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AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRIHALOMETHANES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING WATERS

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CSIR

DIVISION OF WATER TECHNOLOGY

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by

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AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRI-HALOMETHANES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING WATERS

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

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AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRIHALOMETHA--NES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING-WATERS

EXECUTIVE SUMMARY

1. Motivation for research

As far back as 1974 it was discovered that when chlorine is added to drinking-water supplies in the concentrations required for disinfection, it reacts with the organic content of the water to produce trihalomethanes (THM's). Of these THM's, chloroform usually accounts for at least 75 per cent of the total THM's.

For human consumption, the THM's should possibly be regarded as potential carcinogens i.e. compounds shown to have caused cancer in one or more species of laboratory animals but not yet in humans. However, the statements encountered from various epidemiological authorities on this topic namely, that seventy to ninety per cent of human cancer is caused by contact with chemical substances, should be taken seriously and all efforts must be made to limit these compounds in drinking waters.

THM formation is influenced by, inter alia, temperature, pH, chlorine dosage and by seasonal changes. Systematic studies have also indicated that THM production could be roughly proportional to the initial dissolved organic carbon (DOC) concentration. High levels of THM's in final drinking waters would, therefore, be an indicator of inefficient treatment processes concerning the removal of organic materials. The latter raises the question as to whether our present conventional water purification treatment plants are capable of effectively removing organic material from water.

To limit the long term exposure of the public to THM's, the United States Protection Agency (USEPA) promulgated a maximum contaminant level in 1979 of 100 microgram per litre total trihalomethanes (THM's) in drinking waters. Examples of other countries who have subsequently set guidelines for THM's include West Germany (25 μ g/l), Switzerland (25 μ g/l) and the Netherlands (1 μ g/l). In South Africa there are no official criteria or guidelines for THM's but the trend until now by various organizations was to use the USEPA THM value as a guideline when judging water quality.

2. Objectives and procedures

The overall objective of this study was to determine the occurrence and concentration of THM's in South African drinking waters over a two year period in order to quantify the THM problem. The research included the following:

- sample sites were selected throughout the country and as large a percentage of the population as possible was included, forty sampling sites were chosen;
- the sample sites were selected where qualified personnel could take the samples, measure the free chlorine on site and dispatch the samples (in most cases municipalities, water boards and research organizations collaborated);
- apart from the determination of THM's; pH, DOC, bromide and free residual chlorine were also measured i.e. the determinands which could influence THM formation;
- the influence of the diversity of physical/chemical treatment processes on THM values was investigated; and

 efforts were made to determine the relationship, if any, between DOC and THM concentrations.

3. Results and discussion

- 3.1 Based on average results, 36 out of 40 sample sites contained less than 100 µg/l THM.
- 3.2 Since few samples contained free chlorine when sampled for THM's, samples were re-chlorinated in the laboratory to 1 milligram per litre residual chlorine. In the latter case 32 out of 40 sample sites contained less than 100 µg/l THM.
- 3.3 The eight sample sites which were subjected to rechlorination in the laboratory and which exceeded 100 μ g/l THM were those sites where the raw water sources were known to be recipients of treated sewage effluents.
- 3.4 On average, waters direct from the tap contained 45 ug/l THM. Upon post chlorination to 1 mg/l residual chlorine this value rose to 74 µg/l.
- 3.5 The assumption that high THM values coincide with high DOC concentrations when waters are disinfected with chlorine, was confirmed. This emphasizes the importance of DOC removal in a water purification process to inhibit THM formation.
- 3.6 The probability level of the relationship between THM and DOC values of samples taken from the tap, was in the order of 90 per cent. Reasons why only 16 per cent of the THM values could be directly ascribed to the DOC content was the

exclusion in the statistical evaluations of seasonal influences, consideration of different raw water sources, different chemical treatments and chlorine dosages at the treatment plants.

- 3.7 Forty five per cent of the treatment plants encountered, used aluminium sulphate while a further 40 per cent used a poly-electrolyte. The other 15 per cent represented ferric chloride, polyaluminium chloride, lime and combinations of the flocculants mentioned. It is at this stage therefore not possible to correlate THM removal with the chemicals used as flocculants.
- 3.8 The presence of bromide, when re-chlorination was applied favoured the formation of bromoform to that of chloroform when no bromide was present.
- 3.9 The influence of pH on THM formation could not be established due to most of the final waters having virtually the same pH.
- 3.10 The THM values obtained are in most instances on par with those reported by overseas authorities. South African drinking-waters appear to be well within the USEPA criterium of 100 μ g/l.

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AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRIHALOMETHANES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING WATERS

SUMMARY

Statements encountered from various epidemiological authorities emphasise that between seventy and ninety per cent of human cancer is caused by contact with chemical substances and that all efforts be made to limit these compounds in the environment. Drinking-water supplies are especially susceptible to contamination by such substances when potable water supplies are disinfected with chlorine. chemical by-products formed are the reaction products produced The when chlorine reacts with specific organic molecules in the water to form trihalomethane (THM) compounds, the most predominant species being chloroform. Although THM's are regarded as presumptive carcinogens many countries have taken precautions to limit their occurrence by law or by setting guidelines. The objective of this study was to determine the occurrence and concentration of THM's in South African drinking waters to enable us to establish our own A THM survey conducted from 40 drinking-water sites criteria. throughout South Africa showed a concentration range of 9 to 182 ug/1 with more than 50 percent of all values being below 74 ug/1. This study also made it possible to propose a maximum THM level of 100 ug/1 for treated South African drinking waters and that DOC measurements could be used as a predictor of THM concentration.

1. INTRODUCTION

Halogenated compounds of varying structure have been most valuable in many situations - as pesticides, solvents, chemical intermediates, polymer ingredients, medicinals, fireproofing agents, and others. The realization has grown, however, that some of these materials or their contaminants pose a threat to the environment or to the health of individuals exposed to them. Additional forces are now also being directed at the

phenomenon that when chlorine is added to drinking-water supplies in the concentrations required for disinfection it reacts with the organic content of the water to produce a variety of volatile and non-volatile chlorinated compounds. The trihalomethanes (THM's) are by far the largest part of these chlorinated products with chloroform normally accounting for at least 75% of the total.

A survey in the USA,¹ of water from 80 drinking-water treatment plants were analyzed. Table A shows the mean and range of levels of the four major trihalomethanes detected.

	Chloroform	Bromodichloro- methane	Dibromochloro- methane	Bromoform
Mean	21	6	1.2	ND in 68% of samples
Range	<0,1-311	ND-116	ND-100	ND-92

TABLE A. Haloforms in chlorinated drinking-water (ug/1)

ND = Not detected

In the above study the highest concentration of trihalomethane (THM's) were found in water from treatment plants which used surface or shallow ground water with a large content of organic material, and where the water was treated with high doses of chlorine. The nine highest chloroform levels were in the range 103 to 311 ug/1.

In 1976, the National Cancer Institute of the USA announced that chloroform had been found to be carcinogenic to mice.² This finding was soon followed by the United States

Environmental Protection Agency (USEPA) recommendation, designed to limit the long term exposure of the public to THM's via the drinking-water supply. In November 1979³, a maximum contaminant level (MCL) equal to 100 ug/l of THM in drinkingwater was set, for treatment works supplying more than 75 000 households. The USEPA lead has been followed by Canada (MCL 350 ug/l), West Germany (MCL 25 ug/l), and Switzerland (MCL 25 ug/l). The EEC has set a 'guide level' of 1 ug/l for THM's and the World Health Organization, as part of a general review of water quality criteria, has suggested a guideline of 30 ug/l for chloroform only.

For human consumption, the THM's should possibly be regarded as presumptive carcinogens i.e. compounds shown to have caused cancer in one or more species of laboratory animals but not yet in humans. However, the statements encountered from various epidemiological authorities⁴ on this topic namely, that seventy to ninety per cent of human cancer is caused by contact with chemical substances, should be taken seriously and all efforts must be made to limit these compounds in our drinking waters.

The objective of this study was therefore to determine the occurrence and concentration of THM's in South African drinking waters, thereby enabling local authorities to compare our values with these of overseas and establishing local guidelines for these compounds in SA drinking-water supplies. With the financial assistance of the Water Research Commission, the Division of Water Technology commenced this survey in July 1986.

1.1. THM Formation - the haloform reaction

Haloforms are produced by the reaction of chlorine with organic precursor molecules, since they are not present in significant concentrations in non-chlorinated water. Tannic acid, and nitrogen-containing compounds have been shown to produce THM's on chlorination.⁵ The major THM precursors, however, appear to

be the aquatic humic substances and the presence of halogenated organics, both volatile and non-volatile in drinking water can be used as an indicator of water quality i.t.o. organic material.

High levels of THM's are usually indicative of high levels of organic matter in the finished water, which in turn is indicative of an ineffective treatment process in respect of the removal of organic matter. Since the aim of municipal drinking-water utilities is to produce a safe and high quality product by using the most efficient and cost effective treatment methods, the formation and removal of THM's and their precursors can serve as a good indicator as to whether this aim is being achieved.

1.2 Definition of trihalomethane (THM)

Trihalomethanes are the by-products formed when hypochlorous acid reacts with specific organic materials in a water. The rate and extent of formation of the THM's is dependant upon the chlorine dose, temperature, pH, reaction time, and the amount and type of organic material present. The four major trihalomethane components generally found in water after disinfection with chlorine, in descending concentrations are chloroform, dichloro-bromomethane, dibromochloromethane and bromoform. This concentration order could be reversed if bromide ions were present in the water to be chlorinated.

1.3 Factors affecting the rate of THM formation

It has been hypothesized that THM's are formed by the wellknown haloform reaction between chlorine or any other halogen oxidant and the organic precursor compounds. If this were simply the case, the rate of formation of THM's in the haloform reaction would be independent of the applied chlorine dose, because the rate of haloform reaction is apparently controlled by an initial enolization step.⁶

Practice has, however, shown that THM formation is dependent on the chlorine dosage, and increases as the chlorine dose increases. This indicates, therefore, that THM formation also occurs through reaction pathways other than the haloform reaction.⁷

Systematic studies have furthermore shown that THM production time is roughly proportional to the initial TOC with concentration, and is pH and temperature dependent.⁸ The presence of both bromide and ammonia strongly affect THM formation because they compete with the THM precursor sites on the humic polymers for the oxidizing potential of chlorine, Α substantial proportion of the bromide (15-30%) in water is converted upon chlorination to bromine or hypobromous acid, which can react with THM precursors to form the brominated THM's.

In a surface supply, thousands of organic compounds may exist in varying concentrations and at various times of the year. While organic compounds may originate from man-made or natural sources not all produce significant amounts of THM's on chlorination.

Humic and fulvic acids are classes of compounds found in abundance in surface water supplies. As first identified by Rook in 1974,⁹ humic acids have shown a great potential in THM production and are a class of large molecular weight organic acids derived from the decomposition of plant and animal matter. These compounds are usually the largest contributors to the organohalogen precursor concentration.

1.4 Seasonal variations in THM formation

Several researchers have demonstrated that a definite seasonal variation in the formation of THM's in a potable water supply exists.^{10,11}

It is also known that higher THM levels occur during the warmer months with lower concentrations occurring in the colder months. It has been postulated that this decrease in concentration in the colder months could be a result of decreased THM precursor concentrations or the result of lower temperatures on the rate of THM formation. During the summer months when algal growth is at its peak the THM formation potential was also at its greatest indicating a contribution of extracellular material from algae to the organohalogen precursor concentration.¹²

1.5 THM formation in relation to wastewater reuse

As a result of increasing demands on the limited natural water sources in South Africa, the reuse of water on a rapidly increasing scale is inevitable. The experience of the recent drought in South Africa has increased the importance of, and reliance on, treated wastewater reuse as a means to overcome water shortages.

Wastewater reuse can be achieved directly, by reclaiming the wastewater for potable use, or indirectly by treating source waters into which wastewater has been released.

The recycling of wastewater may have serious implication in terms of the levels of THM's and chlorinated organics in the finished water. If chlorine is used in the water treatment process, wastewater reuse may result in a gradual build-up of chlorinated products, to levels which could exceed suggested maximum contaminant levels, unless adequate barriers to remove THM's or their precursors are built into the treatment system. In a direct reuse system these barriers would include either physical-chemical methods, such as coagulation, activated carbon adsorption, air stripping, or a combined physical chemical/biological barrier such as biological activated carbon (BAC). In an indirect reuse system the barrier to the build-up of chlorinated products would be the capacity of the natural

aquatic environment to disperse these products.

1.6 The South African scene concerning trihalomethanes

The facilities to evaluate the occurrence and concentration of THM's, organohalogen precursors and dissolved organic carbon concentrations in South African water sources are extremely limited. due to the sophisticated measuring instruments required. A considerable amount of information on the PWV area, in Windhoek and various other areas is available which was obtained by being involved with contract work where these type of analyses were done on special request. Except for water supplies in Windhoek and in the Pretoria area little is known about the occurrence of the discussed determinands in other parts of the country. Before we can even decide whether THM's are a problem in SA or not, we have to determine their occurrence and concentrations. We have until now used overseas criteria as guidelines for the concentration of THM's in our waters but may find that, after having conducted a national survey, we could set our own THM criteria taking into account our own environmental conditions. Considerations for THM removal could only be investigated if we knew their occurrence and concentrations.

Limited results available for South African drinking-water supplies indicate the following: 1. a drinking-water supply derived by conventional treatment of dam water in Windhoek often has THM values in excess of 100 ug/1; 2. a drinkingwater supply in Windhoek derived by direct reclamation from wastewater generally has THM values below 100 ug/1; 3. drinking water derived by conventional treatment of water from the Vaal River system has THM values close to the level of 100 ug/1¹³. In view of this situation the Rand Water Board is conducting research into the use of activated carbon in its treatment system, a step which could increase the cost of water supplied by the Board to is users by 28 percent.¹⁴

2. SELECTION OF SAMPLING SITES

During the first year of the survey, twenty five sites were sampled once a month. During the second year, the sample sites were increased to forty and sampled twice a month. The selection of sampling sites was aimed at incorporating as large a portion of the domestic sector as possible. Only tap waters from drinking-water reticulation systems were sampled.

3. SAMPLING PROCEDURES

Sampling was carried out by trained persons and included members of the DWT as well as many Municipalities who took part in this survey (see acknowledgements). Special designed reinforced cardboard boxes containing four glass bottles each were sent to each site on a regular basis. Samples were taken on the 10th and 20th of each month. Free chlorine was measured and recorded when the sample was taken. The distribution of sample sites is illustrated in Figure I.

4. DETERMINANDS SELECTED FOR THE SURVEY AND ANALYTICAL PROCEDURES FOLLOWED

The determinands-selected for regular analysis were those that are directly related to the production of THM's in water i.e. pH, dissolved organic carbon (DOC), bromide, and free residual chlorine. The terminology THM represents the sum of the following components: chloroform, dichlorobromomethane, dibromochloromethane and bromoform.

