

Article

Evaluation of River and Groundwater Quality in the Mzimvubu to Tsitsikamma Water Management Area (WMA7)

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Abstract: This paper assessed and evaluated the river and groundwater quality of five major catchments in the Mzimvubu to Tsitsikamma Water Management Area (WMA7). The river assessment and evaluation considered the present state maximum, minimum and mean seasonal values of physiochemical parameters (EC, NO₃ + NO₂, Cl, pH, NH₄-N, PO₄-P and Mg). The study was able to successfully make use of statistical analysis and a water quality index in order to explain seven-year trends and the present state of all five catchments within the study area. The statistical analysis results showed that water quality parameters such as PO₄, NH₄ and NO₃ + NO₂ were not complying with the South African Water Quality Guidelines (SAWQG) limits, suggesting that the study area was impacted by anthropogenic activities such as agriculture, sewage works, etc. The application of WQI showed that the Gamtoos catchment was in a good water quality state (49.71) while the other four catchments were in a poor to very poor state, according to the WQI classification. Based on the groundwater quality assessment, the physicochemical parameters (NH₄, EC, Ca, NO₃ + NO₂, pH, Na, Cl, Mg, F, K, SO₄ and CaCO₃) were selected and the main parameters of concern were EC (salinity), NO₃ + NO₂ and SO₄. However, groundwater assessment revealed that groundwater quality was chemically suitable for drinking purposes in most parts of the study area. Therefore, the study recommended resource-directed measures to improve surface and groundwater resource protection, especially in areas where surface and groundwater quality for other uses remains a challenge. Further, strong water resource compliance monitoring and enforcement to control water resource pollution sources is critical.

Keywords: catchment; groundwater quality; physicochemical parameters; resource-directed measures; water management area; water quality index; water quality; water resource classification; resource quality objectives



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1. Introduction

Water is life to human societies, and critically important to food production, economic development and ecosystem functioning [1–3]. Halder and Islam [1] reported that cities in the world are facing water shortages and more than 40% of the food supply grown under irrigation is water-dependent. Water plays a significant role in sustainable development and poverty reduction [4]. Globally, water resource exploitation has increased and threatened prospects for socio-economic development, political stability and ecosystem integrity [5]. Given the need for sustainable water management worldwide, practical and reliable water quality assessment for sustainable water resource use is important [6,7].

Water quality issues have become a global challenge in both developed and developing nations, undermining the potential for economic growth and the physical and environmental health of billions of people [3,8]. For many years, the world's primary focus has been on

water quantity, water use efficiency and allocation challenges; progressive water quality deterioration has created an unprecedented water crisis [1,8]. Water quality is affected by both anthropogenic and natural sources, through point and non-point sources [9,10]. Studies by De Necker et al. [9], Mishra et al. [2], Rahman et al. [11] and Yotova et al. [10] reported that poor water quality conditions, due to natural and anthropogenic sources can be exacerbated by climatic conditions such as atmospheric precipitation and drought, which reduce flow, adding stress on water resources already affected by anthropogenic activities. Further, Mishra et al. [2] reported that the constraints on the quality of water and availability/quantity have the potential to threaten secured access to water resources by different water users. Moreover, approximately 1.2 billion people have reported that they live in areas where there is limited water supply to meet their water demand. The study [2] revealed that global groundwater use has increased by 50% due to its good quality and ease of access. Further, contamination of groundwater and surface water becomes a great threat to freshwater availability. Mishra et al. [2] noted that for developing nations to minimise the water crisis associated with poor water quality and quantity, understanding of poor water quality and quantity sources, trends and better management options is important.

In South Africa, Griffin et al. [12] reported that the country is faced with a number of water quality challenges such as eutrophication, acid mine drainage (AMD) and anthropogenic salinisation. Eutrophication is a consequence of nutrient enrichment that leads to changes in ecology, such as algal bloom [12,13]. Further, eutrophication has the potential to impact ecological systems, human health, agriculture and recreation. In South Africa, AMD is caused by coal and gold mining activities and is a major environmental problem because of its ability to persist after mines have closed [12]. The study revealed that AMD led to water quality issues in the rivers of Mpumalanga and Gauteng Provinces.

A recent study [14] reported that water quality in the Mzimvubu to Tsitsikamma Water Management Area (WMA7) is deteriorating daily due to water use taking place in some catchments. The report also found that some catchments of the study area have problems with siltation (turbidity), nutrients and ammonium. Agricultural use of chemical fertilizers and pesticides and the rapid growth of industrialisation in the country caused heavy and varied pollution in water resources leading to deterioration of water quality and depletion of aquatic biota [14]. The eastern part of the study area saw increased groundwater pollution and over-abstraction, which presented a serious water problem [15]. The study by Cobbing [16] revealed that groundwater levels and spring flow had dropped significantly as a result of overuse for irrigation in major Karst aquifers. It further revealed that high nitrate levels were observed in groundwater in several parts of the study area and could be due to anthropogenic activities such as agricultural waste, and industrial and domestic effluents. Ji et al. [7] reported that to effectively address water quality concerns, it is important to provide a critical assessment to evaluate water quality conditions and pollution sources. Therefore, in the absence of resource-directed measures (RDM), such as water resource classification and resource quality objectives (RQOs), it is necessary to conduct an evaluation and assessment of water resources, both surface and groundwater, to provide practical and accurate characterisation of the water quality status in the study area. In view of the above considerations, the central aim of this investigation was to assess and evaluate water quality changes over a seven-year period, for both surface and groundwater, in the Mzimvubu to Tsitsikamma Water Management Area (WMA7). The specific objectives were (1) to determine spatial and temporal variations of physicochemical properties of the WMA7 over a seven-year period, achieved by sourcing historical data from the Department of Water and Sanitation Water Management System (WMS), Hydstra and other research papers. The Hydstra monitoring sites provided a time series of water level data to the current study, whilst WMS monitoring sites provided a time series of water quality data. (2) To evaluate surface and groundwater overall water quality status of all five drainage regions. The evaluation process was realised through a water quality index, which presented levels of water quality in an understandable and useable format to the public. It was expected that the study outcomes could provide water quality status for all

catchments within the WMA7, to guide water resource management and pollution control measures in the area.

2. Materials and Methods

2.1. Description of the Study Area and Selection of Sampling Sites

The WMA7 is situated mainly in the province of the Eastern Cape and some parts of the study area fall into the KwaZulu Natal, Western Cape Province and Northern Cape Province [14]. Further, the WMA7 is comprised of several catchments: Mzimvubu, Sundays, Great Kei, Keiskamma, Great Fish, Tsitsikamma, Swartkops, Bushmans, Algoa and Gamtoos. However, for the purpose of the current study, the following major drainage regions were considered: the Sundays, Great Fish, Great Kei, Gamtoos and Mbashe; the smaller drainage regions were not considered due to lack of data. The study area consists of over 300 quaternary catchments, covering a total catchment area of more than 124,730 km² [14]. The study area's topography is hilly to mountainous with plains and hills of the Groot Karoo, with the Drakensberg Mountains along the northeastern boundary of the study area. Further, the rivers are deeply incised in the coastal strip [14]. Figure 1 shows a locality map of the study area.

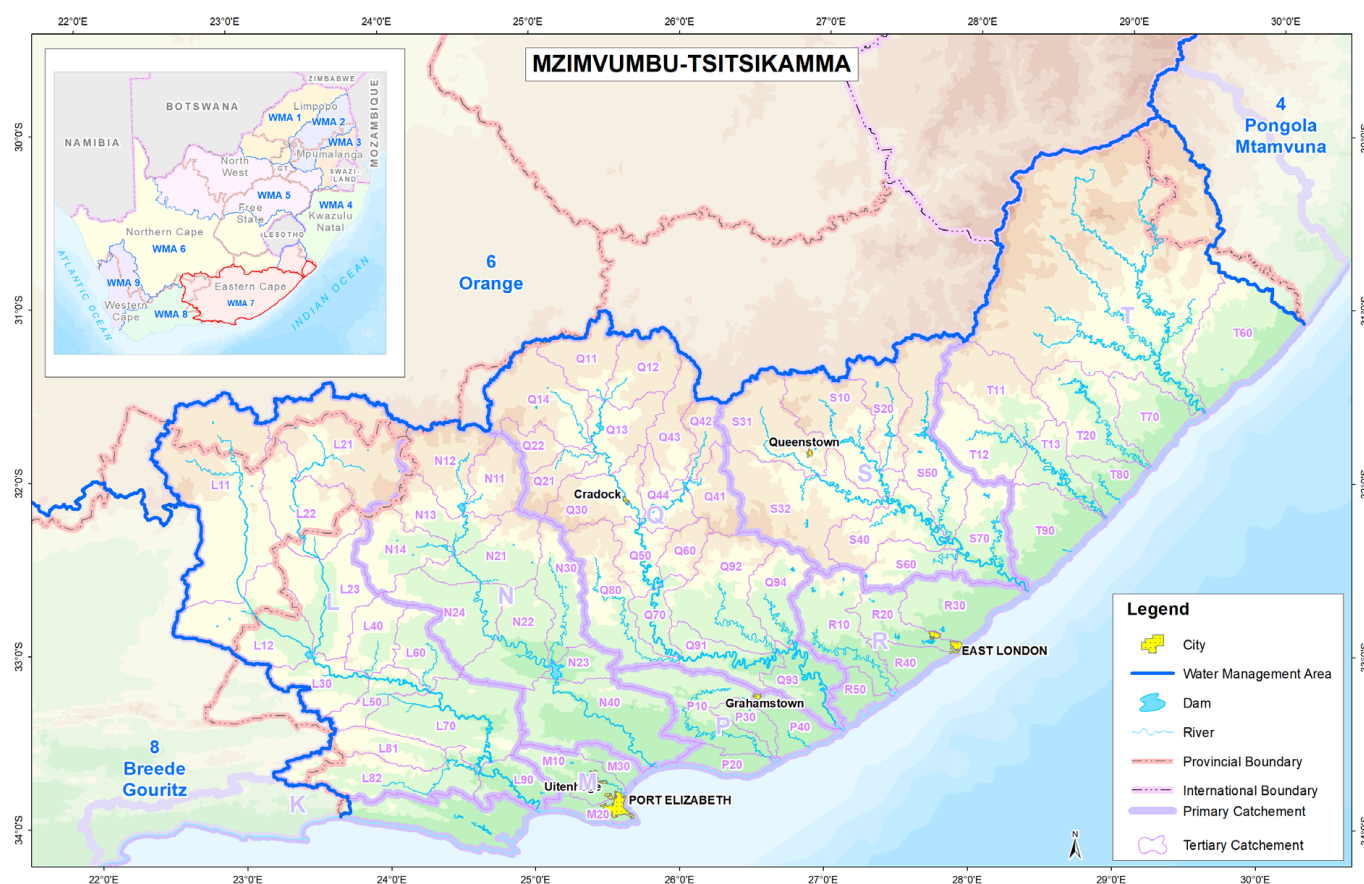


Figure 1. The locality map of the Mzimvubu to Tsitsikamma WMA.

The climate of the Mzimvubu to Tsitsikamma WMA is variable due to topography of the area and proximity to the sea. The inland part of the study area experiences hotter climate conditions while the coastal parts enjoy both subtropical and Mediterranean climate conditions [15]. The study area experiences maximum temperatures (38 °C) in January (summer months) and minimum temperatures (−2 °C) usually occur in July (winter months) [17]. In some parts of the study area, summer temperatures regularly exceed 40 °C, while some parts experience occasional snowfalls in winter months, e.g., Amathole mountain range and Keiskamma to the Hogsback area [17]. The study area has a varied

rainfall pattern throughout the year due to topographic zonation [17]. In the northern, northeastern, northwestern and central parts of the study area, rainfall generally occurs late in summer months with peak rainfall in December and January.

2.1.1. Regional Geology

The Department of Water and Sanitation [14] reported that the study area's basement rocks consist mainly of quartzite, limestone and phyllite, which are unconformably overlain by the Cape Supergroup, the Table Mountain, Bokkeveld and Witteberg Groups of alternating quartzitic sandstone and shale. The Cape Supergroup is overlain by the Eccia, Beaufort, Stormberg and Drakensberg Groups. Further, the Uitenhage Group unconformably overlies older deposits of the Cape Supergroup in small rift basins, i.e., Algoa and Gamtoos Basins; and comprises poorly sorted conglomerate and subordinate sandstone, siltstone and mudstone. These rift basins formed mainly due to normal faulting during the break-up of Gondwana. Unconsolidated to semi-consolidated, palaeo-coastal calcareous sand and conglomerate deposits of the Algoa Group occur within the eastern portion of the Algoa Basin and the Bushman's coastal plain. Table 1 shows the regional geological succession of the study area.

Table 1. The regional geological succession of the Mzimvubu to Tsitsikamma WMA7.

