CHAPTER 4

LABORATORY INVESTIGATIONS

RESULTS AND DISCUSSIONS

Results were analysed to establish the effect of chlorination, pH and coagulants on;

- the removal of different algal groups and species
- the removal of chlorophyll-*a* and
- the formation of THMs.

4.1 THE REMOVAL OF DIFFERENT ALGAL GROUPS AND SPECIES

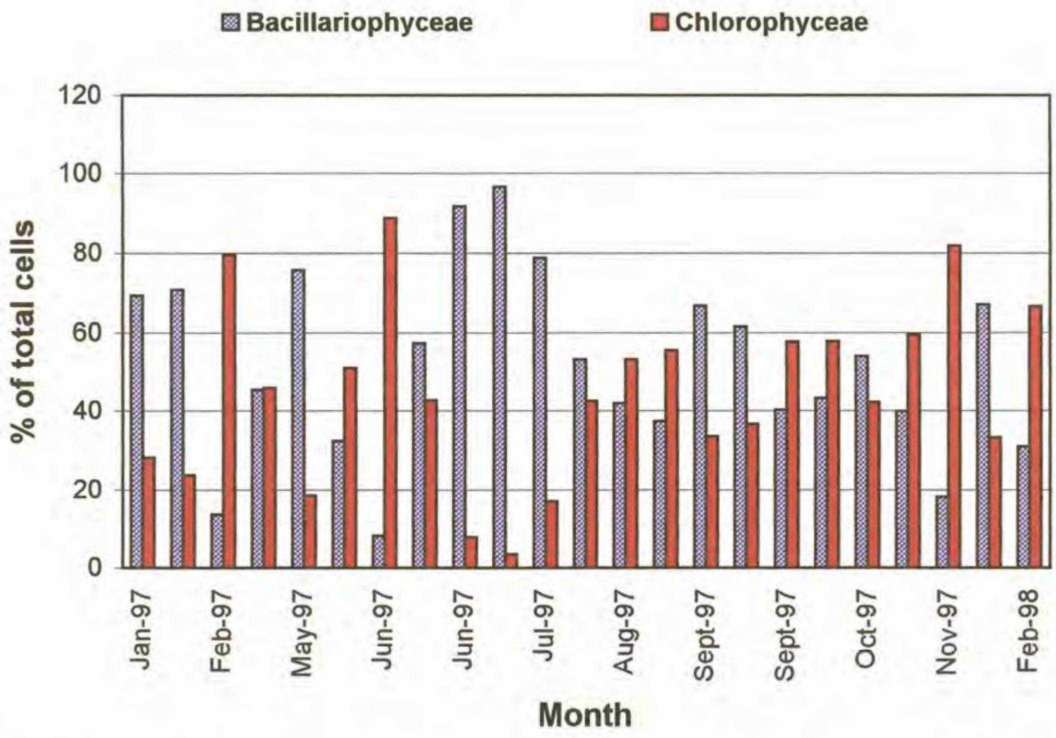

Figure 12: The presence of Bacillariophyceae and Chlorophyceae expressed as a percentage of the total algal cells present in the raw water.

Six different algal groups were found to be present in the Vaal River for most of the time. This is in confirmation with the findings by Visser (1997). Bacillariophyceae and Chlorophyceae (green algae) were the two dominant groups present for the period January 1997 to February 1998.

The occurrence of these two groups, expressed as a percentage of the total cells, is shown in Figure 12. Bacillariophyceae dominated during January 1997, followed by an increase in Chlorophyceae during February 1997. A dominance of Bacillariophyceae occurred during June and July 1997 with an increase in green algae and diatoms during September 1997. The pattern during early 1998 showed similarity to that observed for the same period during 1997.

4.1.1 THE REMOVAL OF BACILLARIOPHYCEAE

Bacillariophyceae cells in the raw water varied between 215 and 6420 cells/ml during the period January 1997 to February 1998. The maximum concentration of cells was observed during October 1997.

The role of chlorination, pH and coagulants in the removal of Bacillariophyceae is illustrated in Figures 13 to 20.

The effect of chlorination

Figure 13 shows that, although chlorination proved to be of a slight advantage in the removal of Bacillariophyceae, removal rates (calculated as monthly averages) of approximately 90% could be obtained by coagulation and sedimentation, without implementing chlorination. Mouchet and Bonnélye (1998) reported removals of 90% with pre-chlorination, but found that removals for diatoms never exceeded 85% without pre-chlorination. The average removal rate of 40-80% for diatoms (Bacillariophyceae), as reported by Mouchet and Bonnélye (1998), is much less than that obtained in this study by sedimentation.

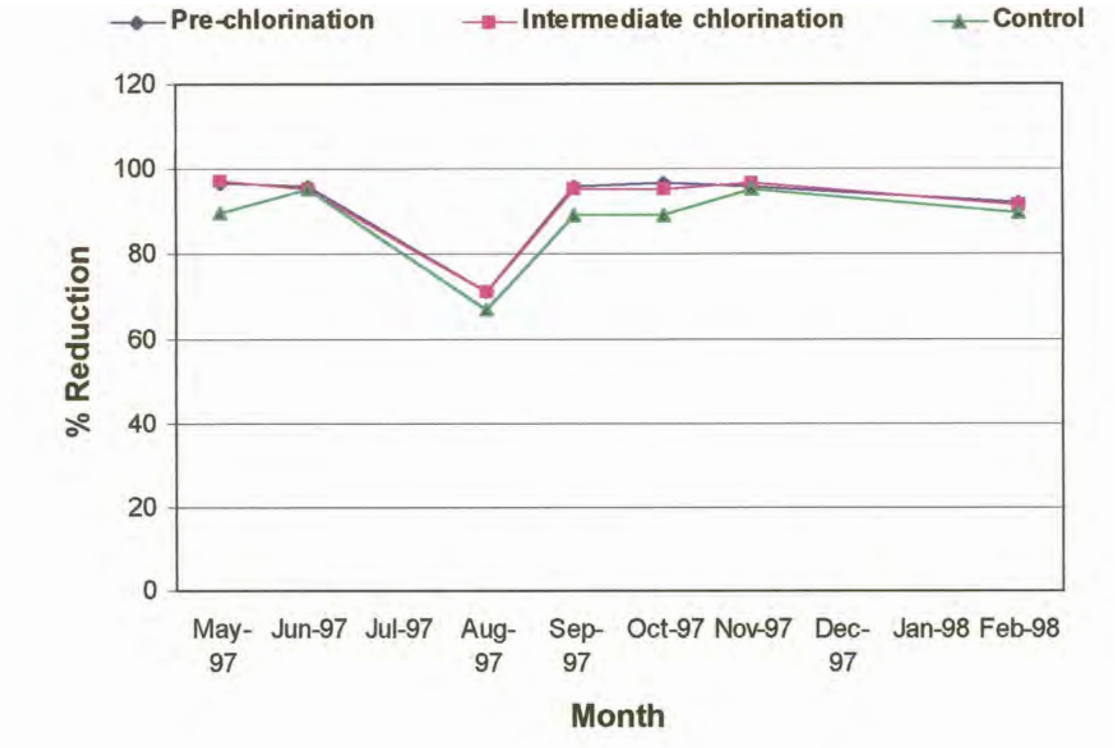

Figure 13: The effect of chlorination on the removal of Bacillariophyceae from the raw water by coagulation and sedimentation.

The increase in cell numbers, which occurred during September and October 1997, were responsible for the lower reductions obtained in the control samples during this period. This indicates that chlorination enhances the removal of Bacillariophyceae by coagulation and sedimentation when cell numbers increase.

The cell numbers in the settled samples were reduced by more than 95% by filtering the supernatant through a Whatman no. 1 filter paper (Figure 14). This implies that in total, even without chlorination, approximately 99 % of the cells could be removed. Better reductions in cell numbers were obtained in the samples where intermediate chlorination was applied.

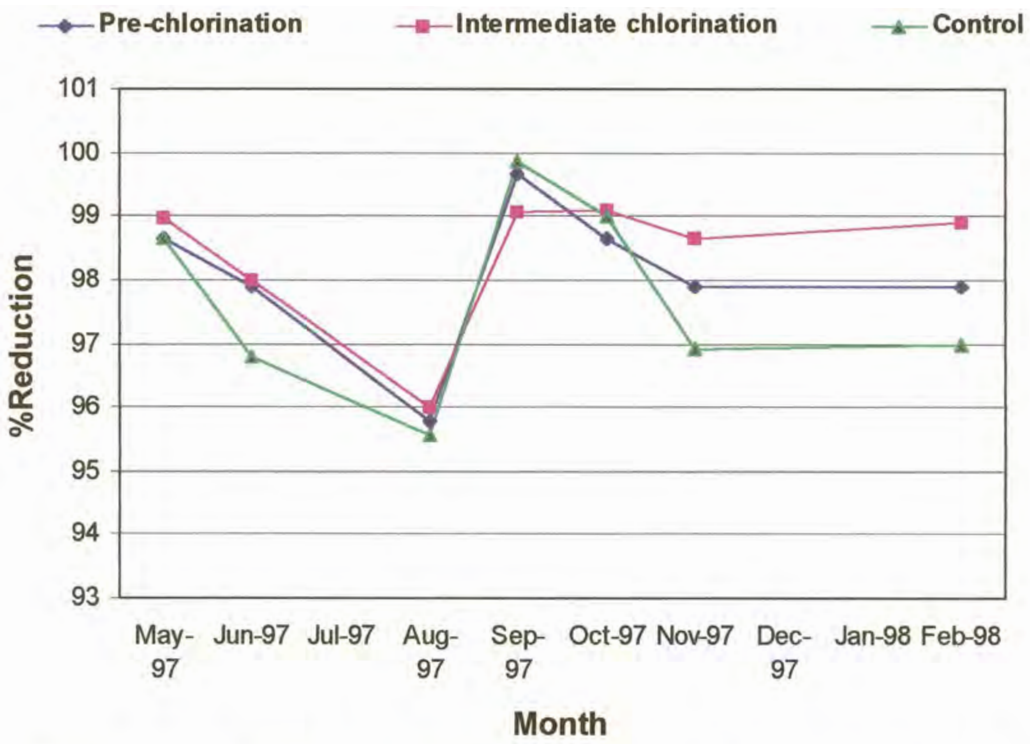

Figure 14: The removal of Bacillariophyceae from settled samples by means of filtration.

The removal rates of two Bacillariophyceae species namely *Cyclotella* and *Nitzschia* are shown in Figures 15 and 16.

Cyclotella

Cyclotella was the dominant Bacillariophyceae species present during this study. Cell numbers varied between 90 and 6210 cells/ml. Cell numbers started increasing during September 1997 and were relatively high throughout the summer. The highest concentrations were observed during October 1997.

The effect of chlorination on the removal of *Cyclotella* cells is shown in Figure 15.

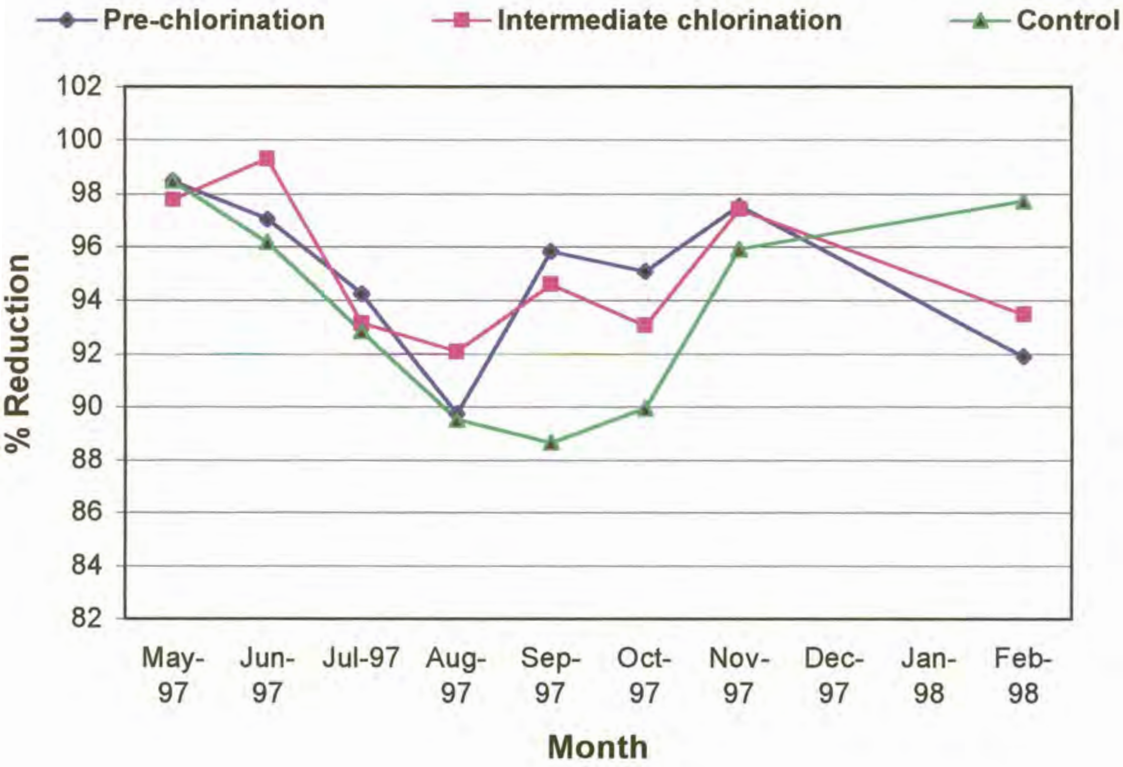

Figure 15: The effect of chlorination on the removal of *Cyclotella* cells from the raw water by coagulation and sedimentation.