4.1 Trihalomethane determination

Samples were collected in 50 ml dark glass bottles and capped with teflon liners. Ascorbic acid was added to each bottle to destroy free chlorine when the sample was taken. The determination was done by gas chromatography according to the method described by Van Rensburg *et al.*¹⁵ The latter described

method was modified by replacing the 50 m SP2100 flexible fused silica column by a 30 m x 0,32 mm ID J & W DBI fused silica column with 1 um film thickness.

Water samples were extracted with an azeotrope mixture consisting of isopropylether (53%) and hexane (47%).

4.2 Dissolved organic carbon analysis

Samples were collected in all glass containers. The determination was based on ultraviolet/peroxodisulphate oxidation according to the method described by Van Steenderen & Lin (1981)¹⁶

5. **RESULTS AND DISCUSSION**

Few samples taken during the survey contained free chlorine although all the water purification plants used chlorine disinfection as a final process (Table B). It was for this reason that after 12 months into the survey, it was decided to take two samples at each site. One was analyzed for THM's as taken, the other one was chlorinated to 1 mg/1 free chlorine residual and left standing at room temperature for 2 days before analysis. All results are presented in Tables 1 to 40.

5.1 Chemical Treatments

Of particular interest was the number of different chemical treatments those waters received (Table B). Forty five per cent of the treatment plants used aluminium sulphate while an equal amount used one or other type of polyelectrolyte. The other ten per cent represented ferric chloride, polyaluminium chloride, lime and combinations of various of the flocculants mentioned. A relationship between THM's and chemical treatments used was not determined because of the vastly different water characteristics.

Tabl	e B: Chemicals used in treatment processes throughout the country
Code	Treatment
1.	Ferric chloride, lime, chlorine
2.	Aluminium sulphate, sodium aluminate, lime, carbon dioxide, chlorine
з.	Chlorine
4.	Aluminium sulphate, lime chlorine
5.	Aluminium sulphate, lime, chloramination
6.	Floccotan FB50, Aluminium sulphate, lime, chlorine
7.	Superfloc C577, Aluminium sulphate, lime, chlorine
8.	Ultrafloc 5105, Aluminium sulphate, lime, chlorine
9.	Anikem polyelectrolyte, chlorine
10.	Ferric chloride, chlorine
11.	Aluminium sulphate, lime, sodium silicate, ferrous sulphate, chlorine and chloramination
12.	Aluminium sulphate, chlorine
13.	Ferric chloride, powder activated carbon, polyelectrolyte, lime, chlorine
14.	Cyanamid C579, lime, chloramination
15.	Ultrafloc polymer, chlorine
16.	Prechlorination, polyaluminium chloride, granular activated carbon, chlorine
17.	Aluminium sulphate, Aecipol electrolyte, lime, chlorine
18.	Aluminium sulphate, lime, carbon dioxide, chlorine
19.	Aluminium sulphate, polyelectrolyte, lime to pH 9,0 - 9,5, chlorination
20.	Ferric chloride, polyelectrolyte, lime, chlorine
21.	Lime, carbon dioxide, chlorine
22.	Polyaluminium chloride P30, lime, chlorine.

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5.2 THM Concentrations

Only 10 per cent of the THM values direct from the tap exceeded 100 ug/l total THM's while this increased to twenty percent when samples were chlorinated to 1 mg/l (Figure 2). At 75 per cent of the sites chloroform was the predominant compound (>60%), Tables 1-40. At the other 25 per cent of the sites, all four THM compounds were more evenly distributed. The sites where values of >100 ug/l THM's were recorded were also known to be recipients of secondary treated sewage. The highest DOC values also occurred at these sites.

5.3 DOC Concentrations

Site 9 recorded the third highest DOC value (6 mg/l) but one of the lowest THM values. An explanation for this was the use of chloramination in place of chlorination thereby eliminating the formation of THM's.

Sites 29 and 40 drew from the same source (Hartbeespoort Dam), yet the THM and DOC values at site 29 were considerably lower than at site 40. The difference in treatment was the use of the powder activated carbon at site 29. The granular activated carbon at site 40 was obviously exhausted in respect of THM removal.

5.4 Relationships between THM and other measured determinands

To determine whether any relationship existed between THM and the other measured determinands, simple and multivariate regression analysis was applied. In the calculation, sample sites at which only one observation was made during the survey Tables 41 to 48 summarize ignored. the average were concentrations of the measured determinands per sample site and details of the spread and distribution of the present determinands. Tables 49 to 54 relate to intercorrelation regression analysis of the measured determinands. Statistical



Sample site Table number

Figure 2: Average concentrations of THM's at sampling sites. (Numbers allocated to histograms follow Tables 1-40.)

THM



ήνεrage TIHM (ug/l)

Average concentrations of THM's at sampling sites. (Numbers allocated to histograms follow Tables 1-40.)

Figure 2: (Continued)

evaluations did not accommodate factors such as seasonal influences, the different sources of raw water, different chemical treatments or the final chlorination dosages at the treatment plants. The box-and-whisker plots indicate a considerable skewness around the inter-quartile ranges for all determinands which can directly be attributed to the above mentioned factors (Box & Whisker Plot explanation in Figure 3).

Although analysis of variance only indicates a 16,24 per cent THM depending on the DOC content, the probability level of the relationship between the observed THM and DOC values is in the order of 90 per cent (Table 49). The probability level of this relationship increases further to 99,9 per cent under controlled chlorination conditions (Table 50).

The effect of chlorine on the formation of dibromochloromethane and bromoform in the presence of bromide was also demonstrated (Table 51). Although r-squared only indicated a 5,57 per cent dependency of the formation of bromonated compounds in the presence of bromide, the probability level of a relationship was 84 per cent and increased to 96 per cent under controlled chlorination conditions (Table 52).

The formation of chloroform and dichlorobromomethane upon chlorination was not influenced by the presence of bromide (Tables 53 and 54).

6. CONCLUSIONS

Only four sample sites out of a total of forty recorded THM values >100 ug/1. The same sites were also among the highest THM values recorded when samples were laboratory chlorinated to a 1 mg/l residual level. The percentage of sites with values of <100 ug/l THM concentrations could possibly be further increased if the sites now producing THM's in excess of 100 ug/l experimented with some of the purification techniques employed by the other treatment plants. Until now, no

scientific evidence has been forthcoming as to why the same flocculant should remove THM precursors at one purification plant and not at another. Sixty seven per cent of treatment plants referred to used aluminium sulphate alone or in combination with other flocculants.

Based on regression results, DOC could serve as a useful parameter to estimate the concentration of THM's in the final waters or as a operational tool in process control.

On average, waters direct from the tap contained 45 ug/1 THM. Upon post chlorination to 1 mg/1 residual chlorine this value rose to 74 ug/1. Based on this data, South African drinking waters appear to be well within the United States EPA criterium of 100 ug/1 THM.

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> Port Elizabeth Cape Town East London George Kimberley Brits Upington Prieska



Figure 1: Sample site distribution in South Africa.

Douglas Rustenburg Volksrust.

Towards the end of the survey the number of THM analysis became too large to handle and the Hydrological Research Institute gratefully come to our assistance to share this load of analyses.

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TABLE 1: THM analysis of sample taken from the distribution system at Cape Town (Bellville). Source of raw water Voëlvlei, Wemmershoek and Teewaterkloof mixture. Treatment process code is 1, 2 and 18, obtained from Table B.

(Number	of	samples	taken:	4)	
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Determinands	Minimum	Maximum	x	Unit
CHC13	13	54	41	ug/1
CHC1 ₂ Br	3	26	11	ug/l
CHC1Br ₂	1	3	1	ug/l
CHBr ₃	0	13	0	ug/1
Total THM	16	83	56	ug/1
рH	8,4	8,7	8,5	
DOC	1,4	2,6	1,8	mg/1
Bromide	0,2	0,4	0,3	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	63	66	65	ug/1
CHC1 ₂ Br	8	12	10	ug/l
CHC1Br ₂	1	1	1	ug/1
CHBra	ND	ND	ND	ug/1
Total THM	71	79	75	ug/1

ND = Not determined.

TABLE 2: THM analysis of sample taken from the distribution system at Paarl. Source of raw water Wemmershoek Dam. Treatment process code is 2 obtained from Table B.

(Number of samples taken: 5)

Minimum	Maximum	x	Unit
34	42	37	ug/1
4	12	7	ug/1
1	1	1	ug/l
0	13	0	ug/l
41	60	47	ug/1
8,2	. 8,8	8,4	
1,4	8,6	3,2	mg/l
0,2	0,3	0,2	mg/l
<0,1	0,1	-	mg/1
	34 4 1 0 41 8,2 1,4 0,2	34 42 4 12 1 1 0 13 41 60 8,2 8,8 1,4 8,6 0,2 0,3	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC13	45	46	45	ug/1
CHC1 ₂ Br	9	13	11	ug/1
CHC1Br ₂	2	3	3	ug/1
CHBr₃	ND	ND	ND	ug/1
Total THM	55	61	58	ug/1

ND = Not determined.

TABLE 3: THM analysis of sample taken from the distribution system at Cape Town (Strand). Source of raw water Steenbras Dam Treatment process code is 2, obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHC13	28	45	34	ug/1
CHC1 ₂ Br	5	10	7	ug/1
CHC1Br ₂	1	3	1	ug/1
CHBr ₃	0	13	7	ug/l
Total THM	40	54	45	ug/l
pH	6,5	8,0	7,3	
DOC	2,0	8,5	4,1	mg/1
Bromide	0,3	2,1	0,7	mg/1
Free chlorine	<0,1	<0,1	-	mg/l

Above water chlorinated to a residual of 1 mg/1 free chlorine

			20	
CHC1 ₃	31	33	32	ug/l
CHC12Br	9	10	9	ug/1
CHC1Br ₂	2	2	2	ug/1
CHBr ₃	ND	ND	ND	ug/1
Total THM	43	44	43	ug/1

ND = Not determined.

TABLE 4: THM analysis of sample taken from the distribution system at Cape Town (Sybrand Park). Source of raw water Wemmershoek Dam, Steenbras Dam. Treatment process code is 2 obtained from Table ^B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	14	56	40	ug/1
CHCl ₂ Br	6	12	8	ug/1
CHC1Br ₂	1	3	2	ug/l
CHBr ₃	0	13	7	ug/l
Total THM	20	78	52	ug/1
pH	6,9	8.8	8,0	
DOC	1.5	8,0	3,3	mg/1
Bromide	0,2	0,6	0,4	mg/l
Free chlorine	<0,1	<0,1	_	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

•	•			
CHC1 ₃	53	64	59	ug/1
CHC1 ₂ Br	18	19	18	ug/1
CHC1Br ₂	6	7	6	ug/1
CHBr ₃	0	1,2	1	ug/l
Total THM	79	88	84	ug/1

TABLE 5: THM analysis of sample taken from the distribution system at Cape Town (Mitchell's Plain). Source of raw water Teewaterskloof Dam. Treatment process code is 18, obtained from Table ^B.

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	32		36	ug/1
CHC1 ₂ Br	3	16	• 9	ug/l
CHC1Br ₂	0	3	1	ug/1
CHBr ₃	0	13	7	ug/1
Total THM	43	59	48	ug/l
рН	7,7	8,8	8,5	
DOC	1,2	2,2	1,6	mg/1
Bromide	0,2	0,6	0,3	mg/1
Free chlorine	0.1	1,1	-	mg/1

(Number of samples taken: 5)

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Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	47	50	49	ug/1
CHC1 ₂ Br	10	14	12	ug/1
CHC1Br ₂	2	4	3	ug/l
CHBr ₃	ND	ND	ND	ug/l
Total THM	61	64	63	ug/1

ND = not determined.

TABLE 6: THM analysis of sample taken from the distribution system at Cape Town (Atlantis). Source of raw water, groundwater. Treatment process code is 3 obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHC1,	5	7	6	ug/1
CHC1 ₂ Br	1	4	3	ug/1
CHC1Br ₂	5	13	8	ug/1
CHBr ₃	16	43	26	ug/l
Total THM	7	65	29	ug/1
pН	7.4	7,9	7,6	
DOC	4,9	15,3	7,2	mg/1
Bromide	0.6	0,8	0,7	mg/l
Free chlorine	<0,1	1,0	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

7	8	7	ug/1
3	4	3	ug/1
19	25	22	ug/1
40	68	54	ug/1
73	107	90	ug/1
-	40	19 25 40 68	19 25 22 40 68 54

TABLE 7: THM analysis of sample taken from the distribution system at Seshego (Pietersburg). Source of raw water Bloed River water plus Groundwater. Treatment process code is 4, obtained from Table B.

(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit
CHC13	1		6	ug/1
CHC1 ₂ Br	0	7	3	ug/l
CHC1Br ₂	0	5	2	ug/l
CHBr ₃	0	6	2	ug/1
Total THM	1	27	9	ug/1
рН	7,5	8,1	7,8	
DOC	2,0	3.0	2,7	mg/1
Bromide	0,3	1,4	0,7	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

		··· ·· ·· ··· ··· ··· ··· ···	
5	16	11	ug/l
3	13	7	ug/1
3	14	7	ug/l
7	13	10	ug/l
19	55	34	ug/1
	3 3 7	3 13 3 14 7 13	3 13 7 3 14 7 7 13 10

TABLE 8: THM analysis of sample taken from the distribution system at Pietersburg (Boreholes). Source of raw water Groundwater. Treatment process code is 4, obtained from Table B.

(Number	of	samples	taken:	5)	

Determinands	Minimum	Maximum	x	Unit
CHC13	5	14	10	ug/1
CHC1 ₂ Br	1	5	3	ug/1
CHC1Br ₂	0	0	0	ug/1
CHBr ₃	0	4	1	ug/1
Total THM	11	19	15	ug/1
φH	7,9	9,6	8,7	
DOC	1,2	3,5	2,1	mg/1
Bromide	0,3	0,7	0,4	mg/1
Free chlorine	<0,1	0,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	21	26	24	ug/1
CHC1 ₂ Br	6	11	9	ug/l
CHC1Br ₂	1	6	3	ug/1
CHBr ₃	0	2	1	ug/l
Total THM	30	40	35	ug/1

TABLE 9 : THM analysis of sample taken from the distribution system at Pietersburg. Source of raw water Ebeneser Dam. Treatment process code is 5, obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHCl ₃	10	20	14	ug / 1
CHC1 ₂ Br	3	8	5	ug/l
CHC1Br ₂	0	1	1	ug/1
CHBr ₃	0	0	. 0	ug/l
Total THM	13	29	20	ug/l
рH	8,4	9,0	8,8	
DOC	1	21	6	mg/1
Bromide	0,2	1,6	0,6	mg/1
Free chlorine	<0,1	0,3	_	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	-19	28	23	ug/l
CHC1 ₂ Br	5	9	7	ug/1
CHC1Br ₂	1	2	2	ug/1
CHBr₃	0	0	0	ug/1
Total THM	24	39	32	ug/1

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TABLE 10: THM analysis of sample taken from the distribution system at Nelspruit. Source of raw water Crocodile River. Treatment process code is 5 obtained from Table ^B.

