A COMPARATIVE STUDY OF CHLORINE DIOXIDE AND OTHER OXIDANTS IN POTABLE WATER TREATMENT

by

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in collaboration with

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and

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EXECUTIVE SUMMARY

BACKGROUND

The runoff and sewage returns from the major industrialised centres in South Africa has rapidly increased in volume and pollution load over recent years, and has resulted in the deterioration of the water quality in the receiving rivers and streams. One of the rivers most affected is the Vaal River as it passes through the PWV complex. This river is still the primary source of water for many downstream users. The increased organic and inorganic load has been a matter of growing concern, especially since South Africa is a water scarce country and in most cases alternative sources of water supply are extremely costly to develop.

Research in South Africa and world wide has resulted in a better understanding of the consequences of the increase in the organic and inorganic loading of river courses. The problems and costs associated with removing these contaminants, or in preventing the formation of new undesirable byproducts in the water treatment process, has been receiving much attention. It has become possible to evaluate the efficacy of various treatment processes, even in terms of micro variations in contaminant levels.

This project has attempted to focus on water treatment in the lower Vaal River regions where the increased levels of pollution emanating from the PWV area is resulting in particular water treatment problems to the water authorities and municipalities who rely on the Vaal River for their water supply. Some of the problems being encountered are algal blooms at certain times of the year, high manganese levels, high trihalomethanes (THMs) in the final treated water, tastes and odours, and continued biological activity in the distribution pipelines. THM levels are often above the present USA limit of 100μg/l. Algal blooms cause rapid changes in raw water pH, and the algae are difficult to remove from the water in the treatment process. Manganese too is difficult to remove by conventional means, and chlorine is much less effective as an oxidant and disinfectant at the higher pH's encountered.

The use of alternative oxidants to chlorine was seen as a possible way to overcome some of these problems. The Western Transvaal Regional Water Company on the lower Vaal River was already using ozone (O_3) for pre-oxidation on one leg of their water treatment plant at Stilfontein. It was possible to compare the water quality from the two legs of the plant, i.e. with chlorine and ozone pre-oxidation respectively. In addition a pilot plant which had been "moth balled" was available to carry out further comparative work. The use of chlorine dioxide (ClO_2) as a pre-oxidant was implemented on the pilot plant so that comparisons could be made with the two legs of the main plant. It was expected that chlorine dioxide would result in substantially less trihalomethanes being formed in the treatment process. Other benefits of the use of chlorine dioxide were also expected.

Consequently discussions were held with Floccotan, the CSIR, and the Western Transvaal Regional Water Company where it was agreed that if financing for the study could be obtained, the pilot plant would be commissioned and such an investigation undertaken over at least a full operating year. Results from the study would prove most valuable for the future planning of water treatment in the lower Vaal River and other similarly contaminated waters. The Water Research Commission agreed to help finance the study, and preparations to carry out the study began in January 1988.

OBJECTIVES

The objectives of the research project were to evaluate the use of alternative oxidants to chlorine in the treatment of the more polluted surface waters. In particular the following parameters were to be carefully monitored:

- THM formation
- affect of oxidants on algae
- manganese reduction
- disinfection
- TOC removal

RESULTS AND CONCLUSIONS

This project set out to assess whether alternative combinations of oxidants could result in a significant improvement of the treatment process for eutrified source waters such as found in the lower Vaal River. The results of the study indicated that while some parameters indicated a significant improvement, others were less significant. The additional costs associated with the use of alternative oxidant combinations would need to be carefully assessed against the benefits which will be achieved before a decision on the use such alternatives is taken. The table below indicates the relative performance of the various combinations in terms of the parameters measured.

	ClO_2 ClO_2	ClO_2 Cl_2	Cl_2 Cl_2	O_3 ClO_2	O_3 Cl_2
THM formation	+	+++	+++++	++	+++++
Chlorophyll removal	++++	++++	++++	+++++	+++++
Algal cell damage	+++++	+++++	+++++	++++	++++
Manganese removal	++++	++++	+++++	+++++	+++++
Iron removal	++++	++++	++++	++++	+++++
TOC removal	+	+	+	+	+
Biofouling control	++	++	++	-	-
Disinfection	+++++	+++++	+++++	+++++	+++++
Operational costs	+	++	++++	+++	+++++
Capital costs	+++++	+++++	+++++	+	+
Total costs	+	++	+++++	++	+++

NOTE: The 3 streams with chlorine and ozone as pre-oxidants were also treated with between 0.1 and 0.8 mg/l of $KMnO_4$ to aid manganese removal in particular.

+ implies low efficiency or high costs
+++++ implies high efficiency or low costs
++, +++, and ++++ are relative positions between these two extremes

A brief summary of the results from the use of different combinations of oxidants at Stilfontein on the lower Vaal River are then as follows:

ClO_2 - ClO_2 : THM formation is significantly minimised (when compared to the other treatment lines) to values well within the 100 µg/l level (average of 20 µg/l). Algae deactivation and subsequent chlorophyll removal is very effective. Manganese and iron removal is good - without the aid of $KMnO_4$. Biofouling is controlled to a limited extent in the raw water lines. Disinfection is excellent. Running costs, however, are extremely high (± R110/Ml for pre-oxidation and post-disinfection with ClO_2).

ClO_2 - Cl_2 : THM formation is minimised to values at the 100 µg/l level. Algae deactivation and subsequent chlorophyll removal is very effective. Manganese and iron removal is good - without the aid of $KMnO_4$. Biofouling is controlled to a limited extent in the raw water lines. Disinfection is excellent. Running costs are also very high due to the high cost of ClO_2.

Cl_2 - Cl_2 : THM formation is high with values well above the 100 µg/l level (average of 155 µg/l). Algae deactivation and subsequent chlorophyll removal is very effective. Manganese and iron removal is good - but with the aid of $KMnO_4$. Biofouling is controlled to a limited extent in the raw water lines. Disinfection is excellent. Running costs are low (± R13/Ml).

O_3 - ClO_2 : THM formation is low (average of 57 µg/l), although slightly higher than for the ClO_2-ClO_2 treatment. This is primarily due to the fact that no free chlorine is added to the water. However, ClO_2 and O_3 will convert bromides to free bromine, and hence result in some THM formation. In addition the ozone treated stream on the main plant is not totally isolated from the chlorine treated stream, and hence some of the THMs measured may have resulted from the chlorine treated stream. Ozone was the most effective for chlorophyll removal, despite cell damage often appearing to be only slight. Manganese and iron removal is good, again in combination with $KMnO_4$. Biofouling is not controlled with pre-ozonation, and may even be slightly enhanced. Excellent disinfection was achieved. Running costs are medium when compared with the other treatment options. Capital costs for the generation of ozone are very high, and make a significant impact on the overall cost of ozone treatment. However, the total costs (± R67/Ml) are significantly less than when ClO_2 is used for pre-oxidation.

O_3 - Cl_2 : THM formation is the highest of all the treatment combinations (average of 160 µg/l), although only slightly higher than the chlorine-chlorine treatment. Ozone, as found in other studies reported in the literature, increases the formation of THMs when post treated with chlorine. This is most likely due to the modification of the organics present when exposed to ozone, so that they become more susceptible to THM formation. However the effect when compared to chlorine pre-oxidation is only slight. Chlorophyll removal was very good through pre-ozonation. Manganese and iron removal, with the aid of $KMnO_4$, is very good, maintaining levels well below 0.1mg/*l*. Biofouling is as for ozone treatment stated above. Disinfection was excellent, and running costs low. However capital costs for the generation of ozone are very high, and make a significant impact on the overall cost of ozone treatment (± R48/Ml).

From the above the following conclusions can be drawn:

1 The use of chlorine dioxide does result in a substantial reduction in the formation of THMs when treating enriched lower Vaal River water for domestic use. In particular the combinations ClO_2-ClO_2 and O_3-ClO_2 resulted in THM levels well within the 100 µg/l level which is set as a maximum in the USA.

2 When ClO_2 was used as a pre-oxidant with chlorine for final disinfection, THM levels were relatively high (100 µg/l). The literature has reported that the ClO_2-Cl_2 combination can result in substantial THM reductions. However, the high TOC levels in the raw water (10-15 mg/l) is probably responsible for the higher than expected THM levels in this stream.

3 Pre-ozonation does appear to increase the THMFP of the water obtained from the Vaal River at Stilfontein. Hence post-chlorination of ozone treated water results in even higher THM formation than for the Cl_2-Cl_2 treatment.

4 The presence of bromides in the raw water will result in some formation of THMs, even when only ClO_2 is added for oxidation and disinfection.

5 Algal cells were successfully removed by all the treatment lines being evaluated. Chlorophyll removal of more than 95% was consistently achieved. Overall, ozone treated water gave slightly better chlorophyll removal than chlorine or chlorine dioxide.

6 Algal cell damage and internal bleaching was evident for all pre-oxidants. Overall, ClO_2 appeared to result in more severe damage than the other two oxidants.

7 Manganese was substantially removed by all treatment lines, although better results were obtained on the ozone-$KMnO_4$ and chlorine-$KMnO_4$ treatment sequences. Levels of >0.1 mg/l were not found in the final water.

8 Iron, although less successfully removed than manganese, was generally within the limits in the final waters (i.e. <0.1 mg/l).

9 Organic carbon was not significantly removed in any treatment process. However, some modification of the organics present was taking place as a result of the different oxidation treatments. Chlorine addition tended to result in chlorine addition type reactions, whereas ozone and chlorine dioxide tended to result in oxidation of the organics (i.e. breaking of some of the bonds).

10 It was not possible to limit the formation of chlorine dioxide byproducts (chlorite and chlorate), and still achieve adequate treatment of the Vaal River water when ClO_2 is used as the pre-oxidant. ClO_2 doses of up to 3.5 mg/l are required for

pre-oxidation, and 1 mg/l for post-disinfection, resulting in combined chlorite and chlorate levels of up to 3.5 mg/l. This is far in excess of the recommended maximum of 1 mg/l.

11 Chlorine and chlorine dioxide were able to reduce the formation of biological slimes in the pipelines following pre-oxidation. However ozone addition enhanced the formation of bacterial slime layers after a short distance from the point of ozone addition. Chlorine and ClO_2 were able to limit bacterial slimes more easily on stainless steel and PVC surfaces than on mild steel surfaces.

12 The cost of using alternative oxidants to chlorine was found to be substantially higher. Overall costs for oxidation and disinfection were in the ratio 1.0 : 3.5 : 5.0 : 6.0 : 8.5 for the treatment lines Cl_2-Cl_2 : O_3-Cl_2 : O_3-ClO_2 : ClO_2-Cl_2 : ClO_2-ClO_2.

Hence the following recommendations are proposed with respect to the use of alternative oxidants in the treatment of water in the lower Vaal River for potable use:

1 Should THM limits of 100 μg/l be enforced in South Africa, ozone pre-oxidation followed by ClO_2 post-disinfection could most economically be proposed to achieve this target in high TOC source waters where chlorine treatment results in THM values above the limit.

2 ClO_2 is not recommended for use as a pre-oxidant in the treatment of lower Vaal River water because of the high dose required and the resultant high level of chlorite and chlorate, as well as the very high costs.

3 Chlorine is still one of the most effective oxidants for the treatment of the lower Vaal River water in terms of chlorophyll removal, biofouling control, disinfection, lowest cost, and, with the aid of $KMnO_4$, iron and manganese removal.

4 Alternatives to chlorine should be further researched to try and obtain a more economical way of reducing the formation of THMs, and to deal with the occasional problem of high pH of the raw water. Other combinations which could be considered are direct UV radiation, hydrogen peroxide, peroxone, and combinations of these.

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

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LIST OF SYMBOLS

The following symbols are used in the text, and should be read as given below:

THM = trihalomethane
TOX = total organo-halogens
THMFP = trihalomethane formation potential
O_3 = ozone
Cl_2 = free chlorine
ClO_2 = chlorine dioxide
ClO_2^- = chlorite
ClO_3^- = chlorate
$NaClO_2$ = sodium hypochlorite
$KMnO_4$ = potassium permanganate
HCl = hydrochloric acid
TOC = total organic carbon
Mn = mangaanese
Fe = iron
CT = concentration x time for disinfection reactions
MIB = 2-Methylisoborneol
IPMP = 2-isopropyl-3-methoxy pyrazine
TCA = 2,3,6-trichloroanisole
IBMP = 2-isobutyl-3-methoxy pyrazine
SS = stainless steel
MS = mild steel
PVC = poly-vinyl chloride

pre-oxidation refers to the addition of an oxidant to the raw water prior to any other treatment (coagulation, pH correction, flocculation, etc.).

post-disinfection refers to the addition of a disinfectant to maintain the microbiological quality of the final water untill it passes through the consumer's tap.

1. INTRODUCTION

The quality of water supplied to consumers by the municipalities in South Africa has been of a very high standard for many years. Water supply companies and municipalities have striven to deliver a safe and acceptable supply of water to their consumers at all times.

Over the past 4 to 5 decades South Africa has rapidly become more industrialised in the major metropolitan areas, and has resulted in the urban populations in these centres increasing at an alarming rate, often beyond that at which adequate sanitation services could be provided. The runoff and sewage returns from these areas has resulted in the deterioration of the water quality in the receiving rivers and streams. One of the rivers most affected is the Vaal River as it passes through the PWV complex. These rivers are often the primary source of water for downstream users. The increased organic and inorganic loads in these rivers has been a matter of growing concern, especially since South Africa is a water scarce country and in most cases alternative sources of water supply would be extremely costly to develop, or are simply not available. Hence downstream users have little alternative but to incur the additional costs associated with the treatment of these more contaminated water sources, or to gradually accept a worse and worse quality of water for domestic and other uses.

Research in South Africa and world wide has resulted in a better understanding of the consequences of an increase in the organic and inorganic loading of river courses, particularly in the process of water purification. The problems and costs associated with removing these contaminants, or in preventing the formation of new undesirable byproducts in the treatment process, has been receiving much attention. New techniques have been developed to be able to identify a large number of organic compounds present in the water at the micro-gram and even nano-gram per litre levels. Hence it has become possible to evaluate the efficacy of various treatment processes, even in terms of micro variations in contaminant levels.

This project has attempted to focus on water treatment in the lower Vaal River regions where the increased levels of pollution emanating from the PWV area is resulting in particular water treatment problems to the water authorities and municipalities who rely on the Vaal River for their water supply. Some of the problems being encountered are algal blooms at certain times of the year, high manganese levels, high trihalomethanes (THMs) in the final treated water, tastes and odours, and continued biological activity in the distribution pipelines. THM levels are often above the present USA limit of 100µg/l. Although no limit has been set for South Africa as yet, these high levels are of concern because of their possible long term health effects. Algal blooms cause rapid changes in raw water pH, and the algae are difficult to remove from the water in the treatment process. Manganese too is difficult to remove by conventional means, and chlorine is much less effective as an oxidant and disinfectant at the higher pH's encountered.

The use of alternative oxidants to chlorine was seen as a possible way to overcome some of these problems. The Western Transvaal Regional Water Company on the lower Vaal River was already using ozone (O_3) for pre-oxidation on one leg of their water treatment plant at Stilfontein, as opposed to chlorine which was being applied as a pre-oxidant on the other leg. Potassium permanganate ($KMnO_4$) was being used on both legs of the plant in combination with chlorine and ozone to aid oxidation of the relatively high levels of manganese in the raw water. Hence it was possible to compare the water quality from the two legs of the plant, i.e. with chlorine and ozone pre-oxidation respectively. In addition a pilot plant which had been "moth balled" was available to carry out further comparative work. The use of chlorine dioxide (ClO_2) as a pre-oxidant could be a promising alternative, especially in terms of trihalomethane control.

Consequently discussions were held with Floccotan (Mr Hugh Mitchell), the CSIR (Ian Pearson), and the Western Transvaal Regional Water Company (Mrs Marina Kruger) on the possible use of chlorine dioxide on the pilot plant as a comparison with the chlorine and ozone treatment legs on the main plant. It was agreed that if financing for the study could be obtained, the results from the study would prove most valuable for the future planning of water treatment in the lower Vaal River and other similarly contaminated waters. The Water Research Commission was approached to help finance the study whereby various combinations of oxidants for pre- and post- treatment could be evaluated. The agreement was signed in 1987, and preparations to carry out the study began in January 1988.

