THE EFFECT OF PRE-OZONATION ON THE PHYSICAL CHARACTERISTICS OF RAW WATER AND NATURAL ORGANIC MATTER (NOM) IN RAW WATER FROM DIFFERENT SOUTH AFRICAN WATER RESOURCES

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"Life is not a race, but a journey to be savoured each step of the way"

ABSTRACT

Research in the use of ozone in water treatment conducted by many authors support the idea that the nature and characteristics of natural organic matter (NOM) present in raw water determines the efficiency of ozonation in water purification.

An ozone contact chamber was designed and made to allow pre-ozonation of water to take place. The concentration of ozone in the chamber was determined using the Indigo method. For the duration of one year, water samples were collected from four different sampling sites and analyzed to determine their overall ecological status with regard to several variables such as pH, chlorophyll-*a*, SAC254, turbidity, DOC, algal species composition and sum of NOM. Two dams sites and two riverine sites were chosen, Hartbeespoort Dam (a hyper-eutrophic impoundment), Boskop Dam (a mesotrophic impoundment), Midvaal Water Company at Orkney and Sedibeng Water at Bothaville. The samples were treated in Jar Tests with $FeCl_3$ and the same variables were measured. Pre-ozonation followed by Jar Tests was performed on each sample at twoconcentrations of ozone and the variables were measured to examine the efficiency of ozonation.

In general, the ph was high and stayed the same for all the samples and for all the treatments. DOC was variable and showed no relatiohship to any other variable or to the treatments.

Hartbeespoort Dam was found to be a eutrophic impoundment characterized by high algal bloom of the cyanobacteria *Microcystis* sp.. Turbidity, SAC254, and the sum of NOM were lower than for the riverine sites but higher than for Boskop Dam. The NOM constituted more intermediate molecular weight(IMW)and low molecular weight (LMW) fractions than the riverine sites. Ozone was effective in reducing chlorophyll-*a*, turbidity and SAC254 from Hartbeespoort Dam, but the presence of large numbers of algal cells interferes with its efficiency. Release of cell-bound organics after ozonation can lead to increases instead of decreases in these variables. Jar Test results demonstrate that ozonation improves water quality when compared to conventional treatment although the interference of algal cells can alter results.

Boskop Dam is a mesotrophic impoundment characterised by low productivity, low SAC254, low turbidity and low sum of NOM. However, it has a large portion of the LMW fraction of NOM present. This LMW fraction affects the treatment process as this fraction is not acted upon by ozone. Therefore it was found that ozonation did not improve the quality of the water when compared to conventional treatment.

The two riverine sites, Midvaal and Sedibeng were similar to each other. Both sites had high algal productivity with high chlorophyll-*a* values indicative of algal blooms observed at certain times. These blooms consisted either of members of Bacillariophyceae or Chlorophyceae. High turbidity and SAC254 was observed during the rainy season and was related to the high percentage HMW and IMW fractions of NOM present. There was correlation between the turbidity and SAC254 of these sites leading to the assumption that the turbidity of the river is due to the presence of HMW humic fractions of NOM. Ozonation was effective in improving water quality with respect to turbidity, SAC254 and chlorophyll-*a* removal, both on its own and after conventional treatment when combined with a coagulant. However, the species of algae present affects ozonation as members of Bacillariophyceae are not affected by the actions of ozone because of the presence of a silica frustule whereas members of Chlorophyceae are easily removed by ozone.

In general, ozone acts upon the HMW and LMW fractions of NOM causing them to breakdown into smaller fractions. Ozone has no effect on samples that have a high percentage of the LMW fraction of NOM. This LMW fraction is more readily removed by conventional treatment than by ozonation. The presence of large numbers of algal cells as well as the species of cells can negatively affect the treatment process with regard to ozone.

KEYWORD: ozone, Natural organic matter (NOM), algal cells, Jar test, chlorophyll-*a*, SAC254, turbidity,

OPSOMMING

Navorsing, oor die gebruik van osoon in watersuiwering, ondersteun die idee dat eienskappe van natuurlike organiese boustowwe (NOB) teenwoordig in die water, die doeltreffendheid van die osoneringsproses in watersuiwering beïnvloed.

'n Osoon-blootstellingskolom is ontwerp en vervaardig om die pre-osonering van water moontlik te maak. Die konsentrasie osoon teenwoordig in die kolom is bepaal deur middel van die 'Indigo' metode. Watermonsters is oor 'n tydperk van een jaar versamel op vier verskillende monsterpunte, en analises is gedoen om die ekologiese status van die water te kan bepaal. Veranderlikes soos pH, chlorofil-*a*, SAC254, troebelheid, opgeloste organiese koolstof, algsamestelling en die som van NOB is bepaal. Twee dam-monsterpunte (Hartbeespoortdam- 'n hiper-eutrofiese dam en Boskopdam -'n mesoeutrofiese dam) en twee rivier-monsterpunte (Midvaal Water Maatskappy naby Orkney en Sedibeng Water naby Bothaville) is gekies. Die monsters is ook in 'n roertoetsapparaat getoets deur gebruik te maak van $FeCl_3$ as koagulant en bogenoemde veranderlikes is weer bepaal. Die monsters is ook blootgestel aan osoon by twee verskillende konsentrasies en die veranderlikes is weer bepaal.

Oor die algemeen was die pH van die al vier die monsterpunte hoog en geen noemenswaardige verandering is waargeneem na enige van die behandelings nie. Die opgeloste koolstof metings het baie gewissel en daar was geen ooreenkoms met enige van die ander veranderlikes nie.

Daar is aangetoon dat Hartbeespoortdam 'n hiper-eutrofiese dam is, gekenmerk deur groot opbloeie van die sianobakterium *Microcystis sp.*. Die troebelheid, SAC254 en die som van die NOB was laer as die van die rivier-monsterpunte maar hoër as die van Boskopdam. Die NOB van Hartbeespoortdam het uit meer intermediêre molekulêre massa (IMM) en lae molekulêre massa (LMM) fraksies bestaan as dit wat in die rivier-monstepunte is. Osoon het veranderlikes soos chlorofil-*a*, troebelheid en SAC254 suksesvol verlaag, maar die teenwoordigheid van 'n groot aantal algselle het die effektiwiteit van die osoon beïnvloed. Die vrystelling van organiese materiaal vanuit selle na osonering kan lei tot die verhoging van in die veranderlikes in plaas van 'n verlaging daarvan. Die roertoets het aangetoon dat, in teenstelling met gewone behandeling, behandeling met osoon die waterkwaliteit kan verbeter ten spyte van die feit dat algselle die resultaat kan beïnvloed.

Boskopdam is 'n mesotrofiese dam wat gekenmerk word deur lae produktiwiteit, lae SAC254, lae

troebelheid en 'n lae som van NOB. Dit verskil van die ander monsterpunte omdat daar hoër LMM fraksies van die NOB teenwoordig is. Hierdie LMM fraksies beïnvloed die suiweringsproses, omdat osoon nie op hierdie fraksie kan inwerk nie. Dus, in vergelyking met die gewone suiweringsproses, kon osoon nie bydra tot die verbetering van die waterkwaliteit nie.

Die twee rivier-monsterpunte (Midvaal en Sedibeng), het vergelykbare resultate aangetoon. Albei monsterpunte het met hoë chlorofil-*a* waardes,'n hoë produktiwiteit getoon, wat beduidend is van die algopbloeie wat gedurende sekere tye van die jaar waargeneem is. Hierdie opbloeie bestaan uit die alge behorende tot die klasse Bacillariophyceae of Chlorophyceae. Hoë troebelheid en SAC254 is ook gedurende die reënseisoen waargeneem en hierdie veranderlikes toon 'n verwantskap met die hoë persentasie hoë molekulêre massa (HMM) en IMM fraksies van die NOB wat in die water teenwoordig was. Goeie korrelasie is ook gevind tussen troebelheid en SAC254 by hierdie monsterpunte, wat lei tot die aaname dat die troebelheid van die rivier deur die HMM humus fraksie van die NOB veroorsaak word. Die gebruik van osoon as behandeling was effktief en het tot die verbetering van waterkwaliteit gelei. Dit het 'n verlaging van chlorofil-*a*, troebelheid en SAC254, in beide die osoonbehandelings, asook in samewerking met die gewone koagulantproses veroorsaak. Die algsamestelling in die water het egter 'n groot invloed op die osoneringsproses gehad, aangesien osonering Chlorophyceae maklik verwyder het, maar geen invloed op Bacillariophyceae gehad het nie, vanweë hulle harde silika selwande.

In die algemeen het die toediening van osoon gelei tot die afbraak van die HMM en IMM fraksies van die NOB en dit omgeskakel na LMM fraksies. Osonering het geen invloed op monsters wat 'n hoë persentasie van die LMM fraksie van NOB bevat, gehad nie. Hierdie LMM fraksie van NOB word meer geredelik deur die konvensionele suiweringsmetodes as deur osonering verwyder. Die teenwoordigheid van groot getalle algselle, sowel as die spesifieke algsoort kan die doeltreffendheid van die osoonbehandeling beïnvloed.

Sleutelwoorde: osoon, Natuurlike Organiese boustowwe (NOB), algselle, Roer toets, klorophyll-a, SAC254, troebelheid

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List of Abbreviations

AOP's	Advanced Oxidation Processes
BK	Boskop Dam
DBP	Disinfection by-products
DBPF	Disinfection by-product formation potential
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
HB	Hartbeespoort Dam
HMW	High molecular weigh fraction of NOM
HPSEC	High performance size exclusion chromatography
IMW	Intermediate molecular weight fraction of NOM
LMW	Low molecular weight fraction of NOM
MIB	Methylisoborneol
MV	Midvaal Water Company at Orkney
NOM	Natural Organic Matter
PCA	Principal Component Analysis
PSS	Polystyrene sulfonates standards
SAC254	Spectral Absorbance coefficient at 254 nm
SB	Sedibeng Water at Bothaville
THM	Tri-halo methane
THMFP	Tri-halo methane formation potential

LIST OF FIGURES

Figure 2.1: Schematic representation of how ozone is formed from oxygen in an electrical field WEDECO information brochure 2004). 6

Figure 2.2: Oxidation reactions of compounds (substrate) during ozonation of water (USEPA Guidance Manual 1999). 8

Figure 2.3: Internal structure of the Sterizone ozone generator showing the position of the corona disk (Sterizone 2004). 9

Figure 2.4: Hypothetical structure of Humic acids showing the aromatic groups (Weber 2005 from Stevenson, F.J. 1979. Humus, The encyclopaedia of Soil Science Part 1. Dowden, Hutchinson and Ross, Pennsylvania). 19

Figure 2.5: Hypothetical structure of Fulvic acids showing aromatic and aliphatic structures (Weber 2005 from Buffle J.A.E. (1977): "Les substances humiques et leurs interactions avec les ions mineraux", w: Conference Proceedings de la Commission d'Hydrologie Appliquee de A.G.H.T.M.. l'Universite d'Orsay, 3-10). 18

Figure 2.6: Relationship between humic acids, fulvic acids and humin, based on colour, molecular weight and other variables (Weber 2005 from Stevenson, F.J. 1979. Humus, The encyclopaedia of Soil Science Part 1. Dowden, Hutchinson and Ross, Pennsylvania). 19

Figure 3.1: Sterizone Buddy ozone generator with a capacity to produce 300mg ozone/h. Mass= 3.9kg, Dimension= 109mmX180mmX150mm. 25

Figure 3.2:
a) Photograph of the constructed ozone contact chamber set-up in the laboratory.
b) Schematic representation of ozone contact chamber with dimensions = 1.2mhigh, internal diameter of 6cm and a capacity of 3 litres. 26

Figure 3.3: Photographs showing the effect of increasing ozone concentration on indigo dye. As the concentration of ozone increases in the flasks from left to right, the colour of the indigo decreases. 27

Figure 3.4: Concentration of ozone present in the distilled water after different exposure times and showing the regression line. 29

Figure 4.1: Map showing the location of sampling points along Middle Vaal region between North West and Free State i.e. Boskop Dam, Midvaal Water Company and Sedibeng Water. 34

Figure 4.2: Map showing the location of Hartbeespoort Dam in North West Province, South Africa. 34

Figure 4.3: Variation in the pH ranges of the four sampling sites for a period of one year from October 2005 to September 2006 (n=12).HBP=Hartbeespoort Dam, BK= Boskop Dam, MV=Midvaal and SB=Sedibeng. 41

Figure 4.4: The change in dissolved oxygen of the four sample sites for a period of one year from September 2005 to August 2006.HBP=Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng.42

Figure 4.5: Variation in the turbidity of the four sampling sites for a period of one year from October 2005 to September 2006 (n=12) HBP=Hartbeespoort Dam, BK= Boskop Dam, MV=Midvaal and SB=Sedibeng. 43

Figure 4.6: Variation in the turbidity of the four seasons for a period of one year from October 2005 to September 2006 (n=12)Var1= Spring, Var2=Summer, Var3=Autumn and Var4=Winter. 44

Figure 4.7: The change in turbidity of the four sample sites for a period of one year from October 2005 to September 2006. HBP= Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng. 44

Figure 4.8: Variation in the SAC254 of the four sampling sites for a period of one year from October 2005 to September 2006 (n=12) HBP=Hartbeespoort Dam, BK= Boskop Dam, MV=Midvaal and SB=Sedibeng. 46

Figure 4.9: Variation in the SAC254 of the four seasons for a period of one year from October 2005 to September 2006 (n=12) Var1= spring, Var2=Summer, Var3=Autumn and Var4=Winter 46

Figure 4.10: The change in SAC254 of the four sample sites for a period of one year from October 2005 to September 2006. HBP=Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng. 47

Figure 4.11: Variation in the Chlorophyll-a of the four sampling sites for duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort Dam, BK=Boskop Dam, MV=Midvaal and SB=Sedibeng. 50

Figure 4.12: Variation in the Chlorophyll-a concentration of the four seasons for the duration of one year from October 2005 to September 2006 (n=12) Var1=Spring, Var2=Summer, Var3=Autumn and Var3=Winter.
50

Figure 4.13: The change in chlorophyll-a of the two dam sites for a period of one year from October 2005 to September 2006. MV=Midvaal, SB=Sedibeng. 51

Figure 4.14: PCC ordination biplot showing the algal species composition for Hartbeespoort Dam, Midvaal and Sedibeng for the duration of one year from October 2005 to September 2006. The Eigenvalues for the PCC are given above. Explanation is given in 4.5.6HBP=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng. 52

Figure 4.15: Variation in the DOC of the four sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort Dam, BK=Boskop Dam, MV=Midvaal and SB=Sedibeng. 56

Figure 4.16: Variation in the DOC of the four seasons for the duration of one year from October 2005 to September 2006 (n=12) Var1=Spring, Var2=Summer, Var3=Autumn and Var4=Winter. 56

Figure 4.17: Typical chromatograms of humic fractions of lake water (S3), artificially recharged groundwater (A6), groundwater (G1), and drinking water originating from surface water (S3) (Nissinen et al. 2001). 57

Figure 4.18: Variation in the Sum of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng. 59

Figure 4.19: Percentage composition of the %NOM for Hartbeespoort dam for a period of one year from October 2005 to September 2006. 60

Figure 4.20: Percentage composition of the %NOM for Boskop dam for a period of one year from October 2005 to September 2006. 60

Figure 4.21: Percentage composition of the %NOM Midvaal dam for a period of one year from October 2005 to September 2006. 61

Figure 4.22: Percentage composition of the %NOM for Sedibeng for a period of one year from October 2005 to September 2006. 61

Figure 4.23: Variation in the percentage HMW fraction of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng. 62

Figure 4.24: Variation in the percentage IMW fraction of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng. 63

Figure 4.25: Variation in the percentage LMW fraction of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng. 64

Figure 4.26: Sum of NOM of the four sampling sites for duration of one year from October 2005 to September 2006. HBP=Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng. 65

Figure 4.27: PCA ordination biplot showing the 4 sampling sites and the variables that were measured for the four sampling sites for the duration of one year from October 2005 to September 2006. HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng. 69

Figure 4.28: PCA ordination biplot showing the environmental variables measured at Boskop Dam for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation. 70

Figure 4.29: PCA ordination biplot showing the environmental variables measured at Hartbeespoort Dam for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation. 71

Figure 4.30: PCA ordination biplot showing the environmental variables measured at Midvaal for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation. 72

Figure 4.31: PCA ordination biplot showing the environmental variables measured at Sedibeng for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation. 73

Figure 4.32: PCA ordination biplot showing the environmental variables measured at Midvaal and Sedibeng for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation. 74

Figure 5.1: Jar Test Apparatus that was used in this study. It consists of 6 beakers, with paddles and speed gage. 76

Figure 5.2: Schematic flow diagram of experimental procedure that was followed every month for the raw water received from the different sampling sites. Twenty liters of water was sampled and this is called Raw water. Six liters of raw water was used in the Jar Test. A further six liters each were exposed to the two ozonation treatments and then used for Jar Test. 77

Figure 5.3: The change in turbidity of the raw water of Hartbeespoort Dam with ozonation. The duration of the study was from October 2005 to September 2006.TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 82

Figure 5.4: The change in percentage turbidity removal for Midvaal, showing the effect of ozonation on raw water for the duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 83

Figure 5.5: The change in Chlorophyll-a concentration of Hartbeespoort Dam showing the effects of ozonation for duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.
85

Figure 5.6: The change in Chlorophyll-a concentration of Sedibeng showing the effects of ozonation for the duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.
86

Figure 5.7: Graph of change in SAC254 for Hartbeespoort Dam after ozonation for duration of one year from October 2005 to August 2006. TR1=0.5mg/l ozone, TR2=>0.5mg/l ozone. 87

Figure 5.8: The changes observed in the Sum of NOM of Hartbeespoort Dam after ozonation for the duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 90

Figure 5.9: The changes observed in the Sum of NOM of Boskop Dam after ozonation for the duration of one year from October 2005 to September 2006. 90

Figure 5.10: The changes observed in the Sum of NOM of Midvaal after ozonation for the duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 91

Figure 5.11: The changes observed in the Sum of NOM of Sedibeng after ozonation for the duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 91

Figure 5.12: The change in the %HMW fraction of NOM for Hartbeespoort Dam for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 94

Figure 5.13: The change in the %HMW fraction of NOM for Boskop Dam for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 94

Figure 5.14: The change in the %HMW fraction of NOM for Midvaal for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 95

Figure 5.15: The change in the %HMW fraction of NOM for Sedibeng for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 95

Figure 5.16: The change in the %IMW fraction of NOM for Hartbeespoort Dam for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 96

Figure 5.17: The change in the %IMW fraction of NOM for Boskop Dam for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 96

Figure 5.18: The change in the %IMW fraction of NOM for Midvaal for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 97

Figure 5.19: The change in the %IMW fraction of NOM for Sedibeng for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 97

Figure 5.20: The change in the %LMW fraction of NOM for Hartbeespoort Dam for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 98

Figure 5.21: The change in the %LMW fraction of NOM for Boskop Dam for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 98

Figure 5.22: The change in the %LMW fraction of NOM for Midvaal for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 99

Figure 5.23: The change in the %LMW fraction of NOM for Sedibeng for duration of one year from October 2005 and September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. 99

LIST OF TABLES

Table 2.1: The classification of NOM based on the organic compound class that is present and the reference sources for that classification (Swietlik et al. 2003). 21

Table 3.1: Composition of Flasks showing amount of ozone-containing water. 27

Table 3.2: Summary of observed concentration of ozone in the contact chamber after contact time of 2, 3, 4 and 5 minutes, respectively. 29

Table 4.1: List of algal species identified from water samples collected at Boskop Dam (BK), Midvaal (MV), Sedibeng (SB), and Hartbeespoort Dam (HBP) from September 2005 to September 2006, and their presence at the different sampling locations. The "Unit" column indicates whether the species was found as cells (cell), filaments (fil), or colonies (col). 53

Table 5.1: The change in pH after ozonation as observed for the four sampling sites from October 2005 to September 2006. Raw=raw water, TR1= 0.5mg/l ozone, TR2=>0.5mg/l ozone. 80

Table 5.2: The efficiency of ozone treatment with regard to percentage removal of SAC254, Turbidity, Chlorophyll-a and DOC of the two dam sites for the duration of the study.TR1= 0.5mg/l Ozone, TR2= >0.5mg/l ozone. HB=Hartbeespoort Dam, BK=Boskop Dam. 102

Table 5.3: The efficiency of ozone treatment on the two riverine sites with regard to percentage removal of SAC254, Turbidity, Chlorophyll-*a* and DOC for the duration of the study.TR1= 0.5mg/l Ozone, TR2= >0.5mg/l ozone. 103

Table 5.4: Changes observed in SAC254, turbidity, chlorophyll-a concentration and DOC after ozonation of the two dam sites Hartbeespoort Dam and Boskop Dam for one year. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. The symbols shown depict the following:
0=no change in the variable
+= Increase in the variable
- = decrease in the variable
X=no readings available 104

Table 5.5: Changes observed in SAC254, turbidity, chlorophyll-a and DOC after ozonation of the two riverine sites Midvaal and Sedibeng for one year. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. The symbols shown depict the following:
0=no change in the variable
+= Increase in the variable
- = decrease in the variable
X=no readings available or value was zero (for chlorophyll-a) 105

Table 5.6: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Hartbeespoort Dam for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l). 111

Table 5.7: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Boskop Dam for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l). 112

Table 5.8: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Midvaal for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l). 113

Table 5.9: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Sedibeng for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l). 114

Table 5.10: Table of largest variation in Chlorophyll-*a* concentration observed during Jar Tests for the four sampling sites for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l).HB=Hartbeespoort Dam, BK=Boskop, MV=Midvaal and SB=Sedibeng.
115

TABLE OF CONTENTS

ABSTRACT		**iii**
OPSOMMING		**v**
ACKNOWLEDGEMENTS		**vii**
LIST OF ABBREVIATIONS		**ix**
LIST OF FIGURES		**x**
LIST OF TABLES		**xvii**
TABLE OF CONTENTS		**xix**
Chapter 1: INTRODUCTION		**1**
Chapter 2: LITERATURE REVIEW		**4**
2.1	**Conventional Water Treatment**	**4**
2.2	**Review on the use of Ozone**	**5**
2.2.1	History of Ozone use in water purification	6
2.2.2	How does Ozone work	7
2.2.3	Ozone generator technology	9
2.2.4	Mass transfer of ozone into water	10
	i) Dome diffusers	11
	ii) Venturi Injectors	11
	iii) Static mixers	11
2.3	**Effect of ozone on water quality parameters**	**12**
2.3.1	Algae control and disinfection	12
2.3.2	Colour removal	13
2.3.3	Removal of taste and odour	13
2.3.4	Effect of ozone on Coagulation/Flocculation	14
2.3.5	Effect of ozone on particle destabilisation	15
2.4	**Natural Organic Matter**	**16**
2.4.1	Background	16

a) Humic acids 18
b) Fulvic acids 18
c) Humin 19
2.4.2 Characterisation of NOM 20
a) Fractionation 20
b) High performance size exclusion Chromatography (HPSEC) 22
2.4.3 Effect of ozone on NOM 22

Chapter 3: DETERMINATION OF OZONE CONCENTRATION 24

3.1 Introduction 24
3.2 Aims 24
3.3 Materials 24
3.4 Method for determination of ozone 26
3.5 Results and discussion 28

Chapter 4: ECOLOGICAL OVERVIEW OF THE SAMPLING SITES 31

4.1 Introduction 31
4.2 Aims 32
4.3 Sampling Sites 33
a) Hartbeespoort Dam 35
b) Middle Vaal Region 35
i) Vaal River at Stilfontein, Midvaal 36
ii)Vaal River at Balkfontein, Sedibeng 36
c) Boskop Dam 37
4.3 Materials and Methods 38
1) pH 38
2) Conductivity 38
3) Turbidity 38
4) Dissolved oxygen 38
5) Chlorophyll-*a* 38

	6) SAC254	39
	7) Dissolved organic carbon (DOC)	39
	8) Determination of Natural Organic Matter (NOM)	39
	9) Algal identification and enumeration	40
4.5	**Results and Discussion**	**40**
4.5.1	pH	40
4.5.2	Conductivity	41
4.5.3	Dissolved oxygen	41
4.5.4	Turbidity	42
4.5.5	SAC254	45
4.5.6	Chlorophyll-*a* and algal species composition	47
4.5.7	DOC	55
4.5.8	Natural Organic Matter	57
	a) High Molecular Weight Fraction (HMW)	62
	b) Intermediate Molecular Weight Fraction (IMW)	63
	c) Low Molecular Weight Fraction (LMW)	64
4.5.9	PCA Ordination Discussion	66
4.6	**Conclusion**	**67**
Chapter 5:	**EFFECT OF OZONE ON SAMPLES AND JAR TEST RESULTS**	**75**
5.1	**Introduction**	**75**
5.2	**Aims**	**76**
5.3	**Outline of experimental procedure**	**77**
5.4	**Methods**	**77**
5.5	**Results**	**78**
5.5.1	Effect of ozone on raw water	79
	a) pH	79
	b) Turbidity	80
	c) Chlorophyll-*a*	83
	d) SAC254	86
	e) DOC	87
	f) Determination of NOM	88

i) High molecular weight fraction (HMW) 92
ii) Intermediate molecular weight fraction (IMW) 92
iii) Low molecular weight fraction (LMW) 93
g) Summary of results for ozonation of raw water 100
5.5.2 Jar Test Results 106
a) Hartbeespoort Dam 106
b) Boskop Dam 107
c) Midvaal 108
d) Sedibeng 108
e) Discussion and conclusion 109

Chapter 6: CONCLUSION **116**

REFERENCES **11**

CHAPTER 1: INTRODUCTION

"*Everyone has the right to have access to sufficient water*".
(Bill of Rights, Constitution of South Africa, Section 27(1) (b)).

All over the world, water is a basic human right and it is the giver of life. Disturbingly though, is the fact that in South Africa, drinking water is a scarce and diminishing resource. Our country is globally considered to be a semi-arid country with a mean annual precipitation of 487 mm per year compared to a world average of 860mm per year. There is also strong seasonal distribution of rainfall resulting in 65% of the country receiving less than 500mm of rain annually and 21% receiving less than 200mm annually (Kidd 1997). Many of our large rivers such as the Orange/Senqu and Limpopo are also shared with other countries. Eleven of the 19 water management areas in the country are presently facing a water deficit where demand exceeds its availability (River Health Programme 2005).

Furthermore, the increase in human demand for water resources will increase in the future for domestic, industrial and agricultural use and this will be in existing urban/industrial areas (Basson 1997). In future, the availability of water promises to set a finite limit upon the size of a population that can be supported at an acceptable standard. Fresh water is therefore set to play a pivotal role in the future socio-economic development in South Africa.

With expanding human population, there is a concurrent increase in activities that leads to a deterioration of water quality. These activities lead to eutrophication, increased salinity, acid mine drainage, the presence of radioactive materials and faecal pollution (Davis and Day 1998). It is therefore becoming increasingly difficult to provide clean water using conventional methods. However, to sustain the demand for clean water in South Africa, no potential source of fresh water should be disregarded because of inadequate purification methods and new methods will have to be investigated.

Conventional treatment plants use coagulation, flocculation, sedimentation, sand filtration and chlorination to produce potable water. However, with the decrease in water quality, these conventional methods have proved inadequate in treating problems such as the presence of iron and manganese, taste and odour problems and the presence of cyanobacterial toxins, and advanced methods have to be used. Advanced treatment processes refer to more sophisticated and often costly processes used for specific purposes. Examples include membrane processes such as reverse osmosis, nanofiltration and ultrafiltration, ultra-violet disinfection, on-site chlorination systems, activated carbon absorption, and the use of ion exchange resins.

Pre-ozonation is effectively used to enhance coagulation and flocculation, oxidise organic substances including iron and manganese, and combat taste and odour problems in drinking water. In South Africa, only two plants use ozone for bulk water treatment, namely Wiggins Water Works in Cato Manor (KwaZulu Natal), and Midvaal in Stilfontein (North West Province).

Ozone is used extensively in Europe and North America as a standard procedure in water purification (Geldenhuys *et al* 2000). According to the United States Environmental Protection Agency, as of April 1989, 264 operating plants in the United States use ozone. Despite the ability of ozone to perform its functions, it is dependant on a number of variables such as:

- the nature and characteristics of Natural Organic Matter (NOM),
- the nature and characteristics of the algae present in the water and
- the pH and alkalinity of the water.

These variables will affect the efficiency and resulting cost of all water purification processes. Due to the high initial cost in setting up an ozone plant, characterisation of these variables is essential to obtain optimal efficiency of the ozone process. Several South African studies have recommended that all of the above variables be measured to ascertain whether ozone can be successfully used to treat a particular water source. These include the following, as quoted by Geldenhuys *et al.* (2000): "Before considering application of ozone for water treatment the potential advantages or disadvantages and the following must be considered: effect of ozone on coagulation and flocculation, effect of ozone on organic matter present, effect of ozonation on concentration of assimilable organic carbon compounds in water. Very little is known about the nature of the organic material in the Vaal Dam. The organic compounds in Vaal Dam ... should be characterized and potential influence on water treatment processes and water quality determined."

Pryor and Freeze(2000) noted that the effect of ozone on trihalomethane formation potential, TOC (total organic carbon) and DOC (dissolved organic carbon) was dependant on the nature and concentration of the NOM and the effect of ozone on the optimum coagulant dose was dependant on the type of coagulant, the water source, and for eutrophic waters, on the cyanobacterial species and concentration.

Other studies have also recommended the measurement of the same variables: Rositano *et al.* (2001) noted that the main parameters that influence the effect of ozonation are the character of the NOM, pH and alkalinity of the raw water. Wildrig *et al.* (1996) concluded that treatment strategies, which employ enhanced coagulation with or without preozonation, are strongly influenced by the chemical nature of the organic matter. Mysore and Amy (1996) showed results that flocculation is enhanced by ozonation but this is dependant on the specific NOM types present.

It is therefore important to determine the nature and characteristics of NOM found in a water sample before and after treatment processes when using ozone or other Advanced Oxidation Processes (AOPs). The objectives of this study was firstly to characterise the NOM present in the samples from specific South African water sources as well as measure the associated physical-chemical properties of those water samples. Secondly, this study will also examine the effect of ozonation on water quality using the Jar Test as test method. It is envisaged that the results obtained will enable water purification plants to make more informed decisions on the implementation of ozone and other AOPs based on nature and characteristic of the NOM and the physical-chemical properties of the water source.

The objectives of this study will be reached by achieving the following aims:

A) To determine the overall ecological state as well as the algal species composition for all sampling sites.

B) To determine the effect of ozone on the physical-chemical characteristics of the sampling sites.

C) To determine the nature and characteristics as well as the effect of ozone on the NOM of the sampling sites.

D) To determine the effect of ozone on the Jar test results for the different sampling sites.

CHAPTER TWO: LITERATURE REVIEW

2.1: CONVENTIONAL WATER TREATMENT

The term: "conventional water treatment", refers to the treatment of surface waters by a series of processes that are aimed at removing suspended and colloidal material from the water, disinfecting it and stabilising the water chemically (Quality of domestic water supplies (2) 2000).

Suspended and colloidal matter present in surface water includes inorganic silt and clay particles, algae, bacteria and other micro-organisms and decaying plant material. The size and charge of the suspended and colloidal matter are very important in determining the type of treatment process that can be used to treat the water. Very coarse particles can be removed by settling whereas finer particles have to be treated chemically to remove them from the water. Colloidal particles are very small (<0.1 μm) and are electrically charged so they do not readily settle out. Therefore, they have to be destabilised or coagulated to neutralise the charge so that they can form larger flocs and settle out (Schutte 2006).

Algae usually produce oxygen during photosynthesis and some species such as cyanobacteria, produce gas vacuoles, which cause them to float and remain in suspension. It is therefore difficult to settle the algae and a good alternative is to use dissolved air flotation (DAF) before coagulation.

Coagulation is the process of adding chemicals to water to collect matter and colloids into clusters that can then be removed later by other processes (Viessman *et al.* 1998). There are two parts to this process. The first part is coagulation, which reduces the net electrical repulsive forces at particle surfaces by the addition of coagulant chemicals such as ferric chloride, lime, aluminium sulphate and polyelectrolytes. The second part is flocculation, which is the agglomeration of the destabilised particles by means of chemical joining and bridging. This is achieved by agitation of the chemically treated water so that very small, suspended particles collide and agglomerate into heavier flocs that then settle out due to gravity.

The flocs are then removed from the water by means of a sedimentation and sand filtration. Sedimentation involves the removal of flocs from suspension by gravity. The flocs collect at the bottom of the sedimentation tanks from where they are removed on a regular basis. The clean water leaves the sedimentation tanks from troughs at the top of the tank. This water then proceeds through to filtration where the water is allowed to filter through a layered bed of granular media, usually a coarse anthracite coal underlain by finer sand (Viessman *et al.* 1998). During this process, the small remaining floc particles are removed by the sand grains and are retained in the bed of sand while clean water flows out through the bottom of the sand bed.

There are two types of sand filters namely:

a) Rapid gravity sand filtration: This normally follows sedimentation as the final 'polishing' step in conventional water treatment, and requires back-washing of the filter at intervals of a few hours.
b) Slow sand filtration: This method has a slow filtration rate and can be employed as a stand-alone treatment process. The filter is cleaned by removal of the top layer of sand at long intervals (weeks).

Many bacteria and viruses still remain in the water after filtration; therefore it is essential to disinfect water to prevent the possibility of spreading pathogens. Disinfection of water entails the addition of chemical agents to the water and allowing specific contact time to enable the disinfectant to be effective in destroying all pathogens. In South Africa, chlorine is the preferred disinfectant and can be added in a number of different forms e.g.: chlorine gas, calcium hypochlorite (HTH), sodium hypochlorite and monochloramine (Quality of domestic water supplies (2) 2000). Other methods of disinfection include boiling water or irradiation with ultra-violet light.

Water can then be stabilised. This refers to the chemical stability of water with respect to its corrosive properties and to form chemical scales in pipes and fixtures. Stabilisation is achieved by the addition of chemical to the water e.g. lime, carbon dioxide, sodium carbonate and sodium hydroxide.

Advanced processes can also be used when specific objectives are required or when conventional treatment processes are not capable of producing potable water. These processes include desalination, reveres osmosis, electrodialysis, activated carbon adsorption, nano- and ultrafiltration and ozone (Quality of domestic water supplies (1) 1998).

2.2: REVIEW ON THE USE OF OZONE

Ozone is a naturally occurring component of fresh air. It can be produced by the ultra-violet rays of the sun reacting with the Earth's upper atmosphere, creating a protective ozone layer, or it can be created artificially with an ozone generator (Sterizone 2004) as seen in Figure 2.1.

Ozone (O_3) is made up of three oxygen molecules and has a molecular weight of 48g/mol (Air-Liquide 2005). It is a colourless gas at room temperature, and has a characteristic pungent odour, readily detectable at concentrations as low as 0.01 to 0.05 parts per million. It is often detected in the atmosphere after electrical storms and around electrical discharges (Lenntech 2006). The odour can be detected by humans at concentrations between 0.02 and 0.05 parts per million or $1/100^{th}$ of the recommended 15 minutes exposure level of 0.3 parts per million.

Ozone is partially soluble in water (about 20 times the solubility of O_2). At 20°C, the solubility of 100% ozone is only 570 mg/L. Although ozone is more soluble than oxygen, chlorine is twenty times more soluble than ozone in water (USEPA Guidance Manual 1999).

Ozone is a powerful oxidizing agent, second only to the hydroxyl free radical, among chemicals typically used in water treatment. Only Fluorine, F_2O and O have higher electronegative oxidation potentials. Ozone has an oxidation potential of 2.07 Volts (Miller *et al* 1978) and is therefore a dangerous material, capable of oxidising many types of organic materials, including human body tissue. Ozone will oxidise all bacteria, endotoxins, mould and yeast spores, organic material and viruses (SEDAB 2004).

At the relatively low concentration of ozone produced by commercial generation equipment (1-3% in air: 2-6% in oxygen), no explosive hazard exists, but mixtures of ozone concentrated to 15-20% or higher in air can be explosive. Ozone is an unstable gas, which decomposes to two molecules of oxygen at normal temperatures (Lenntech 2006). According to the USEPA the half-life of ozone in ambient atmosphere is about 12 hours. In aqueous solutions, ozone is relatively unstable, having a half-life of about 20-30 minutes in distilled water. Factors such as temperature, pH, concentration and solutes present can influence the half-life of ozone.

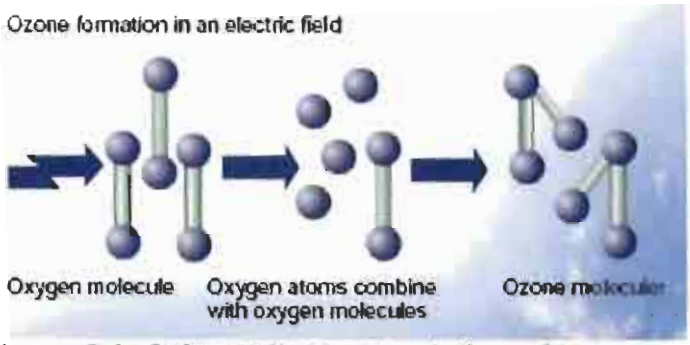


Figure 2.1: Schematic representation of how ozone is formed from oxygen in an electrical field (WEDECO information brochure 2004)

2.2.1: History of Ozone use in Water Purification

In 1893, the first drinking water treatment plant to employ ozone was erected at Oudshoorn in the Netherlands. The Rhine River water was treated with ozone, after settling and filtration. Siemens & Halske then built treatment plants at Wiesbaden (1901) and Paderborn (1902) in Germany, which also employed ozone. In 1906, the Bon Voyage plant was constructed in Nice, France. Since then ozone has been used continuously at the Nice plant and it is referred to as "the birthplace of ozonation in drinking water treatment". By the late 1980s there were more than 1000 drinking water treatment plants throughout the world employing ozone for one or more reason (Miller *et al* 1978).

In 1991, approximately 40 water treatment plants, each serving more than 10000 people in the United States, utilised ozone. According to the USEPA manual, this number has grown significantly and as of April 1998, 264 operating plants in the United States were noted to use ozone.

The Charles-J. des Baileletes Montreal plant is one of the biggest, with an ozone production of 300kg/hour and is one of the largest drinking water treatment plants in the world using ozone.

In South Africa, Midvaal Water Company in Stilfontein has been using ozone since the late 1980s to treat 120ML/day of raw water. The plant has a capacity to produce 30kg/hr of ozone. Pre-ozonation is used at Midvaal in order to reduce problems associated with high concentrations of iron and manganese, as well as reducing taste and odour causing compounds (Lombard *et al* 1992).

Wiggins Waterworks in Cato Manor (KwaZulu Natal) has 3 Trailigaz oxygen–fed generators, each with a capacity of 30kg/hour production of ozone to treat 350 ML/day of raw water- the use of ozone for water treatment on this scale is an African first. Its primary reason for using pre-ozonation is for the oxidation of iron and manganese, reduction of trihalomethane (THM) precursors, and taste and odour compounds like geosmin and 2-methylisoborneol (MIB), (Water, Sewage & Effluent, September 1998).

The new Roodeplaat Water Treatment Plant at Roodeplaat Dam in Pretoria will be able to purify 90ML of water and will employ ozone primarily for the removal of odours from the water (Meyer 2006).

2.2.2: How does Ozone Work

Ozone is an allotrope of oxygen and consists of three oxygen atoms. It is a highly reactive gas formed by electrical discharges in the presence of oxygen. However, the ozone molecule is very unstable and will decay after some time into its original form: O_2 (Lenntech 2006).

The following reactions show the production and the decomposition of ozone:

Production: $3O_2 + \text{energy} \longrightarrow 2O_3$

Decomposition: $2O_3 + 2H^+ + 2e^- \longrightarrow H_2O + O_2 + \text{energy}$ (ΔG = -400kJ/mol)

The thermodynamic free energy of the reaction, ΔG is very high and defines the potential ozone has to act as an oxidant (Glaze 1987).

The rate of decomposition of ozone depends on a number of factors such as temperature, pH, and concentration of organic solutes and inorganic constituents (Miller *et al* 1978).

During decomposition, the single highly reactive oxygen atom combines with any materials present and oxidises them.

However, once ozone diffuses into solution, it decomposes spontaneously into OH radicals, which are the strongest oxidants in water. Therefore, in water, ozone can decompose in two ways, either by direct oxidation to oxygen or by decomposition via hydroxyl radicals (Glaze 1987). These processes are shown in Figure 2.2:

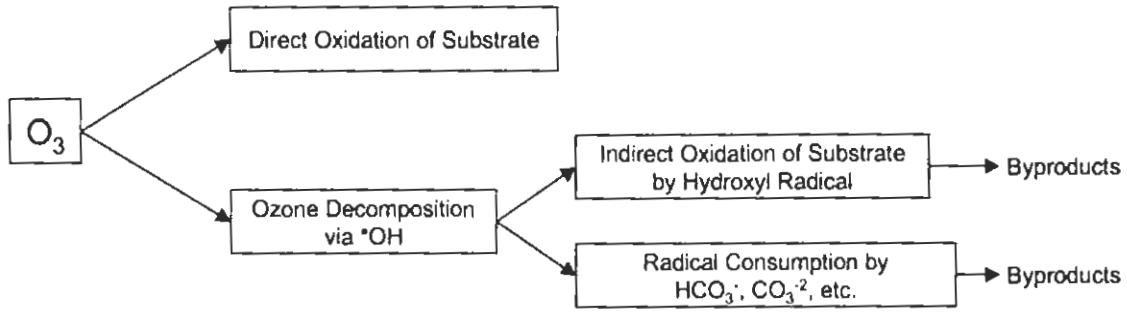


Figure 2.2: Oxidation reactions of compounds (substrate) during ozonation of water (USEPA Guidance Manual 1999)

Ozone is thought to decompose according to the following steps (Miller 1978).

$O_3 + H_20 \rightarrow \quad H0_3^{\bullet} + OH^-$

$HO_3^{\bullet} + OH^- \leftrightarrows 2HO$

$O_3 + HO_2 \rightarrow HO + 2O_2$

$HO + HO_2 \rightarrow \quad H_2O + O_2$

The hydroxyl (OH) radicals that are formed are one of the strongest oxidants in water (von Guten 2003). The hydroxyl radical has an oxidation potential of 2.8V compared to oxidation potential of ozone of 2.07V. This means that the hydroxyl radical may be the species responsible for the very strong anti-microbial action of ozonated water and not the free O_3 itself (Carlsson 2003).

The way that ozone reacts in water is dependant on a number of variables. The process of direct oxidation of ozone occurs rather slowly but the concentration of aqueous ozone is relatively high (USEPA 1999). Conditions of low pH favour the direct oxidation reactions involving ozone and disinfection occurs predominantly through ozone. Conditions that favour the auto-decomposition of ozone include high pH, exposure to UV, addition of hydrogen peroxide, presence of inorganic radicals and high concentrations of hydroxide ions (USEPA 1999). But at the same time, the hydroxyl radical is scavenged by carbonate and bicarbonate ions to form carbonate and bicarbonate radicals. These radicals are of no consequence in organic reactions and therefore, high carbonate concentrations in water reduce the decomposition of ozone (Glaze 1987). The hydroxyl radicals and organic radicals produced by auto-decomposition become chain carriers and enter back into the auto-decomposition reaction to accelerate it (Van Staden 1996).

