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Assessment and Evaluation of Surface Water Quality and Human Health Risk in the Inkomati River Catchment Basin, South Africa

Ernestine Atangana[1] and Rodrigue G. Batogna[2,*]

[1] *Centre for Environmental Management, Faculty of Natural and Agricultural Sciences, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa.*
[2] *Mathematics Statistics and Actuarial Science, Namibia University of Science and Technology, Private Bag 13388, Windhoek, Namibia.*

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Abstract. Multivariate statistical methods, dimensionality reduction, clustering techniques, water quality indices (WQIs) of the Canadian Council of Ministers of the Environment (CCME), comprehensive pollution index (CPI), and human health risk assessment indices for carcinogenic risk of heavy metals, using the hazard index (HI), are utilized in this work to assess the surface water quality of the Inkomati catchment. Six physicochemical parameters – EC, pH, SO_4, Fe, Mn, and Cu were measured monthly from January 2015 to June 2019 from two sites Crocodile and Sabie rivers. The outcomes were compared to standard regulatory guidelines values. Recommended parameter values from US-EPA and peer-reviewed literature were used for the HI. The findings indicated that the river water was turbid and suffered from EC, specifically distressed due to trace metals. The US-WQI range (103.15-431.38) showed that the water quality level of the catchment was in the poor category but excellent during the winter. Water quality improved from marginal to good, according to the CCME-WQI scores, whereas the CPI scores (2.359-8.459) showed that the catchment's water quality was in a very poor condition. The US-WQI suggested that the overall quality of the basin has declined in both the upper and lower portions. The hazard quotient through ingestion exposure did not exceed the threshold limit of 1 for children. This implies there is no potential carcinogenic health risk from trace elements via ingestion of drinking water for children. However, cancer risk for children was computed in relation to Cu, Fe, Mn, and levels. It did not exceed the carcinogenic threshold limit of 10^{-4} for both sites.

AMS subject classifications: 9008, 9010, 9011, 65K05

Key words: Inkomati catchment, river water quality, water quality indices, robust statistical techniques, health risk assessment.

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*Corresponding author. *Email address:* `rgbatogna@yahoo.fr` (R. G. Batogna)

1 Introduction

The availability of clean water is essential for nature as well as for people. The world's aquatic ecosystems are under tremendous stress because of large-scale urbanization, industrial and agricultural expansion, and rising water demand [56]. Population increases and their effects on the economy have threatened the availability of clean water in many parts of the world [69]. Changes in water quantity and quality threaten the availability of clean water. About 25 million people die from water contamination each year. In many nations, such as South Africa, industrial and residential human activity-related water contamination is a severe issue [25]. The growing pollution affecting water resources is due to anthropogenic activities such as industry, urbanization, afforestation, mining, agriculture, and unintentional water contamination (Khatri and Tyagi [36]). Anthropogenic activity has drastically decreased the surface water quality in catchments that support the aquatic ecosystem (Akhtar *et al.* [1]). Watershed water resources are essential to absorb or move runoff from agricultural land, as well as urban and industrial waste. According to Malaj *et al.* [43] and Anh *et al.* [4], river inflows considerably contaminate the water supply of a catchment, increasing the risk of severe ecological and sanitary issues. As towns and companies grew with collected rubbish in populous regions in the first half of the 19th century, environmental pollution issues in South Africa became apparent [16]. The biodiversity of water resources is currently in danger due to human-caused river pollution. It is possible to directly or indirectly alter the physical, chemical, or biological properties of a water resource to reduce its suitability for the intended use (National Water Act 36 of 1998 [62]). Rahman [51] stated that water is considered polluted if it has been affected by contaminants and is either unusable for human needs, such as drinking water, or has significantly lost the ability to support its constituent biotic communities, such as fish and macroinvertebrates. In terms of the National Water Act, the Department of Water Affairs and Forestry (DWAF) had to grant permission for any operations that could contaminate or degrade water resources to ensure proper management of the river. Even though a water usage license includes a requirement for water quality monitoring, rivers like the Crocodile River and Sabie River are still worsening. Though licensed, these activities could contaminate the river through seepage and the release of wastewater. The study area is situated in the Inkomati basin in South Africa, which was the subject of concern due to pollution from mining activities and agricultural sources (Jarmain [30]). The Inkomati basin in South Africa is primarily located within the Mpumalanga province, which has a semi-urban population. It comprises most of the water management area. The Mahala, Mapulanneng, Nsikazi, Nkomati, and Mswati regions are home to numerous rural communities. Some of the main metropolitan areas in the water management area are Nelspruit, White River, Komatipoort, Carolina, Badplaas, Barberton, Sabie, Bushbuckridge, Kanyamazane, and Matsulu. An area of 50,000 km^2 (19,000 sq mi) is thought to exist in the river basin. Despite the substantial amount of water used for diverse purposes, the river continues to experience problems directly related to water scarcity, leading to a decline in water quality, saltwater intrusion, and subsequent environmental and socio-economic repercussions [19]. The chemical water contamination of the river caused these effects to worsen. Some of these consequences resulted from the river's catchment water contamination. Surface water pollution in the Inkomati River basin is mainly brought on by domestic, industrial, and agricultural returns flows; suspended particles and sediment constituents are only a minor contributor [19]. The three principally independent catchments that make up the river basin are the Komati, Crocodile (East), and Sabie – Sand River catchments. These rivers combine to form the Inkomati River in Mozambique, which drains the water management area and discharges into the Indian Ocean. The surface water quality of the Sand River sub-catchment is not as good as that of the Sabie River sub-catchment because of over-abstraction, which reduces the river's natural capacity for assimilation. The Sand River occasionally exhibits high nutrient levels, and unofficial housing projects are thought to be the culprit. When the Inyaka Dam was completed, there was plenty of assimilative capacity to keep the water quality in the Sabie River at its current high level [17]. If proper sanitation is not done upstream of the Kruger National Park, water entering the Park would be a serious hazard. For several years, effluents have been disposed of through irrigation; however, the soil has become saturated with salt (particularly chlorine), which drain out and reach the Elands River and the Crocodile River (Ferreira [23]). The lower Kaap River, which frequently has high arsenic levels, and the lower Crocodile River have also experienced some quality decline. Return flows from upstream users, such as irrigation, urban areas, and former gold mining operations, are to blame. During low flow, irrigation return seepage is apparent (Heath and Claassen [26], Topal and Onac [67]). The Inkomati Catchment Management Agency, the DWA, and the municipalities of Ehlanzeni and Mbombela were compelled to act by issuing orders to noncompliant water users due to the state of the local river. Leestemaker and Tauacale [39] claimed that the eutrophication seen in the Inkomati River is caused by the leaching of agricultural fertilizers or by excessive waste, sewage, and residues created by the sugar industry at Xinavane. However, comparing the numerous water quality measures acquired over time and space can make it challenging to establish the water quality state of a particular reservoir (Uddin *et al.* [68], Yang *et al.* [81]). Environmental techniques such as water quality index (WQI) models have been used to correctly understand the change in the water quality state of surface water bodies. The Horton index, the index developed by the Scottish Research Development Department (known as the SRDD index), the Canadian Council of Ministers of the Environment (CCME - WQI), the National Sanitation Foundation WQI, the Comprehensive Pollution Index (CPI), Organic Pollution Index (OPI), and Eutrophication Index (EI) are the WQIs most frequently used to assess the water quality of surface water bodies (Matta *et al.* [45], Mishra *et al.* [47], Tang *et al.* [65]). Son *et al.* [61] evaluated the water quality of the Cau River in Vietnam using various indices, such as the WQI, CPI, OPI, EI, and the Trace Metal Pollution Index (TPI). They found severe organic pollution and eutrophic conditions downstream. The water quality status of the Qilu Lake in China was evaluated by Tang *et al.* [65] using the CPI. The CPI was employed by Matta *et al.* [45] to assess the water quality state of the Henwal River in India, where they found moderate and severe contamination at various sampling locations. To evaluate the water quality of the Sukhna Lake in India, Mishra *et al.* [47] used combined indices (CPI, OPI, EI, and TPI). They discovered that the lake was significantly polluted and eutrophic. In addition, multivariate statistical techniques, such as linear correlation, principal component analysis, factor analysis, and cluster analysis, enable the identification of potential factor sources that affect water systems and offer a useful tool for dependable problem-solving by assisting with the interpretation of intricate data matrices to understand the quality and ecological status of the water (Lee *et al.* [38], Reghunath *et al.* [53], Vega *et al.* [75], Wunderlin *et al.* [80]). Surface runoff from different farmlands along the river's path, open dumping of solid waste, and open grazing of free-ranging animals are additional possible causes of pollution. Since there are, as far as we know, few studies on the water quality status in the Upper Inkomati River catchment (van der Laan *et al.* [74]), it is crucial to report on the water quality status of the water resource in a semi-arid region of South Africa. Consequently, we present our research on the physicochemical properties of the Inkomati River (Crocodile River and Sabie River). Furthermore, we provide the overall condition of the river's water utilizing a variety of water quality indices (WQI, CCME-WQI, and CPI) and multivariate techniques, which are a flexible way to summarize the state of a river system's water quality and identify its sources. Furthermore, we calculated the possible carcinogenic and noncarcinogenic health risks associated with drinking water based on the trace metal levels obtained because they are utilized for multiple reasons.

