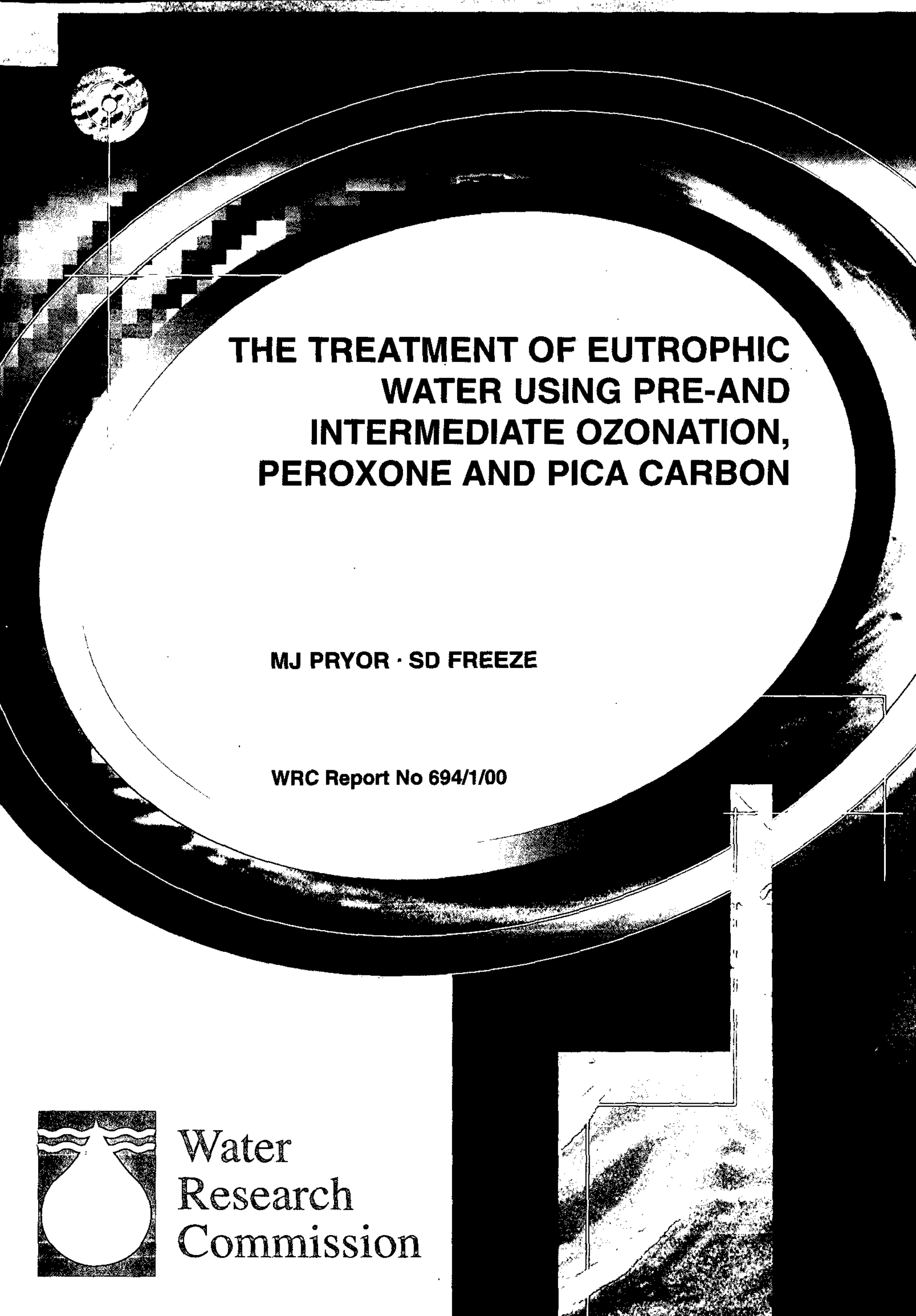

THE TREATMENT OF EUTROPHIC WATER USING PRE-AND INTERMEDIATE OZONATION, PEROXONE AND PICA CARBON

MJ PRYOR · SD FREEZE

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Water
Research
Commission

THE TREATMENT OF EUTROPHIC WATER USING PRE- AND INTERMEDIATE OZONATION, PEROXONE AND PICA CARBON

Final Report

to the

Water Research Commission

by

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Executive Summary

In a water scarce country such as South Africa, where there are rapidly growing informal settlement communities, generally possessing poor sanitation services, as well as discharges to rivers by industries and agricultural runoff, deteriorating water quality is a serious problem. It was therefore realised that it may become necessary in the future to use more advanced water treatment processes in order to produce potable water of an acceptable quality.

A series of laboratory tests were conducted into the effects of ozone and peroxone on various raw water types, whilst pilot scale tests were carried out to assess advanced treatment processes employing ozone and granular activated carbon (GAC).

OBJECTIVES

The objectives of this study were to:

- Assess the effect of ozone on the coagulant demand and background organics of waters containing two predominant taste and odour causing algal species in Southern Africa, namely *Mycrocistis* sp. and *Anabaena* sp.
- Investigate the difference between inorganic and organic coagulants in treating eutrophic waters after ozonation.
- Determine the effect of hardness to organic carbon ratios for both pre- and intermediate ozonation.
- Determine the significance of ozone to organic carbon ratios.
- Assess the effect of ozone on background organics and biodegradation at laboratory and pilot scale.
- Assess the effect of peroxone relative to ozone.
- Assess the use of Pica carbon as a means of reducing the need to regenerate granular activated carbon used for water treatment.
- Develop design criteria for GAC, detailing the sizing parameters and important properties specific to South African conditions.
- Produce a set of guidelines for the process design and operation of water treatment plants treating eutrophic waters.

LABORATORY INVESTIGATION

Laboratory tests were conducted on three basic water types, namely:

1. a eutrophic water containing predominantly *Microcystis* or *Anabaena* species (DOC approximately 3 to 10mg/ℓ),
2. a clean water low in organic content (DOC approximately 3 to 8mg/ℓ) and
3. an industrially polluted water (DOC approximately 10 to 20mg/ℓ).

Since a constant source of eutrophic water was not available during the period of this investigation, the levels of algae were increased by spiking Inanda Dam water with cyanobacterial scums containing predominantly either *Microcystis* or *Anabaena*. Inanda Dam water without any algal cell addition was used as the second water type, while water from the Sterkspruit River, a stream which runs through the industrial area of Hammarsdale and which is contaminated with industrial effluents, was used for the third water type. Tests were performed to assess the effect of pH on ozonation by adjusting the pH to 7, 8 and 9 using either hydrochloric acid (0,1N) or sodium hydroxide (0,1N). In all other tests the pH of the water was adjusted to 8.

A number of simulations was carried out in which the three water types were pre-ozonated followed by laboratory scale coagulation with either a polymeric coagulant or ferric chloride, flocculation, settling and filtration. Pre-ozonation doses varying between 0,25 and 5 mg/ℓ were used and the water was carefully monitored after treatment for a number of determinands including total organic carbon (TOC), dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), biodegradable dissolved organic carbon (BDOC), UV absorption (254nm), geosmin, 2-methylisoborneol (2-MIB) and atrazine. Laboratory tests in which the effect of intermediate ozonation was investigated were also performed. These tests were carried out on Inanda Dam water which had been treated on a pilot plant. Intermediate ozone concentrations varying between 0,2 and 4 mg/ℓ were applied and the water was then analysed for a number of variables, including the organic matter indicators mentioned above. The intermediate ozonation tests were expanded to include advanced oxidation tests in which peroxide was used in conjunction with ozone.

Investigations were also carried out into the effect of hardness on the impact of ozonation of a water. Since no suitable source of hard water was readily accessible, the hardness of Inanda Dam raw water was artificially increased using salts and/or carbon dioxide. Samples of naturally hard waters were also obtained.

Summary of Results of Laboratory Investigation

- Ozonation was not found to have a significant effect on THMFP, TOC or DOC, although decreases in TOC and DOC of up to 25% were possible depending on the nature and concentration of the natural organic matter (NOM) present in the water. Pre-ozonation followed by conventional treatment consisting of coagulation, flocculation, sedimentation and filtration could result in TOC and DOC removals of up to 50%.
- BDOC was found to increase with increasing ozone concentration, generally stabilising at ozone to DOC ratios of between 0,3 and 0,5. The effect of ozone on BDOC was more variable in industrially polluted waters and in some cases was found to decrease at higher ozone doses. This effect might be due to the inhibitory effect of ozonation by-products.
- Ozone proved effective in reducing UV absorbance (254nm) and the micro-pollutants of atrazine, geosmin and (2-MIB). At ozone to DOC ratios of between 0,5 and 1,5, reductions in UV absorbance of up to 70% were possible and removals of micro-pollutants in excess of 70% were achieved. Conventional treatment without pre-ozonation did not result in significant removal of micro-pollutants, but could effect a reduction in the UV absorbance of up to 65%, with ferric chloride proving more effective than the polymeric coagulant. Pre-ozonation followed by conventional treatment could reduce UV absorbance by as much as 90%.
- Colour removal using ozone was generally effective, with reductions of 40 to 60% possible at ozone to DOC ratios of 0,1 to 0,4. Using pre-ozonation followed by conventional treatment, it was possible to reduce colour by between 70 and 90%.
- A small reduction in the THMFP, TOC, DOC and UV absorbance was often observed at ozone to DOC ratios of 0,01 to 0,15 which correlated with the ozone dose at which an improvement in coagulant demand was sometimes observed.
- Reductions obtained in DBP precursors, pesticide/herbicide contaminants, taste and odour compounds and NOM using enhanced coagulation were compared to those achievable using ozone or advanced oxidation followed by GAC. The enhanced coagulation project was another WRC project (TT 105/98) and the same waters were used for the enhanced coagulation investigation as were used for this investigation.
- Enhanced coagulation was found to be very effective for the removal of THMFP (up to 40% reductions), TOC and DOC (up to 60% reductions), BDOC (70 to 90% reductions), colour (up to 50% reductions) and algal cells (> 90% reductions) using coagulant doses 2 to 5 times the optimum dose in terms of turbidity removal. These results were confirmed in pilot plant enhanced coagulation studies. These results are significantly better than those possible using pre-ozonation alone and are comparable with removals achieved in the pilot plant studies using conventional

treatment, ozonation and GAC filtration. Enhanced coagulation was not successful in reducing micro-pollutants such as geosmin, 2-MIB and atrazine.

- Ozone was not found to impact greatly on the polymeric coagulant, but the inorganic coagulant demand usually increased with increasing ozone concentration. The ozone to DOC ratio was found to be important in determining this increase, the higher this ratio the greater the increase. A small decrease in the ferric chloride optimum dose sometimes occurred at applied ozone to DOC ratios of between 0,01 and 0,15 (i.e. 0,25 and 1 mg/ℓ applied ozone). This mirrored the small decrease observed in THMFP, TOC, DOC and UV.
- The effect of ozone on the coagulant demand was also dependent on the species and concentration of cyanobacteria present. Ozonation of *Microcystis* sp. generally had a significant effect on the coagulant demand, although this was dependent on the ozone concentration. Ozonation of *Anabaena* sp. also resulted in increases in coagulant demand, but the effect of ozonation was much smaller than with *Microcystis* sp. The coagulant dose for an unozonated water containing predominantly *Microcystis* sp. was always lower than that for a water containing predominantly *Anabaena* sp. at similar cell concentrations. After ozonation however, the coagulant demands for water containing predominantly *Microcystis* sp. or *Anabaena* sp. at comparative cell concentrations were much closer in value, especially at the greater cell concentrations. The laboratory results suggested that *Microcystis* sp. are more susceptible to lysis by ozonation.
- High hardness concentrations in the water were not found to significantly impact on the effect of ozone on most NOM surrogate parameters, although BDOC generally decreased, rather than increased after ozonation.
- When comparing peroxone to ozone, it was generally found that peroxone results in the same NOM reductions as those obtained using ozone alone, but these were achieved at lower ozone doses. Increasing the peroxide to ozone ratio beyond 0,3 did not increase the advantages of adding peroxide during ozonation at the optimum ozone dose of 1,5 to 2,0 mg/ℓ.

PILOT PLANT INVESTIGATION

A pilot plant was constructed at the Umgeni Water Process Evaluation Facility at the Wiggins Waterworks to assess the benefits of using GAC in conjunction with ozone for water treatment. The use of ozone prior to GAC is reported to have significant benefits in reducing the need for frequent regeneration of the carbon by promoting biologically activated carbon (BAC).

The raw water from the Inanda Dam was treated by coagulation and sand filtration. A portion of the water was then filtered directly using GAC. The rest of the water was ozonated prior to GAC filtration. This allowed direct comparison of GAC filtration with and without ozonation. Two types of carbon were assessed in the GAC pilot plant; a wood based carbon (PICA) considered to beneficial in promoting biological activity and a coal based carbon specifically designed for the adsorption of organic contaminants.

The granular carbon filters were designed and constructed in the following arrangement.

Column 1	Ozonation and GAC filtration using PICA carbon (wood based carbon)
Column 2	Ozonation and GAC filtration using Coal based carbon WCM 106
Column 3	GAC filtration using PICA (wood based carbon) - no ozonation.
Column 4	GAC filtration using Coal based carbon WCM 106 - no ozonation.

Following initial recommendations from PICA regarding encouraging biological removal of contaminants, an EBCT of 10 minutes was designed.

In a separate pilot plant filtered water was dosed with organic micro-pollutants and passed through a series of GAC mini-columns where the adsorption of contaminants onto GAC was studied.

Summary of Results of Pilot Scale Investigation

A number of conclusions could be drawn from the pilot-scale experiments:

- Granular activated carbon can effectively be applied for the adsorption of taste and odour compounds as well as pesticides and herbicides (e.g. atrazine) from surface water. This is particularly beneficial in the treatment of eutrophic waters where the extent of the taste and odour problems cannot be overcome using powdered activated carbon alone. At high concentrations PAC becomes prohibitively expensive and impractical.
- The combination of ozone and GAC showed significant advantage and provided a more reliable treatment process than GAC alone.
- PICA carbon when used specifically as biologically activated carbon (BAC) did not appear to be beneficial for the application at Umgeni Water in terms of NOM removal and little or no biological activity was observed on any of the types of carbon investigated. The lack of biological activity was most probably due to a long retention time in the impoundment prior to the water entering the works. Although levels of BDOC of up to 1 mg/ℓ were measured in the raw water, much of this was removed by coagulation and sand filtration.
- The coal based carbons performed significantly better than the PICA carbon for the removal of organic micro-contaminants due to a higher bulk density and a larger adsorption capacity.

- GAC provides a benefit in the reduction of chlorine demand and once installed at a works should be utilised continuously to gain benefit even when the extent of eutrophication and pesticide problems is insignificant.
- Careful selection of GAC is required to be able to select the type of carbon which is most suitable to the treatment objective of the works. Where biological activity is observed, the use of PICA carbon may prove to be beneficial for the reduction of BDOC, but where the adsorption of contaminants is the main objective the most suitable carbon should be selected.

DESIGN CONSIDERATIONS FOR OZONE/GAC

The design and selection of a particular water treatment process or train depends on a number of factors with the main objectives being :

1. to improve the aesthetic acceptability of the water,
2. to remove any toxic or hazardous materials and
3. to remove or inactivate any disease-causing organisms.

Typical situations where ozone and GAC may be applied are:

- in the oxidation of iron and manganese in raw water using ozonation.
- for the removal of organic carbon, using pre-ozonation, conventional treatment and GAC filtration (preferably preceded by ozonation).
- for the removal of algae by pre-ozonation, conventional treatment and GAC filtration.
- to reduce taste and odour compounds and other micro-pollutants such as pesticides and herbicides, ozone and GAC filtration being suitable processes for these applications.
- for the inactivation of microbilogical contamination, especially pathogenic protazoa such as cryptosporidium and giardia, which ozone is effective in removing.
- to reduce DBP precursors, using ozone and GAC.

Design guidelines for a treatment plant incorporating advanced treatment processes such as ozonation and GAC are provided. Ozone treatability tests on a laboratory scale can be used to determine the optimum ozone concentration for NOM and micro-pollutant removal, an ozone to DOC ratio of 1 being recommended. For improvement in coagulation however, an ozone to DOC ratio of between 0,05 and 0,3 is recommended. Pilot plant tests can be used for confirmation of laboratory results and to determine parameters such as the type of reactor, the reactor depth and volume, liquid flow rate, gas flow rate and bubble size, gas to liquid ratio and the performance indicators required to monitor the system .

For selection of the correct type of GAC, adsorption isotherm tests using the test water containing specific target compounds can be used to get an indication of the effect of the background organics and adsorption capacity of the GAC. Better still are pilot plant tests, but these are significantly more time consuming. However, a pilot plant will allow for more accurate determination of parameters such as EBCT, linear filtration velocity and backwashing of the GAC filters.

Based on the results of this investigation, recommendations are made regarding the following:

- empty bed contact time (EBCT)
- bed depth
- backwashing operation
- filter configurations
- carbon handling and regeneration.

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Table of Contents

PAGE NO

Executive Summary i

Acknowledgements viii

Table of Contents ix

List of Figures xiv

List of Tables xvii

Glossary xviii

1 INTRODUCTION 1

1.1 Introduction into the use of Ozone 2

1.2 Introduction into the use of Granular Activated Carbon 3

1.3 Objectives 3

2 LITERATURE REVIEW 7

2.1 Ozone and Peroxone Effects 7

2.1.1 Effects on THMFP and DBP 7

2.1.2 Pre-Ozonated and Effects on TOC, NOM and Coagulant Dose 8

2.1.3 Advanced Oxidation- Hydroxyl Radicals and the Impact of Hardness 11

2.1.4 Intermediate Ozonation 11

2.2 Granular Activated Carbon 12

2.2.1 Removal of Organic Carbon 12

2.2.2 Removal of Organic Micro-pollutants 13

2.2.3 Laboratory and Pilot-scale Experiments 15

2.2.4 Biologically Activity on GAC 16

2.2.5 Regeneration of GAC 17

2.2.6 Replacing filter and sand with GAC 17

3 ANALYTICAL METHODOLOGY 19

3.1 Organic Analyses 19

3.1.1 TOC, DOC and BDOC Analysis 19
3.1.2 AOC Analysis 19
3.1.3 THMFP Analysis 20
3.1.4 UV Absorbance 20

3.2 Micropollutants: Geosmin, 2-MIB and Atrazine 20

3.3 Algal Indentification and Enumeration 21

3.4 Chemical Analyses 21
3.4.1 pH 21
3.4.2 Turbidity 21
3.4.3 Colour 21
3.4.4 Calcium, Magnesium and Hardness 21
3.4.5 Iron 21
3.4.6 Manganese 21
3.4.7 Alkalinity 21

3.5 Determination of Ozone and Hydrogen Peroxide 22
3.5.1 Iodometric Tritration for the Determination of Ozone 22
3.5.2 Indigo Colorimetric for the Determination of Ozone 22
3.5.3 Iodometric Titration for the Determination of Hydrogen Peroxide 23

3.6 Granular Activated Carbon Analytical Procedures 23
3.6.1 Iodine Number Determination of GAC 23
3.6.2 Methylene Blue Number Determination of GAC 23
3.6.3 Ash Content of GAC 24
3.6.4 Adsorption Isoterm Tests for GAC 24

4 LABORATORY INVESTIGATION 25

4.1 Introduction 25

4.2 Methods and Materials 28
4.2.1 Standard Jar Test (Coagulation Test) 28
4.2.2 Ozonation Procedure 28
4.2.3 Peroxone Procedure 30
4.2.4 Hardness Adjustment 30

4.2.5 Agal Cell Collection and Spiking 30
4.2.6 GAC Equilibrium Tests 31

4.3 Results and Discussion 32
4.3.1 Effect of Ozone on NOM 32
4.3.1.1 THMFP 32
4.3.1.2 DOC, TOC and BDOC 33
4.3.1.3 BDOC and AOC 35
4.3.1.4 UV Extinction (254 nm) 37
4.3.1.5 Atrazine, Geosmin and 2-Methylisoborneol 39
4.3.1.6 Colour 39
4.3.1.7 Effects of Enhanced Coagulation Compared to Advanced Treatment Processes 40
4.3.1.8 Cost Comparison between Treatment Process and Enhanced Coagulation 44
4.3.2 Effect of Ozone on Coagulant Type and Optimum Dose 45
4.3.3 Impact of Algal Type and Concentration on Ozonation Effects 47
4.3.4 Effect of hardness on ozone efficiency 52
4.3.5 Comparision of Ozone and Peroxone Effectiveness 55

4.4 Summary of Conclusions 60

5 PILOT PLANT INVETIGATION 61

5.1 Introduction 61

5.2 Method and Materials 61
5.2.1 Water Treatment Pilot Plant 62
5.2.2 Ozonation Pilot Plant 63
5.2.3 GAC/BAC Pilot Plant 63
5.2.4 Mini-column Adsorption Pilot Plant 66
5.2.5 Dosing of Micro-pollutants 68
5.2.6 GAC Equilibrium Tests 68

5.3 **Results and Discussion** 69
5.3.1 Water Treatment Pilot Plant 69
5.3.2 Dosing of Atrazine and 2-MIB 71
5.3.3 Ozone Pilot Plant Operation 73
5.3.4 GAC Column Operation 75
5.3.4.1 Total Organic Carbon and Dissolved Organic Carbon 75
5.3.4.2 Tri-halomethane formation potential 77
5.3.4.3 UV absorbance (254 nm) 78
5.3.4.4 Biodegradable Dissolved Organic Carbon (BDOC) 80
5.3.4.5 Biological Growth on the GAC Filters 81
5.3.4.6 Chlorine Demand 82
5.3.4.7 Removal of Pesticides 83
5.3.4.8 Iodine Number, Methylene Blue Number and Ash Content 86
5.3.4.9 Backwashing of the GAC Filters 86
5.3.5 EBCT and Bed Depth Consideration 87
5.3.6 GAC Adsorption and Breakthrough Experiments 89

5.4 **Summary of Conclusions** 94

6 **DESIGN CONSIDERATIONS FOR OZONE AND GAC** 95

6.1 **Selection of Water Quality Parameters** 95

6.2 **Identifying a Treatment Objective** 98
6.2.1 The benefits of ozone and GAC 99
6.2.2 Typical Areas where Ozone and GAC are applied 99
6.2.3 Treatment Philosophy for the Umgeni Water Wiggins Waterworks 101

6.3 **Laboratory Studies** 103
6.3.1 Ozone Treatability Tests 103
6.3.2 Granular Activated Carbon 103

6.4 **Pilot Scale Studies** 105
6.4.1 Ozonation Pilot Studies 105
6.4.2 Granular Activated Carbon Pilot Studies 106

6.5 Process Considerations 108
6.5.1 Enhanced Coagulation 108
6.5.2 Ozone 108
6.5.2.1 Pre Ozonation 109
6.5.2.2 Intermediate / Post Ozonation 111
6.5.3 Granular Activated Carbon 112
6.5.3.1 Converting from Powdered Activated Carbon to GAC 112
6.5.3.2 GAC Filter Sizing and Specification 113
6.5.3.3 Reactivation and Regeneration 120
6.5.3.4 Selection of Carbon for GAC Treatment 121

7 CONCLUSIONS AND RECOMMENDATIONS 123

7.1 Laboratory Investigation 123

7.2 Pilot Scale Investigation - GAC 124

7.3 Design Recommendations 125

REFERENCES 127

List of Figures

PAGE NO

Section 4

Figure 4.1 Flow diagram of laboratory scale ozonation apparatus 29

Figure 4.2 Effect of ozone on the THMFP of a final filtered water 33

Figure 4.3 Effect of ozone on the THMFP of a eutrophic water (Inanda Dam Water contaning 100 000 *Microcystis* cell/mℓ) 33

Figure 4.4 Effect of pre-ozonation and conventional treatment on the THMFP of an industrially polluted water 34

Figure 4.5 Effect of ozone on the TOC of a eutrophic water containing 100 000 *Microcystis* cells/mℓ) 34

Figure 4.6 Effect of ozone on the TOC of a eutrophic water (Inanda Dam water containing 500 000 *Microcystis* cells/mℓ) 35

Figure 4.7 Effect of ozone on the BDOC of a final filtered water 36

Figure 4.8 Effect of ozone on the BDOC of an industrially polluted water 36

Figure 4.9 Effect of ozone on the UV absorbance at 254 nm of a final filtered water 38

Figure 4.10 Effect of ozone on the UV absorbance at 254 nm of an industrially polluted water 38

Figure 4.11 Effect of ozone on atrazine, geosmin and 2-MIB of a final filtered water 40

Figure 4.12 Effect of ozone on colour in an industrially polluted water 40

Figure 4.13 Effect of ozone on the coagulant demand of a eutrophic water (Inanda Dam water containing 10 000 *Microcystis* cells/mℓ) 46

Figure 4.14 Impact of algal cell concentration and pH on the effect of ozone on the DOC of eutrophic water 48

Figure 4.15 Impact of algal species on the effect of ozone o the optimum ferric chloride coagulant demand of eutrophic waters (Inanda Dam water containing either 100 000 *Microcystis* sp. or 100 000 *Anabaena* sp. cells at 100 000 cells/mℓ) 49

Figure 4.16 Impact of algal cell concentration and algal species on the effect of ozone o the optimum ferric chloride coagulant demand of eutrophic water 50

Figure 4.17 Impact of algal species and pH on the effect of ozone on the optimum ferric chloride caogulant demand of eutrophic water 51
Figure 4.18 Effect of ozone and conventional treatment using ferric chloride on algal cell concentrations 52
Figure 4.19 Effect of ozone on the THMFP of a naturally hard water (Klip River water, hardness 315 mg/ℓ $CaCO_3$) 52
Figure 4.20 Effect of ozone on the BDOC of a naturally hard water (Suikerbos RandRiver, hardness 385 mg/ℓ $CaCO_3$) 54
Figure 4.21 Impact of hardness on the optimum coagulant dose before and after ozonation 55
Figure 4.22 Effect of peroxone on the THMFP of a final filtered water using a constant ozone dose (1,5 mg/ℓ) and varying peroxide to ozone ratios 57
Figure 4.23 Effect of ozone and peroxone on the TOC of a final treated water from an industrially polluted source 57
Figure 4.24 Effect of peroxide to oxone ratio on the BDOC 58
Figure 4.25 Effect of ozone and peroxone on the UV absorbance 59
Figure 4.26 Effect of the peroxide to ozone ratio on the geosmin concentration 59

Section 5

Figure 5.1 Flow Diagram of Water Treatment Pilot Plant 62
Figure 5.2 Flow Diagram of Ozonation Pilot Plant 63
Figure 5.3 Electron Micrographs of the Surface of the GAC 64
Figure 5.4 Flow Diagram for the GAC Pilot Plant 65
Figure 5.5 Backwashing Procedure of the pilot-plant GAC Filters 66
Figure 5.6 Mini-column Pilot Plant for evaluating adsorption onto GAC 67
Figure 5.7 Filtered water turbidity entering the GAC / Ozone pilot plant 71
Figure 5.8 Dosing of 2-MIB into the Raw water 72
Figure 5.9 Dosing of Atrazine into the Raw water 72
Figure 5.10 Consistency of the ozone dose for the pilot plant operation 73
Figure 5.11 Calculation of the C-T value for the ozonation pilot plant 74
Figure 5.12 Reduction in TOC during the first three months of operation 76
Figure 5.13 Erratic nature of Total Organic Carbon Measurement of water filtered through GAC after ozonation 76

Figure 5.14 Comparison of the fromation of THMs in the GAC filtered water to the THM formation in the Raw water 77
Figure 5.15 Comparison of the THMFP for PICA carbon and the coal based carbon after ozonation 78
Figure 5.16 UV absorbance measurement for comparison of the process operation 79
Figure 5.17 Cumulative UV extinction 80
Figure 5.18 The effect of Ozone and GAC on the levels of BDOC in Inanda Dam Water 81
Figure 5.19 The effect of different processes using ozonation and GAC on the Chlorine Demand of the water 83
Figure 5.20 Comparison of ozonation and GAC processes for the removal of Atrazine 84
Figure 5.21 Cumulative atrazine concentration for GAC filtration with and with out ozonation 85
Figure 5.22 levels of Atrazine and Geosmin dosed into the water 91
Figure 5.23 Breakthrough of Atrazine using different carbons 92
Figure 5.24 UV extinction @ 254 nm measured on samples form GAC mini-columns 93

Section 6

Figure 6.1 Treatment Process for the upgrade of the Umgeni Water Wiggins Waterworks 102
Figure 6.2 Diagram of a Single Flow GAC Filter Configuration 116
Figure 6.3 Single Stage - Dual Bed GAC Filter 118
Figure 6.4 Tow Stage GAC Filtration 119
Figure 6.5 Typical GAC Pressure Filter 120

List of Tables

PAGE NO

Section 4

Table 4.1 Typical water quality data for the three types of water investigated 26

Section 5

Table 5.1 Properties of the coal and wood based carbon used in the plant study 64
Table 5.2 Raw water quality entering the Wiggins Waterworks (pilot plant feed water) 70
Table 5.3 Microbiological Examination of GAC filter backwash waters 82
Table 5.4 Analyses of the carbon from the GAC / Ozone Pilot Plant 86
Table 5.5. Typical values for GAC absorber parameters 88
Table 5.6 Configuration of the pilot plant to monitor performance of different EBCT 88
Table 5.7 Freundlich Isotherm Constants for Inanda Dam Water 89

Glossary

2-MIB	2-Methylisoborneol
Alum	Aluminium sulphate
AOC	Assimilable organic carbon
ASTM	American Society for Testing and Materials
BAC	Biologically activated carbon
BDOC	Biodegradable dissolved organic carbon
CFU	Colony forming units
COD	Chemical Oxygen Demand
C • t	Concentration time product
DBP	Disinfection by-product
DCBR	Differential column batch reactor
DDT	Dichlorodiphenyltrichloroethane
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
GAC	Granular activated carbon
g/h	Grams per hour
g/ℓ	Grams per litre
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
ℓ	Litres
MCL	Maximum Contaminant Level
mg/ℓ	Milligrams per litre
mℓ	Millilitres
N	Normal (concentration)
NOM	Natural organic matter
NOX	*Spirillium* NOX strain of bacteria
PAC	Powdered activated carbon
P17	*Pseudomonas fluorescens* P17 strain of bacteria
RSSCT	Rapid small scale column tests
SABS	South African Bureau of Standards
SANAS	South African National Accreditation Services

SDWA	Safe Drinking Water Act (1974)
SSCT	Small Scale column test
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TOC	Total organic carbon
USEPA	United States Environmental Protection Agency
UV	Ultraviolet irradiation
µg/*l*	Micrograms per litre
VOC	Volatile organic carbon
WRC	Water Research Commission

1. Introduction

South Africa is a country with limited water resources and therefore does not have the freedom to reject available supplies on the basis of strict quality parameters. In addition the relatively small flows in many of the major rivers leads to disproportionately large effects from diffuse and point source pollutants. These pollutants and in particular the nutrients, lead to eutrophication problems in impoundments, which in turn cause treatment problems at many of the country's waterworks. The difficulties in treatment and the need to comply with increasingly stringent water quality standards has focused attention on a number of new and advanced water treatment techniques.

Umgeni Water was formed in 1974, with the main function to supply bulk treated water to the Greater Durban and Pietermaritzburg regions in KwaZulu Natal. Umgeni Water is also responsible for wastewater treatment and lately, reticulation of treated water to rural and peri-urban communities. Most of the water is obtained from the Mgeni River which flows through a number of catchment areas originating in the Natal Midlands and flowing into the Indian Ocean at Durban. Effluent from the Darvill Wastewater Works is discharged into the Mzunduzi River at Pietermaritzburg. This effluent together with pollution from informal settlements along the river banks, as well as agricultural runoff results in increased levels of pollutants and nutrients entering the Inanda Dam.

Since the completion of the Inanda Dam on the Mgeni River (1987), water quality and water catchment monitoring has led to predictions that the Inanda Dam is most likely to become eutrophic. Predictions were that *Microcystis* would be the predominant algal genus present in the Inanda Dam, although it may be possible that *Anabaena* concentrations would periodically also be significant and this genus may even predominate. The presence of algal by-products and other known organic pollutants such as herbicides and pesticides, warranted an investigation into advanced water treatment processes. A laboratory investigation was initiated to investigate the factors which may affect the treatment of highly eutrophic Inanda Dam water.

Water from the Inanda Dam in KwaZulu Natal is transferred to the Umgeni Water Wiggins Waterworks via a series of tunnels and aqueducts which were commissioned in August 1994. The Umgeni Water Process Evaluation Facility at the Wiggins Waterworks provides an opportunity for interesting and useful project work to be undertaken on a pilot scale using the same raw water as the main works. In order to determine the long term adsorption of organics, especially taste and odour compounds on granular activated carbon (GAC) and the factors which affect the frequency of regeneration, a pilot scale project was initiated to assess the different process options.

1.1. Introduction into the use of Ozone

The use of ozone in water treatment has increased significantly since it was first used for disinfection in 1893 and it is now used extensively, especially in Europe where pollution and subsequent eutrophication have complicated water treatment. Although ozone was initially used only for disinfection, the usefulness of ozone in other aspects of water treatment became more apparent. Pre-ozonation is often used to enhance coagulation and flocculation, oxidise soluble iron and manganese, remove taste, odour and colour and oxidise specific micropollutants such as pesticides and phenolic compounds. The use of intermediate ozonation prior to GAC filters, to reduce the amount of biodegradable organic carbon by biologically activated carbon (BAC) and improve the stability of the water, is rapidly expanding. Other benefits such as the effectiveness of ozone to inactivate protozoa and immobilise bacteria and viruses has resulted in a greater awareness of ozone for use in water treatment.

Preliminary investigations into pre-ozonation carried out by Umgeni Water revealed that, contrary to reports of several authors who found that ozone improved coagulation and flocculation (Langlais *et al*, 1991), ozone impaired flocculation and led to an increased coagulant demand (Rencken, 1992). These results have been confirmed in subsequent laboratory experiments carried out by Umgeni Water. Hoyer *et al* (1987) observed that both the algal species and the ozone dose influenced the effect that ozone has on the coagulation and flocculation of water. It would appear that the effect that ozone has on the treatment of water is dependent on a number of different factors and this has important implications for Southern Africa, especially in light of deteriorating water quality.

This report details the laboratory investigation which was carried out on small scale ozonation columns designed for batch treatment with ozone. Investigations into the different process options of ozone, peroxone and coagulation were performed. Water was spiked with algal scums to produce algal cell concentrations of 10 000, 100 000 and 500 000 /mℓ. The effect of two algal genera, *Mycrocyctis* and *Anabaena*, which most often give rise to taste and odour problems in Southern Africa, were assessed. Other types of water investigated included a clean water low in organic content and a water high in organic concentration from an industrial source. The waters were spiked with atrazine and geosmin.

1.2. Introduction into the use of Granular Activated Carbon (GAC)

The use of GAC for water treatment on a full scale has not yet been undertaken by any of the major water utilities in Southern Africa. The ever increasing incidence of eutrophication coupled with more stringent potable water standards for organic pollutants will necessitate the use of GAC in the future. This type of water treatment technology has been avoided because of the cost. Literature quotes the capital cost of regeneration equipment as contributing up to 40% of the total capital cost when using GAC technology.

Recent full scale experience in France using the Picabiol process at a number of major water treatment works, indicates the need for regeneration can be substantially minimised. One major water treatment facility has not regenerated the PICA carbon for more than six years. The Picabiol process uses ozone which enhances the biological activity in the carbon bed by oxidizing organic molecules and making them more amenable to biodegradation.

Research was undertaken on a pilot scale at the Umgeni Water Process Evaluation Facility. A GAC pilot plant, consisting of four columns was built to study the removal of organic contaminants using GAC. The comparative processes with and without ozone, for PICA carbon and a coal based carbon were assessed. The GAC backwashing strategy was similar to that used in Europe to encourage biological activity on the GAC, so that the advantages of using PICA carbon for treating South African waters could be assessed.

1.3. Objectives

The objectives of the project were to :

- Assess the effect of ozone on the coagulant demand and background organics of waters containing two predominant taste and odour causing algal genera in Southern Africa, namely *Mycrocistis* and *Anabaena*. The coagulant demand was to be measured using the standard jar test procedure after spiking water samples with atrazine and geosmin, adjusting the pH to

8 using sodium hydroxide so as not to affect the alkalinity of the water and applying ozone at concentrations between 0,25 and 5,0 mg/ℓ.

- Monitor the water quality before and after ozonation and after coagulation-flocculation-filtration for a number of determinants, including :
    - total and dissolved organic carbon (TOC and DOC)
    - biodegradable dissolved organic carbon (BDOC)
    - turbidity
    - pH
    - alkalinity
    - geosmin, 2-methylisoborneol (2-MIB) and atrazine
    - algal cell concentration, including identification of predominant species
    - trihalomethane formation potential (THMFP)
    - UV absorbance at 254 nm
    - hardness
    - colour
    - iron and manganese

- Investigate the difference between an inorganic coagulant (ferric chloride) and a blended polymeric coagulant (DMDAAC / polyaluminium chloride blend, Zetachem, Z464N) in treating eutrophic waters after ozonation. Past experience has shown that Z464N appears to cope fairly well with increases in algal cell concentration.

- Determine the effect of hardness to organic carbon ratios for both pre- and intermediate ozonation. This effect was to be measured by increasing the ambient hardness from between 60 and 80 mg/ℓ as $CaCO_3$ to approximately 250 mg/ℓ using calcium and magnesium salts.

- Assess the significance of ozone to organic carbon ratios from the data collected.

- Investigate the effect of ozone on background organics on a laboratory and pilot scale. Final treated water after filtration but prior to ozonation is to be ozonated in the laboratory at various ozone concentrations and then analysed for TOC, DOC, BDOC, THMFP, UV absorbance, geosmin, 2-MIB and atrazine. These results were to be confirmed using ozonation on a pilot scale in conjunction with GAC for organics removal.

- Evaluate the effect of adding hydrogen peroxide in conjunction with ozone on a laboratory scale by using the optimum ozone dose and varying the addition of hydrogen peroxide. The effect of whether the peroxone process assists in reducing the ozone dose was to be determined by maintaining a constant hydrogen peroxide to ozone ratio whilst decreasing the ozone dose.

- Investigate the effect of using PICA carbon as a means of reducing the frequency of GAC regeneration. Samples of the carbon from the GAC pilot scale investigation were to be analysed for activity (Iodine No., Methylene Blue No.) as well as geosmin and atrazine isotherms. The reduction in activity would provide an indication of the effectiveness of the carbon for organics removal and the frequency of regeneration.

- Develop design criteria for the removal of algogenic pollutants such as taste and odour compounds, THM precursors as well as atrazine using ozone and GAC. Based on the results obtained from both the laboratory and pilot scale investigations specific information critical to the design of GAC installations would be highlighted.

- Produce a set of guidelines for the process design and operation of water treatment plants treating eutrophic waters. Specific consideration is to be given to the overall process (from pre-treatment and coagulation to post treatment and GAC filtration). The effectiveness of each is related to design parameters and operation strategy. These guidelines would enable water authorities to more accurately assess their situation and establish suitable process options.

2. Literature Review

2.1. Ozone and Peroxone Effects

Ozone has been used over the years to improve the physical-chemical qualities of water such as colour, taste and odour and as a disinfectant. Its strong oxidising properties make it particularly effective against bacteria and viruses. Even at low residuals applied for short contact times ozone can inactivate even the most resistant of human viruses.

2.1.1. Effects on THM and DBP Formation

Increased interest in the use of ozone for water treatment applications resulted from the discovery in the mid seventies that the reaction of the disinfectant with natural organic matter (NOM) in water can lead to the formation of disinfection by-products (DBPs) (Miltner *et al*, 1992; Symons *et al*, 1975). Some DBPs such as trihalomethanes and haloacetic acids, formed during chlorination are suspected to be carcinogens and are therefore a health concern (Crozes *et al*, 1995; Najm *et al*, 1994; Symons *et al*,1994; Szpyrkowicz *et al*, 1992). Their presence in potable water has been regulated or in many cases is in the process of being regulated, with a tendency for the regulations to become increasingly strict (Crozes *et al*, 1995; Goel *et al*, 1995; Jacangelo *et al*, 1995; Krasner *et al*, 1994; Miltner *et al*, 1992; Najm *et al*, 1994; Najm & Krasner, 1995; Speitel *et al*, 1993; Symons *et al*, 1994; Szpyrkowicz *et al*, 1992). In order to minimise DBP formation while maintaining a properly disinfected drinking water, it has been necessary to find alternative treatment methods which will provide more efficient removal of DBP precursors and alternative disinfectants which will result in the formation of fewer DBPs (Miltner *et al*, 1992). Ozone satisfies both of these criteria, because not only is it a very strong disinfectant, but it also has the capability to oxidise many DBP precursors (Miltner *et al*, 1992; Najm & Krasner, 1995).

Pollution of raw water supplies has led to an increase in NOM, which in turn gives rise to higher DBP formation as well as many other water treatment problems. Eutrophication, often a result of water pollution, gives rise to the presence of algogenic compounds, some of which cause taste and odour problems and which can also be toxic. Matters are further complicated by the fact that these algogenic compounds are difficult to remove using traditional water treatment processes. Agricultural run off into raw water supplies results in pesticide and herbicide contamination of the water, while chemicals originating from industrial pollution can cause taste and odour problems as well as being harmful. Ozone, because of its strong oxidising powers is able to oxidise many of these organic contaminants, while at the same time producing less DBPs than disinfectants such as chlorine. As a result of increasingly stringent DBP regulations for water and increases in NOM and pollutant concentrations, ozone has gained much popularity over the past decade as both an oxidant and disinfectant.

Ozone, although giving rise to lower chlorinated DBP, in converting NOM to simpler compounds forms non-halogenated DBP, which include aldehydes, ketones and carboxylic acids (Fiessinger *et al*, 1980; Goel *et al*, 1995; Krasner *et al*, 1993a; Meijers *et al*, 1993; Miltner *et al*, 1992). Toxicological data on ozone DBP, including formaldehyde, acetaldehyde, glyoxal and methylglyoxal, indicate that they are mutagenic or carcinogenic (Andrews & Huck, 1994) and are therefore a health concern.

Another disadvantage of using ozone that has come to light over the last decade is the formation of bromates when bromide is present in the water (Glaze *et al*, 1993; Haag and Hoigne, 1983; Krasner *et al*, 1993b; Kruithof *et al*, 1993; Miltner *et al*, 1992; Siddiqui & Amy, 1993; von Gunten & Hoigne, 1992; von Gunten & Hoigne, 1994). Bromate formation is proportional to the bromide concentration in the water and the ozone dose (Najm & Krasner, 1995; Shukiary *et al*, 1994) and is affected by pH and DOC concentrations. The formation of bromate decreases as the pH is lowered, because bromate is predominantly formed by reaction of ozone, hydroxyl radicals and hypobromite and as the pH decreases, so the amount of hypobromite declines (Kruithof *et al*, 1993; Symons *et al*, 1994; von Gunten & Hoigne, 1994). Certain types of NOM are known to act as initiators for hydroxyl radical formation (Staehelin & Hoigne, 1985) and since bromate is formed by reactions involving hydroxyl radicals, the increase in bromate formation with increasing DOC concentration can be attributed to the hydroxyl radical promotion by NOM (Najm & Krasner, 1995). Their findings are in agreement with those of other researchers (von Gunten & Hoigne, 1994).

2.1.2. Pre-Ozonation and Effects on TOC, NOM and Coagulant Dose

Pre-ozonation is also used prior to conventional water treatment to enhance coagulation and flocculation and a number of references describing this effect can be found (Farvardin & Collins, 1989; Jekel, 1994; Langlais *et al*, 1991; Richard, 1992). However, reports of impairment of coagulation and flocculation by pre-ozonation can also be found (Edwards *et al*, 1993; Rencken, 1992) and it is clear that the mechanisms of ozone reactions need to be understood if the effect of ozone on coagulation and flocculation is to be explained. It has also been found that pre-ozonation affects total organic carbon (TOC) removal, the rate of head loss build-up during filtration and the final water quality. These effects were found to depend on the nature and concentration of NOM in the water (Edwards *et al,* 1994; Jekel, 1994).

The coagulants commonly used in potable water treatment include iron and aluminium salts (e.g. ferric chloride and aluminium sulphate [alum]) and organic polymers which are usually cationic in nature. These coagulants enable the conversion of soluble NOM into insoluble coagulant-NOM reaction products, either by precipitation or adsorption of NOM onto the coagulant particles. Parameters such as pH, coagulant type and dosage and the nature of the NOM will determine which of these mechanisms (i.e. precipitation or adsorption) predominate. Precipitation is defined as the insolubilisation of NOM due to interaction with coagulant molecules and in general, the tendency of NOM to precipitate increases as the molecular weight of the NOM molecules increases and the functional group concentration decreases (Edwards *et al,* 1994). Adsorption also tends to increase with increasing molecular weight and lower functional group activity (Owen *et al*, 1995).

Cationic polymers do not usually provide effective adsorption of NOM and therefore precipitation is generally the predominant mechanism when using a cationic polymer as the sole coagulant (Edwards *et al,* 1994). Ferric chloride and alum tend to remove large molecular weight organic compounds that have a low functional group density by both precipitation and adsorption, while smaller more polar organics are removed primarily by adsorption. Using inorganic iron or aluminium based coagulants, the maximum NOM removal is generally obtained at slightly acidic pH values and is found to increase with increasing coagulant dose. Some of the NOM, however, between 5 and as much as 60% is not removed by coagulation, even at very high doses (Randtke, 1988), indicating the possibility that some NOM compounds are not able to undergo either adsorption or precipitation reactions.

It has been found that when using alum or ferric chloride, ozonation usually increases or has no effect on coagulant demand, provided that the pH is kept constant (Edwards, 1990; Edwards & Benjamin, 1991, 1992; Reckhow *et al,* 1991). Ozonation has on occasion been found to increase coagulant demand even though TOC removal decreases, although this can be explained by the effects ozonation has on precipitation and adsorption reactions. Investigations were carried out into the effects of ozonation on coagulation of waters containing both particles and NOM to quantify changes in both coagulant demand and TOC removal (Edwards & Benjamin 1992). It was 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 is the case when polymeric coagulants are used), and tends to increase coagulant demand when adsorption dominates.

When water containing NOM is ozonated, the larger molecular weight compounds are partially oxidised into smaller, more polar organics (Edwards *et al*, 1994; Jekel, 1994; Reckhow & Singer, 1984). The decrease in molecular weight and increase in functional group density or polarity decreases the amount of NOM removed by both precipitation reactions and adsorption (Edwards *et al*, 1994; Jekel 1994). Coagulant demand will also increase with increasing polarity, although at very low ozone doses (0,1 to 0,3 mg/ℓ) decreases in the colloidal charge density of certain organic compounds can result in a lower coagulant demand and an increased NOM removal (Farvadin & Collins, 1989). It is therefore obvious that the nature of the NOM, the ozone dose and the pH will all affect the treatment process and final water quality and anticipating the effect that ozonation will have on a water is further complicated by the difficulty in characterising NOM.

