DURBAN UNIVERSITY OF TECHNOLOGY

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Impact of anthropogenic activities affecting the water quality of Umhlathuze River in KwaZulu Natal

By

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A dissertation submitted to Faculty of Applied Science, Durban University of Technology in fulfilment of the requirements for the degree of

Master of Applied Science in Chemistry

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science at Durban University of Technology, Faculty of Applied Science, KwaZulu Natal, South Africa. It has been published at Environmental Geochemistry and Health, https://doi.org/10.1007/s10653-025-02830-0

I declare that "Impact of anthropogenic activities on the water quality of uMhlathuze River in KwaZulu Natal, South Africa" is my own original work conducted by myself at Durban University of Technology. All sources that I have used or quoted have been indicated and acknowledged by means of complete references. Furthermore, I declare that I have not previously submitted this work, or part of it, for examination at DUT for another qualification or any other tertiary institution in South Africa

Makhosonke Bhengu

26th day of October 2025

LIST OF MANUSCRIPTS

The current study has been published in the Environmental Geochemistry and Health from which the candidate is the principal author. Environmental Geochemistry and Health is a recognized journal under Springer Nature. The published paper is included as part of the **Appendix** and may be examined as part of the thesis.

1. **MS Bhengu**, P Ntolo, S Ncube, **2025**. Anthropogenic impact assessment on the water quality of uMhlathuze River in KwaZulu Natal Province, South Africa, *Environmental Geochemistry and Health*,47 (11), 1-18.
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ABSTRACT

UMhlathuze River and its three main tributaries experiences various anthropogenic activities including agriculture, urbanization and industrialization before forming an estuary with the Indian Ocean. This River which is in the northern part of KwaZulu-Natal, South Africa supports a rapidly growing agricultural, domestic and industrial community. The comprehensive study was aimed to assess the potential impact of these anthropogenic activities over a 12-months period in 2023/4. The study showed that elementary levels were mostly within the permissible limits along uMhlathuze River, but the impact of anthropogenic activities along its tributaries was evident. Chlorides ranged between 400 and 655 mg/L along the Mholweni tributary during the rainy season while Na, Mg and Ca were also consistently above permissible limits along Mholweni and Ntambanana tributaries. Among non-toxic trace elements, only Fe exceeded its health-based precautional value during the rainy season for all sites. Trace toxic metal levels were also within permissible limits. Hg was only detected along the tributaries in the 0.017 - 0.399 $\mu g\ L^{-1}$ range. The source of elevated levels of parameters along the tributaries was linked to quarry and agricultural activities and the wastewater effluents and urban runoff. The WQI values were in the 10.7 - 36.1 range implying the river water could be classified as good to excellent. The possibility of using these waters for agricultural purposes was assessed by calculating the Sodium Adsorption Ratio (SAR). The SAR results of the present study ranged from 29.5 to 76.3 which indicated that the water from the three tributaries (NTA, MH and EM) was unsuitable for irrigation. A health risk assessment identified that the river water was safe for domestic use to adults but infants and children were more likely to develop non-carcinogenic effects with HI values of 1.07 - 3.28. The ILCR values ranged between 1.20 and 9.93 indicating that consumption of unprocessed water from UMhlathuze and its tributaries will result in carcinogenic effects over one’s lifetime with infants and children affected most.

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This work is dedicated to my mom, Hlomuka, my wife Sindi and my beloved children whose unwavering support and encouragement have been the driving force behind my academic pursuits". A special thank you to my mentor Dr. S Ncube and Dr P Ntola, whose guidance and expertise have been instrumental in shaping my research unconditionally.

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LIST OF ABBREVIATIONS

DWS	Department of Water and Sanitation
EC	Exposure Cancer risk
EDI	Estimated Daily Intake
HI	Hazard Index
HPI	Heavy Metal Pollution Index
HQ	Hazard Quotient
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ILCR	Incremental Lifetime Cancer Risk
LIMS	Laboratory Information Management System
LOD	Limit of Detection
LOQ	Limit of Quantification
MDL	Method Detection Limit
MQL	Method Quantification Limit
PCA	Principal Component Analysis
(R)SD	(Relative) Standard Deviation
SAR	Sodium Adsorption Ratio
SAWQG	South African Water Quality Guidelines

SD	Standard Deviation
TOC	Total organic carbon
TWQR	Target Water Quality Range
USEPA	United State Environmental Protection Agency
WHO	World Health Organization
WSP	Water Service Provider
WW	Water Works
WWW	Waste Water Works

1 INTRODUCTION

1.1 Background

Pollution of water resources results from anthropogenic activities including agricultural runoff, poorly managed wastewater infrastructure, mining, industrial activities as well as urbanisation. (Enitan *et al.*, 2018; Kubra *et al.*, 2022; Atangana, 2023; Rahmani and Hadi, 2024). Every day copious amounts of effluent are discharged into rivers either down the drains or via the wastewater treatment plants (Halder and Islam, 2015; Agoro *et al.*, 2020). In recent years, South Africa has shown a significant decline in water quality status of water resources (Ntombela *et al.*, 2016; Harding, Chivavava and Lewis, 2020). This is caused by poorly maintained wastewater operated and managed by municipalities (van Rensburg, Barnard and Krüger, 2016). Heavy metals which could be attached to sediments end up being released into the water column due to the change in environmental circumstances such as temperature and pH, or other physical or biological disturbances (Ahmed *et al.*, 2020; Kubra *et al.*, 2022). The level of heavy metal contamination in aquatic systems fluctuates seasonally due to changes in precipitation and human behaviour.

UMhlathuze River in northern part of KwaZulu-Natal, South Africa supports a rapidly growing agricultural, domestic and industrial community (Mokoma and Tilahun, 2022).

A previous study conducted by Mthembu, Djarova and Basson (2012) at uMhlathuze River indicated that the river has shown an increase in contamination levels. The study investigated six metals (Mn, Pb, Al, Hg, Cu and Cd) and observed that all the metal levels were higher than guideline limits. The study further confirmed that the main sources of anthropogenic activities were agriculture, industrial development as well as expanding human settlements. As a result, there was a need for further studies to be conducted at this river to assess the water quality changes since 2012. Some developments have taken place in the region including drought between 2014 and 2020, new industrialization and establishment of new settlements that have emerged as well as extreme KZN floods in April 2022 (Mashao *et al.*, 2023, Ndlovu M, 2020). During drought, the levels of Gouderetrouw dam dropped to about 30%, resulting in stratification of the uMhlathuze River. The effect of stratification include increased salinity, high nutrients accumulation to bottom waters as well as increased concentration of dissolved solids, the effect which can be disastrous to the aquatic ecosystem (Kim, Kim and Hwang, 2025). Also, heavy metal accumulation from the bottom of a dam has a potential to pollute the river and cause harm to aquatic life (Goyal *et al.*, 2022). In an article by local newspaper, it was reported that fish died at one of uMhlathuze River Weir Pumpstation (Zululand Observer, April 12, 2023, https://www.citizen.co.za/zululand-observer/news-headlines/local-news/2023/04/12/city-residents-warned-as-dead-fish-found-in-nsezi-weir/ cited 6 Sep 2025). There are various anthropogenic activities upstream of the uMhlathuze Weir which include mining, industries with ponds along river, wastewater works as well as agriculture which may release trace metals that may negative impact aquatic environment hence died fish were taken along these areas as part of investigation. During heavy rains toxic chemicals which may include heavy metals may be washed into the uMhlathuze River and cause environmental damage to aquatic species including fish death. The uMhlathuze Weir also has an extensive growth of invasive plants including hyacinth which may absorb trace metals from wastewater discharge and later release them to water. The invasive plants including hyacinth could be linked to nutrients from wastewater works as well as industries upstream (uMhlathuze Integrated Waste Management Plan 2022/23). Another motivation for further studies to be conducted at the uMhlathuze River relates to some historic events such as the floods of April 2022. During these floods, wastewater infrastructure was unable to contain storm water, resulting in scores of wastewater effluents polluting rivers and streams (Dlamini, Nhleko and Ubisi, 2024). In addition, dissolved heavy metals may also get introduced into rivers after floods due to rock weathering, soil erosion and dissolution of water soluble salts (Inengite, Abasi and Walter, 2015). In the current study, 22 metals were analysed at various sampling points purposefully selected along uMhlathuze River including some of its tributaries based on the activities in the vicinity. The current study was aimed to provide a recent state of pollution along uMhlathuze River by investigating 22 selected metals including the ones previously investigated by Mthembu and colleagues in 2012. The metals include macro elements which are sodium (Na), magnesium (Mg), potassium (K) and calcium (Ca). Essential elements conducted include copper (Cu), cobalt (Co), iron (Fe), manganese (Mn), nickel (Ni), and zinc (Zn). Trace metals which were conducted included chromium (Cr), cadmium (Cd), mercury (Hg), arsenic (As), lead (Pb), and uranium (U). Other elements conducted were aluminium (Al), selenium (Se), antimony (Sb), barium (Ba), boron (B), strontium (Sr) (Zoroddu *et al.*, 2019). In this study, uMhlathuze River was evaluated based on metal levels and physicochemical properties within the river catchment. With 13 sites monitored, the idea was to get a comprehensive assessment of the entire catchment in terms of status of water quality from source of Babanango Mountains to estuary at Richards Bay coastal town. The monitoring of river water samples provided valuable information on a variety of pollution and its extent to biodiversity. The human health risk assessment approach developed by the United States Environmental Protection Agency (USEPA) has been used to estimate the potential health risk. In addition, regular monitoring was required to avoid potential ecotoxicological effects on aquatic life and the human population that depends on the uMhlathuze River for survival (Kinuthia *et al.*, 2020). Measurement of the levels of these 22 selected metals was conducted using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). In addition, some physicochemical parameters including pH, temperature, and dissolved oxygen were conducted and results were linked to the measured levels of the metals. Other nutrient chemicals like chloride (Cl), nitrate (NO_3^-), sulphate (SO_4^{2-}) fluoride (F) and phosphates (PO_4^{3-}) were also analysed and results used to check correlation with metal analysis. The results were required to provide data on the extent of metal contamination along the river in comparison with WHO and SAWQ guideline limits.

1.2 Problem Statement

Trace metals contamination to river water systems due to anthropogenic activities has long been a concern since it is directly related to human and environmental health risk. These anthropogenic activities including agricultural runoff, industrial waste and domestic wastewater discharges may all release trace metals into the river. Metals have known health side effects if present above certain levels in drinking water sources. With 13 sampling sites and 22 metals investigated, the aim was to assess the level of metals (including trace metals) present in the river water based on anthropogenic activities including agricultural, industry and wastewater discharges.

1.3 Research Question

What are the primary anthropogenic sources (mining, industrial, or agricultural) contributing to the trace metal pollution in the uMhlathuze River and its tributaries

1.4 Aims and objectives

Aim: To determine the levels of selected trace metals along uMhlathuze River taking into consideration the impact of anthropogenic factors along the river, and further assess any potential ecotoxicological and health risks to humans and aquatic organisms.

Objectives: The objectives of this study are:

- To measure the levels of 22 selected metals in water using ICP-MS
- To compare the seasonal and spatial variations in water quality throughout the catchment
- Compare results against WHO and SAWQ guideline limits
- To identify sources of pollution along the river based on the results

- To perform a risk assessment on human health and aquatic environment using predictive models like water quality index and hazard quotient pollution indices.

2 LITERATURE REVIEW

2.1 UMhlathuze River

UMhlathuze River is situated on the north coast of KwaZulu-Natal with its catchment area of 4 209 km^2. UMhlathuze River rises between Nkandla and Babanango Hills at an altitude of 1 519 m above sea level and flows over 100 km eastwards towards Richards Bay where it forms an estuary with the Indian ocean as shown in figure1 (uWASP, 2016). Agricultural activities, paper mill, sugarcane process plant, municipal wastewater works and abattoir are located along uMhlathuze River. From eNkandla to Gouderetrouw dam (eShowe north) there are 2 tributary rivers, Madiyana and uMvuzane. Madiyana River receives final effluent from Nkandla town whilst uMvuzane River receives water from uThukela River through a pipeline managed by DWS and uMngeni uThukela Water (UUW) and both rivers join uMhlathuze River upstream of Gouderetrouw dam. The sampling point called Gouderetrouw upstream (GDS) was then established to monitor these rivers for the study. From Gouderetrouw dam to Empangeni, the area has agricultural activities including citrus and sugarcane plantations as well as a fruit processing factory. The area from Empangeni until the estuary in Richards Bay is considered urban and uMhlathuze River is mainly affected by industrialization which include chemical industries, sugarcane processing plants, refuse dumbs, abattoirs and three municipal wastewater works. All these anthropogenic activities have the potential to release pollutants into the river thus affecting the aquatic ecosystems including people who may drink the water from the river especially in rural communities where there are no tapped water sources.

One of the pollutants with a potential to make it to the river due to these anthropogenic activities are metal elements. In a study performed in 2012, Mthembu, Djerova and Basson (2012) sampled four sites and measured the concentration of only six metals. All the six metals (Mn, Pb, Al, Hg, Cu and Cd) were above guideline limits and the authors reported agricultural and industrial development as a major contribution to the deterioration of water quality with the River(Mthembu, Djarova and Basson, 2012). Since then there was no follow up or any other studies that investigated the entire river. This therefore calls for detailed studies to give a better understanding of an impact of anthropogenic activities on metal pollution levels along uMhlathuze River.

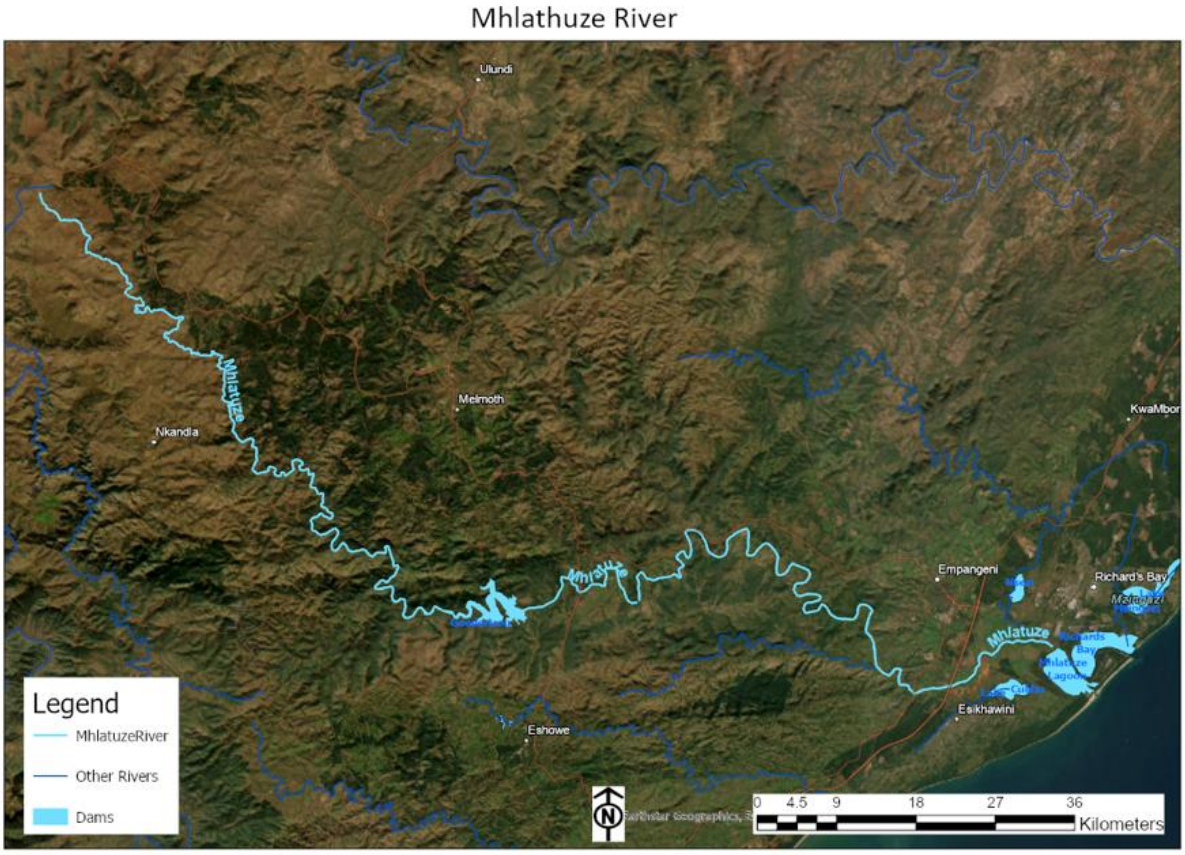

Figure 1: uMhlathuze River from Nkandla to Indian Ocean

There are various types of elements which can be classified as macro-elements, essential metals and toxic metals. The essential and toxic metals exist in water and food sources in trace amounts and therefore are both classified as trace metals. The potential health risks of elements selected for this study and their permissible limits in food sources are discussed in Section 2.2.

2.2 Classification of elements

2.2.1 Macro elements

Macro elements are those natural elements available in water, meat and vegetables etc, and are much needed by the body more than the other minerals (Molnár and Pal, 2024). They are also referred to as macronutrients and help the body to maintain its structure and systems (Madilonga *et al.*, 2021). In this study, macro elements that were investigated are K, Ca, Mg and Na.

Potassium (K) which is found in water originates from rocks as well as anthropogenic activities such municipal or industrial discharge. Municipal domestic waste has been known to release K into the rivers that receive the effluents (Skowron *et al.*, 2018). At high concentrations K makes the water to taste bitter. The SAWQG target range for K in water is 50 mg/L (DWAF, 1996). Above 50 mg/L, K in water can become dangerous to infants. Calcium (Ca) is found in most minerals including lime and gypsum (Khanoranga and Khalid, 2019). In water, Ca ranges between 15 mg/L in fresh water and can go as high as 500 mg/L in ground water (Adbarzi *et al.*, 2020). At high concentrations, Ca is responsible for the hardness of water. Hard water is water containing high concentrations of dissolved minerals usually Ca and Mg. As per SAWQG, the target range for Ca in drinking water is 30 mg/L (DWAF, 1996). Above 30 mg/L, increased scaling problems and lathering of soap is observed. Magnesium is an alkaline earth metal found in water and minerals (Thavrin Manickum, 2020). Ca and Mg ions are primary contributors to water hardness when combined with carbonates (Hammoumi *et al.*, 2024). Sodium is mostly found as sodium chloride (NaCl) in the environment. When present in water at high concentration like in sea water, it is called brine. Ground water from areas with coal deposits or closer to sea is usually very high in Na as NaCl. In addition, high Na may be deposited to river systems from industrial or municipal discharges. The acceptable standard concentration of sodium in water as per SAWQG is 100 mg/L. Above 100 mg/L up to 400 mg/L, the taste of water becomes salty (DWAF, 1996). Above 400 mg/L of Na, the water becomes so salty such that it is impossible to consume.

Ntanganedzeni and colleagues conducted a study along Tugela catchments where Mg, Ca, Na and Cl were reported to be above SAWQG (Ntanganedzeni, Elumalai and Rajmohan, 2018). Reasons given included impact of wastewater infiltration from domestic waste as well as agricultural activities in the area. Skowron and colleagues conducted a study at Bystrzyca River in Poland where K was reported to be high due to impact of huge amount of wastewater entering the river (Skowron *et al.*, 2018).

2.2.2 Trace essential elements

Essential elements are those elements which are required by living organisms to maintain their normal growth, metabolism and development. Whilst these elements are essential, higher concentrations and prolonged consumption may affect human health and aquatic life. Trace essential elements involved in the study are discussed.

2.2.2.1 Iron

Iron (Fe) is found in water and soil either in the soluble ferrous or insoluble ferric form. Rust is an iron oxide which can be seen as reddish-brown colour (Gareev, 2023). This is formed by reaction of iron and oxygen in the presence of water or moisture. In human body, iron plays a crucial role in oxygen transportation, oxidative metabolism, cellular proliferation and other catalytic reaction (Yiannikourides and Latunde-Dada, 2019). The drinking water standard limit for Fe is 0.30 mg/L. Excessive ingestion of iron may result in haemochromatosis where tissue damage occurs as a result of iron accumulation (Lal, 2020).

2.2.2.2 Manganese

Manganese (Mn) is a naturally occurring mineral found in water, soil and rocks. Mn is involved in the synthesis and activation of some enzymes including regulation of the metabolism of glucose and lipids in humans (Li and Yang, 2018). The drinking water standard limit for Mn is 0.10 mg/L (DWAF, 1996). Rainwater that passes through rocks containing Mn ores, industrial discharge and well as agricultural landfills can result in increased concentrations of Mn in drinking water sources. Mn can cause a disorder disease called manganism (Andruska and Racette, 2015), (Kulshreshtha, Ganguly and Jog, 2021). An unpleasant taste has been observed on Mn concentrations exceeding 0.15 mg/L.

2.2.2.3 Copper

Copper (Cu) is a natural metal found in water, soil, rock including sediments. Found in all body tissues, Cu plays a key role in making red blood cells and maintaining nerve cells and immune system (Chen *et al.*, 2020). Most of household plumbing material is made of Cu and at low pH, the copper linings from plumbing material may leach into water (DWAF, 1996). The recommended WHO limit for Cu in drinking water is 2 mg/L. High levels of copper may negatively affect male fertility and damage red blood cells including reducing their ability to carry oxygen (Andrea *et al.*, 2021).

2.2.2.4 Cobalt

Cobalt (Co) is found in water in small amounts. In the human body, Co is involved in the production of red blood cells, the production of antibacterial and antiviral compounds that prevent infections (Zoroddu *et al.*, 2019). In higher concentrations, cobalt is chronic and can be toxic to humans and aquatic life, causing health issues including heart problems, thyroid dysfunction and damage to liver and kidneys (Kosiorek and Wyszkowski, 2016). Permissible WHO limit for cobalt in water is 0.05 mg/L (WHO, 2017).

2.2.2.5 Zinc

Zinc (Zn) is one of micro nutrients found in water, soils and earth crust. It is needed for the body's defensive system to function well. It plays a role in cell division, cell growth, wound healing and the breakdown of carbohydrates (Chasapis *et al.*, 2020). Zn can enter water systems through activities including weathering, erosion, industrial waste disposal and urban runoff.

Water with high levels of Zn may taste metallic or astringent. Also, when high it can cause health risks including stomach cramps, nausea and nervous system disorders (Schoofs, Schmit and Rink, 2024). The WHO limit for Zn in drinking water is 3 mg/L (WHO, 2017).

2.2.3 Trace toxic elements

Trace metals are those with known toxic effects to humans and aquatic organisms even if they are present at low concentrations. Trace metals can be found in water naturally or through anthropogenic activities including municipal wastewater effluents, municipal runoff, agricultural and industry discharge. Those included in this study are discussed in Sections 2.2.3.1 - 7.

2.2.3.1 Cadmium

Cadmium (Cd) is naturally occurring in the earth's crust, mixed with zinc oxide (Surbakti *et al.*, 2021). Cd has toxic effects and causes health issues including kidney damage, bone disorders and disruption of Ca metabolism (Ibe *et al.*, 2019). It can induce various epigenetic changes in mammalian cells, both in vivo and in vitro which then cause pathogenic risks and the development cancer related diseases (Schoofs, Schmit and Rink, 2024). The body can still withstand traces of Cd and its permissible limit in water as per WHO guidelines is 0.03 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.2.3.2 Chromium

Chromium (Cr) occurs naturally in water, soil, rocks, plants and animals. It can exist in trivalent (Cr III) as well as in hexavalent states (CrVI) (Ibe *et al.*, 2019). CrVI is the toxic version of Cr and can lead to stomach and lung cancer, kidney damage, liver damage, skin irritation and gastrointestinal problems due to its toxicity (Tumolo *et al.*, 2020). In an aquatic environment, Cr exposure to fish can lead to uneven swimming behaviour, mucous discharge and change in body colour (Garai *et al.*, 2021). The permissible limit for Cr in water is 0.05 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.2.3.3 Lead

Lead (Pb) is a toxic metal that can be found as a pollutant on earth including water. Pb can enter body through inhalation and ingestion whereas in water, it can arise from industrial, agricultural and wastewater discharges. Pb can cause serious health problems even when present in trace levels to both humans and animals. Pb can severely damage the brain and central envious system causing coma, convulsions and even death (Pratush, Kumar and Hu, 2018). Lead can affect bodily functioning of different types of cells, including immune system cells, modification of immune reactivity by affecting T cell precursor lymphocyte differentiation and can also inhibit cell growth. (Metryka *et al.*, 2018). The guideline limit for lead in water as per WHO is set at 0.01 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004). Above this limit, possible neurological damage may occur on nerve and brain tissues especially on the young and the pregnant women (Xing *et al.*, 2022).

2.2.3.4 Arsenic

Arsenic (As) is a natural element which can be found in minerals, soil and rock. It can dissolve into groundwater and find its way to rivers and streams due to industrial effluent disposal, mining activities and borehole erection. When present at concentration exceeding permissible limits, As can cause health problems including kidney failure (Rehman *et al.*, 2018). Other health effects of As include weariness, colitis, loss of reflexes, weight loss, weakness, anorexia, gas-trisis, hair loss and anorexia (Fatoki and Badmus, 2022). According to WHO, the permissible limit for As in drinking water is 0.01 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.2.3.5 Nickel

Nickel (Ni) can be found in water by leaching from rocks and plumbing material such as pipes and fittings. It is found in many objects of general use such as coins, earrings, watches, mobile phones, batteries and more (Das *et al.*, 2019). Ni is used as a catalyst for various biochemical reactions and forms part of active sites of metallo-enzymes such as urease (Zambelli, Uversky and Ciurli, 2016). Activities such as mining, industrial waste and coal burning can also result in the rise in Ni levels in air and water. Pollution from Ni can cause a variety of side effects to human health including allergy, cardiovascular, kidney failure, lung fibrosis and nasal cancer (Zambelli, Uversky and Ciurli, 2016). Ni acute toxicity to human health results from absorption through the gastrointestinal tract or inhalation through lungs. Symptoms include stiffness of the chest, constant cough, sweating and weakness (Rehman *et al.*, 2018). The WHO recommendation for Ni in drinking water is 0.07 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.2.3.6 Mercury

Mercury (Hg) is a naturally occurring toxic metal found in soil and rock deposits and does not break down in the environment and in the body (WHO, 2021). Hg can also be discharged into a river system through industrial and agricultural activities. When consumed, Hg can have serious health risks on humans and aquatic life. This includes damage to the nervous system affecting brain development in foetuses and young children (Henriques *et al.*, 2019). Hg can also affect the digestive and immune system including eyes, skin and kidneys (Balali-mood *et al.*, 2021). Poisoning with mercury may occur through breathing contaminated air or consuming water of food like contaminated fish (Kumar, Sharma and Sedha, 2022). Indigenous people in the Arctic regionare showed exposed to Hg resulting in health effects including neurology and cardiovascular health effects through dietary pathways from animals harvested (Basu *et al.*, 2022). Permissible guideline limit for mercury as per WHO in water is 0.01 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.2.3.7 Uranium

Uranium (U) is a radioactive metal that can be found in water through erosion of rocks containing U. It can also enter water source through activities such as mining, coal burning and application of fertilizers. U entering human body is mostly in the form of hexavalent oxide uranyl ions (Shaki *et al.*, 2019). In the human body, U causes damage to kidneys and other organs and tissues with effects on pulmonary, hepatic, hematopoietic, neurological and reproductive organs (Zhang *et al.*, 2022). Its toxicity can also lead to infertility by decreasing the levels of sex hormones and impaired expression of genes responsible for production (Wang *et al.*, 2020). Permissible limits for U in water as per WHO is 0.03 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.2.4 Other trace metals

There are other elements in aqueous environments that cannot be classified under trace toxic or trace essential metals. It is important to point out that these elements can still have health effects but the effects are low to moderate. To ensure humans are totally protected from potential effects of such elements, WHO has also set the permissible limits in water sources for some of these elements while others do not have set limits (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004). For the purpose of this study, 6 metal elements with minimal effect in the body were included and classified as other trace metals. These were aluminium (Al), boron (B), barium (Ba), strontium (Sr), antimony (Sb) and Selenium (Se). These metals do exist naturally but industrial, municipal and human activities can result in their elevated levels in drinking water sources. For example, Al is used in water treatment as a coagulant called alum to aid in the removal of organic matter, turbidity, colour and microorganisms, and has the potential to reach the receiving river systems as part of effluents (Krupińska, 2020). Elevated concentrations of Al in water used for consumption may pose a potential risk to human health, resulting in brain changes characteristics of Alzheimer's disease (Izabela Krupinska, 2020). Target limit for Al in water as per SAWQG is 0.150 mg/L (DWAF, 1996).

The element, B occurs naturally in the earth's crust and can also be found in fruits and vegetables. The health benefits of B include improved bone density, reproduction, growth, embryonic development, wound healing and cancer therapy (Biţă *et al.*, 2022). High intake of B may cause diarrhoea, kidney injury or even death from circulatory failure (Bolan *et al.*, 2023). The WHO permissible limit for B in drinking water is 0.5 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004). Another element without known direct benefits to human health is Ba. It can be released into the environment through human activities including mining, industrial effluent discharge and urban runoff (Adams *et al.*, 2024). Once in water at elevated amounts, Ba can cause vomiting, muscle weakness and changes in hearth rhythm or paralysis (Al osman, Yang and Massey, 2019). The WHO permissible limit of Ba in drinking water is 2 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

Strontium (Sr) is another element common in groundwater and surface water along coastal regions. In the body, it can stimulate the growth of osteoblast cells and prevent reabsorption of bone and thus stop osteoporosis (Mukherjee and Mishra, 2021). However, if present in elevated levels, it can potentially replace Ca in bones leading to skeletal problems and defects (Silva *et al.*, 2018). The recommended limit for Sr in drinking water is 4 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004). Selenium (Se) is another element of relatively low toxicity that can enter water through natural processes like weathering of rocks or by human activities including mining, industrial wastewater or disposal of hazardous waste. In the body, Se is incorporated into selenoproteins involved in antioxidant defence systems (Genchi *et al.*, 2023). High intake of Se have been reported in populations exposed to toxic element complexes that are known to interact with Se. In the body, Se may alter the composition of the gut microbiota on very young children (Rayman, 2020). WHO guideline limits for Se in drinking water is 0.04 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004). Another element that exists naturally and can make its way to drinking water sources is antimony (Sb). Water bodies can be contaminated with Sb from sources including mining waste, industrial effluent, leaching of fertilizers as well as burning of fossil fuel (Li *et al.*, 2018). Elevated levels of Sb in the body can cause nausea, vomiting and diarrhoea (Natasha *et al.*, 2019). The WHO guideline limits for antimony in drinking water is 0.02 mg/L (WHO Guidelines in DW 4th edition, Overview *et al.*, 2004).

2.3 Trace metals in rivers

Pollution of river resources remain as one of the greatest hindrances to economic progress, poverty eradication and sustainable development (Enitan *et al.*, 2018; Rahman *et al.*, 2022, Halder and Islam, 2015; Agoro *et al.*, 2020). In recent years, there has been a significant decline in water quality status from water resources due to large amounts of effluents from industry and municipal wastewater treatment plants being discharged into rivers and dams used as drinking water sources in South Africa (Ntombela *et al.*, 2016; Harding, Chivavava and Lewis, 2020). This is caused by non-compliant wastewater treatment works (WWTW) operated and managed by municipalities who do not maintain their aging infrastructure (van Rensburg, Barnard and Krüger, 2016) resulting in discharge of improperly treated waste into rivers and dams that are the major sources of water for domestic, agricultural and industrial purposes (Yohannes and Elias, 2017).

This study was conducted along uMhlathuze River in northern part of KwaZulu-Natal, a river which flows from rural areas of Babanango and Nkandla through various agricultural areas between Eshowe and Empangeni and finally the urban and industrial community of Richards Bay before finally flowing into the Indian ocean (Mokoma and Tilahun, 2022). A previous study conducted by Mthembu and colleagues along uMhlathuze River indicated that the river has shown an increase in metal contamination levels (Mthembu, Djarova and Basson, 2012). Their study observed that the levels of the investigated metals (Mn, Pb, Al, Hg, Cu and Cd) were higher than WHO guideline limits. They further confirmed that the main sources of these anthropogenic activities were agriculture, industrial development as well as expanding human settlements. As a result, there is a need for further studies to be conducted at this river to assess water quality changes since the last study was performed in 2012. Thereafter, there has been notable changes in the area including the drought of 2014 – 2018, a surge in industrialization and settlement as well as extreme KwaZulu Natal floods since 2022 (Mashao *et al.*, 2023). The previous study investigated six metals and focussed on four sites in the industrialized area of Richards Bay only. In the current study, the sampling sites were increased to thirteen which included parts where the river passes through rural areas. It is important to point out that pollution research in rural areas remains limited yet most residents in rural areas consume unprocessed water directly from rivers.

Studies have also reported metal pollution on rivers in other parts of South Africa. A study conducted by Addo-Bediako and colleagues at Steelpoort River, Limpopo reported Cr, Cu, Mn and Zn which exceeded South African Water Quality (SAWQ) guidelines (Addo-Bediako, Matlou and Makushu, 2018). Their study reported fertilisers and pesticides from discharge of agricultural wastes as well as from the mine and domestic and industrial wastes as reasons for high concentrations metals. Edokpayi conducted a study along Mvudi River in Thohoyandou where it was reported that the concentrations of Al, Cr, Fe, Mn and Pb were all above the DWARF permissible limits for domestic water use (Edokpayi *et al.*, 2017). Partially-treated wastewater and agricultural runoff were some of the reasons given. In a study conducted by Madikizela and colleagues along the Bizana and Mthatha Rivers in the Eastern Cape Province, the levels of Cd, Pb and Se were reported to be above the guideline limits (Madikizela, Chimuka and Ncube, 2023). The authors cited wastewater works, municipal dumpsite leachate and agricultural activities as some of the reasons for high concentration levels of metals in the river.

Metal pollution have also been reported elsewhere in the world. Mokarram and colleagues conducted a study along the Kor River in southern Iran where trace metals like Cd, Cu Mo, As and Ni were reported to have higher concentrations at points which were associated with industrial activities, abattoir effluents as well as agricultural runoff (Mokarram, Saber and Sheykhi, 2020). Hussain and colleagues conducted a study on the Godavari River in India and Ni and Cu concentrations exceeded the WHO acceptable limits in water (Hussain *et al.*, 2017). The study pointed out population growth and industrialization as the main reasons for increased concentration of these trace metals. In view of these recent observations, it is therefore important to regularly monitor metal pollution in important rivers such as uMhlathuze in the KwaZulu Natal Province.

2.4 Water Quality Parameters

During metal analysis in an aqueous environment, it is important to check other water quality parameters such as pH to determine any interrelationships with the metal concentrations observed in that aqueous environment. Water quality parameters can be subdivided into physical and chemical parameters. Physical parameters are parameters which include temperature, dissolved oxygen (DO), electrical conductivity (EC) and turbidity. Chemical parameters are parameters which measure chemicals in water. Examples include pH, chloride, sulphate, fluoride, nitrate and total organic carbon (TOC) among others. Physicochemical properties of water especially the physical parameters are usually determined onsite as they may deteriorate during transportation to the laboratory (Ahmed *et al.*, 2020). Some important physicochemical parameters including those done in the current study are presented in Sections 2.41 and 2.4.2.

2.4.1 Physical Parameters

Temperature of water is one of the important physical parameters during environmental water analysis. It is the measure of the degree of coldness or hotness of water. An increase in temperature produces an increase in solubility of solids and may also affect the biosorption process of the dissolved heavy metals (Pilla *et al.*, 2018). Dissolved oxygen (DO) is another important parameter which measures the amount of oxygen present in water. Testing DO is important in understanding and managing the ecology of a river and to be able to identify any possible contamination which can affect aquatic life. Levels of DO above 5 mg/L are good for aquatic organisms whereas if below 2, aquatic life is affected negatively (Zhong *et al.*, 2021). Dead fish at a river signifies less oxygen in water which may be caused by industrial or municipal waste discharge (Ali, Anushka, Mishra, 2022).

Electrical conductivity (EC) is another common water property in water analysis. It is a measure of the ability of water to pass an electrical current (Rusydi, 2018). Dissolved solids which are present in water highly affect conductivity of water if present at large quantities, meaning both are correlated. The conductivity of metal ions in solution depends on the solubility of a particular metal. The more the solubility of metal, the more it will conduct electricity (Belashchenko, 2023). Conductivity in lakes, dams and streams ranges between 0 and 70 mS/m. The South African water quality guideline for EC is 150 mS/m (DWAF, 1996). Known as freshwater salinization syndrome, elevated levels of EC can cause significant infrastructure and ecological damage including accelerated corrosion and toxicity to aquatic organisms.

The measure of clarity of water, referred to as turbidity is another important property of water that is considered during metal analysis. Metals can bind with suspended particles in water which will then contribute to turbidity. When water is more turbid, there is a possibility that suspended particles present can carry metals with them. Hence there is a positive relationship between turbidity and metals in a water sample. Analysis for metals can therefore be conducted either in dissolved state in which turbidity is removed by filtration or particulate form where sample is preserved without removing turbidity (Javed, Cuss and Shotyk, 2020).

2.4.2 Chemical Parameters

Chemical parameters include pH. The pH of a solution is its measure of the concentration of hydrogen ions, indicating whether the solution is acidic or basic (Zhang *et al.*, 2018). The pH scale normally ranges between 0 and 14. pH plays a critical role in determining the solubility and availability of metals. Together with salinity and suspended solids, pH greatly affects the migration and transportation processes of heavy metals (Zou *et al.*, 2024). Acidic environments represented by low pH values increases the bioavailability of metals. Therefore, understanding pH before conducting analysis is essential.

Total organic carbon (TOC) which measures the amount of carbon in organic compounds in aqueous systems is also important during water analysis. Measuring TOC during metals analysis is important because organic matter can significantly affect the extraction and measurement of metals (Hu *et al.*, 2018; Tian *et al.*, 2022). Samples high in TOC may require pre-treatment to break down the organic matter which includes acidification or digestion before analysis.

Determining ammonia is another common practice during metal analysis in water samples. Ammonia is a colourless gas that dissolves in water and forms ammonium hydroxide solution (Kinuthia *et al.*, 2020). It can enter water systems from sources including organic waste decomposition, industrial effluents, municipal effluent discharges, animal and human waste. When ammonia is dissolved in water, it raises the pH of the water solution, making it alkaline. At $pH < 8.75$, the ammonium ion (NH_4^+) is the predominant form while at $pH > 9.7$, it is mainly present in the form of NH_3 (Li *et al.*, 2020). At higher pH levels ($pH>9.7$), most of metals exist as hydroxides and are less available in solution (Edokpayi *et al.*, 2018). As a result, it is crucial to monitor ammonia during metal analysis.

The presence of anions is essential during metal analysis in aqueous systems. Anions are negatively charged ions in aqueous solution including Cl, F, PO_4^{3-}, SO_4^{2-} and NO_3^- (Hammoumi *et al.*, 2024). Cl occurs in water naturally either as NaCl or a combination with K and Ca. In humans, consuming high amounts of sodium chloride may raise blood pressure and lead to obesity disorders (Shahid *et al.*, 2023). Guidelines by Department of Water and Fisheries in SA states that between 100 - 200 mg/L Cl concentration is tolerable as there are no aesthetic or health effects except the intense salty taste when concentrations are above 200 mg/L (DWAF, 1996).

Another mineral found naturally in water and soil is F. Ground water from various areas around mines and along sea have high amounts of F. The acceptable limit of F in drinking water is 1.5 mg/L and higher concentration levels, F may interfere with the metabolism including skeletal fluorosis (DWAF, 1996). Nitrates also occur naturally in water and soil but their main contributor to drinking water sources are mainly agricultural and industrial activities. These ions are the main reason for promoting growth of hyacinth in dams and lakes (Wijayanti, Sediawan and Prasetya, 2019). SAWQ permissible limits for nitrates in drinking water is 15 mg/L (DWAF, 1996).

Sulphates can be found in water and minerals or through discharge by urban or industrial waste. Sources of sulphates include magnesium sulphate commonly used in households as Epsom salts, as well as from calcium sulphate commonly known as gypsum. Sulphate levels above 250 mg/L can give water a bitter taste and prolonged use may result in running stomach (Ubong *et al.*, 2021). The phosphates are also responsible for growth of algae and hyacinth in lakes and dams.

2.5 Ecotoxicological assessment for metals in aqueous environments

2.5.1 Water quality assessment

The most common water quality assessment tools in relation to metal pollution are the water quality index (WQI) and the Heavy Metal Pollution Index (HPI). WQI is a tool that summarizes large amounts of water quality data into a single score and assist in evaluating the water quality of a water body (Lukhabi *et al.*, 2023). The WQI is mainly used to classify water quality in relation to chemical, physical and biological characteristics, and helps classify its possible use or allocations for use (Uddin, Nash and Olbert, 2021).

The HPI is a calculation which uses a formula that considers the concentration of trace metals (heavy metals) and their potential to harm human health or the environment (Raja *et al.*, 2021). Various studies have used the HPI model to predict potential impact of metals in river and dam systems. For example, a study conducted in Ghana by Appiah-Opong and his colleagues in Ghana reported heavy metals (As, Cu, Pb, Se, Zn and Hg) in drinking water with HPI values which were above the critical limit of 100 for both wet and dry season (Appiah-Opong *et al.*, 2021). A-Hejuje and his colleagues studied variation of seven eco-toxic elements (Cd, Cu, Fe, Mn, Ni, Pb, and Zn) at Shatt Al-Arab River and concluded that the water was not suitable for consumption based on HPI calculations (Appiah-Opong *et al.*, 2021). In Sasolburg, South Africa, a study observed that HPI values for major and trace metals (Al, As, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti and V) were low and concluded that the water system was not polluted by heavy metals (Mollo, Nomngongo and Ramontja, 2022). WQI and HPI are therefore important estimation tools for investigating pollution in water systems and should be included in water pollution studies.

2.5.2 Health risk assessment

The most common tools for assessing the potential non-carcinogenic and carcinogenic risks associated with ingesting and absorbing metals through the skin and via the consumption of drinking water include the Hazard Quotient (HQ). An HQ is a ratio that compares the potential exposure to a substance to the level at which adverse health effects are not expected (Emmanuel *et al.*, 2022). This ratio is used to assess the potential of non- carcinogenic health hazards from exposure to any contaminant including trace metals. When HQ < 1, this indicates that no adverse health effects are expected, while HQ > 1, indicates adverse health effects are possible. Therefore, a more representative extent of risk is the sum of all HQ value for all the metals, referred to as the total hazard quotient or the hazard index (HI).

Another important risk assessment tool is the Incremental Lifetime Cancer Risk (ILCR). The ILCR predicts cancerous risks based on cancer slope values for those metals known to cause cancer in the body (Ashraf *et al.*, 2021). Metals with known cancerous effects include Cd, As, Pb and Cr. The ILCR values above 1 represent a serious risk for cancer while below 0.1, the risk is minimal. Between 0.1 and 1, the values represent a potential to cause cancer in the body and extra care should be taken to avoid over exposure.

2.6 Method validation and statistical analysis

To ensure reliable results, both ICP-OES and ICP-MS instruments were validated using parameters which include detection limits, linearity, working range, accuracy, reproducibility and repeatability (Ismail and Afify, 2022). Performing method validation of an analytical instrument before analysis are conducted confirm that the instrument is operating correctly and that the method is sensitive to detect the analyses of interest. Furthermore, performing validation ensure that potential interference are accounted for and that accuracy and reliability of results is achieved (Juliasih *et al.*, 2021; Rusiniak *et al.*, 2024). Validation parameters conducted included detection limit, linearity, working range, accuracy and precision which is very important when analysing trace elements at very low concentrations (Ismail and Afify, 2022). Kilic conducted validation of ICP-MS for the analysis of Cs, Rb, Tl, Co, As, Cr, Pb, Ga, V, Ag, Cd, U, Th, and Mo in natural mineral water and validation parameters conducted included linearity, recovery, limit of detection, trueness and repeatability (Kilic, 2019).

An understanding of interrelationships between pollutants and the physicochemical parameters is essential for a better understanding of the pollution of the water system. Various statistical tools can be used to understand these interrelationships but the most appropriate when handling large datasets is Principal Component Analysis (PCA). PCA is a linear dimensionality reduction technique which compresses large datasets for easy handling and interpretation of interelationships (Jollife and Cadima, 2016). Simple correlation graphs and scatter plots are not easy to interpret if the study has large datasets due to multicollinearity problems (Naangmenyele *et al.*, 2021). In this regard, the PCA approach can be used to counteract these problems by transforming correlated variables into smaller manageable variables called Principal Components (PCs). The first two PCs usually contribute a large proportion of the variance in the dataset and are used to plot biplots to visualize the interrelationships. In the current study, PCA was utilized and performed on RStudio statistical software, an open source Integrated Development Environment (IDE) for R programming language.

3 MATERIALS AND METHODS

3.1 Sampling area

For this study, the uMhlathuze River was divided into three segments based on the anthropogenic activities as shown in Figure 2. The segments selected were referred to as the upstream (represented by rural areas), the interior (represented by agricultural areas), and the downstream (represented by industrial areas) as seen on Figure 3. Thirteen sampling points (Figure 3) were investigated for this study. Three were selected in Segment 1, six in Segment 2 and four in Segment 3. The GPS coordinates for the sampling sites are given in Table 1. The choice of sampling sites in each segment are discussed in Section 3.1.1 – 3.1.3.

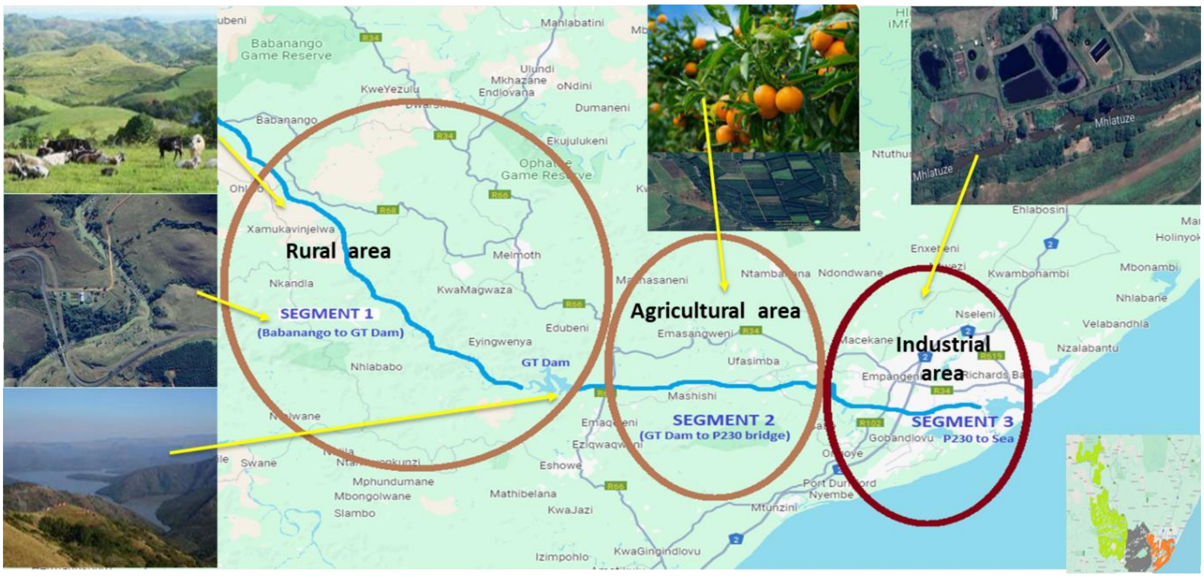

Figure 2: Anthropogenic activities per segment along uMhlathuze River

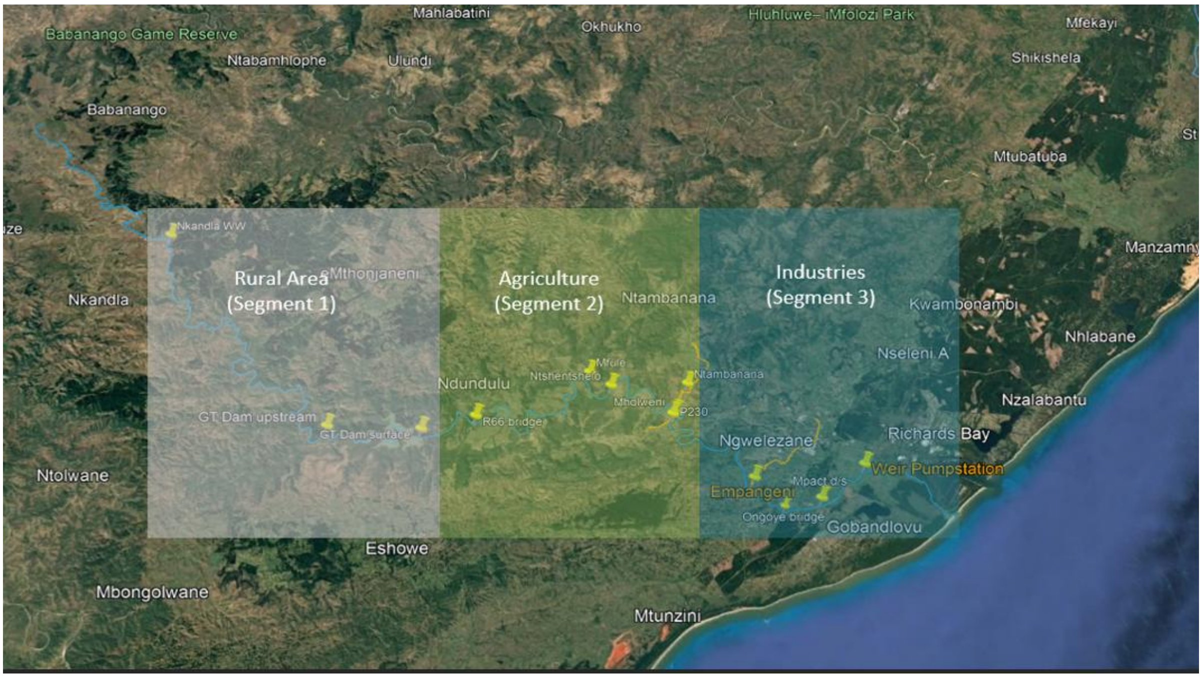

Figure 3: Sampling points along uMhlathuze River from Babanango & Nkandla to the Richards Bay estuary then to Indian Ocean

Table 1: The GPS coordinates for the 13 sampling sites along uMhlathuze River

Segment	Site Name	Site id	Co-ordinates Latitude	Co-ordinates Longitude
1	Nkandla	NKA	28º32’56.64’’S	31º9’33.51”E
	Gouderetrouw dam upstream	GDU	28º46’22.66’’S	31º22’5.42”E
	Gouderetrouw dam surface	GDS	28º46’12.79’’S	31º28’1.82”E
2	R66 bridge	RB	28º45’19.74’’S	31º31’34.80”E
	Mfule River	MF	28º45’19.74’’S	31º39’6.17”E
	Ntshentshelo	NTS	28º43’7.30’’S	31º39’24.37”E
	Ntambanana River	NTA	28º42’53.57’’S	31º45’42.48”E
	Mholweni River	MH	28º44’52.68’’S	31º44’36.25”E
	P230 bridge	PB	28º44’56.58’’S	31º44’42.92”E
3	Empangeni River	EM	28º49’19.41’’S	31º50’7.75”E
	Ongoye	ON	28º50’44.96’’S	31º51’59.26”E
	Industrial monitoring point	IMP	28º50’18.48’’S	31º54’22.67”E
	Weir Pumpstation	WP	28º48’4.23’’S	31º57’20.03”

3.1.1 Segment 1 – Rural areas

This segment represents rural areas between Babanango mountains where uMhlathuze River originates, up until Gouderetrouw Dam which is about 60 km from uMhlathuze River. Three sampling sites were selected. First site is Nkandla (NKA), situated upstream of R68 road bridge which is the upstruction point for raw water to Nkandla Water Works. The site is unknown to any anthropogenic activities hence served as a baseline. The second site called Gouderetrouw Dam upstream (GDU) is located upstream of the Gouderetrouw Dam where two tributary rivers (Madiyana River and uMvuzane River) meet uMhlathuze River. Madiyana River originates from Nkandla sewage ponds. Mvuzane River receives water from Tugela River through a pipeline and pours it into uMhlathuze River just before the dam. The third sampling site is located inside Gouderetrouw Dam, close to the dam wall and is called Gouderetrouw Dam site (GDS). From the dam, uMhlathuze flows into Segment 2 of the study marked by agricultural activities.