Therefore, when there are many compounds present in the water, decomposition of ozone into hydroxyl occurs. Unfortunately, this can lead to the formation of disinfectant by-products (DBP) such as hypobromous acid, hypobromite ions, and other bromine products in the presence of bromide ion in the raw water (USEPA 1999). There can be formation of aldehydes, carboxylic acids

and other aliphatic, aromatic and mixed oxidised forms. However, none of these compounds appear to be in toxic concentrations (Glaze 1987). Chiang *et al.* (2002) reported that disinfection-by-product-formation-potential varies with the sources of water samples, but both pre- and post-ozonation processes can reduce some DBP precursors better than conventional treatment and are more reliable at reducing overall disinfection-by-product-formation-potential. The occurrence of DBP is related to pH, alkalinity and nature of organic materials present in the water. Under conditions of low pH, Lee *et al.* (2001) found that disinfection-by-product-formation-potential was reduced when molecular ozone dominated instead of hydroxyl radicals. According to the USEPA 1999, at low pH levels, ozone is effective in precursor destruction, but at some critical pH it can increase the amount of chlorination by-products.

Increased alkalinity has a beneficial effect on trihalomethane formation potential (THMFP) because the alkalinity scavenges the hydroxyl radical, leaving molecular ozone as the sole oxidant. Therefore, neutral pH and moderate levels of alkalinity can reduce THMFP by about 3 to 20 % for ozone dosages ranging from 0.2 to 1.6 mg ozone per mg carbon (USEPA 1999). Carlsson (2003) noted that the examination of ozonated water using the Ames mutagenicity test, shows that ozone is the disinfectant least prone to forming mutagenic by-products.

2.2.3: Ozone Generator Technology

The Department of Astro-Physics at the North-West University, Potchefstroom developed one of the smallest ozone generators available today. The units are manufactured by a local company called Ozone Assembly, which was set up in partnership between the university and an industrial partner, called Sterizone, with shares held by the Mark-Shuttleworth Company HBD (Sterizone 2004).

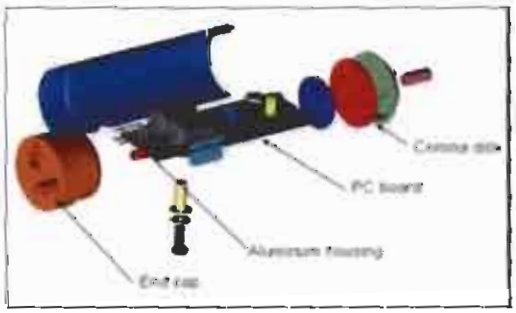


Figure 2.3: Internal structure of the Sterizone ozone generator showing the position of the corona disk (Sterizone 2004)

The Sterizone ozone generator produces ozone by changing the oxygen in the air to ozone using a corona electrical discharge (Figure 2.3). Corona discharge, also known as silent electrical discharge, consists of passing an oxygen-containing gas through two electrodes separated by a dielectric and a discharge gap. High Voltage is applied to the electrodes, causing an electron flowthrough across the discharge gap. The electrons provide the energy to disassociate the oxygen molecule, leading to the formation of ozone (USEPA manual 1999).

The ozone generator houses the corona discharge tubes, solid-state high frequency power supply, run light and a cooling fan. Ozone is produced when the air-feeded gas is exposed to a high voltage low current electrical field. Units producing 2-5 g of ozone per hour are available.

According to Sterizone, a specialised technology is employed to manufacture the Sterizone range of ozonators, which succeeds in stripping the electron from an oxygen molecule, before coulomb collisions proceed. The latter process normally results in unwanted energy losses, which explains the problem of efficiency in most ozone generators. The effect of this is a high ratio of ozone production relative to the energy requirement. A number of patents have been registered for protection purposes. There are many other advantages of the Sterizone generator; it is lightweight, compact form, low power consumption, efficient, environmentally friendly, competitively priced and produced in South Africa. The Sterizone range of generators is produced and sold locally and internationally with applications in spa baths, air conditioners, swimming pools, laundries and dishwashers.

2.2.4: Mass transfer of Ozone into Water

Miller *et al.* (1978) states that because ozone is only slightly soluble in water at the partial pressure at which it is generated and applied, contacting ozone with water involves bringing bubbles of ozone-containing oxygen or air into intimate contact with the water. This mass transfer of ozone from the gaseous bubbles occurs across the gas/liquid interface into the water and depends on a number of factors which are themselves affected by design and operation of the contactor systems. These factors include:

-the miscibility with water and ozone demand of substances to be ozonated,

-concentration of ozone in the gas,

-method and time of contact,

-bubble size,

-pressure and temperature, and

-presence of interfering substances.

In designing an ozone contacting system, there should be maximum solubility of ozone into water with little or no off-gas production (Ozone Disinfection 2006). If bacterial disinfection is required, a

contactor, which causes rapid mass transfer of ozone, should be used (Ozone Tech Brief 1999). If the aim is for oxidation of biorefractory organic materials, the rate of ozone mass transfer is less important than maintaining a specific concentration of ozone for a longer contact period. There are different types of gas/liquid contacting systems. The most common are based on some method for dispersing gas bubbles within a liquid (Miller 1978). Generally there are two ways of accomplishing this:

a) Gas is transferred initially into the liquid as bubbles of the desired size for optimum ozone dispersion into the liquid, called diffuser/sparger type. In this type, ozone is added at the bottom of the contact chamber, through a porous medium (ceramic, Teflon, stainless steel, etc), and the gas bubbles rise through the water, which is passed co-currently, or counter-currently through the chamber. Many installations utilise multiple diffuser chambers, alternating liquid flow with the gas stream. Diffusers can be operated with little energy being added, and are especially useful when large volumes of water are being passed through the plant by gravity flow, and are also flexible in terms of changing flow rates. This method offers the advantages of no additional energy requirements, high ozone transfer rates, process flexibility, operational simplicity, and no moving parts (USEPA 1999).

b) The injector contacting method is commonly used in Europe, Canada and the United States. A massive bubble of gas stream is disintegrated into the fluid called the injector/eductor type. Injectors require added energy, the simplest involving pumping of water to be ozonated rapidly past a small orifice through which the ozone is forced into the liquid under pressure or drawn into the liquid by the vacuum created by the rapid flow of water past the orifice. Injectors are inflexible, however, in terms of changing flow rates (USEPA 1999).

Contact time for pre-ozonation is specified to achieve maximum efficiency of the ozone. Sufficient time should be allowed firstly to maximise the dissolution of ozone into the water, and secondly to allow it to react with any dissolved species.

The main types of commercially available ozone contacting systems are described as follows:

i) **Dome Diffusers**: A bubble diffuser is made from a porous material such as glass or titanium. Ozone is pushed through the small pores in the diffuser, which creates a column of fine ozone bubbles. Many small bubbles produce a larger surface area resulting in increased mass transfer of ozone. This usually takes place in a counter-current direction to the water flow and depends on the height of the water column above the diffuser. Bubble diffusers usually have no moving parts and require no additional energy, but do require cleaning. Ozone transfer efficiencies greater than 90% are common; up to 99% has been obtained using this method (Schoville 2006).

ii) **Venturi injectors**: A Venturi injects the ozone gas in the water via a vacuum. The Venturi creates suction through the hose connecting the generator and the injector, and ozone is drawn

from the generator and mixed with water (Lenntech 2006). This system requires a large side-stream flow of water and is usually associated with a large additional pumping cost. These are particularly useful where the water is highly polluted and large ozone doses are required. The maximum attainable efficiency is limited to approximately 85% and can be applied to relatively shallow reaction chambers. This system is employed to make Sterizone water purification systems in New Zealand (SEDAB 2004).

iii) Static mixers: The static mixer is designed to dissolve gases efficiently in fluids. Both gas and fluid are injected into the static mixer under pressure. A series of baffles converts the kinetic energy into turbulence, which results in improved mixing of the solution (Static mixer 2006). High transfer efficiency can be achieved but the performance is very dependant on the design of the mixer.

2.3: EFFECT OF OZONE ON WATER QUALITY PARAMETERS

Ozonation is used in drinking water treatment to achieve a variety of goals. These include the following:

a) Disinfection and algae control, including destruction of bacteria and viruses.
b) Oxidation of inorganic pollutants such as iron, manganese and sulphide.
c) Oxidation of organic pollutants including taste and odour compounds, phenolic pollutants and some pesticides.
d) Oxidation of organic macropollutants that include colour removal, increasing the biodegradability of organics, reduction of trihalomethane formation potential, and reducing chlorine demand.
e) Improvement of coagulation.

A number of these are of particular importance in water treatment and are discussed below.

2.3.1: Algae Control and disinfection.

Ozone, like other oxidants such as chlorine had a lethal effect on most algae and limits their growth (Ozone Disinfection 2006). Geldenhuys *et al.* (2000) reported that ozonation improved the physical removal of algae by sedimentation and filtration by 17.7 and 17.0 percent respectively, but ozone by itself did not reduce the total chlorophyll values much. They also demonstrated that ozone had the following effect on cell structures of *Monoraphidium* sp. cells: cell wall swelling and increase in elasticity, cytoplasm appears more granular, nuclear membrane becomes swollen and chloroplast grana become swollen and disintegrated. This shows that ozone attacks the membrane system of the algal cells which results in the death of the cells. Pryor *et al.* (2000) reported that with regard to the effect of ozone on coagulant demand, *Microcystis* sp. was more susceptible to lysis by ozonation compared to *Anabaena* sp.. According to Wildrig *et al.* (1996), pre-ozonation enhanced

DOC removal to varying degrees but this was strongly influenced by solution pH and the type of algae present. It was noted that under acidic conditions, DOC removal was enhanced for *Microcystis aeruginosa* and *Scenedesmus quadricauda* but at pH of 8 pre-ozonation had no effect on DOC removal of *Microcystis aeruginosa.*

Ozone can also destroy the toxins produced by blue-green algae. Rositano *et al.* (2000) noted that water containing lower DOC required lower ozone dose to destroy microcystin toxins present. An ozone concentration of 0.2 mg/l with a contact time of 5 minutes should be sufficient to destroy all algal toxins to below detectable level.

Ozone has a high germicidal effect against most pathogenic organisms including bacteria, protozoa and viruses (USEPA 1999). It is more effective than chlorine for removal of *Giardia* sp., which causes gastrointestinal disease (Glaze 1987). Ozone has also been found to be effective against *Cryptosporidium* sp. oocysts that are resistant to conventional chlorination. The cyst wall is reactive to hydroxyl radical and ozone itself (Carlsson 2003).

2.3.2: Colour removal

Naturally occurring colour is often caused by dissolved organic matter in the water, usually humic and fulvic acids (Wetzel 2001). Blooms of algae can also contribute a green colour to the water. Most of the colour-causing compounds include numerous conjugated double bonds, which are readily split by ozone oxidation. Cleavage of only one double bond generally destroys the chromophoric properties of the molecule (Van der Walt 1997). According to Van Staden (1996), although 70 % or more of true colour can be removed thorough direct filtration, conventional treatment or activated carbon, ozone remains the most efficient oxidant, and ozonation is the treatment most often mentioned in the literature for oxidative colour removal. When treating highly coloured water, colour removal will require a treatment sequence containing several steps with ozone used either with slow sand filtration or the use of multistage ozonation.

Although low molecular weight fulvic acids are very hydrophobic and not amenable to removal by coagulation or adsorption, they do respond well to ozonation. Pryor *et al.* (2000) noted that there was a reduction of 40-60 % in colour of industrially polluted water at ozone to DOC ratios between 0.1 and 0.4. This can be increased to 70-90 % if ozonation is followed by conventional treatment using an inorganic or blended polymeric coagulant. Removals of colour by ozonation at doses of 1-3 mg O3/mg DOC are reported to produce almost complete removal of colour. Van der Walt (1997) reported that colour is more susceptible to oxidation with ozone than with Peroxone. Under neutral conditions and at ozone dosage of 6.8mg/l, 100% removal of colour was achieved using ozone, while only 50% removal was obtained using Peroxone. Bessarabov (2002) showed that effluent water from RFF foods show quick and considerable removal of colour and odour after ozonation.

2.3.3: Removal of Taste and Odour

A large proportion of consumer complaints received by water treatment plants is related to taste and odour (AWWARF 1 2006). Many of these are attributed to the presence of metabolites of various organisms such as actinomycetes and cyanobacteria. These compounds, of which geosmin and 2-methylisoborneol (MIB) give rise to the most complaints, are detectable at nanogram per litre concentrations (Stargate 2006). The elimination of taste and odour causing compounds is dependent on the nature of the compound and either non-oxidative or oxidative processes are used. Oxidation processes including ozone, which has been shown to be effective in controlling these compounds. However, results are variable due to differences in water quality. According to Geldenhuys *et al.* (2000), these results vary from 85-100% removal of geosmin and MIB at 2mg/l ozone to 50% removal up to 10mg/l ozone. Removal of 80-90 % MIB and nearly 100% of geosmin was achieved by applying a 5mg/l ozone dose for a 10-20 minute contact period (Geldenhuys *et al.* 2000). According to Hoigne and Bader (1976), ozone reacts following two different pathways: a direct reaction with molecular ozone and an indirect reaction of hydroxyl radicals. Geosmin and MIB, which are tertiary alcohols, are non-reactive towards molecular ozone, but can be removed by hydroxyl radicals formed during ozone decomposition in water (Van der Walt 1997). Therefore, parameters such as pH and bicarbonate content have an influence on the hydroxyl production and scavenging, and variations in these parameters may explain the differences observed (Van der Walt 1997). Ozone has been successfully used to reduce the off-flavour of catfish fillets as well as reducing taste and odour problems in a number of American cities' water treatment plants (Xi *et al.* 2005).

Carlsson (2003) noted that ozone is effective in removing odours due to MIB and geosmin but at a relatively high dosage of 4mg/l, and it has increased effectiveness when combined with peroxide.

NOM fractions that are more highly coloured and have higher molecular weights showed higher ozone demand than the low aromatic fractions. This is linked to the ability of ozone to destroy MIB and geosmin present, as the level of destruction of these two products was higher in the fraction with the highest colour and molecular weight. Therefore, the nature of the NOMs present also affects the efficiency of ozone to destroy MIB and geosmin (Ho *et al.* 2001).

2.3.4: Effect of Ozone on Coagulation/Flocculation

Coagulation reduces the net electrical repulsive forces at particle surfaces by adding coagulant chemicals, whereas flocculation is agglomeration of destabilised particles by chemical joining and bridging (Viessman *et al.* 1998). The removal of contaminants by coagulation depends on their nature and concentration, pH, temperature and ionic strength. Algae contribute the largest portion of contaminants that are removed by coagulation and flocculation.

Engineers at European plants are finding that pre-ozonation enhances the flocculation of suspended particles in surface water and are using ozone for this purpose (Glaze 1987).

However, a number of contradicting reports showed that ozone may or may not benefit coagulation. Technical briefs on water treatment such as Ozone Tech Brief (1999), note that the benefits of using ozone to enhance coagulation are not always observed and pilot studies should be undertaken to determine the effects of pre-ozonation. These differences in response of coagulation to ozone are due to differences in the nature and characteristics of the NOM present in the water.

Geldenhuys *et al.* (2000) reported a number of contradicting observations on the effect of ozone on coagulation. The results showed that Vaal Dam water was affected negatively and fewer macro particles were formed after pre-ozonation in contrast to Klip River water, which was affected positively by ozonation, and spontaneous flocculation occurred at low coagulant doses.

Pryor *et al* (2000) found that when using polymeric coagulants alone, ozonation decreased the coagulant demand by up to 45% while at the same time decreasing TOC removal. The observations were explained by concluding that ozonation almost always decreases coagulant demand when precipitation reactions dominate (as in the case when polymeric coagulants are used), and tend to increase coagulant demand when adsorption dominates.

Wildrig (1996) noted that pre-ozonation for coagulation enhancement was shown under some conditions to improve DOC removal compared to conventional coagulation. As with conventional treatment, improved performance of the action of ozone was dependant on algal source, coagulant dose, and solution pH. The results suggest that coagulation with or without pre-ozonation are strongly influenced by the chemical nature of the organic matrix and this is linked to changes in algal dominance.

Van Staden (1996) observed that although ozone had little effect on particle removal, ozone often facilitated the removal of readily coagulatable materials resulting in savings in coagulant, sludge treatment and sludge disposal costs.

Van der Walt (1997) suggested that the production of acid from reactions between ozone and organic matter increases at higher pH and a decrease in pH improves the efficiency of the metal salts in coagulants. Therefore, increases in solution pH during ozonation resulted in increased coagulant demand.

Tobiason *et al.* (1994) concluded that pre-ozonation lowers the required cationic polymer dose for effective turbidity removal but resulted in decreased DOC removal but the required dose of alum for effective turbidity removal is either unaffected or slightly increased by pre-ozonation with a minimal effect on DOC removal.

2.3.5: Effect of Ozone on Particle Destabilization

There are a number of proposed mechanisms that show how ozone plays a role in particle destabilisation.

The first mechanism of how ozone destabilises particles is that oxidants like ozone cause an increase in the concentration of carboxylic acids and other such oxygenated functional groups (Van der Walt 1997). The carboxylic and phenolic functional groups in the natural organic matter form complexes with polyvalent cations like calcium, magnesium, iron aluminium and manganese aluminium oxide and clay surface, and lead to the formation of insoluble organo-metal complexes. These insoluble compounds can be readily filtered (Ozone drinking water 2006).

The flocculation benefits derived from use of ozone are associated with calcium association with NOM present. Calcium association with NOM increases after ozonation if the ozone affects the number of functional groups that specifically complex calcium and this is related to the oxygen content of the NOM (Mysore *et al.* 1996)

The second mechanism of ozone action on particle destabilisation is that ozone causes a decrease in the size and hence molecular weight of the particles. This causes the lowering of steric hindrances and surface charges and thereby reduces the barriers between particles leading to increased flocculation (Currie *et al.* 2001).

Another mechanism is the formation of meta-stable organics e.g. ozonides, organic peroxides and organic free radicals that contribute to interparticle bridges. These meta-stable organics act like conventional coagulants and promote rapid floc formation and creation of heavier floc particles (Van der Walt 1997).

The fourth mechanism is that organo-metal complexes in natural waters are disrupted during ozonation and this leads to the release of free metal species that can act as coagulants (Currie *et al.* 2001).

The last mechanism proposes the release of the biopolymers from algal cells due to cell lysis or cell aggravation. These polymers can then act as natural coagulants (Currie *et al.* 2001). However, there are conflicting ideas on this mechanism as studies have shown that ozonation of water containing high concentration of algal cells leads to an increase in UV 254, DOC, THM and extracellular toxins compared to water that has NOM only. Lysis of algal cells leads to release of cell-bound organic matter that necessitates greater ozone demand as well as an increase in coagulant demand (Schmidt 2001).

2.4: NATURAL ORGANIC MATTER (NOM)

2.4.1: Background

Natural organic matter (NOM) refers to the complex matrix of organic compounds present in natural waters, soil, sediment and air, and as such, the definition is rather ambiguous (Marhaba *et al.*

2006). NOM has a profound influence on many biophysico-chemical processes in the environment and affects soil quality and health by regulating bioavailability of metals and vital elements. NOM is also a major source of Nitrogen, Phosphorous and Sulphur for plants and a primary food and energy source that controls the ecological dynamics of soil biota (IUPAC 2006). In water, NOM impacts on the efficiency of water treatment processes and affects the quality of final tap water in a number of ways. Water high in NOM may be more costly to treat because of increased demand for coagulants, activated carbon and disinfectant chemicals as well as the need to clean filters more frequently. One of the main concerns is the possible role of NOM in the formation of disinfection by-products and possible support of bacterial regrowth in the distribution system (AWWARF 2 2006).

NOM acts as a pH buffer and binds and transports metals and these dissolved, organically-bound metals may contribute to elemental concentrations. The low-weight molecular fraction is also important in soil development (Natural Organic Matter in the Nordic countries 2006). NOM complexes with trace metals can be a source of methyl groups for the production of chlorinated methanes, and are implicated in the complexation or solubilisation of pesticides and hydrocarbons in the aqueous environment (Thurman *et al.* 1980).

The nature, distribution and reactivity of organic matter in source water are determined by a variety of biogeochemical phenomena occurring in the natural water system and its watershed, namely the nature and strength of interactions among organic source materials, biological cycles, soil chemistry, and hydrology. As organic matter enters the water, they undergo further transformation and finally end up in the sea. Nearly all the organic carbon in natural water comes from the surrounding land and almost all the DOC is from dead detrital organic matter (Wetzel 2001).

Organic matter of soils comes from living organisms and soil organic matter. The transformed product (humus) of soil organic matter can be divided into two categories: Nonhumic and Humic substances (Weber 2005).

Nonhumic substances: These are molecular-weight organic substances and include carbohydrates, proteins, peptides, amino acids, fats, waxes, resins, pigments and other low molecular-weight substances. These substances are generally easily utilised and degraded by hydrolytic enzymes produced by micro-organisms and often exhibit rapid flux rates (Wetzel 2001).

Humic substances form 70-80% of organic matter of soils and water. Humic substances are naturally occurring, biogenic, heterogeneous organic substances that are generally dark-coloured, recalcitrant to biological degradation, and high in molecular weight (Wetzel 2001). The formation of humic substances is not well understood and several theories exist for their formation. The classical theory is that humic substances represent modified lignins formed by microbial degradation of cellulose and lignin of plant material (Weber 2005). However, the majority of present-day investigators favour a mechanism involving quinones. The phenolic aldehydes and acids, which are

released from lignin during microbial degradation, undergo enzymatic conversion to quinones, which polymerize to form humic-like macromolecules. Another theory is that humic substances are formed from sugars. Reducing sugars and amino acids, which are formed as by-products of microbial metabolism undergo nonenzymatic polymerization to form brown nitrogenous polymers (Weber 2005).

Because humic substances are formed by secondary synthesis reactions, they can be divided into a number of fractions based on solubility characteristics:

a) Humic acids – This is the fraction of humic substances that are not soluble in water under acidic conditions (pH<2), but are soluble at higher pH values (Wetzel 2001). Humic acids are the major extractable components of soil humic substances. They are dark brown to black in colour. Humic acids are thought to be complex aromatic macromolecules with amino acids, amino sugars, peptides, and aliphatic compounds involved in linkages between aromatic groups. The hypothetical structure of humic acids is shown in Figure 2.4. It contains free and bound phenolic OH groups, quinine structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings (Weber 2005)

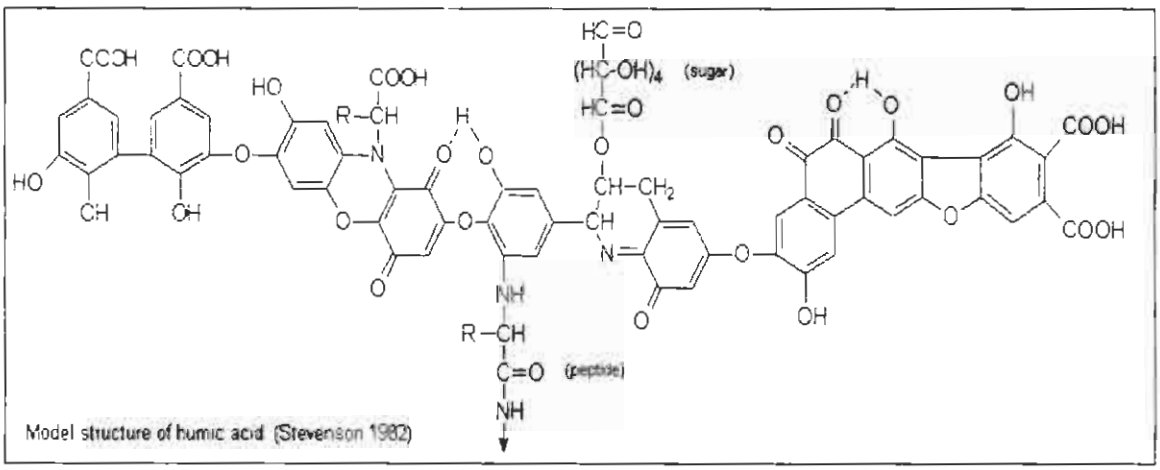


Figure 2.4: Hypothetical structure of Humic acids showing the aromatic groups (Weber 2005 from Stevenson, F.J. 1979. Humus, The encyclopaedia of Soil Science Part 1. Dowden, Hutchinson and Ross, Pennsylvania).

b) Fulvic acids – The fraction of humic substances that is soluble in water under all pH conditions (Wetzel 2001). They remain in solution after removal of humic acids by acidification. Fulvic acids are light yellow to yellow-brown in colour. The hypothetical model structure of fulvic acids contains both aromatic and aliphatic structures, both extensively substituted with oxygen-containing functional groups.

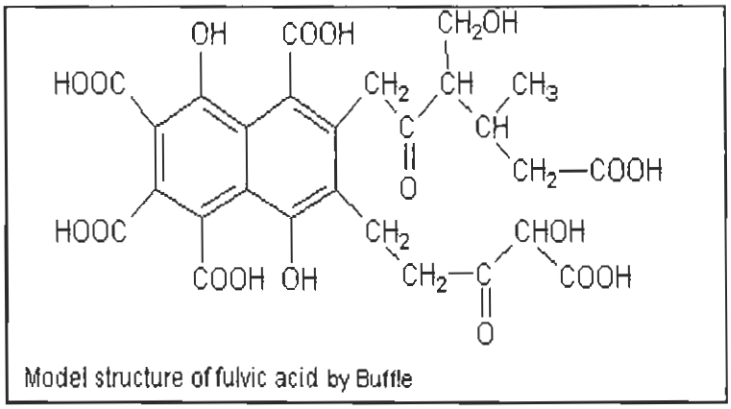


Figure 2.5: Hypothetical structure of Fulvic acids showing aromatic and aliphatic structures (Weber 2005 from Buffle J.A.E. (1977): "Les substances humiques et leurs interactions avec les ions mineraux", w: Conference Proceedings de la Commission d'Hydrologie Appliquee de A.G.H.T.M.. l'Universite d'Orsay, 3-10).

c) Humin – The fraction of humic substances that is insoluble in water at any pH value and in alkali (Wetzel 2001). Humins are black in colour.

Differences between humic acids and fulvic acids can be explained by variations in molecular weight, numbers of functional groups and extent of polymerisation.

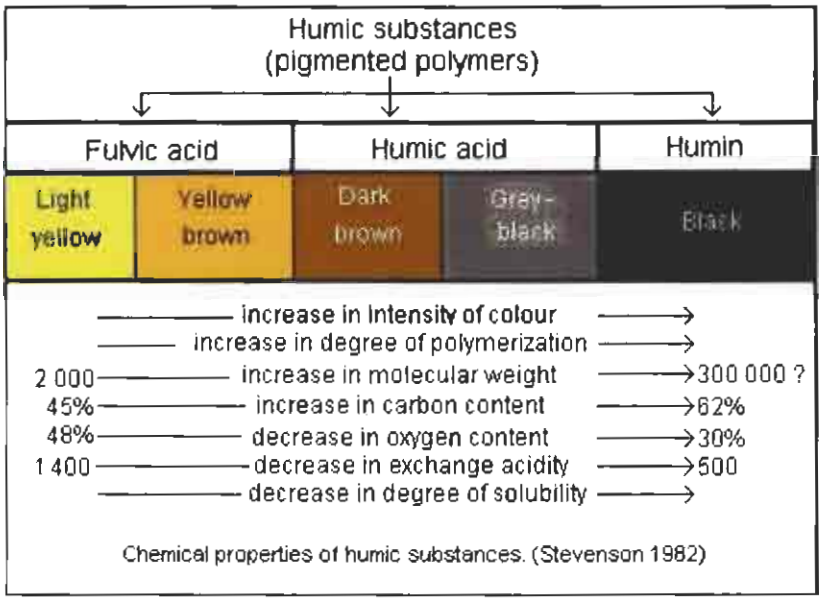


Figure 2.6: Relationship between humic acids, fulvic acids and humin, based on colour, molecular weight and other variables (Weber 2005 from Stevenson, F.J. 1979. Humus, The encyclopaedia of Soil Science Part 1. Dowden, Hutchinson and Ross, Pennsylvania).

This classification of humic substances can also be based on hydrophobic and hydrophilic fractions depending on the way in which they can be separated. This classification is shown in Table 2.1.

2.4.2: Characterisation of NOM:

Although organic matter that enters the aquatic ecosystem is made up of humic and non-humic fractions, only the higher molecular humic substances are of importance and referred to as NOM. Because of the heterogeneous nature of NOM, no single analytical tool can provide definitive or functional information and a combination of methods can be applied. The reactivity of NOM is closely tied to its physicochemical properties such as molecular weight, aromaticity, elemental composition and functional group content (Swietlik *et al.* 2003). The diluted nature of NOM necessitates a concentration and isolation step before fractionation into the different components. Measurement of bulk properties of NOM such as molecular weight, light absorptivity and fluorescence can give important information on the character of NOM (Chin *et al.* 1994). The two frequently used methods used for characterisation of NOM are fractionation of the NOM into hydrophobic and hydrophilic fractions, followed by size distribution on the basis of molecular weight using High Performance Size Exclusion Chromatography (HPSEC).

a) Fractionation:

Fractionation of total NOM offers advantages by selectively separating one group of organic compounds from the other on the basis of their physical and chemical properties. Relatively well defined NOM subcomponents or fractions are thus obtained, and their chemical and structural features can be better characterised. This process is based on column sorption techniques, which simultaneously concentrate and fractionate specific solutes from most other dissolved constituents (Swietlik *et al.* 2003). Non-ionic macroporous copolymers such as XAD resins analogues, in conjunction with ion-exchange resins under the pre-adjusted conditions can classify organic solutes into different hydrophobic and hydrophilic fractions. Most references in the literature use the Amberlite XAD-8 resin technique (Leenheer, 1981) and ultrafiltration together.
The particular fractions obtained by Swietlik *et al.* (2003) are shown below in Table 2.1.

Table 2.1: The classification of NOM based on the organic compound class that is present and the reference sources for that classification (Swietlik et al. 2003)

Fraction	Abbreviation	Organic compound class	Reference
Humic acid	HA	Portion if humic substances precipitated at pH1	Peuravuori *et al.*
Hydrophobic acid	HOA	Soil fulvic acids, C_5-C_9 aliphatic carboxylic acids, 1-and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols.	Leenheer, Marhaba *et al.*, Barber *et al.* and Aiken *et al.*
Hydrophobic base	HOB	Portion of the humic substances retained by XAD-8 resin at pH~7 which can be eluted by HCl; 1- and 2-ring aromatic amines except pyridine, proteinaceous substances	Leenheer, Marhaba *et al.* and Barber *et al.*
Hydrophobic neutral	HON	A mix of hydrocarbons; > C_5 aliphatic alcohols, amides, esters, ketones, aldehydes; long chain (>C_9) aliphatic carboxylic acids and amines; > 3-ring aromatic carboxylic acids and amines.	Leenheer, Marhaba *et al.* and Barber *et al.*
Hydrophilic acid	HIA	< C_5 aliphatic carboxylic acids, polyfunctional carboxylic acids, mixture of various hydroxyl acids	Leenheer, Marhaba *et al.*, Barber *et al.* and Aiken *et al.*
Hydrophilic base	HIB	Amphoteric proteinaceous materials containing aliphatic amino acids, amino sugars, peptides and proteins;<C_9aliphatic amines; pyridine	Leenheer, Marhaba *et al.* and Barber *et al.*
Hydrophilic neutral	HIN	Short chain aliphatic amines, alcohols, aldehydes, esters, ketones; < C_5 aliphatic amides; polyfunctional alcohols; carbohydrates; cyclic amides; polysaccharides	Leenheer, Marhaba *et al.* and Barber *et al.*

b) High Performance Size Exclusion Chromatography (HPSEC):

HPSEC is a rapid and reproducible method for characterising macromolecules according to their molecular weight (Vuorio *et al.* 1998). HPSEC is based on differential permeation of molecules of various sizes into a porous matrix. As the sample traverses the column, smaller compounds move into matrix pores better than larger components and are retained longer. Elution order is therefore determined by molecular size, with larger compounds eluting first, and smaller compounds last (Pelekani *et al.* 1999). During analysis, there must be no chemical interactions between the column packing material, the solvent, or the organic components (Vuorio *et al.* 1998).

An important part of HPSEC is molecular weight calibration. Commercially available standards that have hydrodynamic and chemical properties comparable to those of the sample solutes have to be used. It has been reported by Peuravuori *et al.* (1996) that aquatic humic solutes and polystyrene-sulfonates (PSS) behave similarly during chromatographic elution on HPSEC and have similar hydrodynamic properties. They concluded that although both humic solutes and PSS standards have a random coil-like shape, humic solutes are more branched and cross-linked. Therefore most HPSEC studies use PSS standards and commercially bought humic acids for calibrating the column.

2.4.3: Effect of ozone on NOM

In water treatment processes, coagulation preferentially removes higher molecular weight UV absorbing particles, leaving lower molecular weight, less UV absorbing particles in the water. Coagulation removes some of this organic material but there is always some recalcitrant NOM that remains (Natural Organic Matter 2006).

When water containing NOM is ozonated, the larger molecular weight compounds are partially oxidised into smaller, more polar organics (Swietlik *et al.* 2003). Generally, humic substances extracted from highly coloured water show a large reduction in molecular size after ozonation. Ground and surface water with low or moderate organic content shows only moderate effects on molecular size distribution at ozone doses of 0-1.2 mg ozone/mg C (Bose *et al.* 1993).

The decrease in molecular weight and increase in functional group density or polarity can, however, decrease the amount of NOM removed by both precipitation reactions and adsorption. Coagulant demand will also increase with increasing polarity, although at low ozone doses (0.1-0.3mg/l) decreases in the colloidal charge density of certain organic compounds can result in lower coagulant demand and an increased NOM removal. Therefore the nature of the NOM, the ozone dosage and the pH will all affect the treatment process as well as final water quality (Pryor *et al.* 2000).

Humic substances generally show strong absorbance in the UV region and this is because of the presence of aromatic chromophores (Chen *et al.* 2001). Ozone causes a decrease in the UV-absorbing properties of the NOM (Vuorio *et al.* 1998). Rositano *et al.* (2001) observed that the major site of attack of NOM by ozone were the structures that absorb UV light at a wavelength of 270-290 nm and this was similar to results for reaction of chlorine with NOM.

Ozone reacts rapidly with the aromatic fractions of NOM resulting in a significant decrease in UV 254 (Karnik *et al.* 2005). Huang *et al.* (2005) noted that after ozonation there was a decrease in the percentage of aromatic groups while an increase was observed in phthalates, acids and aldehydes, which can be expected in a process of oxidation. Phthalic acid has been identified as an initiator and promoter of hydroxyl radical chain reactions at low pH and is present in considerable concentrations in ozonated solutions of fulvic acids (Huang *et al.* 2005). Aldehydes are formed at high ozone dosage rather than at lower ozone dosage as aldehydes are easily oxidised by ozone to corresponding carboxylic acids and other organic acids.

Ozonation can cause reduction of hydrophobic compounds and a significant increase in the hydrophilic fractions (Swietlik *et al.* 2003) as the hydrophobic fraction of NOM is sharply reduced and there is a mass transformation to hydrophilic fraction. Chemical changes also occur resulting in more oxalic acid type compounds formed that have more oxygenated moieties making it more amenable to biodegradation (Marhaba *et al.* 2006). It was noted that the hydrophobic acid fraction was also reduced by ozone but to a lesser degree because of the smaller molecular weight which does not have the surface area to provide the large reaction sites needed for targeting ozone. The hydrophilic base component shows an increase after ozonation. This is due to the break-up of the fraction into small molecular sizes and the transformation of materials from non-biodegradable to biodegradable.

Ozonation of humic substances lead to hydrophilic acid fraction forming oxalic acid. Formation of oxalic acid is of great significance to water treatment as this leads to an increase in organic charge of the particles (Bose *et al.* 1993).

Acidity of fractions generally increases after ozonation. This increase in acidity of the hydrophobic acid fractions is mainly due to an increase in strong carboxylic acidity (Bose *et al.* 1993). Bose *et al.* (1993) note that ozone has an impact on removal of organics during coagulation and this probably occurs mainly by adsorption on aluminium hydroxide flocs. Aluminium hydroxide is rather polar and capable of forming complexes and hydrogen bonds with organics. Increased acidity of the organics after ozonation will help the adsorption process because of the increase in the number of sites on a given organic molecule that can potentially interact with the aluminium hydroxide surface.

CHAPTER 3: DETERMINATION OF OZONE CONCENTRATION

3.1: INTRODUCTION

Ozone has been used as a disinfectant in water treatment since 1906 and since then, more than 1000 facilities throughout Europe have adopted the practice (Glaze 1987). The number of ozonation plants in the United States has increased from 5 in 1977 to 40 in 1990 with the Los Angeles plant being the third largest ozone producing facility in the world (Langlais 1991). There are currently about 1500 plants worldwide that use ozone; among them cities such as Budapest, Montreal, Moscow, Paris and Zurich (Strydom 2004). One of the main reasons for the increased interest in ozone treatment is the need to decrease the use of free chlorine in water treatment in keeping with legislated maximum contaminant levels for trihalomethanes (THMs) (Glaze 1987). Ozone has also been shown to be superior to chlorine as a coagulant as it partially oxidises organic material, which becomes more polar and then actively combines with polyvalent coagulants (Ozone tech brief 2006). In addition, because ozone breaks down into oxygen, there is no ozone present in the treated water to affect taste or cause corrosion (SEDAB 2004). Ozone also oxidises metals such as iron and manganese as well as hydrogen sulphide, which can give water a foul odour (Ozone tech brief 2006). Ozone is successful in controlling pathogens like *Cryptosporidium* sp. and *Giardia* sp., which are normally resistant to conventional treatment (Lenntech 2006).

3.2: AIMS

To achieve the aims set out on page 3, an ozone contact chamber had to be designed and constructed. Therefore the aims of this section are as follows:

a) to design and construct an ozone contact chamber, and

b) to determine the concentration of ozone in the contact chamber.

3.3: MATERIALS

An apparatus was required to treat the water with ozone i.e. an ozone contact chamber had to be designed and manufactured. The design of the apparatus was based on the contact chamber used by Pryor *et al.* (2000), which consisted of two glass contact columns fitted with a circulation pump. Pryor *et al.* (2000) also used a Sorbios ozone generator which generates ozone from oxygen with a potassium iodide trap for capturing the off-gas. The ozone contact chamber used was designed at the North-West University, Potchefstroom Campus in consultation with the Department of Astro-Physics and built by Department of Engineering, Instrument Making unit.

Because ozone is such a powerful oxidant, all the materials used had to be non-oxidisable materials such as glass and silicon. A single chamber was constructed from glass, as this was

sufficient for the amount of water that was required, and a glass diffuser was used to allow the ozone to diffuse into the water. The glass tube had a capacity of 3l, was 1,2m high and had an internal diameter of 6 cm.

A Sterizone buddy ozone generator was used to produce ozone using air (see Figure 3.1). It does not require an additional oxygen source. The Sterizone buddy is produced locally by Ozo Clear Marketing (Pty) Ltd trading as Sterizone and is capable of generating 300 mg ozone/hr. The Sterizone buddy uses 110/220 AC voltage and has a power consumption of 39-Watt 50 HZ (Sterizone 2004).

A circulation pump was not required because the concentration of ozone was high enough to promote effective mixing of the sample in a few seconds. The off-gas was discharged outside using silicone tubing (figure 3.2).

The next step was to determine the concentration of ozone in the chamber for a specific contact time using distilled water.

Figure 3.1: Sterizone Buddy ozone generator with a capacity to produce 300mg ozone/h. Mass= 3.9kg, Dimension= 109mmX180mmX150mm.

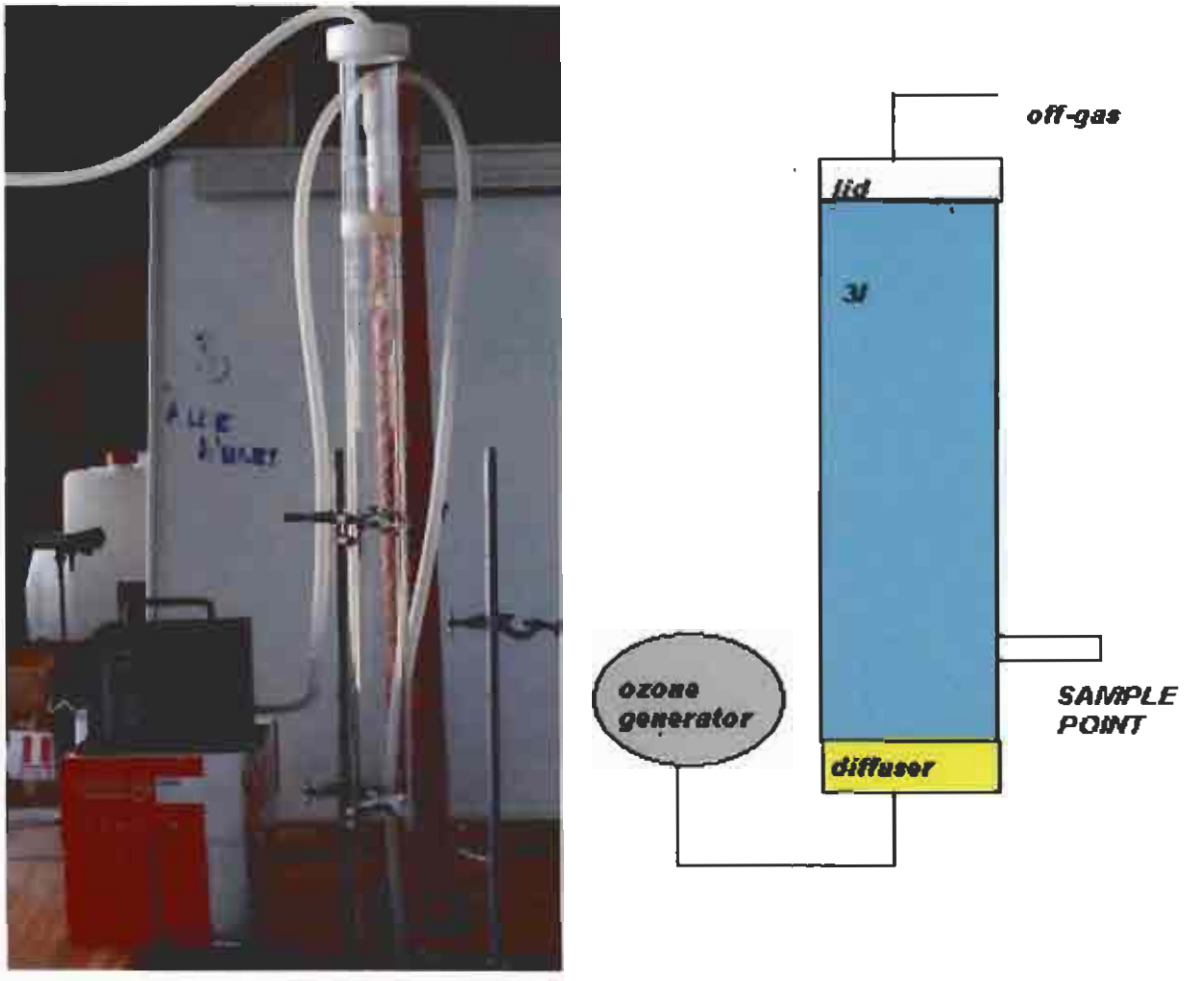


Figure 3.2:

a) Photograph of the constructed ozone contact chamber set-up in the laboratory.

b) Schematic representation of ozone contact chamber with dimensions = 1.2m high, internal diameter of 6cm and a capacity of 3 liters.

