Chapter

An Assessment of Land Use and Land Cover Changes and Its Impact on the Surface Water Quality of the Crocodile River Catchment, South Africa

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Abstract

The degradation of surface water by anthropogenic activities is a global phenomenon. Surface water in the upper Crocodile River has been deteriorating over the past few decades by increased anthropogenic land use and land cover changes as areas of non-point sources of contamination. This study aimed to assess the spatial variation of physicochemical parameters and potentially toxic elements (PTEs) contamination in the Crocodile River influenced by land use and land cover change. 12 surface water samplings were collected every quarter from April 2017 to July 2018 and were analyzed by inductive coupled plasma spectrometry-mass spectrometry (ICP-MS). Landsat and Spot images for the period of 1999–2009 - 2018 were used for land use and land cover change detection for the upper Crocodile River catchment. Supervised approach with maximum likelihood classifier was used for the classification and generation of LULC maps for the selected periods. The results of the surface water concentrations of PTEs in the river are presented in order of abundance from Mn in October 2017 (0.34 mg/L), followed by Cu in July 2017 (0,21 mg/L), Fe in April 2017 (0,07 mg/L), Al in July 2017 (0.07 mg/L), while Zn in April 2017, October 2017 and April 2018 (0.05 mg/L). The concentrations of PTEs from water analysis reveal that Al, (0.04 mg/L), Mn (0.19 mg/L) and Fe (0.14 mg/L) exceeded the stipulated permissible threshold limit of DWAF (< 0.005 mg/L, 0.18 mg/L and 0.1 mg/L) respectively for aquatic environments. The values for Mn (0.19 mg/L) exceeded the permissible threshold limit of the US-EPA of 0.05 compromising the water quality trait expected to be good. Seasonal analysis of the PTEs concentrations in the river was significant ($p > 0.05$) between the wet season and the dry season. The spatial distribution of physicochemical parameters and PTEs were strongly correlated ($p > 0.05$) being influenced by different land use type along the river. Analysis of change detection suggests that; grassland, cropland and water bodies exhibited an increase of 26 612, 17 578 and 1 411 ha respectively, with land cover change of 23.42%, 15.05% and 1.18% respectively spanning from 1999 to 2018. Bare land and built-up declined from 1999 to

2018, with a net change of - 42 938 and − 2 663 ha respectively witnessing a land cover change of −36.81% and − 2.29% respectively from 1999 to 2018. In terms of the area under each land use and land cover change category observed within the chosen period, most significant annual change was observed in cropland (2.2%) between 1999 to 2009. Water bodies also increased by 0.1% between 1999 to 2009 and 2009 to 2018 respectively. Built-up and grassland witness an annual change rate in land use and land cover change category only between 2009 to 2018 of 0.1% and 2.7% respectively. This underscores a massive transformation driven by anthropogenic activities given rise to environmental issues in the Crocodile River catchment.

Keywords: water quality, potential toxic element contamination, land use and land cover (LULC) change, electrochemical detection

1. Introduction

The availability of clean water sources is essential for the survival of any living species. Rivers play a significant role in maintaining human health and has been recognized as the fundamental right of all living beings [1]. Improved access to clean water contributes towards achieving the 2030 agenda for sustainable development goals (SDGs) particularly SDG 6.1 and 6.2 [2]. However, river deterioration due to anthropogenic activities remains one of the contemporary challenges faced by river basin management both at regional and global scale [3–5]. Anthropogenic activities have been exacerbated over the past decades by socio-economic drivers such as the intensification and expansion of irrigation systems for agricultural purposes, increase in population and pressure on existing freshwater usage, climate variability through uneven distribution of precipitation, floodgate constructions, and untreated wastewater disposal into receiving waters bodies [6, 7]. Because of the misuse of river water resources driven by the need to sustain our economies, water resources are one of the most rapidly declining and degrading in our environment [8]. Thus, recognizing the devastating effects of river pollution on human health demands that the main cause of the problem be identified, managed effectively and efficiently [9, 10].

Globally, is estimated that 2 million tons of sewage, industrial, and agricultural wastewater is discharged into rivers leading to the death of at least 1.8 million people with diseases related to unsafe water [11, 12]. In 2012, it was estimated that 842 000 people died of diarrhea due to directly or indirectly consuming poor water quality, of which 43% of the mortality case reported were children. According to Dube, Shoko [13], 29.9% of global freshwater is reserved underground, being a critical source of water supply and a buffer against drought in rural communities, where surface water is limited especially in developing countries [14]. However, most of the rural communities in developing countries are now at threat and vulnerable from the effect of climate change which affects people's daily water availability and consumption. For instance, it is estimated that the daily intake of drinking water by a human being is 7% of the body weight which is essential for the person's healthy growth and existence [15].

Opportunities to address outstanding water issues in Africa have been undercut by intense and prevalent poverty hampering many cities and communities' capacity to make available services for sanitation and potable water, adequate for economic activities, and further forestall deterioration of water quality [16]. These factors, including finance and poor water management, and lack of proper coordination, has further deepened the water crises in Sub-Sahara Africa, thereby undermining any hope of making potable water available in the near future for the populace [17, 18]. This situation is further compounded by several environmental issues arising in the 21st century including climate change, eutrophication, salinization, toxic metal contamination, *E*-coli, phosphate, nitrate, amongst others [19].

The impact of water pollution in different parts of the world can be grouped under two broad themes according to published literature; Increase public health awareness of the negative impact of river pollution from different governmental and non-governmental agencies through education and mass sensitization. Secondly, through the development of sustainable management practices and models to mitigate the impact of river pollution [20]. Surprisingly, all these measures have yielded less results most probably because of the point and non-point sources of pollutants and also because developing and implementing sustainable mitigation measures requires a sound knowledge of the linkages between the different types and diffuse sources of pollutants, conveyor and sinks. Correspondingly also, the need for constant, effective, low cost and outdoor assessment of any available water in circulation in the ecosystem has emerged as a crucial concern for economic development and biological survival [21, 22].

1.1 Fate of African water bodies

In particular, "Africa is the fastest urbanizing continent on the planet and the demand for water and sanitation is outstripping supply in cities" quoted Joan Clos, Executive Director of UN-HABITAT [23]. Northern Africa and Sub-Saharan Africa although in the same continent, have attained different degrees of progress towards the Millennium Development Goal (MDG) on water. With ninety-two percent coverage, North Africa was already on the way to achieve their stipulated ninety-four percent target prior to 2015 [24, 25]. On the contrary, the experience of Sub-Saharan Africa is a dissimilar situation with forty percent of the 783 million people, not having access to better sources of drinking water in the whole region. Sub-Saharan Africa, operates far below the MDG on the water with only sixty-one percentage coverage, and consequently may not have attained the seventy-five percent regional coverage target following their current pace. Available data from 35 countries in Sub-Saharan Africa, which covers a swooping eighty-four percent of the population of the region, reflects high discrimination between the poorest and the richest twenty percentage of the populace in both rural and urban areas. More than ninety percent of the richest quintile (twenty percent) in urban places have access to better water supply, and more than sixty percent have piped water in the environs. Meanwhile, forty percent of the poorest in the rural areas do not have piped water network in their premises and not up to half of the population make do with any form of an improved water source.

Another concern is poor sanitation that overwhelms the safety of our usable water. African was and likely, is one of the two main continents with the least performance in fulfilling the MDG on sanitation as at 2015. This calls for serious concern sequel to the concomitant health challenge, a lot of people who do not have fundamental sanitation orientation indulge in unhealthy sanitary activities such as, indiscriminate disposal of solid waste and wastewater, and open defection [26]. Additionally, Africa's increasing population is driving more the need for water and expediting the depletion of available water sources. Amidst the regions still developing, Sub-Saharan Africa has a projected highest commonness of urban slums and it is likely to double to around 400 million by this year (2020) [27]. Notwithstanding the attempts by some Sub-Saharan African countries and cities, to broaden fundamental services and make reasonable urban housing conditions improvements. Precipitous and unplanned growth of housing, at the urban areas, has heightened the figure of settlements on uneven, floodable, and high-risk zones where natural incidents such as landslides, rains, and earthquakes have demoralizing after-effects. Settlers at such dysfunctional environment resort to any available water supply for both domestic and possibly drinking uses.

Furthermore, need for constant, effective, low cost and outdoor assessment of any available water in circulation in the ecosystem, has emerged a crucial concern for both economic development and biological survival [21, 22].

As part of remediation measures to this overwhelming challenge, in recent times, there has been a strong interest in investigating the impact of land use and land cover (LULC) on water quality [28, 29]. This is because land use and land cover is an integral component of the global environmental changes that affects ecosystems processes at various levels such as hydrological dynamics, sustainability of water bodies to mankind, increasing demand for agricultural cultivated products, shift in grassland to urban and agricultural land [6, 30]. LULC changes provide first-hand information on the transformation of the natural environment due to anthropogenic activities [31]. A range of studies has investigated the association of land use and land cover change that affect water quality in different environments [19, 28, 32–34]. This has been made possible by emerging developments in the use of spatial data acquisition technologies where different attributes of the landscape configuration can be analyzed more effectively by acquiring satellite imagery [35]. This has enabled land use planners to better interpret and to explain the interaction between hydrological components and land uses activities in a catchment and allow better water conservation strategies to be formulated. However, the perusal of literature suggests that the LULC impact of change has not been previously investigated in the upper Crocodile River catchment thus a study of this kind is necessary.

1.2 PTEs in water and adverse health effects

Generally, most elements are classified as been potentially toxic. These elements are grouped into transition metals, metalloids, lanthanides and actinides. Most of these metals occur naturally in soils, and their concentrations are highly dependent on the parent material through weathering processes, while others are included in the environment through anthropogenic activities [36]. The presence of toxic elements in water typically compromises the quality traits expected to be good for drinking, industrial processing and for biodiversity purposes [37]. However, human-induced activities have modified the natural level, biochemical balance and geochemical cycling of PTEs in the environment [38]. A good number of the metals associated with biodegradable organic and inorganic contaminants are themselves not biodegradable and hence cannot be removed or deactivated through naturally occurring processes [39, 40]. Hence, once exposed to the environment, these metals can stay for decades or centuries due to the fact they are not biodegradable [36]. Although the presence of some of these metals is essential to the ecosystem and are still needed in organisms and human body, beyond which level referred to as maximum concentration limit (MCL), they pose a threat to human health and the environs.