3.1.2 Segment 2 – Agricultural areas

The second segment starts at about 5km downstream of Gouderetrouw Dam towards Empangeni area up to P230 road bridge crossing (Figure 2 & 3). This segment has 6 sampling sites. The first site called R66 road bridge (RB) is located closer to a citrus fruit factory and alongside are orange and sugarcane fields. The second site is along Mfule River, a tributary to uMhlathuze River. Mfule River originates from north of Melmoth town, and runs along sewage ponds from Melmoth town. This site was marked as MF, an abbreviation for Mfule River. The third site is called Ntshentshelo (NTS). At the NTS site, uMhlathuze River is surrounded by sugarcane fields whilst rural people access water directly from the river for domestic use. Sampling was also done on Ntambanana River, which is a tributary to uMhlathuze River. This fourth site was marked as NTA as an abbreviation for Ntambanana River. The river originates from rural Ntambanana, with sugarcane fields (Figure 4). Further down uMhlathuze River just before P230 bridge, a stream called Mholweni emerges from Dlangubo rural areas (Figure 4) and passes through a quarry. This stream also receives discharges from a nearby factory that makes rural toilet structures. Water samples were collected just before the stream joins uMhlathuze River, and was marked as MH as an abbreviation for Mholweni. The last site at this segment is located across the P230 road bridge and was abbreviated as PB. This site is used as an upstruction point for water to the quarry and also used by farmers to draw water for irrigation purposes in the area.

Figure 4: Map showing Ntambanana and Mholweni tributaries to uMhlathuze River and the sampling sites in the region

3.1.3 Segment 3 – Urban/industrial area

The third segment covers areas around Empangeni town to Richards Bay estuary. This is an urban area with a variety of chemical and processing industries, three wastewater treatment plants and various informal settlements. Four sites were selected in this segment

(Figure 5). The first site is Empangeni River (EM), a tributary to uMhlathuze River. The river receives wastewater effluents from Empangeni and Ngwelezane wastewater works, and runoff from Empangeni business area. The second sampling site along uMhlathuze River is at Ongoye bridge and was labelled as ON (Figure 5). This site occurs just before uMhlathuze River meets a small stream that recieves wastewater effluents from an academic institution and the surrounding townships. The third sampling site labelled as IMP was done at bridge dowstream of two industries located along uMhlathuze River. The last site is called uMhlathuze Weir Pumpstation which is located just before the river forms the estuary with the Indian ocean, and was named WP.

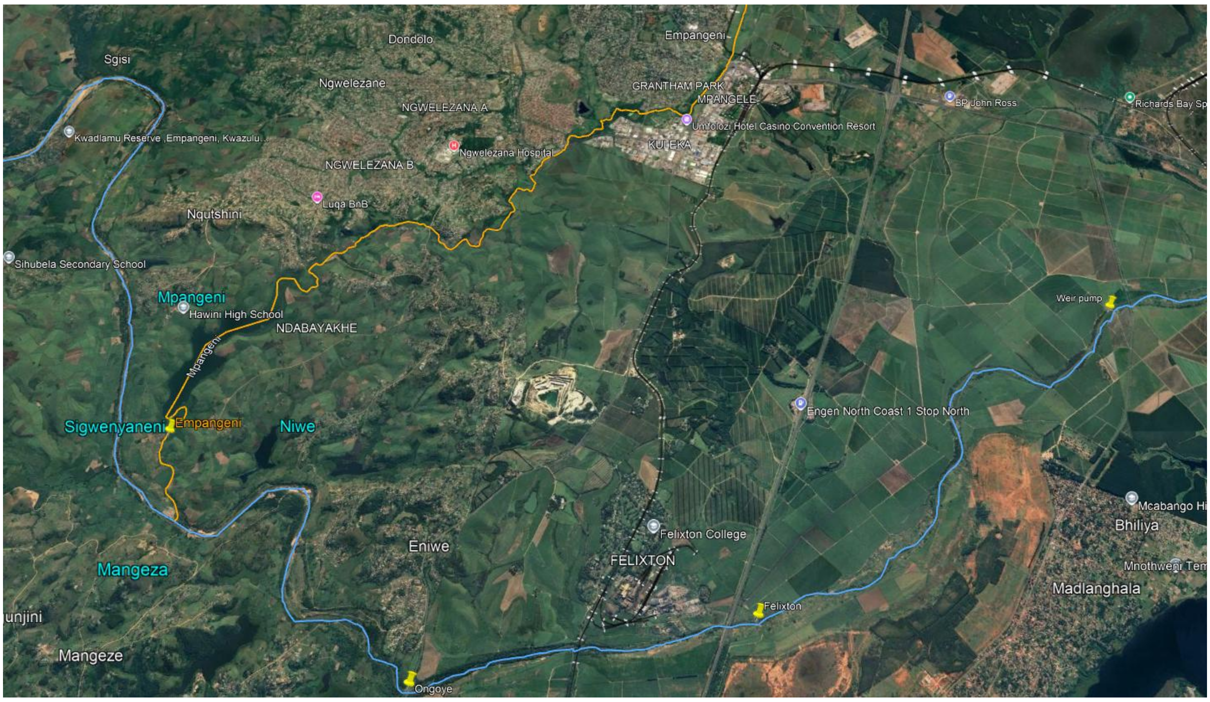

Figure 5: Map showing sites on segement 3 from Ongoye bridge until uMhlathuze Weir Pumpstation

3.2 Sample collection, processing and analysis

Before collecting samples, sampling apparatuses including bailer and bottles were washed with simple liquid soap and rinsed thoroughly with deionized water. Polyethylene plastic sampling bottles of capacity 250 mL were used to collect water samples for metal analysis and the water was preserved with 1% nitric acid. A separate 2 L plastic bottle was used to collect water samples for chemical parameters. Samples were transported in cooler boxes to a SANAS 17025 accredited laboratory and analysed within 48 h. Determination of the physical parameters including DO and temperature were performed onsite using an Aquaread meter from Geowater, Johannesburg, South Africa. An effort was made to maintain collection of samples on the same days monthly which was between the 12th and the 18th of each month for a period of 12 months.

3.3 Sample treatment and analysis

At the laboratory, about 500 mL of water samples was filtered through 0.45 µm filters and analysed for anions including F, Cl, NO_3^- and SO_4^{2-} using a Dionex ICS 1600 Ion Chromatograph by Anatec Suppliers, Johannesburg, South Africa. From same filtered sample, PO_4^{3-}, and ammonia were analysed on a Gallery Plus Discrete Analyser, Anatec Suppliers, Johannesburg, South Africa. From the nitric acidified samples, metal analysis was conducted using ICP-OES from Perkin Elmer, Johannesburg, South Africa to measure the macroelements (K, Na, Mg and Ca). ICP-OES instrument conditions were RF power 1.5 KW, plasma flow 8 L/min, auxiliary flow 0.2 L/min, nebuliser flow 0.7 L/min, pump rate 1 mL/min. Elemental wavelengths selected were Ca (317.933 nm), Mg (285.213 nm), Na (589.592 nm) and K (766.490 nm). ICP-MS from Perkin Elmer, Johannesburg, South Africa was used to analyse trace metals that include Al, Cu, Co, Fe, Mn, Cr, Cd, Hg, As, Se, Sb, Pb, Ni, Ba, B, U, Sr, and Zn. Instrument conditions for ICP-MS were RF power 1.55 kW, carrier gas 2 L/min, helium flow 4.5 mL/min and pump rate of -3 rpm. Gas used for both ICP-OES and ICP-MS was argon at 99.99% purity from Air Product, Richards Bay, South Africa. For both instruments, results were exported from instrument to LIMS system, then exported as excel for further processing.

3.4 Standard preparations

Using individual 1000 mg/L stock solutions (K, Na, Mg & Ca) purchased from Merck Pty Ltd, Johannesburg, South Africa, four working standards were prepared and preserved in 1% HNO_3. Ultrapure water from MiliQ Integral water purification system Merck Millipore, Johannesburg, South Africa was used to prepare standards. The calibration range for Ca and Mg was 5 – 60 µg/mL, for K it was 0.25 – 30 µg/mL while for Na was 25 – 200 µg/mL. For trace metals, mixed stock solutions of Al, As, Hg, B, Ba, Cd, Co, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, U & Zn using Inorganic Ventures brand from Separations, Johannesburg, South Africa were used. Intermediate standards of 10mg/L were prepared and preserved in 1% HNO_3. The calibration range for all trace metals was 1 - 1000 ng/mL except for Hg which was 0.1 – 50 ng/mL. Both instruments were set to accept the linearity of the calibration curves only for $R^2 > 0.999$.

3.5 Method validation

Both ICP-OES and ICP-MS was validated using parameters including LOQ, linearity, correlation of coefficient, working range, accuracy, repeatability and recovery. Acceptability criterion for calibration linearity was set to correlation coefficient ($R^2 \geq$ 0.999. LOD was determined by preparing blank solution (deionised water preserved with 1% nitric acid) and analysed on instrument. Then LOD and LOQ were calculated based on the linear regression method using Eqn 1. Accuracy and repeatability were calculated by running known concentration of standard 10 times on the same day. Accuracy as the percentage relative error (%RE) and relative standard deviation (RSD) were calculated as per Eqn. 2 & 3, respectively.

$$LOD = \frac{3.3 \text{ x } \sigma}{S}\ ;\quad LOQ = 10 \times \frac{\sigma}{S} \tag{1}$$

where S is slope and σ is the standard deviation of the response

Accuracy = $\frac{True\ Value - Mean}{True\ Value} \times 100$ (2)

RSD = $\frac{SD}{Mean} \times 100$ (3)

Since the study was done in a SANAS-accredited laboratory, the instrument was validated and set to accept the results only if accuracy was set at relative error less than 10% (RE ≤10%) and relative standard deviation less than 20% (RSD < 20%).

3.6 Ecotoxicological risk assessment

3.6.1 Water quality

The WQI which summarizes the overall quality of water was calculated using Eqn. 4, taking into consideration average values of pH, EC, TOC, ammonia, Cl, F, NO_3^-, SO_4^{2-}, K, Na, Mg and Ca. Table 2 provides useful info on how to rate water parameters based on determinants investigated. HPI that assesses the impact of heavy/trace metals on water quality was predicted using Eqn. 5. The implications of HPI values are summarized in Table 3.

$$WQI = \sum_{i=1}^{n}(S_i W_i) \quad (4)$$

where WQI is there water quality index, S_i is the sub-index value for parameter i, W_i (which ranges from 0 to 1) is the corresponding parameter weight value and n is the total number of parameters.

$$\text{HPI} = \frac{\sum_{i=1}^{n} (WiQi)}{\sum_{i=1}^{n} Qi} \quad (5)$$

where HIP is Heavy Metal Pollution Index, Q*i* is the sub index of the *i*th parameter. W*i* is the unit weight of the *i*th parameter and n is the number of parameters considered. The sub index Q*i* of the parameter was calculated using Eqn 6.

$$Qi = \frac{Vi}{Si} x\ 100 \quad (6)$$

where Qi is the sub index of the parameter, V_i is the monitored value of the metal of *i*th parameter and S_i is the standard value

Table 2: WQI Rating

WQI Value	Rating	Grading
0 - 25	Excellent	A
26 - 50	Very good	B
51 - 75	Good	C
76 - 100	Poor	D
Above 100	Very poor	E

Table 3: HPI guidelines

HPI Value	Water Quality
<15	Excellent
15 < HPI < 30	Good to intermediate
> 30	Poor to unsuitable
76 < HPI < 100	Very poor

3.6.2 Health risk assessment

Health risk assessment was predicted using three models; HQ, HI and ILCR. The three models give a prediction of the potential health risks to humans due to consumption of contaminated water (Emmanuel *et al.*, 2022). Firstly, the measured concentrations in water samples were used to estimate the chronic daily intake as an exposure concentration (EC) to a metal per day using Eqn. 7. The HQ which estimates the non-carcinogenic risk due to exposure to individual metals was then calculated as a ratio of the EC to the reference dose (RfD) of that metal using Eqn. 8 (US Environmental Protection Agency, 2011). The RfD values for elements investigated in this study are given in Table 5. Hazard index (HI) which is the comprehensive evaluation of multiple metals was calculated using Eqn. 9. The ILCR which represents the probability that someone will develop cancer due to continuous exposure over a particular period was calculated by comparing the EC values with cancer slope factor (CSF) values using Eqn. 10 (Room *et al.*, 2023). The CSF values for trace metals with known carcinogenic effect in the body are given in Table 5.

$$EC = \frac{Cm.DI.ABS.EF.EP}{BW.AT} \tag{7}$$

where EC is the exposure concentration (mg/kg(bw)/day), C_m (mg/L) is the concentration of the metals in water, DI (L/day) is the daily intake average, EF (days/year) is annual exposure frequency, ABS (no units) is dermal absorption factor, EP (years) is the exposure duration, BW (kg/person) is the body weight and AT (days) is average time (365 days/year x 65 years = 23,725 days).

$$HQ = \frac{EC}{RfD} \tag{8}$$

where HQ was the Hazard Quotient, EC is the Exposure Concentration (mg/kg(bw)/day), RfD is the Reference Concentration (mg/kg(bw)/day).

$$HI = \Sigma HQ \tag{9}$$

where HI is the Hazard Index

$$ILCR = EC.CSF \tag{10}$$

where ILCR is the incremental lifetime cancer risk, EC is the exposure concentration (mg/kg(bw)/day) and CSF is the cancer slope factor (mg/kg(bw)/day). Table 5 lists the RfD and CSF for selected metals (Mohammadi *et al.*, 2019).

Table 4: Parameters used for estimating exposure assessment of heavy metals in drinking water

Parameter	Units	Value
Water ingestion rate (IR)	L/day	2.2
Exposure frequency (EF)	Day/year	365
Average exposer time (adults) (AT)	days	10950
Average exposure time (children)	days	2190
Exposure duration (adults)	years	30
Exposure duration (children)	years	6
Average body weight (adult)	kg	70
Average body weight (children)	kg	15
Oral reference dose (Cd)	mg/kg/day	0.0005
Oral reference dose (lead)	mg/kg/day	0.0003
Oral reference done (mercury)	mg/kg/day	0.001

Ref: EPA 2011

Table 5: Reference dose and cancer slope factor values for some metals

Element	Rfd_{oral}	Rfd_{dermal}	CSF (mg/kg (bw)/day)
Pb	1.4	0.42	8.5
Cr	3	0.015	41
Cd	0.5	0.005	6.1
Ni	20	5.4	0.84
Zn	300	60	
Cu	40	12	
Ba	70	14	

Rfd – reference dose; CSF - cancer slope factor

3.7 Environmental Risks

In this study, environmental risks will include assessment of river water quality required to meet irrigation requirements. One parameter to be studied is sodium adsorption ratio (SAR) which is a measure of the sodium content relative to calcium and magnesium (Shakir, Zahraw and Al-Obaidy, 2017). SAR assesses suitability of water for irrigation. SAR can be calculated using Eqn. 11.

$$\text{SAR} = = \frac{[Na]}{\sqrt{\frac{(Ca)+(Mg)}{2}}} \qquad (11)$$

where

- SAR is Sodium Adsorption Ratio
- [Na] is the concentration of sodium
- (Ca) is the concentration of Calcium
- (Mg) is the concentration of magnesium

The %Na is the general Water Quality Index (WQI) used for drinking water, but it is a separate and important calculation used to assess the suitability of water for irrigation. It is calculated by dividing the concentration of sodium by the total concentration of all major cations as per Eqn. 12.

$$\%Na = \frac{[Na]+[K]}{[Na]+[K]+[Mg]+[Ca]} \qquad (12)$$

Water can be classified based on its SAR which ranges from excellent to unsuitable (Tahmasebi *et al.*, 2018). Water is considered suitable for irrigation if SAR<10 and %Na<60 (Mandal *et al.*, 2019). Water with SAR>10 can result in compact and impenetrable soil and %Na>60 can lead to alkaline or saline soils all of which are not suitable for plant growth (Ali and Ali, 2018).

Table 6: Classification of water based on sodium adsorption ratio

Type of water	Classification	SAR Value
Low Sodium Water	Excellent	Below 10
Medium Sodium Water	Good	10-18
High Sodium Water	Doubtful	18-26
Very High Sodium Water	Unsuitable	Above 26

SAR - sodium adsorption ratio

3.8 Principal component analysis

PCA was done on Rstudio statistical software to understand the interrelationships between the following:

- metal concentrations only
- physicochemical properties only
- metals and physicochemical properties of the river

The excel results from ICP analysis and field measurements were converted into a .csv format and imported into RStudio for statistical analysis using the *gplot* package as the R-environment. The dataset was partitioned such that 80% was used as training data and 20% as testing data. The PCA of the parameters (metals and physicochemical) was investigated and summarized using the *prcompt* command. Several PCs were generated but, in most cases, PC1 and PC2 accounted for 50 - 90% of cumulative variance for the respective dataset depending of the size of the data set. This indicated that the PC1 vs PC2 could be a reasonable summary of the data set. In this regards the PCA results were summarized and visualized in terms of biplots of PC1 and PC2 only.

4 RESULTS AND DISCUSSION

4.1 Physicochemical parameters

Table 7 represents minimum, maximum and median values for physicochemical parameters over a 12 months period from December 2023 to November 2024. Results show that temperature ranged from 11.6 to 32.5°C, at all sites. The minimum temperature was observed at Nkandla (NKA) sampling site which is in the rural area, whilst the maximum was recorded at Mfule (MF) which is in the agricultural area. The DO values ranged from 0.1 to 10 mg/L. The lowest DO was recorded at Empangeni River (EM site) which is located in the urban and industrial area. The highest dissolved oxygen was recorded at Nkandla and P32 bridge sites which are at rural and agricultural areas, respectively.

Turbidity values ranged from 0.8 to 252 NTU. The maximum recorded turbidity values were all above SAWQ guideline limits. The median values were also above SAWQ guideline limits, but the minimum values for three sites (GDU and GDS in rural, and MH in the agricultural area) were within SAWQ guideline limits. The recorded pH ranged between 5.8 and 8.6 which were all within SAWQ and WHO guideline limits. The conductivity was also observed to be within the SAWQ guideline limits for rural and agricultural region except for Ntambanana River (NTA site) and Mholweni River (MH site) which are tributaries to uMhlathuze River in the agricultural area. Considering the WHO guidelines of 40 mS/m, all the samples collected after NTA and MH sites and the urban region showed maximum values above the limits. NTA and MH were also observed to have TOC values above SAWQ guideline limit. Two other sampling points in the rural areas, Nkandla (NKA) and Gouderetrouw dam upstream (GDU) were also above the TOC guideline limits. The detailed discussion of each physicochemical parameter is given in Section 4.1.1 to 4.1.6. Site MH was dry during the months of April to July hence there were no results recorded.

Table 7: Minimum, maximum and median values for physicochemical parameters over 12 months

	Site	Temperature ºC			Dissolved oxygen (mg/L)			Turbidity (NTU)			TOC (mg/L)			pH			Conductivity (mS/m)		
Segment	Name	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med
Rural	NKA	11.6	26.6	20.2	5.0	10.0	7.4	10.6	237	23.1	1.5	20.1	2.1	6.04	8.32	7.7	12.8	24.4	15.9
	GDU	16.4	30.3	23.1	5.9	9.6	8.3	2.85	314	12.5	1.0	22.6	1.5	5.95	7.99	7.4	8.85	27.7	15.4
	GDS	17.6	27.8	22.9	5.0	9.1	7.5	3.1	26.1	7.8	2.2	3.8	2.8	6.8	8.0	7.5	11.8	16.7	14.8
Agricultural	RB	16.6	25.4	19.3	5.1	9.3	8.2	7.5	38.1	13.4	2.3	6.4	3.0	6.9	7.9	7.5	12.9	35.3	18.1
	MF	19.6	32.5	24.0	5.6	9.1	7.9	5.4	231	7.8	2.4	7.8	3.9	7.0	8.6	7.6	17.1	39.4	23.9
	NTS	15.6	26.6	20.8	5.5	9.1	8.0	6.2	133	14.5	2.8	7.6	3.3	6.5	7.9	7.6	16.6	29.4	24.4
	NTA	16.7	27.1	21.6	3.5	9.1	6.1	9.0	247	27.0	8.2	21.0	12.1	7.5	8.4	8.2	121	248	172
	MH	17.2	27.4	22.2	2.9	9.1	5.4	0.8	153	10.6	6.0	12.3	9.0	7.5	8.5	8.0	130	309	235
	PB	16.1	28.6	21.1	2.8	10.0	8.3	6.9	252	16.5	2.8	9.8	3.1	7.3	7.9	7.7	19.3	65	30.1
Urban and	EM	13.4	26.6	23.1	0.1	9.4	2.6	7.3	47.7	18.6	7.5	12.3	10.2	7.0	8.2	7.6	55	77	69
Industrial	ON	13.3	25.5	23.3	4.8	8.9	7.1	10.7	53	31.9	3.5	6.4	4.4	6.6	8.0	7.6	25.7	42.7	35.5
	MP	14.7	26.5	22.9	4.2	8.9	7.6	11.1	58	26.8	3.7	6.6	4.6	6.8	7.7	7.6	26.4	43.4	37.9
	WP	19.2	25.6	22.0	5.4	8.1	6.4	9.8	49.6	18.5	3.8	5.5	4.6	6.1	7.5	7.2	26.5	43.1	38.2
SAWQ Guideline		-			-			5			10			6.5 – 8.5			150		
WHO Guideline											-			6.5 – 8.5			40		

TOC = Total organic carban

4.1.1 Temperature

Temperature variations along uMhlathuze River over the 12-months sampling period are summarized in Figure 6. The results show that the temperature values were low in most sites during the winter months (June - July) with the lowest temperature of 11.6^{o}C recorded at Nkandla (NKA) sampling site in June (Figure 6A). The NKA site is closer to Babanango mountains which are known to be cold in winter (Wilkins, Howe and Smith, 2021). Warm to hot temperatures were recorded during summer months for all sites (Figure 6A, B & C). Figure 6C shows that the temperatures in urban and industrial areas did not vary much between the sampling sites from Empangeni River (EM) up to industrial monitoring point (MP) site. However, the temperature at the Weir pump station (WP) where the water is kept for upstruction purposes was consistently warm throughout the year, ranging between 19 and 26^{o}C (Figure 6C). In general Figure 6D shows that Mfule River (MF) in the agricultural region was the hottest ranging between 19 and 32^{o}C while Nkandla (NKA) in the rural areas recorded the coldest temperature as low as 11^{o}C in June. Figure 6D also indicates that there were no extreme cases of temperature along the river. Studies have been conducted at Bojonegara coastal waters as well as Mimica waters during summer months where temperature ranged from 27 to 39^{o}C (Tanjung, Hamuna and Alianto, 2019; Surbakti *et al.*, 2021).

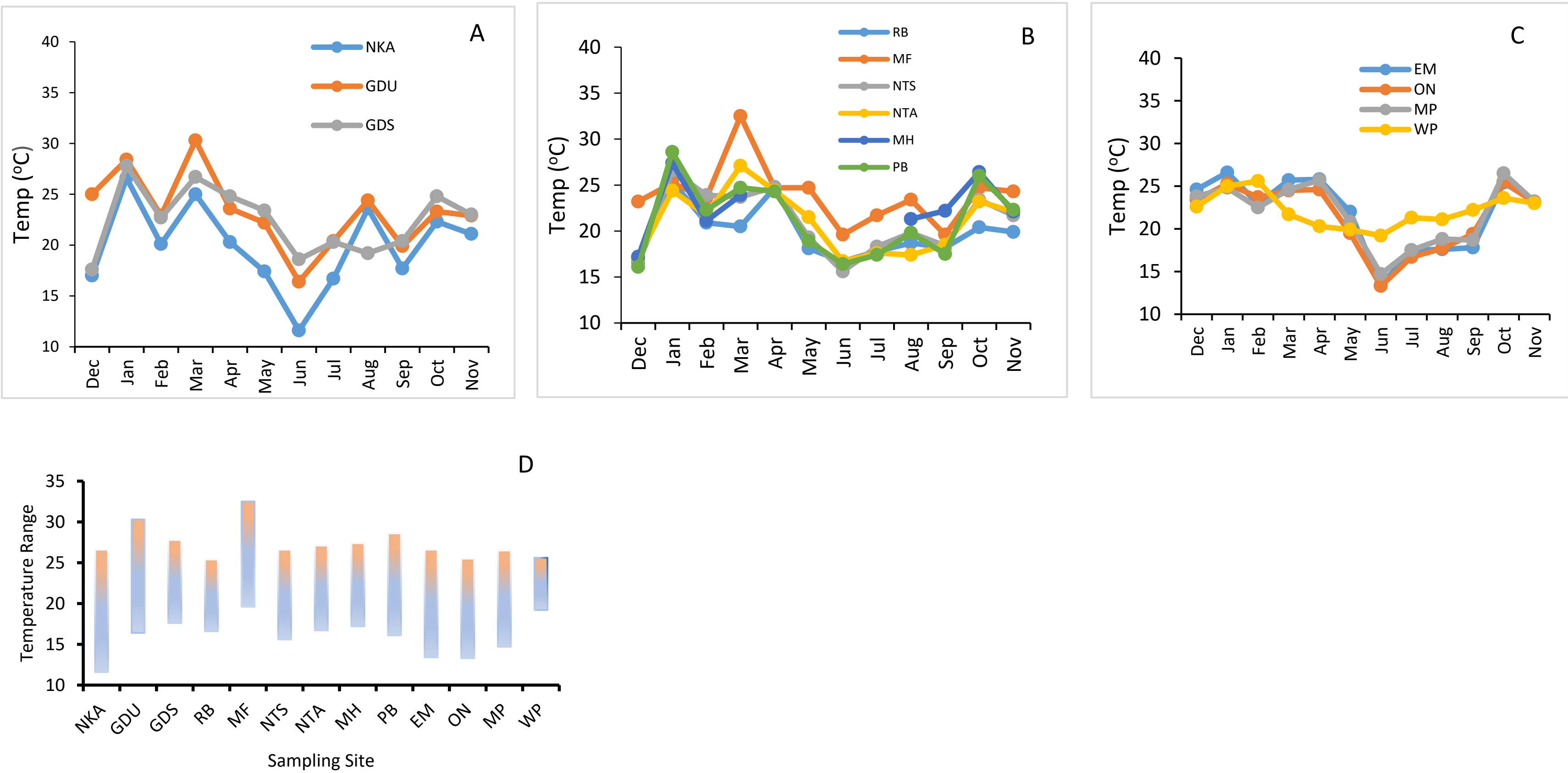

Figure 6: A – yearly temperatures for rural areas, B – yearly temperatures for agricultural areas, C – yearly temperatures for the urban/industrial areas, D – tempertaure range for all sampling areas over 12 months

4.1.2 Dissolved oxygen

Figure 7A shows that DO was between 5 and 10 mg/L for sampling sites in the rural areas. The recorded values were relatively lower during the high flow season (December - March) and increased signicantly during the cold low flow season (April - July). In the agricultural area, DO readings were also between 4 and 10 mg/L throughout the year except two tributaries of Mholweni River (MH) and Ntambanana River (NTA) where DO droped below 4 mg/L (Figure 7B). This was an indication of the impact of quarry and agricultural activities at Mholweni and Ntambanana tributaries respectively. A single spike at the P32 bridge (PB) site in June may indicate the impact from NTA site. An exception at the urban and industrial sites was observed for Empangeni River (EM) site where most of DO concentrations were below 4 mg/L for most of the year except in June (Figure 7C & D). Empangeni River receives wastewater discharge from two municipal wastewater works which could be responsible for the low DO levels (Adbarzi *et al.*, 2020). A study conducted at Lake Taihu reported effect of low DO conditions combined with ion excange and anaerobic reduction lead to significant release of As in water (Zeng *et al.*, 2023). Low DO values attributed to organic polluting constituents of sewage have also been reported elsewhere (Adbarzi *et al.*, 2020). Low DO values in water may indicate contamination due to wastewater discharges which negatively affect aquatic environment because aquatic organisms require DO for respiration, and when levels drop, it leads to widespread stress and mortality (Ntanganedzeni, Elumalai and Rajmohan, 2018).

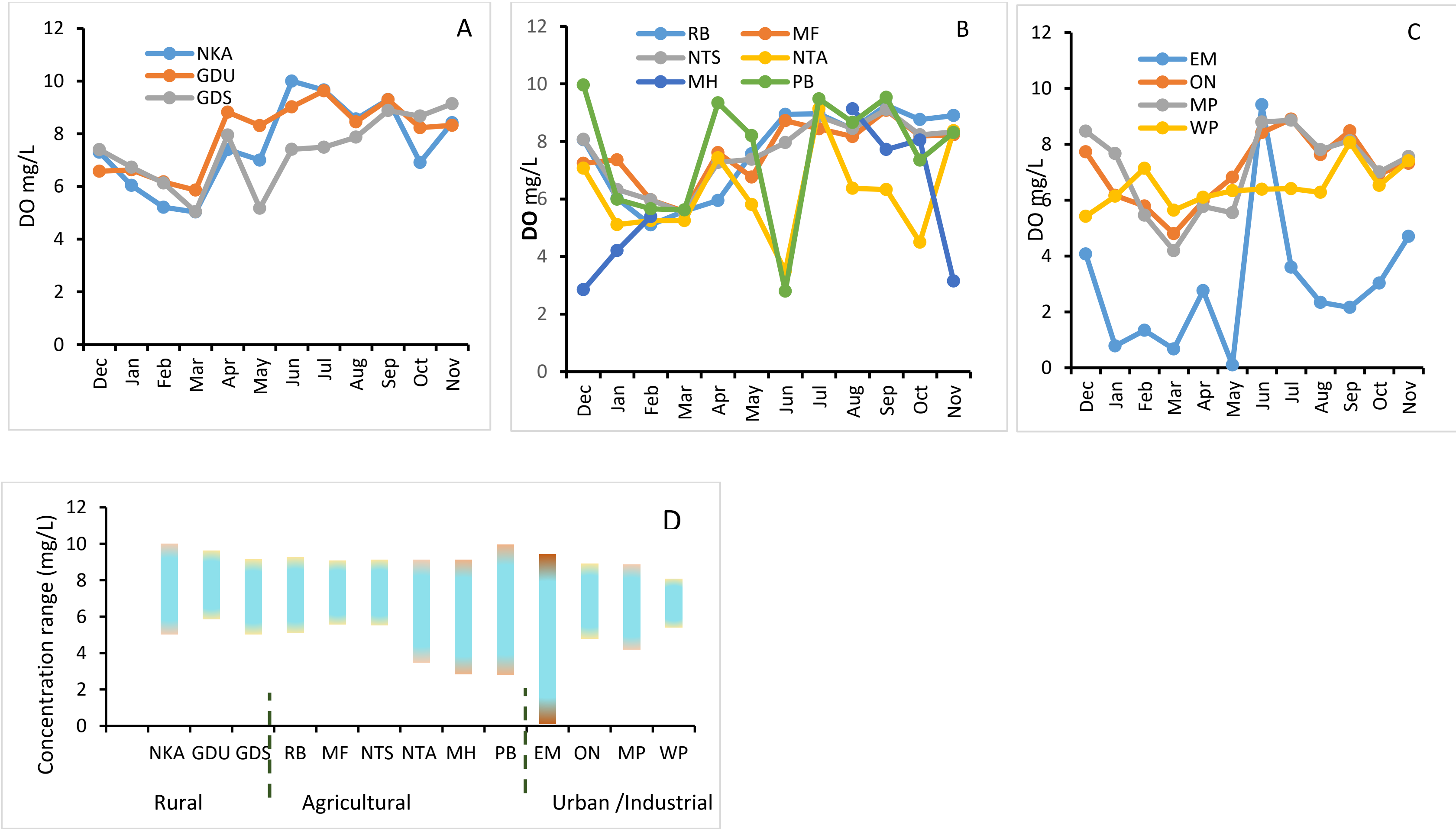

Figure 7: A – yearly dissolved oxygen levels for rural areas, B – yearly dissolved oxygen for agricultural areas, C – yearly dissolved oxygen for the urban/industrial areas, D – dissolved oxygen range for all sampling areas over 12 months

4.1.3 Turbidity

Water at the NKA and GDU sites in the rural areas were highly turbid from the beginning of the rainy season in November until January with values above 50 NTU (Figure 8A). These areas have clay soils which get washed into the river during the rainy season which could explain the elevated values for turbidity. However, at the Gouderetrouw dam (GDS site), the water has been diluted and the turbidity drops down to about 30 NTU. At the agricultural area, the highest turbidity values were experienced during the wet season for MF, MH and P32 bridge (PB) sites (Figure 8B). The water in these rivers was visibly brownish in colour. This could be attributed to the clay soils in this region and the agricultural activities leading to leaching of soil into the rivers during heavy storms (Akoto *et al.*, 2017). Soil erosion and runoff from tributaries could be the source of high turbidity experienced at uMhlathuze River. In a study at tropical coastal zones in Mexico, Romero-Rodriguez and colleagues reported turbidity peaks in spring and summer months, and identified horizontal transport of river discharges and coastal upwelling that generate high biological productivity as the major cause (Romero-Rodríguez *et al.*, 2020). At the urban and industrial sites, turbidity values were below 60 NTU throughout the study due to increase in river level with higher dilution taking place (Figure 8C). While most of the turbidity values were relatively low (<50 NTU), they were still above the SAWQ guideline value of 5 NTU for drinking water indicating a serious challenge for locals who rely on source of untreated water direct from river (Geere and Cortobius, 2017). Studies been conducted elsewhere on physicochemical properties where turbidity of river water was similar to the current study (Akoto *et al.*, 2017; Marina *et al.*, 2020; Madilonga *et al.*, 2021).

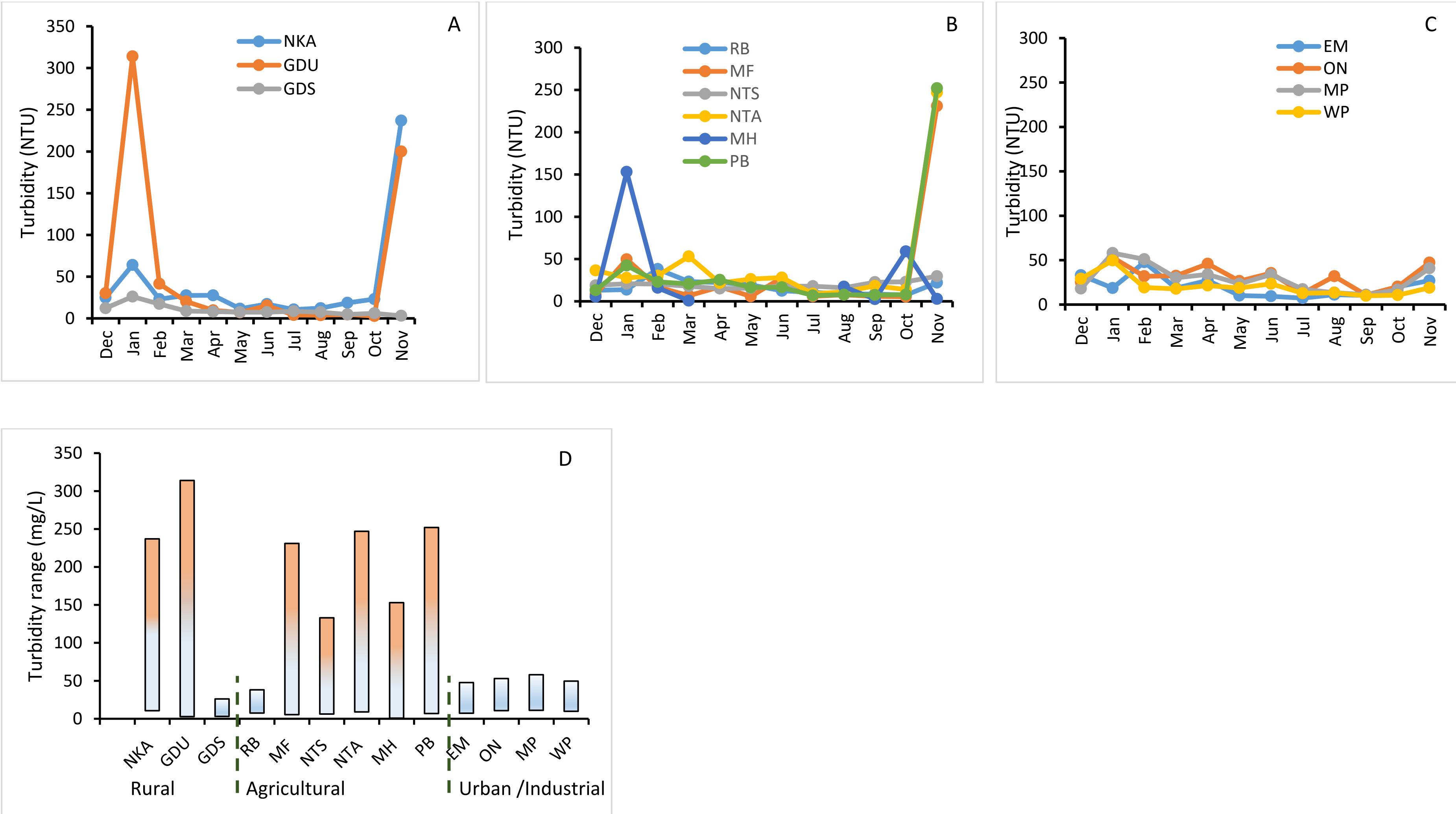

Figure 8: A – yearly turbidity for rural areas, B – yearly turbidity for agricultural areas, C – yearly turbidity for the urban/industrial areas, D – turbidity range for all sampling areas over 12 months

4.1.4 pH

The lower and upper limits for pH were within SAWQ guidelines for all sites except for two instances at the NKA site in July, the GDU site in December and the WP site during the months of June and July where pH values (6.0 - 6.5) which were slightly acidic (Figure 9A – D). Both NKA and GDU sites in the rural areas are located closer to mountains of Babanango and receive spring water from the region. Spring water pH tends to be slightly acidic due to natural factors including type of rocks and minerals as well as presence of gases like carbon dioxide (Novikov, Shirokaya and Slukovskaya, 2022). A study by Khadka and colleagues in Napoli reported pH values on spring water between 5.5 and 7 and reasons given were due to presence of bicarbonate ions that formed carbonic acid (Khadka and Rijal, 2020). The relatively low pH value at the WP site in the industrial area during the cold dry season could be attributed to the impact of industrial effluents during the low flow season. Generally, the pH range of this river was between 6 and 9 (Figure 9D), indicating that water from most parts of the uMhlathuze River could be utilized for industry purposes taking into account the SANS 241 requirements (Ndlangamandla, Sukdeo and Mukwakungu, 2024). Previous studies which included monitoring of pH were conducted at Subin River (Apau *et al.*, 2022), Jhelum River (Gull, Shah and Dar, 2023), Hindon River (Gupta and Gupta, 2023) and Nzhelele River (Edokpayi *et al.*, 2017).

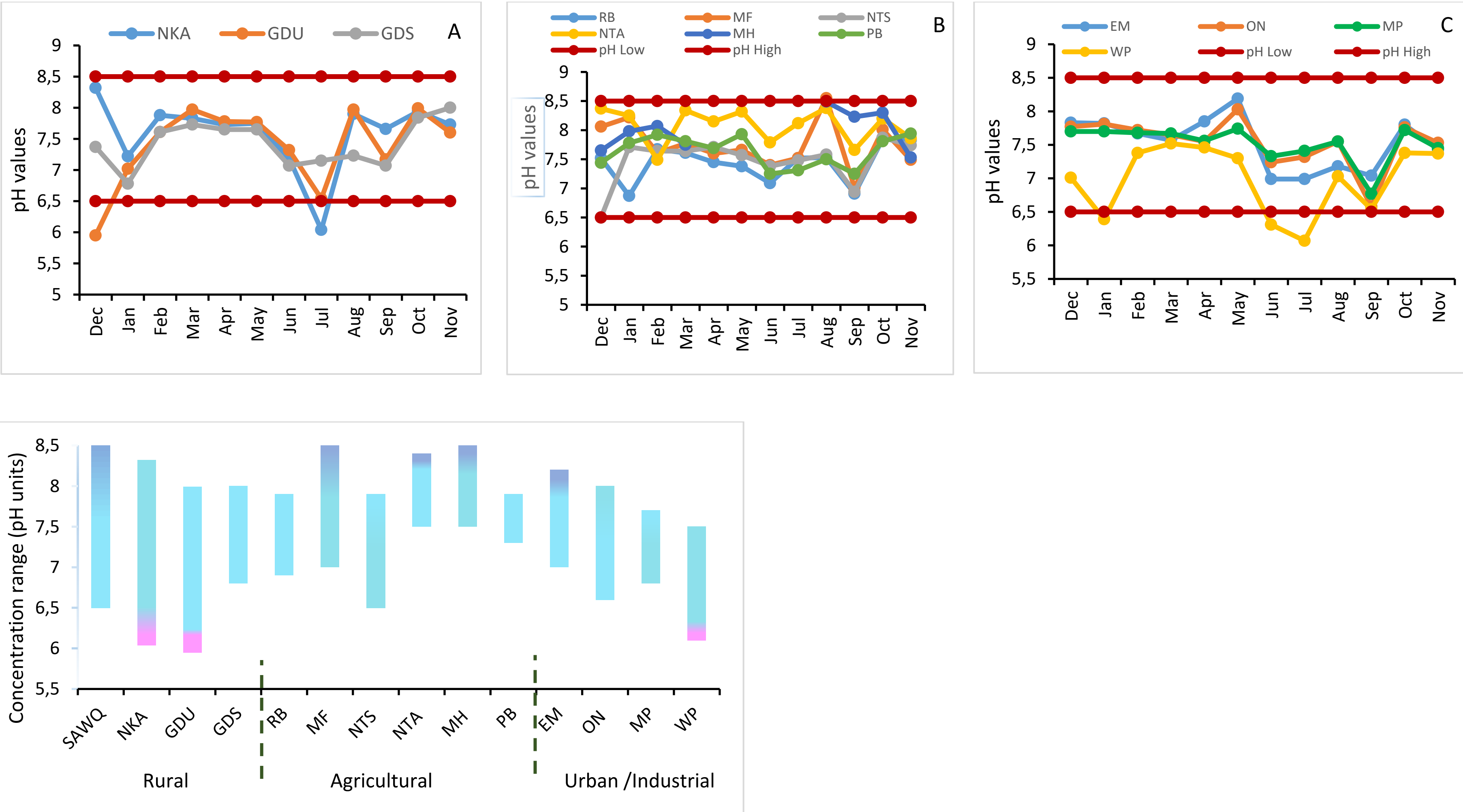

Figure 9: A – yearly pH for rural areas, B – yearly pH for agricultural areas, C – yearly pH for the urban/industrial areas, D – pH range for all sampling areas over 12 months.

4.1.5 Total organic carbon

Organics in the form of total organic carbon (TOC) were within the SAWQ guideline limits in the rural areas except for the unexpected spike measuring about 22 mg/L at NKA and GDU sites in February (Figure 11A & D) and this may indicate presence of decay organic matter in water. These levels cannot be linked to any activity in the rural area except that during the wet season, runoff from the region can end up in river. The TOC values were high along the tributaries with NTA site which flows through agricultural areas consistently recording TOC values above guideline limits (Figure 11B). The TOC chart for EM site in urban and industrial section of the study (Figure 11C) fluctuated above and below the guideline limit. The river receives wastewater discharge from the local municipality through the Empangeni tributary. Other studies elsewhere have recorded higher TOC values than those observed along uMhlathuze River. For example, Khalil and colleagues measured TOC levels at 36.65 mg/L at the Nile River in Egypt and identified wastewater discharge as the main source (Khalil *et al.*, 2023).

