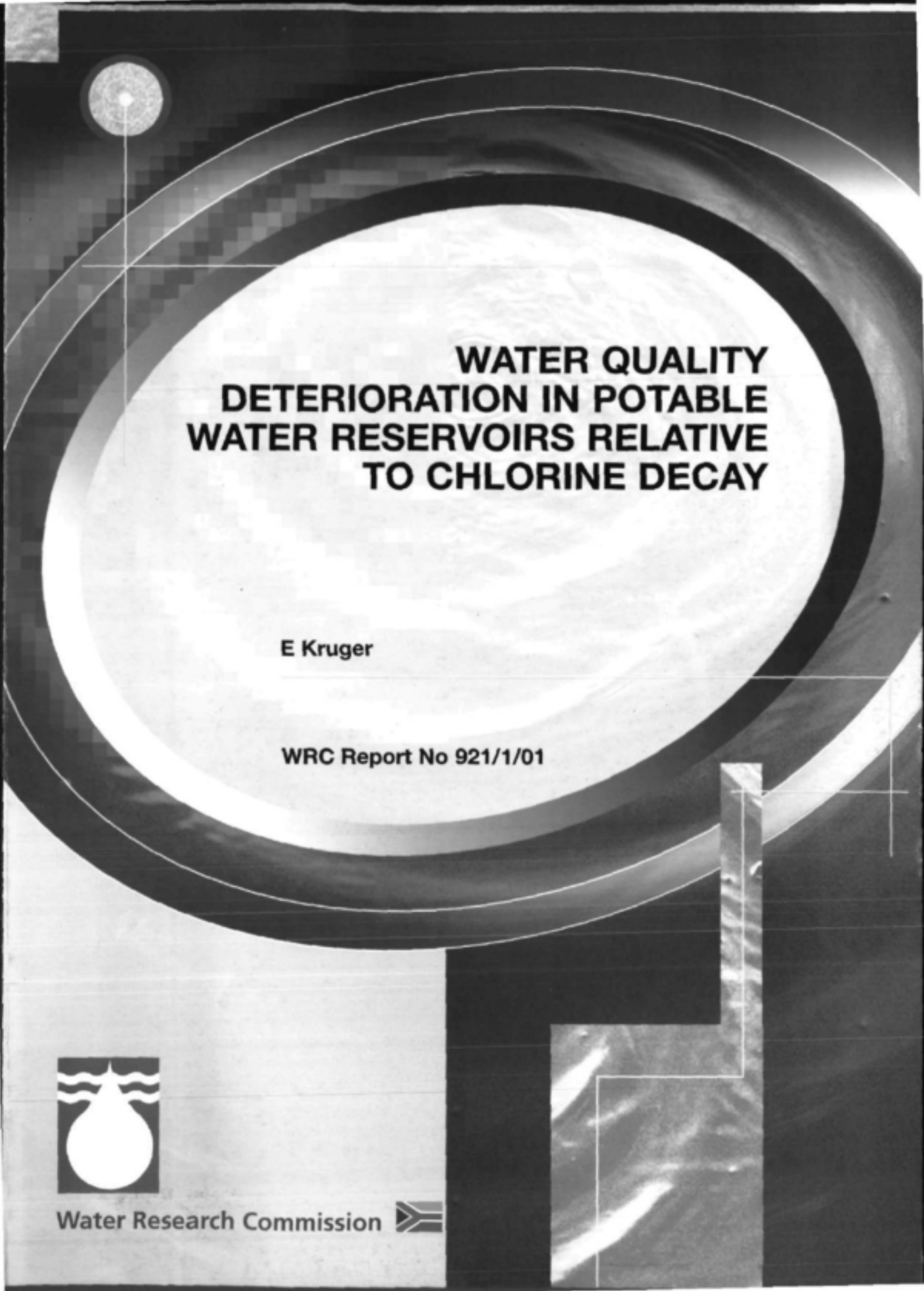

WATER QUALITY DETERIORATION IN POTABLE WATER RESERVOIRS RELATIVE TO CHLORINE DECAY

E Kruger

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Water Research Commission

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by

E Kruger

Rand Water, Experimental Plant, Vereeniging

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EXECUTIVE SUMMARY

1.1. Abstract

The proper understanding, characterisation and prediction of water quality behaviour in drinking water distribution systems are critical in meeting regulatory requirements and ensuring customer oriented expectations. Quality control through the modelling of water quality in distribution systems storage facilities is a relatively new field. Realising that the water quality after treatment deteriorates with time, the distributor cannot always guarantee the quality at the end of the distribution network. For this reason, it is necessary to monitor water quality throughout the distribution network. Reservoirs are an important part of the distribution network, as they represent the final point at which the water quality can be modified before it reaches the consumer. Therefore special attention must be paid to the quality deterioration in and around reservoirs. It is becoming increasingly important to design and manage reservoirs carefully so as to ensure safe drinking water right up to the consumer's tap.

Since chlorine content is one of the most important variables used to indicate water quality, special attention should be paid to its decay and factors influencing its decay in reservoirs. As chlorine concentrations deplete within the reservoir, the overall quality of the water deteriorates as a result of increasing microbial flora. This study investigates the factors contributing to the loss of chlorine residuals in water storage facilities.

The starting point in resolving these problems is the analysis of the decay rate of chlorine in water. Factors that influence the chlorine decay rate are:

- The reaction between chlorine and compounds in the water. This reaction is independent of the storage medium.
- The reaction between the chlorine and the reservoir's walls and base is a function of the area/volume relationship of the reservoir, the reservoir material, the presence and nature of biofilm on the walls and the presence, nature and thickness of the organic layer on the reservoir floor.
- The diffusion of chlorine from the water surface into the atmosphere. This diffusion is dependent on temperature, the turbulence in the reservoir and the concentration gradient.

1.2 Objectives of the study:

The aims of the project were to:

- Characterise the flow patterns in reservoirs in terms of residence time distribution (RTD)
- Relate chlorine losses of the water age (based on RTD-values and kinetic models)
- Account for chlorine losses due to the wall and the bottom effects

- Account for atmospheric losses
- Relate the bacteriological quality of the water to the levels of chlorine in the reservoirs
- Compare the bacteriostatic effect of monochloramine and free residual chlorine in reservoirs

1.3 Summary of major findings and conclusions reached:

- Characterise the flow patterns in terms of residence time distribution (RTD)

From case studies performed it was evident that water selects the route of least resistance to the outlet of a reservoir, the exact nature of this route being determined by the inlet and outlet configurations. It is therefore of utmost importance in reservoir design to ensure that the internal arrangements are designed optimally to prevent short-circuiting as well as the formation of stagnant water pockets. Reservoirs must be designed to ensure plugflow. Computational fluid dynamic (CFD) software packages can be used to compute fluid flow, Flo++, and Flow are two examples of CFD packages. Flo++ is an effective tool to use in determining the optimum flow conditions in the reservoir design process. Specifically, it can be used to optimise internal arrangement conditions, minimise detention time and reduce stagnant pockets, all of which would contribute to improved water quality. When generating a mesh structure for CFD analysis, care must be taken to include detail such as roof support columns, because these finer details can bore significant scientific effects on the results.

- Relate chlorine losses to the water age (based on RTD-values and kinetic models)

Chlorine loss or chlorine decay is influenced by a variety of factors. Two of these are the detention time and temperature. From the kinetic models examined it was noted that the effect of temperature were not built into the decay models. From the studies performed it is apparent that when determining the decay constants of chlorine under conditions of controlled temperature, very reliable first order data fits results. However, when decay studies were subjected to (simulated) natural conditions n^{th}-order decay rates resulted.

- Account for chlorine losses due to the wall and the bottom effects

Under the conditions investigated, it was found that relatively deep penetration of water into the concrete structure took place. This results in a very slow, "3-dimensional" exchange of dissolved substances in the pores of the concrete. A state of equilibrium is therefore only reached over a long period. Empirically it was found that the concrete accelerates the loss of chlorine and that aged concrete has a lesser influence on the chlorine decay than freshly made concrete. Different mathematical models were fitted, but no single model seems to give a good fit of the overall process and therefore a suitable model was developed. Examination of alternative mathematical models indicates that the decay in the bulk fluid is the main reason for the reduction of chlorine concentration in a reservoir. Therefore the influence of concrete in the structure is negligible compared to the decay in the bulk fluid.

- Account for atmospheric losses

Indications that chlorine could be lost to the atmosphere are substantiated by the fact that chlorine concentrations as high 1 ppm was measure in laboratory tests above the water within an hour after dosing with chlorine. These concentrations increased with surface movement. According to mathematical models tested chlorine losses to the atmospheric headspace are negligible compared to bulk decay losses.

- Relate the bacteriological quality of the water to the levels of chlorine in the reservoirs

Very little correlation was found between the bacteriological quality and chlorine levels inside reservoirs. Any apparent correlation found was actually so insignificant that it could be dismissed. Although the percentage samples containing high microbial counts were far fewer in the presence of high chlorine levels, these raised chlorine doses do not necessarily guarantee low microbial counts.

- Compare the bacteriostatic effect of monochloramine and free residual chlorine in reservoirs

Some organisms do survive the disinfection process. These surviving bacteria serve as an inoculum for biofilms and aftergrowth in the distribution system. Bacteria that grow in the distribution system propagate under conditions where chlorine is present and consequently, over a period of time, these could become more resistant towards such a disinfectant. Much higher chlorine doses would thus be required to kill these organisms. However, the bacteria did show more sensitivity towards other disinfectants such as monochloramine. It is therefore very important to optimise the treatment process to ensure that maximum inactivation occurs in the treatment plant. The resistance of bacteria to chlorine is thus relevant in water purification and distribution. At high enough chlorine concentrations micro-organisms will be killed by disinfectants, but it is not possible to determine the increasing demand of bacteria that survived the first disinfection step.

1.4 Review of project in terms of initial objectives:

In terms of the original contract with the Water Research Commission, the objectives were to:

- Characterise the flow patterns in terms of residence time distribution (RTD)
- Relate chlorine losses of the water age (based on RTD-values and kinetic models)
- Account for chlorine losses due to the wall and the bottom effects
- Account for atmospheric losses

- Relate the bacteriological quality of the water to the levels of chlorine in the reservoirs
- Compare the bacteriostatic effect of monochloramine and free residual chlorine in reservoirs

Upon completion of the project it was clear that significant progress was made in terms of the above objectives. The following specific contributions were made:

- Flow patterns inside a reservoir play a significant role in the determination of the residence time and water quality. Inlet/outlet configuration and positioning, as well as the positions of the roof supporting columns are very important factors that influence the flow patterns inside a reservoir.
- Temperature conditions and initial chlorine concentrations play an important role in the determination of best-fit decay models.
- Chlorine losses due to reaction with concrete are insignificant in reservoirs, but significant in pipelines – volume/ surface and flow tempo play a role.
- Chlorine loss to the atmosphere above the water is negligible in large reservoirs with minimal surface movement.
- A model is currently being developed to determine the best-fit for bulk chlorine decay in reservoirs.

1.5 Recommendations for future study:

- Development of a more accurate chlorine decay test method and a chlorine decay model which includes the influence temperature and initial concentration. This will provide more realistic decay values.
- Use of CFD in optimisation of flow patterns and detention times in current structures by optimising operation and internal arrangements of reservoirs.
- Optimum operational conditions for a distribution system that is cost effective and minimises water quality deterioration.
- Optimisation of treatment processes to prevent or minimise aftergrowth within the distribution system.
- Investigate differences and similarities in the operation of small and large distribution systems for optimum water distribution and quality.
- Investigate differences and similarities in the water quality parameters of small rural water storage tanks and large reservoirs.

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

Dr I Msibi	Water Research Commission (Chairman)
Dr G Offringa	Water Research Commission
Dr A Kühn	Dept. of Water Affairs & Forestry
Mr CS Crawford	Dept. of Water Affairs & Forestry
Ms S Freese	Umgeni Water
Prof. CF Schutte	University of Pretoria
Mr R Rimmer	Johannesburg Metro
Mr JC Geldenhuys	Rand Water
Mr L Pelepele	Bloem Water
Dr PL Kempster	Dept. of Water Affairs & Forestry
Prof. J Haarhoff	Rand Afrikaans University
Mr S Pieterse	Cape Metropolitan Council
Mr DJ Marais	Water Research Commission (Secretary)

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Abs 1	Indigo absorbance experiment 1
Abs 2	Indigo absorbance experiment 2
Abs 3	Indigo absorbance experiment 3
Abs 4	Indigo absorbance experiment 4
Abs 5	Indigo absorbance experiment 5
Abs 6	Indigo absorbance experiment 6
Abs 7	Indigo absorbance experiment 7
Abs 8	Indigo absorbance experiment 8
θ	Fractional coverage
θ_{max}	Surface concentration at monolayer coverage and represents the maximum value of θ that can be achieved as C_e is increased.
b	Energy of adsorption and increase as the strength of the adsorption bond increases
Bacteriostatic	The ability of a disinfectant to prevent further reproduction and growth
Bacteriosidic	The ability of a disinfectant to kill bacteria present
Bp	Breakpoint
c	residual disinfectant concentration (mg/ℓ)
C	residual chlorine concentration (mg/ℓ)
C_e	Solution concentrations at equilibrium surface
C_1	Constants related primarily to the capacity of the adsorbent for the adsorbate
C_{d1}	Concentration of chlorine in distilled water without concrete, experiment 1
C_{d2}	Concentration of chlorine in distilled water without concrete, experiment 2
C_{dc1}	Concentration of chlorine in distilled water with concrete, experiment 1
C_{dc2}	Concentration of chlorine in distilled water with concrete, experiment 2
C_{t1}	Concentration of chlorine in reservoir water without concrete, experiment 1
C_{t2}	Concentration of chlorine in reservoir water without concrete, experiment 2
C_{tc1}	Concentration of chlorine in reservoir water with concrete, experiment 1

C_{tc2}	Concentration of chlorine in reservoir water with concrete, experiment 2
CFU	Colony forming units
CFD	Computational fluid dynamics
$\delta\theta/\delta t$	Rate of adsorption
FC	Faecal coliform
HPC	Heterotrophic plate count
K	Dissociation constant
K_H	Hydrolysis constant
k	rate constant characteristic of the type of disinfectant
k'	rate constant characteristic of the type of disinfectant
k	first-order decay rate constant (1/h)
k'	second-order decay rate constant
k''	n^{th}-order decay rate constant
k_w	Decay due to the chlorine demand of the pipe, known as the wall decay
k_b	Bulk decay constant
n	reaction order
$\frac{1}{n}$	Function of the strength of adsorption
N	number of organisms present at time t
N_0	number of organisms present at time 0
$N(1-\theta)$	Number of vacant sites
N	Total number of sites
R_o	the combined chlorine residual immediately after satisfaction of the instantaneous chlorine demand
R_a	Rate constants describing adsorption
R_b	Rate constants describing desorption
ρ	Partial pressure
RTD	Residence Time Distribution
SPC	Standard plate count
τ	an environmental coefficient or induction time, minutes
t	time
TC	Total coliform
Temp	Temperature (°C)

Chapter 1

1. Introduction

1.1. Motivation

Potable water received by a consumer should comply with certain minimum quality standards. In most cases, selecting a suitable raw water source, treatment process and appropriate dosing chemicals should ensure an adequate control of final water quality. The actual operation of a treatment plant should also be optimised to ensure better quality water.

However, once the water has been distributed, very little control can be exercised over changes in quality. One of the major contributing factors to the deterioration of water quality is the loss of chlorine from the water. Once the disinfection potential of chlorine is reduced, an aftergrowth of micro-organisms in the water may lead to poor microbiological quality. However, once the water has been distributed, very little control can be exercised over changes in quality. One of the major contributing factors to the deterioration of water quality is the loss of chlorine from the water. Once the disinfection potential of chlorine is reduced, an aftergrowth of micro-organisms in the water may lead to poor microbiological quality. However, high standard plate counts do not necessarily mean that the water poses a health risk, as this depends on the type of micro-organisms present. According to the SABS 241:1999 Standards for Classes I to III drinking water, class III drinking water may have a maximum standard plate count of 10000 cfu/ml. Moreover, certain species could produce odours or other non-palatable metabolites resulting in aesthetically unacceptable water quality. A further problem is the possible presence and aftergrowth of opportunistic pathogens such as the *Aeromonas* and *Pseudomonas* species.

In a recent study by Viljoen et al. (1998), "The prediction of chlorine decay from potable water in the pipeline systems", it was found that the rate of chlorine decay is not necessarily a first-order reaction rate as generally accepted in published literature. Rather, it was found that it is possible to predict the rate of chlorine losses in a pipeline accurately, once the n^{th}-order kinetic constants for a particular water sample have been determined experimentally. The decay rate can be expressed in terms of the chlorine demand, losses in the bulk water and reactions with the walls of the pipelines. With the dimensions of the pipeline and the flow rate and kinetic constants known, the required dosing rate can easily be calculated to compensate for the expected losses.

This has a major implication in the design and operation of reservoirs. It is often found that the bacteriological quality of the water deteriorates significantly after the water has passed through a reservoir. The reasons for these observations could be a combination of the following:

- Stagnant water pockets may exist in a reservoir, where the chlorine is depleted more than in mixed areas.

- When poorly mixed, some stratification may occur, with "older", chlorine depleted water forming a layer near the surface (stratification may also be caused by a volume of colder water entering the reservoir that contains a slightly warmer water).
- Even when completely mixed, the residence time in the reservoir may be so long that high losses of chlorine may occur. This is especially significant during low demand periods.
- Particulate material may settle and accumulate on the bottom of the reservoir. It has been observed that this sediment contains large numbers of living organisms and may serve as a continuous inoculating source of micro-organisms for water leaving the reservoir.

The major differences between the hydraulic effects in pipelines and reservoirs are the following:

- The water flow in pipelines is laminar whereas the water in a reservoir is almost stagnant. This implies that the major mode of transport in a pipeline is by turbulence, while diffusion dominates the distribution of the dissolved species in a reservoir.
- The surface to volume ratio in a pipeline is much larger than in reservoirs, implying higher wall losses in pipelines.
- A pipeline is a closed system. A reservoir has an open surface area through which chlorine can be lost to the atmosphere.

From the above discussion, it is clear that a knowledge of the residence time distribution (RTD), the kinetics of bulk chlorine losses, the chlorine demand of the water and chlorine losses to the atmosphere whould allow one to calculate the amount of chlorine required to ensure a residual in the water reaching the consumer. It will also provide information on the requirements for additional dosing points in the reservoir.

1.2 Research objectives

The aims of the project were:

- Characterise the flow patterns in terms of residence time distribution (RTD)
- Relate chlorine losses to the water age (based on RTD-values and kinetic models)
- Account for chlorine losses due to the wall and the bottom effects
- Account for atmospheric losses
- Relate the bacteriological quality of the water to the levels of chlorine in the reservoirs
- Compare the bacteriostatic effect of monochloramine and free residual chlorine in reservoirs

Chapter 2

2 LITERATURE REVIEW

2.1 Chemistry of chlorination

Late in the nineteenth century, electrolytic generation of chlorine and hypochlorites became sufficiently competitive with the synthetic chemical oxidation routes to spur the use of chlorine compounds in disinfection. The acceptance of chlorine, or chlorine-derived compounds, as a disinfectant was extremely rapid. Among the many methods available today for the disinfection of water chlorination is the most commonly used as a continuous process in water treatment.

2.1.1 Reaction with water

Chlorine is used for water disinfection in either the gaseous form (Cl_2), or as the hypochlorite salts, of which NaOCl (sodium hypochlorite or common bleach) and $Ca(OCl)_2$, (calcium hypochlorite) are the most common. All these forms of chlorine hydrolyse in water to form an oxidising agent, hypochlorous acid (HOCl), and either an acidic or basic component. In the case of chlorine, one atom is oxidised to Cl^+, the other reduced to Cl^- (White, 1992). The reactions are as follows:

$$Cl_2 + H_2O \rightleftharpoons (H^+ + Cl^-) + HOCl \qquad (2.1a)$$
$$NaOCl + H_2O \rightleftharpoons (Na^+ + OH^-) + HOCl \qquad (2.1b)$$
$$Ca(OCl)_2 + 2H_2O \rightleftharpoons (Ca^{2+} + 2OH^-) + 2HOCl \qquad (2.1c)$$

The hydrolysis constant for reaction (2.1a) is:

$$K_H = \frac{[H^+][Cl^-][HOCl]}{[Cl_2(aq)]} \qquad (2.2)$$

The reaction is very fast and substantially complete in less than one second at 1°C. It is further pH and temperature dependent (Palin, 1974). The equilibrium of this reaction is in favour of free chlorine since $K_H<<1$. This often results in the development of compounds such as nitrogen trichloride, NCl_3. To minimise these effects, high quality water is often used as chlorinate feed water. Flash mixing is required at the point where the chlorine water is applied to prevent the development of localised low pH conditions and subsequent chlorine losses. In dilute solutions and at pH levels above about 4, the equilibrium shown in equation 2.1 is displaced greatly to the right and very little Cl_2 exists as such in solution (White, 1992).

The HOCl formed is completely dissociated under normal dilute aqueous solution conditions. However, hypochlorous acid is a relatively weak acid and is very poorly dissociated at pH levels below 6 (Sawyer et al, 1978).

$$HOCl \rightleftharpoons H^+ + OCl^-, \text{pKa } 7{,}5 \text{ at } 25°C \qquad (2.3)$$

This reaction again is pH dependent and the percentage of hypochlorous acid versus pH is shown in Table 2.1.

Table 2.1: Dissociation of hypochlorous acid versus pH at 20°C.

pH	%HOCl
6	96.8
7	75.2
7.5	48.93
8	23.3
9	2.9

Equations 2.1a and 2.1c therefore indicate that the relative amount of the various oxidised chlorine species is a function of the pH of the water (White, 1992)

From the pKa value (at 25°C), the assumption can be made that at pH 7.5 the activities of HOCl and OCl^- are equal. When the pH drops below 7.5, HOCl predominates while OCl^- is the predominant species at pH above 7.5 (White, 1992). It is therefore evident that HOCl can react in three distinct ways:

(a) At high pH levels ($pH>8$) OCl^- is the dominant species.

(b) At low pH levels ($pH<8$) HOCl is the dominant species.

(c) At very low pH levels ($pH<1$) Cl_2 is the dominant species

The distribution of various chlorine species can be illustrated using a distribution diagram, Figure 2.1, in which the fraction of the total aqueous chlorine (particularly the species Cl_2, OCl, or OCl^-) is plotted against the pH of the water for a fixed chorine concentration.

Figure 2.1 shows that under typical natural water conditions, HOCl and OCl^- are the major chlorine species. The predominant form at pH below 2 is Cl_2. At pH 7.4 HOCl and OCl^- are about equal while above this pH increasing portions of OCl^- are present. As HOCl and OCl^- differ greatly in their ability to disinfect water, pH control is a critical factor in determining the degree of disinfection achieved by a certain level of chlorine (White, 1992).