3.4: METHOD FOR DETERMINATION OF OZONE CONCENTRATION

The method used for the determination of ozone concentration was the indigo colorimetric method as described in Standard Methods for the Examination of Water and Wastewater, AWWA (1995), 4500 - O_3B. This method is based on the principle that, in acidic solutions, ozone rapidly decolourises indigo. There is a linear relationship between the decrease in indigo absorbance and the increase in the concentration of ozone. The volume of sample added to the indigo solution can be varied so that for higher concentrations of ozone, a correspondingly smaller volume of sample is used.

Figure 3.3 shows how ozone decolourises indigo dye, which is blue in colour and used to dye blue

jeans. An indigo stock solution with 1:100 dilution was used which corresponds to 770mg potassium indigo trisulfonate made up to 1 litre with distilled water. In each flask, 10ml indigo solution was added together with a known amount of ozone-containing water and distilled water to make up the final volume to 250ml. The amount of ozone-containing water was increased from left to right. The flasks were made up as follows:

Table 3.1: Composition of Flasks showing amount of ozone-containing water

	Amount of indigo (ml)	Amount of ozone-containing water (ml)	Amount of distilled water (ml)
Flask 1	10	0	240
Flask 2	10	25	215
Flask 3	10	50	190
Flask 4	10	100	140
Flask 5	10	150	90

Figure 3.3: Photographs showing the effect of increasing ozone concentration on indigo dye. As the concentration of ozone increases in the flasks from left to right, the colour of the indigo decreases.

The method for determining the concentration of ozone in water requires the following reagents:

a) Indigo stock solution: Five hundred ml distilled water was added to 1ml concentrated phosphoric acid in a 1l volumetric flask. While stirring, 770mg potassium indigo trisulfonate, ($C_{16}H_7N_2O_{11}S_3K_3$) was added to the flask. The flask was then filled to the mark with distilled water. Generally, a 1:100 dilution exhibits an absorbance of 0.2 $\pm$ 0.01 at 600nm. The stock solution is stable for about 4 months and was stored in the dark. The stock solution was discarded when the absorbance was below 0.16.

b) Indigo reagent II: Hundred ml indigo stock solution, 10g sodium dihydrogen phosphate (NaH_2PO_4), and 7ml concentrated phosphoric acid were added to a 1l volumetric flask and diluted with distilled water to the mark. A fresh solution was prepared when the absorbance decreased to less than 80% of its original value, typically within a week.

The contacting column was filled with 3l of distilled water and ozonated for a contact time of 1 to 5 minutes. After the generator was switched off, the sample was allowed to decanter into a glass flask for at least one minute until no ozone bubbles were seen. A glass pipette was used for obtaining the sample of ozonated water which was first rinsed out with the sample. Ten ml of indigo reagent II was added to five 100ml volumetric flasks. Distilled water was used as the blank in the first flask. The other four flasks were filled with different volumes of the ozone-containing water using the glass pipette while keeping the pipette tip below the surface of the indigo reagent. The flasks were then made up to a volume of 100ml with distilled water. The absorbance of the samples and sample blank was measured at 600nm on a Genysis II spectrophotometer using a plastic cuvette with a path length of 1cm. The ozone concentration in the sample was then calculated from the difference in absorbance between the blank and the sample using the flowing equation. Different volumes of ozonated water were used to obtain accurate results because the volume of the sample used should not affect the concentration of ozone present.

Calculations

$$\text{mg } O_3/l = \frac{100 \times \Delta A}{f \times b \times V}$$

Where:

ΔA =difference in absorbance between sample and blank,

b =path length of cell in cm

V =volume of sample in ml (normally 90ml), and

f =0.42 which corresponds to an absorption coefficient of aqueous ozone, ε=2950/M.cm at 258nm..

3.5: RESULTS AND DISCUSSION

Trial runs were conducted to determine the concentration of ozone in the column starting at contact time of two minutes. The method was repeated a number of times to obtain repeatable results.

For the first few runs, measurements were taken and analysed using different spectrophotometers:

1) Genysis II and 1cm plastic cuvettes, and
2) Spectroquant photometer using 10cm glass cuvettes.

However, there was no difference in the observed values and the Genysis II spectrophotometer and 1cm plastic cuvettes were used for the duration of the experiment.

The results obtained for the concentration of ozone at contact time of 2,3,4 and 5 minutes are summarised and presented in Table 3.2 where n = 11.

Table 3.2: Summary of observed concentration of ozone in the contact chamber after contact time of 2, 3, 4 and 5 minutes, respectively.

TIME(min)	2	3	4	5
Mean	0.475217391	1.170833333	1.614286	1.5927578
Standard Error	0.015715725	0.058535904	0.081778	0.105072
Standard Deviation	0.07536997	0.202774318	0.305984	0.393142
Sample Variance	0.005680632	0.041117424	0.093626	0.15456

The values indicated that after a contact time of two minutes, the minimum concentration of ozone is 0.5mg/l O_3. After 3 minuttes, the average concentration is 1mg/l O_3 and after 4 minutes the average concentration is 1.5mg/l O_3. This concentration is maintained even after a longer contact time. The average values of the concentration of ozone over time are presented in Figure 3.4.

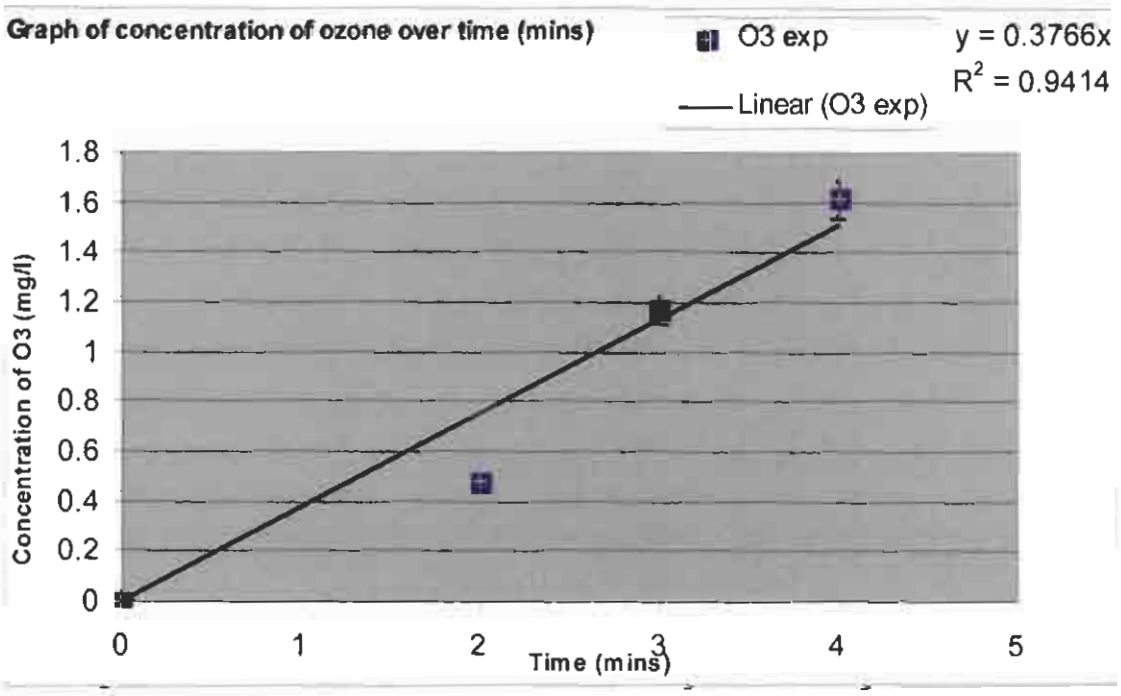


Figure 3.4: Concentration of ozone present in the distilled water after different exposure times and showing the regression line

A contact time longer than 4 minutes produced the same result as for 4 minutes indicating that the maximum concentration of ozone that can be produced in the column was 1.5 mg/l I O_3. If a higher concentration of ozone is required there would have to be modifications made to the apparatus such as using two generators instead of one, changing the diffuser to a venturi system to improve dissolving of ozone into water, or using an oxygen source instead of air for more efficient ozone production from the generator.

Ozone decomposes spontaneously in water to form oxygen and this rate is affected by the presence of any oxidisable material. Therefore the exact measurement of dissolved ozone in water is very difficult. Most water treatment plants use on-line monitors to keep the concentration of ozone constant (Ozone Solutions 2004). The use of an on-line monitor was not an option for this experiment because of cost.

This study examines the general effect of ozone on water treatment variables where ozone is used for pre-ozonation. The minimum concentration required for pre-ozonation is <1mg/l (USEPA Manual 1999), but all samples have different oxidant demands depending on the organics present. A contact time of 4 minutes exposure to ozone is required so that ozone can act on the organics in the sample (The Use of ozone in water and wastewater treatment: 1992). The minimum amount of ozone that can be produced after 2 minutes by the Sterizone generator in the contact chamber was 0.5mg/l O_3. Therefore, all samples were exposed to ozone for 2 minutes to obtain a minimum concentration of 0.5mg/l O_3 and will then be exposed for a further 4 minutes contact time so that ozone can act on the sample. This means that the total contact time was 6 minutes. Subsequently, samples were exposed to 7 minutes contact time to observe the effect of ozone at concentrations of >0.5mg/l O_3.

CHAPTER FOUR: ECOLOGICAL OVERVIEW OF THE SAMPLING SITES

4.1: INTRODUCTION

Aquatic ecosystems are open and receive a continual input of energy in the form of organic matter from the surrounding land. According to Wetzel (2001), the geomorphology of the land, biotic factors such as vegetation, abiotic factors such as soil composition and anthropogenic factors determine the characteristics of rivers. The quality of our water supply is thus to a large extent influenced by human activity and NOM.

The ecological state of South Africa's raw water is firstly affected by a limited water supply with an average rainfall of just over half of that of the world average of 860mm per year (Basson 1997). These water resources are also characterised by several water quality problems including salinisation, eutrophication and high turbidity (Basson 1997). The low mean rainfall values and intermittent flow of South African rivers enhance these problems and add to the stress on the ecology of rivers and dams.

The River Health Programme (RHP) of South Africa provides information about the ecological state of our rivers based on the measurement of several biological indices such as: habitat integrity, riparian zone vegetation index, fish assemblages, water quality and macro-invertebrate integrity. River Health is an integrated measure of various conditions that are necessary for proper ecosystem functioning and the ability to supply good quality water and other services. Poor river health reflects a drop in one or more of these conditions, which may in turn, lead to a disturbance in trophic level interactions, loss of predator or prey species, reduced ability to regulate water quality and flow, and reduced water availability for human consumption (State of the Rivers report 2 2006).

Dams are a major source of drinking water in South Africa with about 50% of South Africa's annual rainfall being stored in dams. There are 550 government dams in South Africa with a total capacity of 37 billion m^3 (South Africa's water sources 2006). The landscape of South Africa is, however, not suited to dams as it lacks deep valleys and gorges. The result is that most dams are shallow with a large surface area resulting in high water loss due to evaporation. Poor farming methods, arid climate and steep river gradients result in a high silt load to rivers, which then further lead to the diminished capacity of South African dams.

One of the most important dams in South Africa is the Vaal Dam, which supplies the Gauteng province with water. Rapid urbanisation and industrialisation in this area have led to increased demand for water in the Vaal River System Supply Area. These factors have necessitated various inter-basin transfers. This can, however, lead to additional water quality problems if the water being transferred is of a poor quality. Inter-basin transfer in the Western Cape has resulted in increased

turbidity and salinity, altering the structure of aquatic macro-invertebrate communities and the transfer of alien fish species (State of rivers report 1 2006).

Most of the major rivers in South Africa have dams built in them and the water quality of the river directly affects the water quality of the dam. Pollutants that flow constantly through rivers can accumulate in the sediment of dams and affect the ecology of the dam, especially heavy metals. Inflow of excessive nutrients can lead to eutrophication of dams. This is evident in Hartbeespoort Dam and leads to massive cyanobacterial blooms and proliferation of water hyacinth (Dower 2005).

NOM occurs in all natural waters when animal and plant materials break down (AWWARF 2 2006). Therefore, NOM present in the water is impacted on by the surrounding soil and vegetation, by seasonal variations and by the geology of the surrounding areas. NOM in water is a complex mixture of organic material such as lipids, humic acids, hydrophilic acids and hydrocarbons (Cranfield University 2006). The character of the NOM is an important factor in their removal from water during the purification process. High concentrations of NOM in the water require an increased demand for coagulants and disinfection chemicals and may necessitate the addition of activated carbon during the purification process. NOM also plays a role in the formation of disinfection by-products and can support bacterial growth in the distribution system (AWWARF 2 2006). According to the Corporative Research Centre for water quality in Australia: "Monitoring NOM character by measuring the very hydrophobic fraction will allow operators to better control coagulant dose to optimize DOC removal" (Natural Organic Matter 2006).

The ecological state of the raw water as well as the nature of NOM determine the quality of the water and this ultimately affects the water purification process. Therefore, knowledge of the ecological state of study areas as well as the characteristics of the NOM found is important in any study that looks at water purification methods.

4.2: AIMS

To determine the overall ecological state of the four different sampling sites by measuring the following variables:

a) pH
b) Conductivity
c) Dissolved oxygen
d) Turbidity
e) *Chlorophyll-a*
f) SAC 254
g) Dissolved Organic Carbon (DOC)

h) Determination of Natural Organic Matter (NOM)

i) Algal identification and enumeration.

4.3: SAMPLING SITES

The four sampling sites chosen for this study are found in and around the North West Province and Gauteng. The study areas were chosen so as to reflect possible differences in NOM found in these areas. Two sites were chosen from riverine areas and two from dams. Other factors such as transport cost and proximity of sample sites were also taken into consideration.

The sites are:

a) Hartbeespoort Dam: a highly eutrophic dam that is part of the Crocodile Marico catchment area and receives water from urban and industrial areas.

b) Middle Vaal Region: Riverine areas

Both river sites are situated on the Vaal River at water purification works. However, different strategies to purify the raw water are used at both sites because of the different substances present in the water.

i) **Stilfontein at Midvaal Water Company** that receives water rich in manganese and iron from surrounding mines.

ii) **Balkfontein at Sedibeng Water Company**, which is downstream of Midvaal and is surrounded by agricultural areas especially maize farming.

c) Boskop Dam: a mesotrophic dam that drains from dolomitic areas.

In Figures 4.1 and 4.2: the location of these sampling sites are indicated as they occur in the different water management areas.

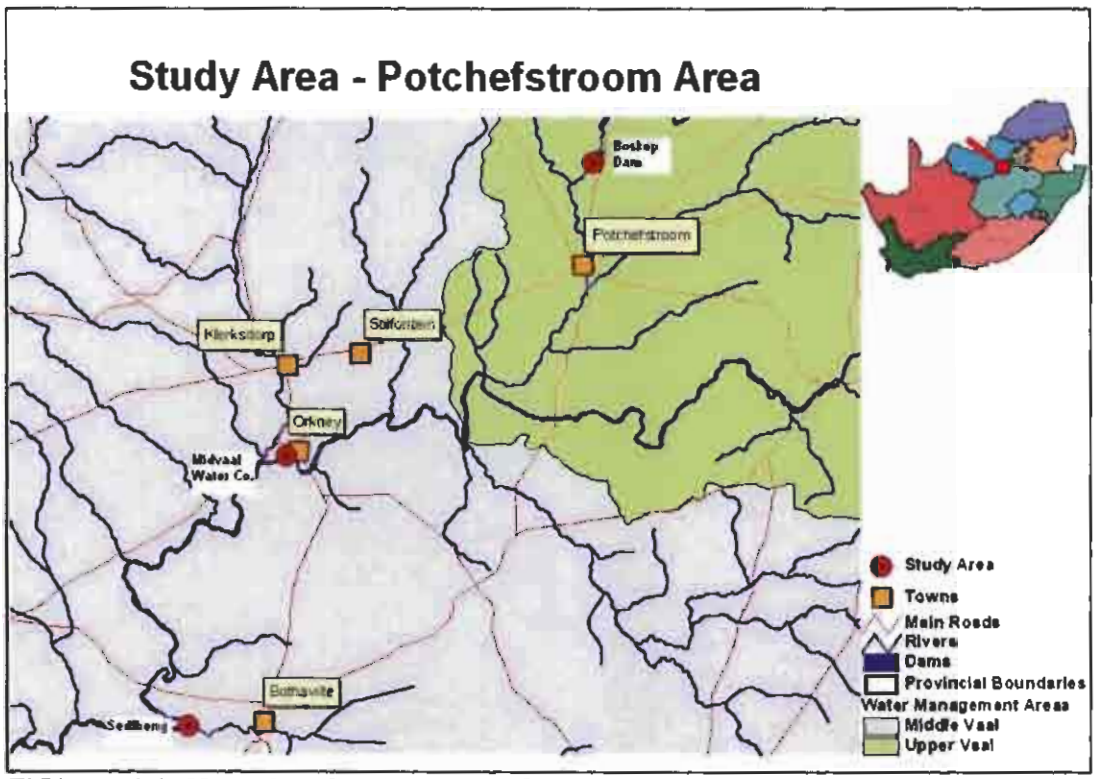


FIGURE 4.1: Map showing location of sampling points along Middle Vaal region between North West and Free State i.e. Boskop Dam, Midvaal Water Company and Sedibeng

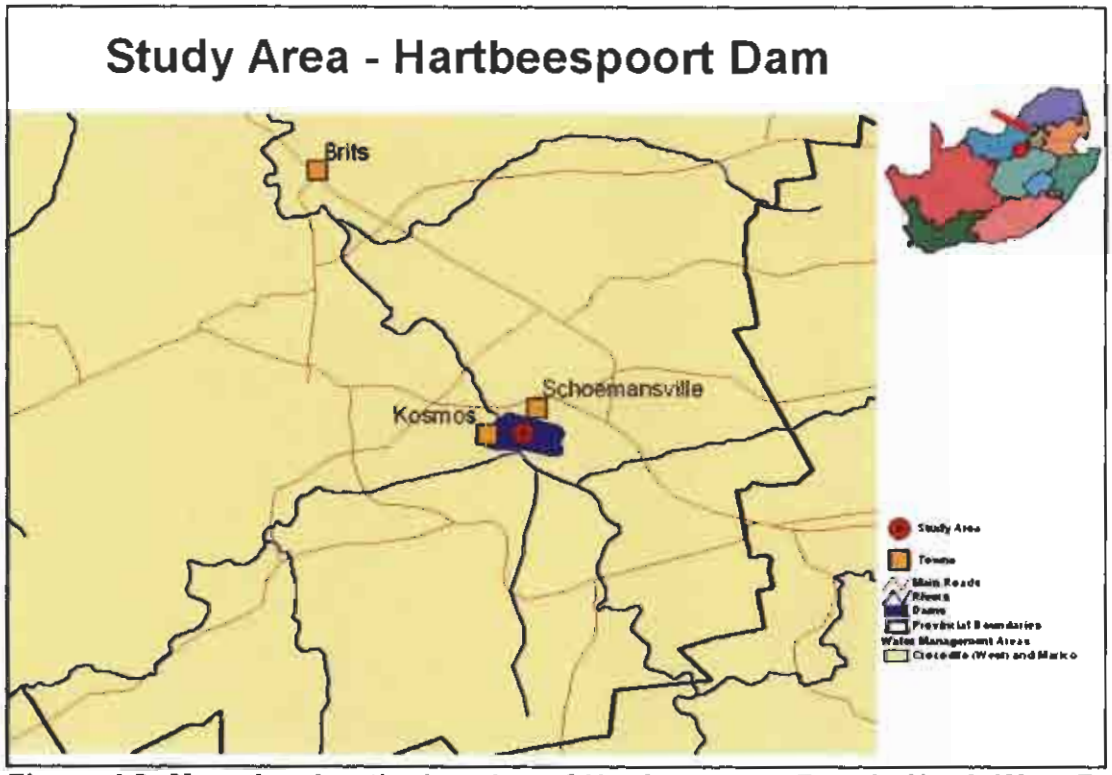


Figure 4.2: Map showing the location of Hartbeespoort Dam in North West Province, South Africa.

a) Hartbeespoort Dam

Hartbeespoort Dam has a surface area of 2034 ha and a capacity of 195 million m^3(Hartbeespoort Dam remediation project 2006). It was constructed during the 1920s and completed in 1925. The dam is located west of Pretoria in Gauteng, close to Brits in the North West Province. Hartbeespoort Dam is located in the Crocodile River catchment downstream on the confluence of the Crocodile River with the Jukskei and Hennops rivers.

Hartbeespoort Dam lies in the Crocodile (West) Marico WMA and according to the RHP; this WMA is classified as having a good to fair overall Eco-Status (State of the Rivers report 2 2006). The Crocodile (West) Marico WMA is highly developed with about 25% of the Gross Domestic Product (GDP) of South Africa originating from here. Riparian habitats and vegetation appear to suffer most in this catchment, mainly due to alien infestation and clearing of ground cover (State of the Rivers report 2 2006).

The diverse geology of this WMA has some of the richest mineral deposits in the World (State of the Rivers report 2 2006). North of the Magaliesberg the geology is dominated by the Bushveld Igneous Complex, which is extremely rich in minerals and mined for platinum, chrome and vanadium in particular (State of the Rivers report 2 2006). Dolomitic rock is found in the Rietvlei Dam catchment towards Krugersdorp, the Marico and Molopo catchments and north of Randfontein and Krugersdorp. Dolomitic rock is also found at the confluence of Pienaars and Crocodile rivers as well as at the confluence of the Tolwane and Pienaars rivers. The rest of the catchment consists of sedimentary rock, the quartsitic Magaliesberg being the prominent feature and regarded as being 2.5 billion years old (State of the Rivers report 2 2006).

Hartbeespoort Dam is a highly eutrophic dam with excessive nutrient loading originating largely from point source discharges into the Jukskei River (State of the Rivers report 2 2006). Two hundred metric tones of phosphorous as P are discharged annually into the dam. This has lead to dense colonies of cyanobacteria, most notably one species, *Microcystis* sp. present for most of the year, which eventually forms a thick sludge of rotting algae that produces foul smells. The result is lack of recreational use of the dam and thus falling property prices around the dam area (Dower 2005).

The abbreviation used for this sampling site will be "HBP".

b) Middle Vaal Region

The Middle Vaal Water WMA is part of the Vaal, Harts and Skoonspruit Catchments. It is located downstream of the confluence of the Vaal and the Rietspruit Rivers at the Barrage and upstream of the Bloemhof Dam (DWAF Report No. P WMA 09/000/00/0304). The Middle Vaal is part of the Vaal River System that forms the main tributary to the Orange River. The Vaal River is probably the

most developed and regulated river in Southern Africa and forms part of extensive inter-basin transfer of water.

The overall health of the Middle and Lower Vaal River is fair to poor (DWAF Report No. P WMA 09/000/00/0304). The Vaal River downstream of the Barrage, which is where the study areas are situated, is impacted on and controlled by activities and effluent discharges from Southern Gauteng. The Klip River and Blesbok Spruit systems drain large areas of southern Gauteng affected by urban development, mining, and industrialisation.

The Vaal River is one of the biggest rivers in South Africa and is the main supply of water for the economic heartland of South Africa, namely Gauteng. The Vaal River comprises 192 000km^2 and is divided into the upper, middles and lower Vaal (Kruskopf 2002). The quality of the water in the Vaal River deteriorates downstream and the major problems are increased salinity and eutrophication (Janse Van Vuuren 2001).

According to DWAF reports, the geology of the area is varied with a large dolomitic intrusion occurring in the Orkney area of the WMA. The area south of the Vaal River is underlain by fine sedimentary rocks of the Karoo System, which represents about 80% of the Vaal River Basin. To the north of the Vaal River igneous and metamorphic rocks predominate but there are extensive dolomitic exposures in the northerly part of this WMA and also east of Klerksdorp (DWAF report no. P WMA 09/000/00/0304). The soil types are predominantly sandy loam, clay loam and clay soil. The Witwatersrand Basin is part of the WMA and gold is extensively mined around Klerksdorp, Orkney and in the Free State. The reefs mined at the Vaal River operations are the Vaal Reef, the Ventersdorp Contact Reef (VCR) and the 'C" Reef (Anglogold Ashanti country report: Vaal River 2005).

i) Vaal River at Stilfontein, Midvaal Water Company

Midvaal Water Company is situated in the Middle Vaal region, 160km downstream from the Barrage and 115km downstream from Parys 26°56'S, 26°55'E) (Kruskopf 2002). Water is abstracted from the Vaal River approximately 15km south of Stilfontein. A volume of 320 000 kl (320 million liters) can be treated daily by Midvaal Water Company. Treatment involves the following processes:

-oxidation by ozone to remove algae and manganese,

-chemical dosing to coagulate suspended solids into flocs,

-sedimentation / flotation, whereby the flocculated particles are separated from the water,

-filtration to remove remaining fine particles, and

-disinfection to kill harmful bacteria.

The abbreviation used for this sampling site will be "Midvaal" or "MV".

ii) Vaal River at Balkfontein, Sedibeng Water Company

Sedibeng Water Company is situated on the Middle Vaal, downstream from Midvaal Water Company. Water is extracted at Balkfontein 270km downstream from Barrage and 110km downstream from the Stilfontein sampling locality (Janse Van Vuuren 2001), (27°23'S, 26°30"E) (Kruskopf 2002). The width of the river at the sampling locality is about 77 m, with a maximum depth of 5 m.

Sedibeng Water supplies water to the Welkom, Virginia and Bothaville areas, as well as the Leeudoringstad, Wolmaransstad, and Makwassie areas. Irrigation farmers along the river and on the Vaalharts Government Water Scheme are also supplied with water from the Vaal River (Traute 2005).

The water treatment process at Sedibeng is as follows:

-prechlorination,

-coagulation,

-sedimentation,

-rapid sand filtration, and

-post-chlorination.

The abbreviation used for this sampling site will be "Sedibeng" or "SB".

c) Boskop Dam

Boskop dam is situated 20km north of Potchefstroom in the North West Province, (26°32'S, 27°6'E) (UNEP 2006). Boskop dam is the receiving water body for the Wonderfontein Spruit (Onstott 2002). The Wonderfontein Spruit originates in Krugersdorp (Mogale City), from where it drains the Western Gauteng and Eastern parts of the North West Province. Some of the richest gold-bearing ores occur in this area and it is extensively mined. The Transvaal Sequence, with outcrops of the associated dolomite of the Malmani Subgroup, also occurs in this area (Centre for Environmental Management 2006). Numerous vertical and subvertical dykes are found in the Witwatersrand Supergroup, and a number of these extend into the overlying dolomite. The result is water bearing dolomitic compartments from which the Wonderfontein Spruit occurred. Groundwater moves rapidly in large volumes through large solution cavities in the dolomite. This groundwater flow, along with the Wonderfontein Spruit, forms a continuous link between mining areas with the result that mines have to pump out large volumes of water to de-water the dolomites. The dewatering of these compartments has a severe impact on both quality and quantity of the Wonderfontein Spruit, especially an increase in salinity and high sulphate concentration (Ontstott 2002).

The annual rainfall in this area is 600mm and occurs mainly during summer (October-April). There is reed encroachment at main angling areas and an increase in agricultural activities such as maize farming upstream from the Dam. The immediate surrounding area forms part of Boskop Dam Nature Reserve that is managed by North West Provincial Government. There is an abundance of bird life and it is a popular fishing destination for Carp and Barber. Boskop Dam was chosen for the study to represent a mesotrophic impoundment as it was identified as such by Department of Water Affairs and Forestry (Howard *et al.* 2002).

The abbreviation used for this sampling site will be "BK".

4.4: MATERIALS AND METHODS

Water samples of 20 liters were collected on a monthly basis for the duration of a year from the surface water of 4 different sampling sites, namely:

-Hartbeespoort Dam (eutrophic dam), sample taken from dam wall

-Boskop Dam (mesotrophic dam), surface water sample

-Sedibeng raw water

-Midvaal raw water

The water of each site was mixed in a 25-litre can to get a homogenised sample.

The following variables were then determined:

a) **pH** – using pH meter pH 330/SET-1,WTW.

b) **Conductivity** – using Hanna HI9033 conductivity meter.

c) **Dissolved oxygen**- using YSI dissolved oxygen meter Model 50B.

d) **Turbidity**- using HACH 2100P Turbidimeter.

e) ***Chlorophyll*-a concentration**- was determined according to the method described by Sartory (1982). A known volume of sample, usually 200ml, was filtered, with the aid of a vacuum pump, through Whatman GF/C filter. The chlorophyll gathered on the filter was extracted with 10ml, 95% ethanol, in a water bath at 78°C for 5 minutes. The samples were removed and left in the dark to cool down. The chlorophyll-extracts were placed in cuvettes and the difference in absorbance of the extract was determined at 665 and 750 nm respectively using 95% ethanol as the blank. A drop of (0.3M) HCl was added to the cuvettes and the difference in absorbance was measured again after 2 minutes.

The following calculation was used to determine the Chlorophyll-*a* concentration:

$$\text{Chlorophyll-}a\ (\mu g/l) = \frac{[(A_{665}-A_{750}) - (A_{665a}-A_{750a}) \times 28.66 \times \text{extract volume}}{\text{Volume of sample}}$$

Where:

A_{665} = Absorbency at 665nm before acidification

A_{750} = Absorbency at 750 nm before acidification

A_{665a} = Absorbency at 665nm after acidification

A_{750a} = Absorbency at 750nm after acidification

Extract volume = 10ml 95% ethanol

Volume of sample` = Volume of water sample filtered in liters

f) **SAC 254**- Spectral absorption coefficient determination was done as described by Traut (2002). This gives an indication of the amount of dissolved organics present in the water. Ten milliliters of supernatant was filtered through a Whatman Membra-fil (MF) membrane made of mixed esters of cellulose with a pore size of 0.65µm. The absorbency of the membrane-filtered water was measured at 254nm using a Genysis II spectrophotometer and a quartz cuvettes. SAC 254 of the membrane-filtered water is taken to represent total particulate and dissolved organic matter, and is often used as a simple surrogate method for DOC. SAC 254 (m^{-1}) was calculated using the following formula:

$$\text{SAC 254}(\text{SAC } m^{-1}) = \frac{\text{ABSORBANCE (254nm) X 100(cm)}}{\text{1(cm: cuvette length)}}$$

g) **Dissolved Organic Carbon (DOC)**. Samples were collected and refrigerated.

Midvaal Laboratory Services using method number AAL, performed the DOC measurements every month. Midvaal Water Company supplied the following description of the method.

Total organic carbon (TOC) and dissolved organic carbon (DOC) determination by the Persulphate - ultraviolet oxidation method. Organic carbon is oxidized to carbon dioxide (CO_2) by persulphate in the presence of ultraviolet light. The UV light is submerged in a continuously gas - purged reactor that is filled with a constant-feed persulphate solution. A non-dispersive infrared analyser measures the CO_2 produced. The sample is introduced into the reactor by an automatic syringe injection. The CO_2 produced is sparged continuously from the solution and is carried in the gas stream to the infrared detector. The instrument's microprocessor calculates the area of the peaks produced by the analyser and compares them to the peaks of the calibration standard stored in memory.

The working range for total and dissolved organic carbon is 0.5 - 20mg/l for this method. The method detection limit is 0.5mg/l.

h) **Determination of Natural Organic Material (NOM)**. A High performance size exclusion chromatography (HPSEC) method was used to determine NOM present in the sampling water and was according to the work of Nissinen *et al.* (2000).

Before separation with HPSEC, the samples were filtered through a 0.45μm membrane. Molecules are separated using a TSK G300SW column (7.5mm X 300mm), and guard column TSK G3000SW (7.5mm X 70mm). TSK gel consists of porous silica with hydrophilic bonded phase, with rigid microparticulate packing. Sodium acetate (0.01M) was used as the effluent with a flow rate of 0.7-1ml/min. The pH of the sodium acetate was adjusted to 7.0 using acetic acid. The injection volume was 20-25μL. The samples were run in duplicate and the analysis time was 35min.
Molecular size calibration was done with polystyrene sulfonates, with molecular weight dispersity of 1,300-2,500,000 obtained from Separations.

i) **Algal identification and Enumeration:** The phytoplankton species composition was determined for the four sampling sites each month, using the method described by Kruskopf (2002). Between 1-5ml of sample water were pipetted into sedimentation tubes together with 2 drops formalin, then covered with distilled water and a glass slide. Gas vacuoles of the cyanobacteria were pressure-deflated in a steel-container. The sedimentation tubes were left for two days in a desiccator before analysing the samples. The enumeration was performed using an inverted Zeiss light microscope. The phytoplankton species present were then identified with the aid of algal key: "A photo guide to algal genera most commonly found in DWAF samples", Jansen Van Vuuren, S. *et al.* (2004). Where possible, cell enumeration was also conducted to determine the value of cells/ml and a species list was compiled for all four sites.

4.5: RESULTS AND DISCUSSSION

The data was analysed using several statistical programmes. Statistical analyses were done in Statistica for Windows version 7. Normality of the data was tested using Shapiro-Wilk's W Test. Since most of the data sets were not normally distributed, non-parametric tests such as Kruskal-Wallis ANOVA were performed. For multivariate analysis, Canoco for Windows version 4.5 was used to perform Principal Component Analysis (PCA) on the four sampling sites.
Graphical representations have been done is Statistica release 7 and Excel 2000 for Windows XP.
The results reported for seasons in the following section represent the following months:
Spring = September, October and November 2005, Summer= December, January and February 2006, Autumn= March, April and May 2006, Winter= June, July and August 2006

4.5.1: pH

The pH of a water body is a logarithmic expression of the hydrogen ion concentration in the water and reflects that degree of acidity (<7) or alkalinity (>7) (Quality of domestic water supplies 1 1998). The geology of the catchment area as well as the amount of dissolved salts affects the pH of the water. High rates of photosynthesis commonly cause a high pH value (Wetzel 2001). The

acceptable range for drinking water is 6.5-8.5 (Quality of domestic water supplies 1 1998).
The range of pH measured at the various sampling sites ranged from 7.66 to 9.97, with a maximum value of 9.97 recorded at Boskop Dam in November 2005 (Figure 4.3). The range of pH measured shows similar distribution to those recorded by Taylor (2004) and Janse van Vuuren (2001). Jansevan Vuuren (2001) noted that pH in the Middle Vaal River ranged between 7.0 and 10.0.

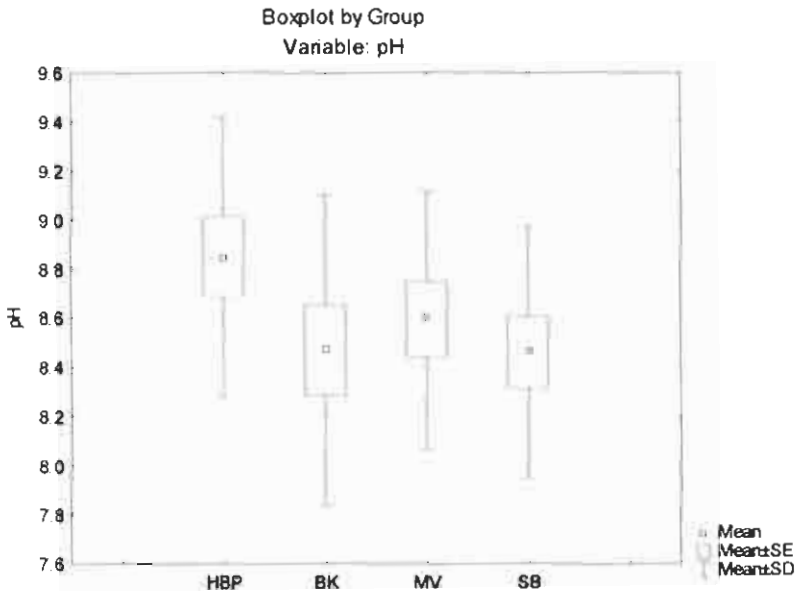


Figure 4.3: Variation in the pH ranges of the four sampling sites for a period of one year from October 2005 to September 2006 (n=12).
HBP=Hartbeespoort Dam, BK= Boskop Dam, MV=Midvaal and SB=Sedibeng.

4.5.2: Conductivity

Conductivity of water indicates the ease at which water conducts electricity as it estimates the total dissolved salts present in the water. We cannot, however, use the conductivity values measured because after month six of the experiment, the conductivity probe was found to be faulty and recalibrated.

4.5.3: Dissolved Oxygen

Oxygen dissolved in water is essential for metabolism of all aerobic aquatic organisms. The amount of oxygen present is governed by a balance between the amount required for respiration and the amount produced by photosynthesis (Wetzel 2001). Temperature affects the amount of dissolved oxygen and the solubility of oxygen decreases as temperature increases. The increase in organic material leads to increase in consumption of dissolved oxygen by bacteria that breakdown the material and lead to anoxic conditions that are detrimental to all aerobic organisms.

The concentrations of dissolved oxygen recorded for the dams are higher than those of the rivers. The values for the river sites range from 3.5-8.3mg/l O_2, with a mean of 5.69mg/l O_2. Hartbeespoort Dam shows similar results with a mean of 5.85mg/l O_2. The results for Boskop Dam are higher, but this may be because the values were recorded *in situ* at the site as can be seen in Figure 4.4. The other samples were delivered by courier and therefore show the value of the sample typically after 24 hours.

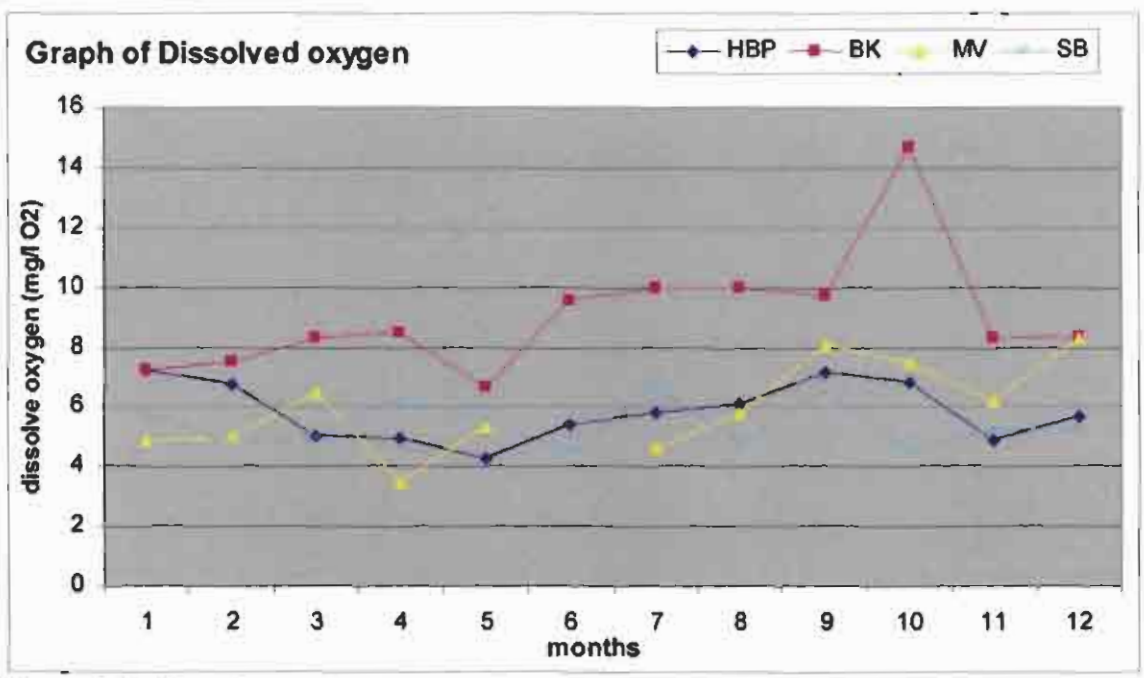


Figure 4.4: The change in dissolved oxygen of the four sample sites for a period of one year from September 2005 to August 2006. HBP=Hartbeespoort, BK=Boskop,MV=Midvaal, SB=Sedibeng.

4.5.4: Turbidity

Turbidity is defined as the light-scattering ability of water and is a measure of how clear or cloudy the sample is (Quality of domestic water supplies 1 1998). Turbidity is caused by the presence of suspended solid matter and gives an indication of the amount of suspended particles present in the sample. Turbidity varies from <1 NTU in spring waters to many hundreds or even thousands of NTU in muddy water that is laden with sand after a storm. Acceptable levels of turbidity for drinking water are 0-1 NTU (Quality of domestic water supplies 1 1998).

As seen in Figure 4.5, the dam and riverine sites differ in turbidity values. Typically dams have lower turbidity values as most of the suspended particles have time to settle and become part of the sediment. Boskop dam shows very low turbidity throughout the year with an average value of 3.32 NTU. There was a slight increase observed in January 2006 during the rainy season, with a

maximum of 5.15 NTU. Hartbeespoort dam has a moderate turbidity with an average of 9.32 NTU. There are increases in turbidity during January to March 2006 due to the rainy season with a maximum of 28 NTU observed in February 2006. There are also higher turbidity values during June and July 2006 averaging 17 NTU. This is due to the presence of *Microcystis* sp. forming extensive blooms and imparting a green colour to the water.

The two riverine sites show much higher turbidity values especially during the rainy season when large amounts of sand, silt and organic matter are suspended in the river (Figure 4.7). The values for Midvaal range from 6.15 NTU to a maximum of 224 NTU during February 2006 at the height of the rainy season, when the river water was brown in colour. Sedibeng had values ranging from 3.47 NTU to a maximum of 112 NTU in March 2006.

There was an observed seasonal change in turbidity in all four sampling sites as seen in Figure 4.6. During spring, turbidity was low before the rains. During summer and autumn, there was an increase in turbidity due to high rainfall, especially in the riverine sites. This is expected because rivers have more suspended particles than dams where the particles have time to sediment out. Turbidity decreased again in winter, this time due to lack of rains.

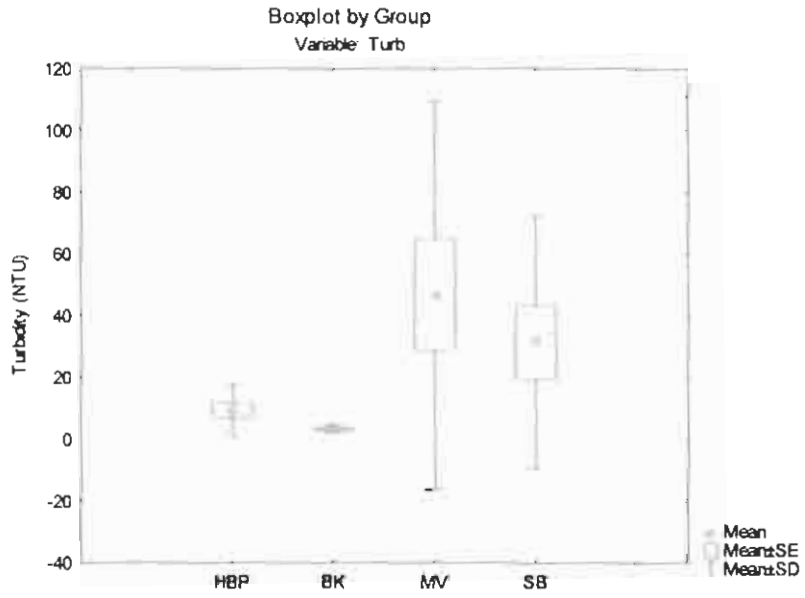


Figure 4.5: Variation in the turbidity of the four sampling sites for a period of one year from October 2005 to September 2006 (n=12)

HBP=Hartbeespoort Dam, BK= Boskop Dam, MV=Midvaal and SB=Sedibeng.