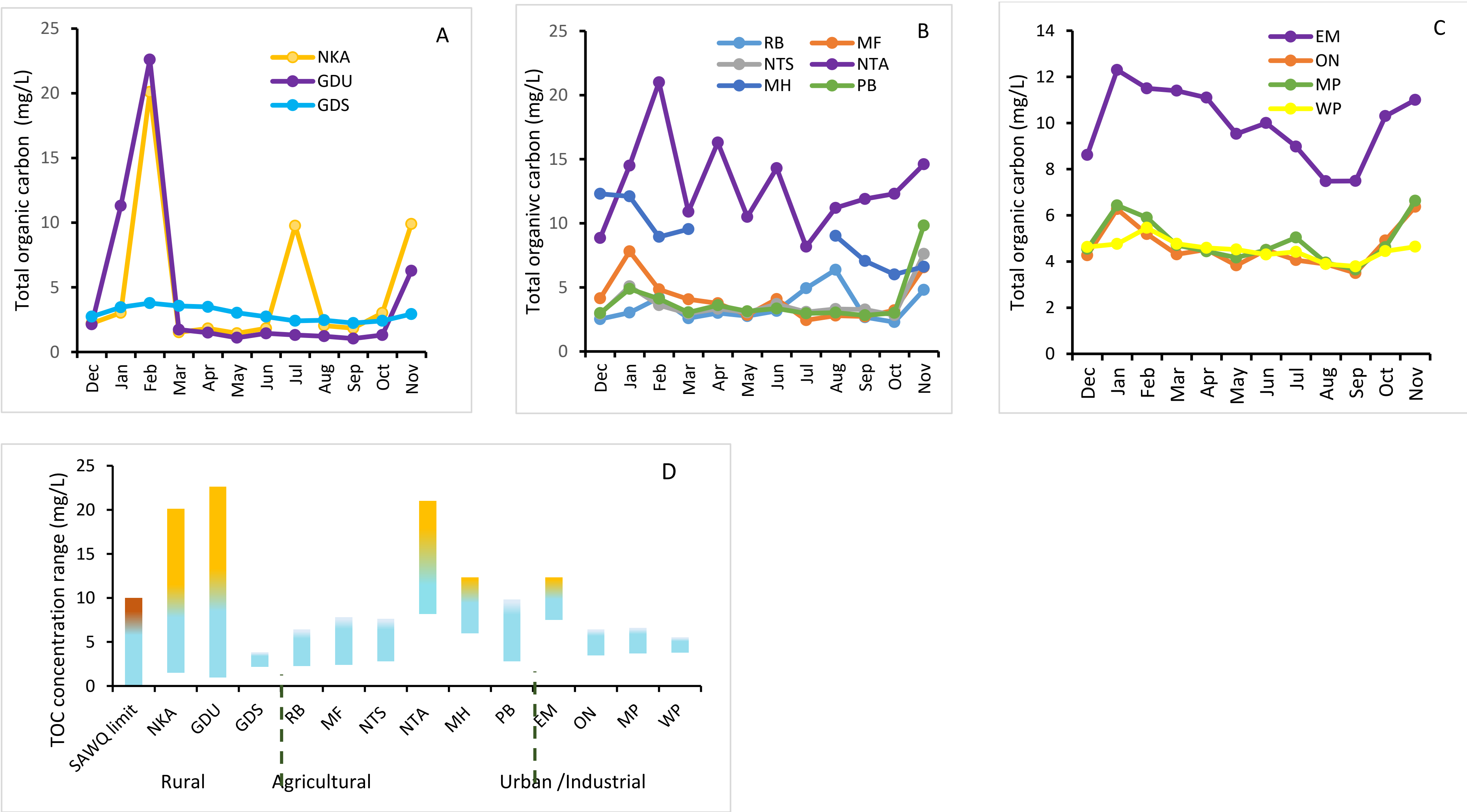

Figure 10: A – yearly total organic carbon for rural areas, B – yearly total organic carbon for agricultural areas, C – yearly total organic carbon for the urban/industrial areas, D – total organic carbon range for all sampling areas over 12 months

4.1.6 Electrical conductivity

Electrical conductivity (EC) along uMhlathuze River was within the WHO and SAWQ guidelines throughout the year except at the two tributaries represented by NTA and MH sites (Figure 10D). The lowest EC range (8 to 28 mS/m) was observed at the rural area (Figure 10A). At the agricultural area, the EC for the tributaries (NTA and MH sites) were above guideline levels (Figure 10B). This could be attributed to anthropogenic activities including the quarry activities along MH as well as the geographical location and agricultural activities along NTA site. Sikakwe and colleagues conducted a study on the effect of agricultural and quarry activities where they reported EC ranging from 290 to 342 mS/m on surface samples, above WHO guidelines (Sikakwe and Ilaumo, 2021). Due to dilution effects, the EC recorded at P32 bridge (PB site) had dropped down to within guideline levels. In the urban and industrial areas, the EC values were above WHO guidelines only along Empangeni tributary (EM site) ranging between 55 and 77 mS/m throughout the year (Figure 10C). This is due to wastewater discharge from local municipal wastewater treatment works. Ibe and colleagues conducted a study at Inyibe River where EC values recorded were high and exceeded WHO guidelines. Reasons provided were due to the effect of wastewater effluent discharge from an aluminium extrusion company (Ibe *et al.*, 2019).

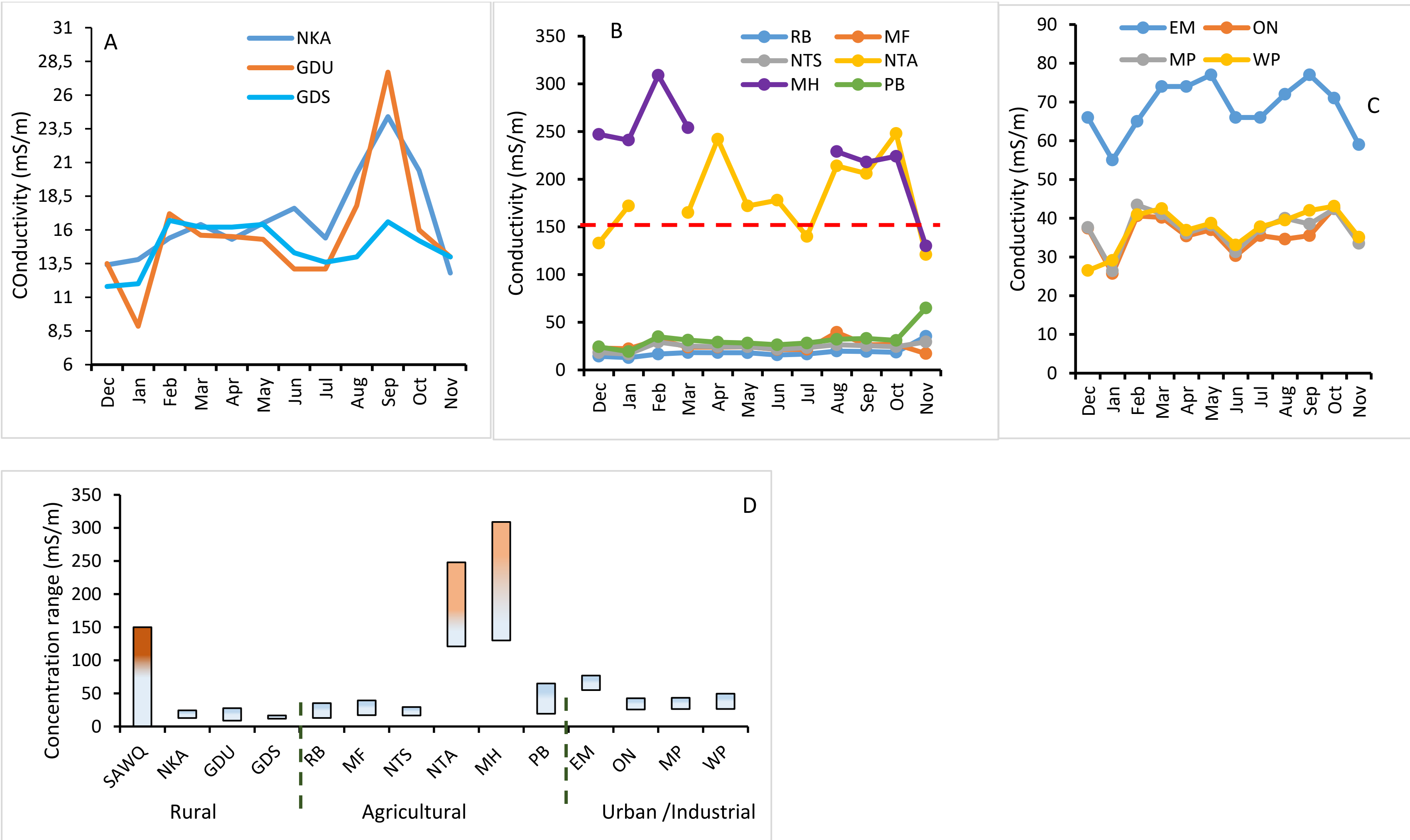

Figure 11: A – yearly conductivity for rural areas, B – yearly conductivity for agricultural areas, C – yearly conductivity for the urban/industrial areas, D – conductivity range for all sampling areas over 12 months

4.2 Anions

Minimum, maximum and median values for four anions included in the current study are summarized in Table 8. Fluoride concentrations were within SAWQ guideline limits for all sites along the uMhlathuze River. The lowest chloride concentration (7.19 mg/L) and sulphate (2.3 mg/L) concentrations were recorded in the rural areas. Concentration levels for chlorides exceeded SAWQ and WHO guideline limits for tributaries only in the agricultural section (MH and NTA sites), while in the urban region the levels at Empangeni tributary EM tributary (EM site) were elevated but within the guideline limits. The sulfate levels were also within guideline limits but elevated levels were observed along the NTA and MH sites. On the urban and industrial segment, concentrations for all anions were within guideline limits even though sulfates, nitrates and chlorides were slightly elevated at the EM site and the WP site which was the last sampling site of uMhlathuze River before it pours into the Indian ocean. Detailed concentration levels for the four anions are discussed in Section 4.2.1 to 4.2.4.

Table 8: Minimum, maximum and median values for anion parameters over 12 months

Segment	Site Name	Chloride (mg/L)			Fluoride (mg/L)			Nitrate (mg/L)			Sulphate (mg/L)		
		Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med
Rural	NKA	7.19	22.3	11.2	0.07	0.70	0.28	0.08	0.87	0.13	2.3	7.1	3.6
	GDU	11.8	18.1	15.2	0.10	0.70	0.34	0.05	0.87	0.25	2.3	8.0	3.8
	GDS	10.4	30.3	16.9	0.15	0.70	0.40	0.07	0.87	0.19	3.2	11.1	5.5
Agricultural	RB	15.0	29.7	18.4	0.14	0.69	0.33	0.13	0.87	0.27	3.9	7.9	6.2
	MF	26.5	53	40.0	0.08	0.74	0.27	0.08	0.87	0.22	2.6	11.9	5.4
	NTS	25.7	37.2	32.5	0.15	0.68	0.26	0.09	0.87	0.30	5.7	10.7	7.8
	NTA	127	422	277	0.09	0.69	0.28	0.15	5.0	0.92	10.5	113	37.8
	MH	205	655	340	0.07	1.4	0.30	0.07	2.4	0.36	111	218	130
Urban and Industrial	PB	21.5	117	35.9	0.13	0.74	0.36	0.11	0.87	0.28	6.6	11.6	8.7
	EM	85	131	104	0.17	0.68	0.33	0.09	1.04	0.45	19.9	29.6	23.3
	ON	42.0	60	51	0.11	0.76	0.34	0.11	0.88	0.30	8.3	14.1	11.0
	MP	42.5	65	52	0.13	0.68	0.31	0.05	0.89	0.30	8.3	14.2	10.3
	WP	42.7	97	58	0.20	0.95	0.37	0.02	0.93	0.30	8.9	28.5	11.8
SAWQ Guideline		300			1.5			15			250		
WHO Guideline		250			1.5			50			500		

4.2.1 Chlorides

Chlorides in the rural areas were within guideline limits. However, a general downward trend was observed from all 3 sites where chlorides were on the high side in summer, stable in winter season then dropped again during the start of the rainy season (Figure 12A). The highest Cl in summer cannot be explained as there are no known activities in the area except weathering, dissolution, leaching which occur during heavy rains. For the agricultural region, the levels of chloride were extremely high in the tributaries compared to sites along uMhlathuze River (Figure 12B & D). During the rainy season, the levels along MH site were above the guideline limits reaching 600 mg/L probably due to water washing from the quarry activities. Similar chloride concentrations above WHO guideline limits were reported by Reghunadh in Kerala River, India (Reghunadh *et al.*, 2023). The reasons provided were related to silicate weathering, dissolution, leaching, and infiltration from hard rock and soil quarries (Reghunadh *et al.*, 2023). Ntambanana tributary (NTA site) which flows mainly through agricultural fields had chloride levels which ranged from 127 to 422 mg/L (Figure 12B). The elevated chloride concentration at this tributary is probably from natural sources considering that this area is known for its salty water such that local people in the area do not rely on river or borehole water for domestic use. (https://www.news24.com/citypress/voices/democracys-surplus-people-20190321 - Last accessed on 23 February 2025). In addition, sugarcane farmers in the area are also not using water from Ntambanana River for irrigation, but water is pumped from uMhlathuze River to reach all irrigated farms in the area (Wadghane and Madguni, 2023).

At the urban and industrial segment, the chloride levels were within guideline limits (Figure 12C). However, the levels at EM site along Empangeni tributary that flows from Empangeni town and the surrounding areas were relatively higher and ranged from 80 to 141mg/L compared to other sites throughout the year. The elevated chloride levels could be arising from the wastewater plants (Adbarzi *et al.*, 2020). An assessment conducted on treated wastewater in Iran reported elevated chlorides levels required for irrigation water (Rahimi *et al.*, 2018).

The elevated chloride concentrations along the three tributary rivers (MH, NTA and EM sites) had limited impact on the quality of uMhlathuze River because the levels recorded on uMhlathuze River after receiving water from these tributaries were within the guideline limits (Figure 12C). However, it was noted that even though the results were within limits, the levels were now higher compared to levels in the rural areas upstream. A study was conducted to check the effect of wastewater discharge on river water and reported chloride levels ranging from 26-68.5 mg/L, within permissible limits (Adbarzi *et al.*, 2020)

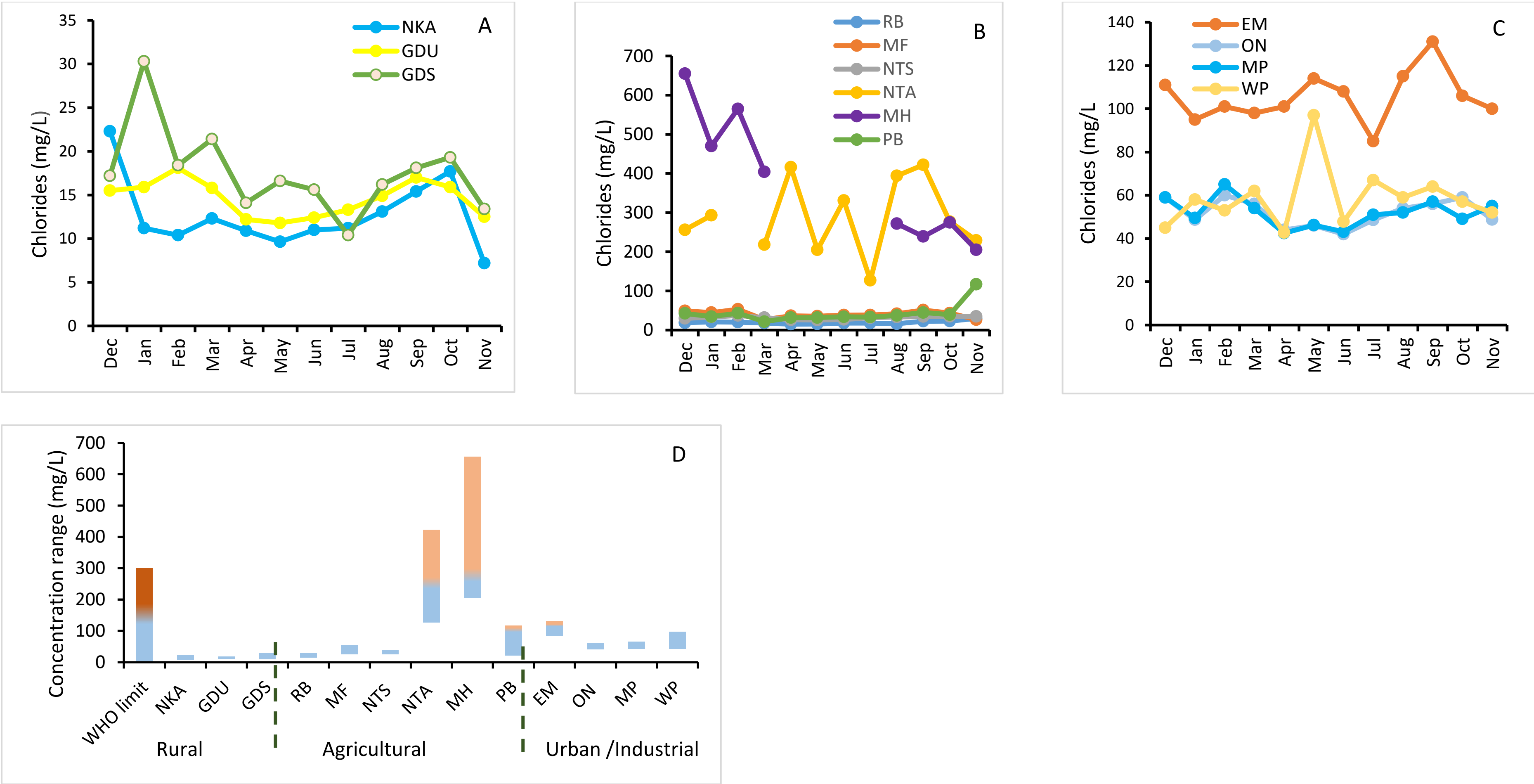

Figure 12: A – yearly chlorides for rural areas, B – yearly chlorides for agricultural areas, C – yearly chlorides for the urban/industrial areas, D – chlorides range for all sampling areas over 12 month

4.2.2 Fluorides

Fluoride concentrations were within guideline limits for all sampling sites along uMhlathuze River and its three tributaries (Figure 13A – D). A general trend was observed with the levels relatively higher during the rainy season and recording the lowest levels during the dry cold season (May – July). The levels then increased recording the highest levels during the spring season when the river is in its lowest flow just before the start of the rainy season in September.

There were spikes, which occurred along the Mholweni tributary (MH site) reaching 1.4 mg/L in February (Figure 13B). Another spike was observed at an urban and industrial segment, where up to 0.95 mg/L was recorded at the WP site in May (Figure 13C). These observations were once off and could not be linked to any source except that Mholweni tributary (MH site) emanates from a quarry mining area, while the WP serves as a reservoir for water upstruction purposes. Elevated levels of fluorides that exceeded WHO guidelines up to 1.6 mg/L were reported by Adbarzi at two river sites in India and the reasons provided were due to stone crushing and quarry activities along the rivers (Adbarzi *et al.*, 2020). This is similar to what was observed in this study along Mholweni tributary (MH site) that is also affected by quarry activities. A study conducted at Molo River in Kenya reported fluoride values ranging from 2.76 to 3.28 mg/L (Chebet, Kibet and Mbui, 2020). Another study showed high levels of fluoride in borehole water and pit latrines was identified as the main source (Odiyo and Makungo, 2018)

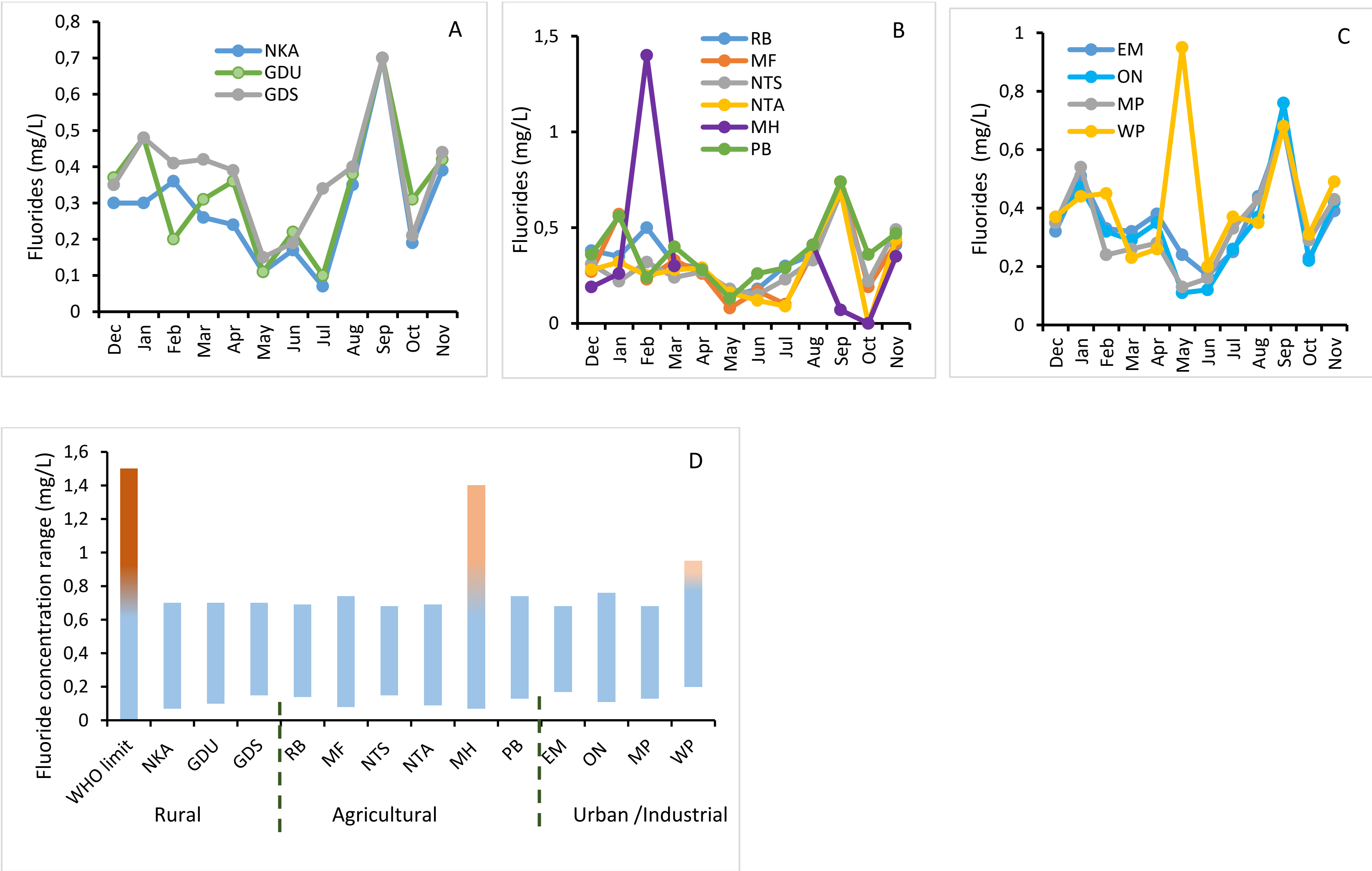

Figure 13: A yearly fluorides for rural areas, B – yearly fluorides for agricultural areas, C – yearly fluorides for the urban/industrial areas, D – fluorides range for all sampling areas over 12 months

4.2.3 Nitrates

Nitrate levels were also within SAWQ and WHO guideline limits throughout uMhlathuze River and its tributaries (Figure 14A – D). In the rural segment, the levels were below 0.4 mg/L throughout the year except for one spike of about 0.8 mg/L which occurred for both sites during the spring season in August (Figure 14A). The levels in the agricultural segment (Figure 14B) were generally similar to those recorded in the rural areas except for the levels in the Mholweni and Ntambanana tributaries (MH and NTA sites). The levels at NTA site were consistently above 1 mg/L indicating the potential impact of farming activities in the area, reaching a maximum of about 5 mg/L in September. Agricultural activities along the Ntambanana tributary as well as the waste coming from nearby quarry activities near the Mholweni tributary may have contributed to the relatively higher levels of nitrates. In the urban and industrial area, there was notable variance in the levels of nitrates on Empangeni tributary (EM site) throughout the year compared to other sites with levels ranging between 0.09 and 1.04 mg/L during spring, while for the Weir Pumpstation (WP site) the variation was observed from April to November ranging 0.36 to 0.93 mg/L (Figure 14C). The EM site receives effluents from nearby wastewater treatment works which has an impact of polluting river with nutrients including nitrates (Jin *et al.*, 2017). Nitrates levels up to 751 mg/L were reported on ground water samples and authors indicated agricultural activities, leachate from landfills domestic sewage leakage as the main source (Suvarna, Sunitha and Reddy, 2020).

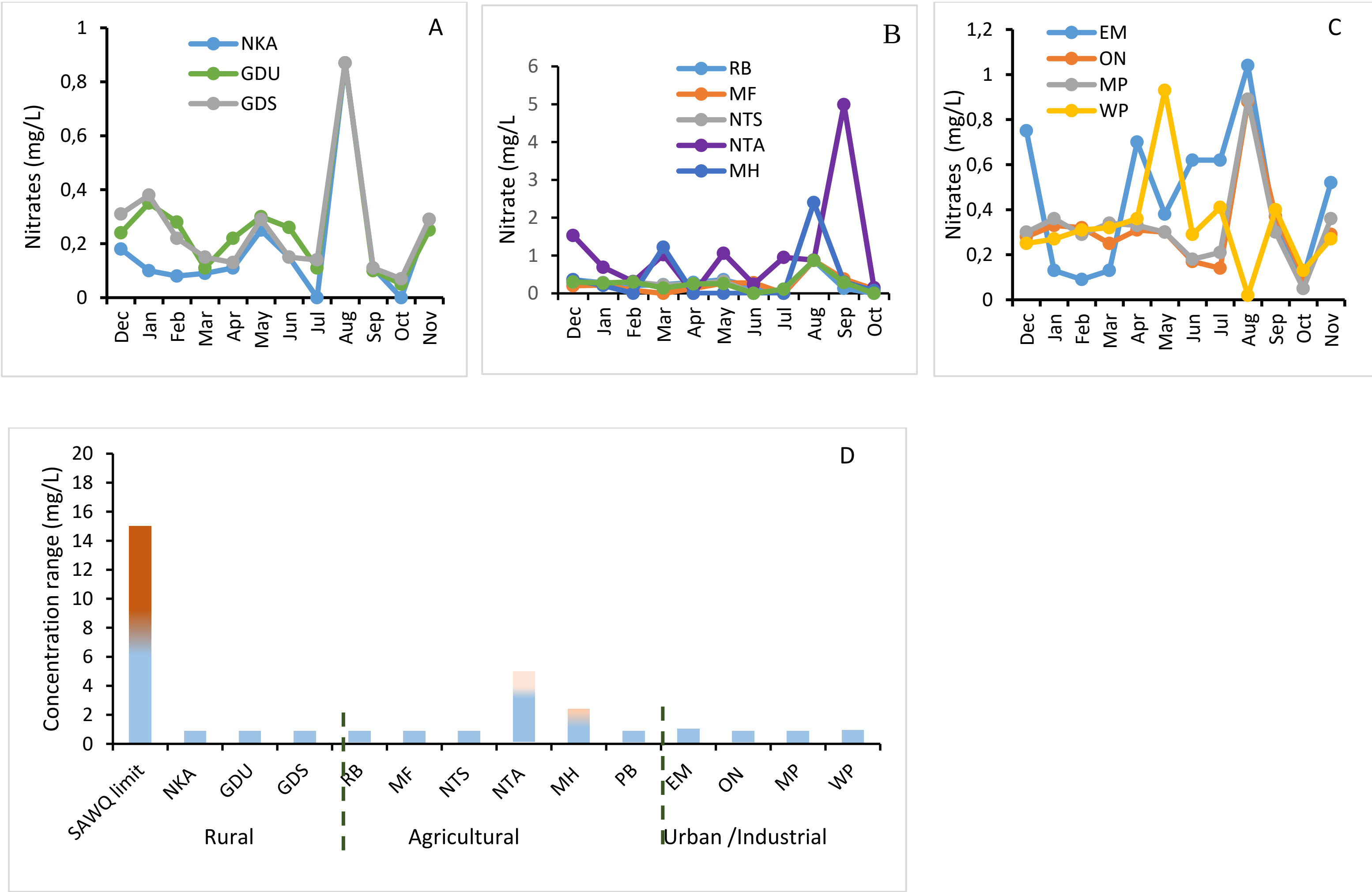

Figure 14: A yearly nitrate for rural areas, B – yearly nitrate for agricultural areas, C – yearly nitrate for the urban/industrial areas, D – nitrate range for all sampling areas over 12 months

4.2.4 Sulphate

Sulfate concentrations were all within guideline limits for all study sites along uMhlathuze River as well as its tributaries (Figure 15A – D). The lowest levels were observed in rural areas (Figure 15A). If the tributaries are not considered, it was observed that the levels generally increased downstream of the uMhlathuze River with the urban and industrial segment recording high levels compared to rural and agricultural segments (Figure 15A – C). The levels in the urban and industrial segment were consistently above 10 mg/L (Figure 15C), the agricultural segment had about 10 mg/L (Figure 15B), while the rural areas had levels consistently below 10 mg/L (Figure 15A). However, Figure 15B & D show that elevated concentrations were observed along Mholweni tributary (MH site) and Ntambanana tributary (NTA site). The agricultural activities along Ntambanana tributary (NTA site) led to sulfate levels up to 113 mg/L while the quarry activities near Mholweni tributary (MH site) resulting in sulphate levels ranging between 111 and 218 mg/L. These levels were however still within the guideline limits. Like chlorides, sulfates can also be linked to quarry activities around Mholweni tributary (Eyankware *et al.*, 2020).

In the urban and industrial segment, the Empangeni tributary (EM site) recorded between 20 and 30 mg/L of sulfates (Figure 15C). These elevated levels compared to other sites in this segment could be due to wastewater discharge from Empangeni town and the surrounding areas where the river passes through. The Weir Pumpstation (WP site) which serves as a reservoir for two waterworks experienced spikes of sulphate concentrations during summer, winter and spring. However, these increments could not be linked to the elevated levels from the tributaries, but could be directly linked to industrial effluents within area close to the pump station. Even though there were spikes, the levels were still within the guideline limits. A study was conducted at Ankora River and surrounding where 338 mg/L levels of sulphate was reported and the reason provided was due to mining activities, welding and other mechanical activities (Saalidong *et al.*, 2022). Another study along Yamuna River reported sulphate levels up to 99 mg/L and the reasons provided were industrial effluents from major drains and canals carrying sewage and agricultural discharges (Parween, Ramanathan and Raju, 2017)

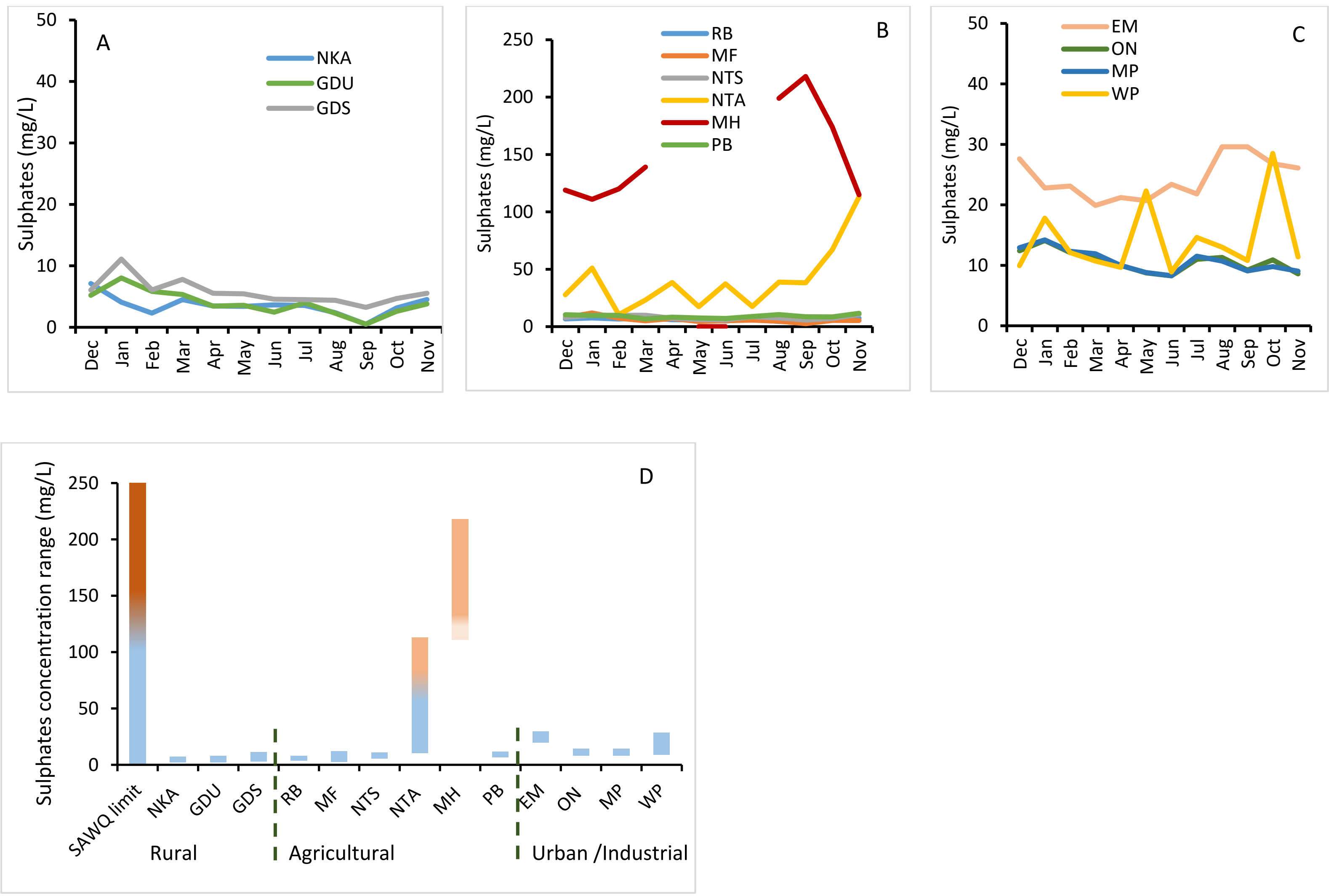

Figure 15: A - yearly sulphate for rural areas, B – yearly sulphate for agricultural areas, C – yearly sulphate for the urban/industrial areas, D – sulphate range for all sampling areas over 12 months.

4.3 Interrelationships between anion and physicochemical properties

4.3.1 Rural areas

Figure 16 shows interrelationships between physicochemical parameters for uMhlathuze River in the rural area. The turbidity and sulphate trends were strongly correlated in all sites even though this was more pronounced upstream at NKA and GDU sites (Figure 16A & B). Besides a spike in turbidity in January and November (Figure 8A), there was a general decline throughout the year which was the case with sulfate levels as seen in Figure 15A. Fluoride and nitrate trends were also strongly correlated to each other (Figure 16A & B) at the NKA and GDU sites but were negatively correlated to pH (Figure 16B & C). A negative correlationship between fluoride and pH has also been reported by Morovati in Iran (Morovati *et al.*, 2024).

At the NKA site, chloride was also strongly correlated with fluorides and nitrates, whilst at the GDU site, chlorides were correlated with turbidity and sulphates (Figure 16A). Other correlationships observed were at the GDU sites between pH and EC, and between TOC and temperature. Notably, dissolved oxygen was not correlated with any of the other parameters for both the NKA and GDU sites. Anions that show a correlation are suggestive of a common source. The correlation between physicochemical properties including pH and conductivity with anions has been observed elsewhere in river water (Obiri *et al.*, 2021; Gull, Shah and Dar, 2023; Iqbal *et al.*, 2023; Li *et al.*, 2025).

At the Gouderetrouw Dam (GDS site), turbidity and sulfates were still correlated but the interrelationship was weaker. Sulfates were no longer correlated with fluorides and chlorides (Figure 16B). However, a weak correlation was observed for nitrates, chlorides and fluorides, with conductivity and TOC also having an impact on the levels of these anions. Within this group, a strong correlation was observed for TOC and fluorides, and for conductivity and nitrates (Figure 16C). None of the anions were correlated. At this site, the pH trend was not correlated with any of the other parameters or anions. Considering that at the dam (GDS site), samples were collected at the surface without disturbing or stirring the water, these results could probably not be representative of the true situation at the dam. The correlationship between pH and conductivity have also been reported elsewhere on ground and surface water (Thavrin Manickum, 2020; Saalidong *et al.*, 2022).

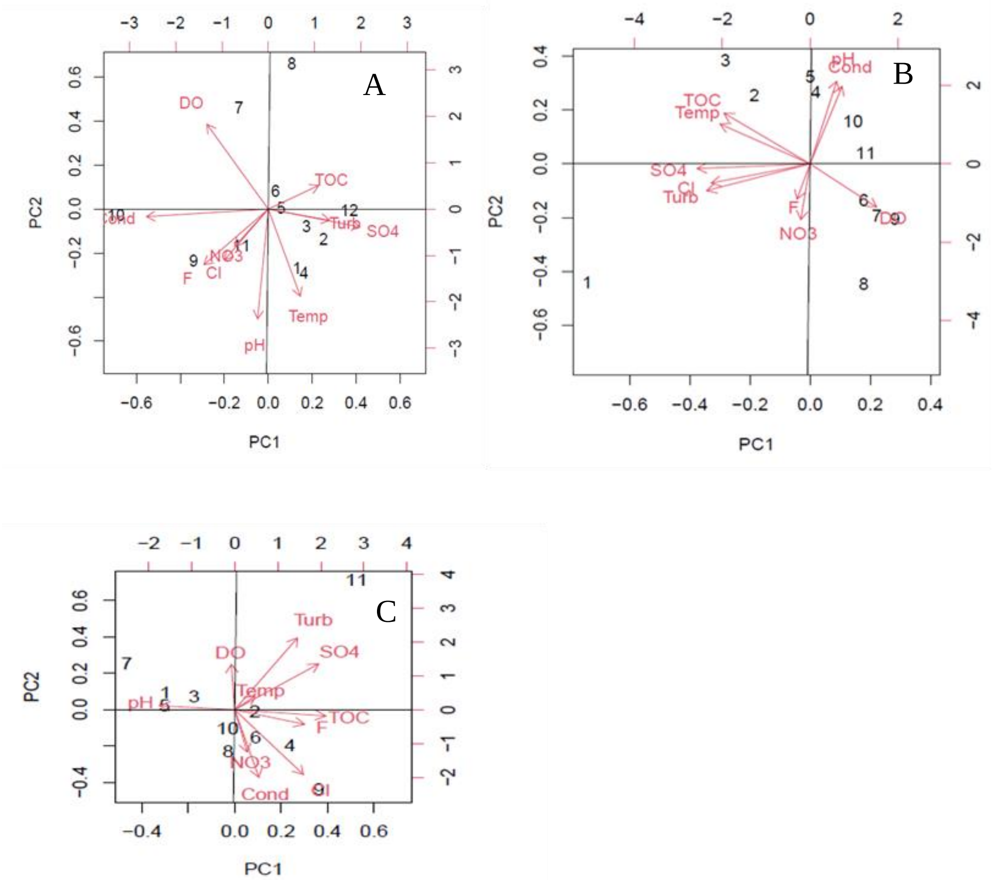

Figure 16: Physicochemical biplot charts for uMhlathuze River in the rural areas (A-Nkandla (NKA); B - Gouderetrouw upstream (GDU); C - Gouderetrouw dam surface (GDS)

4.3.2 Agricultural areas

Figure 17 presents interrelationships between physicochemical parameters and anion levels for uMhlathuze River in the agricultural area. The TOC trends in this region were strongly correlated with either fluorides or chlorides. The TOC-fluoride/chloride correlation was observed throughout this region with the TOC-fluoride stronger at the RB site (Figure 17A) and the NTA site (Figure 17D) while the TOC-chloride correlation was stronger for the other sites. At the RB and NTA sites (Figure 17A & D), conductivity, nitrates and chlorides were strongly correlated. In these two sites, pH trends were not correlated with any of the other parameters or the anions.

A strong correlation was observed between DO, pH, nitrates and sulfates at the MF site (Figure 17B). This behaviour was similar to trends at the MH site (Figure 17E). A positive correlationship between pH and anions (nitrate and sulphates) from agricultural activities have been reported locally and abroad (Patience *et al.,* 2021; Saalidong *et al.,* 2022). At the NTS site there was a strong correlation between TOC, conductivity, turbidity, fluorides, chlorides and nitrates indicating possibility of the same source (Figure 17C). At the last site in the agricultural area (PB site), the correlation between TOC and Cl now included conductivity and turbidity (Figure 17F). Still correlated with this group but forming a clear strong relationship were DO, fluorides, nitrates and sulphates. A negative correlation between temperature, pH and TOC was observed from all sites in the agricultural segment. However, some authors have reported positive correlation between these three parameters in a similar environment affected by agricultural activities (Sakizadeh and Chua, 2020).

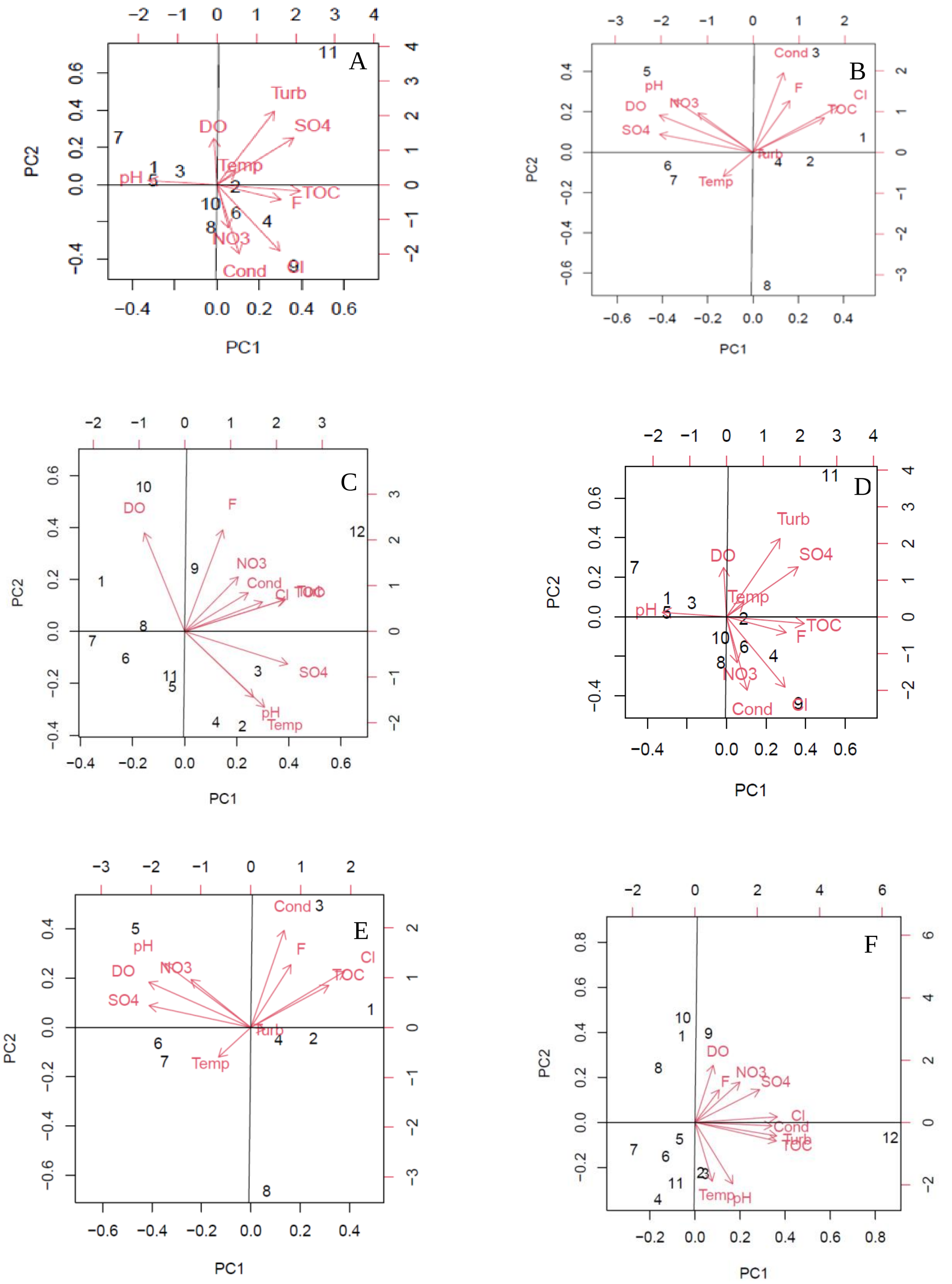

Figure 17: Physicochemical biplot charts for uMhlathuze River in the agricultural areas (A- R66 bridge (RB); B - Mfule (MF); C - Ntshentshelo (NTS); D – Ntambanana (NTA); E – Mholwerni (MH); F – P230 bridge (PB)

4.3.3 Urban and industrial areas

The correlationships due to urban and industrial activities on physicochemical parameters is shown on Figure 18. The anions (fluoride, chlorides and sulphates) were strongly correlated with EC at the EM site (Figure 18A). This correlation corresponds to levels of EC and anions along Empangeni River (EM site) due to wastewater source. At the ON site, the similar correlation between EC and anions was observed with the exception of sulphates (Figure 18B). However, at the ON site, EC was not correlated with any of the anions (Figure 18C). At the same site, fluorides and nitrates were negatively correlated to chlorides and sulphates. At the Weir Pumpstation (WP site), EC was not correlated to any of the anions. Instead, the four anions were strongly correlated to each other (Figure 18D). Turbidity and sulphates were not correlated to each other at this segment except at MP site (Figure 18C). Correlations between physicochemical parameters in river water samples have been conducted elsewhere (Khanoranga and Khalid, 2019; Obiri *et al.*, 2021; Atangana, 2023).

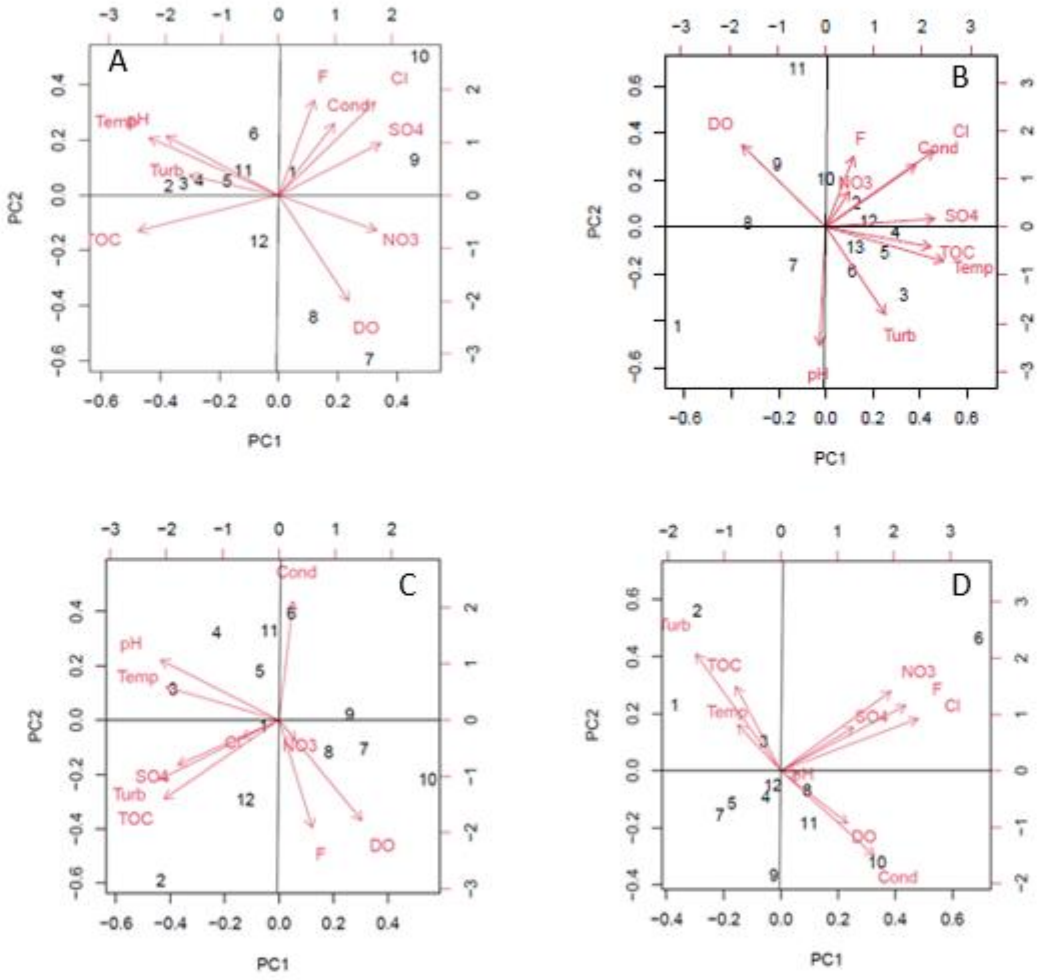

Figure 18: Physicochemical biplot charts for uMhlathuze River in the urban/industrial area (A- Empangeni (EM); B- Ongoye (ON); C- Chemical industry (MP) and Weir Pumpstation (WP).

4.4 Spectroscopic instrument calibration and method validation

The calibration results for the macro elements presented in Table 9 show that calibration standards were 5 – 60 µg/mL for Ca and Mg, 0.25 – 30 µg/mL for K and 25 – 200 µg/mL from Na. Calibration curves were all linear with $R^2 > 0.999$ (Table 8). The LOQ values for Ca, Mg, K and Na were 0.2, 0.2, 0.1 and 1 µg/mL, respectively. Good reproducibility was observed with RSD <10% achieved for all the macro elements. The ICP-MS instrument also produced good linear curves for trace metals with R^2 > 0.999 for all trace elements (Table 10). A previous study by Cengiz and colleagues in Bogacayi River included method validation of ICPMS where correlation coefficient (R^2) of 0.999 and LODs lower than 2.85 µg/L for some trace metals were reported (Cengiz *et al.*, 2017). The reported validation parameters were similar to the current study.

