QUANTIFICATION OF FACTORS AFFECTING COAGULATION OF WATER WITH CATIONIC POLYMERS AND LABORATORY METHODS FOR DETERMINING THESE EFFECTS

Final Report

Prepared for the

WATER RESEARCH COMMISSION

by

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Executive Summary

Coagulation is one of the most important aspects of potable water treatment, being essential in the separation of solids and providing a primary barrier against waterborne diseases. Iron and aluminium salts are often used as primary coagulants and the reactions that occur with these coagulants are fairly well elucidated. More recently, organic polyelectrolyte coagulants have become more widely used, but the reactions of these chemicals are not as well understood as those for their inorganic counterparts.

Anomalies have been observed in Umgeni Water's operational area, which complicate coagulant selection and dose optimisation. For example, augmentation of uMngeni River water in Midmar Dam with water from the Mooi River results in a significant change in coagulant dose and the type of coagulant best suited for the treatment of the water changes, despite the fact that no noticeable changes to the obvious water quality parameters occur and that the volume of Mooi River water added to Midmar Dam has been relatively small.

Tests have been conducted on water samples from three areas where anomalies have been observed, namely the Midmar/Mearns system, the Durban Heights/Amanzimtoti/Nungwane system in the greater Durban area and the Mvoti/Makovane system on the KwaZulu-Natal North Coast, but on the advice of the Steering Committee, testing was concentrated on the Midmar/Mearns system.

In addition to this, the evaluation of operational data acquired over the years by Umgeni Water was carried out. Certain sample points within the Umgeni Water Operational area have been monitored for a number of years and this data has been analysed in order to assist in identifying factors which are important in terms of coagulation. Data were analysed for the Midmar Dam raw water and Mearns sampling sites from the Midmar-Mearns system. In the case of the Midmar Dam raw water, this data includes the coagulant type and dose being used as well as a number of water quality parameters and the flow rates of the Midmar and Mearns water into Midmar Dam.

The jar test, which has always been used successfully for dose selection when using inorganic coagulants, is often inadequate for coagulant type and dose selection when using polyelectrolytes. Modifications to the jar test are described which improve correlation between this test and full-scale operation. This was carried out in order to address the aim of the second research product and to meet the third objective if this investigation.

A better understanding of the factors affecting coagulation with organic polyelectrolytes would allow for more rapid and accurate selection of the correct type of polyelectrolyte and dose. This investigation was conducted in an attempt to provide the answer to some of these questions.

1.1. Project Objectives

The objections of this project as specified in the original project proposal are as follows:

1. Elucidate the chemical reactions that occur during coagulation using polyelectrolytes.
2. Characterise Southern African waters in order to determine the effect of natural organic matter on polyelectrolyte coagulants.
3. Produce procedures and tests to enable accurate and easy selection of polyelectrolyte coagulant type and dose for a particular water type.

The two predominant research products that the researchers hoped to produce from this project were:

1. Assessment of the effect of natural organic matter (NOM) on coagulation when using polyelectrolyte coagulants.
2. Procedures for the rapid and accurate selection of polyelectrolyte type and dose.

In conjunction with the laboratory tests conducted for this project, an in-depth data analysis was conducted on a large database of historical data, including both water quality and operational data. The objectives of this data analysis and interpretation were to assess:

1. Differences in land cover and water quality in the upper Mooi and upper Mngeni catchments that will provide an indication of the cause of the Waterworks (WW) coagulant dose during transfer periods.
2. Historical WW coagulant dose during transfer and non-transfer periods.

3. The relationship between coagulant dose and selected water quality constituents to assist in predicting changes in coagulant dose during transfer periods.

1.2. Results and Discussion

At the start of this project, systems where anomalies in coagulation existed were identified and the raw waters from these systems, as well as mixtures of these waters were assessed in terms of optimal polyelectrolyte coagulant dose and most suitable coagulant, with special emphasis being placed on the impact that mixing of the different waters has on both factors. The systems chosen were the Mvoti-Makovane system, the Durban Heights- Amanzimtoti-Nungwane system and the Midmar-Mearns system.

The Mvoti-Makovane system is being planned for water storage in the Stanger area on the KwaZulu-Natal North Coast. The Durban-Amanzimtoti-Nungwane system includes the Durban Heights and Amanzimtoti Water Works as well as water from the Nungwane Dam and although all three of these waters come from different sources, they are geographically all within fairly close proximity on the coast of KwaZulu-Natal and in terms of water quality parameters are very similar. Despite this, these waters respond very differently to polyelectrolye coagulants.

The Midmar Dam supplies the greater Pietermaritzburg area with water and on account of its strategic importance, an augmentation scheme was commissioned in 1983 as an emergency measure during the drought experienced in the uMngeni catchment. This scheme allows water from the Mooi River at Mearns to be pumped into the Lions River which in turn flows into the uMngeni River shortly before it enters Midmar Dam. It has been observed that whenever water from the Mooi River has been used to augment Midmar Dam, the water responds very differently to coagulation when treated at the nearby Midmar Water Works, despite no obvious changes in the water quality of the raw water and the fact that the Mooi River water accounts for only a small proportion of the total (less than 10%). At the start of this project in 2001, water from the planned Springrove impoundment area were included in the tests, but in later tests, the Springrove water was excluded as the Springrove development has been placed on hold indefinitely. The later tests conducted after mid 2001 included waters and blends of waters from only the uMngeni River, both above

and below the confluence of the Lions River, Midmar Dam itself and the Mearns weir, where water is taken for augmentation of Midmar Dam.

1.2.1. Methodology

The tests on initially the three water systems and then later on only the Midmar-Mearns system, were conducted at laboratory scale using jar tests and although it had originally been planned to conduct pilot plant tests as well, once the results of the laboratory tests were known, the pilot-plant tests were abandoned.

Standard jar tests were performed on each raw water source and, where relevant, any blends of these waters, using a range of polyelectrolytes and aluminium sulphate. Tests to assess variations in coagulant demand were conducted using polyelectrolytes which were chosen to cover the variety currently available on the Southern African market, namely:

1. A polyamine (PA)
2. A dimethyldiallyl ammonium chloride (DMDAAC)
3. A blended PA and polyaluminium chloride (PACl)
4. A blended DMDAAC and PACl.

Aluminium sulphate, an inorganic coagulant, was used in these tests.

Comprehensive analysis of the various water quality parameters was carried out together with characterisation of the natural organic matter present in the water. The analyses used to assess general water quality of the water samples both before and after treatment as well as before and after blending, included the following:

1. turbidity
2. pH
3. alkalinity
4. calcium, magnesium, hardness
5. colour
6. conductivity
7. iron, manganese (total)
8. suspended solids
9. total dissolved solids

In order to achieve the first research product of this study, characterisation of the natural organic matter (NOM) present in the water was done by analysing for the following;

1. total and dissolved organic carbon (TOC and DOC)
2. biodegradable dissolved organic carbon (BDOC)
3. trihalomethane formation potential (THMFP)
4. absorbance at 254 nm
5. chlorine demand
6. lime demand
7. zeta potential
8. gas chromatograph-mass spectrometry (GC-MS) fingerprinting

“Titration” curves were obtained for various blends of water samples taken from the Midmar-Mearns system, in which incremental amounts of one water sample would be added to another, until a 1:1 blend had been achieved. After each incremental addition, the turbidity, pH, conductivity and zeta potential were measured.

Tests were conducted on organic polymeric coagulants which varied in molecular mass, charge density and constituents in an attempt to determine the impact of these factors in the coagulant reaction. A variety of laboratory jar tests were conducted using a range of these coagulants and again the determinands described above were analysed.

Enhanced coagulation tests were conducted on water from the Midmar-Mearns system with a view to identifying differences within the organic constituents of the different waters. Ozonation of the various waters from the Midmar – Mearns system was carried out in order to identify any differences in the NOM present in these waters.

Tests to assess the effect of removal of the particulate matter prior to coagulation were conducted by filtering the individual waters and blends with GF/C filters (1,2 µm) and Whatman No. 1 equivalent filter paper before coagulant addition.

In addition to the laboratory tests which were conducted, a detailed data analysis and interpretation study was conducted. A large database of historical data, including both water quality and operational data were used for this purpose.

Laboratory tests were carried out in an attempt to improve the correlation between the jar test results and full-scale operation. These included laboratory-scale clarifiers as well as filtration tests conducted in conjunction with full-scale operation.

1.3. Summary of the Results

As mentioned above, three systems were originally included in the investigation. These were the Mvoti/Makovane system near Stanger, the Durban Heights/ Nungwane system near Amanzimtoti and the Midmar/Mearns system Inland of Pietermaritizburg. A first set of tests was carried out on all three systems and showed a confirmation of the dosage anomalies previously noted.

1.3.1. Mvoti/Makovane System

The first set of results taken confirmed the anomalies previously noted, but results tended to be somewhat unpredictable. As the system did not have a large database of previous results and was remote from the laboratories, leading to practical difficulties in sampling and logistics, it was agreed at the first steering committee to drop this system from the list and no further investigations were carried out.

1.3.2. Durban Heights/Nungwane System

The second system investigated, comprising Durban Heights water and water from Nungwane Dam treated at the Amanzimtoti works, had a certain amount of previous data and works records which clearly showed anomalies in the coagulant demands between the Durban Heights and Nungwane water despite superficially similar physical and chemical characteristics. These anomalies were also apparent in the first set of tests carried out. However, when the amount of data processing to produce meaningful results from the historical data became apparent, it was evident that it

would not have been possible to fully investigate more than one system. The decision was therefore taken at the steering committee to limit work to the Midmar/Mearns System which was closest to the laboratories, and had by far the largest base of historical data.

1.3.3. Midmar/Mearns System

After the first set of investigational tests, work concentrated on the Midmar/Mearns System. As a first step and in parallel with the investigation on parameters which were not normally analysed routinely, a detailed analysis of all historical data was carried out on water treated in the Midmar system. Samples taken over a five-year period on a weekly basis were analysed for correlation between coagulant demand and the various parameters normally measured. These data are presented in the body of the report as **Chapter 4** and summarises the problem experienced. In this study an attempt was made to correlate coagulant demand with all routinely measured variables. Correlation coefficients were calculated between each variable and the correlation coefficients are presented in the body of the report. Virtually no correlation was evident between any of the variables measured although a weak correlation (correlation coefficients between 0,25 and 0,3) was found for several parameters including TDS (but not Conductivity), Sodium, Barium, Colour and Nitrate.

It was considered that the correlation for Barium was fortuitous and this aspect was not pursued as the concentrations under consideration were very low and only partial data were available. A weak correlation between turbidity and coagulant demand was expected based on previous experience but this was not established. It had been noted on previous routine samples that a weak correlation exists between dissolved solids content and coagulant demand. The correlation with sodium is an echo of this relationship in that the sodium content would be expected to increase with TDS. No correlation was found to exist, with the limited work done, between organic content of the water although the correlation between nitrate was indirectly indicative of possible organic enrichment. This work was then expanded in the investigational work carried out and reported subsequently.

1.3.4. Midmar/Mearns Experimental Work

Tests carried out over the period of the project, which encompassed two years and therefore two full seasonal variations, showed confirmation that the presence of Mearns water had a disproportionate effect on the coagulant demand when mixed with water from the uMngeni River and Lions River which is the normal supply to Midmar Dam. This however was expected as it was the observation which led to motivation for the investigation in the first place. It was also confirmed that the effect of Mearns water on the coagulant demand was stronger then would be expected in proportion to the amount of water present in the various blends.

It had been anticipated that the difference in coagulant demand may have been due to organic content which is not normally measured in routine testing. The characterisation of natural organic material (NOM) was measured in this investigation in a number of ways. It was found with the experimental work that generally no correlation existed between the organic surrogates and coagulant demand. Although a weak correlation existed between UV absorption and turbidity, this was insufficient to be significant. The second objective, which would have resulted in the first research product of this investigation was not then fully realised.

The investigational work was largely confined to the use of polyelectrolytes for coagulation as these tended to display a greater anomaly in demand compared to the inorganic coagulants such as aluminium sulphate. No significant correlation existed between the molecular mass and charge density of the polyelectrolytes, or whether these consisted of a DIMDAAC or a polyamine in origin and the coagulant demand. To further explore this, special samples were obtained from one of the chemical suppliers who produced a range of polymers for our purposes consisting of the same chemical but having different molecular masses and surface charges ranging from very low molecular mass to a very high molecular mass with accompanying variation in surface charge. Again no significant effects or correlations were noted although a higher coagulant dose was evident with the low molecular mass product, this did not vary significantly between the different samples analysed. Thus there were no marked changes in reactions obtained with different formulations of polymers. This had been intended for investigation as part of the first objective of this study.

It was decided to test the waters using dosages in the enhanced coagulation range to see whether the anomalies persisted at higher organic compound removals. Aluminum sulphate was used for this purpose as restabilisation of polyeletrolytes

occurs before the enhanced coagulation effect becomes apparent. Again in this case no trends were noted and results tended to echo the results obtained at the normal dosages for turbidity removal.

It had been hoped that the availability of a zeta potential meter and streaming current analyser would assist in characterising the waters in such a way that some explanation for the anomalies related to surface charge could be provided. Zeta potential measurements were carried out on all samples tested from the date the meter was received and no significant correlation was obtained with any of the samples. All raw water samples tended to have similar zeta potentials prior to addition of coagulant and similar zeta potentials at the point of optimum turbidity removal. There was no difference between the zeta potentials of the different water samples that could significantly account for the differences in coagulant demand. The results with the streaming current analyser were almost identical to those obtained using the zeta potential meter, but this is to be expected as they measure the same effect, one in terms of potential and one in terms of current. The difference in either the zeta potential or streaming current detector (SCD) measurement of the raw water and the treated water appears to be related to the coagulant rather than the water.

Ozonation of samples was carried out to check whether the modification of the organic species in the samples would affect the coagulant demand. Again, no significant differences between the different types of water were noted.

It had been postulated by other researchers in the field that coagulant demand for polyelectrolytes was governed by organic rather than inorganic suspended solids, and at the suggestion of the steering committee an additional series of tests was carried out where the raw water was filtered to remove TOC. By doing this it was hoped that a correlation between coagulant demand and TOC removal could be identified. The results however indicated a greater effect by filtration on inorganic matter than on TOC, as nearly all the organic carbon appeared to be in the dissolved form, and no readily identifiable correlations occurred.

GC-MS screening of the different raw water samples was carried out in order to ascertain whether this might have yielded a reason for the difference in coagulant demands. The scanning curves are presented in the body of the report and it was

apparent on examination of these that all the peaks could be adequately accounted for by impurities in the solvent used to extract the samples.

1.4. Conclusions

The general conclusion which can be drawn from all the work carried out in this investigation is that the tools used to measure differences in water quality for correlation with coagulant demand were not significant in their effects as far as predicting the coagulant demand is concerned. It had been hoped that measuring of the organic species or the zeta potential and streaming current would yield a reason why the coagulant demands varied. But this was not apparent in the tests. It can therefore be concluded that more detailed work would need to be carried out into fundamental characteristics of the particles in suspension to possibly account for the differences noted in coagulant demand. Thus the third objective and the second research product were not fully realised and achieved.

1.5. Recommendations for Future Work

As mentioned in the conclusions the parameters measured did not significantly account for the differences noted in coagulant demand. Future research could possibly take into account molecular formulae, crystal structures and charges on the inorganic particles present in suspension in the water and could also be extended to other water systems where these effects have been noted. The catchments could be studied to note whether there are any differences in geology of the two catchments which could yield dissimilar particles which could give rise to the differences in coagulant demand.

Another possibility would be to examine in detail the spread of algal populations in the water and to establish whether any correlation exists between a particular algal species and coagulant demand.

A third possibility would be to investigate the nature of the organic material present in the water in solution or in colloidal form, such as humic substances and attempt to correlate these with coagulant demand in some way. It was mentioned in the report that fractionation of the organics measured by TOC and BDOC would not have yielded anything significant, but it is possible that concentration of the organics or more sensitive analysis of the organics present might yield information of interest.

Acknowledgements

The research in this report emanates from a project funded jointly by the Water Research Commission and Umgeni Water and entitled:

Quantification of Factors Affecting Coagulation of Water with Cationic Polymers and Laboratory Methods for Determining these Effects

The Steering Committee responsible for this project consisted of the following persons:

Dr I M Msibi.....	Water Research Commission (Chairman)
Mr S A Pieterse.....	City of Cape Town
Mr J Pietersen.....	Midvaal Water
Mr V Botes.....	Mhlathuze Water
Prof J Haarhoff.....	Rand Afrikaans University
Prof W A Pretorius.....	University of Pretoria
Prof C A Buckley.....	University of Natal, Durban
Mr G Gericke.....	ESKOM
Ms S Chetty.....	Water Research Commission (Committee Secretary)

The financing of the project by the Water Research Commission, the provision of laboratory, analytical facilities and office space and equipment by Umgeni Water and the contribution of the members of the Steering Committee are gratefully acknowledged.

The assistance of the Umgeni Water Analytical Services Laboratories for many of the analyses is gratefully acknowledged and the dedication of D L Trollip and F Mthombo in conducting laboratory tests and analyses is greatly appreciated .

Capacity Building

Ms Nonto Simelane, a previously disadvantaged individual, has been involved in this project. Ms Simelane has a BSc (Hons) degree and is currently working as a Scientific Assistant in the Water Quality Planning section of the Water Quality and Environmental Department. She has received training on statistical and graphical methods of data analysis.

Mrs F Mthombo and Mr S Makhavhu, also both previously disadvantaged individuals, were involved in the laboratory tests conducted for this project. Both received training in a variety of laboratory test procedures and analyses, including zeta potential and streaming current measurements, ozonation of water and enhanced coagulation, to mention a few. Mr Makhavhu has since left Umgeni Water's employment to take up a higher level post with Rand Water.

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Abbreviations and Glossary

BDOC	Biodegradable dissolved organic carbon
DADMAC	Diallyldimethyl ammonium chloride
DBP	Disinfection by-product
DLVO	Derjaguin, Landau, Verwey and Overbeek Theory/Model
DOC	Dissolved organic carbon
DWAF	Department of Water Affairs and Forrestry
Epi-DMA	Epichlorhydrin – dimethylamine
GC-MS	Gas chromatography – mass spectroscopy
MAR	Mean annual runoff
MCL	Maximum contaminant level
NOM	Natural organic matter
PA	Polyamine
PACl	Polyaluminium chloride
SANAS	South Africa National Accreditation Services
SCD	Streaming current detector
SS	Suspended solids
TDS	Total dissolved solids
THMFP	Trihalomethane formation potential
TOC	Total organic carbon
USEPA	United States Enviromental Protection Agency
UV	Ultraviolet irradiation
WW	Waterworks

1. INTRODUCTION

Coagulation forms an important part of the water treatment process, being essential in the separation of solids and providing a primary barrier against waterborne diseases. Metal salts such as those of iron and aluminium are widely used as primary coagulants and optimal performance is determined by factors such as coagulant concentration, pH and mixing intensity. The reactions that occur when using these types of coagulants have been studied for many years and are fairly well elucidated. However, over the past few years, organic polyelectrolyte coagulants have become more popular, but the reactions that occur in water when these chemicals are used, are not as well understood as those for their inorganic counterparts.

Anomalies have been observed in the Umgeni Water operational area, which complicate coagulant selection and dose optimisation. For example, augmentation of uMngeni River water in Midmar Dam with water from the Mooi River results in a significant change in coagulant dose and the type of coagulant best suited for the treatment of the water changes, despite the fact that no noticeable changes to the obvious water quality parameters occur and that the volume of Mooi River water added to Midmar Dam has been relatively small.

Anomalies have also been found to occur in the greater Durban area, where three different water works, all treating raw water sources which are similar in quality according to the normal water quality parameters, require different types of polyelectrolytes and quite different concentrations in order to achieve optimal treatment conditions.

A third site where anomalies have been found to occur is the Mvoti/Makovane system, which is being planned for water storage in the Stanger area on the KwaZulu-Natal North Coast.

Initially tests were conducted on water samples from all three of the areas where anomalies have been observed, namely the Midmar/Mearns system, the Durban Heights/Amanzimtoti/Nungwane system in the greater Durban area and the Mvoti/Makovane system on the KwaZulu-Natal North Coast, but on the advise of the Steering Committee, subsequent testing concentrated on the Midmar/Mearns system.

The preliminary results obtained for the other systems is however described in this report wherever relevant.

An important aspect of this investigation was the evaluation of operational data acquired over the years by Umgeni Water. Certain sample points within the Umgeni Water operational area have been monitored for a number of years and this data have been analysed in order to assist in identifying factors which are important in terms of coagulation. Data were analysed for the Midmar Dam raw water and Mearns sampling sites from the Midmar-Mearns system. In the case of the Midmar Dam raw water, these data includes the coagulant type and dose being used as well as a number of water quality parameters and the flow rates of the Midmar and Mearns water into Midmar Dam.

In addition to this, the jar test, which has always been successfully used for dose selection when using inorganic coagulants, is often inadequate for coagulant type and dose selection when using polyelectrolytes. It is suspected that this may be due to the fact that the floc blanket which forms in a clarifier, is far more important in the flocculation process when using polyelectrolytes than when using inorganic coagulants, although this has not been proved. A modified jar test, capable of accurately determining the most suitable polyelectrolyte and dose would greatly facilitate water treatment in these cases.

A better understanding of the factors affecting coagulation with organic polyelectrolytes would allow for more rapid and accurate selection of the correct type of polyelectrolyte and dose. This investigation was conducted in an attempt to provide the answer to some of these questions.

1.1. PROJECT OBJECTIVES

The objections of this project as specified in the original project proposal are as follows:

1. Elucidate the chemical reactions that occur during coagulation using polyelectrolytes.
2. Characterise Southern African waters in order to determine the effect of natural organic matter on polyelectrolyte coagulants.

3. Produce procedures and tests to enable accurate and easy selection of polyelectrolyte coagulant type and dose for a particular water type.

The two predominant research products that the researchers hoped to produce from this project were:

1. Assessment of the effect of natural organic matter (NOM) on coagulation when using polyelectrolyte coagulants.
2. Procedures for the rapid and accurate selection of polyelectrolyte type and dose.

In conjunction with the laboratory tests conducted for this project, an in-depth data analysis was conducted on a large database of historical data, including both water quality and operational data. The objectives of this data analysis and interpretation were to assess:

1. Differences in land cover and water quality in the upper Mooi and upper Mngeni catchments that will provide an indication of the cause of the increased WW coagulant dose during transfer periods.
2. Historical WW coagulant dose during transfer and non-transfer periods.
3. The relationship between coagulant dose and selected water quality constituents to assist in predicting changes in coagulant dose during transfer periods.

2. LITERATURE SURVEY

2.1. INTRODUCTION

Cationic polymeric coagulants, unlike their inorganic counterparts, are not affected by the pH of the water and on account of their much higher charge density, can be applied in much lower doses than aluminium and iron salts (Lind, 1994a and 1994b). Another benefit of these chemicals is that they tend to produce stronger, larger and better settling flocs (Ghosh et al, 1985). Furthermore, for surface waters low in suspended solids, like many of those in used as a raw water source in Southern Africa, polyelectrolytes can be used in conjunction with direct filtration, which can allow for significant savings in water treatment plant construction (Ghosh et al, 1985).

Because of the lower doses employed when using these polymeric coagulants and the fact that they do not affect the pH of the water, these chemicals can lead to significant cost savings. Less coagulant is required, lime or soda ash is only needed in cases where stabilisation of the water is required and not for pH correction due to the effect of the coagulant, and a significant reduction in sludge production is obtained. This can also lead to substantial reductions in energy consumption during sludge disposal (Ghosh et al, 1985).

Many of the chemical reactions which take place when polymeric coagulants are added to a water, are not well elucidated. Therefore selection of the correct type of polyelectrolyte and dose for a particular raw water can be problematic and time consuming. Numerous reviews of the fundamental theory and mechanisms of coagulation can be found in the literature identifying the mechanisms for the destabilisation of contaminants in water using chemical coagulants (Armirtharajah and Mills, 1982; Armirtharajah and O'Melia, 1990; Dempsey, 1984; Dempsey, 1989; Johnson and Armirtharajah, 1983; O'Melia, 1972). These mechanisms include double-layer compression, adsorption-charge neutralisation, sweep coagulation and interparticle bridging. The type of interaction between the coagulant and contaminant determines the mechanism of coagulation and although the mechanism of the reactions occurring between the inorganic coagulants and contaminants in water have largely been identified, this is not the case for organic polymeric coagulants.

Another important factor that can affect coagulation is natural organic matter (NOM), but this is made up of a complex mixture of organic substances that occur in natural waters and for this reason is very difficult to characterise (Jekel, 1994; Owen et al, 1993). It is therefore necessary to use surrogate parameters for NOM quantification and these include UV absorbance at 254 nm, TOC, DOC, 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). Measurement of the zeta potential of a water may also provide useful information regarding the characteristics of particles in a water.

NOM can be divided into two major classes, these being hydrophobic and hydrophilic compounds. The hydrophobic fraction is less soluble than the hydrophilic compounds and is also of higher molecular mass, containing a greater degree of aromaticity than the hydrophilic fraction (Singer and Harrington, 1993). The hydrophobic fraction consists mainly of humic and fulvic acids, the humic acid fraction being more highly reactive and generally easier to remove by coagulation. The fulvic acid component in contrast, is less reactive (Randtke, 1988).

The nature and structure of the organic polymeric coagulants has an impact on the way in which they react with contaminants in the water and therefore a description of the various types of polymeric coagulants available on the market is provided.

2.2. POLYELECTROLYTES FOR WATER TREATMENT

The polyelectrolytes used in water treatment are derived from petrochemicals and carry ionic charges along the polymer chains which render them water-soluble. They are high molecular mass, synthetic organic polymers, produced by the polymerisation of one (homopolymer) or more (copolymer) types of monomer units. Since the type and number of monomer units can be varied during the manufacture of polyelectrolytes, a wide variety of polymers can be produced. In addition to this the polymer chains can be linear, branched or cross-linked, adding to their complexity (Letterman and Pero, 1990).

The molecular mass, solubility and electronic charge can provide useful information regarding the toxicity of a particular polymer and therefore this information is important in considering these chemicals for use in potable water treatment applications (Nabholz et al, 1993). Polymers can contain both negatively and

positively charged sites and are usually classified accordingly, cationic having an overall positive charge, anionic an overall negative charge, non-ionic being neutral and amphoteric having both positive and negative sites (Letterman and Pero, 1990; Hamilton et al, 1994). The more highly charged a polymer, the more soluble it is likely to be and therefore also the more bioavailable to aquatic organisms (Hamilton et al, 1994). The term “polymeric coagulants” is generally used for the cationic polyelectrolytes which behave as primary coagulants, while non-ionic and anionic are referred to as coagulant aids or flocculants and these have relatively high molecular mass, often in the region of ten times or more that of the typical primary coagulant (Letterman and Pero, 1990). Biodegradation tends to decrease as the molecular mass increases and amorphous polymers generally biodegrade more rapidly than their crystalline counterparts. As halogenation of a polymer increases, biodegradation also tends to decrease (Hamilton et al, 1994).

Polyelectrolytes often contain contaminants derived from the manufacturing process, which can pose a health threat. These include (Letterman and Pero, 1990):

- residual monomers, for example acrylamide, ethylenimine and diallyldimethylammonium chloride,
- unreacted chemicals used in the production of the monomers such as epichlorhydrin, dimethylamine and formaldehyde,
- degradation products of residual monomer.
- inorganic salts, organic solvents and by-products of the organic catalysts used in the polymerisation reaction.

The polymeric coagulants used in this investigation consist mainly of blended or unblended cationic polyamines and poly-DADMACs, which are described below.

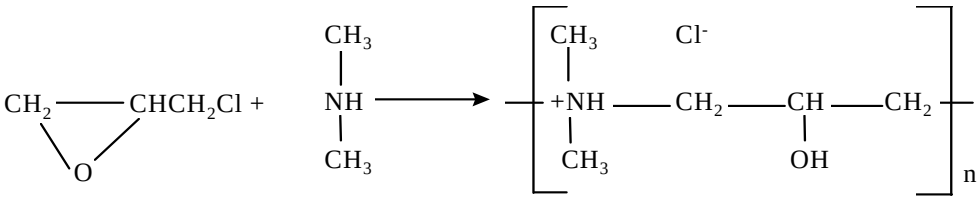
2.2.1. Polyamines

Manufacture of quaternary polyamines occurs by a ring-opening condensation polymerisation of epichlorhydrin and a secondary amine, such as dimethylamine, at

elevated temperatures in concentrated aqueous solution (up to 50% w/w active polymer). The molecular mass can be varied from 10 000 up to 250 000 Da by controlling the sequence of addition of the monomers to the reaction vessel. The polymer formed has a structure quite different from that of most other polyelectrolytes, possessing cationic charges situated along a the backbone chain, as opposed to being on branched side groups. Dimethylamine can be replaced, either in part or completely by other amines, and branched polymers can be made by altering the reaction conditions.

Epichlorhydrin-dimethylamine (epi-DMA) is the common name of a polyamine-type polymer formed by the step-reaction synthesis of 2-hydroxi-3-dimethylaminopropyl, a monomer formed by the reaction of epichlorhydrin and dimethylamine. The process tends to produce a linear quaternary ammonium polymer of low to moderate molecular weight.

Epichlorhydrin + Dimethylamine → Polyamine



The molecular mass per monomeric unit is 102 Da and products of this type tend to have molecular masses of approximately 750 000 Da.

2.2.2. Poly-DADMAC

Poly(diallyl dimethyl ammonium chloride). The other coagulant used in drinking water treatment is polydimethylamine diallyldimethylammonium chloride (poly-DADMAC) (also referred to as poly- DADMAC). Diallyl dimethyl ammonium chloride (DADMAC) is synthesised from allyl chloride and dimethylamine.

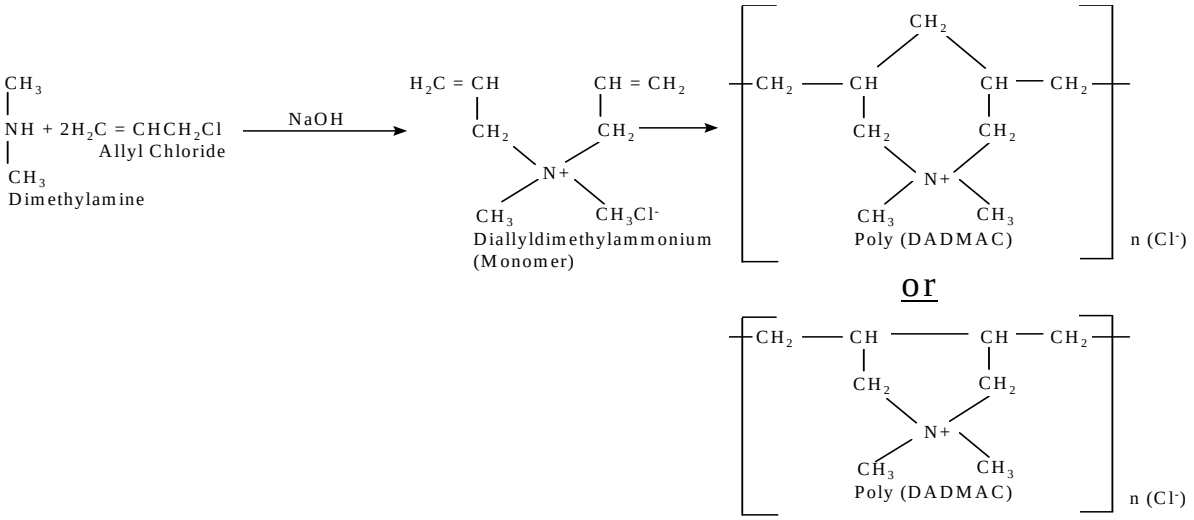
In common with other monomers containing allyl groups, DADMAC forms a relatively stable allyl radical during vinyl polymerisation and homopolymers have an upper molecular mass limit of around 500 000 to 2 000 000 Da.

The manufacture of polyDADMAC involves two sequential steps; the formation of the monomer and its polymerisation. The monomer is usually formed by a reaction of a stoichiometric mixture of allyl chloride with dimethylamine in an aqueous solution. These are available as viscous aqueous solutions at concentrations up to 40% w/w. The preferred representation of the structure of poly-DADMAC is the six-membered ring although a five-membered ring can be postulated.

NaOH

Dimethylamine + Allyl Chloride → Diallyldimethylammonium Chloride → Polymerisation

(Monomer) Poly (DADMAC)



The molecular mass per monomeric unit is 161.5 and a typical molecular mass of a polyDADMAC is 2 to 3 million Da.

2.3. PARTICLES CONTRIBUTING TO TURBIDITY

2.3.1. Characteristic Properties of Particles

Particles in a raw water supply may be composed of inorganic materials, pathogens, or toxic materials. These particles may also provide sorbent sites for pesticides and other synthetic organic chemicals and heavy metals. Particles are undesirable not only for the turbid appearance they impart to finished water, but because they also have the ability to shelter microorganisms from inactivation by disinfectants. Consequently, a principal objective in supplying quality drinking water is the maximum removal of particles. To establish or optimise a particle removal process, it is important to understand the physical properties of particles.

Particles suspended in water can be categorized into three classes based on their origin:

1. Inorganic materials, such as silt or minerals;
2. Organic matter; and
3. Biotic material including algae, viruses and bacteria.

2.3.2. Particle Settling

Particle settling, or sedimentation, may be described for a singular particle by the Newton equation for terminal settling velocity of a spherical particle. A knowledge of this velocity is basic in the design and performance of a sedimentation basin.

The rate at which discrete particles will settle in a fluid of constant temperature is given by the equation:

$$V = \left[\frac{4g\,(p_5 - p)d}{3C_d p} \right]^{0.5}$$

Where V = terminal settling velocity

g = gravitational constant

p_5 = mass density of particle

p = mass density of the fluid

d = particle diameter

C_d = Coefficient of drag (dimensionless)

The terminal settling velocity is derived by equating the drag, buoyant, and gravitational forces acting on the particle. At low settling velocities, the equation is not dependent on the shape of the particle and most sedimentation processes are designed so as to removal small particles, ranging from 1.0 to 0.5 µm, which settle slowly. Larger particles settle at higher velocity and will be removed whether or not they follow Newton's law, or Stoke's law, the governing equation when the drag coefficient is sufficiently small (0.5 or less) as is the case for colloidal products (McGhee, 1991).

Colloids are very fine solid particles, typically between 10 and 0.001 µm in diameter, which are suspended in solution. Colloidal particles may not be visible even with the aid of high-powered microscopes (Sawyer and McCarty, 1978). Colloids will not settle by gravitational forces and may not be removed by conventional filtration alone. The removal of colloidal particles is typically achieved by coagulation to form larger destabilised particles, which then may be removed by sedimentation and/or filtration. Coagulation, as defined by Kawamura (1991), is the "destabilisation of the charge on colloids and suspended solids, including bacteria and viruses", and is further discussed in Section 2.3.5, "Electrokinetic Properties of Particles".

2.3.3. Particle Density and Size Distribution

Typically, a larger range of particle sizes will exist in the raw water supply. Type 1 settling is the designation given to discrete particles of various sizes, in a dilute suspension, which settle without flocculating. Dilute suspensions of flocculating particles, where heavier particles overtake and coalesce with smaller and lighter particles, are given the designation of Type 2. As there is no mathematical equation which can be applied to the relationships of Type 1 and 2 sedimentation, statistical analysis is applied to predict the settling velocities for particles in water having a broad range of size and density. Particle size distribution analysis (Type 1) or settling-column analysis (Type 1 and 2) is applied and a settling velocity cumulative frequency curve is obtained and used in settling basin design. A comprehensive resource for understanding the use of settling column analysis, and discrete particle settling is given by Gregory and Zabel (1990).

Type 3a and 3b, or hindered settling, occur when high concentrations of particles in suspension result in an interaction of particles. The displacement of water produced

by the settling of one particle affects the relative velocities of its neighbors (McGhee, 1991). A zone is formed in which more rapidly-settling particles act as a group with a reduced settling velocity. However, even at fairly high concentrations, the reduction in settling velocity is not significant. The following equation from McGhee (1991) gives and estimate of the magnitude for hindered settling:

$$V_h/V = (1 - C_v)^{4.65}$$

Where V_h = hindered settling velocity

V = free settling velocity

C_v = volume of particles divided by total volume of the suspension

2.3.4. Inorganic Particles

Inorganic particles in water are produced by the natural weathering of minerals, including both suspended and dissolved materials. Inorganic particles may consists of iron oxides, salts, sulphur, silts and clays such as bentonite or muscovite. Depending on the concentration of organic particles present in raw water sources, human health effects can vary from beneficial to toxic.

2.3.5. Naturally Occurring Minerals

Naturally occurring minerals find their way into raw water sources either naturally through the breakdown of minerals in rock, or through industrial process discharges which have contaminated a raw water source. Industrial contributors can include mining, smelting, coal burning power producers, oil and gas companies, and electroplating operations.

Clays, metal hydroxides, and other particles originating from mineral sources typically vary from several nanometres to several micrometres in diameter, with a continuous size distribution over this range. In surface waters, the majority of these particles are within a 0.1 to 1 µm size range. As a result of their settling characteristics, particles in this size range have the ability to remain in suspension in moving water. Particles of this size range scatter visible light efficiently, due to the larger surface areas which are created as particles decrease in size. This scattering gives the water a turbid, or cloudy, appearance at very low concentrations. However, Wiesner and Klute (1998) suggest that the real threat of these particles is their adsorptive properties. The large

surface areas created by even a small mass concentration of the colloid particles provide abundant adsorption sites for natural and synthetic organic matter, metals, and other toxic substances. Bacteria and viruses can also attach to these particles, and there is some concern that inorganic particulate contamination has the ability to shield microorganisms from inactivation by disinfectants.

Dissolved inorganic compounds known to have adverse health effects on humans when ingested include aluminium, arsenic, cadmium, copper, fluoride, lead, and mercury. The United States Environmental Protection Agency (USEPA) has established maximum contaminant levels (MCLs) for a variety of inorganic contaminants and is in constant review of health advisories to determine the health effects from inorganics ingested in drinking water (Tate and Arnold, 1990). The inorganic materials for which MCLs have been established are toxic to humans in some form.

2.3.6. Organic Particles

Organic materials are compounds, natural or manmade, having a chemical structure based upon the carbon atom. Millions of organic compounds containing carbon have been identified and named, including; hydrocarbons, wood, sugars, proteins, plastics, petroleum-based compounds, solvents, pesticides and herbicides.

2.3.7. Natural Organic Matter (NOM)

In the majority of raw water sources, the largest fraction of all organic particles is due to NOM originating form the degradation of plant or animal materials (Wiesner and Klute, 1998). NOM is undesirable in raw water for a variety of reasons, ranging from undesirable color to providing adsorption site for toxic substances. NOM will also adsorb to inorganic particles present in raw water, reducing the settling properties of those particles. Aiken and Evangelo (1995) recognised numerous studies supporting the importance of NOM in mobilisation of hydrophobic organic species; of metals (lead, cadmium, copper, zinc, mercury, and chromium); and radionuclides through the treatment process. Elevated levels of certain NOM constituents require additional coagulants in order to destablize the particles and remove them in sedimentation and/or filtration basins.

NOM is also present in raw water supplies as colloidal organic carbon in the form of humic materials. Humic substances have generated considerable attention due to their disinfection by products (DBP) formation potential (Amirtharajah and O'Melia, 1990).

2.3.8. Coagulants

The coagulation of water generally involves the chemical addition of either hydrolysing electrolytes or organic polymers for the destablisation of colloids in suspension. Some common coagulants are those based on aluminum, such as aluminum sulfate and those based on iron, such as ferric and ferrous sulfate. The action of metallic coagulants is complex and is dependent on the fact that colloid particles are charged entities in water solution. In addition, the use of bentonite, and activated silica for coagulation enhancement will increase the particle loading in the treatment stream (Wiesner and Klute, 1998).

2.3.8.1. Polymers

Natural and synthetic coagulant aids are known as "polyelectrolytes", because they have characteristics of both polymers and electrolyte. Polyelectrolytes are long-chain, high-molecular-weight molecules which bear a large number of charged groups. The net charge on the molecule may be positive, negative, or neutral. The chemical groups on the polymer are thought to combine with active sites on the colloid, combining them into a larger particles which will then settle by gravitational force. Both the molecular weight of the polymer and charge density influence the effectiveness of polyelectrolytes.

Polyeletrolytes may be used alone or in tandem with metallic coagulants. Optimal doses for polymeric coagulant are typically determined in bench-scale or pilot-scale plants testing utilising source water. Use of quantities in excess of the optimal does will not increase coagulation and instead will create unnecessary loading of particles to be removed.

2.3.8.2. Lime

Lime is calcinated chemical material used in lime or lime soda ash water treatment processes to add alkalinity to the water and adjust the pH value. Lime treatment has the incidental benefits to remove iron, aid in clarification of turbid waters, and minimal bactericidal benefit (Logsdon et al, 1994). Lime has a tendency to deposit solids at

points of change of direction and will precipitate out of solution in regions where the velocity decreases. The precipitates formed in the lime-soda softening process consist principally of calcium carbonate and magnesium hydroxide with size ranges from 15 to 20 µm. If lime is dosed in quantities greater than the water supply requires, residual lime particles will increase the turbidity in treated water effluent.

2.3.9. Electrokinetic Properties of Particles

Colloidal particles comprise a large portion of the turbidity-producing substances in waters. Examples of colloidal particles include color compounds, clays, microscopic organisms and organic matter from decaying vegetation or municipal wastes. Colloidal dispersions are stable in water, as they possess a large surface areas relative to their mass. Therefore, gravitational forces alone will not remove colloids during sedimentation. Effective removal of these colloidal dispersions is greatly impacted by the electrokinetic properties on the surface of the colloids.

Each colloid carries a similar electrical charge that produces a force of mutual electrostatic repulsion between adjacent particles. If the charge is high enough, the colloids will remain discrete and in suspension. The addition of coagulants or polymers reduces or eliminates this charge and colloids will begin to agglomerate and settle out of suspension or form interconnected matrices which can then be removed during filtration. This agglomeration causes the characteristics of the suspension to change by creating new particle viscosity, settling rates and effective size properties for the colloids.

Colloids are classified as hydrophobic (resistant to water bonding) or hydrophilic (affinity for water bonding). Hydrophilic colloids are stable because their attraction to water molecules will overcome the slight charge characteristics they posses. This attraction makes hydrophilic colloids difficult to remove from suspension. Examples of hydrophilic colloids include soaps and detergents, soluble starches, soluble proteins and blood serum. On the other hand, hydrophobic particles are dependent on electrical charge for their stability in suspension. The bulk of inorganic and organic matter in turbid raw water is of this type.

2.3.10. Electrical Potential

Most colloidal particles in water are negatively charged as a result of differences in electrical potential between the water and the particle phases. This charge is due to an unequal distribution of ions over the particle surface and the surrounding solution.

The charge on a colloidal particle can be controlled by modifying characteristics of the water which holds the particles in suspension. Modifications include changing the pH of the water or changing the ionic species in solution. Another, more direct technique is to use surface-active agents, such as coagulants, that directly adsorb to the surface of the colloid and change its characteristics.

2.3.11. Electrical Double Layer Theory

The double layer model explains the ionic environment surrounding a charged colloid and explain how the repulsive forces are set up around a colloid.

A single negative colloid will initially attract some of the positive ions in the solution to form a firmly attached layer around the surface of the colloid, known as the *Stern layer*. Additional positive ions are still attracted by the negative colloid, but are also repelled by the Stern layer as well as by other positively charged ions trying to get close to the negatively charged colloid. This constant attraction and repulsion results in the formation of a *diffuse layer* of charged ions surrounding the colloid and Stern layers.

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid. Together, the attracted positively charged ions in the Stern layer and the charged atmosphere in the diffuse layer is referred to as the *double layer*. The charge is a maximum at the particle surface and decreases with distance form the surface. The thickness of this layer depends on the type and concentration of ions in solution.

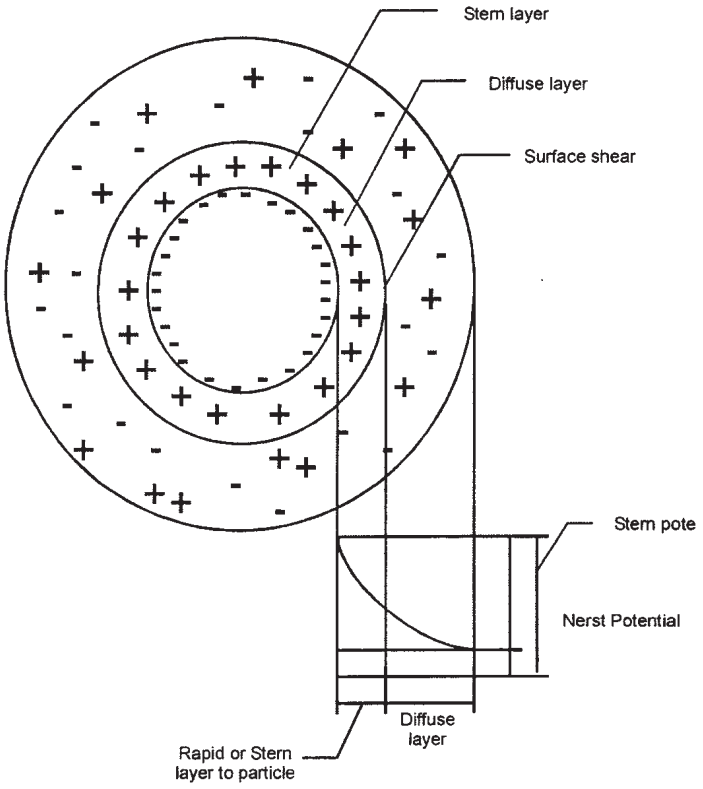


FIGURE 2.1: Diagram of electrical double layer model.

