

Master of Science Dissertation

*For the purpose of completing the program of Master of Science by Dissertation in the
School of Geography, Archaeology and Environmental Studies at the University of
the Witwatersrand.*

Research Title:

**The influence of a chemical treatment plant and an existing wetland ecosystem on AMD
pollution and water quality along the Blesbokspruit, South Africa**



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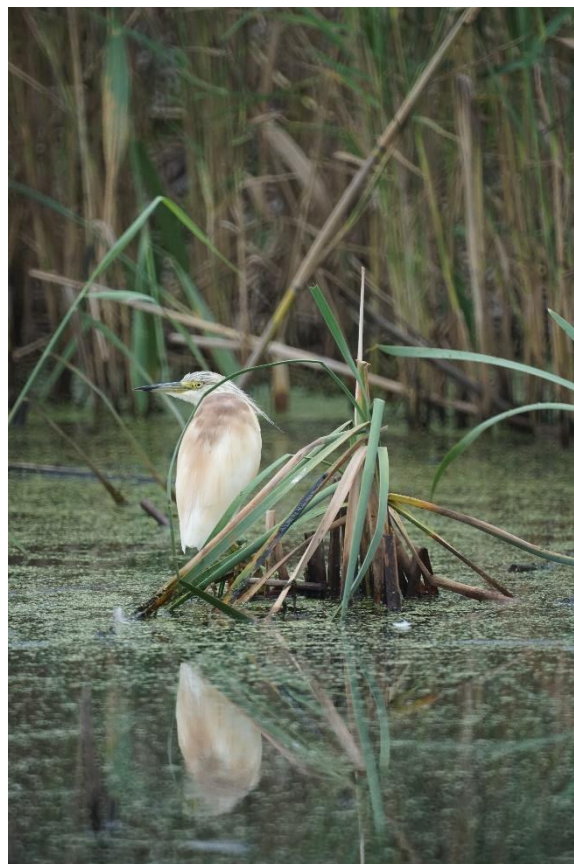


Figure 1: Squacco Heron at Marievale Bird Sanctuary.
Photograph taken by Professor C. Curtis in
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Abstract

The influence of the Eastern Basin Acid Mine Drainage (AMD) chemical treatment plant and the Blesbokspruit Wetland ecosystem in remediating AMD pollution has been determined. The research process involved making land use maps, using historical Rand Water quality data, and collecting water, sediment and soil samples along the Blesbokspruit. Being in operation since August 2016, the Eastern Basin chemical AMD treatment plant has had a major influence on water quality, and this influence is not entirely positive. The introduction of the treatment plant was completely necessary at the time due to the possible decant of AMD water from the abandoned Grootvlei mine into the Blesbokspruit wetland. However, phase one of treatment which makes use of chemical mechanisms to firstly neutralise the water with lime and thereafter remove the toxic metals that precipitate out of the solution has negatively influenced conductivity, magnesium, chloride and sulphate levels downstream. Over time, the concentrations of these parameters have increased to worse management level targets set out by the Blesbokspruit Forum. Conductivity and sulphate have reached unacceptable management target levels since the introduction of the chemical treatment plant. The reduction of iron, manganese, ammonium, nitrate and phosphate downstream of the AMD treatment plant is due to dilution caused by increased discharge from the treatment plant and due to the wetland ecosystem removing these contaminants. The greater Blesbokspruit Wetland and the Marievale Wetland have a very low influence on improving water quality within the area. The wetlands do reduce nutrient levels according to Rand Water data, but the water quality in this study area is mainly influenced by what is occurring upstream of the wetlands at the AMD treatment plant. There are numerous environmental concerns within this study area which includes the Marievale Bird Sanctuary. Soil quality results suggest that the Blesbokspruit has a high influence on soil conductivity. River sediment heavy metal analysis results suggest that the river sediments collected from the eight sampling sites are highly polluted and have a low to moderate potential for ecotoxicity. Sediment trace metal concentrations are also highly concentrated near mine dumps and historical mine decant points. Increased soil conductivity and heavy metal contamination may have a negative impact on the waterfowl living at the Marievale Bird Sanctuary. Ground truth water sampling also identified that there is a seasonal signal of increased conductivity and sulphate during the dry winter months. The results of this research have highlighted the need for phase two of treatment (which would implement desalination infrastructure) to begin at the chemical AMD treatment plant as well as increased monitoring and protection of the wetland ecosystem within the study area.



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Research Title: The influence of a chemical treatment plant and an existing wetland ecosystem on AMD pollution and water quality along the Blesbokspruit, South Africa.

1. Introduction

The biggest threat to a sustainable water supply in South Africa is not a lack of storage but the contamination of available water resources through pollution (Claassen, 2010). South Africa has been well documented as a water scarce nation (Claassen, 2010). Along with scarcity of water, our water quality is continually being compromised due to many factors. These include issues of acidification through acid mine drainage, acid rain and industrial waste, increased salinisation, eutrophication and disease-causing micro-organisms (Oberholster, 2010). Acid Mine Drainage (AMD) is one of the most destructive pollutants on our water quality (Oberholster, 2010). The process of AMD is well understood: through mining activities, water used in coal and gold mines contains sulphuric acid and toxic heavy metals (Ochieng, 2010). If this water is left untreated, it could pose serious health risks to communities, and cause major contamination in the natural environment (Ochieng, 2010). The current and most common remediation technique used for the treatment of AMD water in South Africa is the use of chemical mechanisms to firstly neutralise the water with lime and thereafter remove the toxic metals that precipitate out of the solution (McCarthy, 2011). Although this treatment has its benefits, it does not solve the problem entirely. This process leads to increased salinity as well as promoting high concentrations of sulphate in the water (McCarthy, 2011). Wetlands are described as being effective in attenuating AMD pollution (Humphries et al., 2017). The use of wetlands as a bioremediation option has been described as being able to reduce AMD pollution through biological processes occurring within wetlands (Johnson and Hallberg, 2005).

2. Problem statement

In South Africa, AMD is a very broad geographic problem due to the numerous gold and coal mines that span the provinces of Gauteng, North West, Mpumalanga and Limpopo (McCarthy, 2011). Specifically, within the Witwatersrand Eastern Basin; Brakpan, Springs and Nigel are historic gold mining towns (McCarthy, 2011). Defunct mines have promoted the mobilisation of AMD water in the area and this has prompted national government to act by launching the largest AMD treatment plant of its kind in the world in August 2016 (DWS, 2017). This plant is situated within the Blesbokspruit (spruit translates to a small water course from Afrikaans which is used to describe small rivers) wetland, near the inoperative Grootvlei Gold Mine, and is upstream of the Marievale Bird Sanctuary that lies within the southern half of the greater Blesbokspruit wetland (DWS, 2017). The AMD treatment plant has been operational since its completion, which was extremely necessary at the time. During that time, the abandoned Grootvlei mine was being flooded and there was a huge potential that AMD water would decant into the surrounding Blesbokspruit wetland (Kruger, 2017; Solomons, 2017). The Blesbokspruit wetland was first accepted as a Ramsar Wetland of International Importance in 1986 due to the important biodiversity (mainly waterfowl) it supported during the accreditation period (Ambani and Annegarn, 2015). By 1996, after extensive mining and industrial activities, the wetland was placed on the Montreux Record, a register which lists potentially threatened or degraded Ramsar sites that no longer agree with the Ramsar Convention standards (Ambani and Annegarn, 2015). This research project therefore poses as an opportunity to consider the influence of both chemical (through the new AMD treatment plant) and biological (through the existing wetland) remediation processes on water quality within the Blesbokspruit. As

research within this specific area of study is limited, it is of great interest to determine the influence these two processes have on water quality within the Blesbokspruit. Improvements in water quality could trigger similar strategies taken up by national government at other historic defunct mining sites that are spread across South Africa's gold and coal fields.

2.1 Research questions

1. What influence does the combination of both the chemical treatment plant and the existing wetland have in improving water quality and remediating AMD pollution along the Blesbokspruit?
2. What is the spatial extent and impact of historic and current AMD pollution within the Marievale Bird Sanctuary wetland itself and beyond the wetland further downstream?
3. To what extent does the Blesbokspruit wetland provide an ecosystem service by improving water quality linked to AMD pollution?

3. Research aims and objectives

3.1 Research Aim

- To determine whether the Eastern Basin AMD Treatment Plant and the existing Blesbokspruit wetland have an influence on improving water quality and reducing AMD pollution in the Blesbokspruit. Also, to determine the spatial extent of pollutants within the river sediment and soils of the greater Blesbokspruit wetland area and further downstream at Marievale Bird Sanctuary.

3.2 Research objectives

- Data compilation and analysis of historic Rand Water quality datasets along the Blesbokspruit. The datasets are specific to upstream and downstream datapoints of the new Eastern Basin AMD Treatment Plant and the Marievale Bird Sanctuary. Monthly ground truth sampling of water along the Blesbokspruit system. Ground truth sample points are also focused specifically at points which are upstream and downstream of both the Eastern Basin AMD treatment plant and the Marievale Bird Sanctuary.
- Sampling of soils within Marievale bird sanctuary to quantify soil pH and soil conductivity. This is a spatial assessment of the current soil pH and soil conductivity and can be used as a baseline for future changes.
- Sampling of river sediments along the Blesbokspruit system and wetland, this is to determine whether toxic heavy metals have been deposited in the sediments of the wetland.

4. Literature review

4.1 Background information of AMD pollution within South Africa

The Witwatersrand Basin is made up of the East, Central and West Rand basins, and is famous for its outstanding gold, coal and uranium deposits (McCarthy, 2011). Mining in the basin began in late eighteen hundred, but most of the mines on the East Rand are currently inactive, closed or abandoned (McCarthy, 2011). The Witwatersrand rocks contain varying proportions of sulphide minerals, the major mineral being pyrite and other base metal sulphides that contain metals of iron, nickel, lead, copper, cobalt and arsenic. Radioactive uranium occurs within the leachable oxides within the reef (Robb and Meyer, 1995). AMD is a well understood process; it occurs when pyrite comes into contact with oxygenated water. The pyrite undergoes oxidation in a two-stage process, the first producing sulphuric acid and ferrous sulphate, and the second process producing orange-red ferric hydroxide and more sulphuric acid (McCarthy, 2011).

The generalized overall chemical equation: $4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3 + 8\text{H}_2\text{SO}_4$ (1) (Garland, 2011). This acidic water is able to dissolve toxic heavy metals within the reef (McCarthy, 2011). Consequently, groundwater movement through the mineral reef has high levels of sulphate and heavy metals, and subsequent effluent pumping of groundwater results in the dumping and distribution of heavy metals in the surface water system (Robb and Meyer, 1995; McCarthy, 2011). Grootvlei Gold Mine was one of the largescale working mines in the area that regularly dewatered underground workings and disposed of the effluent in the Blesbokspruit (Roychoudhury and Starke, 2006). The Blesbokspruit, a former Ramsar certified wetland site, had been directly contaminated with AMD metal pollution produced from mine operations in the area. In 1996, the wetland was put on the Montreux Record List of Wetlands of International Importance due to the uncontrolled disposal of untreated mine effluent (Roychoudhury and Starke, 2006). Since being placed on the record, the disposal of treated mine effluent has been closely regulated and monitored (Roychoudhury and Starke, 2006).

Mining in the East Rand basin has produced a significant amount of sand and rock piles in mine dumps on the ground surface, and back-fill rock piles underground (McCarthy, 2011). Apart from the direct route of groundwater movement and effluent pumping, heavy metals are also introduced into the surface water system from water seepage through these mine dumps as well as via atmospheric fallout of fine particulates from the large-scale mine dams (McCarthy, 2011). Specific to the Blesbokspruit, this contamination is made worse as metals are also introduced nearby by sources other than mining. The stream flows through multiple settlements and industrial areas before it passes through the wetland (Roychoudhury and Starke, 2006). Once introduced into the aquatic environment, heavy metals cannot be degraded and they accumulate in sediments (Schulin et al., 1995). Over time, chemical reactions may occur which effect heavy metal toxicity and bioavailability. With continued accumulation, metal concentration in the sediment often exceed environmental thresholds causing acute toxicity levels (Schulin et al., 1995). To add, often biogeochemical conditions can easily change in aquatic environments causing the stored trace metals to remobilise. This makes the metal-rich sediment a potential long-term source of pollution from where the metals can move along the food chain causing toxicity among living organisms (Schulin et al., 1995). The situation of Blesbokspruit is of growing concern as the poor water quality has impacted on the freshwater resources in the area and downstream of the Blesbokspruit. The Blesbokspruit is a tributary of the greater Vaal river system which provides essential drinking water to the people of Gauteng province (Roychoudhury and Starke, 2006).

4.2 Previous studies conducted along the Blesbokspuit

In a study conducted by Roychoudhury and Starke (2006), a suite of heavy metals was analysed in sediment samples from the Blesbokspuit wetland area to assess the impact of mining on the sediment quality. Gold and silver were identified as being the most enriched metals in the sediment and ranged by an enrichment factor of 20–400 compared to the surrounding region (Roychoudhury and Starke, 2006). Significant enrichment of uranium, mercury, vanadium, chromium, cobalt, copper and zinc was also observed in the sediments (Roychoudhury and Starke, 2006). The calculated geo-accumulation indices suggest that the sediments are very lightly to lightly polluted with respect to most heavy metals and highly polluted with respect to gold and silver. The highest metal pollution index values were found at sites that were close to mine dumps (Roychoudhury and Starke, 2006). Sediment eco-toxicity was also calculated during the research process and results determine that the sediments in the study area have low to moderate potential for eco-toxicity (Roychoudhury and Starke, 2006).

In a more recent paper by Ambani and Annegarn (2015), monthly historical water quality records from 2000 to 2011 were examined within the Blesbokspuit Wetland. Three separate Rand Water historical sites were chosen; site B5 at the stream inflow to the wetland, site B16 just after the discharge point of pumped underground mine-water at Grootvlei Mine Shaft No. 3, and site B11 at the stream outflow from the designated wetland area (Ambani and Annegarn, 2015). The study provided evidence that surface water quality (for parameters pH, electric conductivity, sulphate, sodium, chlorine and magnesium) followed distinct spatial patterns from the inlet, past the underground mine-water discharge point to the outlet of the Blesbokspuit wetland (Ambani and Annegarn, 2015). Values for pH had a narrow range of 6.7 to 8.5, a neutral to basic tendency which is uncommon for AMD water. AMD water is also expected to have high levels of electric conductivity, but the results of this paper reveal that only part of the electric conductivity is attributable to AMD processes. The high levels of electric conductivity were attributed to high sodium and chlorine concentrations and the source was determined to be from an upstream industrial paper pulping plant (Ambani and Annegarn, 2015). Seasonally, the highest levels of conductivity occurred during the dry periods. During these periods rainwater and surface runoff were low and could not dilute contaminated stream discharges (Ambani and Annegarn, 2015). As mentioned, the water quality issue within the wetland is described as having high conductivity rather than low pH. This was seen during the pumping of underground mine-water, and after the pumping terminated at Grootvlei Mine Shaft No. 3 in December 2010. The decommissioning of the paper pulping plant coincided with the termination of pumping at Grootvlei Mine from December 2010 to January 2011. Coincidentally, during this time there was a large reduction in conductivity from upstream industries and mining (Ambani and Annegarn, 2015).

In a study centred around biomonitoring, metal concentrations within selected organs and tissues of five Red-knobbed Coot (*Fulica Cristata*) populations were examined (Van Eeden, 2003). The aim of this investigation was to determine whether these birds can accumulate metals from their surrounding habitat, and therefore be able to reflect upon the geographical trends of their population area (Van Eeden, 2003). One such population originated from the Marievale Wetland and it was discovered that there was cadmium, copper, nickel and lead metal contamination found within kidney, bone, blood and liver samples of the bird species (Van Eeden, 2003). The results from the study suggest that the Red-knobbed Coots collected from the five localities within the Gauteng

province were most likely exposed to chronic low levels of metal toxicity (Van Eeden, 2003). The metal-containing diets that these birds were exposed to are believed to have originated from anthropogenic sources such as mining waste dumps, industry, sewerage works, agriculture and residential areas (Van Eeden, 2003). Although this master's dissertation does not make use of biomonitoring, the sediment and water pollution data obtained from this study can be used to infer whether the animal life (predominantly birdlife) along the Blesbokspruit is under threat of being exposed to toxic metal pollution.

In a recent paper by Humphries et al. (2017), a wetland exposed to mining operations and increased levels of metal pollution was identified as being able to sequester metals from polluted water. The results suggested that, through multiple mechanisms, wetlands play a crucial role in reducing metal contamination within AMD polluted environments (Humphries et al., 2017). The study confirmed the effectiveness of wetland ecosystem services linked to improved water quality (Humphries *et al.*, 2017). The common wetland plants that dominate in the reed beds along the Blesbokspruit are *Typha* and *Phragmites* vegetation, which are both well known for their efficiency in removing heavy metals from polluted water (Roychoudhury and Starke, 2005; Kumari and Tripathi, 2015). However, there is speculation on the positive influence of these common wetland plants, specifically within the Blesbokspruit wetland.

In a technical report written by McKay et al. (2018), the importance of these common wetland plants was discussed. The report mentions that excessive nutrients within the Blesbokspruit have promoted the growth of *Phragmites australis* and *Typha capensis* (McKay et al., 2018). Both these common reeds flourish in unfavourable conditions. These unfavourable conditions include anaerobic and disturbed soils, anthropogenic influences such as AMD water pollution and high concentrations of heavy metals (McKay et al., 2018). These plants are considered highly invasive due to their resistance to unfavourable conditions as well as rapid colonization and domination over other aquatic plants. Invasion of these plants is associated with reduced biodiversity and these plants present significant challenges to wetland ecosystems as a whole (McKay et al., 2018). One of the objectives of the technical report was to calculate the changes in the open water area seen at Marievale Bird Sanctuary from 2002 to 2013 (McKay et al., 2018). A total close to nine hectares (11%) of open water was lost, and this was attributed mainly due to the dominance of these two common reeds in the area (McKay et al., 2018). The report mentions that reed spraying in the area is inconsistent, and measures need to be put in place to prevent *Phragmites australis* and *Typha capensis* from continual domination of open water bodies (McKay et al., 2018). As Marievale Bird Sanctuary is a highly important refuge to waterfowl, these reed beds need to be maintained in order to keep the birdlife from migrating to other water bodies in surrounding areas (McKay et al., 2018). The area of open water is also reduced during months of drought and this may force birds to migrate permanently, causing damaging consequences to the Marievale Bird Sanctuary tourist attraction (McKay et al., 2018).

4.3 The Eastern Basin AMD chemical treatment plant in Springs

Construction of the AMD Eastern Basin treatment plant began in June 2014 and the plant was completed in August 2016 (Kruger, 2017; Solomons, 2017). The plant has been operational since its completion which was extremely necessary at the time. During that time, the abandoned Grootvlei mine was being flooded and there was a huge potential that AMD water would decant into the

surrounding Blesbokspruit Wetland (Kruger, 2017; Solomons, 2017). The R1 billion plant, which is the largest of its kind in the world, has the capacity to pump 108 ML of water per day to mitigate against the pollution of underground water sources (DWS, 2017). The plant is part of the short-term solution (phase one) of the Witwatersrand Goldfields that is aimed at preventing decant in the Western Basin and breaching of the environmental critical level in the Central and Eastern Basins (DWS, 2017). The environmental critical level is the water level in mine voids at the critical location which needs to be maintained and not allowed to rise in order to protect the environment, including groundwater resources (Department of Water Affairs, 2012). The areas at risk are those that have the lowest elevations near the mine voids (Department of Water Affairs, 2012).

Speaking at the official launch in February 2017, the former Minister of the Department of Water and Sanitation (DWS), Ms Nomvula Mokonyane mentioned that over the last six years, working with the Trans Caledon Tunnel Authority (TCTA), the DWS has successfully initiated and implemented successful short-term interventions within the three basins, which have paved the way for the long-term solutions (DWS, 2017). The short - and long-term solutions to AMD are expected to cost R10-12 billion which will be funded by the state, mining sector and water users. The long-term (phase two) solution involves the use of desalination processes such as reverse osmosis to reduce salinity in the water (DWS, 2017). Mokonyane mentioned that the treatment of AMD water is part of government's plan to secure Gauteng's future water resources for the next 30 years (DWS, 2017). The short-term plan makes use of lime to firstly neutralise the water and thereafter remove the toxic metals that precipitate out of the solution (McCarthy, 2011). Although this treatment has its benefits, it does not solve the problem entirely; this process leads to increased conductivity as well as high concentrations of sulphate left behind in the water (McCarthy, 2011). Being operational since August 2016, media reports have stated that the plant is successfully reducing AMD within the mine shaft by reducing iron and manganese concentrations and raising the pH of the water that is discharged from the plant (Kruger, 2017). This would indeed be beneficial to the Blesbokspruit, but the very recent launch of the treatment plant has meant that there is no scientific evidence/literature published on the plant. However, within multiple media reports there have been highly controversial reviews of what the treatment plant is actually able to produce in terms of reducing AMD pollution in the area.

4.4 Mixed media reports of the Eastern Basin AMD chemical treatment plant

In an interview by the AMD Eastern Basin treatment plant manager for *Mining Weekly Online*, the manager described the inner workings and processes of the treatment plant. He mentioned that the plant runs 24 hours per day and is running at 85% of its 108 ML per day capacity, treating 94 ML per day of AMD from the old Grootvlei No. 1 shaft (Solomons, 2017). This shaft has a depth of 1 km and three heavy duty pumps (150m deep) are pumping out the AMD water to the surface. He explained that the AMD water is transferred to a splitter box and is separated across three reactor circuits, which include pre-neutralisation, neutralisation and gypsum crystallisation. The plant consumes an average of 35 tonnes of lime and 500 kg of polymer per day. From the splitter box, the water is put into large diameter tanks where the water is clarified using thickeners to be discharged at a later stage (Solomons, 2017). From the thickeners section of the plant, a clean overflow and a low-quality underflow is produced, this low-quality water is recycled back into the plant for processing purposes and the precipitated metal-containing "sludge" is re-injected and disposed down shaft 1 to a depth of 700 meters below the surface (Solomons, 2017). Currently the clean overflow that the plant

produces is not potable; a second treatment phase (phase two) to produce potable water has been awarded but has not started as yet (Solomons, 2017). The plant manager also mentioned that the AMD water had a pH of 6.2 and an iron content of roughly 115 mg/L, and after being treated the pH increased to 8.8 and the iron content decreased to 0.1 mg/L. However, the treated water the plant releases has a high salinity of 1100 mg/L (Solomons, 2017). The treated water contains aluminium concentrations at levels lower than laboratory detection levels and to date the biweekly tests had detected zero traces of radioactive uranium according to the plant manager (Solomons, 2017). He mentioned that if pumping were to stop, it would take only 3 weeks for the toxic water to decant onto the surface. In his opinion, the ground water level needs to remain 120 m below surface to ensure that the ground water flow decants into the mine shafts and not into the surrounding low-lying areas of the Eastern Basin causing potential environmental damage (Solomons, 2017).

The following figure describes the originally proposed process flow diagram for the treatment and transportation of high-density sludge (HDS) for disposal:

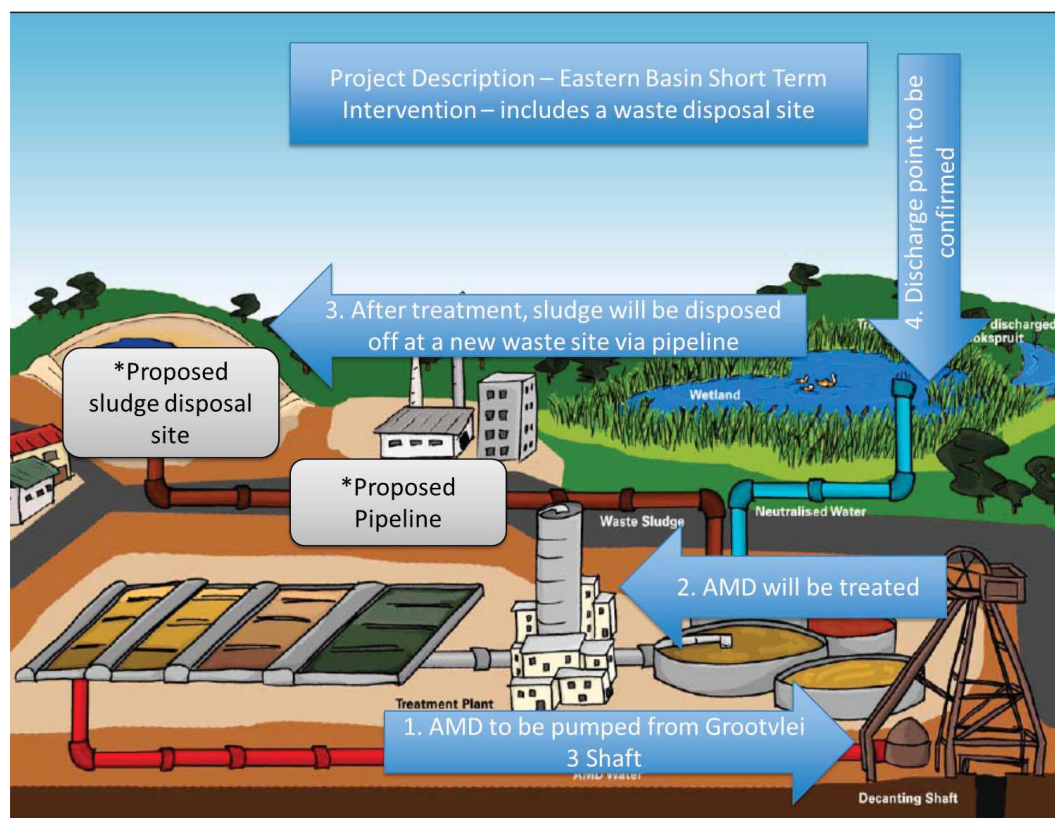


Figure 3: Originally proposed process flow diagram for the treatment and transportation of high-density sludge for disposal. Figure obtained from the Digby Wells EIA for the construction of the originally proposed sludge disposal facility and pipeline associated with the Eastern Basin AMD Treatment Plant. Available online from: https://sahris.sahra.org.za/sites/default/files/additionaldocs/AEC2588_Draft_Scoping_Report_Draft_Public_Review.pdf

The figure above indicates that the high-density sludge will be disposed of at an external site, but as mentioned by the plant manager: the sludge is re-injected and disposed of down shaft 1 to a depth of 700 meters (Solomons, 2017). There is criticism in this as the EIA original flow diagram above does not account for sludge to be disposed down shaft 1. Although being disposed 700 meters below surface, the high-density sludge is not entirely eliminated and has the potential to impact the

environment, especially through ground water movement (Bega, 2017). Figure 2 below is a photograph taken of the lime thickener tanks at the Eastern Basin AMD treatment plant.



Figure 4: The lime thickener tanks at the new Eastern Basin AMD Treatment Plant, the wetland can be seen behind the treatment plant in the background. Photo taken by Professor C. Curtis in 2017.

In a short article written by the Federation for Sustainable Environment, a consulting mining hydrologist described that the DWS has used a R1 billion “sledgehammer” to fix the highly dangerous and complicated situation within the Eastern Basin (Bega, 2017). The “sledgehammer approach” involves pumping that reduces the water table to 120 meters below the surface, and in her opinion, this exposes more pyritic rich rock to oxygen and water and increases the potential for even more environmental damage (Bega, 2017). This directly contradicts the opinion of the treatment plant manager. Another critique by the mining hydrologist is that the plant is not actually treating the water to a better state. The water cannot be used for human consumption and is toxic to the environment (Bega, 2017). In her opinion, large sums of money are being used to purchase expensive lime that is used to raise the pH level of the water, and the metals that precipitate out as sludge are disposed underground which could easily pollute groundwater within the Eastern Basin (Bega, 2017). She recommends that a more effective solution would be to closely monitor the entire area, and rather treat the water at each decant point and remove all the valuable metals and sulphates for resale (Bega, 2017). Within the same article, an attorney who represents the communities of Springs, is highly concerned due to the Blesbokspruit being in close proximity to the suburb of Strubenvale. He mentioned that the possibility of flooding in the area has a high potential of causing devastating mobilisation of toxic metals to both the communities and the surrounding environment which includes the Marievale Bird Sanctuary (Bega, 2017).

4.5 Historical and current data for the Blesbokspuit

The historical and current data are made available from *The Reservoir* website. This is a water resource information centre for the catchment forums that operate within the Vaal Barrage and Vaal Dam catchment of the Upper Vaal Water Management Agency (Reservoir, 2018). The data from this website includes the Blesbokspuit Catchment and water quality reports from the Department of Water and Sanitation, Rand Water and Ekurhuleni are made available online on a quarterly basis (Reservoir, 2018). What is of interest is to determine whether the introduction of the Eastern Basin AMD treatment plant in August 2016 has had a positive influence on water quality downstream. Making use of the historical data helps determine what influence the treatment plant has had downstream along the Blesbokspuit. An example of the water quality report from Rand Water is as follows:

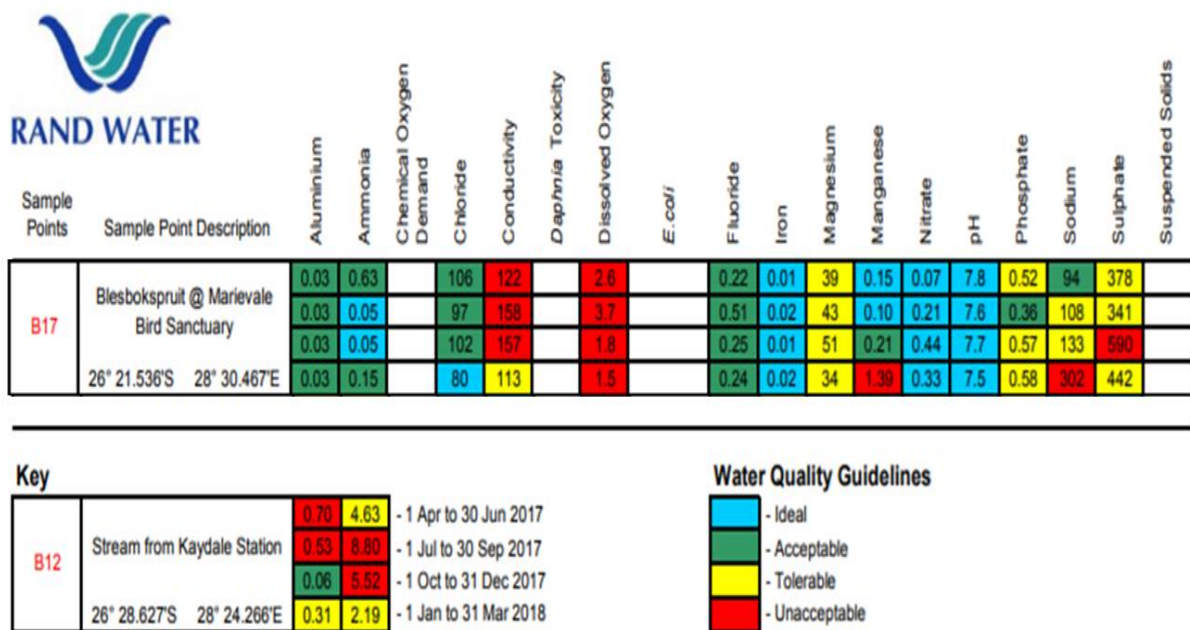


Figure 5: Rand Water quality report for the Blesbokspuit at Marievale Bird Sanctuary from 01 April 2017 - 31 March 2018. Available online from: http://www.reservoir.co.za/forums/vaalbarrage/blesbok_forum/blesbok_reports/current/RW_Blesbok_Jan-Mar2018.pdf

The water quality report above provides essential data that has been made of use for this research project. The water quality parameters include metals such as iron and manganese, sulphate content, conductivity and pH, which are the water quality parameters needed to determine the impact of AMD pollution within the area (McCarthy, 2011). The units for each of these parameters are given in the in-stream water quality guidelines section on the following page. The sample points are also given with GPS coordinates and these are used to determine the water quality along the entire river system in the catchment. Of all the data that are made available, the Rand Water quality reports are the most complete and comprehensive, and these are used for the purpose of this research.

4.5.1 In-stream water quality guidelines

In-stream Water Quality Guidelines for the Blesbokspruit Catchment			Effective: June 2003		
Variables	Measured as	Ideal Catchment Background	Acceptable Management Target	Tolerable Interim Target	Unacceptable
Physical					
Conductivity	mS/m	< 45	45 - 70	70 - 120	> 120
Dissolved Oxygen (Q)	mg/l O ₂		> 6.0	5.0 - 6.0	< 5.0
pH	pH units	6.5 - 8.5			< 6.5; > 8.5
Suspended Solids	mg/l	< 20	20 - 30	30 - 55	> 55
Organic					
Chemical Oxygen Demand (COD)	mg/l	< 20	20 - 35	35 - 55	> 55
Macro Elements					
Aluminium (Al)	mg/l		< 0.3	0.3 - 0.5	> 0.5
Ammonia (NH ₄)	mg/l	< 0.1	0.1 - 1.5	1.5 - 5.0	> 5.0
Chloride (Cl)	mg/l	< 80	80 - 150	150 - 200	> 200
Fluoride (F)	mg/l	< 0.19	0.19 - 0.70	0.70 - 1.00	> 1.00
Iron (Fe)	mg/l	< 0.1	0.1 - 0.5	0.5 - 1.0	> 1.0
Magnesium (Mg)	mg/l	< 8	8 - 30	30 - 70	> 70
Manganese (Mn)	mg/l	< 0.2	0.2 - 0.5	0.5 - 1.0	> 1.0
Nitrate (NO ₃)	mg/l	< 0.5	0.5 - 3.0	3.0 - 6.0	> 6.0
Phosphate (PO ₄)	mg/l	< 0.2	0.2 - 0.4	0.4 - 0.6	> 0.6
Sodium (Na)	mg/l	< 70	70 - 100	100 - 150	> 150
Sulphate (SO ₄)	mg/l	< 150	150 - 300	300 - 500	> 500

Figure 6: In-stream water quality guidelines for the Blesbokspruit Catchment (Effective: June 2003). Available online from http://www.reservoir.co.za/forums/vaalbarrage/blesbok_forum/blesbok_documents/BF_WQGGuidelines.pdf

The above water quality guidelines are used as an indication of the raw/ in-stream water quality specifically within the Blesbokspruit Catchment. Water quality parameters are described as ideal, acceptable, tolerable and unacceptable for each water quality parameter as seen above. These guidelines have value in that they are unique to the Blesbokspruit raw water quality management targets set out by the Blesbokspruit Forum (Reservoir, 2018). However, the guidelines are limited in that they are far less strict than those of the standard water quality guidelines set out by the Department of Water and Sanitation for Aquatic Ecosystems (DWAf, 1996; McKay et al., 2018). These guidelines have been altered due to the mining and industrial processes occurring along the Blesbokspruit (McKay et al., 2018). The Blesbokspruit can therefore be described as a hard-working river, whereby the ecosystem services provided by the stream help meet the reserve (McKay et al., 2018). The reserve is defined as the quality and quantity of water required to meet basic human needs and to protect aquatic ecosystems (Claassen, 2010). The concept of the reserve is controversial in that aquatic ecosystems (ecological reserve) are often overlooked compared to human needs (human needs reserve) (van Wyk *et al.*, 2006). Considering that the ecosystem itself sustains and provides for basic human needs, sufficient water of a high quality is needed for a sustainable future (Claassen, 2010). Another limitation is that these guidelines are for raw water and not drinking water.

The Blesbokspruit is a tributary to the Vaal system which provides drinking water to the people of Gauteng (Roychoudhury and Starke, 2005). Domestic drinking water quality guidelines set out by the Department of Water Affairs are highly comprehensive and detailed with many water quality parameters beyond the scope of this master's dissertation (DWAf, 1996). Considering this, and that the Blesbokspruit is not used directly for domestic drinking purposes, the raw water quality guidelines set out by the Blesbokspruit Forum are those used as a determination for water quality

for this research. The Blesbokspruit Forum promotes the aims of the National Water Act (Act 36 of 1998) and the role players include government departments, non-governmental organisations, mines, industries water users and the general population (Reservoir, 2018). Although the historical and available data is comprehensive and detailed, sample points along the Blesbokspruit used by Rand Water are spread widely apart to cover the entire catchment area. This research project is primarily focused on the areas around the Eastern Basin AMD treatment plant and Marievale Bird Sanctuary Wetland. Therefore, more samples around these areas have been collected from the field to add to the historical data that is currently available. This year-long monthly collection of samples adds value to the research as it provides ground truth data and accounts for seasonal changes in water quality within the Blesbokspruit. The water quality parameters listed in the table above will be explained in terms of possible pollution sources as well as impact on aquatic ecosystems.

4.6 Water quality parameters

4.6.1 Physical water quality parameters

4.6.1.1 Conductivity

Conductivity is a measure of the water's ability to pass an electric current (Light *et al.*, 2005). This is directly linked to the concentration of conductive ions within the water. These ions/electrolytes come from dissolved salts and inorganic compounds such as alkalis, chlorides, sulphides and carbonates (Light *et al.*, 2005). There is a direct relationship between the number of ions and conductivity; the more ions that are present, the higher the conductivity. Conductivity is measured in millisiemens per metre which is standard for freshwater systems (Light *et al.*, 2005). High levels of conductivity are usually as a result of pollution in the area (Akcil and Koldas, 2006). Natural causes such as excessive rainfall or drought can also lead to high conductivity values (Akcil and Koldas, 2006). Most aquatic species have evolved in environments with specific conductivity levels. Conductivity levels outside of the normal range can be damaging to the aquatic life within the water. As a result, only hardier species may be able to survive in environments with high conductivity levels (Ochieng, 2010). With reference to the Blesbokspruit, conductivity levels are hypothesised to increase due to the way in which water is treated at the Eastern Basin AMD treatment plant. The use of lime to neutralise AMD water is hypothesised to lead to increased salinity in the water, which directly impacts on conductivity as more dissolved ions are introduced into the water (McCarthy, 2011).

4.6.1.2 pH

pH is a measure of the concentration of protons (H^+) in a solution (Akcil and Koldas, 2006). The pH scale indicates either acidity or alkalinity of water-soluble substances. The pH scale is numbered from 1 to 14, the pH of pure water has a value of 7, water with a pH value lower than 7 is considered acidic and water with a pH value higher than 7 is considered alkaline (Akcil and Koldas, 2006). This is not a linear scale, but rather a logarithmic scale which means that two adjacent values of pH increase or decrease by a factor of 10. The normal pH range of freshwater systems is between 6.5 and 8.5, which is ideal for most aquatic animals and plants (Akcil and Koldas, 2006). In a typical AMD environment water is acidic. Acidic water has the potential to dissolve toxic heavy metals and this could result in the water containing elevated levels of iron, cobalt, lead, manganese, aluminium and magnesium (Akcil and Koldas, 2006). Specifically, in the Blesbokspruit, the recent paper by Ambani

and Annegarn (2015) concluded that over the period 2000-2011, pH values for all the sampling locations had a range of 6.7-8.8 which suggests a neutral to alkaline pH level. The seasonal variation of pH was also not highly variable, and this was attributed to both the naturally alkaline geology of the area as well as the treatment process of mine waste whereby lime is added to the wastewater to raise the pH level towards neutral/alkaline (Ambani and Annegarn, 2015). This indicates that AMD water was already being treated at the Grootvlei mine before the Eastern Basin AMD Treatment plant came into operation.

4.6.1.3 Dissolved oxygen

Dissolved oxygen, measured in milligrams per litre (mg/L), refers to the level of free oxygen present in water (Chislock et al., 2013). It is an important water quality parameter due to its direct influence on the aquatic organisms within the water. A dissolved oxygen level that is too high or too low can harm aquatic life and affect water quality (Oberholster, 2010). Dissolved oxygen is necessary to many forms of life including fish, invertebrates, bacteria and plants. The amount of dissolved oxygen required varies between species; bottom feeders, crabs and worms need minimal amounts of oxygen (1-6 mg/L), while shallow water fish need higher levels (4-15 mg/L) (Oberholster, 2010). The level of free oxygen is naturally maintained either through diffusion of oxygen rich air from the surrounding atmosphere into the water or can be produced as a result of photosynthesis from aquatic plants (Chislock et al., 2013). Diffusion of oxygen into the water is also promoted by increased flow rates (Chislock et al., 2013). Dissolved oxygen levels can alter due to the process of eutrophication. Eutrophication is a process whereby freshwater systems become laden with nutrients (Chislock et al., 2013). Sources of excess nutrients include agricultural runoff, over-use of synthetic fertilizers, septic tank or sewage leaks, and erosion (Oberholster, 2010). When this occurs, large blooms of algae and aquatic plants thrive as they are fed with excess phosphorous and nitrogen (Oberholster, 2010). When the algae and aquatic plants die, micro-organisms in the water start feeding on the organic remains as part of the decomposition process. Consequently, the decomposition process uses up the available oxygen in the water. This leaves little dissolved oxygen for fish and other aquatic animals, resulting in possible suffocation and death of aquatic life (Oberholster, 2010).

4.6.2 Major Ions

4.6.2.1 Aluminium (Al)

Although aluminium is commonly found throughout the earth, high concentrations can lead to serious health problems within aquatic ecosystems (Poléo et al., 1997). The water-soluble form of aluminium such as aluminium chloride and other ions are those that cause harm to both humans and the environment (Poléo et al., 1997; Exley, C., 2013.). Toxic aluminium is often found in mining and industrial areas where aluminium is used during production processes (Exley, 2013). In the environment, aluminium rich water has proven to have devastating consequences on fish populations (Poléo et al., 1997). Fish and other aquatic organisms such as amphibians and crayfish population numbers decline due to reactions of aluminium ions with proteins in the gills of fish and frog embryos (Alexopoulos et al., 2003). Consequently, birds that eat the contaminated fish and amphibians also suffer. Bird eggshells become extremely thin and brittle and newly born chicks are underdeveloped (Alexopoulos et al., 2003).

4.6.2.2 Ammonium (NH₄⁺)

There are numerous forms of nitrogen that occur within aquatic environments, one such is ammonium. Ammonium is different to most forms of nitrogen in that high concentrations cause a

direct toxic effect on aquatic life (US EPA, 2013). This form of nitrogen also provides excess nutrients within a water body and indirectly affect aquatic life through the process eutrophication (US EPA, 2013). Anthropogenic sources of ammonium include its production for commercial fertilizers and from sewage and industrial discharges (DWAF, 1996). Natural sources of ammonium include the decomposition or breakdown of organic waste matter, gas exchange with the atmosphere, forest fires and from animal and human waste (US EPA, 2013). When ammonium is present in water at high enough levels, it is difficult for aquatic organisms to sufficiently excrete the toxic substance. This leads to toxic build up (bioaccumulation) in the internal tissues and blood, and potentially death (US EPA, 2013).

4.6.2.3 Chloride (Cl⁻)

Chloride is highly reactive in nature and reacts with other elements once in air and water forming compounds (Henschler, 1994). It reacts with inorganic matter in water to form chloride salts, for example, with sodium to form table salt which is nontoxic. When chloride reacts with organic matter in water to form what are known as chlorinated organic compounds, these are very harmful to organisms living in water and in soil (Henschler, 1994). These compounds have been highly documented for toxicity within the literature. General conclusions have been made on the compounds; many of these are toxic to humans and the environment. More and more of these compounds are shown as being carcinogenic and mutagenic (Henschler, 1994). Many of these compounds are highly stable and accumulate in the environment, affecting humans through the food chain. Important examples of these compounds include chlorinated pesticides such as the highly documented DDT (Dichlorodiphenyltrichloroethane), biphenyls, dibenzodioxins and dibenzofurans (Henschler, 1994). These compounds and chloride levels are high risk to the environment.

4.6.2.4 Fluoride (F⁻)

In a review of fluoride toxicity to aquatic organisms by Camargo (2003), fluoride pollution is described as being more likely to effect aquatic organisms living in soft waters (water with little dissolved minerals/salts) than those living in hard (water that contains a high quantity of dissolved minerals/salts) or seawater (Camargo, 2003). This is due to fluoride ions having reduced concentrations with increasing water hardness (Camargo, 2003). In aquatic organisms, fluoride accumulates on the exoskeleton of invertebrates and in the bone tissue of fish. Fluoride is toxic in that it acts as an enzymatic poison which inhibits enzyme activity and interrupts metabolic processes (Camargo, 2003). Increasing fluoride concentration, exposure time and water temperature increases toxicity levels in aquatic ecosystems. Fluoride toxicity is offset by increased animal body size as well as increases in calcium and chloride levels (Camargo, 2003). Some aquatic plants are also effective in reducing fluoride concentrations from polluted water. Due to increased fluoride availability in soft waters with low ionic content, a fluoride concentration as low as 0.5 mg/L can cause harmful effects on aquatic invertebrates and fish (Camargo, 2003).

4.6.2.5 Iron (Fe)

Iron is a highly common element and an important component in soils and rocks. Iron in water may be present in variable quantities due to the surrounding regional geology (DWAF, 1996). It is an essential trace element for dietary requirements for all vertebrate and some invertebrate animals. Iron in the body is used an important oxygen transport mechanism that occurs within the haemoglobin in the blood of animals (DWAF, 1996). It is also a limiting factor for the growth of plants and algae (Zaw and Chiswell, 1999). Fe²⁺ and Fe³⁺ are of concern in the aquatic environment as these persist in waters with low levels of dissolved oxygen. Oxidized Fe³⁺ cannot be consumed by

organisms either, except at very low pH values (Zaw and Chiswell, 1999). However, iron is an essential element for life and only poisonous in extreme concentrations (Zaw and Chiswell, 1999).