Table 9: ICP-OES calibration and validation

Element (nm)	Calibration Range	Calibration equation	Correlation coefficient, R^2	LOD (µg/mL)	LOQ (µg/mL)	%RSD
Ca 317.933	5 - 60	y = 11545x + 1655.1	0.9998	0.5	1.7	6.3
Mg 285.213	5 - 60	y = 23293x + 3778.4	0.9996	0.5	1.6	0.9
K 766.790	0.25 - 30	y = 2487.5x + 2.2597	0.9997	0.4	1.4	6.4
Na 589.592	25 - 200	y = 9448.7x + 1935.1	0.9997	1.2	4.1	9.0

Table 10: ICP-MS calibration and validation

Element (m/z)	Calibration Range (ng/mL)	Calibration equation	Correlation Coefficient (R^2)	LOD (ng/mL)	LOQ (ng/mL)	%RSD
Al 27	10 - 1000	y = 0.0122x + 0.0831	0.9999	0.59	1.78	6.8
As 75	10 - 1000	y = 0.0005x + 0.0009	0.9996	0.08	0.25	8.2
B 11	10 - 1000	y = 0.0036x + 0.0152	0.9998	0.35	1.06	4.4
Ba 138	10 - 1000	y = 0.0109x + 0.0175	0.9999	0.40	1.22	6.4
Cd 114	10 - 1000	y = 0.0011x + 0.0016	0.9999	0.44	1.32	3.0
Co 59	10- 1000	y = 0.0073x + 0.0144	0.9999	0.28	0.86	5.9
Cr 52	10 - 1000	y = 0.0048x + 0.0157	0.9998	0.45	1.36	7.6
Cu 63	10 - 1000	y = 0.0024x + 0.0137	0.9992	0.44	1.35	3.3
Fe 56	10 - 1000	y = 0.0001x + 0.0005	0.9995	1.06	3.22	5.0
Hg 202	0.1 - 50	y = 0.0015x + 0.0002	0.9996	1.05	3.18	1.5
Mn 55	10 - 1000	y = 0.0083x + 0.0239	0.9998	0.52	1.58	1.4
Ni 58	10 - 1000	y = 0.0015x + 0.0029	0.9998	0.55	1.67	2.2
Pb 208	10 - 1000	y = 0.0084x + 0.0184	0.9999	0.62	1.89	1.9
Sb 121	10 - 1000	y = 0.0031x + 0.0065	0.9998	0.33	0.99	8.5
Se 82	10 - 1000	y = 0.0008x + 0.0003	0.9997	0.29	0.89	8.7
Sr 88	10 - 1000	y = 0.0011x + 0.0151	0.9999	0.38	1.16	2.5
U 238	10 - 1000	y = 0.0184x + 0.0025	0.9998	0.23	0.68	2.2
Zn 64	10 - 1000	y = 1855x + 14046	0.9996	0.19	0.56	1.3

4.5 Macro elements

The levels of macro elements (K, Na, Ca & Mg) for a 12 months period are summarised in Table 11 and Figure 19. All macro elemental results in the rural areas were within SAWQ guidelines for all seasons (Figure 19 A-E). In the agricultural area, the levels were relatively higher at MH and NTA sites which represent the Mholweni and Ntambanana tributaries respectively. Ranges at NTA site were 31-46 mg/L (Ca), 30-58 mg/L (Mg), 189-554 mg/L(Na) and 59-354 mg/L (hardness). These levels exceeded SAWQ and WHO guidelines (Figure 19 A, B, D and E). Reasons for such levels could be due to agricultural activities as well as the geological zone. Higher levels have been reported in literature. For example, Chebet and colleagues reported Na levels up to 1800 mg/L at Molo River, Kenya and attributed findings to runoff from agricultural farms as reasons for such levels (Chebet, Kibet and Mbui, 2020). The elevated levels at the MH site can be linked to quarry works along the Mholweni stream, which discharges its waste into uMhlathuze River. Similarity levels of Ca above WHO guidelines were reported by Reghunadh in Achenkovil River Basin, India. The reason provided was due to possible silicate weathering, dissolution, leaching, and infiltration from hard rock and soil quarries (Reghunadh *et al.*, 2023).

The impact of elevated levels of macro elements from the tributaries (MH and NTA sites) on uMhlathuze River is minimal because the levels recorded at P32 bridge (PB) site were within guideline values suggesting dilution effects due to larger volumes of water along uMhlathuze River. The PB site is a point along uMhlathuze River after it has received water from the two tributaries. Dilution effects on water quality in rivers have been reported locally and abroad (Odiyo and Makungo, 2018; Zhou *et al.*, 2022). Within the urban and industrial area, the EM site along Empangeni River that pours into uMhlathuze River had elevated levels of macro elements (Figure 20E), but these were still within the limits. The elevated levels along the

Empangeni tributary (EM site) might have been caused by wastewater discharge from local wastewater works and possible runoff form Empangeni town and surrounding informal settlements.

While dilution effects were observed for uMhlathuze River after receiving polluted water from its tributaries, other studies have noted sharp spikes of these macro elements especially in drought-stricken areas (Mandal *et al.*, 2019). Peña-Guerrero and colleagues studied drought effect on a river water quality in Chile where the major ions analysed in the irrigation districts increased during drought periods, reaching values that surpassed the Chilean regulation for agricultural water uses (Peña-Guerrero *et al.*, 2020).

Table 11: Minimum, maximum and median values for macro elements over 12 months

	Site	Calcium (mg/L)			Magnesium (mg/L)			Sodium (mg/L)			Potassium (mg/L)			Hardness (mg/L)		
Segment		Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med	Min	Max	Med
Rural	NKA	5.2	11	7.6	4.3	9.1	6.1	11	18	15	0.8	2.6	1.0	31	64	45
	GDU	3.3	7.9	6	2.1	5.9	4.6	11	16	13	0.8	2.4	1.0	17	44	34
	GDS	5.1	7.1	5.8	3.7	11	5.3	11	17	15	1.5	2.1	1.4	29	40	33
Agricultural	RB	4.9	12	6.9	3.7	11	5.3	14	48	17	1.5	2.7	1.8	27	72	39
	MF	5.5	8.5	6.9	4.8	7.4	5.9	24	32	28	1.5	3	1.8	34	51	42
	NTS	7.2	10	8.5	5.8	8.5	7.1	22	40	26	1.7	3.1	2.0	42	60	51
	NTA	31	46	37	30	58	41	189	554	289	1.2	8.4	2.0	59	354	274
	MH	51	91	68	54	89	85	179	552	324	1.7	3.5	3.4	349	585	507
	PB	7.6	14	9.1	6.3	15	7.7	26	92	31	1.6	3.2	2.6	45	98	55
Urban and industrial	EM	17	21	20	16	20	18	78	101	90	4.3	6.9	2.0	98	134	120
	ON	9	13	11	8	12	10	34	52	40	2	3.4	5.4	55	84	71
	MP	9.4	14	12	8	13	10	33	54	43	2.3	3.2	2.3	56	86	71
	WP	7.5	7.5	12	6.4	13	10	28	54	41	2.2	3.4	2.8	45	87	73
SAWQ Guideline		32			30			200			50			200		
WHO Guideline					30			200			12			120		

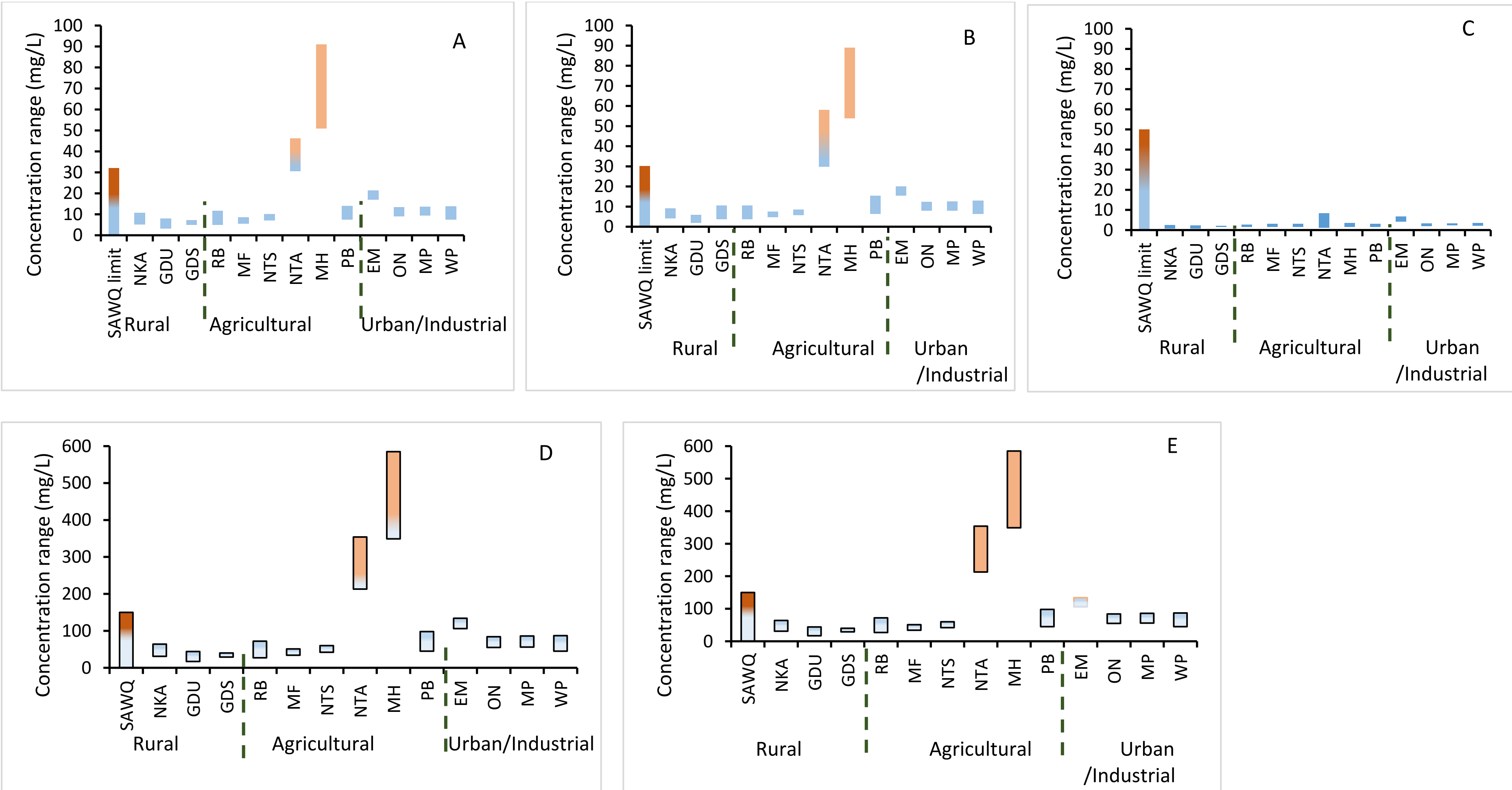

Figure 19: Range of macroelements along the uMhlathuze River (December 2023 to November 2024) A – Calcium (Ca); B – Magnesium (Mg); C – Potassium (K); D – Sodium (Na); E – Hardness ($CaCO_3$)

4.6 Interrelationships between macro elements using principal component analysis

Figure 20 represents interrelationship between macro elements at the rural area. All four macro elements were not correlated to each other at the NKA site (Figure 20A). At GDU and GDS sites, a strong interrelationship was observed between K and Na as well as between Ca, Mg and $CaCO_3$. These observations were an indication of similar trends between Na and K throughout the year while Ca, Mg and $CaCO_3$ which represent water hardness also had similar trends. Similar trends between Mg, Ca and $CaCO_3$ were also observed in the agricultural segment (Figure 21), except for the MH site which is on the Mhoweni tributary (Figure 21E). Potassium and Na also had a strongly correlation at NTS and NTA sites, but they also showed a fair correlation with the other macro elements (Figure 21C & F). Potassium trends seemed not correlated or had minimum correlation with other macro elements at four of the six sites in the agricultural segment of the study. A similar trend was observed at the urban and industrial segment except for EM site (Figure 22B, C & D). Along the EM site (Empangeni tributary), all the macro elements were relatively correlated but the relationship was less pronounced compared to other sites in this segment. Positive interrelationships between macro elements were also discussed by Li and colleagues in ground and surface water, China (Li, Tian and Liu, 2019).

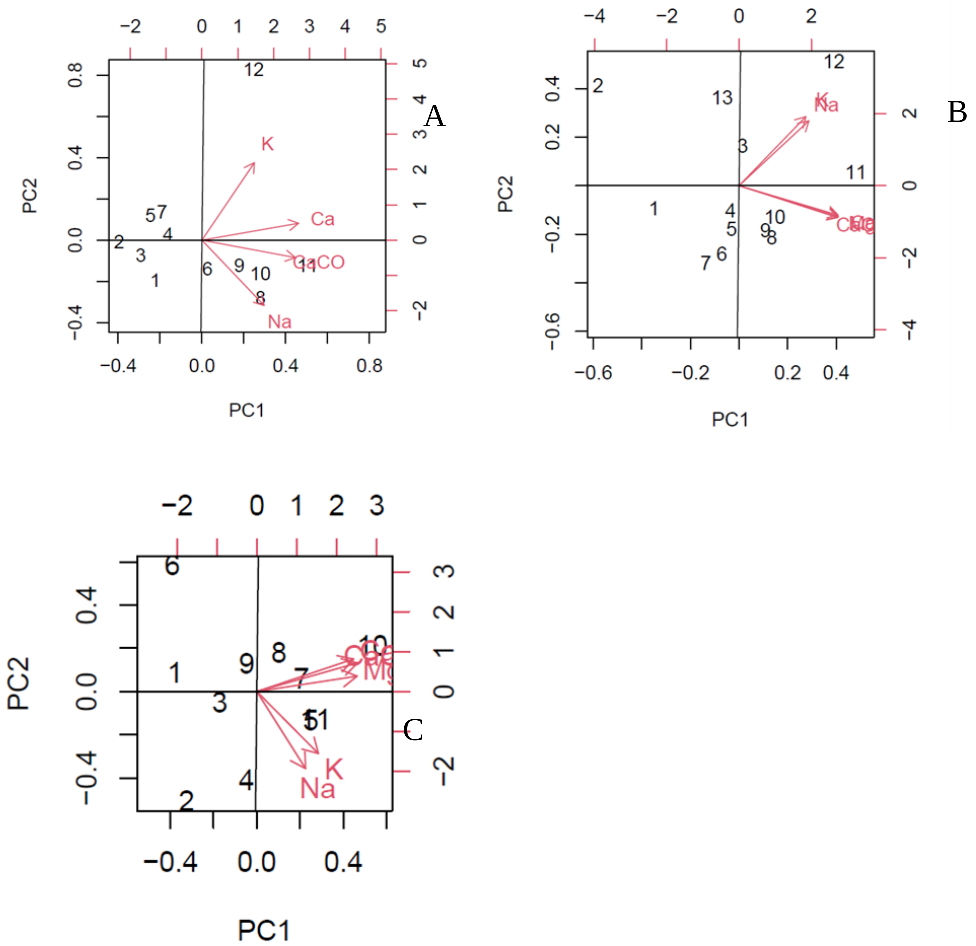

Figure 20: Biplot charts for macro elements in the rural areas (A-Nkandla (NKA); B - Gouderetrouw dam upstream (GDU); C - Gouderetrouw dam surface (GDS)

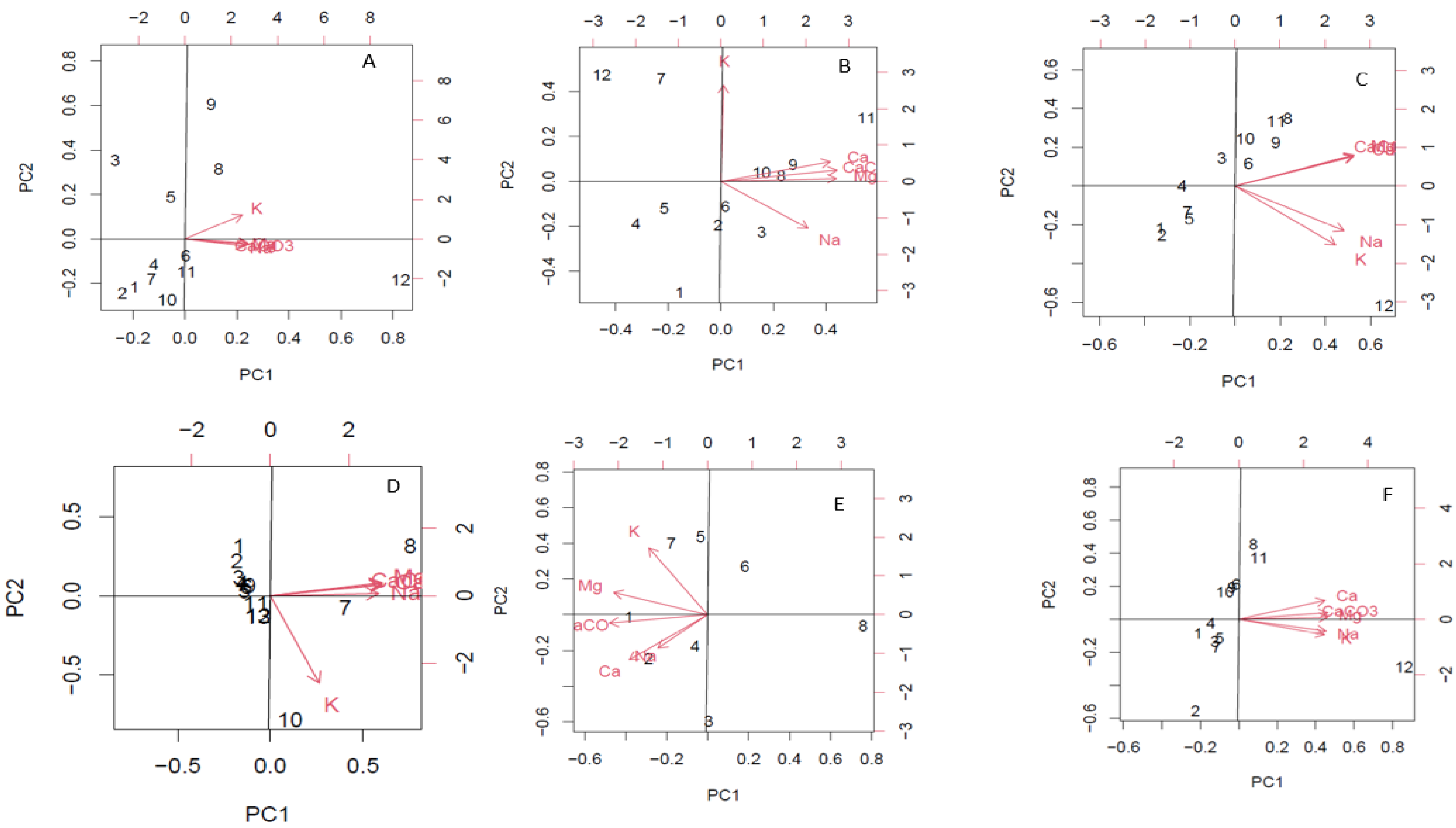

Figure 21: Biplot charts for macro elements in agricultural areas (A- R66 bridge (RB); B – Mfule (MF); C – Ntshentshelo (NTS); D – Ntambanana (NTA); E – Mholwemi (MH); F – P230 bridge (PB)

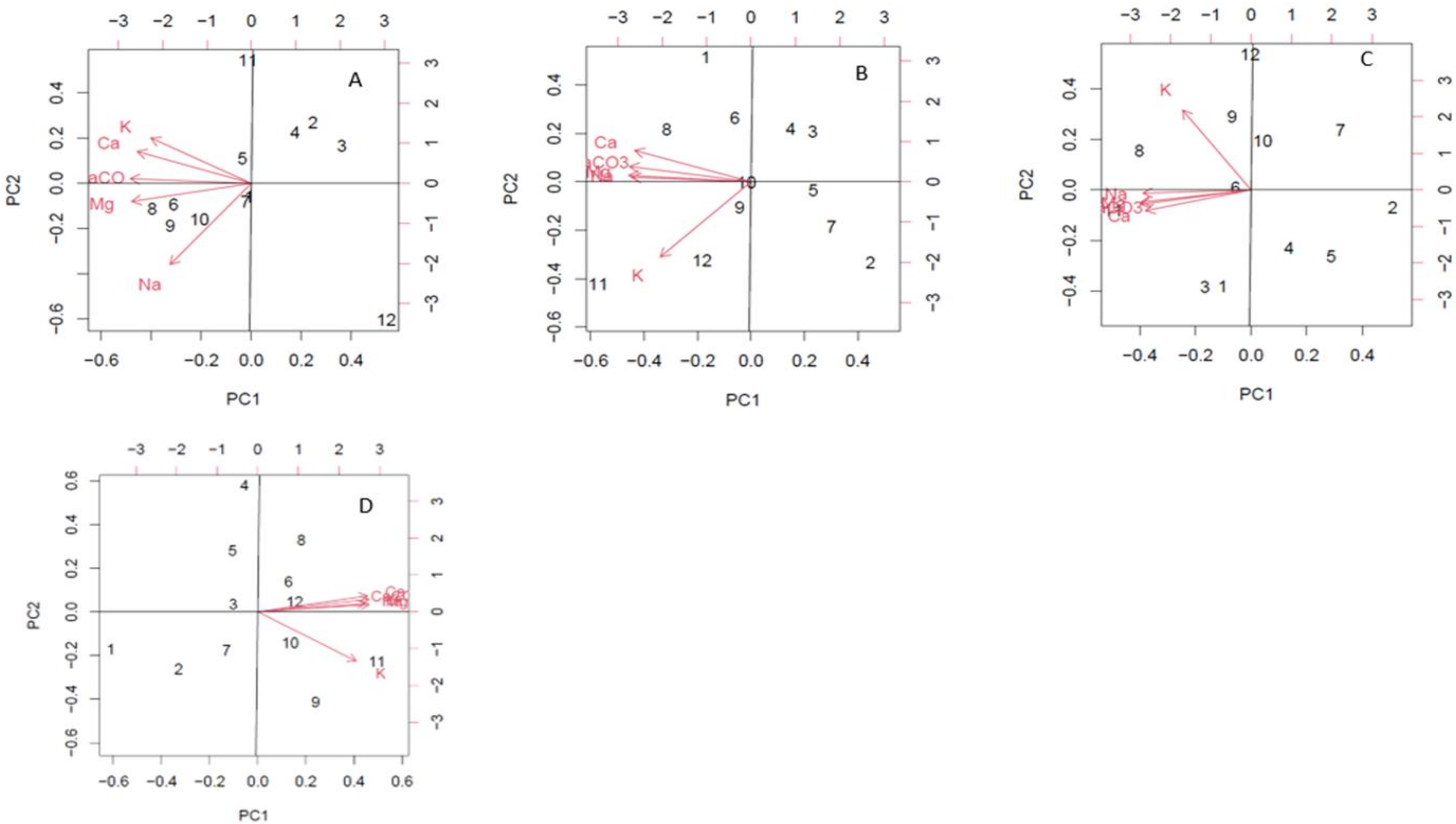

Figure 22: Biplot charts for macro elements in urban/industrial area (A-Empangeni (EM); B – Ongoye (ON); C – Chemical industry (MP); D - Weir Pumpstation (WP)

4.7 Levels of trace essential elements

Table 12 shows minimum, maximum and median values for six trace essential elements investigated in this study over a period of 12 months in 2023/24. Copper, Co, Ni and Zn levels were within WHO guideline limits at all sites throughout the year. Iron exceeded WHO guideline limits on all 13 sampling sites whilst Mn exceeded WHO limits on 9 sites. The detailed discussion of the levels of each of these trace elements (Cu, Cu, Fe, Mn, Ni and Zn) is given in Sections 4.7.1 – 4.7.6.

Table 12: Minimum, maximum and median values for trace essential elements over 12 months

Segment	Site	Copper (µg/L) Min	Max	Median	Nickel (µg/L) Min	Max	Median	Iron (µg/L) Min	Max	Median	Manganese (µg/L) Min	Max	Median	Zinc (µg/L) Min	Max	Median	Cobalt (µg/L) Min	Max	Median
Rural	NKA	0.7	5.0	2.7	0.3	21.7	2.3	17.4	2155	504	1.0	713	38.9	1.5	29	5.6	nd	2.5	0.4
	GDU	0.3	69.9	1.6	0.2	38.8	1.0	6.0	3894	123	0.4	633	8.6	0.1	59	1.6	nd	6.7	0.2
	GDS	0.4	7.0	1.9	0.6	27.8	1.3	138.4	880	309	0.8	32	10.2	0.6	5.2	2.7	nd	0.7	0.1
Agricultural	RB	0.6	4.6	1.9	0.5	28.1	1.9	1.2	1256	432	0.7	69	36.7	nd	7.1	2.3	nd	1.2	0.2
	MF	1.2	5.5	2.1	0.3	20.3	1.5	0.7	2298	423	1.3	158	24.6	nd	4.4	2.4	nd	1.7	0.2
	NTS	0.3	3.1	1.8	0.3	29.4	1.5	0.1	1967	448	0.2	209	15.4	nd	3.0	1.6	nd	1.0	0.2
	NTA	0.8	5.1	2.3	0.3	33.8	2.3	0.1	2160	432	0.3	539	68	0.1	5.5	2.3	nd	5.3	0.6
	MH	nd	8.6	2.9	0.2	59.9	6.1	nd	2583	48	0.1	260	19.2	nd	16.9	5.0	nd	9.1	0.6
	PB	0.8	4.4	2.1	0.6	33.5	2.4	145	2143	774	1.5	268	41.2	1.2	10.0	2.6	nd	2.3	0.4
Urban and industrial	EM	0.7	6.2	3.1	0.9	15.8	3.7	1.5	1347	691	0.1	177	44.8	nd	234	2.9	nd	1.2	0.7
	ON	0.4	11.6	2.5	0.4	26.2	2.0	1.1	1688	548	0.1	205	10.7	nd	427	2.8	nd	2.0	0.4
	MP	0.4	6.3	2.5	0.4	24.9	3.6	14.2	2507	1349	0.1	159	97	nd	6.0	2.9	nd	2.0	0.5
	WP	nd	3.7	2.2	nd	7.2	2.5	1.4	2317	828	0.0	142	39.2	nd	8.1	2.7	nd	1.2	0.4
WHO guidelines		2000			70			300			100			3000			50		

4.7.1 Copper

Copper levels were below guideline limits of 2000 µg/L from all sites (Table 11) in all seasons. The levels were very low except for a spike observed at the GDU site in March where the concentration was up to 70 µg/L (Figure 23A). Another spike was observed at the same site in November recording 30 µg/L. These concentration levels are still within the WHO permissible limits, and were not linked to any anthropogenic activities along uMhlathuze River. Other studies have reported similar results in which Cu levels in a river were within guideline limits (Munene, Hashim and Ambusso, 2023) in Kenya, whilst others reported Cu levels exceeding guideline limits (Siddiqui and Pandey, 2019) in India.

At the agricultural section of the uMhlathuze River, Cu was relatively higher during the high flow season and lowest during the cold low flow season (Figure 23B). However, a single spike was observed at the GDU site in March, but could not be linked to any anthropogenic activities. A similar spike was also observed at the ON site at the urban and industrial segment of the river in April (Figure 17C). The EM site which is along Empangeni tributary had relatively higher Cu levels during the low flow season compared to the other sites in the urban and industrial segment. This might have been an indication of the impact of wastewater effluents from Empangeni Town. Elevated concentrations of copper exceeding guideline limits due to wastewater discharge have been reported in other studies in Nigeria (Iloms *et al.*, 2020; Mshelia, 2024).

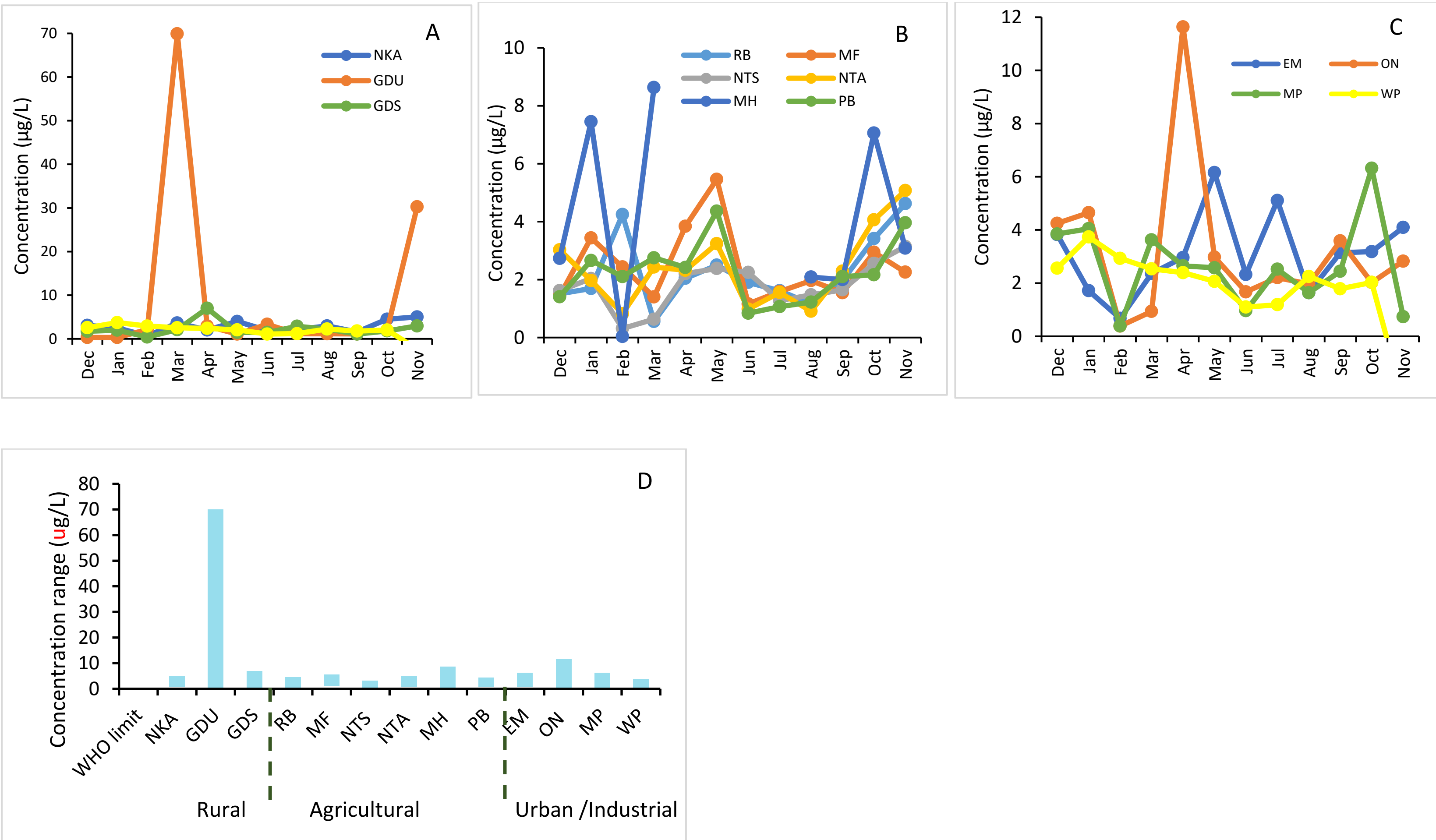

Figure 23: Concentration levels for copper in rural areas (A), agricultural areas (B), urban /industrial area (C).

D is the annual concentration range for each site

4.7.2 Cobalt

Cobalt concentration levels were below WHO guideline limits of 50 µg/L at all sampling sites along uMhlathuze River and its tributaries (Table 11). The Co levels were generally higher during the rainy high flow season and lowest during the cold low flow season which occurs in June and July. Figure 24 shows that there were spikes at some sites in November especially in the rural and agricultural sections (Figure 24A & B). These spikes may have indicated effects of the start of the rainy season but the impact on quality of uMhlathuze River was minimal with the levels still within the WHO permissible limits (Figure 24D). Some studies have observed similar trends of Co in river water systems where the levels were within the WHO guidelines limits (Skorbiłowicz, Skorbiłowicz and Misztal, 2020).

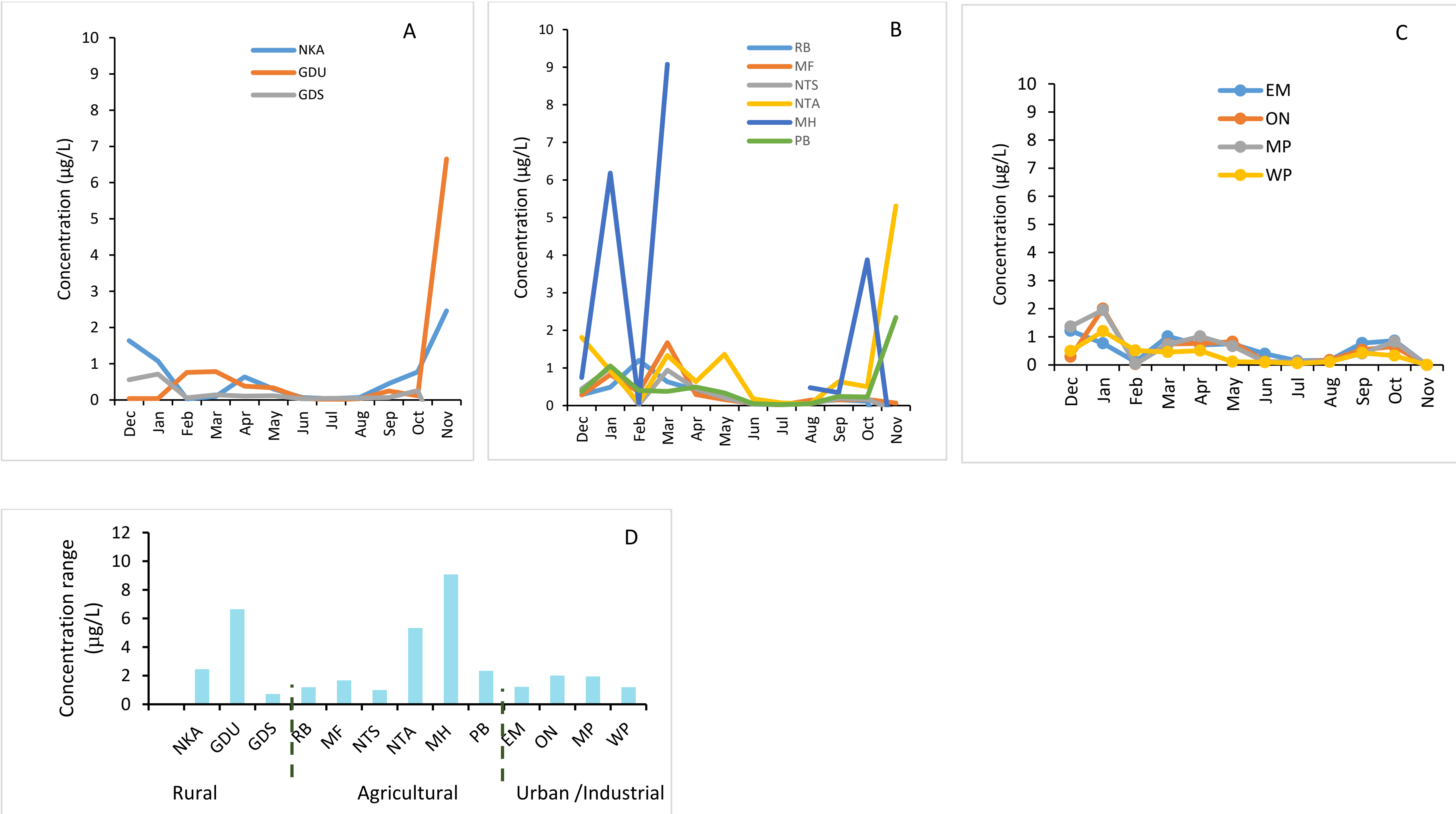

Figure 24: Concentration levels for cobalt in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.7.3 Iron

The Fe levels were relatively high but within the 2000 µg/L limit except for a few instances during the rainy season where this limit was exceeded. Generally, the levels were highest during the rainy season from November to January and then started to drop until from June to August when they would fall below 300 µg/L. The highest Fe concentration of 3894 µg/L was recorded at the GDU site at the start of the rainy season in November (Figure 25A). The area around uMhlathuze River has brownish soils with a possibility to have iron oxide together with organic matter which are responsible for brownish colour. This could be the reason for higher levels of Fe reported in the river in this study. As rainwater infiltrates the soil and underlying geological formations, it can leach Fe to rivers as part of surface run-off (Conrad *et al.*, 2020; Tashiro *et al.*, 2020). Similar studies have observed elevated levels of Fe in rivers that receive water from brownish soils. For example, researchers in Russia reported an increase in dissolved Fe from 2 to 6.90 mg/L in subsurface soil pore waters due to rainwater infiltrating soil in the region (Tashiro *et al.*, 2020).

Besides the spike that occurred in November at the GDU site, the levels of Fe in the rural section of uMhlathuze River were generally lower compared to other sections downstream (Figure 25A) with the levels at the urban and industrial section relatively higher than the agricultural section (Figure 25B & C). Elevated levels of Fe due to anthropogenic activities have recently been reported in other rivers within South Africa including the Vaal River Basin (Moloi, Ogbeide and Voua Otomo, 2020), Nzhelele River (Edokpayi *et al.*, 2017), the Kaap River (Maphanga *et al.*, 2024) and Mthatha River (Madikizela, Chimuka and Ncube, 2023), while lower levels have been recorded elsewhere including Mohlapitsi River (Addo-Bediako, 2024).

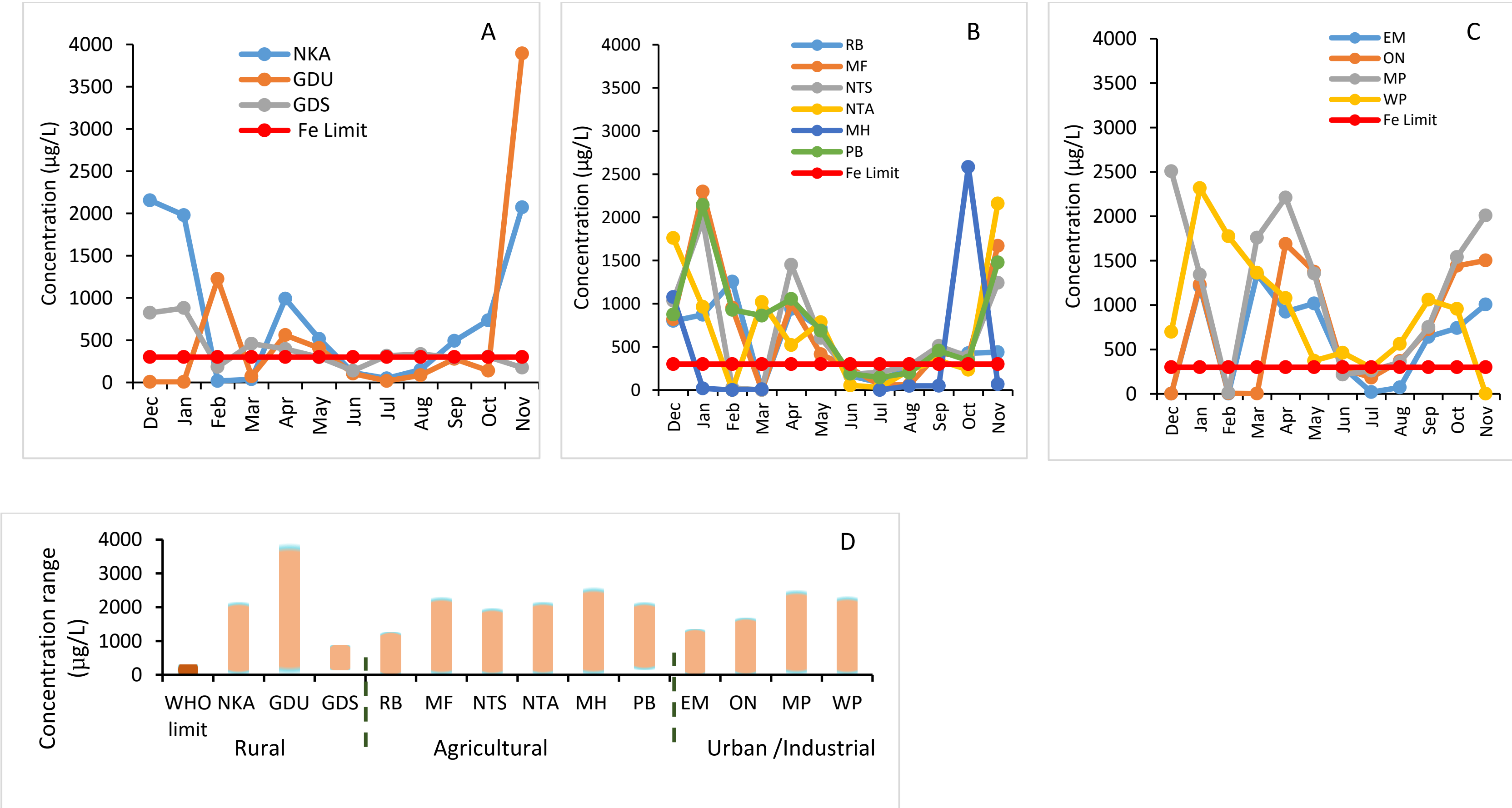

Figure 25: Concentration levels for iron in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.7.4 Manganese

The levels of Mn along uMhlathuze River and its tributaries are summarized in Figure 26. In the rural and agricultural sections of the study, the levels of Mn were within the WHO health-based precautional limit (400 µg/L) for most of the year except during November which marks the beginning of the rainy season (Figure 26A & B). This was also observed for the urban and industrial section but the elevated levels were still within the WHO precautional limits. This could have been an indication of the impact of the first rains on the uMhlathuze River. The spike in the rural areas was huge increasing from <100 µg/L up to 633 and 713 µg/L at GDU and NKA sites, respectively. Some studies have reported discharge of waste from industries to be responsible for higher levels of Mn in water (Goyal *et al.*, 2022).

Besides the few spikes observed in the rural and agricultural sections, the Mn levels were generally higher in the urban and industrial section of the uMhlathuze River. With no evidence of the impact of wastewater effluents on the EM site along the Empangeni tributary, the Mn levels could have emanated from local industries within the urban and industrial sections of the study. Industrial areas have previously elevated levels of Mn in river systems (Edokpayi *et al.*, 2018; Shapi *et al.*, 2021).

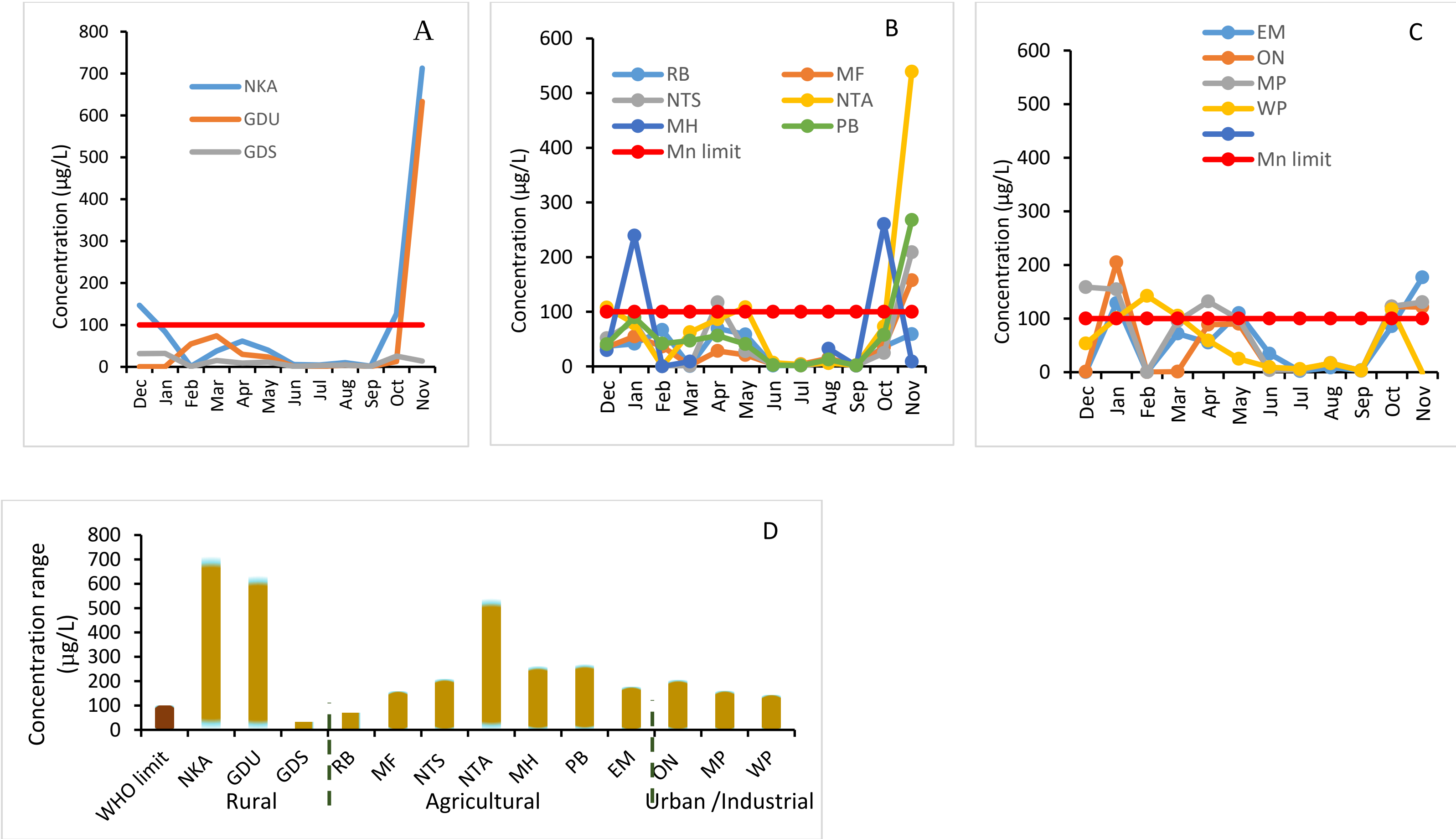

Figure 26: Concentration levels for manganese in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.7.5 Nickel

Nickel concentration levels were below WHO guideline limits of 70 µg/L in water from all sites (Figure 27). However, it was observed that the beginning of rainy season led to significant spikes in levels of Ni for all sites except the WP site which was the last sampling site for this study before uMhlathuze River pours into the Indian Ocean. The spikes were much significant at the agricultural section with the Mholweni River tributary (MH site) increasing up to a concentration of 60 µg/L (Figure 27B). Mholweni River has quarry activities which could potentially result in leaching of Ni into the river system. Studies on impact of quarry activities on heavy metals in water have been conducted elsewhere where Ni was reported to be above WHO guideline limits (Hassan, 2022). Besides the observed spikes during the start of the rainy season in the agricultural section, there is no evidence of agricultural activities impacting on the quality of uMhlathuze River due to Ni pollution. A study was conducted on Lom River, Cameroon which indicated that heavy metals including Ni were within WHO guidelines (Sayom *et al.*, 2023).

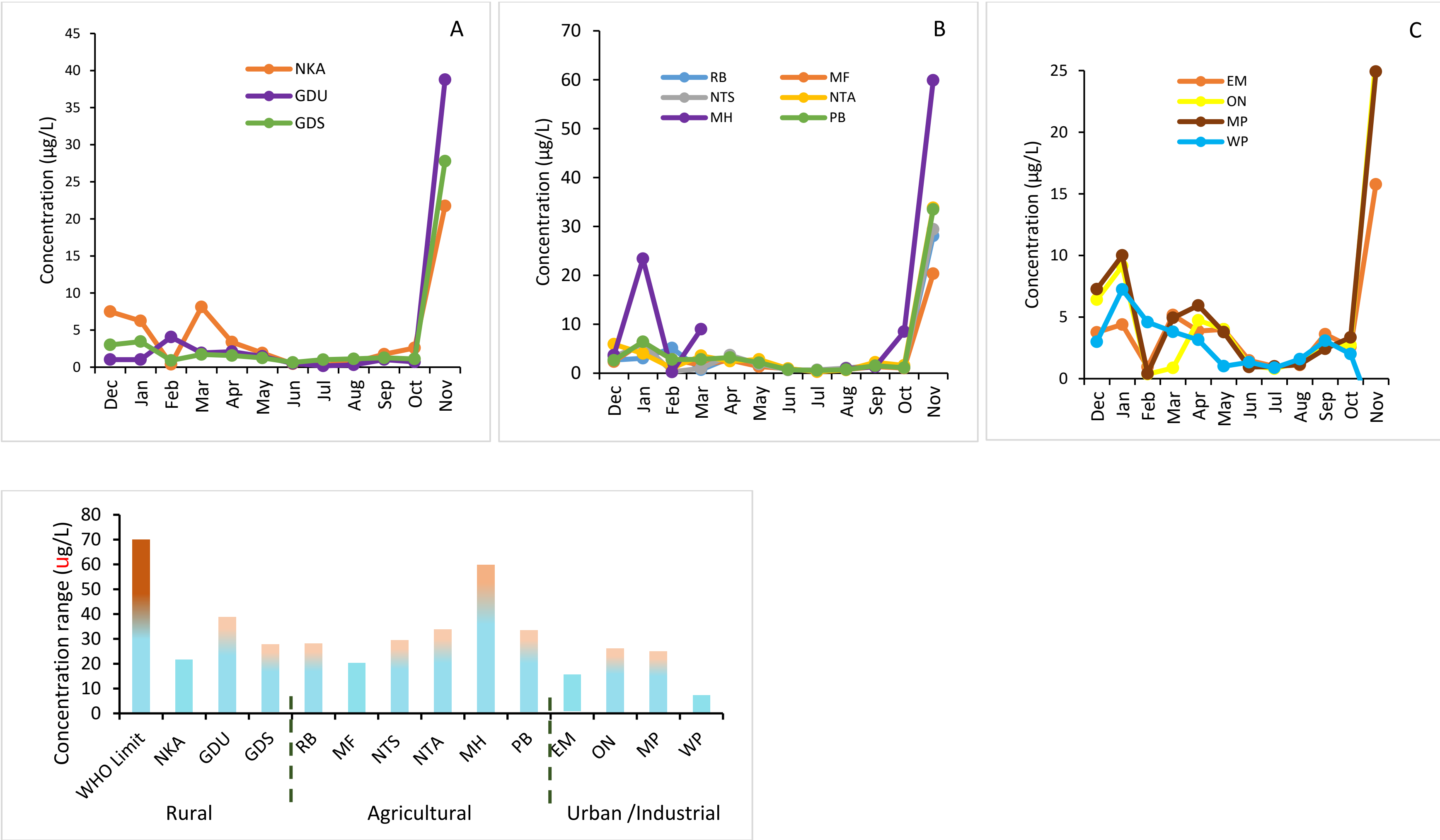

Figure 27: Concentration levels for nickel in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.7.6 Zinc

Zinc was also within the WHO guideline limits of 2000 µg/L from all sites throughout the year (Figure 28). In an urban and industrial area, the EM site (234 µg/L) and ON site (427 µg/L) were the only sites with elevated Zn concentrations (Figure 28C & D. On the EM site which lies along Empangeni tributary, the observed spike could be due to wastewater discharge from wastewater works and direct runoff from galvanised steel structures within Empangeni town. Consequently, the spike at the ON site could be due to accumulation from Empangeni River since it occurs downstream after uMhlathuze River has met with the Empangeni River. Besides the spikes at the EM and ON sites, the concentration of Zn was very low, below 60 µg/L for all the other sites throughout the seasons. Studies that have been conducted on water sources and Zn was reported to be within guideline levels (ElKashouty *et al.*, 2023; Munene, Hashim and Ambusso, 2023). Anthropogenic activities including agricultural, wastewater and quarry activities reported higher concentration of Zn in water (Patel *et al.*, 2018; Mshelia, 2024).