Nickel surpassing its necessary level could cause critical kidney and lung problems, besides distress in the gastrointestinal, skin dermatitis and pulmonary fibrosis [41–44]. Zinc as a trace element, is important for human health. It is essential for the physiological functioning of living tissues and many biochemical processes depend on it for regulation. However, beyond the MCL, zinc can pose serious threat to health like stomach cramps, vomiting, nausea, skin irritation and anemia [45, 46]. Copper is crucial to animal metabolism. Nonetheless, excessive exposure could cause serious toxicological threats like convulsions, vomiting cramps and can be in some severe cases lethal [47]. On the other hand, some metals like lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr) are highly toxic even in minute amount and could critically affect the process of biological degradation of organic matters and severely harm humans [36]. Pb could cause pathological alterations in the endocrine system and kidney that lead to failure in reproduction [48]. With the exception of passage through urine, which is usually extremely slow, there is no other means of eliminating the lead in humans [49]. The irrevocable tubular damage in kidney, caused by exposure to increased level of Cd in the body can no longer be denied. The stability of genes could be negatively impacted by the inhibition in the repair of damaged DNA leading to increased chances of mutations [50]. In the disruption of the endocrine, precisely affects the reproductive system of men, thereby reducing semen quality [51, 52].

The exposure to Cd occupationally, not even involving changes proven to be clinically pathogenic, also threatens to result in visual motor function impairment, promoting changes in emotional balances and causes loss of concentration [53]. Hence these metals including Cd, Pb, As, and Cr are seen as the "Environmental health hazards" having a ranking of the first ten on the list from "Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances", relative substance toxicity and possible exposure to infested soil, air and water [54–56]. Various global agencies such as Joint Food and Agricultural Organization (FAO)/WHO Expert Committee on Food Additives (JECFA), and International Agency for Research on Cancer (IARC), Centre for Disease Control (CDC) and World Health Organization (WHO), United Nations Environmental Protection Agency (US-EPA,) have been actively involved in the control of its pollution in the environment.

1.3 PTEs sources in African water bodies: an overview

The water bodies in Africa are increasingly at the risk of PTEs exposure [57], a sequel to the growing human population leading to broadening settlement, urbanization and concomitant industrialization [58–60]. The general result is commonly the increasing discharge of completely untreated or poorly treated domestic and industrial effluent, responsible for the largest origin of heavy metal contamination and consequently, generate a continuous rise in metallic contamination in water bodies in most of the globe [59, 61]. In particular, sources of heavy metal pollution are either natural or anthropogenic [59], which are distributed across settlements. The greatest source of heavy metal pollution in the rural settlements are natural while that of the urban areas are fundamentally anthropogenic [59, 60]. However, 'bossy' and at times illegal mining activities, in some of the rural areas can also contribute to heavy mining pollution of some fresh water bodies [62].

Natural Sources of toxic elements in most rural African countries include weathering of mineral deposits, bush burning and windblown dust, comets, leachate, wet and dry fallout of atmospheric particulate matter, and volcanic eruptions [59, 62]. The anthropogenic sources on the other hand seem, to be as large as the development of the societies in most African countries where environmental protection, waste management, and disposal are still poorly managed. These include activities directly or indirectly connected with, industrial effluents, fossil fuel and coal combustion, mining and metal processing, solid waste disposal, fertilizers, battery and paint manufacturing, petroleum refining, cement and ceramic production, and steel production [62]. Others include mineral exploitation, ore transportation, smelting and refining, disposal of the tailings and waste waters around mines, weathering of rocks, and heaped waste materials in mining sites [63, 64]. The list goes on to include draining of sewerage, dumping of hospital wastes, recreational activities, shipping, mining, breweries, tanning, fishing, and agro-processing factories [64, 65]. Further activities include urban storm water runoff, atmospheric sources, boating, biocides runoff, nutrients and pathogens from agricultural lands, urban areas and informal settlements [60], metal fabrication and scraping industries, and indiscriminate use of heavy metal-containing fertilizer and pesticides in agricultural fields [65]. For instance, Reza and co-worker [65] reported that mine water, run-off from abandoned watersheds and associated industrial discharges are the major source of heavy metal contamination, total dissolved solids (TDS) and low pH of streams in the mining area [66–69]. The rivers in urban areas have also been associated with water quality problems. This is due to the practice of discharging of untreated domestic and small scale industries into the water bodies, which leads to the increase in the level of metals concentration in river water [70–74]. It may hence, not be an overstatement to assert that the risk of toxic metals pollution is to the degree, of the number of any chemical process going on in the society, especially in the Sub-Saharan region [75, 76]. The list appears intimidating and further strengthens the need for constant environmental monitoring the presence of the heavy metal in our water bodies.

1.4 Aim and objectives of the study

The upper Crocodile River catchment has witnessed an increase land use and land cover change mainly because of the increased population, increase agricultural practices along the Crocodile River, increase in private resort accommodation and other developmental projects over the past few decades. Regarding the worsening situation on site, the National Environmental Act (Act of 108 of 1998) governs the overall conservation, correct utilization of natural resource and management of natural resource, promote sustainable development, and prohibit activities that will affect the environment. In this regards it requires an Integrated Water Resource Management (IWRM) geared towards maximizing water resource in a sustainable manner, which vital for ecosystems conservation. The key question to be asked is; *is water and other conditions in the Crocodile River have been altered by human activities*? *What are the sources of the potentially toxic element in the river?* Rustenburg is one of the fastest-growing towns in the North-West Province in South Africa and hosts most of the country operating mining and agricultural activities. Due to the ongoing anthropogenic activities bringing about changes in land use pattern (mining and intensive cultivation), irrigation from the Crocodile River, resultant dynamics stable river system will be distinctively different from what would be present under natural setting in the catchment. However, estimated changes in land use and land cover has not been reported to assess the overall impact on the surface water quality of the Crocodile River. Hence the knowledge of LULC dynamics is thus necessary to safeguard the health of the riverine population and to inform management of appropriate measures where mitigation action is necessary. This study aims to: [1] Assess the spatial distributions of physicochemical parameters and PTEs concentrations in the Crocodile River, [2] To evaluate LULC change in the catchment for the period of 1999–2018 using geographical information system (GIS) techniques.

2. Material and methods

2.1 Study area

The upper Crocodile River catchment is situated in Rustenburg, the economic hub of the North-West Province, South Africa (**Figure 1**). The area hosts a number

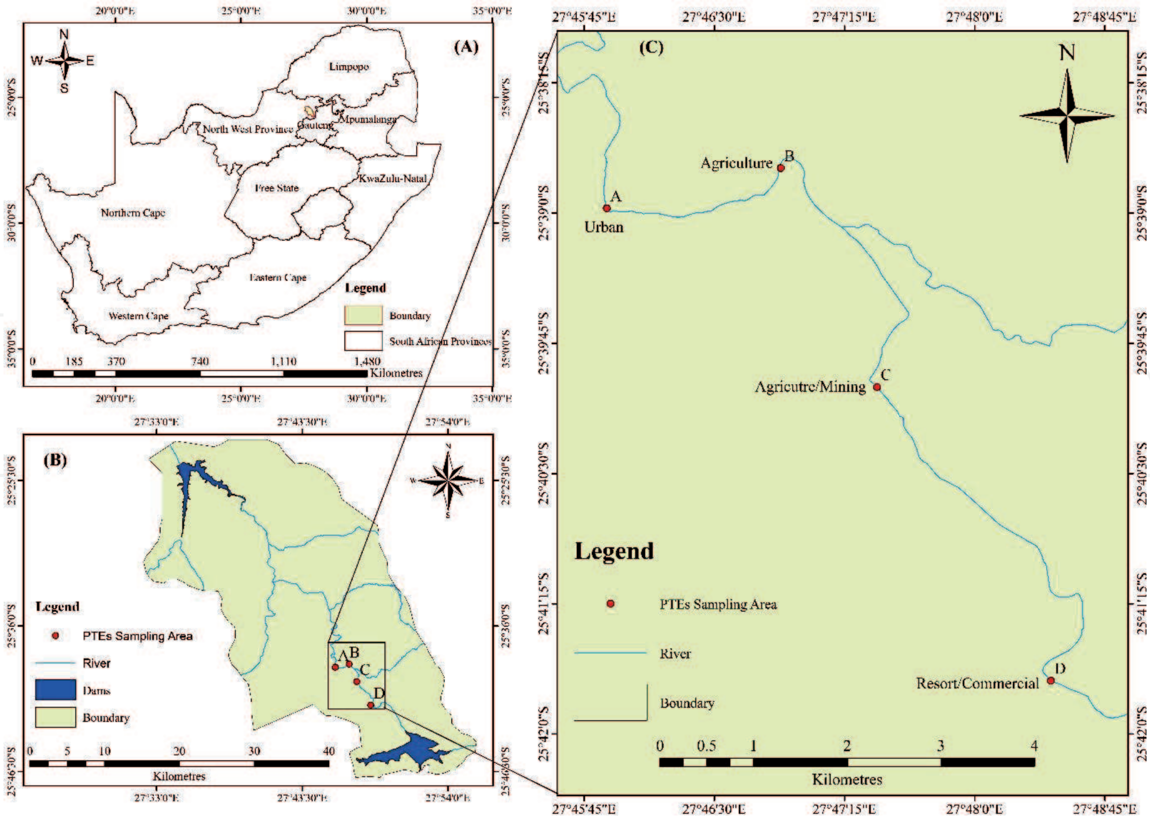

Figure 1.
Study area.

of manufacturing industries, steel and iron smelting, mining and intensive commercial and subsustence agriculture along the Crocodile River. The sub-catchment has two major dams (Roodekopjes and Hartbeespoort) with scattered dams throughout the catchment (**Figure 1B**). These dams act as a source of water supply to the cultivated farmlands and additional water supply is sourced from the borehole and artificial dams. An increasing number of resort accommodations located close these major dams and along the Crocodile River for local and international tourists. The resultant effects of these anthropogenic activities in the marine environment have been reported to be a regular occurrence of filamentous cyanobacteria also known as blue-green algae with several highly toxic biologically active compounds [77–79].