2 Materials and methods

2.1 Description of the study area

The Inkomati River watershed basin is situated in the Mpumalanga province. It is made up of the Komati, Crocodile (East) and Sabie – sand rivers, as well as the Komati, Uanetze, and Mazimichopes rivers, the three most distinct catchments (Fig. 1). These rivers and tributaries all flow into the water management area, which merges to form the Inkomati River in Mozambique, which then flows into the Indian Ocean. The two main catchments in the Inkomati basin in South Africa are the Crocodile River close to Kwena Dam and the Sabie wastewater treatment works (WWTW) close to the Sabie River. The Crocodile River (East) is in the province of Mpumalanga in the northeastern part of South Africa (Fig. 1). The coordinates of the river are shown in Table 1. The Crocodile River, one of the most economically productive rivers in the country with a vast river basin, gives life to everything in this area [11]. It has a total length of about 320km and drains an area of 10450km^2. Due to the range of habitats, the river has at least 49 different fish species, making it one of South Africa's most biologically diverse streams [16]. Agricultural runoff, return flows, and additional mining activities impact the lower reaches of the Crocodile River water quality. Flows from many tributaries during winter, including the main stem of the Crocodile River, have been drastically reduced due to increased afforestation and the

Table 1: Geolocation of sample sites.

Site name	Abbreviation	Coordinates	Description
Sabie River wastewater treatment works (Sabie-Sand)	Sabie WWTW (Site 1)	−25.08897 30.77794	Site 1 is situated downstream at a high relief along the upper Sabie River (Sabie-Sand) between forestry plantations. At the time of sampling, Site 1 was mainly surrounded by deforested plantations.
Crocodile River (East) at the Kwena dam	Croc-K (Site 2)	−25.3632 30.38966	Site 2 lies ∼6.7 km below the Sabie WWTW, which is situated at −25.0912441 S; 30.7942149 E.S. This site is situated in the upper reaches upstream from the Kwena Dam and has a low diversion of species (such as fish) and agricultural activities.

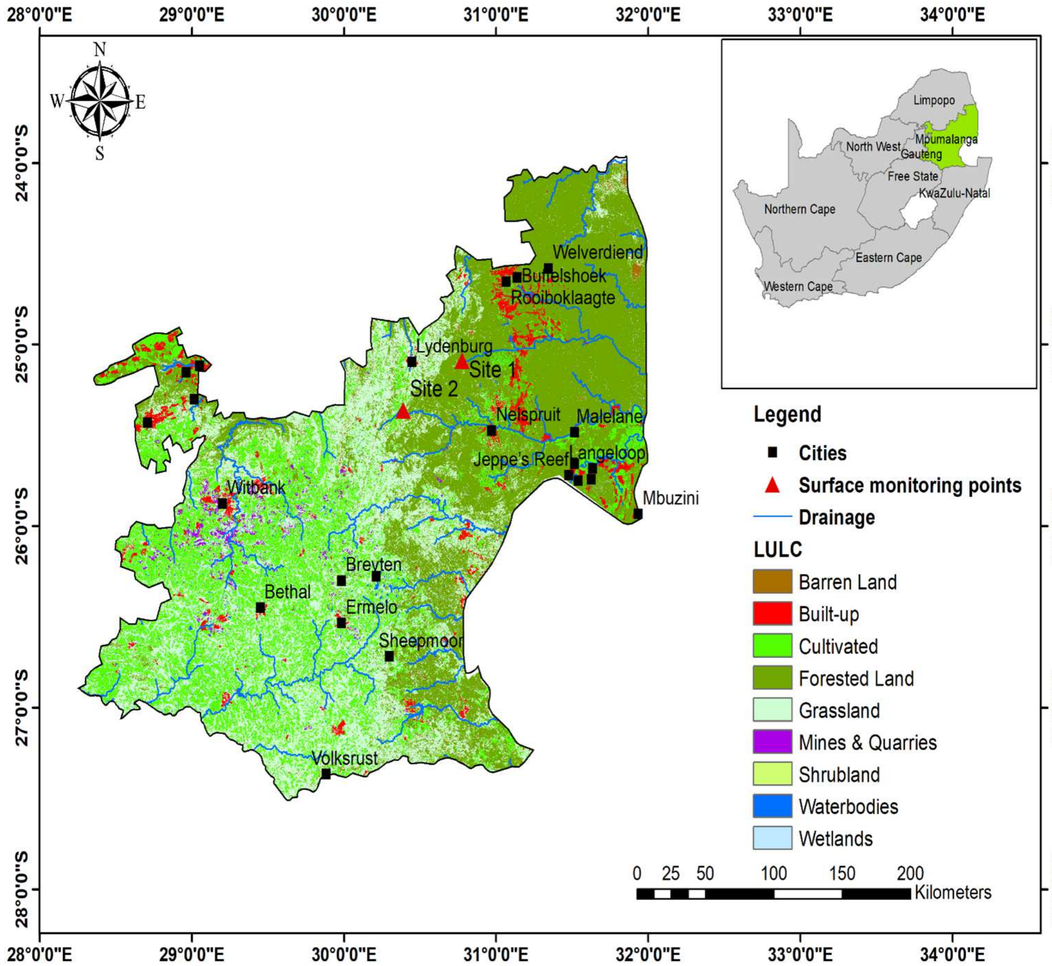

Figure 1: Maps showing the location of the study area - Sabie River (Site 1) and Crocodile River (Site 2).