2. RECENT LITERATURE

Recent literature on the aspects dealt with in this project has been surveyed during the course of the project. The important findings are summarised below. A more comprehensive literature survey on the use of chlorine and chlorine dioxide for pre-oxidation can be found in the WRC report "The influence of water quality on the efficiency of chlorine dioxide as pre-oxidant and algicide with the production of potable water" (project no. K5/281/4/1 undertaken by the Rand Water Board).

2.1 THM formation

Graham et al (1989) found in laboratory tests on organically enriched lowland water of East Anglia (UK) that:

- THMs were formed in the pre-oxidation phase when chlorine was used as the pre-oxidant, but not when ClO_2, O_3 or $KMnO_4$ were used.

- Only low concentrations of THMs were formed after post- chlorination following pre-oxidation with ClO_2, O_3 or combined chlorine (chloramines). However, pre-oxidation with $KMnO_4$ had little effect on THM formation following post-chlorination.

- Levels of total THMs appeared to be similar in winter and summer, i.e. the water temperature made little difference to the formation of THMs in the water treatment process.

- Approximately 60% of the variation in THM formation arising from pre- and post - chlorination on winter samples could be related to sample TOC and chlorophyll 'a'.

- When a limit of 0,5 mg/l ClO_2 was used for pre-oxidation, post chlorination THM levels are generally greater than when applying ozone at 3 mg/l. This indicates that sufficient ClO_2 must be added to overcome the immediate demand and leave a residual before it can have an effect on the THM precursors.

Werdehoff and Singer (1987) similarly found in organically contaminated water in the U.S.A. that:

- ClO_2 can reduce THM and TOX precursor concentrations provided the ClO_2:TOC weight ratio is greater than 0,4.

- ClO_2 does not form THMs and produces only a small amount of organic halogens (TOX).

Grasso et al (1989) in tests with ozone on organically contaminated waters in the U.S.A. found that:

- Trihalomethane formation potential (THMFP) was reduced by pre-ozonation, but this reduction was less for two stage ozonation.

Huck et al (1989) found that chlorination produced mutagenicity most frequently, whereas chloramination, ClO_2 and O_3 only very occasionally.

Summary : THMs should not be formed in the pre-oxidation phase except when chlorine is used as pre-oxidant. After post-chlorination it can be expected that THM levels of the final waters will be low in the case of pre-ozonation (except if 2 phase ozonation is practised), pre-ClO_2 (except in the case of ClO_2 doses being < 0.5mg/l, or < 0.4 x TOC). A relationship may exist between THM formation (when using chlorine for pre-oxidation and post-disinfection) and TOC and chlorophyll 'a'. $KMnO_4$ will not affect THM formation.

2.2 Algae

Recent publications report on the effect of oxidants in the removal of algae in the conventional water treatment process. Of interest are the following:

- pre-oxidation is considered essential as an algal control measure so that the algae are killed prior to entering the plant (Weber and Smith, 1986);

- the use of chlorine for pre-oxidation of algae can lead to the formation of undesirable THMs, and tastes and odours in some cases (Culver 1975);

- certain algae are less affected by chlorine and may pass through the treatment plant maintaining viability, especially when the pH of the raw water is high;

- ozone may be less effective than chlorine for rendering cells non-viable, but more effective in minimizing tastes and odours (however, geosmin and MIB are resistant to oxidation by chlorine, ozone, ClO_2 and $KMnO_4$) (Sukenik et al, 1987, Culver, 1975, and Joubert et al, 1978);

- ClO_2 may destroy certain THM precursors resulting from algae activity, and is markedly more effective than chlorine for algal chlorophyll reduction and prevention of algae re-growth (Masschelein, 1978, and Geldenhuys and van der Merwe, 1987);

- ClO_2 is less effective for algae removal in more polluted water sources (Steynberg et al, 1989);

- both ozone and ClO_2 improve algal flocculation (Sukenik et al, 1987).

Summary : algal removal will be enhanced by any pre-oxidation step. However, pre-chlorination may have little effect when the pH is high, and may give rise to tastes and odours and increased THMs. Ozone may also not be as effective as desired for the rendering of algal cells non-viable, but is likely to result in less taste and odour problems than chlorine. ClO_2 may be more effective for algal control than either chlorine or ozone, provided the water is not too polluted. With ClO_2, THM precursors from algae may be destroyed, and tastes and odours minimised.

2.3 Manganese Removal

In a paper by Knocke et al (1987), it was found that:

- free chlorine was not an efficient oxidant for the removal of manganese unless the pH was alkaline;

- high chlorine levels and extended contact times were required to achieve complete Mn oxidation;

- $KMnO_4$ efficiently oxidized manganese, but the efficiency was considerably reduced at higher TOC levels due to the need to satisfy the oxidant demand; and also at low temperatures;

- ClO_2 was effective in oxidizing Mn, but not as efficiently as $KMnO_4$ (at least twice the stoichiometric amount was required). However, ClO_2 was little affected by lower temperatures or varied pH, but as with $KMnO_4$ higher doses were required at higher TOC levels.

Summary : $KMnO_4$ should effectively remove manganese when applied after chlorine or ozone, although longer contact times may be required in cold weather. ClO_2 should effectively remove Mn, provided the dose was high enough (i.e. above the stoichiometric amount for Mn removal).

2.4 Disinfection

Mc Guire et al (1990) found that concentration.time (CT) values for achieving 90% inactivation of Giardia were lowest for ozone (CT<1) followed by ClO_2 (CT <15) then chlorine (CT <150) and finally chloramines (CT <1200). ClO_2 and ozone are also extremely effective bactericides and virucides (Aieta and Berg, 1986, Berg et al, 1979, and Katz, 1980).

2.5 By-product formation

Besides THM formation, other disinfection by-products are of concern in water disinfection. In particular inorganic by-products from the use of ClO_2 are of concern. Werdehoff and Singer (1987) found that:

- residual chlorite (ClO_2) was consistently about 70% of the ClO_2 consumed;

- once formed, ClO_2 will be maintained in the water supply with minimal decay with time, unless further treatment takes place;

- ClO_2 and chlorite may further breakdown to chlorate (ClO_3).

Condie (1986) found that chlorite was more potent in causing hemolytic anemia (oxidative damage to the red blood cell membrane) than either chlorate or ClO_2.

- In addition, ClO_2 can produce quinones and benzoquinones from a variety of substrates in source waters (esp. phenols);

Summary : the ClO_2 byproducts chlorite and chlorate must be closely monitored when using ClO_2 in a potable water treatment process. Maximum levels of 1 to 2 mg/l of ClO_2 are recommended to limit the presence of chlorite and chlorate in the final water to levels of less than 1 mg/l.

2.6 Taste and odour control

It has already been mentioned that by-products from certain algae species (geosmin and MIB) are poorly oxidized by chlorine, ClO_2, ozone and $KMnO_4$. Work carried out by Lalezary et al (1986) indicated the following when various oxidants were evaluated for the removal of five earthy-musty compounds (IPMP, IBMP, MIB, TCA, Geosmin):

- ClO_2 performed best overall for compound removal;

- $KMnO_4$ oxidation was inefficient for the removal of the compounds of interest;

- Ozone displayed fair removal efficiencies, but less efficient than ClO_2;

- Chlorine was found to be economically inefficient for the removal of the organics of interest;

- At best (ClO_2), geosmin and MIB showed removal levels of 30% or less.

Glaze et al (1990) found that conventional oxidants such as Cl_2, chloramines, ClO_2, $KMnO_4$ and H_2O_2 cannot control taste and odour problems in water supplies. They found ozone to be more effective, especially for the removal of MIB and geosmin 40% and 90% removals were achieved respectively.

Summary : The tastes and odours (MIB and geosmin) from certain algae species may not be removed with oxidation techniques. However, other odours may be more effectively removed with ozone and ClO_2 than with chlorine.

2.7 Biofouling

Mayack et al (1984) found a significant difference in biofouling control when ClO_2 was compared with chlorine, with ClO_2 being more effective in controlling biofouling on 304 SS than chlorine.

Ozone is usually considered a poor candidate for biofouling control as ozonation of water produces increases in organic carbon compounds which can be utilised by various bacteria.

3. Methodology and Approach of Research

The approach adopted for this research project was to utilise the existing water treatment plant of the Western Transvaal Regional Water Company at Stilfontein on the lower Vaal River and to commission the pilot plant at the treatment plant. By using chlorine dioxide as pre-oxidant on the pilot plant, and by transferring a small stream of ozone treated filtered water from the main plant to the pilot plant, be able to evaluate the following five combinations of pre-oxidation and post-disinfection treatments (with flocculation, sedimentation and filtration) of the Vaal River water:

chlorine - chlorine (main plant)
ozone - chlorine (main plant)
ozone - ClO_2 (main plant/pilot plant)
ClO_2 - ClO_2 (pilot plant)
ClO_2 - chlorine (pilot plant)

The following parameters would be monitored to compare the efficacy of the various treatments:

THM levels
manganese
chlorophyll
byproducts
tastes and odours (if problem conditions arose)
biofouling

In addition various other parameters were monitored routinely to assess the performance of the treatment processes.

4. MATERIALS AND METHODS

The water treatment plant at Stilfontein of the Western Transvaal Regional Water Company is situated on the Lower Vaal River some 120 km below the Vaal Barrage. The two legs of the treatment plant (approx. 100 Ml/d each), and a smaller 7 m^3/h pilot plant were sampled routinely and the samples analysed for various parameters to assess the treatment performance. The laboratory facilities and personnel at the water treatment plant carried out the bulk of the routine analyses as well as some of the non-routine analyses. Back-up analyses, particularly of THMs and TOC, were carried out by the CSIR.

4.1 Pilot Plant Design and Operation

The 7 m^3/h pilot plant was supplied with raw water from the Vaal River, and consisted of the following treatment stages (figure 1):

pre-oxidation (ClO_2)
mixing (pipe mixer)
coagulant dosing (ferric sulphate)
mixing (pipe flocculator)
pH correction (lime dosing)
settling (upflow through tube settler)
sand filtration (downflow, constant rate)
post disinfection (chlorine, ClO_2)
storage (approximately 30 minutes)

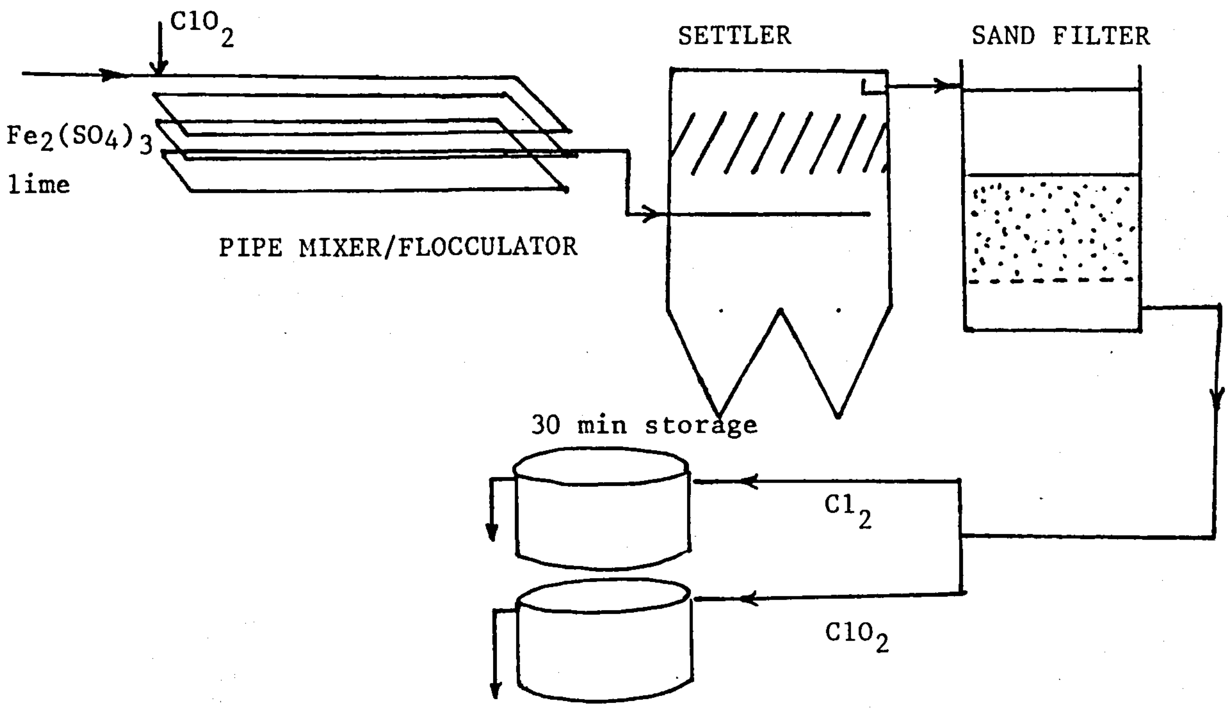


Figure 1 : Pilot plant configuration

Hence in combination with the main plant, the treatment sequences as depicted in figure 2 were obtained:

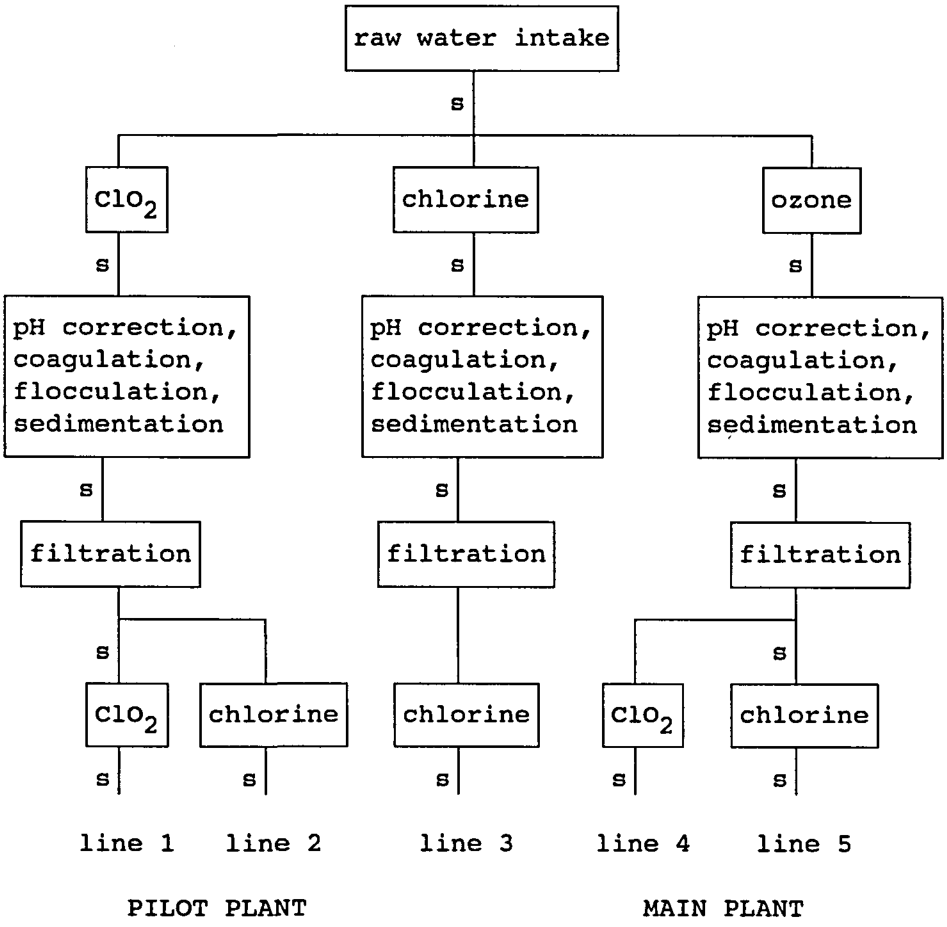


Figure 2: Pilot and main plant treatment block diagram
(note : s refers to sampling points)

The main plant consists of two legs of equivalent size, each treating approximately 100 Ml per day. The coagulant and lime dosing on the pilot plant corresponded to what was being added on the main plant. These dosages were varied depending on the river conditions and hence the quality of the raw water. The ClO_2 dosing on the pilot plant was firstly kept at a level of 0.5 mg/l for pre-oxidation, and a maximum of 1.0 mg/l for post-disinfection so that byproducts (chlorite and chlorate) in the final water would not be above 1.0 mg/l. However this was later adjusted to meet the demand of the raw water (approximately 3.0 mg/l as pre-oxidant and 1.0 mg/l for post disinfection).

