

The dynamics of fluvial transportation of uranium in the Rietspruit River system in South Africa

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Declaration 1 - Plagiarism

I, Iyioluwa Busuyi Raji, hereby declares that this thesis presented to North-West University (NWU) for the degree of Doctor of Philosophy in the Faculty of Natural and Agricultural Sciences, School of Environmental Science, and the study therein is my novel study and neither the unabridged study nor any part of it has been, is being or is to be submitted for alternative degree at this or any other university.

Declaration 2 – Publications

This section includes specifics of articles that make up part of the research presented in this thesis. This thesis includes published and submitted articles. All publications are written by the student, Iyioluwa Busuyi Raji in collaboration with Prof Frank Winde and Dr Adeline Ngie and assisted by Mr Emile Hoffmann and Mr Ewald Erasmus.

Publication 1: I. B. Raji, E. Hoffmann, A. Ngie, F. Winde – “assessing health risk associated with uranium in Rietspruit water, Far-West Rand Goldfield, South Africa”. International Journal of Environmental Science and Technology, 2022, 1-14. <http://doi.org/10.1007/s/3762-022004673-z>.

Publication 2: IB Raji, E. Hoffmann, A. Ngie, F. Winde – “assessing uranium pollution levels in the Rietspruit river, Far-West Rand Goldfield, South Africa”. International Journal of Environmental Research and Public Health, 2021, 18(16), 8466. <http://doi.org/10.3390/ijerph18168466>.

Publication 3: IB Raji, E. Hoffmann, A. Ngie, F. Winde – “Assessing uranium remobilization in water-sediment system and diurnal dam water chemistry”. Under preparation for submission.

Publication 4: IB Raji, E. Hoffmann, F. Winde, A. Ngie – “Assessing uranium mobility within the Rietspruit system, Far West Rand Goldfield, South Africa”. Under preparation for submission.

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Dedication

I dedicate this research work most especially to my entire family members for giving me the inspiration and drive to pursue this career. Without their support, I will not be able to achieve my academic goals.

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Abstract

Mining of precious metals started many years ago, for instance, gold (Au) and the offshoot uranium (U) mining in South Africa's Witwatersrand Basin. Consequently, mining activities contaminate the environment with potentially toxic elements, which could be useful but dangerous as well. The presence of U in the atmosphere, biosphere, lithosphere, and hydrosphere has a negative impact on the exposed population. The main aim of this research is to investigate the dynamics of fluvial transportation of U in the Rietspruit river system located in the Gauteng Province of South Africa.

In this study, the concentrations of U in the Rietspruit fluvial system were quantified using an inductively coupled plasma mass spectrometry (ICP-MS) machine at the Eco-Analytical Laboratory of the North-West University, August 2020. The river is an important stream because it is utilized for various purposes which include domestic, farming, and spiritual purposes. However, the main source of the water stems from the Peter Wright dam which is on the premises of a Au and U mine.

Within the mining impacted source area, elevated concentration of U was logged. Uranium concentration of about 781 µg/L was logged in the furrow taking water to the Peter Wright dam. In the slimes dam and sand dump, a concentration of 72.7 mg/kg and 1043 mg/kg were recorded, respectively. The highest concentrations of U were however recorded about 6 km and 24 km downstream of the mining area in a marshland, with concentration above 1200 mg/kg recorded at both sites. This shows that dams and wetland are sinks for U leading to the immobilization of U in the dam's and wetland's sediments. Other toxic elements such as arsenic, cadmium, mercury and lead were also recorded in the Rietspruit water and sediment at a concentration exceeding the acceptable limits.

In regions where human contact was observed, the amount of U in the collected water sample was over the acceptable limit of U in drinking water 30 µg/L. Due to this, both carcinogenic and non-carcinogenic health risk assessment was done based on the recorded concentration of U in the water. The result showed that the observed human exposure is more at risk of chemical toxicology than radiological toxicology.

To study the mobility of U in the water-sediment system, a large amount of sediment was collected from a U polluted dam downstream of the Rietspruit. After drying under normal atmospheric conditions, the sediment was rewetted with rainwater. Uranium concentration of 1211 µg/L was logged in the water sample collected instantly after rewetting. This was mainly

due to the dissolution of the salt crust rich in the U. This was the highest concentration of dissolved U recorded after rewetting the sediment. It was observed that the release of U into the water column was not linear due to the different phases that U was adsorbed into, for example, iron oxide, manganese oxide, sulphates and carbonates which all have different dissolving rates in water.

In conclusion, the Rietspruit is polluted by the U because of the Au mining operations that took place around the Rietspruit headwater. About 24 km downstream of the Rietspruit, the water is not suitable for domestic, agricultural, and religious activities. Residents of Lawley, farmers, and worshippers, observed using the Rietspruit water, should be sensitized about the dangers involved in the continuous usage of the Rietspruit water. Further study that will quantify the concentrations of U and other toxic alloys in agricultural products – crops and animals within this environment should be done.

Keywords: Uranium, Rietspruit, health, risk, contaminant, immobilization, remobilization, sinks, wetland

Preface

This thesis is written in an article format. All the articles were composed and written by the student under the guidance of the supervisors. Two of the articles, assessing uranium pollution levels in the Rietspruit River, Far West Rand Goldfield, South Africa and assessing health risk associated with uranium in Rietspruit water, Far West Rand, Goldfield, South Africa have been published by International Journal of Environmental Research and Public Health, and International Journal of Environmental Science and Technology, respectively. Chapter 3 and 4 are being prepared for submission to a peer-reviewed journal. There is information overlap between chapters. This is because the study area is the same and some methodologies were repeated in this study. The co-authors of the published articles are the supervisors except Mr Emile Hoffmann who assisted the student during different phases of this study and Mr Ewald Erasmus who gave technical advice on the outcomes of chemical analyses.

Chapter 1

1.1. Introduction

The exploitation of mineral deposits such as gold, uranium, platinum, diamonds, coal, copper etc. has been an eminent foundation of the South African financial system for over a century (Fedderke & Pirouz, 2002; Stilwell et al., 2000), contributing to the elevation of the country as the most industrialized nation on the continent. Mining not only contributes to the development of first-class infrastructures like hospitals, schools and roads but also creates employment for locals and migrants (Eisler, 2003). The Mineral Council South Africa stated that R351 Billion was contributed to the South African Gross Domestic Product (GDP) in 2018 alone by the mining sector. A total of 456,438 people worked in the mining sector in 2018 (Cole & Broadhurst, 2020).

In the 19th century, gold (Au) was discovered in economically viable quantities in the Witwatersrand Basin, South Africa (Durand, 2012; Rösner & van Schalkwyk, 2000). South African Au contributes about 4.2 % of international Au production and the Witwatersrand Basins remains home to the world's largest Au deposit (Nhleko & Neingo, 2020). Notable Au mines within this Basin include Sibanye Gold, AngloGold Ashanti, Harmony Doornkop Gold, South Deep Gold, Libanon Gold, Savuka Gold and many more. Two Au mines are found within the study area: South Deep Gold and Cooke 4 Ezulwini Plant. While South Deep Gold Mine is still operational, Cooke 4 Ezulwini Plant was decommissioned in 2016 (Kritzinger, 2017).

The Black Reef Formation of the Witwatersrand Basin contains a huge concentration of Au and uranium (U) (Fuchs et al., 2016). They are found in association with a variety of other ore minerals such as pyrite, chromite, galena, and sphalerite (Fregola et al., 2023). The mining of Au and U together started in the late 1950s on a small scale. According to Coetzee et al., 2006, U is being mined in the country as a by-product of Au mining.

Mining and industrial activities have consequently added to the gradual rise of potentially toxic concentrations of elements in the environment which have impacted negatively on lives, including humans, plants, and animals (Jacob et al., 2018; Fashola et al., 2016; Kamunda et al., 2016; Wang and Wan, 2015; Fasinu & Orisakwe, 2013; Fernandez-Luqueno et al., 2013; Munnik, 2010; Yabe et al., 2010; Rebecca A. Adler, 2007; Ramadan, 2003; Fatoki &

Mathabatha, 2001; Förstner, 1976). Kamunda et al., (2016) reported that Au mine tailings in the Witwatersrand Basin constitute the major origin of heavy metal contamination of the ecosystem. Wang & Wan (2015) concluded that the manufacturing of nuclear-powered weapons and fuel have left soils and sediments at several locations contaminated with poisonous concentrations of U. Uranium could become mobile because of changes in the oxidation state, the presence of terminal electron acceptors and the concentrations of complexant - a substance that forms complexes with molecules or ions of a kind. This is a proof that the effect of heavy metal pollution is not limited to the contaminated surroundings, but it could extend regionally several kilometres away from the source of pollutant(s).

The potentially toxic elements find their way to contaminate soils, water, and air, which ultimately end up being consumed by humans, either directly or indirectly (Jacob et al., 2018; Fashola et al., 2016; Fernandez-Luqueno et al., 2013; Winde & van der Walt, 2004a; Ramadan, 2003). Naturally, soil contains minimal concentrations of potentially toxic elements depending on the parent materials. Soil is formed from rocks because of either physical, biological or chemical weathering. However, the concentration of these potentially toxic elements has escalated due to anthropogenic activities such as mining, farming, and industry (Gronowski, 2013).

Heavy metals (sometimes referred to as potentially toxic elements) are metals of high density or relative atomic mass (Alloway, 2012). Examples of heavy metals are U, lead (Pb), mercury (Hg) etc. Toxic elements have been known to be the genesis of several health issues in humans, causing series of cancers of several vital body organs and brain damage (Machate, 2023; Mohammadnezhad et al., 2023; Parida & Patel, 2023; Kamunda et al., 2016). These health issues are ultimately terminal in most cases. Uranium, a radioactive heavy metal, for example causes kidney damage in humans and animals after the inhalation or ingestion of U compounds (Keith et al., 2013). Inhalation of U is largely from polluted air from a mining area (Brugge & Buchner, 2011; Ahmed, 1981) while ingestion of U is mainly from drinking mine polluted water and consuming agricultural products irrigated by polluted water or plants grown on polluted soil (Schonfeld et al., 2014; Winde, 2011a; Winde, 2004a). As U in surface water and sediment is the focus of this study, U will be discussed extensively in the literature review of this study. Uranium in air exists as tailings dusts that eventually fall into surface water, on plants or on soils through settling or rainfall (Zupunski et al., 2023; Winde & de Villiers, 2002a; Haschke, 1998; Bennett et al., 1975). It will then accumulate in the sediment or soil of streams.

Uranium will eventually be absorbed by the roots of plants in such environments and stored in edible parts of the plants like leaves and fruits (Lauria et al., 2009). The leaves and fruits will end up being consumed by animals and humans, therefore increasing the U concentration in human and animals, which can lead to several illnesses (Faa et al., 2018; Schnug & Lottermoser, 2013; Winde, 2011a; Parrish et al., 2008; Callahan et al., 2004; Bleise et al., 2002).

Also, U from the eroded tailings moves into the water body which eventually enters the food chain via irrigation (Schonfeld et al., 2014; Winde, 2011a; Anke et al., 2009; Arogunjo et al., 2009; Zikovsky, 2006). In addition, seepage from tailings dams infiltrates the aquifers, thereby elevating the concentration of U in the groundwater (Winde, 2004a; Winde & van der Walt, 2004a). People who live near hazardous waste sites and mines, work in the mining industries, eat crops grown on contaminated soil or drink water from a U waste disposal point have higher exposure (Winde, 2010). The health effects of U consumption will be discussed later in this study.

1.2. Problem statement

Mining operations have detrimental impacts on the environment, most especially on scarce ground- and surface water resources. The negative impacts are not limited to the immediate area or location of the mine but rather, these extend to virgin areas where no mining operation has ever taken place. For example, dewatering, which is a process whereby more water is released from underground mining shafts than naturally can be replenished in the dolomitic aquifers, causes the continuing reduction of the groundwater table. This could result in the drying up of irrigation boreholes and springs, plus massive ground movement in near-karst environments in the form of sinkholes and dolines (Winde & Erasmus, 2011).

The water-solubility of a U compound determines its mobility in the environment as well as its toxicity (Blake et al., 2017; Cumberland et al., 2016; Gronowski, 2013; Winde & van der Walt, 2004a). Other factors that affect the mobility of U in aquatic environments include the number of suspended particles, pH, oxygen and carbonate concentration, the chemistry of the sediment, and the electrical conductivity of the stream water. Uranium may also be released back into the water through plausible environmental changes such as acidification and oxidation (Winde, 2010).

However, the exact pathway mechanisms and dynamics of fluvial transportation of U in the Rietspruit are under-reported. There is a need to quantify the concentration of uranium and other potentially toxic elements in the Rietspruit. This is essential because the Rietspruit is a stream that is being used for various purposes which include agricultural, domestic, and religious. Due to human exposure, there is a need to calculate the health risk based on the concentration of U determined to exist in the Rietspruit water.

1.2.1. Research questions

These following questions necessitated this research:

- a. What is the extent of U pollution in the Rietspruit fluvial system?
- b. What are the possible sources of U pollution in the Rietspruit fluvial system?
- c. Is there a possibility of human exposure to U from the Rietspruit – if yes, to what extent?
- d. Which health risk is more prevalent – carcinogenic or non-carcinogenic health risk?
- e. What are the pathways, mechanisms, and dynamics of U in the Rietspruit?
- f. If the Rietspruit becomes a non-perennial stream, is it possible for U to be remobilised from solid wastes and dry river channels after a rain event?
- g. What are the concentrations of other potentially toxic elements in the Rietspruit?

1.3. Research aim and objectives

The main aim of this research was to investigate the dynamics of fluvial transportation of U in the Rietspruit river system located in the Gauteng Province of South Africa.

The specific research objectives of this study are:

- 1) To determine the U concentration along a longitudinal profile in sediments and stream water of the Rietspruit.
- 2) To establish the impact of rain events on U-pollution by tailings (first-flush event).
- 3) To assess the health risk associated with U.
- 4) To assess U remobilisation in water-sediment systems.

The Rietspruit River flows through the Highveld region of South Africa. The headwater of the Rietspruit is the Peter Wright dam, a farm-dam with an elevation of approximately 1680 m above sea level, in the West Rand of Gauteng and flows south for about sixty (60) km, until it joins the Vaal River (Figure 1.1).



5

Gauteng is the smallest Province in terms of land area of all the provinces in the Republic of South Africa, bordered on the north by Limpopo, Mpumalanga on the east, Free State on the south and North-West on the west (Katima et al., 2018). It is established on the Highveld of South Africa and extends northward from the Vaal River. The climate of Gauteng is warm and temperate (Scott, 1999). Rainfall averages 650 mm annually. Despite the highly urbanised status of the province, commercial farming of wheat, corn, sorghum, groundnut, and dairy farming is still practised. Gauteng has a vast amount of Au in the ridge of Au-bearing rock of the Witwatersrand and other minerals such as platinum, chromite, iron ore and U in commercial deposits. The catchment was characterised as being largely rural, with mostly grassland-type cover and with surrounding plots of agriculture and portions of mining. The vegetation is limited to natural Grassveld with no large trees or any other significant natural obstacles.

The Witwatersrand plateau is made up of a 7000 m thick layer of sedimentary rock laid down about 260 million years ago (McCarthy, 2013). The Witwatersrand Supergroup consists of quartzite, banded iron stones and some marine lava deposits interspersed with softer and easily eroded mudstones, tillites and conglomerates. Gold is found in the conglomerate strata of the newer members of the Supergroup.

The Witwatersrand Basin (Figure 1.2) is one of the oldest geological formations on the planet and was formed during the Archaean Eon (Truswell & Harris, 1977). It was laid down in two phases, over 260 million years. The first phase, which continued for about 60 million years, is made up of sedimentary deposits in shallow seas; it resulted in a 4500 m thick layer of sediment called West Rand Group of Witwatersrand rocks. The second phase resulted from the withdrawal of the Witwatersrand Sea, which hosts a rich deposit of Au. This formed the Central Rand Group of about 2500 m thick layer of rock. The West Rand Group and Central Rand Group of rocks together form the Witwatersrand Supergroup (Norman & Whitfield, 2006).

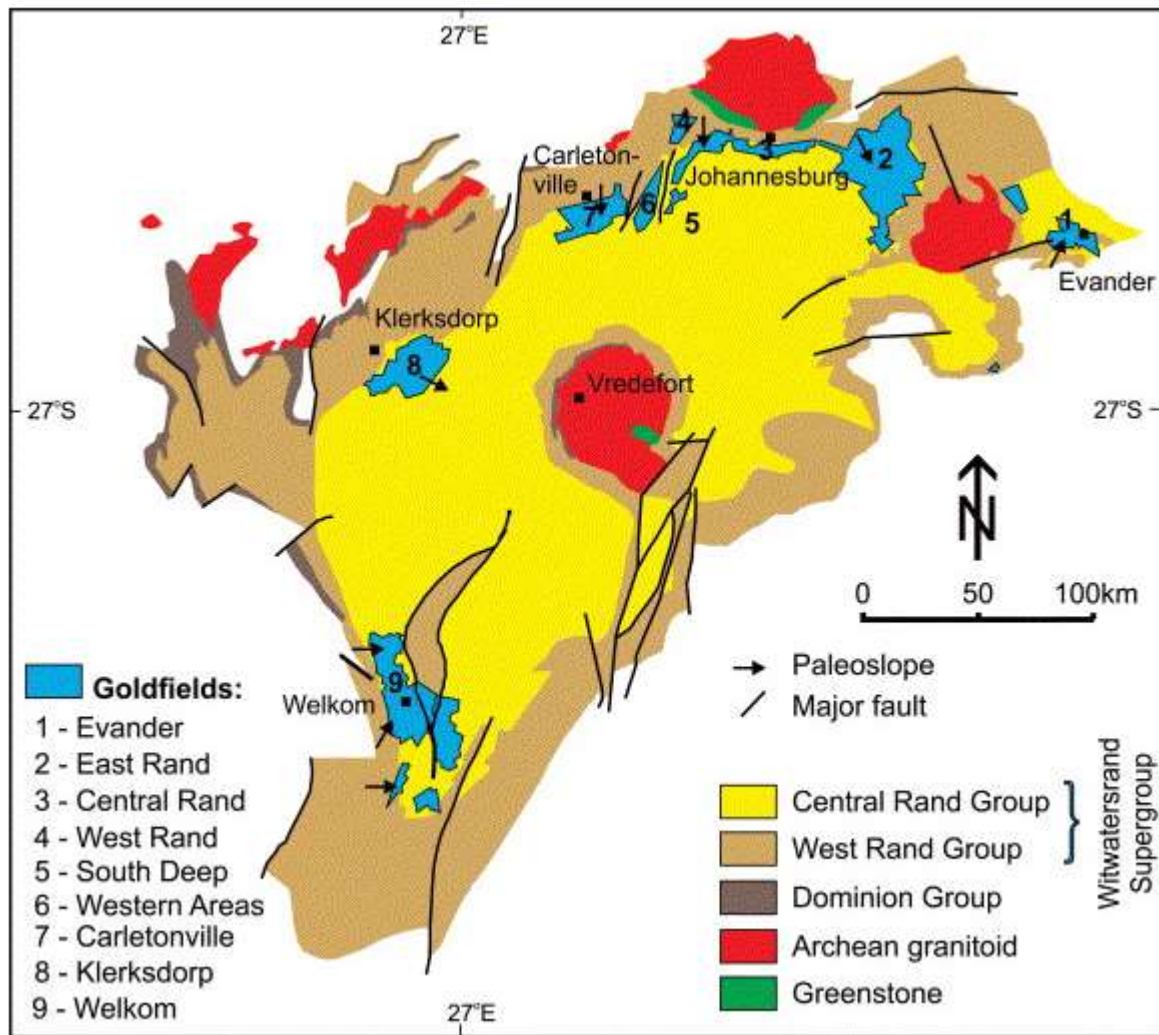


Figure 1.2: Surface and subsurface geological map of Witwatersrand Basin and major goldfields (Source: Frimmel & Minter, 2002)

The Peter Wright dam is in the West Rand Group of the Witwatersrand Supergroup. The Ezulwini Gold Mine is established a few metres from the dam. Discharge from the mine is channelled into the dam through artificial furrows and pipelines. The South Deep Gold Mine is located southwest, a few kilometres from the Ezulwini Gold Mine and it also releases its wastes from the mining activity into the Leeuspruit Dam, which flows down the Leeuspruit stream to join the Rietspruit. The Rietspruit is also joined by the Klein-Rietspruit downstream and flows southwards to the Vaal River. Figure 1.3 below shows the study area map and the major tributaries.

Due to the mining of Au in the environment of the Rietspruit, several informal settlements have been established within the catchment area. An informal settlement is an area with groups of housing units that were constructed illegally without government approval (Huchzermeyer,

2003). These informal settlements are characterised by non-existence of potable water (piped water systems/potable drinking water), giving rise to the utilization of untreated river water for drinking and personal hygiene, and for various agricultural purposes in the Rietspruit catchment, like fishing and irrigation. An example of the informal settlements found in the study area is Lawley (Figure 1.3).

The leading sources of U pollution from the Au mining site are the pumped underground water, tailings deposit from the mines, rock, and sand dumps (Coetzee 2002). In most cases, this results in the enhanced release of leached U and other toxic elements from the tailings particles. Due to the various activities of the Au mines abundant in the study area, tailings within the area constitute a major potential source of U pollution of water. Other sources of U pollution of water include run-off from contaminated surfaces such as slimes dam, rock dumps, ore piles, seepage from unlined return-water dams, and leakages from broken canals, pipelines etc. Knowing the sources of U pollution is important but it is of greater importance to understand the mechanism and dynamics of U pollution.

Sediments found in dams, wetlands, and the streambed of the Rietspruit river act as sinks for dissolved U transported in stream water (Humphries et al., 2017; Winde & Erasmus, 2011). Under certain changes in the environmental conditions such as pH, electric conductivity, oxidation and reduction potential, temperature and in most cases flooding and cattle grazing, such sediments release the U, which was trapped in them, back into the water column. This ultimately turned the sediments from a sink into a secondary source of U pollution.

Uranium can enter the human via several exposure paths from the source, being largely tailings dams in the catchment, through groundwater, to soil, and to river water (Boelee et al., 2019; Winde, 2011a). Contaminated groundwater may also be used unknowingly by humans for agricultural and domestic purposes. Uranium pollution is not limited to humans residing within the environment of the mines but also people staying at a far distance from the mining area who rely on flowing water or groundwater that, unknowingly, has already been contaminated by U.

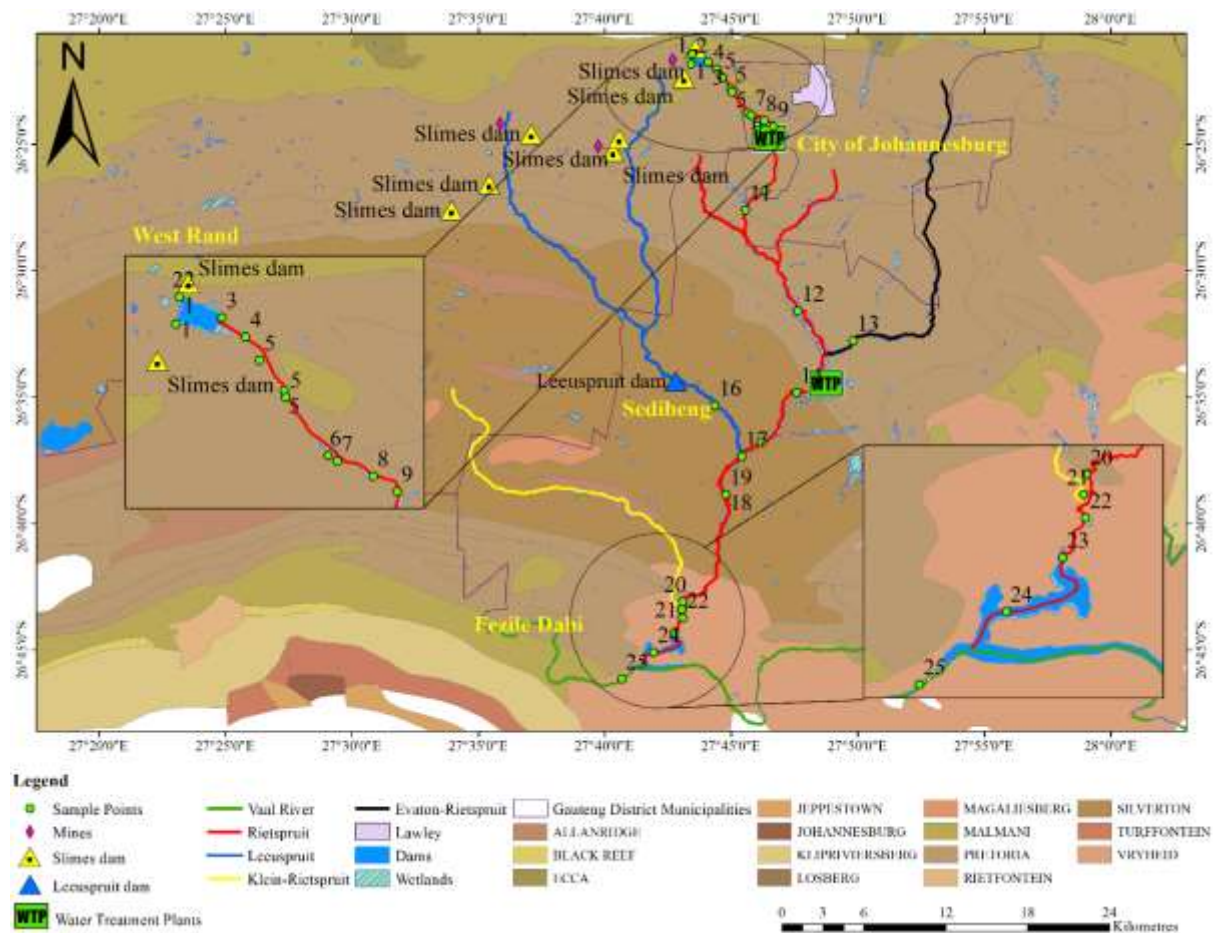


Figure 1.3: Map of the study area showing all the sampled sites (Adapted base geological map created by South African National Space Agency, SANSA, 2018)

This study area was chosen because it has experienced many years of Au mining and the environment has diverse land uses. For example, there is a large-scale wheat farm very close to the mining site, cattle grazing is very common, there is fishing activity at the Peter Wright dam, informal settlements have been established, religious activities are conducted along the Rietspruit, cooking is done using the water from the stream, and drinking the stream water and bathing in the stream. All these activities were observed during sampling. Due to these mining activities and human use of the water, it is crucial to study the dynamics of fluvial transportation of U in the Rietspruit to contribute to knowledge and make public the result of the findings.

1.5. Experimental group sites

In August 2020, sediment and water samples were collected from thirty (30) sites which are found in four different catchment areas downstream of the Rietspruit and several locations within the Peter Wright dam (Figure 1.3). For example, the tailings, acid mine drainage found

along the trough which is channelled to the Peter Wright dam and a broken pipeline carrying water from the dam to the wheat plantation. The study area is divided into ten (10) experimental group sites to reflect the potential sources of the pollutant (U), the Rietspruit headwater (Peter Wright dam), the U sinks (wetlands and dam), and the impact of the tributaries (Evaton-Rietspruit, Leeuspruit, Klein-Rietspruit and Vaal River) as well as the effect of the water treatment plants that discharge municipal waste into the Rietspruit. Sample locations were systematically selected based on accessibility to the stream, human and animal exposure, presence of dams and wetlands, and safety, in no order. A similar approach was used in the study of Windisch et al., 2022 where river confluences, dams and farmlands were used in selecting sample sites.

Cooke 4 Ezulwini Plant environment: Within the mining environment (Figure 1.4) are a residence for mining staff, two evaporation dams and the Peter Wright dam. We also have two mining tailings located at the north and south of the Peter Wright dam. A commercial wheat plantation is established within the environment as well, which utilizes Peter Wright dam water for irrigation purposes. Grazing of cattle was also seen during sampling activity next to the channel taking water from the mine to the dam. Due to cracks on the walls of the channel, water spills to the ground surface keeping the grass evergreen, therefore encouraging the cattle to feed there (Figure 1.5).

The establishment of uncovered tailings close to the residence of the mine poses a health risk. This is because U daughter cell (radon) is readily available in the air most especially within a Au mining area. Also, tailings dust will settle down on the water bodies and the wheat farm, most especially during the windy winter season.

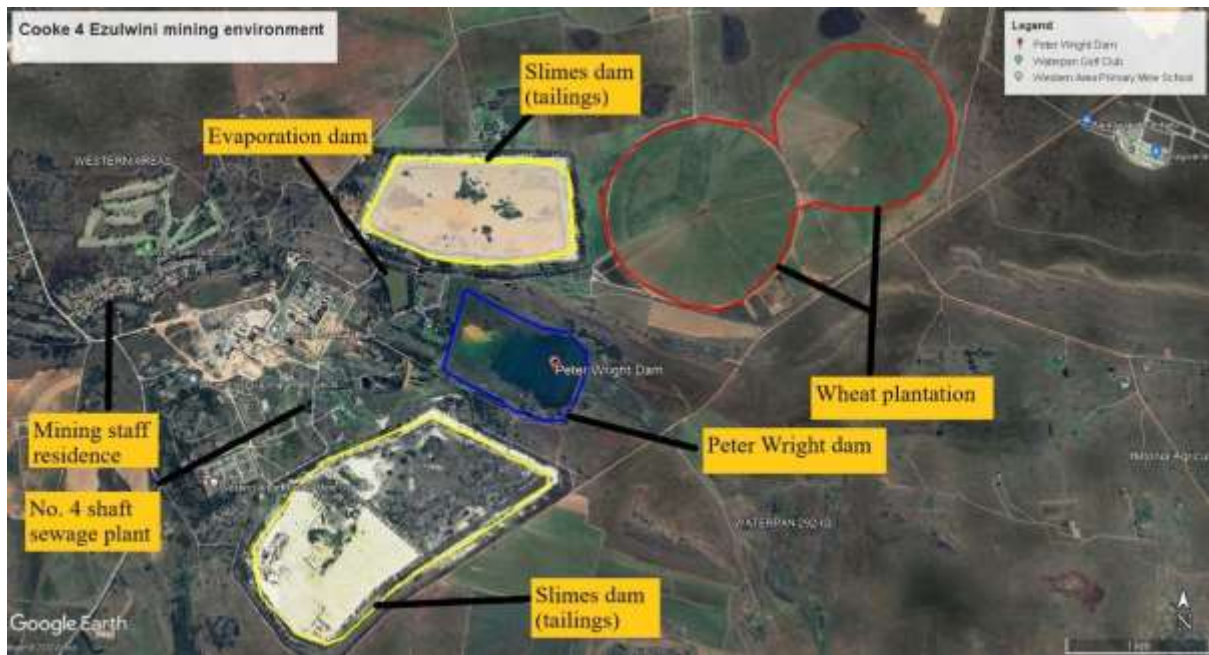


Figure 1.4: Google Earth Pro (2022) aerial map of the Cooke 4 Ezulwini Plant and environment



Figure 1.5: Cattle grazing next to the PW dam inflow water channel October 25th, 2020

Peter Wright dam inflow and outflow: The Peter Wright (PW) dam has two feasible inflows of water. Site one (1) is the man-made furrow called PW dam inflow and the other (site 2) is the channel water. Site three (3) is the PW dam outflow (Figure 1.6B). Fishing activities (Figure 1.6A) and religious activities were witnessed around the PW dam. In addition, the worshippers were observed drinking the water during sampling. Water from the dam flows out through a large concentrate channel (site 3). This is the main source of the stream water, and it is in the C22H Quaternary Catchment. The entire dimension of the C22H Catchment is 454.14 km².



Figure 1.6: Fishing activity at the PW dam (A) and PW dam outflow (B)

Wetlands: Downstream of the PW dam outflow (Figure 1.6(B) above) the first wetland is located, approximately 1.5 km from PW dam, (site 4) and the second wetland, approximately 1 km from the first wetland, (site 5) which were sampled (Figure 1.7A). Cattle grazing was witnessed around the first wetland during the second visit to the site, but none was witnessed around the second wetland. However, since the area is an open field, it is expected that animal grazing will also occur around the second wetland. Wetlands and dams are important for sampling because they serve as sinks for U (Humphries et al., 2017; Ross & Dudel, 2008; Coetzee et al., 2002). This is due to the limited supply of oxygen which will reduce U from its oxidized and mobile soluble state (U^{6+}) to the reduced and immobile and less soluble state (U^{4+}). This will be discussed further in the literature review section and result discussion of this study. During sampling of the first wetland (site 4), the site was widely burnt (source of fire was not investigated) and this was done during the winter season when there was no rainfall (Figure 1.7A). Due to the uptake of toxic elements by plants, it is expected that U will be remobilised from the plant's ashes. The second wetland was sampled during the rainy season (Figure 1.7B). The impact of rainfall is one of the research questions of this study and the result

will be discussed in the later chapters of this study. The wetlands are also located within the C22H Quaternary Catchment.

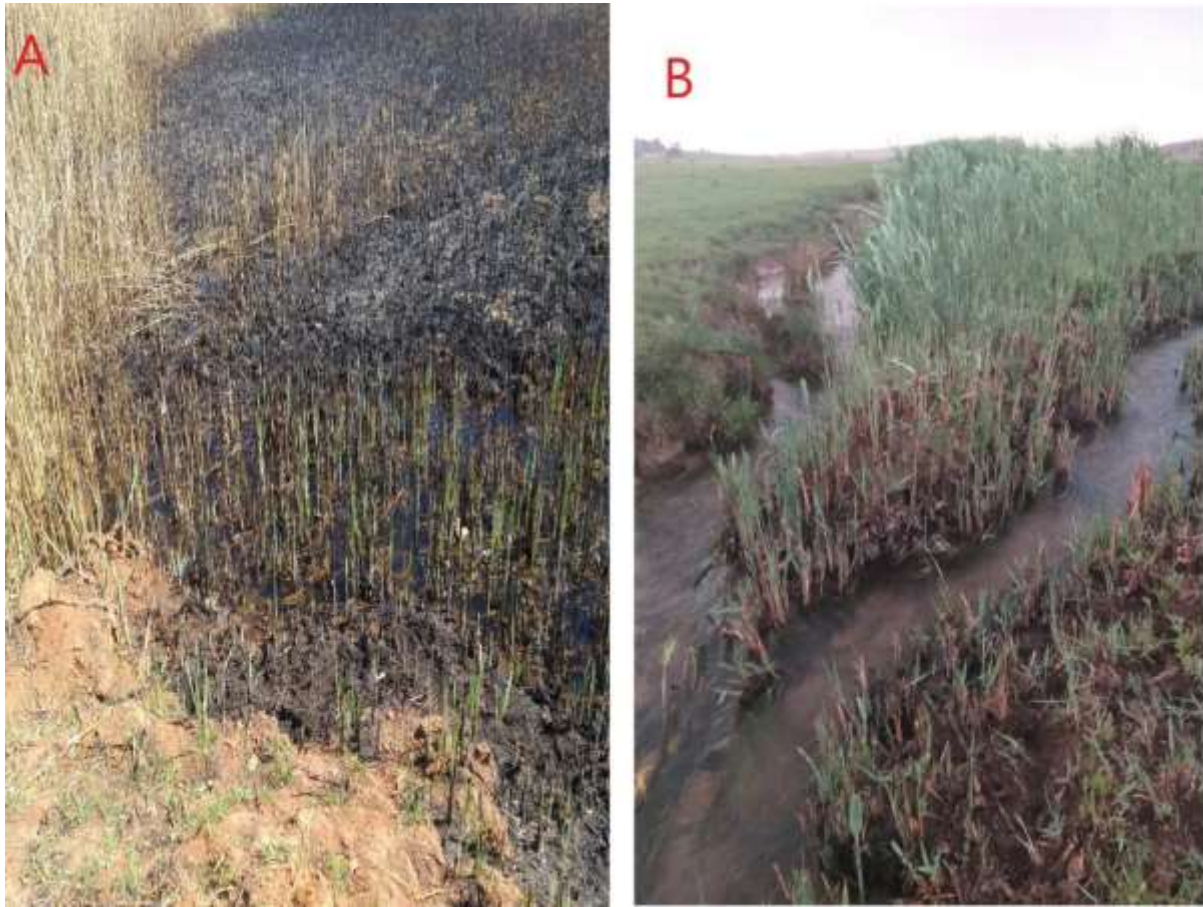


Figure 1.7: Wetlands after PW dam outflow. (A) The first wetland (B) The second wetland

Damlit environment: About 6 km from the PW dam the sixth (site 6) sampled site of this study is located. The site is called damlit due to the small size of the dam as the dam is not specifically named. A farm is located southeast of the damlit and on the eastern part of the damlit. The farm owner reliably informed us that the water from the damlit is used for irrigation of their farm (depending on the season, crops of maize or potatoes are planted) and drinking water for cattle. Fishing activities also take place in the dam, but none was witnessed during sampling, we were informed by the farm owner. A mini-hydropower station is also situated there, which provides electricity to the residents of the area (Figure 1.8). Two hundred meters (200 m) downstream of the damlit (Figure 1.8) was another sampled location (site 7). This was chosen because religious activities are prominent there.

The eighth (8) sampled site is located 7.8 km downstream of the PW dam. Large congregations of worshippers were witnessed during every visit to the site. Worshippers were drinking the

stream water, and praying to the stream, using the water for ablutions, bathing and cooking with the water were all observed. Thus, the worshippers are exposed to U unknowingly. Depending on the total dose accrued during the duration of the exposure from the exposure pathway (ingestion from drinking water, dermal contact, cooking with polluted water), the worshippers could be in danger of U toxins. Cattle grazing was also seen within the environment, but none was witnessed on the water channel.



Figure 1.8: Mini-hydropower station

Further downstream is the next sampled site (site 9), about 8 km from the PW dam (Figure 1.9). Traditional worshippers were seen in units praying and drinking from the stream. This will be tabulated and discussed in the later chapter of this study. The area also falls within the C22H Quaternary Catchment.

