THE INFLUENCE OF WATER QUALITY ON THE EFFICIENCY OF CHLORINE DIOXIDE AS PRE-OXIDANT AND ALGICIDE IN THE PRODUCTION OF POTABLE WATER

BY

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EXECUTIVE SUMMARY

INTRODUCTION

Development in the Witwatersrand took place rapidly since 1880 after the discovery of gold. Unfortunately the mining and associated industrial and domestic development of the past 100 years resulted in a dramatic deterioration of the water quality of the rivers draining the Witwatersrand area. One such catchment is that of the Vaal River Barrage Reservoir.

Excessive enrichment of the tributaries of the Vaal River Barrage Reservoir draining the Witwatersrand with plant nutrients, resulted in algal blooms. This causes for algal related water purification and quality problems. Research done by Rand Water indicated that a catchment management option, such as a 1 mg/ℓ orthophosphate standard for effluents, will not ensure compliance to the annual average chlorophyll guideline value of 20 μg/ℓ set by Rand Water for the Vaal River Barrage reservoir. Rand Water is therefore compelled to develop and optimise algal removal technologies to ensure that the chlorophyll guideline concentration of 1 μg/ℓ for potable water is not exceeded. For this purpose Rand Water considered several purification technologies and its effect on water purification costs. The present study showed that pre-oxidation of algal laden water could be an effective algal control measure.

At Rand Water, and many other similar institutions, chlorine is used as pre-oxidant. The major disadvantage associated with pre-chlorination is the formation of high concentrations of trihalomethanes (THMs) which is regarded by some researchers to be carcinogenic. Experience at Rand Water indicated that it is not always effective in inactivating algae escaping the different unit processes. A literature study indicated chlorine dioxide as an alternative oxidant, which does not form THMs and is a stronger oxidant of the two.

The purpose of this study is therefore to compare the efficiency of chlorine and chlorine dioxide as pre-oxidants and algicides in raw water abstracted for production of potable water. The following aspects received special attention. Comparison of the :

a) algicidal efficiency of the oxidants,
b) combined effect of water quality on the efficiency of the oxidants,
c) sensitivity of different algal species to the oxidants, and

d) the advantages and disadvantages of pre-oxidation with chlorine and chlorine dioxide in the removal of algae, and the formation of oxidation by-products.

RESULTS AND CONCLUSIONS

To meet the aims of this study the following species of algae, differing in size, shape and surface charge characteristics were used in experiments :

Chlamydomonas sp
Chlorella minutissima
Cosmarium laeve var *distentum*
Cyclotella meneghiniana
Euglena gracilis
Monoraphidium minutum
Scenedesmus quadricauda
Pandorina morum

All the algae except *Euglena gracilis* were isolated from the Vaal River Barrage Reservoir. Physiological active algae cells, were used in the experiments.

The influence of water quality on the efficiency of chlorine and chlorine dioxide was evaluated using different mixtures of waste water treatment plant effluent and Vaal Dam Water. The mixtures represented the variety of water qualities observed in the Vaal River Barrage Reservoir. Oxidant efficiency was measured as the free residual oxidant available after a specific treatment time interval. Results from these studies indicated that

a) the residual oxidant concentrations decreased with time with the highest decrease during the first moments after oxidant addition,
b) residual oxidant concentrations after contact time decreased inversely with increases in the effluent concentration,
c) after the same contact period, significantly higher chlorine dioxide concentrations than chlorine concentrations were present at equivalent dosages, and
d) more trihalomethanes (THMs) are formed with increased effluent ratios and higher chlorine concentration in water mixtures. The highest concentrations were recorded after 24 hour contact time, using 10 mg/ℓ chlorine. No THMs were formed when chlorine dioxide was used.

Results on the oxidation of algal suspension indicated the following:

a) A contact time up to 30 minutes is necessary to inactivate algae with chlorine, compared to a maximum of 10 minutes needed when chlorine dioxide was used at equivalent dosing rates.

b) Residual oxidant concentration decrease exponentially over time with the highest rate of oxidant consumption in the first minutes of contact and with high biomass concentrations. The chlorine dioxide demand exercised by the algal suspension was less than that for chlorine.

c) Chlorine dioxide was two to ten times more effective than chlorine as an algicide. This variation in efficiency is dependant on the algal concentration and algal species.

d) Algae differed regarding their resistance to oxidation. *Cosmarium laeve* var *distentum* was the most resistant algae against the action of chlorine, while *Scenedesmus quadricauda* was the most resistant against chlorine dioxide.

e) Electron microscopical investigations showed limited external damage to the cells due to oxidation. Significant damage to the membrane systems of the cells was, however, observed. Difference in ultra-structure damage of the cells have not been quantified. The true locus of damage caused by either chlorine dioxide or chlorine and the effect on the algal cell could not be determined. Further research, using technologies to measure changes in differential permeability of the membranes would be needed.

f) THMs (a maximum of 35 $\mu g/\ell$) were formed by chlorination of algal suspensions after 2 hours contact time. No THMs were formed when chlorine dioxide was used as pre-oxidant.

Results from this study indicate that chlorine dioxide would be the best oxidant for pre-oxidation. Little information is, however, available on the effect of pre-oxidation by chlorine dioxide on the unit treatment processes of Rand Water. To determine the effect of pre-oxidation on the efficiency of the unit processes to remove algae, laboratory scale coagulation/flocculation, sedimentation and filtration experiments were done. Experiments using unoxidised algae at different concentrations indicated that

a) not all algae was removed to the same extent by the different unit processes,

b) sedimentation was responsible for the bulk of the algae removed, and

c) filtration efficiency increased with an increase in algal cell size and with algal load onto the filter.

The difference in removal efficiency of the different algae by the sedimentation process could be related to the physical interference of the algal cells with the coagulation and the flocculation process. Cells with non-spherical shapes, spines, that are motile or that can change their shape were not flocculated well and therefore did not settle as well as colloidal particles.

Two algae, *Euglena gracilis* and *Chlamydomonas* sp, were selected to evaluate the efficiency of chlorine and chlorine dioxide as pre-oxidants on their removal through the unit processes. These algae were selected on the bases of their ability, possibly due to motility by means of flagella, to penetrate through unit processes. Tests done at three different oxidant and coagulant (lime) concentrations indicated that pre-oxidation improved the removal of algal cell significantly. One of the main reasons for this improvement may be the fact that these specific algae lose their motility, this was confirmed by experiments in which the flagella of the algae (not oxidised) was removed by means of ultrasonic sound treatment after which the removal efficiency was increased.

Pre-oxidation with chlorine dioxide compared to chlorine resulted in a 40 per cent improvement in the removal of *Chlamydomonas* sp. In the case of *Euglena gracilis* the improved removal was only significant at low coagulant dosages (low pH). This is due to the fact that the surface charges of *Euglena gracilis* become more negative with an increase in pH (increase in lime dosage), which may be responsible for a decrease in removal efficiency of *Euglena gracilis*. It was only at the high oxidant dosage (Cl_2 = 2,0 mg/ℓ; ClO_2 = 0,8 mg/ℓ), that the effect of the increased negative surface charge at higher pH on the removal of the algal cells were cancelled.

Limited tests done on pilot plant scale confirmed the improvement in removal of algae and colloidal particles when pre-oxidised. The pilot plant tests should, however, be repeated over a longer period to evaluate the long term effect of pre-oxidation of the water quality produced.

The use of chlorine dioxide as a pre-oxidant will be influenced by the potable water quality guidelines for trihalomethanes, chlorite and algae. A trihalomethane level of less than 100 μg/ℓ and a chlorophyll-a value of 0,1 μg/ℓ for potable water will force the use of chlorine dioxide as pre-oxidant, while a chlorite concentration of less than 0,4 mg/ℓ will not allow its use as pre-oxidant.

Production cost of oxidants will also play an important role in the choice of oxidant. A cost comparison was done, given the following conditions:

a) Pre-oxidation of 1000 Mℓ/d.

b) Oxidant concentration : Cl_2 = 3,5 mg/ℓ; ClO_2 = 0,8 mg/ℓ.

c) Amount used per day: Cl_2 = 3500 kg; ClO_2 = 800 kg.

d) Chlorine purchased in bulk at R2,20/kg.

e) Process used to produce chlorine dioxide

$$Cl_2 + 2NaClO_2 \text{ -----> } 2ClO_2 + 2NaCl.$$

The cost comparison indicated that chlorine dioxide will approximately be 1,61 times more expensive to use as an oxidant.

From this study it was evident that the removal of algae by different unit processes should in future not be evaluated on chlorophyll-a concentration only. Cognizance must to be given to the specific algae present in the raw water. In this regard similar research as reported in this report should be done on other problematic algae in water purification plants. Of special importance would be the development of a system based on the physical characteristics of algae which could interfere with specific unit processes when specific coagulants are used. Recommendations regarding the removal of those algae, given a specific water purification technology, should be included in such a system.

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

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INTRODUCTION

The history of the world's developing areas are intricately bound with the need for, and assurance of, adequate water supplies. A study of a world atlas will show that virtually all cities and towns of any size are located close to fresh water supplies. Natural mineral and vegetable resources could not be exploited to any great extent if an assured, adequate and safe supply of water was not relatively close by.

Although water availability was a limiting factor and several inherent geographical difficulties hindered the supply of water, development in the Witwatersrand proceeded rapidly in the 1880's after the discovery of gold (Laburn, 1979). Unfortunately, mining and associated industrial development of the past 100 years has resulted in a dramatic deterioration of water quality of rivers draining the Witwatersrand area (Steynberg *et al.*, 1991).

Water quality is a function of the interactions between the non-living (abiotic) and the living (biotic) factors of the water ecosystem. If the balance between these factors is disturbed, the water quality always deteriorates. This deterioration of raw water quality directly affects the quality of the potable water produced. This may be demonstrated by the correlation of Cyanobacteria blooms, due to nutrient enriched water, and the presence of odour producing compounds, such as geosmin, in potable water (van der Ploeg *et al.*, 1992).

Enrichment of the water habitat with plant nutrients (eutrophication) is an appropriate example of a mainly anthropogenic process that disturbs the balance in the water habitat (Vollenweider, 1968). The increased nitrogen and phosphorus concentrations under favourable conditions result in a population explosion of the primary producers (algae and macrophytes). A heavy burden is then placed on the potable water purification systems to remove the algae and associated compounds.

Algal related water purification and water quality problems have often been referred to (Steynberg and Viljoen, 1990; Steynberg, 1986; Pieterse, 1989; Viljoen and Haynes, 1985). These problems may be summarised as follows:

a) Algae and their extra cellular products interfere with physical/chemical water purification processes.

b) Algae pass through purification systems resulting in water of aesthetically unacceptable quality being produced.

c) Algae not only produce neuro- and heptoxins that could be detrimental to the consumer's health, but algal products may also act as trihalomethane precursors and as a source of carbon for microbiological and other heterotrophic growth.

At Rand Water algal related potable water quality problems have been experienced since the mid seventies. These problems were initially identified as to be colour and turbidity related. Staining of materials in the textile industries were also reported (Dr F C Viljoen - personal communication)[1]. More recent observations indicated an increase in the standard plate count, a few days after chlorophyll values in excess of 1 $\mu g/\ell$ were recorded in the distribution network.

Based on the above information and experience of Rand Water's personnel, a recommended algal guideline for potable water, expressed as 1 μg chlorophyll/ℓ, was formulated and implemented in the latter half of the seventies. To ensure a 95 percent compliance to this guideline, copper sulphate was added during secondary sedimentation and the coagulant dose increased as soon as chlorophyll values in excess of 1 $\mu g/\ell$ were detected. In recent years, pre-chlorination are also practised as soon as raw water chlorophyll values exceeded 30 $\mu g/\ell$. This procedure was implemented based on research that indicated that the potable water chlorophyll guideline is most likely to be exceeded when the raw water chlorophyll exceeds 30 $\mu g/\ell$.

Algal related problems in the purification process have presented many challenges to the scientific and engineering community. These varied from the development and implementation of new water purification technologies (symptom treatment) (van Vuuren *et al.*, 1983) to defining and applying of more scientifically based catchment and water resource management (preventative procedures) (Vollenweider, 1968).

As a preventative procedure the Department of Water Affairs imposed a 1 mg orthophosphate/ℓ standard in 1985 for effluents form waste water treatment plants in the RSA (Water Amendment Act, 96 of 1984). This procedure was adopted so as to limit eutrophication related water quality problems in catchments dominated by point sources. One such catchment is that of the Vaal River Barrage Reservoir (Steynberg, 1986), which is an important raw water source to Rand Water. Research done by Rand Water (Steynberg and Viljoen, 1991) indicated that only 24 per cent of the waste water treatment plants in the Vaal River Barrage Reservoir catchment area are able to meet the orthophosphate standard for more than 75 per cent of the time. Due to the non-compliance of the

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waste water treatment plants, the reduction of orthophosphate loads entering the Vaal River Barrage Reservoir catchment was 1788 tons per annum less than expected and the annual average chlorophyll concentrations in the Vaal River Barrage Reservoir were accordingly 10 $\mu g/\ell$ higher than predicted. Indications are that a 100 per cent compliance with the set orthophosphate standard by the year 2000 will not ensure the required annual average chlorophyll concentration of less than 20 $\mu g/\ell$ in the Vaal River Barrage (Steynberg and Viljoen, 1991). Therefore, other options will have to be considered to help to combat the algal related water purification problems.

From the above it is evident that Rand Water should develop and optimise internal algal and algal product removal technologies so as to ensure that its recommended chlorophyll guideline of 1 $\mu g/\ell$ for potable water is not exceeded. For this purpose Rand Water investigated several purification technologies and their effect on water purification costs (Steynberg and Viljoen, 1990). This investigation showed that pre-oxidation of algal laden water could be a cost effective algal control measure.

At present Rand Water is using chlorine gas as pre-oxidant at its Vaal River Barrage Reservoir intakes. Other oxidants such as chlorine dioxide (Masschelein, 1979), ozone (Richard and Darga, 1992), potassium permanganate, hydrogen peroxide and perozone (Glaze *et al.*, 1990) is used as oxidants to treat water quality problems. These oxidants are not only used to control algae, but also as flocculation aids, for oxidation of natural and synthetic organics, oxidation of inorganics, colour removal and for taste and odour control (Glaze *et al.*, 1990).

To ensure that pre-oxidation of raw water is to the best interest of Rand Water's consumers, a project was formulated to investigate the effect of oxidants such as chlorine, chlorine dioxide and ozone as pre-oxidants, on the efficiency of water purification processes and water quality.

The purpose of this specific study is to compare the efficiency of chlorine and chlorine dioxide as pre-oxidant and algicide in raw water abstracted by Rand Water for potable water production. The following aspects will receive special attention:

a) The algicidal efficiency of the two oxidants and sensitivity of different algal species to the two oxidants will be determined by specially designed oxidation experiments in which algal species, algal concentration, oxidant type, oxidant concentration and contact time will be variables of concern.
b) The combined effect of several water quality variables on the availability of the oxidants for algal

control will be determined using different mixtures of treated sewage and Vaal Dam water, simulating different raw water qualities at the Rand Water's intakes.

c) The advantages and disadvantages of pre-oxidation with chlorine and chlorine dioxide on the removal of algae, the efficiency of purification processes and the formation of oxidation by-products will be investigated using standard laboratory stirring tests and pilot plant facilities.

LITERATURE SURVEY

For this study it was considered necessary to define the different aspects that will be dealt with. It is also of importance to compare results available from a limited number of pre-oxidation studies where chlorine and chlorine dioxide were used to prevent algal related water purification problems.

2.1 ALGAE

This study predominantly deals with algae. It is therefore important to first define what is, for this study, regarded as algae.

Because of it's use as an indicative term, algae has been applied to such a variety of groups of organisms, and has been given so many interpretations, that it has no precise meaning. In the broadest sense it may refer to all chlorophyll bearing thallophytes and protista, including their colourless relatives (Prescott, 1973). To confuse the matter further life history studies have established genetic relationships between definitely plant like and animal-like "algae".

Phycologists generally distinguish between eight different groups (see Table 2.1) of algae based on size, cell wall composition, motility, pigments present and morphology (Prescott, 1973).

TABLE 2.1 : DIFFERENT GROUPS OF ALGAE.

TAXONOMIC GROUP	COMMON NAME AND DESCRIPTION
Chlorophyta	Green algae; motile and non-motile cells and colonies; Filamentous algae.
Chrysophyta	Yellow-green and golden-yellow algae; diatoms
Euglenaphyta	Motile cells which can change shape
Chloromonodaphyta	Chloromonads
Pyrrhophyta	Yellow-brown algae
Phaeophyta	Brown, marine algae
Cyanophyta	Blue green bacteria
Rhodophyta	Red algae, mostly marine

In this study the term algae refers to all autotrophic microscopic aquatic, plant-like organisms that are

suspended (planktonic) in the water column or attach themselves to surfaces in the aquatic systems.

Algae are common inhabitants of surface waters exposed to sunlight. Using sunlight energy, the carbon dioxide present in the water is converted into carbohydrates (Vollenweider, 1974). Oxygen is released into the aquatic environment as a by-product. Algae may thus alter the oxygen and carbon dioxide contents of the water, causing the pH to fluctuate, and in other ways initiate a series of cause-effect interactions.

One such cause-effect interaction due to the activities of man in the catchments of impoundments in the past 30 years, is the increase in the nitrogen and phosphorus concentration of the rivers and impoundments, resulting in algal blooms. This has lead to an imbalance in the aquatic environment, resulting in nuisance conditions, such as:

a) aesthetic problems associated with massive growths of algae (Walmsley *et al.*, 1979),
b) interferences with recreational use of rivers and impoundments (OECD, 1982),
c) the production of extensive anaerobic conditions in the hypolimnion of impounded waters (Dehavay, 1983) and
d) several algal related water purification problems (Fayed, 1983; Thomas *et al.*, 1980).

The latter nuisance condition has specific financial and potable water quality implications which will be discussed in the following sections (Viljoen and Haynes, 1985).

2.2 WATER PURIFICATION AND ALGAE

Understanding how algal-laden waters are purified, requires an understanding of the purification processes involved, and the characteristics of the algae that must be removed. This knowledge is also of paramount importance for the correct planning and interpretation of the results of this project.

During the water purification process, substances that are regarded detrimental to domestic utilisation or that are aesthetically not acceptable, are removed to acceptable levels (AWWA, 1990). One of the oldest and simplest ways to remove these undesirable substances is direct slow filtration with no other pre- or post-treatment. However, the deterioration of the raw water quality necessitated the implementation of other purification practices. Depending on the quality of the raw water being treated, the treatment technology used to remove the different substances, may vary from very simple

such as filtration and chlorination, to comprehensive treatment processes such as denitrification, pre-oxidation, coagulation, flocculation, sedimentation, filtration, activated carbon filtration and disinfection (AWWA, 1990).

Algae, especially phytoplankton and their by products, form part of the raw water quality variables that determine the water treatment technology used to produce an acceptable water quality (Bernhardt and Clasen, 1991). Algae are therefore considered to be unacceptable substances as they affect the quality of the potable water in several ways. Algae may also cause physical problems in the purification plant, aspects that will be reviewed in the following paragraphs.

2.2.1 CHARACTERISTICS OF ALGAL SUSPENSIONS AND THEIR IMPLICATIONS FOR WATER PURIFICATION PROCESSES

A suspension of planktonic algae may be regarded as a suspension of biological particles. Some of the differences between suspended biological and inorganic particles are discussed by Haarhof (1988) and can be summarised as follows:

a. The *particle diameter* of algae varies from a minimum of 2 μm to a average of 10 μm. On average this is between one and two order of magnitude larger than that of inorganic colloidal particles.
b. The *specific gravity* of algae should be close to that of water to ensure its optimum vertical position in the water . In the case of larger cells this is achieved by regulated gas vesicles, lightweight oils or mucilaginous sheets which are lighter than water. Oblong cell shapes or spinelike appendages can increase the larger cell's hydrodynamic drag while other species are motile by means of flagella. In contrast to the elaborated mechanisms used by algae to maintain natural buoyancy, silicate clays have a specific gravity in the region of 2 600 kg/m^3. As a result, the mechanisms whereby algae and clay particles are transported through the different purification processes, should be substantially different and will be addressed in this study.
c. Most particles occurring naturally in water have a negative *electrical surface charge*. Parallels between true colloidal suspensions and algae for their removal by means of flocculation and filtration are quoted by Haarhoff (1988). This point will receive special attention during the study.
d. Algae is responsible for the increase of *dissolved organic carbon* which is not associated with model clay suspensions. The effect of this algal related material on the purification process will be discussed later.

2.2.1.1 Algae and slow (direct) filtration

Filtration, as a water purification process, dates back to 1804 but was first used in public water supplies in 1829 (Baker, 1949). Water was directly filtered through a sand filter with a large area surface (0,5 acres) at a very slow rate (0,1 m/h) without any pre-treatment. In slow sand filtration the interaction between physico-chemical factors and biological factors are important so as to ensure the quality of the filtrate. Bellinger (1979) gave a detailed description of the role of algae in this filtration process. Although algae contribute to a high dissolved oxygen concentration in the filtrate, they may interfere with the filtration process by blocking the filter. High algal concentrations in the raw water will contribute significantly to the wet load on the filter. This will necessitate more frequent filter cleaning which is costly. According to Bellinger (1979) the contribution of dissolved organic carbon (DOC) by algae to the water may be as high as 1 kg DOC/day from *Chlamydomonas* sp. He also lists several algal species responsible for the penetration or blockages of filters.

According to Letterman (1987), direct filtration becomes impractical, based on area requirements and maintenance cost if the total coliform count exceeds 50 organisms/mℓ and the phytoplankton biomass is more than 20 mg C/ℓ. The deterioration of the raw water quality caused by these organisms, lead to the implementation of different pre-treatment processes, which will be discussed in the following paragraphs.

2.2.1.2 Algae and coagulation/flocculation

A high load of suspended particles will cause slow sand filters to block frequently and will increase the maintenance cost of these filters. In cases of high water demand, the area of slow sand filters is not always available. It is therefore necessary to remove most of the particles by another process so that water can be filtered at a higher rate through a smaller area surface. Most of the particles are affected by and removed by a process known as coagulation/flocculation. Coagulation describes the process whereby very fine particles of colloidal size adhere directly to each other as a consequence of Brownian movement, once the mutually repulsive electrical surface forces have been sufficiently depressed by the addition of ions (Purchas,1981). Coagulation is followed by the agglomeration of particles (flocculation) to a settleable size (Purchas and Wakeman, 1986).

Algae may be regarded as particles suspended in the water which can be removed by coagulation and precipitation. Ayoub and Koopman (1986) concluded from a literature study that "algae may be considered hydrophillic biocolloids that carry negative surface charges over the normally encountered

pH range". This confirmed work done by Mc Garry (1970), Tilton *et al.* (1972) and Tenney *et al.* (1972). Ives (1959), however, showed that *Asterionella* sp has a zeta potential of 11.6 mV at a pH of 8,2. The existence of positively charged algal cells was confirmed by Friedman *et al.* (1977) because it was demonstrated that the addition of anionic poly-electrolytes were moderately effective as a flocculation aid using lime as flocculant. Whether the success of the anionic poly-electrolyte is due to positive charged algal cells or to the charge of all the particles as well as chemical compounds in the water, is not clear. Gimmler *et al.* (1991) showed positive zeta potentials for the acid resistant *Dunaliella acidophila* at low pH values. These results indicates that, if the electrical charge on an algal cell is a significant factor in chemical coagulation, considerable variation in algal removal would occur depending on the algal species present and specific coagulant used. In this context Friedman *et al.* (1977) demonstrated that algae are most efficiently removed between lime concentrations of 300 mg/ℓ to 500 mg/ℓ resulting in pH values between 11,5 and 11,8. Ives (1956) showed that the amount of chemical coagulants required to allow an algal material to settle, is largely determined by the number and size of the algae present. The algal concentration and growth phase, surface to volume ratios, algal cell size as well as temperature, played important roles when polyelectrolyte was used as a flocculant (Benderliev and Iossifova, 1982; Borchardt and O'Melia, 1961; and Tilton *et al.*, 1972).

Different electrical surface charges on the algal cell surfaces may affect the coagulation/flocculation process, but so will algal metabolic products. According to Bernhardt *et al.* (1985), algogenic substances, especially neutral or acidic polysaccharides, can influence flocculation according to the ratio of their occurrence to the flocculant used (iron or aluminium salts) and to the surface concentration of the negatively charged particles in the water to be treated. Bernhardt and co-workers showed that algogenic substances at high concentrations ($>$1-2 mg carbon/ℓ) form colloidal substances that penetrate sand filters, thus affecting water quality. The algogenic matter also contributes to an increase in the negative charge density of all particles present, significantly obstructing the destabilisation process during coagulation. Correspondingly more flocculant and, depending on the situation, additional amounts of cationic polyelectrolyte are needed to allow all particles to coagulate and flocculate.

In this study, the effectiveness of coagulation, using line as coagulant, and flocculation at Rand Water, to remove different algal species from the water phase, be will be investigated.

2.2.1.3 Algae and sedimentation

Settling of coagulated and flocculated particles (sedimentation) is governed by their concentration and their relative tendency to cohere (Purchas and Wakeman, 1986). From personal observation and work done by Pieterse (1989) it is evident that the most significant decrease in the algal concentration during water purification takes place during sedimentation. There is, however, indications that some motile algae may be able to escape floc formation and sedimentation. Experience at Rand Water indicated that *Chlamydomonas* spp., *Carteria* spp. and other motile algae are responsible for the algal-related water quality problems in other sections of the purification plant because they are inadequately removed in the sedimentation process.

Sufficient nutrients remain in the water after sedimentation to support algal growth. As most of the suspended inorganic material is removed, optimal light conditions in the sedimentation basins may promote algal growth. These variables, favourable for algal growth, may be responsible for the excessive growth of algae (epiphytic and planktonic), which were not removed by the coagulation and sedimentation process, observed in the rest of purification plant (Pieterse *et al.*, 1993). These algae may be responsible for the algogenic substances that is known to interfere with filtration and increase the oxidant demand of the water.

2.2.1.4 Algae and rapid gravity sand filtration

The sedimentation process, as indicated above, remove the bulk of the coagulated suspended matter, including algae, from raw water. Rapid gravity filtration is used to remove the remaining flocculated suspended particles. During rapid gravity filtration water gravitate through sand at a rate of ± 4 $m^3/m^2/h$ (an area of ± 40 m^2). Algae, not removed by sedimentation, could cause higher algal loads on the rapid gravity sand filters and may cause the same type of problem as encountered in slow sand filters (See 2.2.1.1). Naghavi and Malone (1986) showed that running time, at a fixed head loss, is greatly affected by higher influent algal concentration. High algal concentration in the influent are responsible for the poor removal efficiency of the sand filter (Davis and Borchardt, 1966). Watson (1989) showed that *Microcystis aeruginosa, Oocystis sp, Stephanodiscus astraea* and *Aphanizomenon flos-aquae* penetrate rapid gravity filters. *Anabaena sp, Scenedesmus* sp and *Ankistrodesmus* sp concentrations increase in the filter effluent as available removal sites in the sand filter are occupied (Borchardt and O'Melia, 1961).

Factors responsible for the removal of algae by sand filtration are the sand grain size as well as the

size and shape of algae. A sand grain size less than 200 μm are required to remove *Scenedesmus quadricauda* (Naghavi and Malone, 1986). Small green algal cells are particularly difficult to remove (Foess and Borchardt, 1969). Pennate diatoms were removed better than the centric diatoms because the former group of diatoms consisted of cells that were up to ten times longer than the centric *Stephanodiscus* sp (Kalbe, 1981).

When the chlorophyll concentration in the potable water at Rand Water exceeds 1 $\mu g/\ell$, *Carteria* sp. and *Chlamydomonas* sp. are frequently observed in the filtrate. Sometimes big colonies of *Coelastrum* sp. are found in the potable water, giving rise to colour problems in the production of ultra white fabrics in the textile industry (Dr F C Viljoen - personal communication)[1]. This algal species could only be present in the filtered water due to inadequate filtration.

To comply to the aims of this project, specific experiments were done to compare the filterability of non-oxidised algae as well as pre-oxidised algae.

2.2.1.5 Algae in the treated water

From the information presented above it may be concluded that algae, which can not be coagulated, will not be sedimented and may therefore penetrate through the sand filters, effecting the quality of the treated water. As algae and algogenic matter comprise complex organic material, it is evident that they will contribute to the chlorine demand of the water. Observations made at Rand Water indicated that the algal concentrations in the potable water contribute to assimilable carbon in the water, which in turn may enhance bacterial growth in the distribution network.

Algogenic material from specific algal species is responsible for colour and odour/taste in the final water. Geosmin was identified as the main cause of odour related problems in the potable water at Rand Water. In most cases *Microcystis sp, Oscillatoria* sp and *Anabaena* sp were present in the water at concentrations in excess of 10 μg chlorophyll/ℓ where geosmin was detected.

Information presented in 2.2.1.2 to 2.2.1.4 suggests that algae and the algogenic matter interfere with the purification processes, thus explaining the presence of algae in potable water. Algal related water purification and potable water quality problems were presented by Steynberg and Viljoen (1990) and can be summarised as follows:

---

[1] Dr F C Viljoen, Rand Water, P O Box 1127, Johannesburg. 2000 South Africa.

i. blocking of microscreens and increased operational costs,
ii. increasing the oxidant demand of the water,
iii. dictating the oxidant and the concentration used to allow sedimentation of algae,
iv. interference with the filtration process,
v. acting as THM precursors upon pre-oxidation and disinfection of the water,
vi. releasing of neuro- or hepatoxins, the effect of these toxins at low concentrations on consumers, is still unknown,
vii. causing tastes and odours in the potable water,
viii. producing colour,
ix. blocking and penetration of slow as well as rapid gravity filters. This results in reduced filter running times, increased backwashing as well as increased use of chemicals to disinfect filters, and
x. suspended algae contributes to turbidity in the potable water.

2.2.1.6 Characteristics of algae responsible for their resistance against removal

Except for the metabolic products of algae which may interfere with the coagulation/flocculation process (see 2.2.1.2), some of the algae may possess physical and morphological characteristics which interfere with removal processes.

Bernhardt and Clasen (1991) suggested that the removal of bacteria and certain algae by flocculation and filtration conforms to the same laws as the elimination of colloidal and finely dispersed substances, irrespective of their inorganic or organic nature. Deviations from the described flocculation of algal cells (Bernhardt and Clasen, 1991) may occur in the presence of mobile algae or algae that are not spherical. Such algal may contain "bristles" (spines up to $\pm$ 40 μm in length) which prevent direct contact between adjacent cell surfaces as well as bridging or cross linkage during the flocculation process. Bernhardt and Clasen (1991) also supplied information on long filamentous algae (*Oscillatoria rubescence*) and large colonial algae (*Fragilloria crotonensis*) which clearly indicate that flocculant requirement is not in accordance with stoichiometric laws. Flocculation of cells in colony form, embedded in a gelatinous layer, like *Dictyosphaeriem* sp has been shown not to follow the principle of adsorption coagulation with charge neutralisation (Bernhardt and Clasen, 1991).

According to Bernhardt and Clasen (1991) algae which are motile (by means of flagella), are able to liberate themselves from floc aggregates. These observations is in accordance with the experience at

Rand Water (see 2.2.1.3). Bernhardt and Clasen (1991) is also of the opinion that these algae will only be removed if the motility of the algal cells is inhibited prior to flocculant dosage by means of oxidising agents. For this project, it was therefore necessary to compare the effect of pre-oxidation with respectively chlorine and chlorine dioxide on motility of algae in relation to their removal by coagulation, sedimentation and filtration.

2.3 PRE-OXIDATION AS AN ALGAL REMOVAL AID

As mentioned in chapter 1, the implementation of algal control measures in the catchment of the raw water sources, to limit nutrients that support algal growth, may not always safeguard potable water treatment works against algal related water quality problems. Work done by Rand Water indicated that pre-oxidation with chlorine can be one of the less expensive algal control measures at the purification plants of Rand Water (Steynberg and Viljoen, 1990; Table 2.2).

TABLE 2.2: EXPECTED ALGAL REMOVAL COSTS TO RAND WATER (CALCULATED ON VOLUME OF WATER PRODUCED AND COSTS CALCULATED FOR 2290 Mℓ/d).

PURIFICATION TECHNOLOGY	COST (c/kl)
Pre-oxidation on 1000 Mℓ/d at 5 mg/ℓ (50% *)	0,27
DAFF on 600 Mℓ/d (100 % *)	3,4
Granular activated carbon on 2290 Mℓ/d	9,9
Costs of covering filters	0,13

* Percentage of time technology required during a year.

Pre-oxidation of raw water (oxidation before coagulation) may also be practised for the following reasons (Hoehn *et al.*, 1987).

a) Removal of iron and manganese.
b) Disinfection aid.
c) Preventing proliferation of bacteria in settled solids.
d) Stopping excessive biological growth in filter basins.

e) Lengthening filter runs.

f) Helping with sludge management.

Ma and Li (1992) also indicated that pre-oxidation with permanganate result in lower residual turbidity of settled water for any flocculant dose (20 to 80 mg Alum/ℓ) used. Richard and Darga (1992) have shown that the use of ozone as pre-oxidant, with optimal coagulant dose, may result in an improved algal removal from 75 per cent to 98 per cent. Sukenic *et al.* (1987) indicated that flocculation of algal cells is enhanced during pre-treatment with chlorine dioxide, because it supposedly modifies the cell envelope, thus reducing the colloidal stability of the algae. Pre-oxidation may therefore be used as a method to improve algal removal at water purification plants. For this study it is essential that the possible contribution of chlorine and chlorine dioxide to the removal of algae in the purification plants of Rand Water is evaluated. As these oxidants differ in composition and action, the properties of chlorine and chlorine dioxide will be discussed in the following paragraphs.

2.3.1 CHLORINE

The use of chlorine as a pre-oxidant is strongly recommended by Ibrahim *et al.* (1982). To understand the functioning of chlorine as a pre-oxidant during the water purification process, it is necessary to briefly discuss the important properties of chlorine.

The properties of chlorine differ widely, depending on the gaseous, liquid or aqueous state. Chlorine gas was discovered in 1774 by Karl W. Scheele, a Swedish chemist, when he heated a black oxide of manganese with hydrochloric acid (Baldwin, 1927). The chlorine liberated was a strong smelling, greenish yellow gas with a pungent odour; extremely irritating to mucous membranes. A detailed and interesting history of the application of chlorine gas is presented by White (1972).

Chlorine is a halogen and occurs in nature only in combination with other elements as the negative chloride ion with a valence of -1. It is estimated to account for 0,15 per cent of the earth's crust in the form of soluble chlorides, such as common salt, carnallite and sylvite (White, 1972). Chlorine has the periodic number 17, indicating that there are 17 positively charged protons in the nucleus of the chlorine atom. Depending on the exchange of the negative electrons with other atoms, the chlorine atom can have a valence ranging from +7 to -1.

Normally all molecules and compounds must have a valence of zero. The chlorine molecule (Cl_2) can

be considered as two chlorine atoms, Cl^+ Cl^-, respectively having a positive and a negative valence, balancing to zero. This property of the chlorine molecule characterises it as an oxidising agent as the Cl^+ gains two electrons in a chemical reaction.

During pre-oxidation of water, chlorine is added to water in elemental gaseous form, or as a liquid hypochlorite solution. When chlorine gas dissolves in water a special type of oxidation-reduction reaction takes place; it hydrolyses rapidly as follows:

$$Cl_2 + H_2O \text{ ----> } H^+ + Cl^- + H^{+1}O^{-2}Cl^{+1} \quad (1)$$

According to a survey done by White (1972), the hydrolysis of chlorine has been studied by many investigators and the speed of this hydrolysis is extremely rapid. The rapid rate of this reaction is best explained by the reaction mechanism where the chlorine molecule reacts with the hydroxyl ion rather than with the water molecule:

$$Cl_2 + OH^- \text{ ----> } HOCl + Cl^-. \quad (2)$$

Equation 2 shows that the concentration of HOCl, the more active compound in oxidation, depends on the total chlorine concentration and the pH. HOCl is a weak acid and will therefore tend to undergo complete dissociation, depending on pH of the solution to produce a hypochlorite and a hydrogen ion.

$$HOCl \text{ <----> } H^+ + OCl^- \quad (3)$$

The same phenomenon occurs when hypochlorite is used instead of gaseous chlorine. When sodium hypochlorite is used, it undergoes the following reactions in water:

$$NaOCl + H_2O \text{ ----> } HOCl + NaOH \quad (4)$$
$$HOCl \text{ ----> } H^+ + OCl^-$$

Although both the elemental and hypochlorite forms produce hypochlorous acid, they tend to drive the pH in opposite directions. Reaction 1 produces protons, and reaction 4 consumes protons. The high pH is caused by the excess NaOH present in sodium hypochlorite and possibly by the formation of NaOH.

Reactions 1 to 4 are pH dependent and are incomplete with concentrations of a few milligrams per litre and at pH 5 to pH 9. The relative availability of hypochlorous acid or the hypochlorite ion at pH varying from 4 to 11 is illustrated in Figure 2.1. This dissociation reaction clearly shows that the ratio of OCl^- to HOCl increases as the pH increases.

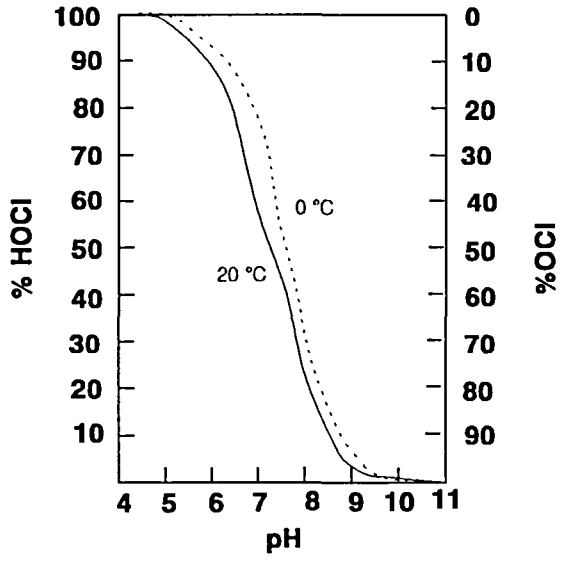

FIGURE 2.1 : DISSOCIATION OF HYPOCHLOROUS ACID VERSUS pH (FROM WHITE, 1972).

Both the hypochlorous acid and hypochlorite ion take part in chemical reactions. They are measured and reported together as free available chlorine. Free chlorine reacts with various chemicals in water. Detailed descriptions, regarding these reactions are presented by various authors, (White, 1972; Morris, 1978; Johnson, 1978; Christman *et al.*, 1978) and will not be discussed in this section. It must however, be stated that the reaction of chlorine with ammonia, amino acids, proteins, carbonaceous materials, nitrates, iron, manganese, hydrogen sulphide, cyanides and other substances will affect the chlorine concentration available to oxidise compounds and kill organisms.

Several papers presented at the Second Conference on Environmental Impact of Water Chlorination, Gatlingburg, Tennessee (Proceedings by Jolley *et al.*, 1978) discussed the health effects of chlorinated water. From these papers it is evident that chlorination (disinfection) of water may contribute to an increased risk of chronic disease but also decrease the risk of waterborne infectious diseases (Figure 2.2).

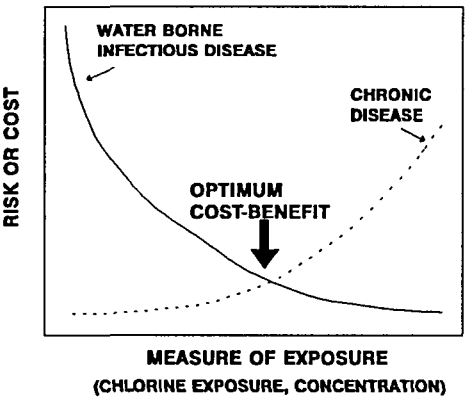

FIGURE 2.2 : RISK-BENEFIT ASSESSMENT ANALYSIS OF THE HEALTH EFFECTS OF WATER CHLORINATION (SCHNEIDERMAN, 1978).

To what extent these risks apply to pre-oxidation of raw water and algal suspensions, is not clear from the available literature. The consequences of pre-chlorination on algae and the water treatment processes will be discussed below.

2.3.1.1 The effects of chlorine on algal cells

According to Green and Stumpf (1946) chlorine completely bleach algal cells and is adequate to sterilise the water. White (1972) mentioned several studies which researched the nature of the inactivation mechanism of chlorine on bacteria, cysts and spores. The action of chlorine on algal cells has not been clearly defined. Hypothesis such as oxidation of algae's food source (Griffin, 1947) and cell damage (Sukenik *et al.* 1987) were presented. Work done by Brooks and Seegret (1978) and Brooks and Liptak (1979) suggested that chlorophyll-a destruction is the principal cause of reduced photosynthetic rates with increasing chlorine concentrations. The concept of cell lysis upon chlorination (Ringer and Campbell, 1955), mentioned in many studies (Haarhof, 1988), offer an explanation for the release of algal material after chlorination. The release of material may be explained by the relative ease with which HOCl can penetrate cell walls. The penetration is comparable to that of water, and can be attributed to both modest size (low molecular weight) and electrical neutrality of HOCl (White, 1972). After penetrating the cells, HOCl would then be able to destroy membrane and enzyme systems within the algal cells. White (1972) stated that it is generally agreed that the relative efficiency of the various disinfecting compounds is a function of the rate of diffusion of the active agent (HOCl in the case of chlorine) through the cell wall.

Research by Echelberger *et al.* (1971), using only algal cells without extra-cellular organic matter, suggested the presence of nitrogenous groups on the algal cell wall, which are complex macromolecules are not readily susceptible to oxidation. The slow rate of the decrease in free chlorine residual during experiments Echelberger and co-workers, indicate a more complex movement of the HOCl through the algal cell walls than is suggested by White (1972).

The OCl^- ion, because of its inability to diffuse through the cell walls of micro-organisms, is a relatively poor disinfectant. This is mainly due to the negative electrical charge of the OCl^- ion (White, 1972).

From the above it is evident that the algicidal efficiency of chlorine will depend on the:

a) ratio of HOCl and OCl^- which is a function of the pH of the water, and
b) the HOCl and OCl^- demand exercised by other substances in the water.

Bernhardt and Hoyer (1979) also suggested that the algicidal efficiency of chlorine is determined by different first order reaction rate constants that could be a function of the different chemical compounds in the water. If the reaction rate constant indicates a faster reaction for the other substances, chlorine will be consumed by these compounds in preference and less free chlorine will be available to oxidise algal cells. The oxidant demand of the water in which the algicidal efficiency of chlorine and chlorine dioxide will be compared, has therefore to be taken in consideration.

2.3.1.2 The consequence of pre-chlorination of algal-laden water

One of the reasons for pre-chlorination, is to prevent algae from penetrating the water purification processes. A number of references on the consequences of chlorination of algal suspensions were found and will be discussed briefly in the following paragraphs.

a. Coagulant dose

Although the algicidal effect of chlorine was found to be irreversible (Sarkiskova and Skripnik, 1988) chlorination of microalgae is known to impair the capability of cationic polyelectrolytes to flocculate algae (Echelberger *et al.*, 1971). Pretreatment with 10 - 20 mg/ℓ chlorine increased the required alum dosage by 15 per cent (Sukenik *et al.*, 1987). The effect of pre-chlorination on the lime dosage (coagulant used by Rand Water) will have to be investigated.

b. Algal species selection

Work done by Sukenic *et al.* (1987) indicated that the dominant algal species in the water being treated can change after chlorine treatment to smaller algal species, which are supposedly more problematic in the purification system. It would therefore be essential to determine the sensitivity of algae to chlorine, so to identify the most chlorine resistant algae which may cause purification problems in the other unit treatment processes.

c. Trihalomethane production

Trihalomethanes are halogen-substituted, single carbon compounds having the general formula CHX_3, where X may be fluorine, chlorine, bromine, or iodine, or combinations thereof (WHO, 1984). With respect to potable water, only the following compounds are applicable (WHO, 1984):

i. Chloroform ($CHCl_3$)
ii. Bromodichloromethane($CHBrCl_2$)
iii. Dibromochloromethane($CHBr_2Cl$)
iv. Bromoform($CHBr_3$)

Fiessinger *et al.* (1981) presented data that shows that pre-chlorination contributes to the formation of chloroform in the final product (Figure 2.3).

Trihalomethanes in drinking water occur as products of the reaction of chemicals used in oxidative treatment, reacting with the naturally occurring organic materials present in the water. Their formation is particularly associated with the use of chlorine. Trihalomethane (THM) formation from organic sources is primarily a function of the nature and concentration of organic material, pH, temperature, the nature of the chlorine species, and the Cl_2:C ratio (Christman *et al.*, 1978).

At this stage there is a difference in opinion on what effect trihalomethanes in potable water may have on human health. This is reflected by the different guidelines for THMs in different countries (Table 2.3). Although chloroform has been proved to be toxic to man (WHO, 1984), their is a difference in opinion on the carcogenic effect of THMs. A recent major study concluded that an increased incidence of bladder and rectal cancers can be seen in populations drinking chlorinated surface waters for many years (Morris *et al.*, 1992). An evaluation by the International Agency for Research on Cancer (IARC, 1991) indicated that the degree of evidence for such an association was inadequate.

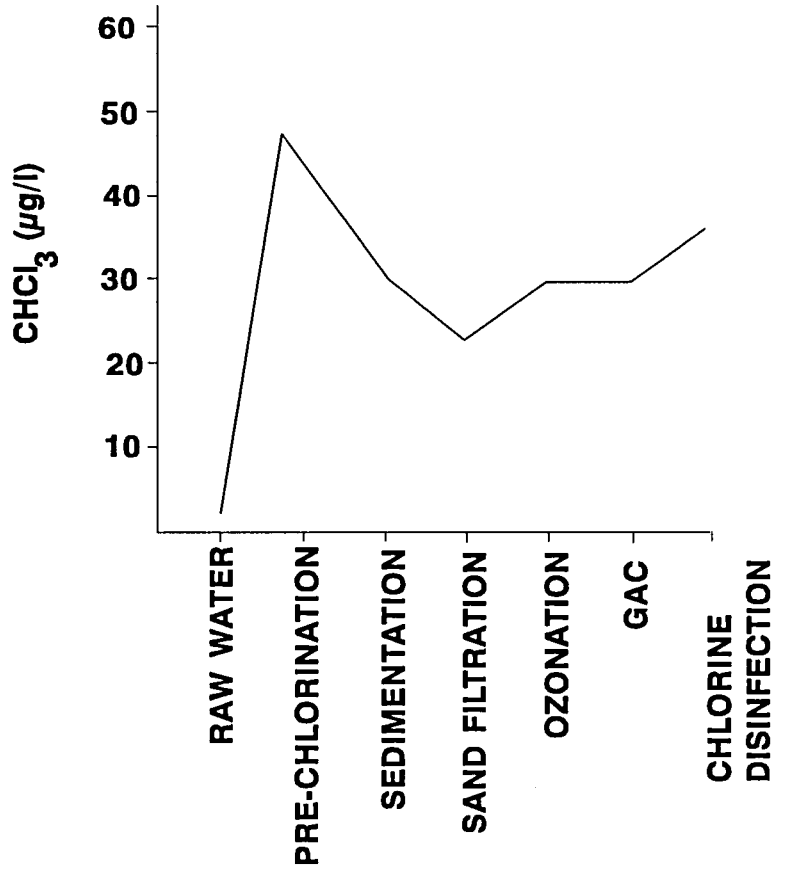

FIGURE 2.3 : CHANGES IN CHLOROFORM CONCENTRATION THROUGH TREATMENT PROCESSES (Fiessinger *et al.*, 1981).

