Mapping the dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom

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DECLARATION

I, Alusani Manyatshe, hereby declare before a Commissioner of Oaths:

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2. That this submission takes place with due recognition being given to my copyright, where applicable

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PREFACE

Introduction

This dissertation is submitted in article format as allowed by the North-West University (NWU). The traditional chapters of materials and method, results and discussion are not included in this dissertation, since this information is presented as articles (Chapters 3 - 5). However, the background to and motivation of the study, objectives, research questions and problem statement (chapter 1) are discussed, and a literature review relevant to the research is presented in chapter 2. It has to be noted that the numbering and headings of the articles (Chapters 3 - 5) are different from the rest of this document, since they appear in the format that they were submitted in to the journal. The conclusion and recommendations for further studies are also included.

Rationale in submitting dissertation in article format

The NWU requires M.Sc candidates to prepare a draft article. However, these draft articles rarely get submitted to peer-reviewed ISI international accredited journals. The authors of the above mentioned articles (Chapter 3 - 5) are:

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Contribution to articles

The author was responsible for the collection of all data, experiments and analyses performed both on the field and in the laboratory. Prof Elvis Fosso–Kankeu was the supervisory author on this project and he was involved throughout the project, in the concept formation and composition of the manuscript. Prof Frans Waanders and Prof Hlanganani Tutu were the co-supervisory authors and they were also involved throughout the project. Divan van der Berg and Nico Lemmer helped with the collection of data and analysis of the data in the laboratory.

Current status of article

Article 1: The paper has been submitted to be peer-reviewed in The Journal of Physics and Chemistry

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Article 3: The paper has been accepted for publication by The Journal of Desalination and Water Treatment.

ACADEMIC AND TECHNICAL OUTPUTS

PUBLICATIONS

Manyatshe, A., Fosso-Kankeu, E., Van der Berg, D., Lemmer, N,. Waanders., F. and Tutu, H. **2016.** Dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom. Physics and Chemistry of the Earth, 65. *Personal contribution: performed the experimental work, wrote the initial draft manuscript and compiled the revised manuscript.*

Manyatshe, A., Fosso-Kankeu, E., Van der Berg, D., Lemmer, N,. Waanders., F. and Tutu, H. 2016. Temporal variation of metal speciation in the Vaal and Mooi Rivers based on the seasonality. Physics and Chemistry of the Earth, 66. *Personal contribution: performed the experimental work, wrote the initial draft manuscript and compiled the revised manuscript.*

A. Manyatshe, E. Fosso-Kankeu, D. van der Berg, N. Lemmer, F. Waanders and H. Tutu, Metal retention potential of sediment and water quality in the Mooi River, South Africa, Desalin. Water Treat. 2016. *Personal contribution: performed the experimental work, wrote the initial draft manuscript and compiled the revised manuscript*

CONFERENCE PROCEEDINGS

Manyatshe, A., Fosso-Kankeu, E., Van der Berg, D., Lemmer, N,. Waanders, F. and Tutu, H, **2015.** Contaminants in Sediments across the Mooi and Vaal Rivers Network in The Vicinity of Potchefstroom, proceeding of the 7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015), Irene, Pretoria, South Africa, pp. 64–69. *Personal contribution: performed the experimental work, wrote the initial draft manuscript and compiled the revised manuscript.*

OTHER PUBLICATIONS RELATED TO THIS WORK

Fosso-Kankeu, E., Van der Berg, D.P., Waanders, F., Manyatshe, A., Lemmer, N. and Tutu, H. **2015.** Mapping of Surface Water Quality in the Vicinity of Potchefstroom based on Mining Pollutants, proceeding of the 7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015) Irene, Pretoria, South Africa, pp. 43–48. *Personal contribution: performed the experimental work, assisted in compiling the initial draft manuscript.*

Fosso-Kankeu, E., Manyatshe, A., Munyai, A. and Waanders, F. 2016. AMD formation and dispersion of inorganic pollutants along the main stream in a mining area. Proceedings IMWA 2016, Freiberg/Germany Drebenstedt, Carsten, Paul, Michael (eds.) Mining Meets Water – Conflicts and Solutions, pp. 391–397. *Personal contribution: performed the experimental work, assisted in compiling the initial draft manuscript.*

Fosso-Kankeu, E., Manyatshe, A. and Waanders, F. 2016. Mobility potential of metals in acid mine drainage occurring in the Highveld area of Mpumalanga Province in South Africa: Implication of sediments and efflorescent crusts. International Biodeterioration & Biodegradation, 1–10. *Personal contribution: performed the experimental work, assisted in compiling the initial draft manuscript*.

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Abstract

South Africa is a country with fewer water resources, as large parts of the country are semi-arid, and the scarcity of water is exacerbated by the pollution of surface water, largely by anthropogenic sources, especially mining activities. In the North West Province, the effluent of acid mine drainage from mining activities is regarded as the major source of pollution in the aquatic environment, as it contains metals such as iron and sulphate and has a low pH (< 2.5). Various mines, especially the gold mines, are situated near the Wonderfonteinspruit (WFS) catchment, which is a tributary to the Mooi River upstream of Potchefstroom. During heavy rainfalls the Mooi River receives large volumes of wastewater from the WFS, which reduces the quality of the surface water. The Mooi River in turn contaminates the Vaal River downstream of Potchefstroom. However, these rivers also receive water pollution from other sources such as the municipal sewage works, industries and agricultural land.

The main objective of this study was to determine the main sources of pollutants and the extent of contribution to the contamination of the surface water in the vicinity of Potchefstroom. This objective was achieved by systematic sampling along the Mooi and Vaal Rivers. The measured physico-chemical parameters were compared with the SANS guideline for drinking and irrigation water, in order to assess the suitability of the surface water for human consumption and agricultural uses. A statistical analysis was also done in order to obtain a good knowledge of the relationship of the water quality indicators. About 44 water samples were collected seasonally (wet and dry) to be analysed for physico–chemical parameters. In addition, 9 sediment samples were selected in the dry season and assessed using a four-stage sequential extraction method. The reason for collecting the water samples seasonally was to assess the variation in chemistry between the two seasons. A pH combined electrode with an integrated temperature probe was used *in situ* to measure parameters such as temperature (˚C), pH, electrical conductivity (EC), dissolved oxygen (DO) and oxidation-reduction potential (ORP). At the laboratory, a COD and Multiparameter Bench Photometer HI 83099 were used to analyse the water for sulphate, nitrate and cyanide. The total content of metals was analysed using inductively coupled plasma spectroscopy (ICP-OES). Parameters such as chloride and the total alkalinity were measured through the titration method. The sediment samples were characterised using the X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier transformed infrared (FTIR) spectroscopy to determine the mineralogical composition, major components, and functional groups, respectively. The total organic carbon was also determined in the sediments by using the Walkey Balk titration method.

Results obtained from the water analyses showed high concentrations of trace metals (Ca, Mg, As, Cd, Fe, Pb, U) and major anions (SO_4^{2-}, CN^-, NO_3^- and Cl^-) mostly in sampling points situated near the mining activities. A decreasing trend of concentrations was observed when moving downstream of the study area. The significant decrease observed in Potchefstroom can be explained by two factors. Firstly, it can be due to the dilution effects by the Mooi River and secondly, it could be because mining activities are much less evident in this area. However, the concentration increases again when moving downstream of Potchefstroom. The elevated concentrations recorded at these points can be attributed to the mining activities at Orkney and its vicinity or wastewater from municipal and domestic sewage. A significant decrease of pollution was observed in the dry season, suggesting that the level of pollution was mainly influenced by large effluents caused by heavy rainfall. The PHREEQC data results revealed that high percentages of Ca and Mg were present as free hydrated species, whereas the Fe, Pb, As and U concentrations were mostly present as carbonate or hydroxide species in both the wet and dry seasons, respectively. However, some percentages of Fe were also present as free hydrated species and thus likely to cause toxicity in the surface water.

The sequential extraction results revealed that metals such as Ca and Mn were mostly associated with the exchangeable fraction while iron and manganese are dominantly found in the oxide fraction. Mg, Fe and Cr were mostly bound to the residual fraction. Metals associated with the exchangeable fraction show higher bioavailability and these metals are likely to increase the level of toxicity in the water, while metals associated with the residual fraction are strongly bound to the sediments and less susceptible to mobilization. The XRF and XRD results showed that the sediment samples consisted predominantly of SiO_2, CaO, Fe_2O_3, MgO, MnO, Cr_2O_3 oxides and quartz minerals, respectively. FTIR results revealed that the sediments mostly contained inorganic materials such as clay and quartz, and this was substantiated by the bands at 788.40 cm^{-1}, 690.00 cm^{-1}, 688.33 cm^{-1}, 629.56 cm^{-1} and 629.25 cm^{-1}, which represented AA, BB, CC and DD, respectively in all the sediment samples. In conclusion, it was observed that the water quality in the studied areas was poor, rendering it unfit for drinking and irrigation purposes according to the SANS/WHO guidelines. Elevated pollution was observed in the sampling areas situated near the mining area. However, the runoffs from agricultural land and municipal sewages have an impact, especially during the wet season, as some elevated concentrations were observed in the sampling points situated near these areas.

Keywords: Wonderfonteinspruit**,** mining activities, Mooi River, Potchefstroom, Vaal River, physico-chemical parameters, sequential leaching

Table of contents

DECLARATION i

PREFACE ii

- Introduction ii
- Rationale in submitting dissertation in article format ii
- Contribution to articles iii

ACADEMIC AND TECHNICAL OUTPUTS iv

- PUBLICATIONS iv
- CONFERENCE PROCEEDINGS iv

OTHER PUBLICATIONS RELATED TO THIS WORK v

ACKNOWLEDGEMENTS vi

Abstract vii

Table of contents ix

List of Figures xiv

List of Tables xviii

List of abbreviation xx

Chapter 1 Background and motivation 1

- 1.1 Introduction 1
- 1.2 Problem statement 2
- 1.3 Aims and objectives 3
  - 1.3.1 Main aim 3
  - 1.3.2 Specific objectives 3

1.4 Research questions 3
1.5 Dissertation structure 3
1.6 References 6
Chapter 2 Literature Review 8
2.1 Introduction 8
2.2 General information on sources of pollution 8
2.3 Impacts of non-point source pollution 9
2.4 Effects of non-point pollution 9
2.5 Mining activities and its impact on water systems 10
2.6 Mining activities in the vicinity of Potchefstroom 11
2.7 Weathering of tailings dumps and impacts on the water system 11
2.8 Formation of acid mine drainage 12
2.9 Impacts of acid mine drainage on the environment 13
2.10 Mine effluents contaminating the water system 14
2.11 History of mine related water pollution and incidents in the North West Province 14
2.12 Geochemistry of the water systems and relevance 15
2.13 The seasonal effect on the dispersion of inorganic contaminants in surface water 16
2.14 Impact of the sediment on the distribution of contaminants in the river 16
2.15 Speciation of metals using geochemical modelling 17
2.16 Piper diagram 17
2.17 Conclusion 17
2.18 REFERENCES 19
Chapter 3 Article 1: Dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom 29
General overview of article 1 29

1 Introduction 31
2 Materials and methods 32
  2.1 Sampling 32
  2.2 Data analysis 34
  2.3 Data treatment 35
3 Results and discussion 35
4 Conclusion 47
Acknowledgement 48
References 48
Chapter 4 Article 2: Temporal variation of metal speciation in the Vaal and Mooi Rivers based on the seasonality 52
  General overview of article 2 52
ABSTRACT 53
1 Introduction 54
2 Materials and method 55
  2.1 Sampling site description 55
  2.2 Sampling procedure 59
  2.3 Laboratory analysis 59
  2.4 Data treatment 60
    2.4.1 Statistical analysis 60
    2.4.2 Geochemical modelling 60
3 Results and discussion 60
  3.1 Spatial and temporal variation 60

3.1.1 Major anions 64

3.1.2 Major cations 68

3.1.3 Trace elements 71

3.1.4 Metal speciation in surface water 71

4 Conclusion 74

Acknowledgement 74

References 74

Chapter 5 Article 3: Metal retention potential of sediment and water quality in the Mooi River, South Africa 78

General overview of article 3 78

Abstract 79

1 Introduction 80

2 Study area 81

3 Methodology 82

3.1 Sampling 82

3.2 Experimental protocol 83

3.3 Reagents 83

3.4 Fourier transform infrared spectroscopy (FTIR) method 83

3.5 Sequential extraction method 84

4 Results and discussion 86

4.1 XRD analysis of mineralogical composition 86

4.2 XRF analysis of major components 86

4.3 Metal speciation in sediment 87

4.4 Total organic carbon in sediments 89
4.5 FTIR spectroscopy 89
4.6 Water quality 91
5 Conclusion 95
Acknowledgements 96
References 96
Chapter 6 CONCLUSION AND RECOMMENDATIONS 100
6.1 Conclusion 100
6.2 Recommendations 101
Appendix A Pictures of sampling site 102
Appendix B Experimental calculations 118

List of Figures

Article 1: Dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom

Figure 1: Map of the Study area in the North West Province South Africa…………………………………………………………………….. 34

Figure 2: Piper diagram of water samples from upstream, Potchefstroom and downstream areas 46

Article 2: Temporal variation of metal speciation in the Vaal and Mooi Rivers based on the seasonality

Figure 1: Google Earth Map showing the Mooi River upstream of Potchefstroom 57

Figure 2: Google Earth Map showing the Boskop Dam...57

Figure 3: Google Earth Map of Potchefstroom (Lakeside) Dam...58

Figure 4: Google Earth Map showing the Potchefstroom area..58

Figure 5: Google Earth Map showing the downstream area..59

Figure 6: Seasonality of pollution: (a) pH; (b) EC (mS/cm) and (c) sulphate (mg/L 68

Article 3: Metal retention potential of sediment and water quality in the Mooi River, South Africa

Figure 1: The study area in the North West Province of South Africa (the Mooirivierloop is now known as the Wonderfonteinspruit)..81

Figure 2: Map of the study area showing sampling points (1- 9) 84

Figure 3: Flowcharts for the BCR speciation scheme of sediments…………………………….85

Figure 4: Mineralogical composition of the sediments (fraction <63 µm) from the Mooi River...86

Figure 5: Selected major and trace components of sediments (fraction < 63 µm) 87

Figure 6: Metal distribution among the different fractions: (A) Calcium, (B) Magnesium, (C) Iron, (D) Total Chromium and (E) Manganese) 88

Figure 7: FTIR spectra of samples: (A) Upstream, (B) Midway and (C) Downstream.............90

Appendix A

Figure A:1: Sample point 1 and 2 (Klerskraal Dam) 102

Figure A:2: Sample point 3 (Driefontein mine canal) 102

Figure A:3: Sample point 4 (Downstream of mine canal) 103

Figure A:4:Sampling point 5 (Mooi River) 103

Figure A:5: Sampling point 6 (Turffontein upper eye)...104

Figure A:6: Sampling point 7 (Turffontein lower eye)...104

Figure A:7: Sample point 8 (Gerhardminedorom eye) 105

Figure A:8: Sampling point 9 – 17 (Boskop Dam)...105

Figure A:9: Sample point 18 (origin of Boskop canal next to Dam wall) 106

Figure A:10: Sample point 19 (Upstream of Potchefstroom Dam) 106

Figure A:11: Sample point 20 (Boskop Dam canal at Potchefstroom)....................................107

Figure A:12: Sample 21 – 25 (Potchefstroom Dam) 107

Figure A:13: Sample point 26 (Potchefstroom Dan canal)...108

Figure A:14: Sample point 27 (Origin of Mooi River after Potchefstroom Dam)...................108

Figure A:15: Sample point 28 (Mooi River)..109

Figure A:16: Sample point 29 (Mooi River meet Ikageng canal)..109

Figure A:17: Sample 30 (Mooi River)...110

Figure A:18: Sample point 31 (Mooi River)..110

Figure A:19: Sample 32 (Mooi River)...111

Figure A:20: Sample 33 (Ikageng canal) 111

Figure A:21: Sample 34 (Boskop Dam canal downstream of Potchefstroom) 112

Figure A:22: Sample point 35 (Boskop Dam canal downstream of Potchefstroom)...............112

Figure A:23: Sample point 36 (Vaal River upstream) 113

Figure A:24: Sample point 37 (Vaal River at bridge)..113

Figure A:25: Sample point 38 (Vaal River downstream) 114

Figure A:26: Sample point 39 (stream at Orkney area) 114

Figure A:27: Sample point 40 (stream at Orkney)...115

Figure A:28: Sample point 41 (Mine canal) 115

Figure A:29: Sample point 42 (Stream) 116

Figure A:30: Sample point 43 (Downstream of Water retain Dam) 116

Figure A:31: Sample point 44 (Upstream of Water retention Dam) 117

List of Tables

Article 1: Dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom

Table 1: Geochemical parameters and major anions of surface water and maximum permitted concentration in drinking water. 37

Table 2: Trace element concentrations in surface water and the maximum permitted concentration in drinking water 40

Table 3: The statistical parameters of all the measured variables in the surface water in the vicinity of Potchefstroom: Statistical summary of parameters.................................43

Article 2: Temporal variation of metal speciation in the Vaal and Mooi Rivers based on the seasonality

Table 1: Description and locations of the sampling sites..55

Table 2: Seasonal variation of *in situ* parameters measured in surface water in the vicinity of Potchefstroom and maximum permitted concentration (mg/L) in drinking water...61

Table 3: Alkalinity (mg/lCaCO3) and major anions (mg/L) measured in the vicinity of Potchefstroom during wet and dry season and maximum permitted concentration in drinking water (mg/L). 65

Table 4: Seasonal variation of major cations and trace metals (mg/L) measured in surface water in the vicinity of Potchefstroom and maximum permitted concentration in drinking water (mg/L)...69

Table 5: Range of highest percentages of speciated forms of metals measured in surface water in the vicinity of Potchefstroom. 71

Article 3: Metal retention potential of sediment and water quality in the Mooi River, South Africa

Table 1: Sampling point description and coordinates 82

Table 2: Total organic carbon of sediments samples from the Mooi River 89

Table 3a: Physico-chemical parameters and major anions concentrations in water samples 93

Table 3b: Major anions and heavy metals concentration in the water sample…………………….94

List of abbreviation

NRF	National Research Foundation
WFS	Wonderfonteinspruit
SANS	South African National Standards
WHO	World Health Organisation
EC	Electrical Conductivity
DO	Dissolved Oxygen
ORP	Oxidation – reduction potential
ICP-OES	Inductively coupled plasma spectroscopy
XRD	X- ray diffraction spectroscopy
XRF	X-ray Fluorescence spectroscopy
FTIR	Fourier transformed infrared
NWU	North – West University
AMD	Acid mine drainage
BCR	Community Bureau of Reference
PS	Point source
NPS	Non – point source
As	Arsenic
Cd	Cadmium
Pb	Lead
U	Uranium

TDS	Total dissolved solid
TOC	Total organic carbon

Chapter 1

Background and motivation

1.1 Introduction

Since the discovery of gold in the Witwatersrand in 1886 (Winde & Sandham, 2004), the gold-bearing conglomerates of the Witwatersrand super-group have been mined (Holland & Witthuser, 2008; Naicker *et al*., 2002; Opperman, 2008). After a year, with the establishment of West Rand consolidate in 1887, gold-mining reached the Wonderfonteinspruit area (Coetzee *et al*, 2006). These gold mines played a crucial role for the development of South African economy (Schonfeld *et al*., 2014). However, they have the negative impact of contaminating the environment, especially water (Durand, 2012). The situation in the environment has exacerbated for the past few years due to the abandonment of some of the gold mines (Van Eeden *et al*., 2009). Large volumes of underground water have been discharged into the Wonderfonteinspruit during the process of dewatering the dolomitic groundwater compartment overlying auriferous reefs at gold mines (Malan, 2002). This process of dewatering has hugely changed the land-usage patterns in the area, because it led to a lack of water available for agricultural uses and to the formation of sinkholes (Coetzee *et al*., 2006). Many of these sinkholes have not yet been rehabilated (Van Eeden *et al*., 2009). The sinkholes, which are filled with tailings, could become a secondary source of uranium and other heavy metals contamination when the mines close.

The Wonderfonteinspruit (WFS) originated from the surface water divide immediately to the south of Krugersdorp in the Gauteng Province and flows into the Mooi River, close to Potchefstroom in the North West Province, South Africa. The Mooi River flows into the Klerkskraal Dam, Boskop Dam and Potchefstroom Dam, and finally into its tributary, which is the Vaal River (Malan, 2002). For more than a century, a large amount of tailings dumps containing elevated amount of uranium and other heavy metals which are toxic, have been produced by the gold mines (Winde & Sandham, 2004). A large amount of these metals gain entry into the Wonderfonteinspruit through point discharges and non-point discharges (Barthel, 2011). It is estimated that these point sources release approximately 50 tons of these radioactive metals into the aquatic environment every year (Winde, 2006).

Elevated concentrations of radionuclides like uranium and other heavy metals have been detected in streams situated in the proximity of the gold mining activities (Wade *et al*., 2002). Therefore, these inorganic contaminants are reducing the quality of water resources used by the community in the vicinity of Potchefstroom for various purposes including the maintenance of their livestock. For example, the Mooi River supports the famers with water for irrigation; and the local community relies on the water for drinking purposes and other essential uses. The contamination of this catchment can pose a serious risk to the health of people who reside in the proximity, especially in the informal settlements in which polluted water is often consumed without genuine treatment (Winde & Van der Walt, 2003). In addition, communities living around the tailings may be exposed to contained contaminants through various pathways, which include the intake of contaminated water and foodstuffs and the breathing of tailings dust (Schonfeld *et al*., 2014).

High levels of metal pollution from gold mines in the catchment area of the Wonderfonteinspruit have attracted the attention of media at some time, which suggested that there is a huge work that still needs to be done in order to protect the aquatic environment in this area (Department of Water Affairs and Forestry, 2009). The pollution from these gold mining activities and other alternative sources like domestic sewage, water treatment plants, industries and runoffs from agricultural land are major concerns, as they play a vital role to the reduction of the water quality. In South Africa, one of the countries that has a shortage of water (Nare *et al*., 2011), it is vital to know the quality of the

water. Water pollution can have a major impact on the future of socio-economic development, since a country needs good water quality to develop. The major aim of this study was to identify the source of pollution in the water systems and to investigate how much of these contaminants are contributing towards poor water quality. Most of the water supplied to communities originates from surface water, therefore; it is very important to protect these water resources. In addition, knowing the concentrations of toxic metals in the surface water could assist water managers in the vicinity of Potchefstroom to have a sound knowledge about the quality of the water.

1.2 Problem statement

The discharge of waste water, which comes from the gold mining activities situated around the Wonderfonteinspruit area, reduces the quality of the surface water in the vicinity of Potchefstroom. Gold mining activities in Carletonville have been implicated in the contamination of the catchment areas of the Boskop Dam, Mooi River, streams in Potchefstroom connected to the Mooi River, and Potchefstroom Dam. In addition, there could be a potential impact on streams supplying Potchefstroom with water as a result of the mining activities around Orkney. However, the exact contribution from these sources as well as alternative sources such as sewage, industrial effluent, agricultural runoff and solid waste is not well known, and the behaviour of contaminants along the river basin is not clearly established. The researcher expected that systematic sampling across the area of concern and the use of geochemical models would shed some light on this quest.

1.3 Aims and objectives

1.3.1 Main aim

The central aim of this study was to discover the source of pollutants and the extent of their contribution to the contamination of the surface water in the vicinity of Potchefstroom.

This aim was achieved by addressing the following specific objectives.

1.3.2 Specific objectives

The specific objectives were:

i. To determine the fitness of water for various uses
ii. To determine the potential of pollutants dispersion through speciation
iii. To identify the seasonal impact on the pollution of surface water

1.4 Research questions

The research aimed at addressing the following questions:

i. What are the main sources of pollutants?

ii. What is the quality of surface water in the vicinity of Potchefstroom?

iii. How is the metal speciation in the surface water?

iv. What is the level of contamination that these sources cause in the surface water in the vicinity of Potchefstroom?

v. What are the mineralogical composition and major components of the metals in the sediments?

vi. What is the mobility potential of metals in the sediments?

1.5 Dissertation structure

All the research work presented in this dissertation has been conducted both on site and in the laboratory. Three papers were written for this dissertation and they are arranged in chronological order to conform to the requirements of the North-West University (Potchefstroom Campus) for the degree of Master of Science. This dissertation comprises of six chapters; a summary of each chapter is provided:

CHAPTER 1: Background and motivation

This chapter provided a background of polluting sources in the vicinity of Potchefstroom, especially gold mining activities, as they are potential sources of pollution in this area. The motivation for the study was provided. The problem statement or hypothesis, objectives and research questions were also briefly discussed.

CHAPTER 2: Literature review

In this chapter, literature about the research topic was discussed and information from previous studies was provided. It mainly focused on the acid mine drainage (AMD) from abandoned and currently active mines, as this is regarded as the main cause of elevated concentrations of heavy metals in surface water.

CHAPTER 3: Dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom

This chapter investigated the sources of pollutants and their level of contribution to contamination, and how they were dispersed in the surface water in the vicinity of Potchefstroom. This section mainly discusses the impact of mining activities on the water sources in the vicinity of the study area. The measured concentrations were compared with the SA/WHO water guideline in order to assess whether the water was fit for human uses and irrigation purposes. The pictures of the sampling sites are presented in Appendix A. The proceeding paper of this article was presented by Divan van der Berg at an international conference held in Pretoria, South Africa.