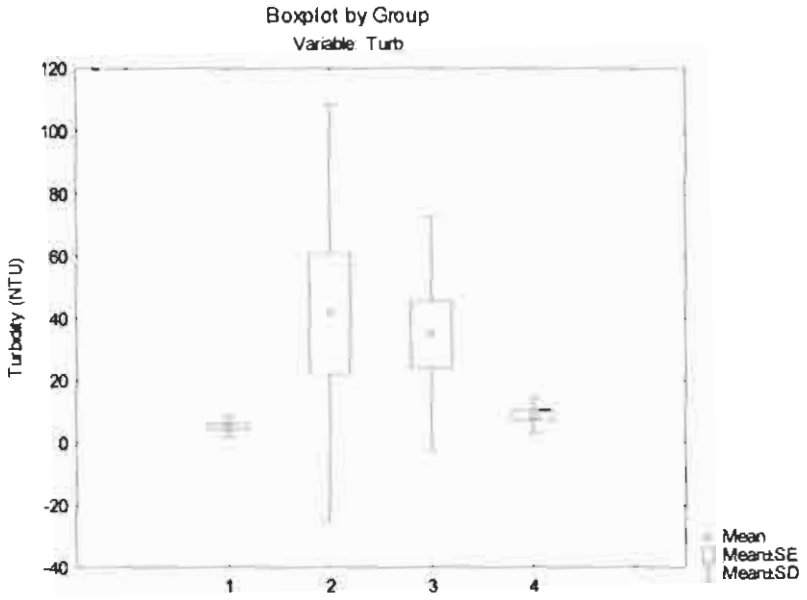


Figure 4.6: Variation in the turbidity of the four seasons for a period of one year from October 2005 to September 2006 (n=12)

Var1= Spring, Var2=Summer, Var3=Autumn and Var4=Winter.

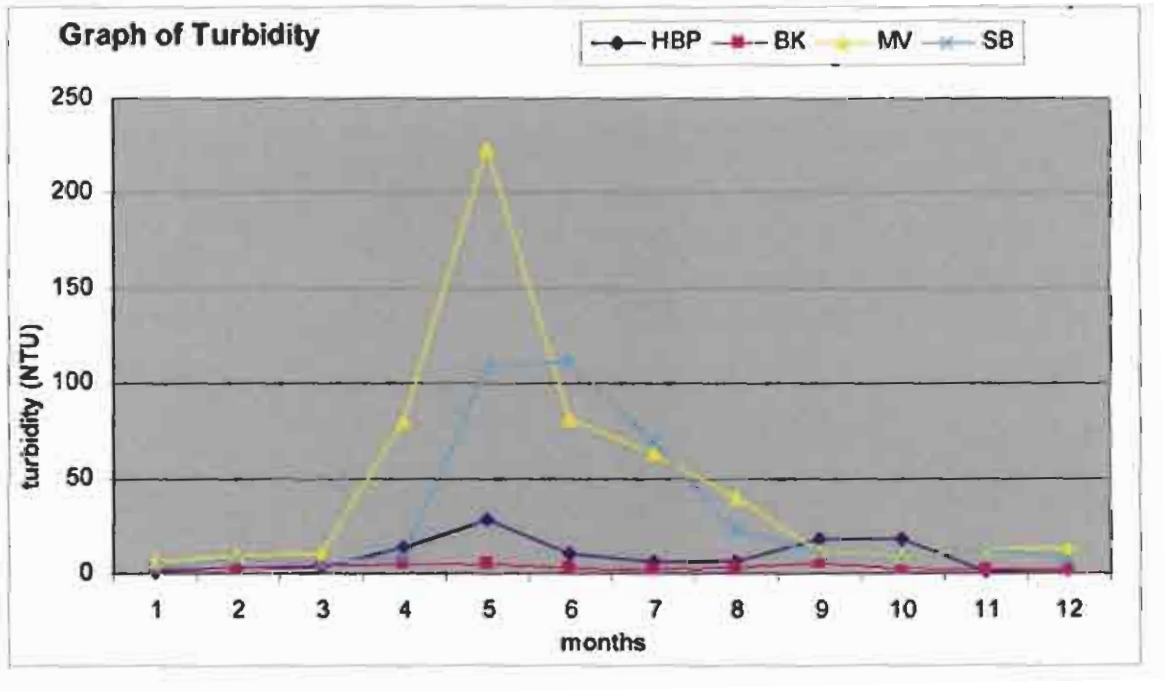


Figure 4.7: The change in turbidity of the four sample sites for a period of one year from October 2005 to September 2006. HBP= Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng

4.5.5: SAC 254

Organic compounds commonly found in water strongly absorb ultraviolet (UV) radiation. UV absorption is therefore a useful surrogate measure of selected organic constituents in water (Standard Methods 1995). This parameter is called UV $_{254}$ or SAC254, as the wavelength of UV light used is 254 nm. SAC254 can be used as a measure for DOC, but good correlation can only be obtained with similar water quality as it only includes the more complex nature of NOM present (Natural Organic Matter 2006). This method requires simple instrumentation and is simple to perform by operators in the treatment plant and is therefore widely used to indicate the presence of organics compounds.

As seen in Figure 4.8, the SAC254 results for Hartbeespoort Dam show a minimum of 16m^{-1} from May to September 2006, and a maximum of 26.5m^{-1} in December 2005 and an average value of 18.67 m^{-1}. Boskop dam exhibited the lowest values with a maximum of 15 m^{-1} in October 2005, a minimum of 9.15 m^{-1} in July 2006, and an average of 12.06 m^{-1}. The maximum value was observed when the water level was at its lowest.

Both riverine sites had higher average values than the dams. Midvaal had a maximum of 108.75m^{-1} during February 2006, a minimum of 21.1 m^{-1} in June 2006 and an average value of 36.53 m^{-1}. Sedibeng had a maximum of 39.3 m^{-1} in March 2006, a minimum of 19 m^{-1} in August 2006 and an average of 26.35 m^{-1}.

Figure 4.7 and Figure 4.10 show the general trends in change in turbidity and SAC254 for the duration of the study. There is a good correlation between these two variables for Midvaal and Sedibeng, with a correlation value of 0.92, n=12. However, there is little or no correlation between turbidity and SAC254 for the dam sites.

There is a seasonal variation in SAC254 with lower values for spring and winter and much higher values for summer and autumn as can be seen in Figure 4.9.

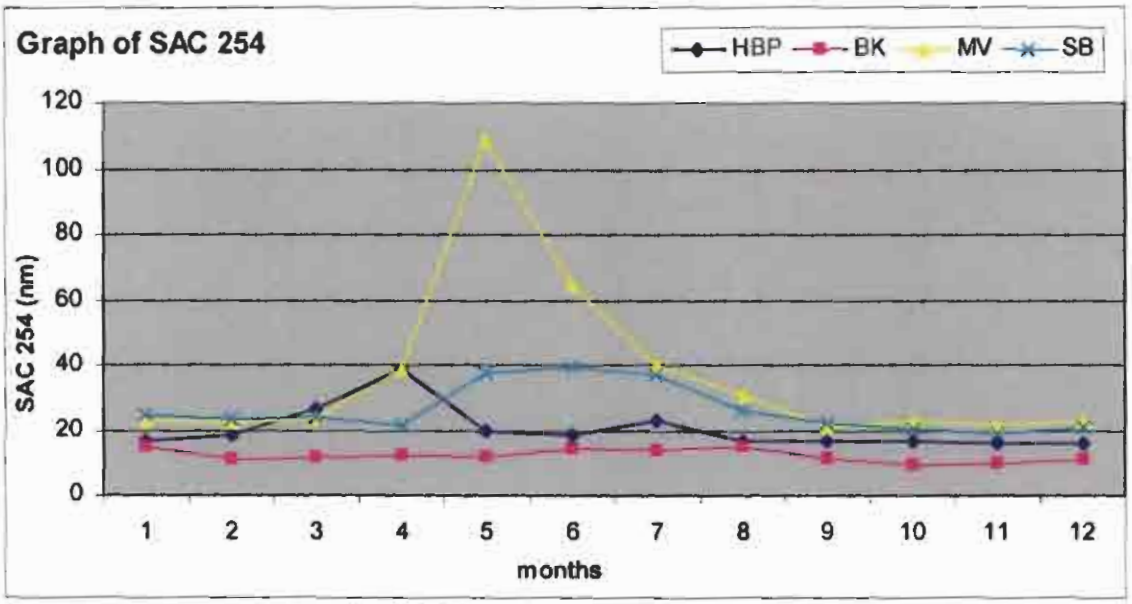


Figure 4.10: The change in SAC254 of the four sample sites for a period of one year from October 2005 to September 2006. HBP=Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng

4.5.6: Chlorophyll-*a* concentration and Algal Species Composition

Chlorophyll-*a* concentration is the primary photosynthetic pigment of all oxygen-evolving photosynthetic organisms and the measure of chlorophyll-*a* present in the water gives an indication of algal biomass. The composition of algal species in a water body is dependant on the environmental conditions in that body of water. They have different physiological requirements and vary in response to several parameters including light, temperature and nutrients available (Wetzel 2001). Therefore, the observed algal species composition is directly related to the chlorophyll-*a* values .DWAF (1993), states that chlorophyll-*a* concentrations in raw water vary from 1μg/l in clear water to over 50 μg/l in conditions of algal blooms. Walmsley (2000) noted that mean annual chlorophyll-*a* value between 8-25 μg/l and annual maximum of 25-75μg/l indicate eutrophic conditions. Figure 4.11 shows the variation observed in the chlorophyll-*a* values of the four sampling sites. Boskop Dam shows very low chlorophyll-*a* values with either zero or 28.66μg/l. This is as expected because of its status as a mesotrophic dam with moderate productivity. The algal species present were mainly of the class Bacillariophyceae (diatoms) and Chlorophyceae (green algae), the former were dominant because sampling was conducted close to the shore near shallow rocks where benthic forms of diatoms are common. In November 2005, *Spirogyra* sp. was present in large amounts on the banks of the dam with Cynaophyceae species such as *Anaebena* sp.and *Arthrospira* sp. present as well.

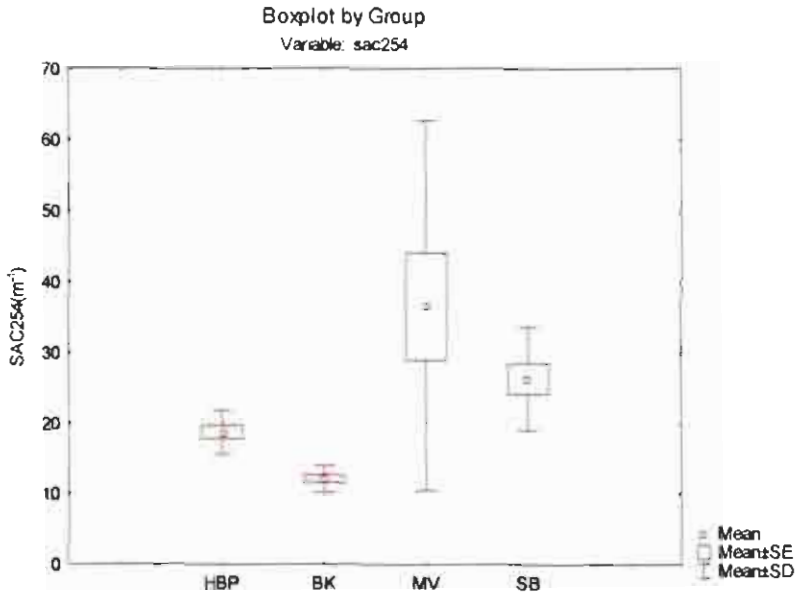


Figure 4.8: Variation in the SAC254 of the four sampling sites for a period of one year from October 2005 to September 2006 (n=12)

HBP=Hartbeespoort Dam, BK= Boskop Dam, MV=Midvaal and SB=Sedibeng

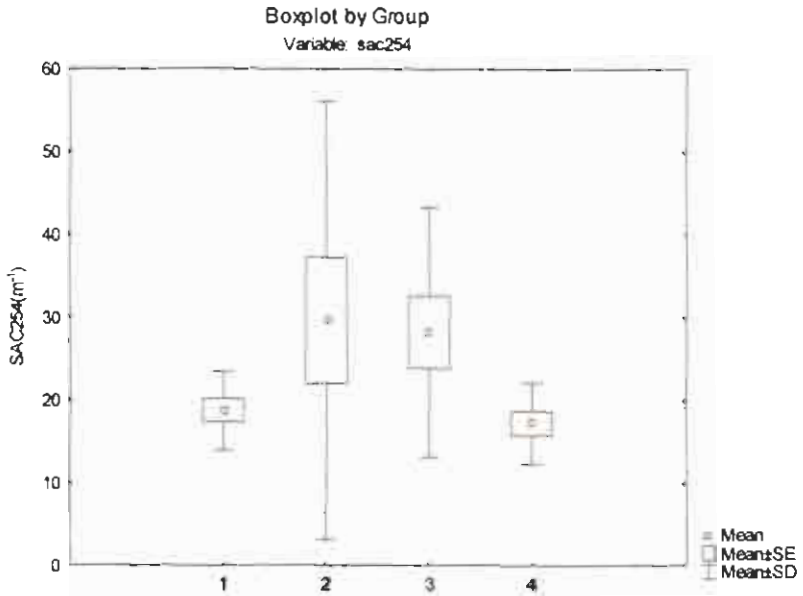


Figure 4.9: Variation in the SAC254 of the four seasons for a period of one year from October 2005 to September 2006 (n=12)

Var1= Spring, Var2=Summer, Var3=Autumn and Var4=Winter

Hartbeespoort Dam is a eutrophic dam and shows high chlorophyll-*a* values with an average of 78.81µg/l and a maximum of 171.96µg/l in June 2006. Values higher than 28.66µg/l occur from November 2005 to July 2006 when there were blooms of *Microcystis sp.* Hartbeespoort dam receives water from the Crocodile River that is rich in phosphorous and nitrogen. One can speculate that in summer, the deeper layers of the dam become anoxic and cause the nutrients that are trapped in the sediment to be released (Dower 2005). *Microcystis* sp. produces gas vacuoles, which help them to move vertically in the water and utilise all the available nutrients including those from the sediment. This leads to the formation of dense blooms of *Microcystis* sp. under warm conditions. However, when they move to the surface, they become photo-oxidised and start to decompose. This adds to the formation of algal scums that give off offensive smells (Dower 2005). Hartbeespoort Dam had a maximum chlorophyll-*a* value of 171.96µg/l in February 2006 and June 2006. This corresponds to >100 000 cells/ml of *Microcystis* sp. being present in the sample. Colonies were made up of thousands of cells and could be viewed with the naked eye, and gave a greenish tint to the sample. August and September 2006 had low values because of the absence of the cyanobacteria: the water was clear with no visible colonies. In the absence of *Microcystis* sp., several Chlorophyceae species were present, notably *Cosmarium* sp. and *Ankyra* sp. during November 2005.

The chlorophyll-*values* of the rivers were variable. Midvaal results show an average value of 90.75µg/l but there is a distinct decrease noticed during the rainy season from January to April 2006. The minimum observed value was zero in March 2006 and the highest values were observed in December 2005, June and September 2006 respectively, with a maximum of 257.94µg/l in September 2006. These values correspond to algal blooms of *Cyclotella* sp. with approximately 2000-10 000 cells/ml, which resulted in the water having a yellowish tint. *Aulacoseira* sp. was dominant in November and December 2005 while several Chlorophyceae were also present at the same time. The diatom *Surirella* sp. was observed in July 2006 with a concentration of 533 cells/ml. Sedibeng had high values in December/January 2005, May/June and August/September 2006, but the values were lower than those observed for Midvaal (Figure 4.13). The average value for Sedibeng was 57.32µg/l. The minimum was 28.66µg/l and the maximum value was 114.64µg/l in May and September 2006. There was greater variation in algal species composition of Sedibeng compared to that of Midvaal. In December 2005, the dominant algae were *Aulacoseira* sp. and *Cyclotella* sp. In January, *Chlorella* sp. was present in concentrations of 8368 cells/ml as well as large numbers of *Aulacoseira* sp. and *Cyclotella* sp. In May, June and July 2006, *Cyclotella* sp. was dominant. In September 2006, the class Chlorophyceae dominated with *Actinastrum* sp., *Coelastrum* sp. and *Scenedesmus* sp. Both Midvaal and Sedibeng show algal blooms of the class

Bacillariophyceae. *Aulacoseira* sp. is a pennate, filamentous diatom and *Cyclotella* sp. is a centric diatom that is planktonic. Janse van Vuuren (2001) found that diatoms were the main phytoplankton groups in the Middle Vaal River, and there was a succession between unicellular centric species like *Cyclotella* sp. and *Aulacoseira* sp. Both these species are also indicative of eutrophic conditions (Janse van Vuuren 2001). In the Vaal River System, cyanobacteria and *Aulacoseira* sp. often dominated during warm water summer periods and were replaced as the dominant species by unicellular centric diatom species when the water temperature was low during the winter and spring (Janse Van Vuuren, 2001). This statement is in agreement with our observations, which show an increase in *Cyclotella* sp. during winter from May to September, and *Aulacoseira* sp. dominated in summer from October to January. There were no blooms from February to April 2005 because of high rainfall and a dramatic increase in turbidity of the Vaal River due to sand and silt. There was little seasonal variation in chlorophyll-*a* values for the sites, with a slight decrease in winter as seen in Figure 4.9.

Figure 4.14 shows the PCC ordination for the species composition of the sampling sites. Boskop Dam is not included because there were very few species present in the sample as can be seen by the low chlorophyll-*a* values. The sample was taken close to the banks of the river and those species found were examples of benthic diatoms. Hartbeespoort Dam shows close association to the presence of Cyanophyceae species especially *Microcystis* sp. which dominated in the samples for most of the year along with Chlorophyceae species of *Ankyra* sp. and *Cosmarium* sp.. Janse van Vuuren (2001) noted that the abundance of Cyanophyceae is indicative of eutrophic water bodies, of which Hartbeespoort Dam is a prime example.

Midvaal and Sedibeng water associate with high concentrations of Bacillariophyceae species especially *Cyclotella* sp. and *Aulacoseira* sp. Both these species are also indicative of eutrophic conditions (Janse van Vuuren 2001). *Cyclotella* sp. is also an indicator of high levels of TDS in the river. *Aulacoseira* sp. dominates during the warmer periods of summer and is replaced as the dominant species in the Vaal River system, by centric diatoms such as *Cyclotella* sp. during the periods when the temperatures are lower. This is in agreement with the results reported by Janse van Vuuren (2001). Sedibeng and Midvaal shows close association with several species of Chlorophyceae which were present in the samples for most of the year. Cyanophyceae members, *Ankyra* sp. and *Cosmarium* sp., lie close to the first axis that explains 25.6% of the variation. The second axis explains 49.9% of the variation in the data and is associated with Chlorophyceae and Bacillariophyceae. Green algae are able to tolerate a wider temperature range than other classes and are found in most parts of the world (Wetzel 2001). A complete list of algal species present in the sample sites is given in Table 4.1.

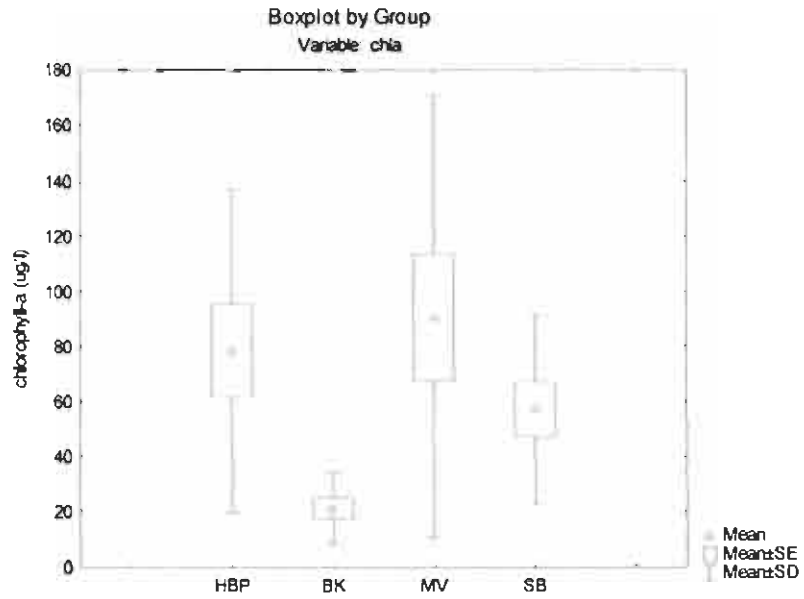


Figure 4.11: Variation in the Chlorophyll-*a* concentration of the four sampling sites for duration of one year from October 2005 to September 2006 (n=12)
HB=Hartbeespoort Dam, BK=Boskop Dam, MV=Midvaal and SB=Sedibeng.

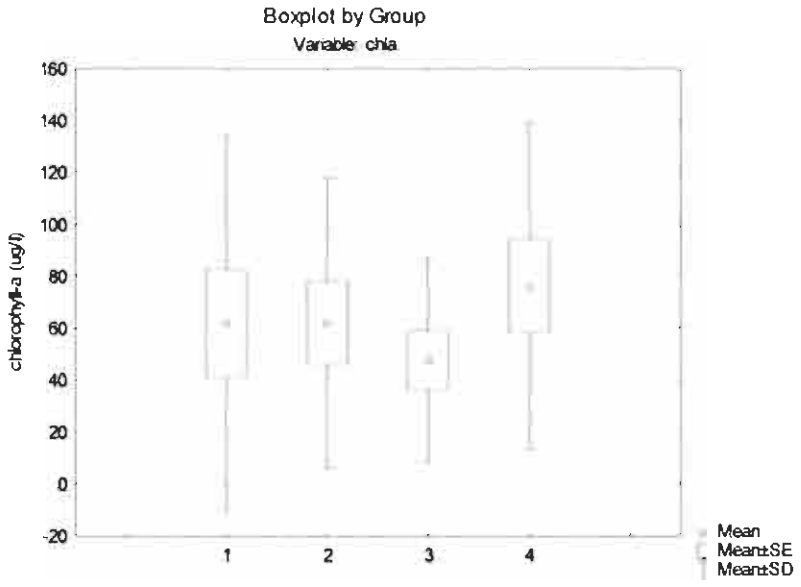


Figure 4.12: Variation in the Chlorophyll-*a* concentration of the four seasons for the duration of one year from October 2005 to September 2006 (n=12)
Var1=Spring, Var2=Summer, Var3=Autumn and Var3=Winter.

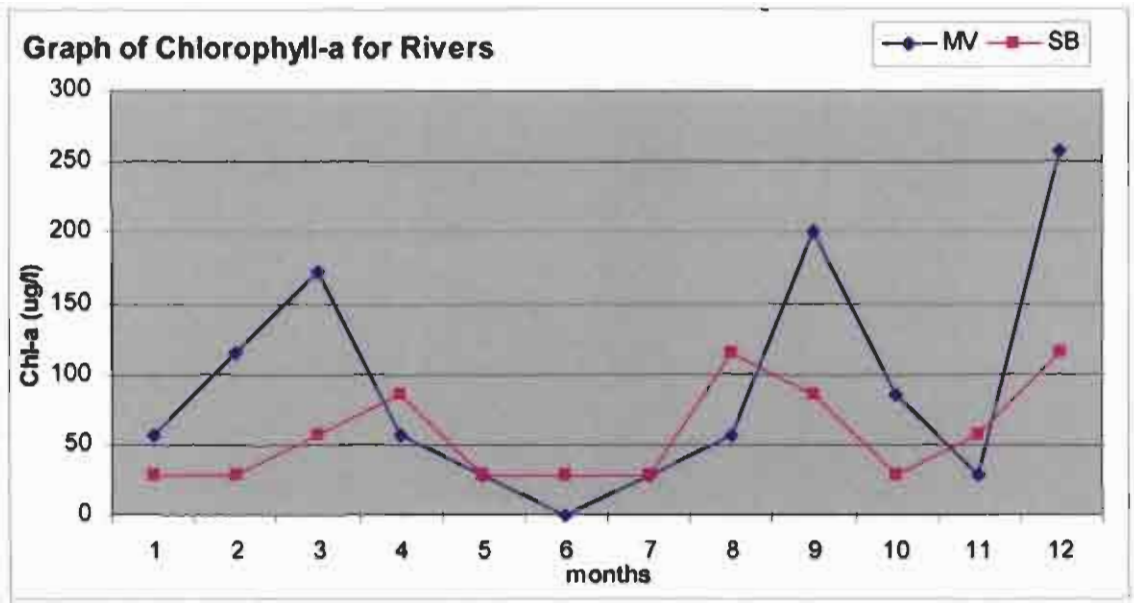
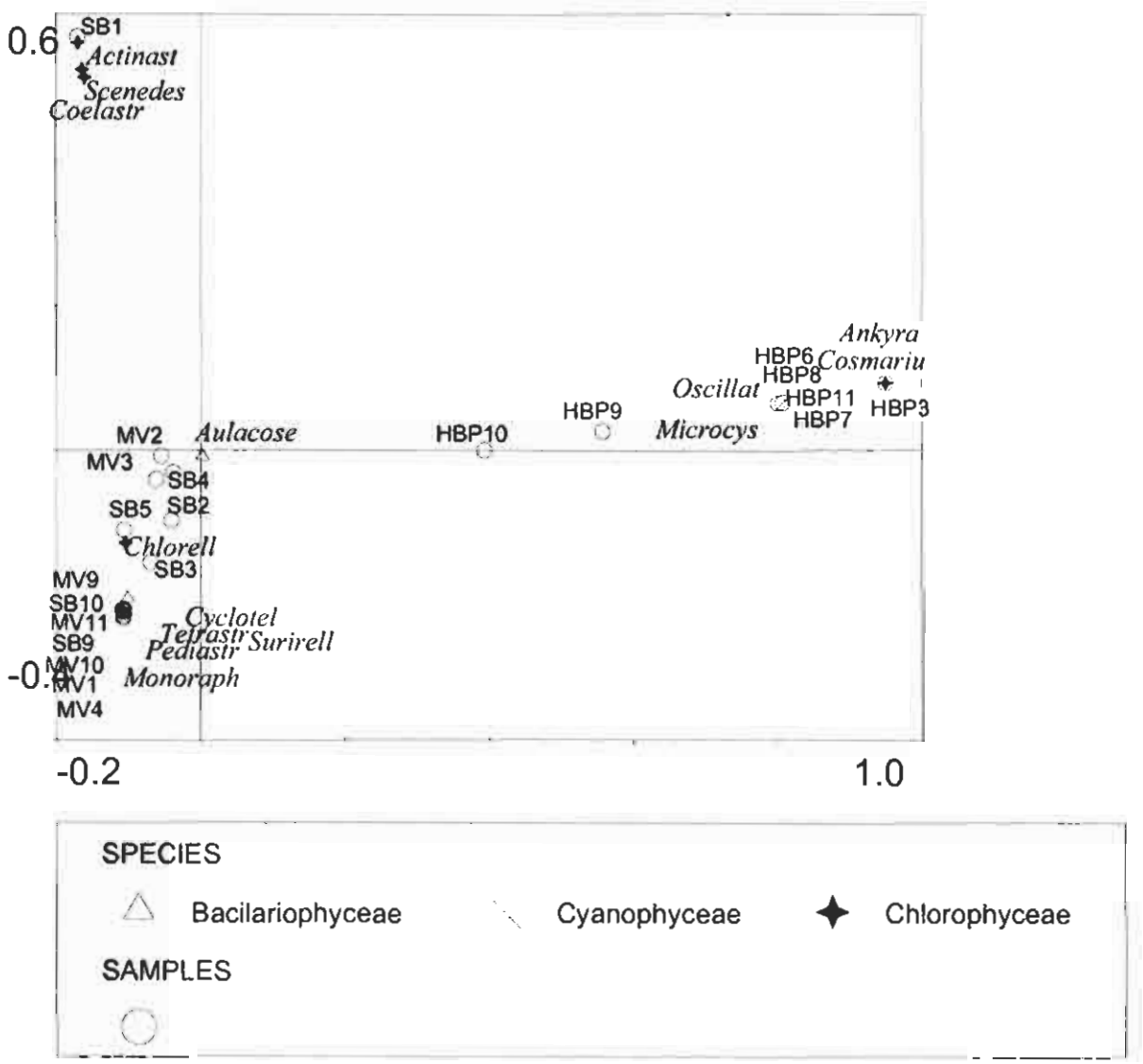


Figure 4.13: The change in chlorophyll-*a* of the two river sites for a period of one year from October 2005 to September 2006. MV=Midvaal, SB=Sedibeng.



Axes		1	2	3	4	Total inertia
Eigenvalues	:	0.943	0.895	0.660	0.614	3.684
Cumulative percentage variance of species data	:	25.6	49.9	67.8	84.5	
Sum of all eigenvalues						3.68

Figure 4.14: PCC ordination biplot showing the algal species composition for Hartbeespoort Dam, Midvaal and Sedibeng for the duration of one year from October 2005 to September 2006. The Eigenvalues for the PCC are given above. Explanation is given in 4.5.6 HBP=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng.

Table 4.1: List of algal species identified from water samples collected at Boskop Dam (BK), Midvaal (MV), Sedibeng (SB), and Hartbeespoort Dam (HBP) from September 2005 to September 2006, and their presence at the different sampling locations. The "Unit" column indicates whether the species was found as cells (cell), filaments (fil), or colonies (col).

Class	BK	MV	SB	HBP	Unit
BACILLARIOPHYCEAE					
Aulocoseira	X	X	X	X	fil
Cyclotella	X	X	X	X	cell
Cymbella	X	X	X		cell
Diadesmus	X				cell
Diatoma	X				cell
Fragilaria	X				cell
Gomphonema	X				cell
Gyrosigma	X				cell
Navicula	X	X	X	X	cell
Nitzchia	X	X	X	X	cell
Pleurosigma			X		cell
Sellaphora			X		cell
Surirella		X			cell

Class	BK	MV	SB	HBP	Unit
CHLOROPHYCEAE					
Actinastrum	X	X	X	X	col
Ankyra			X	X	cell
Carteria			X		cell
Chlamydomonas	X	X	X		cell
Chlorella	X	X	X	X	cell
Coelastrum	X	X	X	X	col
Cosmarium				X	cell
Micractinium	X	X			col
Microspora				X	col
Monoraphidium	X	X	X		cell
Pandorina		X	X		col
Pediastrum	X	X	X	X	col

Scenedesmus	X	X	X	X	col

Class	BK	MV	SB	HBP	Unit
Spirogyra	X				fil
Straurastrum	X	X			cell
Tetraedron	X				col
Tetrastrum			X		col
Treubaria		X			cell
Zygnema				X	fil
CHRYSOPHYCEAE					
Mallamonas	X				cell
Dinobryon	X				col
CRYPTOPHYCEAE					
Cryptomonas	X		X	X	cell
CYANOPHYCEAE					
Anabaena	X			X	fil
Merismopedia	X	X			col
Microcystis				X	col
Oscillatario				X	fil
Spirulina	X				fil
DINOPHYCEAE					
Ceratium				X	cell
Peridinium	X	X			cell
Sphaerodinium	X				cell
EUGLENOPHYCEAE					
Trachelemonas		X		X	cell

4.5.7: DOC

Dissolved organic carbon (DOC) is used to describe the organic material from plants and animals that is dissolved in water. DOC comes from allochthonous sources derived from soils and vegetation as well as autochthonous sources derived from stream biota such as algae. DOC is an important component of the carbon cycle. It is a primary food source in the aquatic food web and may affect light and acid-base chemistry as well as complex with trace metals (Dissolved organic carbon 2006). The limit of DOC for drinking water is 0-5mgC/l (Quality of domestic water supplies 1 1998). There was little variation in the DOC values for all the sites with an average value of 7.43mgC/l (Figure 4.15). Although Boskop had the lowest average DOC of 6.15mgC/l, it also exhibited the highest DOC value of 24mgC/l in October 2005. Midvaal and Sedibeng have very similar DOC values that increased slightly in February and March 2006 and again in September 2006. Hartbeespoort Dam has an average DOC of 7.33mgC/l and a maximum of 9.2mgC/l in November 2005. There is a seasonal change in DOC with an increase in summer as seen in Figure 4.16. This is due to the summer rains that contribute to allochthonous input of organic carbon.

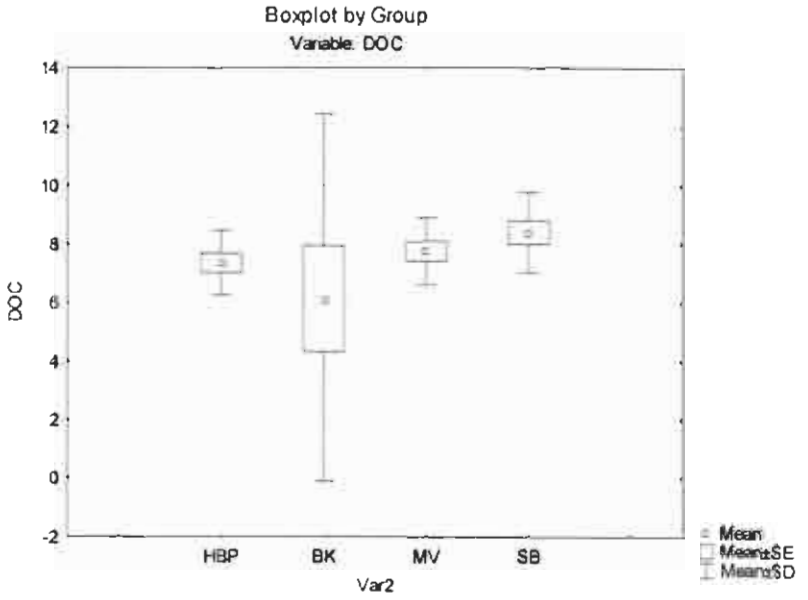


Figure 4.15: Variation in the DOC of the four sampling sites for the duration of one year from October 2005 to September 2006 (n=12)

HB=Hartbeespoort Dam, BK=Boskop Dam, MV=Midvaal and SB=Sedibeng

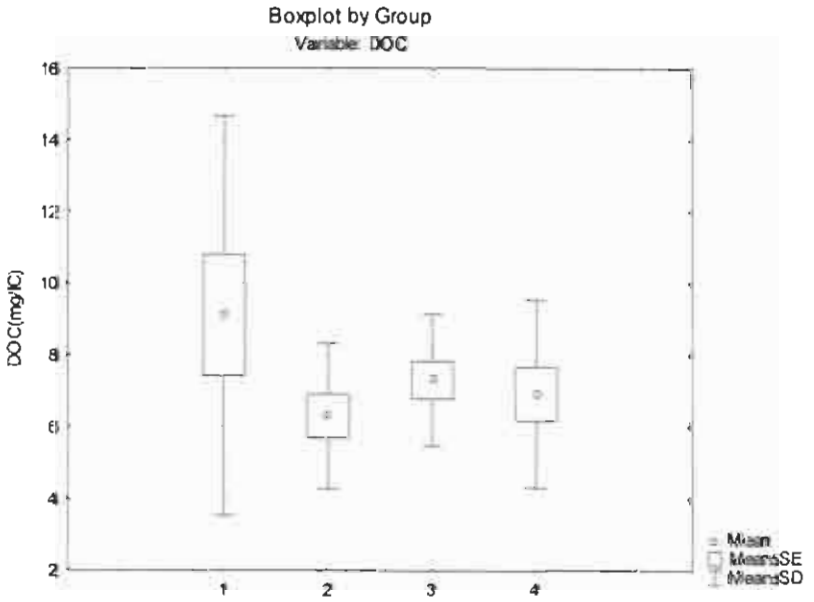


Figure 4.16: Variation in the DOC of the four seasons for the duration of one year from October 2005 to September 2006 (n=12)

Var1=Spring, Var2=Summer,Var3=Autumn and Var4=Winter.

4.5.8: Natural Organic Matter (NOM)

The NOM of the four sample sites were characterised by HPSEC on the basis of molecular weight distribution. This technique focuses on the high molecular humic fraction that forms 70-80% of soils and water (Wetzel 2001). The typical chromatogram obtained for natural organic matter shows six distinct peaks, which represent six fractions, based on different molecular weights (Vuorio *et al.* 1998). The sum of all the peak heights in the chromatogram represents the total amount of NOM in the sample (Matilainen *et al.* 2002). An example of the chromatography picture is given below in Figure 4.17. The fractions obtained can be classified as follows:

High Molecular Weight (HMW)	= Fraction I + Fraction II
Intermediate Molecular Weight (IMW)	= Fraction III + Fraction IV
Low Molecular Weight (LMW)	= Fraction V + Fraction VI

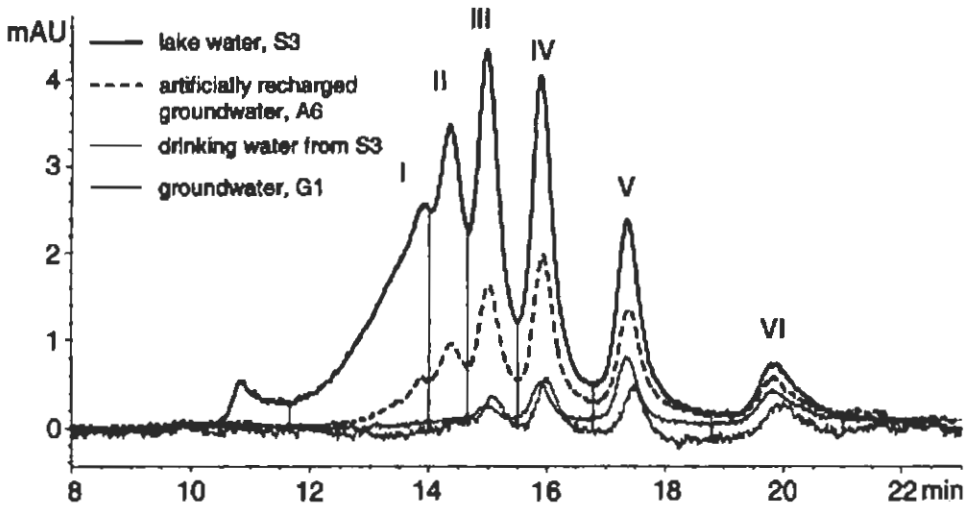


Figure 4.17: Typical chromatograms of humic fractions of lake water (S3), artificially recharged groundwater (A6), groundwater (G1), and drinking water originating from surface water (S3) (Nissinen *et al.* 2001).

According to Nissinen *et al.* (2001), the percentage of the two largest molecular size fractions (I and II=HMW) is higher in rivers than in lakes, whereas in lakes the percentages of the two smallest fractions (V and VI=LMW) were somewhat higher than in rivers. The sum of the fractions was higher in rivers than in lakes as well. The observation that raw water from rivers consisted mainly of larger molecular size fractions was shared with Vuorio *et al.* (1998).

It is therefore expected that the fractions present in each sampling site will differ from site to site.

Aquatic ecosystems are open and require a continual input of energy in the form of organic matter that usually comes from terrestrial sources. This non-living organic matter is degraded and contributes to the primary production of aquatic ecosystems. The productivity of aquatic systems is therefore generally low to intermediate, depending on the amount of organic matter coming into the system (Wetzel 2001). The sum of NOM present gives an indication of the amount of organic material that is present to form detritus. Detritus consists of all dead particulate and dissolved organic matter, which is the primary source of organic carbon for aquatic ecosystems. Most of the biotic metabolism that occurs in aquatic systems is supported by this organic material that originates from allochthonous sources and is imported into rivers and dams- this the NOM. NOM is therefore important for primary productivity and is a major source of organic carbon in aquatic systems. The NOM present is changed from HMW and IMW to LMW fractions. The humic substances that constitute NOM are recalcitrant to biological degradation and persist in the water body for a long time, usually days and weeks (Wetzel 2001).

The percentage contribution of each molecular weight fraction is important to water purification processes because the removal efficiency of each fraction is different. HMW fraction is more amenable to removal than LMW. Also, water with HMW is a good candidate for chemical coagulation. The LMW is more adsorbable, probably because more surface area is accessible to the coagulant (Matilainen *et al.* 2002).

The sample sites were examined for NOM composition and the sum of the NOM as well as the percentage contribution of each fraction to the total NOM was determined.

Figure 4.18 to Figure 4.22 as well as Figure 4.26, show the change in the sum of the NOM for the four sampling sites. It can be observed that the sum of NOM for the riverine sites shows higher values than of the dam sites. Midvaal had an average value of 75.97, a minimum value of 14.13 in June 2006 and a maximum value of 127.20 in August 2006. The minimum observed value could be due to an experimental error as it deviates from the rest of the observed data. Excluding that value changes the average to 81.59, with a minimum of 64.88. Sedibeng had an average value of 69.95 with a minimum value of 42.01 observed in July 2006 and a maximum value of 89.92 observed in March 2006. These values indicate that there is an influx of organic matter into the riverine system which can promote primary production.

The sum of NOM for Hartbeespoort dam was slightly lower with an average value of 59.95, a minimum value of 43.24 in December 2005 and a maximum value of 113.93 observed in August 2006. This shows that Hartbeespoort Dam receives NOM comparable to the rivers and therefore has enough organic matter to support the high primary productivity found in such a eutrophic impoundment. However, the eutrophic status of the dam is based on the influx of nutrients such as

phosphorous and nitrogen, not only on NOM present.

Boskop dam had the lowest values with an average value of 22.80, minimum value of 6.16 in December 2005 and a maximum value of 65.67 observed in January 2006. This high value could be due to high rainfall at that time resulting in an influx of NOM. Therefore the amount of available organic matter for primary production is low and this is demonstrated by the low chlorophyll-*a* values.

There is little seasonal variation in the sum of NOM values. The average value for all seasons is 57.17. Average values for spring and summer are 55.57 and 54.28 with a slight increase in the average to 63.22 during autumn. In winter there was a decrease in the average value to 55.60. This shows that the sum of NOM present in the sampling sites remains fairly constant.

Figures 4.19 to 4.22 give a graphical representation of the distribution of the 3 fractions of NOM present in Hartbeespoort Dam, Boskop Dam, Midvaal and Sedibeng. In general, the riverine sites show a larger percentage of HMW and IMW fractions of NOM than the dam sites that have higher percentages of IMW and LMW fractions of NOM. Boskop Dam is characterised by the highest percentage LMW fraction of NOM for all the sampling sites.

