Sustainable drinking water supply service and development in the face of different resource challenges. A case study of Midvaal Water Company, South Africa

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PREFACE AND ACKNOWLEDGEMENTS

PREFACE

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ABSTRACT

Water quality of resources in large parts of South Africa is declining. The Vaal River is heavily polluted when it reaches its mid-section at Midvaal Water Company in the North-West Province. Midvaal, a water service provider, abstracts and treats water from the Middle Vaal to supply bulk potable water in compliance with the South African National Standard 241:2015 for drinking water. The main objectives of the case study were to investigate water treatment challenges at Midvaal due to changes in source water quality, to evaluate wastewater recycling at the plant and the effect thereof on sustainable drinking water supply and to determine the impact of the Koekemoerspruit on the Middle Vaal River by an integrated study of phytoplankton assemblages and water physico-chemistry. The dissolved air flotation process, since 1997, had the most significant impact since it accounts for almost 70% total chlorophyll removal. Surface water samples were sampled on a monthly basis at sites located in the Koekemoerspruit and on a daily basis from the Middle Vaal River intake as well as sites within the plant for the different sections of this study. Sampling frequency, durations and required analytical methods were based on monitoring programs for each system. Samples were analysed at Midvaal Water Company Scientific Services. The phytoplankton identification and enumeration were performed at the North-West University, Potchefstroom campus. The yearly average total chlorophyll concentrations of the source water gradually increased from 33 µg/L (1984) to 133 µg/L (2014). The treatment facility suffers from severe taste and odour episodes during summer due to the presence of 2-methylisoborneol (MIB), released by Cyanophyceae. Concentrations of > 300 ng/L MIB were recorded. The processes of the wastewater recycling system did not compromise final water quality. Total chlorophyll concentration was identified as the principal risk during wastewater recycling, especially after filtration. Results from the Koekemoerspruit indicated that target water quality objectives for orthophosphate, nitrate and nitrite and ammonia were exceeded during 2014 and 2015, indicating severe organic pollution. Colour, ammonia and total chlorophyll concentrations displayed significant increasing trends over time and increased drastically after 2012. Average phytoplankton concentrations of 1 410 069 cells/ml and 417 931 cells/ml were determined for the Middle Vaal and Koekemoerspruit respectively. A total of 86 phytoplankton genera were collectively identified. A redundancy analysis confirmed that water quality had a definite effect on the phytoplankton assemblages (*p*-value of 0.08). The treatment process changes enabled the plant to manage the increasing phytoplankton load in the source. Wastewater recycling was both operational- and cost-effective. The Koekemoerspruit, suffering severe organic pollution, did not impact significantly on the water quality of the Middle Vaal, except for total chlorophyll. The Chlorophyceae taxon (48%) and *Scenedesmus* spp. genus dominated in the nutrient enriched Middle Vaal River. The Cyanophyceae taxon (45%) and *Nitszchia* spp.

genus were dominant in the Koekemoerspruit. This study highlighted how the eutrophication of water resources and associated chlorophyll concentrations escalate to have multidimensional effects on sustainable drinking water supply. Stricter regulation by authorities concerning wastewater discharges are recommended to protect South-African water resources.

Key terms:

Chlorophyll, compliance, dissolved air flotation, ecological indicators, eutrophication, phytoplankton assemblages, taste and odours, wastewater recycling, water quality monitoring, water treatment

LIST OF ACRONYMS AND ABBREVIATIONS

ANOVA	Analysis of variance
AOP	Advanced oxidation process
CCA	Canonical Correspondence Analysis
CSIR	Council for Industrial and Scientific Research
DAF	Dissolved air flotation
DOC	Dissolved organic carbon
DWS	Department: Water and Sanitation
E.coli	*Escherichia coli*
EC	Electrical conductivity
GAC	Granular activated carbon
ICP-OES	Inductively coupled plasma – Optical emission spectroscopy
IRIS	Integrated regulatory information system
IWRM	Integrated water resources management
KOSH	Klerksdorp, Orkney, Stilfontein and Hartbeesfontein
LIMS	Laboratory information management system
MIB	2-methylisoborneol
NOM	Natural organic matter
NTU	Turbidity
PAC	Powdered activated carbon
RDA	Redundancy Analysis
SANAS	South African National Accreditation System

SANS	South African National Standard
SBD	Sludge balancing dam
SD	Standard deviation
SE	Standard error
SS	Suspended solids
T Chl	Total chlorophyll
TOC	Total organic carbon
UV	Ultraviolet
WTR	Water treatment residue

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CHAPTER 1 INTRODUCTION AND AIMS OF STUDY

A healthy river ecosystem is an essential resource for surrounding communities in terms of drinking water, agriculture and industries. According to Marais *et al*. (2018) fresh water drinking sources are a precious commodity but scarce or completely unavailable in many arid regions of the world while pollutant loads may make water unsuitable for conventional drinking water treatment in areas where fresh water sources are indeed available. Human activities and natural disasters have limited the quantity and quality of water (Marais *et al*., 2018). South Africa is a water scarce country with very little surface water resources that can be used for drinking water purposes without prior treatment. Surface water sources are reduced in South Africa due to a significant decline in the total amount of rainfall and number of rain days over the years (MacKella *et al*., 2014). Population growth and forecasted decline in rainfall due to climate change are expected to increase the water demand in South Africa. The consequences of limited water supply were first hand experienced during 2018 by the City of Cape Town in the Western Cape Province when local government enforced severe water restrictions. Rapid industrialisation and agricultural activities increase the variety of pollutants in South African aquatic systems (Marais *et al*., 2018). Challenges related to water quality are worsened by the inability of water treatment facilities to achieve the required quality of water fit for potable use (Marais *et al*., 2018). Another cause for water quality deterioration in South Africa is the failure of wastewater treatment plants and the discharge of wastewater effluents that do not comply with relevant limits. More people will increase the existing pressures, on diminishing water resources, of deteriorating water quality, which consequently escalate to an inevitable water crisis. The current water related challenges on national and global level endanger the sustainable operations of water treatment facilities together with the associated cost implications to consumers.

Integrated water resources management (IWRM) was introduced to improve management of the physical environment and its use by the different water divisions (Bartram & Balance, 1996). IWRM has to take into account both economic benefits and ecological concerns (CCME, 2015). The unfortunate reality is that the ecological health of rivers and streams are usually not well documented in many developing countries, including South Africa, by municipal and/or national government (van der Hoven *et al*., 2017). IWRM and strategies are severely compromised when information regarding the ecological health of water resources and the effect of different land uses on water quality are not available (van der Hoven *et al*., 2017). There can be no future projections and effective, proactive management without sound, scientific monitoring.

Monitoring water quality and anthropogenic disturbances on essential water resources are crucial to determine whether water quality and quantity meet standards for domestic use. According to

Bartram and Ballance (1996), water quality monitoring is the “long-term, standardized measurement and observation of the aquatic environment in order to define status and trends.” South Africa has overarching national legislation to enforce a nationally coordinated framework for monitoring, assessing and reporting on resource water quality (DWS, 1997; Hallett *et al*., 2016). Regulatory requirements such as drinking water limits (SANS, 2015) and target water quality objectives (DWS, 2016) were amended recently in 2015 and 2016 respectively and both incorporate a risk based approach.

The mid-section of the Vaal River is an essential source of drinking water for consumers in a part of the North-West Province, South Africa. It is currently not fit for this purpose without extensive treatment by Midvaal Water Company. Midvaal Water Company is an example of a water treatment plant that successfully managed source water quality challenges in the past and their operational history is of value to the water industry at national and international level. Midvaal Water Company’s chemical and microbiological water quality analyses are performed at their on-site testing facility. A variety of databases, as a result of water quality monitoring, have been compiled and developed over years and some contain data of more than 30 years. These databases need to be analysed to determine increasing/decreasing trends in water quality parameters. However, the question consequently remains that if further deterioration of the Middle Vaal River occurs, which parameters would be of concern and how should the processes at the plant change to adapt?

The increased demand for fresh water due to continuous worldwide population increase, coupled with the scarcity of clean water, compel stakeholders to explore alternative water sources, especially in South Africa (Marais *et al*., 2018). Midvaal Water Company piloted the recycling of the waste generated from the dissolved air flotation, sedimentation and filtration processes in June 2013 as an initiative to promote cost-effective water utilisation. Herselman (2013) defines water treatment residue (WTR) as "the accumulated solids or precipitate removed from a sedimentation basin, settling tank, or clarifier in a water treatment plant" but WTR of Midvaal Water Company includes the waste/residue from the dissolved air flotation and filtration processes as well, which renders it more of a wastewater than a residue. However, this is a rare practise in South Africa and the efficacy thereof need to be determined.

Besides wastewater recycling, Midvaal Water Company does not have an alternative to their current source of water, the Middle Vaal River, not even the option to abstract water from various depths. Therefore, the preservation together with the understanding of source waters should be a priority for stakeholders and subsequently necessitates the studying of the water quality of water sources to determine pollutant composition and ultimately ensure improved design of water treatment systems (Marais *et al*., 2018). It has been well documented that harmful phytoplankton blooms have increased in frequency, duration and magnitude worldwide (Lundgren *et al*., 2013; O'Neil *et al*., 2012; Paerl & Huisman, 2008). In South Africa, the observed increase in the number of cyanobacterial bloom events (Downing & van Ginkel, 2003) together with high nutrient enrichment and eutrophication related problems observed in many rivers and impoundments are a cause of great concern. By making use of an integrated study of phytoplankton assemblages and water physico-chemistry, a more accurate and comprehensive assessments of the water quality of the Middle Vaal River and its tributaries can be accomplished. Claassens *et al*. (2016) conducted a study on the Koekemoerspruit and identified effluents from mining activities and wastewater treatment plants as stressors. The Koekemoerspruit monitoring program of Midvaal Water Company may require revision in light of changes since the Koekemoerspruit is a possible pollution source upstream of the abstraction point in the Middle Vaal River. The impact of the Koekemoerspruit on the Middle Vaal River is not clear and dominant phytoplankton genera, as indicators of water quality, might contribute to the understanding of the dynamics of these two streams.

Midvaal Water Company has previously been identified on numerous occasions as a sampling site when studies were conducted on either source waters or a specific water treatment process (Haarhoff, *et al*., 2008; Pearson & Swartz, 1992; Rajagopaul *et al*., 2008; van der Walt *et al*., 2009) but a holistic case study of the operations and water quality monitoring has not been conducted before.

The objectives of this case study at Midvaal Water Company were to:

- Investigate challenges that changes in source water quality presented over time and how the water treatment processes at Midvaal Water Company had to change in order to adapt
- Evaluate wastewater recycling at Midvaal Water Company and the effect thereof on safe drinking water supply
- Asses water quality of the Middle Vaal River and Koekemoerspruit at Midvaal Water Company in the Middle Vaal Catchment to determine overall water quality of the two streams and the subsequent impact of the Koekemoespruit on the Middle Vaal River by making use of an integrated study of phytoplankton assemblages and water physico-chemistry
- Evaluate the water quality monitoring program of the Koekemoerspruit
- Identify dominant phytoplankton genera as indicators of water quality in the differentially impacted Middle Vaal River and Koekemoerspruit

CHAPTER 2 MATERIALS AND METHODS

2.1 Description of study area

The Vaal River is the third largest river in South Africa, it originates in the Mpumalanga Province of South Africa and flows westwards over a distance of 1 120 km to its confluence with the Orange River near Douglas in the Northern Cape Province. The mid-section of the Vaal River in the study area has been subjected to upstream agricultural, domestic, industrial and mining uses in the Gauteng province and associated pollution by the time it passes the Midvaal Water Company water treatment plant.

The Koekemoerspruit is a tributary of the Middle Vaal River in the Middle Vaal Catchment (Figure 2-1). It originates from a natural underground source between the towns of Klerksdorp and Ventersdorp in the North-West Province and flows over a distance of approximately 50 km in a south-south-westerly direction before it flows into the Middle Vaal River in the North-West Province about 1.6 km upstream of Midvaal Water Company's abstraction point. The Koekemoerspruit's embankments and flood plains are almost completely covered with *Phragmites australis*, a perennial reed. The groundwater of the Koekemoerspruit area is easily polluted because of the permeability of the underlying dolomitic soils, which are prone to sinkhole formation. Dolomitic soils are characteristic of this environment together with gold mining activities which downscaled substantially over the past few years. The Koekemoerspruit, upstream of the study area, is surrounded by closed goldmines and the urban village of Khuma, with a population of approximately 46 000 people. The study area covered the section of the Koekemoerspruit below Khuma up to the confluence with Middle Vaal River, as well as a section of the Middle Vaal River upstream and downstream of the confluence. The land use of the study area is mostly natural land with some cultivation at the confluence.

The Middle Vaal River (site 2) is the sampling point for this study with the most data (since 1984) and is included in the catchment monitoring, water treatment and wastewater recycling systems.

Five sampling sites were identified (Figure 2-1) at the onset of the Koekemoerspruit water quality monitoring program in 2002. The town of Stilfontein and Khuma are situated upstream of sites 4 and 5 in the Koekemoerspruit. Water from the Enviroclear canal (site 3) flows into the Koekemoerspruit from the west between sites 4 and 5 from time to time. The Enviroclear overflow is more or less a 9 km cement canal that occasionally transfers water from a nearby mining plant to the Koekemoerspruit. Vermaasdrift Bridge (site 1) is situated in the Middle Vaal River, upstream of the confluence of the Koekemoerspruit with the Middle Vaal River, and site 2 is situated downstream of the confluence in the Middle Vaal River at Midvaal Water Company's abstraction point. The sampling frequencies of sites 1 to 5 are indicated in Table 2-1.

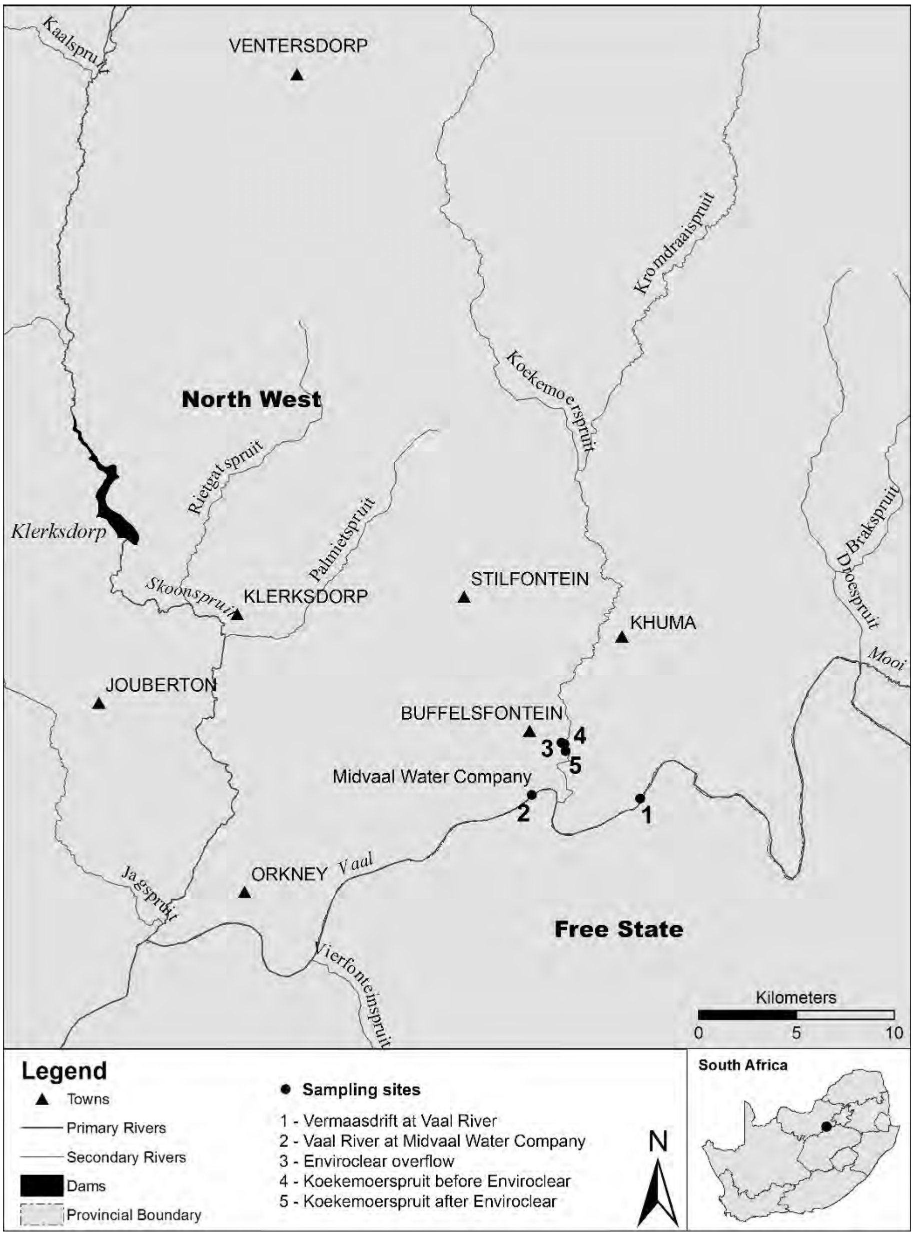


Figure 2-1: **Koekemoerspruit study area indicating the five sampling sites, streams of the catchment and surrounding towns. Samplings sites 4 and 5 along the Koekemoerspruit that flows into the Middle Vaal River between study sites 1 and 2**

Midvaal Water Company is situated in the North-West Province of South Africa on the banks of the Middle Vaal River, 14 km from the small town of Stilfontein, at 26°55'59.3" S and 26°47'51.8" E. The study area is situated in the summer rainfall region of the country and an average annual rainfall of 732 mm was recorded from 2002 to 2017 at Midvaal Water Company's weather station. This is more than the average annual rainfall for South Africa (464 mm) but less than the global average of 860 mm.

2.1.1 Water treatment plant

Water treatment at Midvaal Water Company currently consists of the following processes and the sequence of these processes has remained in this specific order since 2007 with wastewater recycling on the west side of the plant (Figure 2-2):

(1) Abstraction from source (Middle Vaal River) at intake tower

(2) Pre-ozonation by means of a radial diffuser

(3) Primary addition of water treatment chemicals for coagulation and flocculation.

A combination of all or some of the following chemicals are used in this process depending on the water quality: lime, ferric chloride, polyelectrolyte and aluminium sulfate. The polyelectrolyte is a cationic polymer named poly quaternary amine solution.

(4) Dissolved air flotation (DAF)

(5) Intermediate ozonation in two U-tube reactors

(6) Secondary addition of water treatment chemicals (optional).

A combination of all or some of the following chemicals are used in this process depending on the water quality: lime, ferric chloride, polyelectrolyte, aluminium sulfate and powdered activated carbon (PAC)

(7) Sedimentation in 12 circular clariflocculators and one horizontal flow sedimentation dam

(8) Filtration in rapid gravity sand filters

(9) Disinfection by means of chlorine gas

(10) Pump station for distribution of the final water to 11 reservoirs in the Klerksdorp, Orkney, Stilfontein and Hartbeesfontein (KOSH) area as well as Vierfontein

Figure 2-2: **An aerial view of Midvaal Water Company (2010). The water treatment plant abstracts on average 130 ML/day, has a design capacity to treat 320 ML/day and a supply area that extends over more than a 1 000 km^2**

Midvaal Water Company recycled wastewater, produced at three drinking water treatment processes (dissolved air flotation, sedimentation and filtration), parallel with treatment (Figure 2-3).

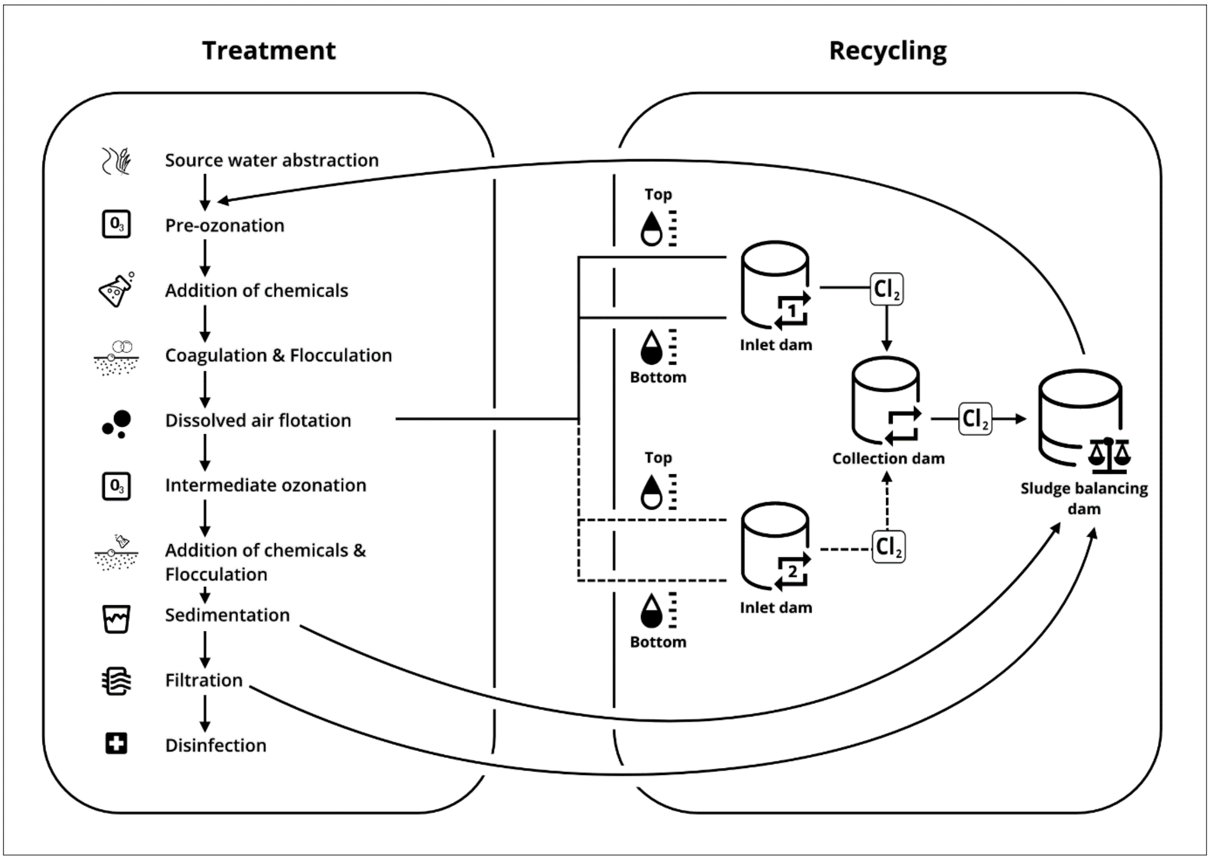


Figure 2-3: **Sequence of the various treatment processes at the Midvaal Water Company and the flow of the wastewater recycling system**

2.2 Description of sampling sites and sampling regime in the plant

Sampling sites and their respective locations have been carefully selected after each of the ten processes on the water treatment plant together with six sampling points at the wastewater recycling system to ensure samples with representative water quality after each step, enabling successful monitoring of plant operations on a continuous basis.

Midvaal Water Company Scientific Services sampled water from the river (also site 2), recycle stream and after each water treatment process on a daily basis and surface water samples on a monthly basis at Vermaasdrift Bridge (sites 1), Enviroclear overflow (site 3), Koekemoerspruit before Enviroclear overflow (site 4) and Koekemoerspruit after Enviroclear overflow (site 5). Midvaal Water Company's process controllers sampled the DAF top, DAF bottom, east wastewater, west wastewater and the collection dam overflow on a weekly basis (Table 2-1).

Table 2-1: A total of 20 sampling sites were investigated for this case study along with abbreviations, to which system(s) it belongs as well as sampling frequency

Sampling site name		Abbreviation or reference in text	System	Sampling frequency
1	Abstraction from source (Middle Vaal River) at intake tower	R / Site 2	Water treatment, wastewater recycling and catchment monitoring	Daily
2	After pre-ozonation	-	Water treatment	Daily
3	Before flotation	-		Daily
4	After chemical dosing	-		Daily
5	After flotation	-		Daily
6	After intermediate ozonation	-		Daily
7	After settling	-		Daily
8	After filtration	-		Daily
9	Storage reservoirs 1 to 4	-		Daily
10	Final after pump station	-		Daily
11	DAF top	DAF-T	Wastewater recycling	Weekly
12	DAF bottom	DAF-B		Weekly
13	East sludge	ES		Weekly
14	West sludge	WS		Weekly
15	Collection dam overflow	CDO		Weekly
16	Recycle stream	RS		Daily
17	Vermaasdrift Bridge	Site 1	Catchment monitoring	Monthly
18	Enviroclear overflow	Site 3		Monthly
19	Koekemoerspruit before Enviroclear overflow	Site 4		Monthly
20	Koekemoerspruit after Enviroclear overflow	Site 5		Monthly

2.3 Analytical methods

The following chemical and microbiological analyses were performed by Midvaal Water Company Scientific Services (Table 2-2), which was established in the 1970s and has been an accredited South African National Accreditation System (SANAS) testing laboratory (T0132) since 2002 based on the International Organisation for Standardisation 17025 (SANAS, 2018). The method numbers in Table 2-2 refer to the SANAS accredited method as indicated on the facility's scope of accreditation.

Table 2-2: The unit and method of each variable that was monitored and statistically analysed in this study

Determinant		Unit	Method/Instrument	Method number
1 2 3 4 5 6 7 8	Aluminium Arsenic Copper Iron Manganese Sodium Uranium Zinc	mg/L	Determined either by atomic absorption spectroscopy or inductively coupled plasma optical emission spectroscopy (ICP-OES)	ICP-A-1 ICP-A-3 ICP-A-1 ICP-A-1 ICP-A-1 ICP-A-2 ICP-A-4 ICP-A-1
9 10 11 12	Ammonia Chloride Nitrate and nitrite Sulfate	mg/L	Determined by colorimetric method on a discreet analyser	GL 7-1 GL 7-5 GL 7-2 GL 7-4
13	Chlorophyll-*a*	µg/L	In-house extraction and absorption method	AL1*
14	Colour	mg/L Pt	Determined with colorimeter	WL4*
15 16	*Cryptosporidium* oocysts and *Giardia* cysts	count/10L	Analyses performed by the Council for Industrial and Scientific Research (CSIR)	Outsourced
17 18	Cyanide recoverable Orthophosphate	mg/L	Determined by colorimetric method on a continuous flow analyser	CFA-1D CFA-1B
19	Dissolved Inorganic Nitrogen	-	Calculation (Nitrate and nitrite + Ammonia)	-
20	*E. coli*	MPN/ 100 mL	Colilert®	BL5-1
21	Electrical conductivity (EC) at 25°C	mS/m	Determined with electrode	WL2
22	Faecal coliform bacteria	cfu/100 ml	Membrane filtration	BL3
23	Geosmin	ng/L	Analyses performed by Rand Water Scientific Services by means of a purge-and-trap system coupled to gas chromatography–mass spectrometry	Outsourced
24	2-methylisoborneol (MIB)	ng/L	Analyses performed by Rand Water Scientific Services by means of a purge-	Outsourced

Determinant		Unit	Method/Instrument	Method number
			and-trap system coupled to gas chromatography–mass spectrometry	
25	pH at 25°C	pH units	Determined with electrode	WL1
26	Spectral absorbance coefficient 254	m^{-1}	Absorption method	AL6*
27	Suspended solids (SS)	mg/L	Gravimetric method	WL5
28	Total chlorophyll (T Chl)	µg/L	Determined by Sartory's extraction method (Swanepoel *et al*., 2008)	AL2
29	Total organic carbon (TOC) and dissolved organic carbon (DOC)	mg/L	Determined by a persulfate–ultraviolet oxidation method	AAL5
30	Turbidity (NTU)	NTU	Determined with turbidity meter	WL3

* indicates methods that are not SANAS-accredited

2.4 Approach and statistical methods

Data were obtained from Midvaal Water Company and the duration for each chapter were as follows, based on the availability of data (see sections 3.2, 4.2.3, 5.2.3 and 6.2.3):

- Chapter 3, data ranged from 1984 to 2015 (31 years)
- Chapter 4, data ranged from 2012 to 2017 (5 years)
- Chapter 5, data ranged from 2002 to 2015 (13 years)
- Chapter 6, data ranged from 2012 to 2014 (2 years)

The following statistical methods were used to analyse data throughout the study. The statistical methods relevant to each section are discussed separately in each chapter (see sections 3.2, 4.2.4, 5.2.4 and 6.2.4).

Results that were below the quantification limit were divided by two to be included in data processing, whereas those that were above the quantification limit were multiplied by two. Microsoft Excel was used to compile data spreadsheets and charts for illustrations.

Statistica software (version 13) was used to determine descriptive statistics (mean, minimum, maximum, standard deviation, variance and confidence intervals) and to create scatter plots (Dell Inc., 2016). The Shapiro–Wilks test for normality was used to determine whether the data were distributed parametrically. Since most of the data did not meet the assumptions of normality in the distribution of all variables, the Kruskal–Wallis analysis of variance (ANOVA) (nonparametric statistics) for comparing multiple independent groups was used to determine differences. The significance of the results of a Kruskal-Wallis ANOVA can be determined as a *z*-value and/or a 2-tailed *p*-value. The *p*-values of these comparisons are listed in Annexures C and D. All multi-variate analyses were done using the CANOCO version 4.5 software program (Ter Braak & Šmilauer, 2002).

CHAPTER 3 WATER TREATMENT AT MIDVAAL WATER COMPANY AND CHALLENGES DUE TO CHANGES IN SOURCE WATER QUALITY

3.1 Introduction

The erstwhile Western Transvaal Regional Water Company was established in 1954 to address drinking water needs of various mining companies at the time. The name was changed to Midvaal Water Company in 1998, with the new name derived from its location. Midvaal Water Company supplies bulk potable water to the local municipality, Vierfontein and the mining industry in the surrounding area. The local municipality is the City of Matlosana Municipality which serves the towns of Klerksdorp, Orkney, Stilfontein and Hartbeesfontein (the KOSH area), which includes approximately 500 000 consumers. Vierfontein, in the Free State Province, has about 1 500 consumers. Anglogold Ashanti represents the majority of the mining industry in the area and is also responsible for the company Mine Waste Solutions which deals with tailing storage facilities reclamation. The Vaal River is both heavily used and polluted by the time it passes the treatment works close to Stilfontein. The eutrophic water from the Middle Vaal River serves as their only water source and is purified by means of various conventional (coagulation and flocculation, sedimentation, filtration and disinfection) and advanced treatment processes (dissolved air flotation (DAF) and ozonation) prior to distribution.

The first aim of this study was to identify the prior objectives, criteria and indicators of water treatment for Midvaal Water Company, and to show how the water treatment processes of the plant have changed over time to adapt to the varying water quality of the Middle Vaal River. The second aim was to consider both current and future concerns and possible solutions regarding water quality and treatment.

3.2 Materials and methods

The source water (Middle Vaal River) database from Midvaal Water Company dates back to 1984. Operational data have been captured and were available on the Laboratory Information Management System (LIMS) of Midvaal Water Company Scientific Services from 2010. All the available data until 2015 was combined for statistical analyses.

See Figure 2-2 for an illustration of the distribution of the ten sampling sites on the water treatment plant, Table 2-1 for sampling sites and the sampling regime and Table 2-2 for the analytical methods. The following variables were investigated to determine changes in the source water quality and operational performances regarding water quality:

Colour

Electrical conductivity

Iron

Manganese

Nitrate and nitrite

Orthophosphate

pH

Total chlorophyll

Turbidity

All the general statistical methods of this study (see section 2.4) were applied to process the data.

3.3 Results: How the water treatment processes at Midvaal Water Company have changed to adapt to the varying water quality of the Middle Vaal River

3.3.1 Water treatment concerns for Midvaal Water Company: Water quality of the source water

Table 3-1 indicates how the water treatment processes of the plant have been changed over time in order to address treatment problems encountered due to varying source water quality over a timeline of 53 years. To summarise changes in source water quality, the data available from 1984 until the end of 2014 were grouped into 4 time periods which match significant changes in water treatment:

- Group 1: 1984–1991 (pre-chlorination, pre-ozonation, KMnO4 oxidation)
- Group 2: 1992–1996 (only pre-ozonation)
- Group 3: 1997–2006 (only DAF)
- Group 4: 2007–2014 (pre-ozonation and DAF)

The mean manganese concentrations declined over time (Figure 3-1). This decrease may be ascribed to the enforcement of the National Environmental Management Act (107 of 1998) as well as the National Water Act (36 of 1998). Interventions by mining companies to comply with regulations resulted in diminishing pollution of underground water that feeds the source. Since 2007 the manganese concentration has no longer posed any concerns to the treatment process.

The turbidity of the source water fluctuates continuously (Figure 3-1), and it is the extreme and unexpected spikes that are a cause for concern, considering that a maximum value of 1 226 NTU has been recorded (Figure 3-2).The water source is a river and rainfall patterns in the catchment, influenced by the effects of climate change, will in future continue to contribute to unpredictable spikes in turbidity levels.

As seen in Figure 3-1 and Figure 3-2, the total chlorophyll concentrations remain on the increase and subsequently result in an increase in pH levels as carbon dioxide is consumed by more algal cells during photosynthesis.

The mean orthophosphate concentration shows a gradual increase from Group 2 (1992–1996) to Group 3 (1997–2006) to Group 4 (2007–2014) (Figure 3-1). The mean nitrate and nitrite concentrations show an increase between Group 3 (1997–2006) and Group 4 (2007–2014) (Figure 3-1). Therefore, these nutrients will continue to sustain algal growth in the source water.

Table 3-1: A summary of the water treatment process train at Midvaal Water Company from 1954–2015

Process	**Plant 1954**	**Plant 1978**	**Plant 1980**	**Plant 1985**	**Plant 1992**	**Plant 1997**	**Plant 2007-2015**	**Treatment objective**
Abstraction	✓	✓	✓	✓	✓	✓	✓	
Pre-chlorination		✓	✓	✓				Removal of algal related problems e.g. colour and filter capacity
Pre-ozonation				✓	✓		✓	Improve colour & oxidise manganese, iron and total chlorophyll (1985–1997) Enhance algal removal by DAF (2007)
Primary addition of chemicals	✓	✓	✓	✓	✓	✓	✓	Coagulation and flocculation to remove turbidity/suspended matter
$KMnO_4$ oxidation			✓	✓				Manganese removal
Dissolved air flotation (DAF)						✓	✓	Separation and removal of light

Process	Plant 1954	Plant 1978	Plant 1980	Plant 1985	Plant 1992	Plant 1997	Plant 2007-2015	Treatment objective
								particulate matter and algae
Intermediate ozonation						✓	✓	Manganese & iron removal, colour, taste and odour improvement
Secondary addition of chemicals						✓	✓	Flocculation of particulate matter/solids after the oxidation step
Sedimentation	✓	✓	✓	✓	✓	✓	✓	Separation of solids from water
Filtration	✓	✓	✓	✓	✓	✓	✓	Removal of remaining particulate matter and removal of micro-organisms which might pose a health risk
Disinfection	✓	✓	✓	✓	✓	✓	✓	Pathogen removal

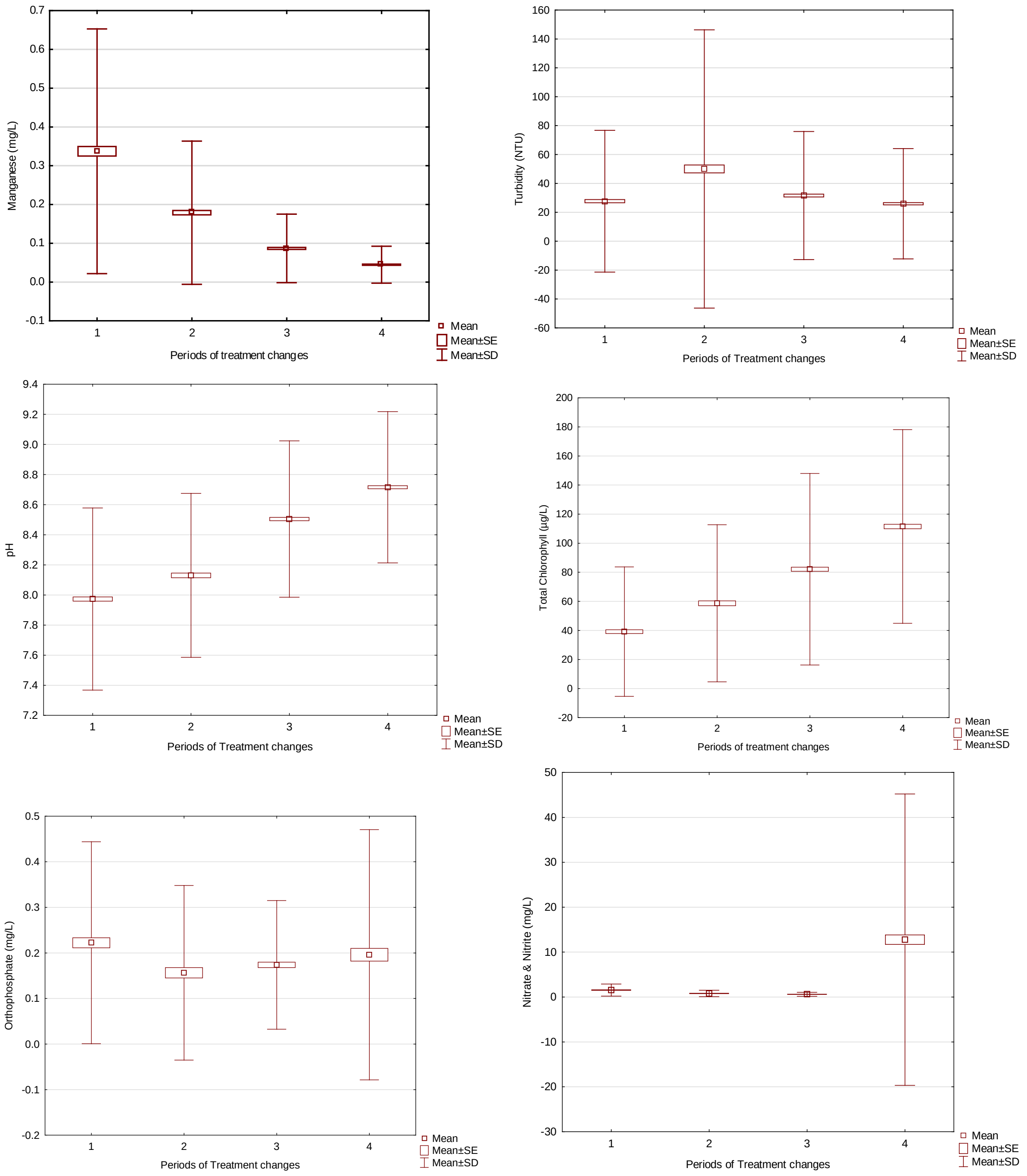


Figure 3-1: Box and whisker plots that compare means, standard errors (SE) and standard deviations (SD) for manganese, turbidity, pH, total chlorophyll, orthophosphate and nitrate and nitrite values of the source water from 1984 till the end of 2014 for Group 1 (1984–1991), Group 2 (1992–1996), Group 3 (1997–2006) and Group 4 (2007–2014)

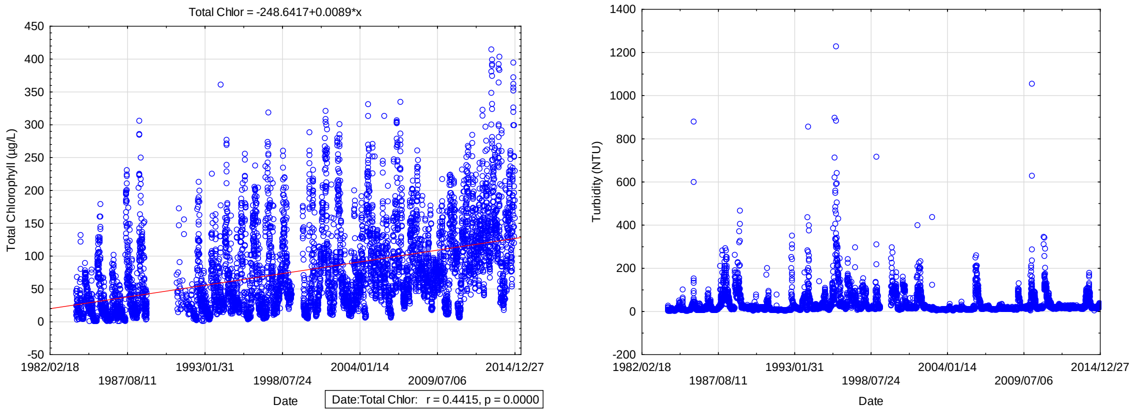


Figure 3-2: **Scatter plots for total chlorophyll concentrations in the source water, which increased significantly (*r* = 0.4415 and *n* = 6268) and for turbidity levels (*r* = −0.0445 and *n* = 7 830), showing extremely high turbidity spikes at times**

It appears from Figure 3-2 that the presence of algae and the subsequent total chlorophyll concentrations will continue to increase in future, increasing the risk for colour as well as taste and odour episodes. Higher algal concentrations in the source water, together with increased spikes in turbidity levels, will ultimately put more pressure on the existing treatment processes, similar to when the DAF process was temporarily out of order from 14 February 2015 to 6 March 2015.