CHAPTER 4: Temporal variation of metal speciation in the Vaal and Mooi Rivers based on the seasonality

This chapter concentrates on assessing the temporal and spatial variations of pollution between the wet and dry period, respectively. The variation of metal speciation was also calculated using the PHREEQC computer model. This model predicted the speciation of the studied metals by showing how these metals will behave in surface water. The sampling sites are presented in Appendix A.

CHAPTER 5: Metal retention potential of sediment and water quality in the Mooi and Vaal Rivers

In this chapter, both the sediments and surface water samples were investigated to assess the metal retention potential of the sediments and the water quality. The sediment samples were analysed to determine the chemical partitioning of selected heavy metals by using the BCR sequential extraction method, while the surface water samples were analysed for the physico-chemical parameters and content of heavy metals. The proceeding of this paper was presented by the author at an international conference held in Pretoria, South Africa.

CHAPTER 6: Conclusion and recommendation

This section provides a conclusion of the findings obtained during the investigation and makes some recommendations that can benefit the affected stakeholders.

1.6 References

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Chapter 2

Literature Review

2.1 Introduction

An overview of the available literature on non-point and point sources of pollution will be discussed, since they are regarded as the main causes of contamination in the aquatic environment. This section will also focus on the impact caused by the mining activities on the water system. Mining activities in the vicinity of Potchefstroom will be discussed, especially the gold mine activities, since gold mines are predominantly found in the study area. More attention will be given to the acid mine drainage (AMD) from abandoned and currently active mines, as this is regarded as the main cause of elevated concentrations of heavy metals in surface water. This section will also discuss the formation of acid mine drainage and the impact it has on the aquatic environment. The history of mine related water pollution and the incidents thereof in the North West Province will be presented. Furthermore, the researcher will focus on the seasonal effects in the dispersion of inorganic contaminants in surface water, impacts of sediments on the distribution of contaminants in the river, and then finally the background of geochemical modelling and Piper diagrams will be discussed.

2.2 General information on sources of pollution

The pollution of surface water by anthropogenic activities like domestic and commercial sewage, water treatment plants, industries, mining activities and agricultural runoffs are the major concerns when determining the quality of water or the lack thereof, both locally and worldwide (Korfali and Davies, 2003; Magu *et al.*, 2015). These anthropogenic sources are separated into the following categories; non-point and point sources (Esen & Uslu, 2008): Point source (PS) pollution is easy to identify and control as it flows into the water system from one direction. In contrast to point source pollution, non-point source (NPS) pollution can be very difficult to regulate, as it flows into the water system through many ways (Chen *et al.*, 2014). Examples of point source pollution include effluents from industries, combine sewer and wastewater treatment plants (Ritter *et al*., 2011), whereas examples of non-point pollution include effluents from mining areas as well as fertilizers and pesticides from agricultural lands (Carpenter *et al.*, 1998; Karan & Samadder, 2016; Xiao & Ji, 2006). The quality of the surface water can usually be attributed to the pollution arising from these sources, because surface water is easily exposed to the environment (Hamman, 2012). Polluted water from these sources contains some toxic chemicals that cause major threats to the quality of the aquatic environment (Ouyang *et al.*, 2016). For example; mining activities, industries and agricultural effluents contribute to the degradation of water quality, since their treated and untreated waste effluents contain toxic metals (Kar *et al.,* 2007). Acid mine drainage (AMD), which flows from closed and currently active mines, is the main source of pollution that has raised major concerns in the aquatic environment worldwide (Department of Environmental Affairs and Tourism, 2008). The effluents from agricultural activities also cause major impacts, as the fertilizers and pesticides increase the level of nitrates in surface water (Esen & Uslu, 2008).

2.3 Impacts of non-point source pollution

The discharges from agricultural lands and urban and mining activities have long been regarded as the main sources of non-point pollution (Mencio & Mas-Pla, 2008; Xiao & Ji, 2006). Among these sources, discharges from agricultural lands have been considered as the main contributors to non-point pollution around the world (Liu *et al*., 2012), as most of the farmers use chemical fertilisers and pesticides to increase their production without considering the impact that it can have on the aquatic environment (Rao *et al*., 2011). The development of agriculture has increased the watershed soil erosion and this releases more associated non-point source pollutants, such as nitrogen, phosphorous and heavy metals (Ouyang *et al*., 2016). However, the abandoned and currently active mines are also important sources that elevate the level of toxic metals often recorded in soils and adjacent river systems (Beane *et al*., 2016). For example, seepages from slime dams, contaminated rainwater runoffs from rocks and tailing dumps, ore piles, and uranium production are accountable for the degradation of the surface water and soil quality in the Wonderfonteinspruit area, South Africa (Winde, 2006). In addition, uranium and various other heavy metals that are carried by the effluents from mines can be very harmful to the living organisms in the water and can also disturb the aquatic environment (Coetzee *et al*, 2006). However, the level of contamination depends on the crop type, the soil properties, characteristics of the water bodies, and the land close to the water bodies (Bermudez-Couso *et al*., 2013). The non-point sources are causing the most concern in the aquatic environment, because their pollutant concentrations are not easy to quantify when compared to those of point sources (Malan, 2002).

2.4 Effects of non-point pollution

The concentrations of nitrogen and phosphorous that flow from the agricultural land, have a huge effect on the aquatic environment (Esen & Uslu, 2008). For example, elevated concentrations of nitrogen and phosphorous are the main source of eutrophication in lakes, reservoirs and on other water surfaces (Guo *et al*., 2013). Furthermore, heavy metals such as, Fe, Ca, Zn, U and others that are carried in the effluents from tailings dumps can cause greater effects in soil and surface water, as they have the ability to reduce the quality of both the water and soil (Navarro *et al*, 2008). Therefore, soil pollutants generally inhibit the enzymatic activity in soils, because they cause more stress on the microbiota (Maboeta *et al*., 2006). Mining dumps are regarded as having a high potential to release radon, especially during the mining of uranium (Ongori *et al*, 2014). Radon can cause serious health damage after long-term exposure.

2.5 Mining activities and its impact on water systems

Mine wastes have been generated from mining activities for several centuries, and their impact can be observed in both surface water and groundwater (Ledin & Pedersen, 1996). Mining itself affects a relatively small area, however; their sand dumps and waste rock deposits adjacent to the mining area are major sources of toxic metals in the environment (Solomons, 1994). In an open cast mine, the waste materials are piled on the soil surface and during runoffs these piled materials pollute and alter the flow paths of local streams (Karan & Samadder, 2016). Mine discharges have a direct impact on the environment, as it affects the water system and its ecosystem in diverse ways: the hydrological pathways can be disrupted, the rate of groundwater recharge may enhance and water pollution may occur (Robles-Arenas *et al*., 2006). The large amounts of toxic waste materials that are produced during the exploration of mines have become the main sources of environmental pollution, especially with regard to the contamination of rivers and other water bodies (Islam *et al.*, 2014). Most of these metals are highly toxic in water and have major effects on the living organisms in the water: they can (Sharma & Agrawal, 2004), for example, affect the reproduction of fish (Kashulin *et al.*, 2007).

In the United States and other European countries, they are facing the result of the pollution from tailings dumps that were mined hundred years ago. The waste waters from these tailings dumps have been reported to have a significant impact on the environment and water bodies in these countries (Resongles *et al*, 2014). The water quality of the wetlands, rivers and groundwater has worsened over the past decades as a results of effluents from mines in the North West Province, South Africa; (Durand, 2012); as these mines' effluents contain radioactive metals (Wade *et al*., 2002), which can be potentially detrimental to human health and to livestock (Durand, 2012). In addition, the effluents from mines have a negative impact of increasing the level of suspended solids; this results in the mobilization of toxic elements such as iron, aluminium, cadmium, cobalt, manganese and zinc (Ochieng *et al*., 2010).

2.6 Mining activities in the vicinity of Potchefstroom

Mining activities, such as gold mining, can be dated back to 1886 in the Johannesburg area, South Africa (Naicker *et al*., 2002). These gold mines produced tailings that are piled in large dumps, known as tailings dumps (Tutu *et al*., 2008). These large dumps have been leaching the toxic metals into the rivers and streams for decades (McCarthy, 2011). Drainage from tailings dumps and waste rock produced by mining activities generally contain elevated concentrations of heavy metals and has an acid pH, because of the various microbiological, chemical and hydrological weathering processes that act on the waste (Ledin & Pedersen, 1996). The gold mines in the Witwatersrand are associated with pyrite (FeS_2); however, this pyrite, which constitutes up to approximately 3 percent of the gold bearing reefs (Hansen, 2015), and other sulphates remain unshaken underground, but it produces iron hydroxide and sulphuric acid when it comes to contact with the oxygen and water (Durand, 2012). The gold mining activities in the West Wits near Carletonville, South Africa, are accountable for the high levels of toxic metals found in the water and sediment of the Mooi River (Van Ardt & Erdmann, 2004).

Most of the Witwatersrand mines have been using a cyanide for the extraction of gold ores for many years (Durand, 2012; Tutu *et al*., 2008). However, some of these mines also uses the mercury for the extraction of gold in this area (Lusilao – Makiese *et al*., 2013). After extraction of the gold, the crushed rock is deposited on waste heaps known as tailing dumps and this posed a negative impact to the nearby environment (Khamar *et al*., 2015, McCarthy, 2011). Therefore, liquid wastes discharged during the extraction of gold ore often contain significant amount of heavy metals (Patil & Paknikar, 2000). The presence of cyanide in natural waters is a matter of major concern, since it can be detrimental to aquatic ecosystems and to human health (Hijosa – Valsero *et al.*, 2013). In addition, the exposure to metal such as mercury can cause development of autoimmunity, in which a person immune system attacks its own cells (Barakat, 2010). Many studies have discovered high concentrations of radioactive heavy metals in groundwater and surface water (Winde & Sandham, 2004), which were mainly attributed to the effluence of wastewater from mines (Coetzee *et al*., 2006; Van Aardt & Erdmann, 2004; Van Eeden, 1997; Wade *et al*., 2002; Winde & Sandham, 2004; Winde, 2006). This radioactivity is a major concern to the local residents and those living downstream, such as the Potchefstroom residents, because it increases the level of toxins in the water (Winde, 2006).

2.7 Weathering of tailings dumps and impacts on the water system

Mining activities around the world produce different types of mine wastes that include the tailings dumps, which act as main sources of environmental contamination, and impact on the water system (Bempah *et al*, 2013). These tailings dumps are responsible for the acidification of water due to the oxidation of pyrite and other sulphide minerals found in the tailings ores (Camden-Smith & Tutu, 2014).

Oxidation of the sulphides in tailings is accountable for the mobilization and migration of metals into the aquatic environment (Candeias *et al*., 2013). The growth of mining activities in some African countries like Botswana, the Democratic Republic of the Congo and South Africa has generated an increase in tailings dumps, which cause contamination of surface water and groundwater (Ekosse *et al.*, 2004).

The chemical weathering of tailings releases metallic elements such as Cd and Zn into the water surface (Kossof *et al.*, 2008), and these mine tailings are regarded as the sources of potentially toxic metallic elements such as arsenic, iron, lead and others when they are directly discharged into the water surface during tailings dump spills (Akcil & Koldas, 2005). In South Africa, most of the tailing dams in the Witwatersrand basin, occupy approximately 400 km^2 (Van Eeden *et al*., 2009), and these dams are situated next to urbanised areas or valuable agricultural areas (Rosner & Van Schalkwyk, 1999). Poor management of tailings dumps in South Africa has resulted in the contamination of soil and reduces the quality of surface water and groundwater in many parts of the country (Opperman, 2008).

2.8 Formation of acid mine drainage

Acid mine drainage (AMD) is a long-term environmental concern connected with mines throughout the world (Balintova *et al*., 2012; Myers, 2015). However, it can also occur wherever sulphide materials are exposed to oxygen, for example during the construction of a tunnel (Candeias *et al.*, 2013; Simate & Ndlovu, 2014). Acid mine drainage resulted from the oxidation and hydrolysis of sulphide minerals like a pyrite (FeS_2) (Pellegrini *et al.*, 2015), when exposed to atmospheric oxygen, water and microorganisms (Gray, 1997; Simate and Ndlovu., 2014). When the mineral pyrite (FeS_2) is mixed with water containing oxygen, the reaction happens in two stages: the first stage is the production of sulphuric acid and ferrous sulphate, and secondly there is the production of orange-red ferric hydroxide and more of sulphuric acid (McCarthy, 2011). This process of oxidation may continue for decades or even centuries after the closure of the mine (Christensen *et al*., 1996; Galan *et al*., 2002). Naturally-occurring bacteria, such as *acidophilic* and *archaebacterial* catalyse the process of oxidation (De la Torre *et al.*, 2013).

The process of AMD is complex, as it involves chemical, biological and electrochemical reactions that vary with environmental conditions (Candeias *et al.*, 2013). In surface and groundwater, acid mine drainage is often characterised by elevated concentrations of iron and sulphate, a low pH, a high conductivity and a wide variety of metals, depending on the host rock geology (Achterberg *et al*., 2002; Akcil & Koldas, 2005; Balintova *et al.*, 2012; Gray, 1997). The oxidation of pyrite can be summarised by the following reactions (Singer & Stumm, 1970):

$FeS_2 + {}^{7}/_{2}\, O_2 + H_2O \rightarrow Fe^{2+} + 2\, SO_4^{2-} + 2\, H^+$ (1)

$Fe^{2+} + {}^{1}/_{4}O_2 + H^+ \rightarrow F^{3+} + {}^{1}/_{2}H_20$ (2)

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ (3)

$Fe^{3+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H^+$ (4)

Reaction (1) shows that mineral pyrite will react with the oxygen and water to produce the ferrous iron. Therefore, reaction (2) indicates that the ferrous iron will oxidize to ferric iron, but the rate of oxidation of the ferrous iron into ferric iron is too slow at a low pH. However, if the pH is very low, oxidation can take place, since it is mediated by Fe-oxidising bacteria (Moreno & Neretnieks, 2006). In reaction (3), the dissolved ferric iron (Fe^{3+}) from reaction (2) is the oxidizing agent for pyrite and reaction (4) portrays that part of the Fe precipitates as $Fe(OH)_3$. The rate-determining step in this whole sequence is the formation of Fe(III). These stages are the primary factors directly involved in the acid production process (Solomons, 1994).

2.9 Impacts of acid mine drainage on the environment

Acid mine drainage (AMD) is a major concern for a number of countries having past or current mining industries, because it enhances the level of toxic elements in the aquatic environment (Willscher *et al.*, 2010; Jonson & Hallberg, 2004; Zhang *et al.*, 2013), although the overall impact of acid mine drainage depends on the local conditions that include the geomorphology and the distribution of this AMD along the environment (MacCarthy, 2011). Acid mine drainage is recognised as one of the most challenging environmental concern facing the world today, because it is difficult to control once it invades the environment and the cost of treatment is highly expensive (Aguiar *et al*., 2016). In addition, acid mine drainage can have long-term impairments to watercourse and biodiversity (Akcil & Koldas, 2005). It is in the nature of mining to consume, divert, and cause significant pollution in water (Ochieng *et al*., 2010). Acid mine drainage can for example introduce high concentrations of iron, copper, zinc, aluminium, sulfuric acid, and metalloids, such as arsenic in the aquatic environment (De la Torre *et al.*, 2013). Therefore, elevated concentrations of these metals lowered the concentration of the pH in natural water (Kim, 2014) and this makes the water unsafe for other aquatic organisms.

AMD is not only causing problems in water systems, but it is also accountable for the degradation of soil quality (Department of Environmental Affairs & Tourism, 2008). AMD can have a long-term environmental impact, causing problems like revegetation and rehabilitation difficulties (Name & Sheridan, 2014). AMD is reported to cause a significant problem in developing countries, especially to people living in the proximity of the mine sites (Ochieng *et al*., 2010). There are many abandoned and closed mines around the world that are draining acidic water loaded with huge amounts of toxic heavy metals to the environment; in the year 2000; Japan has closed down and abandoned approximately 5 487 mines (Pepe *et al.*, 2007). In South Africa, environmental impacts are mainly caused by the AMD emitted from the coal and gold mines, more especially in the areas of Mpumalanga (Ochieng *et al*., 2010), Gauteng and the North West Province (Name & Sheridan, 2014). AMD contains heavy metals like uranium and because it is not biodegradable, the AMD tends to assemble in the environment and this enhances the uptake of heavy metals by soil and plants (Winde, 2006).

2.10 Mine effluents contaminating the water system

Water pollution is a global challenge threatening sustainable development and in order to solve this problem, all the stakeholders who are responsible for providing safe water need to work together in order to overcome these great obstacles (Karan & Samadder, 2016). The waste water from mines is the biggest source of environmental contamination, mostly in the form of acid mine drainage (Sanchez Espana *et al*., 2005). According to Solomon (1994), when the leachates of AMD reach rivers, a wider dispersion of the metals, both in solution and (after adsorption) in particulate form, is possible. Acid mine drainage has the potential to disturb the normal functioning of the rivers and lakes (Lim *et al*., 2007; Peng *et al.*, 2008), as it contains elevated concentrations of heavy metals (Fernandez-Caliani *et al*., 2008). Furthermore, elevated concentrations of heavy metals can potentially be detrimental to human health if humans drink water directly from the source without any proper treatment (Akpor & Muchie, 2010). High concentrations of metals in water and sediment can result in the loss of the aquatic flora and fauna (De la Torre *et al*., 2013).

The waste water from mines can have a severe impact on the aquatic environment due to its salinity (Broder & Hasche-Berger, 2008; Chalupnik *et al*, 2000). High concentrations of metals such as U, Fe, Al, Cd and Pb have been transported from the gold slime dams and rock dumps as runoffs in water systems of the North West Province (Durand, 2012). Therefore, the chemical leaching of uranium and other heavy metals from tailings dumps can be potentially detrimental to the health of the people who reside in Carletonville, Potchefstroom and other close areas (Winde, 2009).

2.11 History of mine related water pollution and incidents in the North West Province

For more than a century, the process of dewatering the dolomitic karst aquifers have reduced the quality of potable water and the availability of water in the North West Province (Winde, 2006). Elevated concentrations of heavy metals have been produced from gold mines since 1886 (Winde & Sandham, 2004). Uranium, for example, has mainly been produced as a by-product of gold mining in South Africa, with approximately 170 000 t of U_3O_8 that has been produced between 1952 and 1991 (Winde & Van der Walt, 2003). Therefore, people living closer to the gold mines are at risk of getting sick if they directly use the surface water without any proper treatment for domestic purposes (Winde *et al*., 2004). Elevated concentrations of heavy metals and radionuclides from the gold slime dams were reported by other studies examining the sediments of the catchment areas of the Wonderfonteinspruit (Coetzee *et al*, 2006; Marara *et al*., 2011; Winde, 2006; Hamman, 2012).

One of the gold mine activities, the process of dewatering a dolomite rock, has been reported to cause a significant impact on the environment as it leads to the formation of sinkholes and many of these sinkholes have not been rehabilated, while new ones are still forming on the West Rand (Van Eeden *et al*., 2009). Therefore, the presence of oxidized slime materials in sinkholes and dewatered aquifers is of major concern, because toxic metals like uranium are likely to leach out and cause contamination of the aquatic environment (Winde, 2006).

This process of dewatering dolomite rock decreases the availability of water, as the surface water runoffs flow into the sinkholes that were formed during the process (Durand 2012). In addition, this process also lowered the original groundwater table by more than 300 m in some areas (Coetzee *et al*., 2006). This process also affected the farmers badly, as it led to the drying up of irrigation boreholes and dolomitic springs (Winde, 2006). In the 1960s, farmers had to depend on water from the gold mines for the irrigation of their crops and this affected them negatively, as most of the farmers complained that the waste from the respective mines contains harmful elements such as boron and aluminium, which have affected their vegetation and animal life (Van Eeden, 1997).

2.12 Geochemistry of the water systems and relevance

According to Glynn and Plummer (2005), geochemistry has contributed significantly to the improved interpretation of the hydrochemical characteristics of water systems over the past 50 years and this also improved people's understanding of how the structural, geological, mineralogical, and hydrological features affect the flow and chemistry of the water system. Natural processes such as precipitation rate, weathering process and the effluents from mining, industries and agricultural activities control the chemical composition of surface water and its properties (Garizi *et al.*, 2011; Qadir *et al*., 2007). It is vital to determine the chemical, physical and bacteriological quality of a water system, as this can help to have a better understanding of the suitability of the water for essential purposes such as drinking, domestic, industrial and agricultural uses (Engle *et al.*, 2016; Opperman, 2008; Thilagavathi *et al.*, 2012).

2.13 The seasonal effect on the dispersion of inorganic contaminants in surface water

The dispersion of inorganic contaminants in surface water may be controlled by the seasonal variations in precipitation (Varol *et al*., 2011), surface runoff, interflow, groundwater flow and pumped in- and outflows (Shrestha & Kazama, 2006). Seasonal changes to the geochemical and hydrological conditions can affect the leaching of metals from the streams sediment into the aquatic environment through the process of mineral dissolution (Zhang *et al*., 2013). According to Meza-Figueroa *et al.* (2009) the dispersion of trace metals into the aquatic environment is also affected by climatic effects such as heavy winds and heavy rainfall. Therefore, due to the spatial and temporal variations in chemistry of water (Simeonov *et al.,* 2003), it is necessary to have long-term surveys and monitoring programs of the water quality, as this will also help to have a better knowledge of the hydrochemistry of water and pollution (Vega *et al.,* 1998). It is essential that water managers utilise long-term monitoring programs, as it can provide them with enough evidence concerning the quality of the water (Zhang *et al.,* 2010).

2.14 Impact of the sediment on the distribution of contaminants in the river

Trace metals become part of the water sediment system when entering natural water and their distribution processes are influenced by a dynamic set of physico-chemical interactions and equilibria (Jain, 2003). The contaminants of the riverine sediments reflect the history of river pollution (Singh *et al.,* 2005). When trace metals enter the sediments, they are further partitioned into different fractions (Okoro *et al.,* 2012); therefore, the process of metal speciation may head to the self-purification of streams from metal pollution (Korfali & Davies, 2003; Ozkan, 2011). The speciation of metals in sediments plays an important role for the understanding of the bioavailability and toxicity of particular metals in the water system (Thanh *et al.,* 2015). According to Singh *et al.* (2005), sediments can operate both as a carriers and sinks for contaminants in the aquatic environment. Therefore, trace metals may re-enter the water column due to physical, chemical and biological processes (Nwiineewii & Edem, 2014). According to Zhang *et al*. (2013), the understanding of the physical-chemical processes controlling the distribution of trace metals is a starting point for developing the remediation strategies.

2.15 Speciation of metals using geochemical modelling

Geochemical modelling is a reliable object that can be utilised to test the physical-chemical conditions of the mine waste materials piles (Carrillo-Chavez *et al*., 2014). In addition, it can be used to understand and predict the leaching of toxic contaminants in soils, sediments and water systems (Cornelis *et al.*, 2008). The aqueous speciation of metals can be predicted by using AQUACHEM software interfaced with the PHREEQC geochemical computer model (Betrie *et al.,* 2015; Korfali & Jurdi, 2010; Korfali & Davies, 2003; Maleke *et al.,* 2014). Metals in the water system undergo some speciation during their transportation due to precipitation, dissolution, sorption and other complex phenomena (Islam *et al.*, 2014). Metal speciation plays an important role in the understanding of metal bioavailability (Magu *et al*., 2015), toxicity, transference of trace metals into aquatic organisms, risk evaluation and remedial strategies (Korfali & Davies, 2003; Thanh *et al*., 2015). The speciation of a metals in surface water may affect its kinetic and thermodynamic properties (Magu *et al.,* 2015). The speciation of metal in surface water is influenced by pH, alkalinity and the presence of natural organic matter (Charkhabi *et al.,* 2005).

2.16 Piper diagram

According to Teng *et al*. (2016) a piper diagram is a generic design tool that is used to trace the changes of composition of the process stream. There are several graphical methods that are used for the visualization and classification of hydrochemical data, however; the Piper diagram is the most widely accepted method (Ray & Mukherjee, 2008). This piper diagram is often used to investigate the similarities and variations in the compositions of water and categorised them into certain chemical types (Alexakis, 2011). These diagrams can also help people to understand several geochemical processes along the flow path of the water system (Karmegan *et al*., 2010). It can display the important chemical characters of the different constituents in percentages of reacting concentrations, which is presented in milligrams equivalent for each water type (Candeias *et al,*. 2013).

2.17 Conclusion

According to the literature survey, anthropogenic sources, more specifically mining activities, are responsible for the degradation of water quality. The waste water from mines contains elevated concentrations of inorganic contaminants; this causes a major problem for the aquatic organisms and human beings. It was revealed by the literature that acid mine drainage from abandoned and currently active mines contains elevated concentrations of toxic metals. Once this acid mine drainage invades the aquatic environment, it is very difficult to control.

The literature review indicated that gold mines situated in the area of the Wonderfonteinspruit are likely to be responsible for the inorganic contaminants present in the surface water and sediments of the study area. These gold mines produce tailings dumps, which are responsible for the acidification of the water as a result of the oxidation of pyrite and other essential sulphide minerals contained in the sand dumps. Furthermore, the literature review revealed that many studies have found elevated concentrations of uranium and other radioactive minerals, making the results of gold mining activities a major concern. Some serious incidents have been reported since the mines begun their activities in the vicinity of the study area, such as the dewatering of dolomite rock, which has led to a shortage of water, environmental pollution and the formation of sinkholes.