The DLVO theory (for Derjaguin, Landau, Verwey and Overbeek) is the classic model which describes the balance of forces between charged colloid particles. Amirtharajah and O'Melia (1990) provide a thorough discussion of the electrostatic theory of colloidal stability from the DLVO model and other works.

When two similar colloidal particles with similar primary charge approach each other, their diffuse layers begin to interact. The similar primary charges they posses result in repulsive forces. The closer the particles approach, the stronger the repulsive forces. Repulsive forces which keep particles from aggregating are counteracted to some degree by an attractive force termed *van der Waals* attraction. All colloidal particles possess this attractive force regardless of charge and composition. As van der Waals forces tend to be relatively weak attractions, the force decreases rapidly with an increasing distance between particles.

The balance of the two opposing forces, electrostatic repulsion and van der Waals attraction, explains why some colloidal systems agglomerate while others do not. As

particles with similar charge approach one another, the repulsive electrostatic forces increase to keep them separated. However, if they can be brought sufficiently close together to get past this energy barrier, the attractive van der Waals force will predominate, and the particles will remain together. The random motion of colloids caused by constant collision with water molecules, termed Brownian Movement, will bring particles in close proximity and aggregation may occur. However, the addition of coagulant and polymers is typically used to lower the energy barriers between particles and provide efficient agglomerations for settling.

2.4. ZETA POTENTIAL

The Stern layer is considered to be rigidly attached to the colloid, while the diffuse layer is a dynamic layer of charged particles. The Nernst Potential is the measurement of voltage (the order of millivolts) in the diffuse layer. The potential is a maximum at the Stern layer and drops exponentially through the diffuse layer. The zeta potential is the electrical potential representing the difference in voltage between the surface of the diffuse layer and the water. It is important to know the magnitude of the zeta potential, as it represents the strength of the repulsion between colloid particles and the distance which must be overcome to bring the particles together.

If we imagine measuring the potential as a function of distance from the surface it will initially rise quite steeply to a maximum at the so-called Helmholtz plane and then relax to a value of the surface potential itself. At some distance from the surface of the so-called Shear Plane, the ions are no longer dragged along with a moving particle but remain in the bulk solution. The potential at this distance is by definition ξ the zeta potential. It so happens that of the range of potentials associated with the particle it is the zeta potential which we can measure most readily and fortunately it is also the potential which is often most important in governing charge mediated particle interactions and hence the behaviour of a suspension

The primary charge on a colloid cannot be measured directly. However, the zeta potential can be computed from measurements of particle movement within an electrical field (electrophoretic mobility). Therefore, the zeta potential, 'ς' is defined by the equation:

$$\varsigma = \frac{4\pi\delta q}{D}$$

where q = charge of the particle

δ = thickness of the zone of influence of the charge on the particle

D = dielectric constant of the liquid

Zeta potential measurements can be made using a high-quality stereoscopic microscope to observe colloidal particles inside an electrophoresis cell (Zeta-Meter 1998). An electric field is created across the cell and charged particles move within the field. Their velocity and direction are then related to the zeta potential. Measurements of zeta potential can give an indication of the effectiveness of added electrolytes in lowering the energy barrier between colloids, and can direct the optimization of coagulant dose in water treatment.

The destabilization of colloids is accomplished by the reduction of the zeta potential with coagulants such as alum ferric chloride and\or cationic polymer. Once the charge is reduced or eliminated, no repulsive forces exist. Gentle agitation in a flocculation basin will cause numerous, successful colloid collisions (Zeta-Meter Inc., 1998).

2.5. STREAMING CURRENT DETECTOR

A streaming current is generated by electrically charged particles in the sampled water, which momentarily attach to a reciprocating piston within the streaming current detector (SCD). Electrodes in the surrounding cylinder measure this current. The signal is electronically processed and the output is the “streaming current”. Because this current is due to electro-double layer characteristics of the particles, the SCD output is related to zeta potential or electrophoretic mobility. However, there are also some important differences between the two measurements, which will be described in this section.

As originally developed, streaming current measurement utilized a capillary passage or porous plug of the material of concern, through which the bulk fluid can be forced by an applied pressure. Counter-ions in the diffuse layer surrounding the material then migrate with the fluid, creating an electrical potential or current, either of which can be measured. If the current is measured, it is termed the streaming current. Thus

the SCD measures current as opposed to the voltage which could be used to express the zeta potential and these can be mathematically related.

In any SCD the measured current is generally proportional to the average particle zeta potential in an analogous fashion.

2.5.1. Description of a SCD

There are several different SCDs currently being marketed, but all of them essentially consist of a sensor and a signal processor. The sensor and its function will first be considered.

A simplified picture of the sensor chamber is presented in **Figure 2.1** below. Water which contains the particles to be characterized flows through this chamber, typically at a rate of about 1 – 3 litres per minute. Inside the chamber is a small piston which reciprocates vertically. Above the piston, the piston rod is attached to an eccentric point on a wheel driven by a motor. The piston's velocity is thus sinusoidal in nature.

The piston moves up and down inside a cylinder which is closed at the bottom. The space between the piston and the cylinder is called the annulus, and this is the heart of a streaming current detector. The annulus has the shape of a thin, cylindrical "shell", which contains sample fluid and particles. Clearance between the piston and cylinder walls is of the order of hundreds of microns. As the piston moves, it acts as a pump: when moving downward, it forces sample out of the volume below the piston, upward through the annulus. Due to the narrow width of the annular gap, the average upward fluid velocity is much faster than the downward velocity of the piston. After the piston has reached its furthest downward position, it them proceeds upward, pulling fluid downward into the increasing volume below the piston. All directions are thus reversed in this stage of the piston's travel.

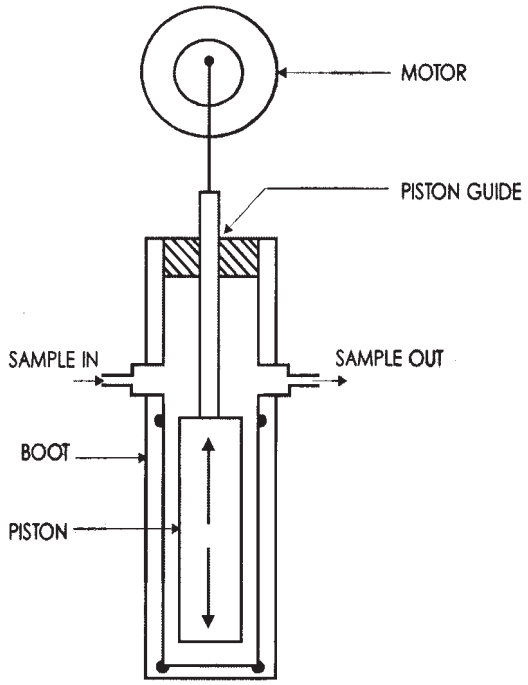


FIGURE 2.2: Sensor of the SCD. Dimensions differ according to manufacturer. Some types can be used in batch mode (beaker sample) as well as the indicated flow-through configuration.

It may be assumed that the surfaces of both the piston and cylinder become “coated” with particles from the water. There are other, more complex ways of viewing the phenomenon, but this assumption provides a workable explanation.

Using the “coating” assumption, the charge density on the annular surfaces should be the same as the average charge density for charged particles which would be found in most raw waters: their charge density, and zeta potential, are both negative, and the annular charge density would be the same negative value as the for the particles.

Because the overall electrical charge in this system must be neutral, the negative charge density must be balanced by a positive charge density, located further outward from the particles (or annulus). This opposing charge density is caused by counter-ions in the water. The simplest way to look at this is to imagine that there is a layer of negative charge near the particles, and a layer of positive charge further from the particles (hence the term “electro-double layer”). Between these two layers is the shear plane.

A shear plane results from fluid motion. Because fluid is stationary right next to a stationary surface, there must be some location or layer outward from the surface beyond which there is motion. This is when the fluid is shearing, and it is the shear

plane. In the annulus of an SCD, the fluid moves between the piston and the cylinder, and there are two shear planes – one near the cylinder wall, and the piston wall. These shear planes are cylindrical in shape and go all the way around the annulus.

The critical point is that the two layers of charge are moving relative to each other because the shear plane is between them. Furthermore, the outer layer of charge is moving relative to the solid surface (of the piston or cylinder). When electrical charges move, this creates an electrical current. If electrodes are placed in proper locations in this system, this current can be measured.

There are two metal electrode rings inserted in upper and lower areas of the cylinder. If the piston is moving downward (and therefore the fluid motion is upwards), and the attached particles are negatively charged (and therefore the outer charged layer is positive), then according to convention the electrical current is traveling from the lower electrode to the upper one. This current is dependent on the fluid velocity and on the charge density. Because the fluid velocity is sinusoidal, so is the current, and the resulting signal is thus an alternating current. The magnitude of the charge density determines the magnitude of the streaming current at any point, and thus determines the amplitude (peak height) of the alternating current signal.

Thus the sensor, although similar in principal to the streaming current apparatus described initially, differs in to important respects. First, because the surfaces to be characterized are those of the particles suspended in water, it is necessary that these particles adhere to the wall of the passage, thereby imparting these characteristics to the coated wall. The annulus is therefore equivalent to the capillary passage of the earlier apparatus. Second, the fluid motion is imparted by a reciprocating piston rather than a directly applied pressure.

The first of these modifications enables continuous renewal of sample such that changes in particle characteristics can be monitored; and second provides an alternating rather than direct current, which can more easily be separated from constant background effects.

2.5.2. Signal Processing

The processing of this alternating current is the other important aspect of an SCD. The current generated in the sensor is on the order of 10^{-12} amps, which is extremely low, and a sensitive amplifier must therefore be used (the wires carrying the current from the sensor to the amplifier must also be well shielded). In order to measure the signal, the amplifier must be low impedance; this is because, in its absence, the circuit would be completed by conductance back through the liquid. Essentially, the amplifier must have a lower conductance than the water in order to complete the circuit and measure the current.

By rectifying the entire signal the signal is simply changed to a positive value whenever it is negative. It is then filtered, or 'time-smoothed", to give a constant reading. This reading can be output to a meter, a chart recorder, or a control system for chemical feed.

The value of this "streaming current" is in relative units. The instrument is not calibrated to numerically relate this to the actual current or charge density that exists in the sensor, primarily because the calibration would be sensitive to small differences in the physical dimensions of the annulus. However, the unit typically includes a sensitivity or span adjustment that allows the output to be varied by a factor of up to 30 or 50.

2.5.3. Application in Process Monitoring and Control

One important mechanism by which coagulants may function is by altering the charge on particles in the raw water. This has been documented using zeta potential measurements, both in water treatment plans and in research laboratories (e.g. Black and Chen 1965; Faust and Aly 1983; Narkis and Rebhun 1983; Dentel and Gossett 1987). Other factors, such as the total volume of floc, can also be important (Letterman and Iyer 1985), but it is often observed that the coagulant dose for best flocculation and sedimentation corresponds to a zeta potential somewhere between plus and minus 14 millivolts (James et al, 1977). Unfortunately, measurement of zeta potential is time-consuming and can be difficult around the zero point which is precisely the range of interest). Thus, although there are a number of water treatment

plants that monitor zeta potential, few plants attempt to use it for constant control of coagulant dosage.

As shown in the previous chapter, streaming current is directly proportional to zeta potential. Furthermore, since the SCD is capable of continuous evaluation of particle charge characteristics, it can be used for constant monitoring and control of coagulant dose.

A typical application of the streaming current detector in a water treatment plant is where the sample for the SCD is taken downstream of the point of coagulant addition, and after the coagulant has been completely dispersed throughout the water. In fact, the sampling location is critical for successful use of the SCD.

With this arrangement, the operator can observe the streaming current and, based upon a previously determined value associated with optimal plant performance, readjust the coagulant dose until the reading matches this target value, or “set point”. Alternatively, the SCD output may be connected to an electronic controller which automatically readjusts the coagulant feed rate until the set point is attained. Such a control system dose not replace the operator, who must on occasion ensure that the set point is proper, based upon jar tests or observed plant performance.

When monitoring settled turbidity at a plant, an excessive turbidity level only tells the operator that the dose is wrong. Operators have observed that the chief value to the streaming current reading is that it indicates whether the coagulant dose is too high or too low.

3. INVESTIGATION METHODOLOGY

3.1. INTRODUCTION

At the start of this project, systems where anomalies in coagulation existed were identified and the raw waters from these systems, as well as mixtures of these waters were assessed in terms of optimal polyelectrolyte coagulant dose and most suitable coagulant, with special emphasis being placed on the impact that mixing of the different waters has on both factors.

Initially, the systems chosen for investigation were the Mvoti-Makovane system, the Durban Heights- Amanzimtoti-Nungwane system and the Midmar-Mearns system.

3.1.1. The Mvoti - Makovane System

The Mvoti-Makovane system is being planned for water storage in the Stanger area on the KwaZulu-Natal North Coast. A number of options have been considered for the Mvoti catchment. These include construction of a mid-catchment storage impoundment (iSithundu) which will release water to the Mvoti river. This water will be abstracted in the Welverdient area, pumped to an off-channel storage dam (Makovane) and treated at a nearby waterworks. It was proposed that by 2005, 32% of the water would come from the Makovane catchment, and 68% from the Mvoti, and by 2040 the proportions would be 5% Makovane, 95% Mvoti. The future of this scheme is being reconsidered based on demand from Stanger, the town that would be supplied by the scheme. Here too, mixtures were made up based on the proportions of each water source that could be expected under typical conditions. Tests were only conducted on this water during the first few months of this investigation, since after the first Steering Committee Meeting, the decision was taken to concentrate on the Midmar-Mearns System. However, where relevant, the results of the preliminary investigation into this system, are reported.

3.1.2. The Durban Heights – Amanzimtoti - Nungwane System

The Durban-Amanzimtoti-Nungwane tests were carried out on water from the Durban Heights and Amanzimtoti Water Works as well as water from the Nungwane Dam. All three of these waters come from different sources, but geographically are all within fairly close proximity on the coast of KwaZulu-Natal and in terms of water quality parameters are very similar. Despite this, these waters respond very differently to polyelectrolye coagulants; for example at Durban Heights WW a coagulant dose of less than 2 mg/ℓ is usually required for optimal turbidity removal, while at Amanzimtoti, the optimum coagulant dose is usually in double figures.

As with the Mvoti-Makovane system, after the first Steering Committee Meeting, work on this system ceased, in order to allow the project team the opportunity to concentrate on the Midmar-Mearns system. However, here too, any relevant data from the preliminary tests have been included in this report.

3.1.3. The Midmar - Mearns System

The Midmar Dam supplies the greater Pietermaritzburg area with water and on account of its strategic importance, an augmentation scheme was embarked upon recently to allow water from the Mooi River at Mearns to be pumped into the Lions River which in turn flows into the uMngeni River shortly before it flows into Midmar Dam. The Department of Water Affairs and Forestry (DWAF) has already completed construction of a small impoundment at Mearns (wall height 12 m, and retention time 2 to 8 weeks) which coincided with the raising of the Midmar impoundment wall by 3,5 m to accommodate the additional transfer volume. The construction of the Mearns impoundment is scheduled for completion by 2003. Another development, the Springrove impoundment was scheduled for completion by 2005, but this stage of the development has now been indefinitely placed on hold. The Mearns impoundment will allow pumped transfer of 67 million m^3 per year by 2003 from Mearns, and if and when the Springrove impoundment is constructed, the pumped transfer volume will be increased to 101 million m^3 per year using the combined Mearns and Springrove impoundment storage. The developed mean annual runoff (MAR) from the uMngeni catchment to the Midmar impoundment is 170 million $m^{3.}$

As mentioned previously, it has been observed that whenever water from the Mooi River has been used to augment Midmar Dam, the water responds very differently to

coagulation when treated at the nearby Midmar Water Works, despite no obvious changes in the water quality of the raw water and the fact that the Mooi River water accounts for only a small proportion of the total flow. During the first year of this investigation, laboratory tests were carried out in which water samples from Midmar Dam, Mearns (from the Mooi River transfer) and Springgrove were studied together with blends of these water, which were made up to simulate conditions that could be expected to occur. However, at that stage of the project, the Springrove development was still on schedule. Since this development was placed on indefinite hold, waters and blends of waters from only the Lions River which is one of the main supply rivers flowing into Midmar Dam, Midmar Dam itself and Mearns have been used.

3.2. HISTORICAL DATA ANALYSIS

In addition to the laboratory tests, a detailed data analysis and interpretation study was conducted. A large database of historical data, including both water quality and operational data, which Umgeni Water has for the D. V. Harris Water Works (WW) and the Midmar WW (both of which are supplied with water from the Midmar Dam) has been processed in an attempt to find correlations between water quality and coagulant type, as well as for elucidation of some of the reactions which occur during coagulation with organic polyelectrolytes. This work is presented **Chapter 4**.

3.3. LABORATORY METHODOLOGY

The tests on initially the three water systems and then later on only the Midmar-Mearns system, were conducted at laboratory scale using jar tests and although it had originally been planned to conduct pilot-plant tests as well, once the results of the laboratory tests were known, the pilot-plant tests were abandoned, as the results would have been of limited value. The laboratory tests were carried out in the Research and Development Laboratories of Umgeni Water at the Darvill Wastewater Works.

In all cases standard jar tests were performed on each raw water source and, where relevant, any blends of these waters, using a range of polyelectrolytes as well as aluminium sulphate. Tests to assess variations in coagulant demand were conducted using polyelectrolytes which were chosen to cover the variety currently available on the Southern African market, namely:

1. A polyamine (PA)
2. A diallyldimethyl ammonium chloride (DADMAC)
3. A blended PA and polyaluminium chloride (PACl)
4. A blended DADMAC and PACl.

Aluminium sulphate, an inorganic coagulant, was also used in these tests.

The products used were:

LP526: This is a DADMAC and PACl blended product. It is a non-toxic, low molecular mass, liquid grade cationic polyelectrolyte. It has a low viscosity, a specific gravity of 1,1 and is effective for flocculation throughout a wide range of pH.

C7750: This is a PA and PACl blended coagulant. It is described as a liquid, cationic aluminium chlorhydrate coagulant blend. It has minimal effect on the pH of the treated water and has an SG of between 1,13 and 1,21.

Sudfloc 3850: This is a DADMAC/PACl blended product. It is a highly charged liquid cationic polyelectrolyte with a specific gravity of between 1,1 and 1,2 and a negligible effect on the pH of the water.

U5000: This is an unblended polyamine coagulant. It is a high molecular mass liquid cationic polyelectrolyte and is also described as a polyquarternary amine in water solution. It has a specific gravity of between 1,1 and 1,2.

Comprehensive analysis of the various water quality parameters was carried out together with characterisation of the natural organic matter present in the water. Fractionation of the organics present in the water had been proposed originally if the organic compounds were found to be a influencing factor in the anomalous reaction observed with the different coagulants, but since this was not the case, fractionation was considered pointless in terms of this investigation. The analyses used to assess general water quality of the water samples both before and after treatment as well as before and after blending, included the following:

1. turbidity
2. pH
3. alkalinity
4. calcium, magnesium, hardness
5. colour

6. conductivity
7. iron, manganese
8. suspended solids
9. total dissolved solids

These tests were carried out in Umgeni Water's Analytical Services Laboratories using South African National Acceditation Services (SANAS) accredited methods.

Characterisation of the natural organic matter (NOM) present in the water was done by analysing for the following;

1. total and dissolved organic carbon (TOC and DOC)
2. biodegradable dissolved organic carbon (BDOC)
3. trihalomethane formation potential (THMFP)
4. absorbance at 254 nm
5. chlorine demand
6. lime demand
7. Zeta potential
8. Gas chromatograph-mass spectrometry (GC-MS) fingerprinting

All of these analyses, except for the GC-MS fingerprinting were conducted in the Research and Development Laboratories of Umgeni Water using standard procedures. The GC-MS fingerprinting was conducted in the Analytical Chemistry Laboratories, Umgeni Water.

In other tests, "titration" curves were obtained for various blends of water samples taken from the Midmar-Mearns system. Tests would start with one water sample and then incremental amounts of a second water sample would be added to the first, until a 1:1 blend had been achieved. A second test would then be carried out in which the first sample was added to the second until a 1:1 blend had been obtained. After each incremental addition, the turbidity, pH, conductivity and zeta potential were measured.

Tests were also conducted on organic polymeric coagulants which varied in molecular masst, charge density and constituents in an attempt to determine the impact of these factors in the coagulant reaction. The coagulants were supplied by Zetachem and the following details were supplied regarding their molecular weight and constituents:

1.	A50H	High molecular mass, high viscosity	Polyamine
2.	A50	Molecular mass less than A50H	Polyamine
3.	A50ML	Molecular mass less than A50	Polyamine
4.	A50L	Molecular mass less than A50ML	Polyamine
5.	A50VL	Very low molecular mass	Polyamine
6.	LP226	Molecular mass approximately between A50H and A50	100% DADMAC
7.	LP526	Molecular mass a little lower than LP226	LP226:A50 1:1

A variety of laboratory jar tests were conducted using a range of these coagulants and again the determinands described above were analysed.

Coagulation is traditionally used for the removal of turbidity, but it can also been used for the removal of NOM and under these conditions is referred to as enhanced coagulation. Enhanced coagulation is defined as the addition of excess coagulant for the improved removal of organic contaminants by conventional filtration treatment (Crozes et al, 1995). Enhanced coagulation occurs in the “sweep coagulation” part of the coagulation diagram described by Amirtharajah and O’Melia (1990). Pryor and Freese (1998) found that organic polymeric coagulants were not successful when used for these applications, restabilisation occurring before any significant NOM removal was obtained. Therefore most of these tests were conducted using only an inorganic coagulant, namely aluminium sulphate, although some preliminary test work using polymeric coagulants was also carried out. Enhanced coagulation tests were conducted on water from the Midmar-Mearns system with a view to identifying differences within the organic constituents of the different waters.

Ozonation of the various waters from the Midmar – Mearns system was also carried out in order to identify any differences in the response of NOM present in these waters.

It had been postulated by other researchers in the field that coagulant demand for polyelectrolytes was governed by organic rather than inorganic suspended solids, and therefore, at the suggestion of the steering committee, an additional series of tests was carried out, in which the raw water was filtered to remove TOC. Water from the Mearns impoundement, the inflow to Midmar Dam and a 1:1 blend of these two

waters were filtered through Whatman GF/C filter paper (1,2 µm) under vacuum to remove all particulate organic matter and also through Whatman No. 1 equivalent filter paper (gravity filtration), which served as a control. The water was coagulated using LP526 (a DADMAC and PACl blended polyelectrolyte) both before and after filtration. The water samples, before and after filtration, and before and after coagulation, were analysed for pH, turbidity, conductivity, colour, zeta potential, UV absorbance at 254 nm, TOC, DOC and THM.

Laboratory tests have also been conducted in an attempt to improve the correlation between the jar test results and full-scale operation. Jar tests were carried out at three of the Umgeni Water WW, all three of which received their raw water supply from the Midmar WW. Coagulant dose ranges were used which encompassed the coagulant dose being used on the plant at the time of testing. The water after the jar test treatment was then filtered through a variety of commercially available filters varying in effective pore size from 0,45 µm to 6 µm. Overflow from the various clarifiers/pulsators on the plant was also filtered through these filters. The turbidity of the jar test treated and clarifier/pulsator overflow water was measured after filtration and compared to the turbidity of the water after filtration on the plant through rapid gravity filters. Emphasis was placed on finding ways to mimic the effect of the floc blanket in the standard jar test, since this was suspected of being the major cause of poor correlation between the jar test and full-scale performance when using organic polymeric coagulants. The results of this investigation are presented in Chapter 5.

4. HISTORICAL DATA ANALYSIS AND INTERPRETATION

4.1. INTRODUCTION

The Mearns Emergency Pumping Scheme from the Mooi River was commissioned in 1983 as an emergency measure during the drought experienced in the uMngeni catchment. The Mearns Pump station is located a few kilometers south of the town of Mooi River just below the confluence of the Mooi and Little Mooi Rivers. The station has a maximum pumping capacity of 3,2 cumecs. Water is pumped from a 12 m high weir through a pipeline over a distance of approximately 20 km to the Mpofana River, a tributary of the Lions River. The Lions River flows into the uMngeni River and then into Midmar Dam, where it is abstracted for treatment by the DV Harris and Midmar WW (see **Figure 4.1**).

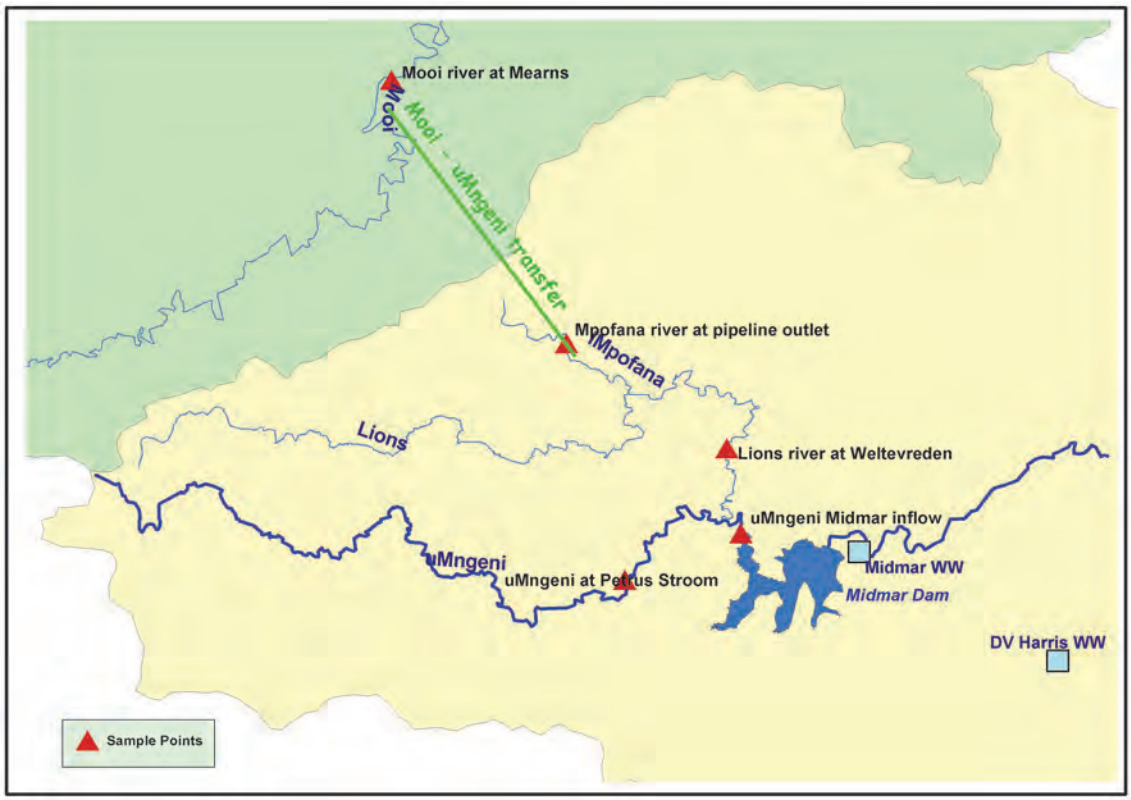


FIGURE 4.1: Map 1: Overview of Mooi-uMngeni transfer scheme including sample points

Water quality in the upper Mooi and upper uMngeni catchments is generally considered to be good, with low to moderate concentrations of bacteriological, physical and chemical constituents. The coagulant demand for water abstracted from Midmar Dam has historically been low. However, during drought periods when interbasin transfer has been undertaken, a significant increase in WW coagulant dose as well as a change in type of coagulant best suited to the treatment of the water has been noted. Investigating the reason for this change in coagulant demand and type forms the basis of this study.

Figure 4.2 illustrates historical abstractions at the Mearns pump station. Historically, transfer occurred during the summer months when yield was available in the Mooi River catchment.

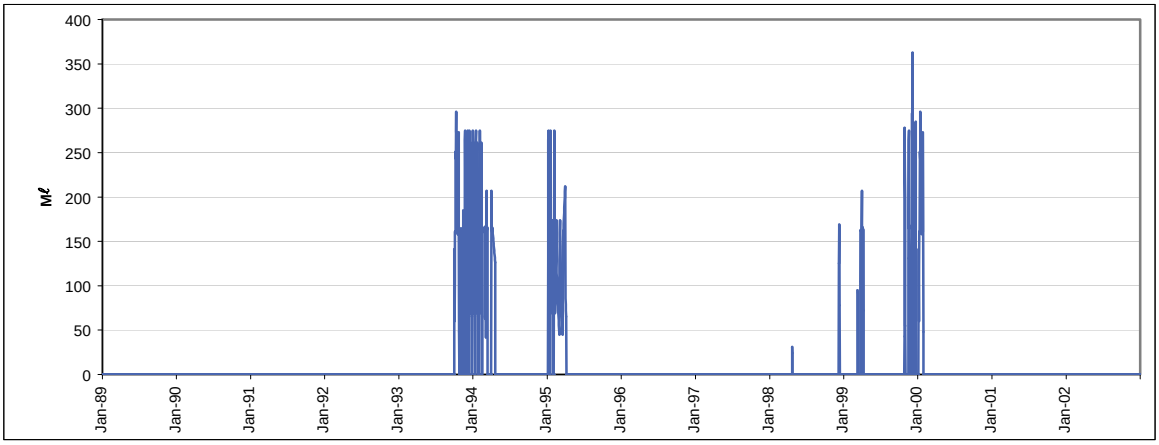


FIGURE 4.2: Time series plot of volumes (Mℓ per day) pumped from Mearns weir to the Mpofana River

4.2. OBJECTIVES OF THE HISTORICAL DATA ANALYSIS AND INTERPRETATION

The objectives of this component of the study were to assess:

1. Differences in land cover and water quality in the upper Mooi and upper uMngeni catchments that may provide an indication of the cause of the increased WW coagulant dose during interbasin transfer.
2. Historical WW coagulant dose during interbasin transfer and non-transfer periods.

3. Possible relationships between coagulant dose and selected water quality constituents to assist in predicting changes in coagulant dose during transfer periods.

4.3. METHODOLOGY

4.3.1. Data Sources

4.3.1.1. Land Cover Data

Land cover data were obtained from the National Land Cover Database developed by Environmentek - CSIR in 1996 and represented using a GIS.

4.3.1.2. Water Quality Data

Umgeni Water has monitored water quality at daily, weekly or quarterly frequencies since 1988 at a number of sites in the upper Mooi and uMngeni catchments as well as at the WW supplied by Midmar Dam. For this investigation, water quality data from the following sites were used:
Mooi River at Mearns
uMngeni inflow to Midmar Dam
DV Harris WW raw
Midmar WW raw (since commissioning in 1997)

There are thus extensive water quality data available to permit good characterisation of water quality during both the summer high rainfall and the drier winter periods.

4.3.1.3. Flow Data

Daily transfer volumes from Mearns weir from January 1989 until December 2002 were obtained from Umgeni Water Operations Division.

4.3.1.4. Coagulant Dose Data

Daily coagulant dose concentrations for the two WW supplied from Midmar Dam (DV Harris WW and Midmar WW) were obtained from Umgeni Water Operations Division.

4.3.2. Data Analyses

4.3.2.1. Comparison of Catchment Land Use and Water Quality

The proportion of area per land cover category in the upper Mooi and upper uMngeni catchments were compared. Paired water quality data (using non-transfer periods only) from the uMngeni inflow to Midmar Dam and the Mooi River at Mearns were compared using the following techniques:

1. Summary statistics
2. Time series plots
3. Percentile plots
4. Statgraphics non-parametric comparison of medians test: This test was used to statistically determine whether the two data sets have similar medians. If the resulting Z-statistic is large (>1,96), the data are significantly different (95% confidence level), but if the Z-statistic is small (<1,96), the data may be considered to be statistically similar.

Only data from non-transfer periods were used for this comparison, as the impact of interbasin transfer from the Mooi River would have been included in the uMngeni inflow to Midmar Dam during transfer periods (see Map 1).

4.3.2.2. Assessment of Coagulant Dose During Transfer Periods

Time series plots were prepared illustrating coagulant dose relative to transfer periods for both the DV Harris and Midmar WW.

4.3.2.3. Assessment of Relationship Between Coagulant Dose and Other Water Quality Constituents

Regression plots were prepared to assess the relationship between coagulant dose and individual water quality constituents at both the DV Harris WW and the Midmar WW.

4.4. RESULTS AND DISCUSSION

4.4.1. Catchment Land Cover

The dominant land uses in both the upper Mooi and upper uMngeni catchments are unimproved grassland / bushland, cultivated lands, forestry and wetlands (see **Figure 4.3**). **Table 4.1** shows the percentage area of each land use in these catchments.

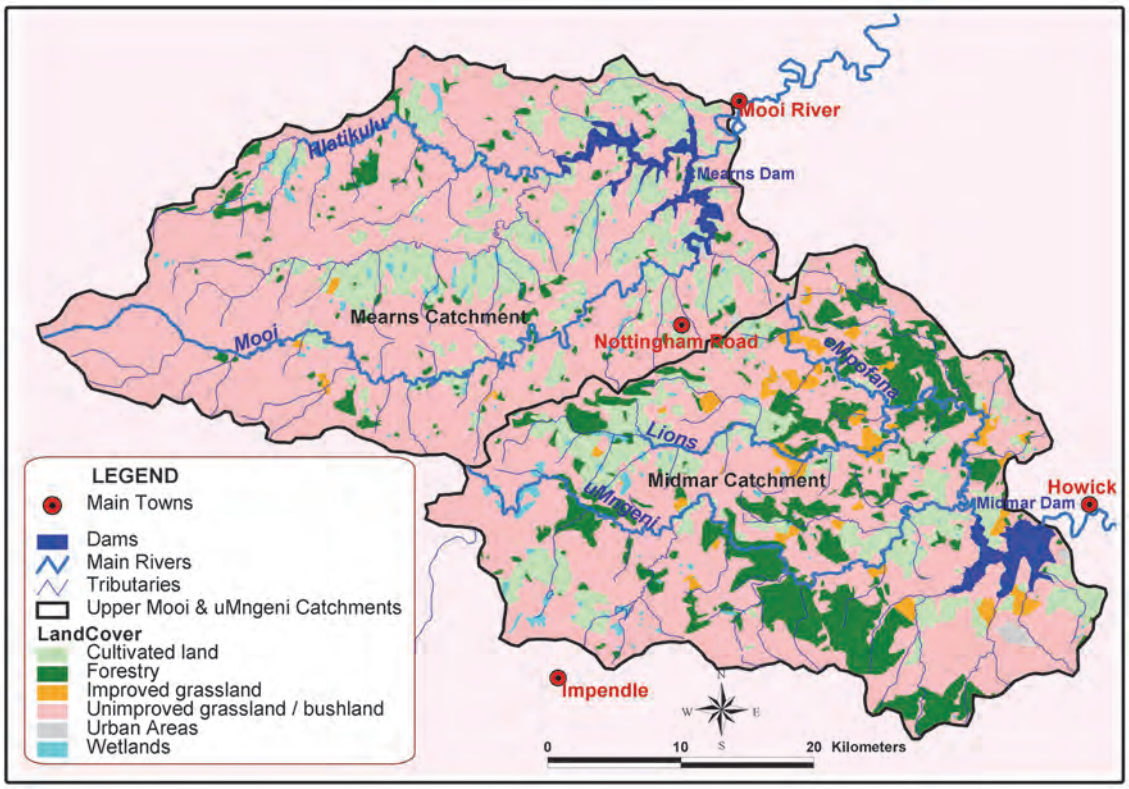


FIGURE 4.3: Map 2: Land cover in the upper Mooi and upper uMngeni catchments

From **Figure 4.3** (Map 2) and **Table 4.1**, it can been seen that large areas of the upper Mooi and upper uMngeni River catchments are classified as unimproved grasslands, but that the catchments are also fairly extensively utilised for agricultural

purposes. In the upper uMngeni catchment, 19,4% of the catchment is classified as forestry (compared to 3,4% in the upper Mooi catchment), but both the agricultural and forestry activities are generally well-managed commercial ventures, with a low pollution potential. Population in both catchments are low and limited to farm worker quarters and freehold areas, which are unlikely to have significant water quality impacts. There are no significant industries in either catchment, and no mining activities are known, other than some quarrying for road materials. In general, upper Mooi and upper uMngeni catchment quality is good.

TABLE 4.1: Percentage area per land cover category in the upper Mooi and uMngeni catchments

	Upper Mooi catchment	**Upper uMngeni catchment**
Unimproved grassland/bushland	77,0	59,7
Cultivated lands	17,6	13,9
Forest/Plantations	3,4	19,4
Improved grassland	0,1	3,7
Wetlands	0,3	0,4

4.4.2. Comparison of Catchment Water Quality

Appendix 1 illustrates summary statistics, time series plots, percentiles plots and the results of the Statgraphics Comparison of Medians test for water quality constituents measured at the Mooi River at Mearns and the uMngeni inflow to Midmar Dam. Where data were below the analytical detection limit, half of the detection limit was used to calculate statistics. **Table 4.2** summarises the median, 95th percentile and the Comparisons of medians test results.

TABLE 4.2: A summary of the comparison of Water Quality data at uMngeni Midmar inflow and the Mooi River at Mearns

	Median		95th percentile		Statgraphics
	uMngeni Midmar Inflow	Mooi River at Mearns	uMngeni Midmar Inflow	Mooi River at Mearns	Non-parametric Comparison of medians
Temperature (°C)	17,1	16,1	5,1	27,0	SD
Coliforms (per 100 mℓ)	300	250	2075	2715	SD
***E. coli* (per 100 mℓ)**	206	177	1190	1800	SS
***F Streptococci* (per 100 mℓ)**	92	52	609	597	SD
Algal counts (per mℓ)	501	433	4326	1041	SS*
pH	7,4	7,6	8,0	8,1	SD
Colour (°H)	14,1	16,9	35,5	32,8	SD
Turbidity (NTU)	8,1	8,9	44,8	43,6	SS
Conductivity (mS/m)	6,9	5,8	9,5	8,5	SD
Total Aluminium (ug/ℓ)	69	74	276	311	SS
Alkalinity (mg/ℓ)	29,0	26,0	42,3	40,1	SD
Total Hardness (mg/ℓ)	24,8	21,8	34,0	32,4	SD
Calcium (mg/ℓ)	5,00	4,70	7,12	7,30	SD
Magnesium (mg/ℓ)	2,90	2,38	3,83	3,40	SD
Sodium (mg/ℓ)	4,58	3,30	5,82	4,71	SD
Potassium (mg/ℓ)	1,10	0,77	1,79	1,77	SD
Iron (mg/ℓ)	0,65	0,75	1,35	1,30	SD
Manganese (mg/ℓ)	0,03	0,04	0,09	0,14	SD
Silica (mg/ℓ)	5,00	5,00	5,97	5,87	SS
Nitrate (mg/ℓ)	0,28	0,17	0,54	0,41	SD
Nitrite (mg/ℓ)	0,025	0,025	0,025	0,025	SS
Ammonia (mg/ℓ)	0,04	0,05	0,14	0,13	SS
Chloride (mg/ℓ)	4,39	3,03	5,86	5,18	SD
Fluoride (ug/ℓ)	50,0	50,0	50,2	52,2	SS
Sulphate (mg/ℓ)	1,23	0,90	2,13	1,93	SD
Total Phosphorus (ug/ℓ)	28,4	30,0	80,1	90,8	SD
Sol. Reactive Phosphate (ug/ℓ)	5,00	6,00	13,94	18,72	SD
Total Dissolved Solids (mg/ℓ)	49,6	44,9	79,3	57,8	SD
Suspended solids (mg/ℓ)	8,4	8,4	37,8	38,2	SS
Boron (mg/ℓ)	10,0	10,0	49,1	37,4	SS
Total Organic Carbon (mg/ℓ)	3,14	3,14	5,33	5,58	SS
BOD (mg/ℓ)	0,87	1,30	2,62	2,70	SS
COD (mg/ℓ)	10,0	10,0	26,4	31,6	SS
Dissolved oxygen (mg/ℓ)	8,1	8,2	9,4	8,5	SS*
	Median		**95th percentile**		**Statgraphics**

	uMngeni Midmar Inflow	Mooi River at Mearns	uMngeni Midmar Inflow	Mooi River at Mearns	Non-parametric Comparison of medians
Copper (mg/ℓ)	<0,05	<0,05	<0,05	<0,05	Data below detection limit
Zinc (mg/ℓ)	<0,03	<0,03	0,02	<0,03	Data below detection limit
Lead (ug/ℓ)	<4	<4	<4	<4	Data below detection limit
Cadmium (ug/ℓ)	<1	<1	<1	<1	Data below detection limit
Chromium (ug/ℓ)	<3	<3	<3	<3	Data below detection limit
Mercury(ug/ℓ)	<0,05	<0,05	<0,05	<0,05	Data below detection limit
Arsenic (ug/ℓ)	<2	<2	<2	<2	Data below detection limit
Selenium (ug/ℓ)	<1	<1	<1	<1	Data below detection limit
Cyanide (ug/ℓ)	<10	<10	<10	<10	Data below detection limit
Phenols (ug/ℓ)	<5	<5	<5	<5	Data below detection limit
Total Pesticides (ng/ℓ)	<20	<20	<20	<20	Data below detection limit
Atrazine (ng/ℓ)	<5	<5	7,75	<5	Data below detection limit

SD – Statistically significantly different • SS – Statistically significantly similar • * - Statistics were calculated with < 10 results

The comparison of water quality between the upper Mooi and uMngeni catchments indicate similar water quality for a number of constituents (data sets not significantly different), but small differences for other constituents (data sets statistically different) (**Appendix 1** and **Table 4.2**). The data showed similarity between some solids-related constituents such as suspended solids, turbidity, total organic carbon and COD, but there were statistically significant differences for soluble constituents such as inorganic ions (calcium, magnesium, sodium, potassium, chloride and sulphate) as reflected by the differences in conductivity and total dissolved salts. These differences in water quality constituents between the upper Mooi and uMngeni catchments, albeit small, may provide a clue to the different coagulant demands on treatment.

These small differences in catchment land use and water quality suggest that water transferred via the Mooi-uMngeni transfer scheme should not significantly impact the water quality in the Midmar impoundment. However, in practice, interbasin transfer has resulted in a significant change in coagulant dose and type of coagulant best suited to the treatment of the water, despite the fact that the volume of Mooi River water augmenting the inflow to Midmar Dam is small (see **Figure 4.4**).

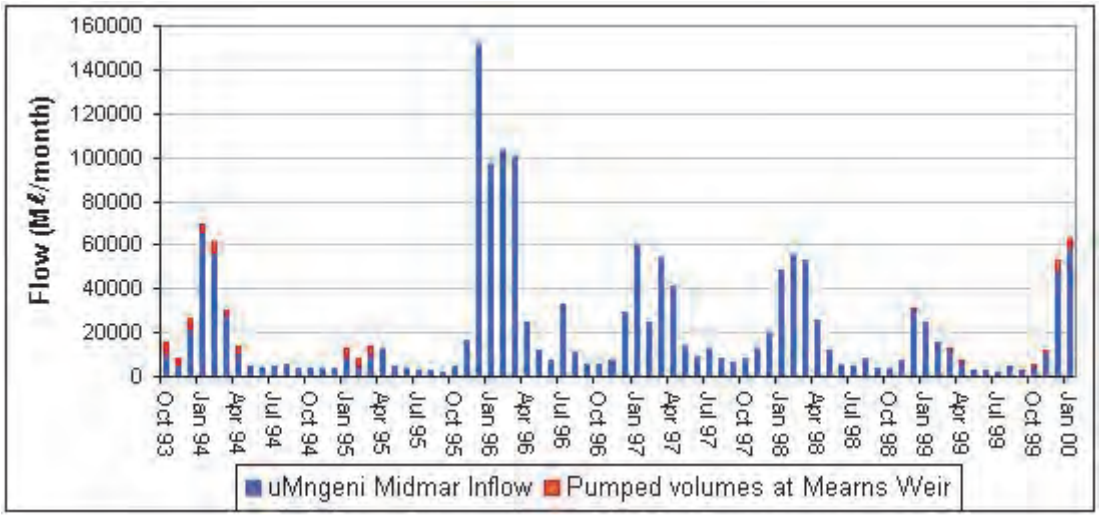


FIGURE 4.4: Proportion of water pumped from Mearns weir relative to the uMngeni Midmar inflow

4.4.3. Assessment of Coagulant dose during transfer periods

Historical coagulant dosage at the DV Harris WW and Midmar WW are shown in **Figures 4.5** and **4.6:**

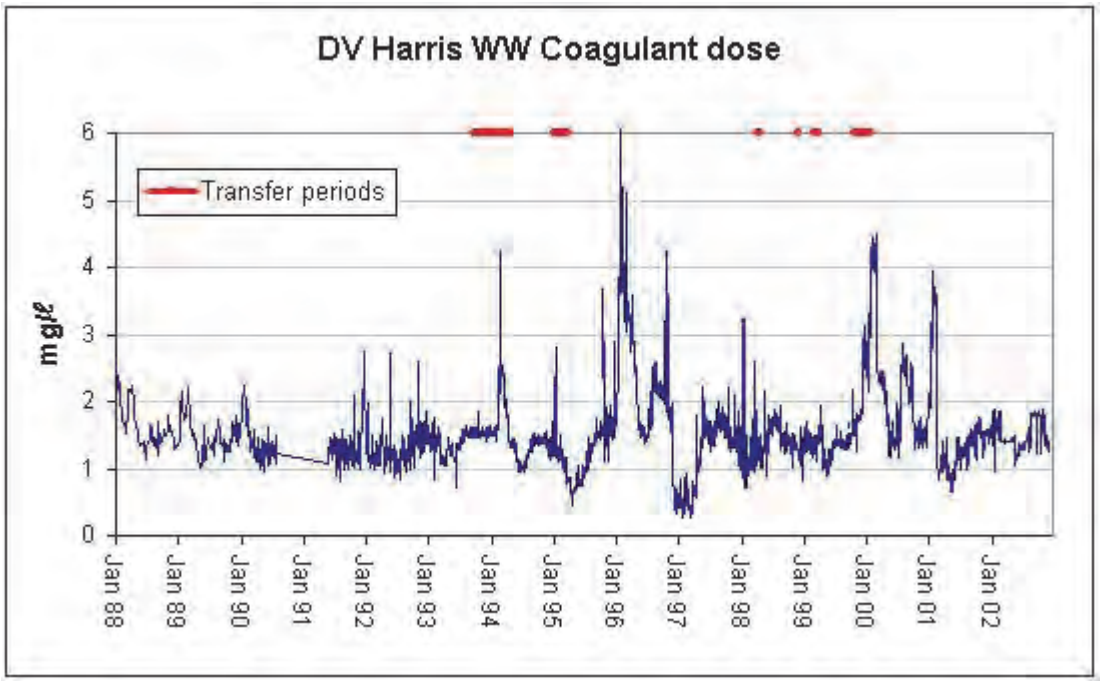


FIGURE 4.5: Time series plot of coagulant dose at the DV Harris WW.