Hudson (2015) conducted a study from January 2010 to December 2011 and determined an average geosmin concentration of 4.083 ng/L (< 5 ng/L) for the Middle Vaal River. Studies by Morrison (2009) and Hudson (2015) stated that Chlorophyceae and Bacillariophyceae are the dominant algal classes in the Middle Vaal River. *Planktothrix* spp. is usually identified in the raw water during taste and odour episodes (when geosmin and 2-methylisoborneol (MIB) can be detected). The MIB concentrations indicated in Table 3-2 confirms that taste and odour problems mostly occur during the months of January, February and March, and also indicate an increase in the frequency of taste and odour problems.

Table 3-2: **A summary of geosmin and MIB concentrations in the source water from 2004 when Midvaal Water Company began to experience taste and odour incidents**

Date	Geosmin (ng/L)	MIB (ng/L)
2004/01/23	36.4	51.9
2012/01/09	<6	255

Date	Geosmin (ng/L)	MIB (ng/L)
2012/01/10	<6	335
2012/01/25	19	325
2012/02/09	<6	27
2012/03/02	<6	125
2012/03/05	<6	130
2013/02/04	5.8	20
2015/01/19	<5	245
2015/02/02	<5	28

3.3.2 Water quality and the use of oxidants

The treatment processes, including oxidants, have varied over time to adapt to the ever-changing quality of the source water as well as to ensure optimal, cost-effective operations (Table 3-1).

Consumer complaints in the late 1970s about brown stains on bathtubs as well as on laundry treated with household bleach lead to the discovery of high and fluctuating concentrations of dissolved manganese in the source water. The average manganese concentration in the source water from 1984 to 1992 was 0.34 mg/L (± 0.3), which ranged from a minimum of 0.01 mg/L to a maximum of 2.84 mg/L and varied at different depths. Low flow conditions during winter due to low rainfall and low release from the Vaal River Barrage together with windy conditions disturbed the source water and resulted in isolated peak manganese concentrations ranging from 4 mg/L to 8 mg/L at times. An oxidation step using potassium permanganate was implemented from 1980 to 1992 for the removal of manganese and ± 1.2 mg/L was dosed with other water treatment chemicals after pre-chlorination and the addition of lime. Manganese concentrations below ± 1.5 mg/L could successfully be removed with the potassium permanganate. For higher concentrations, the required dose resulted in the treated product having a brown/purplish colour; structures that came into contact with it were stained and a manganous oxide layer formed on filter sand. The manganese was bound in tough organic complexes and a more powerful oxidation was required.

A pre-chlorination step was implemented from 1978 to 1992 to alleviate colour problems and filter blockages caused by high total chlorophyll concentrations in the source water. The total chlorophyll concentrations in the source water increased progressively (Figure 3-2) as maximum total chlorophyll concentrations of 132 µg/L, 179 µg/L, 230 µg/L and 305 µg/L were recorded in 1984, 1985, 1987 and 1988, respectively. The pre-chlorination dosages ranged from 1.5 mg/L to

5 mg/L at the time and were positioned after the source water abstraction and prior to the addition of other water treatment chemicals.

In order to try to address these problems with manganese and high chlorophyll concentrations it was decided to add an advanced treatment process in the form of pre-ozonation. The configuration of the plant allowed for a pre-chlorination line (east) and a pre-ozonation line (west) to be separated from the point of abstraction up to the filtration process. A pre-ozonation step was implemented from 1985 to 1997 as this powerful oxidant could improve the colour of the water and also address the manganese, iron and total chlorophyll problems. Pre-ozone was dosed at ± 2.5 mg/L with a contact time of 4 min. The effectiveness of these two oxidants was compared from 1985 to 1992, as far as the removal of total chlorophyll, manganese and iron were concerned. The effect of the pre-chlorination was found to be different for each algal species and, as the algal composition of the source water varies seasonally (Figure 6-2), the effectiveness of pre-chlorination was therefore inconsistent and unreliable. The colour removal also showed limited success. Ozone clearly proved to be more effective and the decision was made to terminate pre-chlorination and utilise pre-ozonation only, as from 1992 to 1997 (Krüger & Pietersen, 2006).

3.3.3 Water quality and the combined use of oxidants and DAF

A DAF plant was implemented in 1997 as a first treatment step to address the high algal load present in the Middle Vaal River and the inability of conventional water treatment methods (including pre-chlorination) to remove algae effectively. The pre-ozonation was redirected to an intermediate ozonation step, after DAF and prior to sedimentation to enhance the conventional processes (sedimentation, filtration and disinfection) that follow. Intermediate ozonation dosages of ± 1.8 mg/L to 2.5 mg/L together with the DAF resulted in favourable removal of total chlorophyll, iron, manganese, micro-organisms and colour. The removal of taste and odour compounds, mainly MIB, has however not been desirable at these ozone dosages but a significant saving in other water treatment chemicals (± 30%) was achieved by the application of DAF and intermediate ozone. The ferric chloride and chlorine demand decreased because less suspended matter had to be flocculated during the sedimentation process and some disinfection had already taken place with ozonation. The disinfection demand after filtration was collectively reduced by both pre-ozonation and intermediate ozonation as ozone is a more powerful oxidant than chlorine; however ozone fails to provide a residual disinfectant concentration which is possible with the use of chlorine.

A case study was conducted by Morrison (2009) from October 2007 to September 2008 to determine the influence of ozone on water purification processes. The average total chlorophyll concentration of the source water during the study was 104 µg/L, reduced to 32 µg/L after DAF (69% removal) and further reduced to 27 µg/L after intermediate ozonation (an additional 5% removal). The average manganese and iron concentrations of the source water during the study were 0.05 mg/L and 0.02 mg/L, respectively, and even though there was no cause for concern the manganese and iron concentration averages as well as concentration ranges decreased after the intermediate ozonation process.

DAF is an advanced water treatment process whereby small air bubbles are introduced to the water after the primary addition of water treatment chemicals for coagulation and flocculation (Table 3-3). The air bubbles attach to the flocs (containing organic material and algae) and rise to the water surface where the froth is collected and removed. Heavier particles settle to the bottom of the flotation units as sludge.

Table 3-3: Design specifications of the DAF plant (Midvaal Water Company, 2014)

Parameter	Specification
Design	Modular, 5 x 50 ML/day units
Capacity	250 ML/day
Retention time	± 1 h
Recycle stream	7 to 10% v/v
Bubble size	0.5 mm
Pressure vessels	500 kPa
Sludge concentration	1.5 to 2%
Flocculation method	Serpentine channels; adjustable outlets
Air : water ratio	1:1

A pre-ozonation step, prior to the DAF, was implemented in 2007. Pre-ozone is currently dosed at a range from 1 mg/L to 1.5 mg/L with a contact time of 2 min in order to enhance the DAF, and intermediate ozone dosages of 2.5 mg/L with a contact time of 4 min are maintained. Pre-ozonation enhances the DAF process by inactivating algal cells and does not necessarily reduce total chlorophyll concentrations of the source water immediately, as was confirmed by Morrison *et al*. (2012).

3.3.4 Temporary shutdown of the DAF and the effects thereof

The DAF process together with the pre-ozonation process was out of operation from 14 February 2015 up to 6 March 2015 due to maintenance on the DAF plant. During this period flocculated material had to be removed in the conventional clarifiers by means of settling. The effect was evident in the higher turbidity levels in the four Midvaal Water Company reservoirs as well as the final water (Figure 3-3). The turbidity of the final water did however comply with the limit of ≤ 1 NTU during the DAF shutdown, but more pressure was placed on the other treatment processes during this period. Higher turbidity levels added to other treatment problems on the plant, e.g., shorter filter runs, increased backwashing, the generation of larger volumes of wastewater and a higher demand for water treatment chemicals and energy. The usage of chlorine gas increased by about 30% during the DAF shutdown whilst the requirement for flocculants increased by 15%. In spite of the additional chemical additions, the average turbidity of the final water 3 months before the DAF shutdown could not be maintained (Figure 3-3). Figure 3-4 shows improved total chlorophyll removal in 3 Midvaal Water Company reservoirs as well as the final water after maintenance had been completed.

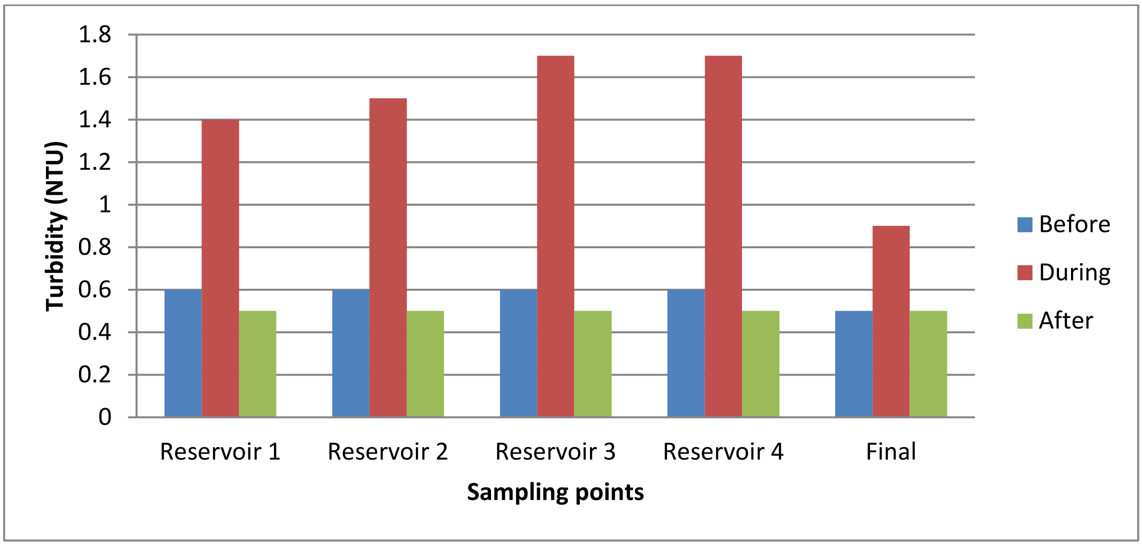


Figure 3-3: **The average turbidity levels three months before, during and three months after the DAF shutdown for four Midvaal Water Company reservoirs, and for the final water**

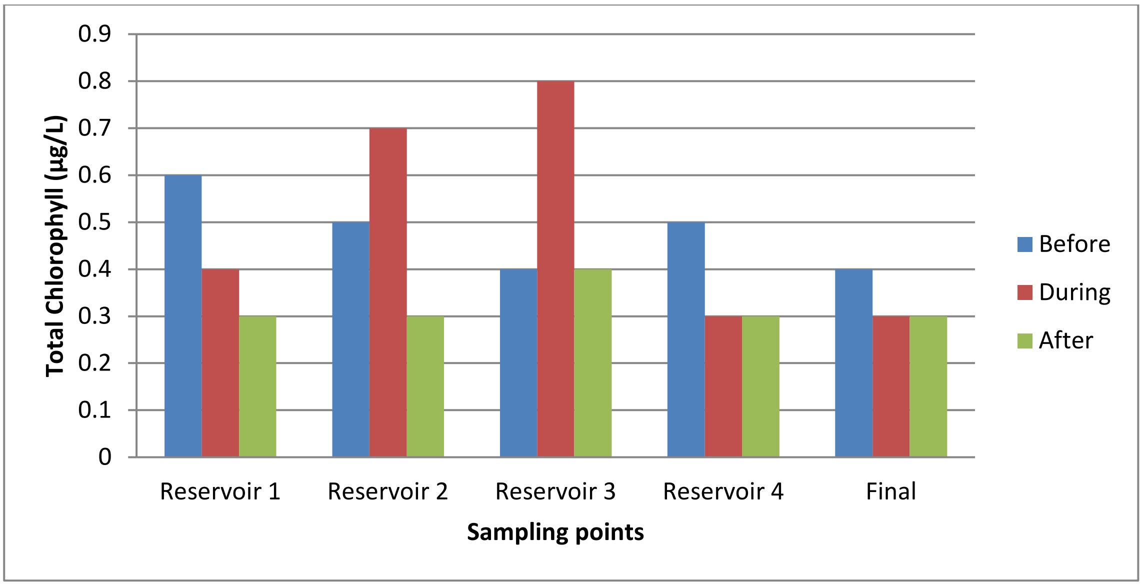


Figure 3-4: **The average total chlorophyll concentrations three months before, during and three months after the DAF shutdown for four Midvaal Water Company reservoirs, and for the final water**

3.3.5 Operational monitoring at Midvaal Water Company: Water quality of various processes

Midvaal Water Company uses pH, electrical conductivity, turbidity and total chlorophyll as operational indicators to monitor the effectiveness of the various treatment processes. The average total chlorophyll concentrations after pre-ozonation, before flotation and after chemical dosing are higher than the average total chlorophyll concentration of the source water (Table 3-4). This could possibly be the result of lyses of algal cell material due to damaged algal cell walls combined with a reaction between the source water and the ozone and chemicals. It is also difficult to ensure that samples are always homogenous and representative of the source water. In water treatment the desired outcome is often not immediately evident as the cumulative effects are only visible right at the end of the treatment train.

Table 3-4: **The average concentrations for pH, electrical conductivity, turbidity, total chlorophyll, manganese, iron and colour indicate the effectiveness of the various water treatment steps from 2010–2014 (± standard deviation)**

Processes/ Sampling points	pH	Electrical conductivity (mS/m)	Turbidity (NTU)	Total chlorophyll (µg/L)	Manganese (mg/L)	Iron (mg/L)	Colour (mg/L)
Source	8.76 (±0.53)	57 (±15)	30 (±44)	127 (±72)	0.04 (±0.04)	0.12 (±0.29)	119 (±96)

Processes/ Sampling points	**pH**	**Electrical conductivity (mS/m)**	**Turbidity (NTU)**	**Total chlorophyll (µg/L)**	**Manganese (mg/L)**	**Iron (mg/L)**	**Colour (mg/L)**
After pre-ozonation	8.82 (±0.49)	58 (±14)	30 (±42)	122 (±72)	-	-	-
Before flotation	8.80 (±0.48)	58 (±14)	32 (±43)	145 (±70)	-	-	-
After chemical dosing	8.94 (±0.46)	59 (±13)	33 (±42)	138 (±79)	-	-	-
After DAF	8.82 (±0.45)	59 (±14)	12 (±25)	39.86 (±35.97)	-	-	-
After intermediate ozonation	8.61 (±0.49)	61 (±13)	14 (±24)	39.48 (±31.40)	0.03 (±0.04)	0.05 (±0.09)	-
After settling	8.55 (±0.47)	60 (±13)	3.3 (±4.0)	15.33 (±42.67)	-	-	-
After filtration	8.17 (±0.43)	62 (±17)	0.6 (±0.9)	1.64 (±4.5)	-	-	-
Storage	8.20 (±0.39)	60 (±13)	0.5 (±0.9)	0.81 (±5.1)	-	-	-
Final after pump station	8.23 (±0.39)	60 (±13)	0.5 (±0.2)	0.55 (±0.6)	0.02 (±0.02)	0.03 (±0.03)	2.65 (±0.8)

The South African National Standards (SANS) for drinking water 241 (2015) requires the pH to range from ≥ 5 to ≤ 9.7 pH units, electrical conductivity at 25°C to be ≤ 170 mS/m and turbidity to be ≤ 1 NTU and ≤ 5 NTU for operational and aesthetic risks, respectively. Midvaal Water Company aims for the pH to range from 7.8 to 8.1 pH units, as the efficacy of chlorine as a disinfectant decreases when pH increases above pH 8.0. The average electrical conductivity (60 mS/m) and turbidity (0.5 NTU) of the final water, as indicated in Table 3-4, comply with the national limits. Even though there is no national limit for total chlorophyll, Midvaal Water Company has an internal limit of ≤ 1.0 µg/L in the final water which was also met with an average of 0.55 µg/L according to Table 3-4.

3.4 Discussion

Algal assemblages and spikes in turbidity levels seem to be the greatest water quality concerns for Midvaal Water Company. Unacceptably high pH levels (Figure 3-1), which affect treatment processes and influence scaling properties of the final water, are attributed to the excessive algal activity and are intensified during periods of low rainfall. Untreated or partially treated sewage effluents and over-fertilised agricultural run-off contribute to the nutrient load of the Middle Vaal River. Due to this nutrient enrichment, the only source of drinking water for consumers in this area of supply is a eutrophic water system. However, nutrient concentrations do not appear to be a cause for concern as such, but result in high algal activity which confirms the presence of nutrients. Increasing total chlorophyll concentrations also hold a threat for taste, odour and colour problems. The abundance of Cyanophyceae species and higher microcystin levels in the source water of the Vaal River Barrage (Hudson, 2015) pose a risk for Midvaal Water Company as the point of abstraction is situated downstream of Vaal River Barrage. Not only is Midvaal Water Company at risk for taste and odour problems but consumers will perceive the drinking water as unsafe. SANS 241 (2015) regulates that water services institutions shall use a risk-based management approach to ensure that safe drinking water is produced at all times and that public health is protected.

Conventional water treatment processes are simply not adequate to supply safe and healthy drinking water anymore when the source water is heavily polluted. Zabel (1985) recorded an average of 93% algal cell reductions for *Aphanizomenon* spp., *Microcystis* spp., *Stephanodiscus* spp. and *Chlorella* spp. in water treatment by DAF at the time. DAF and ozonation are absolutely essential water treatment processes at Midvaal Water Company. This was confirmed by elevated total chlorophyll concentrations and turbidity levels when the DAF was temporarily out of operation (Figure 3-3 and Figure 3-4). Pantelić *et al*. (2013) emphasized the importance of removing cyanobacteria without cell lysis and subsequent release of intracellular metabolites, thereby confirming the value of a DAF process at Midvaal Water Company. The difference in colour of the final water is also noticeable during ozone plant shutdowns. The water treatment processes of the Midvaal Water Company plant have adapted successfully to the varying water quality of their source water, as their compliance with SANS 241 (2015) proves. Climate change has however resulted in dry periods being experienced regularly during recent years as well as occasional floods, causing spikes in turbidity levels, and together with the increase in total chlorophyll concentrations, Midvaal Water Company would most probably be required to consider additional treatment processes to ensure continued compliance with the required standard.

Powdered activated carbon (PAC) could be dosed at the secondary chemicals addition point and removed at the sedimentation stage. The dosing point of PAC in water treatment has to take the degree of mixing, the adequacy of the contact time, the PAC residence time and the minimization of interference of treatment chemicals with the adsorption process in consideration (Najm *et al*., 1991). The application of activated carbon to alleviate taste and odour problems has to be weighed against the cost implications for the consumers, the correct type to be purchased for the organic molecules to be adsorbed, the interference of natural organic matter (NOM) and formation of additional sludge mass, as well as the intensity and duration of taste and odour episodes. The type and concentration of the taste- and odour-causing compounds determine the varying efficiencies of removal by PAC in water treatment (Najm *et al*., 1991). Srinivasan and Sorial (2011) refers to the optimisation of granular activated carbon (GAC)/PAC adsorption but the sporadic and seasonal taste and odour events at Midvaal Water Company do not allow for frequent monitoring of geosmin and MIB concentrations present in the influent, and prevent proper research on the application of GAC/PAC adsorption, or any other advanced process, in this regard.

Advanced oxidation processes (AOPs) in drinking water are used to degrade primarily organic chemical contaminants, e.g., taste- and odour-causing compounds (Linden & Mohseni, 2014). Ozone and ultraviolet (UV) light constitute the main AOPs and are increasingly being used at a large scale for the degradation of contaminants in water and wastewater (Linden & Mohseni, 2014). Wang, Bolton *et al*. (2015) compared UV/chlorine to UV/hydrogen peroxide (H_2O_2) at various pH concentrations, as UV/H_2O_2 is becoming more popular. Approximately 20% and 10% of spiked geosmin and MIB, respectively, were destroyed by UV exposure alone and when an AOP was applied, geosmin and MIB destruction was increased because of the additional hydroxyl radical oxidation (Wang, Bolton *et al*., 2015). The UV/H_2O_2 process is used at the City of Cornwall Water Purification Plant (Ontario, Canada) for the control of seasonal taste and odour events that occur in late summer, but this process does also pose operational problems (Wang, Bolton *et al*., 2015). Similar to GAC adsorption, presence of NOM in water can influence AOPs as well (Srinivasan & Sorial, 2011). According to Srinivasan and Sorial (2011), the capital and operating costs associated with these AOPs can be significantly high, especially at the higher dosages required for MIB/geosmin removal, and they could also result in the formation of disinfection by-products which could be of health or regulatory concerns. Zong *et al*. (2015) established that chlorination was an effective treatment option for removing microcystin but it is important for water suppliers to be aware of the secondary pollution of microcystin-associated disinfection by-products.

More research is required on the use of ultra-filtration for treatment of taste and odour problems at water treatment plants, as very few research results were available on this advanced treatment process for this case study. Currently Midvaal Water Company should ensure that MIB/geosmin is not produced or intensified on-site. Srinivasan and Sorial (2011) stated that although some technologies are more effective and applicable than the others, a completely accepted technology that could be used in any drinking water treatment facility still does not exist. The odour threshold concentration for MIB/geosmin ranges from 4 ng/L to 20 ng/L (Srinivasan & Sorial, 2011) and the treatment of these taste and odour compounds is only required at Midvaal Water Company during increased concentrations. The recommended process, or perhaps combination of technologies, would therefore be expected to deal with concentrations which have been recorded as greater than 300 ng/L MIB (Table 3-2) at times, and even if 80% removal of MIB could be achieved on a source water concentration of 150 ng/L this would still result in a MIB concentration which exceeds the odour threshold concentration. Srinivasan and Sorial (2011) stated that current practice most commonly followed is application of PAC during severe taste and odour outbreaks which is similar to the current situation at Midvaal Water Company. Srinivasan and Sorial (2011) also confirm the view of this case study when it concludes that it would not be economical or practical for water treatment facilities to install a technology exclusively for treatment of MIB/geosmin, but should rather optimise the technology they are currently using for MIB/geosmin treatment. Midvaal Water Company remains a bulk potable water supplier and therefore has to consider the socio-economic status of their consumers where water pricing is concerned, as any additional advanced treatment steps will increase costs. The availability of accurate information and communication with consumers during taste and odour episodes remains imperative for Midvaal Water Company as they have managed to supply wholesome drinking water for many years in spite of the ever increasing pollution of the source, the Middle Vaal River.

3.5 Conclusion

Since 1978 pre-chlorination was applied in addition to the conventional treatment processes to deal with algal related problems. Pre-chlorination was later replaced by pre-ozonation as the algal related problems persisted and intensified up to the point where DAF was introduced and pre-ozonation redirected to an intermediate ozonation process. Currently, pre-ozonation, DAF and intermediate ozonation are applied because the quality of the already eutrophic source water seems to deteriorate continuously with increasing total chlorophyll concentrations. Until now Midvaal Water Company has managed to treat the water successfully, with ozonation and dissolved air flotation being key processes. The operational monitoring of these processes are effective and contribute to a dataset that will enable informative decision-making in future. There is the possibility that organic content of the final water is also at risk of increasing due to the increasing algal load of the source water and therefore chlorine dioxide might have to be considered in future with regard to the subsequent risk of trihalomethane formation. The need for more advanced and expensive processes seem to be inevitable in order to maintain final water quality in future with such unstable source water quality but this has to be considered carefully, keeping in mind the cost implications for consumers.

CHAPTER 4 THE FEASIBILITY AND VALUE OF WASTEWATER RECYCLING WITHIN A WATER TREATMENT PLANT: CASE STUDY OF MIDVAAL WATER COMPANY

4.1 Introduction

Recent droughts and associated conditions in South Africa have increased water users' awareness of current water demands, which are likely to increase in the future. Deteriorating source water quality together with population increases and high water quality standards have led to greater expenses in the production of drinking water. According to Reissmann and Uhl (2006), this has led to numerous efforts to implement water reuse systems in treatment plants all over the world. Sludge produced by water treatment plants is mainly intended for disposal in sanitary landfills but the recycling of spent water produced at different stages of the drinking water treatment process can be applied by water treatment plants to reduce water treatment expenses prior to exploring water reuse systems (Cremades *et al*., 2018; Wang *et al*., 2018). Clarified spent filter backwash water has frequently been returned to the inflow of a water treatment plant after a sedimentation process (Reissmann & Uhl, 2006). However, most studies related to potable water treatment waste refer to the treatment, utilisation or disposal of the residue/sludge (Cremades *et al*., 2018; Herselman, 2013; Zhou *et al*., 2018). In the Water Research Commission report Herselman (2013) acknowledged that there are still information gaps regarding the characteristics of South African water treatment residue and its beneficial use. To the authors' knowledge Midvaal Water Company is the only water treatment plant in South Africa to include sludge/wastewater from the DAF process for recycling. Other bulk water treatment plants recycle wastewater from sedimentation and filtration processes only, such as Virginia and Balkfontein water treatment plants in the Free State Province (Oosthuizen & Janse van Vuuren, 2014) .The Rand Water water treatment plants in the Gauteng Province recycle wastewater from filtration processes and the wastewater from sedimentation are transferred to sludge plants (Swanepoel, 2018).

Midvaal Water Company purchases raw water from the Department: Water and Sanitation (DWS), treats it and sells bulk potable water to the local municipality and surrounding mining industries. The majority of the company's income is dedicated to the purchase of raw water, electricity, chemicals, maintenance and human resources. In an attempt to reduce operational expenses, Midvaal Water Company investigated and implemented an upgraded recycling system for wastewater produced in the water treatment plant (Table 4-1). The mean daily wastewater flow from the different unit processes amounted to ± 22 500 kL/day (9.03% of maximum operational plant capacity) and justified a business case for the recycling of this wastewater. The challenge at the onset of the new recycling system was to integrate the sludge from the DAF process, as this contributed to around 46% of the total wastewater flow per day (Table 4-1). The upgraded wastewater recycling system was in operation from June 2013 to February 2016, recycling waste flows from DAF units, desludging of sedimentation dams and backwashing of sand filters. Since quantity and quality aspects of wastewater can be managed, large quantities of river water can be saved by wastewater recycling, thus lowering input costs, reducing environmental pollution and contributing to water security.

Table 4-1: Wastewater volumes generated per day at the dissolved air flotation (DAF), sedimentation and filtration process units of Midvaal Water Company water treatment plant

Process unit	**Volume (m^3/day)**
DAF scum	5 208
DAF sludge	5 220
Sedimentation	973
Filtration	11 175
Total wastewater (daily flow)	22 576
As % of 250 ML/day (maximum operational plant capacity)	9.03%

It is imperative that the recycling of wastewater should not deteriorate the source water and/or impact on final water quality (with special reference to taste and odours) over and above the benefits of saving water and associated costs. The aims of this study were to determine the functionality and water quality of the recent wastewater recycling system at Midvaal Water Company, and to determine its effect on the overall treatment processes and associated risks regarding wastewater recycling. The wastewater recycling system was partly placed on hold after February 2016 and thus presented an opportunity for evaluating the failures, benefits and future considerations of this process.

4.2 Materials and methods

4.2.1 Description of study site

The study site, as was described in chapter two sections 2.1 and 2.2, was the Midvaal Water Company water treatment plant and its wastewater recycling system (Figure 2-3). It consists of a network of gravity pipelines, pumping systems and sludge-handling infrastructure. A sludge-thickening plant and pond system has been in operation since 1994 but has limited capacity for treating the total wastewater, especially since the DAF process was implemented in 1997 to address the high algal load in the Middle Vaal River and due to the inability of conventional water treatment to effectively remove algae (Janse van Rensburg *et al*., 2016). An upgrade to Midvaal Water Company's water treatment plant commenced in 2013 and entailed the provision of infrastructure to transfer wastewater from the DAF process units to a series of dams and, after some retention, to the sludge balancing dam (SBD). The recycling system comprised two inlet dams and a collection dam. The two inlet dams are fed alternately and chlorine is dosed between the inlet dam in use and the collection dam. Chlorine is dosed again in the canal between the overflow of the collection dam towards the sludge balancing dam by means of sodium hypochlorite tablets; dosing concentrations range from 6 to 10 mg/L. The wastewater from the sedimentation and filtration processes gravitates directly to the sludge balancing dam without any treatment. The sludge balancing dam thus receives the total volume of wastewater produced during plant operation from where the recovered water is pumped to the source water inlet pipe, prior to pre-ozonation.

4.2.2 Description of sampling sites

Seven sampling sites were identified at the onset of the wastewater recycling system in 2013 (Table 4-2 and Figure 2-3) to determine the water quality of the spent water generated during each of the targeted treatment processes.

Table 4-2: Sampling sites at the Midvaal Water Company wastewater recycling system

Sampling site name	Abbreviation	Description
DAF top	DAF-T	Sludge is withdrawn at top of DAF units due to flotation and transferred to inlet dam
DAF bottom	DAF-B	Sludge is withdrawn at bottom of DAF units due to sedimentation and transferred to inlet dam
East sludge	ES	Combined wastewater from east side sedimentation and filtration of plant transferred to SBD
West sludge	WS	Combined wastewater from west side sedimentation and filtration of plant transferred to SBD
Collection dam overflow	CDO	Second retention dam that overflows into canal towards SBD
Recycle stream	RS	Water from SBD combined with river water prior to any treatment
Middle Vaal River	R	Source water abstracted from Middle Vaal River for treatment prior to introduction of recycle stream

4.2.3 Sampling regime and methods

To determine the impact of the recycled water (from the sludge balancing dam) on the water treatment plant, water quality data from the river (source water), after DAF, after west sedimentation and after east sedimentation were collected and statistically analysed. The study period included a year prior to the implementation of the recycling system (June 2012 to June 2013), the operational period of the recycling system (June 2013 to February 2016) and a year after the termination of the wastewater recycling system (February 2016 to February 2017).

The DAF top, DAF bottom, east wastewater, west wastewater and the collection dam overflow were sampled on a weekly basis from June 2013 to February 2016 (Table 2-1).

Data reports for the daily samples were generated from the Scientific Services' Laboratory Information Management System (LIMS) from a year prior to the implementation of the recycling system to a year after its termination for statistical analyses (i.e. June 2012 to February 2017). The wastewater from the east and west wastewaters was recycled from February 2016 to February 2017. The samples were chemically and microbiologically analysed by Midvaal Water Company Scientific Services for the following 11 determinants included in Table 2-2:

Aluminium

Chlorophyll-*a*

Dissolved organic carbon (DOC)

E.coli

Electrical conductivity (EC)

pH

Spectral absorbance coefficient 254

Suspended solids (SS)

Total chlorophyll (T Chl)

Total organic carbon

Turbidity (NTU)

Samples of the final drinking water were submitted to the Council for Industrial and Scientific Research (CSIR) every second month for analyses of protozoan parasites (*Cryptosporidium* oocysts and *Giardia* cysts).

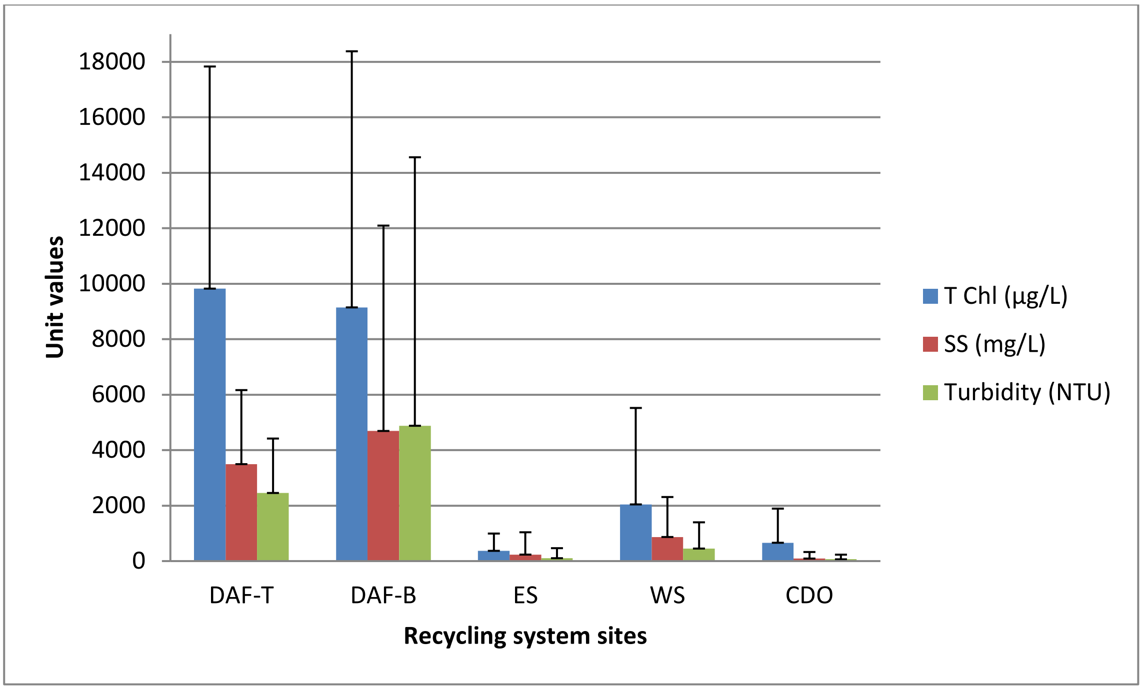
4.2.4 Approach and statistical analyses

All the general statistical methods of this study (see section 2.4) were applied to process the data. The Kruskal–Wallis ANOVA (nonparametric statistics) for comparing multiple independent groups was used to determine differences between unit values of determinants measured after treatment processes prior to, during and after the implementation of the wastewater recycling system.

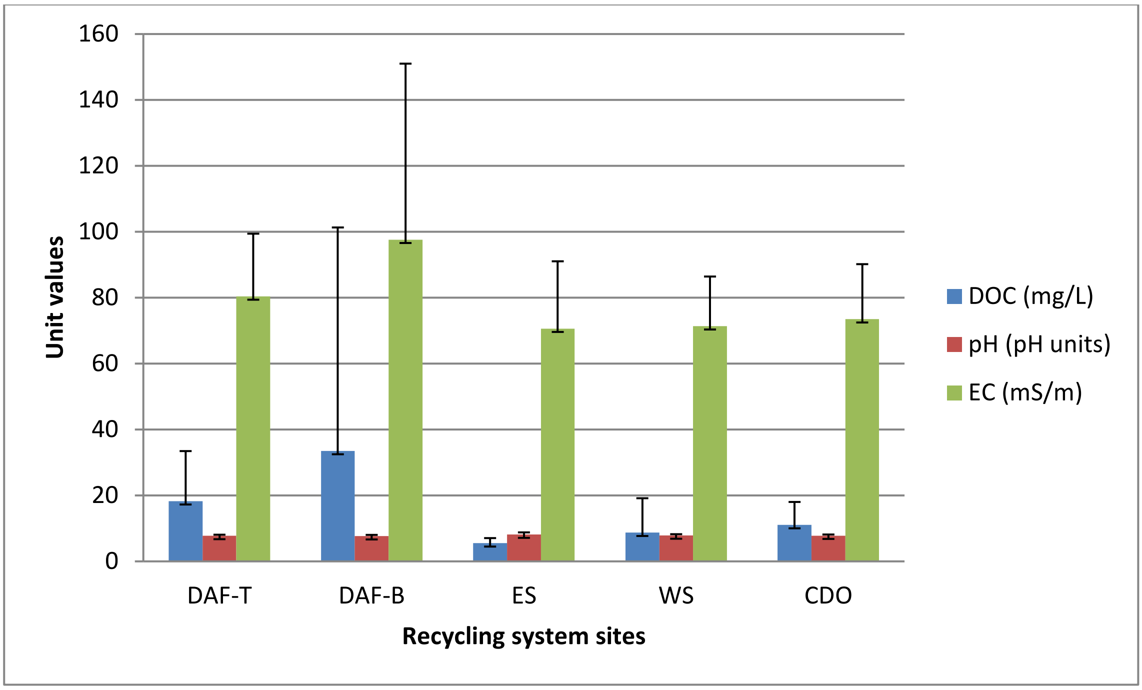
4.3 Results

4.3.1 Water quality of the wastewater

The mean total chlorophyll, suspended solids, turbidity, dissolved organic carbon, pH and electrical conductivity for each section of the wastewater recycling system are compared in Figure 4-1. The wastewater from the DAF top had means of 9 825 µg/L total chlorophyll, 3 497 mg/L suspended solids, 2 457 NTU turbidity and 18 mg/L dissolved organic carbon, whereas the DAF bottom had means of 9 148 µg/L total chlorophyll, 4 693 mg/L suspended solids, 4 880 NTU turbidity and 33 mg/L dissolved organic carbon. The quality of the wastewater (sludge from DAF units) that overflowed from the collection dam to the sludge balancing dam improved significantly with means of 662 µg/L total chlorophyll, 93 mg/L suspended solids, 65 NTU turbidity and 11 mg/L dissolved organic carbon. The total chlorophyll, suspended solids and turbidity of the west wastewater were noticeably higher than those of the east wastewater. The pH and electrical conductivity for each section's wastewater varied very little over the study period.



(a)



(b)

Figure 4-1: **(a and b) Mean total chlorophyll (T Chl), suspended solids (SS), turbidity (NTU), dissolved organic carbon (DOC), pH and electrical conductivity (EC) concentrations with standard deviation error bars of the wastewater sampled at various sites for the water recycling system from 5 June 2013 to 3 February 2016**

Figure 4-2 illustrates the water quality of the recycle stream compared to the water quality of the Middle Vaal River. The mean pH and electrical conductivity of the recycle stream and river differed significantly according to Kruskal-Wallis (see Annexure C, Table C.1) although these differences are small (8.4 vs. 8.7 pH and 62 vs. 60 mS/m electrical conductivity for recycle stream and river respectively). The mean values of total chlorophyll (179 vs. 136 µg/L), suspended solids (75 vs. 29 mg/L), turbidity (46 vs. 22 NTU) and dissolved organic carbon (8.3 vs. 5.7 mg/L) of the recycle stream were higher than that of the river water but only suspended solids and turbidity differed significantly according to Kruskal-Wallis with *p*-values < 0.05 (see Annexure C, Table C.1). The total chlorophyll concentration in the recycle stream ranged from 11 to 6 451 µg/L. The water quality of the recycle stream that originated from the sludge balancing dam represents an improvement compared to that from the collection dam overflow in terms of total chlorophyll (179 vs. 662 µg/L), suspended solids (75 vs. 93 mg/L), turbidity (46 vs. 65 NTU) and dissolved organic carbon (8.3 vs. 11 mg/L). This observed improvement can be ascribed to a dilution effect when water from the collection dam overflow was combined with higher-quality water from the east and west wastewater already present in the sludge balancing dam.