4.6.2.6 Magnesium (Mg)

Magnesium, similar to iron, is an essential mineral used by all organisms except insects, and is also required for plant photosynthesis (DWAF, 1996). Magnesium is found in fresh and saltwater and is spread naturally throughout the environment. Magnesium does not negatively affect human and animal health and can only be poisonous in extreme concentrations (DWAF, 1996). Magnesium and other alkali earth metals are responsible for water hardness. The environmental issues indirectly caused by magnesium are due to softeners being applied to hard, magnesium rich water (DWAF, 1996). In the past, phosphates were used as softeners, but these were discovered to cause eutrophication and are difficult to biodegrade (DWAF, 1996). In the present day, softeners used include synthetic chemicals that do not cause eutrophication and are not toxic. However, some of these synthetic chemicals are difficult to remove through water purification and can persist in the water cycle (DWAF, 1996).

4.6.2.7 Manganese (Mn)

Manganese and manganese compounds exist naturally in the environment as solids in soils and small particles in water. Anthropogenic sources of manganese include industrial pollution, the use of manganese pesticides and burning of fossil fuels (DWAF, 1996). Through these sources, manganese can enter surface water, groundwater and soil. For animals, manganese is an essential component of enzymes that are used for the carbohydrate, protein and fat metabolism (DWAF, 1996). Therefore, too little intake of manganese will lead to growth, bone formation and reproduction deficiencies (DWAF, 1996). However, if essential manganese doses are exceeded, the lethal dose of manganese can be quite low for some animals meaning that natural levels are needed for optimum growth and survival of animals (DWAF, 1996). Manganese and manganese substances can be toxic in high concentration as they cause brain, lung, liver, reproductive and vascular problems leading to tumour development in animals (DWAF, 1996). Manganese can cause both toxicity and deficiency symptoms in plants as well. Between toxic concentrations and concentrations that cause deficiencies, a small area of manganese concentration is needed for optimal animal and plant growth (DWAF, 1996).

4.6.2.8 Nitrate (NO_3^-) and Phosphate (PO_4^{3-})

Nitrate, along with ammonium mentioned previously, are reactive and biologically available forms of nitrogen. Nitrogen is an essential dietary requirement for all plants and animals. Although elementary nitrogen gas takes up a large portion of air, it cannot be taken up directly by organisms (Gilbert *et al.*, 2005). Nitrogen is bound and converted to nitrate by bacteria within soils through the process of nitrification. This process releases energy and adds nitrate to soils that can then be used by plants for growth (Gilbert *et al.*, 2005). Phosphorous can be found in the environment most commonly as phosphates. Phosphorus is an essential nutrient for plants and animals. Anthropogenic influences have changed the natural nitrate and phosphate supply (Chislock *et al.*, 2013). These two nutrients are extensively used in agriculture as nitrate and phosphate (and ammonium) rich fertilizers are required for increased food production (Chislock *et al.*, 2013). When fertilizers are overused or applied outside the growing season, excess nutrients cannot be used and end up in freshwater ecosystems. This process eventually leads to eutrophication whereby freshwater systems become laden with nutrients as mentioned (Chislock *et al.*, 2013). When in deficient concentrations, nitrogen (nitrate and ammonium) levels can be limiting factors for growth in some cases. Phosphate is commonly the limiting factor for algal growth in water bodies (Gilbert *et al.*, 2005). Increasing phosphate concentrations in freshwater ecosystems increases the growth of organisms such as algae and duckweed, which are able to exploit excess phosphate (Gilbert *et al.*, 2005).

4.6.2.9 Sodium (Na)

Sodium compounds are naturally present in the environment and the water cycle, the most common being sodium chloride (table salt) (DWAF, 1996). Sodium compounds serve many different industrial purposes; they are used in metallurgy, applied as a synthetic fertilizer and used in the food industry as a preservative or flavouring agent (DWAF, 1996). Sodium carbonate is applied in water purification to neutralize acids and sodium hydrogen carbonate is used in soap and cleanser production. Sodium is a dietary mineral for animals and humans and is also present in drinking water (DWAF, 1996). Sodium is not considered to be toxic; mammals require sodium for nerve and muscle function as well as maintaining blood pressure levels (DWAF, 1996). Excess sodium can often lead to increased salt levels in the water which can become problematic to organisms that are sensitive to increased salinity (DWAF, 1996). Within an AMD environment, increased sodium levels are expected especially when considering the processes of wastewater treatment. Lime is used to neutralise acidic water, and this generates increased salinity within the treated water (McCarthy, 2011).

4.6.2.10 Sulphate (SO₄)

Sulphate is naturally present in water as some rocks and soils contain sulphate minerals. As groundwater and surface water moves through the rocks and soil, some of the sulphate is dissolved into the water (McCarthy, 2011). The issues surrounding the presence of sulphate within AMD environments have been mentioned; ores rich in sulphide oxidise and cause the chain reaction of AMD (McCarthy, 2011). Therefore, sulphate levels are elevated within these environments and the subsequent processes lead to devastating environmental damage (McCarthy, 2011). Sulphate can also become elevated in industrial areas as sulphur in coal/oil oxidises to sulphur dioxide (SO₂) when burnt. Sulphur dioxide gas then dissolves in rainwater, forming acid rain, which eventually enters into aquatic ecosystems (McCarthy, 2011). However, it is expected that the AMD contribution of sulphate levels are dominant within this study area. The main issue of sulphate surrounds the chemical reaction producing H₂SO₄ (sulphuric acid) during the process of sulphide oxidation (McCarthy, 2011). This process is responsible for AMD and all the issues surrounding AMD which have been mentioned. Sulphate levels within the Blesbokspruit are of high concern and importance.

4.7. River sediment quality - heavy metals

Any metallic element that is highly dense and is toxic at low concentrations is described as a heavy metal (Verma and Dwivedi, 2013). The 17 trace elements that are identified within river sediments in this study are: scandium, vanadium, chromium, cobalt, nickel, copper, zinc, gallium, rubidium, strontium, yttrium, zirconium, niobium, molybdenum, barium, lead, thorium and uranium. These trace elements have been identified using X-Ray fluorescence spectrometry and are measured mg/kg. This common technique is widely used within the literature as an effective way of identifying and quantifying heavy metals within sediments, soils and rocks (Weltje and Tjallingii, 2008). As mentioned, they cannot be degraded or destroyed and they can bioaccumulate, i.e., an increase in the concentration of a certain chemical compound within an organism (Verma and Dwivedi, 2013). The chemical compounds accumulate within the bodies of organisms such as birds and fish faster than they can be broken down/metabolized or excreted (Verma and Dwivedi, 2013). At higher concentrations heavy metals can be poisoning and cause catastrophic damage to the entire food web (Verma and Dwivedi, 2013). River sediments of the Blesbokspruit have been subject to heavy metal contamination over many years of mining activity. River sediment heavy metal analysis is an indication of the potential levels of heavy metal contamination moving downstream through the wetland system.

The most common toxic trace elements that originate from AMD environments within South Africa's gold fields include arsenic, aluminium, manganese, cobalt, copper, nickel, lead, uranium and zinc (McCarthy, 2011; Makgae, 2012). As mentioned, there was significant enrichment of uranium, mercury, vanadium, chromium, cobalt, copper and zinc observed in the sediments of the Blesbokspruit in the study conducted by Roychoudhury and Starke (2006). The highest enrichment factors of each element were also observed in areas near decant points as well as mine dumps (Roychoudhury and Starke 2006). As with the water quality parameters, the river sediment heavy metals will be explained in terms of possible pollution sources as well as impact on aquatic ecosystems.

4.7.1 Cobalt (Co) and copper (Cu)

Cobalt and copper both do not break down in the environment and therefore bioaccumulate. These two elements are enhanced in the environment through human activity such as mining, processing ores and chemical industry (DWAF, 1996). Soils and sediments near these processes are far more likely to accumulate cobalt and copper which can spread through the food chain (DWAF, 1996). Cobalt and copper generally mobilise under acidic conditions that occur during the process of AMD, however, they both generally end up in soil and sediments (DWAF, 1996). When in extreme concentrations, both these elements are extremely harmful to aquatic life and humans. High doses of cobalt have been described as being carcinogenic to aquatic life (DWAF, 1996).

4.7.2 Nickel (Ni) and lead (Pb)

Nickel, lead and the compounds associated with the two elements are toxic to the environment (DWAF, 1996). Although nickel is a dietary requirement for many organisms, it can be toxic in larger doses. Metallic nickel and some other nickel compounds are teratogenic and carcinogenic to mammals (DWAF, 1996). Lead salts and organic lead compounds are described as being extremely dangerous. Low concentrations of lead affect fish as they swim, soluble lead in water causes a mucous to form over the body of the fish and this eventually leads to suffocation and death (DWAF, 1996). If these heavy metals are not removed effectively from decant points and mine dumps, they persist and accumulate in organisms, sediments and water systems (DWAF, 1996).

4.7.3 Uranium (U):

Uranium cannot be found in elemental form within the environment due to its high reactivity (DWAF, 1996). Uranium is dangerous due to its radioactivity and the decay products such as radon gas are highly toxic (DWAF, 1996). Due to the high reactivity of uranium, it usually reacts with other elements and these uranium compounds dissolve in water (DWAF, 1996). Uranium can also occur in air as dust that has the potential to settle in areas far from pollution sources such as mines and mine dumps (McCarthy, 2011). The fallout of uranium dust is especially likely and damaging when mine dumps are unvegetated and near settlements (McCarthy, 2011). Uranium does not bioaccumulate in fish and other aquatic organisms due to its reactive nature; after it is absorbed it is eliminated effectively during waste excretion (DWAF, 1996).

4.7.4 Zinc (Zn):

Zinc is refined from rocks and ores and can enter aquatic ecosystems through erosion of zinc rich rocks or through industry (DWAF, 1996). The element occurs in two oxidation states, as zinc and as Zn^{2+} , and Zn^{2+} is toxic to fish and aquatic organisms at low concentrations (DWAF, 1996). The highest concentrations of zinc occur in waters that are acidic and highly conductive. Both soluble and insoluble zinc salts enter aquatic ecosystems through industrial activity (DWAF, 1996). Examples of common zinc salts include zinc chloride, zinc sulphate, zinc nitrate and zinc sulphide. High toxicity

levels are associated with these zinc salts, in particular, zinc chloride and zinc sulphate (DWAF, 1996).

4.8 Land Use:

Both the water and sediment quality involve physical and elemental parameters as mentioned. These parameters are influenced by the land use/ land cover of the surrounding region. Processes occurring in the surrounding region can impact negatively/ positively on both water and sediment quality and this has been explained for each parameter and macro element previously. Within the literature, the role of land use with regards to general water and environmental pollution has been well documented. It is evident that there are significant relationships between land use and water quality parameters such as nitrogen and phosphorous (Tong and Chen, 2002). Land which is mainly used for agriculture and residential areas influence and increase the amount of nitrogen and phosphorous within water (Tong and Chen, 2002). As mentioned, ammonium, nitrate (both forms of nitrogen) and phosphate (phosphorous) which are the water quality parameters specific to this study, are all heavily influenced by both agricultural and residential land use areas. Land use areas such as mine dumps and industrial areas have been identified as potential hotspots for heavy metal contamination mentioned previously (McCarthy, 2011). Land use/ land cover maps for the entire Blesbokspruit catchment have been created for the purpose of this research. The role of land use/ land cover with regards to both water and sediment quality will be evaluated and discussed in further chapters.

4.9 Sediment quality analysis

The methods used to calculate sediment quality have been adapted from the sediment quality indices used in the paper by Roychoudhury and Starke (2006). This paper has value in that the study was conducted along the Blesbokspruit over ten years ago. These calculations have been adapted from the paper so cannot be directly compared to results of the 2006 study but are useful in describing trace metal pollution along the Blesbokspruit. The following calculations will be used as a determination for sediment quality regarding trace metal contamination:

4.9.1 Enrichment factor (EF)

The EF is a ratio and is determined by dividing the amount of trace metal concentration (TMC) for the individual sample by the TMC of the background region (derived from the natural surrounding geology) in the following simple equation:

$$EF = \frac{TMC(sample)}{TMC(background)} \quad (2) \text{ Adapted from Roychoudhury and Starke, 2006.}$$

Note that the equation does not account for the concentration affected by the variation in mobility of different trace metals (Roychoudhury and Starke 2006). The background value acts as a target value that should be met after remediation of the site. An EF ratio (with respect to each metal and site) that is less than the value of 1 meets this target value and the sample is described as unpolluted. An EF value between 1 and 2 = very lightly polluted, EF between 2 and 3 = lightly polluted, EF between 3 and 4 = moderately polluted, EF between 4 and 5 = highly polluted and an EF greater than 5 = very highly polluted (Roychoudhury and Starke 2006).

4.9.2 Sediment environmental risk factor (SERF)

The SERF is also a ratio and is calculated to determine the ecological risk caused by metal pollution in the study area. The factor has been adapted from the 2006 paper and is calculated as follows:

$$SERF = \frac{TMC(sample)}{TMC(threshold)} \quad (3) \text{ Adapted from Roychoudhury and Starke (2006), where total metal concentration (TMC) threshold represents the concentration of when the specific trace metal}$$

becomes toxic to the environment. The SERF is similar to the enrichment factor calculation; however, the site values are compared to the threshold concentration and not the background concentration (target value) of the trace metal in the region. The threshold value therefore describes the need for human intervention/ remediation (Roychoudhury and Starke 2006). SERF values greater than 1, i.e. the sample value exceeds the threshold for eco-toxicity, suggest that remediation is required at the site. A SERF factor of 1.5 and over would suggest that the sediments have a high potential of being toxic to the environment and remediation is essential. A SERF factor between 0.5 and 1.5 is described as having a moderate potential for toxicity and human intervention would be recommended in the area (Roychoudhury and Starke 2006). SERF Values between 0.2 and 0.5 are described as having a low potential for toxicity and SERF values below 0.2 are described as having a very low potential for toxicity. There is a lack of specific guidelines for trace metal concentrations within South African wetlands, and the eco-toxicity threshold values and background values are those used in the Roychoudhury and Starke (2006) paper. The TMC threshold values are based on Dutch regulations for wetland trace metal remediation and the TMC background values are based on the average composition of the Vryheid Formation which is what the Blesbokspruit is currently eroding (Roychoudhury and Starke 2006).

4.9.3 Limitations in sediment quality analysis

The two sediment quality factors that have been calculated are limited. Although these simple factors provide an effective way of comparing the extent of pollution between different sites, the main limitation is that these factors do not account for multiple metal combinations (Roychoudhury and Starke 2006; Caeiro et al., 2005). Metals that occur together can cause changes to levels of toxicity experienced at the site, changes that cannot be accounted for by using these two factors (Caeiro et al., 2005). It is important to note that these two sediment quality factors are also limited in the sense that they only describe the potential for eco-toxicity and act as guidelines, and not specific toxicity to specific biota such as the bird/ fish species along the Blesbokspruit (Roychoudhury and Starke 2006).

4.10 Soil quality parameters:

4.10.1 Soil pH:

Soil pH is a measure of the acidity and alkalinity in soils. Just as the pH of water, soil pH levels range from 0 to 14, with 7 being neutral, below 7 being acidic and above 7 being alkaline (Akcil and Koldas, 2006). The optimal pH range for most plants is between 5.5 and 7.0 (Akcil and Koldas, 2006). Some plants have adapted outside this pH range but because pH levels control plant nutrient availability, pH levels need to be maintained near this range for optimal plant growth (Akcil and Koldas, 2006). In a study conducted by Naiker et al. (2003) regarding the Witwatersrand gold region, the research concluded that ground water within the mining area was extremely contaminated with heavy metals and highly acidic (Naiker et al., 2003). Where the water table was close to the surface, and in areas near mine dumps and decant points, the upper 20 cm of soil were highly acidic and contaminated with heavy metals (Naiker et al., 2003). The contamination and acidity are made worse through increased capillary action in the soil as well as evaporation over time (Naiker et al., 2003).

4.10.2 Soil electrical conductivity:

Soil electrical conductivity is a measurement of soil quality that directly influences crop productivity, soil texture, cation exchange capacity, organic matter level, salinity, and subsoil characteristics (Frempong and Yanful, 2006). Electrical conductivity represents the ability of an aqueous solution to carry an electric current and represents soil salinity (Light *et al.*, 2005). Within AMD environments, as mentioned, soil pH can be altered drastically as a result of acidic ground-

water movement (Naiker et al., 2003). The acidic nature of soils influence conductivity in that soil minerals such as dolomite, gibbsite, diaspore apatite are dissolved by the acidic ground water moving through the soil (Frempong and Yanful, 2006). This increases soil conductivity in areas exposed to AMD pollution. Some plants are detrimentally affected, both physically and chemically, by excess salts and high levels of exchangeable ions in soils (Frempong and Yanful, 2006).

4.11 Mechanisms by which wetlands purify waste waters containing heavy metals and excess nutrients

The literature shows that natural and artificial wetlands purify waste waters containing heavy metals and excess nutrients (Matagi et al., 1998; Maine et al., 2006). The four main mechanisms by which heavy metals and excess nutrients are removed are physical, chemical, biological and biochemical (Matagi et al., 1998). These mechanisms occur within the water, biota (plants and animals), substratum (underlying bottom layer of sediment) and suspended solids of the wetland (Padmavathiamma and Li, 2007). In most cases these processes are dependent on one another, they occur simultaneously and therefore it is difficult to pinpoint the exact mechanism which is taking place at any given time (Matagi et al., 1998). For example, physical processes such as filtration and sedimentation which occur together as the vegetation (biological mechanism) acts as a hindrance for the water moving through the wetland, slowing its velocity which allows for sediments to be deposited (Matagi et al., 1998; Khanijo, 2002). The substrate then acts as a medium for filtration processes. To add to this example, physical mechanisms are only able to purify water after other chemical mechanisms have aggregated heavy metals into particles large enough to sink (Padmavathiamma and Li, 2007). In this example heavy metals are removed from the water and trapped in the wetland substratum, thus reducing heavy metal mobilization downstream (Matagi et al., 1998). Along with physical mechanisms mentioned, trace metals are also reduced by biological mechanisms such as plant uptake and chemical mechanism during the precipitation of the metal compounds or by exposure to sunlight (Padmavathiamma and Li, 2007). A biochemical mechanism involves a chemical process occurring within a living organism (Khanijo, 2002). For example, floating plants such as water hyacinth, duckweed and water fern store iron and copper found in wastewater (Sakadevan and Bavor, 1999; Maine et al., 2006). *Typha* and *Phragmites* reed beds also aid in the role of heavy metal uptake (Sakadevan and Bavor, 1999; Khanijo, 2002).

A natural function of wetland vegetation is the up-take, store, and remove the nutrients (nitrate and phosphate) found in runoff from the surrounding soil and water (Khanijo, 2002). Nutrients are retained until plants die or are used up by animals or until microbial processes convert soluble nutrients to a gas, as it is the case with nitrate (Maine et al., 2006). The main biological mechanisms occurring in wetlands that results in removal of pollutants and nutrients are photosynthesis, respiration, fermentation, nitrification, denitrification and phosphorus removal (Khanijo, 2002). Photosynthesis helps in maintaining the oxygen supply for plants. Respiration helps in maintaining dissolved oxygen content in the water (Khanijo, 2002). Fermentation leads to decomposition of organic carbon. Nitrification and denitrification are mechanisms of the nitrogen cycle that results in removal of nitrogen (Khanijo, 2002). Phosphorus removal mechanism such as enhanced biological phosphorus removal performed by phosphate accumulating organisms (mainly bacteria) results in removal of phosphorous from the wetland (Sakadevan and Bavor, 1999). In this way wetlands can retain and store both heavy metals and nutrients within the water, reducing heavy metal and nutrient concentrations downstream.

5. Methodology

5.1 Site description

The Blesbokspruit Wetland study area is situated in the East Rand near Johannesburg, just outside the town of Nigel. The riparian wetland along the Blesbokspruit developed as a result of many years of regular pumping and disposal of mine water from Grootvlei Gold Mines and adjacent smaller mines in the area (Roychoudhury and Starke, 2006). The wetland was a designated Ramsar Site due to its ecological importance in supporting the Marievale Bird Sanctuary and a 25 km long green belt (Roychoudhury and Starke, 2006). Historic mine water effluent flowing through the wetland ultimately discharges into the Vaal River, one of the major sources of fresh water supply to Gauteng province (Roychoudhury and Starke, 2006; Ochieng, 2010). The stream flows almost north-south through the study area and because of its low gradient, the river is swampy for most of its course (Roychoudhury and Starke, 2006). The swampy areas are covered with *Typha* and *Phragmites* vegetation (Roychoudhury and Starke, 2006). The building of the new AMD treatment plant near the Blesbokspruit adds a new element to the study area, previous studies involved singling out mines that produce harmful pollution into the wetland. This study identifies whether processes occurring at the Eastern Basin AMD Treatment plant are influencing water quality in the Blesbokspruit wetland downstream. This project has focused sampling specifically at the Marievale Bird Sanctuary and the areas upstream and downstream of the AMD treatment plant along the Blesbokspruit.

5.2 Site Map

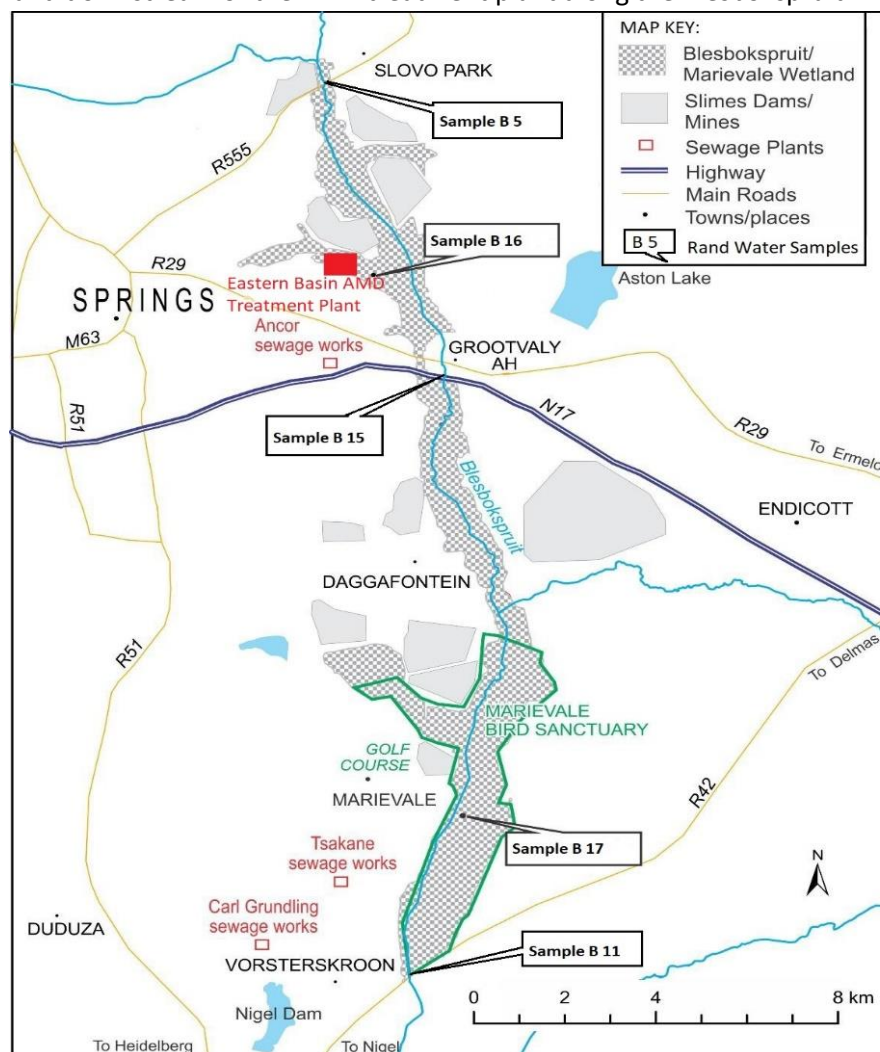


Figure 7: Site map. This site map has been adapted and modified from the map illustrated in the technical report by Mckay et al. (2018).

The site map on the previous page (figure 7) illustrates the complexity of the Blesbokspruit and Marievale Wetland. With reference to the site map, the AMD treatment plant is situated near sample point B16 at the Grootvlei mine which is nearer the northern portion of the wetland area. Several slimes dams/ mine dumps are spread along the stream, and some of these have been reclaimed and reworked in the recent past (McCarthy, 2011). According to the site map, these mine dumps are extremely large, with some spanning areas of over 6 km². The wetland is surrounded by formal and informal residential areas and industrial zones including Slovo Park, Daggafontein and Venterskroon. There are three sewage plants adjacent to the main river, and the Marievale Wetland lies adjacent to large agricultural fields. The Blesbokspruit wetland, therefore, is subject to contamination and pollution from multiple areas, and not just AMD pollution but also sewage, industrial effluent and agricultural pollution such as fertilizers and pesticides. Due to there being multiple sources of possible pollution in the area, sampling points for this research are spread along the entire wetland. There are also historical water quality data for the area and these data are valuable for the purpose of this research.

5.3 Water sampling methods

5.3.1 Historical and current sampling sites:

As mentioned in the literature review, Ambani and Annegarn (2015) used monthly historical Rand Water quality records for the Blesbokspruit Wetland. Three separate Rand Water historical sites were chosen; site B5 at the stream inflow to the wetland, site B16 just after the discharge point of pumped underground mine-water at Grootvlei mine shaft no. 3, and site B11 at the stream outflow from the designated wetland area (Ambani and Annegarn, 2015). For the purpose of this research, the historical data at these three sites will also be used. Two more sites have been included for use in this research: site B15 on the N17 toll road at Springs which is downstream of the discharge point at site B16, and site B17 which is located within Marievale Bird Sanctuary itself.

Table 1: The five historical Rand Water data sites.

No.	Site Name	GPS Location
1.	B5 Blesbokspruit at Welgedacht Inflow into the wetland	S 26.21456 E 28.48008
2.	B16 Blesbokspruit at Grootvlei Mine Train Bridge	S 26.25553 E 28.49889
3.	B15 Blesbokspruit on N17 Toll Road in Springs	S 26.27100 E 28.50400
4.	B17 Blesbokspruit at Marievale Bird Sanctuary	S 26.35900 E 28.50800
5.	B11 Blesbokspruit on R42 bridge at Nigel stream outflow	S 26.39075 E 28.49719

Data from these sites are uploaded quarterly onto the reservoir website by Rand Water. Considering the aims of this project; data provided one and a half years prior (starting 1st January 2015) to the launch of the new AMD treatment plant (August 2016) has been analysed to identify water quality before the launch of the AMD treatment plant. Data spanning nearly three years after the launch (until 31st March 2019) of the treatment plant have been used and analysed to consider whether the introduction of the treatment plant has had an influence on water quality and AMD pollution within the area.

4.3.2 Ground truth water sample sites:

A full year record of monthly water sample collection has been completed in order to cover the full range of seasonality of the area. A total of eight ground truth water sample sites were visited monthly. Five of these eight sites are the same sites used by Rand Water and the remaining three sites lie within the Marievale Bird Sanctuary. These three remaining sites are named according to their surroundings: Marievale Bird Sanctuary Bridge, Duiker Hide, and Hadedda Hide. The sites have been numbered site one through eight according to their position along the stream, from upstream to downstream. The following table provides photos of the eight different sampling sites along with the GPS coordinates and a short description.

Table 2: Sampling site area photos, GPS positions and site descriptions:

No.	Site photo and caption	GPS Location and short site Description
Site 1.	 Figure 8: site B5 Blesbokspruit at Welgedacht Inflow into the wetland. Photo taken in September 2018 by M. Lourenco	S 26.21456 E 28.48008. The first sample site is below the bridge on Welgedacht road in Springs. The site is downstream of a large mine dump and an informal settlement. This site is the inflow point into the Blesbokspruit Wetland. This site is upstream to the Eastern Basin AMD Treatment Plant.
Site 2.	 Figure 9: site B16 Blesbokspruit at Grootvlei Mine Train Bridge. Photo taken in September 2018 by M. Lourenco	S 26.25553 E 28.49889. The Grootvlei mine bridge lies downstream of the Eastern Basin AMD Treatment plant. It is also downstream of Grootvlei Proprietary Mines and east of Strubenvale residential area. The water is collected below the Old Mine Train Bridge.

Site 3.	 Figure 10: B15 Blesbokspruit on N17 Toll Road in Springs. Photo taken in September 2018 by M. Lourenco	S26.27100 E28.50400. The B15 Toll road site is both adjacent and downstream to agricultural land. There are small settlements upstream of the site. The B15 site is approximately 6 km upstream of Marievale Bird Sanctuary.
Site 4.	 Figure 11: Marievale Bird Sanctuary Bridge. Photo taken in September 2018 by M. Lourenco	S 26.33121 E 28.51352. Marievale Bridge (site 4) marks the start of the Marievale wetland area. This site is adjacent to agricultural land, mine dumps and open vegetated land. There is a large mine dump that is less than three hundred meters away from this sample site.
Site 5.	 Figure 12: Duiker Hide in Marievale Bird Sanctuary. Photo taken in September 2018 by M. Lourenco	S 26.34496 E 28.51380. Duiker hide is downstream of the Marievale Bridge and the site extends out into the wetland's main river channel. It is further away (1 km) from the large tailings dam adjacent to the Marievale Bridge site (site 4).

Site 6.	 Figure 13: B17 Blesbokspruit at Marievale Bird Sanctuary. Photo taken in September 2018 by M. Lourenco.	S 26.35900 E 28.50800. The Rand Water B17 site is situated in the centre of the Marievale Bird Sanctuary and the water samples are collected over a small bridge.
Site 7.	 Figure 14: Hadedda Hide in Marievale Bird Sanctuary. Photo taken in September 2018 by M. Lourenco.  Figure 15: Hadedda Hide in March 2019. Photo taken in March 2019 by M.Lourenco	S 26.36723 E 28.51249. The Hadedda Hide site also extends out into the wetland channel. There are missing data from this site due to the site being completely inundated by green algae and duckweed during the months of January 2019 to May 2019. Water was not collected during this time as the water at Hadedda has was not flowing, but stagnant. YSI data was measured at the site. Images of the green algae and duckweed inundation can be seen in the figure 15 to the left.

Site 8.	 Figure 16: B11 Blesbokspruit on R42 bridge at Nigel stream outflow. Photo Taken in September 2018 by M. Lourenco	S 26.39075 E 28.49719. Site B11 marks the end of Marievale Bird Sanctuary and is the last sampling point. The site is below the R42 Bridge in Nigel and the stream water is turbid as it rushes down a fairly steep gradient below the bridge. The stream water continues to flow south from this point and passes through Nigel and Heidelberg.
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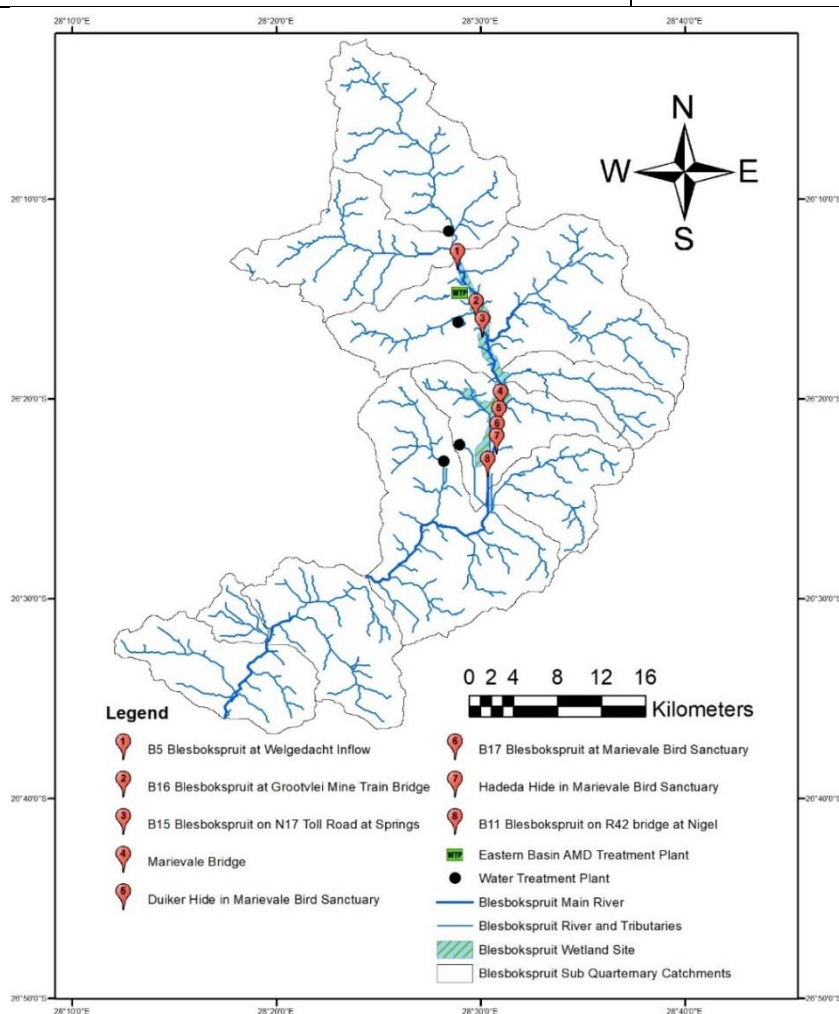


Figure 17: Sample site map showing the Rand water and ground truth water sample sites.

The sample site map above represents the entire Blesbokspruit catchment area along with the main river channel and its tributaries. The small numbered icons on the map represent the locality of the eight sampling sites that have been mentioned in table 2 previously. The map shows the area of the Blesbokspruit wetland. The Marievale Bird Sanctuary Wetland area overlaps the Blesbokspruit Wetland area south of sampling site number 4. The position of the Eastern Basin Water Treatment plant is shown northwest of site number 2 (B16) and four other treatment plants in the area are also represented as black circles. The sub quarternary catchments are also shown in this sample site map.

4.3.3 Sample collection: ground truth water samples

Sample sites were accessible via motor vehicle as sites are located either along main/dirt roads or under bridges. For each sample site (sites one through eight) sterilized 500 ml bottles were used to collect water samples. Upon arrival at the sampling location, the individual bottle for each site was first rinsed with water from the actual stream at least three times before filling bottle to ensure no contamination from previous collections. The bottle was then labelled with tape and the site name and date was written on the tape with permanent marker. Site descriptions were also noted in a field notebook, these included whether the water was clear/turbid, as well as the infield data collection for each sample site. In-field data collection was determined using a YSI multi parameter probe. For water quality parameters pH and conductivity, the YSI needed to be calibrated prior to field work. YSI readings included values for temperature, pH and conductivity. These values were recorded in a field notebook as well as the time of sampling. The labelled 500ml water bottle was then stored in a sealed cooler box and after completing the fieldwork the samples were refrigerated overnight. Within 24 hours of sample collection, the samples were filtered using 0.45 µm pore size filter paper and stored in newly labelled 500ml samples and placed back into the refrigerator between 2 to 4 °C. It is important to note that maximum care for cross contamination was taken as the filtering equipment was cleaned and rinsed with deionised water at least three times before and after each sample was filtered. A new filter paper was also used for each sample.

5.4 Soil sampling methods

Soil samples were collected along two separate river transects during November 2018 and December 2018. These transects ran perpendicular to the stream and each soil sample was collected roughly 20-30 meters apart. The reason for sampling soil along these transects was to provide a spatial assessment of surface soil conductivity and soil pH adjacent to the main river channel. Soil samples were collected using 100 cm³ bulk density cups that have a diameter of 5 cm. The soil was collected as follows: after getting close to the ground, an area in between the vegetation that had bare soil was identified. Once a suitable area was found, loose pebbles and materials, such as twigs or grasses had to be removed from the surface to uncover the bare soil beneath. After noting down the bulk density cup number that was being used, the cup was correctly placed into the bulk density cup holder. Then the bulk density cup holder with the mounted bulk density cup was pushed directly into the bare surface soil. The top of the bulk density cup holder was hammered into the ground until the bulk density cup was filled with the topsoil. The cup extracted soil in the range of 8-10 cm, depending on how easily it was hammered into the ground. When the cup was completely full, the excess soil below the cup was shaved off using the soil shaving tool to ensure that the cup was filled, but not overfilled at the same time. Note that if the cup was not filled correctly, the procedure needed to be re-done near the original site; i.e. no more than two meters from the previous attempt. Once the bulk density cup was successfully filled, it was removed out of the holder and excess soil from the other end was shaved, to ensure the cup was filled correctly. The cup was then enclosed, and the sample was stored in the bulk density cup briefcase. The procedure was completed for a total of 13 sampling sites across the two river transects.

5.5 River sediment sampling methods

The sampling of River sediment heavy metal analysis gives an indication of the potential levels of heavy metal contamination within river sediments due to historic mine pollution. Sediment sampling was carried out in September 2018 during Spring season. The sampling sites are the same sites used for water collection. Sediment was collected from each of the riverbeds at sample sites one through

eight. A cylindrical gravity corer of 8 cm diameter was used to collect approximately the top 5-10 cm of surface river sediment at each sample site. In areas where the stream was under a bridge, the corer needed to be lengthened using 1.5-meter-long poles that screwed onto each other and the corer. In order to extract the sediment, the corer was pushed into the riverbed with reasonable force. The corer then needed to be pulled out of the water and, if successful, the sediment at the bottom of the coring tube acted as a plug so that the sediment and water column would remain intact inside the tube. The water in the tube was then carefully emptied and the top 5-10 cm of sediment was placed into sealed and labelled plastic bags. The eight labelled bags were then stored in a fridge at 2 °C.

5.6 Laboratory methods (water, sediment and soil)

5.6.1 Laboratory methods: water samples

Monthly water samples collected from each sample site in the field were analysed in the Bernard Price Water Laboratory using a Hach test kit. The instrument used is called the Hach DR 2800 Spectrophotometer and the methods used for each water quality parameter were obtained from the DR 2800 procedures manual 2nd edition, written in June 2007. The online web address is as follows: <https://www.Hach.com/asset-get.download-en.jsa?id=7639982436>. The Hach instrument was used to determine phosphate, nitrate, sulphate, iron and chloride (all measured in mg/L) levels in the ground truth water samples that were collected. Samples had been analysed with the Hach test kit within two days after they had been collected from the field and filtered. Each analysis for the individual water quality parameters were carried out in batches. The sample cells used were cleaned thoroughly and rinsed three times over with deionised water between each individual test to avoid cross contamination between samples. A pipette was used to accurately measure liquid quantities and new pipette tubes were used for each of the tests. Laboratory coats, a face mask and gloves were worn throughout the laboratory process as some of the tests make use of hazardous substances. Here is a short description for each water quality parameter. The methods used were followed strictly according to the DR 2800 procedures manual 2nd edition.

5.6.1.1 Phosphate

The method used is the phosphorous reactive (orthophosphate) method which has a detection range of 0.02 to 2.50 mg/L PO_4^{3-} . To begin, the test 490 phosphate reactive was selected on the Hach analyser. 10 mL of an individual water sample was then filled in a clean sample cell. The contents of one PhosVer 3 Phosphate pillow powder was poured into the cell and then the cell was closed and shaken for 30 seconds. The prepared cell was then left undisturbed for a two-minute reaction to take place. In summary, orthophosphate reacts with molybdate in an acid medium to produce a mixed phosphate/ molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue colour. From there, a blank sample cell was used whereby 10 mL of the same sample was filled into a new sample cell. This blank cell was used to zero the instrument. After the two-minute reaction, the prepared sample was then placed into the Hach analyser and the results were displayed in mg/L PO_4^{3-} for the sample. The test results were measured at 880 nm by the Hach analyser. This process is repeated for each sample collected from the field.

5.6.1.2 Sulphate

The method used is the SulphaVer 4 pillow powder procedure to test for sulphate. This method has a detection range of 2 to 70 mg/L SO_4^{2-} . To begin, the test 680 sulphate was selected on the Hach analyser. Due to almost all of the samples having sulphate levels over the limits of detection of the Hach analyser, the samples were diluted with deionised water at a 1:10 ratio. A prepared sample cell was made by filling 1 mL of an individual sample and 9 mL of deionised water into a clean sample cell. A dilution factor of 1:10 was selected on the Hach analyser. The contents of one SulphaVer 4 reagent pillow powder was then added to the sample cell. The sample cell was closed and swirled to mix. A white turbidity formed if there was sulphate present in the sample cell, and the results were not affected by undissolved powder. A five-minute reaction time began, and the sample cell was left undisturbed. In summary, sulphate ions in the sample react with barium in the SulphaVer 4 pillow powder and form a precipitate of barium sulphate. The amount of turbidity formed is proportional to the sulphate concentration. A blank sample then was used in the exact way as that used for the phosphate determination to zero the Hach analyser. After the five-minute reaction time, the sample was placed in the Hach analyser and the results in mg/L SO_4^{2-} were noted for the individual sample with the correct dilution factor. The test results were measured at 450 nm by the Hach analyser. This process was repeated for each sample.

5.6.1.3 Nitrate

The method used is the NitraVer 5 high range nitrate reagent pillow powder procedure. This method has a detection range of 0.3 to 30.0 mg/L NO_3^- . To start, the 355N nitrate high range pillow powder test was selected on the Hach analyser. A sample of 10 mL was prepared and the contents of one NitraVer 5 nitrate reagent high range pillow powder was added to the prepared sample. The sample cell was then closed and shaken forcefully for one minute. Undissolved powder does not affect the results of this test. The sample was then left undisturbed for a five-minute reaction time, during which cadmium metal reduces nitrate ions in the sample to nitrite. The nitrite ions react in an acidic medium with sulphanilic acid to form an intermediate diazonium salt. The salt couples with gentisic acid to form an amber coloured solution. During the reaction period the blank sample cell was prepared to zero the Hach analyser. After the reaction time had ended, the prepared sample was placed in the analyser and the results for mg/L NO_3^- were noted for the individual sample. The test results were measured at 500 nm by the Hach analyser.

5.6.1.4 Iron

The method used is the FerroVer pillow powder procedure for total iron and has a detection range of 0.02 to 3.00 mg/L Fe. To begin, test 265 iron FerroVer was selected on the Hach analyser. A clean sample cell was filled with 10 mL of sample and two drops of phenanthroline indicator solution. The cell was then swirled to mix, and the sample was placed into the Hach analyser to zero the instrument. The same cell was then removed from the Hach analyser and the contents of one FerroVer Iron Reagent pillow powder was added to the sample cell. The cap was then placed on the sample cell and the cell was shaken for 30 seconds, note the accuracy was not affected by undissolved power. The cell was then left for three minutes to react, the FerroVer iron reagent converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron. The ferrous iron reacts with the phenanthroline indicator solution to form an orange colour in

proportion to the iron concentration. The cell was then placed in the Hach analyser and the results in mg/L Fe were noted for each sample. The test results were measured at 510 nm by the Hach analyser for each sample.

5.6.1.5 Chloride

The method used is the Mercuric Thiocyanate method to test for Chloride. The detection range for this method is 0.1 to 25 mg/L Cl^- . Test 70 chloride was selected on the Hach analyser to begin. Similar to sulphate, the samples needed to be diluted in a 1:10 ratio with deionised water as they all had values of chloride that were over the range detection limit of this method. A clean, prepared sample cell was filled with 1 mL of sample and 9 mL of deionised water. Another sample cell, the blank sample, was filled with 10 mL of deionised water. A pipette was used to put 0.8 mL of mercuric thiocyanate solution into each sample cell. A pipette was then used put 0.4 mL of ferric ion solution into each sample cell. The sample cells were then swirled and left undisturbed for a two-minute reaction time. Chloride in the sample reacts with mercuric thiocyanate to form mercuric chloride and liberate thiocyanate ion. Thiocyanate ions react with the ferric ions to form an orange ferric thiocyanate complex. The amount of this complex is proportional to the chloride concentration. The blank sample was then used to zero the Hach analyser. The dilution factor of 1:10 was selected for the Hach analyser and thereafter the prepared sample was placed into the analyser and the results of mg/L Cl^- were recorded for each sample. The test results were measured at 455 nm by the Hach analyser.

Note: the pillow powders from the above analyses contain hazardous substances, for example, cadmium and mercuric thiocyanate. The hazardous waste needs to be disposed of according to local and regional disposal regulations. The waste material was placed into a large sealed container and stored safely for collection by a certified waste management company.

Calibration curves for each of the water quality parameters except for phosphate have been made and are shown in the results section before the Hach water quality results are presented.

5.6.2 Laboratory methods: soil samples

5.6.2.1 Soil pH and soil conductivity

The laboratory method used for quantifying both soil conductivity and soil pH are those described in the soil laboratory manual by Hanlon (2009). These methods have been cited and are very similar to most of the other methods within the literature. These methods also have value in that they can be replicated in the School of Geography water laboratory. Soil pH and soil conductivity analysis have very similar methodology (Hanlon, 2009). The soil samples were first emptied from the individual bulk density cups and placed on clean paper plates to air dry. From there the soil was sieved through a 2mm sieve and 20 grams were taken out of the mixture for analysis (Hanlon, 2009). Both soil pH and soil conductivity methods require 20 grams of soil to be mixed with 40 mL of deionised water. A soil:water ratio of 1:2 was required for each soil sample (Hanlon, 2009). Once the 20 grams of soil from an individual sample was placed in a sterilised plastic cup, the cup was filled with exactly 40 mL of deionised water and then gently stirred with a scraper. The mixture was then left to stand room temperature. After a one-hour reaction period, the mixture was lightly stirred once again and a calibrated (calibrated at 4 pH and 7 pH buffer solutions) YSI probe was placed in the mixture

(Hanlon, 2009). The pH probe was not placed directly into the wet soil layer at the bottom of the plastic cup, but rather held in position just above the soil layer (Hanlon, 2009). After two to three minutes, when the pH reading displayed on the YSI probe had settled, the soil pH was then recorded for the individual soil sample and the method was repeated for each sample thereafter. The same mixture was then left to stand for another three hours. Only after a total four-hour waiting period had passed, the soil mixture could be tested for soil conductivity. The four-hour equilibrium period is essential as it provides enough time for all the soluble compounds within the soil to dissolve (Hanlon, 2009). This four-hour waiting period produces more accurate results, a longer waiting time would not alter results significantly but a shortened waiting time would produce inaccurate results (Hanlon, 2009). After the four-hour waiting period, a calibrated YSI multiparameter probe was placed in the mixture. The conductivity probe needed to be placed in the upper, liquid layer of the plastic cup and not deep within the wet soil layer to provide accurate results. After two to three minutes, once the conductivity readings displayed on the YSI probe had become settled, the soil conductivity was recorded for the individual sample and the method was repeated for the remaining soil samples.