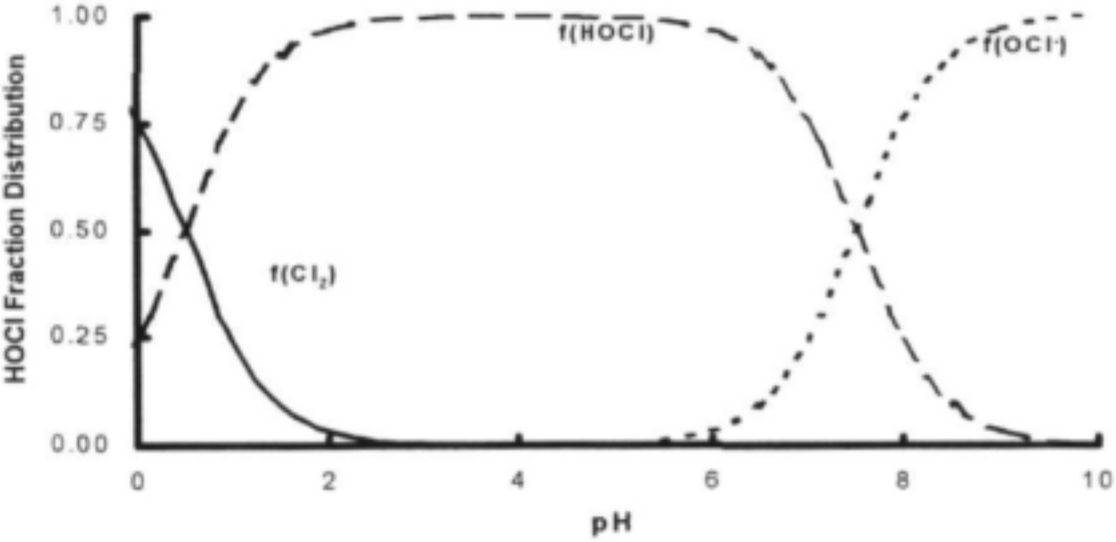


Figure 2.1: Dissociation of hypochlorous acid versus pH at 20°C.

It is thus evident that the equilibrium of the above mentioned reactions are influenced by three parameters, namely:

(a) The pH of the water

(b) The water temperature

(c) The chlorine concentration

White reports that HOCl is about 80 times more effective in destroying *Escherichia coli* than OCl^-. It is therefore clear that the disinfection power of chlorine reduces rapidly with increasing pH. The superior germicidal efficiency of HOCl is due to the relative ease with which it can penetrate the bacterial cell. This penetration is comparable to that of the water molecule and can be attributed to both its modest size and its electrical neutrality.

2.1.2 Reaction with ammonia

Chlorination practices became more sophisticated as time went by. There was widespread adoption of chlorine-ammonia treatment when it was determined that chlorine combined with ammonia produced a more stable disinfecting residual than that produced by chlorine alone.

The reactions of chlorine with any compound containing the nitrogen atom with one or more hydrogen atoms attached to it are very important in any disinfection process. Monochloramine may be either a product or by-product of the chlorination of water. In potable waters it is formed deliberately by the reaction of chlorine in an aqueous solution with either the added ammonium ion or nondissociated ammonia in the potable water or wastewater being treated. Monochloramine is more persistent, although less active, than the "free" chlorine species namely, $Cl_2(aq) + HOCl + OCl^-$. When chlorine (Cl_2) and ammonia (NH_3) are both present in water, they react to form products known collectively as chloramines. To distinguish them from free chlorine, chloramines are usually referred to as combined chlorine. The "total chlorine residual" is a term used to characterise the sum of the combined and free chlorine residuals.

The actual chemical form of ammonia in dilute aqueous suspension depends largely upon pH and temperature. The relative distribution of non-dissociated ammonia and ammonium ion may be defined according to the equation:

$$NH^+_4 \rightleftharpoons NH_3 + H^+ \qquad (2.4)$$

According to the dissociation constant,

$$K = \frac{(NH_3)(H^+)}{(NH_4^+)} = 5x10^{-10} mol/\ell \qquad (2.5)$$

at 20°C, non-dissociated ammonia and ammonium ions are present in equal proportions at pH 9.3. Above this pH, non-dissociated ammonia predominates and below that pH ammonium ion predominates. Reactions between chlorine and ammonia in dilute aqueous solutions that result in the formation of chloramines are the following (Stone, 1978)

$$HOCl + NH_4^+ \rightleftharpoons \underset{\text{(monochloramine)}}{NH_2Cl + H_2O + H^+} \qquad (2.6a)$$

$$HOCl + NH_2Cl \rightleftharpoons \underset{\text{(dichloramine)}}{NHCl_2 + H_2O} \qquad (2.6b)$$

$$HOCl + NHCl_2 \rightleftharpoons \underset{\text{(nitrogen trichloride)}}{NCl_3 + H_2O} \qquad (2.6c)$$

The relative amounts of the chloramine species that exist in solution depend upon certain process variables, including pH, temperature, contact time and the initial chlorine to ammonia ratios. In the pH range 7 to 8,5 and chlorine to nitrogen ratios of less than 5:1 the chief constituent will be monochloramine with the fastest conversion rate ratios at pH 8,3 (fractions of a second); (White, 1992). As the pH decreases dichloramine formation may start at lower chlorine to ammonia-nitrogen mass ratios. As higher chlorine to ammonia-nitrogen ratios are reached, the ammonia is eventually oxidised to nitrogen gas (N_2), a small amount of nitrate (NO_3^+) or a variety of nitrogen containing inorganic oxidation products (Montgomery, 1985).

When the mass ratios exceed 5:1, dichloramine formation will start according to equation 2.6b. This reaction is much slower to take place and at ammonia nitrogen concentrations of less than 1 mg/ℓ and pH values around 8,5 take up to 5 hours to reach completion. Higher ammonia nitrogen concentrations and lower pH values will speed up the reaction appreciably (White, 1992).

2.1.3 Breakpoint chlorination

Breakpoint chlorination occurs when sufficient chlorine has been added to a water or wastewater sample to cause the chemical oxidation of the ammonia in the suspension to nitrogen gas and other end products.

The breakpoint occurs through the sequential formation of monochloramine and dichloramine to end products of nitrogen gas, with a partial return of free residual (HOCl) to the solution.

Breakpoint chlorination of wastewater effluent can result in chemical reaction of ammonia to nitrogen gas. Reaction products and consumption for such reactions are governed by factors such as the type and degree of pre-treatment, initial chlorine to ammonia nitrogen ratio, pH and alkalinity. A summary of the common reactions encountered in breakpoint chlorination is given in Table 2.3.

Table 2.3: Common reactions encountered in breakpoint chlorination:

Description	Reaction Stoichiometry
"Breakpoint Reaction"	$2NH_4^+ + 3HOCl \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^-$ (1)
Nitrogen trichloride formation	$NH_4^+ + 3HOCl \rightarrow NCl_3 + 3H_2O + H^+$ (2)
Nitrate formation from ammonia from nitrite	$NH_4^+ + 4HOCl \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^-$ (3) $NO_2^- + HOCl \rightarrow NO_3^- + H^+ + Cl^-$ (4)
Reaction with inorganic matter	inorganic + HOCl → oxidised inorganic (5)
Chloro-organic reactions	organic + HOCl → oxidised organics (6)

The breakpoint curve:

The breakpoint chlorination curve is a graphic representation of chemical relationships that exist as varying amounts of chlorine are added to dilute solutions of ammonia nitrogen.

The chlorine demand may be related to the breakpoint curve and corresponds to the chlorine required to reach the breakpoint plus such further amount as may be required to produce the desired level of free residual chlorine beyond the breakpoint (Palin, 1974). Chlorine demand is defined as the difference between the amount of chlorine added to water and the amount of free available chlorine remaining at the end of a specified contact period.

The theoretical breakpoint curve shown in Figure 2.2 has several characteristic features.

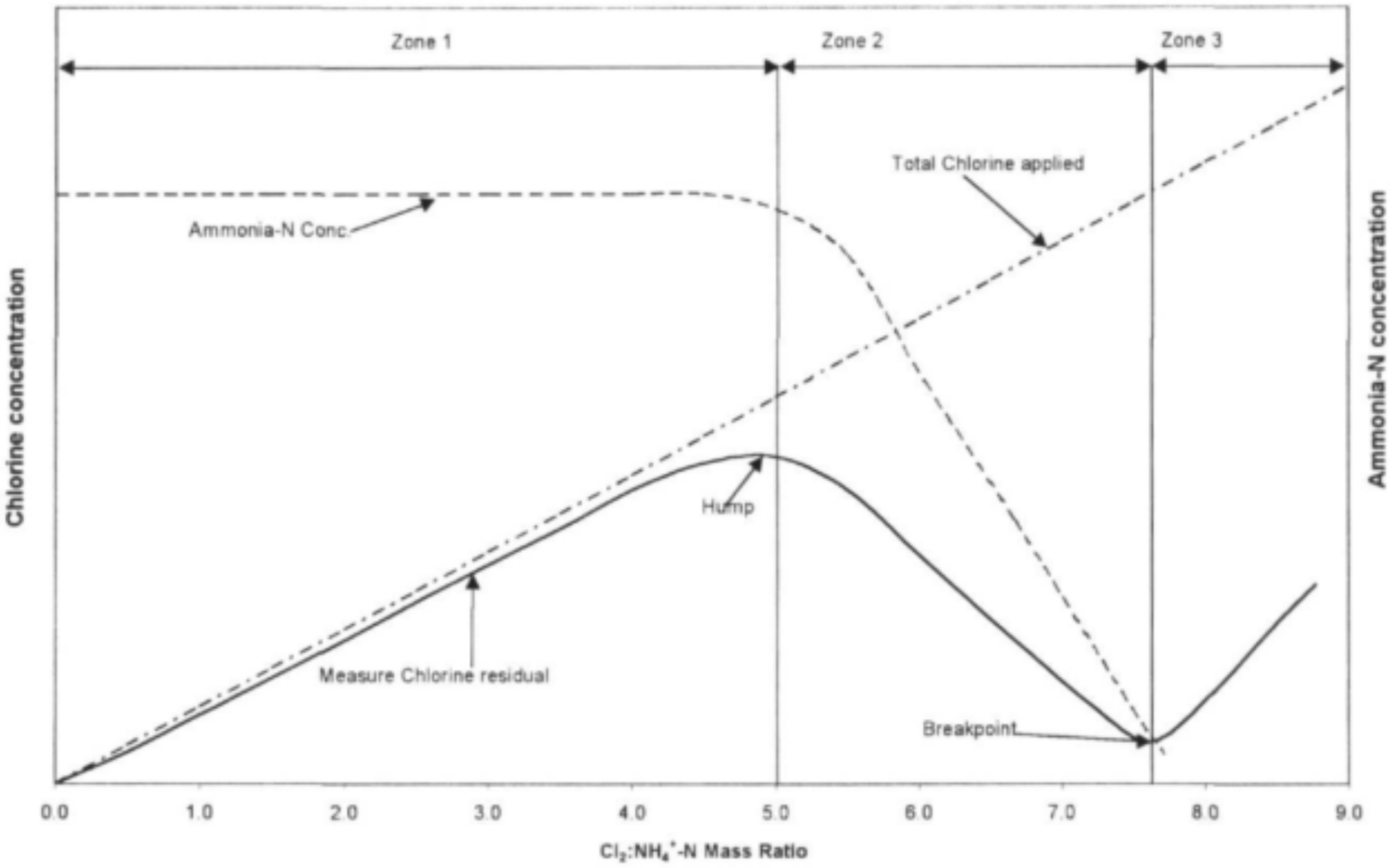


Figure 2.2: Theoretical breakpoint curve

The practical importance of the breakpoint in terms of disinfection is that only after the break point will it be possible to have "free" chlorine (HOCl and OCl^- species) in solution. Before the breakpoint, only "combined" chlorine species (chloramines) will be present.

2.1.4 Reaction with microorganisms

Various disinfection models have been proposed based on laboratory data and refined with field data in an effort to predict the outcome of disinfection (Montgomery, 1985). Following primary disinfection at the point of treatment the two principal strategies for controlling bacterial aftergrowth in distribution systems are chlorination and nutrient control.

Chick's law expresses the rate of micro-organism destruction by the relationship of a first-order chemical reaction:

$$\ln\left(\frac{N}{N_0}\right) = -kt \qquad (2.9)$$

where:

N = number of organism present at time t

N_0 = number of organism present at time 0

k = rate constant characteristic of the type of disinfectant

t = time

Chick-Watson model:

$$\ln\left(\frac{N}{N_0}\right) = -k'c^n t \qquad (2.10)$$

where:

k' = rate constant characteristic of the type of disinfectant

c = residual disinfection concentration

n = reaction order

Unfortunately, the Chick-Watson model is of limited use in most practical disinfection processes. The rate of kill generally does not remain constant. It rather increases or decreases with time depending on the type of micro-organism, the varying concentration or the form of disinfectant used, as well as other operating conditions (Montgomery, 1985, Haas, 1984).

It was shown that free and total chlorine residuals decrease rapidly with distance from the treatment plant and could not be detected in the peripheral parts of the system where HPC levels were highest (Biswas, *et al*, 1993)

Chemical kinetics is concerned with the rate of reactions. Many reactions have rates which at a given temperature are proportional to the concentration of one, two or more of the reactants raised to a small integral power (Swayer, McCarty, 1978).

2.2 Kinetics of chlorine decay in potable water reservoirs

2.2.1 *First-order decay*

The first-order kinetic model for the disappearance of residual chlorine due to reactions with materials in the aqueous phase at different residence times in the network, may be expressed as:

$$\frac{dC}{dt} = -kC \tag{2.11}$$

where:

C = residual chlorine concentration (mg/ℓ)

k = first-order decay rate constant (1/h)

The residence time is defined as the length divided by the mean flow velocity in the pipe (Sawyer, McCarty, 1978).

By integrating equation 2.11 the general first-order decay rate equation can be obtained:

$$C(t) = C_0 e^{-kt} \tag{2.12}$$

where:

C(t) = chlorine concentration(mg/ℓ) at time t

C_0 = initial chlorine concentration (mg/ℓ)

t = residence time in the reservoir

The chlorine decay rate constant k is site specific and must be verified by field measurements (Vasconcelos *et al*, 1995). It was observed that decay of chlorine is more rapid when it is stored in a system than when it is stored in a closed flask, which indicates that the system has an additional chlorine demand.

2.2.2 *Second-order decay*

The second-order decay rate process may be expressed as:

$$\frac{dC}{dt} = -k'C^2 \tag{2.13}$$

By integrating equation 2.13 the equation to determine the concentration at a specific time can be obtained:

$$C(t) = \frac{C_o}{1 + C_o k' t} \tag{2.14}$$

where:

k' = second-order decay rate constant (Vasconcelos *et al*, 1995)

2.2.3 *n^{th}–order decay*

The n^{th}-order decay rate process is describe as:

$$\frac{dC}{dt} = -kC^{n} \tag{2.15}$$

By integrating equation 2.15 an equation to determine the concentration at any time in the distribution system can be obtained:

$$C(t) = \left[(k''t)(n-1) + \left(\frac{1}{C_o}\right)^{(n-1)} \right]^{\left(\frac{-1}{n-1}\right)} \tag{2.16}$$

where:

k'' = n^{th}-order decay rate constant (Vasconcelos *et al*, 1995)

Non-linear least squares regression was used to estimate the order of bulk decay and bulk decay coefficient k for the treated water sources.

2.3 Parameters influencing chlorine losses in potable water reservoirs

2.3.1 Influence of water age

Water bodies, including source water river or lakes as well as storage reservoirs and tanks, age over a relatively long time as a result of natural processes (AWWA, 1990). Chlorine demand and rate of depletion in the water is dependent on the microbiological as well as inorganic quality of the water. Chlorine losses are largely dependent on the age of the water body, as the decay increases with time.

In the water distribution system chlorine also reacts with the pipe wall (Viljoen, *et al.*, 1997; Hua, *et al.*, 1999). To correlate the RTD values with the chlorine losses theoretically the following kinetic models can be used:

a) First-order model: $C(t) = C_o e^{-kt}$

The simplest model for chlorine decay is the first-order model. For a given temperature and initial concentration, the first-order model can give a fair approximation (Hua, *et al.*, 1999; Viljoen, *et al.*, 1997; Kiéné, *et al.*, 1998; Cambers, *et al.*, 1995). Experiments show that the decay constant, k, varies with quality of the source water, the water temperature, the Reynolds number and the construction material properties of the water pipes. Therefore the total decay is expressed as:

- the decay due to the chlorine demand of the pipe, known as the wall decay (k_w)
- and the quality of the water itself, known as the bulk decay (k_b)

so that: $k = k_w + k_b$. (Fang Hua, *et al.*, 1999; Viljoen, *et al.*, 1997; Kiéné, *et al.*, 1998; Cambers, *et al.*, 1995),

b) Second-order model: $C(t) = \dfrac{C_o}{1 + C_o k' t}$

The initial demand of the water after the addition of chlorine is very rapid.

c) Nth order model: $$C(t) = \left[(kt)(n-1) + \left(\frac{1}{C_o}\right)^{(n-1)} \right]^{\left(\frac{-1}{n-1}\right)}$$

The study conducted by Viljoen, et al., (1997) show that in pipelines in Rand Water's distribution system chlorine decays according to the nth order model, were observed.

An RTD value through a pipeline up to the inlet of a reservoir is determined by mathematical modelling. RTD values for specific reservoirs are determined by computational fluid dynamic (CFD) flow modelling (see section 3.2). As soon as the best model is identified, one can use the model to predict the time it will take for chlorine to decay, until no free available chlorine is left.

2.3.2 Influence of concrete from the walls and bottom that is in contact with the water

The presence of concrete accelerates chlorine decay in water, via sorption processes, which include adsorption and absorption. Concrete has a constant demand for chlorine. It is known that in pipelines this demand is significant because of the water volume to pipe surface ratio.

Adsorption is the sticking, or binding, of chlorine molecules to the surface without leading to a chemical reaction. Due to the adsorption in the concrete a concentration gradient exist. Therefore, chlorine will diffuse from the bulk of the water into the concrete.

Diffusion of Free Chlorine

In general, the diffusion process of chloride though water is described by the diffusion laws of Fick. Fick's second diffusion law describes the penetration into concrete

$$\frac{\delta c}{\delta t} = D_c \Delta c \qquad (2.17)$$

where D_c is the chloride diffusion coefficient in concrete, c is the free chlorine concentration, and Δ is the Laplace operator.

The diffusion coefficient is a characteristic of concrete. It is influenced by a number of factors. For example, age and type of the concrete (Bijnen, 1999). Depending on these factors, the order of the diffusion coefficient is $10^{-10} - 10^{-14} m^2 s^{-1}$.

Total Chlorine Content

Total chlorine content in concrete (Tang *et. Al, 1995;* Tang, 1993), consists of two parts, free chlorine and bound chlorine

$$C_{total} = C_{free} + C_{bound} \qquad (2.17)$$

Usually, the total chlorine content and the bound chlorine are expressed in mg(Cl) g^{-1} (cement), respectively mg(Cl) g^{-1} (binder), and free chlorine is expressed in mol ℓ^{-1}. To have the same unit, we rewrite Equation (2.17) to

$$c_{total} = 35.45\, c_{free} \left({}^{1}\!/_{f_c} + W_n^0 \alpha \right) V_p + c_{bound} \qquad (2.18)$$

where W_n^0 in the non-evaporable water, α is the degree of hydration, V_p is the pore content in a dry concrete sample, and f_c is the cement content in concrete by weight. The cement content by weight in defined by

$$fc = \frac{W_{cement}}{W_{cement} + W_{aggregates}} \qquad (2.19)$$

Bound chlorine can be estimated by Freundlich's law ()

$$c_{bound} = f_a c_{free}^B \qquad \text{mg(Cl) g}^{-1}\text{(gel)}$$
$$= \left(1 + W_n^0\right) \alpha f_a c_{free}^B \qquad \text{mg(Cl) g}^{-1}\text{ (binder)}$$

where f_a and B are the adsorption constants. The total chlorine content can now be expressed as

$$c_{total} = 35.45\, c_{free} \left({}^{1}\!/_{f_c} + W_{)n}^0 \alpha \right) V_p + \left(1 + W_{)n}^0\right) \alpha f_a c_{free}^B \qquad \text{mg(Cl) g}^{-1}\text{(binder)}$$

The volume of the concrete, the wet layers in the concrete surfaces in a reservoir, in which the free chlorine is adsorbed, is linear included in these formulas. Compared to the volume of the water this volume is larger in pipelines compared to the volume in reservoirs. Therefore, the concrete will have less influence on the decay of the free chlorine in reservoirs than in pipelines.

2.3.3 *Influence of biofilm on the walls*

Biofilm or microbial films are generally excessive growths of microbial cells held together in polymeric matrices on a surface exposed to an aquatic environment. Several environmental factors: pH, alkalinity, oxygen and ammonia concentration, temperature, organic matter concentration as well as the occurrence of inhibitory compounds (e.g. disinfectants) influence the activity and growth rate of biofilms. Biofilm cell growth and detachment may be more dominant in water distribution systems with low chlorine residuals than chlorine free systems. Biofilm environment is believed to protect cells against the activity of chlorine by diffusional resistance and neutralisation of chlorine as a result of the reaction with biofilm and reservoir wall materials. Thus, sessile microbial growth in the biofilm will be less inhibited than the growth of plantonic cells that one encounters at higher chlorine concentrations. Note that the concrete surface is an ideal surface for bacteria to attach to.

Le Chevalier (1990) found that monochloramine is more successful in penetrating the biofilm than free chlorine. The extent of penetration is dependent on two competing rate processes: diffusion and reaction.

2.4 Relationship between bacteriological quality parameters and chlorine levels in reservoir

Disinfection is not sterilisation therefore micro-organisms will always be present no matter how well the treatment facilities are operated. Thus it is important to control the microbiological quality of the water in the distribution system. This can be done in different ways such as: cleaning and flushing of the system, nutrient control, maintaining a disinfectant residual and corrosion control. See section 2.1.4 for more information.

2.5 The inhibition of microorganisms in reservoirs

2.5.1 Bacterial growth

When one looks at micro-organisms life in a reservoir, it is important to note that micro-organisms will grow on any type of surface in an aquatic environment. Examples of growth in reservoir environments are biofilms on exposed surface, colonies in the sediments and in the water itself. Research shows that bacterial growth can be related to 1) environmental factors such as temperature, 2) the availability of nutrients, 3) the ineffectiveness of disinfectant residuals, 4) corrosion and sediment accumulation, and 5) hydraulic effects (Le Chevalier, 1990). When one looks at the reservoir it is important to note the areas that are infested by these organisms.

Aftergrowth can be defined as the growth of micro-organisms in the distribution system after treatment. It can be due to a) recovery of injured bacteria, b) microbial contamination of distributed water or c) unexplained occurrence of bacteria. For prevention and control of these bacteria it is important to look at the two possible ways that disinfectants influence bacteria a) bacteriostatic effect and b) bacteriosidic effect.

2.5.2 The bacteriostatic effect of disinfectants

Antimicrobial agents are substances that either prevent bacterial growth or kill micro-organisms. Antibacterial agents kill bacteria. The bacteriosidic effect of disinfectants is the ability of a disinfectant to kill all micro-organisms present. The disinfectants that merely inhibit the growth of bacteria are called bacteriostatic agents.

These bacteriostatic agents may be either physical or chemical agents. This project is primarily concerned with chemical agents, more specifically chlorine and monochloramine as disinfectants, and concentrates on the bacteriostatic effect of these disinfectants.

a) Size of the microbial population. The larger the population of micro-organisms the longer the contact time must be between the disinfectant and the micro-organisms.

b) Intensity or concentration of the disinfectant.

c) Time of exposure to the disinfectant. The longer the contact time the more bacteria are killed.

d) Temperature at which micro-organisms are exposed to the disinfectant.

e) Nature of the material containing the micro-organisms.

f) Characteristics of the micro-organisms present. Micro-organisms vary considerably in their resistance to disinfectants.