This graph indicates that on average, in excess of 90% of *Cyclotella* cells were removed by coagulation and sedimentation without chlorination. This is in contradiction with removal rates of 10 – 70% for *Cyclotella* cells mentioned by Mouchet and Bonnélye (1998). Better results were obtained with pre-chlorination when cell counts increased during September and October 1997. The removal rates obtained by intermediate chlorination during this time were however very similar to those obtained by pre-chlorination.

Figure 16 indicates that, although intermediate chlorination slightly enhances the removal of cells by filtration, removal rates in excess of 97% could be obtained in all the samples.

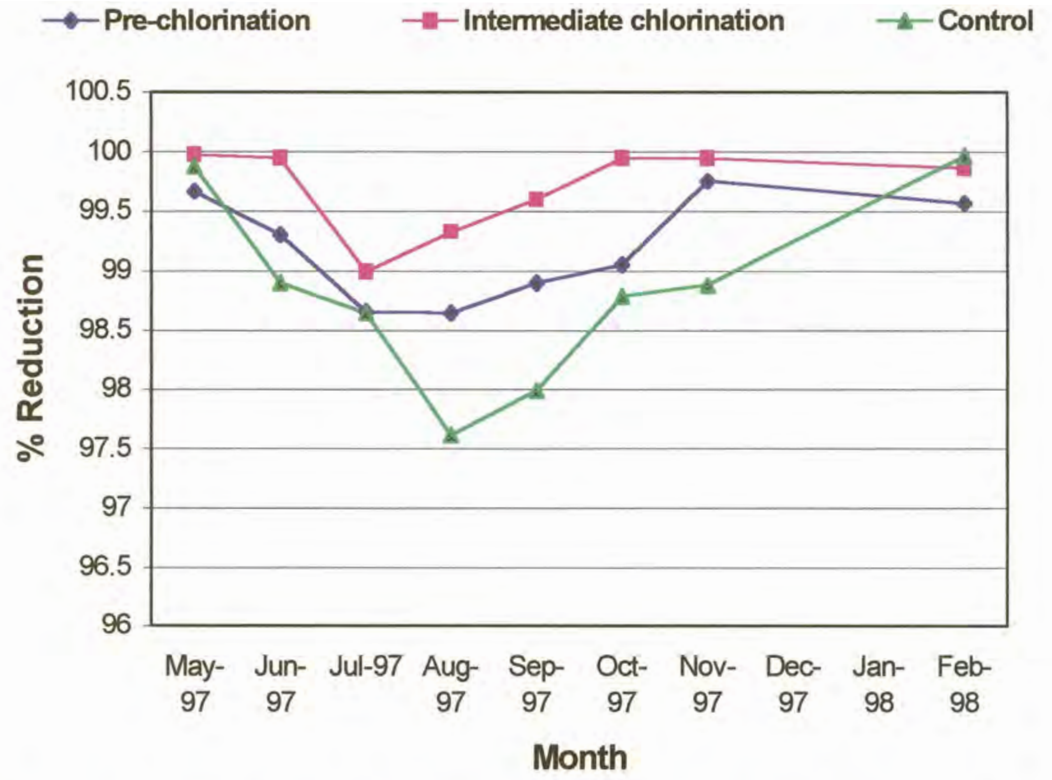

Figure 16: The effect of chlorination on the removal of *Cyclotella* cells from settled samples by means of filtration.

Nitzschia

Figure 17 indicates that chlorination was needed for the removal of *Nitzschia* cells for most of the time.

Cell counts in the river varied between 100 and 328 cells/ml. The poor removals obtained during August and October 1997 coincided with the highest cell numbers observed.

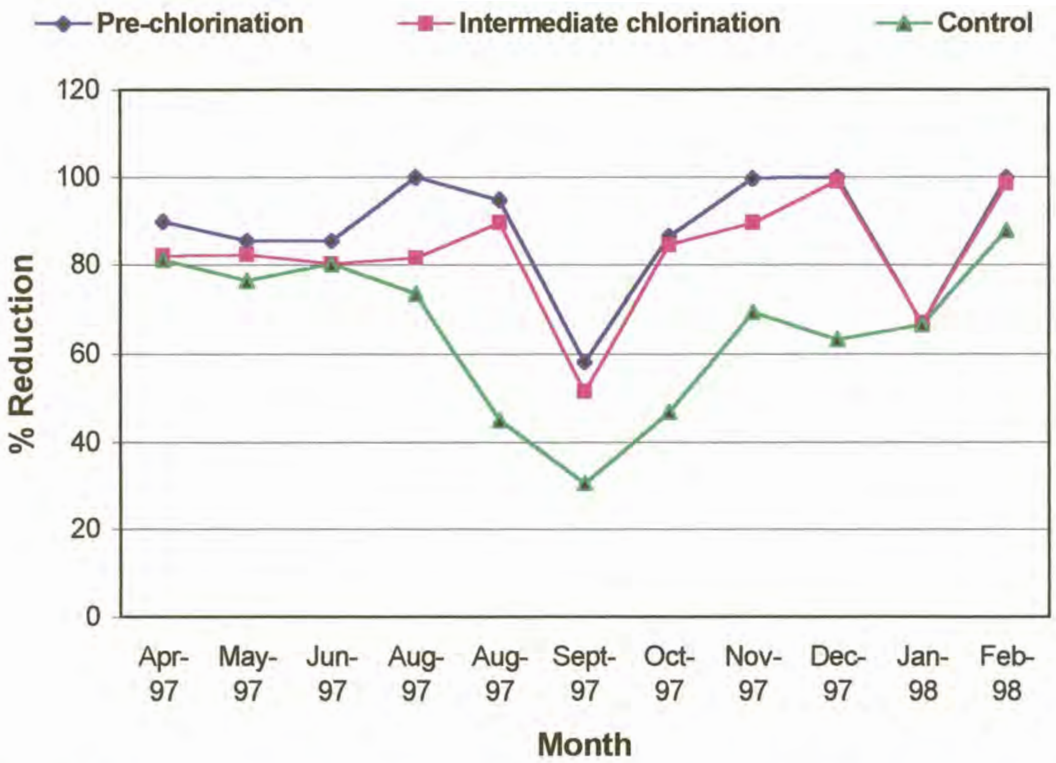

Figure 17: The effect of chlorination on the removal of *Nitzschia* cells. by coagulation and sedimentation.

Discussion

The cells of the Bacillariophyceae family are enclosed by protective cell walls consisting mainly of silica (Wetzel, 1983). These protective walls could cause diatom cells to be more resistant to chlorine. Including chlorination as a treatment process does thus not necessarily contribute to an increased removal of the Bacillariophyceae species. In most cases removals of > 90% were already achieved without pre-chlorination, causing any possible effect of chlorination to be less significant. It must be kept in mind that pre-chlorination was introduced before the removal of any suspended and/or chlorine-consuming substances, and in this way also caused the effect of chlorine to be less significant.

The poorer removal rates obtained when pre-chlorination was excluded during the presence of high cell numbers, as illustrated in Figures 13 to 17, indicate that pre-chlorination could be an attractive option under such circumstances. Removal rates obtained by intermediate chlorination were however very similar to those obtained by pre-chlorination. The removal of chlorine-consuming substances prior to chlorination positively affects the role of chlorine and with reductions in excess of 96% being obtained with intermediate chlorination, this option becomes more attractive and cost-effective than pre-chlorination.

Although chlorination improved the cell removal rates obtained by settling, sufficient reductions could be achieved by filtration of the settled control samples to compare favourable with the reductions in the chlorinated samples. The total removals obtained after filtration indicate that Bacillariophyceae can be removed adequately without incorporating chlorination in the treatment process. Unless the exclusion of chlorination, when cell numbers are high, impacts negatively on filter run times during full-scale operation, the chemical cost can be reduced significantly by omitting chlorination.

The size range of *Cyclotella* cells varies between 5 and 50 µm (Bold and Wynne, 1985) and this characteristic contributes to their better removal in comparison with smaller species. *Nitzschia* sp. is a mobile diatom (Wetzel, 1983) and its mobility causes this species to be more difficult to remove. Chlorination can inhibit the physiological activities of the *Nitzschia* cells, resulting in immobility, and thus more susceptible to removal by sedimentation.

The total cost for chlorine used in the process (pre-oxidation and disinfection) can be reduced by approximately 50% by excluding pre-chlorination when Bacillariophyceae is dominant. Should chlorination however have to be incorporated, intermediate chlorination could be used instead of pre-chlorination. This will reduce the cost for chlorine with approximately 25 - 30 %.

The effect of pH

The effect of pH (9,8) on the efficiency of chlorine in removing *Cyclotella* cells is shown in Figure 18. (The addition of lime is indicated by + and – is used to indicate that no lime was added).

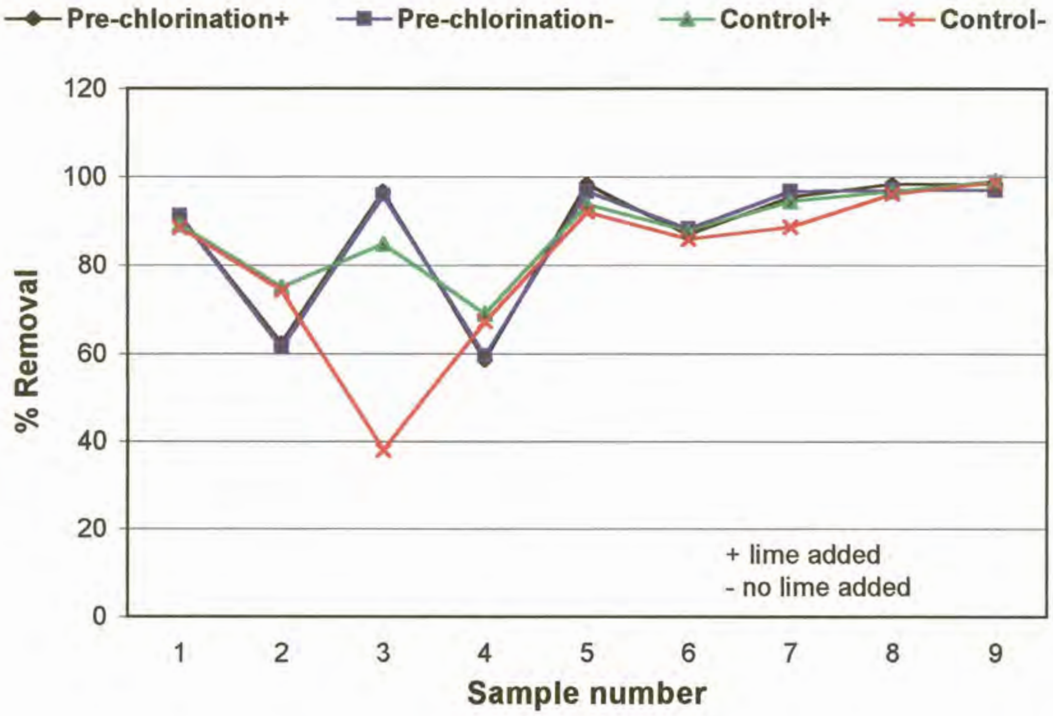

Figure 18: The effect of pH (9,8) on the efficiency of chlorine in the removal of *Cyclotella* cells.