(Number of samples taken: 2)

Determinands	Minimum	Maximum	x ·	Unit
CHC1 ₃	19	30	24	ug/1
CHC1 ₂ Br	6	11	8	ug/1
CHC1Br ₂	1	2	2	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	25	41	33	ug/1
рН	7,8	8,2	8,0	
DOC	3,0	3,4	3,2	mg/1
Bromide	0,5	0,5	0,5	mg/l
Free chlorine	<0,1	<0,1	_	mg/1

CHC1,	34	34	34	ug/l
CHC1 ₂ Br	10	10	10	ug/1
CHC1Br ₂	2	2	2	ug/l
CHBr ₃	0	0	0	ug/l
Total THM	45	45	45	ug/1

TABLE 11: THM analysis of sample taken from the distribution system at KaBokweni (Nelspruit). Source of raw water Crocodile River. Treatment process code is 4, obtained from Table B.

(Number of samples taken: 2)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	14	18	17	ug/1
CHC1 ₂ Br	5	14	9	ug/l
CHC1Br ₂	0	1	1	ug/l
CHBr3	0	0	0	ug/l
Total THM	18	23	21	ug/1
pH	7,6	8,0	7,8	
DOC	2,8	2,8	2,8	mg/1
Bromide	0,2	0,5	0,3	mg/l
Free chlorine	<0,1	<0,1	-	mg/1

CHC1 ₂ Br	11	11	11	ug/1
CHC1Br ₂	2	2	2	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	46	46	46	ug/l

TABLE 12: THM analysis of sample taken from the distribution system at Ladysmith. Source of raw water Spioenkop Dam. Treatment process code is 6 obtained from Table B.

(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	9	38	21	ug/1
CHC1 ₂ Br	1	6	4	ug/1
CHC1Br ₂	1	2	1	ug/1
CHBr ₃	0	0	0	ug/l
Total THM	15	32	21	ug/1
рH	7,7	8,6	8,1	
DOC	1,4	2,8	1,9	mg/l
Bromide	0,2	0,7	0,3	mg/l
Free chlorine	<0,1	0,3	-	mg/1

CHC1 ₃	18	42	27	ug/l
CHC1 ₂ Br	7	9	8	ug/1
CHC1Br ₂	1	4	3	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	29	52	37	ug/1
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TABLE 13: THM analysis of sample taken from the distribution system at eZakheni (Ladysmith). Source of raw water Tugela River Treatment process code is 7, obtained from Table B.

(Number of samples taken: 9)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	6	54	31	ug/1
CHC1 ₂ Br	1	4	3	ug/1
CHC1Br ₂	0	1	1	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	8	59	34	ug/1
рН	7,5	8,6	8,2	
DOC	1.0	7,4	3,1	mg/1
Bromide	0,1	0,9	0,3	mg/1
Free chlorine	<0,1	3,0	-	mg/1

CHC13	47	109	74	ug/l
CHC1 ₂ Br	12	15	13	ug/1
CHC1Br ₂	1	4	3	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	64	122	90	ug/1

TABLE 14: THM analysis of sample taken from the distribution system at Dimbaza (Ciskei). Source of raw water Sandile Dam. Treatment process code is 1 obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	28	28	28	ug/1
CHC1 ₂ Br	17	17	17	ug/1
CHC1Br ₂	7	7	7	ug/1
CHBr₃	1	1	1	ug/1
Total THM	54	54	54	ug/1
pH	8	8	8	
DOC	3,3	3.3	3,3	mg/1
Bromide	0,3	0,3	0,3	mg/1
Free chlorine			ND	mg/1

CHCl ₃	- 80	80	80	ug/1
CHC1 ₂ Br	40	40	40	ug/1
CHC1Br ₂	21	21	21	ug/l
CHBr ₃	4	4	<u>4</u>	ug/1
Total THM	144	144	144	ug/l

TABLE 15: THM analysis of sample taken from the distribution system at Bloemfontein. Source of raw water Welbedacht Dam. Treatment process code is 1, obtained from Table B.

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(Number of samples taken: 16)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	1	100	63	ug/1
CHC1 ₂ Br	1	19	9	ug/1
CHC1Br ₂	0	7	2	ug/1
CHBr₃	0	0	0	u g/1
Total THM	2	109	74	ug/1
рН	8,1	9,3	8,8	
DOC	2,3	5,7	3,2	mg/l
Bromide	0,1	3,1	0,5	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

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CHC1 ₂	12	120	84	ug/1
CHC12Br	12	22	17	ug/1
CHC1Br ₂	1	17	55	ug/1
CHBr ₃	0	9	1	ug/1
Total THM	50	135	108	u g/1

TABLE 16: THM analysis of sample taken from the distribution system at Bloemfontein (Mazelspoort). Source of raw water Modder River Weir. Treatment process code is 7, obtained from Table B.

Determinands	Minimum	Maximum .	X	Unit
CHC1 ₃	4	81	26	ug/1
CHC1 ₂ Br	0	15	5	ug/1
CHC1Br ₂	0	3	1	ug/1
CHBr₃	0	0	0	ug/1
Total THM	5	97	32	ug/1
рН	7,9	9,3	8,8	
DOC	2	5	3,3	mg/1
Bromide	0,1	0,9	0,4	mg/1
Free chlorine	<0,1	0,1	-	mg/1

(Number of samples taken: 15)

Above water chlorinated to a residual of 1 mg/1 free chlorine

14	64	35	ug/l
1	25	11	ug/1
0	16	4	ug/l
0	2	0	ug/l
16	94	5 0	ug/1
	1 0 0	1 25 0 16 0 2	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE 17: THM analysis of sample taken from the distribution system at Makwarella (Venda) Source of raw water Vondo Dam. Treatment process code is 4, obtained from Table B.

(Number of samples taken: 9)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃		61	30	ug/1
CHC1 ₂ Br	1	25	13	ug/l
CHC1Br ₂	0	13	7	ug/l
CHBr₃	0	4	1	ug/l
Total THM	6	99	51	ug/l
рН	7,1	9,5	8,1	
DOC	1	3,2	1,9	mg/1
Bromide	0,1	0,6	0,3	mg/1
Free chlorine	<0,1	0,1	-	mg/1

CHC1 ₃	6	6 0	39	ug/1
CHCl ₂ Br	9	28	18	ug/1
CHC1Br ₂	3	16	10	ug/l
CHBr₃	0	7	3	ug/1
Total THM	33	102	70	ug/l

TABLE 18: THM analysis of sample taken from the distribution system at Hartswater. Source of raw water Vaal River. Treatment process code is 12 obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
CHC13	18	18	18	ug / 1
CHC1 ₂ Br	13	13	13	ug/l
CHC1Br ₂	13	13	13	ug/l
CHBr₃	7	7	7	ug/l
Total THM	51	51	51	ug/1
pН	7,9	7,9	7,9	
DOC	4,2	4,2	4,2	mg/l
Bromide	0,1	0,1	0,1	mg/l
Free chlorine	<0.1	<0.1	-	mg/l

Above water chlorinated to a residual of 1 mg/l free chlorine

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CHCl3	ND	ND	ND	ug/1
CHC1 ₂ Br	ND	ND	ND	ug/l
CHC1Br ₂	ND	ND	ND	ug/1
CHBr ₃	ND	ND	ND	ug/1
Total THM	ND	ND	ND	ug/1

ND = Not determined.

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TABLE 19: THM analysis of sample taken from the distribution system at Vryburg. Source of raw water Vaal River. Treatment process code is 4, obtained from Table $^{\rm B}\cdot$

(Number of samples taken: 1)

Determinands	Minimum	Maximum	X	Unit
CHC1 ₃	5	5	5	ug/1
CHC1 ₂ Br	1	1	1	ug/1
CHC1Br ₂	0	0	0	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	6	6	6	ug/l
pH	ND	ND	ND	
DOC	4.4	4.4	4,4	mg/l
Bromide	ND	ND	ND	mg/1
Free chlorine	<0,1	<0.1	-	mg/l

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	- ND	ND	ND	ug/1
CHC1 ₂ Br	ND	ND	ND	ug/l
CHCIBr ₂	ND	ND	ND	ug/l
CHBr ₃	ND	ND	ND	ug/1
Total THM	ND	ND	ND	ug/1

ND = Not determined.

TABLE 20: THM analysis of sample taken from the distribution system at Upington. Source of raw water Orange River. Treatment process code is 8 obtained from Table B.

(Number of samples taken: 11)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	7	21	14	ug/1
CHC1 ₂ Br	1	12	8	ug/l
CHC1Br ₂	0	12	4	ug/1
CHBr ₃	0	4	1	ug/l
Total THM	9	41	26	ug/1
рH	7,9	8,2	8,1	mg / 1
DOC	2,5	4,3	3,2	mg/1
Bromide	0,2	3,7	1,0	mg/1
Free chlorine	0,2	0.4	-	mg/1

59 30 20	31 19 12	ug/1 ug/1 ug/1
20	12	ug/1
		₩ Q7 =
19	5	ug/1
105	68	ug/1

TABLE 21: THM analysis of sample taken from the distribution system at Kimberley. Source of raw water Vaal River. Treatment process code is 17, obtained from Table B.

(Number of samples taken: 10)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	10	46	28	ug/1
CHC1 ₂ Br	2	24	16	ug/1
CHC1Br ₂	0	17	8	ug/l
CHBr ₃	0	7	2	ug/1
Total THM	31	70	53	ug/1
рH	7,2	7,9	7,7	
DOC	2,9	7,0	5,0	mg/1
Bromide	0,4	1,1	0,7	mg/1
Free chlorine	ND	ND	ND	mg/1

	·		·	
CHC1 ₃	17	43	29	ug/l
CHC1 ₂ Br	15	32	24	ug/l
CHC1Br ₂	10	23	19	ug/1
CHBr ₃	2	17	8	ug/1
Total THM	53	96	79	ug/1

TABLE 22: THM analysis of sample taken from the distribution system at Prieska. Source of raw water Orange River. Treatment process code is 9 obtained from Table ^B.

(Number of samples taken: 11)

Minimum	Maximum	x	Unit
4	46	19	ug / 1
2	9	5	ug/1
0	3	1	ug/l
0	0	0	ug/1
6	53	24	ug/1
8,0	8,5	8,2	
2,1	5,8	3,2	mg / 1
0	1,1	0,5	mg/1
<0,1	<0,1	-	mg/1
	2 0 6 8,0 2,1 0	2 9 0 3 0 0 6 53 8,0 8,5 2,1 5,8 0 1,1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

28 10	ug/1 ug/1
10	ug/1
4	ug/1
1 .	ug/l
43	ug/1
	1 43

TABLE 23: THM analysis of sample taken from the distribution system at Douglas. Source of raw water Orange River. Treatment process code is 10, obtained from Table ^B.

(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	3	12	6	ug/1
CHC1 ₂ Br	2	6	3	ug/1
CHC1Br ₂	1	3	2	ug/1
CHBr ₃	0	4	1	ug/1
Total THM	10	20	13	ug/l
рH	7,6	8,3	7,8	
DOC	2,1	4,9	3,8	mg/1
Bromide	0,1	2,1	0,6	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

		· · ·	<u>_</u>	
CHC1 ₃	б	15	10	ug/l
CHC1 ₂ Br	6	12	9	ug/1
CHC1Br ₂	7	15	12	ug/l
CHBr ₃	5	26	14	ug/1
Total THM	31	62	45	ug/1

TABLE 24: THM analysis of sample taken from the distribution system at Pretoria (Irene). Source of raw water Vaal Dam water. Treatment process code is 11, obtained from Table B.

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	28	71	51	ug/l
CHC1₂Br	14	24	18	ug/1
CHC1Br ₂	2	10	5	ug/l
CHBr₃	0	0	0	ug/l
Total THM	51	100	74	ug/1
рН	7,6	8,4	8,1	
DOC	2.8	4,7	4,0	mg/1
Bromide	0,2	0,8	0,5	mg/1
Free chlorine	<0,1	<0.1		mg/1

(Number of samples taken: 13)

CHC1 ₃	28	120	65	ug/1
CHC1 ₂ Br	17	80	28	ug/1
CHC1Br ₂	4	10	7	ug/l
CHBr ₃	0	1	0	ug/1
Total THM	55	208	99	ug/l

TABLE 25: THM analysis of sample taken from the distribution system at Pretoria (Montana). Source of raw water Vaal Dam. Treatment process code is 11, obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	28	77	53	ug/1
CHC1 ₂ Br	14	31	20	ug/l
CHC1Br ₂	2	9	5	ug/1
CHBr ₃	0	0	0	ug/l
Total THM	48	114	78	ug/1
pH	7,6	8,9	8,3	
DOC	3,3	4,2	3,7	mg/1
Bromide	0,3	0,7	0,4	mg/1
Free chlorine	<0,1	<0,1	<0,1	mg/1

CHC1 ₃	- 35	89	60	ug/1
CHC1 ₂ Br	17	35	26	ug/1
CHC1Br ₂	4	13	9	u g/1
CHBr ₃	1	2	1	ug/1
Total THM	57	121	95	ug/1

TABLE 26: THM analysis of sample taken from the distribution system at Rietvlei (Pretoria). Source of raw water Rietvlei Dam. Treatment process code is 12 obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	29	29	29	ug / 1
CHC1 ₂ Br	16	16	16	ug/1
CHC1Br ₂	4	4	4	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	49	49	49	ug/1
рH	9,0	9,0	9,0	
DOC	7,0	7,0	7,0	mg / 1
Bromide	ND	ND	ND	mg/1
Free chlorine	0,1	0,1	0,1	mg/1

Above water chlorinated to a residual of 1 mg/l free chlorine

CHC1 ₃	ND	ND	ND	ug/1
CHC1 ₂ Br	ND	ND	ND	ug/1
CHC1Br ₂	ND	ND	ND	ug/1
CHBr₃	ND	ND	ND	ug/1
Total THM	ND	ND	ND	ug/1

ND = Not determined.

TABLE 27: THM analysis of sample taken from the distribution system at Durban (Congella). Source of raw water Nagle Dam. Treatment process code is 4, obtained from Table ^B.