2.6 Influences of reservoir design on water quality parameters

2.6.1 Reservoir geometry, configuration and residence time

From the moment water leaves the treatment plant the quality starts changing as a result of time-dependent chemical and biochemical reactions. Constituents such as free chlorine are relatively unstable, and concentrations decrease with increasing water age. Storage reservoirs can contribute to substantial increases in the residence time of water in the distribution system and depend on factors such as tank geometry, operations and location.

In modelling the effects of reservoirs on water age, complete mixing is usually assumed for simplification. In completely mixed tanks, the water age is uniform throughout the tanks. Because of their large height-to-width ratio, water entering the bottom of standpipes cannot easily mix with water in the upper levels of the tank. The potential plug-flow nature of standpipes during filling and emptying may lead to behaviour that can be characterised as "first in, last out". Thus, the oldest water would reside in the upper levels. In addition to the effect of the tank geometry, residence time or turnover rate has a profound effect on average age of the water that is leaving a tank.

2.6.2 Computational fluid dynamic (CFD) case-study

Flo++ is a computational fluid dynamics (CFD) program for the solution of industrial fluid flow and heat transfer. These fluid flows are complex because of the complex nature of fluids and the many aspects, which can influence them. (Softflo cc, 1998)

CFD is about applying computer solutions to the equations of fluid dynamics and heat transfer. Therefore fluid flow and heat transfer can be simulated and visually represented. Prior to setting up and running a CFD simulation there is a stage of identification and formulation of the flow problem in terms of the physical and chemical phenomena that need to be considered. Then the simulation process is done mathematically by discretizing the flow equations and solving them on a fine grid which covers the flow domain. The results of a simulation contain all the relevant flow variables such as velocities, pressures, temperatures, densities, etc. (Versteeg, 1995, Van der Walt, 1999)

2.7 Previous research and results

In the study "The prediction for chlorine decay from potable water in pipeline systems" by Viljoen O.J., et al, (1997) the following conclusions are of relevance to this project:

Conclusions on the measurement of chlorine decay:

All the chemical reactions associated with free chlorine and monochloramine do not occur at the same rate. To differentiate the initial fast reactions from the medium and long term reactions, the first free available chlorine reading was taken after the first hour only, and thereafter at hourly intervals. In the case of monochloramine, the first reading was taken after four hours, and thereafter at four hourly intervals.

A good estimate of free chlorine decay rates can be made if readings are taken for a period of eight hours (or longer). For monochloramine, the test period should be at least 24 hours and readings taken at four-hourly intervals, and at daily intervals thereafter for five days or longer.

In this study, excellent results were obtained if three initial chlorine concentrations were used. For free chlorine, the initial concentrations used were fixed at 2, 4 and 8 mg/ℓ above the demand experienced after 20 minutes. In the case of monochloramine, the initial concentrations were fixed at 2, 4 and 8 mg/ℓ as Cl_2.

The following contribution was made:

The reaction order of the decay of both free chlorine and monochloramine deviates substantially from first-order decay, which is commonly accepted by most workers in this field. The incorporation of n^{th}-order reaction kinetic into some of the existing mathematical models is quite complicated, but could lead to substantially different results.

It is important to separate the initial fast reactions from the data set from which the medium term chlorine decay is estimated. Failure to do so will significantly distort the reaction order as well as the rate constant.

Monochloramine shows two clearly different sets of behaviour. Up to 24 hours, the reaction order is below 0.3 and varies if working with different chemical compositions. After 24 hours, the decay rates for different sources are essentially the same and the reaction order very close to one.

In the study the "Applicability of Hydrodynamic Reservoir Models for Water Quality Management of Stratified water bodies in South Africa: Application of DYRESM and CE-QUAL_W2" by Bath A.J., et al the following conclusion that is of importance for this project was made about the role of hydrodynamic models in the management of water quality:

Internationally, mathematical modelling has become an accepted part of the process of estimating and evaluating alternative scenarios for water quality management and decision making purposes. These models have been used in the design phase of reservoir construction to pre-empt water quality problems, in the operation of reservoirs and the development of operating rules, destratification systems and the evaluation of management strategies, and to manage the chemical process interactions taking place within a water body.

Some of the conclusions that follow out of this research are not directly applicable but are very useful in the design and management of reservoirs. In the widespread use of models it is recognised that:

- Each and every water body has a unique water quality character and response, and empirical 'rule-of-thumb' methods have certain limitations.
- Reservoirs exhibit comparatively complex interactions between physical, chemical and biological processes that can be explored using models.

- The response of a reservoir to a given management practice is difficult to predict reliably without a detailed understanding of the governing processes and driving forces. Modelling can provide refinement of particular management practices to suit local conditions.
- Reservoir modelling is relatively cheap in comparison to the cost of implementing a management option, the cost of water and wastewater treatment and the cost of water paid for by consumers.
- Reservoir modelling exposes monitoring and data collection inadequacies.

This study clearly shows how hydrodynamic reservoir models can provide information that can be applied in the management of water quality. It also shows the use and difference between one and two-dimensional modelling.

2.8 Conclusion from literature review

From the literature reviewed, the following conclusions that are pertinent to this study can be drawn:

Both free chlorine and monochloramine can be used as disinfectants that produce residual chlorine. The chlorine decay studies reviewed only the decay and modelling of free chlorine in distribution systems, with no attention given to the decay of monochloramine.

A variety of mathematical models can be used to describe the decay of chlorine in bulk solutions. Although first-order decay is commonly adopted as the simplest, easiest model, there are indications that better results are obtained by using more elaborate models, e.g. n^{th}-order decay.

The previous studies concur that the tank geometry does influence chlorine decay. Chlorine profiles revealed some stratification in tanks with large height-to-diameter ratios. Modelling further indicated that that the quality of the effluent from completely mixed tanks deteriorated with decreasing volumetric change.

Chapter 3

3 APPLICATION OF CHLORINE DECAY STUDIES IN THE FIELD AND LABORATORY TO DETERMINE THE WATER QUALITY DETERIORATION IN POTABLE WATER RESERVOIRS

3.1 Selection of reservoirs

Concrete reservoirs of different sizes and shapes are used for drinking water storage in a reticulation system. The experimental work in this study was conducted on water from different types of reservoir, e.g. Daleside (pump storage, balancing reservoir, as seen in Figure 1) and Forest Hill (through-flow reservoir), using distilled water as a control. The reason for evaluating these different reservoirs was to examine water that includes a variety of variables such as distances from the pumping stations, types of circulation in the reservoirs and chlorine species present.

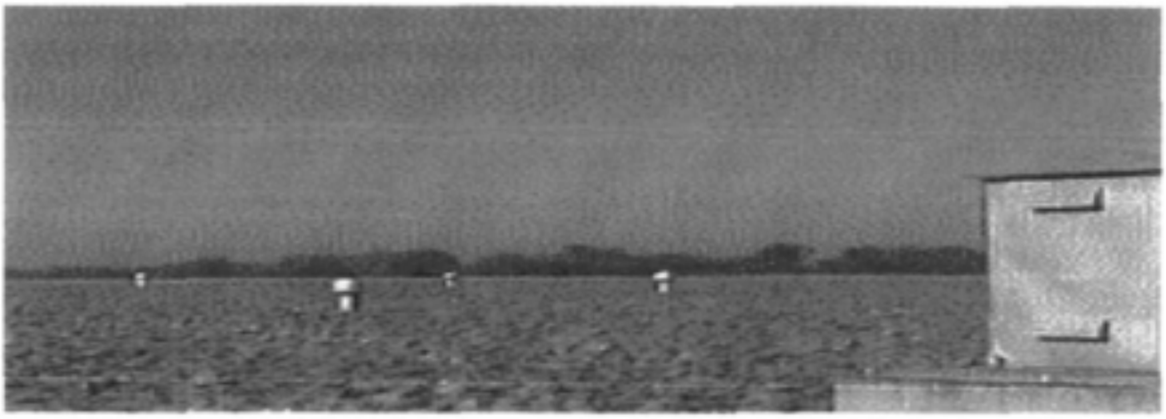


Figure 3.1: Daleside reservoir (45.4 Mℓ, circular reservoir, height of 8.8 m and a diameter of 8.11 m)

A list of every reservoir within the Rand Water distribution system was drawn up. The list contains the following information: Reservoir, type, inlet/outlet configuration, circulation, shape and capacity. Reservoirs for experimental analysis were chosen on the above information. Four reservoirs were selected to perform computational fluid dynamic summations.

The following reservoirs were chosen for experimental examination:

- Daleside is a 45.429 Mℓ circular reservoir, with a common inlet outlet/pipe and by geometric definition a balancing reservoir. The function of this reservoir is to provide water for the pumps at Zwartkopjies pumping station, when there is a water surge. Therefore the reservoir is defined as a pump storage reservoir. Daleside, Sasolburg and Heilbron reservoirs are the only reservoirs in the new system that receives water that containing free available chlorine.

- Forest Hill no 2 is one of three reservoirs at Forest Hill testing rig. All three of the reservoirs, by geometric definition, are throughflow reservoirs. No. 2 was chosen as the water circulation is poorer and some water quality problems were experienced with it over a period of time. The reservoir is circular with separate inlet/outlet pipes and has a capacity of 90 Mℓ. Chloraminated water is received and the reservoir is some 60 km away from the purification works while Daleside is about 25 km away.
- Brakpan, 200 Mℓ reservoir, was chosen because of water quality problems further along in the pipelines being fed by the reservoir. The reservoir is rectangular with a separate inlet/outlet.

3.2 Application of Computational fluid dynamic (CFD) models to determine the characteristics of flow patterns in terms of the residence time distribution (RTD)

3.2.1 Introduction

Rand Water has used CFD (Flo++) since 1998 in the optimisation of flow patterns inside reservoirs. CFD was used in three case studies: 1) Langerand reservoir, 2) Wildebeestfontein reservoirs and 3) Daleside reservoir. The Langerand reservoir is Rand Water's first reservoir where the inlet and outlet configurations were designed using CFD to obtain optimum flow conditions. In the Wildebeestfontein case study Flo++ was used to determine flow patterns inside the current structures, the RTD for the current structures and new possible cost effective inlet/outlets. The proposed new reservoir to be built in Daleside, near Meyerton, was also designed using CFD, to optimise flow inside the reservoirs and minimise the residence time of the reservoir.

All the above-mentioned simulations were done using simplifications. One of the simplifications used in all the simulations was to exclude the roof support columns inside the reservoir. It was decided to use Brakpan 200 Mℓ reservoir for this report and perform a simulation with and without the columns to see if there is an additional influence from the columns on flow patterns inside the reservoir.

Residence Time Distribution (RTD) was used to evaluate the unsteady mixing levels in the reservoir. An operating condition of 90% full was used as a worst case scenario. Arbitrary chlorine decay rates were used to simulate the chlorine decay.

3.2.2 Model input data for Brakpan 200Mℓ

3.2.2.1 Boundary conditions

- Inlet

A steady state solution was obtained for a uniform velocity at the inlet. After the solution was obtained a tracer concentration was set to 0.05mg/ℓ. The uniform velocity was based on 60 Mℓ/d.

The inlet consisted of a 1500mm ∅ pipe that is connected at a T-junction to a 1200mm ∅ pipe. There is four 850mm ∅ perforated inlet holes 15500 mm from each other spaced from the centre of the T- junction as well as open ends (see figure 3.2.1 and 3.2.2).

- Outlet

The outlet was specified as a zero gradient boundary.

There are two outlets, which consist of a sunk in sump with length of 2300 mm and width of 4000 mm. These are situated 30955mm from the centre of the Main 1500 mm ∅ inlet pipe (see figure 3.2.1 and 3.2.2)

3.2.2.2 Computational grid

The side wall geometry was simplified using a rectangular box (width – 143976mm, length – 167226mm, depth – 9450mm). The inlet configuration was constructed and inserted in the structure using arbitrary mesh coupling. The round roof support column structure in the reservoir was also simplified to a square column. These simplifications are believe to have a local effect only as the emphasis of the analysis is on the RTD curves and not on the detailed flow patterns. The final computational grid consisted of cells. The outline of the structures can be seen in figure 3.2.1 and 3.2.2

3.2.2.3 Numerical Aspects

The calculations were done on a Pentium 433 MHz PC with 512 MB RAM.

3.2.3 Model application

Chlorine decay

Theoretical values were used for the decay constants, because experimental values were not available at the time of the simulations. Three values was chosen: k = 0, 0.01, 0.001. These values include a wide spectrum of decay constants.

3.2.4 Description of scenarios

Two scenarios were tested.

- Inclusion of roof supporting columns

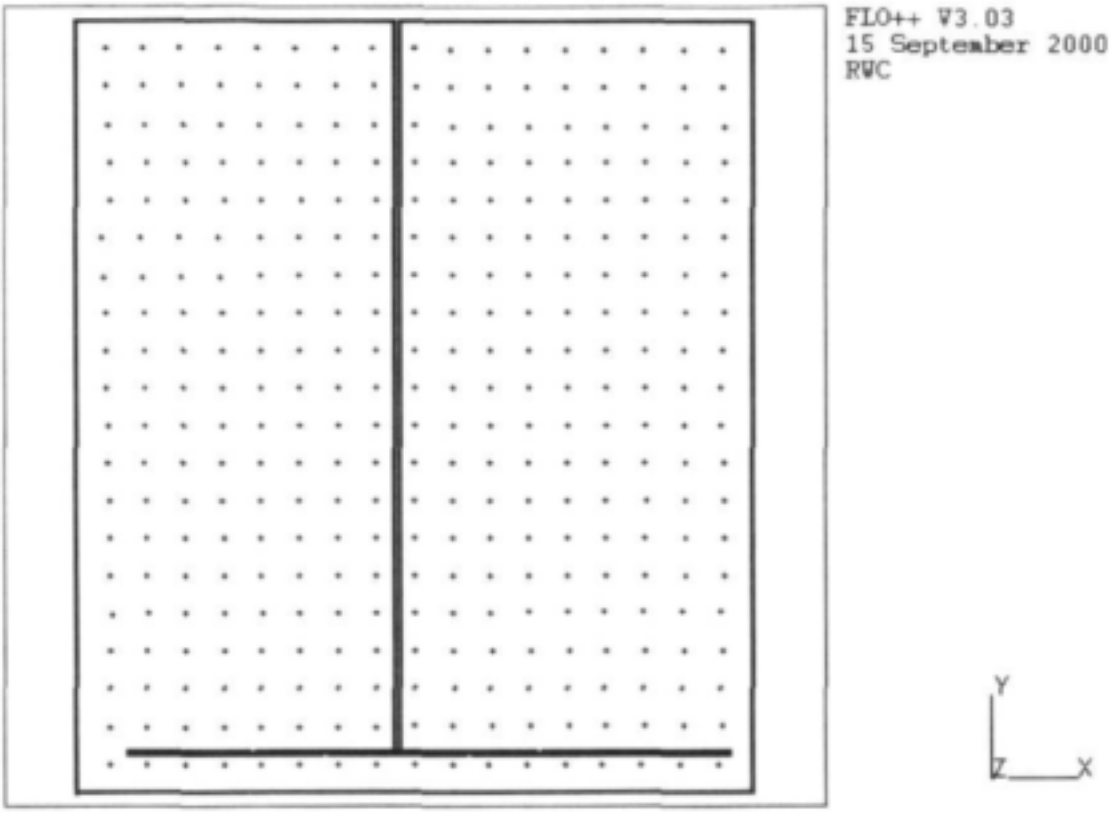


Figure 3.2.1: Brakpan 200 Mℓ reservoir with columns

Excluding columns

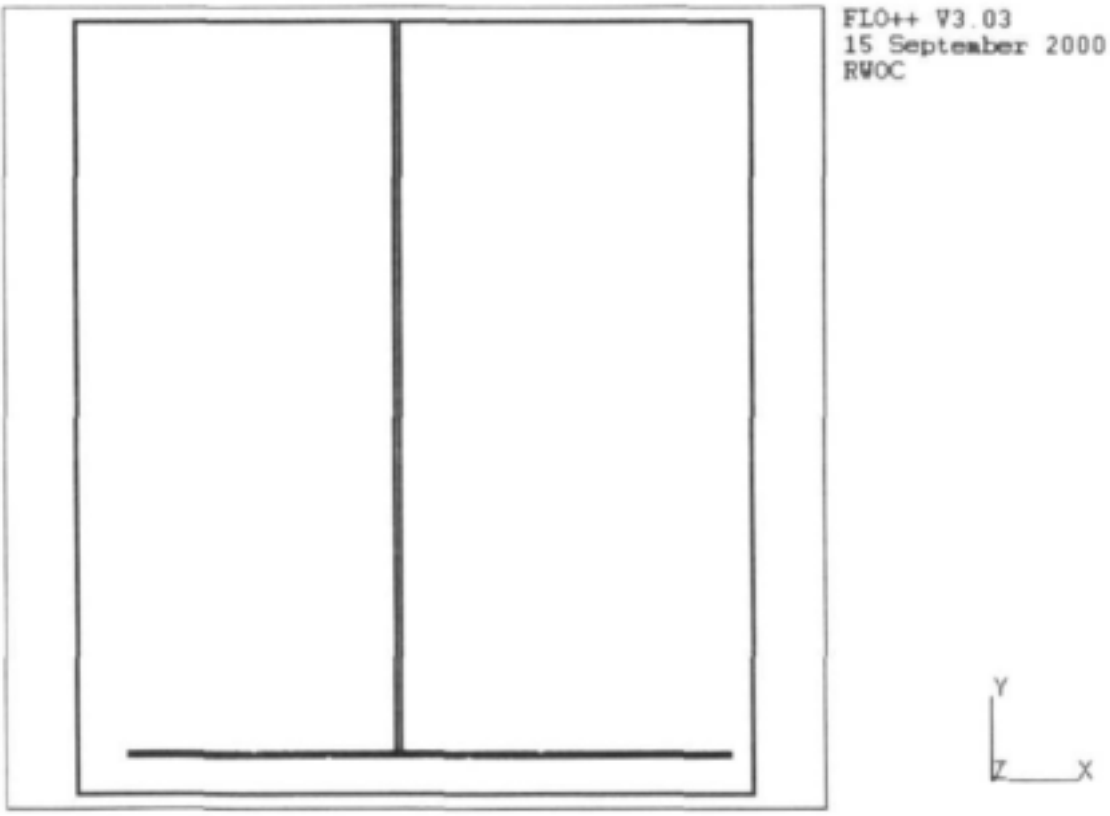


Figure 3.2.2: Brakpan 200 Mℓ reservoir without columns

3.2.5 *Results of scenario testing*

The following results were obtained for scenario 1 (with columns). Contour plots from the steady state solution for the reservoir were drawn at 2, 4,5 and 9 m. The reservoir model was run for the worst case scenario, that is 95% full.

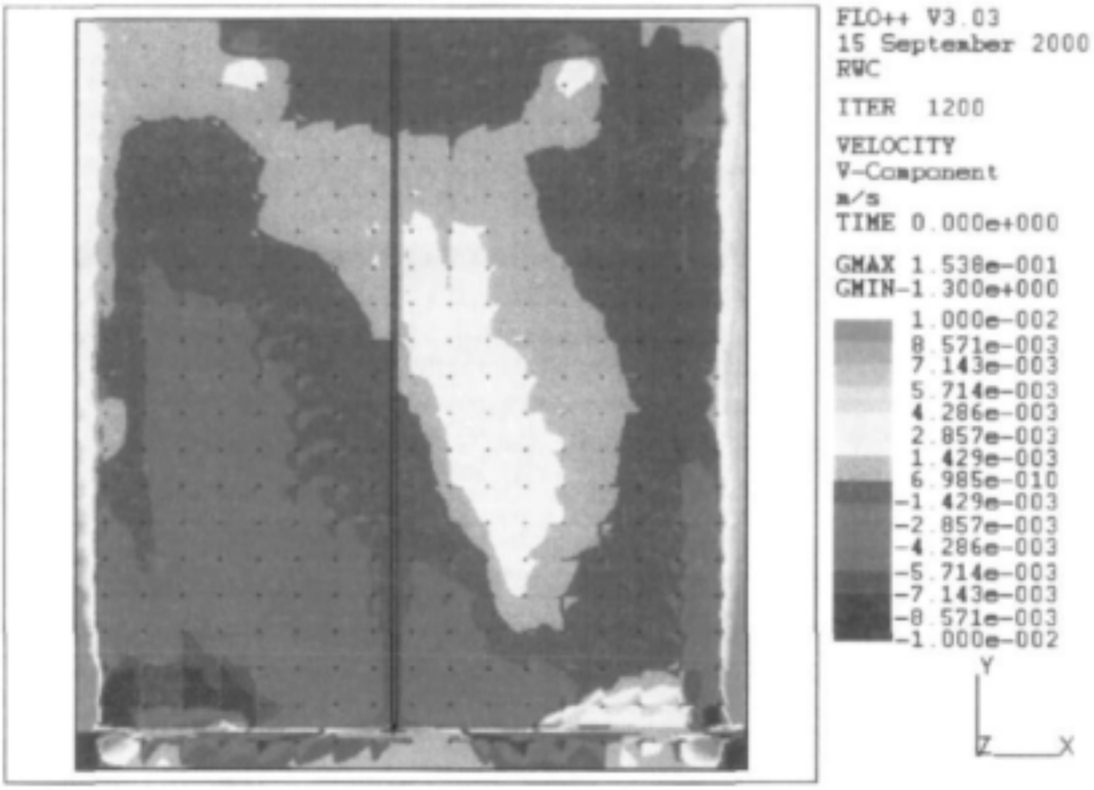


Figure 3.2.3: Horizontal velocity component for scenario 1. Contours at 2 m from bottom, Colour scaling used.

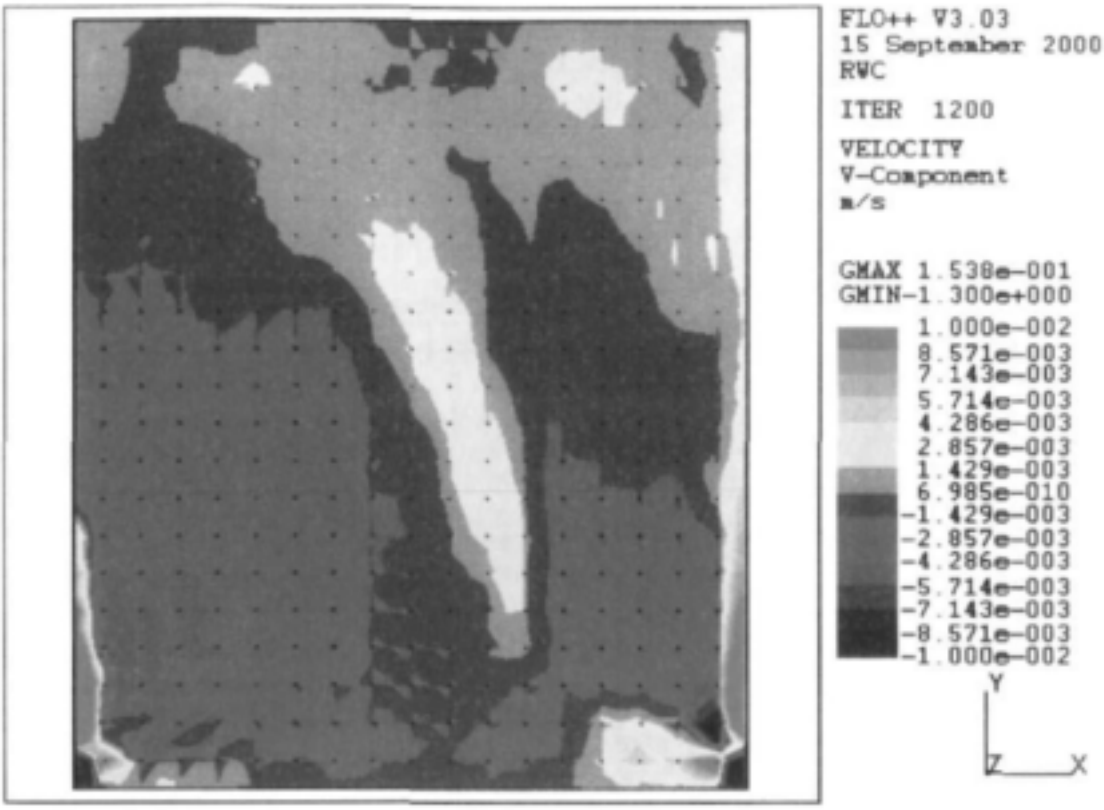


Figure 3.2.4: Horizontal velocity component for scenario 1. Contours at 4,5 m from bottom, Colour scaling used.