NOM consists of a complex matrix of natural organic matter that occurs in natural waters and this is the reason why it is very difficult to characterise (Jekel, 1994; Owen *et al*, 1993). As a result surrogate parameters for NOM quantification have to be employed. These parameters can include UV absorbance at 254 nm, TOC, DOC, THMFP, haloacetic acid formation potential (HAAFP) and other DBP formation potentials, acidity and relative polarity as well as many specific organic compounds (Benoit *et al*, 1993; Jekel, 1994; Najm *et al*, 1994; Owen *et al*, 1993; Tobiason *et al*, 1993). To assess biodegradability of NOM tests such as the assimilable organic carbon test (van der Kooij *et al*, 1982) and the biodegradable dissolved organic carbon test (Servais *et al*, 1987, 1989) are used.

NOM is usually divided into two major classes: hydrophobic and hydrophilic organic matter. The hydrophobic fraction is generally less soluble, of higher molecular size and contains greater aromaticity than the hydrophilic fraction (Singer & Harrington, 1993). The hydrophobic fraction consists basically of humic and fulvic acids, of which the humic acid fraction is more highly reactive and readily removable by coagulation, while the fulvic acid fraction is less reactive (Randtke, 1988). The hydrophobic organics tend to have a higher DBP formation potential and appear to contain a lower carboxylic acid content than the hydrophilic organics (Singer & Harrington, 1993).

2.1.3. Advanced Oxidation - Hydroxyl Radicals and the Impact of Hardness

Ozone reacts with NOM by one of two pathways; the first is by oxidation which is a highly selective direct molecular reaction, while the second is indirectly through non-selective reactions with radical species that are formed during the decomposition of ozone (Hoigne & Bader, 1978, 1983a, 1983b; McKnight *et al*, 1993). The radical reaction proceeds mainly by cycloaddition, with electrophilic attack occurring at sites containing high electron density and nucleophilic attack at sites deficient in electrons (von Sonntag *et al*, 1997). This explains the great affinity of ozone for aromatic compounds (Hoigne & Bader, 1978, 1983a, 1983b). As aromaticity is reduced through ozonation, so the UV absorbance of the solution decreases, making UV absorbance (at 254 nm) a useful parameter for assessing the effect of ozone on NOM (Tobiason *et al*, 1993). Hydroxyl radical formation has been found to increase with increasing pH (Hoigne & Bader, 1978, 1983a), while direct oxidation by ozone predominates at lower pH values (McKnight *et al*, 1993). Bicarbonate ions have also been found to affect the reactions of ozone, since they act as scavengers for hydroxyl radicals (Beltran *et al*, 1994a, 1994b; McKnight *et al*, 1993). The different reaction pathways become important when considering the treatment objectives. The radical pathway is preferable for the destruction of organic molecules. It has been found that removal of pollutants such as the herbicide, atrazine which is fairly resistant to attack by ozone, increases when the radical reaction pathway is encouraged (Hulsey *et al*, 1993; Koga *et al*, 1992; Masten & Davies, 1994; Meijers *et al*, 1993). The use of advanced oxidation techniques in which ozone is used in conjunction with ultraviolet (UV) irradiation or hydrogen peroxide (H_2O_2) enhances hydroxyl radical formation and can improve the removal of atrazine, NOM and other organic pollutants (Beltran *et al*, 1994a, 1994b; Hulsey *et al*, 1993; Koga *et al*, 1992; McKnight *et al*, 1993; Meijers *et al*, 1993; von Gunten & Hoigne, 1994).

2.1.4. Intermediate Ozonation

The DBPs formed as a result of ozonation increase the biodegradability of NOM and can therefore also contribute to regrowth in distribution systems and its resultant problems (Bull & Kopfler, 1991; Miltner *et al*, 1992). However, this increase in biodegradability allows for biological treatment after ozonation, with subsequent increased removal of organics (Huck *et al*, 1990a; Miltner *et al*, 1990), especially when using GAC where the benefits of biological filtration and GAC adsorption are combined (AWWA, 1981; Servais *et al*, 1994). Ozonation when used prior to GAC filters is sometimes referred to as "intermediate ozonation" and generally follows conventional potable water treatment.

A problem encountered in GAC filtration is that pre-loading of background organic matter affects adsorption of the target organic contaminants. Background organic matter refers to all the organic matter present in the water other than the target organic pollutants. This background organic matter is usually present in much higher concentrations than the target pollutants and tends to adsorb onto the GAC before the target compounds such as atrazine and geosmin (Orlandini *et al*, 1997). This results in more frequent regeneration of the GAC, which is both costly and time consuming (Hubele, 1986). Intermediate ozonation prior to GAC filters can be expected to lower background organic matter pre-loading on GAC by increasing the concentration of biodegradable organics, thereby allowing a larger proportion of the NOM to be removed by biodegradation.

2.2. Granular Activated Carbon

A study of the optimisation and economic evaluation of GAC for organic removal, which was sponsored by the American Water Works Association (AWWA), details the important parameters involved in the removal of TOC from potable water supplies (AWWA, 1989). The report describes a mathematical model and bench scale studies for the determination of parameters for the effective sizing and design of a large scale GAC installation.

Instead of building extensive GAC treatment facilities, GAC has been successfully used as a replacement for granular media in filters used primarily for suspended solids removal. It was reported that GAC, as a total or partial replacement for sand, is as effective as conventional media for removing turbidity, provided an appropriate media size is selected (Graese *et al*, 1987). It was also reported that filter absorbers can considerably eliminate taste and odours from water supplies, but do not function well at removing less strongly adsorbed species (such as THM's, volatile organic carbon [VOC] and fractions of TOC). Although these compounds are not easily removed, GAC is preferred to powdered activated carbon (PAC) when high concentrations of VOCs are present in the water, but where water is low in background NOM and contains strongly adsorbing compounds (pesticides), PAC is more efficient (Huber *et al*, 1989).

2.2.1. Removal of Organic Carbon

Adsorption of naturally occurring organic material in water has been studied, and for most organic and taste and odour occurrences PAC or GAC would be capable of removing greater than 90% of the compounds. It was shown that GAC would not totally remove all organic carbon (McGuire *et* *al*, 1991), and that some non-adsorbable TOC can still lead to DBP formation. This may be attributed partially to desorption where in some instances it was found that the effluent concentration of organics exceeded the influent levels if the influent concentrations were low (Yohe *et al*, 1981). This chromatographic effect was most pronounced for variable or poorly adsorbed organics and the mechanism for this phenomenon is called displacement-desorption (Yohe *et al*, 1981).

GAC is an effective means of reducing organic contamination (Hayes & Whitford, 1982), although the lower molecular weight compounds are only reduced efficiently during early bed life. Optimisation of the GAC performance for organics removal is therefore critical to the ultimate cost of treatment.

The use of GAC for the removal of organic compounds has been studied and predictions of the performance of GAC filters have been modelled (Crittenden *et al*, 1978a, 1978b, 1980; Hand *et al*, 1983, 1984) by relating the batch scale adsorption of single and multi-components and performing rate experiments on a small scale. Organic compounds can either diffuse in the adsorbed state along the pore surface (surface diffusion), or within the fluid contained in the pores of the GAC (pore diffusion). The effects of these transport mechanisms were studied and it was found that surface diffusion was many times greater for strongly adsorbed species. Accordingly, the contribution of the pore diffusion in the model was neglected. This led to the Homogeneous Surface Diffusion Model (HSDM) where the adsorbent is distributed homogeneously over the surface and where the surface diffusion flux is described by Fick's Law (Hand *et al*, 1983, 1984).

2.2.2. Removal of Organic Micro-pollutants

The removal of organic micro-pollutants from drinking water can be carried out using GAC (Graese *et al*, 1987; Herzing *et al*, 1977; Huber *et al*, 1989; Lalezary *et al*, 1986; McCreary *et al*, 1977; McGuire *et al*, 1991). This is necessary as many water sources are becoming polluted with synthetic chemical substances and the subsequent proliferation of algae in the catchment can result in the release of taste and odour compounds. The naturally occurring taste and odour causing organics, geosmin and 2-MIB, are believed to be the major causes of consumer complaints.

GAC can also provide a barrier against the formation of potentially harmful DBPs (McGuire *et al*, 1991). THMs are the predominant DBP formed during the disinfection of water using chlorine. The control of THMs using GAC should therefore also limit other DBPs in the distribution systems.

Removal of algal by-products, taste and odour compounds (geosmin and 2-MIB), pesticides as well as herbicides (atrazine) can be achieved using activated carbon. Whereas coagulation is mostly ineffective for solving taste and odour problems, oxidation using chlorine or ozone is sometimes effective for specific compounds and activated carbon is generally but not always effective. The adsorption rate of 2-MIB was found to be slow (Huang, 1996), and predictions of 2-MIB concentrations in the GAC filtered water were lower than actually measured on a pilot-plant scale. It was predicted that the use of GAC filters for removing 2-MIB and geosmin would be effective for a period of less than 10 months using an EBCT less than 13 minutes (Newcombe *et al*, 1996). By increasing the EBCT of the GAC filters to 20 minutes the period of effectiveness of the GAC for removing 2-MIB would still be less than 18 months, but for removing geosmin the life of the filter would be longer than 18 months. These predictions were made by spiking the water with 2-MIB and geosmin at concentrations between 30 and 60 ng/ℓ.

It was shown that by increasing the EBCT by a factor of 3, the filter life can be increased by up to 10 times (Hopman *et al*, 1994). Other significant observations were that by pre-treating the water by membrane filtration for example, prior to GAC filtration, the life of the GAC could be extended by up to 4 times, simply by the removal of some of the background organics in the water. The efficiency of GAC adsorption can be significantly affected by the nature of the NOM in the water (Muller *et al*, 1996). By ensuring that the NOM consisted of weakly adsorbing components, the removal of atrazine improved, compared to the treatment of a water containing NOM which adsorbs more strongly.

Similarly the extent of NOM loading was found to have an effect on the removal of atrazine. The GAC filtration of a surface water containing intermittent levels of a pesticide was compared to the performance of a GAC filter which was continuously exposed to the pesticide (Matsui *et al*, 1994). The removal efficiency of the two processes was almost identical, and indicated that the adsorption behavior was mainly a function of the background organic material loaded onto the carbon.

Ozonation can change the nature of the NOM in the water by converting it to more polar substances of a lower molecular weight. Although ozonation increased the biodegradation of dissolved organic carbon (Maloney et al, 1985), it was shown that the ozone process interfered with the ability of the GAC to adsorb volatile halogenated organics. It was concluded that the ozonation created a larger number of low molecular weight organics, thereby increasing the competition for adsorption sites between the volatile halogenated organics and the NOM.

2.2.3. Laboratory and Pilot-Scale Experiments

Design engineers require specific information when deciding whether to implement GAC, or whether to retrofit existing sand filters (Graese *et al*, 1987). Operations personnel require specific information on the effective operation of plants involving ozone and GAC. For this reason laboratory or pilot plant trials are necessary to determine the performance of filtration and adsorption systems for controlling levels of pollutants.

The use of pilot studies to predict plant performance can be very time consuming and more often than not the full scale plant has to be implemented before adequate research is completed. The use of Rapid Small Scale Column Tests (RSSCTs) (McGuire *et al*, 1991), have proven to be advantageous in producing sufficient data in a short time such that scale up and design parameters can be determined. Comparison of these results with pilot-plant studies and full scale operation has been successful for the removal of single micro-pollutants such as geosmin, 2-MIB and atrazine, in conjunction with NOM and global organic parameters such as TOC and DOC.

Normally, the influent absorbate concentrations in surface and ground waters are not constant, and as such RSSCTs may not be able to produce an accurate breakthrough profile. Although RSSCTs can be used to predict GAC performance and can be performed in a short time, the effects of changing water quality also need to be verified (Cummings *et al*, 1994).

RSSCT's however do have the potential to predict the behavior of full scale GAC columns (Crittenden *et al*, 1991). The test assesses both the adsorption capacity and the kinetics of adsorption; has a low capital and operating cost; and does not require the use of numerical models. Several problems still exist however with the design of RSSCTs for the removal of specific components due to the presence of interfering background organic matter, as well as the particle size dependence of intra-particle diffusivity on the adsorption. Nonetheless, the test can provide a reasonable representation provided the external mass transfer resistance to adsorption is limiting.

RSSCTs have been used to predict the performance of different GAC's for humic acid adsorption (Yuasa *et al*, 1995), and to simulate a 5 month pilot-scale trial in a period of several days (Crittenden *et al*, 1987). During these studies RSSCTs were found to be reproducible and were not affected by small amounts of biodegradability that occur during pilot-scale or full-scale plant operation.

2.2.4. Biological Activity on GAC

Where ozonation is used for water treatment, organic material in the water is oxidised and levels of assimilable organic carbon (AOC) are increased, thereby increasing the likely incidence of bacterial growth in distribution systems. Increased levels of AOC, elevated by ozonation, return to influent levels after dual media (GAC and sand) filtration provided no disinfectant residual is maintained through the filter (McGuire *et al*, 1990). Furthermore aldehydes produced by ozone or peroxone are also removed if biological activity is maintained in the filters. Beds of activated carbon were found to be a convenient place for microbial activity (Schulof, 1979), and the process of ozonation followed by GAC is termed biologically activated carbon (BAC). Bacteria and other micro-organisms attach themselves to the irregular surface of the carbon particles and feed on nutrients in the water.

This was confirmed by measuring AOC on a number of filters of different media types (Krasner, 1993a), and it was observed that GAC filters developed biological activity sooner and showed longer-term stability. Although biological activity was established sooner on slow rate filters, the high rate filters in time achieved a comparable capability.

Dissolved organic compounds present in the water are complex, and are composed of two classes, biodegradable or assimilable organic carbon, and non biodegradable or refractory organic carbon (Galey *et al*, 1991). The role of ozonation prior to biological filtration is to transform some of the refractory molecules into products that can be assimilated by the bacteria. Contact time is an important parameter for the removal of BDOC, and in cold waters a contact time of at least 15 minutes should be allowed.

Washing of the GAC was found to be required to maintain the bacterial balance and avoid the development of other forms of life higher than bacteria (Galey *et al*, 1991), with particular attention being paid to protozoans that are bacteria predators, and algae which provide food for organisms like Naises.

The benefits of using BAC as opposed to GAC without ozone are varied. The use of ozonation and BAC for the removal of chlorine demand was studied (Prevost *et al*, 1990), and it was found that ozone increases both the short and long-term chlorine demand, whereas BAC always reduced the chlorine demand. Maximum reduction of chlorine demand occurred with an EBCT of about 20 minutes.

2.2.5. Regeneration of GAC

After the exhaustion of its adsorption capacity, activated carbon must be removed from the contactor and replaced with fresh or reactivated carbon. The terms regeneration and reactivation are often synonymously used, but regeneration is the process of removal of adsorbed molecules from the carbon without a change in the carbon surface. Reactivation however is the restoration of the adsorption capacity by partial desorption and then burn-off of the carbonaceous residue on the carbon surface. This often results in a loss of carbon from the carbon surface and a change in the pore size distribution of the GAC (van Vliet *et al*, 1991). The main advantage of using GAC over powdered carbon is that, although it requires a higher capital cost, it can be removed and regenerated. This also incurs an additional operating cost which should be carefully evaluated before deciding to implement GAC for water treatment. The critical decision on when to reactivate will depend on the criterion used during plant operation. This may be breakthrough of organic contaminants or the chlorine demand of the treated water (Shulof, 1979). A wood based GAC has been applied in the production of potable water at Choisy-le-Roi water treatment plant for longer than 6 years and has significantly reduced the need for regeneration (PICA, 1994). The carbon has a specific surface structure which is beneficial for maintaining sufficient biomass and promotes the optimisation of the BAC process. These processes have been found to be effective for the treatment of European waters containing elevated levels of organic carbon and ammonia.

The RSSCT technique was used to evaluate the adsorption capacity of GAC after regeneration (Yuasa *et al*, 1995) and showed that regeneration usually resulted in a complete recovery of the adsorption capacity for humic substances. This is contrary to other reports where up to 10% loss in adsorption capacity may occur during each regeneration cycle and up to 7% of the carbon may be lost due to attrition (Geldenhuys, 1980; Sontheimer, 1988).

2.2.6. Replacing Filter Sand with GAC

Specific removal of components can be achieved by the use of different types of GAC as a replacement for silica sand in rapid gravity filters. Four different types of GAC were compared for humic acid removal (Yuasa *et al*, 1995). The breakthrough curves produced in laboratory small scale column tests showed clear differences in the adsorbability of the GACs. One type was significantly less efficient than the other three types. The use of PAC for Microcystin LR adsorption was studied (Donati *et al*, 1994), and it was found that wood based carbon was more effective than coal based carbon, followed by coconut shell and peat carbons. This was attributed to the pore size distribution within the wood based carbon, which contained a higher percentage of mesopores.

A synthetic carbonaceous adsorbent was used for the removal of synthetic organic compounds from contaminated ground waters (Hand *et al*, 1994). The adsorbent was less prone to becoming saturated with NOM and showed only a 12% reduction in performance when a water saturated with naturally occurring organics was passed through the carbon.

A dual-layer filter of GAC and sand performed significantly better than a sand filter with respect to the removal of suspended solids and ammonia (Bablon *et al*, 1988). The GAC also removed appreciable quantities of assimilable carbon and consequently had a positive effect on the final water quality.

3. Analytical Methodology

3.1. Organic Analyses

3.1.1. TOC, DOC and BDOC Analysis

TOC and DOC concentrations were determined using the persulphate-ultraviolet oxidation method (method 5310C in Standard Methods for the Examination of Water and Wastewater, 1995) utilising an Aquadoc Total Organic Carbon Analyser. Prior to analysis of DOC, samples were filtered through 0,45 μm membrane filters (Millex, Millipore). All analyses were performed in at least duplicate.

Biodegradable dissolved organic carbon (BDOC) is defined as the fraction of DOC that is removed by heterotrophic microorganisms over a period of 28 days and analyses were performed according to the method described by Servais *et al* (1989). 200 mℓ of sample was sterilised by filtration through 0,2 μm membrane filters (Sartorius cellulose acetate membrane filters), carefully rinsed first with ultrapure water (Millipore Milli-Q) and then with water sample. An inoculum was prepared by filtering a raw water obtained from the same environment as the sample through a 1,2 μm membrane filter (Sartorius cellulose acetate membrane filter). The method described by Servais *et al* (1989) called for a 2,0 μm filter for filtration of the inoculum, but despite repeated efforts to obtain these filters, it became necessary to use the 1,2 μm filters instead. 2 mℓ of inoculum were added to 200 mℓ of sterilised sample, part of which was then placed in a 100 mℓ glass stoppered reagent bottle and water sealed. The sample was incubated in the dark at between 20 and 22 °C for 28 days. Analysis of the DOC was carried out on a subsample of the water collected prior to incubation and on the sample at the end of the incubation period. In this case filtration was obviously through a 0,2 μm membrane filter and not a 0,45 μm membrane filter as described above for DOC analysis The BDOC value was calculated as the difference between the initial and final DOC results.

3.1.2. AOC Analysis

The method used for assimilable organic carbon analysis was based on that proposed in section 9217A of Standard Methods (1995) with slight modifications introduced from the procedure proposed by van der Kooij *et al* (1982). The samples were inoculated with between 50 and 500 CFU/m*l* each of *Pseudomonas fluorescens* P17 (P17) and *Spirillum* NOX (NOX), stock cultures and incubated in the dark at between 15 and 25°C for a period of approximately 3 weeks until maximum density growth had occurred. Enumeration of the test bacteria during the incubation period was carried out as described in Standard Methods (1995). Calculation of the AOC was carried out using the equation proposed by van der Kooij *et al* (1982).

3.1.3. THMFP Analysis

THMFP was determined using the THMFP test described in section 5710B of Standard Methods (1995), although the test was carried out at a pH of 9,2 ± 0,2 as recommended in section 5710C of the 18th Edition of Standard Methods (1992) for the basic THMFP test. This test simulates the conditions experienced in high pH waters and accelerates THM formation. A measured amount of the water sample was placed in a glass stoppered bottle and sufficient chlorine added to the water sample to ensure that a chlorine residual of at least 3 mg/ℓ, but not more than 5 mg/ℓ, remained at the end of the 7 day incubation period. The pH of the chlorinated water sample was raised to 9,2 ± 0,2 and the bottle was water sealed and incubated in the dark at 25 ± 2°C for 7 days. The THM concentration of the water sample prior to chlorination and at the end of the 7 day incubation period was measured and the THMFP calculated from the difference between these THM concentrations. THMs were determined on a Varian 3600 gas chromatograph using direct aqueous injection with a suitable thermal programme and an internal 1,2-dibromomethane standard.

3.1.4. UV Absorbance

UV absorbance of water samples, after filtration through 0,45 μm membrane filters (Millex, Millipore), was measured at 254 nm using a Pharmacia Ultraspec III spectrophotometer and Autofill III autosampler with a 10 mm quartz cell. The UV light source was provided by a deuterium lamp. The procedure followed is described in section 5910B of Standard Methods (1995).

3.2. Micropollutants: Geosmin, 2-MIB and Atrazine

1 ℓ of the sample was extracted with three 50 mℓ portions of dichloromethane and then concentrated under vacuum on a rotary evaporator, to produce a final concentrate solution of 1 mℓ. The geosmin, 2-MIB and atrazine concentrations were determined on a Hewlett-Packard 5890/5970 gas chromatograph-mass selective detector according to a South African National Accreditation Services (SANAS) accredited procedure for geosmin and 2-MIB and an Umgeni Water method for atrazine.

3.3. Algal Identification and Enumeration

Algal identification and enumeration was carried out by the Hydrobiology section of the Scientific Services Division of Umgeni Water using an SANAS accredited procedure

3.4. Chemical Analyses

3.4.1. pH

pH was measured on a Radiometer PHM 95 pH/ion meter.

3.4.2. Turbidity

Turbidity was determined using a Hach Ratio/XR model 43900 turbidity meter.

3.4.3. Colour

Samples were filtered through a 0,45 μm membrane filter (Millex, Millipore) prior to colour measurement. Colour was determined relative to a chloroplatinate standard at 400 nm on a Shimadzu UV 2100 spectrophotometer according to a SANAS accredited procedure.

3.4.4. Calcium, Magnesium and Hardness

Calcium and magnesium were determined using ICP-AES on a Varian Radial ICP according to a SANAS accredited method. Hardness was calculated from the calcium and magnesium analyses.

3.4.5. Iron

Iron was analysed by ICP-AES on a Varian Radial ICP according to a SANAS accredited method.

3.4.6. Manganese

Manganese was analysed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) on a Varian Radial ICP according to an SANAS accredited method.

3.4.7. Alkalinity

Alkalinity analyses were performed on a Mettler DL25 Autotitrator using 0,02 N hydrochloric acid and titrating to the m-value (approximately pH 4,6) to allow for determination of the total alkalinity according to a SANAS accredited method.

3.5. Determination of Ozone and Hydrogen Peroxide

3.5.1. Iodometric Titration for the Determination of Ozone

An iodometric titration method was used for measuring ozone concentration in the reactor column during calibration or for determination of the ozone concentration in the off-gas from the reactor column. The method involves the liberation of iodine from potassium iodide by ozone, followed by titration of the liberated iodine with sodium thiosulphate. The titration is carried out at a pH of between 3 and 4 since the reaction is not stoichiometric at neutral pH as a result of partial oxidation of the thiosulphate to sulphate. This method is suitable for measuring concentrations of ozone of around 1 mg/ℓ or higher, but is subject to interference from strong oxidising agents, such as chlorine and hydrogen peroxide.

The method used is described in section 4500-Cl B of Standard Methods (1995). It was not necessary to add KI to the sample prior to titration since this procedure was only used in cases where ozone was passed through KI solutions, as was the case during calibration of the ozone apparatus or for the KI trap used to measure the ozone concentration of the off-gas from the ozone reactor column. A measured volume of the KI-iodine solution was placed in a flask together with 5 ml glacial acetic acid and titrated against 0,01 N sodium thiosulphate until the yellow colour of the liberated iodine had almost disappeared. 1 mℓ of starch was then added and titration continued until the blue colour had completely disappeared.

3.5.2. Indigo Colorimetric Method for the Determination of Ozone

The indigo colorimetric method was used for measurement of dissolved ozone in water samples. This method is based on the principle that under acidic conditions, ozone rapidly decolorises indigo dye and the decrease in absorption is linearly proportional to the ozone concentration. The method used is described in section 4500-O_3 B of Standard Methods (1995).

10 mℓ of indigo reagent were placed in a 100 mℓ volumetric flask and the flask was filled to the mark with the ozone-containing sample or a dilution of the sample, ensuring that complete decoloration of the indigo did not occur. A sample blank was prepared by adding ozonated sample from which the ozone was first removed by the addition of sodium thiosulphate, to a flask containing 10 mℓ indigo reagent and filling the flask to the mark. The absorbance of the samples and sample blank were measured at 600 nm on a Pharmacia Ultraspec III spectrophotometer and Autofill III autosampler using a 10 mm quartz cell. The ozone concentration in a sample could then be calculated from the difference between the blank and sample absorbance.

3.5.3. Iodometric Titration for the Determination of Hydrogen Peroxide

An iodometric titration was also used for standardisation of the hydrogen peroxide solution used in the advanced oxidation investigations. The principle of the method is similar to that described above section 3.5.1 in that under acidic conditions hydrogen peroxide reacts with iodide to release iodine, which can then be measured by titration against sodium thiosulphate. The method used is described in section X, 123 of Vogel's Textbook of Quantitative Inorganic Analysis (1993). The hydrogen peroxide solution to be standardised was diluted to approximately 0,3%. 25 mℓ of diluted solution was added gradually with constant stirring to a solution of 1 g potassium iodide in 100 mℓ of sulphuric acid (1:20) contained in a stoppered bottle. The mixture was allowed to stand for 15 minutes after which the liberated iodine was titrated with standard 0,1 N sodium thiosulphate with the addition of 2 mℓ starch solution when the colour of the iodine was almost completely discharged.

3.6. Granular Activated Carbon Analytical Procedures

All tests listed in this section were carried out on GAC that had been ground and sieved through a 45 µm stainless steel sieve (BS 410/1986 325 mesh sieve) until at least 95% of the original GAC sample had been passed through the sieve.

3.6.1. Iodine Number Determination of GAC

The iodine number of activated carbon is a measurement of the amount of iodine adsorbed by 1 g of carbon and gives an indication of the total adsorption capacity of the carbon. The method used was the American Society for Testing and Materials (ASTM) D 4607-86 Standard Method for the Determination of Iodine Number of Activated Carbon. The method is based upon a three point adsorption isotherm in which a standard iodine solution is treated with three different weights of activated carbon. The carbon-treated solutions are then filtered to separate the carbon from the treated iodine solution, after which the remaining iodine is measured by titration against a standard sodium thiosulphate solution. The data is used to plot an adsorption isotherm and the amount of iodine adsorbed per gram of carbon at a residual iodine concentration of 0,02 N is reported as the iodine number.

3.6.2. Methylene Blue Number Determination of GAC

Methylene blue number of activated carbon is a measurement of the amount of methylene blue that is adsorbed by the carbon. It gives an indication of the adsorptive capacity of the carbon for larger molecules as opposed to the iodine number which is a much smaller molecule. The method used involves the addition of a standard solution of methylene blue to a weighed amount of activated carbon. After filtration, 1 mℓ of the treated methylene blue filtrate is diluted to 100 ml using 0,25% acetic acid solution and the absorbance measured at 620 nm on a Pharmacia Ultraspec III spectrophotometer and Autofill III autosampler using a 10 mm quartz cell. The residual methylene blue solution is calculated from a calibration curve prepared from standard methylene blue solutions.

3.6.3. Ash Content of GAC

The ash content of the GAC was determined using the ASTM method D 2866-83. An accurately weighed sample of dried activated carbon is ashed in a controlled-temperature muffle furnace until constant weight has been achieved. The ash content is expressed as a percentage of the weight of the original carbon sample.

3.6.4. Adsorption Isotherm Tests for GAC

Adsorption isotherm tests were based on the procedure described in the Chemviron publication titled "The Laboratory Evaluation of Granular Activated Carbons for Liquid Phase Applications" and were carried out using a number of target compounds, either singly or in combination. The organic contaminants used were geosmin, chloroform, bromoform, bromodichloromethane, chlorodibromomethane and atrazine and combinations of these chemicals. The concentrations of trihalomethanes used were 1000 µg/ℓ and 250 µg/ℓ, atrazine was used at concentrations of 1000 µg/ℓ and 5 µg/ℓ and geosmin at concentrations of 100 µg/ℓ and 0,5 µg/ℓ. A standard solution of the target compound or compounds was prepared and varying amounts of carbon were carefully weighed and added to measured amounts of the isotherm solution (150 mℓ, 500 mℓ or 1000 mℓ) in screw cap Schott bottles. The bottles containing the carbon isotherms were agitated on a mechanical shaker for 24 hours at 22 to 24 °C. After agitation the samples were filtered under vacuum through Whatman No. 3 filter paper on a Buchner flask. The filtrates were then analysed for the relevant contaminants using the procedures described above (see **Section 3.1.3** for analysis of THMs and **Section 3.2** for analysis of geosmin and atrazine).

4. Laboratory Investigation

4.1. Introduction

Laboratory testing allows for more comprehensive testing of a system than can generally be achieved at full scale or on a pilot plant. For example a much wider dose range can be investigated and laboratory testing enables one to assess the effect of a much greater number of variables than would otherwise be possible. However, simulation of the full-scale process tends to be less precise in laboratory tests than in pilot-plant studies and therefore every effort needs to be made to reproduce the full-scale conditions as accurately as possible when carrying out laboratory tests.

The aim of this project was primarily to investigate the various options available for the treatment of eutrophic surface waters, especially where these contained nuisance levels of organoleptic taste and odour compounds and high concentrations of natural organic matter. Excessive phosphorus loading of surface impoundments combined with high temperatures and extended periods of sunlight gives rise to algal blooms, which in turn can produce taste and odour compounds. The production of odorous compounds by algae has been well documented world-wide (Persson, 1983) and a number of references to this problem occurring in South Africa can be found. Joubert and co-workers (1989) reported a taste and odour incident which occurred in Nagle Dam, the cause of which was a geosmin-producing strain of *Anabaena* (a cyanobacterium or blue-green alga). Geosmin incidents have also occurred in a number of impoundments and lakes throughout South Africa and in 90% of cases another cyanobacterium, *Microcystis aeruginosa* has been identified as the predominant algal species. Water quality studies for the Umgeni River catchment area, from which water for this investigation was obtained, indicated that severe eutrophication of the Inanda Dam would occur during the investigation period.

However, due to unusually high rainfall incidents very few algal blooms have occurred in the area during the period in which this investigation was conducted. This made it necessary to obtain algal cultures from alternative sources, including laboratory cultured samples. The sources of algae and the method of algal cell spiking of the water are described in **Section 4.2.5.** This problem obviously complicated the test procedures and was detrimental to efforts to simulate the "real" situation.

During the investigation three basic water types were tested:

1. a eutrophic water containing predominantly *Microcystis* or *Anabaena* species,
2. a clean water low in organic content and
3. an industrially polluted water.

Since a constant source of eutrophic water was not available during the period that this investigation was carried out, eutrophic samples were produced by spiking Inanda Dam water with cyanobacterial scums containing predominantly either *Microcystis* or *Anabaena* to produce water with varying algal cell concentrations. Inanda Dam water without any algal cell addition was used as the second water type, while water from the Sterkspruit River, a stream which runs through the industrial area of Hammarsdale and which is contaminated with industrial effluents, was used for the third water type. Tests were performed to assess the effect of pH on ozonation and for these tests the pH of the water was adjusted to 7, 8 and 9 using either hydrochloric acid (0,1N) or sodium hydroxide (0,1N). In all other tests the pH of the water was adjusted to 8. A set of typical water quality data for the three different water types used appears in **Table 4.1**. Unless otherwise stated all data presented was carried out at a pH of 8.

Table 4.1 Typical water quality data for the three types of water investigated.

Determinand	Units	Eutrophic Water	Clean Water	Polluted Water
Turbidity	NTU	23,3	19,9	11,9
pH		7,7	7,8	8,09
TOC	mg/ℓ	6,33	6,63	19,2
Colour °Hazen	° Hazen	5,79	3,19	46,67
Iron	mg/ℓ	0,75	1,12	0,47
Manganese	mg/ℓ	0,05	0,09	0,05
Akalinity	mg/l $CaCO_3$	51,6	49,8	160,1
Calcium	mg/ℓ	9,91	10,81	13,23
Hardness	mg/l $CaCO_3$	48,76	44,91	77,56
Conductivity	mS/m	18,6	20,0	127,0

In order to ensure that the water samples contained geosmin, 2-MIB and atrazine, these were added to the water prior to treatment at concentrations of 100 ng/ℓ for geosmin and 2-MIB and 5 µg/ℓ for atrazine. Atrazine was obtained from Riedel-de Haen (98% 2-chlor-4-ethylamino-6-

isopropylamino-1,3,5-triazin) and geosmin and 2-MIB were obtained from Wacko Chemicals in Japan.

A number of simulations were carried out in which the three water types were pre-ozonated followed by conventional treatment including coagulation with either a polymeric coagulant or ferric chloride, flocculation, settling and filtration. Pre-ozonation doses varying between 0,25 and 5 mg/ℓ were used and the water was carefully monitored after treatment for a number of determinands including TOC, DOC, THMFP, BDOC, UV absorption, geosmin, 2-MIB and atrazine. Laboratory tests in which the effect of intermediate ozonation was investigated were also performed. These tests were carried out on Inanda Dam water which had been pre-ozonated as described in **Section 4.2.2** and conventionally treated using a jar test procedure as described under in **Section 4.2.1**. Intermediate ozone concentrations varying between 0,2 and 4 mg/ℓ were applied and the water was then analysed for a number of variables, including the organic matter indicators mentioned above. The intermediate ozonation tests were expanded to include advanced oxidation tests in which peroxide was used in conjunction with ozone.

Investigations were also carried out into the effect of hardness on the impact of ozonation of a water. Since no suitable source of hard water was readily accessible, the hardness of Inanda Dam raw water was artificially increased prior to ozonation and conventional treatment according to the procedure described in **Section 4.2.4**. Samples of naturally hard waters were also obtained from the Klip River and Suikerbos Rand River with the assistance of Rand Water.

A number of GAC equilibrium studies were carried out in which Freundlich isotherm tests were conducted to assess the adsorption capacity of the GAC for geosmin, 2-MIB, atrazine, trihalomethanes and combinations of these chemicals. Unfortunately the results of these tests were not conclusive, primarily because the concentrations of geosmin and 2-MIB in particular were often at or near the detection limits of the analytical method and small differences in the result could give rise to significant differences in the slope or intercept of the Freundlich plot. These tests are described in **Section 4.2.6**.

4.2. Methods and Materials

4.2.1. Standard Jar Test (Coagulation Test)

A standard jar test procedure (Black *et al*, 1957; Hudson and Wagner, 1981) was used to simulate the conventional treatment processes of coagulation, flocculation and settling. Jar tests were carried out on an Aztec or a Phipps and Bird 6 paddle jar stirrer apparatus with varying speed control. 800 mℓ samples of the water were placed in 1 ℓ capacity cylindrical glass beakers and stirred at 300 rpm (corresponding to a G value of between 200 and 300 s^{-1}). The coagulant was added and stirring at 300 rpm was continued for 2 minutes after the addition of coagulant, after which the stirring speed was reduced to 40 rpm. Stirring at 40 rpm continued for another 15 minutes. The floc size and settling rate were noted and the water was allowed to settle for 15 minutes before being filtered through Whatman number 1 equivalent filter paper (M&N Rundfilter). The pH and the turbidity of the filtrate were measured.

Both an inorganic coagulant ($FeCl_3$) and a blended inorganic-organic polymeric coagulant (a blend of polyaluminium chloride and dimethyldiallylammonium chloride) were used with a range of coagulant concentrations in order to determine the optimum dose, which was accepted as being the minimum coagulant concentration which would produce a final filtered water turbidity of less than 0,5 NTU. The polymeric coagulant was diluted to a 0,08% solution so that 1 mℓ of this solution corresponded to a coagulant dose of 1 mg/ℓ when added to an 800 mℓ sample of water. The ferric chloride, which was supplied as approximately 14,8% as Fe^{3+} was diluted to 0,03% as Fe^{3+} (i.e. 0,08% as $FeCl_3$).

4.2.2. Ozonation Procedure

A schematic figure of the apparatus used for the laboratory ozonation tests appears in **Figure 4.1**. Ozonation was carried out in one of two glass contact columns. The smaller column was 1,40 m high with an internal diameter of 6 cm and a capacity of 4 ℓ, while the larger column, which had a capacity of approximately 10 ℓ, was 1,57 m high with an internal diameter of approximately 9 cm. A Sorbios laboratory ozone generator model GSG 1.2 capable of producing 1 g ozone per hour was used to generate ozone from oxygen (>99.5% oxygen, <10 mg/ℓ moisture) at a pressure of 0,5 bar and a flow rate of 15 ℓ/h. The apparatus consisted of glass, stainless steel or teflon with silicon tubing.

The ozone was introduced into the column through a sintered glass diffuser (number 1 diffuser) positioned at the base of the column. Gas exiting the column was fed through a potassium iodide trap before passing through a gas flow meter (Alexander Wright Model Number DM3 B). The contact column was calibrated by filling it with a solution of potassium iodide and passing a measured volume of ozone-containing gas through the column. During ozonation the solution was recirculated from the bottom of the contact column to the top using a peristaltic pump. Ozone liberates iodine from potassium iodide and the amount of liberated iodine after ozonation was measured using an iodometric titration as described in **Section 3.5.1**. The process was repeated until at least three calibrations varying not more than 5% in concentration had been obtained. It was then possible to calculate the amount of ozone-containing gas that would have to be added to the sample for a particular applied ozone dose.

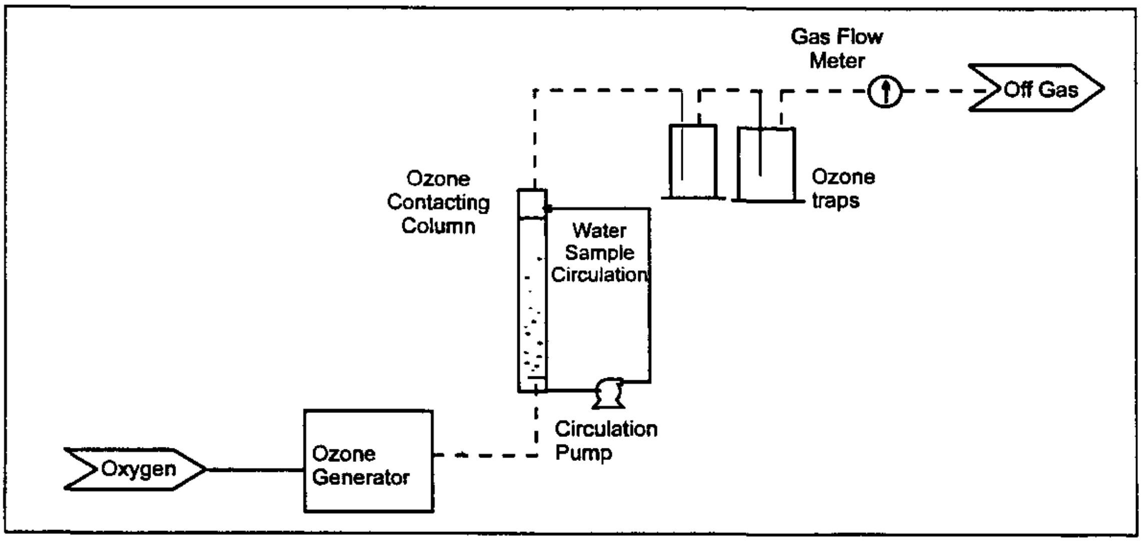


Figure 4.1 Flow diagram of laboratory scale ozonation apparatus.

When ozonating a water sample, a measured volume of the water was placed in the column after calibration had been completed, the water was recirculated to prevent the formation of concentration gradients and the required amount of ozone-containing gas was passed through the contact column. Recirculation of the sample continued for a period of four minutes after onset of ozonation regardless of how long it took to add the ozone-containing gas (it never took more than four minutes to add the ozone). The ozone residual was measured at the end of the four minute recirculation period using the indigo trisulphonate method as described in **Section 3.5.2** and thereafter at four minute intervals for a period of up to 16 minutes. The amount of unreacted ozone exiting the column in the gas phase was also determined by measuring the amount of liberated iodine in the potassium iodide trap at the exit from the column using an iodometric titration (**Section 3.5.1**).

4.2.3. Peroxone Procedure

Advanced oxidation tests in which ozone was used in conjunction with hydrogen peroxide were performed using the ozone apparatus described above in **Section 4.2.2**. Calibration of the system and ozonation of the sample were performed as described in **Section 4.2.2**. Hydrogen peroxide was obtained as a 100 volume solution (30% H_2O_2, Saarchem UnivAR) and was standardised using the iodometric titration described in **Section 3.5.3**. The required amount of hydrogen peroxide was added to the water sample in the contact column immediately before applying the ozone dose. Tests were performed in which a constant peroxide to ozone ratio of 0,5 was used with varying ozone concentrations in three ranges i.e. 0,20 to 1,0; 0,5 to 1,5 and 1,5 to 4,0 mg/ℓ. Tests were also undertaken in which a constant applied ozone concentration of 1,5 mg/ℓ was applied while the peroxide to ozone ratio was varied between 0,3 and 5.

4.2.4. Hardness Adjustment

In tests carried out to assess the effect of hardness on the impact of ozonation, the hardness of the water was raised from ambient hardness (generally 60 to 80 mg/ℓ $CaCO_3$) to approximately 250 mg/ℓ $CaCO_3$ using calcium and magnesium salts in a ratio of 2:1 calcium to magnesium. In order to determine the effect of both non-carbonate hardness and carbonate hardness, hardness adjustment was made in three different ways. In the first only calcium hydroxide and magnesium sulphate were added to assess the effect of permanent hardness only. In the second, sodium bicarbonate was added as well as calcium hydroxide and magnesium sulphate to assess the effect of bicarbonate hardness. The third method involved the addition of all three salts ($Ca(OH)_2$, $MgSO_4$ and $NaHCO_3$) prior to bubbling liquid carbon dioxide through the water until stable pH had been attained. Liquid carbon dioxide was bubbled through an aquarium air bubbler placed at the bottom of a bucket containing 22 ℓ of water sample.

Samples of naturally hard waters were obtained through Rand Water from the Suikerbos Rand and Klip Rivers. Tests were carried out on these water samples without any modification of the natural hardness of the samples.

4.2.5. Algal Cell Collection and Spiking

A number of difficulties were experienced in obtaining algal cell cultures of predominantly *Microcystis* or *Anabaena* cyanobacteria. As it was not possible to find eutrophic water of a consistent source, it became necessary to obtain algal cultures from any available source. Cultures containing predominantly *Microcystis* were obtained from Inanda, Shongweni and

Hazelmere Dams as well as from the maturation ponds at the KwaMakhuta Wastewater Works. Predominantly *Anabaena*-containing cultures were obtained from Inanda and Albert Falls Dams and pure cultures of *Anabaena* were also grown in the Hydrobiology Section of the Umgeni Water Analytical Services Laboratories and used for this project.

The algal scum samples were identified and enumerated as described in **Section 3.3**. The algal cell count was then used to calculate the amount of algal scum that needed to be added to a measured volume of water to yield a final cell count of ten thousand, one hundred thousand and five hundred thousand *Microcystis* or *Anabaena* cells per millilitre. In general 22 ℓ of water sample was measured into a 25 ℓ capacity bucket. The algal scum was mixed well and the required amount was measured and added to the water. The water was well mixed prior to sample extraction to ensure even dispersion of the algal cells. Algal cell counts were carried out on the algal spiked water both before and after any treatment had been performed on it.

4.2.6. GAC Equilibrium Tests

Equilibrium tests were carried out using Chemviron Filtrasorb 400 granular activated carbon which had been ground in a laboratory grinder so that 95% passed through a 45 µm sieve (BS 410/1986 325 mesh stainless steel sieve). The carbon was then dried to constant weight in an oven set at 150 °C .

Single isotherm tests were carried out using trihalomethanes (chloroform, bromoform, dichlorobromomethane and dibromochloromethane) at 1000 and 250 µg/ℓ, atrazine at 1000 and 5 µg/ℓ, and geosmin at 100 and 0,5 µg/ℓ. These contaminants were added to final treated water collected from the Wiggins Water Works at a point prior to chlorination. The volume of water used in the tests depended on the concentration of the contaminant; 150 mℓ water was used at the higher concentrations, while 500 mℓ or 1 ℓ of sample was used at the lower concentrations. It was necessary to increase the volume of water used at the lower concentrations in order to allow sufficient sample for determination of the contaminants and to allow for the accurate weighing of the relatively smaller amounts of carbon which were used under these conditions.

The contaminant-containing water together with the GAC was placed in a glass screw cap bottle of a suitable capacity (150 mℓ, 500 mℓ or 1 ℓ) and if necessary the pH of the water was adjusted to approximately 8. The bottles were placed on a mechanical shaker and shaken for 24 hours at a temperature of between 22 and 24°C. The samples were then filtered through

Whatman number 3 filter paper on a Buchner flask under vacuum. The water was analysed for the relevant contaminants using the procedures described in **Section 3**.

Mixed isotherm tests were carried out as described above using chloroform, bromoform, atrazine and geosmin in both the high and low concentration ranges mentioned above and in various mixtures of two and three of these contaminants.

4.3. Results and Discussion

4.3.1. Effect of Ozone on Natural Organic Matter (NOM)

On account of the difficulty in analysing NOM, a number of surrogate parameters are used for characterisation of the wide variety of organic compounds that occur in water. THMFP, TOC and DOC, BDOC, UV absorbance at 254 nm, chlorine demand and optimum coagulant dose are amongst the surrogate parameters used for NOM characterisation .

4.3.1.1. Trihalomethane Formation Potential (THMFP)

Pre-ozonation was not found to have a significant effect on THMFP, although a weak trend indicating a slight increase in THMFP with increasing ozone concentration was sometimes evident in algal-laden waters. Furthermore, coagulation with either an inorganic or a blended inorganic-organic polymeric coagulant, followed by conventional treatment (flocculation, settling and filtration) was not found to remove any significant amount of THMFP. In tests carried out to assess the effect of enhanced coagulation (WRC Project TT 105/98 *Enhanced Coagulation for the Removal of Disinfection By-Product Precursors)* it was possible to get up to 50% reduction in THMFP using ferric chloride at concentrations of between 1,5 and 5 times that required for optimal turbidity removal. However, little if any THMFP was removed at the ferric chloride doses used for conventional treatment.