2.2 Surface water sampling

Surface water pollution has been reported as the direct consequence of anthropogenic activity [80–82], and has significantly contributed to the deterioration the Crocodile River [37]. The surface water sampling framework along the Crocodile River was developed based on two considerations; firstly, a proper understanding of the contributing sources as the river traverses the different land uses [20]. Secondly the duration of the sampling framework should be long enough to account for seasonal variation physicochemical parameters and PTEs concentrations in the river. Thus, a longitudinal transect was adopted based on the different land uses within the vicinity of the river. Four sampling point were chosen along the Crocodile River during the field survey to ensured that each of the sampling points was within the vicinity of the different land uses (**Figure 1C**) as prescribed by Chetty and Pillay [83]. Those land uses which overlay each other were considered as areas of non-point sources contributing to the contamination of the river [37]. From the stratified sampling sites, surface water was collected on a quarterly basis for 15 months from April 2017 to July 2018. A handheld GPS (Garmin E-Trex 12 channel) was to record the coordinates for each of the sampling points. A total of 72 surface water samples was collected at different points along the Crocodile River. All the water samples were collected in three litter polyethylene bottles, pre-washed with HNO_3. Surface water quality was analyzed according to the physicochemical parameters that is temperature, pH, electrical conductivity (EC), total dissolves solids (TDS) and potentially toxic elements.

2.2.1 In situ and laboratory analysis

The pH, electrical conductivity (EC) total dissolved solid of the surface water freshly collected at each sampling sites were measured in situ using a multi-meter (CRISON MM40+). Prior to each reading, the meter probe was rinsed with distilled water and immersed in the collected water sample for approximately one minute to reach equilibrium. The reading of each parameter was recorded in a data sheet when the measurement was constant.

2.2.2 ICP-MS analysis

In the laboratory, the surface water samples were first filtered to remove all solid and impurities through a (number 42) filter paper. For each sample, 10 mL of nitric acid was added to a 50 mL of water samples as prescribed by [37] and was analyzed using the inductively coupled plasma spectrometry-mass spectrometry (ICP-MS) (Perkin-Elmer Nixon 300Q) for the following elements; copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), arsenic (As), chromium (Cr), aluminum (Al), manganese (Mn) and iron (Fe). The instrument was calibrated using a standard calibration solution as the atomic spectrometric standard of the mass calibration stability measured using 10 mg/L multi-element standards solution Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U and Zn. The instrument was set to run a blank and a standard check for ten samples for quality control for each measurement. Based on three times the standard deviation of the blank using three second integration time and peak hopping at 1-point per mass. The detection limit (mg/l (ppb)) of the selected metals; Ni (< 0.5), Fe (< 1.5), Cu (0.5) and As (< 0.25) and were then converted to mg/L.

2.2.3 Statistical analysis

The statistical analysis was employed using Microsoft Excel (version 2016) and Stata (version 13). Significant relationships between the physicochemical parameters and PTEs was performed using the person's correlation matrix at 95% confidence level ($p > 0.05$).

2.3 Remote sensing data collection

In order to monitor the LULC change, data sets spanning from two time periods for comparison is needed [84]. Suitable images for the following years, 1999, 2009, and 2018 of the study area was acquired from the South African National Space Agency (SANSA) archive. In order to quantify the LULC changes in the study area, remote sensing approach was employed as it involves the usage of satellite images of multiple dates [84]. Landsat and Spot imagery are readily and freely available in South Africa. However, SPOT images were preferred due to high spatial resolution and to ensure consistency in the cover classes and phenology dates of imagery were selected between May and July for all the three images.

2.3.1 Image processing and analysis

ERDAS Imagine 2020 software package was used for image analysis and processing. A subset of the images corresponding to the study area was created after converting all images to a common format. Subsequently, a pre-processing procedure was necessary to make comparable satellite images obtained from different sensors (SPOT) with different radiometric characteristics and acquisition conditions. Moreover, much of the pre-processing, radiometric, and geometric corrections were accomplished using ERDAS Imagine 2020. Additionally, due to the differences in radiometric resolution, the technique adopted to fit this purpose involved the calibration of the digital numbers (DN's) were converted in the image data from to at-sensor radiance (L_{SAT}) units (W m^{-2} sr^{-1} μm^{-1}).

2.3.2 Geometric corrections and image segmentation

Since the images had different spatial resolution, it became necessary for the images to be geometrically corrected [85]. In order to bring the pixel sizes to a common value, due to differences in date, the Root Mean-Square Error (RMSE) was used. The reason is to avoid registration errors to be interpreted as LULC change which can lead to an overestimation of actual change. Because Landsat data series is characterized by spectral bands which are very sensitive to both vegetation and other earth related features, this was central to the study in mapping the LULC changes [29]. To accurately measure the LULC change, a topographic map with a scale of 1:50,000 produced in 1996 was used for geometric correction using GCP (Ground Control Points) to geocode the image of 2009. The image was then used to register the image of 1999 and 2018, using a nearest-neighbor algorithm. From the three images, the RMSE was less than 0.4 pixel which is acceptable [86]. Image segmentation was conducted using the multiresolution segmentation algorithm [87]. The algorithm requires the specification of the weights of the band, the shape (and its mutual color), the scale parameter and the compactness (and its mutual smoothness), which are expounded by Benz and co-workers [88].

2.3.3 LULC cover change classification and accuracy assessment

In order to investigate changes that would have occurred in the study area, the maximum likelihood classifier (MLC) was used. This method provides an effective and robust supervised classification method. This method has widely been used by different scholars as it evaluates both the variance and covariance of spectral response pattern whereby each pixel is assigned to the class for which it has the highest possibility of association and is considered to be most accurate classifier [29, 84]. MLC assumes that spectral values of the pixels are statistically distributed according to a multivariate normal probability density. Accuracy assessment used an error (confusion) matrix, in which producer's accuracy (PA, %), user's accuracy (UA, %), the Kappa coefficient (K), and overall accuracy (OA, %) were computed [29]. Using ground checkpoints and digital topographic maps of the study area, supervised classification was made use of. The area was classified into five main classes: water bodies, cropland, grassland, bare land, and built-up, as presented in **Table 1** with the description of the land cover classes given therein. To represent different land cover classes of the study area, the assessment of 200 random points was generated for the MLC of the study area per image date using the random stratified method. The "create precision points" function in ERDAS Imagine 2020 was used on the MLC classified images to generate a set of random points.

Class	Description
Water bodies	An area containing open bodies of water, which includes brackish, streams, rivers, dams, and natural ponds as well as artificial ponds.
Cropland	Areas cultivated with annual crops, vegetables, or fruit. These crops are irrigated mainly from the water of the Crocodile river and/or groundwater. Most of the cultivated area is newly reclaimed.
Grassland	For the study area, the plants can be classified into nine life forms such as evergreen non-succulent perennial sub-shrubs, evergreen succulent perennial sub-shrubs, annuals perennial grasses, perennial herbs, evergreen succulent perennial shrubs, evergreen non-succulent perennial shrubs, deciduous perennial shrubs and partially deciduous perennial sub-shrubs.
Bare land	Land areas of exposed soil surface as influenced by human impacts and/or natural causes as well as changes in topsoil that comprises areas with active excavation and quarries and opencast mines. These areas contain sparse vegetation with very low plant cover value as a result of overgrazing, woodcutting, etc.
Built-up	Includes construction activities of all kinds in the study area such as apartment buildings, single houses, shacks, shopping centres, industrial and commercial facilities as well as highways and major streets be it tarred or gravel.

Table 1.
Description of different land cover classes in the study area.

The reference data against which to judge the correctness of classification were obtained from 10 m resolution images on Google Earth® of dates close to the SPOT images. Ancillary data and the result of visual interpretation was integrated with the classification result using GIS in order to increase the accuracy of land cover mapping of the three images and improve the classification accuracy of the classified imagery.

2.4 Quality control/quality assurance

This study has established a sound quality control/quality assurance over a similar study and is references therein [37].

3. Results and discussion

3.1 Spatial variation PTEs in the Crocodile River and its implication to water quality from 2017 to 2018

The results of the trend analysis of the PTEs concentrations in the Crocodile River are presented in order of abundance of Mn in October 2017 (0.34 mg/L), < Cu in July 2017 (0.21 mg/L), < Fe in April 2017 (0.07 mg/L), < Al in July 2017 (0.07 mg/L), and < Zn in April 2017, October 2017 and April 2018 (0.05 mg/L) respectively (**Figure 2**). Similar findings was also reported by Marara and Palamuleni [89] in which Mn, Fe and Zn were amongst the most abundant element in the Klip river in South Africa. This results shows an increase in metal concentrations during the first quarter in the sampling months, owing to low rainfall intensities and runoff [81]. Non-point sources of PTEs in the river might be attributed to dust blown into the river from the cultivated field and mining areas, runoff, iron smelting and exhaust automobile [90]. During the second quarter of the sampling months, changes in rainfall pattern might have influenced the PTEs concentrations in the river due to the diluting effect from the different land uses. Usually, the rainfall season begins in October and peaks in intensity from October to February.

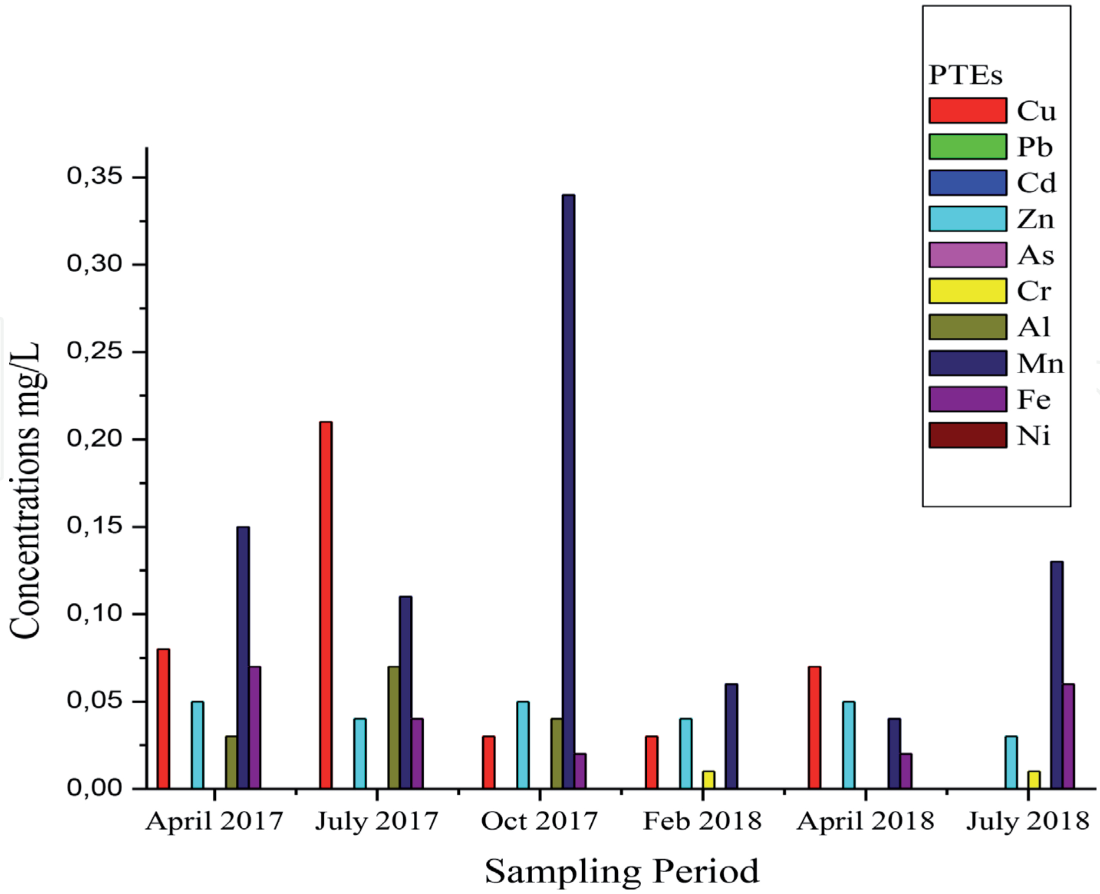

Figure 2.
Trend analysis of PTEs concentrations during the sampling periods.