The literature review also indicated that the sediments play an important role in the contamination of the surface water, as it was revealed that the sediments reflect the history of the river’s pollution. Furthermore, the literature survey showed that geochemical modelling, such as PHREEQC, can be used to understand and predict the speciation of metals in water. It is very important to know the speciation of metals, as that could enhance the understanding of metal behaviour, bioavailability and toxicity in the water system. The Piper diagram was also shown as the generic design tool which can be used to trace the changes of composition of the process stream.

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Chapter 3

Article 1

General overview of article 1

This paper addresses the dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom

The investigation for this paper was done to achieve the following objectives:

To determine the sources of pollutants in surface water in the vicinity of Potchefstroom
To assess the behaviour and extent of the distribution of these pollutants.

The following findings resulted from the investigation:

It was found that the main source of pollution in the surface water of the study area were effluents from gold mining activities, agricultural runoffs, and municipal and domestic sewage. This was substantiated by the elevated concentrations of arsenic (As), cadmium (Cd), lead (Pb), uranium (U), sulphate (SO_4^{2-}), cyanide (CN^-) and nitrate (NO_3^-) observed at the sampling points situated in the proximity of these sources. The results showed a decrease in concentrations when moving downstream of the study area, especially in the Potchefstroom area, where the pollution from mines was less evident. However, an increasing trend was observed downstream from Potchefstroom (Orkney area) and the pollution in this area can be attributed to the tailings dumps piled around the sampling area. The quality of the water was unfit for human consumption and other essential purposes.

Dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom

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Abstract

Potchefstroom and its neighbouring cities mostly rely on the Mooi River and Vaal River to satisfy their water needs. These rivers flow through gold mining areas and farms, and are therefore likely to be contaminated with substantial amounts of inorganic pollutants. Water was collected along the rivers' networks, streams, canals and dams in Potchefstroom and its vicinity. The samples were characterized for geochemical parameters, metals and anions concentrations. The results showed high concentrations of potentially toxic metals such as Cd (0.25 mg/L – 0.7 mg/L); As (4.53 mg/L – 5.74 mg/L), Pb (1.14 mg/L – 5.13 mg/L) and U (0.04 mg/L – 0.11 mg/L), which were predominantly found around the mining areas. Elevated concentrations of anions such as SO_4^{2-} and CN^- were detected around the mining areas, while NO_3^- was dominant near the farms. The relatively high concentrations of anions and trace metals in the surface water made it unfit for domestic or agricultural use. The study showed that contaminants from the mining and agricultural facilities were potentially mobilised, thus impacting the nearby water systems.

Keywords

Inorganic pollutants, Potchefstroom, Mooi River, Vaal River, sources of water pollution

1 Introduction

Water has always been regarded as an essential raw material for social development and organization (Sabhapandit et al., 2010). The accessibility of quality water for drinking and other crucial purposes is a great problem worldwide due to population increase and the rapid development of industries (Fu and Wang., 2010), particularly in developing countries (Mohsin et al., 2013). Water quality can be affected by effluents from anthropogenic sources that include domestic sewage, wastewater treatment plants, agricultural land usage, industrial and mining activities; sources which may discharge pollutants into the aquatic environment through various pathways (Manickum et al., 2014). The weathering of crustal materials and erosion are two of the natural processes that may also contribute to the degradation of water quality (Simeonova et al., 2003). The discharge of wastewater from anthropogenic sources into water bodies is of concern in most of countries worldwide (Lescesen et al., 2014). South Africa falls under the countries with water shortages, as most parts of the country are semi –arid (Nare et al., 2011). It is crucial to prioritise the protection of the available water resources, as there is a view of potential climate changes that may cause a serious threat in the near future (Kusangaya et al., 2013). High level of metals that are available in the aquatic environment world-wide are due to the extraction and processing of respective minerals from the hard rock mines (Zhang et al., 2013). Gold mining activities in South Africa produce large volumes of tailings and leachates from these, e.g. acid mine drainage (AMD), that is implicated in the impairment of many water resources (Rosner and Schalkwyk, 1999). The acid mine drainage (AMD) is a strong acidic wastewater that contains elevated concentrations of dissolved ferrous and non-ferrous metal sulphates and salts (Simate and Ndlovu, 2014). Acid mine drainage (AMD) often occurs when sulfide-bearing materials (mostly pyrite) are exposed to both oxygen and water (Jonson and Hallberg, 2004; Akcil and Koldas, 2005). These pyrites can be oxidized by oxygen according to the following reaction (Singer and Stumm, 1970; Stumm and Morgan, 1996):

$$FeS_{2(s)} + 7/2O_{2(aq)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

The ferrous iron that is released, as is seen in eq.1, can be further oxidized into ferric iron according to eq. 2. However, these reactions of ferrous iron to form ferric iron will depend on the presence of oxygen and the correct pH (Stumn and Morgan, 1996). At a low presence of oxygen, ferric iron will not be formed until the pH increases to 8.5. This oxidation of ferrous iron into ferric iron is also a slow process, unless the reaction is catalysed by bacteria such as *Acidithiobacillus ferrooxidans* (Singer and Stumm, 1970).

$$Fe^{2+} + ¼\, O_{2\,(aq)} + H^+ \rightarrow Fe^{3+} + ½H_2O \qquad (2)$$

Ferric iron is soluble at a pH value below 3, and it will continue to be soluble until the pH increases to above 3. At a pH ranges between 2.5 and 3.5, the ferric iron will then precipitates as ferrihydrate (eq.3).

$$Fe^{3+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H^+ \qquad (3)$$

The ferric iron that does not precipitate from the solution is capable to oxidize an additional pyrite according to the following reaction (Name & Sheridan, 2014):

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

This is a self-perpetuating reaction that is actually the driving reaction in the oxidation of pyrite, making AMD to be persistent over a long period of time. The precipitation of $Fe(OH)_3$ decreases the mineral acidity in the water and it thus reduces the toxicity of ferric iron in the water.

The presence of AMD on the Witwatersrand has been reported on and documented by many studies (Naicker et al., 2002; Durand, 2012; Name and Sheridan, 2014). The West Rand Goldfield has been known to contain significant amounts of uranium (Winde and Van der Walt, 2003; Winde et al., 2004). Elevated contamination levels resulting from the activities of gold mines in many catchment areas of the North West Province, South Africa, have attracted the attention of media at some time, indicating that a lot of effort needs to be done to protect the water bodies in this area (Naicker et al., 2002; Department of Water Affairs and Forestry, 2009; Durand, 2012). Since 1952, the gold mines in the West Rand have been extracting and producing uranium as a by-product of gold (Winde and Van der Walt, 2003). A significant amount of uranium that is formed as a by-product by these gold mines is entering the Wonderfonteinspruit and it poses a potential health risk to humans who drink the water without proper treatment (Maleke et al., 2014). Pollution of uranium is a major threat to the environment due to the fact that it can accumulate in the sediment and continue to leach out of the slime dams for decades to come (Van Eeden et al., 2009). The notable challenge about the West Rand situation is that most of the water bodies in the vicinity of mining activities are sources of drinking water for towns and communities located along them. The area also has many farm holdings with significant agricultural activity. The present study aimed to identify the sources of pollutants in surface water in the vicinity of the city of Potchefstroom and to assess the behaviour and extent of the distribution of these pollutants.

2 Materials and methods

2.1 Sampling

The study area consisted of forty four sampling sites that covered rivers, dams, canals and natural eyes. Natural eyes are defined as areas in which depressions allow the shallow water table to intersect the surface, thus releasing water into pools. For practical reasons, the study area was divided into three sub-areas connected by the Mooi River upstream and the Vaal River downstream of Potchefstroom (Figure 1). The sub-areas were: upstream of the Potchefstroom area; the Potchefstroom area; and downstream of the Potchefstroom area.

Sampling was conducted in April, at the end of the wet season. From the farthest point upstream, the first site of sampling expand from the Klerkskraal Dam (sample points 1 and 2), includes the Carletonville area (sample points 3 and 4) and ends in the Potchefstroom area. Streams flowing from the Klerskraal Dam and the Carletonville join approximately 6 km upstream of the Boskop Dam to form part of the Mooi River. The Mooi River then passes through the Boskop Dam and the Potchefstroom Dam before continuing flowing along the city of Potchefstroom. The Mooi River flows into the Vaal River in the Potchefstroom area (sample point 32), the latter continuing as the main river through Orkney and Stilfontein. Samples points 36 to 44 were located in the Orkney area, also known as the downstream area. This area is heavily mined and surrounded by a number of mine tailings. The mining activities are in close proximity of the Vaal River that flows through the area.

In the dams, the samples were collected along the dam and at various depths ranging between ±1 m and 4 m. Samples 9 to 17 were collected in the Boskop Dam, while samples 21 to 25 were collected in the Potchefstroom Dam.

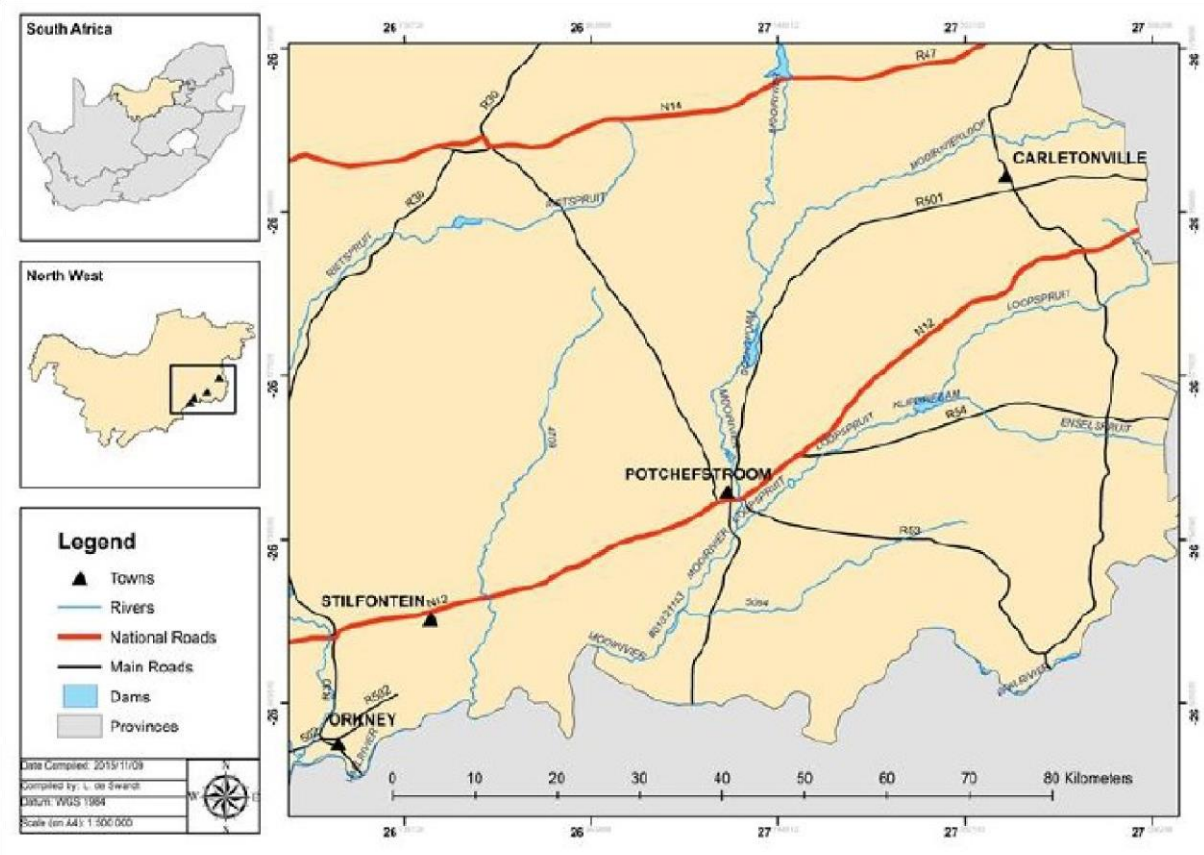

Figure 1: Map of the study area in the North West Province of South Africa

The numbering of the samples followed the order of the sampling points from sample one, which is the furthest upstream to sample forty four, the furthest downstream. Surface water samples were collected in clean 500 mL plastic bottles according to accepted methods (Hermond and Fechner-Levy, 2000). In Dams, surface water samples were taken at various depths (± 1 - 4 m). The depths were: (a) – 1 m; (b) – 2 m, (c) – 3 m and (d) – 4 m. Immediately after the sampling, the following physico-chemical parameters were measured using appropriate probes and meters (Hanna Instruments Inc., USA): pH, electrical conductivity EC (mS/cm), Temperature (°C), redox potential Eh (mV) and dissolved oxygen (mg/L). The probes were calibrated before they were used in the field. The water samples were then stored in the cooler boxes packed with ice to ensure the proper preservation before transportation to the laboratory prior to further analyses.

2.2 Laboratory analysis

The total alkalinity were determined through titration with 0.1 M H_2SO_4 acid. The value of major anions (sulphate, nitrate and cyanide) were analysed using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA). The chloride concentrations were determined through titration using a potassium dichromate and silver nitrate solutions. The trace elemental content was measured using an inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies, USA).

2.3 Data analysis

The statistical analysis of the data was done using Microsoft Excel 2010. Mean, standard deviation, and minimum and maximum of metal and anion concentrations were calculated and considered to determine the source of the pollutants. A Piper diagram was used to investigate the similarities and variances in the composition of the different surface water samples and to classify them into different water types (Candeias et al., 2013).

3 Results and discussion

The results of the geochemical parameters that were determined in the water samples are presented in Table 1. The water temperature ranged from 14.70 ℃ to 27.00 ℃. The highest temperature recorded at sample point 3 is the result of a very hot summer. In general, most of the sampling points showed temperature values which were close to the ambient air temperature. The pH values ranged from 7.39 to 9.34. All the water samples, including those collected at different depths (± 1 to 4 m deep) of the dams, showed a general trend in pH value, indicating alkalinity. The pH values fell within the recommended limits (ranges from 5.00 to 9.50) of the SANS water guideline. According to Patil et al. (2012), pH is an important parameter that can be used to determine the corrosive nature of the water. Enuneku et al. (2013) also present similar results of high pH values in surface water containing elevated alkalinity. The value of total alkalinity ranged between 140 mg/L and 1136 mg/L in this study. It is apparent from Table 1 that the value of alkalinity was very high. However, there is no specific limit for total alkalinity in water set by either the SANS or the WHO drinking water guidelines. According to WHO (2011), a high alkalinity indicates that there is more total dissolved solids (TDS) in the water that can cause the hardness of water. Apparently, no health-based guideline associated with high levels of TDS and water hardness in drinking water is available. However, consumers may object to the presence of high concentration of TDS in the water and the degree of hardness in the water may also affect its acceptability to consumers with regards to taste and scale deposition (WH0, 2008). According to Lawson (2011), a high level of alkalinity usually correlates to high values of pH, hence the researchers observed pH values which were above neutral at most of the sampling points. Similar results of high alkalinity in surface water were presented by Addo et al. (2011), with the water exhibiting pH levels above neutral.

The value of electrical conductivity ranged (EC) from 0.37 mS/cm to 3.36 mS/cm. These values are within the permissible limit of the SANS drinking water guideline, which ranges from 1.50 mS/cm to

3.70 mS/cm. It is apparent from the table of results that there was no significant difference in the value of electrical conductivity in surface water samples collected at different depths of the dams. According to Addo et al. (2011), a high value of EC suggests that there is a relatively high salt content in the water. The values of oxidation reduction potential (ORP) ranged from 81.57 mV to 204.57 mV. These low values of ORP correspond with the high pH values that were above neutral. There is no specific standard set by the SANS drinking water guideline with regard to oxidation reduction potential.

The concentrations of dissolved oxygen vary from 4.70 mg/L to 9.00 mg/L. There is no specific standard for dissolved oxygen set by either the SANS or WHO drinking water guidelines. According to Addo et al. (2011) a dissolved oxygen concentration of below 2.00 mg/L can cause aquatic organisms to perish. It is apparent from Table 1 that the concentrations of dissolved oxygen were fairly high at most of the sampling points. At different depths of the dams, values of DO tended to decrease with an increase in depth. The reason for lower concentrations at deeper depths could be the lack of oxygen and sunlight in the water. According to Patil et al. (2012), sunlight seems to speed up the photosynthesis by phytoplankton, utilizing CO_2 and giving off oxygen. Oxygen is vital in controlling the quality of aquatic ecosystems and it is also crucial for the respiration of aquatic organisms (Lescesen et al., 2014).

Table 1: Geochemical parameters and major anions of surface water and maximum permitted concentration in drinking water.

Sample numbers	Parameters						Major anions			
	pH	Temperature	Eh	Ec	DO	Alkalinity	SO_4^{2-}	Cl^-	NO_3^-	CN^-
		°C	mV	mS/cm	mg/L	mg/LCaCO3	mg/L	mg/L	mg/L	mg/L
1(c)	8.37	21.20	149.57	0.45	5.90	880.00	0.00	13.33	0.00	3.00
2(a)	8.39	20.70	147.57	0.43	7.50	624.00	0.00	10.00	2.50	2.00
3	9.22	27.00	94	1.40	6.70	608.00	595.00	76.67	0.20	3.00
4	8.80	25.20	122	0.37	7.00	836.00	525.00	73.33	0.00	3.00
5	8.03	19.80	167.57	1.11	6.10	796.00	315.00	66.67	2.40	3.00
6	7.39	20.90	204.57	0.82	6.80	856.00	150.00	43.33	18.80	2.00
7	7.40	20.90	204.57	0.81	4.70	1012.00	140.00	33.33	8.40	3.00
8	7.41	21.20	203.57	0.85	7.00	938.00	160.00	43.33	3.10	2.00
9(d)	8.15	18.00	156.57	0.72	6.70	1136.00	110.00	30.00	4.30	1.00
10(a)	8.31	17.90	156.57	0.74	7.40	916.00	110.00	33.33	0.00	2.00
11(a)	8.28	18.00	147.57	0.72	7.40	812.00	100.00	36.67	6.30	1.00
12(c)	8.34	17.90	144.57	0.69	6.80	848.00	100.00	40.00	0.20	1.00
13(a)	8.40	18.00	142.57	0.70	7.00	756.00	110.00	36.67	0.80	1.00
14(d)	8.38	18.40	142.57	0.69	7.20	788.00	100.00	40.00	0.00	1.00
15(a)	8.44	18.70	139.57	0.69	7.30	724.00	110.00	40.00	0.90	1.00
16(c)	8.32	20.30	153.57	0.68	6.20	744.00	110.00	33.33	8.50	1.00
17(a)	8.35	19.80	150.57	0.67	7.30	828.00	110.00	33.33	2.00	1.00
18	8.15	20.20	162.57	0.70	7.60	832.00	120.00	40.00	0.20	2.00
19	8.19	19.60	159.57	0.71	7.60	732.00	110.00	33.33	1.60	2.00
20	8.32	18.30	153.57	0.71	7.70	220.00	120.00	33.33	4.10	2.00
21(c)	8.37	17.30	142.57	0.70	8.80	1040.00	90.00	36.67	21.60	1.00
22(c)	8.39	18.30	142.57	0.75	7.40	1112.00	100.00	56.67	5.50	1.00
23(c)	8.38	18.40	142.57	0.69	6.00	992.00	110.00	36.67	0.00	1.00

24(a)	8.40	17.70	142.57	0.72	6.90	1120.00	100.00	36.67	0.00	0.00
25(b)	8.45	18.30	138.57	0.71	8.40	1016.00	110.00	43.33	1.90	0.00
26	8.47	19.40	146.57	0.71	7.00	2200.00	100.00	36.67	11.20	1.00
27	8.50	19.40	142.57	0.71	7.60	244.00	95.00	30.00	2.20	0.03
28	8.41	18.70	148.57	0.71	7.60	216.00	100.00	40.00	4.70	1.00
29	8.29	18.00	158.57	0.77	7.90	236.00	180.00	46.67	0.60	2.00
30	8.26	20.10	152.57	0.76	7.50	264.00	120.00	26.67	0.00	2.00
31	8.06	20.40	164.57	0.76	7.50	228.00	120.00	43.33	0.00	1.00
32	8.15	17.20	162.57	0.82	6.00	264.00	110.00	53.33	5.80	0.00
33	8.50	21.80	140.57	0.78	7.60	364.00	550.00	150.00	6.50	33.00
34	8.37	20.80	144.57	0.71	7.80	220.00	160.00	40.00	0.00	1.00
35	8.43	19.80	138.57	0.72	7.80	220.00	100.00	43.33	28.00	1.00
36	8.95	20.70	117.57	0.75	7.80	140.00	120.00	56.67	0.00	1.00
37	9.00	20.50	113.57	0.76	7.00	160.00	130.00	60.00	0.30	1.00
38	9.08	18.50	81.57	0.77	7.80	336.00	130.00	60.00	0.60	1.00
39	7.88	17.90	176.57	1.34	7.90	296.00	160.00	133.33	3.10	1.00
40	7.57	18.20	193.57	1.27	7.50	264.00	170.00	136.67	10.00	1.00
41	9.34	20.40	95.57	1.38	7.90	240.00	255.00	106.67	7.20	3.00
42	7.67	14.70	190.57	1.39	9.00	368.00	150.00	120.00	0.00	1.00
43	7.74	21.10	183.57	3.36	7.90	232.00	1360.00	180.00	8.50	65.00
44	7.61	22.40	189.57	3.36	5.90	240.00	1280.00	183.33	13.10	78.00
SANS(2005)	9.50	-	-	3.00	-	-	600.00	600.00	20.00	0.07
WHO(2011)	8.80	-	-	-	-	-	500.00	300.00	50.00	-

Note: (a): ± 1 m; (b): ± 2 m; (c): ± 3 m and (d): ± 4 m depth

The concentrations of sulphate vary from 0.00 mg/L to 1360.00 mg/L. A trend of sulphate concentration decreasing when moving downstream (Potchefstroom area) was evident; however, an increasing trend was observed again in Potchefstroom and downstream of the study area (Orkney area). There was no significant variation in sulphate concentration at different depths of the dams and all the dam samples were within the required limit. According to the SANS drinking water guideline, the permissible concentration of sulphate ranges from 400.00 mg/L to 600.00 mg/L. It is apparent from Table 1 that samples 43 (1360.00 mg/L) and 44 (1280.00 mg/L) had concentrations of more than double the standard.

The nitrate concentration fluctuates between 0.00 mg/L and 28.00 mg/L. The researchers observed a variation at the different depths in the dams, as high concentrations of nitrate were mostly recorded at deeper depths (± 3 m), while low concentrations were recorded at lower depths (± 1 m). The recommended limit of nitrate concentration recommended by the SANS drinking water guideline ranges from 10.00 mg/L to 20.00 mg/L. It is apparent from Table 1 that the concentrations at some of the sampling points have exceeded the permissible limit provided by the drinking water guideline. High concentrations of nitrate can cause serious health threats to human beings, like blue baby syndrome, gastric cancer, meningitis and Parkinson’s disease (Gaurav et al., 2015).

The cyanide concentration fluctuates from 0.00 mg/L to 78.00 mg/L. A decreasing trend was observed when moving downstream; however, an increasing trend was observed further downstream, especially at sampling points 33, 43 and 44. Water samples collected from different depths of the dams, showed an almost uniform concentration. Most of the sampling points show concentrations of cyanide that were above the recommended limit. According to the SANS drinking water guideline, the values of cyanide range from 0.05 mg/L to 0.07 mg/L. Cyanide is one of the most toxic and lethal chemicals on earth (Patil and Paknikar, 2000).

The concentrations of chloride vary between 10.00 mg/L to 183.33 mg/L. According to the SANS drinking water guideline, the concentrations of chloride range from 200.00 mg/L to 600.00 mg/L. It can be clearly seen from Table 1 that all the water samples fell within the permissible limit. There was no significant variation at the different depths of the dams, as a uniform concentration in some of the samples from different depths was observed.