5.6.2.2 Laboratory methods: river sediment samples

Sediments were analysed using X-Ray Fluorescence (XRF) spectrometry by the School of Geosciences at Wits University. After the sediment had been collected from the riverbed, it was stored in a refrigerator at 2 °C. Prior to analysis, the 8 sediment samples were dried in a fan oven at 100 °C for 6 hours in order to remove the water content within the sediment. After the sediment was completely dried, the sediment samples were then crushed using a mortar and pestle. The XRF spectrometer requires 6 grams of very fine-grained material so the sediment that was put through a sieve with 100 µm apertures. The fine-grained sediment samples were then placed in new plastic bags, labelled and sealed. The sediment was then given to the School of Geosciences for XRF Spectrometry analysis. The methods used by the School of Geoscience laboratory are as follows: heavy metal elements were determined on pressed pellets using a Moviol solution binder. Standardization was carried out using International Reference Materials USGS series (USA) and NIM series (South Africa). Precision was determined on the basis of counting time and is taken as 5% for elements in abundance greater than 100 mg/kg, and 10% for elements in abundance between 10 and 100 mg/kg. The instrument used was the Philips PW2404 x-ray spectrometer.

5.7 Data utilisation and statistical analysis

The statistical analysis for this research project was completed using Microsoft Excel program. Multiple data analysis tools and add-ins were used within the excel program. This paragraph highlights the methods/tools that were used for each statistical analysis. Data summaries for both Rand Water data and ground truth water quality data were completed using the descriptive statistics tool within the data analysis tab of Microsoft excel. Normality tests were completed using the NumXL add in programme to test whether the data followed a normal distribution. Non-parametric hypothesis tests were completed using the XLStat add in on excel. The non-parametric comparison of two samples tests were used for both independent (Mann-Whitney test) and dependent (Wilcoxon test) samples. Historical data provided by *The Reservoir* website was pivoted using the Power Pivot and Power Query add ins to aggregate certain water quality parameters and sample sites. Time series graphs were generated from the pivoted water quality data. The Blesbokspruit

Forum management targets shown behind the time series graphs was completed using Microsoft excel graph shading technique to indicate which values meet certain management targets. The Blesbokspruit Forum water quality guidelines act as a threshold of potential concern for individual water quality parameters and each statistical test refers to these water quality guidelines.

Soil and river heavy metal sediment data analysis were also completed using the Microsoft excel program. Simple line graphs were generated from raw data which were collected and analysed in the field. Sediment trace metal results received from the Wits School of Geoscience laboratory were also graphically presented using Microsoft excel program. Land use pie charts were generated using the insert pie chart tool on Microsoft excel. Data obtained for the land use pie charts came after land use maps had been created using the ArcMap program.

5.8 Manual land classification methodology

The purpose of creating land use/ land cover maps for this research is to demonstrate the complex land use / land cover surrounding the Blesbokspruit Wetland. Land use for the entire Blesbokspruit catchment was classified manually due to lack of accurate, up to date and available land use/ land cover data for the region. The land use classification was also completed manually due to the multiple mine dumps within the region that were essential to classify accurately for the purpose of this research. National land cover maps classify mine dumps simply as bare land which would lead to inaccurate results. This manual classification was completed manually by creating hundreds of land use/ land cover polygons across the entire study area on the Google Earth program, using the add polygon tool. For example, a polygon was manually drawn on Google Earth around the perimeter of an individual land use zone that was identified, such as a mine dump. 260 individual polygons were manually created to cover the entire Blesbokspruit catchment area, i.e. no gaps between each land use polygon. The edges of the individual polygons needed to be extremely close to one another to avoid creating small gaps within the catchment area. Every section of land across the Blesbokspruit catchment was manually classified into individual land use polygons. Land use was classified into eight land use classes which are typical for most land use maps. The eight land use classes are: agricultural land, open vegetated land, residential area, water body, mine dump, industrial area, bare land and lastly wetland/riparian zone. Great efforts were made over a long period of time to successfully and accurately classify land use within the entire Blesbokspruit catchment. Google earth imagery, site visits and recent topographical maps were used to aid in the manual classification of land at areas which were difficult to classify. Each land use was identified according to specific criteria.

5.8.1 Agricultural land

Agricultural land was identified when the land area on google earth showed clear evidence of being manipulated by man. Most often agriculture was easily identified by looking at crop rows on the ground or definite circular structures spanning wide open spaces. It was noted on field trips that shepherds and herdsmen take their livestock to open grass fields to graze in multiple areas within the Blesbokspruit catchment. Majority of these open grassland spaces were classified as open vegetated land and not agricultural land. Therefore, there may be some overlap between these two land use classes as herdsmen make use of open vegetated grasslands for pasture. Subsequently, the agricultural land use class only represents arable land that has been clearly worked on by humans for crop growth.

5.8.2 Open vegetated land

In general, open vegetated land was easy to classify by identifying land with green vegetation such as forests, grasslands or bushveld that had no clear indication of being worked on by man. As mentioned, open land may have been used by herdsman as pastureland for their agriculture and this is where the two land use classes can overlap in some areas. Land use which was clearly recreational such as golf courses and sports field were also classified as open vegetated land.

5.8.3 Residential area

Residential areas were classified by using google earth imagery. Both formal and informal settlement names are displayed on google earth imagery and the extent of these settlements were all classified under the residential areas land use type. In some cases, a location would have features that resembled both residential and industrial areas. During these cases efforts were made to successfully split residential and industrial area polygons as accurately as possible. It is possible that there may be some overlap between residential and industrial areas.

5.8.4 Water body

Water bodies occupied only a small fraction of the Blesbokspruit catchment. The water bodies classified include only permanent water bodies such dams. Dam names are indicated on google earth imagery and water bodies are generally simple to identify from google earth images.

5.8.5 Mine dump

One of the major reasons why the land use was manually classified is due to the mine dumps land classification. Mine dumps are easily identifiable both on the ground and on Google Earth. The yellowish-beige colour and scoured land are characteristic of both abandoned mines and mine dumps which fall into this classification. The extent and overall land cover of these mine dumps is extremely important for this research as these areas may negatively impact on water, sediment and soil quality.

5.8.6 Industrial area

Industrial areas were identified by looking for areas with large buildings, and where they land was clearly being used for something other than residential or agricultural purposes. These areas were also identified by looking for flat surface areas with clearly built up structures that were near transport routes on Google Earth. As mentioned, it is possible that industrial and residential areas overlap.

5.8.7 Bare land

As most of the catchment area is vegetated, bare land makes up for a small percentage of land cover. Areas were categorised as bare land when they were clearly unvegetated and had no evidence of being worked on by humans (areas which could be classified as mine dumps). There are a few rocky outcrops in the southern portion of the catchment and these outcrops were classified as bare land.

5.8.8 Wetland/ riparian zone

Land adjacent to the Blesbokspruit and tributaries was classified as wetland/ riparian zones. These zones represent the wetlands of both the greater Blesbokspruit and Marievale Wetland. Areas adjacent to the main river channels which looked highly vegetated and lush were categorised in this land use zone.

5.9 Methodology of creating land use maps

The following paragraph will describe how land use maps were created using the ArcMap 10.4.1 program. After manually creating 260 individual land use polygons on Google Earth, the polygon file was saved as a KML file. Within ArcMap tools, the KML file was converted to a map layer using the “KML to layer tool”. The KML file also included the exact positions of the individual Rand Water and ground truth sampling sites as well as the Eastern Basin AMD treatment plant and other treatment plants within the Blesbokspruit catchment. Once the KML was converted to a layer, the land use polygons were converted to raster pixels using the “layer to raster conversion tool” within ArcMap. The land use raster layer was then clipped using the “clip tool” to occupy the Blesbokspruit sub quaternary catchment area shapefile obtained from the Department of Water and Sanitation website. Individual sub catchments for each water sample site were then created using spatial analysis tools. Individual sampling site locations were represented by “pour” location points which were inputted into the “hydrology watershed (catchment) tool” within the spatial analysis toolbox in ArcMap. This tool uses flow direction and relief to draw the perimeter of the sub catchment for each “pour” location which represented the individual Rand Water and ground truth sampling locations. After the sub catchments had been created for each water sampling site, the original land use cover map for the Blesbokspruit was then clipped to fit into each of these sample site sub catchments. The Blesbokspruit and tributaries shapefile was obtained from the Department of Water and Sanitation website, and the spatial extent of the Blesbokspruit wetland was obtained from the Ramsar Wetlands information website.

6. Results section

The results section for this research project is lengthy and consists of maps and land use results, rand water quality results, ground-truth water quality results, soil quality results and sediment metal analysis results.

6.1 Maps and land use results

6.1.1 Map of sampling sites

The following map shows the eight individual ground truth water sampling sites that follow along the Blesbokspruit within the Blesbokspruit Wetland Site. The five individual Rand Water sites (B5, B16, B15, B17 and B11) are included within these eight ground truth sampling sites and all eight sampling sites are numbered according to the sampling position along the stream. The stream flows in a south direction and the location of the Eastern Basin AMD Treatment plant is shown with a green icon upstream of site 2 on the map below. Four other treatment plants (black dots) are also shown on the map but only the two immediately south and north of the Eastern Basin Treatment Plant fall within the catchment area of the sampling sites.

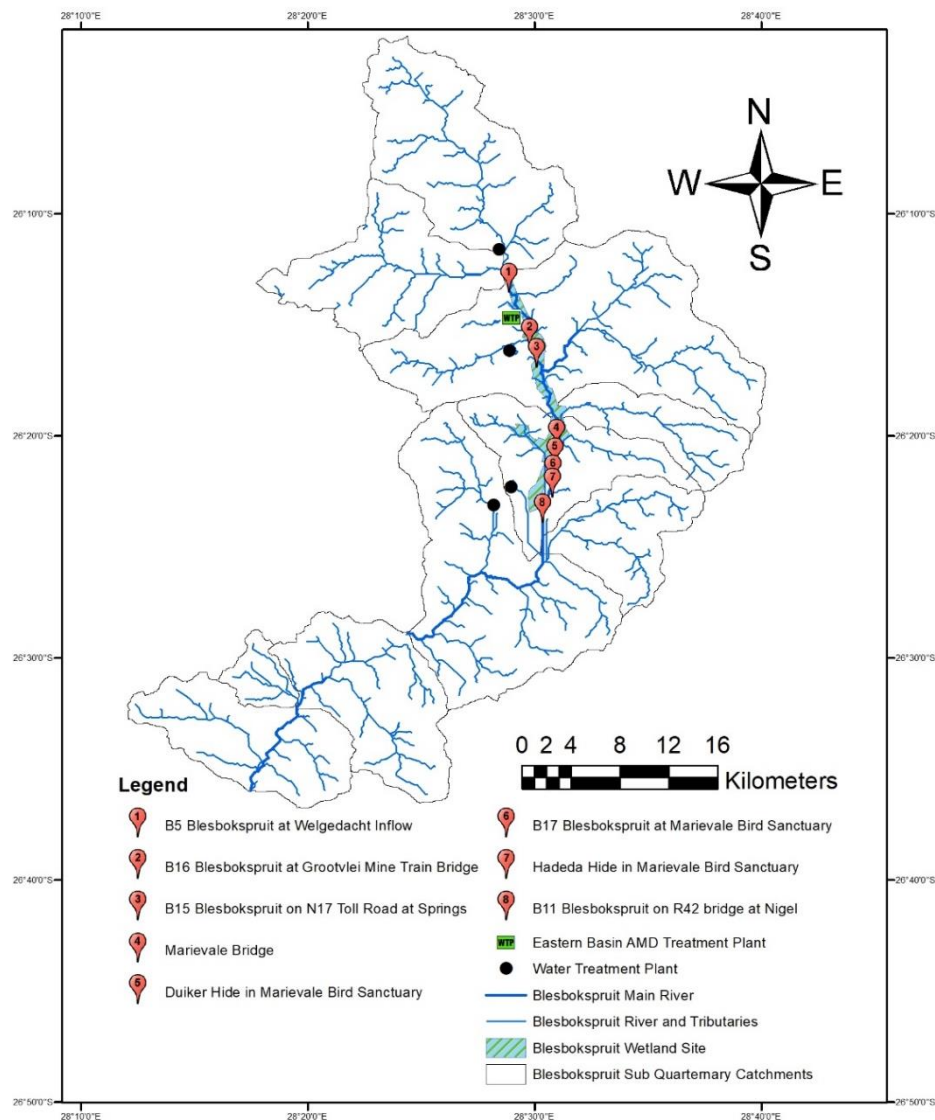


Figure 18: Map showing the location of the eight individual ground truth and Rand Water sampling sites along the Blesbokspruit.

6.1.2 Blesbokspruit catchment land use map:

The following map describes the land use cover within the entire Blesbokspruit catchment. Individual pixel colours represent eight different land use classes shown in the map legend. The study area includes the main Blesbokspruit as well as its tributaries within the Blesbokspruit sub quaternary catchments.

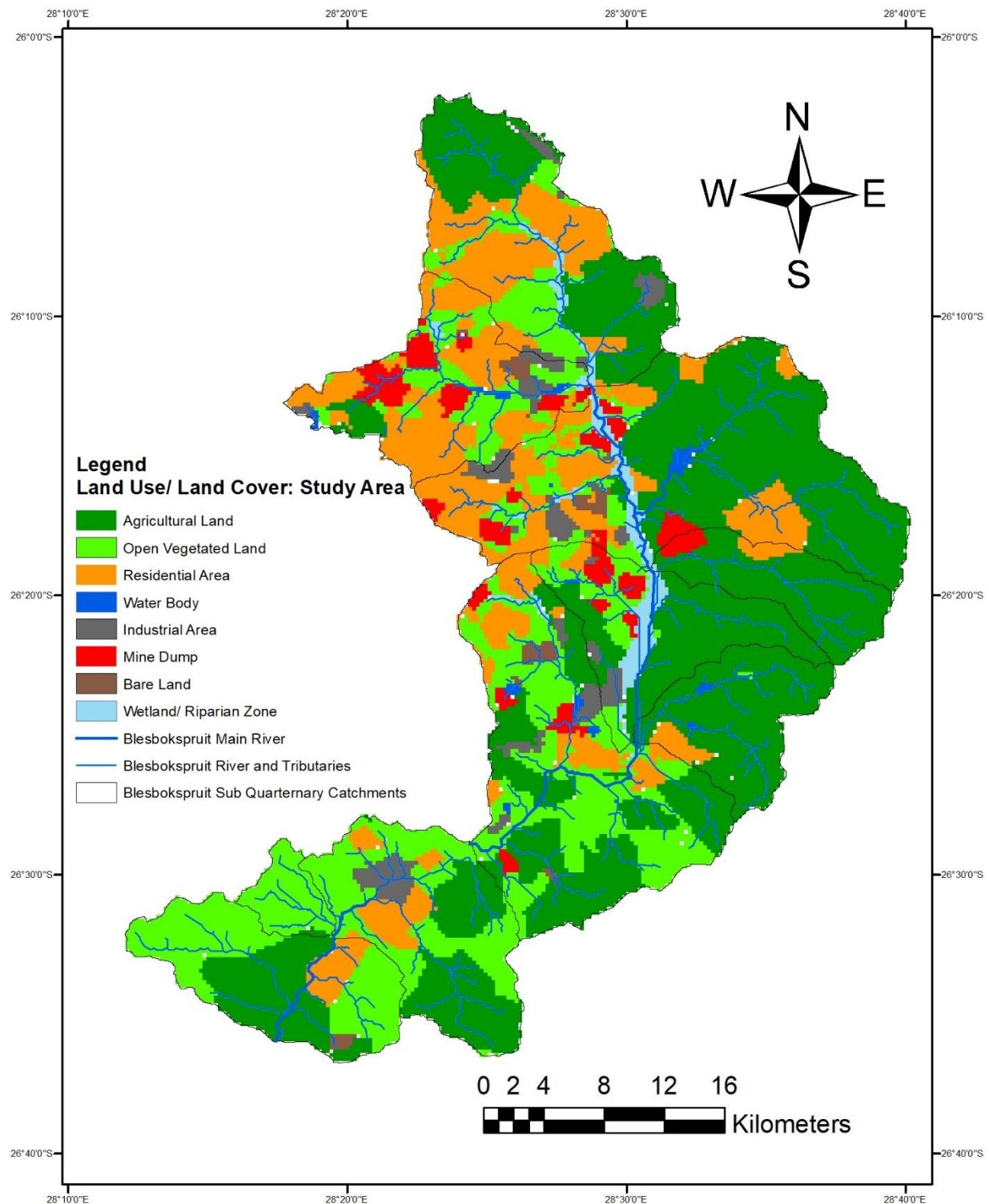


Figure 19: Map of land use/ land cover across the entire catchment area of the Blesbokspruit.

Land use/ land cover percentages for the previous site map of the entire Blesbokspruit catchment are shown in the simple pie chart below:

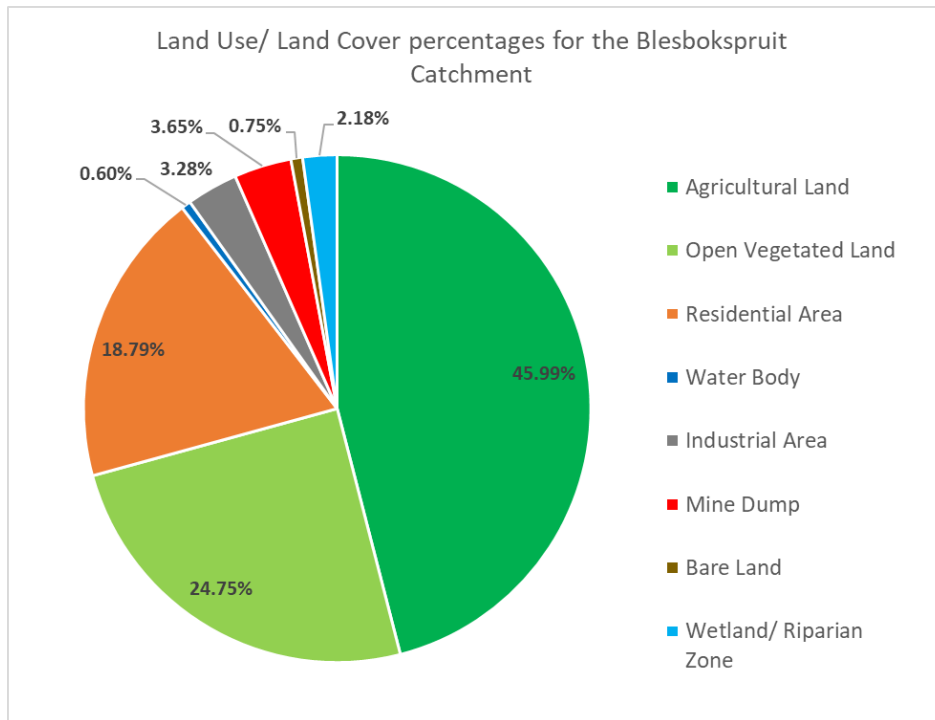


Figure 20: Land Use/ land cover percentages for the Blesbokspruit Catchment.

The study area shown in figure 19 is defined as the area occupied by the Department of Water and Sanitation (DWS) tertiary catchments for the Blesbokspruit. This large catchment includes areas downstream of the Rand Water and ground truth sampling sites specific to this study. The areas downstream have been included to demonstrate the complex land use within the DWS tertiary catchment for the Blesbokspruit. According to the pie chart above, a large portion of land within the Blesbokspruit catchment is used for agriculture (45.99%), open vegetated land (24.74%) and residential areas (18.79%). Land is also occupied by mine dumps, industrial areas, bare land, water bodies and wetland/riparian zones. Individual sub-catchments have been created for each Rand Water and ground truth sampling site. These will be shown with pie charts indicating the percentage land use per sample site sub catchment.

6.1.3 Sub catchments and land use maps

6.1.3.1 Sub catchment of sample site 1 and land use map

The following map shows the sub catchment, land use area and land use percentages of sample site 1: site B5 Blesbokspruit at Welgedacht inflow. This is the first water sampling site for this research project. The map below, therefore, describes the upstream land use areas that influence the Blesbokspruit wetland. The pie chart indicates that residential areas (38%), open vegetated land (28%), agriculture (21%) and mine dumps (6%) account for most of the land use upstream of site 1. There is a large mine dump and a water treatment plant (shown with a dark black dot) upstream from this site.

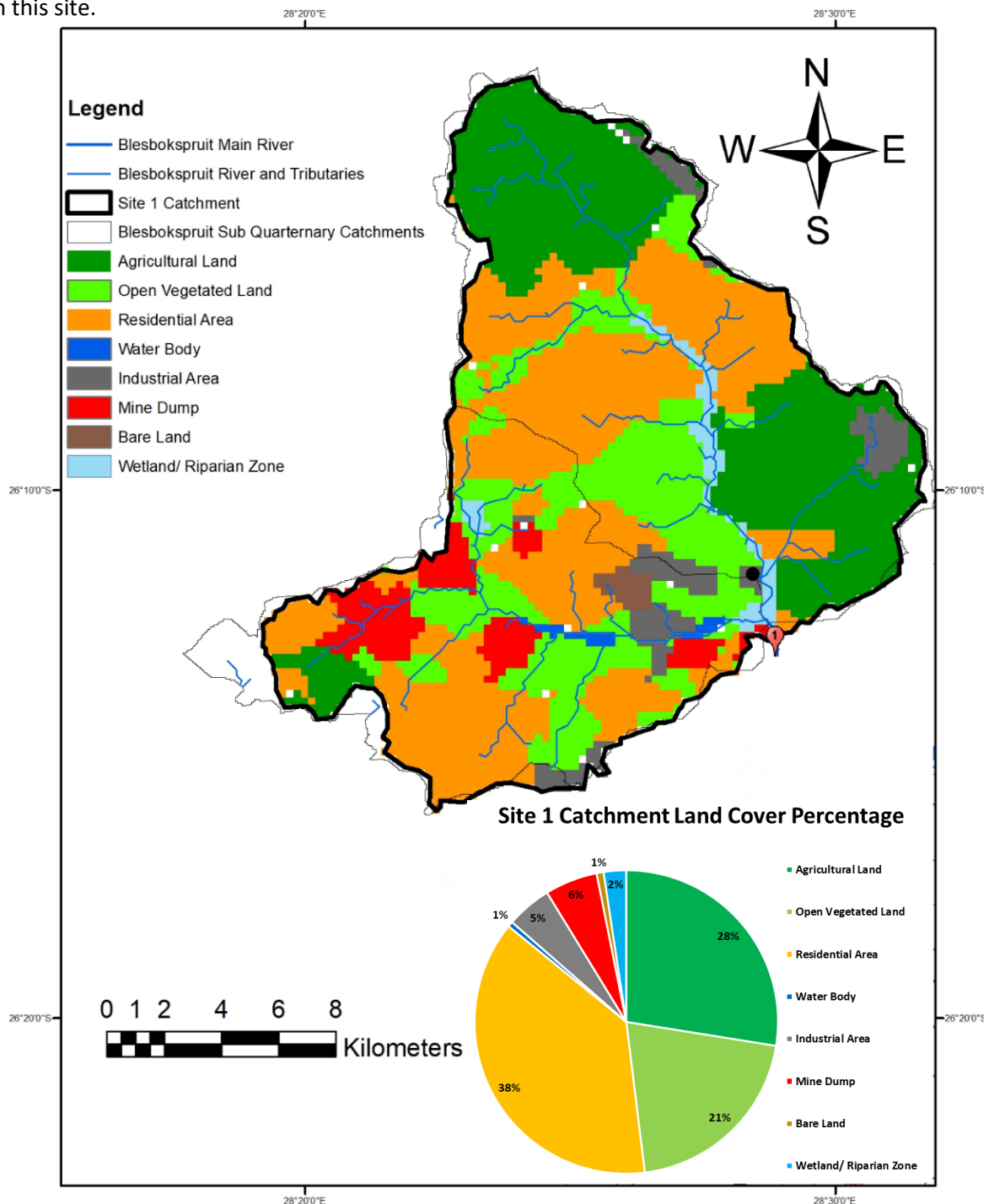


Figure 21: Sub catchment of site 1 land use map and land cover percentage

6.1.3.2 Sub catchment of sample site 2 and land use map

The following map shows the sub catchment and land use area of sample site 2: B16 Blesbokspuit at Grootvlei Mine Train Bridge. This site is downstream of the Eastern Basin AMD treatment plant. As shown in the map below, the sub catchment for sample site 2 includes the upstream sub catchment of sample site 1. This is the case for all the remaining sub catchments from sites 1 to 8. The pie chart indicates that residential areas (37%), agriculture (28%), open vegetated land (20%) and mine dumps (6%) account for most of the land use upstream of site 2. The land use cover is similar to the land use percentages for site 1 previously.

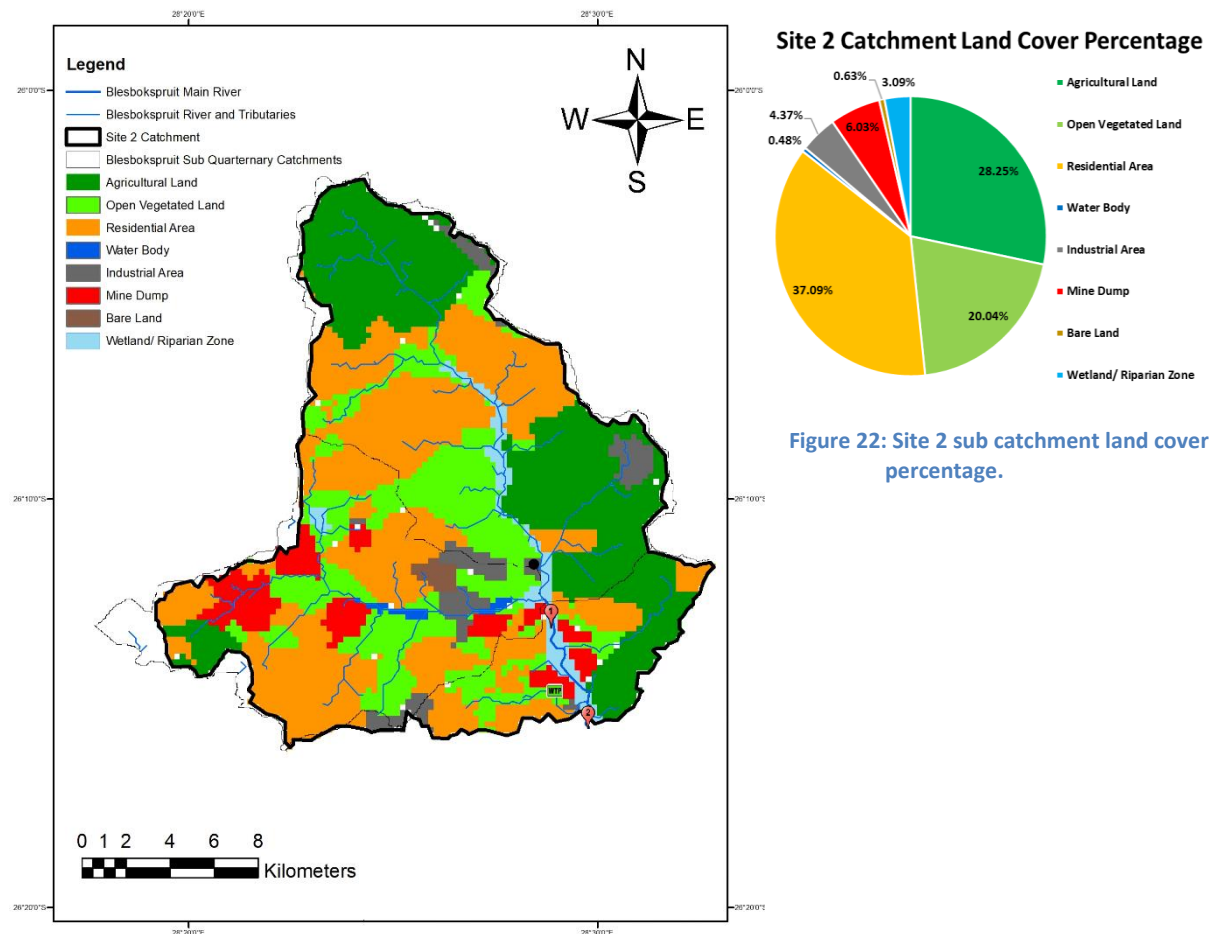


Figure 22: Site 2 sub catchment land cover percentage.

Figure 23: Sub catchment of site 2 and land use map.

6.1.3.3 Sub catchment of sample sites 3 and 4, and land use maps

The map shown on the next page (figure 25) is a map of the sub catchment and land use area of sample site 3: site B15 Blesbokspuit on N17 toll road in Springs. This site is also downstream of the Eastern Basin AMD treatment plant. The pie chart indicates that residential areas (39.5%), agriculture (25%), open vegetated land (20%) and mine dumps (6.5%) account for most of the land use upstream of site 3. There is a third water treatment plant that is included within this sub catchment (shown with a black dot west of sample site 3). Figure 27 is the map of the sub catchment of site 4: Marievale Bridge. The land use class percentages for the site 4 sub catchment is different to site 3. Residential areas which occupy 39.5% at site 3, only occupy 30.5% of site 4 sub catchment. Agricultural land occupies 25% at site 3 and occupies 40.92% of site 4 sub catchment. These two maps with the respective land use percentages can be seen on the following page.

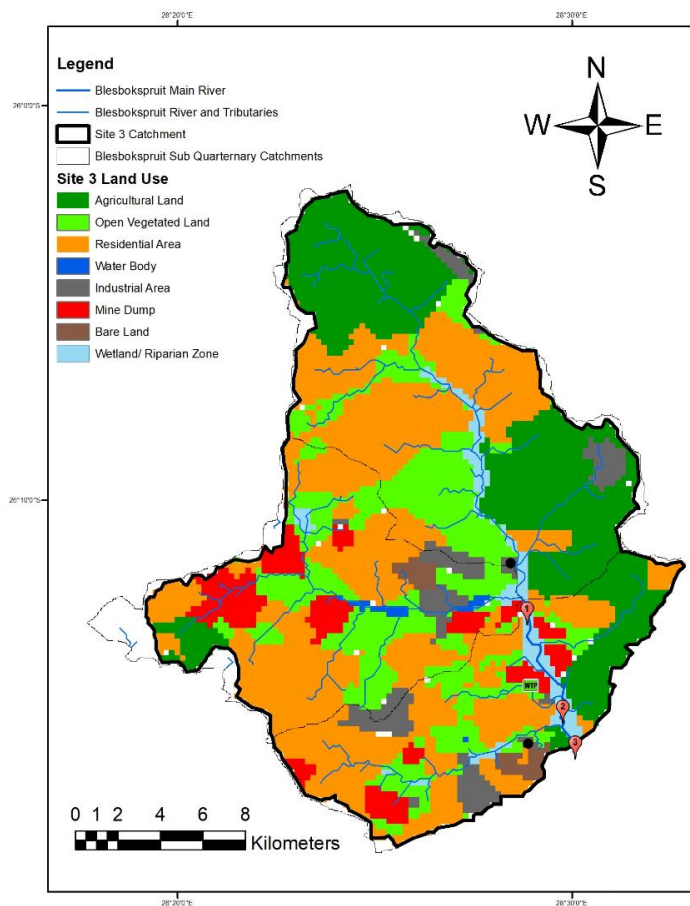


Figure 25: Sub Catchment of sample site 3 and land use map

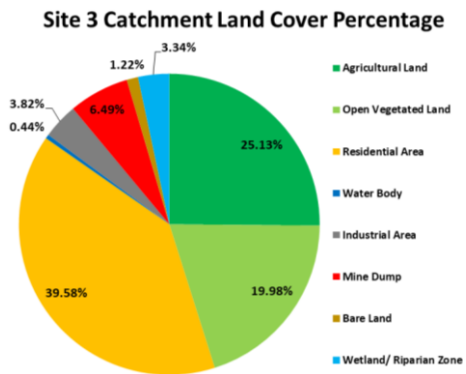


Figure 24: Sample site 3 sub catchment land cover

The differences between site 3 and site 4 sub catchment areas are demonstrated by the respective sub catchment maps and pie charts. Agricultural land occupies a larger percentage than residential areas at catchment 4. There is a clear increase in agricultural land use percentage between these two catchments. Agricultural land has increased at the expense of residential areas between site 3 and site 4 catchment areas.

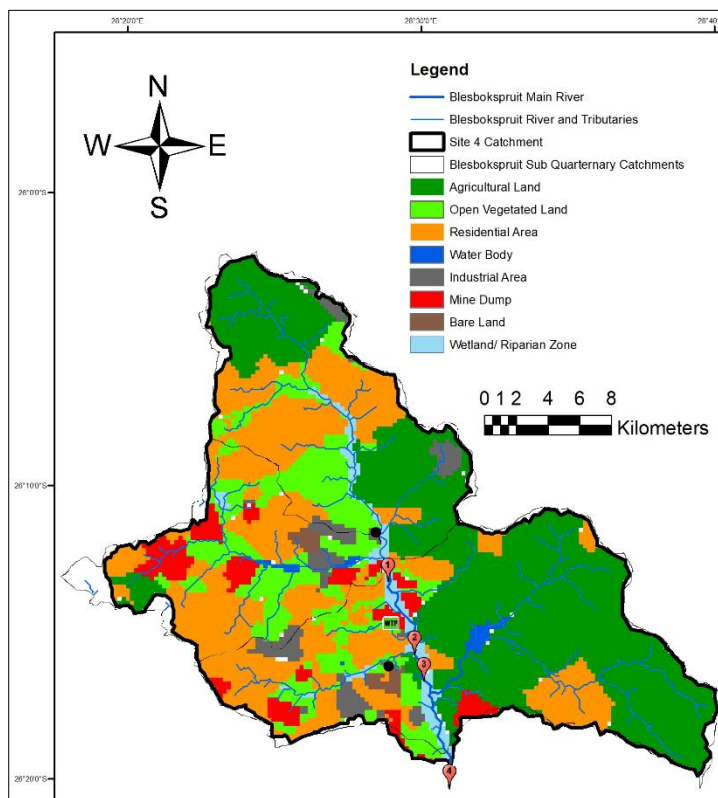


Figure 27. Sub catchment of sample site 4 and land use map

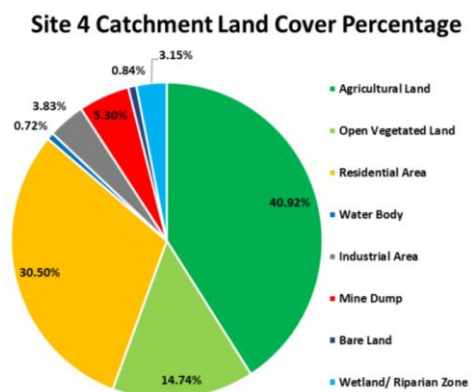


Figure 26: Sample site 4 sub catchment land cover percentage

6.1.3.4 Sample Sites 5, 6 and 7 land cover percentage

The sub catchments of sites 5,6 and 7 are similar to the site 4 catchment on the previous page, and these will not be shown to avoid repetition. However, the pie charts for these three site catchments is shown below in figure 28.

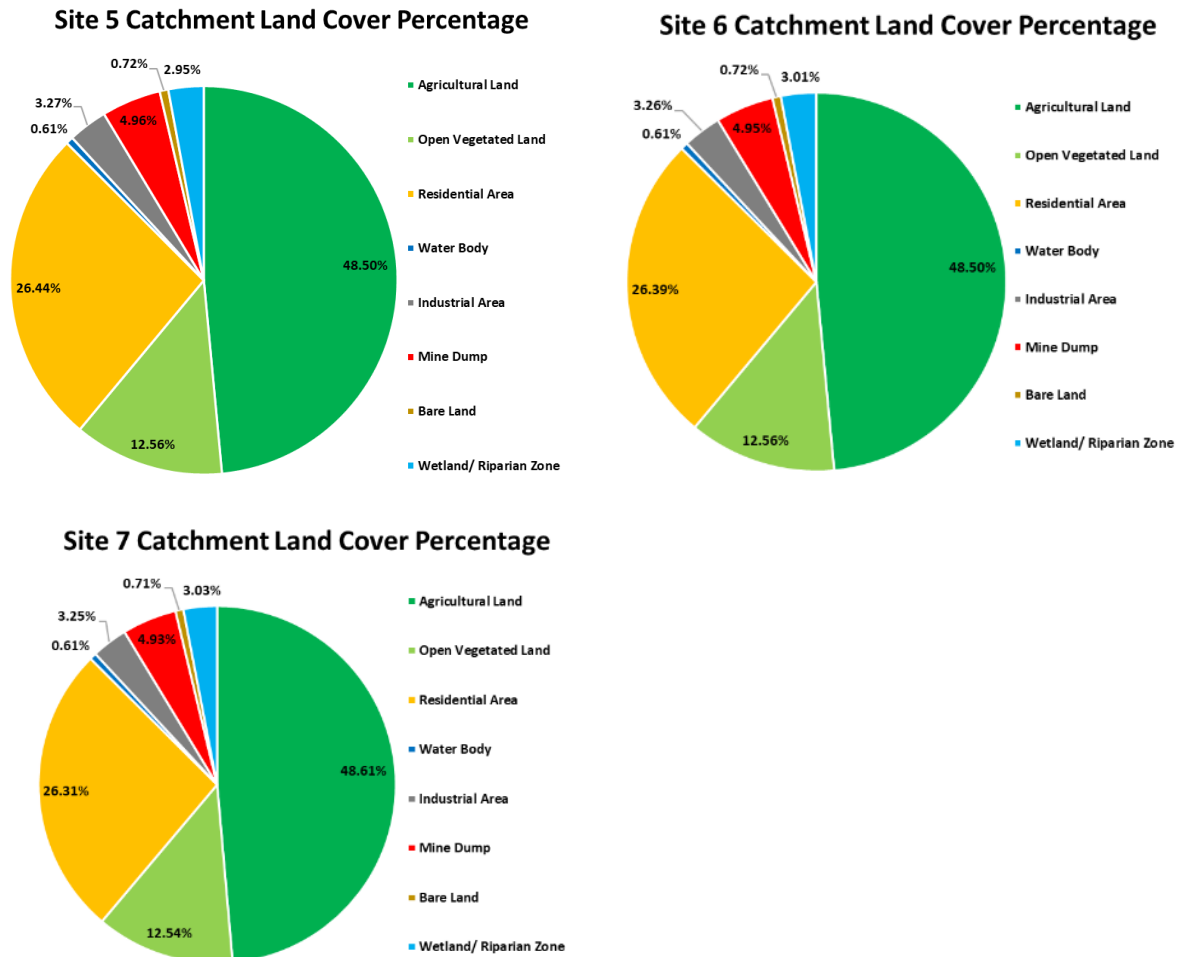


Figure 28: Land use percentage of site 5,6 and 7 sub catchments

According to the pie charts, agriculture for these three site catchments is approximately 48.5%. Residential areas occupy 26.4 % of these catchment areas and open vegetated land occupies 12.5%. Mine dumps occupy 5% of the catchment area. The final site catchment is site 8 which is shown on the next page. The site 8 map represents the accumulation of catchments of all the sites before site 8. Therefore, the land use percentage of site 8 describes the entire land use for the Blesbokspruit wetland study area.

6.1.3.5 Sample site 8 sub catchment and land use map:

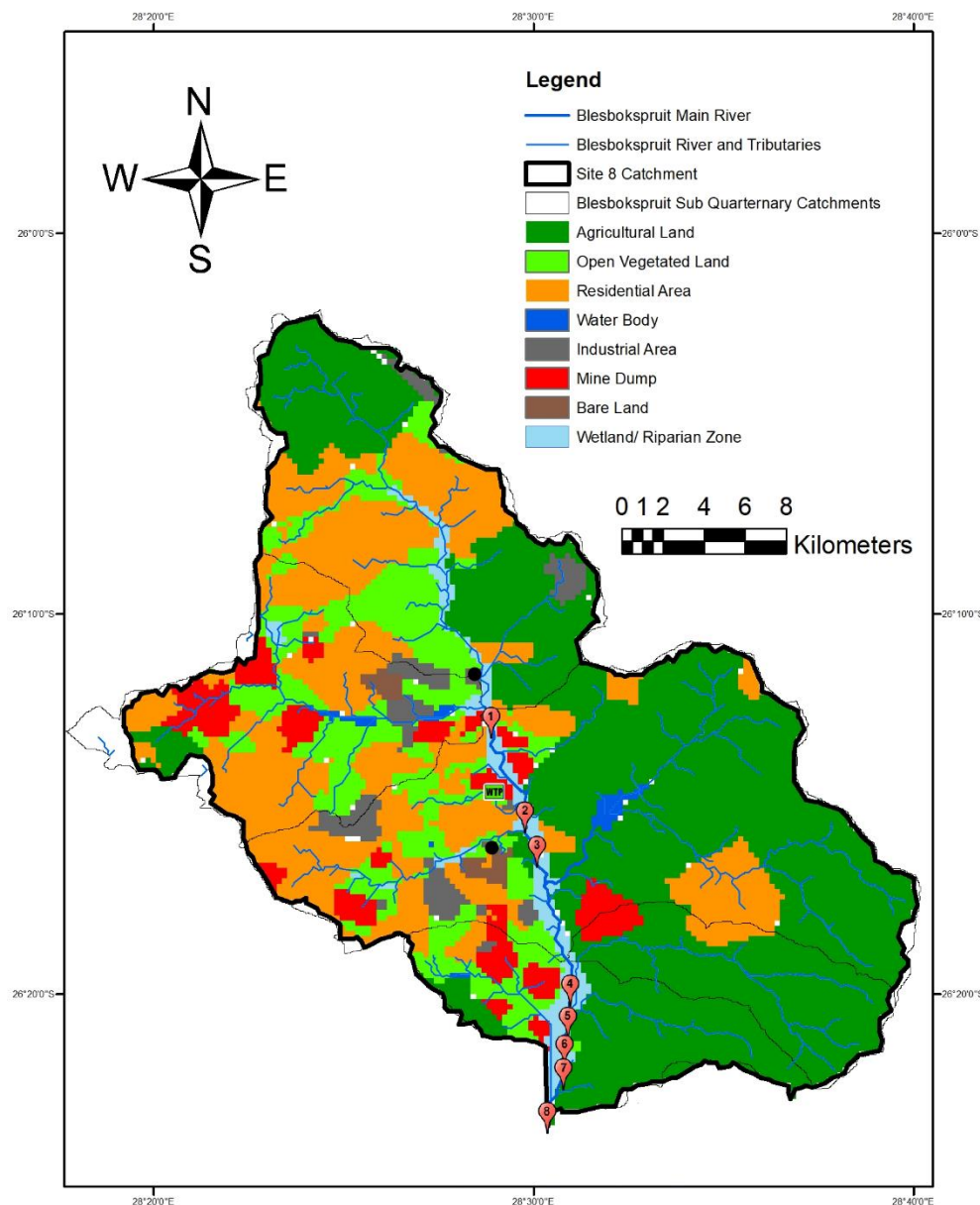


Figure 29: Sample site 8 sub catchment and land use

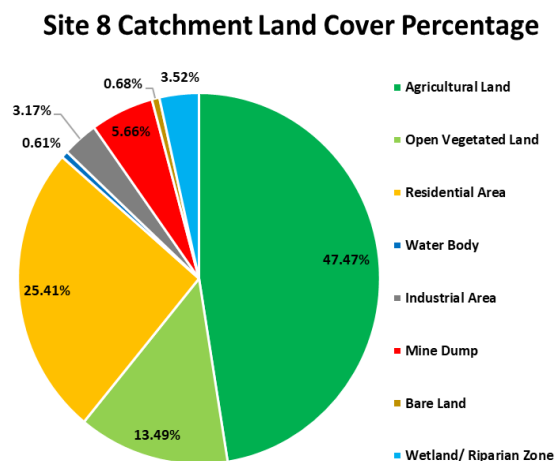


Figure 30: Site 8 sub catchment land cover percentage

This map represents the sub catchment of site 8. The land use percentage of site 8 describes the entire land use for the study area (Blesbokspuit wetland). Agriculture (47.47%), residential (25.41%), open vegetated land (13.49%) and mine dumps (5.66%) make up the bulk of the catchment areas land use. A summary table for each of the site sub catchments and the Blesbokspuit catchment is shown on the following page.

6.1.4 Summary of the land use cover percentages

Table 3: Summary table for the land use/ land cover percentages for each of the sample site sub catchments and the entire catchment area.