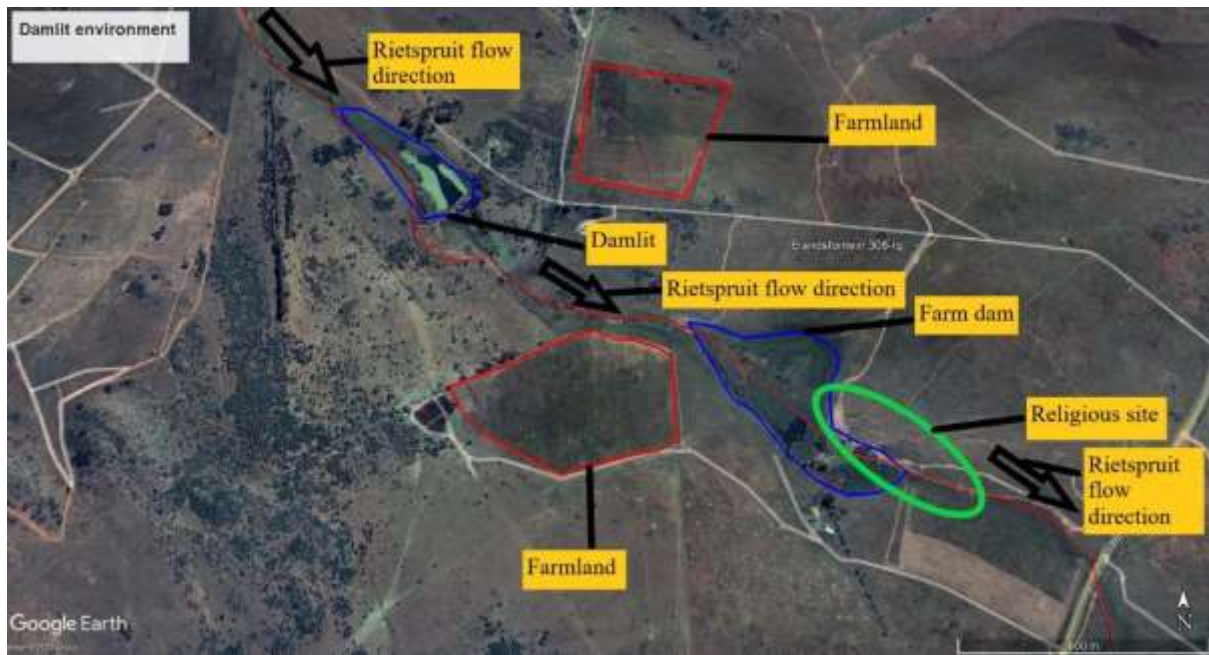


Figure 1.9: Google Earth Pro (2022) aerial map of the Damlit and environment

Post damlit and environment: Downstream of site 9 is Ennerdale Waste Water Treatment Plant, about 1 km from the seventh site. The effect of this water treatment plant will be discussed in the result discussion section of this study. Also, there are small tributaries that joined the Rietspruit before the eighth sampled site. However, they were all dry when sampling took place during winter, August of 2020 (Figure 1.10). So, the tributaries will have no effect on the concentration of U during this study. This could change during the rainy season. There is no mining operation upstream of the tributaries but waste from the communities (Lawley and Ennerdale) in the area could be a considerable factor that may affect the concentration and mobility of U in the area.



Figure 1.10: Two dry tributaries located in the study area

Of note is the change in coloration of the Rietspruit from clear and odourless water to black and with an odour of sewage. This is a result of the Ennerdale Waste Water Treatment Plant discharging wastewater into the Rietspruit.

The tenth sampled site is located about 12 km from the PW dam after the Ennerdale Waste Water Treatment Plant. No animal grazing nor religious activities were witnessed during sampling. This could be due to the stream odour, colouration, and distance from the road. Also, there was no farming activity within the area. Two (2) km from this site is Poortjie township (site 11). Samples were taken along the stream very close to the road bridge. Also, no activity of interest was noticed on this site.

Evaton and environment: Sites 12 and 13 are within the axis of Evaton township. In site 12, animal grazing along the water channel was witnessed (Figure 1.11), and worshippers praying and drinking the stream water less than fifty (50) m apart were also observed. As cattle create disturbance when walking inside the stream channel, this releases sediments and toxic elements that could be trapped within the sediment back into the water column. Depending on the speed of water flow and the chemistry of the environment, the toxic elements released back into the water column could travel for some kilometres before they could be deposited back into the sediment. Therefore, the worshippers drinking the water could be exposed to high concentrations of toxic elements. The concentration of U found in this area will be discussed in detail later.



Figure 1.11: Cattle grazing along Rietspruit stream

Site 13 is located on the R553 near Evaton township. It is a stream that flows through Evaton, Sebokeng, Lakeside, Stretford, Boitumelo and Orange Farm townships. There is no established industrial firm within a radius of 30 km upstream of the tributary (Evaton-Rietspruit) before the confluence with the Rietspruit. The stream transports waste from the two communities downstream into the Rietspruit. The Evaton-Rietspruit joins the Rietspruit about 28 km from the PW dam. The effect of the Evaton-Rietspruit on the Rietspruit will be discussed in the result discussion of this study.

About three (3) km downstream of the confluence Sebokeng Water Treatment plant (Figure 1.12) is located. The water treatment plant controls the wastes from the above-named communities and discharges it into the Rietspruit downstream where the next sampled site (site 14) is located about 2.5 km from the plant. Efforts to take samples very close to the wetland within the water treatment plant were rebuffed by the residents of the area. The site 14 sample was taken downstream of the water treatment plant along the N1 road. There was no animal grazing nor religious activity witnessed during sample collection in site 13 and 14. The coloration of the water body is black with a sewage smell.

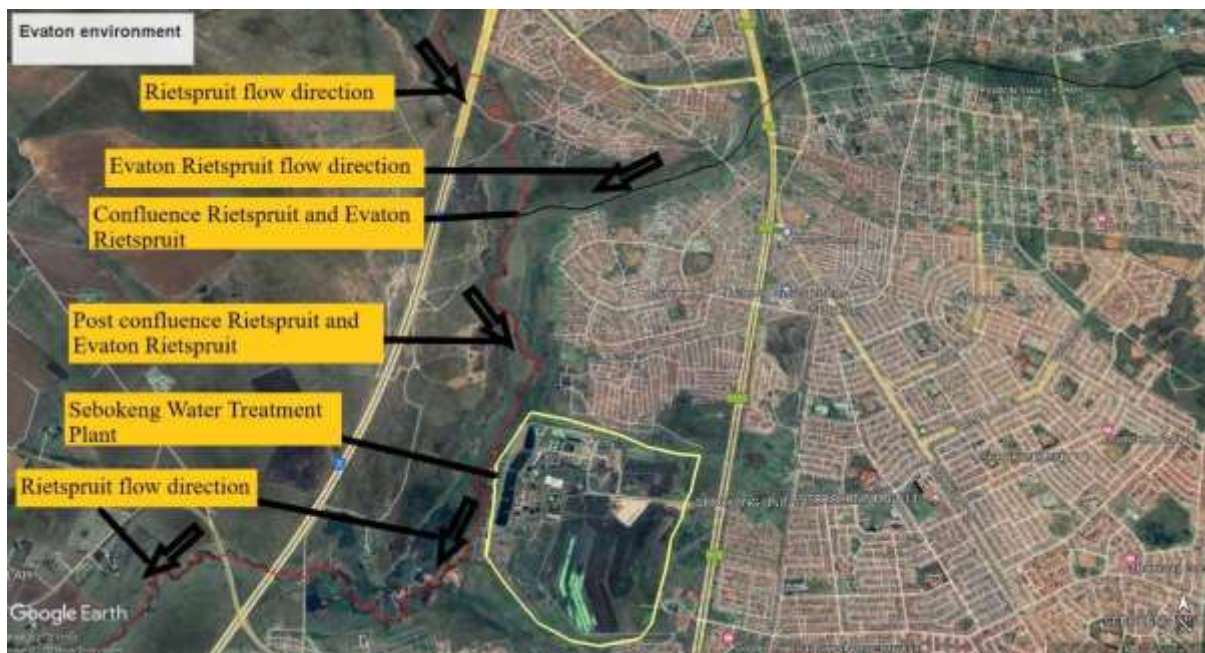


Figure 1.12: Google Earth Pro (2022) aerial map of Evaton and environment

Leeuspruit and environment: About 38 km downstream of the PW dam the next sampling site (site 15) is located. It is called Pre-confluence Rietspruit and Leeuspruit. This is the final sampled site in the C22H Quaternary Catchment. It is about 2 km before the Rietspruit confluence with Leeuspruit. No animal grazing or religious activity was witnessed during

sampling. However, since the environment is an open field (without fence), cattle grazing activity might occur.

Leeuspruit is found in the C22J Quaternary Catchment area. The magnitude of the catchment is about 669 km², meaning it is bigger than the C22H Quaternary Catchment and therefore will have a greater effect on the chemistry of the Rietspruit. About 29 km upstream of the sampled site along the Leeuspruit the South Deep Gold Mine (Figure 1.13) is located. The origin of water for farm irrigation within the area is undetermined; however, a dam is located upstream of the sampled site (site 16). It is believed that the condition upstream of the sampled site will be like Rietspruit, which is the focus of this study. As a result of this, a site (site 16) was sampled during the winter season about 6 km upstream of the Rietspruit confluence and it is called Leeuspruit. The water is clear and odourless. Fochville township (southwest of the South Deep Gold mine) in the map (Figure 1.13) has no effect on the Leeuspruit as it falls outside of the C22J catchment area.

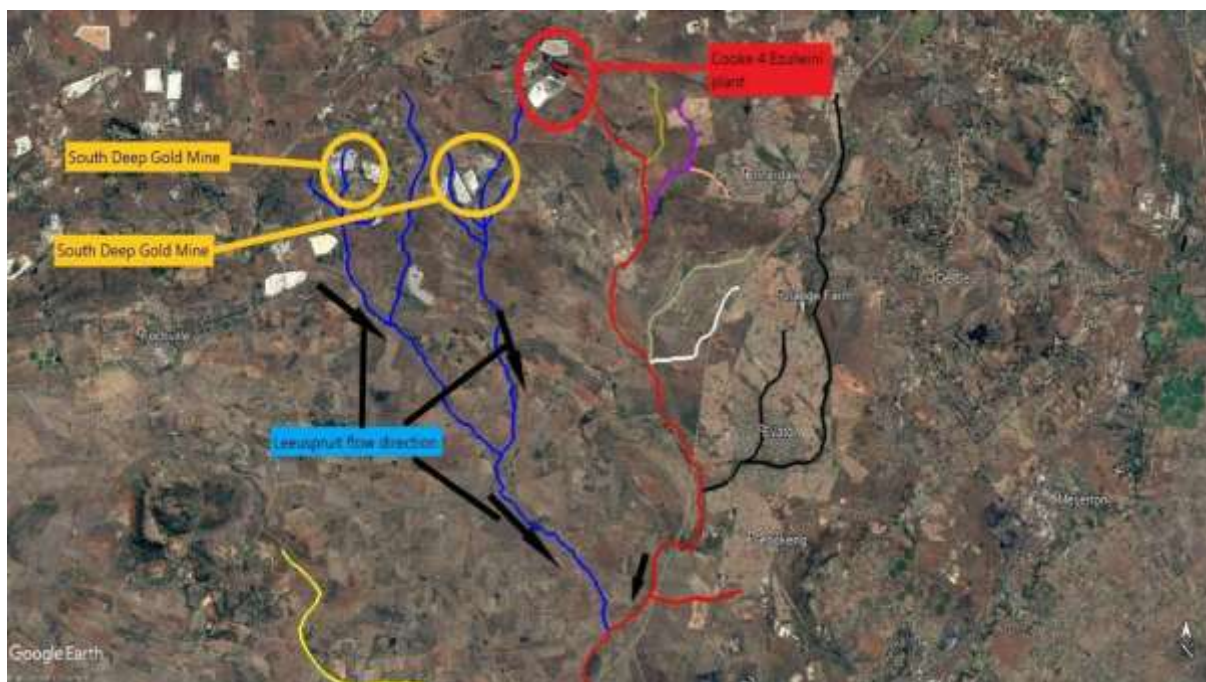


Figure 1.13: Google Earth Pro (2022) aerial map of Leeuspruit and environment

Site 17 is located less than 1 km downstream of the Leeuspruit and Rietspruit confluence and it is located about 39 km from the PW dam. Besides a steel manufacturing company (Arcelor Mittal) that also releases its wastes into the Rietspruit downstream, no animal grazing or worshippers were seen within the sampled sites.

Post-confluence Leeuspruit and Rietspruit: Site 18 is located about 43 km downstream from the PW dam before the confluence of the stream with the Arcelor Mittal discharge (Figure 1.14). Site 19 is after the Rietspruit and Arcelor Mittal discharge confluence about 53 km from the PW dam.



Figure 1.14: Google Earth Pro (2022) aerial map showing the location of Arcelor Mittal

Klein-Rietspruit and environment: Site 20 is located less than 1 km before the confluence with Klein-Rietspruit on the Potchesfroom road. Site 21 is located on the Klein-Rietspruit. The river water is clear and odourless. There is no mining firm located upstream of the river within the catchment (C22J). However, farms are located upstream. The river is seasonal; it was drying up when samples were collected during the winter season before any rainfall within the environment (9th August 2020). It was undetermined if the farmers utilise the water for agricultural purposes. Site 22 is after the confluence of the Rietspruit and Klein-Rietspruit, located about 55 km downstream of the PW dam. Like the Rietspruit located upstream, it is black with a sewage odour. Site 22 was the final sampled site located on the C22J Quaternary Catchment. The overall area of C22H and C22J catchment is 1128 km².

Lochvaal and environment: The next three sites are located on two different Quaternary Catchments. Sites 23 and 24 are found on the C22K Quaternary Catchment with a total size of 433.8 km². Site 23 is the inflow of the Rietspruit into Lochvaal before the Rietspruit makes a confluence with the Vaal River (Figure 1.15). The area is noted for recreational activities like boat cruises, fishing, and camping. The water body is typically black in colour with no odour.

Due to the depth of the river, no sediment sample was collected at site 24. Even though the recreational activities like boat cruises might have an impact on the hydrosphere of the area due to boat fuel discharge and oil leaks, this will not be analysed as it falls out of the study focus, which is based on U. The distances of Site 20 and Site 21 from the PW dam are 56 km and 60 km respectively.



Figure 1.15: Google Earth Pro (2022) aerial map of Rietspruit and the Vaal River

Site 25 is after the confluence of the Rietspruit and the Vaal River (Figure 1.15), located about 63 km downstream of the PW dam. Less than 1 km upstream of site 25 is the Rand Water Barrage Depot. Upstream of the Vaal River, Lethabo Power Station and Sigma colliery are located, but on a different catchment area. While Sigma Colliery is on C22K Quaternary Catchment, Lethabo Power Station is on C22F Catchment. Site 25 is in the C23B, which has a total size of 701 km². This is the only location with a different Tertiary Catchment (C23) from the other catchments mentioned, which all belong to the same Tertiary Catchment (C22) (Figure 1.15).

Each site number is not the same as the field number of each sample. Each sample is given a unique number for easy identification for the researcher. Site details and field numbers are

shown in the table below with the distance from the PW dam as well as Rietspruit's elevation downstream (Table 1.1).

Table 1.1: Table showing the site details with distance from the mining site

Site number	Site name	Water number	Field number	Soil number	Field number	Distance from PW dam (km)	Elevation (m)
Site *0	Tailings (first flush event)		*10		0	0	1681
Site 0	Slimes dam tailings				0	0	1672
Site 1	PW dam inlet		1		1	0	1671
Site 2	Channel water		*1		*1	0	1671
Site 2	Corner of dam		*2		*2	0	1671
Site 3	PW dam outflow		2		2	1	1662
Site 4	Wetland 1		3		3	1,5	1659
Site 5	Wetland 2 inflow		*8		*5	2,5	1643
Site 5	Wetland middle		*7		*4	3	1635
Site 5	Wetland outflow		*6		*3	3,7	1629
Site 6	Damlit outflow		4		4	5,9	1609
Site7	Between damlit		5		5	6,2	1605
Site8	Religious site		5B		5B	7,8	1592
Site9	Post religious site		6		6	7,9	1590
Site10	Post bridge		7		7	12,2	1558
Site11	Poortjie		8		8	14	1540
Site12	Pre Evaton		9		9	23,7	1489
Site13	Evaton		10		10	NA	1489
Site14	Post confluence		11		11	32	1467
Site15	Pre confluence Rietspruit & Leeuspruit		13		13	37,4	1454
Site16	Leeuspruit		12		12	NA	1462
Site17	Post confluence Rietspruit & Leeuspruit		14		14	39,3	1450
Site18	Post confluence Rietspruit & Leeuspruit		15		15	43	1446
Site19	Rietspruit (Potch Road)		16		16	49	1436
Site20	Pre-confluence Rietspruit & Klein-Rietspruit		18		18	53	1430
Site21	Klein-Rietspruit		17		17	NA	1431
Site22	Post-confluence Rietspruit & Klein-Rietspruit		22		22	55	1426
Site23	Lochvaal inflow		19		19	56	1427
Site24	Lochvaal		20		NA	60	1424
Site25	Post confluence Rietspruit & Vaal River		21		21	63	1422

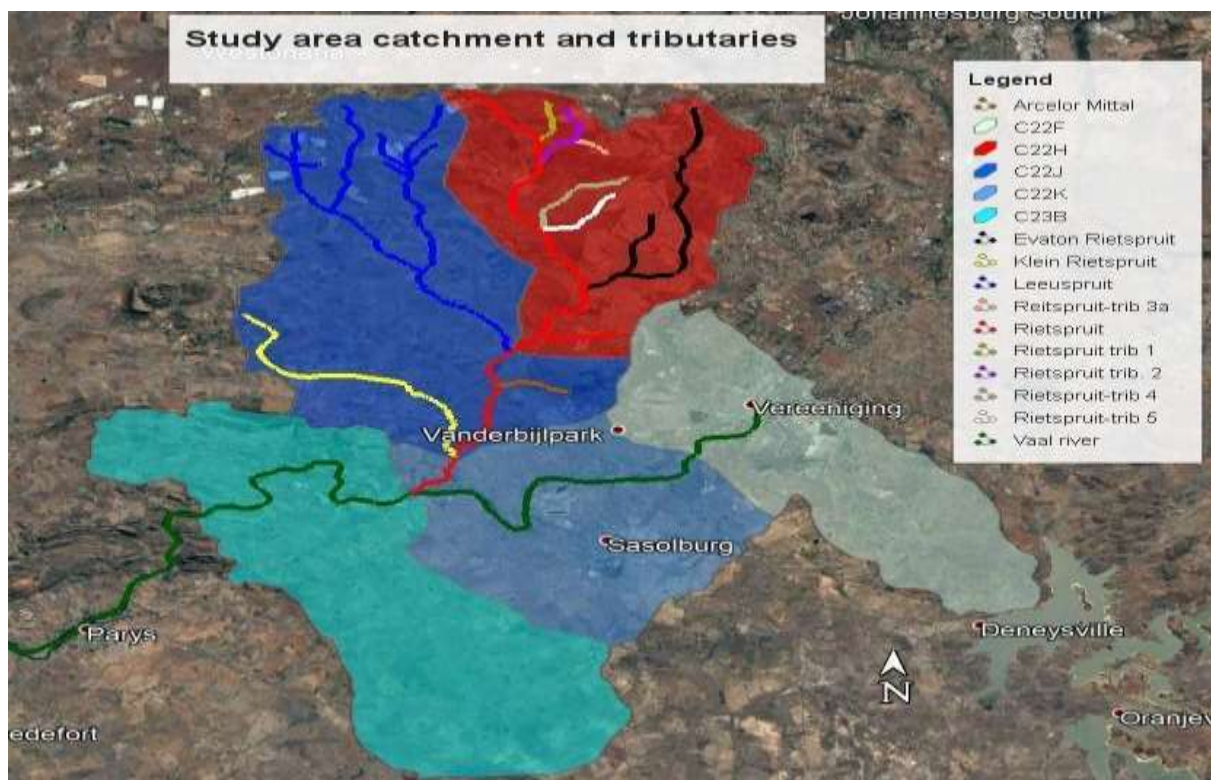


Figure 1.16: Google Earth Pro (2022) aerial map of the study area catchment and tributaries (data set published by Water Research Commission, 2012)

1.6. Organization of chapters in the thesis

This thesis is separated into seven chapters.

Chapter 1 provides an overview of the study, the problem statement, and the aim and objectives, and description of the study area.

Chapter 2 focuses on a literature review, consisting of the findings of similar studies in the mining environment and factors influencing the mobility of U.

Chapter 3 assesses the mobility of U within the Rietspruit system.

Chapter 4 assesses U remobilisation in the water-sediment system and the diurnal dam water chemistry. This chapter is under review by Current Pollution Report, a peer-reviewed journal of Springer.

Chapter 5 discusses the health risk, both carcinogenic and non-carcinogenic, related to U in the Rietspruit system. This chapter has been published in an accredited peer-reviewed journal under Springer.

Chapter 6 discusses U pollution levels in the Rietspruit system. This chapter has been published in an accredited peer-reviewed journal under MDPI.

Chapter 7 presents the overall conclusions of this study and the recommendations.

1.7. General material and methods

Table 1.2 details the material and methods used during this study.

Table 1.2: Study methodologies for each chapter and study objectives

Chapter	Main objectives	Samples collected	Methodology
3	Assessing uranium mobility within the Rietspruit system, Far West Rand Goldfield, South Africa	Both water and sediment samples were collected in August 2020 using a water bottle and an augur respectively. Collected samples were labelled onsite. At every sampled location, water pH, and electrical conductivity readings were taken using a WTW 350i handheld probe-meter. Samples were collected in the middle of the stream in most cases (depending on the site depth) to avoid sampling the riverbank.	ICP-MS was used to determine the concentrations of trace elements in the samples which include U. The concentration of U and the coordinates of the sample sites were used to create a map showing the profile of U concentrations in the Rietspruit river.
	Establish the impact of rain events on U pollution.	Water samples were collected in a furrow leading to the PW dam in September 2020 after a rain event. Before the rain-event, a sample of the mine waste next to the furrow was collected to determine the	The concentrations of other toxic elements recorded in both collected water and sediments samples were tabulated.

		concentration of U and other toxic elements in the mine waste.	ICP-MS was used to determine the concentrations of dissolved U in the water sample and in the suspended particles of the water.
4	Assess U remobilisation in water-sediment systems.	Sediments were collected from a farm dam located downstream of the PW dam	ICP-MS was used to determine the concentration of U in the dried sediment.
	Assessing diurnal dam water chemistry	Water samples were collected every hour continuously for 24 hours at the same spot of the dam. Onsite measurements of water's pH and electrical conductivity were done at the same spot where water samples were taken.	Sediment was rewetted using rainwater to determine the amount of dissolved U remobilised into the water column every hour.
			ICP-MS was used to determine the concentrations of dissolved uranium in the collected water samples. The result was correlated with the water's pH and electrical conductivity to establish the effects of changes in the water's pH and electrical conductivity on U.
5	Assessing health risk associated with uranium in the Rietspruit water,	Water samples collected in August 2020	The concentrations of dissolved uranium in collected water samples were used to determine the health risks – both carcinogenic and non-carcinogenic.
6	Assessing uranium pollution levels in the Rietspruit River,	Water and sediment samples collected in August 2020	ICP-MS was used to determine the concentrations of trace elements in the samples which include U. The results were displayed graphically

			against the distance from the PW dam – source of U in the Rietspruit
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1.8. Chapter summary

The exploitation of economic minerals such as gold, has been a key influence enhancing the economic growth of South Africa. However, the effect of this activity led to the release of poisonous toxic elements into the environment. Uranium is one of these toxic elements. Elevated levels of U have been reportedly logged in fluvial systems within a goldmining environment in the country. Due to the impacts of U on exposed populations, it is crucial to investigate the dynamics of this heavy metal in the Rietspruit fluvial system, found in the Gauteng Province of South Africa.

In chapter one of this study, the scope of this research was introduced, stating the problem statement and the importance of the study. The next chapter presents the literature relevant to this present study done by various researchers.

Chapter 2

Literature review

2.0. Introduction

This chapter discussed previous studies on heavy metals (toxic elements), uranium as an example of toxic elements, sources of uranium in the environment, the exposure pathways of uranium for human and health risk, the mobility of U in a fluvial system and factors contributing to the mobility of uranium in the fluvial system, for example, water's pH, electrical conductivity, concentration of iron and manganese, organic carbon, and the roles of major anions and cations. These were all used to interpret the results of chemical analysis from collected water and sediment samples in this study, based on the study's aim and objectives. Reported studies by several researchers on uranium pollution in South Africa concluded this chapter.

2.1. Heavy metals (potentially toxic elements)

With no clear definition, heavy metals can be regarded as chemical elements with high density when compared with water (Fasinu & Orisakwe, 2013; Alloway, 2012; Ramadan, 2003). Heavy metals are found naturally within the earth-crust throughout the world at a minimal amount, depending on the chemistry of the parent rock. However, due to different human activities (anthropogenic activities), the concentration of toxic elements within the earth-crust has increased (Cumberland et al., 2016). Examples of these activities include mining, farming, industrial and smelting operations, and urbanization (Akoto et al., 2023). Toxic elements include arsenic, (As), cadmium, (Cd), lead, (Pb), mercury, (Hg), zinc, (Zn), Uranium, (U), , iron, (Fe) etc.

Toxic elements are grouped into essential toxic elements and non-essential toxic elements (Tchounwou et al., 2012; Rengel, 2004). Essential toxic elements such as Fe, Zn, and calcium, (Ca), are beneficial to human and plant health at low concentrations, while non-essential toxic elements such as U, Cd, Hg, Pb, chromium, (Cr), and nickel, (Ni) are harmful to humans as well as plants and in most cases, toxic to humans even at low concentrations when ingested. Iron is required for the synthesis of protein in humans and promotes the flow of oxygen in the

blood to vital human organs and tissues (Kassa et al., 2019; Percy et al., 2017), zinc is good to produce different enzymes needed in humans, and calcium is essential for bone development (Noorazar et al., 2020; Hara et al., 2017; Wani et al., 2017).

However, at high concentrations, these essential elements become toxic to human health (Mishra et al., 2019; Rai et al., 2019). High concentrations of Fe (hemochromatosis) in humans can lead to high concentrations of Fe stored in the liver and heart of humans. This will result in liver diseases, heart problems and diabetes (Allamehet al., 2022; Katsarou et al., 2019). Zinc toxicity is caused due to the high concentration of Zn in humans; this leads to nausea, vomiting, loss of appetite, headache, and low absorption of Cu and Fe in the body (Dumrongwongsiri et al., 2022; Ho et al., 2022; Hara et al., 2022; Aggett & Comerford, 1995). Hypercalcaemia is caused by elevated amounts of Ca in humans, which can cause excessive thirst, stomach pain, digestive problems, muscle weakness as well as depression (Turner, 2017).

Non-essential toxic elements such as Cd, As, Cr, Ni, are reported to be carcinogenic (IARC, 2012), Hg damages the nervous system, digestive system, immune system, lungs and kidneys (Raji & Palamuleni, 2023; Adams et al., 2010), Pb affects the brain, and central nervous system (most especially in children) and is highly terminal (Hsiang & Diaz, 2011). Survivors may suffer from permanent brain retardation and behavioural disorder. Uranium exposure leads to kidney and lung damage as well as lung cancer and cancer of the bones (Faa et al., 2018; Kreuzer et al., 2015; Brugge & Buchner, 2011; Callahan et al., 2004; Bleise et al., 2002). This study focused on U as an example of a heavy metal and more details of the occurrence of U, mobility of U, exposure pathways for humans and the health risk associated with human exposure to U will be discussed in detail.

2.2. Uranium occurrence in the earth-crust

Uranium is an isotopic, radioactive chemical element with U as the chemical symbol (Grenthe et al., 2008). It is one of the heaviest naturally occurring toxic elements and is found at low concentrations in soil, rock, and water. As an isotopic element, U exists mainly in two unstable forms; U^{238} (the most abundant in the earth-crust with 99.3 % occurrence) and U^{235} having about 0.7 % abundance in the earth-crust (Závodská et al., 2008). Isotopic elements have different amounts of neutrons (uncharged particles) in the nucleus of the atom.

Due to this instability, the U is weakly radioactive. According to Cheg et al. (2000), the time taken (half-life) for U to decay into its progeny (daughter) to achieve chemical stability is about 4.5 billion years. Uranium²³⁵ has a shorter half-life (about 704 million years) than U²³⁸ (4.5 billion years). Uranium decays by releasing alpha particles, He²⁺. The progeny of U in descending order are thorium, (Th), protactinium (Pa), radium, (Ra), radon, (Rn), polonium, (Po), bismuth, (Bi) and the last, most stable progeny is the isotope of lead, (Pb²⁰⁶). While U decays by emitting alpha particles, the progeny decay by emitting both alpha particles and beta particles, β^- particles. This study is based on U²³⁸.

Over the years, the concentration of U in the earth-crust has increased due to the importance of the element and the exploration of associated metals like gold, Au (Winde, 2004b). Uranium is used in many developed countries such as the United States of America, France, China, Russia, South Korea, Canada, Ukraine, Germany, Japan and developing countries such as South Africa, Mexico, Romania, Iran, and Armenia to generate electricity by nuclear fission (Davenport, 2019; Settle, 2009). Nuclear fission is a chemical process whereby the nucleus of an unstable element splits into two or more smaller stable elements and generates a lot of energy (Smyth, 1945). Using a nuclear reactor, the energy generated during this chemical process (nuclear fission) is used to generate electricity.

Uranium can also be enriched to produce nuclear weapons (Davenport, 2019; Gibson, 2015). Countries having nuclear weapons include the United States of America, Russia, United Kingdom, France, China, India, Pakistan, and North Korea (Waltz, 1981). South Africa developed nuclear weapons during the apartheid regime, but it is one of the countries worldwide to dismantle their nuclear arsenals and discontinue the program due to the United Nation Treaty on the Non-proliferation of Nuclear Weapons, whose goal was to reduce the nuclear weapons race among nations (Cochran, 1994).

In nature, U occurs in two oxidation states, U⁴⁺ and U⁶⁺ (Liu et al., 2017; Cumberland et al., 2016; Bowie, 1979). The U⁴⁺ is stable in reducing conditions while the U⁶⁺ is more stable in oxidising conditions. A reducing condition occurs when an atom accepts a free electron and in an oxidising condition, an atom donates its free electron (Marcus, 1956). U⁴⁺ is highly insoluble in most geological environments while the U⁶⁺ is very soluble (Cumberland et al., 2016). A significant concentration of U is found in phosphate-rich rock deposits and ores, for example, lignite and monazite sands in U-rich ores (Jerden et al., 2003).

Uranium is found in different concentrations and quantities worldwide. It is more abundant than Au, silver, (Ag) and Hg (Keith et al., 2015). The average concentration of naturally occurring U in the earth-crust is < 2 to 4 mg/kg (Turekian & Wedepohl, 1961). In decreasing order of abundance worldwide, Australia, Kazakhstan, Russia, Canada, South Africa, Niger, and China have the highest deposits of U (Dahlkamp, 2013).

Uranium exists in the environment through the erosion of water, wind, and volcanic eruptions (Anke et al., 2009; Bowie, 1979; Crawford & Paone, 1956). Uranium is found in the air as dust from the various activities of mining, milling, and processing of U and precious metals like gold (Zupunski et al., 2023). Small amounts of uranium found in dust later fall onto surface water, plants, and land. Rain aids the settling of U on the ground. Industrial discharge of waste from mines also releases U into ground and surface water. Uranium in surface water can be transported to a larger extent depending on the chemistry of the water and sediment. Some proportion of the U in water will stick to the sediment and other particles in the water which can act as a secondary U pollution source (Winde et al., 2004a).

High concentrations of U can also be found in wells drilled in U-rich rock formation (Kennedy & Drage, 2020; Bjørklund et al., 2017; Corlin et al., 2016). Volcanic eruptions and rock weathering are sources of U in the soil because U is naturally present in nearly all rocks. Previous studies have confirmed the concentration of U in black shales, breccias, clays, limestone, phosphorites and sandstones, which are all sedimentary rocks (Alloway, 2013; Cuney, 2010; Davis et al., 2003; Hobday & Galloway, 1999). Hobday & Galloway (1999) revealed high U level in some igneous rocks (basalt, granites, rhyolites) while Davis et al. (2003) concluded that U can be discovered at a substantial level in metamorphic rocks (zircon) because of tectonic process and volcanic activity deep in the earth-crust. Examples of U existing in metamorphic rock are found in the Forstau deposit, Austria, and the Mary Kathleen deposit, Australia. Deposited U can mix with soil on land, could be washed into surface water or stick to plant roots (Dangelmayr et al., 2018; Chen et al., 2017; Corlin et al., 2016; Alloway, 2013; Bleise et al., 2002). The roots uptake the U from the soil and store it within the edible parts of the plants (Shtangeeva, 2010; Ramaswami et al., 2001). Humans get exposed to U through numerous pathways (WHO, 2001).

2.3. Exposure pathways for humans and health impact

Humans are exposed to the toxins of U through several pathways, which include inhalation of U contaminated dust in the air, ingestion via drinking of U contaminated water, consuming of contaminated plants and animals (food intake) and direct ingestion of contaminated soil, most especially by infants (Boelee et al., 2019; Kamunda et al., 2016; Winde, 2011a; Winde & van der Walt, 2004a). The other human exposure pathway is dermal contact (Keith et al., 2015). However, the risk due to dermal exposure to natural U is slow because natural U emits alpha particles which cannot penetrate the skin (Katz, 2014).

Mining operations release dust into the atmosphere depending on the type of metal being explored. Many studies relating to the concentration of U in air come from mining environments which produce U rich dusts. The concentration of background U in air is generally low except within the mining site (Keith et al., 2015; Basha et al., 2014; Tracy & Meyerhof, 1987). People working and living within such an environment will experience a higher exposure than other people.

The toxicity of U exposure because of inhalation will depend on the oxidation state of the U (Faa et al., 2018; Bjørklund et al., 2017; Katz, 2014). Soluble U compound (U^{6+}) will be absorbed into the blood while the insoluble U compound (U^{4+}) may remain in the lung tissue for several days or years resulting in the accumulation of U in the lung. This leads to a higher dose of alpha radiation in the lung. Above half of the U that is absorbed into the blood will be filtered by the kidney and leaves the body within a day (ATSDR, 2014), while the rest are stored in the bone, liver, and kidney. Human exposure to U via inhalation is little when compared to human exposure from drinking contaminated water and food (ATSDR, 2014).

Another exposure pathway for humans is the consumption of U contaminated water. Uranium is found in water because of soil and rock leaching as well as discharge from processing plants, release in mill tailings, and agricultural farmland runoffs (ATSDR, 2014). There are many U standards in drinking water from different countries. The World Health Organisation, WHO, recommended a U standard of 30 µg per litre of water with an assumption of the average human consumption of water as 2 litres per day (WHO, 2012). The standard for U in drinking water is 20 µg/L in Canada (maximum acceptable concentration), 30 µg/L in USA (EPA), 10 µg/L in Germany and 20 µg/L in Australia (ATSDR, 2014). However, higher concentrations of U

than the standards have been recorded in drinking water worldwide (Muikku et al., 2009; Kurttio et al., 2002; Zamora et al., 1998). Also, elevated amounts of U have been found in surface water and groundwater (Gronowski, 2013; Winde & van der Walt, 2004b; Winde, 2010). Winde (2010) reported an elevated amount of U in the Wonderfonteinspruit, South Africa, because of goldmine discharge into the water body and contaminated water emptying from the waterlogged mine void into the environment.

Uranium in surface water can be mobilised and transported far away from the source of contamination. Some of the U in water will stick to the sediment and other particles in the water (Cumberland et al., 2016; Gronowski, 2013; Winde et al., 2004b). Uranium in sediments can act as a secondary contaminant source (Luo & Gu, 2009; Hobday & Galloway, 1999;). Uranium trapped in sediment could be freed back into the water column whenever a variation in the stream's chemistry occurs. These can constitute a health risk to the biosphere.

Plants uptake nutrients from the soil using their root system (Ratnikov et al., 2020; Anke et al., 2009; Rengel, 2004; Ramaswami et al., 2001). The roots of a plant do not differentiate between the types of nutrients to be absorbed and because of this, U and several toxic elements are absorbed by the root, and they are stored in the plant. Plants as direct and indirect food paths for humans and due to the harmfulness of U and the potential bioaccumulation of U in plants, humans can be exposed to increased concentrations of U through consumption of plants. Different sources of U in soil have been discussed; however, U can still be added to the soil through the irrigation of farmland with U contaminated water (Lauria et al., 2009).

Humans have different exposure pathways to U through food intake:

- a. Direct consumption of fresh vegetables planted on U contaminated soil (Hill et al., 2020; Venus et al., 2019; Lauria et al., 2009).
- b. Consumption of animals that fed on plants with high concentrations of U as well as meat prepared using U contaminated water (Anke et al., 2009; Winde, 2011a; WHO, 2001).
- c. Consumption of processed meals produced using contaminated plant and animal produce e.g., consumption of pulverised maize, wheat, rice, tea leaf, bread, milk, cheese etc (Xiao-teng et al., 2019; Wang et al., 2017; Giri et al., 2011; Anke et al., 2009; Wappelhorst et al., 2002).

- d. Consumption of seafood and fish (Annamalai et al., 2017; Bellés et al., 2013; Al Kaddissi et al., 2012; Guérin et al., 2011).

Geophagia is the direct consumption of soil (Ghorbani, 2009). This is a general practice worldwide and more common among infants. Children regularly put unwashed hands in their mouths and U may be present in this dirt at high concentrations, especially residents close to a gold mine. Consumption of unwashed fruits and vegetables can also lead to indirect consumption of dirt which may contain high U concentrations (ATSDR, 2014).

Due to the availability of U at every sphere of the earth (lithosphere, hydrosphere, atmosphere, and biosphere), humans are exposed in many ways to the toxicity of U. Vital organs like the kidney, brain, lungs, liver, and heart are the target of U in the body (ATSDR, 2014; WHO, 2001). The health effect of U is dependent on the exposure dose, exposure duration, exposure pathway, age, gender, food intake, lineage, routine, and state of personal well-being (ATSDR, 2014). Some percentages of U which humans are exposed to are egested, however, some are absorbed and deposited throughout the body with peak concentrations recorded in the bones, liver, and kidneys, in no order (WHO, 2001).

Several studies have linked the damage of the kidney and lung to U exposure (Zamora et al., 1998; Bjørklund et al., 2020; Keith et al., 2015). There is considerable evidence confirming that U is genotoxic (Bjørklund et al., 2020; Dewar, 2019; Keith et al., 2015; Katz, 2014). Uranium exposure is not limited to the immediate source of pollution owing to the mobility of U in different media (Blake et al., 2017; Cumberland et al., 2016; Gronowski, 2013). This is because U is highly mobile, and several factors influence the mobility of U in a fluvial system.

2.4. Uranium mobility in the fluvial system

Multiple factors play vital roles in the mobility of U in fluvial systems. Some of these factors include pH, sediment composition, organic carbon, concentrations of some chemical elements e.g., Fe, manganese, (Mn), mineral solubility, the kind, and the intensity of chemical bond to ligands like oxygen and silica (Cumberland et al., 2016; Gronowski, 2013; Winde & van der Walt, 2004b). Also, the oxidation state of the U is also a factor to consider, with U^{6+} being more mobile than U^{4+} .