Geological Time Scale (Period)	Lithological Unit		Description
	Sedimentary and Volcanic Rocks	Intrusive Rocks	
Quaternary	Aeolian sand	-	Aeolian sand
	Alluvium		Unconsolidated sediments
Nanaga	Nanaga Formation		Calcareous sandstone, sandy limestone
Cretaceous	Mbotyi Formation		Dark greyish conglomerate sandstone
Jurassic	Uitenhage Group: Kirkwood Formation	Dolerite	Reddish greenish mudstone and sandstone
	Drakensberg Formation		Dolerite dyke and sills
			Basaltic lava, tuff, and agglomerate
Triassic	Clarens Formation		Yellowish-grey, pale-orange, or pink, very fine-grained sandstone
	Elliot Formation		Brownish-red and grey mudstone, sandstone
	Molteno Formation		Gritty sandstone, grey mudstone, shale, and occasional coal seams
	Beaufort Group: Katberg Formation		Fine-grained sandstone and red and green-grey mudstone
Permian	Beaufort Group: Adelaide Formation	-	Red, purple, grey, and blue green mudstone subordinate sandstone
	Eccia Group		Alternating succession of sandstone, siltstone and mudstone
Carboniferous	Dwyka Formation		Tillite
Carboniferous/Devonian	Witteberg Group: Weltevrede Formation		Shale, quartzite
Devonian	Witteberg Group:	Mapumulo Metamorphic Suite	Sandstone, feldspathic sandstone, arkose
Devonian	Bokkeveld Group		Claystone, mudstone, shale
Silurian/Ordovician	Table Mountain Group		Quartzite
Namibian	Mpambanyoni Formation		Quartz feldspar gneiss
		-	Biotite garnet cordierites sillimanite gneiss and migmatite subordinate hornblende gneiss
	Gamtoos Group: Klein River Formation		Quartzite, limestone and phyllite

2.1.2. Geohydrology

The Cape and Karoo Supergroups are the major aquifer systems in the study area. The Karoo Supergroup constitutes intergranular and fractured aquifer over large parts of the study area, associated with extrusive and intrusive igneous rocks [14]. The aquifer systems are mainly of a fractured type, where groundwater occurrence is a result of secondary deformation relating to faults, fissures, fractures, bedding planes and joints [14]. The study by Murray et al. [18] revealed that favourable geological conditions and drilling targets of the Karoo sediments are dolerite ring structures, thick alluvial deposits, dolerite dykes, dolerite sill margins (inclined sheets) and folded and faulted formations.

2.1.3. Land Uses

DWS [15] reported that irrigated lands within the study area occupy about 948 km² in the Great Fish and Sunday Rivers using water from the Orange River, with the main crops such as vegetables, citrus and lucerne. Pineapple and chicory are found in the Albany Coast area. Further, the study by DWS [15] reported that afforestation occupies land of about 417 km² in the Tsitsikamma area. There are few mining activities in the study area, consisting of a limestone quarry near Hankey, Steytlerville, Makhanda and Uitenhage. These mining operations have been reported to have caused concerns (to downstream water users) and negative impact on the ecology of the river. There are no major power stations in the study area, and major industries are situated in cities such as East London and Gqeberha [15].

2.1.4. Water Resources Infrastructure

In terms of water quantity, DWS [15] reported the largest transfer of water from the Gariep Dam (Upper Orange) into the study area (to the upper reaches of the Great Fish River). Large volume of water is used for irrigation within the Great Fish and Lower Little Fish Rivers catchments, with some domestic water used by the towns in the area. In the water transfer scheme into the Algoa System, the water is used for domestic purposes by urban and rural communities [15]. These water transfer schemes are essential for socio-economic development of communities in the Amathole and Algoa water systems. However, these transfers have effects on the water resource health [15].

2.2. Major Catchments and Associated Monitoring Points

The main catchments and associated rivers of the study area are shown in Table 2 for further detail.

Table 2. Major catchments and associated rivers in the WMA7.

Primary Catchment	Sub-Catchment	Main River	Associated Rivers	Catchment Area (km ²)
L	L11, L12, L21–L23, L30, L40, L50, L60, L70, L81, L82, L90	Gamtoos	Baviaanskloof, Groot, Kariga, Buffels, Sout, Kouga, Heuningklip	34,816
N	N11–N14, N21–N24, N30, N40	Sundays	Voel, Bul, Kamdeboo, Kariaga, Gats	21,248
Q	Q11–Q14, Q21, Q22, Q30, Q41–Q44, Q50, Q60, Q70, Q80, Q91–Q94	Great Fish	Tarka, Kat, Koonap, Groot-Brak, Little Fish, Pauls, Baviaans	30,243
S	S10, S20, S31, S32, S40, S50, S60, S70	Great Kei	Kubusi, Tsomo, Smit, Black-Kei, Indwe, Klaas, Klipplaat, Gcuwa, White-Kei	20,485
T	T11–T13, T20, T60, T70, T80, T90	Mbashe	Nenga, Shixini, Qhorha, Xora, Mdumbi, Msikaba, Mtentu, Kobonqaba, Mntafufu, Mthatha, Mngezi, Xuka, Mncwasa	17,938

The study area has 2909 active surface water quality monitoring points (Figure 2). However, for the purpose of the current study, 37 monitoring sites were selected across all five catchments within WMA7. The selection of the sites was based on data availability, water use types and position of the monitoring site, whether the site is on the mainstream or not. These surface sampling sites were sourced from Water Monitoring System (WMS). Table 3 presents water quality monitoring sites, global positioning system (GPS) coordinates (latitude and longitude) and drainage region name of the study area.

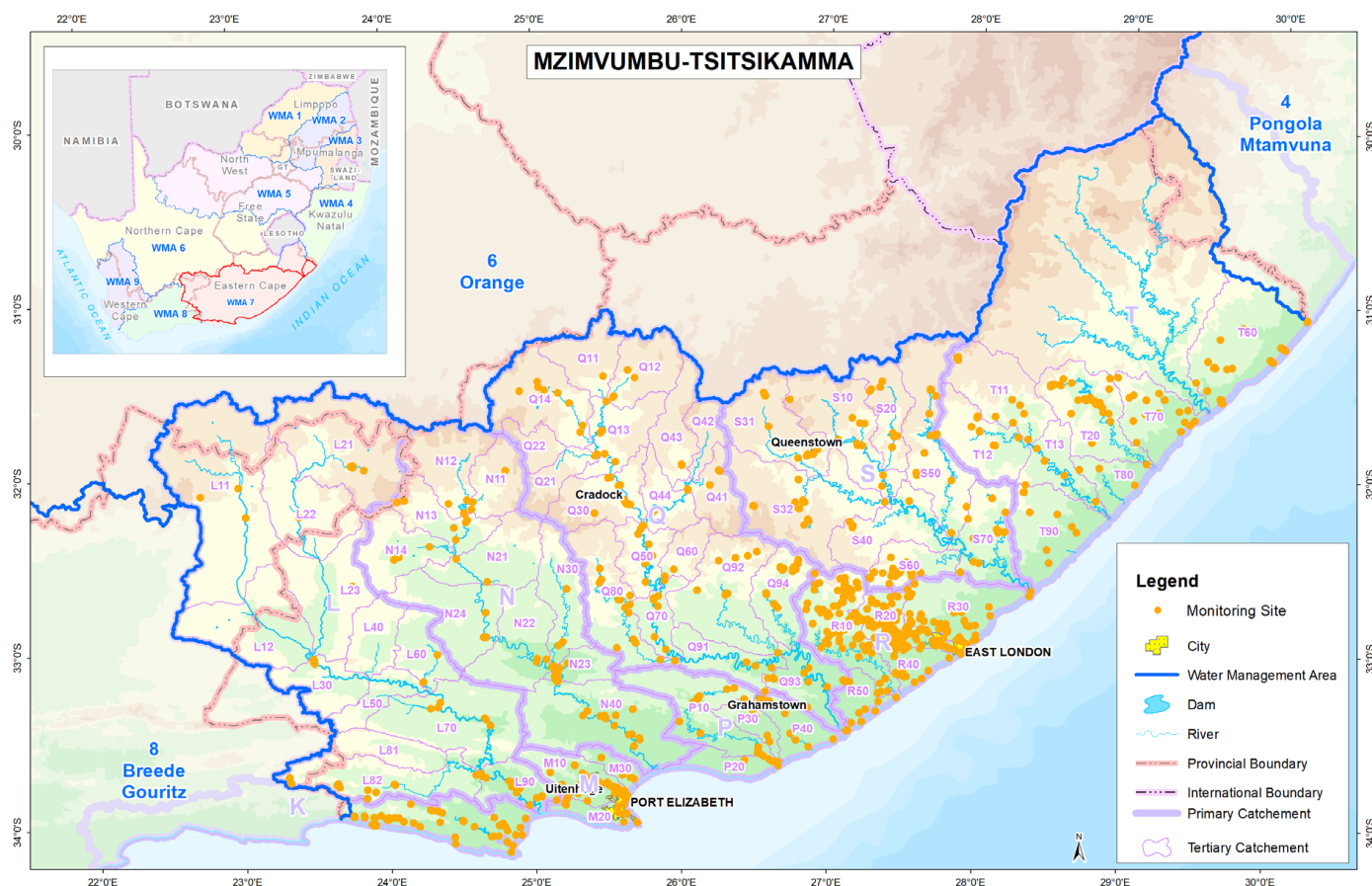


Figure 2. The locality map of the Mzimvubu to Tsitsikamma WMA and associated water quality monitoring points.

Table 3. Surface water monitoring points in the Mzimvubu to Tsitsikamma WMA.

Monitoring Site	Resource Name	Latitude	Longitude	Drainage Region Name
L8H001Q01	Wabooms river (l8)	−33.865833	23.836111	L82D
L8H005Q01	Kouga	−33.790556	24.030556	L82D
L9H004Q01	Gamtoos	−33.914444	24.954167	L90C
S3H004Q01	Swart—Keirivier	−32.05	26.788056	S32C
S3H012Q01	Oskraal	−32.20133889	26.75861111	S32G
S5H004Q01	Tsomo	−31.7875	27.679167	S50G
S6H001Q01	Kubusi	−32.579167	27.366667	S60A
S6H003Q01	Toise	−32.516111	27.524722	S60D
S7H001Q01	Gcuwa	−32.3275	28.144722	S70E
S1H004	Wit kei	−31.847444	27.185222	S10H
S3H013	Swart—Kei Rivier	−32.173889	27.3725	S32M
S5H002Q01	Tsomo	−32.043333	27.822778	S50J
S1H004	Wit Kei	−31.847444	27.185222	S10H

Table 3. Cont.

Monitoring Site	Resource Name	Latitude	Longitude	Drainage Region Name
S3H013	Swart—Kei Rivier	−32.173889	27.3725	S32M
N2H009Q01	Volkers Skoenmakers River	−33.103611	25.2225	N23B
N3H002Q01	Voel	−33.001667	25.161389	N30C
N4H001Q01	Sondags	−33.377778	25.354722	N40B
N4H003Q01	Sondags	−33.581389	25.674444	N40F
N4H005Q01	Coerney River	−33.5125	25.659167	N40E
T1H001	Xuka	−31.671944	28.110833	T11C
T1H007Q01	Mgwali	−31.787778	28.266667	T12G
T6H001Q01	Mntafufu	−31.494444	29.529167	T60K
T6H004Q01	Xura	−31.327778	29.528611	T60F
T7H001Q01	Mngazi	−31.554722	29.245556	T70B
T2H010Q01	Cicira	−31.5567	28.7372	T20C
T1H015Q01	Mbashe	−32.00055556	28.58166667	T13D
T1H013Q01	Mbashe	−31.79966667	28.33302778	T11H
T1H012Q01	Tsomo	−31.78688889	27.70638889	T12C
Q1H012Q01	Teebus River	−31.570028	25.543889	Q12C
Q3H004Q01	Pauls River	−32.035556	25.520833	Q30B
Q4H013Q01	Tarka River	−32.313889	25.741389	Q44C
Q7H003Q01	Great Fish River	−32.778333	25.839722	Q70A
Q7H005Q01	Klein-Visrivier	−33.0275	25.89360556	Q80G
Q8H008Q01	Little Fish River	−32.786111	25.615	Q80E
Q9H002Q01	Koonap River	−32.713889	26.296667	Q92C
Q9H018Q01	Great Fish River	−33.23778	26.99472	Q93C
Q9H029Q01	Kat River	−32.761111	26.629444	Q94F

As for groundwater, 877 water quality monitoring sites were identified and sourced from the WMS and Hydstra (Figure 3). Hydstra is a commercial hydrological information system for the storage, editing, retrieval, manipulation, and analysis of surface water, water quality, and groundwater time series data and related hydrological information in support of water resources management [19]. It is important to note that not all monitoring sites have long-term data as some sites have been discontinued but have historical data. A total of 248 sites were deemed active sites, and for the purpose of the current study, 30 monitoring sites were identified with long-term data availability. These monitoring sites provide time series data on water levels and water quality of the study area [20]. The groundwater monitoring sites for the Mzimvubu to Tsitsikamma WMA are presented in Table 4.

Table 4. Groundwater monitoring sites in the Mzimvubu to Tsitsikamma WMA.

Site Name	Latitude	Longitude	Monitoring Site Type	Quaternary Catchment	Location Description
S7N0001	−32.57722	27.88444	Borehole, water quality	S70A	Upstream of Tsomo River
S27007	−32.52694	27.45750	Borehole, water quality	S60C	In the Imvani Forest
S18930	−31.92500	26.81639	Borehole, water quality	S31G	Upstream of Komani Dam
S19406	−31.92250	26.65194	Borehole, water quality	S31E	Queenstown Town
S19097	−32.02056	26.90639	Borehole, water quality	S31A	Farm in Quaggafontein
S19119	−32.08389	26.81833	Borehole, water quality	S32H	Mountain in Tambo Village
ZQMADK1	−32.70750	26.29444	Borehole, water quality	Q92C	At Adelaide Gymnasium
Q1N0055	−32.01306	26.25417	Borehole, water quality	Q41C	Farms in Tarkastad
Q1N0059	−31.65528	25.81528	Borehole, water quality	Q13A	Tarkastad Town, WWTW
T9N0001	−32.47020	28.31941	Borehole, water quality	T90G	KwaMaciba Village

Table 4. Cont.