amount of water utilised for agriculture. The catchment receives an average of 880mm of precipitation annually, with variations from 1200mm in the west and center to 600mm in the drier Lowveld in the east. The summer (October-April) has higher rainfall rates than the winter (May to September). According to [18], the catchment's average daily temperature varies from 14°C to 22°C during the dry season and from 20°C to 42°C during the wet season and summer months. The Crocodile River watershed and its many tributaries have experienced decreased flows because of afforestation and irrigation abstraction. The $167\times10^6\mathrm{m}^3$ capacity of the Kwena Dam makes a significant contribution to river flow regulation. To provide water to irrigation farmers along the middle and lower sections of the river and to aid in the flushing away of wastewater effluent discharge, water is released from the dam to ensure a minimum flow of $7\mathrm{m}^3\mathrm{s}^{-1}$ throughout the winter months. Salinity and eutrophication are the two main issues with this river's water quality. Low river flow due to anthropogenic activities combined with high pollution loads from point and non-point sources have worsened water quality (Deksissa *et al.* [10]). According to Olbrich and Hassan [49], the main crops grown in the river catchment are maize, cereals, sorghum, citrus, mangoes, bananas, and avocadoes. There are also roughly 12500 ha of irrigated sugarcane. Additionally, the area has around $1775\mathrm{km}^2$ of exotic wood [18]. This catchment is the most water-stressed in South Africa. This raises severe concerns given the rising population that depends on it for survival and the significant demand for water from new farms. If completely implemented, the biological reserve will compete for water with both present and future consumers [18]. The Sabie River Catchment, another sampling site, stretches west to east from the Drakensberg escarpment to the Lebombo Mountains bordering Mozambique (Fig. 1). The geological coordinate of the sampling point is given in Table 1. The mean annual precipitation in the area is about 74.7 mm. The temperature in the area ranges from 12°C to 28°C (winter season) and from 18°C to 40°C (summer season). The elevation along the Drakensberg escarpment is approximately 2200m and gradually descends to 150m in the eastern parts of the catchment. The western side of the catchment is mountainous, and the topography towards the east flattens to a pediplain, commonly known as the Lowveld. A pediplain refers to an extensive flat terrain formed by weathering, transporting, and depositing bedrock material below a mountain slope. The pediplain is, therefore, characterized by the coalescence of numerous pediments forming a gentle plain as described by Oberlander, cited by White [77]. Elevation and topography have a significant effect on the climate of the area. In contrast, the western side has a temperate to subtropical climate, and the eastern side is semi-arid and hot. The average rainfall within the catchment decreases along the topographical gradient from 1500mm to 900mm per annum and in the mountainous areas from 600mm to 348 mm per annum toward the lower, flatter portions of the Sabie River watershed through the foothills. The summers are hot, and winters are moderate and frost-free. Evapotranspiration rates follow the same trend towards the east [18]. Evapotranspiration rates increase from 1400 mm to 1700 mm per annum in an eastward direction Jewitt *et al.* [31] (cited by [18]). Rainfall variability is high within the Lowveld region; droughts occur every three to four years (DWAF 2004). The Lowveld is a water insecure and a high-risk water quality region due to the low and variable rainfall and the expansion of rural settlements bordering the Kruger National Park (Pollard and Walker [50]).

2.2 Site selection

The activities in the catchment and the primary goal of the study were considered when choosing the study site (Fig. 1). To reflect on the various river segments and catchment activities, two locations from the main stems of the Crocodile River and Sabie River were chosen. Additionally, the accessibility and safety of the sites were considered. The river was divided into two pieces, Site 1 and Site 2: Site 1, the lower reaches, included the Sabie WWTW, closer to the upper Sabie River (Sabie-Sand) between forestry plantations, and Site 2, the higher reaches, which are above the Kwena Dam.

2.3 Sample collection and analysis

Monitoring stations of the Department of Water and Sanitation of South Africa provided the historical data used in this analysis. Historical data for the Sabie WWTW and the Crocodile River at Kwena Dam, water samples were collected downstream and upstream of the surface point at the mainstream, 2015–2019 (Table 1). Water quality sampling was done once per month for 5 years for each sampling site (upstream label Site 1 and another downstream label Site 2) using polyethylene bottles. A grab sample of sixty surface water samples in total was taken during the entire study period. Samples were obtained using a bucket attached to a rope to track the water collection from bridges. The samples were transferred into allocated containers. The samples were collected in triplicates using one-liter plastic bottles each and were sterilized with dilute nitric acid every month between January 2015 and December 2019. Samples were gathered for physicochemical and metal examination. Concentrated nitric acid (65%, $0.1M$) was used to preserve water samples for the metals. In an approved analytical chemistry facility in Nelspruit, Mpumalanga, collected samples were maintained in ice cooler boxes and kept cold until analysis. Physicochemical parameters, including metals, were analyzed during this study. Using an Extech multimeter (EC 400, instrument, Nashua, NH, US), pH and electrical conductivity were measured outdoors. An atomic absorption spectrophotometer (900H, Perkin Elmer, Akron, OH, USA) was used to evaluate heavy metals – iron (Fe), copper (Cu), and manganese (Mn). Calibration standards were created from a stock solution in a 100ml volumetric flask to identify the metals. Ion chromatography equipment was used to find anions (SO_4) concentration. A 15mm filter paper (125mm) was used to filter the water samples.

2.4 Water quality indices

The water quality indices were calculated using five years of historical data from the 60 water sample parameters mentioned above. The WQI method is frequently used to assess surface water quality.

2.4.1 US water quality index model

The US-WQI, which gauges the total impact of a number of water quality standards, is easy for water administrators to understand and apply. WQI was developed using the six water sample metrics from five years of historical data. The WQI was calculated in three phases. The first step was to assign a weight (Wi) to each of the six parameters based on their relative importance in the overall quality of drinkable water (Eq. (2.1)). A parameter was given a maximum weight of five due to the significance of the parameter in determining the water quality. The parameters that were assessed to have little impact on the overall quality of the water were given a minimum weight of 1. Based on their relative importance in the water quality assessment, other parameters were given weights ranging from 1 to 5. The formulae below (Eqs. (2.1)-(2.3)) show the mathematical formula used to calculate the WQI (Alobaidy *et al.* [3], Kanga *et al.* [32], Dharma *et al.* [57], Rakishness *et al.* [52])

$$RW_i = \frac{W_i}{\sum_{i=1}^{n} W_i}, \tag{2.1}$$

where RW_i – the relative weight of the pollutant parameter, W_i – the assigned weight of each pollutant parameter, and n – number of pollutant parameters. For all the factors (aside from pH), a quality rating scale (Q_i) was calculated using the formula

$$Q_i = \left(\frac{C_i}{S_i}\right) \times 100, \tag{2.2}$$

where C_i is the i-th parameter's observed value, and S_i is the standard value. The given equation was used to determine the Q_i for pH

$$Q_i = \left(\frac{C_i V_i}{S_i V_i}\right) \times 100, \tag{2.3}$$

where V_i is the ideal value, which is considered 7.0 for pH. For computing the WQI, first, the sub-indices (SI_i) were calculated for each parameter using the following equation:

$$SI_i = RW_i \times Q_i.$$

Finally, WQI was calculated using the equation

$$WQI = \sum_{i=1}^{n} SI_i. \tag{2.4}$$

The WQI values were classified into different categories, according to Rakishness *et al.* [52].

2.4.2 Canadian Council of Ministers of the Environment water quality index (CCME-WQI) model

The CCME-WQI model was used to assess the surface water quality of river lakes and streams (Ramakrishnaiah *et al.* [52]). The calculations were done using the Eqs. (2.5)-(2.11) (Ramakrishnaiah *et al.* [52]). The CCME-WQI method model was obtained by using the following equation:

$$\text{CCME-WQI} = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right), \tag{2.5}$$

F_1 (scope) is the number of variables whose objectives were not met

$$F_1 = \left(\frac{\text{Number of failed variables}}{\text{Total number of variables}} \right) \times 100, \tag{2.6}$$

F_2 (frequency) is the number of items the objectives did not meet

$$F_2 = \left(\frac{\text{Number of failed tests}}{\text{Total number of tests}} \right) \times 100, \tag{2.7}$$

F_3 (amplitude) is the amount by which the objectives were not met. F_3 is obtained in a three-step calculation that shows how extremely failed test numbers deviated from the standards:

Step 1. The term excursion describes the number of times a person's concentration exceeds the objective (or falls short of, if the target is minimum). When the test value cannot be greater than the objectives, then

$$\text{Excursion}_i = \left(\frac{\text{Failed test value}_i}{\text{Objectives}_j} \right) - 1. \tag{2.8}$$

When the test value should not be lower than the recommended value, then

$$\text{Excursion}_i = \left(\frac{\text{Objective}_j}{\text{Failed test value}_i} \right) - 1. \tag{2.9}$$

Step 2. The collective amount by which individual tests are out of compliance is calculated by summing the excursions of individual tests from their objectives and dividing it by the total number of tests (both those meeting the objectives and those not meeting the objectives). This variable, referred to as the normalized sum of excursions (NSE), is calculated as

$$\text{Normalized sum of excursion} = \frac{\sum_{i=1}^{n} \text{excursion}_i}{\text{Number of tests}}. \tag{2.10}$$

Step 3. An asymptotic function determines F_3 after scaling the normalized sum of the excursions from objectives to obtain a range between 0 and 100

$$F_3 = \left(\frac{\text{NSE}}{0.01 \text{ NSE} + 0.01} \right). \tag{2.11}$$

The computed CCME-WQI was classified according to CCME ([21]).