The concentrations of PTEs during this sampling month might likely have had some diluting effect in the river metals concentration. A similar study by du Preez and co-workers [91] asserts that a reduction in nutrients in the Crocodile River could be attributed to the diluting effect, especially during periods of high current flow.

Further, Ogoyi and co-workers [92] examined the content of PTEs in water, sediment and microalgae from Lake Victoria, which is the largest tropical fresh water lake in the world [93], representing an exceptional ecosystem with the largest fresh water fishery in the continent [92]. It is located in East Africa and surrounded by Uganda on the North West, Kenya on the North East, Rwanda on the far West and Tanzania on the South–South [94, 95]. They collected water samples from two different points namely from Winam and Mwanza gulf and using atomic absorption spectrophotometry (AAS) examined the level of heavy metal pollution of lead, cadmium, chromium, mercury and zinc. The analysis of the water sample as summarized in **Table 2** indicates that the presence of lead, cadmium and chromium at the Mwanza gulf point (LVEA-MGP) were 2.2, 2.3 and 1.4 times respectively higher than the recommended permissible threshold standard by WHO (**Table 2**), while the mercury and zinc were within the recommended limit for safe water. At the Winam gulf point (LVEA-WGP), the level of PTEs concentration for lead and chromium was 82.3 and 3.56 times respectively higher than the recommended permissible threshold limit by WHO while the rest were within safe limits. They argued that there is a link between PTEs pollution and anthropogenic activities like waste disposal and mining in the environs [75]. They concluded that the PTEs pollution at these points of the lake was relatively low, but emphasized the need for continuous monitoring of the PTEs pollution in the lake [65]. Chief Albert Luthuli Local Municipality is situated on the eastern scarp of Mpumalanga Province of Republic of South Africa. The Municipality covers a land area of nearly 5.560km^2,

PTES/water Source	$\frac{W_{Pb}}{WHO_{Pb}}$	$\frac{W_{Cd}}{WHO_{Cd}}$	$\frac{W_{Hg}}{WHO_{Hg}}$	$\frac{W_{Cr}}{WHO_{Cr}}$	$\frac{W_{Cu}}{WHO_{Cu}}$	$\frac{W_{Zn}}{WHO_{Zn}}$	$\frac{W_{Fe}}{WHO_{Fe}}$	$\frac{W_{Mn}}{WHO_{Mn}}$	$\frac{W_{As}}{WHO_{As}}$	References
LVEA-MGP	2.2	2.3	0	1.4	—	0.006	—	—	—	[92]
LVEA-WGP	82.3	0	0	3.56	_	0.017	—	—	—	[92]
BHMPRSAJ	>8	—	—	>0.2	>0.01	>0.03	—	>1		[64]
DZindi River	3	—	—	—	0.025	0.033	4.433	1.5		[62]
AAP	—	1.7	2	—	—	0.043	2.233	8.54	0.3	[94]
OAP	—	1.7	3	—	—	0.00167	3.11	7.92	0.3	[94]
US	—	1.7	2	—	—	0.00167	4	7.23	0.3	[94]
MS	—	5666.7	9	—	—	0.0097	4.74	5.77	0.2	[94]
DS	—	1.7	154	—	—	0.0547	22.2	8.72	0.2	[94]
AB	—	2.7	2	—	—	0.0013	5.9	1.13	0.4	[94]
LWW	102	183.3	—	22	0.255	1	—	—		[98]
PBW	279	476.7	—	100	1.51	4	45.4	175		[99]
BH	455	463.3	—	326.8	0.58	4.923	77.5	991.4		[99]
STREAM	29	746.7	—	402.2	1.755	2.063	20	113.2		[99]
RIVER	669	1546.7	—	101.2	1.075	1.547	105.8	61.2		[99]
HDW	401	320	—	2275.6	23.175	49.1	47.1	936.5		[99]
Crocodile River	**2**	**—**	**—**	**—**	**0.01**	**0.017**	**—**	**1.9**		**Present work**

LVEA-WGP: Lake Victoria East Africa-Winan Gulf Point; LVEA-MGP: Lake Victoria East Africa-Mwanza Gulf Point. BHMPRSAJ: Borehole at Mpumalanga South Africa, ELH: East London Harbor, PEH: Port Elizabeth Harbor; Accra Abandoned Pit (AAP), OAP: Obuasi Abandoned Pit, AB: Accra Borehole, US: Up stream, MS: Main Stream, DS: Down Stream; LWW: Lagoon Waste water; BH: Borehole, HDW: Hand dug well; PBW: Pipe Borne Water.

Table 2.
Heavy metal pollution level in some selected African water bodies.

and a report from the Stats SA 2016 Community Survey, indicates its home to some 187,630 people, which have increased. The Municipality is made up of various communities confronted with a society that faces sundry economic, social, environmental, and governmental challenges. Approximately 80% of the populace live in the rural areas concentrated in the east of the area; the two main service centres of Emanzana and Carolina provide a home for 15% of the people while the remaining population are found in the forestry and farming areas of the Municipality [96]. Nthunya and co-workers [64] investigated the source of toxic metals in drinking water in this Chief Albert Luthuli Local Municipality in Mpumalanga, South Africa. Their work was so detailed and captured five different points over four seasons of the year, winter, spring (August 2014), summer (November 2014), autumn (February 2015). The sampling points included a drinking water treatment plant in Eerstehoek bout 5 km from Lochiel, a 50 m deep open well used largely by the community and the students of a nearby school designated as well 1; an open shallow well located in the upper part of Lochiel and used by the residents designated as well 2; Tanks 1 and 2 located in the Lochiel Primary school premises and the community respectively. The latter of the two tanks is being used by the larger part of the community and finally a borehole in Masakhane primary school supplying water to the school tank and taps. Using ICP-OES spectrometer suited with iTEVA software for measurements of all the analytes at maximum wavelength, they investigated the presence of nine heavy metal pollutants in the drinking water which are namely: cadmium, chromium, copper, cobalt, iron, manganese, nickel, lead and zinc (**Figure 3**).

Figure 3 represents the physical properties of the various water samples and the concentration of toxic metals in ppm. Their results indicate that the concentration of toxic metals varied across the seasons and sources. The lead concentration was found to be above WHO limit for drinking water in well 1 & 2, Tanks 1 & 2, surprisingly in both raw and treated water in February 2015, and bore hole for all seasons considered. In autumn, the level of Manganese rose above the WHO limit in the untreated water. Cobalt for most of the periods of the year considered remained above WHO limits for safe and potable water. The rest of the metals were largely within the WHO drinking water limit. The borehole is ground water mainly used by a greater percentage of African populace as already established in the earlier part of the review [97]. **Table 2** indicates that the borehole water taken in July designated as BHMPRSAJ has a lead and cobalt concentration that is greater than the WHO limit by a factor greater than 8 and 1 respectively as at 2014/2015. They argued that the source of these toxic metal accumulation in this locality is both natural and anthropogenic, which include weathering of mineral rich rocks and indiscriminate disposal of metal rich wastes at the landfills. In conclusion, they underscored that long-term exposure to the toxic heavy metal can be fatal and hence, the need to further purify and monitor the quality of drinking water regularly.

Another detailed work was done on the assessment of heavy metals in drinking water, at Datuku in the Talensi-Nabdam District in the Upper East region of Ghana by Cobbina and co-workers [94]. They aimed to evaluate the impact of small scale gold mining on the drinking water quality in that community. Samples were collected from six sources namely: Accra abandoned pit (AAP), Obuasi abandoned pit (OAP), mainstream (MS), upper stream (US), Accra borehole (AB) and down stream (DS). Using the Shimadzu model AA 6300, they evaluated the trace concentration of Zn, As, Cd, Fe, Mn and Hg in these five places. Their results show that Cd, Fe, Hg and Mn level was higher than the standard for safe water by WHO, while As and Zn were within the limit safety for all the sources (**Table 2**). The level of Cd concentration on the mainstream source (MS) was 5666.7 times higher than the WHO standard for safe water. The level of Fe contamination was taken with