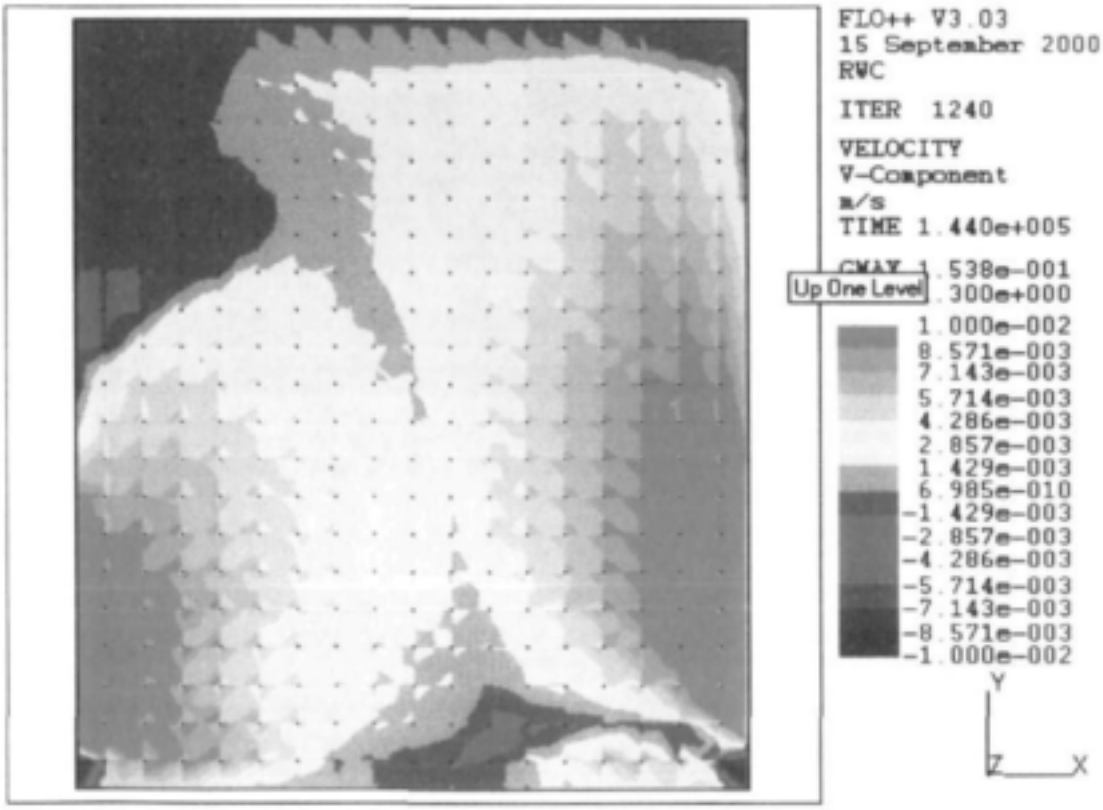


Figure 3.2.5: Horizontal velocity component for scenario 1. Contours at 9 m from bottom, Colour scaling used.

The following results were obtained for scenario 2 (without columns). Contour plots from the steady state solution for the reservoir was drawn at 2, 4,5 and 9 m. The reservoir model was run for the worst case scenario, that is 95% full.

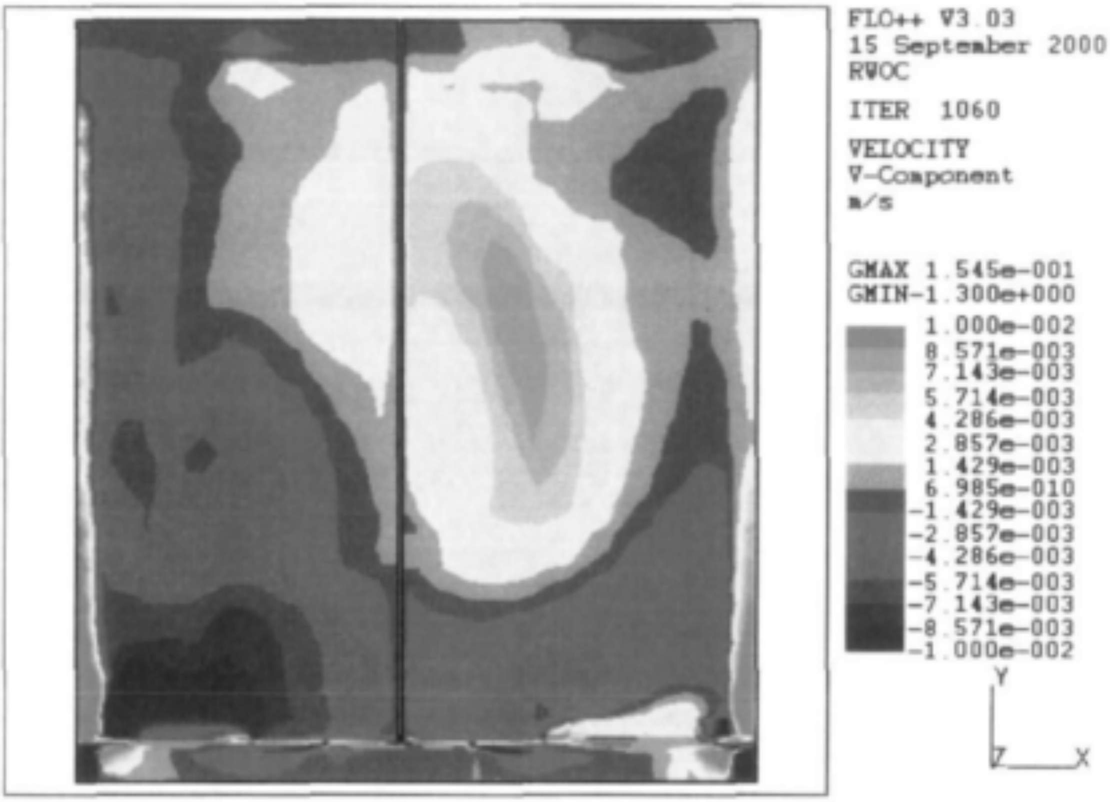


Figure 3.2.6: Horizontal velocity component for scenario 2. Contours at 2 m from bottom, Colour scaling used.

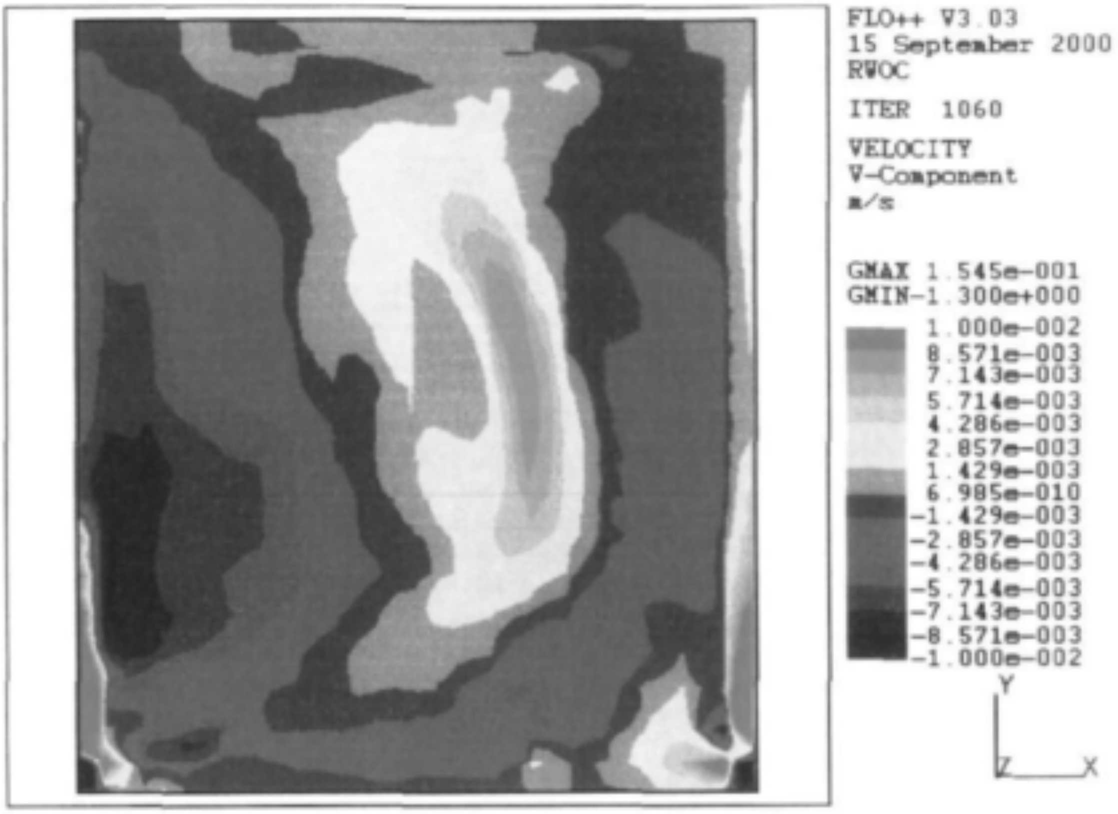


Figure 3.2.7: Horizontal velocity component for scenario 2. Contours at 4,5 m from bottom, Colour scaling used.

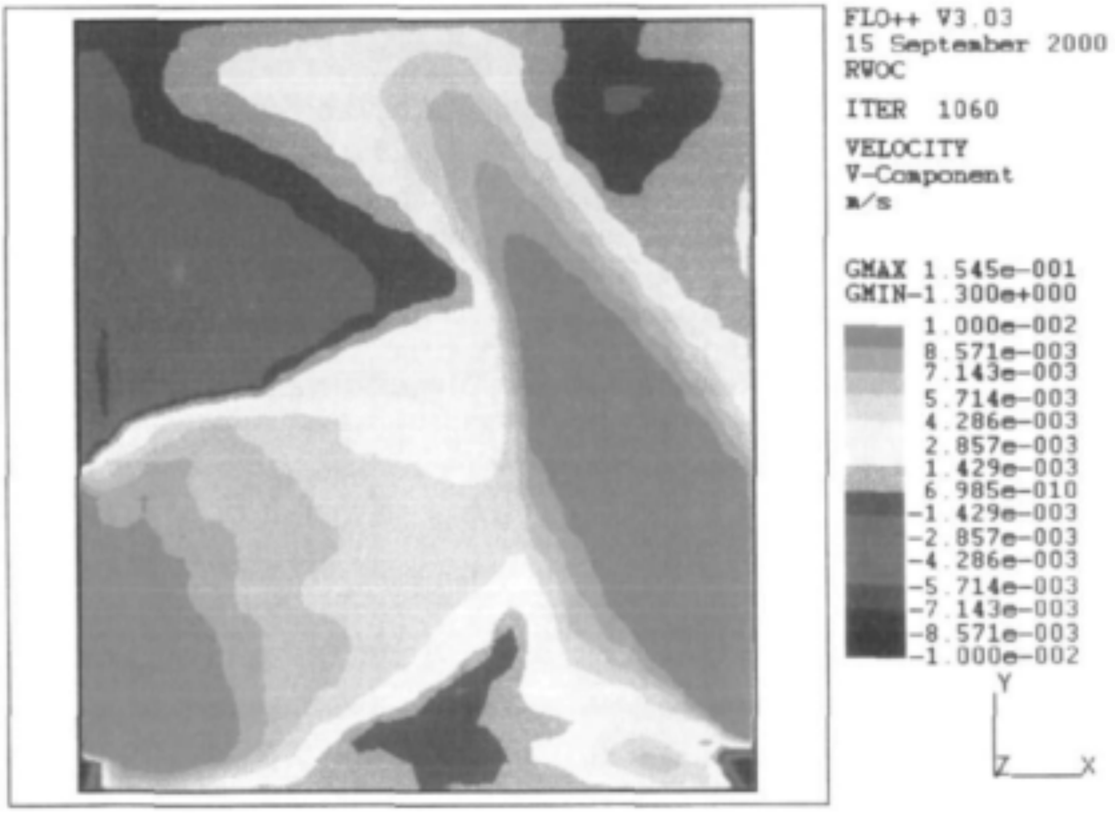


Figure 3.2.8: Horizontal velocity component for scenario 2. Contours at 9 m from bottom, Colour scaling used.

The results from the tracer injection can be seen in figure 3.2.9.

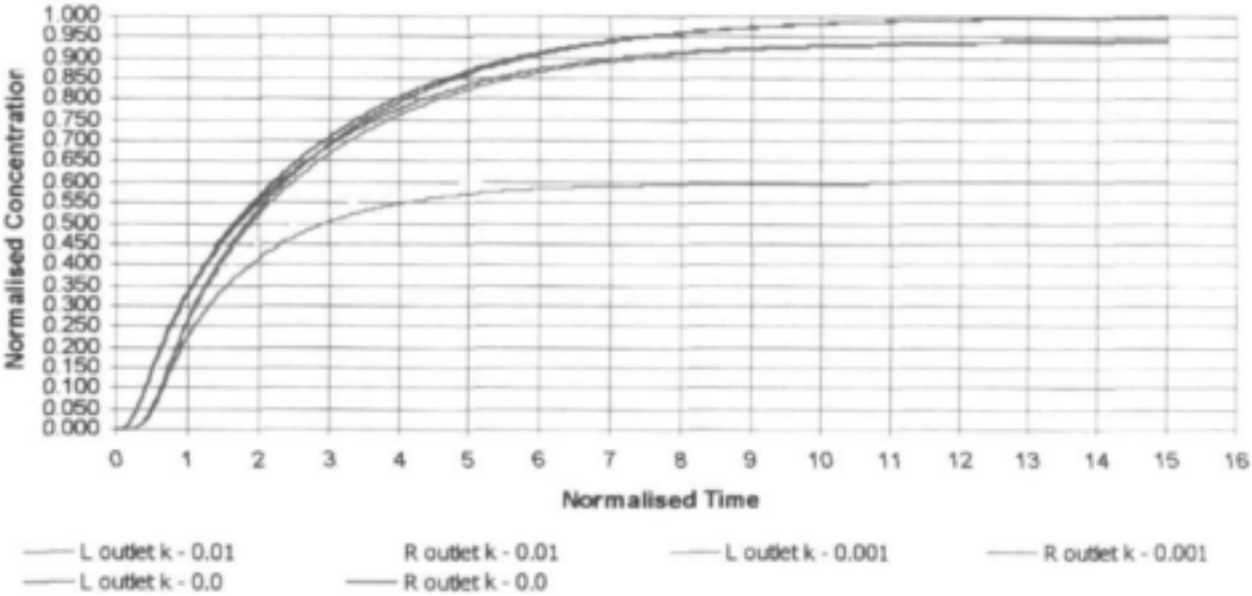


Figure 3.2.9: RTD curve for tracer injection in Brakpan 200 Mℓ reservoir

3.3 Determination of the relationship between chlorine losses and water age

3.3.1 Objectives

The objective was to determine the relationship between chlorine losses and water age.

Chlorine loss (decay) can be defined as the decrease in chlorine concentration in the water body under observation. These losses can be due to natural decay, losses to the atmosphere, reaction with inorganic and organic material as well as reaction with micro-organisms. Water age was based on the time that had elapsed since chlorination took place and is defined as zero at the point of chlorination. Therefore water age is equal to the residence time of that particular volume of water since chlorination, otherwise known as residence time distribution.

3.3.2 Mathematical models

To theoretically correlate the RTD values (water age) with the chlorine losses the following kinetic models can be used:

First-order model:

$$C(t) = C_0 e^{-kt}$$

Second-order model:

$$C(t) = \frac{C_0}{1 + C_0 k' t}$$

nth order model:

$$C(t) = \left[(kt)(n-1) + \left(\frac{1}{C_o} \right)^{(n-1)} \right]^{\left(\frac{-1}{n-1} \right)}$$

Decay constants and reaction order (n) is determined using the least squares method.

3.3.3 *Results*

The following results were obtained in the experiments done to determine the chlorine decay constant and determination of the best-fit model. The experiments were conducted on samples from Daleside reservoir, Forest Hill reservoir and consumer's taps in Vanderbijlpark and Heilbron.

Table 3.3.1: Experiment 1.1. Free chlorine decay profile of Daleside reservoir water (see figure 3.3.1)

Time (h)	Free available chlorine Demand + 2 mg/ℓ	Free available chlorine Demand + 4 mg/ℓ	Free available chlorine Demand + 8 mg/ℓ
0	2.40	4.40	8.20
1	2.00	4.10	7.60
2	1.80	3.80	7.20
3	1.60	3.60	7.20
4	1.60	3.50	6.80
5	1.60	3.50	6.80
6	1.50	3.20	6.80
7	1.40	3.20	6.80
8	1.30	3.20	6.80

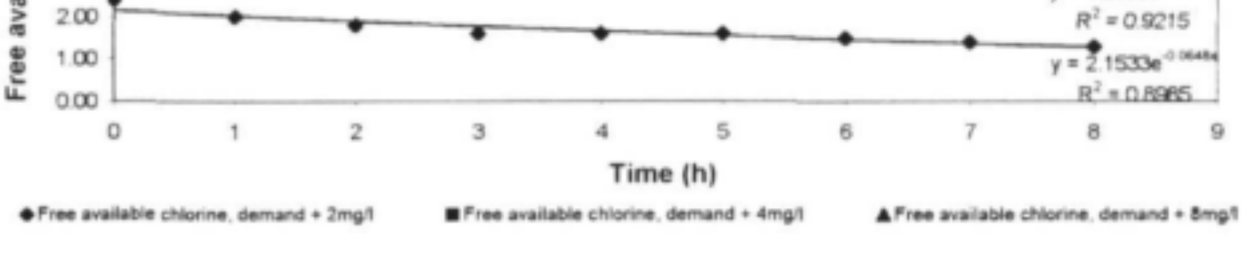


Figure 3.3.1: Free chlorine decay profile of Daleside reservoir water. Fit to a first-order decay model (see Table 3.3.1)

Data was fit with SAS and PROC NLIN.

3.4 Determination of wall consumption parameters

3.4.1 Objectives

When chlorine is in contact with concrete the following possibilities exist:

- Chlorine is absorbed by concrete and the concrete becomes saturated.
- Chlorine is adsorbed in an isothermal way and equilibrium is established.
- Chlorine decay is enhanced on the surface of the concrete.
- Chlorine losses occur, aggravated by pH

The following experiments were conducted on the concrete to determine how the concrete influences the chlorine concentration:

- Concrete blocks submerged in chlorine solutions of different concentrations in 10ℓ aspirators to see if there is an increase in rate and quantity of chlorine lost.
- Chlorine solution pumped through a concrete structure and a glass control structure. To see the change over time in effluent composition.

3.4.2 Mathematical models

The total chlorine content can be expressed as

$$c_{total} = 35.45\, c_{free}\left({}^{1}\!/_{f_c} + W_{jn}^{0}\alpha \right) V_p + \left(1 + W_{jn}^{0}\right)\alpha f_a c_{free}^{\,B} \qquad \text{mg(Cl) g}^{-1}\text{(binder)}$$

3.4.3 Results

Concrete blocks submerged in solutions of different chlorine concentrations in 10 ℓ aspirators.

The following results were obtained from experiments done in the determination of the influence of concrete on chlorine concentrations in the water. In the experiments, aspirators 1 – 4 were filled with 10ℓ distilled water and aspirators 5 – 8 were filled with tap water. A concrete block was added to aspirator 3,4, 7 and 8 All eight aspirators were dosed with the same chlorine concentration and tested on the same time scale under identical conditions.

Table 3.4.1: Experiment 1.1. Influence of concrete on chlorine concentration. 10ℓ of distilled water dosed with 0.91 mg/ℓ chlorine. Reaction time 3120 h. (see figure 3.4.1)

Time (min)	C_{d1} (mg/ℓ)	C_{d2} (mg/ℓ)	C_{dc1} (mg/ℓ)	C_{dc2} (mg/ℓ)	C_{t1} (mg/ℓ)	C_{t2} (mg/ℓ)	C_{tc1} (mg/ℓ)	C_{tc2} (mg/ℓ)
0	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91
120	0.88	0.87	0.76	0.77	0.73	0.73	0.66	0.65
244	0.88	0.88	0.77	0.77	0.72	0.68	0.60	0.59
344	0.86	0.86	0.71	0.69	0.61	0.61	0.52	0.52
1320	0.73	0.72	0.38	0.38	0.25	0.25	0.06	0.06
1440	0.70	0.69	0.34	0.34	0.18	0.18	0.04	0.04
1560	0.70	0.70	0.34	0.34	0.18	0.18	0.04	0.04
1680	0.70	0.70	0.34	0.34	0.16	0.16	0.05	0.04
1750	0.70	0.70	0.34	0.32	0.15	0.16	0.05	0.05
2760	0.68	0.65	0.20	0.20	0.10	0.08	0.05	0.05
2880	0.67	0.66	0.16	0.16	0.07	0.06	0.04	0.04
3120	0.66	0.66	0.15	0.16	0.06	0.06	0.04	0.03

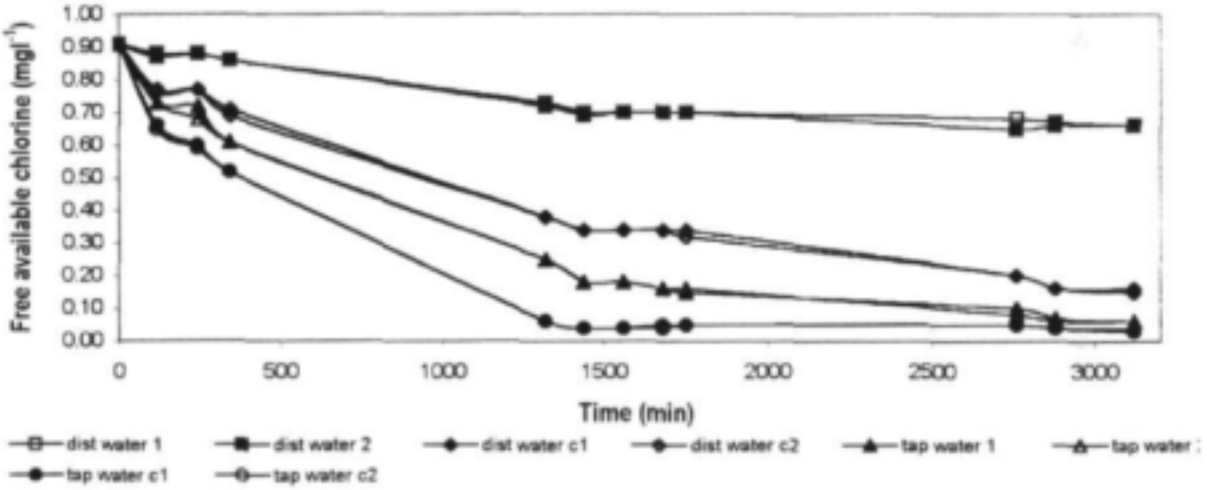


Figure 3.4.1: Chlorine decay profile of distilled water and reservoir water in contact with concrete (see Table 3.4.1)

Chlorine solution pumped through a concrete structure and a glass control structure to see the change over time in discharge composition.