(Number of samples taken: 12)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	27	85	57	ug/1
CHC1 ₂ Br	10	25	20	ug/1
CHC1Br₂	1	8	5	ug/1
CHBr ₃	0	1	0	ug/1
Total THM	52	116	81	ug/1
рН	7,8	8,9	8,3	
DOC	0.8	3,9	2,1	mg/1
Bromide	0,1	0,7	0,3	mg/1
Free chlorine	<0,1	0,3	-	mg/1

CHC13	38	101	73	ug/l
CHC1 ₂ Br	13	32	26	ug/l
CHClBr ₂	1	9	7	ug/l
CHBr₃	1	2	0	ug/1
Total THM	77	136	106	ug/1

TABLE 28: THM analysis of sample taken from the distribution system at Rustenburg. Source of raw water Vaal Dam. Treatment process code is 11 obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
CHC13	39	75	58	ug/1
CHC1 ₂ Br	11	21	18	ug/1
CHC1Br ₂	2	8	5	ug/1
CHBr ₃	0	0	0	ug/l
Total THM	53	92	77	ug/1
рН	7,9	8,2	8,0	
DOC	2,9	5,7	4,4	mg/1
Bromide	0,33	1,4	0,7	mg/1
Free chlorine	<0,1	<0,1	<0.1	mg/1

54	80	67	ug/1
14	29	23	ug/l
3	17	9	ug/l
0	2	0	ug/1
90	116	99	ug/l
	3 0	3 17 0 2	3 17 9 0 2 0

TABLE 29: THM analysis of sample taken from the distribution system at Schoemansville. Source of raw water Hartbeespoort Dam. Treatment process code is 13, obtained from Table B.

(Number of samples taken: 8)

Minimum	Maximum	x	Unit
3	23	11	ug/1
1	15	8	ug/l
1	10	4	ug/l
0	4	2	ug/1
6	52	25	ug/1
7,1	8,3	7,5	
3,8	5.8	4,5	mg/1
0,1	0,4	0,3	mg/l
<0,1	<0.1		mg/1
	3 1 1 0 6 7,1 3,8 0,1	3 23 1 15 1 10 0 4 6 52 7,1 8,3 3,8 5,8 0,1 0,4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

			• •	
CHC13	7	28	14	ug/1
CHC1 ₂ Br	3	20	9	ug/1
CHC1Br ₂	2	16	8	ug/1
CHBr ₃	1	8	4	ug/1
Total THM	15	68	36	ug/1

TABLE 30: THM analysis of sample taken from the distribution system at Temba (Hammanskraal). Source of raw water Pienaars River. Treatment process code is 1 obtained from Table B.

(Number of samples taken: 2)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	58	62	60	ug/1
CHC1 ₂ Br	53	69	61	ug/1
CHC1Br₂	37	56	47	ug/1
CHBr ₃	10	18	14	ug/l
Total THM	158	205	182	ug/1
рH	8.0	8,4	8,2	
DOC	7,7	8,3	8,0	mg/1
Bromide	0,5	0,5	0,5	mg/1
Free chlorine	0,2	0,2	0,2	mg/l

CHC13	.82	82	82	ug/l
CHC1 ₂ Br	87	87	87	ug/1
CHC1Br ₂	67	67	67	ug/1
CHBr₃	20	20	20	ug/1
Total THM	257	257	257	ug/1

TABLE 31: THM analysis of sample taken from the distribution system at Pietermaritzburg. Source of raw water Midmar Dam. Treatment process code is 14, obtained from Table B.

(Number of samples taken: 12)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	6	93	34	ug/1
CHC1 ₂ Br	1	17	7	ug/1
CHC1Br ₂	0	7	1	ug/l
CHBra	0	0	0	ug/1
Total THM	7	117	43	ug/1
pH	8,1	9,5	9	
DOC	1,4	4,6	2,7	mg/1
Bromide	0	1,8	0.5	mg/1
Free chlorine	<0,1	0,7	-	mg/1

CHCl ₃	7	142	42	ug/1
CHC1 ₂ Br	1	28	10	ug/l
CHC1Br ₂	0	15	3	ug/l
CHBr ₃	0	0	0	ug/l
Total THM	9	185	59	ug/1

TABLE 32: THM analysis of sample taken from the distribution system at Newcastle. Source of raw water Chelmsford Dam. Treatment process code is 21, obtained from Table ^B.

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(Number of samples taken:	10)
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Determinands	Minimum	Maximum	x	Unit
CHCl ₃	23	53	37	ug/1
CHC1 ₂ Br	9	23	13	ug/1
CHC1Br ₂	1	5	2	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	33	69	53	ug/1
рH	8,1	8,9	8,6	
DOC	3,2	4,9	3,7	mg/1
Bromide	0,1	0,9	0,5	mg/1
Free chlorine	<0,1	<0,1	-	mg/l

CHC1 ₃	37	61	51	ug/1
CHC1 ₂ Br	16	49	22	ug/1
CHC1Br ₂	4	10	5	ug/1
CHBr ₃	0	2	0	ug/1
Total THM	66	114	78	ug/1

TABLE 33: THM analysis of sample taken from the distribution system at Volksrust. Source of raw water Schuilhoek Dam. Treatment process code is 22, obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit ,
CHC13	31	31	31	ug/1
CHC1 ₂ Br	4	4	4	ug/1
CHC1Br ₂	0	0	0	ug/1
CHBr₃	0	0	0	ug/1
Total THM	35	35	35	ug/1
рН	8,0	8,0	8,0	
DOC	2,1	2,1	2,1	mg/1
Bromide	0,4	0,4	0,4	mg/1
Free chlorine	ND	ND	ND	mg/1

CHC13	44	44	44	ug/l
CHC1 ₂ Br	6	6	6	ug/1
CHC1Br ₂	1	1	1	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	51	51	51	ug/1

TABLE 34: THM analysis of sample taken from the distribution system at Port Elizabeth. Source of raw water, Churchill and Elandsjagt works. Treatment process code is 19, obtained from Table ^B.

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Determinands	Minimum	Maximum	x	Unit	
CHCl ₃	7	57	43	ug/1	
CHC1 ₂ Br	15	34	28	ug/1	
CHC1Br ₂	13	39	27	ug/1	
CHBr ₃	6	30	· 18	ug/1	
Total THM	91	150	119	ug/1	
рH	8,1	8,8	8,4		
DOC	3,4	6,3	4,6	mg/1	
Bromide	0,1	1,1	0,6	mg/1	
Free chlorine ·	<0,1	<0,1	-	mg/1	

(Number of samples taken: 8)

			<u> </u>	
CHC1,	20	63	46	ug/1
CHC1 ₂ Br	26	46	35	ug/l
CHC1Br ₂	32	57	46	ug/1
CHBr ₃	27	45	37	ug/l
Total THM	142	195	168	ug/l

TABLE 35: THM analysis of sample taken from the distribution system at Port Elizabeth. Source of raw water Loerie Works. Treatment process code is 19, obtained from Table ^B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x Uni	
CHCl ₃	23	82	57	ug/1
CHC1 ₂ Br	21	33	28	ug/1
CHC1Br ₂	8	28	19	ug/1
CHBr ₃	2	23	7	ug/1
Total THM	79	138	112	ug/1
рН	7,8	9,1	8,5	
DOC	1,0	6.3	3,5	mg/1
Bromide	0,1	1,7	0,7	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

CHC13	-31	91	71	ug/1
CHC1 ₂ Br	27	45	37	ug/l
CHC1Br ₂	19	43	28	ug/l
CHBr ₃	4	32	11	ug/1
Total THM	109	183	147	ug/1

TABLE 36: THM analysis of sample taken from the distribution system at George. Source of raw water Swart River Dam and Tuin Roete Dam. Treatment process code is 4 obtained from Table B.

(Number of samples taken: 9)

Determinands	Minimum	Maximum	X	Unit	
CHC1 ₃	12	57	30	ug/1	
CHC1 ₂ Br	2	12	8	ug/1	
CHC1Br ₂	0	4	1	ug/l	
CHBr ₃	0	0	0	ug/1	
Total THM	17	72	39	ug/1	
рH	7,9	8,8	8,5		
DOC	1	4,3	3,1	mg/1	
Bromide	0,1	1,6	0,6	mg/1	
Free chlorine	<0,1	<0,1	-	mg/1	

CHC13	22	100	56	ug/1
CHC1 ₂ Br	4	27	16	ug/1
CHC1Br ₂	1	13	4	ug/1
CHBra	0	0	0	ug/1
Total THM	27	139	76	ug/1

TABLE 37: THM analysis of sample taken from the distribution system at East London. Source of raw water Bridle Drift Dam. Treatment process code is 7, obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit	
CHC1,	2	14	10	ug/l	
CHC1 ₂ Br	2	8	6	ug/1	
CHC1Br ₂	1	2	1	ug/1	
CHBr₃	0	2	1	ug/1	
Total THM	5	29	18	ug/1	
pH	8,1	8,6	8,3		
DOC	3,4	5,5	4,3	mg/1	
Bromide	0,1	2,4	1,2	mg/1	
Free chlorine	<0,1	<0,1	-	mg/1	

CHC1 ₃	12	21	15	ug/l
CHC1 ₂ Br	9	15	13	ug/l
CHC1Br ₂	5	21	15	ug/1
CHBr₃	2	25	13	ug/1
Total THM	28	73	57	ug/l

TABLE 38: THM analysis of sample taken from the distribution system at King William's Town. Source of raw water Laing Dam. Treatment process code is 15 obtained from Table ^B.

(Number of samples taken: 3)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	17	22	20	ug/1
CHC1 ₂ Br	12	19	15	ug/1
CHC1Br ₂	7	13	11	ug/l
CHBr ₃	1	3	3	ug/l
Total THM	43	57	48	ug/1
рН	8,0	8,2	8,1	
DOC	0,9	2,1	1,7	mg/1
Bromide	0,3	0,8	0,5	mg/1
Free chlorine	<0,1	<0,1		mg/1

CHC13	32	47	29	ug/1
CHC1 ₂ Br	12	19	15	ug/1
CHC1Br ₂	7	13	11	ug/1
CHBr ₃	1	3	3	ug/1
Total THM	74	122	91	ug/1 -

TABLE 39: THM analysis of sample taken from the distribution system at Beestekraal (Western Transvaal). Source of raw water Vaalkop Dam. Treatment process code is 20, obtained from Table B.

(Number	of	samples	taken:	7)
•				

Determinands	Minímum	Maximum	x	Unit
CHC1 ₃	42	111	69	ug/1
CHC1 ₂ Br	3	23	15	ug/l
CHC1Br ₂	0	6	4	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	56	137	88	ug/1
рН	7,9	9,0	8.6	
DOC	1.7	4.6	2,9	mg/1
Bromide	0,3	1,1	0,6	mg/1
Free chlorine	0,8	1,0	. –	mg/1

CHC13	62	184	118	ug/1
CHC1 ₂ Br	14	25	21	ug/1
CHC1Br ₂	2	13	7	ug/l
CHBr ₃	1	1	0	ug/1
Total THM	95	200	146	ug/1

TABLE 40: THM analysis of sample taken from the distribution system at Brits. Source of raw water Crocodile River. Treatment process code is 16, obtained from Table B.

(Number of samples taken: 6)

Determinands	Minimum	Maximum	x	Unit	
CHC1 ₃	47	82	61	ug/1	
CHC1 ₂ Br	41	51	47	ug/1	
CHC1Br ₂	25	48	35	ug/1	
CHBr ₃	4	7	5	ug/1	
Total THM	131	165	148	ug/1	
рН	7,7	7,7	7,7		
DOC	4.5	5,9	5,1	mg/1	
Bromide	0,3	1,1	0.7	mg/1	
Free chlorine	<0,1	0,2	-	mg/l	

CHC1 ₃	- 48	99	71	ug/1
CHC1 ₂ Br	40	55	46	ug/1
CHC1Br ₂	26	49	37	ug/1
CHBra	4	9	6	ug/l
Total THM	144	187	160	ug/1



Concentration range of determinand \longrightarrow

Table 41. Statistical calculations on average DOC results from 37 sample sites.

37 (1) 1.8 (19) 5 (37) 5.1 Sample size Box-and-Whisker Flot (2) 3.2 (20) 3.2 Average 3.52162 Median 3.2 (3) 4.1 (21) 3.8 Mode (4) 3.3 (22) 4 3.2 Geometric mean 3.27512 (5) 1.6 (23) 3.7 Variance 2.03285 (6) 7.2 (24) 2.1 Standard deviation 1.42578 (7) 2.7 (25) 4.4 Standard error 0.234397 (8) 2.1 (26) 4.5 Minimum 1.6 (27) 8 (9)6 Maximum 8 (10) 3.2 (28) 2.7 Range 6.4 (11) 2.8 (29) 3.7 Lower quartile 2.7 (12) 1.9 (30) 2.1 Upper quartile 4.1 (13) 3.1 (31) 4.6 (14) 3.3 (32) 3.5 Interquartile range 1.4 Ō. 2 4 Skewness 1.2987 (15) 3.2 (33) 3.1 DOC mg/1 Standardized skewness 3.22503 (34) 4.3 (16) 3.3 Kurtosis 2.27938 (17) 1.9 (35) 1.7 Standardized kurtosis 2.83016 (18) 3.2 (36) 2.9

DOC=dissolved organic carbon

Table 42. Statistical calculations on average THM results from 37 sample sites.

(Sample site) DOC

(Sample site) THM Statistical calculations

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THM=CHC13+CHC1Br2+CHC12Br+CFBr3

Statistical calculations

Table 43.Statistical calculations on average THMC results from 37 sample sites.

(Sample site)	THMC	Statistical calc	ulations	
(2) 55 (20) 4 (3) 43 (21) 4 (4) 84 (22) 9	9 6 7 9 8 1 8 1 8 7 6 7 1	Sample size Average Median Mode Geometric mean Variance Standard deviation Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Upper quartile Interquartile range Skewness Standardized skewness Kurtosis Standardized kurtosis	37 52.8108 75 45 72.3962 2255.94 47.4967 7.80841 32 257 225 46 93 53 1.69424 4.20727 3.81283 4.73416	Box-and-Whisker Plot

HMC=CHCl3+CHClBr2+CHCl2Br+CHBr3 chlorinated

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Table44. Statistical calculations on average Br results from 37 sample sites.

(Sample site) Br	Statistical calculations			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sample size Average Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Upper quartile Interquartile range Skewness Standardized skewness Kurtosis Standardized kurtosis	37 0.489189 0.5 0.3 0.447596 0.040991 0.202462 0.0332846 0.1 1.2 1.1 0.3 0.6 0.3 1.00456 2.49459 2.81993 3.50134	Box-and-Whisker Plot	

Br=bromide

Table 45. Statistical calculations on average Br3Br2 results from 37 sample sites.

(Sample site)	Br3Br2	Statistical calcu	lations	-
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(37) 40	Sample size Average Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Interquartile range Skewness	37 8.97297 4 1 0 196.138 14.0049 2.3024 0 61 61 61 5 7 2.456	Box-and-Unisker Plot
(16) 1 (34) 2 (17) 8 (35) 14 (18) 5 (36) 4		Standardized skewness Kurtosis Standardized kurtosis	6.09892 5.67305 7.04387	

Br3Br2=CHC1Br2+CHBr3

Table 46.Statistical calculations on average Br3Br2C results from 37 sample sites.