As an algal cell contains organic material one may expect that algae can contribute to the formation of THMs after chlorination. Morris and Baum (1978), investigated the potential of chlorophyll to produce chloroform. A suspension containing 1700 µg of chlorophyll-a/ℓ, obtained from an aqueous paste of which the solid content was unknown, was used. The suspension was mixed with a 40 mg/ℓ aqueous chlorine solution at the following pH values: 5,8, 6,6, 7,0, 9,2 and 10,0. The mixtures were allowed to stand for 100 hours. At the respective pH values, 12 µg/ℓ, 32 µg/ℓ, 56 µg/ℓ, 260 µg/ℓ and 320 µg/ℓ chloroform was produced.

Bernhardt and Hoyer (1979) chlorinated suspensions of *Fragilaria crotonensis, Carteria radiosa, Pandorina morum* and *Pseudoanabaena galeata*. The particular organic carbon (POC) content of each algal suspension was approximately 60 mg/ℓ, while that of the *Pseudoanabaena* sp suspension was only 40 mg POC/ℓ. The total organic chlorinated products (TOCl) formed were high (Figure 2.4). The bulk of the TOCl was formed during the first 5 hours of the chlorine reaction.

TABLE 2.3 : THM LIMITS IN DRINKING WATER FOR DIFFERENT COUNTRIES (Rand Water Board, 1993)

Country/Organisation	Criteria	Compound	Concentration ($\mu g/\ell$)
WHO	Guideline	$CHBr_3$	100
		$CHBr_2Cl$	100
		$CHBrCl_2$	60
		$CHCl_3$	200
		TOTAL	1000
Rand Water Board	Guideline	$CHBr_3$	50
		$CHBr_2Cl$	50
		$CHBrCl_2$	50
		$CHCl_3$	50
		TOTAL	100
Australia	Guideline	THMs	200
Canada	Guideline	THMs	350
EEC	Guideline	THMs	1
Italy*	Maximum value	THMs	30
UK*			No limit
USA	Maximum contaminant level	THMs	100

* Information from Contu *et al.*, 1990

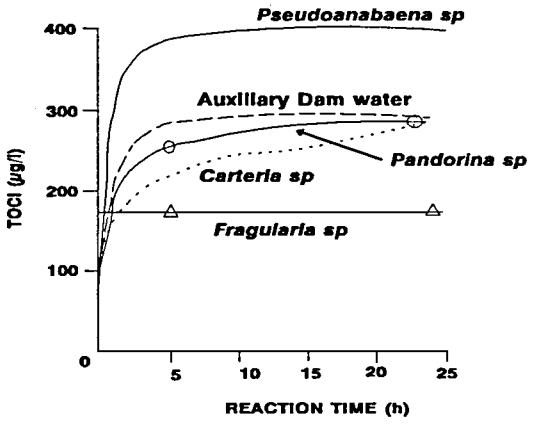

FIGURE 2.4 : TOTAL ORGANIC CHLORINATED (TOCl) PRODUCT FORMATION AS A FUNCTION OF CHLORINE CONSUMPTION AND TIME IN UNFILTERED ALGAL CULTURES AND IN DAM WATER DURING AN ALGAL BLOOM (200 000 cells/mℓ) (FROM BERNHARDT AND HOYER, 1979).

If the halogen formation ($\mu g/\ell$) is plotted against the exposure time to chlorine (Figure 2.5), it can be noted that, with the exception of the *Fragilaria* sp suspension and the dam water, the concentrations of haloforms produced in this series of experiments were low and even decrease with time. Bernhardt and Hoyer (1979) explained these results by proposing that the haloforms formed are bound to algal particles and cell fragments and are therefore not extracted during the analytical method used. These results were supported by a second set of experiments (Table 2.4). The TOCl and the haloform formation potential in the water obtained from filtered algal suspensions were higher than that from unfiltered suspensions. Bernhardt and Hoyer (1979) regarded this as an indication that haloforms precursors may be removed by particulate organic substances (detritus) that can be flocculated and filtered off.

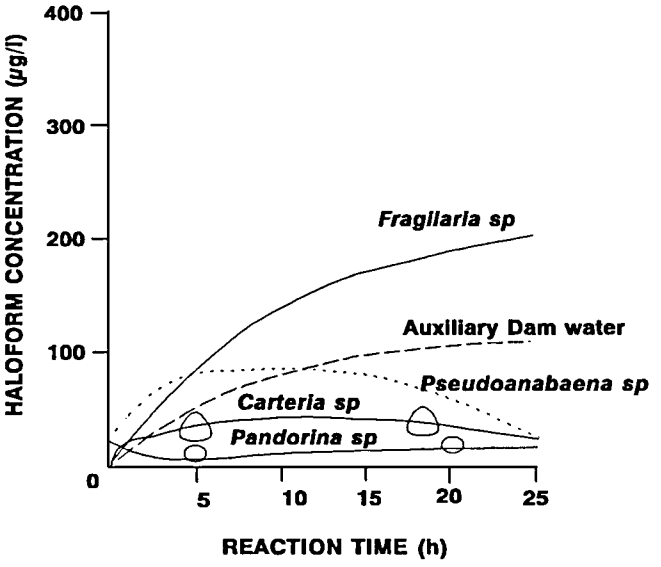

FIGURE 2.5: HALOFORM FORMATION AS A FUNCTION OF THE CHLORINE CONSUMPTION AND REACTION TIME IN UNFILTERED ALGAL CULTURES AND IN DAM WATER DURING AN ALGAL BLOOM (200 000 cells/mℓ). FROM BERNHARDT AND HOYER, 1979.

TABLE 2.4: TOCl AND HALOFORM FORMATION POTENTIAL (20 h EXPOSURE TIME) IN ALGAL SUSPENSIONS IN COMPARISON WITH THE CORRESPONDING MEMBRANE FILTRATES (0,45 μm) (FROM BERNHARDT AND HOYER, 1979).

Sample	Species of algae	Unfiltered				Membrane filtered			
		POC mg/ℓ	TOCl μg/ℓ	Halof μg/ℓ	DOC mg/ℓ	TOCl μg/ℓ	Halof μg/ℓ	TOC %unit	Halof %unit
Fragilaria	Siliceous algae	57	265	174	1,7	165	30	62	36
Fragilaria	Siliceous algae	62	166	192	2,1	87	32	52	27
Pseudoana-baena	Blue algae	40	400	22	1,1	173	106	43	480
Carteria	Green algae	63	300	18	5,0	155	92	52	510
Pandorina	Green algae	57	290	6	6,5	165	44	57	720
Auxiliary dam	Micro-algae	-	292	106		151	197	52	186

POC = Particular organic carbon
TOCI = Total organic chlorinated products
Halof = Haloform

Bernhardt and Hoyer (1979) concluded that the formation of haloforms during the treatment of various algal suspensions with chlorine proceeded with varying degrees of intensity and that allowance should be made for interference in the analytical determination of haloforms by cellular fat and oil substances, so that the haloform concentrations as measured appear to be low. These results strongly suggest that algae may be sources of haloforms precursors in the treatment of water if chlorine is used as oxidant. As chlorine is used as an oxidant in this study, the chlorinated by-products will have to be monitored.

d. Release of cellular material

Sukenik *et al.* (1987) reported an increase in dissolved organic carbon (DOC) upon chlorination of algal suspensions. After a contact time of 10 minutes, chlorine dosages of 2 mg/ℓ, 10 mg/ℓ and 20 mg/ℓ resulted in increases in DOC of respectively 5 per cent, 20 per cent and 15 per cent. The significance of the increase in DOC could not be determined as the DOC concentrations were not given.

Evidence of the release of cellular material upon chlorination is given by Hom (1972). A chlorine dosage of 32 mg/ℓ, and a contact time of 20 minutes in sewage pond effluent containing 2,6 x 10^6 cells/mℓ of *Chlorella* sp, increased the BOD value from 20 mg/ℓ to 100 mg/ℓ. Echelberger *et al.* (1971) and Akiba *et al.* (1990) also demonstrated the release of cellular material after chlorination.

The effect of the release of the extra-cellular organic material (EOM) in raw water after chlorination on the purification processes may be significant. Bernhardt *et al.* (1985) demonstrated that these substances result in negative surface charges on the suspended inorganic particles, which would require more coagulant in cases where aluminium and iron salts are used (See paragraph 2.2.1.2). In contrast Echelberger *et al.* (1971) demonstrated that the EOM released after chlorination, caused significant flocculation and settling when compared to an unchlorinated control.

It is not only the release of organic material by algal cells that may affect the surface charge densities of the suspended particles. Ives (1956) showed a marginal increase in the negative surface charge of algal cells when oxidised with ozone. This increase was however, not enough to change their physical behaviour. It is assumed that oxidants such as chlorine and chlorine dioxide will have the same effect, but the effect thereof on the flocculation process is unknown. The effect of released algogenic material, after chlorination, on the coagulation/flocculation process will be investigated in this project.

The interaction between chlorine and a mixed green algal culture was also researched by Echelberger *et al.* (1971). Algal cells without extracelluler organic material, suspended in organic free water, were examined. This suspension showed a typical breakpoint curve, similar to that of ammonia. A linear relationship was indicated between the chlorine dosage to obtain a specific free chlorine residual after a given time and specific algal concentration. The free chlorine residual also decreased with time (3 hours). The role of algae, exerting a chlorine demand component, will also be studied in this project.

e. Taste and odour production

It is known that the chlorination of filtered water which contains low concentrations of organic material (e.g. phenol) may impart objectionable taste and odours to the water. To what extent this is also true for the chlorination of algae, is unknown. Research at Rand Water indicated that chlorination of water containing algal products, such as geosmin, may intensify the odour.

It is evident that reactions between chlorine and algae are as complex as reactions of chlorine with other organic material. Not only are undesirable products formed, but the efficiency of the chlorine is also effected by pH. As a result researchers investigate the use of alternative oxidants for either disinfection or pre-oxidation (Table 2.5).

TABLE 2.5: ALTERNATIVE OXIDANTS USED FOR PRE-OXIDATION OR DISINFECTION IN THE PRODUCTION OF POTABLE WATER.

Oxidant	Pre-oxidant	Disinfection	References
Ozone	√	√	Sauner *et al.* (1983)
	√	√	van Leeuven (1989)
Chlorine dioxide	√	√	Masschelein (1979)
Ultra violet		√	Wolfe (1990)
Peroxone		√	McGuire and Davis (1988)
Hydrogen peroxide		√	Berglind *et al.* (1979)
Potassium Permanganate	√	√	Kötter (1979)

It is beyond the scope of this report to discuss and compare all the oxidants listed. Because the aim of this study is to compare the algicidal efficiency of chlorine and chlorine dioxide, only chlorine dioxide and its reactions will be discussed in the following paragraphs.

2.3.2 CHLORINE DIOXIDE

An awareness of the potential health hazards caused by the presence of halogenated compounds in drinking water has led public health authorities and water suppliers to investigate all possible means

of reducing their concentrations in water (Culp, 1984). As mentioned above, there is ample evidence that the use of chlorine for disinfection and pre-oxidation of water contributes significantly to the formation of halogenated compounds.

Renewed interest, in chlorine dioxide, as a drinking water oxidant and disinfectant was stimulated by the U.S. Environmental Protection Agency's amendment to the National Interim Primary Drinking Water Regulations which set a maximum contaminant level of 100 $\mu g/\ell$ for total trihalomethanes (THMs). Chlorine dioxide was found to be an alternative, or supplemental, oxidant disinfectant, most suited for treatment to reduce for THM formation in potable water (Aieta and Berg, 1986).

The history of chlorine dioxide, as presented by Aieta and Berg (1986), is summarised in Table 2.6. The rapid growth in the use of chlorine dioxide is an indication of its potential as oxidant disinfectant in the water treatment industry.

TABLE 2.6 : SUMMARY OF THE HISTORY OF CHLORINE DIOXIDE (AEITA AND BERG, 1986)

Date	Event	Person/Place
1811	Recording of "green-yellow euchlorine" gas	Sir Humphrey Davy
1881	Millon's gas (ClO_2 + Cl_2)	Garzarolli-Thurnlackhi
1940	Release of ClO_2 gas from sodium chlorite upon acidification or with reaction with chlorine	Taylor
1944	Application of ClO_2 to drinking water treatment	Niagara Falls, N.Y.

The chlorine atom, with the 7 electrons in the M layer (valence of -7), is capable of forming seven binary simple oxy-compounds, of which chlorine dioxide is one. A detailed description of the physical and chemical properties of these oxy-compounds is presented by Masschelein (1979). A summary of this information is presented in Table 2.7 and will not be discussed.

TABLE 2.7: PHYSICAL AND MOLECULAR PROPERTIES OF CHLORINE OXIDES (FROM MASSCHELEIN, 1979).

Name	Monoxide	Dioxide	Trioxide	Heptoxide	Chlorite
Formula	Cl_2O	ClO_2	$2ClO_2 = Cl_2O_6$	Cl_2O_7	ClO_2^-
Molecular weight	86,91	67,47	83,46 166,92	182,91	
MOLECULAR STRUCTURE AND PROPERTIES*					
Symmetry	C 2v	C 2v		C 2v	C 2v
Geometry d(C-0)A	1,7±0,02	1,49±0,14		1,709±0,004	1,57±0,03
α	110°8±1°	117°±0°5		118°6±0,7 (115°2±0,2)	110°
v1cm 1	631 (g)	945 (g)		595 (g)	790 (s)
v2cm 1	296 (g)	445 (g)		195 (g)	400 (s)
v3cm 1	970 (g)	1,108 (g)		695 (g)	840 (s)
(ClO_4)				sym	
				1,034-1,057	
				anti	
				1,270-1,295	
UV-Vis.mu	395	355	305	(350)	260 (H_2O)
(CC_{14})	415	375	340	(385)	
PHYSICAL PROPERTIES OF CHLORINE OXIDES					
Melting point (C°)	-111 to -116	-59	+3,5	-91,5	
Boiling Point (°C)	+2	+11	+203#	+80	
Density liquid (°C)	-	1,64	2,02	1,805	
Vapour	3	2,4	-	-	
Heat of Evaporation (kcal/mole)	6,20	6,52	9,5	8,3	
Critical T	139	153	-	256	
Trouton Constant (e.u.)	22,5	23,0	21,0	23,4	
Vapour Pressure (Torr at O°)	699	490 or 512	0,31	23,7	
Heat of Dissolution in Water (O°C) kcal/mole	9,44	6,6	-	50 (at 25°)	
Physical Aspect					
Solid	-	red	red	-	
Liquid	brown	orange	reddish brown	colourless (oily)	
Gas	brown	orange	-	-	

* For general relationships for the thermodynamic functions of oxides of chlorine or oxychlorine, see Masschelein, 1979

$H°(ClO_4^-) = 34,1\ n - 44,4$ kcal/mode
$H°(ClO_n) = 12,1\ n + 0,7$ kcal/mole

\# As calculated, unstable component which decomposes when reaching 15°C.

Chlorine dioxide, as used for the treatment of potable water, is obtained from sodium chlorite, by either acidification or oxidation with chlorine (Masschelein, 1979). In contrast to chlorine (equation

1), chlorine dioxide does not hydrolyse but exists as a dissolved gas in water at the range, pH=2 to pH=10. Chlorine dioxide disproportionates in alkaline solution to give a 1:1 molar ratio of chlorite and chlorate.

$$2ClO_2 + 2OH^- \text{---> } ClO_2^- + ClO_3^- + H_2O \quad (5)$$

The oxidation-reduction reactions of chlorine dioxide in water result in the formation of chlorite ion:

$$ClO_2 + e \text{ ---> } ClO_2^- \quad (6)$$

The chlorite ion is an effective oxidising agent as well. It will, however, be consumed at a slower rate as chlorine dioxide in oxidation reduction reactions.

$$ClO_2^- + 4H^+ + 4e = Cl^- + 2H_2O \quad (7)$$

Approximately 50 to 70 per cent of the chlorine dioxide added to water will appear as chlorite, the remainder as chloride, with chlorate at undetectable concentrations once the reaction has gone to completion (Masschelein, 1979).

Chlorine dioxide is applied to the raw water, before sedimentation or in water prior to filtration, for disinfection, taste and odour control, oxidation of iron and manganese, colour removal, organic oxidation, enhanced coagulation and filtration, and for in-plant control of micro- and macro-biofouling (Aieta and Berg, 1986). Detailed descriptions of the chemical reactions between chlorine dioxide and other oxochlorine compounds, inorganic and organic compounds are presented by Masschelein (1979) and Aieta and Berg (1986). These reactions will only be discussed when and where applicable to the present study.

In general chlorine dioxide reacts primarily by oxidation reactions, resulting in volatile and non-volatile organic compounds. Chlorine dioxide also appears to be more selective or less reactive than chlorine as is evident from the somewhat lower demand for chlorine dioxide than for chlorine. Aieta and Berg (1986) concluded, after an intensive literature survey, that chlorine dioxide

a) was an extremely effective bactericide,
b) was unaffected by pH conditions normally encountered in potable water (pH 6 to pH 8,5),
c) reacted extremely rapidly in inactivating bacteria, and

d) was equal to, or superior to, chlorine on a mass-dose basis.

2.3.2.1 The effect of chlorine dioxide on algal cells

Ringer and Campbell (1955) reported on the use of chlorine dioxide for algal control in reservoirs. They found chlorine dioxide to be more effective than copper sulphate at comparable treatment costs.

The reaction mechanism of chlorine dioxide with algal cells is not yet clear. One may, however, make certain assumptions on the mode of actions based on work done by researchers on the chlorine dioxide and bacterial/virus-interactions. Two main reaction mechanisms are suggested. The first is a specific chemical reaction between chlorine dioxide and organic compounds. Chlorine dioxide was shown to react with amino acids such as tryptophan, cystine, ribonucleic acid (RNA; Noss *et al.*, 1986). It is however, unclear whether the primary target of the ClO_2 is to disrupt amino acids and the protein synthesis systems, which will contribute to cell mortality.

The second reaction mechanism, suggested by Berg *et al.* (1986) shows that chlorine dioxide disrupts outer membrane permeability as measured by rapid afflux of potassium. Other researches (Ghandbari *et al.*, 1983 and Olivieri *et al.*, 1985) also showed that chlorine dioxide may alter outer membrane proteins and lipids to such an extent that membrane permeability increases.

2.3.2.2 The consequences of chlorine dioxide pre-oxidation of algal laden water.

From the literature survey done for this study it is evident that little is known about the consequences of pre-oxidation of algae with chlorine dioxide. It is assumed that, as the algal cells die, they will also release organic matter into the water. The available chlorine dioxide will then react with these organic materials, but will not form THMs (Masschelein, 1979).

The major disadvantage of using chlorine dioxide is the toxicity of the chlorite ion (equation 5) (Masschelein, 1979). Chlorite can cause haemolytic anaemia by oxidising haemoglobin to the non-functional pigment methaemoglobin (Couri *et al.*, 1982 and Condie, 1986). Masschelein (1979) reported a LD_{50} dose of sodium chlorite for rats of 140 mg/kg body weight. It is further assumed that after it's reaction in water treatment, all of the chlorine dioxide have been converted into chlorite, the LD_{50} of which is 105 mg ClO_2/kg. Masschelein (1979) concluded that at conventional doses ($<$ 1 mg chlorine dioxide/ℓ) there appears to be no health hazard (toxicity) concerning the use of chlorine dioxide in water treatment, but recommended a residual concentration for chlorite of less than

0,5 mg/ℓ. In Belgium, the maximum allowed concentration in drinking water, distributed by public services, is 0,25 mg/ℓ (Masschelein, 1979). Above this level a certain acerbity of taste may result. Work by Daniel *et al.* (1990) showed no acute toxic effect on Sprague-Dawley rats even at chlorine and chlorine dioxide concentrations in their drinking water as high as 250 mg/ℓ. There were however, clear differences in the toxicological effects of the disinfectants. Chlorine dioxide produced dosage-related decreases in body and organ weight at concentrations as low as 25 mg/ℓ, but its most significant toxic effect was the induction, at all concentrations, of nasal lesions. The oxidant concentrations used above are much higher than quoted by Masschelein (1979), thus giving wrong perceptions on the toxicity of chlorine dioxide concentrations (< 1 mg/ℓ) used in the potable water industry.

Chlorine dioxide, due to the dissociation into the chlorite ion, may not only be toxic but may also contribute to the mutagenicity of the potable water. An extensive literature survey done by Noot *et al.* (1989) on the use of the Ames test to determine mutagenicity, indicated the following relative order in which the following chemicals could contribute to increased mutagenicity when used as primary disinfectants: ozone < chlorine dioxide < chloramine < chlorine. The latter information would promote the use of chlorine dioxide as pre-oxidant in water purification.

2.4 COMPARISON OF CHLORINE AND CHLORINE DIOXIDE AS PRE-OXIDANTS

From the above discussions on chlorine and chlorine dioxide it is evident that they differ in many aspects. Most of the information in literature deals with disinfection of potable water and the consequences thereof on water quality. It will be to the benefit of this study to compare the advantages and disadvantages associated with the pre-oxidation, using chlorine and chlorine dioxide. A summarised comparison is presented in Table 2.8. From this comparison it can be concluded that although chlorine dioxide is by weight ten times more expensive to manufacture than chlorine, it is a stronger oxidant than chlorine which result in less chlorine dioxide used as biocide. Chlorine dioxide only react with a one electron acceptor, which result in fewer chlorinated products being formed. This characteristic of chlorine dioxide is responsible for no THMs being formed and for water being oxidised with chlorine dioxide to contain less mutagenic properties than water being treated with chlorine. Table 2.8 also indicates that chlorine dioxide, being a stronger oxidant, may enhance several of the water purification processes. It will therefore be necessary to take these aspects into consideration for this project.

TABLE 2.8: SUMMARY AND COMPARISON OF VARIOUS CHEMICAL, PHYSICAL AND OTHER PROPERTIES OF CHLORINE AND CHLORINE DIOXIDE AND THEIR PRODUCTS.

Characteristic	Chlorine	Chlorine Dioxide	Reference
1. CHEMISTRY			
1.1 Dissociation	$Cl_2 + H_2O$ ---> HOCl + HCl HOCl <---> $H^+ + OCl^-$	$2ClO_2 + 2OH^-$ ---> $ClO_2^- + ClO_3^- + H_2O$	
1.2 Oxidising agent	HOCl and OCl	ClO_2 and ClO_2^-	
1.3 Theoretical oxidising power	ClO_2 = 263% that of Cl_2		Geldenhuys (1986)
Redox potential	$Cl_2 + 2e$ ---> $2Cl^-$ = 1,359v	$ClO_2 + e$ ---> ClO_2^- = 0,95v	
1.4 Residuals	HOCl; OCl^-; Cl^-; NH_2Cl; $NHCl_2$; NCl_3	ClO_2^-; ClO_3^-; Cl^-; $HClO_3$	
1.5 Solubility	Less soluble than ClO_2	More soluble than Cl_2	Fiessinger *et al.* (1981)
1.6 Interference			
1.6.1 Physical			
a. Temperature	More HOCl at lower temperatures than OCl^-	Higher solubility at high temperatures	
b. pH	At pH $\geq$ 8 more than 68% of Cl_2 as OCl^- ion	Biocidal effects independent of pH	Fiessinger *et al.* (1981)
c. UV	Less sensitive to sunlight	Breaks down ClO_2^-	
1.6.2 Chemical	Reacts with Nitrogen (Ammonia)	Does not react with NH_3	
	Demand for chlorine higher than for chlorine dioxide		Rav-Acha (1984)

TABLE 2.8: (continued) SUMMARY AND COMPARISON OF VARIOUS CHEMICAL, PHYSICAL AND OTHER PROPERTIES OF CHLORINE AND CHLORINE DIOXIDE AND THEIR PRODUCTS.

Characteristic	Chlorine	Chlorine Dioxide	Reference
1.7 By Products			
THM formation	Chlorine reacts via a variety of electrophilic, oxidative and radical pathways with other organics (Reckhow and Singer, 1990)	Only reacts with a one electron acceptor. Forms fewer chlorinated products	Rav-Acha (1984)
Brominated THMs	Much higher (> 10x) formed	Only at high pH Neglectable	Kühn and Sontheimer (1981)
TOCl formation	10 x higher	At all pH; most at pH = 2	
THM precursor		Destroys THM precursors (Copper, 1990)	
COD	COD increases with increased Cl_2 dosed, free residual and increased contact time		Wight *et al.* (1978)
1.8 Free residual Disinfectant	Remains for short period in distribution network	Stays 3 x longer in water distribution	Fiessinger *et al.* (1981)
	Chloramines remains for longer periods		
1.9 Taste & Odours			
1.9.1 Control		Removes phenolic compounds	Fiessinger *et al.* (1981)

TABLE 2.8: (continued) SUMMARY AND COMPARISON OF VARIOUS CHEMICAL, PHYSICAL AND OTHER PROPERTIES OF CHLORINE AND CHLORINE DIOXIDE AND THEIR PRODUCTS.

Characteristic	Chlorine	Chlorine Dioxide	Reference
		Successful for control of taste & odours associated with street runoff	Walker *et al.* (1986)
		Incapable of removing geosmin or MIB	Fiessinger *et al.* (1981)
	Efficiency for taste and odour treatment		
		IPMP: $ClO_2 > Cl_2 > MnO_2 > O_3 > KMnO_4$	
		IBMP: $ClO_2 > Cl_2 > Cl_2 > O_3 > KMnO_4$	
		MIB: $ClO_2 > O_3 > Cl_2 > MnO_2 > KMnO_4$	
		TCA: $ClO_2 > MnO_2 > Cl_2 > O_3 > KMnO_4$	Lalezary *et al.* (1986)
		Geosmin: $ClO_2 > O_3 > MnO_2 > Cl_2 > KMnO_4$	Fiessinger *et al.* (1981)
1.9.2 Cause of tastes/odours		Bad taste at 0,1 mg/ℓ ClO_2 > 0,5 mg/ℓ objectional taste	Masschelein (1979)
	Offensive tastes and odours occur after chlorine addition	Cause of chlorinuous odours above 0,2 mg/ℓ kerosine like and chlorine like odours = a product of gas phase reactions between ClO_2 and air inside customers residence (new carpets)	Levi and Jeslin (1988) Hoehn *et al.* (1990)

TABLE 2.8: (continued) SUMMARY AND COMPARISON OF VARIOUS CHEMICAL, PHYSICAL AND OTHER PROPERTIES OF CHLORINE AND CHLORINE DIOXIDE AND THEIR PRODUCTS.

Characteristic	Chlorine	Chlorine Dioxide	Reference
1.10 Chemical Oxidation		Manganese removal superior to Cl_2 when ClO_2 added prior to coagulation	Hoehn *et al.* (1987)
2. STABILITY	Stability ranking: Chloramines > Chlorine dioxide > free chlorine > ozone		Aieta & Berg (1986)
3. TOXICITY	Subchronic toxicity for rats: Chlorine dioxide > monochlormaine > chlorine. Toxic to all aquatic life. Concentrations - Maximum permissible in air is 0,1 mg vary depending on pH, temperature and DO. ClO_2/m^3 ClO_2-$LC_{(50)}$ for rats = 140 mg/kg		Masschelein (1979)
4. MUTAGENICITY	Ranking at primary disinfection: ozone < chlorine dioxide < chloramine < chlorine		Noot *et al.* (1989)
		ClO_2 of < 1 mg/ℓ not more mutagenic than Cl_2 at 1 mg Cl_2/ℓ	Kool *et al.* (1985)
5. MEASUREMENT			
6. BIOCIDAL EFFICIENCY			
6.1 Algicide	Prechlorination on full scale required 0,8 mg/ℓ residual chlorine - continuous dosing (Ibrahim *et al.*, 1982). Effective algal control: 30 minute contact with residual above 1 mg/ℓ	ClO_2 more efficient than Cl_2 or $CuSO_4$	Ringer and Campbell (1955)

TABLE 2.8: (continued) SUMMARY AND COMPARISON OF VARIOUS CHEMICAL, PHYSICAL AND OTHER PROPERTIES OF CHLORINE AND CHLORINE DIOXIDE AND THEIR PRODUCTS.

Characteristic	Chlorine	Chlorine Dioxide	Reference
6.2 Other organism		Low residuals provide efficient disinfection (0,1 - 0,3 mg/ℓ) prior to coagulation	Copper (1990)
		Short contact times for disinfection (2-5 minutes)	Copper (1990)
	Biocidal efficiency ranking (pH6 - pH9): chlorine > chloramines	oxone > chlorine dioxide > free	Aieta & Berg (1986)
7. COAGULATION	Impair the capability of cationic poly-electrolytes to flocculate algae		Echelberger *et al.* (1971)
9. FILTRATION			
9.1 Direct	Increase in turbidity with pre-chlorination		Haarhof (1988)
9.2 Slow		Longer filter runs with 0,6 mg/ℓ ClO_2 pre-oxidation	Hoehn *et al.* (1987)
10. DISINFECTION		Short contact time required	Copper (1990)

TABLE 2.8: (continued) SUMMARY AND COMPARISON OF VARIOUS CHEMICAL, PHYSICAL AND OTHER PROPERTIES OF CHLORINE AND CHLORINE DIOXIDE AND THEIR PRODUCTS.

Characteristic	Chlorine	Chlorine Dioxide	Reference
11. SLUDGE DISPOSAL		Pre-oxidation resulted in a. Faster alum sludge dewatering rates with chlorine b. Better sludge settlement c. Manganese release from sludges to overlaying water may be suppressed.	Hoehn *et al.* (1987)
12. COST		Chlorine dioxide 10 x more expensive to manufacture than chlorine	Geldenhuys (1986)
13. DANGERS		Explosive at concentrations above 10% in air and temperature above 45°C	Masschelein (1979)

2.5 WATER PURIFICATION AT RAND WATER

The present study is aimed at comparing the possible algicidal effect of chlorine and chlorine dioxide under experimental conditions as an indication of the results to be expected on a full scale plant. A brief description of some physical and chemical aspects of water purification as practised by Rand Water are given as a background to clarify the experimental approach adopted.

Rand Water abstracts virtually all of its water to be clarified and disinfected from the Vaal Dam and the Vaal River Barrage Reservoir. Vaal River Barrage Reservoir water is normally of lower quality compared to water abstracted from the Vaal Dam. This water, which contains a high proportion of treated domestic and industrial effluent contains high concentrations of algae, dissolved inorganic salts, organic material but contains low concentrations of suspended matter. The Vaal Dam water is relatively unpolluted and contains high concentrations of suspended solids.

Rand Water currently applies the following conventional purification processes to produce potable water: pre-chlorination, coagulation, flocculation, sedimentation, stabilisation, filtration, disinfection by breakpoint chlorination at the purification works and chloramination after 6 to 8 hours contact at the booster pumping stations. Each of these processes will be briefly discussed in the following paragraphs.

2.5.1. COAGULATION AND FLOCCULATION

One of the principal problems of purifying Vaal River and Vaal Dam water is the removal of the suspended matter. Suspended matter in the Vaal River water has colloidal properties and remains in suspension for long periods. The colloidal material in the Vaal River varies in diameter between 10 and 1000 nanometre and will under normal circumstances remain suspended for periods of up to 2 years. Therefore, colloidal property is in fact of greater significance than the quantity of the suspended material.

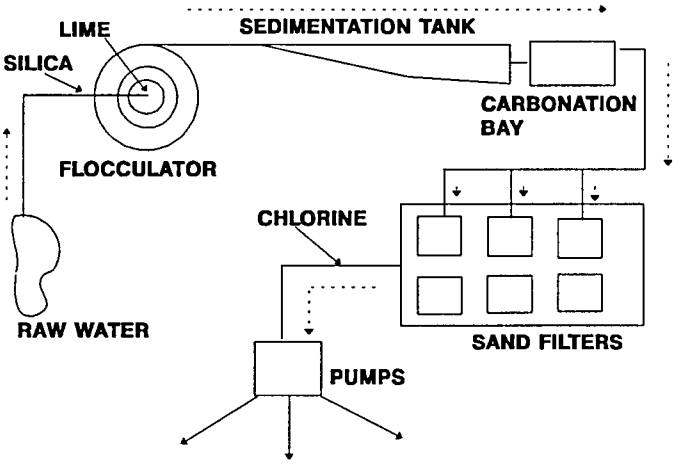

FIGURE 2.6 : A DIAGRAM OF A PURIFICATION PLANT AT RAND WATER

To achieve efficient removal of these solids, Rand Water uses hydrated lime for coagulation and flocculation and activated sodium silicate as an aid to flocculation. The average dosage rate of calcined lime varies between 55 and 70 mg/ℓ as calcium oxide and the silica dosage rate between 1 and 3 mg/ℓ as silicon dioxide. The high pH of between 10 and 11 obtained during lime coagulation limits algal growth and is very effective towards the removal of heavy metals, some organic material, bacteria and viruses.

Considering the various mechanisms which are involved during the destabilisation process with lime, rather low energy conditions are required for optimum coagulation. For lime a G value of 600 per second with a Camp Number (Gt value) of 18 000 is considered ideal in Rand Water's systems. For maximum efficiency, the lime should be added not more than 60 seconds before the point of maximum energy dissipation. The activated sodium silicate should be added prior to the lime, and it is now established practice in Rand Water to add the silica about 15 seconds before the lime (See flocculator, Figure 2.6).

Rand Water has on occasion used high molecular weight cationic polymers as the primary coagulant. A high energy input is required to operate the systems at the optimum polyelectrolyte dosage which will prevent polyelectrolyte carry over into the distribution system. Ideally, G values should be about 2 500 per second and Gt value of 50 000. The use of polyelectrolytes appears very attractive in many

ways as they are easy to handle, require less capital outlay and produce less settleable material which reduces the quantity of sludge to be removed in the sedimentation process. However, these coagulants have many disadvantages - such as high dosages required for high turbidity water, flotation problems, manganese and iron deposition in water supply pipelines and corrosion problems. Experience has shown that the water produced by polyelectrolyte treatment is more corrosive and therefore inferior in quality to that produced using lime and activated silica. Polyelectrolytes are therefore only used in a limited capacity.

2.5.2 SEDIMENTATION

Sedimentation is the oldest known method of water purification and has been employed extensively for thousands of years. Although it is a natural phenomenon, it is aided by the addition of chemical coagulants to produce flocs which are allowed to settle in specially designed tanks from which settled sludge can be removed. Rand Water uses horizontal flow tanks (see sedimentation tank, Figure 2.6) with retention times of 4 hours and produces a water with a turbidity of 5 NTU at the outlet weirs which is considered acceptable for filtration.

2.5.3 STABILISATION

The water after leaving the sedimentation systems has a pH value of about 10,5 and is very unstable and conducive to scale forming. To stabilise it, the pH is reduced with carbon dioxide (see carbonation bay, Figure 2.6) to a pre-determined value, normally between 8,0 and 8,4. The carbon dioxide used for stabilisation is not pure but a mixture of carbon dioxide and other furnace gases. The percentage of carbon dioxide in the lime kiln exhaust gases at the Zuikerbosch treatment plant is between 20 and 30 per cent. At the Vereeniging works, the carbon dioxide obtained from the boiler flue gases has a concentration of between 8 and 12 per cent.

If the concentration of carbon dioxide in the mixture is 20 per cent and absorption efficiencies of 75 per cent are achieved at the carbonation bays, then the volume of carbon dioxide:air mixture required for pH correction at ambient conditions is calculated as 22,5 m^3/minute per 100 Mℓ of water per day.

The carbonation bays are up to 3,0 m deep, and the carbon dioxide is transferred into the water through a series of PVC pipes, with 4,8 mm holes at the bottom of the pipes, under a positive pressure of 40 kPa. There are on average 13,3 holes per m^2. Absorption efficiencies vary between 70 and 80 per cent.

2.5.4 FILTRATION

Rand Water uses rapid gravity sand filters (see sand filters, Figure 2.6) for the final removal of suspended material. The latest filters constructed have a fine sand layer 600 mm thick supported on a 500 mm gravel layer. Typical filter runs of between 48 and 120 hours are achieved depending on the quality of the water being filtered. The filters may be washed in any one of three instances: at a fixed time, when there is loss of head, or because of high turbidity in the filtrate. Washing of the filters is carried out by first using air to loosen the sand and then water at 32 m/h to wash away all the collected dirt. Filters are covered to exclude light to less than 25 lux to prevent algal growth on the filters. After filtration, the water normally has a residual turbidity of 0,3 - 0,5 NTU.

2.5.5 PRIMARY DISINFECTION

The water leaving the purification works is disinfected with chlorine. The required concentration of chlorine is determined in such a way that the number of bacterial colony forming units determined by the standard plate count technique, 48 hours incubation at 37°C, is less than 10 after 20 minutes' contact with the chlorine. The low count will also ensure that minimal resuscitation occurs in the distribution system. Chlorine dosage may vary between 1,5 and 4,0 mg/ℓ depending on the raw water quality to provide a residual concentration of between 1 and 2,5 mg/ℓ after 20 minutes' contact. Pipelines in the distribution system serves as chlorine contact chambers.

2.5.6 POST DISINFECTION OR CHLORAMINATION

Chlorine, although an excellent disinfectant, is consumed rapidly and may be depleted within 6 - 8 hours. To prevent bacterial aftergrowth post-disinfection is done with a less powerful agent that will remain active for long periods so that the water may be protected right up to the end consumer. This is achieved by dosing chlorine and ammonia at the booster pumping stations in the correct mass ratio of not less than 4:1 to form monochloramine *in situ*. The monochloramine, although less active than chlorine, will under ideal conditions prevent bacterial regrowth for long periods.

The chlorine/ammonia dosing rates are aimed at maintaining a 0,5 to 1,0 mg/ℓ monochloramine concentration in the water at the time it enters the municipal distribution network.

2.5.7 SLUDGE DISPOSAL

The sludge settling in the sedimentation tanks is hydraulically scoured in the older systems and removed by pumps through a suction lift in the newer systems. The latter consists of a moving bridge spanning the sedimentation tanks with 6 pumps placed along its width, each pump removing sludge at a rate of 900 ℓ/min. Radio isotope sensors maintain the concentration of the sludge removed at between 5 and 8 per cent while also determining the progress of the bridge along the length of the sedimentation tank.

The sludge consists mainly of calcium carbonate, magnesium hydroxide and complex silicates containing aluminium and iron. The total amount of sludge removed is a function of the raw water turbidity and varies between 500 - 1000 tons of dry sludge per day. Phase separation of the sludge is enhanced by the addition of between 0,3 and 0,5 kg per ton polyacrylamide which is dosed prior to passing through a static mixer. The sludge is presently disposed of in settling ponds from which the clear decanted water is recovered. Plans are presently in hand for the construction of a thickening plant using polyacrylamide as a flocculant at a dosage rate of 0,5 to 0,8 kg per ton dry solids. The thickened sludge produced from this plant will be spread in 200 mm layers over an area of 140 hectare and sun dried. It is expected that a 2 m thick layer of dried sludge will build up after 10 years in the drying beds, after which a second set of drying beds will be developed.

2.5.8 ADDITIONAL TREATMENT

In order to maintain the chlorophyll value in the final water to below 1 $\mu g/\ell$ it is necessary to chlorinate the raw water when the chlorophyll values are higher than 30 $\mu g/\ell$. Lime addition might also be increased to reduce algal concentrations prior to sand filtration (see 2.5.1).

This project will evaluate pre-oxidation as an additional water purification process to control algae at Rand Water, and will also compare the effect of pre-oxidation with chlorine on the other purification processes with that of chlorine dioxide.

MATERIALS AND METHODS

Several methods were used in this project to compare the efficiency of chlorine and chlorine dioxide as algicides. Some of these are not necessarily the best analytical methods or technology available, but had to be implemented based on experimental procedure, costs, time constraints and manpower availability. In the description of some of these methods, reasons were given for the selection of the specific methods and where applicable, comparisons with similar methods are supplied. To evaluate the results meaningfully, appropriate statistical analysis were done.

In this chapter only methods used frequently in all the different experiments will be discussed. The specific protocol and method used for a specific experiment will be discussed prior to the results of the specific experiment, to enhance better understanding and interpretation of results.

3.1 ALGAL DESCRIPTION AND BIOLOGICAL METHODS

A brief description of the algae used, the methods used to determine biomass and to cultivate the algal species, are presented.

3.1.1 ALGAL SELECTION AND DESCRIPTION

In algological investigation researches tend to select algae which is well researched and easily cultivated. Such an approach in this project would not supply all the relevant information because specific algae in the Vaal River Barrage Reservoir and Vaal Dam are responsible for eutrophication related water purification problems. Algae were selected using specific criteria given in Table 3.1.

Information regarding the taxonomy of the algae and micrographs[1] of the algae are presented in Appendix A. The selection of algae was mainly done on the basis of their nuisance potential, size, shape and morphological differences compared to that of suspended inorganic particles.

Although *Euglena* spp are present in the Vaal River Barrage (Steynberg, 1986), *E. gracilis* was the only algal species used that was not isolated from the Vaal River Barrage Reservoir. *Euglena* spp are

[1] Micrographs by Dr P W J van Wyk, Department of Botany and Genetics, University of the Orange Free State, Bloemfontein. South Africa.

frequently found in potable water produced by Rand Water when the 1 μg chlorophyll/ℓ guideline is exceeded. This algae differ markedly from inorganic suspended particles, in that it can change shape and is motile by means of a flagella, thus having the potential not to be removed by the coagulation-sedimentation process (Bernhardt and Clasen, 1991).

TABLE 3.1: SELECTION CRITERIA AND ALGAE USED IN EXPERIMENTS

CRITERIA	Mono	Chla	Sce	Cos	Chlo	Cycl	Eugl	Pan
1. Isolated from Vaal River Barrage	X	X	X	X	X	X		X
2. Algal blooms in raw water and in sedimentation dams		ϕ				ϕ		
3. Penetrate sand filters		ϕ					ϕ	
4. Motile by means of flagella		ϕ					X	X
5. Shape								
5.1 Round-spheric	✓	✓			✓	✓		✓
5.1 Changing							✓	
5.3 "Irregular"			✓	✓				
6. Size ≤ 3 μm	X				ϕ	X		
$3 \leq 6$ μm		X	X					
≥ 10 μm				X			X	X
7. Cell protection				ϕ				ϕ
8. International algal norm	ϕ						X	

Mono	=	*Monoraphidium minutum*	Chlo	=	*Chlorella minutissima*
Chla	=	*Chlamydomonas* sp	Cycl	=	*Cyclotella meneghiniana*
Sce	=	*Scenedesmus quadricauda*	Eugl	=	*Euglena gracilis*
Cos	=	*Cosmarium laeve* var *distentum*	Pan	=	*Pandorina morum*
ϕ	=	Most important selection criteria.	✓	=	specific shape

Chlamydomonas sp is usually the dominant algal species in the potable water when Rand Water chlorophyll guideline is exceeded. This algal species is motile as *Euglena gracilis,* but do not change shape, thus also having the potential not to be removed by the coagulation-sedimentation process.

In the case of *Cosmarium leave* var *distentum* the distinct mucus layer around the cell motivated its selection as this layer could influence its oxidation and removal potential (see 2.3.1.1) and is known to cause green foam during coagulation/flocculation (Pieterse - personal communication[2]).

Except for *Cyclotella meneghiniana* all the algae are members of the Chlorophyceae group (green algae). *C. meneghiniana* is a member of the Bacillariophyceae (diatoms) which differ from the

[2] Prof A J H Pieterse, Department of Botany and Genetics, University of the Orange Free State, Bloemfontein. South Africa.

Chlorophyceae not only in morphology, but also in the requirement for silicon. As a large percentage of the outer covering of the diatom cells (the epi- and hypotheca) consists of silicon, the dissolved silicon requirement of these organisms is higher than that of other algae (Reynolds, 1984). This difference in composition of the outer covering compared to that of other algae and its ability to penetrate and block sand filters, contributed to its selection as test organism.

Due to the difficulty to culture and quantify *Cyclotella meneghiniana,* this specie was replaced by *Pandorina morum*, which was used in the coagulation and filtration experiments. This algae, is a green motile colony, consisting of small pyriform cells, enclosed by a common gelatinous envelope. Two anterior flagella are present and is responsible for the colony moving in a rolling or tumbling fashion. This algal specie is frequently observed during algal blooms in the raw water and in the potable water produced from algal laden water. The occurrence of this algae in potable water, it's motility and gelatinous envelope were the major characteristics considered in its selection as a test organism.

Both *Chlorella minutissima* and *Monoraphidium minatum* are frequently used in algological research and may therefore be referred to as "algal standards". Both these species are relatively small compared to the other algae used (Table 3.1) but differ in shape. *Chlorella minutissima* is spherical while *Monoraphidium minutum* has a comma shape. Not only were these algae used as "algal standards", but was the effect of the differences in shape on coagulation and filtration investigated.

It is anticipated that the differences in morphology, shape, size and physiological characteristics of the various algal cells will influence their removal potential during the different purification stages. It is also anticipated that the effect of chlorine and chlorine dioxide on the removal efficiency of the algae during the different purification stages, may also be explained by these differences between the algae.

3.1.2 BIOMASS DETERMINATION

The amount or number of algae present in the water may be determined by using microscopic counts (Lund *et al.*, 1958), fluorescence microscopy (Tsuji and Yanagita, 1981), image analysis (Brown *et al.*, 1989), electronic particle counting techniques (Evans and McGill, 1970), light scattering methods (Krüger, 1978) as well as the chlorophyll extraction. From the literature it is evident that the best way to quantify algae is by microscopic counts (Utermöhl, 1958). This method is however, time consuming. The chlorophyll-a extraction method was therefore used (Sartory, 1982) in the

monocultures and the laboratory scale experiments as a quantitative indication of biomass.

To determine the expected variance in chlorophyll-a results, different concentrations of *Scenedesmus quadricauda* were made from stock cultures. Chlorophyll-a extractions were done on several replicates of each algal concentration and the concentrations calculated. From these chlorophyll-a results, statistics were calculated (Table 3.2).

TABLE 3.2: STATISTICS FOR THE CHLOROPHYLL-a METHOD (SARTORY, 1982) AS OBTAINED DURING ROUTINE LABORATORY PROCEDURES USING DIFFERENT CONCENTRATIONS OF *Scenedesmus quadricauda*.

Run number	Number of samples (n)	Average (x)	Standard Deviation (SD)	Coefficient of variation (%)
1	8	8,8	0,53	6
2	5	30	1,11	3,7
3	5	56	2,82	5,05
4	7	85	3,59	4,22
5	6	107	5,38	5,0
6	5	200	6,2	3,1

Table 3.2 shows that a variance of less than 6 per cent in the results could be ascribed to the execution of the method. Differences in chlorophyll-a results of a control and an experiment, greater than 6 per cent, could therefore be interpreted as a deviation of the specific extraction method used under the specific conditions.

During the algological studies, use was also made of an electronic particle counter (Coulter Counter, Industrial D) to determine the number of algal cells present and to confirm the relationship between chlorophyll-a and cell numbers. The instrument was calibrated such that it would count all particles in the water exceeding the smallest dimension of the specific algal species to be counted. The algal biomass was calculated using the following formula.

$$A = (CA - CB) \cdot (DF/SV) \qquad (8)$$

where

A = number of cells/mℓ

CA = count of sample containing algae

CB = count of sample without algae (background)

DF = dilution factor

SV = sample volume

Information regarding the variability in cell counts of different algal species, using the Coulter Counter method, are supplied in Table 3.3. It is evident that the variation in cell concentrations, ascribed to the method used, can be regarded as 1 per cent, 2 per cent and 7 per cent for the 3 μm, 6 μm and 10 μm biological particles, respectively. Differences, greater than that indicated, may therefore be regarded as significant.