The pH is key to U mobility because it controls every single factor that affects the mobility of U in the fluvial system. pH is the indicator of acidity and alkalinity of the environment (Cumberland et al., 2016; Meride and Ayenew, 2016).

Organic carbon is an organic material from plants which produces silt or humus on water sediment (Cumberland et al., 2016). The humus breaks down into dissolved carbon which can bond to heavy metal through a process called chelation. Sources of organic carbon in the water-sediment system include the atmospheric carbon dissolved in rainfall, litter and crop residues, fertilisers from farm run-offs plus the decomposition of soil organic matter (Trenfield et al., 2011).

Dissolved organic carbon (DOC) facilitates the transportation of toxic elements such as U in aquatic systems. Uranium forms complexes with DOC which enhance metal solubility and reduce metal bioavailability. Total carbon present in an environment is made up of both the organic carbon and inorganic carbon. Examples of inorganic carbon include carbon dioxide, bicarbonate, and carbonate. While organic carbon immobilises U, inorganic carbon increases U mobility. Organic carbon helps to maintain a reducing condition by making available electron donor for microbes, therefore inhibiting the likelihood that reduced U^{4+} will get re-oxidised, which promotes the solubility and desorption of U, leading to an upsurge in U mobility (Cumberland et al., 2016).

Oxidation state of U: The oxidation state of U is important in knowing the solidity and mobility of U (Ray et al., 2011; Wellman et al., 2008). Uranium exists majorly in two states as previously mentioned, U^{4+} and U^{6+} . The oxidation state of U is controlled by the availability of oxygen (Gronowski, 2013; Winder & van der Walt, 2004a). When the availability of oxygen in the environment increases, U can be oxidised and become more mobile and soluble. Once U is mobilised, soluble U will be redistributed and precipitate either as U^{6+} or U^{4+} onto the streambed. U^{6+} is more soluble and mobile than U^{4+} , which has low solubility and as a result, is immobile (Cumberland et al., 2016). The change of U^{4+} to U^{6+} always occurs naturally under oxidising conditions and U^{6+} will change to U^{4+} in reducing conditions (Murakami et al., 1997).

Carbonates: Carbonates, CO_3^{2-} , influence the mobility of U due to its ability to make U more soluble by forming carbonate complexes (Adam et al., 2014; Zhou & Gu, 2005; Min et al., 2000). According to Cumberland et al. (2016), carbonates improve the mobility of U in an alkaline condition (pH above 7). The existence of carbonates in sediment counterbalances

every integral sediment property, therefore inhibiting the sorption of U to anionic and clay minerals in an alkaline condition (Echevarria et al., 2001).

Phosphate: Phosphate PO_4^{3-} , minerals prevent the mobility of U in groundwater (Pinto et al., 2012; Wellman et al., 2010). When U forms complexes with phosphate, uranyl phosphate is formed. In a study, Vazquez et al. (2007) determined that the solubility of uranyl phosphate is pH reliant. In their study, it was concluded that at a pH value of less than 5, the precipitation of uranyl phosphate occurs while the solubility of uranyl phosphate occurs at pH above 6 (Vazquez et al., 2007). Due to the affinity of phosphate to U, rock containing phosphate deposits always contains high concentrations of U (Alloway, 2013). This is the source of U in phosphate rich fertilisers, which could lead to U enrichment in agricultural soil and food output (Adam et al., 2010). Beazley et al. (2011) reported that phosphate and carbonate always compete for U. At high concentrations of carbonate, phosphate desorbs from uranyl phosphate to allow the adsorption of carbonate, which will encourage improvement in the mobility of U.

Silicate: Silicate, SiO_4^{4-} , is less competitive for U in the environment than both carbonate and phosphate (Cumberland et al., 2016). Uranyl silicate complexes can be formed when silicate is abundant in solution. Uranyl silicate has lower solubility than uranyl carbonate but more soluble than uranyl phosphate (Maher et al., 2013; Gorman-Lewis et al., 2007). The pH and organic matter of water have an active role in the founding of the uranyl silicate complex (Deditius et al., 2008; De Windt et al., 2003). A pH value of less than 9 promotes the establishment of a uranyl silicate complex in the abundance of silica. Deditius et al. (2008) found that organic matter shields U^{4+} minerals from oxidising in uranyl silicate complexes.

Sulphates: Uranium is less likely to form complexes with sulphates, SO_4^{2-} , than carbonate, phosphate, and silicate (Gorman-Lewis et al., 2008). According to Zammit et al. (2014), uranyl sulphate plays a key role in acidic environments and is prevalent in acid mine conditions.

Iron chemistry: As the fourth most abundant element in the earth-crust and a redox element, iron, Fe, plays an active role in the mobilisation of U (Roden et al., 2010; Weber et al., 2006). Uranium adsorption to the Fe mineral surface is pH dependent (Behrends et al., 2012, Zhao et al., 2012). Ulrich et al. (2006) reported that U^{4+} is absorbed into ferric oxide at a pH range of 5 - 8. Iron mineral surfaces are liable to act as a catalyst during ion exchange for a redox reaction to occur. Alam & Cheng (2014) in their study, reported that iron hydroxides are valuable for hosting U minerals in sediment. However, the natural concentration of organic

matter prevents the sorption of U to Fe mineral surface at low pH (Lenhart et al., 2000). Iron compound has the possibility to lower the mobile U^{6+} to insoluble U^{4+} .

In conclusion, the most prominent factors altering U solubility and mobilisation are pH, oxidation state of U, organic matter, redox and complexing ions. The pH threshold for U solubility is around 6; above 6, the U becomes increasingly soluble and mobile (Cumberland et al., 2016). Redox affects U mobility by changing the oxidation state of U. The organic carbon effect on U^{6+} form depends on the complexing ions and concentration of organic matter. At low organic carbon concentration, U solubility is advanced, whereas at high concentration, organic carbon may immobilise U due to complexation and mineral formation (Cumberland et al., 2016). All these factors were considered when the writer interpreted the concentrations of U in water and sediment samples.

2.5. Uranium pollution in South Africa

Several studies have been done on the pollution of U in the country. This is facilitated by the environmental influences of mining and the toxic nature of the element and associated toxic elements that have been mined in-situ with gold. A few of these studies will be highlighted with the findings of their study.

Durand (2012) studied the gold found in the Witwatersrand Supergroup in correlation with pyrite (FeS_2). It was concluded that the Witwatersrand Supergroup contains more U than gold. Uranium is mainly exploited as an offshoot of gold mining in South Africa (Winde & van der Walt, 2004a). Consequently, extracted U is released in slimes dams which contain about 100 000 tons of U (Coetzee et al., 2006). The slimes dams and rock dumps in this area leach U and its daughter products.

Run-off from the mine wastes, including dust, contains as much as 50 tons of U, which are released year after year into nearby surface water, into which effluent drains from the slimes dams (Coetzee et al., 2006). Potential receptors in this study include the rural area close to the mine and downstream of the mines that use the water for consumption, cattle watering and to irrigate crops. Coetzee et al. (2006) suggested that most people living in informal settlements close to rivers depend on water from streams and boreholes that is polluted by U. Informal settlers were observed fetching water from the river for various domestic purposes during field work.

A geochemical model to study the seepage from a tailing's impoundment of a gold mine in the Witwatersrand was carried out by Hansel (2015). He characterised the slimes dam in the study area into different zones- oxidised zone, transitional zone, and reduced zone. The oxidation zone was established at the top of the tailings. The pH increases from the oxidation zone to the reduced zone due to the slower pyrite oxidation. It was found in the study that the tailings are acidic and consist of excessive concentrations of U and other toxic metals. Hansel (2015) established that the amount of U in groundwater cannot be used as a factor to characterize tailings due to the interaction of water and sediment.

In the study of Hedden & Cilliers (2014), focusing on the water crisis in South Africa, they noted the impact of mining activity which results in acid mine drainage (AMD). They noted that despite the compromised water quality in the country because of low rainfall and high evaporation, the status of water is changed by the AMD which is often linked with high concentrations of U. Hobbs et al. (2010) in their study stated that gold mines make up the biggest source of pollutant (47 % of all mineral waste) in South Africa and this is due to AMD. There are over 270 slimes dams in the Witwatersrand Basin covering about 400 km² earth surface. The majority of these tailings dams are unlined and lack top vegetation which eventually results in air, soil and both surface and groundwater pollution (Hobbs et al., 2010).

Maleke et al. (2012) established that the U concentration in the Witwatersrand Basin is because of goldmining activities which constituted a major environmental stressor. They noted that the high concentration of U that frequently contaminates nearby streams originates because of mining activity in the Witwatersrand Basin, a Basin that is dominated by gold mines. Manders (2009) estimated that about 350 ML of mine effluent which is highly rich in U, is being released into nearby stream water.

McCarthy (2011) studied the impact of gold exploration in South Africa focusing on the role of rainfall on slimes dams and mine dumps which are rich in pyrites. It was concluded that rainwater dropping on the dumps or slimes dam oxidises the pyrite, resulting in sulphuric acid which infiltrates through the dump or slimes dam, dissolving U and other toxic metals in the process. The seepage from the slimes dam and mine dumps joins the nearby surface water and / or groundwater as U-plume, leading to the stream being acidic with extreme amounts of sulphate, U, and supplementary toxic alloys.

In an assessment on the complications of decommissioned mines in South Africa around the Far West and West Rand (both in Witwatersrand) by Mhlongo & Amponsah-Dacosta (2016), it was reported that the water contains elevated concentrations of U ranging from 900-1000 mg/kg. Other carcinogenic toxic elements like arsenic, cadmium and mercury in elevated concentrations were also found at the tailings of an abandoned gold mine in the Wonderfonteinspruit Catchment. This poses a significant health challenge to the residents of the area, among other inherent social-economic challenges being faced by the local people of the area such as HIV/ AIDS and chronic malnutrition.

Njinga et al. (2016) in their study assessed the intensity of U around Princess Gold Mine in Roodeport, Gauteng using ICP-MS. Uranium concentration of 868 µg/L was found about 100 m from the tailings in water while a lower concentration of 155 µg/L was found about 1 km from the tailings. The amount of U decreased as the kilometres from the tailings site increased. This work is like the current study; however, the maximum distance from the tailings studied was 1 km while the whole length of the Rietspruit and the contributing tributaries were investigated in this study.

In 2002, Wade and associates studied the transportation of U in the Mooi River Catchment, focusing on the wetland in the Catchment. It was found that U was immobilised in the wetland within the Mooi River Catchment. It was concluded in the study that U immobilised in wetland sediment, could be released (remobilised) back into the water column if there is a change in the water chemistry. Therefore, uranium immobilisation in wetlands is not permanent. Temporal fluctuations in water chemistry and climatic factors could remobilise U in the wetland water-sediment system. This could cause the pollution of downstream water (Wade et al., 2002).

A study done by Coetzee and associates for the Council of Geoscience (CGS) on the downstream pollution of the Potchefstroom water supply concluded that U concentration is above the natural concentration of U (<4 mg/kg) in sediment by several orders of magnitude (Coetzee et al., 2006). In the same study, other carcinogenic toxic elements were found associated with U. This presents a massive danger to the biosphere. Finally, their laboratory studies coupled with chemical modelling, point to the fact that U can be absorbed to the sediment phases from water and can be remobilised back into the water column because of geochemical processes.

2.6. Chapter summary

Heavy metals (toxic elements) can be classified into two broad types – essential and non-essential toxic elements. At a minute concentration, an essential heavy metal is beneficial to human health, however, at an elevated concentration, it becomes toxic, while non-essential toxic elements like U is poisonous even in minimal amounts.

Humans are exposed to U through different pathways, which include untreated water from streams and rivers, air, meat, and food. Due to the mobility of the U, the immediate source of pollution is not the only contaminated site. In a fluvial system, the mobility of U is controlled by several factors which include the water pH, EC, organic carbon, water flow rate, iron and manganese chemistry, carbonates, silicates, phosphates etc. These factors influence the immobilisation and possible remobilisation of U in a fluvial system and were considered in the interpretations of U concentrations in sampled water and sediment in this study.

This chapter highlighted several studies that have been done on U and factors that contribute to the mobility of U in the fluvial system. The next chapters discuss the findings of this study based on the set-out objectives. Each chapter is written in an article format, while chapters 3 and 4 are under preparation for submission to a peer-reviewed journal(s). Two of the chapters (chapter 5 and 6) have already been published in peer-reviewed journals.

Chapter 3

Assessing uranium mobility within the Rietspruit system, Far West Rand Goldfield, South Africa

Abstract

Many years of gold mining within the Witwatersrand Basin have resulted in the release of uranium (U) into water used for irrigation, domestic and religious activities. The assessment of Rietspruit water and sediment samples by inductively coupled plasma mass spectrometry revealed high concentrations of U in collected samples. Within the mining environment, a concentration of 1043 mg/kg was logged in a sand dump and 1143 mg/kg was logged in the crust of a concrete canal taking fissure water into the Peter Wright (PW) dam. A uranium concentration of 781.9 µg/L was recorded at the PW dam inflow. High concentrations of arsenic, cadmium, lead, and mercury were also recorded in collected samples. A secondary accumulation of U was found about 2 km and 6 km post PW dam, that is, in a swamp, 1237 mg/kg and in a dam, 1251 mg/kg. Adsorption, precipitation, and co-precipitation are some of the factors believed to be responsible for the immobilisation of uranium in this study. Uranium mobility is induced by the water pH, electrical conductivity, iron and manganese composition, organic carbon, and the amount of clay and silt in the sediment. Besides the release of mine water into the PW dam, the leaching of U from mine wastes during rainfall also contributes to the amount of uranium found in the Rietspruit system. High concentrations of arsenic, cadmium, lead and mercury, above their permissible limits, were also recorded in the Rietspruit. The result of the health hazard assessment based on the amount of U recorded in Rietspruit water, revealed that chemical risk outweighed radiological risk.

Keywords: Uranium, mobility, immobilisation, remobilisation, Rietspruit, wetland, dam

3.1 Introduction

Uranium (U), a radioactive heavy metal, is mined in South Africa as an offshoot of gold mining (Coetzee et al., 2006). Since the dawn of gold exploration in the Witwatersrand Basin, South Africa, over a century ago (Neingo & Tholana, 2016; Hobbs et al., 2010), a high concentration of U has been registered in this Basin (Du Preez et al., 2016; Durand, 2012; Winde & Sandham, 2004). Gold is mainly mined in South Africa through underground mining and open-pit mining. These activities brought a huge underground waste product to the earth's surface. This waste could be in the form of rock dumps, sand dumps, slimes dams, and underground mine-water discharge. In the Witwatersrand Basin with a total surface area of about 1600 km², slimes dams cover about 400 km² of the total surface area (Phillips, 2013). The discharge of mine water (processed water) through pipes and concrete canals into dams and nearby-surface water can be regarded as a direct source of water contamination. The dissolution or leaching and transportation of uranium and other toxic elements from solid mine wastes to nearby surface water can be regarded as indirect contamination of surface water within the Witwatersrand Basin.

Numerous research has been reported on the effects of gold mining as a source of both surface water and sediment pollution (Raji & Palamuleni, 2023; Humphries et al., 2017; Durand, 2012; Hobbs et al., 2010; Tutu et al., 2008). Durand (2012) reported that the major issue associated with gold-mining processes in the Witwatersrand Basin is the contamination of water bodies and pollution caused by acid mine drainage, which eventually impacts negatively on human lives. Uranium concentration above the allowed limit in sediment, 16 mg/kg, was reported in the Basin (Durand, 2012). In 2010, Hobbs et al. (2010) reported that over 270 slimes dams contain about half of the mineral wastes produced in South Africa and are a foremost concern for both surface and groundwater contamination. Humphries et al. (2017) reported high metal accumulation in the wetland because of polluted surface water and seepage from underlying dolomitic rock through tributaries draining the Central Rand Goldfield, Witwatersrand Basin. Precipitation of gypsum, metal sulphides, iron, manganese hydroxides and phosphate were reported to be among the factors responsible for the heap of toxic elements in the wetland (Humphries et al., 2017). Tutu et al. (2008) recognized tailings dumps as a major source of pollution in the Witwatersrand Basin due to the chemistry of tailings and the continuous discharge of water from underground mine shafts to nearby water bodies as another source of heavy metal pollution.

An excessive amount of U was reported in surface water and sediment in the Basin. Tutu et al. (2008) reported a U concentration of about 9.82 mg/L in their findings of the chemical characteristics of acid mine drainage in the Witwatersrand Basin. Winde & de Villiers (2002a) in their study of U contamination in streams within the Witwatersrand Basin, reported about 161 mg/kg concentration of U in a collected portion of a slimes dam. Njinga et al. (2016) registered an activity concentration of U of about 6390 mBq/L in a surface-based drinking water source because of past activities of a decommissioned gold mine.

In addition to the numerous reports on U pollution in the Witwatersrand Basin, a few reports have been found on U pollution in the Rietspruit. This stream is perennial, and it is found in the Far West Rand Goldfield of the Witwatersrand Basin due to the discharge of mine water into the stream. In this study, factors that influenced U mobility in the Rietspruit will be reported as well as the result of the impact of rainfall on U mobility. Knowing the factors that influence U mobility is important to understand U immobilization and possible remobilisation in the Rietspruit. Due to the chemical and radioactive impacts of U on human health, this study is important because the stream is used for agricultural, domestic, and religious activities. This is because of water scarcity in the country, with the annual potential evaporation being almost triple the annual potential rainfall (Kritzinger, 2017) and the demand for water outweighing the supply.

Therefore, the objectives of this section are:

- 1) To determine U concentration and mobility in the Rietspruit system.
- 2) To determine the concentrations of other toxic elements in the Rietspruit system.
- 3) To assess the health impacts of U and potential receptors and exposure pathways.
- 4) To assess the impact of rainfall (first flush event) on mine wastes.

Study area

The study area has been reviewed in the preceding study of Raji et al. (2021).

3.2 Material and method

3.2.1 Sampling

In total, 30 sediment and 28 water samples were collected on 28th August 2020. Five sediment and four water samples were collected within the mining environment. Two dry sediment samples were from a slimes dam and sand dump while others were from the same site where water samples were taken (PW dam inflow and outflow and concrete canal sediment). Eight sediment and water samples were collected at dams and wetlands in the Rietspruit system and another three sediment and water samples from the Leeuspruit, a tributary of the Rietspruit. An active gold mine was established upstream of the Leeuspruit. One sampled site was at the pre-confluence of Evaton-Rietspruit and Klein-Rietspruit. Other sampled sites were all taken in the Rietspruit downstream. Rural settlers and informal settlements are abundant within these communities and based on observation, they depend on the Rietspruit water flowing close to their settlements for their basic domestic and agricultural needs.

Sampled sites were selected systematically based on accessibility, human exposure, presence of dams and wetlands, proximity to farmlands, and animal grazing. It is crucial to sample dams and wetlands because they are sinks for heavy metals in a fluvial system. Also, in order to evaluate the health risk due to the consumption of a toxic element, there is a need to establish human exposure. Farmlands irrigated with contaminated water also pose a health risk, hence the importance to confirm the source of water used for irrigation of a farmland.

A 100 mL bottle was used to collect water samples, while sediment samples were taken using an auger at the exact site where the water sample was collected. Sediment samples were stored in a zip-lock bag. Each water bottle was cleaned with Rietspruit water prior to water samples being grabbed. This was done to remove any foreign particle in the water bottle in order to avoid cross-contamination. The bottle was submerged under the water surface, once full, and the bottle was capped below the water surface. To avoid water turbulence, a water sample was collected first before a sediment sample was taken. Both samples were collected at the centre of the stream. To avoid skin exposure, protective clothes were worn with hand gloves. After sampling, the auger was rinsed with the stream water outside of the stream.

At each of the sampled sites, water pH, electrical conductivity (EC), and temperature readings were measured using a WTW multi 350i water probe-meter. The WTW multi 350i water probe-meter has been used in a similar study by Molina et al. (2022). The probe-meter was standardized by application of the standard measurements recommended in the manual before water samples were taken and all readings were referenced to 25 °C. A Global Flow Probe FP 101 was used to measure water flow velocity. A handheld GPS was used to measure each sampled site's coordinates.

Water and sediments were labelled at each sampled site and stored in a cooler box covered with ice. No preservation was done because laboratory analysis commenced the next day after sampling. Samples analyses were carried out at the Eco-Analytical laboratory of North-West University, Potchefstroom Campus.

3.2.2 Laboratory analysis

Before the analysis of sediment samples, each collected sediment was put into a branded petri-dish and assembled in an oven at 50 °C for 24 hours to remove the moisture content. After drying, the sediment was loosened using a mortar and pestle then sieved through a mesh of 2 mm. About 0.2 kg of the sieved sediment was placed in a Teflon Tube and 9 mL of nitric acid and 3 mL of hydrochloric acid was added to the Tube, capped, and placed in a Milestone Ethos UP, Maxi 44 microwave digestion.

After digestion, an Agilent 7500 CE ICP-MS was used to establish the amount of dissolved U in the sediment and major cations. The ICP-MS was standardized using Ultraspec certified custom mixed multi-element stock standard solution manufactured by De Bruyn Spectroscopic Solutions, Midrand, South Africa.

Water samples were first filtered to remove suspended particles. As a result, only dissolved uranium concentration was determined. 1 mL of the filtered water was then mixed with 9 mL of HNO₃. While ICP-MS was utilized to quantify the concentration of dissolved uranium, Ion Chromatography was utilized to quantify the concentrations of the major anions.

To further justify the factors that played a role in the immobilisation of U in sediments, a wet sieving method was used to determine the amount of sand, clay, and silt in each sediment

sample (particle size distribution). Sand is made up of grains of particle size ranging from 0.0625 to 2 mm. Silt is made up of grains of particles ranging from 0.008 to 0.0625 mm while clay consists of grains of particle size between silt and colloid. It is preferable to use the wet sieving method when research on sediment is done ((Park et al., 2019; Chen et al., 2014; Huang et al., 2014).

Loss on ignition (LOI) is one of the most widely used methods for measuring organic matter content (carbon content) in soils (de Caritat et al., 2023; Mularski & Li, 2023; Baker et al., 2023). To measure the organic carbon in the sediment, 15 g of the prepared sediment was measured out and placed in an already weighted crucible. The total weight of the sediment plus crucible was weighed and recorded. Thereafter, the sediment-filled crucibles were placed in an incinerator oven at a temperature of 450 °C for a duration of six (6) hours. After six hours, the oven was allowed to cool down before the crucible was removed. The weight of the crucible was then taken and recorded. The amount of organic carbon present in the soil was determined by subtraction of the weight of the sediment- filled crucible after burning, from the weight of the sediment-filled crucible before burning (Baker et al., 2023).

3.2.3. Quality control

All the equipment used was calibrated with reference standards. Glassware used for oven drying, digestion and analysis of samples were rinsed in dilute HNO₃ before use. All the reagents and heavy metal standards used were of analytical grades.

Recoveries ranging from 67 – 89 % were obtained for the measured trace elements. During analysis, calibration verification standards were regularly used to evaluate the calibration curve. The minimum correlation coefficient of the calibration curve accepted was 0.999.

3.3. Results and Discussion

3.3.1. Surface water chemistry

3.3.1.1. pH

The Rietspruit pH ranged from 6.0 to 8.8 (Figure 3.1). A noticeable increase in the pH was observed at sunrise with the maximum pH recorded at noon when the sun was at the maximum.

At sunset, the pH drops. The increase in the water pH is a consequence of photosynthesis of water plants and algae, which increases as the sun becomes available.

At low pH, U will be released into the water column, leading to an elevated amount of dissolved U in the water column. However, this relationship between U and pH cannot be proven in this study because different sites were sampled. The mobility of U improves in neutral to alkaline conditions because of the formation of stable negative complexes with oxygen and carbon (WHO, 2001).

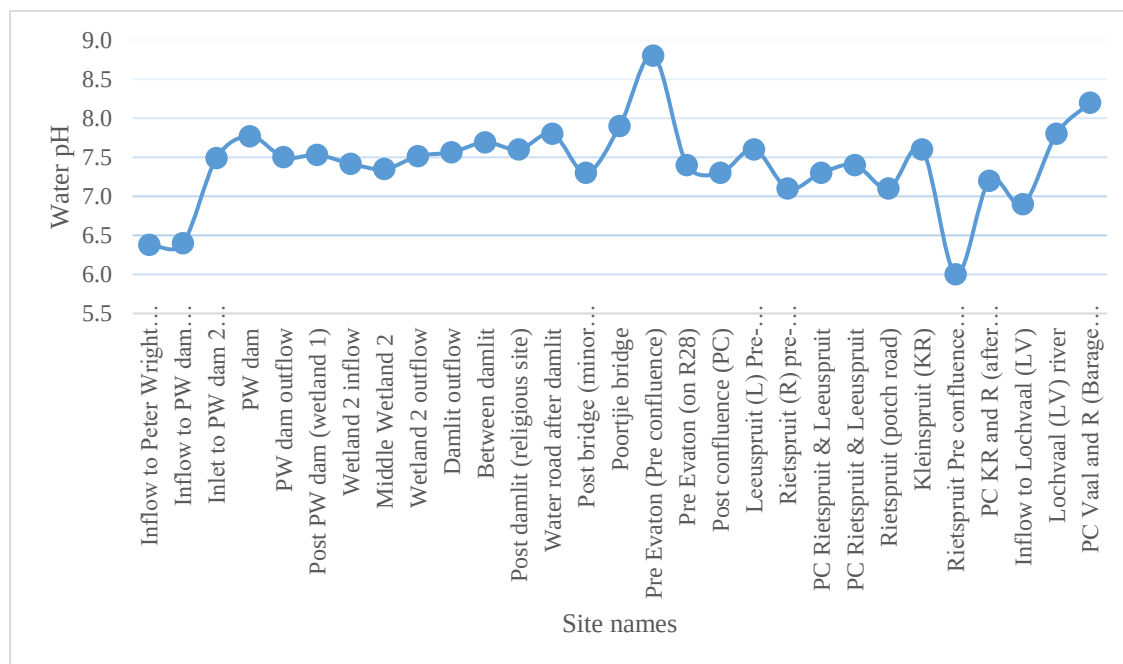


Figure 3.1: Rietspruit water pH

Using Excel for Microsoft 365 MSO (Version 2307), pH has a weak negative correlation with U, - 0.23, and a positive correlation with water temperature, + 0.61. Similar negative correlations between pH and U in water have been reported worldwide (Bhavya et al., 2023; Pandey et al., 2022; Malikova et al., 2020; Zhou et al., 2020).

3.3.1.2. Electric conductivity (EC)

The water EC ranged from 443 – 1358 $\mu\text{S}/\text{cm}$ (Figure 3.2). Water EC relates to the water salinity and can be used to quantify the pollution load (dissolved solids) in water (Chusov et al., 2014). At a high EC value, the rate of U immobilisation is reduced because of the water salinity which lowers the sorptive competence of stream sediment. Consequently, higher concentrations of U will be recorded in the water column than when the EC is lower, and low

concentrations of U will be logged in the underlying sediment because of the low sorptive strength of the sediment.

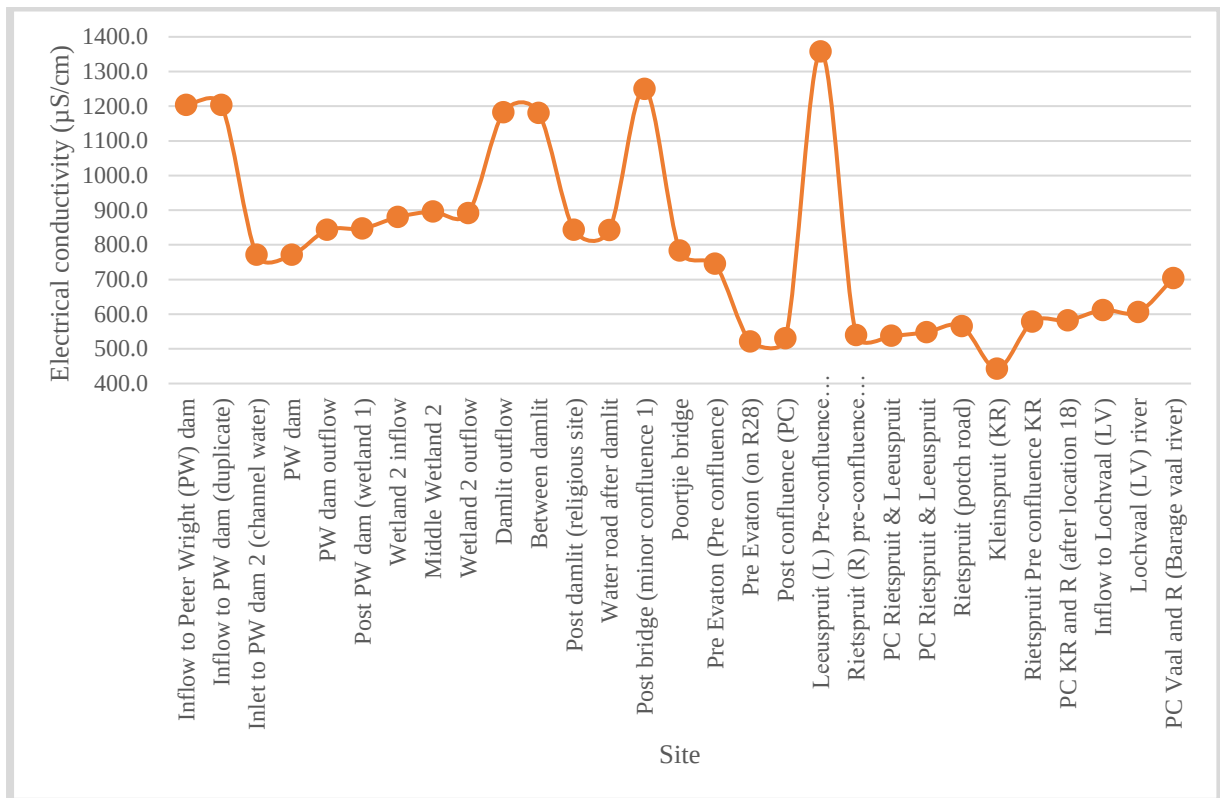


Figure 3.2: Rietspruit water electrical conductivity

Using Excel, EC has a positive correlation with the concentration of U, + 0,52. This indicates that water salinity plays a major role in the mobility of U in a fluvial system. Similar reports have been published with similar positive correlation between EC and U in both surface and groundwater (Kumar et al., 2023; Menaria et al., 2023; Tanwer et al., 2023).

Table 3.1 shows the correlations between U and the stream water pH, EC, and water temperature.

Table 3.1: Correlation of uranium and stream water chemical properties based on results from sampled sites

	pH	EC	Temp	U
pH	1.00			
EC	0.09	1.00		
Temp	0.61	-0.24	1.00	
U	-0.23	0.52	-0.44	1.00

One-way ANOVA is an established statistical tool used to compare the mean values of samples to check whether they are significantly different. The result is significant if the F-statistic is larger than the F-value. Using Excel, the result (Table 3.2) of the one-way ANOVA revealed

that the F-statistics is greater than the F-value. With the alpha value (0.05) greater than the p-value, we can reject the null hypothesis.

Table 3.2: One-way ANOVA showing the significant different between U concentrations and pH, EC, and water temperature

One-way ANOVA						
Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	10595380	3	3531793	126.00	3.64E-33	2.70
Within Groups	2690988	96	28031.12			
Total	13286368	99				

3.3.1.3. Anion and cation concentration

Major anions include SO_4^{2-} , Cl^- and HCO_3^- while major cations include Ca^{2+} , Mg^{2+} , Na^+ and K^+ . The determined levels of the anions and cations were utilized to establish the cause of water pollution in the Rietspruit by mapping a Trilinear Diagram using Grapher 18. The trilinear diagram gives a visual representation of the sampled water chemistry (Figure 3.3). This has been used in several studies to characterise the source of water pollution ((Ratombo, 2019; Du Preez et al., 2016; Hobbs & Cobbing, 2007).

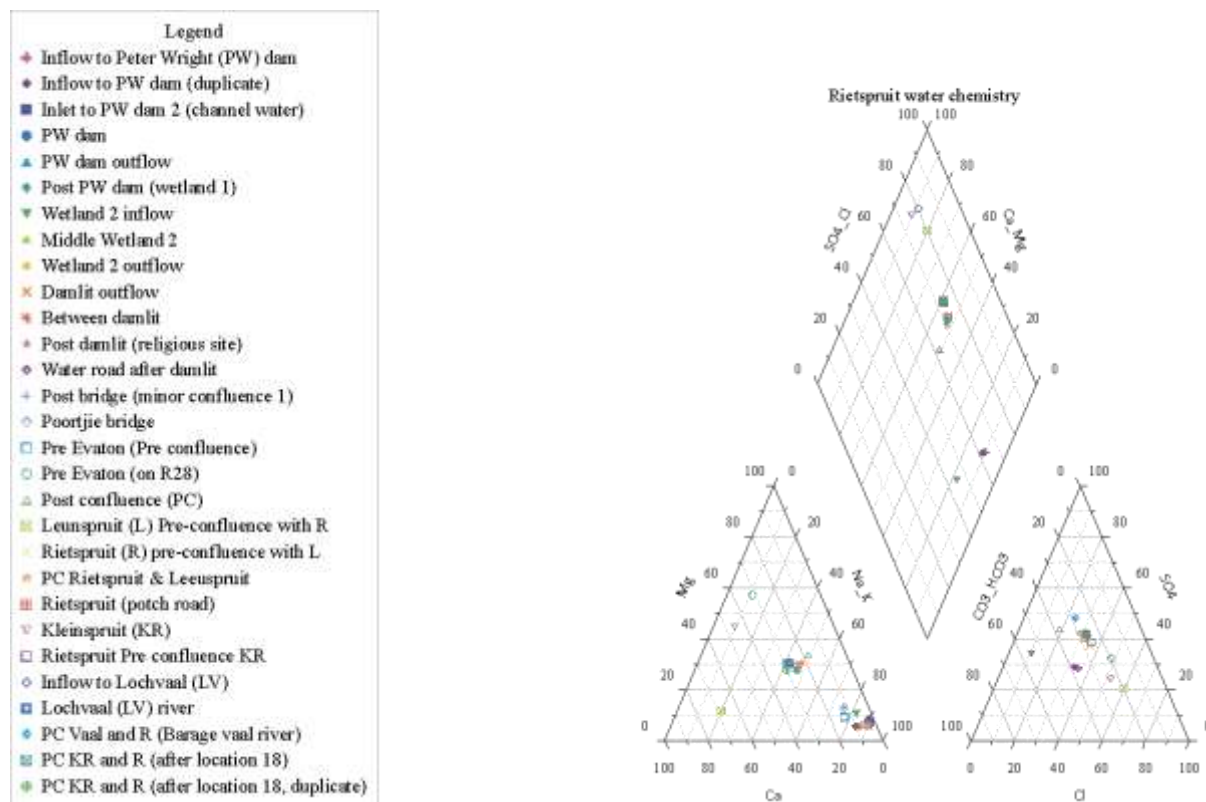


Figure 3.3: Trilinear diagram of the Rietspruit anions and cations

The Trilinear Diagram shows that the water is dominated by calcium sulphate (CaSO_4), which is a standard indicator of mine drainage water. Ratombo (2019) concluded that CaSO_4 rich (apologies, no hyphen here) water sampled downstream of a gold mine is proof of mining pollution. This is like the reports of Hobbs & Cobbing (2007) and Du Preez et al (2016). Despite the difference in the study area within the Witwatersrand Basin, it can be concluded that most of the streams within the Basin have been polluted because of gold mining activities that became operational about a century ago and have continued until the present day.

3.3.2 Inventory of uranium sources and concentrations

Within the study area, the primary sources of U, are the mine wastes and water released from the underground shafts of the gold mine. In the sampled slimes dam and sand dump, the U amount recorded was extreme. While the amount of U logged in the slimes dam was 72.7 mg/kg, in the sand dump, the level of U was 1043 mg/kg (Figure 3.4). Since U is mined as an offshoot of gold operations and the mine being a gold and uranium mine, it can be concluded that the slimes dam has been reworked to remove the U constituents. The total percentage of clay and silt in the sand dump, 44.6 %, is much higher than in the slimes dam, 13.1 %. Due to the high adsorptive capacity of silt and clay because of the surface area, U is adsorbed to clay and silt, leading to the accumulation of U in the sediment.

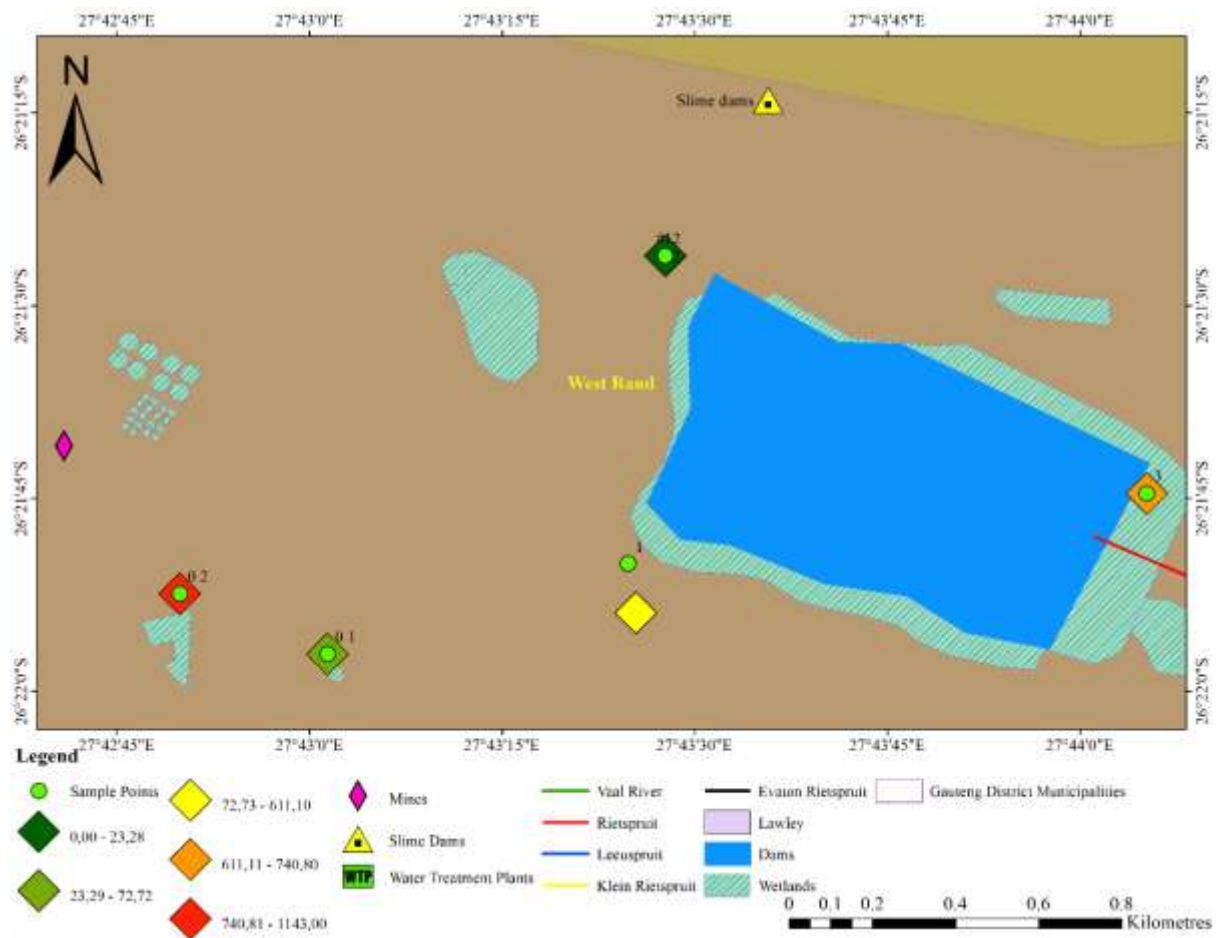


Figure 3.4: A study map showing the concentrations of uranium in sediment around the gold mine (Adapted base geological map created by South African National Space Agency, SANSA, 2018)

Water is discharged from the underground shaft to prevent shaft flooding. This is because the gold deposit within the Witwatersrand Basin is located beneath karst aquifers which flood the mine constantly. To prevent shaft collapse because of flooding, the water must be pumped out. Due to the mixture of U ore with the water, the water holds a high concentration of U. A Uranium concentration of 52.7 $\mu\text{g/L}$ was logged in the concrete canal through which the mine discharges more than 60 ML of fissure and processed water daily into the PW dam, the headwater of the Rietspruit.