(Sample	site)Br3Br2C	Statistical calc	ulations	-
(1) 1 (2) 3 (3) 2 (4) 7 (5) 3 (6) 76 (7) 17 (8) 4 (9) 2 (10) 2 (11) 2 (12) 3	(19) 27 (37) 43 (20) 5 (21) 26 (22) 7 (23) 10 (24) 7 (25) 9 (26) 12 (27) 87 (28) 3 (29) 5 (30) 1	Statistical calc Sample size Average Median Mode Geometric mean Variance Standard deviation Standard deviation Standard error Minimum Maximum Range Lower quartile	ulations 37 17.7568 7 3 8.47027 542.023 23.2814 3.82743 1 87 86 3	Box-and-Whisker Flot
(13) 3 (14) 25 (15) 56 (16) 4 (17) 13 (18) 17	(31) 83 (32) 39 (33) 4 (34) 28 (35) 14 (36) 7	Upper quartile Interquartile range Skewness Standardized skewness Kurtosis Standardized kurtosis	25 22 1.93644 4.80872 3.0173 3.7464	L

Br3Br2C=CHC1Br2+CHBr3 chlorinated

Table 47. Statistical calculations on average Cl3Cl2 results from 37 sample sites.

<u>(Sample site)Cl3Cl2</u>	Statistical calcu	lations	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	•	37 45.5405 41 9 37.3304 758.255 27.5364 4.52696 9 121 112 25 69 44 0.88159 2.18923	Pox-and-Whisker Plot
(17) 43 (35) 35 (18) 22 (36) 84	Kurtosis Standardized kurtosis	0.447336 0.55543	

C13C12 = CHC13 + CHC12Br

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Table ⁴⁸.Statistical calculations on average Cl3Cl2C results from 37 sample sites.

(Sau	nple	sit	<u>a)C1</u>	30120	Statistical calcu	lations	
(1) (2)	75 56	(19) (20)	53 38	(37) 117	Sample size Average	37 65.1251	Box-and-Whisker Plot
(3) (4)	32 77	(21) (22)	19 93		Median Mode	56 44	••••••••••••••••••••••••••••••••••••••
(5)	61 10	(23) (24)	86 99		Geometric mean Variance	55.1163 1314.62	
(7)	18	(25)	90		Standard deviation	36.2577	
(8) (9)	33 30	(26) (27)	23 169		Standard error Minimum	5.96073 10	
(10) (11)	44 44	(28) (29)	52 73		Maximum Range	169 159	
(12) (13)	35 87	(30) (31)	50 81		Lower quartile Upper quartile	38 87	
(14) (15)	120 101	(32) (33)	108 72		Interquartile range Skewness	49 0.832532	30 90 150 0 60 120 180
(15) (17)	46 57	(34) (35)	28 44		Standardized skewness Kurtosis	2.06741 0.533066	C13C12C ug/1
18)	50	(36)			Standardized kurtosis	0.661875	

C13C12C=CHC13+CHC12Br chlorinated
Table 49. Correlation regression of THM on DOC.

Dependent variable:		THM	Independent variable:		DOC
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	15.6549 10.7273	15.6138 4.11751	1.00263	0.322922 0.0133881	

Regression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source Model Error	Sum of Squares 8421.5237 43425.557	Df 1 35	Mean Square 8421.5237 1240.730	F-Ratio 6.7876	Prob. Level .01339
Total (Corr.)	51847.081	36			<u> </u>

Correlation Coefficient = 0.403026 Stnd. Error of Est. = 35.224 R-squared = 16.24 percent



Confidence limits: 95% Prediction límits: 95%

THM = CHC13 + CHC1Br2 + CHC12Br + CHBr3

Table 50. Correlation regression of THMC on DOC.

Sependent variable:		THMC	Independent variable:		DOC
Parameter	Estimate	Standard Error	T Value	Prob. Level	<u> </u>
Intercept Slope	30.2218 14.9332	19.0871 5.03343	1.58336 2.9668	0.122334 5.39426E-3	

Regression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source Model Error	Sum of Squares 16319.759 64893.917		Mean Square 16319.759 1854.112	F-Ratio Pro 8.802	b. Level .00539
Total (Corr.)	81213.676	36		╶╾╾═ _{╼╴╓┑} ╴╴╴╴ [┲] ┷ _{┙┹} ╶╖╴╸	, <u></u>

Correlation Coefficient = 0.448273 Stnd. Error of Est. = 43.0594 R-squared = 20.09 percent



Confidence limits: 95% Prediction limits: 95%

THMC=CHC13+CHC1Br2+CHC12Br+CHBr3 chlorinated

Table 51. Correlation regression of Br3Br2 on Br.

Dependent va:	riable:	BR3BR2	Independen	t variable:	- B1
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	0.987363 16.3242	6.00356 11.3621	0.164463 1.43672	·0.870313 0.159678	<u></u>

Regression Analysis - Linear model: Y = a+bX

	Analysis	of Va	ariance		
Source Model Error	Sum of Squares 393.23616 6667.7368	Df 1 35	Mean Square 393.23616 190.5068	F-Ratio 2.06416	Prob. Level .15968
Total (Corr.)	7060.9730	36			

Correlation Coefficient = 0.23599 Stnd. Error of Est. = 13.8024 R-squared = 5.57 percent



Confidence limits: 95% Prediction limits: 95%

Br3Br2=CHC1Br2+CHBr3

Table 52. Correlation regression of Br3Br2C on Br.

Regression Analysis - Linear model: Y = a+bX

Dependent variable:		BR36R2C	Independer	nt variable:	BI
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	-1.27234	9.66474	-0.131648 2.12667	0.896017	

Analysis of Variance

Source Model Error	Sum of Squares 2232.9231 17279.888		Mean Square 2232.9231 493.711	F-Ratio 4.5227	Frob. Level .04057
Total (Corr.)	19512.811	36			

Correlation Coefficient = 0.338281 Stnd. Error of Est. = 22.2196 R-squared = 11.44 percent



Confidence limits: 95% Prediction limits: 95%

Br3Br2C=CHC1Br2+CHBr3 chlorinated

Table 53. Correlation regression of C13C12 on Br.

Dependent va:	riable:	CL3CL2	Independe	nt variable:	BI
Parameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept	41.9881	12.1299	3.46152	1.43362E-3	. <u>.</u>
Slope	7.2619	22.9567	0.31633	0.753631	

Regression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source Model Error	Sum of Squares 77.820142 27219.369	Df 1 35	Mean Square 77.820142 777.696	F-Ratio .100065	
Total (Corr.)	27297.189	36			
Correlation Coef Stnd. Error of E	ficient = 0.0533933 st. = 27.8872		R-squared	= .29 p	ercent



Confidence limits: 95.00 Prediction limits: 95.00

C13C12 = CHC13 + CHC12Br

Table 54. Correlation regression of C13C12C on Br.

Dependent varia	able:	CL3CL2C		Independ	ent variab	le:		BI
Parameter	Estimate	Stand Err		T Value		rob. evel	<u></u>	
Intercept Slope	72.0456 -14.1264	15.9 30.1		4.51847 -0.468127	6,8123 0,64	1E-5 2596		
	A	nalysis	of Va	riance				
Source Model Error		uares 47762 1.847	Df 1 35	Mean Square 294.47762 1343.767	F-Ratio .21914		Level 64260	
Total (Corr.)		6.324	36			•		
	4732 ≘fficient = -0	6.324	36	R-squared	= .62	percent	t.	

Cl3Cl2C=CHCl3+CHCl2Br chlorinated

Br ug/l

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Table 41. Statistical calculations on average DOC results from 37 sample sites.

(Sample site) DOC

Statistical calculations

			
1 1/ 1.8	(19) 5 (37) 5.	1 Sample size	37
(2) 3.2	(20) 3.2	Average	3.52162
	(21) 3.8	Median	3.2
(4)3.3	(22) 4	Mod∈	3.2
(5)1.6	(23) 3.7	Geometric mean	3.27512
(6) 7.2	(24) 2.1	Variance	2.03285
(7) 2.7	(25) 4.4	Standard deviation	1.42578
(8) 2.1		Standard error	0.234397
(9)6		Minimum	1.6
(10) 3.2	(28) 2.7	Maximum	8
(11) 2.8		Range	6.4
(12) 1.9		Lower quartile	2.7
(13) 3.1		Upper quartile	4.1
	(32) 3.5	Interguartile range	1.4
(15) 3.2		Skewness	1.2987
(16) 3.3		Standardized skewness	3.22503
	(35) 1.7	Kurtosis	2.27938
(18) 3.2	(36) 2.9	Standardized kurtosis	2.83016



DOC=dissolved organic carbon

Table⁴². Statistical calculations on average THM results from 37 sample sites.

(Sample site) THM

Statistical calculations

				*		
1)	56	(19)	53	(37) 148	Sample size	37
2)	47	(20)	24		Average	53.4324
3)	45	(21)	13		Median	47
4)	52	(22)	74		Mode	43
5)	43	(23)	78		Geometric mean	42,8706
6)	29	(24)	81		Variance	1440.2
7)	9	(25)	77		Standard deviation	37.9499
8)	15	(26)	25		Standard error	6.23893
97	20	(27)	182		Minimum	9
10)	33	(28)	43		Maximum	182
11>	21	(29)	53		Range	173
12)	21	(30)	35		Lower quartile	26
:3)	34	(31)	119		Upper quartile	74
14)	54	(32)	112		Interquartile range	48
15)	74	(33)	39		Skewness	1.65458
16)	32	(34)	15		Standardized skewness	4.10878
17)	51	(35)	48		Kurtosis	3.11447
18)	26	(36)	88		Standardized kurtosis	3.86704



Box-and-Whisker Plot



THM=CHC13+CHC1Br2+CHC12Br+CHBr3

Z

Table 43. Statistical calculations on average THMC results from 37 sample sites.

(Sample	site) THMC		Statistical calc	ulations	
<pre>(1) 75 (1) 75 (2) 58 (3) 43 (4) 84 (5) 63 (6) 90 (7) 34 (8) 35 (9) 32 (10) 45 (11) 46 (12) 37 (13) 90 (14) 144</pre>	<pre>(20) 43 (21) 45 (22) 99 (23) 95 (24) 106 (25) 99 (26) 36 (27) 257 (28) 59 (29) 78 (30) 51 (31) 169 (32) 147</pre>	37) 160	Sample size Average Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Interguartile range	37 22.8108 75 45 72.3962 2255.94 47.4967 7.80841 32 257 225 46 93 53	Box-and-Whisker Plot
(15) 108 (16) 50	(33) 76 (34) 57		Skewness Standardized skewness	1.69424 4.20727	50 150 250 0 100 200 300
(17) 70 (18) 68	(35) 91 (36) 146		Standardized Skewness Kurtosis Standardized kurtosis	4.2012) 3.81253 4.73416	THMC ug/1

THMC=CHC13+CHC1Br2+CHC12Br+CHBr3 chlorinated

Table 44. Statistical calculations on average Br results from 37 sample sites.

(Sample site) Br

Statistical calculations

Box-and-Whisker Plot

0.6 0.8

Br mg/1.

1

1.2

0.2

0

	(19) 0.7	(37) 0.7	Sample size	37
(2) 0.2	(20) 0.5		Average	0.489189
(3)0.7	(21) 0.6		Median	0.5
4) 0.4	(22) 0.5	•	Mode	0.3
5) 0.3	(23) 0.4		Geometric mean	0.447596
6) 0.7	(24) 0.3		Variance	0.040991
(7)0.7	(25) 0.7		Standard deviation	0.202462
(8)0.4	(25) 0.3		Standard error	0.0332846
9) 0.6	(27) 0.5		Minimum	0.1
10) 0.5	(28) 0.5		Maximum	1.2
(11) 0.3	(29) 0.5		Range	1.1
(12) 0.3	(30) 0.4		Lower quartile	0.3
(13) 0.3	(31) 0.6		Upper quartile	0.6
(14) 0.3	(32) 0.7		Interquartile range	0.3
(15) 0.5	(33) 0.6		Skewness	1.00456
(16) 0.4	(34) 1.2		Standardized skewness	2.49459
(17) 0.3	(35) 0.5		Kurtosis	2.81993
(18) 0.1	(36) 0.6		Standardized kurtosis	3.50134

Br=bromide

Table 45. Statistical calculations on average Br3Br2 results from 37 sample sites. .

(Sample	site)Br3Br2	Statistical calcu	lations	-
(1) 1 (2) 1	(19) 10 (37) 40 (20) 1	Average	37 8.97297	Box-and-Whisker Plot
(3) (3)	(21) 3	Median	4	
(4) 9	(22) 5	Mode	1	
(5)8	(23) 5	Geometric mean	0	<u>}</u>
(6)34	(24) 5	Variance .	196.138	
(7)4	(25) 5	Standard deviation	14.0049	
< < < < 1 < < < > < < < < < < < < < < <	(26) 6	Standard error	2.3024	
(9)1	(27) 61	Minimum	0	
(10) 2	(28) 1	Maximum -	61	
(11) 1	(23) S	Range	61	
(12) 1	(30) 0	Lower quartile	1	
(13) 1	(31) 45	Upper quartile	8	
(14) 8	(32) 26	Interquartile range	7	0 20 40 60 80
(15) 2	(33) 1	Skewness	2.456	Br3Br2 ug/1
(16) i	(34) 2	Standardized skewness	6.09892	
(17) 8	(35) 14	Kurtosis	5.67305	
(18) 5	(36) 4	Standardized kurtosis	7.04387	

Br3Br2=CHC1Br2+CHBr3

Table 46. Statistical calculations on average Br3Br2C results from 37 sample sites.

(Sample	site)Bı	3.Br2C	Statistical calc	ulations	
(Sample) (1) 1 (2) 3 (3) 2 (4) 7 (5) 3 (6) 76 (7) 17 (8) 4 (9) 2 (10) 2 (11) 2 (11) 2 (12) 3 (13) 3 (14) 25	site)Br (19) 27 (20) 5 (21) 26 (22) 7 (23) 10 (24) 7 (25) 9 (26) 12 (27) 87 (28) 3 (29) 5 (30) 1 (31) 83 (32) 39	<u>3Br2C</u> (37) 43	Statistical calc Sample size Average Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Interquartile range	ulations 37 17.7568 7 3 8.47027 542.023 23.2814 3.82743 1 87 86 3 25 22	Box-and-Whisker Plot
(15) 56 (16) 4 (17) 13 (18) 17	(33) 4 (34) 28 (35) 14 (36) 7		Skewness Standardized skewness Kurtosis Standardized kurtosis	1.93644 4.80872 3.0173 3.7464	Br3Br2C ug/1

Br3Br2C=CHC1Br2+CHBr3 chlorinated

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Table 47. Statistical calculations on average Cl3Cl2 results from 37 sample sites.