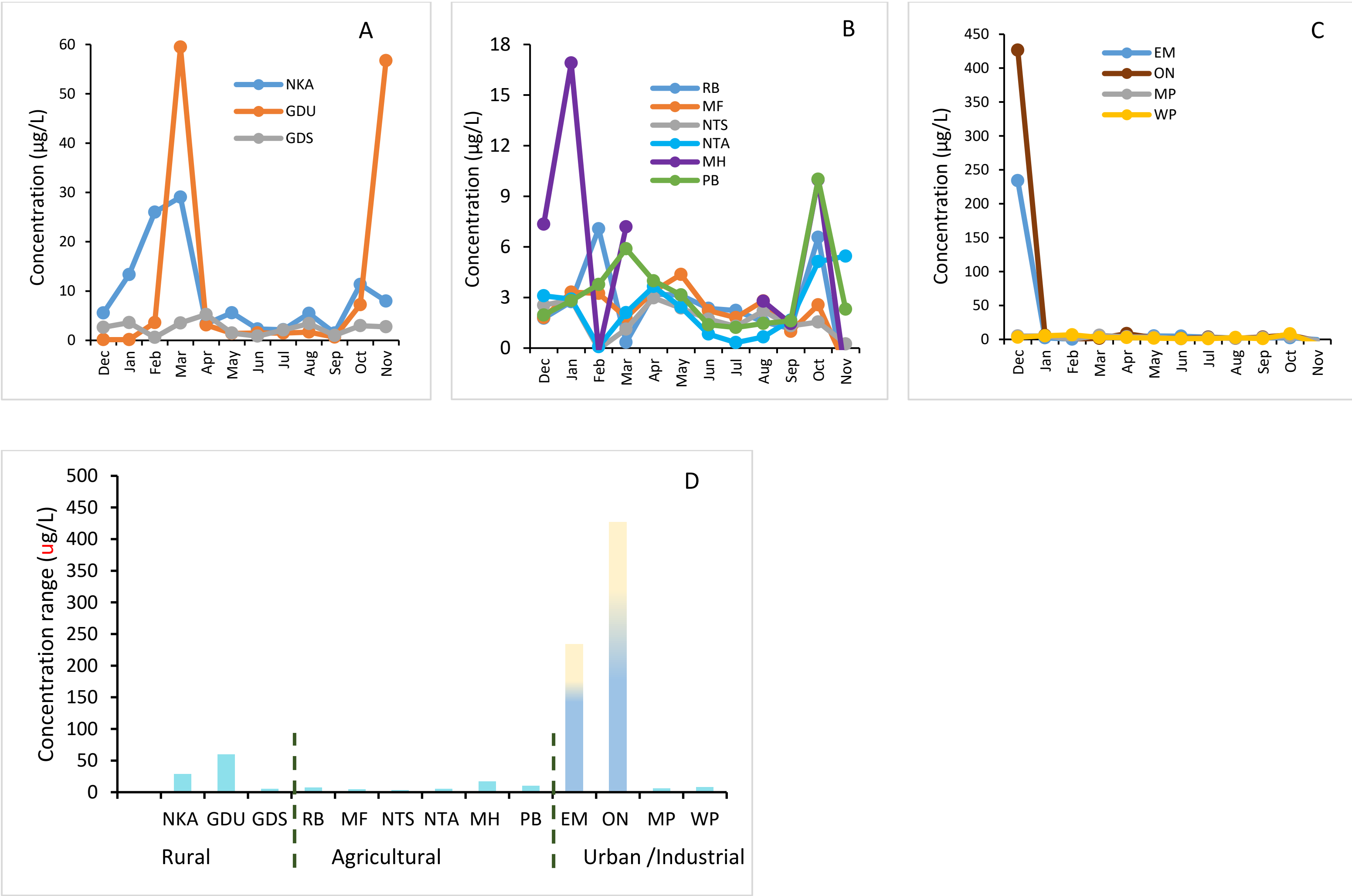

Figure 28: Concentration levels for zinc in the rural segment (A), agricultural segment (B), urban /industrial segment (C). D is the annual concentration range for each site

4.8 Interrelationships between trace essential elements

4.8.1 Rural areas

Figure 29 show the interrelationship between essential metals in a rural area. The results show that there was a strong correlation among Cu, Co, Ni, Fe and Mn trends throughout the year from the NKA site in Nkandla area (Figure 29A), implying that there is a possibility that they came from the same source. With limited anthropogenic activities in rural areas, these metals could be arising from geological properties of the area. However, the Zn trends were different from that of the other metals as observed between January and March. There is no definite explanation on this behaviour. At GDU site (Figure 29B), the Zn trends were now correlated with Cu. This interrelationship was due to a high spike for the two metals in February. At GDS site (Figure 29C), the Zn and Cu trends were still not interrelated with other metals. However, their interrelationship was now relatively weak compared to the GDU site. The Ni trends were also not related to any other metals at GDS site due to the high spike observed in November compared to other sites. A previous correlation analysis study conducted with heavy metals including Cd, Pb, Cr, Co, Mn, Zn and Cu showed that there was no strong correlation reported among these elements (Raja *et al.*, 2021). However, a weak correlation was reported between Co-Ni, Zn-Co and Cu-Mn suggesting that they might come from different sources (Raja *et al.*, 2021).

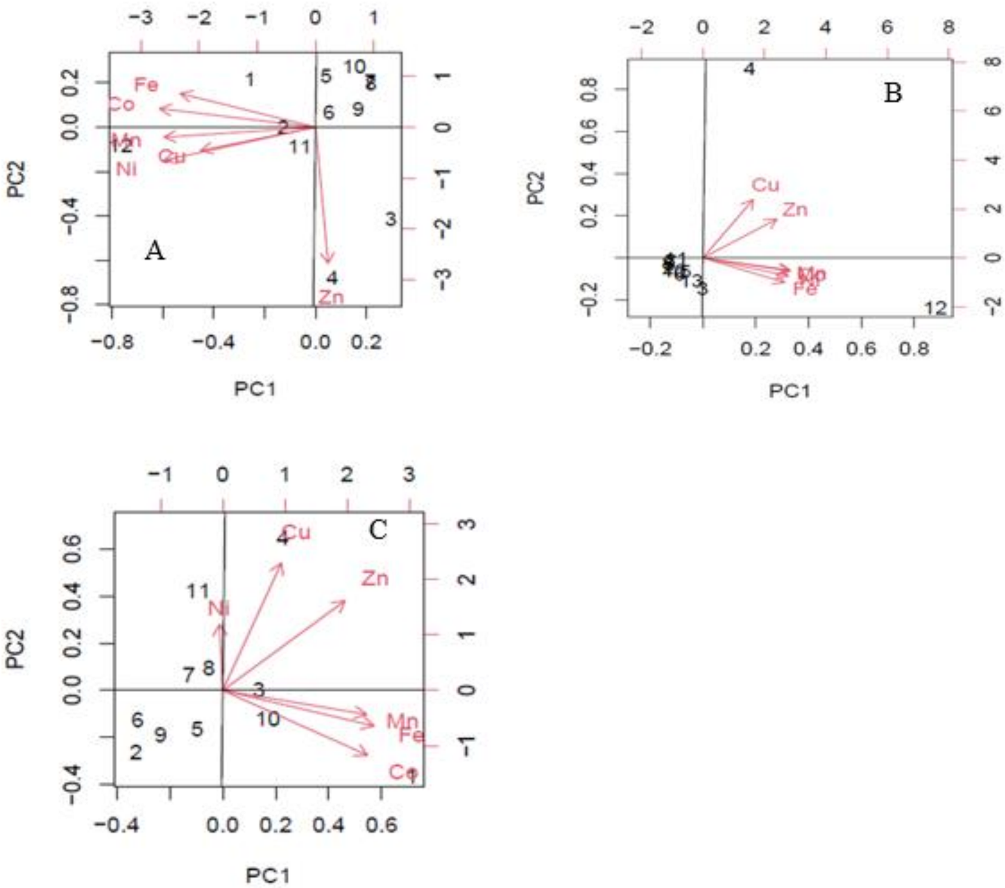

Figure 29: Trace essential elemental biplot charts for uMhlathuze River in the rural areas (A-Nkandla (NKA); B - Gouderetrouw upstream (GDU); C - Gouderetrouw dam surface (GDS

4.8.2 Agricultural areas

Interrelationship between trace essential metals in the agricultural area are summarized in Figure 30. It was observed that Cu and Zn were still not interrelated with the other metals at the R66 bridge (RB) site as shown in Figure 30A. The same behavior was observed at the Mfule site (Figure 30B). The Fe trend was no longer correlated with the other metals. This was due to a high spike observed in November. This Fe behavior was also observed at Ntshentshelo (NTS) sampling site (Figure 30C). Generally, interrelationships at NTS site were different from other sampling sites. For example, the Zn trend was now strongly correlated with Co, whilst the Cu trend was interrelated with Mn. There was a spike for Cu and Mn levels in November and this was not the case with Zn and Co.

The unique interrelationship between the Zn and Cu trends was observed again along Ntambanana tributary (NTA site) (Figure 30D). Along the Mholweni tributary (MH site) (Figure 30E), most trace essential metals were not interrelated except for Cu and Co whose levels were relatively higher from December to March. These levels may be related to quarry activities in the area. There were no samples collected during the dry season, which could have affected potential interrelationships between the essential elements. At the PB site (Figure 30F), the Zn and Cu trends were not interrelated with other metals and were also not related to each other whilst the other metals were all interrelated. Very strong correlation between Zn and Co have also been reported by Kubra and colleagues when assessing heavy metals along the Brahmaputra River, Bangladesh (Kubra *et al.*, 2022).

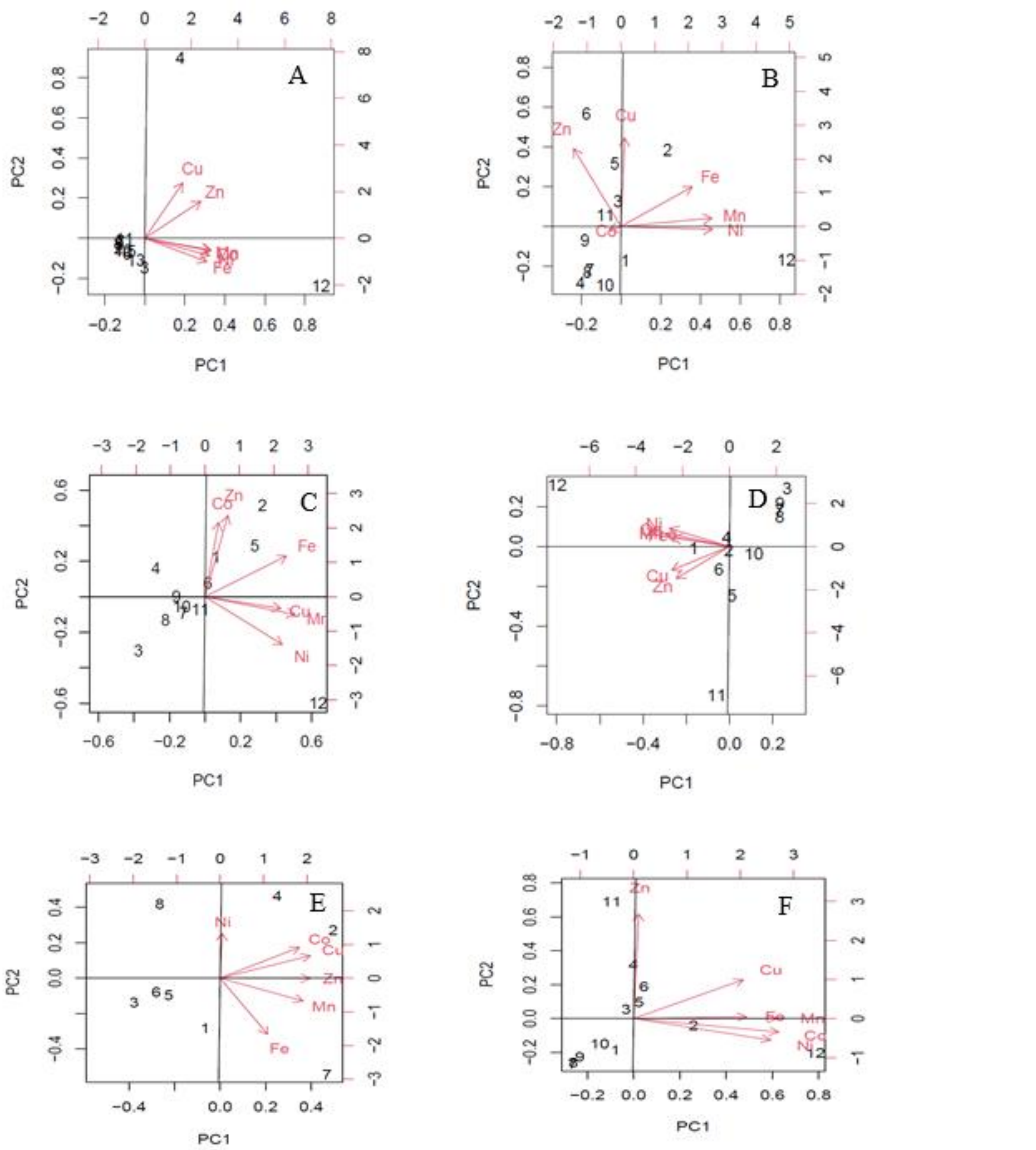

Figure 30: Trace essential elemental biplot charts for uMhlathuze River in the agricultural areas (A-R66 bridge (RB); B - Mfule (MF); C - Ntshentshelo (NTS); D – Ntambanana (NTA); E – Mholweni (MH); F – P230 bridge (PB)

4.8.3 Urban and Industrial areas

Figure 31 represents interrelationships between trace essential metals along the uMhlathuze River in the urban and industrial area. The Zn and Cu trends had a strong interrelationship at Empangeni (EM) site (Figure 31A). The Mn and Fe trends were also interrelated. Both Mn and Fe were lowest in the dry season (June to August). This suggests that Mn and Fe might have come from the same source considering the area is from an urban and industrial area coupled with wastewater discharge from Empangeni town. The same behaviour of Mn and Fe was observed at the ON site (Figure 31B), but the Zn and Cu trends were no longer interrelated. At the MP site (Figure 31C), the Mn and Fe trends were still interrelated and recorded lowest levels in the dry season. The Ni trends were not related to the other metals. There were very low levels for Ni from the months of April to August compared to other metals. At the Weir Pumpstation (WP) site (Figure 31D), the Zn trend was now interrelated with Mn. The Zn and Mn levels were both high in February and October compared to other metals. In a similar environment with sources of pollution from industrial discharges as the current study, there was no correlation between Zn & Mn or Fe & Mn, instead a moderate correlation was between Zn & Co as well as Zn-Cd as well as Zn-Cr (Raja *et al.*, 2021).

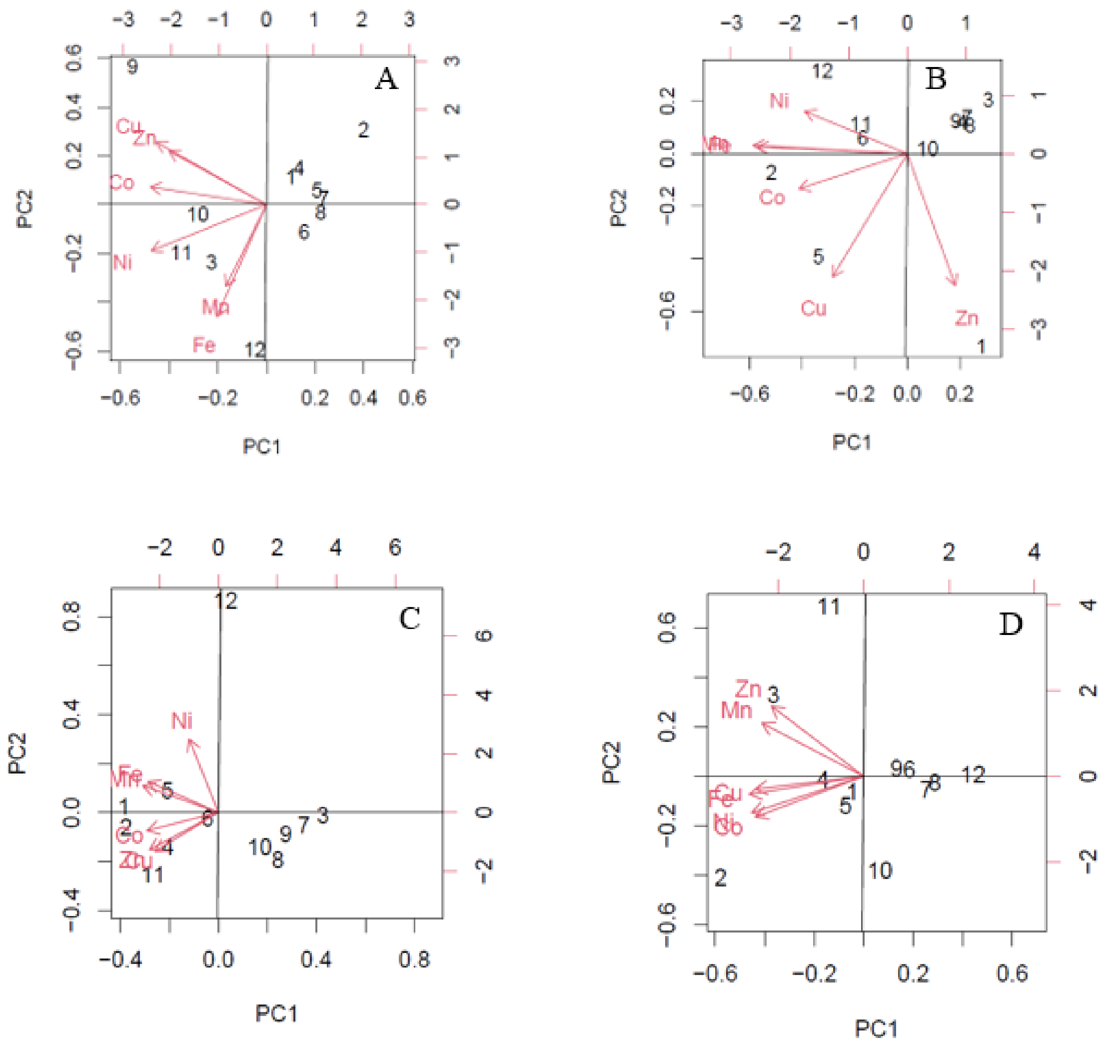

Figure 31: Trace essential biplot charts for uMhlathuze River in the urban/industrial area (A-Empangeni (EM); B- Ongoye (ON); C- Chemical industry (MP) and Weir Pumpstation (WP)

4.9 Trace toxic elements

Table 13 represents minimum, maximum and median values for trace toxic elements over the 12 months sampling period from December 2023 to November 2024. Lead exceeded WHO guideline limits in agricultural and urban and industrial areas. Arsenic, U, Cd and Cr were all below WHO guideline limits. Mercury results were below detection limits from all except the EM site (Empangeni tributary) where 0.4 µg/L was detected. Detailed discussion for trace toxic elements is given in section 4.9.1 – 4.9.6.

4.9.1 Cadmium

Figure 32A – C show concentration levels for Cd along uMhlathuze River and its tributaries. Figure 32D shows the annual concentration range for each site from December 2023 to November 2024. The trends show that Cd concentrations were below 0.05 µg/L from summer to winter months in the rural area (Figure 32A). A spike up to 0.1 µg/L occurred in spring on the GDU and NKA sites. This spike is low, and did not have a marked impact on the quality of uMhlathuze River. In the agricultural and urban/industrial area, the concentration of Cd was below detection limits during winter months (Figure 32B & C). There was a spike up to 2 µg/L which occurred in autumn at Mfule Stream (MF site). Mfule Stream receive some runoff from Melmoth town. However, the impact on uMhlathuze River is minimal, possibly due to dilution effects. A previous study by Mthembu and colleagues on uMhlathuze River in 2012 reported 4 µg/L at WP site which was above guideline limits (Mthembu, Djarova and Basson, 2012). Reasons provided was due to agricultural and industrial development. Their study included sample collection between February and November 2009. Fifteen years later, this study indicates no threat to water quality due to Cd at the same sites and the rest of uMhlathuze River upstream. A study by Cengiz and colleagues on 13 heavy metals including Cd at Bogacayi River, Turkey indicated the results were below detection limit (Cengiz *et al.*, 2017).

Table 13: Minimum, maximum and median values for trace toxic elements over 12 months

Segment	Site	Lead (µg/L)			Arsenic (µg/L)			Mercury (µg/L)			Uranium (µg/L)			Cadmium (µg/L)			Chromium (µg/L)		
		Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median
Rural	NKA	0.1	7.4	1.7	0.3	1.2	0.4	n.d	n.d	n.d	0.1	0.8	0.1	n.d	0.1	n.d	n.d	6.3	0.9
	GDU	0.1	59.0	1.0	0.2	1.9	0.4	n.d	n.d	n.d	n.d	0.7	0.1	n.d	0.1	n.d	0.2	3.6	0.6
	GDS	n.d	5.9	1.0	0.3	0.6	0.5	n.d	0.07	n.d	n.d	0.1	n.d	n.d	n.d	n.d	n.d	2.1	0.7
Agricultural	RB	n.d	13.7	1.1	0.3	1.0	0.4	n.d	n.d	n.d	n.d	0.6	0.1	n.d	0.5	n.d	n.d	3.2	0.8
	MF	0.2	5.0	0.8	0.5	2.0	0.8	n.d	n.d	n.d	n.d	1.9	0.1	n.d	2.0	n.d	n.d	2.6	0.7
	NTS	n.d	11.2	0.9	0.4	1.3	0.5	n.d	0.02	n.d	n.d	0.9	0.1	n.d	0.9	n.d	n.d	3.2	0.5
	NTA	0.2	4.1	0.6	0.5	2.4	1.2	n.d	0.02	n.d	0.1	4.5	1.3	n.d	0.2	n.d	n.d	3.2	0.7
	MH	n.d	10.6	2.7	0.4	6.9	0.7	n.d	n.d	n.d	1.3	7.8	2.4	n.d	n.d	n.d	n.d	14.6	0.4
	PB	n.d	8.0	1.2	0.5	1.5	0.6	n.d	n.d	n.d	0.1	0.9	0.2	n.d	n.d	n.d	n.d	3.9	1.0
Urban and industrial	EM	n.d	5.8	1.0	0.8	6.6	1.4	n.d	0.40	n.d	0.2	0.4	0.3	n.d	1.4	n.d	n.d	3.8	1.4
	ON	n.d	6.7	1.3	0.5	6.4	0.6	n.d	0.03	n.d	n.d	0.7	0.2	n.d	2.0	n.d	n.d	5.0	1.0
	MP	n.d	12.4	1.5	0.4	1.1	0.8	n.d	n.d	n.d	0.1	0.3	0.2	n.d	0.1	n.d	n.d	5.9	1.4
	WP	n.d	5.6	1.2	0.4	0.9	0.7	n.d	n.d	n.d	0.1	0.3	0.2	n.d	0.2	n.d	n.d	3.8	0.6
WHO guidelines		10			10			6			30			3			50		

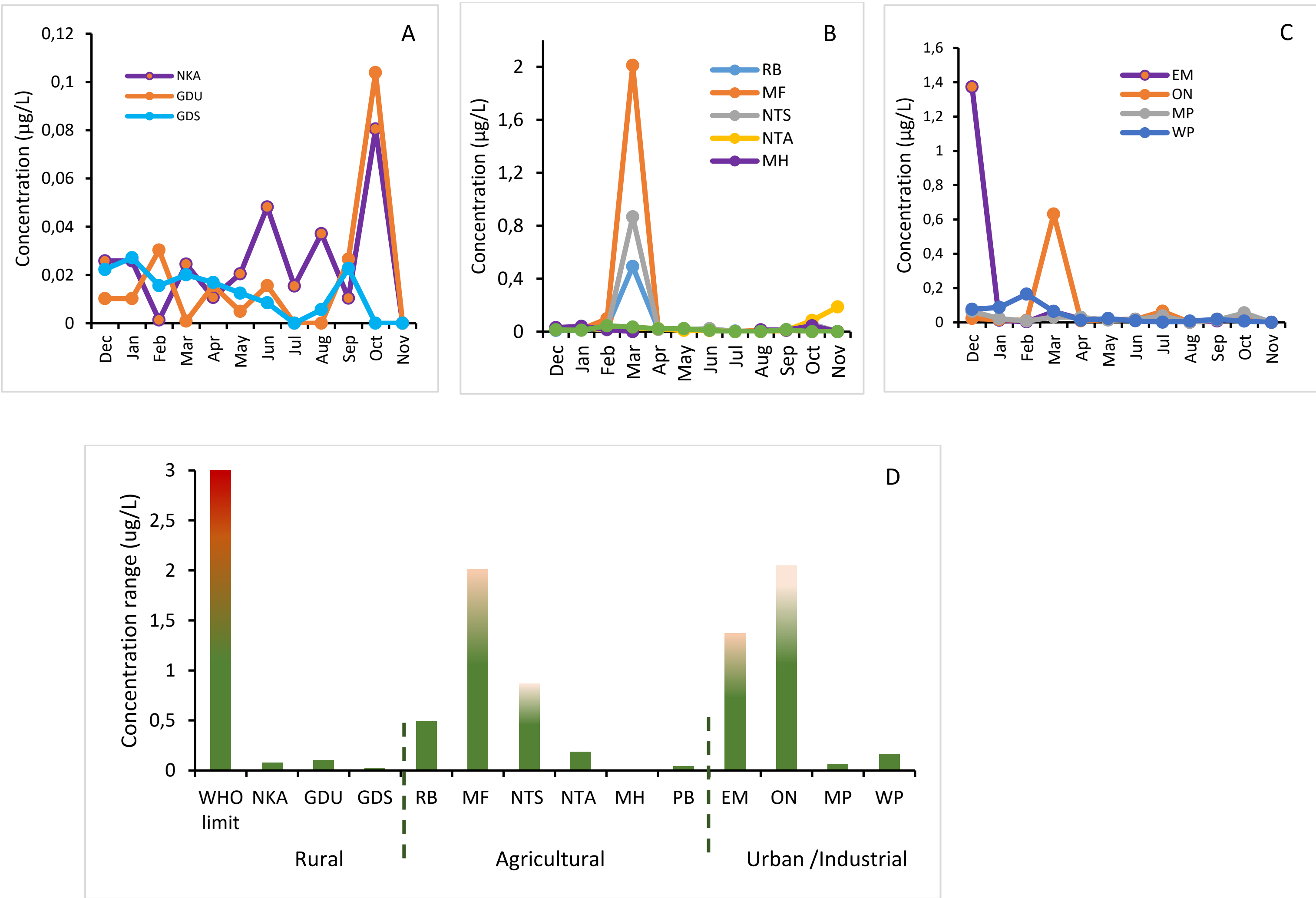

Figure 32: Concentration levels for cadmium in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site.

4.9.2 Chromium

Figure 33A – C show concentration levels for Cr in rural areas, agricultural areas and urban and industrial areas for the period December 2023 to November 2024. From all the 3 segments, the Cr results were below WHO guideline limit of 50 µg/L. During summer, each segment experienced a spike for Cr concentration up to 15 µg/L recorded at RB site. Concentration levels for Cr were below 2 µg/L in winter months, for all segments. Based on these trends, anthropogenic activities at uMhlathuze River had no effect on Cr concentration levels throughout the study. Mthembu and colleagues reported Cr concentration levels which were within the guideline limits at the same river in 2012 (Mthembu, Djarova and Basson, 2012) and that was confirmed in the current study. The sites investigated were ON, MP and WR, and for this study, the same sites showed very low Cr levels.

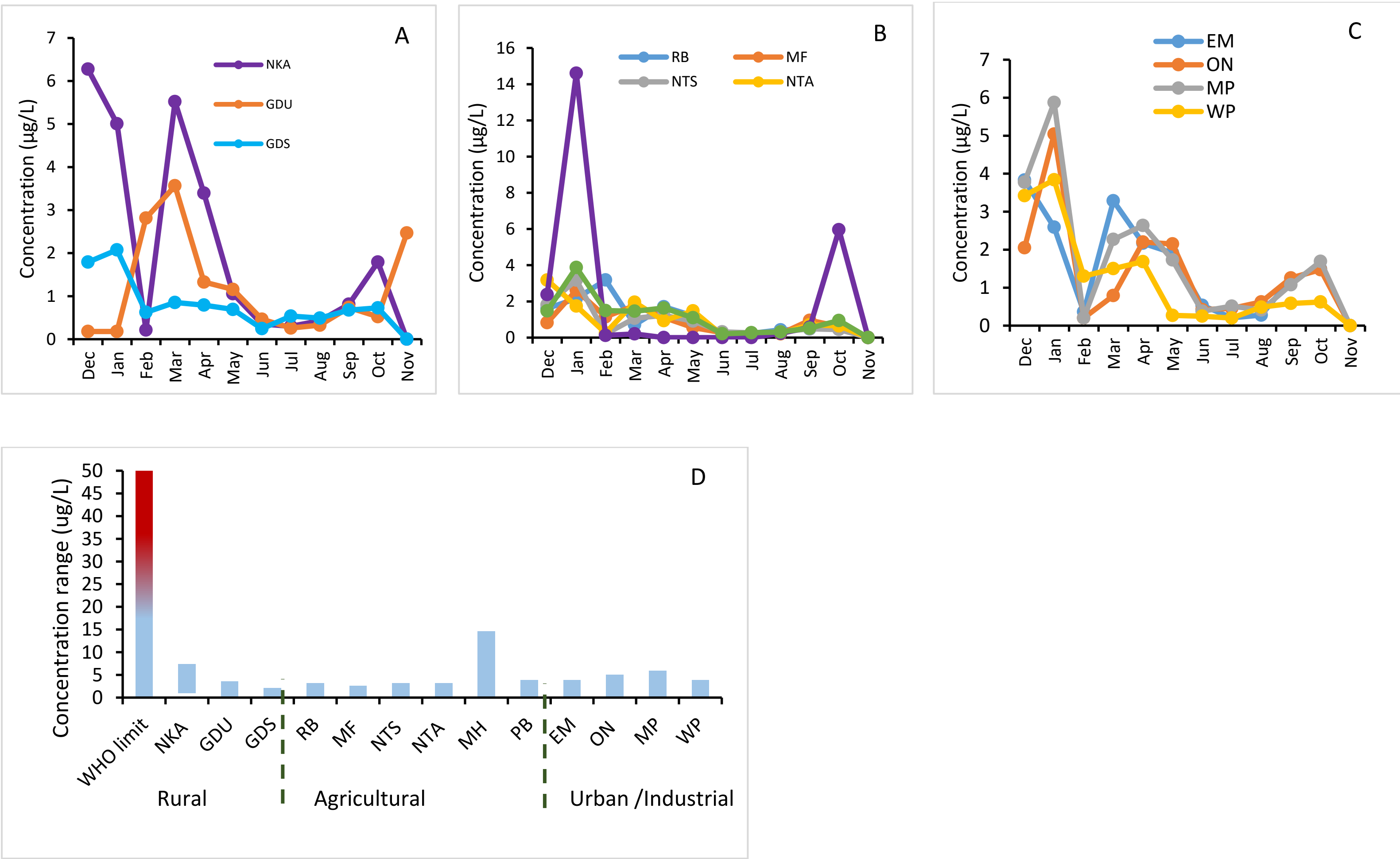

Figure 33: Concentration levels for chromium in rural areas (A), agricultural areas (B), urban / industrial area (C), D is the annual concentration Range for each site

4.9.3 Lead

Figure 34 A, B, C & D) show Pb concentration levels which exceeded WHO guideline limits in autumn (rural area) and winter months (agricultural and urban areas). From spring to early summer, Pb results were approximately 5 µg/L or lower, which was within guideline limits. At the rural areas, Pb levels were within the WHO guideline limits throughout the 12 months period except for a single spike which was observed at the GDU site (upstream of Gouderetrouw dam) in March. This could not be explained. Agricultural activities and wastewater discharge from wastewater works as well as industry could be the reason for Pb spikes reported at segment 2 and 3 which exceeded guideline limits. Lead exceeding guideline levels was reported by Raja in ground water study, India. Reasons provided were due to industrial activities and dumpsite leaches (Raja *et al.*, 2021). Higher levels of Pb in the current study were also reported by Mthembu and colleagues in 2012 where 280, 380 and 500 µg/L Pb at ON, MP and WP sites respectively exceeded guideline limits. Reasons provided were due to agricultural activities and industrial development which negatively impacted quality of uMhlathuze River (Mthembu, Djarova and Basson, 2012). With the elevated concentrations reported from sites upstream of WP, Pb concentration at this site (WP) was below guideline limit. This could be caused by the level of river which provide dilution to those tributaries joining uMhlathuze River, keeping concentration of trace elements at low levels.

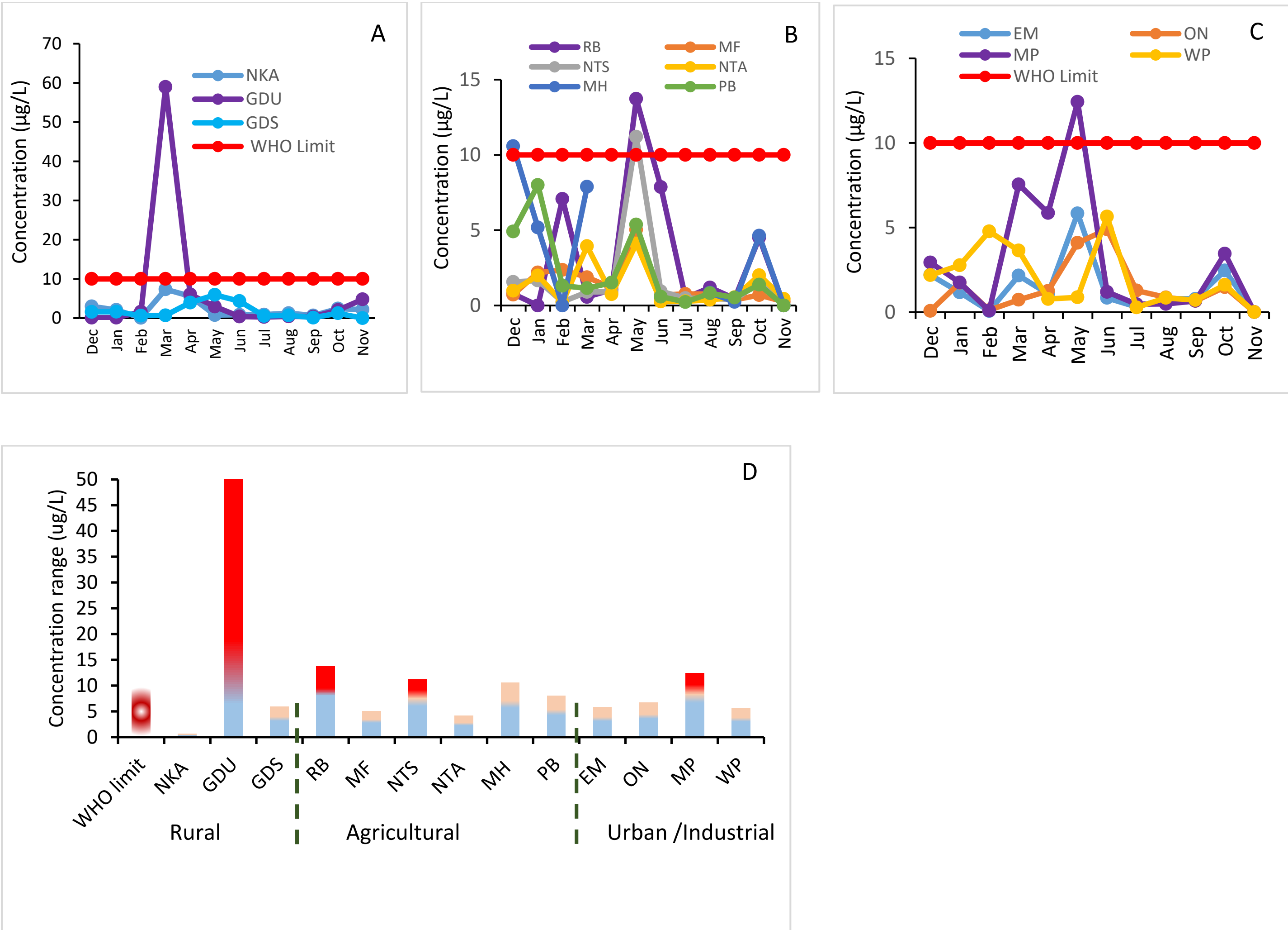

Figure 34: Concentration levels for lead in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.9.4 Arsenic

As results were below WHO guideline limit of 10 µg/L on all sites. A single spike between 4 and 6 µg/Lµ was observed at rural area in winter at the GDS site (Figure 35A). Single spikes were also observed in autumn at the MH site in an agricultural area (Figure 35B) as well as at the EM and ON sites in an urban and industrial area (Figure 35C) where about 7 µg/L was recorded in March and December respectively. These concentrations are below guideline limits but may be linked to anthropogenic activities especially quarry mining along Mholweni tributary and urban runoff and wastewater effluents that enter Empangeni tributary. Besides the spikes at MH, EM and ON sites (Figure 35D), the concentration of As remained below 2 µg/L for all sites, possibly due to dilution from uMhlathuze River. Other studies conducted on rivers have reported As below contamination levels including Cengis in Turkey (Cengiz *et al.*, 2017) and parts of Lake Victoria (Outa *et al.*, 2020). Higher levels of As in water with reasons stated as mining activities were reported in Cross River, Nigeria (Adamu, Nganje and Edet, 2015).

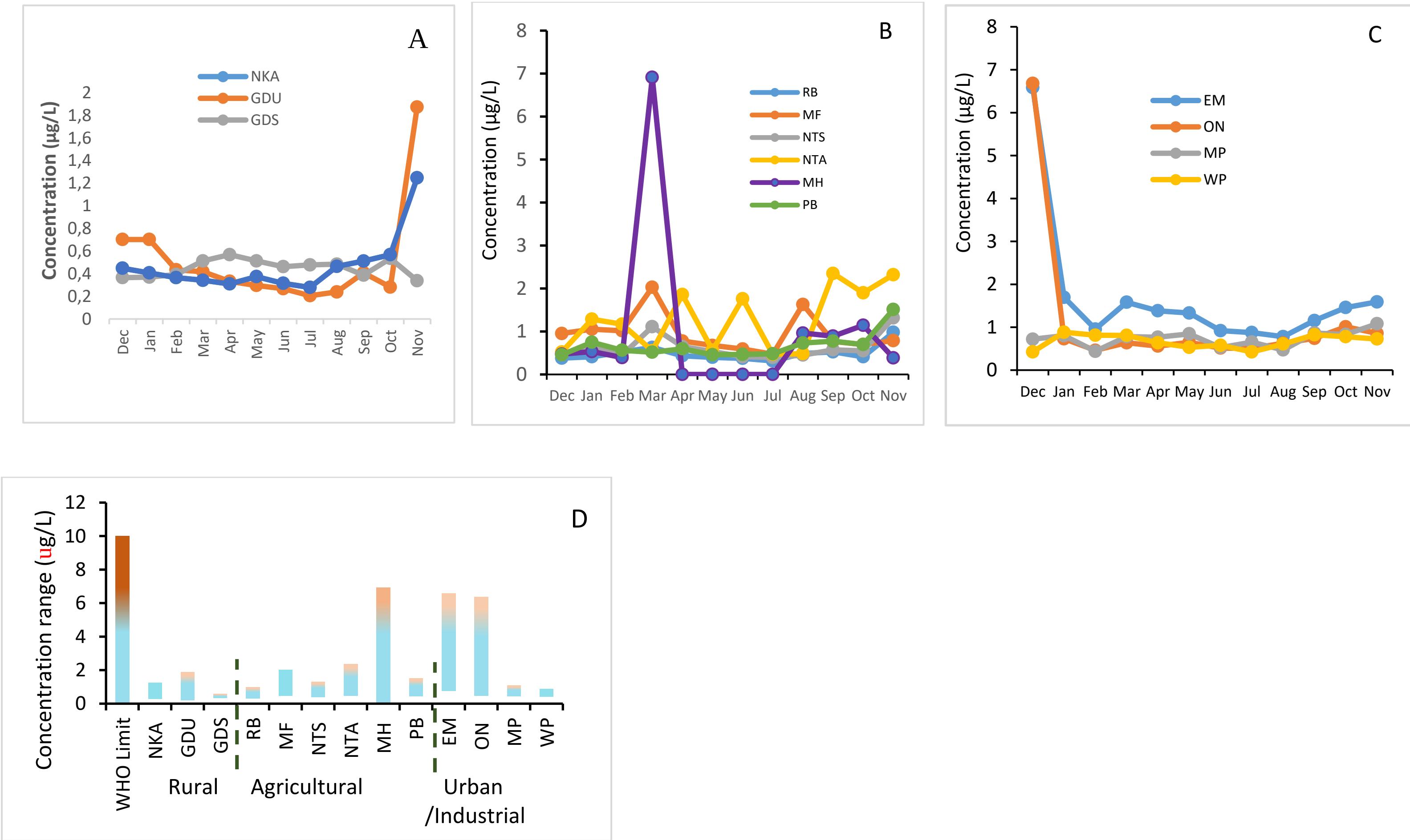

Figure 35: Concentration levels for arsenic in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.9.5 Uranium

Uranium concentration was below 8 µg/L from all sites and mostly within 0.2 µg/L except for tributaries (Figure 36A, B, C & D). These concentrations were all within WHO guideline limits of 30 µg/L. Uranium spikes up to 0.8 µg/L were observed in the rural area during the start of the rainy season in November. The levels along the Mholweni and Ntambanana tributaries (MH and NTA sites) were consistently around 2 µg/L (Figure 36B) which can be translated to the impact of quarry mining and agricultural activities. Studies conducted near U mining area as well as areas with chemical factories and fertilizer indicated levels of U beyond background values of surface water (Bajwa *et al.*, 2017; Yi *et al.*, 2020).

4.9.6 Mercury

Hg levels were all within the WHO permissible limits. Mercury was not detected except along the Empangeni tributary (EM site) where 0.399 µg/L was recorded along Empangeni River (EM site) in the month of March. This falls within the WHO permissible limit of 6 µg/L (WHO, 2017). Traces of Hg were also detected at the ON site which occurs after the Empangeni-uMhlathuze juncture recording 0.014 and 0.033 µg/L in the months of January and June, respectively. Traces of Hg were also detected on the Mholweni tributary in March (0.112 µg L^{-1}) and along the Ntambanana tributary (0.017 µg L^{-1}) in the month of May. Mthembu and colleagues from their study at the same river also reported Hg concentration levels within guideline limits (Mthembu, Djarova and Basson, 2012).

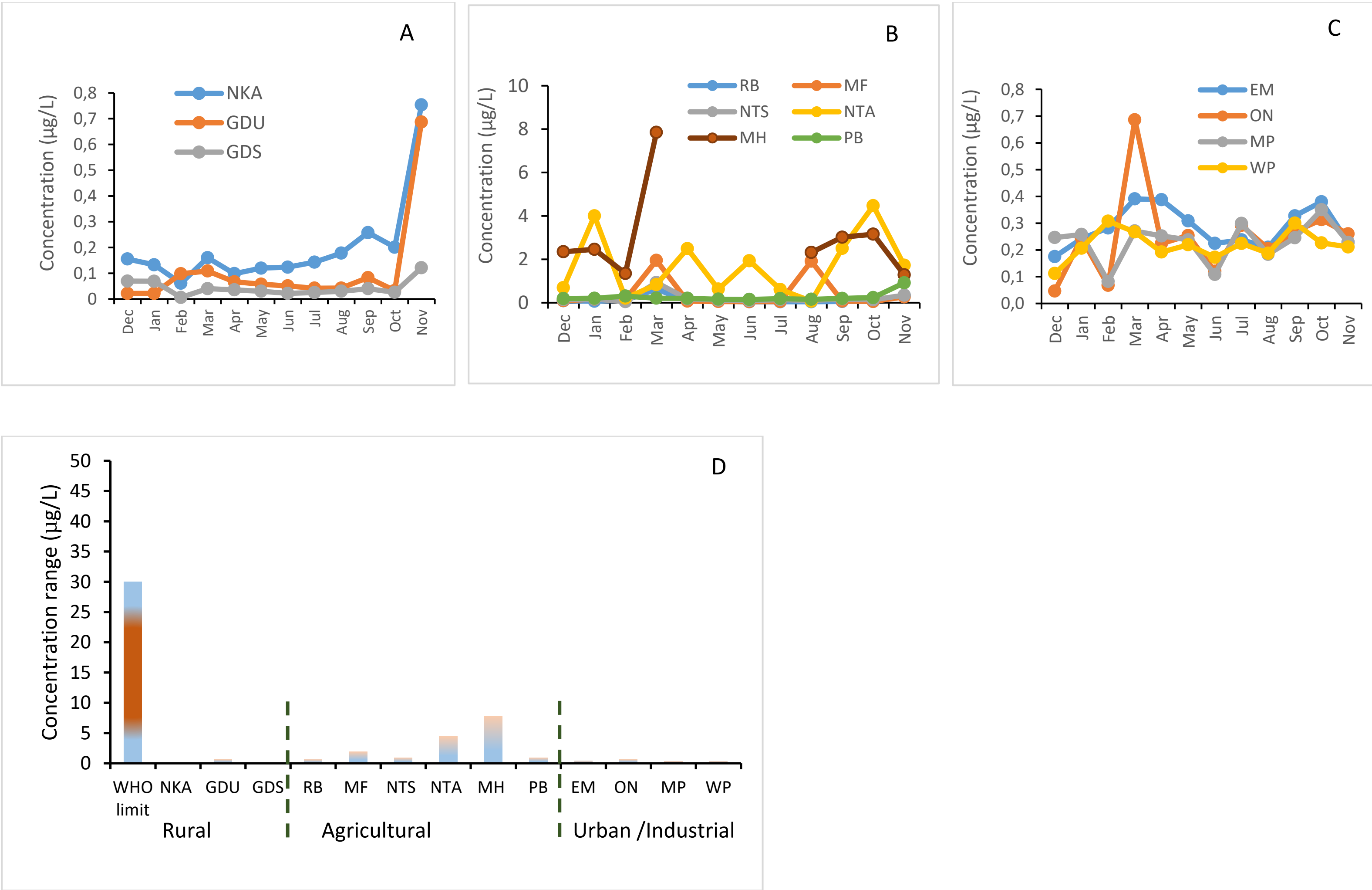

Figure 36: Concentration levels for uranium in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.10 Interrelationships between trace toxic elements

4.10.1 Rural areas

Figure 37 shows the interrelationship between toxic metals in the rural section. The As and U trends show a very strong interrelationship at the NKA site compared to other elements (Figure 37A). This behaviour was observed between Aug and Oct where there was an upward trend from these two elements (Figure 35A & 36A). Besides the fact that both As and U levels were low, this upward trend cannot be linked to any anthropogenic activity, as the area is rural. Cadmium was not interrelated to any metal element which could be attributed to the two spikes in June and October (Figure 32). Equally, the Cd levels at NKA were low and cannot be linked to any anthropogenic activity. At the GDU site, As and U trend still had a strong interrelationship, whilst Cd remained isolated and not related to any element (Figure 37B).