In the crust found on the concrete wall of the canal, a concentration of 1143 mg/kg U was logged. The precipitation of calcium carbonate (CaCO_3) which was formed because of the fractional dissolution of dolomitic host rock and because of changes in the atmospheric condition, led to the formation of the crust on the concrete canal. In the process, U was also isolated from the water column. Uranium immobilised in the crust is considered as another

source of U in this study. This is because the U adsorbed by calcium carbonate in the concrete canal's crust will be liberated or dissolved into the water column during a rain event or when there is fluctuation in the water released by the mine.

The other source of U in this investigation is the erosion of mine wastes littering the lithosphere and the release of water from the sewage plant through the trough to the PW dam. Most of the eroded wastes contain U and are washed to the furrow. In the furrow, a U concentration of 782 µg/L was logged in the water and 611.1 mg/kg of U was logged in the sediment (Figure 3.5). Due to the elevated concentration of organic carbon, 6.7 %, in the furrow's sediment (Table 3.3) and the fact that about 45 % of the sediments were composed of fine units of clay and silt, combined with the low water flow velocity, less than 1 m/s, it is believed that suspended particles rich in U precipitated, ensuing in the elevated amount of U found in the PW dam inflow. The sediment is also rich in Mg, 1669 mg/kg, and Ca, 9746 mg/kg, which is indicative of dolomitic source rock.

Table 3.3: A Table showing the particle size distribution (GS % - grain size percentage) and organic carbon (OC) content of collected sediment samples

Sediment - Location	U (mg/kg)	OC (%)	GS%- Sand	GS% -Silt	GS%- Clay
Tailings 1	72.7	0.8	86.9	8.8	4.3
Tailings 2 (first flush site)	1043.0	1.5	55.4	39.9	4.7
Peter Wright (PW) inflow	611.1	6.7	NA	NA	NA
channel sediment	1143.0	9.3	80.6	10.4	9.0
corner PW dam	23.3	0.5	74.9	16.7	8.4
PW outflow	740.8	10.5	NA	NA	NA
Wetland 1 (after PW dam)	1237.0	6.7	NA	NA	NA
Wetland 1 (after PW dam)	1126.0	3.4	51.0	42.6	6.4
Wetland 2 outflow	13.8	0.3	83.2	1.8	14.9
Middle wetland 2	15.8	0.5	90.5	-0.5	10.0
Wetland 2 inflow	102.4	1.6	80.7	10.2	9.2
Damlit outflow	1252.0	0.6	68.9	21.6	9.5
Between damlit	16.5	1.0	62.7	8.0	29.3
Post damlit (religious site)	9.5	0.6	81.2	4.7	14.1
Water road after damlit	25.1	1.2	71.6	10.4	18.0
Post bridge (minor confluence 1)	5.5	0.6	65.6	8.0	26.4
Poortjie bridge	8.1	0.5	93.6	2.2	4.3
Pre Evaton (Pre confluence)	1.9	1.4	80.6	2.4	17.0
Pre Evaton (on R28)	0.7	0.5	73.6	12.0	14.3
Post confluence (PC)	3.4	0.6	91.1	2.2	6.7
Leeuspruit (L) Pre confluence	0.8	1.3	78.3	7.3	14.5
Rietspruit (R) pre confluence	1.4	0.7	65.0	8.1	26.9
Post confluence (PC) Rietspruit and L.	5.6	0.9	93.5	0.0	6.5

Post confluence Rietspruit and L.	2.5	0.6	66.4	10.4	23.2
Rietspruit (Potchefstroom Road)	1.9	0.4	85.3	8.4	6.3
Rietspruit (Potchefstroom Road)	0.2	0.2	79.6	9.1	11.3
Klein Rietspruit (KR)	0.6	0.7	71.0	9.7	19.3
Rietspruit Pre confluence KR	51.2	8.8	NA	NA	NA
Rietspruit Pre confluence KR	7.4	2.2	58.3	25.1	16.6
PC KR and R (after location 18)	5.2	1.3	74.0	14.2	11.7
Inflow to Lochvaal (LV)	15.2	2.4	47.5	26.3	26.2
PC Vaal and R (Barrage Vaal River)	1.2	1.2	8.0	41.2	30.8

The co-precipitation of U with the gel of Fe and Mn oxyhydroxide plays a role in removing dissolved U from the water column and trapping it in the sediment, per U immobilisation (Coetzee et al., 2006). In Figure 3.6, the crust of iron gel was found in the trough connecting to the PW dam. An elevated amount of both Fe and Mn were also found in the trough, 35 214 mg/kg, and 4349 mg/kg respectively. Also, a high concentration of Fe was recorded in the concrete canal, 39 421 mg/kg, and in the sand dump, 38 130 mg/kg. With the strong positive relationship (Table 3.4) between U and Fe, 0.8, U and Mn, 0.6 and U and organic carbon, 0.7, it is hereby concluded that Fe, Mn, and organic carbon played a dynamic role in the immobilisation of U in the study area. In the study of Windisch et al., a similar positive correlation was recorded between U and OC, Fe and Mn.

Table 3.4: The correlation matrix between U and OC, Mn, Fe, and gold

	OC	Mn	U	Fe	Au
OC	1.0				
Mn	0.4	1.0			
U	0.7	0.6	1.0		
Fe	0.7	0.5	0.8	1.0	
Au	0.5	0.7	0.9	0.7	1.0

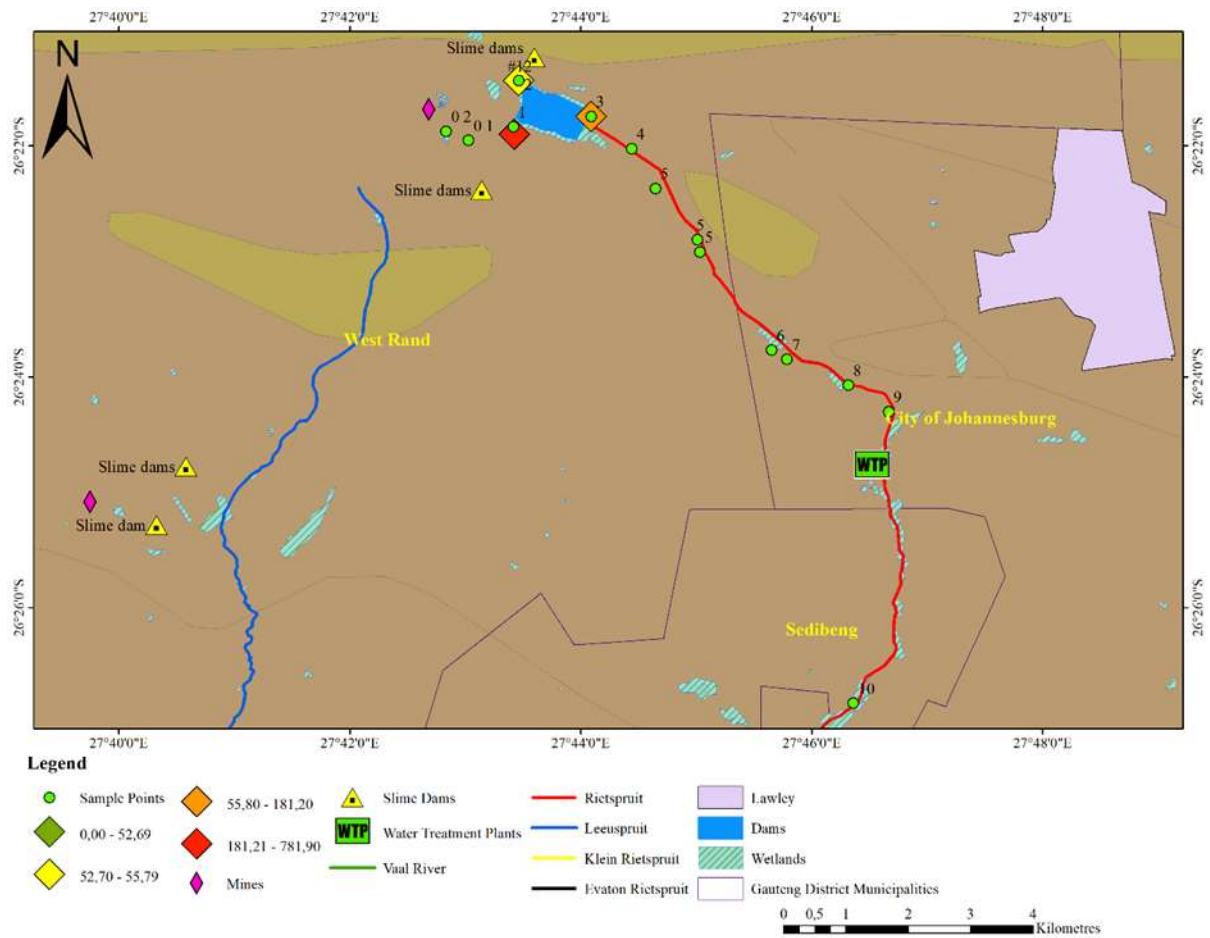


Figure 3.5: A study map showing the concentrations of uranium in water around the gold mine (Adapted base geological map created by South African National Space Agency, SANSA, 2018)



Figure 3.6: Crust of iron gel found in the furrow taking water to the PW dam (Acid mine drainage site with gel of iron hydroxide on the surface)

The PW dam outflow serves as the main water source of the Rietspruit. It is assumed that the Rietspruit will become a seasonal stream if the mine halts the release of water into the PW dam (Kritzinger, 2017). The amount of U recorded in the PW dam outflow is 181 µg/L in the water and 740.8 mg/kg in the sediment. The percentage of organic carbon was 10.5 % while the sediment was made up of about 36 % of clay and silt. The amount of Fe and Mn was 35 330 mg/kg and 146.8 mg/kg, respectively. The PW dam outflow can be safely considered to be the principal cause of U in the stream.

3.3.3 Inventory of uranium sinks and concentrations

Dams and wetlands are deemed to be accumulators of U and other harmful alloys (Raji et al., 2021). Mining activities lead to a lowering of the water table, which causes a scarcity of water. Because of this and the low annual potential rainfall, several farm dams were constructed to save water for different agronomic and domestic uses. In this study, the peak amount of U, 1252 mg/kg, was logged in the dam (called damlit henceforth) about 6 km from the Ezulwini gold and uranium mine. While the percentage of organic carbon was low in the sampled sediment, 0.6 %, the level of Fe and Mn were 30 630 mg/kg and 2029 mg/kg correspondingly. Slow water flow, less than 2 m/s, and high percentage of silt and clay, 31.1 %, U precipitation and co-precipitation with the oxyhydroxides of Fe and Mn, could have influenced U immobilisation in the damlit (Coetzee et al., 2006). The removal of U by adsorption is another factor that could have influenced the accumulation of U in the dam sediment (Coetzee et al., 2006). Downstream of the damlit, the maximum level of U logged was 15.2 mg/kg in the Rietspruit sediment. In the damlit water sample, U concentration was 49.2 µg/L.

In the wetland sediment, U concentration was 1237 mg/kg. This is the second highest amount of U documented within the entire reach of the sampled locations of the Rietspruit. Like the damlit, the amounts of Fe, 35 111 mg/kg and Mn, 9332 mg/kg were quite high. With reeds covering the peat's surface and the hydraulic control point established because of the road culvert impeding the free flow of water, U was able to be deposited in large concentrations because of precipitation and co-precipitation. The amount of organic carbon in the wetland 6.7 % was also high, coupled with the high percentage of clay and silt, 49 %, the sediment of the wetland has a high sorptive capacity which promoted the adsorption of U (positively charged) to the negatively charged wetland sediment (ionic bonding) (Table 3.3 above).

Another factor that plays a critical part in the immobilisation of U is the water salinity. High water salinity reduces the sorptive capacity of sediment resulting in a low concentration of U in sediment (Coetzee et al., 2006). This was observed in the Leeuspruit dam, a tributary of the Rietspruit, with an active gold mine upstream. Despite the high concentrations of Fe, 26 080 mg/kg, and Mn, 963,4 mg/kg logged in the dam's sediment, the peak concentration of U recorded in the Leeuspruit dam was 3.12 mg/kg. The amount of silt and clay was about 44.6 % while a higher percentage of organic carbon was recorded, 1.41 % when compared with the damlit. The sole justification for the minimal U amount is the water salinity which is influenced by dissolved major anions in the water. In the Leeuspruit dam, the concentration of NO₃, 90.14 mg/l, Cl, 241.5 mg/L was greater than the concentration of NO₃, 3.4 mg/L and Cl, 26.2 mg/L recorded in the damlit. This resulted in higher EC recorded in the Leeuspruit dam, 1614 mS/cm. It has been reported that NO₃ prevents the reduction of U which favours immobilisation (Senko et al., 2002). With the elevated amount of U recorded in the water of the Leeuspruit dam, 131.2 µg/L, and the minimal amount of U in the sediment, 3.12 mg/kg, it is resolved that water salinity is a valuable factor influencing the immobilisation of U.

In conclusion, wetlands and dams are considered as secondary sources of U pollution in this investigation. This is because U that was immobilised can also be remobilised back into the water column whenever an alteration in the water chemistry and / or an increase in water salinity takes place. Also, with the proposed halting of fissure and processed water release into the PW dam, the Rietspruit will turn into a seasonal stream, meaning that the dryness of the Rietspruit in winter will eventually oxidize the exposed sediment. During a rain event, U trapped in oxidised sediment will be freed back into the water column, which will be harmful to the wellbeing of downstream dependents.

3.3.4 Uranium distribution in the Rietspruit water

A continuous reduction of dissolved U was logged in the river downstream of the mine (Figure 3.7). This indicated that U is being detached from the water column and trapped in the stream floodplain by either adsorption, precipitation and or co-precipitation. About 24 km downstream of the mine, the level of dissolved U was more than the acceptable threshold of U in water utilized for irrigation, 10 µg/L and drinking, 30 µg/L (DWAF, 1996a; DWAF, 1996b). This is due to the varying stream water-sediment interplay, which removes U from the water column

as explained earlier. This includes the adsorption of U by river sediment, and the precipitation and co-precipitation of U with insoluble oxyhydroxides of Fe and Mn.

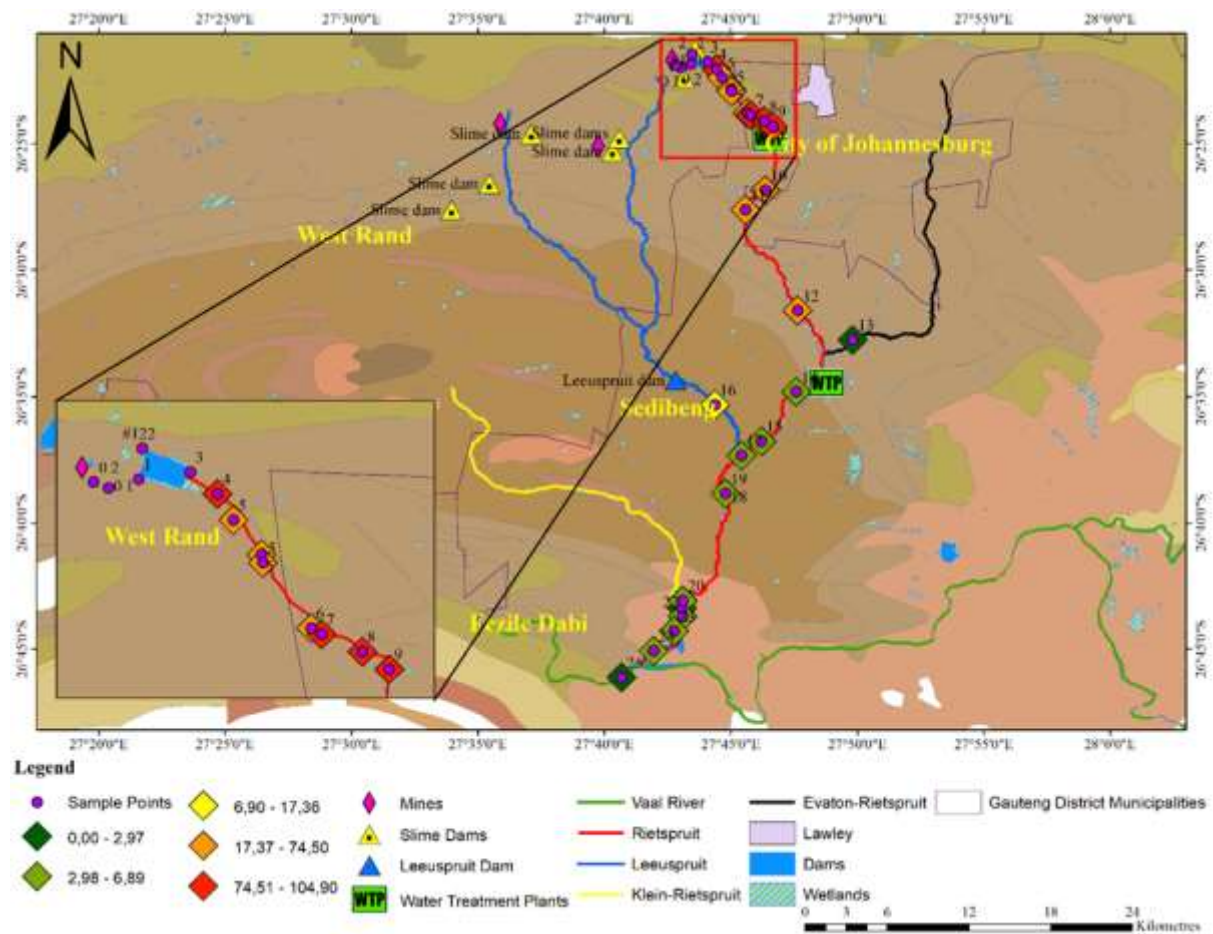


Figure 3.7: Longitudinal profile of dissolved uranium in the Rietspruit water (Adapted base geological map created by South African National Space Agency, SANSA, 2018)

Two water treatment plants, Ennerdale Water Treatment Plant and Sebokeng Water Treatment Plant (Figure 3.7) are established downstream of the Rietspruit. They both discharge about 2324.2 ML of water per month (Kritzinger, 2017). With the combined discharge from the water treatment plants being higher than the average monthly outflow from the PW dam, 159.4 ML, they dilute the concentration of U in the stream. After the confluence of the Rietspruit and Evaton-Rietspruit, the amount of U dropped to 4.9 µg/L from the 71.1 µg/L documented in the Rietspruit before the confluence (Figure 3.7). A similar drop in the level of dissolved U downstream of the gold mine in the Leeuspruit was also observed.

At sites specified as this study's natural concentration of dissolved U, Evaton-Rietspruit and Klein-Rietspruit, the amounts of dissolved U at these sites were 0.3 µg/L and 0.7 µg/L

respectively. These sites were designated as the expected natural concentrations of U due to the absence of mining and industrial activity upstream of the selected sites.

There was a significant decrease in the water EC recorded downstream which indicates the reduction in water pollution loads. There was an increase in EC recorded downstream of the water treatment plants, which will potentially result in the limited immobilisation of U by the stream sediment, as discussed earlier.

3.3.5 Uranium distribution in the Rietspruit sediment

The drift of U distribution in the Rietspruit sediment was not linear as observed in the U distribution in the stream's water (Figure 3.8). This is due to several factors that played a part in the immobilisation of U. As explained earlier, wetlands and dams are sinks for U, therefore U concentrations were very high in the wetland and dam. After the farm-dam, the levels of U logged in sampled sediments were less than 15 mg/kg (Figure 3.8).

At one of the sampled sites, post bridge, downstream of the Ennerdale Water Treatment Plant, the concentration of U was 5.5 mg/kg. Despite the elevated number of fine particles of silt and clay, 34.6 %, there was extreme concentration of U in the water, 70.2 µg/L, and elevated amounts of Fe, 8846 mg/kg and Mn, 42.8 mg/kg. The reason for the low concentration determined in the sediment was the high water salinity characterised by NO₃ concentration of 11.2 mg/L and chlorine, 54.6 mg/L. The EC measured was 1250 mS/cm. This is further proof of the consequence of water salinity on the immobilisation of U. At Evaton-Rietspruit and Klein-Rietspruit, the level of U was less than 1.0 mg/kg. The concentrations of U recorded here were described as the control concentration of U in this study.

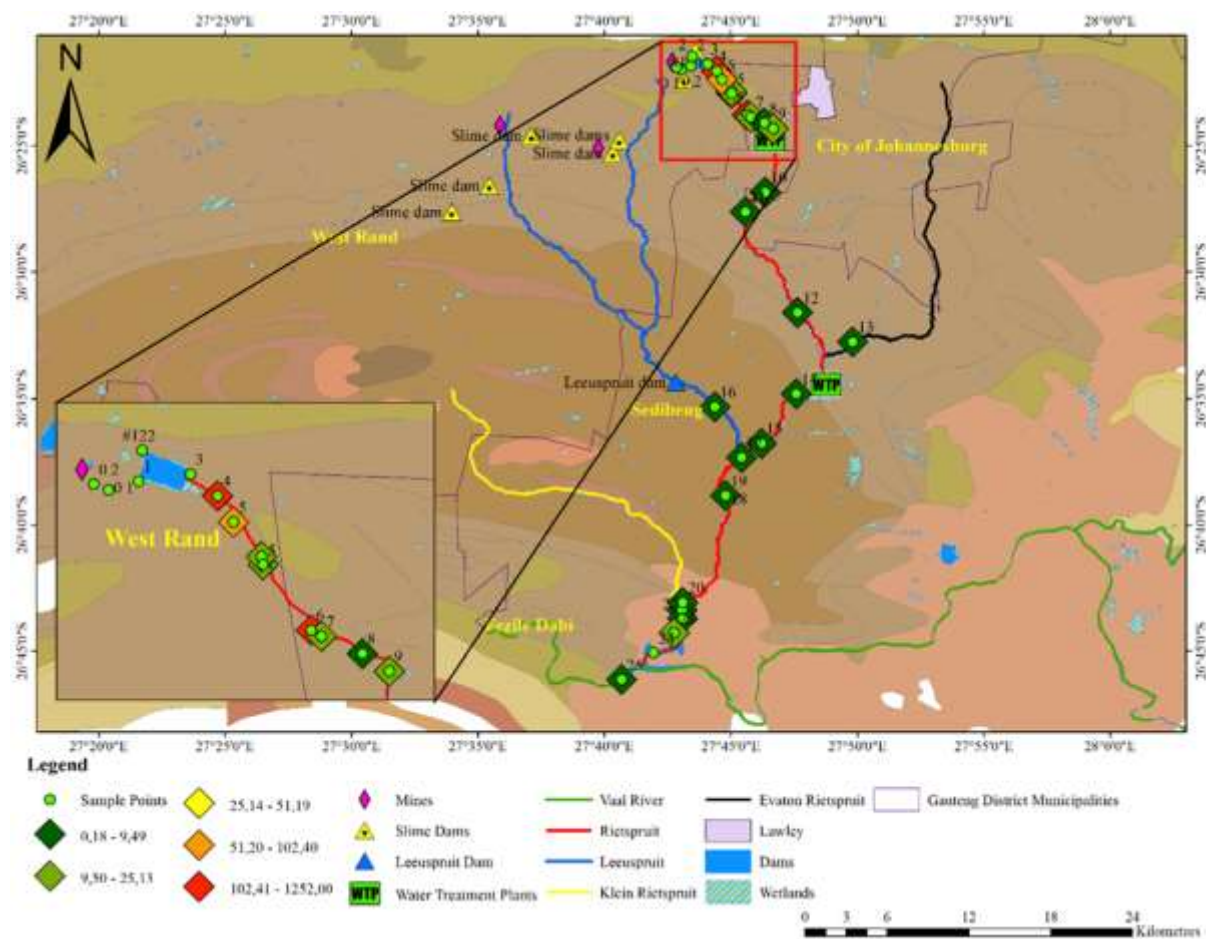


Figure 3.8: Longitudinal profile of uranium in the Rietspruit sediment (Adapted base geological map created by South African National Space Agency, SANSA, 2018)

3.3.6 The concentration of other potentially toxic elements in the Rietspruit water and sediment

According to the World Health Organisation, arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb), are regarded as the most extremely poisonous alloys (Tchounwou et al., 2012). These stated toxic elements have been associated with environmental pollution due to goldmining operations (Raji & Palamuleni, 2023; Maseki et al., 2017; Du Preez et al., 2016; Bakatula et al., 2012; Oelofse et al., 2007). While elevated amounts of these toxic alloys were recorded at sampled sites close to the mine, and which were above the recommended permissible limit in water and sediment, their concentrations decreased further downstream in the stream's water as well as sediment.

The levels of these toxic metals were less than the permissible limit within the proximity of the gold mine in the water samples collected and analysed. When compared with U concentration in the Rietspruit, it can be concluded that U is more mobile than As, Cd, Hg and Pb. High

concentrations of U above the permissible limit were recorded in water about 24 km away from the Cooke 4 Ezulwini Plant. The peak concentration of As was logged in the PW dam furrow; at other sampled sites, the concentrations recorded were lower than the acceptable threshold of As, 10 µg/L. Cadmium being a highly insoluble heavy metal, the concentrations recorded were all below the permissible limit, 5 µg/L in all the collected water samples. While the concentrations of Pb were all below the permissible limit in water, 10 µg/L, the concentration of mercury was high within the mining environment but after about 2 km away from the PW dam outflow, the concentrations recorded were lower than the acceptable threshold in water, 1 µg/L (Table 3.5).

Table 3.5: Concentrations of selected toxic metals in the Rietspruit water

Sampled sites	As	Cd	Hg	Pb
	(µg/L)			
Inflow to PW dam	45.5	0.1	11.8	0.2
Channel water	6.2	0.4	3.7	2.1
PW dam	3.5	0.1	1.7	1.3
PW dam outflow	4.3	n/a	3.4	1.0
Wetland 1	2.6	n/a	1.7	n/a
Wetland 2 inflow	0.7	0.06	0.4	1.5
Middle wetland 2	0.1	0.01	0.5	1.1
Outflow wetland 2	0.5	0.03	0.5	1.0
Damlit outflow	0.5	n/a	1.1	0.4
Between damlit	0.9	n/a	0.6	0.1
Religious site	0.8	n/a	0.5	0.7
Water road after damlit	0.7	n/a	1.5	0.8
Post bridge	0.8	n/a	0.4	0.2
Poortjie bridge	0.9	n/a	0.3	0.5
Pre-confluence Evaton	1.2	n/a	0.3	0.6
Evaton- Rietspruit	0.7	n/a	0.2	0.0
Post-confluence Evaton	0.5	n/a	0.3	0.4
Leeuspruit Pre-confluence with Rietspruit	0.7	n/a	0.3	0.9
Rietspruit Pre-confluence with Leeuspruit	0.7	n/a	0.2	1.6
Post confluence Rietspruit and Leeuspruit	0.5	n/a	1.2	1.2
Post confluence Rietspruit and Leeuspruit	0.7	n/a	0.2	1.7
Rietspruit (Potch Road)	0.6	n/a	0.8	0.2
Klein-Rietspruit	0.4	n/a	0.5	0.6
Rietspruit pre-confluence with Klein-Rietspruit	0.6	n/a	0.7	1.0
Post confluence Rietspruit and Klein-Rietspruit	0.6	n/a	0.1	n/a
Post confluence Rietspruit and Klein-Rietspruit	0.8	n/a	0.2	0.4
Lochvaal inflow	0.8	n/a	0.2	1.8
Lochvaal River	0.9	n/a	0.4	0.1
Vaal River	0.9	n/a	0.1	3.5

Maximum	45.52	0.4	11.79	3.5
Average ± MU	3.12 ± 2.67	0.12 ± 0.16	1.14 ± 1.96	0.91 ± 0.85
Minimum	0.15	0.01	0.08	0.04

n/a means concentration of heavy metal in the sample was below detection limit, MU is the measured uncertainty.

In the sediment, the maximum concentrations of As, Cd, Hg and Pb verified were approximately 550 mg/kg, 3.9 mg/kg, 2.0 mg/kg, and 184 mg/kg respectively (Table 3.6). These concentrations were all recorded within the proximity of the mine. These were all greater than the acceptable maximums of these metals, As, 6 mg/kg; Cd, 0.6 mg/kg; Hg, 0.2 mg/kg and Pb, 31 mg/kg. (Persaud et al., 1993). Like U, high concentrations of the investigated toxic metals were logged in wetland, dams, and mine waste. The peak concentrations of Cd were logged in the wetland and damlit, 3.9 mg/kg and 3.5 mg/kg, respectively. The peak level of Pb was recorded in the sand dump while high concentrations of As were also recorded in the sand dump, crust of the concrete canal and the wetlands.

Table 3.6: Concentrations of selected toxic elements in the Rietspruit sediment

Sampled sites	As	Cd	Hg	Pb
	(mg/kg)			
Slimes dam	61.74	0.15	0.40	12.15
First flush	550.40	1.66	0.42	184.3
PW dam inflow	214.20	1.48	0.44	90.52
Channel sediment	415.30	3.40	0.42	8.382
Corner PW dam	14.46	0.09	0.19	10.24
PW dam outflow	54.81	0.73	0.18	18.75
Wetland 1	223.10	3.53	0.29	120.9
Wetland 1 duplicate	158.30	2.17	0.16	84.41
Wetland 2 outflow	2.25	0.02	0.13	8.77
Middle wetland 2	2.09	0.04	0.09	4.48
Wetland 2 inflow	46.05	0.54	0.09	17.90
Damlit outflow	62.56	3.88	0.12	24.20
Between damlit	5.10	0.01	2.44	9.56
Religious site	3.82	0.02	0.10	21.41
Water road after damlit	4.85	0.02	0.07	12.67
Post bridge	2.55	0.07	0.07	14.2
Poortjie bridge	3.18	0.07	0.09	26.25
Pre-Evaton	1.76	0.01	0.05	8.01
Evaton-Rietspruit	3.73	0.08	0.10	17.67

Post confluence Evaton-Rietspruit and Rietspruit	1.21	0.02	0.07	6.39
Leeuspruit Pre-confluence	2.17	0.02	0.02	8.85
Rietspruit pre-confluence with Leeuspruit	3.46	0.04	0.04	23.42
Post confluence Rietspruit and Leeuspruit	1.03	0.04	0.08	5.49
Post confluence Rietspruit and Leeuspruit	1.08	0.02	0.04	7.70
Rietspruit (Potch Road)	0.52	0.02	0.05	3.20
Rietspruit (Potch Road)	0.31	0.01	0.03	4.06
Klein-Rietspruit	4.62	0.04	0.03	17.15
Rietspruit Pre-confluence with Klein-Rietspruit	3.76	0.27	0.57	19.09
Rietspruit Pre-confluence with Klein-Rietspruit	1.72	0.11	0.16	13.39
Post confluence Klein-Rietspruit and Rietspruit	1.43	0.27	0.12	13.36
Inflow to Lochvaal	2.89	0.18	0.19	20.97
Vaal River	2.01	0.06	0.04	12.53
Maximum	550.40	3.88	2.44	184.30
Average ± MU	58.01 ± 2.19	0.60 ± 1.87	0.23 ± 1.86	26.57 ± 1.47
Minimum	0.31	0.01	0.03	3.20
SD	127.21	1.11	0.43	39.08

3.3.7 Health impact of uranium

It has been reported that U has both radiological (carcinogenic) and chemical (non-carcinogenic) impacts on human health (Bjørklund et al., 2020; Corlin et al., 2016; ATSDR, 2014; Callahan et al., 2004). The chemical health impact of U includes kidney damage, which leads to the impaired functioning of the kidney and the nervous system (ATSDR, 2014). The radiological health impact of U includes liver cancer, bone cancer, lung cancer, as well as a change of or damage to the deoxyribonucleic acid, DNA, (ATSDR, 2014).

Within the study area, U can infiltrate the food chain in two different ways, which include the following:

- 1) Uranium enters the food chain directly through the soil → plant → animal pathway.
- 2) Indirectly using the Rietspruit water for irrigation purposes or as drinking water.

Mathematically, if the concentration of U recorded where human exposure was observed in this study remains the same, and the exposed population drink the water throughout their lifetime, the chemical (non-carcinogenic) risk due to the ingestion of dissolved U will outweigh the radiological (carcinogenic) risk (Raji et al., 2022). Using the concentration of U recorded at the religious site in the form of drinking water from the stream, the chemical risk (the ratio of lifetime average daily dose and the reference dose of U^{238} , 0.6 µg/kg/day) was greater than

1. The cancer risk at the site was however lower than the radiological risk limit for both mortality and morbidity cancer risk, $1.0E - 03$. Full details of the report have been published by Raji et al (2022).

3.3.8 Potential receptors and water-related exposure pathways

The water from the PW dam is used for irrigation. There is a commercial wheat plantation that uses the PW dam water for irrigation. In one of the water samples collected from a pipe leakage supplying water to the farm, a concentration of about 53 µg/L dissolved U was logged. This is above the acceptable threshold of U in water utilized for farmland watering, 10 µg/L (DWAF, 1996b). This is because plants absorb U from the soil and water used to irrigate the plant. Since wheat is used to produce bread, biscuits and flours and is consumed nationwide, this could have an adverse effect on the healthiness of people consuming such products.

Furthermore, the water from the damlit is used for animal watering, most especially cattle. Cattle grazing is also a general phenomenon observed around the mining site and further away. This is another observed exposure route for the introduction of U to the food chain. Also, because of the wealth imbalance in the country, many people reside in informal settlements around the mine. An example of such an informal settlement in this study is Lawley (Figure 3.8). Due to the lack of potable water at such settlements, residents were observed fetching water from the stream for various domestic purposes. High rates of HIV and tuberculosis have been reported in informal settlements (Chimoyi et al., 2020) and all over the country (Pillay et al., 2021), with malnutrition expected within this community. Therefore, the residents can be assumed to have a compromised immune system, which could be triggered further by the consumption of polluted water.

In addition, religious activities were observed within the study area during field work. Religious worshippers were observed drinking the stream water and bathing in the stream. Cooking activities using the stream water were also observed. Within these environments, the minimum level of U determined was 70.1 µg/L which is double the acceptable threshold of U in water utilized for drinking, 30 µg/L (DWAF, 1996a). This could result in the introduction of U to the human body.

3.3.9 Motivation and result of first flush sampling (impact of rainfall)

In a mining environment, rainfall percolates through mine wastes such as slimes dams and mine dumps, releasing the toxic elements embedded in such wastes. Many studies have been done to reflect the impact of rainfall on slimes dams and mine dumps found in a mining environment (Durand, 2012; McCarthy, 2011; Manders et al., 2009; Tutu et al., 2008). However, this study focused on the first rain event after a winter season, which is characterized by limited rainfall for 4 - 5 months.

The result revealed that the concentration of dissolved U in the water was 387.7 µg/L while the concentration of U in the suspended particle was 242.4 mg/kg. This is higher by several degrees of magnitude than the recommended limits of U in water utilised for drinking and irrigation purposes (Table 3.7).

Table 3.7: A comparison between remobilized U and prescribed limits

Concentration of dissolved uranium in water	Concentration of U in suspended water particles	World Health Organisation (WHO) guideline of U in water (WHO, 2012)	Department of Water and Forestry (DWAF) guideline of U used for irrigation purposes (DWAF, 1996b)
387.7 µg/L	242.4 mg/kg	30 µg/L	10 µg/L

Rainwater mixes with atmospheric CO₂, thereby making the water acidic. The pH recorded was 4.1 using a WTW Multi350i probe-meter. Thus, acid mine drainage is formed (Figure 3.6). Oxidation of sulphide in the mine wastes occurred, resulting in the release (dissolving) of U trapped in the mine waste. Even though a high volume of rainfall is expected to dilute contaminated stream water, run-offs eroding a mining environment serve as a pathway of stream water pollution by U and other HM. While some run-offs get evaporated or seep below the surface, most join a flowing water body. In this study, the run-offs go directly through the observed furrows into the PW dam, the headwater of the Rietspruit.

The site of Figure 3.6 is a few metres away from the sand dumpsite. As aforementioned, the site was dry before the rain-event. The amount of U determined in the water sample after rainfall at the site (Figure 3.6) was 185,7 µg/L while in the suspended particle, composed

mainly of the gel, a higher concentration of U was recorded, 205.5 µg/L. As expected in the suspended particles, the amount of Mn and Fe particle were 1289 mg/L and 57 490 mg/L, respectively.

Gold deposit is associated with pyrite (FeS₂) in the Witwatersrand Basin which is stable underground. However, when pyrite encounters rainwater, for example, iron hydroxide and sulphuric acid are released, forming an acidic solution (Durand, 2012). This solution dissolves the mineral ores in the sand dump, releasing U and other poisonous toxic elements (Durand, 2012).

Other toxic metals were also recorded in the sand dump at concentrations above the permissible limit of the heavy metal in sediment. For example, the concentration of arsenic, (As), lead, (Pb), cadmium, (Cd), and mercury, (Hg) were 550.4 mg/kg, 184.3 mg/kg, 1.7 mg/kg, and 0.42 mg/kg respectively. All these toxic elements were many degrees of magnitude higher than their permissible limits (Balali-Mood et al., 2021; Persaud et al., 1993).