				ج مجمع منظري	<u>■■■■₩₽₩₽₽₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩</u>		
(1)	52	(19)	44	(37) 108	Sample size	37	
(2)	44	(20)	24		Âverage	45.5405	Pox-and-Whisker Plot
(3)	41	(21)	9		Median	41	
(4)	48	(22)	69		Mode	3	
(5)	45	(23)	73		Geometric mean	37.3304	
(6)	9	(24)	77		Variance	758.255	
(7)	9	(25)	76		Standard deviation	27.5364	
(8)	13	(26)	19		Standard error	4.52696	
(9)	19	(27)	121		Minimum	9	┝────┤╴│╷┟╾┤┤
:10)	32	(28)	41		Maximum	121	
(11)	26	(29)	50		Range	112	
(12)	25	(30)	35		Lower quartile	25	
(13)	34	(31)	71		Upper quartile	69	
(14)	45	(32)	85		Interquartile range	44	Lecter Lecter
(15)	72	(33)	38		Skewness	0.88159	0 30 60 90 120 150
(16)	31	(34)	16		Standardized skewness	2.18923	C13C12 ug/1
(17)	43	(35)	35		Kurtosis	0.447336	
(18)	22	(36)	84		Standardized kurtosis	0.55543	

C13C12 = CHC13 + CHC12Br

Table 48.Statistical calculations on average Cl3Cl2C results from 37 sample sites.

(Sam	ple	sit	e)C1	<u>3c12c</u>	Statistical calcu	ulations	
(1) (2) (3) (4) (5) (5) (7) (8) (10) (11) (11) (12) (13) (14)	1p1e 75 56 32 77 61 10 18 33 30 44 35 87 120 101 46	sit((19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (27) (28) (29) (30) (31) (32) (33) (34)	<pre>>) C1 53 38 19 93 86 99 90 23 169 52 73 50 81 108 72 25</pre>	<u>3C12C</u> (37) 117		37 65.1351 56 44 55.1163 1314.62 36.2577 5.96073 10 169 159 38 87 49 0.832532 2.06741	Box-and-Whisker Flot
17) 18)	57 50	(35) (36)	44 139		Kurtosis Standardized kurtosis 	0.533066 0.661875	

C13C12C=CHC13+CHC12Br chlorinated

Table 49. Correlation regression of THM on DOC.

Regression Analysis - Linear model: Y = a+bX

<i>Dependent</i> variable:		THM	Independent	t variable:	DOC
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	15.6549	15.6138 4.11751	1.00263 2.60529	0.322922 0.0133881	

Analysis of Variance

Source Model Error	Sum of Squares 8421.5237 43425.557	Df 1 35	Mean Square 8421.5237 1240.730	F-Ratio 6.7876	Prob. Level .01339
Total (Corr.)	51847.081	36			*

Correlation Coefficient = 0.403026 Stnd. Error of Est. = 35.224 R-squared = 16.24 percent



Confidence	limits:	95%
Prediction	limits:	95%

THM=CHC13+CHC1Br2+CHC12Br+CHBr3

Table 50. Correlation regression of THMC on DOC.

Segression Analysis - Linear model: Y = a+bX

Jependent variable:		THMC	Independen	DOC	
Parameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept	30.2218	19.0871	1.58336	0.122334	
Slope	14.9332	5.03343	2.9668	5.39426E-3	

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratic	Prob. Level
Model	16319.759	1	16319.759	8.802	.00539
Error	64893,917	35	1854.112		
Total (Corr.)	81213.676	36			

Correlation Coefficient = 0.448273 Stnd. Error of Est. = 43.0594 R-squared = 20.09 percent



Confidence limits: 95% Prediction limits: 95%

THMC=CHC13+CHC1Br2+CHC12Br+CHBr3 chlorinated

Table 51. Correlation regression of Br3Br2 on Br.

Regression Analysis - Linear model: Y = a+bX

Dependent va	riable:	BR3ER2	Independen	t variable:	BI
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	0.987363 16.3242	6.00356 11.3621	0.164463 1.43672	·0.870313 0.159678	

Analysis of Variance					
Source Model	Sum of Squares 393.23616	Df 1	Mean Square 393.23616	F-Ratio 2.06416	Prob. Level .15968
Error	6667,7368	35	190.5068		
Total (Corr.)	7060.9730	36			

Correlation Coefficient = 0.23599 Stnd. Errcr of Est. = 13.8024 R-squared = 5.57 percent



Confidence limits: 95% Prediction limits: 95%

Br3Br2 = CHC1Br2 + CHBr3

Table 52. Correlation regression of Br3Br2C on Br.

Dependent va	riable:	BR3BR2C	Independer	t variable:	BR
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept	-1.27234	9.66474	-0.131648	0.896017	
Slope	38.8993	18.2911	2.12667	0.0405728	

Regression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source Model Error	Sum of Squares 2232,9231 17279,888	-	Mean Square 2232.9231 493.711	F-Ratio 4.5227	Frob. Level .04057
Total (Corr.)	19512.811	36	- <u> </u>		

Correlation Coefficient = 0.338281 Stnd. Error of Est. = 22.2196 R-squared = 11.44 percent



Confidence limits: 95% Prediction limits: 95%

Br3Br2C=CHC1Br2+CHBr3

chlorinated

Table 53. Correlation regression of Cl3Cl2 on Br.

Dependent v	variable:	CL3CL2	Independe	nt variable:	BI
Parameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	41.9881 7.2619	12.1299 22.9567	3.46152 0.31633	1.43362E-3 0.753631	

Regression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source Model Error	Sum of Squares 77.820142 27219.369	Df 1 35	Mean Square 77.820142 777.696	F-Ratio .100065	Prob. Level .75363
Total (Corr.)	27297.189	36			· · · · · · · · · · · · · · · · · · ·
Correlation Coeff Stnd. Error of Es	icient = 0.0533933 :t. = 27.8872		R-squared	= .29 1	ercent



Confidence limits: 95.00 Prediction limits: 95.00

C13C12 = CHC13 + CHC12Br

Regression Analysis - Linear model: Y = a+bX CL3CL2C Dependent variable: Independent variable: BR Standard T Prob. Estimate Error Value Parameter Level 72.0456 15.9447 4.51847 6.81231E-5 Intercept -14.1264Slope 30.1763 -0.4681270.642596 Analysis of Variance Source Sum of Squares Df Mean Square F-Ratio Prob. Level Model 294.47762 294.47762 .21914 .64260 1 47031.847 1343.767. Error 35 47326.324 Total (Corr.) 36 Correlation Coefficient = -0.0788814 R-squared = .62 percent



Stnd. Error of Est. = 36.6574

Confidence limits: 95% Prediction limits: 95%

Cl3Cl2C=CHCl3+CHCl2Br chl

chlorinated

Table 54. Correlation regression of C13C12C on Br.

CSIR

DIVISION OF WATER TECHNOLOGY

AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRIHALOMETHANES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING WATERS

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Contract report for the Water Research Commission

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AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRI-HALOMETHANES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING WATERS

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

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EXECUTIVE SUMMARY

1. Motivation for research

As far back as 1974 it was discovered that when chlorine is added to drinking-water supplies in the concentrations required for disinfection, it reacts with the organic content of the water to produce trihalomethanes (THM's). Of these THM's, chloroform usually accounts for at least 75 per cent of the total THM's.

For human consumption, the THM's should possibly be regarded as potential carcinogens i.e. compounds shown to have caused cancer in one or more species of laboratory animals but not yet in humans. However, the statements encountered from various epidemiological authorities on this topic namely, that seventy to ninety per cent of human cancer is caused by contact with chemical substances, should be taken seriously and all efforts must be made to limit these compounds in drinking waters.

THM formation is influenced by, inter alia, temperature, pH, chlorine dosage and by seasonal changes. Systematic studies have also indicated that THM production could be roughly proportional to the initial dissolved organic carbon (DOC) concentration. High levels of THM's in final drinking waters would, therefore, be an indicator of inefficient treatment processes concerning the removal of organic materials. The latter raises the question as to whether our present conventional water purification treatment plants are capable of effectively removing organic material from water.

To limit the long term exposure of the public to THM's, the United States Protection Agency (USEPA) promulgated a maximum contaminant level in 1979 of 100 microgram per litre total trihalomethanes (THM's) in drinking waters. Examples of other countries who have subsequently set guidelines for THM's include West Germany (25 μ g/l), Switzerland (25 μ g/l) and the Netherlands (1 μ g/l). In South Africa there are no official criteria or guidelines for THM's but the trend until now by various organizations was to use the USEPA THM value as a guideline when judging water quality.

2. Objectives and procedures

The overall objective of this study was to determine the occurrence and concentration of THM's in South African drinking waters over a two year period in order to quantify the THM problem. The research included the following:

- sample sites were selected throughout the country and as large a percentage of the population as possible was included, forty sampling sites were chosen;
- the sample sites were selected where qualified personnel could take the samples, measure the free chlorine on site and dispatch the samples (in most cases municipalities, water boards and research organizations collaborated);
- apart from the determination of THM's; pH, DOC, bromide and free residual chlorine were also measured i.e. the determinands which could influence THM formation;
- the influence of the diversity of physical/chemical treatment processes on THM values was investigated; and

efforts were made to determine the relationship, if any, between DOC and THM concentrations.

3. Results and discussion

- 3.1 Based on average results, 36 out of 40 sample sites contained less than 100 µg/l THM.
- 3.2 Since few samples contained free chlorine when sampled for THM's, samples were re-chlorinated in the laboratory to 1 milligram per litre residual chlorine. In the latter case 32 out of 40 sample sites contained less than 100 µg/l THM.
- 3.3 The eight sample sites which were subjected to rechlorination in the laboratory and which exceeded 100 µg/l THM were those sites where the raw water sources were known to be recipients of treated sewage effluents.
- 3.4 On average, waters direct from the tap contained 45 ug/l THM. Upon post chlorination to 1 mg/l residual chlorine this value rose to 74 µg/l.
- 3.5 The assumption that high THM values coincide with high DOC concentrations when waters are disinfected with chlorine, was confirmed. This emphasizes the importance of DOC removal in a water purification process to inhibit THM formation.
- 3.6 The probability level of the relationship between THM and DOC values of samples taken from the tap, was in the order of 90 per cent. Reasons why only 16 per cent of the THM values could be directly ascribed to the DOC content was the

exclusion in the statistical evaluations of seasonal influences, consideration of different raw water sources, different chemical treatments and chlorine dosages at the treatment plants.

- 3.7 Forty five per cent of the treatment plants encountered, used aluminium sulphate while a further 40 per cent used a poly-electrolyte. The other 15 per cent represented ferric chloride, polyaluminium chloride, lime and combinations of the flocculants mentioned. It is at this stage therefore not possible to correlate THM removal with the chemicals used as flocculants.
- 3.8 The presence of bromide, when re-chlorination was applied favoured the formation of bromoform to that of chloroform when no bromide was present.
- 3.9 The influence of pH on THM formation could not be established due to most of the final waters having virtually the same pH.
- 3.10 The THM values obtained are in most instances on par with those reported by overseas authorities. South African drinking-waters appear to be well within the USEPA criterium of 100 μ g/1.

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AN INVESTIGATION INTO THE OCCURRENCE AND CONCENTRATION OF TRIHALOMETHANES AND THEIR PRECURSORS IN SOUTH AFRICAN DRINKING WATERS

SUMMARY

Statements encountered from various epidemiological authorities emphasise that between seventy and ninety per cent of human cancer is caused by contact with chemical substances and that all efforts be made to limit these compounds in the environment. Drinking-water are especially susceptible to contamination by supplies such substances when potable water supplies are disinfected with chlorine. The chemical by-products formed are the reaction products produced when chlorine reacts with specific organic molecules in the water to form trihalomethane (THM) compounds, the most predominant species being chloroform. Although THM's are regarded as presumptive carcinogens many countries have taken precautions to limit their occurrence by law or by setting guidelines. The objective of this study was to determine the occurrence and concentration of THM's in South African drinking waters to enable us to establish our own criteria. A THM survey conducted from 40 drinking-water sites throughout South Africa showed a concentration range of 9 to 182 ug/1with more than 50 percent of all values being below 74 ug/1 . This study also made it possible to propose a maximum THM level of 100 ug/l for treated South African drinking waters and that DOC measurements could be used as a predictor of THM concentration.

1. INTRODUCTION

Halogenated compounds of varying structure have been most valuable in many situations - as pesticides, solvents, chemical intermediates, polymer ingredients, medicinals, fireproofing agents, and others. The realization has grown, however, that some of these materials or their contaminants pose a threat to the environment or to the health of individuals exposed to them. Additional forces are now also being directed at the

phenomenon that when chlorine is added to drinking-water supplies in the concentrations required for disinfection it reacts with the organic content of the water to produce a variety of volatile and non-volatile chlorinated compounds. The trihalomethanes (THM's) are by far the largest part of these chlorinated products with chloroform normally accounting for at least 75% of the total.

A survey in the USA,¹ of water from 80 drinking-water treatment plants were analyzed. Table A shows the mean and range of levels of the four major trihalomethanes detected.

	Chloroform	Bromodichloro- methane	Dibromochloro- methane	Bromoform
Mean	21	6	1.2	ND in 68% of samples
Range	<0,1-311	ND-116	ND-100	ND-92

TABLE A. Haloforms in chlorinated drinking-water (ug/1)

ND = Not detected

In the above study the highest concentration of trihalomethane (THM's) were found in water from treatment plants which used surface or shallow ground water with a large content of organic material, and where the water was treated with high doses of chlorine. The nine highest chloroform levels were in the range 103 to 311 ug/1.

In 1976, the National Cancer Institute of the USA announced that chloroform had been found to be carcinogenic to mice.² This finding was soon followed by the United States

Protection Agency (USEPA) Environmental recommendation. designed to limit the long term exposure of the public to THM's via the drinking-water supply. In November 1979³, a maximum contaminant level (MCL) equal to 100 ug/1 of THM in drinkingwater was set, for treatment works supplying more than 75 000 households. The USEPA lead has been followed by Canada (MCL 350 ug/1), West Germany (MCL 25 ug/1), and Switzerland (MCL 25 The EEC has set a 'guide level' of 1 ug/1 for THM's and ug/1). the World Health Organization, as part of a general review of water quality criteria, has suggested a guideline of 30 ug/1for chloroform only.

For human consumption, the THM's should possibly be regarded as presumptive carcinogens i.e. compounds shown to have caused cancer in one or more species of laboratory animals but not yet in humans. However, the statements encountered from various epidemiological authorities⁴ on this topic namely, that seventy to ninety per cent of human cancer is caused by contact with chemical substances, should be taken seriously and all efforts must be made to limit these compounds in our drinking waters.

The objective of this study was therefore to determine the occurrence and concentration of THM's in South African drinking waters, thereby enabling local authorities to compare our values with these of overseas and establishing local guidelines for these compounds in SA drinking-water supplies. With the financial assistance of the Water Research Commission, the Division of Water Technology commenced this survey in July 1986.

1.1. THM Formation - the haloform reaction

Haloforms are produced by the reaction of chlorine with organic precursor molecules, since they are not present in significant concentrations in non-chlorinated water. Tannic acid, and nitrogen-containing compounds have been shown to produce THM's on chlorination.⁵ The major THM precursors, however, appear to

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be the aquatic humic substances and the presence of halogenated organics, both volatile and non-volatile in drinking water can be used as an indicator of water quality i.t.o. organic material.