2.4.3 Comprehensive pollution index

Matta *et al.* [45] and Mishra *et al.* [47] used the CPI to categorize the status of the water quality. It was determined using the following equation:

$$\text{CPI} = \frac{1}{n} \sum_{i=1}^{n} \text{PI}_i. \tag{2.12}$$

Here, PI stands for the individual parameter's pollution index, and n is the number of parameters

$$\text{PI}_i = \frac{C_i}{S_i}. \tag{2.13}$$

In this case, the i-th parameter's observed value is C_i, while S_i, is the standard value of the i-th parameter. Various groupings of CPI numbers were created, according to Sharma *et al.* [57].

More information about the water quality rating with Table 2, see supplementary files.

Table 2: Water quality scale of the selected indices in the study ([2]).

Water quality rating	CCME-WQI	US-WQI	CPI
Excellent	95-100	<50	<0.20
Good	80-94	50-100	0.21-0.40
Fair	60-79	100-200	0.41-1.00
Poor	45-59	200-300	1.01-2.0
Very poor	0-44	>300	>2.01

2.5 Multivariate statistics

With the objective of evaluating significant differences to identify the relationship among water quality parameters among sampling sites in the Inkomati catchment and their possible sources, principal component analysis (PCA), cluster analysis (CA), and Pearson's correlation coefficient analysis, were performed using the commercial statistics package IBM SPSS version 27 for Windows 10. The data were analyzed using a significance level of 0.01%. The use of PCA and CA for the multivariate analysis of the data obtained for the surface water quality was beneficial in identifying the sources of the constituents because they helped distinguish between the natural and anthropogenic pollutant contributors to the surface water, which is typically based on the variable's association level.

The correlation matrices on the variables were used in the PCA and CA to determine the many associations that might be feasible, as well as the sources of the pollutant elements' input (Yongming *et al.* [82]). PCA and CA are the most common multivariate statistical methods for environmental studies (Meza-Figueroa *et al.* [46], Kartal and Tokalıoğlu [33]).

PCA is widely used to reduce data and to extract a smaller number of independent factors (principal components) for analyzing relationships among observed variables (Astel *et al.* [7], Kartal and Tokalıoğlu [33]). PCA begins by extracting the eigenvalues and eigenvectors from the correlation matrix, which describes the dispersion of the original variables (Astel *et al.* [7]). An eigenvector is a collection of coefficients that multiply the correlated variables to produce new, uncorrelated (orthogonal) principal components, weighted linear combinations of the original variables. It is easier to evaluate a specific multidimensional system using PCA to reduce the number of associated variables to a more manageable set of orthogonal elements by displaying the correlations between the original variables. Principal component eigenvalues must be higher than 1 (Kartal *et al.* [33]). Many environmental media, including sediments (Tahri *et al.* [64]), soil (Facchinelli *et al.* [22]), and water (Tahri *et al.* [64]), have been subjected to PCA and derivative approaches to identify pollution sources and allocate natural versus human contributions.

Cluster analysis was done using a similar approach and precepts as factor analysis, pooling together the seasonal data of the two sites, with the goal of clustering parameters affecting water quality most reliably and faithfully as suggested by the available data. Before the analysis, the variables were standardized to their z-scores, and then the procedure computed Euclidean distances to discriminate or identify similarities among the variables. Hierarchical clustering grouping using Ward's method was done on the standardized data (Kazi *et al.* [34]). CA separates data into two or more mutually exclusive groups based on a combination of internal variables. PCA and CA are routinely coupled to evaluate findings and classify certain variables and parameters (Facchinelli *et al.* [22]). CA aims to identify a framework for grouping observations into multiple groups or variables that share observed attributes. The most popular way to summarize hierarchical clustering is with a dendrogram. In the current investigation, CA was employed to assess the similarities between water quality metrics at upstream and downstream stations.

2.6 Human health risk assessment

Given the data availability, human health risk assessment for both carcinogenic and non-carcinogenic risks for the three heavy metals Cu, Fe, and Mn were considered and assessed (Table 6). Although the report of the International Agency for Research on Cancer ([28]) did not classify Cu, Fe, and Mn as heavy metals that are carcinogenic, possibly carcinogenic, or presenting noncarcinogenic risks, the calculations were made for all three, using chronic daily intake (CDI), hazard quotient (HQ), and hazard index. The reference values of the parameters originated from the US EPA ([71]), the US EPA Exposure Factor Handbook ([73]), the World Health Organization ([78]), Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (US EPA, [71]) and guidelines for drinking-water quality (WHO, [79]), as well as reference values from peer-reviewed articles in the literature where no value was found elsewhere. Carcinogenic risks were calculated as follows:

$$CR=\begin{cases} CDI\times SF, & \text{if} \quad CDI\times SF<0.01, \\ 1-e^{CDI\times SF}, & \text{if} \quad CDI\times SF\geq 0.01, \end{cases} \tag{2.14}$$

where we have

$$CDI_{ingestion}=\frac{c_i\times IR\times ABS_{in}\times EF\times ED}{BW\times AT}, \tag{2.15}$$

$$CDI_{dermal}=\frac{c_i\times SA\times K_p\times ABS_{dex}\times ET\times EF\times ED\times CF}{BW\times AT}, \tag{2.16}$$

where $CDI_{ingestion}$ is the exposure dose through ingestion of water (mg/kg-day); CDI_{dermal} is the exposure through dermal absorption (mg/kg-day); C_{water} is the average concentration of the estimated metals in water (μg/L), and Kp is the dermal permeability coefficient in water (cm/h): 0.001 for Cu, Fe, and Mn. The other constants in those equations are shown in Table 3.

By comparing the estimated contaminant exposures from each exposure route (ingestion and dermal) with the reference dose (RfD), potential noncarcinogenic hazards associated with trace metal exposure were identified. Cu, Mn, and Fe have RfD ingestion constants of 40,24, and 700, respectively, whereas the RfD dermal values of the trace elements that were examined are 40,0.96, and 140 (US EPA, [72]). Eqs. (2.17) and (2.18) can be used to calculate the hazard quotient (HQ) toxicity potential of an individual's average daily intake to reference dosage via the two pathways (Edokpayi *et al.* [20]).

$$HQ_{ingestion}=\frac{CDI_{ingestion}}{RfD_{ingestion}}, \tag{2.17}$$

$$HQ_{dermal}=\frac{CDI_{dermal}}{RfD_{dermal}}, \tag{2.18}$$

where RfD ingestion/dermal is the reference dose for ingestion/dermal toxicity (mg/kg/day), the literature provided the RfD ingestion/dermal values (Li and Zhang [40], Iqbal and Shah [29]). According to US EPA ([72]), an $HQ<1$ is considered safe and significantly non-carcinogenic. However, $HQ>1$ suggests that exposure to the pollutant levels represents health concerns. The total of the calculated HQs across metals was expressed as the hazard index (HI) to evaluate the overall possible non-carcinogenic consequences

Table 3: Parameter values for health risk in the Crocodile and Sabie River catchment.