Note that the approximate contact times for the pre-oxidants on each leg before the addition of coagulants, potassium permanganate and lime were as follows:

chlorine	10 minutes
ozone	4 minutes
chlorine dioxide	10 minutes

4.2 Chlorine dioxide generating facility

Chlorine dioxide was generated on-site using an acid - sodium chlorite generator. This was modified during the course of the project to be able to produce small quantities of solution which could be dosed at variable rates without changing the solution concentration. Although initial commissioning of the system was problematic, the following generation system proved to be reliable and consistent in the long term with the production of a minimum of byproducts (chlorite and chlorate less than 5% of product solution):

- stock solutions of HCl and $NaClO_2$ made up to 2%
- solutions added into rapid mix regime
- slow mix in packed bed (50 minutes)
- retention period (2 hours)
- fixed 1:6 dilution through double siphon system

The final model of the generator, depicted in figure 3, was virtually maintenance free since all parts in contact with the ClO_2 solution were of plastic. The dosing pumps which supplied the precursor chemicals (HCl and $NaClO_2$), as well as the ClO_2 solution dosing pumps, did however, require routine maintenance.

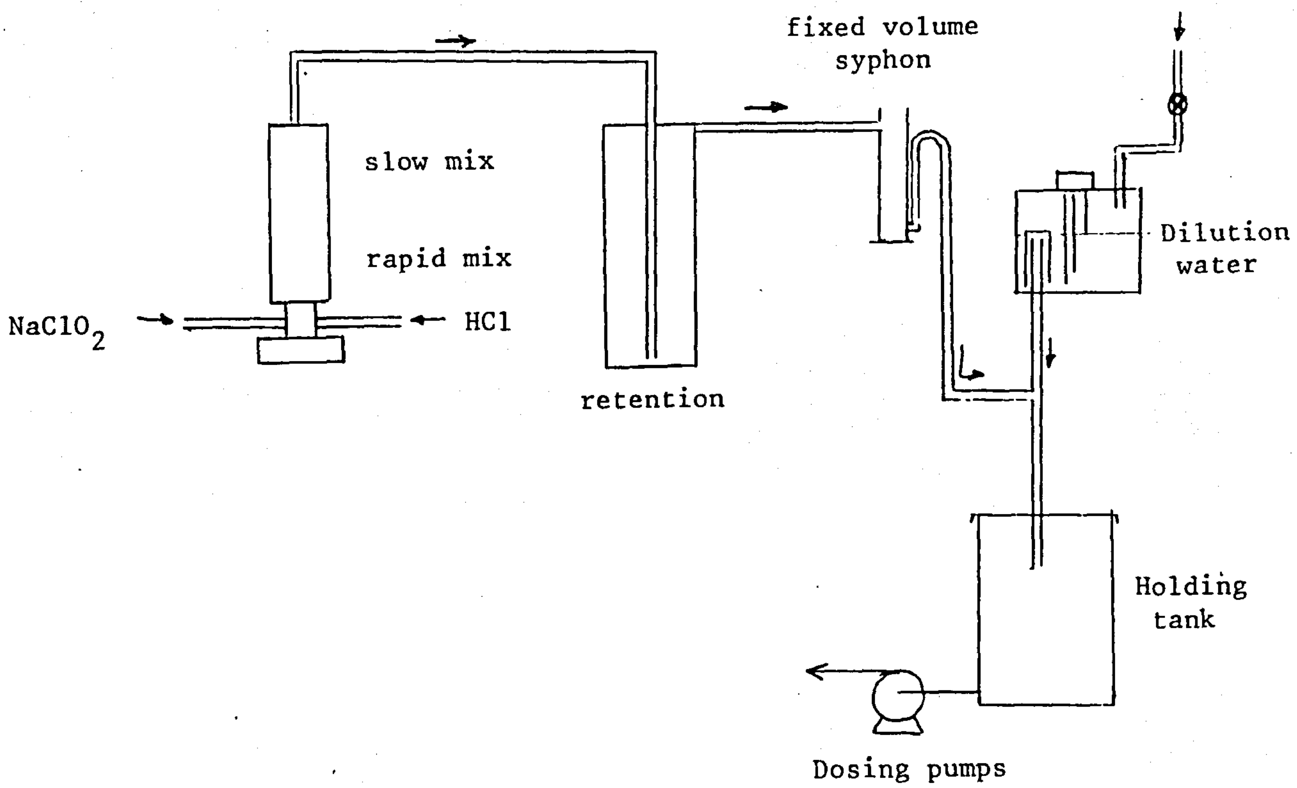


Figure 3 : Chlorine dioxide generator (acid - chlorite)

4.3 Sampling and analyses

A sampling programme was adhered to where daily, weekly and monthly samples were taken and analysed by the Western Transvaal Regional Water Company's laboratory at the treatment plant, and certain samples by the CSIR in Pretoria. Routine analyses were carried out to determine the following parameters:

pH)
conductivity) for process control
turbidity)
residual disinfectants)
manganese
iron
TOC
chlorophyll
THMs

In addition the following were evaluated on a non-routine basis:

algal genera
ClO_2 byproducts (chlorite and chlorate)
scan of organic constituents
microbial fouling

The following analytical methods were employed:

pH - glass membrane probe;
conductivity - conductivity meter corrected for temperature;
turbidity - nephelometric turbidity meter
residual disinfectants:
 chlorine - DPD chlorine comparator/spectrophotometer
 ozone - DPD chlorine comparator/spectrophotometer
 ClO_2 - chlorophenol red titration
manganese - atomic adsorption
iron - atomic adsorption
TOC - DOC analyser employing combustion-infrared
chlorophyll a- spectrophotometric (trichromatic method) corrected for pheophytin
THMs - gas chromatography on extraction
algal genera - microscopic examination with phase contrast microscope
ClO_2^- acid/starch titration with thiosulphate (pH2)
ClO_3^- acid/starch titration with thiosulphate (pH 0.5), both after Aieta et al (1984)
organics - GC-MS scan
microbial fouling - Pedersen's devices

The sampling schedule is shown in appendix A. Generally most analyses were carried out on the final product water of each treatment process, with inter-process sampling being primarily for process control purposes. However, the inter-process samples also provide useful information regarding the effect of the different processes on the water quality.

The test programme ran from June 1988 till October 1990. However technical hitches on the pilot plant resulted in the results of 1988 being too haphazard to be of use. Hence results presented in this report are for the period January 1989 to October 1990.

5. ANALYTICAL RESULTS

The results of the analyses are presented below.

5.1 THM tests and results

The results of the THM analyses for the period January 1989 to October 1990 are shown in figures 4a and 4b. Of interest are the average THM levels resulting from the various treatments.

line 1 : ClO_2 - ClO_2 = 20,2 $\mu g/l$
line 2 : ClO_2 - Cl_2 = 104,2 $\mu g/l$
line 3 : Cl_2 - Cl_2 = 154,8 $\mu g/l$
line 4 : O_3 - ClO_2 = 57,5 $\mu g/l$
line 5 : O_3 - Cl_2 = 160,0 $\mu g/l$

The only two treatments consistently minimizing the formation of THM's are pre- and post-ClO_2, and pre-ozone post-ClO_2. Except for a few 'outliers', these treatment sequences result in final THM values consistently below 100 $\mu g/l$. The use of the ClO_2- sequence results in average THM values of below 25 $\mu g/l$. The conventional treatment sequences are unable to achieve this. Figure 4c indicates the average THM values of the final treated water for each treatment line, and the THM formed, being the difference between the final water and raw water THM values.