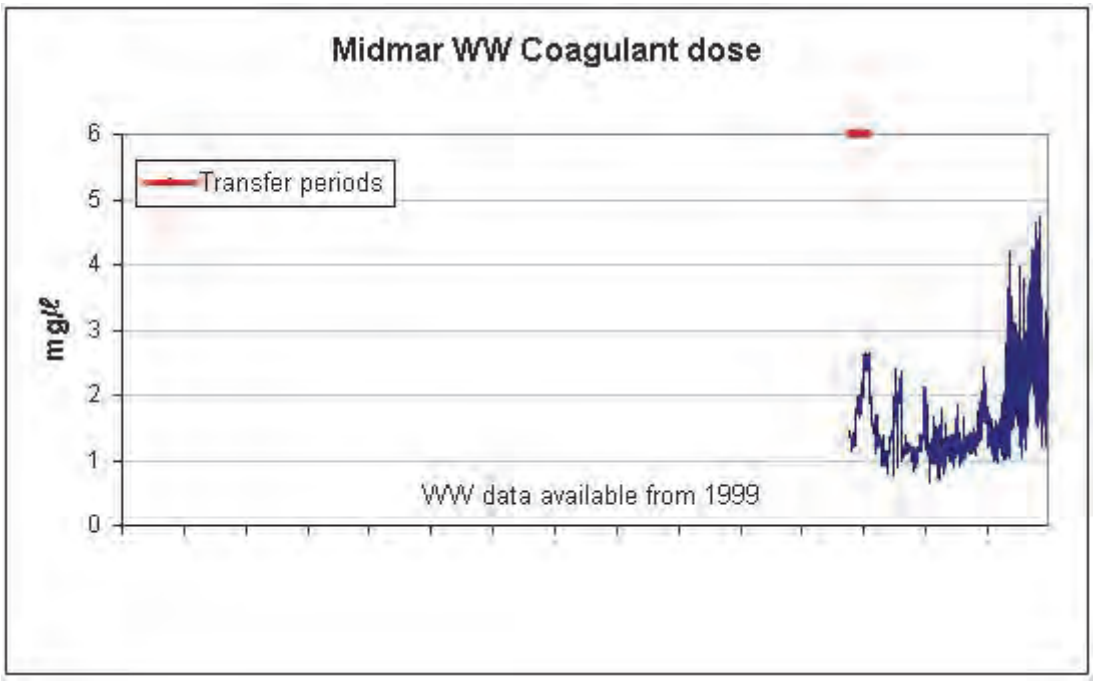


FIGURE 4.6: Time series plot of coagulant dose at the Midmar WW

Figures 4.5 and **4.6** appear to support the contention that interbasin transfer from the Mooi river into Midmar dam (amongst other factors) increased the coagulant dose required at DV Harris and Midmar WW. The significant increase in coagulant dose recorded at the DV Harris WW during December 1995 and January 1996 was due to an extreme rainfall event.

This increase in coagulant dose was particularly noticeable during the November 1999 to January 2000 transfer at both the DV Harris and Midmar WW (see **Figures 4.7** and **4.8**).

It is also notable that, since the retention time in the Midmar dam (prior to raising of the wall in 2003) is approximately one year, there does not appear to be an appreciable lag period between the interbasin transfer period and the increase in coagulant dose at the WW. **Figures 4.7 and 4.8** show an increase in coagulant dose soon after the commencement of interbasin transfer. Not all increases in coagulant dose at the WW, however, can be attributed to interbasin transfers as increases in coagulant dose can also be seen during non-transfer periods, particularly during the summer high rainfall-runoff months (see **Figure 4.5** and **4.6**).

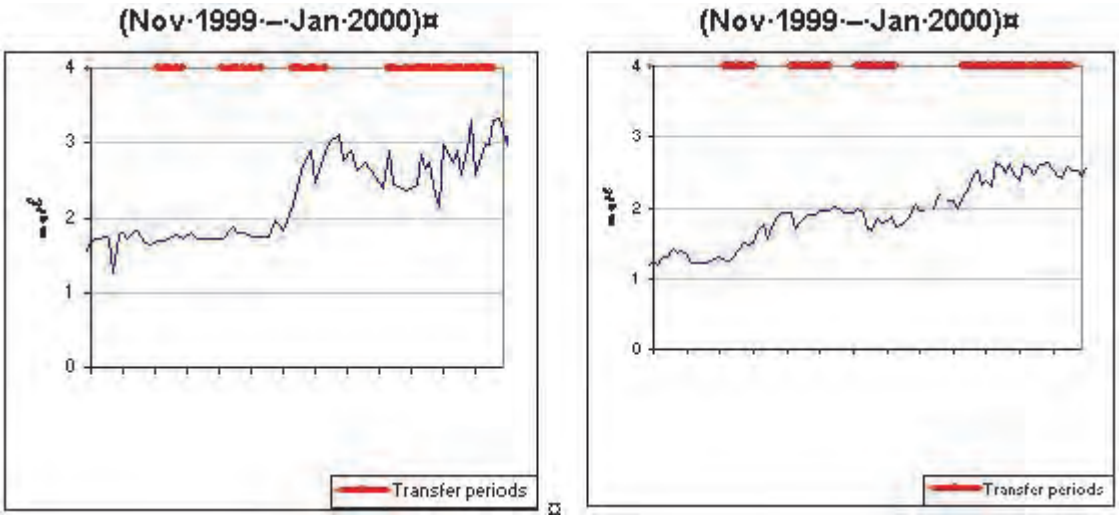


Figure 4.7 and 4.8: Time series plot of coagulant dose at the DV Harris and Midmar WW during transfer periods

4.4.4. Assessment of Relationship Between Coagulant Dose and Other Water Quality Constituents

Regression analyses illustrating the strength of the relationships between coagulant dose and water quality constituents are shown in Appendix 2a for DV Harris WW and in **Appendix 2b** for Midmar WW. A summary of the R^2 values for these regression analyses is shown in **Table 4.3**:

TABLE 4.3: Summary of R^2 values for the regression analyses for dependence of coagulant dose on water quality constituent values

	R^2 value	
Determinand	**DV Harris WW**	**Midmar WW**
Temperature (°C)	0,0073	0,0112
Coliforms (per 100mℓ)	0,0011	0,0083
E. coli (per 100mℓ)	0,0046	0,0003
F. Streptococci (per 100mℓ)	0,0002	0,0013
Algal Count (cells/mℓ)	0,0023	0,0065
pH	0,0036	0,0037
Colour (^{0}H)	0,0026	**0,3254**
Turbidity (NTU)	0,0004	0,127
Conductivity (mS/m)	0,0275	0,0536
Total Aluminium (ug/ℓ)	0,0038	0,1121
Alkalinity (mg/ℓ)	0,0429	0,0096
Total Hardness (mg/ℓ)	0,0297	0,0319
Calcium (mg/ℓ)	0,02	0,0219

	R^2 value	
Magnesium (mg/ℓ)	0,0213	0,0352
Sodium (mg/ℓ)	0,0508	**0,251**
Potassium (mg/ℓ)	0,0214	0,1064
Iron (mg/ℓ)	0,0034	0,1612
Manganese (mg/ℓ)	0,0097	0,0415
Silica (mg/ℓ)	0,0004	0,0006
Nitrate (mg N/ℓ)	0,0006	**0,3337**
Nitrite (mg N/ℓ)	0,0092	-1,00E-15
Ammonia (mg N/ℓ)	0,002	0,0003
Chloride (mg/ℓ)	0,0027	0,0287
Fluoride (µg/ℓ)	0,0038	0,0158
Sulphate (µg/ℓ)	0,0076	0,0567
Totally Dissolved Solids (mg/ℓ)	0,0018	**0,2612**
Suspended Solids (mg/ℓ)	0,0033	0,0018
Copper (mg/ℓ)	0,0017	All data below detection limit
Zinc (mg/ℓ)	0.0019	-1,00E-15
Lead (µg/ℓ)	0.1495	All data below detection limit
Cadmium (µg/ℓ)	1.00E-04	All data below detection limit
Chromium (µg/ℓ)	0,008	All data below detection limit
Mercury (µg/ℓ)	6,00E-06	All data below detection limit
Arsenic (µg/ℓ)	0,0106	All data below detection limit
Selenium (µg/ℓ)	0,0548	All data below detection limit
Nickel (µg/ℓ)	0,0006	All data below detection limit
Barium (µg/ℓ)	0,0005	0,2439
Silver (µg/ℓ)	0,0024	All data below detection limit
Antimony (µg/ℓ)	0,0075	All data below detection limit
Boron (µg/ℓ)	0,0276	All data below detection limit
Total Recoverable Cyanide (µg/ℓ)	0,0002	All data below detection limit
Total Organic Carbon (mg/ℓ)	0,0019	0,013

There were no significant relationships between coagulant dose and any water quality constituent for DV Harris WW as shown by the R^2 values in **Table 4.3** and **Appendix 2a**. However, some relationships between Midmar WW coagulant dose and water quality constituents were shown. These are shown in bold type in **Table 4.3** for colour, sodium, nitrate and total dissolved solids, with R^2 values ranging from 0,25 to 0,33, explaining 25 to 33% of the variability in coagulant dose. Although these relationships cannot be described as highly significant, the plots all show increasing coagulant dose with concentrations of the water quality constituents.

Surprisingly, the turbidity and suspended solids relationships are weaker. It would appear that Midmar WW coagulant demand is related to ionic constituents in a positive manner (colour excepted). However, this finding does not concur with the observation that coagulant demand increased when Mooi river water was introduced to Midmar dam, since all the above constituent (colour, sodium, nitrate and total dissolved salts) concentrations are lower for the Mooi river compared to the uMngeni inflow to Midmar dam (see **Table 4.2**). In other words, introduction of lower ionic strength water from the Mooi river catchment should have reduced the coagulant demand at the Midmar WW, but the reverse was true. Other factors in the Mooi river water must therefore be responsible of the increased coagulant demand.

As recommended by the Steering Committee for the project, further subsetting of the WW raw water quality data was undertaken to assess whether seasonal turbidity, pH range data, or subsetting of the data into upper and lower quartiles would correlate better with WW coagulant dose. The results of this subsetting of the data are shown in **Appendix 3** and are as follows:

- Subsetting of turbidity data into seasons slightly increased the proportion of variability in coagulant dose that could be explained by turbidity for the Midmar WW winter period, but no improvement in R^2 values were noted for the DV Harris WW.
- No improvement in R^2 values were noted by subsetting the pH data into ranges at either the DV Harris WW or the Midmar WW.
- No improvement in R^2 values were noted by subsetting the turbidity, conductivity or TOC data into upper and lower quartiles at either the DV Harris WW or the Midmar WW.

4.5. CONCLUSIONS

The following conclusions may be drawn from the analysis and interpretation of historical water quality, flow and coagulant data:

1. The results of the comparison of catchment land use and water quality data between the upper Mooi and upper uMngeni catchments indicate similar, good water quality at both sites, suggesting that water transferred via the Mooi-uMngeni transfer scheme should not significantly impact the water quality in the Midmar impoundment to the detriment of treatment of potable water.

2. In practice, interbasin transfer has resulted in a significant increase in coagulant demand and a change in type of coagulant best suited to the treatment of the water, particularly during the November 1999 – January 2000 transfer period.
3. No significant relationships were noted between coagulant dose and water quality constituents at DV Harris WW.
4. At Midmar WW, positive but significant relationships were noted between coagulant dose and colour, sodium, nitrate and total dissolved salts, with approximately 25 to 33% of the variability in coagulant dose explained by the variability in these constituents.
5. Subsetting the data into seasonal turbidity, pH ranges or upper and lower quartiles id not improve their relationship to coagulant dose.

5. LABORATORY RESULTS AND DISCUSSION

5.1. THE MVOTI – MAKOVANE SYSTEM

Anomalies were observed in this system, although more data would be required in order to confirm these. There were few differences in the water quality parameters of the two waters or the blends of the two, namely Mvoti:Makhovane at 68:32 and 95:5. The hardness and alkalinity of the Mvoti water was usually a little lower than that of the Makhovane, but not significantly so and the turbidity values of the two waters were generally similar. Even in terms of chlorine demand, the two waters were similar. It was interesting to observe however that the effect that the blending of the waters had on the turbidity was often unexpected. In some cases the blending of the waters would cause a small increase in the turbidity relative to both the original waters, while in others, blending resulted in a significant decrease in turbidity. Blending could also have the effect of reducing the chlorine demand.

In terms of coagulant demand, the Mvoti water was generally conducive to treatment with all the coagulant types tested, having very low demands when using polyelectrolytes (between 1 and 2 mg/ℓ), and aluminium sulphate demands in the region of 10 to 12 mg/ℓ. The Makhovane water however, was generally not suitable for treatment with most of the polyelectrolytes, except the blended PA/PACl, but at concentrations significantly higher than those required for treatment of the Mvoti water (4 to 10 times). The aluminium sulphate demand of this water was about double that of the Mvoti water.

Blending of the waters had no beneficial effect on the coagulant dose relative to the waters prior to mixing. The 68:32 Mvoti:Makovane mixture was similar in terms of coagulant demand to the Makovane water, while the 95:5 Mvoti:Makovane mixture was similar to that of the Mvoti water. One would have expected the Makovane water to have had less influence on the Mvoti water in the 68:32 mix, but otherwise these results were not unusual. Of greater interest is the fact that despite both waters coming from river sources in the same area and being very similar in terms of water

quality parameters, the reaction of various coagulants with these waters is significantly different.

5.2. THE DURBAN HEIGHTS - AMANZIMTOTI - NUNGWANE SYSTEM

Only very preliminary testing was conducted on this system and these results did not indicate the evidence of any anomlalies. The water quality parameters of the three waters were fairly similar, except that the alkalinity and hardness of the Amanzimtoti and Nungwane waters were generally lower than those of the Durban Heights water, while the turbidities of these two waters were quite a bit higher. Past experience at Umgeni Water has shown that even in cases where the turbidity values of the Durban Heights and Amanzimtoti waters have been similar, the coagulant demand at Durban Heights has usually been in the order of 1,5 to 3 mg/ℓ, while that at Amanzimtoti is often in double figures

It was interesting to note that for the Durban Heights water, the coagulant demand of all the polyelectrolyte coagulants was similar, but for the Amanzimtoti and Nungwane waters, the demand when using a blended PA/PAC/ was in the region of 60 to 80% higher than that of the other polyelectrolytes that were used. This indicates that there is some factor present in the Amanzimtoti and Nungwane waters which respond differently to these coagulants.

5.3. THE MIDMAR - MEARNS SYSTEM

5.3.1. Variations in coagulant demand

In the initial tests, which were conducted on Midmar Dam, Mearns and Springgrove water, a number of interesting anomalies were observed. The results of four of the trials conducted on these waters were averaged and this showed that in terms of the usual water quality indicators, there were in fact very few differences between the three waters and the three blends of waters used, namely Midmar:Mearns at 72:28, Midmar:Mearns:Springrove at 63:27:10 and Midmar:Mearns:Springrove at 63:22:15 (i.e. a total of six different waters). Small, but insignificant differences, were present in the conductivity and alkalinity, but all other water quality parameters were very similar, the most noticeable difference in the averaged values being in the turbidity of

the Springrove water, but this was mainly as the result of a sample of Springrove water in one of the sets of water samples having a much higher than normal turbidity.

The lime demands of the six water samples were generally very similar, while the chlorine demand was far more variable. In almost all cases the chlorine demand of the Midmar water was significantly lower than that of the Mearns, while that of the Springrove water varied, sometimes being higher than the Midmar water and in other cases lower. Blending of the waters, usually had the expected result. In other words, the chlorine demand of the mixture would be approximately an average of the blend, based on the proportions used.

The anomalies observed were in terms of coagulant demand. In general, the coagulant demand of the Mearns water was in the region of 100% greater than that of the Midmar Dam water when using diallyldimethyl ammonium chloride (DADMAC) and DADMAC blends and approximately 40% higher when using polyamine (PA) or PA blended coagulants. The increase in aluminium sulphate demand of the Mearns water relative to Midmar water was less than 10%. When blending the Midmar and Mearns waters at a rate of 72:28, the Mearns water had a significant effect on the coagulant demand of the mixture, far greater than one would have anticipated, since Mearns contributed only 28% of the mixture. The coagulant demand when using DADMACs and DADMAC blends increased by approximately 70 to 80% relative to that of the Midmar water, while the demand of the PA and PA blends increased by 15 to 20%.

Another interesting observation was that the Springrove water, although having a DADMAC and DADMAC blend demand similar to that of the Mearns water, caused the coagulant demand with these chemicals to decrease when it was added to the Midmar and Mearns mixture. The PA and PA blend demand of the Springrove water was approximately 50 to 60% higher than that of the Midmar water and 10 to 20% higher than that of the Mearns water. When blended with the Midmar and Mearns water, the PA and PA blend increased as was expected. A graphic representation of the coagulant demands for the various polyelectrolytes when used on the waters in this system appear in **Figure 5.1** below.

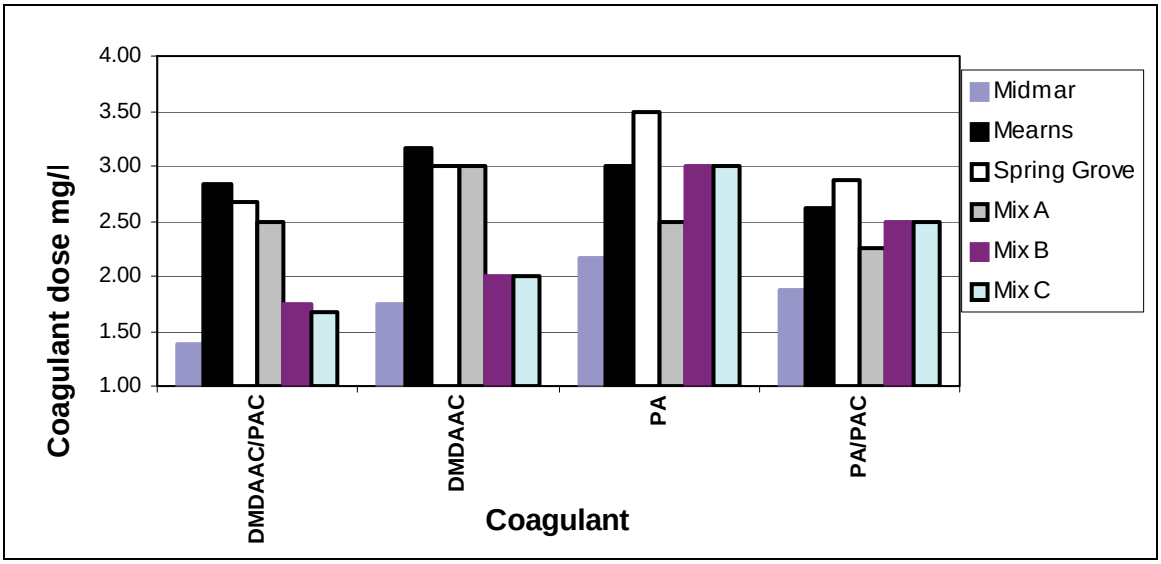


FIGURE 5.1: Optimum coagulant doses for various polyelectrolytes on Midmar, Mearns and Springrove water and three blends of these waters (averaged values).

Where: Blend A is Midmar:Mearns at 72:28
Blend B is Midmar:Mearns:Springrove at 63:27:10
Blend C is Midmar:Mearns:Springrove at 63:22:15

At the time of conducting the tests described above, no zeta potential meter was available, but thereafter a zeta potential meter was acquired. It was hoped that the zeta potential might be a parameter that would explain some of the differences observed in the response of the various waters in the Midmar/Mearns system to different poyelectrolyte coagulants.

Once the decision had been taken to concentrate only on the Midmar-Mearns system and to exclude Springrove, samples were taken from the following sites (see **Figure 4.1**):

- The Mooi River at the Mearns weir (Mearns).
- The uMngeni River at a point just below the confluence of the Lions and uMngeni Rivers but just prior to the point where the uMngeni River flows into Midmar Dam (Infow).
- The raw water inflow to the Midmar Water Works (raw water supply from Midmar Dam) (Midmar).
- The raw water inflow to the D V Harris Water Works (raw water supply from Midmar Dam).

During these trials no pumping took place at the Mearns augmentation scheme, since work had already started on the upgrade of the weir and the water level in Midmar Dam had been lowered to allow work on the raising of the dam wall. This meant that it was possible to study the Midmar-Mearns system without any Mooi River water being in the system. It was realised that there would be a problem in studying the system when pumping from the Mooi River into the Lions River was taking place, since the sample point at the inflow to Midmar Dam would already consist of water from all three rivers, namely the uMngeni, Lions and Mooi Rivers. Initially the uMngeni River was only sampled at a point below the confluence of the uMngeni and Lions Rivers, but at a later stage sampling at a point above this confluence was also included so that the impact of the uMngeni River, without Lions River or Mooi River water could be assessed.

Tests were conducted on all the water samples, as well as on blends of the water samples from Mearns and uMngeni River inflow to Midmar Dam (3:1, 1:1 and 1:3). The coagulants used were aluminium sulphate, a PA (U5000), a DADMAC and PACl blend (Sudfloc 3850), a blended PA and PACl (C7750) and a blended DADMAC (LP526). (these are described in more detail in **Section 3.3** of this report).

The optimum coagulant doses of both the unblended and blended water samples were determined for each coagulant, the optimum dose being considered the minimum dose which would produce a filtered water turbidity of less than 0,5 NTU. The water was then also treated at half and double the optimum dose and the final treated water in each case also analysed as described above in Section 5.1.4.

Despite comprehensive analysis, very little in the way of unexpected or unusual trends have been observed. For most of the determinands, including TOC, DOC, UV and zeta potential, there was generally very little difference between those for each of the waters and the blends and even where small differences were found, the variation in these determinands was expected. Typical examples are listed in **Table 5.1**.

Anomalies were however observed for turbidity, colour and suspended solids, where the results for the blended samples did not follow the expected trend. In many cases these determinands were lower in the blended samples than they were in either of the waters prior to blending. Typical examples can be seen in **Figures 5.2 and 5.3**.

TABLE 5.1: Typical variations in determinands for Mearns water and uMngeni River (Inflow to Midmar Dam) and blends of the two.

Determinand	Mearns	3 Mearns 1 Inflow	1 Mearns 1 Inflow	1 Mearns 3 Inflow	Inflow
Sodium mg/ℓ	2,7	2,9	3,3	3,9	4,4
Cond. mS/m	3,87	4,17	4,48	4,88	5,46
Hardness mg/ℓ	13,1	14,9	16,0	17,2	17,3
Chlorides mg/ℓ	1,65	2,12	2,58	3,11	3,14

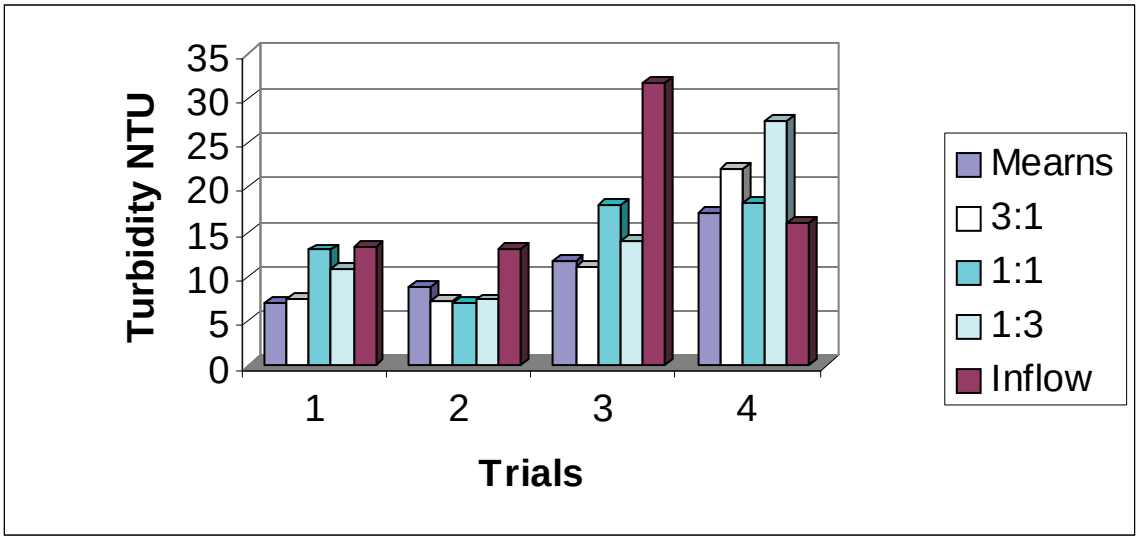


FIGURE 5.2: Turbidity of Mearns (Mooi River) and Midmar Dam Inflow water and 3:1, 1:1 and 1:3 blends of these waters.

Tests were also conducted at half and double the optimum coagulant dose, in order to determine whether anomalous effects occur at these concentrations. However, the trends observed were as expected, with variables such as zeta potential showing a gradual change from the lowest coagulant dose (half the optimum) through to the highest dose (double the optimum).

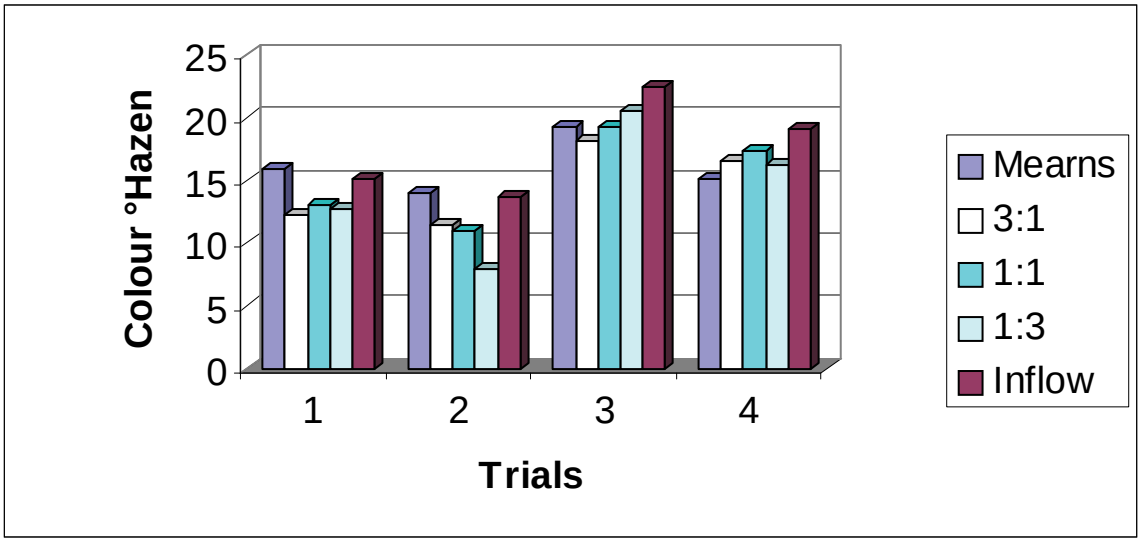


FIGURE 5.3: Colour of Mearns (Mooi River) and Midmar Dam Inflow water and 3:1, 1:1 and 1:3 blends of these waters.

Much attention was focussed on the coagulant demands of the various waters and their blends. Standard jar tests were performed on each raw water source and, where relevant, on the blends of these waters, using a range of polyelectrolytes as well as aluminium sulphate. The polyelectrolytes used are described above in **Section 5.1.4.**

Initial tests had shown that Mearns (Mooi River) water had a much higher polymeric coagulant demand than the water being extracted at the Dam wall. Subsequent tests included water from the uMngeni River at the inflow to Midmar Dam and the polymeric coagulant demand of this water was found to be even higher than that of the Mearns (Mooi River) water (see **Figure 5.4**). During the 2 month period that these tests were carried out, no Mooi River water was being pumped into the Lions River, so this would not explain the higher coagulant demand of the uMngeni River inflow to the dam. The reduced coagulant demand at Midmar WW (water extracted from the Dam wall) is not unusual, since an improvement in water quality after impoundment is expected, but the even higher coagulant demand of the Midmar Dam inflow water is interesting. Experience has already shown that when pumping of Mooi River water into the Lions occurs, water treatment at the plants abstracting from Midmar Dam is significantly affected. Blending of the inflow water and Mooi River water revealed some interesting variations in the coagulant demand of the water. The average coagulant demand data obtained during trials conducted during January and February 2002 are graphically represented in **Figure 5.4**. Very little variation in the coagulant demand for each coagulant and for each sampling site were observed

during this period and therefore averaging of the data was considered acceptable. As can be seen in **Figure 5.4**, blending of Mearns and inflow water yields unpredictable results. In some cases the resultant blend has a lower coagulant demand than either of the two waters prior to blending and in other cases the water has a higher coagulant demand than either of the unblended waters. Certainly no predictable trends are evident. In an attempt to draw a correlation with zeta potential, the average zeta potential at the coagulant demand was plotted for the same samples and compared to Figure 5.9 (see **Figure 5.5**). Again, since the variation in zeta potential for at each coagulant demand and for each water was small during these trials, averaging the data in this manner was considered acceptable. However, no correlation was evident.

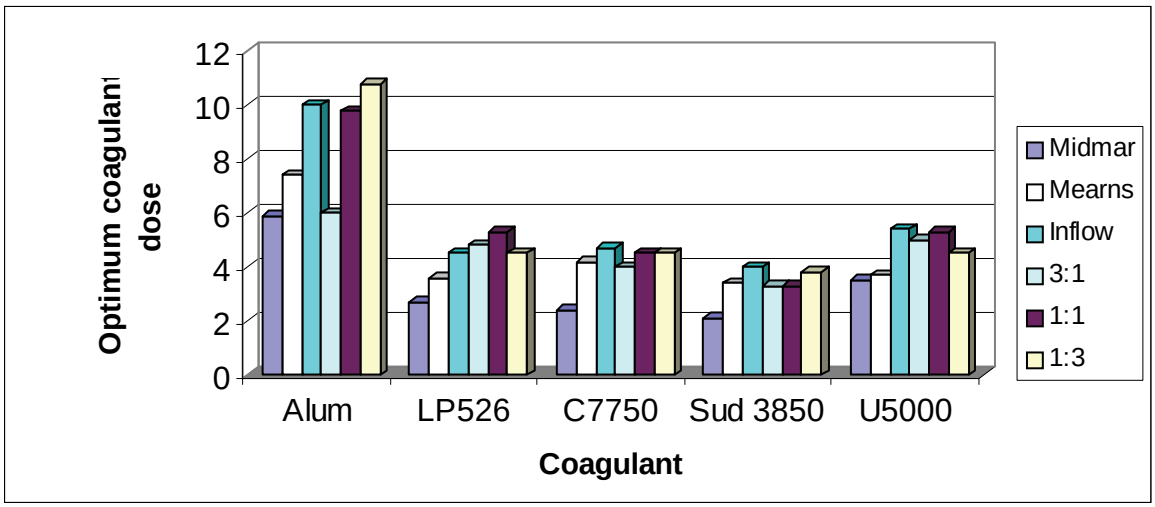


FIGURE 5.4: Average coagulant demand for water from Midmar WW, Mearns (Mooi River), Midmar Dam inflow and blends of Mearns and Midmar Dam inflow water.

Where: 3:1 is Mearns:Inflow 3:1
3:1 is Mearns:Inflow 3:1
3:1 is Mearns:Inflow 3:1

The only correlations which could be found were weak. For example, a weak correlation was found between the aluminium sulphate demand and the raw water turbidity, but this is to be expected. A loose correlation was also observed between the polymeric coagulant demand and the raw water turbidity, although since the polymeric coagulant demands were always much lower than the aluminium sulphate demand, these trends were even less pronounced than for aluminium sulphate.

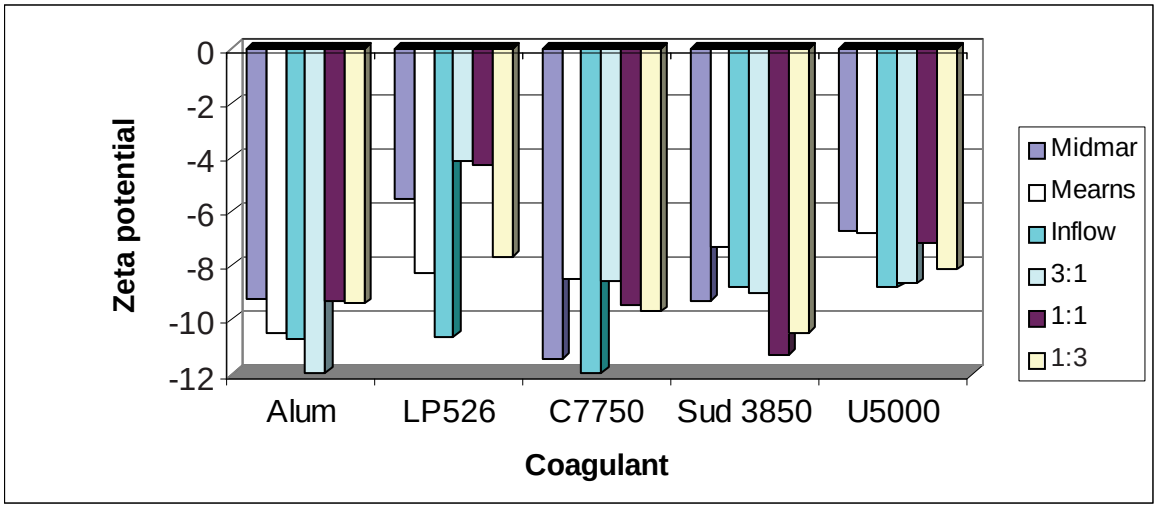


FIGURE 5.5: Average zeta potential at the optimum coagulant demand for water from Midmar WW, Mearns (Mooi River), Midmar Dam inflow and blend of Mearns and Midmar Dam inflow water.

A weak trend was sometimes observed between the zeta potential and the turbidity of the raw water samples, but not always. More interesting was the fact the zeta potential at the coagulant dose appears to be dependent on the coagulant itself. As can be seen in **Figure 5.5**, the zeta potential at the coagulant demand when using aluminium sulphate, the PA/PACl blend and the DADMAC blend was almost always more negative than –8 mV, while that for the DADMAC/PACl blend and the PA was often more positive than –8 mV. This may be related to the charge density of the coagulant and warrants further investigation.

A number of "titration' curve tests were conducted, in which Mearns (Mooi River) and Midmar Dam inflow water was blended starting with 500 mℓ of one water and adding the other in 50 mℓ increments until a total volume of 1 L of blended water had been obtained. After each incremental addition the blended sample was measured for pH, turbidity, UV absorbance, conductivity and zeta potential. The tests would then be repeated but this time changing the waters around (i.e. starting with 500 mℓ of the second water and adding the first in increments of 50 mℓ). Despite the unusual effects observed for turbidity and colour of blended waters when conducting the jar tests described above, nothing unusual was detected in these "titration" tests. A typical example of a turbidity curve obtained in one of these "titration" tests is depicted in **Figure 5.6** and shows a gradual increase in turbidity from that of the

Mearns sample (lower turbidity) to that of the Midmar Dam inflow sample (higher turbidity).

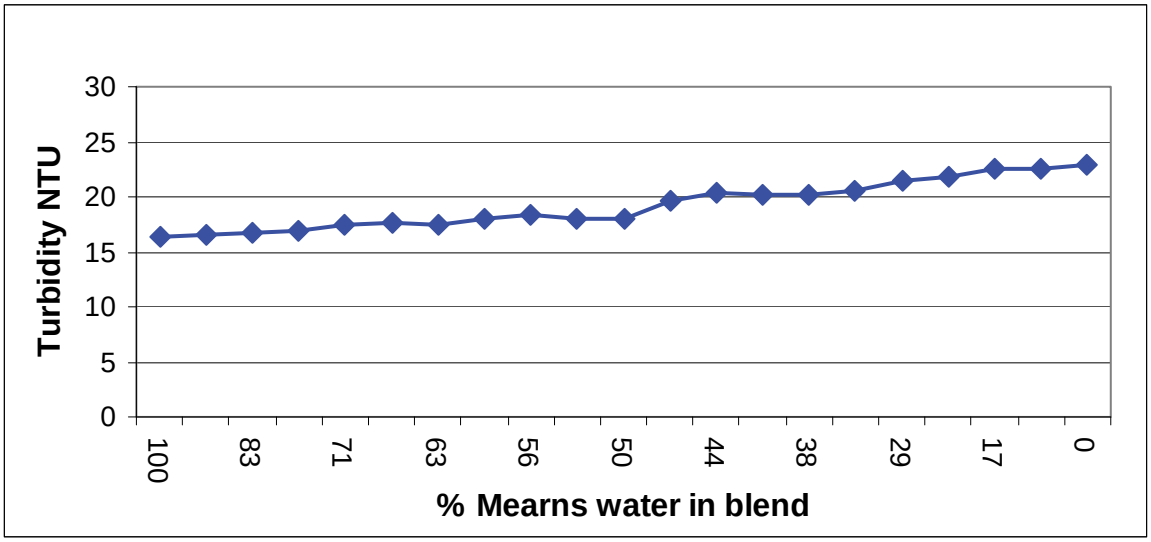


FIGURE 5.6: Turbidity of "Titration" curve of Mearns and Midmar Dam inflow water.

5.3.1.1. Impact of molecular mass and charge density of polymeric coagulants

Since it was considered feasible that the varying effects noted with the different polymeric coagulants might be dependent on molecular weight and possibly also on surface charge, tests were carried out using a range of polymeric coagulants of differing molecular weights and surface charges (these are described in **Section 5.1.4**) in an attempt to quantify these effects. Aluminium sulphate was included in these tests, so that the impact on an inorganic coagulant could also be assessed. The water samples tested included the Midmar Dam inflow, the Lions River, Mearns and 3:1, 1:1 and 1:3 blends of the Midmar Dam inflow and Mearns waters.

These tests revealed very little information. There were no trends evident that could be attributed to the differences in molecular weight and charge density of the coagulants, except that the optimum dose for the very low molecular weight polyamine, A50VL was generally much higher than that of the higher molecular weight coagulants. It was also possible in some cases to achieve a final turbidity of less than 0,5 NTU using the A50VL even when this was not possible using the higher molecular weight products. It was unfortunate that in many of the tests, these coagulants were found to be unsuitable for the treatment of these waters, although it should be pointed out that they were generally successful for the treatment of the

Midmar water. This is not surprising, since the Midmar sample is in fact the raw water supply to Midmar Water Works, which is collected at the outflow from Midmar Dam and an improvement in the quality of the water is expected after impoundment..

The zeta potential also failed to reveal any trends of interest. The zeta potential at the optimum dose (where achievement of the 0,5 NTU standard was not possible, the optimum dose was that dose which yielded the lowest filtered turbidity) was generally between approximately –0,5mV and just above zero, although it was often more negative when using aluminium sulphate. No trends that could be attributed to the variation in molecular weight of the coagulants were evident.

The UV absorbance at 254nm was found to be a consistent indicator of the optimum dose when using polymeric coagulants. The optimum dose almost always occurred at, or near, the lowest UV absorbance value. In fact, by using UV absorbance only, it would be possible in almost every case to determine the optimum dose. However, it was not possible to determine from the UV absorbance whether the filtered turbidity was less than 0,5 NTU or not. UV absorbance could not be used in this way when employing inorganic coagulants, since unlike the polymeric coagulants, they do not generally result in rapid restabilisation and so the UV absorbance continues to decrease at concentrations higher than the optimum (i.e. the dose yielding a filtered turbidity of less than 0,5 NTU). The removal of colour was erratic and pH and conductivity remained unaffected by the different polymeric coagulants.

5.3.2. Enhanced coagulation effects

The enhanced coagulation tests conducted on the Midmar-Mearns system indicated that the best aluminium sulphate dose in terms of overall treatment was generally between the optimum dose defined in terms of turbidity removal (i.e. the minimum dose required to reduce the turbidity of the water to below 0,5 NTU) and three times the optimum dose. This is in agreement with the findings of Pryor and Freese (1998). At aluminium sulphate doses greater than three times the optimum, restabilisation often occurred and turbidity removal deteriorated. However, the same trends were observed for all the waters investigated, there being no marked differences between the Midmar WW raw, the Mearns water, the uMngeni inflow to Midmar Dam or their blends.

Polymeric coagulants were also investigated for enhanced coagulation, but apart from the fact that these were not always suitable for the treatment of the water and therefore did not always achieve an optimum dose in terms of turbidity removal, restabilisation occurred rapidly at doses above the optimum dose, making enhanced coagulation difficult if not altogether impossible.

The parameters studies closely during these enhanced coagulation tests were zeta potential, streaming current, UV absorbance at 254nm, conductivity, suspended solids and total and dissolved organic carbon. The zeta potential and streaming current followed the expected trend, becoming more positive the higher the aluminium sulphate dose. The only difference between zeta potential and streaming current was in terms of scale. The zeta potential of all the raw waters investigated in the enhanced coagulation trials (total of 13, including unblended and blended raw water samples) was -14,8mV, while the average at the optimum dose was –1,14mV (the zeta potential generally varied between –5mV and a little over zero at the optimum dose), rising to an average of 3,6mV at seven times the optimum dose. Again no trends relating to water source were evident. The streaming current for the same samples gave an average of – 1,89mV for the raw samples, -1,15mV at the optimum doses and 0,62mV at seven times the optimum dose. The polymeric coagulants, although not effective for enhanced coagulation, were interesting in that the effect on the zeta potential and streaming current at concentrations much higher than the optimum dose was far more significant. At seven times the optimum dose, the zeta potential was generally around 20 to 40mV and the streaming current between 3 and 4mV, an indication of the much higher charge density of the polymeric coagulants.

The UV absorbance of the water generally decreased with increasing aluminium sulphate dose up to seven times the optimum dose, even though the turbidity of the water sometimes increased at five, or seven times the optimum dose. In this aspect, the correlation observed between turbidity and UV absorbance which was observed for the polymeric coagulants, was not as good using aluminium sulphate.

Conductivity, as to be expected, increased with increasing aluminium sulphate dose, increases being in the region of 20 to 60% (an average increase of 42% at seven times the optimum dose was observed for all the samples used in the enhanced

coagulation trials). The suspended solids content was generally too low for any trends to be observed.

The TOC and DOC removals achieved were similar for all the waters tested, including both the unblended and the blended samples. Removals were generally between 25% and 60%, which is the same as that reported by Pryor and Freese (1998) for enhanced coagulation. The average TOC removal calculated for all the water samples investigated in the enhanced coagulation trials was 45%.

The enhanced coagulation trials merely served to confirm the findings of other researchers regarding enhanced coagulation and failed to identify any significant differences between the various water types present in the Midmar-Mearns system.

5.3.3. Effect of ozone

Preliminary tests were conducted in which water samples from the Midmar-Mearns system were ozonated prior to coagulation with aluminium sulphate or LP526 (a DADMAC/PAC blended polymeric coagulant). Ozone affects the organics present in water, partially oxidising larger molecular weight compounds, into smaller, more polar organics (Edwards et al, 1994; Reckhow and Singer, 1984). It was therefore considered possible that if there were any significant differences in the organic constituents in any of the water samples, they would react differently with ozone and in turn respond differently to coagulation. Samples of the Midmar WW raw, the uMngeni River inflow to Midmar Dam and Mearns were ozonated at 0,25; 0,5 and 1,0 mg/ℓ ozone before coagulation with either aluminium sulphate or the polymeric coagulant.

The ozone was not found to have any significant effect on each water type in terms of coagulant dose, zeta potential, conductivity, turbidity or UV absorbance at 254nm. Ozone was found to bring about a small reduction in the UV absorbance of each water, but this is in agreement with the literature (Hoigne and Bader, 1983). Pryor and Freese (2000) found that usually a small decrease in UV of the water occurred up to applied ozone dose to DOC ratios of between 0,1 and 0,3. At an applied ozone dose of 1 mg/ℓ, the ozone to DOC ratio of these waters fell into this range. Coagulation of the ozonated water obviously brought about further reductions in the UV absorbance, the reduction in UV being greater the higher the ozone dose. This was observed for

all three water types and both for aluminium sulphate and the polymeric coagulant. At low concentrations ozone has been found to decrease the colloidal charge density of certain organic compounds, which can give rise to a lower coagulant demand and improved NOM removal (Farvadin and Collins, 1989), which may explain the reduction in UV absorbance observed as the ozone dose was increased. More importantly though, these trials did not show any evidence of significant differences in the various water types which occur in the Midmar-Mearns system.