TABLE 3.3: VARIATION IN COULTER COUNTS (CELLS/mℓ) USING TEN REPLICA FROM THE SAME CONCENTRATION OF DIFFERENT SIZE ALGAE

No	*Monoraphidium minatum* (> 3 μm)				*Scenedesmus quadricauda* (> 6 μm)			*Euglena gracilis* (> 10 μm)		
	n	x	SD	COV(%)	x	SD	COV (%)	x	SD	COV (%)
1	10	$162{,}2\times10^4$	$0{,}637\times10^4$	0,4	$760{,}9\times10^3$	$4{,}499\times10^3$	0,6	$457{,}9\times10^3$	$16{,}66\times10^3$	3,6
2	10	$83{,}43\times10^4$	$0{,}088\times10^4$	1,05	$42{,}66\times10^3$	$0{,}554\times10^3$	1,3	$25{,}35\times10^3$	$1{,}788\times10^3$	7,0
3	10	$6{,}58\times10^4$	$0{,}104\times10^4$	1,58	$34{,}18\times10^3$	$0{,}833\times10^3$	2,4	$20{,}46\times10^3$	$1{,}45\times10^3$	7,1
4	10	$2{,}68\times10^4$	$0{,}014\times10^4$	0,5	$18{,}64\times10^3$	$0{,}411\times10^3$	2,2	$10{,}89\times10^3$	$0{,}562\times10^3$	5,2
5	10	$1{,}11\times10^4$	$0{,}014\times10^4$	1,3	$9{,}579\times10^3$	$0{,}081\times10^3$	0,8	$6{,}763\times10^3$	$0{,}317\times10^3$	4,7

n = number of samples
x = average
SD = standard deviation
COV = coefficient of variation

To confirm the relationship between chlorophyll-a and cell counts, chlorophyll-a and cell count results of specific algal species used, were correlated. A meaningful correlation was found between cell counts and chlorophyll-a (Table 3.4). These good correlations justify the use of chlorophyll-a as an indicator of biomass for this study.

TABLE 3.4 CORRELATION BETWEEN CELL COUNTS (COULTER COUNTER) AND CHLOROPHYLL-a DETERMINATIONS

Algae	n	r	r^2
Scenedesmus quadricauda	15	0,84	0,71
Chlorella minutissima	16	0,84	0,71
Monoraphidium minatum	16	0,91	0,84

3.1.3 ISOLATION AND CULTURING OF ALGAE

Except for *Euglena gracilis*[3] all the algae used in the present study, were isolated from the Vaal River Barrage Reservoir. Water samples containing the relevant algae were streaked on agar plates (Belcher and Swale, 1982), with BG 11 media (Barlow, 1978) as nutrient source. After repeating the streaking procedure several times over a period of weeks, an algal colony, free of bacteria, fungi and other algae, was inoculated into 100 mℓ BG11 in a 250 mℓ wide neck Erlenmeyer flask. The agar plate cultures and liquid algal cultures, known as the primary algal culture, were kept at the conditions given in Table 3.5.

TABLE 3.5: SPECIFIC CONDITIONS AND MEDIA USED TO CULTIVATE ALGAE (SEE APPENDIX B FOR NUTRIENT MEDIA CONSTITUENTS)

Algal species	Light $\mu E/m^2/sec.$	Temperature °C	Media	
			Maintenance	Experiment
Monoraphidium minutum	80 ± 10	23 ± 2	BG11	BG31
Chlamydomonas sp	80 ± 10	23 ± 2	BG3	BG31
Scenedesmus quadricauda	80 ± 10	23 ± 2	BG11	BG31
Cosmarium laeve var *distentum*	80 ± 10	23 ± 2	BG11	BG31
Chlorella minutissima	80 ± 10	23 ± 2	BG11	BG31
Cyclotella meneghiniana	64 ± 4	23 ± 2	MBG	MBG
Euglena gracilis	80 ± 10	23 ± 2	Euglena broth (10%)	Euglena broth (10%)

Cool white and Toshiba plantlux 20 watt light tubes were used as light source. A light cycle of 16 hours light and 8 hours darkness was maintained for all experiments.

The cultures were either maintained in a liquid medium or on agar plates. Stock cultures, from which cultures for experimentation (experimental cultures) were inoculated, were maintained axenically in 250 mℓ Erlenmeyer flasks. Stock cultures were re-inoculated every 2 weeks to ensure availability of healthy cells for the experiments.

Cells in stock cultures, from which experimental cultures were inoculated, were kept in the

[3] Culture 1224/52; Culture Centre of Algae and Protozoa. The Botany School of the University of Cambridge, Cambridge, Great Britain.

exponential phase. Based on practical considerations it was decided not to use continuous culturing techniques to supply algae for the experiments. For most of the algae, a nutrient rich medium (BG31) containing three times the nitrogen and phosphorus concentrations of BG 11, was used to ensure the availability of 4 day old algae in exponential growth phase on the day of experimentation. Several experimental cultures were prepared by inoculating 15 mℓ of stock culture into 200 mℓ BG31, in a 500 mℓ Erlenmeyer flask. The flask was closed using a cotton plug. On the day of the experiment the different experimental cultures were added together and used as inoculum.

In the case of *Euglena gracilis*, axenic stock and experimental cultures were maintained in 10 per cent Bacto Euglena Broth (Difco 0690-01).

Cyclotella meneghiniana culture was maintained on the BG 11 media enriched with 20 mg silica/ℓ (MBG media).

3.2 PHYSICAL AND CHEMICAL METHODS

3.2.1 WATER ANALYSIS

All physical and inorganic chemical analyses were performed by Scientific Services of Rand Water using methods published in Standard Methods (A.P.H.A., 1989). Detailed analysis were done on Vaal Dam water and waste water treatment plant effluent used in the oxidation experiments.

From chapter 2 it was evident that dissolved organic carbon (DOC) play an important role in the efficiency of the oxidant as well as in the by-products formed. To be able to determine the interaction between the pre-oxidant and the organic content of the water, the dissolved organic carbon (DOC) content of the water was measured using an automated technique (Rand Water[4]). With the same method the extracellular algal products (EAP) were measured. To determine significant differences between DOC results, sample containing DOC of different origin, were used. From Table 3.6 it is evident that the variation due to the DOC method is significantly less than 5 per cent. Differences of more than 5 per cent in results can therefore be regarded as meaningful and not a function of the execution of the method.

[4] Chief Scientist (Quality), Rand Water, P O Box 1127, Johannesburg, 2000 South Africa.

TABLE 3.6: VARIATIONS IN DOC RESULTS FOR THE ANALYTICAL METHOD USED

Run No	Number of Samples	Mean (mg/ℓ)	Standard Variation	Coefficient of variation (%)	Sample Type
1	5	5,24	0,0894	1,7	Algae
2	5	5,20	0,14	2,7	EAP
3	5	4,48	0,1095	2,4	BG11 Nutrients

Oxidation of some organic compounds with chlorine, result in the production of trihalomethanes (THMs). These organic compounds were measured using predominantly gas chromatographic head space analysis. In some experiments a liquid-liquid extraction method was used due to breakdown of instrumentation or unavailability of instrumentation.

As chloroform was shown to be the dominant constituent of the THMs present in the source waters of Rand Water treated with chlorine (unpublished results), statistics on the variability of chloroform analysis, obtained from the two methods, using chlorinated algae as precursor to THMs formation, are presented in Table 3.7. It is evident from the results that the head space extraction method has far less variation and show higher chloroform concentrations than the liquid-liquid extraction method. In the evaluation of the THMs results, this variability will have to be taken into account when decisions regarding significant differences between results is important.

TABLE 3.7: THE VARIATION IN THM RESULTS

ALGAE		Cl_2-DOSING		CHLOROFORM FORMED (µg/ℓ)				METHOD USED
Species	Chlorophyll-a (µg/ℓ)	mg/ℓ	Time (h)	n	x	SD	COV (%)	
Chlorella minutissima	100	4	2	10	13,9	4,15	30	$+Na_2S_2O_3$*
	100	4	2	10	10,3	4,47	43	+Ascorbic acid*
Scenedesmus quadricauda	100	4	2	10	57,3	6,5	11,4	
			24	9	195,3	17,72	9,1	Liquid-liquid extraction
Chlorella minutissima	102	2,5	2	6	40	0,82	2	Head space
Chlamydomonas sp	82	2,6	2,5	6	42,85	1,23	3	Head space extraction

n = number of samples x - average SD = standard deviation COV = coefficient of variation

* = to neutralise chlorine

3.2.2 DETERMINATION OF OXIDANT CONCENTRATIONS

Both chlorine and chlorine dioxide concentrations were determined using the DPD method 4500-ClG (A.P.H.A., 1989) as adapted by Geldenhuys (1986).

The purity of the chlorine dioxide stock solutions were determined by means of a potentiometric method (Aieta *et al.*, 1984). With this method it is possible to distinguish between the chlorine, chlorine dioxide, chlorite and chlorate, which can be present in chlorine dioxide solution or if the oxidant was not prepared correctly.

3.2.3 PREPARATION OF OXIDANTS

3.2.3.1 **Chlorine**

Chlorine gas was bubbled through water to form a chlorine stock solution from which working solutions were prepared for the different experiments. The stock solutions were kept in a sealed, amber bottle at 4°C.

During the pilot plant experiments several technical problems were experienced and associated safety precautions had to be adhered too. Chlorine could neither be dosed as described above nor could chlorine gas be injected directly into the raw water. During pilot plant runs HTH powder, containing $Ca(OCl)_2$, was used to prepare a solution of chlorine, which was dosed into the raw water pipeline.

3.2.3.2 **Chlorine dioxide**

For experiments performed in the laboratory, chlorine dioxide was produced using sulphuric acid (H_2S0_4) and sodium chlorite ($NaCl0_2$; Geldenhuys, 1986). A stock concentration was kept at 4°C in a sealed amber bottle. The stock solution was frequently tested for by-products of chlorine dioxide to ensure high purity.

Chlorine dioxide for pilot plant experiments was produced by a Alldos Oxiperm S C 164 automatic chlorine dioxide compact system. The production of chlorine dioxide is based on the chlorite - hydrochloric acid method in accordance with the following reaction:

$$5NaClO_2 + 4HCl \quad \text{----->} \quad 4Cl0_2 + 5NaCl + 2H_20 \qquad (9)$$

Solutions containing specific concentrations of sodium chlorite and hydrochloric acid, i.e. 7,5 per cent and 9 per cent respectively, were injected simultaneously into the reactor at a 1:1 ratio. This ensures an excess ratio of about 3:1 HCl to $NaClO_2$ in the reactor to result in total conversion of the $NaClO_2$. Further details of the instrument operation are available from Rand Water [5] .

The chlorine dioxide was prepared one day in advance of the performance of experiments and was analysed to assure the purity of the mixture (see 3.2.2).

3.3 VARIATION IN OXIDANT AND ALGAL DOSING

Owing to time constraint and limitations set by the experimental procedures, it was in most cases not possible to report the experiments. To ensure sound interpretations of results, the precision with which oxidants and algae were dosed, had to be determined.

3.3.1 VARIATION IN OXIDANT DOSING

Table 3.8 reports some statistics on the variation in dosing accuracy and repeatability of chlorine and chlorine dioxide into 100 mℓ oxidant free and demand free water. This was done by dosing ten 100 mℓ water samples with chlorine or chlorine dioxide so to achieve a specific concentration. For each selected oxidant concentration this procedure was repeated.

The high percentage variation in the achieved oxidant concentrations at the low oxidant concentration levels is probably not due to inaccurate dosing, but to the analytical method which is not sensitive enough to detect low oxidant levels. This is confirmed by the 5,4 per cent and less variation in absorbence readings at the higher concentrations for both oxidants.

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[5] Chief Scientist (Process), Rand Water, P O Box 1127, Johannesburg, 2000 South Africa.

TABLE 3.8 : VARIATION IN OXIDANT CONCENTRATION DUE TO VARIATION IN DOSING OF THE OXIDANT

OXIDANT	NUMBER OF SAMPLES	MEAN CONCENTRATION (mg/ℓ)		STANDARD DEVIATION	COEFFICIENT OF VARIATION (%)
		Planned	Achieved		
Chlorine	10	0,1	0,107	0,046	43
	10	1,0	0,98	0,051	5,2
	10	5,0	5,0	0	0
Chlorine dioxide	10	0,1	0,67	0,0179	26
	10	0,51	0,557	0,0301	5,4
	10	1,0	1,052	0,0282	2,7
	10	1,50	1,526	0,045	3,0

3.3.2 VARIATIONS IN ALGAL DOSING

Experience at Rand Water show that large variations in the biomass added to carry out specific experiments, may lead to results that are difficult to interpret. This variation was minimized by using larger than the required volumes of algae or water samples to prepare large volumes of a specific concentration of algae. The variation in algae dosing was determined by dosing a known volume of an algal suspension, obtained from a continuously stirred algal culture, into a specific water volume. This procedure was repeated a few times. The variation in algal dosing are presented in Table 3.9. The low variations in algal dosing, as indicated by the coefficient of variation of the chlorophyll-a concentrations, may be attributed to accurate pipetting and continuous stirring of the algal culture.

TABLE 3.9: VARIATION IN ALGAL CONCENTRATIONS EXPRESSED AS CHLOROPHYLL-a (μg/ℓ) AND COUNTS (Cells/mℓ).

Algae	Volume		Number of sample	Mean		SD		COV (%)	
	Inoculum	Sample		Counts	Chl-a	Counts	Chl-a	Counts	Chl-a
Euglena gracilis	5	200 l	10	11489	136	212	3,4	1,8	2,5
Scenedesmus quadricauda	10	5 l	3	-	47	-	1,6	-	3,4
	10	5 l	3	-	23	-	0	-	0
	24	5 l	3	-	100	-	5	-	5

SD = Standard variation
COV = Coefficient of variation
Chl-a = Chlorophyll-a (μg/ℓ)

METHODS AND RESULTS OF DIFFERENT EXPERIMENTS

As mentioned in chapter 3, several experiments, each with it's own method, had to be done to fulfil the aims of this study. In this chapter the specific methodology and results for each experiment will be presented.

4.1 GROWTH CHARACTERISTICS OF ALGAL CULTURES

Setlik (1979) indicated that different patterns of algal cell growth and reproduction may entail important differences in population behaviour under certain conditions. This includes an alteration in the ratio of cell constituents in cells and also the distribution of cells of various age groups in cultures. The author also showed that the composition of cells in various growth phases varies considerably. Although it falls outside the aim of this project to identify all the growth characteristics and associated physical and chemical changes in batch algal cultures, it is essential to identify the different growth phases of the different algae and to note the changes in reproduction and biomass over a 24 hour period, so that comparisons with future studies would be possible.

4.1.1 LONG TERM GROWTH EXPERIMENTS

The typical growth of algal batch cultures is best described by Figure 4.1. During the lag and stationary phases (see A and C in Figure 4.1), physiological and growth processes are possibly inhibited by the age and physiological condition of the algal cells. In the stationary phase most of the available nutrients have been taken up by the algae. Biomass increase is therefore limited (Wetzel, 1983). Algal cells show optimal physiological rates during the exponential growth phase. Algal cultures in the exponential growth phase should therefore be used to investigate the influence of any treatment on the algal cells. Algae in the lag or stationary phases may be less, or more sensitive, for changes in the environment.

As the growth characteristics of the algae, cultured under specified conditions, were not known, a major part of the first phase of the project was spent to determine the growth characteristics of the algae used. The following procedures were followed.

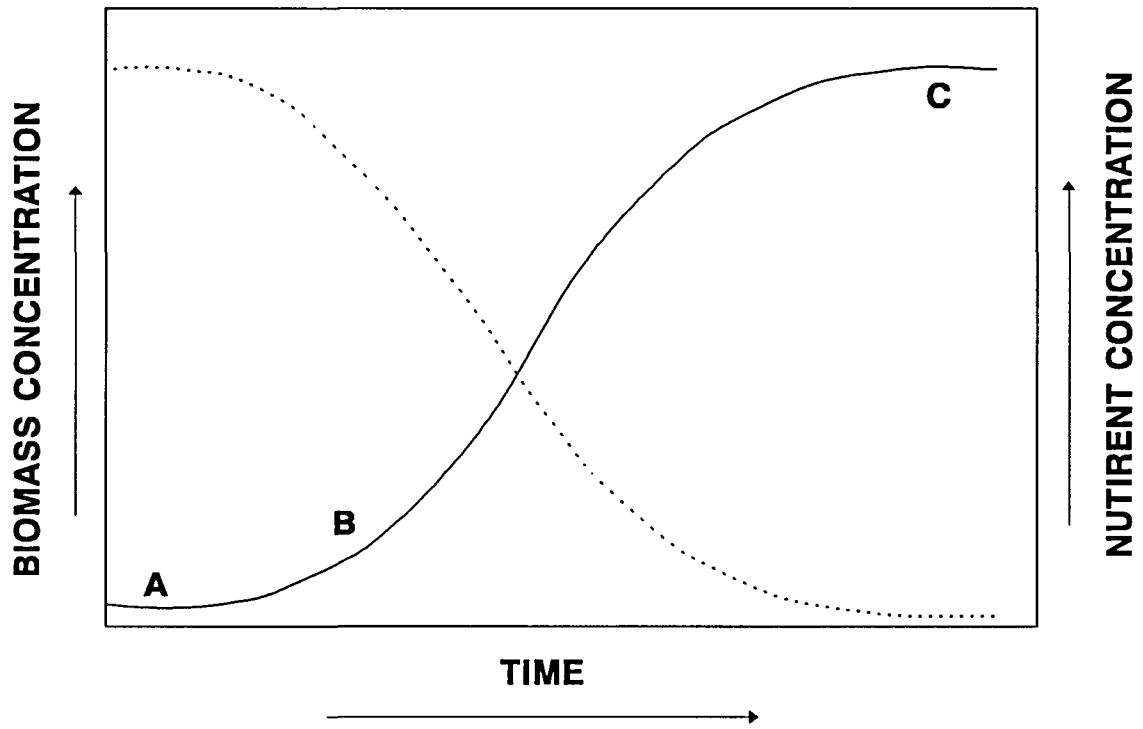

FIGURE 4.1 : **TYPICAL GROWTH CURVE FOR A BATCH CULTURE (___ = algal biomass; .... = nutrient concentration; A = Lag phase; B = Exponential phase; C = Stationary phase).**

a. To have sufficient algae available to determine growth characteristics over a period of 20 days, ten 200 mℓ cultures of each algal species examined, were prepared from 2 litre stock cultures in a 500 mℓ wide neck Erlenmeyer flasks. The stock cultures were prepared using a nutrient medium and a 4 day old algal culture (see Table 4.1)

b. Ten controls, consisting of nutrient media only, were also prepared in the same way as described above. These controls were used to obtain background counts for Coulter Counter analyses.

c. The cultures and controls were kept under the same light and temperature conditions as described under 3.1.3.

TABLE 4.1 : NUTRIENT MEDIA AND INOCULUM VOLUME USED FOR THE DIFFERENT LONG TERM ALGAL GROWTH CURVES (SEE APPENDIX B FOR CONSTITUENTS OF NUTRIENT MEDIA)

SPECIES	NUTRIENT MEDIA	INOCULUM VOLUME (mg/ℓ)
Chlamydomonas sp	BG31	20
Chlorella minutissima	BG31	12
Euglena gracilis	Euglena broth	8
Monoraphidium minutum	BG31	6
Scenedesmus quadricauda	BG31	50
Cosmarium laeve var *distentum*	BG31	20
Pandorina morum	BG31	25
Cyclotella meneghiniana	MBG	20

d. From the day of inoculation (day 0) up to day 20, 100 mℓ per day was removed from the flasks to do chlorophyll-a and Coulter Counter analyses. Therefore the volume in a specific culture flask could be used on two successive days.

e. On day 7 and 14 all the respective remaining cultures of each algal species and controls were pooled separately into a sterilised container and redistributed into the existing culture flasks. This was done to ensure uniformity in biomass between the different culture flasks of each algal species.

When compiling data for growth curves, it is essential to keep the volumes of the cultures constant and uncontaminated. It is also critical to inoculate from an axenic culture which is in the exponential growth phase as cultures, contaminated by bacteria and fungi, may produce a lower final biomass due to competition.

Twenty day growth curves for the different algae are illustrated in Figure 4.2. These curves, based on cell counts and chlorophyll-a concentrations, show that no lag phase lasted longer than four days and on day four all the algal cultures were in the exponential growth phase.

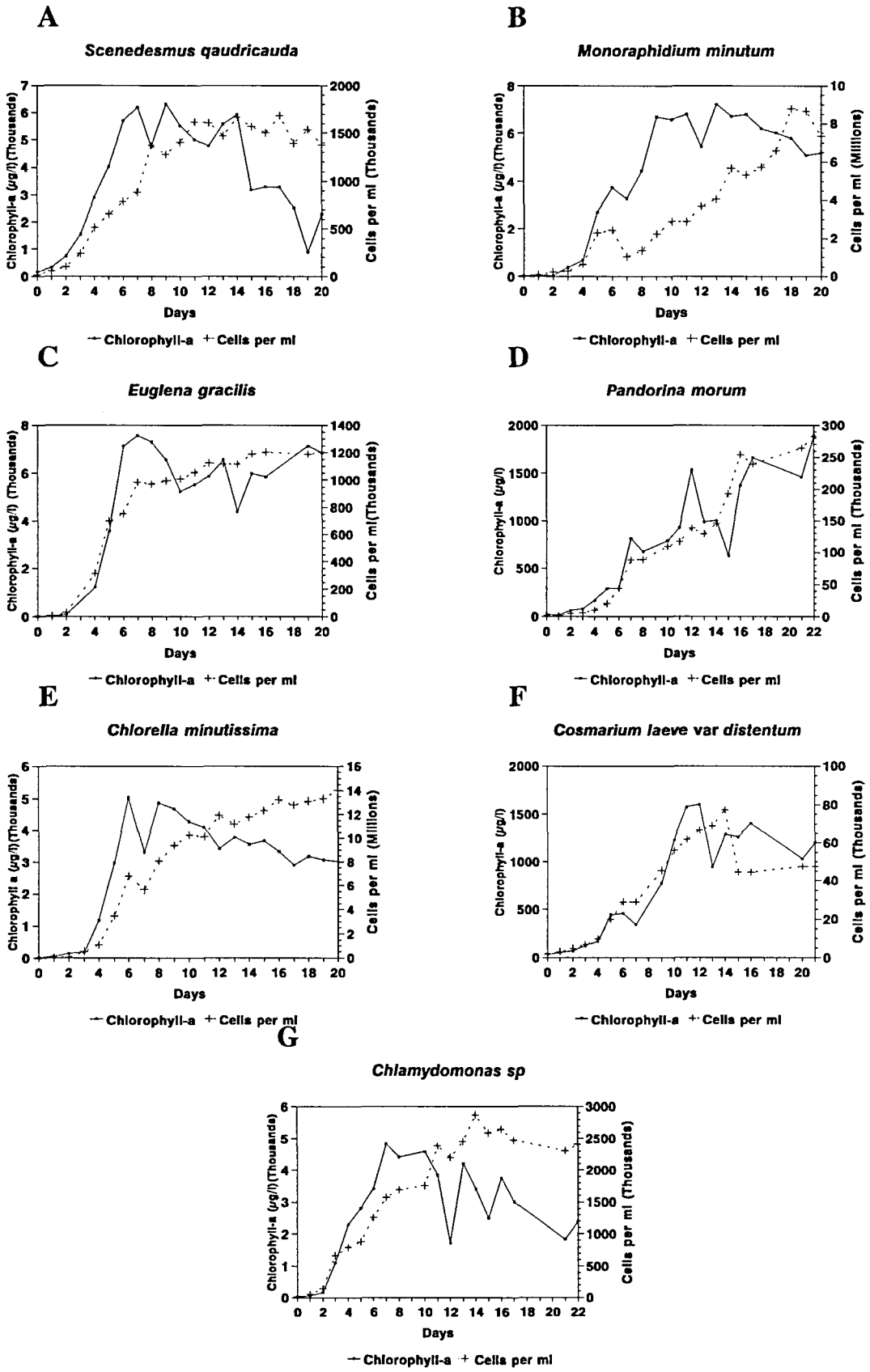

FIGURE 4.2 : LONG TERM GROWTH CHARACTERISTICS OF THE DIFFERENT ALGAE USED

TABLE 4.2A : GROWTH CHARACTERISTICS OF ALGAE BASED ON CHLOROPHYLL-a

Characteristic	Chlamydomonas sp		Chlorella minutissima		Cosmarium laeve var distentum		Euglena gracilis		Monoraphidium minutum		Scenedesmus quadricauda		Pandorina morum	
	Day No	Chl-a (µg/l)	Day No	Chl-a (µg/l)	Day No	Chl-a (µg/l)	Day No	Chl-a (µg/l)	Day No	Chl-a (µg/l)	Day No	Chl-a (µg/l)	Day No	Chl-a (µg/l)
Start biomass	0	36	0	17	0	34	0	12	0	11	0	155	0	23
Lag phase end	1	57	1	52	2	69	1	12	2	23	0	155	3	80
Exponential phase end	4	2287	6	5033	10	1232	6	7127	5	2694	5	4024	7	814
Exponential phase growth rate (Chla/d)	-	743	-	996	-	145	-	1423	-	890	-	774	-	183
End biomass	22	2379	20	3009	21	1204	20	6850	20	5188	20	2293	22	1891

TABLE 4.2B : GROWTH CHARACTERISTICS OF ALGAE BASED ON CELL NUMBERS

Characteristic	Chlamydomonas sp		Chlorella minutissima		Cosmarium laeve var distentum		Euglena gracilis		Monoraphidium minutum		Scenedesmus quadricauda		Pandorina morum	
	Day No	Cells/ ml	Day No	Cells/ ml	Day No	Cells/ ml	Day No	Cells/ ml	Day No	Cells/ ml	Day No	Cells/ ml	Day No	Cells/ ml
Start biomass	0	15180	0	24500	0	2040	0	1300	0	21880	0	16360	0	1240
Lag phase end	1	52400	1	29800	4	9760	1	4250	0	21880	0	52320	3	5280
Exponential phase end	3	668080	6	6831420	9	445500	5	699920	5	2296120	4	513180	7	88420
Exponential phase growth rate (Cells/d)	-	307840	-	1360304	-	7148	-	173917	-	454848	-	115215	-	20785
End biomass	22	2406600	20	14022200	21	47600	20	1205320	20	7356100	20	1375520	22	282720

From Table 4.2 it is evident that the length of exponential growth phases differed for the different algae. In the case of *Chlamydomonas* sp the exponential growth phase lasted for one to two days, compared to that of most of the other algae which lasted four to five days. The rate of growth of the different algae in the exponential phase also differed significantly with that of *Cosmarium laeve var distentum* (7 148 cells/d) the lowest and that of *Chlorella minutissima* (1 360 304 cells/d) the highest.

From Figure 4.2 A - G it is clear that during the exponential growth phase, increase in cell numbers were associated by an increase in chlorophyll-a concentration. This relationship changed during the stationary phase with a decrease or levelling off of chlorophyll-a with a lesser increase or levelling off of cell numbers. In most cases, except *Pandorina morum*, the decrease in cell numbers in the last part of the stationary phase, were preceded by a decrease or levelling off of the chlorophyll-a concentration (compare Figure 4.2 A - G).

From the above it is evident that four day old cultures used for the pre-oxidation experiments will be in an exponential growth phase, thus ensuring physiological healthy cells for experimental purpose.

4.1.2 DIURNAL GROWTH CURVES OF ALGAE

Pieterse & Schmidt[1] (personal communication) found that in a 24 hour cycle, the rate of physiological processes and the growth rate in an algal population, changes significantly during light/dark cycles between day and night. It has also been shown that these physiological rhythms do not change when cultures are exposed to continuous light. Schmidt[1] also showed that different algal species in culture were most sensitive to the inhibition of copper during change-over from dark to light and light to dark conditions. For this study, it was therefore necessary to determine whether the cells were actively dividing (physiologically active) in the time period of the day in which the experiments were to be performed, as they might be more sensitive to the oxidants than during the dark period.

To determine the active dividing period of the algal culture the following experiments were done. Five 200 ml cultures in 500 ml wide neck Erlenmeyer flasks were prepared for each algal species, using media (Table 3.5) and conditions (Section 3.1.3) as described previously. Four day old cultures of each algal species were pooled, mixed and redistributed into the 500 ml flasks. At 90 minute

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intervals a 30 ml sub-sample was taken on which chlorophyll-a and direct cell counts were done. Every 24 hours the remaining cultures of each algal species were pooled, mixed and redistributed again. This was done to prevent potential differences in the individual cultures being amplified over the 48 hour period and to ensure similar conditions in the different culture vessels.

Differences in the physiological behaviour of cells in dark and light conditions were expressed as a function of the change in chlorophyll-a during the period of investigation. Growth rate, indicating conditions stimulating or inhibiting growth, was calculated using the equation (Welch, 1980):

$$\mu = \frac{\ln X_t - \ln X_o}{t}$$

where:

μ = growth rate
t = time
X_t = biomass at t = 1
X_o = biomass at t = 0

As this experiment lasted for 48 hours, growth rates for each of the two light (05:00 to 20:00) and two dark (20:00 to 5:00) phases were calculated and compared.

TABLE 4.3 GROWTH RATE OF DIFFERENT ALGAE OVER A 48 HOUR PERIOD

ALGAL SPECIES	AVERAGE GROWTH RATE FOR	
	NIGHT	DAY
Euglena gracilis	0,24	5,27
Cosmarium laeve var *distentum*	2,91	0,83
Cyclotella meneghiniana	2,10	1,80
Chlamydomonas sp		**
Scenedesmus quadricauda	3,24	0,60
Monoraphidium minutum	0*	2,40
Chlorella minutissima	0	5,50
Pandorina morum	0	3,34

* = Time period 20:00 to 02:00
** = Data not available due to experimental error

The results of the 48 hour growth curves of the 4 day old algal cultures are depicted in Figure 4.3, A to H and summarised in Table 4.3 and Table 4.4. In all the cultures the increase in the number of cells were matched by an increase in the chlorophyll-a concentration during the 48 hour period. The most significant increase of chlorophyll-a took place during the day time (Table 4.4). This confirmed the fact that the chloroplast are only active under light conditions (Robards, 1970).

The tempo of biomass increase, as indicated by the growth rate in Table 4.3, did not take place in all the algal species under the same light conditions. *Cyclotella meneghiniana* (Figure 4.3G) did not show a significant difference in growth rate under dark or light conditions. The highest growth rate for *Cosmarium laeve* var *distentum* (Figure 4.3E) and *Scenedesmus quadricauda* (Figure 4.3C) were observed during the night, while that of *Euglena gracilis* (Figure 4.3F), *Monoraphidium minutum* (Figure 4.3D) and *Pandorina morum* (Figure 4.3H) occurred during the day. In the case of *Chlamydomonas* sp (Figure 4.3A) results obtained during the second 24 hour of the 48 hour experiment differ from those obtained during the first 24 hours. Although the experiments with this species were repeated 3 times, the same trends and fluctuations in data were observed. *Chlamydomonas* sp cells tend to stick to the glassware. The culture flasks were put into an ultrasonic bath before sampling to free the algae from the glass. The effect of this treatment on *Chlamydomonas* sp in a specific culture flask, compared to the others treated in the same way, was not monitored. The effect of the ultrasonic treatment and the mixing of all the respective cultures may explain the variation in the results obtained with *Chlamydomonas* sp (See Figure 4.3A).

TABLE 4.4 CHLOROPHYLL-a CHANGES IN DIFFERENT ALGAL CULTURES OVER A 48 HOUR PERIOD

ALGAL SPECIES	AVERAGE RATE OF CHLOROPHYLL-a CHANGES (μg/l/h) IN	
	LIGHT	DARK
Euglena gracilis	136	-131
Cosmarium laeve var *distentum*	23	3
Cyclotella meneghiniana	*	*
Chlamydomonas sp	83	14
Scenedesmus quadricauda	82	-11
Monoraphidium minutum	37	-36
Chlorella minutissima	62	16
Pandorina morum	19	9

* = Chlorophyll-a not done.
Note: Minus figure indicate decrease in chlorophyll-a

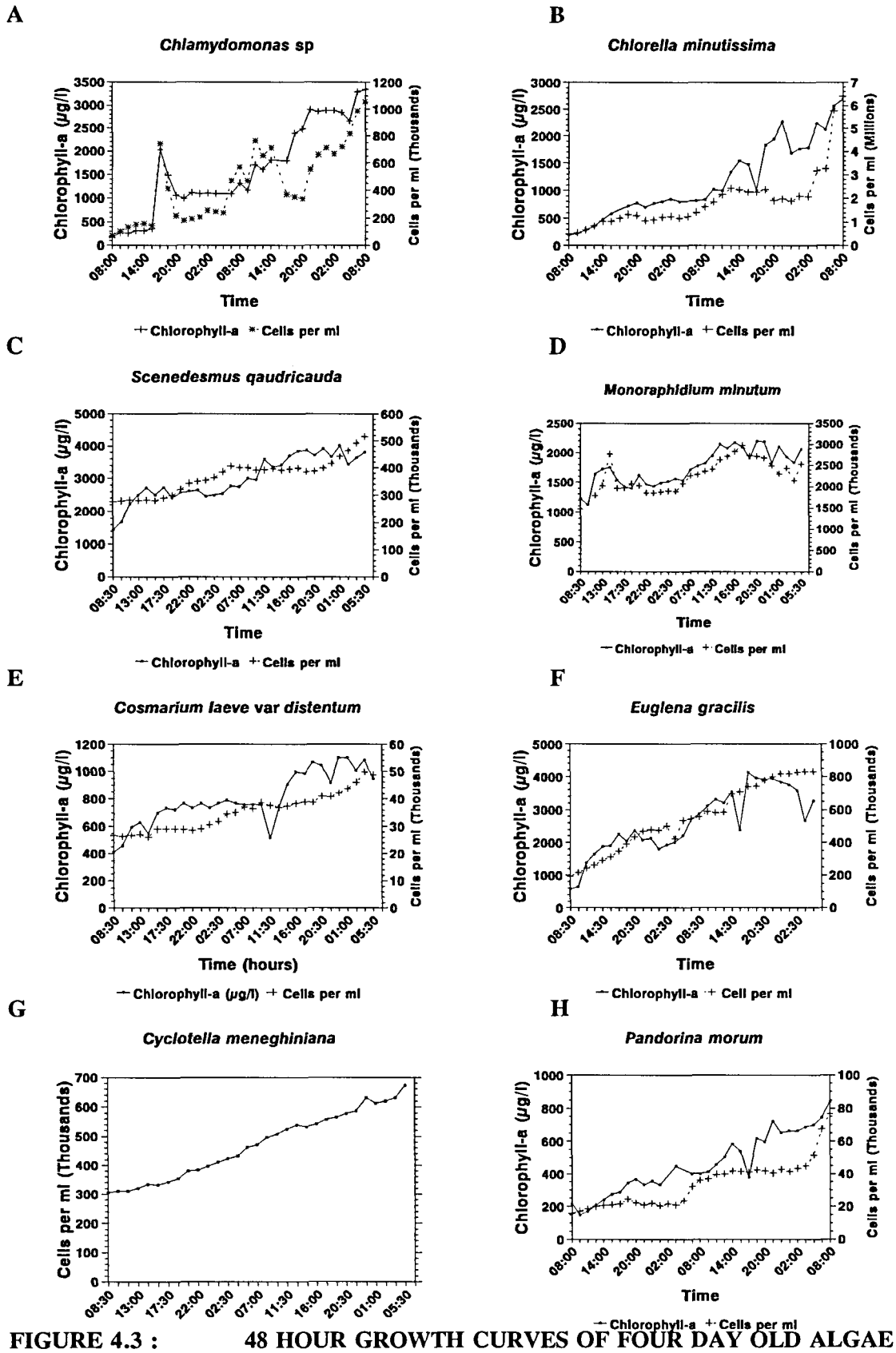


FIGURE 4.3 : 48 HOUR GROWTH CURVES OF FOUR DAY OLD ALGAE

In the case of *Chlorella minutissima* it is clear that most cell divisions take place during early morning to midday (Figure 4.3B). The growth rate in the period when the culture was exposed to light during the second 24 hour period confirms that the increase in cell numbers took place during the light period.

From the above it is evident that the algae would be at the start or end of an actively dividing phase and all the algae will be "physiologically active" (in chlorophyll increase) in the mornings when the oxidation experiments were performed. It may therefore be postulated that, as the algae is physiological active, dissolved substances will be taken up by the algae to satisfy their needs. The fact the algal cells are actively dividing or at the end of their dividing phase, may make them more sensitive for the chemicals used, than mature cells, which may have build up some kind of protection (physiological or physical), making it more resistant to the chemicals.

4.2 ZETA POTENTIALS OF ALGAL SUSPENSIONS

A factor that may influence the removal of algae by the purification techniques used by Rand Water, are the electrical charge densities on the surfaces of the algae (Bernhardt and Clasen, 1991; see 2.2.1.2).

Zeta potentials were determined using a Malvern particle sizer running in default mode[1]. An initial set of experiments were done to determine the Zeta potentials of a 4 day old culture at pH 4 to 12 at intervals of 1. This was done to determine the extent of surface charge density changes over a wide pH range.

The second set of experiments were aimed at determining the effect of algal culture age on the surface charge density of the cells - older cultures containing more extra cellular products, is known to increase surface charge densities (see 2.2.1.2). For this purpose, the Zeta potential of 4 day, 14 day and 28 day old cultures, at the same pH for each algal species, was determined.

For all Zeta potential determinations, algal cultures were diluted with 10 per cent BG31 to a

[1] Work done with the assistance of Mr A Viette, De Beers Diamond Research, Johannesburg.

concentration of $\approx$ 500 μg chlorophyll-a/ℓ. This ensured an algal concentration of an acceptable particle density, which was also determined automatically by the Zeta potential meter. The required pH, was obtained, by the addition of either 1 N NaOH or a 1 N H_2SO_4 solution, added to the algal suspensions.

In addition, tests were set up to determine the variation in results obtained by the Malvern particle sizer. Five replicates of each algal suspension of *Chlorella minutissima* and *Cosmarium laeve* var *distentum* were prepared and analyzed (Table 4.5). The results indicate that the variation in Zeta potentials, due to the method use, was less than 5 per cent.

TABLE 4.5: VARIATION IN ZETA POTENTIAL RESULTS USING TWO 4 DAY OLD ALGAL CULTURES.

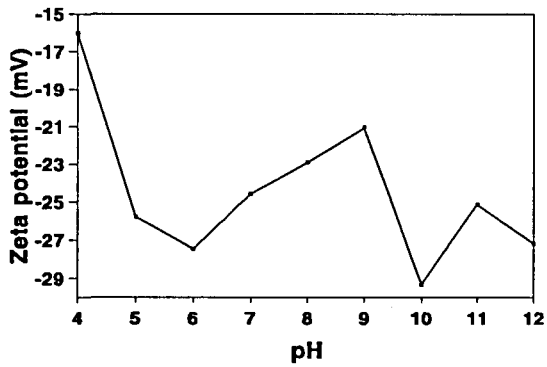
ALGAE	pH	STATISTICS			
		Number	Average	Standard deviation	Coefficient of variation (%)
Chlorella minutissima	9,9	5	-29,15	0,66	2,3
Cosmarium laeve var *distentum*	8,9	5	-28,85	1,00	3,5

Zeta potential studies were performed on six of the eight algal species. The *Cyclotella meneghiniana* culture was heavily contaminated with bacteria and was therefore considered to be unsuitable for this determination. *Pandorina morum* was introduced as a test organism after the completion of the zeta potential studies and were therefore not available for these tests.

4.2.1 ZETA POTENTIALS OF 4 DAY OLD CULTURES

The Zeta potentials measured on all the algae investigated were negative (Figure 4.4). Except for *Euglena gracilis* (Figure 4.4C), most of the algal species displayed a zeta potential of less than -20 mV at pH 7 to pH 9. In the case of *Chlorella minutissima* (Figure 4.4E), values of -30 mV were recorded. The Zeta potentials at pH 4 and pH 12 are significantly less negative than in the range pH 7 to pH 9 (*Cosmarium laeve* var *distentum* being the exception). In the case of *Euglena gracilis* (Figure 4.4C), the relationship between pH and Zeta potentials differed from that of the other algae.

A



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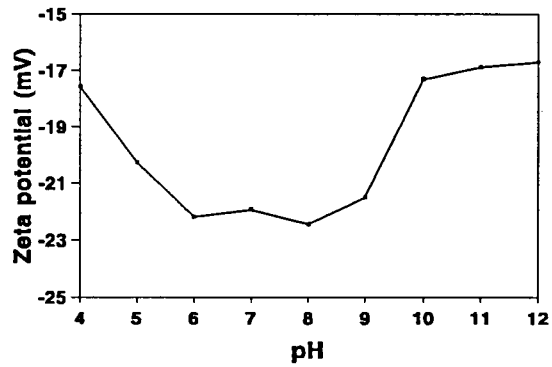

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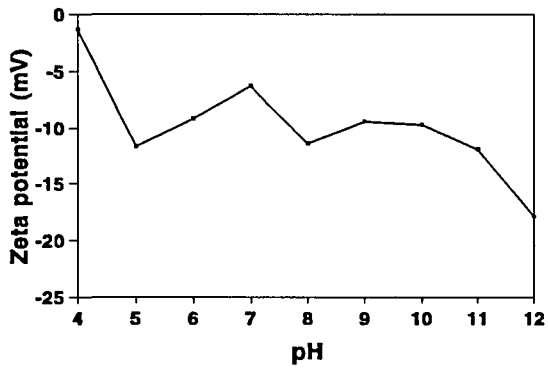

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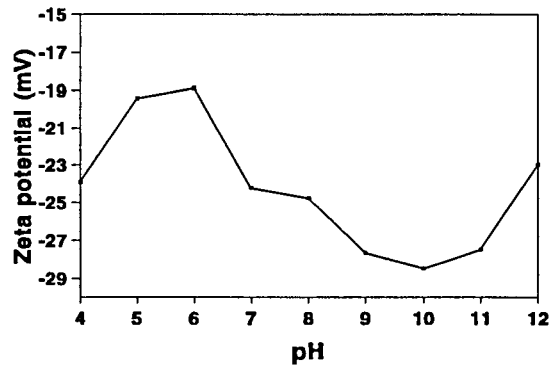

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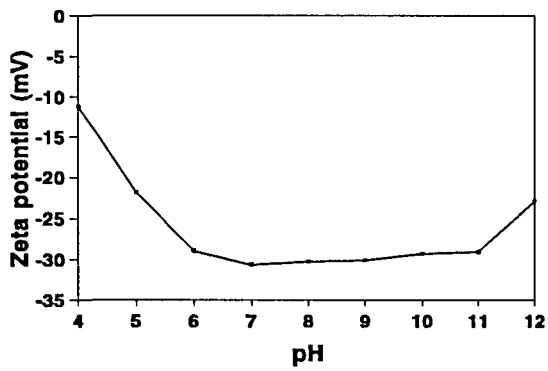

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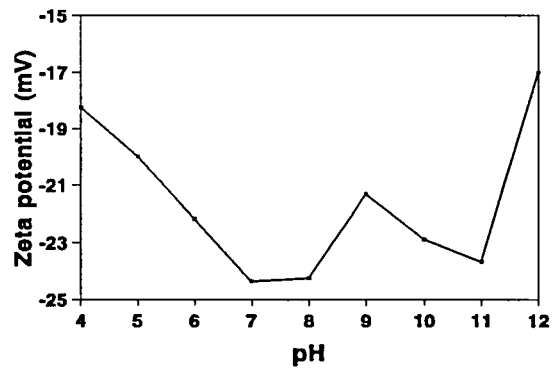


FIGURE 4.4 : ZETA POTENTIALS OF 4 DAY OLD ALGAL CULTURES AT DIFFERENT pH CONDITIONS

The highest Zeta potential was recorded for *Euglena gracilis* at pH 4 (-1,32 mV) which decreased to -17,8 mV at pH 12. These values are less negative than that recorded for the other algae.

The range of zeta potentials were different for the various algal species at similar pH conditions. *Chlamydomonas* sp (Figure 4.4F), *Cosmarium laeve* var *distentum* (Figure 4.4D) and *Monoraphidium minatum* (Figure 4.4B) showed a variation of less than 10 mV over the pH 4 - pH 12 range. The other algae showed wider variations with *Chlorella minutissima* being the highest (19,4 mV). These results confirm the Zeta potential figures quoted in 2.2.1.2 .

4.2.2 ZETA POTENTIALS OF ALGAL CULTURES OF DIFFERENT AGES

Data in Table 4.6 shows that the surface charge density of algae may increase (become more negative) with age. Whether this increase is a function of cell and cell "wall" age or the increase in EAP was not investigated. These results may therefore indicate that algal laden water, containing a two to three week old algal colony, may require more coagulants to be coagulated than a four day algal population. As four day old cultures were used in the oxidation and coagulation experiments for this project, these experiments should also be done at a later stage using different age cultures, so as to test the above.

TABLE 4.6 ZETA POTENTIAL OF CULTURES AT DIFFERENT AGES

ALGAE	pH	ZETA POTENTIAL (mV) OF CULTURE		
		4 Days	14 Days	28 Days
Chlorella minutissima	9,0	-31,07	-33,5	-39,98
Chlamydomonas sp	9,1	-25,95	-26,63	-28,67
Euglena gracilis	5,0	-13,14	- 3,29*	- 5,76*
Cosmarium laeve var *distentum*	9,5	-20,88	-30,79	-41,52
Scenedesmus quadricauda	9,3	-29,33	-30,16	-34,63
Monoraphidium minutum	9,6	-25,19	-31,3	-32,53

* Two zeta potential peaks influence results

4.2.3 THE EFFECT OF SODIUM SILICATE AND LIME ON THE ZETA POTENTIAL OF *Chlamydomonas* sp

From the work of Tilton *et al.* (1972) and Tenney *et al.* (1969) it is evident that an increase in coagulant dose results in an decrease in surface charge density and in an increase in algal removal.

To test this principle, a high concentration of a motile algae, *Chlamydomonas* sp (= 650 μg Chla/ℓ), prepared in 10 per cent BG31, was used to determine the influence of sodium silicate and lime on the Zeta potential of algae. As time only allowed for one algal species to be tested, the motile *Chlamydomonas* sp was selected because motility was suspected by Bernhardt and Clasen (1991) to interfere with the coagulation process. Results in Table 4.7 indicate a decrease in Zeta potential as more lime is added (increased pH) to the culture. The least negative Zeta potential was observed at pH 12, which indicates that the algal cells should be easily coagulated as a significant surface charge neutralisation has taken place. This statement will be tested in the oxidation and coagulation experiments. Operating the coagulation stage of a purification plant at pH 12 is unpractical in terms of chemical cost and sludge disposal, and therefore cannot be considered.

TABLE 4.7 THE EFFECT OF INCREASED LIME (pH) AND SILICA DOSAGE ON THE ZETA POTENTIAL OF *Chlamydomonas* sp

CHEMICAL ADDED	pH	Zp (mV)
(Culture)	9,2	-27,5
Silica (3 mg/ℓ)	9,2	-28,12
Different lime dosages	10,1	-24,29
	11,1	-18,63
	11,5	-14,40
	12,0	- 6,94

4.3 OXIDATION OF RAW WATER

In the literature study, reference was made to the effect of various inorganic and organic variables on the efficiency of the oxidant to inactivate organisms and also on the by-products formed during oxidation. In the case of the Vaal River Barrage Reservoir, the water quality can change in a relative short time due to changes in the Vaal Dam to Klip River volume ratio's (Steynberg, 1986). The aim of this set of experiments was to simulate the different water qualities to be expected in the Vaal River Barrage Reservoir and to determine the influence of these different water qualities on the oxidant available to inactivate algae. Samples of water containing different ratios of Vaal Dam water and

treated waste water treatment plant effluent, equivalent to Klip River water, were prepared. The different water samples were oxidised with different concentrations of chlorine and chlorine dioxide. Immediately after the oxidant was added and at three time intervals thereafter(1, 2 and 24 hours), oxidant residual and certain chemical variables were monitored. Chemical analysis of the un-oxidised water samples was also done. Details regarding Vaal Dam - effluent ratios, contact times and variables monitored are presented in Appendix C.