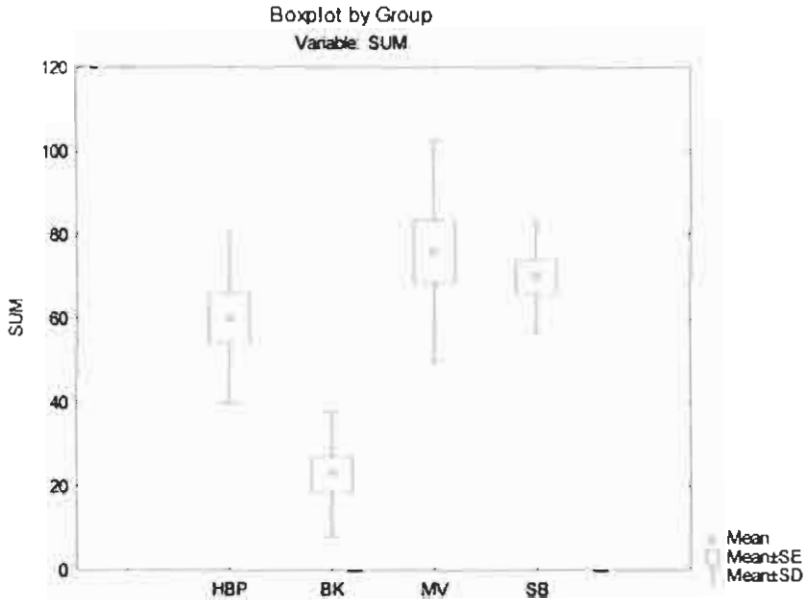


Figure 4.18: Variation in the Sum of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12)
HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng.

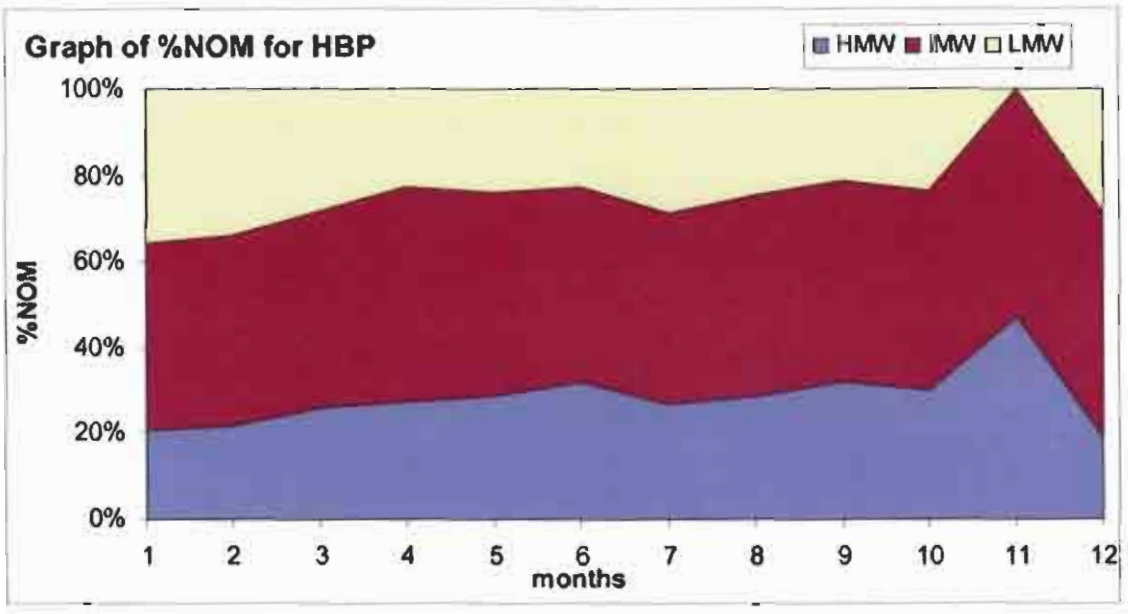


Figure 4.19: Percentage composition of the %NOM for Hartbeespoort dam for a period of one year from October 2005 to September 2006.

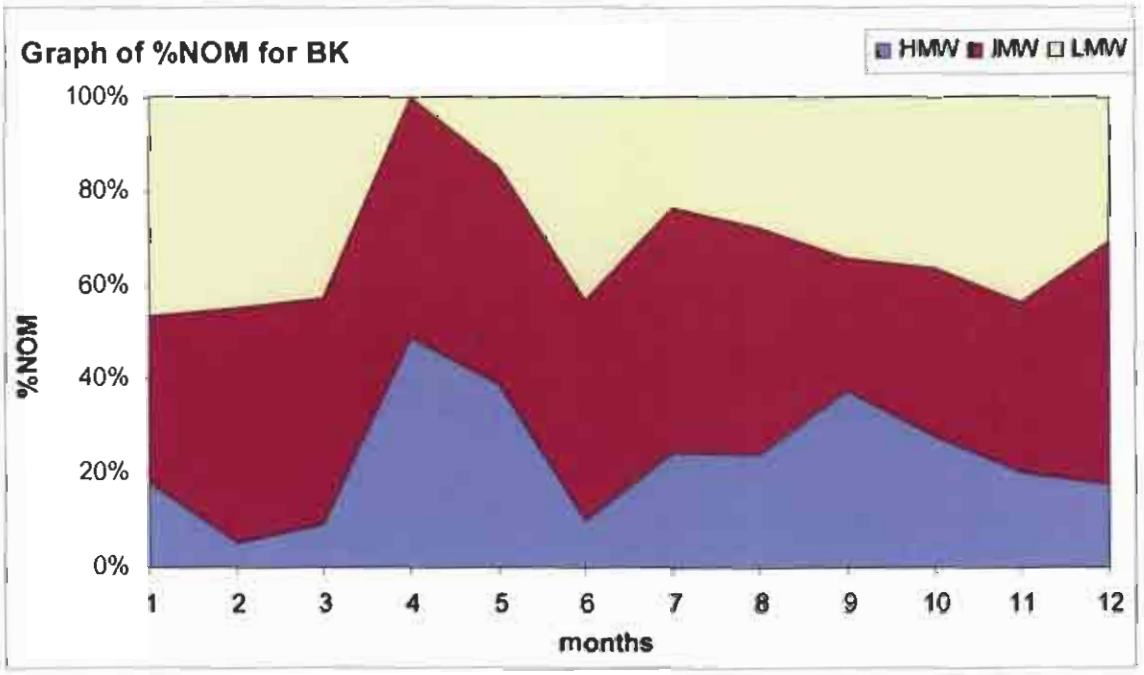


Figure 4.20: Percentage composition of the %NOM for Boskop dam for a period of one year from October 2005 to September 2006

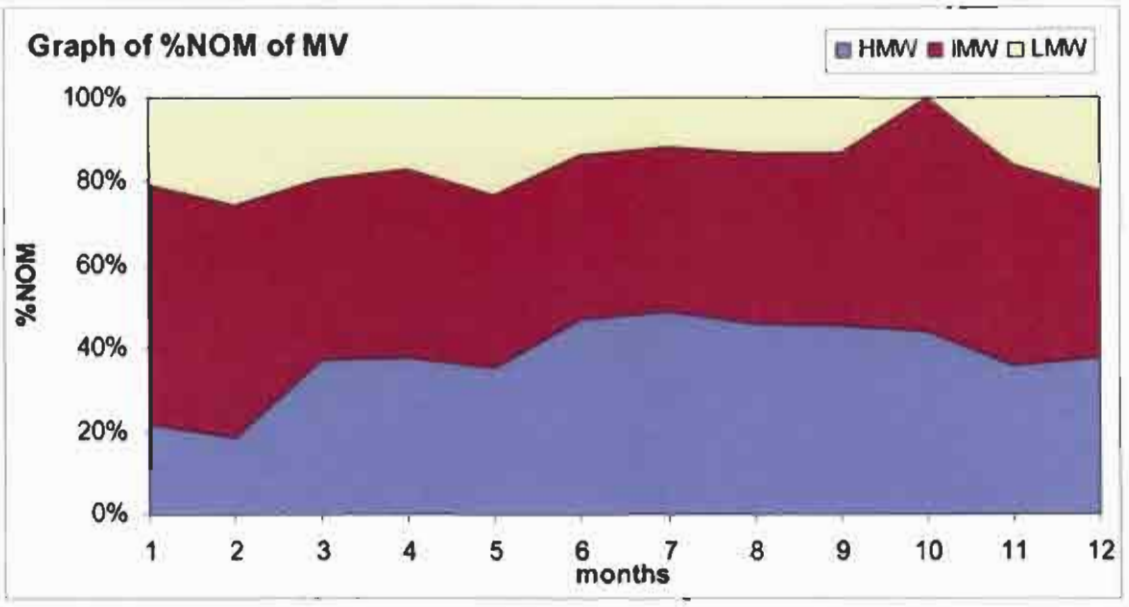


Figure 4.21: Percentage composition of the %NOM Midvaal dam for a period of one year from October 2005 to September 2006.

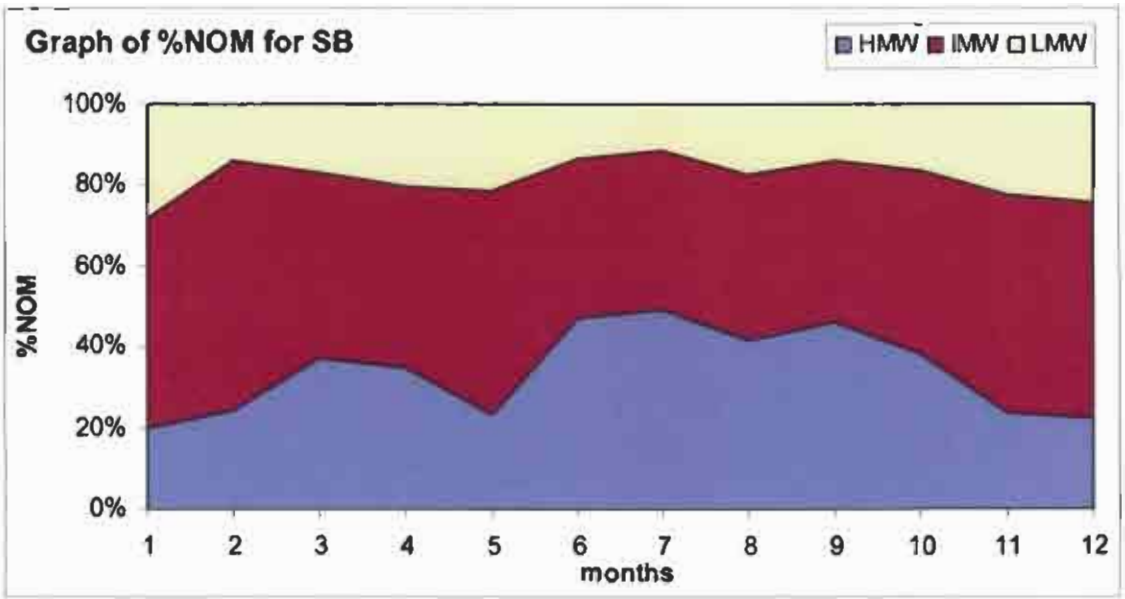


Figure 4.22: Percentage composition of the %NOM for Sedibeng for a period of one year from October 2005 to September 2006.

A) High Molecular Weight Fraction (HMW)

The percentage contributions of the HMW fraction to the total NOM show that the riverine sites have a higher percentage HMW than the dam sites (Figure 4.23). The average percentage HMW for Boskop Dam is 23.4% indicating that Boskop Dam has a low overall HMW fraction. However, in December 2006, the percentage HMW fraction increased to 50%, and this is probably due to heavy rains at the time of sampling. Hartbeespoort Dam has an average percentage HMW of 28.21%. Midvaal and Sedibeng, the riverine sites, have higher percentage HMW fractions with values of 37.96% and 33.92% respectively.

The percentage contribution of the HMW fraction to the total sum of NOM shows a low value of 25% for spring due to low water levels and no rainfall in the previous months. Once the rains began in summer, the percentage HMW fractions increased to 38% and 40 % respectively during summer and autumn. This decreased to 35% in winter once some of the HMW fraction had settled out of the water column.

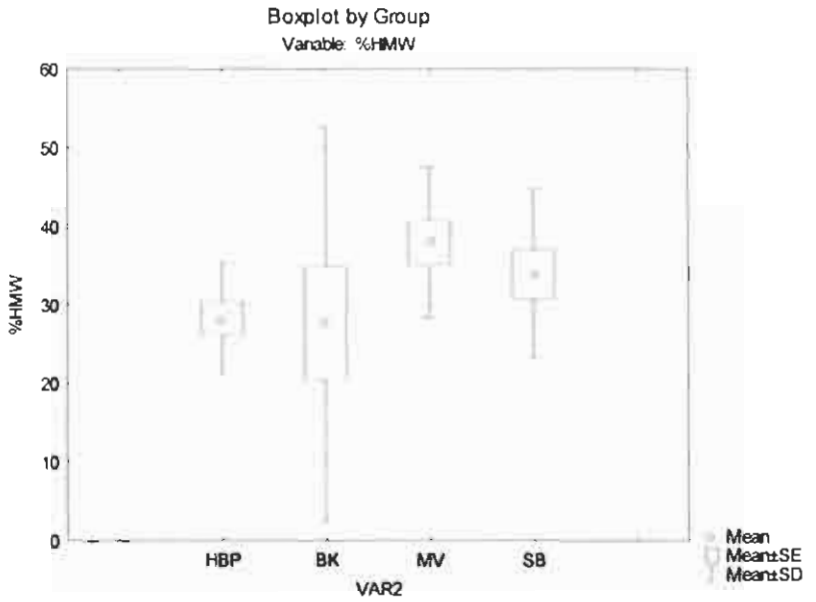


Figure 4.23: Variation in the percentage HMW fraction of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng.

B) Intermediate Molecular Weight Fraction (IMW)

Figure 4.24 shows that the percentage IMW is similar for all sampling sites with an average of 45%, although Boskop Dam shows the most variance. These values indicate that most of the NOM present in the sampling sites is constituted of the IMW fraction.

The percentage seasonal distribution indicates that IMW contributes more than 50% to the total NOM during spring. This contribution then decreases through summer and is lowest in autumn with a contribution of 44%. The IMW fraction increases to 50 % again in winter.

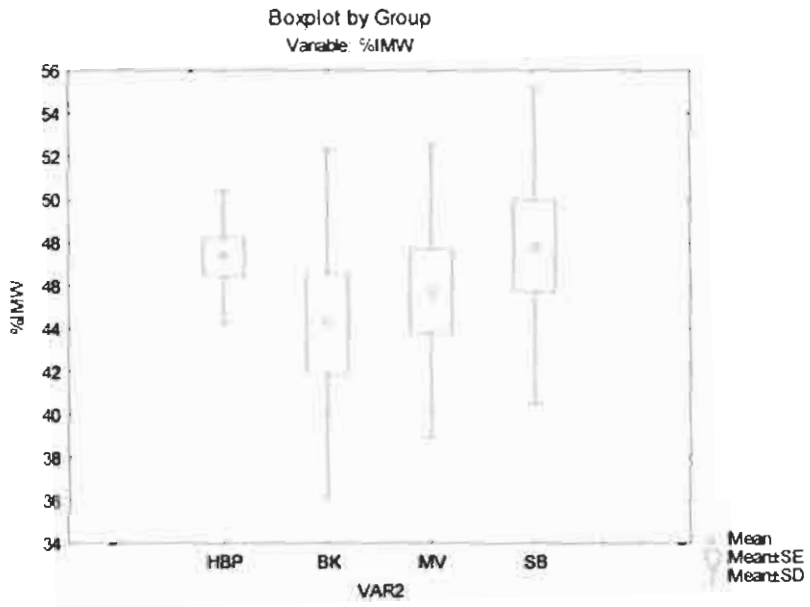


Figure 4.24: Variation in the percentage IMW fraction of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng.

C) Low Molecular Weight Fraction (LMW)

The results show that Boskop Dam has the highest percentage of the LMW fraction with an average of 32.40% (Figure 4.25). Hartbeespoort dam is lower at 24.2%. These values are typical of impoundments as the HMW and IMW fractions sediment out and are degraded by microbial organisms leading to the availability of organic carbon for other organisms. The two riverine sites show much lower percentages of LMW fractions than the dam sites. The average values for Midvaal and Sedibeng are 16.28% and 18.23%, respectively.

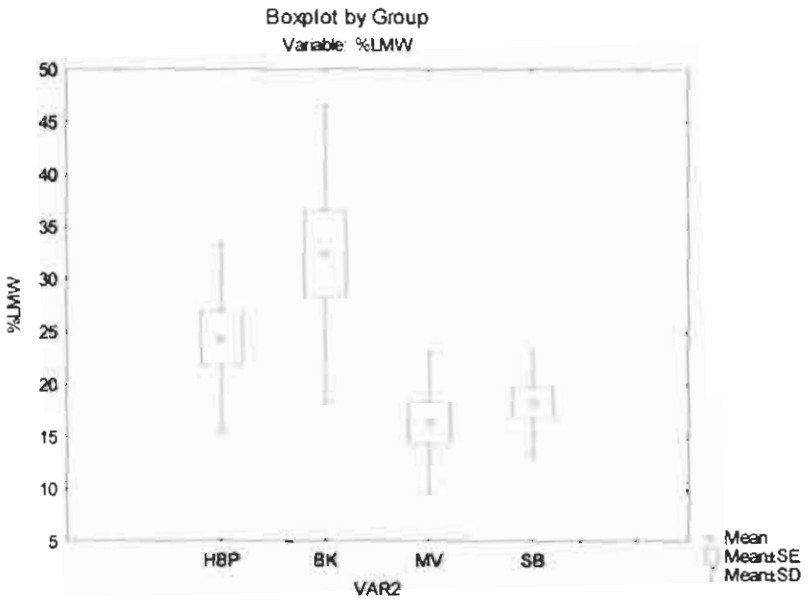


Figure 4.25: Variation in the percentage LMW fraction of NOM of the different sampling sites for the duration of one year from October 2005 to September 2006 (n=12) HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng.

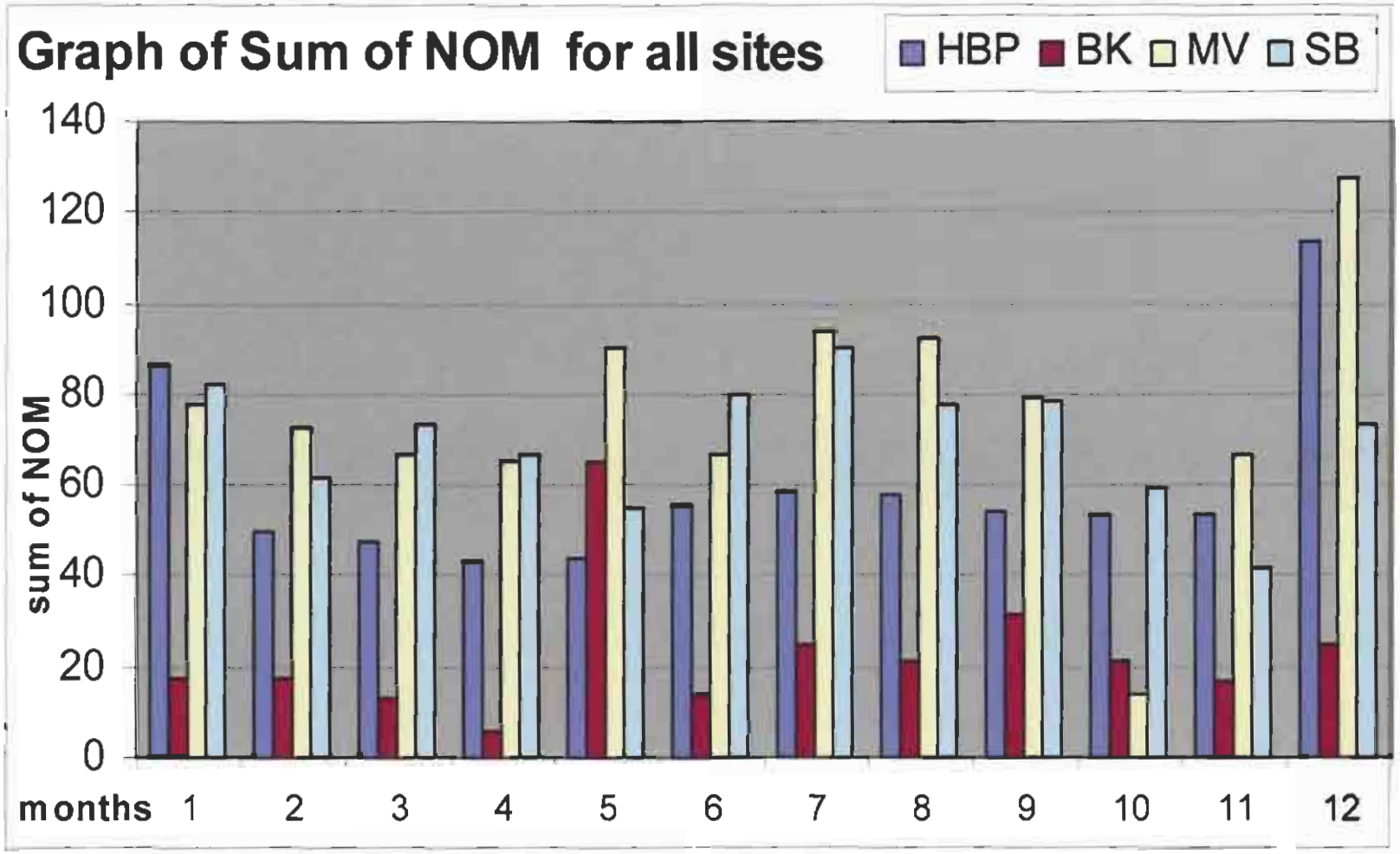


Figure 4.26: Sum of NOM of the four sampling sites for duration of one year from October 2005 to September 2006. HBP=Hartbeespoort, BK=Boskop, MV=Midvaal, SB=Sedibeng.

4.5.9: PCA Ordination Discussion

The Principal Component analysis was performed using Canoco version 4.5 for Windows and is shown in Figures 4.27-4.32. The component that indicates the most variation is DOC. This can be explained by the high value for Boskop Dam for October 2005. At that time, the water level in the dam was very low, as the summer rains had not yet fallen. The dam was characterised by thick mats of live and decaying *Spirogyra* sp. along the banks of the river and an oily sheen was visible on the surface of the water.

Chlorophyll-*a* concentrations, pH and dissolved oxygen associate with the principal axes and lie next to each other. During photosynthesis oxygen is liberated, resulting in high levels of dissolved oxygen in the water, which furthermore suggests an increased rate of photosynthesis explained by high concentrations of chlorophyll-*a* in the water. These variables explain 38.7% of the variance in the data. SAC254 and turbidity lie close to each other and are responsible for high variation as well. The high turbidity can be due to high organics in the water as indicated by SAC254. Both SAC254 and turbidity are closely associated with the sum of NOM as expected.

Because NOM in the water is made up of humic and non-humic substances we would expect some correlation between sum of NOM and SAC254. The correlation value obtained from Excel is low, with a value of 0.41(n=12). This means that the NOM in the water constitutes both humic and some non-humic substances such as carbohydrates, proteins, peptides, amino acids, fats, waxes and other low molecular weight substances. Because of their low molecular weight, these non-humic substances are not readily detected by SAC254, which tends to include the more complex NOM character (Natural Organic Matter 2006).

Interesting to note that the sum of NOM is correlated negatively with Chlorophyll-*a*, pH and dissolved oxygen. This can be expected because the amount of NOM present is not dependant on productivity of the aquatic ecosystem. Rather, the productivity is dependant on the availability of organic matter and the chlorophyll-*a* concentrations present.

In Boskop dam there is a clustered arrangement around the centre of the PCA (Figure 4.27). This is due to the low values of the parameters measured in contributing very little to the variation measured. This is indicative of a mesotrophic dam with low to medium productivity. There is little or no association with any of the components except for DOC. There were high values of DOC recorded of 24mgC/l and 13mgC/l for October 2005 and July 2006, respectively.

Figure 4.29 shows the ordination for Hartbeespoort Dam with a homogeneous spread in the plot indicating the seasonal variations in the dam. This can be expected, as Hartbeespoort dam is a eutrophic dam that has increased productivity throughout the year. Sample 2 for November 2005 associates close to DOC and indicates the high levels of DOC present before the rains. January-March 2006 (samples 4, 5, and 6) and June-July 2006 (samples 9 and 10) show high levels of

chlorophyll-*a*. There was a maximum value of 171.96 μg/l chlorophyll-*a* observed in June 2006. This was due to the presence of *Microcystis sp.* blooms characterised by colonies with 100 000s of cells giving the water a greenish tint. SAC 254 is closely associated with turbidity. Highest values for SAC254 were recorded during December 2005 and April 2006 but there was a general increase in SAC254 during this time, mostly due to the high rainfall.

The two riverine sites Midvaal and Sedibeng show similarities to each other and differ from the dam sites (Figure 4.31). For both sites, points lie close to the axes but are spread out from left to right. They show association with most of the components except DOC. Midvaal shows close association with turbidity, SAC 254 and sum of NOM from January to May 2006. The rest of the time, the association is with chlorophyll-*a*, ph and dissolved oxygen as can be seen in Figure 4.29.

Sedibeng is similarly distributed but has more association with chlorophyll-*a*, pH and dissolved oxygen. Only during February-April 2006 is there a close association with SAC254 and turbidity (Figure 4.30). This was due to high rainfall, which resulted in the water being brown in colour due to high silt load.

The riverine sites are affected by turbidity and SAC254, as well as increased productivity indicative of chlorophyll-*a* and dissolved oxygen. Generally riverine sites have unidirectional flow, high spatial heterogeneity that changes rapidly and frequently and most of the biotic metabolism is supported by organic matter originating for external sources and is imported into the river (Wetzel 2001). Therefore the degree of variability in rivers is always high with regard to physical and chemical properties.

4.6: CONCLUSION

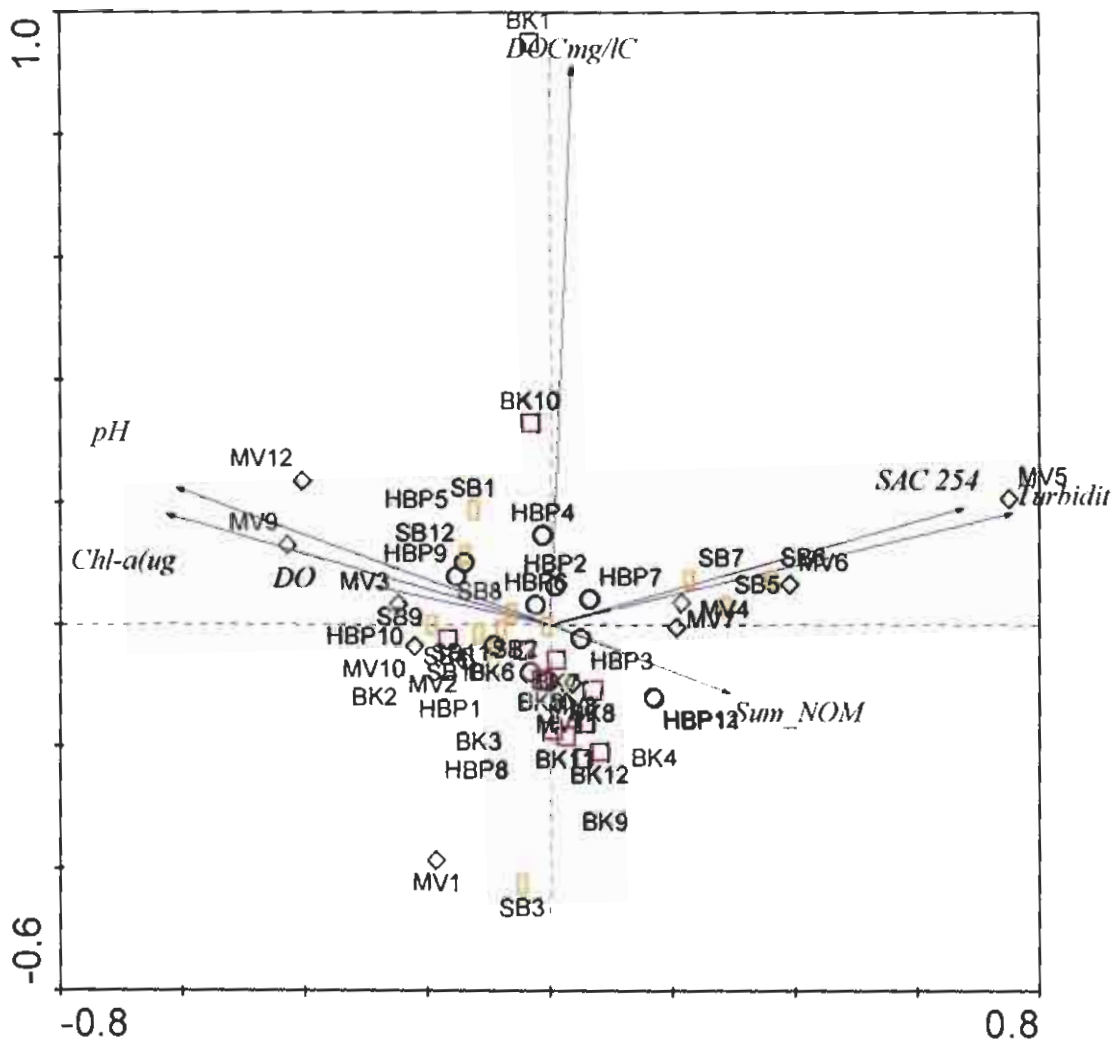
According to the State of Environment report 2002, North West, Hartbeespoort dam is listed as a eutrophic-hypertrophic impoundment associated with algal blooms of cyanobacteria that do lead to toxic incidents from time to time (Howard *et al.* 2002). The trophic status of the dam is affected by treated sewage and industrial effluents, which originate from highly urbanised areas of Gauteng that are situated in the headwaters of the Crocodile River. The results obtained in the study reflect this situation showing the occurrence of high algal blooms and consequently high chlorophyll-values for most part of the year. Seasonal variations occur in most of the variables, but the dam remains eutrophic with annual chlorophyll-*a* values in excess of 25-75μg/l. The dominant algal species was a member of the Cyanophyceae, *Microcystis* sp. There were members of the class Chlorophyceae present but only when no Cyanophyceae was present. Turbidity of Hartbeespoort Dam was moderate with an average of 9.32NTU. SAC254 was lower than for riverine sites but higher than Boskop Dam with an average value of 12.06m^{-1}. Both turbidity and SAC254 increased during the rainy season. DOC was variable and dissolved oxygen was constant. The sum of the NOM for Hartbesspoort Dam was lower than that of the riverine sites but higher than for Boskop

Dam, with more IMW and LMW fractions compared to the riverine sites. Future studies should measure the amount of phosphorous and nitrogen in the dam water.

The results of this study confirm the status of Boskop as a mesotrophic impound with low productivity. There is little or no seasonal variation observed in the measured variables and most of the variables measured remain fairly constant. Chlorophyll-*a*, turbidity and SAC254 were low for Boskop Dam when compared to the other sampling sites. The only notable exception is DOC, which peaked before the rains. This was, however, an extreme situation when the water level was at its lowest after a severe drought period. The algal species found in the study show that the dominant species to be benthic diatoms of the class Bacillariophyceae. This may be because sampling was undertaken along the banks of the river and not in the main stream. This should be investigated further in subsequent studies that examine the water in the main stream as well as the banks for algal classes. Boskop Dam had the lowest sum of NOM values when compared to the other sampling sites, but had the highest percentage LMW fractions present.

According to DWAF (DWAF report no. P WMA 09/000/00/0304), the water quality of the Vaal River in the Middle Vaal is of particular concern especially with regard to increased salinity as well as frequent algal blooms. This is due to nutrient enrichment from water that originates in the Vaal Barrage and the long retention time in the Vaal River promotes algal blooms. The results obtained in this study support the finding of DWAF and demonstrate the eutrophication of the Middle Vaal. Algal blooms occurred throughout the year with an average chlorophyll-*a* value of 90.75μg/l and 57.32μg/l for Midvaal and Sedibeng, respectively. The dominant algal species were members of the class Bacillariophyceae notably, *Cyclotella* sp. and *Aulacoseira* sp., but there was a seasonal succession between these species and several members of the class Chlorophyceae. The members of Chlorophyceae include *Actinastrum* sp., *Scenedesmus* sp., *Monoraphidium* sp. and *Pediastrum* sp. There were reduced values in chlorophyll-*a* concentrations and cell count during the rainy season. Both turbidity and SAC254 were observed to be higher than for the dam sites and were affected by rainfall. During the rainy season both turbidity and SAC54 increased. Midvaal had the highest SAC254 and turbidity readings observed during the study with SAC254 value of 108.75m^{-1} and turbidity of 22NTU recorded in February 2006. There is a good correlation between these two variables for the two riverine sites indicating the correlation between organic material and turbidity in the riverine system. DOC was variable and the dissolved oxygen was lower than for Boskop Dam. The sum of NOM demonstrates that the riverine sites had the largest proportion of HMW and IMW fractions. These HMW and IMW fractions contribute to the increased turbidity of the river and are of allochthonous origin.

Further studies undertaken should measure TDS and alkalinity in addition to the other variables in order to determine their effects.



Axes		1	2	3	4	Total variance
Eigenvalues	:	0.286	0.136	0.124	0.089	1.000
Cumulative percentage variance of species data	:	37.6	55.5	71.7	83.5	
Sum of all eigenvalues						0.762

Figure 4.27: PCA ordination biplot showing the 4 sampling sites and the variables that were measured for the four sampling sites for the duration of one year from October 2005 to September 2006. HB=Hartbeespoort, BK=Boskop, MV=Midvaal and SB=Sedibeng.

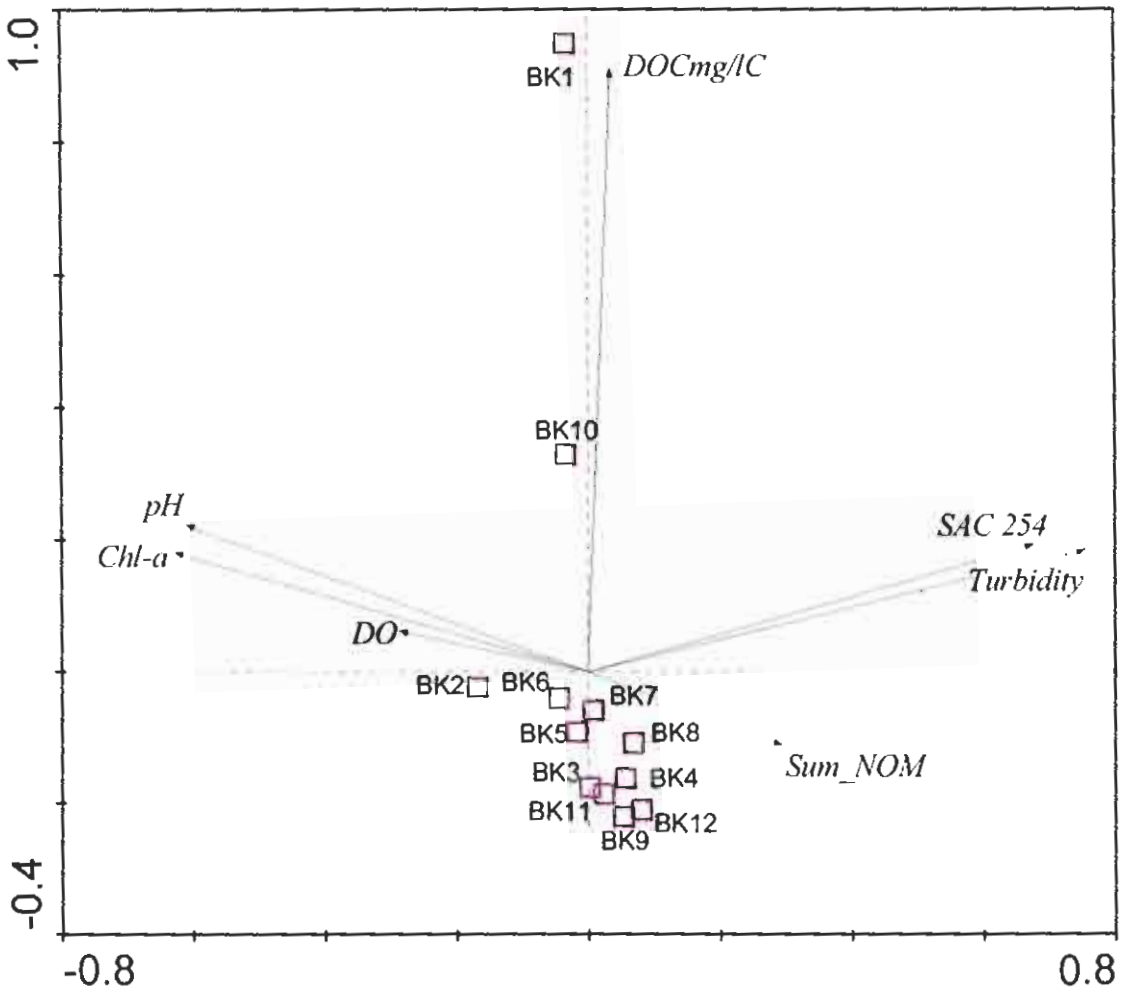


Figure 4.28: PCA ordination biplot showing the environmental variables measured at Boskop Dam for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation.

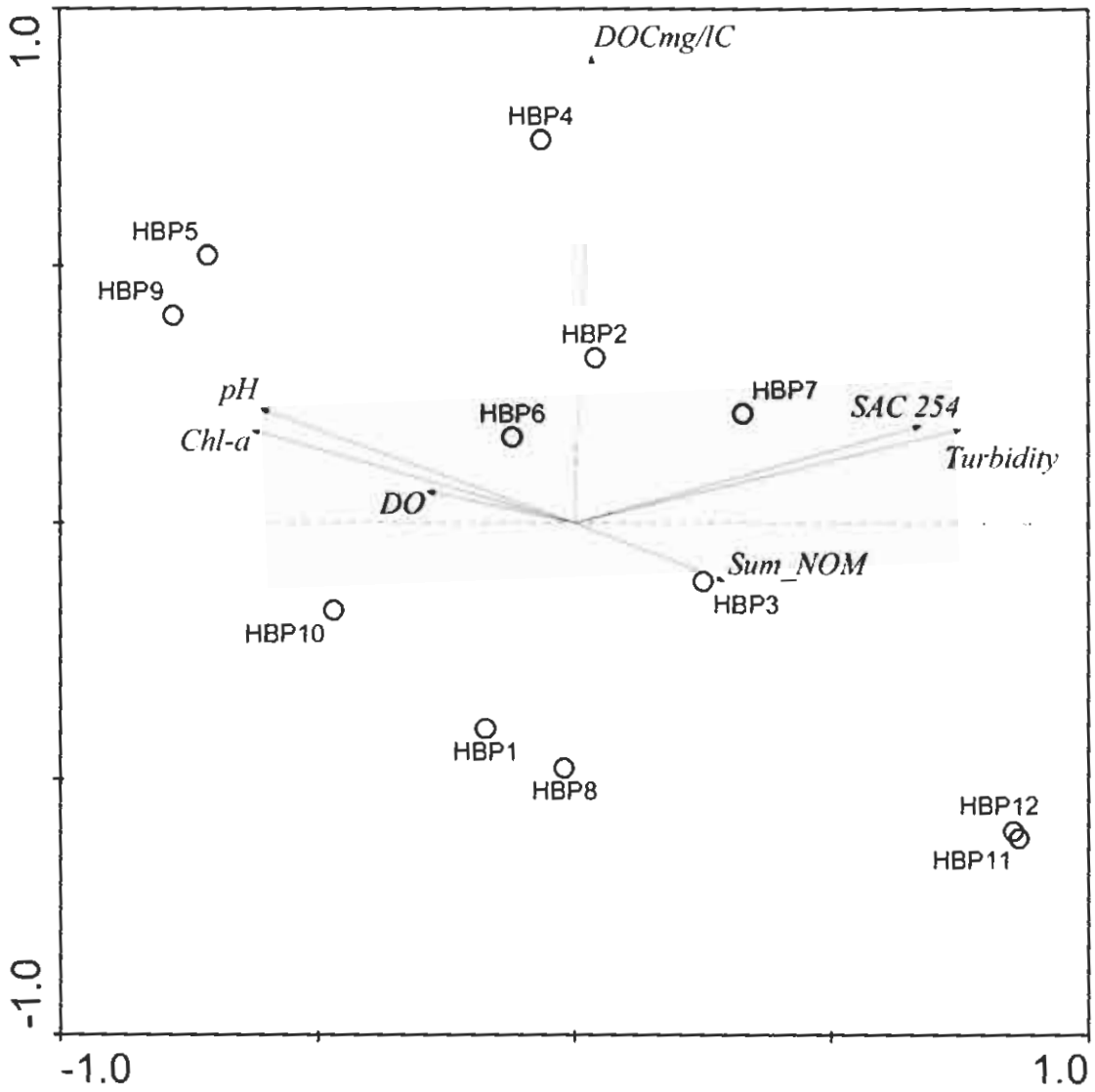


Figure 4.29: PCA ordination biplot showing the environmental variables measured at Hartbeespoort Dam for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation.

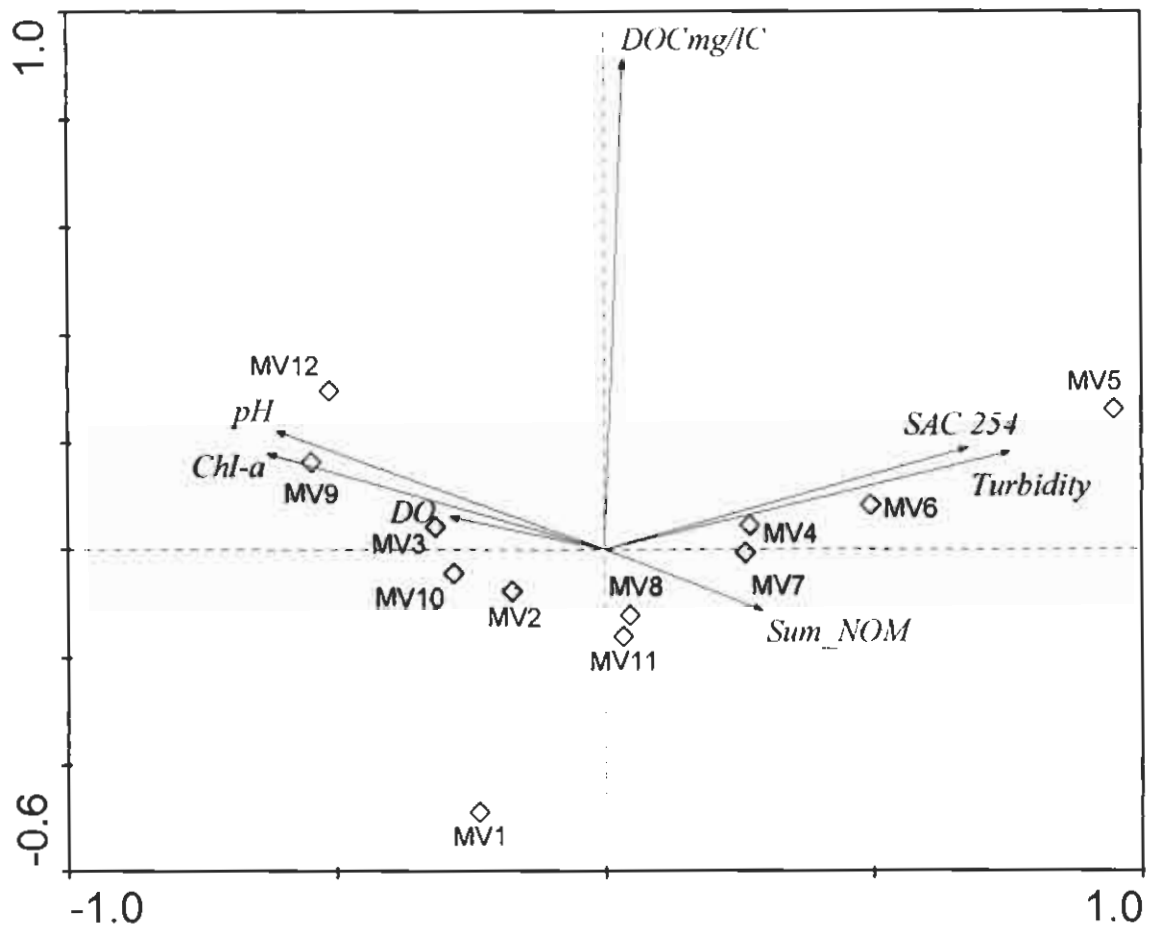


Figure 4.30: PCA ordination biplot showing the environmental variables measured at Midvaal for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation.