Table 2: Trace element concentrations in surface water and the maximum permitted concentration in drinking water

samples Number	Ca	Mg	Na	K	Cd	As	Fe	Pb	U
1(c)	38.43	28.39	3.50	1.43	0.00	0.00	0.00	0.72	0.01
2(a)	37.61	27.67	3.38	9.75	0.17	0.57	0.00	0.32	0.06
3	102.92	72.00	79.00	1.22	0.07	5.00	0.00	0.00	0.04
4	102.25	71.00	70.15	5.38	0.09	2.07	0.00	0.00	0.07
5	78.26	42.02	74.53	5.08	0.05	4.84	0.00	0.21	0.00
6	71.40	38.25	34.61	20.17	0.15	3.51	0.00	0.25	0.00
7	68.45	37.33	28.54	13.14	0.09	4.61	0.00	0.22	0.00
8	68.40	39.85	27.57	12.79	0.01	2.30	0.00	0.00	0.00
9(d)	218.50	195.60	193.04	2.38	0.15	0.84	5.71	0.39	0.05
10(a)	216.60	199.90	197.30	4.93	0.11	0.00	0.10	0.44	0.01
11(a)	217.30	202.00	200.00	13.24	0.14	0.00	11.34	0.70	0.03
12(c)	213.40	199.50	197.83	13.48	0.09	0.00	0.65	1.25	0.00
13(a)	212.50	199.20	197.33	13.02	0.25	0.31	6.90	0.73	0.00
14(d)	210.30	198.00	198.20	16.72	0.08	0.26	0.39	0.67	0.00
15(a)	211.40	198.80	197.29	12.88	0.14	0.95	8.29	0.21	0.00
16(c)	44.35	41.07	26.30	12.98	0.00	2.20	0.00	0.00	0.01
17(a)	45.48	42.09	26.90	12.94	0.24	2.10	0.00	0.00	0.00
18	48.75	39.65	26.22	12.89	0.03	0.00	0.00	0.00	0.00
19	52.80	43.09	25.99	13.11	0.14	0.00	9.45	0.00	0.05
20	51.22	36.56	22.15	3.17	0.03	2.35	8.47	0.00	0.01
21(c)	208.70	188.80	191.97	3.37	0.15	1.43	0.47	0.30	0.00
22(c)	208.40	191.30	191.66	3.54	0.15	0.00	0.68	1.21	0.00
23(c)	210.10	195.00	194.23	2.87	0.09	0.00	0.20	0.89	0.00
24(a)	210.20	199.00	194.77	2.32	0.08	0.00	0.34	0.59	0.00
25(b)	212.00	199.70	196.83	2.07	0.13	0.00	0.69	1.01	0.04

26	48.43	40.37	0.00	11.67	0.20	4.53	22.00	5.13	0.00
27	48.64	39.89	24.23	9.34	0.70	3.67	36.00	0.13	0.00
28	48.73	39.52	24.02	6.85	0.09	2.06	17.80	0.00	0.00
29	66.15	50.53	26.93	39.41	0.15	2.25	7.69	0.00	0.03
30	53.36	20.00	56.85	25.88	0.00	0.97	0.66	1.01	0.00
31	49.88	40.19	22.20	27.93	0.21	1.38	6.95	0.00	0.00
32	38.69	28.33	3.53	0	0.00	0.00	0.00	0.00	0.00
33	185.80	124.10	61.47	0.99	0.10	0.00	15.60	0.00	0.00
34	48.89	35.94	21.96	0.95	0.02	1.76	8.48	0.00	0.00
35	49.26	35.38	22.26	2.56	0.2	1.08	14.00	0.00	0.00
36	352.00	103.20	257.70	10.5	0.00	1.28	0.00	0.85	0.02
37	55.15	20.10	57.22	3.08	0.00	0.00	0.00	0.75	0.00
38	72.52	28.46	99.96	1.93	0.00	0.00	0.00	0.52	0.01
39	60.06	22.66	61.02	21.85	0.00	0.78	0.00	0.68	0.03
40	70.48	28.19	104.89	25.93	0.00	0.42	0.00	0.84	0.00
41	125.60	44.45	36.91	17.82	0.00	2.60	0.00	0.48	0.00
42	121.37	13.83	114.04	9.47	0.00	2.71	0.00	0.40	0.00
43	338.75	22.24	114.01	16.03	0.00	5.74	0.29	0.54	0.11
44	331.70	99.00	240.80	34.23	0.00	0.42	2.53	1.14	0.07
SANS(2005)	300.00	100.00	400.00	100.00	0.01	0.05	2.00	0.05	-
WHO(2011)	-	-			0.003	0.003	0.10	0.01	0.03

Note: (a): ± 1 m; (b): ± 2 m; (c): ± 3 m and (d): ± 4 m depth

Table 2 presents the values of the trace elements that were determined in the water samples. The predominant trace elements decrease according to the following sequence: Ca > Mg > Na> K > Cd> As > Fe> Pb> U. The concentrations of Ca and Mg ranged from 38.43 mg/L to 352.00 mg/L and 13.83 mg/L to 202.00 mg/L, respectively. In this study, Ca and Mg were the most prevalent elements at all the sampling sites. According to WHO (2011), high concentrations of Ca and Mg contribute to the increase of the pH of the water, hence increasing the hardness of the water. The range of other trace elements were: Na: 3.38 mg/L to 257.70 mg/L; K: 0.00 mg/L to 34.23 mg/L; Cd: 0.00 mg/L to 0.70 mg/L; As: 0.00 mg/L to 5.74 mg/L, Fe: 0.00 mg/L to 36.00 mg/L; Pb: 0.00 mg/L to 5.13 mg/L and U: 0.00 mg/L to 0.11 mg/L. There was a slight variation of measured concentrations between the different depths of the dams, as the water samples collected at deeper depths contained elevated concentrations of trace elements. Previous studies have also reported higher concentrations of trace elements in the surface water of the Wonderfonteinspruit area (Winde et al., 2004; Winde, 2006; Winde, 2011; Maleke et al., 2014). In general, the concentrations of all the trace elements, excluding the Na and K concentrations, showed the same trend, as they were above the permissible limit of the SANS/WHO drinking water guidelines.

Table 3: The statistical parameters of all the measured variables in the surface water in the vicinity of Potchefstroom: Statistical summary of parameters

Parameters	Upstream				Potchefstroom				Downstream			
	Mean	Stdev	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev	Min	Max
pH	8.23	0.45	7.39	9.22	8.36	0.12	8.06	8.50	8.32	0.75	7.57	9.34
Alk (mg/l CaCO3)	824.53	124.16	608.00	1136.00	498.50	390.91	216.00	1120.00	252.89	74.4	140.00	368.00
Eh (mV)	155.25	27.02	94.00	204.57	147.63	8.34	138.57	164.57	149.13	46.04	81.57	190.57
EC (mS/cm)	0.73	0.23	0.37	1.40	0.73	0.04	0.69	0.82	1.60	1.03	0.75	3.36
DO (mg/l)	6.85	0.71	4.70	7.60	7.47	0.73	6.00	8.80	7.63	0.83	5.90	9.00
Sulphate (mg/l)	161.84	154.2	0.00	595.00	141.56	111.50	90.00	550.00	417.22	513.76	120.00	1360.00
Chloride (mg/l)	39.82	16.9	10.00	76.67	47.08	28.52	26.60	150.00	115.19	49.05	56.67	183.33
Nitrate (mg/l)	3.17	4.68	0.00	18.80	5.76	8.16	0.00	28.00	4.76	5.03	0.00	13.10
Cyanide (mg/l)	1.84	0.83	1.00	3.00	2.94	8.04	0.00	33.00	16.89	31.14	1.00	78.00
Ca(mg/l)	118.9	76.96	37.60	218.50	108.65	78.16	38.69	212.00	169.74	13.03	55.15	352.00
Mg (mg/l)	100.81	77.83	27.67	202.00	91.54	75.33	20.00	199.70	42.46	34.30	13.83	103.20
Na (mg/l)	95.14	82.59	3.38	200.00	78.44	81.82	0.00	196.83	120.73	77.92	36.91	257.70
K (mg/l)	10.40	5.37	1.22	20.17	8.93	11.71	0.00	39.41	15.65	10.64	1.93	34.23
Cd(mg/l)	0.11	0.07	0.00	0.25	0.14	0.16	0.00	0.70	0.00	0.00	0.00	0.00
As(mg/l)	1.56	1.78	0.00	5.00	1.34	1.39	0.00	4.53	1.55	1.87	0.00	5.74
Fe(mg/l)	2.25	3.88	0.00	11.34	8.75	10.21	0.00	36.00	0.31	0.84	0.00	2.53
Pb(mg/l)	0.32	0.35	0.00	1.25	0.64	1.28	0.00	5.13	0.69	0.23	0.40	1.14
U (mg/l)	0.02	0.02	0.00	0.07	0.00	0.01	0.00	0.04	0.03	0.04	0.00	0.11

From Table 3 it is evident that the values of alkalinity measured in surface water samples collected upstream of the study area were significantly higher than the rest of the sampling sites. This may be due to the dolomite rocks which have covered some part of the upstream area (Malan, 2002). However, the high value of alkalinity measured at the Doornfontein canal (samples 3 and 4) can be attributed to the concrete material or the cement of the canal. The values of pH recorded in all areas show a similar trend that was above neutral. The value of pH upstream and in Potchefstroom range from 7.39 to 9.22 and 8.06 to 8.50, respectively. This was almost similar to the pH range (7.57 to 9.34) recorded downstream of the study area. The impact of mining activities on pH was not apparent, as most of the pH values were quite elevated. However, the trend observed for CN^- suggested that there could be a fresh effluent output from the mines. A fresh output in this instance usually has a high pH value and CN^- concentration (Bakatula et al., 2012). There was a slight difference between the values of the DO measured in the three areas. The values of DO upstream varied from 4.70 mg/L to 7.60 mg/L, in Potchefstroom from 6.00 mg/L to 8.80 mg/L and downstream between 5.90 mg/L and 9.00 mg/L. The highest value of DO was measured at sampling point 42 (downstream area); this can be due to the low value of the temperature at this point. According to Gao and Song (2008), cold water holds much more oxygen than warm water. The value of Eh and EC excluding the EC downstream shows almost a similar values in most of the sampling sites. The highest concentration of EC (3.36 mS/cm) recorded downstream may be due to the contamination from the gold mining activities in the Orkney area (samples 43 and 44). This is substantiated by the elevated CN^-, Ca and Mg concentrations. These sampling points are in a water retention dam that receives excess water flowing out of a tailings dump. These outflows are essentially fresh effluents from the hydrometallurgical process. Water in such dams is usually pumped back to the plant workings, as it contains high levels of CN^- and pH (Bakatula et al., 2012).

It is evident from Table 3 that there was no significant difference in the concentration of sulphate measured in surface water samples from the upstream and the Potchefstroom area. However, high concentration of sulphate was recorded in some of the sampling points. For example, the Doornfontein mine canal (595.00 mg/L) upstream and the Ikageng canal (550.00 mg/L) in Potchefstroom shows the concentration of sulphate which was fairly high. The highest concentration of sulphate recorded downstream of the study area can be attributed to the effluents from the gold mines, with 1360.00 mg/L (sample 43) and 1280.00 mg/L (sample 44) recorded in sampling points within the water retain dam, respectively. This phenomenon has been observed by other researchers elsewhere on the Witwatersrand Basin (Tutu, 2006). Elevated concentrations of chloride were recorded in the canal stemming from Ikageng (150.00 mg/L) and in the water of the retention dam in the downstream area (183.00 mg/l), which indicated the contamination of chloride from the fertilizer plant and the mines, respectively. In addition, elevated concentration of Cl^- can also be attributed to the waste water from the municipal sewage, especially the Ikageng canal since it passes through the town of Potchefstroom. High values of nitrate was mainly recorded in sampling points situated adjacent to the agricultural lands, indicating that the pollution may be flowing from this respective agricultural area as they often use the fertilisers and pesticides to improve their productions. However, elevated concentrations of nitrate were recorded in some of the sampling areas upstream, especially sampling points within or near the farm areas.

It is apparent from Table 3 that there was no significant variation ($P > 0.05$) in the concentration of trace elements recorded in surface water of the study area. However, elevated concentration was mainly recorded upstream and downstream where there are active mines. For example, the mean concentration of U was 0.02 mg/L (upstream), 0.00 mg/L (Potchefstroom) and 0.03 mg/L (downstream), indicating the impacts of mining activities upstream and downstream. Similar case of trace elements dominating mostly upstream and downstream of study area was observed for Na, K, Ca, Mg, Pb and As. Low concentrations of this trace metals can be attributed to the dilution effects of the Mooi River. The concentration of Fe shows to be more dominant upstream and in Potchefstroom. However, the contribution to elevated Fe concentrations in the Potchefstroom area could not be ascertained. In general, the contamination by trace elements was less in the Potchefstroom area than the rest of study areas.

The hydrochemical compositions of the surface water samples collected in the vicinity of Potchefstroom was plotted in the Piper trilinear diagram (Fig. 2).

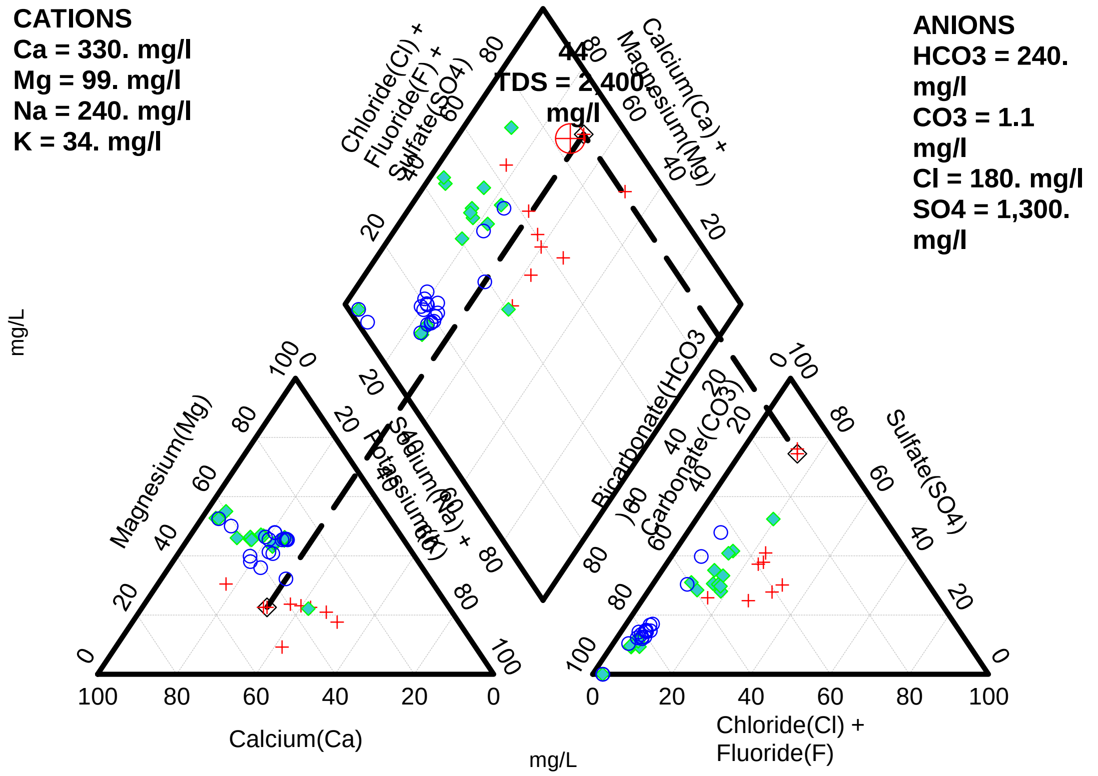

Figure 2: Piper diagram of water samples from upstream, Potchefstroom and downstream areas

The blue circles on the diagram shows the surface water samples recorded upstream of the study area, the squares in green colour indicated the surface water samples collected in midstream (Potchefstroom area), while the surface water samples of the downstream area indicated by the red crosses. It is apparent from the figure above that the inorganic contaminants in surface water samples upstream were predominantly in the Ca-Mg-HCO_3 water type. The number of these surface water samples was closer to one another. High concentration of sulphate, calcium and magnesium were pre-dominantly upstream making them a Ca-Mg-SO_4 water type. The sampling points 3, 4 and 5 were dominated by these trace elements. All of these sampling points are situated closer or near the mining area.

At midstream (Potchefstroom area), the surface water samples were not closer to each other. Elevated concentrations of calcium, magnesium, and sulphate were recorded in most of these sampling points. The less adjacent samples reflected a mixed water type (Ca-Mg-HCO_3 and Ca-Mg-SO_4-Cl). Highest concentrations of these elements were mostly recorded at sampling point 33, which is the canal originated from the Ikageng and is flowing down to meet the Mooi River. Therefore, elevated concentrations of trace elements recorded in some of the sampling points in the Mooi River could be attributed to the effluents from this canal. Downstream, surface water samples were classified as Ca-Mg-SO4-Cl water type. The sampling points 43 and 44 which are situated within the water retention dam are the most contaminated in this area. These two sampling points were the most polluted among all the points considered in this study, and this would be expected as this was at the discharge from a hydrometallurgical plant. It is thus apparent that the study area could be impacted by different sources of contamination. The upstream and Potchefstroom areas were mainly contaminated with elevated concentrations of Ca, Mg, Cd, sulphate and alkalinity. While downstream areas were mainly contaminated with elevated concentrations of Na, K and SO_4^{2-}. Lead (Pb) and uranium (U) were the potentially toxic elements that occurred at high concentrations in the Mooi River and Vaal River.

4 Conclusion

In this study, it was observed that the major sources of pollutants in surface water were the effluents from the gold mines and the agricultural lands. Since high level of contaminants were recorded in sampling points situated at the proximity to these sources. However, alternative sources such as domestic and municipal sewage and industries cannot be ignored. Upstream, the Doornfontein mine canal was identified as the main source of contaminants as it directly flows into the Mooi River. High concentration of calcium, magnesium, sulphate and alkalinity was mostly observed upstream. The dolomite rock which covers most part of the area upstream is likely to contribute to the relatively high level of alkalinity. In Potchefstroom area, the main source of pollution was observed to be the effluents from agricultural lands and the canal from Ikageng, as elevated concentrations of nitrate were mainly recorded in this area. The downstream area was found as the most polluted part of the study area. High concentrations of contaminants recorded in this area can be attributed to the effluents from the gold mining activities. The most contaminated sampling points were 43 and 44 as they are situated within the water retention dam. A slight difference was observed in surface water samples collected at different depths in the dams. However, the water samples collected in deeper depths was observed to be more contaminated in most instances. In general, the Klesrkskraal Dam was observed to be less contaminated compared to the Boskop Dam and Potchefstroom Dam, respectively.

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Chapter 4

Article 2

General overview of article 2

This paper addresses the temporal variation of metal speciation in the Vaal and Mooi Rivers based on seasonality. Physics and Chemistry of the Earth 66.

In this paper, the investigation was conducted on surface water samples collected in two different seasons (wet and dry) to establish the spatial and temporal variation of metal speciation. The main purpose was to evaluate the seasonal impact on the contamination of surface water and to investigate the potential of pollutants dispersion through speciation. The PHREEQC geochemical modelling was used to calculate the data in order to determine the metal speciation.

The following findings were made during the investigation:

The investigation revealed that a larger volume of pollution was observed during the wet season than during the dry season; this can be due to the washout of contaminants from polluting sources, more specifically from gold mining sites. It was also observed that there were no variations in pH, EC, and oxido reduction potential between the surface water samples measured in both seasons. However, for parameters such as the total alkalinity and dissolved oxygen (DO), there were significant variations between the two campaigns. High concentrations of DO were mainly observed in the dry period (corresponding to winter), which can be attributed to the low value of temperature. Therefore, this was expected, because according to the literature, cold water contains more oxygen than warm water. High concentrations of total alkalinity were observed in the wet season and this can be attributed to the elevated concentrations of Ca and Mg recorded. Some of the elements which showed significant variations between the two seasons were: As, Fe and Pb. On the other hand, metals like uranium (U) showed no variation.

The major anions such as sulphate, cyanide and chloride showed no significant difference ($P > 0.05$) between the seasons, however; nitrate was much higher in the wet season than in the dry season, which can be due to the runoff from agricultural land during heavy rainfalls. In addition, the elevated concentration of nitrate could also be attributed to the effluence from domestic or municipal sewages. The investigation showed a variation of metal speciation, which may be due to the disappearance of other metals, especially in the wet season as a result of the dilution effects in some areas. Nevertheless, high percentages of Ca and Mg were present as free hydrated species, whereas Fe, Cd, As and U were predominantly present as carbonate or hydroxide species in both seasons.

Temporal Variation of metal speciation in the Vaal and Mooi Rivers based on the seasonality

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ABSTRACT

Surface water samples were collected in two different seasons (wet and dry season) in the vicinity of Potchefstroom, South Africa. About 44 water samples were collected to be analysed for their physico-chemical parameters, such as the pH, temperature, dissolved oxygen, oxido reduction potential, conductivity, sulphate, nitrate, cyanide, chloride, alkalinity, Ca, Mg, As, Cd, Fe, Pb and U. The objectives of this study were to identify the seasonal impact on the pollution of surface water and to investigate the potential of pollutants dispersion through speciation. It was found that the concentrations of the trace elements measured decreased significantly during the dry season. High concentrations of trace elements in the wet season can be attributed to the high effluents from anthropogenic sources that were flowing into the surface water. Aqueous metal speciation of both seasons was predicted using the geochemical modelling speciation (program PHREEQC version 3.1.6-9191.). There was a variation of species between the water samples collected in the different seasons, and this variation may be due to the disappearance of other trace elements, which can result from the dilution effects, more specifically in the wet season. The water speciation data predicted that a high percentage of Ca and Mg were present as free hydrate species, whereas the Fe, Cd, As and U concentrations were mostly present as carbonate or hydroxide species in both the wet and dry seasons.

Keywords: Wet and dry seasons, metal speciation, surface water, pollution, PHREEQC

1 Introduction

South Africa is a water scarce country dominated by semi-arid areas; it is characterised by high seasonal variability in terms of rainfall and runoff, with high evaporation rates, droughts and floods (Nare et al., 2011). It is therefore critical for water managers to prioritise the protection of surface water (Manickum et al., 2014). Long-term survey and monitoring programs can assist the water managers to have a better knowledge about the quality of the water (Vega et al., 1998). The quality of surface water is impaired by anthropogenic sources such as mining activities, industrial wastewater and agricultural land (Simeonov et al., 2003). These sources produce toxic heavy metals, which are potentially detrimental to human health and aquatic organisms (Patil and Paknikar, 2000). Water pollution by heavy metals remains a serious concern around the world (Zhang et al., 2013), because of their toxicity, persistence and bioavailability (Langston et al., 1998). In surface water, the bioavailability and toxicity of metals can be closely correlated with different physical states, such as free or complexed states, associated with colloids or with particles (Korfali and Jurdi, 2010).

Acid mine drainage (AMD) polluting surface water is a major concern. AMD is formed when pyrite gets exposed to oxygen and water (MacCausland and McTammany, 2006; Balintova et al., 2012; Candeias et al., 2013), and microorganisms (Simate and Ndlovu, 2014). Acid mine drainage is a complex pollutant, characterised by elevated concentrations of iron, aluminium and sulphate, a low pH, and a variety of heavy metals such as uranium (Balintova et al., 2012; Name and Sheidan, 2014). However, mine drainage streams with a high pH also have a negative impact, as the precipitated iron and aluminium may coat the stream substrate and cause an unstable habitat for aquatic macroinvertebrates (MacCausland and McTammany, 2006). AMD impacts negatively on the environment, as it increases the level of suspended solids, leading to the mobilization of metals (Ochieng et al., 2010).

Surface water in the vicinity of Potchefstroom is mainly contaminated by acid mine drainage (AMD) from the gold mining fields of the Witwatersrand (Name and Sheidan, 2014). The activities of these gold mines cause contamination in the Wonderfonteinspruit, and since it is a tributary of the Mooi River, it increases the concentrations of heavy metals, which are further dispersed downstream of Potchefstroom, i.e. in the Vaal River (Malan, 2002; Barnard et al., 2013). AMD pollution has been reported and documented in the Wonderfonteinspruit area by many studies (Naicker et al., 2002; Hobbs and Cobbing, 2007; Opperman, 2008; Ochieng et al., 2010). The toxicity of metals from this AMD does not depend only on the total concentration, but also on its chemical speciation, therefore; analysing the speciation of metals in the water is crucial for better understanding of the metal’s behaviour (Korfali and Davies, 2003). The speciation of metals in water can be predicted using geochemical-based models, for example the PHREEQC model. This model can simulate processes such as geochemical speciation, acid-base equilibrium, redox equilibrium, precipitation/dissolution, adsorption/desorption and transport (Betrie et al., 2015; Thanh et al., 2015). The main objectives of this study was to identify the seasonal impact on the pollution of surface water and to investigate the potential of pollutants dispersion through speciation.

2 Materials and method

2.1 Sampling site description

The mean annual rainfall in the area in which the Wonderfonteinspruit is situated, is about 550 mm to 750 mm, and approximately 90% of the rain falls during the summer season; between October and April. The Wonderfonteinspruit Catchment Area (WCA) is underlain by dolomitic rock (Malan, 2002), which has covered approximately 80% of the area (Winde, 2006). A total of 44 sampling sites were selected between the latitude of 26°15′9.41″ - 26°55′22.9″ southern and longitude of 27°9′32.27″ - 26°48′35.9″ eastern (Table 1) for analysis. Most of the sampling sites were located within the Mooi and Vaal Rivers in the North West Province, South Africa. The surface water samples were collected in dams, rivers, streams connected to rivers, canals and natural eyes. The study area was subdivided into three sections, which include: Mooi River upstream of Potchefstroom, midstream, Potchefstroom area, and downstream of Potchefstroom (the Mooi and the Vaal Rivers). These sites were selected due to the anthropogenic sources such as gold mining and other sources contributing to metal pollution into the Wonderfonteinspruit catchment area, which results in the contamination of the Mooi River downstream of Potchefstroom. The Google earth maps showing these areas can be seen below (Figures 1 - 5).

Table 1: Description and locations of the sampling sites.