	Sample site sub catchments								DWS tertiary catchment area
Land Use Classes	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	DWS Blesbokspruit
Agricultural Land	28%	28%	25%	41%	49%	49%	49%	47%	46%
Open Vegetated Land	21%	20%	20%	15%	13%	13%	13%	13%	25%
Residential Area	38%	37%	40%	30%	26%	26%	26%	25%	19%
Water Body	1%	0%	0%	1%	1%	1%	1%	1%	1%
Industrial Area	5%	4%	4%	4%	3%	3%	3%	3%	3%
Mine Dump	6%	6%	6%	5%	5%	5%	5%	6%	4%
Bare Land	1%	1%	1%	1%	1%	1%	1%	1%	1%
Wetland/ Riparian Zone	2%	3%	3%	3%	3%	3%	3%	4%	2%

Percentages are rounded off to the nearest percent*

The summary table above shows the land use class percentages for each sample site sub catchment sample site catchment and the for the DWS tertiary catchment for the Blesbokspruit. The most significant land use areas within the DWS tertiary catchment area is land used for agriculture, open vegetated land, residential areas, industrial areas and mine dumps. Agricultural land occupies the highest percentage of land use in the DWS tertiary catchment area. With reference to the site sub catchments, agricultural land occupies between 25% and 28% of the land cover at site 1,2 and 3 sub catchments. This increases to 41% at site 4 sub catchment and increase further to 49% at site 5,6 and 7 sub catchment areas and 47% for the site 8 sub catchment. Residential land cover for site 1,2 and 3 sub catchments range between 37% and 40%, and this decreases to 30% for site 4 sub catchment. Site 5 to 8 sub catchment areas have very similar residential cover of 26%. Open vegetated land is at 21% at site 1 sub catchment and decreases to 13% at site 8 sub catchment. The increase of agricultural land between sub catchment sites 1-3 and sub catchment sites 4-8 was at the expense of residential areas and open vegetated land as seen in the summary table above. Both industrial areas and mine dumps have a small range from site 1-8 catchment areas. The role of land use with regards to water and sediment quality will be discussed in the discussion chapter which follows after the water, sediment and soil quality results.

6.2 Water quality results

6.2.1 Rand Water data results

The Rand Water data that is used for the purpose of this research project was published quarterly on *The Reservoir Website*. As mentioned, the data are used to provide for historical and current water quality across the Blesbokspuit wetland. The influence of the Eastern Basin AMD treatment plant is determined using this data. Rand water quality data is split into two periods, the period before treatment plant and the period after treatment plant. The AMD treatment plant came into operation in August 2016. Therefore, dates for the period before the AMD treatment plant start at the 2015 1st January to 31st March quarterly report and end at the 1st April to 30 June 2016 quarterly report. Dates for the period after the treatment plant start from the 1st July to 30th September 2016 quarterly report and finish at the 1st January to 31st March 2019 water quality report. The Rand Water sites 2,3,4 and 5, which are downstream of the Eastern Basin AMD treatment plant, have before and after dates which are used for comparison. The first statistical analysis involved producing summary statistics on the data.

6.2.1.1 Rand Water data summaries

The following data summaries include data from all five historical Rand Water sampling sites. Data summaries include the mean, median, minimum and maximum for each site. The colours of the blocks within the data summaries correspond to the in-stream water quality management targets for the Blesbokspuit Catchment set by the Blesbokspuit Forum shown in figure 6 on page 17.

Table 4: Blesbokspuit Forum water quality management level targets.

Ideal Catchment Background	Acceptable Management Target	Tolerable Interim Target	Unacceptable
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Site 1: Data summary for B5 Blesbokspuit at Welgedacht Inflow into the wetland. This summary includes data from 2015 1st January- 31st March quarterly report to the 2019 1st January-31st March 2019 water quality report. This site is upstream of the treatment plant, therefore data summaries are not separated in a before and after treatment plant comparison.

Table 5: Data summary for site 1: Rand Water site B5 Blesbokspuit at Welgedacht Inflow into the wetland

Site 1. B5 Blesbokspuit at Welgedacht Inflow into the Wetland				
Physical Variables (units)	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	70.65	69	51	99
Dissolved Oxygen (mg/L)	2.12	2.6	0.5	4.5
pH	7.44	7.5	6.3	7.8
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Aluminium	0.06	0.05	0.01	0.15
Ammonium	2.36	2.07	0.34	4.72
Chloride	67.00	63	44	97
Fluoride	0.32	0.25	0.18	0.85
Iron	0.30	0.24	0.07	0.8
Magnesium	17.18	17	11	26
Manganese	0.32	0.32	0.1	0.56
Nitrate	1.13	0.9	0.34	3.83
Phosphate	1.00	0.86	0.46	3.25
Sodium	66.65	70	8	98
Sulphate	116.41	112	49	259

According to the data summary on the previous page, for site 1, the mean for dissolved oxygen and phosphate are both unacceptable. On average, sodium, sulphate, chloride and ph are described as ideal, and conductivity and ammonium are described as tolerable on average. The remaining elements fall into the acceptable management targets on average. This site is extremely important as it is the first sampling site which marks the most upstream site for the Blesbokspruit Wetland. Poor water quality at this site impacts on water quality seen downstream.

Site 2: Data summary for B16 Blesbokspruit at Grootvlei Mine Train Bridge. This summary includes a mean, median, minimum and maximum for each water quality parameter for the period before and after the Eastern Basin AMD treatment plant came into operation. This site is, therefore, downstream of the AMD treatment plant. The before and after treatment plant data summaries have been completed the same way for this site and the remaining three Rand Water sampling sites (3, 4 and 5) as they are all downstream of the AMD treatment plant.

Table 6: Data summary for site 2: Rand Water site B16 Blesbokspruit at Grootvlei Mine Bridge.

S2 (Before and After TP)	Mean		Median		Minimum		Maximum	
Physical Variables (units)	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Conductivity (mS/m)	81	123.36	82	124.0	62	81	102	182
DO (mg/L)	5.15	3.41	5.20	4.00	3.30	0.70	7.30	5.70
pH	7.55	7.55	7.50	7.50	7.50	7.40	7.70	8.00
Major Ions (mg/L)	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Aluminium	0.02	0.03	0.02	0.03	0.01	0.03	0.03	0.07
Ammonium	1.93	0.71	1.92	0.35	1.07	0.11	3.05	4.34
Chloride	62.67	82.27	64.5	78	39	65	83	110
Fluoride	0.34	0.37	0.31	0.30	0.29	0.21	0.43	0.82
Iron	0.11	0.10	0.095	0.08	0.09	0.03	0.14	0.25
Magnesium	18.17	35.82	20	38.0	12	20	23	48
Manganese	0.41	0.23	0.43	0.22	0.11	0.07	0.60	0.57
Nitrate	1.27	0.96	0.86	0.9	0.21	0.54	3.83	1.77
Phosphate	1.11	0.67	1.26	0.58	0.48	0.42	1.69	1.18
Sodium	73.17	95.09	77.00	88.0	41	64	110	132
Sulphate	110.50	342.73	111.50	278	42	99	165	857

*Before TP = period before treatment plant. After TP= period after treatment plant

The summary statistics table above are important as they describe the influence that the AMD treatment plant has had on site 2 which directly downstream from the discharge point of the treatment plant. In terms of negative influences by the AMD treatment plant, on average, conductivity has increased from a tolerable level for the period before the treatment plant to an unacceptable level after treatment plant at this site. Conductivity has clearly increased at this site for the period after the treatment plant when looking at the mean, median, minimum and maximum. Sulphate has also increased from an ideal level before the treatment plant to a tolerable level after the treatment plant on average. The maximum value for sulphate for the period after the treatment plant is 857 mg/L which exceeds the unacceptable level by a large margin of 357 mg/L. On average, chloride and magnesium means have also increased (management target level worsened) for the

period after the treatment plant. The increase in conductivity, chloride, magnesium and sulphate levels were expected due to the manner in which the AMD water is treated at the treatment plant. Once the AMD water that comes from underground is treated, and the sludge is subsequently disposed of underground, a clean overflow of water is produced, and this is discharged into the wetland area downstream (Solomons, 2017). This clean overflow has high levels of conductivity and as a result, have caused conductivity to reach an unacceptable management target. Conductivity relates to chloride, magnesium and sulphate concentrations within the water and the discharge of effluent by the treatment plant has also caused increases in chloride, magnesium and sulphate downstream at site 2. Dissolved oxygen has decreased on average for the period after the treatment plant and is also at an unacceptable level. In terms of positive influences of the AMD treatment plant, both iron and manganese means have improved for the period after the treatment plant. The improvement of iron and manganese was mentioned within media reports in the literature review. Although phosphate is unacceptable on average, it has decreased on average between periods before and after the treatment plant. Noticeability, ammonium and nitrate have also decreased on average for periods before and after the treatment plant. This could signify that as a result of the treatment processes at the treatment plant, the metals of iron and manganese and the nutrients of phosphate, ammonium and nitrate are becoming less concentrated downstream. The reason for the reduction in concentration of these nutrients could be as a result of dilution and increased flow caused by the discharge of the clean overflow by the AMD treatment plant upstream of this site.

Site 3: B15 Blesbokspuit on N17 toll road in Springs. This site marks as the sampling site upstream of the Marievale Bird Sanctuary wetland.

Table 7: Data summary for site 3: Rand Water site B15 Blesbokspuit on N17 toll road in Springs.

S3 (Before and After TP)	Mean		Median		Minimum		Maximum	
Physical Variables (units)	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Conductivity (mS/m)	77.50	123.64	77	122	60	88	96	167
DO (mg/L)	4.58	3.23	4.75	2.70	2.60	0.60	5.90	5.90
pH	7.63	7.56	7.65	7.50	7.50	7.50	7.90	7.80
Major Ions (mg/L)	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Aluminium	0.02	0.04	0.025	0.03	0.01	0.03	0.03	0.12
Ammonium	0.76	0.61	0.89	0.21	0.13	0.05	1.10	4.13
Chloride	63.00	75.36	65.00	85	47	33	78	115
Fluoride	0.35	0.32	0.36	0.28	0.23	0.19	0.44	0.67
Iron	0.06	0.07	0.045	0.05	0.03	0.01	0.10	0.23
Magnesium	18.00	33	19	32	12	20	23	46
Manganese	0.51	0.22	0.47	0.16	0.11	0.09	1.31	0.60
Nitrate	1.44	0.65	0.98	0.63	0.32	0.30	3.62	0.91
Phosphate	1.15	0.66	1.16	0.58	0.59	0.43	1.80	1.04
Sodium	71.00	130.45	72.00	89	42	61	102	557
Sulphate	97.33	324.00	99.00	265	61	136	138	703

The summary statistics above are important as they describe the influence that the AMD treatment plant has had on site 3, which is upstream of the Marievale Bird Sanctuary wetland. In terms of

negative influences, on average, both conductivity and sulphate have increased for the period after the treatment plant. This is a similar increase seen upstream at site 2 indicating that upstream water quality has directly impacted on sulphate and conductivity levels downstream at site 3. On average, conductivity has worsened from a tolerable level to an unacceptable level and sulphate has worsened from an ideal level to a tolerable level. The maximum value of sulphate for the period after the treatment plant is extremely high at 703 mg/L. This high sulphate value was tested during the same quarter as the high sulphate value that was mentioned previously at site 2. This high value occurred during quarter 3 of 2018: 1 July to 30 September. On average, sodium and magnesium both worsened from an acceptable level to a tolerable level. The dramatic increase of sodium was not seen at site 2. Sodium levels increased only slightly at site 2. This dramatic increase could indicate that a source of pollution promoting sodium levels lies downstream of site 2 and upstream of site 3. This increase in sodium also occurred for the period after the treatment plant, indicating that this point source of pollution is a recent occurrence. Dissolved oxygen levels decreased for periods after the treatment plant and are still described as unacceptable. Positive influences indicate that ammonium, phosphate and nitrate values decreased on average. Manganese also improved for this site on average to an acceptable management target for the period after the treatment plant, and iron had maintained an ideal management target. This could be attributed to what was seen at site 2 whereby the discharge of the treatment plant dilutes concentrations of these metals and nutrients and this evidence is seen further downstream at site 3. As seen for this site and the previous two sites, pH means are described as ideal for periods before and after treatment plant.

Site 4: B17 Blesbokspruit at Marievale Bird Sanctuary. This site is in the centre of the Marievale Bird Sanctuary.

Table 8: Data summary for site 4: Rand Water site B17 Blesbokspruit at Marievale Bird Sanctuary.

S4 (Before and After TP)	Mean		Median		Minimum		Maximum	
Physical Variables (units)	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Conductivity (mS/m)	83.33	135.18	81	127	67	102	101	178
DO (mg/L)	5.9	2.48	5.65	1.8	2.9	0.7	10.5	6.1
pH	7.816	7.67	7.85	7.7	7.6	7.5	8	7.8
Major Ions (mg/L)	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Aluminium	0.023	0.03	0.03	0.03	0.01	0.03	0.03	0.03
Ammonium	0.28	0.16	0.25	0.15	0.08	0.05	0.5	0.63
Chloride	69.2	91.27	62	88	50	65	96	122
Fluoride	0.3467	0.41	0.37	0.25	0.28	0.22	0.38	0.91
Iron	0.0533	0.04	0.03	0.02	0.02	0.01	0.18	0.23
Magnesium	20.833	39.18	20.5	40	14	25	27	51
Manganese	0.78	0.39	0.64	0.24	0.16	0.1	1.87	1.39
Nitrate	0.228	0.33	0.24	0.44	0.1	0.07	0.33	0.5
Phosphate	0.846	0.54	0.905	0.57	0.45	0.26	1.15	0.76
Sodium	76.166	140.09	76	94	47	67	101	372
Sulphate	107.166	420.36	111	345	64	237	148	723

This data summary for periods before and after treatment plant at Marievale Bird Sanctuary shows a very similar pattern as those for both sites 2 and 3. In terms of conductivity, sulphate, magnesium and dissolved oxygen, the averages for these parameters have all declined to a worse management target level for periods after the treatment plant. Sodium has increased and moved from an acceptable level to a tolerable level on average. A similar dramatic increase in sodium was identified at site 3 for the period after the treatment plant. As mentioned, this dramatic increase is not seen at site 2 downstream of the treatment plant and therefore, this increase in sodium could be as a result of a recent point source of pollution upstream of site 3. Ammonium, manganese and phosphate have decreased once again, and this may be attributed to the dilution of metals and nutrients seen upstream. Phosphate levels have improved to a tolerable level, this could also be as a result of processes occurring within the wetland whereby wetland plants are using up excess phosphate in the water. On average, pH is described as ideal for this site, this ideal level has been maintained for all the sampling sites upstream to site 4.

Site 5: B11 Blesbokspuit on R42 bridge at Nigel. This is the last Rand Water site used for this research project. This site is significant as it also marks the end of the Marievale Bird Sanctuary Wetland and greater Blesbokspuit Wetland. Water downstream of this site flows past Nigel and Heidelberg and eventually reaches the Vaal system.

Table 9: Data summary for site 5: Rand Water site B11 Blesbokspuit on R42 bridge at Nigel.

S5 (Before and After TP)	Mean		Median		Minimum		Maximum	
	Before TP	After TP	Before TP	After TP	Before TP	After TP	Before TP	After TP
Physical Variables (with units)								
Conductivity (mS/m)	85.83	127.82	81	126	69	67	109	173
DO (mg/L)	7.71	3.25	7.95	2.6	4.5	0.8	10.1	7.4
pH	7.92	7.83	8	7.8	7.6	7.6	8.1	7.9
Major Ions (mg/L)								
Aluminium	0.03	0.04	0.03	0.03	0.01	0.03	0.05	0.08
Ammonium	0.28	0.13	0.25	0.11	0.08	0.04	0.5	0.24
Chloride	75.00	91.09	69	89	54	67	108	117
Fluoride	0.32	0.46	0.32	0.39	0.24	0.22	0.39	1.02
Iron	0.05	0.04	0.03	0.02	0.01	0.01	0.13	0.15
Magnesium	21.83	38.27	21	37	14	25	31	54
Manganese	0.27	0.21	0.15	0.21	0.08	0.05	0.62	0.62
Nitrate	0.26	0.63	0.225	0.46	0.16	0.1	0.42	2.56
Phosphate	0.85	0.54	0.855	0.51	0.58	0.35	1.03	0.77
Sodium	82.50	116.36	79	99	48	66	116	291
Sulphate	110.17	408.82	110.5	372	67	177	162	670

The table above has a very similar results to the data summaries of sites 2, 3 and 4 (upstream) in terms of conductivity, sulphate, chloride, ammonium, phosphate, magnesium, iron, manganese and pH. This demonstrates that the water quality seen at this site is dependent on the water quality upstream. For these parameters, water quality is directly influenced by the AMD treatment plant and this can be attributed to the similar water quality results from site 2 below the treatment plant

to this site (site 5) at the end of the Marievale and greater Blesbokspruit Wetlands. This indicates that the AMD treatment plant has a strong influence on water quality, and that the Marievale wetland has a lesser influence on water quality.

6.2.1.2 Normality test

Hypothesis testing will determine whether there are significant differences between sample sites, and significant differences at individual sites for periods before and after the launch of the treatment plant. In order to test hypothesis, a normality test was conducted on the data to determine whether parametric or non-parametric tests should be performed. The following test was conducted using the NUMXL extension programme in excel. Normality tests were made on the Rand Water data in order to determine if the data follows a normal distribution. Three standard tests (Jarque-Bera, Shapiro-Wilk and Doornik Chi-Square) were performed on each water quality variable and the following results were obtained from the NUMXL programme.

Table 10: Normality test summary for Rand Water quality data.

Water Quality Variable (Rand Water)	Normality Test (H_0 = Follows normal distribution)		
	Jarque-Bera	Shapiro-Wilk	Doornik Chi-Square
Aluminium	Reject	Reject	Reject
Ammonium	Reject	Reject	Reject
Chloride	Reject	Reject	Reject
Conductivity	Reject	Reject	Reject
DO	Reject	Reject	Reject
Fluoride	Reject	Reject	Reject
Iron	Reject	Reject	Reject
Magnesium	Reject	Reject	Reject
Manganese	Reject	Reject	Reject
Nitrate	Reject	Reject	Reject
pH	Reject	Reject	Reject
Phosphate	Reject	Reject	Reject
Sodium	Reject	Reject	Reject
Sulphate	Reject	Reject	Reject

Test interpretation:

Null Hypothesis (H_0): The variable from which the sample was extracted follows a normal distribution.

Alternative Hypothesis (H_a): The variable from which the sample was extracted does not follow a Normal distribution.

Result: As the computed p-value is less than the significance level $\alpha=0.05$ for all the variables, one must reject the null hypothesis, H_0 and accept the alternative hypothesis (H_a). This shows that the data from Rand Water do not follow a normal distribution, and therefore non-parametric tests must be performed on the data.

6.2.1.3 Non-parametric hypothesis tests

Test 1: Comparison of distributions for site 2 (site directly downstream of the AMD treatment Plant) for the periods before and after the launch of the treatment plant. This test is to determine the influence of the treatment plant on site 2. This is a test of two dependent samples, the samples are said to be dependent as the samples come from the same sample site. The two samples differ in the time of sampling (before and after treatment plant). The Wilcoxon signed-rank test / Two-tailed test

is used here. This test is used as the non-parametric equivalent to a parametric t-test for dependent samples. This test is used to determine whether the two samples were selected from populations having the same distribution. This test makes use of the sample medians, and not means which are used in the parametric standard t-test for dependent samples.

Table 11: The Wilcoxon signed-rank test results for all the water quality variables for site 2 before and after treatment plant.

Water Quality Parameter	p-value (Two-tailed)	Null Hypothesis (H_0)
Aluminium	0.059	Accept
Ammonium	0.438	Accept
Chloride	0.031	Reject
Conductivity	0.063	Accept
Dissolved Oxygen	0.292	Accept
Fluoride	0.500	Accept
Iron	0.293	Accept
Magnesium	0.027	Reject
Manganese	0.438	Accept
Nitrate	1.000	Accept
pH	0.257	Accept
Phosphate	0.219	Accept
Sodium	0.141	Accept
Sulphate	0.031	Reject

Test interpretation:

Null Hypothesis (H_0): The two samples follow the same distribution (they have the same median).

Alternative Hypothesis (H_a): The distributions of the two samples are different (they have different medians). If the computed p-value is greater than the level of significance $\alpha=0.05$, one should accept the null hypothesis H_0 . If the p-value is lower than the significance level $\alpha=0.05$, one should reject the null hypothesis (H_0), and accept the alternative hypothesis (H_a).

According to the table above; chloride, magnesium and sulphate are all said to have different populations for periods before and after the launch of the AMD treatment plant at site 2. Different populations may indicate either positive or negative change for periods before and after the treatment plant. In order to establish either a positive or negative influence on water quality parameters, the data summaries shown previously are able to describe means for periods before and after the launch of the treatment plant. The three differing populations mentioned demonstrates the impact of the AMD treatment plant for site 2. All three water quality parameters (chloride, magnesium and sulphate) means increased to an inferior management target level for the period after the treatment plant at site 2.

Although conductivity is said to have the same population in the table above, as mentioned from the data summaries; the mean conductivity for this site had significantly increased to an unacceptable level at site 2 for the period after the launch of the AMD treatment plant. As mentioned from the data summaries, ammonium and phosphate means improved. Chloride, magnesium and sulphate means worsened for the period after the launch of the AMD treatment plant. The remaining variables (including conductivity) have the same populations for periods before and after the launch

of the AMD treatment plant. Overall, the AMD treatment plant has had a positive influence on certain water quality parameters such as manganese, iron and nutrients of ammonium, phosphate, nitrate (through dilution). It has had a negative influence on chloride, magnesium and sulphate, and although not proven to have different populations, conductivity. For the other water quality variables there is no significant influence from the AMD treatment plant.

Test 2: Comparison of distributions for two independent samples. The samples here include site 1 (upstream of the AMD treatment plant) and site 2 (downstream of the AMD treatment plant) for the period after the AMD treatment plant was launched. The test chosen here is a Mann-Whitney test / two-tailed test which is the non-parametric equivalent to the t-test for two independent samples. The samples are said to be independent from one another as each sample represents a different sample site, the samples are relatable by time as data collected from each site was collected on the same day. This test is used to determine if the two independent samples were selected from populations having the same distribution. The test makes use of medians, and not means which are used in the parametric equivalent.

Table 12: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 1 and site 2 for the period after the launch of the treatment plant.

Water Quality variable	p-value (independent samples)	Null Hypothesis (H_0)
Aluminium	0.004	Reject
Ammonium	0.005	Reject
Chloride	0.053	Accept
Conductivity	0.000	Reject
Dissolved Oxygen	0.032	Reject
Fluoride	0.272	Accept
Iron	0.004	Reject
Magnesium	0.0001	Reject
Manganese	0.176	Accept
Nitrate	0.991	Accept
pH	0.138	Accept
Phosphate	0.032	Reject
Sodium	0.006	Reject
Sulphate	0.001	Reject

Test interpretation:

Null Hypothesis (H_0): The difference of location between the samples is equal to 0 (there is no difference between medians).

Alternative Hypothesis (H_a): The difference of location between the samples is different from 0 (there is a difference in medians). If the computed p-value is greater than the level of significance $\alpha=0.05$, one should accept the null hypothesis H_0 . If the p-value is lower than the significance level $\alpha=0.05$, one should reject the null hypothesis H_0 , and accept the alternative hypothesis H_a .

According to the results in the table above; aluminium, ammonium, conductivity, dissolved oxygen, iron, magnesium, phosphate, sodium and sulphate all reject the null hypothesis and accept the alternative hypothesis. The other variables all accept the null hypothesis. Comparison of populations between site 1 and site 2 have again provide evidence of the strong influence of the Eastern Basin AMD treatment plant. Conductivity, sodium, magnesium and sulphate (all relate to one another) means increased between site 1 and 2 and this is attributed to the discharge by the AMD Treatment

plant. Ammonium, nitrate and phosphate levels improved through dilution as mentioned. Iron improved to an ideal level at site 2 for the period after the launch of the treatment plant. It is clear that there are multiple influences on water quality caused by the AMD treatment plant, and these influences are both positive and negative.

Test 3: Comparison of distributions between site 3 and site 5 for the period before the AMD treatment plant launched. Site 3 is upstream to the Marievale Wetland and site 5 is directly downstream of the Marievale wetland. This test, therefore, assesses the role of the wetland in improving water quality in the period before the launch of the treatment plant. The test is also a Mann-Whitney test / two-tailed test for independent samples.

Table 13: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 3 and site 5 for the period before the treatment plant.

Water quality variable	p-value (independent samples)	Null Hypothesis (H_0)
Aluminium	0.426	Accept
Ammonium	0.022	Reject
Chloride	0.394	Accept
Conductivity	0.485	Accept
DO	0.017	Reject
Fluoride	0.558	Accept
Iron	0.089	Accept
Magnesium	0.372	Accept
Manganese	0.370	Accept
Nitrate	0.009	Reject
pH	0.065	Accept
Phosphate	0.310	Accept
Sodium	0.485	Accept
Sulphate	0.485	Accept

The test interpretation is the same as that seen for test 2 previously. According to the table, ammonium, dissolved oxygen and nitrate do not accept the null hypothesis. These three water quality variables all improved on average between site 3 and site 5 for the period before the treatment plant. Ammonium and nitrate levels were reduced on average and this can be attributed to wetland plants taking up these essential nutrients. Ammonium and nitrate, in general, are not of major concern as they maintain an acceptable management target. Dissolved oxygen also improved on average between site 3 and 5 indicating that more oxygen became available within the water as it flowed through the wetland. All the other variables do accept the null hypothesis. This test demonstrates further that the Marievale Wetland has a small, but positive influence on water quality for the period before the launch of the AMD treatment plant. Although only having a small influence, the role of the wetland should not be overlooked.

Test 4: Comparison of distributions between site 3 and site 5 for the period after the treatment plant launched. Site 3 is upstream to the Marievale Wetland and site 5 is directly downstream of the Marievale wetland. This test, therefore, assesses the role of the wetland in improving water quality in the period after the launch of the treatment plant. The test is also a Mann-Whitney test / two-tailed test for independent samples.

Table 14: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 3 and site 5 for the period before the treatment plant.

Water Quality Variable	p-value (independent samples)	Null Hypothesis (H ₀)
Aluminium	0.655	Accept
Ammonium	0.078	Accept
Chloride	0.107	Accept
Conductivity	0.595	Accept
DO	0.970	Accept
Fluoride	0.134	Accept
Iron	0.060	Accept
Magnesium	0.291	Accept
Manganese	0.733	Accept
Nitrate	0.018	Reject
pH	0.000	Reject
Phosphate	0.166	Accept
Sodium	0.340	Accept
Sulphate	0.263	Accept

The test interpretation is the same as that seen for test 2 and test 3 previously. The results indicate that only nitrate and pH do not share the same distribution between site 3 (upstream to the Marievale Wetland) and site 5 (downstream to the Marievale Wetland) for the period after the launch of the new AMD treatment plant. Nitrate was said to have improved between site 3 and site 5 before the launch of the treatment plant. For the period after the treatment plant nitrate has improved only slightly between site 3 and site 5, but it is still within the acceptable management target range. This slight improvement could be due to nitrate levels being reduced further upstream through dilution due the processes of the treatment plant. pH, as mentioned, maintains an ideal management level throughout the Blesbokspruit. Considering that only two water quality variables have differing populations, this test demonstrates that the Marievale wetland has a small influence on water quality compared to the AMD treatment plant. Water quality at these two sampling points is highly influenced by the processes occurring upstream at the treatment plant. In general, water quality parameters do not improve or worsen significantly when passing through the wetland. As mentioned, the role of the wetland should not be overlooked but the high influence of the AMD treatment plant should be noted.

6.2.1.4 Time-series graphs (Rand Water data)

Time-series graphs for each Rand Water quality parameter have been made. These graphs help show whether certain water quality parameters are meeting the required management targets for each sampling site. All 5 Rand Water sample sites are shown on the graphs, and comparisons can be made between sample sites. As there are 14 water quality parameters, only the concerning parameters that lie within the unacceptable and tolerable management target ranges will be shown within the main text, the remaining time-series graphs are shown in the appendix chapter.

Rand Water conductivity time-series graph

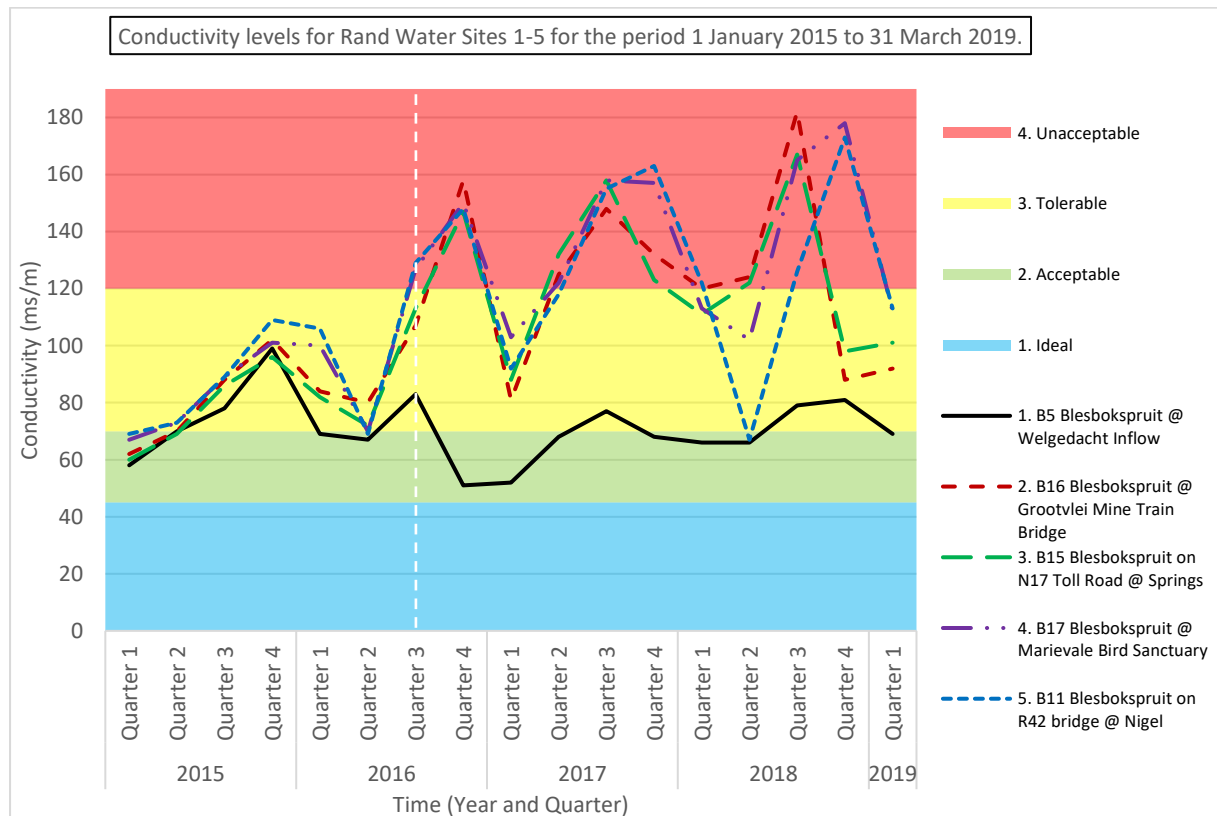


Figure 31: Conductivity levels for Rand Water Sites 1-5 for the period 1 January 2015 to 31 March 2019.

The time-series graph above shows conductivity levels at each of the 5 Rand Water sampling sites. The dotted white line indicates the quarter in which the AMD treatment plant had started, quarter 3 2016, as the plant became operational during August 2016. Site 1, the Welgedacht inflow (black line) which is upstream of the treatment plant is shown to have similar conductivity levels compared to sites 2,3,4 and 5 during the period before the treatment plant became operational. There is an increasing shift in conductivity levels at the start point of the AMD treatment plant. It is noteworthy that conductivity levels reach the unacceptable management target only after the treatment plant becomes operational, and only at sites which are downstream of the treatment plant. The conductivity for the period after the treatment plant is shown to be extremely high and having an increasing trend for all sample sites except site 1. The conductivity raises significantly between sites 1 and 2 especially after the AMD treatment plant became operational. There is direct evidence that processes occurring between sites 1 and 2 are increasing conductivity levels. The explanation for this is increase believed to be due to the discharge from the AMD treatment plant, which was expected

from the literature. What is noticeable is that sites 2,3,4 and 5 all mirror one another to a certain extent. This demonstrates that the wetland has a much lower influence on reducing conductivity between sites 2 and 5. The conductivity is highly influenced by the processes occurring between sites 1 and 2, at the AMD treatment plant, and this influence spreads far downstream to site 5.

Rand Water sulphate time-series graph

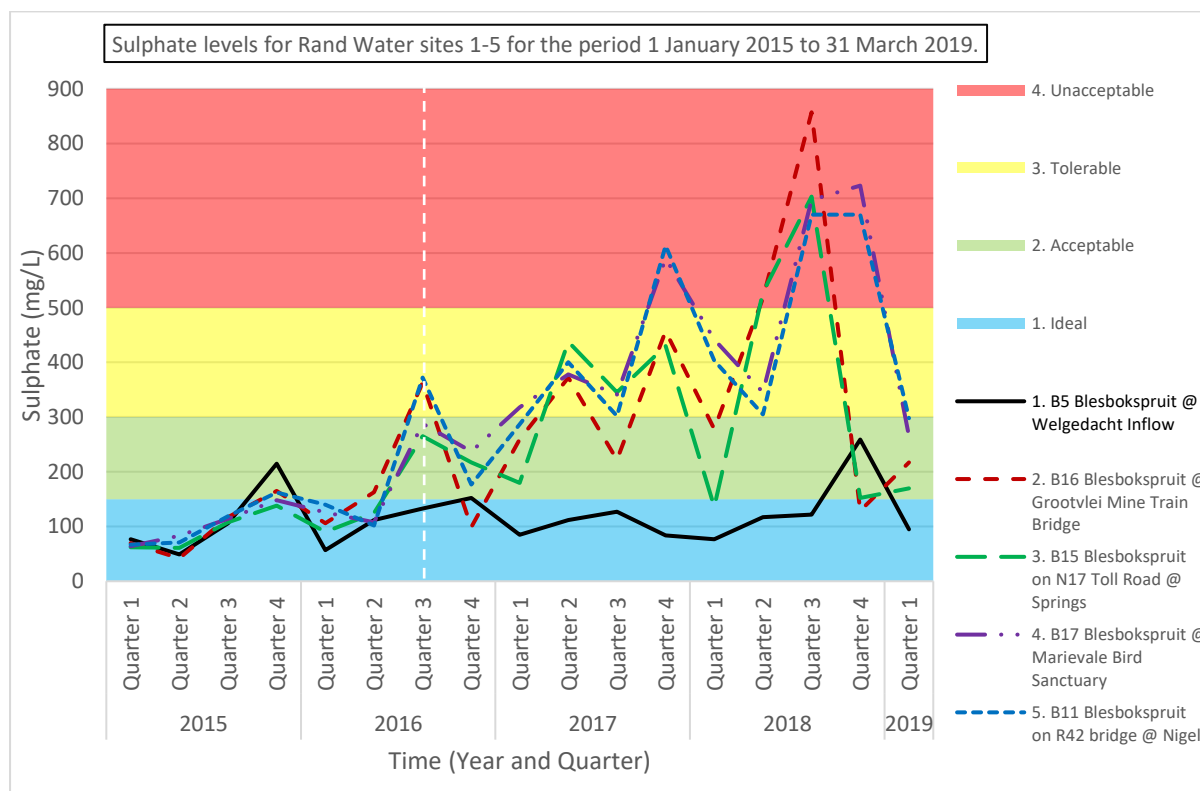


Figure 32: Sulphate levels for Rand Water sites 1-5 for the period 1 January 2015 to 31 March 2019.

The graph above shows the sulphate levels for each of the five Rand Water sites. The dotted white line represents that start of the AMD treatment plant. This graph demonstrates a similar pattern to what was seen in the conductivity time-series graph previously. The solid black line indicating site 1 is between ideal and acceptable management targets over the entire time period. The other four sites have higher sulphate levels than the inflow site and they all eventually reach unacceptable levels over time. As high levels of conductivity can be attributed to high sulphate levels, it is reasonable to suggest that the processes promoting increased conductivity are also responsible for increased sulphate. A definite spike in sulphate level is shown at sites 2,3,4 and 5 at the launch of the treatment plant, and sulphate levels increase dramatically over time after the launch of the AMD treatment plant. Sites 2,3,4 and 5 mirror one another to a certain extent, which demonstrates that the wetland has a small influence on sulphate levels. The mirroring of each wetland site suggests again that processes occurring between site 1 and site 2 at the treatment plant are having a large impact on the sulphate content seen downstream.

Rand Water sodium time-series graph

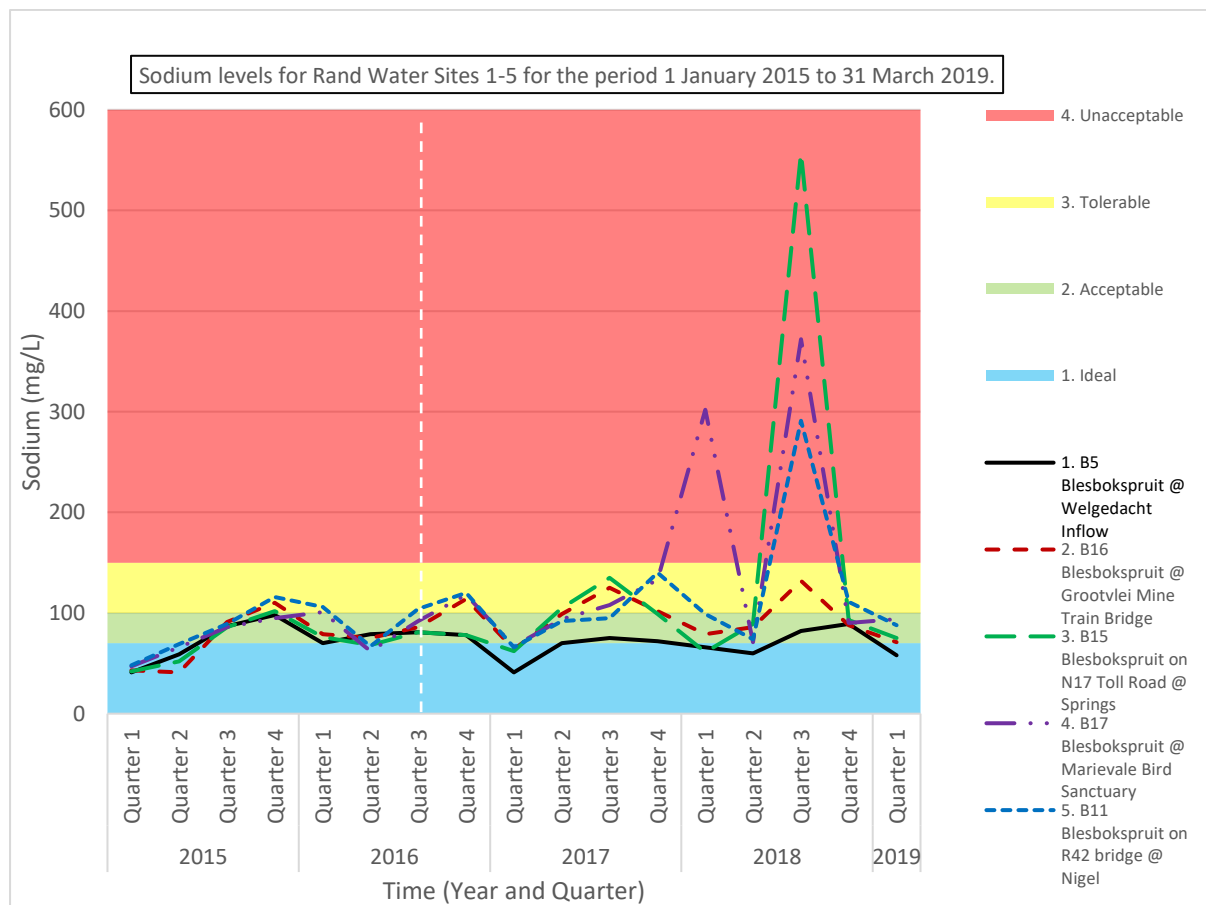


Figure 33: Sodium levels for Rand Water Sites 1-5 for the period 1 January 2015 to 31 March 2019.

The sodium time series graph shows how, in general, sodium values maintain an ideal to tolerable management target. It is clear to see that sodium increased to an unacceptable level during the year 2018. What is significant is that this increase is only seen for sites 3,4 and 5 and not sites 1 and 2. This indicates that a point source of pollution was promoting high levels of sodium upstream of site 3 during 2018. It is difficult to identify exactly what process is responsible for this point source of pollution when looking at the sub catchment land use maps for Rand Water sites 3,4 and 5 due to multiple land use classes within these sub catchments. Point sources of pollution cannot only be attributed to Grootvlei mine/ other mine dumps, the pollution sources can occur anywhere throughout the catchment area which contains residential, industrial and agricultural land use and processes. This gives further evidence to the complexity of the Blesbokspuit wetland catchment, especially with regards to changes in water quality.

Rand Water phosphate time-series graph

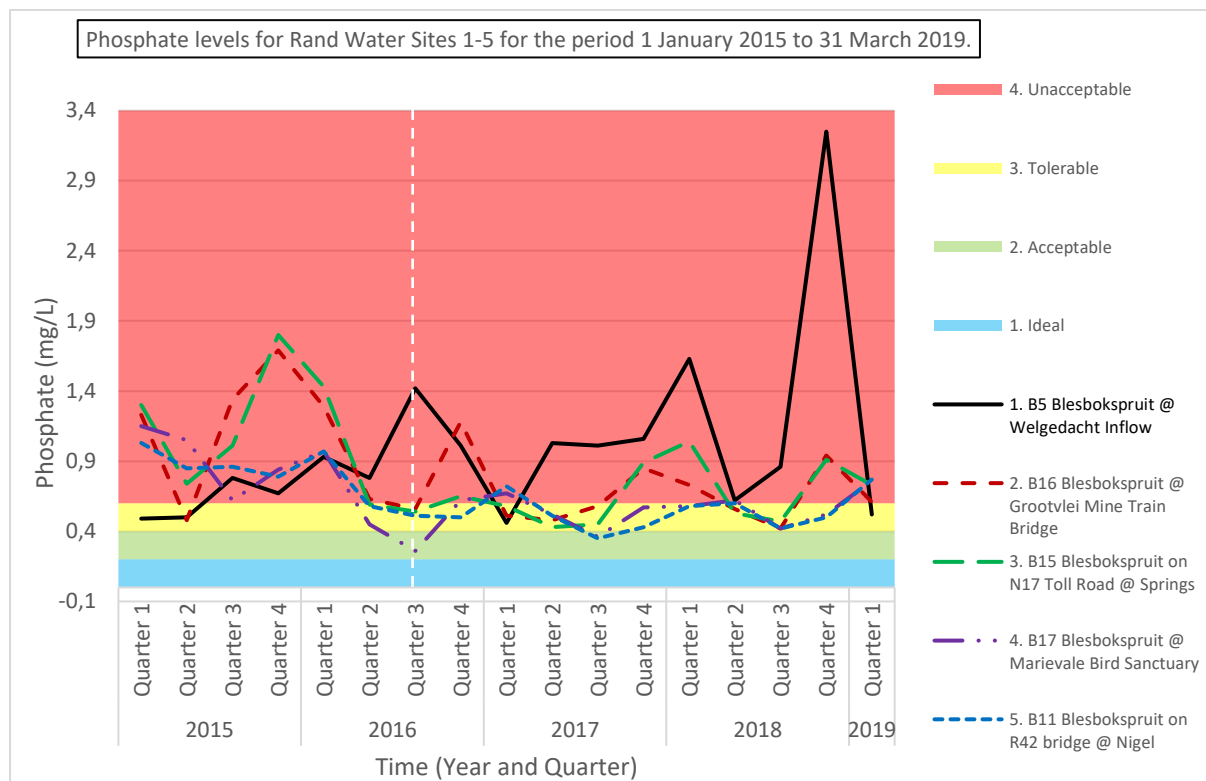


Figure 34: Phosphate levels for Rand Water Sites 1-5 for the period 1 January 2015 to 31 March 2019.

The phosphate Rand Water time series graph shows the elevated levels of phosphate seen at site 1 (Welgedacht inflow). What is significant is that phosphate levels are diminished for the period after the AMD treatment plant between site 1 and site 2 (red dashed line). As mentioned, phosphate, nitrate and ammonium values decreased for the sites downstream of the AMD treatment plant after the treatment plant started. This is due to the discharge of the AMD treatment plant into the wetland which would reduce concentrations of these nutrients downstream. The process of the treatment plant has had an indirectly positive influence on phosphate. It is also noticeable that sites 4 and 5 show the lowest phosphate levels indicating that phosphate levels become reduced as water passes through the Marievale Wetland. This may be as a result of the ecological benefits of a wetland in that excess phosphate is being taken up by wetland plants within the streams of Marievale Bird Sanctuary.