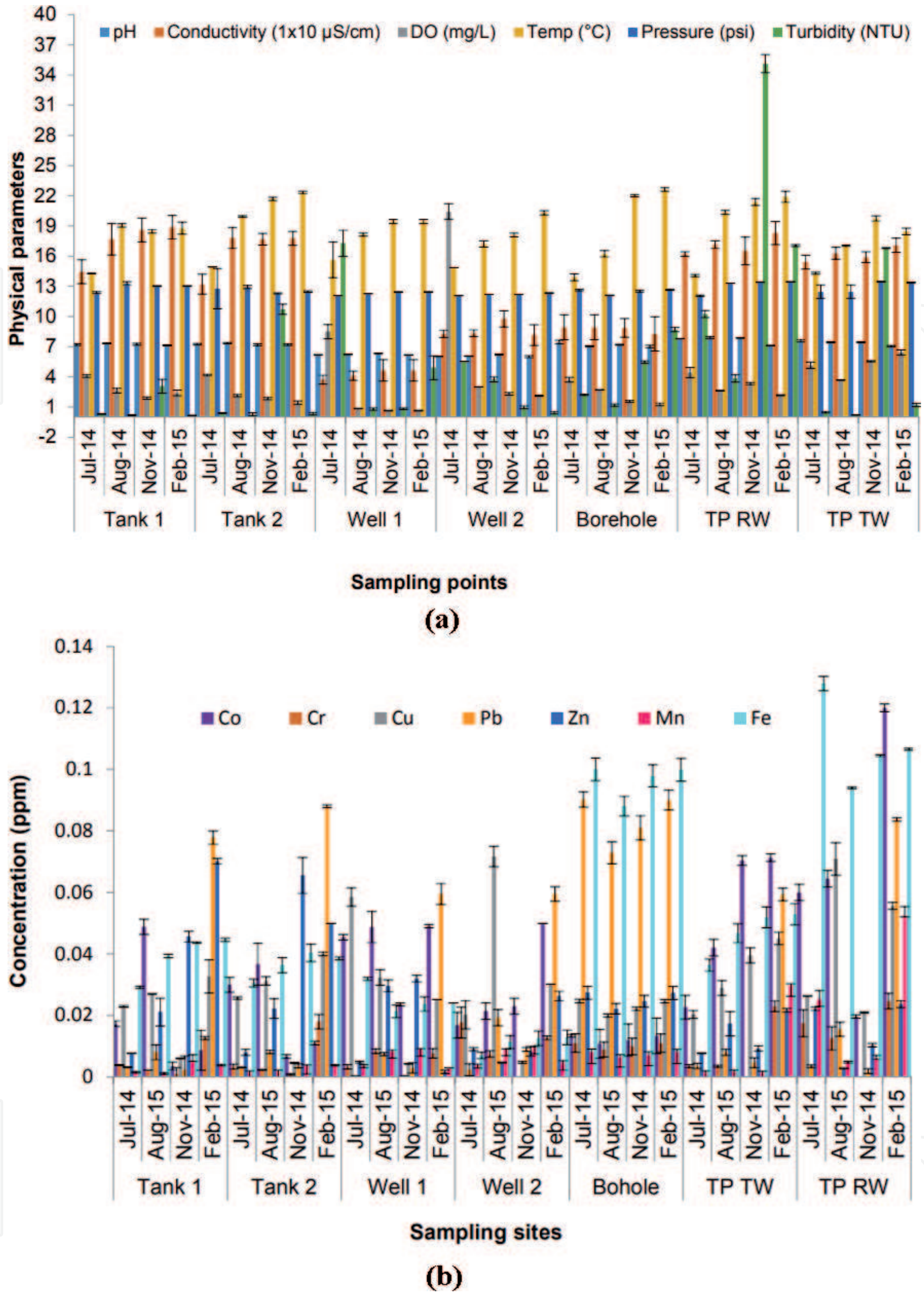

Figure 3.
(a) The physical properties of the various water sources under consideration (b) the number of toxic metals present from the various water sources in winter, spring (August 2014), summer (November 2014), autumn (February 2015). TP TW: Treated Plant Treated Water and TP RW: Treated Plant Raw Water [64].

reference to US-EPA and was also found to be higher than the accepted limit by a factor greater than 2 for all the sources of the water. They opined that cadmium pollution could be as a result of seepage from the parent rock, use of cadmium containing products such as batteries, plastics and mining tools.

Orata and Birgen [98] studied the uptake of heavy metals by different fishes and their tissues in a lagoon waste water (LWW). They proposed that their study would provide a useful tool for envisaging human exposure to PTEs through consuming fish under different contamination scenarios. The lagoon wastewater body had heavy metals concentration of the most lethal class of lead, cadmium, and chromium in an amount that is 102, 183.3 and 22 times respectively higher than the WHO accepted standard of safe water (**Table 3**) and other environmental agencies (**Table 4**). They hence concluded that various species of fishes studied in this scenario were unsafe for consumption sequel to the uptake of heavy metals in various parts of their bodies. Another similar and detailed work was done to inspect the physicochemical properties and heavy metal content of water sources in Ife North Local Government Area of Osun State, Nigeria by Oluyemi and co-workers [99, 100]. While they concluded that the physical parameters of the water collected from pipe borne water (PBW), borehole (BH), stream, river and hand-dug well (HDW) were within limits for potable and household water, the AAS results of heavy metal concentration of Pb, Cd, Cu, Cr, Fe, Mn and Zn is a far cry from safe limits for drinking water (**Table 2**). Pd and Cd levels were 279 and 476.6 times in pipe borne water and 455 and 463.3 times in borehole (BH) above the WHO standard for safe domestic and drinking water. These two sources of water have been validated as the most common sources of water for Africans in rural settings. They opined that such high concentration of these PTEs cannot be disconnected from mining activities, leaching of metals from wastes site to the ground water plus rural and urban water run-off, and possible wearing of lead from metal pipes into the water during the distribution.

In this study, the following elements Cd, As, and Ni, concentrations in all the sampling points were below the detection limits except for Cr (0.1 mg/L) in point C (Agriculture/Mining) and Pb (0.02 mg/L) in point D (Resort/Commercial).

Metal	WHO	EPA	ECE	FTP-CDW	PCRWR	ADWG	NOM-127	DWAF
Aluminum	N/A	N/A	N/A	N/A	N/A	N/A	N/A	< 0.005
Nickel	0.07	0.04	0.020	N/A	0.020	0.020	N/A	< 1
Copper	2	1.3	0.200	0.100	0.200	0.200	0.200	< 2
Zinc	3	5	N/A	5.000	5.000	3.000	5.000	5
Cadmium	0.003	0.005	0.005	0.005	0.010	0.002	0.005	0.003
Lead	0.01	0.015	0.01	0.01	0.05	0.01	0.01	0.01
Mercury	0.001	0.002	0.001	0.001	0.001	0.001	0.001	
Arsenic	0.010	0.010	0.010	0.010	0.050	0.010	0.025	0.01
Antimony	0.020	0.006	0.005	0.006	0.005	0.003	N/A	
Iron	N/A	0.300	0.200	0.300	N/A	0.300	0.300	0.1
Uranium	0.030	0.030	N/A	0.020	N/A	0.017	N/A	
Manganese	0.10	0.500	0.500	0.500	0.500	0.500	0.150	0.18
Thallium	N/A	0.002	N/A	N/A	N/A	N/A	N/A	
Silver	N/A	0.100	N/A	N/A	N/A	0.100	N/A	
Chromium	0.050	0.100	0.050	0.050	0.050	0.050	0.050	0.05

Key: DWAF = Department of Water Affairs and Forestry, South Africa. EPA* = US- Environmental Protection Agency(2011). WHO* = World Health Organization (2011), N/A* = Not reported or Not available and BDL* = Below detection limits, ECE: European Commission Environment (1998), FTP-CDW: Federal-Provincial-Territorial Committee on Drinking Water, Health Canada (2010), PCRWR: Pakistan Council of Research in Water (2008), ADWG: Australian Drinking Water Guidelines (2011), NOM-127: Norma Official Mexicana NOM-127-SSA1–1994 (1994).*

Table 3.
Standards and guidelines for heavy metals in drinking water (mg/L), recommended by the Environmental Protection Agency (EPA) and world health organizations (WHO) for drinking water that is based on data of toxicity and scientific findings.

Metals	Seawater(mg·L^{-1})		Sediment (mg·L^{-1})	
	EEC	ANZECC	CEPA	PSAG
Cd	2.5	2	2	10
Cu	5	5	8	500
Fe	—	—	—	—
Pb	15	5	22	500
Mn	—	—	—	—
Zn	40	50	40	750

Table 4.
Guidelines for metals in seawater and sediment by EEC: European Commission environment; ANZECC: Austrialian and new Zeland environmental conservation council; CEPA: Cannadian Environmental Protection Agency; PSAG: Proposed South African guidelines.

Site ID	Cu	Pb	Cd	Zn	As	Cr	Al	Mn	Fe	Ni
A	0.02	BDL*	BDL*	0.04	BDL*	BDL*	**0.02**	**0.13**	0.02	BDL*
B	0.10	BDL*	BDL*	0.05	BDL*	BDL*	**0.03**	**0.22**	**0.04**	BDL*
C	0.16	BDL*	BDL*	0.05	BDL*	0.01	**0.02**	**0.15**	**0.14**	BDL*
D	0.02	0.02	BDL*	0.05	BDL*	BDL*	**0.04**	**0.19**	**0.09**	BDL*

Table 5.
Average PTEs concentrations (mg/L).

The spatial distribution of Mn, Cu, Fe, Al and Zn along the different land uses in the Crocodile River is presented in **Table 5** and **Figure 4**. The concentration of Mn is quite variable along the different land uses and the highest value of 0.22 mg/L was recorded in point B (Agriculture) while the least value (0.13 mg/L) in point A (Urban). The concentration of Cu also varied spatially along the river with the highest value in point C (Agriculture/Mining) while point A (Urban) and D (Resort/Commercial) had the lowest values of 0.02 mg/L respectively (**Table 2**; **Figure 4**). Fe had the highest concentration in point C, while point A had the lowest concentration value. The concentrations of Al along the different land uses were slightly different from each sampling and point A and C had the lowest concentrations of 0.02 mg/L respectively. The average concentration of Zn in the river indicates that point A, B and C all had the same concentration value of 0.05 mg/L, respectively but with a slight drop in the concentration value of point A (0.04 mg/L) (**Table 2**; **Figure 4**).