5.3.4. Effect of pH

Zeta potential and pH are intrinsically linked. The correlation between these two parameters was investigated in order to determine whether there were any significant differences between the various water types in the Midmar-Mearns system. The pH of water samples taken from the different sources in the system were adjusted between 2,5 and 12,5 using either hydrochloric acid or sodium hydroxide as required and the zeta potential and conductivity at each pH value measured. The zeta potential and conductivity displayed a similar correlation with pH, generally decreasing from a maximum at low pH, reaching a minimum value somewhere between pH 6 and 10, before increasing slightly at higher pH. Typical results are shown in **Figures 5.7** and **5.8**. However, beyond that, no significant differences in the response of the zeta potential and conductivity of the various waters emerged, rather the different waters from the Midmar – Mearns system showed very similar trends with pH.

These results were found to correlate with those of Pieterse (2003) in which the effect of pH on the turbidity of a water was assessed (**Figure 5.9**)

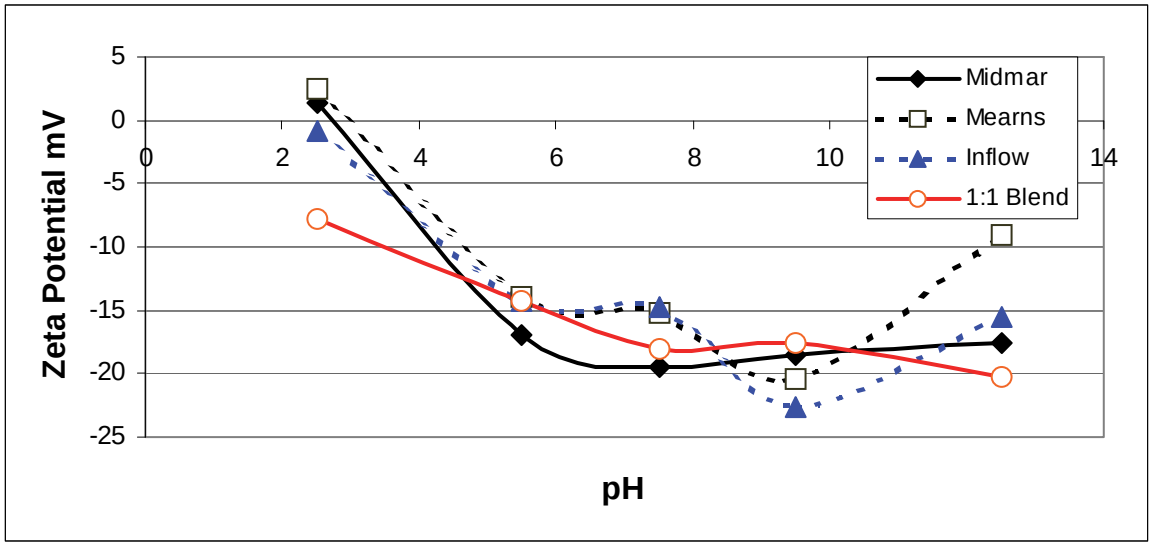


FIGURE 5.7: Effect of pH on the zeta potential of water samples from the Midmar – Mearns system.

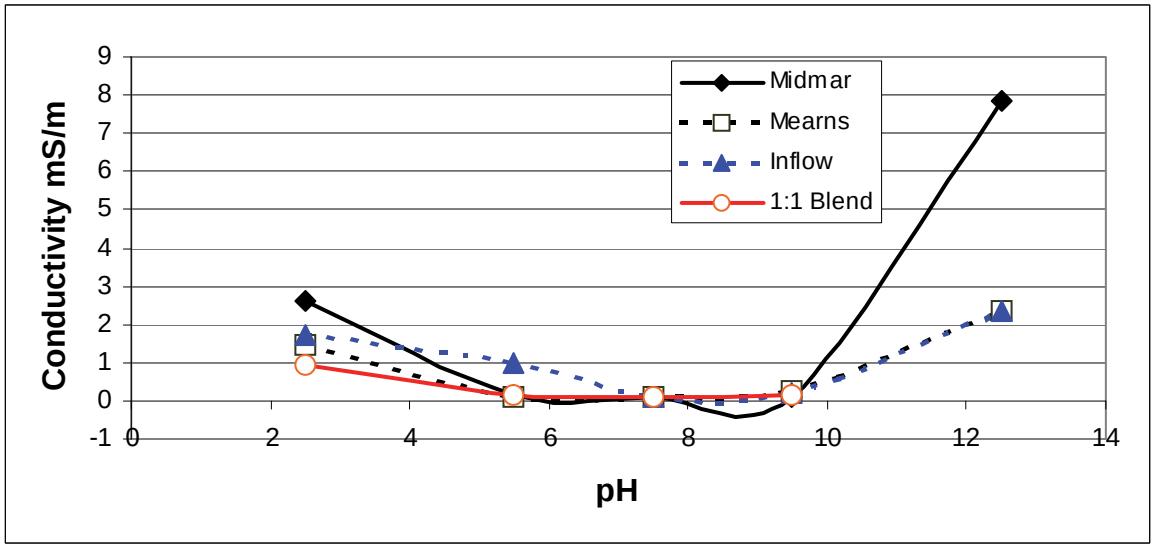


FIGURE 5.8: Effect of pH on the conductivity of water samples from the Midmar – Mearns system.

5.3.5. Effect of Filtration

It had been postulated by other researchers in the field that coagulant demand for polyelectrolytes was governed by the concentration of organic rather than inorganic suspended solids, and at the suggestion of the steering committee an additional series of tests was carried out where the raw water was filtered to remove TOC. By doing this it was hoped that a correlation between coagulant demand and TOC removal could be identified.

The raw water was filtered prior to coagulation with Whatman GF/C (1,2 µm), which had a pore size suitable to remove suspended TOC, as well as through Whatman No. 1 equivalent filter paper as a control. The results however indicated a greater effect by filtration on inorganic matter than on TOC and there was a measurable change in turbidity and zeta potential which changed roughly proportionately to each other. There was however virtually no change in the coagulant demand in these tests, which tends to confirm a relatively minor dependence of coagulant demand on the charged inorganic particles. However, as nearly all the organic carbon appeared to be in the dissolved form and the TOC and DOC were virtually identical in all cases no correlation with organic content could be observed.

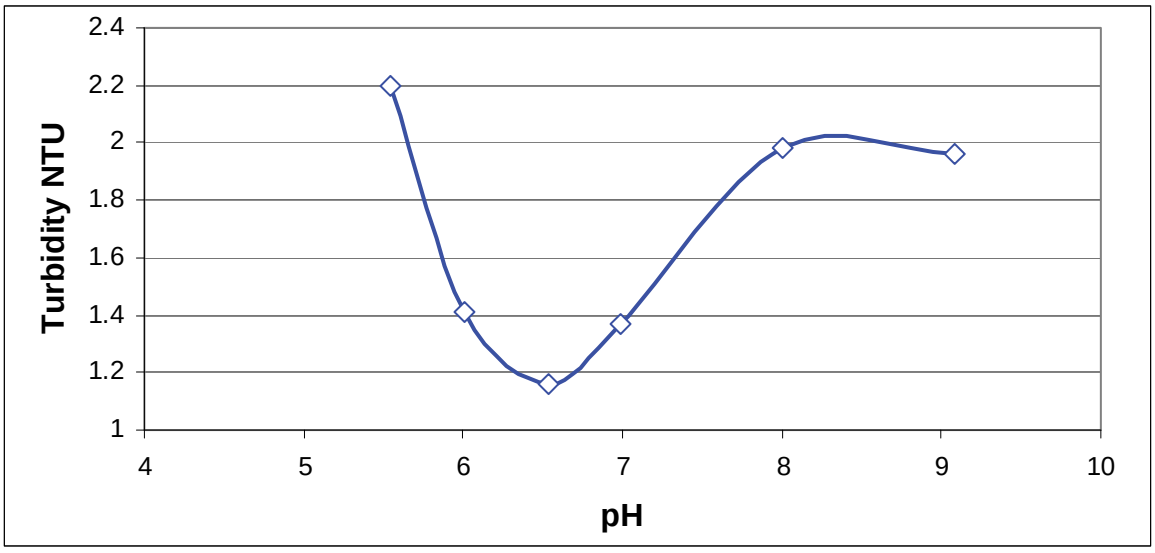


FIGURE 5.9: Effect of pH on the turbidity of a water (Pieterse, 2003).

5.3.6. GC-MS analysis

Gas chromatograph – mass spectroscopy finger-printing was conducted on samples from the Mearns weir (Mooi River), the inflow to Midmar Dam (uMngeni River below the confluence with the Lions River) and the uMngeni River above the confluence. The results of these have been studied, but do not indicate any significant differences in the organic components present in these water samples. Individual chromatograms appear in **Figures 5.10** to **5.13,** while **Figure 5.14** is a combined chromatogram for the three different water types and the control (methylene chloride which was used for extraction of the organic compounds present in the water samples). It was found that

all the peaks present in the chromatograms arose from the sample used for extraction of the samples (only compounds with a quality match above 80% were considered).

Trace analysis of samples was also conducted using the purge and trap technique. This indicated trace quantities of 2,6-di-tert-butyl-p-benzoquinone in the Midmar Dam sample and trace quantities of 2,6-di-buytl-2,5-cyclohexadiene-1,4-dione, but both were in quantities too low to have had any significant effect.

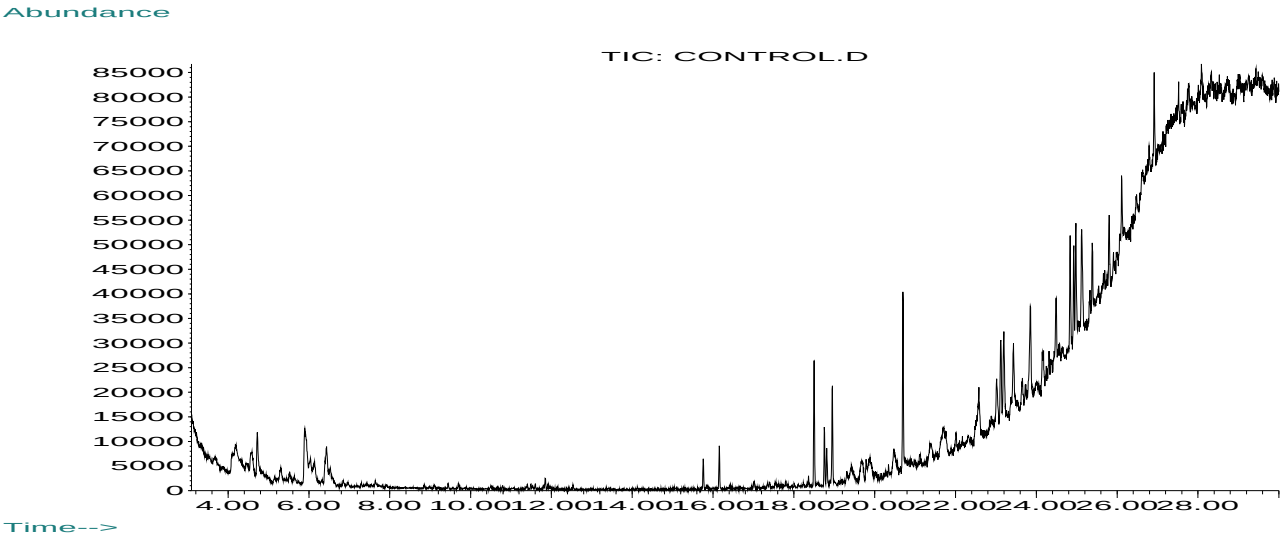


FIGURE 5.10: Chromatogram of control (methylene chloride)

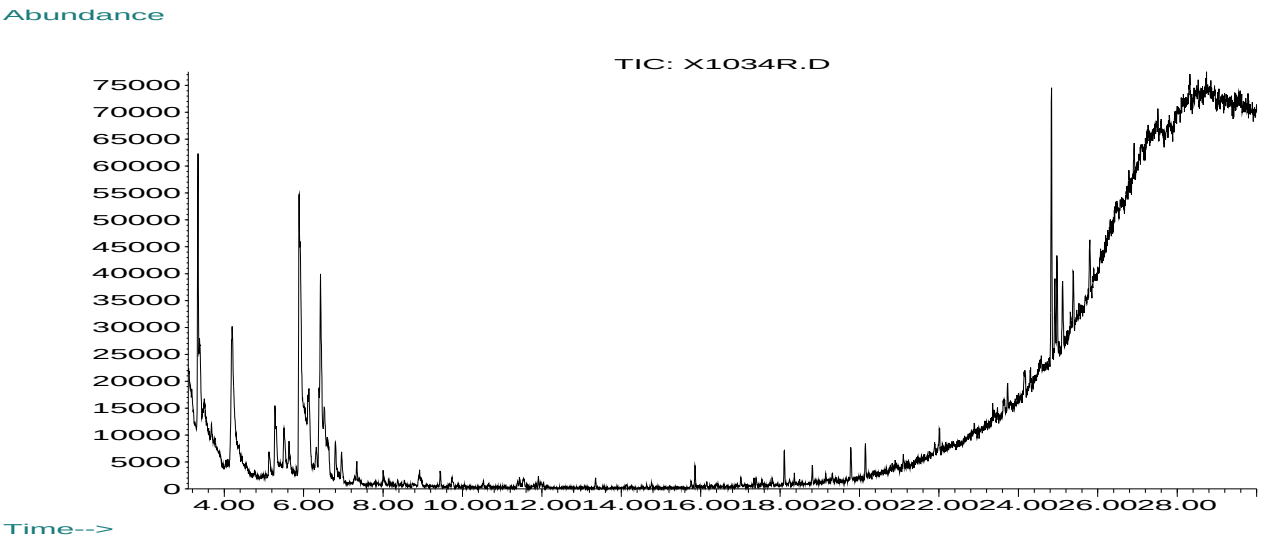


FIGURE 5.11: Chromatogram of Midmar Dam inflow (sampling point 2).

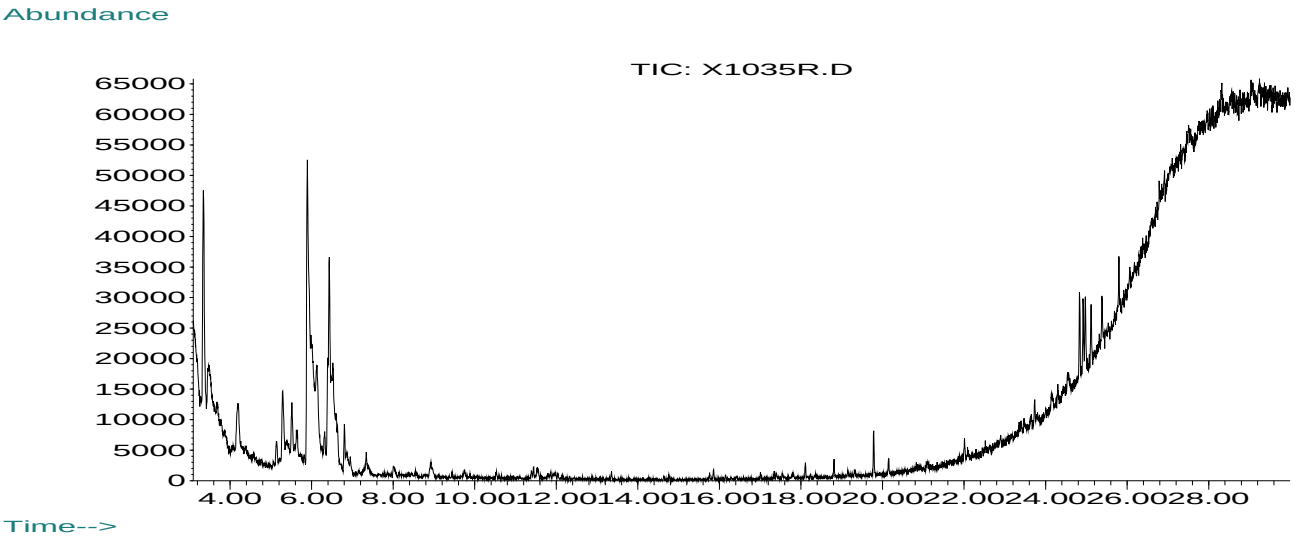


FIGURE 5.12: Chromatogram of uMngeni River above the confluence of the Lions River (sampling point 2.1).

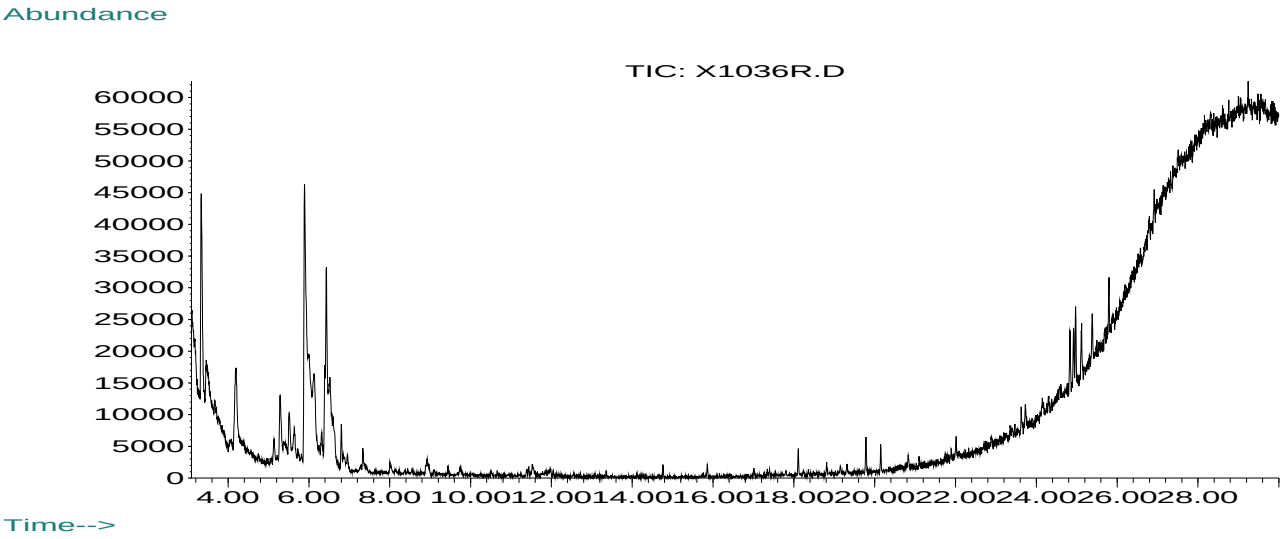


FIGURE 5.13: Chromatogram of Mearns water (sampling point

30).

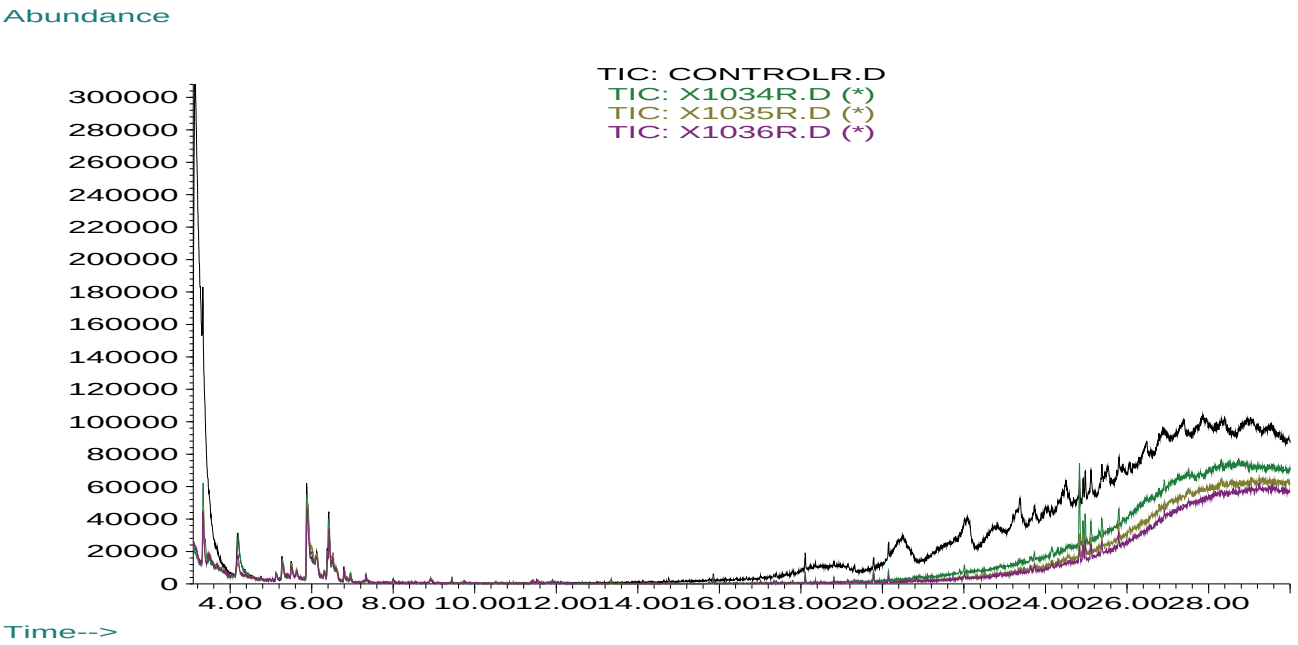


FIGURE 5.14: Overlay of chromatograms.

5.4. REFINEMENT OF THE JAR TEST

Tests were undertaken in an attempt to improve correlation between the jar test and full-scale operation and to allow for accurate and rapid selection of the correct polymeric coagulant dose. Initially attempts were made to use a small laboratory-scale clarifier, which would allow simulation of the floc blanket effect. In the experience of the research team, correlation between the jar test and full-scale plant operation is not always good when using polymeric coagulants, whereas the correlation is usually better when using an inorganic coagulant such as aluminium sulphate or ferric chloride. The mixing energy used during the flash mix period of the jat test has generally been found to have far more of an impact when using polymeric coagulants than it does when using inorganic compounds and it would appear that the effect of the floc blanket is also more important when considering polyelectrolyte compounds. The laboratory-scale clarifier is conical in shape, has a capacity of 1,65 ℓ and is 290 mm tall (from the bottom of the clarifier to the top of the overflow weir). Unfortunately, this was not tall enough to allow establishment of a floc blanket when using realistic upflow rates. Even at an upflow rate of 2 m/h, the total clarifier volume would be replaced almost 7 times every hour, which is far too rapid. Attempts at using lower upflow rates were unsuccessful and it was concluded that simulation of the floc

blanket would not be possible using a simple laboratory test, and that larger pilot-scale equipment would be required to this end.

It was then decided that by simulating filtration more accurately, better correlation might be possible. A series of test were conducted at each of the three waterworks which receive their raw water supply from Midmar Dam, namely the Midmar WW, D V Harris WW and Umlaas Road WW. Jar tests were conducted on site at each plant using the coagulant and dose being used on the plant. The jar-test coagulated and flocculated water was then filtered through a range of filters which had nominal pore sizes varying between 0,45 and 6 µm. The turbidity of the filtered water was then compared to that of the filter underflow on the plant. Simultaneously, water from the clarifier/pulsator overflow was also filtered through the same filters used in the jar tests and the turbidity of this water also compared to that of the rapid gravity filter underflow on the plant. The results indicated that the Whatman Number 1 equivalent filter paper which is routinely used for the jar test, does not give a good correlation with plant performance. Whatman 3V paper gives a better result, but the best results of all, for the tests conducted at all three waterworks, were obtained using a Millipore nitrocellulose filter with a nominal pore size of 0,8 µm. Unfortunately this filter paper is not ideal for general jar test purposes as it does not fold well and so a more suitable filter paper with a similar nominal pore size is recommended. Even when filtering the clarifier/pulsator overflow water, the 0,8 µm filter paper provided the best correlation with the rapid gravity filters. **Table 5.2** shows typical results obtained for the filtration tests.

Tests were also conducted to assess the impact of the shape of the jar. Using raw water samples taken from a Midmar Dam source, jar tests were conducted with a range of coagulants (both inorganic and polymeric organic coagulants) using both round 1 L capacity tall form beakers and square-shaped Consol-type 1 L capacity storage jars. It was in fact these Consol-type jars that were originally used in the jar tests and hence the name of the test. The results showed no significant differences between the tests conducted using each jar type. Typical results are graphically depicted in **Figure 5.15**. Jar shape does not appear to have any major impact on the test.

TABLE 5.2: Comparison of final filtered water from various Waterworks with filtered water obtained using different filters for the jar tests and for the clarifier/pulsator overflow.

Plant	Plant Filter	Source of water	Wht No 1	Wht No 3	Wht 2V	GF/C	G333	0,8 µm	0,45 µm
DVH	0,44	Jar Test	1,55	0,64	0,75	1,75	0,91	0,46	0,43
		Clarifier	0,64	0,73	0,55	1,67	1,08	0,42	0,24
DVH	0,44	Jar Test	2,06	1,45	1,04	3,28	1,14	0,49	0,47
		Clarifier	1,00	0,60	0,68	1,47	0,97	0,43	0,63
DVH	0,32	Jar Test	1,94	0,68	0,93	4,06	1,47	0,26	0,12
		Clarifier	0,73	0,97	-	2,42	3,30	0,33	0,30
DVH	0,33	Jar Test	2,40	0,71	-	2,18	2,58	0,36	0,35
		Clarifier	0,54	0,72	-	3,06	2,48	0,48	0,26
Midmar	0,20	Jar Test	2,07	1,00	0,73	2,98	1,39	0,21	0,02
		Clarifier	0,57	0,36	0,44	2,71	1,29	0,28	0,13
Midmar	0,31	Jar Test	0,70	0,65	0,53	2,52	2,45	0,38	0,28
		Clarifier	0,75	0,58	0,44	1,74	1,72	0,34	0,32
Umlaas	0,39	Jar Test	0,89	0,43	0,36	3,98	2,03	0,35	0,38
		Clarifier	062	0,48	0,31	1,94	4,90	0,61	0,61

Where "Wht" stands for "Whatman".

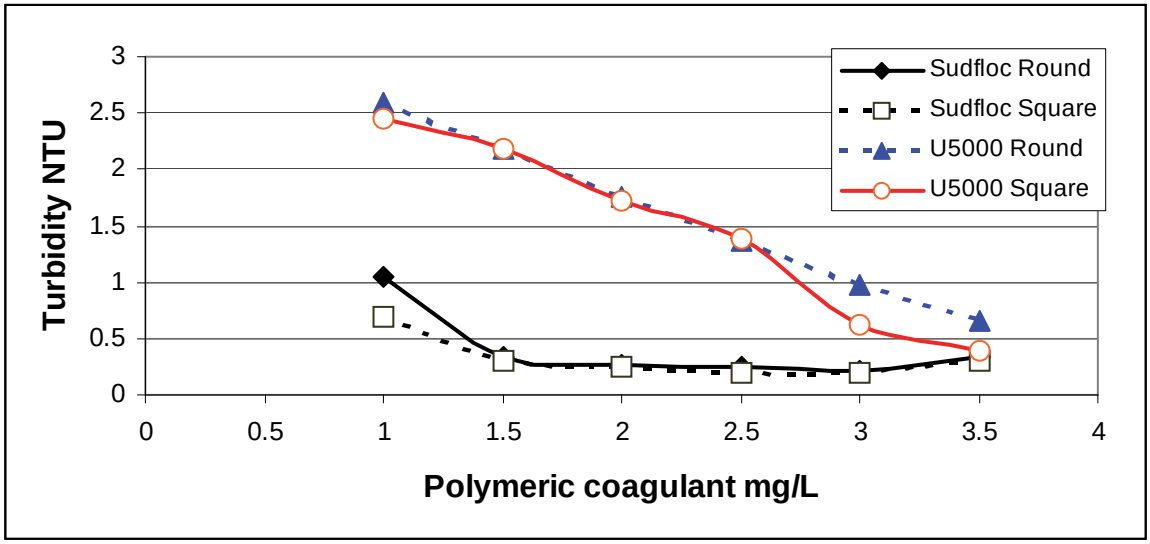


FIGURE 5.15: Comparison of jar test results obtained using round and square jars.

6. CONCLUSIONS

This investigation was initiated on the motivation that a significant difference in coagulant demand had been persistently noted on superficially similar waters which caused disproportionate differences when these were blended. The effect on coagulant demand was stronger than one would expect from averaging calculations on the parameters measured such as would apply to variables such as TDS or conductivity. The project was therefore established in an attempt to find an explanation for this.

As part of the investigation the historical data for the Midmar/Mearns System was carefully investigated and processed. Attempts were made to obtain correlations between all the variables normally measured and the coagulant demand of the water to see whether discrepancies could be accounted for by any of these. From this it was evident that virtually no correlation exists between coagulant demand and most of the variables measured. A very mild correlation was evident for certain parameters where correlation coefficients of 0,25 to 0,3 were measured for sodium, TDS, colour, barium and nitrate. It was considered that the correlation with barium was fortuitous as the amounts of barium present would be unlikely to have any significant effect on the water compared to the other cations present. A weak correlation between total dissolved solids and coagulant demand has been noted in previous work. The correlation with sodium would echo this as the sodium content in the water would be expected to increase together with the TDS. However, the low correlation coefficient indicates that this could not possibly be the major source of the variation in coagulant demand noted. Experience on a large number of water samples has indicated that higher turbidities tend to give rise to higher coagulant demand and that a mild correlation in the present case was therefore anticipated but not measured. However, the present investigation arose because there were significant differences in coagulant demand for waters of similar turbidity. Turbidity cannot therefore be one of the route causes of the difference in coagulant demand noted. The correlation with nitrate may be indirectly indicative of an effect from organic enrichment and this was a confirmation that attention needed to be focused on the organic content of the waters.

It had been anticipated that possibly organic content in the water might be the cause of the differences in coagulant demand and the other anomalies noted. In the laboratory investigation therefore, TOC, BDOC, UV absorption, trihalomethane formation potential (THMFP), chlorine demand and other surrogates for the organic content were measured and it attempts were made to establish whether differences in these could possibly be the cause for the variations in coagulant demand noted between the different waters and blends. No significant correlation was observed between the different parameters measured and the coagulant demand for the various samples. It can therefore be concluded that the surrogate parameters used for measuring organic compounds present in the waters tested were not adequate to explain the main cause of the difference in coagulant demand.

Another possible explanation for the difference in coagulant demand was possibly electrochemical effects and surface charges on the suspended particles present. The purchase of a zeta meter was undertaken as part of this project and this together with measurements using a streaming current detector were used in an attempt to check whether surface charges played a significant role in explaining the differences between the waters. Again, no simple explanation could be found for the differences either when using zeta potential or streaming current. In all cases the raw waters had a negative zeta potential within a fairly narrow range, and all waters at coagulant dosages for maximum turbidity removal had slightly negative zeta potentials within another small range. When trying enhanced coagulation to explore the differences, a similar concentration of zeta potential around yet a third slightly positive point was noted. The differences in zeta potential between the water samples was small and no consistent pattern emerged in the variations. Very similar patterns were noted with the SCD. A simplistic analysis of the surface charge chemistry of the particles does not therefore seem to supply a suitable explanation for the differences.

Finally, an attempt was made to check whether any variation in organic material was present by doing GC-MS scans of the three raw waters. These were carried out and again results were negative in that no significant difference in the peaks were apparent. In fact all the peaks of reasonable size could be accounted for by the present of impurities from the solvent used for extracting the samples.

The final conclusion for this investigation therefore is that the root cause of the differences in coagulant demand and the anomalies between the different waters has

not yet been established. In the absence of a readily available method for characterising water samples, the jar test continues to provide the best estimate of coagulant demand. Its usefulness is enhanced if the supernatant is filtered using a suitable filter which closely simulates the full-scale plant.

7. RECOMMENDATIONS FOR FUTURE RESEARCH

As mentioned in **Chapter 6** this investigation has not determined the reason for the anomalous differences in coagulant demand noted for the various superficially similar water sources in the system tested. This applied both to the routine variables measured as well as to the focus on organics, surface chemistry, and polyelectrolyte characteristics in the investigational work.

It is evident that more fundamental and detailed research may be required to elucidate the differences between the Mearns water and Lions/uMngeni water which supply Midmar Dam. This could also be expanded to include waters which display similar characteristics elsewhere in the country as the reasons for the differences in the other systems may be easier to find. This would apply to inorganic and organic particles present as well as to dissolved and colloidal organics.

Although the waters arise in similar geological regions, there may be differences in the minerals present in the suspended particles in the water and crystallographic or microscopic examination of these and the collection of large quantities of the suspended material by micro-filtration over a long period with analysis of the constituents may be necessary to establish differences which could be correlated on other systems.

A second approach would be to examine the differences in the nature of the algae present in the water. Detailed examination of the algal species present rather than simply recording the dominant species or the two dominant species as is done for routine work, may be necessary. From this it may be possible to correlate the presence of certain species against increase or decrease in coagulant demand.

The third possibility for future work would be to investigate the nature of the dissolved and colloidal organic material present in the different waters including humic substances. The tools available to the present investigation were not sufficient to distinguish any significant differences between the waters and because of the low

organic contents measured in terms of total organic carbon (TOC) or biodegradable dissolved organic carbon (BDOC), fractionation would have yielded results in which the differences would have been masked by random experimental error. It is possible that concentration of the samples to increase the TOC followed by fractionation or other characterisation of the organics may yield results of greater significance.

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9. ANALYTICAL PROCEDURES

9.1. CHEMICAL ANALYSES

9.1.1. 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.

9.1.2. Chlorides

Chlorides were determined by ion chromatography using an anion column, conductivity detector and Millenium Chromatography Manager using a SANAS accredited method.

9.1.3. Conductivity

Conductivity was measured on a conductivity meter in mS/m according a SANAS accredited method. All measurements were conducted at between 21 and 23 °C.

9.1.4. Iron, Manganese, Calcium, Magnesium and Hardness.

Iron, manganese, calcium and magnesium were determined using Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) on a Varian Radial ICP according to a SANAS accredited method. Hardness was calculated from the calcium and magnesium analyses.

9.1.5. pH

pH was measured on a Radiometer PHM 95 pH/ion meter with a temperature compensation probe and thermometer, which was also used to measure the temperature.

9.1.6. Sodium and Potassium

Iron, manganese, sodium and potassium were determined using atomic adsoprtion sprctroscopy with an air/acetylene flame at a suitable wavelength according to a SANAS accredited method.

9.1.7. Sulphates

Sulphates were determined by ion chromatography using an anion column, conductivity detector and Millenium Chromatography Manager using a SANAS accredited method.

9.1.8. Total Dissolved Solids and Suspended Solids

Total dissolved solids were determined on a measured volume of sample which had first been filtered through a 0,45 µm pore size membrane filter. The filtered water was then evaporated at 105 ± 5 °C before being weighed. Suspended solids were determined from the amount of matter in a measured volume of sample which was retained on a GFC 22 µm pore size filter paper, once it had been dried to constant weight at 105 ± 5°C.

9.1.9. Turbidity

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

9.1.10. Zeta Potential Measurements

Zeta potential measurements were made using a Malvern Zetasizer 2000 Zeta Potential Meter.

9.2. NATURAL ORGANIC MATTER SURROGATE TESTS

9.2.1. Biodegradable Dissolved Organic Carbon (BDOC)

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 d. 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.

9.2.2. Chlorine demand test

Chlorine demand tests were conducted using available chlorine concentrations of generally less than 10 mg/ℓ, since the chlorine demand of all the waters was always less than this.. A commercial sodium hypochlorite solution (BDH 10-14% m/v available chlorine) was used for chlorine dosing. This solution was standardised according to the method in Standard Methods for the Examination of Water and Wastewater (1998) (section 2350B(g)), using 0,01N sodium thiosulphate. The chlorine demand tests were carried out according to section 2350B of Standard Methods (1998) using the DPD test for free and total chlorine concentration and a Lovibond comparator, and measuring the free and total chlorine concentrations after a half hour contact period. The chlorine demand was determined by plotting the chlorine residual (total chlorine concentration) against the chlorine added and finding the point at which either the total chlorine concentration approaches zero, or the total chlorine residual starts increasing pro rata with the chlorine addition indicating the chlorine breakpoint and chlorine demand value.

9.2.3. Colour

Samples were filtered through a 0,45 µm pore size membrane filter before measuring the colour at 400 nm on a spectrophotometer equipped with a 50 mm flow cell.

9.2.4. GC-MS Analysis

Fingerprinting was carried out using an HP 6890 GC and HP 5973 Mass Selective Detector (MSD). The samples (1 000 mℓ) were extracted using methylenechloride (50 mℓ). Passing the organic layer over magnesium sulphate dried the extracts. The extraction procedure was repeated twice and the sample extracts were combined in a round-bottomed flask. The combined extracts were then concentrated to 1 mℓ at 35 °C under vacuum. The concentrated samples were transferred to sample vials. One microlitre of the above sample was injected into the HP 6890 series Gas Chromatograph interfaced to an HP 5973 Mass Selective Detector (MSD) and controlled by HP Chemstation software (version b.02.05, 1989-1997). The chromatographic separation was achieved using a DB-5 MS capillary column (30.0 m x 250 µm x 0.25 µm). The column stationary phase comprised of 5%-Diphenyl-95% Dimethylpolysiloxane. The identification of the compounds present in the samples was achieved using the Wiley275 spectral library.

The instrument parameters were as follows:

GAS CHROMATOGRAPH CONDITIONS:	
Oven Temperature Programme:	
Initial Temp:	50°C
Initial Time:	2 minutes
Ramp Rate:	10°C/min
Final Temp:	300°C
Final time:	3 minutes
Injector Conditions:	
Injection mode:	Splitless
Injector Temp:	250°C
Injector volume:	1 µL

9.2.5. Lime Demand

A 0,10% solution of lime was prepared using brown hydrated lime. The lime solution was then added to a 1 000 mℓ subsample of the raw water in incremental amounts up to a concentration of 54 mg/ℓ. The pH of the water after each incremental lime addition was measured and the pH of the water was raised to approximately 10. The conductivity, alkalinity, total hardness, calcium, magnesium iron and manganese concentrations were determined on both the raw water and the water to which 54 mg/ℓ had been added. The pH was measured on a Radiometer PHM 95 pH/ion meter, while conductivity, alkalinity, total hardness, calcium, magnesium, iron and manganese were determined by the Chemistry Laboratory of Analytical Services, UW using South African National Accreditation Systems (SANAS) methods.

9.2.6. Total and Dissolved Organic Carbon

Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were determined using the persulphate-ultraviolet oxidation method (method 5310C in Standard Methods for the Examination of Water and Wastewater, 1998) 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.

9.2.7. Trihalomethane Formation Potential Analysis

Trihalomethane formation potential (THMFP) was determined using the THMFP test described in section 5710B of Standard Methods for the Examination of Water and Wastewater (1998), 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 for the Examination of Water and Wastewater (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 d. 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.

9.2.8. Ultraviolet Absorbance at 254 nm

Ultraviolet (UV) absorbance of water samples was measured at 254 nm using a Cary 50 Conc UV-visible spectrophotometer with a 10 mm quartz cell. The UV light source was provided by a deuterium lamp.

9.3. JAR TESTS

9.3.1. Standard Jar Test Procedure

The standard jar test procedure was carried out on an Aztec jar stirrer apparatus. 0,08% solutions of lime and the polymeric coagulants were prepared so that the addition of 1mℓ of solution to an 800 mℓ volume of raw water sample corresponded to the addition of 1mg/ℓ chemical. The specific gravity of the aluminium sulphate solutions was determined in order to calculate the $Al_2(SO_4)_3.14H_2O$ concentration and then an aluminium sulphate solution containing 0,16% as $Al_2(SO_4)_3.14H_2O$ was prepared so that the addition of 1 mℓ of this solution to 800 mℓ raw water corresponded to the addition of 2 mg/ℓ. Tests were conducted both with and without the addition of lime. When lime was used, it was added while flash mixing to raise the pH of the water to around 8,5 as this is the pH routinely used for water treatment at Umgeni Water. The coagulant was added immediately afterwards. A flash mix speed of 300 rpm was used for 2 minutes followed by a slow mix of 40 rpm for 15 minutes. The floc size and settling rate were then noted and the treated water samples were filtered through M&N 615 Rundfilter filter paper (Whatman N^{o}·1 equivalent) and the turbidity and pH of the filtrate measured. The optimum coagulant dose was taken as the minimum coagulant concentration required to reduce the filtered turbidity of the treated water to below the 0,5 NTU Umgeni Water limit for potable water.

9.3.2. Tests to Improve the Correlation Between Jar Tests and Full Scale Operation

Tests were conducted using a laboratory scale clarifier. This was conical in shape, had a capacity of 1,65 L and was 290 mm tall (from the bottom of the clarifier to the top of the overflow weir).

Tests were also conducted in which the correlation between laboratory treated water and water treated at full scale was assessed. These tests were carried out at each of the three water works which at the time of testing, received their raw water supply from Midmar Dam, namely the Midmar WW, D V Harris WW and Umlaas Road WW. Jar tests were conducted on site at each plant using the coagulant and dose being used on the plant. The jar test coagulated and flocculated water was then filtered through a range of filters which had nominal pore sizes varying between 0,45 and 6 µm. The turbidity of the filtered water was then compared to that of the filter underflow on the plant. Simultaneously, water from the clarifier/pulsator overflow was also filtered through the same filters used in the jar tests and the turbidity of this water also compared to that of the rapid gravity filter underflow on the plant.

Tests were also conducted to assess the impact of the shape of the jar. Using raw water samples taken from a Midmar Dam source, jar tests were conducted with a range of coagulants (both inorganic and polymeric organic coagulants) using both round 1 L capacity tall form beakers and square-shaped Consol-type 1 L capacity storage jars.

9.4. OZONATION TESTS

A schematic figure of the apparatus used for the ozonation tests appears in **Figure 9.1**. Ozonation was carried out in a glass contact column with a capacity of approximately 10 L and 1,57 m in height, with an internal diameter of approximately 90 mm. A Sorbios laboratory ozone generator model GSG 1.2 capable of producing 1 g/h ozone 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.

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 (at ambient temperature and pressure) 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 (Standard Methods for the Examination of Water and Wastewater, 1998). The process was repeated until at least three calibrations varying by 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.

After calibration of the equipment, the reaction column was thoroughly cleaned and 10,6 L of water sample was placed into the column. The amount of ozone-containing gas needed for the required applied ozone dose was passed through the sample.

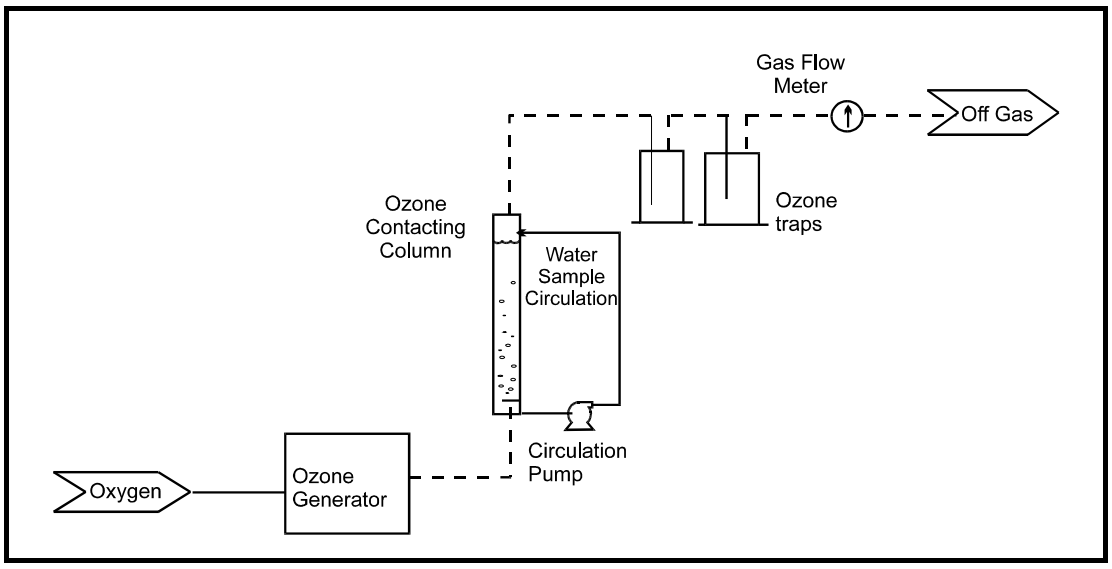


Figure 9.1: Flow diagram of laboratory scale ozonation apparatus.

9.5. DATA ANALYSIS AND INTERPRETATION

9.5.1. Data

The data analysis and interpretation was carried out using the following:

1. **Land Cover Data:** Land cover data were obtained from the National Land Cover Database developed by Environmentek - CSIR in 1996 and represented using a GIS.
2. **Water Quality Data**: Umgeni Water has collected water quality samples at a daily, weekly or quarterly frequency since 1988 at a number of sites in the upper Mooi and uMngeni catchments and at the WW supplied by Midmar dam. For the purposes of this investigation, water quality data from the following sites were used:
   - Mooi River at Mearns
   - uMngeni inflow to Midmar Dam
   - DV Harris WW raw
   - Midmar WW raw (since commissioning in 1997).