A decrease in the THMFP after ozonation was often observed at applied ozone doses to DOC ratios of between 0,01 to 0,15 mg O_3/mg DOC (generally between 0,25 and 1 mg/ℓ applied ozone concentration). This trend was evident for all three types of water investigated and was even observed for ozonation of final filtered waters (i.e. intermediate ozonation) **Figures 4.2, 4.3 and 4.4**. Attempts to correlate the ozone concentration at which this decrease occurs with other water quality parameters have not been successful, but a decrease in coagulant demand appears to coincide with this phenomenon. The decreases in the colloidal charge density at low ozone concentration reported by Farvadin and Collins (1989) may account for this effect, resulting in precipitation of a portion of the THM precursors.

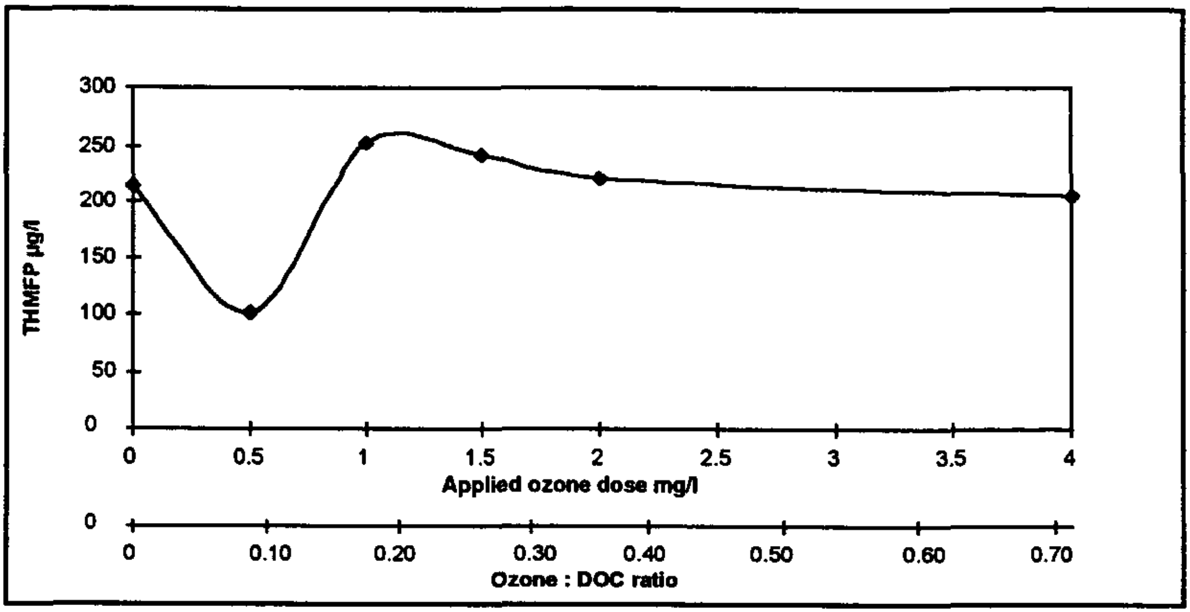


Figure 4.2 Effect of intermediate ozone on the THMFP of a final filtered water.

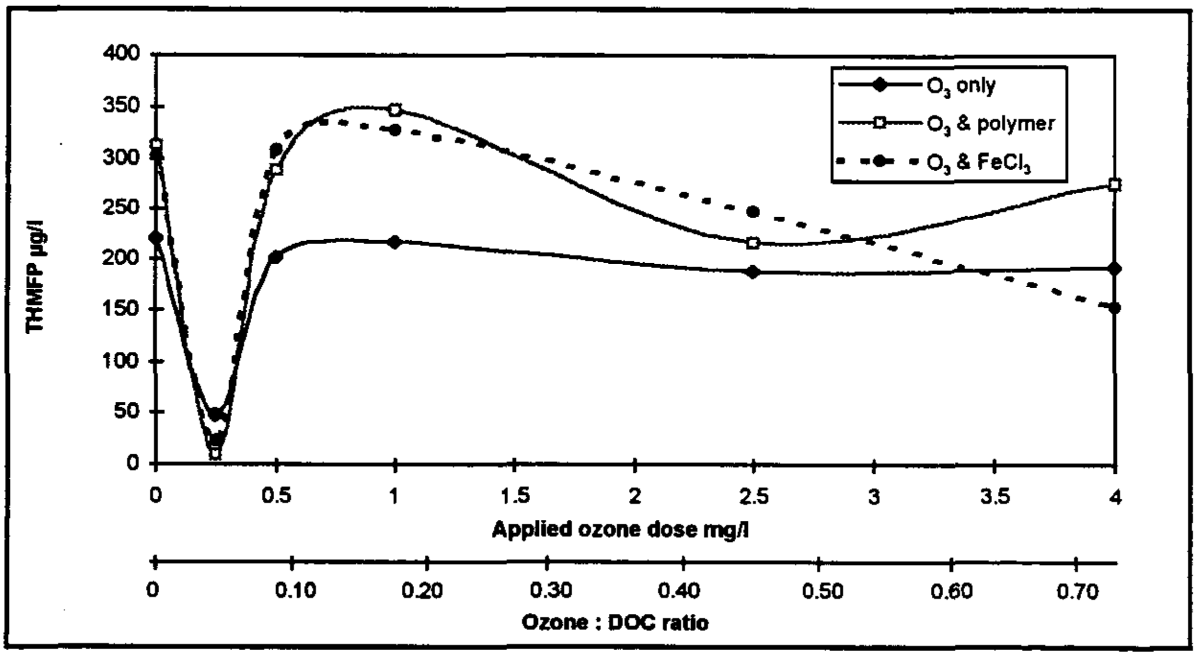


Figure 4.3 Effect of pre-ozonation and conventional treatment on the THMFP of a eutrophic water (Inanda Dam water containing 100 000 *Microcystis* cells/mℓ).

4.3.1.2. Dissolved and Total Organic Carbon (DOC and TOC)

Ozone was often found to have little or no effect on the TOC of a water, although as was found for the THMFP, a small decrease in TOC was often observed at ozone to DOC ratios of 0,01 to 0,15. In cases where the TOC concentrations were higher, such as in algal spiked water and industrially polluted water, a trend was sometimes observed in which the TOC decreased with increasing ozone concentration, with decreases of up to 25% possible at applied ozone concentrations of between 0,3 and 0,5 mg O_3/mg DOC (generally 2 to 4 mg/ℓ O_3) **Figure 4.5**. This correlates with literature reports of TOC removals after ozonation in the region of 20% (Tuhkanen *et al*, 1994) and 30% (Cipparone *et al*, 1997).

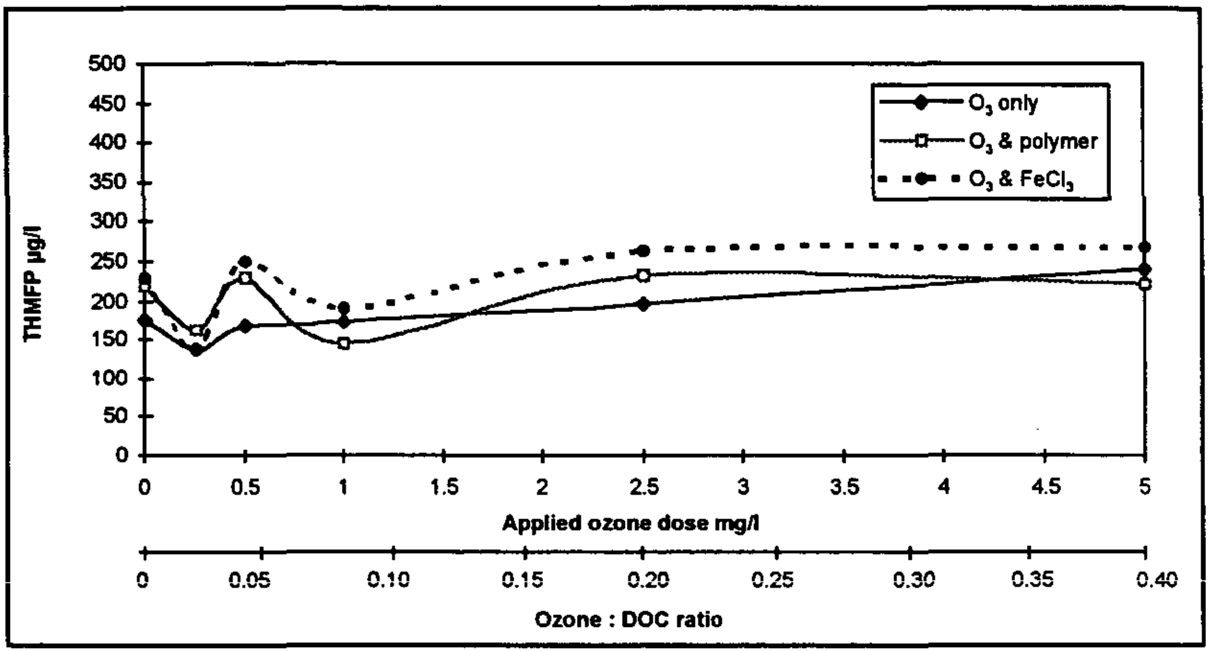


Figure 4.4 Effect of pre-ozonation and conventional treatment on the THMFP of an industrially polluted water.

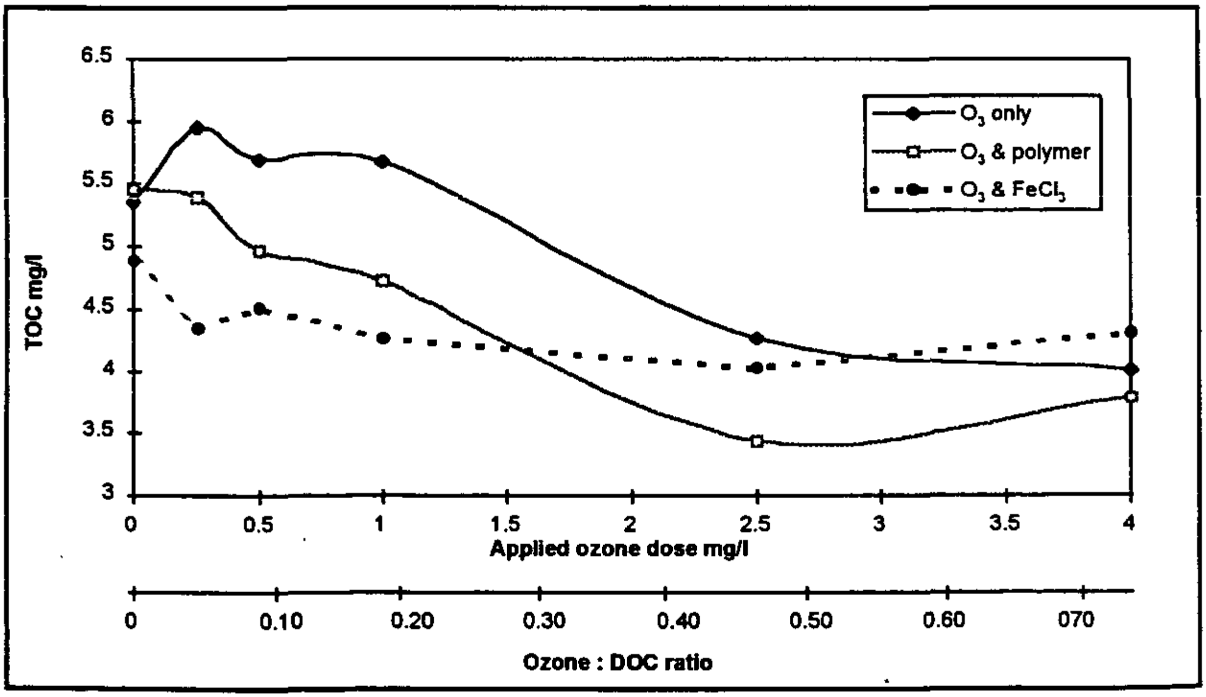


Figure 4.5 Effect of ozone on the TOC of an eutrophic water (Inanda Dam water containing 100 000 *Microcystis* cells/mℓ).

If conventional treatment using either a blended inorganic-organic polymer or inorganic coagulant followed ozonation, it was possible to obtain an overall TOC removal of up to 50% in some instances **Figure 4.6**. The DOC concentrations were found to mirror those for TOC, which is to be expected as in most cases the TOC was found to consist predominantly of DOC. The reason for the DOC and TOC removal after ozonation, but prior to conventional treatment can only be explained by the changes in colloidal properties reported by Farvadin and Collins (1989), which give rise to a lower coagulant demand and an increased NOM removal. The changes that occur in the charge density of NOM at these ozone concentrations possibly have a coagulation effect on the dissolved organic compounds.

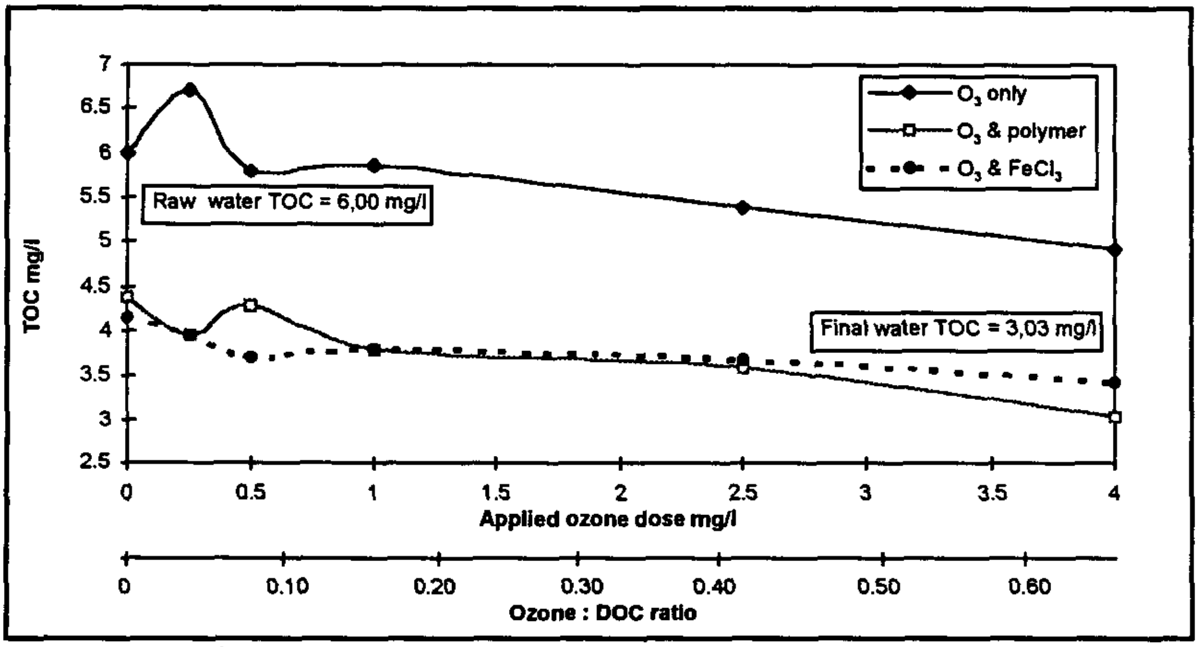


Figure 4.6 **Effect of ozone on the TOC of a eutrophic water (Inanda Dam water containing 500 000 *Microcystis* cells/ml).**

4.3.1.3. Biodegradable Dissolved Organic Carbon (BDOC) and Assimilable Organic Carbon (AOC)

The BDOC was generally found to increase with increasing ozone concentration, stabilising at higher ozone concentrations, which is in agreement with the findings of other authors (Janssens *et al*, 1985; Somiya *et al*, 1986; Sontheimer, 1979). In waters which were fairly low in organic content, such as the Inanda Dam water and algal spiked water, stabilisation of the BDOC concentration was generally found to occur at an applied ozone dose above 1,5 mg/ℓ (i.e. ozone to DOC ratios of approximately 0,3 to 0,5) **Figure 4.7** with ozone having only a small additional effect at higher concentrations. This compares favourably with the findings of other researchers. Brunet and co-workers (1982) found that there was a limit to the ozone dose beyond which no further increase in AOC occurred, while van der Kooij and co-workers (1989) noted an attenuation of the ozone effect on AOC at ozone doses of 0,5 mg O_3/ mg DOC. It was also found that an applied ozone dose to DOC ratio of between 0,2 and 0,5 (generally 1,0 to 1,5 mg/ℓ applied ozone) was required before ozone had any significant impact on the BDOC of the water. In fact many natural organic compounds have been found to show significant improvements in biodegradability at ozone doses of 0,5 mg O_3/mg DOC, while in most cases beyond a dose of 1 mg O_3/mg DOC, all biodegradable organic compounds likely to be formed, have already been transformed (Langlais *et al*, 1991).

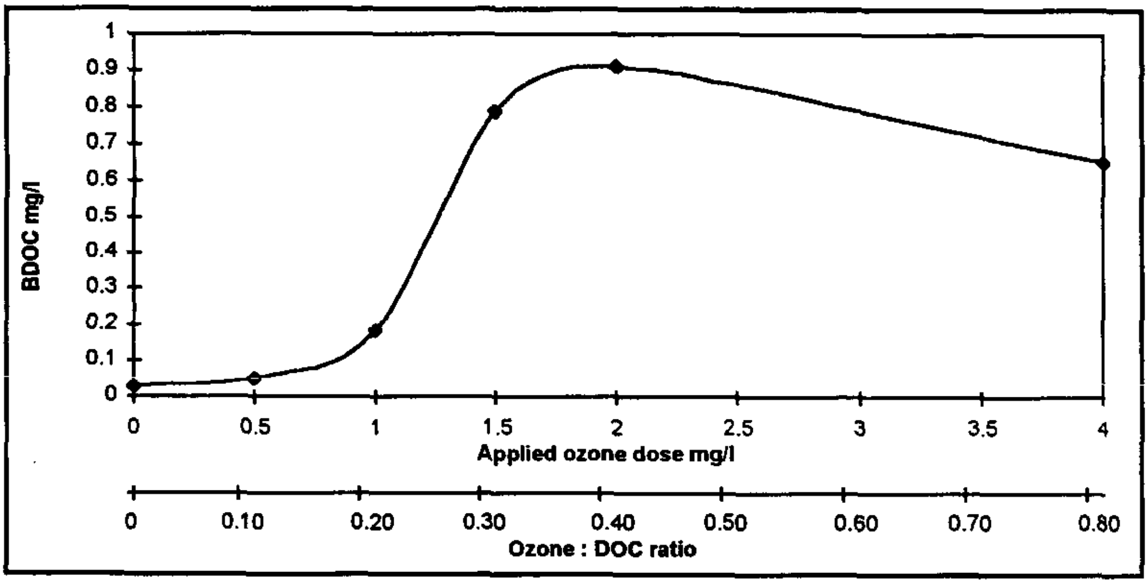


Figure 4.7 **Effect of ozone on the BDOC of a final filtered water.**

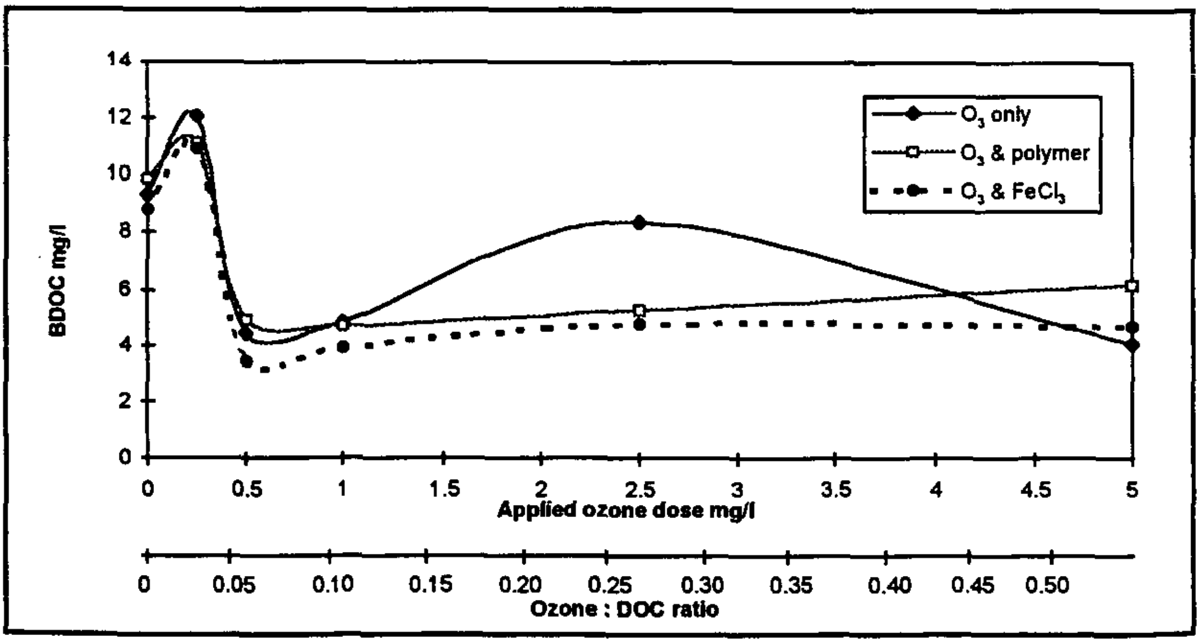


Figure 4.8 **Effect of ozone on the BDOC of an industrially polluted water.**

The trends in BDOC concentration with ozone were much more variable in industrially polluted water. After an initial increase in BDOC at lower ozone doses, the BDOC was sometimes found to decrease at higher ozone doses **Figure 4.8**. Huck and co-workers (1989) observed a similar effect during an investigation into the AOC of water at a Canadian water works and they concluded that this effect could be due to inhibition of the P17 bacteria by an ozonation by-product and may be unrelated to the concentration of biodegradable organic compounds (Huck *et al*, 1990). It is possible that with an industrially polluted water, the ozonation by-products of some of the industrial pollutants may be toxic to the bacteria used during the BDOC test.

AOC and BDOC are both measures of the biodegradable dissolved organic matter present in a water, although these two tests are fundamentally different in measuring biodegradability. BDOC is the portion of DOC that can be mineralised by heterotrophic micro-organisms, while AOC is the portion of DOC that can be converted to biomass (Huck, 1990).

Some AOC tests were carried out in this investigation in order that the BDOC and AOC tests could be compared. Unfortunately it was only possible to perform AOC tests on a few samples, but the AOC results, like the BDOC results, clearly indicated an increase in biodegradability after ozonation.

4.3.1.4. UV Absorbance (254 nm)

UV absorbance at 254 nm was found to decrease with increasing ozone concentration, which is in agreement with the literature (Hoigne and Bader, 1983a). The trend observed in waters with fairly low TOC concentrations (3 to 6 mg/ℓ) was for a small or negligible decrease in UV extinction to occur up to applied ozone dose to DOC ratios of between 0,1 to 0,3, with a fairly significant decrease occurring at higher ozone concentrations. Applied ozone doses higher than this "threshold" concentration did not generally result in much additional reduction in the UV absorbance **Figure 4.9**. In the case of a water polluted with industrial effluent and which had a higher ozone demand than most of the other waters tested, decreases in the UV absorbance had still not stabilised at an applied ozone dose of 5 mg/ℓ as the ozone to DOC ratio at this concentration was often still only about 0,2 **Figure 4.10**. For all waters investigated it was possible to obtain reductions in the UV absorbance of as much as 70% using applied ozone concentrations of up to 5 mg/ℓ (0,5 to 1,5 mg O_3/mg DOC), although a reduction of between 30 and 60% was more common at this ozone dose.

The small decrease often observed in the THMFP, TOC and DOC at low applied ozone concentrations was also evident in the UV absorption, and is obviously due to the effect of ozone on the NOM at these doses **Figure 4.10**.

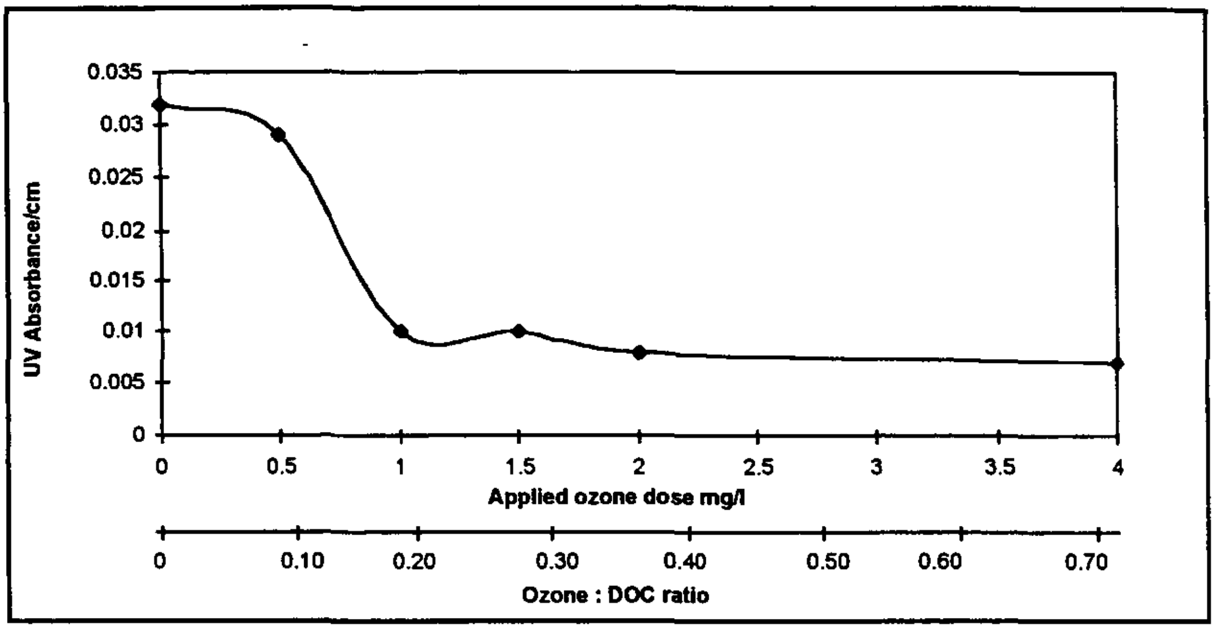


Figure 4.9 Effect of ozone on the UV absorbance at 254 nm of a final filtered water.

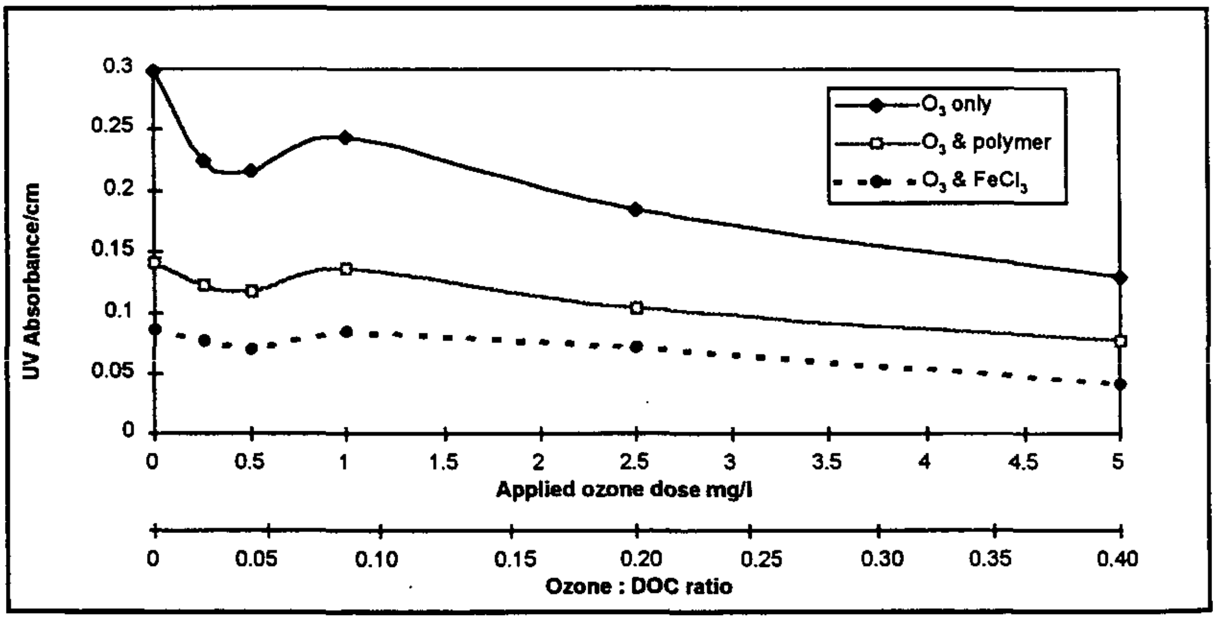


Figure 4.10 Effect of ozone on the UV absorbance at 254 nm of an industrially polluted water.

Conventional treatment consisting of coagulation, flocculation, settling and filtration was found to have a fairly variable effect on the UV absorbance of a water. It was possible to obtain reductions in the UV absorbance of as high as 65% using coagulant without pre-ozonation. The polymeric coagulant sometimes had no effect on the UV absorbance, although in some cases it brought about a fairly significant reduction (up to 60%). Ferric chloride was found to be 10 to

20% more effective than the polymeric coagulant in reducing the UV absorbance **Figure 4.10**. Pre-ozonation followed by conventional treatment could bring about a reduction in the UV absorbance of as high as 90%, although removals of between 40 and 80% were generally obtained. Here too ferric chloride was found to be more effective than the polymeric coagulant.

4.3.1.5. Atrazine, Geosmin and 2-Methylisoborneol

Atrazine, geosmin and 2-MIB were found to decrease with increasing ozone concentration, with an applied ozone concentration of between 0,1 and 0,3 mg O_3/mg DOC generally being required in order to obtain a significant decrease in these compounds (i.e. between 0,5 and 1,5 mg/ℓ applied ozone for the low DOC waters used in this investigation, but between 2,5 and 5,0 mg/ℓ for the higher DOC waters). Applied ozone concentrations higher than this caused further reductions in atrazine, geosmin and 2-MIB, but not much additional removal occurred at applied ozone doses to DOC ratios of above approximately 0,4 **Figure 4.11**. For all three contaminants it was possible to obtain removals in excess of 70% when using applied ozone concentrations of between 0,4 to1,0 mg O_3/mg DOC.

The ozone to DOC ratios at which significant atrazine, geosmin and 2-MIB removal occurred were found to be more variable for pre-ozonation of raw waters. Intermediate ozonation tests carried out on final filtered waters yielded far more consistent ozone to DOC ratios of around 0,2 for the ozone concentration at which significant removal was obtained. This is not surprising since the raw waters were far more variable in NOM content and composition than the final filtered waters and contained turbidity and solids.

Conventional treatment without pre-ozonation did not result in significant atrazine, geosmin or 2-MIB removal.

4.3.1.6. Colour

It was possible at ozone to DOC ratios of between 0,1 and 0,4 to reduce the colour of a water by between 40 and 60% using ozone without additional treatment and to increase this removal to in excess of 70%, and often over 90%, if ozonation were followed by conventional treatment using an inorganic or blended polymeric coagulant. Ferric chloride was found to be more effective than the polymeric coagulant in achieving colour removal.

Removal of colour by ozonation is well documented and ozone doses of between 1 and 3 mg O_3/mg DOC are reported to produce almost complete removal of colour (Killops, 1986).

These doses are significantly higher than those used in this study, but the data obtained in this study indicated that higher ozone concentrations would result in further colour removal **Figure 4.12**.

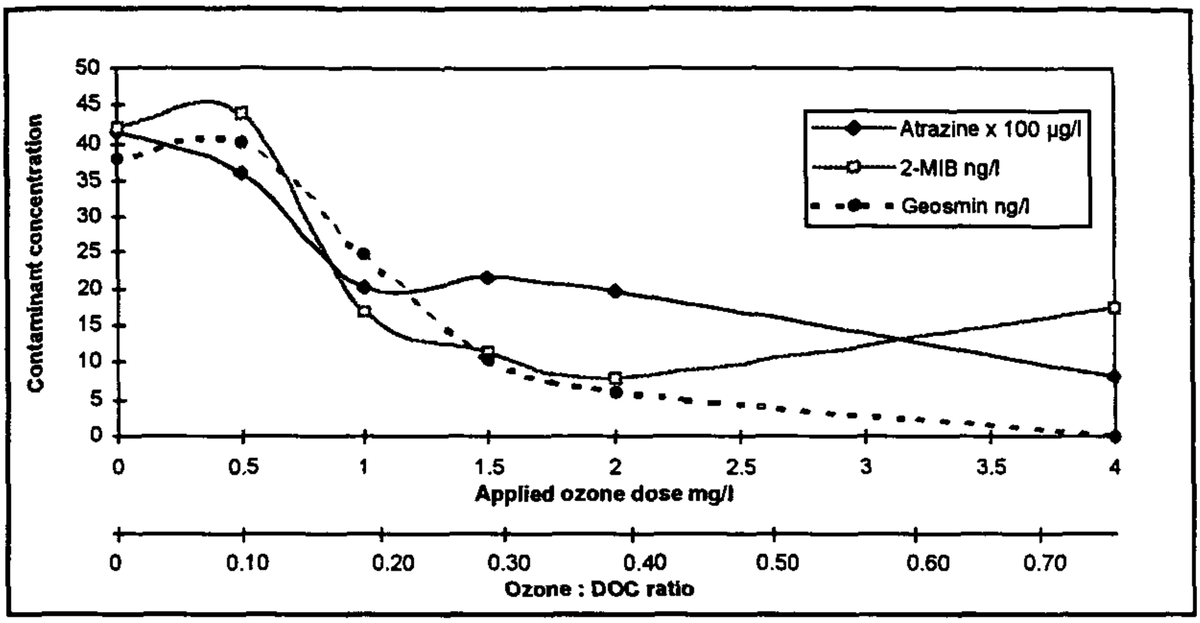


Fig. 4.11 **Effect of ozone on atrazine, geosmin and 2-MIB of a final filtered water.**

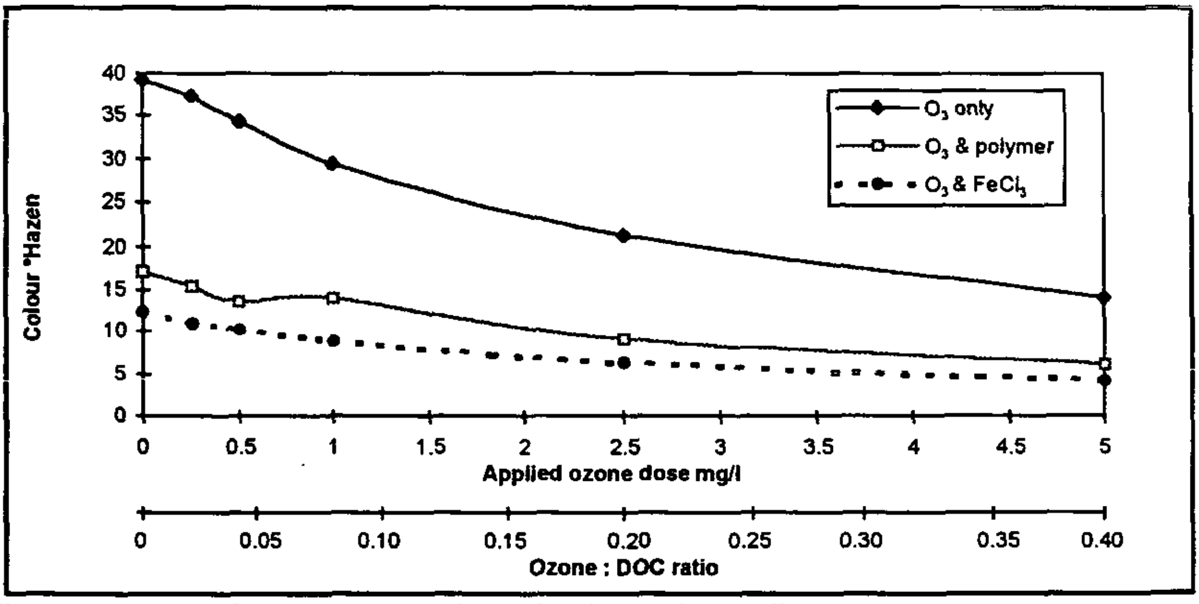


Figure 4.12 **Effect of ozone on colour of an industrially polluted water.**

4.3.1.7. Effects of Enhanced Coagulation Compared to Advanced Treatment Processes.

A brief discussion of the most salient points to come out of a project funded by the Water Research Commission (WRC Project TT 105/98: *Enhanced Coagulation for the Removal of Disinfection By-product Precursors*) and carried out in conjunction with the present project is included here. Conventional coagulation is defined by the conditions that lead to optimal turbidity removal using coagulant alone, while enhanced coagulation is defined by the conditions that lead to optimal NOM or DBP removal using a coagulant (usually inorganic) with or without acid addition (Crozes *et al*, 1995). This project (TT 105/98) investigated the effects of enhanced coagulation as an alternative to the more sophisticated and expensive treatment options of ozone, advanced oxidation and GAC. Reductions obtained in DBP precursors, pesticide/herbicide contaminants, taste and odour compounds and NOM using enhanced coagulation were compared to those achievable using ozone or advanced oxidation followed by GAC.

The same waters as used for this project were used for the enhanced coagulation investigation, namely a water low in organic content, eutrophic water containing either *Microcystis* or *Anabaena* cyanobacteria at concentrations of between 10 000 and 500 000 cells/mℓ and a water high in organic pollutants from an industrial source.

Enhanced coagulation was carried out using alum, ferric chloride, a range of organic polymeric coagulants (both unblended organic cationic polymers and blended inorganic and organic coagulants) and magnetite (Sirofloc).

It was possible in the laboratory tests to obtain up to 50% reduction in THMFP when using ferric chloride for enhanced coagulation of a eutrophic water or an industrially polluted water. This was confirmed by pilot-scale studies in which THMFP removals of up to 40% were obtained when using ferric chloride for enhanced coagulation of waters low in organic content (i.e. Inanda Dam raw water). Removals of between 50 and 75% of DBP have been cited in the literature (Amy and Chadik, 1983; Babcock and Singer, 1979; Dempsey *et al*, 1984; Glaser and Edzwald, 1979; Hubel and Edzwald, 1987; Hundt and O'Melia, 1988; Kavanaugh, 1978; Reckhow and Singer, 1984; Semmens and Field, 1980), although this does depend on the nature of the organic matter present in the water. Enhanced coagulation therefore appears to be more effective for THM precursor removal than ozonation alone. This is probably because enhanced coagulation results in coagulation of some of the THM precursors whereas ozonation would generally only cause conversion of larger organic compounds into smaller more polar compounds and therefore would not be expected to remove THMFP and may even cause a small increase in THMFP.

Pilot-plant studies (**Section 5**) in which final treated water was ozonated prior to filtration through GAC brought about as much as a 40% reduction in THMFP. Enhanced coagulation can therefore compare with the more advanced treatment options of ozone and GAC in terms of THMFP removal.

TOC and DOC removals of between 20 and 40% and even up to 50% were achieved using enhanced coagulation with inorganic coagulants (alum and ferric chloride) for the treatment of waters which had low to moderate TOC and DOC concentrations (i.e. 4 to 8 mg/ℓ). These removals were obtained at inorganic coagulant doses in the region of 1,5 to 5 times the concentration required for optimal turbidity removal. The blended inorganic-organic polymeric coagulant did not bring about more than approximately 10% TOC and DOC removal from the same waters even when using coagulant concentrations of 6 times the optimal dose for turbidity removal. The TOC of these waters consisted predominantly of DOC and therefore both parameters responded in a similar fashion to enhanced coagulation.

Pilot scale tests carried out on Inanda Dam raw water using ferric chloride at concentrations varying between 6 and 30 mg/ℓ as $FeCl_3$, (i.e. 2-10 mg/ℓ as Fe^{3+}) have confirmed the results of the laboratory tests. At concentrations of approximately 30 mg/ℓ $FeCl_3$, it was possible to achieve between 55 and 60% removal of TOC and DOC. These doses were in the region of 2 to 5 times the concentration required for optimal turbidity removal.

TOC and DOC removals of over 60% were achievable using enhanced coagulation with inorganic coagulants for the treatment of industrially polluted waters. The TOC and DOC of these industrially polluted waters was fairly variable, falling any where between 15 and 35 mg/ℓ. For these waters the optimal inorganic coagulant dose for organic carbon removal occurred between 1,5 and 7 times the optimal dose for turbidity removal.

It was also possible to achieve TOC and DOC removals of around 50% from the industrially polluted water when using the blended inorganic-organic polymeric coagulant, although this coagulant was not generally suitable for the treatment of this water in terms of turbidity removal and in most cases it was not possible to produce water of acceptable quality, even at concentrations of up to 70 mg/ℓ .

The effect of pH on NOM removal was investigated in order to determine the optimal pH for maximum NOM removal. It was possible when using the inorganic coagulants (alum and ferric chloride) to adjust the pH to the optimal value using the coagulant alone, or using lower coagulant concentrations together with acid addition. The benefits of each option were then compared. The optimal pH value for organic carbon removal was found to be best at 5 when using ferric chloride and at between 5 and 5,5 when using alum, which is in agreement with the findings of Randtke (1988). The pH was even found to affect NOM removal when using an organic polymeric coagulant, with the optimum pH being around 5. Although NOM removal was generally rather poor when using an organic polymer at the ambient pH of the water (7 to 8), DOC removals could be increased by 15 to 25% by reducing the pH of the water to 5 using acid, without any adjustment to the coagulant dose. Similar increases in DOC removal could be obtained when using pH depression with the inorganic coagulants, again without adjusting the coagulant dose.

Ozonation alone was generally not effective for TOC and DOC removal, although removals of up to 25% could be obtained in waters which were fairly high in organic content. Pilot plant tests (**Section 5**) indicated that TOC and DOC removals after conventional treatment followed by ozonation and GAC filtration were in the region of 15 to 30%, which is no better than that achieved using enhanced coagulation.

BDOC removals were in many cases fairly good (30 to 50%) at the ferric chloride and alum optimal doses in terms of turbidity removal and it was possible to obtain between 70 and 90% removal when using between 2 and 5 times the optimal turbidity removal dose. Ferric chloride generally gave better BDOC removal than did alum, while the organic polymer gave little or no BDOC removal. In contrast to this, ozonation increased the BDOC concentration, but conventional treatment followed by ozonation and GAC filtration could bring about good removals of BDOC, in excess of 80% according to the results of the pilot plant investigation. BDOC removals in the pilot plant tests were however rather variable. The results imply that the BDOC removal achievable using enhanced coagulation may be as good as that obtained using the more advanced treatment options, although enhanced coagulation may be far more cost effective.

Enhanced coagulation using ferric chloride, alum or a polymeric coagulant did not generally give rise to any significant removal of geosmin, 2-MIB or atrazine, despite fairly good removals of TOC and DOC. Enhanced coagulation with ferric chloride and alum gave rise to good colour removal, between 50% and almost complete removal being possible depending on the coagulant dose and the nature of the NOM present in the water. These results have been confirmed in the pilot plant studies where the colour was reduced from values as high as 11,5 ° Hazen to less than 1 ° Hazen at ferric chloride concentrations of between 6 and 30 mg/ℓ as $FeCl_3$ (i.e. 2-10 mg/ℓ as Fe^{3+}) (DOC concentrations of between 3 and 6 mg/ℓ).

Enhanced coagulation was also found to be effective for the removal of algal cells. This is to be expected as "sweep coagulation" which is similar to enhanced coagulation has been used for many years for algal cell and particle removal from water. Pilot plant studies have confirmed the laboratory tests with algal cell removals in excess of 90% and very often complete removals occurring at ferric chloride doses of between 10 and 30 mg/ℓ as $FeCl_3$.

Pre-ozonation of water samples prior to enhanced coagulation with ferric chloride, alum or a polymeric coagulant was carried out in order to determine whether it would be possible to further increase the removal of organic carbon which could be obtained using enhanced coagulation alone. Although ozone was very good for the removal of geosmin, 2-MIB and atrazine, no notable benefit was found for using ozone in terms of organic carbon removal. It should be noted that organic carbon occurred in milligram per litre concentrations as opposed to these micropollutants which were present in nanogram and microgram per litre concentrations. In many cases there was no significant difference in the TOC and DOC removal obtained using enhanced coagulation with or without pre-ozonation. It was possible in some instances to increase TOC/DOC removal achievable with enhanced coagulation alone by between 10 and 15% if the water was first ozonated. However, the capital and running costs of installing an ozone plant could not be justified by such a small improvement in organic carbon removal.

4.3.1.8. Cost Comparison between Advanced Treatment Processes and Enhanced Coagulation

A cost assessment was carried out based on three typical situations in which ferric chloride was used. The first was for a clean water low in organic carbon content (TOC 3-5 mg/ℓ), the second was for a eutrophic water containing approximately 10 000 *Microcystis* cells/mℓ (TOC approximately 8 mg/ℓ) and the third was for a water polluted with industrial effluents (TOC approximately 15 mg/ℓ). Based on optimal doses as shown in Table 1, a ferric chloride cost of R450-00 per tonne at 14,3% iron, a sludge production factor of 0,65 (Geldenhuys,1992) and estimating lime requirements assuming 50% precipitation, the costs shown in **Table 4.2** were obtained. Sludge treatment and disposal costs of R400-00 per 7 m^3 load at 25% solids are based on plant experience.

Cost assessments were also conducted for treatment works in which conventional treatment was followed by ozonation and GAC filtration. For a 350 Mℓ/d plant at a dosage of 5 mg/ℓ, capital costs were estimated at approximately thirty million Rand amortised over 15 years at 15%. Including operating costs into the equation yielded an overall figure of R5-34/Mℓ for ozonation. Costs for GAC filters for a 350 Mℓ/d plant were based on a 20 year amortisation for civils and 15 years for mechanicals and electricals. The first fill of GAC was capitalised. Using an interest rate of 15%, an overall GAC cost of R116-00 was calculated. Costs for a 175 Mℓ/d plant based on the same criteria used above, yielded ozone costs of R8-34 and GAC costs of R174-00.

This implies that advanced treatment processes become economically attractive on large works when treating relatively polluted waters. In all other cases enhanced coagulation is more attractive.

Table 4.2 **Comparison of costs for advanced treatment processes and enhanced coagulation for 350 and 175 Mℓ/d plants.**

Advanced Treatment Processes						Enhanced Coagulation	
350 Ml/d Plant						**350 Mℓ/d Plant**	
Water	**Coag dose mg/ℓ**	**Coag cost R/Mℓ**	**Ozone R/Mℓ**	**GAC R/Mℓ**	**Total cost R/Mℓ**	**Coag dose mg/ℓ**	**Total cost R/Mℓ**
Clean	4	6-80	5-34	116-00	128-14	12	20-40
Eutrophic	25	42-50	5-34	116-00	163-84	60	102-00
Polluted	60	102-00	5-34	116-00	223-34	160	272-00
175 Mℓ/d Plant						**175 Mℓ/d Plant**	
Clean	4	6-80	8-34	174-00	189-14	12	20-40
Eutrophic	25	42-50	8-34	174-00	224-84	60	102-00
Polluted	60	102-00	8-34	174-00	284-34	160	272-00

4.3.2. Effect of Ozone on Coagulant Type and Optimum Dose

The optimum coagulant demand was determined as the minimum coagulant dose which could achieve a final water turbidity of less than 0,5 NTU. The optimum polymeric coagulant demand was generally not greatly affected by ozonation, while the inorganic coagulant demand usually increased with increasing ozone concentration. The ozone to DOC ratio was found to be important in determining the increase that occurs in the optimum ferric chloride dose with ozone (the higher this ratio the greater the increase). Ozone to DOC ratios of less than 0,1 resulted in fairly low increases in the optimum dose, these never being higher than 50%, while ratios in excess of 0,8 generally gave rise to much larger increases, in excess of 1000% in some instances although more commonly between 50 and 300%. For this reason, increases in the ferric chloride optimum dose after ozonation were found to be lower in more polluted waters.