Site Name	Latitude	Longitude	Monitoring Site Type	Quaternary Catchment	Location Description
EC/T90/209	−32.06870	28.33956	Borehole, water quality	T90A	Upstream Gubevu tributary
ZQMLAN1	−31.05944	29.51389	Borehole, water quality	T60B	Sipaqeni farms
ZQMFRR1	−33.05278	26.07111	Borehole, water quality	Q91A	East Cape Game Farm
ZQMHFR1	−31.65278	25.81528	Borehole, water quality	Q13A	Luxolweni surban area
T1N0001	−31.33261	27.85320	Borehole, water quality	T11A	Elliot Town, next to WWTW
T1N0002	−31.86120	27.84752	Borehole, water quality	T12D	Makhuzeni village plots
ZQMSME1	−32.73861	25.60500	Borehole, water quality	Q80D	KwaNojoli residential area
ZQMSTB1	−31.29611	25.83028	Borehole, water quality	Q12B	Steynsburg residential area
ZQMADO1	−33.38944	25.72056	Borehole, water quality	N40D	At Addo Elephant Park
ZQMKWD1	−33.43000	25.44583	Borehole, water quality	N40C	Nqweba Town
3324AB00048	−33.23556	24.30361	Borehole, water quality	L60B	Willowmore community farm
L3324AD00091	−33.26194	24.32806	Borehole, water quality	L70B	At Steytlerville Farm
L8907	−31.80778	23.16583	Borehole, water quality	L11C	Next to Darlington Dam
L9052	−32.23333	22.80000	Borehole, water quality	L11F	Upper Sundays catchment
N2636	−32.18000	24.57833	Borehole, water quality	N11B	Downstream of Nqweba Dam
N3238	−32.32306	24.45167	Borehole, water quality	N13A	Aberdeen Town
3239	−32.34500	24.29333	Borehole, water quality	N14A	Farms in Graaff-Reinet
N3242	−32.39167	24.43056	Borehole, water quality	N13C	Next to farm dam in Kendrew
N3243	−32.36333	24.28417	Borehole, water quality	N14D	Graaff-Reinet Town
L3323DC00007	−33.82194	23.73611	Borehole, water quality	L82D	Downstream of Kouga Dam

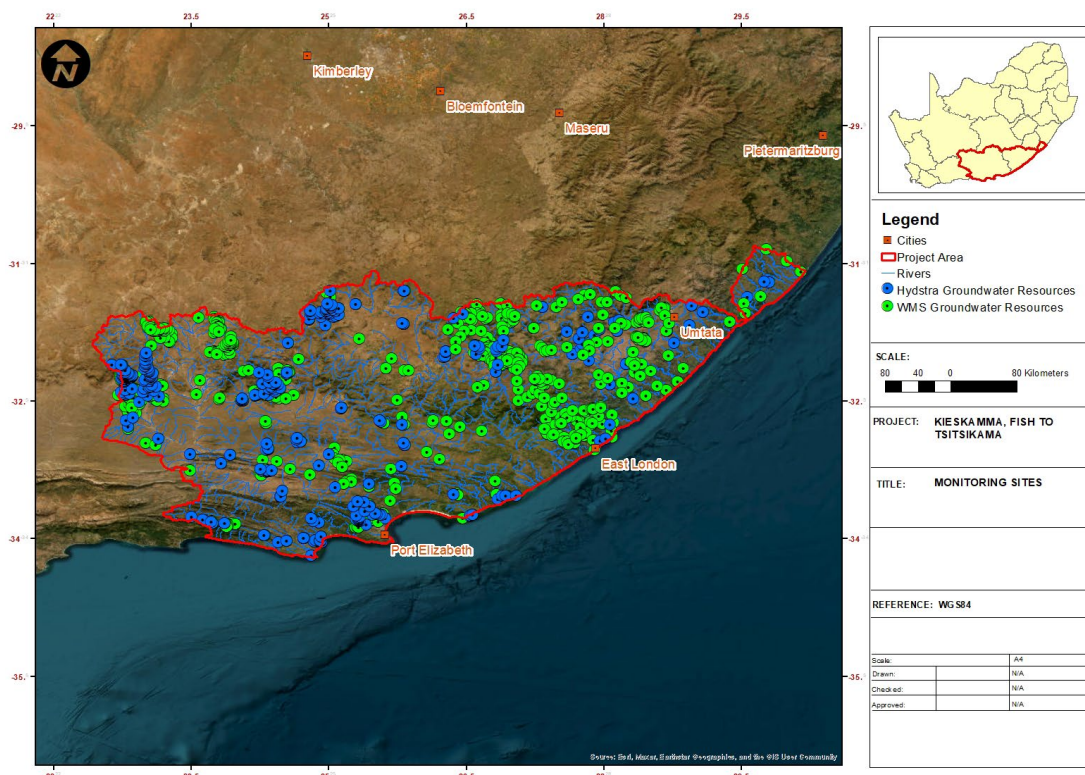


Figure 3. Map showing groundwater monitoring sites in the study area [20].

2.3. Selection of Parameters and Data Collection

Quantitative methodology was used for the study. The study used both primary and secondary water quality data sourced from field assessment and national databases such as the WMS and Hydstra. Historical data from January 2015 to December 2022 were collected following standard surface water quality sampling procedure as indicated in the DWS water quality sampling manual for the aquatic environment [21]. Field investigations were conducted between February 2021 and November 2023 to cover both wet and dry seasons. Briefly, surface water samples were collected using pre-rinsed 500 mL bottles of polyethylene without the addition of any preservatives. Water samples were taken by holding bottle with hand near base and plunging the sample bottle, neck downward, below the water surface. Sample bottles were turned slightly upward, and mouth was directed toward the water current. The bottles were filled to the top with as little air as possible and sealed tightly [13]. Further, every sample bottle contained particulars such as the name of the person who collected sample, date and time of collection, and description of place where samples were taken. The samples were immediately preserved with mercuric chloride (HgCl_2) to prevent uptake of any of the components (especially nutrients) by biological processes.

In terms of groundwater samples, collection technique used by Nzama et al. [19] was followed. Briefly, groundwater quality samples were collected from groundwater sites (boreholes) using a bailer after boreholes had been purged [19]. Multi-parameter probes were calibrated before taking field measurements such as temperature, pH and electrical conductivity. Other physiochemical samples were collected using sterile 250 mL polyethylene sampling bottles. Mercury chloride was added to each sampling bottle to preserve samples from contamination [19]. Further, samples were placed in cooler boxes filled with ice packs to maintain low temperatures, and sampling bailers were rinsed with de-ionised water. Both surface and groundwater samples were transported to the Resource Quality Information Services (RQIS) laboratory of the DWS, where they were stored under darkness at 4 °C until analysis [13].

Further, in Resource Quality Information Service (RQIS) section standard laboratory methods/techniques (such as Flammable Atomic Absorption Spectrophotometry (FAAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)) were applied for chemical analyses. After all laboratory analyses were completed, the results were captured in the WMS national database [13]. The in-situ water quality variables such as pH, electrical conductivity, salinity, clarity, total dissolved solids, temperature and dissolved oxygen were measured in the study area. Mnyango et al. [13] reported that there is no specific rule for selecting water quality parameters to determine the condition of water resources. Moreover, it has been suggested that minimising parameter inputs can significantly save time, effort, and cost of evaluating impacts on the water resources, which translates into feasibly and economically viable process [13]. However, parameter selection for the current study was based on availability of data, water user types in the study area and environmental importance of a parameter. Table 5 shows the suite of physio-chemical parameters that have been identified for the purpose of this study.

Water quality variables such as heavy metals and organic compounds are expensive to analyse and are seldom measured, hence there was insufficient data to report on [20]. Further, heavy metals and most organic contaminants are associated with industrial and mining activities, neither of which is associated with the study area. However, pesticides used in agriculture could affect water quality, but such data are extremely scarce [20]. Due to inconsistent and irregular monitoring across catchments, microbiological parameters such as *E. coli/faecal coliforms* were not considered.

Table 5. Selected water quality parameters and the reasons for their selection.

Parameters	Units	Reason for Selection
pondus hydrogenium (pH)	mg/L	pH provides an indication of alkalinity/acidity, especially for mine operation impacts and other natural variability.
Electrical Conductivity (EC)	mS/m	EC provides an indication of the salinity in a particular catchment.
Orthophosphate as P (PO ₄ -P)	mg/L	Orthophosphate provides an indication of high nutrient value in a particular catchment.
Sulphate as SO ₄	mg/L	Excess amounts of SO ₄ may have a laxative effect to human that can lead to dehydration.
Fluoride as F	mg/L	Excess amounts of fluoride in drinking water can cause human health problems.
Total Alkalinity as CaCO ₃	mg/L	CaCO ₃ indicates value level of all alkaline substances dissolved in the water.
Potassium as K	mg/L	K indicates groundwater quality issues or other problems with the well.
Calcium as Ca	mg/L	Ca is responsible for water hardness and may negatively influence toxicity of other compounds.
Nitrate as N (NO ₃)	mg/L	Nitrate is an indicator of high nutrient value in a particular catchment.
Magnesium (Mg)	mg/L	Important in water pollution and may contribute to water hardness.
Ammonium nitrogen (NH ₄ -N)	mg/L	An indicator of aquatic ecosystem toxicity.
Chloride (Cl)	mmol/L	Chloride provides an indication of impacts associated with industries, agriculture, wastewater treatment works, etc.

2.4. Data Analysis

2.4.1. Descriptive Statistical Analysis

Surface and groundwater water quality raw data were populated and analysed in a Microsoft Excel2016 spreadsheet using descriptive and time series statistical analysis. Data collected in different seasons (wet and dry) were compared to determine spatial and temporal variations of physicochemical properties of the WMA7 over a seven-year period. Due to climatic conditions in the study area, wet season is represented by February month while dry season is represented by June month during data analysis. The South African Water Quality Guidelines (SAWQG) and South African National Standard (SANS) 241 [22] were used as a benchmark. A descriptive statistical analysis provides summary information that quantitatively summarises variables from a dataset, while time series statistical analysis provides time series data and trend analysis [13].

This provided underlying causes of systematic patterns over time. Analysis output was in a table and graphic presentations to show temporal and spatial distribution of the selected parameters. Further, the process considered the maximum, minimum and the mean seasonal values of physiochemical parameters (EC, NO₃ + NO₂, Cl, pH, NH₄-N, PO₄-P and Mg). This was due to water quality sampling being irregular. Moreover, the current study adopted the class description of the water quality status and arithmetic expression as reported by Mnyango et al. [13].

2.4.2. Water Quality Index

Dunca [6] defined water quality index (WQI) as a tool that provides numeric expression that is used to evaluate the quality of water of a particular water resource. The advantage of WQI is that it is easily understood by water resource managers and the public [23]. Further, WQI is well received by many countries in the world because of its capabilities to evaluate overall water quality status by combining complex and technical water quality information into a single meaningful numerical value [23,24]. The application of WQI is a useful tool in assessing and evaluating the water's suitability for various beneficial uses. Moreover, the tool is capable of allowing comparison of spatial and temporal water quality status between catchments [6,24]. The current study assessed overall water quality status of all five drainage basins, using WQI calculations over a seven-year period (2015–2022) in the study area.

Traditionally, the WQI tool follows four common steps, which are (1) parameter selection of interest in the study area, (2) sub-indices generation for each parameter, (3) assigning

parameter weight value, depending on the parameter significance in the assessment, (4) aggregating final water quality index. To achieve evaluation of overall water quality status in the current study, the five-step process was followed to determine the WQI of the catchments in the study area. The first step was to allocate a weight (w_i) to each selected water quality parameter. The weight ranged from 1 to 5, with 1 representing the least important and 5 representing the most important. A weight allocation was on parameter's relative importance for aquatic ecosystems, recreation, domestic, industrial and agriculture as per the SAWQGs. The second step involves calculation of a weight for each selected water quality parameter, through the equation:

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i}$$

where (w_i) represents weight while n represents total number of rated parameters [13]. The third step was to calculate and assign quality rating scale (q_i) for each parameter by dividing the value of each parameter (C_i) by its respective water quality standard (S_i). The results were presented in percentages using equation [13]:

$$q_i = \frac{C_i}{S_i} \times 100$$

The fourth step involved sub-index calculation (S_b) for each water quality parameter. The S_b is calculated using equation:

$$S_b = w_i \times q_i$$

The last step (the 5th) involved determination of WQI for the study area using the equation:

$$WQI = \sum S_b$$

The sub-indices were summed to give overall water quality of the study area. The allocation of final WQI values to classes or categories is known as classification or categorisation [23]. Further, this can be achieved by any of two sets of classification scales, i.e., increasing scale and decreasing scale. In both instances, these scales aim to express the water quality status of water resources by determining the degree of contamination [22]. In general, the WQI index values range between 0 and 100.