Three water quality guidelines permissible threshold values were used to gauge the level of PTEs concentrations in the river (**Table 5**). The results indicate that most of the elements were within the DWAF (Department of Water Affairs and Forestry, South Africa, 1997, and 1997b), stipulated guideline for aquatic environments except for Al, Mn and Fe exhibiting high concentration values above the permissible threshold limit of DWAF of <0.005, 0.18 and 0.1 mg/L respectively (**Table 3**). Similarly, the value of Mn in the Crocodile River exceeded the recommended threshold guideline for EPA of 0.05 mg/L. The concentration of Al in the river exceeded the DWAF guideline in all the sampling points, while Mn concentration exceeded the recommended threshold value by EPA, for all the sampling points, and also that of DWAF at point B (Agriculture) and D (Resort & Commercial). In contrast, the values of Fe exceeded the permissible limit of DWAF

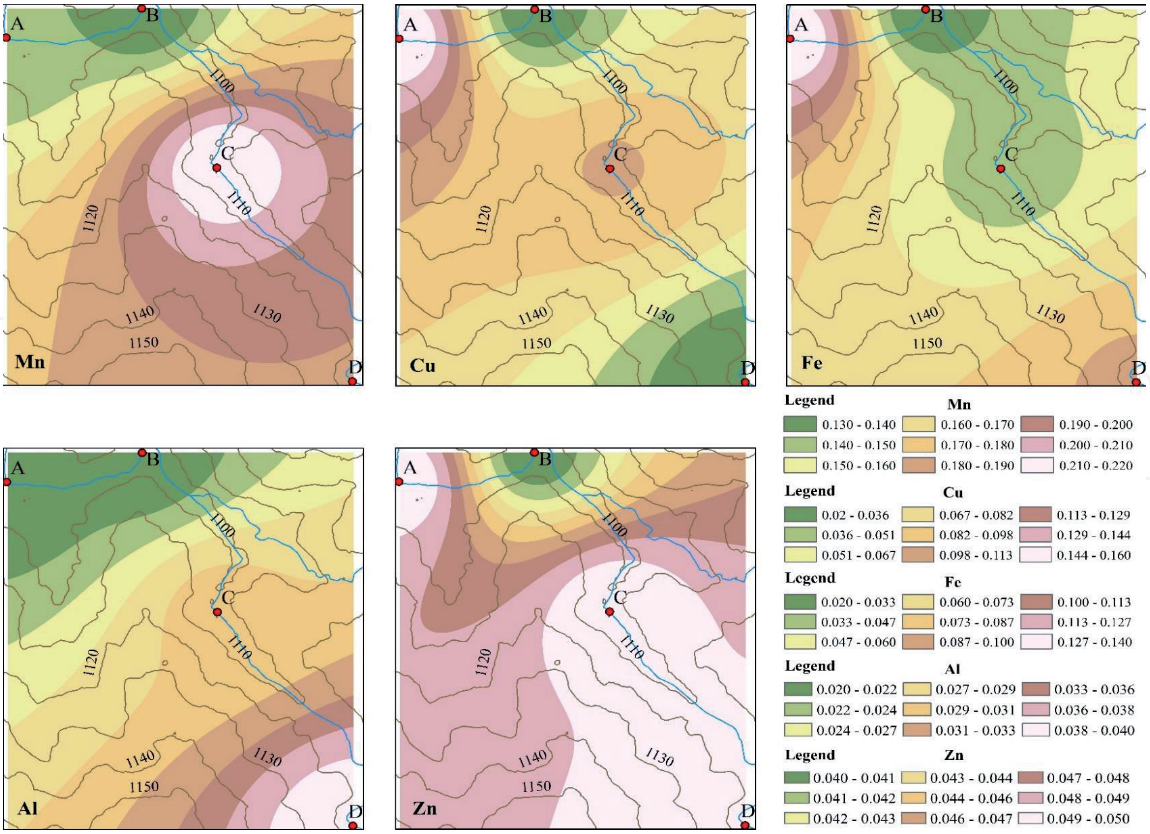

Figure 4.
Summary of the average concentrations (mg/L) of PTEs in the Crocodile River.

at point C (Agriculture/Mining). Cd, As and Ni concentrations in the river were below the detection limit or were not present in the water.

Although the following elements As, Ni, Cd, Pb and Cr analyzed exhibited low concentrations values; however, it cannot be concluded that the river is not contaminated. For instance, Pb concentration in point D (0.02 mg/L) exceeded all the water quality guidelines (DWAF, WHO and EPA) as seen in **Table 3** and a plausible explanation could be attributed to point-source contamination. This is an indication that the river might eventually be polluted in the future if proper mitigation measure is not put in place due to the diverse anthropogenic activities within the vicinity of the river [36]. These changes might also be due to the spatial–temporal input from agricultural areas, surface runoff from different mining areas, untreated wastes disposal from resort accommodation, catchment sensitivity, and settlement dumpsites close to the river [62].

3.2 Seasonal variation of physicochemical parameters and PTEs in the Crocodile River

3.2.1 Physicochemical parameters in the Crocodile River

Studies by Okonkwo and Mothiba [101] and Somerset and co-workers [102] have reported changes in physicochemical and heavy metal concentrations in South African rivers due to changes in the seasons. The results of the physicochemical parameters between the different seasons are shown in **Table 6**. The analysis of the water temperature at the different sampling points was slightly different but was distinctively different between the wet (summer) and the dry season (winter) (**Table 6**). At the time of the water collection, the wet season had a maximum temperature of 28.6°C ± 0.35 while the dry season (winter) had a minimum

Sampling Points		Temp(°C)		EC (µs/cm)		pH		TDS (mg/L)	
	Site ID	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Point A	Urban	28 ± 0.14	19.8 ± 1	520.0 ± 4.24	561.5 ± 51.84	8.2 ± 0.01	7.6 ± 0.29	355.5 ± 34.6	393.0 ± 95.64
Point B	Agriculture	28.6 ± 0.35	20.0 ± 0.91	517.0 ± 0	544.3 ± 37.87	8.5 ± 0.55	7.5 ± 0.41	381.5 ± 71.4	396.5 ± 75.39
Point C	Agriculture/Mining	28.4 ± 0.35	19.9 ± 0.84	509.0 ± 4.24	568.0 ± 25.36	8.4 ± 0.26	7.4 ± 0.57	321.5 ± 0.7	391.0 ± 88.74
Point D	Resort/Commercial	28.3 ± 0	19.6 ± 1.06	533.0 ± 14.14	563.8 ± 54.03	8.1 ± 0.02	7.7 ± 0.41	355.0 ± 0	412.0 ± 97.97
DWAF*		N/A*		400–900		5.0–9.5		450–900	
WHO*		N/A*		N/A*		7.0–8.5		N/A*	
EPA*		N/A*		N/A*		6.5 ≤ pH ≤ 8.5		500	

N/A = Not Available. DWAF* = Department of Water Affairs and Forestry, South Africa. EPA* = (US- Environmental Protection Agency). WHO* = World Health Organization.*

Table 6.
Seasonal variation in the average concentrations of the physiochemical parameters in the crocodile river.

temperature of 19.8°C ± 1. The EC values from across each of the sampling points ranged from 509 μs/cm to 533 μs/cm in the wet season while during the dry season the readings ranged from 544.3 μs/cm to 568 μs/cm.

The pH concentration in the river varied slightly between each sampling points with a maximum value of 8.5 for the wet season and 7.7 for the dry season (**Table 6**). According to du Preez and co-workers [91], an increase in pH concentrations might have a negative impact on water quality and its suitability in watering crops and animals. Although the pH values were generally lower, its value, however, indicates that the water is slightly alkaline in most of the sampling points for drinking water which is deleterious for the animals and human in the catchment. Evidence from the field visit also suggests that the water from the Crocodile River is abstracted and irrigated for agricultural purpose. Bouaroudj and co-workers [103] report that the continuous irrigation of crops with saline waters may lead to a gradual or rapid increase in soil salinity. The concentration of TDS (mg/L) in the river from the different sampling point varied from a 321.5 ± 0.7 to 381.5 ± 71.4 for the wet season while for the dry season it varied from 391.0 ± 88.74 to 412.0 ± 97.97 (**Table 6**). A study by du Preez and co-workers [91], attributed an increase in EC and pH in the Crocodile to anthropogenic activities likely from runoff caused by agricultural activity while Wongsasuluk and co-workers [104] attributed an increase in EC due to seasonal variation, thus confirming the role of seasonal variations in physicochemical parameters.

3.2.2 Seasonal variations in PTE concentrations in surface water

The assessment of PTEs in the Crocodile River suggests there is a significant variation ($p > 0.05$) of each element between seasons (**Figures 5** and **6**). The average concentration of Cu in the dry season ranged from 0.01 to 0.018 mg/L while those for the wet season ranged from 0.03–0.04 mg/L signifying an elevated concentration during the wet season. Although the value of Cu between the two seasons was within the safe permissible limit stipulated by DWAF (< 0.2 mg/L), WHO (< 0.2 mg/L) and EPA (US) (0.3 mg/L). However, a study by Ahmad and Goni [105] states that Cu concentration at 0.01 to 0.02 mg/L might be toxic because of the presence of salts (chlorides and litigates). Analysis of Al in the river for the

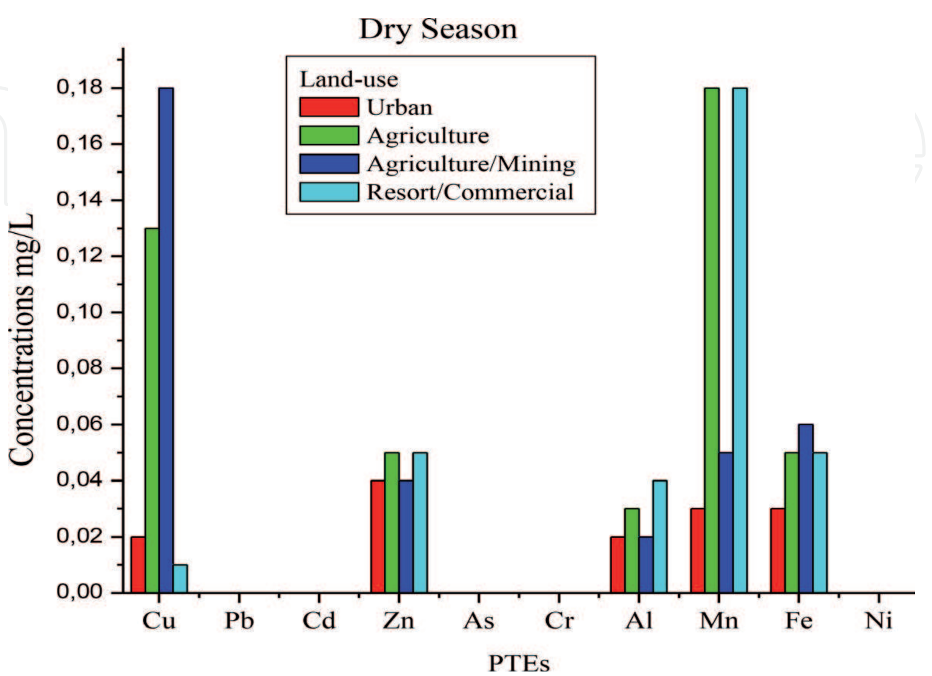

Figure 5.
Average PTEs concentration (mg/L) in surface water.