Sample Numbers	Description	Coordinates	
		S	E
1(c)	Dam	26^{0}15'9.41"	279'32.27"
2(a)	Dam	26^{0}15'9.41"	279'32.27"
3	Mine Canal	26°22'30.71"	27°19'57.34"
4	River	26^{0}22'15.72"	27^{0}15'9.98"
5	River	26°22'13.01"	27°14'53.22"
6	Spring	26°24'51.04"	27°10'13.32"
7	Spring	26^{0}24'52.34"	27^{0}10'4.49"
8	Spring	26°28'47.61"	27° 9'5.70"
9(d)	Dam	26°31'58.54"	27° 7'31.93"
10(a)	Dam	26°31'58.54"	27° 7'31.93"

11(a)	Dam	26°32'22.9"	27°07'39.0"
12(c)	Dam	26°32'59.4"	27°07'15.7"
13(a)	Dam	26°32'59.4"	27°07'15.7"
14(d)	Dam	26°33'56.0"	27°07'13.7"
15(a)	Dam	26°33'56.0"	27°07'13.7"
16(c)	Dam	26°33'43.77"	27° 6'43.96"
17(a)	Dam	26°33'43.77"	27° 6'43.96"
18	Dam canal	26°33'44.43"	27° 6'40.01"
19	Dam	26^{0}38'39.50	27^{0}5'25.52"
20	Dam Canal	26°40'15.7"	27°0522.4"
21(c)	Dam	26°39'55.67"	27° 5'34.14"
22(c)	Dam	26°40'02"	27°06'01.54"
23(c)	Dam	26°40'13.8"	27°05'45.9"
24(a)	Dam	26°40'13.8"	27°05'45.9"
25(b)	Dam	26°40'21.8"	27°05'50.5"
26	Dam Canal	26°40'23.5"	27°05'52.2"
27	Mooi River	26°40'27.5"	27°05'46.4"
28	Mooi River	26°40'55.6"	27°05'53.8"
29	Mooi River	26°42'04.1"	27°06'22.6"
30	Mooi River	26°42'34.1"	27°06'20.2'
31	Mooi River	26°45'10.5"	27°06'01.6"
32	Vaal River	26°52'49.8"	26°57'51.4"
33	Canal	26°42'17.7"	27°05'05.8"
34	Dam Canal	26°43'35.3"	27°04'40.1"
35	Dam Canal	26°44'33.5"	27°03'43.0"
36	Stream	26°56'10.7"	26°50'59.3"
37	Stream	26°56'40.1"	26°46'49.6"
38	Vaal River	27°00'13.5"	26°37'04.4"
39	Stream	26°56'04.8"	26°39'54.4"
40	Stream	26°59'05.0"	26°37'56.2"
41	Mine Canal	26°54'36.8"	26°48'51.4"
42	Stream	26°54'40.2"	26°48'55.0"
43	Water retained Dam	26°55'14.9"	26°48'37.2"
44	Water retained Dam	26°55'22.9"	26°48'35.9"

Note: (a): ± 1m; (b): ± 2 m; (c): ± 3 m and (d): ± 4 m depth

Figure 1: Google Earth Map showing the Mooi River upstream of Potchefstroom

Figure 2: Google Earth Map showing the Boskop Dam

Figure 3: Google Earth Map of Potchefstroom (Lakeside) Dam

Figure 4: Google Earth Map showing the Potchefstroom area

Figure 5: Google Earth Map showing the downstream area

2.2 Sampling procedure

A total of forty-four surface water samples were collected along the Mooi and Vaal Rivers' networks in the vicinity of Potchefstroom during two different seasons: wet (April 2015) and dry (July 2015) seasons. The surface water samples were collected in clean 500 mL plastic bottles according to the accepted method (Hermond and Fechner – Levy, 2000). Before use, the bottles were washed with distilled water and then rinsed with the water of the sampling site. At the dams, water samples were collected at various depths that varied from 1 m to 4 m by using a depth-sampler. The coordinates of each sampling site were determined by using a GPS device. The following physical-chemical parameters were analysed *in situ* by using the appropriate probes, pH meter combined electrode with integrated temperature probe (Hanna Instruments Inc., USA): pH, electrical conductivity EC [mS/cm], Temperature [°C], dissolved oxygen (DO) [mg/L], and redox potential Eh [mV]. The probes were calibrated in the field before use. The samples were then immediately transported to the laboratory in cooler boxes containing ice packs and stored at 4°C prior to analysis.

2.3 Laboratory analysis

The total alkalinity was determined through titration with 0.1 M H_2SO_4 acid. The level of sulphate, nitrate and cyanide were analysed using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA). The concentration of chloride (Cl^-) was measured through titration with silver nitrate and potassium dichromate solutions. The major cations and trace element concentrations were analysed using an inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies, USA).

2.4 Data treatment

2.4.1 Statistical analysis

The statistical analysis of the data was done using Microsoft Excel 2010. A one-way ANOVA was performed to determine the variation between the water samples collected during the wet and dry seasons. A level of $p < 0.05$ was used in all the comparisons. The mean, standard deviation, and minimum and maximum metal and anion concentrations were calculated and considered to determine the variance between the two seasons.

2.4.2 Geochemical modelling

The speciation of metals in surface water was predicted using the AQUACHEM software interfaced with the geochemical modelling program PHREEQC version 3.1.6-9191. In this study, the data base *Minteq.v4.dat* was used. The input data used for the modelling program were temperature, pH, Eh (pE) and the determined concentrations of SO_4^{2-}, NO_3^-, CN^- Cl^-, Al, As, Be, Ca, Cd, Fe, Mg, Mn, Mo, Na, Ni, Pb, U, and Zn.

3 Results and discussion

3.1 Spatial and temporal variation

The summary of geochemical parameter concentrations, showing the spatial and temporal variations of the surface water samples that were analysed during the wet (April 2015) and dry (July 2015) periods, are presented in Tables 2, 3 and 4, respectively. It can be observed from the tables that there was a significant variation in the values of physico-chemical parameters measured during the wet and dry seasons. The values were higher in the wet season compared to the dry season, which may be due to the washout of contaminants from polluting sources into the surface water during the wet season. However, a few sampling points showed elevated concentrations in both seasons, especially those points within or next to the mine canal. The SANS guideline of drinking water showing the minimum and maximum permissible concentrations, is presented in all the tables. .

Table 2: Seasonal variation of *in situ* parameters measured in surface water in the vicinity of Potchefstroom and maximum permitted concentration (mg/L) in drinking water

Sample numbers	pH		T °C		Eh (mV)		Ec (mS/cm)		DO (mg/L)	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
1(c)	8.37	8.50	21.20	11.60	149.57	144.00	0.45	0.42	5.90	9.20
2(a)	8.39	8.50	20.70	11.30	147.57	143.00	0.43	0.49	7.50	8.80
3	9.22	8.50	27.00	18.30	94.00	135.57	1.40	1.21	6.70	8.80
4	8.80	8.48	25.20	16.60	122.00	140.57	0.37	1.31	7.00	7.70
5	8.03	7.97	19.80	12.90	167.57	170.00	1.11	1.17	6.10	7.90
6	7.39	7.34	20.90	19.50	204.57	196.57	0.82	0.79	6.80	7.00
7	7.40	7.25	20.90	19.70	204.57	202.57	0.81	0.78	4.70	5.00
8	7.41	7.24	21.20	16.30	203.57	202.57	0.85	0.82	7.00	5.90
9(d)	8.15	8.12	18.00	12.10	156.57	162.00	0.72	0.76	6.70	8.30
10(a)	8.31	8.17	17.90	12.10	156.57	160.00	0.74	0.73	7.40	8.50
11(a)	8.28	7.99	18.00	13.00	147.57	168.00	0.72	0.77	7.40	7.00
12(c)	8.34	8.57	17.90	13.50	144.57	137.57	0.69	0.71	6.80	8.60
13(a)	8.40	8.58	18.00	13.50	142.57	135.57	0.70	0.70	7.00	8.70
14(d)	8.38	8.55	18.40	12.00	142.57	219.00	0.69	0.71	7.20	9.10
15(a)	8.44	8.54	18.70	12.00	139.57	142.00	0.69	0.72	7.30	8.90
16(c)	8.32	8.39	20.30	13.70	153.57	147.57	0.68	0.69	6.20	9.00
17(a)	8.35	8.40	19.80	13.80	150.57	146.57	0.67	0.70	7.30	8.80
18	8.15	8.43	20.20	12.60	162.57	147.00	0.70	0.68	7.60	9.10
19	8.19	8.20	19.60	14.80	159.57	156.57	0.71	0.70	7.60	9.60
20	8.32	8.65	18.30	9.90	153.57	137.00	0.71	0.72	7.70	9.40
21(c)	8.37	8.45	17.30	10.00	142.57	144.00	0.70	0.74	8.80	9.20
22(c)	8.39	8.49	18.30	9.90	142.57	142.00	0.75	0.70	7.40	10.20
23(c)	8.38	8.50	18.40	10.00	142.57	142.00	0.69	0.71	6.00	8.90
24(a)	8.40	8.51	17.70	9.90	142.57	141.00	0.72	0.71	6.90	8.90
25(b)	8.45	8.53	18.30	10.00	138.57	142.00	0.71	0.71	8.40	8.70
26	8.47	8.57	19.40	9.40	146.57	140.00	0.71	0.67	7.00	8.40
27	8.50	8.64	19.40	9.90	142.57	136.00	0.71	0.73	7.60	8.50
28	8.41	8.64	18.70	10.80	148.57	147.00	0.71	0.70	7.60	9.00
29	8.29	8.45	18.00	10.10	158.57	147.00	0.77	1.00	7.90	7.60
30	8.26	8.30	20.10	11.70	152.57	153.00	0.76	0.74	7.50	8.60
31	8.06	8.25	20.40	11.70	164.57	154.00	0.76	0.78	7.50	9.00
32	8.15	8.12	17.20	12.00	162.57	163.00	0.82	0.84	6.00	9.00

33	8.50	8.66	21.80	11.60	140.57	137.00	0.78	1.96	7.60	12.10
34	8.37	8.54	20.80	11.60	144.57	141.00	0.71	0.72	7.80	8.50
35	8.43	8.65	19.80	11.70	138.57	137.00	0.72	0.70	7.80	9.00
36	8.95	9.00	20.70	11.80	117.57	118.00	0.75	0.78	7.80	9.60
37	9.00	9.14	20.50	11.40	113.57	112.00	0.76	0.78	7.00	9.20
38	9.08	9.12	18.50	10.50	81.57	112.00	0.77	0.78	7.80	9.60
39	7.88	7.71	17.90	10.90	176.57	183.00	1.34	1.45	7.90	3.70
40	7.57	7.55	18.20	11.30	193.57	193.00	1.27	1.34	7.50	8.90
41	9.34	8.97	20.40	9.70	95.57	120.00	1.38	1.54	7.90	9.20
42	7.67	7.74	14.70	8.40	190.57	184.00	1.39	1.28	9.00	8.40
43	7.74	7.64	21.10	12.90	183.57	184.00	3.36	3.06	7.90	7.80
44	7.61	7.60	22.40	13.00	189.57	189.00	3.36	3.00	5.90	7.70
Mean ±SD	8.29 ± 0.44	8.32 ± 0.47	19.59±2.09	12.26±2.55	151.23±27.2	153.52±24.94	0.92 ±0.59	0.97± 0.54	7.27±0.79	8.51±1.33
SANS (2005)	9.50	-	-		-		-		-	
P. Values	> 0.05		> 0.05		> 0.05		> 0.05		< 0.05	

Note: SD – standard deviation, (a): ± 1 m depth; (b): ± 2 m depth; (c): ± 3 m depth and (d): ± 4 m depth pH: The values of the pH in both seasons were alkaline, with mean values of 8.29 in the wet season and 8.32 in the dry season. The variation shows no significant difference ($P > 0.05$) between the wet and dry seasons. It is apparent from a plot that the values of pH for the samples collected during the different seasons were close to the trend line (Fig. 6a). All the pH values collected during the different seasons were within the recommended limit of the SANS drinking water guidelines.

Electrical conductivity (EC): The values of conductivity recorded showed an almost similar trend in both seasons, with means of 0.92 mS/cm and 0.97 mS/cm observed in the wet and dry seasons, respectively. The highest value (3.36 mS/cm) of conductivity was measured in samples 43 and 44 during the wet season; this can be attributed to the elevated concentrations of ions present at these points. However, the variation between the seasons was not significant ($P > 0.05$) and this can be clearly observed on the plot diagram (Fig. 6b). All the values measured in both seasons were within the SANS drinking water guideline.

Total Alkalinity: The concentration of total alkalinity measured in both seasons are presented in Table 3. The concentrations ranged from 140.00 mg/L to 1136.00 mg/L in the wet season and from 160.00 mg/L to 460.00 mg/L in the dry season. Mean values of 582.28 mg/L and 281.21 mg/L were observed in the wet and dry seasons, respectively. The variation was highly significant ($P < 0.01$) between the two seasons. There is no standard for total alkalinity set by the SANS drinking water guideline. The high concentrations of alkalinity that were measured in the wet season can be attributed to the dolomite rock that covers a large part of the study area; especially upstream (Malan, 2002). Hence, elevated values of calcium and magnesium were mostly observed in the water samples collected upstream of the study area.

DO: The values of dissolved oxygen ranged from 4.70 mg/L and 9.00 mg/L, and 3.70 mg/L and 12.10 mg/L in the wet and dry seasons, respectively. The high values recorded in the dry season can be attributed to the low values of temperature in winter. The mean values were 7.27 mg/L and 8.51 mg/L in the wet and dry seasons, respectively. The variation showed a significant difference ($P <0.05$) between the two seasons. The high values of temperature measured in the summer could be responsible for the low values of DO, since according to Gao and Song (2008), water with a low temperature is capable of holding more oxygen.

ORP: The values of Eh ranged from 94.00 mV to 204.57 mV and 112.00 mV to 219.00 mV in the wet and dry seasons, respectively. The mean values were 151.23 mV and 153.52 mV in the wet and dry seasons, respectively. The low values of Eh measured in both seasons can be attributed to the pH values which were alkaline. The variation showed no significant different ($P > 0.05$) between the two seasons.

CN^-: The values of cyanide ranged between 0.00 mg/L and 78.00 mg/L in the wet season and 0.00 mg/L to 73.00 mg/L in the dry season. The mean values were 5.37 mg/L and 4.56 mg/L in the wet and dry seasons, respectively. These variations show no significant difference ($P > 0.05$) between the wet and dry seasons.

3.1.1 Major anions

The statistical summary of the major anions measured in the surface water is presented in Table 3. In general, all the anions, excluding nitrate, showed no significant variations between the two seasons. However, there were variations of concentrations within the sampling points in the different seasons. For example, the concentration of sulphate varied from 0.00 mg/L to 1360.00 mg/L and 0.00 mg/L to 1500.00 mg/L in the wet and dry seasons, respectively. The mean concentrations were 211.51 mg/L in the wet season and 213.14 mg/L in the dry season. Non-significant variation of sulphate concentrations in the water samples collected in the wet and dry seasons is apparent on the plot diagram (Fig. 6c), as the researchers observed samples adjacent to each other. The concentrations of chloride varied from 10.00 mg/L to 183.33 mg/L and 3.33 mg/L to 183.33 mg/L in the wet and dry seasons, respectively. The mean values were 58.91 mg/L and 63.57 mg/L in the wet and dry seasons, respectively. High values of chloride were observed in sampling points close to the anthropogenic sources, especially next to tailings dumps. However, the concentrations observed were within the recommended guideline of drinking water. The concentrations of nitrate ranged from 0.00 mg/L to 28.00 mg/L in the wet season and 0.00 mg/L to 11.20 mg/L in the dry season. Higher concentrations measured in the wet season can be attributed to the washout of nitrogenous fertilisers used in agricultural areas. For example, the concentration of nitrate was 28.00 mg/L at sampling point 35 during the wet season and it decreased to 0.40 mg/L in the dry season. The mean values of nitrate were 4.43 mg/L in the wet season and 1.58 mg/L in the dry season. The variation was significantly different ($P <0.05$) between the two seasons.

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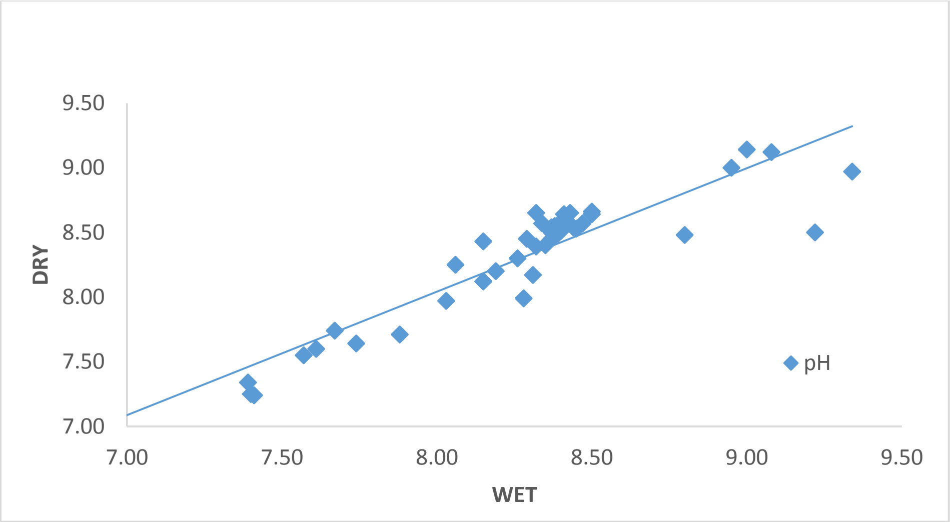
Table 3: Alkalinity (mg/lCaCO3) and major anions (mg/L) measured in the vicinity of Potchefstroom during wet and dry season and maximum permitted concentration in drinking water (mg/L).

Sample numbers	Alkalinity		SO_4^{2-}		Chloride		NO_3^-		CN^-	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
1(c)	880.00	420.00	0.00	0.00	13.33	6.67	0.00	0.00	3.00	3.00
2(a)	624.00	312.00	0.00	0.00	10.00	3.33	2.50	0.00	2.00	3.00
3	608.00	160.00	595.00	420.00	76.67	76.67	0.20	0.00	3.00	1.00
4	836.00	160.00	525.00	420.00	73.33	90.00	0.00	1.40	3.00	2.00
5	796.00	204.00	315.00	325.00	66.67	70.00	2.40	0.00	3.00	1.00
6	856.00	312.00	150.00	120.00	43.33	40.00	18.80	0.00	2.00	2.00
7	1012.00	320.00	140.00	100.00	33.33	33.33	8.40	2.10	3.00	2.00
8	938.00	296.00	160.00	120.00	43.33	50.00	3.10	1.50	2.00	1.00
9(d)	1136.00	344.00	110.00	100.00	30.00	40.00	4.30	0.00	1.00	2.00
10(a)	916.00	304.00	110.00	110.00	33.33	36.67	0.00	0.00	2.00	2.00
11(a)	812.00	288.00	100.00	120.00	36.67	40.00	6.30	0.90	1.00	1.00
12(c)	848.00	276.00	100.00	110.00	40.00	33.33	0.20	0.00	1.00	2.00
13(a)	756.00	308.00	110.00	110.00	36.67	36.67	0.80	4.30	1.00	1.00
14(d)	788.00	304.00	100.00	110.00	40.00	36.67	0.00	11.20	1.00	1.00
15(a)	724.00	300.00	110.00	110.00	40.00	36.67	0.90	2.20	1.00	2.00
16(c)	744.00	280.00	110.00	110.00	33.33	36.67	8.50	0.00	1.00	2.00
17(a)	828.00	324.00	110.00	110.00	33.33	36.67	2.00	1.80	1.00	2.00
18	832.00	248.00	120.00	100.00	40.00	56.67	0.20	0.00	2.00	2.00
19	732.00	300.00	110.00	110.00	33.33	36.67	1.60	0.00	2.00	1.00
20	220.00	248.00	120.00	110.00	33.33	36.67	4.10	0.90	2.00	1.00
21(c)	1040.00	296.00	90.00	90.00	36.67	36.67	21.60	2.20	1.00	3.00
22(c)	1112.00	300.00	100.00	100.00	56.67	36.67	5.50	0.00	1.00	1.00
23(c)	992.00	284.00	110.00	100.00	36.67	36.67	0.00	2.70	1.00	0.00
24(a)	1120.00	288.00	100.00	100.00	36.67	36.67	0.00	0.00	0.00	0.00
25(b)	1016.00	292.00	110.00	100.00	43.33	40.00	1.90	2.10	0.00	1.00
26	2200.00	236.00	100.00	100.00	36.67	46.67	11.20	1.80	1.00	1.00

27	244.00	280.00	95.00	110.00	30.00	53.33	2.20	0.00	0.03	2.00
28	216.00	268.00	100.00	110.00	40.00	36.67	4.70	0.00	1.00	1.00
29	236.00	272.00	180.00	195.00	46.67	53.33	0.60	2.20	2.00	1.00
30	264.00	268.00	120.00	110.00	26.67	43.33	0.00	2.10	2.00	2.00
31	228.00	280.00	120.00	110.00	43.33	40.00	0.00	1.00	1.00	2.00
32	264.00	308.00	110.00	110.00	53.33	63.33	5.80	2.70	0.00	2.00
33	364.00	460.00	550.00	600.00	150.00	183.33	6.50	4.70	33.00	12.00
34	220.00	256.00	160.00	110.00	40.00	36.67	0.00	0.70	1.00	3.00
35	220.00	252.00	100.00	110.00	43.33	40.00	28.00	0.40	1.00	1.00
36	140.00	184.00	120.00	130.00	56.67	76.67	0.00	0.80	1.00	2.00
37	160.00	212.00	130.00	130.00	60.00	73.33	0.30	0.00	1.00	2.00
38	336.00	160.00	130.00	160.00	60.00	73.33	0.60	0.00	1.00	1.00
39	296.00	384.00	160.00	220.00	133.33	140.00	3.10	0.00	1.00	3.00
40	264.00	360.00	170.00	200.00	136.67	123.33	10.00	8.70	1.00	3.00
41	240.00	280.00	255.00	340.00	106.67	166.67	7.20	1.70	3.00	2.00
42	368.00	388.00	150.00	165.00	120.00	120.00	0.00	2.70	1.00	4.00
43	232.00	248.00	1360.00	1500.00	180.00	166.67	8.50	3.40	65.00	73.00
44	240.00	248.00	1280.00	1350.00	183.33	183.33	13.10	3.50	78.00	43.00
Mean ±SD	582.28±335.6	281.21±58.9	211.51±275.5	213.14±292.4	58.91±41.45	63.57±44.69	4.43±6.2	1.58±2.27	5.37±15.63	4.56±12.51
SANS (2005)			600.00		600.00		20.00		0.07	
P. Values	< 0.01		> 0.05		> 0.05		< 0.05		> 0.05	

Note: SD – standard deviation, (a): ± 1 m; (b): ± 2 m; (c): ± 3 m and (d): ± 4 m depth a.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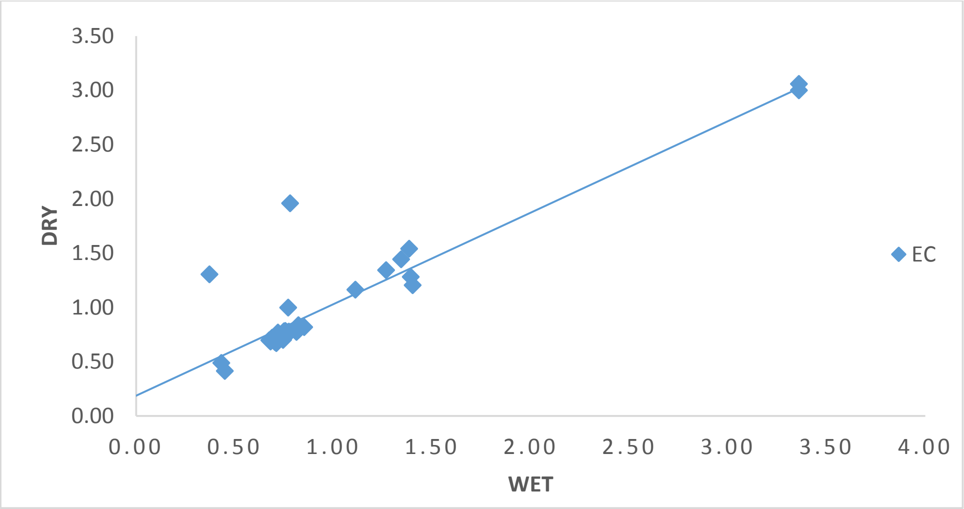
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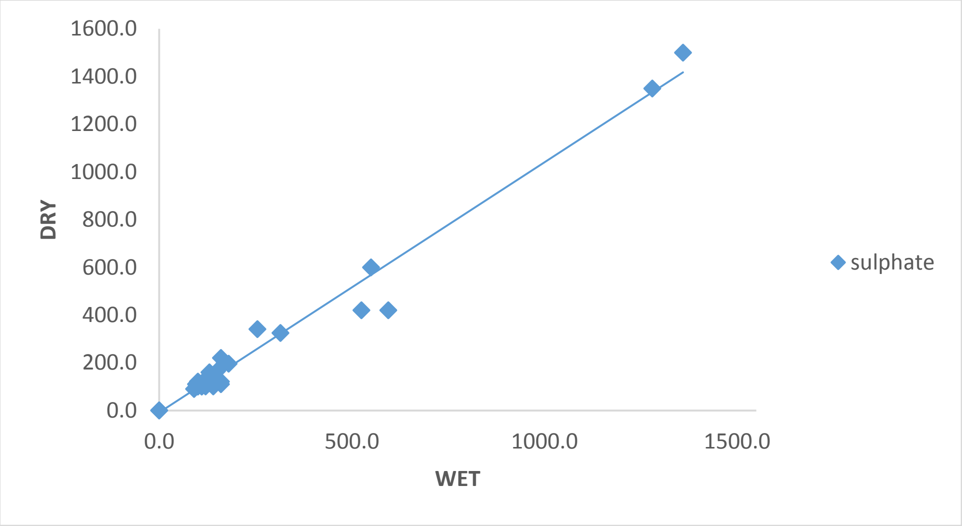

Figure 6: Seasonality of pollution: (a) pH; (b) EC (mS/cm) and (c) sulphate (mg/L

3.1.2 Major cations

The results of major cations concentrations in the surface water shown in Table 4 revealed a significant variation between the wet and dry seasons. The concentration of Ca varied from 37.61 mg/L to 352.00 mg/L and 34.27 mg/L to 308.82 mg/L in the wet and dry seasons, respectively; with a mean value of 125.57 mg/L in the wet season and 54.83 mg/L in the dry season. There was a definite significant variation of Ca concentrations (P <0.01) between the two seasons. It is apparent from Table 2 that the values of Ca measured in the wet season highly exceeded the recommended limit of the SANS drinking water guideline, however; the concentration decreases in the water samples during the dry season. The mean concentrations of Mg were 85.50 mg/L in the wet season and 45.99 mg/L in the dry season. There was a significant variation in the concentration of Mg (P<0.01) between the wet and dry seasons. A similar trend was observed for Mg, as the researchers observed a significant decrease of Mg concentration in the dry season. The highest concentrations of Ca and Mg can be attributed to the dolomite rock which has covered most part of the study area (Malan, 2002).