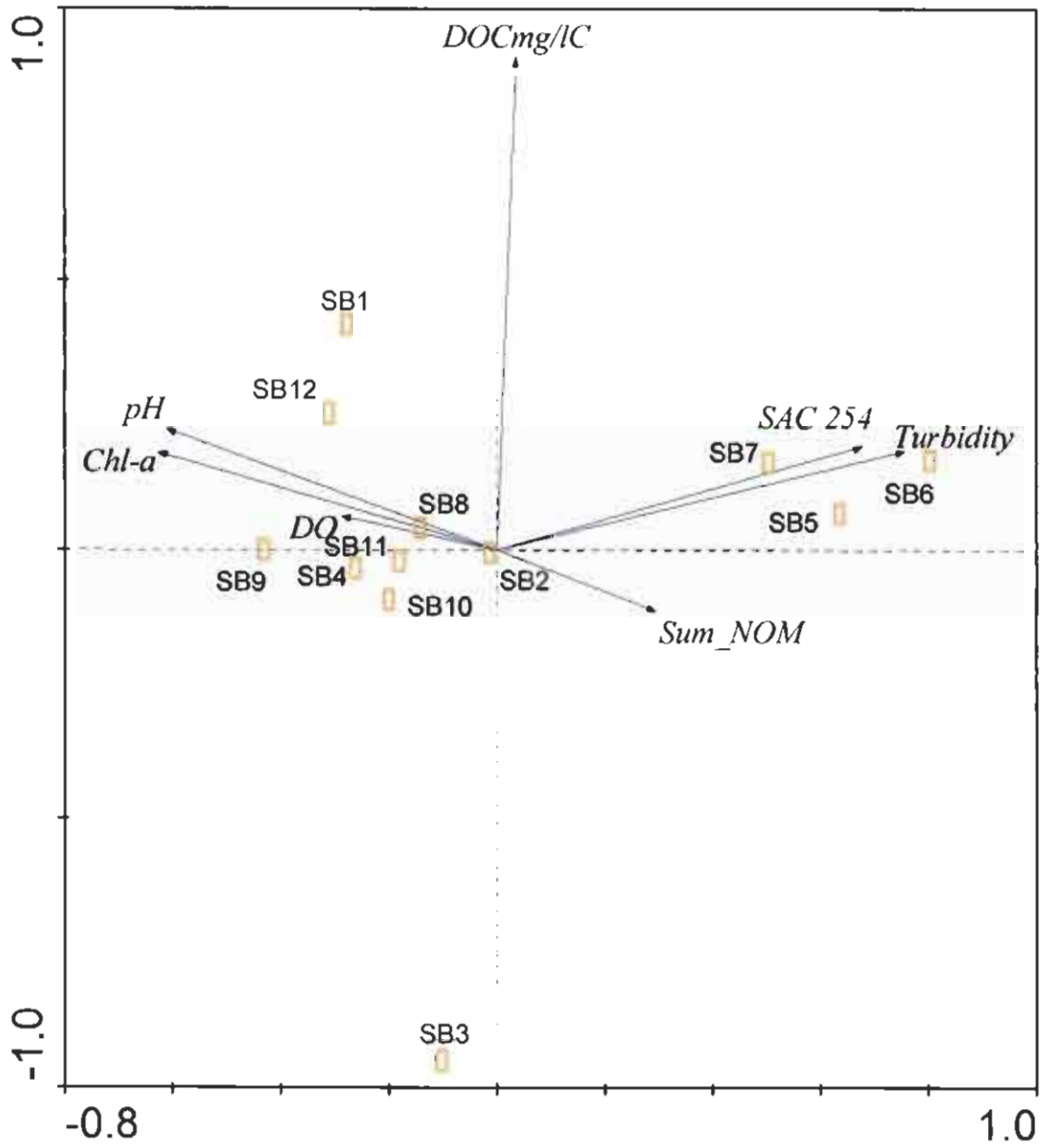


Figure 4.31: PCA ordination biplot showing the environmental variables measured at Sedibeng for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation

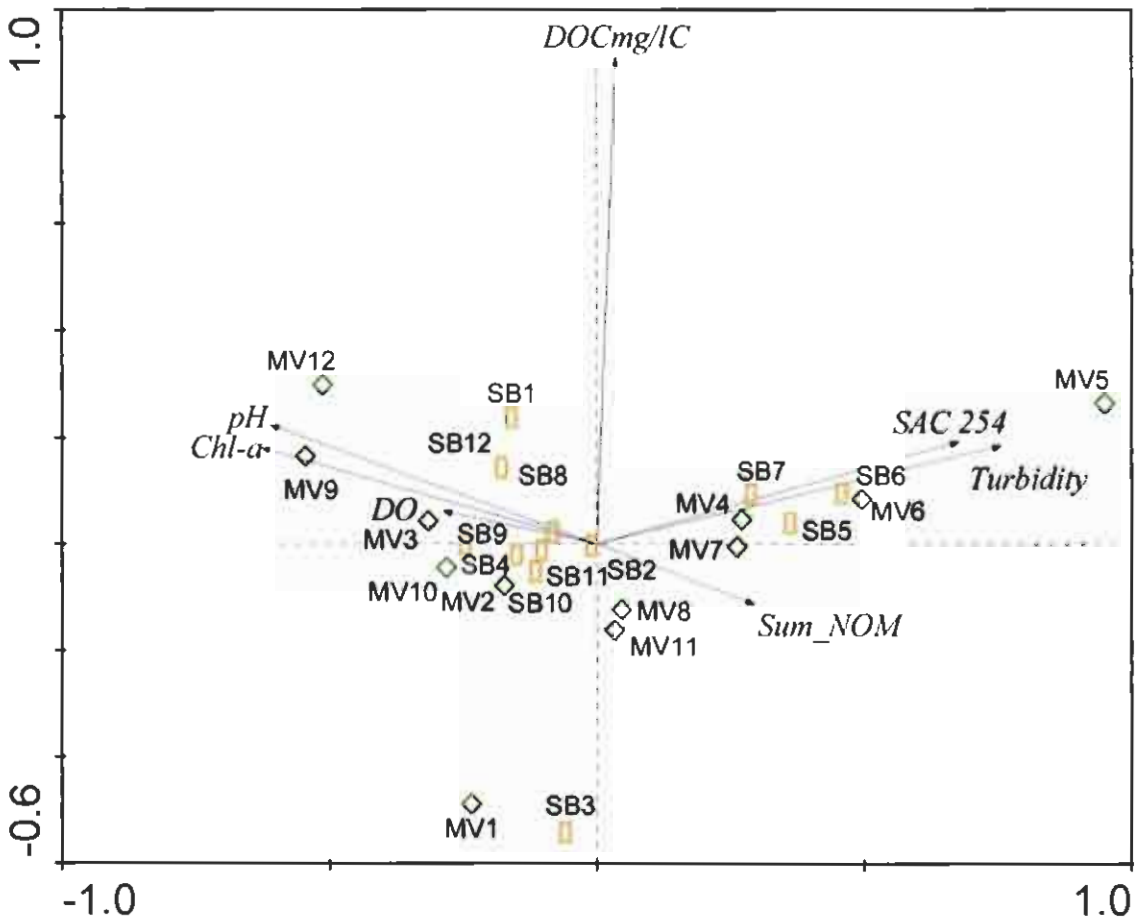


Figure 4.32: PCA ordination biplot showing the environmental variables measured at Midvaal and Sedibeng for the duration of one year from October 2005 to September 2006. See Section 4.5.9 for explanation

CHAPTER 5: THE EFFECT OF OZONE ON SAMPLES AND JAR TEST RESULTS

5.1: INTRODUCTION

Ozone is used in drinking water to achieve a variety of purposes, such as removal of taste and odours, oxidation of iron and manganese, colour removal, improved turbidity and enhanced coagulation. Ozone is typically used in water treatment plants at the head of the operation where it is used on raw water (pre-ozonation) or it can be used after sedimentation (post-ozonation) (USEPA manual 1999). The point of application of ozone is determined by the characteristics of the raw water as water having high turbidity and containing high concentrations of organic and inorganic material has a higher ozone demand. The most effective use of ozone for this type of water would be after sedimentation and filtration. The term 'pre-ozonation" is used when ozone is used before any other conventional treatment processes. Pre-ozonation is used by Umgeni Water's Wiggins Waterworks in Cato Manor, Durban to reduce THM precursors, taste and odour compounds and remove colour (Water Sewage and effluent 1998). Use of pre-ozonation at Midvaal Water Company is primarily for the removal of iron and manganese but contributes to overall improvement in chlorophyll-*a* reduction because algal cells are more stressed after ozonation than after chlorination (Lombard *et al.* 1992).

Coagulation and flocculation are basic processes used in most water treatment plants. The object of these 2 processes is to destabilise the colloidal matter so as to incorporate it into a floc, which can then be removed by sedimentation (Schutte 2006). Different chemicals are used as coagulants such as aluminium sulphate, ferric chloride, lime and polyelectrolytes. Pre-ozonation is used to enhance coagulation and flocculation in water treatment plants. However, there are reports of impairment of coagulation and flocculation by pre-ozonation (Pryor *et al.* 2000). There is a number of mechanisms that explains the observed effects of ozonation on particle destabilisation and these are discussed in Section 2.3.5. Some of these mechanisms involve the direct effects of ozone on the NOM and particles such as the increase in carboxylic acidity of NOM and the decrease in average molecular weight of NOM (Tobiasion *et al.*1994). These factors can affect the coagulation and flocculation processes in water treatment plants.

Jar tests are meant to mimic the conditions and processes that take place in the clarification step of water and wastewater treatment plants. These values can then be correlated and adjusted to account for the actual treatment system (Poland *et al.* 1998). Therefore, the Jar Test is a common lab procedure used in water treatment plants to simulate the coagulation/flocculation process and determine the optimum operating conditions for the plant (Lafleur 2006). This method allows adjustments in pH, coagulant dose, alternating mixing speeds, or testing of different coagulant types on a small scale in order to predict what happens in a large scale treatment plant. The

coagulant dose and paddle speed can be regulated to reflect the specific plant.

The Jar testing apparatus contains six paddles that stir the contents of six 1-liter containers (Figure 5.1). One container acts as a control while the operating conditions of the other containers can be varied. A speed (rpm) gauge at the top of the device allows for uniform control of the mixing speed in all of the containers. The coagulant ferric chloride ($FeCl_3$) was used and dosed at varied concentrations to determine the optimum coagulant dose. After each Jar Test, the supernatant is withdrawn and tested for specific variables.

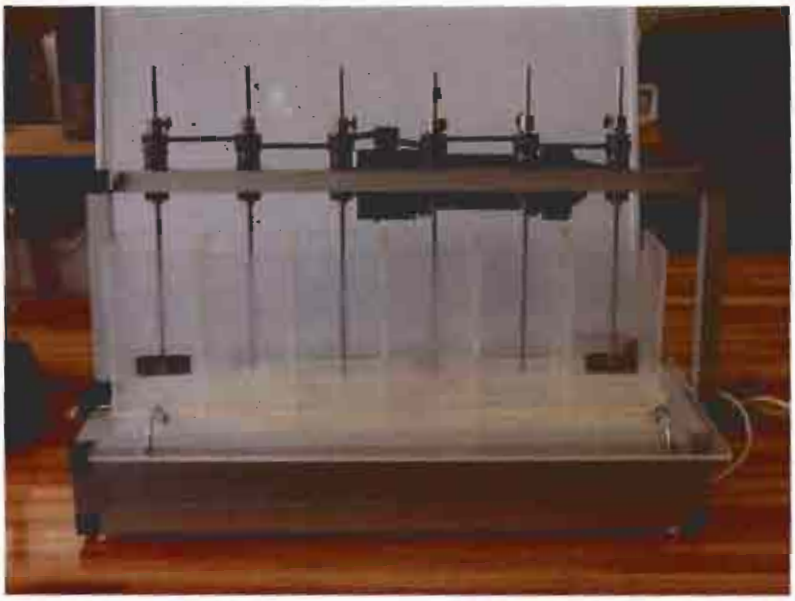


Figure 5.1: Jar Test Apparatus that was used in this study. It consists of 6 beakers, each with a capacity of 1 liter, with paddles and speed gauge.

5.2: AIMS

This study has two main aims.

The first aim is to determine the effect of ozone on raw water with regard to the following variables:

-pH,

-turbidity,

-chlorophyll-*a*,

-SAC254,

-optimum coagulant dose of $FeCl_3$,

-dissolved organic carbon (DOC) and

-Natural Organic Matter (NOM).

The second aim is to determine the effects of ozone on Jar Test results with regard to the lowest observed value for SAC254, turbidity, chlorophyll-*a* in relation to the coagulant dose.

5.3: OUTLINE OF EXPERIMENTAL PROCEDURE

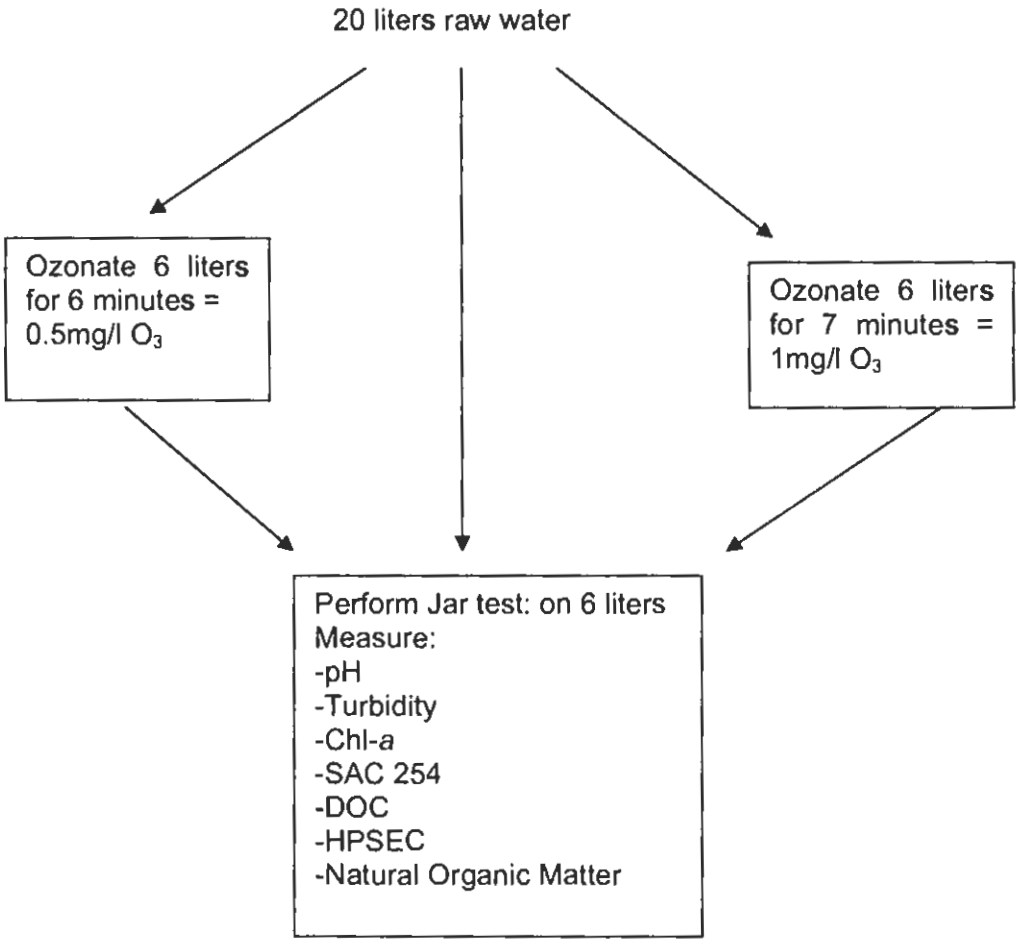


Figure 5.2: Schematic flow diagram of experimental procedure that was followed every month for the raw water received from the different sampling sites. Twenty liters of water was sampled and this is called Raw water. Six liters of raw water was used in the Jar Test. A further six liters each was exposed to the two ozonation treatments and then used for Jar Test.

5.4: METHODS

Water samples of 20 liters were collected on a monthly basis for the duration of a year from 4 different sampling sites, namely:

-Hartbeespoort Dam (eutrophic dam),

-Boskop Dam (mesotrophic dam),

-Sedibeng raw water, and

-Midvaal raw water

The water from each site was mixed in a 25-litre can to get a homogenised sample. Three **Standard Jar tests** were performed on every sample, 1 on the raw water and the other 2 on the samples after they were exposed to ozone at two different concentrations namely 0.5mg/l O_3 (6 minutes) and >0.5mg/l O_3 (7 minutes for concentrations greater than 0.5mg/l but less than 1 mg/l) respectively. These 3 Jar Tests are denoted as follows:

RAW+ = raw water treated with coagulant,

TR1 =raw water + 0.5mg/l ozone + coagulant,

TR2 =raw water + >0.5mg/l ozone + coagulant.

The method used for the Jar Tests was according to the work of Traute (2002).

The flocculant used in the Jar Test was ferric chloride ($FeCl_3$). The $FeCl_3$ stock solution contained 4.8376g $FeCl_3.6H_2O$ made up to 1 litre with distilled water yielding a concentration of 1g/l Fe^{3+}.

For the first treatment, RAW+, each of the 6 jars of the Jar Test apparatus was filled with 1 litre raw water. The first jar acted as a control and no flocculant was added. The water was first rapidly mixed at 350rpm for one minute. Thereafter, rapid mixing at 350rpm for 30 seconds was continued while the coagulant $FeCl_3$ was added simultaneously near the impeller in the 5 remaining jars. The concentration of ferric chloride added to the five jars was 5, 10, 15, 20 and 25mg/l $FeCl_3$ respectively. Subsequently, flocculation was allowed to proceed while the suspension was slowly mixed at 40rpm for 10 minutes. After flocculation, the flocs were allowed to settle for 30 minutes without stirring. Supernatant water was withdrawn with syringes and the following measurements were determined by the methods described in Section 4.3.

1) **pH,**

2) **turbidity,**

3) **Chlorophyll-*a*,**

4) **SAC 254,**

5) **dissolved organic carbon (DOC) and**

6) **determination of Natural Organic Matter (NOM).**

For TR1 and TR2, the raw water was exposed to ozone for 6 and 7 minutes respectively, and then immediately treated in the Jar Test apparatus in the same manner as described above for the raw water.

5.5: RESULTS AND DISCUSSION

These results and discussion are divided into 2 sections: 5.5.1 and 5.5.2.

In the first section, the variables measured for the raw water are compared to that of the ozonated samples before the Jar Test is performed. This will provide information as to the effect of ozone on the raw water with respect to the variables measured. In the second section, the effect of ozone on

Jar Test is examined to determine what the effect of consequent coagulation is towards improving water purification.

The data was analysed using several statistical programmes. Statistical analyses were done in Statistica for Windows version 7 as well as Excel 2000 for Windows XP. Normality of the data was tested using Shapiro-Wilk's W Test and all the data was found to be non-parametric. Graphical representations have been done is Statistica release 7 and Excel 2000 for Windows XP.

5.5.1: The Effect of Ozone on Raw Water

Each raw water sample was exposed to two concentrations of ozone. The results will be compared to raw water and the following abbreviations will be used in the discussion:

Raw water = raw water with no treatment,

TR1 =0.5mg/l ozone, and

TR2 =>0.5mg/l ozone.

A complete list of all the observations is given at the end of the chapter in the form of 2 tables, Table 5.2 and Table 5.3. These tables show the effect of ozone on raw water with regard to percentage removal of SAC254, Turbidity, Chlorophyll-*a* and DOC for the dam and river sites. Tables 5.4 and 5.5 provide a summary of all the values.

a) pH

When ozone decomposes to oxygen, it can either be by direct oxidation to oxygen or by decomposition to hydroxyl radicals. Since this process is dependant on the pH of the sample, the efficiency of ozone is thus affected accordingly (USEPA manual 1999). The pH of most of the samples was moderately high with an average value of 8.50 and it would therefore be expected that the decomposition of ozone to hydroxyl radicals would occur. The results for the change in pH are given below in Table 5.1.

The Hartbeespoort dam measurements exhibit a general decrease in pH after ozonation and there is little difference between TR1 and TR2. An increase in pH was only observed in October 2005 before the rainy season when the water levels were low.

Boskop Dam, however, showed an increase in pH after ozonation except from November 2005 to March 2006 when it was raining. There was no significant difference between the two treatments except in October 2005 when TR2 caused a large increase in pH from 8.56 to 9.21. This sample is characterised by high DOC and a high %LMW fraction of NOM of 52.77%.

Midvaal shows a general decrease in pH after ozonation except in June 2006. There was a large decrease in pH in November 2005 after TR1 and TR2. This value corresponds to low SAC254 removal and negative DOC removal after treatment with ozone.

Sedibeng shows a similar trend to Midvaal results, with a general decrease in pH after ozonation. The notable exception is an increase before the rains in October 2005.

The effect of pH on ozone determines whether ozone itself or hydroxyl radicals will dominate the oxidation reactions. It is expected that hydroxyl radical formation will be favoured in these samples. However, there is a decrease in pH noted for most of the samples after ozonation except for Boskop Dam. This decrease can be due to other factors that scavenge the hydroxyl radical such as bicarbonate or carbonate ions indicative of alkalinity. Therefore measurement of alkalinity can give an indication of whether the alkalinity contributed to formation of carbonate radicals after ozonation with a resulting decrease in pH (USEPA manual 1999).

The major effect of ozone on pH is bromate ion formation if bromine is present in the raw water. This can be reduced by lowering the pH of the sample. However, bromine was not measured in this study. Hence it can be concluded that in this study, the effect of ozone on pH is variable.

Table 5.1: The change in pH after ozonation as observed for the four sampling sites from October 2005 to September 2006. Raw=raw water, TR1= 0.5mg/l ozone, TR2=>0.5mg/l ozone.

	Hartbeespoort			Boskop			Midvaal			Sedibeng		
Months	raw	TR1	TR2	raw	TR1	TR2	raw	TR1	TR2	raw	TR1	TR2
October	8.6	8.9	9.07	8.56		9.12	9.37	9.69	9.43	9.26	9.77	9.59
November	8.13	7.84	7.82	9.97	8.86	8.53	8.38	6.4	7.05	7.87	7.77	7.74
December	8.97	8.73	8.8	8	8.43	8.4	8.7	8.53	7.83	8.31	8.36	
January	9.92	8.78	9.6	8.66	8.43	8.58	8.02	7.95	8.11	8.38	8.54	8.38
February	9.65	9.48	9.46	8.75	8.89	8.36	8.11	8.28	8.06	8	7.36	7.76
March	9	8.15	7.86	8.81	8.59	8.46	8.44	7.69	8.09	7.66	7.16	6.92
April	7.91	7.95	7.73	8.22	8.39	8.09	7.68	7.66	7.62	7.67	7.59	7.56
May	8.18	7.92	7.74	8.12	8.58	8.5	8.23	7.93	7.63	8.7	8.67	8.35
June	9.1	8.83	8.59	7.77	7.78	7.93	9.32	9.52	9.2	9.19	8.94	8.9
July	8.86	8.59	8.49	7.89	8.35	8.16	9.14	9.13	9.11	8.78	8.62	8.67
August	8.14	8.09	8.05	8.16	8.28	8.15	8.22	8.05	8.06	8.66	8.51	8.52
September	8.11	8.1	7.81	7.89	8.06	8.3	9.19	8.97	9.08	8.7	8.43	8.37

b) Turbidity

Turbidity is the measure of the amount of suspended particles in the water and is a good indicator of the efficiency of the purification processes. Drinking water should have a limit of <1NTU and some treatment plants even aim for <0.5NTU (Viessman *et al.*1998).

There was a general decrease in turbidity after ozonation in all the sampling sites with some

exceptions, especially in the Hartbeespoort Dam. As seen in Figure 5.3, Hartbeespoort Dam shows a low average percentage removal of turbidity. For TR1, the average removal is 20% and for TR2 the average removal is 10%. Increases in turbidity were noted at other times such as in January 2006 when the turbidity increased by 36.03% after TR2. This was during the rainy season when there were large numbers of *Daphnia* sp. present in the sample. The *Daphnia* sp. was not affected by either the Jar Test or the ozone treatments and was unevenly distributed in the samples. This could have contributed to the increase in turbidity because there were more *Daphnia* sp. in TR2 than in RAW and TR1. In June 2006 (month 9 in Figure 5.3), ozonation caused the turbidity to decrease by 56.40% after TR1 and then increase by 47.19% after TR2. There was a corresponding increase in SAC254 of 8.54% and 1.83% after TR1 and TR2 respectively, and a decrease in DOC of 2.78% and 6.94% for TR1 and TR2 respectively. The increase in SAC254 indicates that there was an increase in the organic compounds present but this was not associated with any recorded changes in the sum of NOM.

During this month, Hartbeespoort Dam had the highest chlorophyll-*a* concentration of 171.96μg/l recorded, with large colonies of *Microcystis* sp. present. The colonies had over one million cells/ml and were still visible after ozonation although they were smaller in size. The decrease in turbidity can be due to the breakdown of the larger parent colony into smaller colonies. Thereafter, TR2 caused further lysis of individual cells leading to liberation of cell contents and an increase in turbidity. Pryor *et al.* 2000 noted that turbidity of the water was not affected by ozonation but filtered water was found to have more finely dispersed matter suggesting that *Microcystis* sp. cells are susceptible to disintegration by ozone. This is in agreement with our results as seen by the increase in the SAC254 after ozonation by TR1 and TR2, suggesting that ozone did act upon the cell membranes causing oxidation damage.

Boskop dam had an average low turbidity in the raw water but responded well to ozone treatment in general. The average percentage turbidity removal was high for both TR1 and TR2 with 34.82% and 38% removal respectively. The only exception was in August 2006 when the turbidity increased by 9.48%, concurrent with an increase in %LMW fraction of NOM after ozonation at the same time. This increase in turbidity after ozonation can be due to the breakdown of HMW and IMW fractions of NOM into LMW fractions by the actions of ozone. Midvaal water showed positive results with ozone treatment but had a lower percentage removal than that observed for Boskop. Before the rainy season when the turbidity of the raw water was lower, the percentage removal of turbidity was greater after ozonation as seen in Figure 5.4. During the rainy season when turbidity of the raw water was very high as can be seen in section 4.5.4, the percentage removal was lower and this trend continued throughout the year.

There was an exception during February 2006 during the rainy season, when the percentage

removal was higher with 21.88% removal (month 5 in Figure 5.4). This value coincides with a high average removal in SAC254 of 78% for the same time period. At the same time, the %HMW fraction decreased from 49.95 % to 35.50%. This month had the highest recorded values for turbidity and SAC254 (Section 4.5.4). These results indicate that during February 2006 at the height of the rainy season, the organic materials present in the water were HMW fractions of NOM that were effectively removed by ozone, as well as lower molecular-weight compounds that constitute the SAC254 measurements. The increase in turbidity that was visible at Midvaal during that time, is probably due to organic loading of the river. Sedibeng showed a general decrease in turbidity with a low average percentage removal of 15.2% after TR1. However, the percentage removal for TR2 increased to 20.74%. There were few samples that had an increase in turbidity and the percentage increase was low.

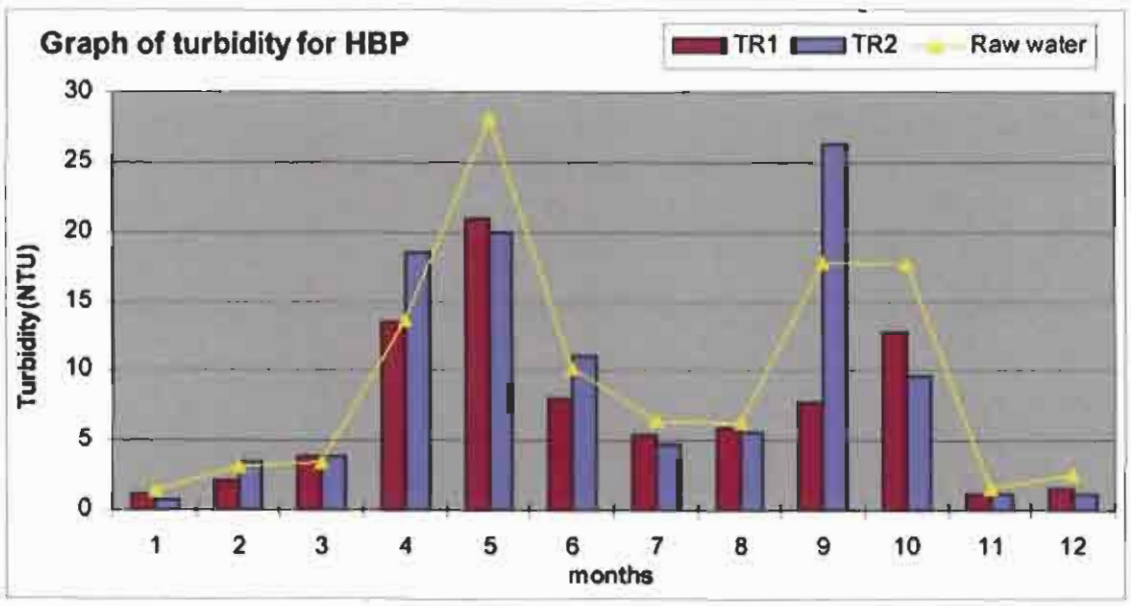


Figure 5.3: The change in turbidity of the raw water of Hartbeespoort Dam with ozonation. The duration of the study was from October 2005 to September 2006.
TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

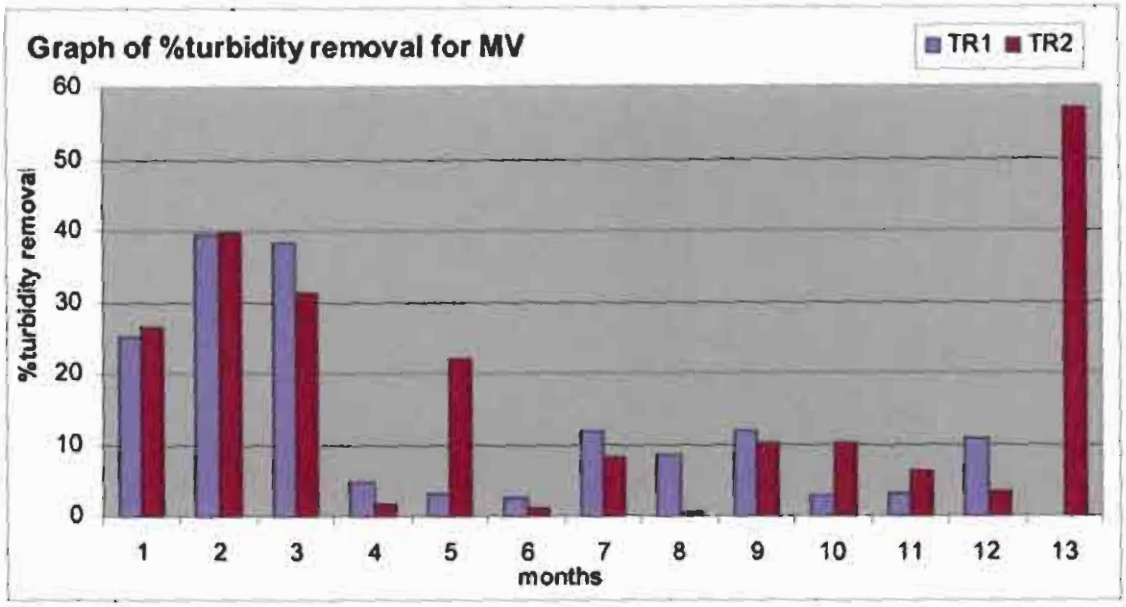


Figure 5.4: The change in percentage turbidity removal for Midvaal, showing the effect of ozonation on raw water for the duration of one year from October 2005 to September 2006. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

c) Chlorophyll-*a*

One of the main uses of ozone is to control the amount of algae in the water. Geldenhuys *et al.* (2000) reported that ozone attacked the membrane systems in algal cells and this resulted in the death of the cells. Results from electron micrographs of *Monoraphidium sp.* cells exposed to ozone show that the chloroplast grana becoming swollen and then disintegrating. Increased ozonation can lead to the destruction of the cell membrane. This destruction can, however, lead to the liberation of organic cellular material that can adversely affect the purification process and contribute to THM production (Plummer *et al.*2001).

Boskop Dam exhibited the lowest chlorophyll-*a* values present in the raw water. There was either 100% removal or no change at all after ozonation. Hartbeespoort dam showed similar results although the raw water had much higher concentrations of chlorophyll-*a* present. The percentage removal of chlorophyll-*a* was high with an average of 51.8% after TR1 and 77.82% after TR2. From Figure 5.5, it can be seen that in June 2006, the chlorophyll-*a* content of the water was at its highest with large colonies of *Microcystis* sp. present. TR1 resulted in 16.67% removal, which was the lowest observed percentage removal for this site during this study. However, TR2 achieved 50% removal of chlorophyll-*a*. From these results we can deduce that concentrations of >0.5mg/l ozone are required to treat water that has large concentrations of *Microcystis* sp. The lower concentration of ozone used in this study caused only a breakdown of the parent colony into smaller colonies but has little effect on the chlorophyll-*a* pigments present.

Midvaal shows a decrease or no change in the chlorophyll-*a* concentration after ozonation. The percentage chlorophyll-*a* removal was 23% for TR1 and 45% for TR2. The lowest percentage removal was in September 2006 with 11.11% for TR1 and 22.22% for TR2 when the chlorophyll-*a* value was at its highest with approximately 15000 cell/ml of *Cyclotella* sp. present.

Similar trends were noted in the results from Sedibeng. There was a general decrease in chlorophyll-*a* after ozonation. The average percentage removal of chlorophyll-*a* was 14.58% for TR1 and 52.78% for TR2 respectively. The highest chlorophyll-*a* value of 114.64µg/l was observed in May 2006 and September 2006. As can be seen in Figure 5.6, there was no removal of chlorophyll-*a* in May 2006 but in September 2006 there was a 25% removal after TR1 and a 50% removal after TR2.

The difference between these two months is the composition of the dominant algal species present. In May, *Cyclotella* sp. which is a member of the class Bacillariophyceae, was the dominant algae present whereas in September 2006, the dominant class was Chlorophyceae, represented by *Actinastrum* sp., *Coelastrum* sp. and *Scenedesmus* sp. Bacillariophyceae are diatoms characterised by the presence of a silica frustule. Each cell is encased by a unique siliceous cell wall that takes the form of a box with an overlapping lid and is called a frustule (Van den Hoek *et al.* 2002). This cell wall is made of polymerised silicic acid, which is amorphous and has no crystalline structure. These silica frustules are resistant to ozone and other oxidants. Members of the Chlorophyceae lack this silica frustule and only possess a normal plant cell wall made up of cellulose and other polysaccharides. Because the silica frustule is more resistant to ozone than the cell wall, members of Chlorophyceae are more easily destroyed than those of the Bacillariophyceae.

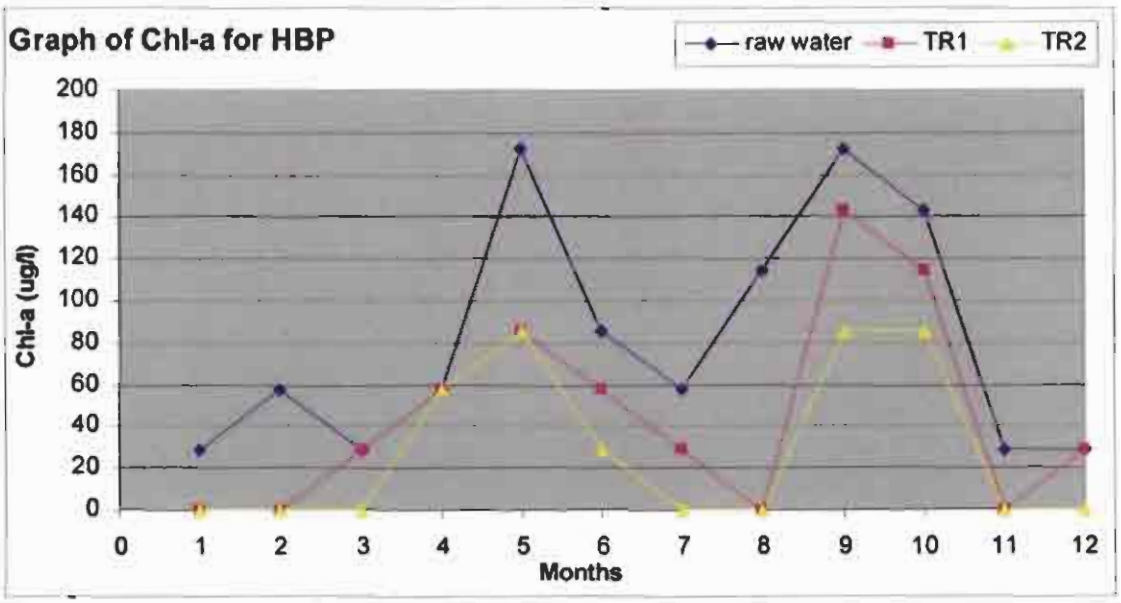


Figure 5.5: The change in Chlorophyll-*a* concentration of Hartbeespoort Dam showing the effects of ozonation for duration of one year from October 2005 to September 2006.
TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

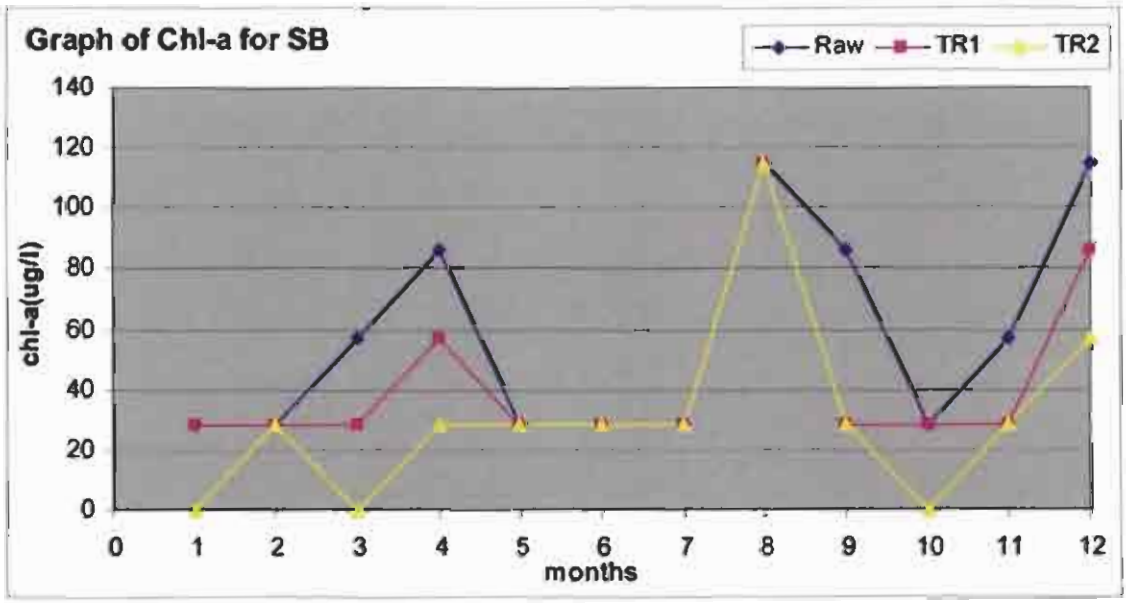


Figure 5.6: The change in Chlorophyll-*a* concentration of Sedibeng showing the effects of ozonation for the duration of one year from October 2005 to September 2006.
TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

d) SAC25

UV absorbance at 254nm is a useful tool and is related to the aromatic fraction of NOM. It is a useful surrogate measure for DOC although it tends to include the more complex NOM character. This technique requires very simple instrumentation and it can be performed by operators in the water treatment plant (Natural Organic Matter 2006). Hartbeespoort Dam samples showed a general decrease in SAC254 after ozonation, with an exception in June 2006 when there was an increase of 8.54% after TR1 and 1.83% after TR2 (Figure 5.7). This corresponds with the highest chlorophyll-*a* value observed. The increase in SAC254 can be due to the liberation of extracellular material when the parent colony of *Microcystis* sp. broke down into smaller colonies after ozonation. Schmidt *et al.* (2001) observed that SAC254 increases after ozonation due to release of cell-bound organics by oxidation of algal cells. The average percentage removal of SAC254 was 15.8% for TR1 and 20.48% for TR2. In January 2006, SAC254 of the raw water was 38.85 m^{-1} and this was the highest observed value for the sampling site. There was 53.8% removal of SAC254 after TR1 and 60.88% removal after TR2. However, this can be related to a decrease in sum of NOM from 43.96 for raw water to 36.32 after TR1 and 35.18 after TR2. It can be concluded that the organics reflected by the SAC254 value are part of the NOM fractions measured by HPSEC and are probably humic substances. Boskop Dam showed a general decrease in SAC254 after ozonation, but with a lower percentage removal than Hartbeespoort Dam. The average percentage removal for TR1 was 11.77% and for TR2 was 13.87%. There was an increase in the values during June and July 2006 of 2.29% and 7.65% after TR1. For the same time period, there were also increases in the percentage of IMW and LMW fractions of NOM after TR1.

Midvaal showed a decrease in SAC254 with an average percentage removal for SAC254 of 21.58% for TR1 and 23.76% for TR2. In February 2006, the river had the highest SAC254 value of 108.75 due to heavy rains. The highest percentage removal was observed in this month with 78.30% for TR1 and 79.03% for TR2. The sample had the highest turbidity value as well. This corresponds to 48.19% HMW and 39.49% IMW fraction of NOM present in the raw water. The values observed suggest that the presences of HMW and IMW fractions of NOM in the river after rainfall are from allochthonous sources and do respond well to ozonation.