In treating a water high in industrial effluent pollution it was noted that the polymeric coagulant was not always suitable for the treatment of this water. Even in cases where this coagulant was capable of producing a final filtered water of less than 0,5 NTU in turbidity prior to ozonation, ozone doses of 0,1 to 0,3 mg O_3/mg DOC (i.e. 2,5 and 5 mg/ℓ applied ozone) rendered the water unresponsive to treatment with this coagulant.

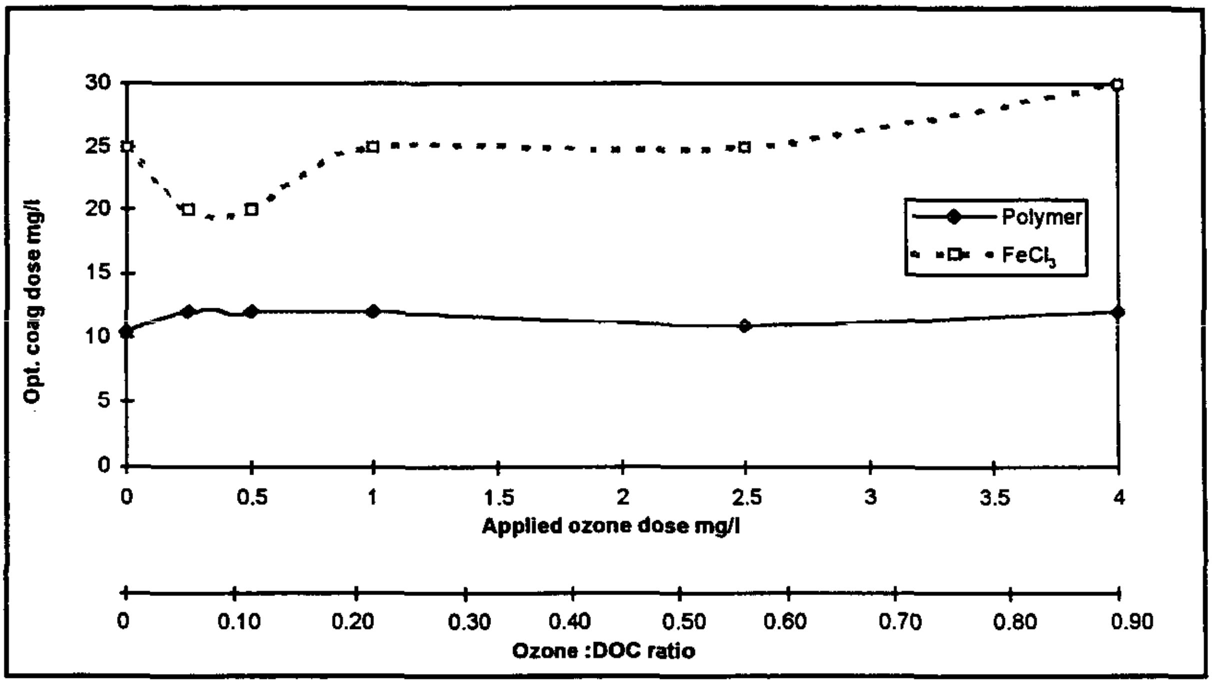


Figure 4.13 Effect of ozone on the coagulant demand of a eutrophic water (Inanda Dam water containing 10 000 *Microcystis* cells/mℓ).

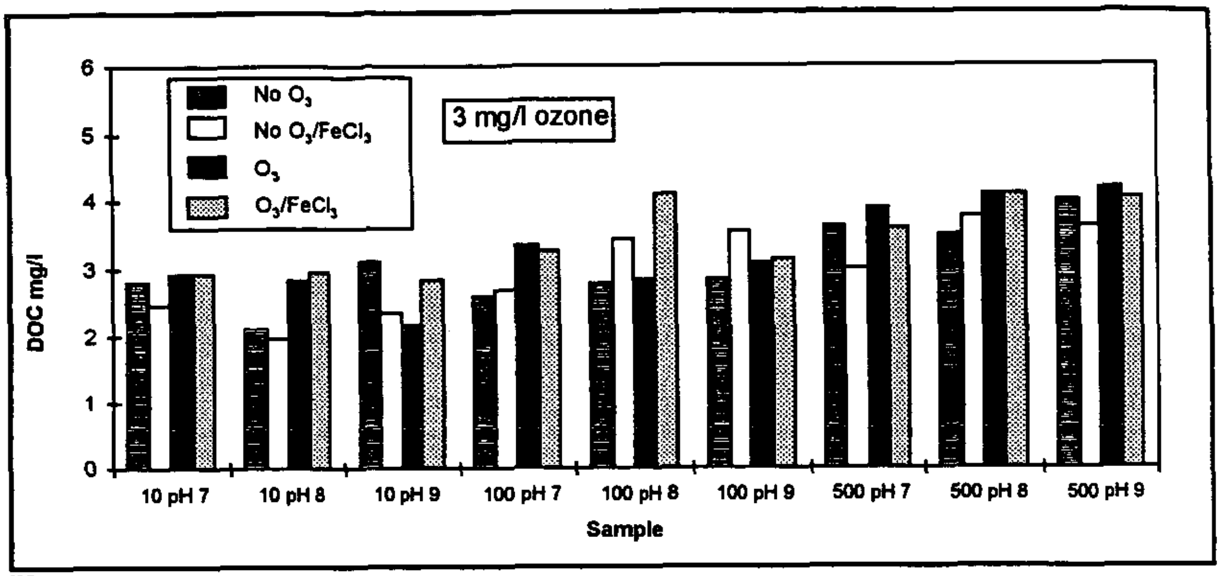
Another interesting observation was that a small decrease in the ferric chloride optimum dose sometimes occurred at applied ozone to DOC ratios of between 0,01 and 0,15 (i.e. 0,25 and 1,0 mg/ℓ applied ozone) **Figure 4.13**. This trend is obviously a function of the NOM in the water and mirrors the reduction observed in THMFP, TOC, DOC and UV absorbance. Farvadin and Collins (1989) reported a decrease in coagulant demand at ozone concentrations of between 0,1 and 0,3 mg/ℓ, while in this study it occurred at higher ozone doses, although the ozone concentration at which a decrease in coagulant demand is observed appears to be related to the ozone demand of the water. A decrease in coagulant demand at low applied ozone doses was only observed for the inorganic coagulant (ferric chloride) and not for the blended polymeric coagulant.

4.3.3. Impact of Algal Type and Concentration on Ozonation Effects

Samples of water were spiked with different concentrations of algal cells as described in **Section 4.2.5**. Samples of the spiked water were treated by different process combinations of ozone and polymeric or inorganic coagulants, and measurements of THMFP, DOC, algal cell concentration and optimum coagulant demand were compared. The effect of ozone on the THMFP or DOC of the water was unaffected by the algal cell type or concentration and the pH of the water had no obvious impact on the effect of ozonation on the DOC of the water. A small increase in the THMFP was sometimes observed after ozonation of algal-laden waters and DOC was generally found to increase slightly with increasing algal cell concentration **Figure 4.14**. There also tended to be a slight increase in DOC after ozonation and DOC removal due to ferric chloride coagulation generally deteriorated after ozonation. As discussed in **section 4.3.1.2** DOC removal by coagulation is dependent on the type of NOM and the ozone dose.

THM concentrations have been strongly correlated to DOC content, but a recent study by Peterson and co-workers (1993) suggests that the average THM yield per mg DOC is approximately 11 µg. The DOC did not generally increase by more than 1 mg/ℓ when the algal cell concentration was raised from *10 000* cells/mℓ to *500 000* cells/mℓ and so according to Peterson *et al* (1993) this would constitute a THM increase of less than 11 µg/ℓ. The THM concentrations in this study were generally between 200 and 600 µg/ℓ, so an increase of 11 µg/ℓ equates to an increase in THM concentration of not more than 6%, which would be too low for the detection of any definite trends. These results would appear to be in conflict with those of van Steenderen *et al* (1988) who reported that *Microcystis aeruginosa*, the species used in this study, gave rise to significant total organic halogen precursors on lysis, but this does not necessarily mean that these precursors were THM precursors.

The geosmin concentration of the water containing predominantly *Microcystis* sp. cells was in many cases below the detection limit of the analytical method. However, geosmin was usually detected in water containing predominantly *Anabaena* sp. cells, indicating that when *Anabaena* is the predominant species, more severe taste and odour problems can be anticipated. *Microcystis aeruginosa* has been found to be the predominant species in the majority of taste and odour incidents that have occurred in South Africa, although it has been pointed out that only circumstantial evidence exists to suggest that it can produce geosmin (Wnorowski & Scott, 1992). On the other hand there is scientific evidence to prove that *Anabaena circinalis*, the species of *Anabaena* that generally gives rise to taste and odour problems in the Umgeni Water operational area, produces geosmin (Bowner *et al*, 1992). Umgeni Water experience has shown that the presence of *Anabaena circinalis* in significant concentrations generally gives rise to geosmin problems, whereas the presence of *Microcystis aeruginosa* in comparable numbers does not always result in a taste and odour problem.



Where:

10 pH 7 = 10 000 cells/mℓ at pH 7
10 pH8 = 10 000 cells/mℓ at pH 8
10 pH 9 = 10 000 cells/mℓ at pH 9
100 pH 7 = 100 000 cells/mℓ at pH 7
100 pH 8 = 100 000 cells/mℓ at pH 8
100 pH 9 = 100 000 cells/mℓ at pH 9
500 pH 7 = 500 000 cells/mℓ at pH 7
500 pH 8 = 500 000 cells/mℓ at pH 8
500 pH 9 = 500 000 cells/mℓ at pH 9

Figure 4.14 Impact of algal cell concentration (*Microcystis*) and pH on the effect which ozone has on the DOC of eutrophic water.

An increase in ozone dosage was generally found to increase the coagulant demand Section **4.3.2**, although for water containing predominantly *Microcystis* cells, it was possible at certain ozone concentrations to obtain a reduction in coagulant demand, which is a trend that had not previously been observed (Freese *et al*, 1996). The coagulant demand of water containing predominantly *Anabaena* cells was always found to increase after ozonation, the increase in demand indicating an almost straight line correlation with ozone concentration **Figure 4.15**.

The algal cell concentration was also found to influence the coagulant demand, the combined effect of algal cell concentration and ozone often resulting in significant increases in the coagulant demand when the algal cells consisted predominantly of *Microcystis* sp. Prior to ozonation, the coagulant demand of water containing predominantly *Microcystis* sp. cells was found to increase with increasing cell concentration, but the increase was always less than 200% and generally much lower. However, after ozonation at an applied dose of 3 mg/ℓ the increase in coagulant demand with algal cell concentration was significantly greater (up to 650% depending on algal cell concentration and pH).

In contrast, ozonation of water containing predominantly *Anabaena* sp. resulted in much smaller increases in coagulant demand (generally below 50%), although prior to ozonation the presence of *Anabaena* sp. resulted in a much higher coagulant demand than for the case of *Microcystis* sp. **Figure 4.16**.

Ozonation of *Microcystis* sp. generally had a significant effect on the coagulant demand, although as mentioned above, this was dependent on the ozone concentration. At ozone concentrations which resulted in an increased coagulant demand, the demand increased almost exponentially with increasing cell concentration when *Microcystis* sp. predominated **Figure 4.16**.

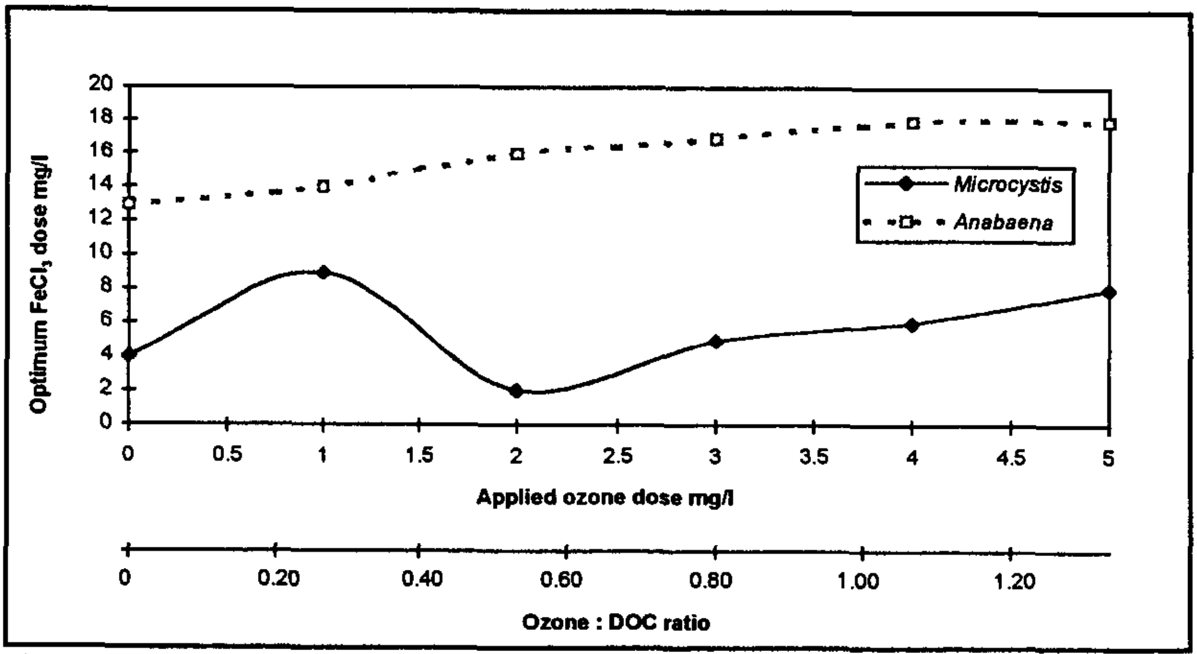


Figure 4.15 Impact of algal species on the effect of ozone on the optimum ferric chloride coagulant demand of eutrophic waters (Inanda Dam water containing either *Microcystis* sp. or *Anabaena* sp. cells at 100 000 cells/mℓ).

Ozonation of *Anabaena* sp. also resulted in increases in coagulant demand, but the effect of ozonation was much smaller than with *Microcystis* sp. As a result, the coagulant dose for an unozonated water containing predominantly *Microcystis* sp. was always lower than that for a water containing predominantly *Anabaena* sp. at similar cell concentrations. After ozonation however, the coagulant demands for water containing predominantly *Microcystis* sp. or *Anabaena* sp. at comparative cell concentrations were much closer in value, especially at the greater cell concentrations **Figure 4.16**. Despite this, the coagulant demand still tended to be lower when *Microcystis* was the dominant species.

The interesting differences observed between the two cyanobacterial species regarding the effect of ozone on the coagulant demand, suggest that *Microcystis* sp. are more susceptible to lysis by ozonation. This would explain why ozone had a greater effect on the coagulant demand when this cyanobacterial type was dominant. However, when *Anabaena* sp. predominated, the coagulant demand was always higher than for the same water containing comparable concentrations of *Microcystis* sp. implying that *Anabaena* sp. are less amenable to removal by coagulation. The results of this study always showed an increase in coagulant demand with ozonation when *Anabaena* sp. predominated, but an improvement in coagulation was possible at certain ozone concentrations when *Microcystis* sp. were dominant **Section 4.3.2.**

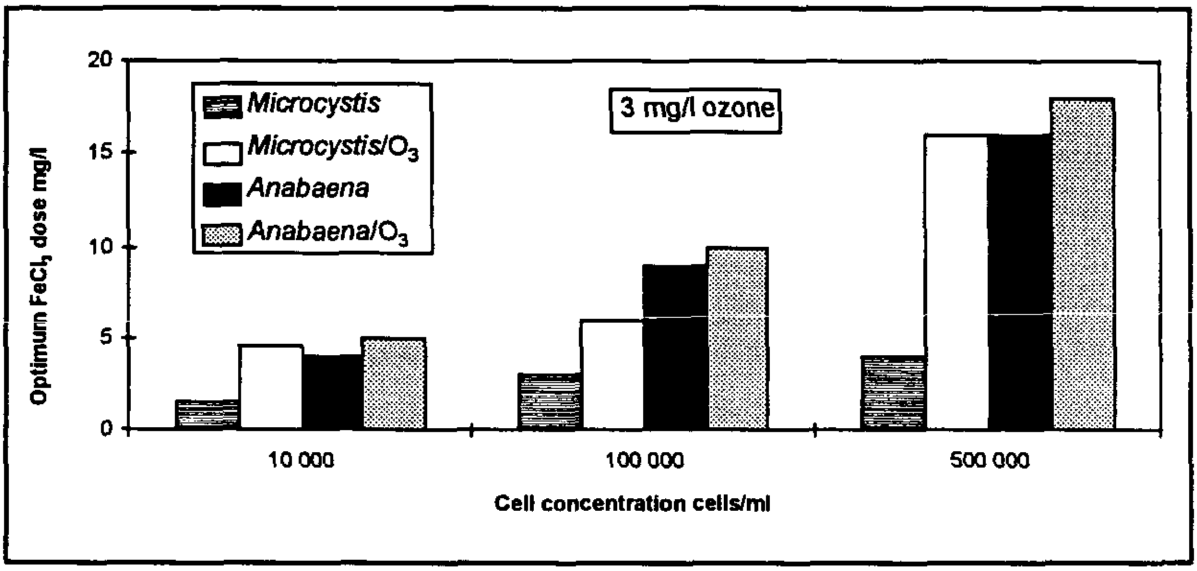


Figure 4.16 **Impact of algal cell concentration and algal species on the effect of ozone on the optimum ferric chloride coagulant demand of eutrophic water.**

The pH was also found to affect the coagulant demand. Where *Anabaena* sp. were dominant, the coagulant demand was found to increase with increasing pH, this effect being particularly noticeable at higher cell concentrations and occurring both before and after ozonation. When *Microcystis* sp were dominant, pH also affected the coagulant demand, but the effect was different before and after ozonation. Prior to ozonation decreases in coagulant demand of between 25 and 70% occurred at a pH of 9 compared to those at pH 7, but after ozonation the coagulant demand was always found to increase at higher pH **Figure 4.17**.

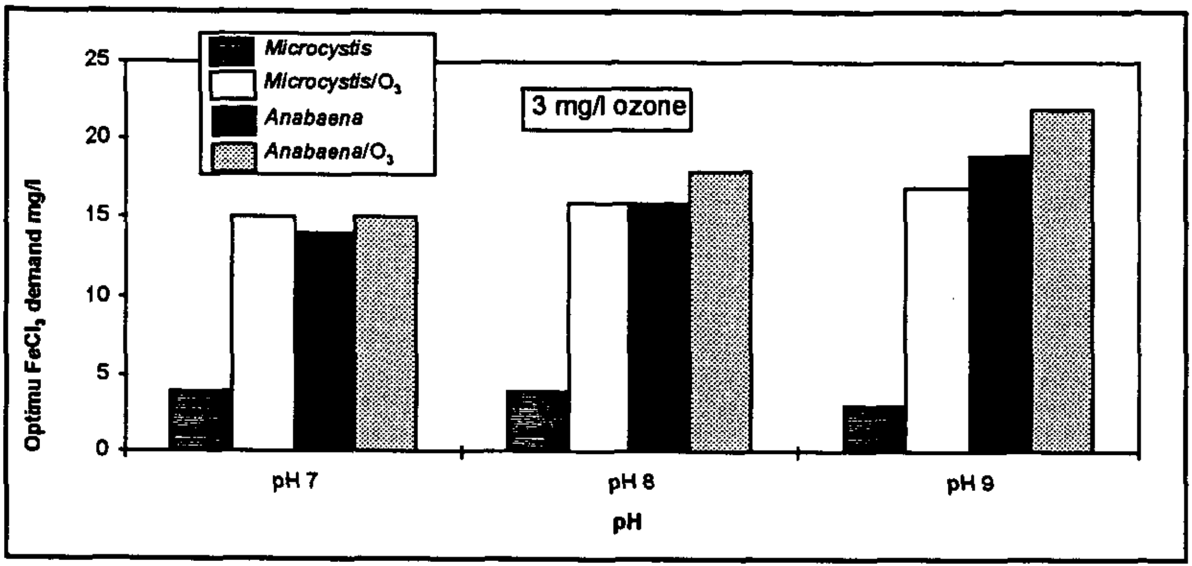


Figure 4.17 **Impact of algal species and pH on the effect of ozone on the optimum ferric chloride coagulant demand of eutrophic water (500 000 cells/mℓ).**

The turbidity of the water was not affected by ozonation, but if the ozonated water was filtered (through Whatman No. 1 equivalent paper) it was found that the amount of finely dispersed matter which passed through the filter generally increased after ozonation. Larger increases in matter passing through the filter were obtained when the water contained predominantly *Microcystis* sp., again implying that *Microcystis* sp. cells are more susceptible to disintegration by ozone than *Anabaena* sp.

The algal cell count determinations were not always found to correlate well with the expected concentrations, but this is not surprising considering that the algal scums used were often very thick and obtaining completely homogenised samples without destroying the cell integrity was difficult. In spite of this, the results indicated good removal of *Microcystis* sp. cells with ozone, removal increasing at higher ozone concentrations. It was possible to obtain removals of as much as 75% at ozone to DOC ratios of between 0,3 to 0,5 (i.e. approximately 2 mg/ℓ applied ozone) and removal was almost complete (>99%) at ozone concentrations of around 1 mg O_3/mg DOC and above (i.e. around 5 mg/ℓ applied ozone). This was in contrast to water containing predominantly *Anabaena* sp. where algal cell removals were never higher than 70%, even at ozone concentrations of up to 5 mg/ℓ and were generally below 40% **Figure 4.18**. Coagulation with ferric chloride, followed by flocculation, settling and filtration was always found to reduce the cell concentration of both *Microcystis* sp. and *Anabaena* sp. with even greater removals occurring when the water was ozonated prior to ferric chloride treatment.

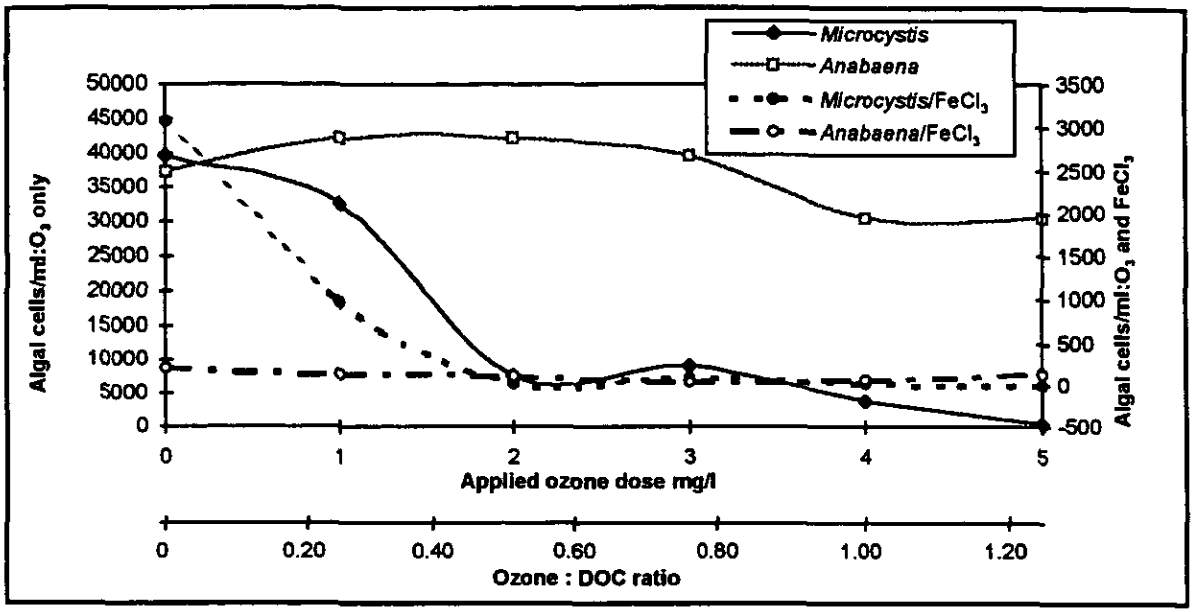


Figure 4.18 **Effect of ozone and conventional treatment using ferric chloride on algal cell concentrations.**

4.3.4. Effect of Hardness on Ozone Efficiency

The hardness of the water was artificially increased to approximately 250 mg/ℓ as CaCO3 using three different methods as described in Section 4.2.4.

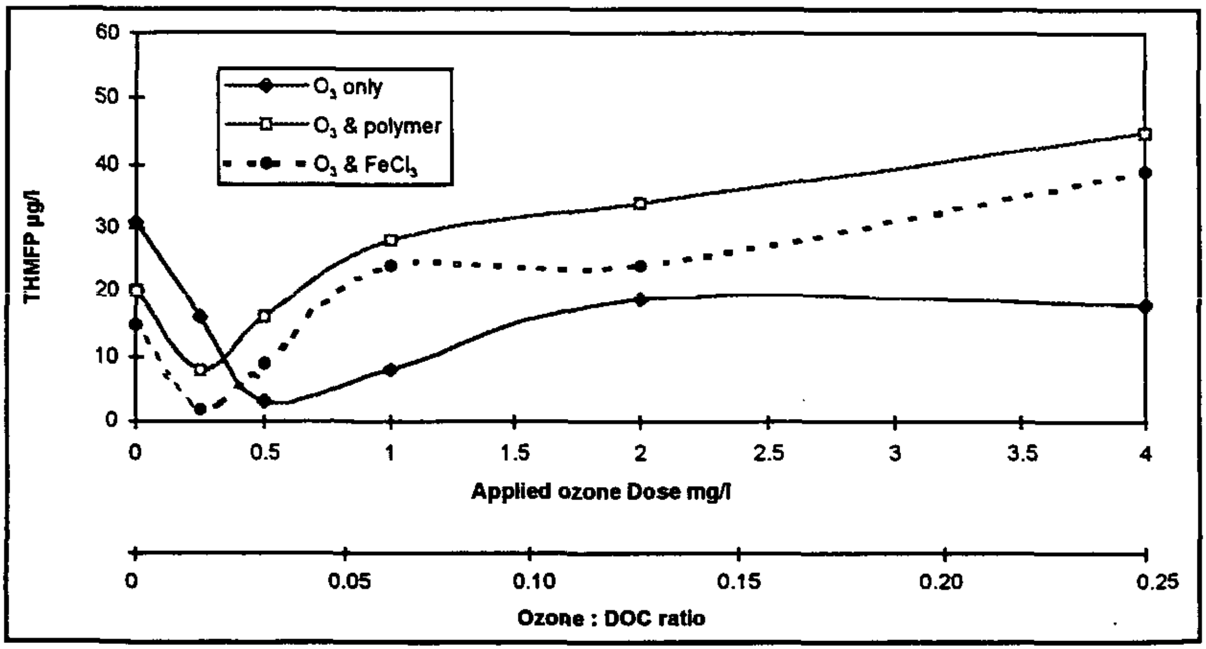


Figure 4.19 **Effect of ozone on the THMFP of a naturally hard water (Klip River water, hardness 315 mg/ℓ $CaCO_3$).**

In all cases, the effect of hardness was not found to impact in any significant way on the THMFP. An increase in THMFP with increasing applied ozone dose was often observed, as was the case in soft waters (total hardness of around 80 mg/ℓ $CaCO_3$) but this was generally small. The small decrease in THMFP at low ozone concentrations (applied ozone doses of 0,01 and 0,15 mg O_3/mg DOC or 0,25 to 1 mg/ℓ applied ozone) was also sometimes observed for hard waters **Figure 4.19**. Hardness was not found to have any noticeable impact on the effect of ozonation on the TOC and DOC of any of the waters investigated.

Hardness was however found to impact on the effect of ozone on the BDOC concentration of the water. In soft waters the BDOC was generally found to increase with increasing applied ozone concentration, but in the naturally hard waters, the BDOC was actually found to decrease with increasing ozone dose **Figure 4.20**. The decrease in BDOC observed for the naturally hard waters may be explained by the fact that the organic compounds formed under these conditions may be less biodegradable or alternatively may actually inhibit the growth of the bacteria during the BDOC test.

Artificially increasing the hardness of the water usually resulted in an increase in the UV absorbance, but it is suspected that this is as a result of the increased salt concentration. The trends in the UV absorbance with ozonation in the artificially hardened waters were found to be very similar to those for the same waters at ambient hardness, regardless of the method used to adjust the hardness, with between 30 and 60% removal in UV occurring at ozone concentrations of 0,5 mg O_3/mg DOC and higher. The DOC concentrations of the naturally hard water samples were fairly high (approximately 15 mg/ℓ and 10 mg/ℓ for the Klip River and Suikerbos Rand samples respectively) and therefore the ozone to DOC ratios used were never higher than 0,4. In spite of this it was still possible to achieve as much as 30% reduction in the UV absorbance at an applied ozone dose of 0,25 mg O_3/mg DOC.

The most interesting observation for these naturally hard water samples in terms of the UV absorbance was that treatment of the water with either a blended inorganic-organic polymeric coagulant or ferric chloride, did not further reduce the UV absorbance, as was the case for the soft and artificially hardened waters. In fact, the UV reduction was often worse after ozonation and conventional treatment than after ozonation alone, implying that the organics are less amenable to removal by coagulation after ozonation. This may be an indication that ozone has reacted differently with the NOM (direct oxidation reaction, rather than the radical reaction) due to the scavenging effect of the bicarbonate ions present in the water. However, it must be remembered that the NOM composition of these naturally hard waters may be quite different from that of the soft waters which were investigated and this may account for these differences.

No obvious trend linking the hardness of the water to the effect of ozone on the concentration of geosmin, 2-MIB and atrazine was evident. It was observed during investigation of soft waters that applied ozone concentrations of between 0,1 and 0,3 mg O_3/mg DOC were required before a significant decrease in these micro-pollutants occurred. The same range of ozone concentrations was also necessary to bring about significant reductions in the harder waters (250 to 385 mg/ℓ $CaCO_3$), with removals in the region of 70% and higher being possible at applied ozone concentrations of 0,5 to 1 mg O_3/mg DOC. This is similar to the reductions in micro-pollutants obtained after ozonation of soft waters.

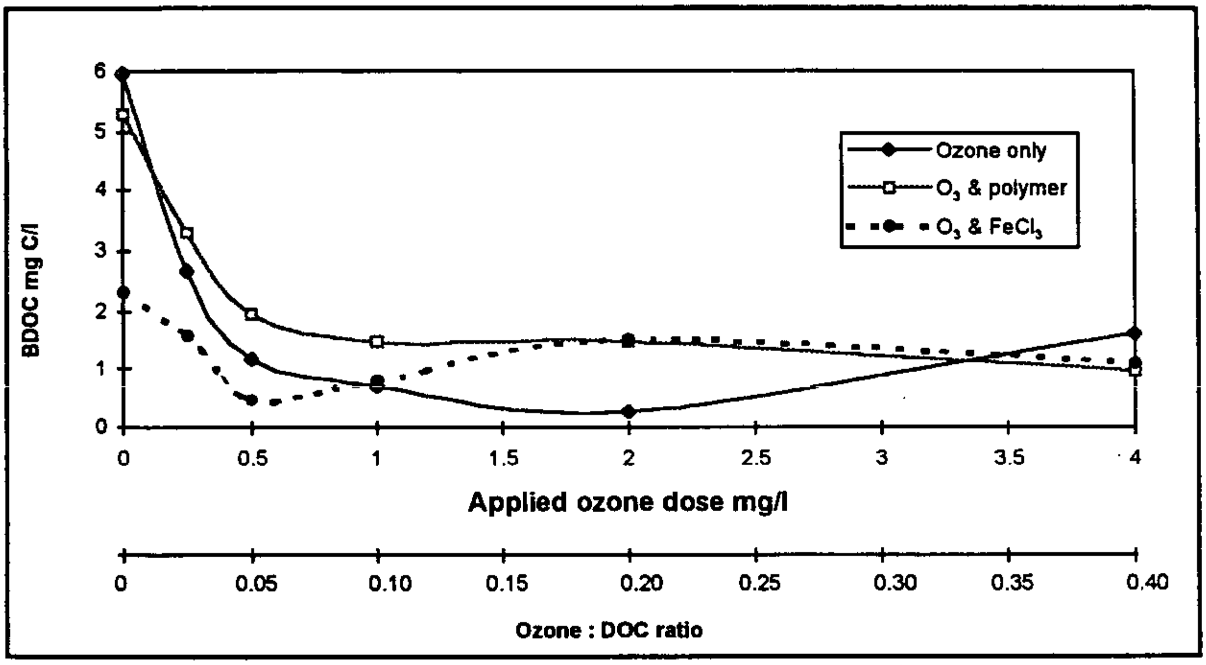


Figure 4.20 **Effect of ozone on the BDOC of a naturally hard water (Suikerbos Rand River, hardness 385 mg/ℓ $CaCO_3$).**

The coagulant demand of the water for which the hardness had been artificially increased was always found to be lower than that for the water at ambient hardness **Figure 4.21**. The lower coagulant demand is probably a function of the coagulant aid effects of the calcium and magnesium salts which were added to increase the hardness.

There are many arguments regarding the effect of hardness on the role of ozone in coagulation, although there is not a great deal of experimental evidence to suggest which conditions are best. Saunier and co-workers (1983) reported that as the raw water pH increased, conditions suitable for rapid ozone decomposition were produced (i.e. high pH and low bicarbonate alkalinity) and the coagulation effects of ozone improved. This may explain the reduction in coagulant demand at higher hardness concentrations observed in these studies, although it is possible that this effect is due to the increase in calcium ion concentration. Hundt and O'Melia (1988) have shown that calcium ions exert a destabilising effect on natural colloidal particles, thereby enhancing removal of fulvic acid.

Increasing the hardness had no apparent impact on the effect of ozone on the algal cell concentration or the colour of the water.

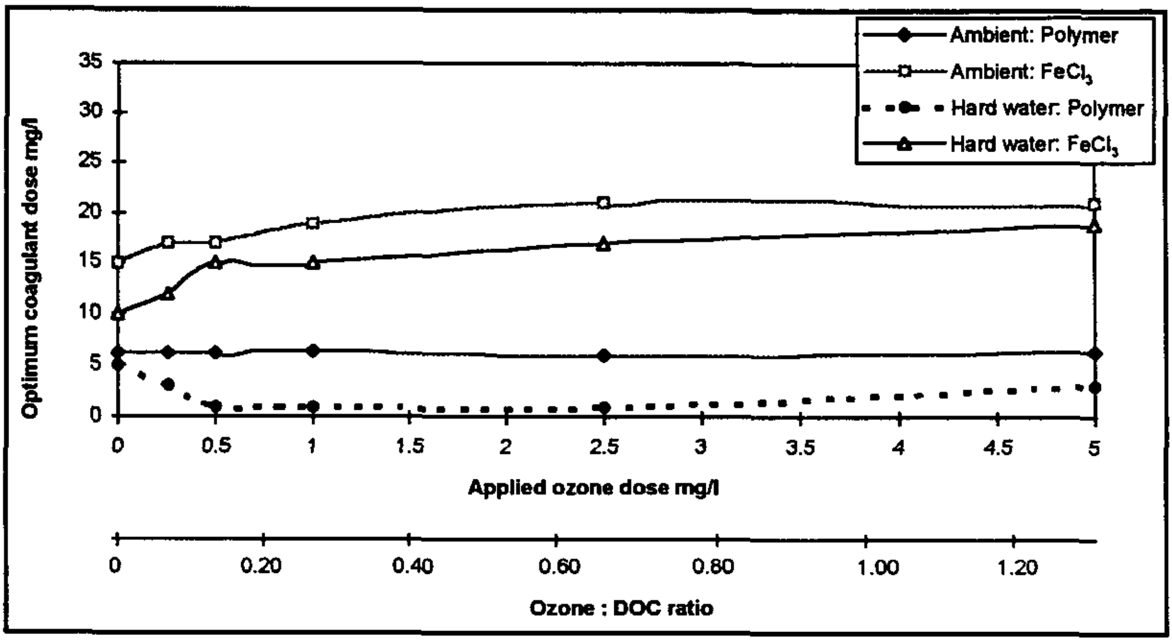


Figure 4.21 Impact of hardness on the optimum coagulant dose before and after ozonation.

4.3.5. Comparison of Ozone and Peroxone Effectiveness

In contrast to bicarbonate ions which inhibit formation of hydroxyl radicals during ozonation, hydrogen peroxide and UV radiation encourage the formation of these radicals. Processes employing ozone in conjunction with hydrogen peroxide, UV radiation or any other factor which enhances the free radical formation are known as advanced oxidation techniques. In this study advanced oxidation using ozone and hydrogen peroxide, also termed peroxone, was compared to ozonation alone in order to determine the added benefits of advanced oxidation.

Hydrogen peroxide [I] is a weak acid and when combined with water, it partially dissociates into the hydroperoxide ion [III] according to the following equation:

$$H_2O_2 \text{ [I]} + H_2O = HO_2^- \text{ [III]} + H_3O^+$$

The hydrogen peroxide molecule reacts slowly with ozone, while the hydroperoxide anion is highly reactive. The rate of decomposition of ozone by hydrogen peroxide was shown to increase as the pH rose (Langlais *et al*, 1991). However, the effect of pH on peroxone was not investigated in this study and was maintained at approximately 8.

Peroxone tests were only carried out on treated filtered waters, since advanced oxidation is more commonly used at an intermediate treatment stage. Both water low in organic content as well as an industrially polluted water were treated conventionally using coagulation, flocculation, settling and filtration prior to peroxone treatment. The tests were performed at constant ozone concentrations and varying hydrogen peroxide concentrations as well as at a constant peroxide to ozone ratio whilst varying ozone concentrations. In this way it was possible to establish the optimum peroxide to ozone ratio for treatment and the optimum ozone concentration.

The addition of hydrogen peroxide with ozone was not found to have any significant effect on the THMFP of the water, provided the peroxide to ozone ratio did not exceed 0,5. When applying ozone at varying concentrations but keeping a constant peroxide to ozone ratio of 0,5, no obvious effect on the THMFP was evident. However, when maintaining a constant applied ozone dose of 1,5 mg/ℓ and using peroxide to ozone ratios varying between 0,3 and 5, the THMFP was found to remain fairly constant up to a ratio of 0,5, but decreased at higher ratios until at a ratio of 2,5 the THMFP was zero **Figure 4.22.**

Chlorine demand tests were carried out on the peroxone treated water in an attempt to confirm the disappearance of the THMFP. These tests indicated a very significant increase in the chlorine demand as the H_2O_2:O_3 ratio increased and at the highest ratio of 5, the chlorine demand was found to be in excess of 10 mg/ℓ, although the chlorine demand of the water prior to treatment was always low (generally not more than 1 mg/ℓ). It seems unlikely that with a fairly low total organic carbon (TOC) concentration of generally between 3 and 5 mg/ℓ that such high chlorine demands are feasible and interference in the measurement of the chlorine due to peroxide ion or peroxone reaction products may explain this effect. No explanation for the decrease in THMFP with increasing H_2O_2:O_3 has been found. It is possible that chlorination of the peroxonated water could give rise to disinfection by-products (DBP) other than THMs, such as haloacetic acids (HAA), but as our Analytical Laboratories have not yet been able to analyse for HAA, confirmation of this theory has not yet been obtained.

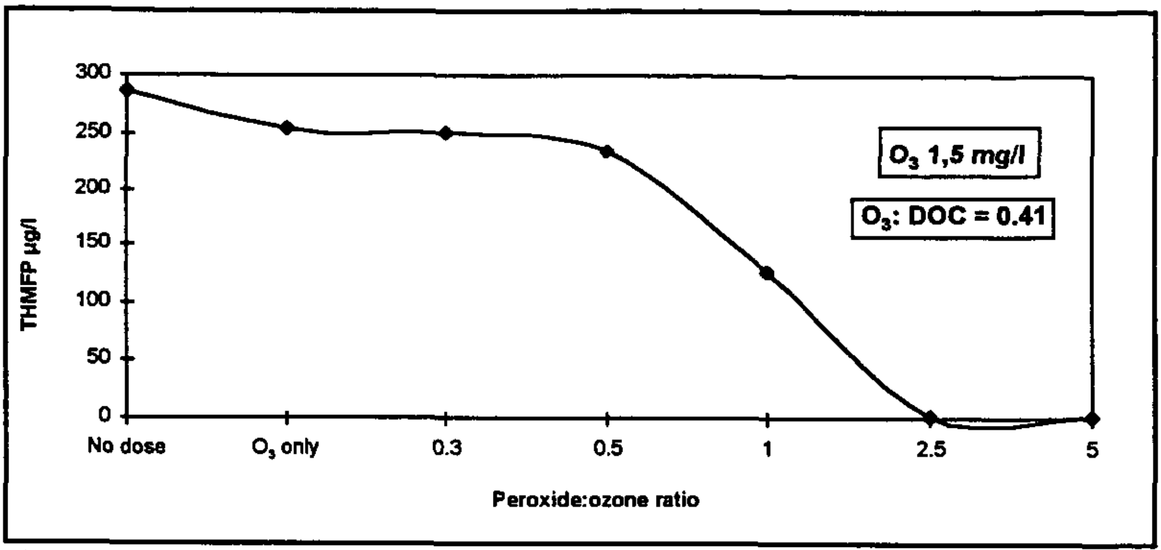


Figure 4.22 Effect of peroxone on the THMFP of a final filtered water using a constant ozone dose (1,5 mg/ℓ) and varying peroxide to ozone ratios.

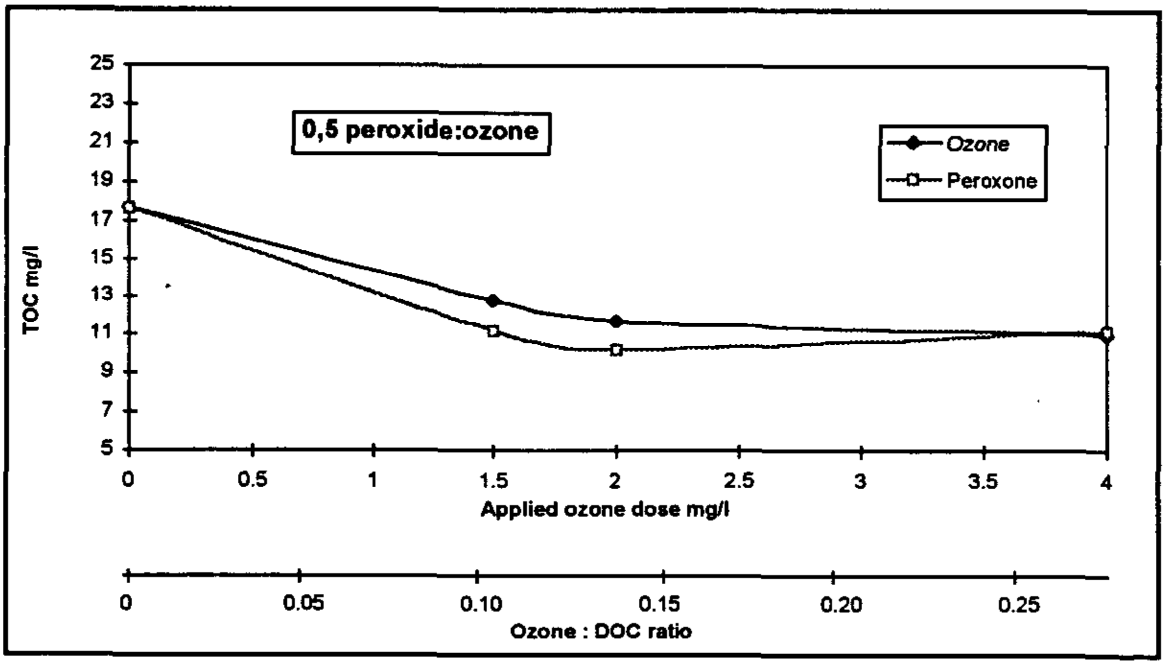


Figure 4.23 Effect of ozone and peroxone on the TOC of a final treated water from an industrially polluted source.

Ozone was not generally found to have a large effect on the TOC and DOC concentrations in waters where these were fairly low (3 to 5 mg/ℓ), although in waters with higher TOC and DOC, decreases of up 25% were obtained. Therefore it is not surprising that peroxone was not found to impact noticeably on the TOC and DOC of waters low in NOM, but in industrially polluted waters, peroxone resulted in a similar reduction in TOC (up to 25%), but this was obtained at a lower applied ozone dose **Figure 4.23**.

No significant differences were observed between the effect of advanced oxidation on the BDOC and that of ozone alone. However, when using varying peroxide concentrations together with a constant applied ozone dose of 1,5 mg/ℓ, the BDOC was found to increase with increasing peroxide concentration up to a H_2O_2:O_3 ratio of between 0,5 and 1,0. The BDOC stabilised at higher ratios **Figure 4.24**, indicating that peroxide concentrations higher than 0,5 to 1,0 mg peroxide/mg O_3 are ineffective in promoting further hydroxyl radical formation.

The impact of peroxide on the effect of ozone on the UV absorbance and micro-pollutants was similar to that for TOC and DOC. Peroxone did not bring about greater reductions in the UV absorbance and geosmin, 2-MIB and atrazine concentrations than were achievable using ozone alone, but the maximum decrease was possible at a lower ozone concentration when using peroxone **Figure 4.25**.

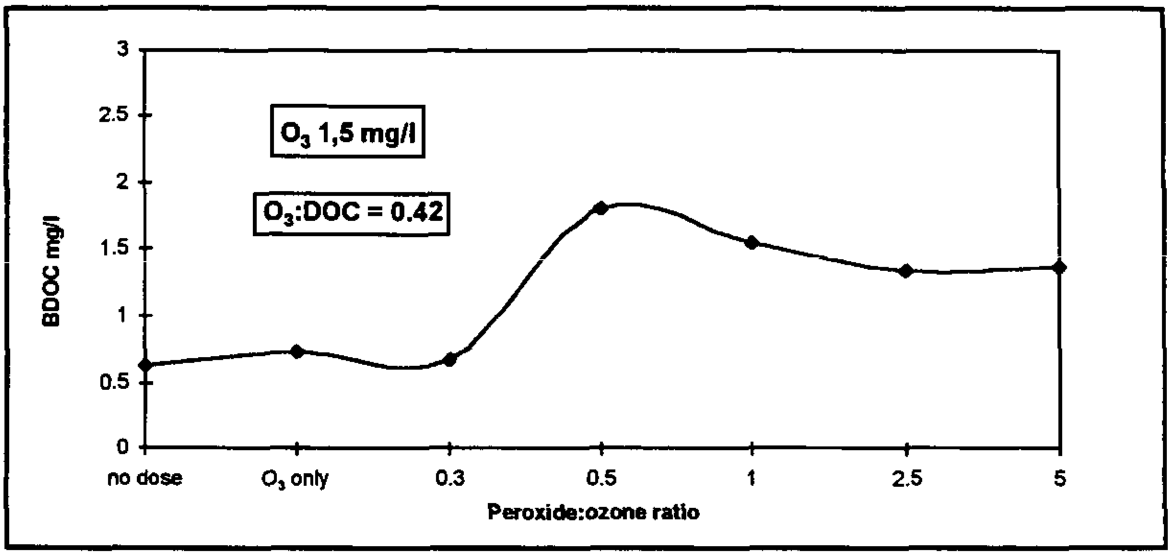


Figure 4.24 Effect of peroxide to ozone ratio on the BDOC.