Table 4: Seasonal variation of major cations and trace metals (mg/L) measured in surface water in the vicinity of Potchefstroom and maximum permitted concentration in drinking water (mg/L)

Sample numbers	Ca		Mg		As		Fe		U		Pb	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
1(c)	38.43	38.85	28.39	31.01	0.00	0.00	0.00	0.00	0.01	0.00	0.72	0.00
2(a)	37.61	42.26	27.67	33.30	0.57	3.05	0.00	0.21	0.06	0.00	0.32	0.00
3	102.92	81.79	72.00	53.93	5.00	0.00	0.00	0.15	0.04	0.00	0.00	0.00
4	102.25	94.76	71.00	63.94	2.07	0.00	0.00	0.00	0.07	0.00	0.00	0.00
5	78.26	76.28	42.02	45.68	4.84	0.00	0.00	0.26	0.00	0.00	0.21	0.91
6	71.40	76.23	38.25	47.75	3.51	4.24	0.00	0.19	0.00	0.06	0.25	0.00
7	68.45	66.84	37.33	38.15	4.61	2.11	0.00	0.09	0.00	0.00	0.22	0.55
8	68.40	65.87	39.85	39.88	2.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9(d)	218.50	48.05	195.60	37.99	0.84	0.00	5.71	0.19	0.05	0.00	0.39	0.00
10(a)	216.60	59.29	199.90	37.01	0.00	0.00	0.10	0.11	0.01	0.00	0.44	0.00
11(a)	217.30	65.18	202.00	41.57	0.00	0.00	11.34	0.00	0.03	0.00	0.70	0.00
12(c)	213.40	48.65	199.50	41.04	0.00	0.00	0.65	0.24	0.00	0.00	1.25	0.00
13(a)	212.50	54.28	199.20	41.43	0.31	7.74	6.90	0.18	0.00	0.00	0.73	0.00
14(d)	210.30	54.93	198.00	39.31	0.26	0.00	0.39	0.00	0.00	0.00	0.67	0.00
15(a)	211.40	55.59	198.80	41.18	0.95	0.00	8.29	0.00	0.00	0.00	0.21	0.00
16(c)	44.35	54.17	41.07	42.88	2.20	4.99	0.00	0.13	0.01	0.00	0.00	0.00
17(a)	45.48	52.19	42.09	41.26	2.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	48.75	55.21	39.65	43.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	52.80	56.66	43.09	43.51	0.00	0.00	9.45	0.00	0.05	0.00	0.00	0.19
20	51.22	54.48	36.56	43.28	2.35	0.00	8.47	0.00	0.01	0.00	0.00	0.00
21(c)	208.70	49.36	188.80	43.33	1.43	0.00	0.47	0.00	0.00	0.06	0.30	0.00
22(c)	208.40	49.29	191.30	40.22	0.00	9.49	0.68	0.00	0.00	0.09	1.21	0.00
23(c)	210.10	57.35	195.00	45.81	0.00	0.00	0.20	0.03	0.00	0.00	0.89	0.00
24(a)	210.20	56.74	199.00	44.50	0.00	3.55	0.34	0.17	0.00	0.00	0.59	0.00

25(b)	212.00	51.29	199.70	41.20	0.00	0.00	0.69	0.08	0.04	0.00	1.01	0.00
26	48.43	57.62	40.37	45.36	4.53	0.00	22.00	0.00	0.00	0.00	5.13	0.00
27	48.64	60.56	39.89	47.63	3.67	0.00	36.00	0.20	0.00	0.00	0.13	0.00
28	48.73	59.86	39.52	48.04	2.06	0.00	17.80	0.00	0.00	0.00	0.00	0.00
29	66.15	81.73	50.53	64.60	2.25	0.00	7.69	0.09	0.03	0.00	0.00	0.00
30	53.36	43.49	20.00	45.40	0.97	0.00	0.66	0.08	0.00	0.00	1.01	0.00
31	49.88	57.58	40.19	48.27	1.38	0.00	6.95	0.00	0.00	0.00	0.00	0.00
32	38.69	42.94	28.33	44.86	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
33	185.80	131.44	124.10	132.90	0.00	0.00	15.60	0.00	0.00	0.00	0.00	0.00
34	48.89	57.79	35.94	47.15	1.76	0.00	8.48	0.00	0.00	0.03	0.00	0.71
35	49.26	51.96	35.38	43.85	1.08	0.00	14.00	0.00	0.00	0.03	0.00	1.17
36	352.00	34.90	103.20	21.89	1.28	0.00	0.00	0.13	0.02	0.00	0.85	0.00
37	55.15	40.95	20.10	24.78	0.00	0.00	0.00	0.22	0.00	0.04	0.75	0.00
38	72.52	37.62	28.46	22.38	0.00	0.00	0.00	0.10	0.01	0.00	0.52	0.38
39	60.06	39.32	22.66	30.59	0.78	0.00	0.00	0.00	0.03	0.00	0.68	0.00
40	70.48	77.00	28.19	33.88	0.42	0.00	0.00	0.00	0.00	0.00	0.84	0.00
41	125.60	120.08	44.45	41.16	2.60	0.00	0.00	42.87	0.00	0.10	0.48	0.00
42	121.37	34.27	13.83	25.82	2.71	0.00	0.00	0.19	0.00	0.00	0.40	0.21
43	338.75	308.82	22.24	95.79	5.74	0.00	0.29	0.05	0.11	0.00	0.54	0.00
44	331.70	295.69	99.00	96.65	0.42	6.24	2.53	0.00	0.07	0.09	1.14	0.00
Mean ±SD	125.57±91.30	70.44±54.83	85.50±72.38	45.99±19.67	1.48±1.63	0.94±2.26	4.22±7.44	1.04±6.45	0.01±0.03	0.01±0.03	0.51±0.82	0.1±0.26
SANS (2005)	300.00		100.00		0.05		2.00				0.05	
P. Values	< 0.01		< 0.01		> 0.05		< 0.05		> 0.05		< 0.01	

Note: SD – standard deviation, (a): ± 1 m; (b): ± 2 m; (c): ± 3 m and (d): ± 4 m depth

3.1.3 Trace elements

The results of trace elements are presented in Table 4. The obtained mean concentrations of arsenic (As) were 1.48 mg/L and 0.94 mg/L in the wet and dry seasons, respectively. The mean concentrations of arsenic were observed to be above the recommended value of the drinking water guideline. It is apparent from the table of results that there was a significant variation between the concentrations of arsenic measured in the wet and dry seasons; this reflects changes in water geochemistry. The concentrations of Fe ranged from 0.00 mg/L to 36.00 mg/L and 0.00 mg/L to 42.87 mg/L in the wet and dry seasons, respectively. The mean concentrations of Fe were 4.22 mg/L in the wet season and 1.04 mg/L in the dry season. There was a significant variation ($P < 0.05$) in Fe concentrations between the wet and dry seasons. It is evident from Table 4 that the concentrations of Fe were above the recommended limit in both seasons. The concentrations of U varied from 0.00 mg/L to 0.10 mg/L in the wet season and 0.00 mg/L to 0.09 mg/L in the dry season. The mean concentrations of U were 0.01 mg/L in the wet season and 0.01 mg/L in the dry season. There is no specific standard for uranium set by the SANS guideline for drinking water. However, according to WHO (2011), the maximum allowable concentration of uranium in drinking water is 0.03 mg/L. It is apparent from Table 4 that the concentrations at some of the sampling points have exceeded the required limit, especially those situated at or close to mining activities. The analysis shows that there was no significant variation between the concentrations of U measured in the wet and dry seasons. The mean concentrations of Pb were 0.51 mg/L and 0.10 mg/L in the wet and dry seasons, respectively. The concentrations of Pb showed a significant variation ($P < 0.01$) between the water samples measured in the wet and dry seasons.

3.1.4 Metal speciation in surface water

The speciation of metal in water is important to understand metal's behaviour in aquatic systems (Korfali and Jurdi, 2010; Korfali and Davies, 2003). This model is capable of predicting the long-term species in water and it also helps to see the form in which metals will be distributed in surface water. The application computes and reports the metals speciation in terms of their free hydrated ion and inorganic complexes (Korfali and Jurdi, 2010; Obiefuna and Orazulike, 2010). In this study, the objective was to investigate the potential of pollutants dispersion through speciation. Table 5 presents the concentrations of metals speciation calculated by the PHREEQC modelling program in the surface water collected during the wet and dry seasons.

Table 5: Range of highest percentages of speciated forms of metals measured in surface water in the vicinity of Potchefstroom.

		Wet season	Dry season
Element	Speciated forms	% Range	% Range

Ca	Ca^{+2}	57.87 -88.95	68.69 - 87.66
	$CaHCO_3^+$	1.88 - 11.64	0.06 - 3.07
	$CaCO_3$	0.25 - 20.92	0.24 - 9.43
	$CaOH^+$	< 1	-
	$CaSO_4$	3.10 - 30.61	6.62 - 29.80
Mg	Mg^{+2}	63.15 - 90.15	70.58 - 90.48
	$MgSO_4$	2.66 - 26.35	5.56 - 27.44
	$MgHCO_3^+$	1.21 - 8.39	1.10 - 3.62
	$MgCO_3$	0.14 - 8.92	0.33 - 2.38
	$MgOH^+$	< 1	-
Fe	Fe^{+2}	0.65 - 21.04	0.04 - 13.31
	$MgFe(cyanide)_6^{-2}$	0.12 - 6.97	0.01 - 40.85
	$Fe(cyanide)_6^{-4}$	1.0 - 14.79	27.50 - 34.13
	CaFe(cyanide)	1.97 - 49.84	17.71 - 42.74
	$Fe(OH)^{2+}$	1.48 - 43.05	0.29 - 7.45
	$Fe(OH)_3$	21.13 - 29.68	0.06 - 8.57
	$Fe(HO)_4^-$	16.59 - 35.61	0.05 - 7.54
	$Fe(cyanide)_6^{-3}$	< 1	< 1
As	$HAsO_4^{-2}$	90.60 - 99.00	73.43 - 98.15
	$H_2As0_4^-$	0.22 - 5.02	1.71 - 26.63
U	$UO_2(CO_3)_3^{-4}$	87.29 - 99.43	60.30 - 96.48
	$UO_2(CO_3)_2^{-2}$	1.81 - 12.93	3.57 - 39.46
Pb	$PbCO_3$	20.99 - 37.49	39.48 - 47.68
	$Pb(CO_3)_2^{-2}$	1.37 - 18.42	0.89 - 3.77
	$PbHCO_3^+$	0.28 - 5.42	-
	Pb^{+2}	-	0.45 - 2.27

Calcium species: The concentrations of Ca chemical species calculated for all the water samples analysed both in the wet and dry seasons showed that the samples were found mostly (> 89 %) in the oxidation state II, the rest being in oxidation state I and forming complexes with the carbonates. The other predicted species of Ca were $CaSO_4$, $CaCO_3$, $CaHCO_3^+$ and $CaOH^+$. The presence of Ca as free aqua ion indicated that the bioavailability will be high in water; thus it is likely to increase the level of toxicity in water. However, the toxicity will be decreased when it forms complexes with the carbonate ($CaCO_3$).

Magnesium species: The most predominant species of magnesium was Mg^{2+}, with over 90% analysed both during the wet and dry seasons. The other chemical species of magnesium were $MgSO_4$, $MgHCO^{3+}$, $MgCO_3$ and $MgOH^+$. The high percentage of magnesium as free aqua ion shows that bioavailability will occur; however, the toxicity will decrease as it also forms complexes with the carbonates.

Iron species: The prime species of Fe in the samples collected were those forming complexes with the carbonates and hydroxides both during the wet and dry seasons. Concentrations of CaFe (cyanide) ranged from 1.97% to 49.84% in the wet season and 17.71% to 42.74% in the dry season. The species of $Fe(OH)_3$ ranged from 21.13% – 29.68% and 0.06% – 8.57 % in the wet and dry seasons, respectively. Among the carbonates and hydroxide species were $MgFe(cyanide)_6^{-2}$, $Fe(cyanide)_6^{-4}$ and $Fe(OH)_4^-$. The free hydrated ion species of Fe were $Fe(OH)^{2+}$ and Fe^{+2}, with the highest percentage mainly observed in the wet season. There was a significant variance between the concentrations of free hydrated (Fe^{+2}) measured in both seasons, with high concentrations mostly calculated in the wet season. This speciation of Fe as free aqua ion shows that bioavailability is likely to occur and that can cause toxicity in water. Similar results were reported in water samples collected in Kwazulu-Natal, South Africa (Magu et al., 2015).

Arsenic species: The arsenic species were mostly distributed as the As (5) in the water samples collected in the wet and dry seasons. Prime species of arsenic that were observed in both seasons were those forming complexes with the hydroxide species ($H_3AsO_4^{-2}$ and $H_2AsO_4^-$). The concentrations of $H_3AsO_4^{-2}$ ranged from 90.60% to 99.00% and 73.43% to 98.15% in the wet and dry seasons, respectively. The dominance of species of As forming complexes with the hydroxides may be attributed to the pH values, which were alkaline in both seasons. However, the lack of free hydrated ions shows that this metal will precipitate and will cause no harm in water. Other authors have reported the tendency of arsenic to form a complex with the hydroxide (Lenoble et al., 2012).

Pb: The speciation modelling predicted that Pb will mostly precipitate as $PbCO_3$ and $Pb(CO_3)_2^{-2}$ in the water samples collected during the wet and dry seasons. The concentrations of $PbCO_3$ ranged from 20.99% to 37.49% in the wet season and from 39.48% to 47.68% in the dry season. The concentrations of $Pb(CO3)_2^{-2}$ ranged between 1.37% and 18.42% and 0.89% and 3.77% in the wet and dry seasons, respectively. The remaining Pb was predicted to be present as free hydrated ions and the predominant species were $PbHCO_3^+$ and Pb^{+2}. However, the species of $PbHCO_3^+$ (0.28% – 5.42%) was only shown in water samples during the wet season while the Pb^{+2} (0.45% – 2.27%) was measured in the dry season only. The presence of free hydrated ion concentrations indicated the possible bioavailability of the metal and its likeliness to increase the level of toxicity in water. Similar results were predicted by Korfali and Davies (2003) in water samples of a river underlain with limestone.

U: The predominant species of uranium in both seasons were those forming complexes with the carbonate species ($UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$). The concentration of $UO_2(CO_3)_3^{-4}$ ranged between 87.29% and 99.43% and 60.30% and 96.48% in the wet and dry seasons, respectively. The concentrations of the species of $UO_2(CO_3)_2^{-2}$ ranged from 1.81% to 12.93% and 3.57% to 39.46% in the wet and dry seasons, respectively. The formation of complexes between uranium and carbonate implies that precipitation will occur and this will result in a decrease of its toxicity in water. The high precipitation of uranium can be attributed to the alkaline pH in both seasons.

4 Conclusion

The study showed that there was a significant difference between the physical-chemical parameters measured in the surface water samples collected in the wet and dry seasons. High concentrations measured in the wet season can be attributed to the large flow of effluents from anthropogenic sources. However, parameters such as pH, EC, Eh, CN^-, Cl^-, SO_4^{-2} and U showed no significant difference between the two seasons. Non-significant differences could suggest that anthropogenic sources contributed mostly to the pollution in both seasons, or some of the parameters were slightly conservative. The significant difference observed for parameters like total alkalinity, calcium, magnesium and lead shows that there was a change in water geochemistry. The PHREEQC modelling shows that there was a slight variation of chemical species in the water samples collected in the wet and dry seasons within the sampling points, which could be due to dilution effects in the wet season. Metals could form complexes with the carbonates, which are likely to reduce its bioavailability in water, however, the presence of other metals as free hydrate ions, indicated their bioavailability and the likeliness to increase toxicity in the surface water of the study area.

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Chapter 5

Article 3

General overview of article 3

This paper addresses the metal retention potential of sediment and water quality in the Mooi Rivers, South Africa.

In this paper, both sediment and surface water samples were selected to be analysed. The sediment samples and water samples were collected along the Mooi River and its connected streams. The main purpose was to investigate how metals will be distributed in different fractions of the sediment, and that was achieved by using the BCR sequential leaching method. Sediment samples were also characterised using XRD, XRF and FTIR spectroscopy. The organics groups, which are likely to bind metals, were also investigated in the sediment. The quality of the water was assessed and compared with the SA/WHO water guidelines to determine its fitness.

The following findings resulted from the investigation:

It was found that metals such as Fe, Cr and Mg were mostly bound to the sediment and this was substantiated by the high percentages associated with the residual fractions. On the other hand, Ca and Mn were mainly associated with the exchangeable fraction, indicating that their bioavailability was high and they were likely to cause toxicity in the aquatic environment, especially in the case of manganese. The characterization results of XRF and XRD revealed that the sediment samples contained predominantly mineral oxides and quartz minerals, respectively. The investigation on the sediment also showed that the composition of organic carbon varied among the sampling sites. The high content of organic carbon observed can be due to the decomposition of organic matter, and this is likely to reduce the bioavailability of metals through complexity. The binding groups revealed by the FTIR analysis also confirmed that metals are likely to be retained in sediment samples. However, the concentrations of the studied metals were observed to render the water unfit for drinking and other essential purposes.

Metal retention potential of sediment and water quality in the Mooi River, South Africa

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Abstract

The potential of sediments to retain metals along the Mooi River and connected streams in the vicinity of Potchefstroom, South Africa, was evaluated using a four-stage sequential extraction procedure. The sediments were characterized using XRD, XRF and FTIR techniques. The physico-chemical parameters and heavy metals content of the water were also measured to evaluate their impact on water quality and fitness for human consumption. The highest percentages of Fe, total Cr and Mg (83.46%, 27.43%, and 88.83%, respectively) were associated with the residual fraction of the sediments. Elements such as Ca and Mn were mostly bound to the exchangeable fraction of the sediments. Association of Fe, total Cr and Mg with the residual fraction as predicted by speciation calculations suggests that these metals are strongly bound to the sediments and therefore less susceptible to cause pollution. The mobility order of the heavy metals in the sediments samples was Ca> Mn> Mg> Fe> Cr. For the first time the implication of organic matter in the sediments along the Mooi River to retain metals was investigated and it was found that organic matter occurring in various concentrations in these sediments, contained binding groups such as C-O, C-C=C, O-H and =C-H that are most likely to contribute to the retention of metals in the exchangeable fraction of the sediments. The amount of inorganic pollutants in the water was found to basically decrease moving downstream, but the water quality remained unfit for human consumption at most of the sampling points.

Keywords— Mooi River, sediments, metals, sequential extraction, fractions, mobility and bioavailability

1 Introduction

The contamination of rivers by heavy metals is a worldwide problem [1]. Heavy metals are carried through the rivers and streams in different forms that include dissolved species or as part of the suspended sediments [2], which contaminate the aquatic environment causing instability of the ecosystem due to their toxicity [3]. Some metals are essential to living organisms when available in small quantities, but they become toxic at higher concentrations [4] and thus they lead to a reduced quality of water, making it unfit for various uses [5]. Water quality is described in terms of the biological, physical and chemical parameters that include the temperature, pH, rainfall, salinity, electrical conductivity, redox potential, dissolved oxygen and carbon dioxide [6]. The quality of water can also be reduced by the local geology; however, human practices have a much larger influence on the reduction of water quality [7]. For example, anthropogenic activities such as mining activities, industrial wastewater, domestic sewage, operation of wastewater treatment plants and agricultural practices are among the most vital sources of heavy metals found in the aquatic environment [8]. Heavy metals are among the major pollutants of the aquatic environment, as they can be potentially detrimental to human health [9], and the situation is exacerbated because they are persistent and bio-accumulative in nature [10]. These heavy metals can be dispersed and accumulated in plants and animals [11], thus entering the food web [12]. The developing countries are affected the most by this metal pollution due to the poor management of their environment as well as the incapacity to afford the operating costs of pollution treatments facilities [13]. When entering into the aquatic environment, metals are partitioned between the water column and sediments [14]. In the sediments, they are further partitioned into different phases that include carbonates, oxides, hydroxides and sulphides [15].

The metal distribution, mobility and their availability in the aquatic environment do not necessarily depend on their total concentrations, but on the physical-chemical forms in which they are partitioned, and this can be studied through sequential extraction and speciation techniques [16,17]. To determine the partitioning of heavy metals, various methods involving both the single and sequential extraction schemes have been employed for the past decades [8]. In this study, a four-stage sequential extraction procedure, proposed by the European Communities Bureau of References (BCR), was employed. This method has been successfully used by other researchers [10, 18].

The high concentration of trace metals found in the Mooi River at Potchefstroom has been reported to be mainly due to the gold mining activities in the vicinity of the Wonderfonteinspruit [19, 20]. However, the degradation of the water quality in the Mooi River, as it flows through the city of Potchefstroom, is also exacerbated by effluents from the municipality's wastewater treatment works and some major industries [21]. Due to this concern, many studies have been conducted in the catchment of the Wonderfonteinspruit (WFS) to determine the level of trace metals in the surface water and sediments [22-25]. However, to the best of our knowledge, no study has so far investigated the typical binding groups contributing to the retention of metals in the sediments along the Mooi River. The objectives of this study were: (i) to investigate the distributions of the selected metals in different fractions of the sediments collected from the Mooi River and connected streams using the BCR extraction procedure, (ii) to characterise the sediment samples using XRD, XRF and FTIR spectroscopy, (iii) to determine the organic groups in the sediment which are likely to bind to metals in solution, and (iv) to assess the quality of water.

2 Study area

The Mooi River originates from a large catchment area from the Bovenste Oog spring as well as the inflow of the Wonderfonteinspruit and the confluence with the Loopspruit, south of Potchefstroom [18]. The study area is situated between the latitudes $26^{o}22'$ and $26^{o}54'$ and longitudes $27^{o}5'$ and $27^{o}57'$ (Table 1). The average temperature of the study area is 16.9°C, and the mean annual precipitation is 663.5 mm, with a reported mean annual runoff into streams of 29.5 mm [26]. The Mooi River catchment contains some reservoirs, the largest of which are the Klerkskraal Dam (8 million m^3), Boskop Dam (21 million m^3) and Potchefstroom Dam (2 million m^3) [27]. The Klerkskraal, Boskop, and Potchefstroom Dams supply domestic and industrial water to Potchefstroom through the Mooi River State Water Scheme [18]. These dams are also used for irrigation purposes in Potchefstroom and the vicinity [28]. Geologically, the Mooi River is partly located on a dolomite rock system which covers almost 75% of the area [27].

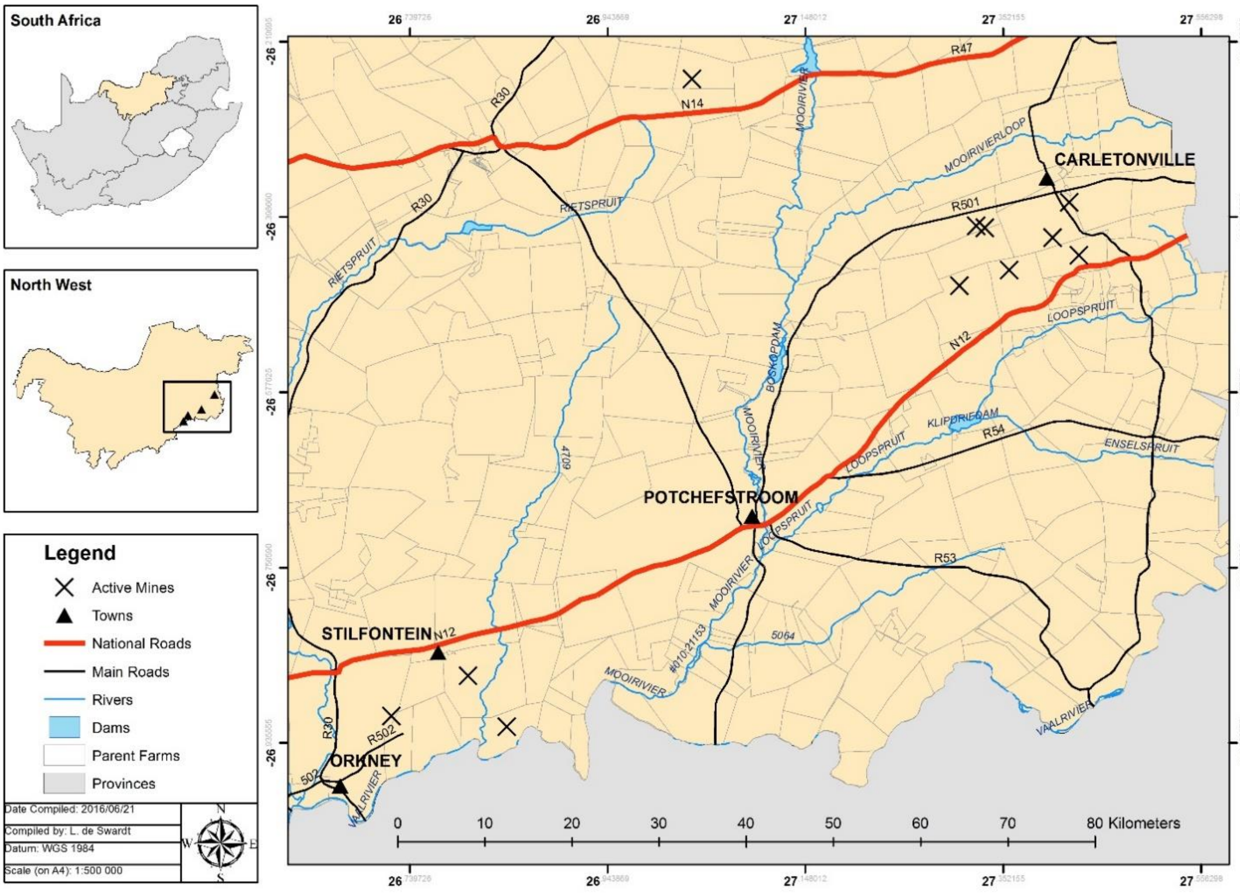


Figure 1: The study area in the North West Province of South Africa (the Mooirivierloop is now known as the Wonderfonteinspruit)

3 Methodology

3.1 Sampling

A total of 9 sampling sites were selected along the Mooi River, karst spring and a mine canal to investigate the contamination of sediments and water by metals (Fig 2). The coordinates of the sampling points are presented in Table 1. Sampling point 1 is at the Driefontein mine canal connection with the Mooi River, samples 2 (connected to the karst spring) and 3 are in streams forming part of the Mooi River system. Samples 4 and 5 are located within the Boskop and Potchefstroom Dams, respectively; both dams are situated along the Mooi River. Sampling points 6 - 9 are located along the Mooi River. These sampling points received effluents from anthropogenic sources such as mining activities (Fig 1). The positions of the collection points were determined by personnel from the Department of Water and Sanitation located at Boskop Dam; these points are mapped for routine monitoring of pollution problems in the area.