   There is thus good water quality data available that permits good characterisation of water quality during of both the summer high rainfall period and the drier winter period.
3. **Flow data:** Daily transfer volumes for Mearns weir from 1989 until December 2002 were obtained from Umgeni Water Operations Division.
4. **Coagulant Dose data**: Daily coagulant dose concentrations for the two WW supplied by Midmar dam (DV Harris WW and Midmar WW) were obtained from Umgeni Water Operations Division.

9.5.2. Data Analysis

The analysis of the data was conducted using the following methods:

1. **Comparison of catchment land use and water quality:** The percentage area per land cover category in the upper Mooi and upper uMngeni catchments were compared. Paired water quality data (using non-transfer periods only) from the uMngeni inflow to Midmar dam and the Mooi river at Mearns were compared using the following techniques:
   - Summary statistics
   - Time series plots

- Percentile plots
- Statgraphics non-parametric comparison of medians test: This test was used to statistically determine whether the two data sets have the same median. If the resulting Z-statistic is large (>1.96), the data are significantly different (95% confidence), but if the Z-statistic is small (<1.96), the data can be considered to be statistically similar.

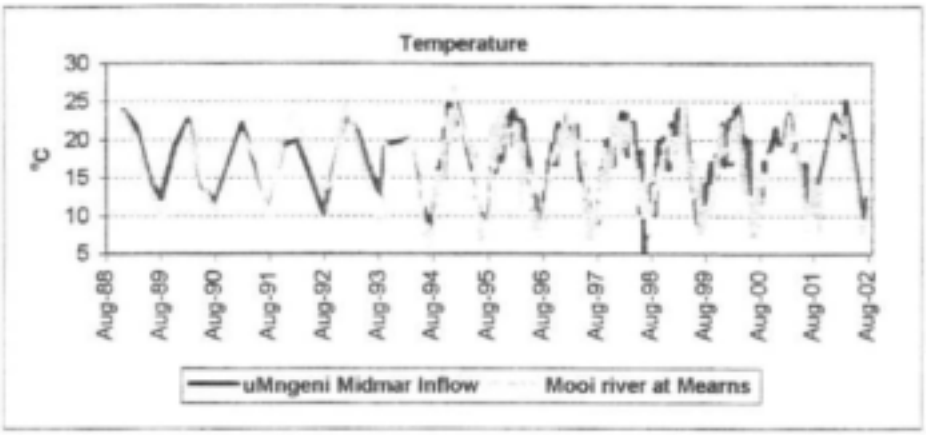
Data from non-transfer periods only were used for this comparison, as the impact of interbasin transfer from the Mooi river will be included in the uMngeni inflow to Midmar dam during transfer periods (see Map 1).

2. **Assessment of coagulant dose during transfer periods**: Time series plots were prepared illustrating coagulant dose relative to transfer periods for both the DV Harris and Midmar WW.
3. **Assessment of relationship between coagulant dose and other water quality constituents:** Regression plots were prepared to assess the relationship between coagulant dose and individual water quality constituents at both the DV Harris WW and the Midmar WW.

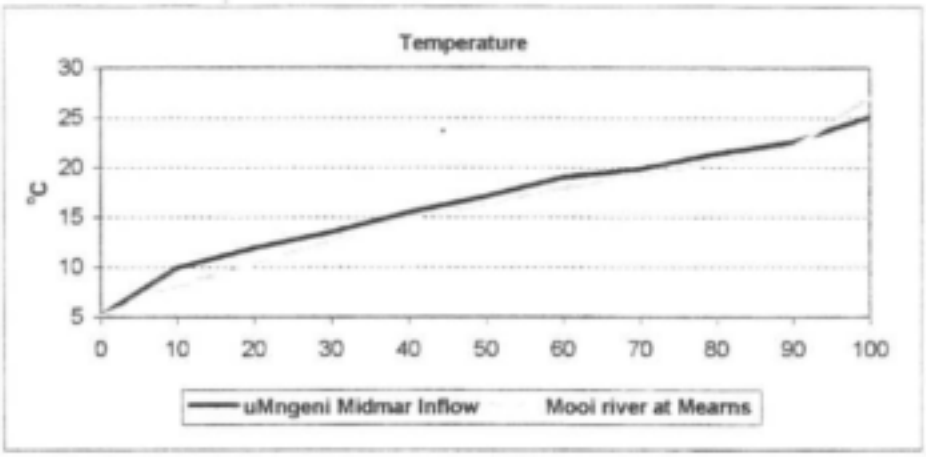
Appendix 1 : Comparison of Water Quality at uMngeni Midmar Inflow and Mooi river at Mearns

Temperature (°C)

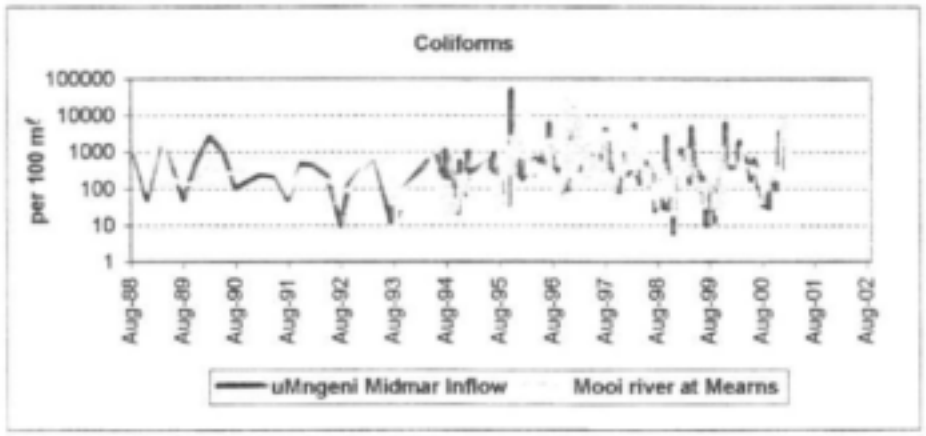
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	335	335
Minimum	5.1	5.1
25th Percentile	12.6	11.2
Median	17.1	16.1
Average	16.6	15.7
75th percentile	20.4	20.0
95th percentile	23.5	23.0
Maximum	25.1	27.0



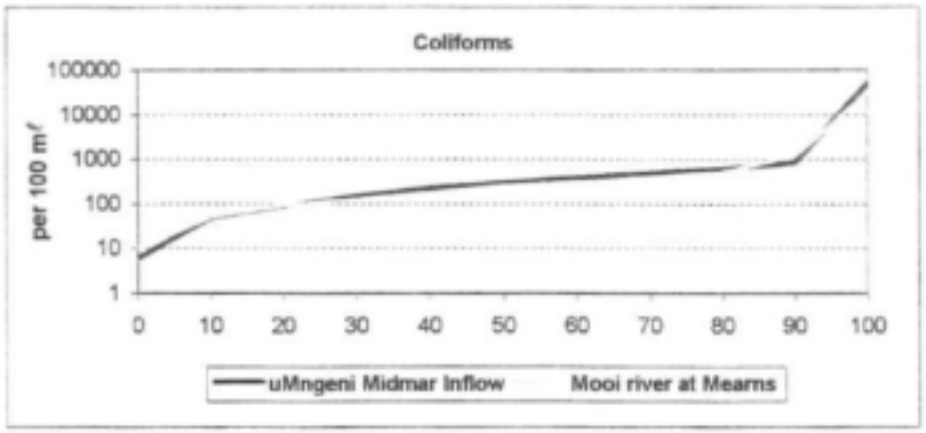
Non parametric comparison of medians
Z = 6.81566 - statistically significantly different



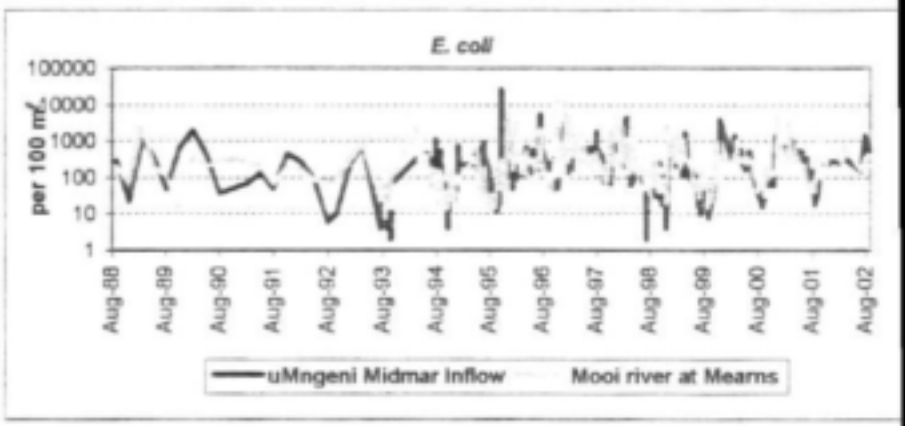
Coliforms (count per 100 m/)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	298	298
Minimum	6	10
25th Percentile	113	113
Median	300	250
Average	731	792
75th percentile	530	428
95th percentile	2075	2715
Maximum	52000	30000



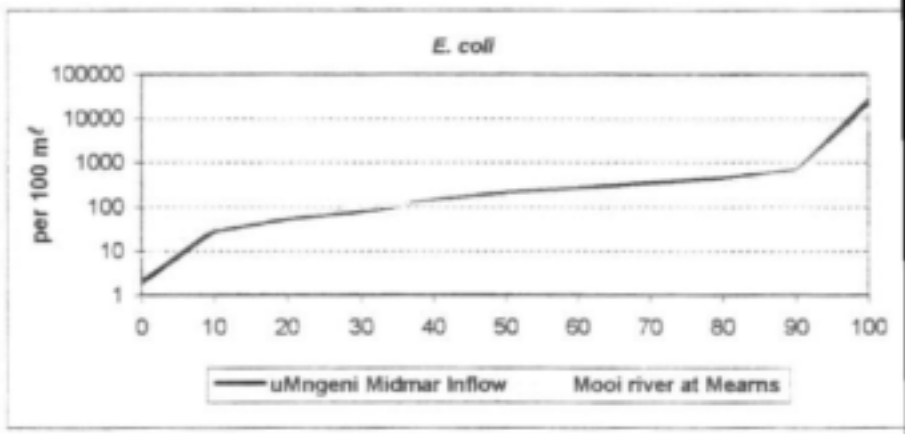
Non parametric comparison of medians
Z = 2.50781 - statistically significantly diiferent



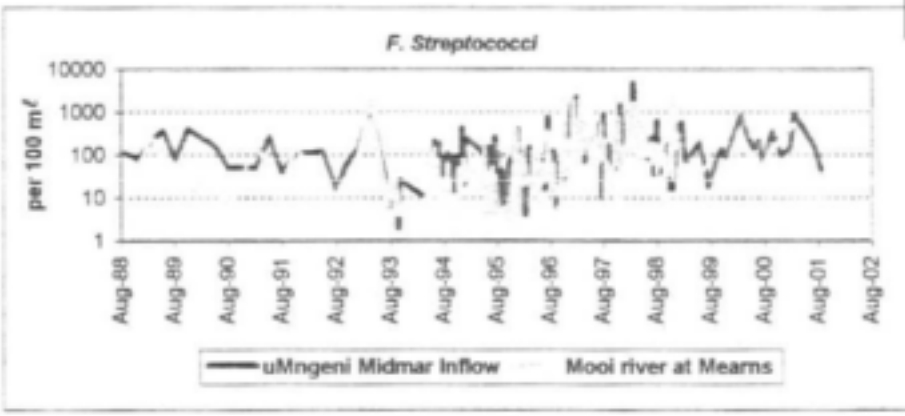
E. coli (count per 100 m*l*)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	328	328
Minimum	2	8
25th Percentile	68	78
Median	206	177
Average	439	473
75th percentile	393	333
95th percentile	1190	1800
Maximum	26000	15800



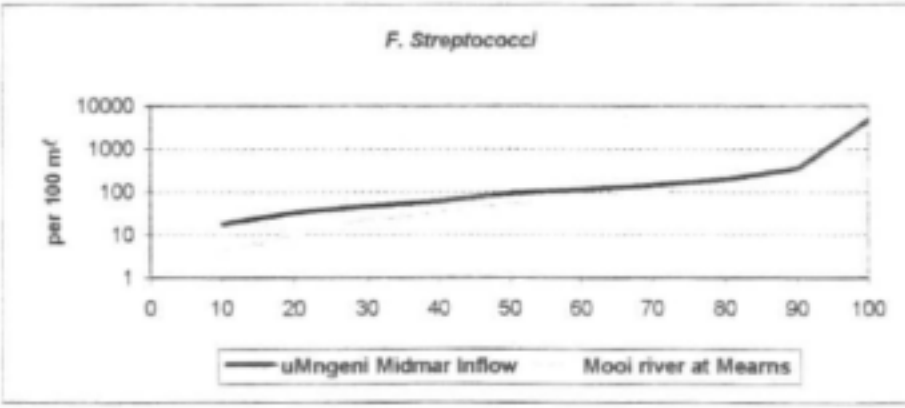
Non parametric comparison of medians
Z = 0.767195 - statistically similar



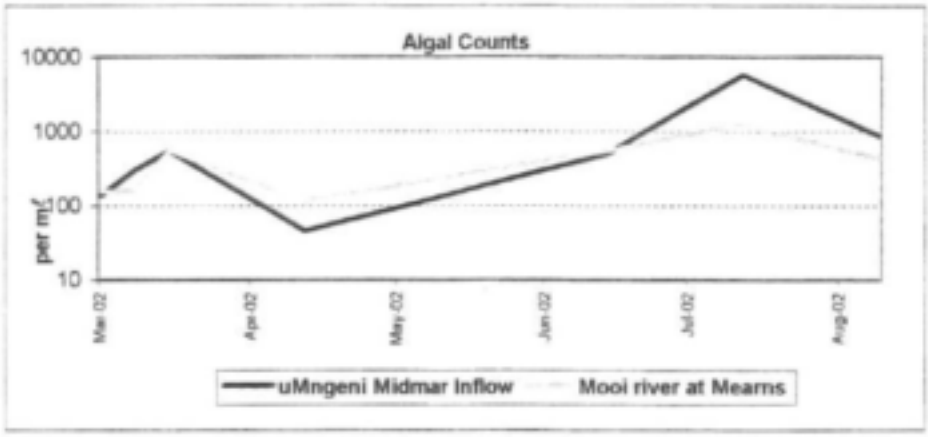
F. Streptococci (count per 100 m*l*)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	249	249
Minimum	0	0
25th Percentile	40	18
Median	92	52
Average	184	157
75th percentile	176	128
95th percentile	609	597
Maximum	4800	2800



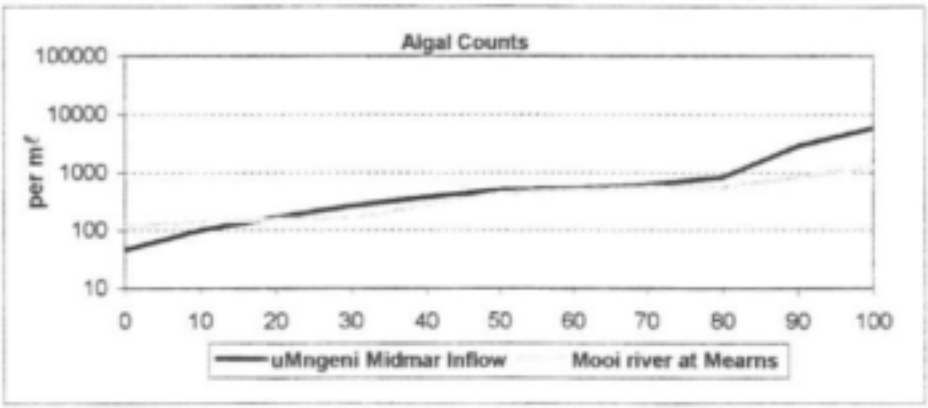
Non parametric comparison of medians
Z = 5.76901 - statistically significantly different



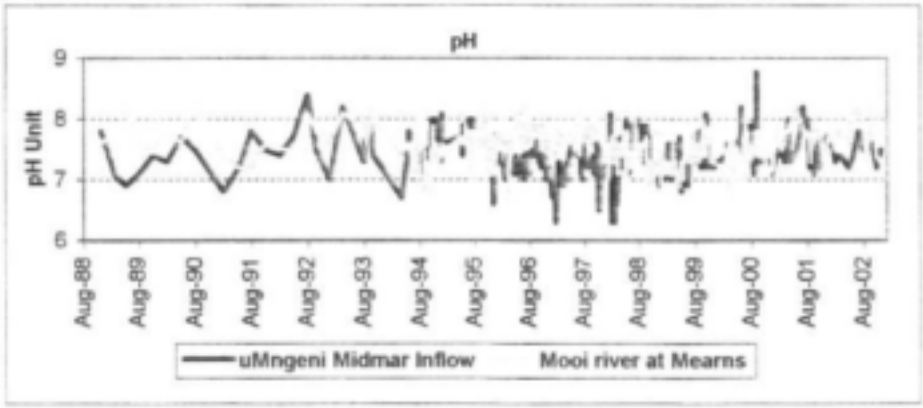
Algal Counts (count per m/)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	7	7
Minimum	46	114
25th Percentile	217	157
Median	501	433
Average	1173	458
75th percentile	718	547
95th percentile	4326	1041
Maximum	5799	1252



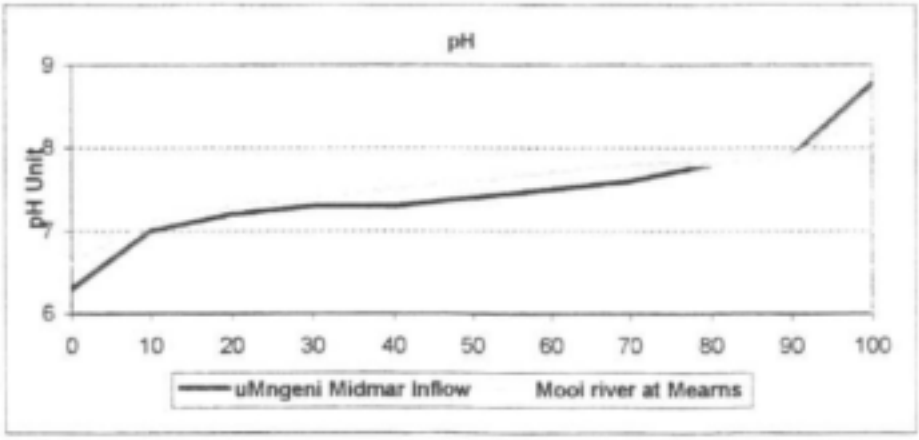
Non parametric comparison of medians
Z = 0.408248 - statistically similar



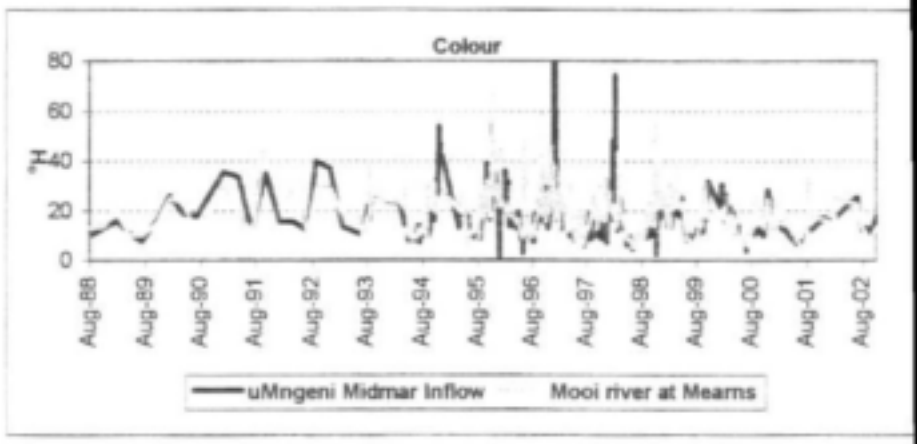
pH (pH unit)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	329	329
Minimum	6.3	6.6
25th Percentile	7.2	7.4
Median	7.4	7.6
Average	7.4	7.6
75th percentile	7.7	7.8
95th percentile	8.0	8.1
Maximum	8.8	8.4



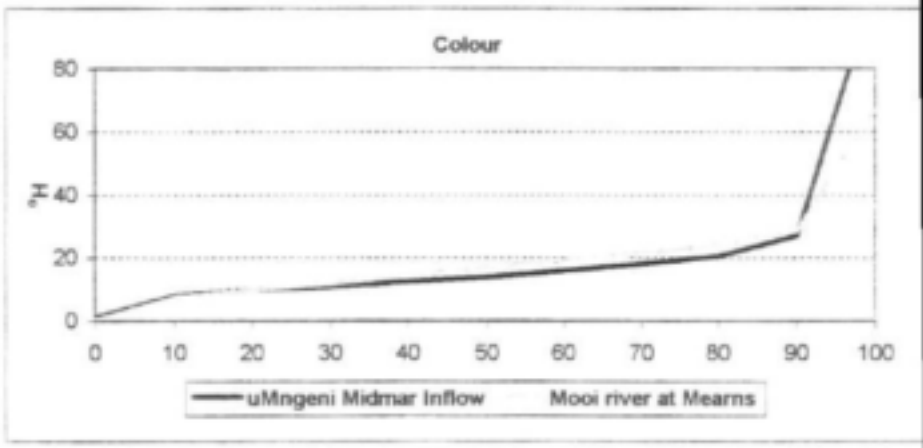
Non parametric comparison of medians
Z = 4.82567 - statistically significantly different



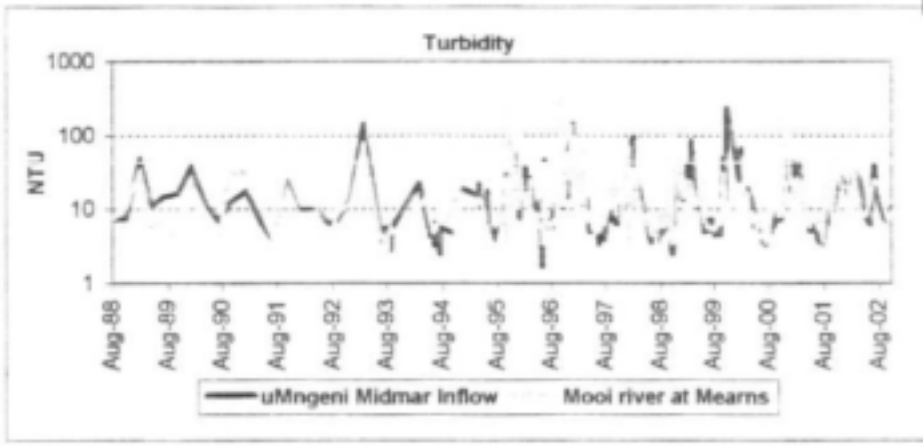
Colour (°H)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	324	324
Minimum	1.2	0.5
25th Percentile	10.5	10.7
Median	14.1	16.9
Average	16.7	17.9
75th percentile	19.7	22.5
95th percentile	35.5	32.8
Maximum	107.6	67.1



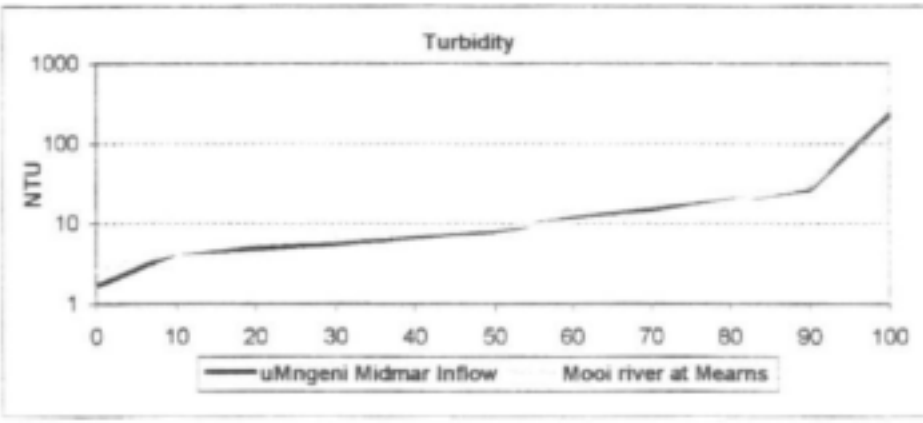
Non parametric comparison of medians
Z = 2.06193 - statistically significantly different



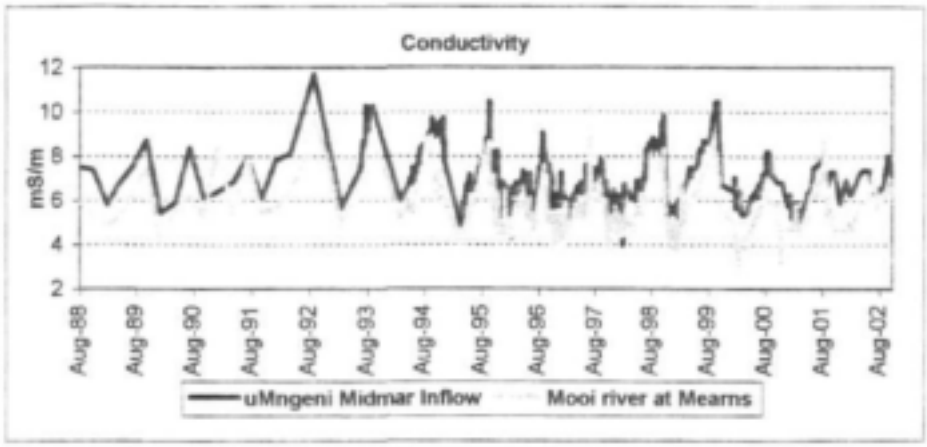
Turbidity (NTU)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	335	335
Minimum	1.7	2.6
25th Percentile	5.3	6.0
Median	8.1	8.9
Average	15.6	16.2
75th percentile	17.1	14.4
95th percentile	44.8	43.6
Maximum	237.0	340.0



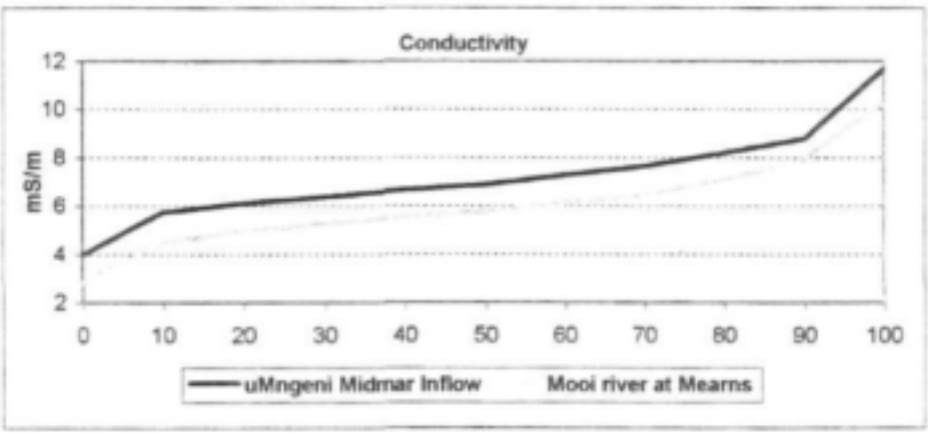
Non parametric comparison of medians
Z = 1.31519 - statistically similar



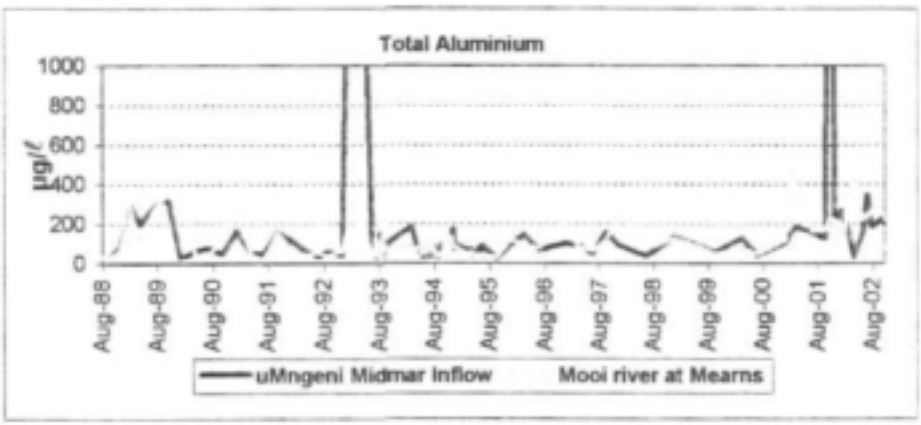
Conductivity (mS/m)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	341	341
Minimum	4.0	2.9
25th Percentile	6.2	5.1
Median	6.9	5.8
Average	7.1	6.0
75th percentile	7.9	6.7
95th percentile	9.5	8.5
Maximum	11.7	10.3



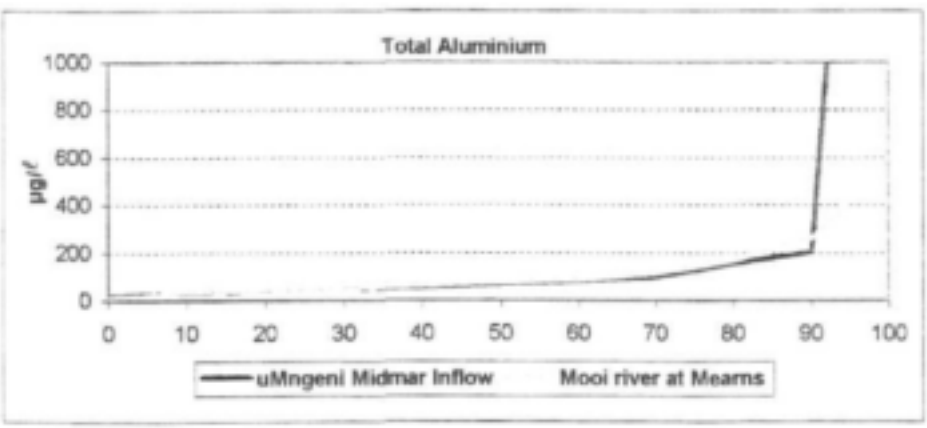
Non parametric comparison of medians
Z = 16.8369 - statistically significantly different



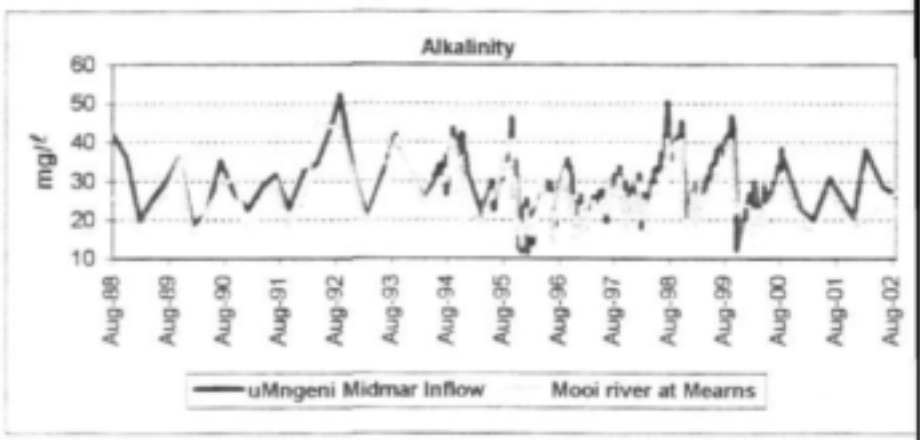
Total Aluminium (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	109	109
Minimum	18	12
25th percentile	45	44
Median	69	74
Average	160	110
75th Percentile	130	131
95th Percentile	276	311
Maximum	4140	595



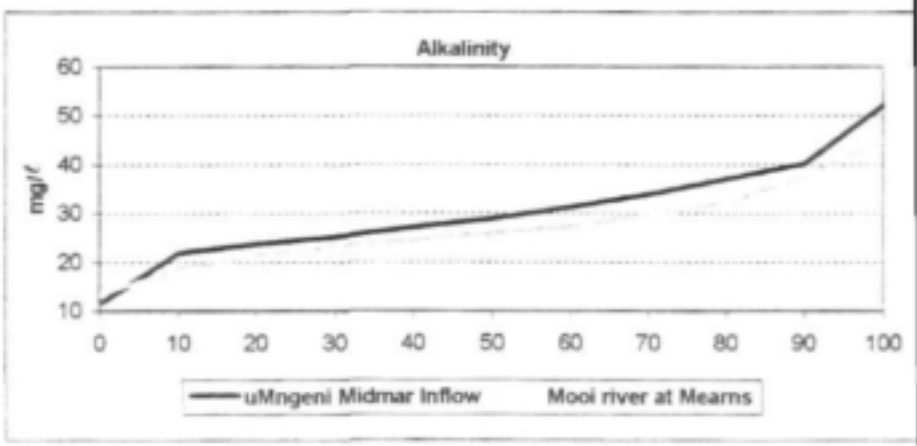
Non parametric comparison of medians
Z = 0.096225 - statistically similar



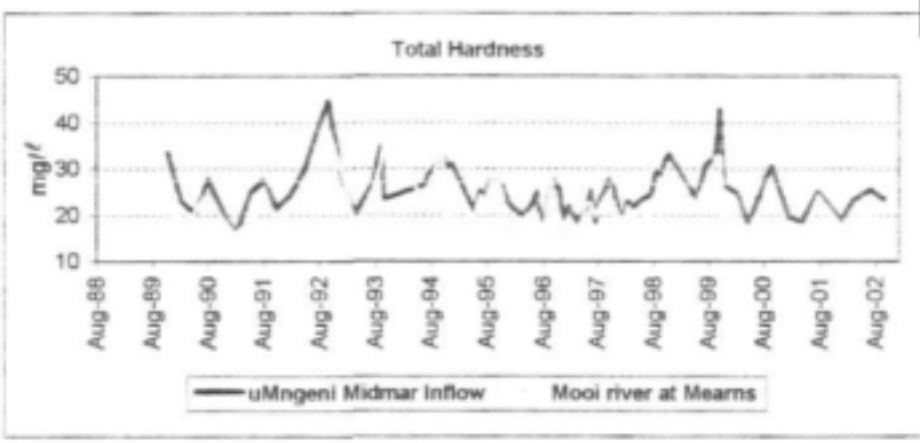
Alkalinity (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	306	306
Minimum	11.4	13.4
25th percentile	24.7	22.3
Median	29.0	26.0
Average	30.0	26.9
75th Percentile	35.4	31.0
95th Percentile	42.3	40.1
Maximum	52.3	45.0



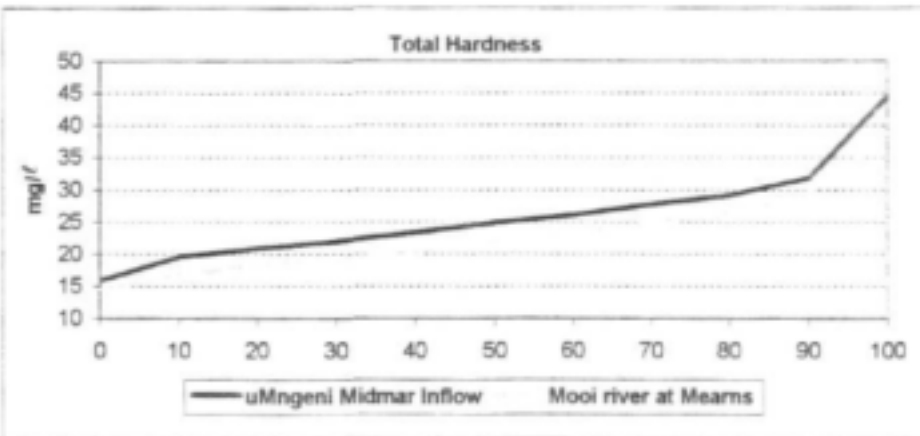
Non parametric comparison of medians
Z = 11.7191 - statistically significantly different



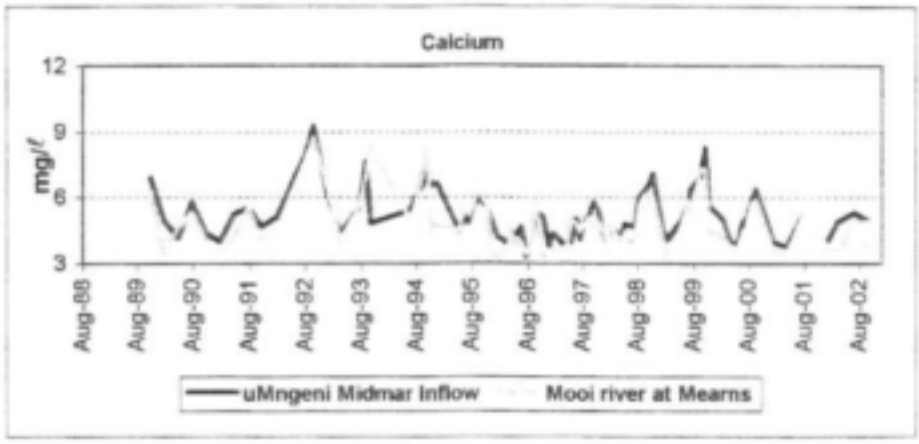
Total Hardness (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	82	82
Minimum	15.9	14.6
25th percentile	21.5	18.5
Median	24.8	21.8
Average	25.5	22.6
75th Percentile	28.3	25.4
95th Percentile	34.0	32.4
Maximum	44.7	38.9



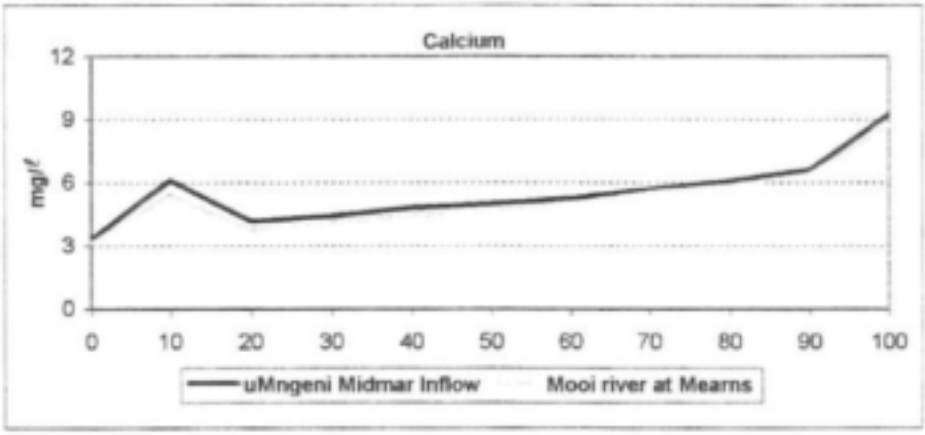
Non parametric comparison of medians
Z = 6.88889 - statistically significantly different



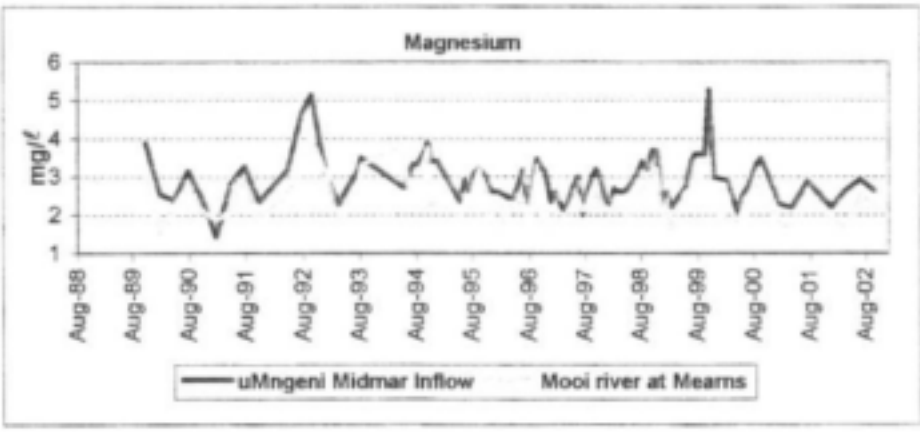
Calcium (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	85	85
Minimum	3.31	3.12
25th percentile	4.36	4.00
Median	5.00	4.70
Average	5.23	4.93
75th Percentile	5.83	5.63
95th Percentile	7.12	7.30
Maximum	9.28	8.72



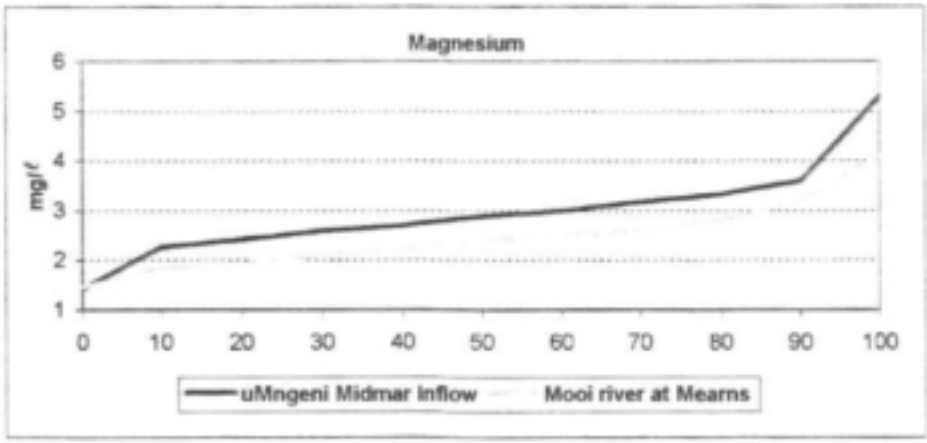
Non parametric comparison of medians
Z =4.13673 - statistically significantly different



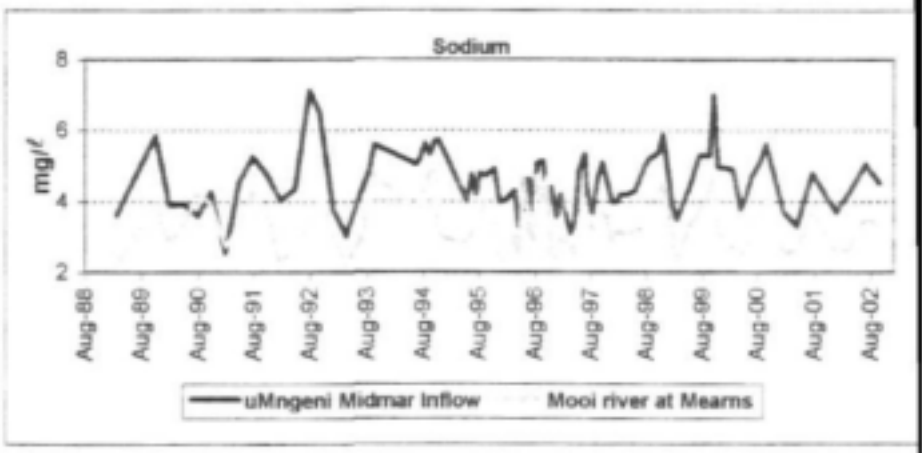
Magnesium (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	87	87
Minimum	1.42	1.46
25th percentile	2.53	2.04
Median	2.90	2.38
Average	2.93	2.43
75th Percentile	3.24	2.70
95th Percentile	3.83	3.40
Maximum	5.30	4.11



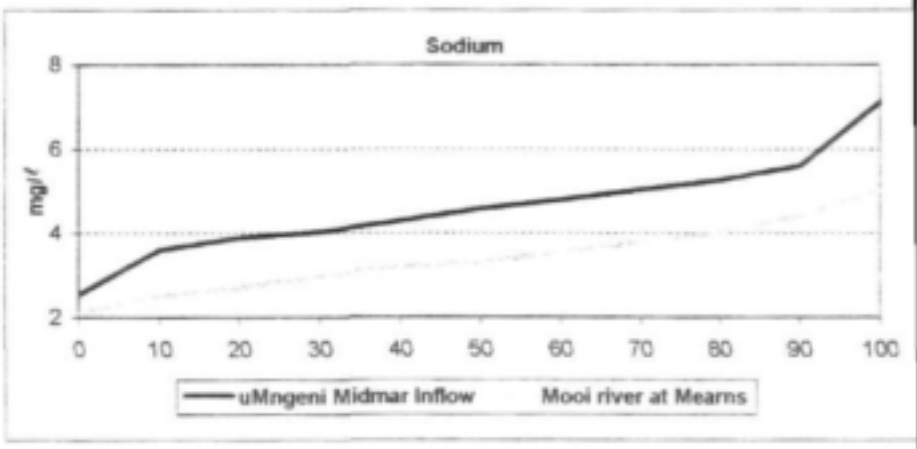
Non parametric comparison of medians
Z =8.36248 - statistically significantly different



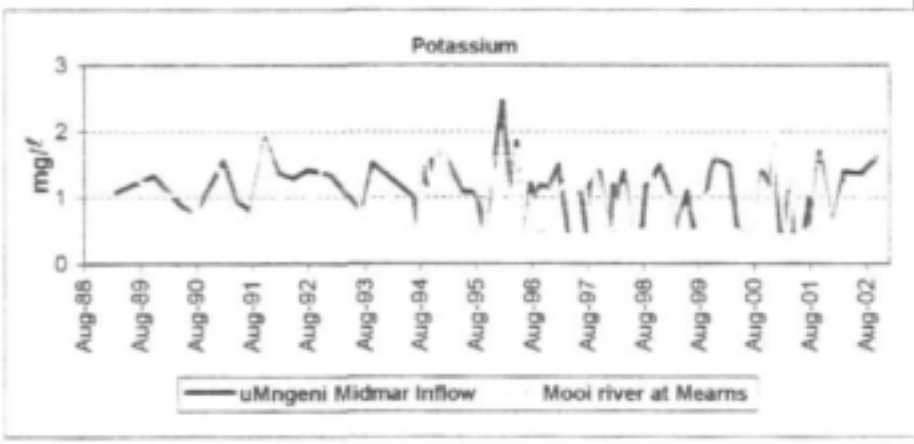
Sodium (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	86	86
Minimum	2.54	2.10
25th percentile	4.00	2.86
Median	4.58	3.30
Average	4.59	3.39
75th Percentile	5.10	3.88
95th Percentile	5.82	4.71
Maximum	7.13	5.02