At the GDS site, there was a different picture on elemental interrelationships compared to NKA and GDU. The elements As and U were now not correlated, but Cd was now strongly interrelated to Cr (Figure 37C). The reason for the Cd and Cr correlationship is that there was a downward trend from January to August followed by a spike in September for both Cd and Cr, but that was not seen from other elements. A study conducted along Gangdese mountain reported a positive correlation among As (93.63%), Cr (93.07%), Mn (73.53%), Fe (59.54%), and Pb (58.28%) and were linked mainly to natural sources (Xing *et al.*, 2022).

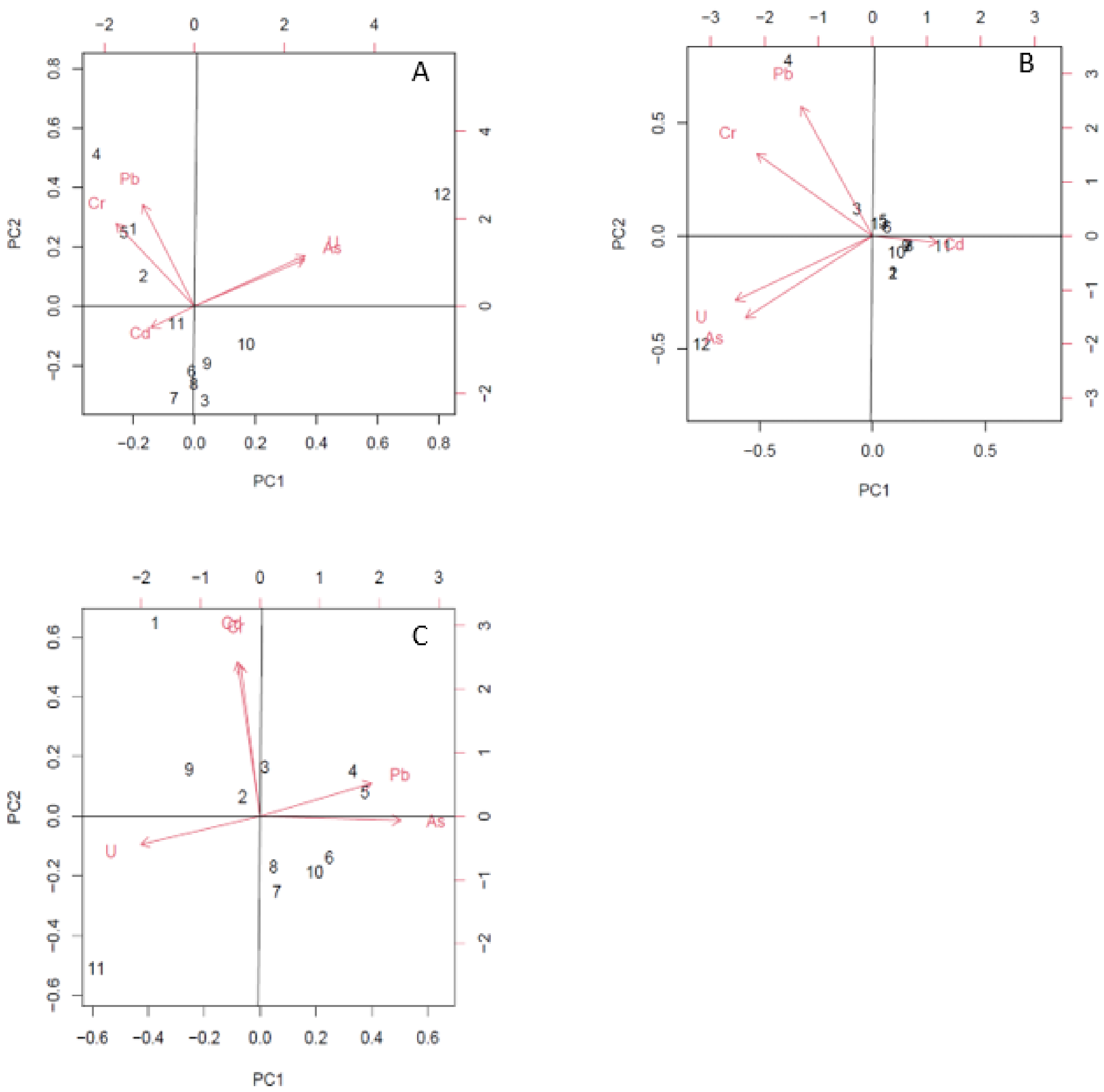

Figure 37: Trace toxic elemental biplot charts for uMhlathuze River in the rural areas (A- Nkandla (NKA); B - Gouderetrouw upstream (GDU); C - Gouderetrouw Dam surface (GDS

4.10.2 Agricultural areas

Figure 38 shows interrelationships between toxic elements within the agricultural area where the interrelationships between toxic elements had a different picture as compared with rural segment. Cadmium was now interrelated with U (Figure 38A), but the relationship was not strong. The correlationship between Cd and U occurred due to the single spikes that occurred for the metals in March (Figure 32B & 36B). At RB site, there was a correlationship between

Pb and Cr. In February and May, there were two spikes for both Pb and Cr, but the Pb spike for May was high and exceeded WHO guideline limits (Figure 33B & 34B). Reasons could be due to agricultural activities around this site. The As metal was not correlated with any element due to its levels being very low compared to other metals. At MF site, there was still a correlationship between the Cd and U trends but the relationship was not so strong. Instead, the strong interrelationship was now between the Cd and As (Figure 38B). In March as well as November, there were spikes for both Cd and As at the MF site hence the correlationship (Figure 32B & 35B). The Cd and As levels were low and within guideline limits, hence these spikes cannot be linked to any activity from this site. The same correlationship reported for Pb and Cr trends at RB site was also observed at the MF site. The correlationship reported between Cd, As and U trends as well as the one between Pb and Cr was still observed at NTS and NTA sites (Figure 38C & D). However, at the NTA site, Cd and As were correlated to each other while U was not correlated to any metal. Reason for U not correlated to any metals was due to its inconsistent trend throughout the seasons. At the MH site, another correlation developed, and was different from other sites within agricultural area. Lead was not correlated to any metal (Figure 38E). This was due to three Pb spikes observed in December, March and October (Figure 34B).

The last site within this area was P32 bridge (PB). At this site, only Cd was not correlated to any metal (Figure 38F). The Cd levels were very low compared to other elements. Uranium which was strong and positively correlation with Pb was reported at Ili and Tekes River, and the reasons provided were due to coal mining (Dong *et al.*, 2021). Another study in a river impacted by agricultural, mining and quarry activities as well as from natural processes revealed that Cr, Pb, and U were positively correlated (Yi *et al.*, 2020). A positive correlation between Cr and Ni was observed and correlation was associated with industrial discharges (Rajasekar *et al.*, 2024).

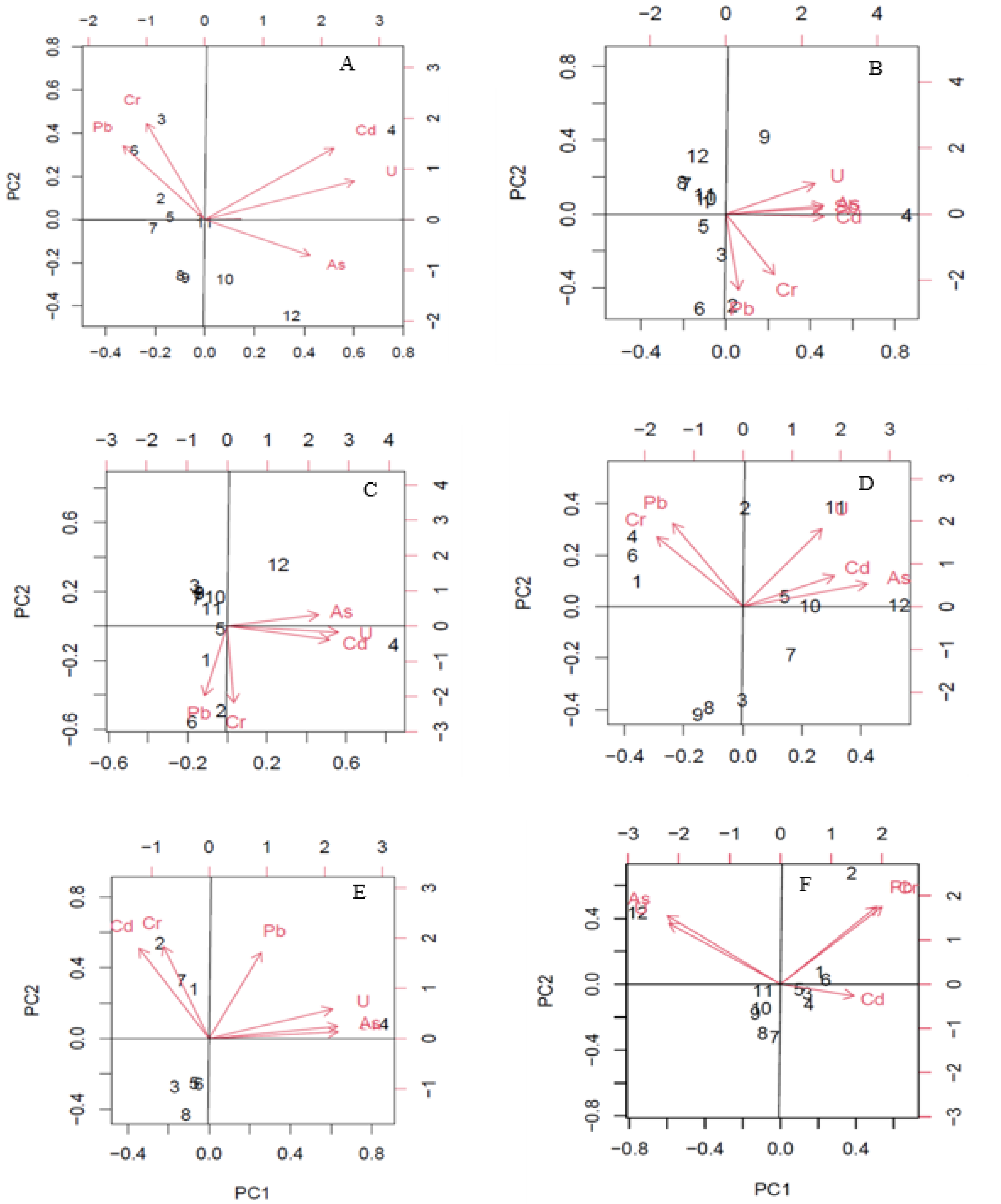

Figure 38: Trace toxic elemental biplot charts for uMhlathuze River in the agricultural areas (A-R66 bridge (RB); B - Mfule (MF); C - Ntshentshelo (NTS); D – Ntambanana (NTA); E – Mholweni (MH); F – P230 bridge (PB)

4.10.3 Urban and Industrial areas

Correlationship between toxic elements within the urban and industrial are represented in Figure 39. The Cd and As trends had a strong correlationship, and the rest were not correlated to each other (Figure 39A). This corelationship was caused by a spike in December observed for both Cd and As, and was not seen from the other metals. Although the levels for Cd and As were low and within guidelines, the spikes seen in December could have resulted from wastewater discharge or solid waste leachate from local municipality via Empangeni tributary (EM site). Positive correlation among Fe, Mn, As, Cd, Cr, Cu, Ni, Pb, and Zn was reported at Ekulu River impacted by coal field and solid waste disposal (Ifediegwu, Ozoko and Aganigbo, 2022). At the ON site, U was the only element which was not correlated with any element (Figure 39B). In March, there was a spike for U at this site, and no other spike for the rest of the year as compared to other elements (Figure 35C). The same behavior was also observed at MP site where U was the only element not correlated to any metal (Figure 39C).

At Weir pump station (WP site), there was a strong interrelationship between Cd and Pb (Figure 39D) and the rest of elements were not correlated to each other. This corelationship was strengthened by a spike which was observed in February, followed by other spikes around June and October (Figure 36C). Sahen conducted a study on heavy metals at Salda River where the PCA analysis revealed correlations among Fe, Mn, As, Cd, Cr, Cu, Ni and Pb (Sahen *et al.*, 2025).

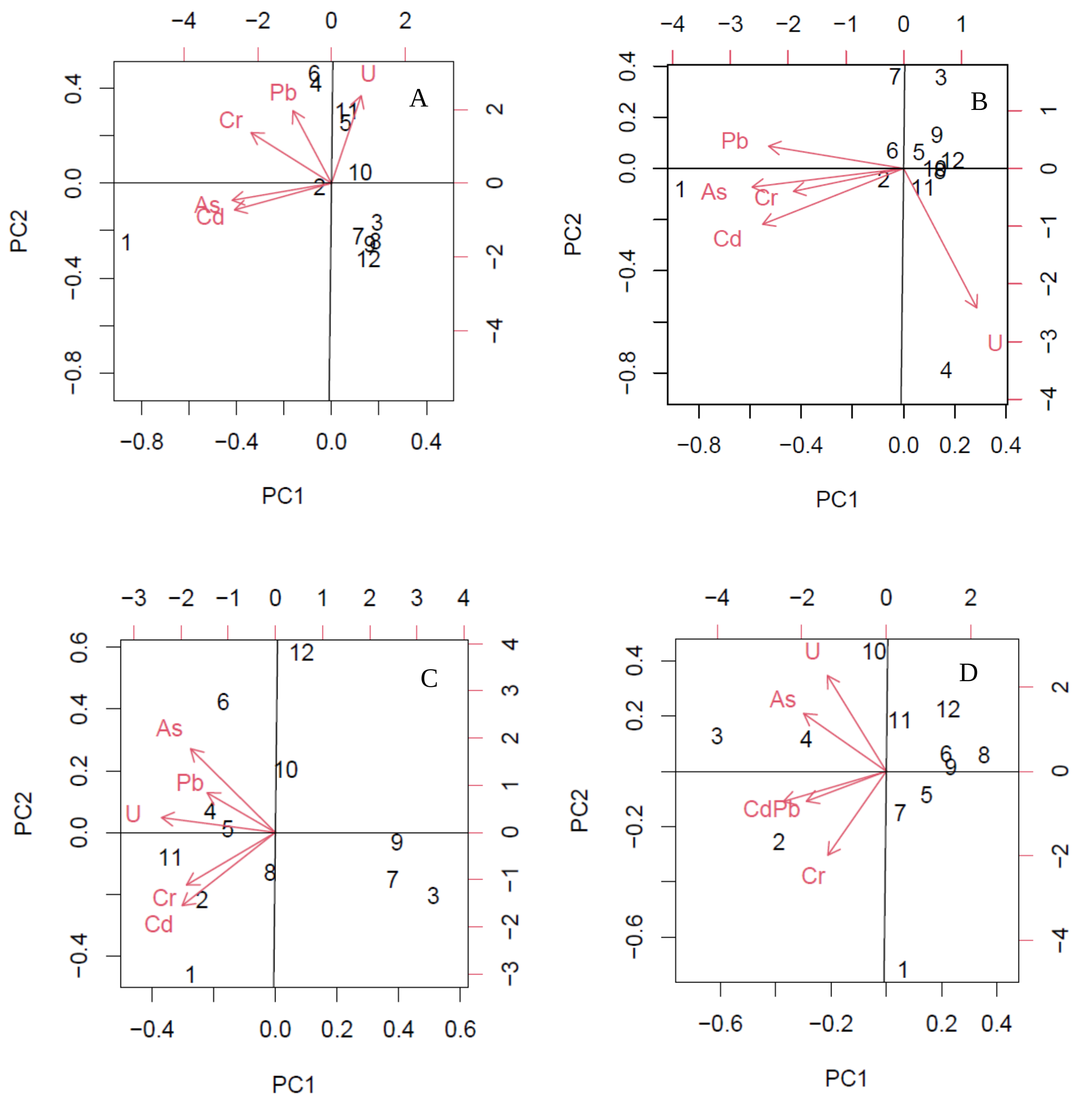

Figure 39: Trace toxic elemental biplot charts in the urban/industrial area (A- Empangeni (EM)); B- Ongoye (ON); C- Chemical industry (MP) and Weir Pumpstation (WP)

4.11 Other trace metals

Table 14 represents minimum, maximum and median values for other trace elements (excluding essential and toxic) over a period of 12 months. There are no guideline limits for Al but a health-based precautional value of 900 µg/L is recognized (WHO, 2017). It was observed that concentration levels of Al during the rainy season from (November - March) were consistently above this value except for Empangeni tributary (EM site) and the Weir Pumpstation (WP site) in the urban and agricultural region (Figure 40A, B & C). The high levels observed in the rural areas could not be linked to any anthropogenic activities (Figure 40A & D). Probably, during heavy rains leachable Al from the geology of Babanango and Nkandla may be washed into Umhlathuze River. Downstream of the river, Al could arise from agricultural, urban and industrial activities (Figure 40B & C). This was mentioned by Mthembu and colleagues in their study at the same river in 2012, where Al was reported in higher concentrations at the ON, MP and WP sites (Mthembu, Djarova and Basson, 2012). Locally, Al have been reported in extremely high levels of 1.172 - 29.094 mg/L (Edokpayi *et al.*, 2017).

.

Table 14: Minimum, maximum and median values for trace toxic elements over 12 months

Segment	Site	Aluminium (µg/L)			Barium (µg/L)			Boron (µg/L)			Strontium (µg/L)			Antomony (µg/L)			Selenium (µg/L)		
		Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median
Rural	NKA	3.2	2463	177	19.5	259	39.7	8.4	43.5	15.6	37.1	99	46.4	n.d	0.5	0.0	n.d	9.4	1.7
	GDU	4.5	1985	106	16.4	140	29.5	8.3	81	17.5	29.4	104	44.6	n.d	2.1	0.1	n.d	9.8	1.5
	GDS	33.7	1191	263	27.9	46.6	37.9	14.7	24.1	18.8	36.5	54	46.5	n.d	0.4	0.0	n.d	8.4	1.7
Agricultural	RB	2.5	1318	201	0.6	66	41.0	3.6	56	21.3	0.7	100	52	n.d	0.4	0.1	n.d	8.0	0.8
	MF	n.d	1173	77	1.9	128	50	n.d	171	29.2	2.0	309	42.4	n.d	1.8	0.1	n.d	9.8	1.5
	NTS	n.d	1357	126	0.9	92	43.0	n.d	55	32	0.9	86	66	n.d	0.8	0.1	0.2	13.8	1.1
	NTA	n.d	2033	221	38.1	281	128	24.3	216	190	40.0	435	250	n.d	3.5	0.2	n.d	20.7	0.8
	MH	n.d	1836	51	8.8	233	119	n.d	228	196	8.8	823	567	n.d	7.4	0.2	n.d	19.4	1.1
	PB	32.7	1713	395	34.2	168	47.9	28.6	80	36.6	58.7	147	72	n.d	0.8	0.1	n.d	26.6	2.3
Urban and industrial	EM	5.3	695	250	n.d	92	65	63.5	83	70	1.2	179	129	n.d	1.2	0.2	n.d	27.8	0.8
	ON	2.3	1892	220	n.d	77	50	2.8	69	42.1	0.9	117	83	n.d	0.6	0.1	0.4	23.2	1.6
	MP	7.8	2206	297	36.7	78	61	34.9	72	43.1	53.1	121	88	n.d	0.2	0.1	n.d	27.9	1.4
	WP	n.d	436	139	0.6	72	47.6	4.3	55	41.4	n.d	134	79	n.d	1.4	0.1	n.d	26.7	1.5
WHO guidelines					1300			2400			4000			20			40		

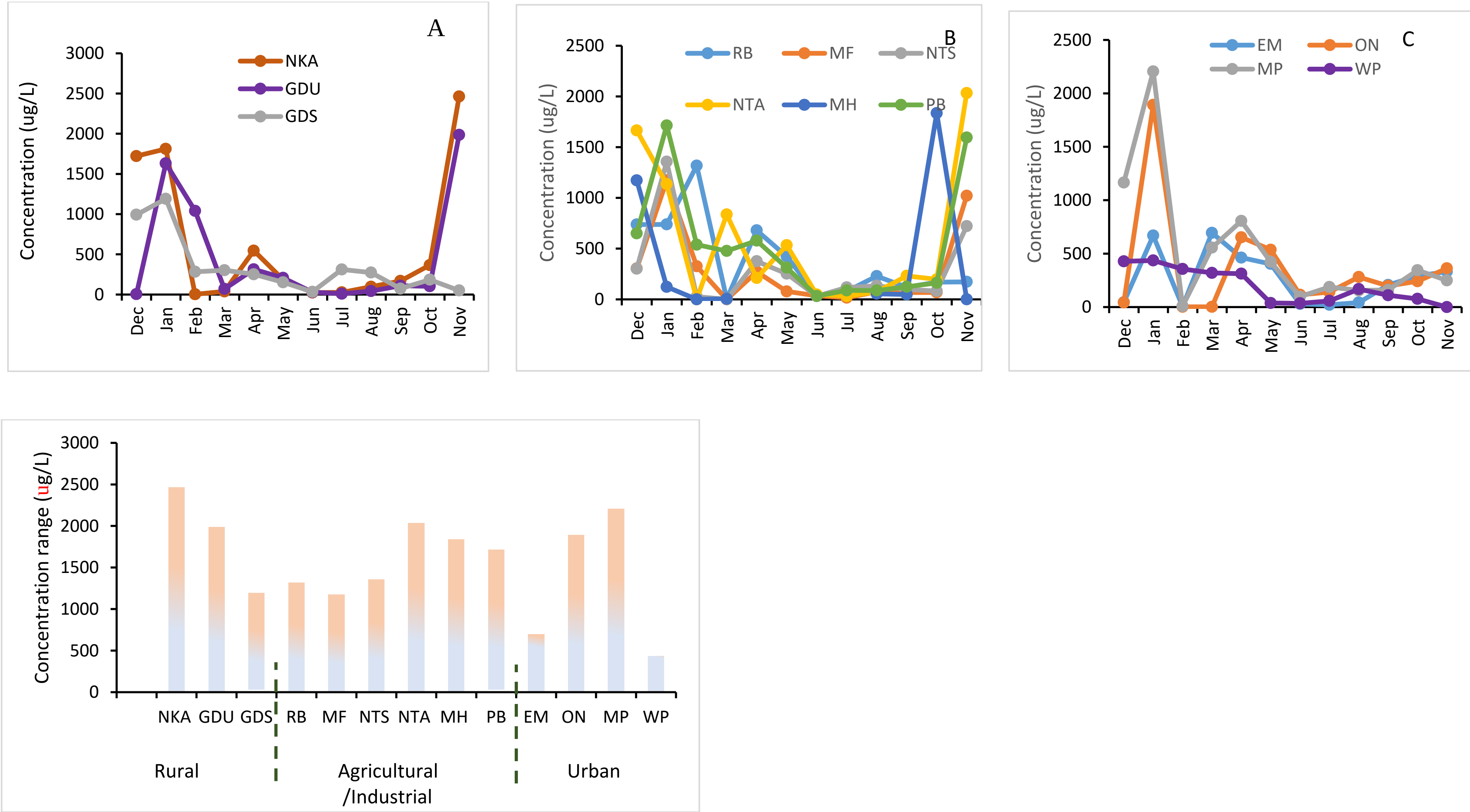

Figure 40: Concentration levels for aluminium in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

Boron concentration levels were within WHO guideline limits throughout the year (Figure 41A-D). It was observed that at the rural and urban areas, B were below 80 µg/L levels (Figure 41A & C). The B levels at Ntambanana and Mholweni tributaries were above 200 µg/L during the wet seasons (Figure 41B). This behavior can be linked to quarry mining and agricultural activities from MH and NTA sites respectively. A spike experienced at MF site in August cannot be explained (Figure 41B). Boron concentration levels from 280 to 1850 µg/L were reported in parts of Iraq and the reason provided were due to geological area of that region (Algrifi and Salman, 2022). Higher concentration levels of B up to 742 µg/L were reported around boron mines in Turkey where the mines were considered to be the cause for the contamination of water, soil and plants in that region (Sasmaz, Senel and Obek, 2021).

Barium concentration levels were within WHO guideline limits from all sites (Figure 42D). Two spikes above 250 µg/L were observed at NKA and NTA sites (Figure 42A & B) during a wet season. The spike from NKA cannot be linked to any activity, whereas levels from NTA could arise from agricultural activities. Barium levels were below 100 µg/L in the urban and industrial area (Figure 42C). Other studies reported Ba levels which exceeded WHO guidelines in Oban Massif and reasons given were due to agricultural and quarry activities in the area (Sikakwe and Ilaumo, 2021).

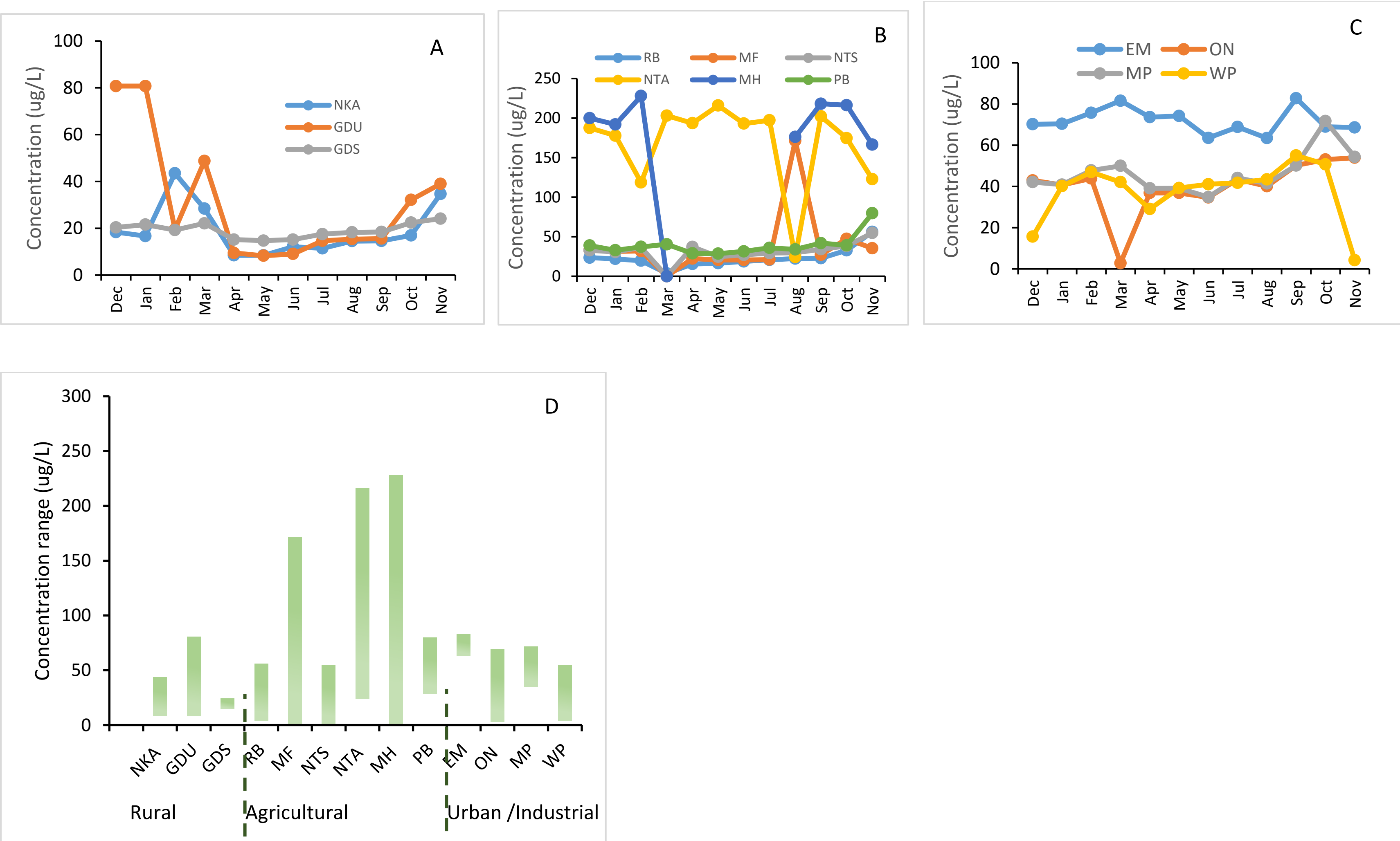

Figure 41: Concentration levels for boron in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

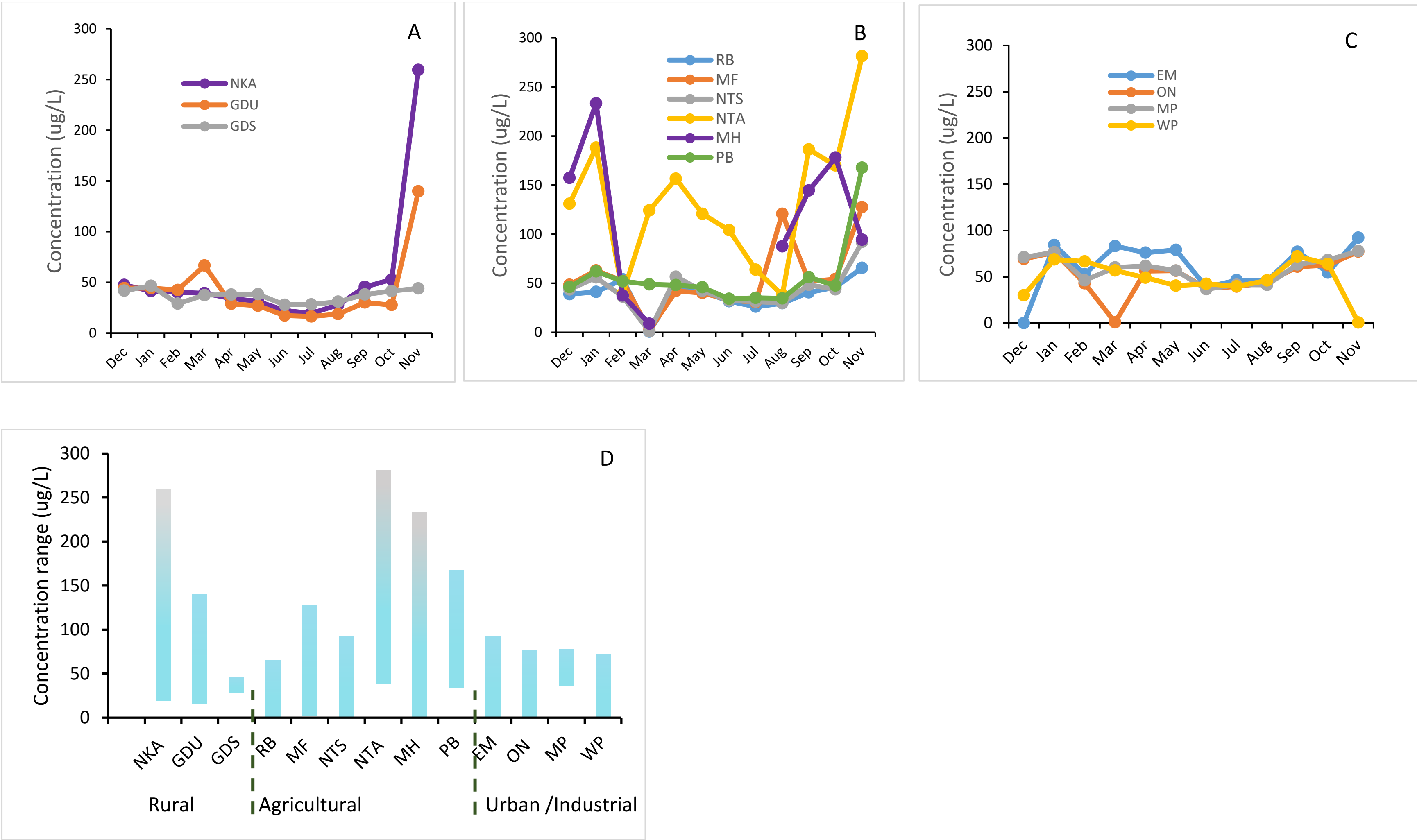

Figure 42: Concentration levels for barium in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

The Sr levels were within 100 µg L^{-1} for most parts of the year except for MH, NTA and EM sites which represent the tributaries to uMhlathuze River (Figure 43A-D). Few spikes above 400 µg L^{-1} were observed at tributaries of Mholweni (MH site) and Ntambanana (NTA site) during wet season (Figure 43B). These spikes can be linked to quarry mining and agricultural activities at MH and NTA sites respectively. Increased levels of Sr up to 500 µg/L have been reported elsewhere and the authors pointed wastewater discharge from mining and quarry activities as well as intrusion from sea water as sources (Malov *et al.*, 2022).

Another study which was conducted in China reported higher levels of Sr and reasons were related to wastewater discharge (Akob *et al.*, 2016; Yang *et al.*, 2023).

The Se levels were below WHO guideline limits throughout the year (Figure 44A-D). The few spikes ranging from of 20 to 30 µg/L were observed at agricultural and urban and industrial area during the wet season (Figure 44B & C). The levels at agricultural area can be linked to quarry mining operations at Mholweni tributary whilst agricultural activities can be a source at Ntambanana tributary. These levels may have impact on PB, ON and WP sites which are within uMhlathuze River, but are within guideline levels.

The Sb levels were mostly around 0.2 µg L^{-1} which is normal for natural unpolluted waters even though a few spikes up to 7.4 and 3.5 µg L^{-1} for MH and NTA sites, respectively were observed (Figure 45A-D). At the Mholweni tributary, a single spike of 8 µg/L in March can be linked to quarry mining activities in the area (Figure 45B). A study conducted at Sakarya River, Turkey reported Se and Sb levels which were low and within WHO guideline limits (Dundar and Altundag, 2018). Elevated Se and Sb levels were reported at floodplain area in Spain and the reasons provided were due to pollution from agricultural sources, uncontrolled fertilization and urban wastewater as sources (Jiménez-Ballesta *et al.*, 2017).

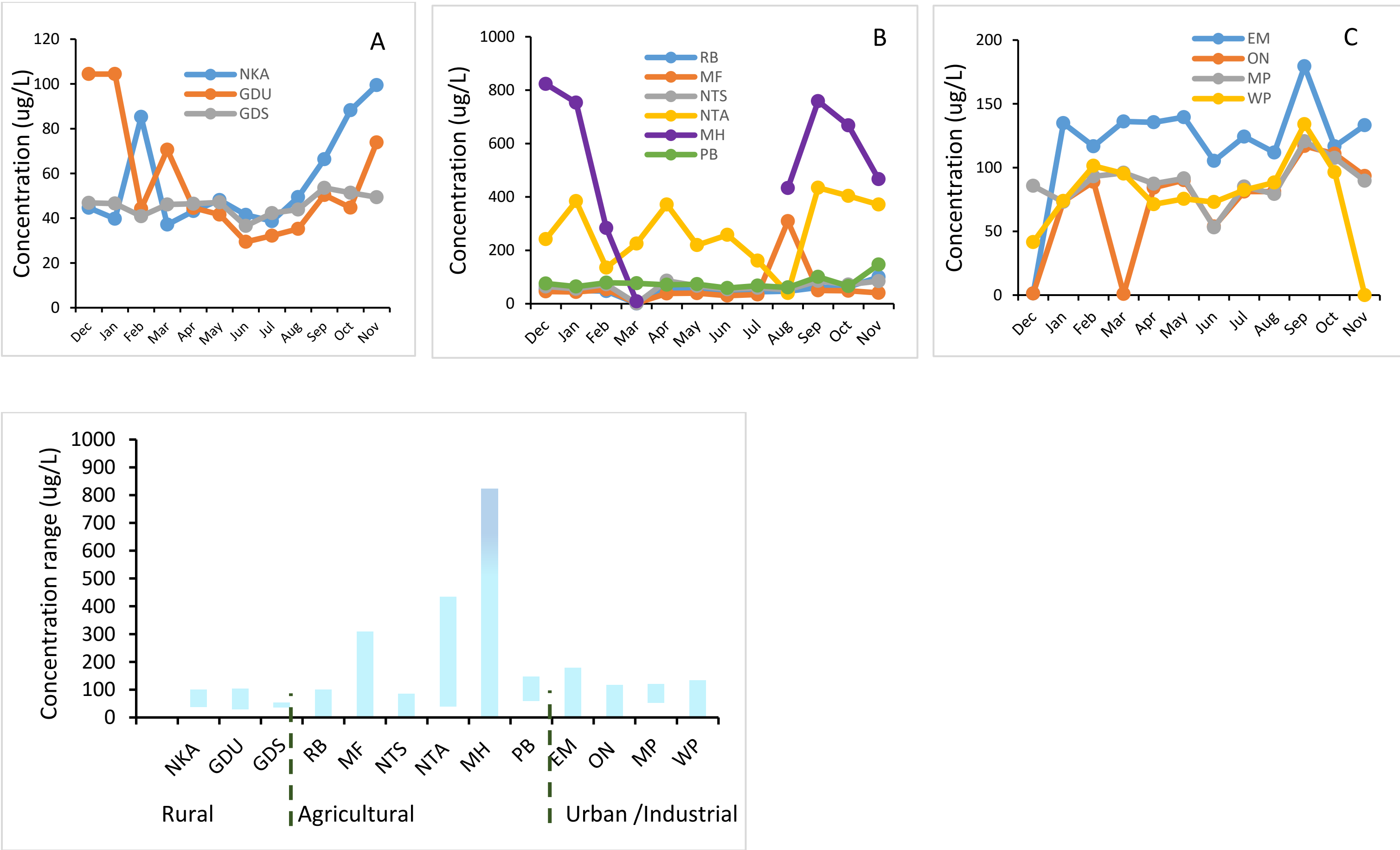

Figure 43: Concentration levels for strontium in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

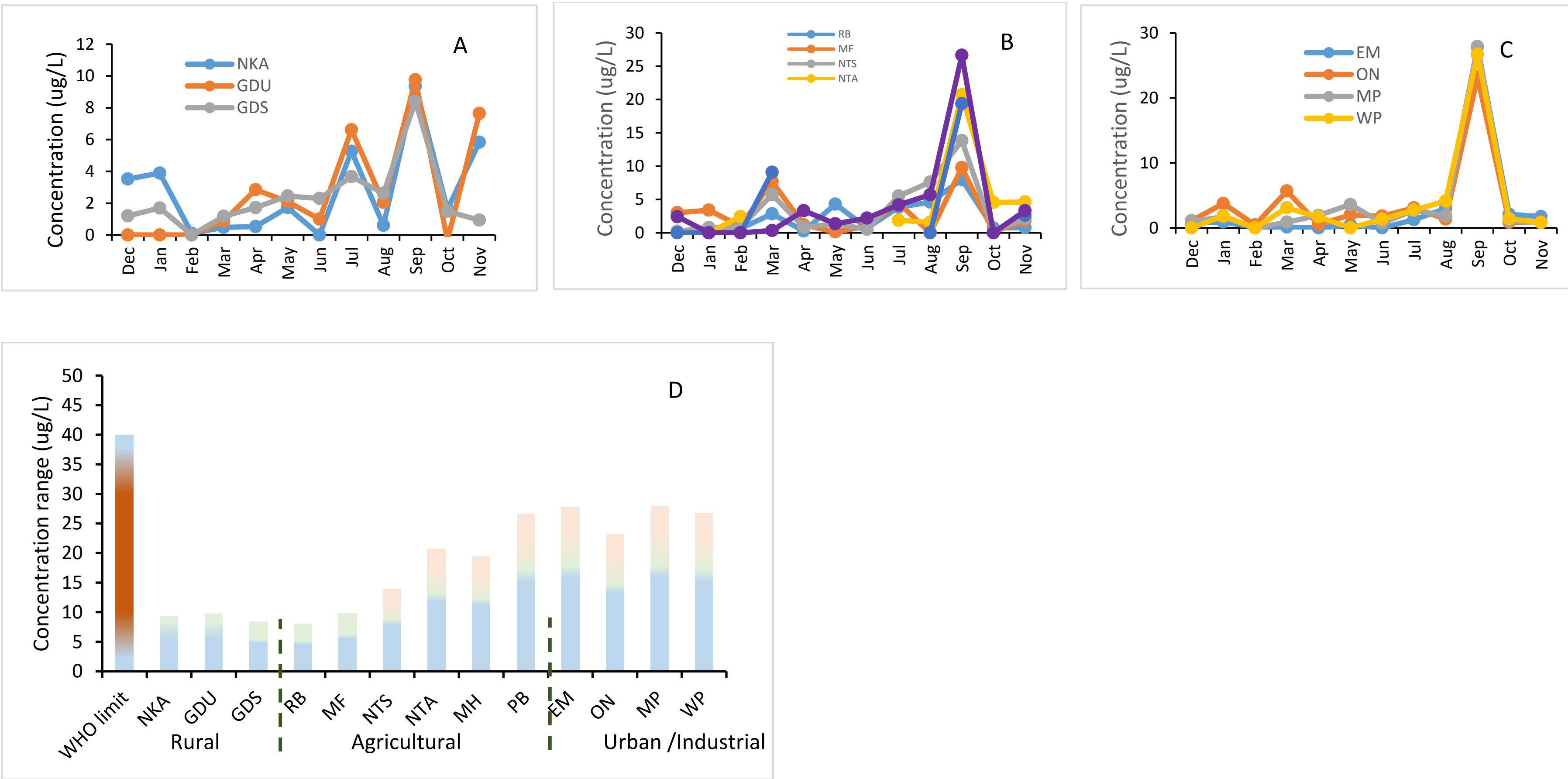

Figure 44: Concentration levels for selenium in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

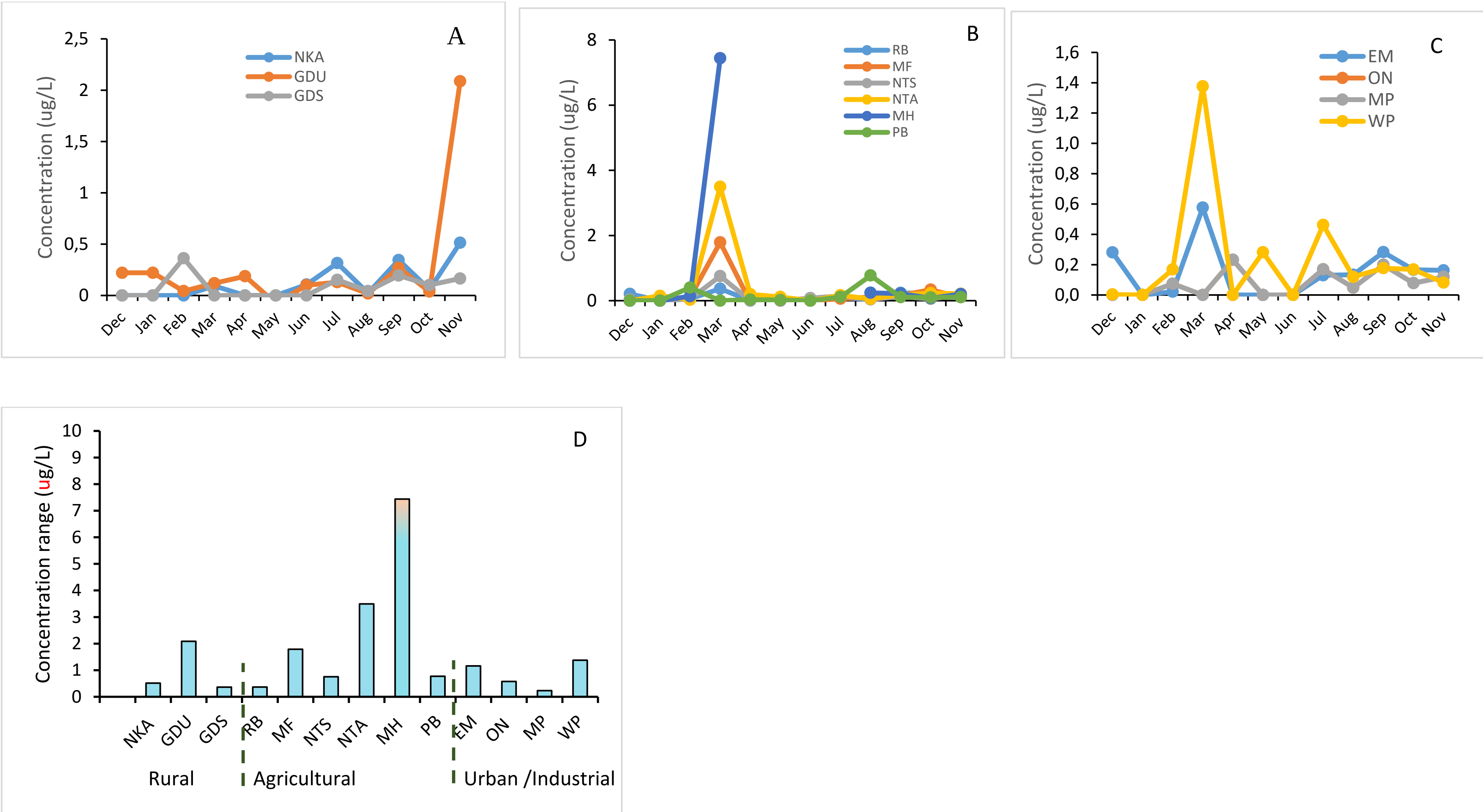

Figure 45: Concentration levels for antimony in rural areas (A), agricultural areas (B), urban /industrial area (C). D is the annual concentration range for each site

4.12 Interrelationship with principal component analysis for other trace metals

4.12.1 Rural areas

Figure 46 show the interrelationships between other trace metals in a rural area. The B and Sr trends were strongly correlated to each other in all three sites at the rural area during the wet season (Figure 46A, B & C). Another strong correlationship was between Al and Ba which occurred at NKA and GDU sites during wet season. The same pair was not correlated at GDS site due to dilution within the dam. These two elements could arise from geological area of Nkandla to Gouderetrouw dam. It was also noted that Al was not correlated to Se from all sites possible through their concentration levels. Positive correlation was observed between the elements Al and B at Coleroon River in an area with had rock formations (Chandrasekar *et al.*, 2021).

4.12.2 Agricultural areas

Figure 47 show the interrelationships between other trace metals in an agricultural area. The B and Sr were still correlated to each other at this segment and levels were notably increased on MH and NTA sites (Figure 48A-F). In contrast, Al and Ba were not correlated to each other at this segment except MH site as opposed to rural area. Other elements were not correlated to each other including a pair between Al and Se. A study conducted on fresh water sources reported a strong correlation among Al, B and Ba and the authors reported anthropogenic activities related to agricultural runoff as sources (Khan *et al.*, 2023).

4.12.3 Urban and Industrial areas

Figure 48 show the interrelationships between other trace metals in an urban and industrial area. The B and Sr trends were still correlated to each other as reported on rural and agricultural areas (Figure 48A-D). The correlationship that has been observed between Al and Ba except at MP site which still occurred at this segment during wet season as it has been reported at rural areas. Reason for the correlation between elements in this area could be related to urban runoff, wastewater discharge from municipal dumpsite as well as discharges from wastewater works.