Parameter	Mean value children	Unit
Metal sample metal value (c_i)	–	Microgram per liter (μg/l)
Ingestion rate (IR)	0.869^a	Liter per day (l/d)
Intestinal absorption factor (ABS_{in})	0.3^a,0.2^a,0.04^a for Cu, Fe, and Mn, respectively	Microgram per kg per day (μg/kg-day)
Dermal absorption factor (ABC_{dex})	0.001^a,0.001^a,0.001^a for Cu, Fe, and Mn, respectively	Microgram per kg per day (μg/kg-day)
Exposure factor (EF)	365^a	Days per year (d/year)
Exposure duration (ED)	49^a	Year
Body weight (BW)	63.6^a	Kilogram (kg)
Average time (AT)	28371.5^b	Days
Skin surface area (SA)	18000	cm^2
Permeability coefficient (K_p)	0.001^a,0.001^a,0.001^a for Cu, Fe, Mn, respectively	Centimeter per hour (cm/h)
Conversion factor (CF)	10^{-3}	Liter per cm^3 (l/cm^3)
Reference dose intestinal ingestion ($RfD_{ingestion}$)	40^a,1000^a,7^a for Cu, Fe, Mn, respectively	Microgram per kg per day (μg/kg-day)
Slope factor ingestion ($SF_{ingestion}$)	0.0017^c,$0.0017\cdot 10^1$,$0.0017\cdot 10^{1^c}$, for Cu, Fe, Mn, respectively	Kilogram day per microgram (kg d/μg)
Slope factor dermal exposure (SF_{dermal})	$0.00425\cdot 10^{1^c}$, $0.00425\cdot 10^{1^c}$, $0.00425\cdot 10^{1^c}$ for Cu, Fe, Mn, respectively	Kilogram day per microgram (kgd/μg)

[a]US EPA ([71]), US EPA Exposure Factor Handbook,
[b] World Health Organization (WHO),
[b]Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (US EPA [71]),
[c]Guidelines for drinking-water quality (WHO [79]).

posed by many metals and pathways (US EPA [70]). According to Li and Zhang [40], $HI>1$ indicates that exposure can potentially have a negative impact on human health.

The overall calculated HQs across metals were expressed as the hazard index (HI) to evaluate the total possible noncarcinogenic consequences posed by several metals and pathways (US EPA [72]). $HI>1$ indicated that exposure can potentially be harmful to human health (US EPA [72]). Eq. 2.19 was used to assess the carcinogenic risk (CR) through the ingestion pathway

$$CR_{ingestion}=CDI_{ingestion}\times SF, \tag{2.19}$$

where $CR_{ingestion}$ is the cancer risk due to ingestion of trace metals contaminated in water, $CDI_{ingestion}$ is the average daily dosage (mg/kg/day) of heavy metals, and SF is the cancer slope factor (mg/kg/day). For both Fe and Mn, the slope factor is 0.017.

3 Results

3.1 Water chemistry

The surface and freshwater quality in the watershed areas has been characterized and evaluated using multivariate statistical approaches. It was employed in the study to confirm temporal and regional differences brought on by seasonality-related anthropogenic causes. The water quality data set, which tracked six parameters across two research locations, was analyzed using Pearson's correlation coefficient, cluster analysis and principal component analysis. The techniques were applied to find potential pollution sources, while spatial and temporal variations were considered (Kazi *et al.* [34]) as well as central tendency and spread measures of physicochemical parameters.

A pH meter measures the acid/base in the solution and is expressed as a negative log of the concentration of H+ ions (Dallas and Day [9]). The average pH recorded during this study ranged from $6.51-8.80$ (supplementary file). The water in the Sabie WWTW and Crocodile River (Kwena Dam) areas was slightly acidic and more often alkaline. According to the five years of data (2015-2019) in Site 1, Sabie River catchment, water samples collected in a treatment plant with a maximum pH of 7.87 mg/l were recorded in spring (September-October), followed by 7.83 mg/l in the winter season (June-August). Similar observations were recorded in the Mutangwi River in Limpopo downstream (Madilonga *et al.* [42]). This contradicts most other studies showing decreased pH in river systems during drought (Mosley [48]). When looking at Site 2 (Crocodile River), samples collected upstream, across the Kwena Dam, the maximum pH value of 8.25 was recorded in spring (September-October), followed by 8.20 in winter (June-August) and the lowest value of 7.95 in summer (November-March). These values were measured and compiled adhering to the standard guidelines of respectively (South African National Standards (SANS) [27], World Health Organization (WHO, [78]).

3.2 Trace and heavy metals contents

The presence of SO_4 anions with a mean value of 24.16 mg/l (summer), followed by autumn 23.60 mg/l (April-May) and 21.27 mg/l (winter), were recorded downstream at Site 1, compared with its 45.78mg/l (winter and 43.35mg/l (spring), at the upper reaches site. These values recorded did comply with agricultural use and guidelines to protect the aquatic ecosystem, mindful of SO_4 concentrations in most seasons (autumn to winter) for Site 2 during the five-year study. In contrast, the opposite was seen in Site 1 (Sabie River WWTW). The flushing of individual solutes such as SO_4 under immediate post-drought conditions due to different hydrological pathways and sediment-solution characteristics has been reported in several studies (Mosley [48]). Heavy metals such as iron (Fe), Manganese (Mn), and Copper (Cu) were also detected during the four-season downstream (Site 1; Sabie River WWTW) and upper reaches (Site 2; Crocodile River catchment) during this research study. This rise in trace elements and nutrients in these areas is connected to agricultural runoff. In both plants and animals, iron is a metal found near the active site of various essential redox proteins (WHO [78]). Iron concentrations ranged from 0.52 mg/l and 1.33 mg/l in the autumn and summer at Site 1 and from 0.08 mg/l to 0.68 mg/l in the winter and spring at Site 2. The SANS recommendation of 2 mg/l associated with chronic effects of Fe consumption through water was not surpassed in any of the study months. The 0.3 mg/l aesthetic recommendation threshold was not exceeded, according to the 2011 WHO study. Manganese toxicity and lower agricultural yield can be seen at concentrations between 0.02 mg/l and 10 mg/l because surface water is also used for irrigation in the catchment areas (Sites 1 and 2) (DWAF [12]). The Mn concentrations used in this investigation were between 0.17 mg/l and 0.26 mg/l, which was within the permissible limit for irrigating fresh vegetables and using aquatic ecosystems. Fe and Mn can negatively impact the flavor and aesthetic qualities of water if their levels exceed the acceptable aquaculture range (DWAF [12]) and exceed the aquatic ecosystem limits (DWAF [12]). The level of Cu 0.01-0.24 mg/l (Site 1) and 0.02-0.25 mg/l (Site 2) in winter and spring, respectively, complied with the regulatory guidelines (SANS [27]) but exceeded the aquatic ecosystem use (less than 0.0012 mg/l).

3.3 Statistical analysis and multivariate results

3.3.1 Water quality indices model

Across the selected sites in the study, the water quality indices ranged from 46.80 to 431.39 for the WQI, from 2.36 to 8.50 for the CPI, and from 49.15 to 68.32 for the CCME–WQI. According to the calculated water indices, the overall water quality of both sites was poor. For the WQI, the measures lay in the range of excellent water quality (6.80 for the winter at the Crocodile River) to other extreme water quality, 431.39 for the autumn at Sabie River WWTW. Only one measure, WQI = 46.8, for one season (winter) and Site 2 only (Crocodile River), indicated excellent water quality. According to a study done in Mutangwi River and Vaalwaterspruit in Mpumalanga, the water is of good quality and can be used for various purposes. However, the water quality of the midstream and downstream of the river was poor, and the overall rating of the water quality of the river was poor. Hence, the river water quality is poor both microbiologically and physiochemically and should not be used without appropriate treatment (Madilonga *et al.* [42].