Rand Water manganese time-series graph

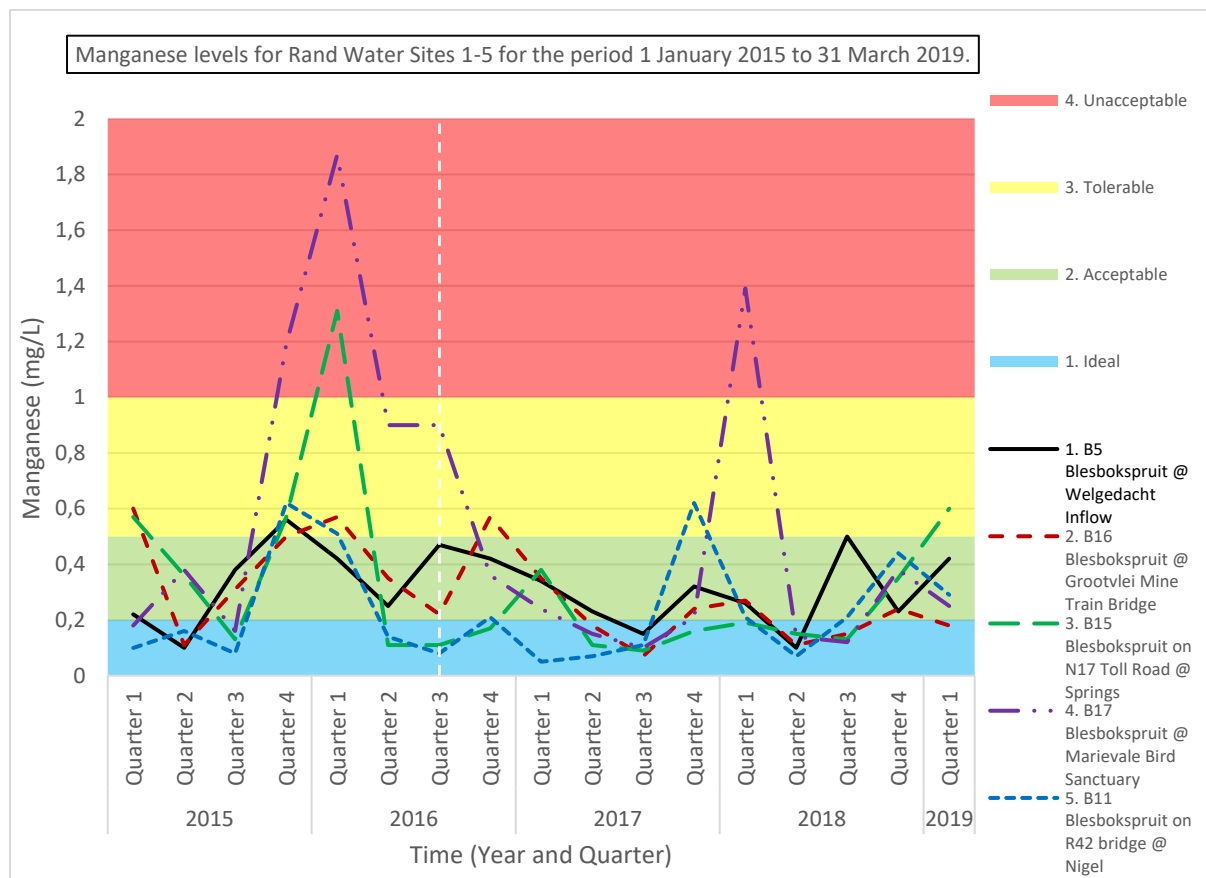


Figure 35: Manganese levels for Rand Water Sites 1-5 for the period 1 January 2015 to 31 March 2019.

The above graph shows manganese values for the five Rand Water Sites. The graph shows that manganese is generally at an ideal to acceptable level. However, two sample sites (sites 3 and sites 4) show spikes in manganese at periods before and after the AMD treatment plant. These spikes cannot be attributed to the AMD treatment plant or Grootvlei mine dump, but rather some other influence or point source promoting manganese pollution especially at site 4. According to the summary statistics, Manganese levels, on average, had decreased (suggested to be as a result of dilution) between site 1 and 2 for the period after the treatment plant had started operating. When looking at the graph, for the period after the treatment plant started, the dotted red line (site 2) is more often below the solid black line (site 1) which enhances the suggestion of dilution. This is an indirectly positive influence that the new AMD treatment plant has had on the Blesbokspruit in reducing manganese concentrations downstream.

Rand Water iron time-series graph

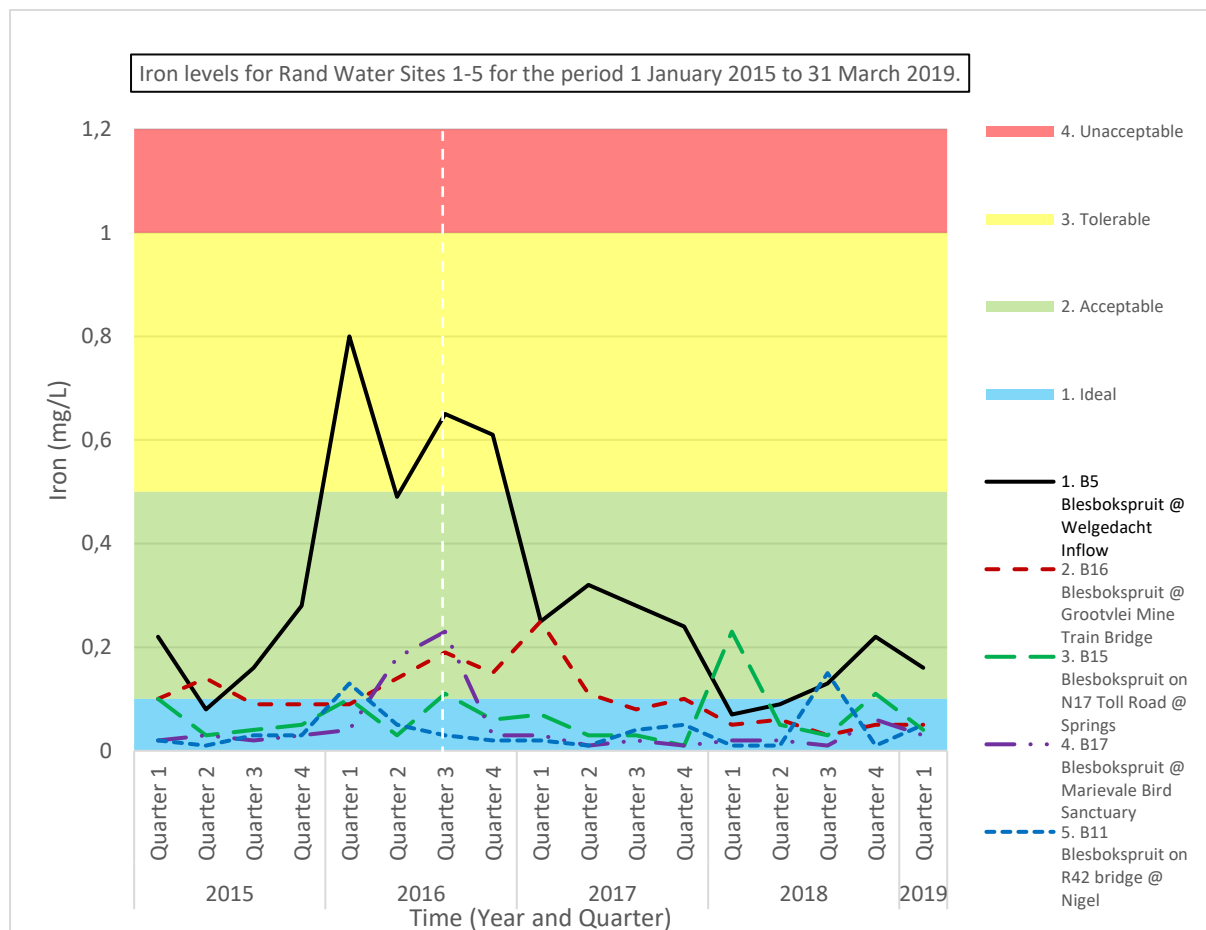


Figure 36: Iron levels for Rand Water Sites 1-5 for the period 1 January 2015 to 31 March 2019

The above graph shows iron values for the five Rand Water Sites. The graph shows that Iron is generally at an ideal to acceptable level. It is noticeable that site 1 has a much higher iron content than all the other sites. The summary statistics results confirmed that the treatment plant has positively reduced iron levels through dilution. One can argue that Iron was being reduced even before the treatment plant became operational according to the time series graph above. Media reports around the AMD treatment plant mentioned within the literature review had reported that the plant was successfully reducing iron and manganese levels within the water (Kruger, 2017). It is reasonable to suggest that the iron and manganese reduction mentioned within the media reports refers to the reduction of these two metals within the AMD water, which is pumped from underground, and not within the river water of the Blesbokspruit itself. The reduction of these two metals is suggested to be through dilution caused by increased flows due to the discharge of the clean overflow of water from the AMD treatment plant into the wetland below.

Rand water pH and dissolved oxygen time-series graph

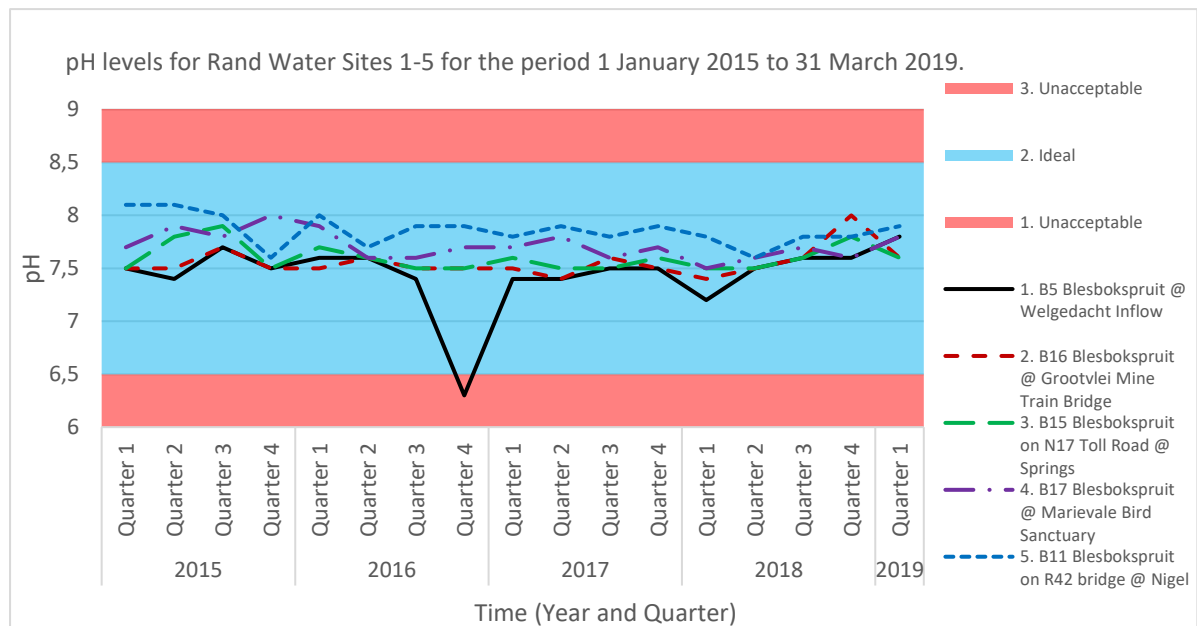


Figure 37: pH levels for Rand Water sites 1-5 for the period 1 January 2015 to 31 March 2019.

The above graph demonstrates how pH maintains an ideal level for all the Rand Water sampling sites. Only one sample was deemed unacceptable and this was for site 1 during the 2016 4th quarter. It is expected that pH in an AMD environment would be a lot lower and more acidic in nature and this is not the case (Ambani and Annegarn, 2015). These results agree with what was mentioned within the literature review with regards to pH (Ambani and Annegarn, 2015).

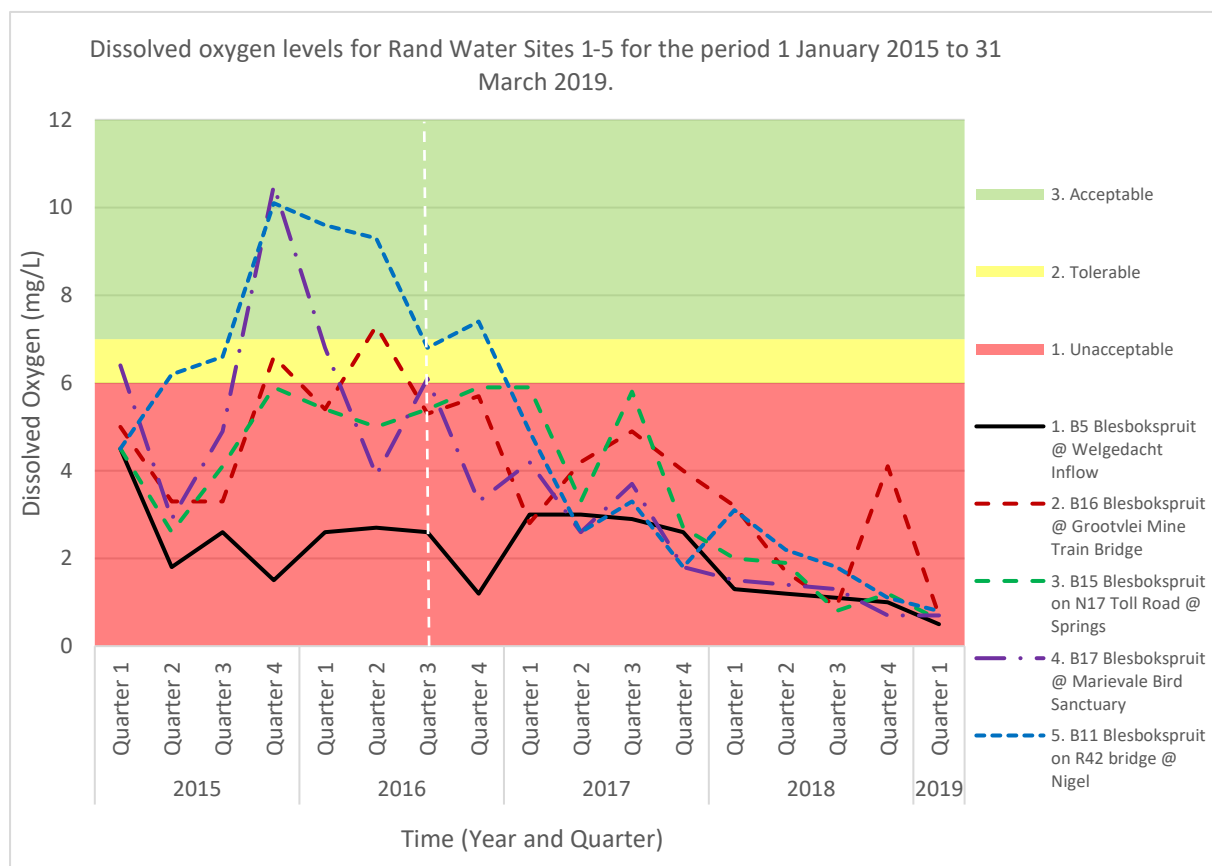


Figure 38: Dissolved oxygen levels for Rand Water sites 1-5 for the period 1 January 2015 to 31 March 2019.

The dissolved oxygen time-series graph on the previous page for the five Rand Water sites demonstrates that dissolved oxygen within the water is decreasing over time. It is important to note that this reduction in dissolved oxygen started before the launch of the AMD treatment plant and has continued decreasing after the launch of the AMD treatment plant. Site 1 has the lowest dissolved oxygen of all the sites, and all of the sites have decreased to an unacceptable level after the launch of the treatment plant. This reduction could be attributed to processes concerning overall stream flow and oxygen circulation within the Blesbokspruit, and not specific processes occurring at the AMD treatment plant.

6.2.1.5 Box plots

These box plots help to better understand the differences between sampling sites of the historical Rand Water data for the individual water quality parameters. As there are multiple water quality parameters, only the parameters that have definite trends will be shown.

Conductivity Box Plots (Before and After Treatment Plant)

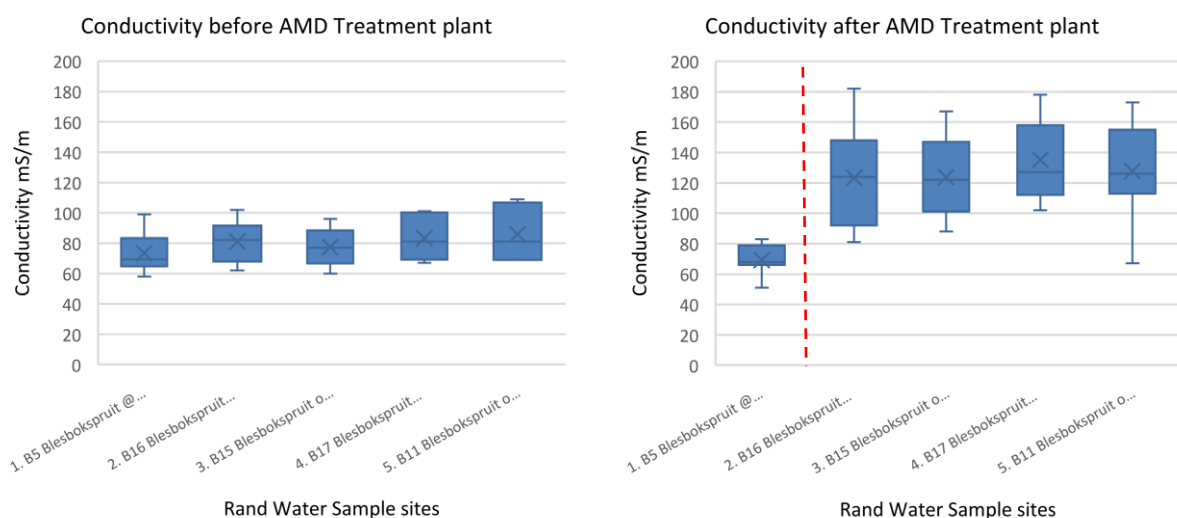
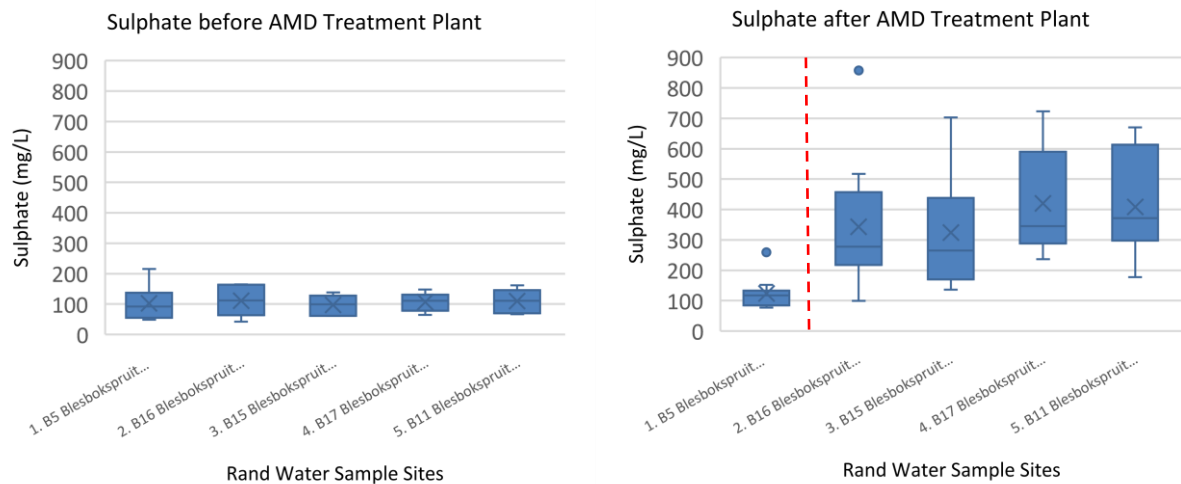


Figure 39: Conductivity box plots during the periods before and after the AMD treatment plant came into operation.

(The dotted red line splits the sites upstream and downstream of the Eastern Basin AMD Treatment plant. Rand Water site 1 is upstream and sites 2,3,4 and 5 are all downstream of the AMD treatment plant.)

The simple box plots above (from high to low values) show maximum, quartile 3 (upper box limit), median (middle box line), mean (marked with an x), quartile 1 (lower box limit) and minimum values at each sample site. These box plots clearly reiterate the results that have been mentioned before. The plots show that conductivity between sites 1 and 2 increased dramatically for the period after the AMD treatment plant came into operation. The values and range of conductivity have clearly increased downstream of the AMD Treatment plant after it came into operation. The high values of conductivity for sites 2,3,4 and 5 also show that the wetland is highly influenced by the processes occurring at the AMD treatment plant. For the period before the AMD treatment plant started operating, conductivity is shown to increase only slightly between site 1 and 2. The box plots either side of the dotted red line clearly demonstrates the influence of the AMD treatment plant after it came into operation.

Sulphate box plots (before and after AMD Treatment Plant)



(Blue dots represent outliers)

Figure 40: Sulphate box plots during the periods before and after the AMD treatment plant came into operation

The box plots above are similar to the conductivity box plots shown previously. These box plots also reiterate the results that have been mentioned before. The plots show that sulphate between sites 1 and 2 increased for the period after the AMD treatment plant came into operation. The high values of sulphate for sites 2,3,4 and 5 show that the wetland is highly influenced by the processes occurring at the AMD treatment plant. For the period before the AMD treatment plant started operating, sulphate values were similar between all the sampling sites. As both sulphate and conductivity relate to one another, they have both shown the same trends over time within the Blesbokspuit.

Ammonium Box Plots (Before and After AMD Treatment Plant)

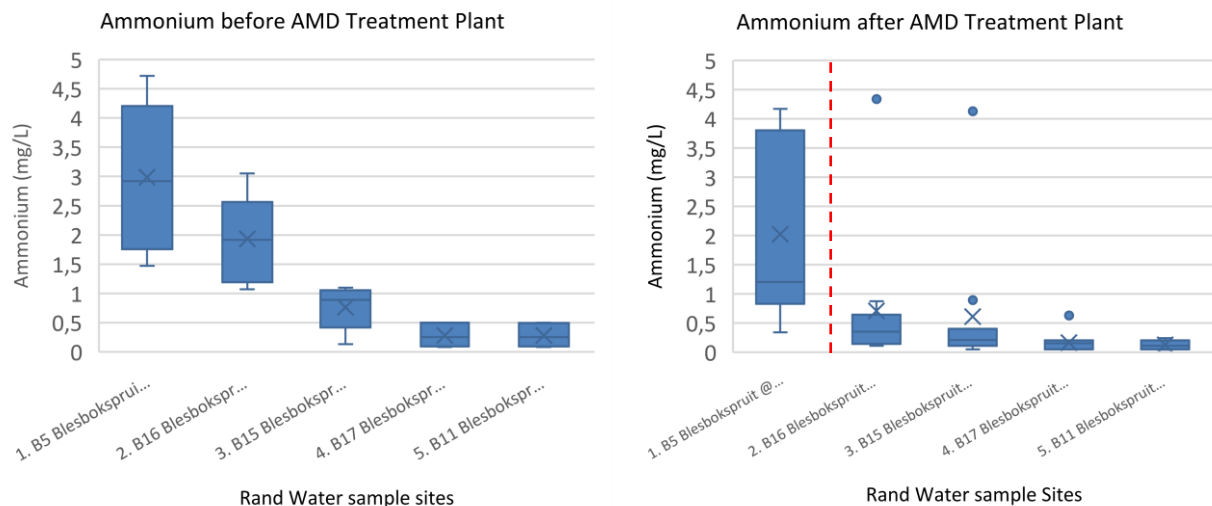


Figure 41: Ammonium box plots during the periods before and after the AMD treatment plant came into operation

Previous results suggested that ammonium had been reduced due to the process of dilution from discharges by the AMD treatment plant between sites 1 and 2. This is shown clearly in the ammonium after AMD treatment plant box plot above. Between site 2 and site 5, ammonium levels are being reduced for both box plots, which can be attributed to processes occurring within the wetland area. For the period before the AMD treatment plant came into operation, ammonium is

also reduced between site 1 and site 2, but not as drastically as the reduction after the treatment plant started operating. Due to dilution from discharge of the AMD treatment plant and processes occurring within the wetland, ammonium levels are being reduced. The combination of the two processes are reducing ammonium within the Blesbokspuit.

Phosphate box plots (before and after AMD Treatment Plant):

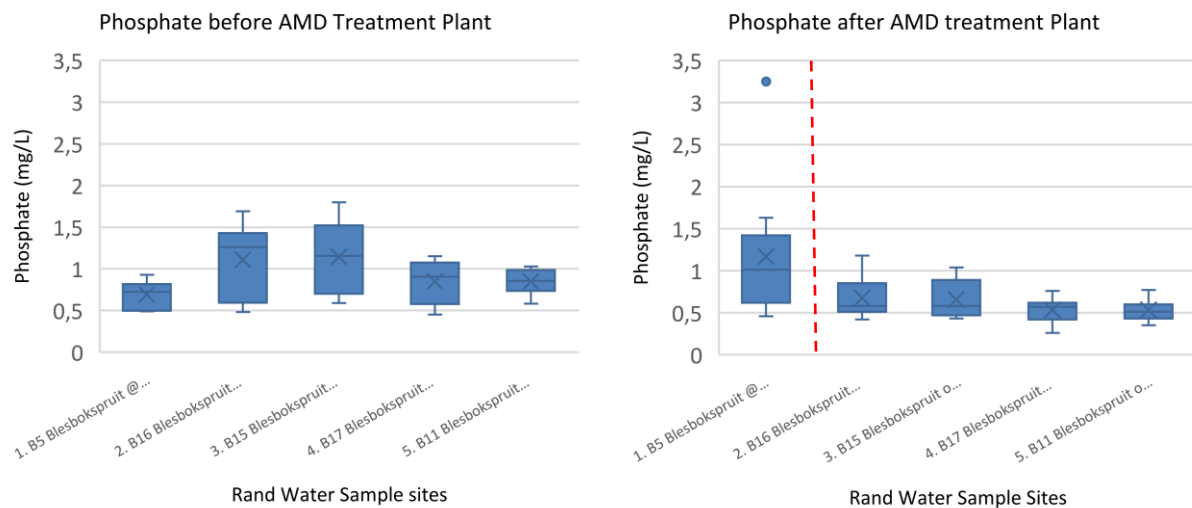


Figure 42: Phosphate box plots during the periods before and after the AMD treatment plant came into operation

The phosphate box plots above for the period before the AMD treatment plant show that phosphate is increasing from site 1, 2 and 3 and only starts decreasing after site 3. For the period after the AMD treatment plant, phosphate is being reduced throughout, especially between site 1 and 2 which enhances the suggestion that the AMD treatment plant is reducing phosphate through dilution as mentioned. Phosphate levels for site 4 and 5 for the period after the AMD treatment plant show decreasing trends which suggests that the wetland is also reducing phosphate levels. The combination of the wetland and indirect dilution caused by the treatment plant has reduced both ammonium and phosphate along the Blesbokspuit.

Nitrate Box Plots (Before and after AMD Treatment plant)

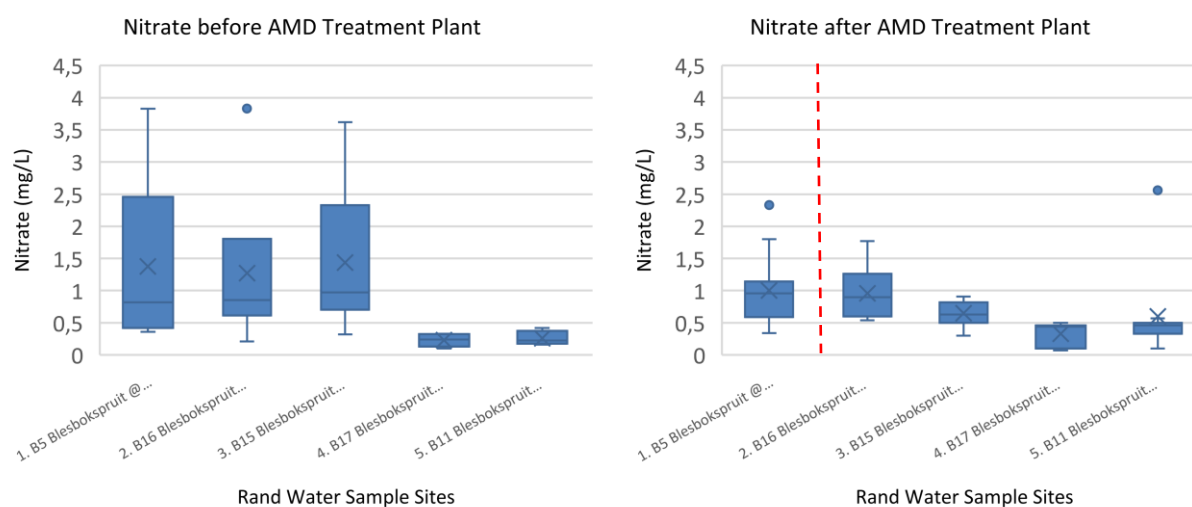


Figure 43: Nitrate box plots during the periods before and after the AMD treatment plant came into operation

The box plots on the previous page for nitrate follow a similar pattern to the box plots of ammonium and phosphate shown before. The combination of the processes occurring at the AMD treatment plant and the Marievale Bird Sanctuary wetland are clearly reducing the nutrients of ammonium, phosphate and nitrate within the Blesbokspruit.

6.2.1.6 Correlation matrix colour plot

The correlation matrix colour plot below in figure 44 has been produced using the XLStat programme. The colours within the legend correspond to the Pearson correlation coefficients of each water quality variable for Rand Water samples over the entire sampling period. The Pearson correlation is a measure of correlation between two variables, in this case water quality parameters. The correlation coefficients range between +1 and -1, where +1 is a complete positive linear correlation (shown in light green), 0 is no linear correlation (shown in black), and -1 is a complete negative linear correlation (shown in red). The actual correlation coefficient values have been produced and this is shown in the appendix section. It is easier to visualise the correlations between variables using this correlation matrix colour plot instead of the actual correlation coefficient values.

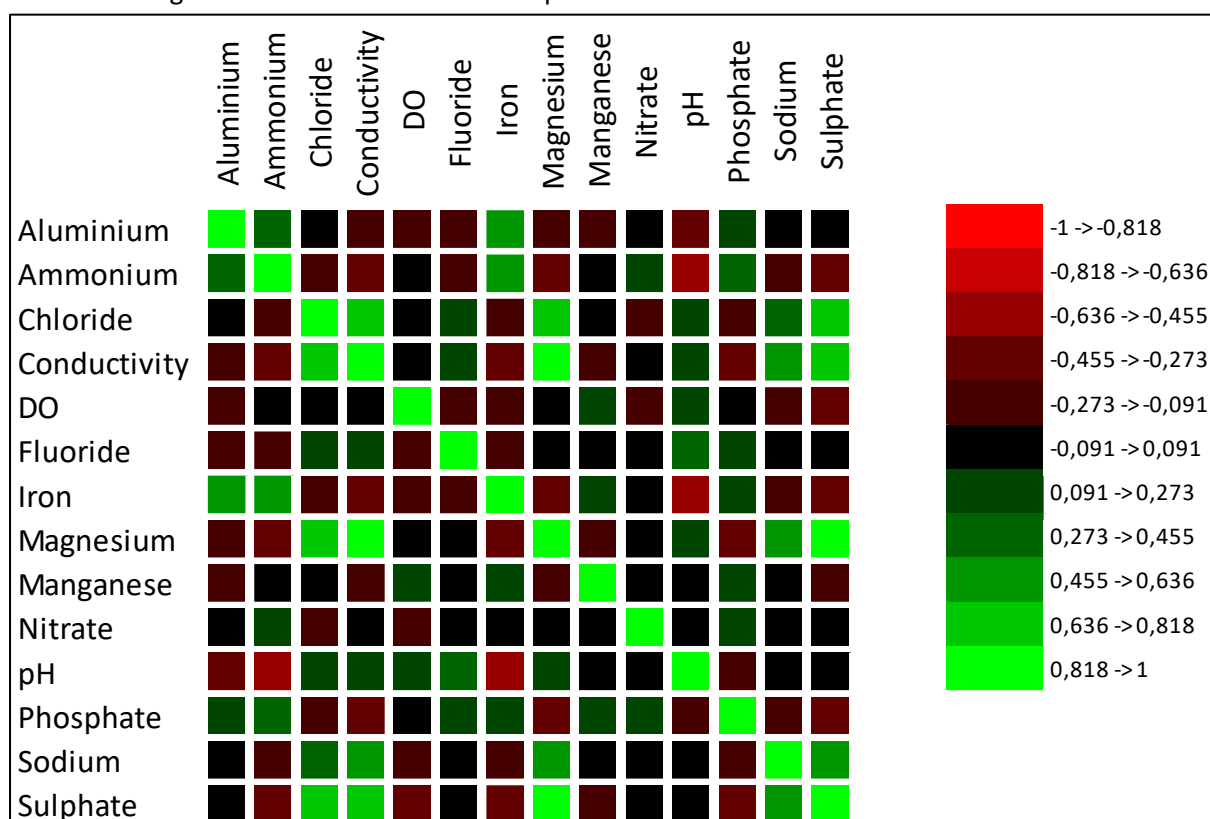


Figure 44: Correlation matrix colour plot for Rand Water data over the entire sampling period.

According to the figure above, there are positive linear correlations (shown in light green) between conductivity and magnesium, magnesium and sulphate, magnesium and chloride, chloride and sulphate, and sulphate and conductivity. Negative linear correlations (shown in red) are between pH and iron, and ammonium and pH. Most of the correlation matrix colour plot suggests that there are multiple water quality parameters that have no linear correlation (shown in black). A principal component analysis has been completed on the above Rand Water data to determine whether there are more clear linkages and correlations between certain water quality parameters.

6.2.1.7 Principal Component Analysis

A principal component analysis (PCA) is a popular tool used to bring out strong patterns from complex multivariable datasets (Wold et al., 1987). It captures the essence of the data in a few principal components, which convey the most variation in the dataset (Wold et al., 1987). A PCA was performed on the Rand Water data using the XLstat program. After the data from both Rand Water were normalized, the program produced a PCA vector plot. The F1 and F2 principal components account for the combined variation in the dataset. Vectors, in this case water quality variables, that are close to the principal components F1 and F2 are those that strongly influence the components (Wold et al., 1987). For the purpose of this research, the main use of the PCA is to account for which vectors (water quality variables) are strongly correlated with one another. There are simplified characteristics of a PCA that one can use to help determine which variables are correlated to one another: 1. When two vectors are close, and form a small angle, the two variables they represent are positively correlated (Wold et al., 1987). 2. If the two variables are at 90° to one another, they are not likely correlated (Wold et al., 1987). 3. When the two variables diverge and form a large angle (close to 180°), they are negatively correlated with one another (Wold et al., 1987).

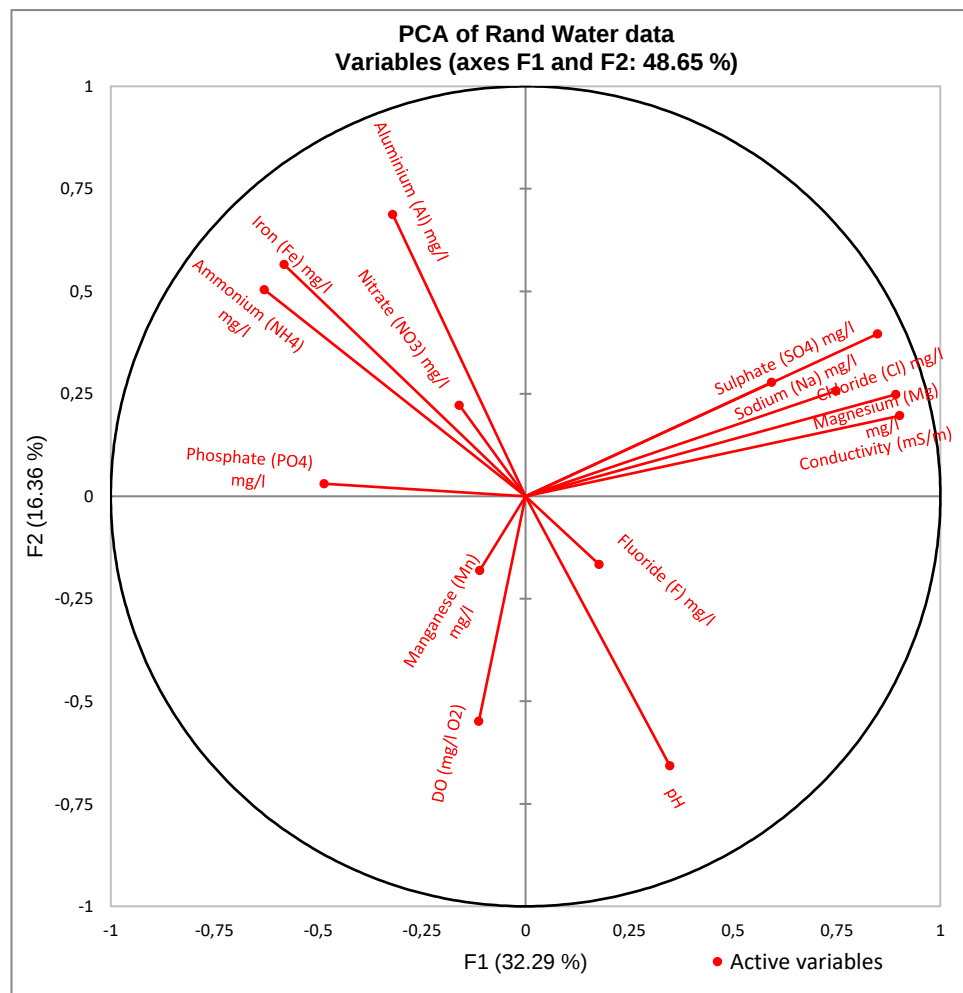


Figure 45: Principal Component Analysis of Rand Water data over the entire sampling period.

When looking at the PCA for the Rand Water quality data, principal component 1 (F1) explains 32.29% of the variance in the dataset and is positively related to high levels of sodium, sulphate, chloride, magnesium and conductivity. These parameters are all grouped together near the F1

component and have small angles between each vector indicating a positive correlation between these water quality parameters and F1. The F1 principal component is negatively related to phosphate, ammonium and nitrate. Component F1 therefore relates to treated AMD water inputs by the treatment plant which increases the levels of sodium, sulphate, chloride, magnesium and conductivity and decrease the levels of phosphate, ammonium and nitrate through dilution. Component 2 (F2) only accounts for 16.36% of the variance in the dataset and is more difficult to interpret. However, this component corresponds to low dissolved oxygen and pH and corresponds to high nitrate, iron and aluminium levels. The high levels of nitrate corresponding to low dissolved oxygen would be indicative of a nutrient input signal related to eutrophication. However, one would expect that phosphate levels would also match up with closely with the high levels of nitrate, but this is not the case. Therefore, this signal is only partly relating to the process of eutrophication due to phosphate not increasing in relation to nitrate. A eutrophication signal would include both increasing phosphate and nitrate levels corresponding to decreasing dissolved oxygen.

In terms of making linkages between specific water quality parameters, the strong positive correlation between sodium, sulphate, chloride, magnesium and conductivity are negatively correlated with the nutrients of phosphate, ammonium and nitrate. This indicates that as the conductivity increases (the parameters of sodium, sodium, sulphate, chloride, magnesium also increasing), which is seen downstream of the treatment plant, the nutrients of phosphate ammonium and nitrate all decrease due to the processes of the AMD treatment plant through dilution. Contributing to this, both iron and manganese are also negatively correlated with the strong sodium, sulphate, chloride, magnesium and conductivity signature. This is significant and directly agrees with the literature in that the treatment plant does remove these two metals (iron and manganese) at the expense of increased conductivity, sodium, sulphate, chloride and magnesium. Overall, the PCA has demonstrated that as a result of the processes of treatment plant, both nutrients (phosphate, ammonium and nitrate) and the metals of iron and manganese are decreasing at the expense of increased levels of sodium, sulphate, chloride, magnesium and conductivity. Although the plant may be removing metals from AMD that would otherwise decant, the main influence on stream chemistry can only come from the discharge from the plant, via dilution of some ions but an increase in others that are not removed in the plant.

6.2.2 Calibration curves for ground truth water quality results

The following calibration curves have been constructed for the major ion determination of sulphate, nitrate iron and chloride. The phosphate curve was not constructed due to the unavailability of phosphate standard solution. Calibration curves have been constructed to demonstrate the accuracy of the Hach instrument in measuring major ion concentrations of certain water quality parameters with known concentrations. Hach standard solutions for each water quality parameter were used and diluted to determine the known concentrations. The measured concentrations were measured in the exact same way as the water samples were measured using the Hach test kit, these methods have been mentioned within the methodology section.

The sulphate calibration curve on the following page made use of the Sulphate Standard solution with 1000 mg/L SO_4^{2-} concentration. The standard solution was diluted with deionised water to concentrations of 100 mg/L, 50 mg/L and 20mg/L at a standard solution: deionised water ratio of 1:9, 1:19 and 1:49 respectively. The red values in brackets represent the three known sulphate

concentrations and the green values represent the respective sulphate concentration measured by the Hach test kit. The percentage error has been calculated for each measurement and is shown after the bracket on the figure below.

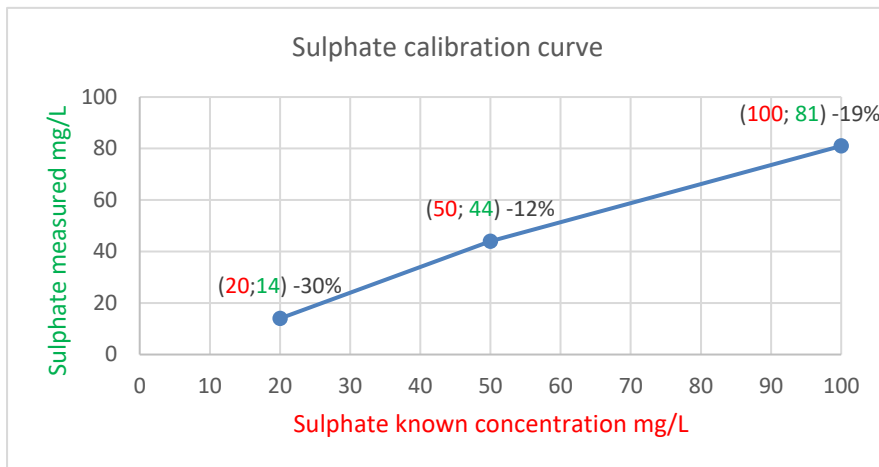


Figure 46: Sulphate calibration curve: The labels on the blue line indicate the measured value vs the known concentration value on the X axis.

According to the figure above, sulphate concentrations are actually being underestimated by roughly 20% shown by the negative percentage error seen above. The results section which follows these calibration curves shows how sulphate from the ground truth water sampling points is at unacceptable levels. This is concerning as this underestimation of sulphate would indicate that the true sulphate concentrations are even higher than what the Hach test kit is detecting.

The nitrate calibration curve below made use of the Nitrate Nitrogen Standard Solution with 4.43 ± 0.04 mg/L NO_3^- concentration. The standard solution was diluted with deionised water to concentrations of 2.215 mg/L, 1.1075 mg/L and 0.443 mg/L at a standard solution: deionised water dilution ratio of 1:1, 1:3 and 1:9 respectively. The red values in brackets represent the three known nitrate concentrations and the green values represent the respective nitrate concentration measured by the Hach test kit. The percentage error has been calculated for each measurement and is shown after the bracket in the figure below.

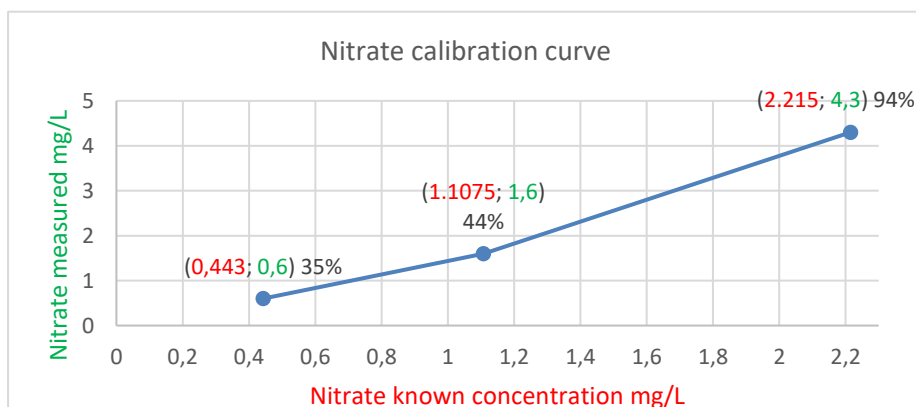


Figure 47: Nitrate calibration curve: The labels on the blue line indicate the measured value vs the known concentration value on the X axis.

According to the figure above, nitrate is being overestimated by the Hach test kit. The results section which follows these calibration curves shows how nitrate is at an acceptable level on average for all

of the ground truth sampling sites. Therefore, even when considering the overestimation, nitrate is not a water quality parameter of high concern with regards to the accuracy of detection by the Hach test kit as seen with sulphate previously.

The iron calibration curve below made use of the Iron Standard Solution with 100 ± 0.5 mg/L Fe concentration. The standard solution was diluted with deionised water to concentrations of 1 mg/L, 0.5 mg/L and 0.1 mg/L at a standard solution: deionised water dilution ratio of 1:99, 1:199 and 1:999 respectively. The red values in brackets represent the three known iron concentrations and the green values represent the respective nitrate concentration measured by the Hach test kit. The percentage error has been calculated for each measurement and is shown after the bracket in the figure below.

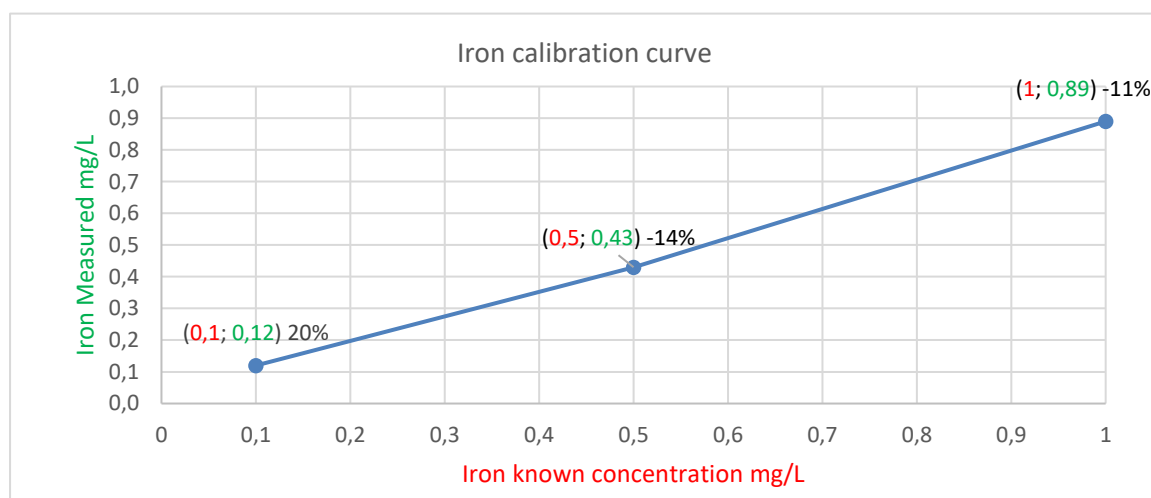


Figure 48: Iron calibration curve: The labels on the blue line indicate the measured value vs the known concentration value on the X axis.