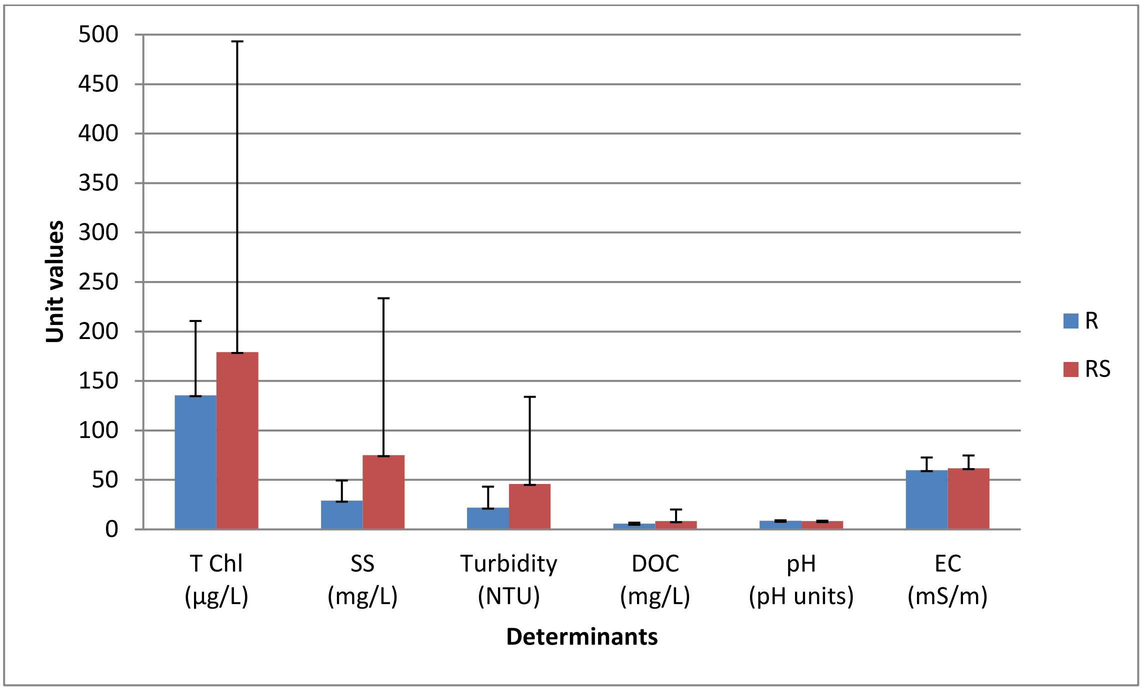


Figure 4-2: **Mean total chlorophyll (T Chl), suspended solids (SS), turbidity (NTU), dissolved organic carbon (DOC), pH and electrical conductivity (EC) concentrations with standard deviation error bars for the Middle Vaal River (R) and recycle stream (RS) from 5 June 2013 to 3 February 2016**

4.3.2 Final water quality failures

To establish whether the recycle stream had any impact on the water quality of the final water produced by the plant, the incidences of water quality failures for the final water were determined. Failures were determined as noncompliance to SANS 241 (2015). SANS 241 (2015) requires aluminium concentrations to comply with a limit of ≤ 0.3 mg/L regarding operational risks and turbidity with limits of ≤ 1 NTU and ≤ 5 NTU for operational and aesthetic risks, respectively. Even though there is no national limit for total chlorophyll, Midvaal Water Company has an internal limit of ≤ 1.0 µg/L in the final water (Janse van Rensburg *et al*., 2016). Aluminium, turbidity and total chlorophyll failures occurred during the entire study period and most failures for all three of these determinants were recorded when the recycling system was in operation (Table 4-3). Despite these failures, the water quality of the final water during the addition of the recycle stream still complied at ≥ 95% for aluminium and turbidity.

Table 4-3: Final drinking water failures from June 2012 to February 2017, considering that the recycle stream was in operation from June 2013 to February 2016 as well as the associated risk-defined compliances, as prescribed by South African National Standard 241:2015

	Pre-recycling	**During recycling**				**Post-recycling**
		From June 2013	**2014**	**2015**	**To February 2016**	
Aluminium						
Total number of analyses	149	82	147	149	14	143
Aluminium failures	0	1	1	4	0	1
% Compliance	100	99	99	97	100	99
Operational compliance	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent
Turbidity						
Total number of analyses	357	203	361	360	34	367
Turbidity failures	6	6	19	6	0	9
% Compliance	98	97	95	98	100	98
Operational compliance	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent
Aesthetic compliance	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent	(≥95%) – Excellent

	Pre-recycling	**During recycling**				**Post-recycling**
		From June 2013	**2014**	**2015**	**To February 2016**	
Total chlorophyll						
Total number of analyses	242	138	224	237	21	235
Total chlorophyll failures	22	44	37	2	0	15
% Compliance	91	68	83	99	100	94

4.3.3 Effect of the wastewater recycling on various treatment processes

Mean aluminium concentrations increased over time in the river and displayed slight increases after DAF and west and east sedimentation during the wastewater recycling process during the same time period (Figure 4-3). However, all mean concentrations were below the limit of ≤ 0.3 mg/L at all times.

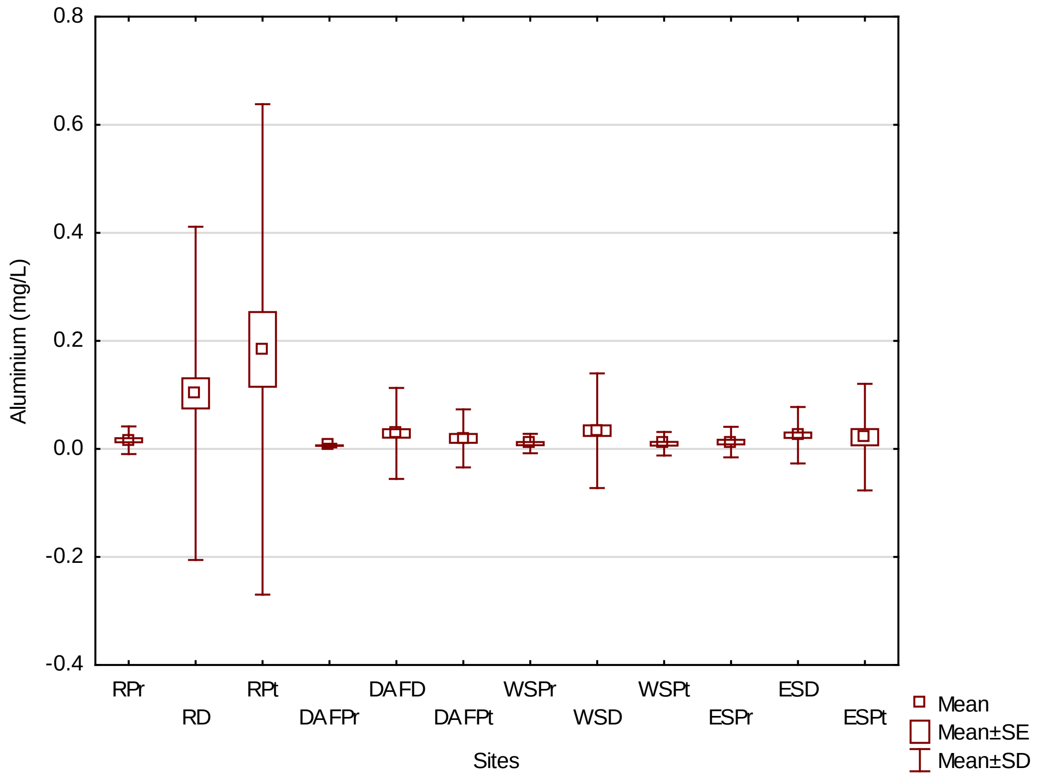


Figure 4-3: **Aluminium concentrations of the Middle Vaal River, after dissolved air flotation (DAF), after west and east sedimentation for the periods prior to, during and after implementation of wastewater recycling; RPr, RD and**

RPt: river pre, during and post recycling system; DAFPr, DAFD and DAFPt: DAF pre, during and post recycling system; WSPr, WSD and WSPt: west sedimentation pre, during and post recycle system; ESPr, ESD and ESPt: east sedimentation pre, during and post recycling system

The increased turbidity levels in the river during the study period were also reflected in the increased turbidity measured after DAF, but the mean turbidity levels remained below 4 and 3 NTU after the west and east sedimentation processes, respectively (Figure 4-4).

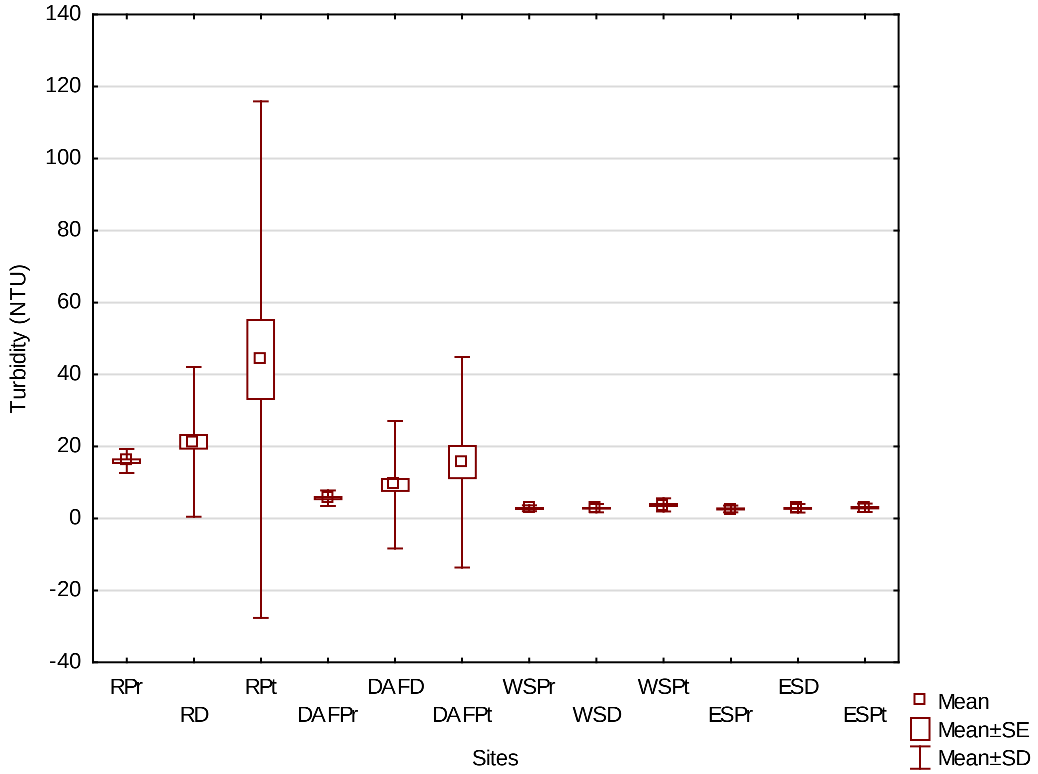


Figure 4-4: **Turbidity levels of the Middle Vaal River, after dissolved air flotation (DAF), after west and east sedimentation for the periods prior to, during and after implementation of wastewater recycling; RPr, RD and RPt: river pre, during and post recycling system; DAFPr, DAFD and DAFPt: DAF pre, during and post recycling system; WSPr, WSD and WSPt: west sedimentation pre, during and post recycle system; ESPr, ESD and ESPt: east sedimentation pre, during and post recycling system**

Mean total chlorophyll concentrations in the river decreased during the study period. This trend was also visible after the west and east sedimentation processes. Total chlorophyll removal was best achieved after DAF during wastewater recycling (Figure 4-5).

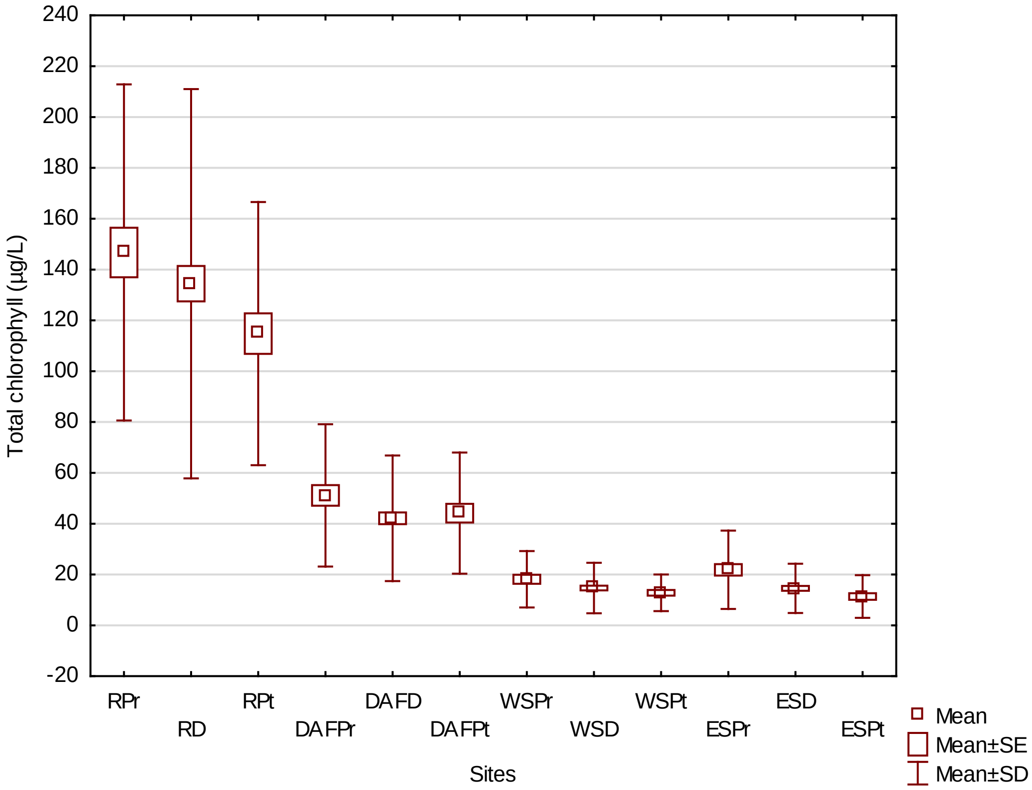


Figure 4-5: **Total chlorophyll concentrations in the Middle Vaal River, after dissolved air flotation (DAF), after west and east sedimentation for the periods prior to, during and after implementation of wastewater recycling; RPr, RD and RPt: river pre, during and post recycling system; DAFPr, DAFD and DAFPt: DAF pre, during and post recycling system; WSPr, WSD and WSPt: west sedimentation pre, during and post recycle system; ESPr, ESD and ESPt: east sedimentation pre, during and post recycling system**

Mean total organic carbon concentrations were consistently higher in the river and during the wastewater recycling process at all study sites (Figure 4-6).

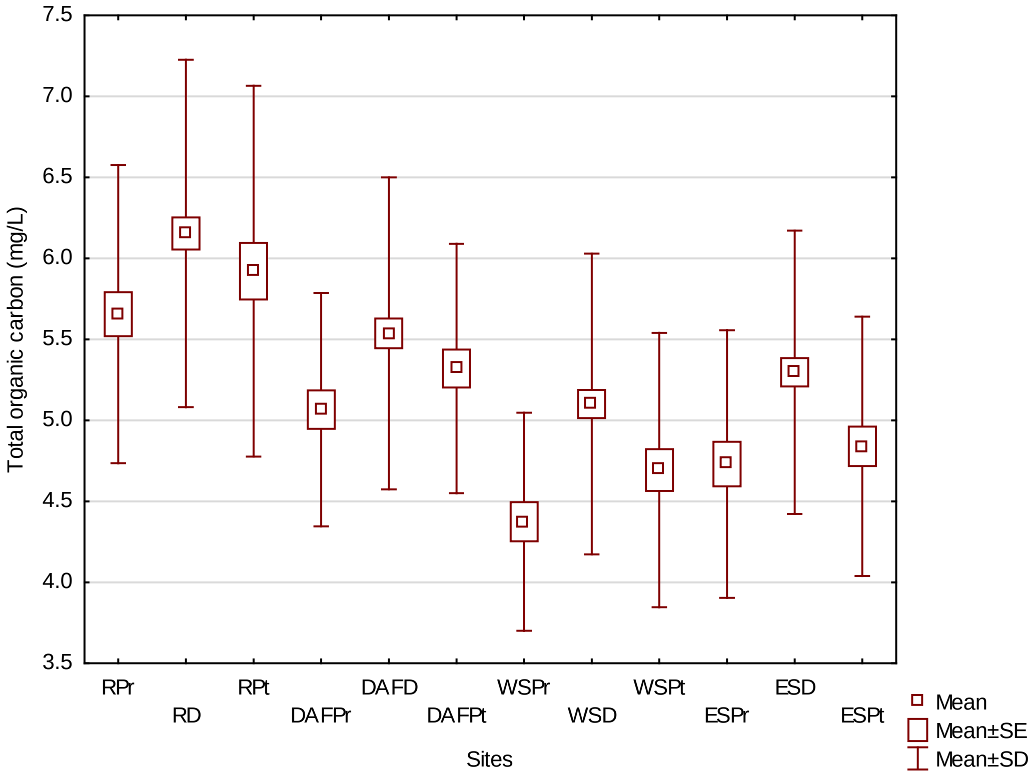


Figure 4-6: **Total organic carbon concentrations of the Middle Vaal River, after dissolved air flotation (DAF), after west and east sedimentation for the periods prior to, during and after implementation of wastewater recycling; RPr, RD and RPt: river pre, during and post recycling system; DAFPr, DAFD and DAFPt: DAF pre, during and post recycling system; WSPr, WSD and WSPt: west sedimentation pre, during and post recycle system; ESPr, ESD and ESPt: east sedimentation pre, during and post recycling system**

Mean *E. coli* concentrations continuously increased over time in the river and after DAF but remained at ≤ 10 MPN/100 mL after the west and east sedimentation processes (Figure 4-7).

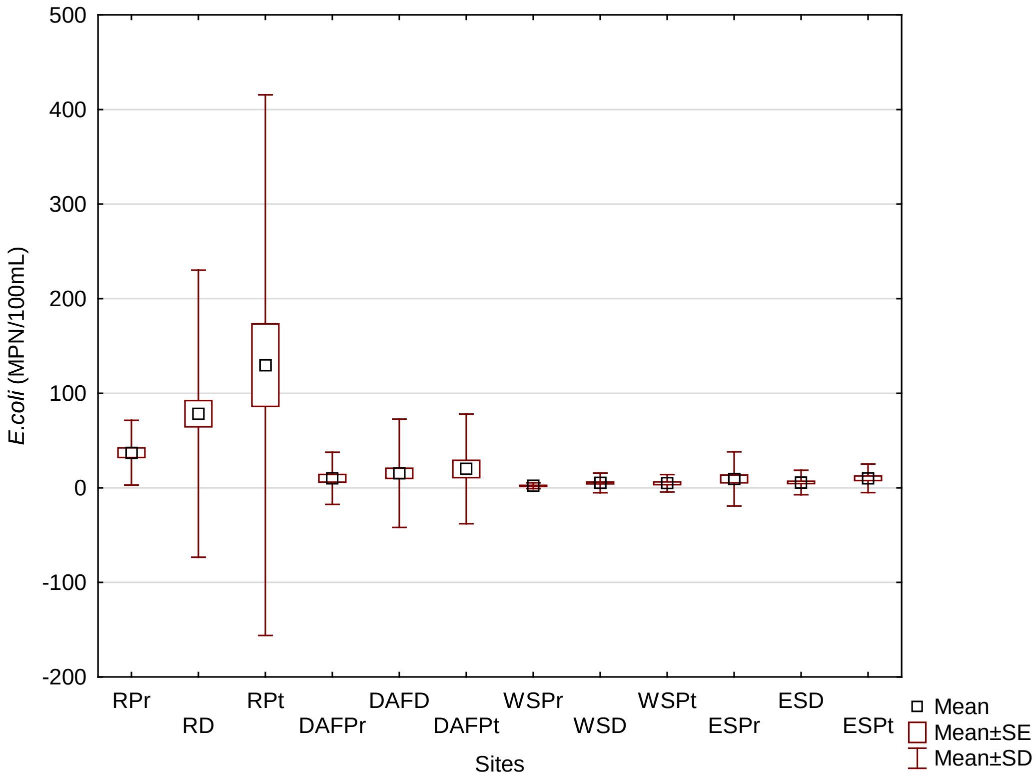


Figure 4-7: ***E. coli* concentrations of the Middle Vaal River, after dissolved air flotation (DAF), after west and east sedimentation for the periods prior to, during and after implementation of wastewater recycling; RPr, RD and RPt: river pre, during and post recycling system; DAFPr, DAFD and DAFPt: DAF pre, during and post recycling system; WSPr, WSD and WSPt: west sedimentation pre, during and post recycle system; ESPr, ESD and ESPt: east sedimentation pre, during and post recycling system**

The Kruskal–Wallis test was applied to data collected for pH, electrical conductivity, dissolved organic carbon, chlorophyll-*a* and spectral absorbance coefficient 254, but no significant differences between unit values of electrical conductivity and chlorophyll-*a* for the treatment processes (DAF and sedimentation) prior to, during and after implementation of the wastewater recycling system were detected (see Annexure C, Table C.2). There were significant differences between dissolved organic carbon concentrations of the river, DAF and sedimentation (west and east) prior to and during implementation of the wastewater recycling system (see Annexure C, Table C.2). Average dissolved organic carbon concentrations were consistently lower in the river, after DAF and after sedimentation before implementation of the wastewater recycling than during the process. The Kruskal-Wallis test indicated various significant differences for pH and spectral absorbance coefficient 254 at west and east sedimentation (see Annexure C, Table C.2).

The water quality after the filtration process was not included in Figure 4-3 to Figure 4-7 as differences between periods prior to, during and after implementation of wastewater recycling were negligible and this water represents the final drinking water, the quality of which is addressed in Table 4-3 and Table 4-4. In Table 4-4 the mean total chlorophyll was highest after west and east filtration during the recycling process but at levels and concentrations that complied with limits. Maximum pH levels and total chlorophyll concentrations exceeded limits throughout the study period except for the maximum total chlorophyll of the west filtration after recycling.

Table 4-4: Descriptive statistics for turbidity levels and total chlorophyll concentrations after west and east filtration processes, where failures are shaded; WFPr, WFD and WFPt: west filtration pre, during and post recycle system; EFPr, EFD and EFPt: east filtration pre, during and post recycle system

	Turbidity (NTU)				Total chlorophyll (µg/L)			
	Mean	**Minimum**	**Maximum**	**Standard deviation**	**Mean**	**Minimum**	**Maximum**	**Standard deviation**
WFPr	0.5	0.2	1.0	0.2	0.6	0.3	2.3	0.5
WFD	0.6	0.2	1.9	0.3	0.8	0.3	14	1.4
WFPt	0.6	0.4	1.0	0.2	0.4	0.3	0.7	0.2
EFPr	0.6	0.3	2.0	0.3	0.6	0.1	3.0	0.6
EFD	0.7	0.2	2.4	0.3	0.8	0.3	3.7	0.6
EFPt	0.7	0.3	2.3	0.4	0.4	0.3	1.5	0.3

No Cryptosporidium oocysts or Giardia cysts were detected in the final water prior to, during or after recycling.

4.4 Discussion

Concerns about water recycling with regards to microorganisms (such as micro-algae and *E. coli*), heavy metals and increasing turbidity are some reasons why many water treatment plants have not returned wastewater to the water treatment process. Reissmann and Uhl (2006) were concerned about the recycling of precursors for disinfection by-products. During this investigation the sludge from DAF largely contributed to the poor water quality of the water recycling system.

The total chlorophyll, suspended solids, turbidity and dissolved organic carbon of the sludge transferred from the DAF top and bottom to the inlet dam were extremely high (Figure 4-1), but the concentrations of these determinants for the wastewater that overflowed from the collection dam to the sludge balancing dam improved significantly. The effect of retention to allow for the settling of suspended matter in the holding and collection dams was noticeable. Haarhoff *et al*. (2001) concluded that the turbidity of the supernatant on the sludge (sedimentation wastewater) and washwater (filtration wastewater) at the Vaalkop water treatment plant was mostly lower than that of raw water abstracted from the Vaalkop dam. The west and east sedimentation and filtration seemed to be equally effective when values were compared during recycling and did not verify the poorer water quality of the west sludge in Figure 4-1. The total chlorophyll, suspended solids and turbidity of the recycle stream were identified as risks due to extreme concentrations (Figure 4-2) together with the outcomes from Janse van Rensburg *et al*.'s (2016) study, which confirmed that increasing total chlorophyll concentrations and turbidity spikes were the main source-water quality challenges for Midvaal Water Company. Haarhoff *et al*. (2001) stated that the rate of solids production, associated with turbidity levels in wastewater, at water treatment plants treating inland surface water are highly variable and occasionally reach extremely high peaks (Haarhoff *et al*., 2001).

Aluminium is introduced as a water treatment chemical (aluminium sulfate) and concentrations were below the required limit for drinking water in the river despite the observed increase during 2012–2017 (Figure 4-3). During the time that aluminium failures were recorded in the final water, neither aluminium concentrations nor turbidity levels were water quality concerns in the river water and it could be ascribed to the dosing of aluminium sulfate during the water treatment process. The turbidity levels of both the river and recycle stream were not significantly high during times when turbidity failures were recorded and no pattern/correlation could be established. Moreover, the turbidity levels of the recycle stream were not necessarily higher than those of the river during times when turbidity failures were recorded. The mean pH of the river was 9.0 and the median 9.1 during times when turbidity failures occurred. The aluminium and turbidity failures only corresponded once (25 February 2015); the same was true for aluminium, turbidity and total chlorophyll failures (14 July 2014).

The total chlorophyll concentrations of the river prior to and after the wastewater recycling ranged from 57 to 373 µg/L and from 68 to 196 µg/L, respectively, during times when failures were recorded. Total chlorophyll concentrations of the river and recycle stream ranged from 57 to 393 µg/L and from 15 to 6451 µg/L, respectively, during recycling at times when failures were recorded and no seasonal correlation could be confirmed. Total chlorophyll concentrations were highest after west and east filtration during the recycling process. The total chlorophyll concentrations increased from 0.6 to 0.8 µg/L after both west and east filtration during the wastewater recycling and is a cause for concern as it is close to the limit of ≤ 1.0 µg/L (Table 4-4). These total chlorophyll concentrations after west and east filtration do not correspond with the decreasing trends depicted in Figure 4-5 after west and east sedimentation. The impact on the filtration process and irregular failures in terms of total chlorophyll have to be monitored and managed closely during wastewater recycling, especially since no particular correlation could be identified from this research. In the event of taste and odour episodes, recycling has to be terminated until the situation is resolved.

Total organic carbon concentrations in the river peaked during the recycling period, but all mean total organic carbon concentrations, including those for the river, were below the limit of ≤ 10 mg/L (Figure 4-6) and complied with SANS 241 (2015) requirements at all times (SANS, 2015). Turbidity and *E. coli* in the river displayed similar increasing trends (Figure 4-4 and Figure 4-7, respectively) as opposed to the decreasing total chlorophyll concentrations (Figure 4-5). Turbidity can inhibit photosynthesis by blocking sunlight and, as algae decay, the decomposition process allows organic particles to release as suspended solids and contribute to turbidity (Fondriest Environmental Inc., 2014).

4.4.1 Supplementary benefits of wastewater recycling

The raw water tariff for 2016 was R 3.22/kL, which results in an average saving of raw water purchases of approximately R 27 million per year when calculated:

22 576 kL/day (Table 4-1) x 365 (days per year) x R 3.22/kL (2016 water tariff) = R 26 533 572.

Recycle stream pumping and dosing costs for 2016 was R 0.23/kL, which resulted in an average cost of approximately R 1,9 million per year when calculated:

22 576 kL/day (Table 4 1) x 365 (days per year) x R 0.23/kL (2016 recycle stream pumping and dosing costs) = R 1 895 256.

The net saving in raw water abstraction, less the costs associated with the pumping and chemical treatment of the recycled water greatly exceeds the capital expenditure that was associated with the new infrastructure.

Wastewater recycling systems have several benefits in addition to reducing water treatment expenses. A system like this allows for suspended solids to settle out and thus contributes to turbidity reduction (Figure 4-1). Natural microbiological processes result in improved microbiological quality of the wastewater due to disinfection via sunlight. Furthermore, the sludge balancing dam attenuates the flow rate of the recycled stream, which results in more consistent and controllable introduction of wastewater into the river water inlet stream. The health-related risks of recycling wastewater are considered manageable as the recycle stream is introduced at the beginning of the treatment process, prior to pre-ozonation and subsequent treatment processes to ultimately produce potable water for consumers.

4.4.2 Future considerations regarding wastewater

In light of the findings of this study, several points regarding the implementation of wastewater recycling systems should be considered since organic fractions, derived from algae and bacteria, are present in the wastewater (Zhou *et al*., 2018). Periodic cyanobacterial blooms and poor raw water quality require temporary termination of the wastewater recycling system, as this has a negative impact on the treated water quality if recycled, e.g. in terms of taste and odour. Water from the recycle dams at Virginia and Balkfontein water treatment plants was discharged into the Vaal River during prevalent algal blooms (Oosthuizen & Janse van Vuuren, 2014). Extension of the dam surface area is necessary as provision for the total wastewater flow to curtail recycling of poor quality water plugs and prevent possible discharge into the environment. Anaerobic/anoxic conditions may develop in the dams and some form of mechanical agitation/aeration has to be considered for the future. Additional disposal sites are necessary for dry sludge, which would subsequently require further analyses and classification. Microbiological monitoring of the recycle stream could expand to include contaminants of emerging concerns, such as endocrine-disrupting compounds and persistent organic pollutants. Trihalomethane formation monitoring is required due to the high organic load (dissolved organic carbon) in the wastewater recycling system and the dosing of chlorine at two points (Figure 2-3).

4.5 Conclusion

It is evident from the available data that wastewater recycling, which included wastewater from the DAF plant, into the main inlet stream of the water treatment plant proved to be effective based on SANS 241:2015 compliance and had no detrimental impact on overall treatment processes or final water quality. The wastewater recycling system operated successfully and was cost-effective due to reduced river water purchases. Total chlorophyll was identified as the most prominent risk when wastewater is recycled due to the high concentration in both the river and recycle stream, borderline concentrations of 0.8 µg/L total chlorophyll after filtration during recycling and total chlorophyll failures during recycling in 2013 and 2014. Water quality of the sludge from DAF units improved significantly after it was subjected to retention in the dam system and dilution with wastewater from the sedimentation and filtration processes. Final water quality failures recorded for aluminium, turbidity and total chlorophyll occurred mostly during the recycling period, but the risk-defined compliances were calculated and categorized as excellent (≥ 95%) for both aluminium and turbidity in the periods prior to, during and after wastewater recycling. The total chlorophyll compliance was 94% in the year prior to the implementation of the wastewater recycling system, 88% during recycling and 96% in the year after recycling. The findings of this case study are, however, based on retrospective data evaluation and could not take all of the factors (e.g. flow, seasonal conditions) that contributed to water quality on the Midvaal Water Company water treatment plant into account.

CHAPTER 5 EVALUATING WATER QUALITY MONITORING OF THE MIDDLE VAAL RIVER AND KOEKEMOERSPRUIT AT MIDVAAL WATER COMPANY IN THE MIDDLE VAAL CATCHMENT

5.1 Introduction

Midvaal Water Company monitors the water quality of the treatment and wastewater recycling operations on the plant (refer to chapter one and two) as well as water quality of the Middle Vaal River and Koekemoerspruit in the Middle Vaal Catchment. Midvaal Water Company has previously initiated seven water quality monitoring programs in total, including the Koekemoerspruit monitoring program, which was of special interest for this section of the case study. The inflow of the highly utilized and impacted Koekemoerspruit (a tributary) into the Middle Vaal River, upstream of the company's abstraction point, is regarded as a possible pollution threat. The monitoring objectives since 2002 have been to determine the water quality of the Koekemoerspruit by means of collecting water quality data. In 2015, the costs of the abovementioned monitoring programs amounted to R 4 985 200, of which R 65 150 (1.3% of the total amount) was spent on analytical costs for monitoring the Koekemoerspruit. As Midvaal Water Company has to consider the stressed socioeconomic status of their consumers regarding water tariffs, cost-effective monitoring and managing of the water resource is of the essence.

Midvaal Water Company's water safety plan identifies, amongst others, the following two risks/hazards: (1) increased eutrophication of the raw water from various sources of pollution and (2) decreased raw water quality due to industrial and mining activities. One of the required measures included in the water safety plan in dealing with these risks/hazards is the evaluation and review of monitoring data to acquire information on the identified risks and hazards. Subsequently, the company's water monitoring program needs to be reviewed periodically to acquire information on the aforementioned risks/hazards. Long-term water quality monitoring data are essential for recognizing trends and adapting water quality monitoring programs in response to new environmental pressures (e.g. evolving pollution sources and chemicals) and emerging sampling tools (Altenburger *et al*., 2015; Brack *et al*., 2015). When optimizing a water quality monitoring program, certain aspects need to be decided on, e.g., determining the sampling site network, selecting the water quality determinants to be measured, establishing sampling frequencies and recurrence and estimating financial resources (Behmel *et al*., 2016). As referenced in Behmel *et al*. (2016), the concept of 'optimizing a water quality monitoring program' refers to the process of reviewing and improving an existing water quality monitoring program. It therefore involves verification to see whether the initial monitoring objectives have been met and whether additional monitoring objectives need to be addressed (Behmel *et al*., 2016).

Environmental monitoring is essential for detecting water quality and land use changes as well as associated pollution sources and other stressors, such as climate change. Monitoring is also needed to evaluate the effects of proposed environmental policies and resource use and management strategies (Lovett *et al*., 2007). Legislation requires evidence of risk-based monitoring and management, but no specific guidelines are available to water service providers and authorities for environmental monitoring. The research in this chapter can therefor serve as a valuable example for such institutions after the water quality of the Koekemoerspruit has been monitored for 13 years.

Consequently, the aims of the study were first to evaluate water quality by determining what parameters were beyond reference limits and establishing trends in the data, secondly to determine impacts on the water quality of the Middle Vaal River (source) to establish if the KMS contributes/exacerbates the poor water quality of the Middle Vaal River and thirdly, to identify shortcomings in the water quality monitoring program for improving water quality monitoring in the study area together with conclusions that are derived from the data during evaluation.

5.2 Materials and methods

5.2.1 Description of study site

The study area is situated in the summer rainfall region of the country and an average annual rainfall of 684 mm was recorded during the study period.

The South African Government Gazette 39943 No. 469 (DWS, 2016) has divided the Middle Vaal Catchment into eight integrated units of analysis, subdivided into smaller resource units, to which classes and target water quality objectives have been assigned. The Vaal River main stem from Vermaasdrift to upstream of the Schoonspruit confluence (downstream of Midvaal Water Company) has been classified as a Class III resource unit, with a largely modified present and recommended ecological state (Table 5-1). The Koekemoerspruit, from its origin to its confluence with the Vaal River, has also been classified as a Class III resource unit. This is the only resource unit in South African Government Gazette 39943 No. 469 (DWS, 2016) whose ecological state is required to be improved, from being seriously modified to being largely modified (Table 5-1).

Table 5-1: Resource unit classification and ecological state of the Vaal River main stem and Schoonspruit resource unit which incorporates the Koekemoerspruit (DWS, 2016)

Integrated unit of analysis	Vaal River	Schoonspruit
Resource unit	Vaal River main stem: from Vermaasdrift to upstream of the Schoonspruit confluence as represented by study sites 1 and 2	Koekemoerspruit: from origin to confluence with Vaal River as represented by study sites 3,4 and 5
Water resource class	III: heavily used; overall ecological condition significantly altered from its predevelopment condition	III: heavily used; overall ecological condition significantly altered from predevelopment condition
Present ecological state	D: largely modified	D/E: largely modified/seriously modified
Recommended ecological state	D: largely modified	D: largely modified

5.2.2 Description of sampling sites

Figure 2-1 illustrates where the study and sampling sites are located in the catchment. Sampling frequencies are indicated in Table 2-1 whereas Table 5-2 gives a more detailed description of the sampling sites for this chapter.

Table 5-2: Sampling sites of the Koekemoerspruit water quality monitoring program

Sampling site number	Site name	Coordinates	Description
Site 1	Vermaasdrift Bridge	26° 56' 10.3" S, 26° 51' 00.8" E	Reference point to determine impacts of Koekemoerspruit on Middle Vaal River; part of Middle Vaal, upstream of confluence of Koekemoerspruit and Middle Vaal River.
Site 2	Middle Vaal River	26° 56' 04.5" S, 26° 48' 01.4" E	Middle Vaal River at Midvaal Water Company’s abstraction point downstream of confluence of Koekemoerspruit and Middle Vaal River. Water quality at this site is critical and determines water treatment processes and operations of Midvaal Water Company.
Site 3	Enviroclear overflow	26° 54' 37.8" S, 26° 48' 50.5" E	Approximately 9 km cement canal downstream from site 4 flowing from nearby mining plant into Koekemoerspruit.

Sampling site number	Site name	Coordinates	Description
Site 4	Koekemoerspruit before Enviroclear overflow	26° 54' 40.3" S, 26° 48' 55.4" E	Koekemoerspruit from below Khuma urban village before inflow of canal; indicates influence of urban village.
Site 5	Koekemoerspruit after Enviroclear overflow	26° 54' 51.7" S, 26° 48' 57.0" E	Koekemoerspruit after confluence of canal with site 4; represents water that will enter Middle Vaal River.

5.2.3 Sampling regime and methods

Samples were chemically analysed at Midvaal Water Company Scientific Services for 20 variables included in Table 2-2.

Aluminium

Ammonia

Arsenic

Chloride

Colour

Copper

Cyanide recoverable

Electrical conductivity

Iron

Manganese

Nitrate and nitrite

Orthophosphate

pH

Sodium

Sulfate

Total chlorophyll

Total organic carbon

Turbidity

Uranium

Zinc

Data from October 2002 to December 2015 were used for this study with the exception of data for uranium, which were collected since April 2005.

5.2.4 Approach and statistical analyses

All the general statistical methods of this study (see section 2.4) were applied to analyse the data and to determine the descriptive statistics for all variables as prescribed and discussed. The application of the Mann-Kendall test and Sen's slope estimates was done as described by the Canadian Council of Ministers of the Environment (CCME, 2015).

A selection of two years (2014 and 2015) were made to evaluate the compliance of different variables with national drinking water standards and environmental target water quality objectives. These two years represented a normal rainfall year (2014) and a low rainfall year (2015). In order to ensure that variables are not removed prematurely after comparison with compliance criteria, the variance of the data collected at each site for each variable were determined (Caldwell Eldridge *et al*., 2014). No data were available on river flow of either the Koekemoerspruit or Middle Vaal River. Therefore, the nonparametric Mann–Kendall test for testing the presence of significant monotonic increasing or decreasing trends and Sen's nonparametric method for estimating the slope of a linear trend were used to discover long-term trends of discrete variables (Caldwell Eldridge *et al*., 2014). The analyses were performed with the Excel application MAKESENS 1.0 and the Mann–Kendall test and Sen's slope estimates for the trend of annual data with version 1.0 Freeware (Salmi *et al*., 2002).

5.3 Results

5.3.1 Water quality of the Koekemoerspruit

The compliance of the measured water quality determinants at sites 4 and 5 in the Koekemoerspruit with the target water quality objectives for this resource unit was evaluated using data obtained during 2014 and 2015 (Table 5-3) to highlight where limits have recently been exceeded. The DWS, as the custodian of water resources, has decided after consultation with relevant stakeholders and research institutions to implement the use of percentile limits for compliance monitoring. The rationale behind this is that the percentile limits give a more accurate reflection of the true situation and eliminates the effects of outliers. Seeing that the target water quality objectives are in many instances stricter than the drinking water limits.

The percentile limits for orthophosphate and ammonia concentrations were excessively exceeded at sites 4 and 5. The 95th percentile limit for nitrate and nitrite were exceeded at site 5. The electrical conductivity, an indicator of salinization, did not comply with limits set for these sites, and the sulfate concentration of site 5 failed to comply with the set limit as well. Even though a target water quality objective for dissolved cyanide exists, only recoverable cyanide was monitored during this water quality monitoring program. The recoverable cyanide concentrations are included in Table 5-3 and Table 5-6 and compared with the target water quality objectives of dissolved cyanide. However, since these concentrations are expected to be higher than those of dissolved cyanide, the worst-case scenarios are portrayed. The 95th percentile manganese and iron concentrations failed to comply with the set limits; in comparison manganese exceeded the limit to a much greater extent.

Table 5-3: Relevant 50th and 95th percentile water quality data for sites 4 and 5 from January 2014 to December 2015 compared with target water quality limits of Government Gazette 39943 No. 469 for the resource unit; noncompliances are shaded

Quality subcomponent	Determinant indicator/measure	Unit	Limit	Percentile	Site 4	Site 5
Nutrients	Orthophosphate	mg/L	≤ 0.125	50th	3.322	3.929
	Nitrate and nitrite	mg/L	≤ 2.5	50th	0.61	0.65
	Nitrate and nitrite	mg/L	≤ 6	95th	5.64	7.2
Salts	Electrical conductivity	mS/m	≤ 85	95th	151	150
	Sulfate	mg/L	≤ 250	95th	236	257
Toxics	Cyanide (dissolved)	mg/L	≤ 0.05	95th	0.03	0.03
	Aluminium	mg/L	≤ 0.1	95th	0.04	0.06
	Manganese	mg/L	≤ 0.25	95th	0.78	0.82
	Iron	mg/L	≤ 0.25	95th	0.29	0.30
	Uranium	mg/L	≤ 0.03	95th	0.03	0.02
	Ammonia	mg/L	≤ 0.1	95th	55	52

The water quality compliance of sites 3, 4, and 5 with SANS 241 (2015) was evaluated for 2014 and 2015 during this study to obtain a recent overview (Table 5-4) and to identify risks since the standard requires a water quality risk assessment that includes evaluation of the catchment and source water. The noncompliant colour, electrical conductivity, turbidity, sulfate, recoverable cyanide and arsenic concentrations of site 3 posed aesthetic, operational, and acute and chronic health risks. The noncompliant colour, turbidity, manganese, and total organic carbon concentrations measured at sites 4 and 5 posed aesthetic, operational, and chronic health risks. The water sampled at sites 3, 4, and 5 in the Enviroclear overflow canal and Koekemoerspruit (Table 5-4) is not suitable for drinking purposes.