For this study, Sabie River WWTW (Site 1), water quality indices values showed poor to worse classifications on the scales. The three different indices measures – WQI, CPI, and CCME-WQI – consistently indicated the season with the most suitable water quality (winter), and each of the three classified it as being poor or worst (winter: WQI=179.33 poor/fair; CPI=4.3 very poor; CCME-WQI=63.6 poor/fair). The three measures – WQI, CPI, and CCME-WQI for Site 1 also agreed on the season with the poorest water quality (autumn: WQI=431.39 unsuitable/poor; CPI 8.5 very poor; CCME-WQI=49.15 very poor/marginal). The available data and the resulting water indices established that at no point in any of the seasons for the five years under consideration was the water quality of the Sabie River WWTW suitable for consumption.

For Station 2, Crocodile River, the three water indices calculated did not all agree with their quality assessment. The lack of consistency in the classification they made resulted from the winter (WQI=46.8), which indicated excellent water quality. In contrast to WQI indicating an excellent Winter water quality, CPI and CCME-WQI showed winter as having the best water quality on Station 2, although classified as very poor (CPI=2.4) and poor/fair (CCME-WQI=68.3), respectively. Winter water quality was not perceived as good or excellent. For Station 2, the three indices – CPI, CCME-WQI, and WQI – all designated spring as having the lowest water quality (CPI=5.3, CCME-WQI=62.7), classifying it as very poor and unsuitable for drinking water, respectively, and WQI=227.84 classifying it as very poor or marginal. The WQI says that winter water quality for the Crocodile River was suitable for consumption and classified as excellent.

In contrast, the two others indicated the category of being fair to poor. Nonetheless, the three indices – WQI, CPI, and CCME-WQI – all along pointed to the same season and water site as being of the best or the worst quality. The index values did not always fall in the same category, the exception being for – Crocodile River: winter WQI=46.8 excellent – otherwise, classifications were in the same qualitative range of poor to lower quality. The research study applied all three indices, WQI, CCME-WQI and CPI, to determine the surface water quality of Vaalwaterspruit in Mpumalanga. It was discovered that the stream was poor/feeble at the up and downstream sites and concluded that it was not suitable for domestic purposes.

3.3.2 Results of statistical multidimensional analysis

3.3.2.1. Correlation analysis

The Pearson correlation coefficients were calculated for all variables using IBM SPSS Statistics version 26. The six parameters – Cu, Fe, Mn, EC, SO_4, and pH – for the overall available data set and according to the four seasons – spring (September-November), autumn (April-June), winter (June-August), summer (December-March) – were correlated against each other to understand the extent of their linear association (Table 4, supplementary file). The coefficients are calculated as the ratios between the covariance of each pair of parameters by the respective product of their corresponding standard deviations. They return values between -1 and 1, reflecting a perfect linear monotonic decreasing relationship between the two parameters at hand, to an ideal linear monotonically increasing relationship between the two parameters.

Taking a glance at the table of correlation results, we notice a reoccurring feature throughout the entire literature. None of the WQIs correlated significantly with any of the parameters. On the other hand, the three different indices' rankings agreed with each other. WQI correlated strongly and positively with CPI. For both indices, smaller values than respective thresholds indicated excellent water quality, and values above corresponding thresholds meant deteriorating quality. The high end of the spectrum showed the best water quality for the CCME-WQI whereas it was the reverse for the CPI and US-WQI. As a result, both WQI and CPI strongly correlated adversely with CCME-WQI.

Fe is moderately correlated with Cu, but a is significant correlation with a p-value less than 1%. Mn has a weak positive correlation with Cu and Fe. The correlations coefficients are 0.196 and 0.211 respectively (Table 4). Electrical conductivity Ec is weakly and negatively correlated with iron (−0.191). Sulphate (SO_4) was significant (1%) but moderately positively correlated with EC, with a coefficient of 0.563. EC and pH were significantly (1%) positively associated, with a coefficient of 0.468.

Table 4: Pearson correlation matrix for water quality parameter concentrations.

	Cu	Fe	Mn	EC	SO_4	pH	WQI	CPI	CCME-WQI
Cu	1								
Fe	0.575**	1							
Mn	0.196*	0.211*	1						
EC	−0.012	−0.191*	0.120	1					
SO_4	−0.070	−0.085	−0.017	0.563**	1				
pH	0.044	0.073	0.031	0.468**	0.167	1			
WQI	−0.045	0.013	0.110	0.087	−0.063	0.097	1	**	
CPI	−0.035	0.011	0.099	0.067	−0.069	0.080	0.991**	1	
CCME-WQI	6.03e-16	−5.78e-16	9.39e-16	−1.31e-15	−1.54e-16	2.67e-15	−1.13e-15	2.81e-15	1

3.3.2.2. Principal component/factor and cluster analysis

A factor analysis was conducted to assess the pertinence of parameters that were monitored to measure each of their contributions to information about water quality (Table 5). Data from the four seasons – autumn (April-May), winter (June-August), spring

Table 5: Rotated components loadings for data of crocodiles at Kwena Dam and Sabie River WWTW catchment (PC loading is more than 0.5 are shown in bold).

Parameter	Component	
	C1	C2
EC	**0.914**	−0.047
SO_4	**0.763**	−0.119
pH	**0.653**	0.177
Cu	−0.024	**0.837**
Fe	−0.133	**0.848**
Mn	0.115	**0.501**
Eigen value	1.919	1.675
% of variance explained	31.98	28.64
% of Cumulative	31.25	59.894

(September-November) and summer (December-March) – were combined and subjected to factor analysis using the PCA approach. Given the data at hand, the idea was to extract the components responsible for variations in water quality as indicated by monitored parameters while minimizing any location or spatial bias that may result from an inefficient measurement practice or recording on-site. PCA is a dimension reduction technique that aims to extract several variables from the data that represents essential information about water quality. These are the so-called principal components that are extracted and explain most of the variations in water quality. Six water quality parameters were recorded seasonally in autumn, winter, spring, and summer for five years from 2015 to 2019 for the two selected sites in the study. Although the Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy did not yield a satisfactory value of 0.46 (less than 0.5), indicating that sampling considerations were not optimal, with a p-value under 0.0009, Bartlett's test of sphericity was very significant. This shows perfect independence of the variables, ruling out multicollinearity and information redundancy and asserting the suitability of data for PCA. The data availability for the two sites restrained severely alternative sampling choices and offered no room to maneuver to get a better sample. PCA was reduced to two principal components responsible for explaining 59.89% of changes in water quality. The PCA rotated plots show two components could account for almost 60% of the total variance in water quality parameters at hand for both sites (Table 5). The scree plot illustrates the two significant components retained (with Eigenvalues above 1) to explain and analyze data structure. The slope in the scree plot changes noticeably only after the third component, whose Eigenvalue is 0.894. Factors loadings are strong and moderate, corresponding in absolute values to the ranges greater than 0.75 and $0.50-0.75$, respectively. Hierarchical cluster analysis results generated a dendrogram showing two clusters: EC, SO_4, and pH, forming the first cluster, and cluster Cu, Fe, and Mn, forming the second cluster. The clustering is parameter-based and geolocation indistinct; it shows two statistically significant groups of parameters that show similar impacts on the water quality, regardless of the sites. For the two sites, it revealed a substantial degree of association between EC, SO_4, and pH parameters on the one side and Cu, Fe, and Mn on the other side.