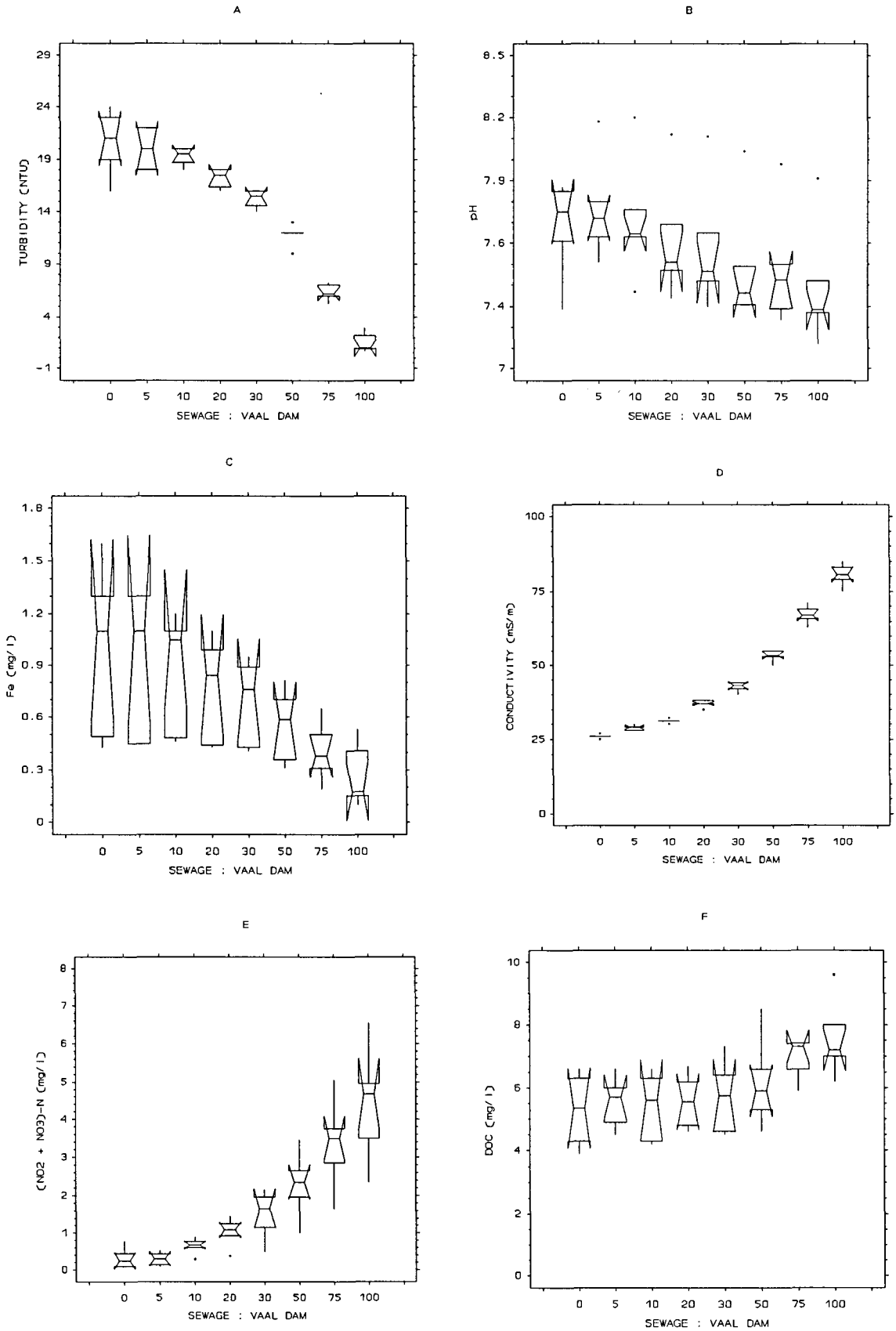
The emphasis was placed on the free available oxidant concentration after specific contact times as an indirect measure of the oxidant demand of the water.

4.3.1 RAW WATER QUALITY

The quality of the samples containing various ratios of treated effluent to Vaal Dam water are presented in Appendix D. From this data it can be seen that the quality of the samples changed through the duration of the experimental period and with an increase in treated effluent. Table 4.8 presents a summary of the general trends observed when the percentage treated effluent was increased.

TABLE 4.8 : CHANGES IN THE CONCENTRATIONS OF WATER QUALITY VARIABLES IN RELATION TO AN INCREASE IN THE PROPORTION OF TREATED EFFLUENT CONCENTRATIONS.

CHANGE	WATER QUALITY VARIABLE
Increase	Conductivity; Ca; Mg; Hardness; Na; K; DOC; $(NO_3 + NO_2)$-N; PO_4-P; SO_4; Cl; F; COD; SiO_2; $tSiO_2$
Decrease	Fe; Turbidity; pH; Alkalinity; Al
No change	Mn; Pb; Zn; NH_3-N; TP; Ni; Cu



(Figure 4.5 continue on next page)

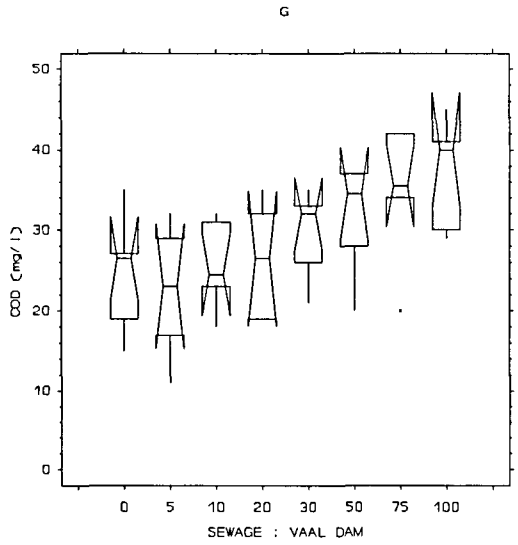


FIGURE 4.5 : BOX PLOTS OF THE VARIATION IN THE DIFFERENT WATER QUALITY VARIABLES THROUGH THE DURATION OF THE EXPERIMENTAL PERIOD AND WITH INCREASE IN THE TREATED SEWAGE TO VAAL DAM RATIO.

Although the quality of different samples prepared at different times were not the same due to changes in the quality of Vaal Dam water abstracted and effluent produced, the information presented in Table 4.8 represents water quality in the Vaal River Barrage Reservoir. The variation in water quality through the duration of the experimental period is indicated by the variation in data as represented by the box plots in Figure 4.5. Figures 4.5A to C shows a decrease in turbidity, pH and iron. Increases in conductivity (Figure 4.4D) nitrite, nitrate (Figure 4.5E), DOC (Figure 4.5F) and COD (Figure 4.5G) are also depicted.

The water of different compositions with specific reference to conductivity produced by changing the ratio of treated effluent:Vaal Dam water is similar to the water quality observed in the Vaal River Barrage Reservoir when Klip River water is present in different proportions compared to Vaal Dam Water.

In the experiments that followed no attempt was made to adjust the water quality to produce mixtures which were exactly the same every time experiments were done.

4.3.2 RESIDUAL OXIDANT AT TIME INTERVALS AFTER OXIDATION

Different oxidant concentrations were dosed into samples containing different ratios of effluent:Vaal

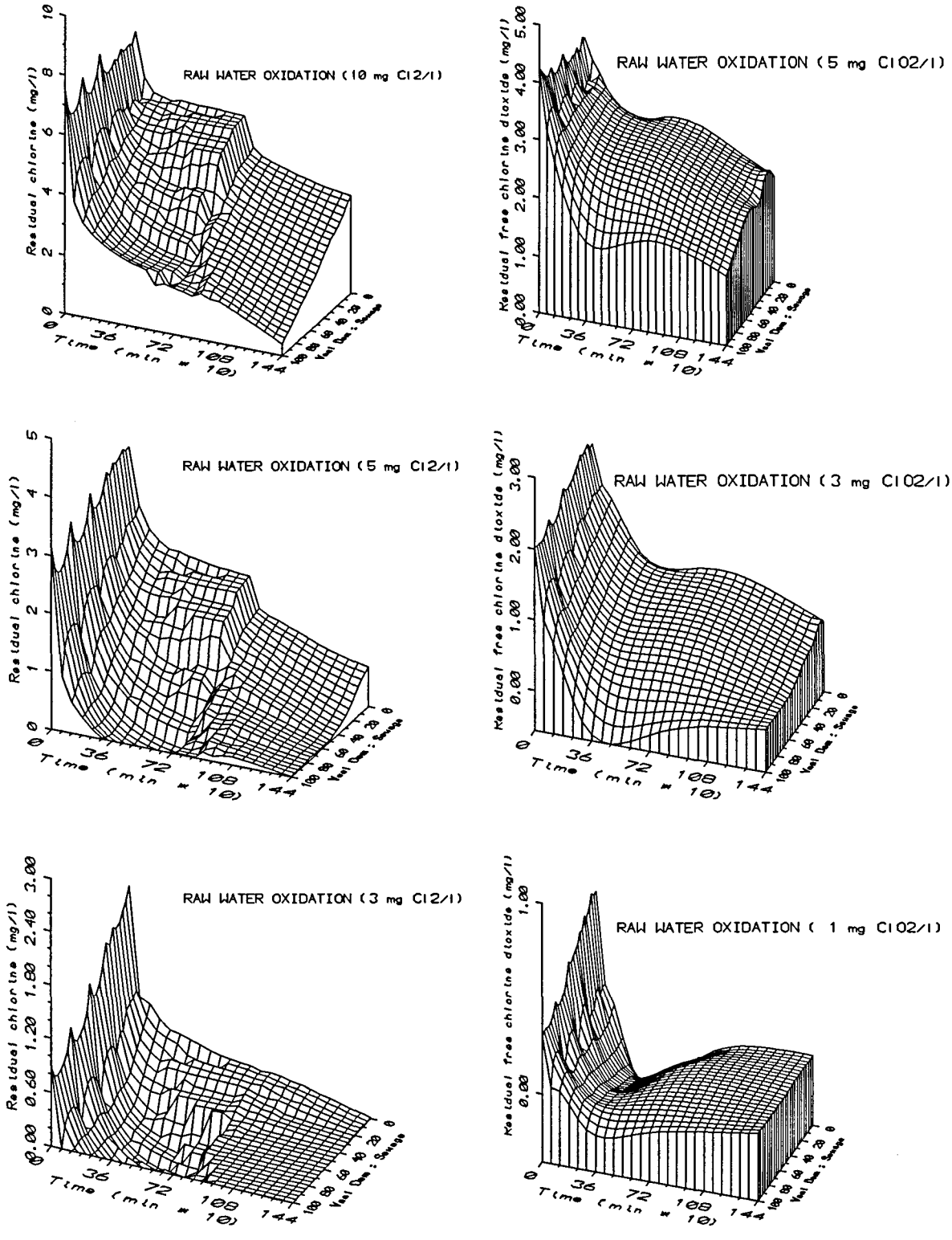


FIGURE 4.6 : RESIDUAL CHLORINE AND CHLORINE DIOXIDE CONCENTRATIONS AT CERTAIN INTERVALS AFTER DOSAGE INTO DIFFERENT MIXTURES OF TREATED SEWAGE AND VAAL DAM WATER.

Dam water. The free residual oxidant concentrations after a specific time is an indirect indication of the oxidant demand. From Figure 4.6 it is evident that the residual oxidant concentration in the samples decreased with higher proportions effluent present as well as an increase in contact time.

If the difference between chlorine dosing rate and residual measured is taken as the chlorine demand, it can be seen that the demand was higher at 10 mg/ℓ dosage compared to 5 and 3 mg/ℓ dosage (See figure 4.7).

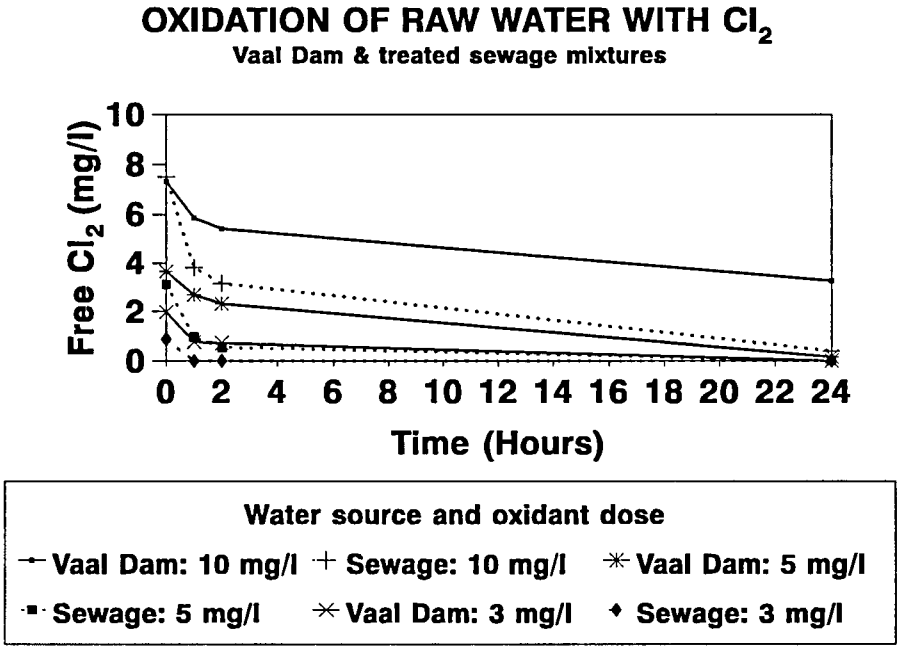


FIGURE 4.7 : RESIDUAL CHLORINE (mg/ℓ) IN VAAL DAM AND SEWAGE EFFLUENT AT DIFFERENT CHLORINE DOSAGES AND AFTER DIFFERENT TIME INTERVALS.

From Figure 4.7 it is evident that, irrespective of chlorine dosage or water quality, the rate of chlorine consumption was the highest in the first moments after contact. During the first two hours after dosage, the rate at which chlorine was consumed, was significantly higher than that measured during the next 22 hours. Similar results were obtained when chlorine dioxide was used (See Figure 4.8). Less chlorine dioxide was consumed during the contact period, compared to similar initial dosages of chlorine.

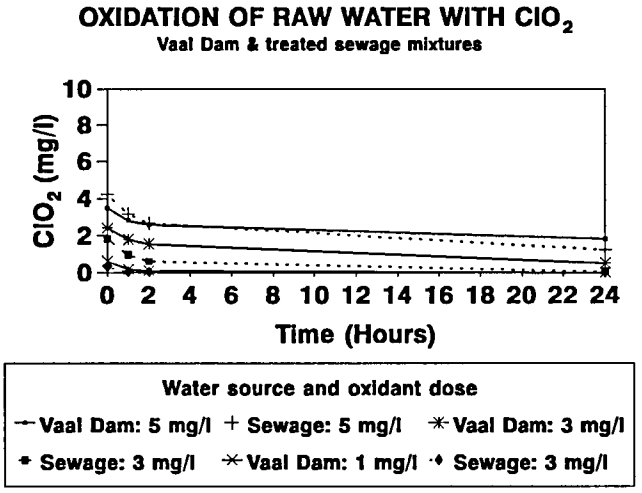


FIGURE 4.8 : RESIDUAL CHLORINE DIOXIDE (mg/ℓ) IN VAAL DAM AND SEWAGE EFFLUENT AT DIFFERENT CHLORINE DIOXIDE DOSAGES AFTER DIFFERENT TIME INTERVALS.

In Figures 4.9 and 4.10 the residual chlorine and chlorine dioxide concentrations after the same initial concentration dosages are compared. From these figures it is evident that irrespective of water quality, substantially more chlorine dioxide than chlorine is available after specific time intervals. This higher residual chlorine dioxide concentration may therefore be available to inactivate algae.

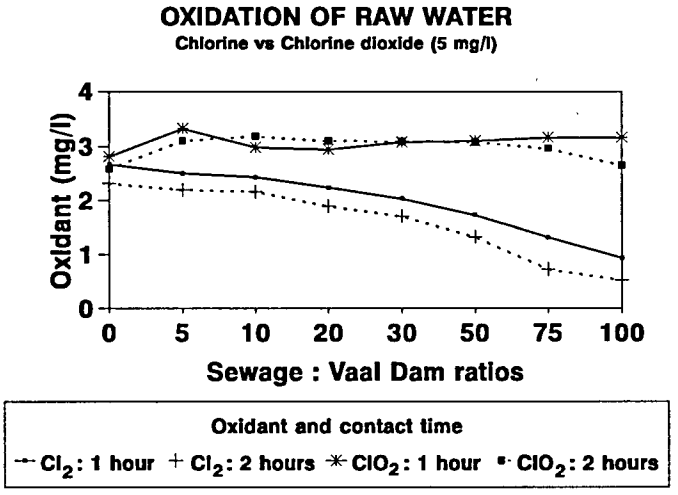


FIGURE 4.9 : RESIDUAL OXIDANT CONCENTRATIONS IN DIFFERENT SEWAGE EFFLUENT - VAAL DAM MIXTURES AT THE SAME INITIAL DOSAGE AFTER 1 AND 2 HOURS.

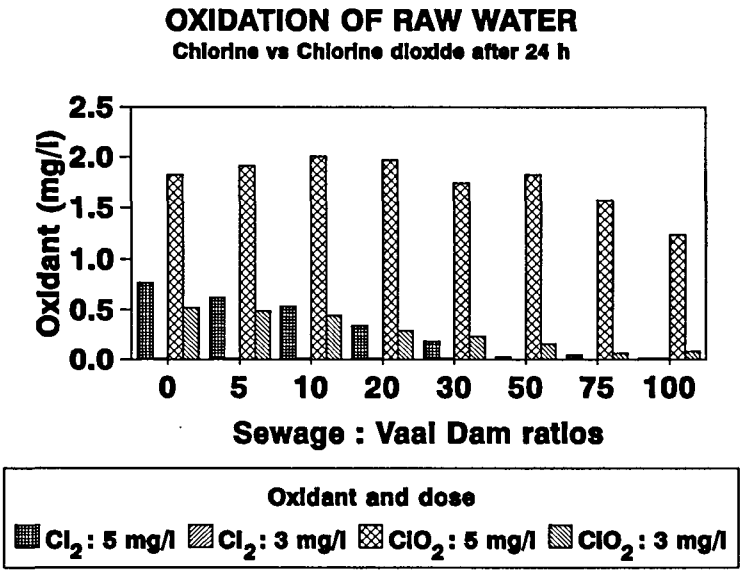


FIGURE 4.10 : RESIDUAL OXIDANT CONCENTRATIONS IN DIFFERENT SEWAGE EFFLUENT - VAAL DAM MIXTURES AT THE SAME DOSAGE AFTER 24 HOURS

4.3.3 THM FORMATION

Due to unforeseen circumstances THM analyses could not be performed during this set of experiments. However, from previous set of experiments done on a similar basis, using oxidised effluent, THM analyses were performed. THMs are formed upon chlorination. From Figures 4.11, 4.12 and 4.13 it is evident that higher chlorine dosages resulted in higher concentrations of THMs being formed. The concentration of THMs formed were not always proportional to the increase in treated effuent ratio in the samples. One possible reason for this is the fact that the treated effluent was chlorinated before sampling and therefore already contained THMs. This can be substantiated as the THMs concentration increased in proportion to the ratio of treated effluent : Vaal Dam water in the samples. It is also evident from the results that more THMs are formed after 24 hour contact time than after 2 hour contact time.

The fact that THMs are not formed upon oxidation with chlorine dioxide is confirmed by the results of this experiment (Figure 4.14). There was no significant increase in THMs after 24 hours contact with chlorine dioxide compared with the THMs value in the control sample to which no oxidant was added.

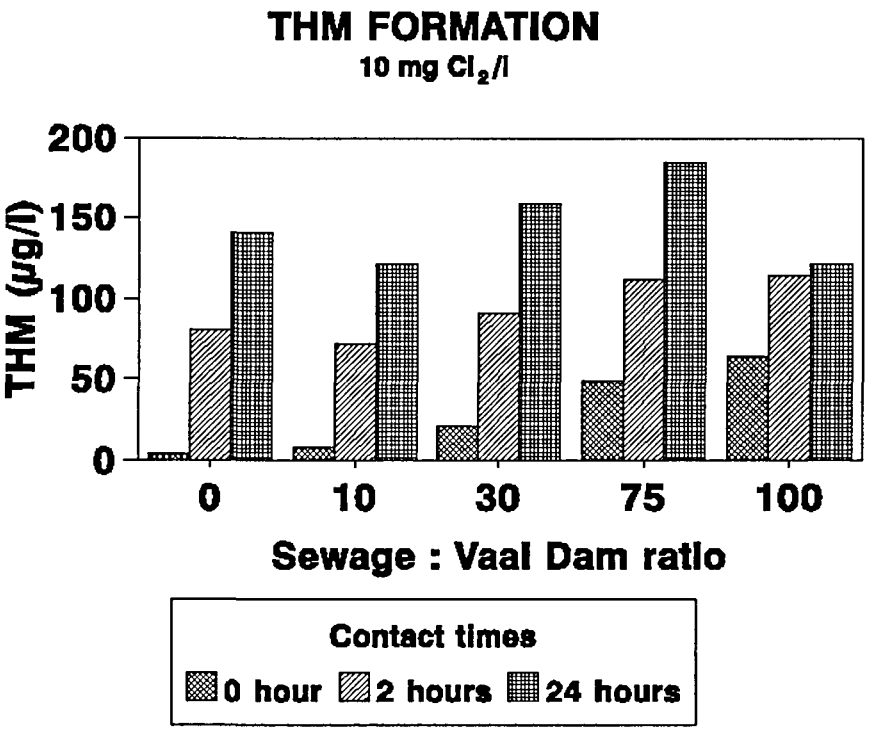


FIGURE 4.11 : THMs PRODUCED AFTER CHLORINATION WITH 10 mg Cl_2/l AT DIFFERENT CONTACT TIMES.

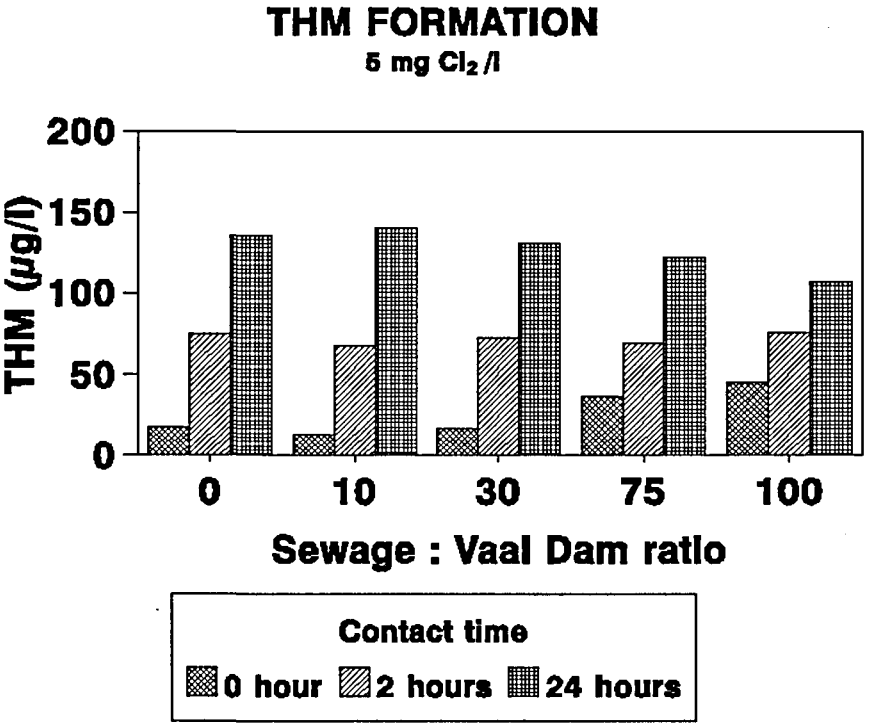


FIGURE 4.12 : THMs PRODUCED AFTER CHLORINATION WITH 5 mg Cl_2/l AT DIFFERENT CONTACT TIMES.

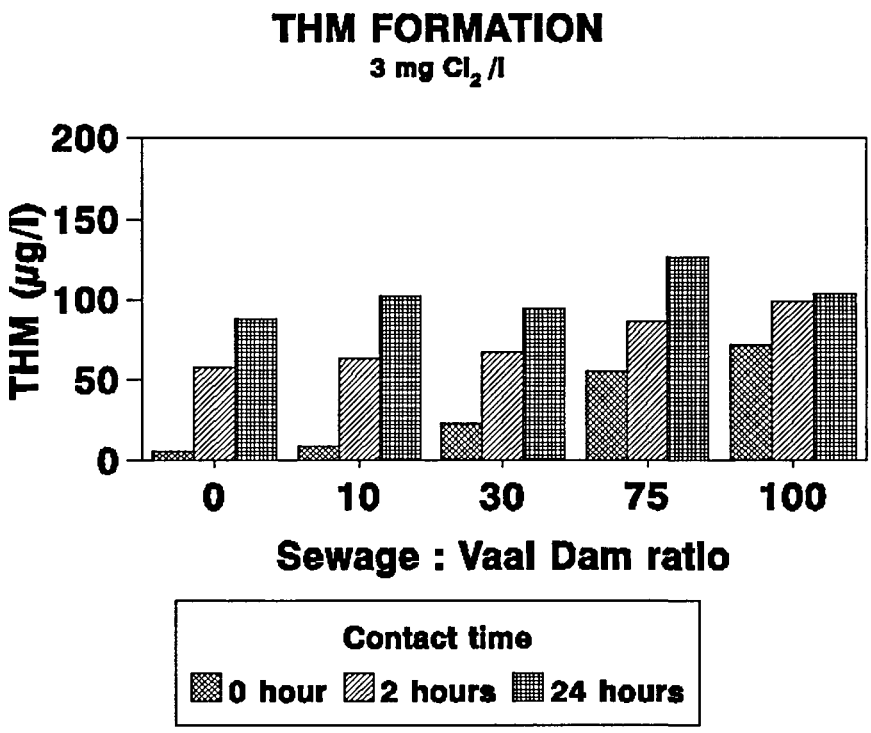


FIGURE 4.13 : THMs PRODUCED AFTER CHLORINATION WITH 3 mg Cl_2/l AT DIFFERENT CONTACT TIMES.

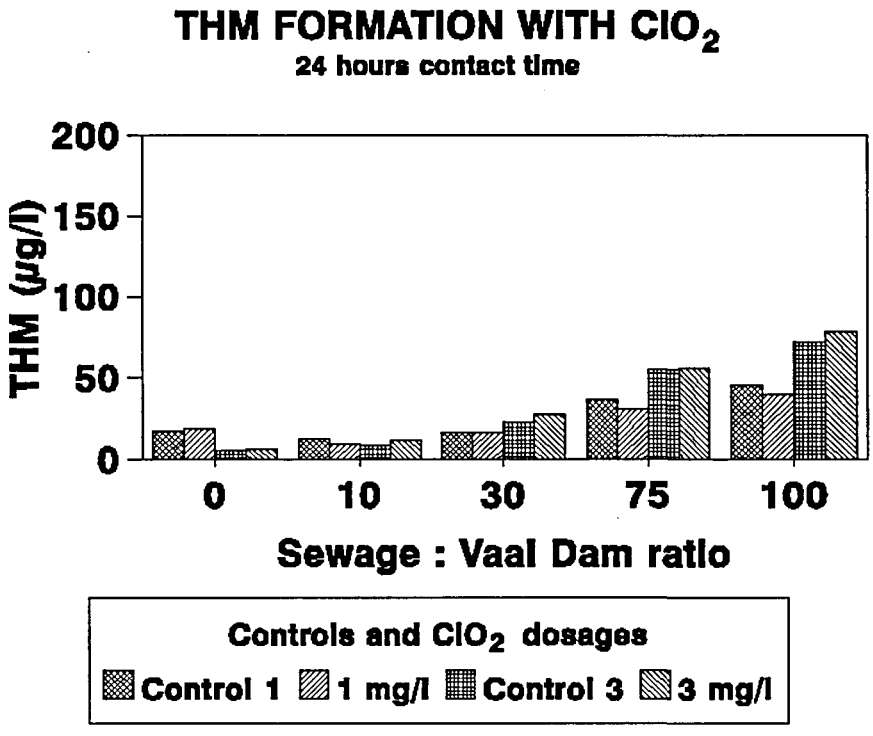


FIGURE 4.14 : CHLORINE DIOXIDE AND THMs FORMATION

4.3.4 OXIDANT REDUCING AGENTS

In these experiments it was not possible to identify specific compounds with which the oxidants reacted. There is, however, several levels of correlation between the residual oxidant consumed and the concentration of specific water quality variables present in the un-oxidised sample (e.g. experiments done on 1991-07-23, Table 4.9).

TABLE 4.9 CORRELATION COEFFICIENTS (r) BETWEEN A SPECIFIC OXIDANT CONSUMED AND SPECIFIC WATER QUALITY VARIABLES ON 1991-07-23

Coefficient	Oxidation with Cl_2 (5 mg/ℓ)	Oxidation with $Cl0_2$ (5 mg/ℓ)
$\geq$ 0,95*	Hardness; Na; K; $tSiO_2$; Turbidity; Conductivity; Ca; (NO_3 + NO_2)-N; SO_4; Cl	(NO_3 + NO_2)-N; SO_4; Conductivity; Hardness; Ca; Na; K; Fe
0,9 - 0,94*	Mg; Fe	Cl; Turbidity; $Tsio_2$
0,8 - 0,89	Alkalinity; PO_4-P; F; COD; Zn	Mg; Zn; PO_4-P; F; Al
$\leq$ 0,79	pH; DOC; NH_3; Al; SiO_2; Mn	pH; Alkalinity; Mn; DOC; NH_3; COD; SiO_2

* Significant correlation with 95 per cent confidence.

It would be dangerous to assume that the variables with the highly significant correlation coefficient had the highest affinity for a specific oxidant. Special kinetic experiments will have to be conducted to determine preferences of these oxidants.

4.4 OXIDATION OF ALGAL SUSPENSIONS

Davis and Middaugh (1978) summarised information on the toxicity of chlorine (Table 4.10), which indicates inactivation of marine algae at chlorine concentrations (0,01 mg Cl_2/ℓ to 12,9 mg Cl_2/ℓ) at different exposure times (2 min to 12 hours). Brooks and Seegret (1978) reported a reduction in the photosynthetic rate (25 to 100 per cent) of Lake Michigan phytoplankton after a 30 min exposure to chlorine ranging in concentration between 0,01 and 1,375 mg/ℓ. The most significant reductions occurred at concentrations above 0,5 mg Cl_2/ℓ.

TABLE 4.10 SUMMARY OF TOXIC EFFECTS OF CHLORINATED WASTES AND WATER ON MARINE PHYTOPLANKTON (FROM: DAVIS AND MIDDAUGH, 1978)

Species	Toxicant	Reported chlorination Level (mg/ℓ)	Duration of test	Effect	Reference
Phytoplankton	Cl_2 injection	0,05-0,40	12hr + 4hr incubation	50-98% loss of productivity	Carpenter *et al.* (1972)
Chlamydomonas sp	Sodium hypochlo-rite solution	0,69-12,90	5 min	Reduced growth rate	Hirayama and Hirano (1970)
Skeletonema costatum		0,18-2,40	5 min	None up to 0,29 mg/ℓ; greater amts. inhibited growth	
Phytoplankton	Sodium Hypochlo-rite solution	0,32	2 min	55% decrease in ATP	Gentile *et al.* (1973, 1976)
		0,01	45 min	77% decrease in ATP	
		0,075-0,25	55% decrease in growth		
Phytoplankton	Cl_2 injection		15 min	91% reduction in photosynthesis	Hamilton *et al.* (1970)

The differences in results reported above, may be due to different experimental procedures, algae, chlorine solutions and chemical composition of water used.

To test the factors influencing the effect of the oxidants on the algae occurring in the Vaal River Barrage Reservoir, sets of experiments were carried out in which as many of the variables as possible were kept constant while changing only one variable at a time. The sets of experiments were done in a solution with a low oxidant demand and were designed so that:

a) a comparison of the efficiency of the two oxidants to oxidise different algal concentrations, could be done,

b) the sensitivity of the different algal to the oxidants could be compared, and

c) the effect of pH, temperature, extracelluar algal products (EAP) and algal cell age on the efficiency of the oxidants could be determined,

The efficiency of an oxidant in inactivating the algal cells was expressed as the percentage survival of algae, 24 hours after the oxidation process had been stopped and the algae had been subjected to optimal light and temperature conditions. This concept of survival differs from the definition of Sykes (1984) viz, "continue to exist, to be alive or in existence" after treatment with the oxidant. A more accurate and direct method to determine viability and the effect of the oxidants on the algal cells is to measure the uptake of ^{14}C (Ross *et al.*, 1988). Only cells that survived the oxidation process would be able to assimilate ^{14}C. As facilities to perform the ^{14}C method were not available chlorophyll-a, associated with living cells, was used to indicated the effect of the oxidants on the viability of algae. It was assumed that cells in the process of dying will contain chlorophyll-a, which will be recorded with that of viable cells if a chlorophyll-a extraction is done directly after the oxidant had been neutralized. The nett effect of the oxidant to kill algae could, therefore, be masked. It is also important to know how pre-oxidation effects the potential of the viable cells to grow in the purification plant, after they survived oxidation. Algal cells were therefore subjected to optimal light and temperature conditions for 24 hours after the oxidation reaction was stopped by the addition of sodium thiosulphate.

The experimental design, procedures and results for each set of experiments are given and discussed below.

4.4.1 A COMPARISON OF THE EFFICIENCY OF CHLORINE AND CHLORINE DIOXIDE TO OXIDISE DIFFERENT ALGAL SPECIES AT DIFFERENT ALGAL CONCENTRATIONS.

In this experiment the following variables were kept constant for the duration of the experiment.

a) Algal cells were suspended in a 10 per cent BG 31 nutrient medium. Although at a lower concentration than the medium in which the algae was cultivated, the 10 per cent BG 31 has the same composition, should be an osmotic balanced solution and may have a relative low oxidant demand. This solution would therefore not put the algal cells under severe

physiological stress. At the same time the solution will not interfere significantly with the reaction between the algae and the oxidants.

b) The pH, after algae was added to the 10 per cent BG 31 media, was adjusted to 8,2 ± 0,2 to represent the pH of raw water sources of Rand Water (water before treatment). Adjustments were made using a O,1N NaOH or a 1N H_2S0_4 solution.

c) Temperature of the culture room in which the experiment were performed was kept constant at 23 °C ± 2 °C .

All the glassware used was rendered oxidant and oxidant demand free (A.P.H.A., 1989). All dilutions and chemicals used, except the 10 per cent BG 31 media, were made up using oxidant and oxidant demand free water (A.P.H.A., 1989).

The following protocol was followed in the experiment with each algal species and oxidant.

a) A 10 ℓ aspirator bottle was filled with sterile 10 per cent BG 31 nutrient media. A 1 ℓ sample was removed as control. This solution was continuously stirred with a magnetic stirrer.

b) Algae from a 4 day old culture (in exponential growth phase; see 4.1.1) was dosed into the aspirator bottle so that the required algal concentration of 30 μg and 100 μg chlorophyll-a per litre could be obtained. These algal concentrations selected were based on the maximum value above which algal related purification problems can be expected (30 μg/ℓ; Steynberg, 1986) and the algal concentrations above the 90-th percentile of algal concentrations occurring in the Vaal River Barrage Reservoir (100 μg/ℓ; Rand Water - unpublished data). The pH of the algal suspension was adjusted to 8,2. One litre of this algal suspension was removed as the algal control.

c) The next step was to dose the oxidant. The oxidant was dosed into oxidant free and oxidant demand free water (ODFW) to determine the volume of oxidant concentrate to dose. This volume was then dosed into ODFW and the BG31 control to determine the influence of the experimental environment on the oxidant. The same concentration of oxidant was also dosed below the water surface into 10 ℓ algal suspension while rapidly stirring the suspension with a magnetic stirrer.

d) The oxidated algal suspension was allowed to mix for 30 seconds. After 30 seconds a sample was taken, the free residual oxidant concentration determined, the oxidation reaction stopped by the addition of sodium thiosulphate and the sample then placed on the light box.

e) Simultaneously with (d), 8 x 1 ℓ bottles were filled with the "oxidised" algal suspension, sealed with screw tops and put into a dark cupboard. After respectively 5, 10, 15, 20, 30, 45, 60 and 120 minutes, one bottle was removed. Free residual oxidant concentration was determined, the oxidation reaction stopped with sodium thiosulphate, the screw tops replaced with a cotton plug after which the bottle was placed on the light box in the culture room.

f) At the specific time intervals, sub-samples were also taken after the oxidation reaction was stopped, to determine THMs, DOC concentrations and pH.

g) The oxidation reaction in the BG31 media and the ODFW (see step c) was stopped after 120 minutes. These samples were treated the same as the other oxidised samples.

h) The algal control (see b) was also subjected to the same conditions as the oxidised samples except that to this control no oxidant was added.

i) After 24 hours on the light cupboard in the culture room, the efficiency of the oxidant dosed was expressed as the percentage survival of the algae (expressed as chlorophyll-a) after a specific contact time, compared to that of the non-oxidised algal control.

Only two experiments could be performed per day. The same algal culture was used to produce algal suspensions for oxidation experiments with chlorine and the oxidation with chlorine dioxide. The experimental procedures for both these oxidants were the same.

4.4.1.1 Chlorine as pre-oxidant

The effect of different chlorine concentrations on the algae is best demonstrated by relating the survival of an algal specie to different chlorine dosages. Figure 4.15 show the reaction of the algal species at different concentrations when oxidised with different chlorine concentrations. Studying the graphs in 4.15 the following general comments regarding the survival of algae can be made:

a) Irrespective of the chlorine dosage, algal concentration, or algal species, an exponential decline in algal survival over time can be observed. These results conform to results presented by Mattice (1978) which indicated that above ± 2,5 mg chlorine/ℓ, increase in exposure time will result in an increase in mortality of aquatic life.

b) Algal biomass is reduced more rapidly at the higher chlorine dosages.

c) At initial chlorophyll-a concentrations of 100 μg/ℓ higher survival rates are observed.

These observations will be discussed in more detail in the following paragraphs.

a. The effect of increased biomass on the oxidation efficiency of chlorine.

The oxidation efficiency of similar chlorine concentrations dosed into algal suspensions containing respectively 30 μg/ℓ and 100 μg/ℓ chlorophyll-a, differ markedly. From Figure 4.15 it is evident that the mortality at the lower biomass concentrations (30 μg Chl-a/ℓ) were 30 per cent higher compared to the reaction in the suspensions with 100 μg Chl-a/ℓ at comparable chlorine dosages and time. Table 4.11 compares the percentage survival of the different algae at the same chlorine dosages at different initial biomass. The comparison was done after 10 minutes and 30 minutes contact time. The effect of the higher biomass (100 μg Chl-a/ℓ) on the efficiency of the oxidant was calculated by deviding the percentage survival of the higher biomass with that of the lower biomass (30 μg Chl-a/ℓ). The answer of this calculation is indicated as the efficiency ratio in Table 4.11.

After either contact times, using 2 mg/ℓ chlorine, the percentage survival at 100 μg Chl-a/ℓ was between 4,4 to 66,7 times that of algae at the lower chlorophyll-a concentration (excluding the results obtained with *Chlorella minutissima* at 10 minutes contact time). At chlorine dosages of 2,5 mg/ℓ the percentage survival of algae in the 100 μg Chl-a/ℓ suspension, was 1,01 to 9,7 times higher than that in the 30 μg Chl-a/ℓ suspension.

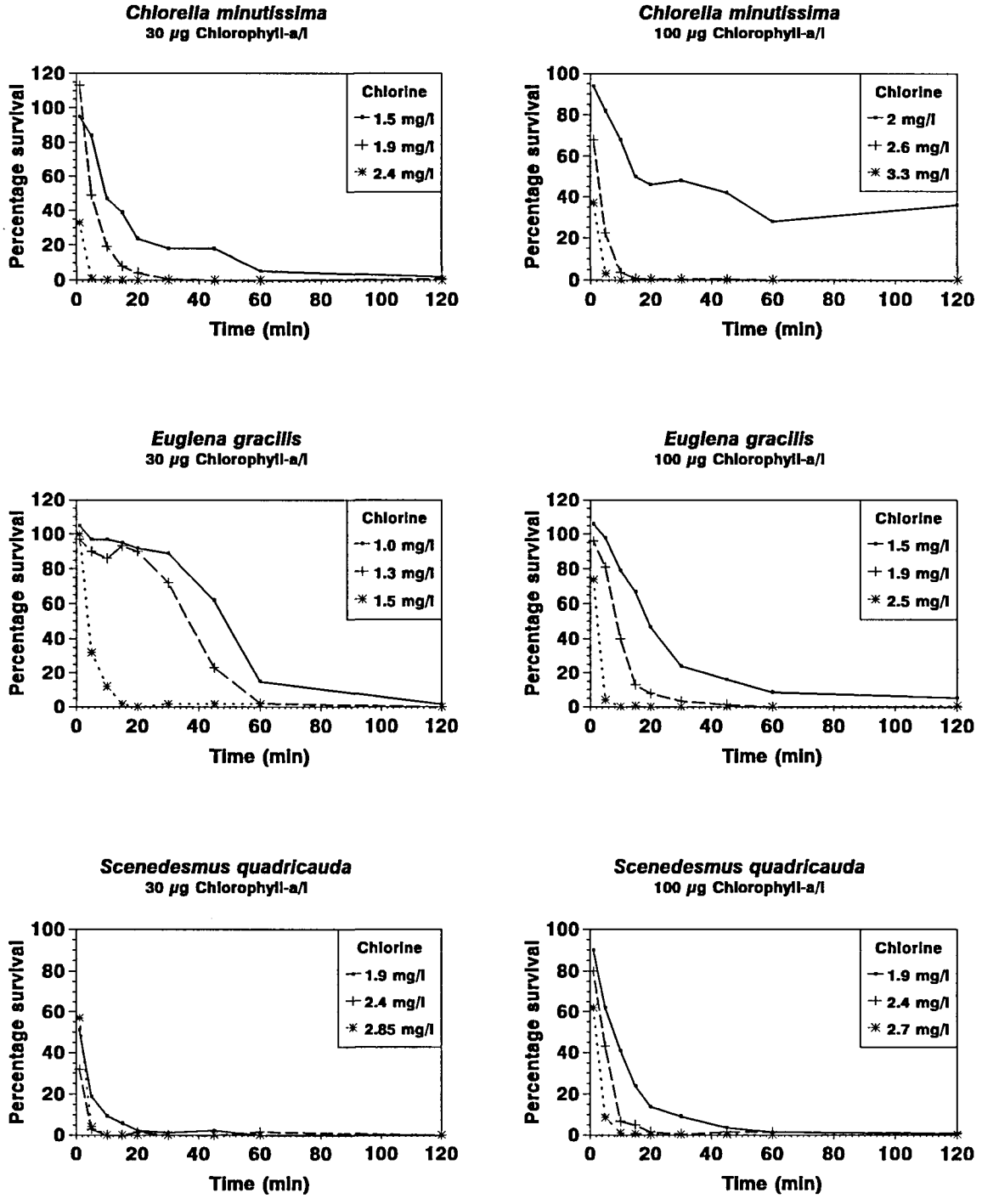
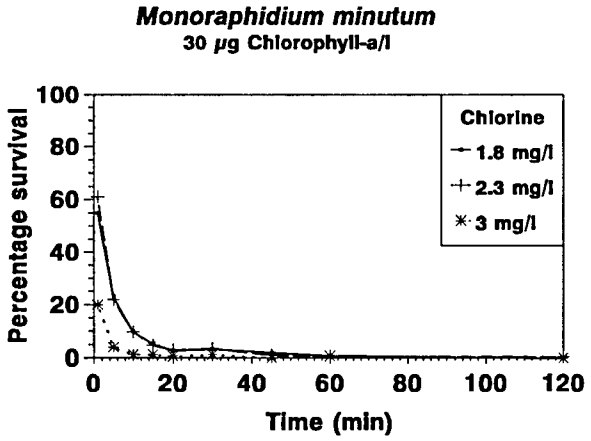
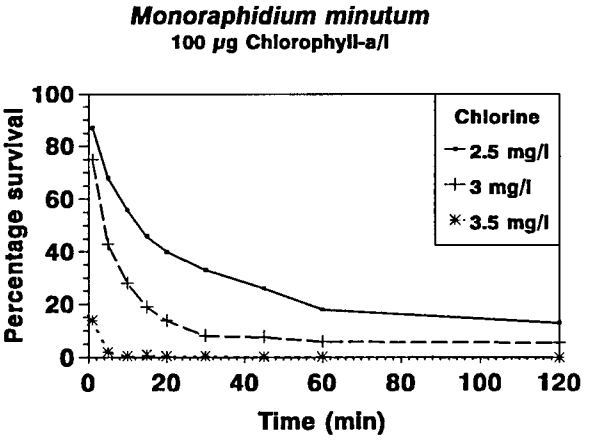
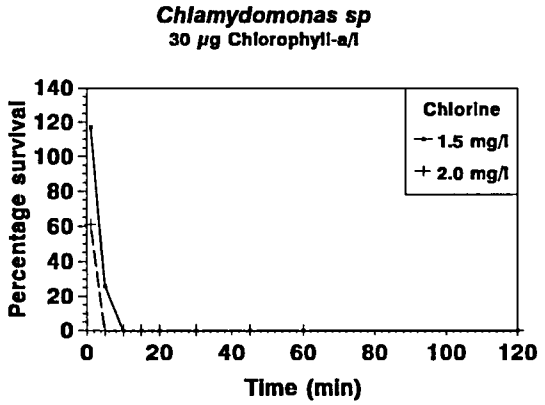
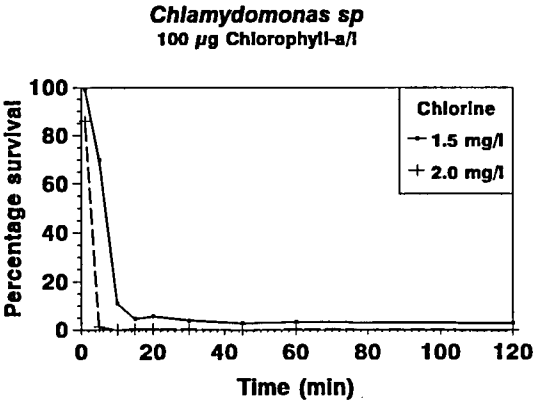


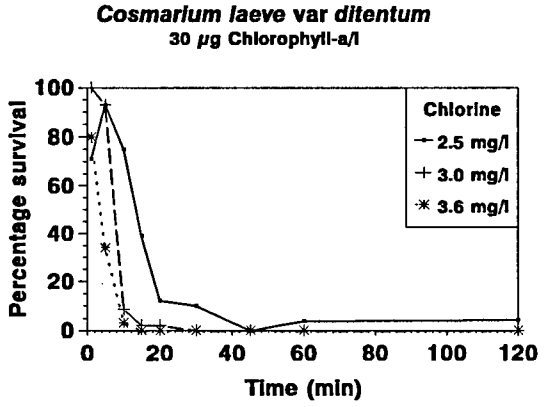
FIGURE 4.15 : THE SURVIVAL OF DIFFERENT ALGAL SPECIES AT DIFFERENT CHLORINE DOSAGES AND CONTACT TIME.











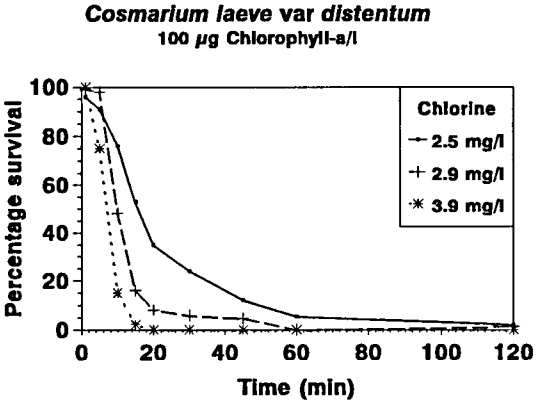


FIGURE 4.15 (CONT.): THE SURVIVAL OF DIFFERENT ALGAL SPECIES AT DIFFERENT CHLORINE DOSAGES AND CONTACT TIME.