Table 1: Sampling point description and coordinates

Sample number	Description	Location	
		S	E
1	Driefontein mine canal	26°22'30.71"	27°19'57.34"
2	Turffontein eye	26°24'51.04"	27°10'13.32"
3	Gerhardminebron eye	26°28'47.61"	27° 9'5.70"
4	Boskop Dam	26°33'56.0"	27°07'13.7"
5	Potchefstroom Dam	26°39'55.67"	27° 5'34.14"
6	Mooi River	26°40'55.6"	27°05'53.8"
7	Mooi River	26°42'04.1"	27°06'22.6"
8	Mooi River	26°42'34.1"	27°06'20.2'
9	Mooi River	26°52'49.8"	26°57'51.4"

The selected samples (collected once) were assessed for their metal retention potential. The sediment samples were collected inside of the Mooi River and connected streams (a few metres away from the bank) at depths varying from 0 cm to 6 cm using a grab sampler. A sub-sampling of the sediments was performed by taking the upper 6 cm of the sample from the grab, where after it was stored in clean plastic bags that quickly tighten to avoid oxygen penetration (preserve biological or chemical equilibria). Sediment samples were then kept at 4ºC prior to their analysis. A large amount of sediment samples was collected (about 3 to 4 kg) at each site in order to have enough samples for experiments such as sequential extraction, mineralogical and chemical compositions, total organic carbon and identification of functional groups using Fourier transform infrared spectroscopy (FTIR). The water samples were collected in 500 mL plastic bottles according to accepted methods [29]. Before use, the bottles were washed with deionised water and then rinsed with the water of the sampling site during sampling. The water samples were collected at the surface of the streams, using 500 mL polyethylene bottles that were rinsed with river water and then also deeper at the subsurface with the mouth of the bottle facing in the direction of the water flow. However, at the dams, samples were collected a few metres from the Dam wall at depths that varied from ±1 m to 2 m using a depth-sampler. Immediately after water sampling, the following physical-chemical parameters were measured using appropriate probes and meters (Hanna Instrument Inc, USA): pH, temperature [°C], electrical conductivity [mS/cm], dissolved oxygen (DO) [mg/L] and redox potential [mV]. The pH meter was calibrated in the field before analysis, using reference buffer solutions. The samples were then stored in cooler boxes packed with ice to ensure proper preservation during transportation to the laboratory where further analyses were done.

3.2 Experimental protocol

The sediment samples were dried in an oven at 50ºC, then it was ground using a mortar and pestle and sieved to particle sizes of <63 µm, which corresponds to the size fraction used in previous studies focusing on the analysis of heavy metals from sediments [30, 31]. The sequential extraction of heavy metals was performed using the BCR sequential extraction method. The mineralogical composition and major components of the metals were determined using XRD and XRF, while the total organic carbon was determined by using the Wakley Balk titration method. The functional groups in the sediments were identified using FTIR spectroscopy (Thermo Scientific, France). The total analysis of heavy metal content in the sediment samples was conducted using ICP-OES (Agilent Technologies, USA).

The total alkalinity (as HCO_3^- and CO_3^{2-}) was determined through titration with 0.1 M H_2SO_4 acid. The concentrations of sulphate, nitrate, and cyanide$^-$ in the water samples were analysed using a COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA). The concentration of Cl^- in the water samples was measured through titration with a silver nitrate and potassium dichromate solution. The heavy metals concentrations (Fe, Ca, Mn, Mg, and total Cr) were measured using ICP-OES. Organic carbon content was determined according to the method reported by Avramidis et al. [32]. The BCR sequential extraction was conducted according to the procedure described in Fig 3.

3.3 Reagents

Sequential extraction: high quality reagents of analytical grade and deionised water, supplied by Oasis Water (Potchefstroom, South Africa), were used for all the preparations and analyses. Diluted standard solutions were prepared from the stock standard solutions. A working solution of 0.11 M acetic acid, 0.1 M $NH_2OH.HCl$ (adjusted to pH 2 with 2 M nitric acid), 8.8 M hydrogen peroxide (pH of 2-3), 1.0 M ammonium acetate (adjusted to pH 2 by adding a concentrated HNO_3) and aqua regia (HNO_3 + 3HCl) was prepared using distilled water.

For the quantification of organic carbon, diluted standard solutions were also prepared from the stock standard solutions. Therefore, solutions of 1.0 M potassium dichromate (dried at 105 °C), sulphuric acid 98%, 0.4 M ferrous sulphate and a ferroin indicator were prepared using the deionised water.

To assess the quality of water, specific test kits were used to measure the level of sulphate, nitrate and cyanide in water. About 20% nitric acid was used to dilute the water samples prior to the analysis of heavy metals by the ICP-OES instrument.

3.4 Fourier transform infrared spectroscopy (FTIR) method

The binding groups in the sediment samples collected from the Mooi River network and connected streams were identified using FTIR spectroscopy (Thermo Scientific Nicolet iS10 FTIR Spectrometer, France). The FTIR spectra were collected within the wavenumber range between 400 and 400 cm^{-1} using the potassium bromide (KBr) pellet technique.

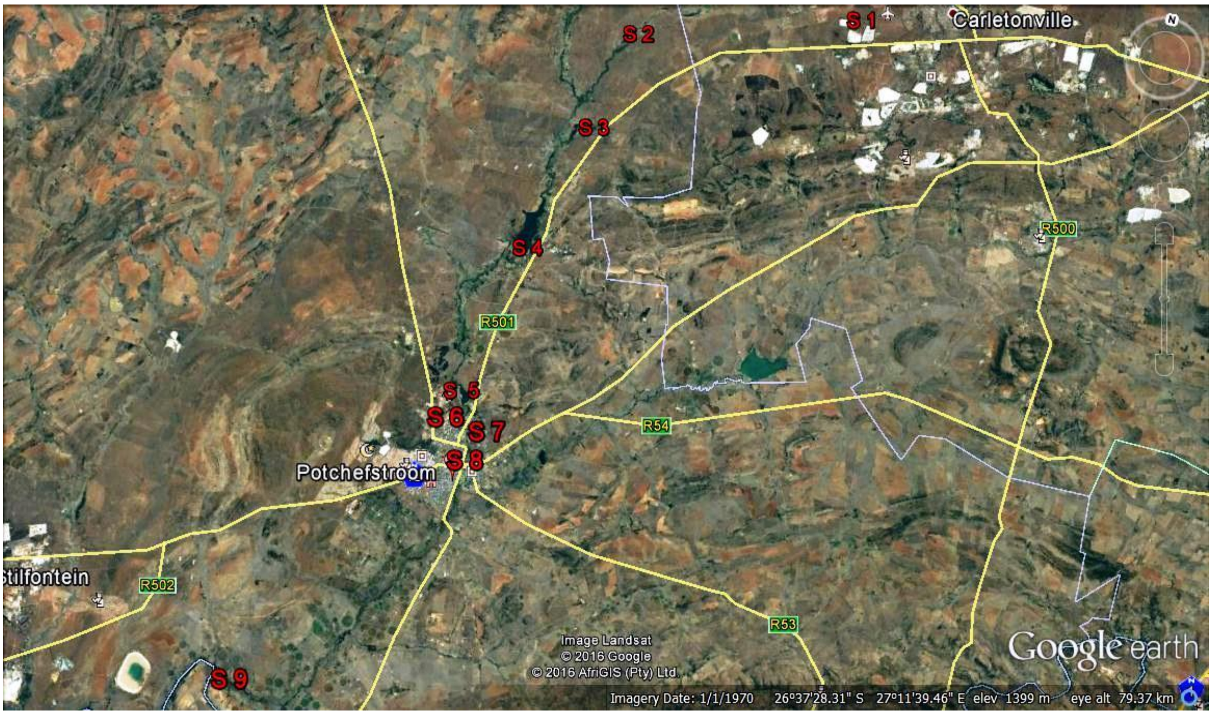
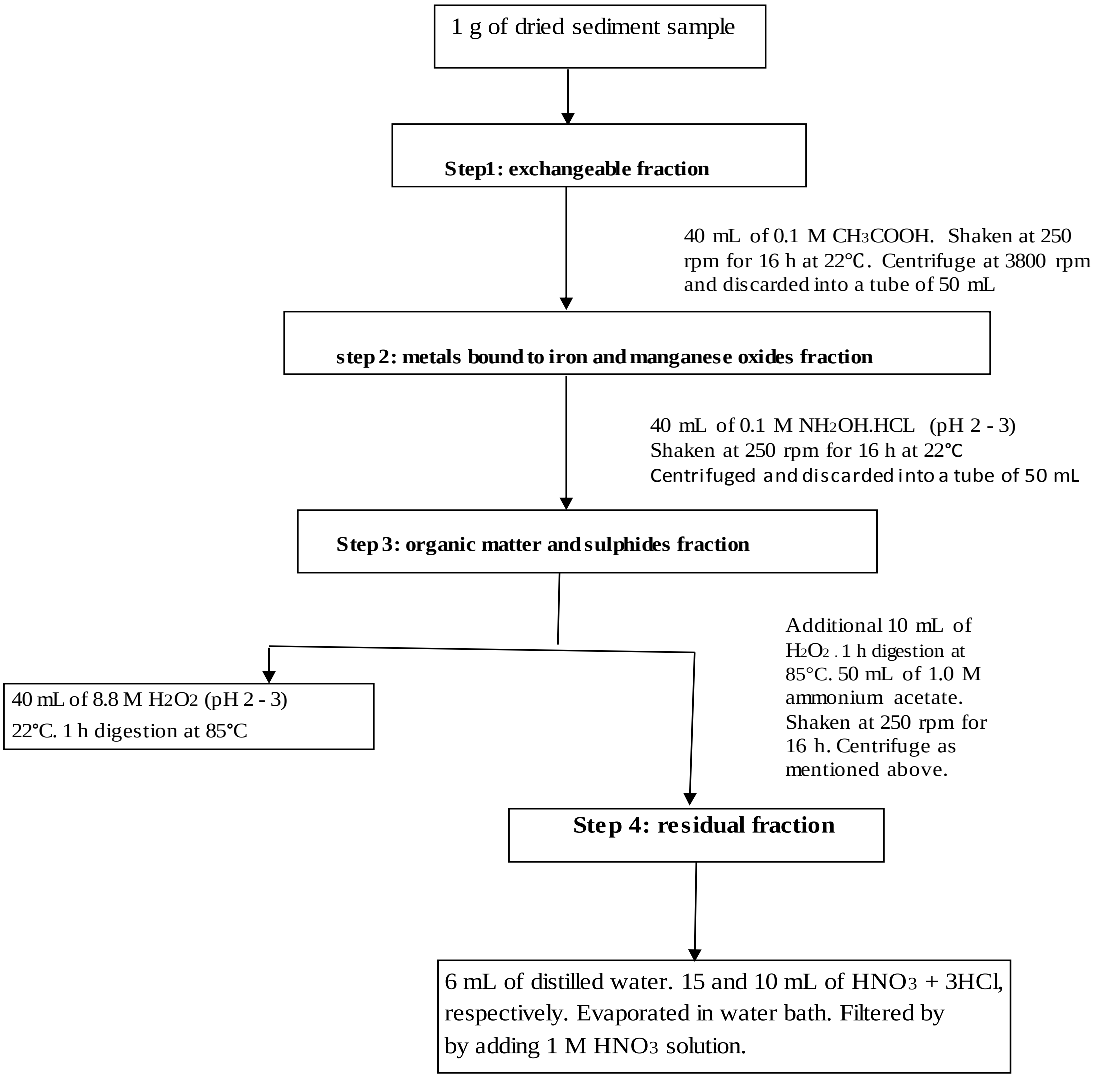


Figure 2: Map of the study area showing sampling points (1- 9)

3.5 Sequential extraction method

To evaluate the binding forms of heavy metals in the sediment samples, BCR sequential extraction was applied. The details of the different steps and reagents used are shown in the following flowchart.



40 mL of 0.1 M CH_3COOH. Shaken at 250 rpm for 16 h at 22°C. Centrifuge at 3800 rpm and discarded into a tube of 50 mL

40 mL of 0.1 M $NH_2OH.HCL$ (pH 2 - 3) Shaken at 250 rpm for 16 h at 22°C Centrifuged and discarded into a tube of 50 mL

40 mL of 8.8 M H_2O_2 (pH 2 - 3) 22°C. 1 h digestion at 85°C

Additional 10 mL of H_2O_2 . 1 h digestion at 85°C. 50 mL of 1.0 M ammonium acetate. Shaken at 250 rpm for 16 h. Centrifuge as mentioned above.

6 mL of distilled water. 15 and 10 mL of HNO_3 + 3HCl, respectively. Evaporated in water bath. Filtered by by adding 1 M HNO_3 solution.

Figure 3. Flowcharts for the BCR speciation scheme of sediments.

4 Results and discussion

4.1 XRD analysis of mineralogical composition

The mineralogical compositions of the sediments are presented in Fig 4. These results show that the most abundant mineral is quartz, within a range of 29% - 89% as determined in the sediment samples collected from the Mooi River and its connected streams. The rest of the minerals such as clinoferrosilite, diopside, welinite, iron silicide, rutile, clinoenstalite, kyanite and calcium oxide iron were detected in one or more samples.

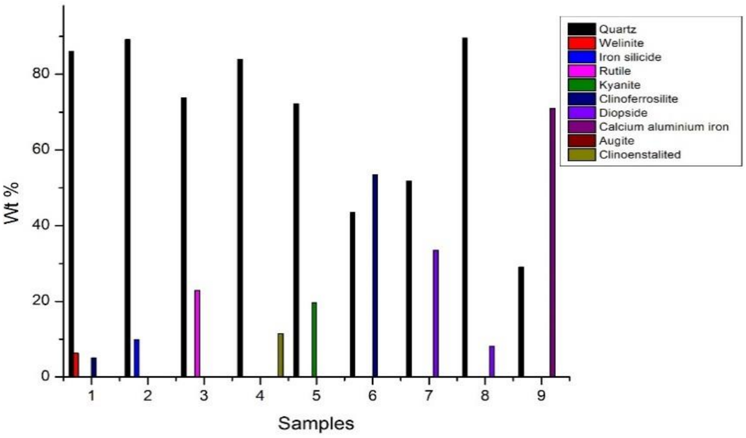


Figure 4: Mineralogical composition of the sediments (fraction <63 µm) from the Mooi River

4.2 XRF analysis of major components

The results of the XRF analysis of the major components are illustrated in Fig 5, presented as percentages of the corresponding oxides. The following oxides were observed to be dominant in all sampling sites studied: SiO_2 (45.72% – 84.13%), CaO (0.62% - 17.96%), Fe_2O_3 (5.73% - 25.51%), MgO (0% – 2.48%), MnO (0.16% – 3.45%) and Cr_2O_3 (0% – 0.25%). Most of these element oxides were mainly dominant in samples 1 to 8 (Mooi River and connected streams); however, higher concentrations of magnesium were found in samples 9 and 8 (Mooi River). The abundance of these elements is likely due to the type of rock, which covers most part of the study area. The dominant elements such as Si, Ca, Fe, Mg, Mn, and Cr can be potentially toxic to the aquatic environment. The nature of the sediments determined in this study is similar to that of the sediments from the four main rivers in Kolovo [30].

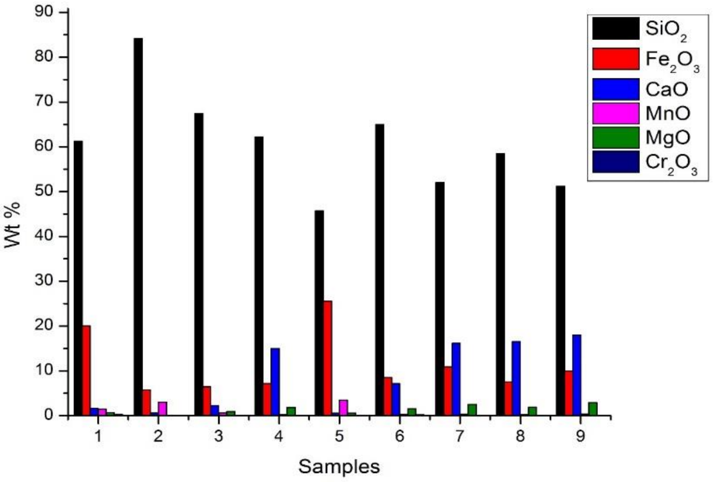


Figure 5: Selected major and trace components of sediments (fraction < 63 µm)

4.3 Metal speciation in sediment

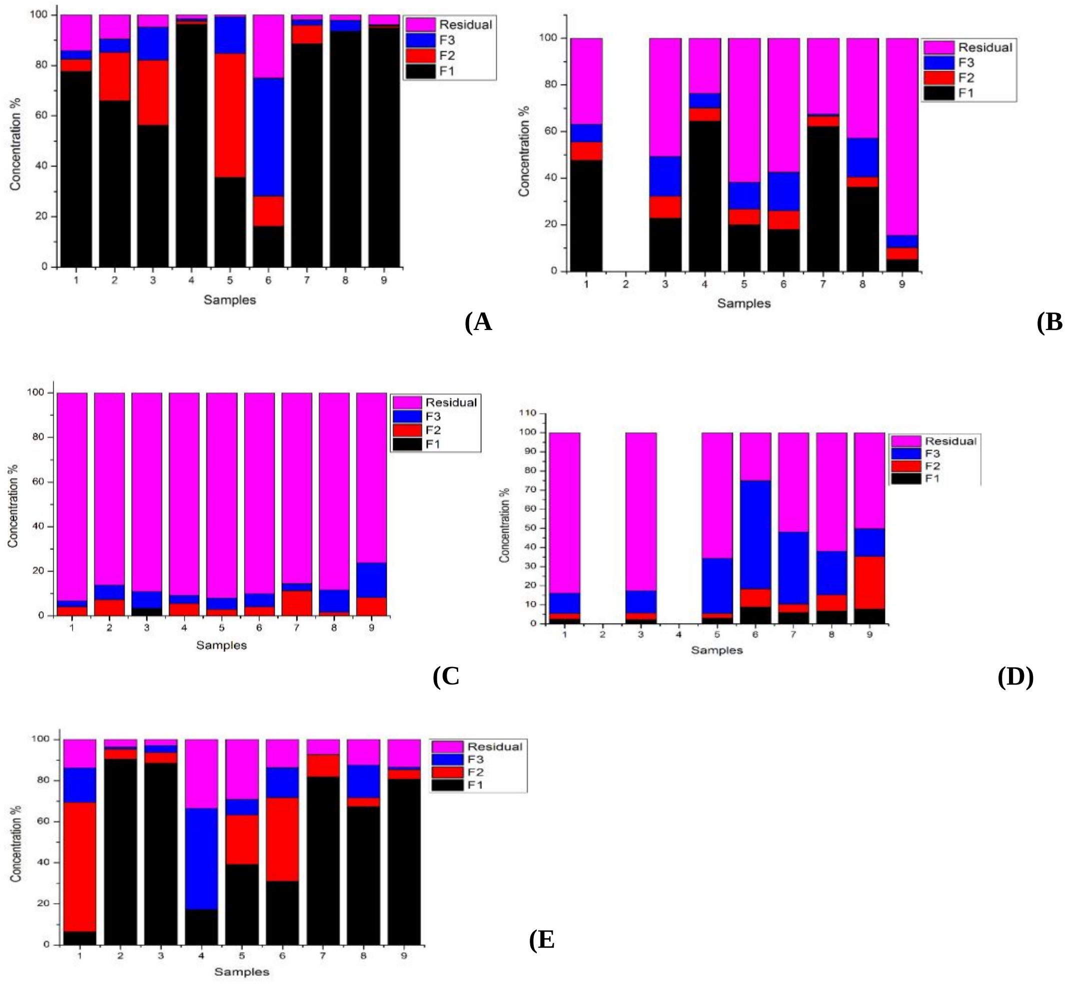
The percentage concentrations of Fe, Ca, Mn, Mg and Cr extracted from the sediments at each step are illustrated in Fig 6. Elements such as Ca and Mn were mostly recovered in fraction 1 of the sediment samples collected from the Mooi River and connected streams. The rest of the metals were found to be strongly bound to the crystalline structure of sediments. Mobility and bioavailability of metals are related to the solubility; therefore, bioavailability decreases in order of exchangeable > reducible > oxidizable > residual. The mobility and bioavailability of metals extracted from the studied sediments samples decreased in the following order: Ca > Mn > Mg > Fe > Cr. In this study, the high concentration of Fe in the sediment samples collected from the Mooi River and connected streams was associated with the residual fraction (83.46%) and to a lesser extent to the exchangeable fraction (1.65%), reducible fraction (5.89%) and oxidizable fraction (7.25%). It therefore ensues that the mobility and bioavailability of Fe will be very low due to the smaller amounts bound to the exchangeable fraction, and this implies that there will be a relatively lower risk of toxicity related to the presence of this element in the surface water. These results were in agreement with the studies performed by Yuan et al. [33] who found that more than 90% of the total Fe was bound to the residual fraction.

Ca and Mg were obtained in all four fractions of the BCR sequential extraction method. In sediments collected from the Mooi River and connected streams, a high recovery percentage of Mg from the residual fraction was 88.83%. Its contribution to exchangeable, reducible and oxidizable was 21%, 9.64% and 16.39%, respectively. Furthermore, the distribution of Ca, as an exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction, was as follows: 72.92%, 83.29%, 45.01% and 10.54%, respectively. The high percentages of Mg and Ca associated with the exchangeable fraction, show that the mobility and bioavailability of these elements will be high, and this tends to increase the hardness of water, which can result in the increase of the pH in surface water. These high values of Mg and Ca extracted from sediments can be attributed to the underlying rocks constituted mainly of dolomite; however, in contrast to Ca, most of the Mg was bound to the residual fraction at sampling point 5, which indicates that only a small amount of Mg could be released into the water at this particular point.

Total Cr was mainly associated with the residual fraction, suggesting relatively low mobility and availability of this metal, with the highest concentration of 27.43% extracted in the sediment samples.

Its contribution to the exchangeable, reducible and oxidizable fractions was 1.27%, 2.20% and 7.75%, respectively. It has been shown in other studies [31, 34] that total Cr binds strongly to the crystalline structure of the sediments.

The distribution pattern of Mn in the sediment samples showed that it was mainly bound to the oxidizable fraction or organic matter and sulphides; with the highest percentage (64.19%) found in sediments from a stream connected to the Mooi River. The concentrations of Mn in other fractions were: 33.84% bound to the exchangeable fraction (at Mooi River), 24.94% bound to Fe and Mn (at a stream connected to the Mooi River) and 43.82% bound to the residual fraction (at the Mooi River). Mn is released from the exchangeable and reducible fractions of these sediment samples and will be bioavailable, implying that it can be harmful to the biota. The distribution of Mn in sediment fractions, as observed in this study, is in agreement with previous studies carried out using the four-step (BCR) sequential extraction procedure in sediment samples from Tokat, Turkey [35], which showed that Mn was mainly bound to the organic matter fraction.



(A

(B

(C

(D)

(E

Figure 6: Metal distribution among the different fractions: (A) Calcium, (B) Magnesium, (C) Iron, (D) Total Chromium and (E) Manganese)

4.4 Total organic carbon in sediments

It has been reported that the organic content is among the key factors influencing the bioavailability of metals in surface and groundwater [36]. The values of total organic carbon (TOC) in the studied sediment samples are presented in Table 2. The variation of the organic carbon content among the different sediment samples was likely due to its origin in the aquatic environment. The values ranged between 0.37% and 2.88%, with the highest percentage recorded in sample 6 (Mooi River). The high content of organic carbon recorded at some of the sampling points indicates the decomposition of organic matter and it is thus likely to reduce trace metal bioavailability through complexation. It is therefore understandable that the impact of organic carbon content on the distribution of elements bound to exchangeable, reducible and organic matter will vary per sampling site. Elements such as Ca and Mg, which were predominantly found in the exchangeable and reducible fractions, are likely to be entrapped in the biological matters forming part of the sediments. The breakdown or degradation of these biological matters by microorganisms often contribute to resuspend (dissolve) the metals into the solution.