In the water, an elevated concentration of toxic elements was also recorded. The concentrations of As, Cd, Hg and Pb logged were 22 µg/L, 0.02 µg/L, 0.3 µg/L and 1.6 µg/L respectively. Only the concentration of As was above the WHO allowable threshold of 10 µg/L (WHO, 2003).

3.3.10. Possible uranium remobilisation

As proposed by the mine, the release of water into the PW dam will end in a few years' time (Krizinger, 2017). If this should happen, outflow from the PW dam, the Rietspruit's main source of water, will be seasonal, happening mainly during the rainy period. Due to potential annual evaporation being nearly triple the potential annual rainfall, it is expected that the Rietspruit would become a non-perennial (seasonal) stream (Krizinger, 2017).

Consequently, the upper part of the Rietspruit, upstream of Ennerdale Water Treatment Plant, will be dry from April to August due to no or limited rainfall, during the winter season (Krizinger, 2017). Wetlands and dams are located within the upper part which helped to remove U from the stream. It will be expected that the wetland will get dry first due to the lack of a

regular supply of water which keeps the environment water-saturated before the dam. Considering the extreme concentration of U logged in the wetland's sediment, 1237 mg/kg, and the damlit's sediment, 1252 mg/kg, this could have a detrimental effect on downstream dependents of the stream water.

Firstly, salt crusts rich in U which are formed on the surface of the dried and exposed wetland and dam sediment will dissolve immediately upon contact with water (Coetzee et al., 2006). This is expected most especially during the first flush event after several months of no rainfall. The quick dissolution of the salt crust rich in U creates a pulse of dissolved U in the stream.

Secondly, the oxidised sediment will react with rainwater, causing the release of U trapped within the sediment. This might not be as immediate as the dissolution of the salt crust. Since U immobilisation and remobilisation occur concurrently, a time frame cannot be proposed to give an estimation when the stream water will be safe for its various uses after a rain event.

Furthermore, the burning of wetland vegetation covers like reeds could result in the remobilisation of U (Coetzee et al., 2006). This was observed during field work. Reeds, like every other plant, absorb uranium and other toxic elements from the sediment of polluted wetlands. During burning, which is a general practice in the study area, U accumulates in the ashes. During a rain event, the ashes will dissolve in water and form part of the stream run-offs (Winde, 2006). This could lead to a temporary increase in the concentration of dissolved U in downstream water.

3.3.11. Limitation

It is common knowledge that oxidation – reduction potential (Eh) plays a role in the mobility of U. However, there are a few limitations that prevented the Eh measurement. One of the limitations was inaccessibility to Eh probe meter and inadequate funding to purchase the instrument. The Eh measurements at all the sampled sites would have been used to determine if a site is undergoing oxidation or reduction. Oxidation promotes U mobilisation while reduction favours U immobilisation in a fluvial system (Gronowski, 2013). Also, the measurement would have been used as one of the parameters required to create a geochemical

model like PH REdox EQUilibrium (PHREEQC), which would have been helpful to solidify some of the findings in this study.

3.4. Chapter conclusion

Uranium mobility in the Rietspruit was discussed in this study. It can be concluded that the main source of U in the stream can be linked to the continuous release of processed water into the PW dam and the leaching of U from sand dumps and tailings which run off into the PW dam. The outflow of the PW dam, which is the key beginning of Rietspruit water, contains an elevated amount of dissolved U. Once inside the stream, the amount of U reduces with distance from the PW dam. This proved that some of the dissolved U was trapped by the highly adsorptive floodplain sediment. Adsorption of U by the negatively charged sediment, precipitation and co-precipitation of U are some of the processes attributed to the removal of U from the water column in this study.

Throughout field works, it was confirmed that water from the dam was being utilized for agricultural, domestic, and religious purposes. In a wheat plantation, the water used for irrigation contained about 53 µg/L of dissolved U which is more than five times higher than the acceptable threshold of U in water designated for farmland watering. At a site where people were observed drinking the stream water, the chemical risk calculated from the amount of U²³⁸ found in the water at the time, was above 1, while the radiological risk was below 1.0 E-3 for both morbidity and mortality risk. This is discussed in detail in Chapter 5 of this thesis.

Other harmful toxic metals were also emitted into the environment because of the gold- mining operations. High concentrations of As, Cd, Hg and Pb were recorded in collected samples found within the immediate mining environment. However, a few kilometres away from the mining location, their concentrations were below their permissible limit except for Cd found in the wetland and damlit sediment. This shows that U is more mobile than As, Cd, Hg and Pb in a fluvial system.

After the first rain-event post a dry season, an elevated amount of dissolved U was logged in water found in a furrow next to a sand dump. This indicated that U can be released from abandoned mine waste. Uranium is released when pyrite meets rainwater, forming a solution

containing iron hydroxide and sulphuric acid. This solution dissolves the mineral constituent of the sand dump, causing the release of U and other toxic elements into the environment.

The proposed discontinuation of water release into the PW dam could make the stream a seasonal stream which only flows during the rainy season. After a prolonged time without rainfall, the stream will be dry, leading to the oxidation of the U polluted sediment. This will result in the remobilisation of elevated amounts of dissolved U trapped in the sediment of wetlands and dams upon contact with water.

In conclusion, the continuous usage of water for the activities should be discouraged due to the health implications. Government should intervene by erecting fences around this environment where human contact with the high concentrations of U was observed. Also, people within the environment must be sensitized about the toxic impacts of U and other toxic heavy metals abundant in the stream. Adequate provision of clean borehole water should be delivered to the residents of the informal settlements.

Chapter 4

Assessing uranium remobilisation in water-sediment system and diurnal dam water chemistry

Abstract

River sediments have been contaminated with uranium, and this is attributable to gold mining exploration in the Witwatersrand Basin. In this study, factors influencing uranium remobilisation from polluted sediments were investigated. To this end, polluted sediment collected from a dam in the Rietspruit system was sampled and dried in a container. Subsequently, the sediment was rewetted with collected rainwater, and U-levels in the dissolved phase were analysed using ICP-MS. Since U mobility in a sediment-water system is controlled by chemical processes, diurnal changes in water chemistry in the dam were also analysed using hourly measurements. Regarding U-remobilisation from rewetted sediments, we found high initial releases of U, about 1200 µg/L, into the dissolved phase for which several underlying mechanisms are proposed. The *in-situ* measurements in the dam indicated significant fluctuations of pH during the day as described in the literature, with potential implications for U-speciation and mobility. Higher concentrations of dissolved U were verified at night than during the day. Given the high rates of U-remobilisation from rewetted sediments, significant U-spikes are to be expected in streams after the first rains, after the dry winter months, during which many streams in the study area tend to at least partly dry out.

Keywords: Uranium, immobilisation, remobilisation, gold, mining, Witwatersrand, dam

4.1 Introduction

Gold mining began several decades ago in the Witwatersrand goldfields, South Africa (Durand, 2012; Hobbs et al., 2010; Phillips & Law, 2000). This has helped to absolutely shape the economy and development of the country (Fedderke & Pirouz, 2002). Since uranium (U) is associated with many gold reefs, fluvial sediments in streams and dams of the Witwatersrand Basin often contain elevated concentrations of U, reaching over 1000 ppm in some places (Winde & van der Walt, 2004a). A major U-source are tailings deposits (termed slimes dam in South Africa) which, in the Witwatersrand Basin alone, cover over 400 km² of land surface (Winde, 2010; Rösner & van Schalkwyk, 2000).

Several studies have been done on the U pollution in the Witwatersrand Basin (Winde & de Villiers, 2002b; Winde, 2004b; Tutu et al., 2009; Winde & Erasmus, 2011, Raji et al., 2021;). Tutu et al (2009) report an ongoing leakage of U from gold tailings in water systems; about 130 mg/kg of U was recorded in tailings. Raji et al (2021) also reported U concentrations above 1048 mg/kg in sand dumps of a decommissioned gold mine and over 1000 mg/kg of U in sediments of a downstream wetland and dam, proving the capability of wetlands and dams to immobilise and accumulate U. However, if the accumulated U is released again, this sediment may become an alternative source of U pollution. In the study of Raji et al. (2021), the background concentration of U in sediment and water within the study area was below 0.7 mg/kg and 0.3 µg/L respectively.

The removal of U from water (immobilisation) can be through physical, chemical, and biological processes. Physical processes include the sedimentation and settling of uranium-bearing particles such as suspended solids (Javed et al., 2019). In standing or slow-flowing water, like we found in dams and wetlands, this may lead to U accumulation. Chemical processes of U immobilisation include sorption, adsorption, precipitation, and co-precipitation (Coetzee et al., 2006). Sorption can be described as binding of U ions from the water column to the sediment due to electro-static forces. In contrast, precipitation occurs due to the formation of compounds with low solubility once critical levels of their dissolved constituents are exceeded in the water (Javed et al., 2019). Factors governing U-precipitation are mainly redox potential and pH with reducing conditions, which favour the formation of tetravalent U-compounds with low solubility.

Co-precipitation of U occurs if the dissolved U-ion is incorporated through adsorption or physical inclusion. For example, U can co-precipitate with the oxides / hydroxides of iron, Fe, and manganese, Mn, which in turn are governed by oxidation-reduction potential (Eh) and pH along with the sorption of U to organic carbon. It was revealed in previous studies that the strong correlation between Fe and U and Mn and U found in sediments of the Klerksdorp Goldfield (Winde & de Villiers, 2002b), and dams and wetlands found downstream of a gold and uranium mine (Raji et al., 2021), are indicators that dissolved U co-precipitated along with the oxide and hydroxide of Fe and Mn.

Uranium can also be released from sediment back into the water column. This process is called remobilisation. Remobilisation involves the desorption of U from polluted sediment, dissolution of solid phase, for example secondary uranium minerals, uranium-bearing calcite, salt crust and the biological decomposition of uranium contaminated sediment rich in organic carbon (Winde, 2004a). The dissolution of U minerals, uranium bearing calcite and salt crust is prominent in environments where months of dry conditions are followed by wet conditions. The dissolution of salt crusts developed on the surface of dried U polluted sediment is very quick when compared with the dissolution of iron oxides and calcites. The dissolution of salt crust leads to pulses of dissolved uranium in water when dry sediment meets water (Winde, 2004b).

Remobilisation of U may occur when there is lowering in water pH and/ or an increase of Eh or the electric conductivity, EC, increases (Winde, 2004a). Electric conductivity indicates the presence of anions that U can bind with, to form uranyl complexes such as carbonates, sulphates, and phosphates. High EC values also show reduced adsorption of U onto potential sorbents due to binding competition by other dissolved cations such as sodium, calcium etc. In the study of Raji et al. (2021), it was confirmed that increase in water EC reduced the ability of Leeuspruit dam sediment (a dam located downstream of a gold mine in Witwatersrand Basin) from adsorbing U despite the high concentration of U in the water, reduction in water flow velocity, abundance of fine particles of clay and silt (40% of the sediment particle was made of clay and silt) and high concentration of Fe, above 20 000 mg/kg, and Mn, above 600 mg/kg.

In this study, the remobilisation of U due to rewetting and the possible impacts of diurnal water chemistry fluctuations were examined in a shallow farm-dam downstream of a

decommissioned gold and uranium mine which discharges some 70 000 m³ of U-containing fissure water – infiltrating groundwater in an underground mine shaft - per day (Kritzinger, 2017). According to the specialist surface water report done by Jones & Wagener Engineering and Environmental Consultants, South Africa, it was concluded that the Rietspruit will become a non-perennial stream after the closure of the gold mine underground workings (Kritzinger, 2017). As this will result in the drying out of highly U-contaminated sediments in dams, wetlands and the stream channel containing over 1000 mg/kg, massive water pollution after rainfall is a potential threat to downstream water users. For that reason, this study investigated the remobilisation of U from a dry U-polluted dam sediment as well as the diurnal stream water chemistry fluctuations.

During field work, it was observed that the dam water is used for irrigation and animal watering and about 50 m downstream of the dam outflow, religious activities were prominent, which involved drinking and bathing in the stream and the usage of the water for domestic purposes. The dam will serve as a water reservoir for all these activities if the Rietspruit becomes non-perennial, most especially during winter and with limited rainfall in summer. Therefore, the focus of this study is:

1. To determine the level of U released from an oxidised stream sediment after rewetting the sediment with rainwater.
2. To determine the hourly changes in dam water chemistry.

4.2. Materials and methods

A uranium contaminated sediment sample of less than 5 kg was collected on 24th June 2021 in a farm dam (26°23'42.59"S 27°45'43.24"E) located approximately 7 km downstream of a decommissioned gold and uranium mine in Gauteng, South Africa. The farm dam is supplied by the outflow from the Peter Wright (PW) dam, a dam into which mine waters from underground shafts are discharged, and thence into the Rietspruit (Raji et al., 2021). The Rietspruit flows close to rural settlements and the settlers within these communities depend on the stream water for their basic agricultural, religious, and domestic needs (Raji et al., 2022).

The sediment sample was stored in an opened container and allowed to dry naturally under atmospheric conditions. A portion of the sediment was taken to the laboratory for chemical

analysis. The sediment was microwave digested with the EPA 3051A method and results were obtained using Agilent inductively coupled plasma-mass spectrometry (ICP-MS). This method has been detailed in the previous study of Raji et al. (2022).

Loss on ignition (LOI) is one of the most widely used methods for measuring organic matter content (chiefly made up of organic carbon content) in soils (Breithaupt et al., 2023; Mozaffari et al., 2023; Hoogsteen et al., 2015). To measure the organic carbon in the sediment, 15 mg of the prepared sediment was measured out and placed in an already weighted crucible. The total weight of the sediment plus crucible was weighed and recorded. Thereafter, the sediment-filled crucibles were placed in an incinerator oven at a temperature of 450 °C for a duration of six (6) hours. After six hours, the oven was allowed to cool down before the crucible was removed. The weight of the crucible was then measured and recorded. The amount of organic carbon present in the soil was determined by subtraction of the weight of the sediment filled crucible after burning, from the weight of the sediment-filled crucible before burning. After two months, the sediment was completely dry and a change in sediment coloration was noticed as the sediment changed from brown (Figure 4.1A) to light brown. There was dry salt crust observed on the dried sediment (Figure 4.1B).



Figure 4.1: Collected dam sediment sample (A) Immediately after collection on 26th June 2021 (B) Fully dried sediment sample on 27th August 2021 under normal atmospheric condition (C) Sediment sample after rewetting on 27th August 2021 (D) Four days after rewetting

The major aqueous compositions of the rainwater used to rewet the sediment were also determined using Agilent ICP-MS. To determine the concentration of dissolved U in the water composition, 0.45 µm nylon filtered pipette was used to measure 1 mL of the water sample. 9 mL of 2 % HNO₃ was added to the 1 mL to bring the volume to 10 mL and remove any dissolved organic material.

After rewetting of the sediment with about 10 L of rainwater, the colour of the sediment was observed to change from the light brown with salt crust on top to dark brown (Figure 4.1C). A dissolved water phase sample was collected immediately after the rewet using a 100 mL brown water bottle and the bottle was labelled. The water bottle was rinsed thoroughly with distilled water manufactured by Powafix, Wandsbeck, South Africa before water samples were collected. Penultimate water samples were collected after 30 minutes for three hours. Thereafter, water samples were taken at 1-hour intervals for the next five hours.

After 8 hours of the rewet, there was insufficient water left in the container (Figure 4.1D). All the water samples were labelled, kept in a cooler-box, and taken to the Eco-Analytica laboratory, North-West University, Potchefstroom campus for analysis the following day. Water samples were not treated nor preserved before chemical analysis.

A handheld Crison MM40+ water probe-metre was used to determine the pH and EC of the water sample. The probe-metre was calibrated accordingly before the reading was taken. The pH was calibrated using pH standards of 4.01, 7.00 and 9.21 according to the probe-metre manual. Electric conductivity was calibrated using 1412 µS/cm and 1228 µS/cm standards. The standards were all manufactured by Crison, Spain. The temperature was compensated to a reference temperature of 25 °C.

To determine the hourly changes in dam water chemistry (the second objective of this study), a total of 24 water samples were collected hourly at the same spot where the sediment used for the rewet procedure was taken. Water samples were collected, unfiltered, in a 100 mL water bottle. The bottle was rinsed thrice with the dam water before water samples below the water surface were taken. Once the bottle was filled with the dam water, the bottle was capped below the water surface.

On-site field reading of the dam's pH, electric conductivity (EC), and water temperature (TW) were recorded hourly using a handheld Crison MM 40+ water probe-metre. The probe-metre was calibrated using the standard calibrating fluid before any reading was taken. A flow probe, FP 101, manufactured by Global Water, California, USA was used to determine hourly, the average flow velocity of the dam. All samples were taken to Eco-Analytica laboratory of North-West University for chemical analysis. To achieve a quantitative result, the ICP-MS was calibrated using ULTRASPEC certified custom mixed multi-element stock standard (De Bruyn Spectroscopic Solutions, Midrand, South Africa) solutions containing all major trace elements, which include U at a concentration of 10 µg/L. The ULTRASPEC standard solution has been reportedly used in several studies (Dada & Kutu, 2022; Coertze & Bezuidenhout, 2021; Dhlamini et al., 2020). The ICP-MS detection limit for U was 0.31 µg/L.

The ULTRASPEC solution is made up of eight custom-made referenced standard mixtures, mixed accordingly to make a standard calibration curve before each run. They are:

1. Au, Pd, Pt, at 10 ppm.
2. Rb at 10 ppm.
3. Mo, Ti, and B at 100 ppm.
4. Ca at 2000ppm, Mg 2 400 ppm, K at 200 ppm and Na at 1000 ppm.
5. Bi, Th at 10 ppm.
6. Sb, Sr at 10 ppm.
7. P at 100 ppm.
8. Ag, Be, Cd, Mn, Co, Tl, U at 10 ppm; Al, As, Ba, Pb, V at 40 ppm; Fe, Se, Zn at 100 ppm.

4.3. Results and Discussion

4.3.1 Remobilisation of U from a rewetted sediment

4.3.1.1. Sediment composition

In the collected dam sediment, U concentration of about 838 mg/kg was logged. Since only a small portion of the total collected sediment was taken for analysis, the concentration recorded may not reflect the concentration of U across the entire volume of sediment. In the study of Raji et al. (2021), it has been concluded that the natural background concentration of U in sediment within the study area is below 0.7 mg/kg. After drying, it was assumed that carbonates and sulphates formed a whitish crust on the sediment's surface, possibly containing U (Coetzee et al., 2006). Table 4.1 shows the detailed selected chemical composition of the collected dam sediment after drying.

Table 4.1: Chemical composition of the collected dam sediment

Sediment composition	Concentrations
Uranium	838 mg/kg
Total silt and clay	26 wt. %
Organic carbon	9.3 wt %
Fe	26 260 mg/kg
Mn	1516 mg/kg

Uranium is adsorbed by finer particles of clay and silt; this is due to the high sorptive capacity of fine particles (Raji et al., 2021). Also, organic carbon helps in keeping an environment in a reduced state, which favours the immobilisation of U (Trenfield et al., 2011; Wan et al., 2008). When reduced Fe and Mn are oxidised by dissolved oxygen, they form gel which traps U. Fine particles of clay and silt, organic carbon, Fe and Mn and the reduction in waterflow velocity have been reported to promote the immobilisation of U in the dam sediment, resulting in high concentrations of U found in the dam (Coetzee et al., 2006). In the study of Raji et al. (2021), the concentration of U recorded in a dam was 1252 mg/kg, in sediment collected August 2020. The percentage of silt and clay recorded in the sediment was 31.1 % and the concentration of Fe and Mn in the sediment were 30 630 mg/kg and 2029 mg/kg, respectively.

4.3.1.2. Rainwater chemistry

Locally collected rainwater was used for rewetting the sediment to resemble natural conditions as much as possible. As expected, the concentration of U in the rainwater used to rewet the dry sediment was very low, 0.21 µg/L. With a pH of 6.1, the water is weakly acidic (Table 4.2). The concentrations of calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) - major cations - are displayed in Table 4.2 as well as the major anions which include SO_4^{2-} , Cl^- , HCO_3^- , NO_3^- . Since the pH is lower than 8.2, there was no carbonate and nitrate, NO_3^- , respectively. The concentrations of the cations and anions were all below the permissible limit recommended by SANS for drinking water (SANS, 2015).

Table 4.2: Rainwater chemistry

U (µg/L)	pH	EC (µS/cm)	Mg	K	Na	Ca	Cl	HCO ₃	SO ₄	NO ₃
(mg/L)										
0.21	6.1	170	2.2	5.1	2.8	23.3	4.9	9.15	55.7	12.4

4.3.1.3. Concentration of dissolved U in water after rewetting

A concentration of 1211 µg/L was recorded in the water sample taken immediately after the rewet. This confirmed that the remobilisation of U into water was rapid. It begins immediately when the dried sediment encounters dissolved oxygen in the rainwater. The dissolution of U

from the sediment is also controlled by the oxidation rate of *in situ* iron and has been reported to take place within seconds for pure iron oxides (Hug et al., 1997). The concentration of Fe recorded in the water immediately after rewetting was 5.01 mg/L from the 0.09 mg/L recorded in the rainwater. The concentration of dissolved Fe recorded immediately after the rewet was the highest concentration of dissolved Fe recorded throughout the rewet procedure and it corresponded with the highest concentration of U remobilised to the water column (Figure 4.2).

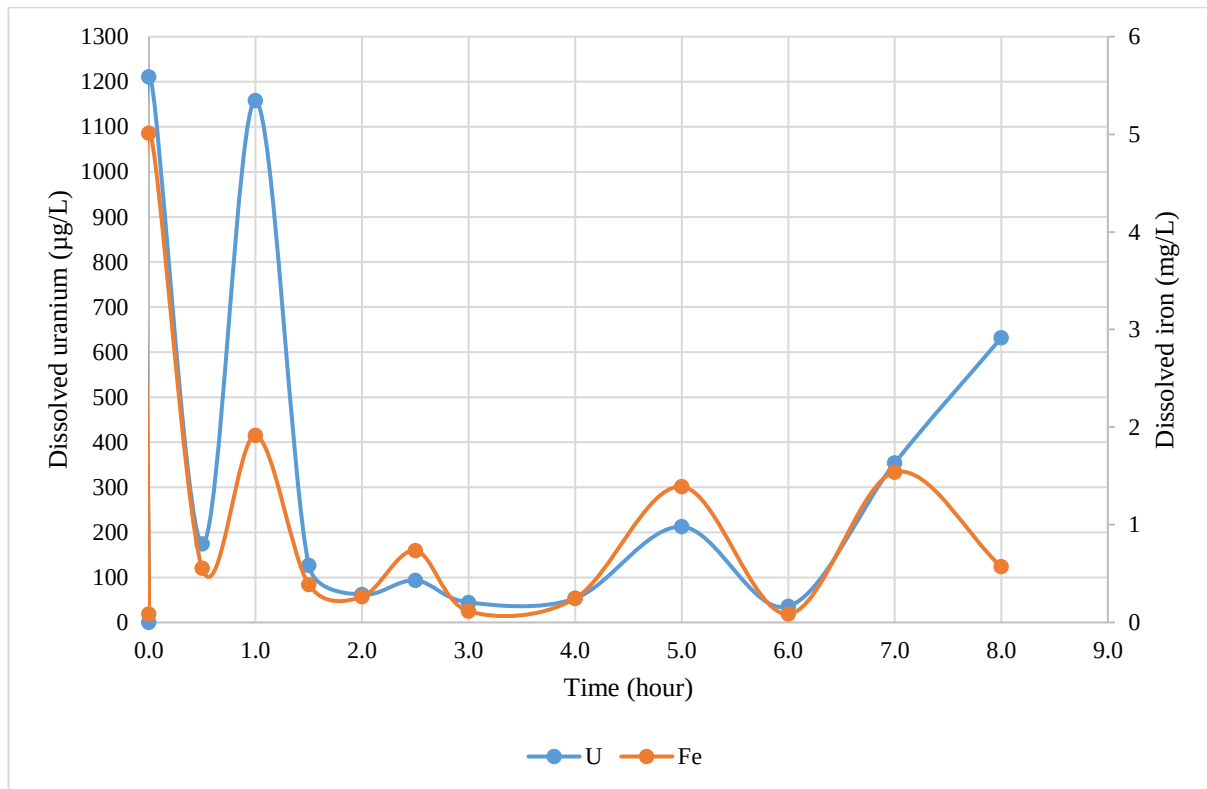


Figure 4.2: Relationship between dissolved uranium and iron

The minimum concentration of dissolved U recorded was 35.96 µg/L, 6 hours after the rewet (Figure 4.2). Coincidentally, the minimum concentration of Fe recorded was found during this time, 0.09 mg/l. With a strong positive correlation (0.8) between dissolved U and Fe, it can be suggested that the oxidation rate of Fe plays an important role in the rapid remobilisation of U. In the study of Szecsody et al (1998), it was confirmed that U precipitate that formed on a reduced sediment will be remobilised when the reductive capacity of the sediment is exhausted and Fe in the sediment is oxidised by oxygen in the water. The rate of U remobilisation from a sediment into the water column will depend on several factors which include the oxidation rate of the different reduced Fe barrier, the oxidation rate of the U (IV) species and the aging of the chemical bond between the U (IV) and the sediment. However, this study mainly focused on the concentration level of U remobilised into the water column without considering the

different Fe and U species that are present in the sediment and water and the Eh of the system. Furthermore, due to the heterogeneity of a sediment, the entire sediment cannot be fully oxidised at the same time. The varying trends of the release of dissolved iron into the water column indicated different phases of oxidised Fe in the sediment, which could lead to different dissolution rates of U in the sediment (Figure 4.2).

In addition, the complexation of U to available ligands in the sediment varies. Uranium complexes with carbonate, which is highly soluble (Cumberland et al., 2016; Winde, 2011b). Bicarbonate concentrations are important in uranium mobility due to the formation of uranyl-carbonate complexes. With an increase in the concentration of HCO_3^- immediately after rewetting, from 9.15 mg/L in rainwater to 39.7 mg/L, the remobilisation / solubility of uranyl-carbonate complexes could also be responsible for the high concentration of dissolved U recorded in the water after rewetting (Figure 4.3). This suggested that dissolved U carbonate complexes were largely dominant. Carbonate which facilitated the dissolution of U in this study is consistent with the renowned ability of uranyl to form soluble complexes with carbonate ions. As explained earlier under the remobilisation of U, the dissolution of salt crust led to a pulse of dissolved U in the water after rewetting. White salt crusts which formed on the sediment after drying, led to efflorescence of salt crust upon contact with water. This resulted in high concentrations of dissolved uranium recorded immediately after the dry sediment was rewetted with rainwater (Figure 4.3).

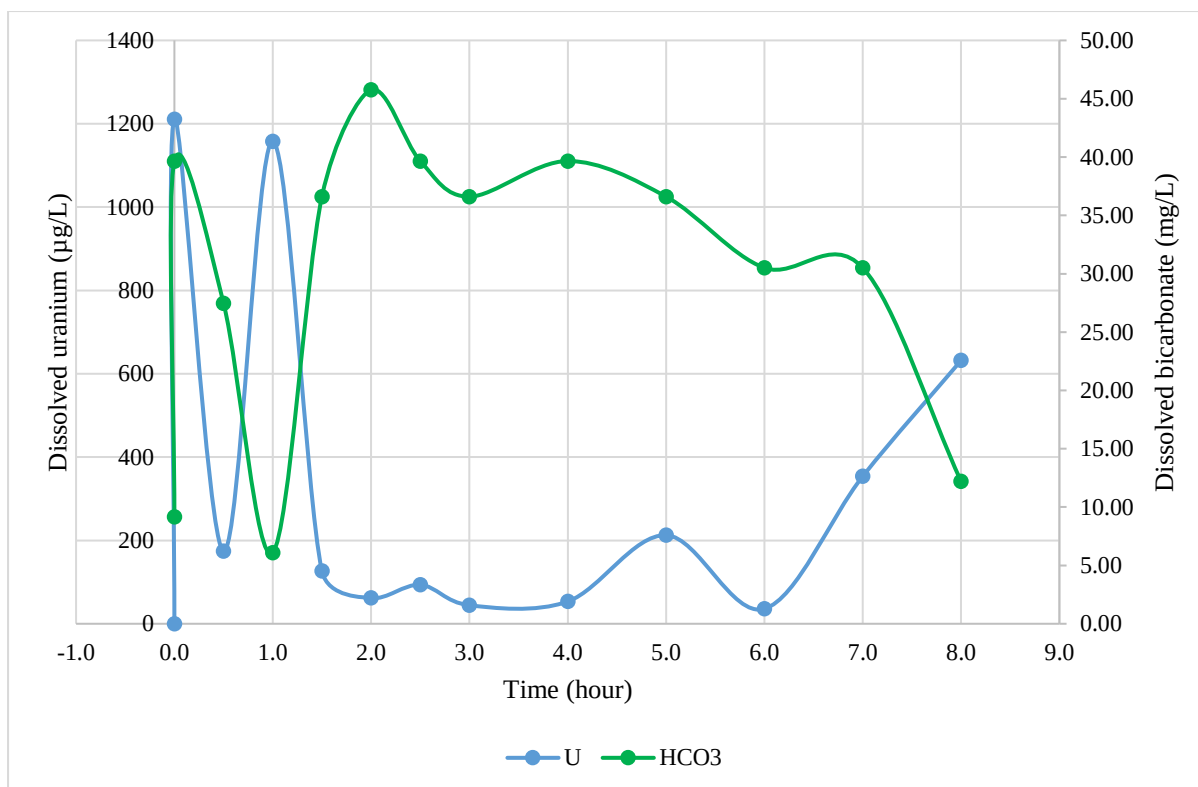


Figure 4.3: Relationship between dissolved uranium and bicarbonate

In the study of Seder-Colomina et al (2018), it was reported that less than 1 % of U was released from the solid phase (sediment) when HCO_3^- was absent in the sediment-water system. A significant increase in the concentration of dissolved U was recorded with gradual increase in HCO_3^- . Regenspurg et al. (2009) concluded that a high bicarbonate concentration was found to increase the U desorption rate by the formation of aqueous U-carbonate complexes. Winde (2011b) also reported that U complexes with carbonate, sulphate, and nitrate, have high solubility.

The remobilisation of U was non-linear, and this indicated that there is more than one type of adsorbing species in the sediment (Figure 4.3). Uranium can form complexes with PO_4^{3-} and SO_4^{2-} with both showing different rates of solubility. Eight hours after the rewet, the concentration of dissolved U in the water was still very high (631.9 µg/L). However, there was about a 50 % reduction in the concentration of dissolved U recorded immediately after the rewet and 8 hours later (Figure 4.3).

According to Senko et al. (2002), the immobilisation of U is prevented by the presence of sulphide and nitrate at high concentrations. They proved that the immobilisation of U was not complete until nitrate was removed. This was related to the finding of Finneran et al. (2002),

which concluded that nitrate subdued the reduction of both U and Fe, and both U and Fe will be reduced when nitrate is completely depleted. With the increase in the concentration of nitrate, chlorine, and sulphate culminating in an increase in the EC (increase in water salinity), immobilisation of U was reduced. The concentrations of SO_4^{2-} , NO_3^- eight hours after rewetting were 1252.65 mg/L and 14.63 mg/L respectively, while the EC was 2.87 mS/cm. In the water used for the rewet, the concentration of SO_4^{2-} , NO_3^- and EC were 55.7 mg/l, 12.4 mg/L and 0.17 mS/cm, respectively. This is like the findings of Raji et al. (2021) which reported limited immobilisation of U despite the abundance of factors that promote U immobilisation in sediment because of water salinity.

After 4 days of rewet, the concentration of U had dropped to 15.53 $\mu\text{g/L}$. This suggested that most of the oxidised dissolved U had been re-adsorbed or precipitated back into the sediment. During the period, the concentration of dissolved Fe dropped significantly to 0.1 mg/L. This was comparable to the concentration of Fe recorded in the rainwater used for the rewet. Similarly, the concentrations of HCO_3 , NO_3 and SO_4 had dropped significantly to 15.25 mg/L, 2.12 mg/L and 941.4 mg/L respectively after 4 days. There was a similar drop in the concentrations of the major cations after 4 days when compared with the concentrations of major cations recorded 8 hours after the rewet.

Based on statistical analysis, it is believed that the dissolution of Fe, NO_3 , HCO_3 and SO_4 played a major role in the remobilization of U. While Fe has a strong positive correlation (+ 0.83) with remobilised U, NO_3 , HCO_3 and SO_4 have a weak negative correlation with remobilised U (Table 4.3). The F-value is greater than the F-critical and the P-value is less than the alpha value (0.05). This means that the measurements are significant, and the null hypothesis can be rejected (Table 4.4).

Table 4.3: The correlation of uranium with iron, nitrate, carbonate, and sulphate

	U	NO_3	HCO_3	SO_4	Fe
U	1.00				
NO_3	-0.50	1.00			
HCO_3	-0.35	0.27	1.00		
SO_4	-0.06	0.69	0.00	1.00	
Fe	0.83	-0.35	0.08	-0.22	1.00

Table 4.4: A single-factor analysis (ANOVA) of variance between uranium, bicarbonate, nitrate, and sulphate

One-way ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3917520	4	979380.1	16.54	3.48E-09	2.53
Within Groups	3553700	60	59228.33			
Total	7471220	64				

4.3.2. Diurnal changes of stream chemistry

4.3.2.1. Dam Water pH

As shown in Figure 4.5, there was a distinct diurnal variation in the pH of the dam water. The water pH was very high during the day; this could be related to the intensity effect of solar radiation. The highest pH reading of 9.01 was recorded by 12:00 noon when sunshine was expected to be at its peak. However, the pH decreases as sunlight reduces. The lowest pH reading, 7.2, was recorded by 6:00 just as the sun rose the following day (Figure 4.5). Similar daily pH variations were observed in the study of Winde & Walt (2004a) and Raji et al., (2021).

Changes in water pH can be related to photosynthetic activities of aquatic microorganisms and plants (Winde 2004a, Javed et al., 2019). As sunlight becomes available, dissolved carbon dioxide is consumed by algae, phytoplankton, and aquatic plants. This caused a shift in carbon dioxide (CO₂) and calcium carbonate equilibrium, leading to an increase in the pH values (Zang et al., 2011). This can be regarded as a biological process.

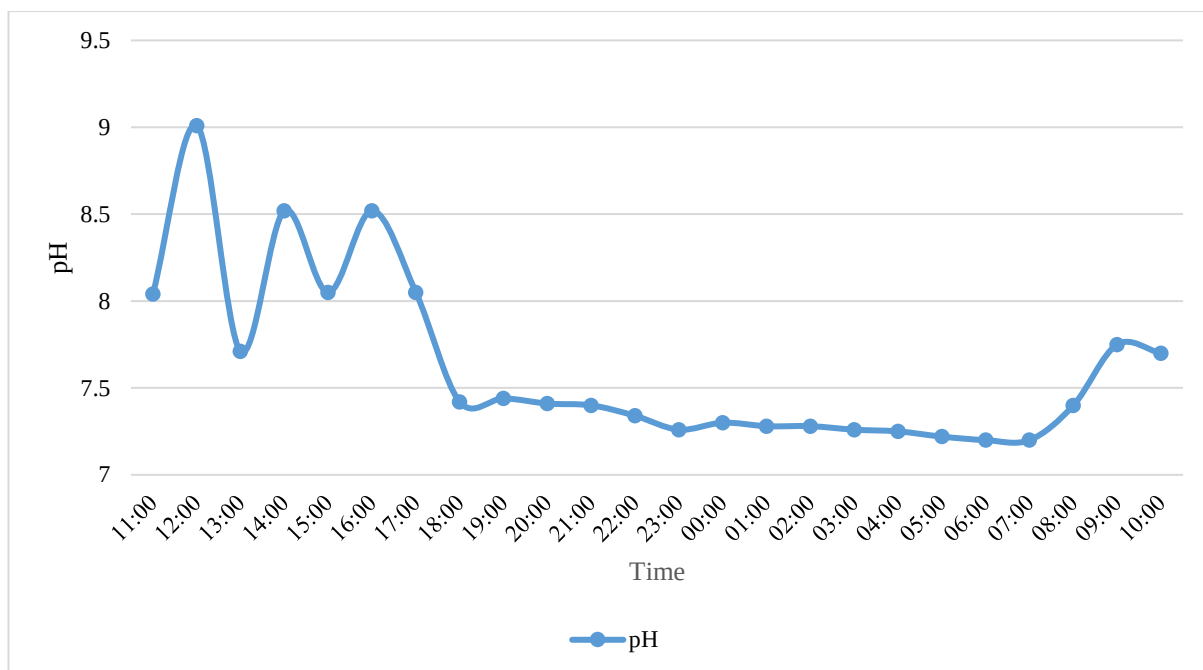


Figure 4.4: Diurnal dam water pH fluctuation

A reduction in pH-values prevents U adsorption owing to binding competition created by increased concentration of hydrogen ions (Winde, 2004a). In this study, a higher concentration of dissolved U was recorded mostly at night when the pH was lower (Figure 4.5). A change in the pH due to the CO_2 changed the U sorption equilibrium point (less sorption equates to more U in the water column). This confirms that a small pH difference can dramatically change U mobility and these pH differences are huge.

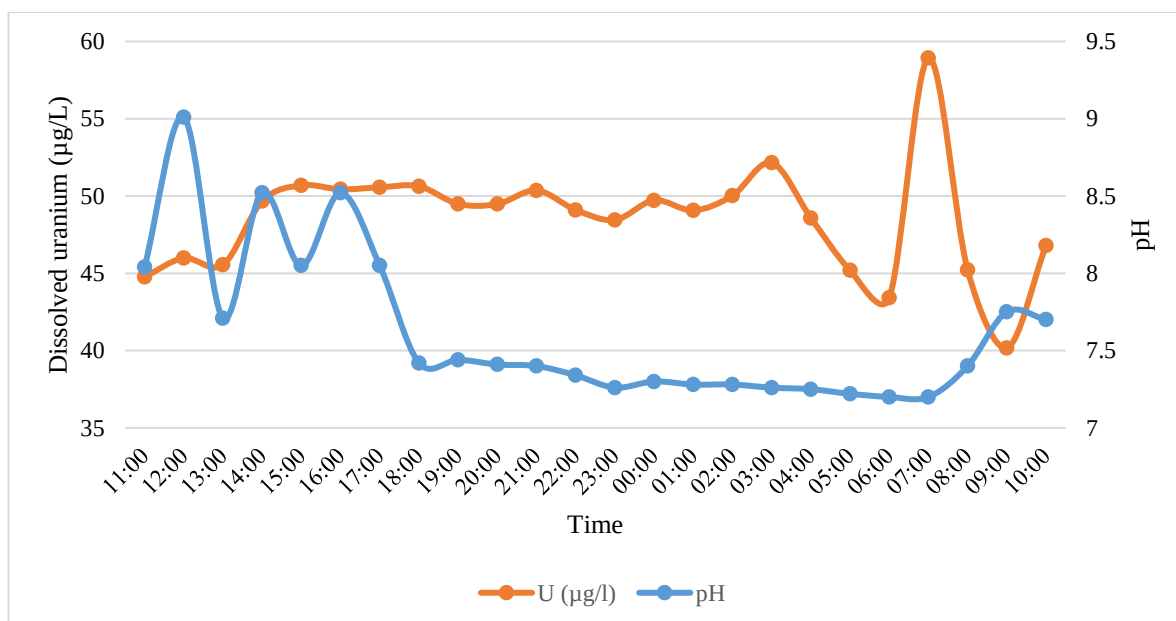


Figure 4.5: Diurnal relationship between dissolved uranium and pH

4.3.2.2. Dam water electric conductivity

Electric conductivity measures the ability of water to pass electrical flow. In the 24 hours' field observation, EC readings were higher at night than during the day when there was sunlight (Figure 4.6). As soon as the sun started to rise, the water EC started to decrease. This could be because of biological decalcification, which is higher during the day due to the consumption of carbon dioxide by aquatic lives and lower at night when carbon dioxide is released.