According to the above, the error percentages suggest that the readings are $\pm 20\%$ of the standard solution values. The results section which follows these calibration curves shows that iron lies within the ideal and acceptable range targets on average with the highest mean value of iron being 0.18 mg/L at both site 1 and site 2. At this concentration iron is being overestimated by the Hach test kit. However, an overestimation of 20% equates to an overestimation of only 0.02 mg/L at the concentration of 0.1 mg/L. Therefore, the overestimation does not change the outcome of the analysis considerably as the low concentrations of iron would remain within an acceptable or ideal management target.

The chloride calibration curve, seen on the following page, made use of the Chloride Reference Standard Solution with 1000 mg/L Cl^- concentration. The standard solution was diluted with deionised water to concentrations of 100 mg/L, 50 mg/L and 20 mg/L at a standard solution: deionised water dilution ratio of 1:9, 1:19 and 1: 49 respectively. The red values in brackets represent the three known chloride concentrations and the green values represent the respective chloride concentration measured by the Hach test kit. The percentage error has been calculated for each measurement and is shown after the bracket in the figure on the following page.

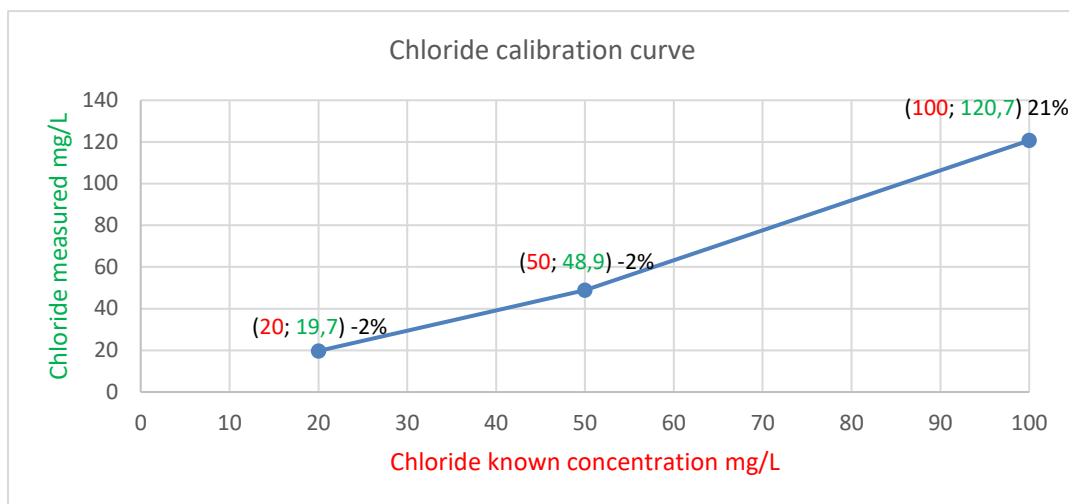


Figure 49: Chloride calibration curve: The labels on the blue line indicate the measured value vs the known concentration value on the X axis.

According to the figure above, the Hach test is able to make very accurate determinations of chloride at concentrations between 20 mg/L and 50 mg/L. At the higher concentration of 100 mg/L, chloride is being overestimated by 21%. The results which follow this section show that mean chloride concentrations lie at 50-60 mg/L concentrations for most of the ground truth sampling sites which would suggest that these values are fairly accurate. The values that lie near the 100 mg/L concentration still achieve acceptable management targets for chloride. The calibration curves show that, out of all the water quality parameters for major ion determination, only sulphate concentrations are of concern with regards to the accuracy of the Hach test kit making considerable changes to the water quality results. The calibration curve for sulphate suggests that the Hach test kit is underestimating sulphate concentrations which already lie within the higher unacceptable management target levels. The results to follow have not been altered according to the calibration curves above. However, the influence of these curves, with regards to sulphate, will be mentioned further within the discussion section.

6.2.3 Ground truth water quality results

A full year record of monthly water sample collection has been completed in order to cover the full range of seasonality experienced in the area as well as providing ground truth data for the purpose of this research. A total of eight sample sites were visited monthly. Five of these eight sites are the same sites used by Rand Water and the remaining three sites lie within the Marievale Bird Sanctuary. These three remaining sites are named according to their surroundings: Marievale Bird Sanctuary Bridge, Duiker Hide, and Hadedda Hide. The sites have been named site one through eight according to their position along the stream from upstream to downstream. The full year record started in June 2018 and ended in May 2019 with samples collected once per month.

6.2.3.1 Data summaries

The following data summaries include data from the eight ground-truth water sampling sites. Data summaries include the mean, median, minimum and maximum for each site for the duration of the full year of ground truth sampling from June 2018 to May 2019. The colours of the blocks within the data summaries correspond to the in-stream water quality guidelines for the Blesbokspruit

Catchment. The following table can be used as a determination of water quality for each water quality parameter:

Table 15: Blesbokspruit Forum water quality management level targets.

Ideal Catchment Background	Acceptable Management Target	Tolerable Interim Target	Unacceptable
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Table 16: Data summary for site 1: B5 Blesbokspruit at Welgedacht Inflow. This site is upstream of the treatment plant.

Site 1.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	57.14	53.50	38	93.5
pH	7.18	7.17	6.41	7.87
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	53.21	50.80	32.2	83.8
Iron	0.18	0.12	0.02	0.83
Nitrate	1.18	1.10	0.4	1.9
Phosphate	1.62	1.51	0.71	3.55
Sulphate	140.67	84.00	50	584

The ground truth data summary above shows that on average; chloride, pH and sulphate are at the ideal management target at site 1. Conductivity, nitrate and iron are described as acceptable on average and phosphate is the only parameter described as unacceptable for site 1.

Table 17: Data summary for site 2: B16 Blesbokspruit at Grootvlei Mine Train Bridge. This site is downstream of the AMD treatment plant and inactive Grootvlei Mine.

Site 2.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	90.29	83.15	67.8	152.9
pH	7.29	7.26	6.95	7.82
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	55.81	51.4	36.1	76.9
Iron	0.18	0.095	0	0.99
Nitrate	1.31	1.25	0.5	2.1
Phosphate	1.85	1.61	0.88	4.27
Sulphate	321.25	295	81	600

The site 2 data summary above shows once again that conductivity means have increased from acceptable levels at site 1 to tolerable levels at site 2 as a result of the AMD treatment plant. The mean sulphate at site 1 is described as ideal and the mean sulphate at site 2 has worsened to a tolerable level. Phosphate means have increased from site 1 and remain unacceptable. The remaining parameters of iron, nitrate, chloride and pH, on average, have maintained the respective original management targets from site 1.

Table 18: Data summary for site 3: B15 Blesbokspuit on N17 toll road in Springs. This site marks as the sampling site upstream of the Marievale Bird Sanctuary Wetland.

Site 3.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	91.91	92.45	71.4	117
pH	7.38	7.31	7.05	7.95
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	59.54	62.55	36	80.6
Iron	0.12	0.09	0	0.56
Nitrate	1.08	0.95	0.5	2.1
Phosphate	1.79	1.48	0.87	3.58
Sulphate	410.42	376.50	110	826

The site 3 data summary is very similar to site 2 means for all the water quality parameters except for sulphate. Sulphate, on average, has increased even more so at site 3 to 410.42 mg/L and is still described as tolerable management target. The maximum value of sulphate for this site is 826 mg/L which exceeds the unacceptable sulphate level by 326 mg/L. These extremely high sulphate levels are highly concerning for the Blesbokspuit.

Table 19: Data summary for site 4: Marievale Bird Sanctuary Bridge. This site marks as the start of the Marievale Bird Sanctuary Wetland.

Site 4				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	101.05	100.85	66.5	131.4
pH	7.64	7.63	6.97	8.1
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	60.67	62.75	36.2	79.6
Iron	0.17	0.04	0.01	1.11
Nitrate	0.78	0.8	0.1	1.4
Phosphate	1.80	1.62	0.75	3.87
Sulphate	488.00	387.5	243	1264

The site 4 data summary is similar to what was shown for the site 2 and 3 water quality means in terms of all the water quality parameters except conductivity and sulphate. Conductivity means have increased from site 3 to site 4. After Sulphate increased on average between site 2 and site 3, it has increased further on average between site 3 and site 4 to 488 mg/L. This suggests that conductivity sulphate levels are actually increasing downstream from the treatment plant according to the ground truth water quality results. The maximum sulphate of 1264 mg/L at site 4 at Marievale Bridge is extremely high and more than doubles unacceptable management target levels for sulphate.

Table 20: Data summary for site 5: Duiker Hide in Marievale Bird Sanctuary.

Site 5.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	101.80	98	68.1	129.6
pH	7.78	7.71	7.48	8.23
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	60.00	61	18.9	90.7
Iron	0.07	0.04	0	0.19
Nitrate	0.94	1	0.3	1.4
Phosphate	1.74	1.79	0.78	3.31
Sulphate	409.92	396.5	200	650

Table 21: Data summary for site 6: B17 Blesbokspuit at Marievale Bird Sanctuary. This site is at the centre of the Marievale Wetland.

Site 6.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	110.78	102.90	72	151.3
pH	7.97	7.95	7.63	8.41
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	58.56	53.40	37.4	78
Iron	0.05	0.05	0	0.14
Nitrate	0.72	0.65	0.4	1.4
Phosphate	1.79	1.64	0.88	4.57
Sulphate	484.58	478.50	209	1023

Both Sites 5 and 6 data summaries show water quality means that are similar to site 4. The mean for Sulphate at site 5 had been reduced from site 4 (409.92 mg/L) but increased at site 6 (484.58 mg/L).

Table 22: Data summary for site 7: Hadeda Hide in Marievale Bird Sanctuary.

Site 7.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	128.58	103.45	77	242.3
pH	7.85	7.89	7.17	8.35
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	76.23	74.4	57.8	102.3
Iron	0.04	0.02	0	0.11
Nitrate	1.31	1.2	0.2	2.5
Phosphate	2.26	1.93	0.99	4.02
Sulphate	527.29	549	350	630

Although the data summary has been completed, this site had missing data values due to the cite having become laden with duckweed and algae. Due to the missing data, this site will not be used for hypothesis testing. However, the site marks as a reference for the potential influence of algae and duckweed seen at Marievale Bird Sanctuary. As shown in the field site photos (figure 15), the algae and duckweed have completely blanketed the water at this location. The data summary for site 7 indicates that Hadeda hide has extremely high conductivity and sulphate means at levels which are unacceptable. These high values can be as a result of slow-moving (stagnant) water at the site. Increased evaporation of the slow-moving water could possibly have resulted in the increased conductivity and sulphate levels at this site.

Table 23: Data Summary for site 8: B11 Blesbokspuit on R42 bridge at Nigel stream outflow.

Site 8.				
Physical Variables with units	Mean	Median	Minimum	Maximum
Conductivity (mS/m)	112.98	101.00	84.8	168.7
pH	7.79	7.76	7.44	8.38
Major Ions (mg/L)	Mean	Median	Minimum	Maximum
Chloride	65.20	60.25	33	90
Iron	0.03	0.03	0	0.1
Nitrate	0.93	0.85	0.1	1.7
Phosphate	1.62	1.54	0.94	2.57
Sulphate	440.00	434.50	168	650

Site 8 marks as the end (downstream point) of the Marievale Bird Sanctuary and is the final sampling site for this research project. The data summary for site 8 shows clearly that between sites 2 through 8, the water quality is more or less maintained for each individual water quality parameter. This agrees with Rand Water data which showed that the wetland has a much lower influence on water quality compared to the AMD treatment plant between site 1 and 2. Hypothesis testing on the ground truth data will prove whether the populations from different sites are the same. Normality tests have been completed for this data to consider whether parametric/ non-parametric hypothesis tests should be used.

6.2.3.2 Normality test:

Normality tests were made on the ground truth data to determine if the data follows a normal distribution. Three standard tests (Jarque-Bera, Shapiro-Wilk and Doornik Chi-Square) were performed on each water quality variable and the following results were obtained from the NUMXL programme.

Table 24: Normality test summary for the ground truth water quality data

Water Quality Variable	Normality Test (H_0 = Follows normal distribution)		
	Jarque-Bera	Shapiro-Wilk	Doornik Chi-Square
Chloride	Accept	Accept	Accept
Conductivity	Reject	Reject	Reject
Iron	Reject	Reject	Reject
Nitrate	Reject	Reject	Reject
pH	Accept	Accept	Accept
Phosphate	Reject	Reject	Reject
Sulphate	Reject	Reject	Reject

Test interpretation:

Null Hypothesis (H_0): The variable from which the sample was extracted follows a Normal distribution.

Alternative Hypothesis (H_a): The variable from which the sample was extracted does not follow a Normal distribution.

Result: If the computed p-value is more than the significance level $\alpha=0.05$, one must accept the null hypothesis (H_0). If the computed p-value is less than the significance level $\alpha=0.05$, one must reject the null hypothesis, H_0 and accept the Alternative Hypothesis (H_a).

According to the result above, both Chloride and pH follow a normal distribution and the remaining five variables do not follow a normal distribution. In order to compare Rand Water data with ground truth data, non-parametric tests will be used on this data.

6.2.3.3 Non-parametric hypothesis tests

Test 1: Comparison of distributions for two independent samples. The samples here include site 1 (upstream of the Treatment plant) and site 2 (downstream of the treatment plant) for the twelve-month sampling period. The test chosen here is a Mann-Whitney test / two-tailed test which is the non-parametric equivalent to the t-test for two independent samples. The samples are said to be independent from one another as each sample represents a different sample site, the samples are relatable by time as data collected from each site was collected on the same day. This test is used to determine if the two independent samples were selected from populations having the same distribution.

Table 25: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 1 and site 2 for the twelve-month sampling period.

Water Quality variable	p-value (independent samples)	Null Hypothesis (H_0)
Chloride	0.580	Accept
Conductivity	0.000	Reject
Iron	0.537	Accept
Nitrate	0.609	Accept
pH	0.551	Accept
Phosphate	0.452	Accept
Sulphate	0.004	Reject

Test interpretation:

H_0 : The difference of location between the samples is equal to 0 (there is no difference between medians).

H_a : The difference of location between the samples is different from 0 (there is a difference in medians).

If the computed p-value is greater than the level of significance $\alpha=0.05$, one should accept the null hypothesis H_0 . If the p-value is lower than the significance level $\alpha=0.05$, one should reject the null hypothesis H_0 , and accept the alternative hypothesis H_a . According to the test result, only conductivity and sulphate are shown to have different populations between site 1 and site 2. The results agree with the ground truth data summaries as well as the Rand Water statistical results. These two parameters have increased between site 1 and site 2 due to the processes occurring at the AMD treatment plant. Elevated conductivity and sulphate levels are a major concern within the Blesbokspruit wetland area.

Test 2: Comparison of distributions between site 3 (upstream of the Marievale Bird Sanctuary Wetland) and site 4 (the start of the Marievale Bird Sanctuary Wetland)

Table 26: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 3 and site 4 for the twelve-month sampling period.

Water Quality variable	p-value (independent samples)	Null Hypothesis (H_0)
Chloride	0.755	Accept
Conductivity	0.183	Accept
Iron	0.975	Accept
Nitrate	0.171	Accept
pH	0.021	Reject
Phosphate	0.932	Accept
Sulphate	0.660	Accept

The test result shown on table 26 on the previous page indicates that only pH has a different population between site 3 and site 4. pH is not a water quality parameter of concern as it maintains an ideal management target throughout the Blesbokspruit Wetland. This test suggests that the Blesbokspruit wetland area between site 3 and site 4 has very little influence on water quality parameters. These results agree with the ground truth data summaries as well as the Rand Water statistical results.

Test 3: Comparison of distributions between site 4 (the start of the Marievale Bird Sanctuary Wetland) and site 8 (the end of the Marievale Bird Sanctuary Wetland).

Table 27: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 4 and site 8 for the twelve-month sampling period.

Water Quality variable	p-value (independent samples)	Null Hypothesis (H ₀)
Chloride	0.514	Accept
Conductivity	0.724	Accept
Iron	0.143	Accept
Nitrate	0.506	Accept
pH	0.378	Accept
Phosphate	0.854	Accept
Sulphate	0.977	Accept

Comparison of distributions between site 4 (the start of the Marievale Bird Sanctuary Wetland) and site 8 (the end of the Marievale Bird Sanctuary Wetland) are the same for all the water quality parameters. Test 3 suggests, once again, that the Marievale Bird Sanctuary wetland has very little influence over water quality parameters.

Test 4: Comparison of distributions between site 5 (Duiker Hide within Marievale Bird Sanctuary) and site 6 (B17 at the centre of Marievale Bird Sanctuary).

Table 28: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 5 and site 6 for the twelve-month sampling period.

Water Quality variable	p-value (independent samples)	Null Hypothesis (H ₀)
Chloride	0.787	Accept
Conductivity	0.347	Accept
Iron	0.658	Accept
Nitrate	0.068	Accept
pH	0.037	Reject
Phosphate	0.887	Accept
Sulphate	0.505	Accept

Comparison of distributions between site 5 and site 6 indicate that only pH has a different population between the two sample sites. This is the same result seen previously for test 2. These results suggest that there is very little influence by the Marievale wetland on water quality between these two sample sites.

Test 5: Comparison of distributions between site 6 (B17 at the centre of Marievale Bird Sanctuary Wetland) and site 8 (the end of the Marievale Bird Sanctuary wetland).

Table 29: The Mann-Whitney test / two-tailed test results for all the water quality variables between site 6 and site 8 for the twelve-month sampling period.

Water Quality variable	p-value (independent samples)	Null Hypothesis (H_0)
Chloride	0.156	Accept
Conductivity	0.887	Accept
Iron	0.465	Accept
Nitrate	0.298	Accept
pH	0.037	Reject
Phosphate	0.989	Accept
Sulphate	0.875	Accept

Test 4 and test 5 were performed to identify whether there were any significant differences in populations for the water quality variables within the Marievale Bird Sanctuary Wetland. The only water quality variable that has a different population is pH, which is not a variable of high concern as mentioned. These results suggest that there is very little influence by the Marievale Bird Sanctuary wetland on water quality, except for pH.

6.2.3.4 Time-series graphs (ground truth data):

Time-series graphs for each water quality parameter have been made for the ground truth sampling period from June 2018 to May 2019. These graphs help show whether certain water quality parameters are meeting the required targets for each sampling site. All 8 sample sites are shown on the graphs, and comparisons can be made between sample sites. As there are seven water quality parameters, only the concerning parameters that lie within the unacceptable and tolerable ranges will be shown. The remaining ground truth time-series are shown in the appendix section.

Conductivity ground truth time-series graph

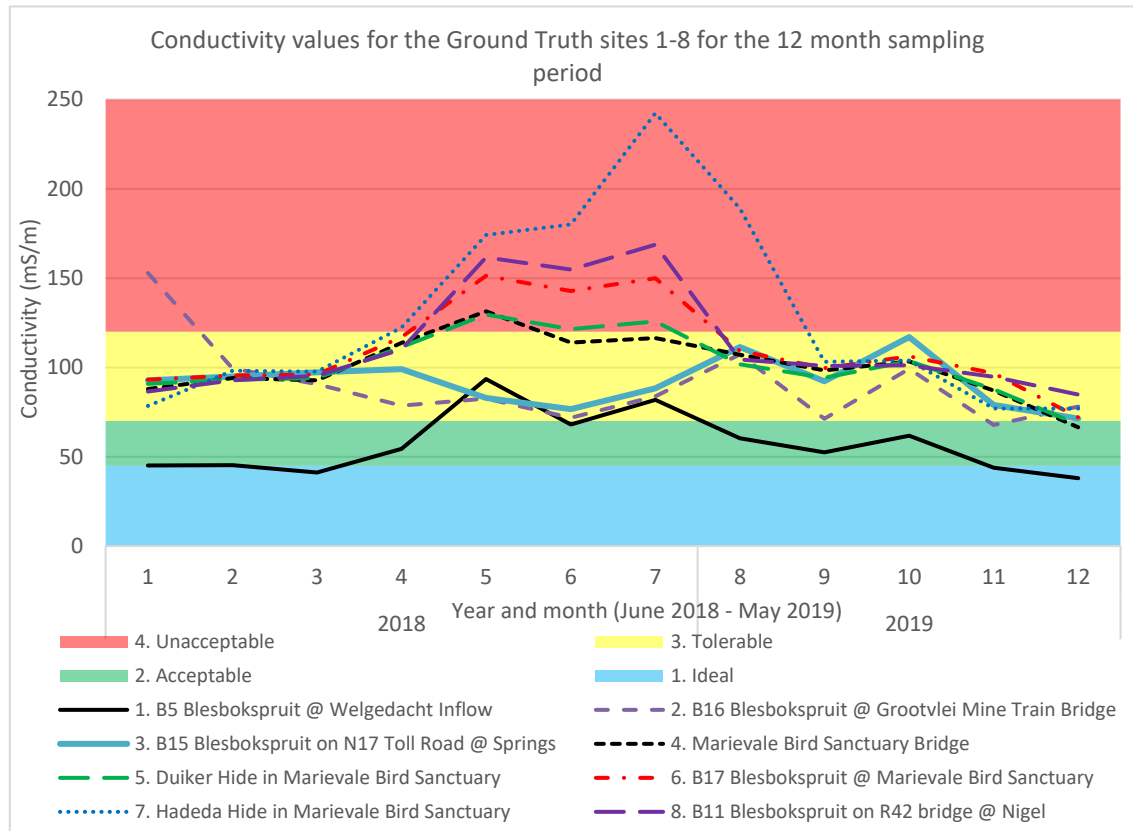


Figure 50: Conductivity values for the ground truth sites 1-8 for the 12-month sampling period.

The time series graph for conductivity shows clearly that conductivity levels are lowest at site 1 and increase from site 2 to site 8. Site 7 (Haded hide) is shown to have the highest conductivity as this is the site where the water became stagnant and conductivity levels are thought to have increased due to increased evaporation. It is noticeable that, moving downstream, sites 4,5,6,7 and 8 (which are all within Marievale Bird Sanctuary) all have high values of conductivity especially during months 5,6,7 and 8 which correspond to the months of October, November, December 2018 and January 2019. During this period, upon site visits to Marievale Bird Sanctuary, the water levels within the wetland streams were low due to very little rainfall over this period. The lack of rain promoted high conductivity values as rainwater from upstream was unavailable to dilute concentrations of dissolved salts. When the summer rains started occurring more frequently at the end of January (month 8) 2019, conductivity levels are shown to decrease during the month of February (month 9) 2019. The seasonal differences in rainfall are highly influential with regards to conductivity levels within the Blesbokspuit. The impacts of seasonal rainfall changes will be further discussed in the discussion chapter to follow.

Sulphate ground truth time series graph

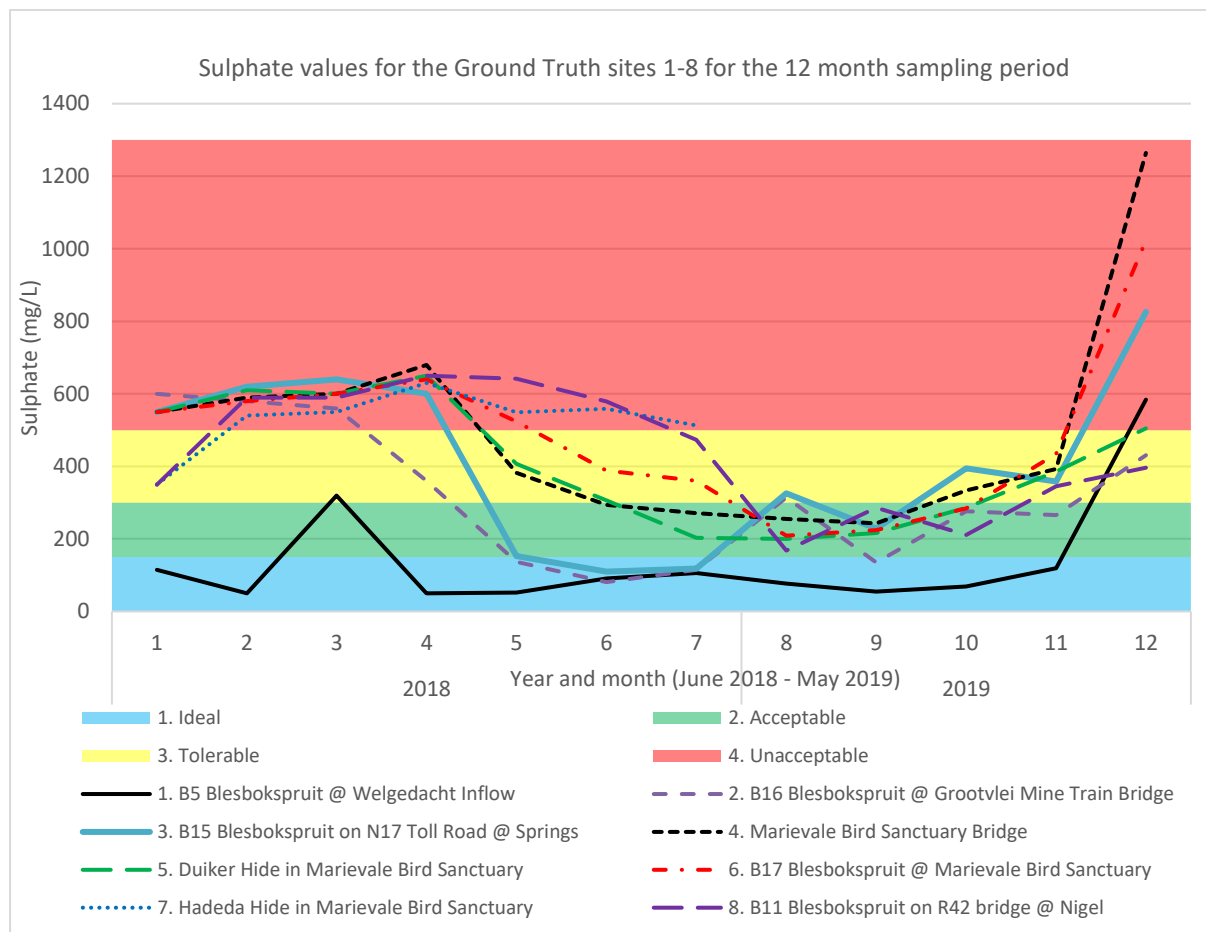


Figure 51: Sulphate values for the ground truth sites 1-8 for the 12-month sampling period.

The time series graph for sulphate shows a clear difference between site 1 (solid black line) and the remaining sample sites. For sample sites 4, 5, 6, 7 and 8 (within the Marievale Bird Sanctuary) high levels of sulphate were recorded from month 1 to month 7 (June 2018 to December 2018). Sulphate has also been underestimated by the Hach kit according to the calibration curves, meaning that true sulphate concentrations would be even higher than the ones shown above. These high sulphate values are relatable to the high conductivity values seen for months 5, 6, 7 and 8 which corresponded to low water levels at Marievale Bird Sanctuary due to a lack of rainfall during that period. The seasonal difference in rainfall had a negative influence on sulphate content. Sulphate was highest during this period as lack of rainfall promoted sulphate concentrations especially at Marievale Bird Sanctuary. When the rainfall started becoming more frequent in the new year, sulphate levels decreased within the Marievale Bird Sanctuary. During the dry season, multiple photographs had been taken of salt crust forming on the ground surfaces adjacent to the main river channel stream. This provides evidence that the Marievale Bird Sanctuary is at risk of becoming a super saline environment whenever water levels drop due to a lack of rain. The highly conductive and saline environment will negatively impact the bird populations that live within Marievale. This will be discussed further in the discussion section. The final month of sampling yielded the highest sulphate concentrations. This was seen across all the individual sites including site 1. The high sulphate values in the last month could be attributed to a combination of processes including high sulphate inputs upstream of site 1, inputs from the AMD discharge, low flow rates or low rainfall within the area.

Phosphate ground truth time series graph

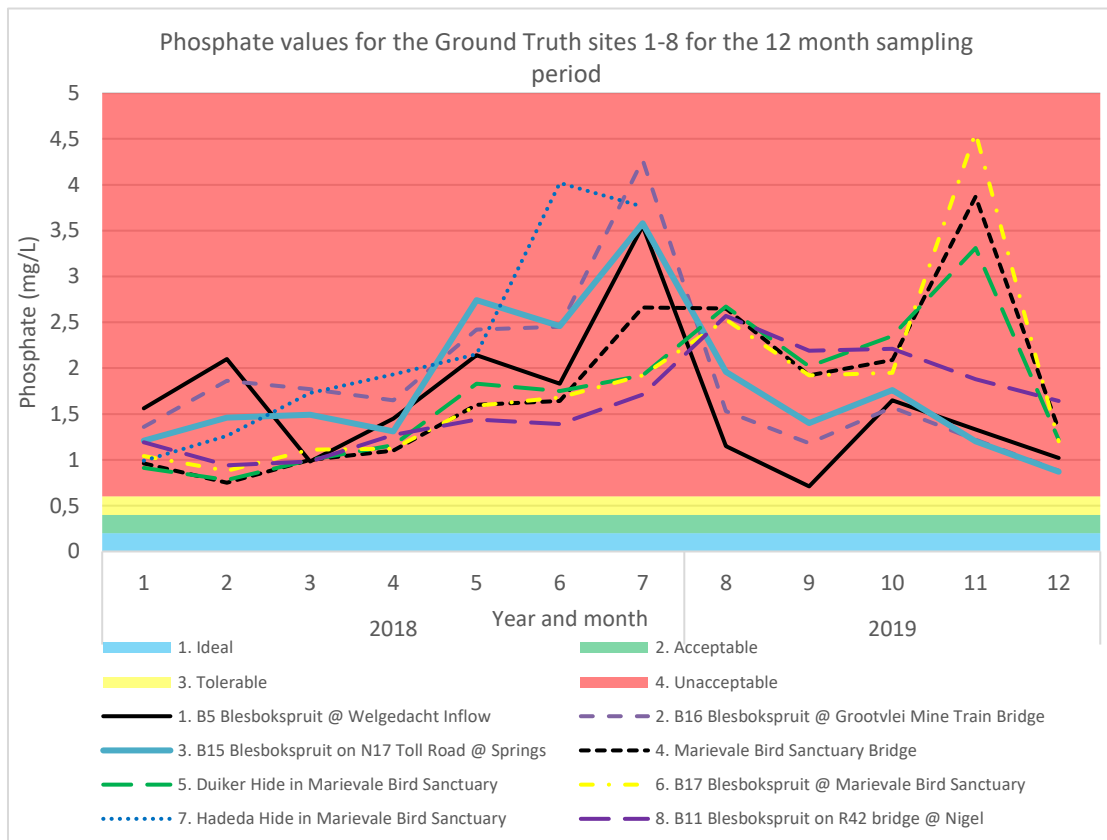


Figure 52: Phosphate values for the ground truth sites 1-8 for the 12-month sampling period

The phosphate time series graph for ground truth samples shows that phosphate is unacceptable for all the sample sites throughout the Blesbokspuit and Marievale wetlands. This does not agree with the Rand Water statistical results. The reason for the difference in phosphate levels between Rand Water and ground truth data could be due to different analytical methods used or different sampling dates/ time periods. Rand Water data indicated that phosphate levels were being diminished due to the dilution cause by the AMD treatment plant as well as phosphate uptake by the wetland. The graph above does not show much improvement between individual sample sites. It does demonstrate the need to closely monitor this water quality variable as a serious problem. Increased phosphate levels could be as a result of agricultural practices and sewage ingress at multiple areas across the greater Blesbokspuit catchment.

pH ground truth time series graph

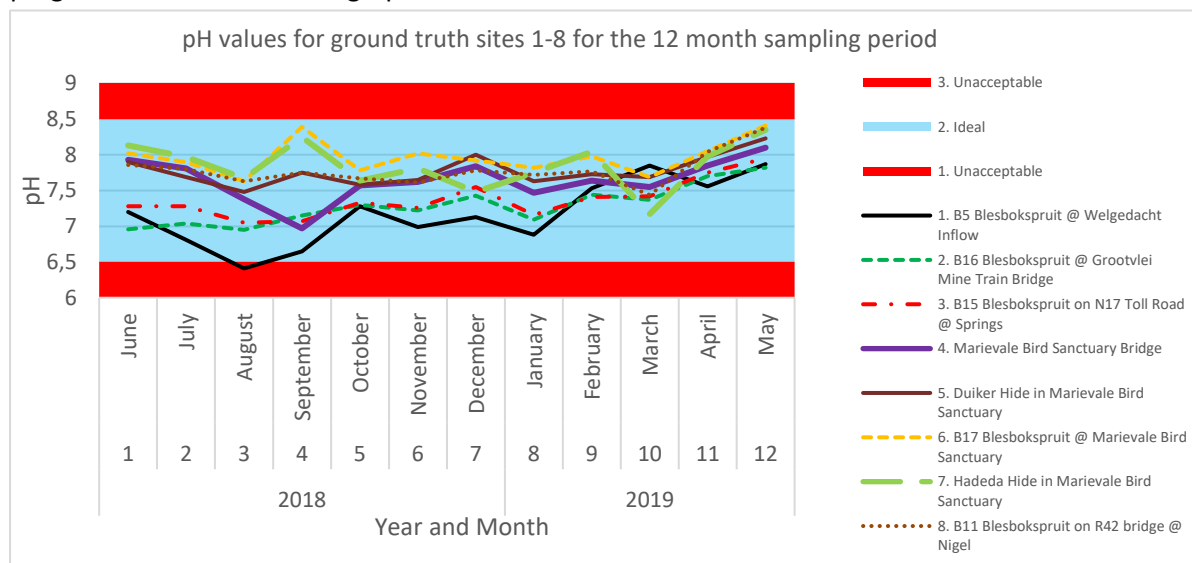


Figure 53: pH values for ground truth sites 1-8 for the 12-month sampling period

The pH time series graph agrees with the Rand Water statistical data in that pH is maintained at an ideal management target. pH increases between site 1 and site 2 which is the action of the AMD treatment plant to raise pH levels downstream through the discharge of treated water.

6.3 Soil data (soil ph and conductivity)

Two separate soil sample collections were completed in November and December 2018 in Marievale Bird Sanctuary. The soils were collected on river transects adjacent to the main river channel. The November transect yielded 9 samples and the December transect yielded 4 samples. The number of samples depended on the distance to the Marievale outer fence/border. Soils were collected roughly between 20m and 30m apart. After completing collection and analysis the following results were obtained.

6.3.1 November 2018 transect results

The November Transect was completed adjacent to Site 4 (Marievale Bridge) at the northern end of the Marievale Bird Sanctuary. A total of 9 soil samples were collected and analysed and the results are shown in the table below:

Table 30: Soil conductivity and soil pH for the November 2018 transect.

Sample No.	GPS Location	Soil Conductivity (mS/m)	Soil pH (pH)	Distance from the river edge (m)
1	S 26.33082 E 28.51320	1560	6.4	15
2	S 26.33072 E 28.51286	250.9	5.28	38
3	S 26.33060 E 28.51243	111.6	5.1	52
4	S 26.33052 E 28.51211	106	5.9	72
5	S 26.33043 E 28.51186	63.4	5.7	90
6	S 26.33030 E 28.51159	4.75	6.05	120
7	S 26.33017 E 28.51136	15.26	6.85	140
8	S 26.33012 E 28.51101	6.13	4.9	170
9	S 26.33000 E 28.51072	5.83	6.18	195

Below is a Google Earth Image illustrating the exact position of the 9 sample sites adjacent to the Marievale Bridge water collection site (site 4). The numbers 1 through 9 correspond to the GPS location and site numbers in the table above. To the West of the transect there is a mine dump as seen in the image below and the transect was performed in this direction to identify whether the mine dump has an influence over soil ph and soil conductivity.



Figure 54: Google Earth image showing the exact positions of the 9 soil sample sites.

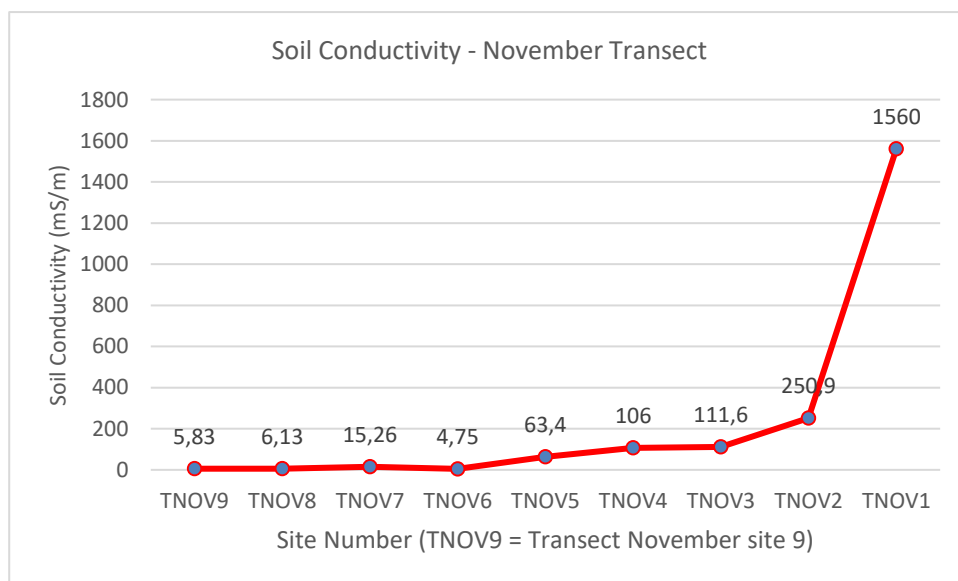


Figure 55: Soil conductivity for the 9 soil samples collected in November 2018.

As can be seen from the simple line graph above, the soil conductivity is extremely high (1560 mS/m) at site 1 closest to the river channel and the conductivity decreases further from the river, eventually decreasing to 5.83 mS/m at site 9. Conductivity follows an increasing trend towards the stream channel and decreases towards the mine dump as shown in the graph. It is possible that the mine dump may have an influence on soil conductivity, however, there is a clear indication that the river has a much greater influence on soil conductivity over the mine dump. Soil conductivity values close to the river's edge are high, indicating that the intermittently wetted areas of the riparian zone may dry up leaving behind high salt content which influences the soil conductivity. Sites 1,2,3,4 and 5 are less than 100 meters from the river's edge, the conductivity of these sites are a lot higher than sites

6, 7, 8 and 9 (which are between 120m -195m from the river). According to this data, one could infer that there is a high level of conductivity within soils adjacent to the river's edge that is a result of the high conductive nature of the water within the stream. This highly saline soil could possibly follow the trend of the flood plain within the Blesbokspruit and can have a major influence on the environment within the area.

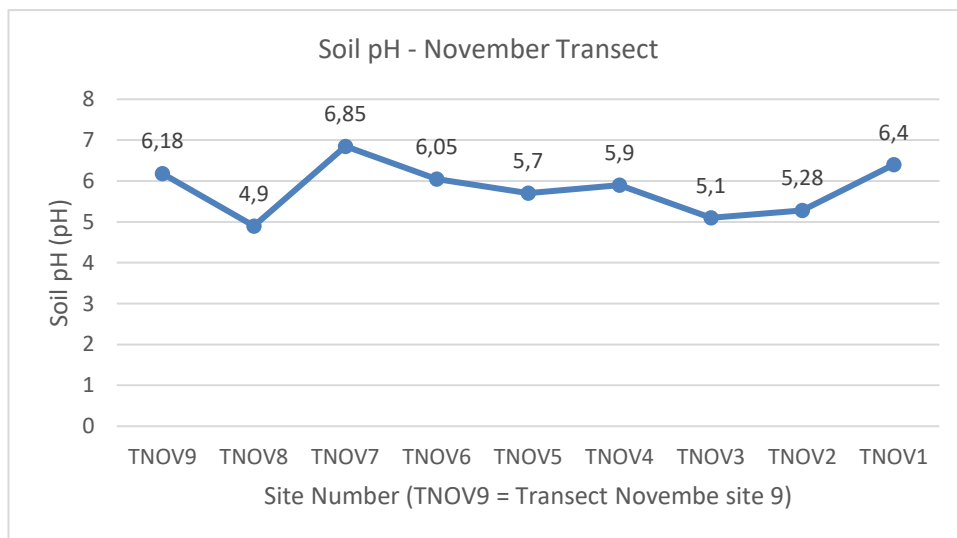


Figure 56: Soil pH for the 9 soil samples collected in November 2018.

The simple line graph above illustrates how soil pH changes from site 1 near the stream to site 9 near the tailings dam. The pH values cover a range of 1.95 pH units with the lowest (most acidic) value of 4.9 at site 8 and the highest value of 6.85 pH (near neutral) at site 7. Unlike the soil conductivity graph, there is no clear linear pattern in pH which might reflect the influence of either the river or the mine dump.

6.3.2 December 2018 transect results

The December Transect was completed roughly a kilometre south of Site 4 (Marievale Bridge) within Marievale Bird Sanctuary. A total of 4 soil samples were collected and analysed and the results are shown in the table below:

Table 31: Soil conductivity and soil pH for the December 2018 transect.

Sample No.	GPS Location	Soil Conductivity (mS/m)	Soil pH (pH)	Distance from the river edge at the time of sampling (m)
1	S 26.33769 E 28.51672	274.3	6.47	10
2	S 26.33765 E 28.51697	290.7	6.33	26
3	S 26.33758 E 28.51718	32	6.7	55
4	S 26.33746 E 28.51743	22.2	6.75	75

Below is a Google Earth Image illustrating the exact position of the 4 sample sites collected in December 2018. The numbers 1 through 4 correspond to the GPS location and site numbers in the table shown previously. At the time of sampling, sites 1 and 2 were dry and not in the river as depicted on the Google Earth Image. The dry riverbeds were due to dry conditions in the area due to lack of summer rainfall experienced in December 2018. The distance from the river's edge given in the table above was the distance from the river at the time of sampling.

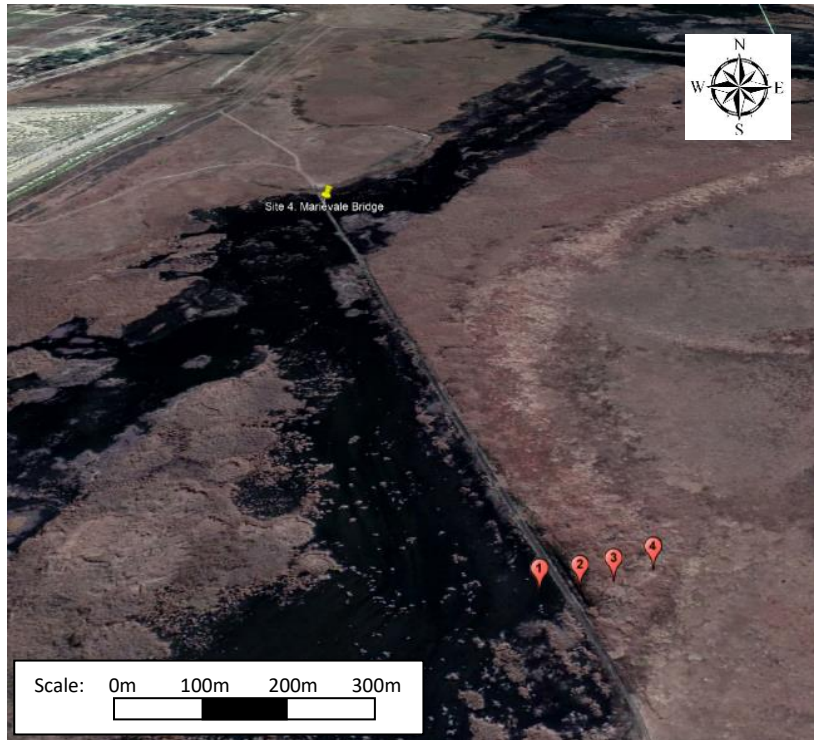


Figure 57: Google Earth image showing the exact positions of the 9 soil sample sites.

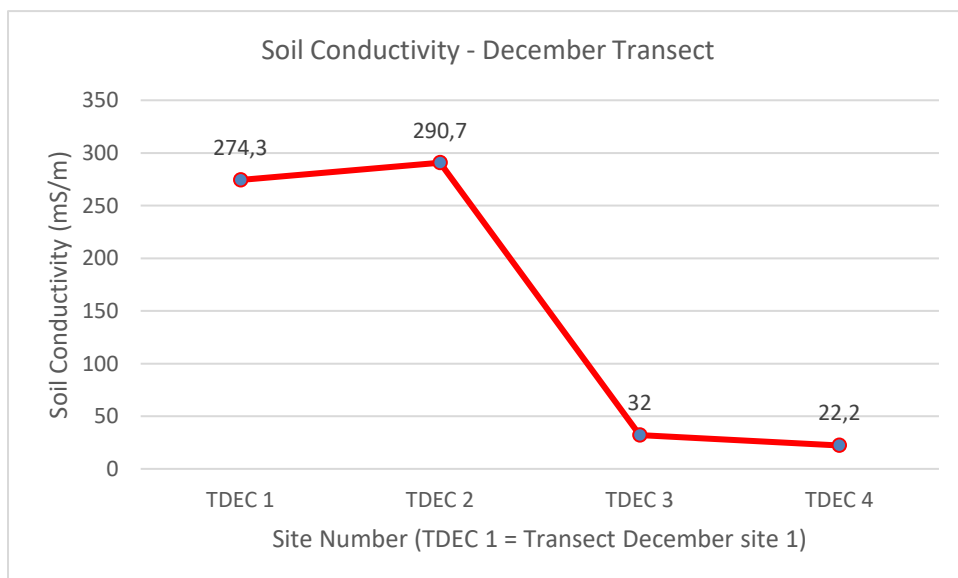


Figure 58: Soil conductivity for the 4 soil samples collected in December 2018.