It is clear from this graph that the increased pH has no effect on the efficiency of chlorine in the removal of *Cyclotella* cells.

Discussion

The pH-dependency of chlorine in killing micro-organisms as described by White (1992) and Steynberg (1994) seems not to play any role in the removal of *Cyclotella* cells. As these cells are relatively easy to remove (as illustrated in Figures 13 to 16), with high removal rates obtained, other influences are less significant.

The effect of coagulants

Cyclotella

Figure 19 shows the improvement in the removal of *Cyclotella* cells which was obtained by increasing the $FeCl_3$ dosage or by adding 1 mg/l of poly-electrolyte as secondary coagulant.

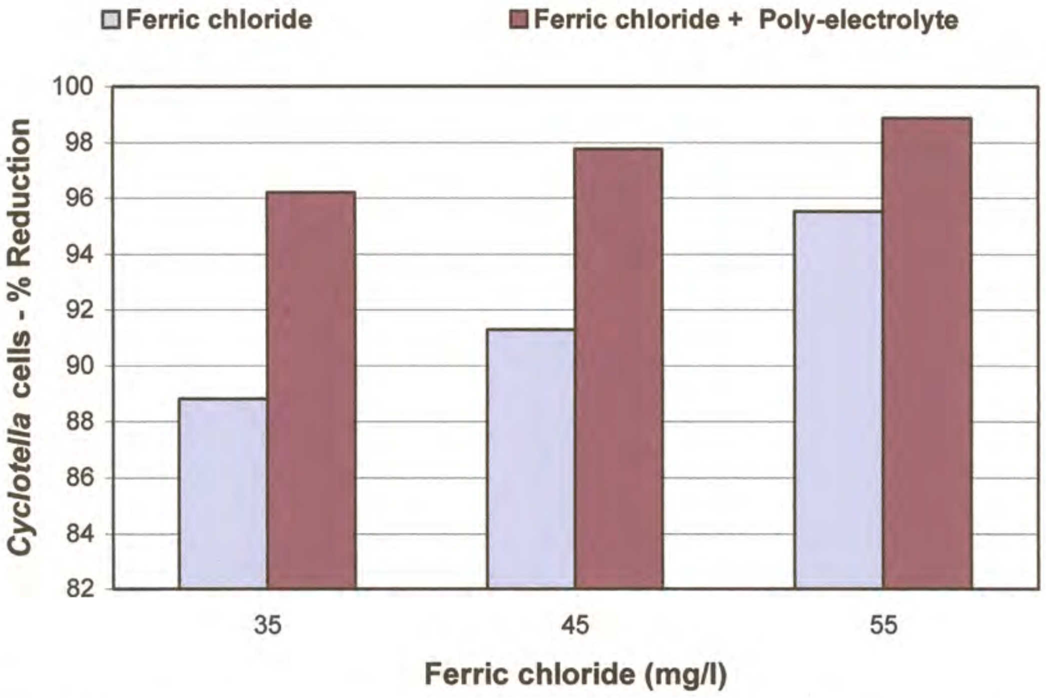

Figure 19: The effect of increased concentrations of $FeCl_3$ dosages and poly-electrolyte on the removal of *Cyclotella* cells (no chlorination).

Figure 19 shows that:

(i) The removal rate of *Cyclotella* cells was improved by a relatively small amount of approximately 6,5% by increasing the $FeCl_3$ dosage from 35 to 55 mg/l.

(ii) The addition of 1 mg/l of poly-electrolyte as secondary coagulant to the $FeCl_3$ dosage of 35 mg/l, improved the cell removal by approximately 7,2%.

(iii) At a $FeCl_3$ dosage of 55 mg/l the cell removal rate was increased by approximately 3,5% by the addition of 1 mg/l of poly-electrolyte.

Nitzschia

The enhancement of the removal of *Nitzschia* cells by the addition of a poly-electrolyte as secondary coagulant, is shown in Figure 20.

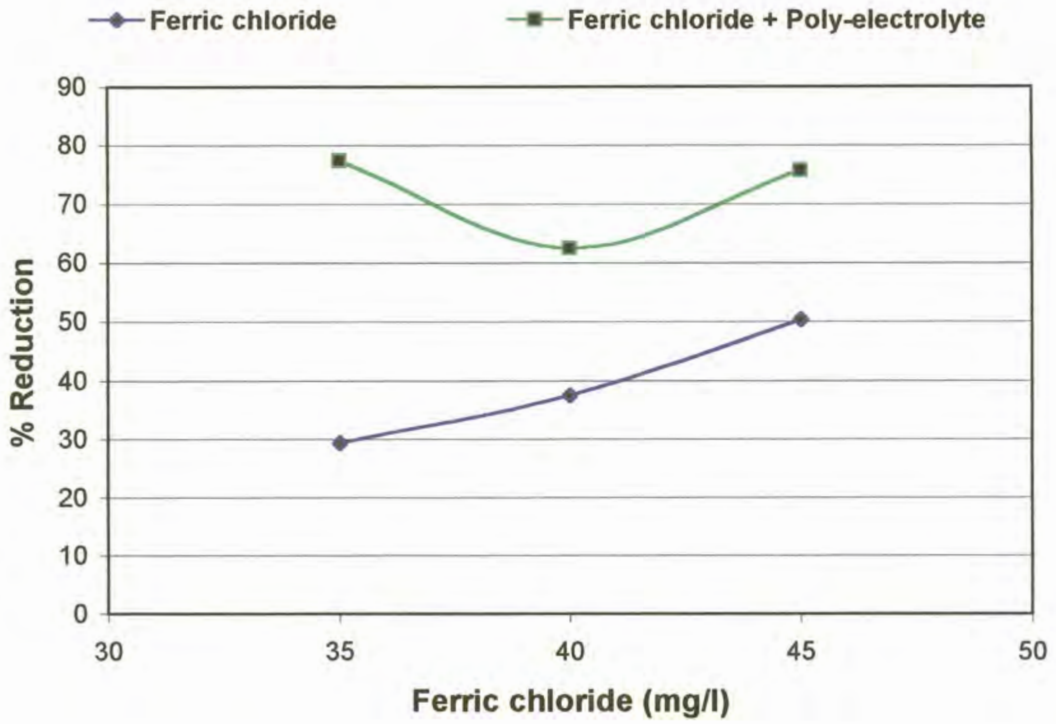

Figure 20: The effect of poly–electrolyte on the removal of *Nitzschia* cells (no chlorination).

Cell removal rates improved by an average of 20-25% by the addition of a poly-electrolyte as secondary coagulant. The improved removal rates obtained for *Cyclotella* and *Nitzschia* are in conformation with research by Basson and Pieterse (1996) and Visser (1997) who found that addition of poly-electrolytes enhances the removal of diatoms.

Discussion

The removal of algae is due to adsorption with charge neutralisation (Edzwald, 1993) and as the latter is also the main coagulation mechanism for organic polymers (Amirtharajah and O'Melia, 1990) this explains the improved removal rates obtained by the addition of a poly-electrolyte.

Almost 90% of *Cyclotella* cells were already removed when 35 mg/l of $FeCl_3$ was dosed, thus causing the effect of increased coagulant dosage to be less significant. The excretion of smaller amounts and fewer organic acids by diatoms than by green algal representatives is according to Basson and Pieterse (1996) the reason for the improvement.

The additional costs of adding 1 mg/l of poly-electrolyte to 35 mg/l of $FeCl_3$, amounts to 50% of the additional costs incurred by increasing the $FeCl_3$ dosage from 35 to 55 mg/l. The removal of *Cyclotella* cells can thus cost-effectively be improved by rather using a poly-electrolyte as secondary coagulant instead of increasing the $FeCl_3$ dosage.

Pre-chlorination enhanced the removal of *Nitzschia* (Figure 17) and as no chlorine was added in experiments illustrated in Figure 20, cell removals were poor. The improvement obtained by the addition of a poly-electrolyte was thus more significant. Chlorination is however also adversely affecting the efficiency of a poly-electrolyte in removing algal cells (Steynberg, 1994) and the significant improvement obtained by adding a poly-electrolyte could be partially due to the fact that no pre-chlorination was applied. *Nitzschia* cells are mobile due to excretions (Bold and Wynne, 1985). Adsorption coagulation (Edzwald, 1993) could be responsible for the loss of mobility of the cells and thus an improved removal rate.

Conclusions

1. Bacillariophyceae can be removed efficiently by sedimentation and filtration without chlorination, resulting in a reduction of approximately 50% in the cost for chlorine.

2. An improvement in cell removal can be obtained by including chlorination when cell numbers increase. Intermediate chlorination is however an economic substitute for pre-chlorination. By choosing this option, a reduction of 25-30% in the cost for chlorine is achievable.

3. Increasing the coagulation pH does not affect the removal rate of Bacillariophyceae when chlorination is applied.

4. Removal of *Cyclotella* and *Nitzschia* is enhanced by the use of a cationic polyelectrolyte.

4.1.2 THE REMOVAL OF CHLOROPHYCEAE

Chlorophyceae cell numbers in the raw water varied between 697 and 5370 cells/ml with the highest concentrations observed during September 1997 and February 1998.

Figures 21 to 29 illustrate the effect of chlorination, pH and coagulants on the removal of Chlorophyceae.

The effect of chlorination

The experimental data calculated as monthly averages and shown in Figure 21, indicates that a significant improvement in the removal of Chlorophyceae could be achieved by applying chlorination.

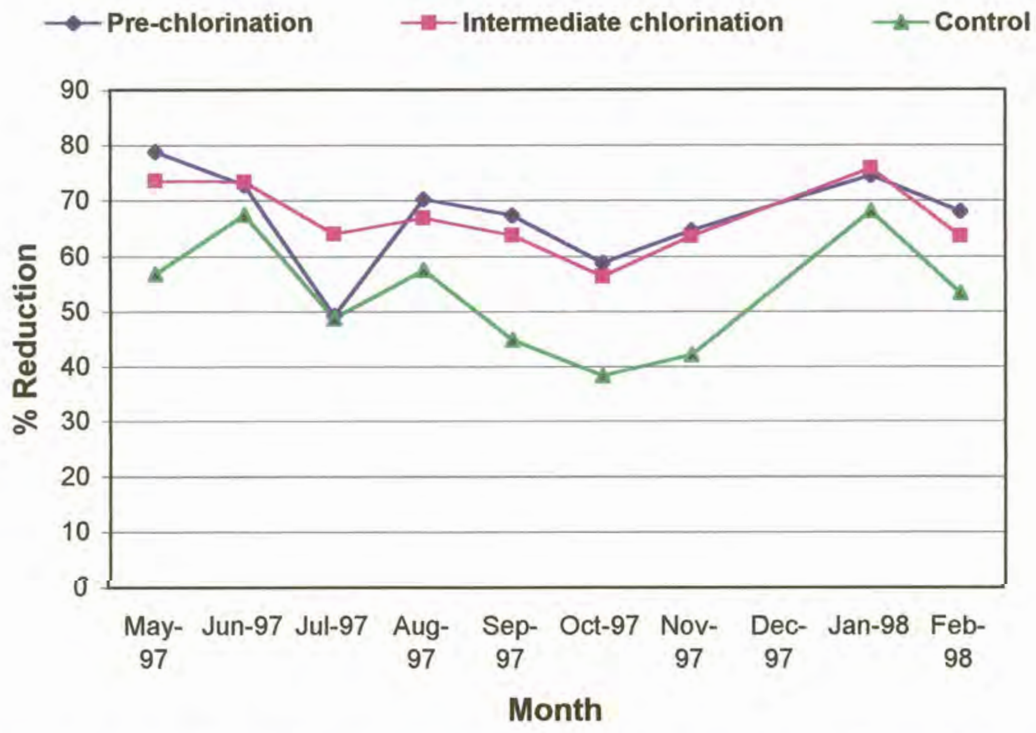

Figure 21: The effect of chlorination on the removal of Chlorophyceae by coagulation and sedimentation.

These results show that, in the chlorinated samples, the average removal rate obtained by sedimentation was less than 70% for most of the time. The average removal rate in the control samples was less than 60%, with the poorer reductions obtained when cell numbers were high (September and October1997, February 1998). These results thus show that Chlorophyceae was not effectively removed by sedimentation, even when pre-chlorination was applied.