Table 5-4: Average values of water quality determinants measured at sites 3, 4, and 5 from January 2014 to December 2015 compared with the limits for drinking water as per South African National Standard 241:2015; shaded values indicate exceeded limits

Determinant	Unit	Limit (associated risk)	Site 3	Site 4	Site 5
Colour	mg/L Pt	≤15 (aesthetic)	22	98	97
pH	pH units	≥5.0 to ≤9.7 (operational)	8.79	7.78	7.78
Electrical conductivity	mS/m	≤170 (aesthetic)	209	124	124
Turbidity	NTU	≤1 (operational)	61	10.6	10.7
		≤5 (aesthetic)	61	10.6	10.7
Chloride	mg/L	-	150	106	106
Sulfate	mg/L	≤500 (acute health)	810	136	163
		≤250 (aesthetic)	810	136	163
Sodium	mg/L	≤200 (aesthetic)	183	87	86
Ammonia	mg/L	-	0.7	37	34
Nitrate and nitrite	mg/L	-	4.8	1.7	1.7
Orthophosphate	mg/L	-	0.12	3.79	4.00
Cyanide recoverable	mg/L	≤0.2 (acute health)	0.43	<0.02	<0.02
Total chlorophyll	µg/L	-	67	93	95
Iron	mg/L	≤2 (chronic health)	0.07	0.14	0.14
		≤0.3 (aesthetic)	0.07	0.14	0.14
Manganese	mg/L	≤0.4 (chronic health)	0.05	0.44	0.45
		≤0.1 (aesthetic)	0.05	0.44	0.45
Zinc	mg/L	≤5 (aesthetic)	0.03	0.03	0.03
Copper	mg/L	≤2 (chronic health)	0.03	<0.01	<0.01
Aluminium	mg/L	≤0.3 (operational)	0.04	0.06	0.06
Arsenic	mg/L	≤0.01 (chronic health)	0.02	<0.01	<0.01
Uranium	mg/L	≤0.03 (chronic health)	0.03	<0.01	0.01
Total organic carbon	mg/L	≤ 10 (chronic health)	6.2	13	12

5.3.2 Environmental concerns and emerging pollution pressures in the Koekemoerspruit affecting water quality

Site 5 represents the water that flows into the Middle Vaal River and that can impact directly on the water quality of the source water destined for drinking water treatment. Determinants that showed a statistically significant increase in concentration over time were viewed as posing a risk to the Middle Vaal River. To determine whether any variables demonstrated an increasing trend over the long term, the temporal version of the nonparametric Mann–Kendall test was performed (Caldwell Eldridge *et al.*, 2014). This was done using the entire dataset (2002–2015) for site 5; only the determinants with statistical significant increases/decreases are listed in Table 5-5. According to the results of the Mann-Kendall test there are statistically significant increases in ammonia (p=0.05), colour (p=0.01) and total chlorophyll (p=0.01) during the study period. Colour and total chlorophyll concentrations exhibited the highest increases (slope estimates of 2.345 and 1.152 respectively) during the study period. The increasing ammonia together with total organic carbon concentrations (Figure 5-1) suggested that upstream domestic wastewater effluent or agricultural runoff currently has the largest impact on the Koekemoerspruit. Domestic wastewater effluent is, however, more likely to be a contributing factor based on the high ammonia concentrations and other sewage-related determinants (Figure 5-1 and Table 5-3).

Table 5-5: Mann–Kendall test and Sen’s slope estimate results showing trends of the entire dataset (2002–2015) for site 5, indicating determinants for which a significant annual trend was observed

Determinant	Mann–Kendall test trend level	Sen’s slope estimate
Ammonia	0.05	0.631
Colour	0.01	2.345
Sodium	0.1	-6.993
Total chlorophyll	0.01	1.152

The colour, ammonia, and total chlorophyll concentrations measured at site 5 not only showed a significant increase over the entire study period but also exhibited drastic increases from 2012 (Figure 5-1) onwards. The total organic carbon concentration measured at site 5 demonstrated a great deal of variability but a general increase as shown in Figure 5-1. The seasonal burning of *Phragmites australis* may also contribute to this variability of the total organic carbon concentrations.

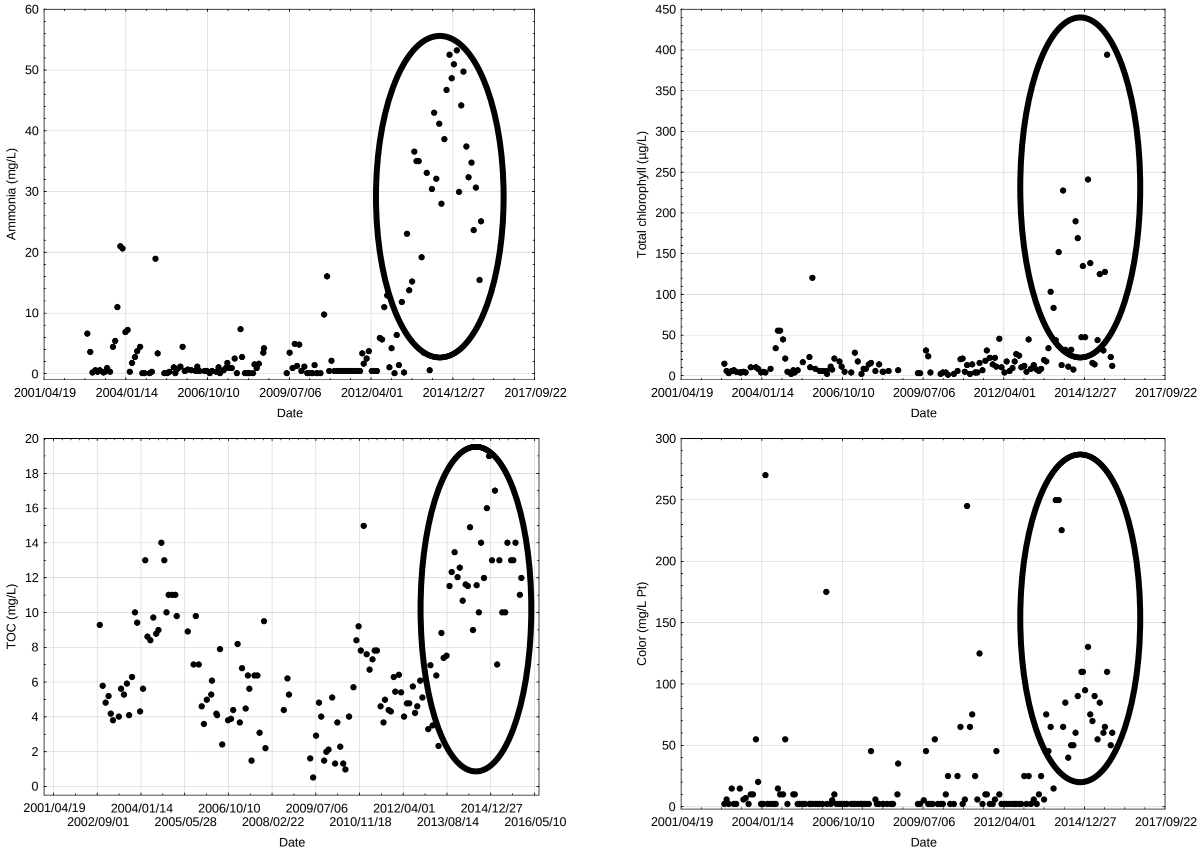


Figure 5-1: **Mean concentrations of ammonia, total chlorophyll, total organic carbon (TOC), and colour revealed drastic increases in the Koekemoerspruit as measured during the water quality monitoring program after 2012 at site 5**

The sulfate, sodium, and chloride concentrations measured at site 5 prior to 2012 were especially high. These determinants showed much lower concentrations from 2012 onwards (Figure 5-2), which was particularly noticeable when compared with the SANS 241 (2015) limits for sulfate and sodium (500 and 200 mg/L, respectively).

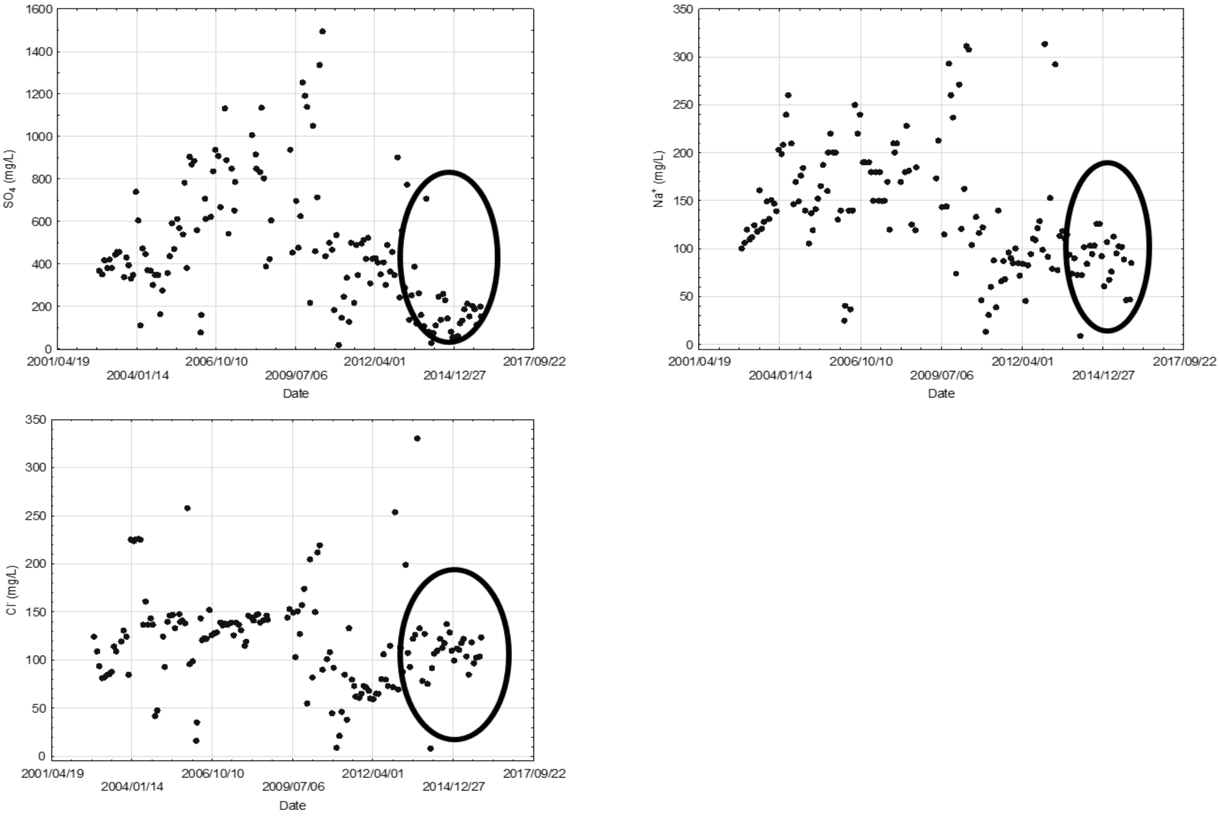


Figure 5-2: **Mean concentrations for sulfate, sodium, and chloride in the Koekemoerspruit were at alarming levels at times during the water quality monitoring program from 2002 to 2015 at site 5 despite a general decrease in concentration over time**

5.3.3 Impact of Koekemoerspruit on water quality of Middle Vaal River source water

The water quality compliance of sites 1 and 2 with target water quality objectives for the Vaal River main stem resource unit was also evaluated for 2014 and 2015 (Table 5-6). This was carried out to highlight limits that have been exceeded and to ascertain the impact of the Koekemoerspruit on the Middle Vaal River. Table 5-6 indicates that the inflow of the Koekemoerspruit did not have an impact on the water quality of the Middle Vaal River, irrespective of whether limits were exceeded, because none of the listed determinants displayed a significant increase from site1 to site 2. Electrical conductivity, nitrate and nitrite, sulfate, iron, and ammonia contents were of concern for both the Middle Vaal River (Table 5-6) and the Koekemoerspruit (Table 5-3). Although orthophosphate and manganese were identified as concerns for the Koekemoerspruit (Table 5-3), levels of these determinants complied with limits set for the Middle Vaal River (Table 5-6). Aluminium content and pH (even though pH is not required as an indicator/measure in Table 5-3) emerged as concerns for the Middle Vaal River but not for the Koekemoerspruit (Table 5-6).

Table 5-6: Relevant 50th and 95th percentile data for sites 1 and 2 from January 2014 to December 2015 compared with target water quality limits of Government Gazette39943 No. 469 for the resource unit; shaded values indicate noncompliance

Quality subcomponent	Indicator/measure	Unit	Limit	Percentile	Site 1	Site 2
Nutrients	Nitrate and nitrite	mg/L	≤ 1.35	50th	1.35	1.46
	Nitrate and nitrite	mg/L	≤ 6	95th	4.1	2.4
	Orthophosphate	mg/L	≤ 0.125	50th	0.117	0.090
Salts	Electrical conductivity	mS/m	≤ 70	95th	79	77
	Sulfate	mg/L	≤ 160	95th	176	183
System variables	pH at 25°C	pH units	7.5	5th	7.9	7.5
	pH at 25°C	pH units	9.2	95th	9.3	9.2
Toxics	Cyanide (dissolved)	mg/L	≤ 0.05	95th	0.01	0.01
	Aluminium	mg/L	≤ 0.1	95th	1.0	1.1
	Manganese	mg/L	≤ 0.25	95th	0.05	0.05
	Iron	mg/L	≤ 0.25	95th	0.71	0.69
	Uranium	mg/L	≤ 0.03	95th	0.01	0.01
	Ammonia	mg/L	≤ 0.1	95th	0.5	0.3

The mean values (Figure 5-3) for all 20 determinants were compared before and after the inflow of the Koekemoerspruit at sites 1 and 2, respectively, to determine the overall impact of the Koekemoerspruit on the Middle Vaal River for the entire dataset (2002–2015), as not all the determinants were assigned within the target water quality objectives. Total chlorophyll values were the only mean and maximum values to show a slight increase in the Middle Vaal River after the inflow of the Koekemoerspruit (Figure 5-3 and Figure 5-4). There were, however, no statistically significant differences between sites 1 and 2 for any of the other variables. The extremely high ammonia concentrations observed at sites 4 and 5 (Table 5-3 and Table 5-4) contributed to nutrient enrichment of the Middle Vaal River and subsequent proliferation of algal growth.

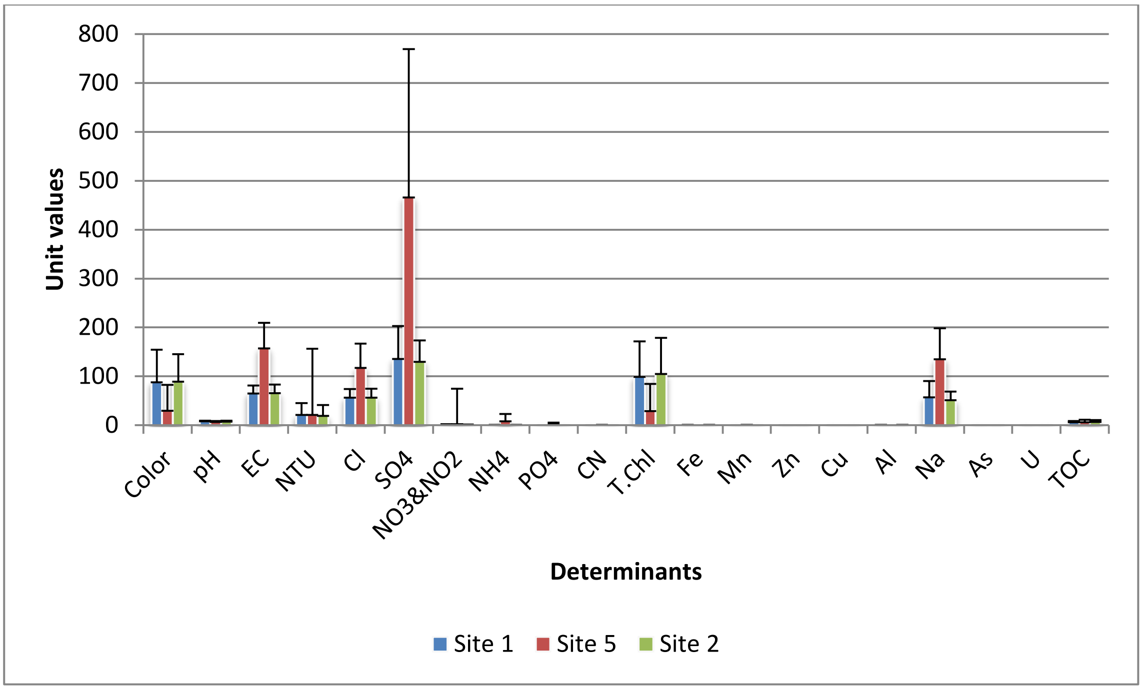


Figure 5-3: **Mean values derived from the water quality monitoring data for sites 1, 5, and 2 from October 2002 to December 2015 (n=130 ±std); Site 1: Middle Vaal River above the confluence of the Koekemoerspruit; Site 5: Koekemoerspruit before the confluence with the Middle Vaal River; Site 2: Middle Vaal River below the confluence of the Koekemoerspruit; electrical conductivity (EC); turbidity (NTU); total chlorophyll (T Chl); total organic carbon (TOC)**

Chloride, sulfate, total chlorophyll and sodium showed large variances in their concentrations from 2002 to 2015 at sites 1 and 2 in the Middle Vaal River and at sites 4 and 5 in the Koekemoerspruit. The maximum concentrations shown in Figure 5-4 for sites 1 and 5 indicate that their respective turbidity, chloride, sulfate, total chlorophyll and sodium concentrations could jointly have contributed to the maximum levels observed at site 2 and would therefore have been able to increase average measured levels of these determinants at site 2.

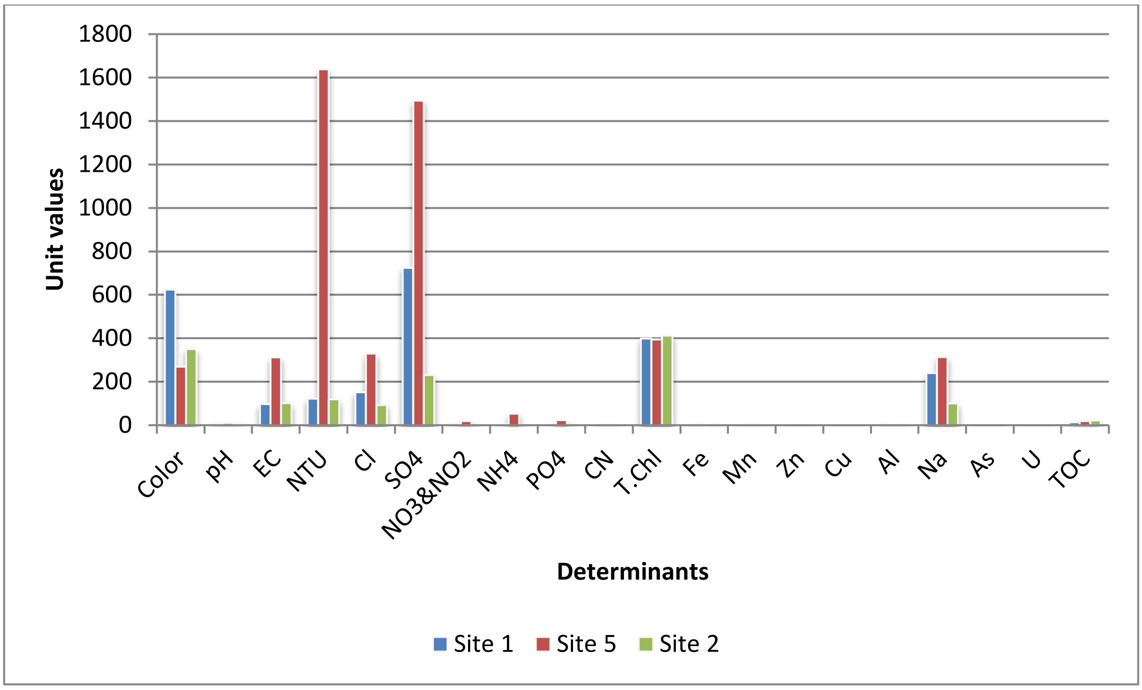


Figure 5-4: **Maximum values derived from the water quality monitoring data for sites 1, 5, and 2 from October 2002 to December 2015; Site 1: Middle Vaal River above the confluence of the Koekemoerspruit; Site 5: Koekemoerspruit before the confluence with the Middle Vaal River; Site 2: Middle Vaal River below the confluence of the Koekemoerspruit; electrical conductivity (EC); turbidity (NTU); total chlorophyll (T Chl); total organic carbon (TOC)**

5.3.4 Gaps identified in the Koekemoerspruit monitoring program

The changes recommended for the water quality monitoring program of the Koekemoerspruit are summarized in Table 5-7. Ammonia was not previously identified as a major concern but, as indicated by Government Gazette 39943 No. 469 (DWS, 2016), should be monitored for the Koekemoerspruit resource unit, along with electrical conductivity, sulfate, magnesium, nitrate and nitrite, orthophosphate, cyanide, iron, manganese, aluminium and uranium. Magnesium has also not been monitored for sites 1, 3, 4, and 5 to date and therefore has to be included in the water quality monitoring program. Recoverable cyanide was monitored for the study period and can be replaced with the analysis of dissolved cyanide according to the target water quality objectives as per Government Gazette 39943 No. 469 (DWS, 2016). The monitoring of colour, total chlorophyll, and total organic carbon has to continue and the frequency cannot be reduced, as these determinants are expected to increase in the future due to ongoing pollution activities upstream; they have subsequently been identified as possible risks. Due to the increasing threat of sewage pollution, additional microbial determinants should be considered for inclusion in the routine water quality monitoring program, in particular *Escherichia coli* (*E.coli*), other coliforms, and cyanobacterial toxins like microcystin. The monitoring of arsenic should continue, as site 3 poses a possible risk to the Koekemoerspruit (Table 5-4). The monitoring of pH, turbidity, chloride, sodium, zinc, and copper can either be reduced to quarterly or annual monitoring or omitted from the monitoring program, because the concentrations of these determinants did not exceed any limits or indicated a concentration increase from 2002 to 2015. During this case study it was the first time that the Koekemoerspruit monitoring program was evaluated and replaced in the water safety plan of Midvaal Water Company and should be evaluated again in future to determine whether the revised monitoring program (Table 5-7) still holds true.

Table 5-7: Proposed revised monitoring program for the Koekemoerspruit after evaluation of data collected from 2002 to 2015 and identification of shortcomings

Determinants	**Existing or new determinant**	**Frequency**	**Adjustment of frequency**	**Regulated by Government Gazette No. 39943**
Ammonia	Existing	Monthly/weekly	Unaffected/ increase	Yes
Electrical conductivity, sulfate, nitrate and nitrite, orthophosphate, iron, manganese, aluminium, uranium	Existing	Monthly	Unaffected	Yes
Colour, total chlorophyll, total organic carbon, arsenic	Existing	Monthly	Unaffected	No
pH, turbidity, chloride, sodium, zinc and copper	Existing	Quarterly/yearly	Decrease	No
Magnesium and dissolved cyanide	New	Monthly	-	Yes
Gross alpha/beta activity	New	Dependent on uranium concentrations	-	No
Algal identification and enumeration, temperature, cyanobacterial toxins,	New	Monthly/Dependent on algal blooms or taste and odour episodes	-	No

Determinants	Existing or new determinant	Frequency	Adjustment of frequency	Regulated by Government Gazette No. 39943
geosmin and 2-methylisoborneol (MIB)				
Escherichia coli and coliforms	Replace faecal coliform monitoring	Monthly		No

5.4 Discussion

The Koekemoerspruit is a polluted water resource and the Middle Vaal River system is the receiving water body. The study area has not only been affected by mining and municipal/urban village developments but also by agriculture. Nutrient enrichment and salinity, as a result of urbanization and gold mining, contributed most to the deterioration of water quality in the Koekemoerspruit. In this case study, the target water quality objectives for Koekemoerspruit (Table 5-3) indicated that orthophosphate, nitrate and nitrite, electrical conductivity, sulfate, manganese, iron, and ammonia exceeded the relevant limits. The inflow of the Koekemoerspruit into the Middle Vaal River did not seem to have a significant impact on the overall water quality of the Middle Vaal River when water quality upstream at site 1 was compared with that downstream at site 2 (Table 5-6). However, total chlorophyll concentrations increased from 100 µg/L at site 1 to 105 µg/L at site 2 after the inflow of the Koekemoerspruit. A previous study on Midvaal Water Company by Janse van Rensburg *et al*. (2016) indicated that increasing chlorophyll concentrations and associated taste and odours, as well as fluctuating turbidity levels, are the main challenges that affect the water treatment process at this water treatment plant.

Although orthophosphate and ammonia concentrations are not directly addressed in South African drinking water standards, together with nitrate and nitrite, they can contribute to nutrient enrichment of a water body and subsequent algal growth. Taste and odours can be associated with nuisance algal blooms, such as that of *Anabaena* spp., *Microcystis* spp., *Oscillatoria* spp. and *Planktothrix* spp. which occur in the Koekemoerspruit. They are responsible for the presence of geosmin and/or MIB. The odour threshold concentrations for these compounds range from 4 to 20 ng/L (Janse van Rensburg *et al*., 2016) and therefore affect downstream drinking water treatment despite dilution of the Koekemoerspruit's inflow into the Middle Vaal River. These species are also known producers of cyanobacterial toxins which can impact on human health.

The extremely high ammonia concentrations suggest discharge of untreated domestic wastewater effluent, which contributes to the increasing total chlorophyll, and results in the eutrophication of the Koekemoerspruit. The increasing population of the Khuma urban village (HDA, 2015), together with doubtful infrastructure and operation of wastewater treatment plants upstream from site 4, most probably contributed to the decline of the Koekemoerspruit's water quality. This is also evident from the upsurges in ammonia, total organic carbon, and colour concentrations observed at site 5, especially since 2012. Sewage discharge is a major component of water pollution, contributing to oxygen demand and nutrient loading of water bodies, promoting toxic algal blooms, and leading to a destabilized aquatic ecosystem (Igbinosa & Okho, 2009). The declining state of municipal wastewater and sewage treatment infrastructure in South Africa is one of the largest contributing factors to the numerous pollution problems and is a major contributor to health problems in poor communities (Mema, 2010), such as that in the study area. Investigations conducted on South African water resources have shown that poor operation and maintenance of domestic wastewater treatment plants have a great impact on both the environment and human health.

Colour, turbidity, manganese, and total organic carbon were the determinants of concern in the Koekemoerspruit when measured against the requirements of the SANS 241 (2015) limits for drinking water (Table 5-4). The alarming electrical conductivity, turbidity, and chloride, sulfate, sodium, recoverable cyanide, arsenic, and uranium concentrations at site 3 are directly associated with mining activities. However, it did not seem to have a significant impact on the water quality of the Koekemoerspruit after the inflow of the canal. This could perhaps be ascribed to the low flow volume of the canal or absence of flow at times, as sampling was possible only 80% of the time. Furthermore, mining activities in the area surrounding the study site have declined over the past five years. City of Matlosana mining activities have downscaled drastically specifically in the year 2011 which lead to 75% of original workforce to be retrenched in 2011 (HDA, 2015). These events are also evident in the decline of sulfate, sodium, and chloride concentrations at site 5 since 2012 (Figure 5-2).

Even though legislation requires evidence of risk-based monitoring and management, no specific guidelines are currently available. In optimizing the monitoring program based on water quality monitoring data the following recommendations could be made:

(i) The monitoring of radio activity in the Koekemoerspruit is recommended due to the borderline uranium concentrations.

(ii) Algal identification, cyanobacterial toxins such as microcystin and geosmin/MIB analyses of the Koekemoerspruit during taste and odour episodes are also recommended to establish possible aesthetic, health and environmental risks. The recording of temperatures together with algal identification and enumeration will enable the investigation into seasonal occurrences of phytoplankton.

(iii) The water safety plan should be revised to state that the decreasing raw water quality is due to upstream domestic wastewater effluent or runoff and not mining activities anymore.

(iv) Site 4 may be omitted from the monitoring program as it did not seem to have a significant impact on the water quality of site 5.

(v) The water quality status of the Koekemoerspruit may be communicated to the community for them to understand the health-related risks and how it may impact their drinking water source.

(vi) Monitoring is imperative for water quality management but can never substitute sound management principles. Monitoring can be significantly reduced if the pollution source of the Koekemoerspruit is remedied.

It remains imperative to be aware that the management of water quality monitoring should never overshadow the management of the water quality itself (Rivett *et al*., 2013) as interventions and corrective actions ensure improvement of water quality. Monitoring programs should however be reviewed and the data continuously evaluated, using at least descriptive statistical methods (confidence interval and variance) to indicate variance in water quality determinants and to determine the level of compliance to set objectives and standards. The review of a monitoring program can be prompted by schedule, new legislation, costs, or an emerging environmental impact.

5.5 Conclusion

Analyses of the water quality datasets (2002–2015) for both the Middle Vaal River and the Koekemoerspruit were used to evaluate the water quality determinants that are a cause for concern (noncompliant to legal limits) and to determine the impact of the Koekemoerspruit on the water quality of the Middle Vaal River. Furthermore, these factors were used to establish whether and how the monitoring program of the Koekemoerspruit can be optimized. Evaluation of the monitoring data showed that the water flowing from Koekemoerspruit into the Middle Vaal River is diluted to a great extent and therefore has a reduced impact on the water quality of the Middle Vaal River, except for mean total chlorophyll concentrations which increased by 5% after the Koekemoerspruit inflow. The impact of the Koekemoerspruit on the Middle Vaal River regarding the average total chlorophyll increase may seem insignificant but together with the organic pollution of the Koekemoerspruit and continuous increase of total chlorophyll in the Middle Vaal River, justifies to be considered as a risk. The risks/hazards addressed in Midvaal Water Company's water safety plan (increased eutrophication of the raw water and decreasing raw water quality) remains relevant and applicable. The application of the target water quality objectives proved to be a valuable tool to evaluate monitoring data. The evaluation and review of monitoring data have identified several shortcomings, and avenues of optimization with regards to the water quality monitoring program for the Koekemoerspruit has been suggested. The monitoring program is both effective and necessary, as the determinants of concern in the Koekemoerspruit pose a risk for the use of Middle Vaal River water as a drinking water source downstream. However, the lack of guidelines on how to review a monitoring program (when to omit a determinant from a monitoring program or how to determine the reduction in monitoring frequency) would contribute significantly to the ongoing optimization of such a water quality monitoring program. The challenges faced by Midvaal Water Company were examined, highlighting the importance of adopting a holistic approach when investigating water quality problems. The focus of water quality monitoring programs should not only be to identify risks but also to protect the environment.

South Africa does not currently have guidelines available on environmental water quality monitoring. The information derived from studies such as those of Altenburger *et al*. (2015); Behmel *et al*. (2016), Brack *et al*. (2015) and Lovett *et al*. (2007) and the availability of a comprehensive, existing database supported and allowed to suggest the following condensed guidelines. The steps for reviewing an existing water quality monitoring program are listed here as supplementary information:

1. Determine any changes in the structural composition and population number of the consumers in order to discover new environmental pressures

2. Verification of the objectives of the existing monitoring program during first review or suggested for every five years

3. Need for long term water quality monitoring program to provide data

4. Evaluation of monitoring data by means of basic statistical analyses to observe and determine differences and trends with multivariate statistics such as principal component analysis or correspondence analysis (CCME, 2015)

5. Determine the variance in data

6. Application of target water quality objectives (In this case study the concentrations of recoverable cyanide have been monitored for the initial monitoring program but was adjusted to monitor dissolved cyanide concentrations based on the requirements of the newly published target water quality objectives.)
7. Set up new objectives and implement a revised monitoring program

CHAPTER 6 COMPARISON OF PHYTOPLANKTON ASSEMBLAGES IN TWO DIFFERENTIALLY POLLUTED STREAMS, MIDDLE VAAL RIVER AND KOEKEMOERSPRUIT, IN THE MIDDLE VAAL CATCHMENT

6.1 Introduction

The importance of phytoplankton (algae) and associated chlorophyll concentrations became increasingly evident throughout the course of this case study as a serious concern in the source water, during wastewater recycling and in a tributary of the catchment. Algae forms a critical living part of aquatic ecosystems that power food webs and biogeochemical cycling but are also major sources of problems that threaten many ecosystems when abundances of nuisance and toxic taxa are high (Stevenson, 2014). Phytoplankton communities respond to changes in environmental parameters, especially nitrogen and phosphorus, as they integrate cumulative impacts that would not be detected in another way or that would be otherwise underestimated (e.g. highly variable pollution levels due to point and non-point pollution) (Shi *et al*., 2012). Studies such as Wu *et al*. (2011) not only studied the relationship between phytoplankton and environmental variables but also identified phytoplankton species that could potentially be used as indicators of specific water chemistry conditions. Eutrophication and cyanobacterial blooms have become the most severe problems affecting the water body's functioning (Wang, Wang *et al*., 2015). Research on phytoplankton assemblages in streams, rivers, dams and lakes have been applied previously to manage blooms (Chalar, 2009) and to determine relationships with different water quality aspects (Vázquez *et al*., 2011). The use of phytoplankton in bio-assessments is a relatively new field of research (Wu *et al*., 2017), necessitated by decreased water quality of freshwater ecosystems due to intensive human disturbances. Understanding phytoplankton ecology is important for managing river ecosystems to protect the goods and services that rivers provide (Stevenson, 2009).

The water quality and phytoplankton composition of the Middle Vaal River and the Koekemoerspruit in the Middle Vaal Catchment were assessed in this section of the case study as both streams are polluted to their own extend and in due course serves as a drinking water source after their convergence. The Vaal River is classified as a largely modified stream and a eutrophic water body, while the Koekemoerspruit is classified as a largely modified to seriously modified stream (Table 5-1). The Koekemoerspruit is considered to contribute to the algal problems experienced by Midvaal Water Company's water treatment plant since it receives the effluent from both a large urban wastewater treatment plant and a canal that occasionally transfers water from a nearby mining plant.

Phytoplankton genera were identified and enumerated and analysed together with the physical and chemical parameters to establish correlations between the physical and chemical water quality and phytoplankton genera observed in each of two heavily polluted streams, the Middle Vaal River and the Koekemoerspruit. The findings of this study will add value to the physical and chemical monitoring data available by incorporating phytoplankton diversity and composition as well as dominance to signify the presence of pollutants and possible dangers of specific genera present. It therefore provides an integrated view of the ecological status of these two streams, not only for Midvaal Water Company and the scientific community but also to create environmental awareness of the unseen effects of pollution among stakeholders in the catchment. Relationships between phytoplankton assemblages and anthropogenic stressors help diagnose stressors and establish targets for protection and restoration (Stevenson, 2014).

The intensity of pollution in the Middle Vaal River and the Koekemoerspruit varies and therefore the aims of the study were thus to determine how the pollution of each of the two streams influenced phytoplankton composition by means of correlations between physical and chemical variables and phytoplankton assemblages and to confirm the dominant phytoplankton genera at each stream as an indicator of the water quality.

6.2 Materials and methods[1]

6.2.1 Description of the study site

See section 5.2.1 for a description of the study site together with Table 5-1. An average rainfall of 607 mm per year was recorded at the study site during the study period.

6.2.2 Description of sampling sites

Figure 2-1 illustrates where the study and sampling sites are located in the catchment. Sampling frequencies are indicated in Table 2-1 whereas Table 6-1 (similar to Table 5-2) gives a more detailed description of the sampling sites for ease of reference in this chapter.

Table 6-1: The relevance and location of each sampling site

Site number	Site name	Coordinates	Description
Site 1	Vermaasdrift Bridge	26° 56' 10.3" S 26° 51' 00.8" E	Reference point to determine impact of Koekemoerspruit on Middle Vaal River

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[1] Ms S Booyens performed phytoplankton identification and enumeration for her dissertation (Booyens, 2015) and is a co-author of the manuscript based on this chapter.

Site number	Site name	Coordinates	Description
Site 2	Middle Vaal River	26° 56' 04.5" S 26° 48' 01.4" E	Water quality at this site determines water treatment processes and operations of water treatment plant
Site 3	Enviroclear overflow	26° 54' 37.8" S 26° 48' 50.5" E	Flows periodically into Koekemoerspruit, downstream from site 4
Site 4	Koekemoerspruit before Enviroclear overflow	26° 54' 40.3" S 26° 48' 55.4" E	Koekemoerspruit from below Stilfontein before inflow of canal; indicates influence of urban activities and reference point to determine impact of Enviroclear on Koekemoerspruit
Site 5	Koekemoerspruit after Enviroclear overflow	26° 54' 51.7" S 26° 48' 57.0" E	Koekemoerspruit after confluence of canal; represents water that will enter Middle Vaal River between sites 1 and 2

6.2.3 Sampling regime and methods

Two litre surface water samples for chemical and total chlorophyll analyses together with a 250 ml microbiological sample in a sterile sampling bag were collected at the five sites on a monthly basis for 24 months from November 2012 to October 2014. The samples were chemically and microbiologically analysed by Midvaal Water Company Scientific Services for the following 21 variables included in Table 2-2:

Aluminium

Ammonia

Arsenic

Chloride

Colour

Copper

Cyanide recoverable

Dissolved inorganic nitrogen (calculation)

Electrical conductivity

Faecal coliforms

Iron

Manganese

Nitrate and nitrite

Orthophosphate

pH

Sodium

Sulfate

Total chlorophyll

Total organic carbon

Turbidity

Uranium

Zinc

Surface water grab samples for phytoplankton analysis were also collected at the five sites on a monthly basis for 24 months from November 2012 to October 2014. No samples could be collected at site 3 from June 2014 to August 2014 as the canal was dry. The grab samples were immediately transferred each time to 250 ml brown polyethylene bottles with each containing 3 ml acidified formaldehyde (2% final preservative concentration) (Throndsen, 1978). The phytoplankton identification and enumeration method as per Lund *et al.* (1958), Swanepoel *et al*. (2008) and Utermöhl, (1958) was performed at the North-West University, Potchefstroom campus with a Zeiss inverted light microscope (40x objective lens and 10x eyepiece). Phytoplankton was identified to genus level and concentrations were expressed as cells/ml. Phytoplankton identification guides such as Croasdale and Flint (1986, 1988), Croasdale *et al.* (1994), Entwisle *et al.* (1996), Gell *et al*. (1999), Guiry *et al*. (2007), Hindák (2008), Janse van Vuuren *et al*. (2006), John *et al*. (2002), Joska and Bolton (1993), Prescott (1983), Taylor *et al*. (2007) and Wehr and Sheath (2002) were used.

6.2.4 Approach and statistical analyses

All the general statistical methods of this study (see section 2.4) were applied to process the data and determine the descriptive statistics for all variables. The Kruskal–Wallis ANOVA (nonparametric statistics) for comparing multiple independent groups was used to determine differences between unit values of physical and chemical variables and phytoplankton concentrations between the different sites (faecal coliform bacteria was included as an environmental variable due to its association with nutrient related concentrations in this study). The identified phytoplankton genera were grouped according to taxon (class) for data analysis.

Canonical Correspondence Analysis (CCA) and Redundancy Analysis (RDA) were carried out using CANOCO version 4.5 (Ter Braak & Šmilauer, 2002). For the RDA the option “Center by species” was selected for the species under Centering and Standardization in CANOCO (Lepš and Šmilauer, 2003). Log transformation, i.e. log(y+1), was applied to deal with zero values in the data set for both the CCA and RDA. A Monte Carlo permutation test (499 permutations) was used to determine the statistical validity of both the RDA and CCA.

6.3 Results

6.3.1 Physical and chemical water quality assessment

The Middle Vaal River at sites 1 and 2 was characterised by high maximum values for pH (9.6), turbidity (120 NTU), colour (300 mg/L Pt), aluminium (1.3 mg/L to 1.6 mg/L) and total chlorophyll concentrations (399 µg/L to 413 µg/L) as seen in Table 6-2. In comparison the Koekemoerspruit (Table 6-3) was characterised by higher electrical conductivity, chloride and sulfate concentrations. The average electrical conductivity of the Koekemoerspruit at sites 4 and 5 (115 mS/m and 129 mS/m respectively) was lower than that of the Enviroclear canal (239 mS/m) but higher than that of the Middle Vaal River (55 mS/m). The elevated ammonia, nitrate and nitrite, orthophosphate and total organic carbon concentrations in the Koekemoerspruit indicates organic pollution (Table 6-3). Extreme average faecal coliform counts at site 4 (3444 cfu/100ml) and 5 (3342 cfu/ml) confirm domestic wastewater effluent to be the source of organic pollution in the Koekemoerspruit. The saline water of the Enviroclear canal at site 3 had the highest average concentrations of sulfate (933 mg/L), chloride (183 mg/L) and sodium (256 mg/L).