When ozonating water at a constant applied ozone dose of 1,5 mg/ℓ and using varying peroxide concentrations it was found that increasing the peroxide to ozone ratio above 0,3 did not result in any significant changes in the UV absorbance or concentration of micro-pollutants **Figure 4.26**. It is interesting to note that this is the stoichiometric ratio for the reaction of ozone and peroxide, which probably explains why peroxide in excess of this was ineffectual in reducing these parameters further.

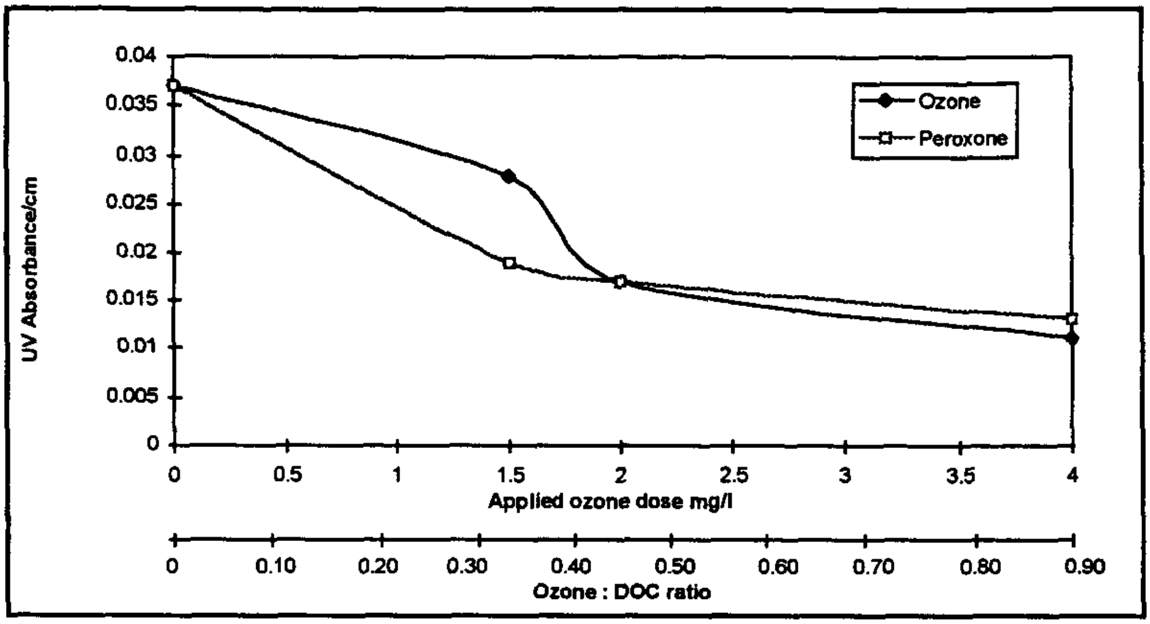


Figure 4.25 **Effect of ozone and peroxone on the UV absorbance.**

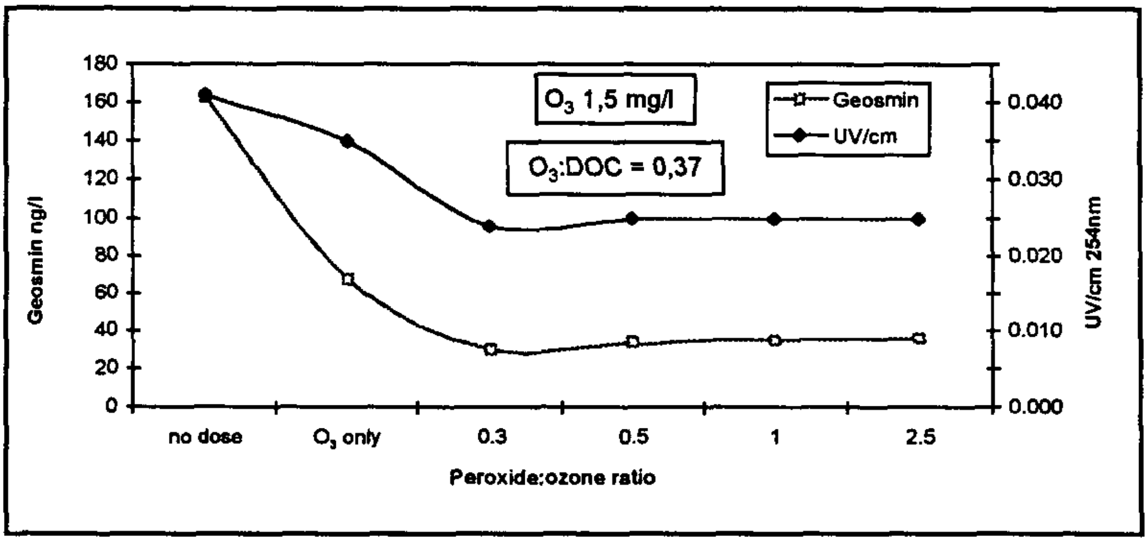


Figure 4.26 **Effect of the peroxide to ozone ratio on the geosmin concentration and UV absorbance at 254 nm.**

It was often difficult to compare the effect of peroxone and ozone on colour removal, as the colour of the treated final water used for the peroxone tests was usually very low (less than 5° Hazen). In those cases where the effect on the colour could be observed, the addition of peroxide to ozone was found to affect the colour in much the same way as it affected the other NOM parameters; maximal colour removal could be achieved at a lower ozone dose when adding peroxide, but the reduction itself was no greater than that obtained using ozone alone. It was not possible to determine the effect of the peroxide to ozone ratio on colour removal, mainly because conventional treatment followed by 1,5 mg/ℓ ozone generally reduced the colour to below the detection limits of the analytical procedure. No trends relating peroxide to the effect of ozone on algal cell concentration, iron or manganese emerged.

4.4. Summary of Conclusions

A number of conclusions can be drawn from the laboratory test results. In summary these are:

- Ozone was not generally found to affect the THMFP, TOC and DOC greatly, although decreases in the TOC and DOC of up to 25% were possible. The effect of ozone on these parameters is dependent on the nature and concentration of the NOM.
- Ozone increases BDOC and brings about reductions in UV absorbance and micro-pollutants (geosmin, 2-MIB and atrazine). Applied ozone doses of between 0,5 and 1,5 mg O_3/mg DOC can reduce UV absorbance by up to 70% and micro-pollutant concentrations by over 70%.
- Ozone is good for colour removal. Ozone concentrations of 0,1 to 0,4 mg O_3/mg DOC can result in 40 to 60% removal of colour, and this can be increased to over 90% if conventional treatment is used after ozonation.
- The effect of ozone on the optimum coagulant dose is dependent on the type of coagulant, the water source and, for eutrophic waters, on the cyanobacterial species and concentration.
- An applied ozone concentration of between 0,1 and 0,3 mg O_3/ mg DOC is usually required before significant decreases/increases in NOM surrogate parameters and micro-pollutants are obtained. Ozone doses higher than this do not generally result in much additional change in these parameters.
- A small decrease in THMFP, TOC, DOC, UV and optimum inorganic coagulant demand was often observed at ozone concentrations of between 0,01 and 0,3 mg O_3/mg DOC.
- High hardness concentrations were not found to significantly impact on the effect of ozone on most NOM surrogate parameters and micro-pollutants, except for the BDOC, which generally decreased, rather than increased, after ozonation.
- Enhanced coagulation was effective for the removal of THMFP (up to 40% reductions), TOC and DOC (up to 60% reductions), and BDOC (70 to 90% reductions), but was not effective in reducing micro-pollutants. The only benefit in pre-ozonation prior to enhanced coagulation is in the removal of micro-pollutants.
- Peroxide used in conjunction with ozone generally results in the same effect as that achieved with ozone alone, but this occurs at a lower ozone dose.
- Peroxide to ozone ratios in excess of 0,3 do not increase the benefit derived from ozone alone.
- Advanced treatment processes become more economically attractive on large works when treating relatively polluted waters.

5. Pilot Scale Investigation - GAC

5.1. Introduction

Powdered activated carbon is commonly used in Southern Africa for the treatment of eutrophic water where problems related to the occurrence of taste and odours in the drinking water have been experienced. Increased recycle of wastewater effluents to the rivers in South Africa, as well as diffuse pollution from informal settlements along the river banks and agricultural runoff, is likely to result in increased levels of nutrients and pollutants in the raw water used for the production of drinking water.

It was predicted that due to increased levels of nutrients entering the Inanda Dam, (mainly from the discharge of wastewater works effluent into the Mzunduzi River in Pietermaritzburg), the dam would become highly eutrophic. The predicted deterioration in water quality, increased levels of algae, natural and synthetic organic compounds as well as taste and odour compounds, meant that excessive amounts of powdered activated carbon (PAC) would be required. The use of granular activated carbon (GAC) should therefore be considered as an economic alternative.

A pilot plant was designed to assess the benefits of using GAC in conjunction with ozone for water treatment. The use of ozone prior to GAC (**Section 2.2.4**) is reported to have significant benefit in reducing the need for frequent regeneration of the carbon, by promoting biologically activated carbon (BAC). The adsorption of organic contaminants onto activated carbon has been well documented. The laboratory determination of adsorption isotherms for single components to predict adsorption behavior is a useful technique, but should be used with caution when designing a GAC contacting system for treating a naturally occurring water where competitive adsorption reactions may significantly alter the performance of GAC in practice. A set of small columns were also constructed and operated for a period to determine the breakthrough characteristics of specific organic compounds.

5.2. Methods and Materials

A pilot plant was erected at the Umgeni Water Process Evaluation Facility at the Wiggins Waterworks and commissioning was completed by the end of September 1994. Raw water from the Inanda Dam was treated by coagulation and sand filtration. The filtered water was then treated directly using GAC or a process comprising a combination of ozonation and GAC. In a separate pilot plant filtered water was dosed with organic micro-pollutants, and passed through a series of GAC mini-columns where the adsorption and breakthrough of contaminants could be studied.

5.2.1. Water Treatment Pilot Plant

Initially the use of filtered water from the Wiggins Waterworks was considered as feed water to the GAC pilot plant, but as the works was being upgraded pre-chlorination of the water was necessary. A completely separate water treatment pilot plant, where the water could be treated without the use of pre-chlorination, was considered to be essential to ensure that biological activity on the carbon would not be affected by residual chlorine in the filtered water.

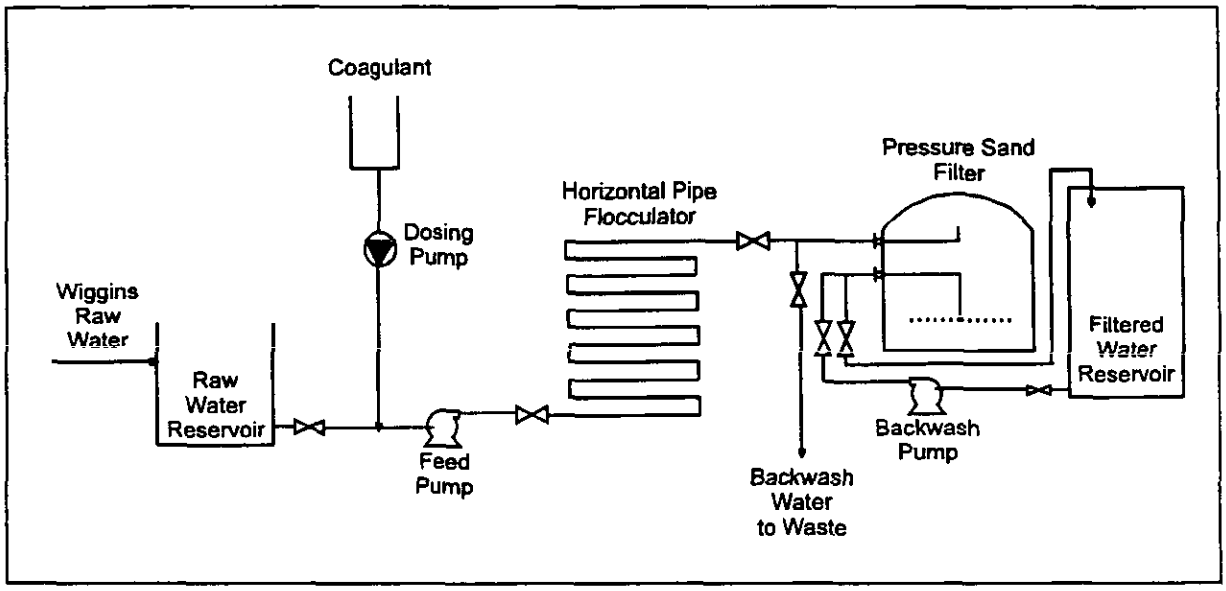


Figure 5.1 Flow Diagram of Water Treatment Pilot Plant

The water treatment pilot plant (**Figure 5.1**) comprises a feed pump and a facility for dosing chemical coagulant and organic contaminants. The water is flocculated in a pipe flocculator, and filtered through dual media filter (anthracite & sand). Filter backwashing is initiated by a differential pressure sensor across the filter. During periods of high turbidity the filter was found to operate poorly and more frequent backwashing was required. The differential pressure switch was replaced with a timer control system where backwashing was initiated more regularly to ensure the quality of the filtered water.

5.2.2. Ozonation Pilot Plant

A SORBIOS ozone generator Model GSF 025.2 (capable of producing 25 g/hr of ozone in oxygen) was operated continuously with oxygen supplied from a liquid oxygen container (**Figure 5.2**). The ozone was bubbled into the bottom of two contact columns resulting in a 12 to 14 minute contact time. The off gases from the columns were fed to a thermal destructor unit before being exhausted to atmosphere. A sample of the water after ozonation was analysed for residual ozone and other routine analyses.

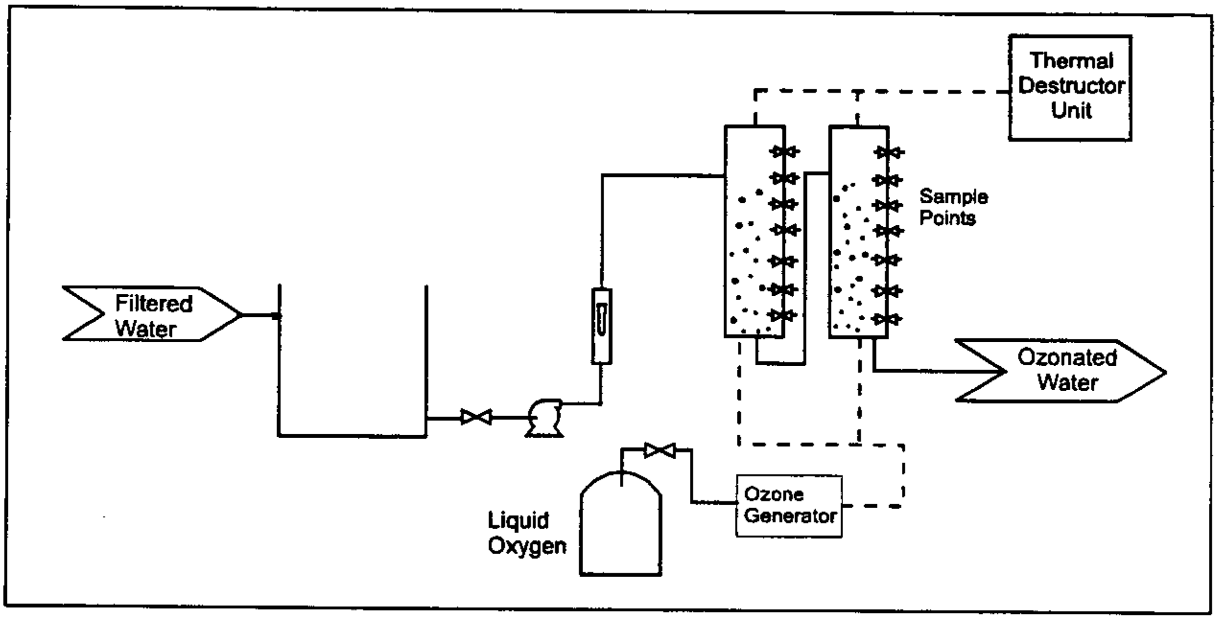


Figure 5.2 Flow Diagram of Ozonation Pilot Plant

Due to limitations in process equipment available to the project only one ozonation step was implemented in the pilot plant configuration. In the application of ozone as well as GAC, water would normally be ozonated twice before entering the GAC filters. Pre-ozonation would be expected to oxidise the algae, iron and manganese present in the water, and perform an initial disinfection of the water thereby improving the overall clarity of the water. The use of a single ozonation stage after filtration but prior to GAC treatment was considered to be a suitable option for comparison of the GAC processes.

5.2.3. GAC / BAC Pilot Plant

The GAC columns were operated continuously (7 days per week) as separate processes with different configurations. The initial pilot plant trials to assess the benefits of biologically activated carbon (BAC) compared two different types of carbon each with or without ozonation prior to the filtration of the water through GAC. The use of wood based carbon (PICA carbon) has been implemented successfully in Europe, and is considered to be beneficial in promoting biological activity in the carbon filters. Other coal based carbons are more specifically designed for the adsorption of organic contaminants and the specifications of iodine number, specific surface area, mean particle diameter, bulk density and ash content (**Table 5.1**) are typical specification parameters. A coal based carbon with typical water treatment grade specification was selected (WCM 106) for comparison with the PICA carbon.

Table 5.1 Properties of the coal and wood based carbon used in the pilot plant study

Description	Coal Based Carbon WCM 106	Wood Based Carbon PICA
Iodine Number (mg/g)	1000	900
Methylene Blue Number (mg/100g C)	37,65 *	46,03 *
Ash Content (%)	3,1 *	1,3 *
Specific Surface Area (m^2/g)	1100	1200
Mean Particle Diameter (mm)	0,9 - 1,1	0,85 - 1,1
Bulk Density - wet (g/l)	520	300

* measured in the laboratory

Figure 5.3 shows the surface of the two types of carbon. The tubular nature of the wood based PICA carbon is claimed to protect the biomass during backwashing, and limits the shearing effects of high water velocities across the surface of the carbon. It is reported by Bablon (1991) that this assists in maintaining a representative population of micro-biological species on the carbon, and promotes biological activity.

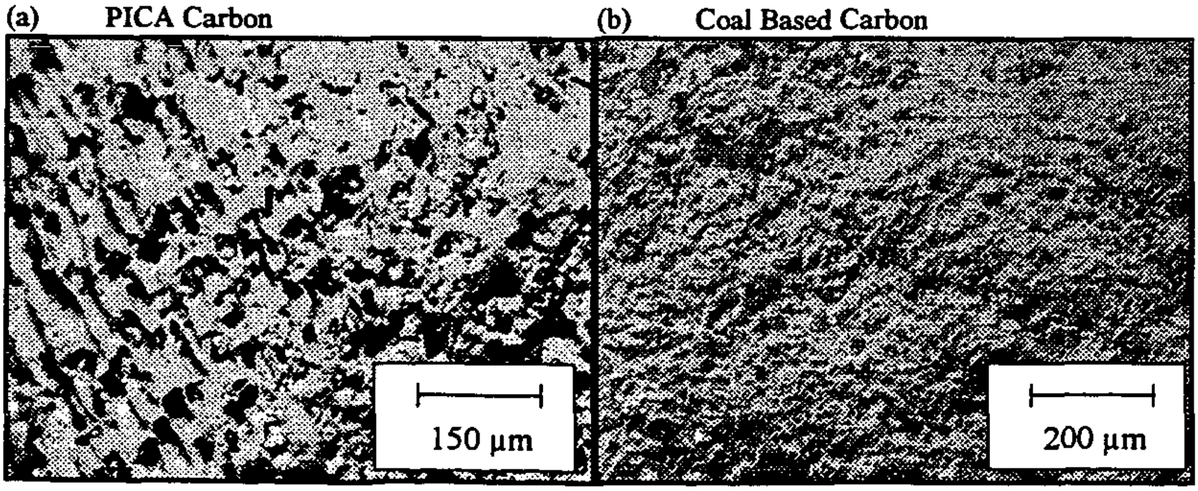


Figure 5.3 Scanning Electron Micrographs of the Surface of the GAC

Four GAC columns (**Figure 5.4**) were constructed and operated in parallel with the following comparative processes :

- Column 1 - Filtered water & Ozonation & PICA carbon
- Column 2 - Filtered water & Ozonation & Coal based carbon
- Column 3 - Filtered water & PICA carbon
- Column 4 - Filtered water & Coal based carbon

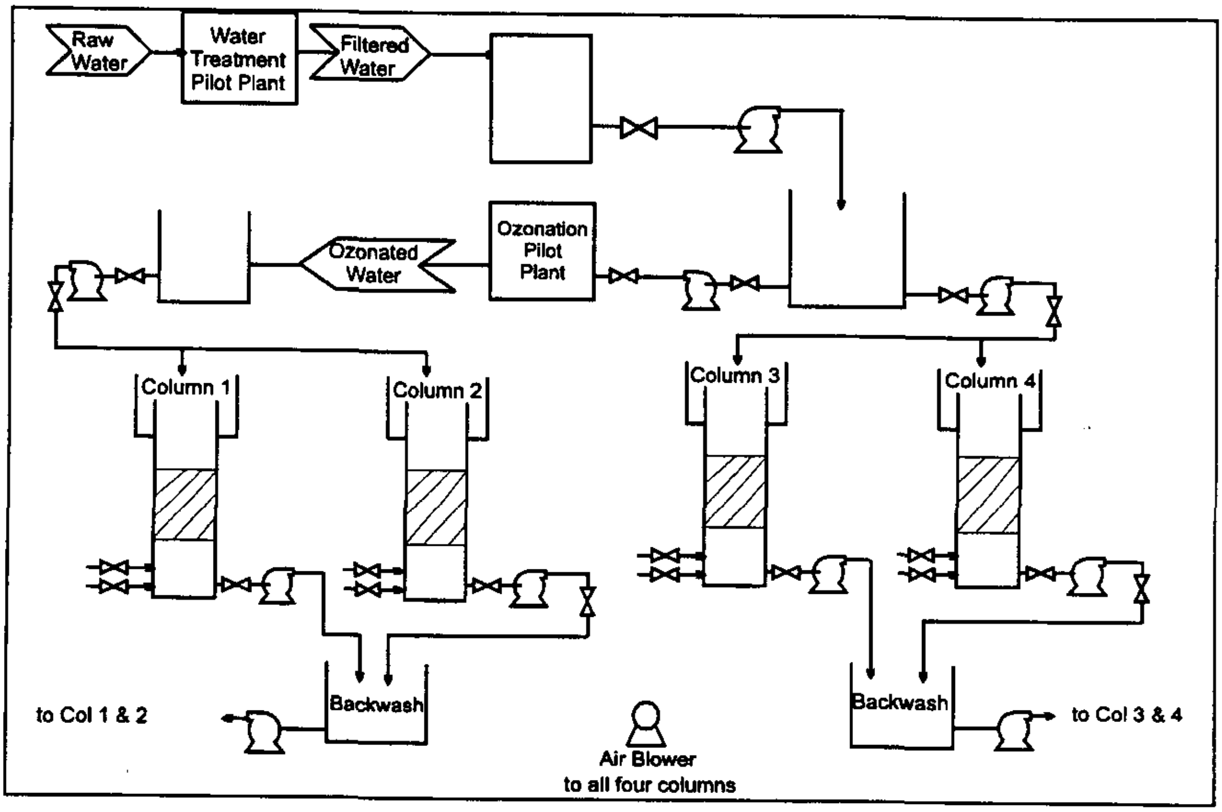


Figure 5.4 **Flow Diagram for the GAC Pilot Plant**

The carbon filters were sized such that they had an empty bed contact time (EBCT) of 10 minutes. The carbon bed depth was 1,0 m and the filtration rate was maintained at approximately 6 m/h. The sequence of backwashing proposed for the PICA carbon was effected by a programmable logic controller (PLC) whereby each column is washed sequentially after a specific time. The backwash procedure (**Figure 5.5**) was as follows :

Step 1 The water level in the filters is lowered to just above the carbon to allow simultaneous air and water scour.

Step 2 When the water level reaches the top of the GAC, air scour is initiated to loosen the carbon granules.

Step 3 Air and water are injected simultaneously. This occurs until a high level of water is obtained in the filter. The air scour is stopped to prevent loss of carbon.

Step 4 The carbon is rinsed with backwash water for a period of between 10 and 20 minutes to ensure adequate removal of biomass and suspended matter from the filter.

Step 5 The carbon is allowed to settle and the first period of filtration is allowed to go to waste. The objective is to discharge the interstitial water before returning the filters to service, as the water is likely to be of a poorer quality, and this allows the carbon to return to its normal state of permeability after disturbance by fluidisation during the backwashing.

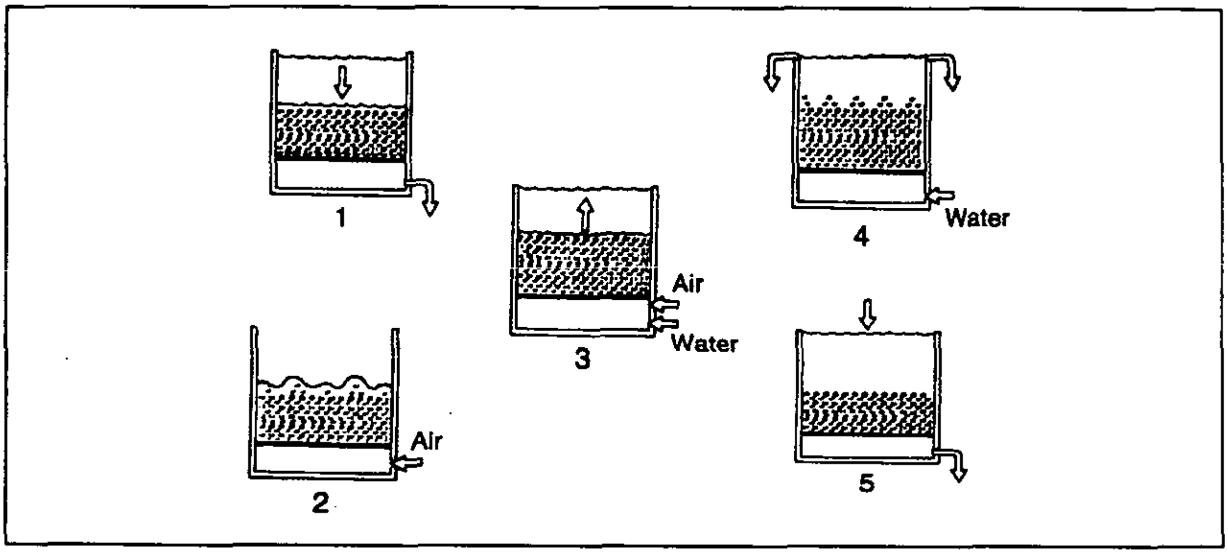


Figure 5.5 **Steps 1 - 5 of the backwashing procedure of the pilot-plant GAC Filters (Langlais et al (Ed), AWWA 1991)**

Backwashing of the pilot-scale GAC filters was initially performed every four days as recommended for water temperatures above 10° Celsius, but the filtration cycle was then lengthened to seven days in an attempt to promote biological activity on the activated carbon in the filters.

5.2.4. Mini-column Adsorption Pilot Plant

During the assessment of GAC for the removal of organic contaminants and the use of biologically activated carbon (BAC) for water treatment, the regeneration of the GAC may be necessary to ensure the effective removal of micro-contaminants. During GAC / BAC filtration the adsorption capacity of the carbon slowly reduces until breakthrough is observed. This can be modelled for single components, but for water treatment the adsorption of naturally occurring organic matter on the carbon may affect the removal of specific known substances.

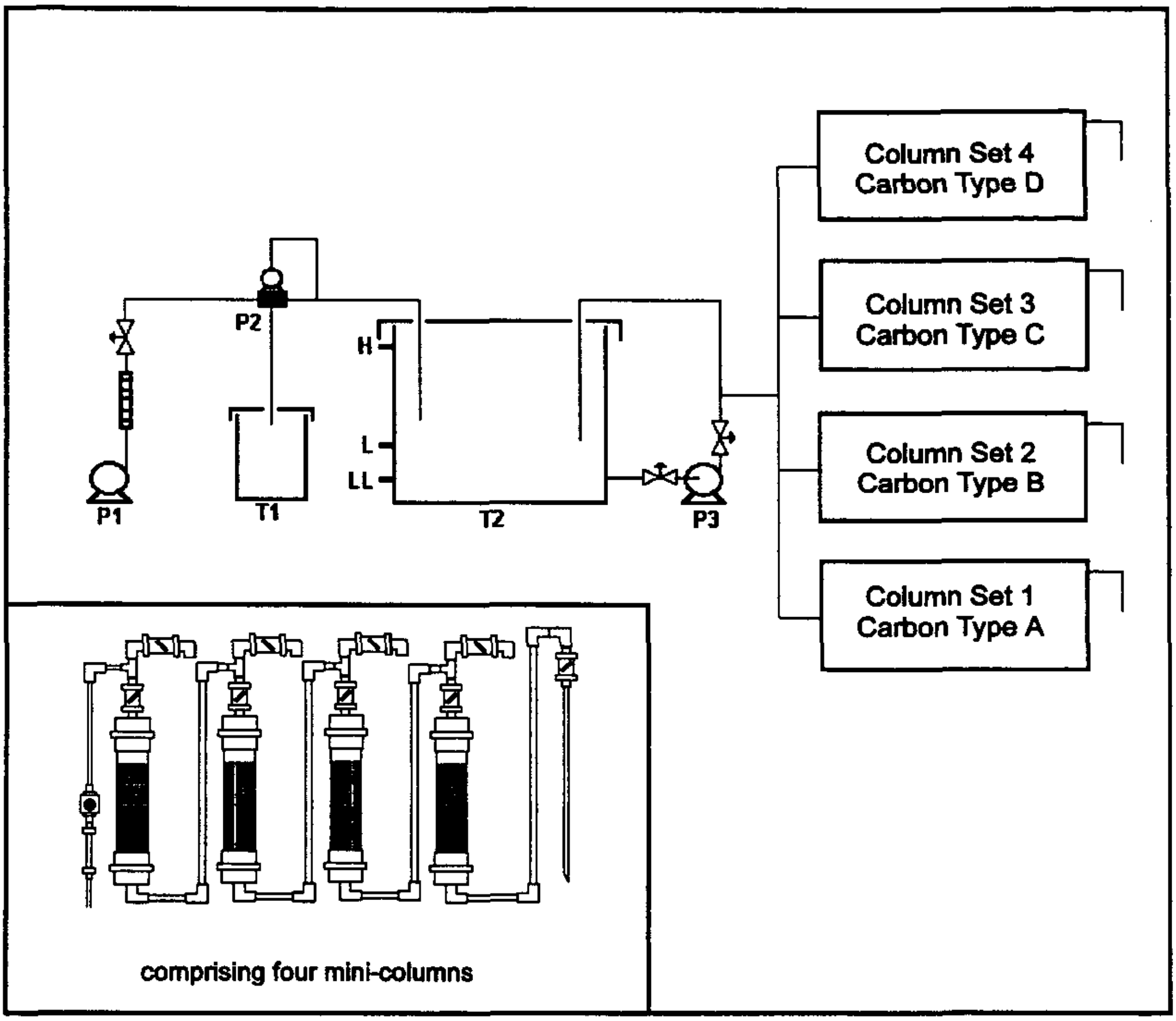


Figure 5.6 **Mini-column Pilot Plant for evaluating adsorption onto GAC**

A mini-column pilot plant (**Figure 5.6**) consisted of four short columns connected in series. A sample point between each column was provided to monitor the breakthrough of micro-contaminants. Due to practical difficulties in maintaining a constant flow of water through the columns, as well as the length of time it may take to reach breakthrough, a shorter EBCT of 6 minutes was designed and the flowrate through the mini-columns was manually controlled at between 9 and 13 ℓ/hr.

The mini-column pilot plant was constructed in four separate sections where the breakthrough of micro-contaminants was monitored for four different types of carbon. Samples of GAC were obtained from four carbon manufacturers, and operated over a period of six months to assess the adsorption performance. The selection of a suitable carbon to achieve particular treatment objective is likely to be expensive and emphasises the need to perform laboratory or pilot scale experiments when considering the selection of GAC for water treatment.

5.2.5. Dosing of Micro-pollutants

The presence of algae in water from the Inanda Dam is known to result in the presence of taste and odour compounds in the water. Organic compounds released when the algae cells are destroyed can be detected as odours at concentrations of less than 20 ng/ℓ. 2-methyl isoborneol (2-MIB) and geosmin are two such organic substances which can be monitored to ensure the acceptability of the water. The presence of other organic compounds in the catchment area of the Inanda Dam are also of concern, especially due to the use of atrazine as a herbicide. Atrazine and other Simazine compounds have also been detected in catchments in Europe.

Samples of geosmin, 2-MIB and atrazine were obtained and these were dosed into the water at concentrations of between 100 and 500 ng/ℓ. The stock solutions were dissolved in an organic solvent before subsequent dilution in water. The procedure was found to be inconsistent, as difficulty in obtaining an even dose and a consistent analysis proved to be mainly due to the sampling techniques. Dosing of atrazine was found to be most consistent as this compound was dosed at higher concentrations in the water and was found to be less sensitive to sampling technique. This is discussed in **Section 5.3.6.**

5.2.6. GAC Equilibrium Tests

Equilibrium tests were carried out using Chemviron Filtrasorb 400 granular activated carbon which had been ground in a laboratory grinder so that 95% passed through a 325 mesh sieve (SABS 53µm stainless steel sieve). The carbon was then dried to constant weight in an oven set at 150° Celsius.

Single isotherm tests were carried out using trihalomethanes at 1000 and 250 µg/ℓ, atrazine at 1000 and 5 µg/ℓ, and geosmin at 100 and 0,5 µg/ℓ. These contaminants were added to final treated water collected from the Wiggins Water Works at a point prior to chlorination. The volume of water used in the tests depended on the concentration of the contaminant; 150 mℓ water was used at the higher concentrations, while 500 mℓ or 1 ℓ of sample was used at the lower concentrations. It was necessary to increase the volume of water used at the lower concentrations in order to allow sufficient sample for determination of the contaminants and to allow for the accurate weighing of the smaller amounts of carbon which were used under these conditions.

The contaminant-containing water together with the GAC was placed in a glass screw cap bottle of a suitable capacity (150 mℓ, 500 mℓ or 1ℓ) and if necessary the pH of the water was adjusted to approximately 8. The bottles were then placed on a mechanical shaker and shaken for 24 hours at a temperature of between 22 and 24° Celsius. The samples were then filtered through Whatman number 3 filter paper. As geosmin is highly volatile extreme care was taken to prevent excessive aeration of the sample. The water was analysed for the relevant contaminant using the procedures described in **Section 3**.

Mixed isotherm tests were carried out as described above using chloroform, bromoform, atrazine and geosmin in both the high and low concentration ranges mentioned above and in various mixtures of two and three of these contaminants.

5.3. Results and Discussion

The pilot plant was operated over a period of two years, comparing the performance of two different types of GAC, and the combination of GAC with intermediate ozonation. The GAC filters were operated as described in **Section 5.2.3** to determine whether a biological mechanism can be beneficial in improving performance of the GAC filters, thereby reducing the frequency of regeneration.

The extent of biological activity on the GAC filters was found to be limited, and a set of mini-columns was designed to assess the adsorption of organic micro-contaminants (geosmin and atrazine) on different types of GAC. An attempt was also made to determine whether EBCT and linear filtration velocity have any noticeable effect on the performance of the GAC processes. The water quality entering the Wiggins Waterworks during the period of operation of the pilot plant is shown in **Table 5.2**.

5.3.1. Water Treatment Pilot Plant

The water treatment pilot plant (**Figure 5.1**) was designed to produce a filtered quality water similar to what would be expected from the rapid gravity sand filters at the Umgeni Water Wiggins Waterworks. A polymeric coagulant was dosed into the water (average dose of 0,7 mg/ℓ) before the centrifugal feed pump. The energy dissipated into the water by the feed pump enables effective flash mixing and dispersion of the coagulant. Flocculation is effected in a horizontal tube flocculator in which the linear velocity is 1 m/s. The water is then filtered at a filtration velocity of 7 m/hr through a 1,2 m diameter dual media sand filter.

Table 5.2 **Raw water quality entering the Wiggins Waterworks (pilot plant feed water)**

Determinant	Units	Maximum	Minimum	Average
Algae Counts	Cells/mℓ	4935	126	1000
Colour	°H	145	1,0	40
Turbidity	NTU	216	2,9	31,5
Total Aluminum	μg/ℓ	1001	27	257
Alkalinity	mg/ℓ as $CaCO_3$	54,4	35,5	42,9
Total Hardness	mg/ℓ as $CaCO_3$	51,2	38,1	45,1
Calcium	mg/ℓ	10,6	7,4	9,0
Magnesium	mg/ℓ	5,9	4,7	5,4
Sodium	mg/ℓ	18,3	12,7	16,4
Iron	mg/ℓ	4,9	0,3	0,8
Manganese	mg/ℓ	0,22	0,.01	0,04
Suspended Solids	mg/ℓ	58	4	15
Total Organic Carbon	mg/ℓ as C	6,2	1,4	3,6

During the operation of the GAC columns, the main emphasis was a comparison of the performance of the different process options. It was however necessary to ensure that the filtered water feeding the columns was representative of what would be expected from an operating plant. The operation of the water treatment plant was therefore considered critical to the success of the project. **Figure 5.7** shows the turbidity removal during the period of operation. In general the plant was operated well, and a filtered water turbidity below 0,5 NTU was maintained. The operation of a sand filter by direct filtration had to be monitored very carefully, and the effectiveness of backwashing was found to be critical to the success of the operation.

On a few occasions an increase in the filtered water turbidity was observed. This was found to be caused by ineffective backwashing of the filter where sections of the filter media had become blocked causing an increased filtration rate in other areas of the filter and poor plant operation. The filter media was removed and replaced with clean sand and fresh anthracite.

The raw water turbidity increased during December 1996 (after 450 days of operation **Figure 5.7**) at which point the dual media direct filtration pilot plant again performed inadequately. The filter media was replaced, a larger filter backwash pump was installed and the operating procedure of the plant was modified. Timers were installed to control the backwash sequence instead of relying on differential pressure measurement.

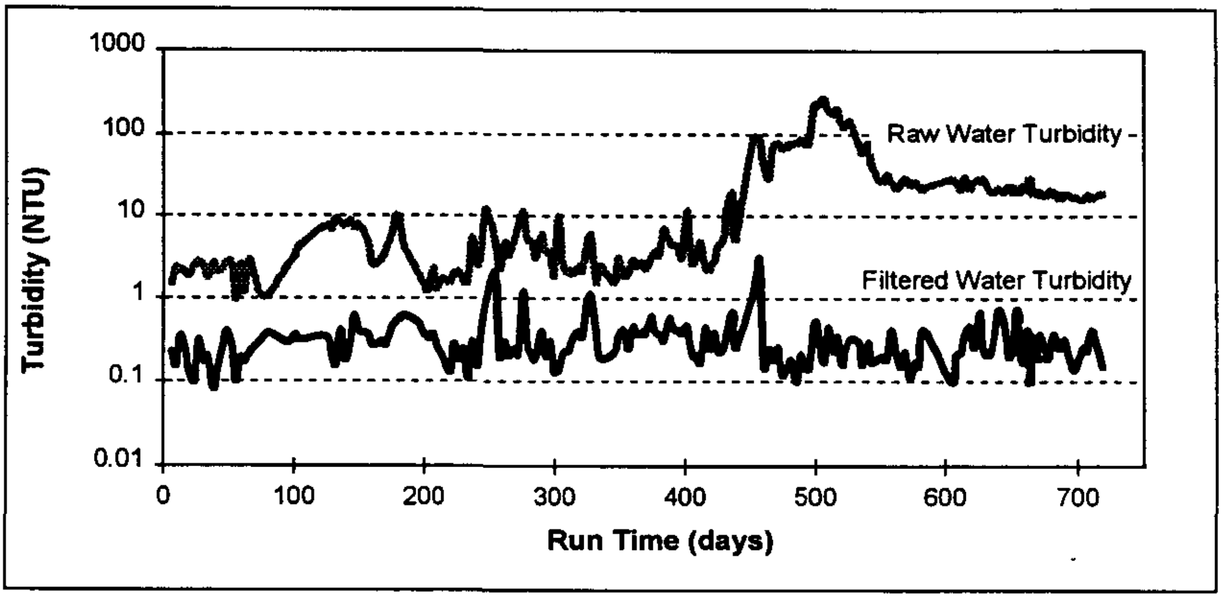


Figure 5.7 **Filtered water turbidity entering the GAC / Ozone pilot plant**

The occasional increase in filtered water turbidity (exceeding the normal range of 0,5 to 1 NTU), did not significantly affect the operation of the GAC filters as they were backwashed automatically once every 7 days.

5.3.2. Dosing of Atrazine and 2-MIB

During the operation of the pilot plant organic micro-contaminants of 2-MIB and atrazine were dosed into the raw water. **Figure 5.8** shows the concentration of 2-MIB that was dosed into the water. Initially 2-MIB was dosed intermittently (points "A") in an attempt to simulate the occurrence of taste and odour compounds resulting from irregular algal blooms in the Inanda Dam, and thus to compare the performance of the carbon at removing 2-MIB from the water over a period of time.

During period "B" (**Figure 5.8**), an attempt was made to maintain the 2-MIB concentration between 60 and 100 ng/ℓ. In order to do this a concentrated solution of 2-MIB had to be made up once per day. Although difficulties were experienced with the dissolution of 2-MIB in water, a procedure was developed to first solubilise the powder in acetone and then dilute with water to the required concentration for dosing. A dosing pump was used to inject the solution into the main flow of water. Due to changes in the water temperature in the reservoir, the extent of vaporisation of 2-MIB could not be controlled, and the concentration of 2-MIB reaching the GAC / Ozone columns was found to be inconsistent.

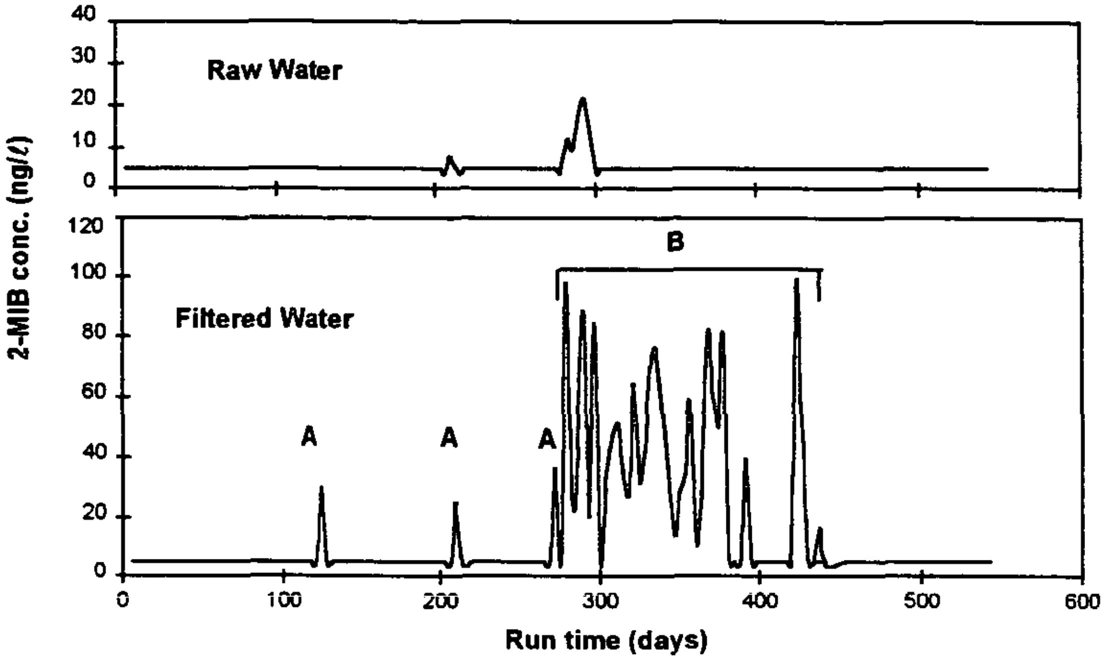


Figure 5.8 Dosing of 2-MIB into the Raw water

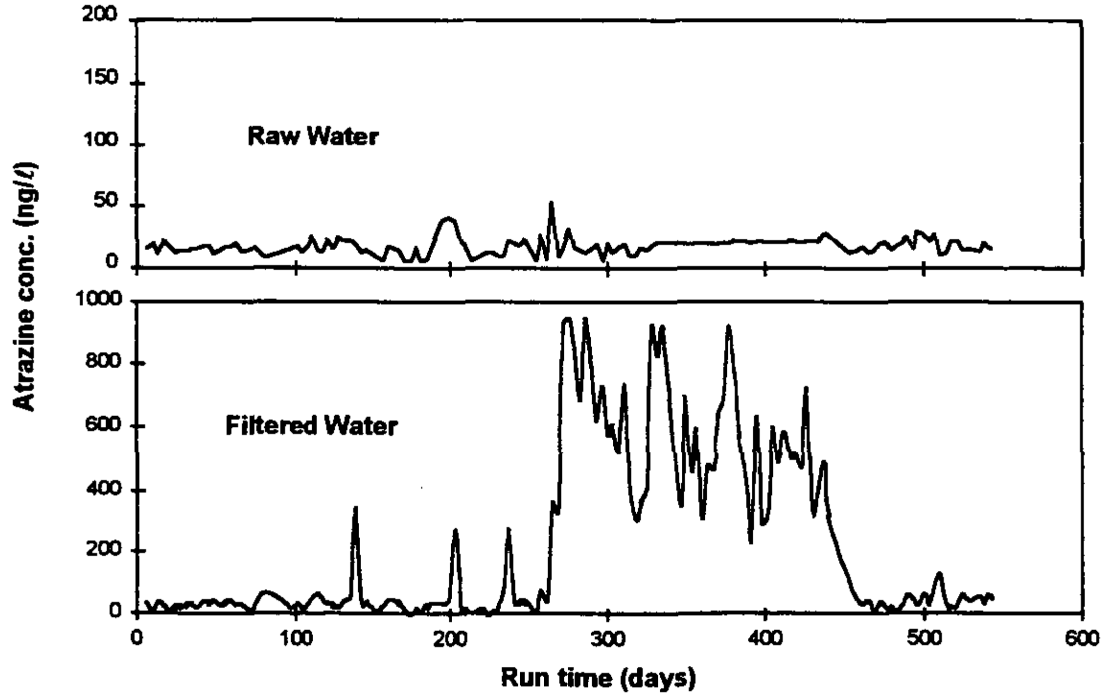


Figure 5.9 Dosing of Atrazine into the Raw water

A solution of commercial herbicide was diluted and the dose was controlled to achieve an atrazine concentration of approximately 400 - 600 ng/ℓ. As can be seen from **Figure 5.9**, similar difficulties were encountered in maintaining an accurate atrazine dose on a small scale.