Figure 22 shows the cell removal obtained by filtration of the settled samples. The results show that better reductions were obtained by filtration when intermediate chlorination was applied. The removal rates obtained by filtration of the settled control samples were less than 90%.

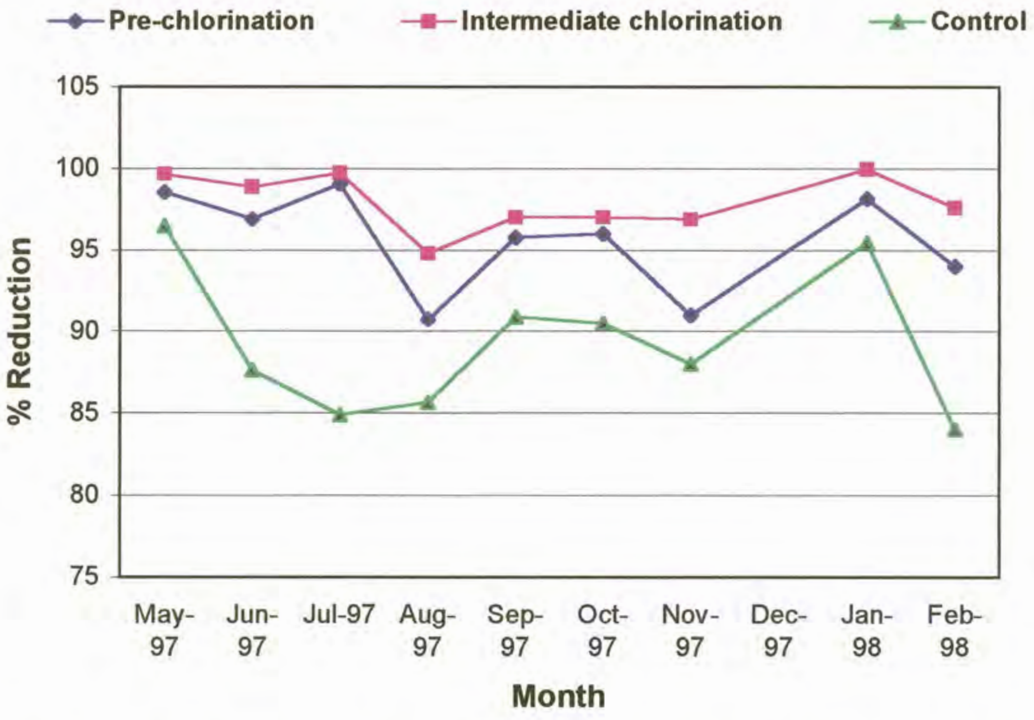

Figure 22: The removal of Chlorophyceae from settled samples by means of filtration.

Chlorella

Chlorella was the most dominant Chlorophyceae species present with cell numbers varying between 25 and 4000 cells/ml. The maximum concentration was present during February 1998 and contributed to 87% of the total Chlorophyceae population.

Figures 23 and 24 show the removal of *Chlorella* cells obtained during laboratory investigations. Less than 65% of the cells could be removed by coagulation and sedimentation for most of the time. The effect of chlorination appeared to be more prominent when cell numbers were high, as was the case from September to November 1997. The results also indicate that the removal rates obtained with intermediate chlorination were at times very close to those obtained with pre-chlorination.

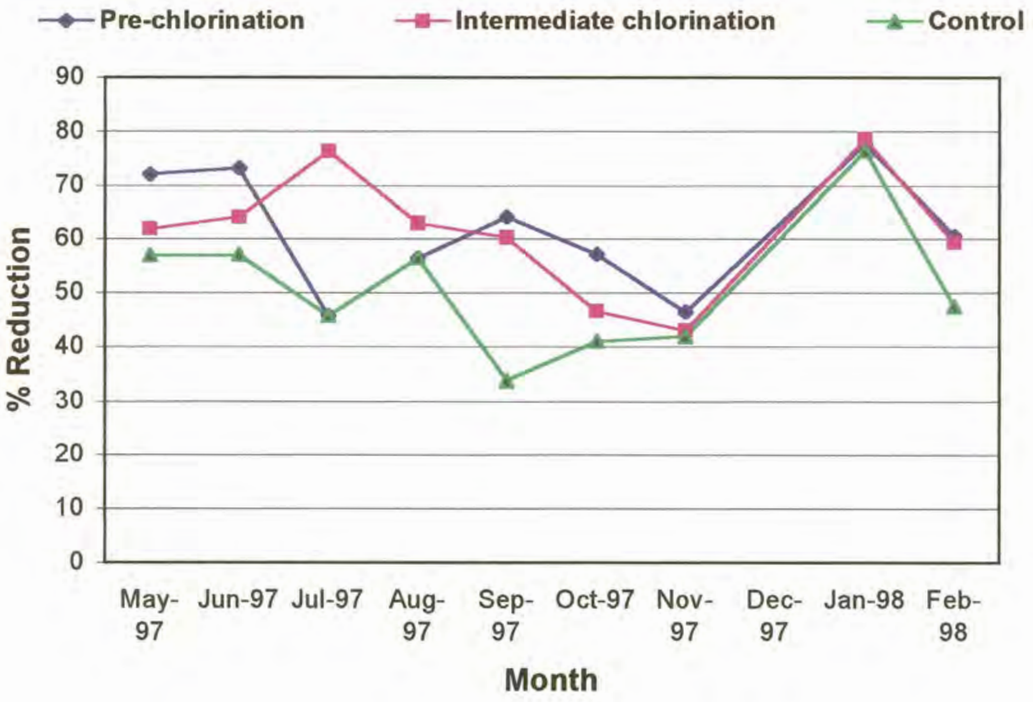

Figure 23: The effect of chlorination on the removal of *Chlorella* cells by coagulation and sedimentation.

Figure 24 illustrates the removal rates obtained by filtration of the settled samples. Reductions were constantly lower in the control samples and intermediate chlorination slightly enhanced the removal of cells by filtration. These results indicate that pre-chlorination or intermediate chlorination should be incorporated for the effective removal of *Chlorella*. The difference in the results obtained by the two different options for chlorination is, however small.

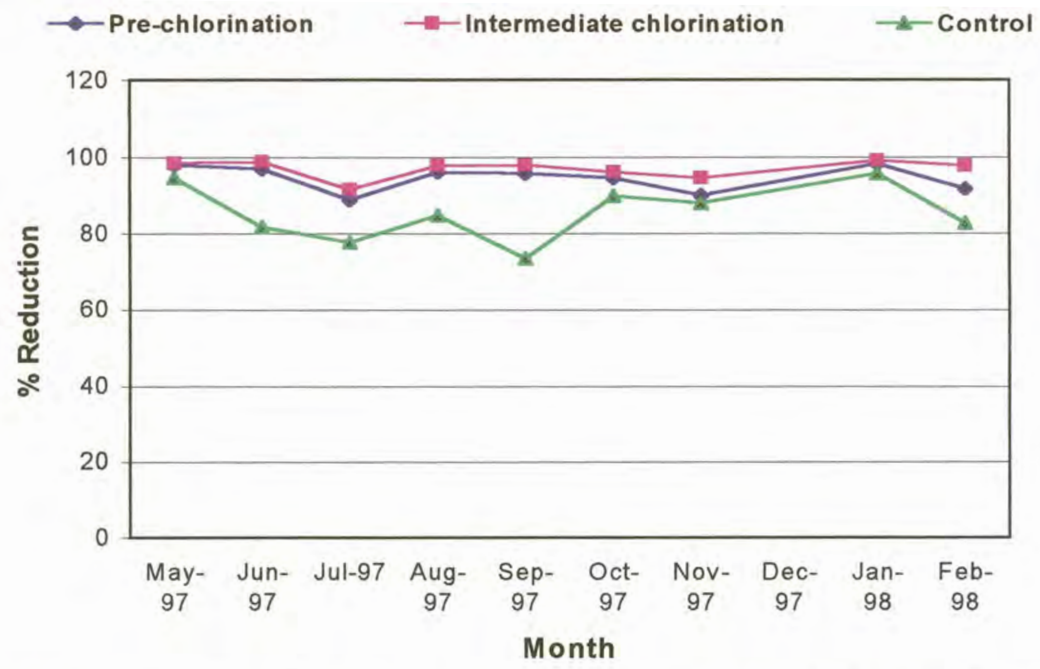

Figure 24: The effect of chlorination on the removal of *Chlorella* cells from settled samples by means of filtration.

Discussion

Edzwald (1993) mentioned size as an important particle property in coagulation. *Chlorella* cells are small with a cell size varying between 4-6 µm (Bold and Wynne, 1985) and therefore more difficult to remove (Mouchet and Bonnélye, 1998). Algae which have a low density are removed poorly by settling. It can be concluded that ineffective aggregation of these cells, resulting in small particle size and low densities, cause their poor removal by settling. The killing of micro-organisms through chlorination (White, 1992 and Steynberg *et al,* 1996) will contribute to more effective aggregation and in this way enhance the removal of the cells. This could explain the positive effect of chlorination on cell removal.

The slightly better removals obtained by filtration when intermediate chlorination was applied is in agreement with the results obtained by Becker and O'Melia (1999) who found that intermediate oxidation results in lower filtered water particle counts.

The effect of pH

Figures 25 and 26 show the efficiency of chlorine in the removal of *Chlorella* and *Monoraphidium* at pH 9,8.

Chlorella

The results obtained indicate that increasing the pH to 9,8, adversely affected the removal of *Chlorella* cells in the pre-chlorinated samples. Decreases in removal rates of up to 20% were observed. In the control samples however, the removal rates decreased by only approximately 5% at the increased pH value.

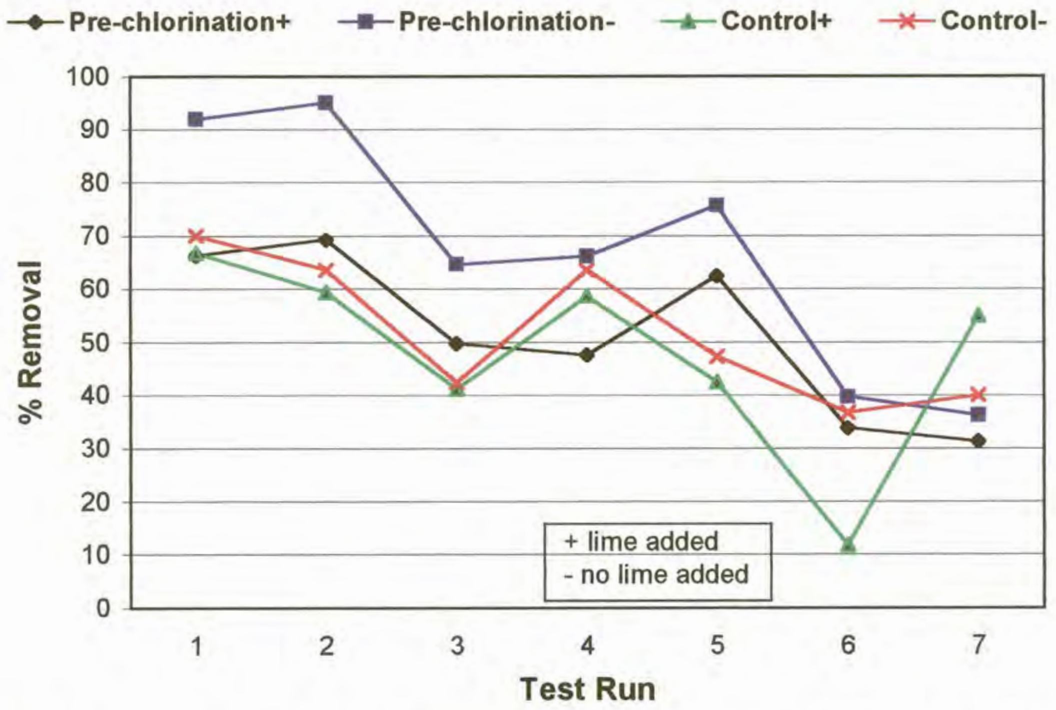

Figure 25: The effect of an increased pH on the removal of *Chlorella* cells by coagulation and sedimentation with pre-chlorination.

Monoraphidium

Figure 26 indicates that the efficiency of chlorine in the removal of *Monoraphidium* was also adversely affected by increasing the pH.