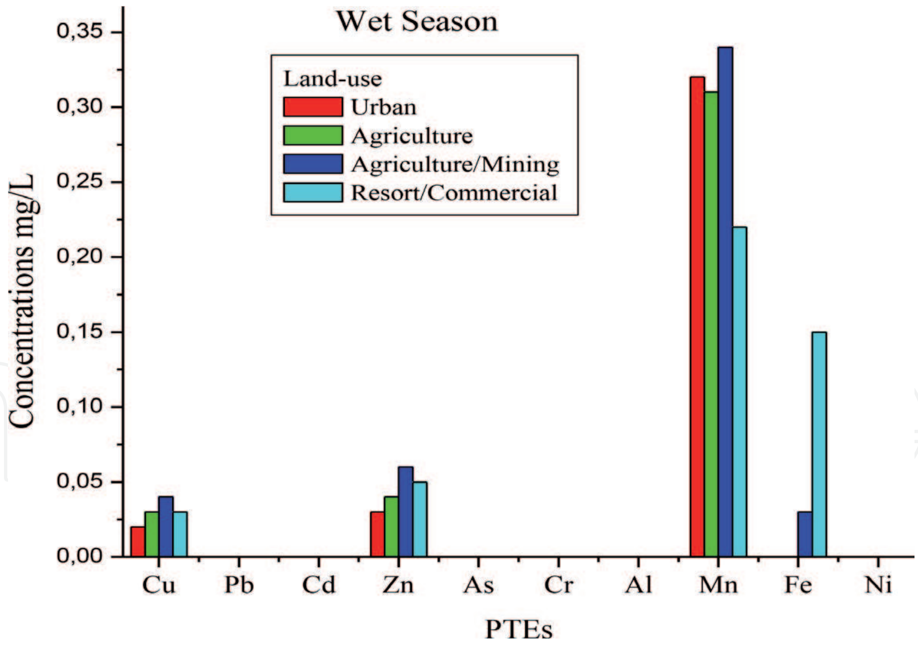

Figure 6.
Average PTEs concentration in the Crocodile River.

dry seasons ranged from 0.02–0.04 mg/L whereas during the wet season it was not detected in the water samples. A plausible reason why Al was found in the water during the dry season might be due to the discharge of waste effluent from nearby private resort accommodation, agricultural surface runoff and commercial waste dumping directly into the river. Marara and Palamuleni [89] reported an increase in toxic element in the Klip river, South Africa to high evaporation rates and low flow rates of water during the season which is similar to the findings of this research.

The average concentration of Mn in the river ranged from 0.03–0.18 mg/L (dry season) while for the wet season it ranged from 0.22–0.34 mg/L. The findings of this study is in line with those reported by Li and Zhang [106], whereby an increase concentration of Mn during the wet seasons in the Upper Han River in China. Fe concentration for the dry season ranged from 0.03–0.05 mg/L while in the wet season, it ranged from 0.03–0.15 mg/L recorded only at points C and D respectively, whereas point A and B were below the detection limit and or might not be available in the water. The observed high concentration of Fe during the dry season compared to the wet season might be attributed to significant anthropogenic disturbance dominated primarily by physical weathering in the river as source areas [89].

3.2.3 Correlation matrix of PTEs in the water samples

The results of the Pearson's correlation coefficients (r) ($p > 0.05$) between the PTEs and the physicochemical parameters are shown in **Table 7**. The results of the physicochemical parameters of the water showed a highly significant positive correlation with each of the parameters with temperature and EC ($r = 0.96$), temperature and pH ($r = 0.99$), temperature and, TDS, ($r = 0.98$) and pH and EC, ($r = 0.99$), TDS and EC ($r = 1$) as indicated in **Table 7**.10. Also, the pH was significantly positively correlated with all the PTEs, thus indicating that the pH influences the concentration of PTEs in the Crocodile River. Similarly, the temperature correlation with the PTEs showed positive to significantly strong positive with Zn, Mn and Cu ($r = 0.63$, $r = 0.64$ and $r = 0.76$) respectively. The correlation between the PTEs showed a significant positive correlation between Mn and Zn ($r = 0.70$), Mn and Al ($r = 0.71$) while Fe and Cu, Fe and Zn showed strong positive correlation **Table 7**.

	Tem	**EC**	**pH**	**TDS**	**Cu**	**Zn**	**Al**	**Mn**	**Fe**
Tem	1								
EC	**0,96**	1							
pH	**0,99**	**0,99**	1						
TDS	**0,98**	**1,00**	**1,00**	1					
Cu	**0,76**	**0,77**	**0,77**	**0,77**	1				
Zn	**0,63**	0,39	**0,52**	0,46	**0,54**	1			
Al	−0,05	−0,31	**−0,17**	−0,24	−0,43	**0,52**	1		
Mn	**0,64**	0,44	**0,55**	0,50	**0,08**	**0,70**	**0,71**	1	
Fe	0,16	0,03	0,10	0,06	**0,62**	**0,65**	0,02	**−0,08**	1

Correlation is significant at the p > 0.05 level. (2-tailed).

Table 7.
Pearson correlation coefficient matrix of the physiochemical parameters and PTEs in the river.

3.3 Land use and land cover change detection in the catchment

The Crocodile River catchment witnessed a considerable change in land use and land cover during the two decades. The results from the observed changes of the land use and land cover in the study area during the selected periods (1999–2009-2018) are illustrated in **Tables 8**–**10** and **Figure 7**. **Table 8** shows the results of the accuracy assessment for the study area. Thematic map of the study area shows the overall accuracy classification of 77% with an overall kappa statistic of 0.7579 in 1999. Cropland and grassland user accuracy yielded 73% and 70% respectively. Bare land was correctly classified at 75% user accuracy, and built-up land yielded a classified user accuracy of 78% as per the actual representation on the ground. Water bodies were correctly classified at 88%, thus making it the highest user's accuracy. Classification of 2009 had an overall accuracy of 84% ($\hat{K}$ = 0.8341), slightly better than the 1999 image. Water bodies had the highest user's accuracy, at 100%. Bare land had a user's accuracy of 73%, built-up area had user's accuracy of 85%, while cropland and grassland had user's accuracy of 75% and 88% respectively. On the other hand, the 2018 image produced an overall kappa statistic of 0.7832 with an overall accuracy of 79%. The built-up class had a user's accuracy of 80%, while the cropland area had 73%. The bare land class, as well as the grassland, were both classified with a user's accuracy of 75%, while the water bodies' class produced a user's accuracy of 93%, which was the highest out of all the five classes.

3.3.1 Change detection in the study area

Tables 8, **9** and **Figure 7** shows all the major land use classes in the area. It was noted that between 1999 to 2009, cropland increased by 25 462 ha and with a land cover change of 21.8% but decreased from 2009 to 2018 by −7 884 ha and with a − 5.5% changes in land cover. However, from 1999 to 2018, cropland witness 15.05% general change land cover and 1.44% change rate. The observed change can be attributed to a number of natural factors such as climate changes, and anthropogenic factors such as loss in soil fertility, changes in land use pattern/management, bush encroachment amongst others. It is also possible that climate change has played a leading role to the loss of cropland from 2009 to 2018. Grassland decreased by −2 159 ha between 1999 to 2009 with a land cover change of −1.9% but increased

Accuracy assessment for study area 1999 MLC classified							
Classification	**Cropland**	**Grassland**	**Bare land**	**Built-up**	**Water bodies**	**Row total**	**User 'accuracy**
Cropland	29	3	3	3	2	40	73%
Grassland	4	28	3	2	3	40	70%
Bare Land	2	4	30	4	0	40	75%
Built-up	3	3	3	31	0	40	78%
Water	2	2	1	0	35	40	88%
Column total	40	40	40	40	40	200	—
Producer's accuracy	73%	70%	75%	78%	88%	—	77%
Overall Kappa ($\hat{K}$) = 0.7579							
Accuracy assessment for study area 2009 MLC classified							
Cropland	30	2	7	1	0	40	75%
Grassland	3	35	1	1	0	40	88%
Bare Land	5	2	29	4	0	40	73%
Built-up	2	1	3	34	0	40	85%
Water	0	0	0	0	0	40	100%
Column total	40	40	40	40	40	200	—
Producer's accuracy	75%	88%	73%	85%	100%	—	84%
Overall Kappa ($\hat{K}$) = 0.8341							
Accuracy assessment for study area 2018 MLC classified							
Cropland	29	4	3	2	2	40	73%
Grassland	6	30	2	1	1	40	75%
Bare Land	3	3	30	4	0	40	75%
Built-up	2	2	4	32	0	40	80%
Water	2	2	1	0	35	40	88%
Column total	40	40	40	40	40	200	—
Producer's accuracy	73%	70%	75%	78%	88%	—	77%
Overall Kappa ($\hat{K}$) = 0.8341							

Table 8.
Accuracy of LULC obtained from satellite data for the selected periods.

from 2009 to 2018 by 28 771 ha having a land cover change of 25.8%. Also, from 1999 to 2018 grassland witness an overall increase of 23.42% change in land cover with an annual change rate of 2.76%. This could be attributed to increased conservation in protected areas for game hunting as the number of privately owned resort accommodation increased for ecotourism [29].

Similarly, between 1999 and 2009 and from 2009 to 2018, bare land decreased from −22 163 ha to −20 775 ha respectively, with an annual negligible land cover

Land cover categories	1999–2009		2009–2018		1999–2018
	Area (ha)	Percentage Change	Area (ha)	Percentage change	Percentage change
Cropland	+25 462	+21.8	−7 884	−5.5	15.05
Grassland	−2 159	−1.9	+28 771	+25.8	23.42
Bare Land	−22 163	−19	−20 775	−22	−36.81
Built-up	−1 978	−1.7	−685	−0.6	−2.29
Water bodies	+838	+0.7	+573	+0.5	1.18

Table 9.
Trend changes in study area land cover categories.

Land cover categories	1999–2009		2009–2018		1999–2018
	Area (ha)	Percentage Change	Area (ha)	Percentage change	Percentage change
Cropland	+2 546.2	+2.2	−876	−0.7	1.44
Grassland	−215.9	−0.2	+3 196.78	+3	2.76
Bare Land	−2 216.3	−1.9	−2 308.33	−2	−3.88
Built-up	−197.8	−0.2	−76.11	−0.1	−0.28
Water bodies	+83.8	+0.1	+63.67	+0.1	0.18

Table 10.
Annual rate of change in land cover categories for study area.