High levels of THM's are usually indicative of high levels of organic matter in the finished water, which in turn is indicative of an ineffective treatment process in respect of the removal of organic matter. Since the aim of municipal drinking-water utilities is to produce a safe and high quality product by using the most efficient and cost effective treatment methods, the formation and removal of THM's and their precursors can serve as a good indicator as to whether this aim is being achieved.

1.2 Definition of trihalomethane (THM)

Trihalomethanes are the by-products formed when hypochlorous acid reacts with specific organic materials in a water. The rate and extent of formation of the THM's is dependant upon the chlorine dose, temperature, pH, reaction time, and the amount and type of organic material present. The four major trihalomethane components generally found in water after disinfection with chlorine, in descending concentrations are chloroform, dichloro-bromomethane, dibromochloromethane and bromoform. This concentration order could be reversed if bromide ions were present in the water to be chlorinated.

1.3 Factors affecting the rate of THM formation

It has been hypothesized that THM's are formed by the wellknown haloform reaction between chlorine or any other halogen oxidant and the organic precursor compounds. If this were simply the case, the rate of formation of THM's in the haloform reaction would be independent of the applied chlorine dose, because the rate of haloform reaction is apparently controlled by an initial enolization step.⁶

Practice has, however, shown that THM formation is dependent on the chlorine dosage, and increases as the chlorine dose increases. This indicates, therefore, that THM formation also occurs through reaction pathways other than the haloform reaction.⁷

Systematic studies have furthermore shown that THM production time is roughly proportional to the initial TOC with concentration, and is pH and temperature dependent.⁸ The presence of both bromide and ammonia strongly affect THM formation because they compete with the THM precursor sites on the humic polymers for the oxidizing potential of chlorine. Α substantial proportion of the bromide (15-30%) in water is converted upon chlorination to bromine or hypobromous acid, which can react with THM precursors to form the brominated THM's.

In a surface supply, thousands of organic compounds may exist in varying concentrations and at various times of the year. While organic compounds may originate from man-made or natural sources not all produce significant amounts of THM's on chlorination.

Humic and fulvic acids are classes of compounds found in abundance in surface water supplies. As first identified by Rook in 1974,⁹ humic acids have shown a great potential in THM production and are a class of large molecular weight organic acids derived from the decomposition of plant and animal matter. These compounds are usually the largest contributors to the organohalogen precursor concentration.

1.4 Seasonal variations in THM formation

Several researchers have demonstrated that a definite seasonal variation in the formation of THM's in a potable water supply exists.^{10,11}

It is also known that higher THM levels occur during the warmer months with lower concentrations occurring in the colder months. It has been postulated that this decrease in concentration in the colder months could be a result of decreased THM precursor concentrations or the result of lower temperatures on the rate of THM formation. During the summer months when algal growth is at its peak the THM formation potential was also at its greatest indicating a contribution of extracellular material from algae to the organohalogen precursor concentration.¹²

1.5 THM formation in relation to wastewater reuse

As a result of increasing demands on the limited natural water sources in South Africa, the reuse of water on a rapidly increasing scale is inevitable. The experience of the recent drought in South Africa has increased the importance of, and reliance on, treated wastewater reuse as a means to overcome water shortages.

Wastewater reuse can be achieved directly, by reclaiming the wastewater for potable use, or indirectly by treating source waters into which wastewater has been released.

The recycling of wastewater may have serious implication in terms of the levels of THM's and chlorinated organics in the If chlorine is used in the water treatment finished water. process, wastewater reuse may result in a gradual build-up of chlorinated products, to levels which could exceed suggested maximum contaminant levels, unless adequate barriers to remove THM's or their precursors are built into the treatment system. In a direct reuse system these barriers would include either physical-chemical methods, such as coagulation, activated carbon adsorption, air stripping, or a combined physical chemical/biological barrier such as biological activated carbon (BAC). In an indirect reuse system the barrier to the build-up of chlorinated products would be the capacity of the natural

aquatic environment to disperse these products.

1.6 The South African scene concerning trihalomethanes

The facilities to evaluate the occurrence and concentration of THM's, organohalogen precursors and dissolved organic carbon concentrations in South African water sources are extremely limited. due to the sophisticated measuring instruments required. A considerable amount of information on the PWV area, in Windhoek and various other areas is available which was obtained by being involved with contract work where these type of analyses were done on special request. Except for water supplies in Windhoek and in the Pretoria area little is known about the occurrence of the discussed determinands in other parts of the country. Before we can even decide whether THM's are a problem in SA or not, we have to determine their occurrence and concentrations. We have until now used overseas criteria as guidelines for the concentration of THM's in our waters but may find that, after having conducted a national survey, we could set our own THM criteria taking into account our own environmental conditions. Considerations for THM removal could only be investigated if we knew their occurrence and concentrations.

Limited results available for South African drinking-water supplies indicate the following: 1. a drinking-water supply derived by conventional treatment of dam water in Windhoek often has THM values in excess of 100 ug/1; 2. a drinkingwater supply in Windhoek derived by direct reclamation from wastewater generally has THM values below 100 ug/1; 3. drinking water derived by conventional treatment of water from the Vaal River system has THM values close to the level of 100 ug/1¹³. In view of this situation the Rand Water Board is conducting research into the use of activated carbon in its treatment system, a step which could increase the cost of water supplied by the Board to is users by 28 percent.¹⁴

2. SELECTION OF SAMPLING SITES

During the first year of the survey, twenty five sites were sampled once a month. During the second year, the sample sites were increased to forty and sampled twice a month. The selection of sampling sites was aimed at incorporating as large a portion of the domestic sector as possible. Only tap waters from drinking-water reticulation systems were sampled.

3. SAMPLING PROCEDURES

Sampling was carried out by trained persons and included members of the DWT as well as many Municipalities who took part in this survey (see acknowledgements). Special designed reinforced cardboard boxes containing four glass bottles each were sent to each site on a regular basis. Samples were taken on the 10th and 20th of each month. Free chlorine was measured and recorded when the sample was taken. The distribution of sample sites is illustrated in Figure I.

4. DETERMINANDS SELECTED FOR THE SURVEY AND ANALYTICAL PROCEDURES FOLLOWED

The determinands selected for regular analysis were those that are directly related to the production of THM's in water i.e. pH, dissolved organic carbon (DOC), bromide, and free residual chlorine. The terminology THM represents the sum of the following components: chloroform, dichlorobromomethane, dibromochloromethane and bromoform.

4.1 Trihalomethane determination

Samples were collected in 50 ml dark glass bottles and capped with teflon liners. Ascorbic acid was added to each bottle to destroy free chlorine when the sample was taken. The determination was done by gas chromatography according to the method described by Van Rensburg *et al.*¹⁵ The latter described

method was modified by replacing the 50 m SP2100 flexible fused silica column by a 30 m x 0,32 mm ID J & W DBI fused silica column with 1 um film thickness.

Water samples were extracted with an azeotrope mixture consisting of isopropylether (53%) and hexane (47%).

4.2 Dissolved organic carbon analysis

Samples were collected in all glass containers. The determination was based on ultraviolet/peroxodisulphate oxidation according to the method described by Van Steenderen & Lin (1981)¹⁶

5. **RESULTS AND DISCUSSION**

Few samples taken during the survey contained free chlorine although all the water purification plants used chlorine disinfection as a final process (Table B). It was for this reason that after 12 months into the survey, it was decided to take two samples at each site. One was analyzed for THM's as taken, the other one was chlorinated to 1 mg/1 free chlorine residual and left standing at room temperature for 2 days before analysis. All results are presented in Tables 1 to 40.

5.1 Chemical Treatments

Of particular interest was the number of different chemical treatments those waters received (Table B). Forty five per cent of the treatment plants used aluminium sulphate while an equal amount used one or other type of polyelectrolyte. The other ten per cent represented ferric chloride, polyaluminium chloride, lime and combinations of various of the flocculants mentioned. A relationship between THM's and chemical treatments used was not determined because of the vastly different water characteristics.

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Tabl	e B: Chemicals used in treatment processes throughout the country
Code	Treatment
1.	Ferric chloride, lime, chlorine
2.	Aluminium sulphate, sodium aluminate, lime, carbon dioxide, chlorine
3.	Chlorine
4.	Aluminium sulphate, lime chlorine
5.	Aluminium sulphate, lime, chloramination
6.	Floccotan FB50, Aluminium sulphate, lime, chlorine
7.	Superfloc C577, Aluminium sulphate, lime, chlorine
8.	Ultrafloc 5105, Aluminium sulphate, lime, chlorine
9.	Anikem polyelectrolyte, chlorine
10.	Ferric chloride, chlorine
11.	Aluminium sulphate, lime, sodium silicate, ferrous sulphate, chlorine and chloramination
12.	Aluminium sulphate, chlorine
13.	Ferric chloride, powder activated carbon, polyelectrolyte, lime, chlorine
14.	Cyanamid C579, lime, chloramination
15.	Ultrafloc polymer, chlorine
16.	Prechlorination, polyaluminium chloride, granular activated carbon, chlorine
17.	Aluminium sulphate, Aecipol electrolyte, lime, chlorine
18.	Aluminium sulphate, lime, carbon dioxide, chlorine
19.	Aluminium sulphate, polyelectrolyte, lime to pH 9,0 - 9,5, chlorination
20.	Ferric chloride, polyelectrolyte, lime, chlorine
21.	Lime, carbon dioxide, chlorine
22.	Polyaluminium chloride P30, lime, chlorine.

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5.2 THM Concentrations

Only 10 per cent of the THM values direct from the tap exceeded 100 ug/l total THM's while this increased to twenty percent when samples were chlorinated to 1 mg/l (Figure 2). At 75 per cent of the sites chloroform was the predominant compound (>60%), Tables 1-40. At the other 25 per cent of the sites, all four THM compounds were more evenly distributed. The sites where values of >100 ug/l THM's were recorded were also known to be recipients of secondary treated sewage. The highest DOC values also occurred at these sites.

5.3 DOC Concentrations

Site 9 recorded the third highest DOC value (6 mg/1) but one of the lowest THM values. An explanation for this was the use of chloramination in place of chlorination thereby eliminating the formation of THM's.

Sites 29 and 40 drew from the same source (Hartbeespoort Dam), yet the THM and DOC values at site 29 were considerably lower than at site 40. The difference in treatment was the use of the powder activated carbon at site 29. The granular activated carbon at site 40 was obviously exhausted in respect of THM removal.

5.4 Relationships between THM and other measured determinands

To determine whether any relationship existed between THM and the other measured determinands, simple and multivariate regression analysis was applied. In the calculation, sample sites at which only one observation was made during the survey Tables 41 to 48 summarize the ignored. were average concentrations of the measured determinands per sample site and details of the spread and distribution of present the Tables 49 to 54 relate to intercorrelation determinands. regression analysis of the measured determinands. Statistical



Sample site Table number

Figure 2: Average concentrations of THM's at sampling sites. (Numbers allocated to histograms follow Tables 1-40.)



(I/Sn) MHII ageravê

allocated to historrams follow Tables (1-40.)
evaluations did not accommodate factors such as seasonal influences, the different sources of raw water, different chemical treatments or the final chlorination dosages at the treatment plants. The box-and-whisker plots indicate a considerable skewness around the inter-quartile ranges for all determinands which can directly be attributed to the above mentioned factors (Box & Whisker Plot explanation in Figure 3).

Although analysis of variance only indicates a 16,24 per cent THM depending on the DOC content, the probability level of the relationship between the observed THM and DOC values is in the order of 90 per cent (Table 49). The probability level of this relationship increases further to 99,9 per cent under controlled chlorination conditions (Table 50).

The effect of chlorine on the formation of dibromochloromethane and bromoform in the presence of bromide was also demonstrated (Table 51). Although r-squared only indicated a 5,57 per cent dependency of the formation of bromonated compounds in the presence of bromide, the probability level of a relationship was 84 per cent and increased to 96 per cent under controlled chlorination conditions (Table 52).

The formation of chloroform and dichlorobromomethane upon chlorination was not influenced by the presence of bromide (Tables 53 and 54).

6. CONCLUSIONS

Only four sample sites out of a total of forty recorded THM values >100 ug/l. The same sites were also among the highest THM values recorded when samples were laboratory chlorinated to a 1 mg/l residual level. The percentage of sites with values of <100 ug/l THM concentrations could possibly be further increased if the sites now producing THM's in excess of 100 ug/l experimented with some of the purification techniques employed by the other treatment plants. Until now, no

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scientific evidence has been forthcoming as to why the same flocculant should remove THM precursors at one purification plant and not at another. Sixty seven per cent of treatment plants referred to used aluminium sulphate alone or in combination with other flocculants.

Based on regression results, DOC could serve as a useful parameter to estimate the concentration of THM's in the final waters or as a operational tool in process control.

On average, waters direct from the tap contained 45 ug/1 THM. Upon post chlorination to 1 mg/1 residual chlorine this value rose to 74 ug/1. Based on this data, South African drinking waters appear to be well within the United States EPA criterium of 100 ug/1 THM.

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Rand Water Board Umgeni Water Board Magalies Water Board DWT Water Care Services, CSIR DWT Branch Laboratory, Bellville, CSIR DWT Branch Laboratory, Durban, CSIR Water Treatment Laboratory, Iscor, Newcastle The Municipalities of : Port Elizabeth

> Cape Town East London George Kimberley Brits Upington

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Figure 1: Sample site distribution in South Africa.

Douglas Rustenburg Volksrust.

Towards the end of the survey the number of THM analysis became too large to handle and the Hydrological Research Institute gratefully come to our assistance to share this load of analyses.

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TABLE 1:THM analysis of sample taken from the distribution systemat Cape Town (Bellville).Source of raw water Voëlvlei,Wemmershoek and Teewaterkloof mixture.Treatment processcode is 1, 2 and 18, obtained from Table B.