Table 3.4.2: Reaction of chlorine with concrete surface (see figure 3.4.3)

	Free available chlorine (mg/ℓ)	
Time (min)	Glass tube	Concrete tube
60	0.98	0.97
90	0.95	0.93
120	0.93	0.88
150	0.85	0.80
180	0.80	0.76
210	0.78	0.74
240	0.74	0.68
270	0.69	0.65
290	0.65	0.50

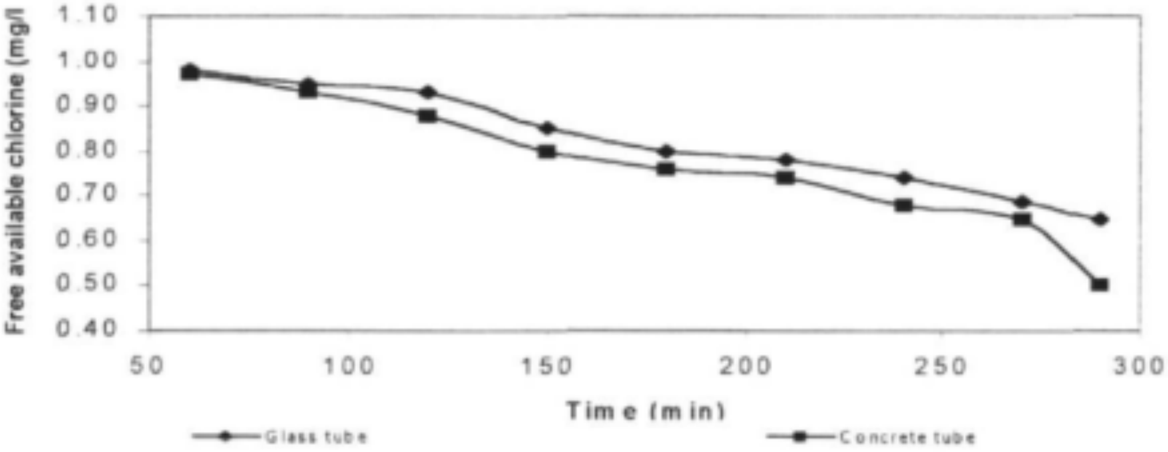


Figure 3.4.4: Reaction of chlorine with concrete and glass surfaces (see Table 3.4.2)

Calculation using mathematical models

Table 3.4.3: Decay of Chlorine in Concrete Reservoirs

C_i	Total Chlorine	Decay in the bulk fluid	% of total	Loss due to adsorption	% of total
0.6	24	15.1	63.0	40	0.16
0.4	16	13.8	86.3	34	0.14
0.2	8	7.9	98.0	26	0.11

Results for the decay of free chlorine in a reservoir for vaporisation in grams, decay in the bulk fluid in kilograms, and adsorption in grams and in percentages of the total amount (total) in kilograms of free chlorine present in the beginning of the day, given a certain initial concentration C_i (mg/ℓ).

3.5 Determination of chlorine losses to the headspace of reservoir

3.5.1 Objectives

In time, chlorine will distribute itself over the entire area of the water body in the reservoir if a concentration gradient exists. Chlorine will also be lost to the headspace, causing a concentration gradient and diffusion throughout the entire atmosphere above the water. The question in mind is how much chlorine is lost to the atmosphere? Increasing turbulence, temperature and circulation will accelerate the loss of chlorine.

3.5.2 Analysis procedures

$$c_{air} = \frac{c}{H_{T_w} s_w R T_{air}}$$

The formula will be used to determine the amount of chlorine that can vaporise.

The amount Q [kmol/m^{2}s] of chlorine that can leave the reservoir per area per second is given by

$$Q = \frac{D_{air}}{\delta}(c_{air} - c_o) \qquad (4.5.1)$$

where D_{air} [m^2/s] is the diffusion coefficient of chlorine in water, δ [m] is the length of the air holes, and c_o [kg/m^3] is the concentration of chlorine outside the reservoir. Since

$c_0 = 0$ mg/ℓ (4.5.1) reduces to

$$Q = \frac{D_{air}}{\delta} c_{air}$$

When we assume that c_{air} and D_{air} are constant during small time intervals, the total amount Q_{dif} [kg] of chlorine that can leave the reservoir due to diffusion through the air holes is given by

$$Q_{dif} = QmA_h t$$

where m [kg] is the mass of 1 kilomol of chlorine, A_h [m^2] is the total area of the air holes, and *t* [sec] is the time period considered.

Convection

First convection through air expansion due to temperature variation in the air layer is considered. The amount Q_{air} [kg] of chlorine in the air layer is given by

$$Q_{air} = c_{air} V_{air}$$

where V_{air} [m^3] is the volume of the air layer. The temperature gradient induces a volume change ΔVair, or

$$\frac{\Delta c_{air}}{c_{air}} = \frac{V_{air}}{V_{air} + \Delta V_{air}} = \left(\frac{1}{1 + \frac{\Delta V_{air}}{V_{air}}} \right) \approx \left(1 - \frac{\Delta V_{air}}{V_{air}} \right)$$

Then the amount Q_{conv} [kg] of chlorine that can leave the reservoir is given by

$$Q_{conv} = c_{air} \Delta V_{air}$$

Secondly, chlorine can leave the reservoir due to airflow in the air layer. The amount Q_{flow} [kg] of chlorine that can leave the reservoir by the airflow is given by

$$Q_{flow} = \frac{1}{2} c_{air} v A_h t$$

where v [m/s] is the velocity of the incoming air, A_h [m^2] the area of the air holes, and *t* [sec] the period considered. The factor ½ comes from the fact that we assume that the air enters the reservoir through half of the air holes and leaves the reservoir through the other half of the air holes.

3.5.3 Results

From the calculations done for the effect of vaporisation it was found that the effect of diffusion only is negligible compared to the effect of convection through expansion of the air layer, see table 3.4.4.

With the data as in the last subsection, calculations are done for a length of stay of one day. The results are given in Table 4.5.1.

Table 3.5.1: Decay of Chlorine in Concrete Reservoirs

C_i	**Total chlorine**	**Losses due to vaporisation**	**% of total chlorine decay**
0.6	24	1.0	0.004
0.4	16	0.7	0.0044
0.2	8	0.3	0.0038

Results for the decay of free chlorine in a reservoir for vaporisation (vap) in grams and in percentages of the total amount (total) in kilograms of free chlorine present in the beginning of the day, given a certain initial concentration C_i (mg/ℓ].

3.6 Determination of the relationship between microbiological quality and chlorine losses in the water

3.6.1 Objectives

Rand Water's distribution system comprises about 55 reservoirs that range in capacity from 11 Mℓ to 650 Mℓ. The number of reservoirs in the system to be examined was reduced to one reservoir per major district in the Rand Water distribution system. The reservoirs were chosen to reflect a variety in terms of type, shape, circulation and capacity. This was done to obtain a representative group of reservoirs that included all the divergent reservoirs. Table 4.6.1 lists the chosen reservoirs and their characteristics.

Table 3.6.1: Chosen reservoirs and their characteristics.

Reservoir	Type	Inlet/outlet	Turnover	Shape	District	Capacity (Mℓ)
Airfield	Throughflow	Separate	Good	Round	Germiston	25
Benoni no. 3	Balancing	Separate	Medium	Rectangular	Benoni	121
Brakpan	Throughflow	Separate	Medium	Rectangular	Brakpan	200
Daleside	Pumpstorage	Common	Medium	Round	Kliprivier	45
Forest Hill No. 2	Balancing	Separate	Poor	Round	Forest Hill	90
Waterval No. 2	Balancing	Separate	Poor	Rectangular	Waterval	61
Witpoortjie	Balancing	Separate	Poor	Rectangular	Krugersdorp	75

3.6.2 Statistical analysis

Data was statistically analysed using STATISTICA software. This user friendly computer package was used because it is generally available and has extended user support.

Correlation matrixes were drawn to see if there was any correlation between the chlorine concentrations and bacteriological quality. Tables 3.6.2 – 3.6.4 show the results for the reservoirs where there were a correlation between the chlorine concentrations and bacteriological quality.

Tables 3.6.5 – 3.6.8 show the comparison of SPC, 37°C and free available chlorine: the figures in these tables indicates the percentage samples that had a SPC in the specified range during the period January 1992 – August 1998.

3.6.3 Results

Table 3.6.2: Correlation matrix for data of **Brakpan reservoir No. 2**.

	Correlations Brakpan reservoir No. 2 **Marked correlations are significant at $p<0.05$** **n=220 (Casewise deletion of missing data)**						
Variable	**Temp**	**Total Residual Chlorine**	**Free Available Chlorine**	**Standard plate counts**	**Total coliforms**	**Faecal coliforms**	**Log(SPC)**
Temp	1.00						
Total Residual Chlorine	0.05	1.00					
Free Available Chlorine	0.16*	0.62*	1.00				
Standard plate counts	-0.01	-0.13*	-0.11	1.00			
Total coliforms	0.05	-0.08	-0.05	0.59*	1.00		
Faecal coliforms	0.07	0.00	0.02	-0.04	0.08	1.00	
Log(SPC)	0.00	-0.03	-0.03	0.64*	0.15*	-0.09	1.00

Table 3.6.3: Correlation matrix for data of **Daleside reservoir**.

	Correlations Daleside reservoir **Marked correlations are significant at $p<0.05$** **n=220 (Casewise deletion of missing data)**						
Variable	**Temp**	**Total Residual Chlorine**	**Free Available Chlorine**	**Standard plate counts**	**Total coliforms**	**Faecal coliforms**	**Log(SPC)**
Temp	1.00						
Total Residual Chlorine	-0.12	1.00					
Free Available Chlorine	-0.07	0.90*	1.00				
Standard plate counts	0.09	-0.20*	-0.14*	1.00			
Total coliforms	0.14*	-0.04	-0.03	0.12	1.00		
Faecal coliforms	0.06	-0.01	-0.02	0.04	0.17*	1.00	
Log(SPC)	0.26*	-0.38*	-0.37*	0.56*	0.15*	0.11	1.00

Table 3.6.4: Correlation matrix for data of **Witpoortjie reservoir**.

	Correlations Witpoortjie reservoir **Marked correlations are significant at $p<0.05$** **n=220 (Casewise deletion of missing data)**						
Variable	**Temp**	**Total Residual Chlorine**	**Free Available Chlorine**	**Standard plate counts**	**Total coliforms**	**Faecal coliforms**	**Log(SPC)**
Temp	1.00						
Total Residual Chlorine	0.15	1.00					
Free Available Chlorine	0.26*	0.62*	1.00				
Standard plate counts	0.13	0.16	0.30*	1.00			
Total coliforms	0.15	-0.08	-0.02	-0.05	1.00		
Faecal coliforms	0.15	-0.08	-0.02	-0.05	1.00*	1.00	
Log(SPC)	0.21	0.16	0.17	0.76*	-0.12	-0.12	1.00

Table 3.6.5: Comparison of SPC 37°C and total residual chlorine: the figures in this table indicate the percentage of samples that had SPC in the specified range during the period January 1992 – August 1998 for **Brakpan reservoir**.

	SPC (CFU/mℓ)						
Total chlorine (mg/l)	**1-21**	**21-41**	**41-61**	**61-81**	**81-101**	**>101**	**Grand Total**
0-0.1	4.4	0.4	0.0	0.4	0.0	1.8	7.1
0.1-0.2	2.2	1.3	0.9	0.4	0.0	3.1	8.0
0.2-0.3	7.1	0.0	1.8	1.3	0.4	4.9	15.6
0.3-0.4	8.0	0.9	2.7	1.3	0.9	4.0	17.8
0.4-0.5	7.1	1.3	0.0	0.0	0.9	3.6	12.9
0.5-0.6	7.1	0.0	0.0	0.9	0.4	0.9	9.3
0.6-0.7	4.0	0.9	0.4	0.0	0.0	0.9	6.2
0.7-0.8	2.2	0.4	0.0	0.4	0.4	0.9	4.4
0.8-0.9	1.8	0.9	0.9	0.0	0.4	3.6	7.6
>0.9	4.0	0.9	0.9	0.9	1.8	2.7	11.1
Grand Total	48.0	7.1	7.6	5.8	5.3	26.2	100.0

Table 3.6.6: Comparison of SPC 37°C and free available chlorine: the figures in this table indicate the percentage of samples that had SPC in the specified range during the period January 1992 – August 1998 for **Witpoortjie reservoir**.

	SPC (CFU/mℓ)						
Total chlorine (mg/ℓ)	**1-21**	**21-41**	**41-61**	**61-81**	**81-101**	**>101**	**Grand Total**
0-0.1	19.3	6.0	2.4	0.4	1.2	1.6	30.9
0.1-0.2	11.2	2.0	4.4	0.4	0.4	0.4	18.9
0.2-0.3	8.8	2.8	2.0	1.6	0.0	0.4	15.7
0.3-0.4	7.2	1.6	0.4	0.4	0.4	0.8	10.8
0.4-0.5	6.0	1.6	0.4	0.4	0.0	0.0	8.4
0.5-0.6	2.4	0.4	0.8	0.0	0.0	0.4	4.0
0.6-0.7	2.4	0.4	0.4	0.0	0.0	0.4	3.6
0.7-0.8	1.6	0.0	0.4	0.0	0.0	0.4	2.4
0.8-0.9	1.2	0.0	0.0	0.0	0.0	0.4	1.6
>0.9	2.8	0.4	0.0	0.0	0.4	0.0	3.6
Grand Total	63.1	15.3	11.2	3.2	2.4	4.8	100.0

Table 3.6.7: Comparison of SPC 37°C and total residual chlorine: the figures in this table indicate the percentage of samples that had SPC in the specified range during the period January 1992 – August 1998 for **Daleside reservoir**.

	SPC (CFU/mℓ)						
Total chlorine (mg/l)	**1-21**	**21-41**	**41-61**	**61-81**	**81-101**	**>101**	**Grand Total**
0-0.1	1.6	2.1	0.4	0.0	0.0	3.7	7.8
0.1-0.2	7.4	2.1	2.9	0.8	0.4	5.8	19.3
0.2-0.3	8.2	0.8	0.8	0.0	0.0	3.7	13.6
0.3-0.4	10.7	1.6	0.4	0.4	0.0	3.7	16.9
0.4-0.5	12.3	1.2	0.4	0.0	0.4	1.6	16.0
0.5-0.6	4.5	0.4	0.8	0.4	0.0	1.2	7.4
0.6-0.7	6.6	1.6	0.0	0.4	0.0	0.4	9.1
0.7-0.8	5.3	0.4	0.4	0.0	0.0	0.4	6.6
0.8-0.9	1.2	0.4	0.0	0.0	0.0	0.0	1.6
>0.9	1.6	0.0	0.0	0.0	0.0	0.0	1.6
Grand Total	59.7	10.7	6.2	2.1	0.8	20.6	100.0

Table 3.6.8: Comparison of SPC 37°C and free available chlorine: the figures in this table indicate the percentage of samples that had SPC in the specified range during the period January 1992 – August 1998 for **Daleside reservoir**.

	SPC (CFU/mℓ)						
Total chlorine (mg/ℓ)	**1-21**	**21-41**	**41-61**	**61-81**	**81-101**	**>101**	**Grand Total**
0-0.1	19.1	6.7	3.6	1.3	0.4	14.2	45.3
0.1-0.2	3.6	1.8	0.4	0.4	0.0	3.1	9.3
0.2-0.3	10.2	0.9	0.4	0.4	0.0	1.3	13.3
0.3-0.4	8.9	0.9	1.8	0.0	0.0	1.3	12.9
0.4-0.5	7.6	0.0	0.0	0.0	0.4	1.3	9.3
0.5-0.6	1.3	1.3	0.4	0.4	0.0	0.4	4.0
0.6-0.7	3.1	0.0	0.0	0.0	0.0	0.0	3.1
0.7-0.8	0.9	0.0	0.0	0.0	0.0	0.0	0.9
0.8-0.9	0.9	0.0	0.0	0.0	0.0	0.0	0.9
>0.9	0.9	0.0	0.0	0.0	0.0	0.0	0.9
Grand Total	56.4	11.6	6.7	2.7	0.9	21.8	100.0

3.7 Determination of the bacteriostatic effect of monochloramine and chlorine

3.7.1 Objectives

The objective of this study was to assess the effectiveness of monochloramine and chlorine as bacteriostatic and bacteriosidic agent. In order to determine the bacteriostatic and bacteriosidic effect of monochloramine and chlorine, a sample of the treated specimen was cultured to determine the number of surviving bacteria (those that can grow and multiply).

The bacterial cultures used in this experiment were cultured in two different ways. The first series of experiments was done on bacteria grown in the microbiological laboratory under ideal circumstances. These data were taken from Geldenhuys (1978). The data is presented in table 3.7.1, and 3.7.3. For the second series of experiments the culture was grown under natural conditions. Vaal Dam water was used as inoculum, and tap water from Vereeniging pumping station was added to this sample. The sample was grown during winter and spring. Tap water was added to replace water that evaporated from the culture. This was done to see if there is a difference in reaction towards disinfectants if microorganisms were cultured under natural conditions in the presence of chlorine compared to using artificial media in the lab.

3.7.2 Analysis procedures

The data accumulated was analysed in the following way. First an arithmetic death of the bacteria in the water was drawn. This is a graph of the number of surviving bacteria against time. The chlorine concentrations were also plotted on this graph. From this graph the following observations can be made: a) the growth pattern of bacteria over time, b) what happens when chlorine is added to the solution.

Secondly a logarithmic death curve was drawn. The reason for this is that on the arithmetic death curve the events in the beginning with the addition of chlorine is not very clear because counts tend to get very high towards the end of the exposed period. The logarithmic death curves were used to put these readings in perspective.

3.7.3 Results

Experiments done to study the bacteriostatic effects of chlorine produced the following results. Experiments 1.1 – 1.5 as well as 2.1 – 2.5 were done on bacteria grown in the laboratory under ideal conditions. Experiments 1.1 – 1.5 were done over a period of 168 hours and Experiments 2.1 – 2.5 were done over a period of 144 hours. Experiments 3.1a – 4.5b were done over a period of 72 hours on bacteria that were grown under natural conditions.

Table 3.7.1: Bacteriostatic effect of chlorine for bacteria grown under ideal conditions in the laboratory.

Time (h)	Counts at 22°C CFU/mℓ	Counts at 37°C CFU/mℓ	Total available chlorine mg/ℓ	Free available chlorine mg/ℓ	Log (Counts at 22°C)	Log (Counts at 37°C)
0	1.80x10^{+2}	1.80x10^{+2}	0.50	0.20	2.26	2.26
1	7.00x10^{+1}	4.50x10^{+1}	0.25	0.20	1.85	1.65
24	6.50x10^{+1}	4.00x10^{+1}	0.10	0.10	1.81	1.60
48	4.00x10^{+1}	5.00x10^{+1}	0.10	0.00	1.60	1.70
72	1.50x10^{+2}	1.40x10^{+2}	0.05	0.00	2.18	2.15
96	1.80x10^{+3}	3.60x10^{+3}	0.05	0.00	3.26	3.56
168	3.60x10^{+3}	3.40x10^{+3}	0.05	0.00	3.56	3.53

Table 3.7.2: Bacteriostatic effect of chlorine for bacteria grown under natural conditions in the presence of chlorine.

Time (h)	Counts at 22°C CFU/mℓ	Counts at 37°C CFU/mℓ	Total available chlorine mg/ℓ	Free available chlorine mg/ℓ	Log (Counts at 22°C)	Log (Counts at 37°C)
0	1.30x10^{+2}	2.20x10^{+3}	1.80	1.15	2.11	3.34
1	2.10x10^{+2}	2.00x10^{+2}	1.22	0.95	2.32	2.30
24	5.70x10^{+3}	2.10x10^{+3}	0.23	0.10	3.76	3.32
48	9.30x10^{+3}	5.80x10^{+3}	0.20	0.04	3.97	3.76
72	9.40x10^{+4}	8.50x10^{+4}	0.12	0.04	4.97	4.93

Experiments done to study the bacteriostatic effect of monochloramine produced the following results. Experiments 1.1 – 1.2 as well as 2.1 – 2.2 were done on bacteria grown in the laboratory under ideal conditions. Experiments 1.1 – 1.2 were done over a period of 192 hours and Experiments 2.1 – 2.5 were done over a period of 240 hours. Experiments 3.1a – 4.5b were done over a period of 96 hours on bacteria that were grown under natural conditions.

Table 3.7.3: Bacteriostatic effect of monochloramine for bacteria grown under ideal conditions in the laboratory.

Time (h)	Counts at 22°C CFU/mℓ	Monochloramine mg/ℓ	Log(Counts at 37°C)
0	$2.60x10^{+3}$	0.80	3.41
24	$1.70x10^{+2}$	0.60	2.23
48	$1.10x10^{+2}$	0.40	2.04
72	$1.20x10^{+2}$	0.30	2.08
96	$4.00x10^{+1}$	0.20	1.60
120	$1.00x10^{+1}$	0.15	1.00
144	$2.00x10^{+1}$	0.10	1.30
168	$2.00x10^{+1}$	0.00	1.30
192	$1.00x10^{+1}$	0.00	1.00

Table 3.7.4: Bacteriostatic effect of monochloramine for bacteria grown under natural conditions in the presence of chlorine.

Time (h)	Counts at 22°C CFU/mℓ	Counts at 37°C CFU/mℓ	Monochloramine mg/ℓ	Log (Counts at 22°C)	Log (Counts at 37°C)
0	$2.20x10^{+4}$	$3.40x10^{+4}$	0.59	3.34	3.53
1	$8.00x10^{+2}$	$3.70x10^{+2}$	0.50	2.90	2.67
24	$7.00x10^{+1}$	$5.00x10^{+1}$	0.45	1.85	1.70
48	$5.00x10^{+1}$	$5.00x10^{+1}$	0.40	1.70	1.70
72	$7.00x10^{+1}$	$2.00x10^{+1}$	0.40	1.85	1.30
96	$1.00x10^{+2}$	$6.00x10^{+1}$	0.30	2.00	1.78

A typical arithmetic death curve for data in table 3.7.1 is shown in figure 3.7.1, table 3.7.2 in figure 3.7.2, table 3.7.3 in figure 3.7.3, and for table 3.7.4 in figure 3.7.4. These graphs were drawn to visualise the change in bacterial counts with the addition of chlorine.