Table 2: Total organic carbon of sediments samples from the Mooi River

Sample number	**TOC %**
1	0.45
2	1.15
3	1.21
4	2.02
5	0.37
6	2.88
7	1.65
8	2.82
9	1.41

4.5 FTIR spectroscopy

It is suggested that the biological factors are poorly understood, while they could strongly influence the bioaccumulation of metals and severely inhibit the prediction of metal bioavailability [37]. It is therefore important to identify the binding groups which are likely to be involved in the bioaccumulation of metals on sediments. In this study, FTIR analysis was conducted in order to confirm the presence of binding groups involved in the retention of metals in the sediments. The spectra of sediment samples collected along the Mooi River and connected streams are shown in Figs 7A, B and C, respectively. In general, the spectra of all the sampling points showed almost the same characteristics in their absorption bands.

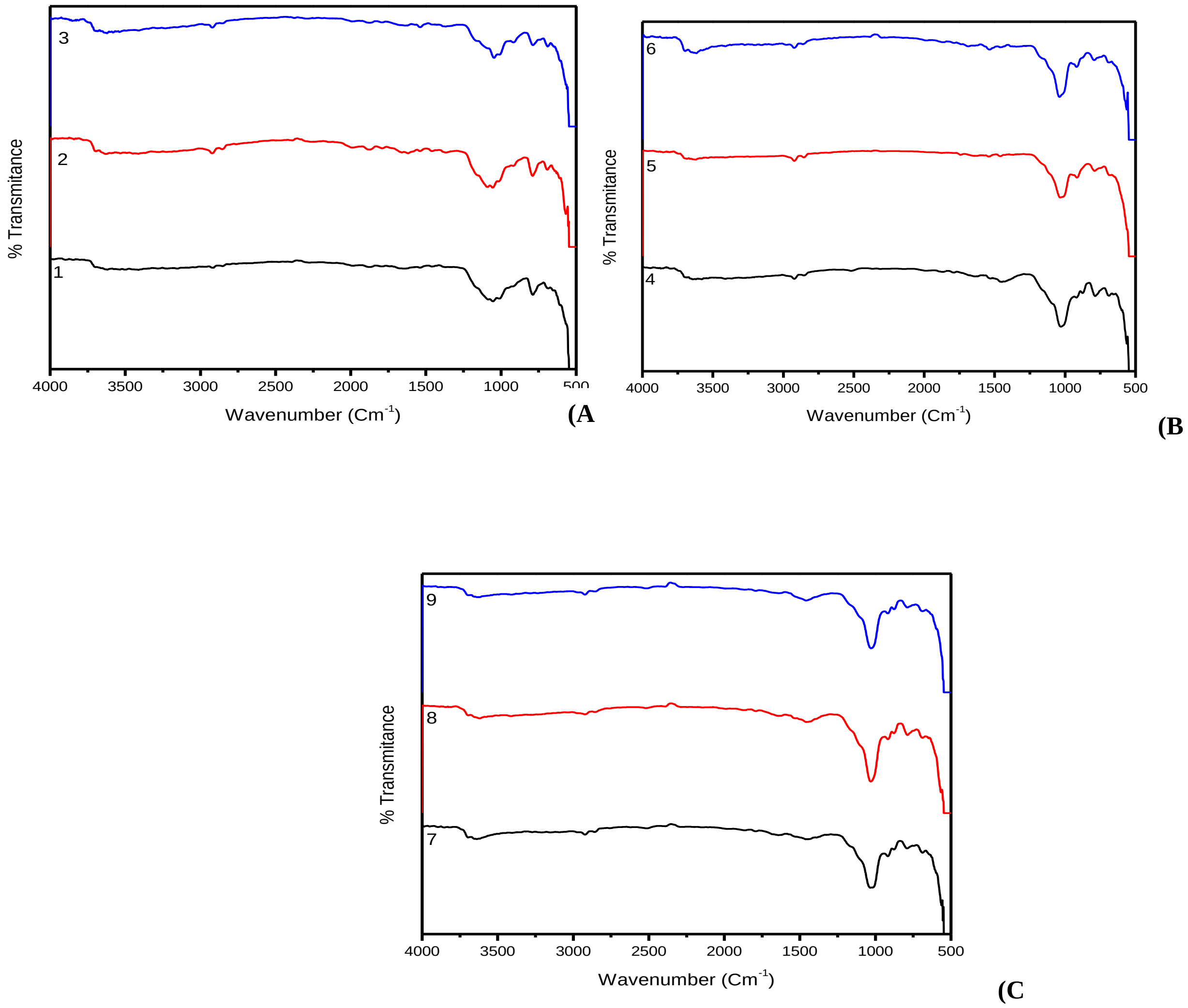


Figure 7: FTIR spectra of samples: (A) Upstream, (B) Midway and (C) Downstream

Fig 7A shows a band between 1300 cm^{-1}and 1000 cm^{-1}, which corresponds to the stretching vibrations of ester groups (C-O). The same trend of results was also observed in Figs 7B and C, respectively. The slight twin peaks seen between 2918.29 cm^{-1} and 3000 cm^{-1}, can be due to the asymmetric and symmetric stretch of Alkanes H-C-H. A band between 1500 cm^{-1} and 1450 cm^{-1} seen in Fig 7C can be assigned to the asymmetric stretch of Aromatic Rings C-C=C group, however, this band was not seen in Figs 7A and B. A wide band, which can be seen between 3500 cm^{-1} and 3000 cm^{-1} in all the figures, is corresponding to the O-H stretch vibration, often found in organic compounds. A band between 1000 cm^{-1} and 650 cm^{-1} can be ascribed to the strong alkenes =C-H group. A band between 690 cm^{-1} and 515 cm^{-1} is corresponding to the medium stretching of the alkyl halides C-Br group. These results are similar to those found in a study done by Reig et al. [38]. These groups have a high binding potential. The bands at 788.40 cm^{-1}, 690 cm^{-1},688.33 cm^{-1}, 629.56 cm^{-1}, and 629.25 cm^{-1} were found in all the sediment samples, and this is due to the inorganic materials such as the clay and quartz minerals [39]. Hence, XRF results in this study show the dominance of SiO_2, CaO, MgO, Fe_2O_3, MnO and Cr_2O_3. This demonstrates that these inorganic metals were retained in the sediment, and the sequential leaching experiment shows that some of these metals, such as Ca and Mg, were mostly bound to the exchangeable fractions and this clearly indicate that their mobility will be high and thus they are prone to increase the hardness of the water, hence, the relatively high pH of the water samples. However, metals such as total Cr and Fe that are being associated with the exchangeable fractions are prone to increase the toxicity in the aquatic environment even at low concentrations, and their mobility will depend on the environmental changes over time. On the other hand, the results obtained are consistent with the presence of total organic carbon in the sediment samples. According to a previous study [40] the organic peaks corresponding to organic compounds are those of aliphatic (3000 cm^{-1} – 2800 cm^{-1}), aromatic and C=O groups (in the region of 1700 cm^{-1} – 1550 cm^{-1}), which are more pronounced in sample 9 than any other sample. According to Galle et al. [41], band characteristics of the groups C=O, -OH and –NH, as well as aliphatic stretches in the 3500 cm^{-1} – 2800 cm^{-1} region are reported to be the most prominent features of microbial spectra, which have a significant correlation with the organic carbon content implicated in the biofilm growth. This clearly supports our findings; demonstrating the retention of metals in the exchangeable fraction mostly made up of organic matters. Furthermore the presence of microorganisms is likely to result in the mobilization of the metals attached to that layer after degradation of the organic matter.

4.6 Water quality

Tables 3a and 3b represent the results of the physico-chemical parameters and heavy metals measured in the surface water of the Mooi River and connected streams, respectively. The results show that there was a significant variation ($P < 0.05$) among the sampling sites. It is apparent from Tables 3a and 3b that most of the parameters were within the recommended limit of the SA drinking and irrigation water guidelines. However; for parameters like the dissolved oxygen, redox potential and alkalinity, there is no specific limit set by the South African water guidelines [42]. The values of surface water temperature ranged from 10.10°C to 19.50°C; these relatively low values can be attributed to the cold weather during a winter season. The mean and standard deviation for recorded concentrations of dissolved oxygen (DO) were 8.24 mg/L and 1.15 mg/L, respectively; with the highest concentrations measured at sampling point 5. The high value of DO at this point can be attributed to the low temperature (12℃). According to Nezlin et al. [43] the concentration of DO is an important water quality parameter, because low DO concentrations can be physiologically stressful or lethal to aquatic organisms. The values of alkalinity varied between 160 mg/L and 312 mg/L, with a mean of 276.00 mg/L and a standard deviation of 46.78 mg/L. The highest value of alkalinity recorded at sampling point 2 can be attributed to the underlying rock constituted mainly of dolomites. High alkalinity can result in physiological stress on aquatic organisms and that may lead to loss of biodiversity [6]. The values of pH ranged from 7.34 to 8.64, with a mean value of 8.18 and a standard deviation of 0.52. It is apparent from Table 3a that all the pH values were above neutral; these values were within the recommended limit of the SA drinking water guideline, however, at some of the sampling sites these values were above the SA irrigation water guideline. According to the South African irrigation water guideline [44], high values of pH can cause foliar damage, which can result in the decrease of yield or damage to fruit or marketable products. The high values of pH measured reflect the relatively high concentrations of Ca and Mg, as high percentages of Ca and Mg were associated with the exchangeable fraction in the sediment samples. The value of EC varied between 0.70 mS/cm and 1.52 mS/cm, with a mean value of 0.83 mS/cm and a standard deviation of 0.17 mS/cm. The highest value of EC was recorded at sampling point 1 and such high value may result from contamination by the gold mine discharge, as sampling point 1 is situated within the mine canal. This is substantiated by elevated concentrations of Ca, Mg, SO_4^{2-} and Cl^- at this point. The value of Eh ranged from 138.00 mV to 205.57 mV, with a mean of 158.30 mV and a standard deviation of 25.68 mV. The highest value of Eh was recorded at sampling point

3 and this correlates with the lowest value of pH (7.24) recorded at this site. Therefore; the low value of Eh measured in the rest of the sampling points can be attributed to the relatively high values of pH that were above neutral.

Table 3a: Physico-chemical parameters and major anions concentrations in water samples

		pH	**T**	**Eh**	**EC**	**DO**	**Alkalinity**	**SO_4^{2-}**	**Cl^-**
Sampling sites			**°C**	**mV**	**mS/cm**	**mg/L**	**mg/LCaCO3**	**mg/L**	**mg/L**
1		8.50	18.30	135.57	1.21	8.80	160.00	420.00	76.67
2		7.34	19.50	196.57	0.79	7.00	312.00	120.00	40.00
3		7.24	16.30	205.57	0.82	5.90	296.00	120.00	50.00
4		8.55	12.00	142.00	0.71	9.10	304.00	110.00	36.67
5		8.45	12.00	144.00	0.74	9.20	296.00	90.00	36.67
6		8.64	10.80	138.00	0.70	9.00	268.00	110.00	36.67
7		8.45	10.10	147.00	1.00	7.60	272.00	195.00	53.33
8		8.3	11.70	153.00	0.74	8.60	268.00	110.00	43.33
9		8.12	12.00	163.00	0.84	9.00	308.00	110.00	63.33
Average ± SD		8.18 ± 0.52	13.63 ± 3.46	158.30 ±25.68	0.83 ± 0.17	8.24 ± 1.15	276.00 ± 46.78	153.89 ± 104.04	48.52±13.96
SA-DWG [a]	Class I	5.00 - 9.50	-	-	< 1.50	-	-	< 400.00	< 200.00
	Class II	4.00 - 10.00	-	-	1.50 - 3.70	-	-	400.00 -600.00	200.00 – 600.00
SA-IWG [b]		6.50 - 8.40	-	-	-	-	-	-	-

Note: SD, Standard deviation; a (South African- drinking water guideline, 2006); b (South African- irrigation water guideline, 1999); Class I (recommended operational limit); Class II (max.allowable for limited duration)

The concentration of nitrate ranged from 0.00 mg/L to 11.20 mg/L, with a mean value of 2.43 mg/L and a standard deviation of 3.46 mg/L. The highest concentration of nitrate was measured at sampling point 4 (11.20 mg/L). However, a decreasing trend was observed when moving downstream of the study area. The concentrations of nitrate were observed to be within the class II limit of the SA drinking water guideline. However, the nitrate concentration at point 4 was above the class I limit of the drinking water guideline and the source of pollution at this point could be the effluent from the agricultural land surrounding the area; agricultural activities have been reported to contribute to more pollution of NH_4 and NO_3^- around the world [45]. In addition, high concentrations of nitrate at this point could also be attributed to contamination from the municipal and domestic sewage in the proximity of the Boskop Dam. The concentration of chloride ranged from 36.67 mg/L to 76.67 mg/L, with a mean and standard deviation of 48.52 mg/L and 13.96 mg/L, respectively. The highest concentration of chloride (76.67 mg/L) was observed at sample point 1 (Table 3a), and the source of pollution could be the effluent from the mines, since this point is situated within a mine canal. However, the level of chloride was observed to be within the recommended limit of the SA drinking and irrigation water guidelines. The value of cyanide ranged from 1.00 mg/L to 3.00 mg/L, with a mean and standard deviation of 1.56 mg/L and 0.73 mg/L, respectively. The relatively low value of SD indicates that there was no significant variation between the sampling points.

High concentrations of cyanide (Table 3b) were recorded at most of the sampling points and this could be ascribed to the contamination from the gold mine effluent, as it is known that some of the mines use cyanide for the extraction of gold from ore [46]. The concentration of CN^- was observed to be above the recommended limit of the SA drinking water guideline. The level of sulphate varied between 110 mg/L and 420 mg/L, with a mean value of 153.89 mg/L. The high value of the standard deviation (104.04 mg/L) clearly shows that there was a significant variation between the sampling sites. The highest concentration was measured at sampling point 1 (420 mg/L), upstream of the study area. This elevated concentration of sulphate can be attributed to the effluent from the gold mines in the vicinity of Carletonville, since this point is located along the mine canal joining the Mooi River. A decreasing trend was observed when moving downstream of the study area. This clearly shows that effluents from the respective mines contribute to the pollution while the sediments may be naturally involved in the mitigation of pollutants dispersion.

The concentration of total Cr ranged from 0.08 mg/L to 0.18 mg/L, with a mean and standard deviation of 0.16 mg/L and 0.03 mg/L, respectively. The low value of SD clearly indicates that there was no significant variation between the sampling sites. The highest value of total Cr was recorded at sampling point 4 (0.19 mg/L). The concentrations of total Cr were observed to be within the recommended class II limit of the SA drinking and irrigation water guidelines. However, all the sampling sites except point 2 showed concentrations above class II of the drinking water guideline, therefore degrading water quality. Total Cr is one of the toxic elements in the aquatic environment, for example Cr (VI) can cause cancer to human beings if a high concentration is ingested in drinking water [47]. The source of total Cr can be effluents from the respective gold mines in the vicinity of the study area. The concentration of Fe ranged from 0 mg/L to 0.19 mg/L, with the mean of 0.51 mg/L and standard deviation of 0.07 mg/L. The elevated concentrations measured at sampling points 1 and 2 can be attributed to contamination by effluents from the gold mines (Fig. 1).

Table 3b: Major anions and heavy metals concentration in the water samples

	$NO3^-$	**CN^-**	**Fe**	**Ca**	**Mg**	**Mn**	**Cr**
Sampling sites	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1	0.00	1.00	0.15	81.79	53.93	0.09	0.15
2	0.00	2.00	0.19	76.23	47.75	0.02	0.08
3	1.50	1.00	0.00	65.87	39.88	0.01	0.15
4	11.20	1.00	0.00	54.93	39.31	0.00	0.19

5		2.20	3.00	0.00	49.36	43.33	0.00	0.17
6		0.00	1.00	0.00	59.86	48.04	0.00	0.16
7		2.20	1.00	0.09	81.73	64.60	0.00	0.18
8		2.10	2.00	0.08	43.49	45.40	0.00	0.18
9		2.70	2.00	0.00	42.94	44.86	0.00	0.17
Average ± SD		2.43 ± 3.46	1.56 ± 0.73	0.51 ± 0.07	61.80±15.49	47.46 ± 7.81	0.01 ± 0.03	0.16 ±0.03
SA-DWG[a]	Class I	< 10.00	< 0.05	< 0.20	< 150.00	< 70.00	< 0.10	< 0.10
	Class II	10.00 – 20.00	0.05 - 0.07	0.20 - 2.00	150.00 – 300.00	70.00 – 100.00	0.10 - 1.00	0.10 - 0.50
SA-IWG[b]		-	-	5.00 – 20.00	-	-	0.02 - 10.0	0.10 - 1.00

Note: SD, Standard deviation; a (South African- drinking water guideline, 2006); b (South African- irrigation water guideline, 1999); Class I (recommended operational limit); Class II (max.allowable for limited duration)

A decreasing trend of Fe concentration was observed when moving downstream of the study area. This may be partly due to the retention on the sediments across the river. Nevertheless, high concentrations of Fe were recorded at sampling point 7 (0.09 mg/L) and point 8 (0.08 mg/L). However, the source of pollution at these points (Potchefstroom area) could not be ascertained. The concentrations of Fe were observed to be within the recommended limit of the SA drinking and irrigation water guidelines. The mean concentration of Mn was 0.01 mg/L, with the highest concentration measured at sampling point 1 (0.09 mg/L). The elevated concentration of Mn could be attributed to the effluent from gold mines in the vicinity of the Carletonville area. However, a decreasing trend was observed when moving downstream of the study area and this may be partly due to the retention on the sediments. The concentration of Ca and Mg ranged from 42.94 mg/L to 81.79 mg/L and 39.31 mg/L to 64.60 mg/L, respectively. These concentrations of Ca and Mg can be ascribed to the nature of the underlying rock constituted mostly of dolomites and they are likely to increase the hardness of the water, hence a relatively high pH value was observed. However, the Ca and Mg concentrations were within the required limit of the SA drinking water guideline.

5 Conclusion

The sediments from the Mooi River and its connected streams are dominated by oxide minerals and contain mainly Fe, Cr, Mg, Mn and Ca. According to the modified BCR sequential extraction results, it is sound to say that the bioavailability tendency of most of the elements except Ca and Mn was on the lower side, as they were predominantly bound to the residual fraction; implying that the major concern may be the continuous increase of water hardness due to high levels of dissolved Ca. Because elements such as Fe, Cr, and Mg are strongly bound to the residual fraction, this indicates that they are less likely to cause pollution of water. However, the portion of Fe and Cr associated with the exchangeable and reducible fractions at some sampling points may be progressively released at a speed that will vary depending on the environmental conditions and could therefore degrade the quality of water. The distribution of metals in the various fractions of the sediments informed the attachment affinity further investigated by FTIR analysis. The FTIR results revealed the presence of binding groups on the organic compounds, which could have been involved in the retention of metals in the sediments. The water quality was found unfit for drinking purposes due to high concentrations of SO_4^{2-}, CN^-, NO_3^- and total Cr above the recommended class I limit at some of the sampling points. The water was observed to be fit for irrigation purposes. It is however noticeable that the interaction of the observed pollutants with the sediments may have contributed to the mitigation of pollution, decreasing metal concentrations across the river.

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Chapter 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

It was concluded in this research that the anthropogenic activities, especially gold mining activities situated in the vicinity of Wonderfonteinspruit are the main sources of inorganic contaminants found in the Mooi River and its tributary, which is the Vaal River downstream of the city of Potchefstroom. However, gold mining activities in Orkney and its vicinity are also responsible for the contamination recorded in the Vaal River and its connected streams. This was substantiated by elevated concentrations of elements such as, Cd, Pb, Fe, Mn, Cr, U, SO_4^{2-}, Cl^- and CN^- recorded in the sampling sites situated in the proximity of the mining activities. However, the elevated concentrations of nitrates recorded in some of the sampling sites indicated that the runoff from agricultural land and domestic and municipal sewage were also responsible for pollution in surface water. The study area was subdivided into three subareas: upstream of Potchefstroom, Potchefstroom area and downstream of Potchefstroom (Orkney). It was found that the surface water in Potchefstroom was less polluted compared to the rest; this was expected since the mining activities are less evident in this area or this could be due to the dilution effect by the less polluted water of the Mooi River. However, the studied water samples of all the subareas showed concentration levels above the recommended limit of the SA/WHO water guideline for drinking and irrigation purposes.

Higher concentrations of pollution were mainly observed in the wet season when compared to the dry season. A significant variation observed could be due to the reason that the surface water received more pollution during the washouts by heavy rainfalls in the wet season. The speciation data results also showed the variation between the two seasons. It was observed that element such as Fe, Cd, As and U were mostly associated with the carbonate or hydroxide species, which is likely to decrease its toxicity in water. While elements such as Ca and Mg were mostly present as free hydrated species and thus likely to decrease the quality of the water.

The sequential extraction by BCR method on sediment samples revealed that high percentages of elements such as the Fe, Cr and Mg were mostly associated with the residual fraction. On the other hand, the high Ca and Mn concentrations were mostly associated with the exchangeable fraction. Therefore, elements associated with the residual fraction showed that they were mostly bound to the sediment and they are less prone to cause toxicity in water. However, the elements associated with the exchangeable fraction had potentially elevated bioavailability, and in the case of Mn, it was likely to enhance the level of toxicity in the water system. The XRD and XRF results revealed that the sediment samples were constituted predominantly of oxide minerals and quartz, respectively. The organic carbon was observed in the sediment at varying concentrations, and the associated binding groups identified by FTIR were likely to contribute to the retention of metals in the organic–bound fraction of the sediments. Therefore, the sediments of the study area will have less impact on the pollution of the surface water, since most of the metals will be retained on the sediment.

6.2 Recommendations

This research shows that the surface water in the vicinity of Potchefstroom is not suitable for drinking and other essential purposes. Anthropogenic activities, especially mining activities will continue to reduce the quality of water unless some serious actions are taken by affected stakeholders, i.e. water managers. It is important to continue to monitor the surface water, especially at those sites that had elevated concentrations of inorganic elements. However, it will be expensive and time consuming to monitor a large number of sites as it was conducted in this dissertation. Therefore, it is recommended that only a few sites are selected, with more attention paid to those polluted areas.

It is recommended that various remediation measures are introduced in order to remediate and mitigate the pollution caused by anthropogenic sources, as this can help to increase the quality of water in the vicinity of Potchefstroom. The water managers of the affected areas need to work with the mining sector, farmers and local communities in order to improve the state of the environment. It is possible to reduce the contamination in surface water, however, this can only be successful if all the parties can work together.

Appendix A

Pictures of sampling site

Figure A:1: Sample point 1 and 2 (Klerskraal Dam)

Figure A:2: Sample point 3 (Driefontein mine canal)

Figure A:3: Sample point 4 (Downstream of mine canal)

Figure A:4:Sampling point 5 (Mooi River)

Figure A:5: Sampling point 6 (Turffontein upper eye)

Figure A:6: Sampling point 7 (Turffontein lower eye)

Figure A:7: Sample point 8 (Gerhardminedorom eye)

Figure A:8: Sampling point 9 – 17 (Boskop Dam)

Figure A:9: Sample point 18 (origin of Boskop canal next to Dam wall)

Figure A:10: Sample point 19 (Upstream of Potchefstroom Dam)

Figure A:11: Sample point 20 (Boskop Dam canal at Potchefstroom)

Figure A:12: Sample 21 – 25 (Potchefstroom Dam)

Figure A:13: Sample point 26 (Potchefstroom Dan canal)

Figure A:14: Sample point 27 (Origin of Mooi River after Potchefstroom Dam)

Figure A:15: Sample point 28 (Mooi River)

Figure A:16: Sample point 29 (Mooi River meet Ikageng canal)

Figure A:17: Sample 30 (Mooi River)

Figure A:18: Sample point 31 (Mooi River)

Figure A:19: Sample 32 (Mooi River)

Figure A:20: Sample 33 (Ikageng canal)

Figure A:21: Sample 34 (Boskop Dam canal downstream of Potchefstroom)

Figure A:22: Sample point 35 (Boskop Dam canal downstream of Potchefstroom)

Figure A:23: Sample point 36 (Vaal River upstream)

Figure A:24: Sample point 37 (Vaal River at bridge)

Figure A:25: Sample point 38 (Vaal River downstream)

Figure A:26: Sample point 39 (stream at Orkney area)

Figure A:27: Sample point 40 (stream at Orkney)

Figure A:28: Sample point 41 (Mine canal)

Figure A:29: Sample point 42 (Stream)

Figure A:30: Sample point 43 (Downstream of Water retain Dam)

Figure A:31: Sample point 44 (Upstream of Water retention Dam)

Appendix B

Experimental calculations

Total Alkalinity

Total alkalinity = (Volume of H_2SO_4 ×1000)/ (Volume of sample)

Chloride

Total chloride = (V_1 × 1000) / (sample volume)

Where V_1 = volume of titration

Organic carbon

Total organic carbon (%) = 0.003 g × N × 10 Ml × (1-T/S) × 100 / ODW

= 3 (1 – T/S) / W

Where: N = Normality of $K_2Cr_2O_7$ solution

T= volume of $FeSO_4$ used in sample titration

S= volume of $FeSO_4$ used in blank titration

ODW = Oven-dry sample weight (g)