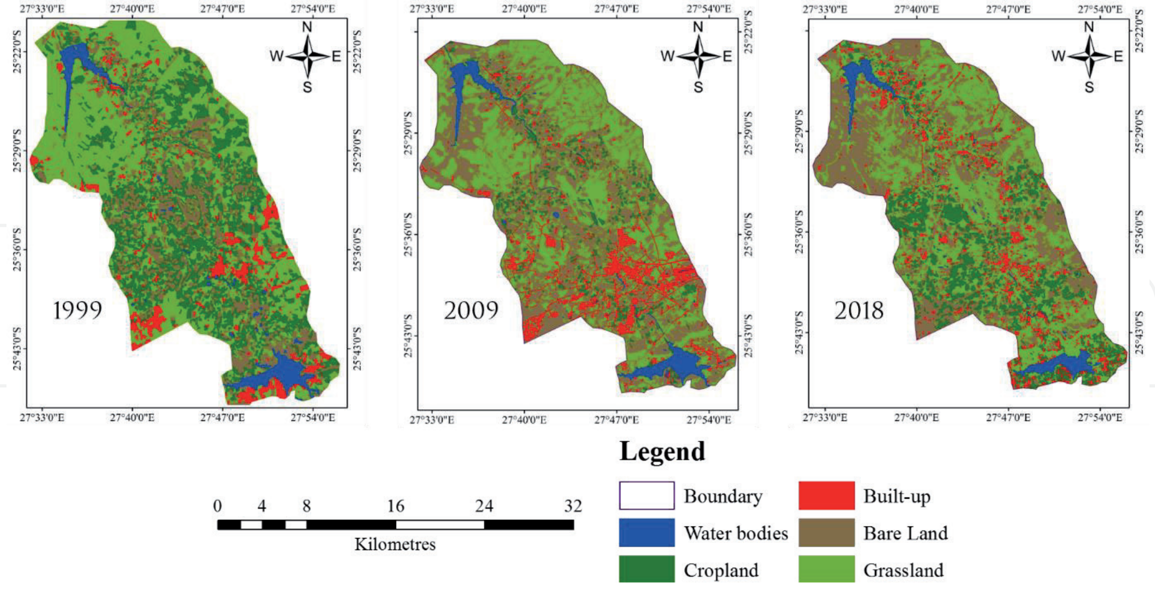

Figure 7.
Land use and land cover map of the upper crocodile river catchment from 1999 to 2018.

change of 1.9% and – 22% respectively and with an overall land cover change of −36.81% and annual change rate of −3.88 spanning from 1999 to 2018. The decrease in bare land suggests that other land uses such as grassland are slowly occupying the bare land. Similarly, Built-up also decrease from 1999 to 2009 by −1 978 ha and between 2009 to 2018 by −685 ha witnessing a change of −2.29% in land cover change and – 0.28% annual change rate from 1999 to 2018. Similar explanation as for bare land hold true with the exception that built-up areas are highly influence by man reconfiguring the environment.

Water bodies increased from +838 ha from 1999 to 2009 and with a slight increment of 0.7% and from 2009 to 2018, it further increased by 573 ha with an overall land cover change of 1.18% and annual change rate of 0.18 spanning from 1999 to 2018. This increase could be attributed to the construction of artificial dams used for irrigation water of crops in the area. The area is known for large scale intensive cultivation of both perishable crops (vegetables) fruits and grains (corn and wheat). Also, river environments are pristine and fragile, thus the restriction of human on these environments critical for sustainability [29]. The reconfiguration of the environments and the land use and land cover change may have had a negative effect on the river most probably influenced by the increased numbers and concentration of privately own accommodation along the river. A similar study by Namugize and co-workers [107], also attributed the deterioration of the uMngeni river catchment in South Africa to the multifaceted relationships between land use and land cover change and water quality parameters to be site specific.

Therefore, these findings help to understand the state of the environment in the upper Crocodile River catchment and aid in decision making on the implication on such findings on water resources which are considered be one of the most critical environmental problems in South Africa. The intensification of agricultural practices along the Crocodile River has had a negative impact on the receiving water through pollution as a result of the use of chemical fertilizers for cultivation profitable and more productive crop varieties (e.g. Fruits, grains and vegetables). The toxicity of water owing to the use of pesticides and other forms of chemical fertilizers draining into water bodies has resulted in the extinction of many marine organisms including serious effect on human health of those depending on the river as source for fish and domestic use [37, 84]. Furthermore, the decline in cropland from 2009 to 2018 may have a serious implication to food security and self-sufficiency for the province. This is further compounded by the increase in population growth urbanization, tourism, and other development activities are the principal drivers of LULC change in the Crocodile River catchment.

3.4 Prospect and implications for future studies

PTEs, even in trace amount in some cases, could pose a great risk to humans, exert harmful effects on the environment and other ecological receptors, as mentioned earlier. With this increased anthropogenic activity, considering the land use and landcover change, spanning from 1999 to 2018, with the concomitant rise in PTEs observed in the study area, as one of the African water bodies, the need for continuous environmental monitoring of the safety of the river water body has emerged, of great importance. Standard techniques for detection of the PTEs such as inductively coupled plasma optical emission spectrometry (ICP-OES) [108], Uv–Vis spectrometry [109], atomic absorption/emission spectroscopy [110], laser-induced breakdown spectroscopy (LIBS) [111] and even the inductively coupled plasma mass spectroscopy (ICP-MS) employed in this study, are not generally suitable for in situ, fast, easy and low cost operations [112]. Gross setbacks like tedious sample preparation and pre-concentration, professionalism needed in personnel operation, and high cost of procuring and maintaining equipment have surrounded the use of such techniques. Such growing mandatory demand for real-time on-site tracking of water quality for human health and the environmental monitoring requires a competitively sensitive and reliable technique which is affordable and exerts less pressure on the environment.

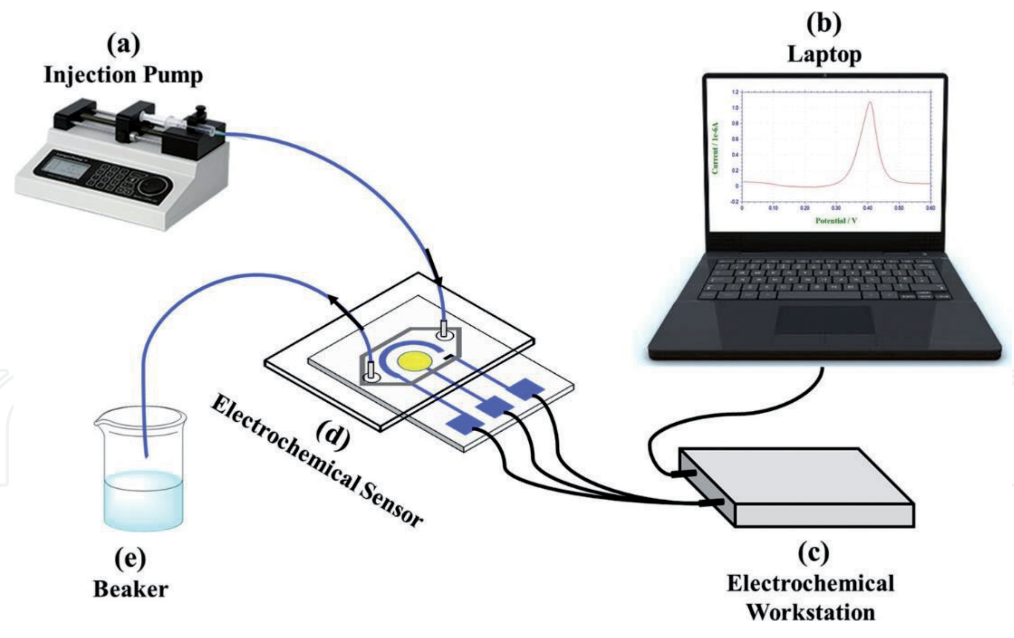

Figure 8.
Typical electrochemical set-up [114].

Hence, it is proposed that electrochemical monitoring technique could be a promising portable, low cost alternative with high selectivity and low detection limit [112]. Consequently, electrochemical sensors could be simply assembled into a compact system that is cheaper, simple to operate and possible for the desirable on-the-field application. These techniques leverage on the electro-catalytic oxidation of pre-concentrated deposited analyte on the surface of a prepared electrode. They have been engaged in extensive scope of applications such as environmental safety monitoring, control of food quality, medical diagnostics, and chemical threat detection. Some of the electrochemical methods most commonly in use nowadays include voltammetry, amperometry, impedemetry, potentiometry and conductometry [113]. Therefore, the safety assessment of African water bodies could profit immensely from the synergic integration of remote sensing and electrochemical technique in a way that is comparably affordable and efficient. **Figure 8** [114] illustrates a typical electrochemical setup.

4. Conclusion

The physicochemical parameters and PTEs contamination in the Crocodile River were analyzed to highlight the effect of the PTEs have on the river health. The results of this study revealed that the Crocodile River is contaminated with the following PTEs, (Al, Mn and Fe) as their contamination level were above the stipulated permissible guideline of DWAF of 0.005, 0.18 and 0.1 mg/L respectively. Non-point sources of metals in the river could possibly be attributed to anthropogenic activities such as agriculture, mining, resorts, and privately owned accommodation, commercial activities and the increasing population along the Crocodile River. A measure to curb metal pollution in the Crocodile River would be to avoid tannery discharge effluent into the river and farmland without prior treatment. Apart from the treatment of wastewater, effluent discharged into the Crocodile River. The different classes of land use and land cover revealed the following change patterns; bare land and built-up declined from 1999 to 2018, with a net change of −42 938 ha and − 2 663 ha respectively. Whereas, land cover category for grassland, cropland and water bodies exhibited an increase of 26 612, 17 578 and

1 411 ha respectively. The LULC changes observed in the upper Crocodile River can be attributed to anthropogenic activities having a range of negative impact on the river and the environment. This result, therefore, serves as an informed guideline for policymakers in understanding the effects of land use and land cover change in designing an eco-friendly land use policy in the Crocodile River. Electrochemical strategy using appropriate sensors has been proposed a congruent technique for periodic monitoring of water quality needed, to inform the local population of the human health risk associated with the use of water derived from the river.

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Conflict of interest

All authors declared no conflicts of interest.

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