The WQI scores of less than 40 represented “no concern” regularly meeting standards set in the SAWQG and SANS 241 [22]. The WQI scores of between 40 and 80 indicated “marginal concern” and WQI scores of above 80 did not meet standards set out in guidelines and indicated “highest concern” [6]. Further, the WQI values were grouped into classes ranging from 1 to 5, subject to which scale the author employed, increasing or decreasing scale. Table 6 showcased the classification of water quality status using increasing scale [23].

Table 6. Classification of water quality status [13].

Class	Value Intervals (%)	Water Quality Status	Possible Water Uses
Class 1	0–25	Excellent	Domestic, recreation, irrigation, industrial, etc.
Class 2	26–50	Good	Domestic, recreation, irrigation, industrial, etc.
Class 3	51–75	Poor	Industrial and irrigation
Class 4	76–100	Very poor	Irrigation
Class 5	≥ 100	Unsuitable	Water treatment is required before use

3. Results and Discussion

3.1. Surface Water Quality Results

The available physiochemical parameters such as EC, $\text{NO}_3 + \text{NO}_2$, Cl, pH, $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$ and Mg were presented in Tables 7–11. Further, the process considered the present state maximum, minimum and mean seasonal values of physiochemical parameters.

Table 7. Summary statistics of the physicochemical parameters determined from the Gamtoos catchment.

						Gamtoos Catchment
Parameters	Units	Max	Min	Mean	Std. Dev	SANS 241: 2015; SAWQG, 1996; WRC, 1998
EC	mS/m	372	4.7	122	3.39	<170
Cl	mg/L	460	12.3	327	1.12	<300
PO ₄	mg/L	7.8	0.05	0.8	0.25	<0.025
Mg	mg/L	292	3.74	20.9	4.3	<100
NH ₄ -N	mg/L	15.2	0.05	5.1	1.5	<1.5
pH		8.2	4.5	7.1	0.9	5–9.7
NO ₃ + NO ₂	mg/L	10.1	0.005	0.7	0.34	<1

Table 8. Summary statistics of the physicochemical parameters determined from the Great Kei catchment.

						Great Kei Catchment
Parameters	Units	Max	Min	Mean	Std. Dev	SANS 241: 2015; SAWQG, 1996; WRC, 1998
EC	mS/m	256	10.6	38	3.4	<170
Cl	mg/L	390	13.7	33.6	5.7	<300
PO ₄	mg/L	3.4	0.01	0.8	1.8	<0.025
Mg	mg/L	132	5.2	13.6	1.7	<100
NH ₄ -N	mg/L	13.4	0.05	2.8	0.88	<1.5
pH		9.1	7.1	7.8	0.56	5–9.7
NO ₃ + NO ₂	mg/L	4.7	0.005	1.6	0.63	<1

Table 9. Summary statistics of the physicochemical parameters determined from the Sundays catchment.

						Sundays Catchment
Parameters	Units	Max	Min	Mean	Std. Dev	SANS 241: 2015; SAWQG, 1996; WRC, 1998
EC	mS/m	640	27.4	239	2.50	<170
Cl	mg/L	1649	19.7	510	6.6	<300
PO ₄	mg/L	3.5	0.05	0.2	0.88	<0.025
Mg	mg/L	126.5	10.8	57.3	5.6	<100
NH ₄ -N	mg/L	4.8	0.05	0.5	0.35	<1.5
pH		8.9	7.7	8.5	0.34	5–9.7
NO ₃ + NO ₂	mg/L	17.54	0.05	1.1	0.27	<1

Table 10. Summary statistics of the physicochemical parameters determined from the Mbashe catchment.

						Mbashe Catchment
Parameters	Units	Max	Min	Mean	Std. Dev	SANS 241: 2015; SAWQG, 1996; WRC, 1998
EC	mS/m	167	7.6	30.2	1.07	<170
Cl	mg/L	156	3.4	21.4	2.6	<300
PO ₄	mg/L	16.2	0.01	0.79	0.20	<0.025
Mg	mg/L	34	3.6	6.7	5.5	<100
NH ₄ -N	mg/L	14.2	0.05	2.9	0.10	<1.5
pH		9	6.5	7.8	0.5	5–9.7
NO ₃ + NO ₂	mg/L	5.7	0.1	1.6	0.16	<1

Table 11. Summary statistics of the physicochemical parameters determined from the Great Fish catchment.

Parameters	Units	Max	Min	Mean	Std. Dev	Great Fish Catchment
						SANS 241: 2015; SAWQG, 1996; WRC, 1998
EC	mS/m	446	11.7	88.6	8.3	<170
Cl	mg/L	303	4.5	86.9	1.10	<300
PO ₄	mg/L	4.2	0.05	0.9	0.21	<0.025
Mg	mg/L	135	4.4	27.2	2.5	<100
NH ₄ -N	mg/L	57	0.03	4.1	1.1	<1.5
pH		10.1	7.4	8.3	0.5	5–9.7
NO ₃ + NO ₂	mg/L	29.3	0.03	2.3	0.77	<1

3.1.1. Gamtoos Catchment

The Gamtoos catchment water quality results showed that EC values ranged from 4.7 mS/m to 372 mS/m with a mean value of 122 mS/m (Table 6). The South African water quality range for EC in water for aquatic ecosystems use is 170 mS/m [25]. The European Union (EU) and World Health Organisation (WHO) also set protection limits of 250 mS/m for fisheries and aquatic life [26,27]. Therefore, the parameter does not pose serious risk but would make the water unsuitable for direct domestic use. EC is an indicator of salinity [28], it fluctuated significantly over the years in the study area. pH values ranged from a minimum of 4.5 to a maximum of 8.2 with a mean value of 7.1. According to Makanda et al. [28] pH is one of the water quality parameters used to determine the alkalinity (pH > 7), acidity (pH < 7) and neutrality (pH = 7) of water. Therefore, the results of the study showed neutral conditions in the Gamtoos catchment. This could be due to the reason that the catchment is characterised by protected areas such as Baviaanskloof Nature Reserve and Tsitsikamma National Park. Based on these guidelines, the pH value of the catchment would not adversely affect its use for recreational, aquatic ecosystems and domestic purposes. The Cl values varied between 12 mg/L and 460 mg/L with a mean value of 327 mg/L which was beyond the target water quality range of 300 mg/L for domestic water supply [29]. The PO₄ values ranged from 0.05 mg/L to 7.8 mg/L with a mean value of 0.8 mg/L, which was over the target water quality range of 0.025 mg/L. The malfunction of Hankey sewage works could be the source of the rise in PO₄ in the study area. The maximum value of Mg was 135 mg/L which was over the target water quality range of 100 mg/L, while the mean value was within the target range. The NO₃ + NO₂ values ranged between a minimum value of 0.005 mg/L and a maximum value of 10.1 mg/L with a mean value of 0.7 mg/L. The presence of high nutrient values in the water resources could lead to the growth of unwanted plants such as blue-green algae. The blue-green algae could release toxic substances such as cyanotoxins into the water systems [30]. According to Fatoki et al. [30], cyanotoxins were reported to have caused the death of farm livestock.

3.1.2. Great Kei Catchment

Water quality assessment in the Great Kei catchment showed nutrient enrichment. The NO₃ + NO₂ values ranged from 0.005 mg/L to 4.7 mg/L with a mean value of 1.6 mg/L (Table 7). The maximum value of PO₄ was 3.4 mg/L and the mean value of 0.8 mg/L. The mean values of these two nutrients exceeded their respective target water quality range. The presence of nutrients in the water systems could pose a problem for aquatic life, and recreational and domestic uses because of eutrophication. The South African Guideline for NO₃ + NO₂ in aquatic ecosystems is 1 mg/L, while aquatic ecosystems' target range for PO₄ is 0.025 mg/L. The values of EC and Cl were recorded at maximum values of 256 mg/L and 390 mg/L, respectively. There was a steep rise of NH₄-N, with a maximum value of 13.4 mg/L and a mean value of 2.8 mg/L. The high presence of NH₄ and NO₃ + NO₂ could be an indication of agricultural contaminants in the study area. The WHO safe limit for

NO_3 for a lifetime is 10 mg/L as N [27]. The results of these parameters concurred with earlier findings by DWS [14] which identified NO_3 , NH_4 and turbidity from agricultural activities as the main sources of pollution in the study area. pH of the catchment showed neutrality with 7.8, while Mg recorded a maximum value of 132 mg/L, which was beyond the target water quality range.

3.1.3. Sundays Catchment

Water quality results in Table 8 showed that EC was higher than the required target water quality range, as it ranged from 27.4 mg/L to 640 mg/L with a mean value of 239 mg/L. The Sundays catchment recorded a great spike of CI with a maximum value of 1649 mg/L and a mean value of 510 mg/L. Sources of the high value of CI in the Sundays catchment could be from weathering of soils, intrusion of salty water from the ocean and contributions from wastewater. The PO_4 value ranged from 0.05 mg/L to 3.5 mg/L with a mean of 0.2 mg/L. The $\text{NO}_3 + \text{NO}_2$ values ranged between 0.05 mg/L and 17.54 mg/L with a mean value of 1.1 mg/L. DWS [15] reported that the lower Sundays River was characterised by irrigation to the upper Sundays in the Darlington Dam [15]. In addition, the drainage region was also dominated by livestock grazing and limited forestry activities. The study area showed alkalinity conditions with a mean pH value of 8.5. The EU sets pH protection limits of 6 to 9 for fisheries and aquatic life [30].

3.1.4. Mbashe Catchment

Water quality results in the Mbashe catchment showed that EC and CI values were compliant with their respective target water quality ranges. The PO_4 results ranged from 0.01 mg/L to 16.2 mg/L with a mean value of 0.79 mg/L, while the value of $\text{NO}_3 + \text{NO}_2$ ranged from 0.1 mg/L to 5.7 mg/L with a mean value of 1.6 mg/L. pH showed alkalinity conditions (7.8) in the study area. Therefore, there were neither major industries nor mining activities in the area that could cause extreme changes in the pH of the effluents and of the receiving river, therefore the results obtained for pH in this study were as expected. The catchment was characterised by subsistence and commercial farming.

3.1.5. Great Fish Catchment

Water quality results in the Great Fish catchment (Table 10) recorded maximum values of EC (446 mg/L) and CI (303 mg/L). Water quality data showed PO_4 ranged from 0.05 mg/L to 4.2 mg/L with a mean value of 0.9 mg/L, while $\text{NO}_3 + \text{NO}_2$ values ranged from 0.03 mg/L to 29.3 mg/L with a mean value of 2.3 mg/L. DWS [15] reported that agriculture was of major importance to the catchment with citrus and vegetable crops being grown. There was a steep rise of NH_4 with a maximum value of 57 mg/L and a mean value of 4.1 mg/L. The steep rise in NH_4 values was attributed to problems associated with the Peddie sewage works and Seymours wastewater treatment works west of the residential area along the R67 to Whittlesea. These values were grossly exceeded in the water resource, and this disqualifies the water for direct domestic use.

3.2. Trends Analysis for Surface Water for All Five Catchments

Figures 4–8 show the findings of the historical trend analysis of the physicochemical parameters for the WMA7. The trend analysis was presented per drainage region.

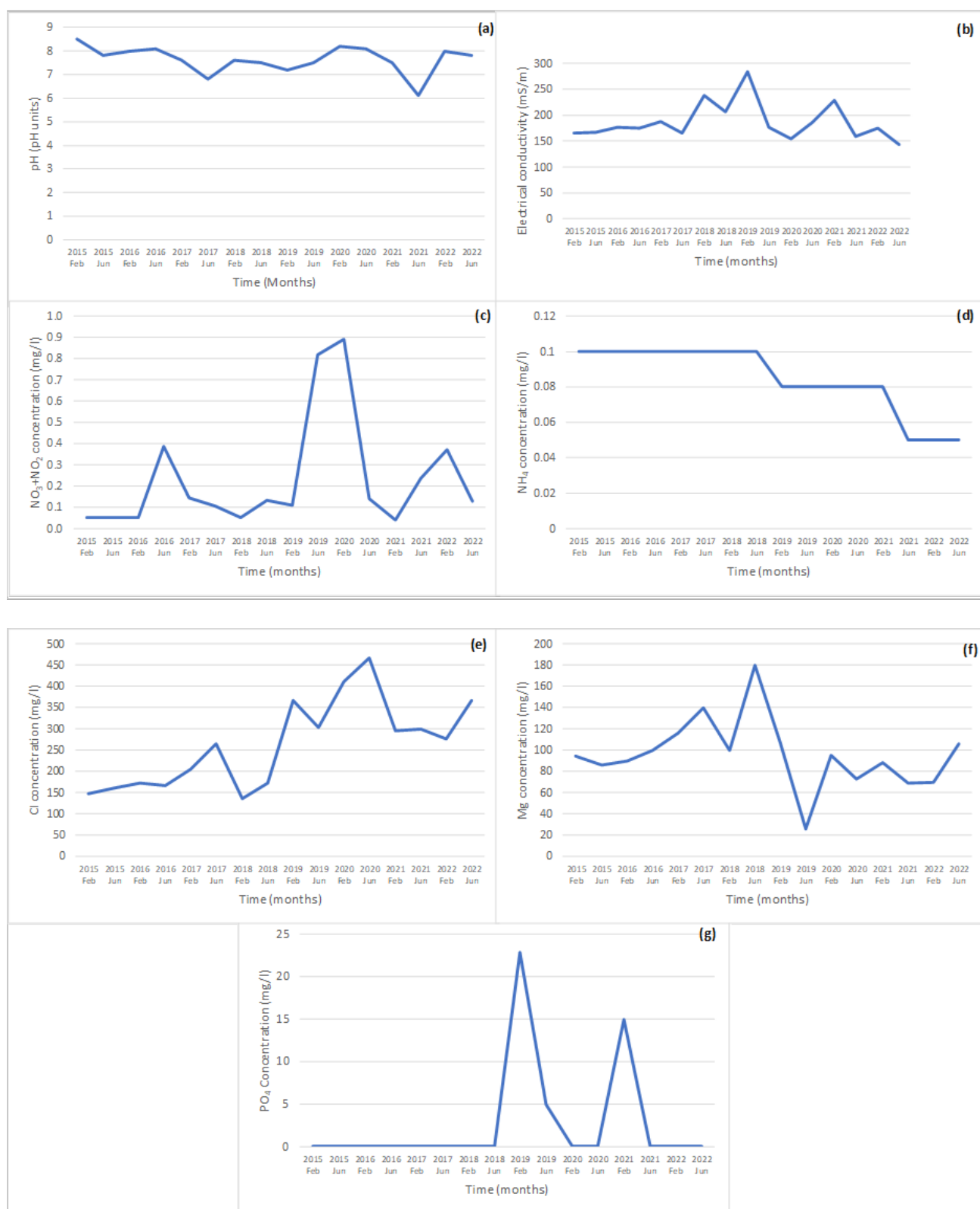


Figure 4. Trends analysis of pH (a), EC (b), NO₃ + NO₂ (c), NH₄ (d), Cl (e), Mg (f) and PO₄ (g) in the Gamtoos catchment.