The line graph above demonstrates a similar linear pattern in soil conductivity as the soils collected during the November Transect. Soils close to the river's edge (no further than 25 m away) at site 1 and 2 have high conductivity values of 274.3 and 290.7 mS/m respectively. Sites 3 and 4 have much

lower conductivities as shown in the line graph with values of 32 and 22.2 mS/m respectively. The results above and the results regarding the November transect both indicate that the high salinity load within the water that is flowing through Marievale and the greater Blesbokspruit Wetland is suggested to have a strong direct influence on the soil quality adjacent to the river channels. Some plants are detrimentally affected, both physically and chemically, by excess salts and high levels of exchangeable ions in soils (Frempong and Yanful, 2006). This will be discussed further in the discussion chapter.

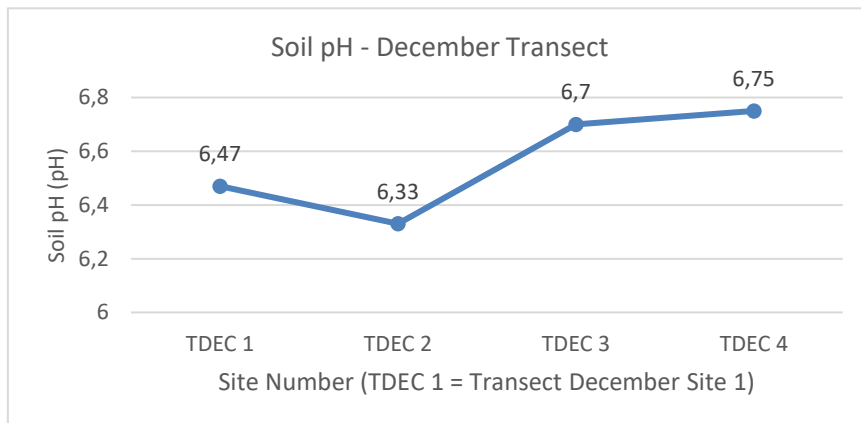


Figure 59: Soil conductivity for the 4 soil samples collected in December 2018.

The line graph above indicates the soil pH of the December Transect. The results indicate that the soil pH has a very low range of 0.28 pH units and there is no clear pattern to suggest that soil pH is highly influenced by the river system. The soil pH minimum value of 6.33 for site 2 and maximum value of 6.75 for site 4 indicate that the soil has a neutral pH. Perhaps if more samples were taken further away from the river's edge there would be a different outcome, but the Eastern boundary of the Marievale Site is no more than 10 meters from site 4 and so the transect could not be extended beyond this point. As mentioned with the December Transect soils, the soil pH within the region may be more greatly influenced by factors other than the river system.



Figure 60, 61 and 62: Photographs which provide evidence of salt crusts that have formed on the surface of the soil after water has evaporated. These photos were taken during August (dry season) 2018 at Marievale Bird Sanctuary and validate the high salinity of the area.

6.4 River sediment results: XRF spectrometry analysis of heavy metals

The sampling of river sediments gives an indication of the amount of heavy metal pollution within the wetland sediments due to historic AMD pollution. Sediment sampling was carried out in September 2018 during Spring season. The sampling sites are the same sites used for water collection. Sediment was collected from each of the riverbeds at sample sites one through eight. A gravimetric corer was used to collect approximately the top 5-10 cm of surface sediment at each sample site. The XRF Spectrometry analysis accounted for 17 different trace elements, however, only six are of importance within AMD environments.

Table 32: Heavy metal analysis for the six metals of importance within AMD environments.

Heavy Metal	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Regional Background mg/kg*	Threshold mg/kg*
Cobalt (mg/kg)	81.55	518.83	80.06	250.36	50.34	106.26	22.25	39.36	9.80	240
Nickel (mg/kg)	215.28	1816.92	243.07	341.07	126.77	223.19	77.61	61.30	36.10	210
Copper (mg/kg)	169.71	248.19	71.18	51.00	49.15	65.62	42.21	28.50	16.90	190
Zinc (mg/kg)	615.22	2803.92	187.57	625.48	493.84	495.05	478.68	139.58	97.70	720
Lead (mg/kg)	229.68	122.97	42.20	38.92	46.76	62.01	34.45	14.92	27.40	530
Uranium (mg/kg)	7.16	66.07	15.18	15.03	11.48	16.07	14.52	3.19	5.10	100

* Regional Background and Threshold values are those used in Roychoudhury and Starke (2006).

6.4.1 Sediment quality results

6.4.1.1 Enrichment factor

The enrichment factor is determined by dividing the total metal concentration of the sediment sample with the regional background. The background value acts as a target value that should be met after remediation of the site (Roychoudhury and Starke, 2006). The table below illustrates what sediment enrichment factor values correspond to the level of pollution at the site.

Table 33: Enrichment factor values and the corresponding pollution level.

Enrichment Factor Pollution Level	EF Value
Unpolluted (Target Level)	<1
Very Lightly Polluted	1 and 2
Lightly Polluted	2 and 3
Moderately Polluted	3 and 4
Highly Polluted	4 and 5
Very Highly Polluted	>5

The enrichment factor pollution levels have been adapted from Roychoudhury and Starke (2006).

Table 34: The enrichment factor for each sediment sample as well as the average enrichment for each metal and at each site.

	Sites								
Metals	S1 EF	S2 EF	S3 EF	S4 EF	S5 EF	S6 EF	S7 EF	S8 EF	Average Metal Enrichment
Cobalt	8.32	52.94	8.17	25.55	5.14	10.84	2.27	4.02	14.66
Nickel	5.96	50.33	6.73	9.45	3.51	6.18	2.15	1.70	10.75
Copper	10.04	14.69	4.21	3.02	2.91	3.88	2.50	1.69	5.37
Zinc	6.30	28.70	1.92	6.40	5.05	5.07	4.90	1.43	7.47
Lead	8.38	4.49	1.54	1.42	1.71	2.26	1.26	0.54	2.70
Uranium	1.40	12.95	2.98	2.95	2.25	3.15	2.85	0.63	3.64
Average Site Enrichment	6.74	27.35	4.26	8.13	3.43	5.23	2.65	1.67	

The table above illustrates the enrichment factors of 6 heavy metals compared to the regional background (target value) at each site. The average EF values for the metals of cobalt, nickel, copper and zinc indicate a very high level of pollution. The average EF for uranium indicates a moderate level of pollution, and the average EF of lead indicates a light level of pollution. From highest to lowest in terms of average metal enrichment; cobalt, nickel, zinc, copper, uranium and lead. When comparing the average EF for each sample site, sites 1,2,4 and 6 are described as very highly polluted with respect to the regional background. Site 3 is highly polluted on average, site 5 is moderately polluted, site 7 is lightly polluted and site 8 is very lightly polluted on average. From highest to lowest EF values with respect to the sample sites; S2, S4, S1, S6, S3, S7 and S8. It is important to note that site 2, which is downstream of the Grootvlei mine dump and its historical mine discharge point has the highest average enrichment factor of 27.35. The second highest is site 4 at the Marievale Bridge which is adjacent to a mine dump and has an average EF of 8.13. It is important to make note that the enrichment factor values downstream of site 6, at site 7 and 8. These two sites mark the end of the Marievale wetland indicating that trace metal concentrations have the tendency to decrease through the course of the wetland. What is of concern is that only 2 EF values are within the target range/background concentration (dark blue colour). Both of these are at site 8 which indicates again that heavy metals are being reduced as they pass through the wetland. However, considering that very few values meet target requirements, the possible remediation of sediments along the Blesbokspruit could be explored, especially downstream of the Grootvlei mine at site 2. What could also be interpreted is that sites 5,6,7 and 8 are further away from the mine dumps and the historical mine discharge points, which are nearer to sites 1, 2, 3 and 4. This suggests that mine dumps and historical mine discharge points have a high influence on heavy metal enrichment factor within the region. The high metal enrichment could be the result of groundwater movement, surface runoff or even windblown dust from the mine dumps and historical mine discharge points whereby heavy metals have been deposited into the Blesbokspruit sediments.

6.4.1.2 Sediment environmental risk factor (SERF)

The SERF is also a ratio and is calculated to determine the ecological risk caused by metal pollution within sediments of the study area. The SERF is determined by dividing the total metal concentration of the sample with the total metal concentration threshold. The concentration threshold value

describes the need for human intervention/remediation, as concentrations exceeding this threshold would signify high ecotoxicity potential (Roychoudhury and Starke, 2006).

The table below illustrates what SERF values correspond with toxicity levels.

Table 35: SERF factor values and the corresponding Potential toxicity level.

SERF. Potential Toxicity Level within Sediments	SERF Value
Very low potential for toxicity	<0.2
Low potential for toxicity	0.2 and 0.5
Moderate potential for toxicity	0.5 and 1.5
High potential for toxicity	>1.5

The SERF factor pollution levels have been adapted from Roychoudhury and Starke (2006).

Table 36: The SERF values of each metal within sediments at each site as well as the average SERF value for each metal and the average SERF value for each site.

	Sites (SERF values for sediments)								
Heavy metals	S1	S2	S3	S4	S5	S6	S7	S8	Average SERF for each metal
Cobalt	0.34	2.16	0.33	1.04	0.21	0.44	0.09	0.16	0.60
Nickel	1.03	8.65	1.16	1.62	0.60	1.06	0.37	0.29	1.85
Copper	0.89	1.31	0.37	0.27	0.26	0.35	0.22	0.15	0.48
Zinc	0.85	3.89	0.26	0.87	0.69	0.69	0.66	0.19	1.01
Lead	0.43	0.23	0.08	0.07	0.09	0.12	0.07	0.03	0.14
Uranium	0.07	0.66	0.15	0.15	0.11	0.16	0.15	0.03	0.19
Average SERF for each Site	0.60	2.82	0.39	0.67	0.33	0.47	0.26	0.14	

The results indicate the level of eco toxicity when comparing metal concentrations at each site with threshold concentrations. When comparing the average SERF for each metal, nickel is described as having a high potential of being toxic, cobalt and zinc have moderate potential for toxicity, copper is described as having a low potential of being toxic and both lead and uranium have a very low potential for ecotoxicity. When comparing average potential of toxicity for each metal, metals follow from highest to lowest in the following order; nickel, zinc, cobalt, copper, uranium and lead. When comparing average SERF values for each site, sites follow from highest to lowest in the following order; S2, S4, S1, S6, S3, S5, S7 and S8. Site 2 is the only site that is described as having a high potential for toxicity. This site is below the Grootvlei mine and its historical mine discharge point, and a high potential for toxicity suggests that remediation may be required in this area. Site 2 has the highest SERF values over all the other sites for all heavy metals except for lead at site 1. This suggests that lead (and other heavy metals) at site 1 reflect pollution from upstream sources. Site 1 and Site 4 fall into the moderate potential for toxicity, and according to Roychoudhury and Starke (2006), remediation is recommended for sites with a moderate potential to ecotoxicity. Sites 3, 5, 6 and 7 are described as having a low potential for toxicity and according to Roychoudhury and Starke (2006), close monitoring is recommended at sites with low potential for toxicity to ensure the toxicity potential does not increase. On average, site 8, with a very low potential for ecotoxicity, has

the lowest SERF value. The average SERF values for each site from upstream to downstream follow a trend whereby S1 has moderate potential, S2 downstream of the Grootvlei mine and its historical discharge point has a high potential for ecotoxicity and thereafter the potential for ecotoxicity diminishes downstream to the lowest value at site 8. These results suggest that the wetland could possibly play a role in reducing the potential for ecotoxicity within the sediments. What could also be interpreted is that sites 5, 6, 7 and 8 are further and further away from the historical discharge point at Grootvlei mine and other mine dumps seen nearer to sites 1, 2, 3 and 4. The distance between sample sites to mine dumps and historic decant points suggest that these mine dumps and historical decant points are highly influential to toxicity potential. These results, therefore, suggest the need to investigate whether remediation of wetland sediments would be beneficial, especially around sites that are nearer mine dumps. Overall, both EF and SERF values show similar trends and outcomes.

The following line graphs illustrates the quantity of each heavy metal within the sediments of each sample site:

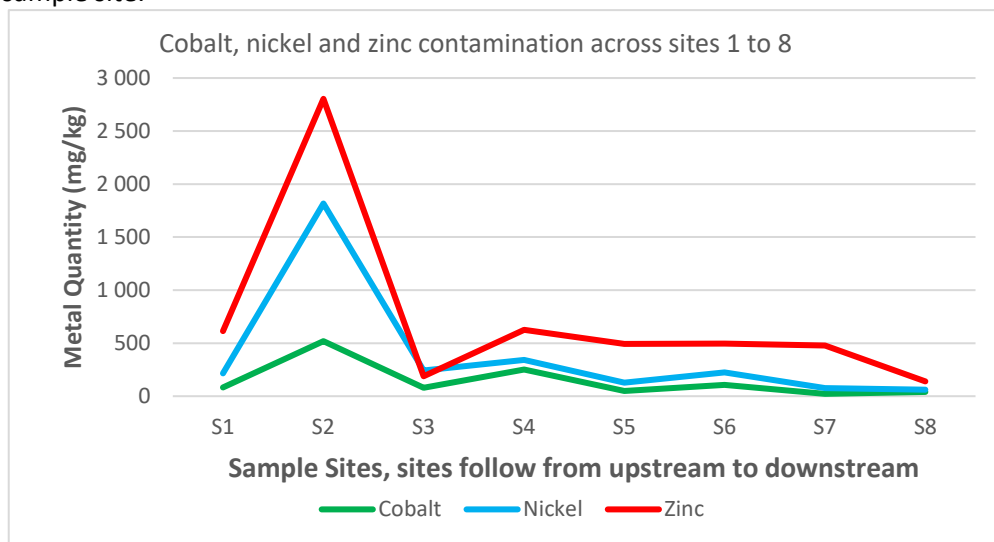


Figure 63: Cobalt, nickel and zinc contamination across sites 1 to 8.

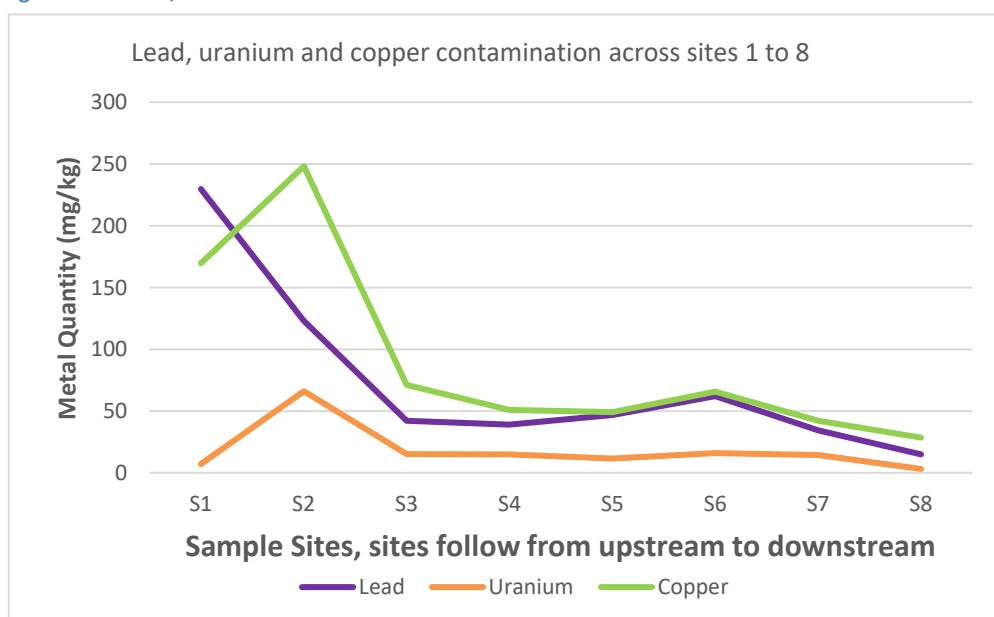


Figure 64: Lead, uranium and copper contamination across sites 1 to 8.

The two line graphs on page 95 tell a similar story to the tables shown before. Considering that the tables show factors that were determined using direct metal values, it is not surprising to see that site 2 has the highest values of metal pollution. Site 2 is also directly downstream of the original discharge point of Grootvlei mine. It is evident that metal concentrations are being reduced further downstream in both graphs. This reduction in metal concentrations could be as a result of metal uptake by the wetlands downstream or due to the sites being further away from the mine dumps and mine discharge points, or a combination of the two cases.

7. Discussion

7.1 Main aim of the study

The main aim of this study was to determine the influence of the introduction of the Eastern Basin AMD treatment Plant and the existing wetland on AMD pollution and water quality within the study area. Peer-reviewed literature concerning the Eastern Basin AMD Treat Plant has not, as yet, been published since its launch in August 2016. This research gap stood as a prospect to explore the influence of the new Eastern Basin AMD Treatment Plant as well as the greater Blesbokspruit wetland in remediating AMD pollution. The prevailing aim of this study is therefore, to examine possible solutions to the very broad geographic issue of AMD as a whole, both in South Africa and throughout the world (McCarthy, 2011). This research is significant as essential freshwater resources all over the world are becoming increasingly damaged through AMD pollution (Oberholster, 2010). Numerous defunct mining areas are spread across South Africa's gold and coal fields (McCarthy, 2011). The results of this research question could inform decision makers in being able to identify the influence these treatment processes have on water quality within AMD environments.

7.2 Summary account of the major findings

The methods used to answer this research question included making use of multiple sources of information. These included making land use/land cover maps, the use of historical water quality data from Rand Water, sampling of water, soil and sediment, laboratory analysis and statistical analysis on the data collected. Strict methods and procedures were followed throughout the research process. With regards to land use results, high percentage coverage of residential and agricultural land use classes within sample site sub catchments can be attributed to the high levels of phosphate within the Blesbokspruit Wetland area. With regards to the historical Rand Water quality results: a major finding was that, since it became operational, the AMD Treatment plant has a significantly higher influence on water quality compared to the Marievale wetland. To add, conductivity, chloride, magnesium and sulphate levels had directly increased as a result of the processes implemented by the new AMD treatment plant. Manganese and iron levels were reduced due to the dilution caused by the AMD treatment plant. Lastly, due to dilution of downstream waters by the AMD Treatment plant and nutrient intake at the Marievale Wetland, nutrients of ammonium, phosphate and nitrate are being reduced within the Blesbokspruit wetland.

With regards to ground truth water sampling data, the AMD treatment plant has a larger influence on water quality over the Marievale wetland which is agreeable to the Rand Water quality results. Both conductivity and sulphate had different populations between the two sites upstream and downstream of the AMD Treatment plant, these two variables increased significantly as a result of the processes implemented by the AMD treatment plant, and this agrees with the Rand Water results once again. Ground truth water quality results did not agree entirely with the Rand Water results in respect of phosphate reduction downstream. This could be due to different analytical methods used by Rand Water to quantify phosphate levels. Phosphate levels for the ground truth water sampling data were not reduced downstream as seen in the Rand water quality results. Soil quality results confirm that soil conductivity is extremely high adjacent to the main river channel in areas that lie within the floodplain. The results suggest that the Blesbokspruit channel has a dominant influence over soil conductivity compared to a nearby mine dump. Sediment trace metal analysis confirmed that trace metals are concentrated downstream of the abandoned Grootvlei

mine. To add, metal enrichment factors and environmental risk factors diminish greatly further away from mine dumps and historical mine discharge points.

7.3 Critical analysis of the major findings with references to previous research

7.3.1 Land Use findings

The land use maps which were generated manually provide a basic reference to the land use of the entire Blesbokspruit catchment area. Within sample site sub catchments, the results identified three major and two minor land use classes. The three major land use classes include: agriculture, residential areas and open vegetated land, and the two minor land use classes include industrial areas and mine dumps. Sub catchments for sites 1, 2 and 3 all have higher residential land use coverage compared to the sub catchments for sites 4,5,6,7 and 8, where agricultural land makes up the majority of the land cover. It was described within the literature review that land which is mainly used for agriculture and residential areas influence and increase the amount of nitrogen (nitrate and ammonium) and phosphorous (phosphate) within water (Tong and Chen, 2002). According to the historical Rand water quality and ground truth water quality results, the means of nitrate and ammonium are generally described as ideal, and phosphate means are described as unacceptable throughout the Blesbokspruit wetland. High values of phosphate seen at sites 1,2 and 3 could be attributed to the high residential land usage within these sub catchments. High values of phosphate seen at sites 4,5,6,7 and 8 could be attributed to the high agricultural land usage within these sub catchments. It is most likely that a combination of both residential and agricultural land use practices across the Blesbokspruit can be attributed to high levels of phosphate entering the Blesbokspruit wetland area.

With regards to sediment quality results, it was evident that the highest metal pollution was found at sites that are near to mine dumps and historical discharge points, and that metal pollution diminishes further from away from mine dumps and historical discharge points. The results of the sediment trace metal analysis do agree with Roychoudhury and Starke (2006) in that the highest metal concentrations were also found near mine dumps. This is especially evident at sample site 2, this site is directly downstream of the Grootvlei mines and showed the highest levels of contamination and metal enrichment compared to the other sampling sites. Due to the “mine dump land use class” having very similar percentage coverage across all 8 site catchments, looking at the percentage alone, does not account for increased metal contamination. The close proximity of sites to the individual mine dumps and the historical discharge point of Grootvlei mine (specific to site 2) is what causes the increased levels of metal contamination, and not just the percentage of mine dump land coverage within individual sub catchment sites. The sediment heavy metal results will be discussed further in this chapter.

7.3.2 Historical Rand Water quality findings

7.3.2.1 Negative influence of the AMD treatment plant

The Rand Water quality data provided historical water quality data for the Blesbokspruit. This data was used to determine changes in water quality for periods before and after the introduction of the AMD treatment plant. In sequence with the results, data summaries from site 2 for periods before and after the treatment plant determined that conductivity, sulphate, chloride and magnesium

means increased to an inferior management level targets after the AMD treatment plant came into operation. In the literature review, the short-term (phase one) remediation processes implemented by the AMD Treatment plant was hypothesised to lead to increased conductivity and high sulphate content and this was confirmed (McCarthy, 2011). The increased conductivity (water hardness) is also caused by elevated chloride and magnesium within discharge waters released by the AMD treatment plant. Hypothesis tests concluded that site 2 (downstream of the AMD treatment plant) had different populations for three water quality parameters: chloride, magnesium and sulphate which all increased and led to inferior management target levels. The Hypothesis test for different populations between site 1 (upstream of the AMD treatment plant) and site 2 (downstream of the AMD treatment plant) confirmed that nine out of the fourteen water quality parameters have different populations. This test and Rand Water time series graphs confirm that the AMD treatment plant has an extremely high influence on water quality in the Blesbokspruit, and the influences are not positive. The dissolved oxygen time-series graph shows how dissolved oxygen has decreased over time throughout the Blesbokspruit, and not just downstream of the treatment plant. This will be discussed further nearer the end of this chapter.

7.3.2.2 Positive influence of the Eastern Basin AMD treatment plant

Peer-reviewed literature concerning the Eastern Basin AMD treatment plant has not been published. However, media reports highlighted that since the treatment plant had come into operation, iron and manganese levels were being reduced and pH levels were being increased at the AMD treatment plant. The Rand Water quality results section had confirmed that both iron and manganese were being reduced, on average, at site 2 for the period before and after the AMD treatment plant began operating. It is reasonable to suggest that this reduction in iron and manganese is due to the dilution of the stream water caused by the AMD treatment plant discharging clean overflow water into the wetland downstream. The iron and manganese that is treated at the plant (referred to in the media reports) originates from the AMD water being pumped up to the treatment plant from underground and the treated metal containing sludge would be disposed of back down the shaft. Therefore, the AMD treatment plant does not directly reduce iron and manganese within the Blesbokspruit stream, but rather reduces the iron and manganese indirectly by diluting stream water when it discharges the clean overflow water from the thickeners section of the plant. The same argument can be made for the reduction in the nutrients of phosphate, ammonium and nitrate considering that the treated water does not originate from the stream itself. AMD water pumped from underground can be assumed to have little to no nutrients, when this water is treated and the subsequent metal sludge is disposed of underground, the clean overflow of water that is produced and later discharged into the wetland is thought to have low concentrations of nutrients (and heavy metals). The reduction of nutrients between site 1 and site 2 can be simply due to the dilution caused when the clean overflow water is discharged into the wetland downstream of the treatment plant. It cannot be overlooked that although phosphate is being reduced, it still does not completely fall into the ideal or acceptable management target levels. pH is being maintained at an ideal level. The neutral to basic pH levels were also described by Ambani and Annegarn (2015) for the Blesbokspruit. Maintaining this ideal target pH level is advantageous as acidic waters have the potential to dissolve toxic heavy metals in the environment (Akciil and Koldas, 2006).

7.3.2.3 Influence of the greater Blesbokspruit and Marievale Wetlands on water quality

With reference to the Rand Water quality results, the influence of the Marievale wetland has much less significance compared to the AMD treatment plant. This was demonstrated in the hypothesis test where the comparison of populations between site 1 (upstream of the treatment plant) and site 2 (downstream of the treatment plant) indicated that nine of the fourteen parameters have different populations. Compare this to only three of the fourteen water quality parameters which were shown to have different populations between site 3 (upstream of the Marievale Wetland) and site 5 (downstream of the Marievale Wetland). The three populations that were shown to have different populations include ammonium, dissolved oxygen and nitrate. It has already been mentioned that both ammonium and nitrate were reduced due to dilution caused by the discharge of the clean overflow into the wetland by the AMD treatment plant. The role of the greater Blesbokspruit and Marievale wetland in reducing these two nutrients is also shown in the Rand Water box plot results. Both ammonium and nitrate are essential for all plants and animals (Gilbert *et al.*, 2005). The reduction of these two nutrients is direct evidence that the Marievale Wetland is promoting ammonium and nitrate uptake within the Blesbokspruit. The exact mechanisms (mainly biological) by which nutrient uptake is taking place are difficult to pinpoint as mentioned within the literature review (Matagi *et al.*, 1998). The main biological mechanisms occurring in wetlands that results in removal of pollutants and nutrients are photosynthesis, respiration, fermentation, nitrification, denitrification and phosphorus removal (Khanijo, 2002). It is possible that a number of these biological mechanisms are taking place simultaneously at different places within the greater Blesbokspruit and Marievale Wetlands.

As far as remediating AMD pollution, the Marievale and greater Blesbokspruit Wetlands are a lot less effective. Irrespective of the management targets achieved, water quality is remains constant between Rand Water site 3 (upstream of the Marievale Wetland) and site 5 (downstream of the Marievale Wetland) over time. The possible cause of little to no influence may be due to little interaction between the flowing river channel and the wetland areas between Rand Water site 3 and site 5. What is significant is that since the AMD treatment plant launched, water quality has been highly impacted. The water quality data obtained from the wetland are a direct result of what is occurring upstream, and the wetland shows little indication of reducing/improving most water quality parameters especially after the AMD treatment plant came into operation. Where there is improvement, in the case of nutrient uptake, these improvements do not directly relate to water quality parameters indicative of AMD pollution such as iron, manganese, magnesium and sulphate.

7.3.3 Ground truth water quality findings:

7.3.3.1 Influence of the AMD treatment plant and the Blesbokspruit Wetland:

Ground truth water quality data were collected in order to identify seasonal changes in water quality as well as making comparisons with the Rand Water quality data. In terms of the influence of the AMD treatment plant, it was demonstrated through hypothesis testing that both sulphate and conductivity have different populations between site 1 and site 2. Between site 1 and 2, on average, sulphate moved from the ideal management target to the tolerable management target and conductivity moved from the acceptable management target to the tolerable management target. According to the sulphate calibration curve, sulphate is also being underestimated by roughly 20% and is a parameter of major concern. The increase of these two parameters agrees with the Rand

Water data as well as the literature. In terms of influence on water quality, the AMD treatment plant has a greater influence on water quality than the Marievale Wetland. This was demonstrated as the hypothesis test between site 4 (upstream of the Marievale Wetland) and site 8 (downstream of the Marievale Wetland) indicated that all the individual water quality parameters have the same population, and this agrees with the Rand water quality results. With respect to phosphate, the ground water sampling data does not agree with the Rand Water data whereby phosphate is being reduced downstream. The phosphate time series graph shows that phosphate is at an unacceptable management level throughout and is a potential environmental issue within the study area. The overall influence of the Marievale wetland is minimal with regards to remediating AMD pollution according to the ground truth data, this is comparable to the Rand Water quality data results mentioned previously.

7.3.3.2 Seasonal variations in water quality:

Both the conductivity and sulphate time series graphs indicated that these two water quality parameters increased during the periods with little rainfall. This confirms the results of Ambani and Annegarn (2015) whereby the greatest values in conductivity occurred during the dry season when rainwater surface runoff was low and could not dilute contaminated stream water. What is significant is that this paper was written before the treatment plant came into operation. This indicates that the high conductivity within the area has been a problem even before the AMD treatment plant started, and now conductivity (including sulphate, chloride and other dissolved salts) is being increased furthermore since the AMD treatment plant came into operation. As mentioned, the sulphate calibration curves also suggest that sulphate concentrations are underestimated by the Hach test kit by roughly 20%. This is a concern as sulphate is being underestimated and is a parameter raising to tolerable management target levels. It should also not go without mention that site 7 (Hadedda Hide) within the Marievale wetland had become completely inundated with both green algae and duckweed from January 2019 to May 2019. The presence of these two problem species is another overriding issue within the Marievale Bird Sanctuary, and these and other issues will be discussed further in this chapter.

7.3.4 Soil quality findings

7.3.4.1 Soil Conductivity

Soil pH and soil conductivity were both obtained from soils collected from two separate soil sampling transects. The results indicated that soil conductivity is highly influenced by the Blesbokspruit channel. The soil sampling transect completed in November 2018 demonstrated that soil conductivity increased towards the river channel and not an adjacent mine dump. This is an important finding in that the stream itself has a stronger influence on soil conductivity compared to an adjacent mine dump. This is something that may have been predicted as the Blesbokpruit water is described as having high conductivity (Ambani and Annegarn, 2015). The results suggest that the stream is a source of increased conductivity. This spatial analysis of soil within the Marievale Bird Sanctuary from this research can be used to compare soil samples collected in the future to consider if the soil may become increasingly saline over time due to the stream. With increasing conductivity of stream water from the upstream source at the AMD treatment plant, one would expect that soil conductivity near the intermittently wetted riparian zones of Marievale Bird Sanctuary to become increasingly saline in the future.

A significant finding regarding soil conductivity was discovered during the December transect collection. The first two samples were collected within the dried-up riverbed. A lack of summer rainfall during this period led to the drying up of the riverbed and the river becoming extremely low with a narrow channel. It is clear that the Marievale Bird Sanctuary has an issue in terms of highly conductive and saline soils from the photographic evidence shown. To add, this increased salinity will become exacerbated during the dry season when water is unable to become diluted from lack of rain and upstream flows within the catchment. The ground truth conductivity and sulphate time-series graphs indicate that during this dry spell both conductivity and sulphate increased within the stream. There is cause for concern with regards to soil conductivity, and this may be aggravated during dry spells. Capillary action of the ground water near the surface soil could be a contributing process that caused these salt crusts to form adjacent to the main river channels. The flat topography of the area may cause highly saline stream water to flow over the intermittently wetted riparian zones in the low-lying areas of Marievale Bird Sanctuary. The water would eventually be evaporated leaving behind conductive salts forming these salt crusts on the topsoil surface layer. There is extensive evidence of salt crusts that have formed adjacent to river streams at the Marievale Bird Sanctuary.

7.3.4.2 Soil pH

In a study conducted by Naiker *et al.* (2003) regarding the Witwatersrand gold region, the research concluded that ground water within the mining area was extremely contaminated with heavy metals and was highly acidic (Naiker *et al.*, 2003). One would expect that the soils collected during the November and December 2018 transect would showcase a similar acidic trend, but this is not the case within the Marievale Bird Sanctuary soils. There is no clear linear trend of decreasing pH levels (acidic levels) in soils approaching the main river stream. The stream may have an influence on soil pH, but this influence is not significant according to the results of this research.

7.3.5 Sediment heavy metal findings

River sediment heavy metal analysis gives an indication of the potential levels of heavy metal contamination within river sediments due to historic mine pollution. Two sediment quality factors were used to determine sediment quality. The factors calculated were the metal enrichment factor (EF) and the sediment environmental risk factor (SERF). These factors were adapted from Roychoudhury and Starke (2006) who analysed sediment within the Blesbokspruit wetland. For the eight individual sampling sites; cobalt, nickel, copper and zinc all represented highly polluted enrichment factors. Site 2, directly downstream of the Grootvlei mine dump and the historical mine discharge point, had an average enrichment factor of 27.35 for all six metals, which exceeds the “very highly polluted” category by an incredibly high 22.35. Cobalt and Nickel at this site are both enriched by a factor of over 50 which demonstrates the highly elevated heavy metal enrichment at this site. In terms of sediment toxicity, nickel was described to have a high potential for toxicity on average. Both cobalt and zinc were described as having a moderate potential for toxicity on average and site 2 was described as having a high potential for toxicity. According to Roychoudhury and Starke (2006), moderate to high potential for toxicity indicates that effective remediation/ human intervention is required. The results of the sediment trace metal analysis do agree with Roychoudhury and Starke (2006) in that the highest metal pollution was found at sites that are near to mine dumps and discharge points, and that metal pollution diminishes further from these areas. It

is possible that the reduction in metal concentrations is not only seen at sample sites further away from mine dumps and discharge points, but also due to metal reduction mechanisms within wetland ecosystems.

As per the literature, the four main metal reduction mechanisms within wetland environments are physical, chemical, biological and biochemical (Matagi et al., 1998). These mechanisms occur within the water, biota (plants and animals), substratum (underlying bottom layer of sediment) and suspended solids of the wetland (Padmavathiamma and Li, 2007). In most cases these processes are dependent on one another, they occur simultaneously and therefore it is difficult to pinpoint the exact mechanism which is taking place at any given time (Matagi et al., 1998). However, due to the results seen, it is conceivable that these mechanisms are in fact occurring within the Blesbokspruit wetland. For example, it is likely that metals that chemically precipitate out of solution aggregate into particles that are large enough to sink and may have become trapped in the wetland substratum. In this case, one would expect that the sediments nearer the metal pollution sources of mine dumps and discharge points would have higher metal pollution, and this is exactly the case seen within the Blesbokspruit. Sediments that were collected further away from pollution sources did indeed have lower metal pollution than those collected nearer pollution sources. Along with physical mechanisms mentioned, trace metals are also reduced by biological mechanisms such as plant uptake. For example, floating plants such as duckweed and water fern store iron and copper found in wastewater (Sakadevan and Bavor, 1999; Maine et al., 2006). *Typha* and *Phragmites* reed beds also aid in the role of heavy metal uptake (Sakadevan and Bavor, 1999; Khanijo, 2002). All the plants mentioned thrive within the Blesbokspruit and Marievale wetlands and it is likely that these plants are aiding in heavy metal intake. Therefore, heavy metals are trapped both mechanically and biologically within the Blesbokspruit and Marievale wetlands, reducing heavy metal mobilisation downstream.

7.4 Environmental problems within the Blesbokspruit and Marievale Wetland

This section will account for the environmental problems within the Marievale Bird Sanctuary. These problems were observed from field visits and are an extension of the main results obtained from this study.

7.4.1 Dissolved oxygen, nitrate and phosphate

Dissolved oxygen has decreased over time throughout the Blesbokspruit wetland. Dissolved oxygen is promoted either through diffusion of oxygen rich air from the surrounding environment or produced as a result of photosynthesis (Chislock et al., 2013). Diffusion of oxygen into the water is also promoted by increased flow rates (Chislock et al., 2013). Dissolved oxygen is necessary for aquatic organisms and can be altered by eutrophication. There is a direct relationship between dissolved oxygen availability and the amount of nutrients (nitrate and phosphate) within the water. Although not directly observed, the promotion of nutrients may be due to sewerage ingress or agricultural practices seen throughout the Marievale and Blesbokspruit Wetland. Figures 18 and 19 within the results section show possible pollution sources across the Blesbokspruit Catchment, including wastewater treatment plants. There is evidence that there are increasing algal and duckweed blooms across the Blesbokspruit wetland, especially within Marievale Bird Sanctuary at Hadedda hide (site 7). The excess nutrients of phosphate and nitrate analysed within these waters may have promoted the growth of these algal blooms, which in turn reduce dissolved oxygen within

the water. The slow flow rates at Hadedda hide can also be attributed to the increased area occupied by common reed beds. McKay et al. (2018) calculated that 11 percent of open water was lost from 2002 to 2013 due to *Phragmites australis* and *Typha capensis* growth. The lack of removal of these reed beds is an issue as they lead to slow flow rates, which would reduce dissolved oxygen availability in the water. The area of open water is also important to waterfowl, and this area is susceptible to shrinkage during the dry season as mentioned. The birds at Marievale may migrate to other water bodies in the surrounding areas leading to permanent damages to the Marievale tourist attraction (McKay et al., 2018).

7.4.2 High levels of conductivity and sulphate

The Blesbokspruit waters were described as being highly conductive within literature that was published before the AMD treatment plant came into operation. The results of this study indicate that the AMD treatment plant is promoting conductivity levels within an existing, highly conductive environment. It is reasonable to deduce that phase one of the AMD treatment plant has beneficial impacts in treating heavy metals from underground AMD water and maintaining ground water below the environmental critical level. However, the processes used by the plant are not improving water quality downstream, especially with regards to conductivity and sulphate. Conductivity and sulphate (sulphate concentrations being underestimated in ground truth water quality data) levels seen at Marievale are of high concern, and for the majority of the Blesbokspruit wetland lies within the tolerable to unacceptable management target levels which have high potential to be damaging to the environment. Soil quality results suggest that stream itself has become a high conductivity source. High conductivity values indicate high total dissolved solids and hence potential salinisation. Most aquatic species have evolved in environments with specific conductivity levels, conductivity levels outside of the normal range can be damaging to the aquatic life within the water. As a result, only hardier species may be able to survive this environment (Ochieng, 2010). The core issue of increased sulphate levels involves the chemical reaction producing H_2SO_4 (sulphuric acid) during the process of sulphide oxidation (McCarthy, 2011). This process is responsible for AMD and all the issues surrounding AMD which have been mentioned. The H_2SO_4 is neutralised within the plant with lime water (dilute aqueous solution of calcium hydroxide, $\text{Ca}(\text{OH})_2$) and what is expected is that through this neutralisation, $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$ (4) calcium hydroxide reacts with sulphuric acid to produce calcium sulphate and water (McCarthy, 2011). The large amounts of calcium sulphate being produced through this reaction are being discharged into the Blesbokspruit Wetland downstream of the treatment plant and increasing the levels of conductivity both within the water and the soil adjacent to the stream.

7.4.3 Heavy metals

Heavy metals within the Blesbokspruit wetland are of high concern. The bioaccumulation of heavy metals cannot be overlooked. According to the results, the sediments are highly polluted with cobalt, nickel, copper and zinc. These metals are highly enriched, on average, with respect to the regional background geology of the area. Nickel was described as having a high potential for ecotoxicity, zinc and cobalt was described as having a moderate potential for ecotoxicity and copper was described as having a low potential for ecotoxicity within the sediments. The toxicity factors were determined using threshold values and are based upon Dutch Regulations for wetland trace metal remediation (Roychoudhury and Starke 2006). From the literature, nickel in high doses are

teratogenic and carcinogenic to mammals (DWAF, 1996). Zinc is toxic to fish and aquatic organisms at low concentrations, and the highest concentration of zinc salts such as zinc sulphate occurs in waters that are acidic and highly conductive (DWAF, 1996). Cobalt and copper generally mobilise under acidic conditions and the accumulate in soil and sediment (DWAF, 1996). The potential for ecotoxicity caused by these metals indicates that effective remediation of sediment heavy metals may be required within the Blesbokspruit.

7.5 Deduction

The introduction of the Eastern Basin Treatment plant was extremely necessary as the abandoned Grootvlei Mine was being flooded, and there was high potential that AMD would decant to the surrounding environment (Kruger, 2017; Solomons, 2017). The introduction of the AMD treatment plant was a step in the right direction. However, the second phase of treatment is becoming more and more essential. The second phase/ long-term solution of treatment is said to incorporate desalination processes (DWS, 2017). It is a problem that the current phase (phase one) of AMD treatment plant is not intended to discharge potable water downstream. Phase two is intended to discharge potable water from the treatment plant downstream (DWS, 2017). This could be highly beneficial and the hopes of securing water supply within Gauteng water supply could be greatly enhanced. Through the AMD treatment process, the discharge that is produced is promoting high levels of conductivity, chloride, magnesium and sulphate downstream. The AMD treatment plant is beneficial in terms raising pH levels through downstream discharges. High levels of pH being maintained within the region reduce the waters susceptibility to dissolve toxic heavy metals. The positive influence that the AMD treatment plant has had on water quality downstream have been indirectly achieved and were unexpected. During the process of treating underground AMD, the clean overflow discharge that is produced enters into the river downstream. The increase in flow caused by the discharge causes heavy metals such as iron and manganese, and the nutrients of ammonium, nitrate and phosphate to become diluted downstream of the AMD treatment plant. This can be investigated and substantiated further if flow data of the Blesbokspruit was available. However, due to the enormous amount of water that is being pumped from underground, some of which is eventually discharged, one would expect that flow rates downstream of the AMD treatment plant have increased since it came into operation.

The overall influence of the AMD treatment plant is extremely high compared to the influence of the Marievale and greater Blesbokspruit wetland. In some cases, nutrient levels are shown to diminish as a result of the wetland. The role of the wetland cannot be overlooked, it is a former Ramsar site with international importance. The Marievale Bird Sanctuary has a high amenity value and promotes tourism and conservation. The Marievale wetland is home to numerous species of waterfowl, fish and other important biodiversity. This wetland is exposed to processes occurring at the AMD treatment plant upstream, some of which have the potential to be highly damaging to the environment. Water quality within the greater Blesbokspruit does not meet acceptable and ideal management targets set out by the Blesbokspruit Forum. Wetland protection and preservation is crucial to improve water quality within this area.

7.6 Limitations of the study

There are some limitations of this study and these will be addressed. Throughout the research process, efforts were made to produce highly accurate data and results. Human error across multiple facets including field and laboratory work may have occurred. With regards to the major ion determination of ground truth water samples, the Hach test kit is not highly accurate and its limitations have been mentioned. However, calibration curves have been made for each water quality parameter and adjustments to the results have been accounted for, especially with regards to sulphate. With regards to the land use/ land cover map, the manual classification of land use classes cannot be considered to be completely accurate. The maps themselves provide an idea of the land use within each sample site catchment but they provided limited assistance in interpreting spatial patterns. However, certain relationships between land use classes and water and sediment quality have been mentioned. With regards to the water quality and trace metal sediment quality guidelines, both of these guidelines have limitations that have been fully explained previously. With regards to the historical water data, the period before the treatment plant spans a time frame that is a lot shorter than the period after the treatment plant came into operation. One can argue that the time frames for before and after the AMD treatment plant came into operation should be the same in order to account for seasonal changes, and this is a limitation of this study. However, the changes in seasonality were examined and discussed according to the ground truth water quality results. With regards to the composition of the salt crusts that have formed throughout Marievale Bird Sanctuary shown in the text. The composition of these salt crusts is unknown. This is due to the limited scope of this project, research into identifying the composition of these salts could be carried out in the future.

7.7 Considerations for future research

In terms of considerations for future research, more projects which have similar aspects such as AMD treatment plants and wetlands can be investigated, especially within the South African context. Further scientific work surrounding the Eastern Basin AMD treatment plant is required to demonstrate its benefits and influences on society and the environment. Projects that are centred around further understanding of the numerous biogeochemical processes occurring within this complex system could be carried out in the future. This would include determining the composition of the salt crusts at Marievale. The Marievale Bird Sanctuary has a large biodiversity and is a tourist attraction, its preservation and future can only be upheld through investigation, conservation and research. The water quality situation is of utmost importance, not only for our current population but increasingly important for future generations. Work around the preservation and upkeep of wetlands and rivers is extremely important no matter the context. Lastly, AMD is an extremely damaging process for both the human and natural environment. Efforts to mitigate and lessen the effects of AMD through research are extremely valuable and important to society and the environment as a whole, especially within South Africa.

8. Conclusion and concluding statements

The main aim of this research project was to determine the influence of a chemical treatment plant and an existing wetland ecosystem on AMD pollution and water quality along the Blesbokspruit. The research process involved making land use maps, using historical Rand Water quality data and collecting water, sediment and soil samples. Several concluding statements have been made regarding the results of the research.

1. The introduction of the Eastern Basin Treatment plant was extremely necessary as the abandoned Grootvlei Mine was being flooded, and there was a high potential that AMD would decant to the surrounding environment. Without the AMD treatment plant, toxic AMD water from the flooded mine reefs would have surpassed the environmental critical level and decanted into the Blesbokspruit. The consequences of AMD decant would have been devastating to both the environment and the surrounding residential areas. Trace elements such as cobalt, lead, nickel, arsenic, zinc, uranium within AMD decant would have mobilised throughout the Blesbokspruit.

2. As a result of the processes implemented by the AMD treatment plant, the in-stream concentrations of the metals of iron and manganese, and the nutrients of ammonium, nitrate and phosphate are being reduced. This reduction was unexpected and is suggested to be as a result of dilution due to increased flow caused by the AMD treatment plant discharges downstream.

3. The negative influences on water quality caused by the AMD treatment plant are due to the increased levels of conductivity, sulphate, magnesium and chloride downstream of the plant. These increases are presumably due to high concentrations of these water quality parameters within the discharge water released by the treatment plant.