Midvaal Water Company’s specific interest lies in significant differences between sites 1 and 2 as that would indicate any influence of the Koekemoerspruit on the Middle Vaal River. Even though, there were no significant differences according to Kruskal-Wallis (see Annexure D, Table D) in the mean values for all variables determined for the Middle Vaal River between sites 1 and 2, there was an increase observed in the mean total chlorophyll concentration from 127 µg/L at site 1 to 148 µg/L at site 2.

As in the case of the Middle Vaal River, the influence of the Enviroclear overflow on the Koekemoerspruit had to be established. The mean sulfate concentration increased from 191 mg/L at site 4 to 291 mg/L at site 5 together with slight increases of chloride, electrical conductivity and sodium (Table 6-3) but there were also no significant differences in the mean values for all variables of the Koekemoerspruit between sites 4 and 5 according to Kruskal-Wallis (see Annexure D, Table D).

Water quality of the Koekemoerspruit from site 5 did not impact on the water quality of site 2 in the Middle Vaal River, except for total chlorophyll concentrations. It seems that the water quality of the canal (site 3) did not impact on the water quality of site 5 in the Koekemoerspruit as well.

Table 6-2: The mean, minimum, maximum and standard deviation of parameters for sites 1 and 2 that indicated differences in the physical and chemical water quality between sites

	Site 1				**Site 2**			
	Mean	**Min.**	**Max.**	**SD**	**Mean**	**Min.**	**Max.**	**SD**
Aluminium	0.16	<0.1	1.3	0.36	0.20	<0.1	1.6	0.44
Ammonia	0.2	0.1	0.3	0.07	0.2	0.1	0.3	0.07
Arsenic	0.01	<0.01	<0.01	0.003	<0.01	<0.01	<0.01	0
Chloride	49	18	81	15.7	49	15	64	12.2
Colour	98	40	300	74.9	111	50	300	86.9
Copper	<0.2	<0.2	<0.2	0.02	<0.2	<0.2	<0.2	0.01
Cyanide recoverable	<0.02	<0.02	<0.02	0.004	<0.02	<0.02	<0.02	0.001
Electrical conductivity	55	25	79	14.4	55	24	77	13.8
Faecal coliforms	235	9	1800	421	119	5	1100	244
Iron	<0.2	<0.2	0.8	0.23	<0.2	<0.2	1.0	0.27
Manganese	<0.1	<0.1	0.1	0.02	<0.1	<0.1	0.1	0.02
Nitrate and nitrite	1.7	0.3	7.9	1.7	1.2	0.3	4.5	0.9
Orthophosphate	0.09	0.03	0.20	0.06	0.08	0.03	0.20	0.04
pH	8.8	7.8	9.6	0.49	8.7	7.4	9.6	0.57
Sodium	47	12	76	17.4	43	12	66	14.3
Sulfate	112	46	218	45.1	95	24	158	29.6
Total chlorophyll	127	8.0	399	82.6	148	30	413	89.0
Total organic carbon	5.8	4.7	7.0	0.72	6.1	4.5	8.4	1.10
Turbidity	29	8.4	120	28.4	27	11	120	28.4
Uranium	<0.05	<0.05	<0.05	0.001	<0.05	<0.05	<0.05	0.001
Zinc	<0.1	<0.1	0.1	0.01	<0.1	<0.1	<0.1	0.01

Table 6-3: The mean, minimum, maximum and standard deviation of parameters for sites 3, 4 and 5 that indicated differences in the physical and chemical water quality between sites

	Site 3				Site 4				Site 5			
	Mean	**Min.**	**Max.**	**SD**	**Mean**	**Min.**	**Max.**	**SD**	**Mean**	**Min.**	**Max.**	**SD**
Aluminium	0.03	<0.1	0.15	0.047	<0.1	<0.1	1.2	0.25	<0.1	<0.1	1.1	0.24
Ammonia	1.3	0.1	11	2.3	23	0.25	47	14.7	21	0.1	47	16.1
Arsenic	0.02	<0.01	0.07	0.02	<0.01	<0.01	0.02	0.005	0.01	<0.01	0.1	0.01
Chloride	183	79	327	54.8	96	9.1	146	29.9	121	8.2	330	64
Colour	6.4	2.5	45	10.2	62	2.5	250	75.1	61	2.5	250	75.0
Copper	<0.2	<0.2	<0.2	0.018	0.02	<0.2	0.2	0.04	<0.2	<0.2	<0.2	0.01
Cyanide recoverable	<0.02	<0.02	0.02	0.004	0.03	<0.02	0.35	0.07	0.02	<0.02	0.10	0.02
Electrical conductivity	239	96	314	50.2	115	29	154	26.4	129	29	279	45.0
Faecal coliforms	420	0	4200	977	3444	20	16000	5814	3342	24	16000	5844
Iron	<0.2	<0.2	0.4	0.09	<0.2	<0.2	0.9	0.19	<0.2	<0.2	0.9	0.18
Manganese	<0.1	<0.1	0.22	0.05	0.29	<0.1	2.0	0.42	0.28	<0.1	2.0	0.42
Nitrate and nitrite	5.4	0.6	11.7	4.1	3.5	0.5	8.5	2.0	3.5	0.5	10.1	2.7
Orthophosphate	0.13	0.03	1.51	0.32	3.2	0.22	19	3.9	3.5	0.05	23	4.8
pH	8.7	7.5	10.6	0.92	7.7	7.2	8.1	0.25	7.7	7.1	8.6	0.35
Sodium	256	104	380	71.8	91	9.0	137	23.9	113	8.9	314	64.5
Sulfate	933	231	1435	245	191	28	375	96.9	291	28	900	232
Total chlorophyll	21	0.3	176	39.7	62	4.0	235	74.7	52.1	5.2	227	66.0
Total organic carbon	2.9	0.3	16	4.03	10	5.8	15	2.65	9.4	2.3	15	3.58
Turbidity	41	1.1	334	78	14	2.9	47	11.9	15	1.1	53	14.5
Uranium	0.04	<0.05	0.14	0.04	<0.05	<0.05	0.03	0.01	<0.05	<0.05	0.1	0.03
Zinc	<0.1	<0.1	<0.1	0.02	0.04	<0.1	0.2	0.04	0.03	<0.1	0.1	0.02

6.3.2 Phytoplankton assemblages and composition

A total of 86 phytoplankton genera were identified during the study and grouped into seven phytoplankton taxa (classes) (12 Cyanophyceae genera, 18 Bacillariophyceae genera, 47 Chlorophyceae genera, two Chrysophyceae genera, two Dinophyceae genera, one Cryptophyceae genus and four Euglenophyceae genera) (Table 6-4).

Table 6-4: The complete phytoplankton composition of this study

Taxon	Genus
Cyanophyceae	*Anabaena* spp.
	Aphanocapsa spp.
	Arthrospira spp.
	Calothrix spp.
	Cylindrospermopsis spp.
	Gloeocapsa spp.
	Merismopedia spp.
	Microcystis spp.
	Nostoc spp.
	Oscillatoria spp.
	Phormidium spp.
Bacillariophyceae	*Achnanthes* spp.
	Achnanthidium spp.
	Amphiprora spp.
	Amphora spp.
	Aulacoseira spp.
	Cocconeis spp.
	Cyclotella spp.
	Cymbella spp.
	Diadesmus spp.
	Fragilaria spp.
	Gomphonema spp.
	Gyrosigma spp.
	Melosira spp.
	Navicula spp.
	Nitzschia spp.
	Pinnularia spp.
	Surirella spp.
	Tabellaria spp.
Chlorophyceae	*Actinastrum* spp.
	Ankistrodesmus spp.
	Ankyra spp.
	Asterococcus spp.
	Binuclearia spp.

Taxon	Genus
	Carteria spp. *Chaetophora* spp. *Characium* spp. *Chlamydomonas* spp. *Chlorella* spp. *Chlorococcum* spp. *Chlorolobion* spp. *Closteriopsis* spp. *Closterium* spp. *Coelastrum* spp. *Cosmarium* spp. *Crucigenia* spp. *Desmodesmus* spp. *Dictyosphaerium* spp. *Didymogenes* spp. *Elakatothrix* spp. *Golenkinia* spp. *Golenkinopsis* spp. *Goniochloris* spp. *Keratococcus* spp. *Kirchneriella* spp. *Klebsormidium* spp. *Lagerheimia* spp. *Micractinium* spp. *Monoraphidium* spp. *Mougeotia* spp. *Nephrocytium* spp. *Oedogonium* spp. *Oocystis* spp. *Pandorina* spp. *Pediastrum* spp. *Pteromonas* spp. *Spirogyra* spp. *Staurastrum* spp. *Staurodesmus* spp. *Stigeoclonium* spp.

Taxon	Genus
	Tetraedron spp. *Tetrastrum* spp. *Treubaria* spp. *Ulothrix* spp.
Chrysophyceae	*Dinobrion* spp. *Mallomonas* spp.
Dinophyceae	*Ceratium* spp. *Peridinium* spp.
Cryptophyceae	*Cryptomonas* spp.
Euglenophyceae	*Euglena* spp. *Phacus* spp. *Strombomonas* spp. *Trachelomonas* spp.

The total phytoplankton cells that were enumerated during the study period from November 2012 to October 2014 in the Middle Vaal River increased from 1 228 827 cells/ml at site 1 to 1 591 311 cells/ml at site 2 and might be ascribed to the influx of nutrients and algae from the Koekemoerspruit. The total cells of the Cyanophyceaea, Bacillariophyceae, Chlorophyceae, Chrysophyceae, Dinophyceae and Cryptophyceae each increased from site 1 to site 2 (Figure 6-1). Site 3 had the lowest total phytoplankton concentration of 84 747 cells/ml (5% of the cells at site 2). The total phytoplankton cells in the Koekemoerspruit also increased from 231 779 cells/ml at site 4 to 604 084 cells/ml at site 5 and these included cells of the Cyanophyceaea, Bacillariophyceae, Chlorophyceae, Chrysophyceae and Cryptophyceae (Dinophyceaea decreased). The cells of the Euglenophyceae decreased from site 1 (28 256 cells/ml) to site 2 (19 255 cells/ml) and from site 4 (26 815 cells/ml) to site 5 (13 541 cells/ml). The Kruskal-Wallis ANOVA indicated no significant difference between the Cyanophyceae, Chrysophyceae, Dinophyceae and Cryptophyceae for all the sites and this is important as algae may indicate certain pollution (see Annexure D, Table D). The total cell concentration for the Cyanophyceae, Chrysophyceae, Dinophyceae and Cryptophyceae ranged from 26 914 cells/ml (site 3) to 497 042 (site 2), 35 cells/ml (site 3) to 3 575 cells/ml (site 2), 42 cells/ml (site 5) to 7 715 cells/ml (site 2) and from 0 cells/ml (site 4) to 18 721 cells/ml (site 2) respectively despite the size of the streams. The abstraction point of Midvaal Water Company (site 2) had the highest phytoplankton concentrations for all the taxa (classes) except for the Euglenophyceae which were most at site 1.

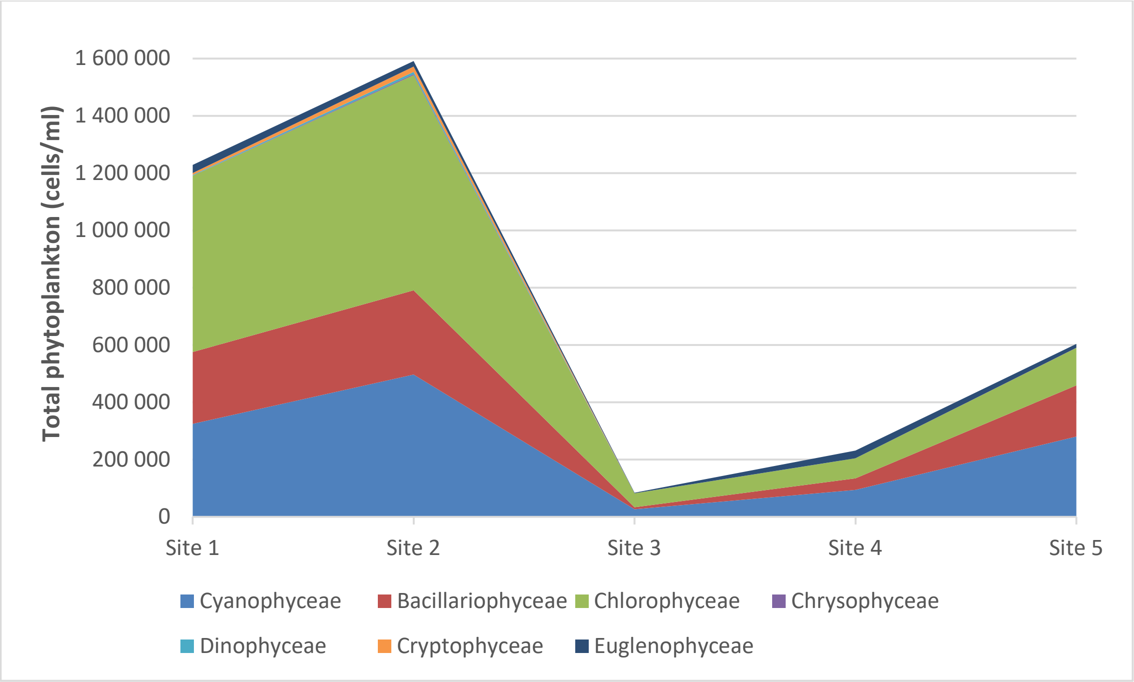

Figure 6-1: **The total phytoplankton cells enumerated and grouped into seven taxa (classes) from November 2012 to October 2014 for site 1 (Vermaasdrift Bridge), site 2 (Middle Vaal River), site 3 (Enviroclear overflow), site 4 (Koekemoerspruit before Enviroclear overflow) and site 5 (Koekemoerspruit after Enviroclear overflow)**

During spring at site 2, Chlorophyceae cells were the most (318 893 cells/ml) and comprised 73% of the total cells (435 894 cells/ml) enumerated (Figure 6-2). The cell concentrations of the Chlorophyceae (239 882 cells/ml) and Cyanophyceae (235 259 cells/ml) were even in the Middle Vaal River (site 2) during summer with a difference of only 4 623 cells/ml. The concentration of Cyanophyceae cells (180 752 cells/ml) exceeded the concentration of Chlorophyceae cells (126 519 cells/ml) during autumn at site 2. Bacillariophyceae cells were the most (144 699 cells/ml) at site 2 during winter and comprised 57% of the total cells (252 218 cells/ml) enumerated, following Chlorophyceae (65 745 cells/ml) and Cyanophyceae (38 145 cells/ml).

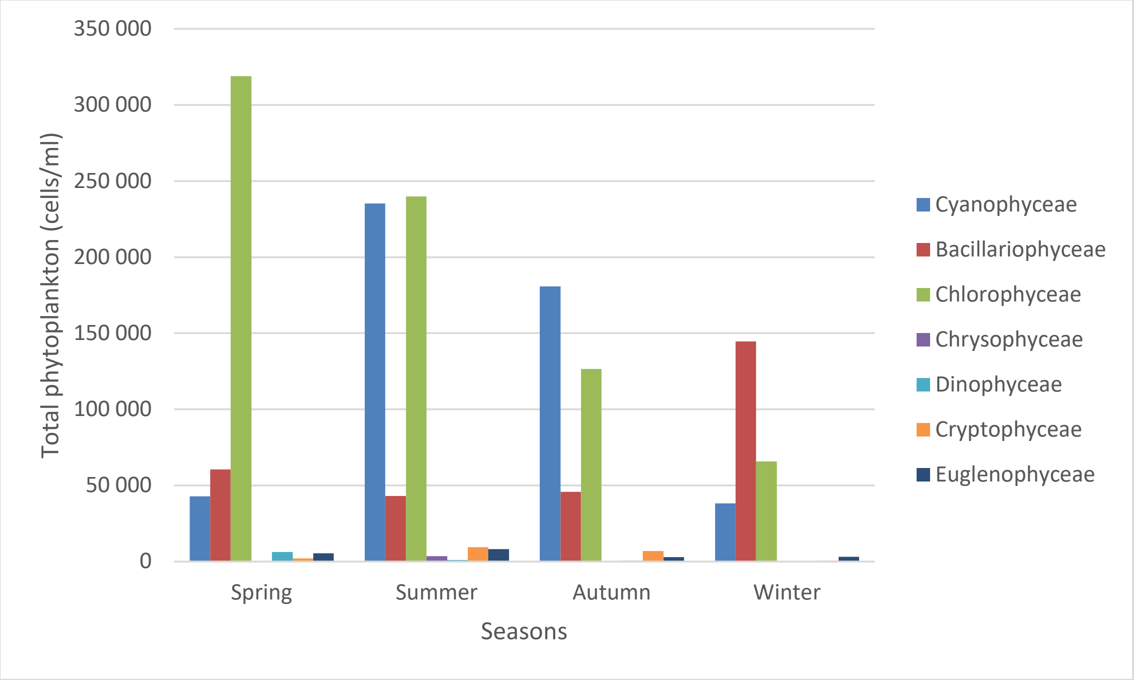

Figure 6-2: **The total phytoplankton cells enumerated and grouped into seven taxa (classes) per season from November 2012 to October 2014 for site 2 (Middle Vaal River)**

During spring, Cyanophyceae cells were the most (238 885 cells/ml) at site 5 and comprised 64% of the total cells (370 395 cells/ml) enumerated (Figure 6-3). The concentration of Cyanophyceae cells (27 513 cells/ml) exceeded the concentration of Chlorophyceae cells (9 416 cells/ml) during summer at the Koekemoerspruit after Enviroclear overflow (site 5) but the Chlorophyceae (16 973 cells/ml) exceeded the Cyanophyceae (12 348 cells/ml) during autumn. Bacillariophyceae cells peaked during the winter season at site 5 with 107 627 cells/ml, 69% of the total cells (156 307 cells/ml).

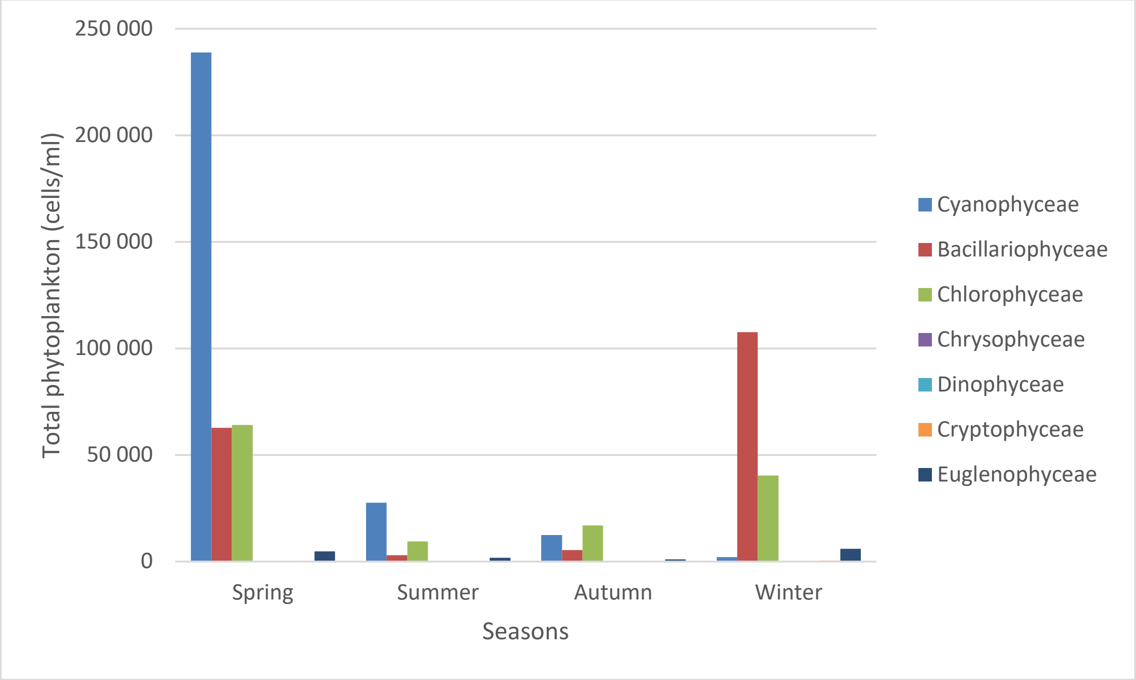

Figure 6-3: **The total phytoplankton cells enumerated and grouped into seven taxa (classes) per season from November 2012 to October 2014 for site 5 (Koekemoerspruit after Enviroclear overflow)**

The Chlorophyceae were dominant at sites 1 (50%), 2 (47%) and 3 (58%) while Cyanophyceae dominated at sites 4 (41%) and 5 (46%) (Figure 6-4). The percentage composition of the Cyanophyceae increased from sites 1 to 2 (26% to 31%) and from sites 4 to 5 (41% to 46%). Site 3 displayed the lowest Bacillariophyceae dominance (8%) and the highest Chlorophyceae dominance (58%) of all the sites.

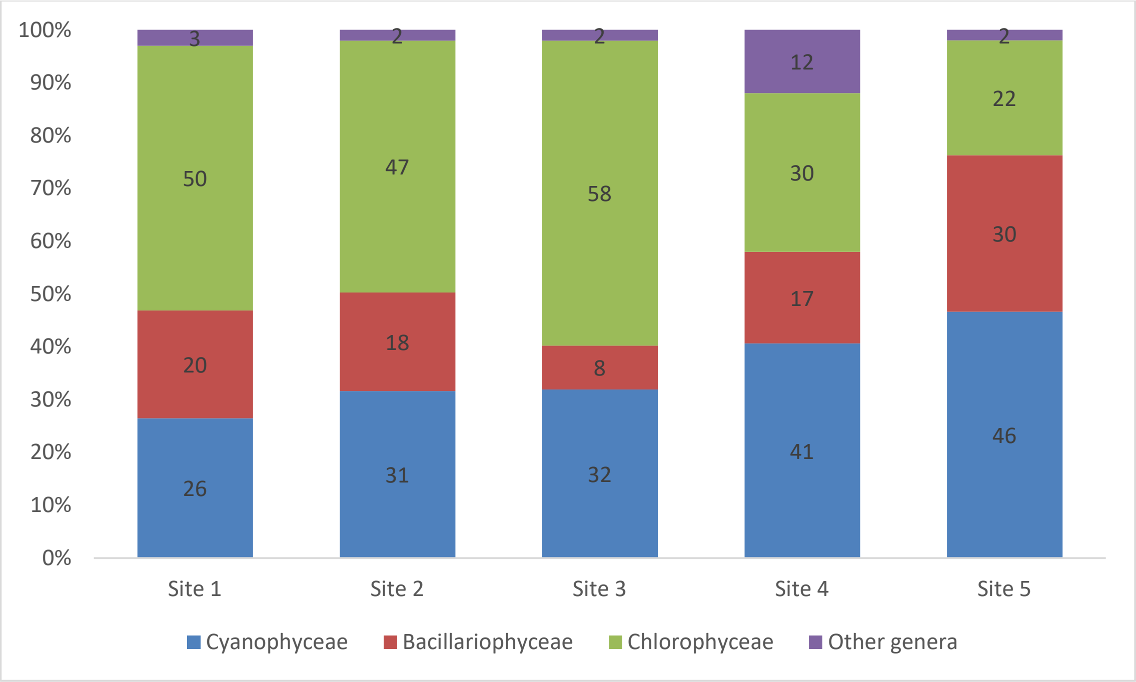

Figure 6-4: **Taxonomic composition of phytoplankton samples collected from November 2012 to October 2014 at site 1 (Vermaasdrift Bridge), site 2 (Middle Vaal River), site 3 (Enviroclear overflow), site 4 (Koekemoerspruit before Enviroclear overflow) and site 5 (Koekemoerspruit after Enviroclear overflow)**

The most abundant genera of the Chlorophyceae were *Scenedesmus* spp. in the Middle Vaal River (sites 1 (40%) and 2 (44%) respectively), *Chlorolobion* spp. in the Koekemoerspruit (sites 3 (41%) and 5 (21%) respectively) and, *Chlamydomonas* spp. (sites 3 (38%), 4 (47%) and 5 (32%) respectively) also found in the Koekemoerspruit (Table 6-5). The most abundant genera of the Cyanophyceae were *Aphanocapsa* spp. (sites 1 (47%), 2 (48%) and 4 (45%) respectively) and *Phormidium* spp. (sites 3 (80%), 4 (37%) and 5 (70%) respectively) (Table 6-5). *Cyclotella* spp. (79% at sites 1 and 84% at site 2) and *Nitzschia* spp. (73% at sites 3 and 4 and 94% at site 5) were the most abundant genera representing the Bacillariophyceae in the Middle Vaal River and Koekemoerspruit respectively (Table 6-5).

Table 6-5: **The dominant genera that were identified for each taxon (class) at all the sites expressed in percentages**

Taxon	Site	Genus	% dominance
Cyanophyceae	1	*Aphanocapsa* spp. *Oscillatoria* spp.	47 23

Taxon	Site	Genus	% dominance
		Merismopedia spp.	18
	2	*Aphanocapsa* spp. *Merismopedia* spp. *Oscillatoria* spp.	48 24 22
	3	*Phormidium* spp.	80
	4	*Aphanocapsa* spp. *Phormidium* spp. *Oscillatoria* spp.	45 37 17
	5	*Phormidium* spp. *Aphanocapsa* spp. *Oscillatoria* spp.	70 16 12
Bacillariophyceae	1 & 2	*Cyclotella* spp.	79 & 84
	3, 4 & 5	*Nitzschia* spp.	73, 73 & 94
Chlorophyceae	1	*Scenedesmus* spp. *Chlamydomonas* spp. *Pediastrum* spp.	40 12 10
	2	*Scenedesmus* spp. *Chlamydomonas* spp. *Pediastrum* spp.	44 12 9
	3	*Chlorolobion* spp. *Chlamydomonas* spp.	41 38
	4	*Chlamydomonas* spp. *Carteria* spp. *Chlorolobion* spp.	47 18 15
	5	*Chlamydomonas* spp. *Chlorolobion* spp. *Carteria* spp.	32 21 14
Crysophyceae	1, 2, 3, 4 & 5	*Mallomonas* spp.	100, 97,100, 100 & 100
Dinophyceae	1, 2, 3, 4 & 5	*Peridinium* spp.	83, 96, 89, 96 & 93
Cryptophyceae	1, 2, 3 & 5	*Cryptomonas* spp.	Only genus identified
Euglenophyceae	1, 2, 3, 4 & 54	*Euglena* spp.	72, 69, 80, 76, & 77

6.3.3 Relationship between physical and chemical variables and phytoplankton communities

Ordinations were interpreted using the following rationale:

(a) Variables are positively correlated with each other if their vectors subtend a small angle and are not correlated if their vectors are arranged greater than 90°apart,

(b) variables are negatively correlated if their vectors are directed oppositely (180°) and

(c) variables with the longest vector relative to an axis have the greatest influence on that axis.

The same principle applies for the clustering of sampling sites, with respect to each other as well as the variables (Bhat *et al*., 2014).

The CCA of the data showed that there was a significant correlation between the water quality parameters and the different classes of algae that were identified and had a *p*-value of 0.02. Therefor the correlations between physical and chemical variables and phytoplankton assemblages of the two streams were then further analysed using RDA ordination. RDA allowed us to simultaneously examine the influences of multiple water quality parameters on all phytoplankton groups (Ding *et al*, 2016). Sites 1 and 2 in the Middle Vaal River are clearly separated from sites 3, 4 and 5 in the Koekemoerspruit. Figure 6-5 illustrates positive associations between pH, turbidity, colour, aluminium, iron, total chlorophyll and the samples from the Middle Vaal River and between samples from the Koekemoerspruit and electrical conductivity, sulfate, chloride and sodium as well as ammonia, nitrate and nitrite, orthophosphate, manganese, total organic carbon and faecal coliforms. The Bacillariophyceae, Dinophyceae and Crytophyceae are positively correlated with and dominate the sites of the Middle Vaal River. The Chrysphyceae are positively correlated with site 3 and the associated sulfate concentrations. The Cyanophyceae and Euglenophyceae are positively correlated with and dominate the sites of the Koekemoerspruit in Figure 6-5. The Chlorophyceae is associated with both the Middle Vaal River and the Enviroclear overflow. The Cyanophyceae and Euglenophyceae are positively correlated with the nutrients containing phosphorus and nitrogen that was found in high concentrations in the samples collected from the Koekemoerspruit. The Chlorophyceae are associated with both the Middle Vaal River and the Enviroclear overflow.

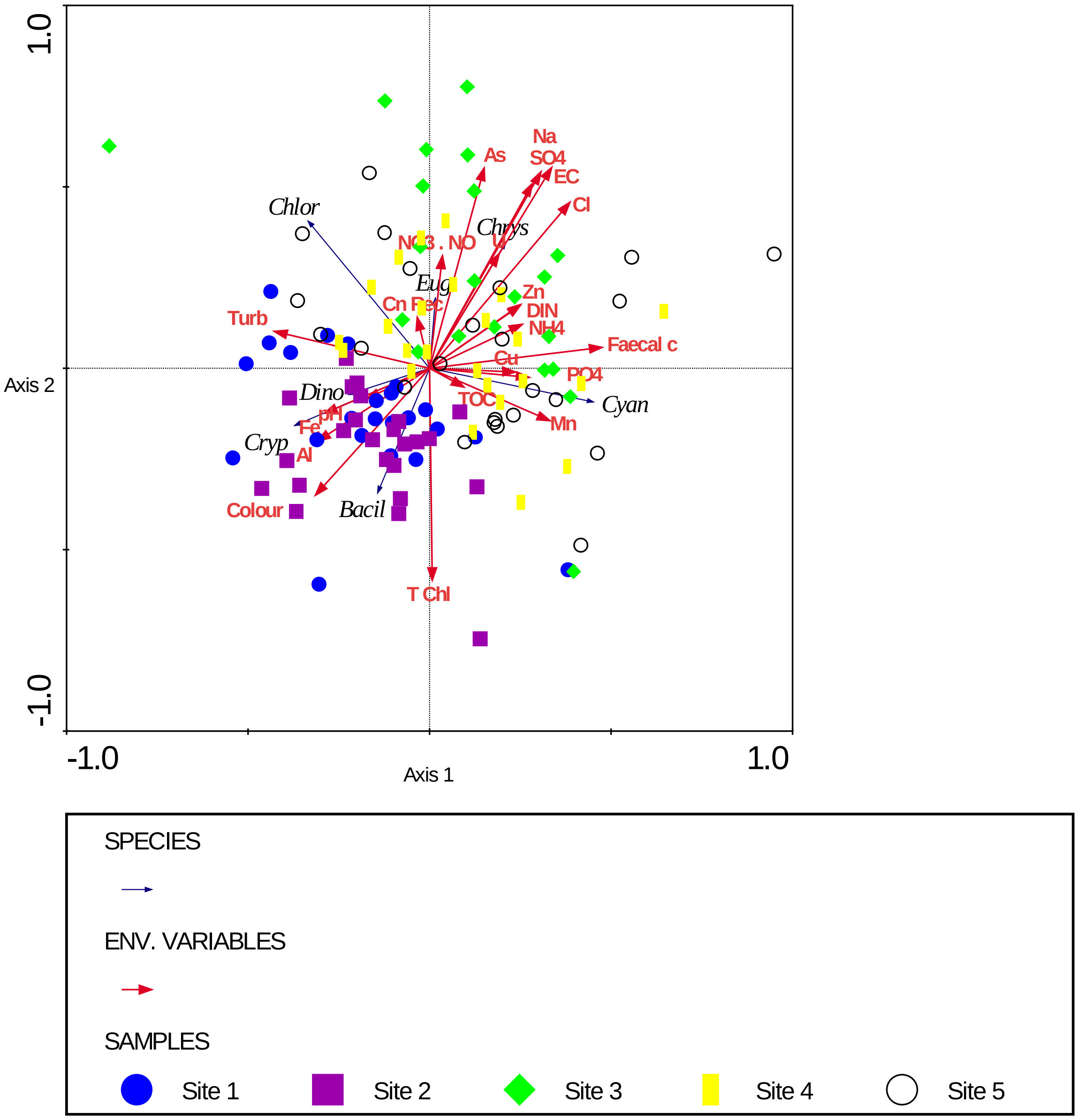

Figure 6-5: **Illustration of the redundancy analysis (RDA) triplot showing axes 1 and 2. (Cyan: Cyanophyceae, Bacil: Bacillariophyceae, Chlor: Chlorophyceae, Chrys: Crysophyceae, Dino: Dinophyceae, Cryp: Cryptophyceae and Eug: Euglenophyceae)**

All four eigenvalues reported in Table 6-6 are canonical and correspond to axes that are constrained by the variables. The first axis accounted for 53.1% of the variance in the data and the second axis for 16.4% of the variance (Table 6-6). Faecal coliforms and Cyanophyceae associate with the first axis and have the greatest influence on the data. The vectors of faecal coliforms and Cyanophyceae indicate that these variables have a strong positive correlation (Figure 6-5). Sulfate, electrical conductivity, sodium and total chlorophyll have the greatest influence on the second axis. There is a positive correlation between sulfate, electrical conductivity and sodium and the dominance of the Chrysophyceae and Euglenophyceae associate closely with these parameters but these three variables have a negative correlation between with total chlorophyll. The Cyanophyceae and Bacillariophyceae also correspond positively with total chlorophyll concentrations taking into account that total chlorophyll is greatest at sites 1 and 2 in the Middle Vaal River where electrical conductivity is lowest, hence the negative correlation.

Table 6-6: Eigenvalues, species-environment correlations and cumulative percentage variance contributed by the four axes on the RDA ordination

Axes	Eigenvalues	Species-environment correlations	Cumulative percentage variance of species data	Cumulative percentage variance of species-environment relation
1	0.122	0.505	12.2	53.1
2	0.038	0.570	16.0	69.5
3	0.030	0.461	19.0	82.6
4	0.023	0.500	21.3	92.7

Summary of Monte Carlo test for all groups as discussed

Test of significance of first canonical axis: eigenvalue = 0.122
F-ratio = 13.097
p-value = 0.1840

Test of significance of all canonical axes: Trace = 0.230
F-ratio = 1.339
p-value = 0.0820

6.4 Discussion

The composition of algal assemblages is affected by water quality and habitat and they can therefore be used to assess the environmental condition of water sources. Because of their dependence on water quality they can also have an effect on recreational and drinking water source uses. The water quality of the sites located in the Middle Vaal River are characterised by high pH (9.6), turbidity (120 NTU), colour (300 mg/L Pt), aluminium (1.6 mg/L) and total chlorophyll concentrations (413 µg/L). High phytoplankton biomass accumulation in eutrophic water bodies such as the Middle Vaal River (sites 1 and 2) contribute to total chlorophyll concentrations and elevated pH levels because algal cells consume carbon dioxide during photosynthesis. In comparison, the sites in the Koekemoerspruit revealed higher electrical conductivity and faecal coliforms than what were observed in the Middle Vaal River. The higher electrical conductivity values of the Koekemoerspruit are most probably due to the alarmingly high average concentrations of sulfate (241 mg/L), chloride (109 mg/L), sodium (102 mg/L), ammonia (22 mg/L), nitrate and nitrite (3.5 mg/L) and orthophosphate (3.4 mg/L) that were measured. In this respect the saline water in the canal of the Enviroclear overflow at site 3 displayed averages of 183 mg/L chloride, 256 mg/L sodium, 933 mg/L sulfate and an electrical conductivity of 239 mS/m (Table 6-3). The water quality of Koekemoerspruit dismally failed the resource water quality objective limits (DWS, 2016) for ammonia, nitrate and nitrate, orthophosphate as well as faecal coliform bacteria. The physical chemical results indicated that organic pollution from domestic wastewater had the largest influence on the Koekemoerspruit and that mining activities influenced the water quality of the Enviroclear overflow canal. This is also evident from other studies showing that South Africa’s rapidly growing population and increase in unregulated industrial and municipal wastewater discharge from ineffective sewage treatment infrastructures cause an increase in water pollution (Mema, 2010; Noel and Rajan, 2015; Van der Hoven *et al*., 2017). These influences were expected since a wastewater treatment plant discharges effluent into the Koekemoerspruit upstream of site 4 and due to the settler plant that transfers mine effluent to the Koekemoerspruit via the Enviroclear overflow canal. The Koekemoerspruit is unable to dilute the nutrient concentrations of the wastewater effluent that is discharged into the stream due to its limited volume even with the added volume from the Enviroclear overflow as the volume transferred from the canal is much less than that of the Koekemoerspruit.

Previous studies (Janse van Rensburg *et al*., 2016; Janse van Rensburg *et al*., 2019) have shown that both the Middle Vaal River and the Koekemoerspruit are experiencing an overall increase in total chlorophyll concentrations. Janse van Rensburg *et al*. (2016) reported an average total chlorophyll concentration of 127 µg/L in the Middle Vaal River (2010 to 2014) compared to the average total chlorophyll concentration of 148 µg/L observed during this study from 2012 to 2014. During this study the average total phytoplankton cell concentrations of sites 1 and 2 in the Middle Vaal River were 1 410 069 cells/ml and 3.4 times higher than the average total phytoplankton cell concentrations of sites 4 and 5 in the Koekemoerspruit (417 931 cells/ml). The potential impacts on the treatment processes, when cell concentrations proliferate in the source water during the occasional events of phytoplankton blooms, are listed:

- Overload of the treatment processes, e.g. algal loads exceed the design capacity
- Over expenditure of chemicals and electricity as chemical dosages either increase or has to be supplemented with other chemicals as well as increased ozonation and chlorination dosages

- Filter blockages that require more frequent maintenance
- Risk of final water quality failures
- Generation of more water treatment waste
- Requires more supervision and laboratory analyses
- The public has to be informed to promote awareness and as required by DWS regulation

Besides the fact that the Koekemoerspruit is a smaller stream than the Vaal River the lower phytoplankton cell concentrations can also be the result of lower residency time since the Koekemoerspruit is also much shorter than the Vaal River (Descy *et al.,* 2017). It is well known that phytoplankton assemblages are affected by high nutrient concentrations and temperature (Zhou *et al*, 2019). Nitrogen and orthophosphate concentrations present in the Middle Vaal River sites are indicative of hypertrophic conditions and will continue to sustain phytoplankton activities of this magnitude but were probably not as apparent in Table 6-2 as for the Koekemoerspruit sites since it is assimilated by phytoplankton. Although the total phytoplankton cells per site relate to the total chlorophyll concentrations (Table 6-2 and Table 6-3), the taxonomic composition (Figure 6-2) and dominance were also investigated in order to determine how dominance of the phytoplankton classes were affected by the water quality of the Vaal River and the Koekemoerspruit respectively.

A total of 86 phytoplankton genera were identified which were grouped into seven phytoplankton classes during the 24-month study period. The dominant genera for each taxon or class were also determined per site. The Chlorophyceae (47%), Cyanophyceae (31%) and Bacillariophyceae (18%) collectively comprised 96% of the phytoplankton composition at site 2 in the Middle Vaal River. This is in contrast to other studies on river phytoplankton that named the Bacillariophyceae as the most important algal group (Descy *et al*., 2017; Duong *et al*, 2019). The phytoplankton data concluded that Chlorophyceae dominated in the Middle Vaal River, sometimes succeeded by Bacillariophyceae and with occasional Cyanophyceae blooms and this tendency was also confirmed as observed by Janse van Vuuren and Pieterse (2005). A particular Cyanophyceae bloom was responsible for a taste and odour episode at Midvaal Water Company during February 2013 of this study. Concentrations of 5.8 ng/L geosmin and 20 ng/L MIB were recorded and was associated with the presence of *Oscillatoria* spp. (Cyanophyceae) at a concentration of 59 059 cells/ml at the time. *Scenedesmus* spp. from the Chlorophyceae, *Aphanocapsa* spp. from the Cyanophyceae and *Cyclotella* spp. from Bacillariophyceae occurred as dominant genera in the Middle Vaal River.

Scenedesmus spp. prefer eutrophic to hypertrophic waters with low salinity, similar to that of the Middle Vaal River water (Janse van Vuuren *et al*., 2006). *Scenedesmus* spp. are associated with wastewater and also known as “green weeds” that are responsible for blooms, fishy odours and capable of clogging sand filters at water treatment plants due to the spines on each terminal cell (Wehr, 2015). *Cyclotella* spp. occurs worldwide in different water bodies, from oligotrophic to hypertrophic and may form blooms and contribute to filter clogging as well (Wehr, 2015).