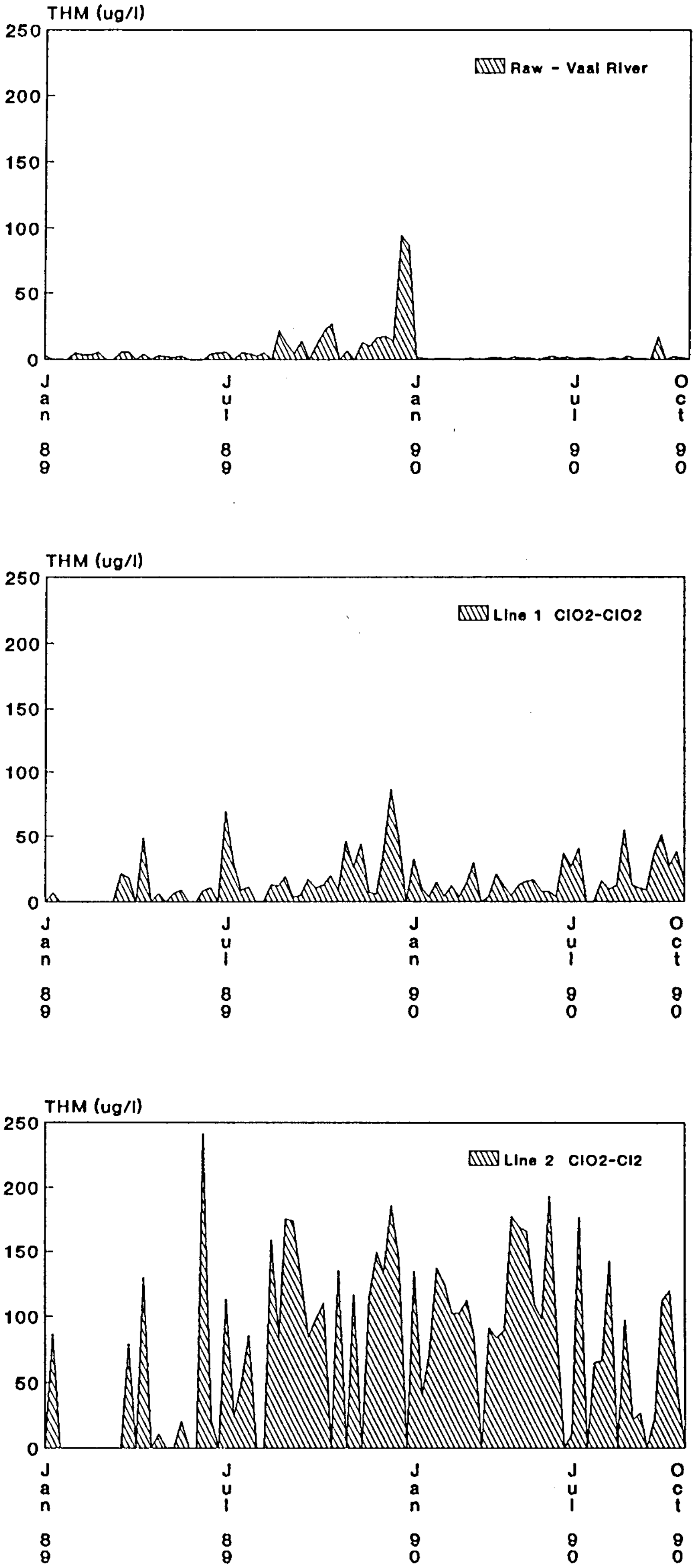


Figure 4a THM concentrations

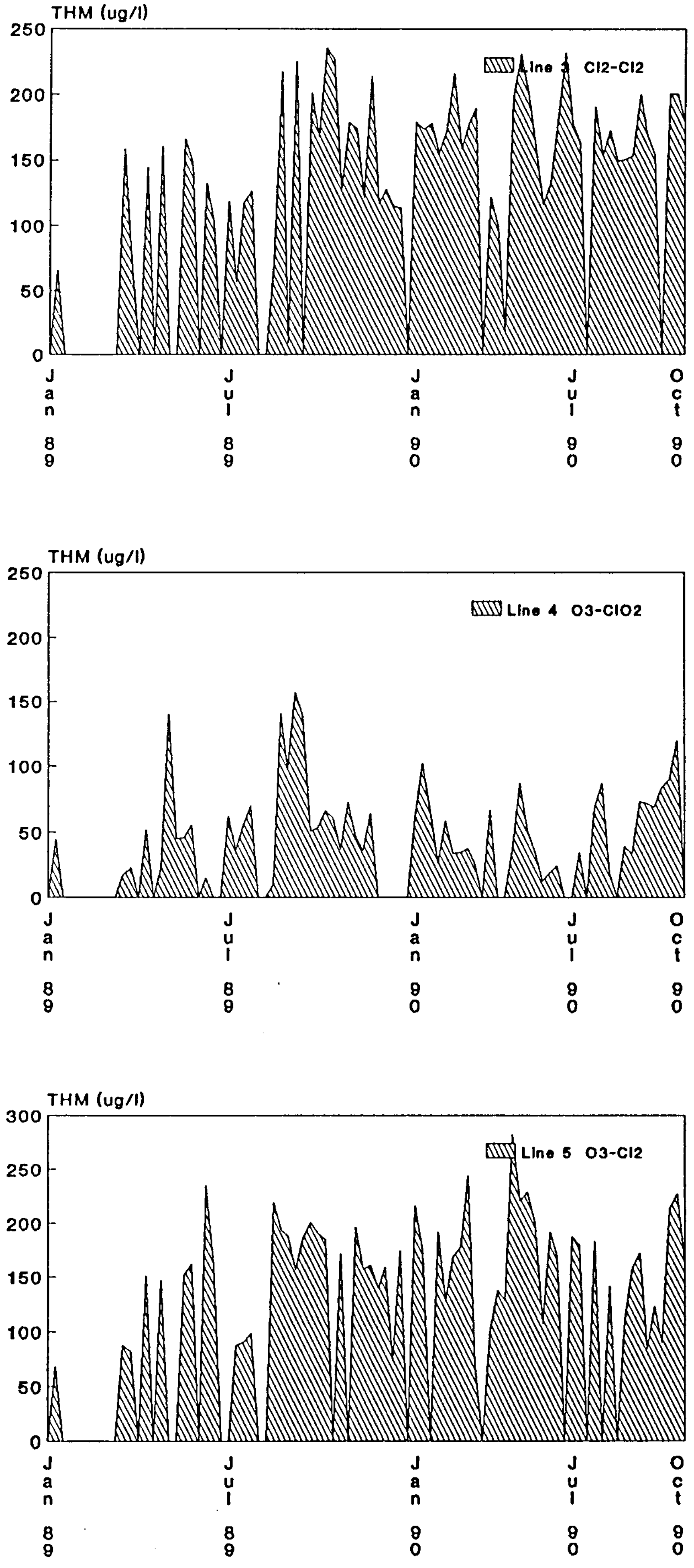


Figure 4b THM concentrations

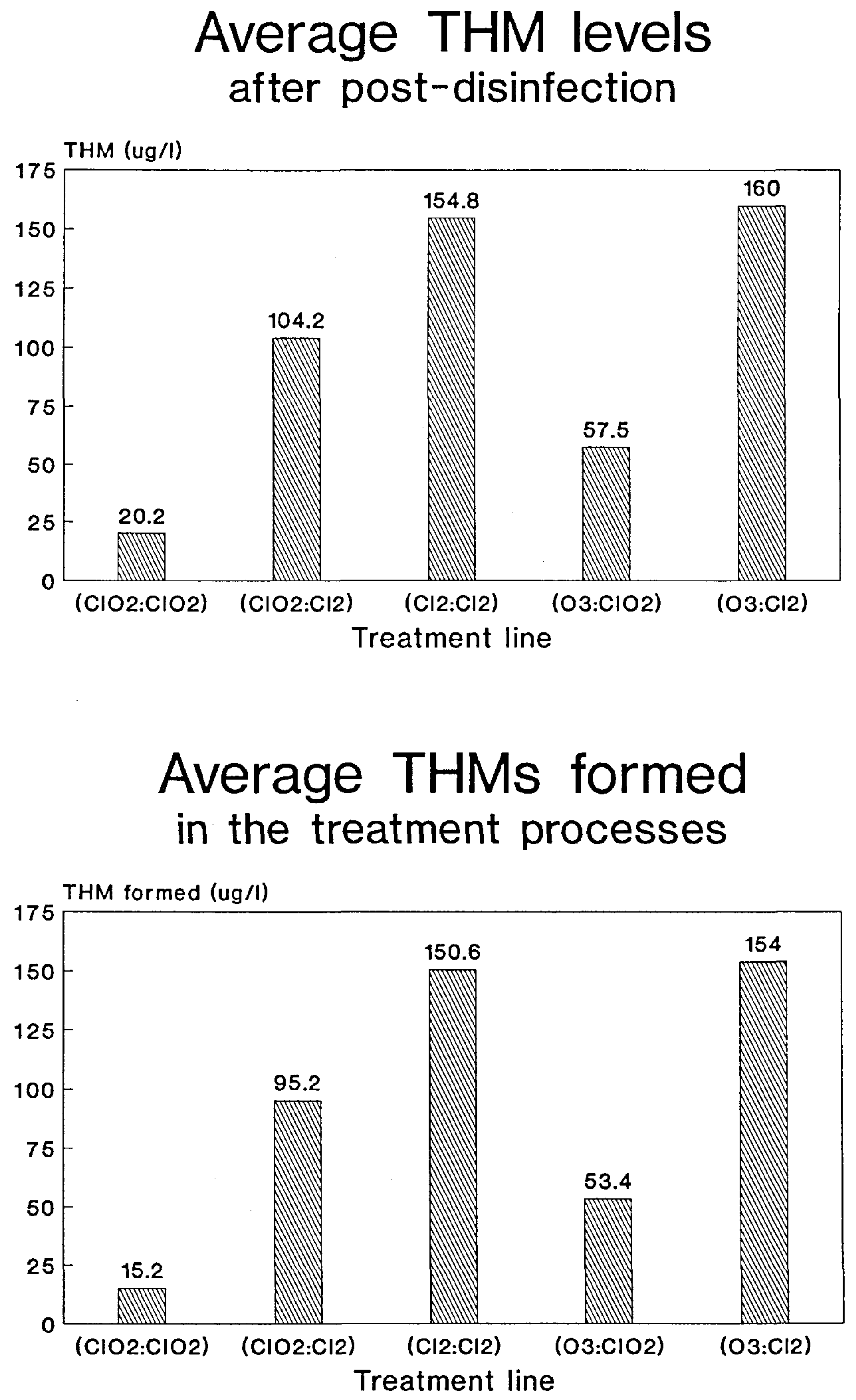


Figure 4c Effect of treatment on THM levels

Note that the pre-ClO_2 dose was often < 0.5 mg/l, and < 0.4 x TOC. The fact that line 2 could not reduce THM levels significantly may be attributed to this. Higher ClO2 dosing could have been applied, but the levels would have been excessive and not practical. On the other hand, despite ozone application being a single phase application, the final THM levels of line 5 are high (higher even than the chlorine-chlorine leg (line 3). This confirms the findings of Werdahoff and Singer (1987), and Graham et al (1989), but contradicts the findings of Grasso et al (1989).

Although the data appears cyclic in nature, there are no definite seasonal trends. The predominant chlorinated species are consistently chloroform and dichlorobromomethane. A typical composition of the THM species is given in table 1.

SAMPLE	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
raw + ClO_2	8	8	0.3	0
ClO_2 - ClO_2	9	5	0	0
ClO_2 - Cl_2	12	13	5	0
raw + Cl_2	35	12	4	0
Cl_2 - Cl_2	53	16	4	0
raw + O_3	6	8	1	0
O_3 - Cl_2	14	18	11	10
O_3 - ClO_2	8	8	2	0

Table 1 : Variation in THM species concentrations (12/12/89)

These results also indicate that when chlorine is added to the water, whether raw or treated, the majority of the chlorinated organics are formed. The GC-MS scan carried out in October 1990 (appendix B) also confirms that of the less volatile organics, the majority of the chlorinated species are to found in the chlorine - chlorine stream.

5.2 Chlorophyll removal, algal genera and algal cell damage

Chlorophyll as found in the algae present in the Vaal River, is removed in the treatment process through the settling and/or filtering of the algal cells in the treatment process. Hence in the final water little or no algal cells, and hence chlorophyll, should be present. However, when small cells remain viable and active they may pass through both the settling stage and the sand filters, and hence be found in the final water. One of the aims of pre-oxidation is to render the cells non-viable so that they may be more easily flocculated and hence removed in the treatment plant. When oxidation results in the rupture of the algae cell walls, flocculation may be enhanced due to the release of cellular polymers which have a natural affinity to other algal cells.

Hence when algal cells are found in great numbers in the final waters it could be that the pre-oxidant is unsuccessful in rendering the cells non-viable.

The results in the figures 5a, 5b and 5c indicate that in all cases chlorophyll removal was excellent, with removals of at least 95% but often 100%. No treatment leg resulted in significantly better results than another, although ozone treatment did give slightly better chlorophyll

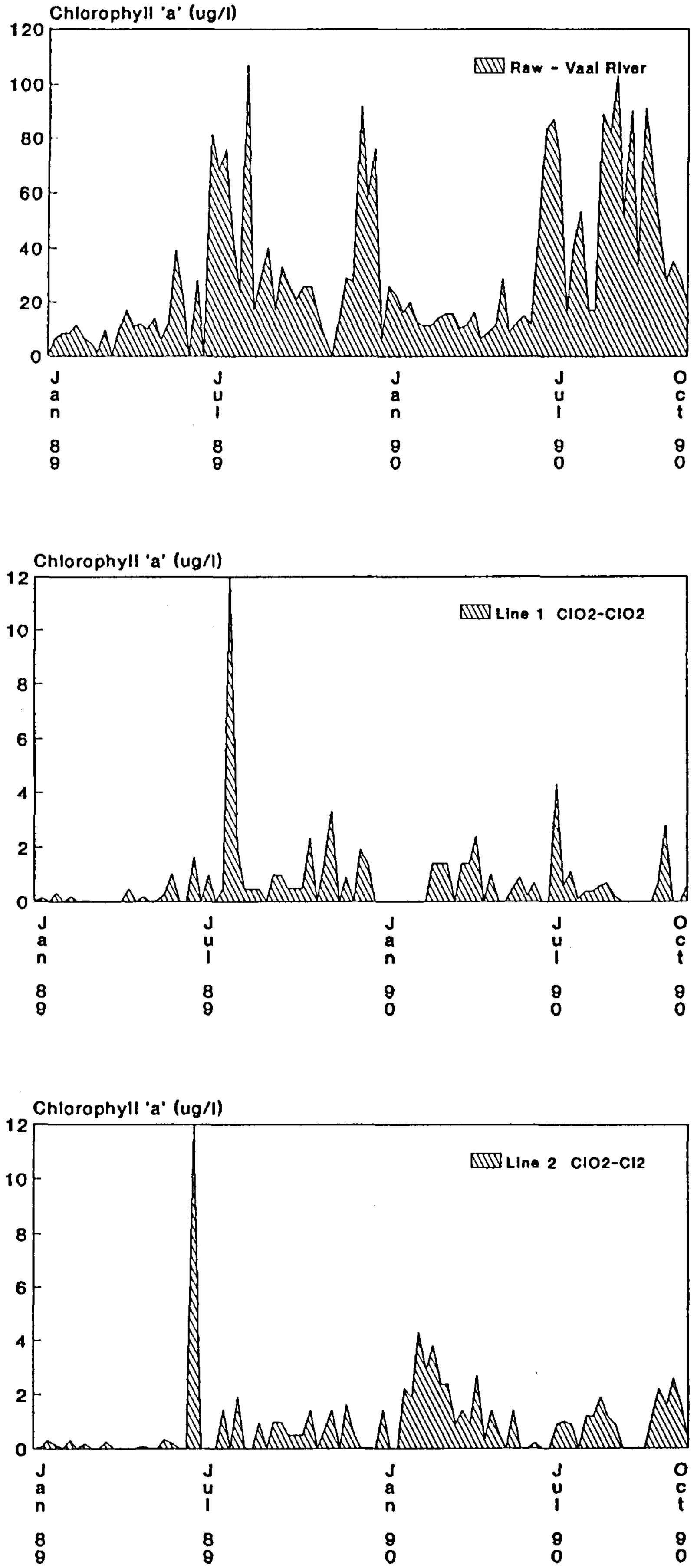


Figure 5a Chlorophyll 'a' concentrations

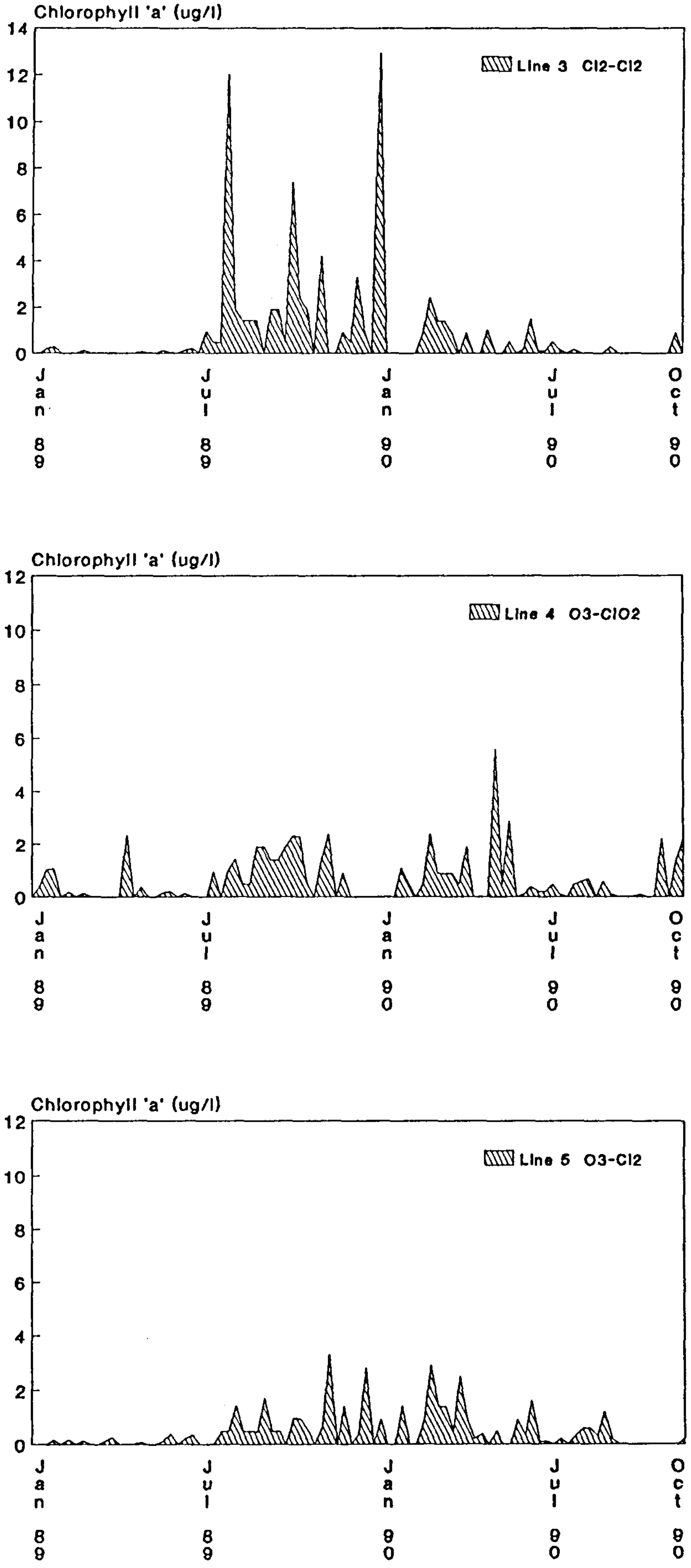


Figure 5b Chlorophyll 'a' concentrations

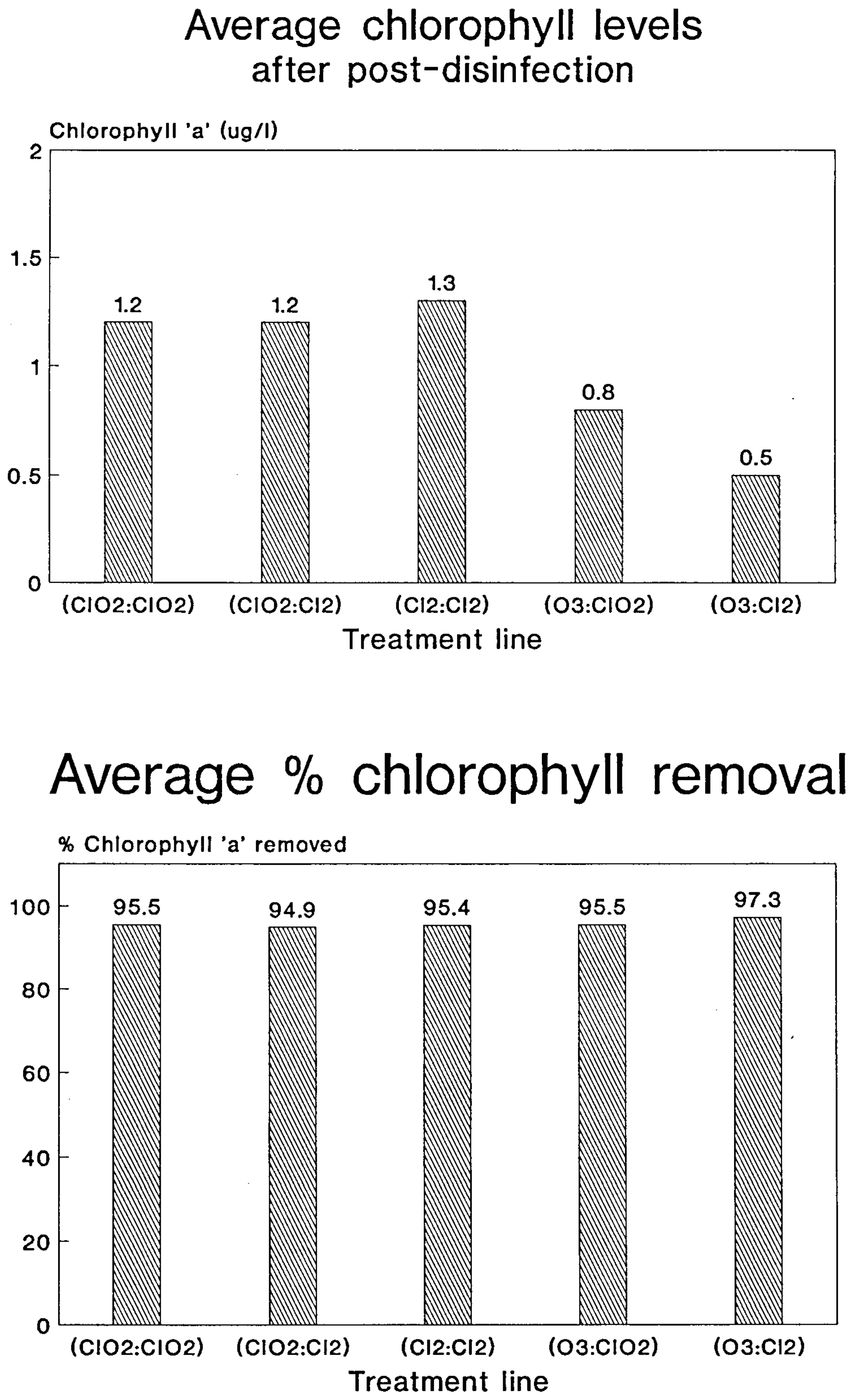


Figure 5c Effect of treatment on chlorophyll levels

removal overall. All algae counts over the period revealed that only small, microscopical cells pass through the filters. Most of these cells are coccus in shape and are difficult to identify. Most of the larger cells found in the raw water do not generally pass through the filters. Cells which have on occasions been found in the final water include Scenedesmus and Coelostrum.