TABLE 4.11 : THE EFFECT OF INCREASED BIOMASS ON THE SURVIVAL OF ALGAE USING CHLORINE AS PRE-OXIDANT

Time	Species	Chlorine (2 mg/ℓ) Chlorophyll-a		Effi-ciency ratio	Chlorine (2,5 mg/ℓ) Chlorophyll-a		Effi-ciency ratio
		30 µg/ℓ	100 µg/ℓ	30:100	30 µg/ℓ	100 µg/ℓ	30:100
10	*Scenedesmus*	9,4	41	4,4	0	6,7	>6,7
	Monoraphidium	-	-	-	9,8	56	5,71
	Chlorella munitussima	19	6,8	0,36	0	3,5	>3,5
	Chlamydomonas sp	0	0	*	-	-	-
	Euglena gracilis#	12	79	6,6	-	-	-
	Cosmarium laeve var distentum	-	-	-	75	76	1,01
30	*Scenedesmus*	1,2	9,3	7,75	0	0,5	>0,5
	Monoraphidium	-	-	-	3,4	33	9,7
	Chlorella minutissima	0,72	48	66,7	0	0,55	>0,55
	Chlamydomonas sp	0	0	*	-	-	-
	Euglena gracilis#	1,7	24	14	-	-	-
	Cosmarium laeve var *distentum*	-	-	-	10	24	2,4

\- No results available

* Efficiency ratio could not be calculated

\# At 1,5 mg/ℓ

From the above it may be concluded that increased chlorine dosages are necessary to kill algal cells, present in increased concentrations (100 µg Chl-a/ℓ). It would therefore be necessary to adjust the pre-chlorination dose as the algal concentration in the raw water change.

b. Chlorine resistance of different algae.

Riedel, (1989) indicated that the concentration of hexavelant chromium, required to cause a 50 per cent inhibition of growth rate, varied by a factor of more than 50 for 10 different species of algae. Sarkiskova and Skripnik, (1988) demonstrated that algal species also differ in their sensitivity to chlorine, i.e. 2 - 4 mg/ℓ stimulated the photosynthetic rate of *Prorocentrum micans*, while 18 - 37 mg/ℓ was lethal for *Prorocentrum micans* and *Nephrochlorio salina*. These marine algae appear to

be less sensitive than the algae as reported in Table 4.11 and the algae used in this study as lower chlorine dosages were required to kill algae selected for this study. Observations (Table 4.11) indicate that *Cosmarium laeve* var *distentum* (after 10 minutes contact time) may be more resistant to chlorine than the other algae species. The relative resistance of the other algae compared to that of *Cosmarium laeve* var *distentum* is given in Table 4.12. The relative resistance factors were calculated by dividing the percentage survival of *Cosmarium laeve* var *distentum* by that of the other algae treated under identical conditions.

The results indicate that after 10 minutes contact time the survival of *Cosmarium laeve* var *distentum* was 75 times higher than that of *Scenedesmus quadricauda*) and after 30 minutes 10 times higher. Comparing the relative resistance factors calculated for *Scenedesmus quadricauda, Monoraphidium minatum* and *Chlorella minutissima* at 30 μg Chl-a/ℓ and 100 μg Chl-a/ℓ it would also seem as if difference in resistance to chlorine became less evident with an increase in biomass. Comparing the resistance of the different algae it is evident that *Cosmarium laeve* var *distentum* is only 0,71 to 7,6 times more resistant to chlorine than *Monoraphidium minatum* compared to resistance factors of 1,7 to higher than 75 for the other algae. *Monoraphidium minatum* may be regarded as the second most resistant algae of the species tested.

From the above it may be concluded that algae differ in their resistance to chlorine. The level of survival may be influenced not only by the algal concentrations, but also at what stage of the oxidation reaction the survival is determined.

TABLE 4.12 RELATIVE RESISTANCE OF *Cosmarium laeve* var *distentum* AGAINST CHLORINE COMPARED TO THE OTHER ALGAE USED

Time (Min)	Algal species	Biomass as chlorophyll-a (μg/ℓ)			
		30 μg/ℓ		100 μg/ℓ	
		Chlorine (mg/ℓ)		Chlorine (mg/ℓ)	
		2,5 mg/ℓ	3,0 mg/ℓ	2,5 mg/ℓ	3,0 mg/ℓ
10	*Monoraphidium minutum*	7,6	6,5	1,4	3
	Scenedesmus quadricauda	>75	>8,5	11,3	1,7
	Chlorella minutissima	>75	>2,6	21,7	48
	Chlamydomonas sp	-	-	-	-
	Euglena gracilis	16,3	-	-	-
30	*Monoraphidium minutum*	2,9		0,72	0,71
	Scenedesmus quadricauda	>10	-	48	16,6
	Chlorella minutissima	>10	-	43,6	-
	Chlamydomonas sp	-	-	-	-
	Euglena gracilis	2	-	-	-

- = No results available.
Resistance of *Cosmarium laeve* var *distentum* = 1.

c. Free residual chlorine.

The chlorine dosed reacts at a specific rate with the oxidant reducing agents present in the water (Bernhardt and Hoyer, 1979). Chlorine not taking part in any chemical reaction at a specific time, is known as free residual chlorine (A.P.H.A., 1989). The free residual chlorine present in the algal suspension after the specified time intervals, may therefore be an indication of the chlorine demand of the algal suspensions and the rate of the reactions between the algae and chlorine. Figure 4.16 shows the residual free chlorine in the different algal suspensions from which the following is noted.

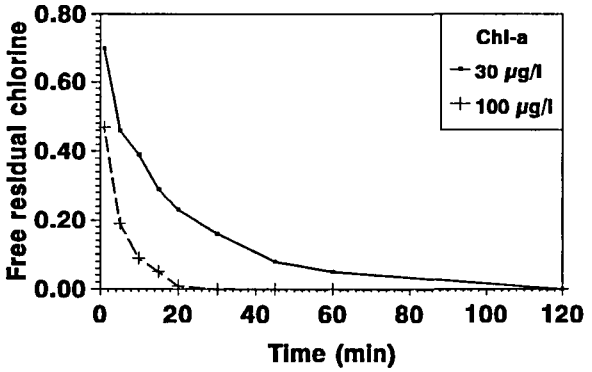
i. The free residual chlorine concentration in the algal suspensions decreases exponentially over time with the highest rate of decrease occurring within the first 30 minutes (Figure 4.16 A - K). Bernhardt and Hoyer, (1979) reported that a spontaneous consumption takes place extremely rapidly in the first few seconds, with a rapid consumption within the first 3 hours, thus confirming the results of these experiments.

ii. The free residual chlorine concentration after a specific time interval and the same initial chlorine dosage, was lower in the 100 μg Chl-a/ℓ suspensions compared to that in the 30 μg Chl-a/ℓ suspension (Figure 4.16 B and C).

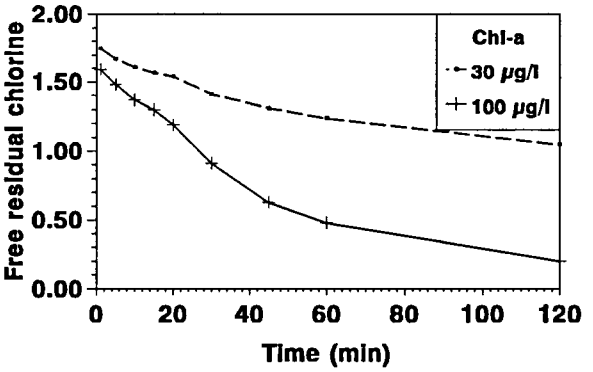
iii. Increasing chlorine dosages resulted in increased free residual chlorine concentration after the similar time interval and biomass concentration (Figure 4.16 D to H).

iv. The rate of chlorine consumption, as indicated by the difference between the chlorine dosed and the free residual chlorine over time, is significantly higher in the 100 μg Chl-a/ℓ suspension in the first minute compared to that in the 30 μg Chl-a/ℓ suspension (Figure 4.16 E to H).

A



B



C

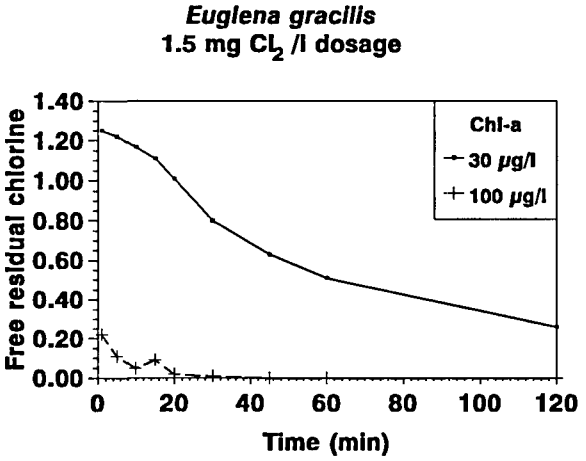
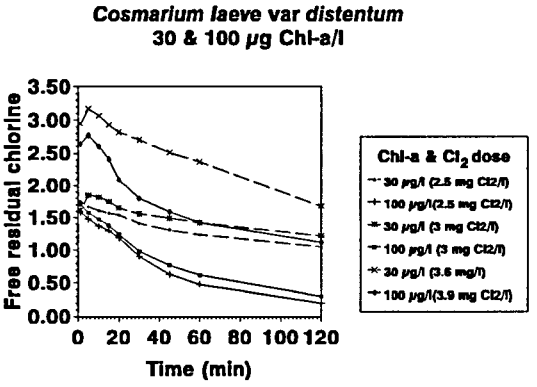
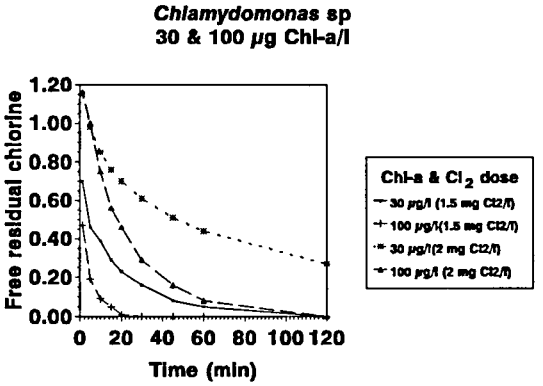


FIGURE 4.16 : FREE RESIDUAL CHLORINE CONCENTRATIONS IN THE DIFFERENT ALGAL SUSPENSIONS.

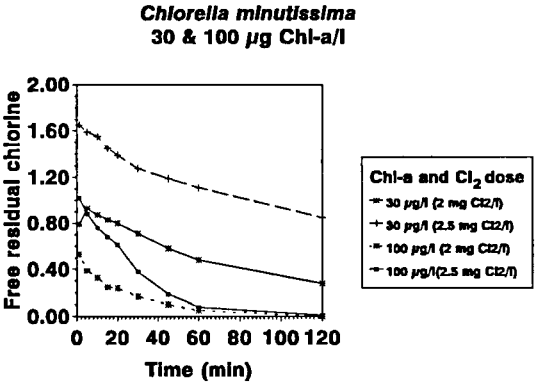
D



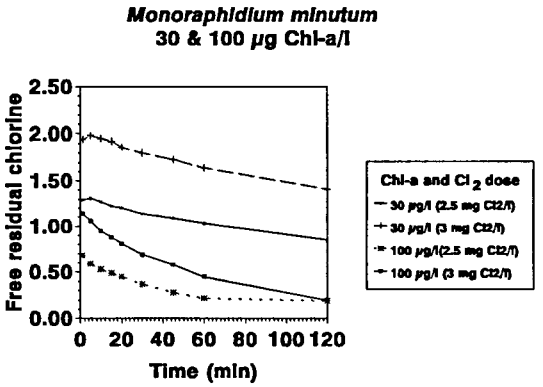
E



F



G



H

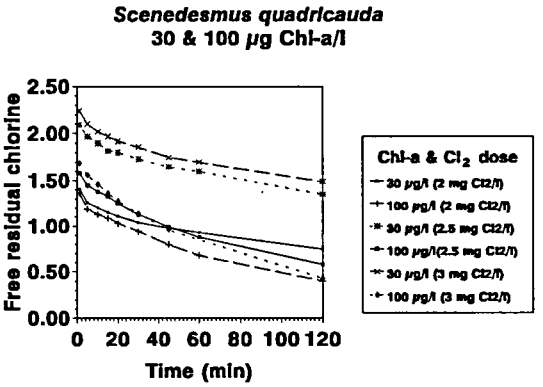
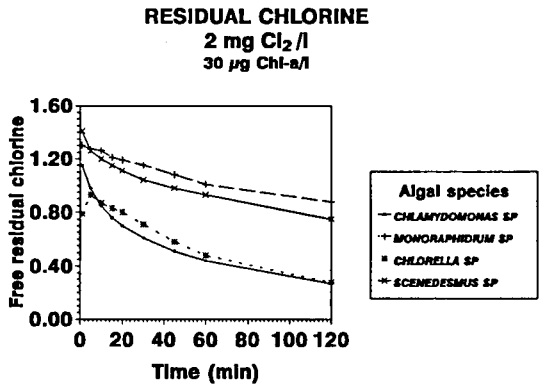
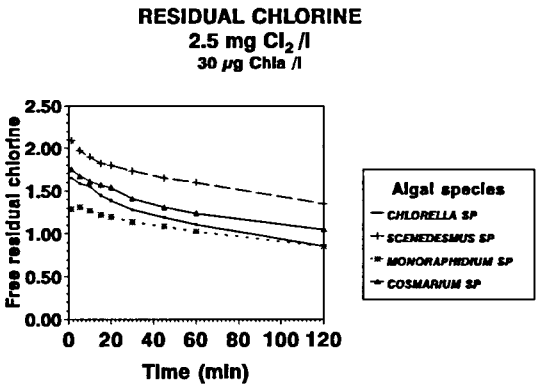


FIGURE 4.16 (CONT.): FREE RESIDUAL CHLORINE CONCENTRATIONS IN THE DIFFERENT ALGAL SUSPENSIONS.

I



J



K

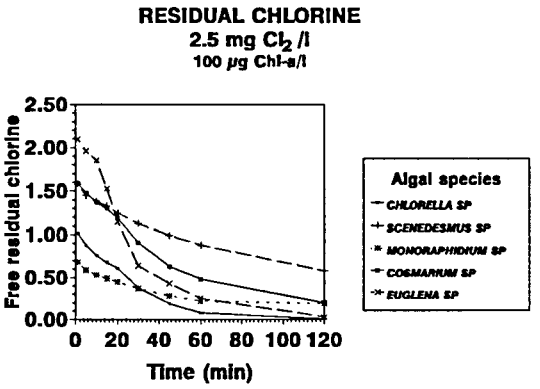


FIGURE 4.16 (CONT.) : FREE RESIDUAL CHLORINE CONCENTRATIONS IN THE DIFFERENT ALGAL SUSPENSIONS.

The above information indicates that algae may play an important role in exercising chlorine demand. This is confirmed by the corresponding increase in survival rate (eg. Figure 4.15 : *Monoraphidium minutum*) with an increase in the algal concentration and a decrease in free residual chlorine (Figure 4.16G). If pre-chlorination is also used for other purposes than for algal control (see 2.3), the high oxidant demand caused by algae will effect the success of those pre-chlorination practices.

d. Residual chlorine vs algal survival

Since chlorine react with algae, it may be postulated that where different suspensions containing algae, which have higher and lower resistance to chlorine, the free residual chlorine concentration in the suspension containing algae with higher resistance may be higher compared to solutions with algae with a low resistance to chlorine, assuming that the algae is the only substance in solution taking part in the oxidation reaction.

Comparing the free residual oxidant concentration under the same conditions (Figure 4.16 I to K) it is evident that the free chlorine in the *Cosmarium laeve* var *distentum* suspension, the most chlorine resistant algae (see 4.4.1.1.b.), is not higher than that of the other algae. In the case of *Monoraphidium minutum*, the second most chlorine resistant algae, the lowest free residual chlorine concentrations of all the experiments were recorded. It would thus not seem as if residual free chlorine and survival correlate.

Factor that complicates the issue is the fact that the pH values recorded during the time related experiments with *Cosmarium laeve* var *distentum*, favoured more of the chlorine to be present in the HOCl form (previously shown to be the effective chlorine species). In other experiments more OCl^- would have been present because of higher pH. From Table 4.13 it is evident that if pH of the solution was responsible for a simulation of resistance, *Scenedesmus quadricauda* (100 µg Chl-a/ℓ) should have had the highest survival. The *Scenedesmus quadricauda* suspension also shows the highest free residual oxidant concentration (Figure 4.16K).

TABLE 4.13: pH VALUES RECORDED DURING THE TIME RELATED EXPERIMENT, DOSING 2,5 mg Cl_2/ℓ TO DIFFERENT ALGAL CONCENTRATIONS.

Algal Species	Chlorophyll-a	
	30 µg/ℓ	100 µg/ℓ
Cosmarium laeve var *distentum*	7,4 - 7,5	7,4 - 7,5
Monoraphidium minutum	7,6 - 7,8	7,5 - 7,8
Scenedesmus quadricauda	7,2 - 7,5	8,4 - 8,0
Euglena gracilis	-	7,3 - 7,8
Chlorella minutissima	7,6 - 7,9	7,5 - 7,7

- = no result available

From the above it may be concluded that the free residual chlorine is not only a function of the resistance of some algae to chlorine. The concentration of free residual chlorine is influenced by other oxidant reducing agents present in the algal suspension as the algae was not washed before suspensions were made. It would therefore be difficult to manage the pre-chlorination of algae in raw water, based on the residual chlorine present in the water after a specific contact time.

Davis and Middaugh, (1978) reported that a chlorine residual of 0,4 mg/ℓ coincided with an 83 per cent decrease in productivity. Ibrahim *et al.* (1982) showed that continuous dosing of chlorine to maintain a residual chlorine level of 0,8 mg/ℓ was found lethal to the algae tested. In an attempt to provide a residual chlorine concentration derived from the results of this study, a three-dimensional presentation of algal concentration against residual chlorine concentration and exposure time was constructed (Figure 4.17). For this purpose the following results were plotted against each other:

a) The free residual chlorine concentrations resulting in chlorophyll-a concentrations (after 24 hours) less than the critical raw water level (30 μg/ℓ) for Rand Water.
b) Oxidation time.
c) Initial algal concentrations (30 or 100 μg Chl-a/ℓ)

Figure 4.17 indicate a strong relationship between residual chlorine, exposure time and the inactivation of the algae. The shorter the exposure time, the higher the residual chlorine concentration needed to ensure an algal concentration of less than 30 μg/ℓ developing in the purification plant, irrespective of the initial algal concentration and species.

For Rand Water where the average residence time in the raw water pipeline is 30 minutes, it is recommended that the residual chlorine concentrations between 0,3 to 1,0 mg/ℓ for algal concentrations between 30 and 100 μg Chl-a/ℓ, irrespective of the algal species present be maintained to prevent algal growth.

Figure 4.17 indicated a minimum residual concentration of 0,3 mg/ℓ for exposure times longer than 30 minutes. For initial algal concentration in the order of 100 μg Chl-a/ℓ, residual chlorine values as high as 1 mg/ℓ may be required for exposure times of 30 minutes and longer to ensure an algal biomass of less than 30 μg Chl-a/ℓ, 24 hours after oxidation.

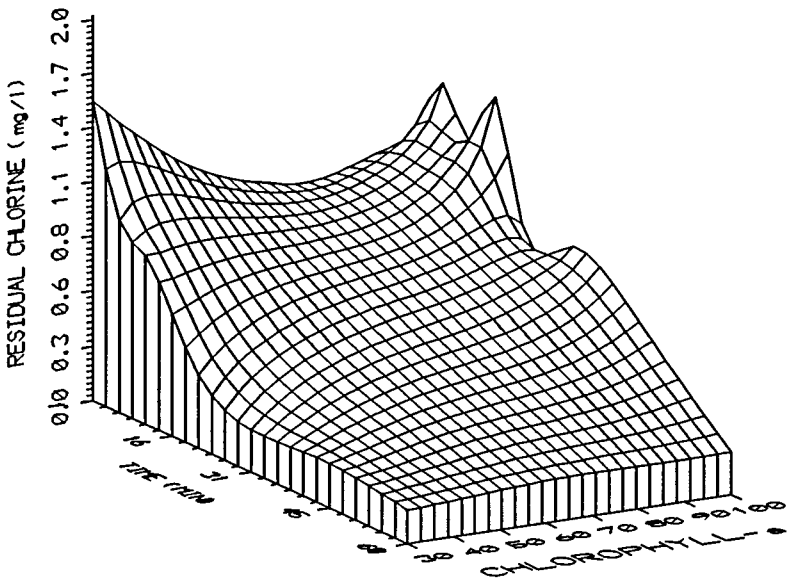


FIGURE 4.17: **A GRAPHICAL PRESENTATION OF THE RELATIONSHIP BETWEEN RESIDUAL CHLORINE, EXPOSURE TIME AND INITIAL ALGAL CONCENTRATIONS TO ENSURE LIMITED GROWTH IN PURIFICATION WORKS.**

4.4.1.2 Chlorine dioxide as pre-oxidant

The same algal species in similar concentrations were exposed to chlorine dioxide, in the same way as with chlorine (4.4.1). General trends regarding the survival of algae when oxidised with different chlorine dioxide concentrations are indicated in Figure 4.18 and can be summarised as follow:

- The efficiency of chlorine dioxide to inactivate algae is apparently not strictly a function of time. The greatest reduction in survival of the algae takes place within the first few minutes after the addition of chlorine dioxide. This is clearly demonstrated by the curves indicating survival of algae at the lower chlorine dioxide concentration dosages.

- In the case of *Cosmarium laeve* var *distentum*, 10 minutes contact time ensured the lowest percentage survival with the specific chlorine dioxide dosage (Figure 4.18 : *Cosmarium laeve* var *distentum*, 30 and 100 μg Chl-a/ℓ).

- A small increase in chlorine dioxide concentration in the order of 0,2 mg/ℓ to 0,3 mg/ℓ, resulted in a dramatic decrease in the percentage survival of the organisms (see Figure 4.18, *Euglena gracilis*, *Chlamydomonas* sp).

- With most of the algal species, chlorine dioxide concentrations, as low as 0,5 to 0,8 mg/ℓ, resulted in percentage survival rate of less than 10 per cent. In the case of *Scenedesmus quadricauda* and *Cosmarium laeve* var *distentum,* chlorine dioxide concentrations in excess of 1 mg/ℓ ensured algal survival rates of less than 10 per cent.

a. <u>The influence of increased biomass on the oxidation efficiency of chlorine dioxide.</u>

The influence of higher algal concentrations on the oxidation efficiency of chlorine dioxide, measured as the percentage survival, is not as clear as in the case of chlorine. It is especially observed in cases where chlorine dioxide dosages exceeded 0,5 mg/ℓ. This may perhaps be due to the higher oxidation power of chlorine dioxide (Table 2.7 : 1.3), compared to that of chlorine, and to the fact that less organic substances interfere with the oxidation of the algal cells than in the case of oxidation with chlorine (Table 2.7 : 1.6). However, at dosages of between 0,3 mg/ℓ and 0,5 mg/ℓ, higher percentage survival rates were observed when the initial algal concentration was 100 μg Chl-a/ℓ (Table 4.13 - *Chlamydomonas* sp).

b. <u>Resistance of different algae to chlorine dioxide.</u>

From Table 4.14 it is clear that *Scenedesmus quadricauda* has a higher resistance against chlorine dioxide compared to that of the other algal species tested. The relative resistance of the algae tested compared to that of *Scenedesmus quadricauda* is given in Table 4.15 which was compiled by dividing the percentage survival of an algal species with that of *Scenedesmus quadricauda* under identical conditions. From this table it is evident that *Scenedesmus quadricauda* may be 1,2 times to 85 times more resistant (higher percentage survival) than the other algae, with the higher resistance observed at the low chlorine dioxide concentration.

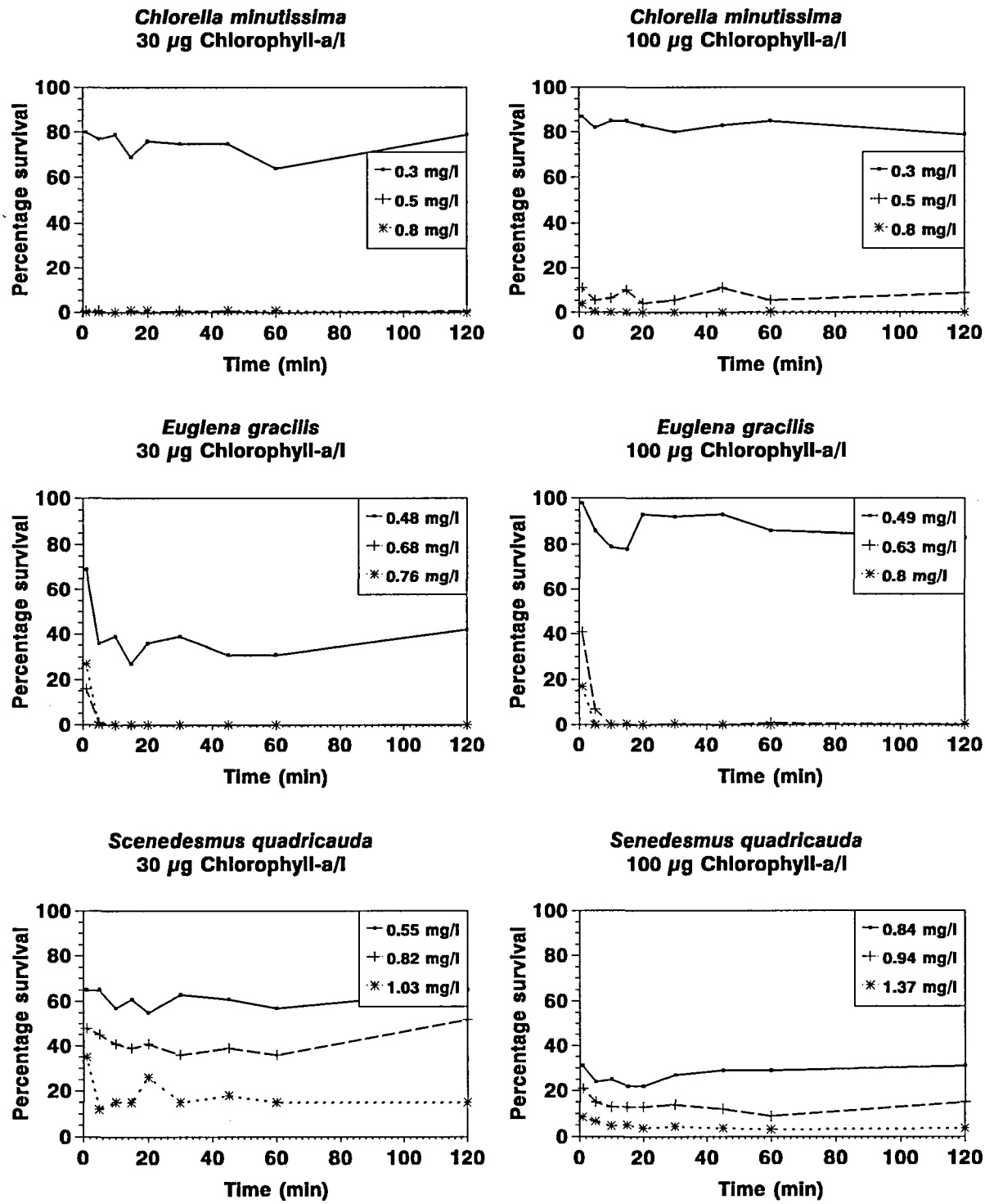


FIGURE 4.18: THE SURVIVAL OF DIFFERENT ALGAL SPP AT DIFFERENT CHLORINE DIOXIDE DOSAGES AND CONTACT TIME.

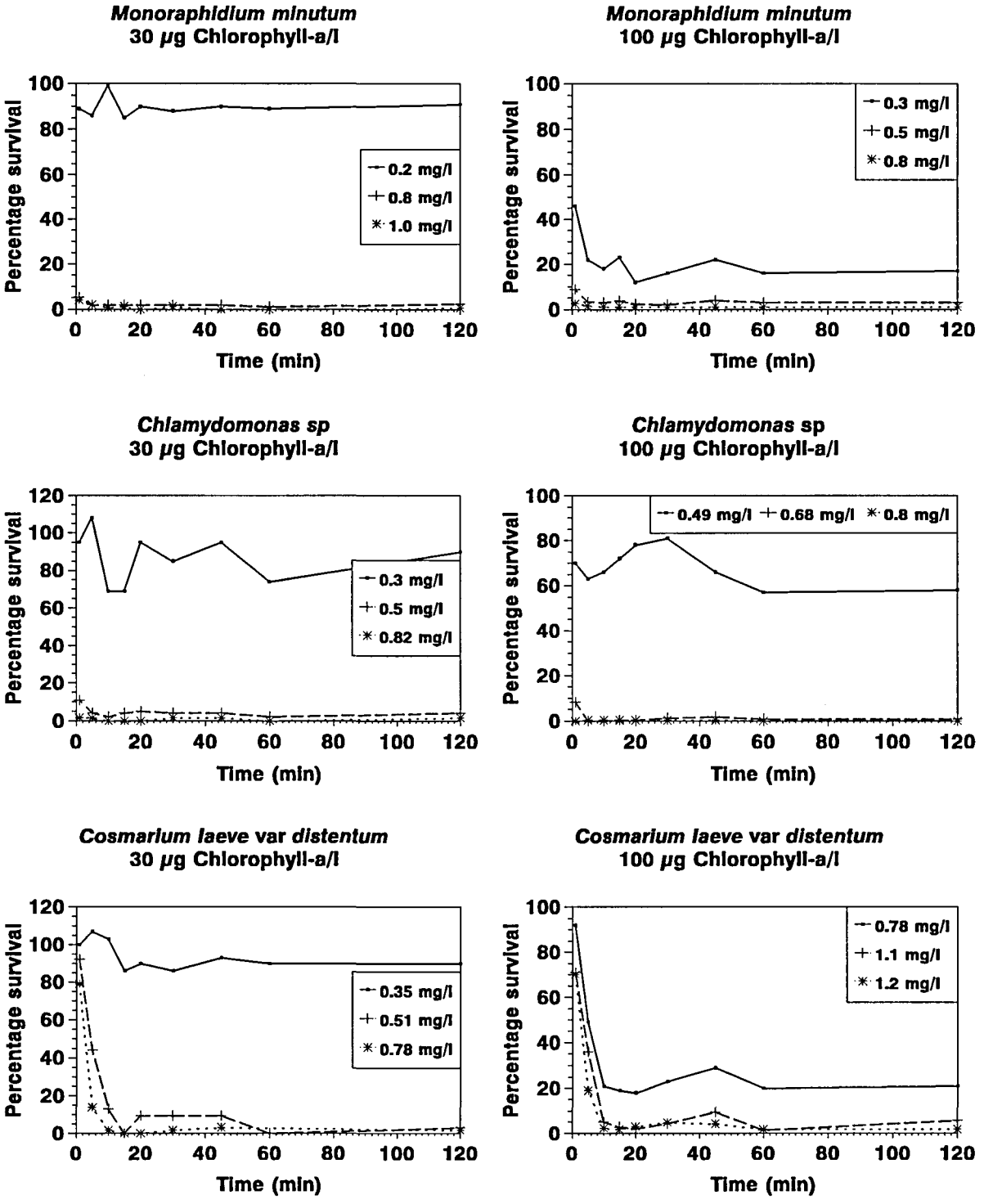


FIGURE 4.18 (CONTINUED): THE SURVIVAL OF DIFFERENT ALGAL SPP AT DIFFERENT CHLORINE DIOXIDE DOSAGES AND CONTACT TIME.

TABLE 4.14 THE INFLUENCE OF HIGHER ALGAL CONCENTRATIONS ON THE OXIDATION EFFICIENCY OF CHLORINE DIOXIDE (AS PERCENTAGE SURVIVAL)

Time (Min)	ALGAE	Chlorophyll-a	30 $\mu g/\ell$				100 $\mu g/\ell$				100 ÷ 30			
		ClO_2 (mg/ℓ)	0,3	0,5	0,8	1,0	0,3	0,5	0,8	1,0	0,3	0,5	0,8	1,0
	Scenedesmus quadricauda	-	-	57	41	15	-	-	25	13	-	-	0,61	0,86
	Monoraphidium minutum	-	-	-	1,8	0,66	-	3	11	-	-	-	0,61	-
10	*Chlorella minutissima*	-	79	0	0	-	85	6,2	0	-	1,07	>6,2	-	-
	Chlamydomonas sp	-	69	2,2	0	-	-	66	0	-	-	-	-	-
	Cosmarium laeve var *distentum*	-	103	13	1,7	-	-	-	21	5,1	-	12,4	-	-
	Euglena gracilis	-	-	39	0	-	-	79	0	-	-	-	-	-
	Scenedesmus quadricauda	-	-	63	36	15	-	-	27	14	-	-	0,75	0,93
	Monoraphidium minutum	-	-	-	1,8	1,33	-	2,1	1,3	-	-	-	0,72	-
30	*Chlorella minutissima*	-	75	0,74	0	-	80	5,3	0	-	1,07	7,16	-	-
	Chlamydomonas sp	-	85	4,3	1,7	-	-	81	1,4	-	-	18,8	0,82	-
	Cosmarium laeve var *distentum*	-	86	9,4	1,7	-	-	-	23	4,4	-	13,5	-	-
	Euglena gracilis	-	-	39	0	-	-	92	0,5	-	-	2,3	70,5	-

- = No results available

100 ÷ 30 = Survival ratio calculated by deciding the percentage survival of 100 μg Chl-a/ℓ by that of 30 μg Chl-a/ℓ

TABLE 4.15: RESISTANCE OF *Scenedesmus quadricauda* TO CHLORINE DIOXIDE MEASURED AS CHLOROPHYLL-a COMPARED TO THE OTHER ALGAE USED.

Time (min)	Chlorophyll-a	30 µg/ℓ			100 µg/ℓ		
	ClO_2 (mg/ℓ)	0,5	0,8	1,0	0,5	0,8	1,0
	ALGAE						
	Monoraphidium minutum	-	23	23	-	23	-
	Chlorella minutissima	>55	>41	-	-	25	-
10	*Chlamydomonas* sp	26	>41	-	-	25	-
	Cosmarium laeve var *distentum*	4,4	24	-	-	1,2	2,5
	Euglena gracilis	1,5	>41	-	-	25	-
	Monoraphidium minutum	-	20	11	-	21	-
	Chlorella minutissima	85	36	-	-	27	-
30	*Chlamydomonas* sp	15	21	-	-	19	-
	Cosmarium laeve var *distentum*	6,7	21	-	-	1,2	3,2
	Euglena gracilis	1,6	36	-	-	54	-

- = No results available

c. Residual chlorine dioxide

Figure 4.20 shows the residual chlorine dioxide present after different contact times with equivalent biomass concentration and chlorine initial dioxide dosages. The following was observed:

- The residual chlorine dioxide concentration in the algal suspensions decreases exponentially over time with the highest rate of decrease within the first 30 minutes.

- The residual chlorine dioxide concentrations after a specific time interval starting off at the same initial chlorine dioxide dosage, was in most of the cases lower in the 100 μg Chl-a/ℓ suspensions than in the 30 μg Chl-a/ℓ suspensions. The exceptions are *Euglena gracilis* (0,5 mg ClO_2/ℓ, Figure 4.19) and *Scenedesmus quadricauda* (0,8 mg ClO_2/ℓ, Figure 4.19).

- Increasing chlorine dioxide dosages resulted in corresponding higher free residual chlorine dioxide concentrations after the same time interval and equivalent initial biomass concentration.

- The rate of chlorine dioxide consumption is significantly higher in the 100 μg Chla/ℓ algal suspensions in the first few minutes compared to the 30 μg Chl-a/ℓ suspension.

A comparison of the exponential decrease of the residual chlorine dioxide concentration (Figure 4.20) with the immediate decrease in survival of the algae (Figure 4.19), may suggests that the reaction between algae and chlorine dioxide is very rapid. The reaction rate between chlorine dioxide and other substances may be slower, therefore the exponential decrease in the residual chlorine dioxide. This is in contrast to chlorine where the free residual chlorine and survival of algae followed the same curve trend. As in the case where chlorine was used, the higher biomass concentration is also responsible for lower residual chlorine dioxide concentrations, as well as for a higher rate of oxidant consumption. More chlorine dioxide may, therefore, be needed to inactivate algae as their concentration increase in the raw water. From the results it seems as though chlorine dioxide reacts much more rapidly with algal cells compared to the reaction of chlorine, thus favouring the use of chlorine dioxide in present pre-oxidation plants which only provide for short residence times.

d. Residual chlorine dioxide vs algal resistance

As in the case when chlorine was used as oxidant, no relationship between the residual chlorine

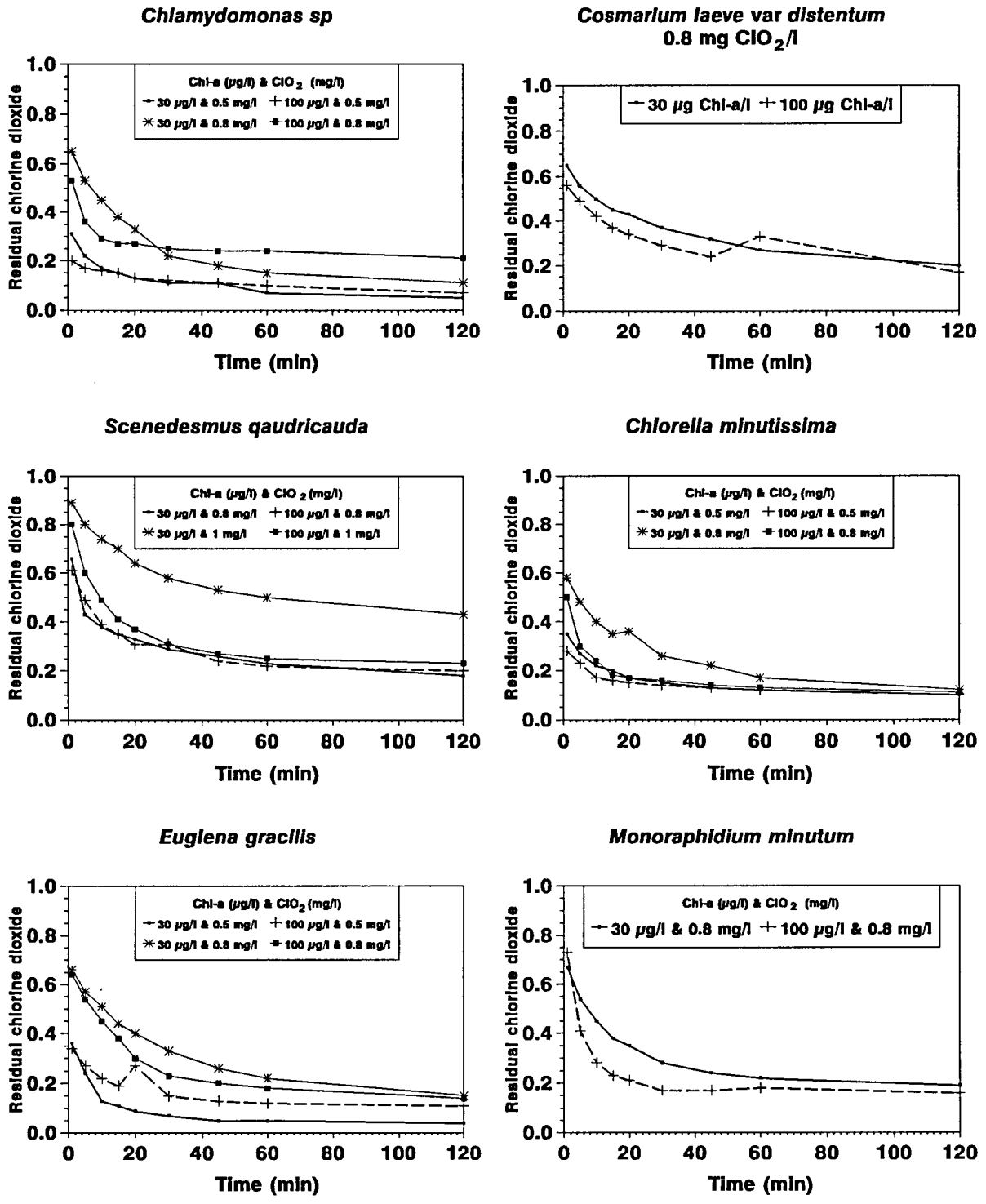


FIGURE 4.19 : RESIDUAL CHLORINE DIOXIDE CONCENTRATIONS IN DIFFERENT ALGAL SUSPENSIONS

dioxide present and the resistance of the algae could be observed. Figure 4.20 clearly indicates that the residual chlorine dioxide in a suspension of a specific algae species does not differ significantly from that present in other algal suspensions under the same conditions. The residual chlorine dioxide is, therefore, not an indicator of the resistance of the algae to chlorine dioxide or the survival of the algae. Residual chlorine dioxide concentration after a specific contact time can therefore not be used as an indicator of how successful algae may be killed.

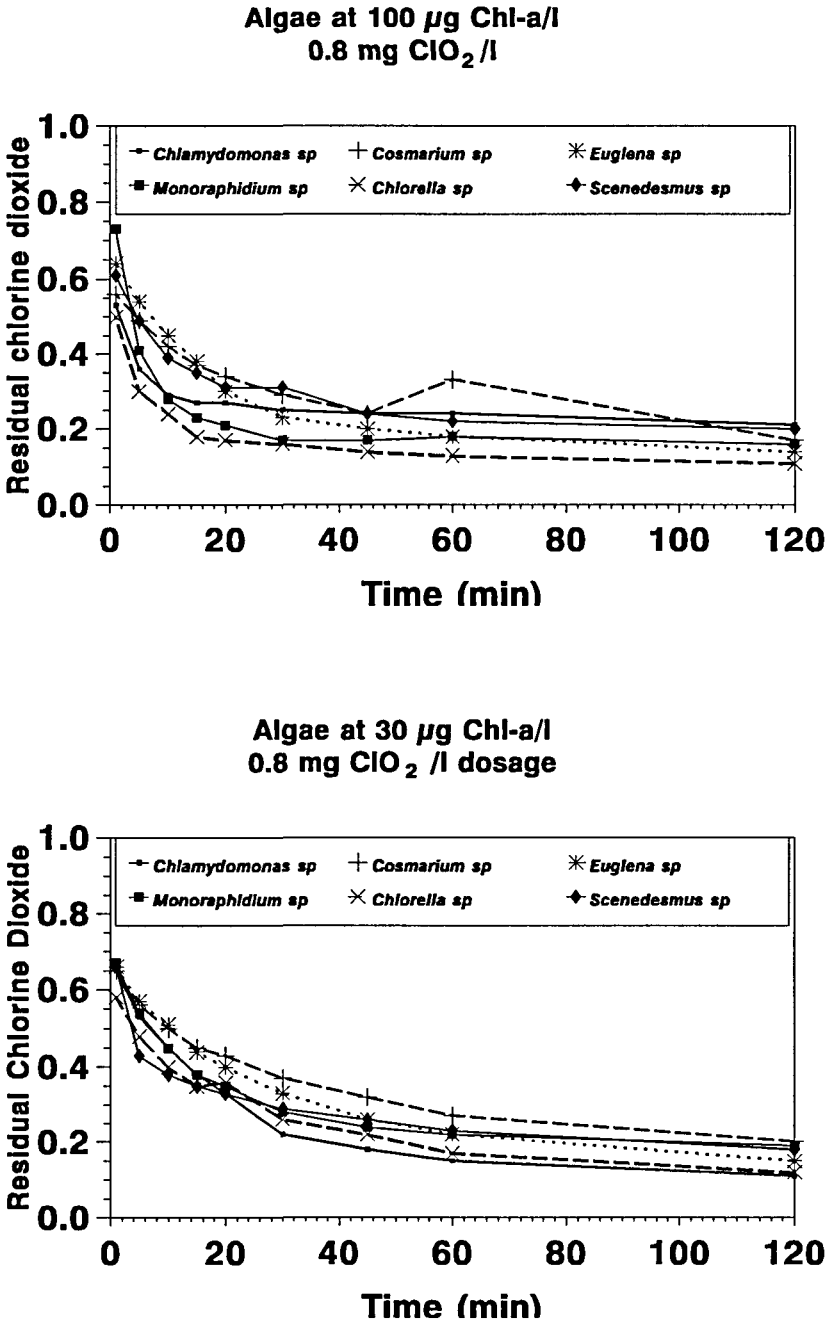


FIGURE 4.20 : A COMPARISON OF THE RESIDUAL CHLORINE DIOXIDE IN ALGAL SUSPENSIONS , STARTING AT THE SAME INITIAL ALGAL AND CHLORINE DIOXIDE CONCENTRATIONS.

4.4.2 THM FORMATION IN SUSPENSIONS OF ALGAE

During the experiments in which pre-oxidation was simulated, samples for THM analyses were taken from controls as well as after specific contact times. Results indicate that chlorine dioxide does not form any THM when used as pre-oxidant, thus confirming results reported by Rav-Acha (1984).

THM are, however, formed when chlorine is used. THM results obtained for similar chlorine dosages, contact times, nutrient media (BG31 only after 120 minute) and algal concentrations for the different algae used are presented in Table 4.16. Chlorine concentrations in all experiments were not the same, resulting in data gaps which interfere with the interpretation of the results. From Table 4.17 the following observations can be made:

a) Significant amounts of THM are present after 60 and 120 minutes contact time. These concentrations vary from 2,5 μg THM/ℓ to 49 μg THM/ℓ.

b) THM concentration increases proportionally with increased chlorine dosage and with longer contact time.

c) Insignificant amounts of THM were formed during 120 minutes when the media in which the algae were suspended was treated with chlorine. It may be concluded that this nutrient media did not significantly contributes to the THM formed.

From this set of results it is not evident whether there is any correlation between increase in biomass and an increase in THM formed at the algal concentrations and chlorine dosages used. These results, however confirm the conclusions presented by Morris and Baum (1978) and Bernhardt and Hoyer (1979) using higher algal and chlorine concentrations (See 2.3.1.2.c), that algae act as THM precursors.

TABLE 4.16: THMs ($\mu g/\ell$) PRODUCED AT DIFFERENT TIME INTERVALS, ALGAL CONCENTRATIONS AND CHLORINE CONCENTRATIONS.

CHLORINE (mg/ℓ)	TIME (MIN)	CHLOROPHYLL											
		30 $\mu g/\ell$						100 $\mu g/\ell$					
		ALGAE											
		Chlam	Cos	Eug	Scene	Mono	Chlo	Chlam	Cos	Eug	Scene	Mono	Chlo
	BG31 (120)	-	-	3	-	-	-	-	-	1,8	-	-	-
1,5	1	-	-	3	-	-	-	-	-	1,5	-	-	-
	60	-	-	4,5	-	-	-	-	-	3	-	-	-
	120	-	-	5	-	-	-	-	-	2,5	-	-	-
	BG31 (120)	2	-	-	-	4	-	2	-	-	5	0	1
2,0	1	2	-	-	-	6	-	2	-	-	5	4	0
	60	8	-	-	-	8	-	12	-	-	31	14	16
	120	12	-	-	-	21	-	13	-	-	49	20	20
	BG31 (120)	-	?	-	4	?	8	-	3,3	3,6	3	5	8
2,5	1	-	2,5	-	1	0	2	-	4,1	3,3	5	9	9
	60	-	8,5	-	3	0	15	-	12	5	18	18	17
	120	-	15	-	18	12	31	-	19	6,0	27	32	20
	BG31 (120)	-	1,9	-	8	9	-	-	2,1	-	3	2	0
3,0	1	-	2,1	-	5	12	-	-	2,1	-	5	5	10
	60	-	11	-	25	17	-	-	22	-	21	13	15
	120	-	19	-	30	30	-	-	34	-	39	23	34
	BG31 (120)	-	2,9	-	-	-	-	-	*3,9	-	-	-	-
3,5	1	-	2,5	-	-	-	-	-	2,9	-	-	-	-
	60	-	14	-	-	-	-	-	26	-	-	-	-
	120	-	46	-	-	-	-	-	33	-	-	-	-

* 3,9 mg/ℓ Cl_2 BG31 (120) = BG31 at 120 min after oxidation

? = determination suspect - = No results available

4.4.3 COMPARISON OF THE EFFICIENCY OF THE OXIDANTS

The information presented in 4.4.1 show that the algicidal efficiency of chlorine is a function of chlorine and algal concentrations as well as contact time. White (1972) and AWWA (1990) quote several studies, showing similar results when viruses, bacteria and pathogenic protozoa were chlorinated. On the other hand, the algicidal efficiency of chlorine dioxide, as presented in 4.4.2, is less contact times. Cronier *et al.* (1978) indicated that 1 mg ClO_2/ℓ at pH 9 inactivates viruses within a few seconds compared to hours when chlorine is used.