The time series indicated a dominant inverse relationship between EC and pH (Figure 4.6). A similar observation was reported in the study of Winde & Van der Walt (2004a). Using Excel, a strong negative correlation was found to exist between the water EC and pH (-0.7) within the 24 hours of observation. Worthy of note is that the maximum EC reading of the dam's water corresponded with the minimum pH reading of the dam's water (Figure 4.6). As a result, higher concentrations of dissolved U will be expected in the water column because low pH and high EC reduce the efficiency of river sediment to immobilise U.

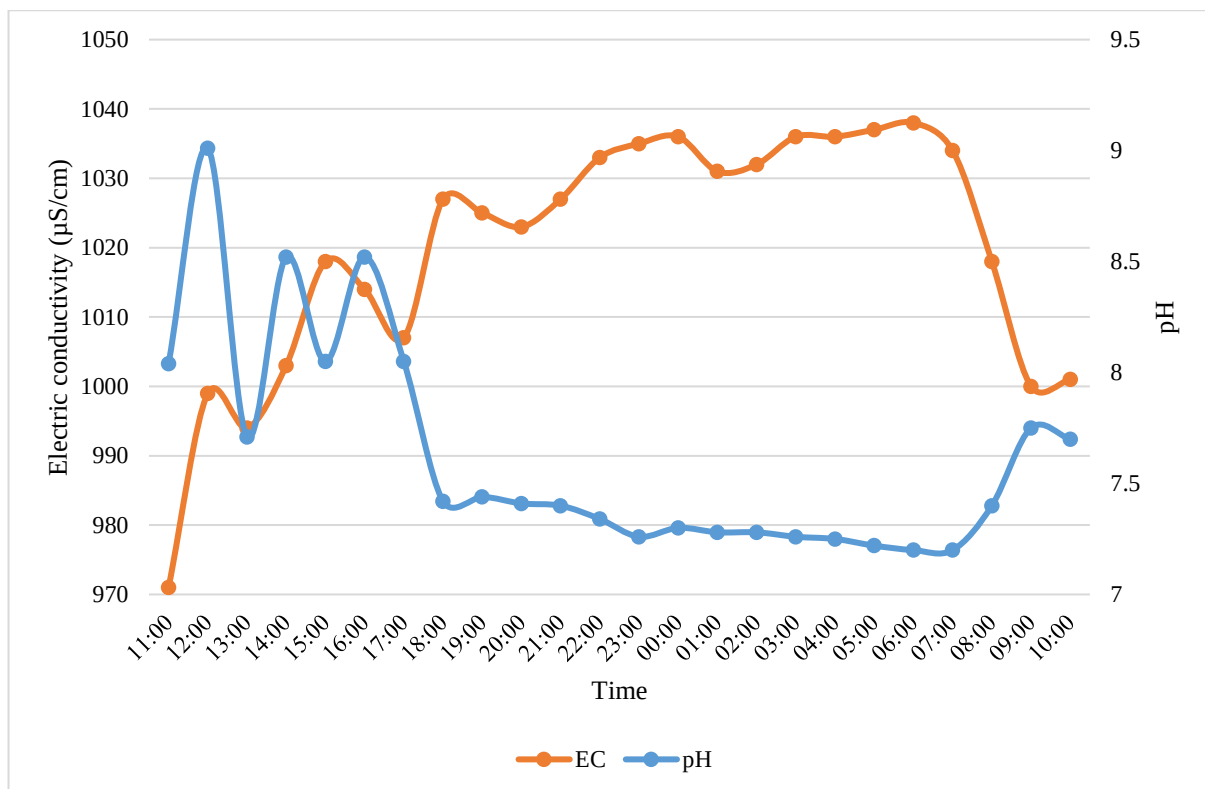


Figure 4.6: Diurnal dam water electric conductivity and pH relationship

Water temperature affects dissolution and solubility of chemical compounds, resulting in increased levels of dissolved solids. Since the water probe-metre was compensated to a reference temperature of 25 °C, any changes in water temperature should not directly affect

EC. Even though the effect of Tw on EC is not important, however from field observations, an inverse relationship was found to exist between the EC and Tw. This is evident as the lowest EC reading coincided with the highest Tw (Figure 4.7). At the same time, the highest EC reading coincided with the lowest Tw recorded in 24 hours (Figure 4.7). Using Excel, EC was found to have a strong negative correlation, - 0.6, with Tw. A similar inverse relationship between EC and Tw was reported in a similar study within the Witwatersrand Basin (Coetzee et al., 2006; Winde & van der Walt, 2004a).

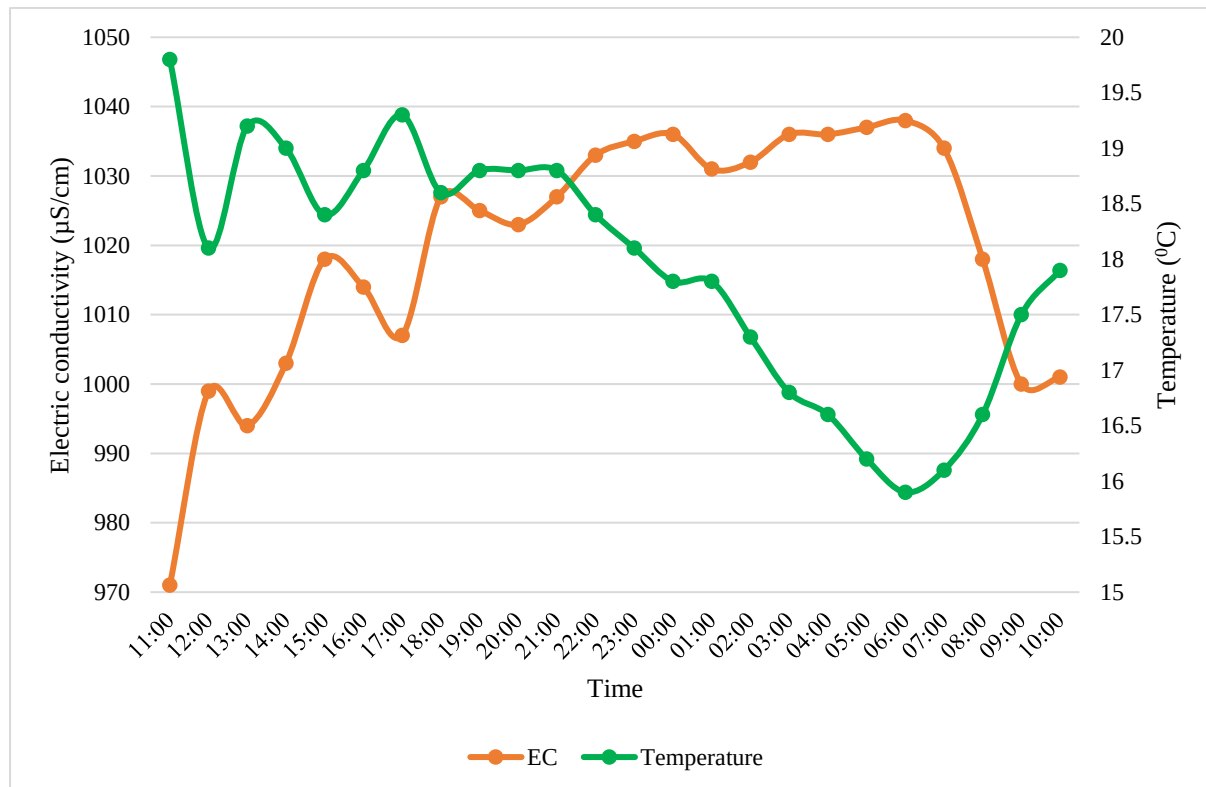


Figure 4.7: Diurnal dam water electric conductivity and water temperature relationship

As aforementioned, an increase in EC leads to desorption of U and reduction in the sorptive capacity of sediment. A higher concentration of dissolved U was recorded after sunset when EC is higher than during the day, when EC is lower (Figure 4.8). This confirms the importance of EC as one of the factors contributing to the immobilisation and remobilisation of U in a fluvial system.

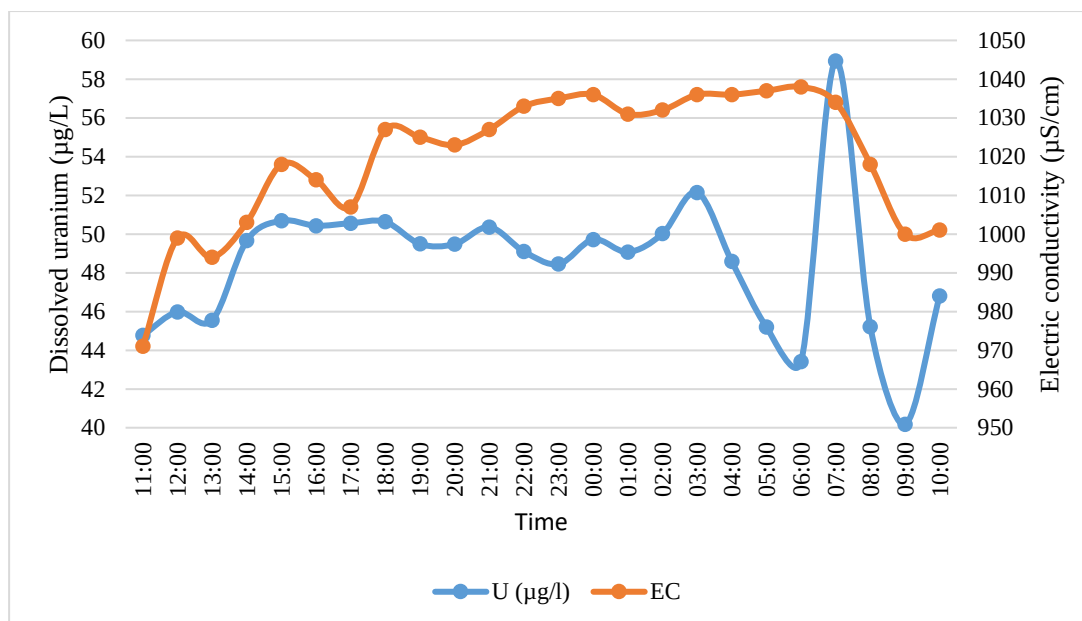


Figure 4.8: Diurnal relationship between dissolved uranium and electric conductivity

4.4. Chapter conclusion

From the rewet experiment carried out to simulate what happens in the natural environment, it can be concluded that the remobilisation of dissolved U from sediment is not linear. This is due to the different dissolution rates of the various constituents of the sediment. The concentration of U was still above the regulated limit prescribed for U in irrigation water (10 µg/L) after 4 days of rewet (DWAF, 1996b) but lower than the permissible limit of U in drinking water (30 µg/L) (DWAF, 1996a; WHO, 2012). The limit of U in water used for irrigation is lower than U limit in drinking water because the concentration of toxic elements (uranium included) found in plants is directly proportional to the concentration of the heavy metal in water used for irrigation. These toxic elements are stored in the edible parts of the plant, while about 70 percent of U ingested by humans from drinking water would be excreted in most cases (WHO 2001).

If the anticipated drying-up of the stream after the cessation of water discharge by the mine into the PW dam should take place and the stream becomes non-perennial, downstream wetlands sediment and dam sediment will become secondary sources of U pollution of stream water that is being used for agricultural and domestic purposes. This is due to the high concentrations of U that have been reported in the wetland and the dam (Raji et al., 2021).

Uranium remobilised into water columns from the stream sediment could be detrimental to human health several hours after an initial rain-event.

Several factors control the remobilisation of U. In this study, the impacts of Fe, HCO_3 , NO_3 , and SO_4^{2-} have been detailed with references to previous studies. However, it is unknown which factor predominates the others. It can be concluded that they all happen concurrently in a natural environment. The site of U adsorption and the complexing ligands determine the rate of dissolution of U from the sediment.

In the diurnal water chemistry fluctuation study, it can be concluded that changes in water pH are mostly controlled by the various activities of aquatic lives because of photosynthesis. The water pH increased during the day and decreased at sunset. Since low pH favours the remobilisation of U from sediment, a greater increase in the concentration of dissolved U was observed at night than during the day. The highest concentration of dissolved U ($58.9 \mu\text{g/L}$) recorded in the 24-hour field investigation coincided with the lowest pH (7.2) and the second lowest water temperature (16.1°C). The lowest water temperature recorded was 15.9°C . This finding points to the most appropriate time for water sampling because most sampling periods occur during the day. With the general practice of sampling during the day, the peak of dissolved U in the stream will be missed.

An inverse relationship was also noticed between water pH and EC. Since EC directly reflects water salinity resulting in limited adsorptive capacity of U by sediment, sediment ability to adsorb dissolved U will be reduced at night, leading to higher concentrations of dissolved U in water at night. Using the combined effect of pH and EC on the immobilisation and remobilisation of U, the rate of U remobilisation will be expected to be higher at night while the rate of U immobilisation will be higher during the day.

Chapter 5

Assessing health risk associated with uranium in the Rietspruit water, Far West Rand Goldfield, South Africa

Abstract

Uranium, U, as a radiologically and chemically toxic element, has detrimental impacts on human health when ingested at elevated concentrations in water. Effluents from an underground gold mine located in the headwater region of the Rietspruit have contaminated the stream with waterborne uranium. The Rietspruit is a tributary of the Vaal River and consequently flows through residential and agricultural land. Water samples from the stream were collected and analysed using inductively coupled plasma mass spectrometry to determine the concentrations of dissolved U. The maximum concentration of U recorded was 781.9 µg/L at the mine, from where it decreases with growing distance from the mine. Results from calculations showed that the maximum annual effective dose at the mine was above the regulatory limit for public exposure for all age groups. The radiological risk associated with consumption of untreated water from the Rietspruit is lower than the chemical risk. The chemical risk ranges from 0 – 37.2 while the highest life-time cancer risk was 1.7 E -03 for morbidity cancer risk and 1.1 E-03 for mortality cancer risk. The chemical risk analysis showed that within 24 km downstream of the mine, stream users are exposed to toxic U levels. Therefore, adequate interventions by relevant government agencies are required.

Keywords: uranium, dose, exposure, pathways, cancer, risk, hazard, gold, mining

5.1. Introduction

The quality of most South African water resources has deteriorated over the years, which poses serious health risks to humans and livestock (WWF-SA, 2016). Due to a strongly negative climatic water balance where potential evaporation exceeds rainfall by several times in large parts of the country, including the study area, much of South Africa is affected by water-scarcity (Bwapwa, 2019). Some 62 % of South Africa's limited water resources are currently used for irrigation and 11 % for mining and industrial use (DWAS, 2020; WWF-SA, 2016). Poor communities like informal settlements often suffer from a lack of piped water. Consequently, residents depend on the use of untreated surface water, as observed in the study area, exposing them to the risk of waterborne diseases (Satterthwaite et al., 2020). In goldmining areas, much of the surface water is polluted with toxic elements, uranium inclusive.

Uranium (U) has been reported to have health impacts on humans exposed to the element (Bjørklund et al., 2020; ATSDR, 2014; Adams et al., 2010; Winde, 2011; Bleise et al., 2003; Zamora et al., 1998). Depending on the solubility of the uranium compound, exposure route, and concentration, kidneys, lungs, and bones are among the targeted vitals that could be damaged by U (Dewar, 2019a; ATSDR, 2014; Keith et al., 2013b; WHO, 2001a). Uranium is mined in South Africa in most cases as the by-product of gold mining (Tutu et al., 2003; Winde & de Villiers, 2002b; Ford, 1993; Krige, 1966). High concentrations of U have been found within gold mines in water and sediment (Raji et al., 2021; Fashola et al., 2016; Kamunda et al., 2016b; Durand, 2012b).

Gold mining has been a large contributing factor to the economy of South Africa; however, large volumes of mine wastes have been deposited as a result (McCarthy, 2011a; Fedderke & Pirouz, 2002). In the Witwatersrand Basin, one of the richest gold deposits worldwide (Tutu et al., 2008), high concentrations of U have been recorded in some of the mined gold reefs. About 70 years ago, the Far West Rand became the first goldfield in South Africa where commercial production of U was established (Coetzee et al., 2006). Winde (2001) reported an average U concentration of about 110 mg/kg in gold tailings, also known as slimes dams, across seven goldfields of the Witwatersrand Basin. Winde (2004a) concluded that for each ton of gold produced, more than 10 tons of U were brought to the earth's surface. Mined gold reefs are therefore regarded as the original source of U (Winde & Sandham, 2004b).

Other sources of U pollution include mine waste deposits such as slimes dams and mine dumps, often located close to streams or rivers. In many cases, these waste deposits are the primary source of U pollution of the nearby water bodies. The process includes the transport of dissolved U via seepage into underlying alluvial aquifers (Winde & van der Walt, 2004a) and of U-bearing tailings particles by wind and water erosion (Winde & Sandham, 2004b). Uranium can be emitted from point sources or from non-point (diffuse) sources. Point sources include the discharge of fissure and processed water through canals and pipelines into nearby streams or dams, as also observed in this study. Even though the mine was decommissioned about 5 years ago, dewatering of underground tunnels is still ongoing. Another example of point source is the storm-water run-off from slimes dams, storm-water retention dams, rock, and sand dumps etc. A typical example of diffuse sources of pollution includes seepage from slimes dams and uncaptured run-off from various mine waste deposits including washed-off tailings material downstream of eroded slimes dams.

Uranium is released into the environment in several ways, which include erosion of slimes dams by wind and water, leading to eroded slimes settling on dams, wetlands, irrigation channels and agricultural land etc. (Coetzee et al., 2006). In addition, there are spillages of tailings associated with burst pipelines, partial dam failures etc.

High concentrations of U have been found several kilometres from the mining site in river sediment, wetlands, and dams as a result of precipitation, adsorption, co-precipitation and bioaccumulation (Winde et al., 2004b). Wetlands and dams have been identified as sinks for U and other toxic elements such as mercury, lead, cadmium, arsenic (Schöner et al., 2009; Ross & Dudel, 2008; Coetzee et al., 2006). Raji et al. (2021) recorded high concentrations of the aforementioned toxic elements above the acceptable limit in a wetland and a dam located about 3 km and 6 km respectively from a mining site. These sites can be a secondary source of U pollution and other toxic elements if there is a change in the water chemistry which could be influenced by the water's pH, electric conductivity, redox state, and seasonal changes (from winter to summer).

The focus of this study is on the Rietspruit, a small stream draining the south-eastern part of the Far West Rand (FWR) goldfield that is impacted by mining-related water pollution. The study explores the main pathways of U entering the Rietspruit system, the concentrations of

dissolved U along the entire longitudinal profile of the Rietspruit as well as both the carcinogenic and non-carcinogenic risk assessment using the concentrations of U found at sampled sites.

Due to human exposure pathways witnessed during fieldwork, and the lack of information on the level of U which users could be exposed to, it is imperative to assess potential health risks associated with ingestion of dissolved U found in the Rietspruit. This study will be used to sensitize the local inhabitants about the dangers involved with the use of the water for domestic, agricultural, and religious purposes. Due to human exposure observed in the field, e.g. ingestion of the water from the stream, both carcinogenic and non-carcinogenic risks were assessed.

The objectives of this study are:

- 1) To determine the concentration of U in the Rietspruit water along its entire longitudinal profile from source to mouth.
- 2) To assess the health risk posed by the U levels in Rietspruit water.
- 3) To propose possible interventions and recommendations to local authorities.

5.2 Study area

The source of the Rietspruit is in Gauteng Province, South Africa about 1 km away from Ezulwini Gold and Uranium Mine. The Ezulwini Gold and Uranium Mine (coordinate: 26°21'46"S 27°42'52"E) was operational for about 56 years before it was decommissioned in August 2016. At the time of study, the mine still discharged its fissure and process water into the Peter Wright dam (PW dam) at a rate of approximately 68 ML per day. The outflow from the PW dam is currently the (man-made) source of the Rietspruit. It is believed that the Rietspruit will become a non-perennial river if the mine should stop discharging water into the PW dam (Kritzinger, 2017).

The river flows south for about 60 km before joining the Vaal River (Figure 5.1). The associated drainage region name is C22H according to the Department of Water Affairs and Sanitation, comprising a catchment area of about 454 km² (Figure 5.2). Tributaries of the Rietspruit include the Leeuspruit, the Evaton-Rietspruit and the Klein-Rietspruit. While the Leeuspruit is also polluted with U because of another gold mine located upstream of the

confluence with the Rietspruit, the Evaton-Rietspruit and Klein-Rietspruit are not polluted as they drain areas without mining activities. The Leespruit is in the C22J Quaternary Catchment, draining some 668.7 km² (Department of Water Affairs and Sanitation, 2011) (Figure 5.2). As there are no mining or industrial activities in the catchments of the Evaton-Rietspruit and Klein-Rietspruit, the concentration of U in the water of these streams was used as the natural background concentration of U. Most farms located in the area depend on water from the Rietspruit for irrigation.

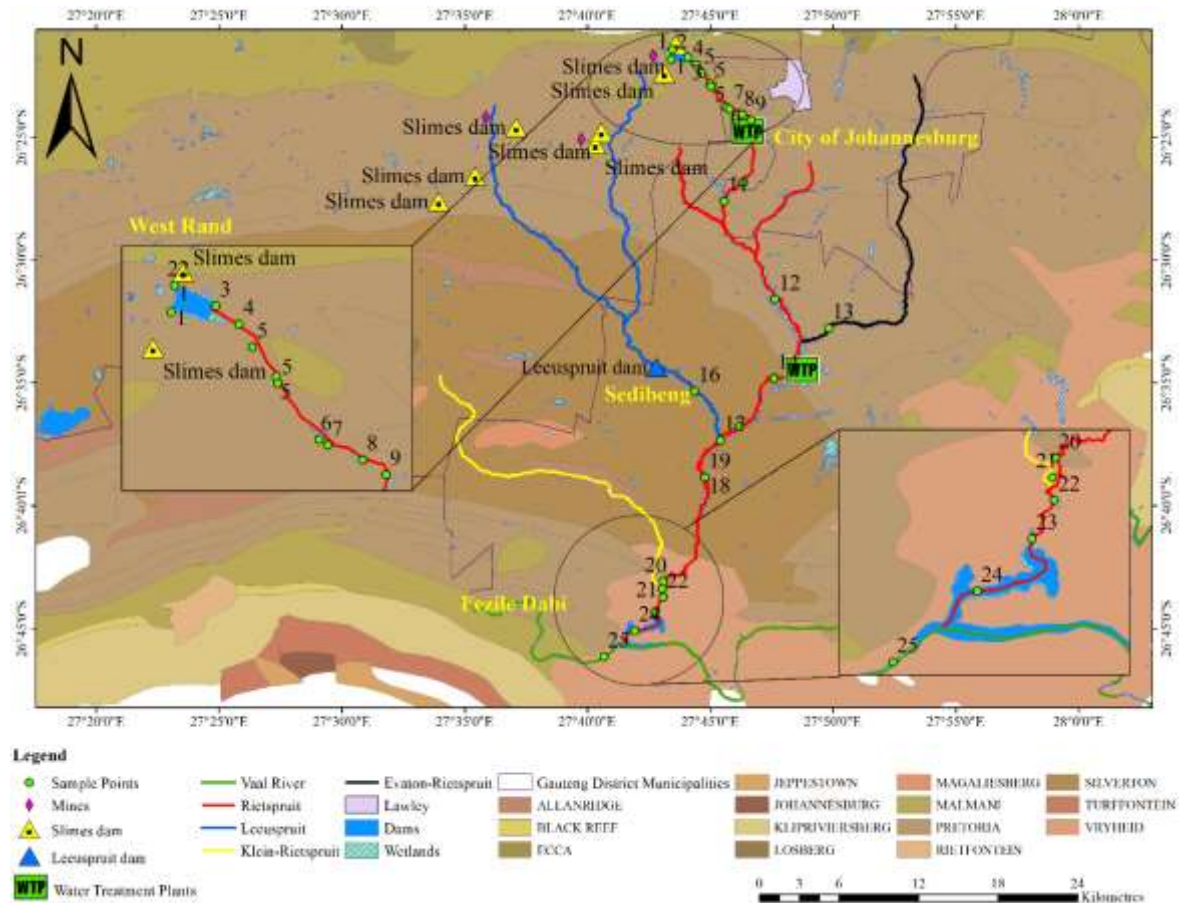


Figure 5.1: Map of the study area (Adapted base geological map created by South African National Space Agency, SANSA, 2018)

The climate of the study area is temperate, defined by moderately cold winters (April to August) and hot summers (October to March). Annual rainfall mainly occurs between October and March and with an average of about 664 mm. Evaporation is about twice the annual rainfall (about 1700 mm). In winter, the average temperature is 13 °C and 24 °C in summer (Kamunda et al., 2016b).

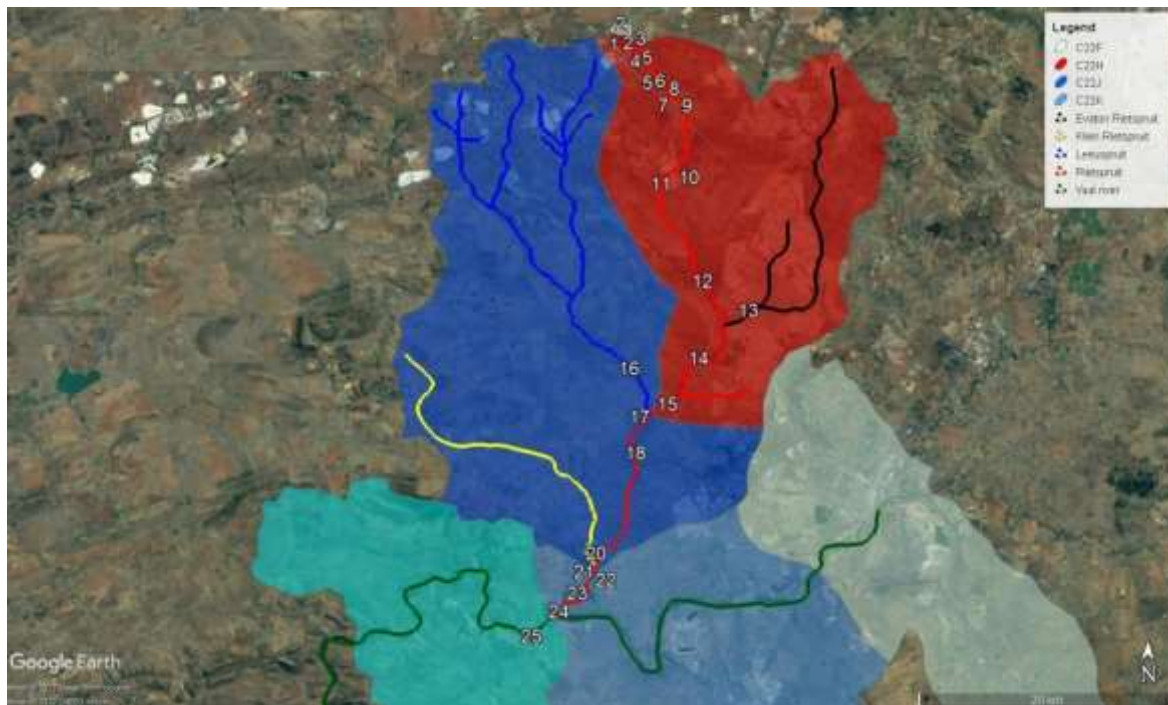


Figure 5.2: A Google Earth Pro (2022) image of the study area catchment showing the sampled sites (Catchment data set published by Water Research Commission, 2012)

The Ezulwini Gold and Uranium mine is located about 40 km South-West of Johannesburg in the Gauteng Province, South Africa. Gold is found in the upper Elsburg in the form of native gold and is associated with sulphide minerals (e.g pyrite). Also, gold is found in the middle Elsburg reefs associated with pyrite underlying the mine. Uranium is mined in the middle Elsburg reef (Kritzinger, 2017) and it is found in the form of uraninite (Kritzinger, 2017). This is the major source of all the U found in the Rietspruit.

Uranium is released from mine waste during a rain event and transported to the PW dam, the Rietspruit headwater. A concentration of about 52.7 $\mu\text{g/L}$ of U was recorded in the fissure water discharged by the mine into the PW dam (Raji et al., 2021). According to Kritzinger (2017), about 68 ML of fissure water is pumped into the PW dam per day; this means the amount of U discharged into the PW dam is about 52 700 mg/L of U per day. Thus, the discharge of fissure water into the PW dam is the most significant U source into the Rietspruit.

The outflow from the PW dam into the Rietspruit makes the Rietspruit a perennial river. Observations during field sampling indicated that the Rietspruit water is used for drinking, cooking, bathing (especially by the residents of informal settlements within the area and religious worshippers) and animal watering, and dam water is used for irrigation of farmland.

The uptake of U by plants from the soil could be a result of air pollution from slimes dams and water used to irrigate such plants (Gupta & Walther, 2020; Anke et al., 2009). Field observation commenced on 13th of July 2020, while water samples were collected on 28th of August 2020, covering the total length of the Rietspruit within the Gauteng Province, South Africa.

5.3 Materials and methods

5.3.1 Field work

A total of 28 water samples were collected on 28th of August 2020 along the entire length of the Rietspruit (Figure 5.2). Water samples were collected in a 100 mL PVC water bottle below the water surface. The water bottle was rinsed three times with river water before water samples were collected. Water samples were taken in the middle of the river, depending on the depth of the site. Each water bottle was labelled accordingly and kept in a cooler box. The samples were taken to the laboratory the following day for chemical analysis. Samples were analysed in the laboratory to determine the concentration of U using inductively coupled plasma mass spectrometry (ICP-MS). At each sampled site, the water pH, electric conductivity, temperature, and coordinates were taken using handheld instruments. The detailed readings and their influence on U concentrations were however published in the first part of this study (Raji et al, 2021).

5.3.2. Laboratory analysis

The water samples were analysed in the Eco-analytical laboratory of the North-West University, Potchefstroom Campus, South Africa. Each water sample was first filtered using a 0.45 µm sieve to remove suspended particles. 1 mL of the filtered water was measured, and 9 mL of nitric acid was added to remove any dissolved organic material in the water. An Agilent 7500 CE ICP-MS with Collision Reaction Cell (CRC) technology for interference removal was used to determine the concentration of U in the water. In order to achieve a quantitative result, the instrument was calibrated using ULTRASPEC certified custom mixed multi-element stock standard (De Bruyn Spectroscopic Solutions, Midrand, South Africa) solutions containing all major trace elements which include U at a concentration of 10 µg/L. The ICP-MS detection limit for U was 0.31 µg/L.

5.3.3. Exposure assessment

According to the US EPA (1992), exposure assessment can be defined as the determination of the magnitude, frequency and duration of exposure and exposure dose (EPA, 1992). Exposure assessment includes identification of all important sources of pollutant, routes of exposure (exposure pathways), the potentially exposed population, mechanisms of pollutant transportation, quantification of exposure, toxicity assessment of pollutants, and risk characterisation. Exposure assessment is one of the most essential steps in human health risk assessment, with hazard identification, dose-response assessment and risk characterization being the other steps (NRC, 2009).

Source of uranium pollution: The main source of uranium, as a contaminant of concern, in the Rietspruit is the Ezulwini Gold and Uranium mine (Figure 5.3). Slimes and waste rock are deposited on the surface. Oxidised mine wastes release U when it encounters water (in the form of rain, pore-water, and seepage), which then runs off into the PW dam. The mine also discharges fissure water with elevated concentrations of U, 52.7 µg/L, into the PW dam as source of the Rietspruit. Fissure water consists of dolomitic water from the overlying karst aquifers that migrate via fractures and faults into the underlying main void. Where this water comes into contact with mined or unmined uraniferous ore, it can become contaminated, resulting in elevated levels of dissolved U (Winde, 2006). Another source of U in the Rietspruit is the injection of washed-off tailings materials eroded by water and wind from nearby mine waste deposits.

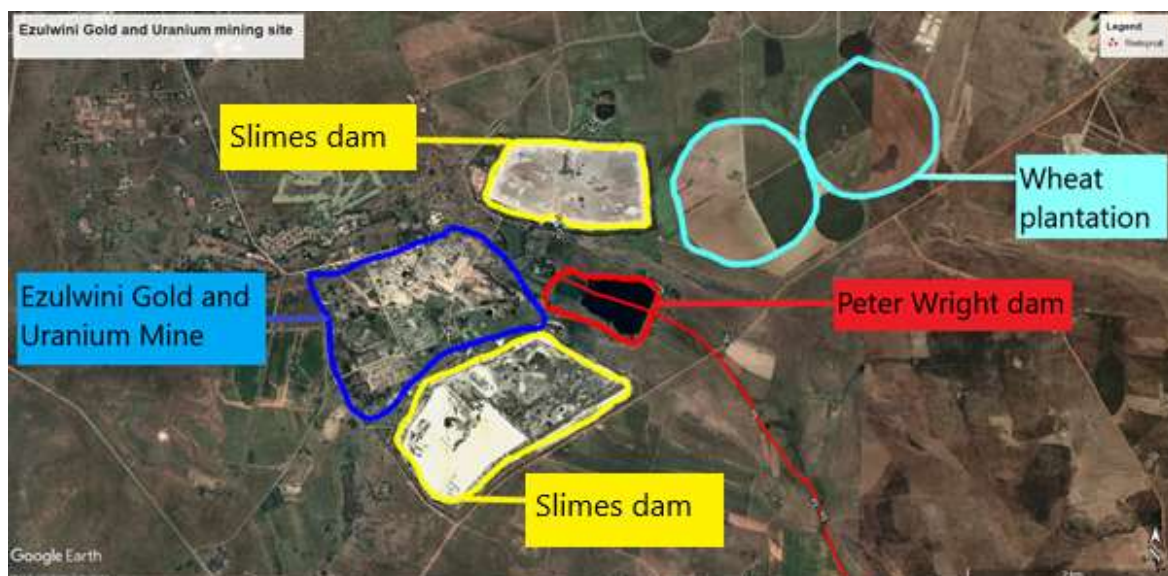


Figure 5.3: Google Earth Pro (2022) image showing source area of the Rietspruit including selected U-sources such as slimes dams

Exposure pathways: In this study, the pathways include the usage of the water for domestic, religious, and agricultural purposes. Domestic and religious activities observed in the Rietspruit include drinking of the Rietspruit water, usage of the water for cooking, bathing in the river, as well as fishing in the dam located downstream of the river (Figure 5.4). The water is also used for the irrigation of farmlands. A commercial wheat plantation located a few kilometres from the Ezulwini Mine uses the water from the dam for irrigation (Figure 5.4B and C). Several studies have been done on the uptake of U and other toxic elements by plants (Edayilam et al., 2020; Gupta & Walther, 2020; Genthe et al., 2018; Dzoma et al., 2010; Hakonson-Hayes et al., 2002).

Wind erosion is another pathway. The deposition of tailings materials on nearby farmland could potentially introduce U into the food chain due to the uptake by plants. The consumption of animals that were fed with plants irrigated with polluted water, is also another route for indirect consumption of U by humans (Figure 5.4A and B). Formal and informal settlers within the immediate environment of the slimes dam could also be exposed because of inhaling dust particles (Figure 5.4E).

The only exposure pathway considered in this study is the oral ingestion of U from drinking water. This is the most prevalent exposure pathway experienced in the Rietspruit by different population groups that depend on the water for both domestic and religious activities, and this exposure pathway is the primary objective of this study.

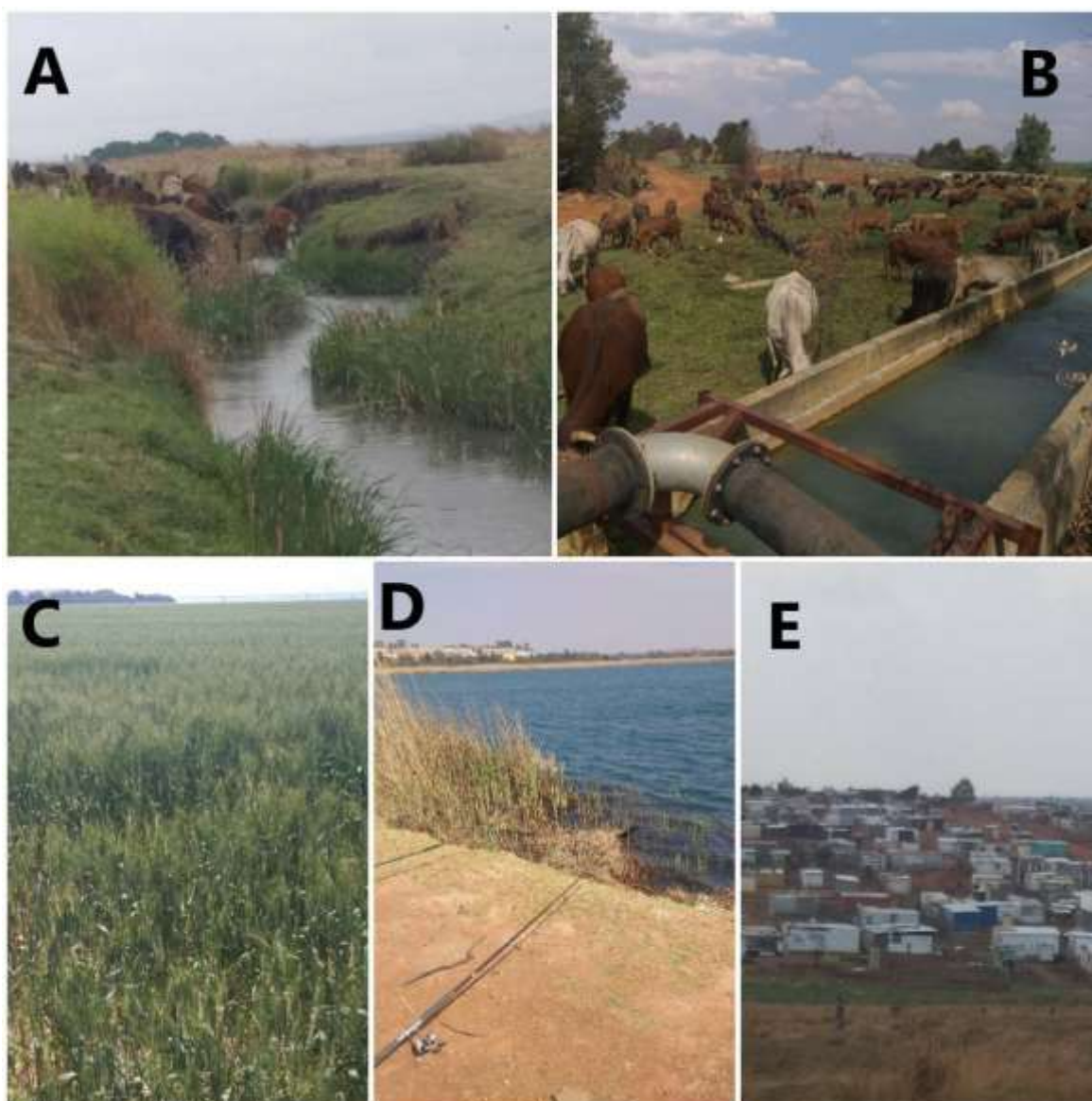


Figure 5.4: Exposure pathways witnessed in Rietspruit; A: Cattle grazing in the Rietspruit river B: Cattle grazing next to the canal used by the mine to discharge water C: Wheat plantation irrigated by water from PW dam, D: Local residents fishing in PW dam, E: Informal settlement within the study area

Mechanism of transport: The major mode of transportation of U from the point source to the Rietspruit is through water and air.