4. The introduction of the AMD treatment plant was a step in the right direction. However, the second phase of treatment is becoming more and more essential. The second phase/ long-term solution of treatment is said to incorporate desalination processes. It is problematic that the current phase (phase one) of AMD treatment plant is not intended to discharge potable water downstream. The intention of phase one is to maintain groundwater levels below the environmental critical level for the Eastern Basin. Phase two is intended to discharge potable water from the treatment plant downstream. This could be highly beneficial and the hopes of securing water supply within Gauteng could be greatly enhanced.

5. Phase two of treatment is intended to discharge potable water into the wetland. The second phase of treatment is becoming more important over time. This is not only demonstrated by the Rand Water and ground truth water quality results, but also by the soil quality results. The spatial analysis of soil salinity (as indicated by conductivity) suggests that the Blesbokspruit is a source of increased soil salinity. Given the history of AMD pollution in the Blesbokspruit, soil salinity may have been elevated even before the AMD treatment plant came into operation. Increased salinisation is known to negatively impact aquatic plants and animals. Analysis of soils in the future may give an indication into the future projections of soil quality within the wetland soils of Marievale Bird Sanctuary.

6. The overall state of the river downstream of the treatment plant and the wetlands in relation to the Blesbokspruit Forum management targets can be described as deteriorating for certain parameters. Certain parameters such as conductivity and sulphate have reached unacceptable

management target levels as a result of the discharge of treated water from the AMD treatment plant. Dissolved oxygen is also at an unacceptable management target, but this is probably not due to the AMD treatment plant as mentioned in the discussion. According to ground truth results, phosphate is also at an unacceptable target level within the Blesbokspuit. Other parameters such as iron and pH are at ideal levels which is positive for the area.

7. River sediment heavy metal analysis gave an indication of the potential levels of heavy metal contamination. Sediment heavy metal analysis results suggest that the sediments collected from the eight sampling sites are highly polluted and have a low to moderate potential for ecotoxicity. The results demonstrated that metal enrichment factors and environmental risk factors increased at sites which were in close proximity to both mine dumps and historical mine decant points. This was especially evident at site 2 which is downstream of the abandoned Grootvlei mine dump and its historical decant point. Sediment heavy metal results also suggested that increased metal concentrations can be attributed to upstream land use areas such as industry within the Blesbokspuit catchment. Future sediment analysis may be of value to identify spatial trends in heavy metal contamination throughout the Blesbokspuit. Such analyses could determine whether remediation of sediments is required within the Blesbokspuit.

8. There are numerous environmental concerns within the Blesbokspuit Wetland and the Marievale Bird Sanctuary. These are demonstrated by water, sediment and soil sample analysis and results mentioned in the above concluding statements. Future research and studies focused on environmental monitoring within these wetland areas may improve the current situation. The continued conservation and protection of the greater Blesbokspuit wetland and Marievale Bird Sanctuary is extremely important, not only to the environment and the biodiversity they support but also to the surrounding communities.

9. The greater Blesbokspuit and Marievale wetlands are far less influential on water quality than the Eastern Basin AMD treatment plant. The wetlands do show evidence of reducing nutrient levels downstream. The AMD treatment plant does not only influence water quality, it may also influence the soils and sediments and hence the ecology of the Marievale Bird Sanctuary reserve. The influences from the AMD treatment plant upstream of the Marievale Bird Sanctuary are not entirely positive as mentioned in the above concluding statements.

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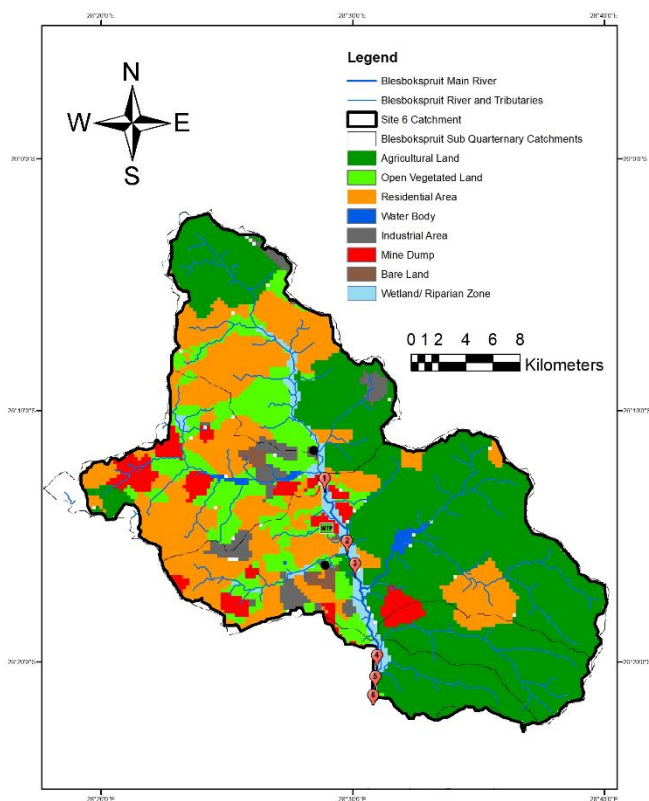
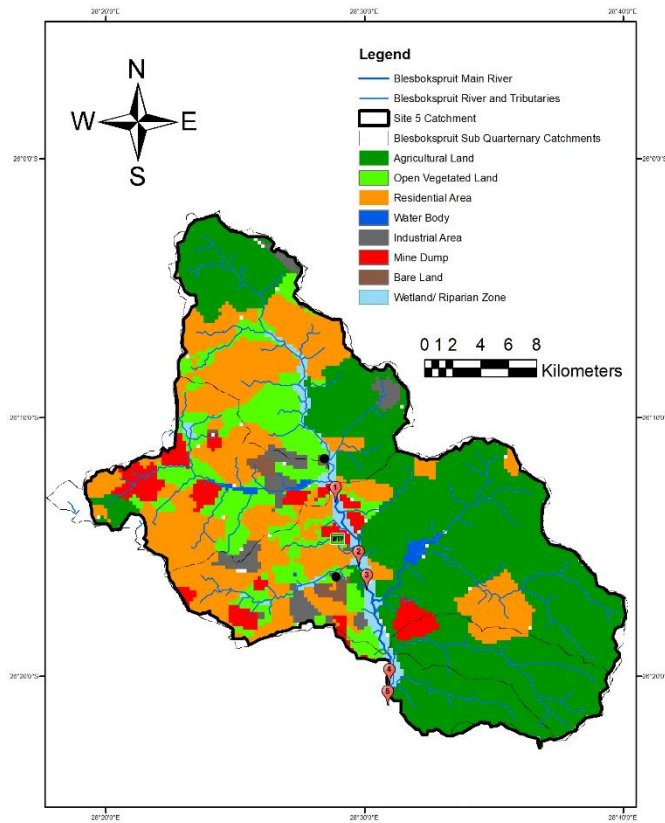
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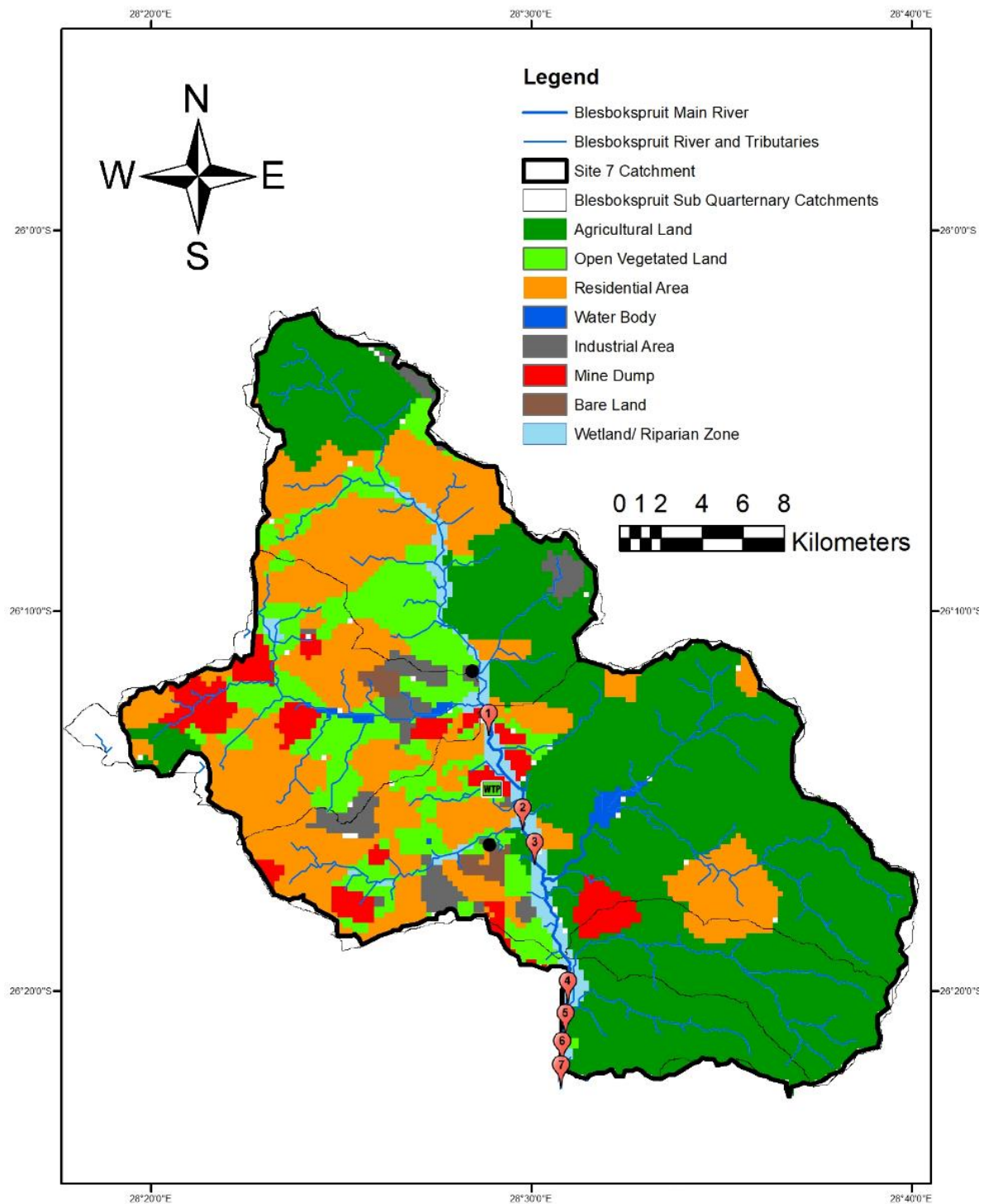
9. Appendix

The appendix includes images and raw data that was not shown within the main text.

Site 5 and site 6 sub catchments



Site 7 sub catchment

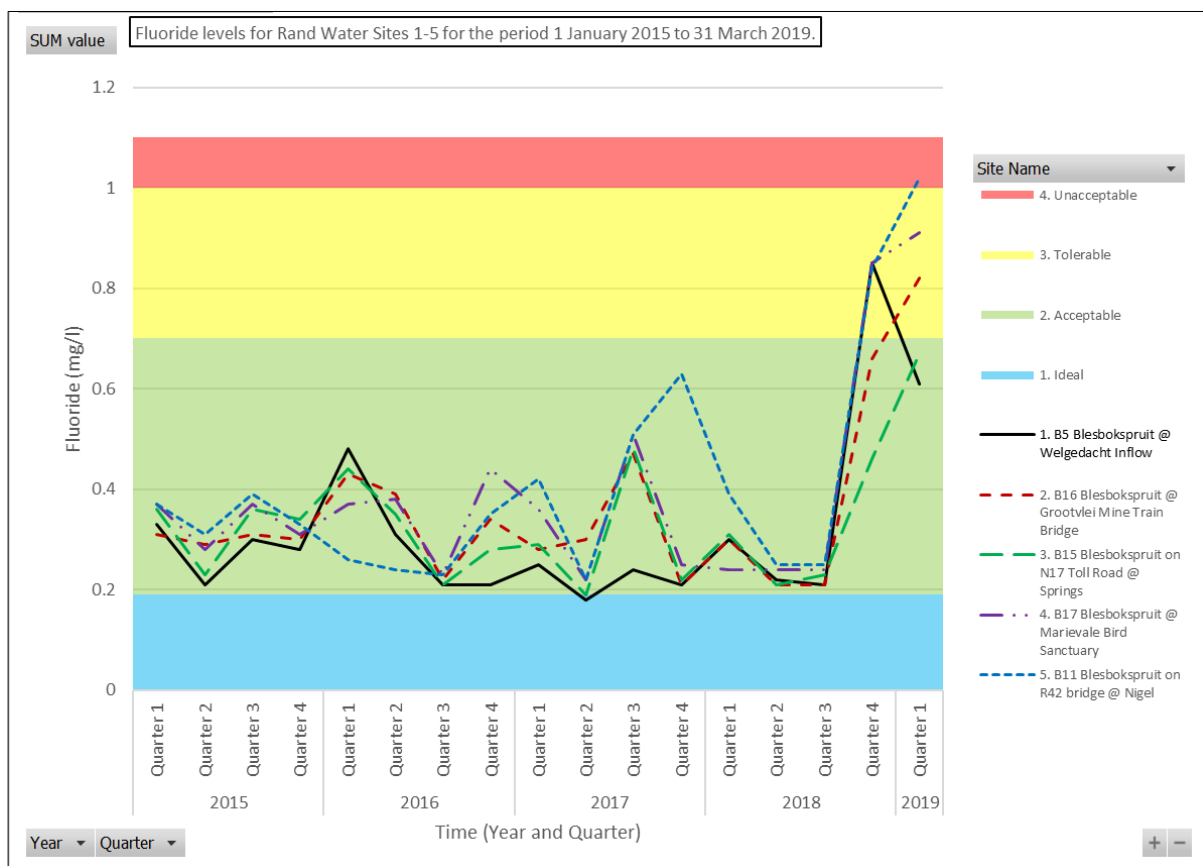
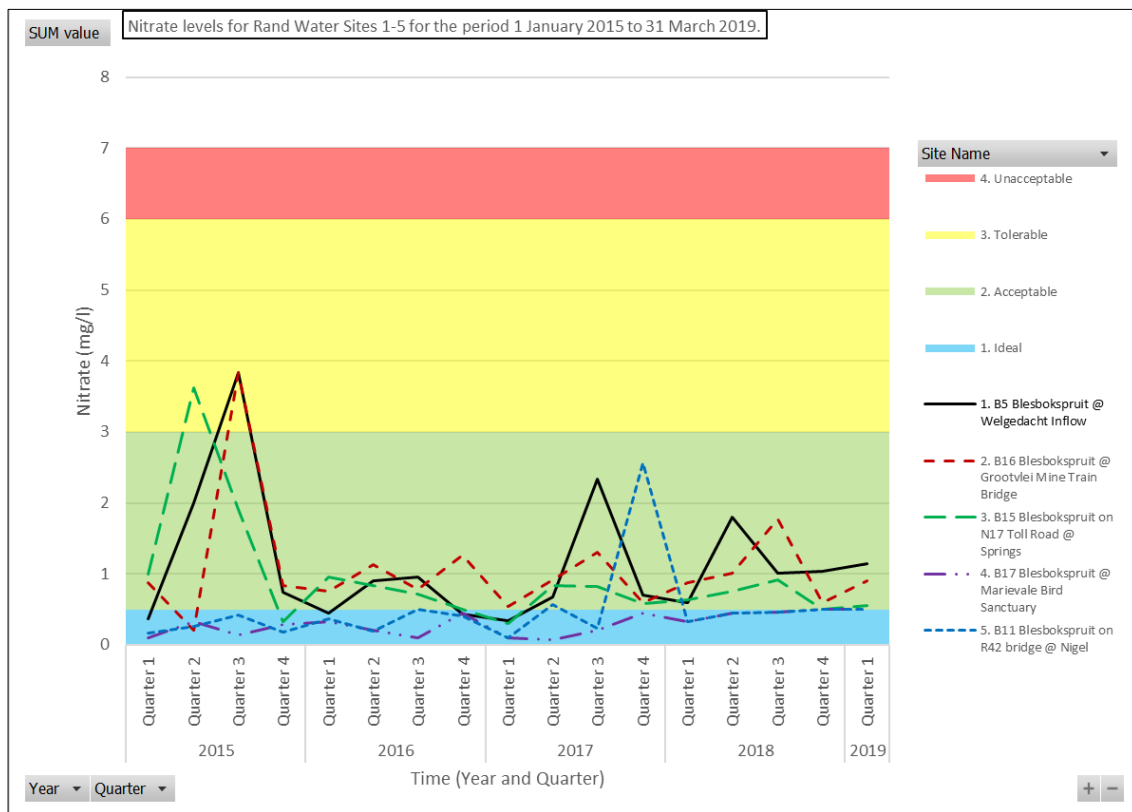


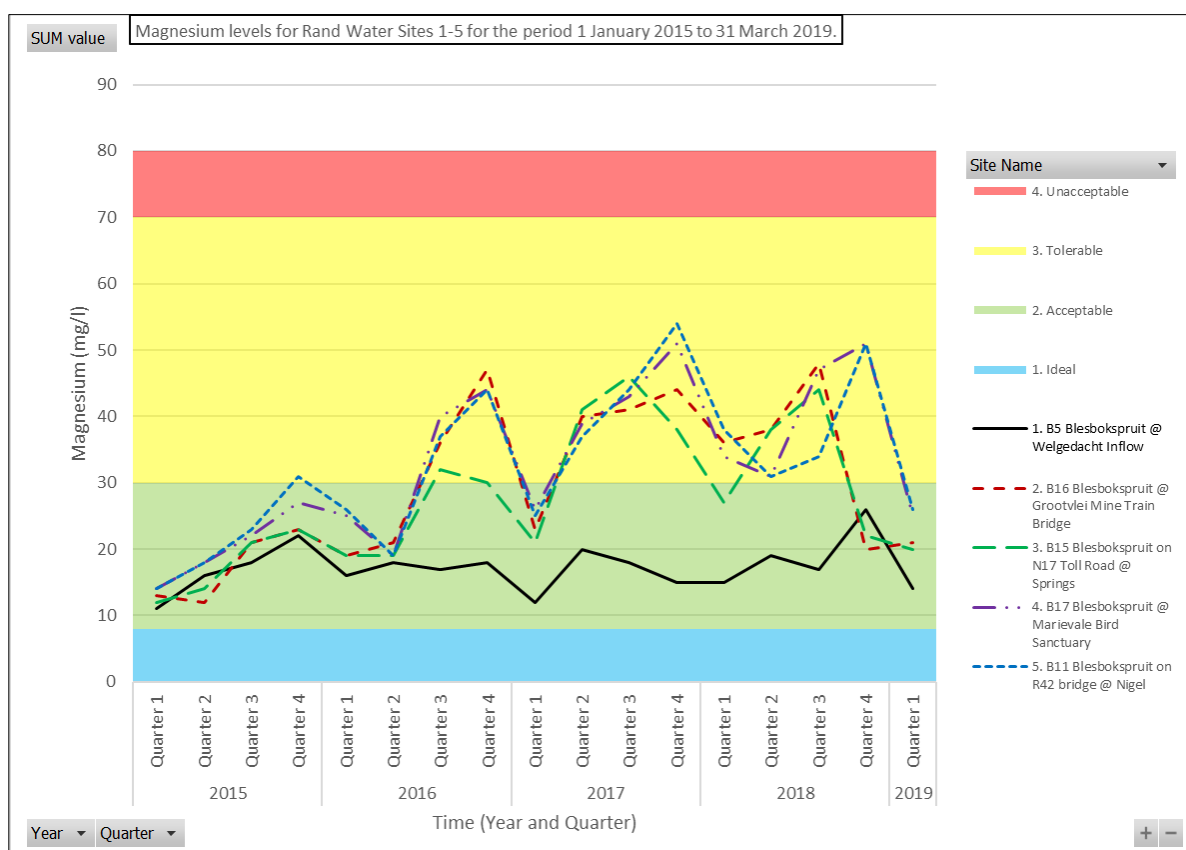
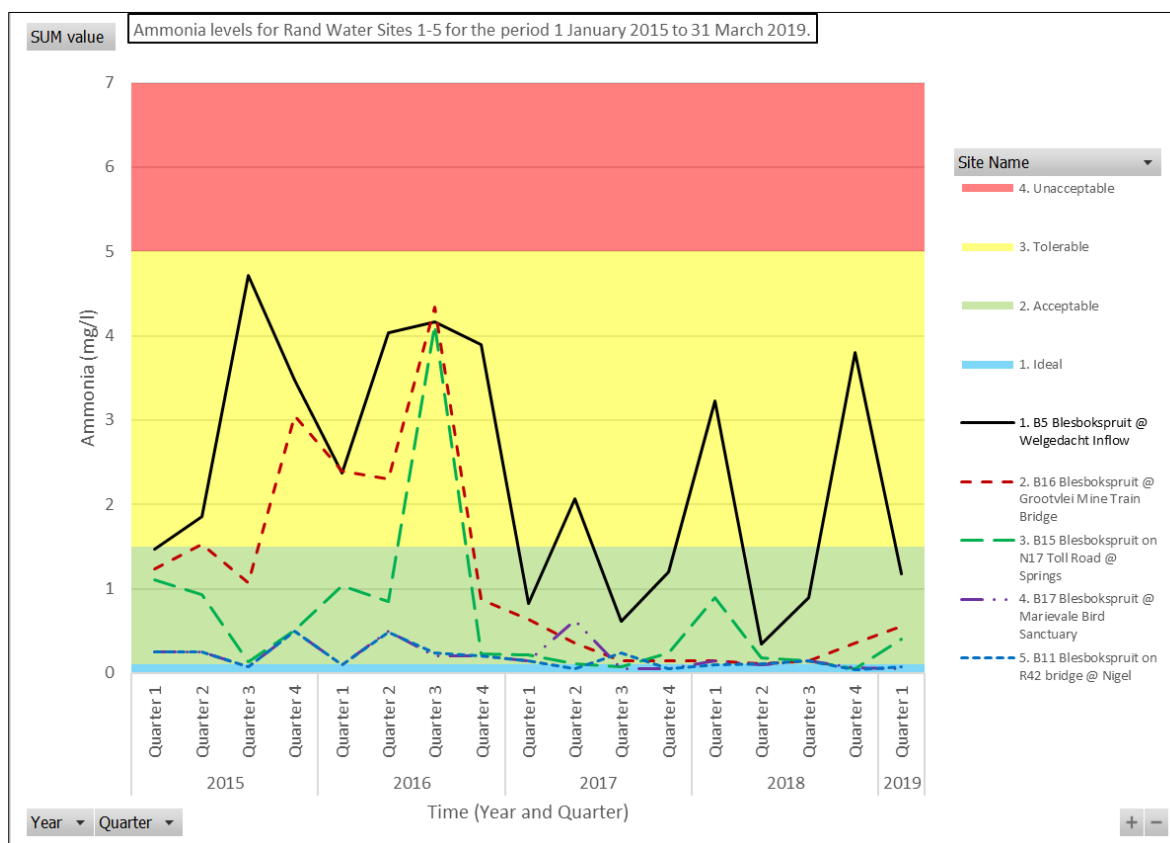
Rand Water site 1 and site 2 raw data (colours correspond to management targets)

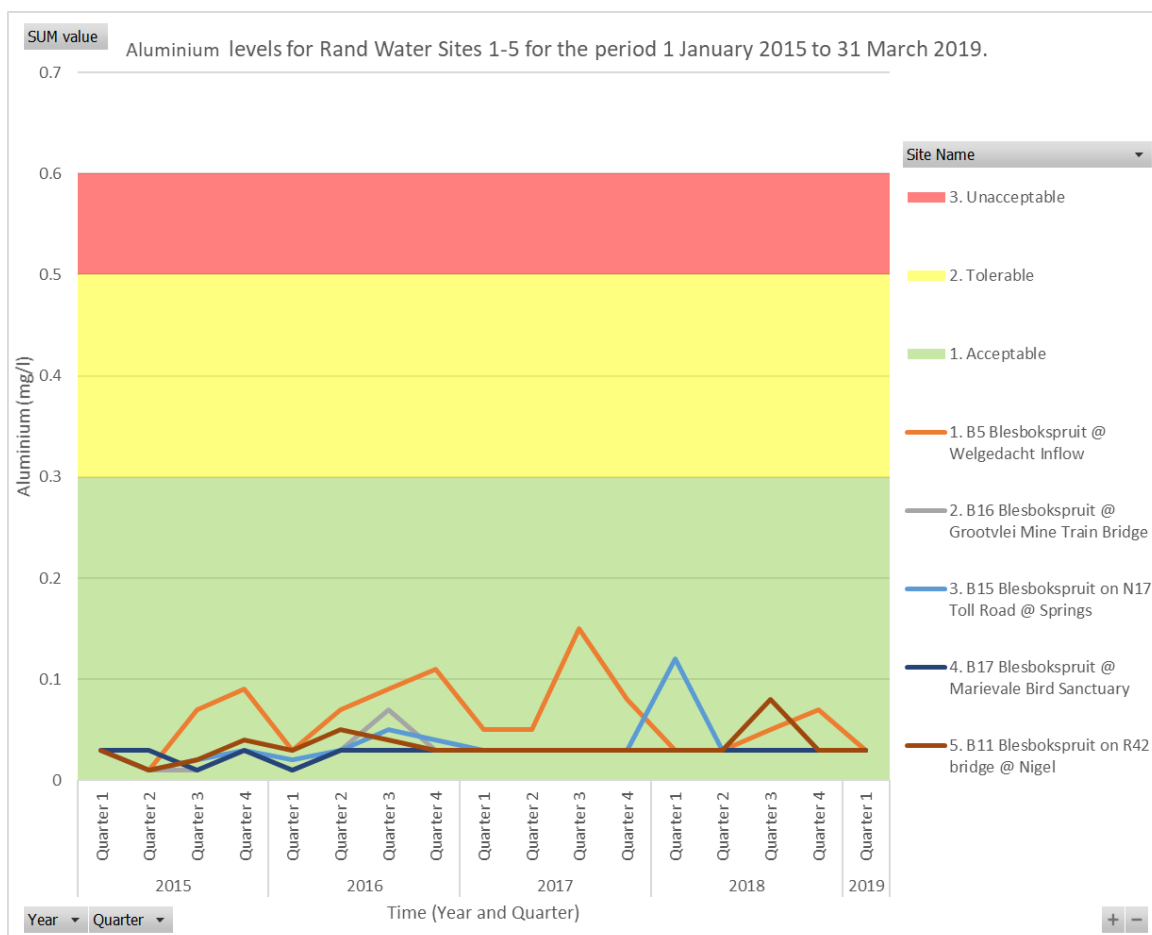
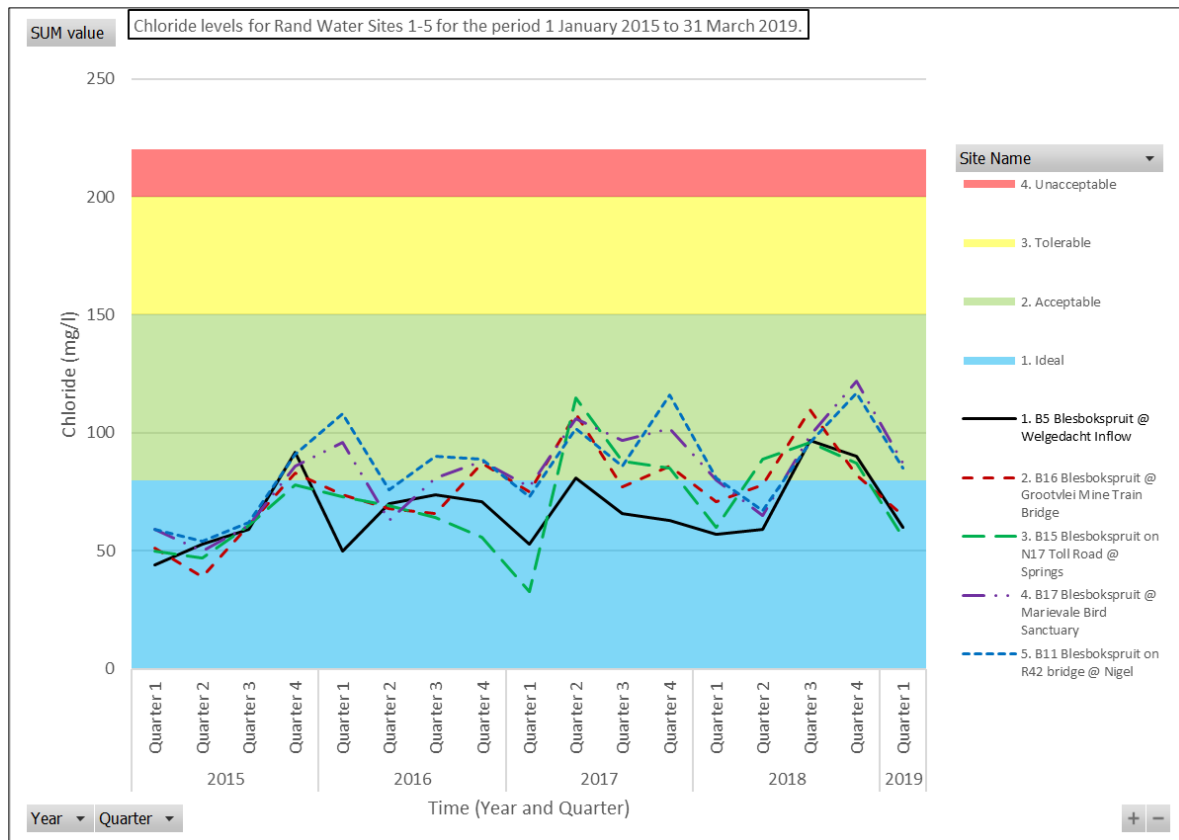
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S15 Blackledge at con N17 off Road @ Springside S26 S27 S28 S29														
Date of Record Water Quality Report														
Minimum (d)	Seminarva (N140) mg/l	Chloride (C3) mg/l	Conductivity (mc/cm)	SDI (mp/d)	Hardness (P1) mg/l	Iron (Fe) mg/l	Magnesium (Mg) mg/l	Sulfate (Me) mg/l	Nitrate (NO3) mg/l	Phosphate (PO4) mg/l	Sodium (Na) mg/l	Sulfate (SO4) mg/l		
1 Jan to 31 Mar 2015	0.018	50	60	6.5	4.5	0.36	0.30	34	1.8	1.3	52	52		
1 Apr to 30 Jun 2015	0.017	49	60	6.5	4.5	0.23	0.30	34	1.6	1.3	52	52		
1 Jul to 30 Sep 2015	0.017	51	60	6.5	4.5	0.36	0.36	34	1.8	1.3	52	52		
1 Oct to 31 Dec 2015	0.018	50	59	5.5	3.5	0.34	0.36	27	1.8	1.3	52	52		
1 Jan to 31 Mar 2016	0.022	50	62	5.4	3.4	0.44	0.30	35	1.9	1.4	50	50		
1 Apr to 30 Jun 2016	0.023	60	60	6.0	5.0	0.35	0.36	35	1.9	1.4	50	50		
1 Jul to 30 Sep 2016	0.025	64	64	6.4	5.4	0.21	0.30	32	1.8	1.3	54	54		
1 Oct to 31 Dec 2016	0.024	56	54	5.5	3.5	0.23	0.36	30	1.7	1.3	56	56		
1 Jan to 31 Mar 2017	0.023	53	53	5.3	3.3	0.29	0.30	27	1.8	1.3	56	56		
1 Apr to 30 Jun 2017	0.023	53	53	5.3	3.3	0.30	0.36	47	1.9	1.4	56	56		
1 Jul to 30 Sep 2017	0.023	58	58	5.8	4.8	0.43	0.36	46	1.9	1.4	56	56		
1 Oct to 31 Dec 2017	0.023	60	60	6.0	5.0	0.27	0.36	36	1.9	1.4	56	56		
1 Jan to 31 Mar 2018	0.023	60	60	6.0	5.0	0.27	0.36	36	1.9	1.4	56	56		
1 Apr to 30 Jun 2018	0.023	60	60	6.0	5.0	0.27	0.36	36	1.9	1.4	56	56		
1 Jul to 30 Sep 2018	0.023	60	60	6.0	5.0	0.27	0.36	36	1.9	1.4	56	56		
1 Oct to 31 Dec 2018	0.023	60	60	6.0	5.0	0.27	0.36	36	1.9	1.4	56	56		
1 Jan to 31 Mar 2019	0.023	60	60	6.0	5.0	0.27	0.36	36	1.9	1.4	56	56		
S17 Blackledge at @ Mainville Brd of Sanctuary S26 S27 S28 S29														
Date of Record Water Quality Report														
Minimum (d)	Seminarva (N140) mg/l	Chloride (C3) mg/l	Conductivity (mc/cm)	SDI (mp/d)	Hardness (P1) mg/l	Iron (Fe) mg/l	Magnesium (Mg) mg/l	Sulfate (Me) mg/l	Nitrate (NO3) mg/l	Phosphate (PO4) mg/l	Sodium (Na) mg/l	Sulfate (SO4) mg/l		
1 Jan to 31 Mar 2015	0.018	50	60	6.5	4.5	0.37	0.30	34	1.8	1.3	49	49		
1 Apr to 30 Jun 2015	0.018	50	60	6.5	4.5	0.26	0.30	34	1.8	1.3	49	49		
1 Jul to 30 Sep 2015	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Oct to 31 Dec 2015	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Jan to 31 Mar 2016	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Apr to 30 Jun 2016	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Jul to 30 Sep 2016	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Oct to 31 Dec 2016	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Jan to 31 Mar 2017	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Apr to 30 Jun 2017	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Jul to 30 Sep 2017	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Oct to 31 Dec 2017	0.018	60	60	6.5	4.5	0.37	0.36	34	1.8	1.3	49	49		
1 Jan to 31 Mar 2018	0.018	60	60											

Rand water time series graphs







Rand Water correlation table

Variables	Aluminium	Ammonium	Chloride	Conduct	DO	Fluoride	Iron	Magnesium	Manganese	Nitrate	pH	Phosphate	Sodium	Sulphate
Aluminium	1	0.444	-0.005	-0.141	-0.184	-0.161	0.555	-0.121	-0.093	0.086	-0.402	0.174	-0.032	-0.038
Ammonium	0.444	1	-0.265	-0.405	-0.065	-0.129	0.620	-0.377	0.037	0.250	-0.462	0.401	-0.211	-0.322
Chloride	-0.005	-0.265	1	0.723	-0.082	0.171	-0.218	0.751	0.076	-0.116	0.154	-0.153	0.414	0.701
Conduct.	-0.141	-0.405	0.723	1	-0.082	0.174	-0.378	0.943	-0.094	-0.070	0.173	-0.364	0.516	0.788
DO	-0.184	-0.065	-0.082	-0.082	1	-0.235	-0.152	-0.083	0.224	-0.229	0.251	0.055	-0.170	-0.361
Fluoride	-0.161	-0.129	0.171	0.174	-0.235	1	-0.124	0.079	0.055	-0.061	0.276	0.153	-0.079	0.068
Iron	0.555	0.620	-0.218	-0.378	-0.152	-0.124	1	-0.350	0.093	0.048	-0.489	0.210	-0.206	-0.292
Magnesium	-0.121	-0.377	0.751	0.943	-0.083	0.079	-0.350	1	-0.116	-0.089	0.103	-0.376	0.478	0.822
Manganese	-0.093	0.037	0.076	-0.094	0.224	0.055	0.093	-0.116	1	-0.056	0.025	0.184	0.035	-0.170
Nitrate	0.086	0.250	-0.116	-0.070	-0.229	-0.061	0.048	-0.089	-0.056	1	-0.035	0.115	-0.027	-0.065
pH	-0.402	-0.462	0.154	0.173	0.251	0.276	-0.489	0.103	0.025	-0.035	1	-0.113	0.068	0.046
Phosphate	0.174	0.401	-0.153	-0.364	0.055	0.153	0.210	-0.376	0.184	0.115	-0.113	1	-0.200	-0.383
Sodium	-0.032	-0.211	0.414	0.516	-0.170	-0.079	-0.206	0.478	0.035	-0.027	0.068	-0.200	1	0.589
Sulphate	-0.038	-0.322	0.701	0.788	-0.361	0.068	-0.292	0.822	-0.170	-0.065	0.046	-0.383	0.589	1

Ground Truth water quality raw data

Sample 1 at Wilgedagt Bridge		26.21474 S 28.47958 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		1.56	0.9	115	0.02	69.3	10:49:00	7.9	NC	NC	7.2	451.1	45.11
	Jul-18		2.1	0.7	50	0.11	53.1	12:00:00	8.2	1.68	20	6.81	453	45.3
	Aug-18		0.98	1.2	320	0.05	55	09:00:00	9	1.35	14.4	6.41	411	41.1
	Sep-18		1.45	1.0	50	0.12	83.8	10:41:00	15.2	1.4	17.1	6.65	545	54.5
	Oct-18		2.14	1.9	52	0.19	69.7	09:25:00	16.7	0.72	9	7.28	935	93.5
	Nov-18		1.83	1.8	91	0.83	67.3	09:30:00	16.3	3	37	6.99	680	68
	Dec-18		3.55	1.5	106	0.11	48.5	10:00:00	19.2	5	50	7.13	818	81.8
	Jan-19		1.15	0.4	77	0.26	44.2	10:00:00	18.5			6.88	603	60.3
	Feb-19		0.71	0.6	55	0.04	32.2	11:30:00	19.9	4.57	60	7.53	525	52.5
	Mar-19		1.65	1.0	69	0.06	37.4	10:00:00	18.8	2.55	35.9	7.85	617	61.7
	Apr-19		1.33	1.7	119	0.18	43.5	11:08:00	15.8	2.32	28	7.56	438.2	43.82
	May-19		1.02	1.5	584	0.15	34.5	10:10:00	13.8			7.87	380	38
Sample 2 at Old Mine Train Bridge		26.25554 S 28.49833 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		1.36	2.1	600	0.02	70.7	11:45:00	11.2	3.3	36.2	6.96	1529	152.9
	Jul-18		1.86	1.3	580	0.08	69.6	12:33:00	11.6	5.67	62.5	7.04	994	99.4
	Aug-18		1.77	1.2	560	0	48.7	09:35:00	12.7	4.56	52.3	6.95	907	90.7
	Sep-18		1.65	0.5	360	0.03	76.9	11:30:00	15.9	7.34	90.7	7.15	787	78.7
	Oct-18		2.42	1.9	137	0.15	46.3	10:05:00	18.4	3.23	41.5	7.3	825	82.5
	Nov-18		2.45	1.2	81	0.99	68	10:05:00	17.5	10.5	130	7.22	718	71.8
	Dec-18		4.27	1.4	115	0.38	51.4	10:54:00	21	10	90	7.43	838	83.8
	Jan-19		1.53	0.6	314	0.11	59.9	10:35:00	20.4			7.09	1073	107.3
	Feb-19		1.18	0.7	135	0.03	42.4	12:00:00	21	4.18	57	7.44	713	71.3
	Mar-19		1.57	0.9	276	0.08	51.4	10:24:00	20	2.1	27	7.37	993	99.3
	Apr-19		1.22	1.8	266	0.13	48.3	11:42:00	17	2.91	36.4	7.7	678	67.8
	May-19		0.88	2.1	431	0.13	36.1	10:45:00	16			7.82	780	78
Sample 3 at N17 Toll Road		26.27152 S 28.50385 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		1.21	1.3	550	0.01	68.6	12:30:00	10	10.41	109.7	7.28	927	92.7
	Jul-18		1.46	1.0	620	0.01	80.6	13:09:00	9.8	10.36	110	7.28	949	94.9
	Aug-18		1.49	0.7	640	0	67	10:10:00	10.6	4.1	43.6	7.05	973	97.3
	Sep-18		1.31	0.5	600	0	69.6	12:40:00	16.6	4.4	61	7.07	991	99.1
	Oct-18		2.74	2.0	153	0.3	44.6	10:20:00	17.6	6.89	87.6	7.33	830	83
	Nov-18		2.46	0.9	110	0.56	71.8	10:30:00	16.8	8.17	100	7.26	766	76.6
	Dec-18		3.58	0.6	118	0.1	49.9	11:15:00	19.5	3.5	40	7.55	883	88.3
	Jan-19		1.96	0.9	326	0.17	58.1	10:54:00	20			7.16	1114	111.4
	Feb-19		1.4	0.9	229	0.07	49.6	12:22:00	20.9	4.4	56.5	7.41	922	92.2
	Mar-19		1.76	1.0	395	0.04	50.2	10:47:00	19.8	3.2	43	7.42	1170	117
	Apr-19		1.2	1.0	358	0.1	68.5	12:00:00	16.8	4.81	61	7.75	790	79
	May-19		0.87	2.1	826	0.1	36	11:15:00	14.8			7.95	714	71.4
Sample 4 at Old Bridge in Marievale		26.33121 S 28.51352 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		0.96	0.6	590	0.02	70.1	13:27:00	9.1	11.51	120	7.93	879	87.9
	Jul-18		0.75	0.3	590	0.01	73.6	14:00:00	9.7	13.5	140	7.81	941	94.1
	Aug-18		1	0.1	600	0.02	61.2	11:20:00	10.1	10.56	112.2	7.38	927	92.7
	Sep-18		1.1	1.4	680	0.02	79.6	14:00:00	20	6.97	92.5	6.97	1138	113.8
	Oct-18		1.6	0.8	382	0.46	54.7	11:50:00	20.3	8.97	116	7.57	1314	131.4
	Nov-18		1.64	1.4	294	1.11	78.3	11:55:00	22.4	7.53	100	7.62	1139	113.9
	Dec-18		2.66	0.9	271	0.03	90.5	12:20:00	21.5	10	100	7.84	1165	116.5
	Jan-19		2.65	0.2	255	0.11	52.7	11:56:00	21.4			7.47	1071	107.1
	Feb-19		1.92	0.9	243	0.02	42.3	13:30:00	23.4	12	160	7.64	984	98.4
	Mar-19		2.09	0.8	334	0.05	64.3	11:44:00	19.5	10.08	133	7.55	1033	103.3
	Apr-19		3.87	0.7	393	0.05	64.5	13:26:00	18.4	9.86	127	7.85	870	87
	May-19		1.33	1.2	1264	0.08	36.2	12:27:00	15.7			8.1	665	66.5
Sample 5 at Duiker Hide		26.34495 S 28.51383 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		0.91	0.7	610	0.01	90.7	14:08:00	10.4	10.4	110	7.9	908	90.8
	Jul-18		0.78	0.7	610	0.01	85.8	15:00:00	9.3	11.05	114	7.69	932	93.2
	Aug-18		1	0.3	600	0	56	11:55:00	10	8.25	87.9	7.48	940	94
	Sep-18		1.16	1.1	650	0	74.8	15:21:00	19.2	6.46	83.6	7.75	1114	111.4
	Oct-18		1.83	1.3	407	0.12	66	12:15:00	20	8.86	113.3	7.58	1296	129.6
	Nov-18		1.75	1.1	306	0.05	81.7	13:10:00	23.7	5.8	80	7.65	1214	121.4
	Dec-18		1.92	1.4	203	0.03	41.1	13:15:00	22.9	9	90	8	1257	125.7
	Jan-19		2.67	1.0	200	0.18	67.6	12:15:00	21.5			7.63	1017	101.7
	Feb-19		2.02	1.0	216	0.02	44.3	13:54:00	22.8	10.52	146.7	7.73	943	94.3
	Mar-19		2.35	0.5	286	0.09	49.9	12:07:00	19.5	10.46	140	7.69	1036	103.6
	Apr-19		3.31	1.3	386	0.16	43.2	14:00:00	17.7	10.31	130	7.97	878	87.8
	May-19		1.22	0.9	505	0.19	18.9	12:48:00	17.2			8.23	681	68.1
Sample 6 at Road Crossing		26.25952 S 28.50861 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		1.04	1.0	550	0.01	74.6	14:27:00	11.6	14.36	159.4	8.02	931	93.1
	Jul-18		0.88	0.6	580	0.01	78	15:20:00	9.8	13.8	140	7.9	954	95.4
	Aug-18		1.11	0.4	600	0	63	12:10:00	11.5	140	12.97	7.63	960	96
	Sep-18		1.12	0.7	640	0	77.7	16:20:00	21.6	7.08	99.6	8.39	1170	117
	Oct-18		1.59	0.8	523	0.14	54.2	12:50:00	21.6	8.7	112.5	7.78	1513	151.3
	Nov-18		1.68	1.1	388	0.05	74	13:40:00	27.6	7.83	115.6	8.02	1428	142.8
	Dec-18		1.92	0.5	360	0.06	48.8	13:32:00	23.9	5.2	80	7.92	1500	150
	Jan-19		2.53	0.4	209	0.1	47.2	12:30:00	23.9			7.82	1093	109.3
	Feb-19		1.92	1.4	224	0.04	47.2	14:11:00	25.5	11.7	173	7.98	995	99.5
	Mar-19		1.95	0.5	284	0.05	48	12:30:00	20.7	9.63	127	7.69	1063	106.3
	Apr-19		4.57	0.7	434	0.07	52.6	14:11:00	20	10.59	140	8.05	967	96.7
	May-19		1.2	0.5	1023	0.04	37.4	13:03:00	19.3			8.41	720	72
Sample 7 at Hadedda Hide		26.36730 S 28.51256 E	Phosphate PO43- (mg/L)	Nitrate NO3- (mg/L)	Sulphate SO42- (mg/L)	Iron Fe (mg/L)	Chloride CL- (mg/L)	Time sampled	Temp Celcius	DO (mg/L)	DO %	pH	Conductivity (µ siemens/ cm)	Conductivity (mS/m)
	Jun-18		0.99	2.3	350	0.03	65.8	14:32:00	8.9	14.57	120	8.13	784	78.4
	Jul-18		1.26	0.5	540	0.02	74.4	15:45:00	13.7	12.85	140	7.97	981	98.1
	Aug-18		1.73	0.2	550	0.02	57.8	12:28:00	14	8.45	98.2	7.67	977	97.7
	Sep-18													

Ground truth time series graphs