Significantly less chlorine dioxide (0,3 mg/ℓ to 1,0 mg/ℓ) than chlorine (1,5 mg/ℓ to 3,5 mg/ℓ) was required in the experiments done in 4.4.1 and 4.4.2 to achieve similar results. This indicated that chlorine dioxide could be a more efficient algicide than chlorine. The relative factor by which chlorine dioxide was more efficient than chlorine was calculated by using the following formula:

$$REF = \frac{Cl_2 t\%}{ClO_2 t\%}$$

where :

REF = Relative efficiency factor of chlorine dioxide.
Cl_2 = Chlorine concentration dosed.
ClO_2 = Chlorine dioxide concentration dosed.
t = contact time.
% = percentage survival.

The relative efficiency factor indicates how much less chlorine dioxide would possible be required to achieve the same algicidal effect as chlorine after the same contact time and with the same percentage survival. As the percentage survival figures were not always the same for chlorine dioxide and chlorine, figures differing the least were used.

From the data in Table 4.17 it is clear that the relative efficiency factor differed for various algae and that chlorine dioxide was more effective.

TABLE 4.17: EFFICIENCY FACTORS OF CHLORINE DIOXIDE BASED ON THE SURVIVAL OF ALGAL CELLS

CONTACT TIME (min)	ALGAE	CHLOROPHYLL 30 µg/ℓ																CHLORINE DIOXIDE EFFICIENCY FACTOR
		CHLORINE								CHLORINE DIOXIDE								
		1,0	1,3	1,5	2,0	2,5	3,0	3,5	4,0	0,2	0,3	0,5	0,8	1,0	1,1	1,2	1,3	
10	*Euglena gracilis*	97	86	12*	-	-	-	-	-	-	-	39	0*	0	-	-	-	>1,9
	Chlamydomonas sp	-	-	0*	-	-	-	-	-	-	-	-	0*	-	-	-	-	>1,9
	Chlorella minutissima	-	-	47	19*	0	-	-	-	-	79	0*	0	-	-	-	-	>4
	Scenedesmus quadricauda	-	-	-	9	0	0	-	-	-	-	57	41	15	-	-	-	1
	Monoraphidium minutum	-	-	-	10	10	1*	-	-	99	-	-	2	1*	-	-	-	3
	Cyclotella meneghiniana	-	-	23	23	5	3	-	-	-	-	-	9	3	-	-	2	3
	Cosmarium laeve var distentum	-	-	-	-	75	9	3	-	-	103	13	2	-	-	-	-	6/4
20	*Euglena gracilis*	92	90	2	-	-	-	-	-	-	-	36	0	0	-	-	-	>2
	Chlamydomonas sp	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Chlorella minutissima	-	-	24	4	3	-	-	-	-	76	0	0	-	-	-	-	4
	Scenedesmus quadricauda	-	-	2	2	0	-	-	-	-	-	55	41	26	-	-	-	≈1
	Monoraphidium minutum	-	-	-	3	3	1	-	-	90	-	-	2	0	-	-	-	2,5-3
	Cyclotella meneghiniana	-	-	-	14	6	2	-	-	-	-	-	8	2	-	-	1	3
	Cosmarium laeve var distentum	-	-	-	-	12	2	0	-	-	90	9	0	-	-	-	-	5
30	*Euglena gracilis*	89	72	2	-	-	-	-	-	-	-	39	0	0	-	-	-	2,25
	Chlamydomonas sp	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Chlorella minutissima	-	-	18	1	0	-	-	-	-	75	0	0	-	-	-	-	2
	Scenedesmus quadricauda	-	-	1	0	0	-	-	-	-	-	63	36	15	-	-	-	≈1
	Monoraphidium minutum	-	-	-	3*	3	1	-	-	88	-	-	2*	1	-	-	-	2,5-3
	Cyclotella meneghiniana	-	-	-	13	5	2	-	-	-	-	-	10	2	-	-	-	3
	Cosmarium laeve var distentum	-	-	-	-	10	0	0	-	-	86	9	2	-	-	-	-	5

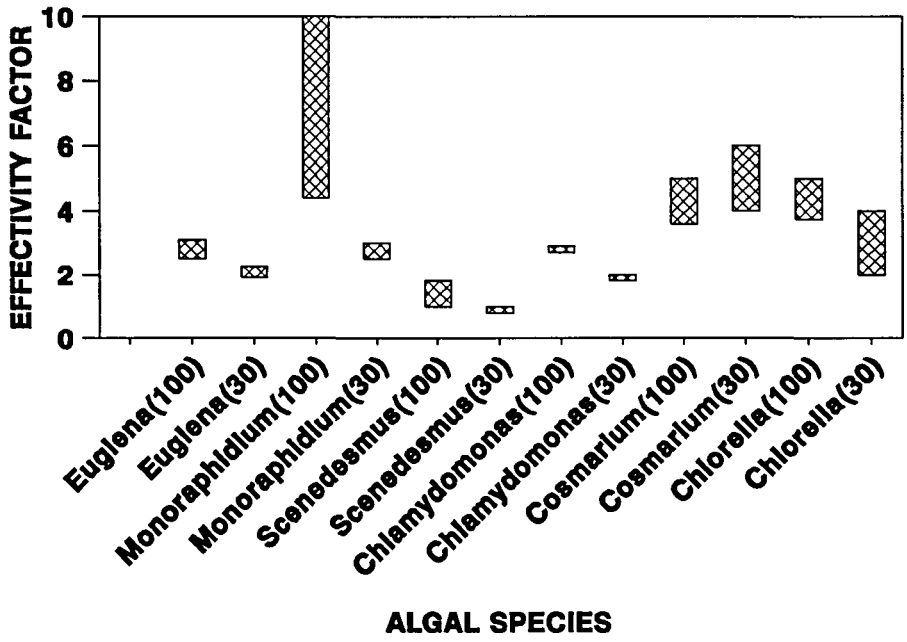
* Oxidant concentrations used in calculations.

- = No results available

TABLE 4.17 (continue)

CONTACT TIME (min)	ALGAE	CHLOROPHYLL 100 µg/ℓ																	CHLORINE DIOXIDE EFFICIENCY FACTOR
		CHLORINE								CHLORINE DIOXIDE									
		1,0	1,3	1,5	2,0	2,5	3,0	3,5	4,0	0,2	0,3	0,5	0,7	0,8	1,0	1,1	1,2	1,3	
10	*Euglena gracilis*	-	-	79	40	0	-	-	-	-	-	79	-	0	0	-	-	-	3
	Chlamydomonas sp	-	-	11	0	-	-	-	-	-	-	66	0	0	-	-	-	-	2,8
	Chlorella minutissima	-	-	-	68	4	0	-	-	-	85	6	-	0	-	-	-	-	5-3,75
	Scenedesmus quadricauda	-	-	-	41	7*	1	-	-	-	-	-	-	25	13	-	-	5*	1,8
	Monoraphidium minutum	-	-	-	-	56	28	1	-	-	18	3	-	1	-	-	-	-	4,4
	Cyclotella meneghiniana	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Cosmarium laeve var distentum	-	-	-	-	76	48	-	15	-	-	-	-	21	-	5	2	-	5
20	*Euglena gracilis*	-	-	47	8	0	-	-	-	-	-	93	-	0	0	-	-	-	2,5-3,1
	Chlamydomonas sp	-	-	6	1	-	-	-	-	-	-	78	0	0	-	-	-	-	2,8
	Chlorella minutissima	-	-	-	46	1	0	-	-	-	83	4	-	0	-	-	-	-	5
	Scenedesmus quadricauda	-	-	-	14	2	0	-	-	-	-	-	-	22	13	-	-	4	1
	Monoraphidium minutum	-	-	-	-	40	14	1	-	-	12	2	-	1	-	-	-	-	10-4,4
	Cyclotella meneghiniana	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Cosmarium laeve var distentum	-	-	-	-	35	8	0	-	-	-	-	-	18	-	2	3	-	3,6
30	*Euglena gracilis*	-	-	24	3	0	-	-	-	-	-	92	-	0	0	-	-	-	2,5-3
	Chlamydomonas sp	-	-	4	0	-	-	-	-	-	-	81	1	0	-	-	-	-	2,8
	Chlorella minutissima	-	-	-	48	1	0	-	-	-	80	5	-	0	-	-	-	-	3,75
	Scenedesmus quadricauda	-	-	-	9	1	0	-	-	-	-	-	-	27	15	-	-	5	1
	Monoraphidium minutum	-	-	-	-	33	8	1	-	-	16	2	-	1	-	-	-	-	4,4-6
	Cyclotella meneghiniana	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Cosmarium laeve var distentum	-	-	-	-	24	6	0	-	-	-	-	-	23	-	4	5	-	3,65

* Oxidant concentrations used in calculations. - = No results available



Algal species(xxx) = Chl-a in μg/l.

FIGURE 4.21 : A COMPARISON OF THE EFFICIENCY OF CHLORINE AND CHLORINE DIOXIDE.

To summarise the information in Table 4.17, the lowest and highest efficiency factor for each algal species and algal concentration, irrespective of contact time, was plotted in Figure 4.21. From Figure 4.21 it is evident that, except in the case of *Cosmarium laeve* var *distentum*, the efficiency of chlorine dioxide at the 100 μg Chl-a/ℓ concentrations was higher than at the 30 μg Chl-a/ℓ concentration. This may be due to oxidant reducing agents being present at higher concentrations in the 100 μg Chl-a/ℓ algal suspension, which affected the oxidation reaction of chlorine more than that of chlorine dioxide. It is also implicated that chlorine dioxide was more effective in killing *Cosmarium laeve* var *distentum*, *Chlorella minutissima* and *Monoraphidium minutum* (100 μg Chl-a/ℓ) than the other algae.

As shown previously *Monoraphidium minutum* has the highest resistance against chlorine while *Scenedesmus quadricauda* had the highest resistance against chlorine dioxide. This is confirmed by information contained in Figure 4.21. Chlorine dioxide was more efficient in reducing *Monoraphidium minutum* than chlorine. Although less chlorine dioxide was needed to kill *Scenedesmus quadricauda* than chlorine the efficiency factor for chlorine dioxide is much less in the case of *Scenedesmus quadricauda* compared to other algae. From these results it may be concluded that although algae may differ in their resistance to the oxidants, chlorine dioxide was shown to be more effective as an algal reducing agent.

From results presented in Figure 4.21 and Table 4.17, it may further be concluded that chlorine dioxide may be 2 to 10 times more effective in reducing algae than chlorine, depending on the algal species and algal concentration. These results should be taken into account when designing contact chambers for new purification works or implementing pre-oxidation for algal control purposes at existing plants.

4.4.4 THE INFLUENCE OF CULTURE AGE ON THE OXIDATION EFFICIENCY OF CHLORINE, CHLORINE DIOXIDE AND THE FORMATION OF BY-PRODUCTS

Algae are distinguished from other forms of plankton by their ability to photosynthesize, i.e. turning light energy and inorganic carbon into organic carbon compounds, used as source to form new cells and as form of energy for other organisms in the food chain. Algae do not convert all product from photosynthesis into new cells, but excrete some into the surrounding water. According to a summery of Lüsse *et al.* (1985), the release of this material can be as low as 5 per cent of the total organic carbon synthesized, or as high as 95 per cent of the total organic carbon for stressed cultures. An extensive survey done by Zlotnik and Dubinsky (1989) confirmed this high variation in organic carbon releases by algae.

In algal batch cultures, the concentration of suspended organic matter and the products excreted over time by the algae follow the same pattern as changes in cell number. The soluble excreted products will be referred to as extra-cellular algal products (EAP). As indicated in 2.3.1.2, EAP may be released upon oxidation and may interfere with the coagulation process. It was, however the purpose of the following experiments to determine whether the efficiency of the oxidants used, were affected by respectively 4, 7 and 14 day old algal cultures containing excreted products.

The same basic experimental procedures as set out in 4.4.1 were performed, using algae which were easily cultivated i.e. *Euglena gracilis*, *Monoraphidium minutum* and *Scenedesmus quadricauda*. The following changes to the experimental procedure were made:

a. The action of the oxidants were stopped after 30 minutes.
b. Algal cultures, 4, 7 and 14 days after inoculation, were used.
c. Only algal concentrations of 100 μg Chl-a/ℓ were used.

To determine the influence of algal culture age on the algicidal efficiency of the oxidant, the experiment was done, using a 100 μg Chl-a/ℓ algal suspension. This was obtained by suspending

algae of their specific age in a 10 per cent BG 31 media. Depending on the algal species, a predetermined oxidant concentration, as determined by previous experiments, was dosed (Table 4.18). After 30 minutes in the dark, residual oxidant concentrations was determined and the oxidation reaction stopped. Samples were taken for THM measurement and the rest of the algal suspension exposed to optimal light and temperature conditions for the 24 hours. After 24 hours chlorophyll-a concentration in these suspensions were determined.

TABLE 4.18: ALGAL SPECIES, THEIR AGE AND OXIDANT CONCENTRATIONS SELECTED FOR EXPERIMENTS TO DETERMINE THE EFFECT OF EAP/ALGAL AGE ON OXIDANT EFFICIENCY.

ALGAL SPECIES	AGE (DAY)	OXIDANT DOSE SELECTED (mg/ℓ)	
		Cl_2	ClO_2
Euglena gracilis	4; 7; 14	2	0,7
Monoraphidium minutum	4; 7; 14	2,9	0,8
Scenedesmus quadricauda	4; 7; 14	2,0	0,9

On the same day when the algal suspension was oxidised, an EAP stock was prepared from the same algal species. The EAP was separated from the algae by filtering the algal culture through a sterilised HA Millipore filter (0,45 μ). From this algal free solution, consisting of EAP and nutrient media, the same volume used to prepare the 100 μg Chl-a/ℓ algal suspension, was used to prepare the EAP solution. This EAP solution was then oxidised and treated in the same way as described above.

From Table 4.19 it is evident that the percentage survival of the algae do not significantly change with culture age. These results, therefore indicate that the efficiency of the oxidants is not influenced by the physiological condition of the algal cells, as *Euglena gracilis* at 4 and 7 days and *Scenedesmus quadricauda* at 12 days should be out of the physiological active growth phase, while *Monoraphidium minutum* was in a active growth phase for the whole period (See Figure 4.2, C, B and A respectively). The efficiency of the oxidants may be affected more by an increased biomass than by the growth phase of the algae. No correlation between algal cultures age and the THM concentrations produced could be detected (Table 4.20). This may be due to the fact that no significant increase in dissolved organics in suspensions of similar concentration, made from the different aged cultures, could be detected (Table 4.21).

TABLE 4.19: ALGAL SURVIVAL OF DIFFERENT AGE CULTURES OXIDISED AT SIMILAR OXIDANT CONCENTRATIONS.

Species	Culture Age (Day)	Chlorine mg/ℓ dosed	Survival %	Chlorine dioxide mg/ℓ dosed	Survival %
Euglena gracilis	4	1,98	0	0,71	0,24
	7	1,88	0	0,66	0
	14	1,87	0,49	0,73	0,54
Monoraphidium minutum	4	2,91	9,35	0,81	8,2
	7	2,89	3,9	0,82	5,7
	14	2,96	5,8	0,81	39
Scenedesmus quadricauda	4	1,69	0,64	0,89	7,0
	7	1,82	1,2	0,89	5,7
	12	1,86	2,8	0,89	6,6

TABLE 4.20: THM CONCENTRATIONS IN ALGAL CULTURES OF DIFFERENT AGES AFTER 30 MINUTE CONTACT TIME AT SIMILAR CONCENTRATION OF CHLORINE.

Species	Oxidant	Culture Age (Day)	THMs in algal suspension			THMs in suspension without algae			Oxidant mg/ℓ
			Control	After 30 min	⌂	Control	After 30 min	⌂	
Euglena gracilis	Cl_2	4	2,3	3,6	1,3	2,3	3,5	1,2	1,98
		7	-	4,7	-	-	4,5	-	1,88
		14	5,4	10,8	5,4	5,7	5,7	0	1,87
Monoraphidium minutum	Cl_2	4	2,7	6,9	4,2	6,2	5,9	-0,3	2,91
		7	2,6	7,1	4,5	1,8	6,3	4,5	2,89
		14	1,5	5,1	3,6	1,3	5,0	3,7	2,96
Scenedesmus quadricauda	Cl_2	4	1,1	6,5	5,4	1,3	5,9	4,6	1,69
		7	1,0	6,3	5,3	1,0	5,0	4,0	1,82
		12	0,8	4,6	3,8	0,8	3,4	2,6	1,86

⌂ = Difference in THM between control and after 30 minutes
- = No results available

TABLE 4.21: DOC CONCENTRATIONS IN THE PRESENCE OF ALGAE AFTER 30 MINUTES EXPOSURE TO CHLORINE OR CHLORINE DIOXIDE.

Species	Oxidant	Culture Age (Day)	DOC in the algal suspension			DOC in suspension without algae			Oxidant (mg/ℓ)
			Control	After 30 min	△	Control	After 30 min	△	
Euglena gracilis	Cl_2	4	4,1	3,1	-1,0	2,9	3,4	0,5	1,98
		7	2,2	2,6	0,4	2,2	2,2	0	1,88
		14	2,5	2,7	0,2	2,1	2,7	0,6	1,87
	ClO_2	4	3,8	3,0	-0,8	3,4	2,6	-0,8	0,71
		7	2,0	2,0	0	2,2	2,2	0	0,66
		14	2,8	3,5	0,7	2,1	11,1	9,0	0,73
Monoraphidium minutum	Cl_2	4	3,0	3,4	-0,4	2,6	2,2	-0,4	2,91
		7	2,0	2,5	0,5	2,2	5,3	3,1	2,89
		14	1,5	1,5	0	1,1	1,5	0,4	2,96
	ClO_2	4	1,9	2,4	0,5	2,2	2,4	0,2	0,81
		7	2,8	2,1	-0,7	2,0	3,1	-1,1	0,82
		14	1,5	1,9	0,4	2,6	1,6	-1,0	0,81
Scenedesmus quadricauda	Cl_2	4	1,9	1,5	-0,4	1,8	2,3	0,5	1,69
		7	3,2	2,3	-0,9	1,9	2,3	0,4	1,82
		12	2,9	2,2	-0,7	1,6	1,3	-0,3	1,86
	ClO_2	4	2,1	1,5	-0,6	1,9	3,7	1,81	0,89
		7	2,3	2,3	0	1,9	2,1	0,2	0,89
		12	1,6	1,6	0	1,5	1,3	-0,2	0,89

△ = Difference in DOC between control and after 30 minutes

For the purpose of this experiment, algae, the nutrient medium (BG31) and the extracellular products were regarded as the only matter that could react with the oxidants. The contribution of each of the agents to the oxidant demand are displayed in Figure 4.22 and 4.23 . An attempt was made to determined the oxidant demand for each of these agents by subtracting the residual oxidant after 30 minutes from the oxidant concentration dosed. The oxidant demand for each of these agents were determined separately and the total demand then calculated. From these figures it seems as though the overall demand after 30 minutes for chlorine dioxide (Figure 4.23) was significantly less than that for chlorine (Figure 4.22). It seems as though the extra-cellular algal products exhibited the highest demand for chlorine compared to algae in the case of *Monoraphidium minutum*. However, no significant difference between the effect of culture age could be detected. Another factor, complicating the interpretation of these results was the high demand by BG31 for chlorine and chlorine dioxide when *Monoraphidium minutum* was used. No logical reasons can be supplied for this.

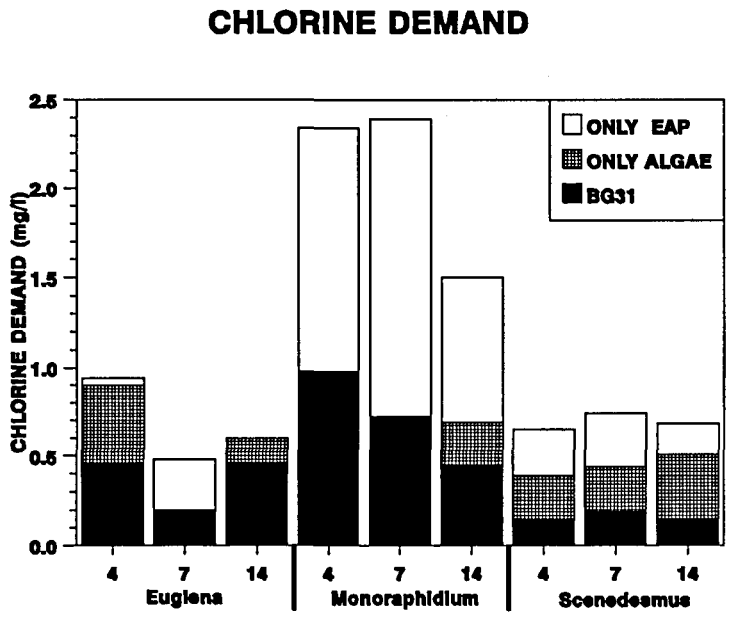


FIGURE 4.22: THE DEMAND FOR CHLORINE BY NUTRIENT MEDIA (BG31), THE EXTRACELLULAR PRODUCTS (EAP) AND THE ALGAL SUSPENSIONS OF DIFFERENT AGES.

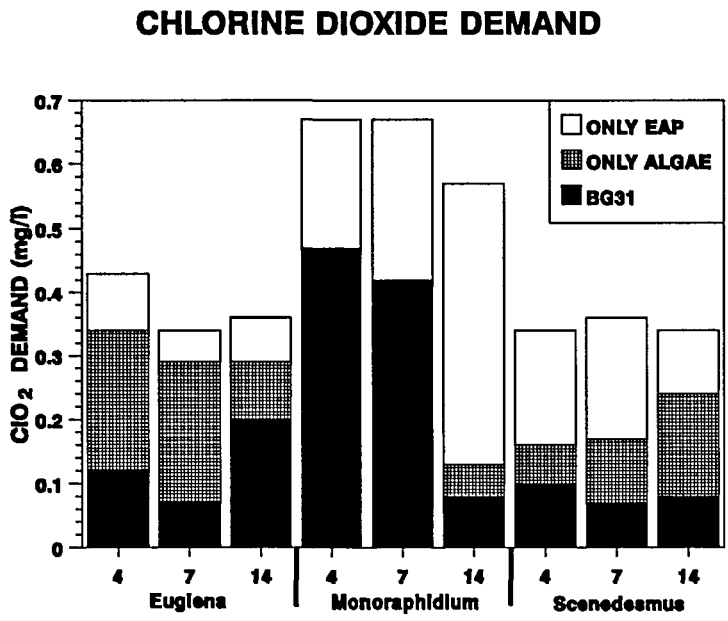


FIGURE 4.23: THE DEMAND FOR CHLORINE DIOXIDE BY NUTRIENT MEDIA (BG31), THE EXTRACELLULAR PRODUCTS (EAP) AND THE ALGAL SUSPENSIONS OF DIFFERENT AGES.

4.4.5 THE EFFECT OF pH AND TEMPERATURE ON THE ABILITY OF CHLORINE AND CHLORINE DIOXIDE TO INACTIVATE ALGAE.

According to White (1972) the efficiency of chlorine to kill micro-organisms is dependant on pH and temperature (See Figure 2.1). These factors determine the relative concentration of HOCl which has been proven to be the effective agent. Although chlorine dioxide is not influenced by pH to the same extent, increased temperature will improve the oxidation efficiency of chlorine dioxide (Masschelein, 1979). The effect of pH and temperature on the inactivation of the polio-virus and bacteria (*Escherichia coli*) by chlorine and chlorine dioxide was also demonstrated by Cronier *et al.* (1978).

To test the effect of temperature and pH on the efficiency of chlorine and chlorine dioxide to kill algae, a 4 day old *Monoraphidium minutum* culture was used to prepare a 20 ℓ algal suspension with a concentration of 30 μg Chl-a/ℓ in a 10 per cent BG31 media. *Monoraphidium minutum* was selected as it was easy to culture. To determine the influence of temperature on the algicidal efficiency of the oxidants, the pH of the algal suspension was changed to 8,2 using the same methods as in 4.4.1. From this algal suspension 3 x 1 ℓ Schott bottles was filled for each experiment to be conducted at a different temperature i.e. 10°C; 17°C and 25°C. These temperatures represents the temperature range of water in the Vaal River Barrage Reservoir during the various seasons. Once the algal suspensions reached the required temperature, oxidants were dosed at respectively 1,8 mg chlorine/ℓ and 0,5 mg chlorine dioxide/ℓ in the two of the 1 ℓ algal suspensions respectively. These concentrations were low enough to ensure that not all the algal material would be oxidised (see 4.4.1). The remaining 1 ℓ samples were used as controls for each temperature treatment. All the bottles were kept in the dark for 30 minutes at the respective ambient temperatures, after which the residual oxidant concentrations were determined, the oxidation process stopped and samples for THM analyses taken. The samples were left under optimal light and temperature conditions for 24 hours after which chlorophyll-a analyses were done.

The same experimental procedure as above was used to test the effect of pH on the algicidal efficiency of the oxidants. In this set of experiments, the temperature was kept constant at 23 $\pm$ 2°C and the pH adjusted to respectively pH 5, pH 7, pH 9,5 and pH 11 using either 0,1 N NaOH or 1N H_2SO_4 solution. After the pH for a specific experiment was stabilised, the algal suspension was oxidised using 1,8 mg/ℓ chlorine, and 0,5 mg/ℓ chlorine dioxide in the same way as described in 4.4.1. Both sets of experiments were done in duplicate.

Results indicate that the growth of algal cells in the controls are inhibited at pH 5 and pH 11,

resulting in chlorophyll-a values close to the 30 $\mu g/\ell$ at which the experiment was started (Table 4.22). In the case of treatments at pH 7 and pH 9,5 the chlorophyll-a concentration in the controls doubled which indicates that the cells were less effected by the change in pH than those exposed to pH 5 and pH 11 conditions. The high percentage survival recorded in the experiments with chlorine at different pH treatments,excluding pH 7, can therefore not be regarded as a function of the percentage HOCl present (see Figure 2.1), but may rather be a function of the effect of sudden change of pH on the cells.

TABLE 4.22: THE EFFECT OF pH ON THE SURVIVAL OF *Monoraphidium minutum* (AS 30 μg CHLOROPHYLL-a/ℓ) UPON EXPOSURE TO RESPECTIVELY 1,8 mg/ℓ CHLORINE AND 0,5 mg/ℓ CHLORINE DIOXIDE.

Treatment		pH	Residual Oxidant	*Residual Chl-a	% Survival
pH 5,5	Control	5,6	-	29	-
	Cl_2	5,7	0,89	25	86
	ClO_2	5,9	0,12	26	90
pH 7	Control	6,9	-	68	-
	Cl_2	6,9	0,70	1,1	1,6
	ClO_2	6,9	0,20	1,1	1,6
pH 9,5	Control	9,4	-	59	-
	Cl_2	9,3	1,33	38	64
	ClO_2	9,3	0,21	2,3	3,9
pH 11	Control	10,9	-	34	-
	Cl_2	10,9	1,47	27	79
	ClO_2	10,9	0,17	2,3	6,8

*Residual chlorophyll after 24 hours

Table 4.23 also indicate that the algicidal efficiency of chlorine dioxide is less effected by an increase in pH, than that of chlorine. The high percentage survival of the chlorine dioxide treated algae at pH 5 can, in this context, not be explained.

At pH 7 a 3,6 times lower chlorine dioxide concentration (0,5 mg/ℓ) resulted in the same reduction in *Monoraphidium minutum* concentration as chlorine (1,8 mg/ℓ). At pH 9,5 the same chlorine dioxide concentration (0,5 mg/ℓ) achieved algal reduction of the same order while the chlorine (1,8

mg/ℓ) was 40 times less effective in killing *Monoraphidium minutum* than at pH 7. At pH 11 the chlorine concentration was 50 times less effective than at pH 7 and the chlorine dioxide only 4 times less effective. These results confirm results reported by Cronier *et al.* (1978), indicating chlorine dioxide efficiency to be less effected by pH than that of chlorine.

Although White (1972) and Masschelein (1979) reported improved mortality when micro-organisms were exposed to chlorine and chlorine dioxide at increased temperatures, similar results on the algicidal efficiency of the oxidants were not observed when *Monoraphidium minutum* was exposed to different temperatures (Table 4.23). The three fold increase of biomass in the controls indicate that the cells were less effected by the sudden change in temperature at which they were exposed to for 30 minutes, than the change in pH, as described above.

TABLE 4.23: THE INFLUENCE OF TEMPERATURE ON THE SURVIVAL OF *Monoraphidium minutum* UPON EXPOSURE TO RESPECTIVELY 1,8 mg/ℓ CHLORINE AND 0,5 mg/ℓ CHLORINE DIOXIDE.

Treatment		Tempera-ture °C	Residual oxidant	Initial pH	*Residual CHl-a	% Survival
	Control	11,9	-	8,3	66	-
10 °C	Cl_2	10,8	1,32	8,3	1,1	1,7
	ClO_2	10,5	0,25	8,0	0	0
	Control	18,6	-	8,3	55	-
17 °C	Cl_2	17,4	1,33	8,2	1,7	3,1
	ClO_2	17,7	0,29	7,9	2,3	4,2
	Control	24,8	-	8,2	57	-
25 °C	Cl_2	24,6	1,38	7,8	1,7	3
	ClO_2	24,5	0,23	7,8	2,3	4

* Residual chlorophyll after 24 hours.

From the above results it may be concluded that pH has a greater affect on the algicidal properties of chlorine than chlorine dioxide, but that temperature is not as an important factor.

4.5 THE REMOVAL OF ALGAE BY SIMULATED UNIT WATER TREATMENT PROCESSES ON LABORATORY SCALE.

The literature reviewed in chapter 2 clearly showed that algae may penetrate water purification

processes resulting in unacceptable algal concentrations in and reduction of potable water quality. To determine what the effect of pre-oxidation on the extend of algal penetration of the purification processes used by Rand Water could be, these purification processes were simulated in the laboratory.

The purification processes used by Rand Water are presented in 2.5. The information can be summarised as follows. At present Rand Water uses activated sodium silicate as coagulant aid which is added 15 seconds prior to the addition of lime (coagulant) to the water. In the purification systems installed since 1977 the addition of these chemicals, and the mixing with raw water thereafter, is done in specially designed flash mixers. Particles are allowed to flocculate in spiral flocculators which discharges the flocculated water into sedimentation basins. After sedimentation the pH of the water is usually above 10 and the water is scale forming. To stabilise the water through recarbonation and reduce the pH, CO_2 is bubbled through the water. In this process the pH is lowered to values between 8,2 and 8,4. Remaining turbidity in the settled water is removed by rapid gravity sand filters at a nominal filtration rate of 4 $m^3/m^2/h$. The effective particle size of the filter medium is between 0,65 mm and 0,75 mm with an uniformity coefficient of less than 1,4.

To simulate the coagulation-flocculation, sedimentation and filtration processes, two Leetech six paddle stirrers and a model of a sand filter were used. Details regarding the purification conditions and technical information of the laboratory scale plant are given in Tables 4.24 and 4.25.

This part of the project was divided into two parts viz.

a) The evaluation of the removal efficiency of algae from Vaal Dam water.

b) From information obtained in the first part, algal species with low percentage removal in the tests, as well as on the full scale plant, was selected. The effect of pre-oxidation on the removal efficiency of this algae by coagulation, at different pH conditions, was evaluated.

4.5.1 THE EVALUATION OF THE REMOVAL OF ALGAE FROM VAAL DAM WATER

Petrusevski *et al.* (1992) demonstrated that the percentage removal of *Chlorella vulgaris* and *Selenastrum capricornutum* differ significantly depending on the chemical composition of the media in which the algae are suspended. For this reason, Vaal Dam water, which has a consistent quality and is the main raw water source of Rand Water, was used.

TABLE 4.24 TECHNICAL INFORMATION AND PURIFICATION CONDITIONS USING THE LEETECH 6 PADDLE STIRRER.

PURIFICATION STEP		TECHNICAL INFORMATION
1. Preoxidation	Time: 30 minutes. Container, 20 ℓ dark aspirator bottle exluding light.	
2. Coagulation	2.1	Coagulation aid: activated silica at pH ≈ 8
	2.2	Coagulant: CaO as $Ca(OH)_2$
	2.3	Coagulation chambers
	2.3.1	Size L ≈ 100 mm; W = 100 mm; H = 200 mm
	2.3.3	Energy conditions
		a) 30 seconds at 300 rpm (G = 179) without chemicals
		b) Add 3 mgℓ activated silica
		c) Wait 30 seconds and add predetermined volume of CaO as $Ca(OH)_2$ to reach pH = 11
		d) Stir 60 seconds at 300 rpm
		e) Total Gt = ± 21 480 s
3. Flocculation	3.1	Reduce rpm down to 200 for 30 seconds (Gt = 2 958 s)
	3.2	Reduce rpm to 60 over a 30 second period and stir at 60 rpm for 7 minutes (Gt = ±12 600 s)
	3.3	Reduce 60 rpm to 30 rpm in 30 second period and stir at 30 rpm for 90 seconds
4. Sedimentation	4.1	Allow 10 minutes for sedimentation, 800 ml of supernatant is withdrawn with special gravity suction
5. Carbonation	5.1	Pure CO_2 is bubbled through the water to change pH > 10 to pH = 8,2 - 8,4

TABLE 4.25 TECHNICAL INFORMATION OF THE LABORATORY SAND COLUMN USED

CHARACTERISTIC		INFORMATION
1. Container	PVC pipe	
2. Diameter	ID = 43 mm	
3. Sand depth	600 mm	
4. Empty bed volume	0,87 ℓ	
5. Filtration rate	at 4 $m^3/m^2/h$ ≡ 97 ml/min	
6. Sand	6.1	Sizes: D10 = 0,66 mm (effective size)
		D60 = 0,916 mm
		D60/D10 = 1,37 mm (uniformity coefficient)
	6.2	Dry weight = 1,391 kg
7. Constant head	330 mm	

In laboratory experiments algal suspensions with chlorophyll-a concentrations of respectively 10 $\mu g/\ell$, 30 $\mu g/\ell$ and 100 $\mu g/\ell$, were prepared from 4 day old cultures in 20 ℓ Vaal Dam water. The chlorophyll-a concentrations represent the range of algal concentrations commonly observed in Rand Water's source waters. These algal suspensions, as well as a Vaal Dam water control with no additional algae added, were treated using the same maximum dosages of lime and activated silica as used in full scale to purify water. Activated sodium silica was dosed at 3 mg SiO_2/ℓ . The volume of lime required to achieve a pH of 11 in the sample, was predetermined for each algal concentration and Vaal Dam water sample respectively. The experiments were performed on each algal suspension using the conditions as specified in Table 4.24.

The algal removal efficiency of the laboratory scale unit was expressed as a function of the change in turbidity and chlorophyll-a after sedimentation and filtration, compared to that of the untreated algal suspensions. The influence of algae on the purification processes was determined by comparing the turbidity and chlorophyll-a results, with that achieved in Vaal Dam water control.

Microscopic observations of algal cultures showed that *Cyclotella meneghiniana* can change its shape, from centric, to cylindric. It was, therefore, decided not to use *Cyclotella meneghiniana* in the laboratory scale tests as it unnatural shape could effect the efficiency of coagulation-flocculation and sedimentation processes, thus preventing valid conclusions being made regarding its removal. Quantification of the *Cyclotella meneghiniana* biomass in the Vaal Dam water was also difficult and large variations in results were observed. *Pandorina morum*, a multicellular, flagellated algal species was used instead (See section 3.1.1).

Vaal Dam water, without algae added, was used as control. The experimental procedure was performed and laboratory scale unit operated such that suspended particles were reduced to a turbidity level of less than 1 NTU after filtration. From Figure 4.24 it is evident that most of the suspended matter is removed by the sedimentation process, the remaining being removed by the sand filter to levels of between 0,7 NTU and 0,9 NTU. Results are indicative of the control which was done in parallel to the Vaal Dam water containing a specific algae.

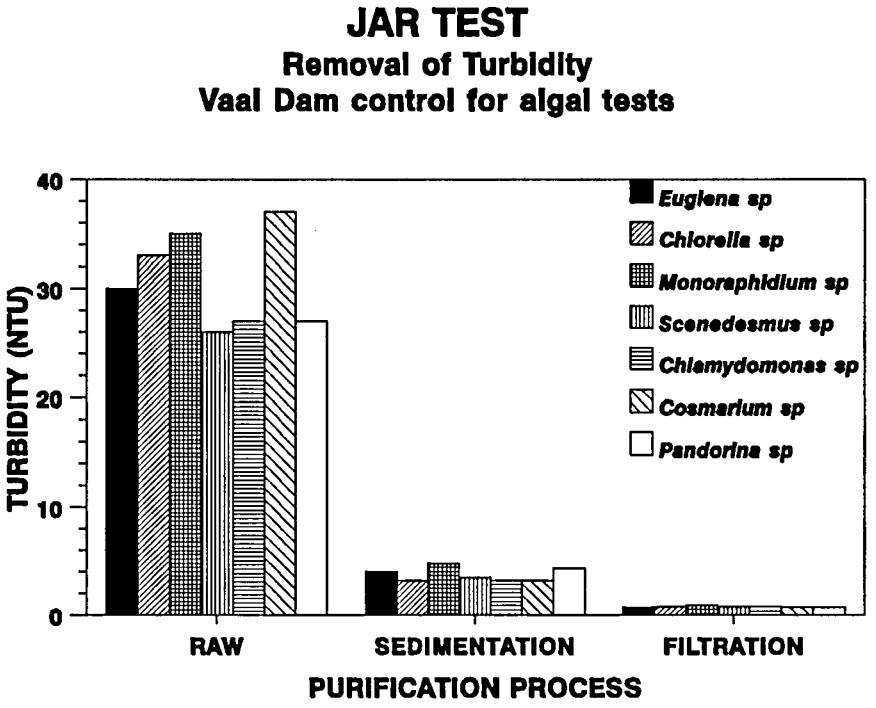


FIGURE 4.24 : REMOVAL OF TURBIDITY FROM THE CONTROLS FOR THE DIFFERENT ALGAL REMOVAL EXPERIMENTS.

The residual algae (μg Chl-a/ℓ, Figure 4.25) and the percentage removal (Figure 4.26) by each purification process were determined. Difficulties were experienced in maintaining algal concentration in the Vaal Dam samples at the same level as a result of fluctuations in the concentration of algae occuring in Vaal Dam water and variations in the algal concentrations added.

The following general remarks can be made on the removal of the different algal species from water:

a. All the algal species at the three concentrations used were removed by the purification process, but not to the same extend (Figure 4.25 and Figure 4.26).

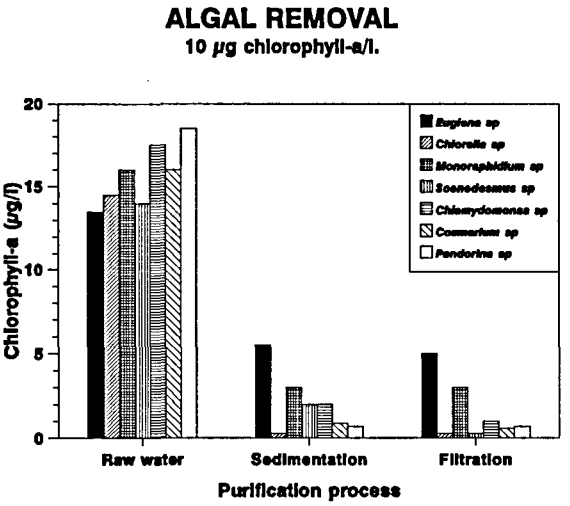
b. Irrespective of the algal species or concentration, the highest proportion algae was removed by the sedimentation process (Figure 4.27 A, B, C).

One of the aims of the purification process at Rand Water, is to remove algae to below Rand Water guideline of 1 μg Chlorophyll/ℓ (total pigment). From Figure 4.25 A, B and C it is clear that *Chlorella minutissima*, *Scenedesmus quadricauda*, *Cosmarium laeve* var *distentum* and *Pandorina morum* are removed to below 1 μg Chlorophyll/ℓ. Where respectively 30 μg/ℓ and 100 μg/ℓ *Scenedesmus quadricauda* was used only about 65 percent of the algae (Figure 4.27 A) was removed by sedimentation, compared to the 94 per cent removal of *Chlorella minutissima, Cosmarium laeve var distentum* and *Pandorina morum* (Figure 4.27 C). Filtration removed 94 to 98 per cent of the remaining *Scenedesmus quadricauda* concentration (Figure 4.26 A to C). Naghavi and Malone (1986) presented average percentage removal of 98,7 per cent for *Scenedesmus quadricauda*, using sand with half the diameter (0,335 mm) used in this study (0,67 mm). In the case of *Chlorella minutissima, Cosmarium laeve var distentum* and *Pandorina morum* less than 40 per cent of the algal concentration present in the water after sedimentation was removed by filtration (See Figure 4.26 A to C).

Results show that in the case of *Euglena gracillis, Scenedesmus quadricaude* and *Monoraphidium minutum* higher biomass concentrations resulted in decreases in the relative percentage removal efficiency by sedimentation and an increased efficiency by filtration (Figure 4.27 A and B). Filtration was efficient to reduce the residual chlorophyll-a to below 1 μg/ℓ in the case of *Scenedesmus quadricauda* (see previous paragraph). The residual chlorophyll concentration after filtration increased with increased initial biomass in the case of *Euglena gracillis* and *Monoraphidium minutum*. When *Chlamydomonas* sp was used as test organism (Figure 4.27 B) the percentage removal by sedimentation decreased with increasing initial biomass. No improvement in removal efficiency (percentage removal) with high algal loading was noticed. However, with *Euglena gracillis, Scenedesmus quadricaude* and *Monoraphidium minutum* an increase in removal efficiency was observed (See Figure 4.27 A and B).

Watson (1989) indicated that the efficiency of rapid-gravity filter beds to remove algae may vary from 89 - 97 per cent for algal species such as *Stephanodiscus* sp to as low as 26 - 45 per cent for *Oocystis* sp. In this study a wide range of removal efficiency by sand filtration was also observed (Figure 4.26). Of the algae fed onto the filters, *Scenedesmus quadricauda* had the highest percentage removal (> 80 per cent) compared to *Chlorella minutissima* (0 per cent - 15 per cent).

A



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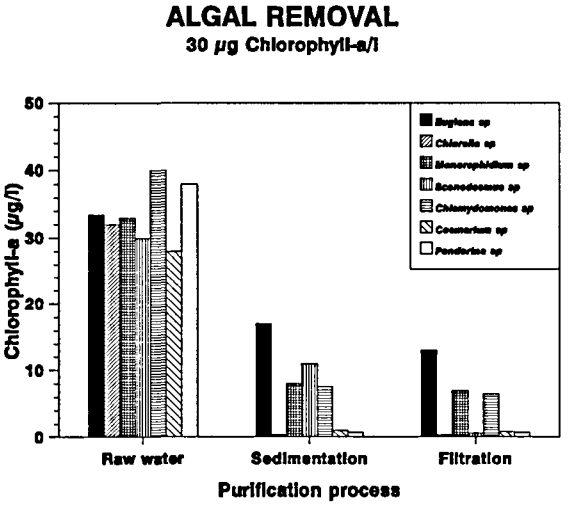

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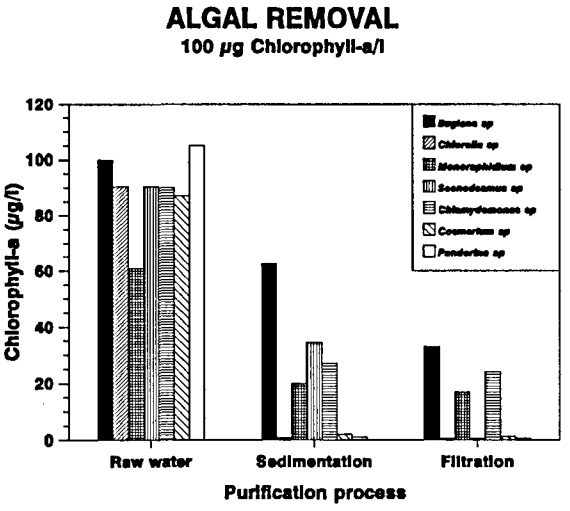
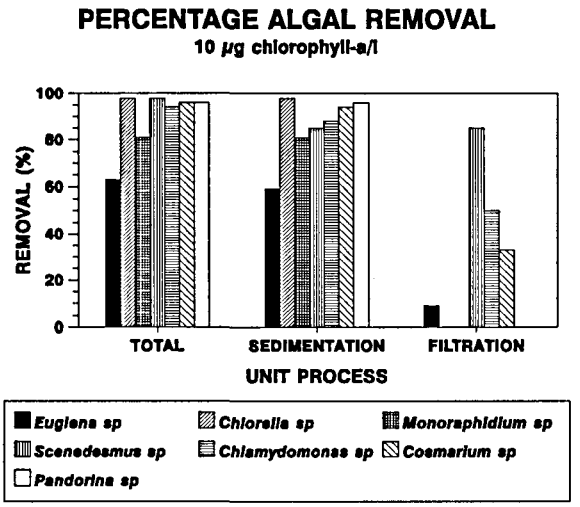


FIGURE 4.25 : ALGAL REMOVAL BY DIFFERENT UNIT TREATMENT PROCESSES

A



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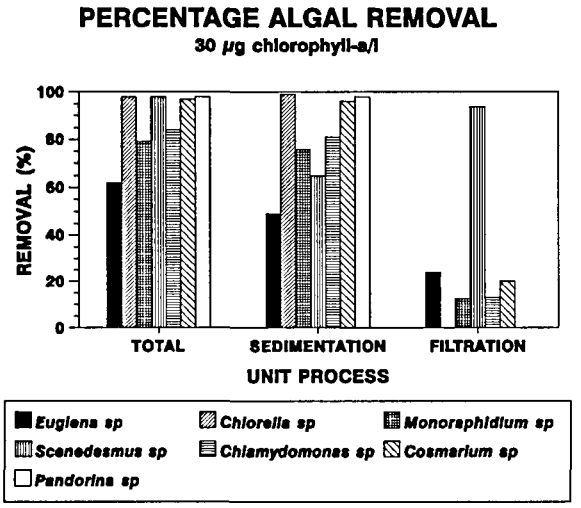

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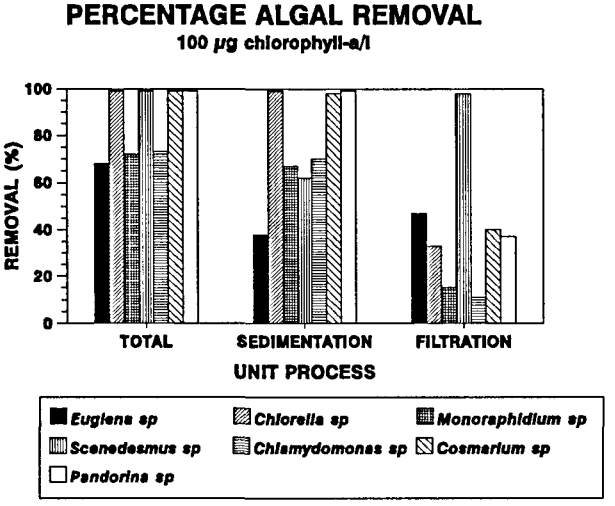
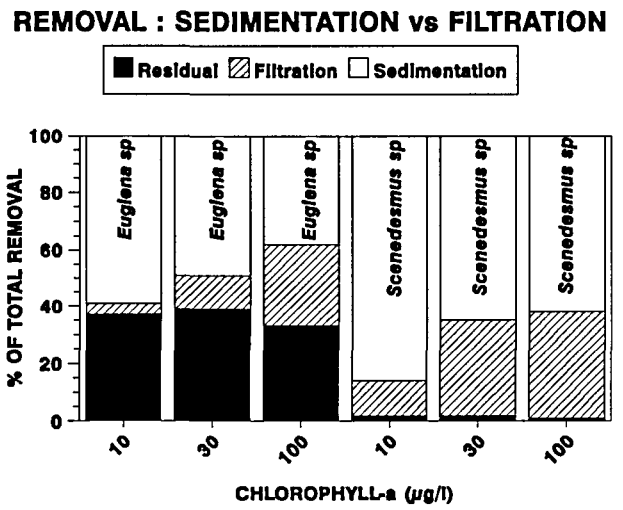


FIGURE 4.26 : PERCENTAGE ALGAE REMOVED BY DIFFERENT UNIT TREATMENT PROCESSES.