The Cyanophyceae (46%), Bacillariophyceae (30%) and Chlorophyceae (22%) collectively comprised 98% of the phytoplankton cell concentration (604 084 cells/ml) at site 5 which represents the water that flows into the Middle Vaal River at the confluence of these two streams in the catchment. *Chlorolobion* spp. and *Chlamydomonas* spp. from Chlorophyceae, *Aphanocapsa* spp. and *Phormidium* spp. from Cyanophyceae and *Nitzschia* spp. from the Bacillariophyceae were identified as dominant genera in the Koekemoerspruit. These genera are also known to grow well in high concentrations of organic wastes (Palmer, 1969). The phytoplankton cells of site 3 were mostly comprised of and dominated by the Chlorophyceae (58%) with *Chlorolobion* spp. and *Chlamydomonas* spp. identified as dominant genera in the Enviroclear overflow canal. The phytoplankton dominance in the Koekemoerspruit and the canal demonstrated that Chlorophyceae are likely to be more tolerant to saline conditions while Cyanophyceae are influenced by the availability of nutrients, as was indicated by Paerl *et al*. (2001).

Chlamydomonas spp. was a dominant genus in sites 3, 4 and 5, the most likely green swimming algal cells to be encountered and able to form very dense blooms according to (Janse van Vuuren *et al*., 2006). *Phormidium* spp. (sites 4 and 5) can form harmful cyanobacterial blooms and release substances such as dimethyldisulphide, dimethylsulphide, dimethyltrisulphide, MIB, geosmin, anatoxin-a, homoanatoxin-a (Wehr, 2015). *Nitzschia* spp. (sites 4 and 5) is also associated with nutrient rich, wastewater and organic pollution and indicators of deteriorating water quality such as that of the Koekemoerspruit (Palmer, 1969; Wehr, 2015). Sen *et al*. (2013) lay emphasis on *Phormidium* spp., *Oscillatoria* spp., *Nitzschia* spp. and *Chlamydomonas* spp., dominant at sites 4 and 5 (Table 6-5), to tolerate organic pollution as well.

Phytoplankton genera are largely seasonal organisms that react to the temperature variations (Figure 6-2 and Figure 6-3). The Chlorophyceae and Cyanophyceae cell concentrations dominated in the Middle Vaal River (site 2) and in the Koekemoerspruit after Enviroclear overflow (site 5) respectively during spring. Chlorophyceae and Cyanophyceae cell concentrations dominated alternately between summer and autumn at both sites 2 and 5. Bacillariophyceae cell concentrations were the highest at sites 2 and 5 during winter. The potential problem or risk periods for cyanobacterial toxins in the Middle Vaal River and the Koekemoerspruit ranged from summer to autumn and from spring to summer respectively and remains dependant on the presence of relevant genera, such as *Microcystis* spp. The highest *Microcystis* spp. count was recorded as 17 875 cells /ml during February 2013 at site 2 during the same time when Midvaal Water Company experienced a taste and odour episode.

The nutrient rich water of the Middle Vaal River promoted algal growth or blooms dominated by the Chlorophyceae. The Koekemoerspruit is on the other hand severely impacted by organic pollution and dominated by Cyanophyceae. The variation within phytoplankton abundances are closely related to environmental variables and can rapidly respond to variations in the water trophic status (Wang, Wang *et al*., 2015). The RDA ordination (Figure 6-5) summarised and confirmed that water quality (predictor variables) has a definite effect on the phytoplankton assemblages (response variables) for the Middle Vaal River and the Koekemoerspruit with a *p*-value of 0.08 (*p*-values of < 0.05 indicate statistically significant correlations). Similar statistical techniques were applied by Wang, Wang *et al*. (2015) to reveal that Cyanophceae, Chlorophyceae and Bacillariophyceae were in the majority with nitrogen and phosphorus as main impact factors. De Sousa Barroso *et al*. (2018) also applied RDA and found that nutrient availability and water transparency influence phytoplankton temporal dynamics.

Stream order reflects an estimate of water volume of a specific stream or river and therefore it ultimately reflects the effect of pollutant dilution within a catchment area such as that of the Middle Vaal Catchment (Dodds, 2002). The stream orders of the Koekemoerspruit (stream order two) and the Middle Vaal River (stream order five) suggest that the Koekemoerspruit (site 5) will have a minimal or no effect on the Middle Vaal River due to dilution that occurs from the confluence up to site 2 and was confirmed with the RDA ordination because the samples of the two streams were clearly separated as seen in Figure 6-5.

The nature of water pollution in this study had significantly different impacts on the water quality in each of the two streams which escalated to ultimately influence the phytoplankton assemblages in response. Phytoplankton communities can subsequently be used as a potential bioindicators of water quality in freshwater river systems (Shi *et al*., 2012) together with differences in phytoplankton abundances and variations over time (Gao *et al*., 2018) as declining species numbers indicate water quality deterioration. Decreasing the input of exogenous nutrients contribute to the prevention and control of phytoplankton blooms (Wang, Wang *et al*., 2015) and this study demonstrated the detrimental effects of eutrophication from a limnological perspective together with the importance of functional wastewater treatment plants, especially in a water scarce, developing country such as South Africa.

6.5 Conclusion

The situation with the Middle Vaal River and the Koekemoerspruit is what Sen *et al*. (2013) referred to when mentioned that two types of large and long-lasting pollution threats can be recognized on global level: organic pollution leading to high organic content (Koekemoerspruit) and, in the long term, to eutrophication (Middle Vaal River). The Middle Vaal River revealed excessive phytoplankton biomass accumulation along with elevated pH levels. The Koekemoerspruit was, in addition to the inflow of saline water from the Enviroclear overflow, severely polluted with domestic wastewater effluent during the extend of the study. Both streams were eutrophic but Chlorophyceae dominated in the Middle Vaal River and Cyanophyceae in the Koekemoerspruit. The dominance of phytoplankton genera such as *Scenedesmus* spp. from the Chlorophyceae in the Middle Vaal River (enriched with nutrients) and *Nitszchia* spp. from the Bacillariophyceae in the Koekemoerspruit (polluted with organics) confirmed the main water quality characteristics of the two streams. The physical and chemical variables expressed statistical correlations with phytoplankton data for each stream to demonstrate that water quality determines phytoplankton assemblages.

CHAPTER 7 GENERAL CONCLUSIONS

The outcomes of this case study presented a holistic overview of the water quality of the Middle Vaal River and Koekemoerspruit in the Middle Vaal Catchment. It highlighted the problems faced by water treatment plants due to deteriorating source water quality and investigated the success and feasibility of different management and operational strategies using water treatment and wastewater recycling operations at Midvaal Water Company for various periods as case studies.

The effects of nutrient enrichment (eutrophication) is evident throughout this study seeing that an increase in total chlorophyll concentrations due to frequent phytoplankton blooms, and the associated risks of tastes and odour problems, would be one of the Middle Vaal Catchment's main concerns when it comes to water treatment and wastewater recycling. Furthermore, it has been shown that changes in land use, as with the case of both the Middle Vaal River and Koekemoerspruit in the study area, has led to changes in abiotic and environmental pollution sources that obliges stakeholders to continuously monitor water quality. It also, once again, emphasised the importance of a well-planned monitoring program together with the selection of representative sampling points to ensure best integrated management practices. The evaluation and review of Koekemoerspruit monitoring data have identified several shortcomings. The monitoring of recoverable cyanide and faecal coliform bacteria have to be replaced by dissolved cyanide and *E.coli* respectively as required by the target water quality objectives of the South African Government Gazette 39943 No. 469 (DWS, 2016). The target water quality objectives require the monitoring of magnesium and since not being done previously, magnesium has to be included in the monitoring program. Water quality concerns pertaining to total chlorophyll and uranium concentrations validate the monitoring of algal identification and enumeration, cyanobacterial toxins, geosmin, MIB, radioactivity and temperature as part of the Koekemoerspruit monitoring program. Avenues are suggested for optimization, as the monitoring program is both effective and necessary as the total chlorophyll concentrations in the Koekemoerspruit pose a risk to the use of Middle Vaal River as a drinking water source downstream.

The continuous increase of total chlorophyll concentrations in the eutrophic Middle Vaal River as source water is the primary challenge for water treatment plants such as Midvaal Water Company. The changes in treatment processes over time at Midvaal Water Company enabled and assured the continuous supply of safe and healthy drinking water and demonstrated sound decision making by the management of Midvaal Water Company. Until recently Midvaal Water Company has managed to treat the water successfully with a variety combinations of water treatment processes in order to comply with national standards for drinking water. The ozonation and dissolved air flotation are crucial processes as flotation accounts for almost 70% total chlorophyll removal prior to conventional methods which significantly reduces the total chlorophyll load on these remaining processes. The first lesson learned was that the cumulative effect of a combination of treatment processes in series produce a better quality of final water opposed to the desired outcome which is not always achieved after a specific treatment process but is only realised towards the end. The improvement of the colour of the water is not necessarily apparent directly after intermediate ozonation as anticipated, but the effect thereof is immediately evident after filtration when intermediate ozonation is not in operation. The second lesson was that the operation of DAF ensures compliant turbidity levels and chlorophyll concentrations of the final drinking water. The third lesson was that the split dosing of ozone (pre-ozonation and intermediate ozonation) contributed more to chlorophyll removal than a single, higher dose at a designated step in the treatment process. The process of a wastewater recycling system can be effective to reduce costs, increase supply and at the same time do not compromise final water quality. Total chlorophyll was however identified as an overarching risk that justifies close monitoring. The use of on-line water quality monitors and adoption of models to create water quality alerts are recommended to continuously manage the operations successfully until such time that source water quality prompts treatment process intervention again.

An assessment of the Koekemoerspruit water quality indicated that target water quality objectives for orthophosphate, nitrate and nitrite and ammonia were often exceeded during 2014 and 2015, which confirm eutrophication due to severe organic pollution. Colour, ammonia and total chlorophyll concentrations displayed significant trends of increase over time and increased drastically after 2012. The Koekemoerspruit did not have a significant impact on the water quality of the Middle Vaal, except for total chlorophyll concentrations which increased in the Middle Vaal River from the Vermaasdrift Bridge to the downstream abstraction point of Midvaal Water Company because of the inflow of Koekemoerspruit in between.

The study on phytoplankton assemblages of the differentially polluted Middle Vaal River and Koekemoerspruit have shown that phytoplankton assemblages can be used as biological indicators of water quality, as well as the impact of land use on water quality. Chlorophyceae (48%) dominated in the Middle Vaal River and Cyanophyceae (45%) in the Koekemoerspruit. The dominant presence of phytoplankton genera such as *Scenedesmus* spp. (42%) from the Chlorophyceae in the Middle Vaal River and *Nitszchia* spp. (90%) from the Bacillariophyceae in the Koekemoerspruit confirmed that the Middle Vaal River is enriched with nutrients and that the Koekemoerspruit suffers from severe organic pollution. The physical and chemical variables expressed statistical correlations with phytoplankton data for each stream by means of a redundancy analysis (*p*-value of 0.08) to demonstrate and confirm that the water quality determines phytoplankton assemblages. Phytoplankton identification and enumeration in the Middle Vaal River on a continuous basis, as part of a monitoring program, is recommended to assess the seasonality of phytoplankton composition in the source water and thereby determine possible risk periods for the occurrence of cyanobacterial toxins, enabling precautionary actions.

The problems that were mentioned at the beginning of this study regarding water quality and quantity, such as eutrophication, pollution, climate change, water scarcity and water demand, allows for exciting water-related scientific research and case studies but also prompts serious reflection on how humans managed to damage and deteriorate one of the very resources they rely on most - water. Balzer (2018) presented as part of the National Water and Sanitation Master Plan that “About 50% of South Africa’s water resources originate from 10% of the country’s land, but many of these ‘water factories’ are under threat. Between 1999 and 2011 the extent of the main rivers in South Africa, being classified as having a poor ecological condition, increased by 500%, with some rivers pushed beyond the point of recovery. Approximately 56% of municipal wastewater treatment works and approximately 44% of water treatment works in the country are in poor/critical condition and need urgent rehabilitation, with some 11% being completely dysfunctional.” The DWS National Water and Sanitation Master Plan outlines a turnaround strategy to intervene with South Africa’s water related challenges.

The discussions and conclusions towards the end of each chapter summarised the symptoms and/or risks associated with water quality problems, which is total chlorophyll in this case. Such a water quality problem is having a significantly detrimental impact on the environment and drives up the cost of water treatment (Balzer, 2018). The root-cause of this water quality problem has to be identified as well in order to finalise a complete case study. The Koekemoerspruit is the only resource unit in South African Government Gazette 39943 No. 469 (DWS, 2016) whose ecological state is required to be improved from being seriously modified to being largely modified but how can this be achieved? The ecological health of the Koekemoerspruit due to the effects of land use is not currently well documented and available at national level since the national monitoring programs of DWS have been temporarily placed on hold in the Middle Vaal Catchment. Therefore, except for the data produced by Midvaal Water Company, valuable information is currently lost when water quality monitoring ceases. Water quality management, especially wastewater discharges, requires monitoring, regulation and enforcement from government as this will ensure the achievement of the target water quality objectives which will be at the heart of improving the current water quality situation in the Middle Vaal Catchment. A multitude of ripple effects for the environment and water service institutions (providers and authorities) may be significantly mitigated if untreated wastewater discharges into natural water resources can be monitored, regulated, managed and improved.

South Africa has exemplary water related laws, standards and initiatives like the Integrated Regulatory Information System (IRIS) for drinking and wastewater but these tools have to be used by stakeholders in order to manage water quality. An additional field to the existing IRIS for environmental data may be a collection point where institutions, such as Midvaal Water Company, could upload monitoring data to assist with the monitoring and evaluation of water quality at national level. Similar water quality data might also be available from other water utilities as a water safety plan obliges monitoring of a catchment to manage risks.

Since the impact of sewage pollution is evident in excessive chlorophyll concentrations, it is highly recommended to initiate the investigation into cyanobacterial toxin concentrations as well as levels of contaminants of concern such as endocrine disruptive compounds and persistent organic pollutants in the Middle Vaal Catchment. The results of this case study, including the identified risks, can be adopted by management of Midvaal Water Company to manage and plan this vital, life-sustaining service that has been successfully delivered to the community of the City of Matlosana and surrounding mines for the past 65 years.

The recent termination of the various national monitoring programs places doubt on upstream water management in the Middle Vaal Catchment. Red warning lights are flashing for the Vaal River as the eutrophication of a water source escalates to have multidimensional effects, especially on sustainable, safe and affordable drinking water supply by Midvaal Water Company, and therefore emphasizes the intrinsic value of protecting water resources not only in South Africa but all over the world.

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ANNEXURE A

Challenges in the potable water industry due to changes in source water quality: case study of Midvaal Water Company, South Africa

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ABSTRACT

Midvaal Water Company treats hypertrophic water abstracted from the Vaal River to supply bulk wholesome potable water to their consumers in compliance with the South African National Standard (SANS) 241:2015 for drinking water. The facility incorporates conventional and advanced treatment processes. The aims of the study were to identify how the water treatment processes of the plant have changed over time in response to the varying water quality of the Vaal River, and to consider both current and future obstacles as well as possible solutions regarding water quality and treatment. Oxidation steps such as pre-chlorination, potassium permanganate addition, pre-ozonation and intermediate ozonation have either been applied in the past or are still operational. The dissolved air flotation plant accounts for almost 70% of total chlorophyll removal and the significance of this process was confirmed during a brief maintenance shutdown during 2015. Total chlorophyll concentrations of the source water have increased extensively since 1984, while turbidity levels have remained fairly constant but with spikes at times. The facility suffers from severe taste and odour episodes during warm periods due to the presence of methylisoborneol (MIB), released by Cyanophyceae, in the Vaal River. Concentrations of > 300 ng/L MIB have been recorded, whereas the odour threshold concentration for MIB ranges from 4 ng/L to 20 ng/L. The additional application of activated carbon to alleviate taste and odour problems has to be weighed against the cost implications for consumers, the correct type to be purchased for the organic molecules to be adsorbed, the interference of natural organic matter, and the formation of additional sludge mass, as well as the intensity and duration of taste and odour events. Midvaal remains a bulk potable water supplier and therefore has to consider the socio-economic status of their consumers where water pricing is concerned. The study ultimately emphasized the intrinsic value of protecting water resources.

Keywords: oxidation processes, dissolved air flotation, chlorophyll *a*, taste and odour

INTRODUCTION

The erstwhile Western Transvaal Regional Water Company was established in 1954 to address the drinking water needs of various mining companies at the time. The company is situated in the North West Province of South Africa on the banks of the Middle Vaal River, close to the small town of Stilfontein. The name was changed to Midvaal Water Company in 1998, with the new name derived from its location. Midvaal Water Company supplies bulk potable water to the local municipality, Vierfontein, and the mining industry in the surrounding area. The local municipality is the City of Matlosana Municipality which serves the towns of Klerksdorp, Orkney, Stilfontein and Hartbeesfontein (the KOSH area), which includes approximately 500 000 consumers. Vierfontein, in the Free State Province, has about 1 500 consumers. Anglogold Ashanti represents the majority of the mining industry in the area and is also responsible for the company Mine Waste Solutions which deals with tailing storage facilities reclamation. The 1 120 km long Vaal River originates in the Mpumalanga Province of South Africa and is both heavily used and polluted by the time it passes the treatment works close to Stilfontein. The hypertrophic water from the Vaal River serves as their only water source and is purified by means of various conventional (coagulation and flocculation, sedimentation, filtration and disinfection) and advanced treatment processes (dissolved air flotation (DAF) and ozonation) prior to distribution.

The first aim of this study was to identify the prior objectives, criteria and indicators of water treatment for Midvaal Water Company, and to show how the water treatment processes of the plant have changed over time to adapt to the varying water quality of the Vaal River. The second aim was to consider both current and future concerns and possible solutions regarding water quality and treatment.

METHODS

The study site is situated 14 km from Stilfontein, at 26°55'59.3" S and 26°47'51.8" E. Vaal River water quality data were available from 1984 and operational data were available from 2010. Water treatment at Midvaal Water Company currently consists of the following processes which have been implemented since 2007 (see Fig. 1 and Table 1):

1. Abstraction from source (Middle Vaal River) at intake tower
2. Pre-ozonation
3. Primary addition of water treatment chemicals for coagulation and flocculation.
   A combination of all or some of the following chemicals are used in this process depending on the water quality: lime, ferric chloride, polyelectrolyte and aluminium sulphate
4. Dissolved air flotation (DAF)
5. Intermediate ozonation
6. Secondary addition of water treatment chemicals (optional).
   A combination of all or some of the following chemicals are

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used in this process depending on the water quality: lime, ferric chloride, polyelectrolyte, aluminium sulphate and powdered activated carbon (PAC)

7. Sedimentation
8. Filtration
9. Disinfection by means of chlorine gas
10. Pump station for distribution of the final water to 11 reservoirs in the Klerksdorp, Orkney, Stilfontein and Hartbeesfontein (KOSH) area and Vierfontein

The following analytical activities were performed by Midvaal Water Company Scientific Services, which was established in the 1970s and has been an accredited SANAS Testing Laboratory since 2002 based on ISO 17025.The source water database dates back to 1984. Operational data have been captured on the Laboratory Information Management System (LIMS) since 2010:

• ph	Determined with an electrode since 1984
• Electrical conductivity	Determined with an electrode since 1984
• Turbidity	Determined with a turbidity meter since 1984
• Total chlorophyll	Determined by means of the Sartory (Swanepoel et al., 2008) extraction method since 1984
• Chlorophyll-*a*	Determined be means of an in-house extraction method since 2006
• Manganese	Determined since 1984 by means of atomic absorption spectros copy and inductively coupled plasma optical emission spectroscopy
• Iron	Determined since 1984 by means of atomic absorption spectroscopy and inductively coupled plasma optical emission spectroscopy
• Colour	Determined with a colorimeter since 1989
• Nitrate and nitrite	Determined by means of a colorimetric method since 1984
• Orthophosphate	Determined by means of a colorimetric method since 1984

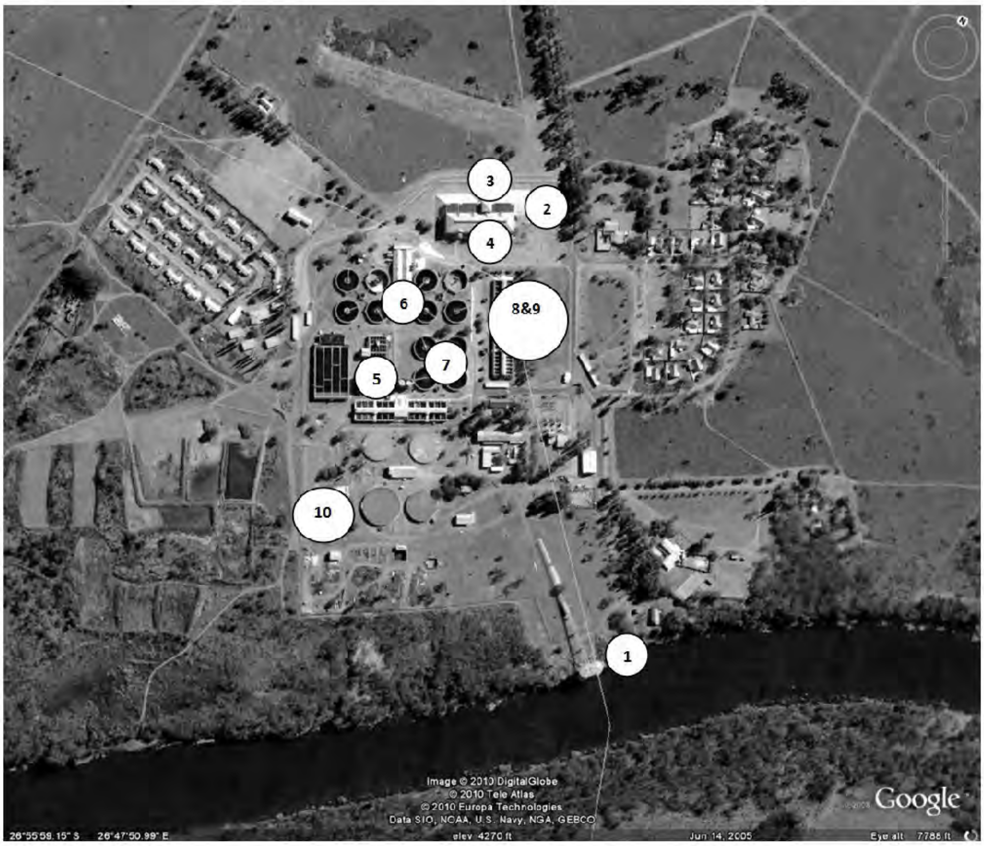

Figure 1

An aerial view of Midvaal Water Company. The treatment plant abstracts on average 130 ML /day, has a capacity to treat 320 ML /day and has a supply area that extends over more than a 1 000 km²^2.

Samples are submitted to Rand Water Scientific Services for the analyses of geosmin and MIB when taste and odour problems occur. Rand Water makes use of the purge-and-trap system coupled to gas chromatography–mass spectrometry in order to determine these taste and odour compounds.

Statistica (Version 13) software was used to determine differences between the different datasets. The Shapiro Wilks test for normality was used to determine if the datasets were distributed parametrically. The data did not meet the assumptions of normality in the distribution of all variables. Therefore the Kruskal-Wallis ANOVA (non-parametric data) for comparing multiple independent samples was used to determine differences between the different periods of treatment changes. This software package was also used to determine descriptive statistics for all variables as well as to create the scatterplots.

RESULTS

How the water treatment processes at Midvaal Water Company have changed to adapt to the varying water quality of the Vaal River

Water treatment concerns for Midvaal Water Company: Water quality of the source water

Table 1 indicates how the water treatment processes of the plant have been changed over time in order to address treatment problems encountered due to varying source water quality over a timeline of 53 years. To summarise changes in source water quality, the data available from 1984 until the end of 2014 were grouped into 4 time periods which match significant changes in water treatment:

Group 1: 1984–1991
Group 2: 1992–1996
Group 3: 1997–2006
Group 4: 2007–2014

The mean manganese concentrations declined over time (Fig. 2). This decrease may be ascribed to the enforcement of the National Environmental Management Act of 1998 (Act No. 107 of 1998) (RSA, 1998a) as well as the National Water Act of 1998 (Act No. 36 of 1998) (RSA, 1998b). Interventions by mining companies to comply with regulations resulted in diminishing pollution of underground water that feeds the source. Since 2007 the manganese concentration has no longer posed any concerns to the treatment process.

The turbidity of the source water fluctuates continuously (Fig. 2), and it is the extreme and unexpected spikes that are cause for concern, considering that a maximum value of 1 226 NTU has been recorded (Fig. 3).The water source is a river and rainfall patterns in the catchment, influenced by the effects of climate change, will in future continue to contribute to unpredictable spikes in turbidity levels.

As seen in Fig. 2 and Fig. 3, the total chlorophyll concentrations remain on the increase and subsequently result in an increase in pH levels as carbon dioxide is consumed by more algal cells during photosynthesis.

The mean orthophosphate concentration shows a gradual increase from Group 2 (1992–2006) to Group 3 (1997–2006) to Group 4 (2007–2014) (Fig. 2). The mean nitrate and nitrite concentrations show an increase between Group 3 (1997–2006) and Group 4 (2007–2014) (Fig. 2). Therefore these nutrients will continue to sustain algal growth in the source water.

It appears from Fig. 3 that the presence of algae and the subsequent total chlorophyll concentrations will continue to increase in future, increasing the risk for colour, taste and odour episodes. Higher algal concentrations in the source water, as well as increased spikes in turbidity levels, will ultimately put more pressure on the existing treatment processes, similar to when the DAF process was temporarily out of order from 14 February 2015 to 6 March 2015.

Hudson (2015) conducted a study from January 2010 to December 2011 and determined an average geosmin concentration of 4.083 ng/L (< 5 ng/L) for the Middle Vaal River.

TABLE 1
A summary of the water treatment process train at Midvaal Water Company from 1954–2015

Process	Plant 1954	Plant 1978	Plant 1980	Plant 1985	Plant 1992	Plant 1997	Plant 2007-2015	Treatment objective
Abstraction	✓	✓	✓	✓	✓	✓	✓	
Pre-chlorination		✓	✓	✓				Removal of algal related problems e.g. colour and filter capacity
Pre-ozonation				✓	✓		✓	Improve colour & oxidise manganese, iron and total chlorophyll (1985–1997) Enhance algal removal by DAF (2007)
Primary addition of chemicals	✓	✓	✓	✓	✓	✓	✓	Coagulation and flocculation to remove turbidity/suspended matter
$KMnO_4$ oxidation			✓	✓				Manganese removal
Dissolved air flotation						✓	✓	Separation and removal of light particulate matter and algae
Intermediate ozonation						✓	✓	Manganese & iron removal, colour, taste and odour improvement
Secondary addition of chemicals						✓	✓	Flocculation of particulate matter/solids after the oxidation step
Sedimentation	✓	✓	✓	✓	✓	✓	✓	Separation of solids from water
Filtration	✓	✓	✓	✓	✓	✓	✓	Removal of remaining particulate matter and removal of micro-organisms which might pose a health risk
Disinfection	✓	✓	✓	✓	✓	✓	✓	Pathogen removal

Studies by Morrison (2009) and Hudson (2015) stated that Chlorophyceae and Bacillariophyceae are the dominant algal classes in the Middle Vaal River. *Planktothrix sp.* is usually identified in the raw water during taste and odour episodes. The MIB concentrations indicated in Table 2 confirms that taste and odour problems mostly occur during the months of January, February and March, and also indicates an increase in the frequency of taste and odour problems.

Water quality and the use of oxidants

The treatment processes including oxidants have varied over time to adapt to the ever-changing quality of the source water as well as to ensure optimal, cost-effective operations (Table 1).

Consumer complaints in the late 1970s about brown stains on bathtubs as well as on laundry treated with household bleach lead to the discovery of high and fluctuating concentrations of

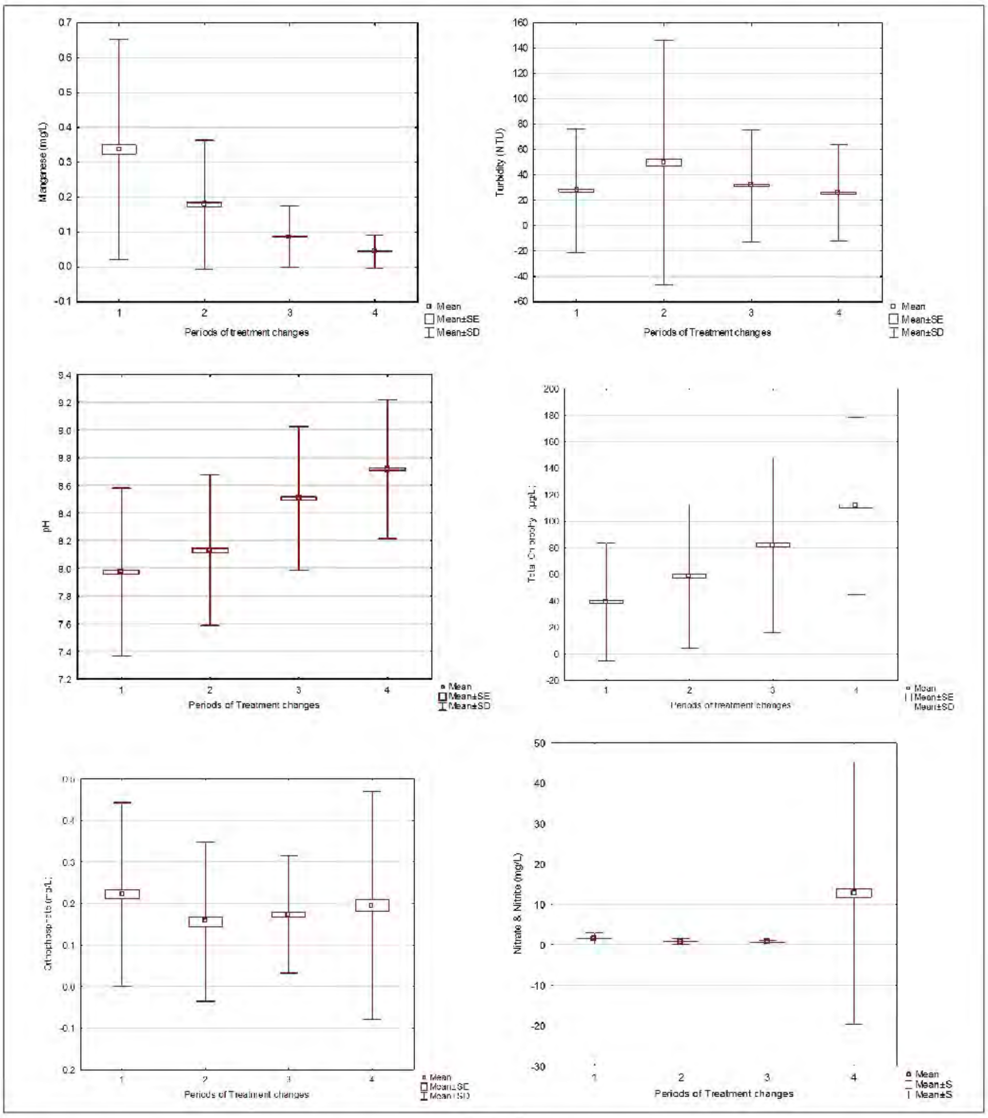

Figure 2

Box and whisker plots that compare means, standard errors (SE) and standard deviations (SD) for manganese, turbidity, pH, total chlorophyll, orthophosphate and nitrate and nitrite values of the source water from 1984 till the end of 2014 for Group 1 (1984–1991), Group 2 (1992–1996), Group 3 (1997–2006) and Group 4 (2007–2014) dissolved manganese in the source water. The average manganese concentration in the source water from 1984–1992 was 0.34 mg/L (±0.3), which ranged from a minimum of 0.01 mg/L to a maximum of 2.84 mg/L. De-stratification of the source water during windy conditions resulted in isolated peak manganese concentrations ranging from 4 mg/L to 8 mg/L at times. An oxidation step using potassium permanganate was implemented from **1980–1992** for the removal of manganese and ± 1.2 mg/L was dosed with other water treatment chemicals after pre-chlorination and the addition of lime. Manganese concentrations below ± 1.5 mg/L could successfully be removed with the potassium permanganate. For higher concentrations, the required dose resulted in the treated product having a brown/purplish colour; structures that came into contact with it were stained and a manganous oxide layer formed on filter sand. The manganese was bound in tough organic complexes and a more powerful oxidation was required.

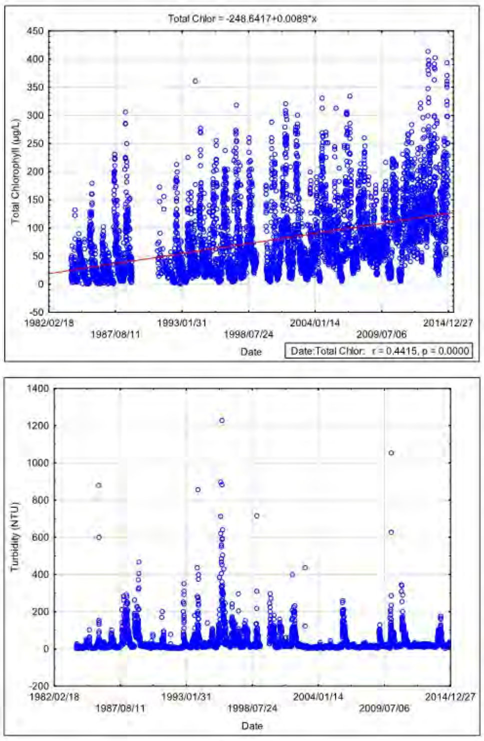

Figure 3

Scatter plots for total chlorophyll concentrations in the source water, which increased significantly (r = 0.4415 and n = 6268) and for turbidity levels (r = −0.0445 and n = 7 830), showing extremely high turbidity spikes at times

TABLE 2
A summary of geosmin and MIB concentrations in the source water from 2004 when Midvaal Water Company began to experience taste and odour incidents

Date	Geosmin (ng/L)	MIB (ng/L)
2004/01/23	36.4	51.9
2012/01/09	<6	255
2012/01/10	<6	335
2012/01/25	19	325
2012/02/09	<6	27
2012/03/02	<6	125
2012/03/05	<6	130
2013/02/04	5.8	20
2015/01/19	<5	245
2015/02/02	<5	28

A pre-chlorination step was implemented from **1978–1992** to alleviate colour problems and filter blockages caused by high total chlorophyll concentrations in the source water. The total chlorophyll concentrations in the source water increased progressively (see Fig. 3) as maximum total chlorophyll concentrations of 132 µg/L, 179 µg/L, 230 µg/L and 305 µg/L were recorded in 1984, 1985, 1987 and 1988, respectively. The pre-chlorination dosages ranged from 1.5 mg/L to 5 mg/L at the time and were positioned after the source water abstraction and prior to the addition of other water treatment chemicals.

In order to try to address these problems with manganese and high chlorophyll concentrations it was decided to add an advanced treatment process in the form of pre-ozonation. The configuration of the plant allowed for a pre-chlorination line (east) and a pre-ozonation line (west) to be separated from the point of abstraction up to the filtration process. A pre-ozonation step was implemented from **1985–1997** as this powerful oxidant could improve the colour of the water and also address the manganese, iron and total chlorophyll problems. Pre-ozone was dosed at ± 2.5 mg/L with a contact time of 4 min. The effectiveness of these two oxidants was compared from **1985–1992**, as far as the removal of total chlorophyll, manganese and iron were concerned. The effect of the pre-chlorination was found to be different for each algal species and, as the algal composition of the source water varies seasonally, the effectiveness of pre-chlorination was therefore inconsistent and unreliable. The colour removal also showed limited success. Ozone clearly proved to be more effective and the decision was made to terminate pre-chlorination and utilise pre-ozonation only, as from **1992–1997** (Krüger et al., 2006).

Water quality and the combined use of oxidants and dissolved air flotation

A dissolved air flotation (DAF) plant was implemented in **1997** as a first treatment step to address the high algal load present in the Vaal River and the inability of conventional water treatment methods to remove algae effectively. The pre-ozonation was redirected to an intermediate ozonation step, after DAF and prior to sedimentation. Intermediate ozonation dosages of ±1.8 mg/L to 2.5 mg/L together with the DAF resulted in favourable removal of total chlorophyll, iron, manganese, micro-organisms and colour. The removal of taste and odour compounds, mainly MIB, has however not been desirable at these ozone dosages but a significant saving in other water treatment chemicals (± 30%) was achieved by the application of DAF and intermediate ozone. The ferric chloride and chlorine demand decreased because less suspended matter had to be flocculated during the sedimentation process and some disinfection had already taken place with ozonation. The disinfection demand after filtration was collectively reduced by both pre-ozonation and intermediate ozonation as ozone is a more powerful oxidant than chlorine; however ozone fails to provide a residual disinfectant concentration which is possible with the use of chlorine.

A case study was conducted by Morrison (2009) from October 2007 to September 2008 to determine the influence of ozone on water purification processes. The average total chlorophyll concentration of the source water during the study was 104 µg/L, reduced to 32 µg/L after DAF (69% removal) and further reduced to 27 µg/L after intermediate ozonation (an additional 5% removal). The average manganese and iron concentrations of the source water during the study were 0.05 mg/L and 0.02 mg/L, respectively, and even though there was no cause for concern the manganese and iron concentration averages as well as concentration ranges decreased after the intermediate ozonation process.

Dissolved air flotation is an advanced water treatment process whereby small air bubbles are introduced to the water after the primary addition of water treatment chemicals for coagulation and flocculation (Table 3). The air bubbles attach to the flocs (containing organic material and algae) and rise to the water surface where the froth is collected and removed. Heavier particles settle to the bottom of the flotation units as sludge.

A pre-ozonation step, prior to the DAF, was implemented in **2007**. Pre-ozone is currently dosed at a range from 1 mg/L to 1.5 mg/L with a contact time of 2 min in order to enhance the DAF, and intermediate ozone dosages of 2.5 mg/L with a contact time of 4 min are maintained. Pre-ozonation enhances the DAF process by inactivating algal cells and does not necessarily reduce total chlorophyll concentrations of the source water immediately, as was confirmed by Morrison et al. (2012).

Temporary shutdown of the DAF and the effects thereof

The DAF process together with the pre-ozonation process was out of operation from 14 February 2015 up to 6 March 2015 due to maintenance on the DAF plant. During this period flocculated material had to be removed in the conventional clarifiers by means of settling. The effect was evident in the higher turbidity levels in the four Midvaal reservoirs as well as the final water (Fig. 4). The turbidity of the final water did however comply with the limit of ≤1 NTU during the DAF shutdown, but more pressure was placed on the other treatment processes during this period. Higher turbidity levels added to other treatment problems on the plant, e.g., shorter filter runs, increased backwashing, the generation of larger volumes of wastewater and a higher demand for water treatment chemicals and energy. The usage of chlorine gas increased by about 30% during the DAF shutdown whiles the requirement for flocculants increased by 15%. In spite of the additional chemical additions, the average turbidity of the final water 3 months before the DAF shutdown could not be maintained (Fig. 4). Figure 5 shows improved total chlorophyll removal in 3 Midvaal reservoirs as well as the final water after maintenance had been completed.

Operational monitoring at Midvaal Water Company: Water quality of the various processes

Midvaal Water Company uses pH, electrical conductivity, turbidity and total chlorophyll as operational indicators to monitor the effectiveness of the various treatment processes. The average total chlorophyll concentrations after pre-ozonation, before flotation and after chemical dosing are higher than the average total chlorophyll concentration of the source water (Table 4). This could possibly be the result of lyses of algal cell material due to damaged algal cell walls combined with a reaction between the source water and the ozone and chemicals. It is also difficult to ensure that samples are always homogenous and representative of the source water. In water treatment the desired outcome is often not immediately evident as the cumulative effects are only visible right at the end of the treatment train.

TABLE 3
Design specifications of the DAF plant (Midvaal Water Company, 2014)

Parameter	**Specification**
Design	Modular, 5 x 50 ML/day units
Capacity	250 ML/day
Retention time	± 1 h
Recycle stream	7 to 10% v/v
Bubble size	0.5 mm
Pressure vessels	500 kPa
Sludge concentration	1.5 to 2%
Flocculation method	Serpentine channels; adjustable outlets
Air:water ratio	1:1

The SANS 241: 2015 (SABS, 2015) requires the pH to range from ≥ 5 to ≤ 9.7 pH units, electrical conductivity at 25°C to be ≤ 170 mS/m and turbidity to be ≤ 1 NTU and ≤ 5 NTU for operational and aesthetic risks, respectively. Midvaal aims for the pH to range from 7.8 to 8.1 pH units, as the efficacy of chlorine as a disinfectant decreases when pH increases above pH 8.0. The average electrical conductivity (60 mS/m) and turbidity (0.5 NTU) of the final water, as indicated in Table 4, comply with the national limits. Even though there is no national limit for total chlorophyll, Midvaal has an internal limit of ≤ 1.0 µg/L in the final water which was also met with an average of 0.55 µg/L according to Table 4.