Algal cell damage following pre-oxidation was observed microscopically. The following was observed:

Scenedesmus:	Chlorine dioxide treatment resulted in definite signs of internal cell damage and bleaching. At lower doses (0.5mg/l) damage was only slight.
	Chlorine treatment resulted in internal cell bleaching and slight damage, but less evident on the larger cells.
	Ozone treatment resulted in internal cell bleaching and cell contraction, but often the damage was minimal.
Cyclotella:	Chlorine dioxide treatment resulted in cell damage and internal bleaching, but less evident on the larger cells.
	Chlorine treatment resulted in cell bleaching in almost all cells, with some signs of cell contraction and damage.
	Ozone treatment resulted in definite internal cell damage and bleaching.
Sphaerocystis: (less common)	Chlorine dioxide treatment resulted in cell bleaching and damage.
	Chlorine treatment resulted in some cell damage.
	Ozone treatment resulted in minimal or no damage.

Other less common algal species showed similar damage to those above, with chlorine dioxide treatment often resulting in more significant damage than chlorine or ozone treatment. It appears that all oxidants cause cell damage and bleaching, provided the dose is sufficient to meet the immediate demand and maintain a residual for a few minutes. Hence while all pre-oxidants are able to render the cells non-viable, cell damage which may result in enhanced flocculation is not always significant.

5.3 Tastes and odours

The project team were not able to carry out taste and odour evaluations, having missed the critical period in June 1989 when odours were prevalent (about one week) due to technical problems with the pilot plant. During 1990 no taste and odour problems with the raw water arose.

5.4 Manganese and iron removal

The WTRWC utilizes $KMnO_4$ addition as a standard treatment step to aid manganese removal on the main plant (on both the chlorine and ozone pretreatment legs). On the pilot plant no $KMnO_4$ was added, and hence all manganese removal was due to oxidation by ClO_2. In general the removal of manganese has been very good on all legs of the plant (figures 6a, 6b and 6c). Where $KMnO_4$ was added (i.e. main plant - lines 3, 4 and 5), removals of 95% on average were achieved. With ClO_2 (pilot plant - lines 1 and 2) average removals of 80% were achieved for post treatment with ClO_2, and 76% with post treatment by chlorine. These percentages could have been even higher, as poor removals were obtained when lime dosing problems and low ClO_2 dosing were experienced on the pilot plant. After the ClO_2 dose on the pilot plant had been increased, manganese levels higher than 0,1 mg/l were not found.

The removal of soluble iron by all legs of the plant was less satisfactory (figures 7a, 7b and 7c). However this could be attributed to both the low levels in the raw water (generally < 0.1 mg/l), and the fact that ferric sulphate is added as a coagulant. Iron levels in the final water were generally below 0,1 mg/l.

5.5 Organic carbon removal

As expected, the removal of dissolved organic carbon by all the treatment processes in use is minimal. In all cases the average removal is approximately 20%. The oxidants do not oxidize the organics to CO_2 and water, but at most modify them to a different molecular form. See figures 8a, 8b and 8c.

5.6 Chlorine dioxide byproducts

The level of byproducts found in the streams treated with ClO_2 was monitored. In some countries the maximum level of ClO_2 and its byproducts (chlorite and chlorate) permitted in drinking water is 1,0 mg/l. However, the measurement of chlorite and chlorate in water samples is somewhat difficult except in the case of pure solutions. In the Vaal River water there exists a number of reducible products which will give false readings in the chlorite and chlorate determinations. This is particularly true at the low pH's at which the tests are carried out (2,0 and 0,5 for chlorite and chlorate respectively), and has resulted in values of total ClO_2 byproducts being more than the actual ClO_2 dosed. The results are presented in figures 9a and 9b. Of interest is that from April to October 1990 very little chlorate was found in the final waters. Chlorite levels were generally higher than chlorate levels.

5.7 Biofouling

Four Pedersen's devices were installed for a period of 4 weeks to monitor the fouling of 3 different materials (mild steel, stainless steel and PVC). The devices were installed on the raw water line (control), and on the 3 lines following pre-oxidation (ClO_2, Cl_2 and O_3). A through flow of 16 l/min was maintained on each device, temperatures were in the range of 23 to 26°C, and the oxidant doses were as follows:

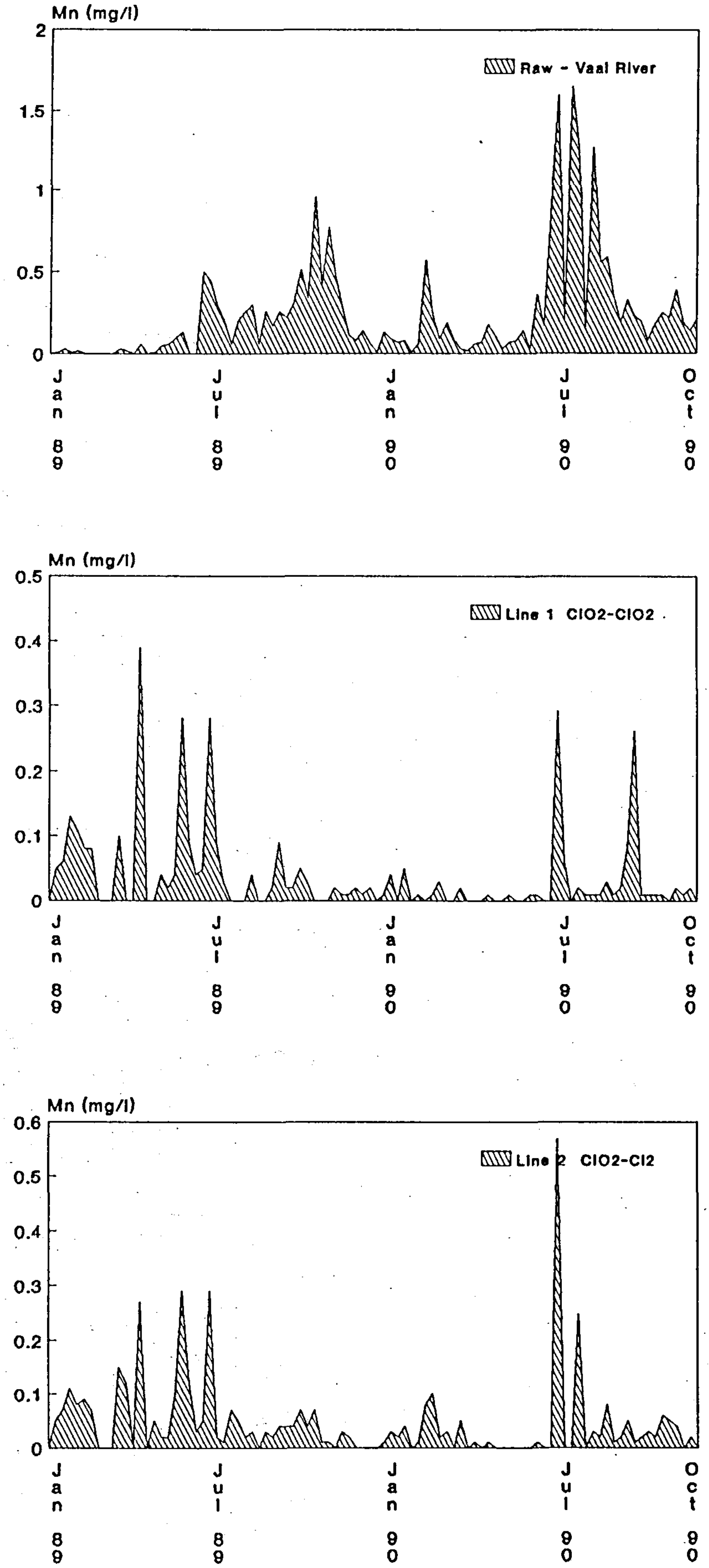


Figure 6a Manganese concentrations

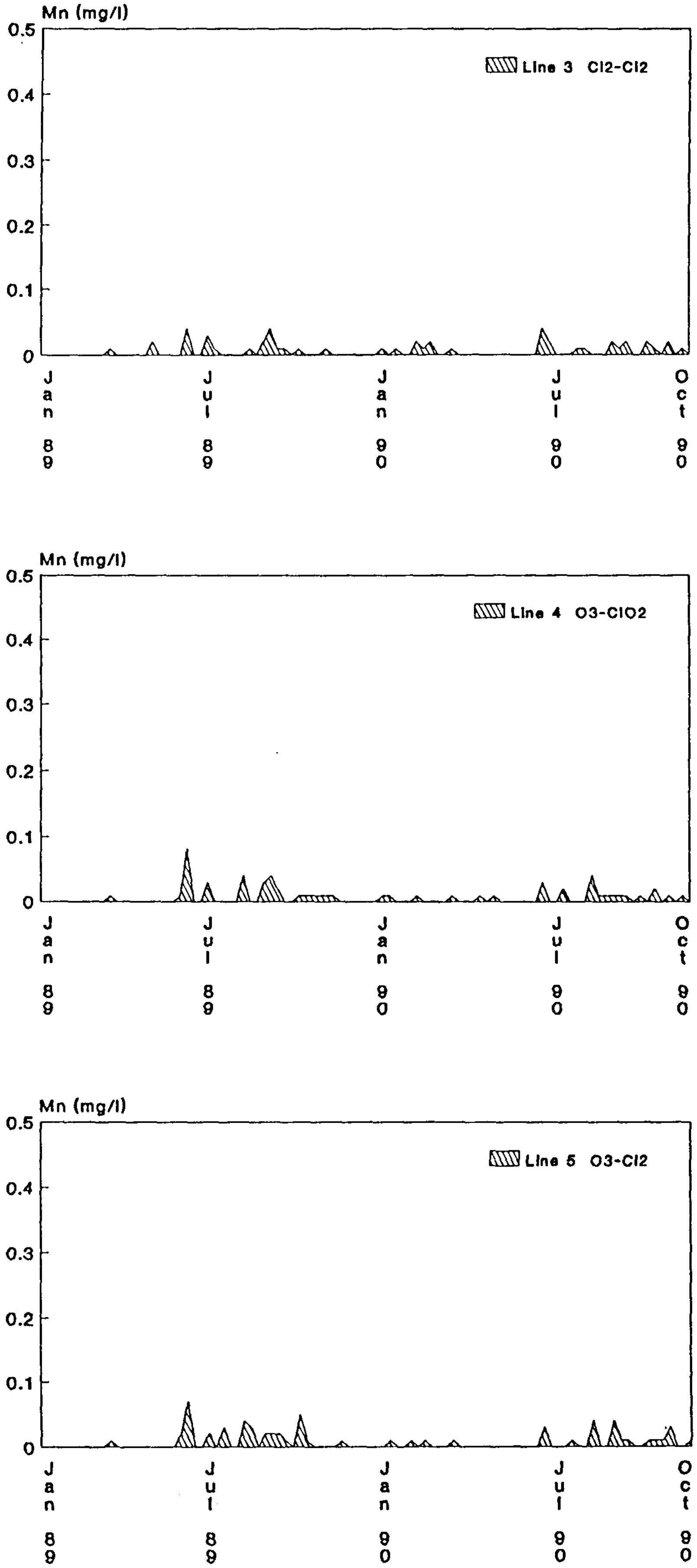


Figure 6b Manganese concentrations

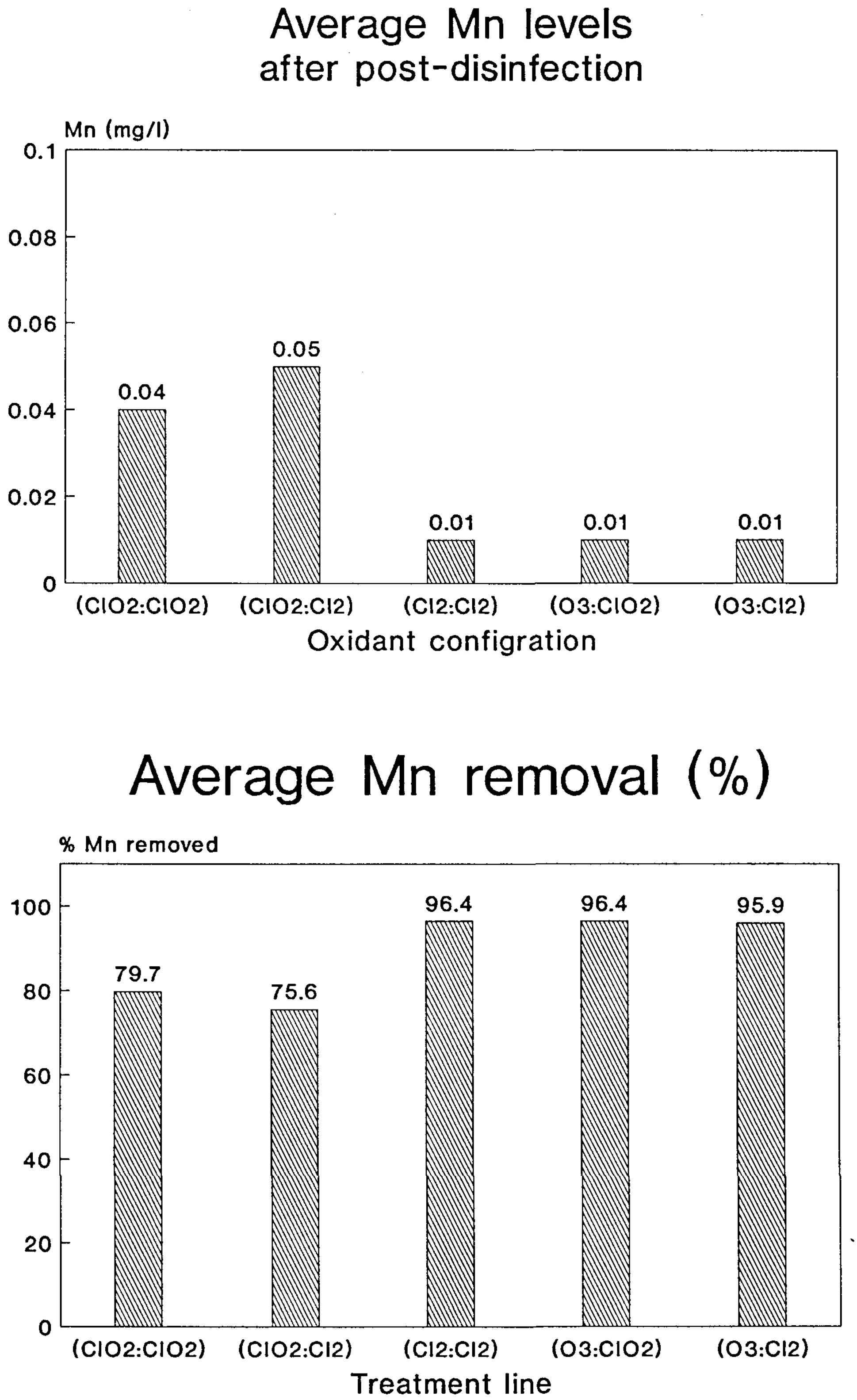


Figure 6c Effect of treatment on Mn levels

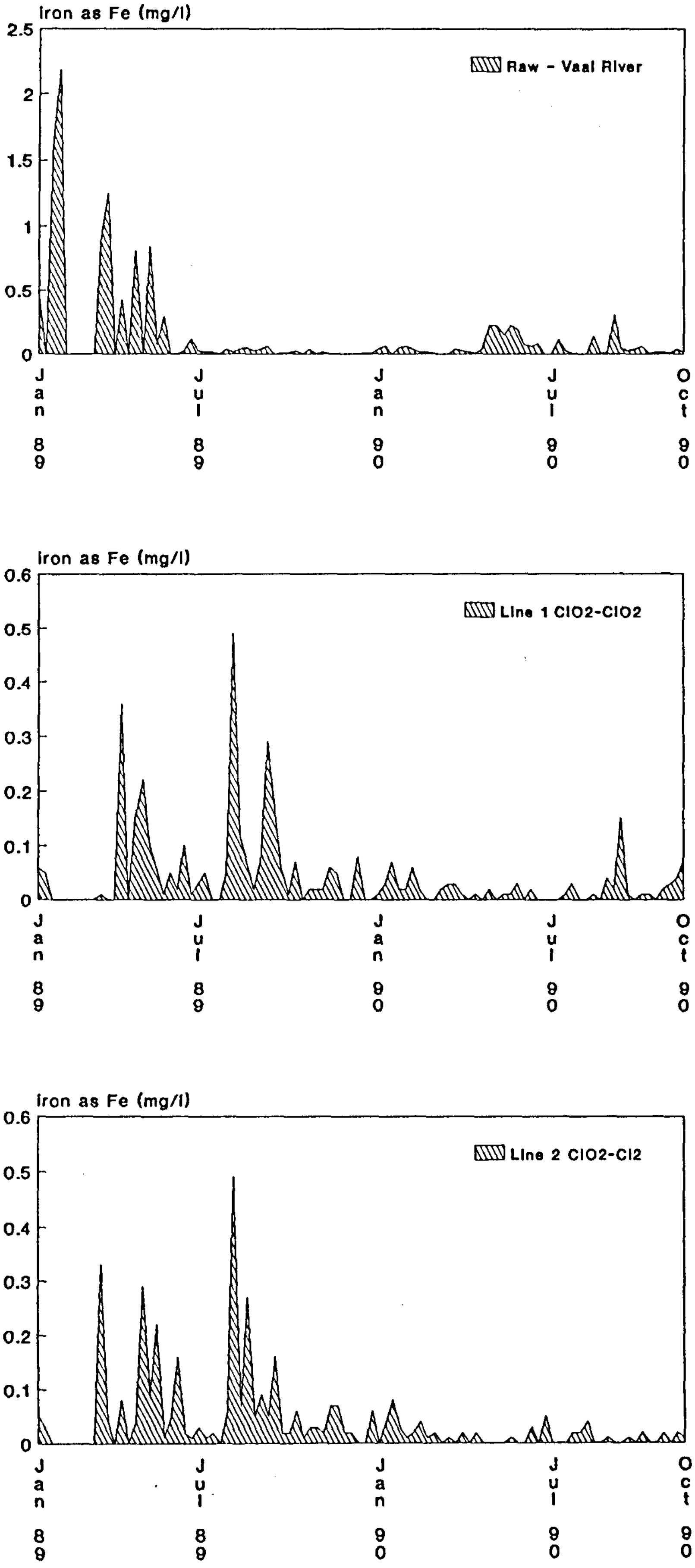
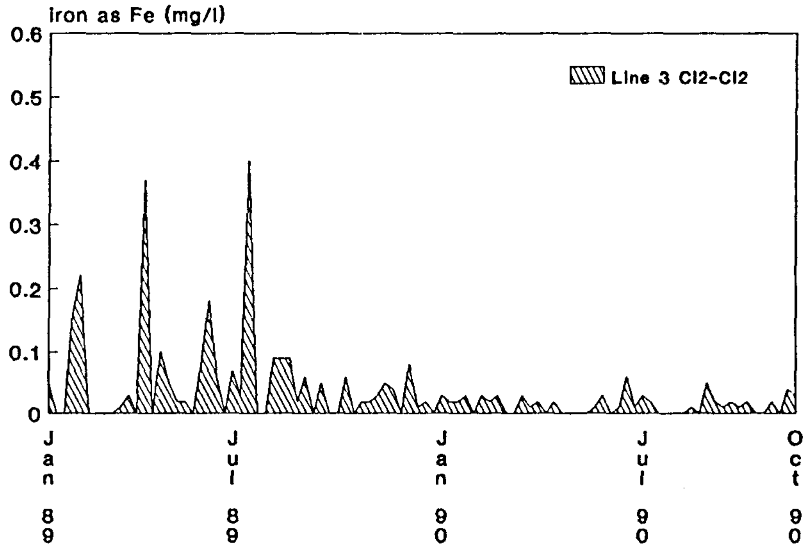
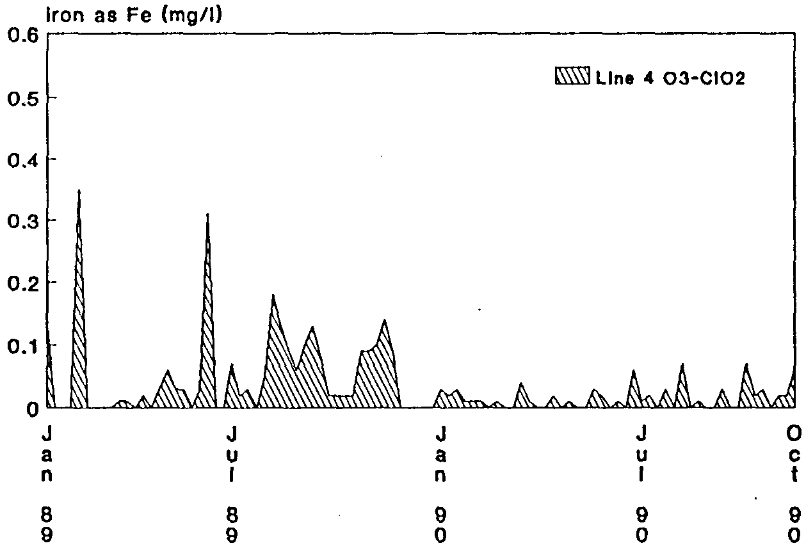