A



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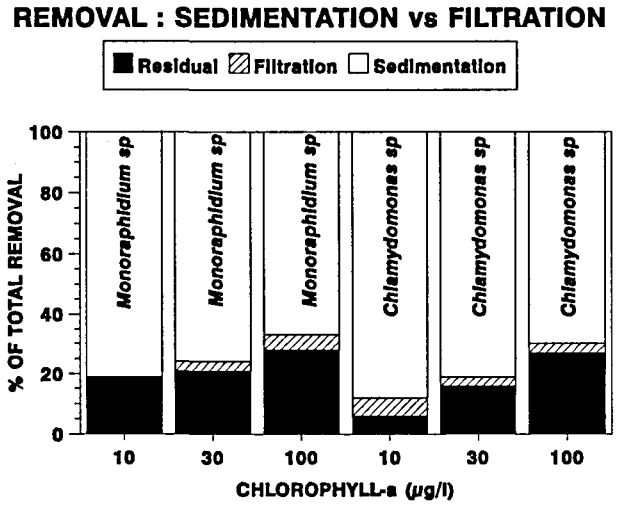

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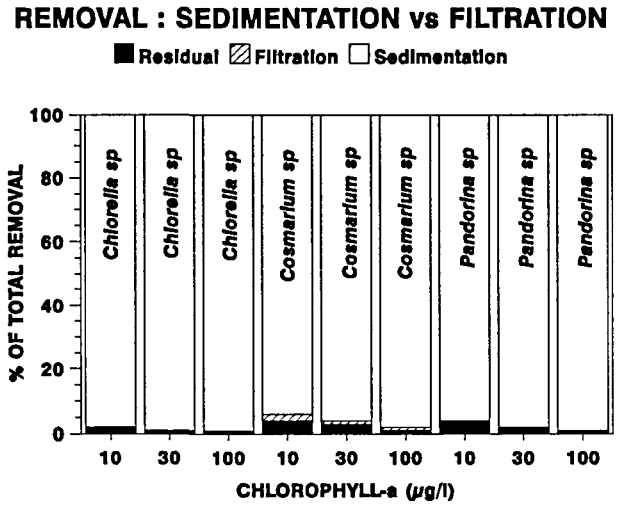


FIGURE 4.27 : RELATIVE REMOVAL EFFICIENCY BY DIFFERENT UNIT TREATMENT PROCESSES EXPRESSED AS A PERCENTAGE OF THE TOTAL REMOVAL

From the foregoing it is clear that an increase in the concentration of *Euglena gracilis*, *Scenedesmus quadricauda*, *Chlamydomonas* sp and to a lesser extend, *Monoraphidium minutum* in the suspension onto the filter, results in an increased percentage removal of these algae by filtration. In the case of *Chlorella minutissima*, *Cosmarium laeve* var *distentum* and *Pandorina morum*, algal concentrations were reduced to $\leq$ 1 μg Chl-a/ℓ by the sedimentation process irrespective of the initial chlorophyll concentration. The effect of filtration on the removal of these algal species could, therefore, not be determined, within the specific experimental set up. Regarding *Chlorella minutissima*, it would seem as no removal by filtration takes place when low algal concentrations are present in the water.

4.5.2 MECHANISMS OF ALGAE RESPONSIBLE FOR RESISTANCE AGAINST REMOVAL

From 4.5.1 it is clear that not all the algae were removed with the same efficiency by sedimentation and filtration. Investigations into the morphology of algae was therefore necessary to explain these observations.

The shape of *Scenedesmus quadricauda* (Appendix A4) possibly prevents the accommodation of several of these cells into a single floc. The terminal cells of *Scenedesmus quadricauda* have distinct spines which may prevent cells approaching each other closely enough to produce a bridging effect or a flocculation support. Bernhardt and Clasen (1991) explain the poor removal of *Stephanodiscus hantzchii*, a diatom with long bristles, in the same way. Microscopic examination of flocculated *Scenedesmus quadricauda*, as in the case with *Stephanodiscus hantzchii*, showed cells entrapped in large heaps of flocs. For efficient flocculation of these algae, the flocculant must be dosed in such large amounts that it fills the gaps between the adjacent cells. Bernhardt and Clasen (1991) also suggest that these cells must likewise be enmeshed in large flocs so that they can be eliminated according to the principle of sweep coagulation described by Stumm and O'Melia (1968). *Scenedesmus quadricauda* is, however, effectively removed by filtration. The effect of high concentrations ($>$ 10 μg/ℓ Chl-a) of *Scenedesmus quadricauda* in water on the filter running time and chemical quality of the filter effluent over an extended period is unknown. It is, therefore, preferred that the algae are removed prior to filtration.

The removal of *Monoraphidium minutum*, a small half-moon shaped cell, through sedimentation, at 75 - 81 per cent was as poor as that of *Chlamydomonas* sp (71 to 88 percent) and *Euglena gracilis* (40 to 67 per cent). The poor removal, compared to that of the small spheric cell, *Chlorella minutissima* (98 to 99 per cent), may be contributed to the shape that does not allow cells to approach each other closely enough to form dense flocs. *Monoraphidium minutum*'s "comma shape" may be

contribute to the penetration through the filter. Forces present in the filter, such as Van der Waals forces, may be incapable of retaining the algae in the pores formed by the sand grains.

Although the shape and size of *Chlorella minutissima* are suitable for removal by coagulation/flocculation followed by sedimentation (> 98 percent) it is not removed by filtration for the same reasons as mentioned for *Monoraphidium minutum.*

The poor removal of *Euglena gracilis* and *Chlamydomonas* sp may be due to the fact that both algae are motile, having whip like appendages (flagella) which propel them through the water. These algae may, therefore free themselves from floc aggregations by virtue of their motility. Bernhardt and Clasen (1991) also experienced low percentage removal of *Cryptomonas* sp and *Rhodomonas* sp (50 percent) using metal salts as coagulant at a pH 7 and suggested that the motile algae will only be removed by flocculation and filtration if the motility of the cells is inhibited. Petrusevski *et al.* (1992) also reported low percentage removal of *Rhodomonas minuta* (5 percent) and of *Chlamydomonas* sp (60 percent).

As motility of the algae was thought to be the cause for the low percentage removal, the flagella of the algae were removed using ultrasonic sound. A 4 day old culture was divided into two equal volumes, the one to be used as the control and the other subjected to ultrasonic sound, using a ultrasonic sound generator (Branson Sonic Power Co) with a metal finger. Ultrasonic sound was applied to the culture for 30 seconds. After 5 minutes the cells were microscopically examined. If cells were still motile, ultrasonic sound was applied for a further 30 seconds. If neither motile nor physical damaged cells were observed, these cultures were used to prepare a $\pm$ 100 μg chlorophyll-a/ℓ suspension in Vaal Dam water. The treated *Euglena gracilis* cells showed movement because they are able of changing shape, and they are not propelled by flagella. The controls, as well as the algae without flagella, were subjected to the same stirring tests as mentioned in 4.5.1.

From results presented in Figure 4.27 A and B it is clear that the removal of flagella improved removal by filtration. Improved removal by coagulation/flocculation and sedimentation of the algae without flagella was observed as well. Comparing the improved removal of algae without flagella by sedimentation, with that by filtration, it would seem as if the percentage removal of algae by sedimentation increased by more than 20 percent while the filter efficiency increased between 10 percent and 17 percent (Figure 4.27 C). The 20 percent improvement in removal by sedimentation confirms the ideas on the removal of motile algae by sedimentation as presented above.

Although coagulation/flocculation and sedimentation is responsible for removing the bulk of *Euglena gracilis*, the further improvement in the removal of deflagellated *Euglena gracilis* cells by filtration (10 percent) is less than observed for *Chlamydomonas* sp. A possible reason is the fact that the deflagellated *Euglena* cells were still able to change their shape, a contributing characteristic which may explain their penetration through sand filters.

It seems possible to increase the overall removed efficiency of *Chlamydomonas* sp and *Euglena gracilis* by more than 20 percent if the cells are immobilised (Figure 4.28 C).

4.5.3 THE EFFECT OF PRE-OXIDATION ON THE REMOVAL OF ALGAE

The previous results indicated *Euglena gracilis* and *Chlamydomonas* sp are algae which penetrate purification systems and that their removal by sedimentation and filtration can be improved if they are immobilised. Petrusevski *et al.* (1992) indicated improvement in the removal of the flagellate, *Rhodomonas minuta* when pre-oxidised with potassium permanganate. The effects of pre-oxidation on the removal efficiency by purification processes were studied on *Euglena gracilis* and *Chlamydomonas* sp cultures at three different levels of either coagulant and oxidant dosages.

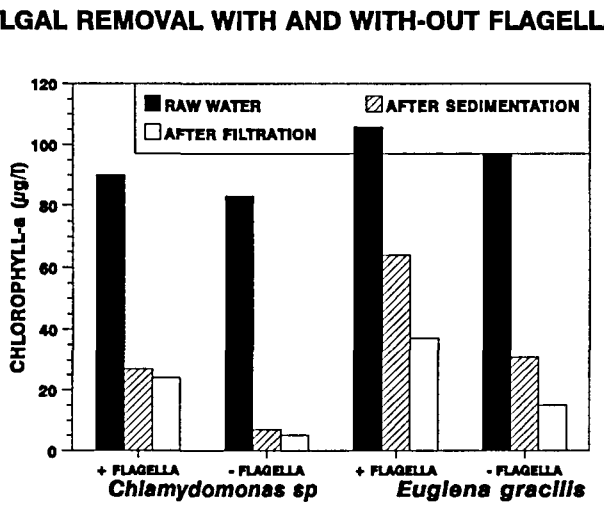
For these experiments 4 day old *Euglena gracilis* and *Chlamydomonas* sp cultures were used. From each algal culture an algal suspension of 50 $\mu g/\ell$ chlorophyll-a in Vaal Dam water was prepared. As control in experiments Vaal Dam water without algae and with algae but not oxidised were used.

The purification process was simulated as described in 4.5.1, but using 3 different concentrations of lime so that a pH = 10, pH = 10,5 and pH = 11 at coagulation were achieved. The following procedures were used.

a. The required algal concentration was made-up and checked.

b. Where pre-oxidation was required the algal suspension was oxidised for 30 minutes at 23 $\pm$ 2°C in the dark. Chlorine, dosages of respectively 1 mg/ℓ, 1,5 mg/ℓ and 2,0 mg/ℓ were used for each lime concentration. When chlorine dioxide was used, dosages of 0,3 mg/ℓ, 0,5 mg/ℓ and 0,8 mg/ℓ were applied. These oxidant concentrations were shown in section 4.4 to inhibit algal survival.

A



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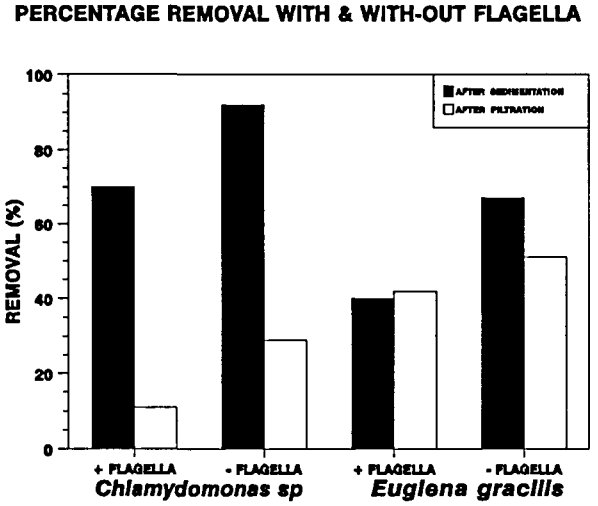

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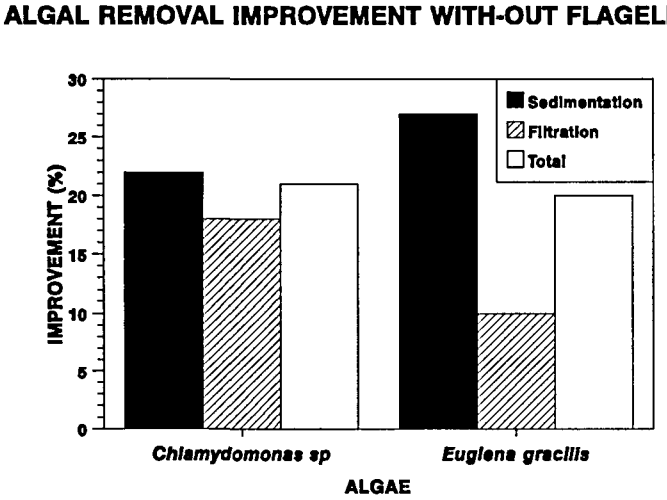


FIGURE 4.28 : THE REMOVAL OF *Chlamydomonas* sp AND *Euglena gracilis* WITH AND WITHOUT FLAGELLA BY SEDIMENTATION AND FILTRATION

c. After the 30 minute pre-oxidation period samples were transferred as quickly as possible to the stirring apparatus where the coagulation/ flocculation and sedimentation procedures described in 4.5.1 were as follows:

d. This procedures were followed for the controls (not oxidised) and the pre-oxidised cultures for each algal specie and lime dosage.

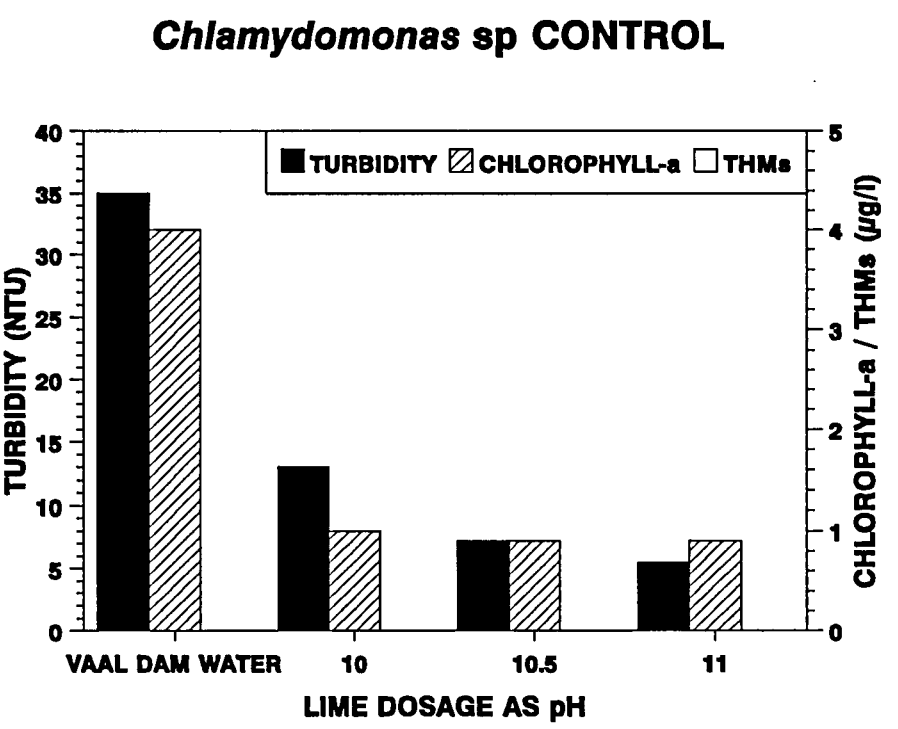
Due to the time span of such an experiment (12 hours) no filtration of the settled water was done. The results, therefore, only indicate the effects of pre-oxidation, including the sedimentation process, up to filtration.

In all experiments Vaal Dam water were used as control, to establish values to which the turbidity and chlorophyll-a could be reduced. From Figure 4.29 A and B a decrease in turbidity with an increase in pH as a result of lime dosed is evident. The algae present in the Vaal Dam water was removed to 1 μg Chl-a/ℓ but did not show any correlation with increased pH. No significant THM concentrations could be detected.

Another set of controls were done to which unoxidised 50 μg Chl-a/ℓ *Chlamydomonas* sp and *Euglena gracilis* were added prior to the addition of the different lime dosages. In the case of *Chlamydomonas* sp more algae were removed by sedimentation at pH 11 than compared to pH 10,5 or 10 (Figure 4.29 A and Figure 4.30 A: 0 μg/ℓ oxidant). In the case of *Euglena gracilis*, 75 percent removal was observed at pH 10 and pH 10,5. At pH 11 the percentage removal decreased significantly to about 40 percent (Figure 4.30 B and 4.31 B).

The 50 μg Chl-a/ℓ suspension of each algal species was exposed to the oxidants for 30 minutes, at

A



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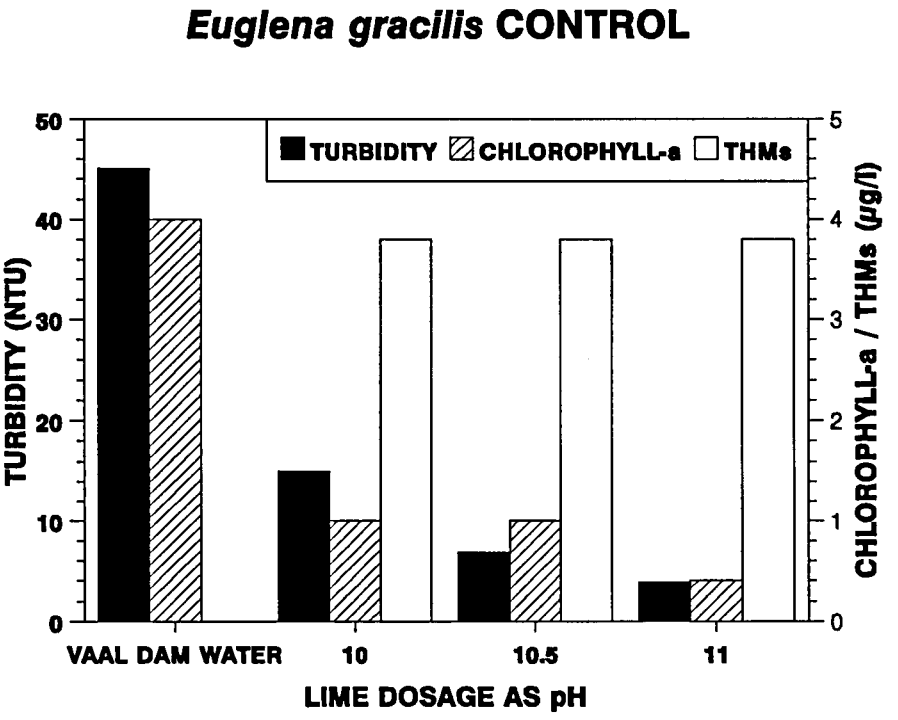
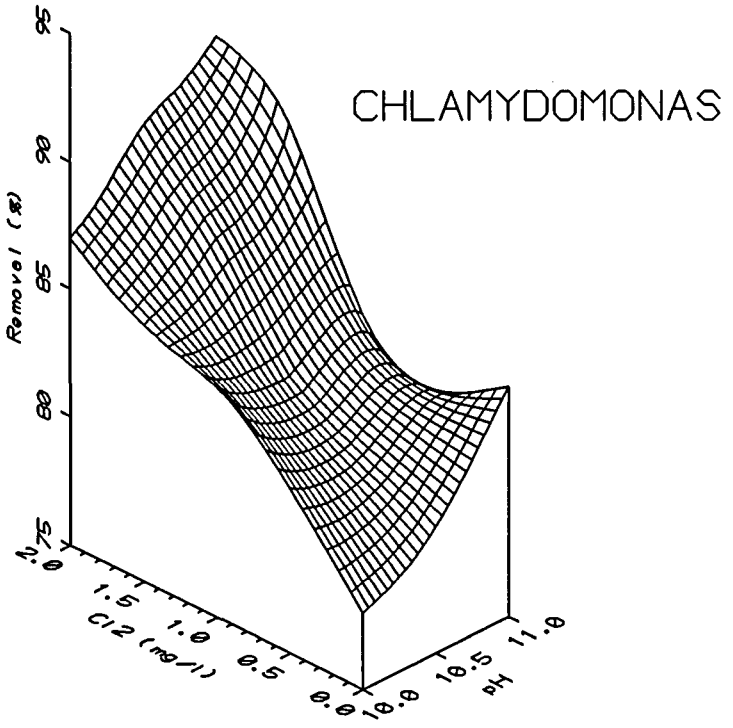


FIGURE 4.29 : RESIDUAL TURBIDITY, CHLOROPHYLL-a AND THMs AFTER SEDIMENTATION RECORDED IN CONTROL EXPERIMENTS TREATING VAAL DAM WATER WITH DIFFERENT CONCENTRATIONS OF LIME.

A



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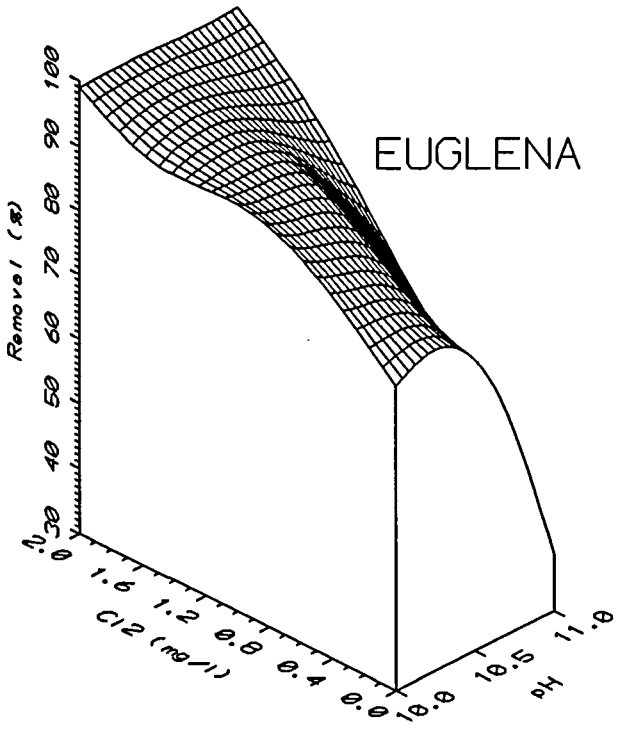
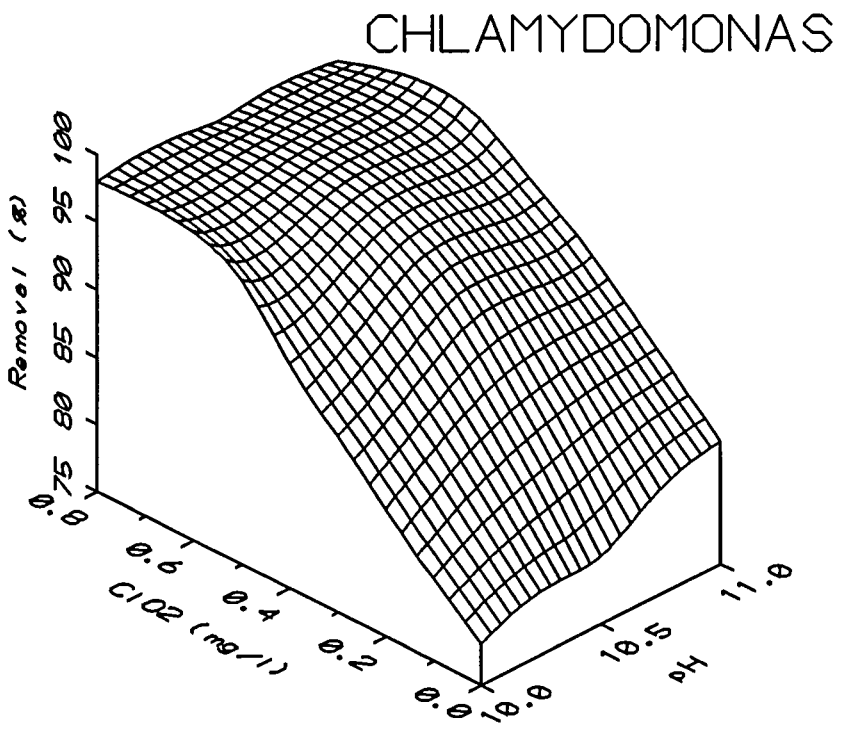


FIGURE 4.30 : **THE PERCENTAGE REMOVAL OF *Chlamydomonas* sp (A) AND *Euglena gracilis* (B) AFTER PRE-CHLORINATION AT DIFFERENT LIME DOSAGES (pH)**

A



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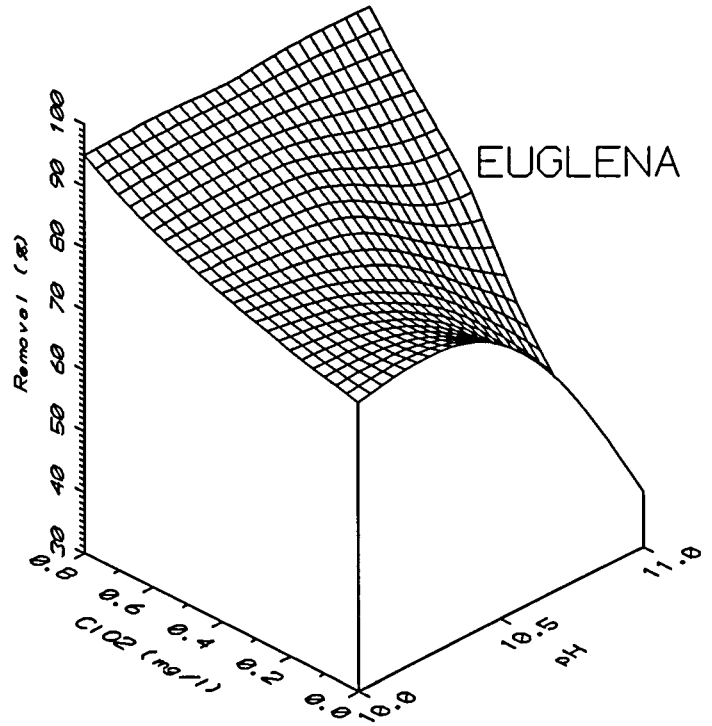

FIGURE 4.31 : **THE PERCENTAGE REMOVAL OF *Chlamydomonas* sp (A) AND *Euglena gracilis* (B) AFTER PRE-OXIDATION WITH CHLORINE DIOXIDE AT DIFFERENT LIME DOSAGES (pH)**

three different concentrations each. From Figure 4.30 A and Figure 4.31 A it is clear that the removal of *Chlamydomonas* sp increases relative in oxidant concentration. Higher percentage removal of algae was observed at increased pH with the best removal efficiency (90 to 98 percent) at pH 11 in combination with an oxidant. Work done by Ayoub and Koopman (1986) also indicated an increase in algal removal at increased pH (pH 11; 84 percent removal).

In contrast results obtained with *Chlamydomonas* sp and that presented by Ayoub and Koopman (1986), the removal efficiency of *Euglena gracilis* decreased with an increase in pH (Figure 4.30 B and Figure 4.31 B). A high removal efficiency was only observed at a chlorine dosage of 2 mg/ℓ and chlorine dioxide dosage of 0,8 mg/ℓ where the percentage removal was the same at pH 10, 10,5 and 11,0.

The effect of pre-oxidation on the removal of *Euglena gracilis* at the different pH values is shown in Figure 4.32 B. From Figure 4.32 B it is evident that the 0,3 and 0,5 mg ClO_2/ℓ dosage had a smaller impact on the removal of algal cells compared to that of chlorine concentrations. However, at pH 11, chlorine dioxide (0,8 mg/ℓ) enhanced the percentage removal by 38 percent (14 μg Chl-a/ℓ) compared to that of the 1 mg chlorine dosage.

Chlamydomonas sp cells exposed to the oxidants were more easily removed and the removal efficiency increased at higher oxidant concentrations (Figure 4.32 A). It would also seem as if the use of chlorine dioxide would enhance the removal of *Chlamydomonas* sp by more than 40 percent compared to chlorine treatment.

From the results illustrated in Figure 4.32 A and B it is clear that the role of increased lime (pH) in the percentage improvement in the removal of pre-oxidised "motile" algal cells is limited. The percentage improvement in the removal of the oxidised cells can directly be correlated to the oxidant type and concentration.

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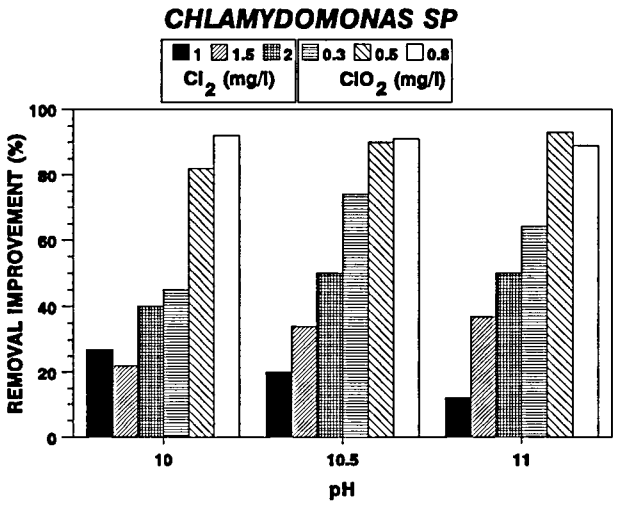

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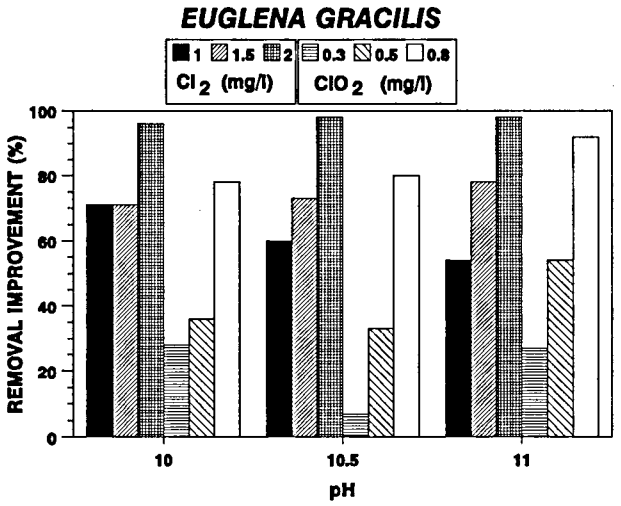


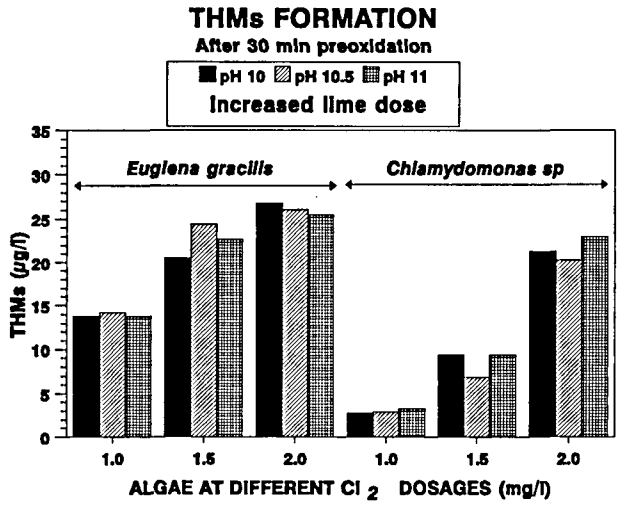
FIGURE 4.32 : PERCENTAGE IMPROVEMENT IN THE REMOVAL OF *Chlamydomonas* sp (A) AND *Euglena gracilis* (B) AS A RESULT OF PRE-OXIDATION WITH CHLORINE AND CHLORINE DIOXIDE.

4.5.4 THE INFLUENCE OF PRE-OXIDATION OF ALGAE ON THE FORMATION OF THMs

No THMs were formed at any stage of the experiment when chlorine dioxide was used as pre-oxidant. THMs were formed by both algal species after pre-chlorination (Figure 4.33). Although there were no significant differences in the THM concentrations at different pH, there was an increase in THMs with increased chlorine dosage.

More THM was formed, especially at chlorine dosages of 1 mg/ℓ and 1,5 mg/ℓ in the *Euglena gracilis* suspensions, compared to *Chlamydomonas* sp.

A



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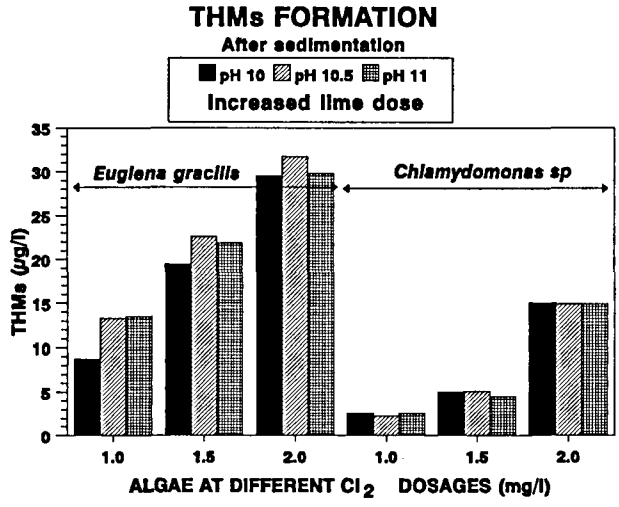

FIGURE 4.33 : THM CONCENTRATIONS IN *Chlamydomonas* sp AND *Euglena gracilis* SUSPENSIONS PRE-OXIDISED FOR 30 MINUTES (A) AND AFTER SEDIMENTATION (B).

The decrease in THM concentration as a result of the sedimentation process was less than 10 µg/ℓ for both algal species and no further THM are formed during the coagulation/flocculation and sedimentation stages.

4.6 PILOT PLANT EVALUATIONS

Research needs of Rand Water necessitated the design and construction of a large pilot plant. Design criteria are based on purification systems presently used by Rand Water. In general the aim was to provide flexibility into the design and operation of the plant to facilitate a wide range of flow rates and the evaluation of modern purification technologies.

The pilot plant simulates the full scale plant and consists of two parallel purification systems, each with a raw water inlet, in line mixer for coagulation, flocculator, sedimentation tank, carbonation tank and a rapid sand filter. Technical information regarding the different water treatment units is given in Table 4.26.

For the purpose of this study raw water for the pilot plant was abstracted from the raw water pipeline supplying water from Rand Water's No. 2 Vaal River Barrage intake to the purification works. This water usually contains higher algal concentrations than other raw water sources. The raw water was oxidised prior to the addition of activated silica and lime in specially constructed PVC contact chambers with a 20 minute retention time (Figure 4.34).

It was not possible to run the pilot plant continuously for several days on end. The operation of the pilot plant had to be stopped at least once a day for maintenance, calibration and for preparing new batches of activated silica and lime. To allow stabilisation of all processes the following basic routine was followed:

a. Operation was started before 17:00 prior to the experiment, dosing the required concentration of coagulant.
b. The next morning at 06:00 samples were taken from the raw water, after sedimentation and after filtration to ensure that the parallel systems parallel produced the same quality water at each monitoring point.
c. Dosing of oxidants at the required concentrations, at points prior to the addition of the coagulant, was then started simultaneously.
d. At approximately 09:00 samples of the raw water were taken. Samples were also taken at all sample points (See Figure 4.34) based on calculated retention time.
e. After step d had been repeated 2 to 3 times, the pilot plant was turned off at 15:00, new batches of chemicals prepared, dosing pumps calibrated and the necessary adjustments done. At 17:00 the plant was started up again.

The above procedures only allowed the pilot plant to run from Tuesdays to Fridays.

TABLE 4.26 : TECHNICAL INFORMATION OF THE DIFFERENT TREATMENT UNITS OF RAND WATER PILOT PLANT.

TREATMENT UNIT	
1. In line static mixer	A 100 mm mixer with helix
2. Flocculator	Linear flow rate = 7,5 m/h
	Flow = 5 m^3/h
	Diameter at top = 921 mm
	Area at top = 0,664 m^2
	Height of conical section = 1110 mm
	Inlet tangential at bottom of conical section
	Adjustable outlet point to achieve retention times respectively of 10, 12,5 and 10 min
3. Sedimentation tanks	Braithwaite type steel tank
	Length = 4,8 m
	Height = 2,4 m
	Width = 2,4 m
	Inlet/outlet height = 2,1 m
	Effective capacity = 24,193 m^3
	Retention time at 5 m^3/h = 4 hours 50 minutes
	Each tank divided in length with retention time of 2 hours 25 minutes within each sections
4. Carbonation tank	Nominal flow rate = 1,7 m^3/h
	Retention time = 20 minutes
	Capacity - 0,566 m^3
	Height = 2 600 mm
	Diameter = 530 mm
5. Rapid sand filter	Diameter = 600 mm
	Surface area = 0,383 m^2
	Total height = 2 500 mm
	Depth of filter bed: Nominal = 600 mm
	Maximum = 2170 mm
	Maximum water head on top of sand = 1570 mm
	Filtration rate = 4 $m^3/m^2/h$

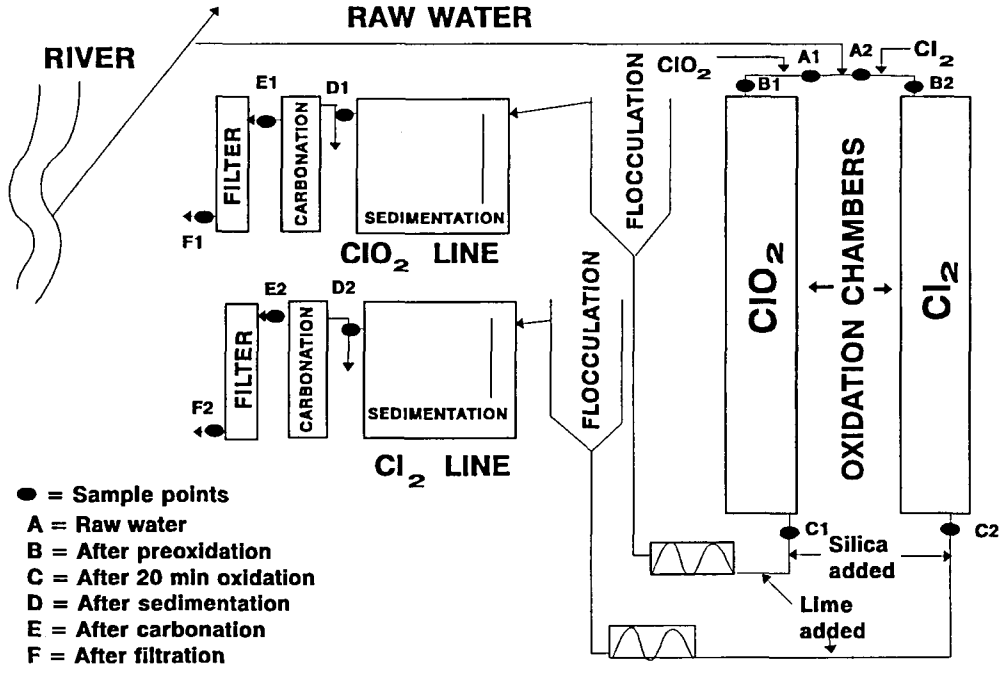

FIGURE 4.34 : LAY-OUT OF TREATMENT UNITS IN AND LOCALITY OF THE SAMPLE POINTS AT THE RAND WATER'S PILOT PLANT.

Direct comparison of the algicidal efficiency of chlorine and chlorine dioxide at the different unit processes were made difficult by:

a. fluctuation in the chlorophyll concentration of the raw water.

b. difference in the residence time through the sections of the plant which were compared, and

c. the availability of a third system, running parallel to the chlorine and chlorine dioxide line, which could serve as a control.

Water quality results obtained from the pilot plant runs, are presented in Appendix E. It is clear that the turbidities were always reduced to below 1 NTU with one exception on 12/11/1991 in the section that served as control. In excess of 75 percent of the suspended material was removed by sedimentation.

From the limited data available it is clear that the 30 minute pre-oxidation treatment was responsible for a significant reduction of chlorophyll-a (Figure 4.35). Pre-oxidation with chlorine was, however, responsible for high concentrations of THMs being formed (>60 $\mu g/\ell$; see Figure 4.36). At times a reduction in THM concentration was observed through sedimentation and carbonation.

The results in Appendix E also indicate that algae were removed to levels of ≈ 1 μg Chl-a/ℓ through the process (except 12/11/1991), the bulk of which was removed by sedimentation. These results, however, do not indicate the improvement of algal removal by sedimentation due to oxidation was demonstrated in jar tests. As the purpose of these experiments were to compare the effect of chlorine to chlorine dioxide no results are available for the efficiency of either oxidant compared to a control or the combined effect of the two oxidants.

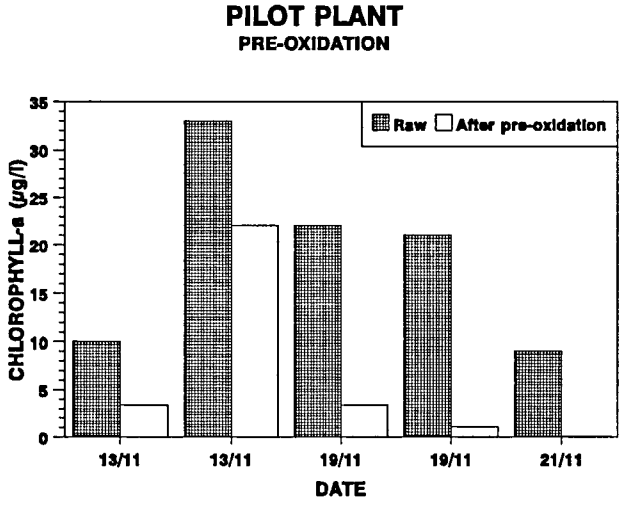

FIGURE 4.35 : REDUCTION IN CHLOROPHYLL-a AFTER 30 MINUTES PRE-OXIDATION WITH CHLORINE DIOXIDE.

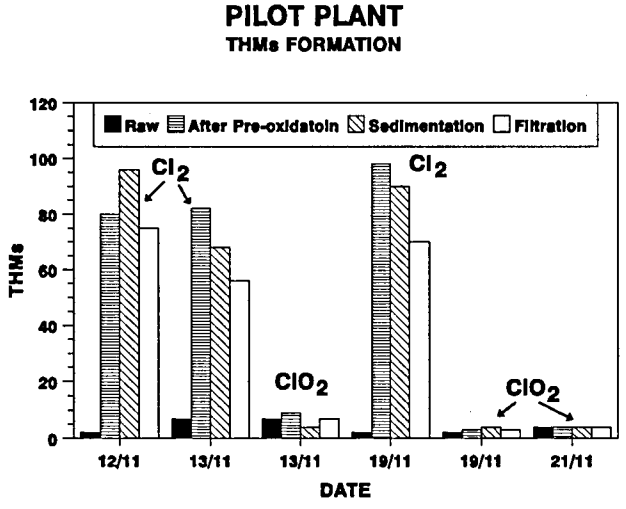

FIGURE 4.36 : THMs FORMED IN DIFFERENT UNIT PROCESSES AFTER PRE-OXIDATION.

It was the intention to monitor the residual chlorine dioxide, chlorite and chlorate concentrations at each purification step. Due to the fact that the titroprocessor was set up to check the purity of the chlorine dioxide stock, the low chlorite and chlorate concentrations (< 1 mg/ℓ) could not be monitored. However, if the disproportionation of chlorine dioxide (Eq.5) is taken into account, the theoretical residual chlorite concentration should have been between 0,38 mg/ℓ and 0,44 mg/ℓ. These levels are less than the 0,5 mg ClO_2/ℓ recommended by Masschelein (1979) for potable water.

4.7 THE EFFECT OF OXIDANT ON THE MORPHOLOGY AND FINE STRUCTURE OF ALGAE

Four day old cultures of all the algae mentioned in Table 3.1 were used to determine the effect of the oxidants on the structure of the algal cells. Algal suspensions of 100 μg/ℓ were oxidised in the dark for 30 minutes using the methods as described in 4.4. Table 4.27 indicates the oxidant concentrations used. These oxidant concentrations were selected based on results obtained in 4.4, ensuring virtually total oxidation of the algae.

TABLE 4.27 : CONCENTRATIONS OF OXIDANT USED TO INVESTIGATE THE EFFECTS THEREOF ON STRUCTURAL CHANGES IN ALGAL CELLS

ALGAL SPECIES	OXIDANT CONCENTRATION (mg/l)	
	Cl_2	ClO_2
Euglena gracilis	2	0,7
Monoraphidium minutum	2,9	0,81
Scenedesmus quadricauda	1,8	0,9
Chlorella minutissima	2,5	0,5
Chlamydomonas sp	1,9	0,82
Cyclotella meneghiniana	2,8	1,0
Cosmarium laeve var *distentum*	2,1	0,8
Pandorina morum	2	0,8

The oxidation reaction was stopped using sodium thiosulphate. As much sample as possible of the oxidised algal suspension was filtered through a 8 μm Millipore filter. The filter membrane with

algae was submerged in 10 mℓ of a 3 per cent gluteraldehide phosphate fixing agent in a sealed bottle. Control samples, without the addition of oxidants, were treated in the same way.

The samples were kept in the dark at 4°C until preparation and electron microscope investigation[1]. The micrographs produced during the investigation, are presented in Figure 4.37 A to H.

The scanning electron microscope (SEM) micrographs show little or no effects of the oxidants on the external structure of the algae. With *Euglena gracilis* (Figure 4.37 A) a rupture between the lorica bands can be observed, where as with *Cyclotella meneghiniana* (Figure 4.37 F) it would seem as if the external silicon and pectin wall (frustule) became brittle when oxidised. The chlorine dioxide treatment affected the mucus layer of *Cosmarium laeve* var *distentum* (Figure 4.37 G) more than the chlorine treatment.

Transmission electron microscope micrographs revealed the effect of the oxidants on the initial fine structure of the algae. In the case of *Euglena gracilis* (Figure 4.37 A), *Scenedesmus quadricauda* (Figure 4.37 C), *Chlamydomonas* sp (Figure 4.37 E), *Cyclotella meneghiniana* (Figure 4.37 F) and *Chlorella minutissima* (Figure 4.37 G) a drastic decrease in cell content or disintegration in membrane systems were observed. A comparison of the effects of chlorine and chlorine dioxide on the fine structure of the algae was not made. This would have been possible if the extent of structural damage to the cells as a function of oxidant concentration could be quantified. It is also not possible to explain the difference in resistance of the different algae to the oxidants based on the visual information presented in Figure 4.37.