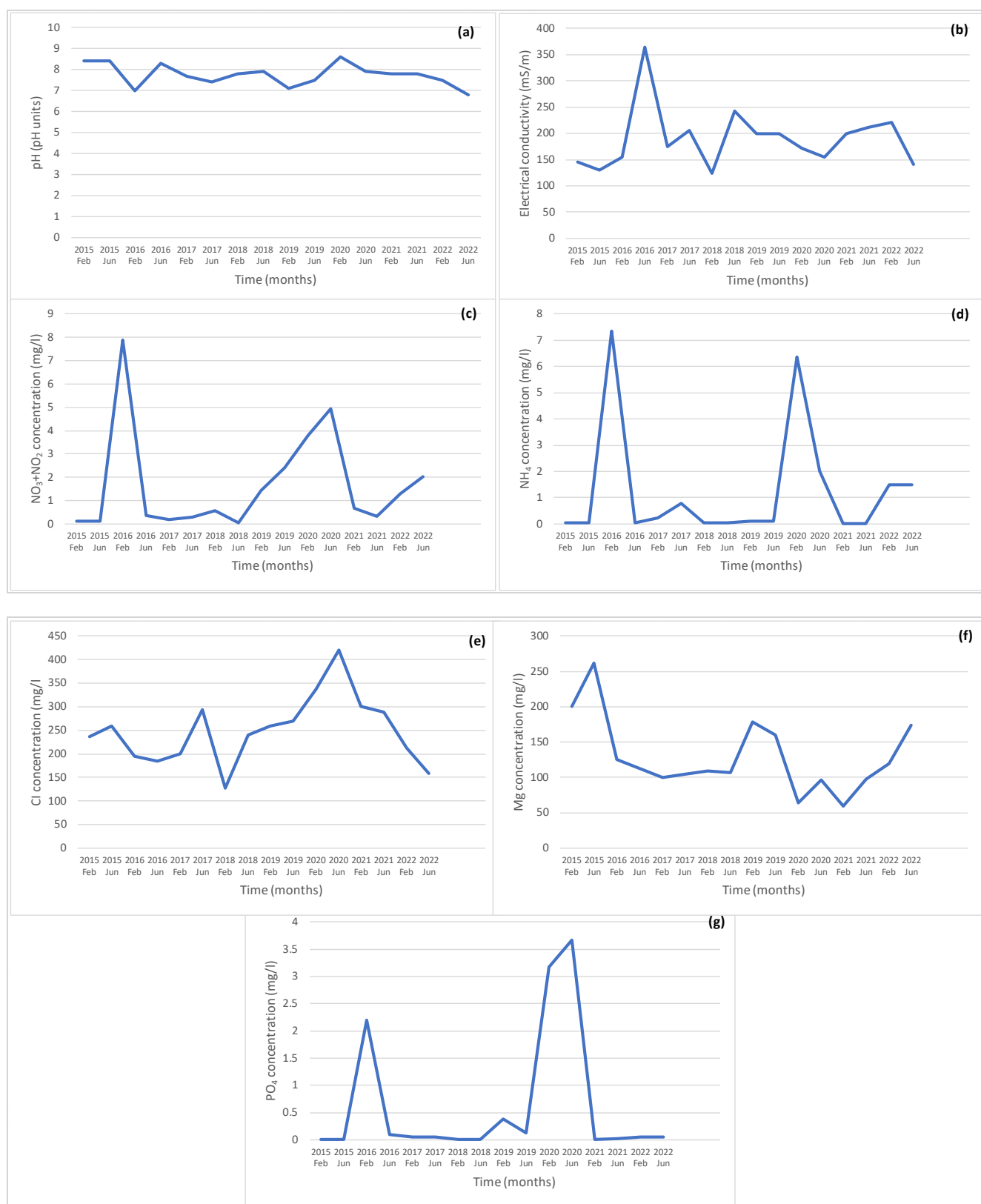


Figure 5. Trends analysis of pH (a), EC (b), NO₃ + NO₂ (c), NH₄ (d), Cl (e), Mg (f) and PO₄ (g) in the Great Kei catchment.

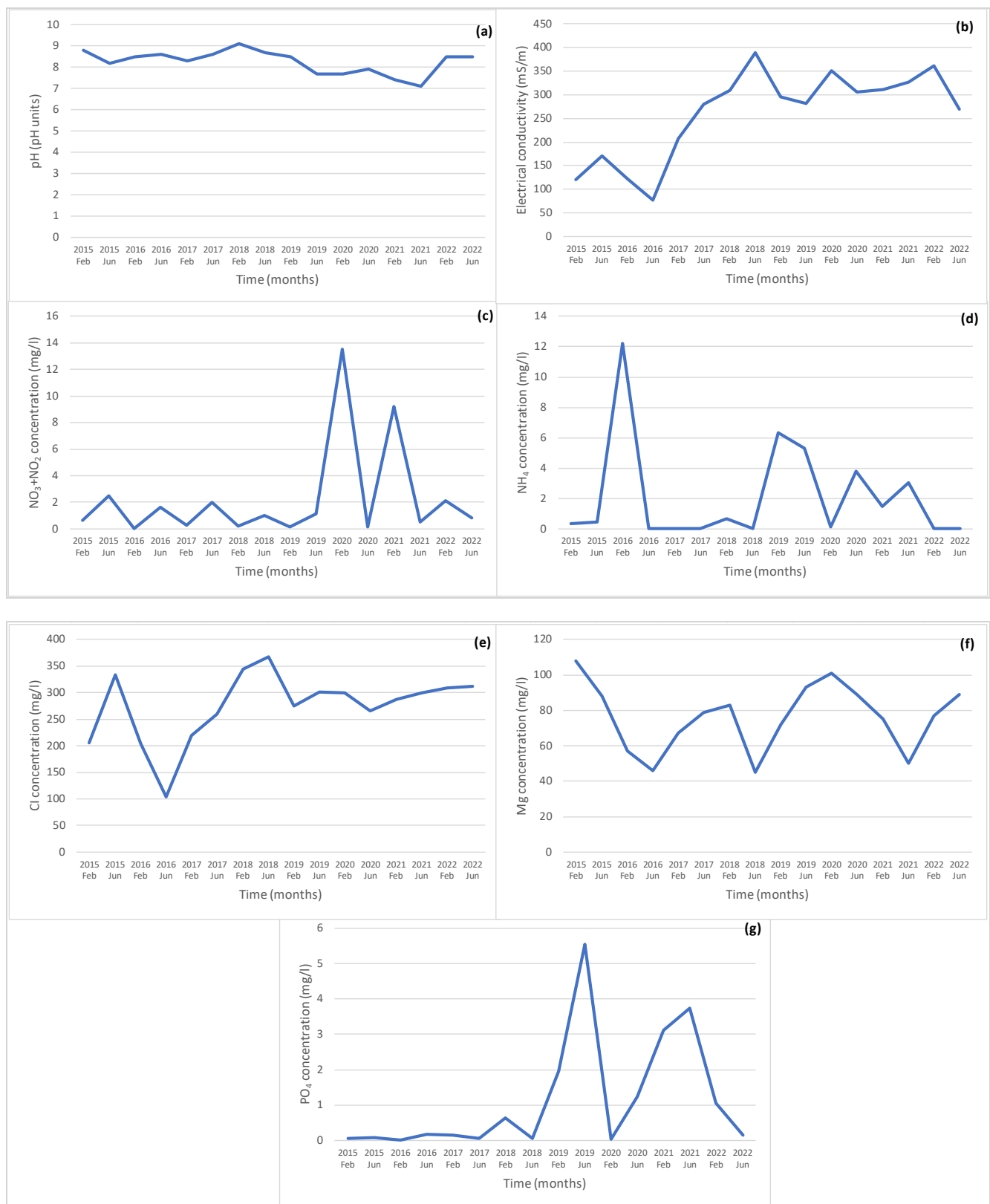


Figure 6. Trends analysis of pH (a), EC (b), NO₃ + NO₂ (c), NH₄ (d), Cl (e), Mg (f) and PO₄ (g) in the Sundays catchment.

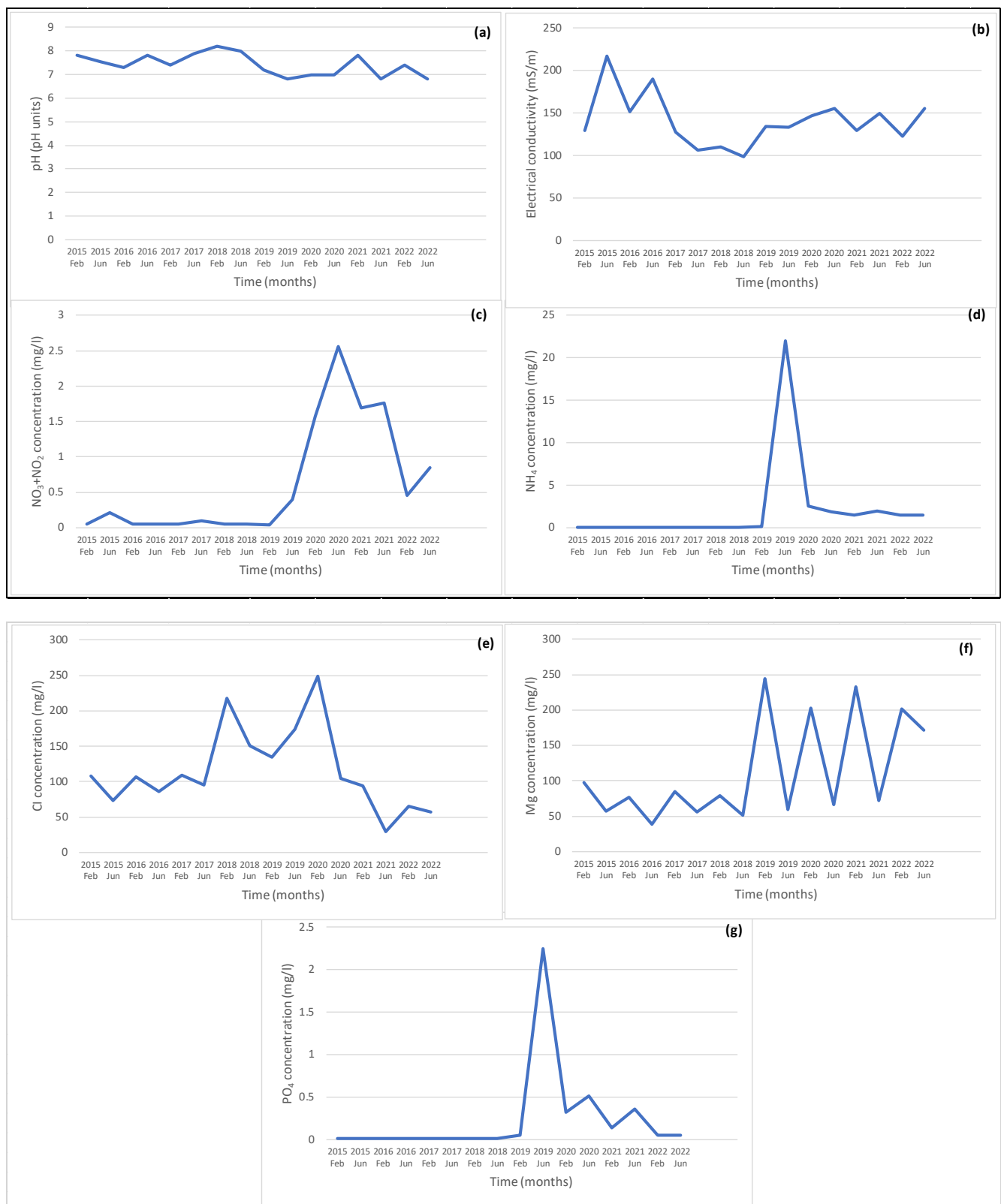


Figure 7. Trends analysis of pH (a), EC (b), NO₃ + NO₂ (c), NH₄ (d), Cl (e), Mg (f) and PO₄ (g) in the Mbashe catchment.