3.3.2.3. Physicochemical data source identification

The statistical results showed a high correlation between Fe-Cu (0.575) and SO_4-EC (0.563); respectively, these metals were of great interest in this study. If we abide by the classification by Liu *et al.* [41], then we have 0.914, 0.848, 0.837, and 0.763 for the strong loadings, 0.653, and 0.501 for the moderate loadings. Component 1 -EC-SO_4-pH- was grouped inside the cluster analysis because of their substantial positive correlations in PCA and correlation coefficient analysis. Component 1 explained 31.98% of the total variance and had a strong favorable loading (>0.7) on EC (0.914), SO_4 (0.763), pH (0.653), and a weak loading on discharge. Thus, this factor contained hadrochemical variables originating from natural and anthropogenic sources. A second group of elements clustering together Component 2 explains 28.64% of the total variance and loads heavily on

Cu (0.837), Fe (0.848), and Mn (0.501). Very weak and negative loading on pH, SO_4, and EC explain that the dilution processes of dissolved minerals increase with discharge. Increased EC and trace metals in this area are related to agricultural operations (industrial effluent and sediment runoff).

3.3.3 Health risk assessment

3.3.3.1. Non-carcinogenic risk

Summary of hazard quotient (HQ) values for some trace elements (Cu, Mn, and Fe) for the four seasons (autumn, spring, winter, and summer) in drinking water through ingestion and dermal routes were computed for children (Table 6). Trace metals can pose potential adverse health effects when the HQ value of a metal is lower than 1 (Atangana and Oberholster [8]). The HQ through ingestion and dermal exposure for child's groups did not exceed 1 in all sampling points. The hazard index HI values $(0.0009-0.0219)$ were relatively low and of the same magnitude as the corresponding hazard quotients of gastrointestinal ingestion. Table 6 shows that for the three metals – Cu, Fe, and Mn – the seasonal hazard quotients from dermal exposure remained consistently below the noticeable 0.0001 level of concern for arsenic. Hence, we did not find evidence for noncarcinogenic risk related to trace elements (Cu, Mn, Fe) in Crocodile and Sabie River. Similar findings have been reported in previous studies (Asare-Donkor *et al.* [5], Saha *et al.* [55]).

3.3.3.2. Carcinogenic risk (CR)

The overall average result showed no carcinogenic health risk to the intake of water containing Fe, Cu, and Mn metals, implying that the children are not vulnerable to carcinogenic health risks associated with drinking water. Similar studies showing the nonvulnerability of children to chemical contaminants in food and water have been reported (Mannzhi *et al.* [44]). Nevertheless, heavy metals consumed in water intake in the study area should still be monitored to prevent any health implications.

4 Discussion

4.1 On the water chemistry

The Crocodile River, which has excellent water quality upstream, was vulnerable to eutrophication due to nearby trout aquaculture, according to Kleynhans [37]. Using cow feed and fertilizer for agricultural purposes led to higher concentrations of these water-quality elements in the upper reaches of the Crocodile River. In addition, development, agricultural pollution, household waste, industrial effluent, and water extraction, according to Ashton [6], threatened South Africa's freshwater ichthyofauna. Whether the animals will survive primarily depends on the success of conservation efforts outside of protected areas (Skelton *et al.* [58]). The upstream regions have a low diversity and abundance of species because of the obstacles. Numerous human activities, including farming

Table 6: Human health risk assessment indices for cancer risks from ingestion and absorption of study metals (Sabie and Crocodile rivers) for children, as well as their seasonal hazard index values.

	Season	Metal	CDI_{in}	CR_{in}	HQ_{in}	HI
Sabie river	Autumn	Cu	0.2545	0.0004	0.0064	0.0064
		Fe	2.2929	-0.0397	0.0023	0.0023
		Mn	0.0899	0.0015	0.0128	0.0128
	Winter	Cu	0.0379	0.0001	0.0009	0.0009
		Fe	0.8992	-0.0154	0.0009	0.0009
		Mn	0.0733	0.0012	0.0105	0.0105
	Spring	Cu	0.6305	0.0011	0.0158	0.0158
		Fe	2.0861	-0.0361	0.0021	0.0021
		Mn	0.1533	0.0026	0.0219	0.0219
	Summer	Cu	0.4057	0.0007	0.0101	0.0101
		Fe	1.9211	-0.0332	0.0019	0.0019
		Mn	0.0582	0.0010	0.0083	0.0083
Crocodile river	Autumn	Cu	0.1499	0.0003	0.0037	0.0037
		Fe	0.3225	0.0055	0.0003	0.0003
		Mn	0.1895	0.0032	0.0271	0.0271
	Winter	Cu	0.0586	0.0001	0.0015	0.0015
		Fe	0.1425	0.0024	0.0001	0.0001
		Mn	0.0779	0.0013	0.0111	0.0111
	Spring	Cu	0.6382	0.0011	0.0160	0.0160
		Fe	1.1680	-0.0201	0.0012	0.0012
		Mn	0.0667	0.0011	0.0095	0.0095
	Summer	Cu	0.3426	0.0006	0.0086	0.0086
		Fe	0.8426	-0.0144	0.0008	0.0008
		Mn	0.0672	0.0011	0.0096	0.0096

and activities such as washing clothes and vehicles in rivers, have been connected to high levels of Fe.

Förstner and Wittmann [24] identified that manganese is vital for using glucose in all living things. According to Stubblefield *et al.* [63] and the WHO ([78]), high dissolved manganese concentrations may also bioaccumulate in the tissue of aquatic creatures, increasing the mortality rate of various marine organisms.

According to Khadse *et al.* [35], at the dam wall of the Inyaka Dam close to the Sabie River WWTW, a very high concentration of iron (540.00 μg/l) and manganese (117.00 μg/l) have been observed at the sampling point. The water is mainly used for drinking water, agriculture, and the development of industries. There is a treatment plant to treat drinking water, but the system is ineffective or broken. The substantial growth of these communities during the past two to three decades raised increasing concerns regarding the demand for water resources (Tlou [66]). Forestry, commercial plantations, cultivated commercial lands, and urban land uses also boost the water availability and quality of the catchment. The upper sections of the Crocodile River have been shown to have high water quality. Heath and Claassen [26] identified domestic runoff, trash, and a rise in nutrients in the segment of the river from Nelspruit to the Kaap River confluence. Manganese levels rise because of industrial effluents from Nelspruit (Kleynhans [37]).

High nutrient loads in the river were also a result of significant sewage treatment facilities in the cities of Nelspruit, Matsulu, and Kanyamazane (Heath and Claassen [26]). Furthermore, Ramshoo and Muslim [54] found that land use practices such as farming affect river nutrient loading and discharge. Their research findings were comparable to those of the investigation by Kleynhans [37]. Since Cu is just slightly necessary for enzyme activity and glucose metabolism in people and other living organisms, the WHO ([78]) classified it as an essential mineral. Solomon [60] has observed that Cu is more poisonous in its cupric (Cu2+) form. Because it will attach to the organic matter, it is present in lower amounts in the water column than in the sediments. Mining operations, electrical wires, water supplies, and alloys are only a few of the many environmental sources it comes from [60].

4.2 Comparison between the water quality indices parameters

The discrepancy between these indices was very significant and should raise more questions. When calculating water quality in relation to physicochemical properties, the WQI is widely utilized. It transfers huge variables into smaller numbers, which indicate the WQI level. This is the main distinction between the WQI, CCME-WQI, and CPI. In the same field of research, CPI is not tied to a particular kind of water characteristic or weight. It is adaptable in terms of the number of parameters used for the computations and can be used for physical, chemical, or even biological aspects of surface water. On the other hand, the three measures (scope, frequency and amplitude) of variance from selected objectives are the focus of the CCME-WQI, a version of the British Colombia WQI (Zandberg and Hall [83]. Combining these three metrics yields a score, with 0 representing the lowest water quality and 100 the greatest, that ranges from 0 to 100. In that regard, the overall water quality level can be used to reduce variables to a smaller amount. Upstream and downstream sites, during winter, WQI indicated about 46% and 179.3% (<50 and 100-200 range) sample categories corresponding to excellent and fairly polluted. In contrast, the CCME-WQI and CPI showed fair and poor water quality. The other season indicated poor water quality throughout the sampling year. This analysis concluded that WQI was best suited to categorize the water quality at the Inkomati catchment even though the CCME-WQI showed fair water quality in summer at Site 2.