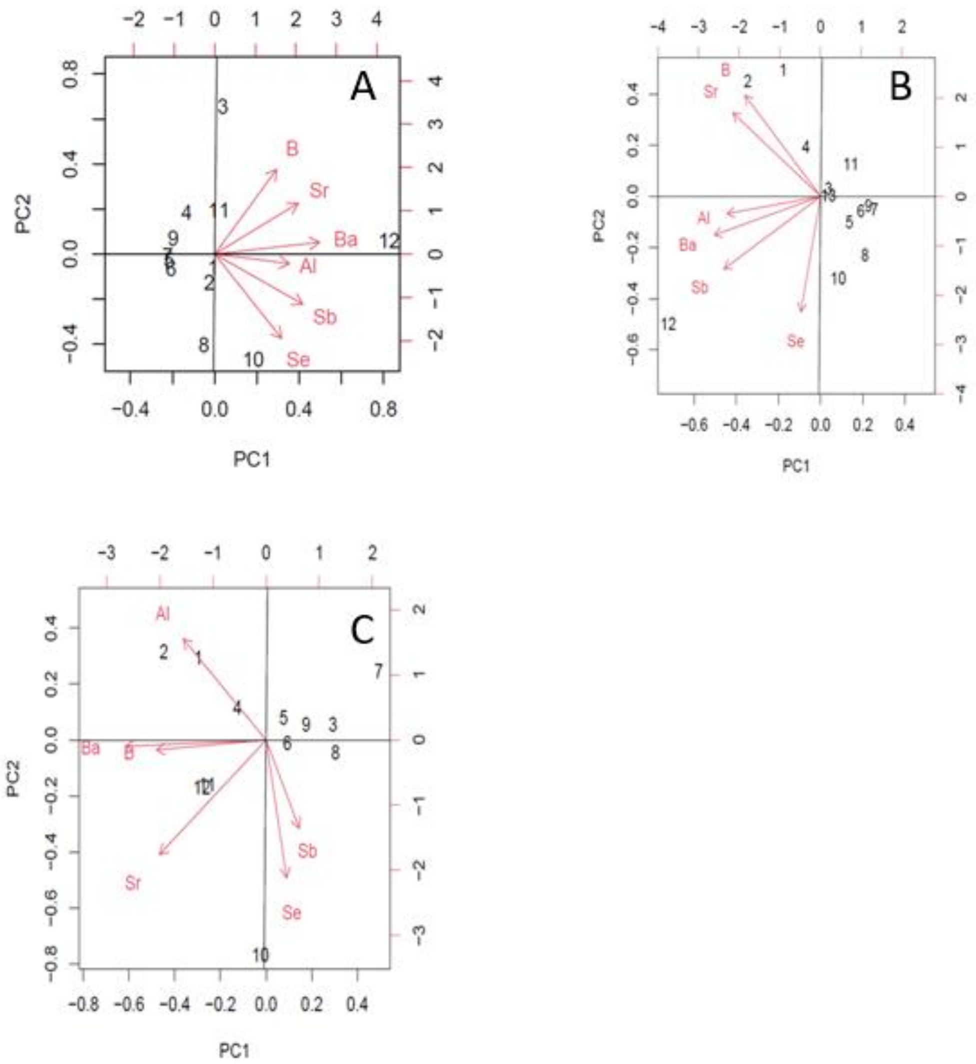

Figure 46: Other trace elemental biplot charts for uMhlathuze River in the rural areas (A- Nkandla (NKA); B - Gouderetrouw upstream (GDU); C - Gouderetrouw dam surface (GDS)

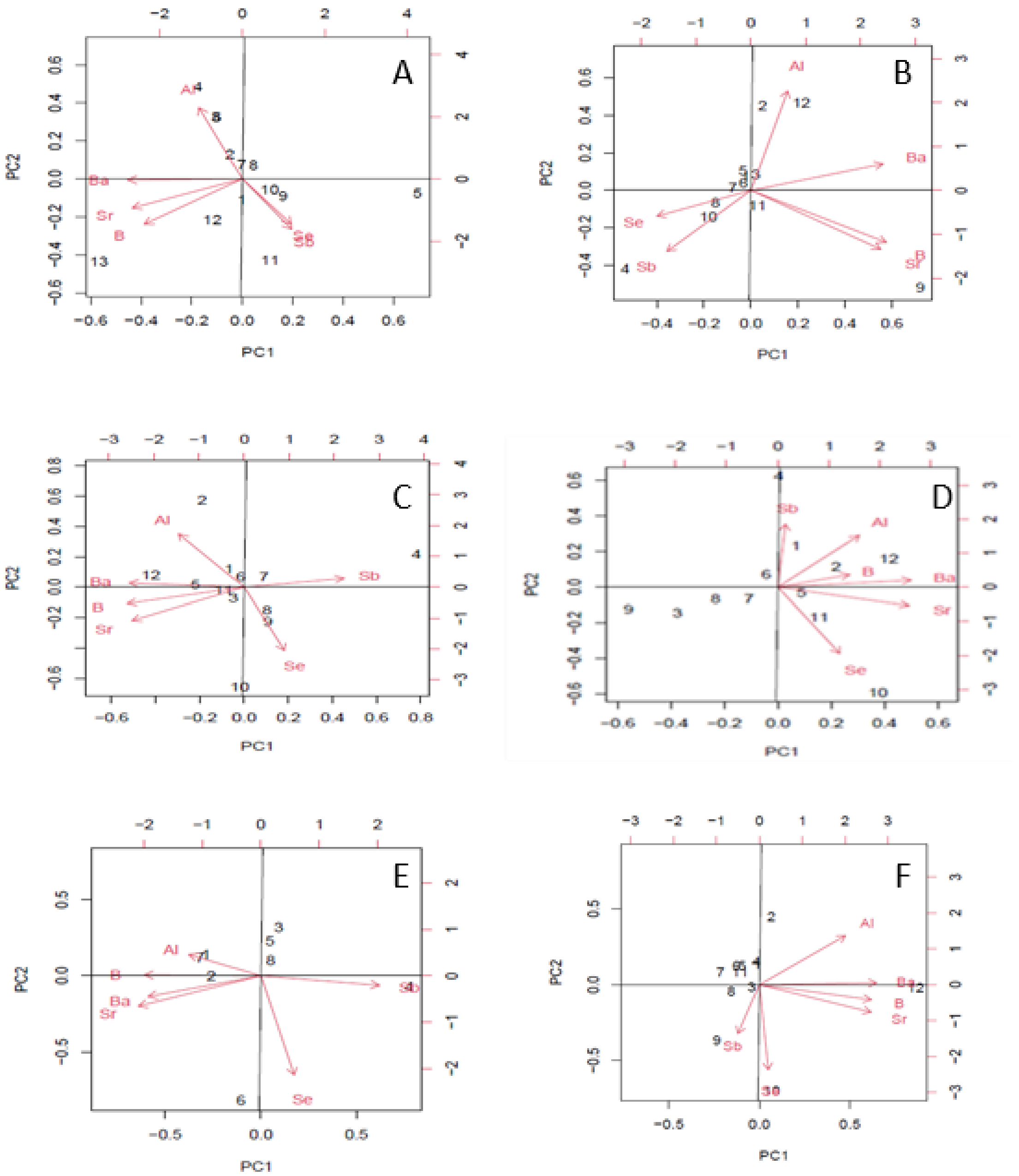

Figure 47: Other trace elemental biplot charts for uMhlathuze River in the agricultural areas (A-R66 bridge (RB); B - Mfule (MF); C - Ntshentshelo (NTS); D – Ntambanana (NTA); E – Mholweni (MH); F – P230 bridge (PB)

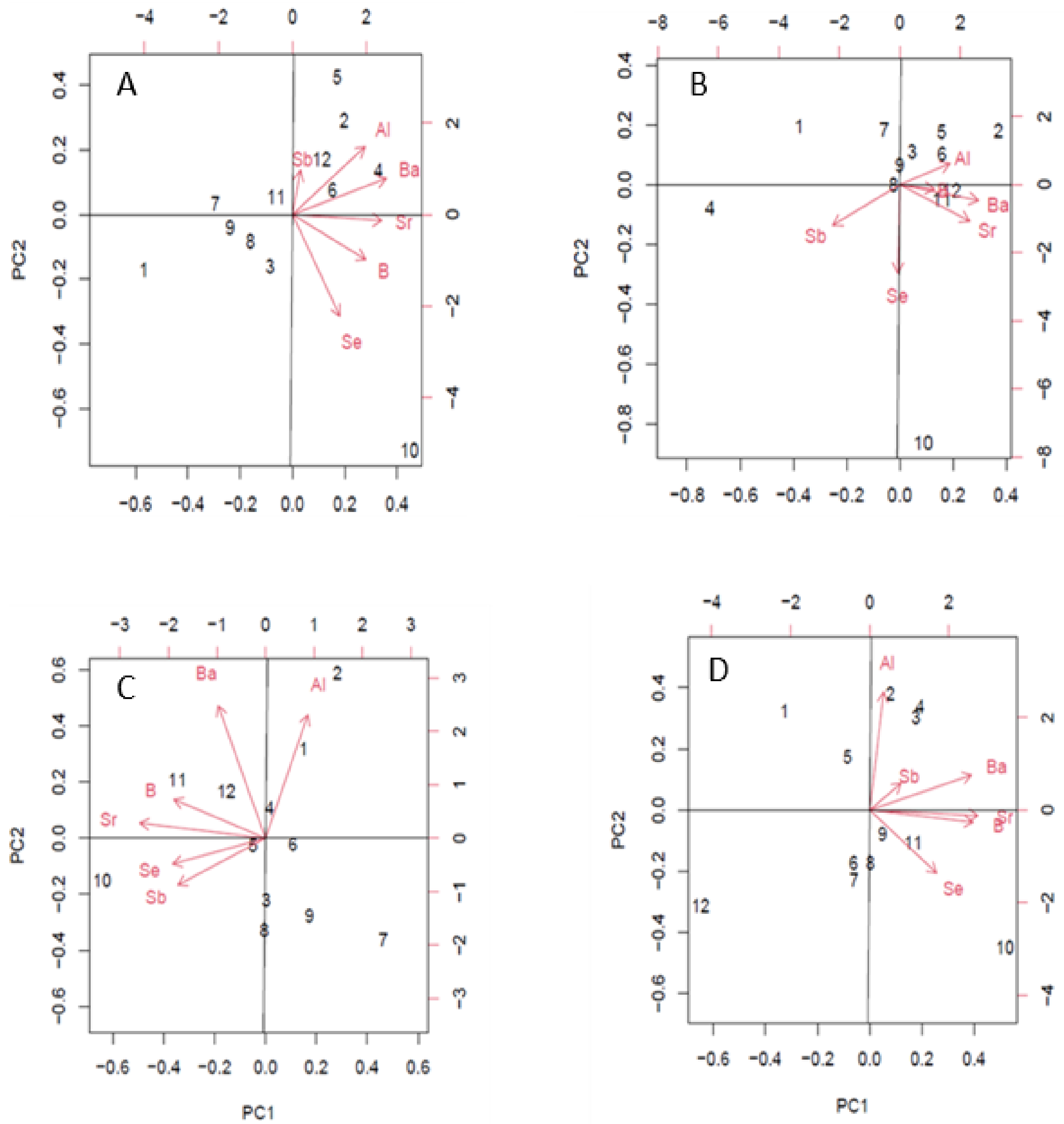

Figure 48: Other trace elemental biplot charts for uMhlathuze River in the urban/industrial area (A- Empangeni (EM)); B- Ongoye (ON); C- Chemical industry (MP) and Weir Pumpstation (WP)

4.13 Interrelationships for all trace elements

4.13.1 Rural areas

Figure 49 show the interrelationships between all trace elements for this study in a rural area. The following interrelationships of Pb-Zn, Cu-Co-Al-Ni-Fe, Mn-Ba-B-U-Sr as well as Se-Sb-Sr were strong at NKA site. The Cd was not correlated to any element at NKA and GDU sites. At GDU site, Cu-Zn-Cr-B-Sr were strongly correlated to each other. These relationships may indicate that the metal elements are coming from common source and similar behaviour in variation (Dhaliwal *et al.*, 2021). A strong interrelationships between metal elements among Fe–Zn, Zn–Pb, Pb–Cr, Cr–Zn, Fe–Cd, Zn–Cd and Cr–Cd were reported where the authors indicated that the elements may have originated from common input sources and have similar geochemical characteristics (Mishra *et al.*, 2018).

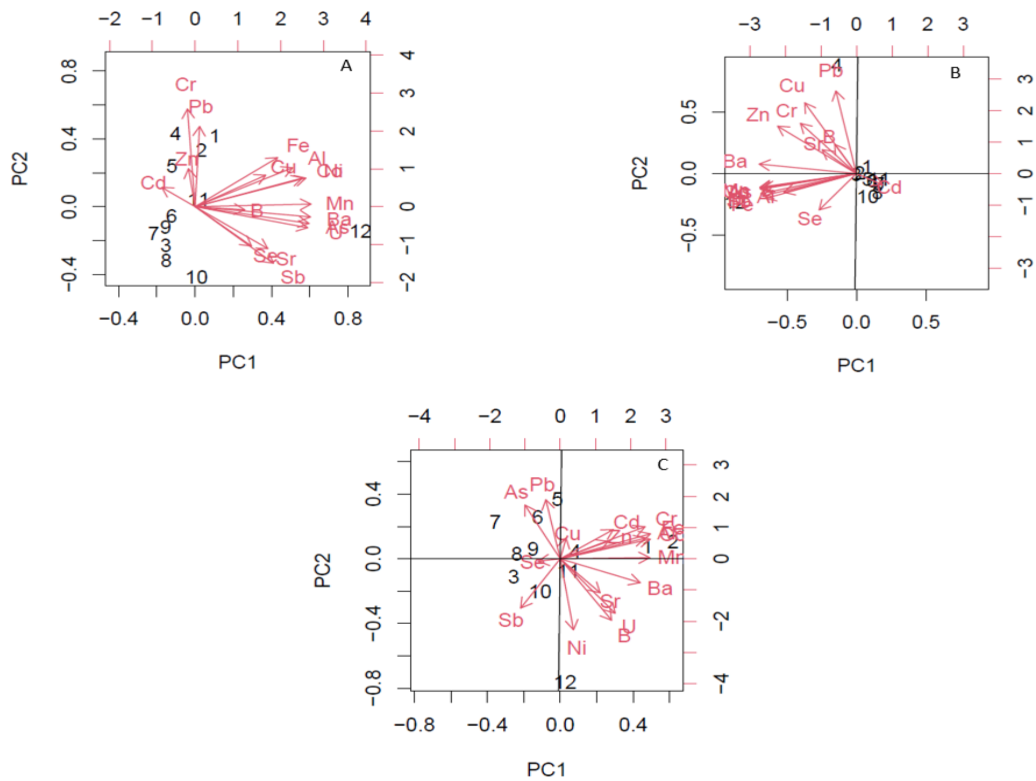

Figure 49: All trace elemental biplot charts for uMhlathuze River in the rural areas (A-Nkandla (NKA); B - Gouderetrouw upstream (GDU); C - Gouderetrouw dam surface (GDS

4.13.2 Agricultural areas

Figure 50 show the interrelationships between all trace metals in an agricultural area. The Al-Ni-Fe-Mn combination were strongly correlated to each other at RB site. At MF site, Cd-Sb, Co-Se, Ba-Ni & Se-B were correlated to each other. At NTS site, Al-Fe-Mn-Ni were correlated to each other. The Al-Fe correlationship was confirmed by increased levels of these elements during the wet season. At NTA site, Cr-Pb-Sb, Al-Fe, Zn-Cd-Ba and Co-Mn-Sb were correlated to each other and their relationship can be related to the geological area of Ntambanana tributary (NTA site) as well as agricultural runoff. At MH site, the correlation was among U-As-Sb, Al-Fe-Mn-Cr-Cd-Ba and Cu-Pb, which may be linked to quarry mining operations along Mholweni tributary. Previous studies have reported correlation between trace metals due to coal mining activities including quarry (Sahoo and Sahu, 2022) whilst some were linked to anthropogenic sources such as agricultural runoff (Dhaliwal *et al.*, 2021).

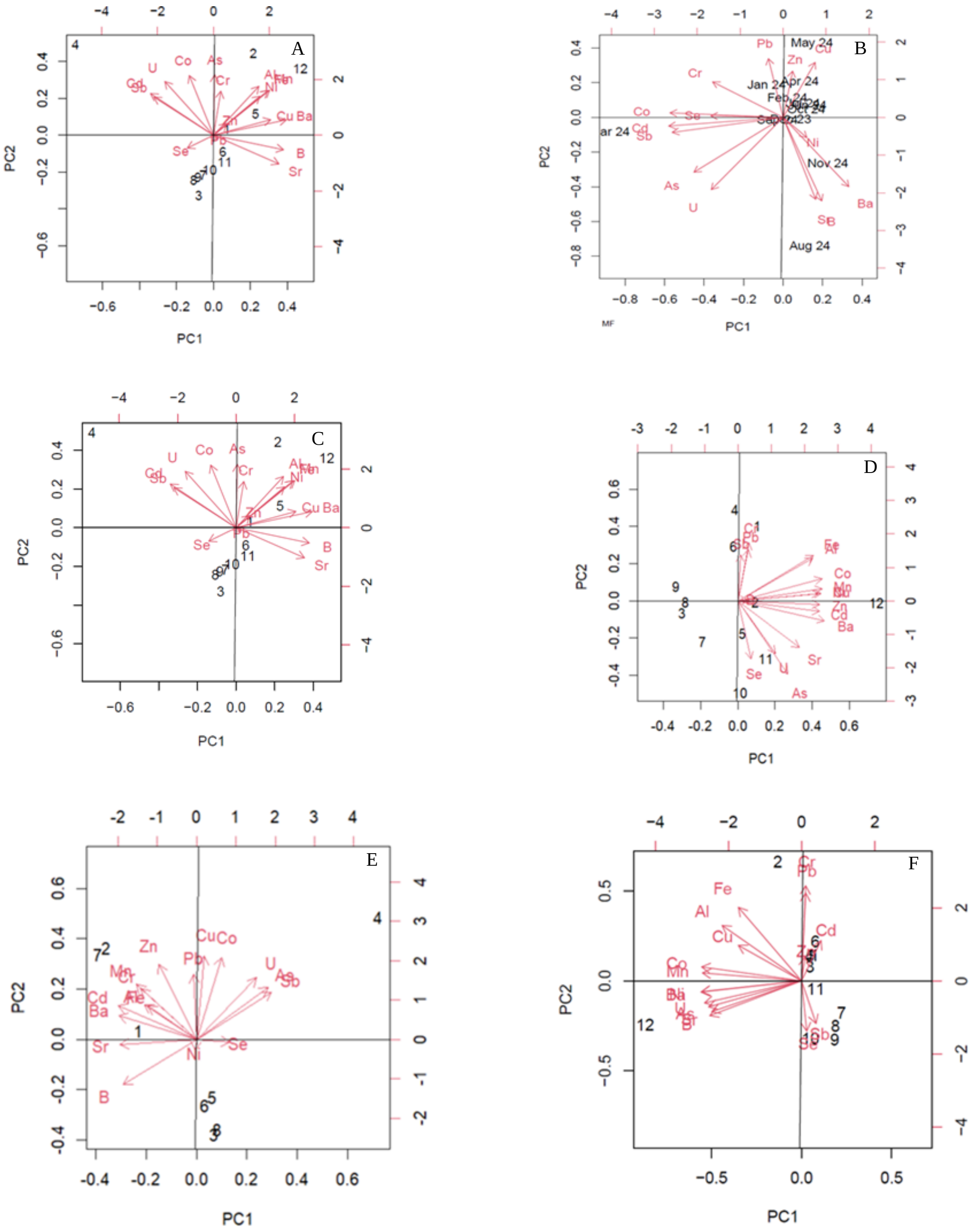

Figure 50: All trace elements biplot charts for uMhlathuze River in the agricultural areas (A- R66 bridge (RB); B - Mfule (MF); C - Ntshentshelo (NTS); D – Ntambanana (NTA); E – Mholweni (MH); F – P230 bridge (PB)

4.13.3 Urban and Industrial areas

Figure 50 show the interrelationships between all trace metals in an urban and industrial area. At the Empangeni tributary (EM) site, the following interrelationships among Al-Fe-Mn-Ni-B, As-Cd, ON site Al-Fe-Mn-Ni-Co and AS-Zn-Cd were observed. The Sb, Sr, Ba were not correlated to any element. At MP site, Se-Sb, B-Sr, As-Ni, U-Ba, Cu-Fe and Al-Co-Cr-Pb were correlated to each other. The WP site has interrelationships of U-Sb, As-Ba, Al-Cr and Co-Cd-Ni-Mn-Zn-Fe. Unlike the macro elements, the observation about trace elements maximizing during the rainy season suggests that the rains accumulate the trace elements into the river as part of surface runoff. Within this group, there were various definite clusters that showed close correlations between certain trace metals.

Correlation analysis among Cu-Ni, Cu-Cr, Fe-Cr , Fe-Cu & Ni-Cr been studied at Yamuna River where it was reported that the correlation was due to the industrial effluents, toxic waste from processing units, untreated domestic sewage discharges as main source (Asim and Nageswara Rao, 2021).

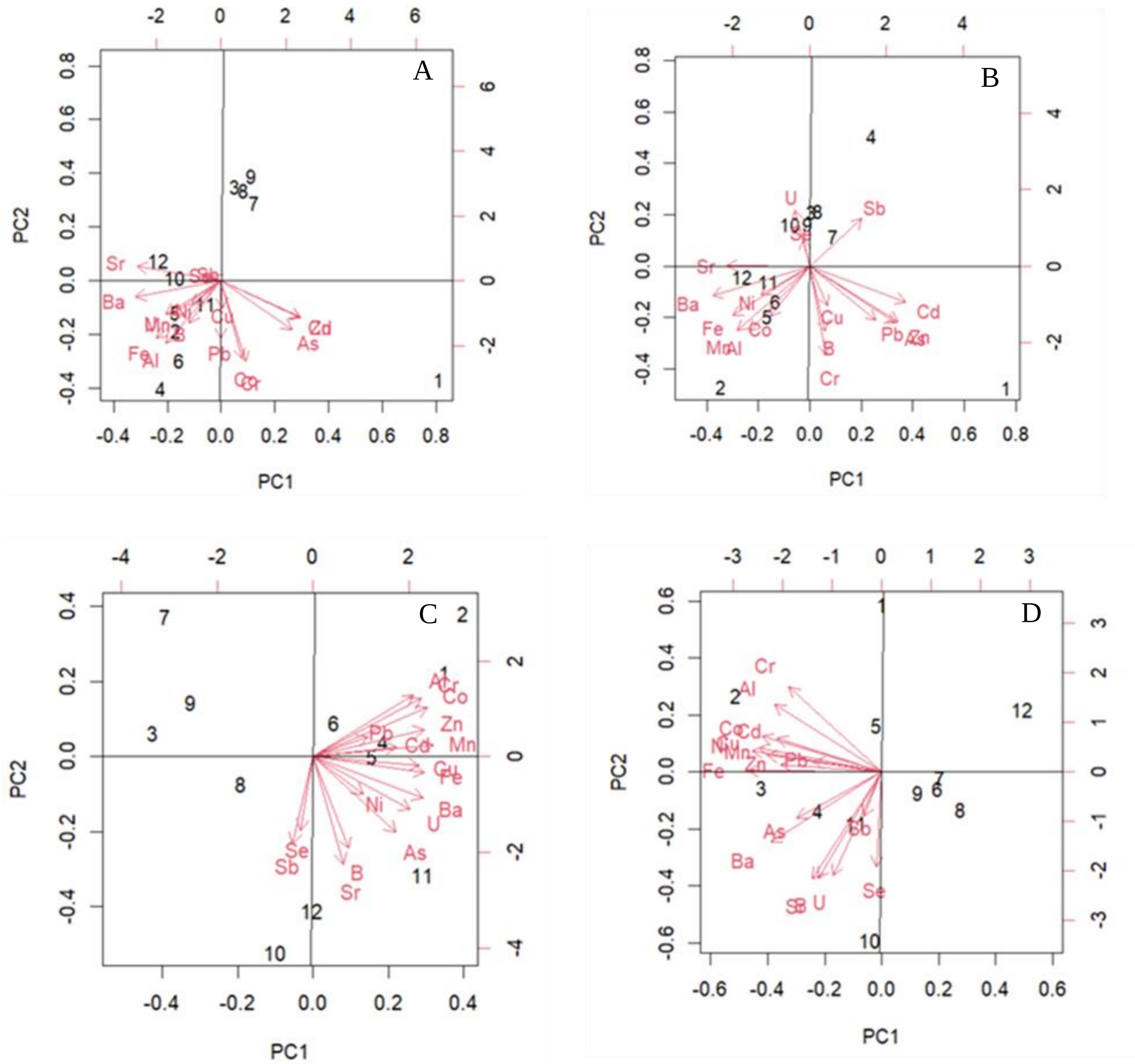

Figure 51: All trace elements biplot charts for uMhlathuze River in the urban/industrial area (A- Empangeni (EM)); B- Ongoye (ON); C- Chemical industry (MP) and Weir Pumpstation (WP)

4.14 Human health risk assessment

4.14.1 Water Quality Index (WQI)

Table 15 represents WQI for uMhlathuze River in rural, agricultural, urban and industrial areas. The parameters used for WQI calculation are presented at Table 16. Most of the sites had WQI<20 (Figure 52) and therefore were rated in the excellent category. Besides elevated concentration levels for physicochemical parameters as well as those from macro elements, the WQI values for NTA, MH and EM sites were still acceptable and rated as good.

Table 15: WQI values along uMhlathuze River from December 2023 to November 2024

Segment	Site	WQI	Grading	Rating
Rural area	NKA	18.8	A	Excellent
	GDU	15.8	A	Excellent
	GDS	10.7	A	Excellent
Agricultural area	RB	15.6	A	Excellent
	MF	17.8	A	Excellent
	NTS	15.4	A	Excellent
	NTA	30.2	B	Good
	MH	36.1	B	Good
	PB	20.2	A	Excellent
Urban and Industrial area	EM	26	B	Good
	ON	20.4	A	Excellent
	MP	18.1	A	Excellent
	WP	18.7	A	Excellent

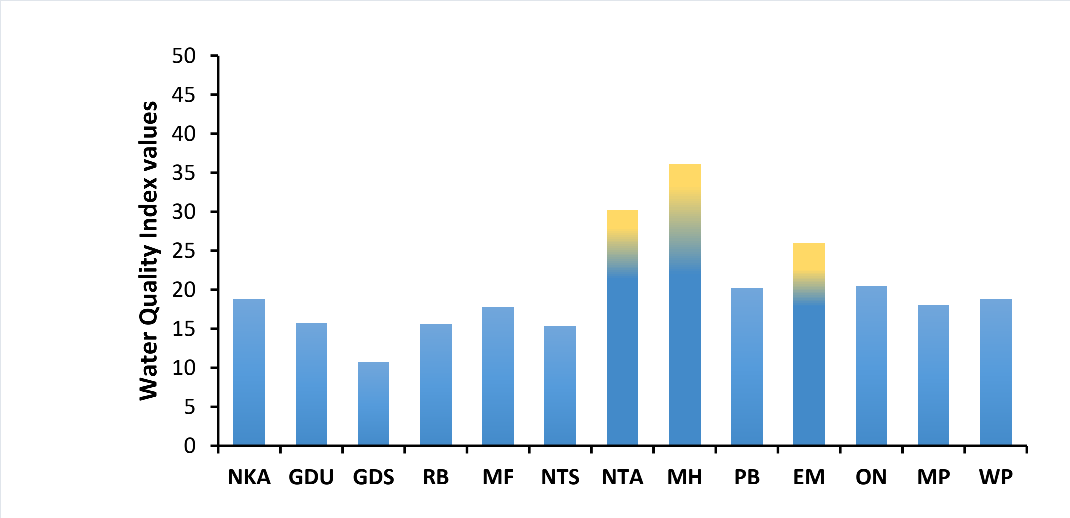

Figure 52: Graphical representation of WQI for uMhlathuze River from December 2023 to November 2024

Table 16: Average physicochemical parameters for uMhlathuze River in rural, agricultural and urban and industrial areas used to calculate WQI

	Levels in Rural area			Levels in Agricultural area						Levels in Urban/Industrial area			
Parameter	NKA	GDU	GDS	RB	MF	NTS	NTA	MH	PB	EM	ON	MP	WP
pH	7.60	7.39	7.43	7.44	7.74	7.48	8.08	8.00	7.64	7.53	7.54	7.52	6.98
Cond (mS/m)	16.8	15.6	14.8	18.6	25.2	24.0	181	130	31.9	69	35.8	37.2	37.1
TOC (mg/L)	4.88	4.41	2.94	3.53	4.11	3.73	12.88	8.95	3.90	9.98	6.34	4.88	4.52
Chloride (mg/L)	12.7	14.6	17.6	19.6	40.4	31.7	288	386	42.6	105	51.8	52.0	58.7
Fluoride (mg/L)	0.29	0.33	0.15	0.34	0.31	0.30	0.30	0.43	0.38	0.36	0.34	0.34	0.43
Nitrate (mg/L)	0.22	0.26	0.26	0.31	0.28	0.35	1.18	3.65	0.33	0.45	0.31	0.33	0.33
Sulphate (mg/L)	3.83	4.23	0.04	6.11	6.08	8.06	40.0	149	8.95	24.4	10.7	10.7	14.1
Ammonia(mg/L)	0.19	0.08	0.09	0.06	0.11	0.07	0.09	0.09	0.15	0.20	0.15	0.08	0.13
Na (mg/L)	14.4	13.6	14.9	19.3	27.9	26.4	310	331	36.4	90	41.3	42.6	41.6
K (mg/L)	1.10	1.39	1.76	1.90	2.09	2.01	3.43	2.62	2.03	5.49	2.44	2.73	2.75
Mg (mg/L)	6.37	4.50	5.58	5.58	5.90	7.08	41.5	80	8.45	17.8	10.1	10.2	9.99
Ca (mg/L)	7.79	6.07	5.94	7.15	6.95	8.47	38.3	70	9.54	19.5	11.4	11.7	11.4
WQI Value	18.8	15.8	10.7	15.6	17.8	15.4	30.2	36.1	20.2	26	20.4	18.1	18.7
Grading	A	A	A	A	A	A	B	B	A	B	A	A	A
Rating	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Good	Excellent	Good	Excellent	Excellent	Excellent

4.14.2 Heavy metal Pollution Indices

The HPI values calculated based on trace toxic metal concentrations are also summarized in Table 17. Overall HPI values were very low for all sites (Figure 53) implying that the anthropogenic activities including agricultural and industrial development had minimal potential to cause pollution concerns due to toxic metals on uMhlathuze River. WQI and HI on river water samples been reported elsewhere (Al-Hejuje, Hussain and Al-Saad, 2017; Gupta *et al.*, 2023; Ikpi *et al.*, 2024).

Table 17: Toxic elemental results with HPI calculation

Site	NKA	GDU	GDS	RB	MF	NTS	NTA	MH	PB	EM	ON	MP	WP
As	0.47	0.51	0.45	0.49	0.95	0.63	1.27	1.46	0.67	1.69	1.14	0.73	0.67
Cd	n.d	n.d	0.00	0.04	0.14	0.07	0.03	n.d	n.d	0.11	0.21	0.00	n.d
Cr	2.01	1.17	0.39	0.68	0.53	0.54	0.73	2.41	0.85	1.18	1.23	1.40	0.65
Pb	2.26	6.51	1.62	3.02	1.41	1.62	1.32	2.69	2.13	1.21	1.76	2.96	1.38
Hg	n.d	0.07	n.d	n.d	n.d	0.02	0.02	n.d	n.d	0.40	0.03	n.d	n.d
U	0.20	0.11	0.04	0.13	0.41	0.21	1.68	2.97	0.26	0.28	0.25	0.23	0.22
HPI	6	9	5	6	8	6	7	9	6	9	10	6	7
Limit	100	100	100	100	100	100	100	100	100	100	100	100	100

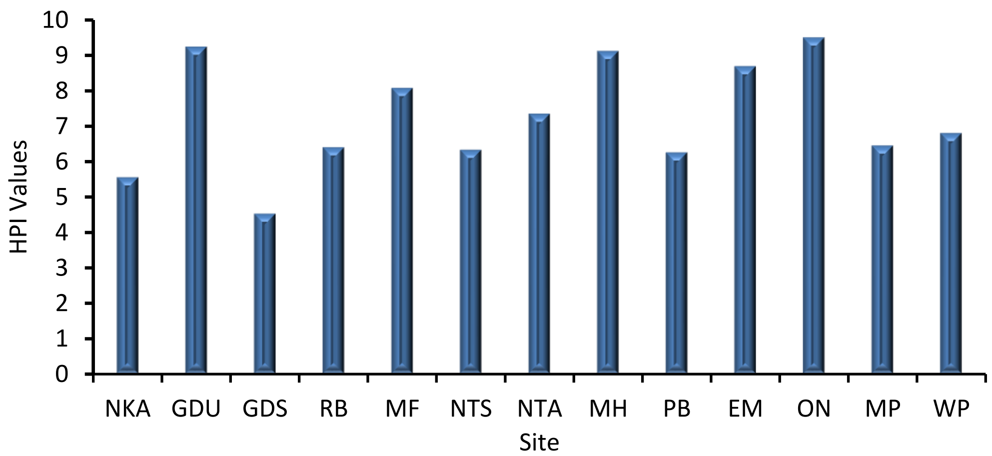

Figure 53: Graphical representation of HPI along UMhlathuze River for a period of 12 months

4.15 Ecotoxicological effects

4.15.1 Hazard Index and Incremental Lifetime Cancer Risk

The HI values based on non-carcinogenic effects and ILCR values based on carcinogenic effects within uMhlathuze River are summarized in Table 18. While there is no evidence of using the raw water from uMhlathuze River for consumption purposes, it was still important to assess the potential risk considering the that river stretches from rural areas where access to treated water may be a challenge. In this regard, the results in Table 18 indicate that water from uMhlathuze River will not cause any health problems related to metal contamination with HI values below 1 for all sites. These values do not take into consideration other pollutants that may enter the river from wastewater treatment plants. In case of children, the water in the rural areas (NKA, GDU and GDS sites) was safe while they were not safe for other regions especially along the three tributaries (MH, NTA and EM sites) whose HI values were between 1.42 and 2.18. It is important to note that it is unlikely that people can drink the unprocessed water from these tributaries. Finally, the untreated river water was found to be unsuitable for consumption by infants throughout the entire sampling region except for the GDU site whose predicted HI value was 0.71. Ecotoxicological effects on river water samples have been reported elsewhere (Ghahramani *et al.*, 2020; Emmanuel *et al.*, 2022; Golaki *et al.*, 2022; Rahman *et al.*, 2022; Moradnia *et al.*, 2024).

Table 18: Hazard Index for carcinogens and non-carcinogens

Site	NKA	GDU	GDS	RB	MF	NTS	NTA	MH	PB	EM	ON	IMP	WP
HI_{adult}	0.29	0.32	0.16	0.24	0.37	0.27	0.47	0.73	0.27	0.48	0.48	0.34	0.26
HI_{child}	0.88	0.97	0.47	0.72	1.12	0.80	1.42	2.18	0.82	1.43	1.43	1.03	0.79
HI_{infant}	1.32	1.46	0.71	1.07	1.68	1.19	2.13	3.28	1.23	2.15	2.15	1.54	1.18
$ILCR_{adult\ x10}{}^{-4}$	1.86	1.71	1.41	0.16	1.62	1.66	2.19	4.99	1.88	2.23	2.15	2.21	1.2
$ILCR_{child\ x10}{}^{-4}$	5.59	5.13	4.23	4.81	4.87	4.98	6.56	4.96	5.65	6.68	6.46	6.62	3.59
$ILCR_{infant\ x10}{}^{-4}$	8.38	0.77	6.35	7.21	0.73	7.47	9.83	22.4	8.47	10.03	9.69	9.93	5.39

4.16 Environmental risks

Water quality at uMhlathuze River and its tributaries as classified in terms of suitability for irrigation as per Table 19. The water quality in relation to irrigation was excellent in the rural areas with the SAR values ranging between 7.6 and 9.2. The river water was still good for irrigation in the agricultural region with SAR values ranging between 10.8 - 17.2, but water along the two tributaries (Mholweni and Ntambanana Rivers) was deemed unsuitable with the potential to harden the soil and reduce internal drainage. In the urban and industrial areas, Empangeni River water was deemed unsuitable with a SAR value of 27.8 while the water along Umhlathuze River was found to be suitable. The Na content as a %Na value was up to 81% for Ntambanana River and its water was deemed unsuitable for irrigation. This value together with the high chlorine levels reported in Section 3.2 indicated that the water from Ntambanana River was likely to be too salty for irrigation purposes. It is important to note that SAR and %Na values are not an indication of pollution but an estimation of water impermeability and saltness which is might hinder plant growth. Other studies have reported similar observations where some parts of a river were unsuitable for irrigation purposes including Molo River in Kenya (Chebet, Kibet and Mbui, 2020). The impact of tributaries on the main river quality have also been reported in literature including the Pechora River in Russia (Yakovlev *et al.*, 2023). Tahmasebi and colleagues conducted classification of ground water samples where the authors reported about 27% of samples which were classified as excellent and good whilst more than 60% were classified as doubtful and unsuitable (Tahmasebi *et al.*, 2018).

Table 19: Sodium Adsorption ratio for uMhlathuze River and its tributaries over a 12-month period

Site Name	SAR	%Na	Rating	SAR Guide
NKA	7.7	52	Excellent	0-10
GDU	8.4	59	Excellent	0-10
GDS	9.3	62	Excellent	0-10
RB	10.8	62	Good	10-18
MF	15.5	70	Good	10-18
NTS	13.4	65	Good	10-18
NTA	76.3	81	Unsuitable	>26
MH	44.2	69	Unsuitable	>26
PB	17.2	68	Good	10-18
EM	29.5	72	Unsuitable	>26
ON	17.9	67	Permissible	18-26
MP	18.2	67	Permissible	18-26
WP	18.0	67	Permissible	18-26

SAR – Sodium Adsorption ratio

5 CONCLUSIONS AND RECOMMENDATIONS

The study has provided insights on the potential impact of anthropogenic activities on the water quality along uMhlathuze River and its three main tributaries based on levels of physicochemical properties, anions, macro elements and trace metals. It was important to note that, the water quality of uMhlathuze River at rural area was in an acceptable condition as per SAWQ guidelines besides. Along the main river, the physicochemical parameters were mostly within guideline limits but during rainy seasons, they were elevated and at times exceed the guideline limits for SAWQ and WHO especially along the tributaries. Agricultural activities, quarrying, wastewater effluents and urban runoff were identified as potential pollution sources. However, a crucial finding is that the elevated pollution levels along the tributaries had minimal impact on uMhlathuze River with the parameters immediately diluted to normal conditions as soon as the water from the tributaries entered the main river. Despite this resilience of uMhlathuze River, dependency on its dilution capabilities cannot be a sustainable management strategy. The tributaries act as critical and chronic pollution hotspots that should be closely monitored to prevent the river from being overwhelmed on the long run.

The environmental risk assessment indicate that anthropogenic activities along uMhlathuze River pose minimal treats to river pollution. Furthermore, the health risk assessment identified that the river water will not cause health problems for adults related to metal contamination. In should however be emphasized that these values do not take into consideration other pollutants that may be present in the river. With respect to children, the water in the rural area (NKA, GDU and GDS site) was safe whilst other regions were not safe especially along the three tributaries (MH, NTA and EM sites) whose HI values were between 1.42 and 2.18. It is important to note that it is unlikely that people can drink the unprocessed water from these tributaries due to elevated concentration levels of some physicochemical parameters including

Cl and Na which are responsible for salty taste of water. Moreover, the untreated river water was found to be unsuitable for consumption by infants throughout the entire sampling region except for the GDU site whose predicted HI value was 0.71. When assessing environmental risk, the water quality from the three tributaries (NTA, MH and EM) was unsuitable for irrigation purposes (SAR >29) hence river water was unsustainable for agricultural purposes.

The study has further demonstrated that water quality along uMhlathuze River and its tributaries is affected by seasonality and anthropogenic activities within its tributaries. Based on principal component analysis, the elementary levels along uMhlathuze River and its tributaries were grouped into three distinct groups; the rainy season (December - April) cluster consisting of trace metals associated with surface runoff; the dry season (May - September) cluster characterized by macro elements that tend to concentrate during the cold low flow season; and the unique first flush event in November marked by those trace elements that experience a spike during the first rains. This insight may be crucial in providing a basis for source control and a more dynamic monitoring schedule that targets pollution sources and the potential impact of episodic pollution spikes along uMhlathuze River and its tributaries. It is recommended that future studies must include sedimentation in order to assess levels of metals bound to sediments as well as organics possible accumulated in river water due to anthropogenic activities reported in this study.

6 REFERENCES

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7 APPENDEX

8 Published Paper

The results of the current study have been published in the Environmental Geochemistry and Health. and. The published paper is included as part of the **Appendix.** The paper can also be accessed via Springer Nature Link: https://link.springer.com/article/10.1007/s10653-025-02830-0

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ORIGINAL PAPER

Anthropogenic impact assessment on the water quality of Umhlathuze River in KwaZulu Natal Province, South Africa

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Abstract Umhlathuze River and its three main tributaries experiences various anthropogenic activities including agriculture, urbanization and industrialization before forming an estuary with the Indian ocean. The current study assessed the potential impact of these anthropogenic activities over a 12–months period in 2023/4. The study found that elementary levels were mostly within the permissible limits along Umhlathuze River, but the impact of anthropogenic activities along its tributaries was evident. Chlorides ranged between 400 and 655 mg L^{-1} along the Mholweni tributary during the rainy season while Na, Mg and Ca were also consistently above permissible limits along Mhloweni and Ntambanana tributaries. Among non–toxic trace elements, only Fe exceeded its health–based precautional value during the rainy season for all sites. Trace toxic metal levels were also within permissible limits. Hg was only detected along the tributaries in the 0.017–0.399 μg L^{-1} range. The source of elevated levels of parameters along the tributaries was linked to quarry and agricultural activities, the wastewater effluents and urban runoff. The WQI values were in the 10.7–36.1 range implying the river water could be classified as good to excellent. The main river water was also found to be suitable for irrigation purposes, but water from the three tributaries was unsuitable with SAR values of 29.5–76.3. A health risk assessment identified that the river water was safe for adults but infants and children were more likely to develop non–carcinogenic effects with HI values of 1.07–3.28. The ILCR values ranged between 1.20 and 9.93 indicating that consumption of unprocessed water from Umhlathuze and its tributaries will result in carcinogenic effects over one's lifetime with infants and children affected most.

Keywords Water quality · Metal pollution · Umhlathuze river · Health risk assessment · Hazard quotient

Introduction

Anthropogenic processes have been reported to contribute to metal pollution of river water systems. Developing countries including South Africa still experience a challenge with metal contamination of surface water resources with researchers identifying wastewater effluents and mine runoff as the major contributors of metal pollution in surface water systems (Dzhangi & Atangana, 2024; Harding et al., 2020; Ntombela et al., 2016; van Rensburg et al., 2016). Metals have known health side effects if present above certain levels in drinking water

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sources (Jomova et al., 2024; Zaynab et al., 2022). Recent studies have been done on metal pollution of important rivers within South Africa with some results reporting metal levels higher than the WHO and the South African Water Quality (SAWQ) guidelines (Edokpayi et al., 2016; Moloi et al., 2020). These observations may still be ignored at legislation level but the potential impact on the aquatic organisms and rural communities that may consume the river water in its raw form cannot be ignored, with more research required to provide more evidence for remedial action.

Umhlathuze River in northern part of KwaZulu–Natal province is currently exposed to anthropogenic activities including the rapidly growing urbanization as well as growth in agricultural and industrial activities all with the potential to release metal elements into the river if not properly managed (Mokoma & Tilahun, 2022). The river has also been impacted by inclement environmental conditions including the drought between 2014 and 2020, extreme floods in 2022 as well as the growth of new chemical industries and urban settlements within its catchment (Dlamini et al., 2024; Mashao et al., 2023). A previous study conducted by Mthembu and colleagues along uMhlathuze River in 2012 investigated six metals (Mn, Pb, Al, Hg, Cu and Cd) at four sampling sites and observed that all the metal contamination levels were higher than the South African Water Quality guideline limits (Mthembu et al., 2012). It is therefore important to perform recent pollution studies to better understand the current state of water quality along Umhlathuze River and assess the impact that these anthropogenic activities and adverse weather conditions could have on the river's ecosystem.

The current study aimed to provide a recent state of water quality along uMhlathuze River by investigating 22 selected metals at thirteen sites strategically selected along the river and its catchment taking into consideration various anthropogenic activities along the river. The metals included the four major macro elements (Na, Mg, K and Ca); six essential trace metals (Cu, Co, Fe, Mn, Ni and Zn); six toxic trace metals (Cr, Cd, Hg, As, Pb, U). Six other elements (Al, Se, Sb, Ba, B, Sr) with limited effect on the human body were included in the study. In addition, some physicochemical parameters including pH, temperature, and dissolved oxygen were conducted and results were linked to the measured levels of the metals. Other nutrient chemicals like chloride, fluoride, nitrate and sulfate were also included in the study. Principal component analysis was used to understand the interrelationships between the various water parameters and the elementary composition. The measured concentrations were used to predict water quality of Umhlathuze River based on water quality indices (WQI) and heavy metal pollution index (HPI), the suitability of the water for irrigation purposes based on the sodium adsorption ratio (SAR), and health risk using the hazard index (HI) and incremental lifetime cancer risk (ILCR).

Materials and methods

Chemicals and reagents

Individual 1000 mg L^{-1} stock solutions (K, Na, Mg & Ca) were purchased from Merck Pty Ltd, Johannesburg, South Africa. A mixed stock solution of Al, As, Hg, B, Ba, Cd, Co, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, U and Zn with concentration range of 1000 mg/L was purchased from Separations, Johannesburg, South Africa. The anion standards were also purchased as 1000 mg/L standards from Merck Pty Ltd, Johannesburg, South Africa.

Instrumentation

A Dionex ICS 1600 Ion Chromatograph by Anatec Suppliers, Johannesburg, South Africa was used for analysis of chlorides, fluorides, nitrates and sulfate. Total organic carbon (TOC) was analysed using Analyticjena Multi N/C 3100 TOC instrument from Spectrometer Technologies, Johannesburg, South Africa. An Inductively Coupled Plasma Optical Emission Spectrometry (ICP–OES) instrument from Perkin Elmer, Johannesburg, South Africa was used for analysis of macro elements. The ICP–OES instrument conditions were RF power 1.5 KW, plasma flow 8 L min^{-1}, auxiliary flow 0.2 L min^{-1}, nebuliser flow 0.7 L min^{-1}, pump rate 1 mL min^{-1}. Elemental wavelengths selected were Ca (317.933 nm), Mg (285.213 nm), Na (589.592 nm) and K (766.490 nm). An Inductively Coupled Plasma Mass Spectrometry (ICP–MS) from Perkin Elmer, Johannesburg, South Africa was used to analyse trace metals that included Al, Cu, Co, Fe, Mn, Cr, Cd, Hg, As, Se, Sb, Pb, Ni, Ba, B, U, Sr, and Zn. Instrument conditions for ICP–MS were RF power 1.55 kW, carrier gas 2 L/min, helium flow 4.5 mL min^{-1} and pump rate of –3 rpm. Gas used for both ICP–OES and ICP–MS was argon of 99.999% purity from Air Product, Richards Bay, South Africa.

The calibration range for Ca and Mg was 5–60 µg mL^{-1}, for K was 0.25–30 µg mL^{-1} while for Na was 25–200 µg mL^{-1}. The calibration range for trace metals on the ICP–MS instrument was 10–1000 ng mL^{-1} except for Hg which was 0.1–50 ng mL^{-1}. Both instruments were set to accept the linearity of the calibration curves only if $R^2 > 0.999$. In this regard, the R^2 values for all the elements varied between 0.9995 (Ba) and 1 (Hg). The limits of detection (LODs) and limits of quantitation (LOQs) for the elements were estimated based on the linear regression method using the LINEST function on Excel. The LODs for trace elements ranged between 0.11 and 0.59 ng/mL, while macro elements were in the 0.41–5.46 mg/L range. The LOQs were 0.36 – 1.90 ng/L for trace elements and 0.36–18.2 mg/L for macro elements. The LODs and LOQs for each element are given in the Supplementary. For precision, all calibration standards and samples were run in triplicate, and the average used in further data processing. A relative standard deviation less than 20% (RSD < 20%) was considered acceptable.

Sampling area

The uMhlathuze River was divided into three segments based on the anthropogenic activities (Fig. 1). The first segment represented rural areas between Babanango mountains where uMhlathuze River originates, up until Gouderetrouw Dam which is about 60 km before uMhlathuze River meets the Indian Ocean. The second segment is an agricultural region in which Umhlathuze River is surrounded by sugarcane fields and citrus farms and processing factories. In this region Umhlathuze river meets with various tributaries with the two major ones (Mholweni and Ntambanana Rivers) selected for sampling just before they meet UMhlathuze River. Mholweni River emerges from Dlangubo rural areas and passes through a quarry. Ntambanana River originates from Ntambanana rural areas and passes through sugarcane fields. The third segment covers areas around Empangeni Town and Richards Bay until the estuary. This is an urban area with a variety of chemical and processing industries, three wastewater treatment plants and various informal settlements. Thirteen sampling points were strategically selected for this study of which three were in Segment 1, six in Segment 2

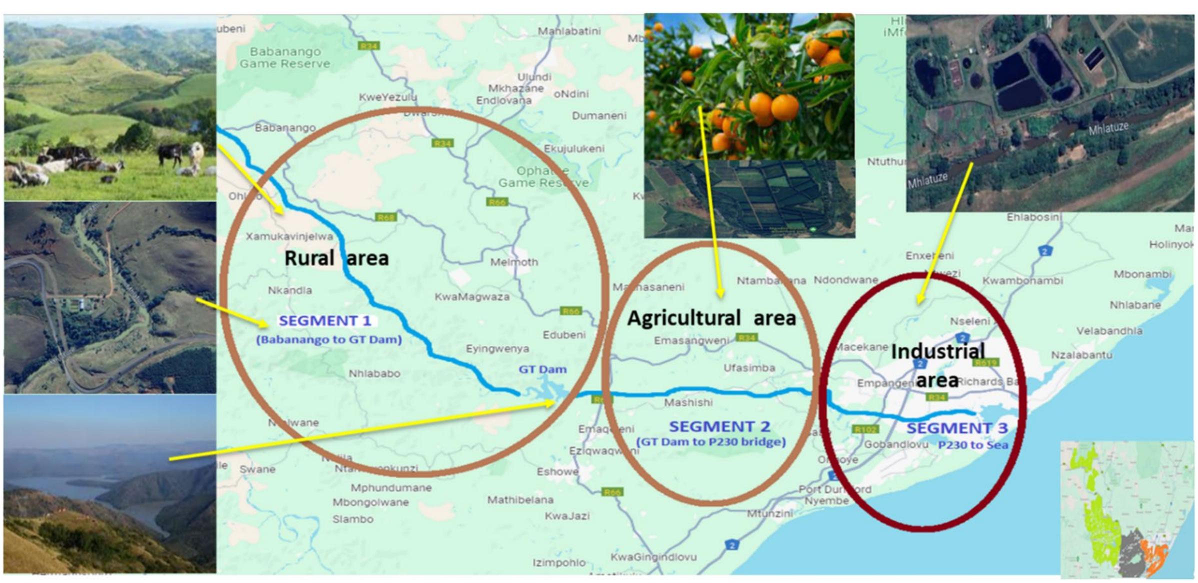


Fig. 1 Anthropogenic activities per segment along uMhlathuze River

and four in Segment 3. The GPS coordinates for each sampling point are given in the Supplementary.