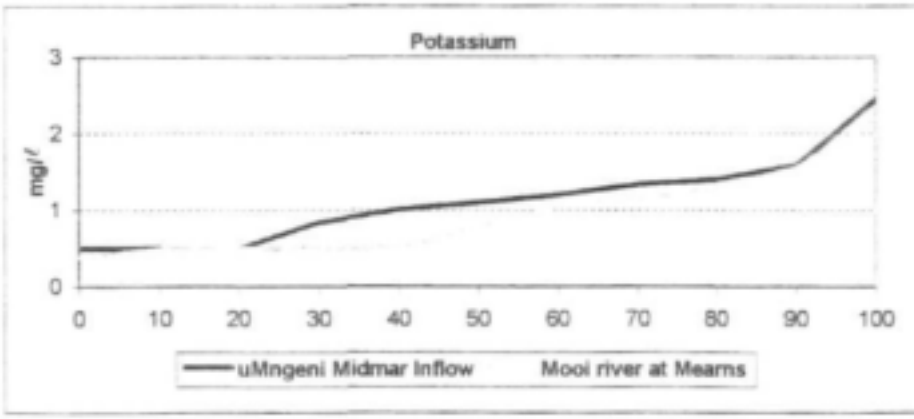
Non parametric comparison of medians
Z =8.30312 - statistically significantly different



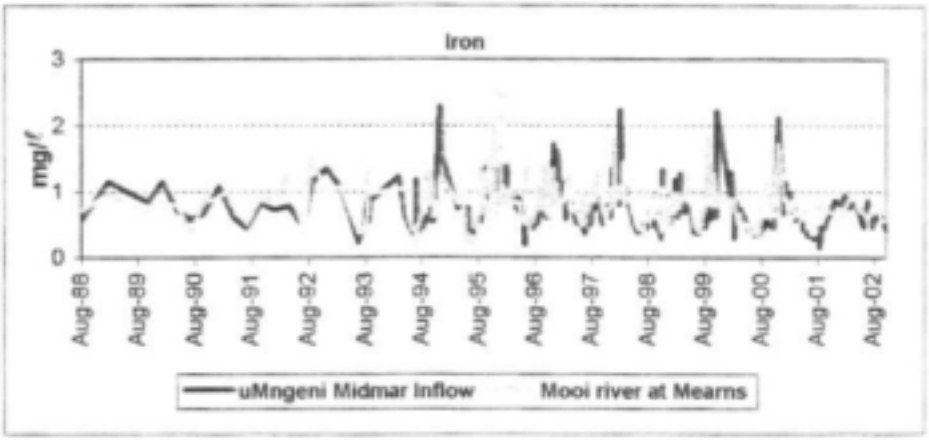
Potassium (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	93	93
Minimum	0.50	0.39
25th percentile	0.50	0.50
Median	1.10	0.77
Average	1.08	0.91
75th Percentile	1.40	1.20
95th Percentile	1.79	1.77
Maximum	2.46	2.20



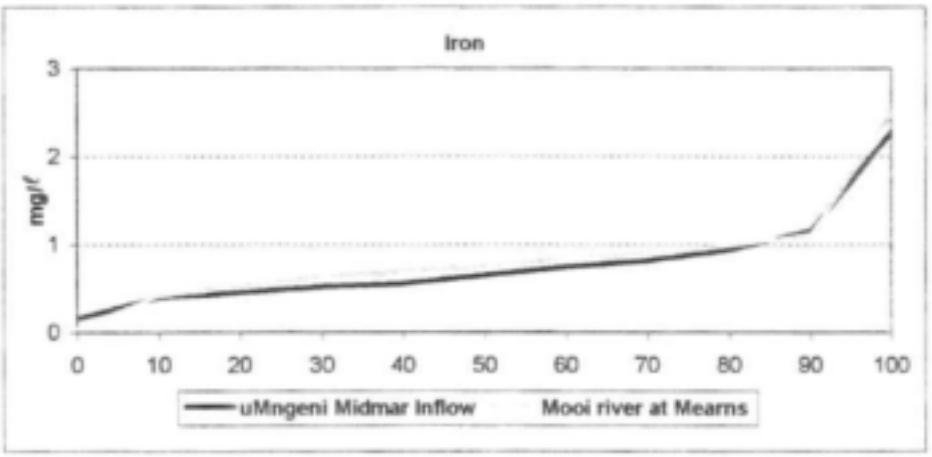
Non parametric comparison of medians
Z =3.70521 - statistically significantly different



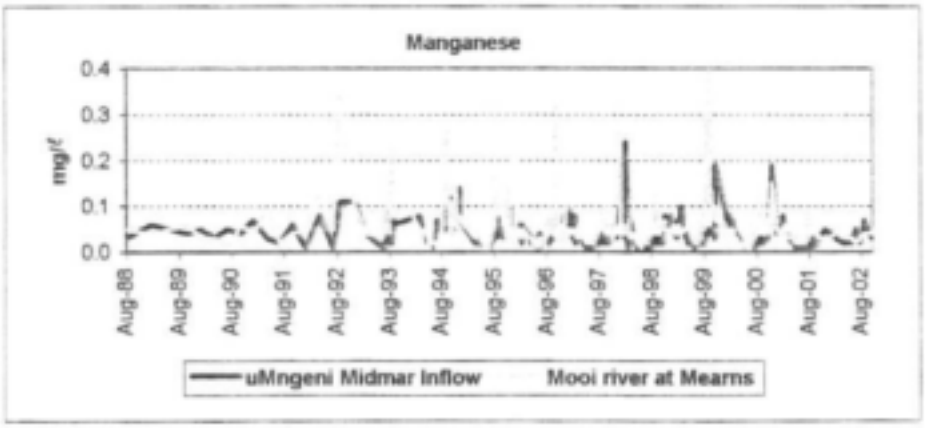
Iron (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	337	337
Minimum	0.16	0.05
25th percentile	0.49	0.56
Median	0.65	0.75
Average	0.73	0.78
75th Percentile	0.89	0.94
95th Percentile	1.35	1.30
Maximum	2.28	2.49



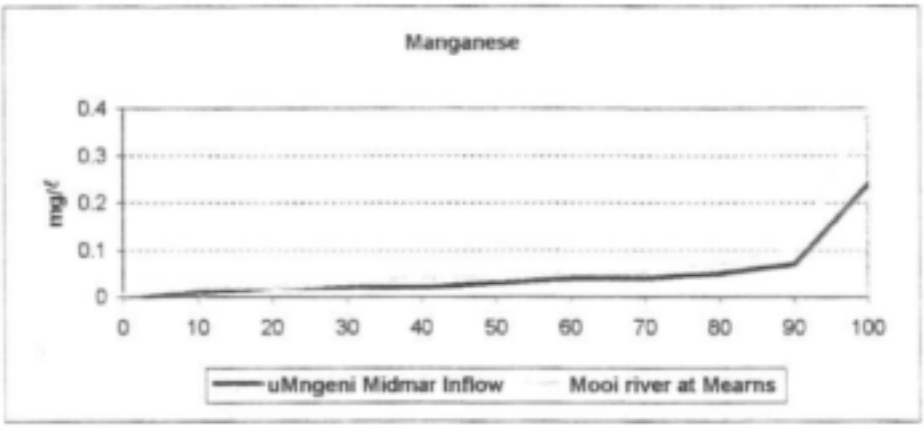
Non parametric comparison of medians
Z =4.61708 - statistically significantly different



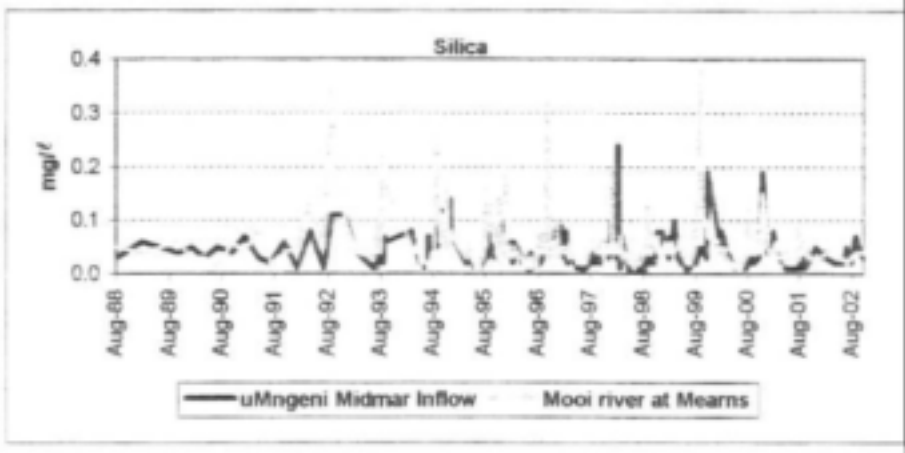
Manganese (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	336	336
Minimum	0.005	0.005
25th percentile	0.020	0.030
Median	0.030	0.040
Average	0.037	0.053
75th Percentile	0.050	0.060
95th Percentile	0.090	0.140
Maximum	0.240	0.400



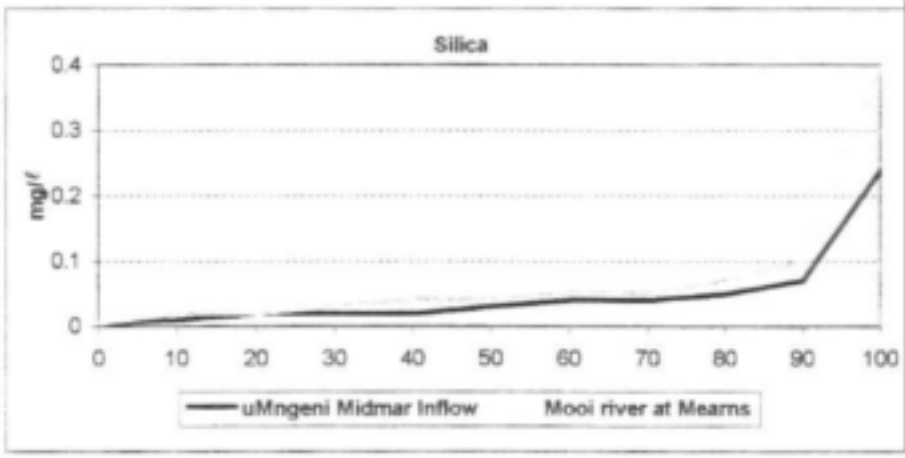
Non parametric comparison of medians
Z =8.15823 - statistically significantly different



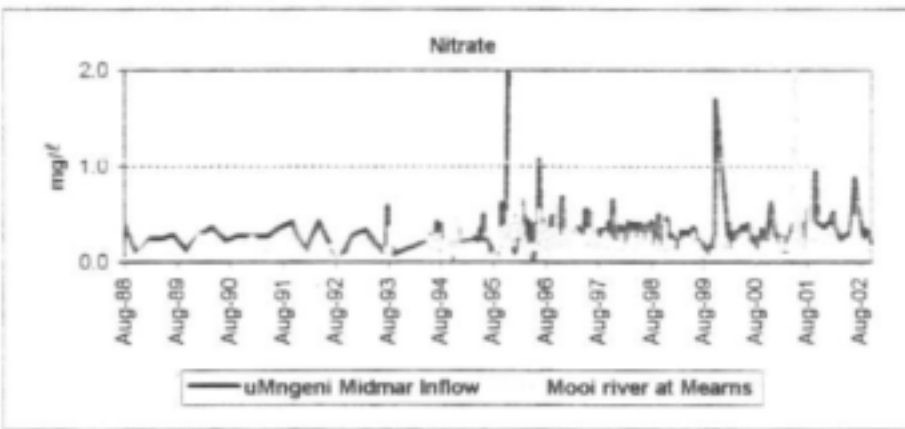
Silica (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	302	302
Minimum	1.90	1.60
25th percentile	4.30	4.40
Median	5.00	5.00
Average	4.80	4.84
75th Percentile	5.40	5.40
95th Percentile	5.97	5.87
Maximum	6.70	9.00



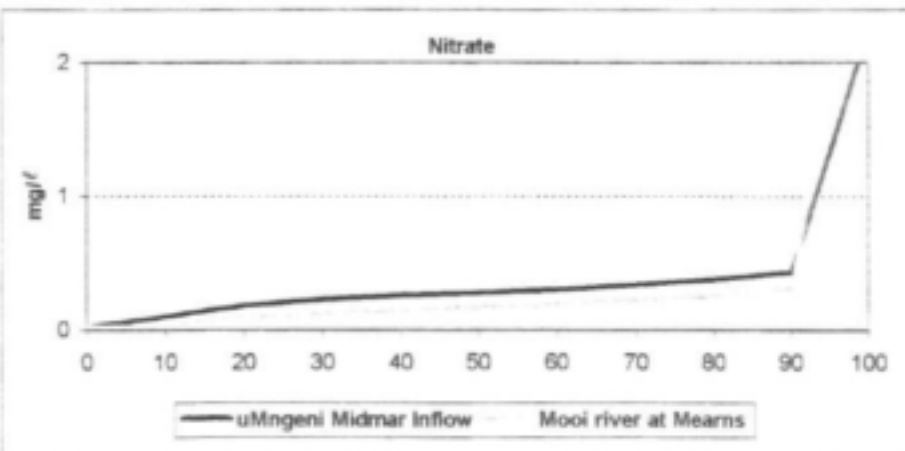
Non parametric comparison of medians
Z =1.22693 - statistically similar



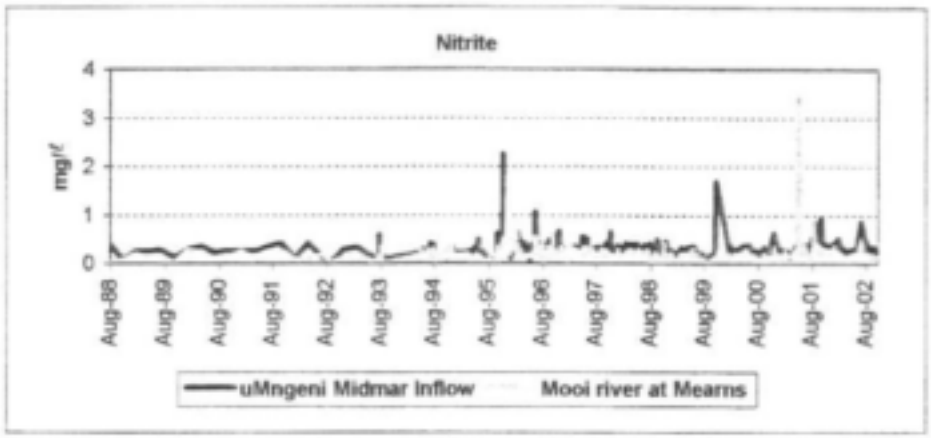
Nitrate (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	341	341
Minimum	0.03	0.03
25th percentile	0.21	0.11
Median	0.28	0.17
Average	0.30	0.20
75th Percentile	0.36	0.24
95th Percentile	0.54	0.41
Maximum	2.26	3.40



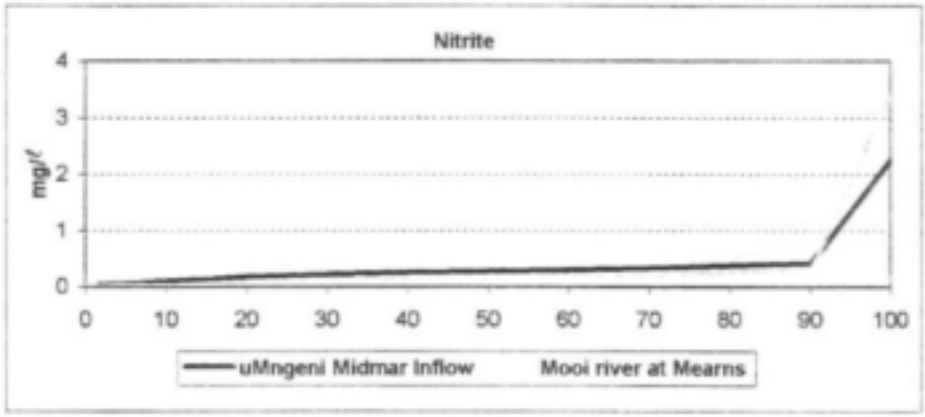
Non parametric comparison of medians
Z =12.2034 - statistically significantly different



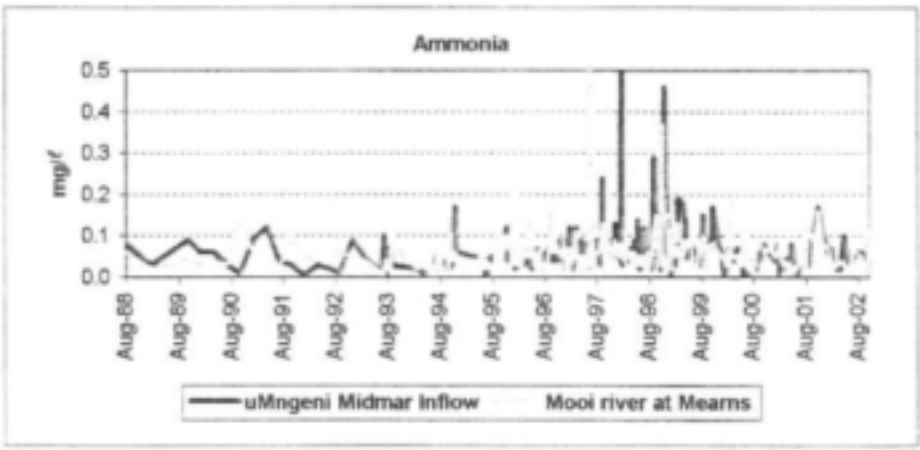
Nitrite (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	342	342
Minimum	0.025	0.025
25th percentile	0.025	0.025
Median	0.025	0.025
Average	0.025	0.027
75th Percentile	0.025	0.025
95th Percentile	0.025	0.025
Maximum	0.070	0.250



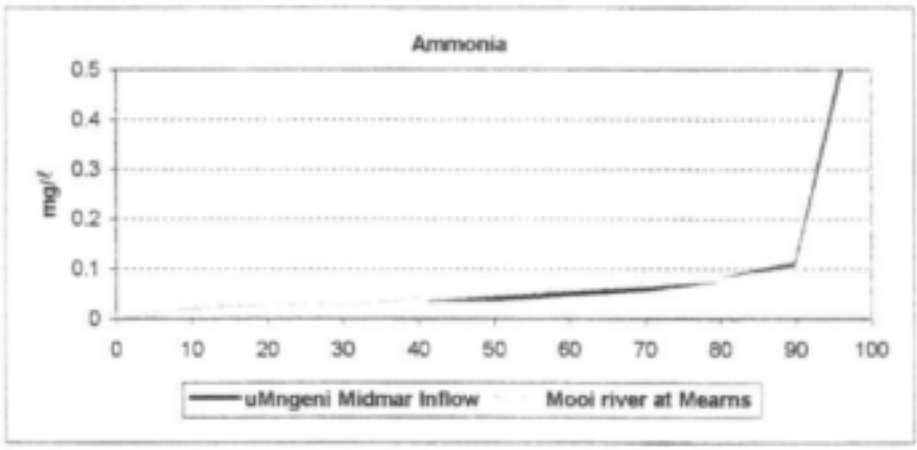
Non parametric comparison of medians
Z = 0.948683 - statistically similar



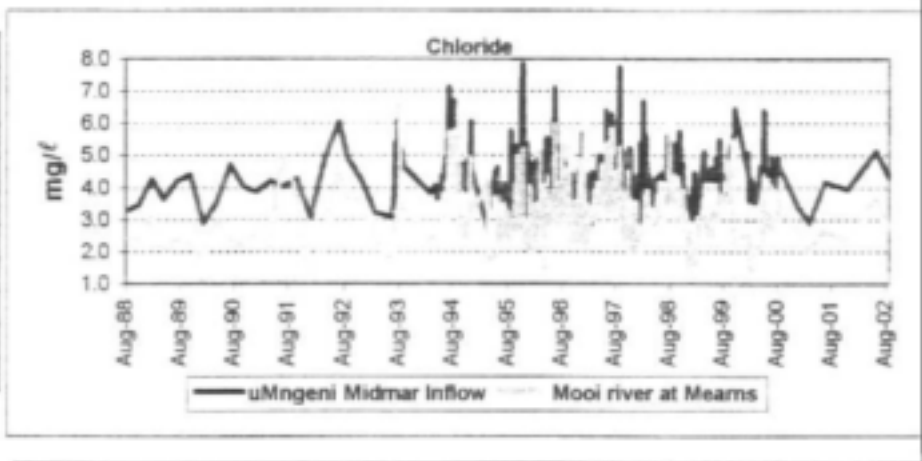
Ammonia (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	328	328
Minimum	0.01	0.01
25th percentile	0.03	0.03
Median	0.04	0.05
Average	0.06	0.06
75th Percentile	0.07	0.07
95th Percentile	0.14	0.13
Maximum	0.77	0.72



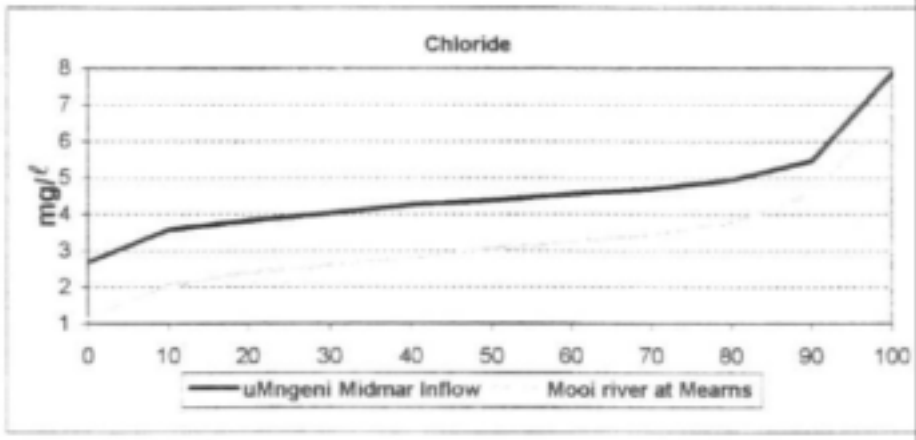
Non parametric comparison of medians
Z =1.06152 - statistically similar



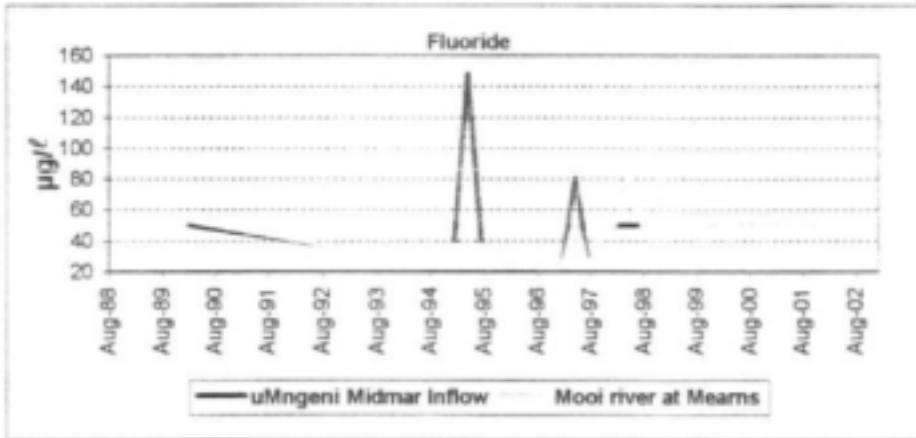
Chloride (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	310	310
Minimum	2.69	1.10
25th percentile	3.93	2.51
Median	4.39	3.03
Average	4.46	3.15
75th Percentile	4.85	3.59
95th Percentile	5.86	5.18
Maximum	7.89	6.84



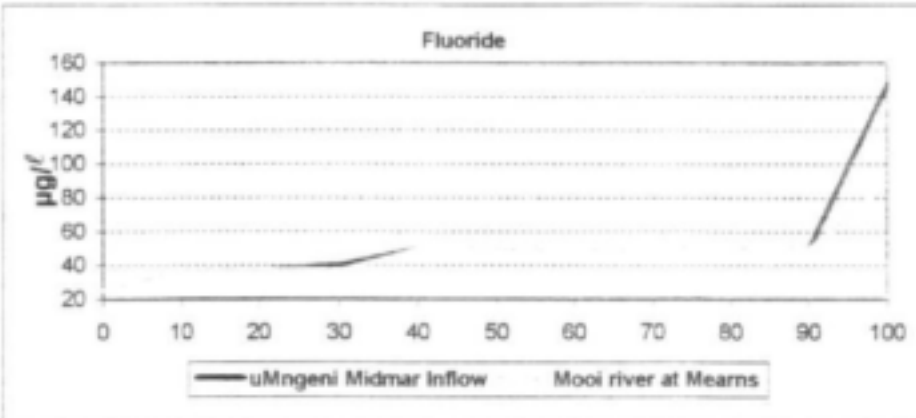
Non parametric comparison of medians
Z =14.7909 - statistically significantly different



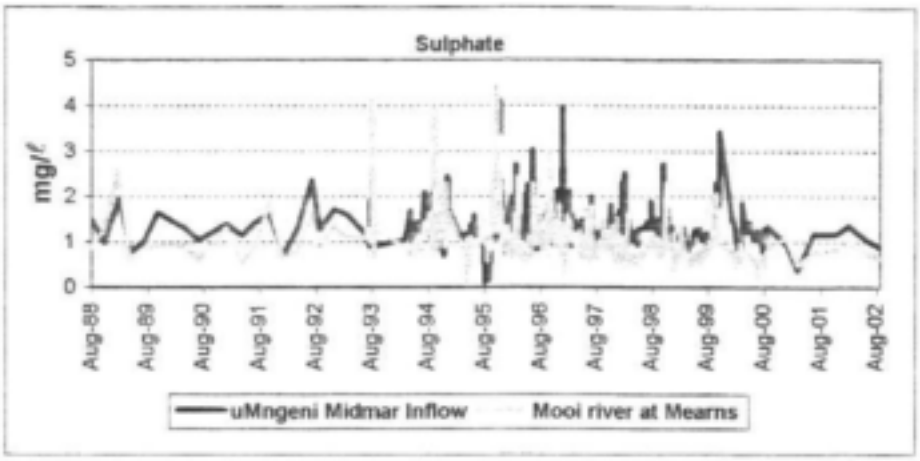
Fluoride (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	45	45
Minimum	25.0	25.0
25th percentile	37.5	37.5
Median	50.0	50.0
Average	47.9	45.7
75th Percentile	50.0	50.0
95th Percentile	50.2	52.2
Maximum	148.0	87.9



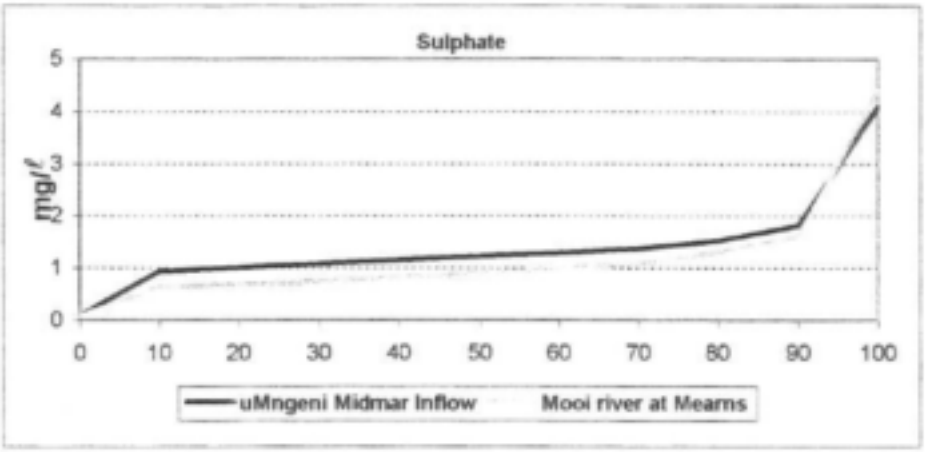
Non parametric comparison of medians
*Z =0 - statistically similar



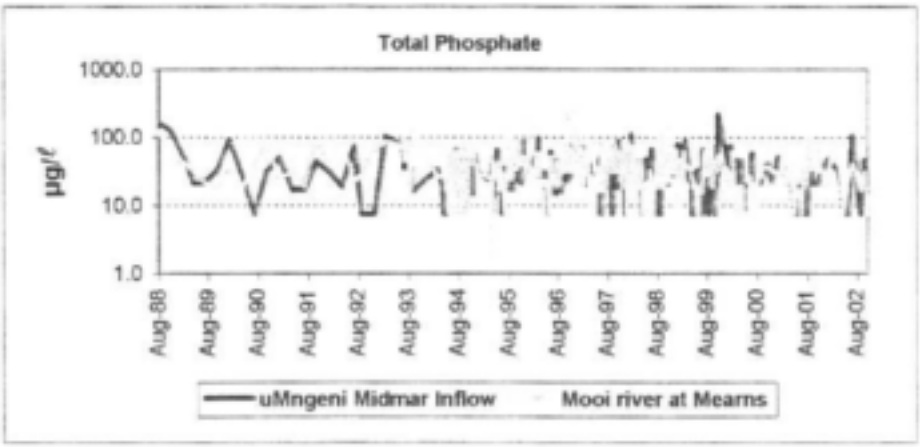
Sulphate (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	310	310
Minimum	0.06	0.06
25th percentile	1.06	0.72
Median	1.23	0.90
Average	1.32	1.04
75th Percentile	1.45	1.18
95th Percentile	2.13	1.93
Maximum	4.11	4.43



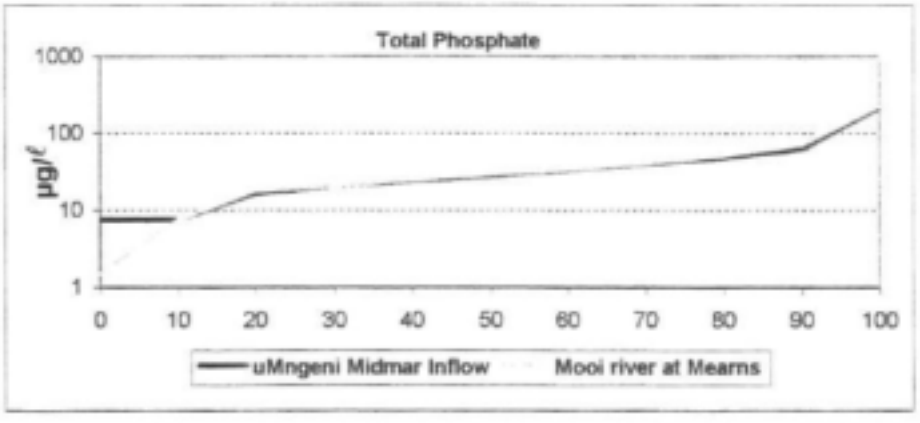
Non parametric comparison of medians
Z =9.89851 - statistically significantly different



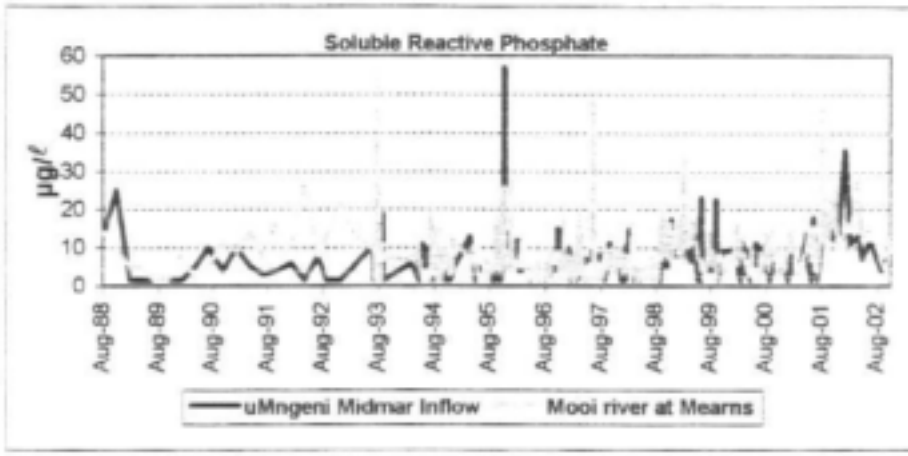
Total Phosphate (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	332	333
Minimum	7.5	1.5
25th percentile	19.0	19.6
Median	28.4	30.0
Average	34.0	37.6
75th Percentile	43.5	45.0
95th Percentile	80.1	90.8
Maximum	220.0	232.0



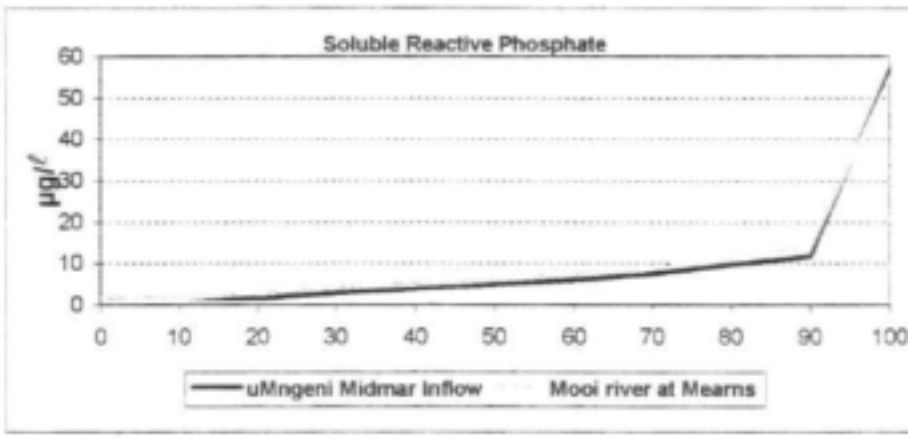
Non parametric comparison of medians
Z =2.04137 - statistically significantly different



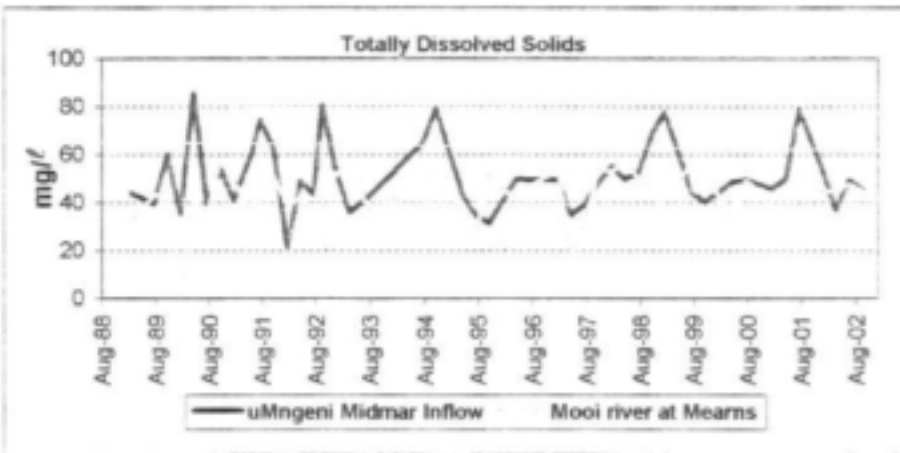
Soluble Reactive Phosphate (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	333	333
Minimum	1.50	1.50
25th percentile	1.50	3.49
Median	5.00	6.00
Average	6.12	7.69
75th Percentile	8.57	10.00
95th Percentile	13.94	18.72
Maximum	57.00	55.00



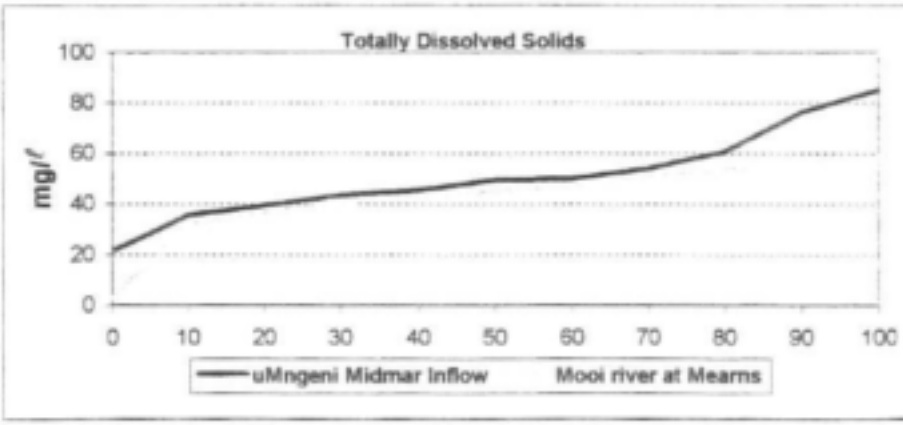
Non parametric comparison of medians
Z =3.87069 - statistically significantly different



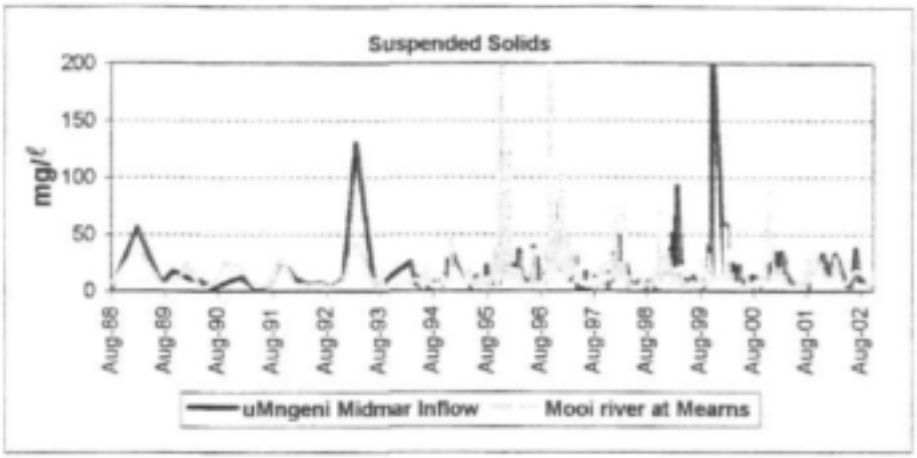
Totally Dissolved Solids (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	45	45
Minimum	21.6	2.8
25th percentile	41.2	37.4
Median	49.6	44.9
Average	51.1	43.9
75th Percentile	55.2	51.8
95th Percentile	79.3	57.8
Maximum	85.3	59.0



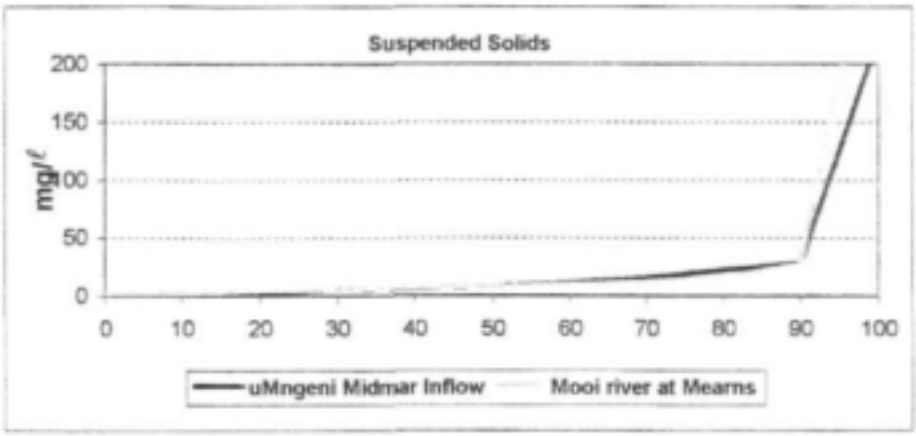
Non parametric comparison of medians
Z =2.96142 - statistically significantly different



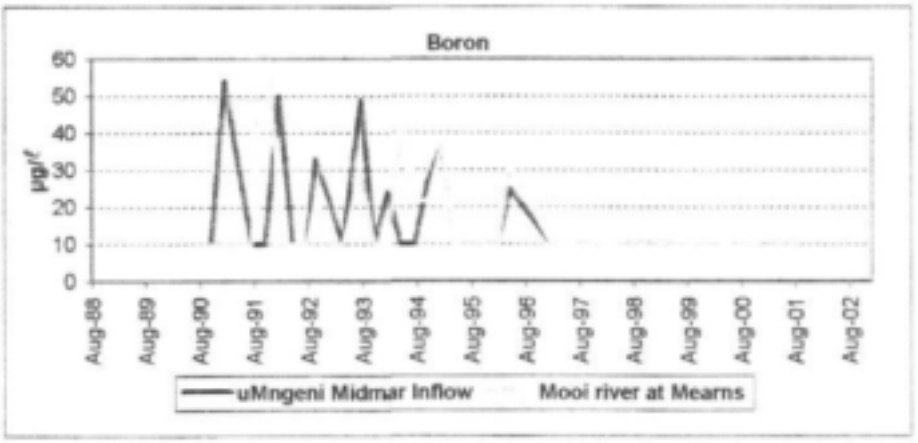
Suspended Solids (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	331	331
Minimum	2.0	2.0
25th percentile	4.8	5.2
Median	8.4	8.4
Average	14.3	14.5
75th Percentile	18.0	14.9
95th Percentile	37.8	38.2
Maximum	224.0	347.0



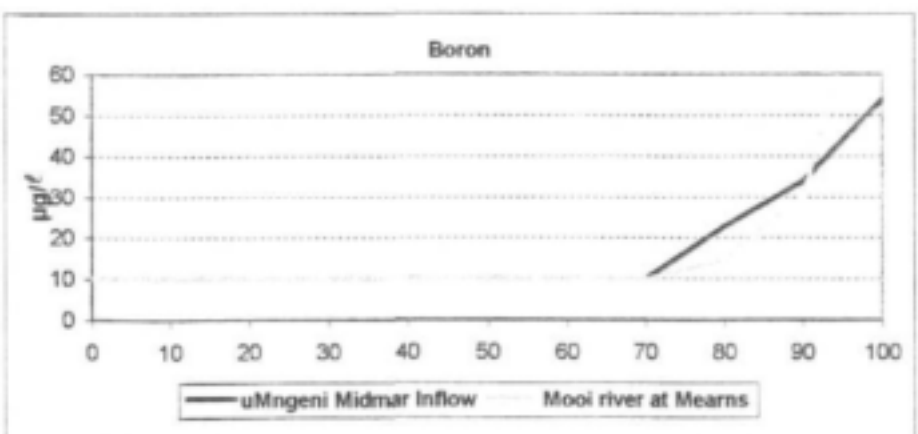
Non parametric comparison of medians
Z =1.18889 - statistically similar



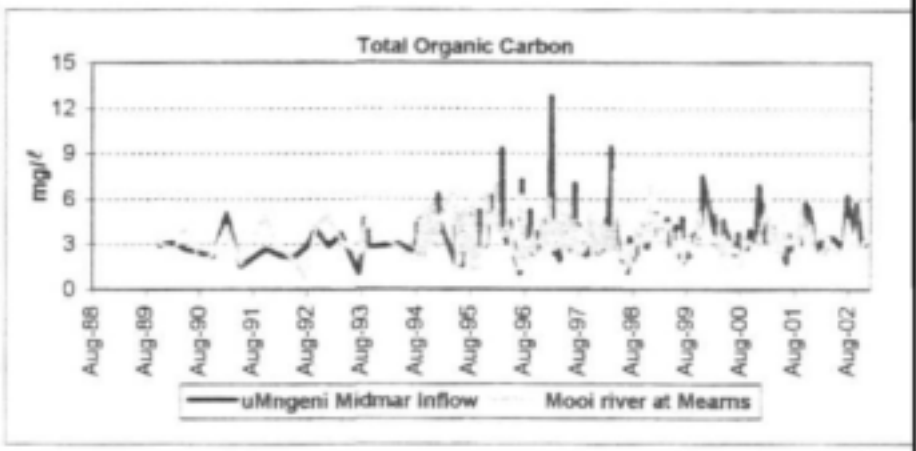
Boron (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	39	39
Minimum	10.0	10.0
25th percentile	10.0	10.0
Median	10.0	10.0
Average	15.9	15.6
75th Percentile	10.0	10.0
95th Percentile	49.1	37.4
Maximum	54.0	97.0



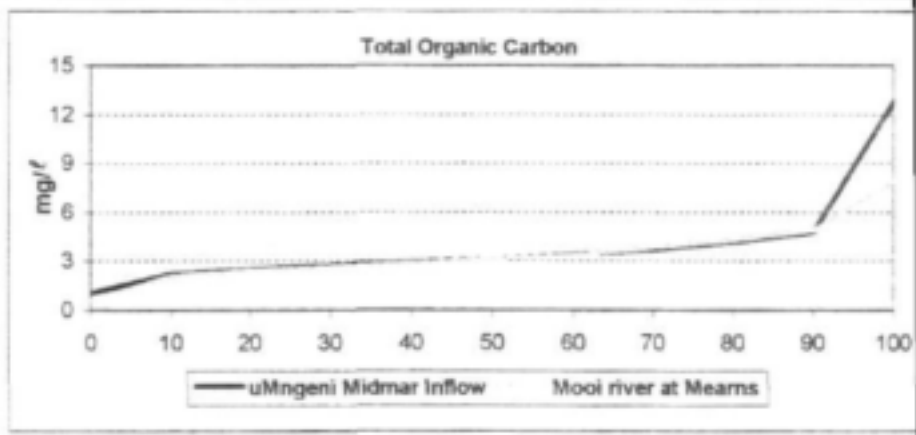
Non parametric comparison of medians
Z =0.2886765 - statistically similar