Figure 7a Iron concentrations





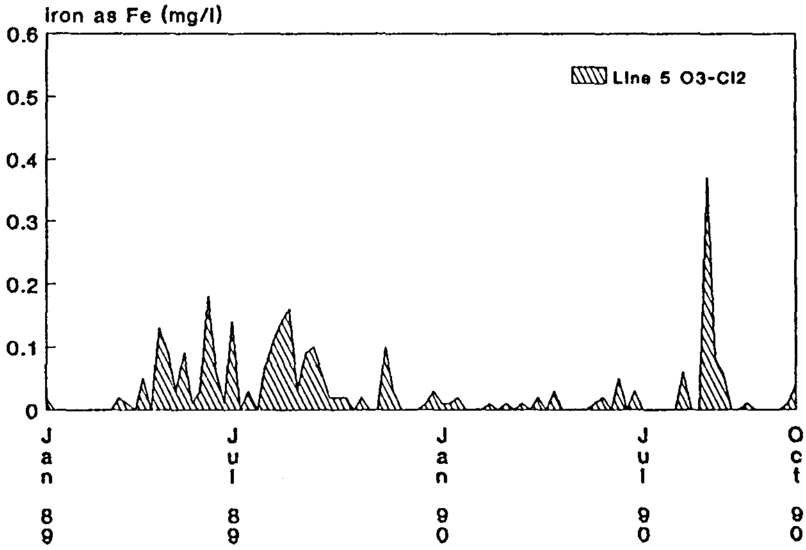


Figure 7b Iron concentrations

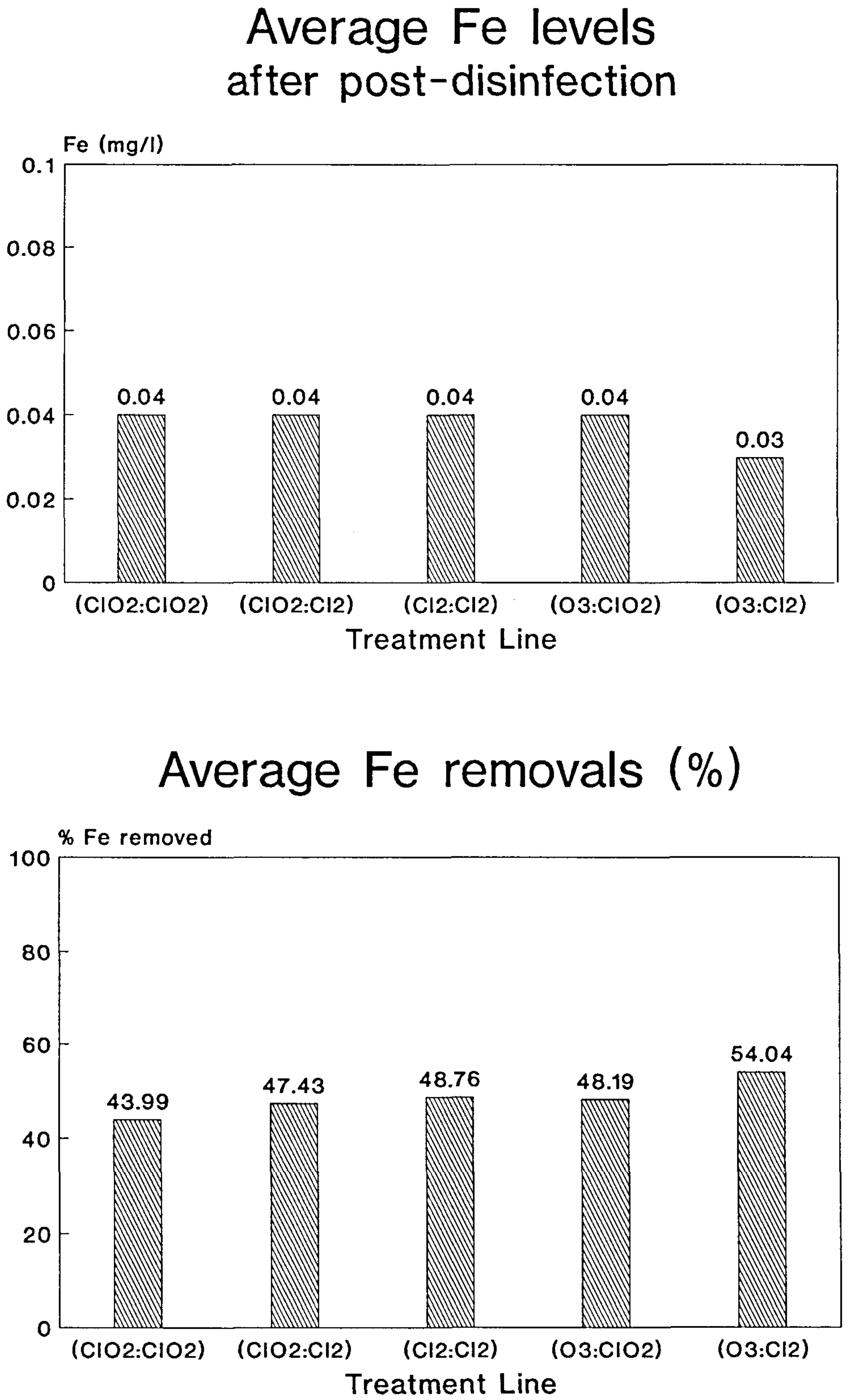


Figure 7c Effect of treatment on iron levels

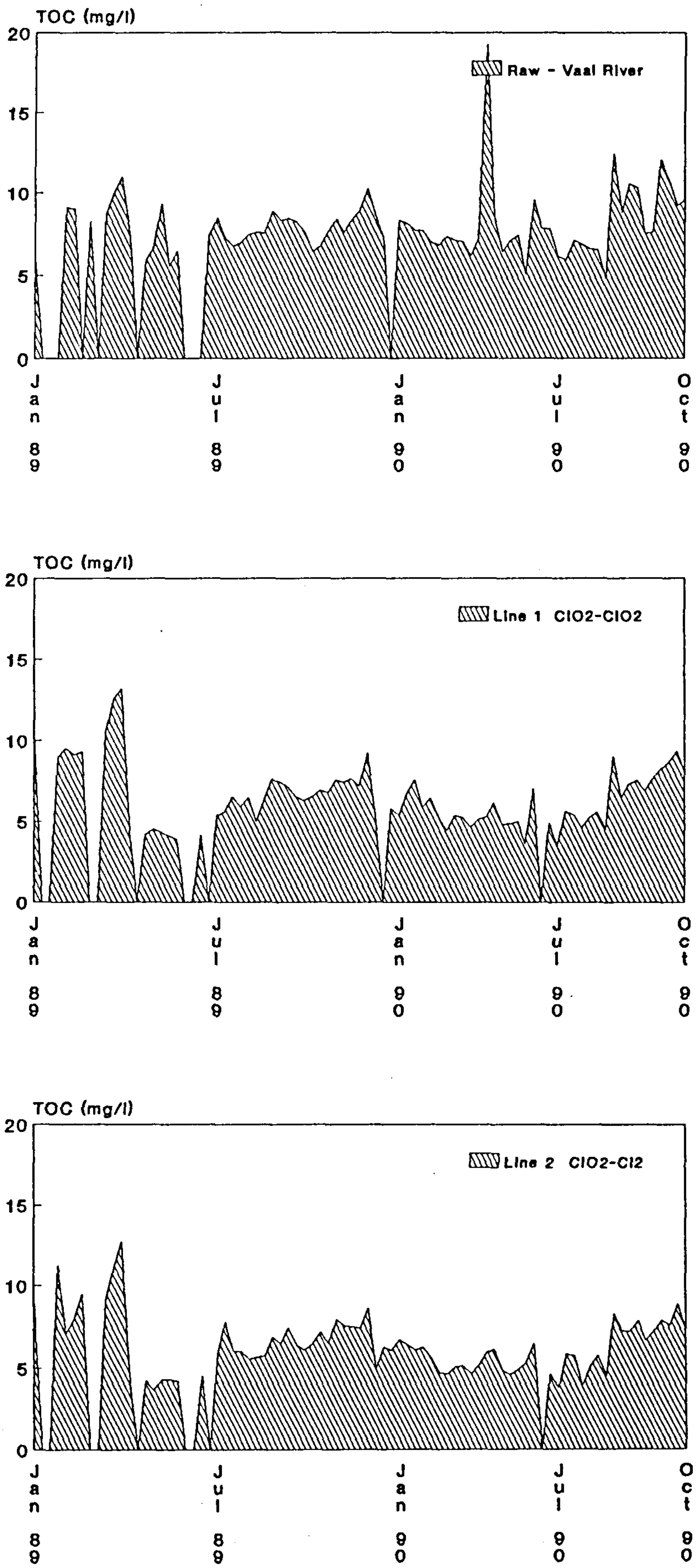


Figure 8a Total organic carbon concentrations

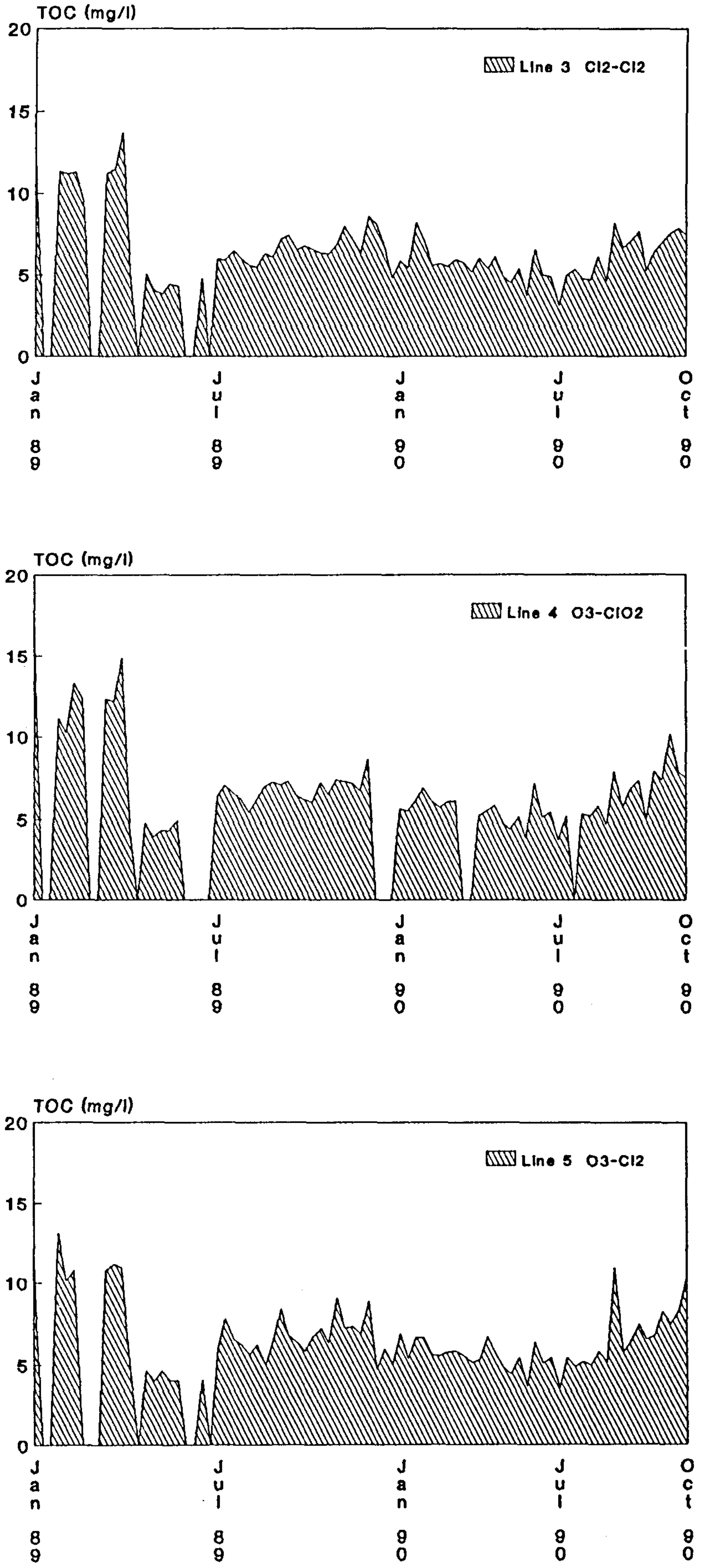


Figure 8b Total organic carbon concentrations

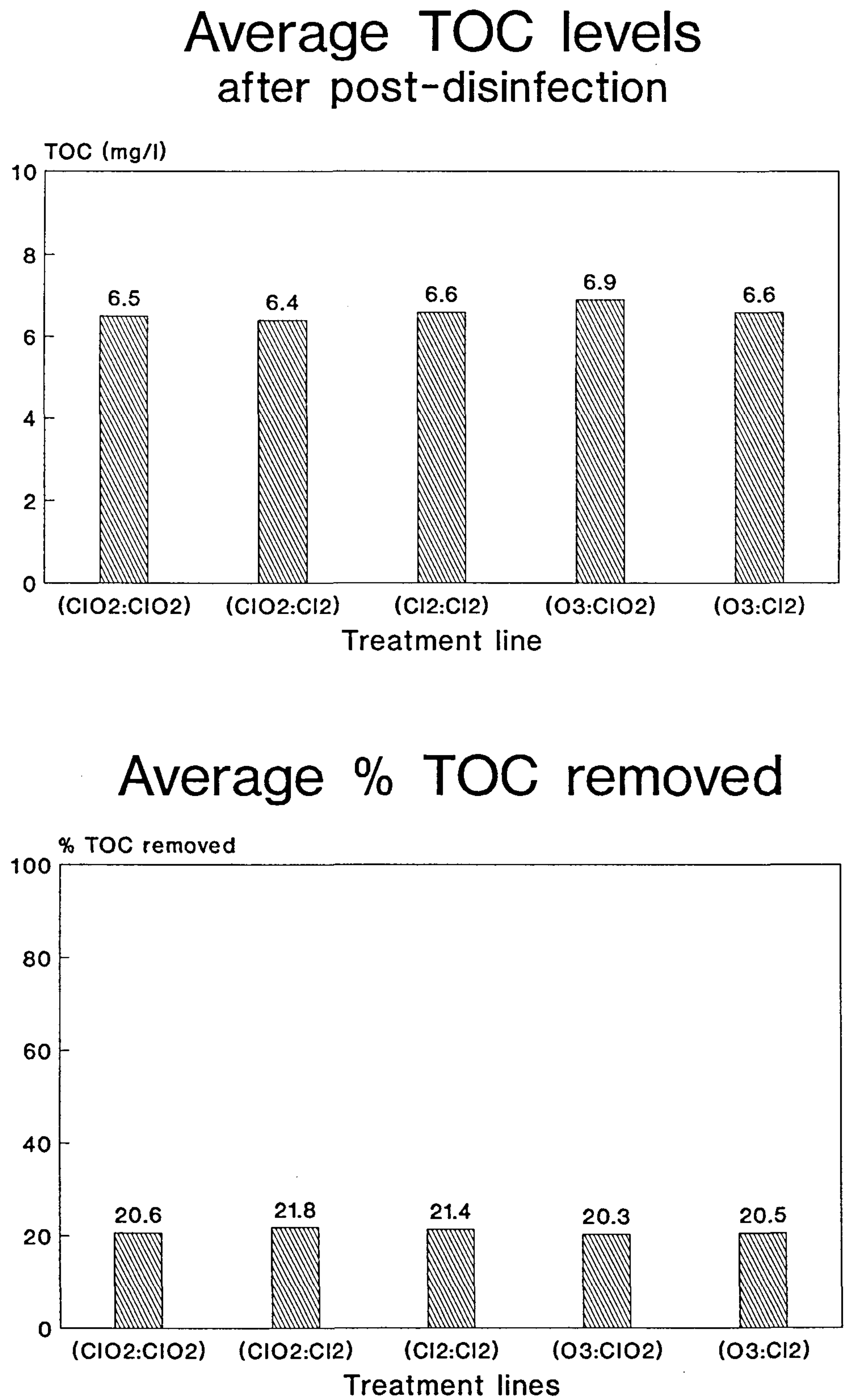


Figure 8c Effect of treatment on TOC levels

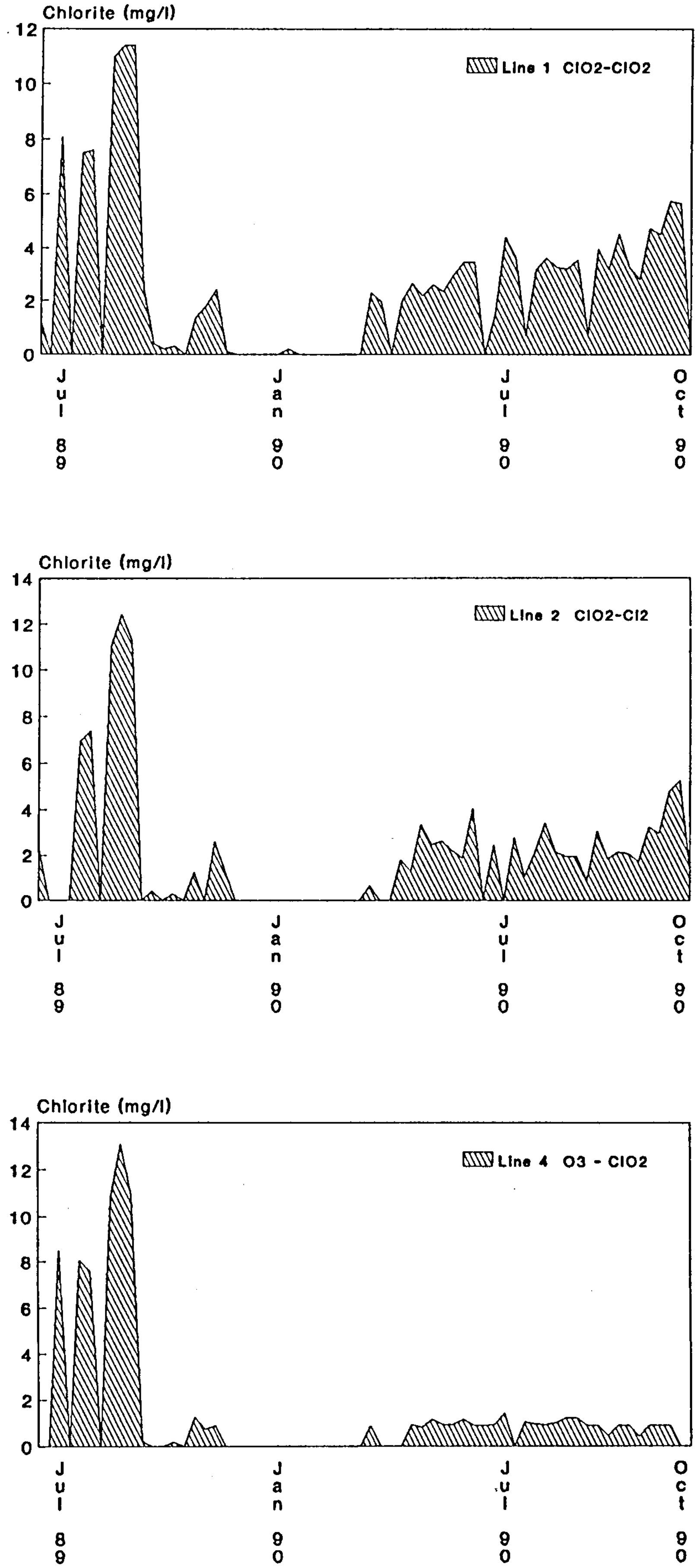


Figure 9a Chlorite levels in streams treated with chlorine dioxide

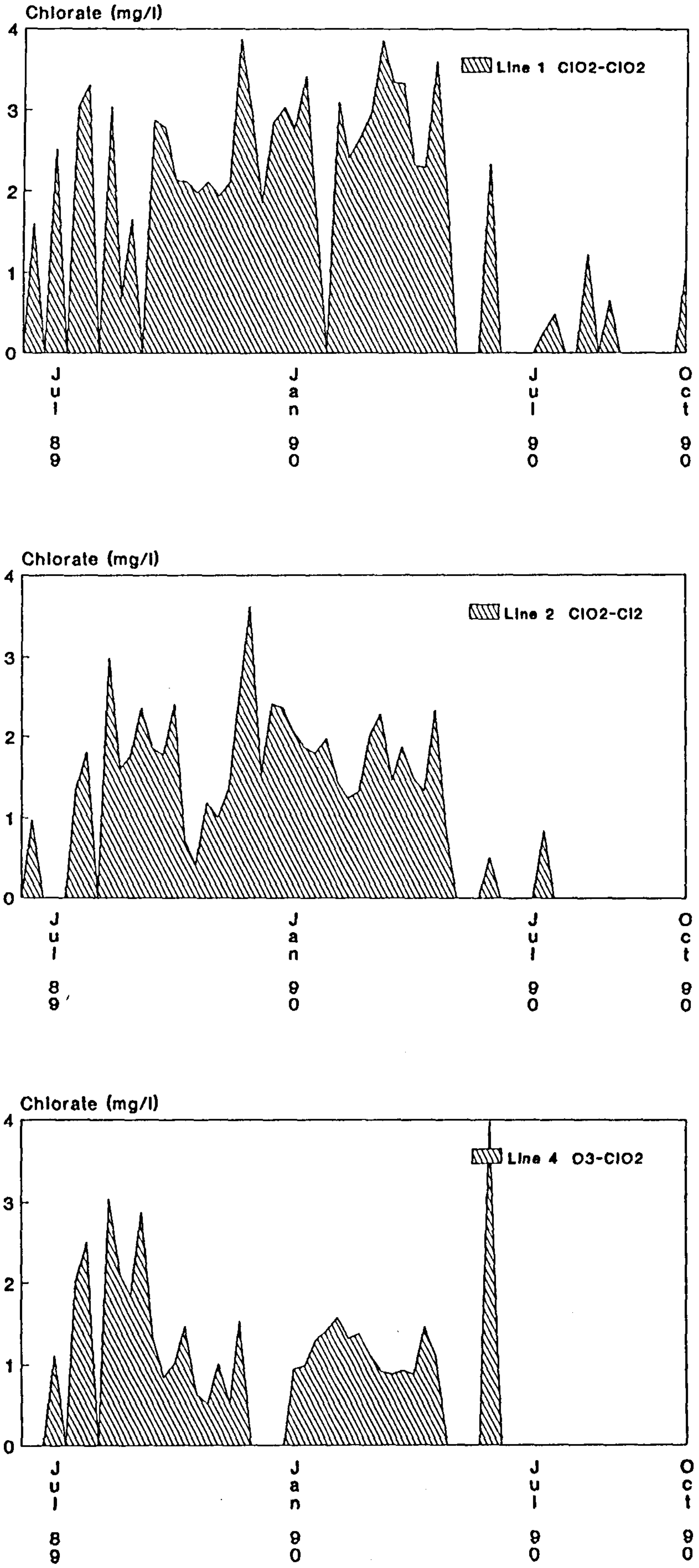


Figure 9b Chlorate levels in streams treated with chlorine dioxide

ClO_2 : 2.5 to 3.0 mg/l (after at least 4
Cl_2 : 3.5 to 5.0 mg/l minutes contact time)
O_3 : 4.5 mg/l

Results are presented in table 2 below:

SAMPLE	RAW	ClO_2	Cl_2	O_3
PC on MS	5.20	1.64	12.30	23.70
PC on SS	8.38	7.92×10^2	7.66×10^2	4.48
PC on PVC	0.87	7.25×10^3	4.38×10^4	2.28

Notes: All valves x 10^6 unless otherwise indicated, counts are as number of cells per cm^2.
PC = plate count, being a count of all the viable bacteria on the test section.
MS=mild steel, SS=stainless steel, PVC=uPVC

Table 2: Bacterial counts on Pedersen's devices after 4 weeks

DAPI tests whereby the bacterial DNA is stained with a fluorescent stain for easier counting were also carried out, but the results were somewhat contradictory. Hence only the standard plate count results are given here.

These results are interesting in that ozonation showed a slight increase in counts on the MS and PVC, probably due to the organics being broken down to more biodegradable forms. Chlorine and chlorine dioxide showed some reductions in counts, especially on SS and PVC. Chlorine dioxide was slightly better than chlorine treatment for preventing biological buildup on surfaces during the test.

5.8 Disinfection

Disinfection of the final water was achieved in all cases, with no coliforms and total counts of less than 40 bacteria per ml. Even after only pre-oxidant addition there were no coliforms present. The disinfection ability of the oxidants was not adversely affected by the water quality conditions existing at the plant.

5.9 GC-MS analysis of organics present

A general analysis of the organics present was carried out to determine the relative effect of the different treatment lines on the organics present in the water. This was undertaken towards the end of the project period, i.e. in September 1990. Samples of the raw and final waters were passed through *Waters* Sep Pak C18 cartridges to extract the organic compounds. The organic compounds on each cartridge were eluted with acetonitrile and analysed by capillary gas chromatography-mass spectrometry. The results (appendix B), although not specific, do indicate some important trends.

- The raw water contains mainly large, longer chain molecules and benzine compounds.

- The chlorine treated stream contains many chloro-substituted compounds as a result of breakages of large molecules, as well as number of shorter chain molecules (including N compounds).

Ethylbenzine and butyl butanoate remain unaffected, but a number of small and large cyclic molecules are being produced. There is a simplification of propyl ester to pentyl ester.

- The chlorine dioxide treated streams do not contain significant amounts of chlorinated compounds. Xylene is relatively unaffected, but as with chlorine propyl esters have been simplified to pentyl esters. There is minimal breakdown of larger molecules to form smaller ones. Sulphur compounds are becoming visible.
- The ozone treated stream is difficult to interpret. Sulphur and silicon compounds are present, and very large complicated molecules. This is possibly the result of the catalytic affect of ozone.

These preliminary results indicate that chlorination tends to result in both chlorine addition and oxidation reactions, whereas chlorine dioxide and ozone treatment results primarily in oxidation reactions.