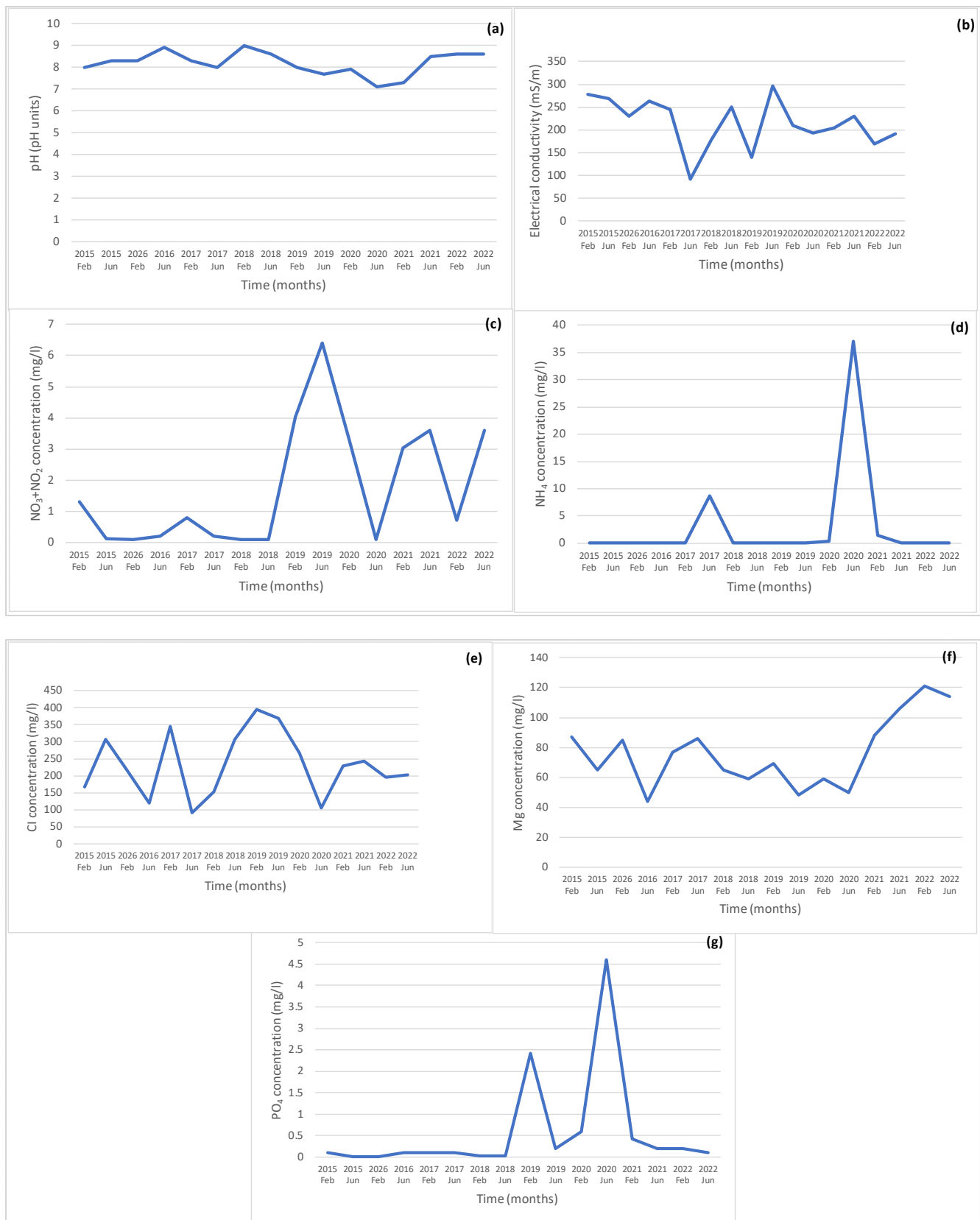


Figure 8. Trends analysis of pH (a), EC (b), $\text{NO}_3 + \text{NO}_2$ (c), NH_4 (d), Cl (e), Mg (f) and PO_4 (g) in the Great Fish catchment.

A trend analysis of water quality parameters from 2015 to 2022 in all five catchments was explored. The analysis was based on the two seasons (wet and dry). The study results showed that the pH condition was constant across all catchments. The results of the trend analysis for Mg, CI and EC showed seasonal variations across all five catchments. EC fluctuation indicated problems with water quality in the study area. The high value of CI concurred with previous studies that water quality impacts of the geological drivers have been observed, with high conductivity and salts in many catchments within the WMA7.

Figure 4 showed that the EC, Mg and CI readings were slightly above the allowable threshold whilst pH, $\text{NO}_3 + \text{NO}_2$ and NH_3 were fair. Water quality measurements of PO_4 reached harmful levels, indicating a serious deterioration in water resource quality. The deterioration of water quality could be attributed to prevalent agricultural activities in the Gamtoos catchment. Pesticides from agricultural activities could eventually drain into the system, explaining the poor quality of water in the catchment.

Water quality results in the Great Kei catchment showed that the EC and $\text{NO}_3 + \text{NO}_2$ readings were unstable and beyond standard limits in many sections of the catchment. Main activities such as irrigation, afforestation, sand mining and human settlements could be the main sources of poor water quality. The Kubusi River (which feeds into the Great Kei) passes near the town of Stutterheim. Spikes of PO_4 and NH_3 during the wet seasons of 2020 and 2021 could be due to flooding events that occurred in the area. DWS (15) reported that sand mining activities modified the landscape in the Queenstown and Stutterheim towns, due to vegetation removal, which led to exposed banks/bank erosion including eroded gullies.

In Figure 6, water quality results showed that $\text{NO}_3 + \text{NO}_2$, EC and NH_3 were not compliant with the standard limits, especially during the wet season. The Sundays catchment is heavily surrounded by agricultural activities, and poor quality of water could be the result of effluent runoff from pesticides and/or other agricultural products. Downstream of the Coega River, there is a dense concentration of urban settlements and industrial areas that stretch from the town of Uitenhage to the City of Gqeberha. The study by DWS [31] revealed that the river quality became significantly poorer as rivers (Riet, Voel and Coega) approached the urban and industrial areas. More likely due to waste generated by industrial processes, urbanisation and the Addo wastewater treatment works return flows discharging into the rivers. The water quality parameters were indicative of chemical imbalances and poor quality of water within the parts of the Sundays catchment. The limestone quarry in the Uitenhage was reported to have caused large-scale sediment deposition within portions of the Chatty wetland originating from the land clearing and development within the systems' catchment areas [31].

The Mbashe water quality is acceptable as shown in Figure 7, though NH_3 , $\text{NO}_3 + \text{NO}_2$ and PO_4 readings showed spikes between 2019 and 2022. This could also be attributed to the heavy rains experienced in the study area. DWS (14) reported that the catchment is characterised by afforestation, limestone quarry activities and agricultural practices, but these practices appeared to be small and sparsely located. Further, a large number of small rural settlements are located alongside many of the rivers (Xora, Nqabara, Mngazi, Mtetu, Msikaba, Mtakatye and Qhorha) within the catchment, and rely on the water provided by these rivers. The study by Kafu and Mlaba [32] reported that quarrying activities in the Siera village have significantly affected the natural environment, such as altering the hydrographic network, losing plants and vegetation, deteriorating ecology and aesthetics, destroying natural habitat, impacting the surface water, etc.

In Figure 8, EC and $\text{NO}_3 + \text{NO}_2$ measurements were beyond the allowable threshold, especially between 2019 and 2022. Water quality results showed a spike in PO_4 in 2020 and 2021, respectively. These water quality differences were results of land use activities such as agriculture, and urban and rural settlements. During the assessment of water quality, long stretches of cultivated land bordering the rivers that feed into the Great Fish catchment were identified.

In conclusion, the results of $\text{NO}_3 + \text{NO}_2$ showed significant differences in almost all catchments. Results of the current study gave evidence that water quality parameters such as $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and $\text{NO}_3 + \text{NO}_2$ were not complying with the SAWQG limits, suggesting that the study area was impacted by anthropogenic activities such as agriculture, mining activities, human settlements and sewage works. The results of pH and EC suggested that mining activities are limited in the area. However, study results suggested strong intervention was required to address identified spikes of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and $\text{NO}_3 + \text{NO}_2$ in the study area. Strong water resource compliance monitoring and enforcement to control water resource pollution sources is critical. However, other water quality parameters did not show significant differences based on wet and dry seasons.

3.3. Overall Assessment of Water Quality Status

The overall assessment was calculated and analysed using Makanda et al. [27], Mnyango et al. [13] and Nzama et al. [18] techniques. Tables 12–16 show overall water quality results for all five catchments in the study area.

Table 12. Water quality index calculated for the Gamtoos catchment.

WQ Parameters	Parameter Value	Target Water Quality Range	Weight	Relative Weight	Quality Rating Scale	Sub-Index	WQI
EC	122	170	3	0.12	71.8	8.6	49.71
Cl	327	300	2	0.08	1.09	0.09	
PO_4	0.8	0.025	5	0.16	32	5.12	
Mg	20.9	100	2	0.08	20.9	1.7	
$\text{NH}_4\text{-N}$	5.1	1.5	5	0.2	34	6.8	
pH	7.1	8.5	4	0.16	83.5	13.4	
$\text{NO}_3 + \text{NO}_2$	0.7	1.00	5	0.2	70	14	

Table 13. Water quality index calculated for the Great Kei catchment.

WQ Parameters	Parameter Value	Target Water Quality Range	Weight	Relative Weight	Quality Rating Scale	Sub-Index	WQI
EC	38	170	3	0.12	22.4	2.7	93.92
Cl	33.6	300	2	0.08	11.2	0.9	
PO_4	0.8	0.025	4	0.16	32.0	5.12	
Mg	13.6	100	2	0.08	13.6	1.1	
$\text{NH}_4\text{-N}$	2.8	1.5	5	0.2	187	37.4	
pH	7.8	8.5	4	0.16	92	14.7	
$\text{NO}_3 + \text{NO}_2$	1.6	1.00	5	0.2	160	32	

Table 14. Water quality index calculated for the Sundays catchment.

WQ Parameters	Parameter Value	Target Water Quality Range	Weight	Relative Weight	Quality Rating Scale	Sub-Index	WQI
EC	239	170	3	0.12	140.5	16.9	92.6
Cl	510	300	2	0.08	170	13.6	
PO_4	0.2	0.025	4	0.16	80	12.8	
Mg	57.3	100	2	0.08	57.3	4.6	
$\text{NH}_4\text{-N}$	0.5	1.5	5	0.2	33.3	6.7	
pH	8.5	8.5	3	0.16	100	16	
$\text{NO}_3 + \text{NO}_2$	1.1	1.00	5	0.2	110	22	

Table 15. Water quality index calculated for the Mbashe catchment.

WQ Parameters	Parameter Value	Target Water Quality Range	Weight	Relative Weight	Quality Rating Scale	Sub-Index	WQI
EC	30.2	170	3	0.12	17.8	2.14	93.54
Cl	21.4	300	2	0.08	7.13	0.6	
PO ₄	0.79	0.025	4	0.16	31.6	5.06	
Mg	6.7	100	2	0.08	6.7	0.54	
NH ₄ -N	2.9	1.5	5	0.2	193	38.6	
pH	7.8	8.5	4	0.16	91	14.6	
NO ₃ + NO ₂	1.6	1.00	5	0.2	160	32	

Table 16. Water quality index calculated for the Great Fish catchment.

WQ Parameters	Parameter Value	Target Water Quality Range	Weight	Relative Weight	Quality Rating Scale	Sub-Index	WQI
EC	88.6	170	3	0.12	52.12	6.3	79.08
Cl	86.9	300	2	0.08	28.96	2.32	
PO ₄	0.9	0.025	4	0.16	3,60	0.6	
Mg	27.2	100	2	0.08	27.2	2.8	
NH ₄ -N	4.1	1.5	5	0.2	27.3	5.46	
pH	8.3	8.5	4	0.16	97.6	15.6	
NO ₃ + NO ₂	2.3	1.00	5	0.2	230	46	

According to the WQI, the water quality status for all five drainage regions ranged from good to very poor water quality conditions. However, the water quality status for the Gamtoos catchment showed an improved result when compared with the other catchments, sitting at 49.71 indicating good water quality condition as per the WQI classification. As reported in the previous study [15], after the confluence of the Kouga and Baviaanskloof Rivers, the quality of water was categorised as good due to protected areas. The overall water quality assessment for the Great Fish catchment was calculated to be 79.08 indicating poor water according to water quality index classification. The water quality status for the Great Kei, Mbashe and Sundays catchments was calculated to be 93.92, 93.54 and 92.6, respectively. The status of these three catchments showed very poor water quality conditions, as per the WQI classification. The overall water quality status showed that the WMA7 is not ideal for users such as domestic, recreational and sensitive aquatic organisms. Therefore, water treatment is required before use.