Exposed population: Most of the inhabitants in the study area live in informal settlements, e.g., Lawley (Figure 5.1). Informal settlements are housing areas often built illegally on municipal land (Huchzermeyer, 2009). Most of the houses in an informal settlement are built out of metal sheets and other materials which are in most cases reused or repurposed (Figure 5.4E).

Another group of exposed residents are the worshippers using the water from the river for their various religious activities which include drinking the water. On several visits to site 6, 7, 8, 9 and 11, cooking activities using water from the river were also witnessed as well as bathing in the river. The worshippers are of different age groups and gender.

5.3.4. Annual effective dose (radiation dose) due to the ingestion of uranium in Rietspruit water

Whenever there is human contact with a hazardous chemical, such as U in this study, there is exposure (Means, 1989). Residents and worshippers using the water for drinking, cooking, and bathing are therefore exposed. To screen the area that could constitute a health risk, radiation doses for all the sampled sites were calculated and compared with the radiation dose limit prescribed by UNSCEAR (2000), 0.1 mSv/y, to control the presence of radionuclide in water used for drinking.

The annual effective absorbed dose is the estimated value of radiation energy absorbed by the human body because of an intake of a certain amount of radioactivity in a year (DWAF, 2002). To calculate the annual effective dose, equation 1 was used.

$$\text{Annual effective dose} = C \times AWI \times DCF \dots \dots \dots \text{equation 1}$$

Where C is the activity concentration of U (Bq/L), DCF is the dose conversion factor for a specific age group (Sv/Bq) and AWI is the age-dependent annual water intake (L/year). The annual water intake default values for different age groups and the dose conversion factor values were obtained from the Department of Water Affairs handbook (DWAF, 2002). The concentration of natural U (U_{nat}) recorded in the water was converted to activity concentration using $1 \mu\text{g/L} = 0.025 \text{ Bq/L}$ as the conversion factor (Duggal et al., 2021; Dowdall et al., 2013).

5.3.5. Lifetime cancer risk (Carcinogenic risk assessment)

The lifetime cancer risk (risk factor) estimates the likelihood of developing cancer due to exposure to a carcinogen (Bleam, 2012). To calculate the lifetime risk factor due to the consumption of the Rietspruit water, equation 2 was used. The concentrations of U in the Rietspruit water were converted to uranium activity concentration (Bq/L). $1 \mu\text{g/L} = 0.025 \text{ Bq/L}$.

As U decays, its decay products such as radon, lead, thorium, radon, radium etc emit alpha, beta and gamma radiation that results in internal exposure to the exposed population once U is ingested. Based on the zero - threshold linear dose model, any absorbed dose of U is believed to result in an increased risk of cancer. The model stipulates that with every exposure to an ionizing radiation, there is a linearly increasing risk of causing cancer. Due to the accumulation of U in certain human organs, the risk of cancer of the bone, liver and blood is believed to increase (Golden et al., 2022; Keith & Faroon, 2022).

The calculation assumes that the activity concentration of U at each site remains constant and the residents only consume untreated stream water of this U-concentration at the specified rate throughout their lifespan (i.e., a highly unlikely scenario that significantly overestimates the true risk). This method was designed by the US EPA (USEPA, 1986) and has been used in several studies (Okeyode & Jibiri, 2013; Bleam, 2012; Giri & Jha, 2012).

Lifetime cancer risk = U intake (Bq/L) over a lifetime × risk coefficient equation 2

To calculate lifetime cancer risk, the activity intake of U must be determined using the concentration of dissolved uranium quantified in the water samples collected at each site. Equation 3 was used to calculate the uranium activity intake:

$$\text{Uranium intake (Bq/l)} = C \times IR \times EF \times ED \dots \dots \dots \text{equation 3}$$

Where C is the uranium activity concentration (Bq/L), ED is the lifetime exposure duration (70 years), and EF is the exposure frequency (365 days per year). Lifetime cancer morbidity and mortality risk coefficients for uranium are 1.3E-09 and 1.73E-09 respectively (EPA; Radiation, 2000).

5.3.6. Hazard quotient (non-carcinogenic risk assessment)

Hazard quotient (HQ) is the ratio of the lifetime average daily dose at each site and the reference dose for U, 0.6 µg/kg/day, (Singh et al., 2021) through the ingestion of drinking water. A reference dose (RfD) is the estimate of the dose level considered safe for human consumption (ATSDR, 2014). It relates the dose at the exposure point to a toxicological

endpoint (Bleam, 2012). Hazard quotient below 1 signifies no risk while above 1 means there is risk. The hazard quotient has been used to assess the health risk of U in several studies (Kamunda et al., 2018; Njinga et al., 2016; Giri & Jha, 2012).

$$\text{Hazard quotient} = \frac{\text{lifetime average daily dose}}{\text{reference dose}} \dots \dots \dots \text{equation 4}$$

5.4. Results and Discussion

5.4.1. Concentration of U in collected water samples

The highest concentration of U (781.9 µg/L) in the water was recorded at the inflow of the PW dam (Rietspruit headwater) (Table 5.1). It decreases gradually with distance from the mine. This is similar to the study of Davidson (2003), which also reported a gradual reduction in the concentration of U moving downstream from the source of pollution.

The concentration of U in the water is above the WHO guideline limit in drinking water, 30 µg/L, (WHO, 2012) and South Africa standards, 10 µg/L in water used for irrigation and 30 µg/L in drinking water, (DWAF, 1996a) for about 24 km away from the point source. The concentration of U in the water used for the irrigation of the wheat plantation (Figure 5.4C) is 52.7 µg/L. Hakonson-Hayes et al (2002), concluded that the concentration of U in plants is directly proportional to the concentration of U in the water used for the irrigation of the plant. The consumption of such plants by humans and animals that fed on the plant could be detrimental to human health (Bjørklund et al., 2020; Corlin et al., 2016b; ATSDR, 2014).

Table 5.1: Concentration of uranium in the stream (28th August 2020)

Site number	Site name	Field number*	Flow distance from PW dam (km)*	U water (µg/L)
Site 1	PW dam inlet	1	0	781.9
Site 2	Channel water	*1	0	52.7
Site 2	Corner of dam	*2	0	55.8
Site 3	PW dam outflow	2	1	181.2
Site 4	Wetland 1	3	2	101.4
Site 5	Wetland 2 inflow	*8	3	62.0
Site 5	Wetland middle	*7	3	63.4
Site 5	Wetland outflow	*6	4	65.6
Site 6	Damlit outflow	4	6	49.2
Site7	Between damlit	5	6	104.9
Site8	Religious site	5B	8	103.3
Site9	Post religious site	6	8	103.8
Site10	Post bridge	7	12	70.2
Site11	Poortjie	8	14	74.5
Site12	Pre Evaton	9	24	71.1
Site13	Evaton-Rietspruit	10	NA	0.3
Site14	Post confluence	11	32	4.9
Site15	Pre confluence Rietspruit & Leeuspruit	13	37	6.0
Site16	Leeuspruit	12	NA	17.4
Site17	Post confluence Rietspruit & Leeuspruit	14	39	6.2
Site18	Post confluence Rietspruit & Leeuspruit	15	43	6.9
Site19	Rietspruit (Potch Rd)	16	49	5.1
Site20	Pre-confluence Rietspruit & Klein-Rietspruit	18	53	3.7
Site21	Klein-Rietspruit	17	NA	0.7
Site22	Post-confluence Rietspruit & Klein-Rietspruit	22	55	5.5
Site23	Lochvaal inflow	19	56	6.5
Site24	Lochvaal	20	60	6.9
Site25	Vaal River	21	63	3.0
Maximum				781.9
Average ± MU				71.9 ± 2.0
Minimum				0.3
SD				146.4

*The field number is the ascribed number on collected water samples and the flow distance is the approximate distance of sampled site from the PW dam, MU is the measurement uncertainty.

The reduction in the concentration of U from the point source downstream is attributed to the dilution effect from unpolluted water (e.g., discharge from water treatment plants and tributaries), infiltrating groundwater and the river water-sediment interplay which removed dissolved uranium from water column into the riverbed and vice-versa. Despite the reduction in the concentration of U in water downstream, the site used for religious activities, Site 8 in Table 5.1, has U concentrations more than twice the guideline limit of U in water. This is about 6 km from the source of the pollutant. Factors responsible for the increase and decrease in the concentrations of U at these sites were discussed in a previous study by Raji et al. (2021).

The concentrations of U at the sites designated as natural background concentration of U, were 0.3 µg/L at the Evaton-Rietspruit and 0.7 µg/L at the Klein-Rietspruit. As mentioned earlier, these sites were selected as the natural background concentration of U because there is no mining activity or industrial operation upstream of the river. At the Leeuspruit tributary, the concentration of U in the river was 17.4 µg/L. A gold mine is located about 24 km upstream of the sampled site (Figure 5.1). Besides the grazing of cattle and the location of farmlands along the Leeuspruit, no human exposure was witnessed. The source of the water used for irrigation of the farmlands is unknown. However, Leeuspruit water might be used by the residents of the informal settlements within this area.

5.4.2. Hazard quotient (non-carcinogenic risk assessment)

The lifetime average daily dose (LADD) of U due to the ingestion of Rietspruit water ranged from 0.0 to 22.3 µg/kg/day of uranium with an average of 2.1 µg/kg/day. As mentioned earlier, the HQ was estimated for uranium using a reference dose of 0.6 µg/kg/day as recommended by EPA OGWDW (2000). The result of the non-carcinogenic risk (chemical risk) ranged from 0 to 37.2 (Figure 5.5). The minimum HQ was recorded at sites selected as the natural background concentration of U in the study area. Like the U concentration in the Rietspruit, the maximum HQ was recorded at the PW dam inlet.

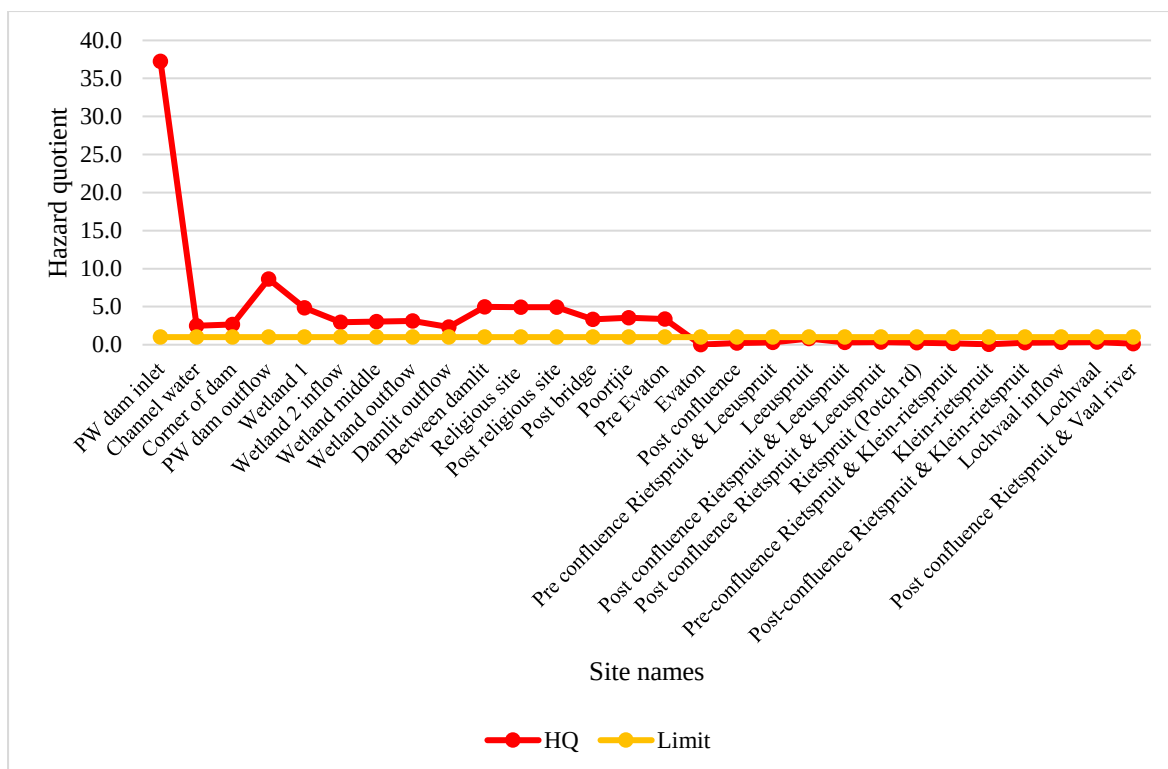


Figure 5.5: Non-carcinogenic risk: via drinking untreated stream water only at site-specific U-concentrations observed on 28th August 2020

In this study, HQ was above 1 for about 24 km from the mining environment (Figure 5.5). With human exposure observed within this radius, it means people drinking from the water could be exposed to chemical toxins because of ingesting U contained in the water.

5.4.3. Annual effective dose due to the ingestion of uranium in Rietspruit water

There are many human exposure pathways for U, however the major pathway witnessed during the field survey was considered in this study, namely ingestion through drinking of water. From Figure 5.6 below, it was confirmed that an individual annual radiation dose limit of 0.1 mSv/year (for members of the public) prescribed by UNSCEAR (2000) was exceeded at the PW dam inlet for all the age groups. At the PW dam outflow, the radiation dose limit was exceeded by the 15 years' age group while the rest of the age groups' annual effective dose was equal to the radiation dose limit, 0.1 mSv/year, (Figure 5.6). This means the ingestion of the water at the observed U activity concentration will cause a proportional increase in the chance of a health effect. Given the numerous exposure pathways that may cause radiation exposure, it was recommended by the International Commission on Radiological Protection

(ICRP) to keep individual exposure doses to a minimum. This is essential in order to keep the total dose received by an individual below the annual dose limit.

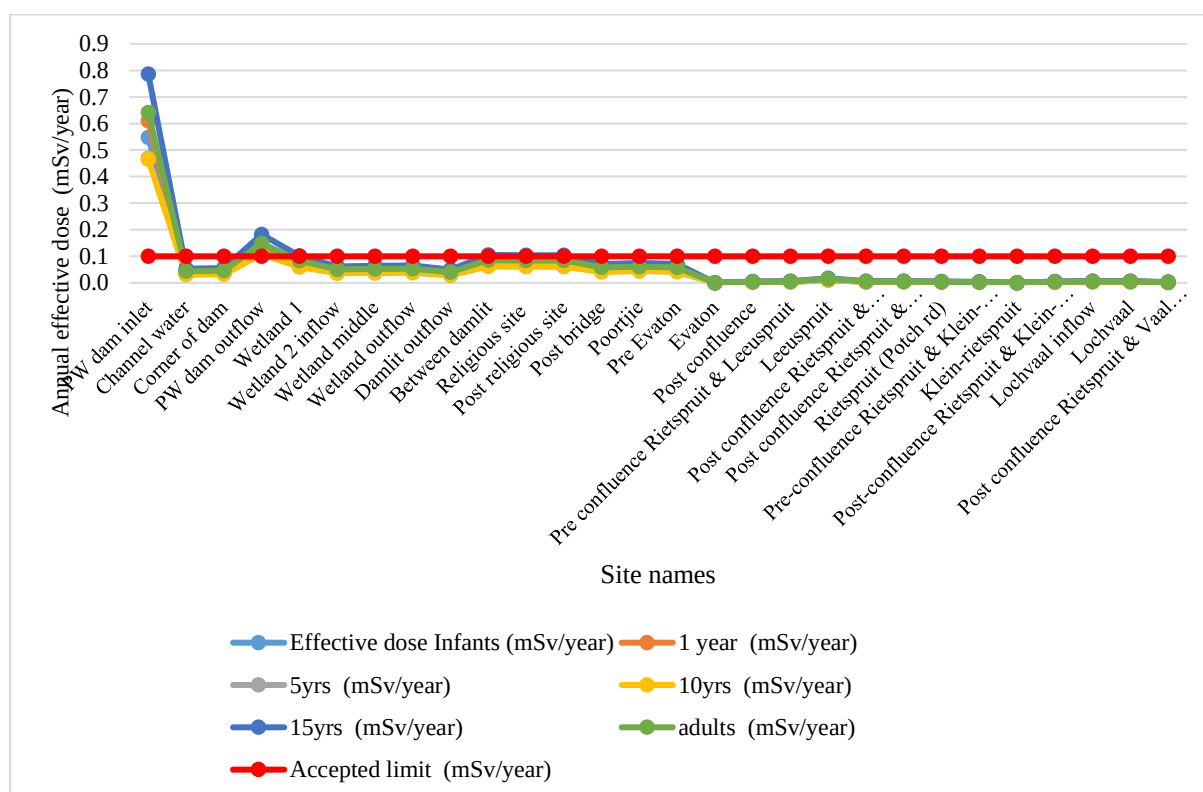


Figure 5.6: Annual effective dose for different age groups: via drinking untreated stream water only at site-specific U- concentrations observed on 28th August 2020

At sites where human exposure was observed, the annual effective dose was not greater than 0.1 mSv/year for all the age groups (damlit outflow, between damlit, religious site, and post religious site). The maximum effective dose was recorded at the PW dam inlet for all the age groups (Figure 5.6). This coincided with the maximum concentration of U recorded in this study. The annual effective dose is in the order 15 years' age group as the highest > adults > 1 year > infants > 5 years and 10 years.

In Table 5.2 below, the values of annual water intake (AWI) and dose conversion factor (DCF) used to calculate the annual effective dose were given. Also included in Table 5.2 are the minimum, maximum, average, and standard deviation for each of the studied age groups.

Table 5.2: Statistics of age-dependent annual effective dose due to the intake of uranium through the ingestion of drinking water

Age group (years)	AWI (L/year) (D WAF, 2002)	DCF (Bq/Sv) (D WAF, 2002)	Minimum	Maximum	Average	Standard deviation
			mSv/year (based on the concentration of dissolved U at sampled sites)			
0 - 12 months	200	1,40E-07	2,00E-04	0,55	0,05	0,1
1 - 4	260	1,20E-07	2,00E-04	0,61	0,06	0,11
5 - 9	300	8,00E-08	2,00E-04	0,47	0,04	0,09
10 -14	350	6,80E-08	2,00E-04	0,47	0,04	0,09
15 - 17	600	6,70E-08	3,00E-04	0,79	0,07	0,15
Adults	730	4,50E-08	2,00E-04	0,64	0,06	0,012

5.4.4. Lifetime cancer risk (Carcinogenic risk assessment)

According to US EPA, 1991, the lifetime cancer risk ranging from $1.0\text{E}-06$ to $1.0\text{E}-04$ is acceptable and above $1.0\text{E}-04$ requires immediate remediation, while a cancer risk below $1.0\text{E}-06$ is not considered to pose any significant health effect (Hu et al., 2012; Fryer et al., 2006). Using equation 2 above, the result of the cancer risk is displayed in Figure 5.7 below.

The highest mortality cancer risk recorded was $1.1\text{E}-03$ and $1.7\text{E}-03$ for morbidity cancer risk. The result revealed that more than 1 person in 1000 persons are at risk for both mortality and morbidity cancer because of ingestion of dissolved U from the Rietspruit water. These values were the only values above the radiological risk limit ($1.0\text{E}-03$) in this study. From the result above, (Figure 5.7), downstream users of the Rietspruit water are below the cancer risk limit and can be considered safe. Comparable to the exposure dose result, the PW dam inlet has the highest cancer risk (Figure 5.7). This means the sites require immediate intervention. Since no human contact was witnessed in this environment, possible human exposure to U will be the consumption of cattle that graze within this environment and consumption of plants irrigated with U-polluted water (Figure 5.4 A to D) - indirect exposure (Dzoma et al., 2010).

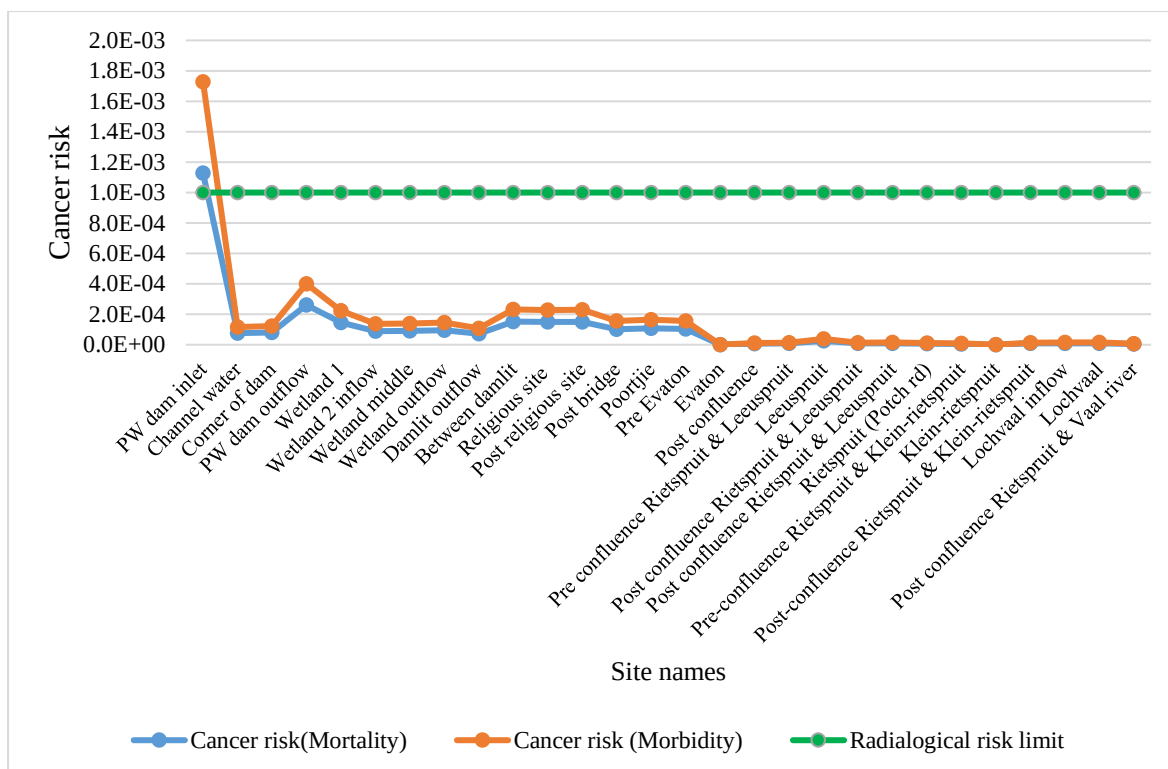


Figure 5.7: Mortality and morbidity cancer risk: via drinking untreated stream water only at site-specific U- concentrations observed on 28th August 2020

5.4.5. Recommendation

Due to the high concentration of U found in the study area, the usage of the water for domestic, agricultural, and religious activities should be discouraged. This could be achieved by educating the inhabitants of the informal settlements, farmers, and worshippers about the health impacts of U and the concentration of U in the water used for these activities. Mining companies in conjunction with relevant government agencies should work together to remediate this situation. This will help in reducing human exposure to the U.

5.4.6. Limitations

The risk assessments are all based on the assumption that the concentrations of U will remain constant, and people consume only Rietspruit water at the given quantity per day throughout their lifespan. This is unrealistic and results in a significant overestimation of actual exposure and associated health risks.

Furthermore, individual risk can be influenced by genetic, age, sex, diet, state of health and lifestyle factors; as a result, lifetime cancer risk does not estimate the actual risk for any

individual (ATSDR, 2013; Bjørklund et al., 2020; WHO, 2001b). Generally, poor communities are particularly vulnerable due to malnutrition, lack of access to adequate health care, poverty related stress levels, and high prevalence of other diseases negatively affecting the immune system, including HIV/AIDS, tuberculosis etc, commonly found in mining areas.

5.5. Chapter conclusion

The maximum concentration of U, 781.9 µg/L, was recorded around the Ezulwini Gold and Uranium Mine, which is the primary source of U in the Rietspruit. Where human exposure was observed, the concentrations of U ranged from 49.2 µg/L to 181.2 µg/L. The affected population is therefore exposed to both chemical and radiological risk from U. The chemical toxicity of U in the Rietspruit has values above the standard limit. The HQ was above 1 about 24 km away from the mine. These are sites where human exposure, cattle grazing, and farmlands were observed.

Radiological (lifetime) cancer risks of mortality and morbidity due to Rietspruit water consumption are above the safe limit of $1.0E3$ within the mining environment. The grazing of cattle within this environment and the use of the water for irrigation activity could be an entry point for the introduction of U into the food chain. Also, people who were observed drinking water at these sites and fetching the water for domestic purposes are at risk of radiological exposure.

This study revealed that the probability of carcinogenic risk is low; however, the non-carcinogenic risk may be due to the chemical toxicity of U. It will be recommended that the mining environment should be fenced to limit cattle grazing, potable water should be provided for the informal settlers, and farming and religious activities along the stream should be discouraged.

Chapter 6

Assessing Uranium Pollution Levels in the Rietspruit River, Far West Rand Goldfield, South Africa

Abstract

The Rietspruit is in Gauteng Province, South Africa, within the Witwatersrand Basin. The basin is noted for its vast gold deposits. The river extends for about 60 km before joining the Vaal River. The aim of this study was to determine the concentration of uranium in the Rietspruit and the factors that influenced the concentration of U at each of the sites. The source of uranium in the river is the discharge from the gold mine and the mine wastes. Inductively coupled plasma mass spectrometry was used for water and sediment analysis to determine the concentration of U. A high concentration of U was found in the river water and sediment, which is above the permissible limit of U. The water is used for irrigation of farmlands, cattle watering and for human consumption despite the high concentration of uranium in it. Ingestion of uranium is dangerous to human health. Due to the toxic nature of uranium, consumption of the water for domestic use and agriculture purposes must be discouraged.

Keywords: Uranium; Pollution; Wetland; Dam; Water Salinity

6.1. Introduction

Uranium (U) is an isotopic radioactive element (Grenthe et al., 2006). This is because of the difference in the number of neutrons in the nucleus of the atom. The natural mean background concentration of U in soil is ≤ 4 mg/kg (WHO, 2001b), and the South African limit of U in water used for drinking and agricultural activities is 30 $\mu\text{g/L}$. However, gold mining operations elevated the concentration of U in sediment and water (Winde et al., 2004c). In South Africa, U is found in association with gold, and South African uranium is mainly produced as a by-product of gold mining (Winde & Sandham, 2004a).

The mining of gold has brought a large concentration of U to the surface. In South Africa, about six million kilograms of U have been brought to the surface and disposed onto slimes dams (Winde & van der Walt, 2004b). Slimes dams contaminate nearby surface water as well as groundwater through different modes of erosion (water and air) and seepage to water systems (Durand, 2012a; Winde, 2010). The contamination of water bodies is hazardous to humans and animals that depend on the water for various uses (Dewar, 2019b; Corlin et al., 2016a; Callahan et al., 2004; Bleise et al., 2003). Due to the mobility of U influenced by the redox state of U, the chemistry of the water and sediment, as well as iron and manganese concentration in the sediment (Boelee et al., 2019; Cumberland et al., 2016), downstream users of the water could also be exposed. Exposure pathways of humans to U include drinking of polluted water, consumption of food rich in U, inhalation of mine dusts and farm produce irrigated with contaminated water (Kamunda et al., 2016a; Keith et al., 2013a; Coetzee et al., 2006).

Several studies have been done on the impacts of gold mining in South Africa focusing on U (Durand, 2012a; Hobbs et al., 2010; Coetzee et al., 2006; Winde & de Villiers, 2002a) reporting high concentrations of U within gold mines; however, no literature has reported on the concentration of U for the entire length of the Rietspruit. As a result of this, it is important to know the concentration of U in the Rietspruit system (water and sediment), and the extent of the pollution plus the factors influencing U concentration. The use of water for irrigation provides a pathway for the introduction of U into the food chain, and drinking the water as a religious rite also makes it crucial for researchers to quantify the level of the pollutant in the water. This is necessary to engage the authority in charge of water to take adequate steps in reducing human exposure. This study focused on the U pollution level of the Rietspruit from

the Peter Wright (PW) dam downstream to the Vaal River, about 60 km, and the factors that affected the U level.

The main objective of this study was to determine the concentration of U in the Rietspruit water and sediment. Factors that play an important role in the mobilization and immobilization of U will also be discussed.

6.2. Materials and Methods

6.2.1. Study Area

The Rietspruit River is in the Highveld region of South Africa. It starts from the Peter Wright dam, a reservoir located at an elevation of 1680 m above sea level, in the West Rand of Gauteng (C22H Quaternary Catchment area according to the Department of Water Affairs and Forestry) and flows south for about 60 km before the confluence with the Vaal River (Figure 6.1C). The Vaal River is located downstream of Vanderbijlpark and extends westwards to the Northern Cape, where it joins the Orange River. As a result of the abundance of gold deposits in this study area, the Rietspruit area has experienced over 60 years of goldmining activity. Notable mines include Cooke 4 Ezulwini Plant and South Deep Gold Mine, which is situated along the Leeuspruit River (Figure 6.1C). The Leeuspruit River formed a confluence with the Rietspruit River, and it is found in the C22J Quaternary Catchment area. The total size of these two catchments is about 1123 km². Other notable tributaries include the Evaton-Rietspruit and Klein Rietspruit (Figure 6.1C).

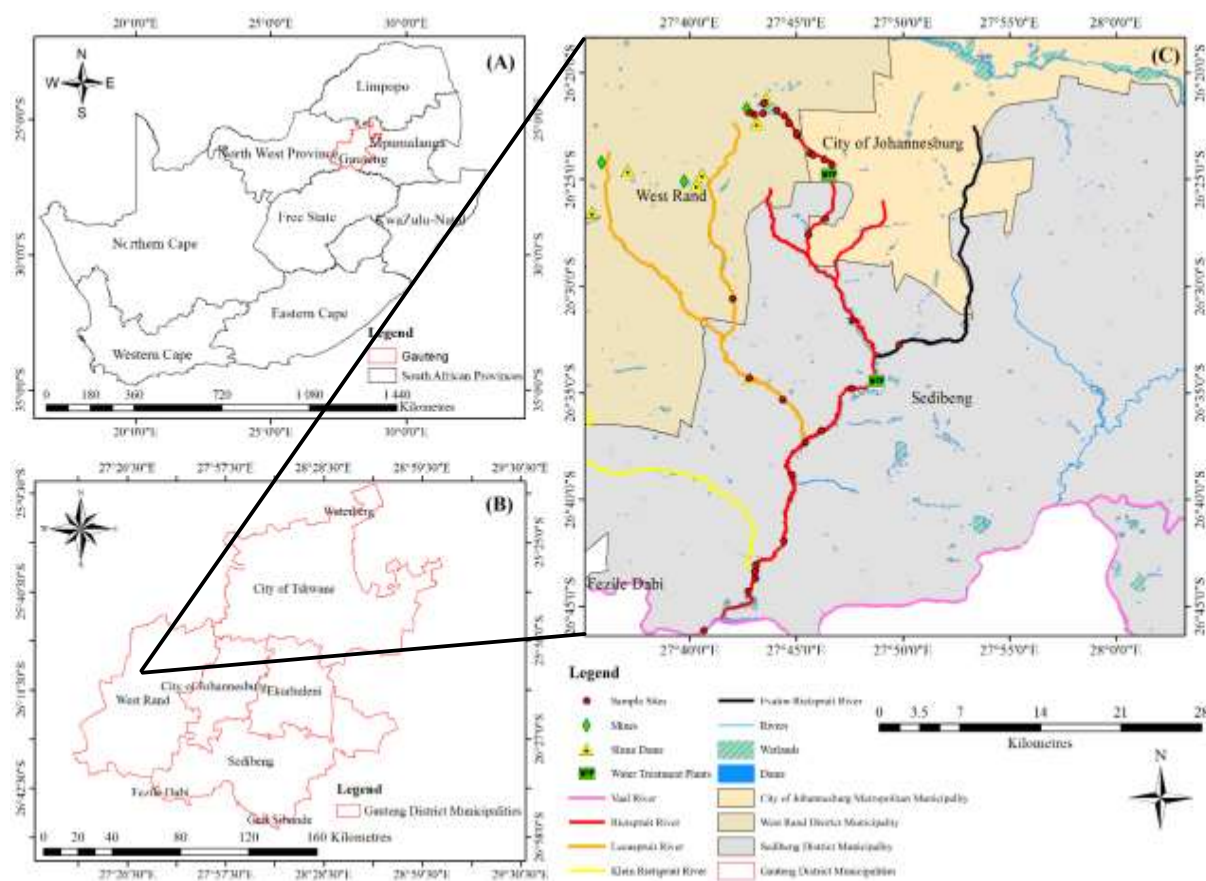


Figure 6.1: Map of study area. (A) shows the map of South Africa. (B) is the map of the Gauteng Province where the mine is located. (C) depicts the Rietspruit river with associated tributaries and the sampled sites

The study area is within the Witwatersrand Basin, an Archean sedimentary basin that contains a stratigraphic sequence about 6 km thick. It is made up of quartzites and shales with minor volcanic unit. Gold is hosted by the upper Elsburg and middle Elsburg reefs. Uranium is also found in the middle Elsburg reef. The gold is found associated with sulphide minerals (pyrite), while U is found in the form of uraninite.

6.2.2. Field Work

In total, thirty soil samples and twenty-eight water samples were collected from the 30 sites downstream of the Rietspruit at varying distances, depending on accessibility while focusing on wetlands, dams, river confluence and places where human exposures were witnessed. Sediments were collected at the same spot where water samples were collected using an auger. Sampling started in the vicinity of the gold mine and continued downstream (Figure 6.1C). Water samples were collected under the water surface using water bottles in the middle of the

river. Water bottles were rinsed three times before water samples were taken. This is done to avoid sampled water contamination. When the water bottle was full, the bottle was capped under water. There were two dry samples from the tailings; each from the slimes dam and mine waste located along the furrow leading to the PW dam inflow, while the rest of the sediment samples were collected under water at the same spot where water samples were collected. The sediment samples were kept in a zip-lock bag, while the water samples were kept in the 500 mL water bottle used to collect the water samples. The pH, electric conductivity and temperature of the water body were taken using the WTW multi 350i at each of the sampled sites (reference temperature: 25 °C). Stream flow velocity was measured using Global Flow Probe FP101 and 201. All samples were taken to the laboratory after sampling.

6.2.3. Laboratory Analyses

Sediment samples were all dried in the oven at a temperature of 50 °C for 24 hours to remove the water content. About 400 g of the sediment was placed in a labelled petri dish. The petri dish was then arranged in the oven. After drying, a mortar and pestle were used to break the particles and a sieve of mesh size 2000 µm was used to remove gravel and plant particles. Sediment samples were digested according to EPA 3050b. About 200 mg of the sieved sediment sample were placed in a Teflon tube. A volume of 9 mL of 65 % nitric acid and 3 mL of 32% hydrochloric acid was added to the tube, capped, and placed in a microwave digestion system (Milestone, Ethos UP, Maxi 44). A period of 20 min allowed the system to reach 1800 MW at a temperature of 200 °C, which was maintained for another 15 min. After cooling, Agilent 7500 CE ICP-MS fitted with Collision Reaction Cell technology for interface removal was used to determine the concentration of U and other trace metals in the samples. To achieve a quantitative result, the instrument is calibrated using ULTRASPEC certified custom mixed multi-element stock standard (De Bruyn Spectroscopic Solutions, Midrand, South Africa) solutions containing all the elements of interest.

Water samples were filtered using a 0.45 µm pre-filter nylon sieve to remove suspended particles. Then, 1 mL of the filtered water was mixed with 9 mL of 2 % HNO₃ to remove organic constituents before ICP-MS was used to determine U concentration. High-performance ion chromatography was used to determine the anion concentration of chlorine (Cl), sulphate (SO₄), nitrate (NO₃), nitrite (NO₂), phosphate (PO₄) and fluorine (F) in the water.

6.3. Results and Discussion

6.3.1. Rietspruit Water Chemistry

The quality of water of the Rietspruit River from twenty-eight (28) water samples is indicated in Table 6.1. The impact of the Rietspruit water chemistry on uranium will be discussed further in the next session.

Table 6.1: Rietspruit water chemistry

Parameters	Water samples (n = 28)				WHO Limit (WHO, 2012)	SANS 241 (SANS, 2015)
	Maximum	Average	Minimum	SD		
pH	8.8	7.4	6	0.7	6–9	5–9.7
EC (µS/cm)	1358	788	443	252	400	
Temp (°C)	26	16	8.8	4	30	
Cl (mg/L)	481.5	56	18.5	85	5	300
SO ₄ (mg/L)	1009	302.2	13.2	241	500	500
NO ₃ (mg/L)	25.1	4	0	6	10	11
NO ₂ (mg/L)	2.9	0	0	1	3	1
F (mg/L)	1.2	0.1	0	0.2	1.5	1.5
PO (mg/L)	14.8	1.1	0	2.8	0.03	

6.3.2. pH Value

The pH of the stream water is weakly acidic to weakly alkaline (6.0 – 8.8) (Figure 6.2). This is within the WHO guideline range (6 – 9) and the South African limit (5 – 9.7). The temperature at which pH readings are taken, should always be reported, since pH measurement is influenced by temperature. The maximum temperature recorded was 26 °C at the channel water, while the minimum temperature was 8.8 °C, which corresponded to the lowest pH reading observed in the field.