6. OPERATION OF THE PILOT PLANT

Since the middle of August 1989, the ClO_2 generator operated well, despite major problems encountered previously. During 1988 results were unreliable due to a number of technical problems being experienced. Initially only relatively short filter runs were possible. However after installing tube settlers in the settler, runs of 24 hours or longer were possible. Perhaps the major problem which has been encountered is the difficulty of dosing low levels of lime into the pilot plant due to dosing pump limitations. In general the pilot plant has not been able to achieve the same turbidity levels as achieved on the main plant, although turbidities have seldom been above 2,5 (figures 10a and 10b). It is felt though that the differences have been minor and the results obtained on the pilot plant would reflect closely the results expected for similar treatments on a large scale.

The chlorine, ozone and chlorine dioxide dosages used on both the main and pilot plants are shown in figure 11. On the pilot plant dosages have been set to give a residual of ± 0,5 mg/l in the raw water before flocculant addition, and a final residual of between 0,1 and 0,5 mg/l.

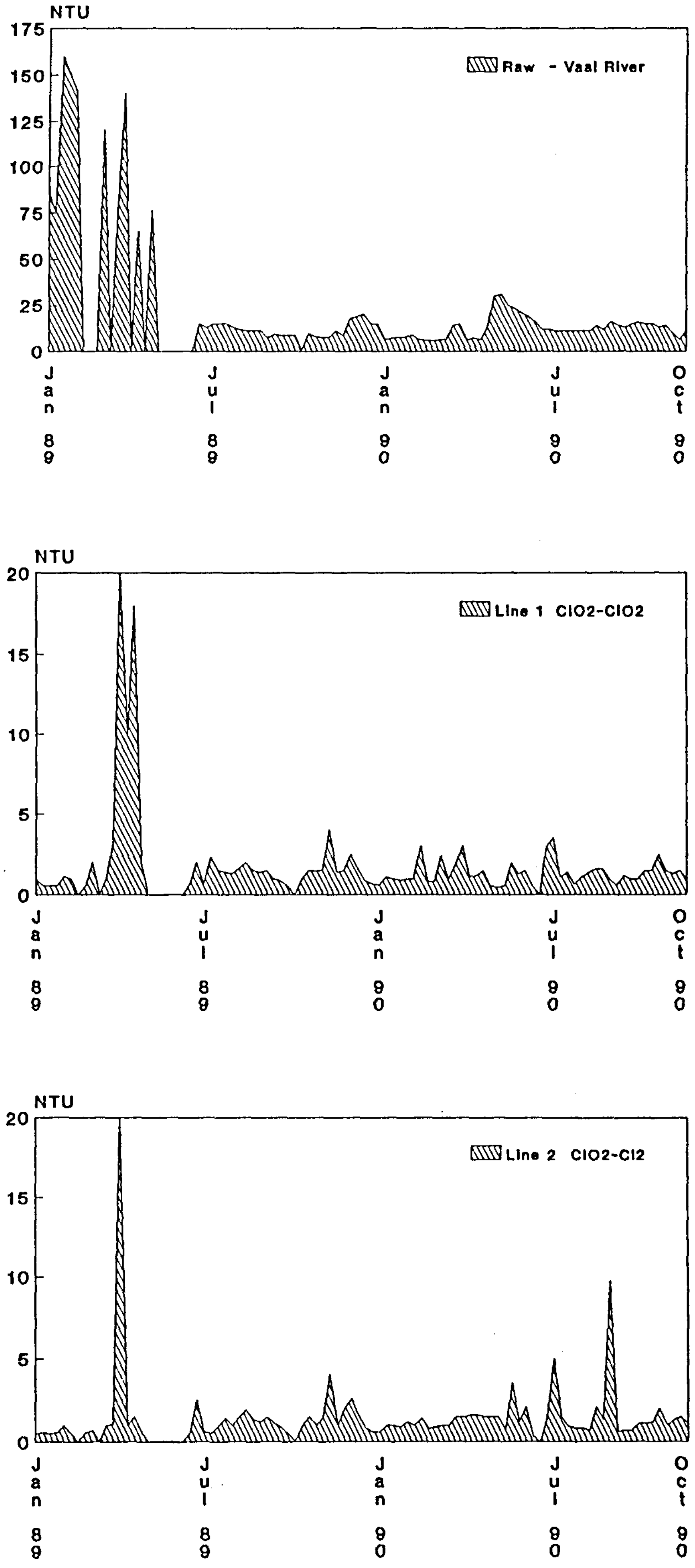


Figure 10a Turbidity levels

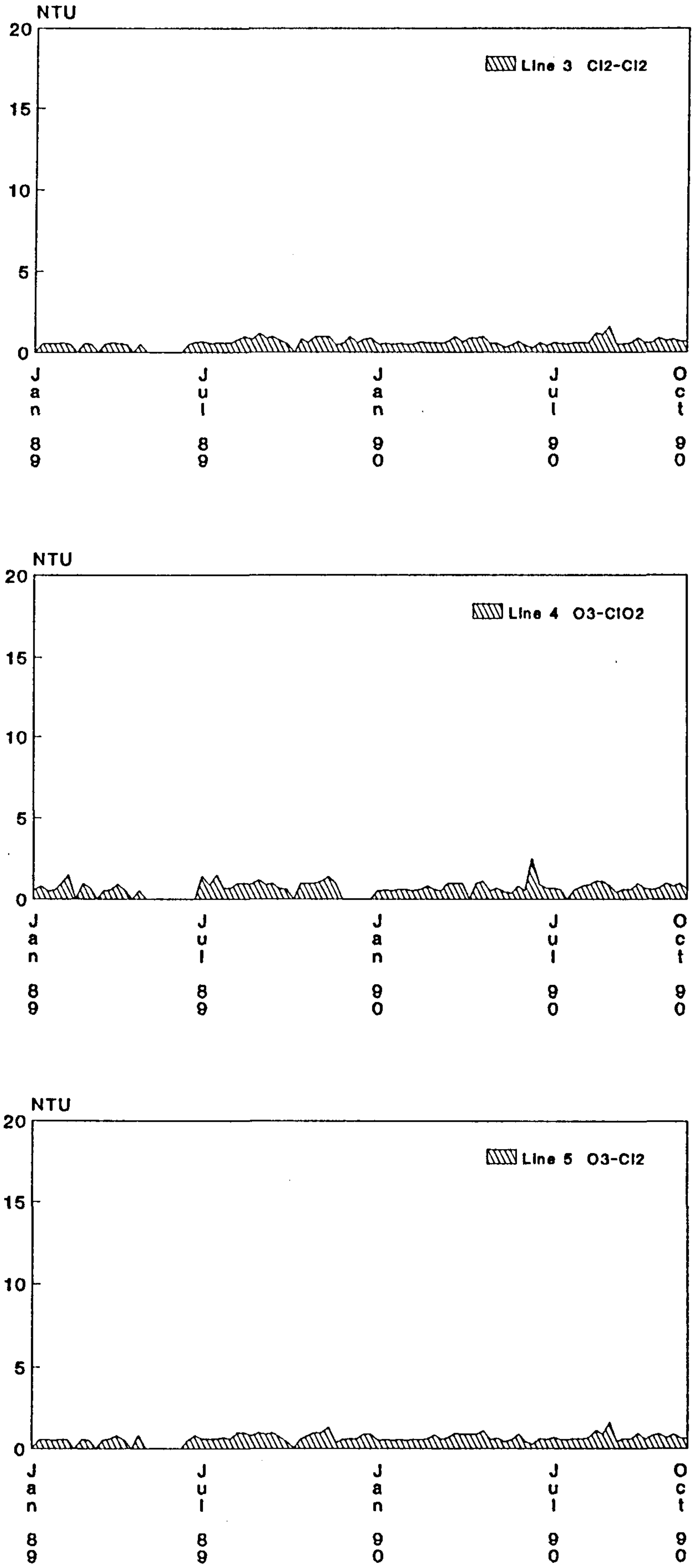


Figure 10b Turbidity levels

7. ECONOMIC CONSIDERATIONS

The relative costs of the different oxidant options based on a 100M*l* per day unit plant size, is as follows (1990 prices):

	DOSE mg/*l*		Op costs R/M*l*		TOT. OP. COSTS R/M*l*	CAPITAL COSTS R	TOTAL COSTS R/M*l*
	pre	post	pre	post			
ClO_2:ClO_2	3.5	1.5	77	33	110	20-50 000	110.20
ClO_2:Cl_2	3.5	1	77	2	79	30-70 000	79.30
Cl_2:Cl_2	4	2.5	8	5	13	20-70 000	13.25
O_3:ClO_2	4	1	5	22	27	4-10m	66.70
O_3:Cl_2	4	1.5	5	3	8	4-10m	47.70

Note: capital redemption is based on a 10 year life time and 16% interest.

Chlorination, as expected, is by far the least cost option. The capital redemption has little effect on the costs of chlorine and chlorine dioxide, but has a significant effect on the cost of ozone. Clearly the high running costs associated with the use of ClO_2 will need to be critically assessed against the benefits achieved.

8.0 CONCLUSIONS

This project set out to assess whether alternative combinations of oxidants could result in a significant improvement of the treatment process for eutrified source waters such as found in the lower Vaal River. The results of the study indicated that while some parameters indicated a significant improvement, others were less significant. The additional costs associated with the use of alternative oxidant combinations would need to be carefully assessed against the benefits which will be achieved before a decision to use the alternatives were taken. The table following indicates the relative performance of the various combinations in terms of the parameters measured.

	ClO_2 ClO_2	ClO_2 Cl_2	Cl_2 Cl_2	O_3 ClO_2	O_3 Cl_2
THM formation	+	+++	+++++	++	+++++
Chlorophyll removal	++++	++++	++++	+++++	+++++
Algal cell damage	+++++	+++++	+++++	++++	++++
Manganese removal	++++	++++	+++++	+++++	+++++
Iron removal	++++	++++	++++	++++	+++++
TOC removal	+	+	+	+	+
Biofouling control	++	++	++	-	-
Disinfection	+++++	+++++	+++++	+++++	+++++
Operational costs	+	++	++++	+++	+++++
Capital costs	+++++	+++++	+++++	+	+
Total costs	+	++	+++++	++	+++

NOTE : The 3 streams with chlorine and ozone as pre-oxidants were also treated with between 0.1 and 0.8 mg/l of $KMnO_4$ to aid manganese removal in particular.

+ implies low efficiency or high costs
+++++ implies high efficiency or low costs

From this the following conclusions can be drawn from the use of the combination of oxidants as tested at Stilfontein on the lower Vaal River:

ClO_2 - ClO_2 : THM formation is significantly minimised when compared to the other treatment lines to values well within the 100 µg/l level. Algae deactivation and subsequent chlorophyll removal is very effective. Manganese and iron removal is good - without the aid of $KMnO_4$. Biofouling is controlled to a limited extent in the raw water lines. Disinfection is excellent. Running costs are extremely high.

ClO_2 - Cl_2 : THM formation is minimised to values at the 100 µg/l level. Algae deactivation and subsequent chlorophyll removal is very effective. Manganese and iron removal is good - without the aid of $KMnO_4$. Biofouling is controlled to a limited extent in the raw water lines. Disinfection is excellent. Running costs are very high.

Cl_2 - Cl_2 : THM formation is high with values well above the 100 µg/l level. Algae deactivation and subsequent chlorophyll removal is very effective. Manganese and iron removal is good - but with the aid of $KMnO_4$. Biofouling is controlled to a limited extent in the raw water lines. Disinfection is excellent. Running costs are low.

O_3 - ClO_2 : THM formation is low, although slightly higher than for the ClO_2-ClO_2 treatment. This is primarily due to the fact that no free chlorine is added to the water. However, ClO_2 and O_3 will convert bromides to free bromine, and hence result in some THM formation. In addition the ozone treated stream on the main plant is not totally isolated from the chlorine treated stream, and hence some of the THMs measured may have resulted from the chlorine treated stream. Ozone was the most effective for chlorophyll removal, despite cell damage often appearing to be only slight. Manganese and iron removal is good, again in combination with $KMnO_4$. Biofouling is not controlled with pre-ozonation, and may even be slightly enhanced. Excellent disinfection was achieved. Running costs are medium when compared with the other treatment options. Capital costs for the generation of ozone are very high, and make a significant impact on the overall cost of ozone treatment. However, the total costs are significantly less than for ClO_2 treatment for pre-oxidation.

O_3 - Cl_2 : THM formation is the highest of all the treatment combinations, although only slightly higher than the chlorine-chlorine treatment above. Ozone, as found in other studies reported in the literature, increases the formation of THMs when post treated with chlorine addition. This is most likely due to modification of the organics present by ozone to be more susceptible to THM formation. However the effect when compared to chlorine pre-oxidation is only slight. Chlorophyll removal was very good through pre-ozonation. Manganese and iron removal, with the aid of $KMnO_4$, is very good, maintaining levels well below 0.1mg/*l*. Biofouling is as for ozone treatment stated above. Disinfection was excellent, and running costs low. However capital costs for the generation of ozone are very high, and make a significant impact on the overall cost of ozone treatment.

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APPENDIX A : SAMPLING SCHEDULE

	pH	cond.	turb.	residual	Mn	Fe	TOC	Chlorophyll	THM	Algae	Tot plate count	Tot coli	Faec coli
Raw	d	d	d		d	d	d	w	w	w	w	w	w
Pilot plant:													
* after pre-ClO_2				d	d	d					w	w	w
* after settling			d										
* after filtration			d		w	w	w	w	w	w			
* after post-ClO_2	d	d	d	d	w	w	w	w	w		w	w	w
* after post-Cl_2				d	w	w	w	w	w		w	w	w
Main plant leg 1:													
* after pre-Cl_2	d	d	d	d	d	d					w	w	w
* after filtration	d	d	d		d	d	w	w	w	w			
* after post-Cl_2	d	d	d	d	w	w	w	w	w		w	w	w
Main plant leg 2:													
* after pre-O_3	d	d	d	d	d	d					w	w	w
* after filtration	d	d	d		d	d	w	w	w	w			
* after post-Cl_2	d	d	d	d	w	w	w	w	w		w	w	
* after post ClO_2	d	d	d	d	w	w	w	w	w		w	w	w

NOTE : d = daily, w = weekly

APPENDIX B

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GC-MS ANALYSIS OF FOUR WATER EXTRACTS

SAMPLE INFORMATION: Four Sep-Pak C_{18} cartridges were submitted for analysis by Mr Ian Pearson on 18 September 1990.

ANALYSIS REQUIRED: Identification of the organic compounds trapped on the cartridges.

METHOD: The organics on each cartridge were eluted with acetonitrile and analyzed by capillary gas chromatography-mass spectrometry.

RESULTS:

SAMPLE	COMPONENTS IDENTIFIED (% PROBABILITY MATCH)
Raw	ethylbenzene (64%) or xylene (60%) 2-methylpropanoic acid, 2,2-dimethyl-1(2-hydroxy-1-methylethyl)propyl ester (59%) butyl butanoate (78%) 10-ethynyl-10-hydroxy-1,8-diphenyl-9(10H)-anthracenone (72%)
Cl_2	1,2-dichloroethane (96%) acetamide (86%) ethylbenzene (46%) butyl butanoate (59%) 1,2-dimethoxycyclopropane (23%) dodecamethylcyclohexasiloxane (64%) 3,4,5-trimethyl-1-hexene (47%) 2-methylpropanoic acid, 3-hydroxy-2,4,4-trimethylpentyl ester (87%) tetradecamethylcycloheptasiloxane (87%) 1-phenylethanone (42%)

ClO_2	xylene (87%) 2-methylpropanoic acid, pentyl ester (47%) 2-methylpropanoic acid, 3-hydroxy-2,4,4-trimethylpentyl ester (87%) 3-methylisothiazole (38%) 2-pentadecyl-4,4,5,5-tetradeutero-1,3-dioxolane (33%) glycine (36%)
O_3	epoxydeacetylgedunin (12%) [2-(ethylthio)ethyl]-benzene (38%) dimethyloctadecyl[(D)methyloctadecylsilyl)oxy]-silane (91%)

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