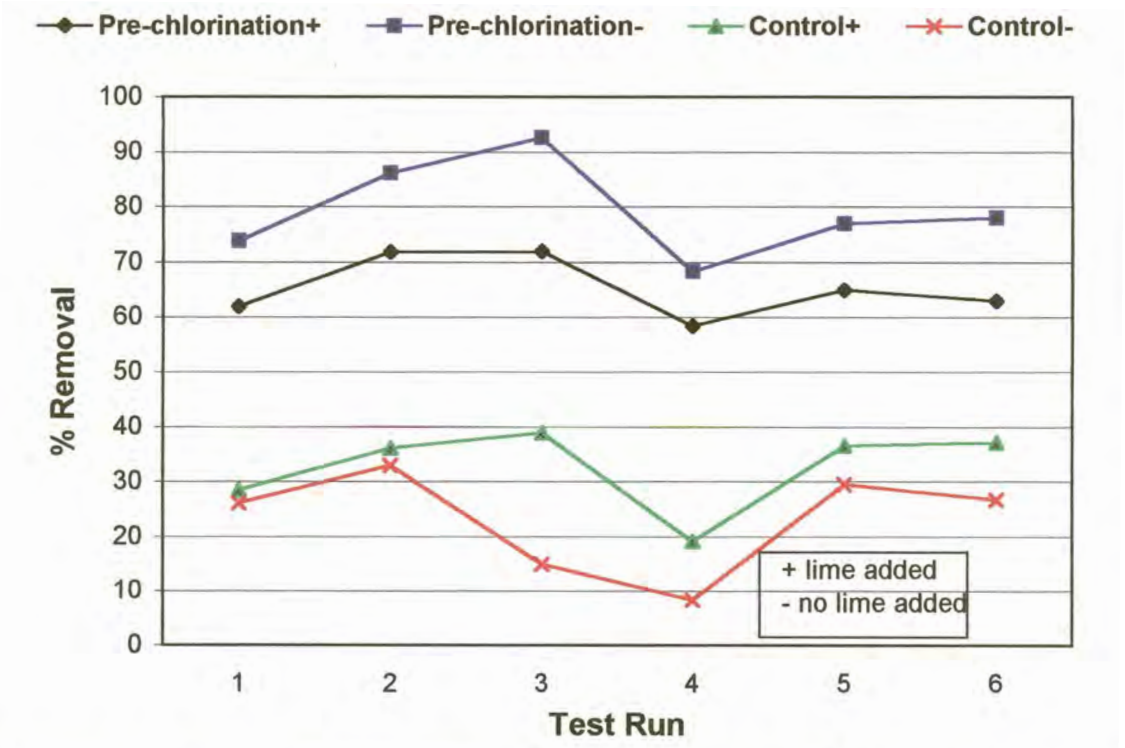

Figure 26: The effect of increased pH (9.8) on the removal of *Monoraphidium* cells by coagulation and sedimentation.

At a pH of 9.8 cell removal rates decreased by 10 to 20% in the chlorinated samples. In the control samples however, increasing the pH contributed to an improvement in cell removal rates.

Discussion

The negative effect of the high pH on the efficiency of chlorine in killing *Chlorella* and *Monoraphidium* is in agreement with findings by Steynberg *et al.*, (1996) and White (1992) who found that the efficiency of chlorine in killing micro-organisms is adversely affected at increased pH values.

The effect of coagulants

The results reported are average values from two or three sets of analyses.

Figures 27 to 29 show the positive effect of an increased coagulant dosage and the addition of a cationic poly-electrolyte on the removal of *Chlorella, Monoraphidium* and *Scenedesmus.*

Chlorella

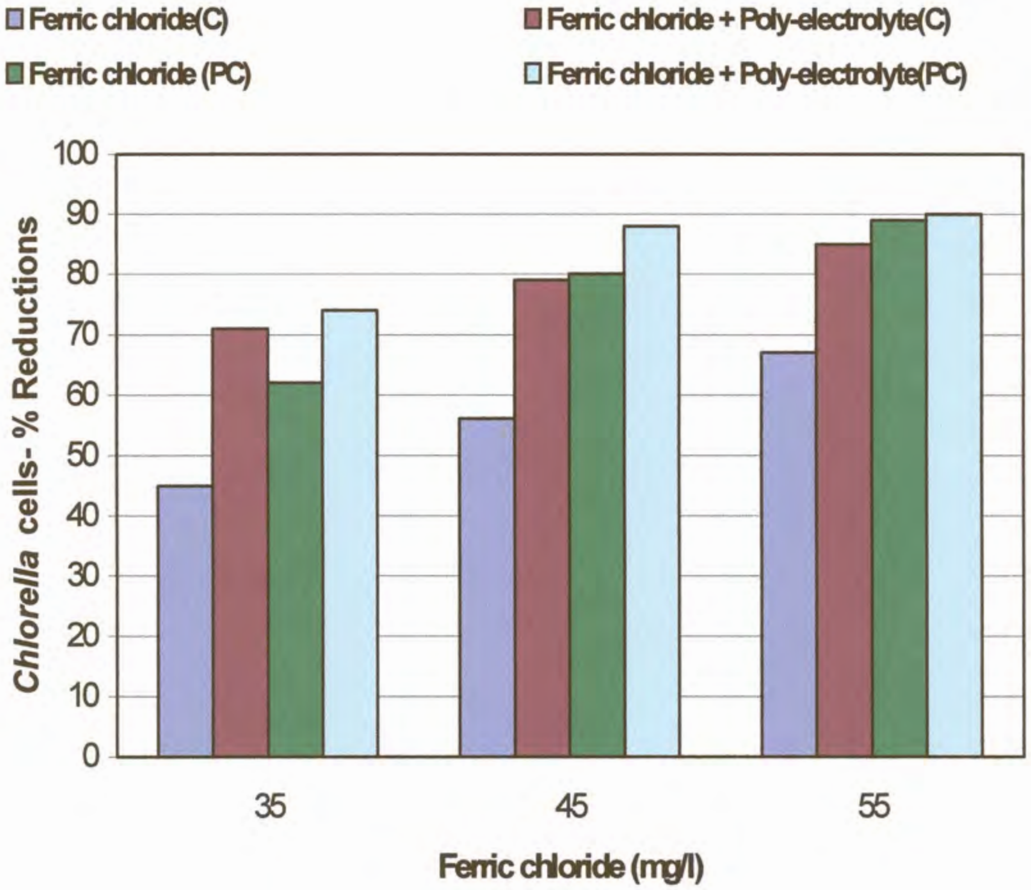

Figure 27: The effect of increased $FeCl_3$ dosages and poly-electrolyte on the removal of *Chlorella* cells.

Figure 27 shows that the effect of the poly-electrolyte on the removal of *Chlorella* was more significant when pre-chlorination was omitted.

Monoraphidium

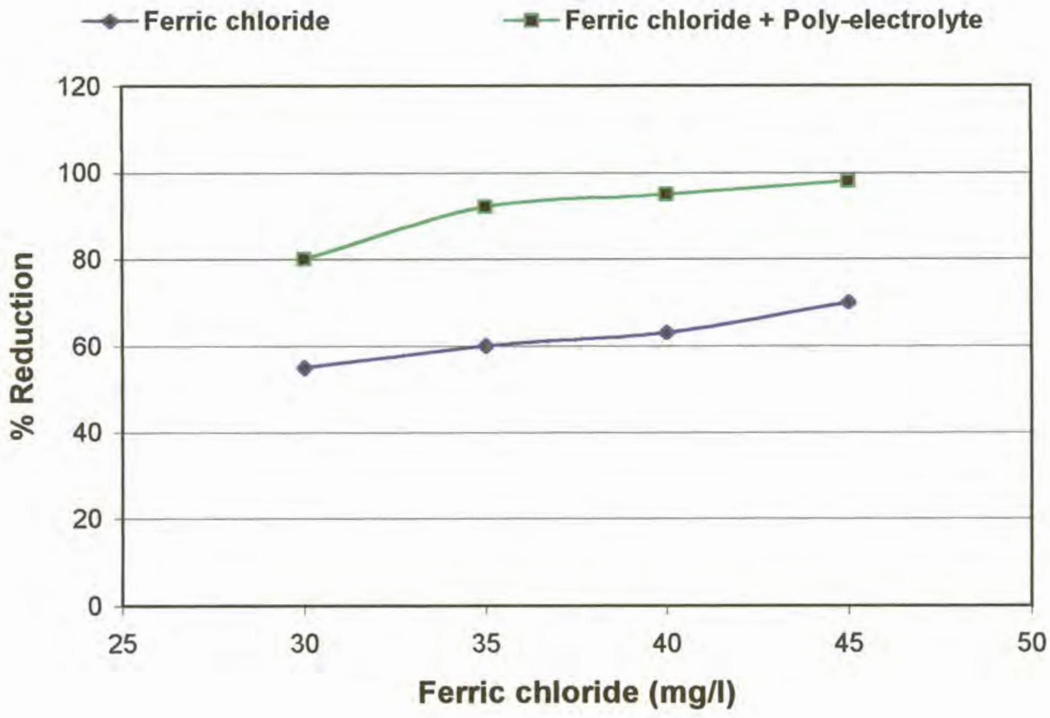

Figure 28: The effect of increased $FeCl_3$ dosages and poly-electrolyte on the removal of *Monoraphidium* cells (no chlorination).

The removal of *Monoraphidium* cells was increased by more than 20% by the addition of a poly-electrolyte as secondary coagulant (Figure 28). Increasing the $FeCl_3$ dosage from 30 to 45 mg/l resulted in an average increase of 15% in the reduction of the cells. It is furthermore clear that with the addition of 1 mg/l of a poly-electrolyte, increasing the $FeCl_3$ dosage from 35 to 45 mg/l did not prove to be of any significant advantage in the removal of *Monoraphidium* cells.

Scenedesmus

Figure 29 shows that the reduction in *Scenedesmus* colonies improved from 35% to approximately 70% by increasing the $FeCl_3$ dosage from 30 to 45 mg/l. The addition of a poly-electrolyte however, improved the removal rate to approximately 90%, irrespectively of the $FeCl_3$ dosage.

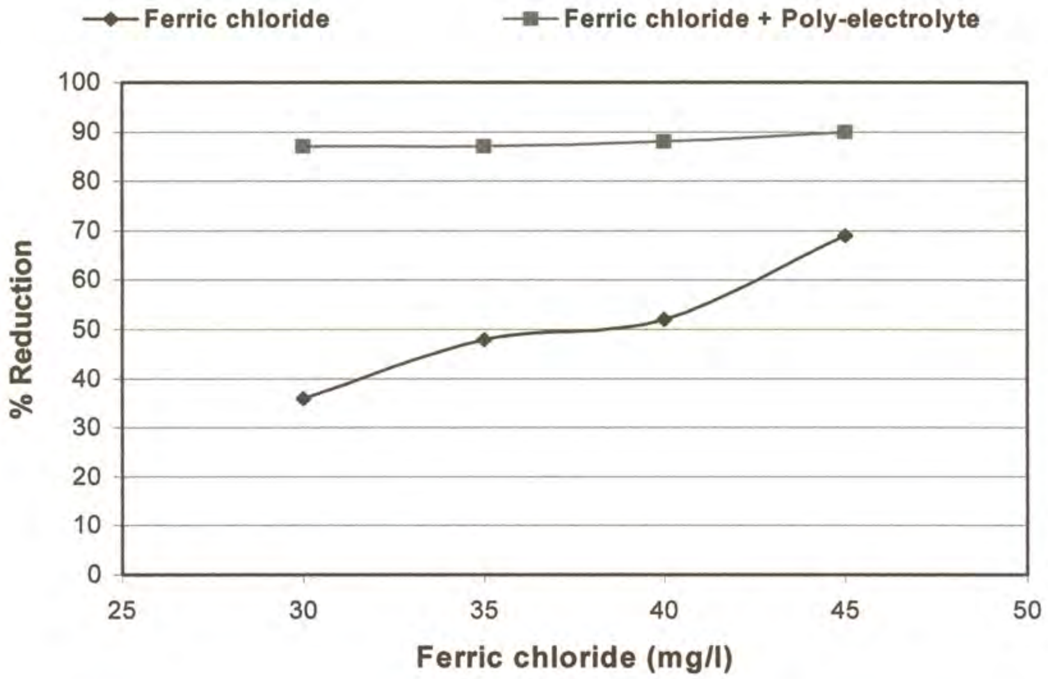

Figure 29: The effect of increased $FeCl_3$ dosages and poly-electrolyte on the removal of *Scenedesmus* colonies (no chlorination).