DISCUSSION

Algal assemblages and spikes in turbidity levels seem to be the greatest water quality concerns for Midvaal Water Company. Unacceptably high pH levels (Fig. 2), which affect treatment processes and influence scaling properties of the final water, are attributed to the excessive algal activity and are intensified during periods of low rainfall. Untreated or partially treated sewage effluents and over-fertilised agricultural runoff contribute to the nutrient load of the Vaal River. Due to this nutrient enrichment, the only source of drinking water for consumers in this area of supply is a hypertrophic water body. However, nutrient concentrations do not appear to be a cause for concern as such, but result in high algal activity which confirms the presence of nutrients. Increasing total chlorophyll concentrations also hold a threat for taste, odour and colour problems. The abundance of Cyanophyceae species and higher microcystin levels in the source water of the Rand Water Barrage (Hudson, 2015) pose a risk for Midvaal Water Company as the point of abstraction is situated downstream of Rand Water Barrage. Not only is Midvaal at risk for taste and odour problems but consumers will perceive the drinking water as unsafe. SANS 241: 2015 regulates that water services institutions shall use a risk-based management approach to ensure that safe drinking water is produced at all times and that public health is protected.

Conventional water treatment processes are simply not adequate to supply safe and healthy drinking water anymore when the source water is heavily polluted. DAF and ozonation are absolutely essential water treatment processes at Midvaal Water Company. This was confirmed by elevated total chlorophyll

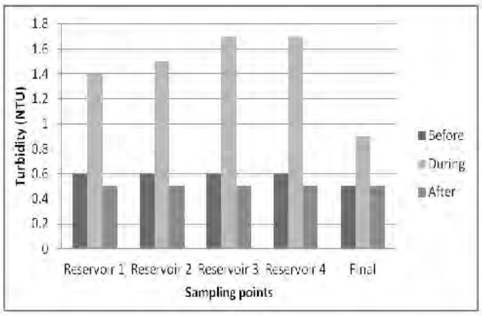

Figure 4

The average turbidity levels 3 months before, during and 3 months after the DAF shutdown for 4 Midvaal reservoirs, and for the final water

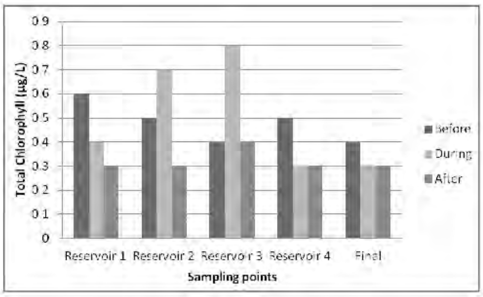

Figure 5

The average total chlorophyll concentrations 3 months before, during and 3 months after the DAF shutdown for 4 Midvaal reservoirs, and for the final water

TABLE 4
The average concentrations for pH, electrical conductivity, turbidity, total chlorophyll, manganese, iron and colour indicate the effectiveness of the various water treatment steps from 2010–2014(± standard deviation)

Processes/ Sampling points	pH	Electrical conductivity (mS/m)	Turbidity (NTU)	Total chlorophyll (µg/L)	Manganese (mg/L)	Iron (mg/L)	Colour (mg/L)
Source	8.76 (±0.53)	57 (±15)	30 (±44)	127 (±72)	0.04 (±0.04)	0.12 (±0.29)	119 (±96)
After pre-ozonation	8.82 (±0.49)	58 (±14)	30 (±42)	122 (±72)	-	-	-
Before flotation	8.80 (±0.48)	58 (±14)	32 (±43)	145 (±70)	-	-	-
After chemical dosing	8.94 (±0.46)	59 (±13)	33 (±42)	138 (±79)	-	-	-
After flotation	8.82 (±0.45)	59 (±14)	12 (±25)	39.86 (±35.97)	-	-	-
After intermediate ozonation	8.61 (±0.49)	61 (±13)	14 (±24)	39.48 (±31.40)	0.03 (±0.04)	0.05 (±0.09)	-
After settling	8.55 (±0.47)	60 (±13)	3.3 (±4.0)	15.33 (±42.67)	-	-	-
After filtration	8.17 (±0.43)	62 (±17)	0.6 (±0.9)	1.64 (±4.5)	-	-	-
Storage	8.20 (±0.39)	60 (±13)	0.5 (±0.9)	0.81 (±5.1)	-	-	-
Final after pump station	8.23 (±0.39)	60 (±13)	0.5 (±0.2)	0.55 (±0.6)	0.02 (±0.02)	0.03 (±0.03)	2.65 (±0.8)

concentrations and turbidity levels when the DAF was temporarily out of operation (Figs 4 and 5). Pantelić et al. (2013) emphasized the importance of removing cyanobacteria without cell lysis and subsequent release of intracellular metabolites, thereby confirming the value of a DAF process at Midvaal Water Company. The difference in colour of the final water is also noticeable during ozone plant shutdowns. The water treatment processes of the Midvaal plant have adapted successfully to the varying water quality of their source water, as compliance with SANS 241: 2015 (SABS, 2015) proves. Climate change has, however, resulted in dry periods being experienced regularly during recent years, as well as occasional floods causing spikes in turbidity levels and, together with the increase in total chlorophyll concentrations, Midvaal would most probably be required to consider additional treatment processes to ensure continued compliance with the required standard.

Powdered activated carbon (PAC) could be dosed at the secondary chemicals addition point and removed at the sedimentation stage. The application of activated carbon to alleviate taste and odour problems has to be weighed against the cost implications for the consumers, the correct type to be purchased for the organic molecules to be adsorbed, the interference of natural organic matter (NOM) and formation of additional sludge mass, as well as the intensity and duration of taste and odour episodes. Srinivasan and Sorial (2011) refers to the optimisation of GAC (granular activated carbon)/PAC adsorption but the sporadic and seasonal taste and odour events at Midvaal Water Company do not allow for frequent monitoring of geosmin and MIB concentrations present in the influent, and prevent proper research on the application of (GAC)/PAC adsorption, or any other advanced process, in this regard.

Advanced oxidation processes (AOPs) in drinking water are used to degrade primarily organic chemical contaminants, e.g., taste- and odour-causing compounds (Linden and Mohseni, 2014). Ozone and ultraviolet (UV) light constitute the main AOPs and are increasingly being used at a large scale for the degradation of contaminants in water and wastewater (Linden and Mohseni, 2014). Wang et al. (2015) compared UV/chlorine to UV/hydrogen peroxide (H_2O_2) at various pH concentrations, as UV/H_2O_2 is becoming more popular. Approximately 20% and 10% of spiked geosmin and MIB, respectively, were destroyed by UV exposure alone and when an AOP was applied, geosmin and MIB destruction was increased because of the additional hydroxyl radical oxidation (Wang et al., 2015). The UV/H_2O_2 process is used at the City of Cornwall Water Purification Plant (Ontario, Canada) for the control of seasonal taste and odour events that occur in late summer, but this process does also pose operational problems (Wang et al., 2015). Similar to GAC adsorption, presence of NOM in water can influence AOPs as well (Srinivasan and Sorial, 2011). According to Srinivasan and Sorial (2011), the capital and operating costs associated with these AOPs can be significantly high, especially at the higher dosages required for MIB/geosmin removal, and they could also result in the formation of disinfection by-products which could be of health or regulatory concerns. Zong et al. (2015) established that chlorination was an effective treatment option for removing microcystin but it is important for water suppliers to be aware of the secondary pollution of microcystin-associated disinfection by-products.

More research is required on the use of ultra-filtration for treatment of taste and odour problems at drinking water treatment plants, as very few research results were available on this advanced treatment process for this case study. Currently Midvaal Water Company should ensure that MIB/geosmin is not produced or intensified on-site. Srinivasan and Sorial (2011) stated that although some technologies are more effective and applicable than the others, a completely accepted technology that could be used in any drinking water treatment facility still does not exist. The odour threshold concentration for MIB/geosmin ranges from 4 ng/L to 20 ng/L (Srinivasan and Sorial, 2011) and the treatment of these taste and odour compounds is only required at Midvaal Water Company during increased concentrations called outbreaks.

The recommended process, or perhaps combination of technologies, would therefore be expected to deal with concentrations which have been recorded as greater than 300 ng/L MIB (Table 2) at times, and even if 80% removal of MIB could be achieved on a source water concentration of 150 ng/L this would still result in a MIB concentration which exceeds the odour threshold concentration. Srinivasan and Sorial (2011) stated that current practice most commonly followed is application of PAC during severe taste and odour outbreaks which is similar to the current situation at Midvaal Water Company. Srinivasan and Sorial (2011) also confirm the view of this case study when it concludes that it would not be economical or practical for water treatment facilities to install a technology exclusively for treatment of MIB/geosmin, but should rather optimise the technology they are currently using for MIB/geosmin treatment. Midvaal Water Company remains a bulk potable water supplier and therefore has to consider the socio-economic status of their consumers where water pricing is concerned, as any additional advanced treatment steps will increase costs. The availability of accurate information and communication with consumers during taste and odour episodes remains imperative for Midvaal Water Company as they have managed to supply wholesome drinking water for many years in spite of the ever increasing pollution of the source, the Vaal River.

CONCLUSION

The quality of the already hypertrophic source water seems to deteriorate continuously but until now Midvaal Water Company has managed to treat the water successfully, with ozone and dissolved air flotation being key processes. The need for more advanced and expensive processes does however seem to be inevitable in order to maintain final water quality in future, but to consider cost implications for consumers during challenging economic times remains a concern.

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ANNEXURE B

Scientific Research Publishing

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Evaluation and Impact of a Polluted Stream on the Integrated Management of a Drinking Water Resource: A Case Study of the Middle Vaal River, South Africa

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Abstract

The Koekemoerspruit is a possible pollution source of the Middle Vaal River, an important drinking water source in South Africa. This case study aimed to establish the water quality of the Koekemoerspruit, to evaluate the impact of the Koekemoerspruit on the Vaal River, and to use this information to identify shortcomings in the monitoring program. Monthly and weekly samples from both the Vaal River and the Koekemoerspruit were analyzed at an accredited testing laboratory based on ISO 17025 for 20 chemical methods. A dataset from 2002 to 2015 was statistically analyzed by means of Statistica software, the Mann-Kendall test and the Sens's slope to determine descriptive statistics and significant trends respectively. The sites' water quality was evaluated by comparison with both national drinking water standards and environmental target water quality objectives. Results indicated that the target water quality objectives for orthophosphate, nitrate and nitrite, and ammonia concentrations were considerably exceeded in the Koekemoerspruit. The drinking water quality of the Koekemoerspruit and the Middle Vaal was noncompliant with South African standards. Color, electrical conductivity, turbidity, sulfate, recoverable cyanide and arsenic at one site posed aesthetic, operational, acute and chronic health risks. Color, mean ammonia and total chlorophyll concentrations displayed significant trends of increase over time and increased drastically after 2012 at the site where water enters the Middle Vaal River. However, the Koekemoerspruit did not seem to have a significant impact on the overall water quality of the Middle Vaal River, except for total chlorophyll concentrations. Moreover, the review and recommendations for optimizing the water quality monitoring program proved that original monitoring objectives have been achieved. The reviewed monitoring program has consequently been adopted in the water safety plan to address the shortcomings that were identified during this case study.

Keywords

Target Water Quality, Eutrophication, Domestic Wastewater, Mining, Pollution

1. Introduction

A healthy river ecosystem is an essential resource for surrounding communities in terms of drinking water, agriculture, and industries. Therefore, Integrated Water Resources Management (IWRM) was introduced to improve management of the physical environment and its use by the different water divisions [1]. IWRM has to take into account both economic benefits and ecological concerns [2]. In this respect, IWRM succeeds in satisfying present needs and usually does not consider future changes. Environmental monitoring is essential for detecting water quality and land use changes as well as associated pollution sources and other stressors, such as climate change. Monitoring is also needed to evaluate the effects of proposed environmental policies and resource use and management strategies [3]. Water related problems are better understood and controlled through the early detection and increased knowledge of the environment. During this study we used Midvaal Water Company in South Africa (a water treatment plant that supplies bulk potable water from the Middle Vaal River to 501 500 consumers), as a case study to show how changes in surface water stressors due to changes in land use and socio-economic issues can impact on the challenge of providing safe drinking water.

According to Reference [4], water quality monitoring is the "long-term, standardized measurement and observation of the aquatic environment in order to define status and trends." South Africa has overarching national legislation to enforce a nationally coordinated framework for monitoring, assessing and reporting on resource water quality [5] [6]. This is of particular importance for multi-stressed rivers, like the Vaal River in South Africa, that serve as drinking water sources to many. The Koekemoerspruit is a polluted water resource that can impact on the Middle Vaal River system. The Koekemoerspruit has not only been affected by mining and municipal/urban village developments but also by agriculture. Nutrient enrichment and salinity, as a result of urbanization and gold mining, has been known to contribute to most of the deterioration of the water quality in the Koekemoerspruit. Thus the inflow of the highly utilized and impacted Koekemoerspruit into the Vaal River, upstream of the Midvaal Water Company's abstraction point from the Vaal River, is regarded as a possible pollution threat. The monitoring objectives since 2002 have been to determine the water quality of the Koekemoerspruit by means of collecting water quality data. In 2015, the costs of the abovementioned monitoring programs amounted to

ZAR 4985200 (USD 363421), of which ZAR 65150 (USD 4749) (1.3% of the total amount) was spent on analytical costs for monitoring the Koekemoerspruit. The existing monitoring program was reviewed and improved after verification to see if the initial monitoring objectives have been met and whether additional monitoring objectives need to be addressed. The statistical methodology applied during this case study (mainly comparisons of descriptive statistics and determination of trends) is fairly easy to use and readily available in the hope that our study might serve as an example to other facilities and enable sensible but practical evaluation and monitoring of water quality to promote integrated water resource management, especially for water services providers and authorities in developing parts of South Africa.

As Midvaal Water Company has to consider the stressed socioeconomic status of their consumers regarding water tariffs, cost-effective monitoring and managing of the water resource is of the essence. In view of these constraints the water quality in Koekemoerspruit has been investigated as possible source of pollution to determine: 1) changing trends in the data and to identify parameters that were beyond reference limits, 2) its impacts on the water quality of the Middle Vaal River, and 3) to identify possible shortcomings in the monitoring program.

2. Materials and Methods

2.1. Study Area

The Koekemoerspruit is a tributary of the Vaal River in the Middle Vaal Catchment area, South Africa. It originates from a natural underground source between the towns of Klerksdorp and Ventersdorp in the North-West Province and flows over a distance of approximately 50 km in a south-south-westerly direction into the Vaal River about 1.6 km upstream of Midvaal Water Company's abstraction point. The Koekemoerspruit's embankments and flood plains are almost completely covered with *Phragmites australis*, a perennial reed. The study area occurs in the summer (December to January) rainfall region of the country and an average annual rainfall of 684 mm was recorded during the study period. The groundwater of the Koekemoerspruit area is easily polluted because of the permeability of the underlying dolomitic soils, which are prone to sinkhole formation. The Koekemoerspruit upstream of the study area is surrounded by closed goldmines and the urban village of Khuma, with a population of approximately 46,000 people. The study area covered the section of the Koekemoerspruit below Khuma up to the confluence with Vaal River, as well as sites upstream (at the Vermaasdrift bridge) and downstream (at the abstraction point of Midvaal Water Company) of the confluence in Vaal River. The land use of the study area is mostly natural land with some cultivation at the confluence (**Figure 1**).

The South African Government Gazette 39943 No. 469 [7] has divided the Middle Vaal Catchment into eight integrated units of analysis, subdivided into smaller resource units, to which classes and target water quality objectives have been assigned. The Vaal River main stem from Vermaasdrift to upstream of the

Schoonspruit confluence (downstream of Midvaal Water Company) has been classified as a Class III resource unit, with a largely modified present and recommended ecological state (Table 1). The Koekemoerspruit, from its origin to its confluence with the Vaal River, has also been classified as a Class III resource

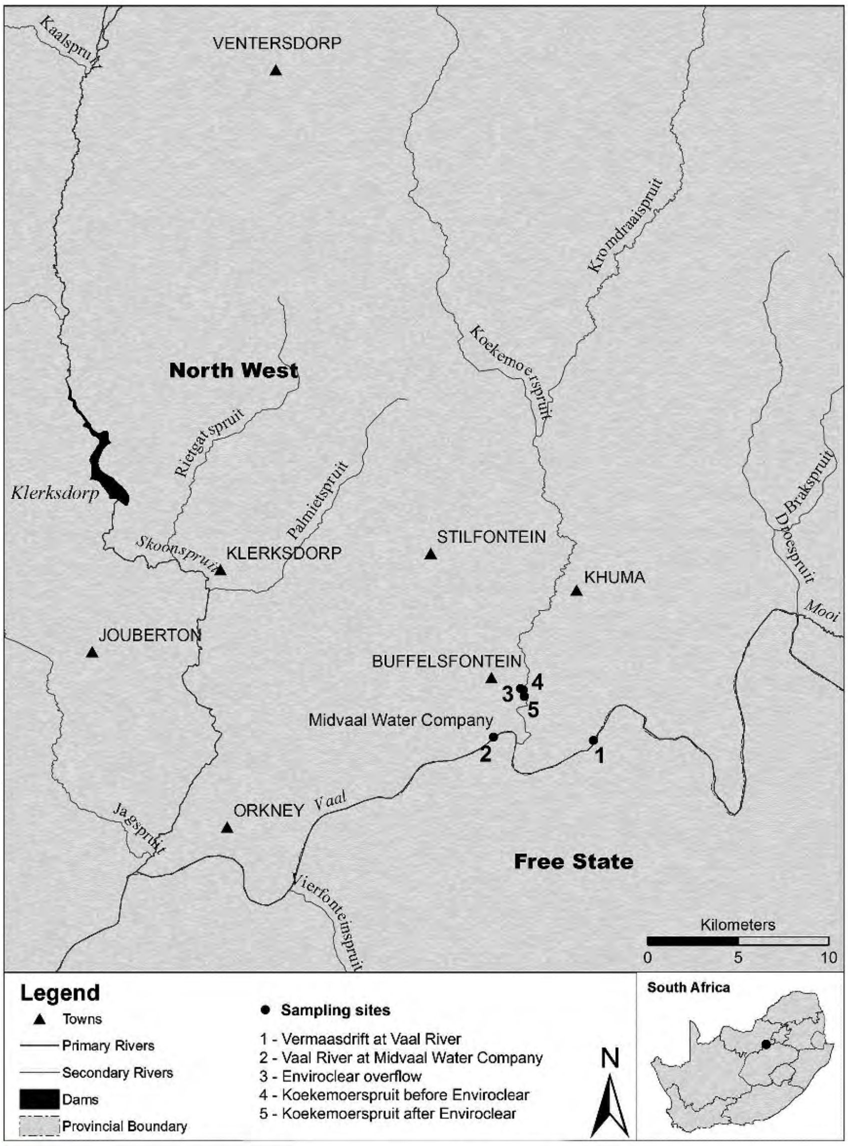

Figure 1. Koekemoerspruit study area indicating the five study sites, streams of the catchment and surrounding towns.

unit. This is the only resource unit in Government Gazette 39943 No. 469 [7] whose ecological state is required to be improved, from being seriously modified to being largely modified (**Table 1**).

2.2. Study Sites

Five study sites were identified at the onset of the water quality monitoring program in 2002 (**Table 2**, **Figure 1**).

2.3. Sampling Regime

Surface water samples were collected by Midvaal Water Company Scientific Services on a monthly basis at sites 1, 3, 4 and 5 and on a daily basis at site 2. Samples were chemically analyzed at Midvaal Water Company Scientific Services for 20 determinants as listed in **Table 3**. Midvaal Water Company Scientific Services has been an accredited South African National Accreditation System (SANAS) testing laboratory (T0132) since 2002 based on ISO 17025. Data from October 2002 to December 2015 were used for this study with the exception of data for uranium, which were collected since April 2005. The method numbers in **Table 3** refer to the SANAS accredited method as indicated on the facility's schedule of

Table 1. Resource unit classification and ecological state of the Vaal River main stem and Schoonspruit resource unit which incorporates the Koekemoerspruit [7].

Integrated unit of analysis	Vaal River	Schoonspruit
Resource unit	Vaal River main stem: from Vermaasdrift to upstream of the Schoonspruit confluence as represented by study sites 1 and 2	Koekemoerspruit: from origin to confluence with Vaal River as represented by study sites 3, 4 and 5
Water resource class	III: heavily used; overall ecological condition significantly altered from its predevelopment condition	III: heavily used; overall ecological condition significantly altered from predevelopment condition
Present ecological state	D: largely modified	D/E: largely modified/seriously modified
Recommended ecological state	D: largely modified	D: largely modified

Table 2. Study sites of the Koekemoerspruit water quality monitoring program.

Site number	Site name	Coordinates	Description
Site 1	Vermaasdrift	26˚56'10.3"S, 26˚51'00.8"E	Reference point to determine impacts of Koekemoerspruit on Vaal River; part of Middle Vaal, upstream of confluence of Koekemoerspruit and Vaal River.
Site 2	Vaal River	26˚56'04.5"S, 26˚48'01.4"E	Vaal River at Midvaal Water Company's abstraction point downstream of confluence of Koekemoerspruitand Vaal River. Water quality at this site is critical and determines water treatment processes and operations of Midvaal Water Company.
Site 3	Enviroclear overflow	26˚54'37.8"S, 26˚48'50.5"E	± 9 km cement canal downstream from site 4 flowing from nearby mining plant into Koekemoerspruit.
Site 4	Koekemoerspruit before Enviroclear overflow	26˚54'40.3"S, 26˚48'55.4"E	Koekemoerspruit from below Khuma urban village before inflow of canal; indicates influence of urban village.
Site 5	Koekemoerspruit after Enviroclear overflow	26˚54'51.7"S, 26˚48'57.0"E	Koekemoerspruit after confluence of canal with site 4; represents water that will enter Vaal River.

Table 3. Determinants monitored from October 2002 to December 2015. Method numbers marked with an (*) have not been accredited by SANAS.

	Determinant	Unit	Method	Method number
1	Aluminum	mg/L	Determined either by atomic absorption spectroscopy or inductively coupled plasma optical emission spectroscopy (ICP-OES)	ICP1
2	Arsenic			
3	Copper			
4	Iron			
5	Manganese			
6	Sodium			
7	Uranium			
8	Zinc			
9	Ammonia	mg/L	Determined by colorimetric method on a discrete analyser	GL 7-1
10	Chloride			GL 7-5
11	Nitrate and nitrite			GL 7-2
12	Sulfate			GL 7-4
13	Color	mg/L Pt	Determined with colorimeter	WL4*
14	Cyanide recoverable	mg/L	Determined by colorimetric method on a continuous flow analyser	CFA-1D*
15	Orthophosphate			CFA-1B*
16	Electrical conductivity	mS/m	Determined with electrode	WL2
17	pH	pH units	Determined with electrode	WL1
18	Total chlorophyll	µg/L	Determined by Sartory's extraction method [9]	AL2
19	Total organic carbon	mg/L	Determined by a persulfate-ultraviolet oxidation method	AAL5
20	Turbidity	NTU	Determined with turbidity meter	WL3

accreditation [8].

2.4. Approach and Statistical Analyses

Statistica software (version 13) was used to determine the descriptive statistics (mean, standard deviation, variance and confidence interval) for all variables as prescribed and discussed by Reference [10] and to create scatter plots. The Shapiro-Wilks test for normality was used to determine whether the data were distributed parametrically. The data did not meet the assumptions of normality in the distribution of all variables. Therefore, the Kruskal-Wallis analysis of variance (nonparametric statistics) for comparing multiple independent groups was used to determine differences between concentrations of determinants measured at the different sampling sites. Results that were below the limit of quantification were divided by two to be included in data processing. Results that were above the limit of quantification were multiplied by two to be included in data processing.

A selection of two years (2014 and 2015) was made to evaluate the compliance of different variables with national drinking water standards and environmental target water quality objectives. These two years represented a normal rainfall year (2014) and a low rainfall year (2015). In order to ensure that variables are not removed prematurely after comparison with compliance criteria, the variance of the data collected at each site for each variable were determined [6]. No data were available on river flow of either the Koekemoerspruit or Vaal River. Therefore, the nonparametric Mann-Kendall test for testing the presence of a significant monotonic increasing or decreasing trends and Sen's nonparametric method for estimating the slope of a linear trend were used to discover long-term trends of discrete variables [11]. The analyses were performed with the Excel application MAKESENS 1.0 and the Mann-Kendall test and Sen's slope estimates for the trend of annual data with version 1.0 Freeware [12].

3. Results

3.1. Water Quality of the Koekemoerspruit

The compliance of the measured water quality determinants at sites 4 and 5 in the Koekemoerspruit with the target water quality objectives for this resource unit was evaluated using data obtained during 2014 and 2015 (**Table 4**) to highlight where limits have recently been exceeded. The National Department: Water and Sanitation, as the custodian of water resources, has decided after consultation with relevant stakeholders and research institutions to implement the use of percentile limits for compliance monitoring. The rationale behind this is that the percentile limits give a more accurate reflection of the true situation and eliminates the effects of outliers. Seeing that the target water quality objectives are in many instances stricter than the drinking water limits. The percentile limits for orthophosphate, nitrate and nitrite, and ammonia concentrations were excessively exceeded at sites 4 and 5. The electrical conductivity, an indicator of salinization, did not comply with limits set for these sites, and the sulfate concentration of site 5 failed to comply with the set limit as well. Even though a target water

Table 4. Relevant 50th and 95th percentile water quality data for sites 4 and 5 from January 2014 to December 2015 compared with target water quality limits of Government Gazette 39943 No. 469 for the resource unit; noncompliances are shaded.

Quality subcomponent	Determinantindicator/measure	Unit	Limit	Percentile	Site 4	Site 5
Nutrients	Orthophosphate	mg/L	≤0.125	50th	3.322	3.929
	Nitrate and nitrite	mg/L	≤2.5	50th	0.61	0.65
	Nitrate and nitrite	mg/L	≤1.35	95th	5.64	7.2
Salts	Electrical conductivity	mS/m	≤85	95th	151	150
	Sulfate	mg/L	≤250	95th	236	257
Toxics	Cyanide (dissolved)	mg/L	≤0.05	95th	0.03	0.03
	Aluminum	mg/L	≤0.1	95th	0.04	0.06
	Manganese	mg/L	≤0.25	95th	0.78	0.82
	Iron	mg/L	≤0.25	95th	0.29	0.30
	Uranium	mg/L	≤0.03	95th	0.03	0.02
	Ammonia	mg/L	≤0.1	95th	55	52

quality objective for dissolved cyanide exists, only recoverable cyanide was monitored during this water quality monitoring program. The recoverable cyanide concentrations are included in Table 4 and compared with the target water quality objectives of dissolved cyanide. However, since these concentrations are expected to be higher than those of dissolved cyanide, the worst-case scenarios are portrayed. The 95th percentile manganese and iron concentrations failed to comply with the set limits; in comparison manganese exceeded the limit to a much greater extent.

The water quality compliance of sites 3, 4 and 5 with the South African National Standards (SANS) [13] for drinking water 241:2015 was evaluated for 2014 and 2015 during this study to obtain a recent overview (Table 5). The

Table 5. Average values of water quality determinants measured at sites 3, 4, and 5 from January 2014 to December 2015 compared with the limits for drinking water as per South African National Standard 241:2015 [13]; shaded values indicate exceeded limits.

Determinant	Unit	Limits (associated risk)	Site 3	Site 4	Site 5
Color	mg/L Pt	≤15 (aesthetic)	22	98	97
pH	pH units	≥5.0 to ≤9.7(operational)	8.79	7.78	7.78
Electrical conductivity	mS/m	≤170(aesthetic)	209	124	124
Turbidity	NTU	≤1 (operational)	61	10.6	10.7
		≤5 (aesthetic)	61	10.6	10.7
Chloride	mg/L	-	150	106	106
Sulfate	mg/L	≤500 (acute health)	810	136	163
		≤250 (aesthetic)	810	136	163
Sodium	mg/L	≤200 (aesthetic)	183	87	86
Ammonia	mg/L	-	0.7	37	34
Nitrate and nitrite	mg/L	-	4.8	1.7	1.7
Orthophosphate	mg/L	-	0.12	3.79	4.00
Cyanide recoverable	mg/L	≤0.2 (acute health)	0.43	<0.02	<0.02
Total chlorophyll	μg/L	-	67	93	95
Iron	mg/L	≤2 (chronic health)	0.07	0.14	0.14
		≤0.3 (aesthetic)	0.07	0.14	0.14
Manganese	mg/L	≤0.4 (chronic health)	0.05	0.44	0.45
		≤0.1 (aesthetic)	0.05	0.44	0.45
Zinc	mg/L	≤5 (aesthetic)	0.03	0.03	0.03
Copper	mg/L	≤2 (chronic health)	0.03	<0.01	<0.01
Aluminum	mg/L	≤0.3 (operational)	0.04	0.06	0.06
Arsenic	mg/L	≤0.01 (chronic health)	0.02	<0.01	<0.01
Uranium	mg/L	≤0.03 (chronic health)	0.03	<0.01	0.01
Total organic carbon	mg/L	≤10 (chronic health)	6.2	13	12

noncompliant color, electrical conductivity, turbidity, sulfate, recoverable cyanide and arsenic concentrations of site 3 posed aesthetic, operational, and acute and chronic health risks. The noncompliant color, turbidity, manganese, and total organic carbon concentrations measured at sites 4 and 5 posed aesthetic, operational, and chronic health risks. The water sampled at sites 3, 4, and 5 in the Enviroclear overflow canal and Koekemoerspruit (**Table 5**) is not suitable for drinking purposes.

3.2. Impact of Koekemoerspruit on Water Quality of Middle Vaal River Source Water

The water quality compliance of sites 1 and 2 with target water quality objectives for the Vaal River main stem resource unit was also evaluated for 2014 and 2015 (**Table 6**). This was carried out to highlight limits that have been exceeded and to ascertain the impact of the Koekemoerspruit on the Vaal River. The Kruskal Wallis ANOVA (results not shown) indicated that the inflow of the Koekemoerspruit did not have an impact on the water quality of the Vaal River, irrespective of whether limits were exceeded, because none of the listed determinants displayed a significant increase from site 1 to site 2. Electrical conductivity, nitrate and nitrite, sulfate, iron, and ammonia contents were of concern for both the Vaal River (**Table 6**) and the Koekemoerspruit (**Table 4**). Although orthophosphate and manganese were identified as concerns for the Koekemoerspruit (**Table 4**), levels of these determinants complied with limits set for the Vaal River (**Table 6**). Aluminum content and

Table 6. Relevant 50th and 95th percentile data for sites 1 and 2 from January 2014 to December 2015 compared with target water quality limits of Government Gazette39943 No. 469 for the resource unit; shaded values indicate noncompliance.

Quality subcomponent	Indicator/measure	Unit	Limit	Percentile	Site 1	Site 2
Nutrients	Nitrate and nitrite	mg/L	≤1.35	50th	1.35	1.46
	Nitrate and nitrite	mg/L	≤6	95th	4.1	2.4
	Orthophosphate	mg/L	≤0.125	50th	0.117	0.090
Salts	Electrical conductivity	mS/m	≤70	95th	79	77
	Sulfate	mg/L	≤160	95th	176	183
System variables	pH at 25˚C	pH units	7.5	5th	7.9	7.5
	pH at 25˚C	pH units	9.2	95th	9.3	9.2
Toxics	Cyanide (dissolved)	mg/L	≤0.05	95th	0.01	0.01
	Aluminum	mg/L	≤0.1	95th	1.0	1.1
	Manganese	mg/L	≤0.25	95th	0.05	0.05
	Iron	mg/L	≤0.25	95th	0.71	0.69
	Uranium	mg/L	≤0.03	95th	0.01	0.01
	Ammonia	mg/L	≤0.1	95th	0.5	0.3

pH emerged as concerns for the Vaal River but not for the Koekemoerspruit (**Table 6**).

The mean values (**Figure 2**) for all 20 determinants were compared before and after the inflow of the Koekemoerspruit at sites 1 and 2, respectively, to determine the overall impact of the Koekemoerspruit on the Vaal River for the entire dataset (2002-2015), as not all the determinants were assigned within the target water quality objectives. Total chlorophyll values were the only mean and maximum values to show a slight increase in the Vaal River after the inflow of the Koekemoerspruit (**Figure 2** and **Figure 3**). There were, however, no statistically significant differences between sites 1 and 2 for any of the other variables. The extremely high ammonia concentrations observed at sites 4 and 5 (**Table 4** and **Table 5**) contributed to nutrient enrichment of the Vaal River and subsequent proliferation of algal growth.

Chloride, sulfate, total chlorophyll and sodium showed large variances in their concentrations from 2002 to 2015 at sites 1 and 2 in the Vaal River and at sites 4 and 5 in the Koekemoerspruit. The maximum concentrations shown in **Figure 3** for sites 1 and 5 indicate that their respective turbidity, chloride, sulfate, total chlorophyll and sodium concentrations could jointly have contributed to the maximum levels observed at site 2 and would therefore have been able to increase average measured levels of these determinants at site 2.

3.3. New Environmental Concerns and Emerging Pollution Pressures in the Koekemoerspruit

Site 5 represents the water that flows into the Vaal River and that can impact directly on the water quality of the source water destined for drinking water use.

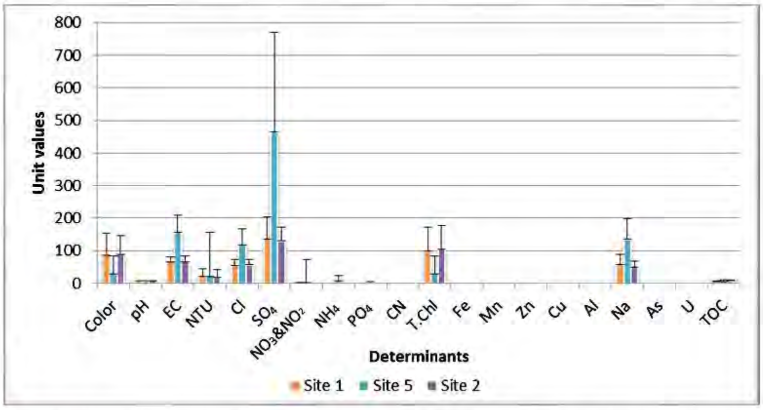

Figure 2. Mean values derived from the water quality monitoring data for sites 1, 5, and 2 from October 2002 to December 2015 (n = 130 ±std); Site 1: Vaal River above the confluence of the Koekemoerspruit; Site 5: Koekemoerspruit before the confluence with the Vaal River; Site 2: Vaal River below the confluence of the Koekemoerspruit; EC: electrical conductivity; NTU: turbidity; T.Chl: total chlorophyll; TOC: total organic carbon.

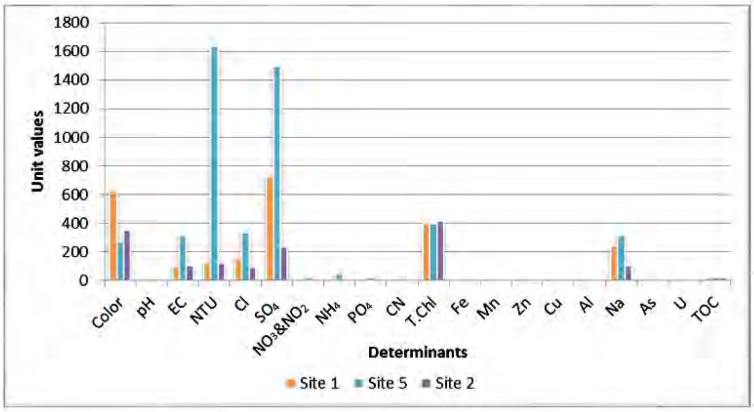

Figure 3. Maximum values derived from the water quality monitoring data for sites 1, 5, and 2 from October 2002 to December 2015; Site 1: Vaal River above the confluence of the Koekemoerspruit; Site 5: Koekemoerspruit before the confluence with the Vaal River; Site 2: Vaal River below the confluence of the Koekemoerspruit; EC: electrical conductivity; NTU: turbidity; T.Chl: total chlorophyll; TOC: total organic carbon.

Table 7. Mann-Kendall test and Sen's slope estimate results showing trends of the entire dataset (2002-2015) for site 5, indicating determinants for which a significant annual trend was observed.

Determinant	Mann-Kendall test trend level	Sen's slope estimate
Ammonia	0.05	0.631
Color	0.01	2.345
Sodium	0.1	−6.993
Total chlorophyll	0.01	1.152

Determinants that showed a statistically significant increase in concentration over time were viewed as posing a risk to the Vaal River. To determine whether any of the variables illustrated in **Figure 3** demonstrated an increasing trend over the long term, the temporal version of the nonparametric Mann-Kendall test was performed [11]. This was done using the entire dataset (2002-2015) for site 5; only the determinants with statistical significant increases/decreases are listed in **Table 7**. According to the results of the Mann-Kendall test there are statistically significant increases in ammonia ($p = 0.05$), color ($p = 0.01$) and total chlorophyll ($p = 0.01$) during the study period. Color and total chlorophyll concentrations exhibited the highest increases (slope estimates of 2.345 and 1.152 respectively) during the study period. Domestic wastewater effluent is, however, more likely to be a contributing factor based on the high ammonia concentrations and other sewage-related determinants (**Figure 4** and **Table 4**).

The color, ammonia, and total chlorophyll concentrations measured at site 5 not only showed a significant increase over the entire study period but also exhibited drastic increases from 2012 (**Figure 4**) onwards. The total organic carbon

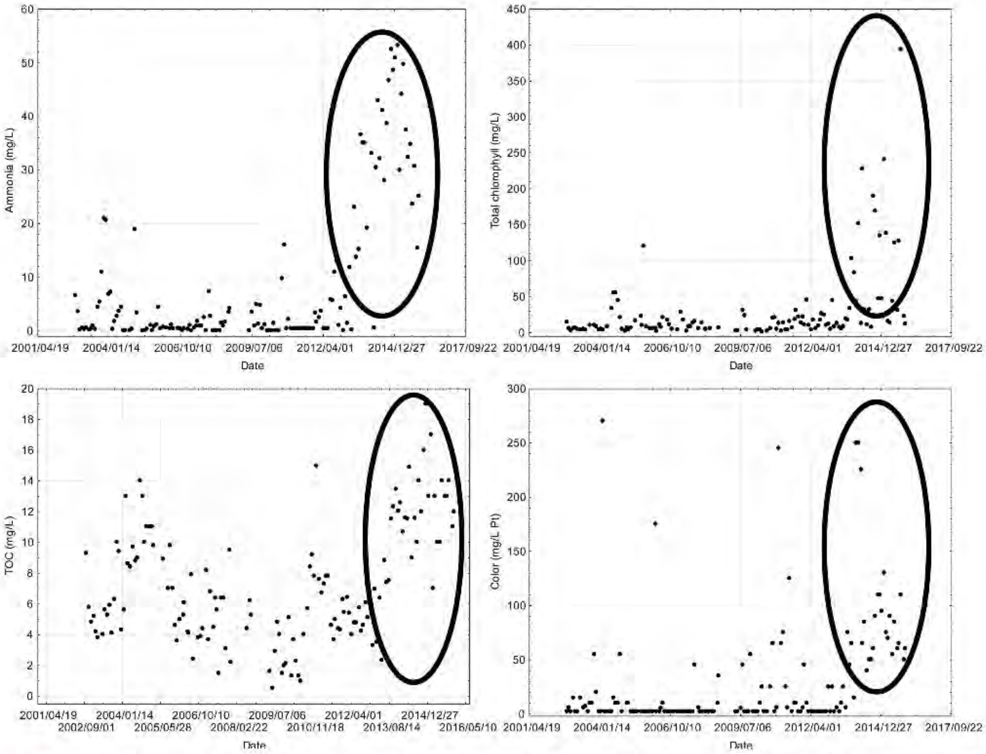

Figure 4. Mean concentrations of ammonia, total chlorophyll, total organic carbon (TOC), and color revealed drastic increases in the Koekemoerspruit as measured during the water quality monitoring program after 2012 at site 5.

concentration measured at site 5 demonstrated a great deal of variability but a general increase as shown in **Figure 4**. The seasonal burning of *Phragmites australis* may also contribute to this variability of the total organic carbon concentrations.

The sulfate, sodium, and chloride concentrations measured at site 5 prior to 2012 were especially high. These determinants showed much lower concentrations from 2012 onwards (**Figure 5**), which was particularly noticeable when compared with the SANS 241:2015 [13] limits for sulfate and sodium (500 and 200 milligrams per liter, respectively).

4. Discussion

Mining activities in the Koekemoerspruit area surrounding the study site have declined significantly over the past five years. The City of Matlosana showed that mining activities have downscaled drastically specifically in the year 2011 which lead to 75% of original workforce to be retrenched [14]. This was also evident in the results of the water quality of the Koekemoerspruit.