A typical logarithmic death curve for: bacteria grown under ideal conditions and dosed with chlorine are shown in figure 3.7.5; grown under natural conditions and dosed with chlorine are shown in figure 3.7.6; grown under natural conditions and dosed with monochloramine are shown in figure 3.7.3.

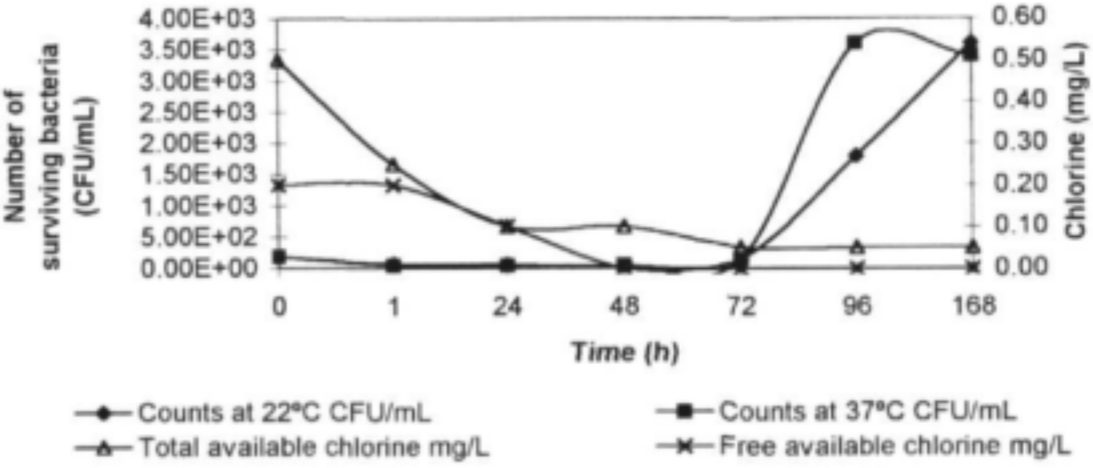


Figure 4.7.1: Bacteriostatic effect of chlorine: Arithmetic death curve of bacteria in water dosed with chlorine. Standard plate counts at 22°C and 37°C, Free and Total available chlorine in mg/ℓ and time up to 168 hours. For bacterial culture grown under ideal conditions in the laboratory.

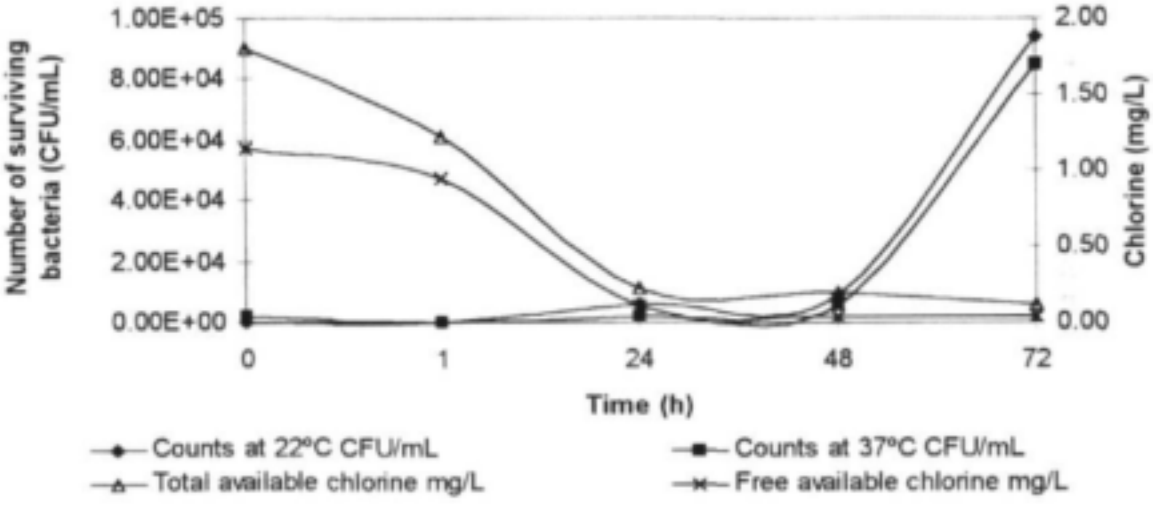


Figure 4.7.2: Bacteriostatic effect of chlorine: Arithmetic death curve of bacteria in water dosed with chlorine. Standard plate counts at 22°C and 37°C, Free and Total available chlorine in mg/ℓ and time up to 72 hours. For bacterial culture grown under natural conditions in the presence of chlorine.

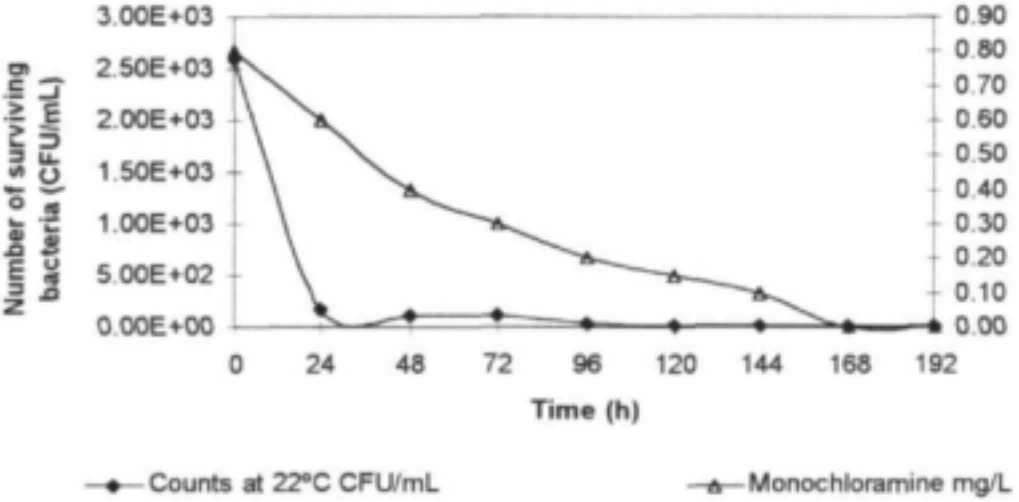


Figure 4.7.3: Bacteriostatic effect of monochloramine: Arithmetic death curve of bacteria in water dosed with chlorine. Standard plate counts at 22°C and 37°C, monochloramine in mg/ℓ and time up to 192 hours. For bacterial culture grown under ideal conditions in the laboratory.

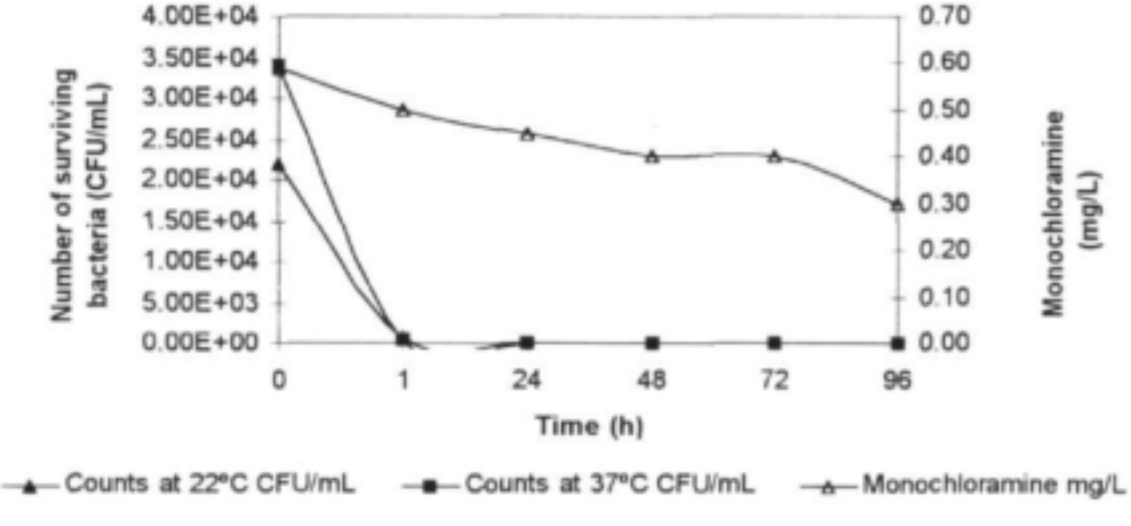


Figure 4.7.4: Bacteriostatic effect of monochloramine: Arithmetic death curve of bacteria in water dosed with chlorine. Standard plate counts at 22°C and 37°C, monochloramine in mg/ℓ and time up to 96 hours. For bacterial culture grown under natural conditions in the presence of chlorine.

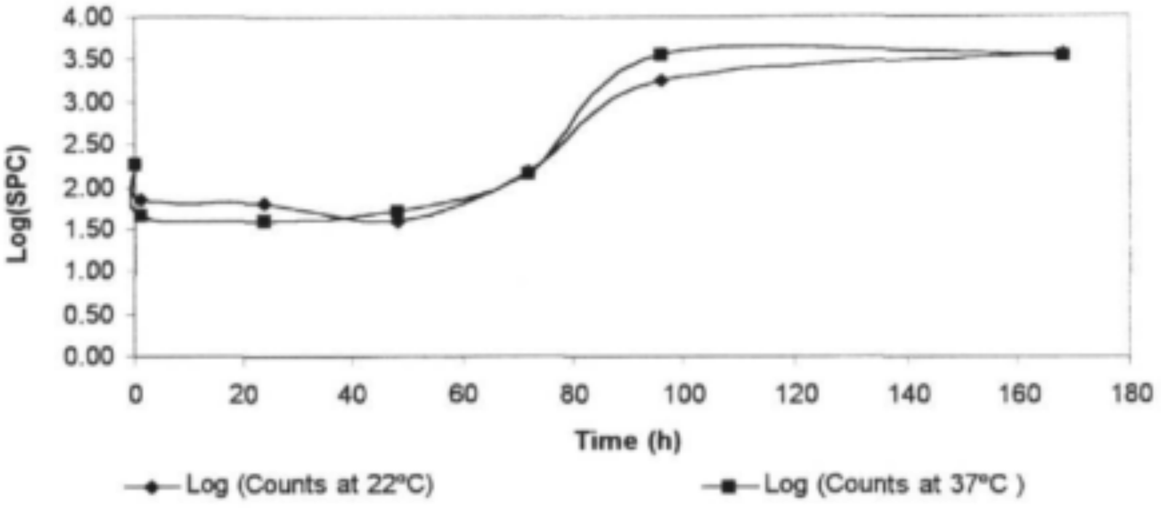


Figure 4.7.5: Bacteriostatic effect of chlorine. Logarithmic death curve of bacteria in water dosed with chlorine. log(SPC) at 22°C and 37°C as a function of time (168 hours). For bacterial culture grown under ideal conditions in the presence of chlorine.

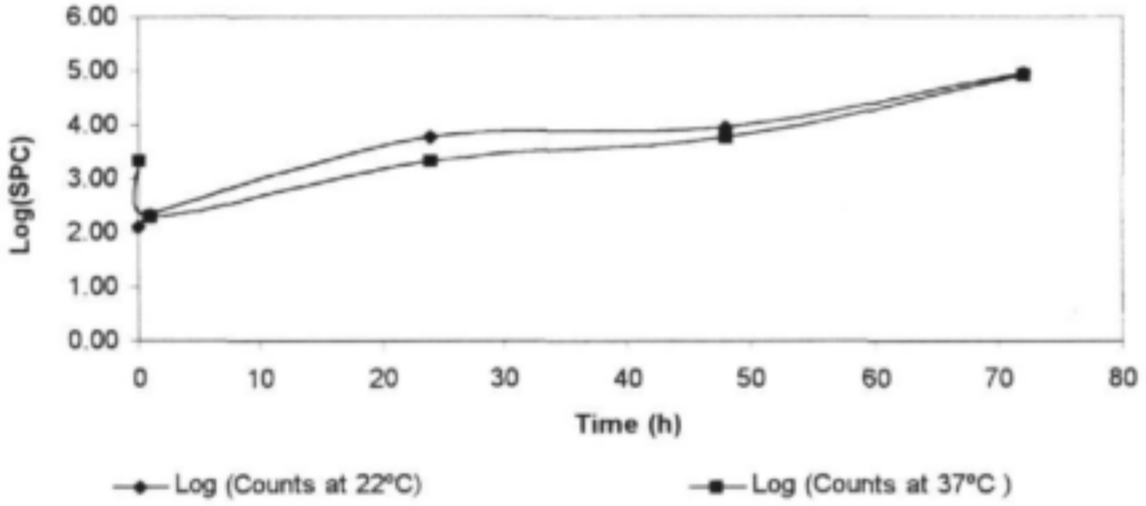


Figure 4.7.6: Bacteriostatic effect of chlorine. Logarithmic death curve of bacteria in water dosed with chlorine. log(SPC) at 22°C and 37°C as a function of time (72 hours). For bacterial culture grown under natural conditions in the presence of chlorine.

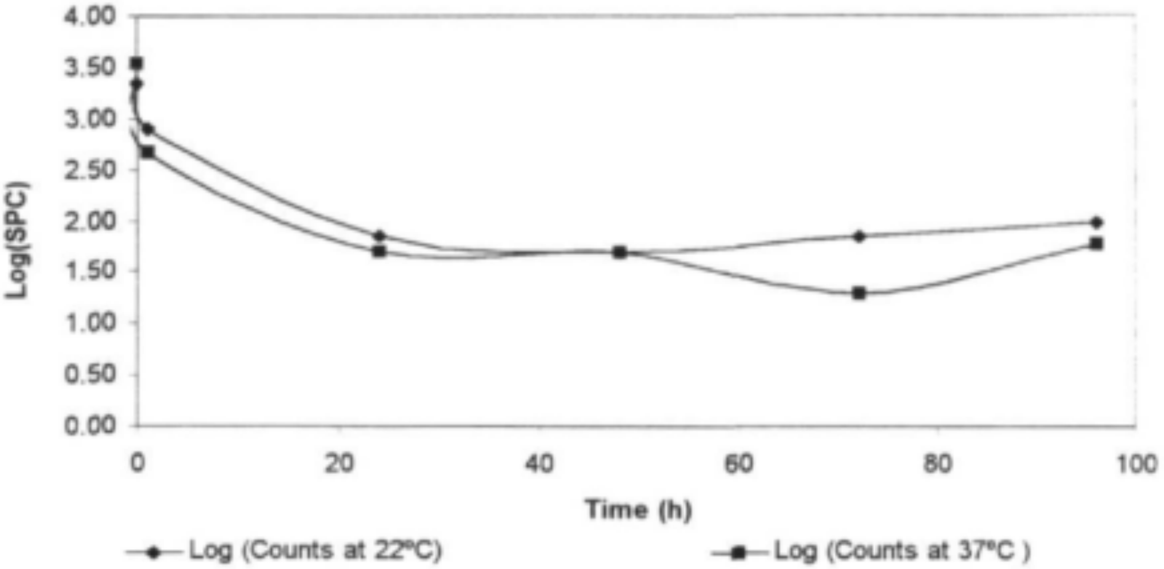


Figure 4.7.7: Bacteriostatic effect of monochloramine. Logarithmic death curve of bacteria in water dosed with monochloramine. Standard plate counts at 37°C as a function of time (96 hours). For bacterial culture grown under natural conditions in the presence of chlorine.

CHAPTER 4

4. DISCUSSION

4.1 Technical discussion of

4.1.1 Relationship between water age and chlorine concentration

The literature reviewed concluded that in water distribution systems chlorine will probably follow a first order decay. Most of the experiments conducted in this study were conducted under controlled temperature conditions. However, in the distribution system itself there is no temperature control. The validity of these reactions can therefore be questioned.

Graphs were drawn from data from different reservoirs and sites in the distribution system with no temperature control; in other words the sample temperatures were not regulated to stay. From these graphs it is seen that the first order model can still be fit to the data, although the fit is not as good as in the case with temperature controlled samples.

Results from SAS's PROC NLIN for data fit to different order models. For first order decay k is 0.005 per time. Best fit n order model $k=-b^{(-a(n-1)}$.

Data analysed on Oakdale Curve fitting program show that about 43 models fit the data, however the first order model is the 25th best fit model.

The decay constant for samples tested is dependent on the initial concentration. For the first order rate the following was found:

- Initial concentration: 0.2 mg/L, then k=0.01 (from experiment 2.2).

- Initial concentration: 0.4 mg/L, then k=0.003 (form experiment 1.4).

- Initial concentration: 0.6 mg/L, then k=0.001.

It is clear that k decreases when the initial concentration is higher.

4.1.2 Chlorine losses due to the concrete that is in contact with the water

Concrete has a definite influence on chlorine levels in the water this can be seen in figure 3.4.1. The following conclusions can be draw from this figure:

- Distilled water has the smallest demand and exhibits the slowest chlorine decay, because there are not many other ions and compounds present that exercise an additional chlorine demand.
- A faster decay is seen in distilled water in contact with concrete. Therefore it seems as through concrete accelerates the decay of chlorine.
- Chlorine decay is faster in reservoir water than in distilled water with concrete, as the additional ions and compounds in water also influence chlorine decay
- The fastest decay of chlorine is seen in tap water in contact with concrete.

It is known that the porosity of concrete changes with age. This could explain the change in sorption and diffusion rates with time.

It is concluded from data in table 3.4.2 that the percentage loss of chlorine inside a reservoir due to adsorption form concrete is negligible for chlorine residual found in reservoirs. It is found that the main decay is due to natural bulk decay, which give 63 – 98 % of chlorine losses inside the reservoir.

4.1.3 Chlorine losses due to the headspace in the reservoir

In laboratory tests conducted on water samples containing 6.5mg/ℓ chlorine, up to 0.8ppm chlorine were measured in the atmosphere above the water inside the container. These tests were done an hour after dosing. These results are higher than results obtained from the model (in table 3.5.1) because the tests were done under control condition, no temperature variations, small surface area and small atmospheric space above the water exist. Therefore diffusions are instantaneous because of this small surface to headspace ratio, and thus the diffusion gradient is much bigger and that lead to the high chlorine concentrations measured in the laboratory. When the same concentrations of chlorine were used and the water surface was stirred, these losses increased by 0.1 – 0.2 ppm, thus diffusion and vaporisation increases. In reservoirs the period of surface exposure is much longer and the chlorine concentrations in the bulk water is much lower than the samples used in the laboratory.

From the results in table 3.5.1 it is seen that the percentage losses into the atmosphere, due to vaporisation is negligible for the highest percentage with a chlorine bulk concentration of 0.6 mg/ℓ is only 0.004%. This is the concentration present inside the reservoirs.

4.1.4 Relationship between microbiological quality and chlorine levels

Microbiological and chemical data from 1992 – August 1998, on the reservoirs mentioned in table 3.6.1, were statistically analysed. These analyses were done to see if there are any relationships between microbiological parameters and chlorine levels.

Correlation matrixes were drawn on above-mentioned data, see in table 3.6.2 – 3.6.4. It can be seen that for the seven reservoirs analysed only data on three of these reservoirs showed any correlation between microbial parameters and chlorine levels. From the data of Brakpan reservoir a negative correlation (-0.13) between total residual chlorine and SPC can be seen. For Daleside there is a negative correlation (-0.20) between total residual chlorine and SPC and a negative correlation (-0.14) between free available chlorine and SPC. There is also a negative correlation (-0.38) between total residual chlorine and log(SPC) and a negative correlation (-0.37) between free available chlorine and log(SPC). For Witpoortjie reservoir there is a positive correlation (0.30) between free available chlorine and SPC. In general the correlations are very poor. and not significant enough to state that there is a definite positive or negative correlation between the microbial parameters and chlorine levels in reservoirs.

The pooled data from these reservoirs were tabulated in Table 3.6.5 – 3.6.8, which indicated that the frequency of occurrence of SPC at 37°C decreases as the chlorine residuals increased. The same phenomena were found at Umgeni Water (Bailey, et al, 1998). At Daleside (Table 3.6.8) and Witpoortjie (Table 3.6.6) reservoirs most of the SPC were detected in the presence of free available chlorine concentration in the 0.0 – 0.5 mg/ℓ range. More than 55 percent of the samples had SPC counts in the 1-21 CFU/mℓ range and a further 20 – 30 percent in the range 21 – 61. The data on Brakpan (Table 3.6.5) and Daleside (Table 3.6.7) show that that most of the SPC detected was in the presence of 0.1 – 0.5 mg/ℓ total chlorine range.

From the free available and total residual chlorine data it can be seen that the numbers of SPC decrease with an increase in chlorine.

4.1.5 Bacteriostatic effect of monochloramine and chlorine

From the laboratory experiments it can be concluded that the largest decrease in bacterial counts takes place in the first few minutes after the addition of chlorine or monochloramine. Thereafter the counts decrease more gradually. For experiments done on bacteria grown in the laboratory under ideal conditions aftergrowth only started after 48 hours (see table 3.7.1 and figure 3.7.1) up to 72 hours. This aftergrowth starts when free available chlorine concentrations are depleted. From the experimental data it seems as through initial chlorine concentrations postpone aftergrowth. With lower chlorine dosages of 0.5 – 0.8 mg/L the first signs of aftergrowth start after 48 hours, but with the higher dosages the first signs of aftergrowth was found after 72 hours. Counts at the lower concentration (0.5 – 0.9 mg/ℓ) was ten fold higher than counts at higher chlorine concentrations.

With bacteria grown under natural conditions the aftergrowth starts at about 24 hours after the addition of chlorine for free chlorine concentration up to 1.10 mg/ℓ, aftergrowth for chlorine dosages higher than 1.10 mg/ℓ is postponed for 48 hours (table 3.7.2, figure 3.7.2). This indicates that the bacteria grown in natural conditions in the presence of chlorine are more resistant towards free available chlorine, than bacterial cultures grown in the laboratory under ideal conditions.

From the logarithmic death curve for chlorine (figure 3.7.5) of experiments done on bacteria grown in the laboratory it can be concluded that: growth occurs in three phases. First there is a very fast decrease in the first hour, secondly a stabilising period where no aftergrowth occurs and then thirdly a sudden increase in growth. The last phase started after ± 55 hours for experiments 1.1 – 1.5 and ± 72 hours for experiments 2.1 – 2.5. The logarithmic death curves (figure 3.7.6) for bacteria grown under natural conditions show a fast decrease in the first hour and then a progressive increase in growth.

In the laboratory experiments done to determine the bacteriostatic effect of monochloramine on laboratory cultures bacteria it is seen that aftergrowth is postponed to about 196 – 216 hours. The decrease in counts is not as fast as the decrease with free available chlorine, but it is a slower, longer lasting, decrease (table 3.7.3, figure 3.7.3). In the laboratory experiments done to determine the bacteriostatic effect of monochloramine on bacteria grown under natural conditions in the presence of chlorine it is seen that the same bacteria that are now more resistant towards chlorine is more sensitive towards monochloramine, which are less oxidative than chlorine. This can be see from figure 3.7.4. For low concentration of monochloramine (about 0.5 mg/ℓ) the first signs of aftergrowth is seen at 96hours, but for higher monochloramine dosages (higher than 1.0 mg/ℓ) bacterial counts are still decreasing after 96 hours.