5.3.3. Ozone Pilot Plant Operation

The ozonation pilot plant was operated between 4 and 7 g/hr. Ozone was bubbled into the bottom of two ozone contact columns, counter-current to the flows filtered water as shown in **Figure 5.2**. During the measurement of the ozone dose, the concentration of ozone in the feed gas and the off-gas was measured.

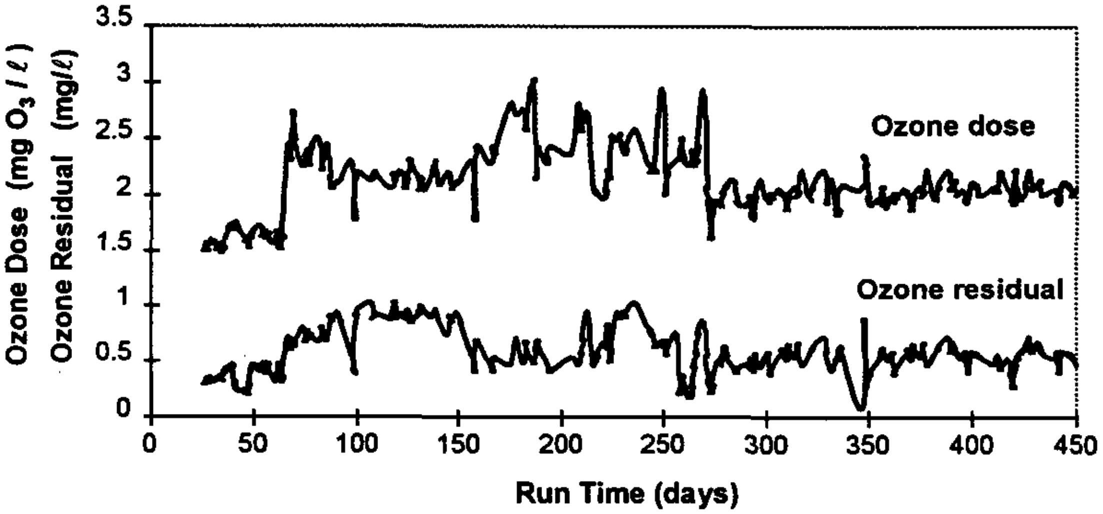


Figure 5.10 Consistency of the ozone dose for the pilot plant operation

Initially the pilot plant was controlled at a dose of 1,6 mg/ℓ ozone, but following results from laboratory work (**Section 4.3.1.5**) which indicated better removal of 2-MIB and atrazine at higher applied ozone concentrations, the dose was increased to 2,5 mg/ℓ (**Figure 5.10**). The ozone transfer efficiency was consistently above 85%. The residual ozone concentration was measured by the indigo trisulphonate method. During the initial period there was a large fluctuation in the ozone residual, and it was feared that high residual concentrations might affect the biological growth in the carbon columns. An operating strategy was adopted to apply a dose of at least 2 mg/ℓ and maintain a residual concentration of approximately 0,5 mg/ℓ (**Figure 5.10**).

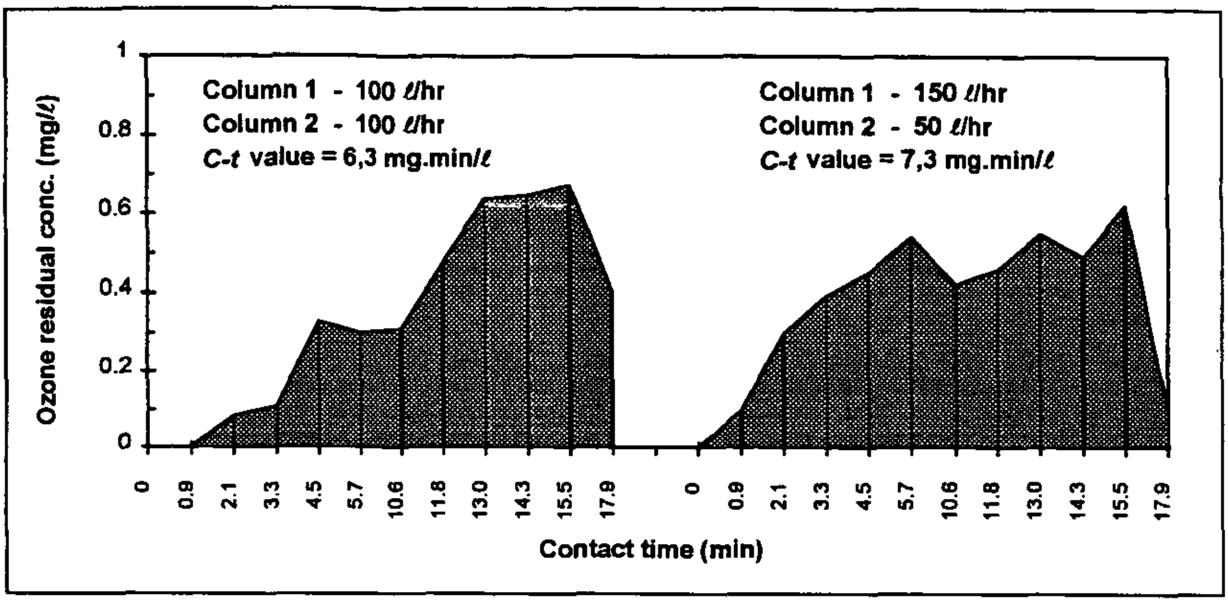


Figure 5.11 **Calculation of the *C•t* value for the ozonation pilot plant**

During the operation of the ozonation pilot plant, the residual ozone concentration at different sample points (**Figure 5.2**) in the ozone contact columns was monitored. Assuming perfect plug flow, the hydraulic residence time in the ozone contact columns (and subsidiary piping) was found to be in excess of 17 minutes.

For disinfection, the U.S. EPA has specified the *C• t* concept, where *C* is the concentration of dissolved disinfectant (mg/ℓ) and *t* is the nominal contact time (min). The *C•t* value was calculated by integrating the residual ozone concentration with respect to time, and determining the area under the graph of residual concentration vs. time (**Figure 5.11**).

Initially the plant was operated with equal gas flow (100 ℓ/hr) into each column. The continual increase in residual concentration in the second column shows that the ozone demand had not yet been met. The operation of the columns was then changed, whereby the gas flowrate into the first column was increased to 150 ℓ/hr and the flowrate to the second column reduced to 50 ℓ/hr. In this instance exactly the same amount of ozone was being dosed (i.e. the same operational costs) but a larger *C•t* value was obtained for the contacting system. The ozone demand was almost completely met in the first contact column and the additional dose in the second column effectively maintained the residual at a constant level of approx. 0,5 mg/ℓ. In this way the effectiveness of the ozonation was controlled and a *C•t* of between 6 and 7 mg.min/ℓ was maintained.

5.3.4. GAC Column Operation

The granular carbon filters were designed and constructed in the following arrangement.

Column 1	Ozonation and GAC filtration using PICA carbon (wood based carbon)
Column 2	Ozonation and GAC filtration using Coal based carbon WCM 106
Column 3	GAC filtration using PICA (wood based carbon) - no ozonation.
Column 4	GAC filtration using Coal based carbon WCM 106 - no ozonation.

Following initial recommendations with regard to the operation of activated carbon filters for the biological removal of contaminants, with TOC concentrations between 4 and 8 mg/ℓ, an EBCT of 10 minutes was designed. The operating strategy for water temperatures above 10°C recommends backwashing every four days. Whereas at lower water temperatures when the metabolic rate of the biomass is slower, a backwashing interval of seven days is recommended.

The main emphasis of the long term operation of the GAC filters was to establish the extent of organic removal, and to determine whether any advantage could be obtained by allowing the filters to operate in a manner which would promote biological activity on the carbon. The organic quality of the water prior to ozonation and GAC filtration, was compared to the final GAC filtered water from each of the treatment processes. The parameters measured were total organic carbon (TOC), UV absorbance at 254nm, total THM formation potential (THMFP), as well as the biodegradable organic carbon content of the water as measured by the method proposed by Servais et al. (1987).

5.3.4.1. Total Organic Carbon and Dissolved Organic Carbon

During the first month of operation, the removal of TOC from the water was significant. The consistency of the analyses for the GAC filtration using a coal based carbon indicates an excellent removal by adsorption initially, with analyses of TOC being as low as the detection limit (0,7 mg/ℓ) (**Figure 5.12**). A subsequent reduction in the removal efficiency as the carbon became saturated with natural organic matter and the TOC in the raw water increased (after 30 to 50 days) was observed. There is also a noticeable difference in the performance of the GAC filtration after ozonation, as a better removal of TOC is observed.

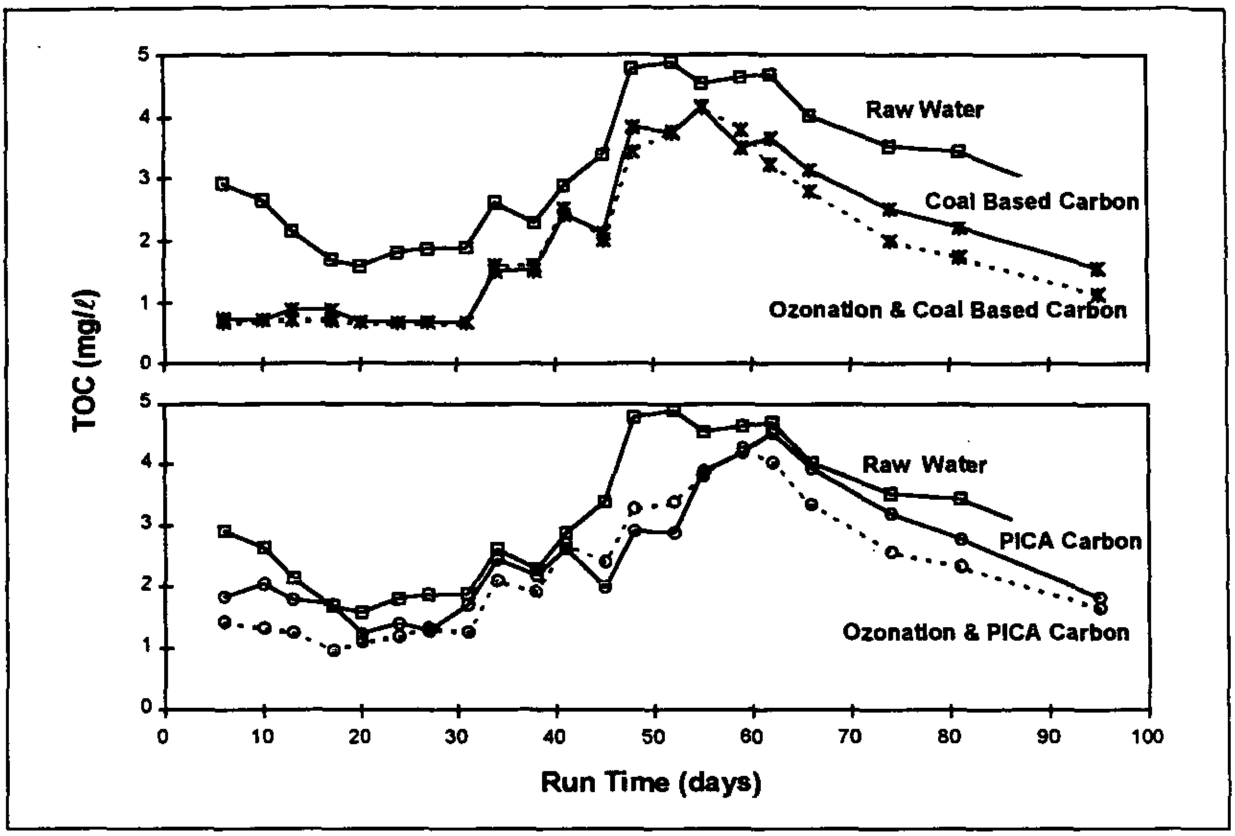


Figure 5.12 **Reduction in TOC during the first three months of operation**

The analysis of TOC in both the raw and filtered water samples was found to be erratic (Figure 5.13). No trends in performance could be established with regards to the effectiveness of the GAC process for controlling the levels of DOC in the water.

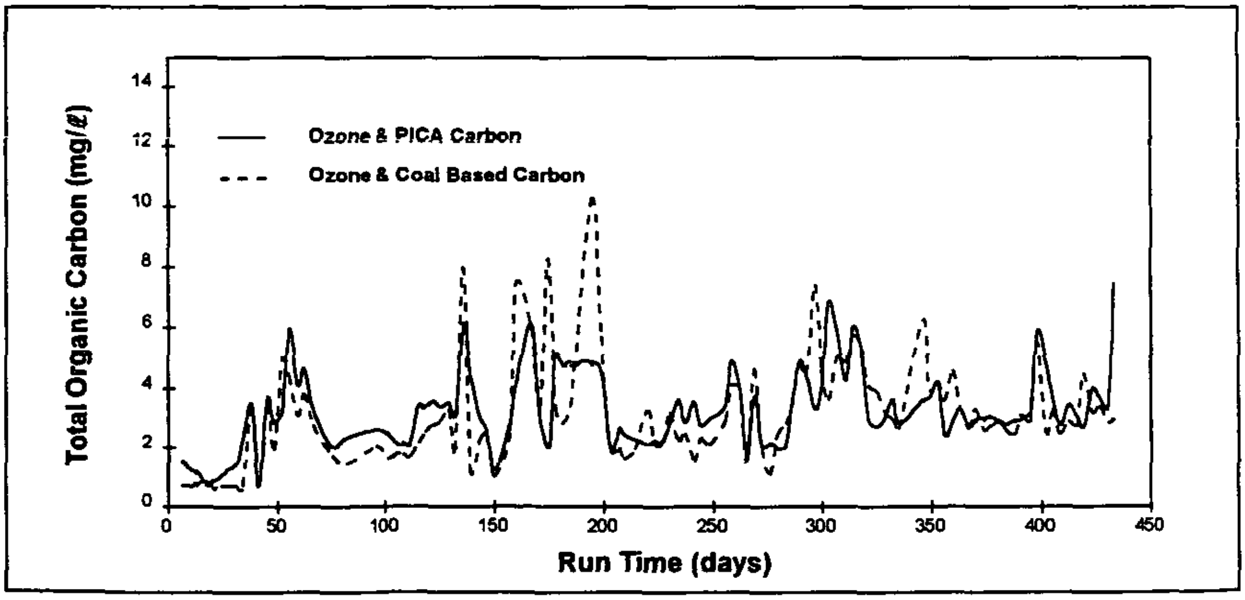


Figure 5.13 **Erratic nature of Total Organic Carbon Measurement of water filtered through GAC after ozonation**

5.3.4.2. Tri-halomethane formation potential

Samples from the GAC filtration columns were chlorinated as described in **Section 3.1.3** to allow the formation of THMs. When the THMFP of the GAC filtered water is compared to the THMFP of the raw water (**Figure 5.14**) a removal of at least 20 % was achieved, indicating that the GAC provides an effective process for limiting the formation of disinfection by-products. The coal based carbon was more effective than the PICA carbon at reducing THM precursors. This is due to the higher capacity of the carbon for adsorption of specific organic contaminants.

As was found by monitoring DOC, the performance of both types of carbon was better during the initial months of operation, but after approximately six months of operation (200 days) there was little difference in the results.

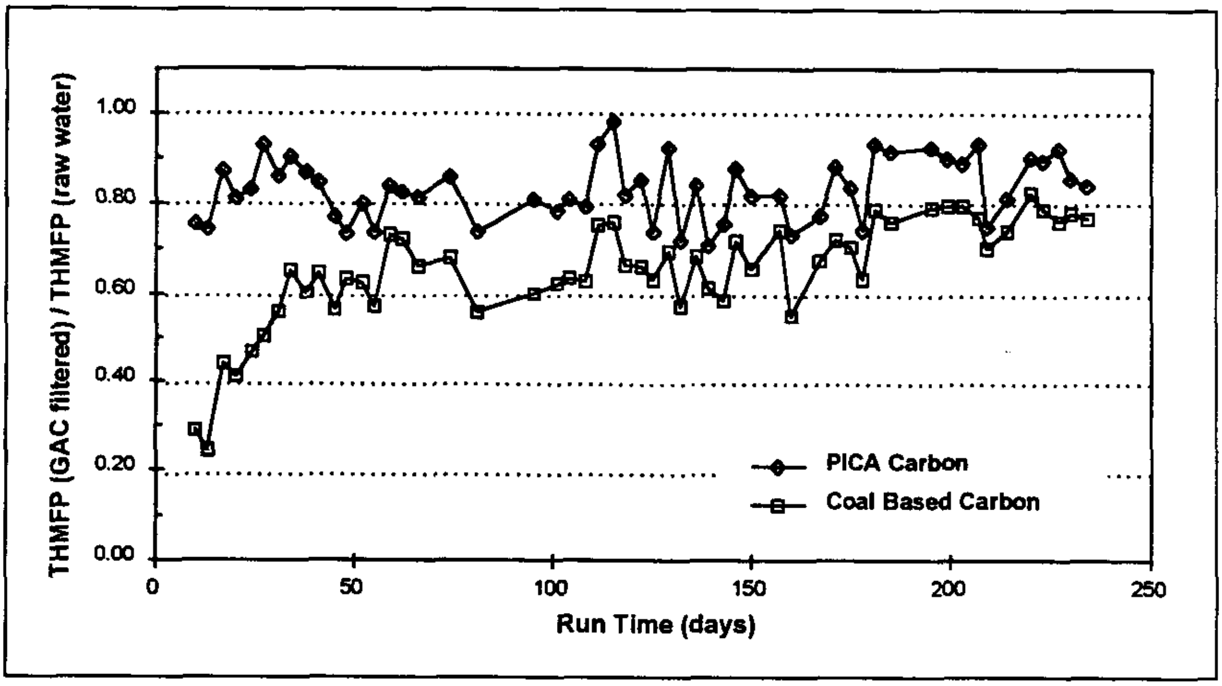


Figure 5.14 Comparison of the formation of THM's in the GAC filtered water without ozone to the THM formation in the Raw water

Figure 5.15 shows the THMFP of the water after ozonation and subsequent filtration through both types of GAC. This also shows an improved reduction in THMFP using the coal based carbon.

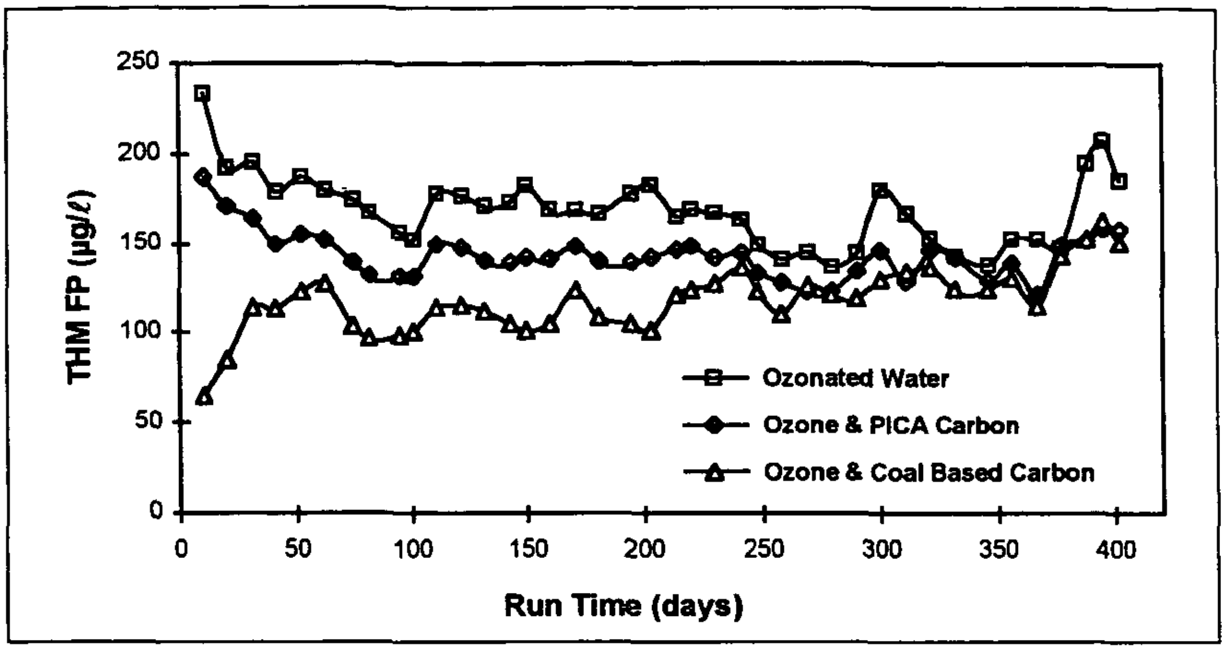


Figure 5.15 **Comparison of the THMFP for PICA carbon and the coal based carbon after ozonation**

5.3.4.3. UV absorbance (254 nm)

Figure 5.16 shows the average monthly measurement of UV absorption @ 254 nm, and the trends are clearly evident. The use of ozone significantly reduces the absorbance and in all cases the use of coal based carbon would appear to be better than PICA for improving the water quality.

The UV extinction data can also be represented in the form of a cumulative plot which indicates the rate of reduction in UV absorbance with time. **Figure 5.17** shows that initially the lines diverge indicating an advantage in implementing GAC as an additional process step. The slope of the lines becomes more parallel towards the end of the pilot plant operation (after 450 days of operation, or after the filtration of 60000 bed volumes), which is an indication that fewer of the contaminants or species are being removed by the GAC. The use of ozonation, however, continues to show benefit in reducing the UV extinction as the lines continue to diverge when compared to the filtered water.

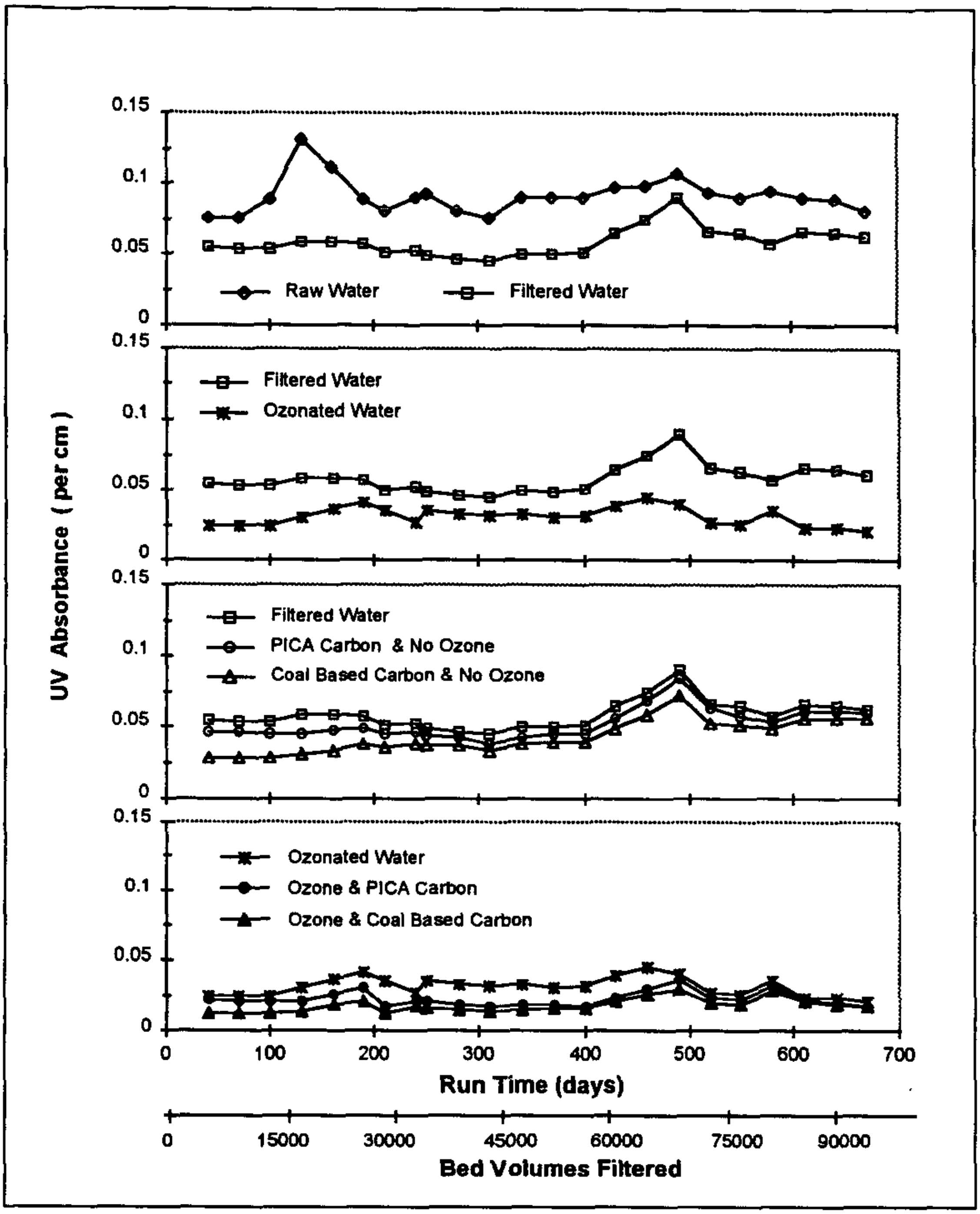


Figure 5.16 UV absorbance measurement for comparison of the process operation

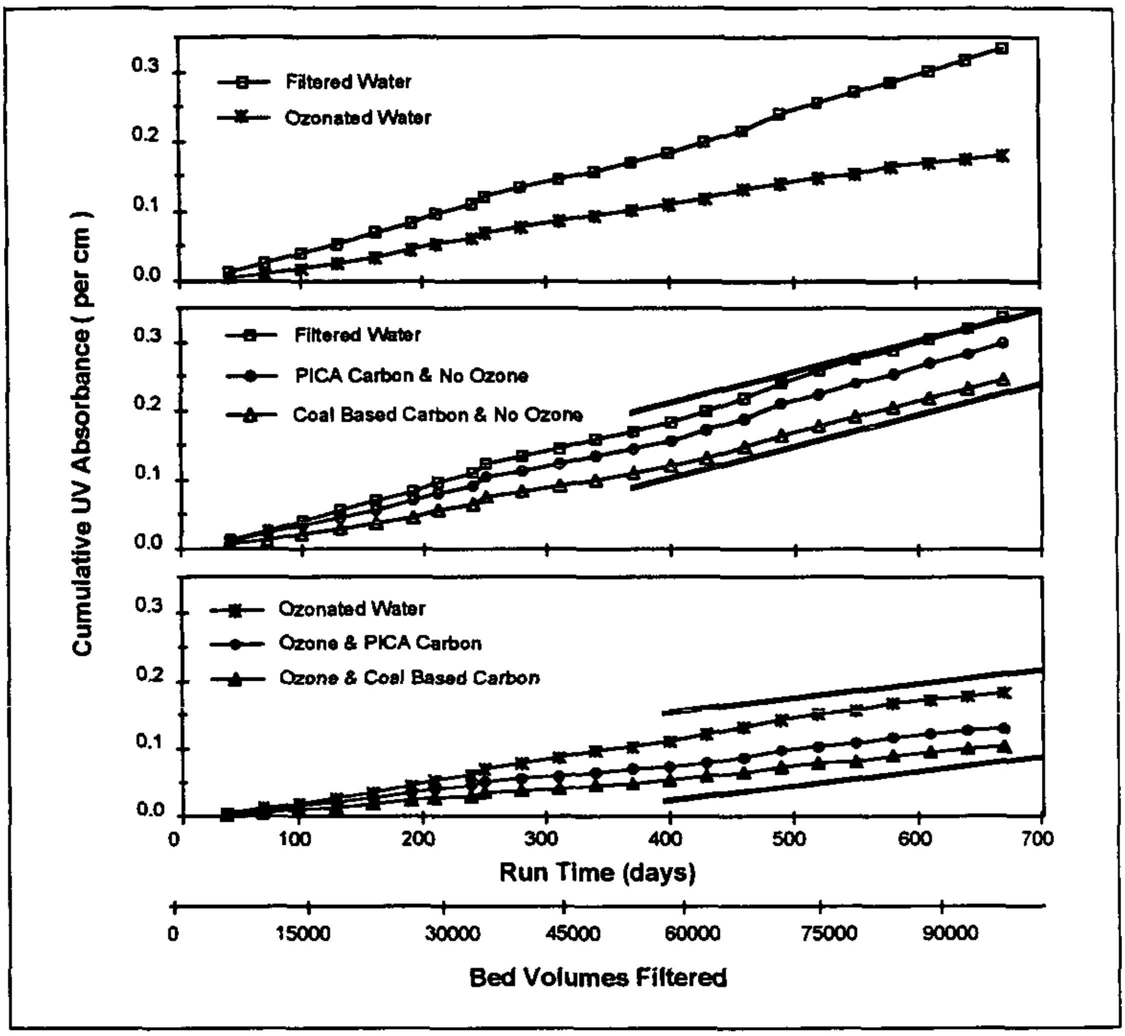


Figure 5.17 **Cumulative UV absorbance**

5.3.4.4. Biodegradable Dissolved Organic Carbon (BDOC)

The analysis of BDOC was implemented to study the biodegradability of NOM in the water **Section 3.1.1**. No significant trends were observed, but the averaged values **Figure 5.18** show a trend which may be expected. A reduction in BDOC during chemical coagulation, flocculation and sand filtration was observed. An increase in BDOC was observed after ozonation, as this transforms refractory (non-biodegradable) substances into compounds which are more readily biodegradable. A reduction in biodegradable NOM after GAC filtration was not evident during the pilot plant operation.

It has been postulated that the water received at the Wiggins Waterworks is biologically stable as the residence time in the Inanda Dam is in excess of 200 days, during which time most biological reactions may have gone to completion.

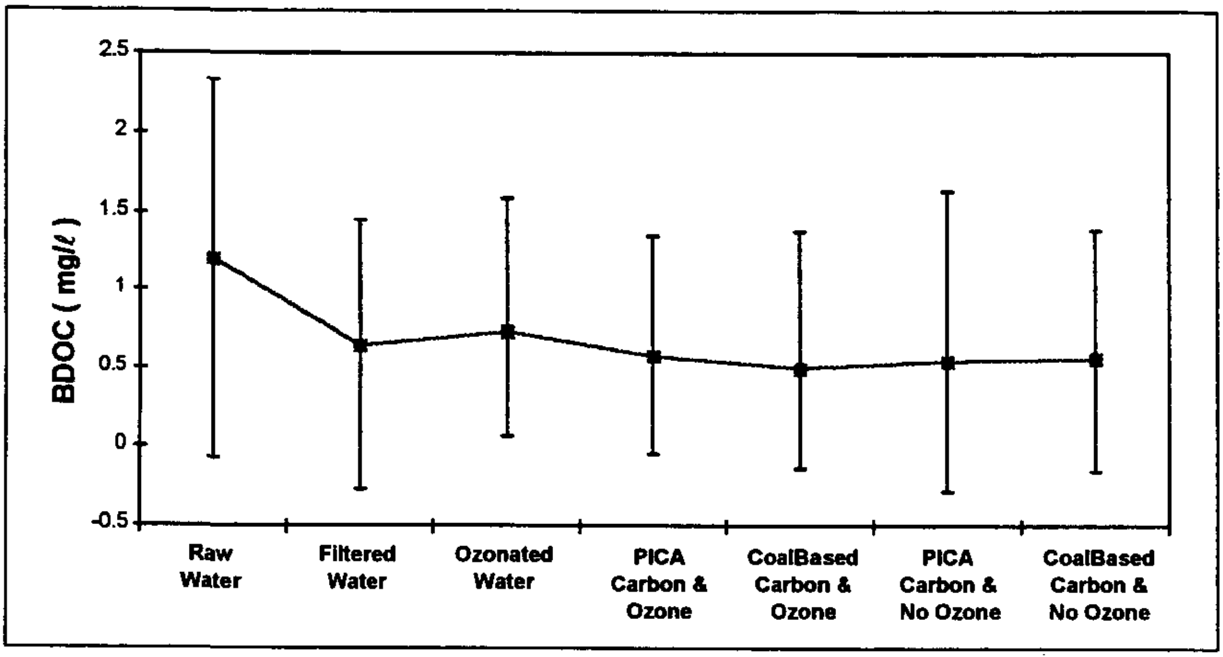


Figure 5.18 **The effect of Ozone and GAC on the levels of BDOC in Inanda Dam Water (error bars showing 95 percentile of a total of 59 determinations)**

These results are consistent with the BDOC trends (**Section 4.3.1.3**) where after coagulation and filtration the BDOC of the water was as low as 0,1 mg/ℓ. The pilot plant was operated to maintain an ozone dose of 2,5 mg/ℓ, and the typical DOC concentration ranged between 3 and 8 mg/ℓ. The ozone to DOC ratio varied between 0,3 and 0,8.

5.3.4.5. Biological Growth on the GAC Filters

The biodegradable organic carbon (BDOC) measurements showed the expected trends but these were not significant enough to indicate that there was definitely an advantage for the operation of GAC filters using PICA carbon for the specific benefit of gaining additional biological activity.

It has been extremely difficult to assess the extent of biological activity on the carbon filters. The reduction of DOC and BDOC indicate that there is very little, if any, biomass on the carbon and that the water at Wiggins Waterworks is very stable. The regular backwashing of the filters as recommended for PICA carbon (**Section 5.2.3**) is designed to maintain a balance of bacteria and protozoa in the filter and thereby provide a balanced ecosystem for the promotion of biological growth. The backwash waters from the columns were sampled and studied for any indication of biological activity **Table 5.3**. As protozoa are larger species and will only exist if there is biomass for them to feed on, the samples were qualitatively examined for protozoan species.

Table 5.3 Microbiological Examination of GAC filter backwash waters

	Sample				Sample		
	1	2	3		1	2	3
PICA carbon + ozone				**GAC carbon + ozone**			
Spirochaetes	–	–	–	Spirochaetes	–	–	–
Ciliates - free & creeping	+	+	+	Ciliates - free & creeping	+	±	+
Ciliates - sessile	–	–	–	Ciliates - sessile	–	–	–
Rotifers	±	+	±	Rotifers	–	±	+
Flagellates	++	++	++	Flagellates	+++	+++	+++
Amoeba	–	–	–	Amoeba	±	±	±
Nematodes	++	++	++	Nematodes	+	++	++
PICA - no ozone				**GAC - no ozone**			
Spirochaetes	–	–	–	Spirochaetes	–	–	–
Ciliates - free & creeping	+	+	±	Ciliates - free & creeping	±	+	+
Ciliates - sessile	–	–	–	Ciliates - sessile	–	–	–
Rotifers	+	±	±	Rotifers	++	+	+
Flagellates	+	±	±	Flagellates	++	+	+
Amoeba	±	+	+	Amoeba	++	++	±
Nematodes	+	+	+	Nematodes	+	+	±

– = not seen ± = incidental + = few ++ = common +++ = abundant

Some analyses of the carbon **Table 5.3** showed small numbers of protozoan organisms but no significant difference was noted between either the two types of carbon or the ozonated process when compared to the non-ozonated process. It was also realised that any granular material in a filter will achieve some biological activity which will benefit the long term operation of a biological process.

5.3.4.6. Chlorine Demand

A secondary benefit in the use of GAC is that by reducing the levels of organics in the water the chlorine demand is reduced. **Figure 5.19** shows a reduction in chlorine demand after ozonation from 1 mg/ℓ to 0,65 mg/ℓ. A further reduction of 0,3 mg/ℓ can be obtained by using either PICA or coal based carbon to between 0,3 and 0,4 mg/ℓ. In processes where ozonation is not used, the activated carbon filtration is able to lower the chlorine demand by approximately 35 % to 0,65 mg/ℓ.

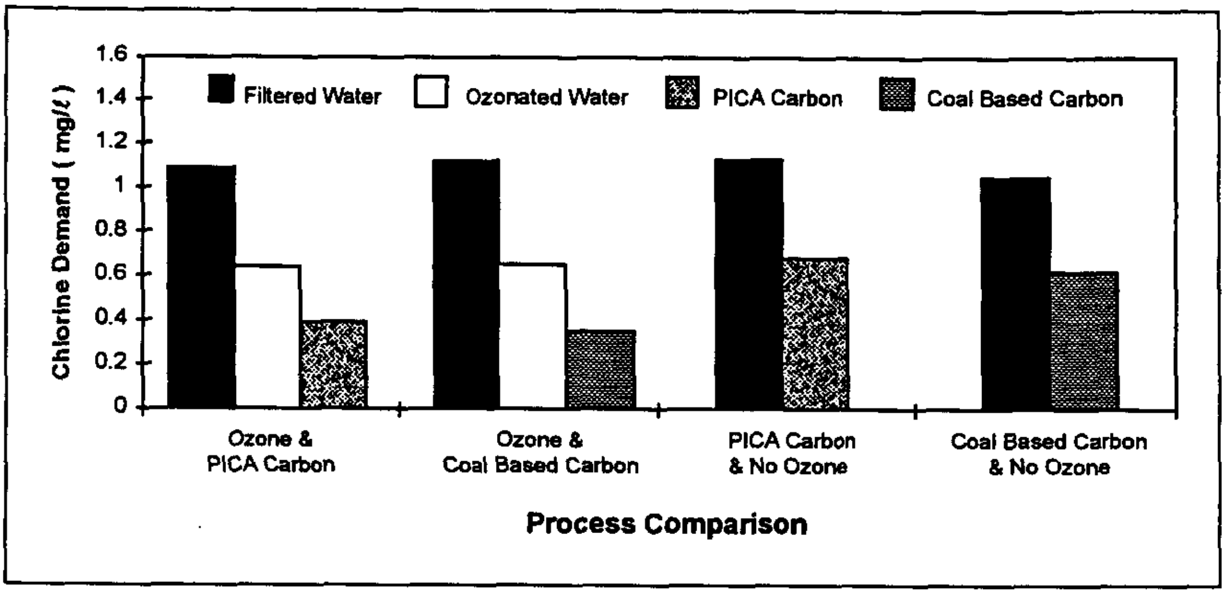


Figure 5.19 **The effect of different processes using ozonation and GAC on the Chlorine Demand of the water**

5.3.4.7. Removal of Pesticides

Section 5.2.5 explains the procedures involved and the complications experienced while dosing Atrazine into the raw water. **Figure 5.20** shows the effectiveness of the processes in reducing the atrazine concentration in the water to below 100 ng/ℓ. Initially whilst the atrazine was being spiked periodically into the water, to represent sporadic occurrences of point source pollution (**Section 5.3.2**), the GAC processes all consistently removed atrazine to below the detection limit of the analytical procedure (<5 ng/ℓ). Ozonation was beneficial in promoting a 75% reduction in atrazine concentration. This is consistent with findings during the laboratory investigation (**Section 4.3.1.5**).

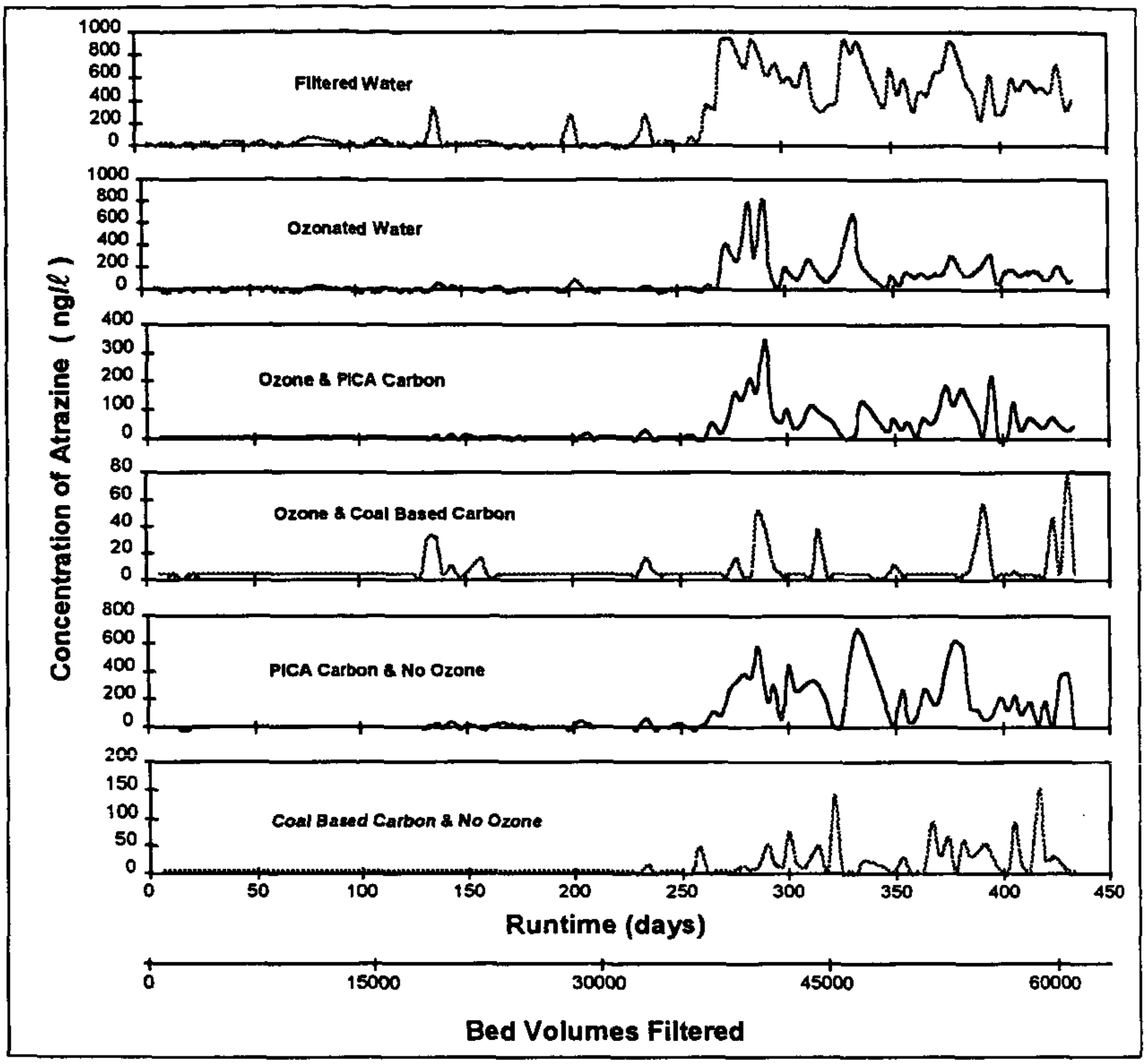


Figure 5.20 Comparison of ozonation and GAC processes for the removal of Atrazine (Note : different scales on axes for atrazine concentration)

Atrazine was then spiked at higher concentrations of between 300 and 900 ng/ℓ. The process comprising ozonation followed by a coal based carbon was most effective at maintaining levels of Atrazine below 100 ng/ℓ over a prolonged time. Occasional breakthrough with atrazine concentrations reaching between 200 and 300 ng/ℓ was observed for ozonated water after PICA carbon filtration.

The performance of the carbon without the use of ozone was significantly poorer with concentrations of atrazine in the final water which exceed the European recommended limit for pesticides (100 ng/ℓ). The coal based carbon reduced the atrazine concentration to levels between 100 and 200 ng/ℓ which was significantly better than the PICA carbon, which at times only reduced the atrazine concentration to 600 ng/ℓ (only a 30% removal from the concentration in the filtered water).

The performance of the GAC filters can also be measured by monitoring the cumulative atrazine concentration **Figure 5.21**.

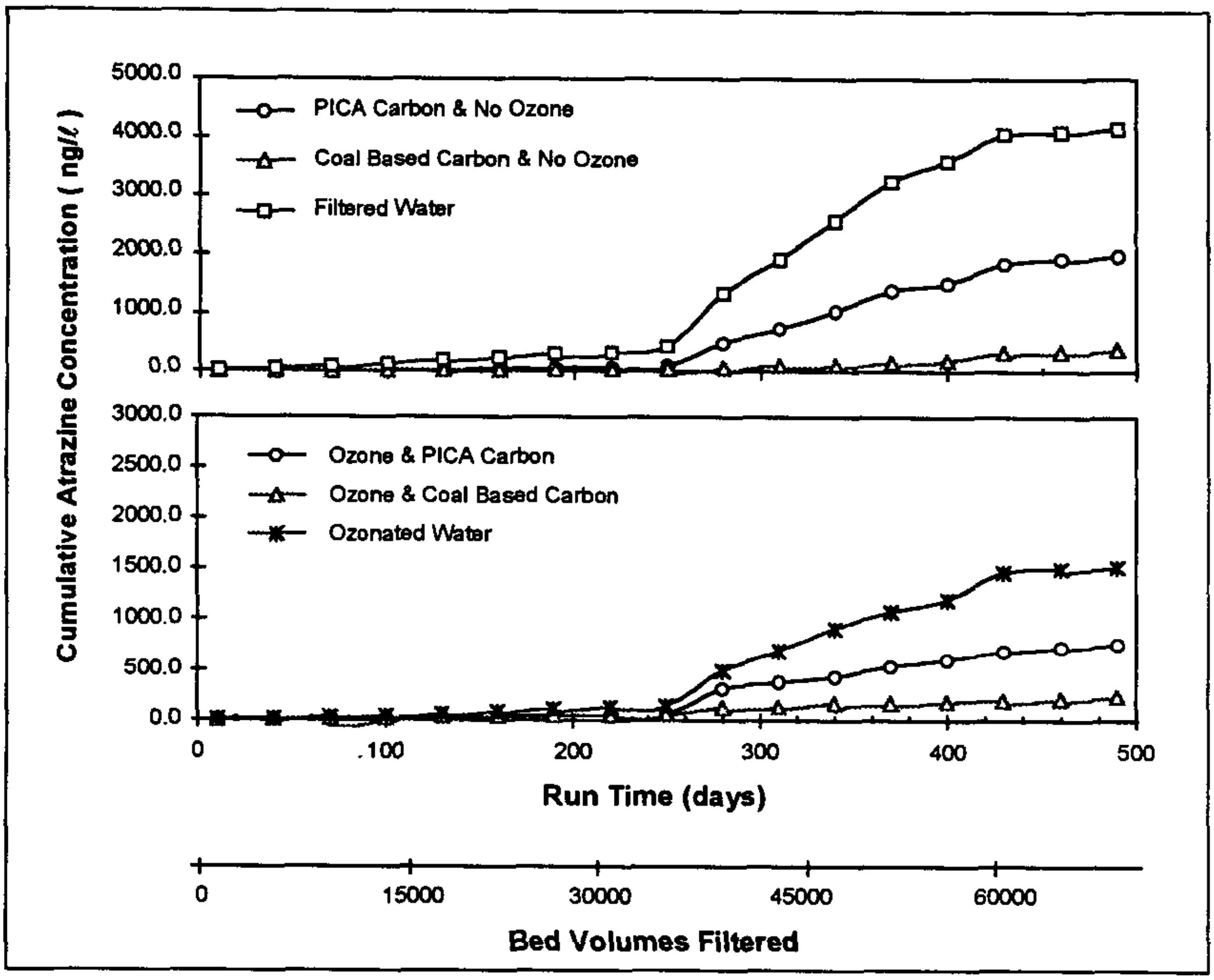


Figure 5.21 **Cumulative atrazine concentration for GAC filtration with and without ozonation**

It should be noted however that at the point where the graphs of the filtered water and the ozonated water level out (after 450 days of operation, > 60000 bed volumes), the excessive dosing of atrazine and 2-MIB was reduced (**Figure 5.8 and 5.9**). Unlike the plot of cumulative UV absorbance (**Figure 5.17**), where the lines become parallel after approximately 60 000 bed volumes. At this point the other graphs still appear to diverge indicating that the adsorption capacity of the carbon for the removal of atrazine may not yet have been exhausted and that further removal of atrazine would have been possible.