Discussion

Charge neutralisation is, according to Amirtharajah and O'Melia (1990), the main coagulation mechanism for organic cationic polymers. The destabilisation and aggregation of algae is brought about by adsorption coagulation with charge neutralisation (Bernhardt *et al.*, 1985; Bernhardt and Clasen, 1991 and Edzwald, 1993) and these processes are positively promoted by the use of a poly-electrolyte. The use of a poly-electrolyte may also cause a decrease in repulsive forces due to reduction of the negative charge of the algae when applying such poly-electrolyte (Tilton *et al.*, 1972 and Bernhardt and Clasen, 1991). The positive effect obtained by adding a poly-electrolyte could thus be due to the specific coagulation mechanism.

The improvement in the removal of *Chlorella* cells obtained by the addition of a poly-electrolyte was however less significant when pre-chlorination was applied. These results confirm the findings by Steynberg (1994) who found that pre-chlorination adversely affects the capability of a poly-electrolyte for the flocculation of algal cells. With

Chlorella being the dominant Chlorophyceae species and pre-chlorination being applied for their removal this also explains why Basson and Pieterse (1996) concluded that poly-electrolytes enhance the removal of diatoms rather than green algae.

Chlorella cells are much smaller than *Cyclotella* cells and therefore only possible to remove when captured within larger flocs, which can be settled out or kept behind in a sand filter. The higher $FeCl_3$ dosages resulted in larger flocs being formed, which settled out in a shorter time period (laboratory investigations for this study; Amirtharajah and O'Melia, 1990 and Edzwald, 1993).

Monoraphidium cells are crescent shaped and difficult to remove (Prescott, 1978). As the shape of *Monoraphidium* prevents their accommodation into a single floc (Bernhardt and Clasen, 1991), the use of a poly-electrolyte could contribute to the formation of a single floc. This could result in an increased density of the aggregated cells, which will result in improved removal by sedimentation (Edzwald, 1993).

The significant improvement in the removal of *Scenedesmus* colonies which was obtained by adding a poly-electrolyte could be due to the morphological characteristics of the colonies and the specific coagulation mechanism.

Conclusions

1. Although the removal of Chlorophyceae is enhanced by pre-chlorination, very similar results can be obtained by intermediate chlorination. The end result, after filtration, indicates that intermediate chlorination is a viable option for the treatment of eutrophied waters. The effect on filter run time in a full-scale operation, when cell numbers are high, will however have to be investigated.

2. Applying intermediate chlorination instead of pre-chlorination could contribute to a reduction of 25-30% in the total cost for chlorine.

3. The removal of certain Chlorophyceae species is enhanced by increased coagulant dosages and the addition of a poly-electrolyte as secondary coagulant.

Chlorination however adversely affects the capability of a poly-electrolyte in removing algal cells.

4. The morphological and physiological properties of algal cells play a definite role in their removal during water purification.

4.2 THE REMOVAL OF CHLOROPHYLL-*a*

Chlorophyll-*a* concentrations in the raw water samples analysed, varied between 14 and 158 µg/l. The peak values were measured during August and September 1997. During this period, between 60 and 95% of the total algae population was from the Chlorophyceae group.

The effect of chlorination

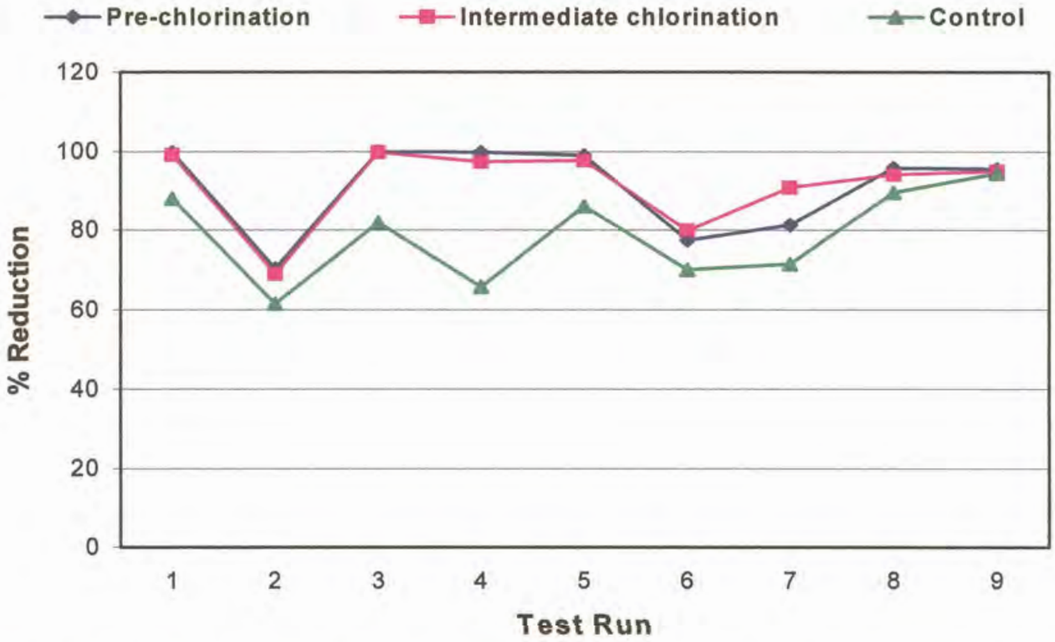

Figure 30: The effect of moving the point of chlorine dosing on chlorophyll-*a* removal (and no lime added).

A comparison between the chlorophyll-*a* reductions obtained when applying chlorine at different dosing points is illustrated in Figure 30 (No lime was added).

These results indicate that chlorination significantly increased the removal of chlorophyll-*a* when no lime was added for pH adjustment. It is also clear from these results that there was almost no difference in the removals obtained by pre-chlorination and intermediate chlorination.

Discussion

Chlorophyll-*a*, mainly due to the presence of Chlorophyceae (Balkfontein laboratory), can be removed cost-effectively with intermediate chlorination. The benefits of pre-chlorination can therefore be obtained at a decreased cost and water quality problems, related to pre-chlorination, could in this way also be over come.

The effect of pH

Figure 31 shows the effect of chlorination on chlorophyll-*a* removal at an increased pH-value.

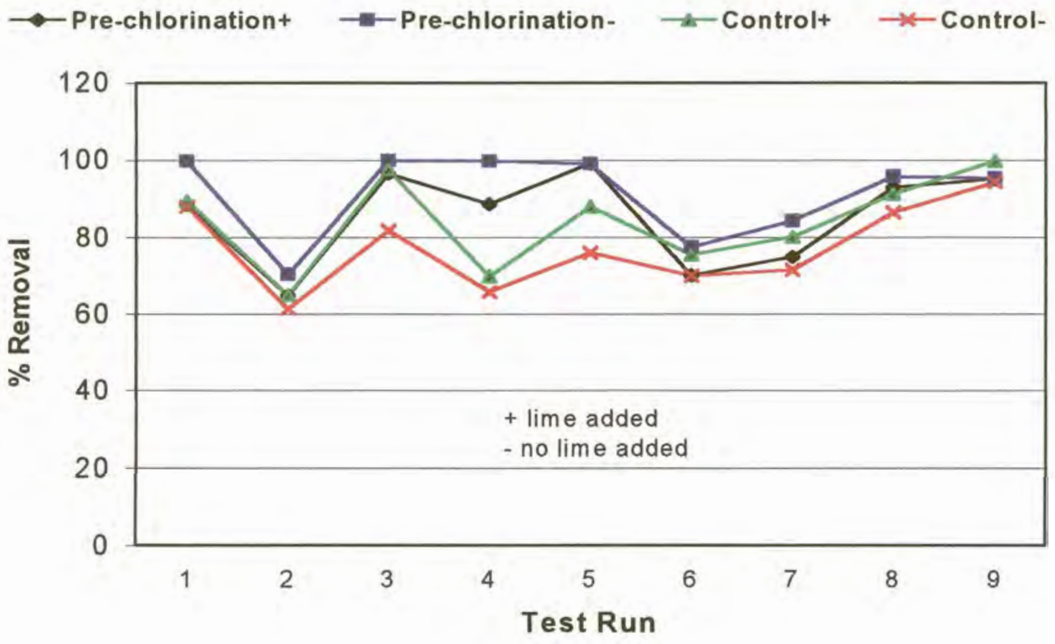

Figure 31: The effect of pH on the efficiency of chlorine in chlorophyll-*a* removal.

This graph illustrates that the increased pH had a slight adverse effect on the role of chlorination in the removal of chlorophyll-*a*. This correlates with research results from literature indicating that, at increased pH values, chlorine is less effective as oxidant (White, 1992) and chlorophyll-*a* removals are less effective when chlorinating at increased pH values (Steynberg *et al*., 1996). Figure 31 also indicates that the removal of chlorophyll-*a* in the control samples is enhanced by the addition of lime (pH to 9,8).

Discussion

Chlorine was less effective in the removal of chlorophyll-*a* at increased pH values. The addition of lime, to obtain a pH of 9,8, proves to enhance the removal of chlorophyll-*a* when pre-chlorination was excluded from the treatment process. It could therefore be concluded that the addition of lime might be used as an alternative treatment option for pre-chlorination in the removal of chlorophyll-*a*.

The effect of coagulants

Figure 32 shows the reduction of chlorophyll-*a* which was obtained by increasing the $FeCl_3$ dosage and by adding 1 mg/l of a poly-electrolyte as secondary coagulant. These results also illustrate the advantage of the effective use of coagulants as a substitute for pre-chlorination in removing chlorophyll-*a*.

Chlorophyll-*a* removal was enhanced by the addition of 1 mg/l of a poly-electrolyte as a secondary coagulant. The improvement obtained was more significant when pre-chlorination was excluded and at the lower $FeCl_3$ dosage concentrations. These results also indicate that poly-electrolyte could be use for the removal of chlorophyll-*a* concentrations exceeding 30 µg/l instead of applying pre-chlorination. Although the chlorophyll-*a* concentration in the raw water was 76 µg/l, efficient removal was obtained even without pre-chlorination. These results are in contradiction with what was found by Steynberg, (1994), who stated that pre-chlorination should be incorporated in the treatment process when chlorophyll-*a* concentrations in the raw water exceed 30 µg/l.

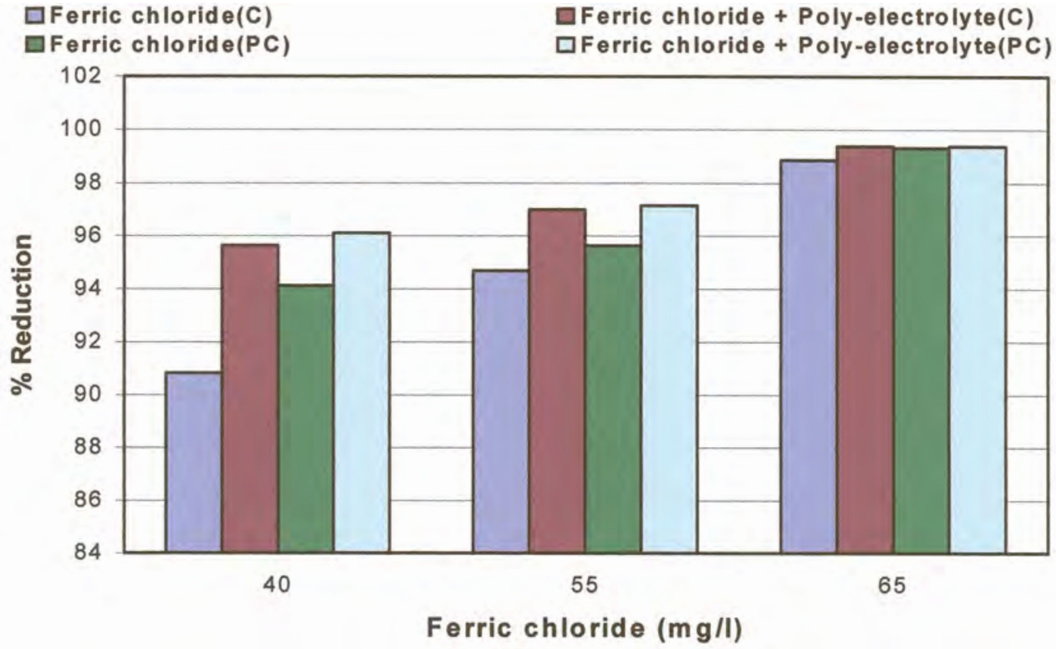

Figure 32: The effect of increased $FeC1_3$ dosages and poly-electrolyte on the removal of chlorophyll-*a* by coagulation and sedimentation.