3.4. Groundwater Quality Results

The physiochemical groundwater quality parameters (pH, EC, Ca, Mg, K, F, Cl, NO₃ + NO₂, SO₄, CaCO₃ and Na) were identified to assess groundwater quality in more detail in all five catchments within the WMA7. Median values of groundwater quality parameters were determined to characterise the dominant groundwater quality in the study area. The results for groundwater quality analysis were presented per catchment. The groundwater quality results are presented in Tables 17–21.

After interrogation of WMS groundwater quality data, the overall groundwater quality of all five catchments within the WMA7 greatly varied.

Table 17. Median value of groundwater quality parameters in the Gamtoos catchment.

Gamtoos Catchment: Groundwater Monitoring Sites							
Parameters	Unit	L3323D	L3324AB	L9052	L332AD	L8907	
Ambient Groundwater Quality or Median							Target Water Quality Range (SANS 241 and SAWQG)
pH		6.40	7.86	7.96	8.06	8.25	5–9.7
Electrical conductivity	mS/m	19.60	307.20	164.00	427.00	72.20	≤170
Calcium as Ca	mg/L	3.65	111.58	146.06	157.35	63.23	≤150
Magnesium as Mg	mg/L	2.38	126.74	38.56	160.27	35.70	≤100
Sodium as Na	mg/L	24.00	351.61	149.77	530.64	39.42	≤200
Potassium as K	mg/L	0.64	4.82	3.17	5.31	1.20	≤12
Total alkalinity as CaCO ₃	mg/L	7.83	421.13	243.85	373.00	250.30	≤200
Chloride as Cl	mg/L	45.97	634.34	215.93	1115.84	47.73	≤300
Sulphate as SO ₄	mg/L	4.20	249.43	254.84	326.84	54.90	≤250
Nitrate + Nitrite as N	mg/L	0.35	0.04	2.12	1.10	2.02	≤1
Fluoride as F	mg/L	0.11	0.60	0.70	1.04	0.59	≤1.5

Table 18. Median value of groundwater quality parameters in the Great Kei catchment.

Great Kei Catchment: Groundwater Monitoring Sites							
Parameters	Unit	S19097	S19406	S18930	S19119	S27007	S7N0001
Ambient Groundwater Quality or Median							Target Water Quality Range (SANS 241 and SAWQG)
pH		8.24	8.02	7.80	7.96	7.86	7.84
Electrical conductivity	mS/m	58.90	84.80	88.90	88.70	120.60	70.00
Calcium as Ca	mg/L	48.90	58.00	62.30	63.51	83.01	35.53
Magnesium as Mg	mg/L	27.35	27.86	35.65	32.80	24.79	20.98
Sodium as Na	mg/L	20.22	89.25	66.15	73.15	144.75	69.58
Potassium as K	mg/L	1.37	7.68	2.17	3.77	1.12	1.28
Total alkalinity as CaCO ₃	mg/L	257.96	332.71	283.00	312.77	308.11	155.00
Chloride as Cl	mg/L	15.35	53.00	79.75	67.53	204.40	103.83
Sulphate as SO ₄	mg/L	15.74	24.61	17.40	20.17	23.10	10.35
Nitrate + Nitrite as N	mg/L	0.14	3.58	2.33	2.72	0.31	4.45
Fluoride as F	mg/L	0.36	0.89	0.57	0.76	0.43	0.21

Table 19. Median value of groundwater quality parameters in the Sundays catchment.

Sundays Catchment: Groundwater Monitoring Sites							
Parameters	Unit	N2636	N3238	N3242	N3243	ZQMKWD1	ZQMADO1
Ambient Groundwater Quality or Median							Target Water Quality Range (SANS 241 and SAWQG)
pH		8.12	8.01	8.29	8.25	8.12	7.94
Electrical conductivity	mS/m	223.80	93.20	322.00	72.50	777.00	277.00
Calcium as Ca	mg/L	82.38	59.50	63.00	63.23	125.46	129.66
Magnesium as Mg	mg/L	88.50	14.40	107.52	35.70	183.70	106.58
Sodium as Na	mg/L	271.86	127.08	489.25	39.42	1363.77	294.26
Potassium as K	mg/L	3.20	0.90	4.01	1.20	18.40	1.88
Total alkalinity as CaCO ₃	mg/L	412.00	258.44	479.00	250.30	462.70	477.00
Chloride as Cl	mg/L	299.18	129.80	545.92	47.73	1734.19	562.93
Sulphate as SO ₄	mg/L	265.01	31.10	362.53	54.90	966.90	110.64
Nitrate + Nitrite as N	mg/L	1.98	0.04	0.06	2.02	0.05	2.13
Fluoride as F	mg/L	0.52	3.12	0.70	0.59	1.14	0.52

Table 20. Median value of groundwater quality parameters in the Mbashe catchment.

Mbashe Catchment: Groundwater Monitoring Sites							
Parameters	Unit	T1N0001	T1N0002	ZQMLAN1	EC/T90/209	T9N0001	
Ambient Groundwater Quality or Median							Target Water Quality Range (SANS 241 and SAWQG)
pH		8.49	8.36	7.58	7.70	8.17	5–9.7
Electrical conductivity	mS/m	42.30	53.90	14.90	112.00	61.30	≤170
Calcium as Ca	mg/L	7.70	45.09	5.49	87.80	37.48	≤150
Magnesium as Mg	mg/L	1.24	24.95	5.09	41.80	25.24	≤100
Sodium as Na	mg/L	82.97	37.24	11.65	238.80	45.05	≤200
Potassium as K	mg/L	0.56	1.00	0.91	4.94	0.62	≤12
Total alkalinity as CaCO ₃	mg/L	140.35	264.47	42.78	298.80	115.60	≤200
Chloride as Cl	mg/L	36.16	18.17	9.85	339.80	71.54	≤300
Sulphate as SO ₄	mg/L	11.40	6.25	2.00	14.85	8.85	≤250
Nitrate + Nitrite as N	mg/L	0.04	0.30	2.49	1.11	15.10	≤1
Fluoride as F	mg/L	3.58	0.34	0.13	0.44	0.18	≤1.5

Table 21. Median value of groundwater quality parameters in the Great Fish catchment.

Great Fish Catchment: Groundwater Monitoring Sites								
Parameters	Unit	ZQMADK1	ZQMFRR1	ZQMSME1	ZQMSTB1	ZQMHFR1	Q1N0055	
Ambient Groundwater Quality or Median								Target Water Quality Range (SANS 241 and SAWQG)
pH		8.07	8.07	7.91	8.20	8.12	8.00	5–9.7
Electrical conductivity	mS/m	111.40	248.00	160.00	99.60	99.50	71.00	≤170
Calcium as Ca	mg/L	118.68	95.30	89.20	83.18	73.50	58.48	≤150
Magnesium as Mg	mg/L	33.23	64.89	63.30	21.22	43.61	31.40	≤100
Sodium as Na	mg/L	133.21	361.70	190.59	116.65	71.39	48.70	≤200
Potassium as K	mg/L	2.59	13.29	2.99	0.95	3.97	1.52	≤12
Total alkalinity as CaCO ₃	mg/L	363.70	480.70	419.75	295.00	272.89	288.50	≤200
Chloride as Cl	mg/L	118.68	492.81	251.20	80.99	117.69	47.55	≤300
Sulphate as SO ₄	mg/L	36.35	131.90	108.50	136.37	75.89	16.20	≤250
Nitrate + Nitrite as N	mg/L	0.37	3.59	3.65	1.00	3.62	1.99	≤1
Fluoride as F	mg/L	0.79	1.59	0.71	0.48	0.60	0.36	≤1.5

3.4.1. Gamtoos Catchment

In the Gamtoos catchment, water quality assessment results showed CaCO₃ was a problem across the catchment. The mean value of CaCO₃ ranged from 243.85 mg/L to 421.13 mg/L in the identified stations within the catchment. This was likely due to geological types and/or land use practices. Groundwater monitoring sites L3324AB and L332AD recorded significantly higher values for EC, Cl and Na, which were beyond their respective standard limits. The mean values of EC were 307.20 mS/m at L3324AB and 427 mS/m at L332AD. The mean value of Cl was 634.34 mg/L at L3324AB and a value of 1115 mg/L at L332AD. The mean values of Na 351.61 mg/L and 530.64 mg/L were recorded at L3324AB and L332AD, respectively. The higher values of EC, Cl and Na at L3324AB and L332AD could be attributed to intense irrigation and citrus farming.

3.4.2. Great Kei Catchment

In the Great Kei catchment, water quality assessment results showed the value of CaCO₃ was beyond the target water quality ranges in all groundwater stations. Non-compliance of CaCO₃ was recorded at 257.96 mg/L (S19097), 332.71 mg/L (S19406), 283 mg/L (S19097), 312.77 mg/L (S19119) and 308.11 mg/L (S27007). The main land use activities at the stations are sand mining and vegetation removal. These activities expose riverbanks and land surface, which caused gullies during erosion. Station S7N0001 was the only monitoring station which complied (155 mg/L) with the target water quality range of 200 mg/L. The mean value of NO₃ + NO₂ showed non-compliance to the target water quality range, with 3.58 mg/L (S19406), 2.33 mg/L (S19097), 2.72 mg/L (S19119) and

4.45 mg/L (S7N0001). The recorded higher values of $\text{NO}_3 + \text{NO}_2$ at the stations could be due to farming and sewage work activities.

3.4.3. Sundays Catchment

In the Sundays catchment, water quality results showed a steep rise in EC mean value with 777 mS/m, at the ZQMKWD1 monitoring station, which was beyond the target water quality range of 170 mS/m. The presence of EC in a resource was an indication of poor water quality conditions. The majority of groundwater monitoring stations in the catchment had EC which was beyond the required limits. The high mean value of CaCO_3 spreads across all monitoring stations in the catchment, exceeding the value target water quality range of 200 mg/L. The mean value of SO_4 was high at the following monitoring stations: N2636 (265.01 mg/L), N3242 (362.53) and ZQMKWD1 (966.90) compared to the target water quality range of 250 mg/L. According to Makanda et al. [28], SO_4 is an indicator of general mining impacts. Results for $\text{NO}_3 + \text{NO}_2$ value varied from 1.98 mg/L to 2.13 mg/L at the stations N2636 and ZQMADO1, respectively. This was likely due to intensive farming practices in the catchment. The water quality results of Na did not comply with the majority of monitoring stations within the study area, except at stations N3238 (127.08 mg/L) and N3243 (39.42 mg/L) which complied with the target water quality range of 200 mg/L.

3.4.4. Mbashe Catchment

In the Mbashe catchment, the monitoring station (EC/T90/209) recorded high values of CaCO_3 (298.80 mg/L), Na (238.80 mg/L), Cl (339.80 mg/L), $\text{NO}_3 + \text{NO}_2$ (1.11 mg/L). The mean value level of $\text{NO}_3 + \text{NO}_2$ was beyond the limit at monitoring stations at T9N0001 (15.10 mg/L) and ZQMLANI (2.49 mg/L), while the mean value of F was non-compliant at station TIN0001 with 3.58 mg/L.

3.4.5. Great Fish Catchment

The results of the water quality assessment in the Great Fish catchment showed a mean value of CaCO_3 which exceeded the target water quality range of 200 mg/L, across the catchment. The mean value ranged from 272.89 mg/L to 480.70 mg/L across all stations. This was a clear indication of the influence of farming practices and geological types in the study area. The ZQMADK monitoring station was a water quality hot spot and the majority of parameters were beyond the target water quality ranges. The station recorded EC of 248 mg/L, Na of 361.70 mg/L, Cl of 495.81 mg/L, NO_3 and NO_2 of 3.59 mg/L and F of 1.59 mg/L. At the station, there is high sedimentation (highly turbid), farming, cattle trampling, and sewage works problems.

In conclusion, areas in the central (Great Fish catchment) and western parts (Gamtoos catchment) of the WMA7 reflected marginal to poor groundwater quality. The $\text{NO}_3 + \text{NO}_2$ value level was marginally high (2.12 mg/L) compared to the required limit of 1.00 mg/L. According to a study by DWS [33], EC spatial distribution in the catchment generally reflected lithological controls, favourable recharge and rainfall conditions. The study by DWS [33] noted that though some parts of the catchments in the WMA7 had poor groundwater quality, it was not always impacted by anthropogenic sources but happened naturally in aquifers, owing to interaction with rock and sediments. However, spatial distributions and quality results of NH_4N , SO_4 and $\text{NO}_3 + \text{NO}_2$ proved to be generally evident that pollution sources were man-made. Therefore, groundwater treatment is recommended to render it suitable for sensitive water users.

3.4.6. Spatial Distribution of Groundwater Parameters

The spatial distribution of groundwater chemical parameters such as nitrate and nitrite, ammonia and sulphate in the study area is presented in Figures 9–11, respectively.