5.3.4.8. Iodine Number, Methylene Blue Number and Ash Content

During the initial months samples of carbon were taken from the carbon columns and submitted for analysis of methylene blue number, iodine number and ash content. The results of these tests are summarised in **Table 5.4**.

Table 5.4 **Analyses of the carbon from the GAC / Ozone Pilot Plant**

Sample	Methylene Blue Number (g/100gC)		Iodine Number (mg.ℓ/g^{C})		Ash Content (%)	
	with ozone	without ozone	with ozone	without ozone	with ozone	without ozone
Fresh PICA Carbon	46.03	46.03	892.25	892.25	1.3	1.3
PICA (1 month)	49.90	52.70	840.86	840.86	3.3	2.8
PICA (2 months)	44.63	43.79	554.89	631.99	8.8	8.4
PICA (5 months)	44.39	43.67	488.28	538.92	9.7	9.5
Fresh WCM 106	37.65	37.65	1162.34	1162.34	3.1	3.1
GAC (1 month)	35.95	36.66	997.46	1005.55	2.4	2.4
GAC (2 months)	33.48	33.09	935.70	900.72	2.3	2.3
GAC (5 months)	33.67	32.72	935.57	834.43	2.5	2.5

There is a consistent decrease in the methylene blue and iodine numbers for both types of carbon, both with and without ozone. The iodine number of the PICA carbon decreased at a faster rate to approximately 50% of the initial value within 5 months. The iodine number of the coal based carbon only dropped by about 20 % for the ozonated water and 30 % for the process treating filtered water without ozonation. It is surprising to notice a substantial increase in ash content with the PICA carbon. This has been confirmed by analysis of the calcium on the carbon which increased after 1 year operation to 4% m/m as Ca (ash content 11%).

5.3.4.9. Backwashing of the GAC Filters

Biological Activity The GAC filters were operated in accordance with the PICA recommendations for water temperatures above 10° Celsius. Regular backwashing of the filters every four days is recommended whereas at lower water temperatures a backwashing interval of seven days is reported to be better for maintaining biological activity on GAC. The relative performance of the coal based carbon and the PICA carbon after 1 year of operation (approximately 50000 bed volumes) indicated that the coal based carbon performed significantly better due to a higher bulk density and better adsorption of organic contaminants. Although BDOC was detected in the water after ozonation, the presence of biological activity on the carbon filters was difficult to confirm.

In an attempt to encourage biological activity on the carbon, the aggressive backwashing conditions especially during air-scouring were minimised, and the bed expansion during rinsing was reduced from 30% to 10% bed expansion. Another aspect which may have limited the biological activity was the fact that the water may have been biologically stable, and the mechanisms which promote biological activity may have been nutrient limiting. The length of the filter operation between successive backwashes was also lengthened to 7 days to establish whether this would encourage microbial growth on the carbon. Following a further period of operation of the GAC filters under the modified operating conditions, there was still no evidence of improved biological activity.

Carbon Abrasion - It was observed that the particle size of the carbon in all four filters reduced significantly during the 18 months operation. The vigorous backwash strategy initially adopted (3 minutes air scour and 30% bed expansion during the rinsing) also contributed to the excessive abrasion of the carbon particles. Some carbon manufacturers do not recommend the use of air during backwashing in order to limit carbon abrasion. The automatic backwashing was reliant on the correct functioning of level probes in the pilot-plant filters. On one occasion, the air blower was allowed to blow continually for a period of 48 hours over a weekend, during which time the carbon was abraded to such an extent that after subsequent backwashing, approximately 8% of the carbon had to be replaced. This indicated that the air scouring effect is extremely vigorous, and definitely contributes to overall carbon loss.

5.3.5. EBCT and Bed Depth Consideration

To characterise the size and operation of a GAC adsorber (filter) the following design parameters are used :

- Volumetric Flowrate
- GAC Bed length and depth of Carbon
- Volumetric Flowrate
- Filter Velocity (surface loading rate)
- Empty Bed Contact Time (EBCT)

Depending on the type of water to be treated, the pre-treatment processes, the specific reason for the use of activated carbon (TOC removal or biological stabilisation of the water), the process parameters may be considerably different. **Table 5.5** shows typical values for these parameters, and the EBCT can vary from 5 to 10 minutes in France to as high as 40 minutes in the Netherlands.

Table 5.5 ***Typical values for GAC adsorber parameters (Sontheimer et al, 1984)***

Parameter	**Units**	**Typical values**
Filtration velocity	m/hr	5-15
Filter GAC density	kg/m^3	350-550
Empty Bed Contact Time (EBCT)	min	5-30
Effective contact time	min	2-10
Operation time before Reactivation	days	100-600

In the initial study significant advantage of using ozone with GAC was observed and therefore the use of ozone is recommended. The operation of the pilot plant was then changed to assess differences in the performance of the GAC filters when operated under varying operating conditions (EBCT, GAC depth and filtration velocity). The following configuration was adopted :

Table 5.6 **Configuration of the pilot plant to monitor performance of different EBCT**

	CARBON	DEPTH	EBCT	VELOCITY	FEED WATER
Column 1	Coal Based Carbon	1,5m	10 min.	9 m/h	Filtered / Ozonated
Column 2	Coal Based Carbon	1,5m	20 min.	4,5 m/h	Filtered / Ozonated
Column 3	Coal Based Carbon	1m	10 min.	6 m/h	Filtered / Ozonated
Column 4	PICA Carbon	1m	10 min.	6 m/h	Filtered / Ozonated

Note : Columns 3 & 4 were operated under the same conditions as the initial pilot study (PICA carbon and Coal Based Carbon with ozonation and EBCT of 10 minutes).

The columns were operated for a period of four months, and little difference in the analyses from the columns was observed. A number of problems were experienced which may affect the operation of GAC filters. The filtration through column 1 was regularly affected. Low filtration velocities were observed, and these were caused mainly by filter blinding and gas entrainment within the GAC media. Although GAC filtration rates of up to 15 m/h are reported in the literature, careful design of the height of water above the filter is required to maintain positive pressures through the filter bed, to ensure adequate filtration.

5.3.6. GAC Adsorption and Breakthrough Experiments

It was noted (Section 5.3.4.5) that very little biological activity was evident on the GAC filters. Crittenden et al (1984) predicted adsorption mechanisms by performing laboratory-scale adsorption equilibrium studies as well as laboratory and pilot scale continuous adsorption tests on water containing NOM which was likely to affect GAC adsorption and full scale operation. Laboratory isotherm tests to establish the Freundlich equilibrium constants for geosmin, atrazine, 2-MIB and the four main THM species were performed (**Table 5.7**).

Table 5.7 Freundlich Isotherm Constants for a carbon sample

Contaminant and conditions of Isotherm	Concentration	K (mg/g)(ℓ/mg)$^{1/n}$	1/n
Atrazine (Filtered water from Wiggins Waterworks treating Inanda Dam water)	5 μg / ℓ	3009	0,350
Atrazine (Filtered water from Wiggins Waterworks containing Geosmin at 0,5 μg / ℓ)	5 μg / ℓ	1209	0,682
Geosmin (Filtered water from Wiggins Waterworks treating Inanda Dam water)	0,5 μg / ℓ	281	0.349
Geosmin (Filtered water from Wiggins Waterworks containing Atrazine at 5 μg / ℓ)	0,5 μg / ℓ	365	0.422

These constants may be used for predicting breakthrough once kinetic studies have been performed. The values of the K and 1/n constants also differ for different types of activated carbon, and depending on the accuracy of the analyses of atrazine and geosmin for example, the predicted breakthrough may be inaccurate. The constant K is proportional to the solid phase concentration of adsorbed species, and as shown in **Table 5.7** when geosmin is added to the water, the adsorption of atrazine is affected by a reduction in K from 3009 to 1209 (mg/g) (ℓ/mg)$^{1/n}$. A similar trend was not observed for the adsorption of geosmin onto GAC when atrazine was added to the water.

This could possibly be attributed to errors in the analysis of geosmin causing the regression analysis to be inaccurate. Duplicate experiments are required when performing this type of experiment to be able to obtain a more accurate estimate of the actual isotherm parameters. Small changes in background organic matter may also affect the outcome of the experiment depending on whether the organic compounds are strongly adsorbing and whether competitive adsorption is occurring.

Sontheimer et al (1988) detailed a Rapid Small Scale Column Test (RSSCT) which can be used to assess the adsorption of micro-contaminants onto activated carbon and then by using mathematical scaling techniques a rapid assessment of the full scale operation can be obtained. An attempt was made to conduct these tests in the laboratory but practical problems (grinding of the carbon, column blockages due the fine particle size of the carbon and subsequent tube bursts), resulted in the RSSCTs being abandoned.

A set of small columns were erected to monitor the adsorption of geosmin and atrazine on GAC, and to establish the period of time before breakthrough occurred. Provided sufficient time is available before the implementation of GAC is necessary, the operation of small pilot-scale columns can generate sufficient data for the accurate sizing and design of the full-scale application. Four different samples of GAC were obtained from carbon manufacturers specifically for the adsorption of geosmin and atrazine to establish the differences in the performance of different types of carbon for this application.

Each set of columns was designed to determine the breakthrough of contaminants at four different points in the carbon bed (**Figure 5.6**). Four mini columns were connected in series each with a bed depth of 200 mm representing a total bed depth for adsorption of 0,8m. The EBCT of each column was 1,5 minutes (total per set of columns - 6 minutes). Samples of the water leaving each column were taken on a weekly basis and monitored for geosmin, atrazine and UV absorbance @ 254nm.

Dosing of geosmin and atrazine to maintain a consistent concentration in the water was found to be extremely difficult. The geosmin sampling technique and dilution was particularly sensitive, so that the results of the analyses fluctuated during the trial. **Figure 5.22** shows analyses of geosmin and atrazine that were spiked into the water. Atrazine was easier to dose into the water as it is not as sensitive to temperature and is not as volatile as geosmin.

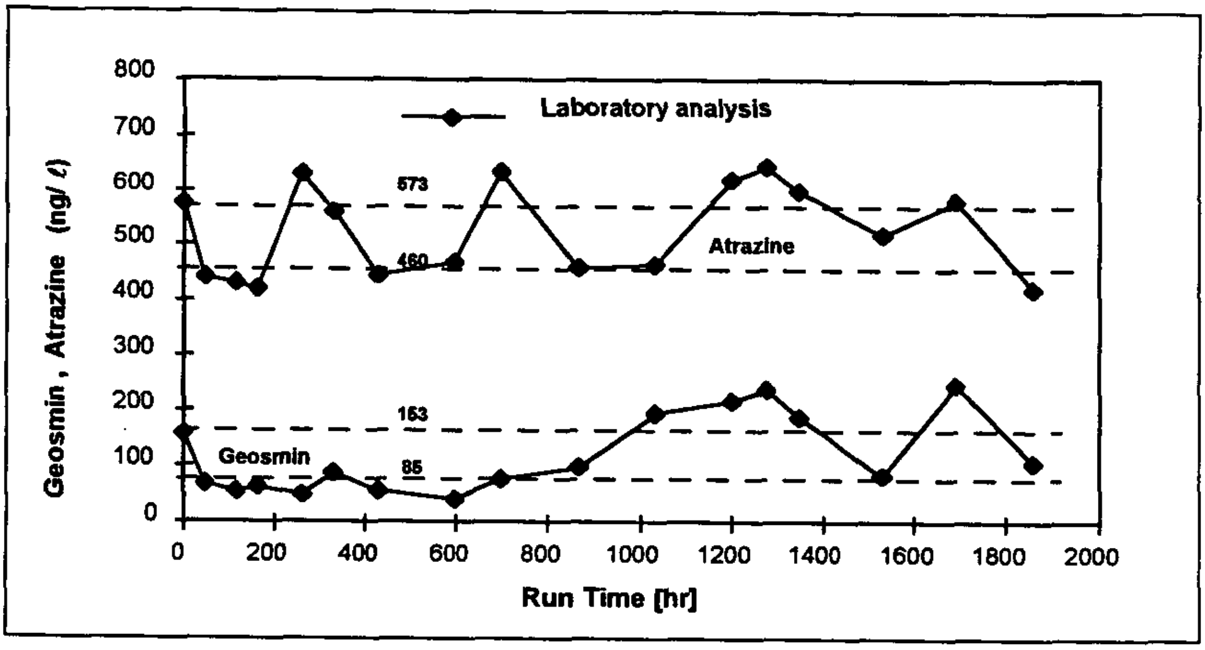


Figure 5.22 Levels of Atrazine and Geosmin dosed into the water

Due to the fact that geosmin was more sensitive to analysis and operator sampling, the breakthrough of atrazine only is shown in **Figure 5.23**. Breakthrough is considered to be the point at which the atrazine concentration exceeds 100ng/ℓ (ECC and EPA specification for total pesticides in water). Carbon types B and C were clearly better with regard to the adsorption of atrazine from the water, and only after 80 days of operation was breakthrough observed through the first mini-column (EBCT = 1,5 min). Carbon samples A and D were not as efficient in the removal of atrazine, and breakthrough was observed in the second column (EBCT = 3,0 min) after approximately 60 days of operation (after the filtration of 28000 bed volumes).

It is noticeable that the time required to achieve breakthrough on the second and third mini-columns appears proportionately longer than the time required to reach breakthrough in the first column. In order to fully predict the length of operation of a GAC filter with an EBCT of 10 or 15 minutes, a detailed model is required. The importance of the correct selection of carbon however is shown to be extremely important when considering the treatment of water. For the application of removing atrazine from Inanda Dam water, clearly carbon type B or C would be preferred to carbon type A or type D.

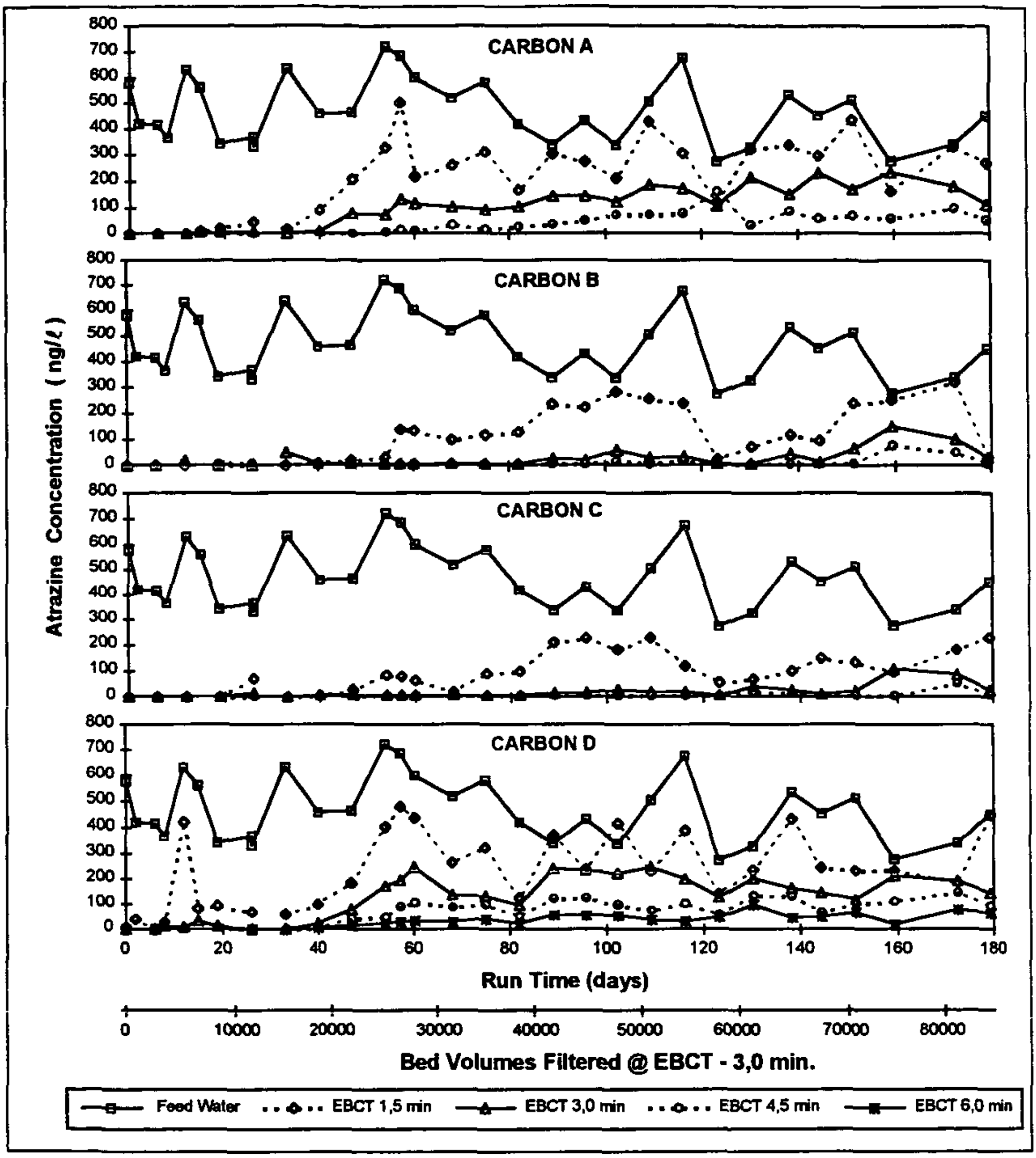


Figure 5.23 Breakthrough of Atrazine using different carbons

The UV absorbance @ 254nm of samples from the GAC mini-columns was also monitored **Figure 5.24**. Due to the amount of data, only the UV absorbance at an EBCT of 3,0 and 6,0 minutes is presented. A similar trend was observed in that carbon types B and C reduced the UV absorbance for a longer period of time than carbon types A and D. Although it was initially believed that UV absorbance may be an appropriate parameter by which a GAC filtration plant can be monitored, (to assess the point at which regeneration is required) no correlation between atrazine concentration and UV absorbance was observed.

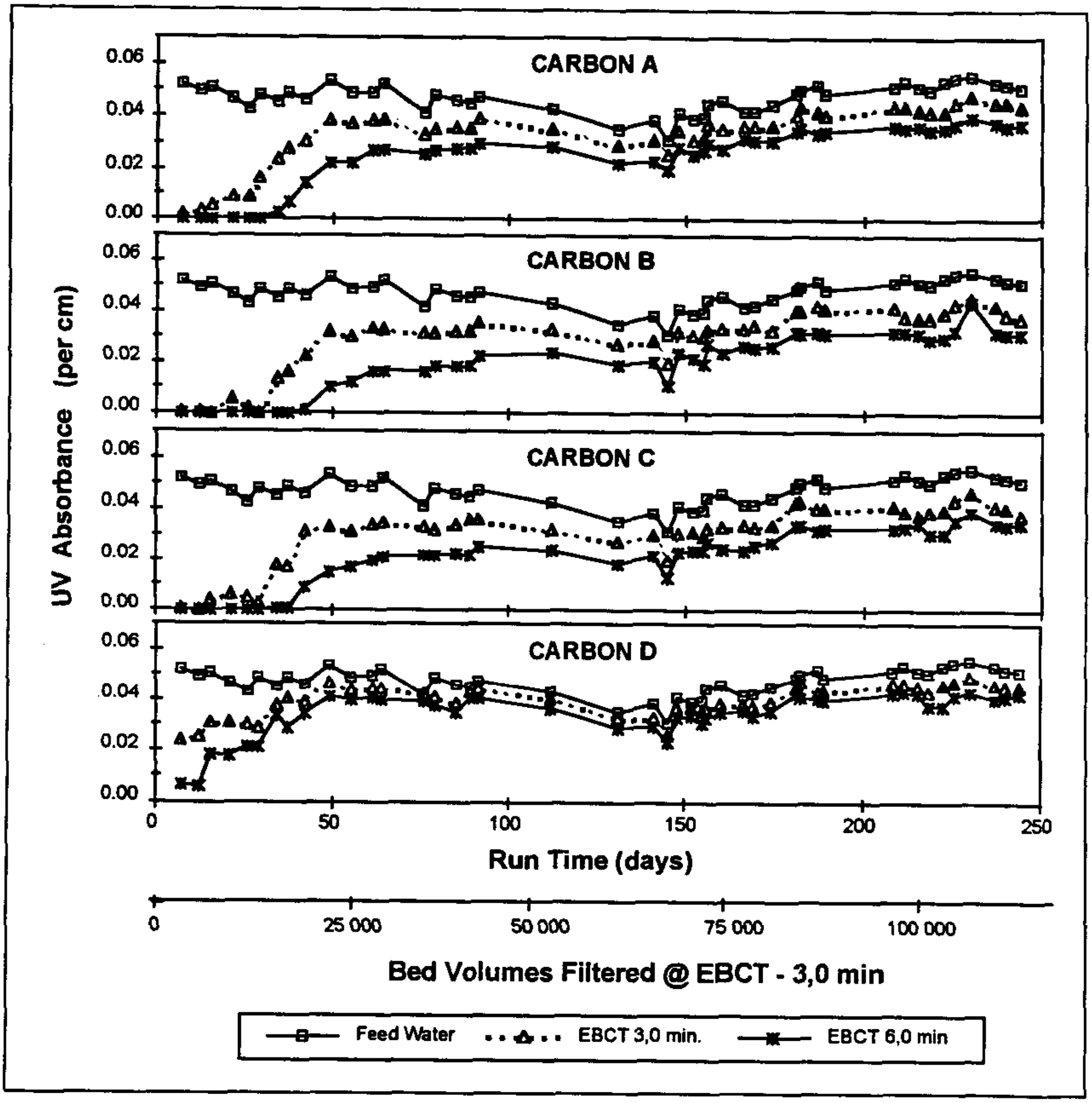


Figure 5.24 **UV absorbance @ 254 nm measured on samples from GAC mini-columns**

UV absorbance @ 254nm **Figure 5.24** shows that carbon D is not suitable for the removal of NOM, when compared to the other carbon samples. The carbon was almost saturated after 25000 bed volumes of treated water had been filtered, whereas at a similar point using carbon C the UV absorbance was reduced to between 50 and 60% of the UV absorbance of the feed water.

5.4. Summary of Conclusions

A number of conclusions can be drawn from the laboratory and pilot-scale experiments into the use of GAC for water treatment. In summary these are :

- Granular activated carbon can effectively be applied for the adsorption of taste and odour compounds as well as pesticides (atrazine) from surface water. This is particularly beneficial in the treatment of eutrophic waters where the extent of the taste and odour problems cannot be overcome using powdered activated carbon alone.
- The combination of ozone and GAC showed significant advantage and provided a more reliable treatment process.
- PICA carbon did not appear to be beneficial for application at Umgeni Water, as little or no significant biological activity was observed. The lack of biological activity was most probably due to a long retention time in the impoundment prior to the water entering the works. Although levels of BDOC of up to 1 mg/ℓ were measured in the raw water, most of this was removed by coagulation and sand filtration.
- The coal based carbons performed significantly better than the PICA carbon for the removal of organic micro-contaminants, due to a higher bulk density and a larger adsorption capacity.
- GAC provides a benefit in the reduction of chlorine demand, and once installed at a works should be utilised continuously to gain benefit even when the extent of eutrophication and pesticide problems are insignificant.
- Careful selection of GAC is required. Where biological activity is observed, the use of PICA carbon may prove to be beneficial for the reduction of BDOC, but where the adsorption of contaminants is the main objective the most suitable carbon should be selected. An attempt was made to assess the adsorption of contaminants using a RSSCT, but due to practical problems with the control of the experiments overnight these were abandoned.
- The effects of operating GAC filters at a higher filtration velocity, or with a deeper bed were not conclusive although some operation difficulties were experienced whereby negative pressures and filter blinding was observed. Specific process and head-loss considerations should be taken into account when specifying the depth of the GAC filters to prevent this from occurring.

6. Design Considerations for Ozone / GAC

The design and selection of a specific water treatment process, depends on a number of considerations and the following main objectives :

1. to improve the aesthetic acceptability of the water,
2. to remove any toxic or hazardous materials, and
3. to remove or inactivate any disease-producing organisms.

Sound engineering practice requires that design towards meeting these objectives should be done with a reasonable factor of safety, and with maximum economy. Information obtained from treatability and pilot-plant studies is essential for the development of a successful design and ultimately, a treatment facility that achieves its water treatment goals.

The use of ozone and granular activated carbon for the treatment of eutrophic water has, during this project, been studied on a laboratory and a pilot-plant scale. The ozonation facility at the Umgeni Water Wiggins Waterworks has recently been upgraded, and a feasibility study on the use of granular activated carbon at the works was completed. The recommendations and experience gained in by Umgeni Water is detailed as a guideline, but under different circumstances, other aspects may need to be considered.

6.1. Selection of Water Quality Parameters

In 1984, the World Health Organisation (WHO) published the first edition of Guidelines for drinking water quality. These define the criteria used to select various chemical, physical, microbiological and radiological contaminants, and describes the approach used in deriving guideline values. Regulating every chemical that may contaminate drinking water and that theoretically may adversely affect human health is impractical and irrational. In South Africa water authorities are guided by the SABS guidelines for water quality and the recent publication by the Departments of Health and Water Affairs and Forestry (1996).

In the United States, the National Drinking Water Advisory Council established the Safe Drinking Water Act (SDWA) in 1974 which requires the USEPA to publish primary drinking water regulations and to specify for each contaminant either a maximum contaminant level (MCL) or treatment techniques for the control of the contaminant. The most relevant considerations in the selection of criteria were the occurrence or the potential for occurrence of contaminants in drinking water, and the potential health risk.

The following principal requirements can be formulated to meet the standards as laid down by the W.H.O.

- Drinking water should be free of pathogens
- Drinking water should be free of micro-organisms
- Drinking water should be colourless, clear, and without objectionable taste and odour
- The dissolved solids content should be limited
- The water should be non-corrosive to the materials of construction of the distribution system
- Drinking water should be delivered in sufficient quantity and at sufficient pressure
- The cost of water should be taken into consideration

In most instances where ozonation and granular activated carbon (advanced water treatment) are considered, water is treated by conventional treatment and sufficient data has been obtained to justify the additional expense of implementing a more sophisticated process. Alternatively, the quality of the source water is such that advanced treatment is required to reliably supply an acceptable quality drinking water. In both instances the specific contaminants should be monitored to ascertain the extent of the pollution of the water supply.

With particular reference to the use of ozonation and granular activated carbon for the removal of organic contaminants, specific compounds should be identified and monitored. The efficient use of these processes requires the ability to accurately determine the concentration of the compounds of concern.

The selection of the proper analytical parameter is most often not straight forward, due to the wide spectrum of compounds, but can be grouped into three types of parameters :

1. **Specific organic compounds** - A single substance of concern may be selected, but normally the effects of the processes on one substance will be affected by the other substances in the water. Efforts are normally directed towards the collective characterisation of substances that are similar in structure and behavior.
2. **Collective parameters** - For the performance evaluation of ozone and activated carbon parameters such as overall dissolved organic carbon (DOC) can be used. These together with other analyses provide a reasonable assessment of the processes.
3. **Characterizing parameters** - Nearly all drinking water sources contain humic and fulvic substances. Characterization and isolation of these may not be practical but general methods like UV absorbance or THM formation potential may be more suitable to

evaluate the effects of ozone and granular activated carbon on the quality of final drinking water.

Some of the more common collective and characterizing parameters are listed below :

- **Dissolved Organic Carbon** - (DOC) This is comprised of both humic and non-humic substances and molecular weight fractionation can be used to determine what proportion consists of the larger more hydrophobic (humic) compounds and the smaller more hydrophilic (non-humic) substances (Owen *et al*, 1993). The humic fraction is more amenable to removal by adsorption or coagulation. The non-humic fraction has always been considered to present less of a problem for drinking water quality, although more recent evidence suggests that DBP can be formed from this fraction and that it may constitute the greater proportion of BDOC. DOC is in any case a good general surrogate parameter for NOM.
- **Chemical Oxygen Demand** - (COD) This test can be very useful for giving an indication of organic matter concentration in waters where COD is fairly high, such as in sewage effluents and highly polluted rivers. However, the test is not particularly accurate in determining the oxidisable organics when COD levels are below 20 mgO_2/ℓ and provides little information on the extent of biodegradation .
- **Organically bound chlorine and organically bound halogens** - disinfection of water using chlorine can give rise to chlorinated organic compounds and other organically bound halogen by-products generally referred to as disinfection by-products (DBP) (Water Quality and Treatment, 1990). These DBP are of concern as many have been found to have negative health implications. Principally these consist of trihalomethanes (THM), but other chlorination DBP, such as haloacetic acids and halonitriles can also be formed.
- **Organic acids** - some organic acids, such as the haloacetic acids (HAA) are formed as a result of chlorine disinfection (Standard Methods for the Examination of Water and Wastewater, 1995). There are a number of HAA, many of which have exhibited carcinogenicity (Water Quality and Treatment, 1990) and therefore constitute a health risk. In much the same way as a THMFP test can be conducted, a formation potential test for HAA can be performed and like the THMFP test, this would provide useful information regarding the concentration and nature of the NOM present in the water.
- **Other group parameters** - These include phenols, detergents, aromatic amines, aldehydes, ketones. Specific organic compound analyses can be undertaken in waters where these have been problematic. In this way, the effect of the various treatment

processes on specific organic compounds can be monitored and a more comprehensive characterisation of the organic matter present in the water can be obtained.

- **UV absorbance** - a number of organic compounds commonly found in water, such as lignin, tannin, humic substances and aromatic compounds absorb strongly in the ultraviolet spectrum and UV absorption is therefore a useful surrogate measure of the presence of certain organic compounds present in a water (Dobbs *et al*, 1972). UV absorbance can often be strongly correlated with organic carbon concentration, colour and THM precursors (Singer *et al*, 1981; Edzwald *et al*, 1985) and as a result provides a rapid and simple method for characterising NOM. For example, it can be used to monitor organic removal from water by coagulation (Edzwald *et al*, 1985), or changes to NOM as a result of ozonation.
- **Trihalomethane formation potential** - The trihalomethane formation potential (THMFP) test measures the potential of a water to form THMs under standard conditions and in the presence of an excess of chlorine. This test gives a good indication not only of the potential of a water to form DBP, but also of the concentration of naturally occurring and synthetic organics present in the water.

Specific organic compounds can be analysed by sophisticated analytical instrumentation, and the methods have been developed to detect these to extremely low levels :

- Pesticides and herbicides
- Taste and odour compounds released by algae - geosmin and 2-MIB
- specific chlorinated organics - chloroform

6.2. Identifying a Treatment Objective

The inclusion of Ozone and Granular Activated Carbon as advanced water treatment process, should be as a result of the identification of a specific need. By implementing a monitoring program and gathering information on the water treatment parameters of concern, a treatment objective can be formulated.

6.2.1. The benefits of ozone and GAC

The benefits of ozonation in the water treatment process or together with granular activated carbon are many and varied :

- Bacterial disinfection
- Inactivation of viruses
- Oxidation of soluble manganese
- Oxidation of soluble iron
- Splitting of organically bound manganese
- Removal of colour (by oxidation)
- Elimination of taste and odour (by oxidation)
- Elimination of algae (by oxidation
- Oxidation of organic substances (phenol, detergents, pesticides)
- Micro-flocculation of dissolved organic substances
- Oxidation of inorganic substances (cyanide, sulfide, nitrite)
- Pre-treatment for biological processes on sand, anthracite or granular activated carbon

Similarly granular activated carbon has specific applications in water treatment:

- Dechlorination
- Removal of taste and odour substances
- Removal of organic pollutants (pesticides, algal toxins)
- Biological stabilisation of the water
- Adsorption of inorganic compounds and heavy metals

6.2.2. Typical Areas where Ozone and GAC are applied

The treatment objective may include the following specific areas of concern :

- **The oxidation of iron and manganese in the raw water** - Iron and manganese are often present in surface waters. Increased pollutant loading with various wastewater, can result in reductive microbiological activity during the passage of the waters through rivers and impoundments. Oxygen rich compounds of iron and manganese can therefore become chemically reduced and dissolve in the water (Rice and Netzer, 1984). Subsequent aeration in the treatment process may be sufficient to oxidise most of the iron at neutral pH, which will hydrolyze, coagulate and precipitate as ferric hydroxide. The divalent manganous compounds however react much slower during aeration, and ozone can be used to improve the oxidation to manganic ions which then hydrolyze, forming an insoluble manganese dioxide.

- **The removal of organic carbon** - No significant benefit can be obtained by using ozone without additional treatment such as coagulation and filtration as there is little evidence showing a removal of organic carbon by ozonation alone (although O_3 may oxidise some to CO_2 at very high ozone dosages >100 mg/ℓ). Ozone provides a mechanism to depolymerise organic molecules, to precipitate dissolved organic carbon, to increase the polarisation of organic compounds. This can result in additional benefit during coagulation and flocculation, by the transformation of some organics into polyelectrolytes, thereby encouraging micro-flocculation, and transforming the dissolved organic carbon providing greater adsorption onto suspended matter. Granular activated carbon provides an adsorption capacity for the removal of organic matter. The use of GAC as a support for microbial growth, has been reported to be specifically beneficial for the removal of biodegradable organic carbon, and the removal of natural organic matter.
- **The removal of algae** - The effect of ozone on algae is dependent on the algal species and concentration. Removals of up to 75% of *Microcystis* is possible at ozone to DOC ratios of between 0,3 and 0,5 and almost complete removal (>99%) is obtained at ozone to DOC ratios of 1. In contrast to this, when *Anabaena* is the predominant species, removals are never greater than 70% and generally less than 40% even at ozone to DOC ratios greater than 1. However, ozonation followed by conventional treatment consisting of coagulation, flocculation, sedimentation and filtration generally resulted in complete removal of algae.
- **The reduction in taste and odour occurrences** - Ozone reacts with the organic taste and odour compounds in the water. These are typically released under certain conditions when algal cells become stressed. The levels of these compounds can be reduced by 50 % by ozonation, and further reduction to below the detection limit can be achieved by either powdered or granular activated carbon.
- **The removal of pesticides** - There are a number of herbicides in particular which have been detected in drinking water. Some pesticides such as aldrin, dieldrin and DDT have been severely restricted or banned in some countries due to their toxicity. Atrazine and other Simazines are of interest particularly in Europe as they are relatively stable in soil and aquatic environments. As with taste and odour compounds, ozone and GAC are suitable processes to ensure the removal of pesticides from drinking water.

- **The inactivation of microbiological contamination (Cryptosporidium & Giardia)** - Pathogens and other organisms have been found to be the cause of infection, diarrhea and disease in humans. These types of organisms are especially resistant to chlorine during disinfection, but the use of ozone (requiring a $C \cdot t$ in excess of 5 mg.min/ℓ) is regarded as being sufficient to inactivate these organisms.
- **The reduction of biofilm growth in distribution systems** - Biofilm growth and contamination of drinking water in distribution systems are caused by residual organic carbon (more specifically biodegradable organic carbon) and other nutrients in the water. These constituents are then a source for the promotion of microbial growth on the surface of pipes, but it is limited by the levels of residual chlorine used during final disinfection. A combination of ozone and GAC is being used extensively in the Netherlands as a secondary process following sand infiltration as a means of reducing the levels of biodegradable organic carbon in the water. The use of chlorine for disinfection is limited, but by significantly reducing the levels of nutrients the microbial contamination of the water in the distribution systems can be limited.
- **The reduction of THM forming compounds** - Where chlorine is used for final disinfection of the water the reduction of organic carbon and the removal of nutrients which may promote microbial growth, will limit the amount of chlorinated disinfection by-products (especially THM's) and at the same time reduce the chlorine demand of the water.

6.2.3. Treatment Philosophy for the Umgeni Water Wiggins Waterworks

A detailed study of the raw water quality from the Inanda Dam was undertaken over the period 1991 to 1993 (Hudson, 1993), where the future quality of the Inanda Dam water was predicted. The Inanda Dam provides a buffering effect for the quality of the water entering the Umgeni Water Wiggins Waterworks, whereby variations in turbidity and suspended solids are less marked than those for the inflowing river. Particulate material settles out rapidly, and extreme conditions are not regularly expected in the main basin.

In Southern Africa, drought cycles exist where over a period of years lower than average rainfall is common, and as the water level is drawn down, the impoundment will behave more like a riverine system, with less buffering effect from the impounded water. Flood events will then alter the water quality more rapidly and more extremely than normal. These events could introduce large volumes of cooler water, causing a density current and resulting in a rapid change in water quality.

Conclusions of the raw water quality study were the following :

1. Future raw water quality will be determined by the quality of the water impounded in the Inanda Dam, the management strategies in the upper catchment and the selection of draw off level.
2. Concentrations of iron, suspended solids and manganese are present and treatment will have to ensure that manganese can be dealt with during period of dam turnover.
3. Total algae numbers have been significant, where *Mycrocystis* levels in excess of 100,000 cells per mℓ have been measured. These have reduced in recent years, probably due to a reduced nutrient availability and increased sedimentation of nutrients.
4. Sludge loads are expected to be between 100 and 200 % greater during the summer period than the winter period.
5. When the dam is drawn down the impoundment will tend to behave more as a riverine system, with water in or near the main basin being affected more significantly by the inflowing river water.

Consideration of the water quality recommended the following process for the treatment of water from the Inanda Dam.

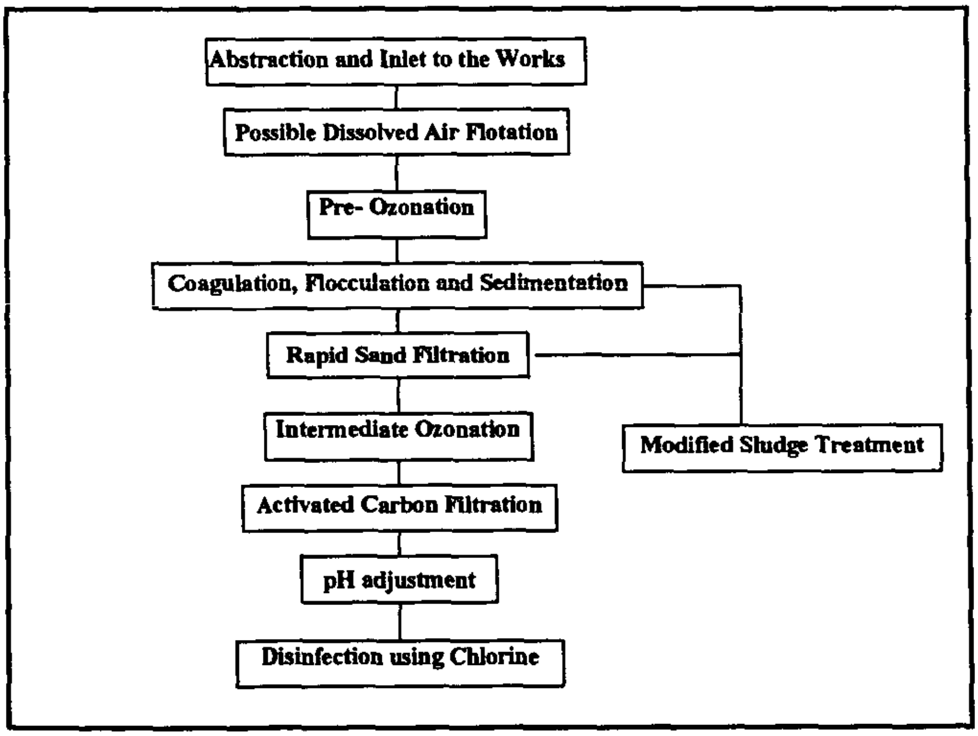


Figure 6.1 **Treatment Process for the upgrâde of the Umgeni Water Wiggins Waterworks**

6.3. Laboratory Studies

6.3.1. Ozone Treatability Tests

Before designing a pilot or full scale plant incorporating pre- or intermediate ozonation the optimal ozone dose in order to meet the treatment objective, needs to be established. Laboratory equipment consisting of an ozone generator and suitable contactor can be used to carry out pre-ozonation tests (on raw waters) or intermediate ozonation tests (on final filtered waters) using a range of ozone concentrations **Section 4.2.2**. Applied ozone doses to DOC ratios of up to 1 mg O_3/mg DOC could be investigated, with careful attention being paid to the low concentration range of around 0,05 to 0,3 mg O_3/mg DOC. Improvements in coagulant demand and reductions in NOM generally occur in this region. The optimum ozone dose is dependent on the treatment objective, but optimal removal of TOC, DOC, UV absorbance, colour and micro-pollutants (atrazine, geosmin and 2-MIB) was shown to occur at ozone to DOC ratios of approximately 0,2 to 0,5 with removals generally in the region of 30 to 60%.

When considering ozonation for NOM removal a number of surrogate parameters can be analysed, since NOM is difficult to characterise. These parameters included THMFP, TOC, DOC, BDOC, AOC, chlorine demand, UV absorbance and colour.

In order to fully optimise the pre-ozonation dose, the effect of additional treatment including coagulation, flocculation, settling and filtration should be assessed. This can be done using jar tests to determine the most suitable inorganic or polymeric coagulant for the treatment of the water, as well as the most effective dose **Section 4.2.1**. Optimal coagulant doses in terms of turbidity removal can be expected to increase removals obtained using pre-ozonation alone to as much as 50% in the case of TOC and DOC, and to 70% and more for UV absorbance, colour and micro-pollutants. Inorganic coagulants are recommended if NOM removal, particularly TOC, DOC and colour, are required.

6.3.2. Granular Activated Carbon

The most efficient way to obtain an indication of the effectiveness of various carbons for the adsorption of specific target compounds is to carry out adsorption isotherm adsorption tests. It is recommended that initial adsorption tests be carried out using ultra pure water to determine how well the test results correlate with literature values. Thereafter tests should be performed using the test water which can be spiked with specific target compounds so that the effects, that the background organics in the water have on adsorption, can be assessed. Adsorption isotherm tests can be performed as described in **Section 4.2.6**.

The results of these tests give an indication of the relative adsorption capacities of the carbon, but a number of repeat experiments should be performed as the nature of the background organics may change with variations in the raw water quality resulting in competitive adsorption and poorer removal of the target compound. It is also important to perform the analyses as accurately as possible as the adsorption parameters are determined by regression on a number of data points and scatter of these points may result in incorrect information. Finally the tests should be performed using concentrations of the target compounds in the range which they may are expected to occur naturally in the water. The temperature and contact time is essential as the isotherm parameters should be calculated once the adsorption has reached equilibrium. Often 12-24 hours is sufficient.

In order to assess the suitability of powdered activated carbon for use at Umgeni Water, other test methods were developed which attempt to simulate the conditions under which the PAC is contacted with the water. A "modified jar test" procedure which takes into account the coagulation and flocculation and the fact that PAC combines with the floc formed during these processes, has been successfully used in the assessment of powdered activated carbon for the reduction of taste and odour compounds.

Small scale column tests (SSCT) or rapid small scale column tests (RSSCT) have been used successfully by some researchers to provide useful information regarding GAC adsorption and regeneration in much shorter periods (4 to 8 days) than is possible on a larger scale. However, in order to determine which modeling equation to use to accurately design a RSSCT, it has to be established whether the carbon displays constant or proportional diffusivity. This is done by performing a differential column batch reactor (DCBR) test (**Section 4.2.7**). However, the DCBR tests were found to be rather problematic and a number of operational problems were experienced as the head build up during the test was often large. As a result, the RSSCT were not found to be particularly effective. Furthermore, small scale tests do not allow one to assess the effect of biological growth on the GAC filters and this can impact on both adsorption and regeneration.

6.4. Pilot Scale Studies

Pilot scale tests take significantly longer to complete that the small scale laboratory tests, and were found to be far more effective for monitoring the effects of biological activity and GAC performance (**Section 5**). Ozonation pilot studies can be used very effectively however to confirm process parameters determined during laboratory investigations, and these will provide sufficient information for final application of ozonation.

6.4.1. Ozonation Pilot Studies

The use of ozonation pilot plant studies are most useful when considering the process implications of ozonation. The pilot plant should be designed to dose at least 1 mg O_3/mg DOC. This will allow for further investigation of the effects of the ozone dose.

When designing and constructing a pilot-scale ozonation facility, ensuring the quality of the equipment will far outweigh the loss of time and frustration encountered for a less easily operable system or one where there are equipment malfunctions. The major expense of any system would in ant case usually be the skilled labour and analytical aspects required to operate the system and collect meaningful data. The design of pilot-scale reactors should follow the following basic guidelines :

- **Type of reactor** - The most commonly used system is a bubble column reactor where the gas is introduced at the base of the column and the water flows longitudinally through the column from top to the bottom. The hydrodynamics of the system can be designed for almost plug flow or totally mixed reactor, and the results from a plug flow reactor may severely underestimate the required ozone dose for a specific application. The hydrodynamics can be determined by tracer tests, once the reactors have been built.
- **Reactor depth and volume** - The reactor depth in a pilot study affects mainly the transfer efficiency. While high transfer efficiencies during pilot-scale experiments are not necessary, measurement of this to calculate the transferred ozone dose is required. The choice of reactor volume is determined by the water flowrate and the range of contact times to be investigated. For oxidation reactions, relatively short contact times are required, but where disinfection is being considered, contact times should be chosen to provide ***C•t*** values sufficient to meet the disinfection needs (inactivation of *Giardia* and *Cryptosporidium* for example). Reactor depths are typically between 3 and 6 meters and the diameter of the column can be between 0,1 and 0,4 m. These are normally manufactured of glass or clear PVC.