4.3 Multivariate statistics

The more solids that are dissolved in the water, the higher the value of the electric conductivity. The sources of ions could be natural, i.e. geological conditions, human activities such as domestic and industrial waste, and also from agricultural activities. The moderately correlated trace metals (Fe-Cu) indicate the presence of anthropogenic activities from industries such as the mining of metals around the study areas. Multivariate statistical techniques, such as linear correlation, PCA, and cluster analysis, are often used to comprehend better the research system's water quality and ecological status. The Crocodile River near Kwena Dam and the Sabie River WWTW made it possible to identify potential sources of influence on the water system. It provided a useful tool for finding a lasting fix for problems with the purity of the water.

4.4 Sources identification

There were similarities between locations in the Crocodile River and its tributaries, according to the Bray-Curtis similarity results for water quality under high and low flow circumstances. Still, there were discrepancies in various percentages from the cluster analysis. This concerns the river's several water use activities, contributing to multiple flows and physicochemical or water quality factors. There was a two-group formation of Sites 1 and 2 (Crocodile and Sabie rivers) at precisely 25%. At the upper sections of the Sabie River, Site 1 downstream along the river created a collection of clusters. This was related to similar water-related activities discovered close to these sites, as they would have a similar effect.

Although there was a 25% commonality, there was also a dissimilarity between the two sampling sites (Crocodile and Sabie rivers), which suggested that the physicochemical components inside a particular site might vary. More similarity was seen at 10%, where two sets of clustered formation sites were found. Sites with components affecting water quality may be connected to the similarity between sites.

According to a research study on the tributaries of the Crocodile River, the Kapp and Eland rivers were the only ones with sites from both the middle and lower reaches. The similarity between 80% and 90% suggested that the physical and chemical properties of the Crocodile River and its tributaries would have similar concentrations. In comparison of land use and water quality studies, cluster analysis results indicated that sites were more similar during the study period in 2017 than during the year 2016 ([59]). This is also evident from the results of the PCA in the study, which was ordinated much closer. This could result from higher river flows from the upper reaches, leading to better mixing in the lower reaches. This is also indicated by the clustering of a study in Sabie headwaters in the Sabie River, upstream from the town of Sabie, which stretches from the headwaters above the town of Sabie to the foothills at Hazyview, unlike the results obtained during the drought conditions when the water quality at Site 1 clustered closer to that of the Inyaka Dam. A PCA was used to analyze the water quality data set at the Crocodile River and Sabie River study sites to get temporal variation and identify potential pollution sources. Spatial variation was assessed in a comparative analysis of each sampling site. The distance between two points in the multivariate space roughly correlated with the Euclidean distance between two observations. As a result, far-apart observations had a considerable Euclidean distance and vice versa

Regarding the source identification of the water quality parameters, two different sources can be identified according to the cluster analysis and PCA analysis. This indicates that EC, pH, and SO_4 have mixed sources of natural and anthropogenic activities (local soils, agricultural, urban, and rural runoff), while Cu, Fe, and Mn have anthropogenic sources (mining industries). EC, SO_4, pH, chlorine, and total dissolved solids were found to correlate with a group of components and water quality indices.

The high positive loading contribution of pH and EC is interpreted as the physicochemical source of variability. As the river flows downstream, it has been discovered that the EC level rises longitudinally. The contribution of non-point source pollution from agricultural areas in the higher reaches, which was connected to fertilizer containing these chemicals of farming uses, is represented by highly favorable loading SO_4. Farmers employ irrigation and surface runoff in these locations.

The Crocodile River has high water quality in the upstream parts but is vulnerable to eutrophication because of trout running nearby (Kleynhans [37]). The application of fertilizer for agricultural purposes and cattle feed was the cause of the elevated concentrations of these water quality constituents in the upper sections of the Crocodile River. Sewage treatment facilities near Nelspruit, Matsulus, and Kanyamazane, sources of significant nutrient loads in the Crocodile River next to Kwena Dam, can be a source of Mn and Cu (Heath and Claassen [26]). Research studies have also indicated that agricultural runoff may be due to increased electrical conductivity, trace metals, and nutrient loads (WRC [76]). High loadings of Fe (0.848) and Mn (0.501) may be due to sediment runoff during high rainfall experience in the Sabie and Crocodile catchment. Thus, this could be geological areas surrounding the sampling sites. This could also be the potential impact of acid rain during acid rainfall, as the catchment is just north of the Olifants River catchment, which is known for the acid rain impacts. According to reports from DWAF, Fe and Mn may occur naturally from soils or caused by abandoned mines and industrial regions near the watershed. Salts from abandoned mines and industrial areas may cause EC (DWAF [13–15]) and Mn because of industrial areas and the abandoned mine.

4.5 On health risk assessment

These overall findings imply that the water is of poor quality and should still need to be treated prior to domestic water use. The use of water with Mn, Cu, and Fe levels lower than the permissible limit can also be of good health risk to the fishes that live in the Crocodile and Sabie water. While acknowledging that for both the Sabie and Crocodile rivers, the readings remained consistently below critical levels of cancer risk, there is a need to monitor the potential effects of long-term exposure to low levels of heavy metals as well as possible harmful interactions with other metals. Given the poor water quality as established by the water quality indices, prolonged or continuous exposure to contaminants interacting with some level of heavy metal is a more than plausible cause of concern.

5 Conclusion

The current study reviewed the water quality conditions of the Inkomati River, which consists of the Sabie WWTW and the Crocodile River at the Kwena Dam. For a period of five years, a seasonal change in the water quality of the rivers was evaluated (2015-2019). During the four seasons of the study, a total of six parameters – pH, EC, Cu, Fe, and Mn – were examined with an increase in river distance upstream (Crocodile River near Kwena Dam) and downstream (Sabie WWTW). The findings showed that among the six physicochemical parameters studied, EC and pH were determined to be within the DWAF acceptable range, albeit at higher concentrations than in prior studies in the catchments. It was discovered that the rivers were naturally alkaline. When compared to other seasons, winter was found to have a favorable effect on the water quality for Fe, Mn, and Cu. The study found that the water usage here would not be suitable for irrigation, agriculture, and aquatic marine organisms. Poor results were reported when various water quality indices were employed to evaluate the temporal fluctuation of the surface water quality. The WQIs of the Sabie and Crocodile rivers showed that the current conditions of the two rivers were unpleasant and fell into the inferior, poor, and marginally fair categories. The winter season had greater water quality and was the best compared to the other seasons, which led to an excellent water quality index. The top reaches of industrial and agricultural activities negatively impacted the water quality in the catchment around both sites on the Crocodile River. Carcinogenic risk was computed for children, there was no potential carcinogenic risk, hazard quotient less than 1 ($HQ<1$) associated with the consumption of river water. However, the monitoring data revealed significant concentrations of these pollutants, with an annual average pH of 7.75 and electrical conductivity (EC) of 25.06, reflecting the river's pollution status.

By addressing the limitations of traditional sampling methods and enhancing the understanding of inorganic pollution, this model offers a robust tool for environmental management. Its predictions can provide valuable data and theoretical guidance for setting surface water standards, particularly for Cu and SO_4 concentrations, ensuring better protection and sustainable use of the Inkomati River's water resources. Overall, this study guides surface water heavy metals regulatory activities and public health surveillance for better monitoring. Therefore, adequate treatment of water from this river is still highly recommended.

A longitudinal study encompassing monitoring data for longer periods unlike the five-year data span used in this study, can be envisaged for further investigations. Such a study could add substantial value to these findings as it will allow us to assess how individual physiochemical parameters change with time and what impact is produced on the water quality.

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