The logarithmic death curves of monochloramine (figure 3.7.7) for bacteria grown under natural conditions show a fast decrease in the first hour and then a progressive decrease period with little to no aftergrowth in first 96 hours.

4.1.6 Influence of reservoir design on flow patterns, RTD values and chlorine levels

From previous studies done for Rand Water it was concluded that directly opposing inlet and outlet pipes in reservoirs are generally not hydraulically efficient especially in reservoirs with a high depth to diameter ratio. Larger reservoirs with lower depth to diameter ratios tend to be more efficient with this type of inlet and outlet arrangements (see figure A1, Annexure B).

Cyclone arrangements are generally more efficient than directly opposing arrangements for smaller reservoirs. Cyclone arrangements for larger reservoirs do not exhibit the same improvement (see figure B1, Annexure B).

Inlet manifold arrangements with inlets pointing towards and away from the outlet are more efficient than manifolds pointing only in one direction. Bi-directional manifold arrangements are less scale dependent than the above-mentioned arrangements (see figure C1, C2, Annexure B).

Near plug flow can be achieved with a labyrinth of internal baffles. This arrangement is far superior to any of the above options, but more costly to implement (see figure D1, Annexure B).

(Van der Walt, et al, 1999)

The flow patterns in Langerand no 2 reservoir were evaluated for the presence of stagnant areas. It was found that by changing the inlet/outlet configurations detention time was reduced from 288 hours to 119 hours and the large stagnant zone was reduced to a small zone in the corner near the outlet.

(Van der Walt, et al, 1998)

The flow patterns in the proposed Daleside reservoir were evaluated and flow patterns were improved to near plug flow conditions. The detention times reduced to 96 hours and stagnant zones reduced to a minimum.

(Otto Langenegger & Partners CC, 1999)

The flow patterns in Brakpan 200Mℓ reservoir were evaluated for the presence of stagnant areas, to visualise the general flow patters throughout the reservoir, and to evaluated the significance of including or excluding roof support columns (see figure 3.2.1 and 3.2.2). Therefore two scenarios were tested, scenario one structure plus roof support columns and scenario two just the structure excluding the roof support columns. From the comparison of the results between scenario one and scenario two (figure 3.2.3 compare with figure 3.2.6, figure 3.2.4 with figure 3.2.7, and figure 3.2.5 with figure 3.2.8), it is evident that the columns does influence the general flow patterns significantly. It is seen that stagnant areas are smaller and that in general the flow velocity is higher in scenario one. Therefore the simplification to exclude roof supporting columns because of their small area, is can not be made without loosing important information.

Because columns influence the general flow patterns significantly tracer studies were only conducted on scenario one. From the results it is concluded that the detention time of the reservoir is 360 hours and large near stagnant areas with very low flow velocities exist. It was found that if the chlorine decay rate is faster than 0.01 1/h only 60 % of the chlorine injected will reach the outlet the other 40% deteriorate before it reached the outlet (see figure 3.2.9). From the lines in the RTD curve in figure 3.2.9 it can be concluded that short-circuiting to the outlets takes place and therefore stagnant of very low velocity zones will co-exist with very high velocity zones.

It must be taken into consideration that the results from the above case study were not verified with a tracer study, because of the financial implication.

4.2 Review of the project in terms of the initial objectives

In terms of the original contract with the Water Research Commission, the objectives were to:

- Characterise the flow patterns in terms of residence time distribution (RTD)
- Relate chlorine losses of the water age (based on RTD-values and kinetic models)
- Account for chlorine losses due to the wall and the bottom effects
- Account for atmospheric losses
- Relate the bacteriological quality of the water to the levels of chlorine in the reservoirs
- Compare the bacteriostatic effect of monochloramine and free residual chlorine in reservoirs

Upon completion of the project it was clear that significant progress was made in terms of the above objectives. The following specific contributions were made:

- Flow patterns inside a reservoir play a significant role in the determination of the residence time and water quality. Inlet/outlet configuration and positioning, as well as the positions of the roof supporting columns are very important factors that influence the flow patterns inside a reservoir.

- Temperature conditions and initial chlorine concentrations play an important role in the determination of best-fit decay models.
- Chlorine losses due to reaction with concrete are insignificant in reservoirs, but significant in pipelines – volume/ surface and flow tempo play a role.
- Chlorine loss to the atmosphere above the water is negligible in large reservoirs with minimal surface movement.
- A model is currently being developed to determine the best-fit for bulk chlorine decay in reservoirs.

Chapter 5

5 CONCLUSIONS

- Characterise the flow patterns in terms of residence time distribution (RTD)

From case studies performed it was evident that water selects the route of least resistance to the outlet of a reservoir, the exact nature of this route being determined by the inlet and outlet configurations. It is therefore of utmost importance in reservoir design to ensure that the internal arrangements are designed optimally to prevent short-circuiting as well as the formation of stagnant water pockets. Reservoirs must be designed to ensure plugflow. Flo++ is an effective tool to use in determining these optimum flow conditions within the reservoir design process. Specifically, it can be used to optimise internal arrangement conditions, minimise detention time and reduce stagnant pockets, all of which contribute to improved water quality. Care must be taken in the generation of the mesh structures for reservoir, from this study it was evident that roof support structures must be included in the mesh.

- Relate chlorine losses to the water age (based on RTD-values and kinetic models)

Chlorine loss or chlorine decay is influenced by a variety of factors. Two of these are the detention time and temperature. From the kinetic models used it is noted that the effect of temperature is not built into the decay models. From the studies performed it is apparent that when determining the decay constants of chlorine under conditions of controlled temperature, very reliable first order data fits result. However, when decay studies were subjected to (simulated) natural conditions the data fit an n^{th}-order decay rather than first order.

- Account for chlorine losses due to the wall and the bottom effects

Under the conditions investigated, it was found that relatively deep penetration of water into the concrete structure took place. This results in a very slow, "3-*dimensional" exchange of dissolved substances in the pores of the concrete.* A state of equilibrium is therefore only reached over a long period. Empirically it was found that the concrete accelerates the loss of chlorine and that aged concrete has a lesser influence on the chlorine decay than freshly made concrete. Different mathematical models were fitted, but no single model seems to give a good fit of the overall process and therefore a suitable model was developed. Results of the investigation for alternative mathematical models indicate that the decay in the bulk fluid is the main reason that the chlorine concentration in a reservoir drops. Therefore the influence of concrete is negligible compared to the decay in the bulk fluid.

- Account for atmospheric losses

Indications that chlorine could be lost to the atmosphere are substantiated by the fact that chlorine concentrations as high 1 ppm was measure in laboratory tests above the water within an hour after dosing with chlorine. These concentrations increased with surface movement. According to mathematical models tested chlorine losses to the atmospheric headspace are negligible compared to bulk decay losses.

- Relate the bacteriological quality of the water to the levels of chlorine in the reservoirs

Very little correlation was found between the bacteriological quality and chlorine levels inside reservoirs. Any apparent correlation found was actually so insignificant that it could be dismissed. Although the percentage samples containing high microbial counts were far fewer in the presence of high chlorine levels, these raised chlorine doses do not necessarily guarantee low microbial counts.

- Compare the bacteriostatic effect of monochloramine and free residual chlorine in reservoirs

Some organisms do survive the disinfection process. These surviving bacteria serve as an inoculum for biofilms and aftergrowth in the distribution system. Bacteria that grow in the distribution system propagate under conditions where chlorine is present and consequently, over a period of time, these could become more resistant towards such a disinfectant. Much higher chlorine doses would thus be required to kill these organisms. However, the bacteria did show more sensitivity towards other disinfectants such as monochloramine. It is therefore very important to optimise the treatment process to ensure that maximum inactivation occurs in the treatment plant. The resistance of bacteria to chlorine is thus relevant in water purification and distribution. At high enough chlorine concentrations micro-organisms will be killed by disinfectants, but it is not possible to determine the increasing demand of bacteria that survived the first disinfection step.

Chapter 6

6 RECOMMENDATIONS FOR FUTURE STUDY

- Development of a more accurate chlorine decay test method and a chlorine decay model that includes temperature and initial concentration influences, which will provide more realistic decay values.
- Use of CFD in optimisation of flow patterns and retention times in current structure by optimising operation and internal arrangements of reservoirs.
- Classify conditions to optimise operational conditions for the distribution system to minimise water quality deterioration inside pipelines and reservoirs.
- Optimisation of treatment processes to prevent/minimise aftergrowth in the distribution system
- Investigate the differences and similarities in the operation of small and large distribution systems for optimum water distribution and quality
- Investigate the differences and similarities in the water quality parameters of small rural water storage tanks and large reservoirs.
- Disinfection procedures for reservoirs in rural communities
- Chlorine losses inside pumps and turbines

Chapter 7

7 TECHNOLOGY TRANSFER

The data of this project can be used by consulting firms that design and develop distribution systems, water boards with large distribution systems and water storage facilities and municipalities with small to extensive reticulation systems.

The data can be applied in:

- Design of new water storage facilities
- Optimise internal arrangements of existing water storage facilities,
- Test different operational procedures for new and existing facilities
- Determination of true residence times for reservoirs
- Optimisation of storage and distribution of water for minimal chlorine loss due to external influences in the water.

Chapter 8

8 REFERENCES

AESØY A, et al, *"The effect of sulphide and organic matter on the nitrification activity in a biofilm process"*, Wat. Sci. Tech., Vol. 37, No. 1, 1998, p 115 - 122

American Association of State Highway and Transportation Offi-cials, *"Standard Method of Sampling and Testing for Total Chloride Ion in Concrete and Con-crete Raw Materials"*, Designation: T 260-84, 1984.

American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), *"Standard Methods for the Examination of Water and Wastewater"*, 16th ed., Washington, 1997, American Public Health Association, p 294 – 319

American Water Works Association (AWWA), *"Water Treatment and Quality"*, Fourth edition, McGraw Hill Inc., 1990

Atkins PW, *"Physical Chemistry"*, Fifth edition, Oxford university Press, Oxford, 1994

AWWARF, *"Characterization and Modeling of Chlorine Decay in Distribution Systems"*, 1996.

Bailey IW and Thompson P, *"Maintaining water quality in distribution systems in hot climates"*, Water Quality Modelling, Rand Afrikaans University, 1998, p 12.1 – 12.8

Bath AJ et al, *"The Applicability of Hydrodynamic Reservoir Models for Water Quality Management of Stratified water bodies in South Africa: Application of DYRESM and CE-QUAL_W2"*, Report to the water Reset Commission Ninham Shand (Pty) Ltd, 1997

Bijnen J, *"Durability of Cement-Based Materials and Corrosion"*, Course Cement-based Composites for the Building Industry (TU Delft), 18-22 January 1999.

Biswas P et al, *"A model for chlorine concentration decay in pipes"*, Water Research, Vol. 27, No 12, 1993, p1715 - 1724

Biswas P, et. al., *"A Model for Chlorine Concentration Decay in Pipes, report on Water Quality Modeling"*, 1998.

Blatchley ER, III and Xie Y, *"Disinfection and antimicrobial processes"*, Water Environmental Research, Vol. 67, No 4, June, 1995, p 475 - 479

Boeker E and Van Grondelle R, *"Environmental Physics"*, John Wiley & Sons, New York, 1995, p 187 - 247

Boucher A, et. al., *"Kinetics of reactions in solution containing monochloramine and bromide"*, Wat. Res., Vol. 23, No. 8, 1989, Great Britain, Maxwell Pergamon Macmillan plc., p 1049 – 1058

Cambers VK et al, *"Modeling free and total chlorine decay in potable water distribution systems"*, J Water SRT-Aqua, Vol. 44, No 2, p 60 - 69

Connell GF, *"The Chlorination / Chloramination Handbook"*, Water disinfection series, 1996, American Water Works Association, Denver,

Dhaliwal BS and Baker RA, *"Role of ammonia-N in secondary effluent chlorination"*, Journal WPCF, Volume 55, No. 5, May, 1983, p 454 – 456.

Dice JC, *"Denver's Seven Decade of Experience With Chloramination"*, Management and Operations, Journal AWWA, January, 1985, p 34 - 37

Grayman WM and Clark RM, *"Using Computer Models to Determine the Effects of Storage on Water Quality"*, Journal of AWWA, July 1993, Management and operations, p 67 – 7

Greenwood NN and Earnshaw A, *"Chemistry of the elements"*, Pergamon Press, Oxford, 1994,p921 - 924

Haas CN and Karra SB, *"Kinetics of Microbial Inactivation by Chlorine – I, Review of Results in Demand-Free Systems"*, Wat. Res., Vol. 18, No. 11, 1984, Great Britain, Pergamon Journals Ltd., p 1443 - 1449

Haas CN and Karra SB, *"Kinetics of Microbial Inactivation by Chlorine – II, Kinetics in the Presence of Chlorine Demand"*, Wat. Res., Vol. 18, No. 11, 1984, Great Britain, Pergamon Journals Ltd., p 1451 – 1454

Hau F, et al, *"Modelling of chlorine decay in municipal water supplies"*, Wat. Res., Vol. 33, No. 132, 1999, Great Britain, Pergamon Journals Ltd., p 2735 - 2746

Hornung U, et. al., *"A Model for Chemical Reactions in Porous Media, in "Complex Chemical Reaction Systems. Mathematical Modeling and Simulation"*, 318-334, Chemical Physics, **47**, Springer-Verlag, Berlin, 1987.

Hornung, U, et. al., *":Diffusion, Convection, Adsorption and Reaction of Chemicals in Porous Media"*, Journal of Differential Equations, **92**, 199-225, 1991.

Jafvert CT and Valentine RL, *"Dichloramine Decomposition in the Presence of Excess Ammonia"*, Wat. Res., Vol. 21, No. 8, 1987, Great Britain, Pergamon Journals Ltd., p 967 - 973

Kennedy MS, et al, *"Assessing the effects of Storage Tank Design on Water Quality"*, Journal of AWWA, July 1993, Management and operations, p 78 - 88

Kerkhof PJAM, *"Lecture notes Stofoverdrachts processen, Module A"*, faculty of Chemistry and Chemical Engineering, Eindhoven University of Technology, 1999.

Kiéné L, et al, *"Relative importance of phenomena responsible of the chlorine decay in drinking water systems"*, Water Quality International 1998, IAWQ, p 214 - 221

Komorita JD and Snoeyink VL, *"Technical Note: Monochloramine Removal From Water By Activated Carbon"*, Research and Technology, Journal AWWA, January, 1985, p 62 - 64

Kreft P, et al, *"Converting From Chlorine's to Chloramines: A case Study"*, Management and Operations, Journal AWWA, January 1985, p 38 – 45

Kruger E, et. al., *"Chlorine Decay on Concrete Surfaces and Losses to the Atmosphere in Water Storage Facilities"*, Rand Water, WISA, 2000.

Le Chevallier MW, *"Coliform Aftergrowth in Drinking Water: A Review"*, Research and technology, Journal AWWA, November 1991, p 74 – 86

Lourent, et al, "

Matin A and Harakeh S, *"Effect of Starvation on Bacterial Resistance to Disinfectants"*, Drinking Water Microbiology, GA McFeters, New York, p 88 – 101

Merck, *"The Testing of Water"*, Darmstadt, Germany 23/4170/3/379 RU, p 47 – 54

Montgomery JM, *"Water Treatment - Principles & Design"*, New York, 1985, John Wiley & son, p 265-274

Muyima NYO and Ngcakani F, *"Indicator bacteria and aftergrowth potential of the drinking water in Alice, Eastern Cape"*, Water SA, Vol. 24, No. 1, January 1998, p 29 - 34

Nilsson L-O, et. al., *"Transport Mechanisms in Porous Material, in "The modeling of microstructure and its potential for studying transport properties and durability"*, 289-311, Kluwer Academic Publishers, The Netherlands, 1996.

Norton CD and Le Chevallier MW, *"Chloramination: its effect on distribution system water quality"*, Journal AWWA, Vol. 89, Issue 7, July 1997, p 66 - 77

Otto Langeregger & Partners cc., *"Daleside Reservoir/ pumpstation investigation"*, Report No: 55A/1, March, 1999

Palin AT, *"Chemistry of modern water chlorination"*, Water Services, January 1974, p. 7 – 12

Palin AT, *"Monochloramine"*, Research and Technology, Journal AWWA, February 1980, p 121 – 122

Polubarinova-Kochina P-Ya, *"Theory of Ground Water Movement"*, Princeton Uni-versity Press, Princeton, 1962. *"Determination of Chloride in Hardened Portland Cement Paste, Mortar and Con-crete"*, FHWA-RD-72-12, PB-219 831, Federal Highway Administration, Department of Trasportation, Washington, 1972.

Rossman LA, et. al., *"Modeling Chlorine Residuals in Drinking-Water Distribution Systems"*, Journal of Environmental Engineering, **120**(4), 803-820, 1994.

Rossman LA, et. al., *"Modeling Disinfectant Residuals in Drinking-Water Storage Tanks"*, Journal of Environmental Engineering, 752-755, 1995.

Saunier BM, et. al., *"The kinetics of breakpoint chlorination in continious flow systems"*, Water Technology/Quality, Journal AWWA, March, 1979, p 164 - 172

Savluk OS, *"Methods of intensifying the antimicrobiel effect of disinfectants"*, Khiniya I Tekhnologiya Vody, Vol. 4, No. 1, 1983, p 79 – 82

Sergi G, et. al., *"Diffusion of Chloride and Hydroxyl Ions in Cementious Materials Ex-posed to a Saline Environment"*, Magazine of Concrete Research, **44**(158), 63-69, 1992.

Shutie X, *"Summer School on Flow and Transport in Porous Media"*, World Scientific, Singapore, 1992.

Skoog DA and Leary JJ, *"Principles of Instrumental Analysis"*, Fourth edition, 1992, p 110.

Softflo cc, *"Flo++"* Users manual, 1999

Swawyer CN and McCartty PL, *"Chemistry for Environmental Engineering"*, 3rd ed., New York, 1978, McGraw Hill Book Company, p 77 - 80, 385 – 394

Tang L, *"A Simple Method for Preparig Reference Concrete Containing Chlorides"*, Chlo-ride Penetration into Concrete Structures - Nordic Miniseminar, edited by L.-O. Nilsson, Publication No. P-93:1, Division of Building Materials, Chamers University of Technol-ogy, 1993.

Tang L, *"Chloride Binding Capacity and Binding Isotherms of OPC Pasters and Mor-tars"*, Cement and Concrete Research, 23, 247-253, 1993.

Tang L, et al, *"A New Approach to the Determination of Pore Distribution by Pene-trating Chlorides into Concrete"*, Cement and Concrete Research, 25(4), 695-701, 1995.

Tang L, et. al., *"Rapid Determination of the Chlorine Diffusivity in Concrete by Applying an Electrical Field"*, ACI Material Journal, **49**(1), 1992.

Trulear MG and Characklis WG, *"Dynamics of biofilm processes"*, Journal WPCF, Vol. 54 No. 9, Sept., 1982, p 1288 – 1300

Trussel RR, et al, *"Rational design of chlorine contact facilities"*, Journal WPCF,April, 1977

Valentine RL, et. al., *"Evaluation of a Chloramine Decomposition Model Incorporating General Acid Catalysis"*, Wat. Res., Vol. 22 , No. 9, 1988, Great Britain, Pergamon Press plc, p 1147 – 1153

Van der Merwe SW, *"The purification and quality of potable water supplied by the Rand Water Board"*, 1978

Van der Walt JJ, et al, *"The simulation of flow patterns in the Daleside Reservoirs"* Report to Rand Water, 1999

Van der Walt et JJ, al, *"The simulation of flow patterns in the Lagerand Reservoir"* Report to Rand Water, 1998

Van der Wende and Characklis, *"Drinking Water Microbiology, Progress and resent Development"*, Springer-Verlag, New York, p 249 – 267, 470 - 473

Vasconcelos JJ, et. al., *" Kinetics of chlorine decay"*, Journal AWWA, Vol. 89, Issue 7, July 1997, p 54 - 62

Vasconcelos JJ, et. al., *"Kinetics of chlorine decay"*, Journal AWWA, Vol. 89, Issue 7, July 1997, p 54 - 62

Versteeg HK, et al, *"An Introduction to Computational fluid Dynamics"*, Longman, England, 1998, p 1 - 9

Viljoen OJ, et al, *"The prediction for chlorine decay from potable water in pipeline systems"*, Report to the water Reset Commission by Rand Water and Rand Afrikaans University, 1997, p 2-1 - 2-13, 4-1 - 4-10

White GC, *"Handbook of chlorination and alternative Disinfectants"*, New York, 1992, Van Nostrand, p 386 – 399

Zhou H, et. al., *"Modeling of Dissolved Ozone Concentration Profiles in Bubble Columns"*, Journal of Environmental Engineering, **120**(4), 1994.

ANNEXURE A

MATERIALS AND METHODS

1 Water sources tested

The experimental work in this study was conducted on water of four different reservoirs, e.g. Brakpan (throughflow), Daleside (balancing), Forest Hill (throughflow), Isando (break pressure tank). The reason for testing these different reservoirs was to includes a variety of variable's such as: differing distances from the pumping stations, different types of circulation in the reservoirs and different chlorine species present.

Table A1: Water Quality of reservoir water

Water quality parameters	Reservoir water
pH	8,26
Conductivity (mS/m)	25,8
Turbidity (NTU)	0,58
mo-Alkalinity (mg/ℓ $CaCO_3$)	94,0
pp – Alkalinity (mg/ℓ $CaCO_3$)	9,0
Ca Hardness (mg/ℓ $CaCO_3$)	89,7
Mg Hardness (mg/ℓ $CaCO_3$)	25,7
Total Hardness (mg/ℓ $CaCO_3$)	115
Free available chlorine (mg/ℓ)	0,65
Total chlorine (mg/ℓ)	0,89

1.1 On-site experimental evaluation

Because chlorine decay is dependent on time, temperature, the medium and way the samples are stored, most of the analysis were conducted on site. These analyses were free available chlorine, total chlorine, pH, turbidity, temperature and conductivity.

1.2 Laboratory batch tests

To bring the whole project in line with the objectives of the study, laboratory batch tests were conducted to determine the decay rate constants and reaction orders of the different water types of the different reservoirs.

1.3 Frequency of testing

Two test series on microbiological quality and chlorine contents, one summer and one winter series were conducted on each reservoir. The wall and bottom effects on the chlorine decay were conducted over a period of 13 weeks where test work were done every second week. Atmospheric studies were done twice, during winter, and summer.

2 Analytical test procedures and reagents

2.1 Chlorine dosing

A chlorine solution was prepared with an initial concentration of 200 mg/ℓ to ensure that the volume of the 100 mℓ water samples needed to test for free and combined chlorine residuals were not increased by more than 5% on addition of the chlorine solution.

Each water sample was treated with a known volume of the chlorine solution to ensure that enough residual chlorine would be present to conduct the tests over desired period of time.

2.2 The DPD ferrous titrimetric method for determination of free and combined chlorine residuals

The DPD ferrous titrimetric method for determination of free and combined chlorine residuals in water are describe below in accordance with Standard Methods for the examination of water and wastewater, 17th edition (APHA et al, 1996).

2.3 Reagents

See Standard Methods for the examination of water and wastewater, 17th edition (APHA et al, 1996).

3. Measurement of chlorine decay

Chlorine free water samples are treated with a known volume of the chlorine solution. Contact times of up to 8 hours are going to be used. After the desired time period elapse, the water sample is tested to determine residual chlorine in the sample. Samples were tested on the hour, every hour for 8 hours, on the second day every three hour and the third day very four hours.