Discussion

The better removals of chlorophyll-*a* at the higher coagulant concentrations could be related to the higher coagulant demand due to organic substances present in the water (Edzwald, 1993)(1). The effect of pre-chlorination on the removal of chlorophyll-*a* was more significant at lower coagulant dosages than at the higher dosages, probably due to the fact that the coagulant demand was not satisfied at the lower dosages and that pre-chlorination, under these circumstances, could add positively to the removal of chlorophyll-*a*. Chlorination however, adversely affects the role of poly-electrolytes (Steynberg, 1994) and therefore the smaller impact on chlorophyll-*a* removal in the pre-chlorinated samples.

Conclusions

1. The removal of chlorophyll-*a* is enhanced by increasing the coagulant dosage or by adding a poly-electrolyte as secondary coagulant.

2. The effect of a poly-electrolyte is more significant at the lower $FeCl_3$ dosages and when pre-chlorination is excluded.
3. Coagulants can be used in such a way that it would be possible to exclude chlorination from the treatment process and still obtain sufficient chlorophyll-*a* removal. Poly-electrolyte can thus be used as an alternative for pre-chlorination in the reduction of chlorophyll-*a*.

4.3 THE FORMATION OF THMs

Results were analysed to establish relationships between the formation of THMs, chlorination, the removal of organic substances, the presence of algae and pH.

The effect of chlorination

The advantage of moving the point of chlorine application to a position after coagulation and sedimentation (Strobel and Dieter, 1990; Carlson, 1991 and White *et al.*, 1997) is illustrated in Table 4 and Figures 33 and 34.

Table 4: The effect of moving the chlorine dosing points on the formation of THMs. (PC = Pre-chlorination; IC = Intermediate chlorination; C = Control)

THM (µg/l)					
Settled Samples			**Filtered Samples (Post-chlorination after filtration) 4mg/l**		
PC (4 mg/l)	**IC (2 mg/l)**	**C**	**PC**	**IC**	**C**
70,5	58,5	2,0	99,5	84,5	74,5
28,5	20,5	2,0	88,5	80,5	64,5
32,5	14,5	5,5	66,0	51,5	42,5
51,5	18,5	2,0	118,5	80,5	76,5

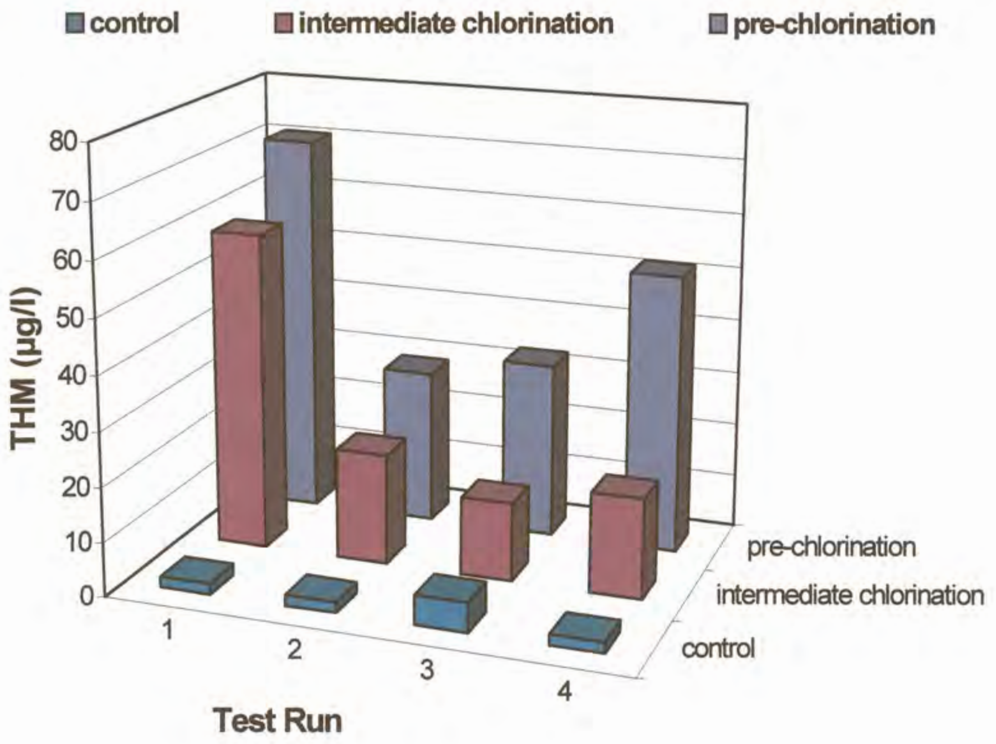

Figure 33: The effect of chlorination on the formation of THMs in settled samples.

Figure 33 shows that chlorination resulted in the formation of THMs. The lower THM yield obtained with intermediate chlorination is in confirmation with the research carried out by Basson and Pieterse (1996), which indicated that increased organic removal (40% DOC removal with the high lime process) before chlorination, resulted in lower THM concentrations in the final water.

Despite the removal of dissolved and particulate substances before chlorination, the impact of post-chlorination on the formation of THMs can be seen in Figure 34. Filtered turbidities indicated that most of the particulate matter were removed by filtration and therefore these results show that dissolved organic substances, which could be due to the production of algogenic organic substances, were still available for reaction with chlorine after filtration (Bernhardt *et al.*, 1986).

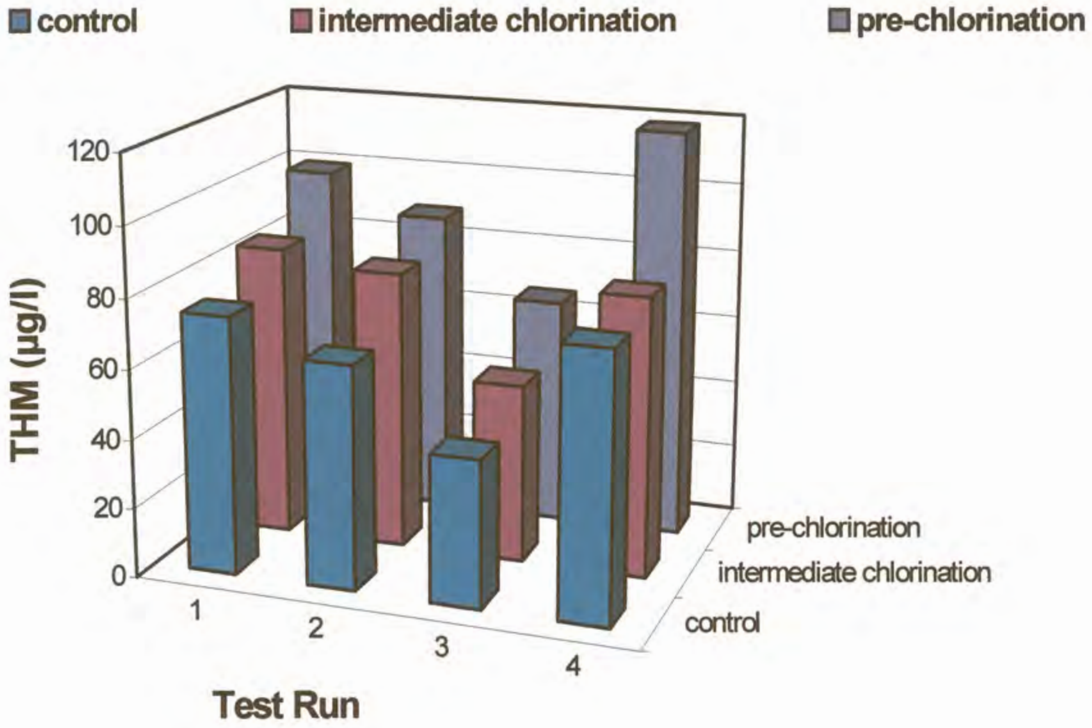

Figure 34: The effect of post-chlorination on the formation of THMs in filtered samples.

Even though a significant increase in the THM values was observed in the control samples after disinfection, the advantage of adding chlorine after primary sedimentation, is evident from the results shown in Figure 34.

The removal of organic substances measured as DOC

Figures 35 and 36 show the results from laboratory experiments conducted to investigate the relationship between DOC removal and the formation of THMs. Increased $FeCl_3$ dosages were used to obtain increased DOC removals.

Figure 35 illustrates that the removal of DOC correlated with the formation of THMs when pre-chlorination was excluded. This indicates the advantage of chlorination after some organic substances have been removed.

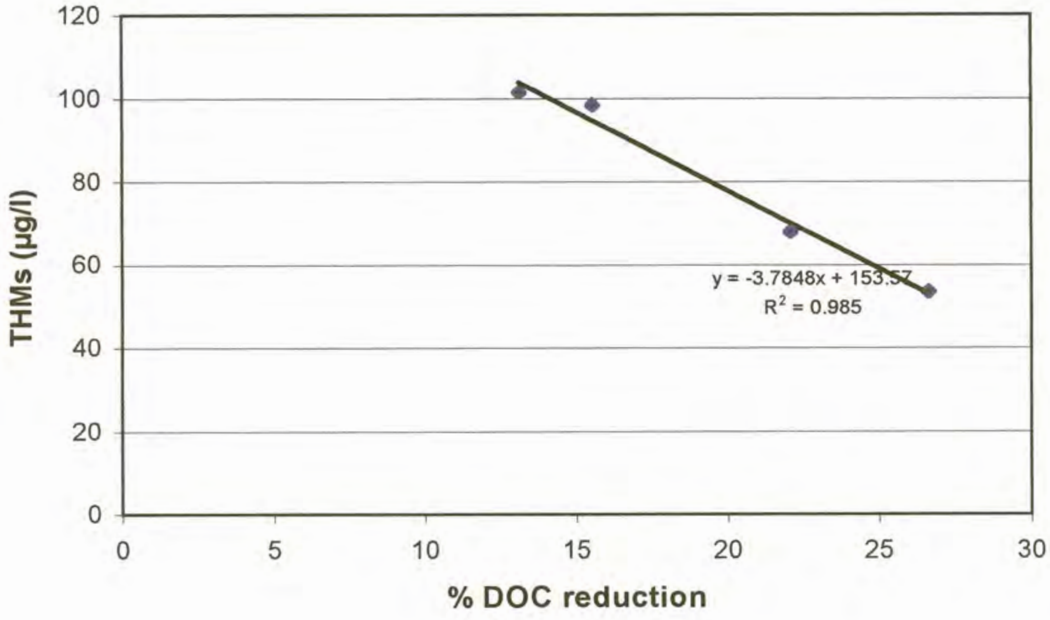

Figure 35: The relationship between DOC removal and the formation of THMs in the control samples.

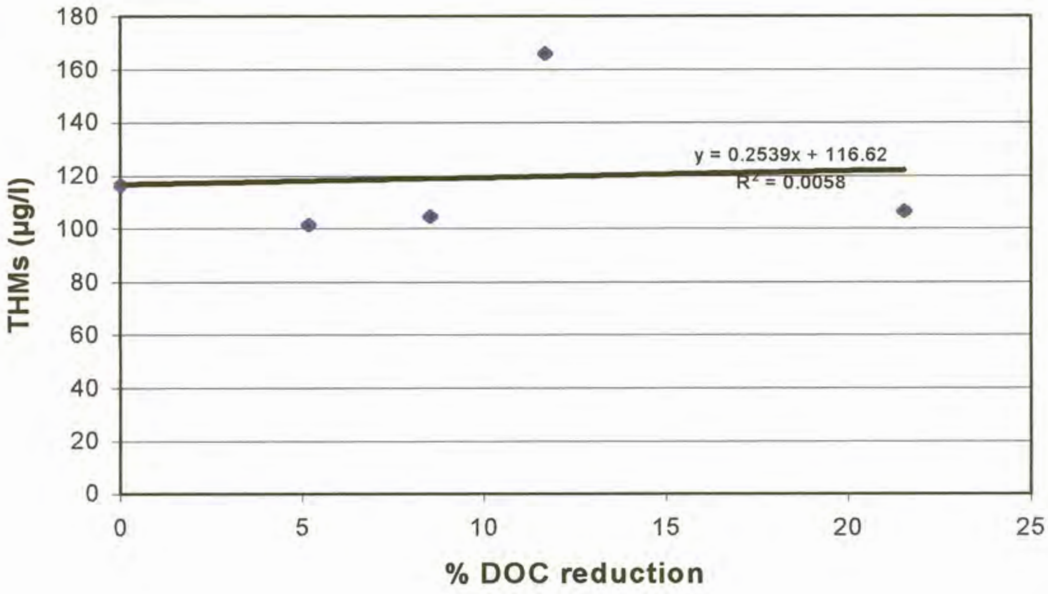

Figure 36: The relationship between DOC removal and the formation of THMs with pre-chlorination.