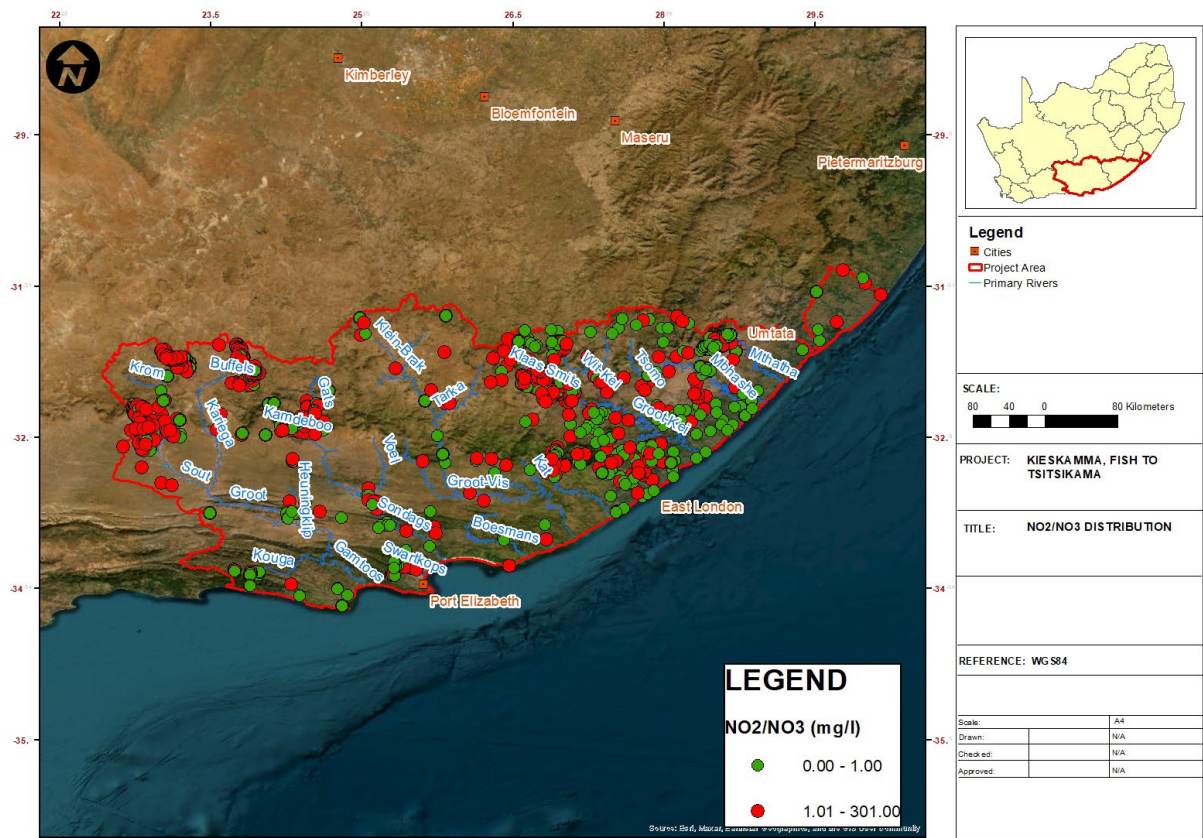


Figure 9. Spatial distribution of nitrate and nitrite within the WMA7 [33].

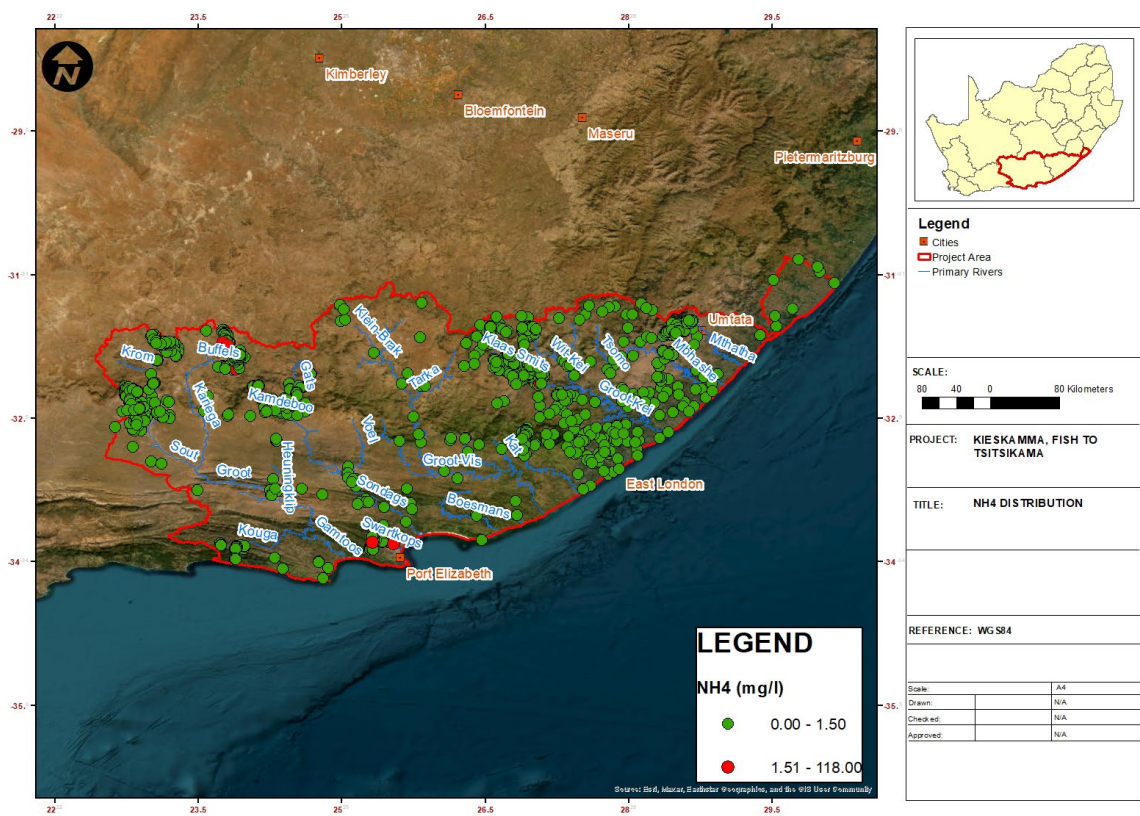


Figure 10. Spatial distribution of ammonia within the WMA7 [33].

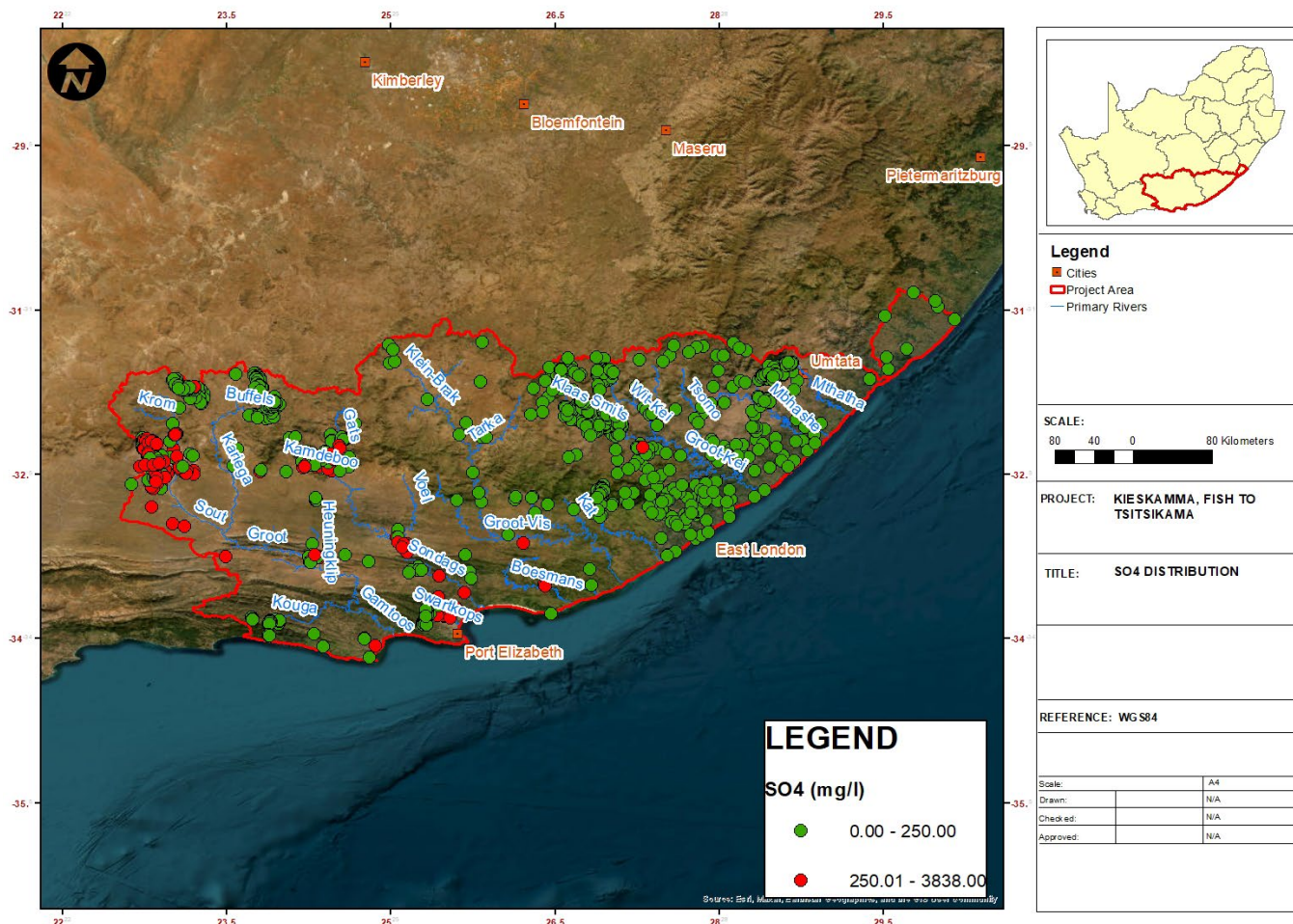


Figure 11. Spatial distribution of sulphate within the WMA7 [33].

The DWS WMS database was interrogated to analyse groundwater quality data in the study area. The spatial distribution of nitrate and nitrite, ammonia and sulphate were assessed to determine potential anthropogenic impacts. Where external sources are impacting negatively on groundwater quality, increases in typical pollution indicators such as nitrate, ammonia and sulphate will generally be evident. The SAWQGs and SANS 241 [22] limits were used to distinguish between acceptable and elevated values, respectively. The results show that elevated nitrate and nitrite values are widespread in the study area, as indicated in Figure 9. This is likely due to the impact of farming practices in the WMA7. The land uses in the WMA7 include extensive subsistence and commercial agriculture, afforestation, irrigation, human settlements, limited mining activities, industries, etc. Groundwater recharge processes are modified during flooding events, causing leaching of salts, including nitrate. This could be the reason considering that the study area is prone to flooding events. Figure 10 shows that ammonia values are generally within the limits in the study area. Figure 11 shows that elevated sulphate values occur mainly in the western half of the study area. These elevated sulphates may potentially be due to external sources, namely agricultural practices or other surrounding land use activities. Groundwater quality in the western and central parts of the study area reflected marginal to poor groundwater quality. This could be due to lithology, limited groundwater recharge and rainfall conditions, which have a bearing on the quality of groundwater. These sections of the study area are associated with the Bokkeveld Group, Uitenhage Group and alluvium (particularly over the more arid western part of WMA7). Therefore, these sections of the study area have poor groundwater quality, owing to greater interaction with rock and sediments. Groundwater quality is not always impacted by anthropogenic sources but naturally occurs in aquifers.

Based on the groundwater quality assessment, the main parameters of concern are EC (salinity), nitrate and nitrite and sulphate. Groundwater with elevated EC, nitrate and nitrite, and sulphate will require treatment prior to use.

4. Conclusions

The current study aimed to assess and evaluate water quality changes, for both surface and groundwater, in the Mzimvubu to Tsitsikamma Water Management Area (WMA7). The current study was able to successfully make use of statistical analysis and a water quality index in order to explain seven-year trends and the present state of all five catchments within the study area. The study results showed that, overall, water quality parameter values of NH_4 , pH, Na, Cl, Mg, F, K, SO_4 and CaCO_3 were within the water quality target range of the South African Water Quality Guidelines and SANS 241. However, the values of PO_4 , $\text{NO}_3 + \text{NO}_2$ and EC vary significantly due to possible sewage works, sand mining, farming and industrial activities in the study area. The application of WQI was explored to determine the overall water quality status of all five catchments within the WMA7. The overall assessment results of all five catchments in the WMA7 showed that the Gamtoos catchment was in a good water quality state while the other four catchments were in a poor to very poor state, according to the WQI classification. Based on the groundwater quality assessment, the main parameters of concern were EC (salinity), $\text{NO}_3 + \text{NO}_2$ and SO_4 . However, groundwater assessment revealed that groundwater quality was chemically suitable for drinking purposes in most parts of the study area. Similarly, the study [33] found that agricultural activities and wastewater treatment works were the main sources of EC and $\text{NO}_3 + \text{NO}_2$ in the Keiskamma River and in the impoundment downstream. The current study findings provided baseline information to assist the National Department of Water and Sanitation in the management of water resources and in making informed decisions regarding identified water quality hotspots, the authorisation of future water use and the magnitude of the impacts of developments. Therefore, the study recommended resource-directed measures to improve surface and groundwater resource protection, especially in areas where surface and groundwater quality for other uses remains a challenge. This will enable management authorities and researchers to focus on potential future threats that need to be addressed to prevent further water quality changes.

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