This chlorine residual was calculated by the DPD ferrous titrimetric method.

Graphs were drawn in the end after all the test are conducted, to calculate the chlorine decay rate constant for each specific sample.

4. Measurement of chlorine losses due to water age

To determine the losses due to water age the following chlorine decay experiments were done:

Measure sample temperature and pH. Keep sample and sample portions at desired temperature and protect from light throughout the procedure. If pH adjustments are desired, prepare a blank distilled water containing the same amount of buffer as sample. Carry blank throughout the procedure.

Determine the demand of the required sample. (That is the free chlorine concentration at breakpoint after 20min.)

For k and n value determinations:

Prepare three samples of water and dose with the initial demand + X mg/ℓ Cl_2, where X = 2,4, and 8mg/ℓ Cl_2 respectively. Make sure samples are sufficient for at least eight tests. Titrate every hour for eight hours and complete the calculations (section 3.3).

5. Measurement of influence of concrete on chlorine decay

Concrete blocks submerge in different chlorine concentration solution in 10 l aspirators.

a) Sampling

Concrete blocks with known dimensions (height, top diameter, bottom diameter and weight) were suspended in a service reservoir. After a known time (± 12 - 50 weeks) the block was transported in water from the reservoir to the laboratory, where the effect of the concrete block on chlorine was tested. New concrete blocks were used as the control. The reason for this was to examine the age factor.

b) Method

A fresh concrete block (with known dimensions) was submerged in a 10ℓ aspirator filled with 10ℓ distilled water and dosed with a known chlorine concentration. As a control an aspirator with 10ℓ distilled water without a concrete block was used. The same chlorine concentration was maintained in the control. Six different concentrations were used, each with its own control and at a specific temperature, being 18°C. The aspirator was stirred before any measurements were taken. Chlorine concentrations were determined with the N,N-diethyl-p-phenylenediamine (DPD) Ferrous Titrimetric Method. The chlorine concentration determinations were conducted at sixty-minute intervals for approximately fifty-five hours.

Series 2:

To test the effect of older concrete the same experiment as above was repeated with aged concrete blocks.

Concrete blocks submerge in an indigo solution.

Fresh new concrete blocks with known dimensions (height, top diameter, bottom diameter and weight) were submerged in 1ℓ beakers with an indigo solution, covered with foil and stirred at a speed of 1 - 3rpm. After 12 hours the blocks were rinsed off with distilled water so that all the indigo that did not undergo sorption was eliminated. The blocks were then suspended in 250mℓ distilled water and stirred while UV measurements were taken with a 10mm optic fibre cell on a Cary 50 Concentration UV-visible Spectrophotometer. Readings were taken at varying intervals (5 sec, 10 sec and 60 sec) until readings stabilised, over a period of 3 to 4 hours. The concrete block was put into a fresh indigo solution for further 12 hours and UV readings obtained. This process was repeated for five weeks to test the effect of the ageing process of concrete

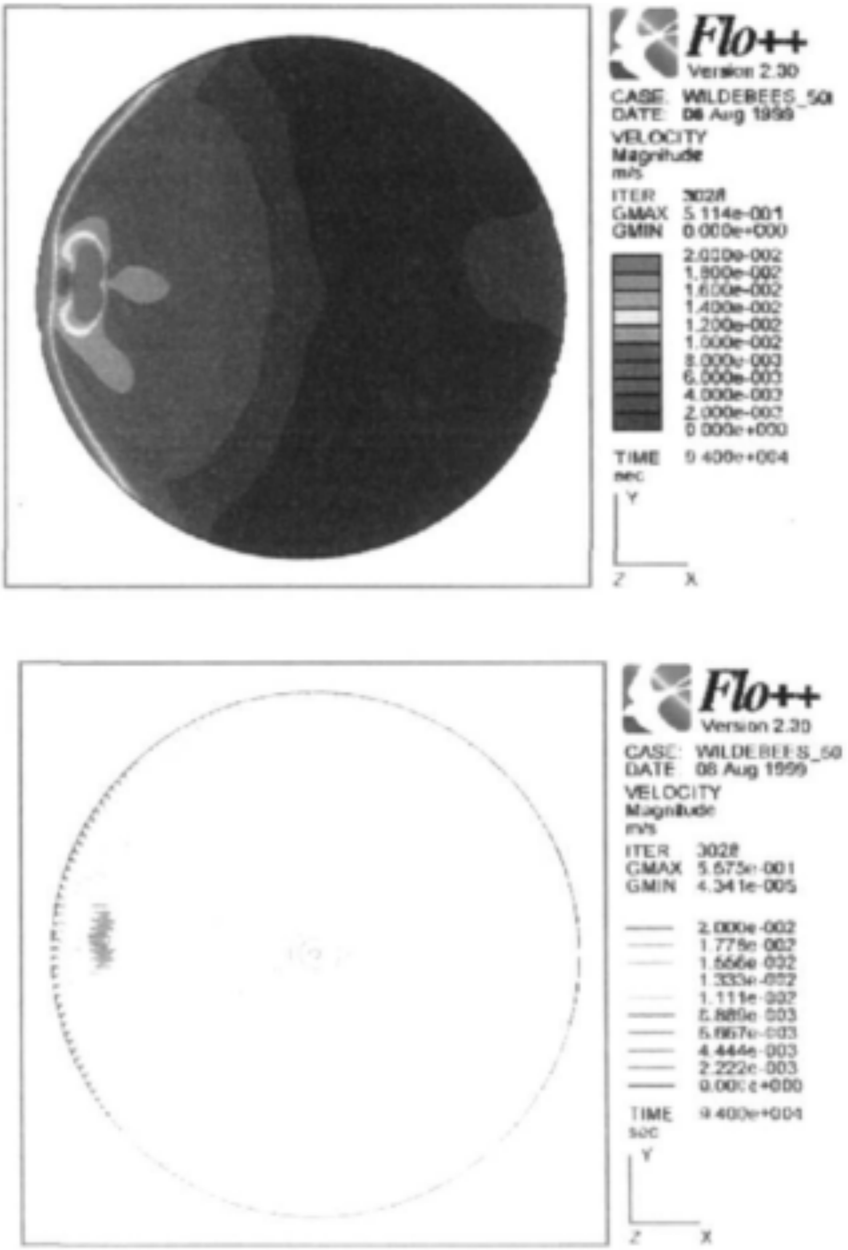
Series 2:

The same experiment was then performed using aged concrete blocks.

ANNEXURE B

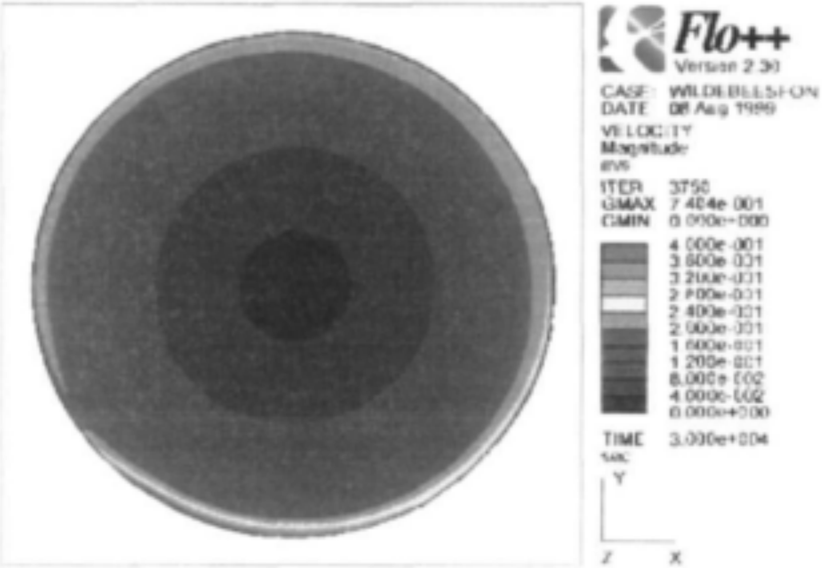
ANNEXURE B – FLOW PROFILES

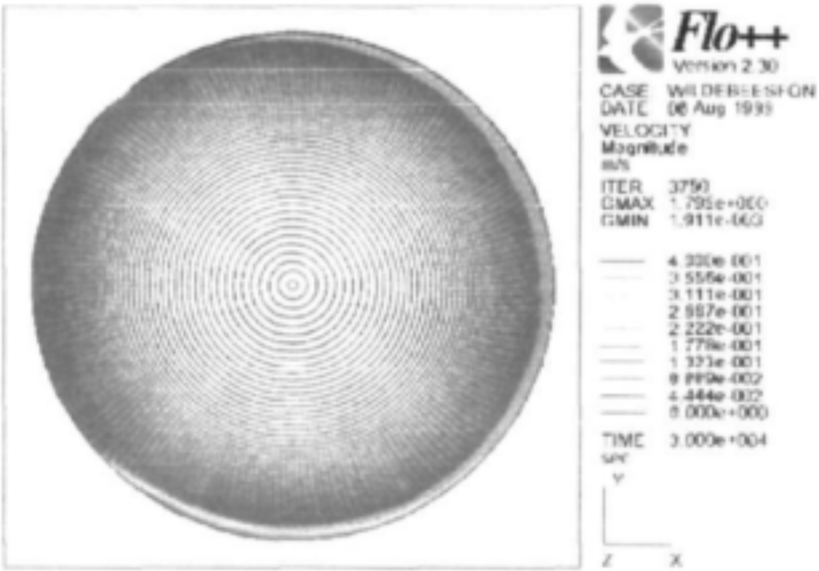
Figure A1 – Typical flow patterns in a existing reservoir (at mid depth)



ANNEXURE B – FLOW PROFILES

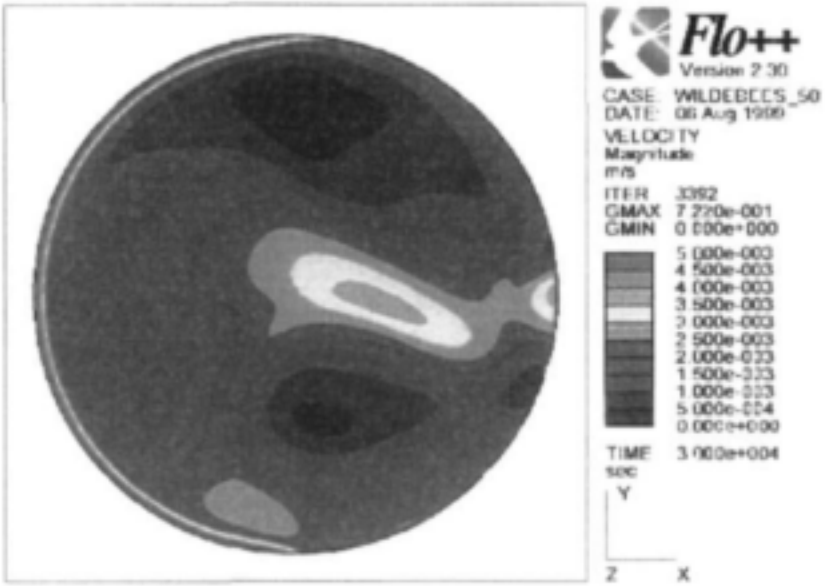
Figure A2 – Typical flow patterns in a cyclone arrangement

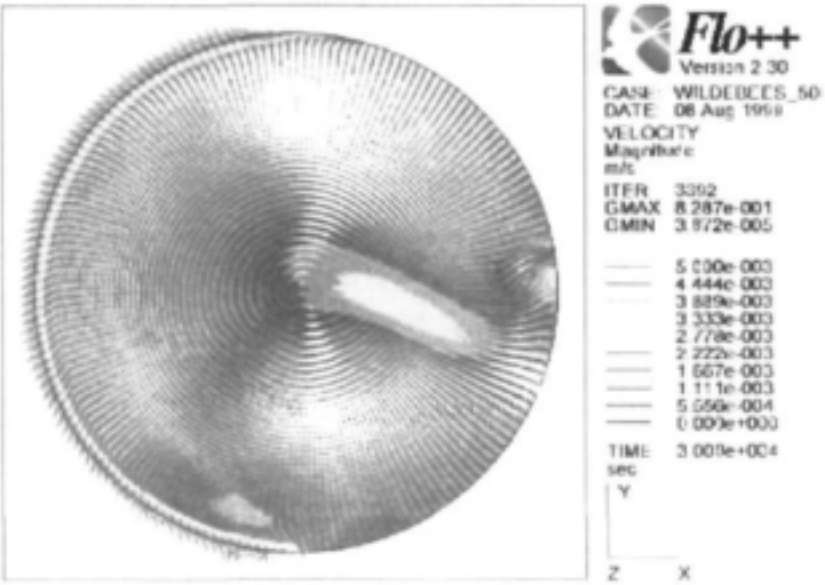




ANNEXURE B – FLOW PROFILES

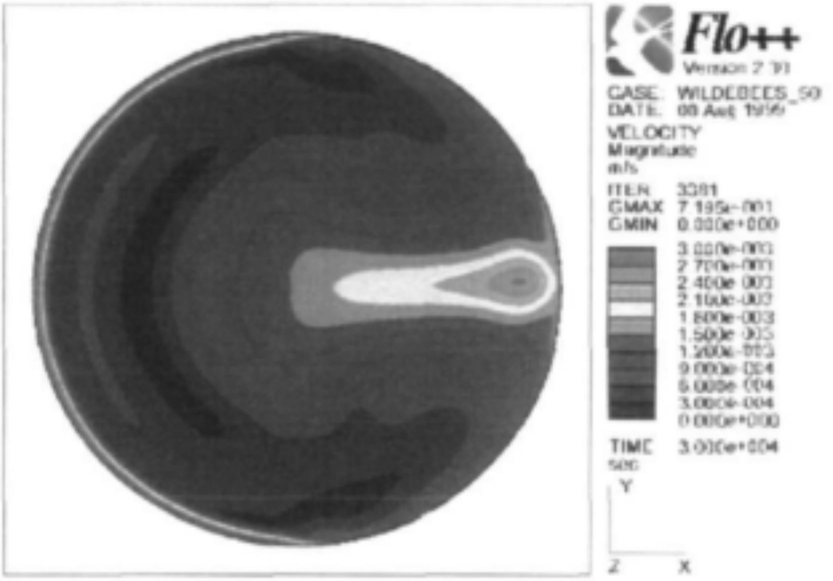
Figure C1 – Typical flow patterns in a one-directional manifold arrangement

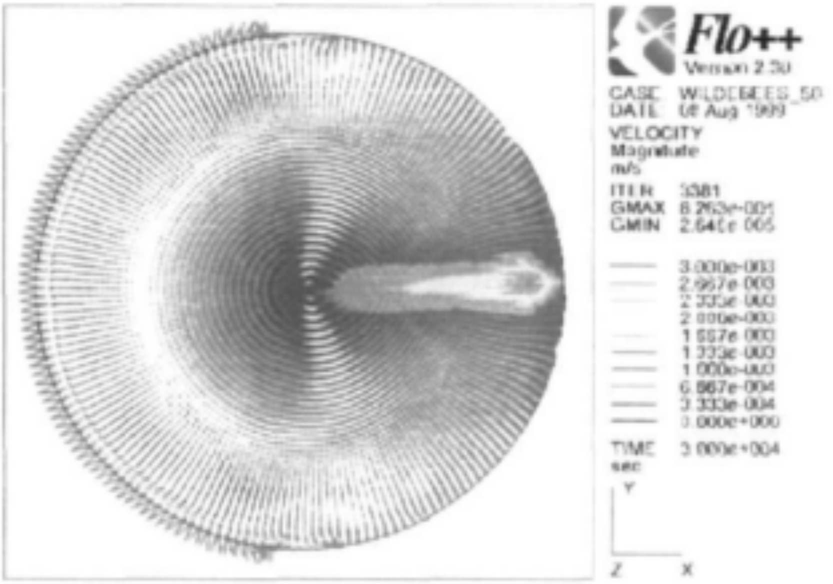




ANNEXURE B – FLOW PROFILES

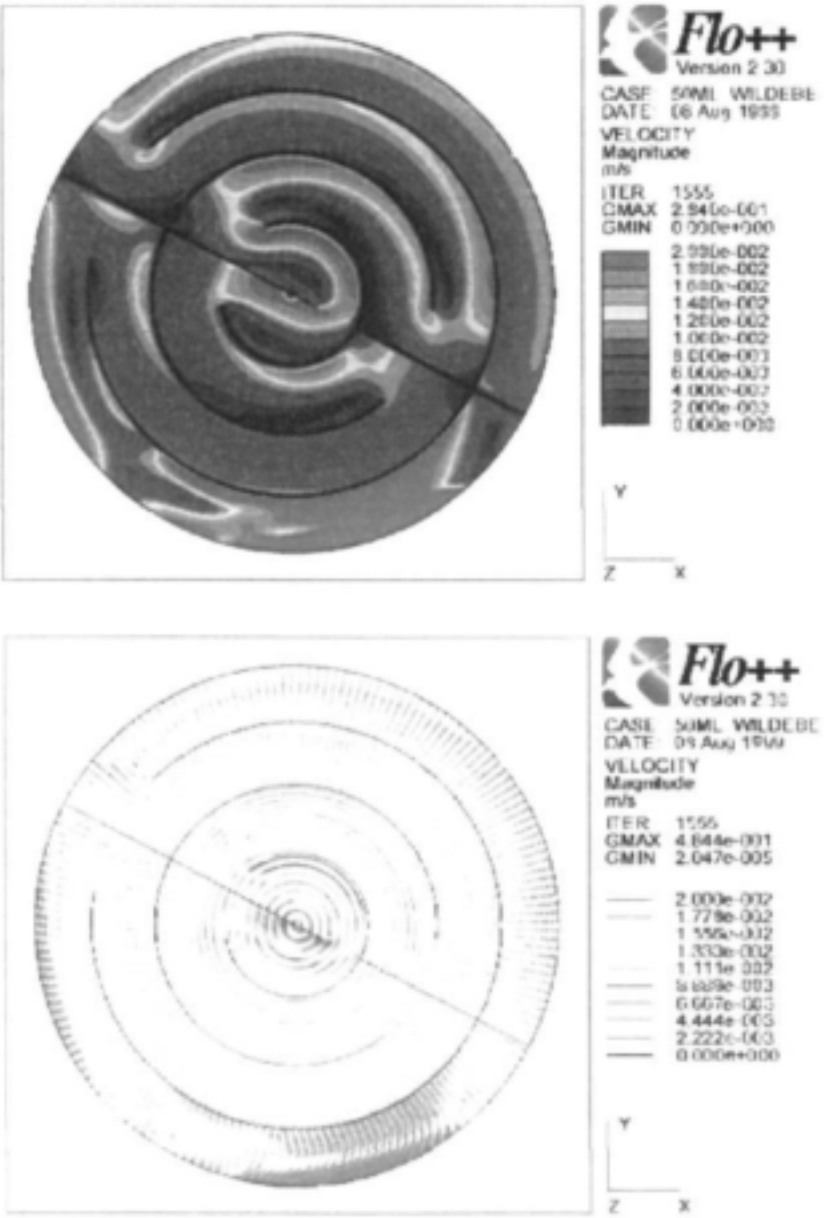
Figure C2 – Typical flow patterns in a bi-directional manifold arrangement.

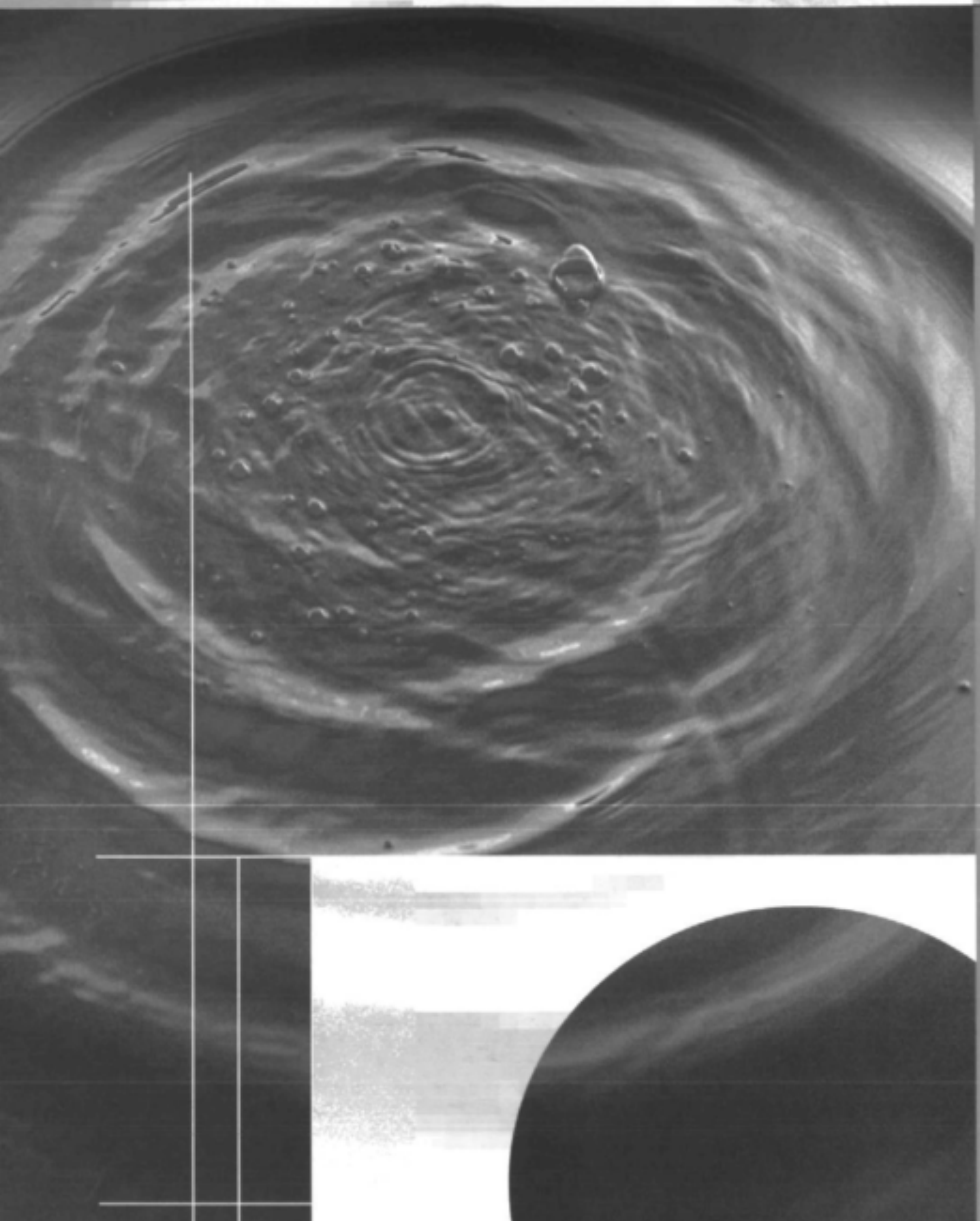




ANNEXURE B – FLOW PROFILES

FIGURE D1 – Typical flow patterns for a concentric baffle arrangement





Water Research Commission
PO Box 824, Pretoria, 0001, South Africa
Tel: +27 12 330 0340, Fax: +27 12 331 2565
Web: http://www.wrc.org.za

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