Sedibeng had an average percentage removal for SAC254 of 13% for both TR1 and TR2. The highest percentage removal was in February 2006 during the rainy season with 30.28% removal after TR1 and 39.44% removal after TR2. There were decreases in percentage removal of SAC254 observed in August 2006 of 8.92% after TR1 and 3.15% after TR2. There was a concurrent increase in DOC after ozonation observed at the same time.

Westerhoff *et al.* (1998) noted that SAC254 appears to correlate well with the sum of NOM. Correlations performed on the four sampling sites in Excel show that this is only true for the riverine

sites. The correlation coefficient for Midvaal and Sedibeng are 0.96 and 0.72 respectively (n=12). The reason for the correlation is that the absorbance wavelength of 254nm falls within the range where the π-electron interactions occur for a number of aromatic substances and SAC254 at these wavelengths has been found to be a good indicator of aromatic carbon contents of both soil and aquatic humic substances. The dam sites do not show a good correlation and suggest that the SAC254 of these sites constitute other organic fractions that are not part of sum of NOM such as non-humic substances.

Karnik *et al.* (2005) stated that even after extensive ozonation, 15% of the UV-254 absorbance of some waters remained, suggesting that while most of the UV absorbing substances react with ozone, there is a recalcitrant fraction that does not react with ozone. It was also observed that a lower ozone dose was not sufficient to remove the reactive UV-254 absorbing compounds. This could be a factor in explaining why some samples did not react to ozonation as well as should be expected.

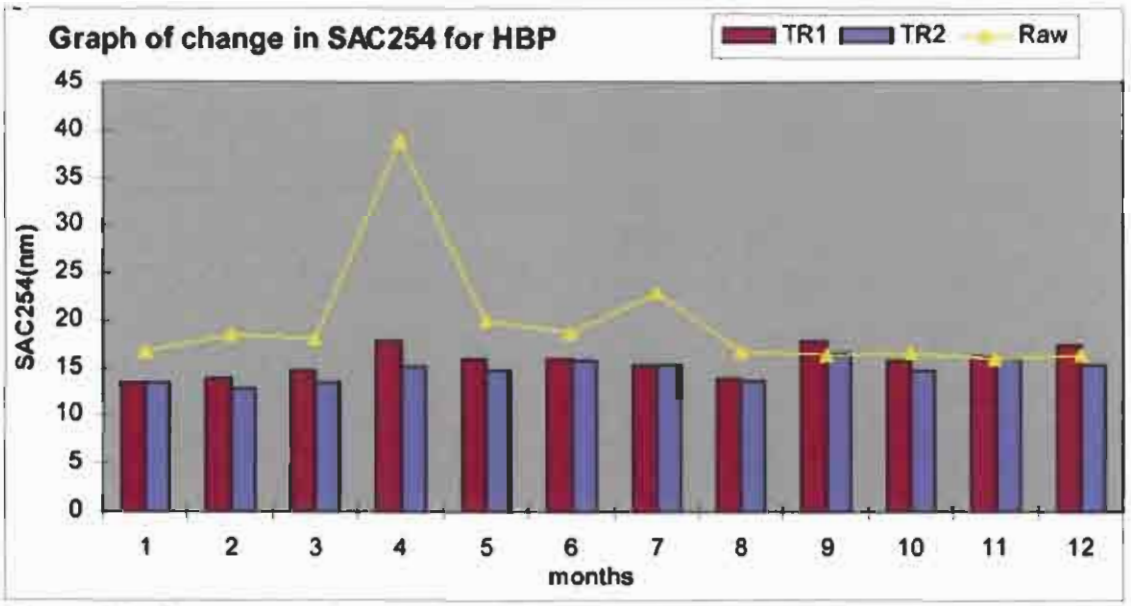


Figure 5.7: Graph of change in SAC254 for Hartbeespoort Dam after ozonation for duration of one year from October 2005 to August 2006. TR1=0.5mg/l ozone, TR2=>0.5mg/l ozone.

e) DOC

DOC gives an indication of the amount of carbon that is available for the biota. This carbon is utilised directly by organisms and is important for maintaining primary production in the aquatic ecosystem. DOC is the most commonly used parameter to quantify NOM, but is not a sufficient measure to determine its impact on water treatment (Natural Organic Matter 2006).

Hartbeespoort Dam had high DOC values for raw water and had a variable response to ozonation

with reported increases and decreases in DOC after exposure to ozone. The biggest decrease in DOC after ozonation appeared in August 2006 with 45% removal after TR1. During this time the water had low turbidity, moderate SAC254 and low chlorophyll-*a* values. There was an absence of any *Microcystis* sp. and the water was very clear. This could account for the high DOC values, as there were no algae to utilise the organic carbon available. This value also corresponds with the highest sum of NOM of 113.93, of which 86.2% was found in the IMW fraction. November 2005 had the highest DOC value for the raw water and had 20% removal of DOC after TR1.

Boskop Dam showed an increase in DOC after ozonation for most samples. There was an increase in DOC from October 2005 to January 2006 after both treatments as well as in March 2006 after TR2. Thereafter, there was a decrease in DOC with a maximum percentage removal of DOC of 36.92% after TR1 in July 2006. This corresponds with the highest percentage LMW fraction of 47.03% found in the sample.

The Midvaal sample results show very little variation in DOC in response to ozone. The percentage removal is below 10% for both treatments except September 2005 and November 2005, which had values of 17.35% and 11.11% removal after TR2. There were increases in DOC in February 2006 and June 2006.

Sedibeng results show no real pattern, having increases and decreases in DOC values after ozone treatment. There was 21.88% removal of DOC after TR2 during April 2006 and an increase of 27.27% after TR1 during October 2005.

There is no correlation between DOC removal and any other variables. Pryor *et al.* (2000) noted that there were decreases of up to 25% in DOC and TOC at ozone concentrations of 2-4mg/l ozone. It is possible to obtain up to 50% removal of TOC if ozonation is followed by coagulation. Geldenhuys *et al.* (2000) reported 6.3% removal of DOC using 1.9mg/l ozone dosage. It is therefore possible to obtain higher percentages of DOC removal after ozonation if the concentration of ozone is increased above 1mg/l.

According to Schmidt *et al.* (2001), SAC254 and DOC increased after ozonation in water containing algae. These workers said that the reason for this is the destruction of algae cells by oxidation causing the release of cell-bound organic matter into the water. Because ozone causes "oxidation and destruction of undesirable components" and "release of cell bound organic matter", there should be careful consideration of the dose of ozone applied as pre-ozonation in water that has a large number of algal cells. The presence of large numbers of algal cells in Hartbeespoort Dam, Midvaal and Sedibeng has an influence on the DOC levels in the water and this can also thus explain the changes in the levels of DOC after ozonation.

f) Determination of NOM

The effect of ozone on NOM is discussed according to the various fractions and how these fractions respond to the two treatments. The sum of NOM and the various fractions have been discussed in Section 4.5.8. The sum of NOM represents the total NOM for the sample and is composed of 3 different fractions based on molecular weight distribution namely: high molecular weight fraction (HMW), intermediate molecular weight fraction (IMW) and low molecular weight fraction (LMW).

It is reported that ozonation could convert NOM from humic to non-humic fractions and from HMW to LMW fractions (Chiang *et al.* 2002). They reported furthermore that they observed high percentages of LMW fractions in surface water of some samples where it was not as expected and concluded that the molecular weight characteristics of samples differ from each other and that they are site specific. Ozone would be expected to be more effective at fragmenting large NOM fractions than small NOM fractions for the same dose (Bose *et al.* 1993). One can envisage that TR2 will show a greater decrease in the sum of NOM than TR1, as the actions of ozone simply convert large molecules into smaller ones (Karnik *et al.* (2005). It is also expected that the sum of NOM for the rivers are higher than dam sites because of a large fraction of HMW which contributes to the total sum of NOM (Bose *et al.* 1994). The changes observed in the sum of NOM after ozonation for the different sampling sites are shown in Figures 5.8 to 5.11 below.

To summarise these results, the following observations were made: the sum on NOM for the rivers was indeed higher than the dam sites and that Hartbeespoort dam had values much higher than Boskop Dam. This is the general trend observed in all the sampling sites, but there are exceptions, which can be attributed to changes in particular fractions of the NOM.

For Hartbeespoort Dam there was a general decrease in the sum of NOM after both TR1 and TR2. There was, however, an increase in sum of NOM in August 2006 but this cannot be explained by rainfall or high concentrations of algae present. As can be seen in Figure 5.9, Boskop showed lower efficiency of TR1 and TR2 to decrease the sum of NOM. Both Midvaal and Sedibeng had higher sum of NOM values with Midvaal showing a greater decrease in the sum of NOM after ozonation.

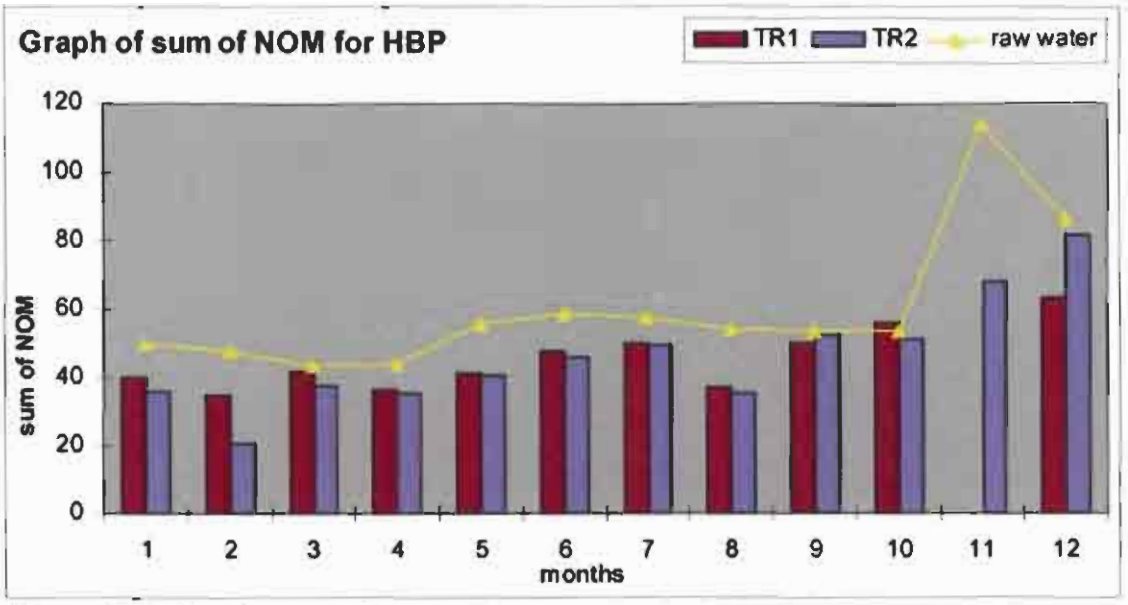


Figure 5.8: The changes observed in the Sum of NOM of Hartbeespoort Dam after ozonation for the duration of one year from October 2005 to September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

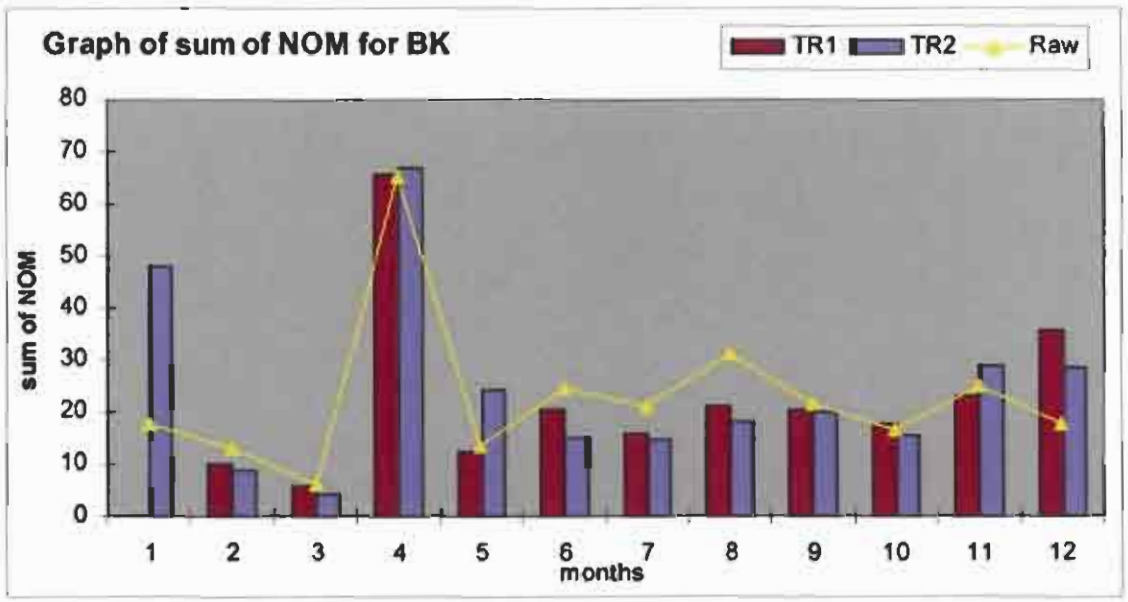


Figure 5.9: The changes observed in the Sum of NOM of Boskop Dam after ozonation for the duration of one year from October 2005 to September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

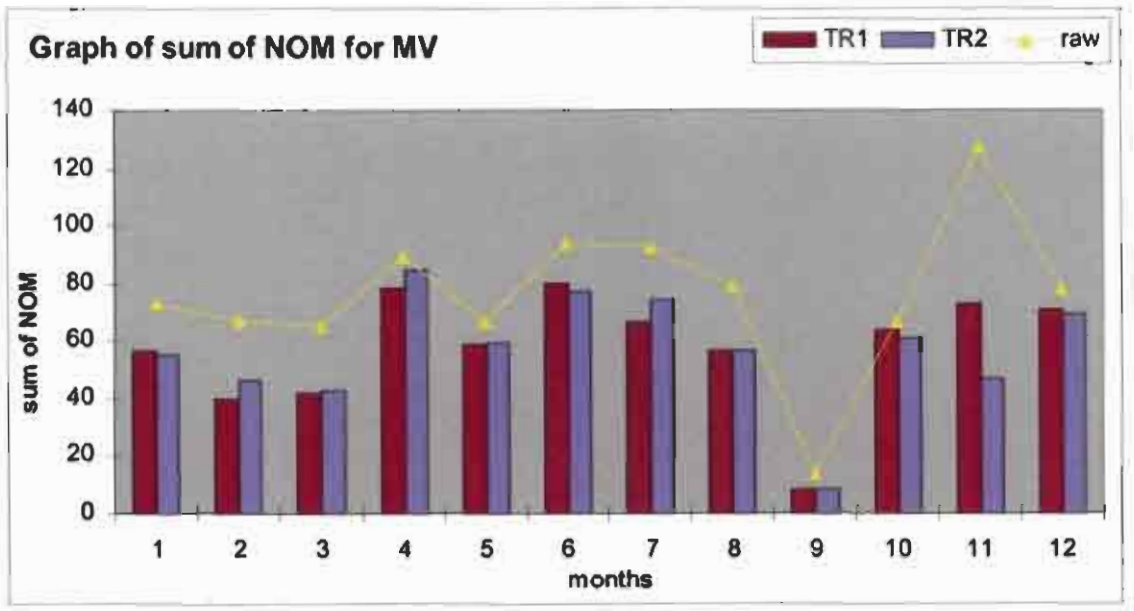


Figure 5.10: The changes observed in the Sum of NOM of Midvaal after ozonation for the duration of one year from October 2005 to September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

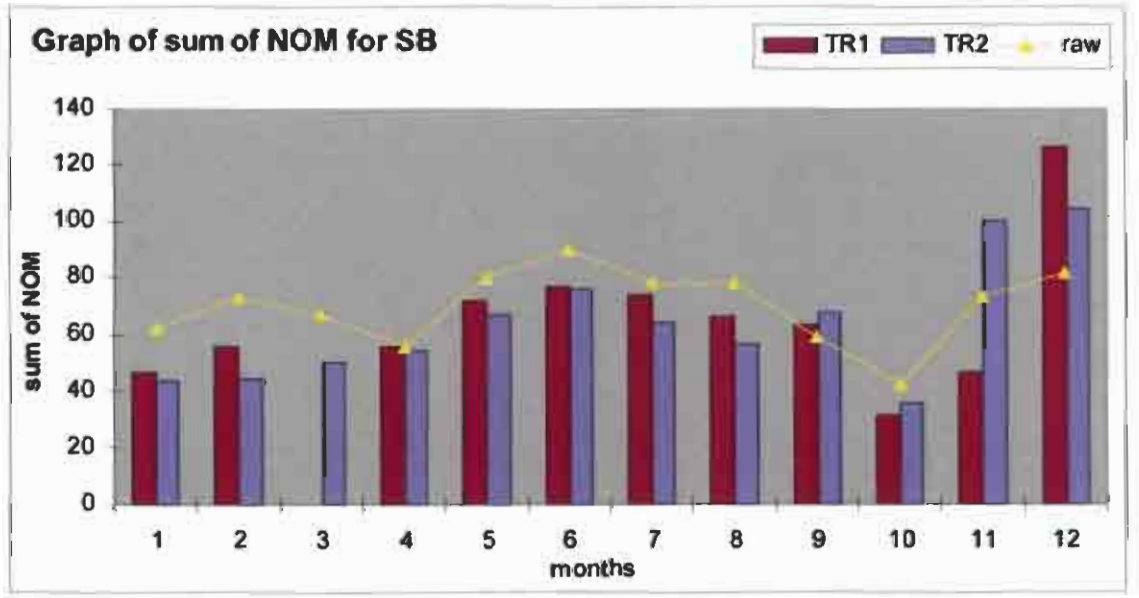


Figure 5.11: The changes observed in the Sum of NOM of Sedibeng after ozonation for the duration of one year from October 2005 to September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

i) HMW Fraction

According to Swietlik *et al* (2003), compounds with HMW fractions were more reactive to oxidants such as ozone. The decrease in SAC254 of these fractions proved that the reactions with ozone proceeded as the removal of SAC254 absorbing compounds occurs predominantly due to the reaction of ozone with these substances (Karnik *et al.* 2005). A common characteristic of drinking water is the absence of the HMW fraction of NOM (Nissinen *et al.* 2000).

Figure 5.12 shows the change in HMW fraction after ozonation for Hartbeespoort Dam. The raw water has an HMW fraction between 12% and 30% and shows a general decrease in the HMW fraction after ozonation. As expected, TR2 is more efficient at reducing the HMW fraction than TR1. The biggest decrease was observed in April and May 2006 with a decrease of 3-5% after ozonation. The increase observed on month 11 cannot be explained.

The Boskop Dam raw water had a lower HMW fraction, but exhibited a bigger change in those fractions after ozonation. Figure 5.13 shows that a decrease in the percentage of the HMW fraction occurred from February 2006 to August 2006 in response to ozonation, especially after TR1. The highest change in the percentage of the HMW fraction occurred in April 2006 for both TR1 and TR2.

Figure 5.14 shows the results obtained for Midvaal. There was a greater change in the HMW fraction after ozonation from October to December 2005 before the rains. Thereafter the percentage change in the HMW fraction after ozonation was low showing no change and even an increase in the HMW fractions. In October 2005 and January 2006, TR2 had the biggest percentage removal of 14.99% of HMW fraction.

Sedibeng had similar results as can be seen in Figure 5.15. The biggest percentage removal after ozonation occurred in April 2006 with a removal of 7.6% after TR1 and 11.92% after TR2.

The results obtained show a change in the HMW fraction of NOM after ozonation, but this change is not as high as expected. Since the presence of a large number of algal cells has an increased demand for ozone, this can lead to a low ozone concentration in the chamber. Studies on humic substance extracted from terrestrial sources show a large reduction in molecular size after ozonation (Nissinen *et al.* 2000). However, surface water with low to moderate organic content has shown only moderate effects on the molecular size distribution at ozone doses between 0-1.2mg ozone/mg carbon (Bose *et al.* 1993). The low ozone dose and low to moderate organic content of the samples may explain why the decrease in the HMW fraction was lower than what was expected after ozonation.

ii) IMW Fraction

Figure 5.16 shows that Hartbeespoort Dam had either no change or negligible decreases in percentage IMW fraction after ozonation.

Boskop dam showed mainly decreases in the percentage IMW fraction after ozonation, the biggest changes being in December 2005, February 2006 and September 2006 (Figure 5.17).

Midvaal and Sedibeng only show negligible changes in the percentage IMW fractions after ozonation as can be seen in Figures 5.18 and 5.19.

iii) LMW Fraction

A larger percentage of LMW fractions is found in dams instead of rivers because the HMW and the IMW fractions have time to settle out of solution and become part of the sediment where they are acted upon by bacterial degradation to form detritus. This detritus is an important source of organic material for the aquatic ecosystem. The LMW fractions seem to be more difficult to remove as they consist mostly of fulvic acids that are more soluble and highly charged compared to humic acids (Matilainen *et al.* 2002). The removal of smaller molecular size humic fractions is lower when using ozone than with other processes like granular activated carbon (Nissinen *et al* .2000), and the removal of NOM in general deteriorates when the size of the fractions becomes smaller. There should be an increase in the LMW fraction after ozonation as the HMW and IMW fractions are oxidised to LMW fractions (Swietlik *et al.* 2003).

This was then also the case for Hartbeespoort Dam as can be seen in Figure 5.20. There was an increase in the LMW fractions after ozonation especially after TR2 from October 2005 to May 2006 when the dam experienced an inflow of organics from rainfall at that time.

Boskop Dam showed a general increase in LMW fraction after ozonation especially in February 2006 at the height of the rainy season and then again in April and May 2006 after the rains. This shows that the organic matter present at that time was amenable to breakdown by ozone and contained a high percentage of the IMW fractions that were subsequently converted to LMW fractions after ozonation (Figure 5.21).

Midvaal showed an increase in the LMW fraction from October 2005 to February 2006, especially after TR2. In June 2006 there was a total removal of LMW fraction after both treatments as seen in Figure 5.22.

Figure 5.23 shows how the LMW of Sedibeng changed after ozonation. There was a general increase in the LMW fractions after ozonation. A reduction in the LMW fraction after TR2 was observed in October 2005 and after TR1 in August 2006.

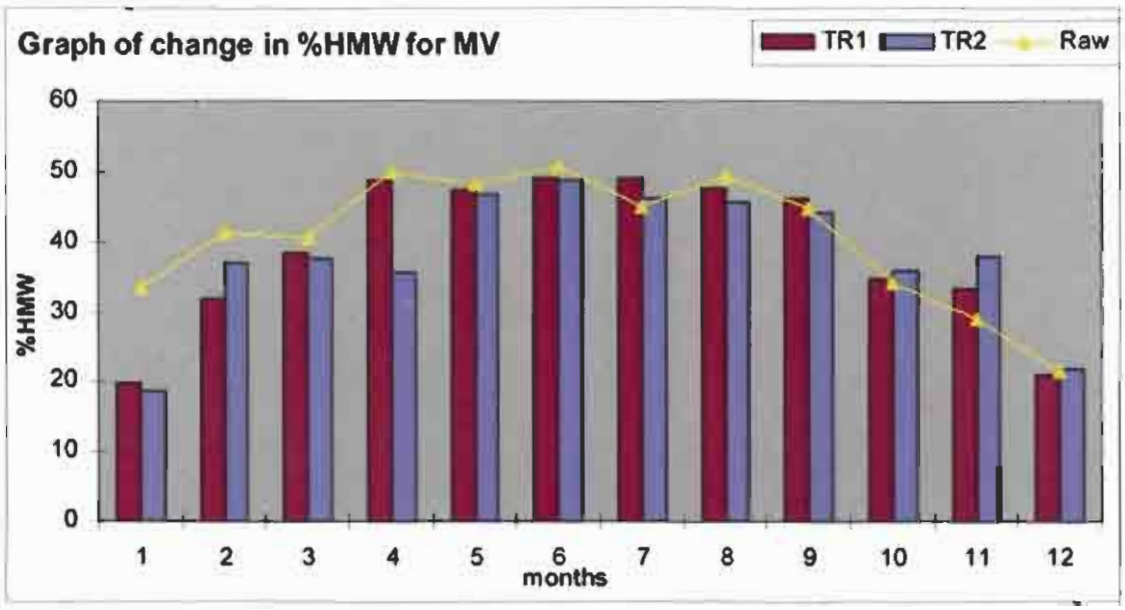


Figure 5.14: The change in the %HMW fraction of NOM for Midvaal for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

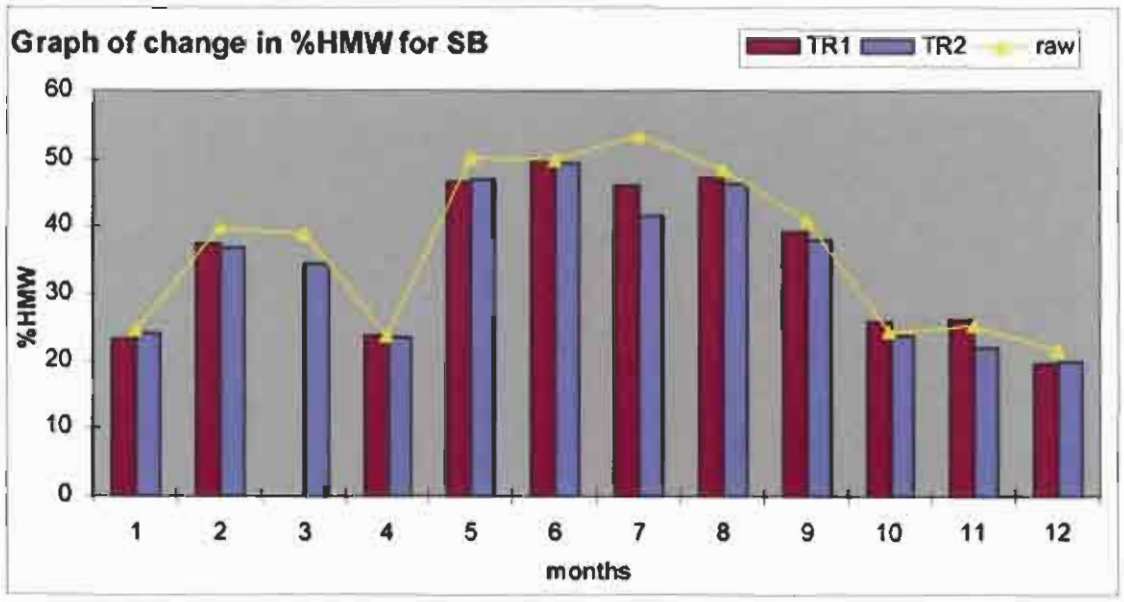


Figure 5.15: The change in the %HMW fraction of NOM for Sedibeng for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

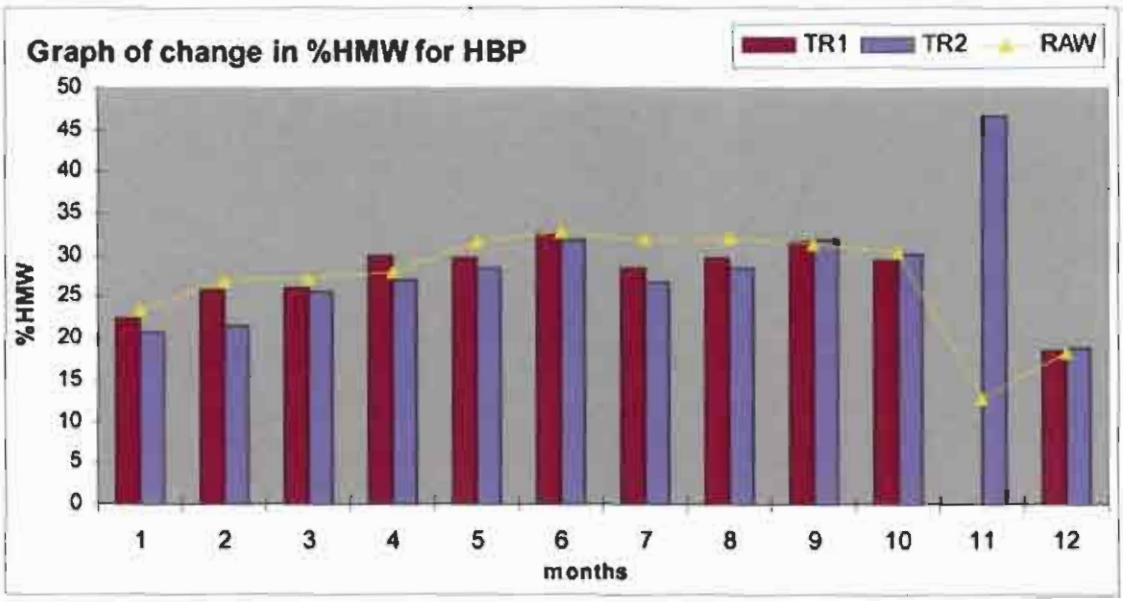


Figure 5.12: The change in the %HMW fraction of NOM for Hartbeespoort Dam for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

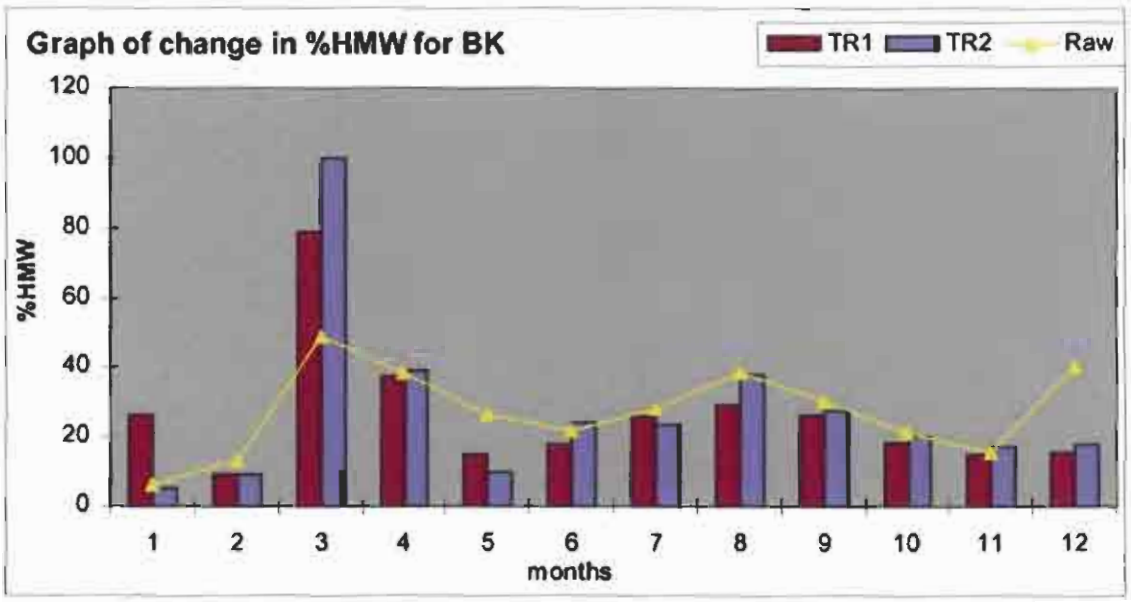


Figure 5.13: The change in the %HMW fraction of NOM for Boskop Dam for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

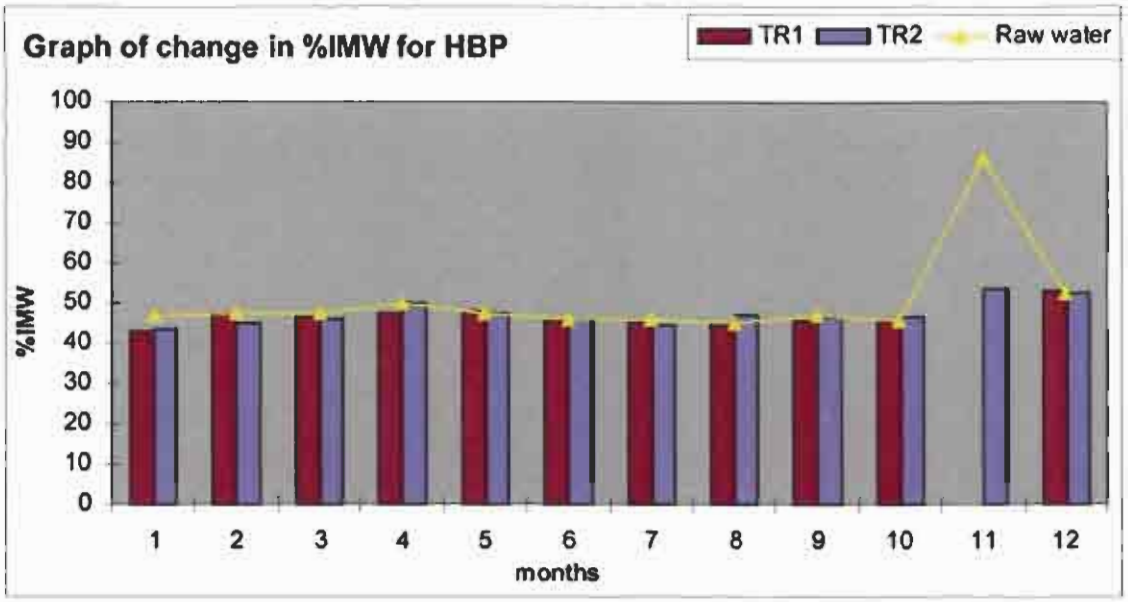


Figure 5.16: The change in the %IMW fraction of NOM for Hartbeespoort Dam for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

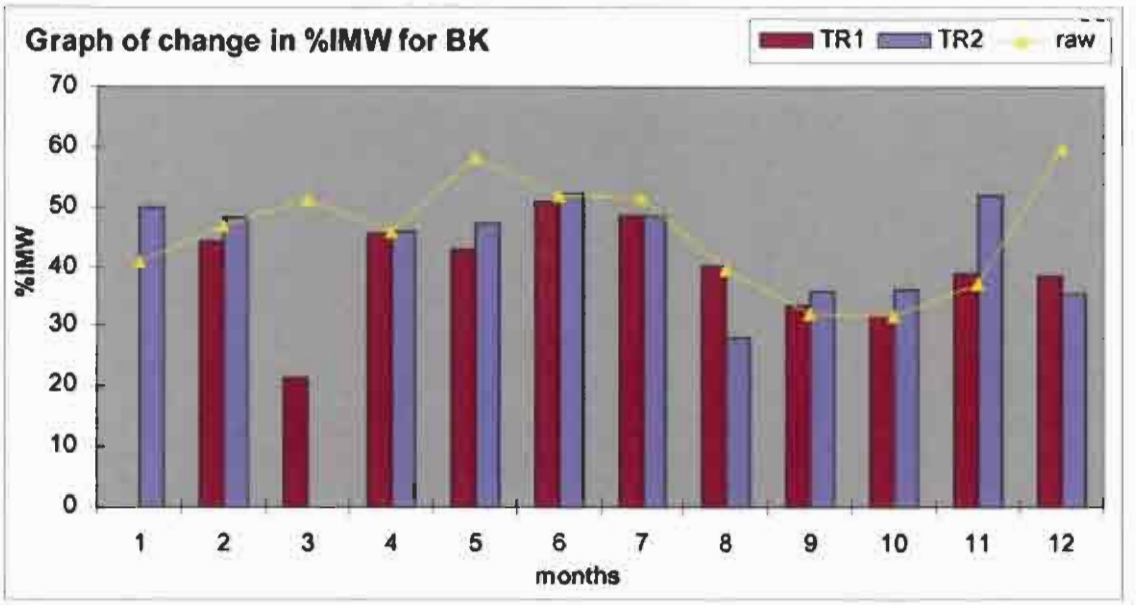


Figure 5.17: The change in the %IMW fraction of NOM for Boskop Dam for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone

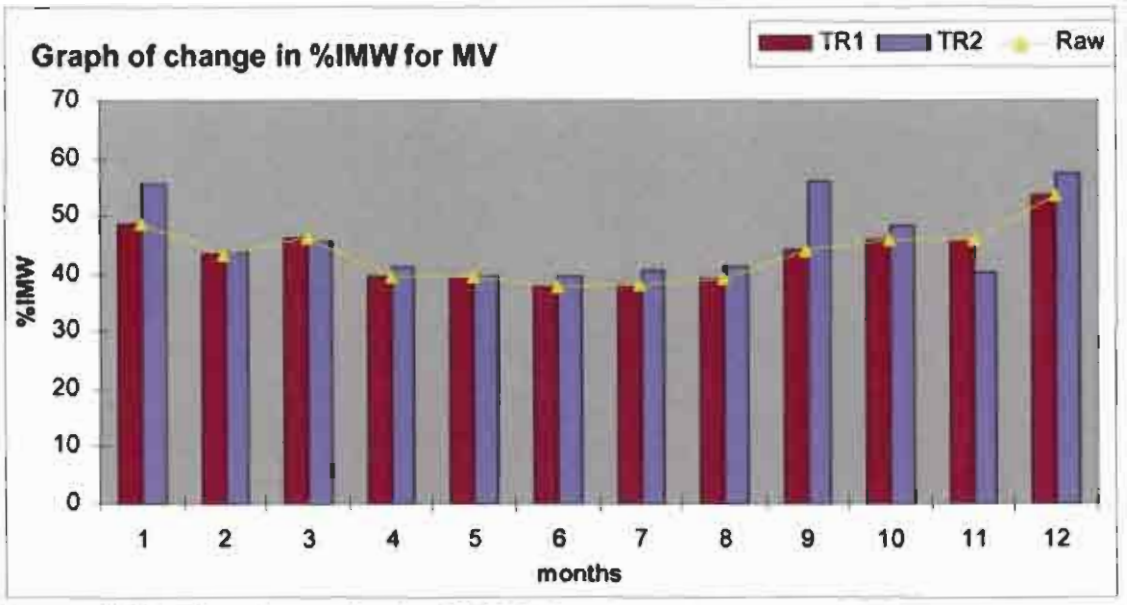


Figure 5.18: The change in the %IMW fraction of NOM for Midvaal for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

Figure 5.19: The change in the %IMW fraction of NOM for Sedibeng for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

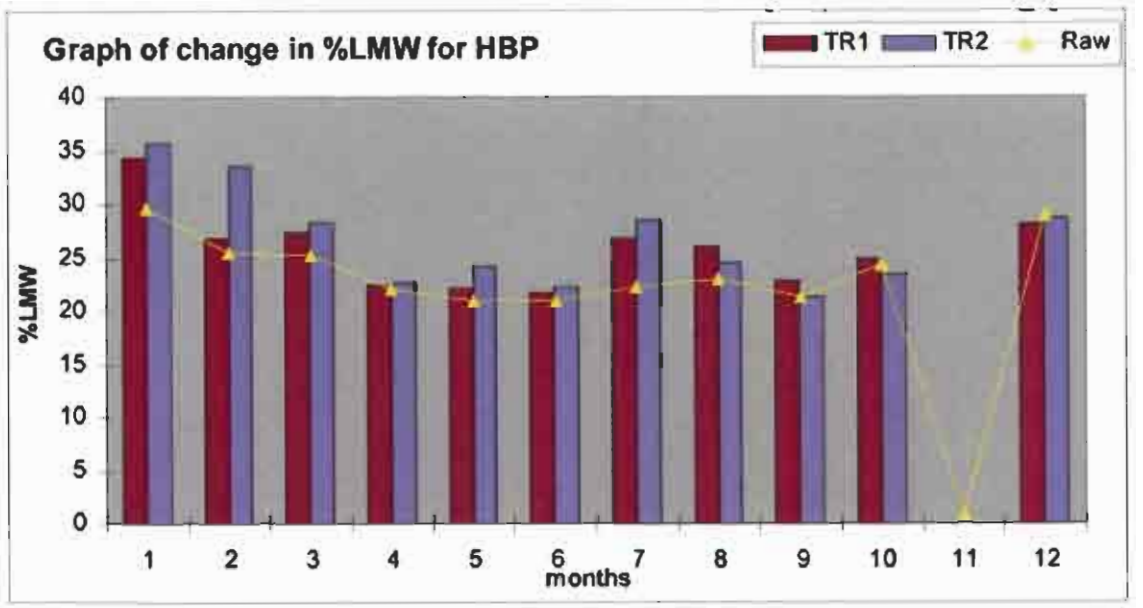


Figure 5.20: The change in the %LMW fraction of NOM for Hartbeespoort Dam for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

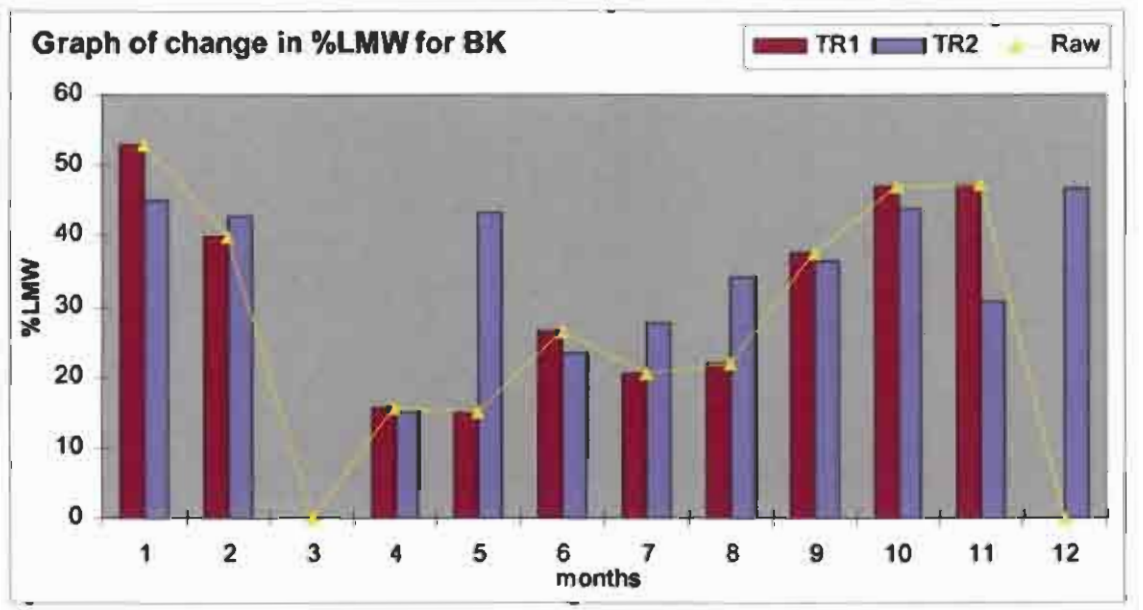


Figure 5.21: The change in the %LMW fraction of NOM for Boskop Dam for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

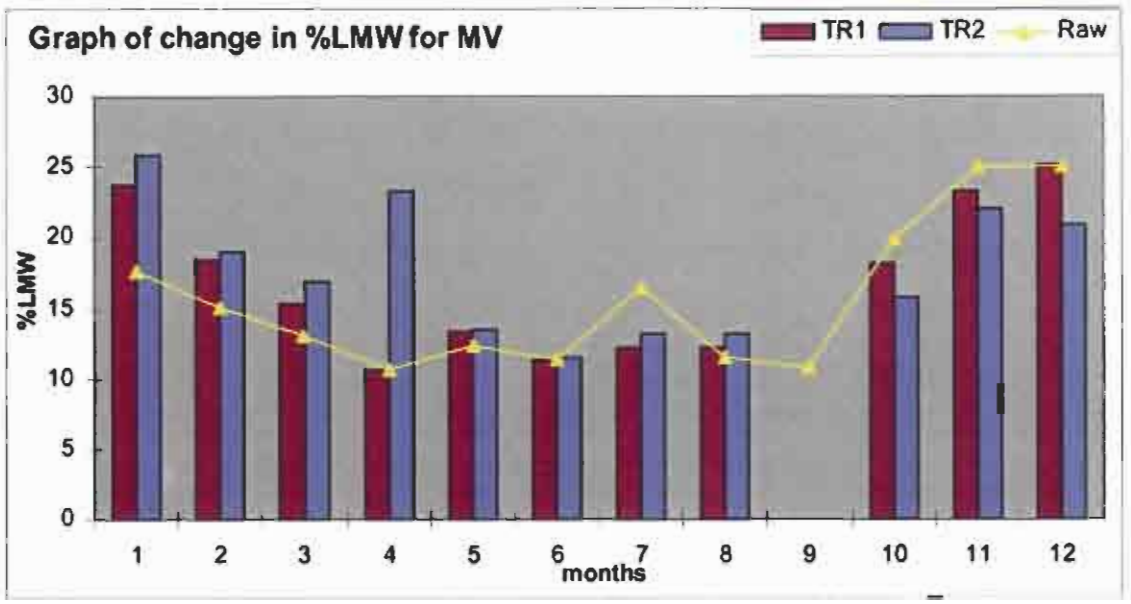


Figure 5.22: The change in the %LMW fraction of NOM for Midvaal for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

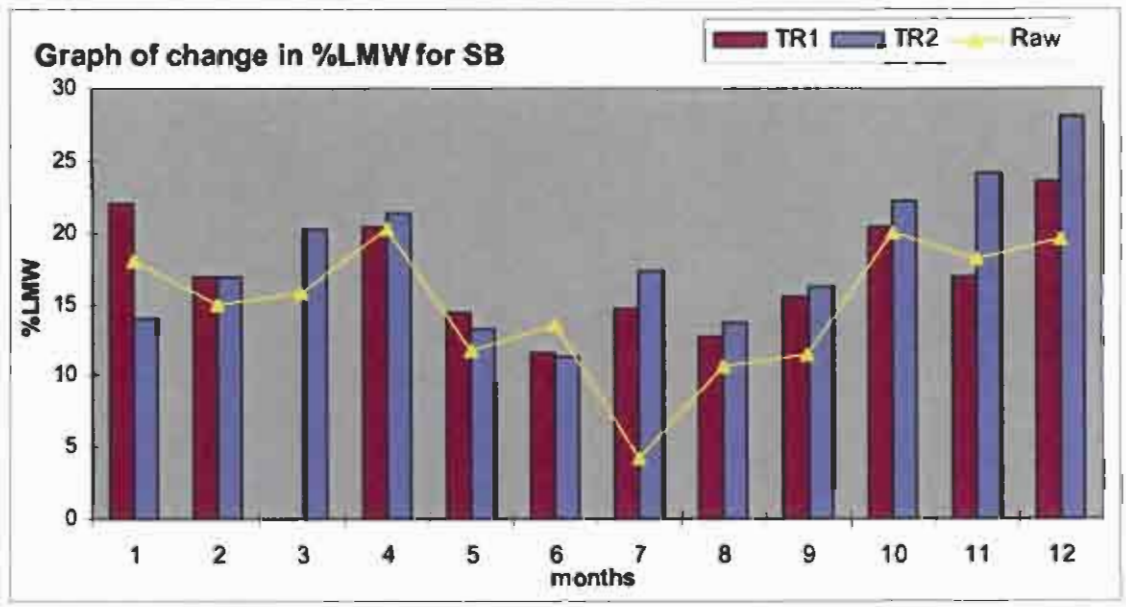


Figure 5.23: The change in the %LMW fraction of NOM for Sedibeng for duration of one year from October 2005 and September 2006.

TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone.

G) Summary of Results for ozonation of raw water

Ozone is used for a variety of purposes and contributes to enhancing the purification process in many ways. The removal of turbidity, SAC254, DOC and chlorophyll-*a* is the primary function of the treatment process and can benefit from pre-ozonation. Tables 5.4 and 5.5 provide a summary of the effect of ozone on the different samples.

In general, ozonation leads to a decrease in SAC24 for all samples. The results obtained in this study show that ozonation enhanced removal of SAC254 for all the samples with Midvaal showing the largest change in SAC254 removal. Karnik *et al.* (2005) reported that the removal of compounds that absorb at UV-254 by ozonation is due to ozone reacting with the aromatic fraction of these compounds resulting in a significant decrease in SAC254 values, even at low ozone dosages. Therefore we can conclude that the organic matter present in the river at Midvaal is of an aromatic nature. In some of the samples, ozonation led to an increase in SAC254 instead of a decrease, but this is probably due to other factors such as the release of algal-derived organic substances and non-humic substances. This is the case for Hartbeespoort Dam where large algal blooms occur.

Turbidity was affected favourably by ozonation for all samples, especially in the riverine samples. The turbidity of Hartbeespoort Dam was reduced by ozonation but in some cases an increase occurred. This was probably due to the release of extra-cellular materials by the broken down cyanobacterial blooms present in the sample. Turbidity of Boskop dam responded favourably to ozonation although the presence of a high percentage of LMW fractions impacted negatively in some samples, as ozonation is more effective in removing the HMW fraction than the LMW fractions (Bose *et al.* 1993).

Ozone is used extensively for algal control but the release of cell-bound organics can lead to an increase in turbidity, SAC 254 and coagulant dose. However, this study found that ozonation was very effective at removal of some of the algal species, especially member of the Chlorophyceae. Members of Cynaophyceae, notably *Microcystis* sp., are destroyed by ozone but at a higher dose of ozone and a reduced percentage when compared to Chlorophyceae. It has been reported by Pryor *et al.* (2000) that *Microcystis* sp. responds well to ozonation and it is possible to obtain removal of as much as 75% or more if concentrations of 2mg/l ozone are applied. We found that the diatoms, which are members of Bacillariophyceae are, however, resistant to ozone, possibly because of the presence of the silica frustule around the cell.

The effect of ozone on DOC was variable with no fixed pattern. SAC254 can be used as a surrogate measure for DOC (Natural Organic Matter 2006), but there were no correlations between the values of DOC and SAC254 observed in any of the samples. DOC did not correlate with any of the other variables measured. There should be a decrease in DOC after ozonation but this was not

the case in all samples. This may be a consequence of low ozone concentrations and interference from the algal species present. Wildrig (1996) observed that the extent of DOC removal after ozonation was determined by the algal species from which it was derived and this can change seasonally depending on the type of algae present.

The effect of ozonation on the sum of NOM was a general decrease in the value for all the sampling sites. Nissinen *et al.* (2000) reported that ozonation, alone or in combination with other treatments such as granular activated carbon, improved the removal of all humic fractions compared to conventional treatment. Ozone causes a move from the HMW to the IMW and the LMW fractions. In most of the samples, the percentage change of the HMW fraction was lower than expected. There was little change in the IMW fraction and a large increase in the LMW fraction of NOM. We can deduce that the ozone concentration was not high enough to break down the large percentage of HMW fractions that was found in the riverine samples. This may be due to a high ozone demand of the samples as a result of large numbers of algal cells being present. The IMW fraction showed either no change or slight decreases in the values while the LMW fraction had the biggest increase. Therefore, ozone led to an increase in the LMW fraction of all the samples.

To summarise, ozonation benefited the samples for water purification with regard to the measured variables, but the interactions with algal cells and other dissolved organics can hinder its effectiveness.

Table 5.2: The efficiency of ozone treatment with regard to percentage removal of SAC254, Turbidity, Chlorophyll-*a* and DOC of the two dam sites for the duration of the study.

TR1= 0.5mg/l Ozone, TR2= >0.5mg/l ozone. HB=Hartbeespoort Dam, BK=Boskop Dam.

Sample	Months	%SAC254 removal		% Turbidity removal		%Chlorophyll-*a* removal		% DOC removal	
		TR1	TR2	TR1	TR2	TR1	TR2	TR1	TR2
HB	October	19.40	20.00	17.93	53.79	100.00	100.00	0.00	0.00
HB	November	25.00	30.71	33.13	-8.12	100.00	100.00	20.65	17.39
HB	December	18.61	24.72	-14.79	-15.68	0.00	100.00	-7.14	-2.86
HB	January	53.80	60.88	0.74	-36.03	-0.16	49.92	5.13	1.28
HB	February	19.85	25.63	25.27	28.83	50.00	50.00	-1.47	1.47
HB	March	14.67	16.27	21.47	-7.84	33.33	66.67	11.54	6.41
HB	April	32.97	33.19	15.63	25.31	50.00	100.00	8.99	5.62
HB	May	17.26	18.75	7.24	10.87	100.00	100.00	3.28	8.20
HB	June	-8.54	-1.83	56.40	-47.19	16.67	50.00	2.78	6.94
HB	July	5.09	12.28	27.27	45.00	20.02	40.01	-3.51	0.00
HB	August	-1.56	0.00	25.83	22.52	100.00	100.00	45.00	11.25
HB	September	-6.75	5.21	38.10	52.78			-16.46	-6.33
BK	October	0.00	3.13	100.00	65.87	100.00	0.00	-4.17	100.00
BK	November	6.48	9.72	30.19	56.51	100.00	100.00	-233.3	-324.2
BK	December	28.09	23.83	25.69	45.09	0.00	100.00	-11.11	-7.41
BK	January	11.25	19.17	47.18	43.30			-25.00	-44.44
BK	February	18.75	24.17	44.00	48.80	0.00	100.00	2.56	10.26
BK	March	17.33	14.80	26.28	41.69	100.00	100.00	10.87	-8.70
BK	April	20.30	22.14	28.85	46.63	0.00	100.00	25.49	19.61
BK	May	28.76	24.08	55.59	16.08			31.91	29.79
BK	June	-2.29	1.38	39.13	67.91	0.00	100.00	0.00	14.81
BK	July	-7.65	3.83	4.14	15.98	0.00	100.00	36.92	23.08
BK	August	1.02	3.57	6.47	-9.48	100.00	100.00	12.90	22.58
BK	September	7.41	16.67	10.36	15.94			15.63	-31.25

Table 5.3: The efficiency of ozone treatment on the two riverine sites with regard to percentage removal of SAC254, Turbidity, Chlorophyll-*a* and DOC for the duration of the study.

TR1= 0.5mg/l Ozone, TR2= >0.5mg/l ozone.

Sample	Months	%SAC254 removal		% Turbidity removal		%Chlorophyll-*a* removal		% DOC removal	
		TR1	TR2	TR1	TR2	TR1	TR2	TR1	TR2
Midvaal	October	16.41	23.76	25.20	26.50	0.00	0.00		
Midvaal	November	21.03	26.40	39.51	39.61	25.00	75.00	6.94	11.11
Midvaal	December	21.87	18.47	38.27	31.25	33.33	33.33	9.21	3.95
Midvaal	January	20.93	27.87	4.76	1.75	50.00	50.00	1.12	2.25
Midvaal	February	78.30	79.03	3.13	21.88	0.00	100.00	-8.20	-9.84
Midvaal	March	24.69	34.63	2.46	1.23			4.55	0.00
Midvaal	April	22.56	21.68	11.91	8.15	100.00	100.00	2.33	-1.16
Midvaal	May	35.78	29.90	8.54	0.50	0.00	50.00	3.03	1.52
Midvaal	June	4.98	4.98	11.97	10.26	0.00	28.56	-2.74	-1.37
Midvaal	July	1.11	13.53	2.71	10.14	33.33	33.33	1.52	6.06
Midvaal	August	7.26	3.04	3.10	6.20	0.00	0.00	2.88	0.00
Midvaal	September	2.12	0.00	10.57	3.25	11.11	22.22	5.10	17.35
Sedibeng	October	15.57	14.96	20.75	56.77	0.00	100.00	-27.27	0.00
Sedibeng	November	23.47	29.60	48.46	65.82	0.00	100.00	1.14	7.95
Sedibeng	December	24.90		10.11		50.00	100.00		
Sedibeng	January	13.49	29.30	34.52	26.73	33.33	66.67	0.00	10.81
Sedibeng	February	30.28	39.44	9.82	9.09	0.00	0.00	7.89	5.26
Sedibeng	March	3.94	4.96	-4.46	-2.68	0.00	0.00	-4.35	-8.70
Sedibeng	April	27.30	31.73	9.90	2.77	0.00	0.00	3.12	21.88
Sedibeng	May	16.06	-14.72	26.29	30.60	0.00	0.00	0.00	2.60
Sedibeng	June	9.66	10.79	10.00	5.05	66.67	66.67	4.62	-4.62
Sedibeng	July	3.41	-0.97	-3.84	7.17	0.00	100.00	2.82	16.90
Sedibeng	August	-8.92	-3.15	20.57	16.39	0.00	50.00	-2.50	-2.50
Sedibeng	September	0.95	6.92	0.28	10.47	25.00	50.00	18.37	10.20

Table 5.4: Changes observed in SAC254, turbidity, chlorophyll-*a* and DOC after ozonation of the two dam sites Hartbeespoort Dam(HB) and Boskop Dam (BK) for one year. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. The symbols shown depict the following:

0=no change in the variable

+= Increase in the variable

- = decrease in the variable

X=no readings available

Sample	Months	SAC254		Turbidity		Chlorophyll-*a*		DOC	
		TR1	TR2	TR1	TR2	TR1	TR2	TR1	TR2
HB	October	-	-	-	-	0	X	-	-
HB	November	-	-	-	+	-	-	+	-
HB	December	-	-	+	+	0	X	+	+
HB	January	-	-	-	+	0	0	-	+
HB	February	-	-	-	-	-	-	+	-
HB	March	-	-	-	+	-	-	-	+
HB	April	-	-	-	-	-	-	-	-
HB	May	-	-	-	-	-	-	-	-
HB	June	+	+	-	+	-	-	-	-
HB	July	-	-	-	-	-	-	-	-
HB	August	+		-	-	-	-	-	-
HB	September	+	-	-	-	0	0	+	+
BK	October	X	-	X	-	X	0	+	+
BK	November	-	-	-	-	0	0	+	+
BK	December	-	-	-	-	-	0	+	+
BK	January	-	-	-	-	X	X	+	+
BK	February	-	-	-	-	0	-	-	-
BK	March	-	-	-	-	-	-	-	+
BK	April	-	-	-	-	0	-	-	-
BK	May	-	-	-	+	X	X	-	-
BK	June	+	-	-	-	0	-	0	-
BK	July	+	-	-	-	0	-	-	-
BK	August	-	-	-	+	-	-	-	-
BK	September	-	-	-	-	0	0	-	+

Table 5.5: Changes observed in SAC254, turbidity, chlorophyll-*a* and DOC after ozonation of the two riverine sites Midvaal and Sedibeng for one year. TR1=0.5mg/l ozone, TR2= >0.5mg/l ozone. The symbols shown depict the following:

0=no change in the variable

+= Increase in the variable

- = decrease in the variable

X=no readings available or value was zero (for chlorophyll-*a*)

Sample	Months	SAC254		Turbidity		Chlorophyll-*a*		DOC	
		TR1	TR2	TR1	TR2	TR1	TR2	TR1	TR2
Midvaal	October	-	-	-	-	0	0		
Midvaal	November	-	-	-	-	-	-	-	-
Midvaal	December	-	-	-	-	-	-	-	-
Midvaal	January	-	-	-	-	-	-	-	-
Midvaal	February	-	-	-	-	0	-	+	+
Midvaal	March	-	-	-	-	X	X	-	0
Midvaal	April	-	-	-	-	-	-	-	+
Midvaal	May	-	-	-		0	-	-	-
Midvaal	June	-	-	-	-	0	-	+	+
Midvaal	July	-	-	-	-	-	-	-	-
Midvaal	August	-	-	-	-	0	0	-	0
Midvaal	September	-	-	-	-	-	-	-	-
Sedibeng	October	-	-	-	-	-	X	+	X
Sedibeng	November	-	-	-	-	0	0	-	-
Sedibeng	December	-	X	-	X	-	X	X	X
Sedibeng	January	-	-	-	-	-	-	-	-
Sedibeng	February	-	-	-	-	0	0	-	-
Sedibeng	March	-	-	-	-	0	0	+	+
Sedibeng	April	-	-	-	-	0	0	-	-
Sedibeng	May	-	+	-	-	-	-	0	-
Sedibeng	June	-	-	-	-	-	-	-	+
Sedibeng	July	-	+	+	-	0	-	-	-
Sedibeng	August	+	+	-	-	0	-	+	+
Sedibeng	September	-	-	-	-	-	-	-	-

5.5.2: Jar Test results

As described in Section 5.4, each sample was subjected to a Jar Test to determine whether ozone application could improve on the conventional coagulation, flocculation and sedimentation processes. Three Jar Tests were performed on each water sample from the four sampling sites for the duration of one year and are denoted as follows:

RAW+ =raw water treated with coagulant,

TR1 =raw water +0.5mg/l ozone + coagulant and

TR2 =raw water + >0.5mg/l ozone + coagulant.

There were a total of 144 Jar tests performed during the experiment and each test made use of five different coagulant doses. It is difficult to show the changes that occurred in each Jar Test and in every jar. Since reductions in turbidity, SAC254 and chlorophyll-*a* are the most important parameters for water treatment plants, these values are examined in the following tables. The value corresponding to the lowest turbidity, SAC254 and chlorophyll-*a* for each test is shown in Tables 5.6-5.10 for the different sampling sites. The raw water value of these variables is given so that a comparison can be made of the efficiency of the 3 treatments. The number given in brackets is the coagulant dose in mg/l $FeCl_3$ at which the minimum value was achieved. It is recommended that turbidity of < 4NTU is achieved after coagulation, flocculation and sedimentation (Schutte 2006) and <1NTU for drinking water. Since the lowest turbidity obtained in all the Jar Tests is far below 4NTU, the optimum turbidity will be taken as <1 NTU.

Each sample site is unique in its response to the treatments and is therefore discussed individually.

a) Hartbeespoort Dam

The results of the Jar Test for SAC 254 and turbidity are given in Table 5.6.

There is a decrease in SAC254 after all 3 treatments with the largest change observed after TR2. The only exceptions are in April and May 2006 when TR1 had lower values. The optimum coagulant dose remained at 25mg/l $FeCl_3$. The largest observed removal of SAC254 was in April 2006, which also had the highest SAC254 value for raw water.

Optimum turbidity of <1NTU was obtained using RAW+, TR1 and TR2 although there were some exceptions. From January to March 2006, TRI and TR2 did not achieve optimum turbidity and this can be due to the high rainfall at that time. In February, the turbidity value for TR2 was 2.23, showing that the coagulant dose of 25mg/l $FeCl_3$ was not effective to obtain optimum turbidity. This was the month with the highest raw water turbidity. The optimum coagulant dose remained the same at 25mg/l $FeCl_3$ for turbidity removal for all 3 treatments.

Table 5.10 shows that chlorophyll-*a* is removed by all 3 treatments. There is, however, a change in

the coagulant dose necessary. In some of the samples, ozonation alone achieves complete removal of chlorophyll-*a* and coagulant is not required. In other instances the coagulant dosage is lower for TR1 and TR2 when compared to RAW+. Therefore it can be deduced that ozonation has some effect on the algal cells making them more amenable to removal by the coagulant. This may be due to the action of ozone on the cell membrane or surface charges and should be investigated. There were some exceptions to this during the months when chlorophyll-*a* values were at their highest. The RAW+ treatment achieved complete removal of chlorophyll-*a* at the lowest coagulant dose. TR1 and TR2 achieved complete removal as well, but at a higher coagulant dose. This may be due to liberation of cell-bound organics after ozonation that required a higher coagulant dose to remove.

To conclude, SAC24 is removed effectively by all 3 treatments but more by the action or TR1 and TR2 than RAW+. Turbidity is reduced by all 3 treatments with no extra benefit from the application of ozone. Chlorophyll-*a* is effectively removed by all 3 treatments, but a lower coagulant dose after TR1 and TR2 except when values are above 143.32 μg/l chlorophyll-*a*.

b) Boskop Dam

Table 5.7 shows that SAC254 is removed by all 3 treatments with TR1 and TR2 being more effective than RAW+. However, the reduction in SAC254 of Boskop Dam was not as good as it was for Hartbeespoort Dam. The biggest change in SAC254 was observed in October 2005 with TR2 with a reduction from 15.5 to 9 after ozonation and the Jar test. The optimum coagulant dose was generally 25mg/l $FeCl_3$.

Although the raw water turbidity of Boskop dam was very low compared to the other sites, optimum turbidity was achieved only a few times. All 3 treatments did not effectively remove the turbidity of the raw water. From June to August 2006, the turbidity of the raw water was very low and both TR1 and TR2 lead to increases in the turbidity values. This could be due to oxidation of dissolved organics that were not incorporated into the flocs by the coagulant. Samples for January to March 2006 showed a positive effect of TR1 and TR2 on reducing turbidity when compared to RAW+. It can be deduced that pre-ozonation had no effect on the Boskop Dam water with regard to turbidity removal from June to August 2006 but had a positive effect on the samples from January to March 2006 when compared to the RAW+ treatment. The organic matter present in the water from January to March comes primarily from allochthonous sources, as this was a period of heavy rainfall. These particles are positively affected by ozone and subsequent coagulation.

According to Matilainen *et al.* (2002), the LMW fraction of NOM is more difficult to remove because of its increased solubility and charge compared to humic fractions. They are also more difficult to destabilise by aluminium coagulation doses used in water treatment plants. Boskop Dam had the

largest fraction of LMW among the samples and this could account for the reduction in turbidity removal especially after TR1 and TR2.

Boskop has low values of chlorophyll-*a* in the raw water and this was effectively reduced by all 3 treatments, although RAW+ achieved the removal at a higher coagulant dose than TR1 and TR2 (Table 5.10).

To summarise, TR1 and TR2 can enhance SAC254 removal while RAW+ is more effective at removal of turbidity. There was some improvement in turbidity removal after TR1 and TR2 but the effect of these treatments is variable and depends on other factors such as nature of NOM. Removal of chlorophyll-*a* was achieved by all 3 treatments.

c) Midvaal.

As seen in Table 5.8, Midvaal exhibited the best removal of SAC254 as achieved by TR1 and TR2 i.e. ozonation was effective in removal of SAC254. However, during August and September 2006, this changed and RAW+ treatment achieved the best removal of SAC254. These two months correspond to the highest values for percentage LMW fraction of NOM in the raw water. There was also a decrease in the percentage HMW fraction and an increase in the percentage IMW and LMW fractions of NOM. These IMW and LMW fractions therefore respond well to removal with $FeCl_3$. The optimum coagulant dose stayed the same for all treatments.

Ozonation had little effect on turbidity of the samples from the Midvaal water. Optimum turbidity was difficult to achieve throughout all 3 treatments but the RAW+ treatment achieved the lowest turbidity for most of the samples except from July to September 2006 when TR2 improved turbidity.

Table 5.10 shows that chlorophyll-*a* removal was achieved by all 3 treatments with TR1 and TR2 having lower coagulant doses than RAW+. The only exceptions were in December 2005, June 2006 and September 2006 when RAW+ achieved total removal of chlorophyll-*a* at the lowest coagulant dose. These samples had high concentrations of the diatom *Cyclotella* sp. of greater than 10 000 cells/ml present at that time. These diatoms are not oxidised by ozone and are therefore effectively reduced by the RAW+ treatment at a lower coagulant dose.

In conclusion, Midvaal water responds well to removal of SAC254 after TR1 and TR2 although there are exceptions. Turbidity removal was greatest after the RAW+ treatment. Chlorophyll-*a* is effectively removed by all 3 treatments but at a lower coagulant dose after TR1 and TR2.

d) Sedibeng

Table 5.9 shows that SAC254 removal was more effectively achieved after TR1 and TR2 than RAW+. TR2 showed better results than TR1 and coagulant dose was the same at 25mg/l $FeCl_3$ for all the samples. However, in September 2006 the lowest value for SAC254 was obtained after the

RAW+ treatment. This corresponds to a decrease in the percentage of the HMW fraction and an increase in the percentage of the IMW and LMW fractions of NOM, which is similar to that found in Midvaal.

Turbidity of Sedibeng water responded well to TR1 and TR2 compared to the RAW+ treatment. The optimum coagulant dose was between 15-25mg/l $FeCl_3$.

Removal of chlorophyll-*a* follows the same trend as for Midvaal (Table 5.10). All 3 treatments removed chlorophyll-*a* effectively with TR1 and TR2, achieving this at the lowest coagulant dose. The exceptions to these observations are when large numbers of diatoms are present and then the RAW+ treatment achieves total removal at a lower coagulant dose.

In summary, Sedibeng water responded better to TR1 and TR2 than RAW+ for removal of SAC254 and turbidity. Chlorophyll-*a* removal follows the same trend as that for Midvaal with all 3 treatments proving effective although coagulant dose is variable.

e) DISCUSSION AND CONLUSION

The effects of pre-ozonation on Jar Test results are variable and site specific. These variations can be due to the nature and characteristics of the NOM and other dissolved particles as well as the presence of algal cells and their metabolites. $FeCl_3$ is a metal salt coagulant that destabilises particles by forming positively charged hydroxide precipitates and removal of NOM occurs by adsorption and precipitation. The tendency of NOM for precipitation and adsorption increases with increasing molecular weight of NOM. When water containing NOM is ozonated, the larger molecular weight compounds are partially oxidised to smaller, polar organic compounds which can lead to a decrease in the amount of NOM removed by precipitation and adsorption (Pryor *et al.* 2000). Since ozonation affects the surface charge and the size of the NOM, it can cause changes in coagulant demand to occur (Tobiason *et al.* 1994). The coagulant demand in this study did not change much with an average optimum coagulant dose of 25 mg/l $FeCl_3$ with regard to turbidity and SAC254 removal.

It is expected that ozone will break down the HMW fractions into smaller fractions. Nissinen *et al.* (2000) noted that ozone breaks up the larger humic molecules and alters the sum of NOM towards smaller molecules. He further observed that ozone decreases the UV-absorbance properties of individual humic fractions, compared to conventional treatment. This explains the efficiency of ozone treatment to reduce SAC254 for most of the samples. The two occasions that ozone did not decrease SAC254 in the river samples were related to a change in the composition of the NOM at that time. During August 2006 (Midvaal) and September 2006 (Midvaal and Sedibeng), there was a higher percentage SAC254 removal with conventional treatment than with ozonation. These samples were characterised by lower HMW fractions and higher IMW and LMW fractions. It can

therefore be deduced that ozone did not act efficiently on these samples because of the lack of the HMW fraction. Therefore the IMW and LMW fractions were successfully coagulated by ferric chloride and removed from the sample. The percentage of the LMW fraction of NOM therefore, can affect the efficiency of ozone treatment. It is advisable that Midvaal Water Company monitors this LMW fraction, as pre-ozonation is part of their purification process.

The effect of the treatments on chlorophyll-*a* removal follows similar patterns for the sampling sites. In general, for Vaal River samples, all the treatments removed some part of the chlorophyll-*a*, but ozonation does so at a lower coagulant dose. This is, however, dependant on the type of algal cells present in the water sample at that time. Members of the class Bacillariophyceae are not reactive towards ozone and when there are large numbers of these species present, conventional treatment achieves total removal of chlorophyll-*a* at a lower coagulant dose. Hartbeespoort Dam responds well to ozonation, but when very high concentrations of cyanobacteria are present, the coagulant dose increases after ozonation. This is probably due to oxidation of the parent colony membrane by ozone, which results in the formation of smaller colonies and some extra-cellular material is liberated. Therefore, the ability of ozone to remove chlorophyll-*a* effectively at the lowest coagulant dose is dependant on the amount and type of algal cells present in the sample.

Table 5.6: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Hartbeespoort Dam for the study period October 2005-September 2006 after different treatments.

RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l).

MONTH	SAC254				Turbidity			
	RAW	RAW +	TR1	TR2	RAW	RAW +	TR1	TR2
Oct	16.75	14(10)	13(20)	12(25)	1.45	0.72(20)	0.80(20)	0.65(25)
Nov	18.4	13(25)	10.9(25)	11(20)	3.20	0.93(20)	1.16(25)	0.65(25)
Dec	18	11.75(25)	10.65(25)	10.25(25)	3.38	0.51(25)	0.72(25)	0.29(25)
Jan	18.65	13.7(25)	10.85(25)	10.1(25)	13.6	0.74(25)	0.73(25)	1.10(25)
Feb	19.9	13.1(25)	10.85(25)	10.55(25)	28.1	0.58(25)	0.72(25)	2.23(25)
March	18.75	12.85(25)	12.25(25)	12.45(25)	10.2	0.52(25)	1.22(20)	0.72(20)
April	22.9	11.7(25)	11.55(25)	11.9(15)	6.40	1.15(15)	0.87(20)	0.47(25)
May	16.8	12.05(25)	10.45(25)	11.05(25)	6.35	0.76(20)	1.34(20)	0.89(20)
June	16.4	10(25)	7.15(25)	10(25)	17.8	1.46(20)	0.53(20)	1.25(20)
July	16.7	10.65(25)	10.85(25)	10.25(25)	17.6	0.55(25)	1.10(25)	1.35(15)
Aug	16	12.75(25)	11.2(25)	11.05(25)	1.51	0.82(20)	0.53(20)	0.57(20)
Sep	16.3	11.95(25)	11.5(25)	11.75(25)	2.52	1.35(15)	1.05(15)	1.12(15)

Table 5.7: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Boskop Dam for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l).

MONTH	SAC254				Turbidity			
	RAW	RAW +	TR1	TR2	RAW	RAW +	TR1	TR2
Oct	15.5	12.2(25)		9(25)	2.52	1.60(20)		1.01(25)
Nov	10.8	9.8(25)	8.8(25)	8.9(25)	3.61	1.96(20)	1.85(20)	0.99(25)
Dec	11.75	8.65(25)	7.9(25)	7.5(15)	3.97	0.93(15)	1.06(15)	1.18(25)
Jan	12.9	9.1(25)	8(25)	8.2(25)	5.15	1.25(20)	0.87(10)	0.96(20)
Feb	12	9.55(25)	8.6(25)	7.95(20)	5	0.71(20)	0.71(25)	0.84(20)
March	13.85	10.25(25)	9.6(25)	9.85(20)	3.31	1.47(20)	0.82(25)	0.83(10)
April	13.55	9.7(25)	9.15(20)	9.7(150	2.08	0.64(25)	0.68(20)	1.77(20)
May	14.95	10.25(25)	9.3(25)	9.4(25)	2.86	1.08(25)	1.58(25)	1.47(5)
June	10.9	8.9(20)	9.25(25)	8(25)	4.83	0.63(20)	2.45(5)	2.19(10)
July	9.15	7.1(25)	6.9(25)	6.3(25)	1.69	0.74(25)	2.63(10)	1.83(5)
Aug	9.8	7.55(25)	7.9(25)	7.2(15)	2.32	0.71(250	2.60(5)	1.70(25)
Sep	10.8	7.7(25)	7.7(25)	7.45(25)	2.51	1.09(15)	1.13(10)	0.95(25)

Table 5.8: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Midvaal for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l).

MONTH	SAC254				Turbidity			
	RAW	RAW +	TR1	TR2	RAW	RAW +	TR1	TR2
Oct	23.75	14.5(25)	14.5(25)	12.8(25)	6.15	0.89(25)	0.95(20)	1.31(25)
Nov	22.35	12.2(25)	15(25)	10(25)	9.87	0.71(20)	0.59(20)	0.68(20)
Dec	23.55	14.60(25)	11.15(25)	10.3(25)	10.4	0.92(250	1.05(20)	2.25(25)
Jan	38.85	11.75(25)	12.95(25)	12.10(25)	79.8	1.03(20)	1.51(20)	2.94(20)
Feb	108.75	10.9(25)	11.5(25)	10.25(25)	224	1.40(25)	1.66(25)	2.07(25)
Marc	64.4	18.15(25)	10.3(25)	11(25)	81.2	2.16(25)	2.36(25)	3.80(20)
April	39.9	14.65(25)	11.5(250	11.9(25)	63.8	5.12(25)	2.12(20)	5.60(25)
May	30.6	12.4(25)	10.5(25)	10.9(25)	39.8	1.81(25)	6.67(25)	2.79(25)
June	21.1	13.85(25)	12.25(25)	11.5(25)	11.7	1.36(20)	1.66(20)	2.50(20)
July	22.5	14.7(25)	12(25)	11.35(25)	8.48	2.67(25)	1.28(25)	0.84(25)
Aug	21.35	11.95(25)	12.9(20)	12.3(25)	12.9	1.82(20)	1.20(20)	1.39(15)
Sep	22.5	13.6(25)	14.3(25)	15.9(25)	12.3	3.35(25)	2.96(20)	2.56(25)

Table 5.9: Table of largest variation in SAC254 and Turbidity observed during Jar Test for Sedibeng for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l).

MONTH	SAC254				Turbidity			
	RAW	RAW +FeCl3	TR1	TR2	RAW	RAW + FeCl3	TR1	TR2
Oct	24.4	17.9(25)	15.9(25)	15(25)	3.47	1.09(25)	0.95(20)	0.96(25)
Nov	23.65	13(25)	12.5(25)	12.5(25)	6.70	1.17(20)	1.06(20)	1.16(20)
Dec	23.9	14.05(25)			5.64	0.74(20)		
Jan	21.5	11.85(25)	10.55(25)	10.45(25)	8.98	1.09(15)	0.89(15)	0.77(15)
Feb	37.65	10.5(25)	10.2(25)	11.3(25)	110	2.41(25)	1.31(25)	2.42(25)
Marc	39.3	11.65(25)	11.2(25)	11.45(25)	112	4.85(25)	2.18(25)	1(25)
April	37	11.25(25)	12.45(25)	10.7(25)	68.7	13.8(25)	1.15(25)	1.80(25)
May	26.15	12.65(25)	12.25(25)	17.1(15)	23.2	1.89(25)	2.30(25)	1.44(25)
June	22.25	10.7(25)	11.95(25)	10.9(25)	10.3	1.38(25)	1.06(25)	1.30(25)
July	20.55	12.35(25)	12.6(25)	11.95(25)	7.81	1.17(5)	0.97(25)	1.05(25)
Aug	19.05	12.35(25)	11.85(25)	12.35(25)	12.2	1.44(25)	1.04(25)	0.93(15)
Sep	20.95	10.65(25)	10.85(25)	11.35(20)	7.07	0.80(25)	0.69(25)	1.03(15)

Table 5.10: Table of largest variation in Chlorophyll-*a* observed during Jar Tests for the four sampling sites for the study period October 2005-September 2006 after different treatments. RAW= raw water, RAW+=raw water + coagulant, TR1= 0.5mg/l ozone + coagulant, TR2= >0.5mg/l ozone + coagulant, value in brackets= (concentration of $FeCl_3$ in mg/l). HB=Hartbeespoort Dam, BK=Boskop, MV=Midvaal and SB=Sedibeng.

Month	HBP				BK			
	RAW	RAW+	TR1	TR2	RAW	RAW+	TR1	TR2
Oct	0	0	0	0	28.66	0(5)	0(c)	0(c)
Nov	57.32	0(5)	0(c)	0(c)	0	0	0	0
Dec	28.66	0(5)	0(5)	X	28.66	0(5)	0(c)	0(c)
Jan	57.32	0(15)	0(10)	0(10)	0	0	0	0
Feb	171.96	0(10)	0(20)	0(10)	28.66	0(5)	0(15)	0(c)
March	85.98	0(5)	0(5)	0(5)	28.66	0(15)	0(c)	0(c)
April	57.32	0(10)	0(5)	0(c)	28.66	0(10)	0(5)	0(c)
May	114.64	0(10)	0(c)	0(c)	0	0	0	0
June	171.96	0(5)	0(10)	0(10)	28.66	0(10)	0(5)	0(c)
July	143.32	0(10)	0(10)	0(15)	28.6	0(10)	0(5)	0(c)
Aug	28.66	0(20)	0(c)	0(c)	28.66	0(5)	0(c)	0(c)
Sep	28.66	0(10)	0(c)	0(c)	0	0	0	0
Month	MV				SB			
	RAW	RAW+	TR1	TR2	RAW	RAW+	TR1	TR2
Oct	57.23	0(15)	0(5)	0(5)	28.66	0(15)	0(10)	0(c)
Nov	114.64	0(25)	0(5)	0(5)	28.66	0(20)	0(5)	0(5)
Dec	171.96	0(20)	0(25)	0(10)	57.32	0(10)	0(5)	X
Jan	57.32	0(5)	0(5)	0(5)	85.98	0(10)	0(15)	0(10)
Feb	28.66	0(5)	0(5)	0(c)	28.66	0(5)	0(5)	0(5)
March	0	0	0	0	28.66	0(15)	0(5)	0(5)
April	28.66	0(5)	0(c)	0(c)	28.66	0(10)	0(5)	0(5)
May	57.32	0(15)	0(15)	0(10)	114.64	0(15)	0(20)	0(15)
June	200.62	0(20)	0(15)	0(5)	85.98	0(15)	0(10)	0(10)
July	85.98	28.66(5)	0(15)	0(10)	28.66	0(15)	0(5)	0(c)
Aug	28.66	0(5)	0(5)	0(5)	57.32	0(10)	0(10)	0(5)
Sep	257.94	0(15)	28.66(15)	0(20)	114.64	0(20)	0(15)	0(15)

CHAPTER SIX: CONCLUSIONS

Ozone, in combination with conventional treatments, is used extensively to purify water in many countries but its use is limited in South Africa primarily because of the capital investment needed to install ozone generators. There are conflicting reports on the effect of ozone on water quality and these must be examined before the decision is made to install an ozone plant as part of the treatment process. The four sampling sites were chosen to demonstrate different types of water that will be uniquely affected by water purification processes due to their characteristics. The sampling sites are located in the North West Province and are Hartbeespoort Dam (a eutrophic impoundment), Boskop Dam (a mesotrophic impoundment), and two riverine sites that are part of the Middle Vaal River namely, Midvaal at Stilfontein and Sedibeng at Bothaville. This study has undertaken to provide some answers with respect to the characteristics of the four different sampling sites and the effect ozone will have on water purification of these sites.

Hartbeespoort Dam is a hyper-eutrophic impoundment characterised by the presence of cyanobacterial blooms for most of the year. It is a vital source of fresh water for Gauteng and poses serious problems for water purification processes. Ozone was found to be effective in the removal of turbidity, SAC254 and chlorophyll-*a* from water samples at Hartbeespoort Dam. However, the presence of *Microcystis* sp. interfered with the efficiency of ozone in some instances. Breakdown of algal cells after ozonation can lead to the liberation of cell-bound organics that adversely affect the treatment process. Schmidt (2001) noted that where an oxidation step like ozone is used in raw water containing algal cells, there is a risk between oxidation and reduction of undesirable components and the release of cell-bound organic matter. The optimum ozone dose must be determined so that there is a reduction in SAC254 and chlorophyll-*a* can be obtained without an increase in turbidity. Ideally the cells should be stressed and the membrane integrity reduced, but there should not be enough ozone available to cause lysis of cell membranes, which will release cell-bound organic compounds. During this study, subsequent coagulation in the Jar Test shows that ozone improved removal of SAC254 and chlorophyll-*a* when compared to conventional treatment. The NOM fractions of Hartbeespoort Dam constituted all 3 fractions, with most of it found in the IMW and LMW fractions. Ozone caused a reduction in the HMW and the IMW fractions as well as an increase in the LMW fraction of NOM. It is therefore beneficial to use ozonation to treat Hartbeespoort Dam water.

Boskop Dam is indicative of a mesotrophic impoundment with high salinity and sulphate concentrations. Ozonation was successful in the removal of SAC254, turbidity and chlorophyll-*a*, but the percentage removal was much lower than for any of the other sites. There were many instances when ozone caused an increase instead of a decrease in the variables. This could be

due to the presence of a high percentage of the LMW fraction of NOM, which is more difficult to remove by the actions of ozone. The effect of alkalinity on ozone was not examined in this study. It is known that high alkalinity decreases the efficiency of ozone as the carbonate and bicarbonate ions scavenge the hydroxyl radicals. The presence of high alkalinity in Boskop Dam due to the geology of the area can be a factor contributing to decreased efficiency of ozonation of the water. Further studies should measure the alkalinity of Boskop Dam and look at possible interactions with the action of ozone. The dam has low turbidity, SAC254 and chlorophyll-*a* for most of the year and this should be noted. The cost of applying ozone in this case does not warrant the observed changes in the water quality due to ozonation.

Both Midvaal and Sedibeng are part of the Middle Vaal region of the Vaal River. These sites are characterised by high algal numbers, increased salinity and eutrophication. The NOM of the rivers is comprised mainly of the HMW and IMW fractions, as it is expected from riverine samples. These samples respond well to ozonation leading to decreases in all the variables except DOC. The removal of SAC254 is indicative of the actions of ozone on the aromatic fractions of NOM. This leads to a decrease in the HMW and the IMW fractions with a subsequent increase in the LMW fraction of NOM. This was the case in both riverine sites. SAC254 has been shown to correlate very well with the sum of the NOM and it can thus be used as a surrogate for this value. Removal of chlorophyll-*a* was increased by the effects of ozonation. However, the algal species composition of the raw water had a major effect on this, as samples with Bacillariophyceae (diatoms) proved to be resistant to the actions of ozone. Cells from the class Chlorophyceae were effectively removed by ozonation. Jar test results showed that ozonation combined with coagulation proved very successful and led to great decreases in the variables i.e. SAC254, turbidity and chlorophyll-*a*. However, when there were more of the LMW fractions present, ozonation did not cause any reduction in these variables. The LMW fractions are therefore not affected by ozonation and conventional treatment alone is effective when these fractions are present in the water samples.

Because each type of water is unique with regard to several variables, the relationship between the actions of ozone and these variables must be examined before a decision is made to use ozone as part of the treatment process. There is a relationship between SAC254, turbidity, chlorophyll-*a* and the effect of ozone. The amount and species of algal cells present can adversely affect the ozonation process and this can change seasonally. The sum of the NOM is also important as the presence of HMW fractions responds well to ozone whereas the presence of LMW fractions does not.

SAC254 has proved to be a good measure of the NOM in the riverine sites and is easy to perform at any treatment plant. This can provide information on the nature of the organics present. It can be concluded that ozonation will improve the purification of Hartbeespoort Dam, Midvaal and Sedibeng

water while the improvement in Boskop Dam is minimal because of variations in its efficiency due to the specific characteristics of the water.

Further studies should investigate the properties of NOM fractions by the process of fractionation as the change in the charge and acidity of the NOM after ozonation may explain some of the variations observed especially with regard to the Jar Test results.
Future studies should also focus on obtaining results for longer periods than one year so that seasonal variations can be observed. Higher concentrations of ozone should be considered by using two generators in parallel at the same time. This can shed light on the effects of ozone on the HMW fraction of NOM as well as the effect on cell lysis and cell-bound organelles.

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