Figure 36 however, shows that the DOC reduction did not correlate with THM formation when pre-chlorination was applied.

Discussions

Chlorination of the untreated water, when dissolved and particulate substances have not yet been removed, will result in a greater potential for the formation of THMs (White *et al.*, 1997).

Some organics are transformed by chlorination from other fractions into hydrophilic neutral or low molecular weight fractions. Amirtharajah *et al.*, (1993), Edzwald, (1993) and Yeh and Huang, (1993) described the removal of dissolved organic matter by coagulation to be proportional to molecular size, with larger molecular weight fractions being more effectively removed. The formation of low molecular weight organic substances on chlorination, is partially the reason for the lower DOC reductions obtained when introducing pre-chlorination. These low molecular weight compounds are also the dominant precursors for THM - and Total Organic Halogens (TOX) formation (Amirtharajah and O'Melia 1990).

Pre-chlorination also causes the excretion of organic substances by algae and the release of organic matter in the form of algal cells being transformed to DOC (Bernhardt *et al.*, 1985; Abika *et al.*, 1991; Steynberg *et al.*, 1994 and Bernhardt, 1996). The release of organic substance due to algal cell lysis and the transformation of organic substances into low molecular weight fractions could also be a reason for poor DOC removals obtained with chlorination. This will affect the correlation between DOC removal and THM formation with pre-chlorination.

By removing organic substances prior to chlorination, as is the case when intermediate chlorination is applied, the advantages of chlorination could be obtained but DBP formation will be reduced (Strobel and Dieter, 1990 and Jiang and Graham, 1992).

The effect of pH

The profound influence of pH on THM yield, as described by El-Dib and Ali, (1994) was investigated by establishing a correlation between pH, DOC removal and the formation of THMs. The results, as shown in Table 5, are average figures calculated from three sets of analyses for each condition.

Table 5: The effect of pH on DOC removal (percentage) and the formation of THMs. (The figures in brackets refer to the formation of THMs after post-chlorination)

	pH		
	8,4	9,8	11,4
Pre-chlorinated	15,5% (99,8 µg/l)	12,7% (118,6 µg/l)	-
Not pre-chlorinated	24,8% (80,8 µg/l)	20,6% (88,6 µg/l)	58,9% (51,7 µg/l)

The results in Table 5 show that less DOC removal was obtained at the higher pH values and when pre-chlorination was applied. This consequently resulted in higher THMs being formed at higher pH values. The removal of organic substance was however enhanced by increasing the pH to 11,4. Removals of approximately 50% were obtained in the laboratory. The enhanced removal of DOC and lower THM concentrations obtained at pH 11,4 confirms the findings by Basson and Pieterse (1996). They found that DOC removals of approximately 40% could be obtained at pH 11,4. These improved removals resulted in decreased THM concentrations being measured in the final water.

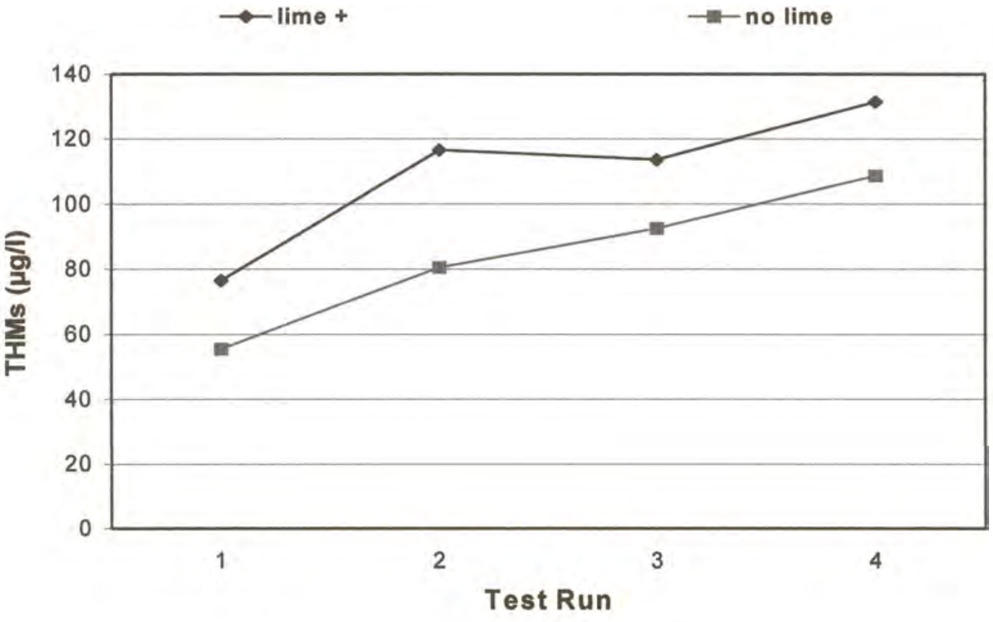

Figure 37: The effect of lime addition (pH 9,8) on THM formation.

Figure 37 shows the effect of pH on the formation of THMs. The addition of lime (to increase the pH by 1 to 1,5 pH units to pH 9,8), resulted in increased THM formation. These results, as illustrated in Figure 37, are in confirmation with the findings by El-Dib and Ali (1994) who found that a reduction of 50% in THM yield could be obtained by decreasing the pH from 9,0 to 7,0.

Discussion

At higher pH values, less cationic species are available for reaction with NOM, and precipitation (Amirtharajah and O'Melia, 1990). This could partially be the reason for poorer removal of organic matter at pH 9,8. The less effective removal of organic material at the higher pH values then contributes to the formation of higher THMs at increased pH values, as illustrated in Table 5 and Figure 37. Raising the pH to above 10,5 implies that the removal of colloidal matter and DOC now occurs in the range of $Mg(OH)_{2(s)}$ precipitation where adsorptive coagulation is favoured and organic substances are removed by co-precipitation (Basson and Pieterse, 1996). The increased removal of organic substances by co-precipitation will result in the production of lower THMs in the final water.

The presence of algae

The relationship between the formation of THMs and the presence of algal cells has been described in literature (Abika *et al.*, 1991; Van Steenderen *et al.*, 1991 and Jiang and Graham, 1992).

Figure 38 and 39 demonstrate the relationship between THMs formed after pre-chlorination and disinfection, and the presence of *Cyclotella* and *Scenedesmus quadricauda* in the river. Although the formation of THMs cannot be attributed to individual parameters, Figures 38 and 39 indicate that a positive correlation exists between the presence of *Cyclotella* and *Scenedesmus* and the formation of THMs on chlorination.

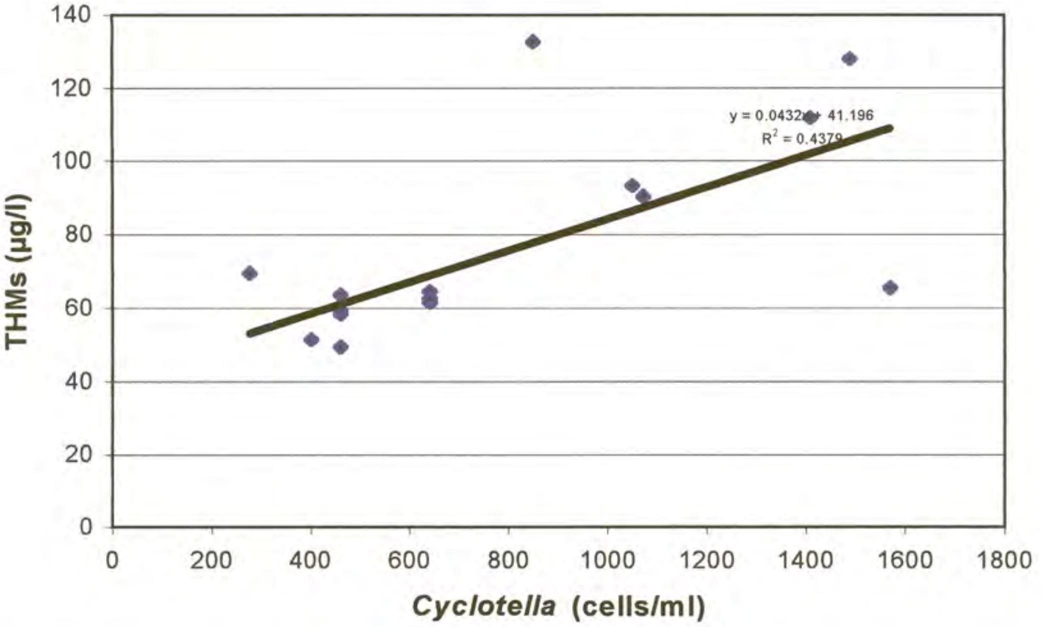

Figure 38: The relationship between the presence of *Cyclotella* cells in the raw water and the formation of THMs on chlorination.

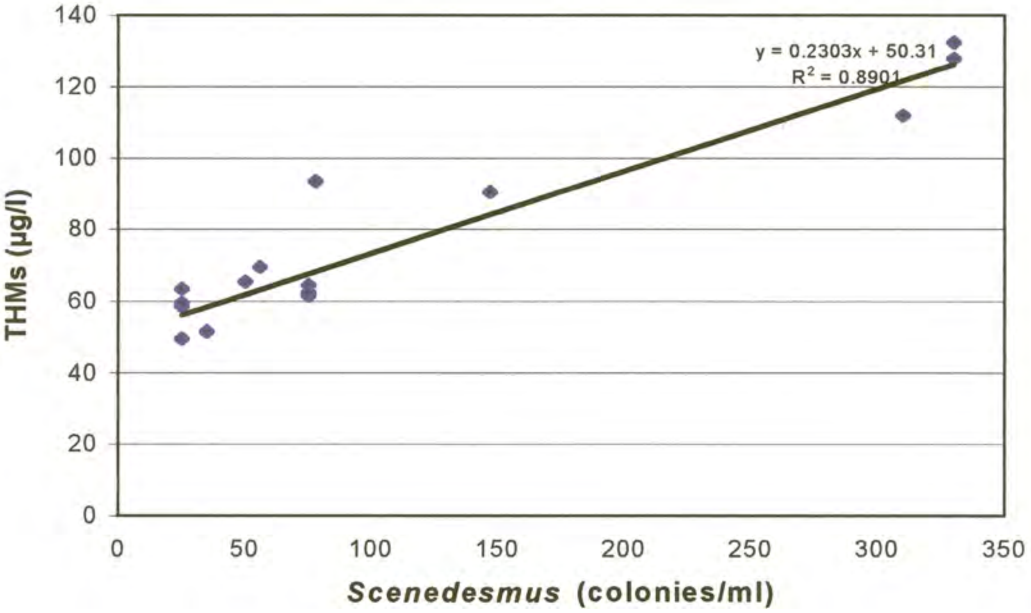

Figure 39: The relationship between the presence of *Scenedesmus* colonies in the raw water and the formation of THMs on chlorination.

Discussions

Edzwald (1993) found that much more EOM was produced by *Cyclotella* and *Scenedesmus* than by *Chlorella*. The molecular weight distribution was shifted to substances of lower molecular weight after ozonation. These lower molecular weight substances are more difficult to remove and act as precursors for THM formation. The effect of chlorination on EOM produced by *Cyclotella* and *Scenedesmus* on their destruction by chlorine, could be similar to that of ozonation, thus resulting in the formation of these lower molecular weight substances and consequently in a higher THMFP.

Conclusions

1. The point of chlorine application affects the removal of DOC and consequently the formation of THMs.

2. The potential for the formation of THMs increases with increased pH values.

3. At pH 11,4 the removal of organic substances by co-precipitation contributes to the lower THM yield in the final water.

4. The formation of THMs is related to the presence of certain algal species in the raw water.