Sample collection and analysis

Water samples were collected into 250 mL clean polyethylene plastic sampling bottles and preserved with 1% nitric acid. A separate 2 L plastic bottle was used to collect water samples for chemical parameters. Samples were transported in cooler boxes and analysed within 48 h. Determination of the physical parameters including dissolved oxygen (DO) and temperature were performed onsite using an Aquaread meter from Geowater, Johannesburg, South Africa. An effort was made to maintain collection of samples on the same days monthly which was between the 12th and the 18th of each month for a period of 12 months.

At the laboratory, water samples were filtered through 0.45 micron and analysed for chlorides, fluorides, nitrates and sulfates using ion chromatograph. The unfiltered samples were analysed for TOC using the TOC instrument. The acidified water samples were analysed for selected macro elements (K, Na, Mg and Ca) using ICP–OES. trace metals that included Al, Cu, Co, Fe, Mn, Cr, Cd, Hg, As, Se, Sb, Pb, Ni, Ba, B, U, Sr, and Zn were analysed using ICP–MS. For both instruments, results were exported from the instrument in excel format for further processing.

Ecotoxicological risk assessment

Water quality

The water quality index (WQI) which summarizes the overall quality of water was calculated using Eq. 1, taking into consideration average values of electrical conductivity, pH, TOC, ammonia, chlorides, fluorides, nitrates, sulfates, K, Na, Mg and Ca. The impact of heavy trace metals on water quality was predicted as the Heavy Metal Pollution Index using Eq. 2. Since the Umhlathuze River has agricultural activities, the suitability of its water for irrigation purposes was estimated as the sodium adsorption ratio (SAR) and the Na content using Eq. 3 & 4, respectively. Water is considered suitable for irrigation if SAR < 10 and %Na < 60. Water with SAR > 10 can result in compact and impenetrable soil and %Na > 60 can lead to alkaline or saline soils all of which are not suitable for plant growth (Ali & Ali, 2018).

$$WQI = \sum_{i=1}^{n} \left(S_i W_i\right) \quad (1)$$

$$HPI = \frac{\sum_{i=1}^{n} \left(W_i \times V_i / S_i \times 100\right)}{\sum_{i=1}^{n} \left(V_i / S_i \times 100\right)} \quad (2)$$

$$SAR = \frac{2 \times [Na]}{\sqrt{[Ca] + [Mg]}} \quad (3)$$

$$\%Na = \frac{[Na] + [K]}{[Na] + [K] + [Mg] + [Ca]} \quad (4)$$

where *WQI* is there water quality index, S_i is the standard value, *Wi* is the unit weight of the i^{th} parameter (ranges from 0 to 1), *n* is the number of parameters. *HPI* is heavy metal pollution index, V_i is the monitored value of i^{th} parameter. *SAR* is the sodium adsorption ratio.

Health risk assessment

Health risk assessment was predicted using three models; the Hazard Index (HI) and incremental lifetime cancer risk (ILCR). The two models give a prediction of the potential health risks to humans due to consumption of contaminated water (Emmanuel et al., 2022; US Environmental Protection Agency, 2011). Firstly, the measured concentrations in water samples were used to estimate the chronic daily intake as an exposure concentration (EC) to a metal per unit body weight per day using Eq. 5. The HI which estimates the cumulative non–carcinogenic risk due to exposure to different metals was calculated as the sum of the ratios of the EC to the reference dose (R_fD) of each metal using Eq. 6. The ILCR which represents the probability that someone will develop cancer due to continuous exposure over a particular period was calculated as the product of the EC values with cancer slope factor (CSF) values for trace metals with known carcinogenic effect in the body using Eq. 7.

$$EC = C_m \times IR/BW \tag{5}$$

where EC is the exposure concentration (mg kg(bw)$^{-1}$.day^{-1}), C_m (mg L^{-1}) is the concentration of the metal in water, DI is the average daily water intake (2 L day^{-1} for adults, 1 L day^{-1} for children and 0.75 L day^{-1} for infants), BW is the body weight (60 kg for adults, 10 kg for children and 5 kg for infants) (WHO, 2017).

$$HI = \sum_{i=1}^{n} \left(EC/R_f D\right) \tag{6}$$

where HI is the Hazard Index, EC is the exposure concentration (mg/kg(bw) $^{-1}$.day^{-1}), RfD is the reference dosage (mg kg(bw) $^{-1}$.day^{-1}).

$$ILCR = \sum_{i=1}^{n} (EC \times CSF) \tag{7}$$

where ILCR is the incremental lifetime cancer risk, EC is the exposure concentration (mg/kg(bw)$^{-1}$ day^{-1}) and CSF is the cancer slope factor (mg/kg(bw)$^{-1}$ day^{-1}) (Mohammadi et al., 2019).

Principal component analysis

Principal component analysis (PCA) was done on RStudio statistical software version 4.4.1 (2024-06–14 ucrt) to explore the seasonal interrelationships between elementary levels along Umhlathuze river. The excel results from ICP analysis were converted into a.csv format and imported into RStudio for statistical analysis using the *ggplot* package as the R–environment. The dataset was partitioned such that 80% was used as training data and 20% as testing data. The PCA of the elementary composition was processed using the *prcompt* command. Several PCs were generated but PC1 and PC2 accounted for most of the cumulative variance for the dataset indicating that PC1 vs PC2 could be a reasonable summary of the data set. In this regard, the PCA results were summarized and visualized in terms of biplots of PC1 and PC2 only.

Results and discussion

Physicochemical parameters

Figure 2 presents the range of physicochemical parameters over a 12 months sampling period from

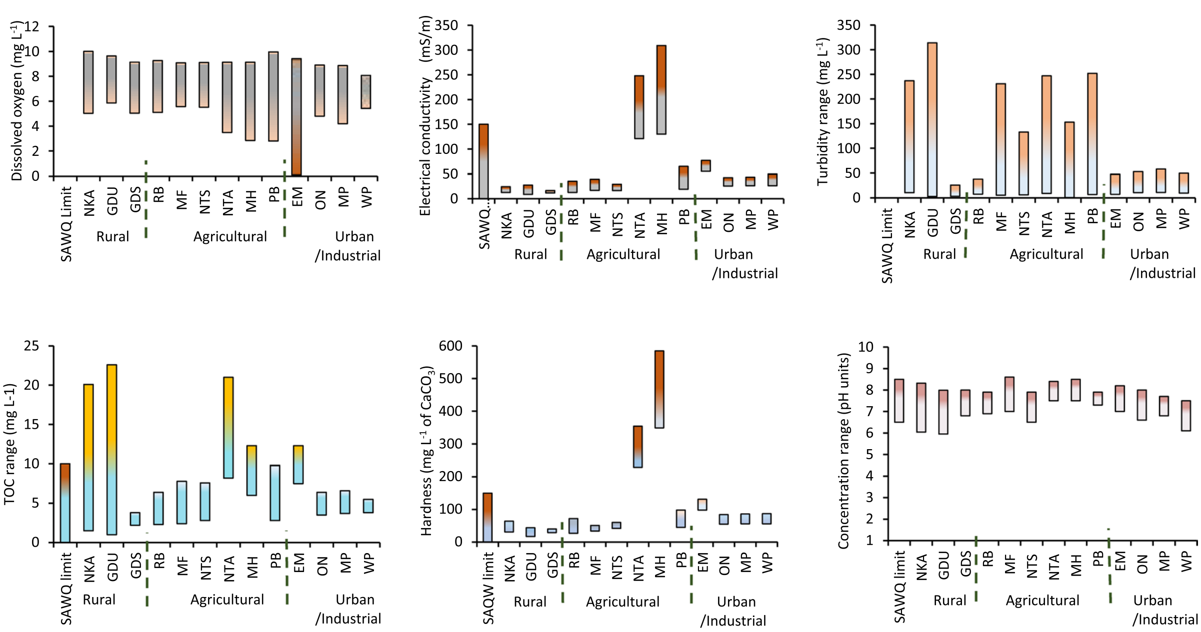


Fig. 2 Annual levels of physicochemical parameters

December 2023 to November 2024. Results show moderate seasonal temperature variations ranging between 11.6 and 32.5 °C indicating a warm temperate climate in the region. The temperatures were relatively mild during the winter (May–July) and warm during the summer months. The minimum temperature was observed at the NKA site in the rural area, whilst the maximum was recorded at the MF site in the agricultural area. Water along the Umhlathuze River was generally soft to moderately hard except for the tributaries with Ntambanana (NTA site) and Mholweni (MH site) rivers recording 229–354 and 349–585 mg L^{-1} of $CaCO_3$, respectively through the year. Water along Empangeni tributary (EM site) was moderately hard recording an annual range of 98–131 mg L^{-1} of $CaCO_3$. Water from the tributaries was therefore not suitable for any domestic purposes.

The DO values ranged from 0.1 to 10 mg L^{-1}. The lowest DO was recorded at EM site along Empangeni tributary with the levels below 4 mg L^{-1} for most of the year except in June (Fig. 2). Empangeni River receives wastewater discharge from two municipal wastewater works which could be responsible for the low DO levels. The DO levels below 4 mg L^{-1} have the potential to cause hypoxia in aquatic organisms in some cases leading to death (Zeng et al., 2023). The lower and upper limits for pH were within SAWQ guidelines for all sites except for three instances at the NKA site in July, the GDU site in December and the WP site during the winter months (June and July) where pH values were slightly acidic. Both NKA and GDU sites in the rural areas are located closer to mountains of Babanango and Nkandla, and receive spring water from the region. Spring water pH tends to be slightly acidic due to natural factors including type of rocks and minerals as well as presence of gases like carbon dioxide (Novikov et al., 2022). The relatively low pH value at the Weir Pumpstation (WP site) in the industrial area during the cold dry season could be attributed to reduced dilution effects on industrial effluents during the low flow season.

The electrical conductivity of uMhlathuze River was within the WHO and SAWQ standards throughout the year except for Ntambanana River (NTA site), Mholweni River (MH site) in the agricultural region, and Empangeni River (EM site) in the urban area. This could be attributed to anthropogenic activities including discharge from the quarry (Mholweni River), and agricultural activities (Ntambanana River). Ibe and colleagues conducted a study at Inyibe River of Nigeria, where EC recorded was high and exceeded WHO guidelines. This was due to the impact of discharge from aluminium extrusion activities (Ibe et al., 2019). The EC values along Empangeni River (EM site) were above WHO guidelines ranging between 55 and 77 mS m^{-1} throughout the year.

NTA and MH sites were also observed to have TOC and hardness values above SAWQ guideline limit. The TOC values on Ntambanana River (NTA site) were consistently above guideline limits. Two other sampling points in the rural areas, NKA and GDU sites experienced a spike of TOC measuring about 22 mg L^{-1} in February. The TOC chart for Empangeni tributary (EM site) in the urban and industrial section fluctuated above and below the guideline limit. The river receives wastewater discharge from the local municipal wastewater treatment plants. Other studies elsewhere have identified wastewater discharge as a major contributor of higher TOC values including 36.65 mg L^{-1} on the Nile River in Egypt (Khalil et al., 2023).

Water turbidity in the agricultural region were within 50 NTU most of the time except spikes observed in November and January in the agricultural region and the NKA and GDU sites in the rural areas. These areas have clay soils and the agricultural activities further loosen the soil which get washed into the river during the rainy season. At the urban and industrial sites, turbidity values were below 60 NTU throughout the study due to increase in river level with higher dilution taking place. While most of the turbidity values were relatively low (< 50 NTU), they were still above the SAQW guideline value of 5 NTU indicating a serious challenge for uMhlathuze River.

Anions

The levels of chlorides, fluorides, nitrates and sulfates along Umhlathuze River and its tributaries are summarized in Fig. 3. The results pointed the impact that Ntambanana, Mholweni and Empangeni tributaries have on Umhlathuze River with the three rivers recording extremely high levels compared to other sites. The chloride levels were between 205 and 655 mg L^{-1} for Mholweni River (MH site) with the rainy season (December – March) consistently

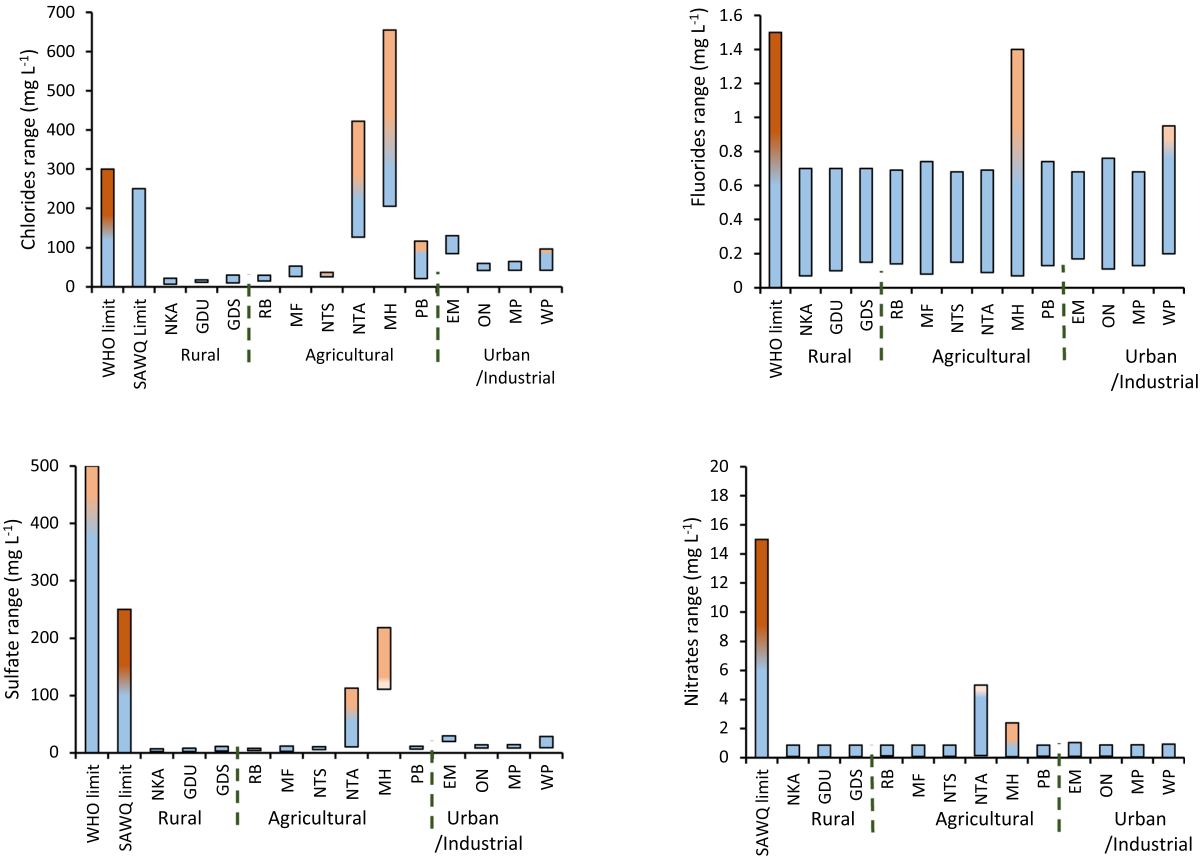


Fig. 3 Annual levels for anions for all sampling areas over a 12 month period

above the SAQW guideline limits. This could have been due to rain water washing from the quarry excavations contaminating Mholweni River with chlorine–rich rock leachates and chemicals used in blasting operations and lubricants. These levels are similar to those reported on the Achenkovil River Basin where 546 mg L^{-1} of chlorine was recorded (Reghunadh et al., 2023). Both rivers received run-off from quarry mining activities. Ntambanana River (NTA site) which flows mainly through agricultural fields had chlorine levels that ranged from 127 to 422 mg L^{-1}. The elevated chloride concentration at this river is probably from natural sources because this area is known for its salty water that has presented challenges for consumers (https://www.news24.com/citypress/voices/democracys–surplus–people–20190321—Last accessed on 23 February 2025). Chloride levels along Empangeni River (EM site) were within guideline limits but ranged from 80 to 141 mg L^{-1} throughout the year.

The elevated chloride levels could be arising from solid waste dumpsite leachates and wastewater plants that discharge their effluent into Empangeni River. The elevated chloride concentrations along the three tributary rivers (MH, NTA and EM sites) had limited impact on the quality of uMhlathuze River because the levels recorded on uMhlathuze River after receiving water from these tributaries was within the guideline limits even though higher compared to levels in the rural areas upstream.

Fluoride levels were within SAWQ guideline limits for all sites. A general trend was observed with the levels relatively higher during the rainy season and recording the lowest levels during the dry cold season (May–July). There were spikes that occurred along the Mholweni River (MH site) reaching 1.4 mg L^{-1} in February. Another spike up to 0.95 mg L^{-1} was recorded at the Weir Pumpstation (WP site) in May. These observations were once off and could not be linked to any source except that Mholweni River emanates from a quarry mining area while the Weir Pumpstation serves as a reservoir for water upstruction purposes. Nitrate levels were also within SAWQ and WHO guideline limits throughout the uMhlathuze River and its tributaries, but the potential impact of quarry activities along Mholweni and farming activities along Ntambanana tributaries were observed with sites slightly higher than other areas along Umhlathuze River.

The sulfate levels were also within guideline limits but elevated levels were observed along the tributaries (NTA and MH sites in the agricultural region, and EM site in the urban and industrial areas. The agricultural activities led to sulfate levels up to 113 mg L^{-1} along Ntambanana River (NTA site) while the quarry activities near Mholweni River (MH site) resulted in sulfate levels ranging between 111 and 218 mg L^{-1}. However, these levels were still within the guideline limits. Like chlorides, sulfates can also be linked to the type of soil in that particular geographical area, but fertilizer runoff from agricultural fields is also a major contributor (Saka et al., 2024; Sukarjo et al., 2025). A general increase in sulfate levels downstream of the uMhlathuze River was observed with the urban and industrial segment recording high levels compared to rural and agricultural segments. The levels in the rural areas were consistently below 10 mg L^{-1}, the agricultural segment had about 10 mg L^{-1}, while the urban and industrial segment were consistently above 10 mg L^{-1}, which could be suggestive of cumulative effects down the river. Accumulation of sulfates in the industrial area (WP site) could also be directly from the industries within industrial area or the result of sea spray since the Weir Pumpstation is closest to the Indian ocean.

Elementary analysis

Macro elements, (major cations)

The concentration range of macro elements for the 12 months period are summarised in Table 1. The levels recorded for each month are given on the Supplementary. Potassium was within the SAQW permissible limits throughout the year for all sampling sites. However, Ca, Mg and Na were recorded above the guideline limits for the Ntambanana (NTA site) and Mholweni (MH site) tributaries throughout the year (Fig. 4). These elevated levels could be linked to quarry works along the Mholweni River and the geochemistry of the area where Ntambanana River emanates. The impact of similar anthropogenic activities on the levels of macro elements in river water including silicate weathering, dissolution, leaching, and infiltration from hard rock and soil quarries has been reported in India (Reghunadh et al., 2023) and Kenya (Chebet et al., 2020). The impact of elevated levels of macro elements from MH and NTA sites is minimal on UMhlathuze River because the levels recorded at PB site along uMhlathuze River after it has received water from the two streams were within guideline values suggesting dilution effects due to larger volumes of water along uMhlathuze River. Despite the dilution effects, the levels of macro elements were relatively higher in the urban and industrial area with Empangeni River (EM site) also pumping more macro elements into Umhlathuze River. The relatively high levels along Empangeni tributary might have been caused by wastewater discharge from local wastewater works and possible runoff form Empangeni town and surrounding informal settlements.

Levels of trace essential elements

The annual trends of trace essential elements are summarized in Table 1. The concentration levels recorded for each month over the 12–month period are given on the Supplementary. The levels of Cu, Ni and Zn were within the WHO permissible limits at all sites throughout the year, while Fe and Mn at times exceeded their WHO precautional limits during the rainy season. There are no WHO guideline limits for Co, but in the current study its levels were mostly within 2 µg L^{-1} except for the MH site along Mholweni River and single spikes on the GDU and NTA sites in November. A significant spike in Zn levels was observed at the EM and ON sites during the month of December recording 234 and 427 µg L^{-1}, respectively while the other sites were consistently below 60 µg L^{-1}. The accumulation of Zn on Empangeni River (EM site) could be due to wastewater effluents and direct runoff from activities and structures that use galvanized steel structures within Empangeni urban area. Consequently, the spike at the ON site

Table 1 Minimum, maximum and median values for non–toxic elements over 12 months

Segment	Site	Concentration of macro elements (mg L^{-1})				Concentration of metals (ug L^{-1})											
		Ca	Mg	Na	K	Al	Ba	B	Sr	Sb	Se	Cu	Ni	Fe	Mn	Zn	Co
Rural	NKA	5.2–11	4.3–9.1	11–18	0.8–2.6	3.2–2463	19.5–259	8.4–43.5	37.1–99	nd–0.5	nd–9.4	0.7–5.0	0.3–21.7	17.4–2155	1.0–713	1.5–29	nd–2.5
	GDU	3.3–7.9	2.1–5.9	11–16	0.8–2.4	4.5–1985	16.4–140	8.3–81	29.4–104	nd –2.1	nd–9.8	0.3–69.9	0.2–38.8	6.0–3894	0.4–633	0.1–59	nd–6.7
	GDS	5.1–7.1	3.7–11	11–17	1.5–2.1	33.7–1191	27.9–46.6	14.7–24.1	36.5–54	nd –0.4	nd–8.4	0.4–7.0	0.6–27.8	138.4–880	0.8–32	0.6–5.2	nd –0.7
Agricultural	RB	4.9–12	3.7–11	14–48	1.5–2.7	2.5–1318	0.6–66	3.6–56	0.7–100	nd –0.4	nd –8.0	0.6–4.6	0.5–28.1	1.2–1256	0.7–69	nd–7.1	nd –1.2
	MF	5.5–8.5	4.8–7.4	24–32	1.5–3	nd–1173	1.9–128	nd–171	2.0–309	nd –1.8	nd –9.8	1.2–5.5	0.3–20.3	0.7–2298	1.3–158	nd–4.4	nd –1.7
	NTS	7.2–10	5.8–8.5	22–40	1.7–3.1	nd–1357	0.9–92	nd–55	0.9–86	nd –0.8	nd –13.8	0.3–3.1	0.3–29.4	0.1–1967	0.2–209	nd–3.0	nd –1.0
	NTA	31–46	30–58	189–554	1.2–8.4	nd–2033	38.1–281	24.3–216	40–435	nd –3.5	nd –20.7	0.8–5.1	0.3–33.8	0.1–2160	0.3–539	0.1–5.5	nd –5.3
	MH	51–91	54–89	179–552	1.7–3.5	nd–1836	8.8–233	nd–228	8.8–823	nd –7.4	nd –19.4	nd–8.6	0.2–59.9	nd–2583	0.1–260	nd–16.9	nd –9.1
	PB	7.6–14	6.3–15	26–92	1.6–3.2	32.7–1713	34.2–168	28.6–80	58.7–147	nd –0.8	nd –26.6	0.8–4.4	0.6–33.5	145–2143	1.5–268	1.2–10.0	nd –2.3
Urban and industrial	EM	17–21	16–20	78–101	4.3–6.9	5.3–695	nd–92	63.5–83	1.2–179	nd –1.2	nd –27.8	0.7–6.2	0.9–15.8	1.5–1347	0.1–177	nd–234	nd –1.2
	ON	9–13	8–12	34–52	2–3.4	2.3–1892	nd–77	2.8–69	0.9–117	nd –0.6	nd –23.2	0.4–11.6	0.4–26.2	1.1–1688	0.1–205	nd–427	nd –2.0
	MP	9.4–14	8–13	33–54	2.3–3.2	7.8–2206	36.7–78	34.9–72	53.1–121	nd –0.2	nd –27.9	0.4–6.3	0.4–24.9	14.2–2507	0.1–159	nd–6.0	nd –2.0
	WP	5.5–7.5	6.4–13	28–54	2.2–3.4	nd–436	0.6–72	4.3–55	nd–134	nd –1.4	nd –26.7	nd–3.7	nd–7.2	1.4–2317	nd–142	nd–8.1	nd –1.2
WHO guidelines		–	–	–	900*	200	1300	–	–	40	40	2000	2000*	400*	3000*	–	
SAWQ Guideline	32	32	200	200													

*WHO health–based precautional limit

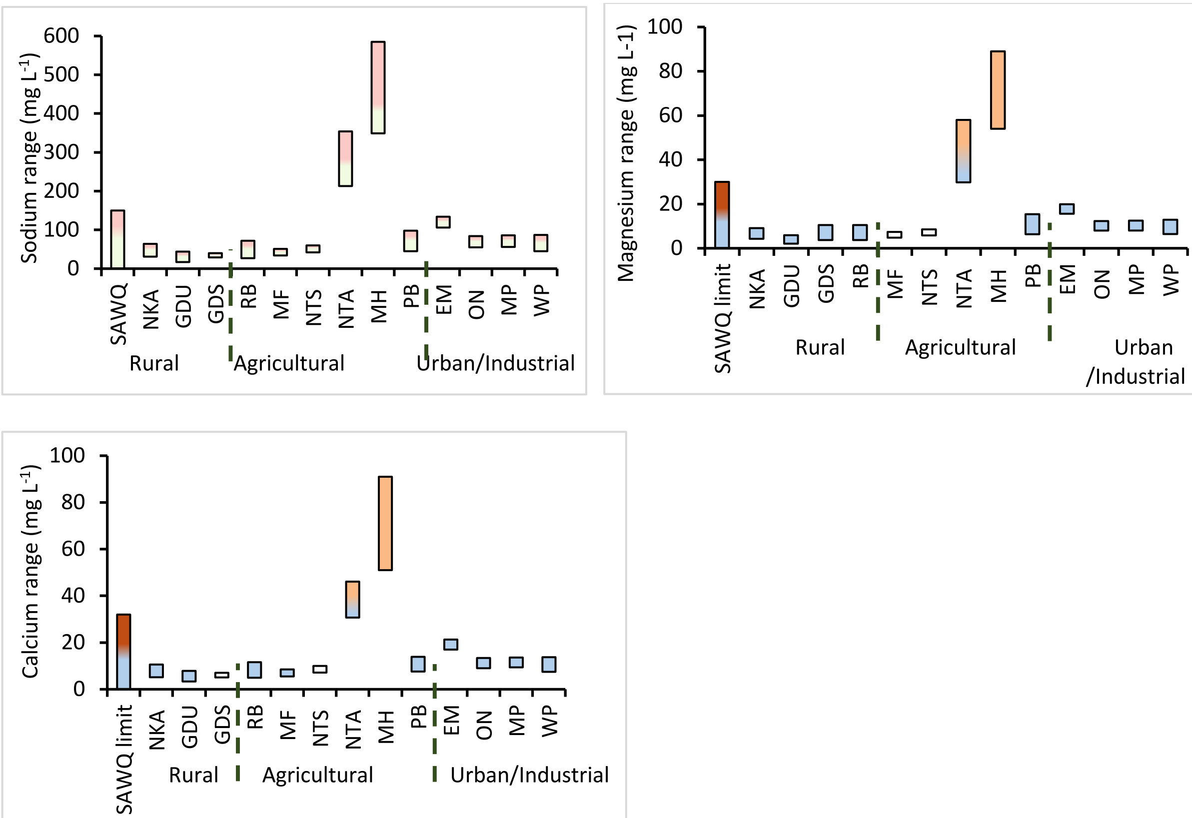


Fig. 4 Annual levels of sodium, magnesium and calcium along the uMhlathuze River

could be due to accumulation from Empangeni River since it occurs downstream after uMhlathuze River has met with the Empangeni River. These spikes may have indicated effects of the start of the rainy season but the impact on quality of uMhlathuze River was minimal with the levels still within the WHO permissible limits. The levels of Ni were within WHO guideline limits and normal drinking levels (<20 µg L^{-1}) throughout the year (WHO, 2017), but significant spikes were observed for all sites during the beginning of the rainy season in November. The spikes were much significant along Mholweni River (MH site) increasing up to 60 µg L^{-1}. Mholweni River has quarry activities which could potentially result in leaching of Ni into the river system.

WHO has no guideline limits for Fe and Mn but has set precautional values of 2000 and 400 µg L^{-1}, respectively (WHO, 2017). The Fe levels were relatively high but within the 2000 µg L^{-1} limit except for a few isolated instances during the rainy season where this limit was exceeded. The area around uMhlathuze River has brownish soils and iron oxide together with organic matter are responsible for this colour which might explain the high levels of Fe in the river. As rainwater infiltrates the soil and underlying geological formations, it can leach Fe to rivers as part of surface run–off (Conrad et al., 2020; Tashiro et al., 2020). Other studies have observed elevated levels of Fe in rivers due to the geochemistry of the region through which the river passes (Aleshina et al., 2024; Vodyanitskii et al., 2018). Besides the spike that occurred in November at the GDU site, the levels of Fe in the rural section of uMhlathuze River were generally lower with the levels continuously increasing downstream. Elevated levels of Fe due to anthropogenic activities have recently been reported in other rivers within South Africa including the Vaal River Basin (Moloi et al., 2020), Nzhelele River (Edokpayi et al., 2017), the Kaap River (Maphanga et al., 2024) and Mthatha

River (Madikizela et al., 2023), while lower levels have been recorded elsewhere including Mohlapitsi River (Addo–Bediako, 2024).

The concentration levels for Mn were also within the WHO health–based precautional limit (400 μg L^{-1}) for most of the year except for isolated spikes observed at NKA, GDU and NTA during November which marks the beginning of the rainy season. The spike in the rural areas was huge increasing from < 100 μg L^{-1} up to 633 and 713 μg L^{-1} at GDU and NKA sites, respectively. Besides the few spikes observed in the rural and agricultural sections, the Mn levels were generally higher in the urban and industrial section of the uMhlathuze River. With no evidence of the impact of wastewater effluents on the EM site along Empangeni River, the Mn levels could have emanated from local industries within the urban and industrial sections of the study. Industrial areas have been reported previously to elevate levels of Mn in river systems.

Other trace metals

There are no guideline limits for Al but a health–based precautional value of 900 μg/L is recognized (WHO, 2017). It was observed that concentration levels of Al during the rainy season from (November–March) were consistently above this value except for Empangeni tributary (EM site) and the Weir Pumpstation (WP) in the urban and agricultural region. The high levels observed in the rural areas could not be linked to any anthropogenic activities. Probably, during heavy rains leachable Al from the geology of Babanango and Nkandla may be washed into Umhlathuze River. Downstream of the river, Al could arise from agricultural, urban and industrial activities. This was mentioned by Mthembu and colleagues in their study at the same river in 2012, where Al was reported in higher concentrations at the ON, MP and WP sites (Mthembu et al., 2012). Elsewhere, Al has been reported in extremely high levels of 1.172–29.094 mg L^{-1} (Edokpayi et al., 2017).

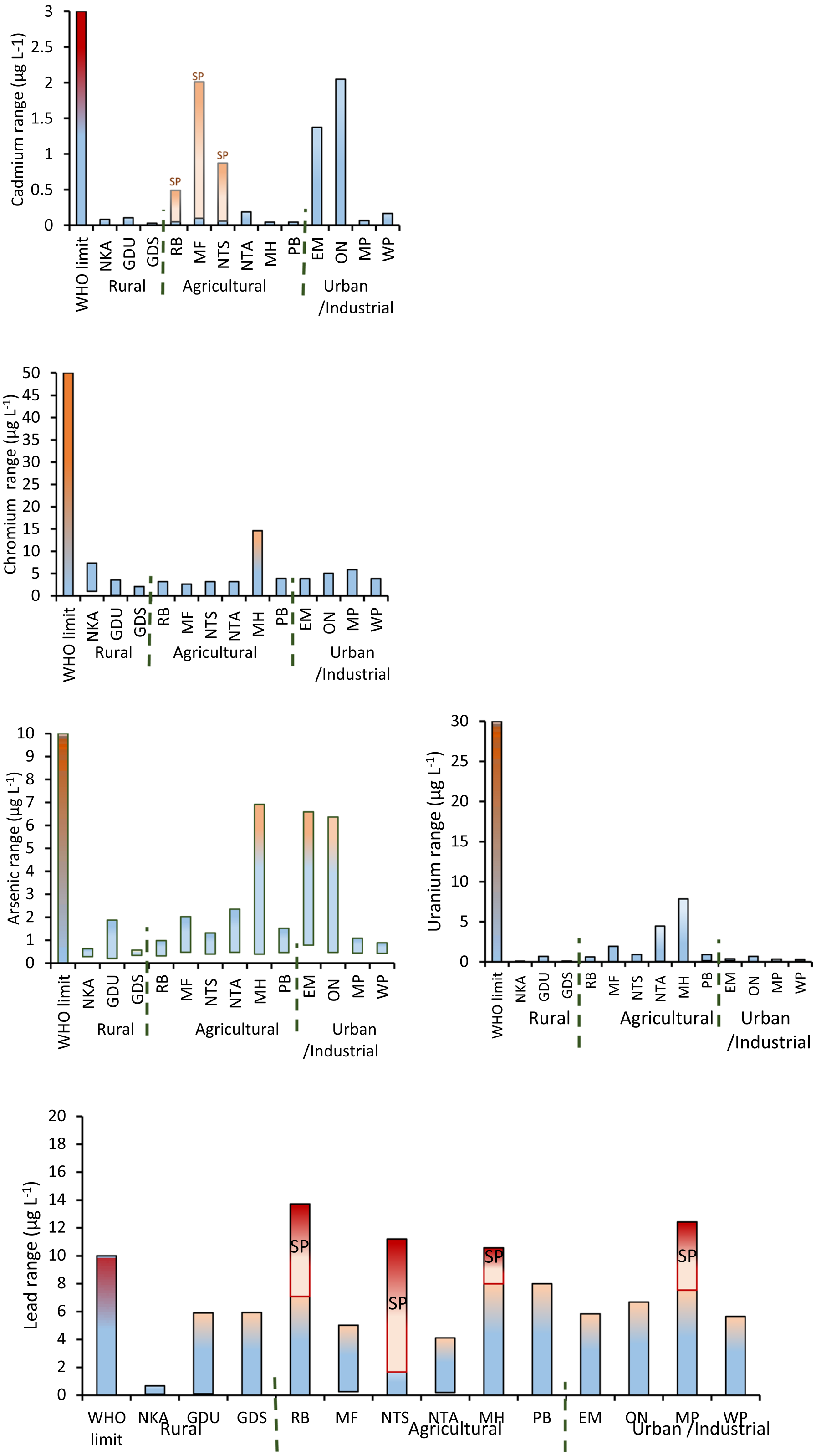
The levels of B and Ba were within WHO permissible limits for all sites throughout the year with a few spikes observed in the rainy season along Mholweni (MH site) and Ntambanana (NTA site) and Empangeni (EM site) tributaries. The levels of B along Empangeni River (EM site) were also a bit elevated compared to other sites ranging between 60 and 80 μg/L throughout the year. The levels of Se were within WHO permissible levels throughout the year. The Sb levels were mostly around 0.2 μg L^{-1} which is normal for natural unpolluted even though a few spikes up to 7.4 and 3.5 μg L^{-1} for MH and NTA sites, respectively were observed. The Sr levels were within 100 μg L^{-1} for most parts of the year except for MH, NTA and EM sites which represent the tributaries to Umhlathuze River. The seasonal concentrations recorded for each month are given on the Supplementary.

Trace toxic elements

Figure 5 represents the concentration range for the trace toxic elements (Cd, Cr, As, Pb and U) over a 12 months sampling period from December 2023 to November 2024. The seasonal concentrations recorded for each month are given on the Supplementary. The results show that the levels of Cd, Cr, As, U and Hg were all within the WHO permissible limits. Mercury was not detected except along the Empangeni tributary (EM site) where 0.399 μg L^{-1} was recorded along Empangeni River (EM site) in the month of March. This falls within the WHO permissible limit of 6 ug/L (WHO, 2017). Traces of Hg were also detected at the ON site which occurs after the Empangeni–Umhlathuze juncture recording 0.014 and 0.033 μg L^{-1} in the months of January and June, respectively. Traces of Hg were also detected on the Mholweni tributary in March (0.112 μg L^{-1}) and along the Ntambanana tributary (0.017 μg L^{-1}) in the month of May. Mthembu and colleagues from their study at the same river also reported Hg concentration levels within guideline limits (Mthembu et al., 2012).

The levels of Pb were within the WHO permissible limits for most of the year (nd–8 μg L^{-1}), but there were a few isolated incidents where the levels were above the guideline limits. For example, in May the RB site in the agricultural region recorded 13.7 μg L^{-1}, while the MP site in the industrial area recorded 12.4 μg L^{-1}. In March, the NTS site recorded 11.02 μg L^{-1} while the MH site affected by quarry activities recorded 10.6 μg L^{-1}. These were isolated incidents and could have resulted from episodic incidents within this region. Similar levels have been reported along

Fig. 5 Concentration range for trace toxic metals over the 12–months period. SP, single spike



Nzhelele River where concentration varied from 1 and 13 μg L^{-1} (Edokpayi et al., 2017) while at Mutangwi River the Pb levels were above 50 μg L^{-1} (Madilonga et al., 2021). A previous study conducted by Mthembu and colleagues reported 280, 380 and 500 μg L^{-1} Pb at ON, MP and WP sites, respectively which exceeded guideline limits and higher than the levels reported in the current study (Mthembu et al., 2012).

The Cd concentrations were very low (< 0.09 μg L^{-1}) in the rural and agricultural areas except for the once–off spikes that occurred in March at the RB site (0.5 μg L^{-1}), MF (2 μg L^{-1}) and NTS (0.9 μg L^{-1}). The spikes were still within the guideline limits but they might indicate the potential impact of runoff from fertilized farms in the area. In the urban and industrial area, the Cd levels were relatively high along Empangeni River (EM) that emerges from Empangeni Town, which could point to wastewater effluents and urban runoff as a source of Cd into Umhlathuze River. The levels along Empangeni River led to higher levels recorded on the ON site that represents a point after the Empangeni–Umhlathuze intersection. The impact is however minimal, with the levels still within guideline limits. Mthembu and colleagues previously reported 4 μg L^{-1} Cd at the WP site which was above permissible limits (Mthembu et al., 2012). Fifteen years later, this study indicates no threat to water quality due to Cd concentration levels at the same sites and the rest of uMhlathuze River sites upstream.

Figure 5 shows that As levels along Umhlathuze River were within the levels expected for natural water which is less than 1–2 μg L^{-1} (WHO, 2017). However, the impact of urban activities including domestic wastewater effluents was evident with Empangeni River (EM site) recording between 0.779 and 6.58 μg L^{-1} throughout the year. The highest concentrations were recorded in November and January reaching 1.59, 6.58 and 1.70 μg L^{-1}, respectively. Likewise, this had an impact on the ON site which also recorded the corresponding levels of 1.01, 6.37 and 0.730 μg L^{-1}, respectively for the same months. It was also observed that the As levels along Mholweni river (MH site) were affected by quarry activities resulting in concentrations of 0.393 to 6.92 μg L^{-1} throughout the year (Fig. 5). Importantly, the impact of these activities was still minimal because the levels were within the guideline limits.

Elementary interrelationships

A summary of the relationships between seasonal levels of metals along Umhlathuze River is presented as a biplot in Fig. 6. PC1 was the most important dimension that captured the largest amount of variation in the levels of metals. In this regard, the plot revealed three distinct seasonal groupings. The months of December–April which represent the rainy season were clustered together and defined by higher levels of Pb, Zn and Cr. This interrelationship between Pb, Zn and Cr could suggest a common source for these metals that is brought to the river by surface runoff during the high flow season. Previous studies on urban river pollution have observed a similar correlation between these metals and identified corrosion of galvanized steel structures from small–scale industries and informal dwellings that make their way into the environment as part of urban runoff as the probably source (Madikizela et al., 2023).

Another distinct cluster occurred from May–September primarily influenced by macro elements as well as Cd. A strong correlation occurs among macro elements suggesting that they were influenced by the low flow along the river. This could suggest that their natural existence in the river overweighs the influx from surface runoff and therefore become concentrated as the river water levels reduce during the dry winter/spring season.

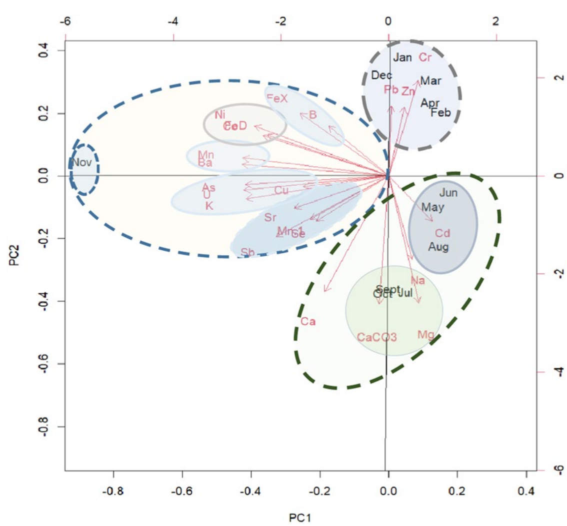


Fig. 6 Interrelationships between elementary levels along Umhlathuze River over a 12–month period

Most studies have found Cd interrelated with other trace elements. Cadmium was not detected in most of the months which could explain its deviation from other trace metals. Other studies have also observed that Cd trends were not corelated with other trace metals (Madikizela et al., 2023).

The final seasonal grouping was clustered in November consisting of most of the trace metals with a surprise of K which is a macro element. November marks the beginning of the rainy season and the high levels of these trace elements could result from the first flush effect where the first rains wash and accumulate the trace metals into the river after a dry spell (Conrad et al., 2020). While most of these elements were within the guideline limits, elevated levels along the tributaries were linked to wastewater effluents and urban runoff (EM site), quarry activities (MH site) and the geochemistry and agricultural activities (mainly NTA site). The levels of these elements remained high throughout the rainy season gradually decreasing until reaching minimum in June/July. Unlike the macro elements, the observation about trace elements maximizing during the rainy season suggests that the rains accumulate the trace elements into the river as part of surface runoff. Within this group, there were various definite clusters that showed close correlations between certain trace metals. For example, B is known to adsorb on iron oxides and expectedly its trend showed a strong relationship with Fe (Demetriou & Pashalidis, 2012).

Risk assessment

Water quality assessment

Table 2 represents WQI for uMhlathuze River in rural, agricultural, urban and industrial areas. Most of the sites had WQI < 20 and therefore were rated in the excellent category. Besides elevated concentration levels for physicochemical parameters as well as those from macro elements, the WQI values for NTA, MH and EM sites were still acceptable and rated as good. The HPI values calculated based on trace toxic metal concentrations are also summarized in Table 2. Overall HPI values were very low for all sites implying that the anthropogenic activities including agricultural and industrial development had minimal potential to cause pollution concerns due to toxic metals on Umhlathuze River.

The water quality in relation to irrigation was excellent in the rural areas with the SAR values ranging between 7.6 and 9.2. The river water was still good for irrigation in the agricultural region with SAR values ranging between 10.8 and 17.2, but water along the two tributaries (Mholweni and Ntambanana Rivers) was deemed unsuitable with the potential to harden the soil and reduce internal drainage. In the urban and industrial areas, Empangeni River water was deemed unsuitable with a SAR value of 27.8 while the water along Umhlathuze River was found to be suitable. The Na content as a %Na value was up to 81% for Ntambanana River and its water was deemed unsuitable for irrigation. This value together with the high chlorine levels reported in Sect. 3.2 indicated that the water from Ntambanana River was likely to be too salty for irrigation purposes. It is important to note that SAR and %Na values are not an indication of pollution but an estimation of water impermeability and saltness which is might hinder plant growth. Other studies have reported similar observations where some parts of a river were unsuitable for irrigation purposes including Molo River in Kenya (Chebet et al., 2020). The impact of tributaries on the main river quality has also been reported in literature including the Pechora River in Russia (Yakovlev et al., 2023).

Hazard index and incremental lifetime cancer risk

The HI values based on non–carcinogenic effects and ILCR values based on carcinogenic effects within uMhlathuze River are summarized in Table 2. While there is no evidence of using the raw water from Umhlathuze River for consumption purposes, it was still important to assess the potential risk considering the that river stretches from rural areas where access to treated water may be a challenge. In this regard, the results in Table 2 indicate that water from Umhlathuze River will not cause any health problems related to metal contamination with HI values below 1 for all sites. These values do not take into consideration other pollutants that may enter the river from wastewater treatment plants. In case of children, the water in the rural areas (NKA, GDU and GDS sites) was safe while other regions were not safe especially along the three tributaries (MH, NTA and EM sites) whose HI values were between 1.42 and 2.18. It is important to note that it is unlikely that people can

Table 2 Water quality and health risk assessment parameters for Umhlathuze River

Segment	Site	Water quality indices				Suitability for irrigation			Hazard index (HI) value				Cancer risk (ILCR value × 10^{-4})		
		WQI	Rating	HPI	Limit	SAR	Rating	Na (%)	Rating	Adult	Child	Infant	Adult	Child	Infant
Rural area	NKA	18.8	Excellent	6	100	7.6	Excellent	52	Permissible	0.29	0.88	1.32	1.86	5.59	8.38
	GDU	15.8	Excellent	9	100	8.3	Excellent	59	Permissible	0.32	0.97	1.46	1.71	5.13	7.70
	GDS	10.7	Excellent	5	100	9.2	Excellent	62	Doubtful	0.16	0.47	0.71	1.41	4.23	6.35
Agricultural	RB	15.6	Excellent	6	100	10.8	Good	62	Doubtful	0.24	0.72	1.07	1.60	4.81	7.21
	MF	17.8	Excellent	8	100	15.5	Good	70	Doubtful	0.37	1.12	1.68	1.62	4.87	7.30
	NTS	15.4	Excellent	6	100	13.4	Good	65	Doubtful	0.27	0.80	1.19	1.66	4.98	7.47
	NTA	30.2	Good	7	100	76.3	Unsuitable	81	Unsuitable	0.47	1.42	2.13	2.19	6.56	9.83
	MH	36.1	Good	9	100	44.2	Unsuitable	69	Doubtful	0.73	2.18	3.28	4.99	15.0	22.4
	PB	20.2	Excellent	6	100	17.2	Good	68	Doubtful	0.27	0.82	1.23	1.88	5.65	8.47
Urban and Industrial	EM	26.0	Good	9	100	29.5	Unsuitable	72	Doubtful	0.48	1.43	2.15	2.23	6.68	10.0
	ON	20.4	Excellent	10	100	17.5	Good	67	Doubtful	0.48	1.43	2.15	2.15	6.46	9.70
	MP	18.1	Excellent	6	100	18.2	Permissible	67	Doubtful	0.34	1.03	1.54	2.21	6.62	9.93
	WP	18.7	Excellent	7	100	18.0	Permissible	67	Doubtful	0.26	0.79	1.18	1.20	3.60	5.39

WQI, water quality index; HPI, heavy metal pollution index; SAR, sodium adsorption ratio; HI, hazard index; TCR, total cancer risk drink the unprocessed water from these tributaries. Finally, the untreated river water was found to be unsuitable for consumption by infants throughout the entire sampling region except for the GDU site whose predicted HI value was 0.71.

Conclusions and recommendations

The study has provided insights on the potential impact of anthropogenic activities on the water quality along Umhlathuze River and its three main tributaries based on levels of physicochemical properties, anions, macro elements and trace metals. Along the main river, these parameters were mostly within guideline limits but they were elevated and at times above the guideline limits along the tributaries. Agricultural activities, quarrying, wastewater effluents and urban runoff were identified as potential pollution sources along the tributaries. However, a crucial finding is that the elevated pollution levels along the tributaries had minimal impact on Umhlathuze River with the parameters immediately diluted to normal conditions as soon as the water from the tributaries entered the main river. Despite this resilience of Umhlathuze River, dependency on its dilution capabilities cannot be a sustainable management strategy. The tributaries act as critical and chronic pollution hotspots that should be closely monitored to prevent the river from being overwhelmed on the long run.

The study further demonstrated that water quality along Umhlathuze River and its tributaries is affected by seasonality and anthropogenic activities within its tributaries. Based on principal component analysis, the elementary levels along Umhlathuze River and its tributaries were grouped into three distinct groups; the rainy season (December–April) cluster consisting of trace metals associated with surface runoff; the dry season (May–September) cluster characterized by macro elements that tend to concentrate during the cold low flow season; and the unique first flush event in November marked by those trace elements that experience a spike during the first rains. This insight may be crucial in providing a basis for source control and a more dynamic monitoring schedule that targets pollution sources and the potential impact of episodic pollution spikes along Umhlathuze River and its tributaries. With the study focusing on the aqueous phase of the river, further studies can be done to include the sediments and microorganisms that exist along Umhlathuze River.

Author contributions M.B did project planning, collected and analyzed samples, processed results, and wrote the initial draft of the manuscript P.N and S.N were the MSc supervisors for M.B, did project planning, approved results, and reviewed the manuscript.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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