- **Liquid flowrate** - This is determined by the hydrodynamic needs of the pilot study, and particular care should be given to the reactor and pipe sizing of the pilot-plant to be able to achieve the required flow.
- **Gas flowrate and bubble size** - The diffuser system which is employed will determine the bubble size for a specific flowrate of gas. Optimum bubble size for an ozone reactor are in the range of 2 mm. Ideally the pilot-scale system should be able to vary the ozone dose by either changing the gas flowrate, or by changing the gas concentration at a specific gas flowrate.
- **Gas/Liquid ratio** - The larger the G/L ratio, the larger the back-mixing in the ozone reactor. Control over the G/L ratio can be achieved by planning for a wide range of gas concentration, thereby allowing a large variation in gas flow, for the specific liquid flow and contacting hydrodynamics.
- **Measurement of process parameters** - adequate provision of sampling points must be included to be able to measure both the gas and liquid flowrates, as well as the ozone concentration in the feed and off-gas from the ozone reactor. These need not be measured on-line but adequate frequency of sampling is required to ensure consistent operation. Measurement of the ozone residual may be necessary and particular attention should be given to the sampling technique as the ozone concentration degrades rapidly after sampling.
- **Performance parameters** - In addition to the ozone analyses, specific sampling and analyses of the water are required to monitor the plant for the specific treatment objective. The water may be treated by coagulation and flocculation to study the effects on optimum coagulant dose, and additional monitoring may then be required. Sampling and analysis of algae in the water, as well as TOC, colour, micro-pollutants and disinfection by-products are typical parameters which can be measured.

6.4.2. Granular Activated Carbon Pilot Studies

The adsorption of organics and micro-pollutants onto GAC depends on the adsorption properties of the GAC, as well as the relative concentrations of the pollutant under consideration, or the application for which GAC is being considered. In most applications viz. removal of DOC, organic micro-pollutants, pesticides and the production of a biologically stable water the benefit of ozonation has been documented (**Section 2.2**).

Two types of GAC pilot plant were considered **(Section 5)**. Initially the effects of biodegradation and subsequently adsorption of micro-pollutants was evaluated by performing a small scale adsorption test with relatively small empty bed contact times. This was performed to be able to assess the differences in the adsorption using different types of GAC. When considering the design of an adsorption system for monitoring the long term operation of GAC, the following parameters should be considered.

- **Empty Bed Contact Time** - This is often not known, and the primary objective of the pilot-scale studies may be to recommend an EBCT for the full-scale system. This is determined by the volume of GAC in the carbon filter and the filtration velocity. Typical values for EBCT's for specific application are mentioned in **(Section 3.2)**, and provision can be made to evaluate the effect of different sized carbon filters.
- **Linear filtration velocity** - This has been found to affect the shape of the adsorption front and breakthrough characteristics. The higher the filtration velocity, the quicker breakthrough may be observed, especially with weaker adsorbing compounds. The stronger the adsorption of the micro-pollutants, the closer the breakthrough is to an ideal (flat) breakthrough curve and an ideal plug flow reactor scenario. Similarly a slower filtration rate will produce a more ideal breakthrough .
- **Shape of the GAC filter** - The shape of full scale GAC filters is normally rectangular, but on a pilot-plant scale this is often difficult to construct. Circular filters are commonly used, whereby sections of pipe are assembled to form the body of the filter. The aim of a pilot scale filter is to obtain as best as possible the same flow through the filter as the full scale units. A ratio of particle size to column diameter of 50 is often designed to ensure that the wall effects are minimised. When considering biological activity a larger surface area of carbon is required, and a minimum column diameter of 300 mm is recommended (Bablon, 1991).
- **Backwashing of the GAC filters** - Routine backwashing of GAC filters is required, to remove suspended particles which are filtered out of the water. Biological growth on the GAC will also result in debris in the filter which needs to be removed. Provision should be made to monitor the head-loss through the carbon filter, and on this basis regularly backwash the filter. Other regular backwashing strategies have been recommended by Bablon et al (1991) whereby the need for backwashing is primarily to maintain an adequate biological population in the GAC and limit the development of higher life forms on the filter (e.g. Protozoa). The period between backwashing may be as long as seven days for water temperatures lower than 10 ^{0}C, and shorter filter run times for warmer temperatures. This procedure is detailed in **(Section 5.2.3)**.

6.5. Process Considerations

6.5.1. Enhanced Coagulation

As an initial consideration, enhanced coagulation is considered to be able to gain additional organic removal without having to incur major capital expenses. By utilising the existing process equipment, and incurring an additional operating expense by the use of higher doses of coagulants some benefit can be obtained.

Enhanced coagulation is effective for the removal of THMFP (up to 50% reductions), TOC and DOC (up to 60% reductions) and BDOC (70 to 90% reductions). If NOM removal is the primary treatment objective then enhanced coagulation using coagulant doses in the region of 1,5 to 7 times the optimal coagulant dose for turbidity removal is recommended, rather than the more expensive treatment processes of ozonation or advanced oxidation and GAC. The use of inorganic coagulants such as ferric chloride or alum are preferable under these conditions.

However, if removals of micro-pollutants such as atrazine, geosmin and 2-MIB are required, then enhanced coagulation would not be a suitable option. In such instances a treatment process incorporating GAC, preferably with both pre- and intermediate ozonation would be recommended.

6.5.2. Ozone

The main components of an ozone system will not be detailed here, but specific attention to the ozone generator, power supply and ozone destruction apparatus need to be addressed when considering an effective process design. The suppliers of equipment normally have the experience with the detailed aspects of these components as well as the design and implementation of a control strategy which will enable the most efficient operation of the equipment. The processes which affect the use of ozone for the treatment of eutrophic water and in combination with GAC are discussed.

Some of the fundamental decisions which may be required when considering the use of ozone are to determine:

- where is the best location(s) to employ ozone in the treatment sequence
- what ozone dose is required and
- what contact time is required

This information should be readily available from laboratory scale investigations, but due to differences in the quality of the water used during the laboratory or pilot-scale investigation, and the expected raw water quality, these need to be specified prior to the design of the system.

6.5.2.1. Pre-Ozonation

The use of ozone prior to coagulation has been used extensively to oxidise manganese, remove colour and oxidise algae. The effects of ozonation on NOM were studied in **Section 4.3.1**, by monitoring the THM formation potential, the UV absorbance of the water, as well as the concentration of micro-pollutants which were spiked into the water. The effects of ozone on the optimum dose of coagulant required is discussed in **Section 4.3.2**, and shows that under certain conditions the optimum dose required increases after ozonation, although at very low ozone doses some benefit can be obtained. When considering the effects of ozone on eutrophic water in particular, the species of algae or cyanobacteria present in the water need to be identified as the effects were found to be different for the species present in the Inanda Dam water. In general the DOC of the water tended to increase after ozonation when large numbers of algae were present in the water.

- **Ozone Requirements** - The amount of ozone is commonly related to the concentration of organic pollutants in the water. The most effective ozone dose to be able to gain advantage in a reduction of coagulant demand is in the low range (0,25 - 1 mgO_3/ℓ), but to obtain other effects at least 0,3 mgO_3/mg DOC is recommended. This is consistent with findings of Singer et al, 1988 who give a range of 0,3 - 0,4 mgO_3/mg DOC. It should be noted that in order to achieve adequate disinfection higher ozone doses may be required. The water quality will also affect the ozone requirements. For example the alkalinity, hardness and pH of the water are known to affect the rate of decomposition of ozone as well as the mechanism of ozone reaction. As a result a larger ozone dose may be required to obtain the required treatment objective. The mechanism of ozone reaction is most critical when there is a risk of forming hazardous disinfection byproducts, as bromates may be formed when bromide is present in the water, by a direct ozonation reaction. These are not formed as readily however when the radical ozone reaction occurs.

- ***Contact Time*** - *The contact time required for pre-ozonation is specified* to achieve maximum efficiency of the ozone. Sufficient time should be allowed firstly to maximise the dissolution of the ozone into the water, and secondly to allow it to react with any dissolved species. For disinfection of Cryptosporidium for example, the $C \cdot t$ of 5 mg.min/ℓ may be required to obtain 90 % inactivation. By maintaining a residual ozone concentration in the water of 0,5 mg/ℓ for a period of 10 minutes would therefore be sufficient to achieve similar results. Pre-ozonation normally aims for a 15 minute retention time.
- **Peroxone** - The use of peroxide in conjunction with ozone may improve the effectiveness of ozone by obtaining the same oxidation at a lower ozone dose The additional capital and operating costs of a peroxide dosing plant need to be considered against the cost of the slightly larger ozone generating facility. Peroxide to ozone ratios not greater than 0,3 (the stoichiometric ratio) are recommended.
- **Pre-ozonation Contact Configuration** - The important parameters to promote a high efficiency of dosing ozone are summarised as follows :
    1. High pressure and low temperature feed gas, with a high ozone concentration
    2. Optimum gas flowrates within the expected operating water flow of the plant
    3. Appropriately sized diffusers or other equipment to optimise the mass transfer
    4. Counter-current contacting with a down flow velocity below 0,2 m/s
    5. Long contact and reaction time for a high disinfection efficiency
    6. A minimum of submerged moving parts to facilitate reliable operation and low maintenance.

Various dosing systems have been used, and the best choice would require a knowledge of local *conditions and the expertise of the operating and maintenance personnel. The main types of ozone* contacting systems are described as follows.

- **Dome Diffusers** - which create a column of fine ozone gas bubbles, operated preferably in counter current to the water flow. Ozone transfer efficiencies greater than 90 % are common, and up to 99% have been obtained.
- **Venturi Injectors** - require a large side-stream flow of water and are 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 approx. 85 % and can be applied to relatively shallow reaction chambers.
- **Radial Injectors** - direct a side-stream flow of water containing ozone to a radial dispersing head which distributes the ozone horizontally through the water. These can be applied to applications where clogging of diffusers is expected and where large numbers

of algae are present in the water. High mass transfer efficiencies similar to diffusers can be obtained, but this requires additional motive water pumps and incurs additional energy consumption.

- **Static Mixers** - are a high shear mixing device used to distribute gas thoroughly in the water. This can be achieved by first injecting ozone into a smaller side stream and then combining this with the main flow of water, or by injecting the ozone directly into the water prior to agitation through a static mixer. A high transfer efficiency can be achieved but the performance is very dependent on the design of the mixer. It is recommended that the supplier give performance guarantees for the application with ozone. These may cost more than other contacting arrangements, and result in a higher head loss for flow of the water through the plant, but are low maintenance items with no moving parts.

6.5.2.2. Intermediate / Post Ozonation

Intermediate ozonation is specifically installed when subsequent processing with GAC is considered. Ozone has shown to be beneficial for the promotion of biological growth on the GAC filters, by converting some of the DOC to a biodegradable fraction which can be assimilated by microbial organisms in the carbon filters. Where GAC is not present the post ozonation treatment can be used specifically for final disinfection where there may still be a risk of contamination of the water in the presence of protozoan parasites. Post ozonation may therefore reduce the amount of chlorine required for the protection of distribution systems.

- **Dosing System** - The dome diffuser system is the most widely used, especially in low turbidity applications and after sand filtration. High mass transfer can be expected and few problems with the blockage of diffusers can be expected. The number of diffusers, the gas flowrate and the size of the diffuser is critical to the effective operation and bubble size generation for effective contacting.
- **Ozone Requirements** - Where pre-ozonation has occurred, the main use of intermediate ozonation would be to stimulate biological activity on GAC, to assist in the removal of DOC and to ensure that the concentration of any taste and odour compounds as well as pesticides are reduced to acceptable levels. In such cases ozone doses up to 0,3 mgO_3 / mg DOC may be required, and possible ozone doses as high as 2 - 3 mg/ℓ may be required to reduce the micro-contaminant levels by up to 70% (**Section 4.3.1.3**). Where pre-ozonation is not implemented the main treatment objective may be final disinfection of the water. Under these circumstances, sufficient attention should be given to the ***C•t*** requirements and the expected contamination of the water supply.

6.5.3. Granular Activated Carbon

6.5.3.1. Converting from Powdered Activated Carbon to GAC

Powdered activated carbon (PAC) is often used when the incidence of taste and odour, and pesticide problems at a waterworks are infrequent. Monitoring of the water quality to detect increases in these compounds, to initiate PAC dosing procedures is common. As the frequency of pollution incidents increase, larger amounts of PAC are required and a more cost effective and reliable means of providing a barrier against contamination of potable water becomes necessary. This is provided by ozonation and GAC.

Ozonation alone can provide a reasonable barrier against micro-pollutants by oxidising them to other by-products, and the need for large amounts of PAC is reduced. The use of GAC however would be significantly more expensive than PAC dosing, but would be permanently in place. The decision to implement GAC would therefore depend on the ease of operation of the GAC when compared to having to make up a slurry of PAC and the associated mechanical maintenance of dosing the PAC.

An economic comparison between PAC and GAC may show that the continuous dosing of PAC at >15 mg/ℓ is more cost effective than the installation of GAC with a regeneration frequency of 18 months. If this was the only basis on which a decision to implement GAC is based then it is unlikely that such filters would ever be constructed.

In most applications PAC should be used where low levels of contaminants are experienced. There are however practical limitations in the design and sizing of PAC dosing installations:

- limitations in the storage and handling of large volumes of PAC.
- excessive dosing of PAC may result in the breakthrough of carbon through sand filters.
- larger volumes of sludge removal from clarifiers.
- possible sludge dewatering and handling difficulties due to the presence of carbon

Similarly the backwashing of GAC filters has been associated with problems in the handling of backwash waters:

- carbon fines entrained in the backwash water do not tend to settle readily, and
- additional treatment of the backwash waters may be required.

The quality of the final water produced using PAC can not really be compared to the quality of water filtered through GAC as the latter provide a number of additional benefits as described in **Section 6.2.1**.

6.5.3.2. GAC Filter Sizing and Specification

Empty Bed Contact Time - The empty Bed Contact Time (EBCT) is the time required for water to pass through the empty filter column or bed, and can range from 5 to 40 minutes. This is commonly designed once information on the specific adsorption characteristics have been determined. The stronger the adsorption of micro-contaminants, the lower the EBCT required. This is often related to the regeneration frequency and a planned procedure of frequent regeneration and minimising the risk of breakthrough should be adopted. In the Netherlands for example, an EBCT of 40 minutes was designed that the carbon would be regenerated over an 18 month cycle. This was designed for a specific feed concentration of pesticide.

The presence of biological activity in a granular media filter will assist in increasing the time between regeneration. To be able to provide a reliable process for taste and odour compound removal (resulting from eutrophic conditions) an operation strategy of frequent regeneration is recommended. The results **(Section 5)**, show that a GAC system using coal based carbon, and operated with an EBCT of 10 minutes was capable of removing atrazine to levels below 0,1μg/ℓ over a period of 60000 bed volumes. The cost comparison of reducing the capital cost by designing a lower EBCT versus a lower operating cost in having to remove and regenerate the carbon less frequently should be assessed.

Bed Depth and Hydraulic Loading - These parameters are related for a specific design flow of water through the plant, and seem to have no effect on the adsorption characteristics of GAC. The headloss in a packed bed is directly related to the hydraulic loading. Where the GAC filters are performing on additional filtration function, the hydraulic loading in deep filters may result in negative pressure in the bed and subsequent filter blinding. The choice of filter configuration, upflow versus downflow, or gravity versus pressurised flow may be considered at this stage. Gravity flow is considered to be feasible up to a hydraulic loading of 12 - 15 m/h, but when a high level of biological activity is expected the hydraulic loading may have to be limited to less than 10 m/hr.

Backwashing Considerations - GAC is sometimes used as a replacement for sand in gravity sand filters and as such will require backwashing at normal intervals. Alternatively, GAC is used as secondary filtration process primarily for the removal of TOC. Biological activity can result and may contaminate the effluent during filter operation. The GAC has also proven to be effective as a polishing filter, and improves the turbidity of the effluent, which results in a gradual head loss development over the filter. Consequently, the carbon must be backwashed periodically to reduce head loss and limit the bacterial counts in the final water.

During start up of a GAC installation, the filters are loaded with carbon, and the carbon should be left for a period to become completely wetted. Thereafter the filters should be backwashed to remove fine carbon particles from the new or regenerated carbons. A stratification of the carbon particles will also occur during the initial backwashing.

- **Frequency** - The frequency of backwashing normally depends on the head loss across the GAC filter. When GAC is used for pre-treatment and turbidity removal, the larger uniformity coefficient of most GAC's when compared to sand can result in a faster build up of head loss. Under these circumstances backwashing every 24 - 48 hours can be expected. When GAC is used for post treatment, the frequency will be significantly lower with filter run times in excess of 7 days. During the GAC pilot plant trials **Section 5.3** a backwashing frequency of 7 days was employed.

  In order to obtain effective biological activity using PICA carbon, Bablon et al (1991) recommend specific backwashing frequency to maintain a specific population of bacteria on the carbon. The limiting factor in this instance is not the head-loss development but the population of bacteria of protozoa in the filter media. The temperature of the water affects the rate of reproduction of the micro-organisms, therefore where the temperature is below 10°C a backwashing interval of 14 days is recommended.
- **Backwashing Rate** - The backwashing rate is primarily determined by the density of the carbon (which will vary depending on the type of carbon), and the bed expansion required to effectively remove the entrained colloidal particles and biomass from the filter. During the GAC pilot plant investigation a backwashing rate of 30 m/hr was used to obtain between a 15% and 30% bed expansion.

  The use of mixed air/water for the backwashing of sand filters can be employed for GAC and is recommended for BAC to introduce aerobic conditions in the GAC bed and assist in the break-up of mud balls or clumps of GAC. This is especially true for GAC filters with high biological activity. The use of air can cause flotation of carbon particles and lead to high carbon losses. Air will also result in higher carbon abrasion and may lead to excessive carbon losses.

- **Control** - The control of backwashing of GAC filters is similar to the control of rapid sand filtration. This is normally timer based for routine backwashing, but can incorporate a head loss monitor which will initiate the backwashing sequence. This may create problems during the operation of more than one filter as more than one filter could backwash simultaneously, thereby requiring a larger volume of backwash water. An automated timer system therefore tends to be more flexible.

Filter Configurations - GAC can be implemented in a number of different configurations :

- **Single bed downflow filters** Traditionally GAC filters have been designed to operate in much the same way as conventional downflow sand filters, with water entering the filters above the carbon and being collected below the carbon after flowing down through it, as shown in **Figure 6.2**. In these filters the size of the filter media particles tend to increase through the filter from top to bottom, as a result of stratification of the filter bed during back washing.

The theory of adsorption of organic compounds onto activated carbon is well described in the literature. From these descriptions it is known that loading of the carbon with organic compounds does not take place uniformly. A particular organic compound develops a "front" as the carbon becomes loaded. The front moves through the bed and when it reaches the bottom of the bed the organic compound associated with the front is released into the product water and "breakthrough" is said to have occurred. This may not mean that the entire carbon filter is saturated with the organic compound concerned. Up to about 50 percent of the carbon in the filter bed could still have a high degree of adsorption capacity, see **Figure 6.2.**

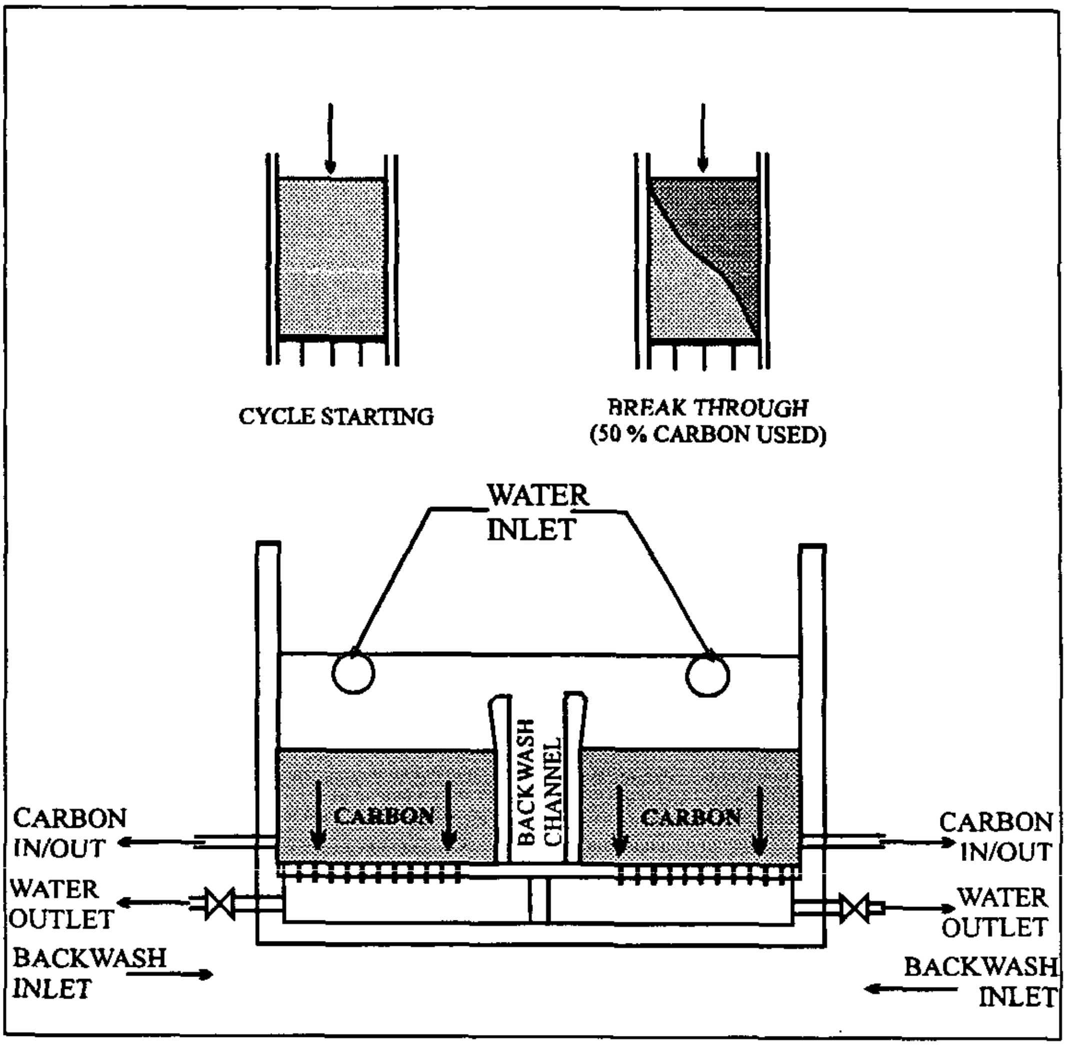


Figure 6.2 **Single Bed Downflow GAC Filter**

The need for more frequent regeneration resulting from uneven loading of the carbon is a disadvantage of this configuration.

- **Dual bed dualflow filters** - Dual bed dualflow filters consist of two equally sized filter cells that are operated in series. Water enters the first cell from below and flows upwards through the carbon before entering the second cell and passing downwards through the carbon in the second cell, as shown in **Figure 6.3.**

The reason for introducing the dualflow filter is to make better use of the total carbon adsorption capacity. As the filtration cycle progresses the first cell (the lead filter bed operating in the upflow mode) becomes progressively saturated with impurities and at some point the adsorption front will break through from the first cell into the second cell (the lag filter bed operating in the downflow mode. It can be presumed that the carbon in the first bed has lost approximately 50 percent of its adsorption capacity. As the filtration cycle continues breakthrough would eventually occur from the second cell. At this point the carbon in the first cell is about 75 percent saturated, while the carbon in the second bed is about 25 percent saturated.

The carbon in the first cell is removed for regeneration. The second cell then becomes the lead filter. This can be achieved by either transferring the carbon hydraulically from the second cell into the first cell, or by designing the filters such that they are able to operate as either lead or lag filters. The carbon removed from the lead filter would be replaced with fresh or regenerated carbon.

The main advantages of the dual bed dualflow GAC filter configuration, when compared with a single bed filter filled with the same type of carbon and operating at the same EBCT are:

1. The time between carbon regeneration is longer because of the better utilisation of the carbon adsorption capacity.
2. Although the amount of ozone released from the water above the single bed filters is not expected to be significant, the dual flow dual bed configuration ensures that the feed water to the GAC always enters the first filter from below the carbon. In this way ensuring that there will be no ozone residual in the vapour above the carbon filter.

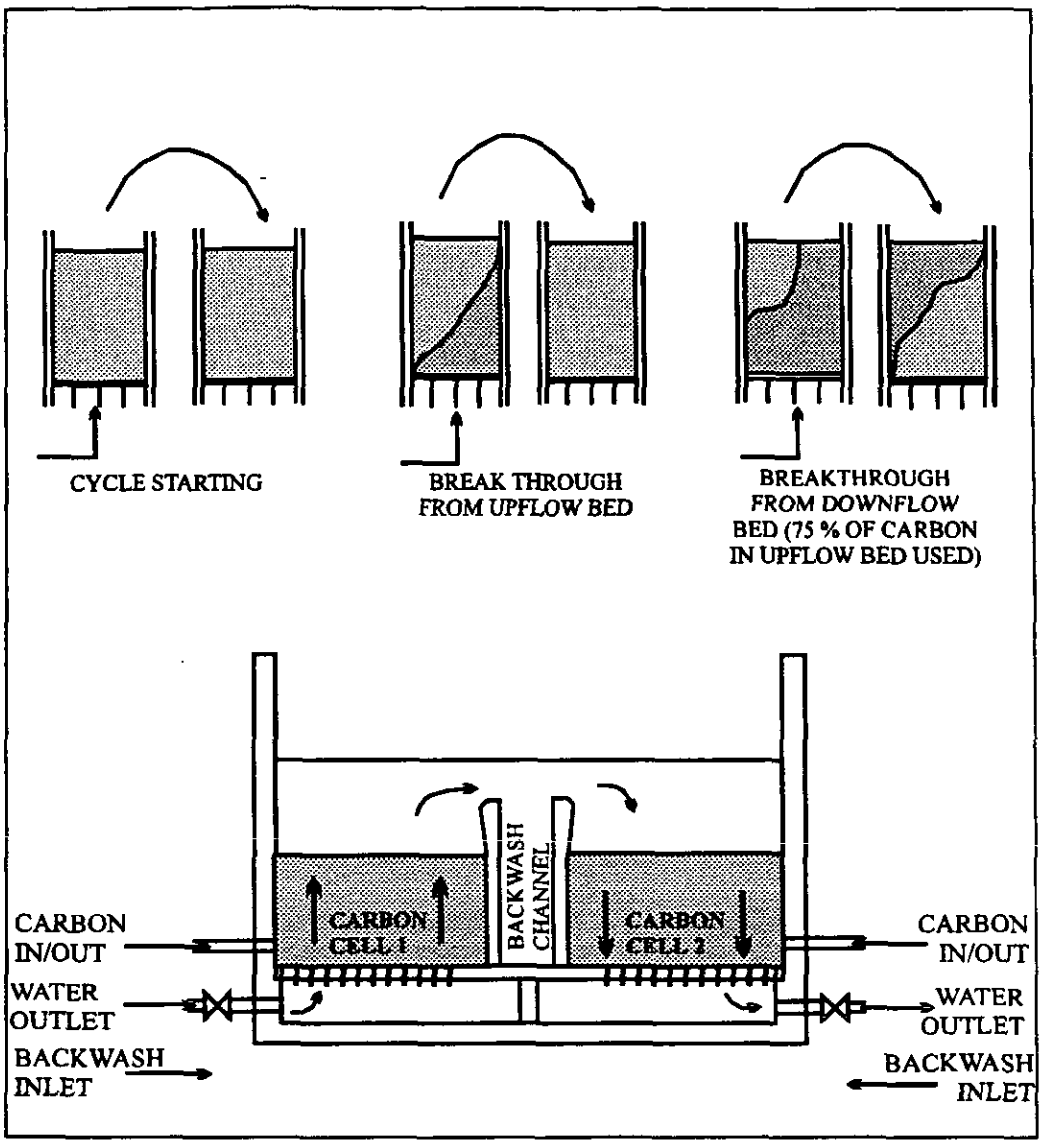


Figure 6.3 **Dual Bed Dualflow GAC Filter**

For this configuration a larger filtration area and infrastructure is required thereby increasing the capital cost for a specific EBCT.

- **Single Bed Two Stage Downflow Filtration** - This configuration is similar to the single bed downflow filtration, except that the water from a first GAC filter is then pumped to a second GAC filter (**Figure 6.4**) to be able to utilise the GAC capacity in a similar way to the second option. In this option the carbon normally remains in a particular filter and an intermediate pumping stage is designed to pump from either of the two filters to the other depending which filter happens to be selected as the lead filter.

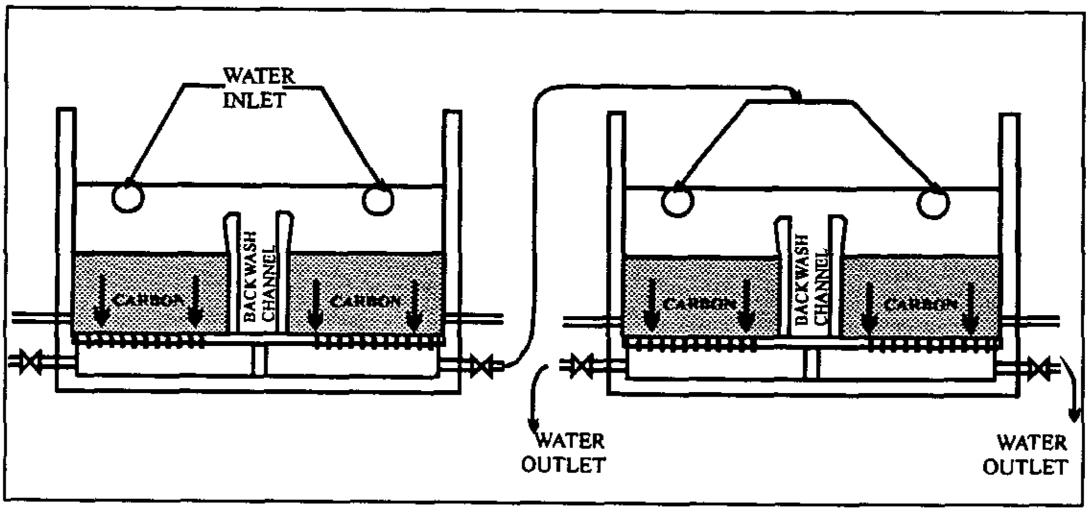


Figure 6.4 **Two Stage GAC Filtration**

The main disadvantage of this is that the filtration area doubles for a specific flow and EBCT, and an additional operating cost is incurred by having to pump between stages. An advantage of this though is that the quality of the water can be monitored between the two filters and breakthrough from the first filter is an advanced warning indication of possible breakthrough through the second filter. The warning may then provide sufficient time to adequately regenerate the carbon in the lead filter before the quality of the final water is affected. The adsorption capacity of the second filter therefore provides the security that regular sampling of the water between the two filters could be performed on a less regular basis.

- **Pressure Downflow Filtration** - A steel fabricated vessel normally with a flanged section, can be provided by most of the carbon suppliers. These are specifically sized and designed, and are easy to install on site. Provision is made for all the necessary connections required for smooth operation and backwashing of the filter (**Figure 6.5**). The filters are modular and can be connected as single stage or dual stage configuration. An adequately sized feed pump is required to pump into each vessel, and in this regard additional operating and maintenance costs will be incurred, when compared to gravity flow filtration.

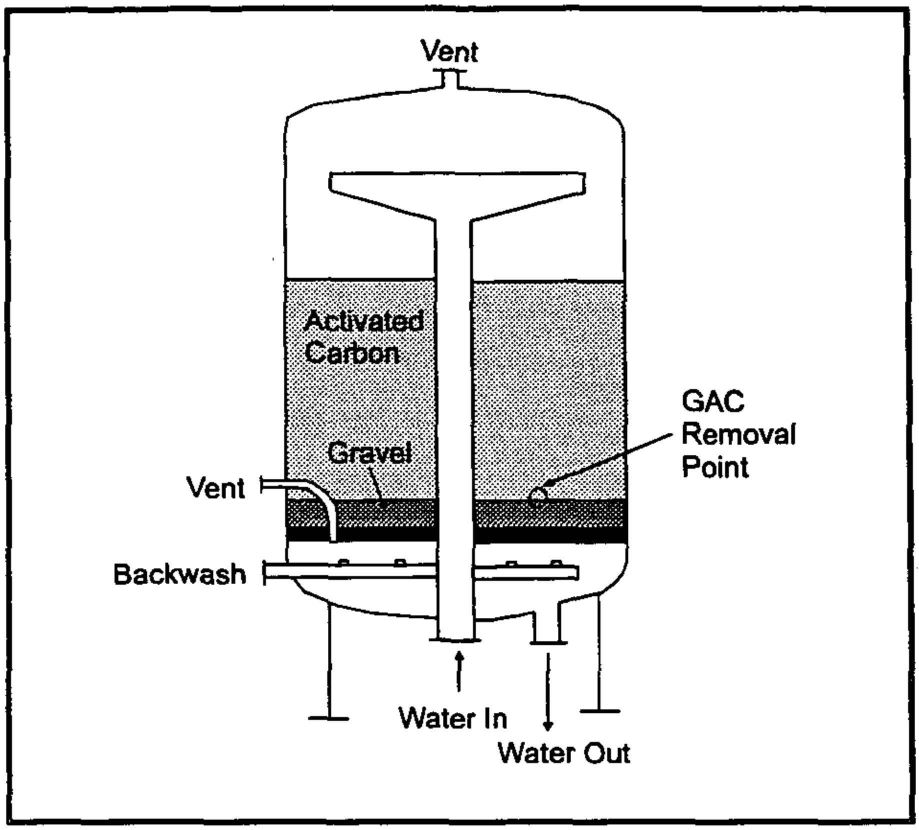


Figure 6.5 **Typical GAC Pressure Filter**

6.5.3.3. Reactivation and Regeneration

Once "breakthrough" has been observed and the resultant water quality does not meet the required standards, the GAC must be removed from the contactor and replaced with fresh or reactivated carbon.

Regeneration methods include steam, thermal and physiochemical regeneration, and these are is followed by thermal reactivation processes which burn off the carbonaceous residual on the carbon surface. The following processes have been applied to water treatment carbons :

- **Steam Regeneration** - Low temperature regeneration using steam at 130 - 200°C is commonly used for the removal or solvents and heavy organics from GAC. The solvents volatilise and are transported out of the carbon with the steam into a condenser. The presence of non-volatile compounds do not desorb under these conditions and reduce the carbon's adsorption capacity.
- **Thermal Desorption** - The carbon is heated to temperatures above 400°C in an inert environment, and at specific temperatures the extent of the desorption of other more strongly adsorbing compounds can be optimised. The desorption of humic substances

from macropores on some carbons may not be efficient however, and other techniques may be necessary.

- **Physiochemical Regeneration** - Various chemical techniques are documented for the removal of specific compounds from ion exchange resins and activated carbons. A shift in the pH by the addition of NaOH for example may result in significant desorption of certain compounds. Acid and base aqueous solutions are reported to reduce the organic matter by only 20 - 30 %. The use of specific solvents can be used but these often result in other substances adsorbing onto the carbon and causing a loss of adsorption capacity. Acid washing is also used to remove metals or metal complexes from the carbon.
- **Thermal Reactivation** - This requires high temperatures and reaction conditions similar to those used for the thermal manufacture of the carbon. The objective of the manufacture is to burn a portion of the carbon to form an optimised structure (i.e. a balance between the number of adsorption sites and the pore size). During the re-activation however the objective is to remove the adsorbed material without altering the carbon structure. The adsorption capacity of the carbon is therefore likely to change after the first reactivation, but after successive reactivations no significant change occurs. A larger pore volume may indicate a benefit in the removal of larger compounds as measured by DOC or UV absorbance, but the removal of smaller compounds and micro-contaminants may be adversely affected.

6.5.3.4. Selection of Carbon for GAC Treatment

The selection of carbon is a consideration which is often overlooked, especially when using GAC for the removal of micro-contaminants resulting from eutrophic water. The type of GAC will affect the removal of taste and odours and other micro-contaminants. Often laboratory experiments are conducted to determine the Freundlich isotherm parameters for the adsorption of micro-contaminants. Although the parameters obtained give an idea as to which type of carbon may be more suitable for the removal of a particular component, other background organics in the water are known to create competitive adsorption and reduce the effectiveness of the GAC.

Competitive adsorption has been shown to affect the less strongly adsorbing species and result in faster breakthrough. Taste and odour compounds (geosmin and 2 MIB) do not adsorb as strongly as pesticides and atrazine for example and for this reason careful selection and pilot scale experiments are required to determine the effectiveness of different carbon types. The carbon manufacturers have rapid assessment techniques which can be useful to be able to obtain a good indication of the effectiveness of the GAC for a specific application. In most circumstances the carbon manufacturers may also give a performance guarantee provided they have performed the tests and assisted in the sizing of the GAC contactors. This may be excessive and greater than required amount of carbon may be specified.

A mini-column pilot plant can be used to compare different types of carbon, and the breakthrough profile of micro-contaminants can be monitored over a period of time. In this way an assessment of the adsorption behavior can be evaluated. **Section 5.3.6** shows the breakthrough of geosmin and atrazine for different EBCT's and shows that the levels of atrazine can be removed using two types of carbon, but the other types performed poorly when the results were compared. The cost of carbon is usually high (approx. R9000/ ton) and the savings that could be derived by selecting the correct carbon could therefore be significant.

7. Conclusions and Recommendations

The following conclusions can be drawn from this project. The laboratory investigation addresses mainly aspects related to ozonation and the pilot plant study aspects related to GAC. In summary these are:

7.1. Laboratory Investigation

The conclusions drawn from the laboratory investigation are :

- Ozone was not generally found to affect the THMFP, TOC and DOC greatly, although decreases in the TOC and DOC of up to 25% were possible. The effect of ozone on these parameters is dependent on the nature and concentration of the NOM.
- Ozone increases BDOC and brings about reductions in UV absorbance and micro-pollutants (geosmin, 2-MIB and atrazine). Applied ozone doses of between 0,5 and 1,5 mg O_3/mg DOC can reduce UV absorbance by up to 70% and micro-pollutant concentrations by over 70%.
- Ozone is good for colour removal. Ozone concentrations of 0,1 to 0,4 mg O_3/mg DOC can result in 40 to 60% removal of colour, and this can be increased to over 90% if conventional treatment is used after ozonation.
- The effect of ozone on the optimum coagulant dose is dependent on the type of coagulant, the water source and, for eutrophic waters, on the cyanobacterial species and concentration.
- An applied ozone concentration of between 0,1 and 0,3 mg O_3/ mg DOC is usually required before significant decreases/increases in NOM surrogate parameters and micro-pollutants are obtained. Ozone doses higher than this do not generally result in much additional change in these parameters.
- A small decrease in THMFP, TOC, DOC, UV and optimum inorganic coagulant demand was often observed at ozone concentrations of between 0,01 and 0,3 mg O_3/mg DOC.
- High hardness concentrations were not found to significantly impact on the effect of ozone on most NOM surrogate parameters and micro-pollutants, except for the BDOC, which generally decreased, rather than increased, after ozonation.
- Enhanced coagulation was effective for the removal of THMFP (up to 40% reductions), TOC and DOC (up to 60% reductions), and BDOC (70 to 90% reductions), but was not effective in reducing micro-pollutants. The only benefit in pre-ozonation prior to enhanced coagulation is in the removal of micro-pollutants.

- Peroxide used in conjunction with ozone generally results in the same effect as that achieved with ozone alone, but this occurs at a lower ozone dose.
- Peroxide to ozone ratios in excess of 0,3 do not increase the benefit derived from ozone alone.
- Advanced treatment processes become more economically attractive on large works when treating relatively polluted waters.

7.2. Pilot Scale Investigation - GAC

A number of conclusions can be drawn from the laboratory and pilot-scale experiments into the use of GAC for water treatment. In summary these are :

- Granular activated carbon can effectively be applied for the adsorption of taste and odour compounds as well as pesticides (atrazine) from surface water. This is particularly beneficial in the treatment of eutrophic waters where the extent of the taste and odour problems cannot be overcome using powdered activated carbon alone.
- The combination of ozone and GAC showed significant advantage and provided a more reliable treatment process.
- PICA carbon did not appear to be beneficial for application at Umgeni Water, as little or no significant biological activity was observed. The lack of biological activity was most probably due to a long retention time in the impoundment prior to the water entering the works. Although levels of BDOC of up to 1 mg/ℓ were measured in the raw water, most of this was removed by coagulation and sand filtration.
- The coal based carbons performed significantly better than the PICA carbon for the removal of organic micro-contaminants, due to a higher bulk density and a larger adsorption capacity.
- GAC provides a benefit in the reduction of chlorine demand, and once installed at a works should be utilised continuously to gain benefit even when the extent of eutrophication and pesticide problems are insignificant.
- Careful selection of GAC is required. Where biological activity is observed, the use of PICA carbon may prove to be beneficial for the reduction of BDOC, but where the adsorption of contaminants is the main objective the most suitable carbon should be selected. An attempt was made to assess the adsorption of contaminants using a RSSCT, but due to practical problems with the control of the experiments overnight these were abandoned.
- The effects of operating GAC filters at a higher filtration velocity, or with a deeper bed were not conclusive although some operation difficulties were experienced whereby negative

pressures and filter blinding was observed. Specific process and head-loss considerations should be taken into account when specifying the depth of the GAC filters to prevent this from occurring.

7.3. Design Recommendations

The design and selection of a water treatment process incorporating ozone and GAC depend on a number of factors with the main objectives being :

1. to improve the aesthetic acceptability of the water,
2. to remove any toxic or hazardous materials and
3. to remove or inactivate any disease-causing organisms.

Typical situations where ozone and GAC may be applied are:

- in the oxidation of iron and manganese in raw water using ozonation.
- for the removal of organic carbon, using pre-ozonation, conventional treatment and GAC filtration (preferably preceded by ozonation).
- for the removal of algae by pre-ozonation, conventional treatment and GAC filtration.
- to reduce taste and odour compounds and other micro-pollutants such as pesticides and herbicides, ozone and GAC filtration being suitable processes for these applications.
- for the inactivation of microbiological contamination, especially pathogenic protazoa such as cryptosporidium and giardia, which ozone is effective in removing.
- to reduce DBP precursors, using ozone and GAC.

It is recommended that when considering an ozone or GAC installation the following be included prior to detailed design stages on the project. Ozone treatability tests on a laboratory scale should be used to determine the optimum ozone concentration for NOM and micro-pollutant removal, an ozone to DOC ratio of 1 being recommended. For improvement in coagulation however, an ozone to DOC ratio of between 0,05 and 0,3 is recommended. Pilot plant tests can be used for confirmation of laboratory results and to determine parameters such as the type of reactor, the reactor depth and volume, liquid flow rate, gas flow rate and bubble size, gas to liquid ratio and the performance indicators required to monitor the system .

For selection of the correct type of GAC, adsorption isotherm tests using the test water containing specific target compounds should be used to get an indication of the effect of the background organics and adsorption capacity of the GAC. Better still are pilot plant tests, but these are significantly more time consuming. However, a pilot plant will allow for more accurate determination of parameters (which include the kinetics of adsorption) such as EBCT, linear filtration velocity and backwashing of the GAC filters.

In summary therefore, there are a number of aspects to be considered when designing systems to incorporate ozone and GAC. These may be site specific and adequate water quality data will be required. It will be necessary to perform an adequate literature study and consult organisations that have implemented ozone and GAC in their treatment processes. It is however recommended that due consideration be given to the selection of the required ozone dose and the type of carbon.

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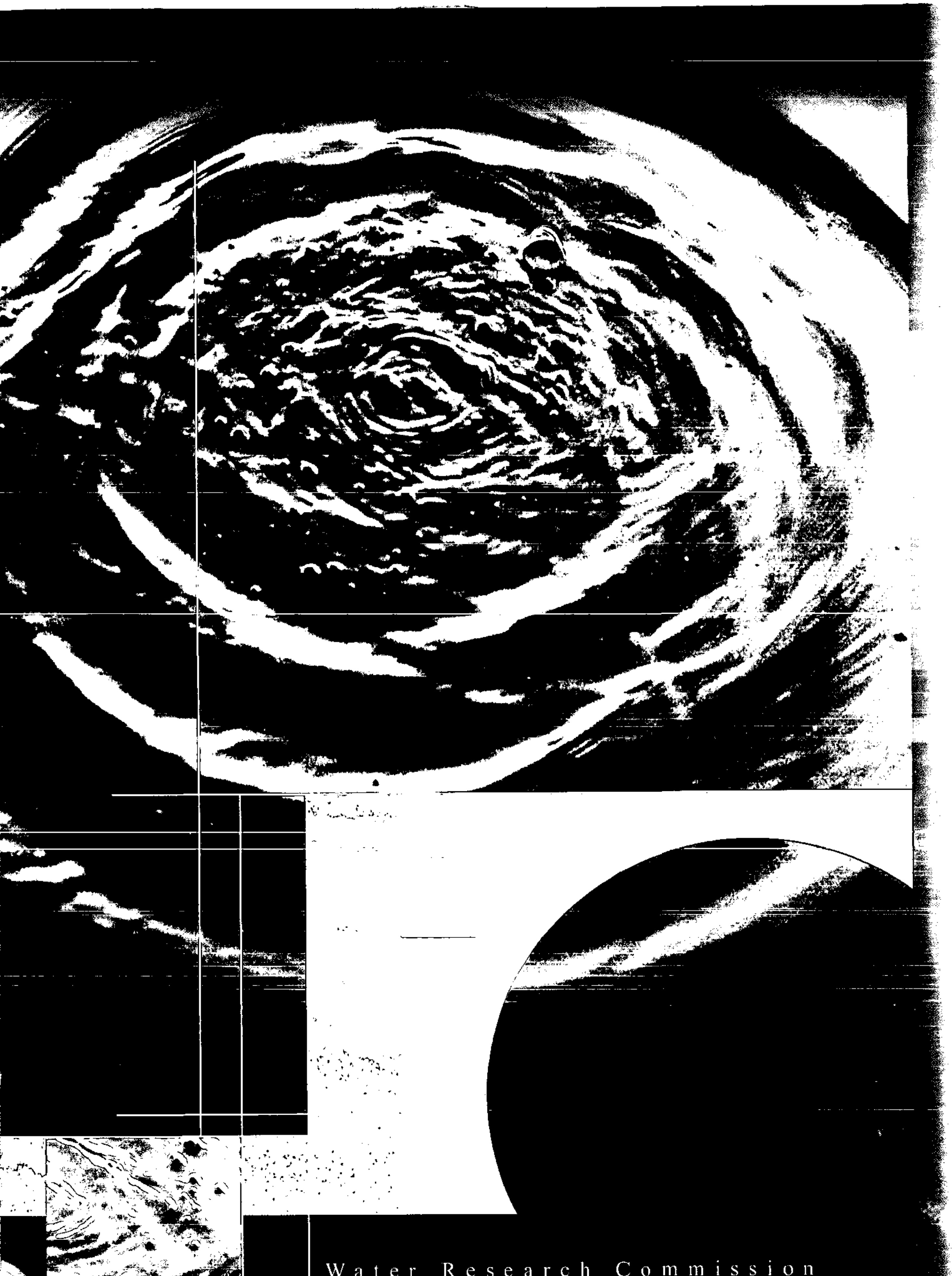

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