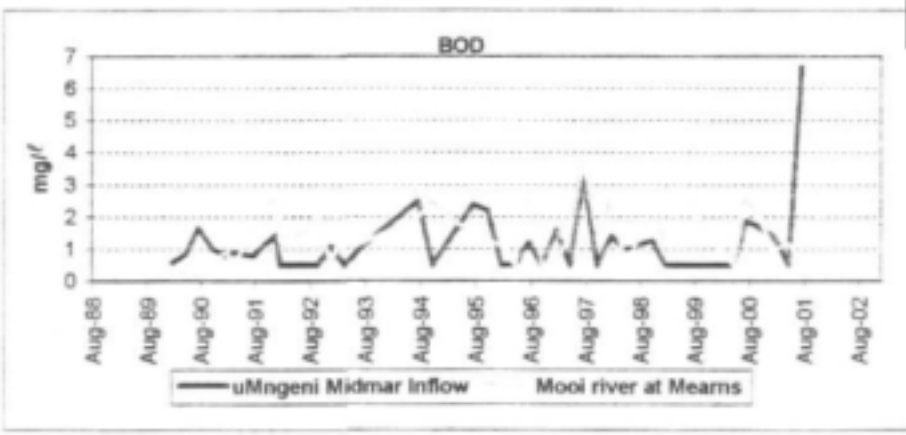
Total Organic Carbon (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	310	310
Minimum	1.06	0.64
25th percentile	2.64	2.55
Median	3.14	3.14
Average	3.41	3.36
75th Percentile	3.88	4.07
95th Percentile	5.33	5.58
Maximum	12.80	7.85



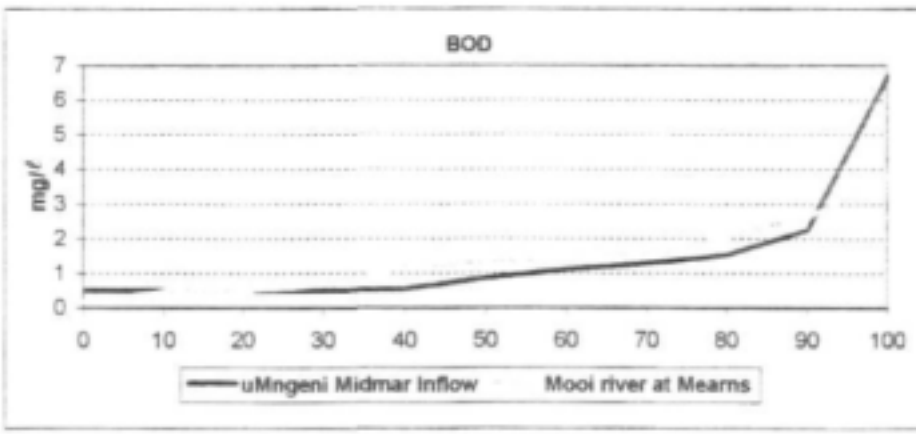
Non parametric comparison of medians
Z =1.02396 - statistically similar



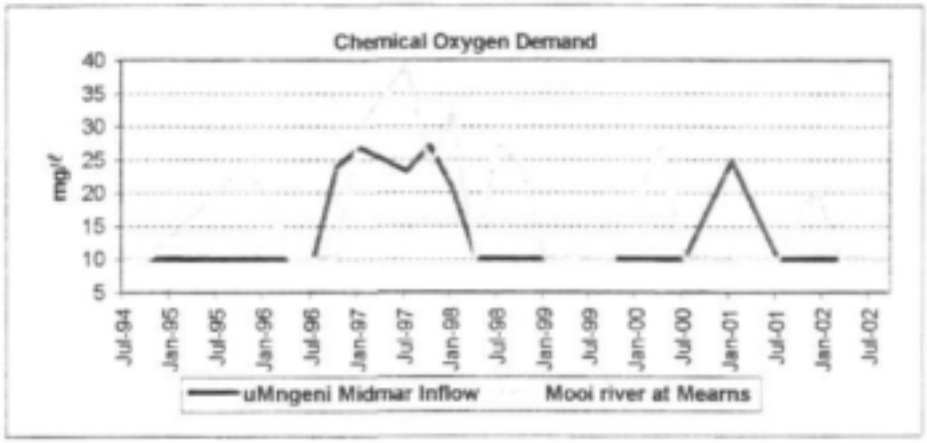
BOD (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	38	38
Minimum	0.50	0.16
25th percentile	0.50	0.50
Median	0.87	1.30
Average	1.20	1.37
75th Percentile	1.40	1.79
95th Percentile	2.62	2.70
Maximum	6.70	3.80



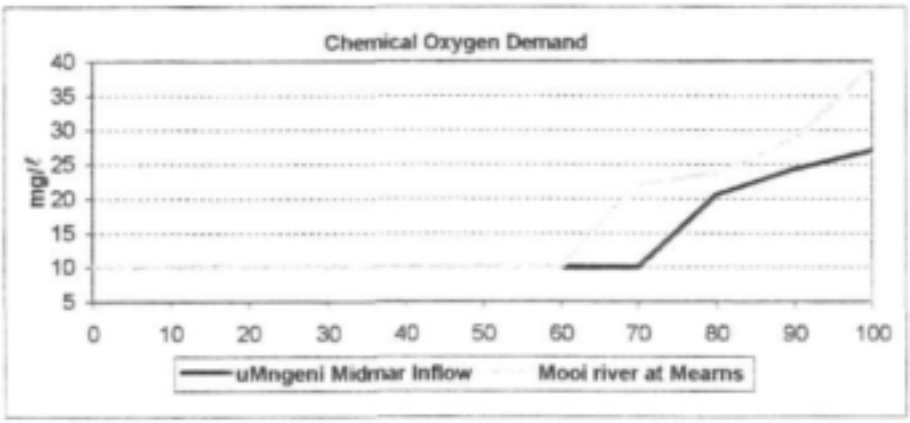
Non parametric comparison of medians
Z =1.35225 - statistically similar



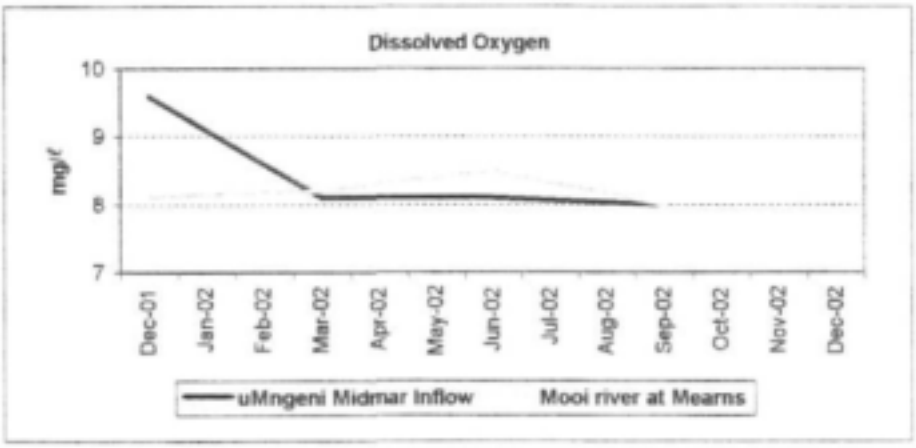
Chemical Oxygen Demand (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	26	26
Minimum	10.0	10.0
25th percentile	10.0	10.0
Median	10.0	10.0
Average	13.3	16.5
75th Percentile	10.0	23.7
95th Percentile	26.4	31.6
Maximum	27.1	39.2



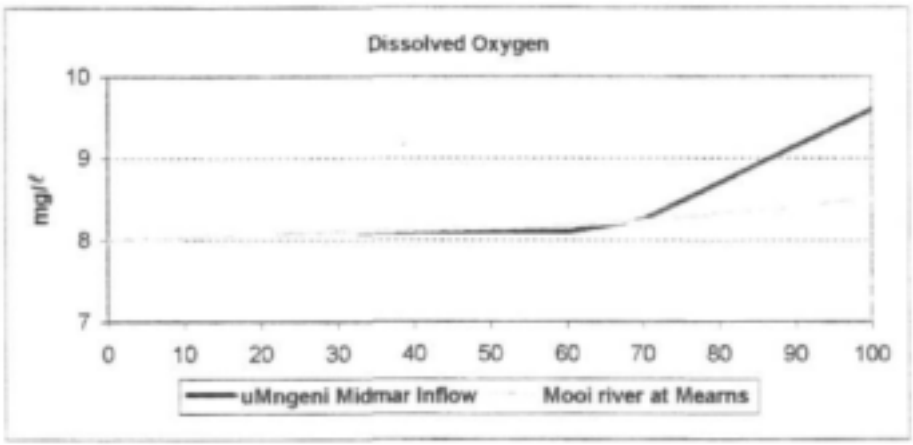
Non parametric comparison of medians
Z =1.44338 - statistically similar



Dissolved Oxygen (mg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	8.0	8.0
25th percentile	8.1	8.1
Median	8.1	8.2
Average	8.5	8.2
75th Percentile	8.5	8.3
95th Percentile	9.4	8.5
Maximum	9.6	8.5



Non parametric comparison of medians
*Z =0



Copper (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<0.05	<0.05
25th percentile	<0.05	<0.05
Median	<0.05	<0.05
Average	<0.05	<0.05
75th Percentile	<0.05	<0.05
95th Percentile	<0.05	<0.05
Maximum	<0.05	<0.05

Zinc (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<0.03	<0.03
25th percentile	<0.03	<0.03
Median	<0.03	<0.03
Average	<0.015	<0.03
75th Percentile	<0.015	<0.03
95th Percentile	0.02	<0.03
Maximum	0.03	<0.03

Lead (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<4	<4
25th percentile	<4	<4
Median	<4	<4
Average	<4	<4
75th Percentile	<4	<4
95th Percentile	<4	<4
Maximum	<4	<4

Cadmium (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<1	<1
25th percentile	<1	<1
Median	<1	<1
Average	<1	<1
75th Percentile	<1	<1
95th Percentile	<1	<1
Maximum	<1	<1

Chromium (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<3	<3
25th percentile	<3	<3
Median	<3	<3
Average	<3	<3
75th Percentile	<3	<3
95th Percentile	<3	<3
Maximum	<3	<3

Mercury (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<0.5	<0.5
25th percentile	<0.5	<0.5
Median	<0.5	<0.5
Average	<0.5	<0.5
75th Percentile	<0.5	<0.5
95th Percentile	<0.5	<0.5
Maximum	<0.5	<0.5

Arsenic (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<2	<2
25th percentile	<2	<2
Median	<2	<2
Average	<2	<2
75th Percentile	<2	<2
95th Percentile	<2	<2
Maximum	<2	<2

Selenium (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<1	<1
25th percentile	<1	<1
Median	<1	<1
Average	<1	<1
75th Percentile	<1	<1
95th Percentile	<1	<1
Maximum	<1	<1

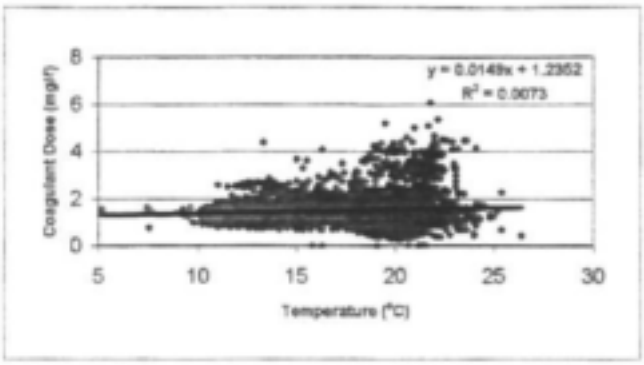
Total Recoverable Cyanide (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<10	<10
25th percentile	<10	<10
Median	<10	<10
Average	<10	<10
75th Percentile	<10	<10
95th Percentile	<10	<10
Maximum	<10	<10

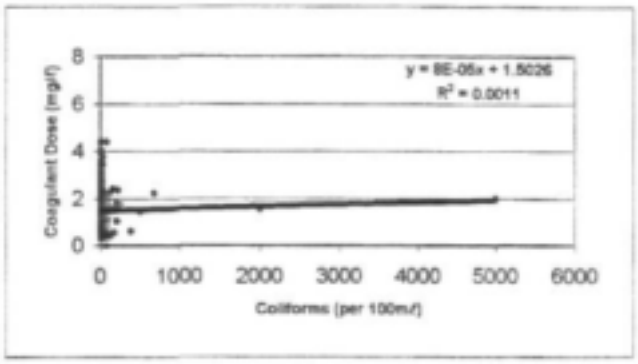
Phenols (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<5	<5
25th percentile	<5	<5
Median	<5	<5
Average	<5	<5
75th Percentile	<5	<5
95th Percentile	<5	<5
Maximum	<5	<5

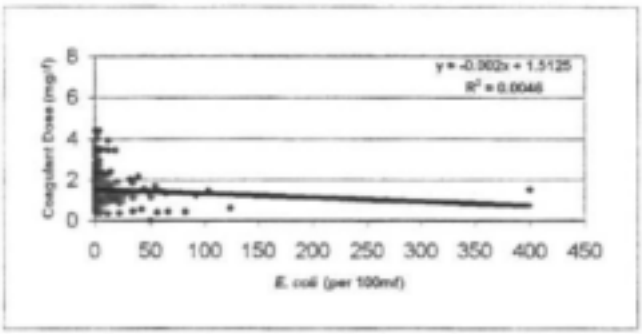
Pesticides (µg/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	3	3
Minimum	<20	<20
25th percentile	<20	<20
Median	<20	<20
Average	<20	<20
75th Percentile	<20	<20
95th Percentile	<20	<20
Maximum	<20	<20

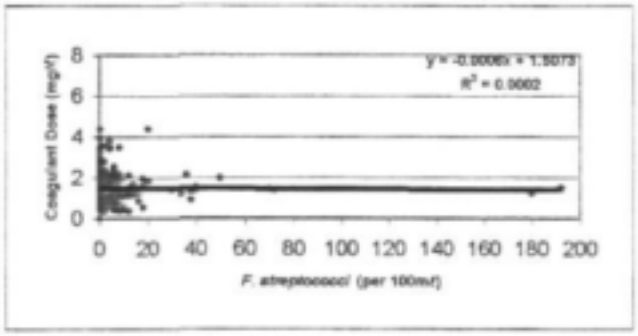
Atrazine (ng/ℓ)		
	uMngeni Midmar Inflow	Mooi river at Mearns
Analyses	4	4
Minimum	<5	<5
25th percentile	<5	<5
Median	<5	<5
Average	<1.25	<5
75th Percentile	<1.25	<5
95th Percentile	7.75	<5
Maximum	10.00	<5

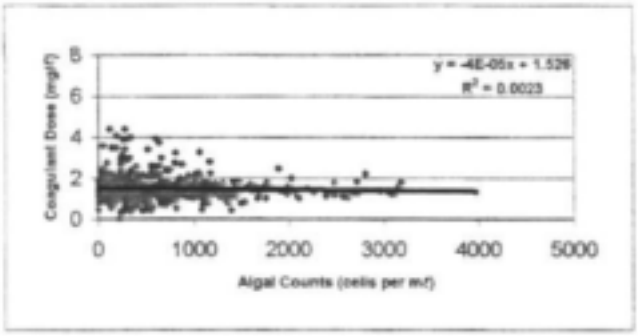
Appendix 2a : DV Harris WW Regression Analysis

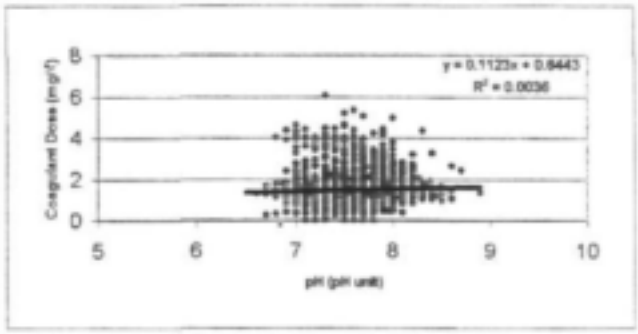


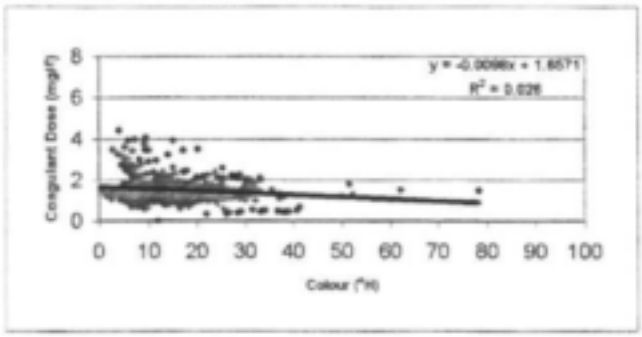


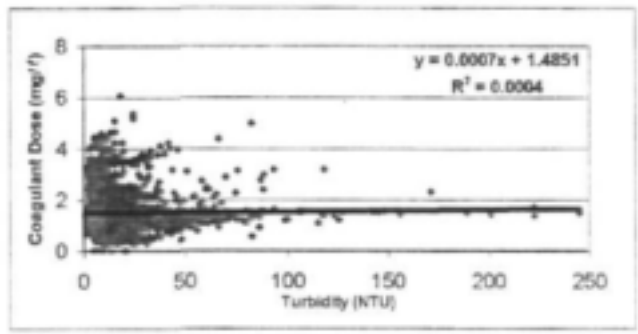


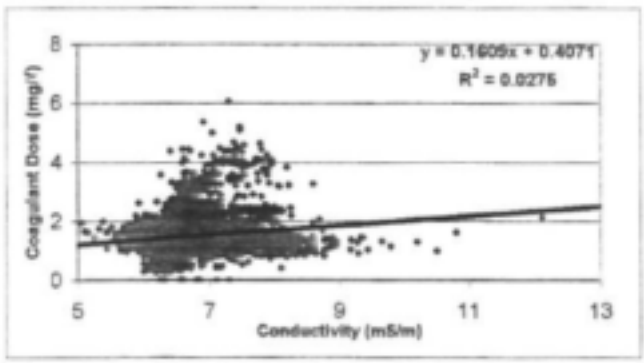


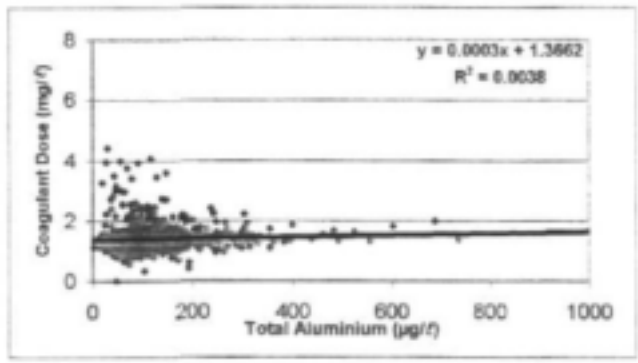


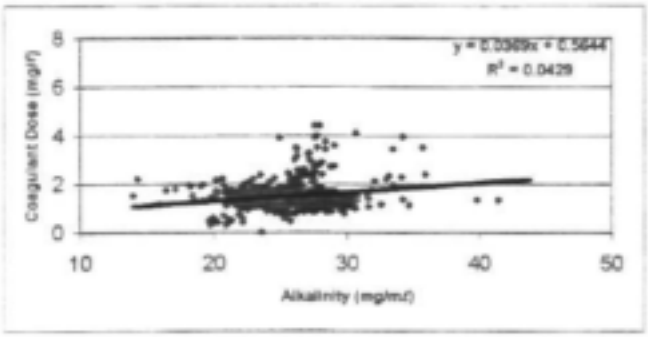


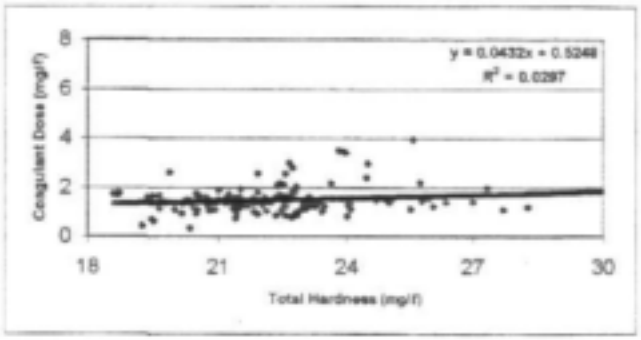


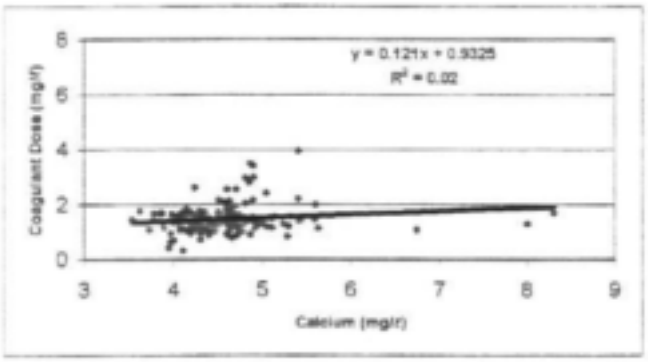


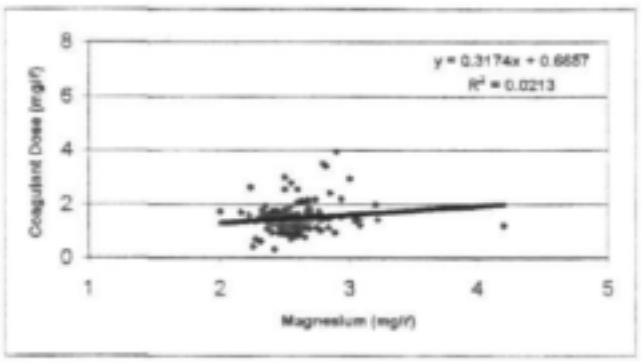


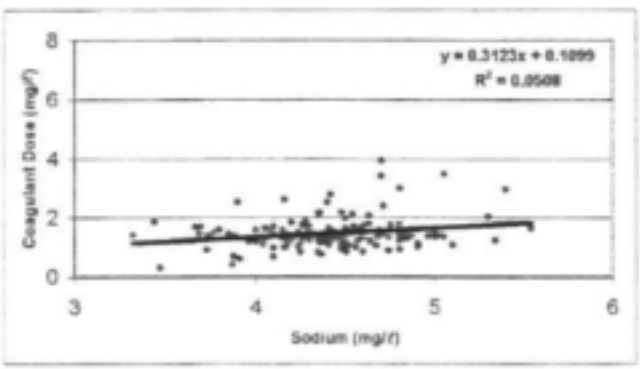


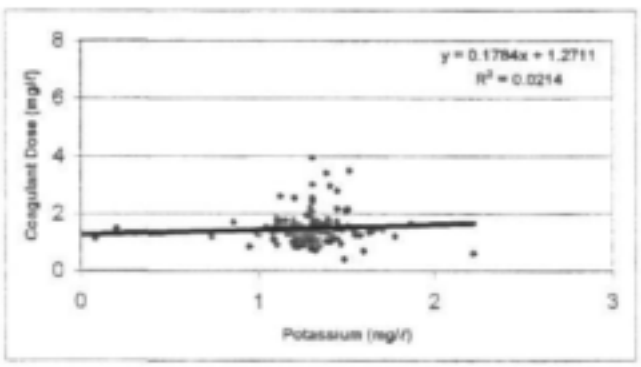

y = 0.0369x + 0.5644
R² = 0.0429
Coagulant Dose (mg/l)
Alkalinity (mg/ml)

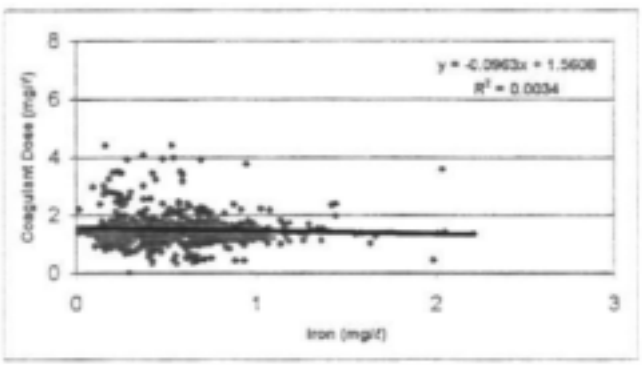

y = 0.0432x + 0.5248
R² = 0.0297
Coagulant Dose (mg/l)
Total Hardness (mg/l)

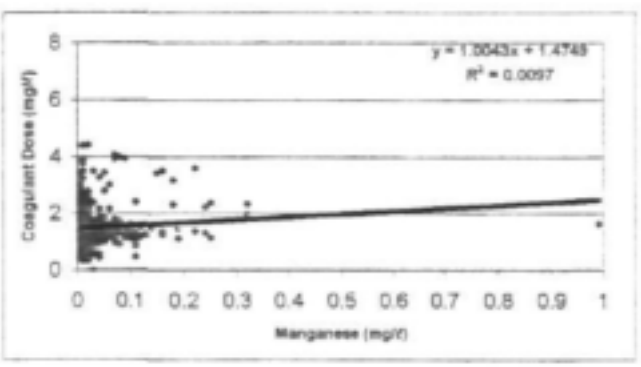

y = 0.121x + 0.9325
R² = 0.02
Coagulant Dose (mg/l)
Calcium (mg/l)

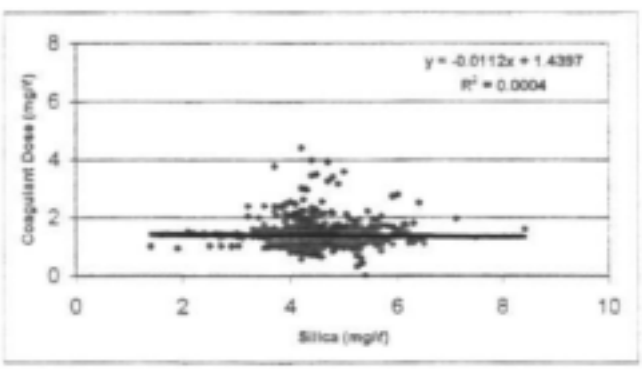

y = 0.3174x + 0.6657
R² = 0.0213
Coagulant Dose (mg/l)
Magnesium (mg/l)

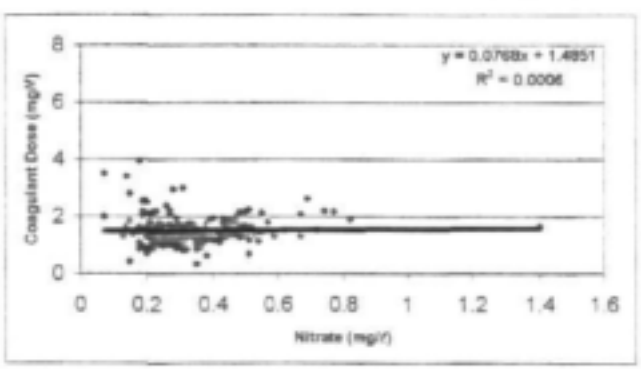

y = 0.3123x + 0.1099
R² = 0.0508
Coagulant Dose (mg/l)
Sodium (mg/l)

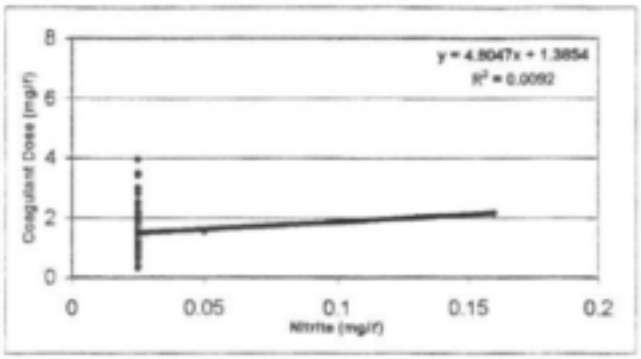

y = 0.1784x + 1.2711
R² = 0.0214
Coagulant Dose (mg/l)
Potassium (mg/l)

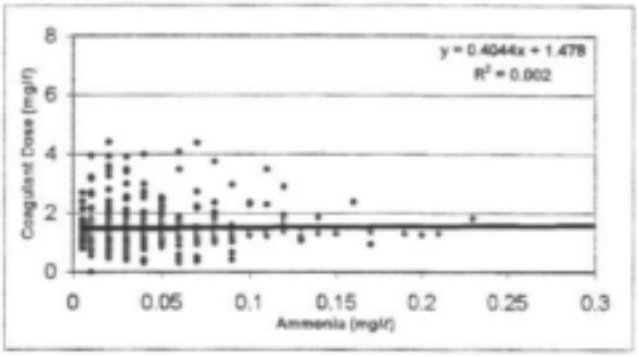

y = -0.0903x + 1.5608
R² = 0.0034
Coagulant Dose (mg/l)
Iron (mg/l)

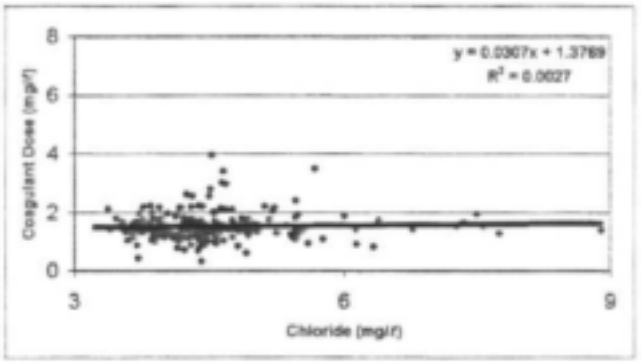

y = 1.0043x + 1.4745
R² = 0.0097
Coagulant Dose (mg/l)
Manganese (mg/l)

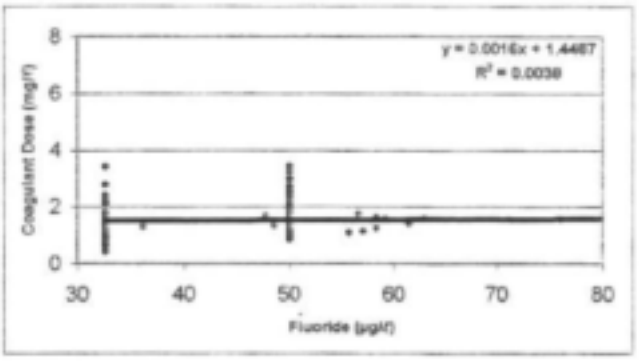

y = -0.0112x + 1.4397
R² = 0.0004
Coagulant Dose (mg/l)
Silica (mg/l)

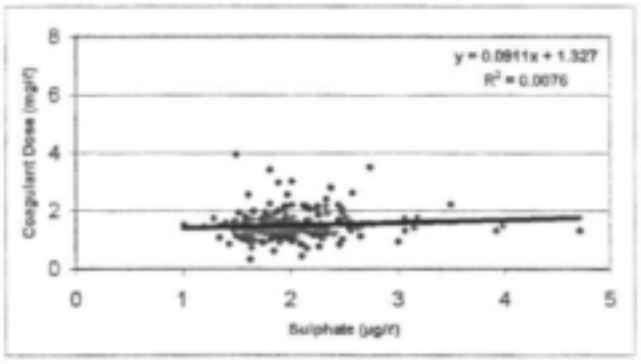

y = 0.0768x + 1.4851
R² = 0.0006
Coagulant Dose (mg/l)
Nitrate (mg/l)

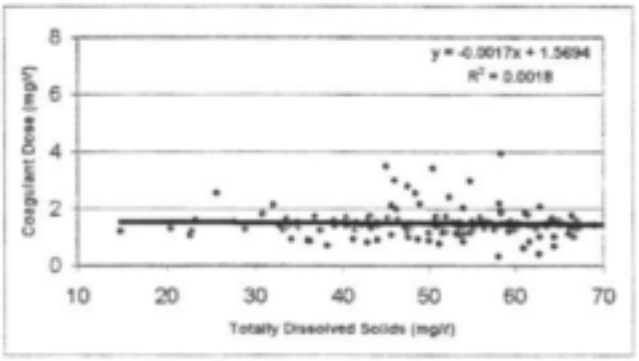

y = 4.8047x + 1.3854
R² = 0.0092
Coagulant Dose (mg/l)
Nitrite (mg/l)

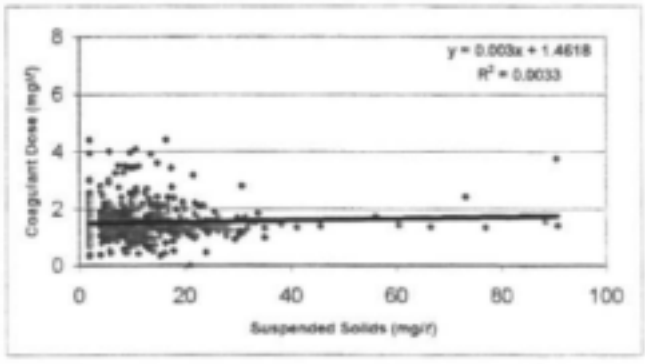

y = 0.4044x + 1.478
R² = 0.002
Coagulant Dose (mg/l)
Ammonia (mg/l)

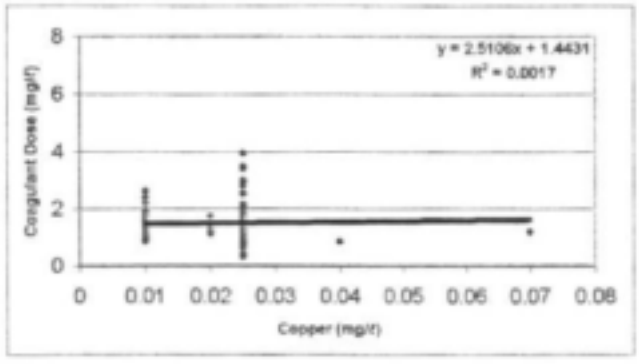

y = 0.0307x + 1.3769
R² = 0.0027
Coagulant Dose (mg/l)
Chloride (mg/l)

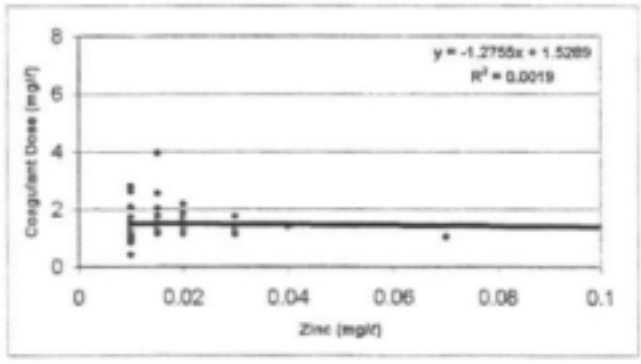

y = 0.0016x + 1.4487
R² = 0.0039
Coagulant Dose (mg/l)
Fluoride (µg/l)

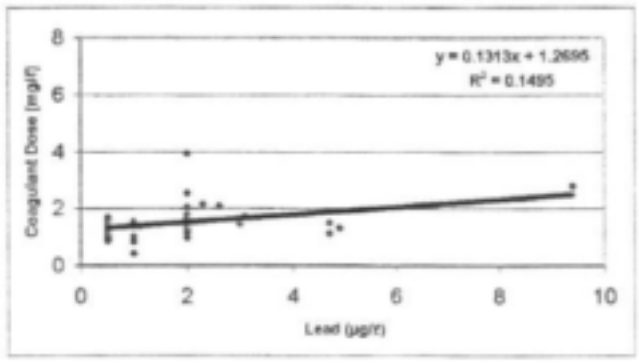

y = 0.0911x + 1.327
R² = 0.0076
Coagulant Dose (mg/l)
Sulphate (µg/l)

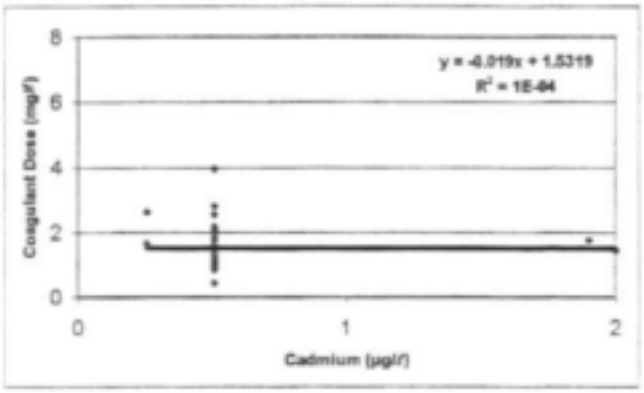

y = -0.0017x + 1.5694
R² = 0.0018
Coagulant Dose (mg/l)
Totally Dissolved Solids (mg/l)

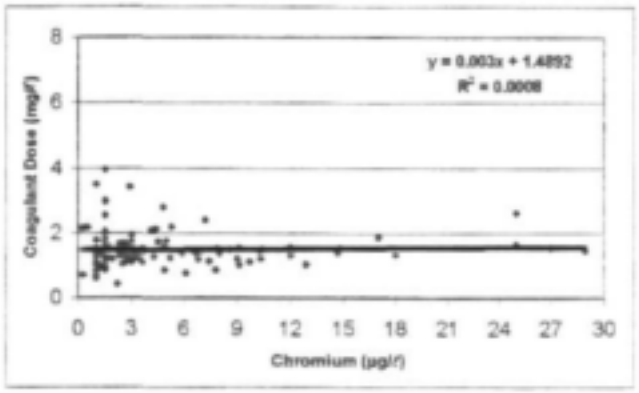

y = 0.003x + 1.4618
R² = 0.0033
Coagulant Dose (mg/l)
Suspended Solids (mg/l)

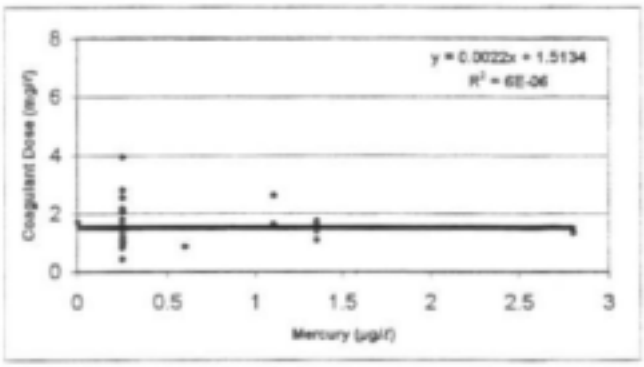

y = 2.5106x + 1.4431
R² = 0.0017
Coagulant Dose (mg/l)
Copper (mg/l)

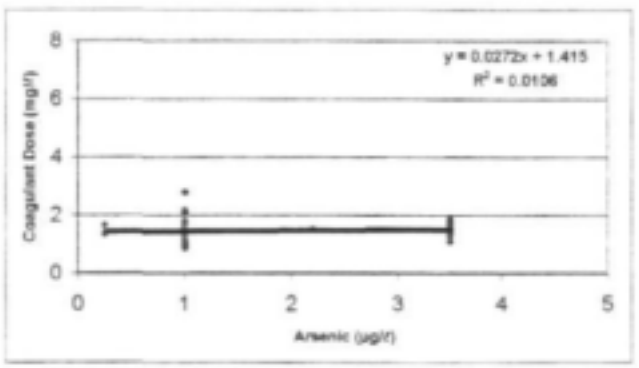

y = -1.2755x + 1.5289
R² = 0.0019
Coagulant Dose (mg/l)
Zinc (mg/l)

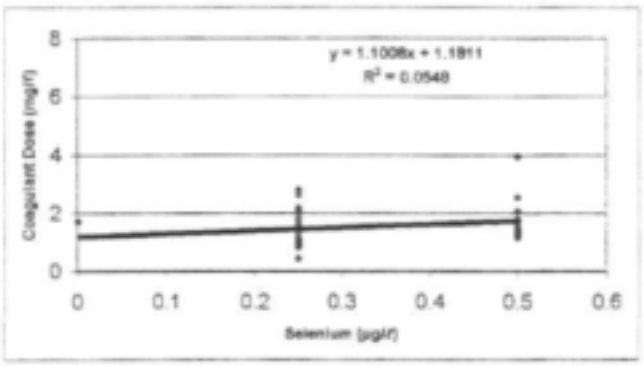

y = 0.1313x + 1.2695
R² = 0.1495
Coagulant Dose (mg/l)
Lead (µg/l)

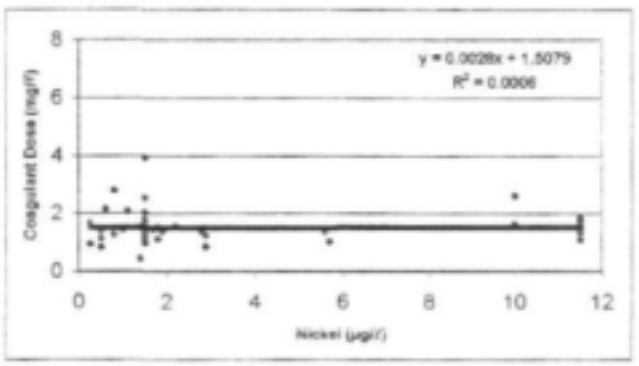

y = -6.019x + 1.5319
R² = 1E-04
Coagulant Dose (mg/l)
Cadmium (µg/l)

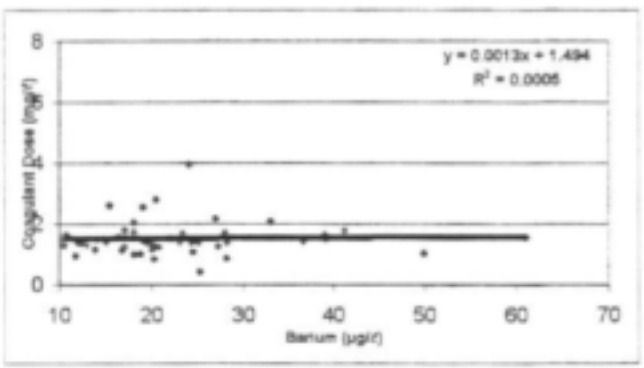

y = 0.003x + 1.4892
R² = 0.0008
Coagulant Dose (mg/l)
Chromium (µg/l)

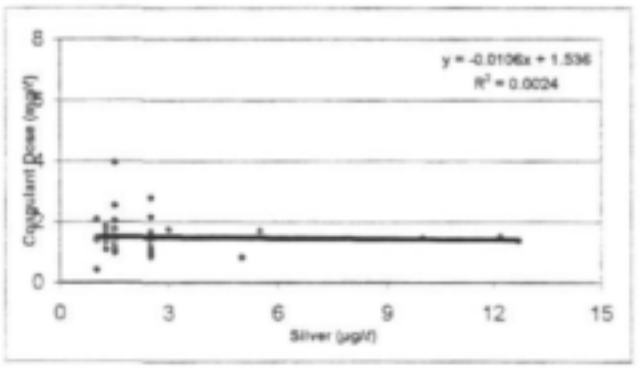

y = 0.0022x + 1.5134
R² = 6E-06
Coagulant Dose (mg/l)
Mercury (µg/l)

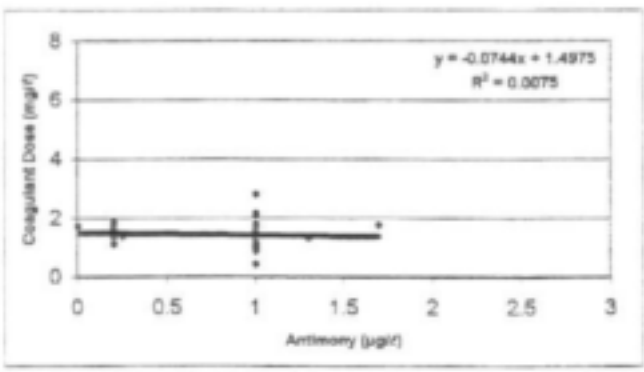

y = 0.0272x + 1.415
R² = 0.0106
Coagulant Dose (mg/l)
Arsenic (µg/l)

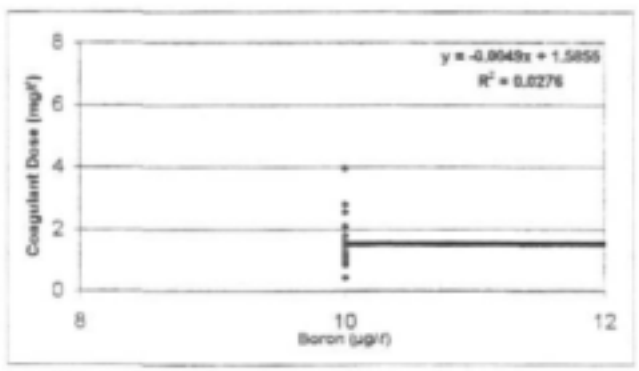

y = 1.1008x + 1.1811
R² = 0.0548
Coagulant Dose (mg/l)
Selenium (µg/l)