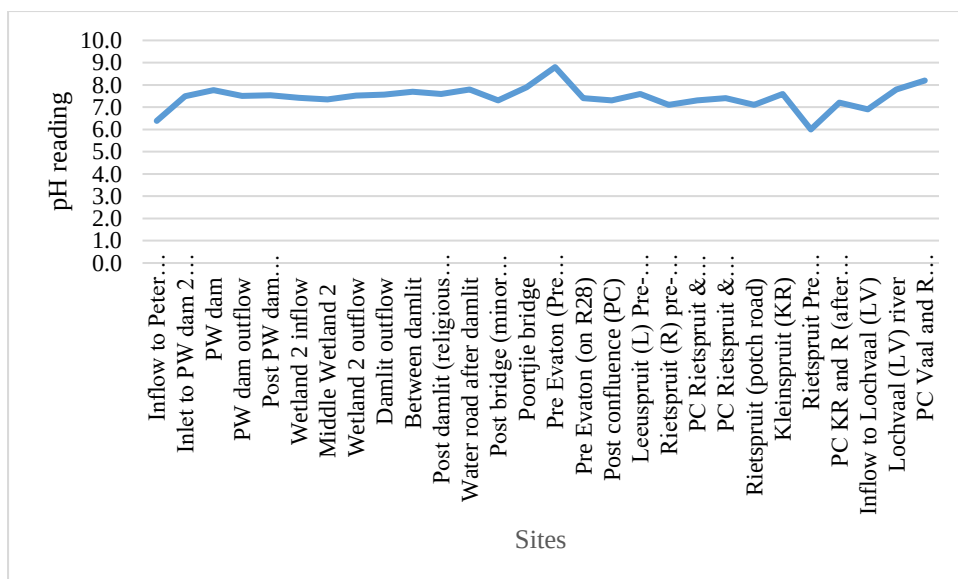


Figure 6.2: pH readings at the sampled sites

The pH of the stream water increases as the sun rises from the first site (inflow to Peter Wright dam) downstream. The maximum pH reading, 8.8, was recorded around noon, when the sun was at its peak (Figure 6. 2). The fluctuation of the pH in stream water is the result of photosynthesis of aquatic plants and algae. The minimum pH reading, 6.0, was recorded in the evening, after sunset. As a result of the reading at sunset, sampling was continued the next day and the trend of the rising pH reading as the sun rises was observed the following day when the last few sites were visited. This is comparable to the finding of Winde et al. (Winde et al., 2004a). However, in his study, pH observation was done in one location, but the pH observations correspond with this study finding.

The reduced species (U (IV), U⁴⁺) typically precipitates from natural waters near neutral pH due to its low solubility, and so is usually characterized as relatively immobile (Silva & Nitsche, 1995). In contrast, the oxidized species of uranium, uranyl (U(VI), UO₂²⁺), typically forms more stable aqueous complexes and is much more mobile in natural waters (Silva & Nitsche, 1995), although there are many known minerals containing uranium in the VI oxidation state (Finch & Murakami, 1999).

6.3.3. Electrical Conductivity

Electrical conductivity (EC) is a measure of the ability of water to conduct an electrical current (Meride & Ayenew, 2016). The range of EC at 25 °C in the water is 443–1358 µS/cm (Figure

6.3). The World Health Organization (WHO) recommends that the value of EC in water should not exceed 400 $\mu\text{S}/\text{cm}$. This means that the EC of the study area is higher than the normal threshold for EC in water. The average of the study area EC (785.1 $\mu\text{S}/\text{cm}$) is above the WHO recommended limit of EC in water (400 $\mu\text{S}/\text{cm}$).

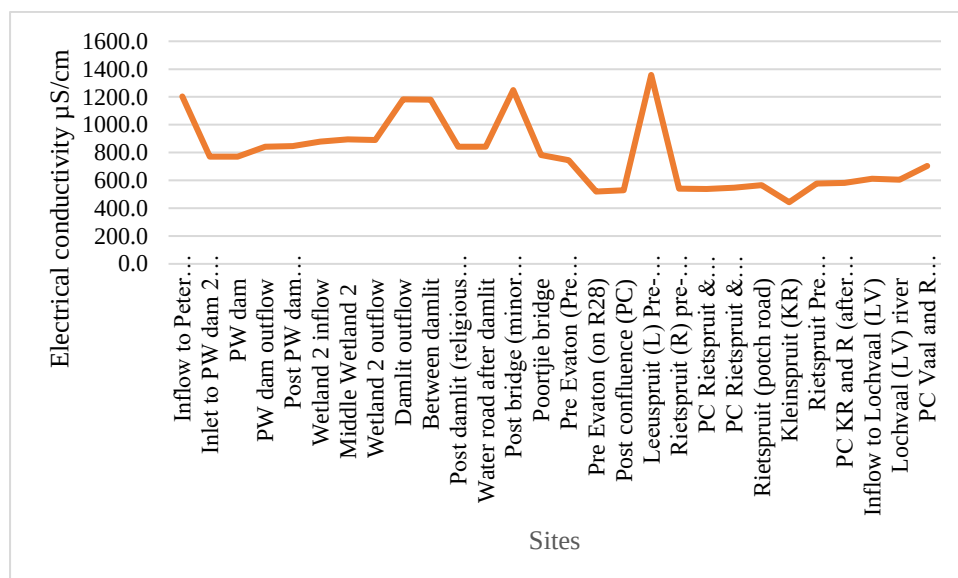


Figure 6.3: EC reading at the sampled sites

Electrical conductivity is influenced by the availability of ions, and it is proportional to the total amount of dissolved solid, positively charged ions like sodium (Na), magnesium (Mg), calcium (Ca), iron (Fe) (cations) and chlorine (Cl), nitrate (NO_3), sulphate (SO_4), and phosphate (PO_4), (anions) in the water. Electrical conductivity is also affected by water temperature; the warmer the water, the higher the conductivity (Winde et al., 2004a). Anions like Cl, NO_3 , SO_4 are synonymous with sewage discharge. High concentrations of these anions were recorded at sites after the two water treatment plants and both sites have high EC (Figure 6.1C).

6.3.4. Anions Concentration

The concentrations of the anion (SO_4 , NO_3 , NO_2 , F, PO_4 , Cl_2) relate to the source of water contamination. Typical sources for this kind of contamination are industrial operations, agricultural practices and mining activities, and municipal waste discharge. The average concentrations of SO_4 (302.2 mg/L), NO_3 (4.2 mg/L), NO_2 (0.3 mg/L), F (0.1 mg/L) are below the WHO guideline limit (500 mg/L, 10 mg/L, 3 mg/L, 1.5 mg/L, respectively); only PO_4 (1.3 mg/L) has a higher average concentration than the WHO guideline limit (0.03 mg/L). Using

the South-African National Standard, SANS 241, the average concentrations of the SO_4 , NO_3 , NO_2 and F in this study are all below the national limit.

The presence of sulphate, nitrate, nitrite, and chlorine in water increases the salinity of the water. An increase in water salinity decreases the ability of U to be adsorbed by the sediment (Coetzee et al., 2006). High concentrations of SO_4 , NO_3 and Cl_2 were recorded at sites downstream of the two water treatment plants along the Rietspruit (Figure 6.1C). At each of these sites, a low concentration of U was recorded in the sediment, despite the high concentration of U in the water column and the high adsorption capacity of the sediment.

6.3.5. Uranium Concentration in the Rietspruit Water

Within the immediate environment of the gold mine, the uranium concentration in the water is very high. At the inflow of the PW dam, a concentration of 781.9 $\mu\text{g/L}$ was recorded in the furrow (Figure 6.4). This is about 200 times higher than the WHO regulatory limit of U in water. The furrow takes discharge from the mine sewage plant to the PW dam. Another contributing factor to the high concentration of U at the furrow is the erosion of mine waste that litters the environment. During rain events, mine wastes are eroded into the furrow. In one of the mine wastes sampled next to a channel that connects with the furrow, a U concentration of 1125 mg/kg was recorded in the sediment. Before the main rain event, the channel was dry, so the water sample collected after rainfall in the channel was analysed. The concentration of U in the water was 387.7 $\mu\text{g/L}$. It confirms that erosion of mine wastes located on the earth surface could contribute to the increase in the concentration of U in water.

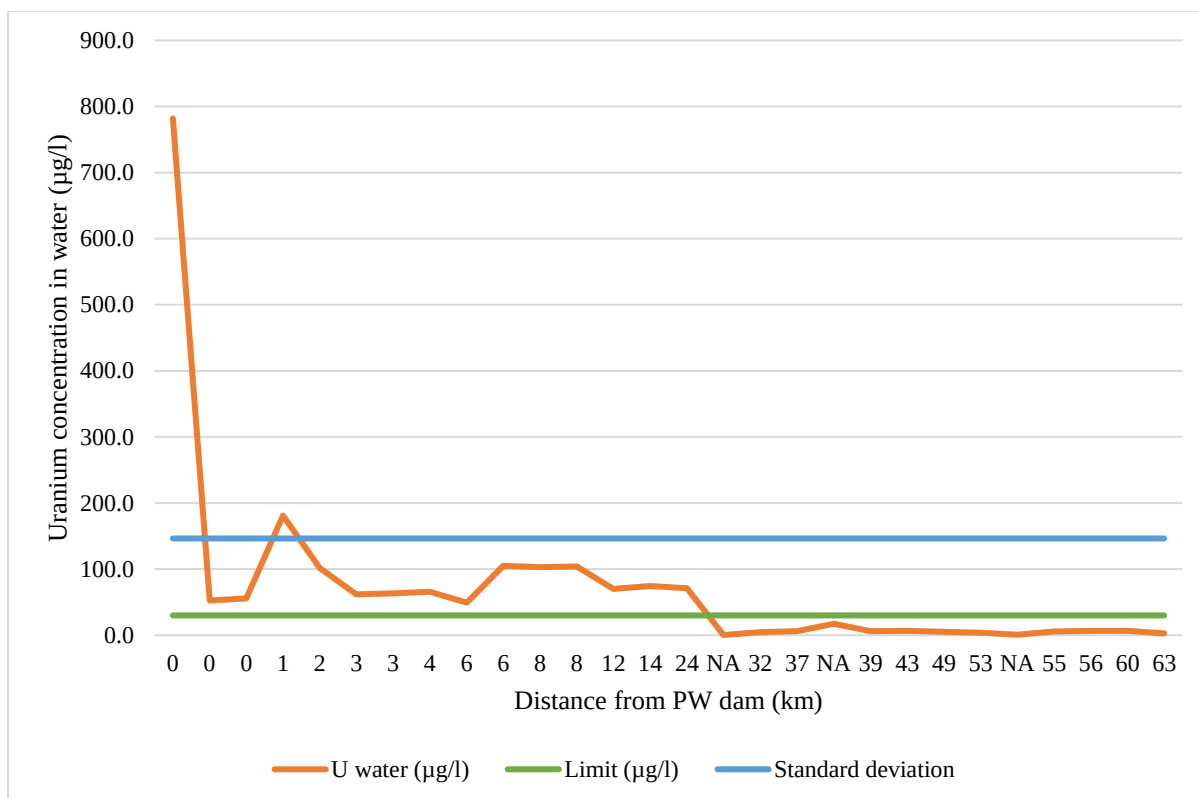


Figure 6.4: Longitudinal profile of U in Rietspruit water

The discharge from the underground shaft has a concentration of 52.7 µg/L. It should be noted that, despite the treatment of fissure water before discharge to remove U, U persists in the water. The Cold Lime Softening process is used by the mine to remove U in the water before discharge (Kritzinger, 2017).

About 1 km from the dam inflow (Figure 6.4), the concentration of U has reduced to 181.2 µg/L. This site is the outflow of the PW dam. It shows the ability of the dam to remove U from the water column. This indicates immobilization of U. Further downstream, the concentration of U reduced further to 101.4 µg/L after another 1 km from the previous site (PW dam outflow). Reduction of U in water concentration as distance increases from the source pollutant, has been reported (Liu et al., 2015). This site is a wetland (Figure 6.1C). The reeds cover of the wetland and the hydraulic control point created because of the road culvert reduced the flow of the water. This allows for the deposition of suspended particles, which U is adsorbed to. The deposition resulted in a high concentration of U being present in the wetland sediment, signalling immobilization of U by wetland sediment.

The reduction trend in the concentration of U continues downstream for another 6 km, where another dam is located (Figure 6.4). We call the dam a damlit because it does not have an official name. The concentration of U in the damlit water is 49.2 µg/L. After the damlit outflow, the concentration of U increased to 104.9 µg/L. This is because of the turbulence created by the damlit outflow slab. After the slab, the flow velocity of the stream increased to 177.9 m/s from 24.7 m/s recorded before the slab. This turbulence was able to re-suspend fine particles of silt and clay which contain U, resulting in a high concentration of U in the water column. The environment of the damlit is noted for a series of religious activities and farming. Many of the worshippers use the water for drinking, cooking, and bathing, whereas the farmers use the damlit water for crop irrigation and animal watering. Due to the high concentration of U recorded in the water, these activities could be toxic to human health.

The concentration of U was consistent for another 2 km before a reduction in concentration was observed. The reduction was caused by the diluting effect of the Ennerdale Water Treatment Plant (Figure 6.1C). The average discharge from the water plant averages about 132,300 m³ per month (Kritzinger, 2017). After the Ennerdale Water Treatment plant, there is a change in water colour, from clearwater to a dark colour, with a sewage odour. As a result of the discharge, the concentration of chlorine and nitrate in the water increased more than twofold. These increased the water salinity and reduced the adsorption capacity of the stream sediment (Coetzee et al., 2006). The concentration of U after the Ennerdale Water Treatment plant was 70.2 µg/L; this value was consistent for another 2 km before the confluence of the Evaton-Rietspruit tributary.

Evaton-Rietspruit has no mining or industrial activity upstream (Figure 6.1C). As a result, the site was selected as this study's background concentration of U. The concentration of U at the Evaton-Rietspruit is 0.3 µg/L. This is the lowest concentration of U recorded in this study. Downstream of the Evaton-Rietspruit is the Sebokeng Water Treatment Plant (Figure 6.1C), with an average monthly discharge of 2,191,867 m³ (Kritzinger, 2017). About 1 km from the Sebokeng Water Treatment Plant is the post confluence of Rietspruit and Evaton-Rietspruit. The concentration of U in the water of this site was 4.9 µg/L. This is a huge decrease in U concentration. Before the confluence, 71.1 µg/L of U was recorded in the Rietspruit. The only reason for the reduction in U concentration is the diluting effect of the Sebokeng Water

Treatment Plant. At a concentration of 4.9 µg/L, the concentration of U falls below the WHO regulatory limit in water.

The Leeuspruit tributary is an interesting tributary of the Rietspruit (Figure 6.1C). This is because of the gold mine established upstream. Uranium concentration in the Leeuspruit also reduces as the distance from the mining site increases. The highest concentration of U recorded in the Leeuspruit water is 50.2 µg/L. This is lower than expected because the mine is operational. At about 6.1 km before the confluence of the Leeuspruit and the Rietspruit, the concentration of U in the water has reduced to 12.81 µg/L. After the confluence, the concentration of U in the Rietspruit was 6.0 µg/L. This is an increase from the 4.9 µg/L U concentration recorded before the confluence of Rietspruit and Leeuspruit.

Going further downstream, the concentration of U ranges from 3.7 µg/L to 6.9 µg/L before the confluence with the Vaal River (Figure 6.1C). After the Vaal River confluence, about 60 km from the Rietspruit headwater, the concentration of U in the water was 3.0 µg/L. At another tributary selected as a natural background concentration of U in the water of the environment, the Klein Rietspruit (Figure 6.1C), the concentration of U recorded was 0.7 µg/L. Low concentrations of U at the sites selected as the natural background concentration of U in the study area water (including the Evaton-Rietspruit, 0.3 µg/L) indicates that the major source of U in the Rietspruit is the gold mine discharge and mine wastes.

6.3.6. Uranium Concentration in the Rietspruit Sediment

Goldmine wastes contain a high concentration of U. For example, in the slimes dam, the concentration of U recorded was 72.7 mg/kg. A higher concentration of U has been recorded in slimes dams in the country (McCarthy, 2011b; Winde et al., 2004a). In another mine dump located beside a water channel that connects with the furrow taking sewage discharge to the PW dam, a concentration of 1043 mg/kg was recorded in the mine waste. Despite the decommissioning of the mine, the waste from mining operations contains a high concentration of U in them. The erosion of these mine wastes into nearby water bodies pollutes the stream, and this is toxic to downstream users of such water.

The scale found on the concrete canal, which takes discharge from the underground shaft, has a U concentration of 1143 mg/kg. The scale is formed because of calcium carbonate

precipitation and changes in the atmospheric pressure (Winde & van der Walt, 2004b). The concentration of calcium in the scale is 20,760 mg/kg. This is the highest concentration of Ca found in this study. During the precipitation of calcium carbonate, U was also removed from the water column. The scale on the concrete canal could serve as another source of U as it could easily dissolve if the water chemistry should change. This could be influenced by a drop in the water pH, and a change in the discharge flow. According to Winde et al. (Winde et al., 2004c), the volume of water discharged by the mines at night and on the weekend is more than water discharged during the day. This is done to save costs spent on electricity.

Unlike the trend of U concentration in the Rietspruit water, which decreases with distance from the mining site, the trend of U in the Rietspruit sediment is not consistent (Figure 6.5). Several factors play an active role in the ability of sediment to retain U in them (immobilization). Some of these factors are sediment texture, organic carbon, water salinity, iron hydroxide/oxide, and water flow velocity.

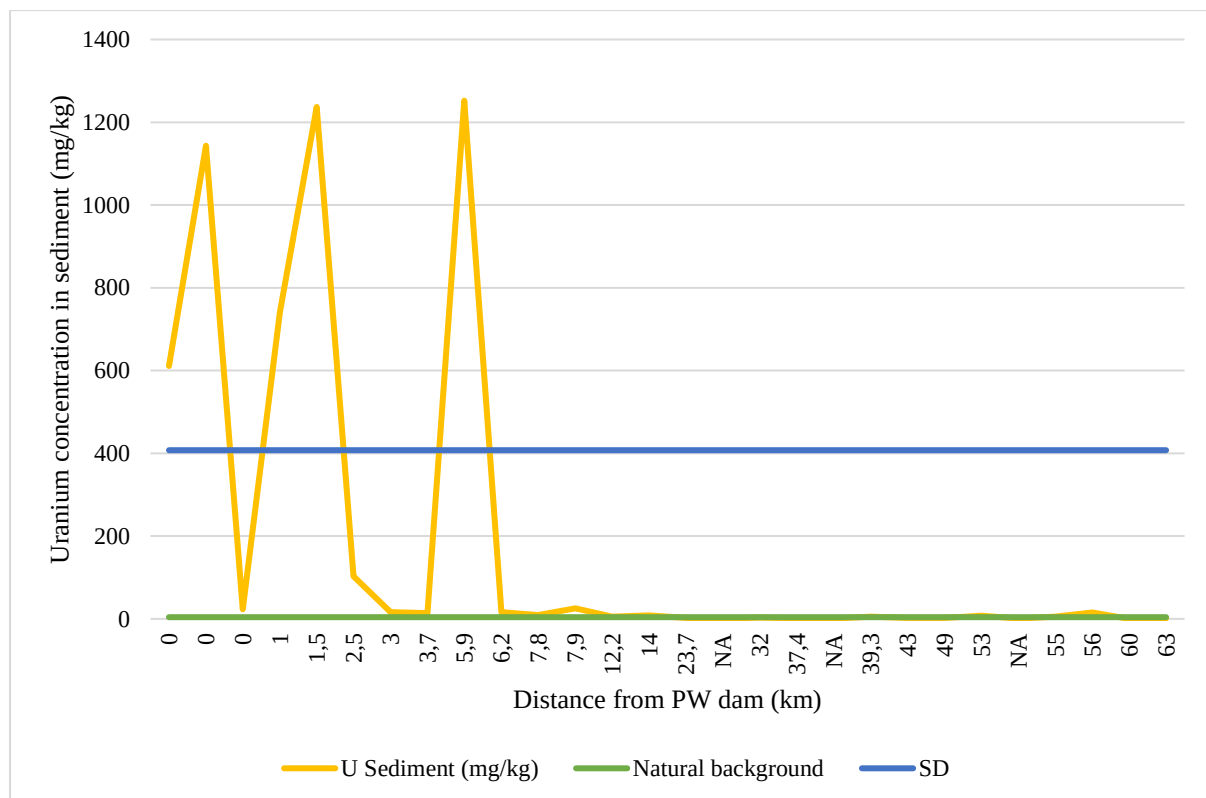


Figure 6.5: Longitudinal profile of U in Rietspruit sediment

At the inflow of the PW dam furrow, the concentration of U recorded was 611.1 mg/kg. All these concentrations were higher than the natural background concentration of U in soil (≤ 4 mg/kg by WHO). The percentage of organic carbon is very high (6.7 %). Organic carbon has been reported to be able to keep an environment in a reducing condition. A reducing condition favours U immobilization. This is because U (VI), which is highly oxidized, soluble, and mobile, will be reduced to U (IV), which is insoluble and immobile (Cumberland et al., 2016). The correlation of U concentration in the sediment and organic carbon is positively strong (+0.7).

At the wetland located about 1.5 km from the PW dam inflow (Figure 6.5), the concentration of U at this site is 1237 mg/kg. This is the second highest concentration of U recorded in this study. Organic carbon plays a role in this site. The percentage of organic carbon here is 6.7 %, which is comparable to the organic carbon at the Peter Wright inflow. Uranium is adsorbed to organic matter, which breaks down to form humus. Furthermore, the high concentration of iron recorded at the wetland indicates co-precipitation of U with iron hydroxide. The correlation of U with OC and Fe is positively strong (+0.7 and +0.8 respectively). This indicates the importance of these two factors in the immobilization of U in the sediment.

The reed cover of the wetland was able to reduce the flow velocity of the wetland water. This resulted in the gravitational settling of fine particles of silt and clay. Fine particles of silt and clay have a higher adsorption capacity than the coarse particles of sand (Coetzee et al., 2006). This is further established by the strong composition of silt and clay in the sediment, which amounts to a total percentage of 49 % of the soil texture. Uranium adsorbed to fine suspended particles of clay and silt will precipitate out of the water column when the flow velocity of water has reduced and there are enough barriers (reeds in the case of the wetland) to impede the flow of the water. All these factors contributed to the reason why a high concentration of U was recorded in the wetland sediment.

Wetlands have been categorized as a sink for U and other toxic elements (Schöner et al., 2009; Ross & Dudel, 2008; Coetzee et al., 2002). Some of the concentrations of toxic elements recorded in the wetland sediment are the highest found in this study (Table 6.2). Water discharged from the mine is the major reason why the stream is perennial. This could change if the discharge from the mine was stopped, which could lead to drying up of the stream during winter, thereby exposing the wetland sediment to atmospheric conditions. With the exposure,

the sediment will become oxidized, and toxic elements stored in the sediment will be released during a rain event. This could be a major problem for downstream users of the stream.

Table 6.2: Concentration of toxic elements in wetland

Heavy Metal	Gold	Arsenic	Lead	Cadmium	Mercury	Cobalt	Manganese
Concentration (mg/kg)	2.3	223.1	120.9	3.5	0.3	4878	47120

The highest concentration of U was recorded in the damlit sediment (Figure 6.5). The concentration of U recorded was 1252 mg/kg. A low concentration of organic carbon was found in the sediment, which indicated that organic carbon does not play any role in this case. Possible factors that played a role here are the adsorption capacity of the damlit sediment and co-precipitation of U with iron and manganese hydroxide.

The total composition of silt and clay in the sediment is 31.1 %. Like the wetland, this is a valid factor responsible for the immobilization of U in the damlit. In addition, the concentration of iron is very high, 30,630 mg/kg. As a result, co-precipitation of U with hardly soluble compounds of iron is possible. Due to the reduction in the flow velocity of water in the damlit, precipitation of U of low solubility could be possible.

After the damlit, the concentration of U decreased to 16.5 mg/kg in the sediment of the next sampled site about 200 m from the damlit outflow. The reduction of U concentration in the sediment could be a result of the dominant coarse particle of sand. This resulted in a decrease in the ability of U to be retained in the sediment despite the high concentration of U found in the water (104.9 µg/L).

At the site after the Ennerdale Water Treatment Plant, the percentage of clay and silt is high, about 34 % of the soil texture, but a low concentration of U was recorded in the sediment. This is because of the increase in the salinity of the water, which reduces the adsorption capacity of the stream sediment. This finding is comparable to the result of the Leeuspruit tributary: a similar tributary of the Rietspruit with an operational gold mine established upstream. The percentage of silt and clay in the Leeuspruit dam is high, above 40 % at the inflow, middle and outflow of the dam. However, a low concentration of U was found in the sediment. This is because of the water salinity. The concentration of chlorine, sulphate and nitrate in the water is very high.

Further downstream of the Rietspruit, the concentration of U was below 4 mg/kg, the natural concentration of U in soil (WHO, 2001b) except at two sites (Figure 6.5), the post confluence of Leeuspruit and Rietspruit (5.6 mg/kg) and the inflow of the Lochvaal (15.2 mg/kg). The inflow of the Lochvaal was able to retain U because of the high composition of silt and clay of the sediment (above 50 % of the soil texture) and the slow flow velocity of the water.

In the sediment of the sites chosen for this study of natural background concentration of U in sediment, the concentrations of U are 0.7 mg/kg at the Evaton-Rietspruit and 0.6 mg/kg at the Klein Rietspruit. It further indicates that the environment has low concentrations of U but, because of gold mining operations in the upstream environment, U was able to infiltrate the water and sediment of the Rietspruit.

6.4. Chapter conclusion

The concentration of U decreases with increasing distance from the gold mine located in the study area. This reduction can be attributed to the water-sediment system interplay (chemistry), and location of wetlands and dams close to the source pollutant. The major source of U in the Rietspruit is the discharge from the Ezulwini plant underground shaft and water treatment plant. Other sources include the leaching of slimes dams and mine dumps into the water channel leading to the PW dam. Underground pollution is another source of pollution but was not considered in this study. Despite the decommissioning of the mine, U trapped in mine wastes still contributes to the concentration of U in the water.

Wetlands and dams provide a medium of filtering U out of water. However, this is not a permanent filtration, as U trapped in sediments can be remobilized back into the water column, thereby contributing to the pollution of the downstream. If the mine should stop discharging water into the PW dam, the stream will become non-perennial, which will increase oxidation. Oxidation favours the remobilization of U trapped in sediment (Cumberland et al., 2016; Coetzee et al., 2006; Winde & van der Walt, 2004b) when in contact with rainwater.

The impact of mining is not limited to the immediate environment. It is confirmed in this study that while a high concentration of U is found in the water about 24 km from the mining site (Figure 6.4), the highest concentration of U is found in the sediment about 6 km away from the mining site (Figure 6.5). As a result, animal grazing and religious activity along the stream

must be discouraged within the environment that has a high concentration of U. The use of billboards and signage within the perimeter should be encouraged and effected. The use of the water from the dam for irrigation purposes should also be discontinued, as well as fishing activity in the dam.

Possible remediation of the mining environment, which must include the removal of the mine wastes that litter the mining sites, must be investigated. Also, possible mechanisms that will ensure the wetland chemistry does not change to prevent the remobilization of U from the sediment, should be considered. This includes keeping the environment in a reduced state by maintaining the concentration of organic carbon and preventing the burning of wetland reeds during winter. In dams, the water level must be maintained to prevent drying out of the dam, which will result in the exposure of oxidized sediment to acid water from the rain.

Conclusion and recommendations

7.1. Study conclusion

The purposes of this investigation were to quantify uranium, U, in the Rietspruit system, to determine the impact of rain events on U pollution, to assess the health risks associated with U, and to assess the mobility of U in a water – sediment system. Based on the objectives, the following conclusions were made:

1. Elevated levels of U were found in the Rietspruit water and sediments. The presence of this toxic metal is owing to the exploitation of gold within the proximity of the Rietspruit headwater, the Peter Wright dam. At locations used as the natural background concentrations of U in the study area, the concentrations of U were below the allowable threshold of U in both the water and sediment. These sites, Evaton-Rietspruit and Klein-Rietspruit, were selected due to the absence of quarrying or industrial activity about 30 km upstream of the river and they both form major parts of the Rietspruit tributaries.
2. Once U is released into the Rietspruit due to the outflow of the Peter Wright dam, the concentration of U in the water reduces with distance away from the source pollutant. However, the concentration of U was double the permissible maximum in water, 30 µg/L, about 24 km from the gold mining surroundings. After the confluence of Evaton-Rietspruit with the Rietspruit, the concentration was below the permissible threshold of U. Dilution of unpolluted water of the Evaton-Rietspruit with the polluted Rietspruit water is a valid cause for the decrease in the concentration of U.
3. In the Rietspruit sediment, a concentration exceeding 1000 mg/kg was recorded in downstream dams and wetlands. The concentrations at these sites were the highest recorded in this study. This is regarded as a secondary accumulation of U outside of the mining environment. Due to this, dams and wetlands can be termed as “sinks” for U. Many factors are responsible for the accumulation of U at these sites, and they include the precipitation of U out of the water column because of the decrease in water flow in wetland and dam, adsorption of U to negatively charged particles, and the richness of clay and silt which influence the immobilization of U.

4. Water salinity controls the capability of sediment to immobilize U. These can be determined by the electric conductivity recorded as well as the number of major anions in the water. For example, despite the similarities in the physical properties of sediments in the damlit (downstream of the Rietspruit) and the Leeuspruit dam, the amount of U in the Leeuspruit dam is just 3.12 mg/kg. However, concentrations of the major anions in the Leeuspruit dam tripled the amount found in the damlit downstream of the Rietspruit.
5. To establish the impact of rain events, a sand dump along a dry furrow leading to the Peter Wright dam was selected. A concentration of 1043 mg/kg was logged in the sand dump. After a rain-event, a water sample was collected from the furrow. The amount of dissolved U recorded in the collected water sample was 387.7 mg/kg. These confirmed that U can be released from a mine waste after rainfall which can be washed downstream to surface water.
6. Based on the utilization of the Rietspruit for various domestic, religious, and agrarian activities, a carcinogenic and non-carcinogenic health risk assessment was done. This was based on the amount of U recorded at a major religious site where worshippers were observed drinking the untreated Rietspruit water amongst several activities. It was concluded that if the amount of U at this site remains constant, and the observed population uses only this water in their lifetime, the non-carcinogenic risk outweighs the carcinogenic risk. This means the observed population are at a higher risk to U-chemical risk than radiological health risk. Due to this, it is proposed that the usage of the Rietspruit for any of the activities must be restricted. Potable water should be supplied consistently to the residents of nearby informal settlements within mining locations.
7. To monitor U-mobility in a water-sediment system, two stages were involved. Firstly, a 24-hour field investigation was undertaken where water samples were collected hourly, and the in-situ water readings were also recorded using the handheld Crison MM40+. Finally, a large portion of the polluted damlit sediment was taken and allowed to dry out at natural atmospheric condition. In the first phase, it was concluded that the pH increased as the sun rose. This is due to biological activities like photosynthesis. At night, the pH of the water reduced. The reduction in water pH coincided with an increase in the amount of U in the water and a gradual reduction in dissolved U at sunrise. In addition, the EC level increases at night and decreases as the sun rises. Due to this phenomenon, it was concluded that low pH and high EC lead to U remobilization and low immobilization. This means that the true reflection of U concentration will be missed during the day when sampling traditionally takes place.

In the second stage of this objective, rainwater was used to rewet the dry sediment. The concentration of U in the rainwater was 0.21 µg/L before the rewet; after the rewet, the concentration increased to 1211 µg/L in the water sample collected the instant after the rewet. The quick dissolution of salt crust, rich in U, that formed on the sediment surface after drying dissolved immediately upon contact with the rainwater. The non-linear graph showing the levels of U in dam water with time proved that U is adsorbed into different phases in the sediment and each phase dissolves in water at different rates of desorption. This process implied that if the Rietspruit should become a non-perennial stream, U that has been immobilized in the sediment will be freed into the water column upon contact with rainwater. This is hazardous to downstream users of the water.

8. Besides U, some toxic elements with concentrations above the permissible limits in the environment were recorded in collected water and sediment samples. This shows that the exploitation of gold in the Witwatersrand Basin pollutes the environment not only with U but also arsenic, As, cadmium, Cd, mercury, Hg, and lead, Pb. In relation to the mobility of these toxic elements, it can be concluded that they are less mobile when compared with U. Extreme concentrations of these toxic metals were found within 6 km of the gold mine while elevated concentrations of U were determined in the Rietspruit water about 24 km away from the gold mine. Also, elevated concentrations of these toxic elements were recorded in the swamp and dam sediment. This shows that factors liable for the deposition of U in the wetland and dam sediment also contributed to the immobilization of these toxic elements.

7.2. Research contribution to knowledge

The findings from this research highlighted the impacts of gold mining on the immediate environment, which includes the biosphere, hydrosphere, and lithosphere. This research also provided fundamental recommendations for government, policymakers, and practitioners within the goldmining sector. This study highlighted the consequences of U for human health and provided the exposure route of U to the biosphere because of gold mining. The research also provided in-depth knowledge on factors that promote the mobility of U from the source pollutant. Despite the closure or the decommissioning of a gold mine, this study confirmed that once U is released into a fluvial system, the pollution is long-lasting, and it is not limited to the immediate goldmining environment. To mitigate the effects of gold mining, this study provided possible ways of reducing the exposure to U from the fluvial system.

While there is a lot of research around mining and its impacts on the natural environment, there is a lack of research work that has quantified the presence and prevalence of heavy metals in river basin systems in South Africa. In view of these, this study contributes to the overall agenda on environmental management systems within the mining setups as well as the formulation of management procedures to manage pollution arising from the mining environments in South Africa and Africa as a whole.

7.3. Research gap filled

By investigating the U pollution levels and mobility from the Rietspruit headwater and further downstream, this study bridged a gap in literature which is limited to the study of heavy metal pollution levels within the immediate environment of a gold mine or a specific location in a stream. This highlighted possible dangers that downstream users of a polluted stream, for example, settlers of informal settlement, farmers, and worshippers, are exposed to, and provided different ways of mitigating these effects. This study also showed that U can be released into the environment from a polluted dry sediment when in contact with water. This is critical in understanding the mobility and the remobilisation of U in a fluvial system.

7.4. Recommendations and future studies

Based on this study's conclusions, the following are recommended:

1. The utilization of the Rietspruit for local, sacred, and agrarian functions ought to be rejected. This can be controlled by the erection of a fence along the Rietspruit channel.
2. Due to the dissolution of U and several toxic metals from mine wastes that litter the mining environment, the immediate environment of the mine should be rehabilitated.
3. Local inhabitants of informal settlements and farmers around the area should be sensitized about the dangers involved with the continuous usage of the Rietspruit water for their basic needs. Potable water should be provided for the residents of Lawley.
4. Further studies should be carried out to verify the amount of U and other toxic elements in agricultural produce from this area which include wheat and maize plantations and cattle farms.

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Appendix



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ETHICS APPROVAL LETTER OF STUDY

Based on approval by the **Faculty of Natural and Agricultural Sciences Ethics Committee (FNAS-REC)**, the Faculty of Natural and Agricultural Sciences Ethics Committee hereby **approves** your study as indicated below. This implies that the North-West University Senate Committee for Research Ethics (NWU-SCRE) grants its permission that, provided the special conditions specified below are met and pending any other authorisation that may be necessary, the study may be initiated, using the ethics number below.

Study title: The dynamics of fluvial transportation of Uranium in the Rietspruit River System															
Study Leader/Supervisor: Dr A Ngie															
Student: IB Raji															
Ethics number:	N	W	U	-	0	1	4	9	9	-	2	0	-	A	9
	Institution				Study Number					Year			Status		
Status: S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation															
Application type: Single					Risk Category: Minimal										
Commencement date: 01/02/2020															
Expiry date: 30/06/2024															
Approval of the study is initially provided for a year, after which continuation of the study is dependent on receipt and review of the annual (or as otherwise stipulated) monitoring report and the concomitant issuing of a letter of continuation.															

Special in process conditions of the research for approval (if applicable):

- The following documentation are archived by FNASREC and should be complete and kept up to date:
 - Research proposal
 - Signed approval from the scientific committee indicating the proposed risk category
- All researchers involved in the study should submit signed NWU code of conduct statements annually.
- All researchers of low risk studies should submit proof of relevant ethics training every two years.
- All researchers that take part in activities that pose a safety and security threat to the researchers or the environment should submit a risk assessment form annually.
- All research involving human interaction should follow best ethical practise and keep documents as proof. This includes informed consent, questionnaires, incorporation of risk-benefit, and responsible data management.
- Any research at governmental or private institutions, permission must still be obtained from relevant authorities and provided to the FNASREC. Ethics approval is required BEFORE approval can be obtained from these authorities.

General conditions:

While this ethics approval is subject to all declarations, undertakings and agreements incorporated and signed in the application form, the following general terms and conditions will apply:

- *The study leader/supervisor (principle investigator)/researcher must report in the prescribed format to the FNASREC:*
 - *annually (or as otherwise requested) on the monitoring of the study, whereby a letter of continuation will be provided, and upon completion of the study; and*
 - *without any delay in case of any adverse event or incident (or any matter that interrupts sound ethical principles) during the course of the study.*
- *The approval applies strictly to the proposal as stipulated in the application form. Should any amendments to the proposal be deemed necessary during the course of the study, the study leader/researcher must apply for approval of these amendments at the FNASREC, prior to implementation. Should there be any deviations from the study proposal without the necessary approval of such amendments, the ethics approval is immediately and automatically forfeited.*
- *Annually a number of studies may be randomly selected for an external audit.*
- *The date of approval indicates the first date that the study may be started.*
- *In the interest of ethical responsibility, the NWU-SCRE and FNASREC reserves the right to:*
 - *request access to any information or data at any time during the course or after completion of the study;*
 - *to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process;*
 - *withdraw or postpone approval if:*
 - * *any unethical principles or practices of the study are revealed or suspected;*
 - * *it becomes apparent that any relevant information was withheld from the FNASREC or that information has been false or misrepresented;*
 - * *submission of the annual (or otherwise stipulated) monitoring report, the required amendments, or reporting of adverse events or incidents was not done in a timely manner and accurately; and / or*
 - * *new institutional rules, national legislation or international conventions deem it.*
- *FNAS-REC can be contacted for further information or any report templates via Roelof.Burger@nwu.ac.za 018 299 4269*

The FNASREC would like to remain at your service as scientist and researcher, and wishes you well with your study. Please do not hesitate to contact the FNASREC or the NWU-SCRE for any further enquiries or requests for assistance.

Yours sincerely,



Prof Roelof Burger
Chairperson Faculty of Natural and Agricultural Sciences Ethics Committee (FNASREC)