From the above information it is evident that oxidation of algal at concentrations of less than 100 μg Chl-a/ℓ with chlorine (< 3 mg Cl_2/ℓ) and chlorine dioxide (< 1 mg ClO_2/ℓ) disrupts the fine structure of the algae.

These observations confirmed that of Ringer and Campbell (1955) who observed severe plasmolyses in cells of different algal species, exposed to different chlorine and chlorine dioxide concentrations for up to 48h.

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[1]Dr P W J van Wyk, Department of Botany and Genetics, University of the Orange Free State, Bloemfontein, South Africa.

FIGURE 4.37: ELECTRON MICROSCOPE PHOTOGRAPHS OF OXIDISED ALGAL CELLS.

A: *Euglena gracilis*

B: *Monoraphidium minutum*

C: *Scenedesmus qaudricauda*

D: *Chlorella minutissima*

E: *Chlamydomonas sp*

F: *Cyclotella meneghiniana*

G: *Cosmarium laeve* var *distentum*

H: *Pandorina morum*

A. *Euglena gracilis*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (µg/l) after

- 0 min :
- 30 min :

Survival (%) :

B. *Monoraphidium minutum*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (μg/l) after

- 0 min :
- 30 min :

Survival (%) :

C. *Scenedesmus quadricauda*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (µg/l) after

- 0 min :
- 30 min :

Survival (%) :

D. *Chlorella minutissima*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (μg/l) after

- 0 min :
- 30 min :

Survival (%) :

E. *Chlamydomonas sp*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (µg/l)
after

- 0 min :
- 30 min :

Survival (%) :

F. *Cyclotella meneghiniana*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (μg/l) after

- 0 min :
- 30 min :

Survival (%) :

G. *Cosmarium laeve var distentum*

CONTROL **Cl_2** **ClO_2**

SEM

TEM

Dosage (mg/l):

Chl-a (μg/l)
after

- 0 min :
- 30 min :

Survival (%) :

H. *Pandorina morum*

CONTROL	Cl_2	ClO_2
SEM		
TEM		

Dosage (mg/l):

Chl-a (μg/l) after

- 0 min :
- 30 min :

Survival (%) :

IMPLICATIONS OF PRE-OXIDATION : GENERAL DISCUSSION

The algal species selected for this study may be regarded as non colloidal particles varying in size from 3 μm to more than 20 μm. These biological particles varied in shape, from orbicular in the case of *Chlorella minutissima* to reniform in the case of *Monoraphidium minutum*. *Scenedesmus quadricauda* and *Pandorina morum* produce colonies consisting of different numbers and shapes of cells. *Euglena gracilis* cells are able to move in the water column by changing their shape, and also by means of flagella. *Chlamydomonas* sp has two flagella with which it moves through the water. The cell surface characteristics of the different algae vary from "smooth" to punctate to heavily decorated with spines on the terminal cells, warts, rosettes and combs (*Scenedesmus quadricauda*). Literature and results from this study clearly indicates that these algae have dominantly negatively charged surfaces.

The above characteristics of the biological particles differ markedly from those of the inorganic particles that could be removed by the unit processes described in 2.5. According to Bernhardt and Clasen (1991) algae cells are colloidal, finely dispersed substances, with spherical shapes. The implication of this statement is that algae conform to the same basic flocculation principles which mean that:

a. the stability of the colloidal and finely dispersed particles is determined by the negatively charged particle surface and is reduced by destabilisation processes, occurring under natural conditions and during coagulation in treatment plants.
b. adsorption and coagulation with charge reduction or neutralisation, forms the basis for destabilisation and aggregation within the flocculation process.
c. a large number of aggregates are formed according to the mechanism of particle bridging. Whilst this aggregation process required only a charge reduction rather than a charge neutralisation, the way in which the flocculant attaches itself to the particle surface is more important than the kind of surface charge.

Results from this study (see 4.6.2), as well as from Bernhardt and Clasen (1991) and Haarhof (1988), indicate that the destabilisation and aggregation of algal suspensions lead to significant deviations from the basic flocculation principle due to the various shapes, sizes and in some cases their motility.

Removal of algae from raw water can be achieved by using treatment options such as an increase

in the coagulant dose (Bernhardt and Clasen, 1991), altering the type of coagulant to facilitate optimum charge reduction (Tilton *et al.*, 1972), changing the effective size of the sand particles and filter depth of rapid sand filters and by oxidising the algal material.

From the results of this study obtained with *Scenedesmus quadricauda* and work done by Bernhardt and Clasen (1991) it is evident that the first two options will not necessarily improve the removal of algae which have shapes that do not allow individual cells to approach each other to facilitate bridging. To achieve this, flocculants must be dosed at such high rates, about 10 times more aluminium sulphate required for *Stephanodiscus hantzschii* (Bernhardt and Clasen, 1991) to fill the gaps between the adjacent cells, that it may become uneconomical. Results of this study indicated that the maximum lime dosage that could be used by Rand Water, is not sufficient to remove high concentrations of *Scenedesmus quadricauda.*

The effective size of the sand particles and filter depth could be changed to improve the removal of the small algae such as *Chlorella minutissima.* No evidence in literature could be found to substantiate this. It would, however, be a costly exercise on existing plants to change the filter design.

Oxidation of algae may improve the removal of motile algae such as *Euglena gracilis* and *Chlamydomonas* sp (Bernhardt and Clasen, 1991). Results of this study indicated that the pre-oxidation of *Euglena gracilis* and *Chlamydomonas* sp would improve their removal through the purification process by more than 20 percent. This improvement in algal removal can be ascribed to the immobilisation of the algae by the oxidants, which was confirmed by similar improvements in the removal efficiency of algae from which flagella were removed.

Criticism has been launched against the use of chlorine as pre-oxidant for algae. The formation of THMs by chlorination of algal suspensions in organic rich water was confirmed by this study (Morris and Baum, 1978; Fiessinger *et al.*, 1981). In this study oxidation of different algae in culture media resulted in THMs of less than 50 $\mu g/\ell$ formed after a contact period of 120 minutes, with maximum dosages of 3 mg Cl_2/ℓ. THMs of about 100 $\mu g/\ell$ were formed by chlorinating raw water, containing high concentrations of organic material (pilot plant run). It is therefore suspected that the THM formation would primarily be a function of the dissolved organics in the water rather than the algae present in the raw water. (Compare THM produced from *Euglena gracilis* and *Chlamydomonas* sp in Vaal Dam water with THM present in 100 percent sewage water and the pilot plant run after chlorination).

Pre-chlorination of high algal concentrations may result in the increase in the dissolved organic material du to the release of organic material by the dying cells. Akiba *et al.* (1990) showed that in chlorinated *Chlorella minutissima* suspensions the DOC fractions were 1,3 to 2,5 times larger than in the unchlorinated samples. Akiba and co-workers also found that the released organic substances and those previously excreted by the algae, did not interfere with coagulation process when pre-oxidation was applied and alum used as coagulant. Liu and Bernardt (1991) found that chlorinated extracelluar organic material did not interfere with the flocculation process using hydrolysed metals salts, as was the case with the non-chlorinated organic material. Results of this study indicated significant change in DOC concentration when the different algae were oxidised. This may be due to the specific analytical method used which might have not been sensitive enough to detect small changes at low concentrations of dissolved organic carbon (<2 mg C/ℓ). Another possible reason for the non-detection of an increase in extracellular material after oxidation may be due to the low algal and oxidant concentrations used compared to that of Akiba *et al.* (1990) and Sukenik *et al.* (1987) (See Table 5.1).

TABLE 5.1: COMPARISON OF EXPERIMENTAL CONDITIONS USED IN TWO OTHER STUDIES WITH THAT OF THE PRESENT STUDY.

Researcher	Oxidant	Dose	Time	Algal Concentration
Akiba *et al.* (1990)	Cl_2	35 mg/ℓ	24 h	40 day old *Chlorella* sp at ± 160 μg Chl-a/ℓ
Sukenik *et al.* (1981)	Cl_2	2, 10, 20 mg/ℓ	10 min	2 x 10^6 cells/ml of *Scenedesmus* sp
	ClO_2	1, 3, 5 mg/ℓ	10 min	
*Present study	Cl_2	3 mg/ℓ	2 h	100 μg Chl-a/ℓ of several algae
		1 mg/ℓ	2 h	

*Maximum concentrations

From the literature study it would also seem as though a number of researchers used either very high algal or oxidant concentrations on which their conclusions regarding THM formation (Morris and Baum, 1978), BOD increase (Hom, 1972) and changes chlorinated organic carbon (Bernhardt and Hoyer, 1979) were based. In this study, however, the effects of pre-oxidation on algal removal and water quality was done based on conditions found in Rand Water's raw water. For example, Morris and Baum (1978) showed that 260 μg $CHCl_3$/ℓ were formed, at pH 10 when 1,7 mg Chlorophyll-a/ℓ

were oxidised with 40 mg Cl_2/ℓ for 100 hours. This chloroform concentration is more than 2,6 times higher than the maximum THMs recorded in the pilot plant runs, using water from the Vaal River Barrage reservoir.

Results of this project indicate that algae do not only differ in the way they are removed by purification processes, but also in their resistance to chlorine and chlorine dioxide. *Cosmarium laeve* var *distentum* and *Scenedesmus quadricauda* had the highest resistance to chlorine and chlorine dioxide respectively. The differences in sensitivity of the algae can perhaps be explained in terms of the chemical composition and nature of their cell covers. In the case of *Cosmarium laeve* var *distentum* the cell is covered by a perforated cell wall, enwraped in a mucilaginous layer. The chemical composition of the mucilaginous layer may be of such a nature that it protects the enclosed cells against the actions of chlorine. This layer may be less resistant to chlorine dioxide, thus making more chlorine dioxide available to inactivate the cells. According to a literature survey done by Dodge (1973) researchers showed that *Scenedesmus* species had a 14 nm thick trilaminar layer outside the cell wall. This layer is extremely resistant and is believed to consist of a polymerised catenoid material similar to sporopollenin. If the latter is applicable to the *Scenedesmus quadricauda* used in this study, it may be possible that chlorine dioxide reacts with this material, resulting in less being available for oxidation of the internal cell matter. Damage to the cell wall of *Scenedesmus quadricauda* could, however, not be confirmed by the electron microscope investigations. In the case of *Cosmarium laeve* var *distentum* more obvious damage to the mucilaginous layer upon chlorine dioxide treatment, compared to that of the chlorine treatment, could be seen.

Irrespective of the specific characteristics of the different algae, the mechanism by which the oxidants inactivate the cells seems to differ between chlorine and chlorine dioxide. At the oxidant and algal concentrations used in the present study it would seem from the electron microscope investigation that no significant external damage due to pre-oxidation took place. These observations do not agree with the observations made by Sukenik *et al.* (1987), who oxidised higher algae concentrations with much higher oxidant concentrations (See Table 5.1), resulting in severe structural damage.

Although the molecular weight of HOCl (35,45) is about 1,9 times less than that of chlorine dioxide (67,43), it is possible that chlorine dioxide is capable of penetrating the cell wall and membrane at a faster rate than chlorine. As a third less time was required to inactivate algae with chlorine dioxide compared to chlorine at a lower concentration, it can be deduced that chlorine dioxide penetrates at a higher rate through the cell wall. It would thus seem as if it is the higher oxidation potential of chlorine dioxide that allow it to penetrate the cells faster. The destruction of membrane systems (e.g.

chloroplast membrane and plasmalemma) is, however, the primary reason for the algae to die. By these means the physiological processes in the cells are disrupted (photosynthesis and protein synthesis) and is the differential permeability of the cell membrane destroyed, allowing free movement of substances in and out of the cells. The possible association of the loss of membrane permeability with the mechanism by which chorine and chlorine dioxide inactivate algae was suggested by Ringer and Campbell (1955) and Berg *et al.* (1986) respectively.

5.1 CONSIDERATION FOR THE IMPLEMENTATION OF PRE-OXIDATION WITH CHLORINE DIOXIDE AT RAND WATER.

From the results of this study it is evident that chlorine dioxide is two to ten times more effective in killing algae depending on the algal species and algal concentration. A third of the time is required for this (See section 4.4.4). It becomes clear that the use of chlorine dioxide will improve the removal of certain algae by more than 40 percent in comparison to the use of chlorine (*Chlamydomonas* sp, Figure 4.31 A). Results show no THMs are formed when chlorine dioxide is used a pre-oxidant compared to 35 $\mu g/\ell$ to 100 $\mu g/\ell$ THMs formed when water of varying quality was oxidised by chlorine. A previous study, however, indicated chlorine dioxide to be ten times more costly to produce than chlorine (Geldenhuys, 1986). Taking all these factors into account, it is clear that the decision, whether to use chlorine or chlorine dioxide as pre-oxidants will be influenced by a combination of factors, i.e. potable water quality standards, cost of the oxidants and use of additional water purification chemicals.

In South Africa there is no potable water standard for THMs. This implies that water containing any amount of THM can be supplied to the consumer. If a standard were to be set for chloroform at a level of 100 μg $CHCl_3/\ell$, equal to Rand Water's guideline value, and no further THMs are produced during disinfection and distribution, water of similar quality to that of the Vaal River Barrage Reservoir, can be pre-oxidised by chlorine. However, if a THM standard of less than 100 $\mu g/\ell$ is adopted, it will force Rand Water to use chlorine dioxide as pre-oxidant. The maximum chlorine dioxide concentration used will be governed by the potable water standard for the chlorite ion, the toxic breakdown product of chlorine dioxide. If the standard is set at 0,5 mg/ℓ, higher maximum chlorine dioxide dosage can be used, assuming a 50 per cent breakdown of chlorine dioxide (Masschelein, 1979). A more stringent potable water standard will limit the percentage time Rand Water would be able to use chlorine dioxide as a pre-oxidant.

A standard for the maximum algal content of potable water (expressed as chlorophyll) will determine

For **chlorine dioxide** as pre-oxidant, the following cost calculations were done.

a)	For the production of 800 kg chlorine dioxide per day	
	4472,74 kg $NaClO_2$ (24 percent) @ R3-21/kg is needed	R14 357-49
b)	Chlorine required is 421 kg @ R2-20/kg	R 926-20
	Direct cost R/kg R19-10	R15 284-69
c)	Capital costs (equipment only (Table 5.3)	92-00
	Total daily costs	R15 376-00
d)	Total dosing cost per kg chlorine dioxide = R19-22	

TABLE 5.2 CAPITAL COSTS FOR EQUIPMENT USED TO DOSE 3500 kg CHLORINE PER DAY.

Loan amount	R350 000-00
Number of years	15
Interest rate (%)	12
Number of payments per year	12
Total amount paid	R756 106-20
Monthly payment	R 4 200-59
Cost per day	R 140-00

TABLE 5.3 CAPITAL COSTS FOR EQUIPMENT USED TO PRODUCE AND DOSE 800 kg CHLORINE DIOXIDE PER DAY.

Loan amount	R230 000-00
Number of years	15
Interest rate (%)	12
Number of payments per year	12
Total amount paid	R496 870-20
Monthly payment	R 2 760-39
Cost per day	R 92-00

From the cost calculations it is evident that for direct and total dosing cost per kg oxidant, chlorine dioxide is respectively 8,68 and 8,58 times (cost factor) more expensive than chlorine.

the frequency and duration of pre-oxidation and the additional use of coagulants. At present, Rand Water uses a chlorophyll guideline of 1 $\mu g/\ell$ for potable water while that of the Wahnbach Reservoir Association is 0,1 $\mu g/\ell$ as chlorophyll-a (Bernhardt and Clasen, 1991). The use of the latter as a standard will require pre-oxidation for 100 percent of the time when Vaal River Barrage Reservoir water is purified. A chlorophyll concentration guideline of higher than 1 $\mu g/\ell$ in potable water will reduce the need and frequency of pre-oxidation significantly.

Assuming a potable water guideline of 1 μg chlorophyll/ℓ, raw water abstracted by Rand Water, has to be pre-oxidised when raw water chlorophyll values exceed 30 $\mu g/\ell$. A THM standard of less than 100 $\mu g/\ell$ and a chlorite standard of less than 0,5 mg/ℓ for potable water will force Rand Water to use chlorine dioxide as pre-oxidant or to implement more costly algal control measures. At present, the water quality guidelines implemented by Rand Water and the cost benefit of using chlorine or chlorine dioxide, will determine the pre-oxidant used.

To determine the cost benefit, given the potable water guidelines, a cost comparison between chlorine and chlorine dioxide was made, using the following assumptions:

a. Amount of water pre-oxidised 1000 Ml/d.

b. Pre-oxidant concentration Cl_2 = 3,5 mg/ℓ; ClO_2 = 0,8 mg/ℓ

Amount used per day Cl_2 = 3500 kg/d; ClO_2 = 800 kg/d

c. Pre-oxidation only required for 25 percent of the year.

d. Process used to produce chlorine dioxide:

$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl$

(71 kg) + (181 kg) ---> (135 kg)

e. Chlorine purchased in bulk at contract price of R2-20/kg.* $NaClO_2$ (24 percent) in liquid form purchased in bulk at R3-21/kg*.

The daily cost of using **chlorine** as pre-oxidant was calculated based on the following:

a) Direct chemical costs : 3500 kg @ R2-20/kg R7 700

b) Capital costs (equipment only - Table 5.2) R 140

Total daily cost **R7 840**

c) Total dosing cost per kg chlorine = R2-24

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* Estimates from supplier, 1991 prices (See acknowledgements)

Results from this study clearly indicated chlorine dioxide to be 3 to 5 times more effective than chlorine as algicide. Using these efficiency factors in the cost calculation, by dividing the chlorine dioxide cost factor by the efficiency factors, chlorine dioxide is shown to be 2,89 to 1,72 times more expensive than chlorine to achieve the same results (Table 5.4).

TABLE 5.4 CHLORINE DIOXIDE COST FACTORS COMPENSATED FOR ALGICIDAL EFFICIENCY

Cost item	Relative cost of ClO_2 compound compared to Cl_2	Relative cost of ClO_2 at various efficiency rates		
		5	4	3
Direct cost	8,68	1,74	2,17	2,89
Total dosing cost	8,58	1,72	2,14	2,86
Total dosing cost including reaction chamber	7,04	1,41	1,76	3,25

The comparative cost of treating one cubic meter of water with either

a) 3,5 mg Cl_2/ℓ @ total cost of R2-24/kg = **0,784 c/m^3**

b) or 0,8 mg ClO_2/ℓ @ total cost of R19-22/kg = **1,5376 c/m^3**

The reaction rate of chlorine dioxide with algal cells is three times that of chlorine. Therefore chlorine required a proportionally larger contact vessel and longer retention time. By installing an oversized pipeline this could be achieved at a capital expenditure of R4,9 M (Table 5.5). This will result in an increase in the total cost for chlorine to R2,73/kg with a decrease in the relative cost of chlorine dioxide being 7,04 times more expensive than chlorine. Using the algicidal efficiency factors of chlorine dioxide in the same way as above (Table 5.4), chlorine dioxide could be 1,41 to 2,35 times more expensive than chlorine. Incorporating this into the calculation, the cost of treating one cubic meter of water with either chlorine or chlorine dioxide is respectively 0,965c/m^3 and 1,547c/m^3, making chlorine dioxide about 1,61 times more expensive.

As a result of the possible benefits i.e. no trihalomethanes produced, the use of chlorine dioxide is favoured. Calculating a cost factor for the presence of the latter is not within the scope of this

project. It can only be postulated that such a cost factor, based on a water quality guideline, could turn to a cost benefit analysis to favour chlorine dioxide.

TABLE 5.5 CAPITAL COSTS FOR EXTENDING THE CONTACT TIME FOR CHLORINE TO THREE TIMES THAT NEEDED FOR CHLORINE DIOXIDE.

Pipeline dimensions	Diameter = 2,3 m		
	Length = 1327 m		
	Capacity = 2083 m^3		
Pipeline construction cost		R3700/m	
Loan amount			R 4 908 975-00
Number of years			25
Interest rate (%)			12
Number of payments per year			12
Total amount paid			R15 510 753-00
Monthly payment			R 51 702-51
Daily cost			R 1 723-42

CONCLUSIONS

At Rand Water as many other similar institutions, chlorine is used as pre-oxidant. The major disadvantage associated with pre-chlorination is the formation of high concentrations of trihalomethanes (THMs) which are regarded by some researchers as being carcinogenic. Experience at Rand Water indicated that pre-chlorination is not always effective in inactivating algae which escapes the different unit processes. A literature study indicated chlorine dioxide as an alternative oxidant, which does not from THMs and is a stronger oxidant.

The purpose of this study was to compare the efficiency of chlorine and chlorine dioxide as pre-oxidant and algocide in raw water abstracted for potable water production. The following aspects have received special attention. A comparison of the:

a) algocidal efficiency of the oxidants,
b) combined effect of water quality on the efficiency of the oxidants,
c) sensitivity of different algal species to the oxidants and
d) the advantages and disadvantages of pre-oxidation with chlorine and chlorine dioxide in the removal of algae, and the formation of oxidation by-products.

To meet the aims of this study several species of algae differing in size, shape and surface charge characteristics were used. The following algae were used:

Chlamydomonas sp.
Chlorella minutissima
Cosmarium laeve var distentum
Cyclotella meneghiniana
Euglena gracilis
Monoraphidium minutum
Scenedesmus quadricauda
Pandorina morum

All the algae except *Euglena gracilis* were isolated from the Vaal River Barrage Reservoir. Tests done on these algae indicated that the methods used to cultivate the algae ensured physiological active algal cells, which were used on the days of the experiments.

The influence of water quality on the efficiency of chlorine and chlorine dioxide was simulated using different mixtures of waste water treatment plant effluent and Vaal Dam Water. The mixtures represented the different water qualities observed in the Vaal River Barrage Reservoir. The efficiency of the oxidant was measured as the free residual oxidant available after a specific treatment time

interval. Results from these studies indicated that:

a) The residual oxidant concentrations decreased with time with the highest decrease in oxidant concentration in the first moments after oxidant addition,
b) Residual oxidant concentrations after contact time decreased with an increase in the proportional effluent concentration,
c) after the same contact period, significantly more chlorine dioxide than chlorine was present at equivalent dosages, and
d) significant concentrations of trihalomethanes (THMs) are formed with increased effluent ratios and chlorine concentration in water mixtures. The highest THM concentrations were recorded after 24 hours contact time, using 10 mg/ℓ chlorine. No THMs were formed when chlorine dioxide was used.

Results of the oxidation of algal suspension indicated the following:

a) A contact time up to 30 minutes is necessary to inactivate algae with chlorine, compared to a maximum of 10 minutes needed when chlorine dioxide was used at equivalent dosing rates.
b) Residual oxidant concentration decrease exponentially over time with the highest rate of oxidant consumption in the first minutes of contact and with high biomass concentrations. The demand for chlorine dioxide by the algal suspension was less than that for chlorine.
c) Chlorine dioxide was two to ten times more effective than chlorine as an algocide. This variation in efficiency is dependant on the algal concentration and algal species used.
d) Algae differ regarding their resistance to oxidation. *Cosmarium laeve var distentum* was the most resistant algae against the action of chlorine, while *Scenedesmus quadricauda* was the most resistant against chlorine dioxide.
e) Electron microscopical investigations showed limited external damage to the cells due to oxidation. Significant damage to the membrane systems of the cells was, however, observed. Difference in ultra-structure damage of the cells have not been quantified. This lack of information made the comparison of damage caused by chlorine and chlorine dioxide impossible.
f) A maximum of 35 μg/ℓ THMs were formed by chlorination of algal suspensions after 2 hours contact time. No THMs were formed when chlorine dioxide was used as pre-oxidant.

Results from this study indicate that chlorine dioxide would be the best oxidant for pre-oxidation. Little information is, however, available on the effect of pre-oxidation by chlorine dioxide on the unit

treatment processes of Rand Water. To determine the effect of pre-oxidation on the efficiency of the unit processes to remove algae, laboratory scale coagulation/flocculation, sedimentation and filtration experiments were done. Experiments using unoxidised algae at different concentrations indicated that

a) not all types of algae were removed with the same degree of efficiency by the different unit processes,
b) the bulk of the algae was removed by sedimentation, and
c) removal efficiency by filtration increased with an increase in algal cell size and with algal load onto the filter.

The difference in removal efficiency of the different algae by the sedimentation process could be related by the physical interference of the algal cells with the coagulation and the flocculation process. Cells with non-spherical shapes, spines, that are motile or that can change their shape were not flocculated well and therefore did not settle as well as colloidal particles.

Two algae, *Euglena gracilis* and *Chlamydomonas* sp, were selected to evaluate the effect of chlorine and chlorine dioxide as pre-oxidants on their removal through the unit processes. The selection of algae were based on their motility by means of flagella, to possibly penetrate through unit processes. Tests done using three different oxidant and coagulant (lime) concentrations indicated that pre-oxidation improved the algal cell removal significantly. One of the main reasons for this improvement may be the fact that these specific algae lost their motility which was confirmed by experiments in which the flagella of the algae (not oxidised) were removed by means of ultrasonic sound treatment.

Pre-oxidation with chlorine dioxide resulted in a 40 per cent improvement in the removal of *Chlamydomonas* sp compared to chlorine. In the case of *Euglena gracilis* the improved removal is only significant at the low coagulant dosages (low pH). This is due to the fact that the surface charges of *Euglena gracilis* become more negative with an increase in pH (increase in lime dosage), which may be responsible for a decrease in removal efficiency of *Euglena gracilis*. It was only at the high oxidant dosage (Cl_2 = 2,0 mg/ℓ; ClO_2 = 0,8 mg/ℓ), that the effect of the increased negative surface charge with pH on the removal of the algal cells were cancelled.

Limited tests done on pilot plant scale confirmed the improvement in the removal of algae and colloidal particles when pre-oxidised. The pilot plant tests should, however, be repeated over a longer period to evaluate the long term effect of pre-oxidation on the water quality produced.

Use of chlorine dioxide as a pre-oxidant will be influenced by the potable water quality guideline for trihalomethanes, chlorite and algae. A trihalomethane level of less than 100 $\mu g/\ell$ and a chlorophyll-a value of 0,1 $\mu g/\ell$ for potable water will force the use of chlorine dioxide as pre-oxidant, while a chlorite concentration of less than 0,4 mg/ℓ will not permit its use as pre-oxidant.

Production cost of oxidants will also play an important role in the choice of oxidants. A cost comparison was done, given the following conditions:

a) Pre-oxidation of 1000 M/d.

b) Oxidant concentration : Cl_2 = 3,5 mg/ℓ; ClO_2 = 0,8 mg/ℓ.

c) Amount used per day: Cl_2 = 3500 kg; ClO_2 = 800 kg.

d) Chlorine purchased in bulk at R2,20/kg.

e) Process used to produce chlorine dioxide.

$$Cl_2 + 2NaClO_2 \quad \text{----}> \quad 2ClO_2 + 2NaCl.$$

The cost comparison indicated that chlorine dioxide will only be 1,61 times more expensive to use as an oxidant.

From this study it was evident that the removal of algae by different unit processes should in future not be evaluated on the basis of chlorophyll-a values only. Cognizance must be given to specific algal species present in the raw water. In this regard similar research as reported in this report should be done on other problematic algae in water purification plants. Of special importance would be the development of a system which would describe possible interferences of algae with specific unit processes and coagulants based on physical characteristics. Recommendations regarding the removal of those algae, given a specific water purification technology, should be included in such a system.

SUMMARY OF RESEARCH NEEDS

The results of this project clearly indicated that of the removal of various algal species by different unit treatment processes can not be based solely on the removal of chlorophyll. More attention should be given to the specific algal species which penetrate through, or interfere with, the different unit processes. In this regard the following aspects need further detailed research:

a. A well-equipped algal culture centre with the capacity to isolate and maintain cultures of algae known to cause problems in water treatment works should be established.

b. The electrical surface charge and other physical characteristics of algae, which may be responsible for penetration through, or interference with, unit processes, should be described. From this description it should be possible, based on surface charge, size, shape, density, motility and excreted products, to predict which unit process will remove algae, with a specific combination of characteristics, the most effectively.

c. All algae are not affected in the same way by chlorine and chlorine dioxide. Research into reasons for this phenomenon will be helpful in studying the effect of other pre-oxidants, such as ozone, on the removal of algae.

d. The research done in this project should be extended to cover other algae, different coagulants and possibly more sophisticated unit processes.

e. Long term pilot plant work is necessary to evaluate the effect of pre-oxidation on aspects such as microbial content of filter effluent, oxidant demand of filtered water before disinfection, influence on sludge production and disposal and general quality of water produced.

f. Methods, other than chlorophyll-a, should be implemented to determine the immediate effect of oxidants on the viability and survival of algal cells. Special attention should be given to the rate of ^{14}C uptake and its practical implementation on the purification plants.

The specific algal control measure or unit treatment process to be used will be largely affected by the algal related water quality standard with which the water purification industry will have to comply with. In this regard it is important that potable water standards in South Africa for THMs, chlorite and algae should be formulated and implemented as soon as possible.

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APPENDIX A

BASIC INFORMATION REGARDING THE TAXONOMY

OF THE DIFFERENT ALGAE USED

APPENDIX B

CONSTITUENTS OF THE DIFFERENT NUTRIENT MEDIA USED.

Constituent	Stock Culture Concentration (g/ℓ)			Stock volume required for 100 % media (ml/ℓ)		
	BG11	BG31	MBG	BG11	BG31	MBG
$MgSO_4.7H_20$	25	25	25	1	3	3
K_2HPO_4	7	5,06	5,06	1	3	3
$Ca(NO_3)_2.4H_20$	235,69	14,87	14,87	1	1	1
NA_2CO_3	100	100	100	1	1	1
$NaCO_3$	-	121,36	121,36	1	3	3
NaH_2PO_4	-	34,53	34,53	1	3	3
Citric acid	12	12	12	1	3	3
EDTA.FE	1,2	1,5	1,5	1	3	3
$Ca_3(PO_4)_2$	23	-	-	1	3	3
$Na_2SiO_3.5H_20$	-	-	7,46			4
MICRO ELEMENTS				1	1	1
H_3BO_3	2,86	2,86	2,86			
$MnCl_2.4H_20$	1,81	1,81	1,81			
$ZnSO_4.7H_20$	0,222	0,222	0,222			
$NaMoO_4.2H_20$	0,39	0,39	0,39			
$CoNO_3.6H_20$	0,049	0,049	0,049			
$CuSO_4$	0,0504	0,0504	0,0504			

APPENDIX C

INFORMATION REGARDING OXIDATION OF EFFLUENT AND VAAL DAM WATER MIXTURES.

1. Ratios in the different mixtures are expressed as

Effluent : Vaal Dam =			
0	is	0% effluent	100% Vaal Dam
5	is	5% effluent	95% Vaal Dam
10	is	10% effluent	90% Vaal Dam
20	is	20% effluent	80% Vaal Dam
30	is	30% effluent	70% Vaal Dam
50	is	50% effluent	50% Vaal Dam
75	is	75% effluent	25% Vaal Dam
100	is	100% effluent	0% Vaal Dam

2. Contact times: 0 min, 60 min, 120 min, 1440 min.

3. Controls used: Oxidant demand free water.

4. For variables monitored see Appendix D.

5. Oxidant concentrations dosed.

   5.1 Chlorine = 10, 5, and 3 mg/l

   5.2 Chlorine dioxide = 5, 3 and 1 mg/l.

APPENDIX D

WATER QUALITY INFORMATION OF THE DIFFERENT EFFLUENT-VAAL DAM MIXTURES USED ON DIFFERENT DAYS OF THE EXPERIMENT.

SEWAGE : VAAL DAM RATIOS

DATE: 230791

Variable	RATIO							
	0	5	10	20	30	50	75	100
pH	7,29	7,63	7,65	7,5	7,42	7,33	7,5	7,27
Alkalinity ($CaCO_3$)	86	92	89	90	90	90	92	92
Conductivity (mS/m)	26	28	30	35	40	50	63	75
Calcium	18	19	20	22	24	27	32	37
Magnesium	9,8	9,9	10	10	10	11	11	12
Hardness ($CaCO_3$)	85	88	91	96	100	115	125	140
Sodium	17	21	24	31	38	52	70	88
Potassium	4,3	5	5,6	6,9	8,1	11	14	17
Copper	*	*	*	*	*	*	*	*
Iron	0,43	0,45	0,48	0,44	0,41	0,36	0,31	0,16
Manganese	0,06	0,06	0,05	0,06	0,05	0,05	0,05	0,05
Lead	*	*	*	*	*	*	*	*
Zinc	0,08	*	0,07	0,08	0,05	0,04	0,04	*
D.O.C.	6,3	6,6	6,2	6,7	7,3	6,6	7,4	9,6
AMMONIA as N	0,08	0,06	0,06	0,05	0,03	0,03	0,05	0,03
Nitrate+Nitrite as N	0,1	0,13	0,29	0,38	0,49	1	1,65	2,35
Ortho Phosphate as P	0,05	*	0,04	0,05	0,24	0,25	0,27	0,28
Total Phosphate as P	*	*	*	*	*	*	*	*
Sulphate	35	67	33	38	38	51	73	80
Chloride	11	18	23	32	41	62	75	100
Fluoride	0,12	0,17	0,21	0,24	0,27	0,31	0,34	0,36
C.O.D	19	21	24	25	33	37	36	41
Turbidity (NTU)	24	22	20	18	15	12	7	0,95
Nickel	*	*	*	*	*	*	*	*
Aluminium	0,45	0,43	0,58	*	0,44	0,39	0,35	0,08
Active Silica	3,3	2,3	3,4	3,6	3,8	4,2	2,9	6,6
Total Silica	6,2	6,4	7,5	7,5	8,1	9	10	11

* Below detection limit

All concentrations in mg/ℓ where applicable

SEWAGE : VAAL DAM RATIOS

DATE: 250791

Variable	RATIO							
	0	5	10	20	30	50	75	100
pH	7,87	7,8	7,64	7,52	7,47	7,31	7,24	7,12
Alkalinity ($CaCO_3$)	90	90	87	86	82	78	71	67
Conductivity (mS/m)	25		31	37		53	66	80
Calcium	18	18	20	22	24	28	33	38
Magnesium	9,8	9,9	10	11	11	11	12	13
Hardness ($CaCO_3$)	85	86	91	100	105	115	130	150
Sodium	16	19	23	30	37	52	70	87
Potassium	4,1	4,6	5,4	6,8	8,2	11	15	18
Copper	*	*	*	*	*	*	*	*
Iron	1,3	1,3	1,2	1,1	0,95	0,7	0,39	0,15
Manganese	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Lead	*	*	*	*	*	*	*	*
Zinc	0,06	0,06	0,06	0,05	0,05	0,05	0,03	*
D.O.C.	6,6	6	6,6	6,2	6,4	8,5	7,4	7,3
AMMONIA as N	*	*	*	*	0,12	0,11	0,1	0,1
Nitrate+Nitrite as N	0,25	0,43	0,89	1,25	1,95	1,95	2,85	3,49
Ortho Phosphate as P	0,17	0,15	0,15	0,07	0,08	0,1	0,1	0,1
Total Phosphate as P	*	*	*	*	*	*	*	*
Sulphate	35	29	27	43	53	51	67	88
Chloride	*	22	30	92	58	92	119	148
Fluoride	0,22	0,24	0,26	0,27	0,28	0,29	0,3	0,3
C.O.D	15	17	18	19	26	20	20	29
Turbidity (NTU)	22	21	19	18	16	12	6,2	0,71
Nickel	*	*	*	*	*	*	*	*
Aluminium	2,1	2	1,9	1,6	1,4	0,96	0,4	*
Active Silica	2,9	2,7	2,9	3,3	3,1	3,5	4,5	6,9
Total Silica	15	15	15	14	14	13	12	11

* Below detection limit

All concentrations in mg/ℓ where applicable

D4

SEWAGE : VAAL DAM RATIOS

DATE: 300791

Variable	RATIO							
	0	5	10	20	30	50	75	100
pH	7,16	7,51	7,37	7,34	7,3	7,31	7,29	7,3
Alkalinity ($CaCO_3$)	90	91	94	91	92	96	96	98
Conductivity (mS/m)	26	28	31	37	43	54	68	81
Calcium	20	20	21	23	26	31	40	43
Magnesium	10	10	10	11	11	12	14	14
Hardness ($CaCO_3$)	91	91	94	105	110	127	160	165
Sodium	18	21	25	32	39	54	78	92
Potassium	4,5	4,9	5,7	7	8,5	11	16	19
Copper	*	*	*	*	*	*	*	*
Iron	0,49	0,45	0,46	0,43	0,43	0,31	0,19	0,1
Manganese	0,06	0,06	0,06	0,06	0,06	0,06	0,05	0,04
Lead	*	*	*	*	*	*	*	*
Zinc	0,08	0,08	0,08	0,07	0,07	0,05	0,04	*
D.O.C.	4,9	5,5	5	5,7	5,7	5,7	6,6	8
AMMONIA as N	0,06	0,14	0,05	0,09	0,03	0,08	0,05	0,05
Nitrate+Nitrite as N	0,1	0,1	0,69	0,93	1,15	2,15	3,35	4,65
Ortho Phosphate as P	0,24	0,24	0,24	0,25	0,25	0,27	0,28	0,28
Total Phosphate as P	*	*	*	*	*	*	*	*
Sulphate	16	40	23	27	34	49	68	87
Chloride	*	14	23	40	56	77	110	130
Fluoride	0,31	0,28	0,29	0,22	0,23	0,25	0,2	0,31
C.O.D	35	11	23	19	21	28	34	30
Turbidity (NTU)	23	22	20	28	18	12	6	1
Nickel	*	*	*	*	*	*	*	*
Aluminium	0,64	0,54	0,56	0,51	0,52	0,32	0,22	0,14
Active Silica	1	2,6	2,4	2,7	2,6	3,2	3,9	4,3
Total Silica	6,6	6,2	6,6	7,1	7,5	7,9	9,4	9,8

* Below detection limit

All concentrations in mg/ℓ where applicable

SEWAGE : VAAL DAM RATIOS

DATE: 010891

Variable	RATIO							
	0	5	10	20	30	50	75	100
pH	7,85	8,18	8,2	8,12	8,11	8,04	7,98	7,91
Alkalinity ($CaCO_3$)	89	86	86	88	85	82	81	77
Conductivity (mS/m)	26	29	31	38	44	55	71	85
Calcium	18	19	20	23	25	31	37	44
Magnesium	9,8	9,9	10	11	11	12	13	14
Hardness ($CaCO_3$)	85	88	91	105	110	130	145	170
Sodium	17	20	24	31	39	54	74	93
Potassium	4,1	4,8	5,5	6,9	8,4	11	15	19
Copper	*	*	*	*	*	*	*	*
Iron	0,41	0,5	0,56	0,74	0,8	1,1	1,3	1,6
Manganese	0,05	0,06	0,06	0,07	0,07	0,09	0,1	0,12
Lead	*	*	*	*	*	*	*	*
Zinc	0,05	0,05	0,05	0,05	0,04	*	0,03	*
D.O.C.	3,9	4,9	4,3	4,6	4,6	5,3	7,4	7
AMMONIA as N	0,09	*	*	0,08	0,09	0,09	0,09	0,05
Nitrate+Nitrite as N	0,87	0,29	0,61	1,45	2,15	3,45	5,05	6,55
Ortho Phosphate as P	*	*	*	*	0,03	0,04	0,07	0,1
Total Phosphate as P	*	*	*	*	*	*	*	*
Sulphate	21	19	20	36	32	46	62	94
Chloride	*	17	26	42	53	84	105	175
Fluoride	0,34	0,33	0,33	0,34	0,35	0,41	0,45	0,47
C.O.D	26	25	31	35	35	33	42	45
Turbidity (NTU)	16	19	20	17	16	13	7,2	2,9
Nickel	*	*	*	*	*	*	*	*
Aluminium	0,49	0,52	0,51	0,58	0,49	0,38	0,22	0,15
Active Silica	3,2	3,2	3,1	3,7	3,2	3,7	5,8	8,5
Total Silica	5,3	5,8	6	7,1	7,3	8,1	9	10

* Below detection limit

All concentrations in mg/ℓ where applicable

SEWAGE : VAAL DAM RATIOS

DATE: 060891

Variable	RATIO							
	0	5	10	20	30	50	75	100
pH	7,77	7,77	7,76	7,69	7,65	7,49	7,45	7,42
Alkalinity ($CaCO_3$)	90	89	86	86	86	84	85	83
Conductivity (mS/m)	26	30	32	38	44	55	69	83
Calcium	18	19	20	22	25	29	35	40
Magnesium	9,9	9,9	10	10	11	11	12	13
Hardness ($CaCO_3$)	86	88	91	96	110	120	140	155
Sodium	17	21	24	32	40	55	74	93
Potassium	4,1	4,8	5,5	6,9	8,2	11	15	18
Copper	*	*	*	*	*	*	*	*
Iron	1,1	1,1	1,1	0,99	0,89	0,81	0,65	0,53
Manganese	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Lead	*	*	*	*	*	*	*	*
Zinc	0,12	0,11	0,1	*	0,09	0,07	0,05	*
D.O.C.	4,3	4,5	4,2	4,8	4,5	4,6	5,9	6,21
AMMONIA as N	*	*	0,05	0,07	0,05	0,05	0,05	*
Nitrate+Nitrite as N	0,24	0,31	0,65	1,01	1,65	2,55	3,75	4,75
Ortho Phosphate as P	0,06	0,05	0,05	0,04	0,15	0,09	0,19	0,06
Total Phosphate as P	*	*	*	*	*	*	*	*
Sulphate	24	21	23	29	40	51	66	78
Chloride	10	17	24	45	54	86	102	130
Fluoride	0,29	0,28	0,29	0,3	0,31	0,32	0,33	0,36
C.O.D	27	29	25	28	32	37	35	41
Turbidity (NTU)	20	18	18	16	14	12	6,2	2,2
Nickel	*	*	*	*	*	*	*	*
Aluminium	1,8	1,7	1,7	1,4	1,2	0,89	0,43	*
Active Silica	3,7	3,6	2,9	3,3	3,2	4	4,2	6,4
Total Silica	13	13	13	12	11	11	10	9,6

* Below detection limit

All concentrations in mg/ℓ where applicable

D7

SEWAGE : VAAL DAM RATIOS

DATE: 080891

Variable	RATIO							
	0	5	10	20	30	50	75	100
pH	7,73	7,67	7,63	7,47	7,46	7,4	7,4	7,27
Alkalinity ($CaCO_3$)	90	89	88	91	91	87	87	85
Conductivity (mS/m)	27	29	31	37	42	53	66	79
Calcium	18	19	20	22	24	29	34	39
Magnesium	9,9	10	10	10	11	11	12	12
Hardness ($CaCO_3$)	86	89	91	96	105	120	135	147
Sodium	17	21	25	32	39	54	74	92
Potassium	4,4	5	5,8	7	8,3	11	14	18
Copper	*	*	*	*	*	*	*	*
Iron	1,1	1,1	1	0,88	0,78	0,61	0,37	0,19
Manganese	0,05	0,05	0,05	0,05	0,05	0,05	0,04	0,04
Lead	0,06	0,06	0,07	0,08	0,06	0,08	0,07	0,06
Zinc	0,17	0,17	0,17	0,15	0,13	0,1	0,06	0,02
D.O.C.	5,8	5,9	6,3	5,4	5,8	6,1	7,2	7,1
AMMONIA as N	*	*	*	*	0,08	*	*	*
Nitrate+Nitrite as N	0,44	0,52	0,77	1,15	1,65	2,65	3,65	4,95
Ortho Phosphate as P	0,07	0,06	0,06	*	*	*	0,06	0,06
Total Phosphate as P	*	*	*	*	*	*	*	*
Sulphate	16	20	18	42	47	40	57	91
Chloride	13	20	24	45	64	69	104	132
Fluoride	0,24	0,27	0,27	0,27	0,28	0,29	0,31	0,32
C.O.D	27	32	32	32	32	36	42	39
Turbidity (NTU)	19	18	18,7	16,4	14,6	10	5,3	0,94
Nickel	*	*	*	*	*	*	*	*
Aluminium	1,8	1,8	1,7	1,5	1,3	0,91	0,46	0,14
Active Silica	2,4	2,3	1,9	2,6	3,2	3,8	3,6	4,9
Total Silica	13	13	13	12	12	11	10	9,8

* Below detection limit

All concentrations in mg/ℓ where applicable

APPENDIX E. WATER QUALITY INFORMATION OF WATER PRODUCED BY THE DIFFERENT UNIT TREATMENT PROCESSES OF THE PILOT PLANT ON SPECIFIC DAYS.

Date	Run	Sample Point		Turbidity (NTU)	pH	Chloro-phyll-a (μg/ℓ)	THM (μg/ℓ)	Residual oxidant (mg/ℓ)	Oxidant Dose (mg/ℓ)
21/11	2	Raw	Chlorine	16	8,1	12	4	-	-
			Chlorine dioxide	16	8,1	9	4	-	0,87
		Post oxidation	Chlorine	16	8,1	12	4	-	-
			Chlorine dioxide	15	7,6	0,07	4	0,18	-
		Sedimentation	Chlorine	4,1	10,4	2	4	-	-
			Chlorine dioxide	2,9	10	3	4	0,02	-
		Carbonation	Chlorine	4,4	10,3	-	4	-	-
			Chlorine dioxide	5,3	9,7	-	4	-	-
		Filtration	Chlorine	0,4	10,1	1	4	-	-
			Chlorine dioxide	0,8	9,6	1	4	0,02	-
19/11	2	Raw	Chlorine	12	8,4	22	1,7	-	1,6
			Chlorine dioxide	12	8,4	21	1,8	-	0,75
		Post oxidation	Chlorine	11	8,4	3,4	98	0,7	-
			Chlorine dioxide	11	7,3	1,1	2,7	0,3	-
		Sedimentation	Chlorine	3,1	10,3	1,1	90	*	-
			Chlorine dioxide	1	10,8	0,14	4	0,02	-
		Carbonation	Chlorine	1,8	7	-	74	-	-
			Chlorine dioxide	0,8	7	-	3	-	-
		Filtration	Chlorine	0,7	8,1	-	70	0,02	-
			Chlorine dioxide	0,2	8,3	*	3	0,08	-

* Below detection limit - No analysis done

E2

Date	Run	Sample Point		Turbidity (NTU)	pH	Chloro-phyll-a (μg/ℓ)	THM	Residual oxidant (mg/ℓ)	Oxidant Dose (mg/ℓ)
13/11	2	Raw	Chlorine	22	8,5	33	7	3,08	3,8
			Chlorine dioxide	24	8,5	33	7	0,6	0,85
		Post oxidation	Chlorine	31	8,6	3,4	82	1,49	-
			Chlorine dioxide	22	7,5	22	9	0,5	-
		Sedimentation	Chlorine	1,9	10,4	2,1	68	*	-
			Chlorine dioxide	2,9	10,7	3,4	4	*	-
		Carbonation	Chlorine	1,6	10,4	-	62	-	-
			Chlorine dioxide	3,1	10,6	-	3	-	-
		Filtration	Chlorine	0,1	10,2	0,9	56	*	-
			Chlorine dioxide	0,1	10,2	0,5	6	*	-
12/11	2	Raw	Chlorine	10	8,6	52	2	3,1	3,5
			Chlorine dioxide	10	8,7	54	2	-	-
		Post oxidation	Chlorine	10	8,6	18	80	1,3	-
			Chlorine dioxide	10	8,6	15	-	-	-
		Sedimentation	Chlorine	3	10,3	0,6	96	*	-
			Chlorine dioxide	12	10,1	1,2	2	-	-
		Carbonation	Chlorine	12	6,9	-	80	-	-
			Chlorine dioxide	11	6,9	-	2	-	-
		Filtration	Chlorine	0,3	8,6	3,8	75	*	-
			Chlorine dioxide	1,6	7,7	1,8	3	-	-

* Below detection limit - No analysis done