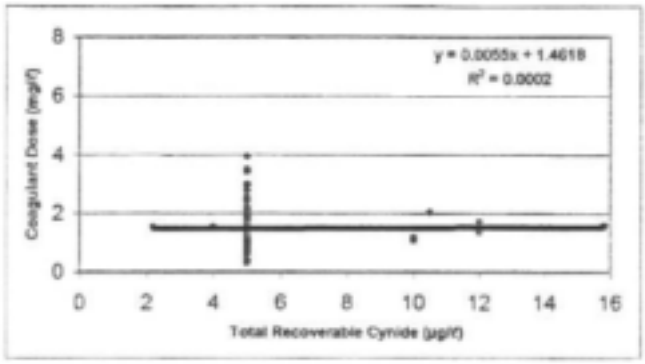

y = 0.0028x + 1.5079
R² = 0.0006
Coagulant Dose (mg/l)
Nickel (µg/l)

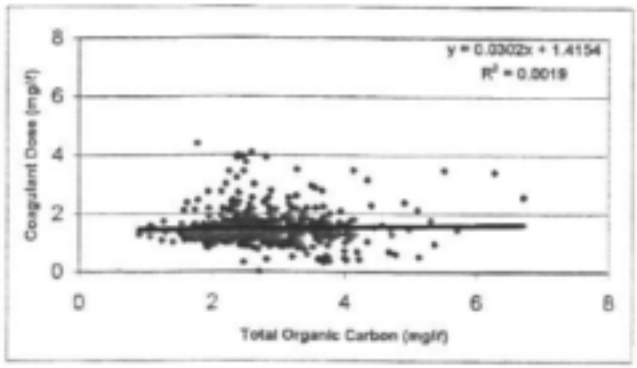

y = 0.0013x + 1.494
R² = 0.0005
Coagulant Dose (mg/l)
Barium (µg/l)


y = -0.0106x + 1.536
R² = 0.0024
Coagulant Dose (mg/l)
Silver (µg/l)

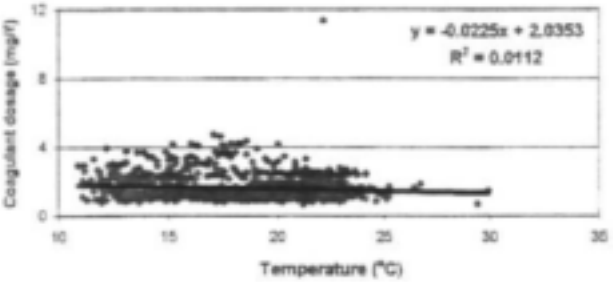

y = -0.0744x + 1.4975
R² = 0.0075
Coagulant Dose (mg/l)
Antimony (µg/l)

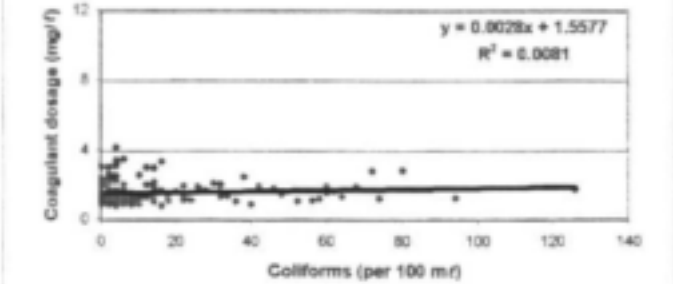

y = -0.0049x + 1.5855
R² = 0.0276
Coagulant Dose (mg/l)
Boron (µg/l)

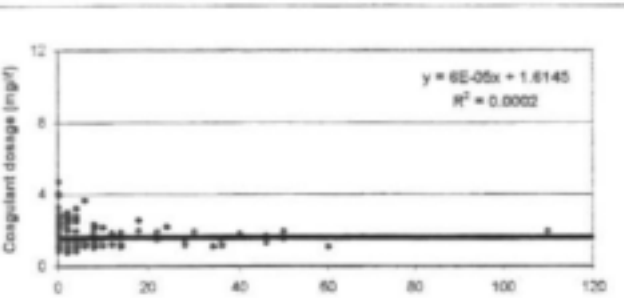

y = 0.0055x + 1.4619
R² = 0.0002
Coagulant Dose (mg/l)
Total Recoverable Cyniide (µg/l)
0
2
4
6
8
10
12
14
16

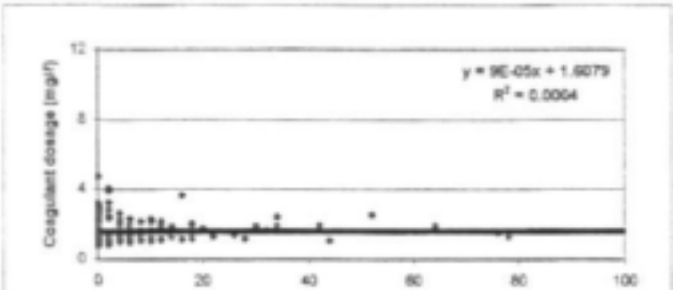

y = 0.0302x + 1.4154
R² = 0.0019
Coagulant Dose (mg/l)
Total Organic Carbon (mg/l)
0
2
4
6
8

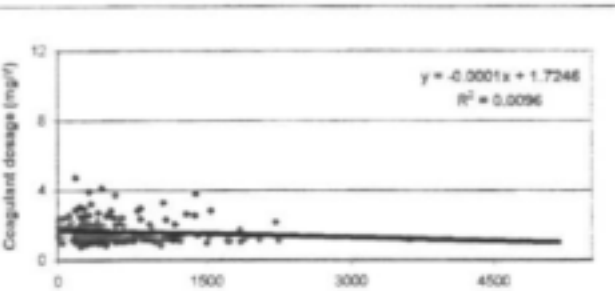
Appendix 2b : Midmar WW Regression Analysis

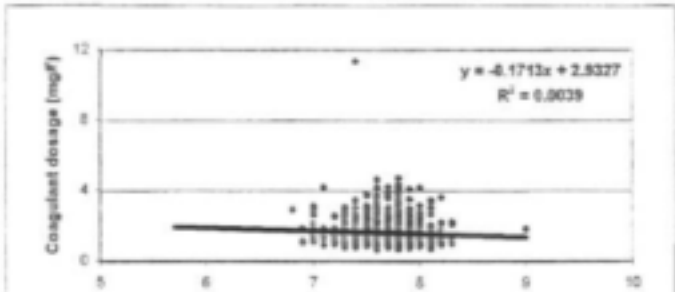


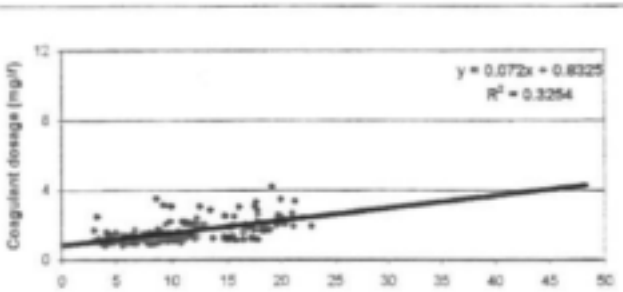


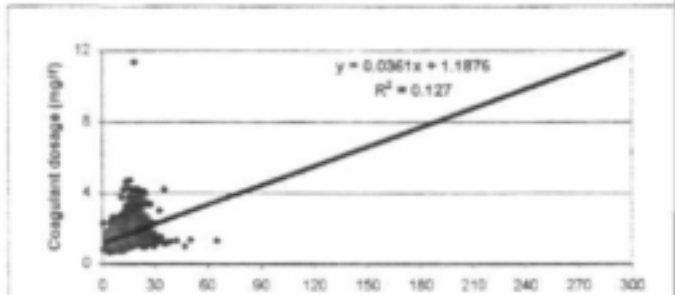


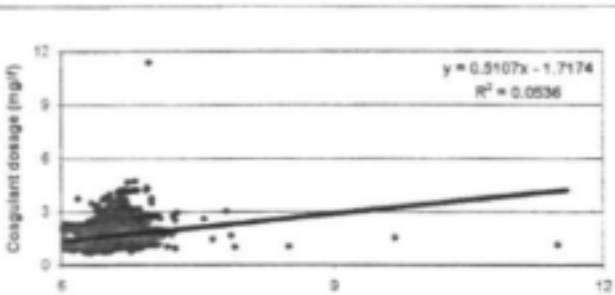


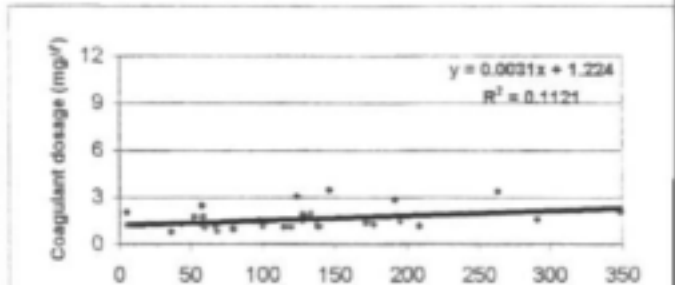


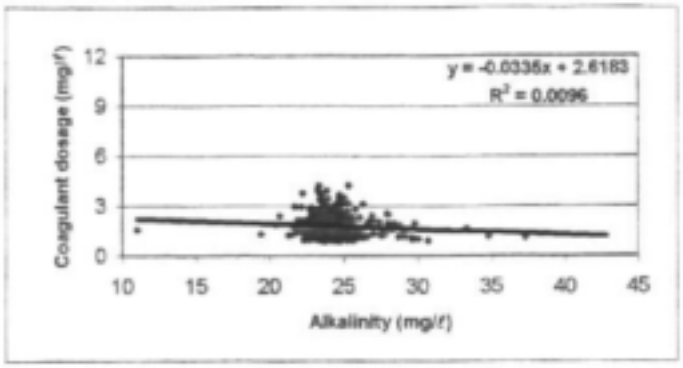


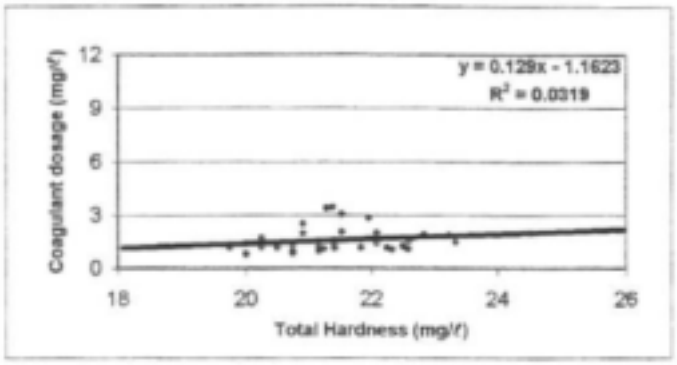


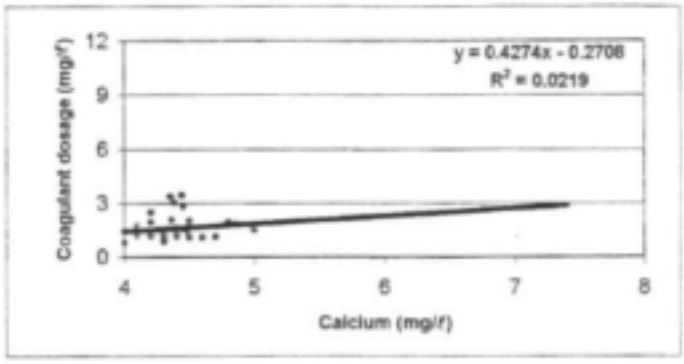


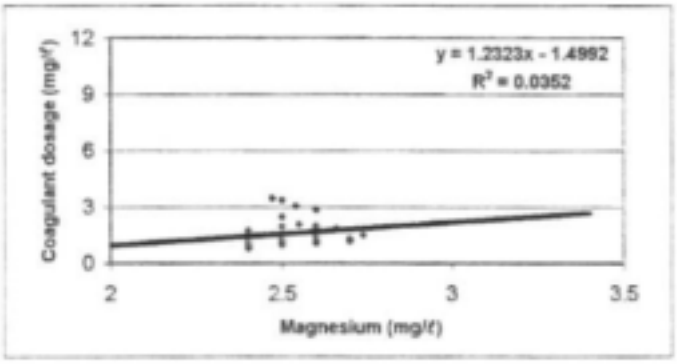


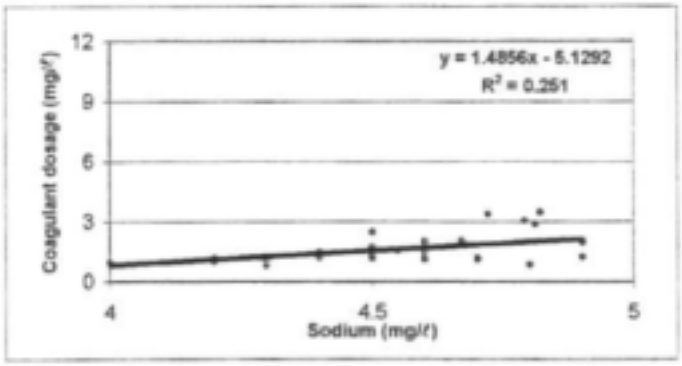


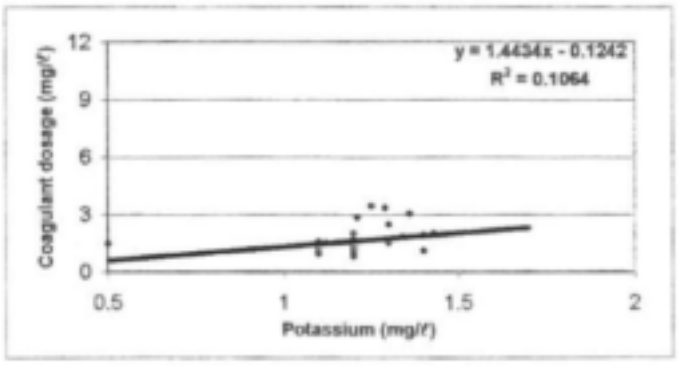

y = -0.0336x + 2.6183
R² = 0.0096
Coagulant dosage (mg/ℓ)
Alkalinity (mg/ℓ)

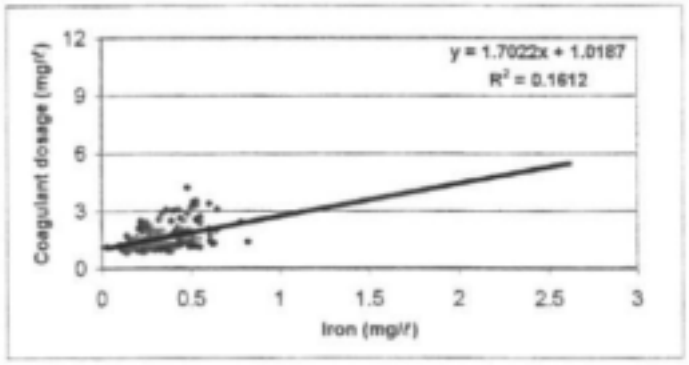

y = 0.129x - 1.1623
R² = 0.0319
Coagulant dosage (mg/ℓ)
Total Hardness (mg/ℓ)

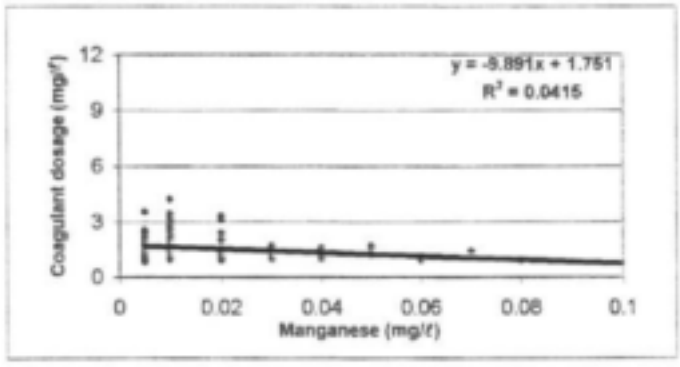

y = 0.4274x - 0.2708
R² = 0.0219
Coagulant dosage (mg/ℓ)
Calcium (mg/ℓ)

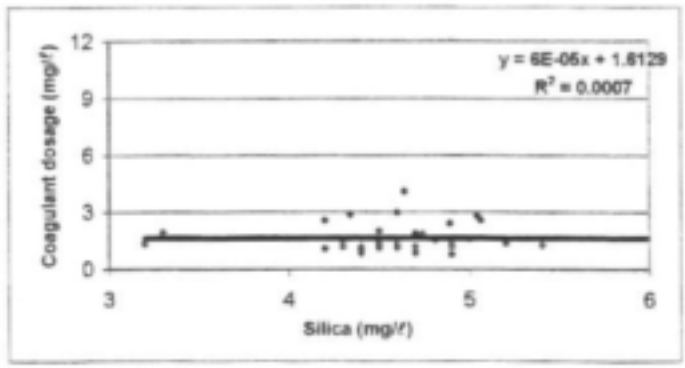

y = 1.2323x - 1.4992
R² = 0.0352
Coagulant dosage (mg/ℓ)
Magnesium (mg/ℓ)

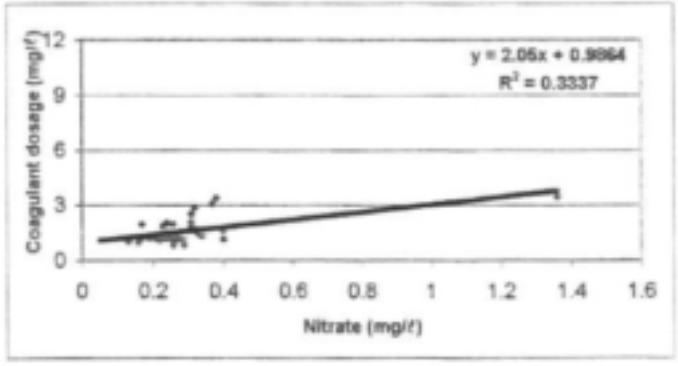

y = 1.4856x - 5.1292
R² = 0.251
Coagulant dosage (mg/ℓ)
Sodium (mg/ℓ)

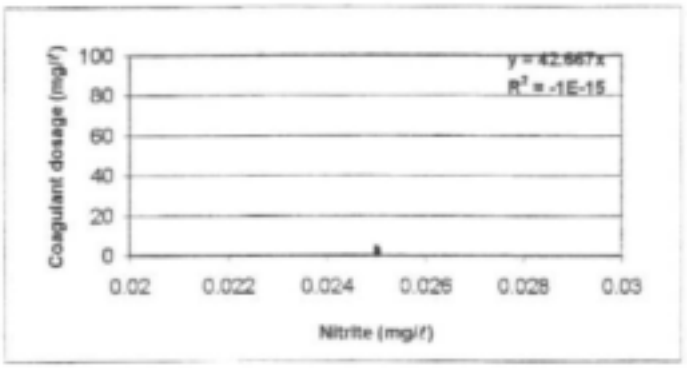

y = 1.4434x - 0.1242
R² = 0.1064
Coagulant dosage (mg/ℓ)
Potassium (mg/ℓ)

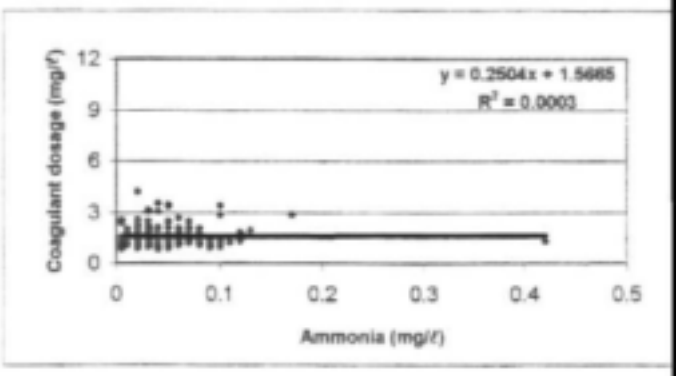

y = 1.7022x + 1.0187
R² = 0.1612
Coagulant dosage (mg/ℓ)
Iron (mg/ℓ)

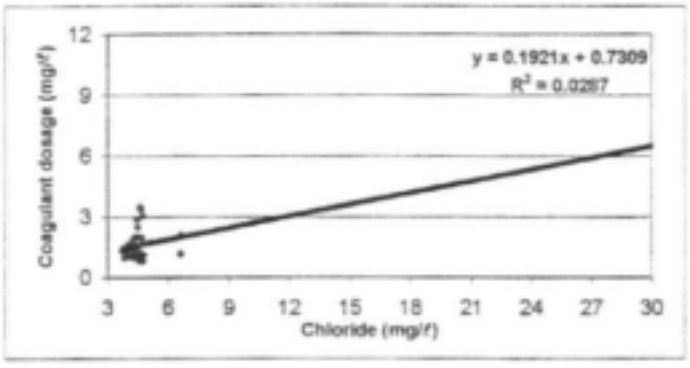

y = -9.891x + 1.751
R² = 0.0415
Coagulant dosage (mg/ℓ)
Manganese (mg/ℓ)

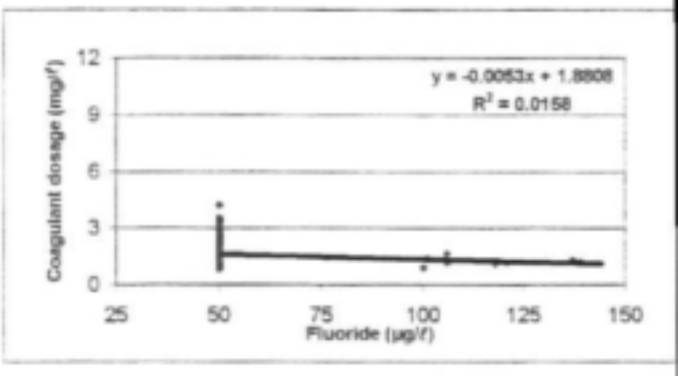

y = 6E-05x + 1.8129
R² = 0.0007
Coagulant dosage (mg/ℓ)
Silica (mg/ℓ)

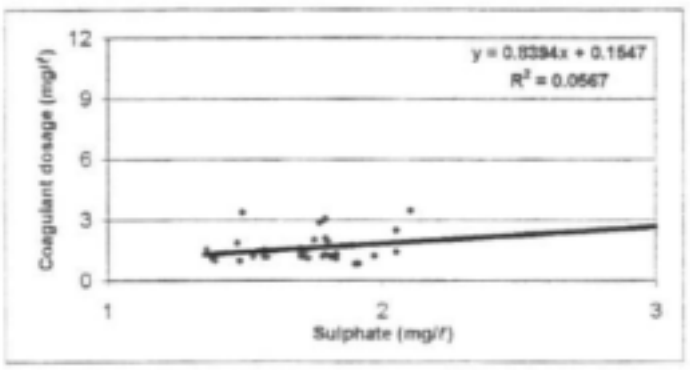

y = 2.05x + 0.9864
R² = 0.3337
Coagulant dosage (mg/ℓ)
Nitrate (mg/ℓ)

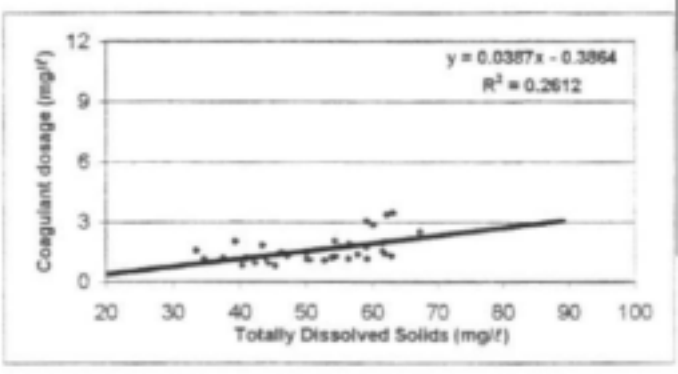

y = 42.667x
R² = -1E-15
Coagulant dosage (mg/ℓ)
Nitrite (mg/ℓ)

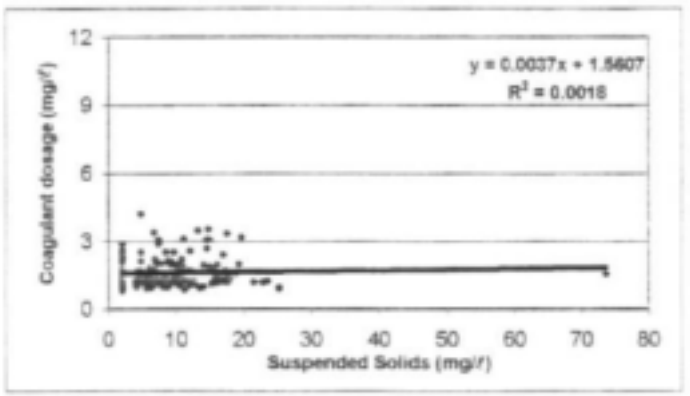

y = 0.2504x + 1.5665
R² = 0.0003
Coagulant dosage (mg/ℓ)
Ammonia (mg/ℓ)

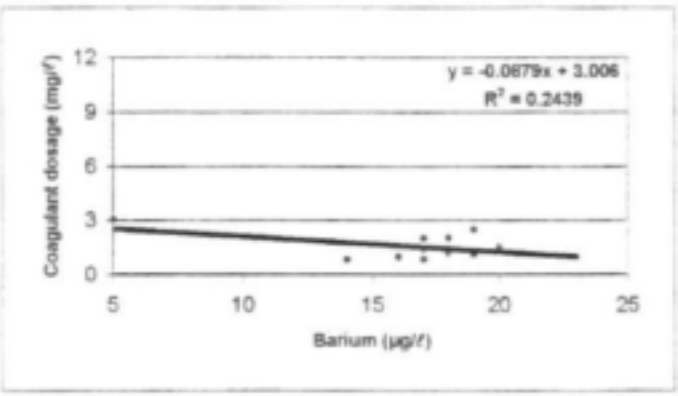

y = 0.1921x + 0.7309
R² = 0.0267
Coagulant dosage (mg/ℓ)
Chloride (mg/ℓ)

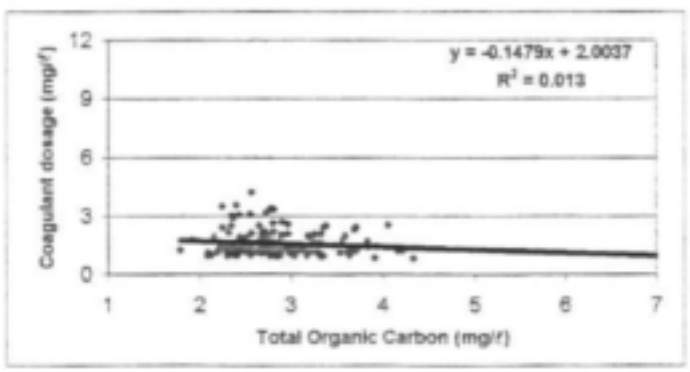

y = -0.0053x + 1.8808
R² = 0.0158
Coagulant dosage (mg/ℓ)
Fluoride (µg/ℓ)


y = 0.8394x + 0.1547
R² = 0.0567
Coagulant dosage (mg/ℓ)
Sulphate (mg/ℓ)


y = 0.0387x - 0.3864
R² = 0.2612
Coagulant dosage (mg/ℓ)
Totally Dissolved Solids (mg/ℓ)

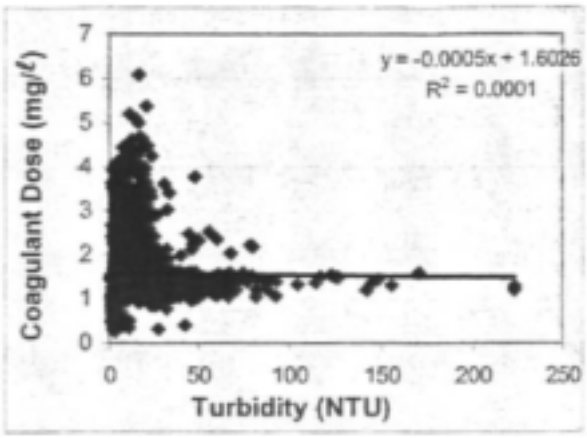

y = 0.0037x + 1.5607
R² = 0.0018
Coagulant dosage (mg/ℓ)
Suspended Solids (mg/ℓ)


y = -0.0879x + 3.006
R² = 0.2439
Coagulant dosage (mg/ℓ)
Barium (µg/ℓ)

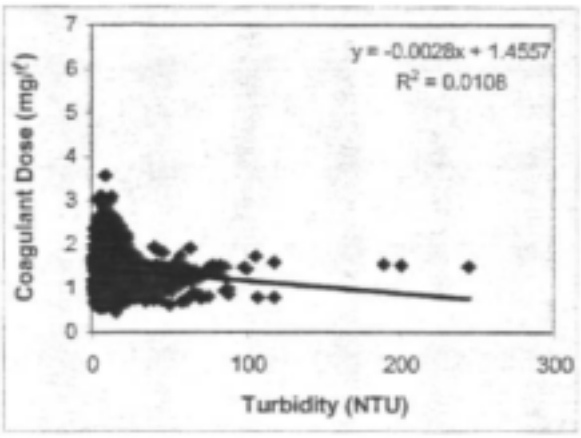

y = -0.1479x + 2.0037
R² = 0.013
Coagulant dosage (mg/ℓ)
Total Organic Carbon (mg/ℓ)

Appendix 3: Regression Analysis using Subsetted Data (1988 - 2002)

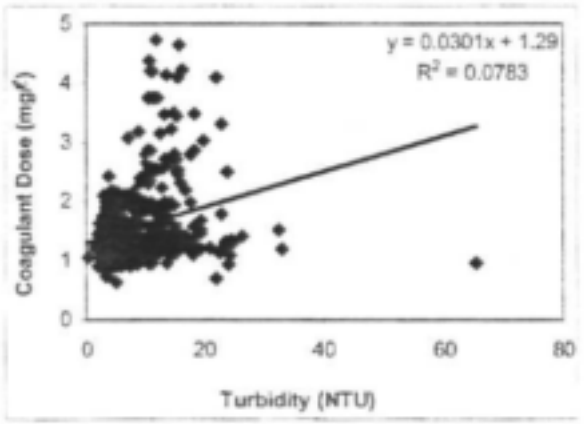
a) Seasonal Turbidity



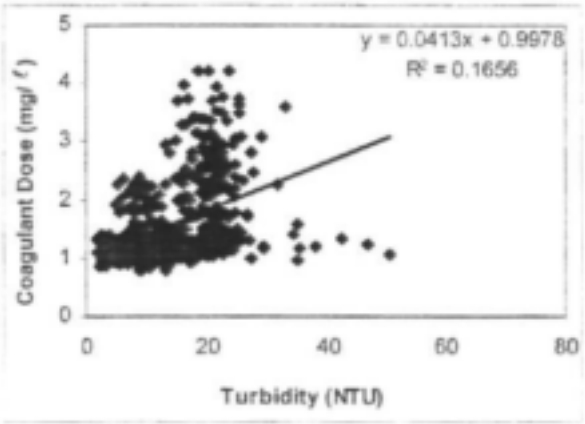
DV Harris WW - Turbidity vs Coagulant Dose
Summer (Oct - Mar)



DV Harris WW - Turbidity vs Coagulant Dose
Winter (Apr - Sep)

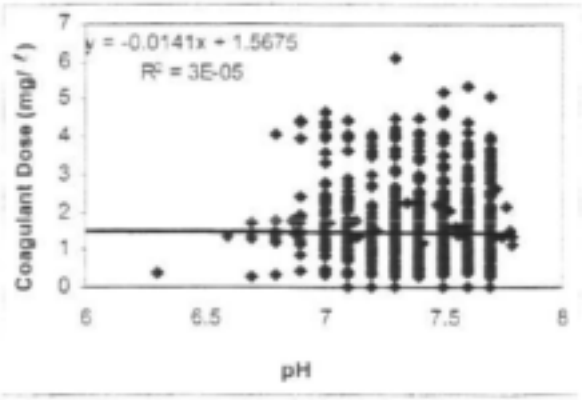


Midmar WW - Turbidity vs Coagulant Dose
Summer (Oct - Mar)

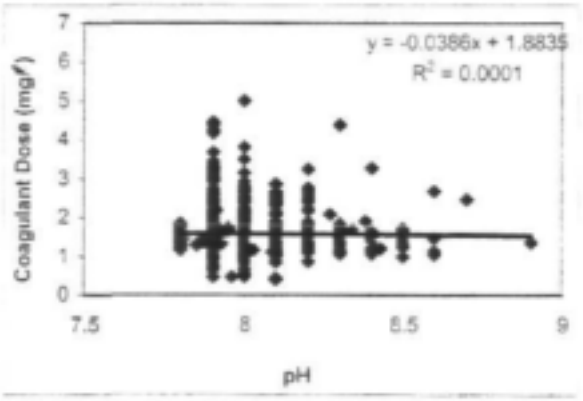


Midmar WW - Turbidity vs Coagulant Dose
Winter (Apr - Sep)

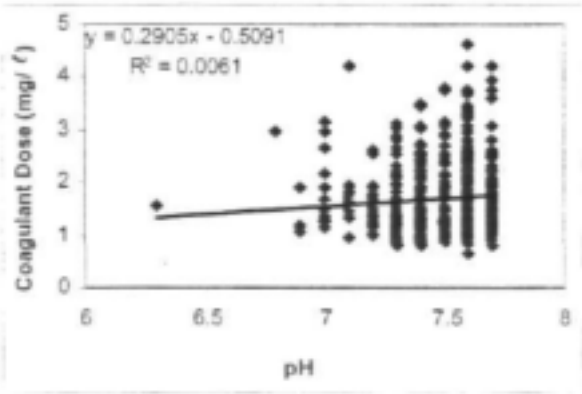
b) pH ranges



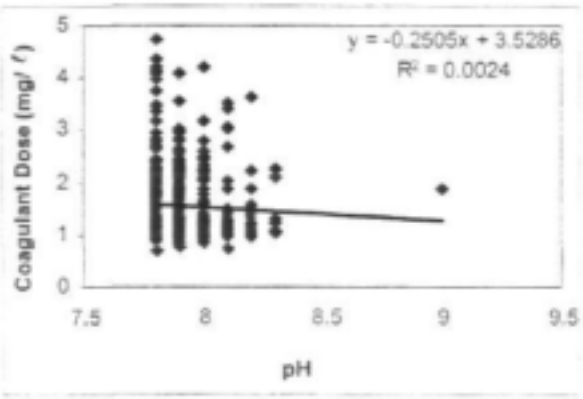
DV Harris WW - pH vs Coagulant Dose
6 - 7.7



DV Harris WW - pH vs Coagulant Dose
7.8 - 9



Midmar WW - pH vs Coagulant Dose
6 - 7.7

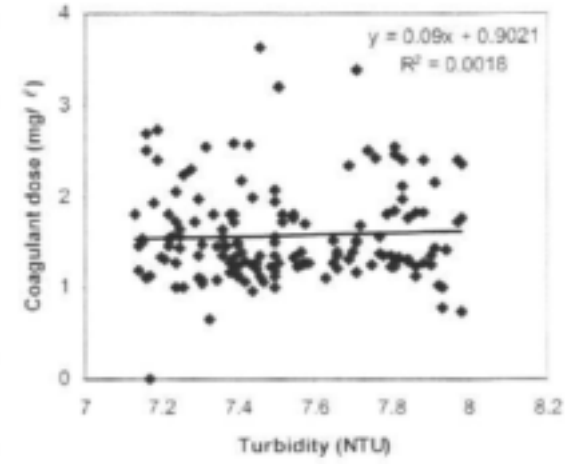


Midmar WW - pH vs Coagulant Dose
7.8 - 9

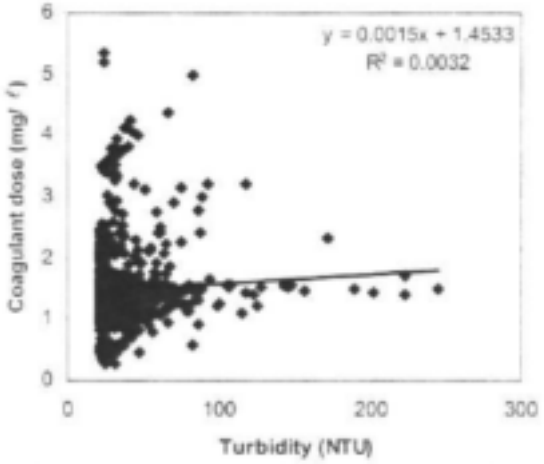
c) Upper and lower quartiles

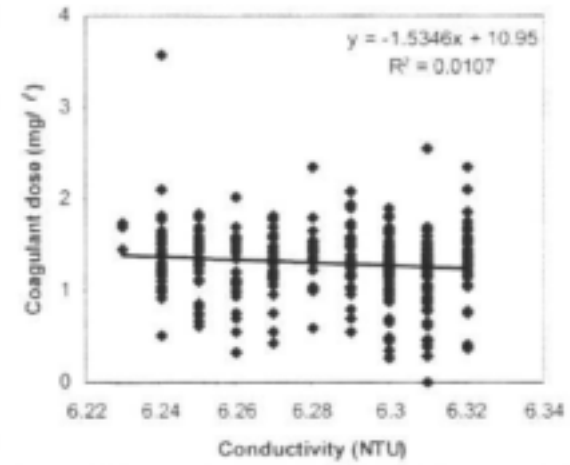
DV Harris WW

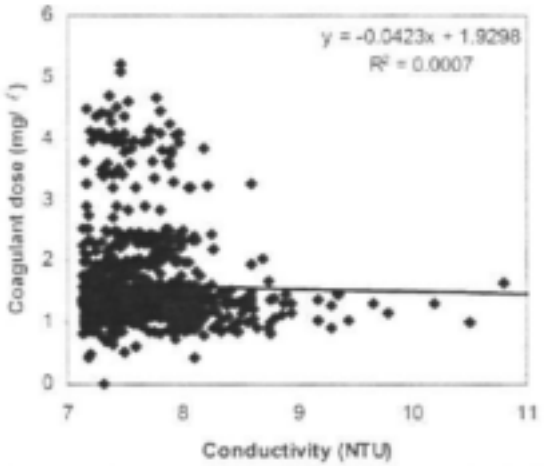
Lower quartile regressions

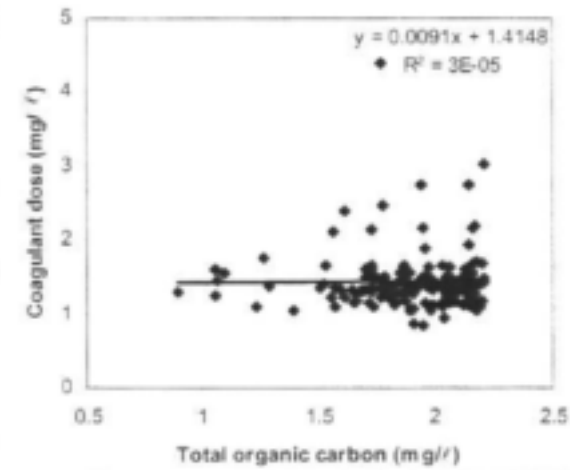


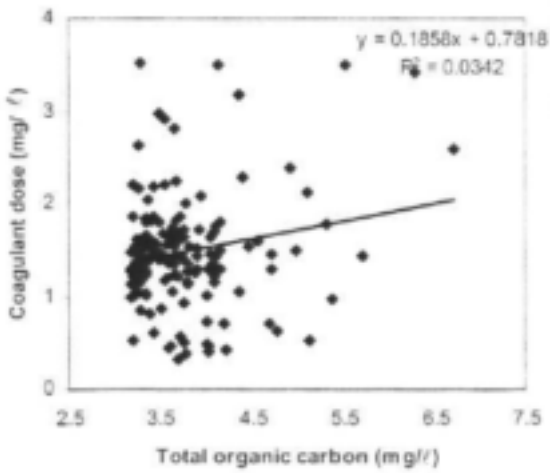
Upper quartile regressions





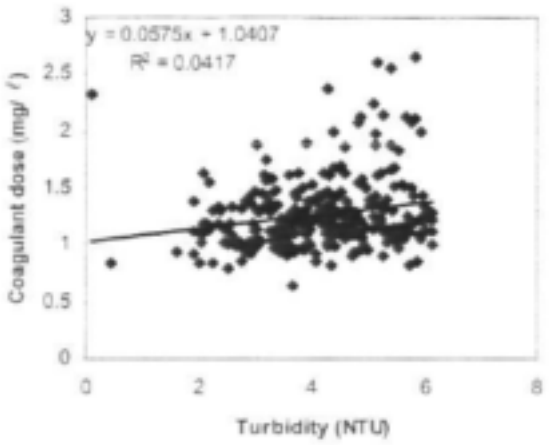




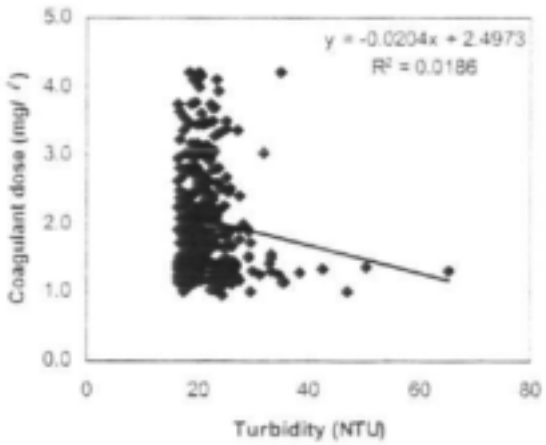


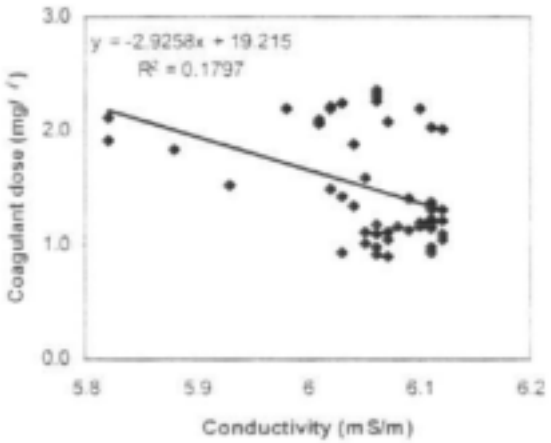
Midmar WW

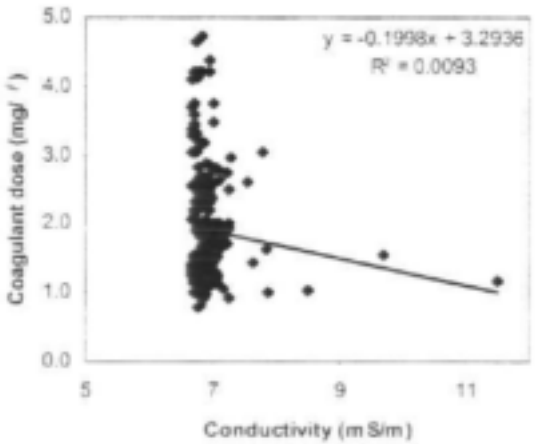
Lower quartile regressions

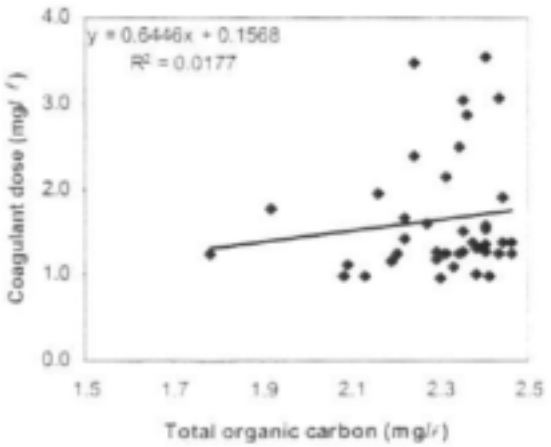


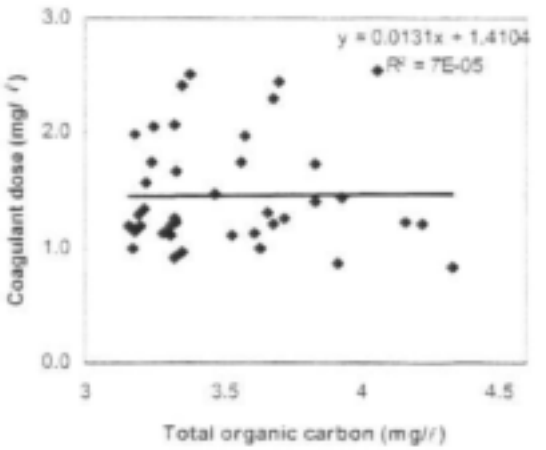
Upper quartile regressions











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Optimization of combined flotation and filtration at a large water treatment plant

JC van Beek; J Haarhoff

Though recently there have been some major advances in the refinement of practical design guidelines for the flotation of eutrophic water, uncertain areas remained, especially with regard to the choice of coagulant and requirements for a good flocculation. In the treatment of eutrophic water, metal complexes formed during flocculation may break through more easily than the sediment formed during flocculation of non-eutrophic water. This raises questions concerning the adjustments of the height loss and effective recovery of filter backwash water. At the same time the accumulation of organisms such as *Cryptosporidium* should be monitored and managed very carefully.

The objectives of this project were to optimise the following conditions and parameters of bench-scale as well as full-scale plant tests for the combined flotation/filtration of a typical eutrophic surface water:

- Optimum flocculation conditions
- Filtrate quality in terms of residual coagulant
- Optimal chemical dosing of filter backwash water.

This project established the protocol for the prediction of full-scale coagulation and flocculation, using an improved bench-scale flocculator for eutrophic waters. The advantages of a dual filter medium and chemical dosing of filter backwash water have also been established.

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