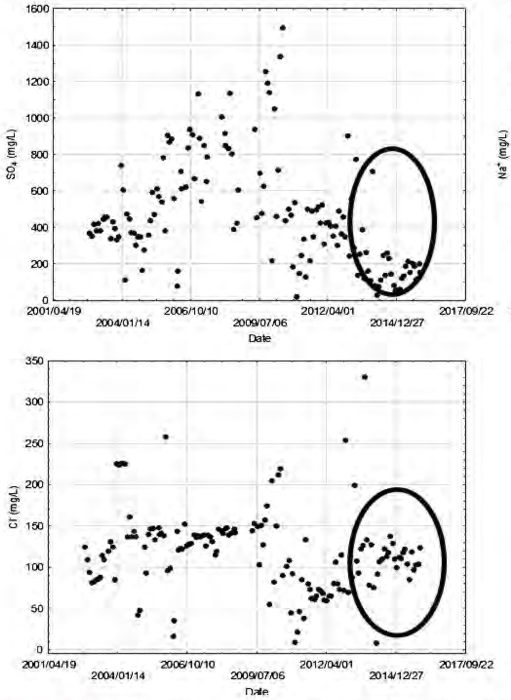

Figure 5. Mean concentrations for sulfate, sodium, and chloride in the Koekemoerspruit were at alarming levels at times during the water quality monitoring program from 2002 to 2015 at site 5 despite a general decrease in concentration over time.

In this case study, the target water quality objectives for Koekemoerspruit indicated that orthophosphate, nitrate and nitrite, electrical conductivity, sulfate, manganese, iron and ammonia exceeded the relevant limits. Color, turbidity, manganese, and total organic carbon were the determinants of concern in the Koekemoerspruit when considering the SANS 241:2015 limits for drinking water. The alarming electrical conductivity, turbidity, chloride, sulfate, sodium, recoverable cyanide, arsenic and uranium concentrations at site 3 are directly associated with mining activities. However, it did not have a significant impact on the water quality of the Koekemoerspruit after the inflow of the canal. This could perhaps be ascribed to the low flow volume of the canal or absence of flow at times as sampling was possible only 80% of the time. The decline in mining activities is evident in the decline of sulfate, sodium and chloride concentrations at site 5 since 2012.

The long term increasing trend demonstrated for ammonia together with total organic carbon concentrations suggested that upstream domestic wastewater effluent or agricultural runoff currently has the largest impact on the Koekemoerspruit. The extremely high ammonia concentrations suggest discharge of untreated domestic wastewater effluent, which contributes to the increasing total chlorophyll, and results in the eutrophication of the Koekemoerspruit. Sewage discharge is a major component of water pollution, contributing to oxygen demand and nutrient loading of water bodies, promoting toxic algal blooms and leading to a destabilized aquatic ecosystem [15]. The declining state of municipal wastewater and sewage treatment infrastructure in South Africa is one of the largest contributing factors to the numerous pollution problems and is a major contributor to health problems in poor communities [16], such as that in the study area. Investigations conducted on South African water resources have shown that poor operation and maintenance of domestic wastewater treatment plants have a great impact on both the environment and human health. The increasing population of the Khuma urban village [14], together with doubtful infrastructure and operation of wastewater treatment plants upstream from site 4, most probably contributed to the decline of the Koekemoerspruit's water quality. This is also evident from the upsurges in ammonia, total organic carbon and color concentrations observed at site 5, especially since 2012.

The inflow of the Koekemoerspruit into the Vaal River did not seem to have a significant impact on the overall water quality of the Vaal River when water quality upstream of the convergence at site 1 was compared with that downstream of the convergence at site 2. However, total chlorophyll concentrations increased after the inflow of the Koekemoerspruit. A significant trend of increase over a long period of time has been demonstrated for chlorophyll concentrations in the Koekemoerspruit and therefore would have a greater impact on the chlorophyll concentrations of the Middle Vaal River. A previous study on Midvaal Water Company by Reference [17] indicated that increasing chlorophyll concentrations and associated taste and odors, as well as fluctuating turbidity levels, are the main challenges that affect the water treatment process at this treatment plant. Although orthophosphate and ammonia concentrations are not directly addressed in South African drinking water standards, together with nitrate and nitrite, they can contribute to nutrient enrichment of a water body and subsequent algal growth. Taste and odors can be associated with nuisance algal blooms, such as that of *Microcystis* sp., *Oscillatoria* sp., and *Planktothrix* sp., which occur in the Koekemoerspruit. They are responsible for the presence of geosmin and/or 2-methylisoborneol. The odor threshold concentrations for these compounds range from 4 to 20 nanograms per liter [17] and therefore affect downstream drinking water treatment despite dilution of the Koekemoerspruit's inflow into the Vaal River.

The changes recommended for the water quality monitoring program of the Koekemoerspruit are summarized in **Table 8**. Ammonia was not previously identified as a major concern but, as indicated by Government Gazette 39943 No. 469 [7], should be monitored for the Koekemoerspruit resource unit, along with electrical conductivity, sulfate, magnesium, nitrate and nitrite, orthophosphate, cyanide, iron, manganese, aluminum and uranium. Magnesium has also not been monitored for sites 1, 3, 4, and 5 to date and therefore has to be included in

Table 8. Proposed revised monitoring program for the Koekemoerspruit after evaluation of data collected from 2002 to 2015 and the identification of shortcomings

Determinants	Existing or new determinant	Frequency	Regulated by Government Gazette No. 39943
Magnesium and dissolved cyanide	New	Monthly	Yes
Escherichia coli and coliforms	Replace faecal coliform monitoring	Monthly	Yes
Microcystin, geosmin & 2-methylisoborneol	New	Dependent on algal blooms or taste and odor episodes	No
Gross alpha/beta activity	New	Dependent on uranium concentrations	No

the water quality monitoring program. Recoverable cyanide was monitored for the study period and can be replaced with the analysis of dissolved cyanide according to the target water quality objectives as per Government Gazette 39943 No. 469 [7]. The monitoring of color, total chlorophyll and total organic carbon has to continue and the frequency cannot be reduced, as these determinants are expected to increase in the future due to ongoing pollution activities upstream; they have subsequently been identified as possible risks. Due to the increasing threat of sewage pollution, additional microbial determinants should be considered for inclusion in the routine water quality monitoring program, in particular *Escherichia coli*, other coliforms and cyanobacterial toxins like microcystin. The monitoring of arsenic should continue, as site 3 poses a possible risk to the Koekemoerspruit. The monitoring of pH, turbidity, chloride, sodium, zinc, and copper can either be reduced to quarterly or annual monitoring or omitted from the monitoring program, because the concentrations of these determinants did not exceed any limits or indicated a concentration increase from 2002 to 2015. The analysis of gross alpha/beta activity is suggested based on elevated uranium concentrations at site 3 to identify the associated risks. It was the first time that the Koekemoerspruit monitoring program was evaluated during this case study and should be evaluated again in future to determine whether the revised monitoring program still holds true.

Even though legislation requires evidence of risk-based monitoring and management, no specific guidelines are currently available. In optimizing the monitoring program based on water quality monitoring data the following recommendations could be made:

1) The monitoring of radio activity in the Koekemoerspruit is recommended due to the borderline uranium concentrations.

2) Algal identification and geosmin/2-methylisoborneol analyses of the Koekemoerspruit during taste and odor episodes are also recommended to establish possible aesthetic, health and environmental risks.

3) The water safety plan should be revised to state that the decreasing raw

water quality is due to upstream domestic wastewater effluent or runoff and not mining activities anymore.

4) Site 4 may be omitted from the monitoring program as it did not seem to have a significant impact on the water quality of site 5.

5) The water quality status of the Koekemoerspruit may be communicated to the community for them to understand the health-related risks and how it may impact their drinking water source.

6) Monitoring can never substitute sound management principles. Monitoring can be significantly reduced if the pollution source of the Koekemoerspruit is remedied.

It remains imperative to be aware that the management of water quality monitoring should never overshadow the management of the water quality itself [18] as interventions and corrective actions ensure improvement of water quality. Monitoring programs should however be reviewed and the data continuously evaluated, using at least descriptive statistical methods (confidence interval and variance) to indicate variance in water quality determinants and to determine the level of compliance to set objectives and standards. The review of a monitoring program can be prompted by schedule, new legislation, costs, or an emerging environmental impact.

5. Conclusion

Evaluation of the monitoring data showed that the water flowing from Koekemoerspruit into the Middle Vaal River dilutes to a great extent and therefore it mostly has a reduced impact. Total chlorophyll concentrations of the Koekemoerspruit did however have a significant impact on the Vaal River and also showed an increasing trend over time. The increasing trends in ammonia and total organic carbon suggested that upstream domestic wastewater effluent or agricultural runoff and not mining, currently has the largest impact on the Koekemoerspruit. The risks/hazards addressed in Midvaal Water Company's water safety plan remains relevant and applicable. The application of the target water quality objectives proved to be a valuable tool to evaluate monitoring data. The evaluation and review of monitoring data have identified several new concerns and avenues of optimization for the Koekemoerspruit water quality monitoring program. The monitoring program is both effective and necessary, as the determinants of concern in the Koekemoerspruit pose a risk for the use of Vaal River water as a drinking water source downstream. However, the lack of guidelines on how to review a monitoring program would contribute significantly to the ongoing optimization of such programs. The challenges faced by Midvaal Water Company were examined, highlighting the importance of adopting a holistic approach when investigating water quality problems. The focus of water quality monitoring programs as part of integrated management should not only be to identify risks but also to protect the environment.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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ANNEXURE C

Table C.1: Kruskal-Wallis multiple comparisons of *p*-values (2 tailed) that indicate significant variable differences (*p*-values < 0.05) between the recycle stream and river from June 2013 to February 2016.

Note that the rank values in red indicate significant differences.

VARIABLE	**SITES**	
	Recycle stream (RS)	**River (R)**
Dissolved organic carbon	**R:248,71**	**R:220,09**
RS		0,107864
R	0,107864	
Electrical conductivity	**R:998,97**	**R:901,47**
RS		0,000107
R	0,000107	
pH	**R:724,81**	**R:1168,4**
RS		0,00
R	0,00	
Suspended solids	**R:407,23**	**R:296,30**
RS		0,000000
R	0,000000	
Total chlorophyll	**R:608,04**	**R:619,82**
RS		0,560319
R	0,560319	
Turbidity	**R:1113,6**	**R:792,11**
RS		0,00
R	0,00	

Table C.2: Kruskal-Wallis multiple comparisons of *p*-values (2 tailed) that indicate significant variable differences (*p-values* < 0.05) between the Middle Vaal River, after dissolved air flotation (DAF), after west and east sedimentation for the periods prior to, during and after implementation of wastewater recycling from June 2013 to February 2016.

Note that the rank values in red indicate significant differences.

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
Aluminium	**R:417,89**	**R:506,82**	**R:463,03**	**R:339,28**	**R:386,60**	**R:370,23**	**R:353,08**	**R:392,24**	**R:338,05**	**R:348,28**	**R:410,64**	**R:346,66**
RPr		1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000
RD	1,000000		1,000000	0,002759	0,004586	0,061087	0,028171	0,009232	0,002814	0,007970	0,115105	0,006788

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
RPt	1,000000	1,000000		0,862655	1,000000	1,000000	1,000000	1,000000	0,837479	1,000000	1,000000	1,000000
DAFPr	1,000000	0,002759	0,862655		1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000
DAFD	1,000000	0,004586	1,000000	1,000000		1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000
DAFPt	1,000000	0,061087	1,000000	1,000000	1,000000		1,000000	1,000000	1,000000	1,000000	1,000000	1,000000
WSPr	1,000000	0,028171	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000	1,000000	1,000000	1,000000
WSD	1,000000	0,009232	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000	1,000000	1,000000
WSPt	1,000000	0,002814	0,837479	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000	1,000000
ESPr	1,000000	0,007970	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000
ESD	1,000000	0,115105	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000
ESPt	1,000000	0,006788	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
Chlorophyll-a	**R:702,83**	**R:675,21**	**R:644,69**	**R:498,74**	**R:474,51**	**R:466,92**	**R:252,80**	**R:229,21**	**R:198,73**	**R:260,17**	**R:207,71**	**R:160,81**
RPr		1,000000	1,000000	0,001249	0,000001	0,000101	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RD	1,000000		1,000000	0,000583	0,000000	0,000031	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RPt	1,000000	1,000000		0,184617	0,003045	0,025928	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
DAFPr	0,001249	0,000583	0,184617		1,000000	1,000000	0,000051	0,000000	0,000000	0,000038	0,000000	0,000000

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
DAFD	0,000001	0,000000	0,003045	1,000000		1,000000	0,000015	0,000000	0,000000	0,000008	0,000000	0,000000
DAFPt	0,000101	0,000031	0,025928	1,000000	1,000000		0,001826	0,000001	0,000006	0,001661	0,000000	0,000000
WSPr	0,000000	0,000000	0,000000	0,000051	0,000015	0,001826		1,000000	1,000000	1,000000	1,000000	1,000000
WSD	0,000000	0,000000	0,000000	0,000000	0,000000	0,000001	1,000000		1,000000	1,000000	1,000000	1,000000
WSPt	0,000000	0,000000	0,000000	0,000000	0,000000	0,000006	1,000000	1,000000		1,000000	1,000000	1,000000
ESPr	0,000000	0,000000	0,000000	0,000038	0,000008	0,001661	1,000000	1,000000	1,000000		1,000000	1,000000
ESD	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	1,000000	1,000000	1,000000	1,000000		1,000000
ESPt	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	1,000000	1,000000	1,000000	1,000000	1,000000	

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
Dissolved organic carbon	**R:385,70**	**R:519,91**	**R:481,98**	**R:267,20**	**R:420,46**	**R:367,48**	**R:137,36**	**R:347,90**	**R:260,83**	**R:204,32**	**R:392,68**	**R:268,10**
RPr		0,024909	1,000000	1,000000	1,000000	1,000000	0,000114	1,000000	0,434565	0,020786	1,000000	0,693273
RD	0,024909		1,000000	0,000000	0,037131	0,005360	0,000000	0,000000	0,000000	0,000000	0,001053	0,000000
RPt	1,000000	1,000000		0,001435	1,000000	0,941395	0,000000	0,035924	0,000146	0,000004	1,000000	0,000311
DAFPr	1,000000	0,000000	0,001435		0,028261	1,000000	1,000000	1,000000	1,000000	1,000000	0,284035	1,000000
DAFD	1,000000	0,037131	1,000000	0,028261		1,000000	0,000000	0,806137	0,002763	0,000061	1,000000	0,006088
DAFPt	1,000000	0,005360	0,941395	1,000000	1,000000		0,000805	1,000000	1,000000	0,091897	1,000000	1,000000

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
WSPr	0,000114	0,000000	0,000000	1,000000	0,000000	0,000805		0,000269	1,000000	1,000000	0,000002	0,854612
WSD	1,000000	0,000000	0,035924	1,000000	0,806137	1,000000	0,000269		1,000000	0,070532	1,000000	1,000000
WSPt	0,434565	0,000000	0,000146	1,000000	0,002763	1,000000	1,000000	1,000000		1,000000	0,054842	1,000000
ESPr	0,020786	0,000000	0,000004	1,000000	0,000061	0,091897	1,000000	0,070532	1,000000		0,001514	1,000000
ESD	1,000000	0,001053	1,000000	0,284035	1,000000	1,000000	0,000002	1,000000	0,054842	0,001514		0,104930
ESPt	0,693273	0,000000	0,000311	1,000000	0,006088	1,000000	0,854612	1,000000	1,000000	1,000000	0,104930	

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
E. coli	**R:638,72**	**R:639,91**	**R:646,85**	**R:326,90**	**R:344,31**	**R:377,79**	**R:212,21**	**R:278,83**	**R:267,55**	**R:323,51**	**R:282,84**	**R:379,68**
RPr		1,000000	1,000000	0,000000	0,000000	0,000008	0,000000	0,000000	0,000000	0,000000	0,000000	0,000013
RD	1,000000		1,000000	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RPt	1,000000	1,000000		0,000000	0,000000	0,000005	0,000000	0,000000	0,000000	0,000000	0,000000	0,000008
DAFPr	0,000000	0,000000	0,000000		1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000
DAFD	0,000000	0,000000	0,000000	1,000000		1,000000	0,123600	1,000000	1,000000	1,000000	1,000000	1,000000
DAFPt	0,000008	0,000000	0,000005	1,000000	1,000000		0,084504	1,000000	1,000000	1,000000	1,000000	1,000000
WSPr	0,000000	0,000000	0,000000	1,000000	0,123600	0,084504		1,000000	1,000000	1,000000	1,000000	0,079801
WSD	0,000000	0,000000	0,000000	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000	1,000000	1,000000

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
WSPt	0,000000	0,000000	0,000000	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000	1,000000
ESPr	0,000000	0,000000	0,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000	1,000000
ESD	0,000000	0,000000	0,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000		1,000000
ESPt	0,000013	0,000000	0,000008	1,000000	1,000000	1,000000	0,079801	1,000000	1,000000	1,000000	1,000000	

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
Electrical conductivity	**R:343,03**	**R:353,20**	**R:493,51**	**R:372,11**	**R:381,71**	**R:505,24**	**R:357,24**	**R:386,62**	**R:523,17**	**R:383,10**	**R:405,87**	**R:524,99**
RPr		1,000000	0,150282	1,000000	1,000000	0,066260	1,000000	1,000000	0,017106	1,000000	1,000000	0,014812
RD	1,000000		0,046890	1,000000	1,000000	0,016095	1,000000	1,000000	0,002712	1,000000	1,000000	0,002243
RPt	0,150282	0,046890		0,881593	0,490881	1,000000	0,551871	0,692888	1,000000	1,000000	1,000000	1,000000
DAFPr	1,000000	1,000000	0,881593		1,000000	0,439796	1,000000	1,000000	0,137252	1,000000	1,000000	0,121159
DAFD	1,000000	1,000000	0,490881	1,000000		0,204716	1,000000	1,000000	0,046684	1,000000	1,000000	0,039814
DAFPt	0,066260	0,016095	1,000000	0,439796	0,204716		0,275959	0,297890	1,000000	0,940199	1,000000	1,000000
WSPr	1,000000	1,000000	0,551871	1,000000	1,000000	0,275959		1,000000	0,087255	1,000000	1,000000	0,077177
WSD	1,000000	1,000000	0,692888	1,000000	1,000000	0,297890	1,000000		0,071207	1,000000	1,000000	0,061021
WSPt	0,017106	0,002712	1,000000	0,137252	0,046684	1,000000	0,087255	0,071207		0,326150	0,362834	1,000000
ESPr	1,000000	1,000000	1,000000	1,000000	1,000000	0,940199	1,000000	1,000000	0,326150		1,000000	0,291086

ESD	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	1,000000	0,362834	1,000000		0,317676
ESPt	0,014812	0,002243	1,000000	0,121159	0,039814	1,000000	0,077177	0,061021	1,000000	0,291086	0,317676	

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
pH	**R:555,04**	**R:525,68**	**R:513,57**	**R:389,27**	**R:421,11**	**R:358,50**	**R:269,85**	**R:326,81**	**R:555,57**	**R:240,29**	**R:300,82**	**R:506,99**
RPr		1,000000	1,000000	0,040234	0,068006	0,005127	0,000001	0,000001	1,000000	0,000000	0,000000	1,000000
RD	1,000000		1,000000	0,045000	0,042326	0,004190	0,000000	0,000000	1,000000	0,000000	0,000000	1,000000
RPt	1,000000	1,000000		0,793410	1,000000	0,150749	0,000166	0,000585	1,000000	0,000003	0,000037	1,000000
DAFPr	0,040234	0,045000	0,793410		1,000000	1,000000	1,000000	1,000000	0,051415	0,136523	1,000000	1,000000
DAFD	0,068006	0,042326	1,000000	1,000000		1,000000	0,031163	0,152634	0,093469	0,000618	0,009223	1,000000
DAFPt	0,005127	0,004190	0,150749	1,000000	1,000000		1,000000	1,000000	0,006985	1,000000	1,000000	0,230208
WSPr	0,000001	0,000000	0,000166	1,000000	0,031163	1,000000		1,000000	0,000002	1,000000	1,000000	0,000307
WSD	0,000001	0,000000	0,000585	1,000000	0,152634	1,000000	1,000000		0,000003	1,000000	1,000000	0,001198
WSPt	1,000000	1,000000	1,000000	0,051415	0,093469	0,006985	0,000002	0,000003		0,000000	0,000000	1,000000
ESPr	0,000000	0,000000	0,000003	0,136523	0,000618	1,000000	1,000000	1,000000	0,000000		1,000000	0,000005
ESD	0,000000	0,000000	0,000037	1,000000	0,009223	1,000000	1,000000	1,000000	0,000000	1,000000		0,000081
ESPt	1,000000	1,000000	1,000000	1,000000	1,000000	0,230208	0,000307	0,001198	1,000000	0,000005	0,000081	

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
Spectral absorbance coefficient 254	**R:633,67**	**R:635,27**	**R:690,59**	**R:345,24**	**R:468,78**	**R:502,27**	**R:90,875**	**R:301,18**	**R:254,15**	**R:120,05**	**R:332,31**	**R:300,99**
RPr		1,000000	1,000000	0,000000	0,003516	0,544271	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RD	1,000000		1,000000	0,000000	0,000004	0,096643	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RPt	1,000000	1,000000		0,000000	0,000009	0,013964	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
DAFPr	0,000000	0,000000	0,000000		0,150934	0,099638	0,000031	1,000000	1,000000	0,000213	1,000000	1,000000
DAFD	0,003516	0,000004	0,000009	0,150934		1,000000	0,000000	0,000004	0,000023	0,000000	0,001026	0,004499
DAFPt	0,544271	0,096643	0,013964	0,099638	1,000000		0,000000	0,000113	0,000070	0,000000	0,004203	0,004955
WSPr	0,000000	0,000000	0,000000	0,000031	0,000000	0,000000		0,000073	0,106502	1,000000	0,000002	0,003266
WSD	0,000000	0,000000	0,000000	1,000000	0,000004	0,000113	0,000073		1,000000	0,000567	1,000000	1,000000
WSPt	0,000000	0,000000	0,000000	1,000000	0,000023	0,000070	0,106502	1,000000		0,463184	1,000000	1,000000
ESPr	0,000000	0,000000	0,000000	0,000213	0,000000	0,000000	1,000000	0,000567	0,463184		0,000017	0,018160
ESD	0,000000	0,000000	0,000000	1,000000	0,001026	0,004203	0,000002	1,000000	1,000000	0,000017		1,000000
ESPt	0,000000	0,000000	0,000000	1,000000	0,004499	0,004955	0,003266	1,000000	1,000000	0,018160	1,000000	

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
Total chlorophyll	**R:709,52**	**R:679,39**	**R:663,44**	**R:500,56**	**R:459,69**	**R:470,64**	**R:264,99**	**R:213,38**	**R:196,39**	**R:296,48**	**R:212,51**	**R:163,02**
RPr		1,000000	1,000000	0,000921	0,000000	0,000104	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
RD	1,000 000		1,000 000	0,000 454	0,000 000	0,000 038	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000
RPt	1,000 000	1,000 000		0,062 238	0,000 085	0,009 936	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000
DAFPr	0,000 921	0,000 454	0,062 238		1,000 000	1,000 000	0,000 155	0,000 000	0,000 000	0,001 311	0,000 000	0,000 000
DAFD	0,000 000	0,000 000	0,000 085	1,000 000		1,000 000	0,000 362	0,000 000	0,000 000	0,003 542	0,000 000	0,000 000
DAFPt	0,000 104	0,000 038	0,009 936	1,000 000	1,000 000		0,004 300	0,000 000	0,000 005	0,028 619	0,000 000	0,000 000
WSPr	0,000 000	0,000 000	0,000 000	0,000 155	0,000 362	0,004 300		1,000 000	1,000 000	1,000 000	1,000 000	1,000 000
WSD	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	1,000 000		1,000 000	1,000 000	1,000 000	1,000 000
WSPt	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 005	1,000 000	1,000 000		1,000 000	1,000 000	1,000 000
ESPr	0,000 000	0,000 000	0,000 000	0,001 311	0,003 542	0,028 619	1,000 000	1,000 000	1,000 000		1,000 000	0,462 815
ESD	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	1,000 000	1,000 000	1,000 000	1,000 000		1,000 000
ESPt	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	1,000 000	1,000 000	1,000 000	0,462 815	1,000 000	

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
Total organic carbon	**R:452,15**	**R:541,14**	**R:484,22**	**R:308,89**	**R:430,56**	**R:383,40**	**R:163,29**	**R:335,93**	**R:234,30**	**R:237,89**	**R:382,54**	**R:264,79**
RPr		1,000 000	1,000 000	0,216 940	1,000 000	1,000 000	0,000 001	0,169 594	0,000 215	0,000 847	1,000 000	0,004 140
RD	1,000 000		1,000 000	0,000 002	0,010 657	0,004 040	0,000 000	0,000 000	0,000 000	0,000 000	0,000 008	0,000 000
RPt	1,000 000	1,000 000		0,026 121	1,000 000	1,000 000	0,000 000	0,011 453	0,000 010	0,000 051	0,752 218	0,000 265

VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
DAFPr	0,216940	0,000002	0,026121		0,245535	1,000000	0,444594	1,000000	1,000000	1,000000	1,000000	1,000000
DAFD	1,000000	0,010657	1,000000	0,245535		1,000000	0,000000	0,088058	0,000050	0,000359	1,000000	0,001954
DAFPt	1,000000	0,004040	1,000000	1,000000	1,000000		0,001522	1,000000	0,114398	0,232096	1,000000	0,838560
WSPr	0,000001	0,000000	0,000000	0,444594	0,000000	0,001522		0,007428	1,000000	1,000000	0,000086	1,000000
WSD	0,169594	0,000000	0,011453	1,000000	0,088058	1,000000	0,007428		0,665389	1,000000	1,000000	1,000000
WSPt	0,000215	0,000000	0,000010	1,000000	0,000050	0,114398	1,000000	0,665389		1,000000	0,014871	1,000000
ESPr	0,000847	0,000000	0,000051	1,000000	0,000359	0,232096	1,000000	1,000000	1,000000		0,048428	1,000000
ESD	1,000000	0,000008	0,752218	1,000000	1,000000	1,000000	0,000086	1,000000	0,014871	0,048428		0,223636
ESPt	0,004140	0,000000	0,000265	1,000000	0,001954	0,838560	1,000000	1,000000	1,000000	1,000000	0,223636	
VARIABLE	**SITES**											
	RPr	**RD**	**RPt**	**DAFPr**	**DAFD**	**DAFPt**	**WSPr**	**WSD**	**WSPt**	**ESPr**	**ESD**	**ESPt**
Turbidity	**R:692,38**	**R:688,08**	**R:695,14**	**R:459,56**	**R:450,80**	**R:507,94**	**R:221,61**	**R:217,14**	**R:321,01**	**R:196,52**	**R:210,77**	**R:233,64**
RPr		1,000000	1,000000	0,000116	0,000000	0,014086	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RD	1,000000		1,000000	0,000001	0,000000	0,001006	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
RPt	1,000000	1,000000		0,000132	0,000000	0,014445	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000
DAFPr	0,000116	0,000001	0,000132		1,000000	1,000000	0,000163	0,000000	0,341675	0,000004	0,000000	0,000339
DAFD	0,000000	0,000000	0,000000	1,000000		1,000000	0,000007	0,000000	0,131312	0,000000	0,000000	0,000015

VARIABLE	SITES											
	RPr	RD	RPt	DAFPr	DAFD	DAFPt	WSPr	WSD	WSPt	ESPr	ESD	ESPt
DAFPt	0,014 086	0,001 006	0,014 445	1,000 000	1,000 000		0,000 002	0,000 000	0,014 749	0,000 000	0,000 000	0,000 004
WSPr	0,000 000	0,000 000	0,000 000	0,000 163	0,000 007	0,000 002		1,000 000	1,000 000	1,000 000	1,000 000	1,000 000
WSD	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	1,000 000		0,866 303	1,000 000	1,000 000	1,000 000
WSPt	0,000 000	0,000 000	0,000 000	0,341 675	0,131 312	0,014 749	1,000 000	0,866 303		0,821 737	0,609 193	1,000 000
ESPr	0,000 000	0,000 000	0,000 000	0,000 004	0,000 000	0,000 000	1,000 000	1,000 000	0,821 737		1,000 000	1,000 000
ESD	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	0,000 000	1,000 000	1,000 000	0,609 193	1,000 000		1,000 000
ESPt	0,000 000	0,000 000	0,000 000	0,000 339	0,000 015	0,000 004	1,000 000	1,000 000	1,000 000	1,000 000	1,000 000	

ANNEXURE D

Table D: Kruskal-Wallis multiple comparisons of *p*-values (2 tailed) that indicate significant variable differences (*p*-value < 0.05) between sites 1 to 5 from November 2012 to October 2014.

Note that the rank values in red indicate significant differences.

VARIABLE	**SITES**				
	1	**2**	**3**	**4**	**5**
Aluminium	**R:65.587**	**R:60.833**	**R:58.952**	**R:52.021**	**R:55.458**
Site 1		1.000000	1.000000	1.000000	1.000000
Site 2	1.000000		1.000000	1.000000	1.000000
Site 3	1.000000	1.000000		1.000000	1.000000
Site 4	1.000000	1.000000	1.000000		1.000000
Site 5	1.000000	1.000000	1.000000	1.000000	
Ammonia	**R:32.043**	**R:31.104**	**R:48.524**	**R:91.667**	**R:86.813**
Site 1		1.000000	1.000000	0.000000	0.000000
Site 2	1.000000		0.830117	0.000000	0.000000
Site 3	1.000000	0.830117		0.000176	0.001389
Site 4	0.000000	0.000000	0.000176		1.000000
Site 5	0.000000	0.000000	0.001389	1.000000	
Arsenic	**R:46.000**	**R:43.500**	**R:84.690**	**R:58.063**	**R:63.000**
Site 1		1.000000	0.001380	1.000000	0.832094
Site 2	1.000000		0.000415	1.000000	0.445793
Site 3	0.001380	0.000415		0.080535	0.308910
Site 4	1.000000	1.000000	0.080535		1.000000
Site 5	0.832094	0.445793	0.308910	1.000000	
Chloride	**R:26.304**	**R:26.625**	**R:100.76**	**R:67.083**	**R:75.667**
Site 1		1.000000	0.000000	0.000325	0.000005
Site 2	1.000000		0.000000	0.000308	0.000004
Site 3	0.000000	0.000000		0.008039	0.125146
Site 4	0.000325	0.000308	0.008039		1.000000
Site 5	0.000005	0.000004	0.125146	1.000000	
Colour	**R:78.522**	**R:85.813**	**R:17.167**	**R:53.979**	**R:52.688**
Site 1		1.000000	0.000000	0.123852	0.084734
Site 2	1.000000		0.000000	0.010418	0.006448
Site 3	0.000000	0.000000		0.002490	0.004081
Site 4	0.123852	0.010418	0.002490		1.000000
Site 5	0.084734	0.006448	0.004081	1.000000	
Copper	**R:51.543**	**R:60.063**	**R:64.095**	**R:61.917**	**R:55.292**
Site 1		1.000000	1.000000	1.000000	1.000000
Site 2	1.000000		1.000000	1.000000	1.000000
Site 3	1.000000	1.000000		1.000000	1.000000
Site 4	1.000000	1.000000	1.000000		1.000000
Site 5	1.000000	1.000000	1.000000	1.000000	
Cyanide recoverable	**R:55.543**	**R:55.167**	**R:60.833**	**R:60.583**	**R:60.542**
Site 1		1.000000	1.000000	1.000000	1.000000
Site 2	1.000000		1.000000	1.000000	1.000000
Site 3	1.000000	1.000000		1.000000	1.000000
Site 4	1.000000	1.000000	1.000000		1.000000
Site 5	1.000000	1.000000	1.000000	1.000000	

VARIABLE	SITES				
	1	2	3	4	5
Electrical conductivity	**R:26.196**	**R:25.646**	**R:103.29**	**R:67.604**	**R:74.021**
Site 1		1.000000	0.000000	0.000245	0.000011
Site 2	1.000000		0.000000	0.000155	0.000006
Site 3	0.000000	0.000000		0.003841	0.035887
Site 4	0.000245	0.000155	0.003841		1.000000
Site 5	0.000011	0.000006	0.035887	1.000000	
Faecal coliforms	**R:44.913**	**R:38.104**	**R:41.619**	**R:82.417**	**R:82.771**
Site 1		1.000000	1.000000	0.001325	0.001144
Site 2	1.000000		1.000000	0.000050	0.000042
Site 3	1.000000	1.000000		0.000491	0.000422
Site 4	0.001325	0.000050	0.000491		1.000000
Site 5	0.001144	0.000042	0.000422	1.000000	
Iron	**R:51.609**	**R:53.229**	**R:48.286**	**R:69.979**	**R:67.833**
Site 1		1.000000	1.000000	0.612044	0.982600
Site 2	1.000000		1.000000	0.844666	1.000000
Site 3	1.000000	1.000000		0.308680	0.517470
Site 4	0.612044	0.844666	0.308680		1.000000
Site 5	0.982600	1.000000	0.517470	1.000000	
Manganese	**R:36.022**	**R:44.292**	**R:42.690**	**R:86.854**	**R:79.729**
Site 1		1.000000	1.000000	0.000002	0.000084
Site 2	1.000000		1.000000	0.000116	0.002620
Site 3	1.000000	1.000000		0.000111	0.002280
Site 4	0.000002	0.000116	0.000111		1.000000
Site 5	0.000084	0.002620	0.002280	1.000000	
Nitrate and nitrite	**R:43.065**	**R:35.583**	**R:77.929**	**R:71.667**	**R:66.042**
Site 1		1.000000	0.005933	0.035616	0.192125
Site 2	1.000000		0.000251	0.002018	0.017047
Site 3	0.005933	0.000251		1.000000	1.000000
Site 4	0.035616	0.002018	1.000000		1.000000
Site 5	0.192125	0.017047	1.000000	1.000000	
Orthophosphate	**R:40.478**	**R:37.542**	**R:29.714**	**R:91.667**	**R:88.750**
Site 1		1.000000	1.000000	0.000002	0.000009
Site 2	1.000000		1.000000	0.000000	0.000001
Site 3	1.000000	1.000000		0.000000	0.000000
Site 4	0.000002	0.000000	0.000000		1.000000
Site 5	0.000009	0.000001	0.000000	1.000000	
pH	**R:84.717**	**R:78.104**	**R:73.548**	**R:29.229**	**R:29.875**
Site 1		1.000000	1.000000	0.000000	0.000000
Site 2	1.000000		1.000000	0.000005	0.000007
Site 3	1.000000	1.000000		0.000103	0.000139
Site 4	0.000000	0.000005	0.000103		1.000000
Site 5	0.000000	0.000007	0.000139	1.000000	
Sodium	**R:28.130**	**R:24.375**	**R:103.90**	**R:67.042**	**R:73.458**
Site 1		1.000000	0.000000	0.000733	0.000039
Site 2	1.000000		0.000000	0.000111	0.000004
Site 3	0.000000	0.000000		0.002441	0.024472
Site 4	0.000733	0.000111	0.002441		1.000000
Site 5	0.000039	0.000004	0.024472	1.000000	
Sulfate	**R:36.826**	**R:30.417**	**R:104.38**	**R:58.750**	**R:66.958**
Site 1		1.000000	0.000000	0.254749	0.021364
Site 2	1.000000		0.000000	0.035174	0.001672
Site 3	0.000000	0.000000		0.000056	0.001961

VARIABLE	**SITES**				
	1	**2**	**3**	**4**	**5**
Site 4	0.254749	0.035174	0.000056		1.000000
Site 5	0.021364	0.001672	0.001961	1.000000	
Total chlorophyll	**R:78.565**	**R:85.167**	**R:24.333**	**R:53.542**	**R:47.458**
Site 1		1.000000	0.000001	0.107726	0.015249
Site 2	1.000000		0.000000	0.011238	0.001027
Site 3	0.000001	0.000000		0.036539	0.213788
Site 4	0.107726	0.011238	0.036539		1.000000
Site 5	0.015249	0.001027	0.213788	1.000000	
Total organic carbon	**R:46.457**	**R:50.188**	**R:22.190**	**R:87.771**	**R:80.854**
Site 1		1.000000	0.168188	0.000255	0.004562
Site 2	1.000000		0.053354	0.001083	0.015841
Site 3	0.168188	0.053354		0.000000	0.000000
Site 4	0.000255	0.001083	0.000000		1.000000
Site 5	0.004562	0.015841	0.000000	1.000000	
Turbidity	**R:76.304**	**R:71.708**	**R:44.786**	**R:50.042**	**R:48.688**
Site 1		1.000000	0.019018	0.074449	0.048890
Site 2	1.000000		0.073812	0.256295	0.177272
Site 3	0.019018	0.073812		1.000000	1.000000
Site 4	0.074449	0.256295	1.000000		1.000000
Site 5	0.048890	0.177272	1.000000	1.000000	
Uranium	**R:43.435**	**R:43.250**	**R:76.333**	**R:59.250**	**R:71.833**
Site 1		1.000000	0.011907	1.000000	0.038047
Site 2	1.000000		0.009940	0.993355	0.032376
Site 3	0.011907	0.009940		0.891299	1.000000
Site 4	1.000000	0.993355	0.891299		1.000000
Site 5	0.038047	0.032376	1.000000	1.000000	
Zinc	**R:41.348**	**R:38.833**	**R:53.714**	**R:82.833**	**R:74.458**
Site 1		1.000000	1.000000	0.000236	0.007406
Site 2	1.000000		1.000000	0.000058	0.002430
Site 3	1.000000	1.000000		0.037590	0.389900
Site 4	0.000236	0.000058	0.037590		1.000000
Site 5	0.007406	0.002430	0.389900	1.000000	
Cyanophyceae	**R:68.957**	**R:70.854**	**R:44.000**	**R:51.146**	**R:56.167**
Site 1		1.000000	0.139453	0.695282	1.000000
Site 2	1.000000		0.075327	0.423503	1.000000
Site 3	0.139453	0.075327		1.000000	1.000000
Site 4	0.695282	0.423503	1.000000		1.000000
Site 5	1.000000	1.000000	1.000000	1.000000	
Bacillariophyceae	**R:83.261**	**R:88.875**	**R:19.452**	**R:46.396**	**R:50.667**
Site 1		1.000000	0.000000	0.001722	0.008955
Site 2	1.000000		0.000000	0.000121	0.000830
Site 3	0.000000	0.000000		0.073356	0.018950
Site 4	0.001722	0.000121	0.073356		1.000000
Site 5	0.008955	0.000830	0.018950	1.000000	
Chlorophyceae	**R:88.261**	**R:91.375**	**R:22.905**	**R:44.188**	**R:42.563**
Site 1		1.000000	0.000000	0.000071	0.000032
Site 2	1.000000		0.000000	0.000012	0.000005
Site 3	0.000000	0.000000		0.341836	0.504427
Site 4	0.000071	0.000012	0.341836		1.000000
Site 5	0.000032	0.000005	0.504427	1.000000	
Chrysophyceae	**R:56.457**	**R:61.396**	**R:61.190**	**R:57.854**	**R:55.854**

VARIABLE	**SITES**				
	1	**2**	**3**	**4**	**5**
Site 1		1.000000	1.000000	1.000000	1.000000
Site 2	1.000000		1.000000	1.000000	1.000000
Site 3	1.000000	1.000000		1.000000	1.000000
Site 4	1.000000	1.000000	1.000000		1.000000
Site 5	1.000000	1.000000	1.000000	1.000000	
Dinophyceae	**R:65.000**	**R:74.146**	**R:49.452**	**R:54.250**	**R:48.792**
Site 1		1.000000	1.000000	1.000000	0.985984
Site 2	1.000000		0.139983	0.404255	0.090116
Site 3	1.000000	0.139983		1.000000	1.000000
Site 4	1.000000	0.404255	1.000000		1.000000
Site 5	0.985984	0.090116	1.000000	1.000000	
Cryptophyceae	**R:64.761**	**R:74.500**	**R:50.000**	**R:50.000**	**R:52.438**
Site 1		1.000000	1.000000	1.000000	1.000000
Site 2	1.000000		0.147665	0.116151	0.230531
Site 3	1.000000	0.147665		1.000000	1.000000
Site 4	1.000000	0.116151	1.000000		1.000000
Site 5	1.000000	0.230531	1.000000	1.000000	
Euglenophyceae	**R:71.457**	**R:75.021**	**R:25.071**	**R:65.188**	**R:52.125**
Site 1		1.000000	0.000049	1.000000	0.488440
Site 2	1.000000		0.000007	1.000000	0.183544
Site 3	0.000049	0.000007		0.000655	0.070989
Site 4	1.000000	1.000000	0.000655		1.000000
Site 5	0.488440	0.183544	0.070989	1.000000	