(Number of samples taken: 4)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	13	54	41	ug/1
CHC1 ₂ Br	3	26	11	ug/1
CHC1Br ₂	1	3	1	ug/1
CHBr ₃	0	13	0	ug/1
Total THM	16	83	56	ug/1
рН	8,4	8,7	8,5	
DOC	1,4	2,6	1,8	mg/1
Bromide .	0,2	0,4	0,3	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC13	63	66	65	ug/l
CHC12Br	8	12	10	ug/1
CHC1Br ₂	1	1	1	ug/1
CHBr ₃	ND	ND	ND	ug/1
Total THM	71	79	75	ug/1

TABLE 2: THM analysis of sample taken from the distribution system at Paarl. Source of raw water Wemmershoek Dam. Treatment process code is 2 obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	X	Unit
CHC1 ₃	34	42	37	ug/1
CHC1 ₂ Br	4	12	7	ug/1
CHC1Br ₂	1	1	1	ug/1
CHBr ₃	0	13	0	u g/1
Total THM	41	60	47	ug/l
рН	8,2	8,8	8,4	
DOC	1,4	8,6	3,2	mg/1
Bromide	0,2	0,3	0,2	mg/1
Free chlorine	<0,1	0,1		mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

45	46	45	ug/l
9	13	11	ug/1
2	3	3	ug/l
ND	ND	ND	ug/1
55	61	58	ug/l
	9 2 ND	9 13 2 3 ND ND	9 13 11 2 3 3 ND ND ND

TABLE 3:THM analysis of sample taken from the distribution systemat Cape Town (Strand).Source of raw water Steenbras DamTreatment process code is 2, obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	X	Unit
 CHCl ₃	28	45	34	ug/1
CHC1 ₂ Br	5	10	7	ug/1
CHC1Br ₂	1	3	1	ug/1
CHBr ₃	0	13	7	ug/l
Total THM	40	54	45	ug/1
рH	6,5	8,0	7,3	
DOC	2,0	8,5	4,1	mg / 1
Bromide	0,3	2,1	0,7	mg / 1
Free chlorine	<0,1	<0,1	_	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC13	31	33	32	ug/1
CHC1 ₂ Br	9	10	9	ug/1
CHC1Br ₂	2	2	2	ug/1
CHBra	ND	ND	ND	ug/l
Total THM	43	44	43	ug/1

TABLE 4: THM analysis of sample taken from the distribution system at Cape Town (Sybrand Park). Source of raw water Wemmershoek Dam, Steenbras Dam. Treatment process code is 2 obtained from Table ^B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	14	56	40	ug/1
CHC1 ₂ Br	6	12	8	ug/l
CHC1Br ₂	1	3	2	ug/1
CHBr ₃	0	13	7	ug/1
Total THM	20	78	52	ug/1
рH	6.9	8,8	8,0	
DOC	1.5	8.0	3,3	mg/1
Bromide	0,2	0,6	0,4	mg/1
Free chlorine	<0.1	<0.1	-	mg/1

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CHC13	53	64	59	ug/1
CHC1 ₂ Br	18	. 19	18	ug/l
CHC1Br ₂	ю́.	7	6	ug/1
CHBr ₃	0	1,2	1	ug/l
Total THM	79	88	84	ug/1

TABLE 5: THM analysis of sample taken from the distribution system at Cape Town (Mitchell's Plain). Source of raw water Teewaterskloof Dam. Treatment process code is 18, Obtained from Table ^B.

(Number of samples taken: 5	Number	of	samples	taken:	5)
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Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	32	40	36	ug/1
CHC1 ₂ Br	3	16	• 9	ug/1
CHC1Br ₂	0	3	1	ug/l
CHBr₃	0	13	7	ug/1
Total THM	43	59	48	ug/l
рН	7,7	8,8	8,5	
DOC	1,2	2,2	1,6	mg/1
Bromide	0,2	0,6	0,3	mg/1
Free chlorine	0.1	1,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 _a	47	50	49	ug/l
CHC1 ₂ Br	10	14	12	ug/1
CHC1Br ₂	2	4	3	ug/1
CHBr ₃	ND	ND	ND	ug/1
Total THM	61	64	63	ug/l

TABLE 6:THM analysis of sample taken from the distribution systemat Cape Town (Atlantis).Source of raw water, groundwater.Treatment process code is 3 obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	5	7	6	ug/l
CHCl ₂ Br	1	4	3	ug/1
CHC1Br₂	5	13	8	ug/1
CHBr ₃	16	43	26	ug/1
Total THM	7	65	29	ug/1
рН	7,4	7,9	7,6	
DOC	4.9	15,3	7,2	mg/1
Bromide	0.6	0,8	0,7	mg/1
Free chlorine	<0.1	1.0	-	mg/1

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CHC1 ₃	7	8	7	ug/l
CHC1 ₂ Br	3	4	3	ug/1
CHC1Br ₂	19	25	22	ug/1
CHBr₃	40	68	54	ug/1
Total THM	73	107	90	ug/l
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TABLE 7: THM analysis of sample taken from the distribution system at Seshego (Pietersburg). Source of raw water Bloed River water plus Groundwater. Treatment process code is 4, obtained from Table B.

(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit
CHC13	1	9	6	ug/1
CHC1 ₂ Br	0	7	3	ug/l
CHC1Br ₂	0	5	2	ug/1
CHBr₃	0	6	2	ug/1
Total THM	1	27	9	ug/1
рН	7,5	8.1	7,8	
DOC	2.0	3.0	2,7	mg/1
Bromide	0,3	1,4	0,7	mg / 1
Free chlorine	<0,1	<0,1	_	mg/1

5	16	11	ug/1
3	13	7	ug/1
3	14	7	ug/1
7	13	10	$\mathtt{ug}/1$
19	55	34	ug/1
	3 3 7	3 13 3 14 7 13	3 13 7 3 14 7 7 13 10

TABLE 8: THM analysis of sample taken from the distribution system at Pietersburg (Boreholes). Source of raw water Groundwater. Treatment process code is 4, obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
ĊHC1,	5	14	10	ug/1
CHC1 ₂ Br	1	5	3	ug/1
CHC1Br ₂	0	0	0	ug/l
CHBr ₃	0	4	1	ug/1
Total THM	11	19	15	ug/l
рН	7,9	9.6	8,7	
DOC	1.2	3,5	2,1	mg/1
Bromide	0,3	0.7	0,4	mg / 1
Free chlorine	<0.1	0,1	-	mg / 1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC13	21	26	24	ug/l
CHC1 ₂ Br	6	11	9	ug/l
CHC1Br ₂	1	6	3	ug/l
CHBr ₃	0	2	1	ug/1
Total THM	30	40	35	ug/l

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TABLE 9 : THM analysis of sample taken from the distribution system at Pietersburg. Source of raw water Ebeneser Dam. Treatment process code is 5, obtained from Table B.

(Number of samples taken: 5)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	10	20	14	ug/1
CHCl ₂ Br	3	8	5	ug/1
CHC1Br ₂	0	1	1	ug/l
CHBr ₃	0	0	0	ug/l
Total THM	13	29	20	ug/l
pH	8,4	9,0	8,8	
DOC	1	21	6	mg/1
Bromide	0,2	1.6	0,6	mg/1
Free chlorine	<0.1	0,3	-	mg/1

CHC13	-19	28	23	ug/1
CHC12Br	5	9	7	ug/1
CHC1Br ₂	1	2	2	ug/1
CHBr₃	0	0	0	ug/1
Total THM	24	39	32	ug/1

TABLE 10: THM analysis of sample taken from the distribution system at Nelspruit. Source of raw water Crocodile River. Treatment process code is 5 obtained from Table ^B.

(Number of samples taken: 2)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	19	30	24	ug/1
CHC1 ₂ Br	6	11	8	ug/1
CHC1Br ₂	1	2	2	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	25	41	33	ug/1
рH	7,8	8,2	8,0	
DOC	3.0	3,4	3,2	mg/1
Bromide	0.5	0,5	0,5	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

CHC13	34	34	34	ug/l
CHC12Br	10	10	10	ug/l
CHC1Br ₂	2	2	2	ug/l
CHBr ₃	0	0	0	ug/l
Total THM	45	45	45	ug/l

TABLE 11: THM analysis of sample taken from the distribution system at KaBokweni (Nelspruit). Source of raw water Crocodile River. Treatment process code is 4, obtained from Table B.

(Number of samples taken: 2)

Determinands	Minimum	Maximum	x	Unit
CHC13	14	18	17	ug/l
CHC1 ₂ Br	5	14	9	ug/1
CHC1Br ₂	0	1	1	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	18	23	21	ug/1
рН	7,6	8,0	7,8	
DOC	2,8	2,8	2,8	mg/1
Bromide	0,2	0,5	0,3	mg/1
Free chlorine	<0,1	<0,1	-	mg/1

CHC13	33	33	33	ug/l
CHC1 ₂ Br	11	11	11	ug/1
CHC1Br ₂	2	2	2.	$\mathtt{ug}/1$
CHBr ₃	0	0	0	ug/1
Total THM	46	46	46	ug/1

TABLE 12: THM analysis of sample taken from the distribution system at Ladysmith. Source of raw water Spioenkop Dam. Treatment process code is 6 obtained from Table B.

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(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	9	38	21	ug/1
CHC1 ₂ Br	1	6	4	ug/l
CHC1Br ₂	1	2	1	ug/1
CHBr ₃	0	0	0	u g/1
Total THM	15	32	21	ug/1
pH	7,7	8,6	8,1	
DOC	1,4	2,8	1,9	mg/1
Bromide	0,2	0,7	0,3	mg/1
Free chlorine	<0,1	0,3	-	mg / 1

CHC1 ₃	18	42	27	ug/1
CHC1 ₂ Br	7	9	8	ug/1
CHC1Br ₂	1	4	3	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	29	52	37	ug/l

TABLE 13: THM analysis of sample taken from the distribution system at eZakheni (Ladysmith). Source of raw water Tugela River Treatment process code is 7, obtained from Table B.

(Number of samples taken: 9)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	6	54	31	ug/1
CHC1 ₂ Br	1	4	3	ug/1
CHC1Br ₂	0	1 ·	1	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	8	59	34	ug/1
рН	7,5	8,6	8,2	
DOC	1.0	7,4	3,1	mg/1
Bromide	0,1	0,9	0,3	mg/1
Free chlorine	<0.1	3,0	_	mg/1

CHC1 ₃	47	109	74	ug/l
CHC1 ₂ Br	12	15	13	ug/1
CHC1Br ₂	1	4	3	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	64	122	90	ug/1

TABLE 14: THM analysis of sample taken from the distribution system at Dimbaza (Ciskei). Source of raw water Sandile Dam. Treatment process code is 1 obtained from Table B.

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(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	28	28	28	ug/1
CHC1 ₂ Br	17	17	17	ug/1
CHC1Br ₂	7	7	7	ug/1
CHBr ₃	1	1	1 .	ug/1
Total THM	54	54	54	ug/1
pH	8	8	8	
DOC	3,3	3,3	3,3	mg/1
Bromide	0,3	0,3	0,3	mg/1
Free chlorine			ND	mg/1

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CHC1,	- 80	80	50	ug/1
CHC1 ₂ Br	40	40	40	ug/1
CHC1Br ₂	21	21	21	ug/l
CHBr₃	4	4	4	ug/1
Total THM	144	144	144	ug/l

TABLE 15: THM analysis of sample taken from the distribution system at Bloemfontein. Source of raw water Welbedacht Dam. Treatment process code is 1, obtained from Table B.

(Number of samples taken: 16)

I 1 0	100 19	63	ug/1
	19	9	
0			ug/1
	7	2	ug/1
0	0	0	ug/1
2	109	74	ug/1
8,1	9,3	8,8	
2,3	5,7	3.2	mg/1
0,1	3,1	0,5	mg/1
<0,1	<0,1	_	mg/1
	2 8,1 2,3 0,1	2 109 8,1 9,3 2,3 5,7 0,1 3,1	210974\$.19.38.82.35.73.20.13.10.5

CHC13	12	120	84	ug/l
CHC1 ₂ Br	12	22	17	$\mathtt{ug}/1$
CHC1Br ₂	1	17	55	ug/1
CHBr ₃	0	9	1	ug/1
Total THM	50	135	108	ug/1
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TABLE 16: THM analysis of sample taken from the distribution system at Bloemfontein (Mazelspoort). Source of raw water Modder River Weir. Treatment process code is 7, obtained from Table B.

(Number of samples taken: 15)

Determinands	Minimum	Maximum .	x	Unit
CHC1,	4	81	26	ug/1
CHC1 ₂ Br	0	15	5	ug/1
CHC1Br ₂	0	3	1	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	5	97	32	ug/1
ρH	7.9	9,3	8,8	
DOC	2	5	3,3	mg/1
Bromide	0,1	0,9	0,4	mg/1
Free chlorine	<0,1	0,1	-	mg/1

CHC1 ₃	14	64	35	ug/1
CHC1 ₂ Br	1	25	11	ug/1
CHC1Br ₂	0	16	4	ug/1
CHBr ₃	0	2	0	ug/l
Total THM	16	94	50	ug/1

TABLE 17:THM analysis of sample taken from the distribution systematMakwarella (Venda)Source of rawwaterVondoDam.Treatment process code is 4, obtained from TableB.

(Number of samples taken: 9)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	4	61	30	ug/1
CHC1 ₂ Br	1	25	13	ug/l
CHC1Br ₂	0	13	7	ug/1
CHBr ₃	0	4	1	ug/l
Total THM	6	99	51	ug/1
рН	7,1	9,5	8,1	
DOC	1	3.2	1,9	mg/1
Bromide	0,1	0,6	0,3	mg/1
Free chlorine	<0,1	0,1	_	mg/1

6	60	39	ug/l
9	28	18	ug/1
}	16	10	ug/l
0	7	3	ug/1
33	102	70	ug/1
	3 0	3 16 0 7	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE 18: THM analysis of sample taken from the distribution system at Hartswater. Source of raw water Vaal River. Treatment process code is 12 obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
 CHCl ₃	18	18	18	ug/1
CHC1 ₂ Br	13	13	13	ug /1
CHC1Br ₂	13	13	13	ug/l
CHBr₃	7	7	7	ug/1
Total THM	51	51	51	ug/1
рH	7,9	7,9	• 7,9	
DOC	4,2	4,2	4,2	mg/1
Bromide	0.1	0,1	0,1	mg/1
Free chlorine	<0.1	<0.1	-	mg / 1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	ND	ND	ND	ug/1
CHC1 ₂ Br	ND	ND	ND	ug/l
CHC1Br ₂	ND	ND	ND	ug/1
CHBr ₃	ND	ND	ND	ug/1
Total THM	ND	ND	ND	ug/1

TABLE 19: THM analysis of sample taken from the distribution system at Vryburg. Source of raw water Vaal River. Treatment process code is 4, obtained from Table ^B.

(Number of samples taken: 1)

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Determinands	Minimum	Maximum	x	Unit
CHC1,	5	5	5	ug/1
CHC1 ₂ Br	1	1	1	ug/l
CHC1Br ₂	0	0	0	ug/1
CHBr₃	0	0	0	ug/1
Total THM	6	6	6	ug/l
рH	ND	ND	ND	
DOC	4.4	4.4	4,4	mg/l
Bromide	ND	ND	ND	mg/l
Free chlorine	<0,1	<0,1	-	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC1 ₃	- ND	ND	ND	ug/l
CHC1 ₂ Br	ND	ND	ND	ug/l
CHC1Br ₂	ND	ND	ND	ug/l
CHBr ₃	ND	ND	ND	ug/l
Total THM	ND	ND	ND	ug/1

TABLE 20:THM analysis of sample taken from the distribution system
at Upington. Source of raw water Orange River. Treatment
process code is 8 obtained from Table B.

(Number of samples taken: 11)

Determinands	Minimum	Maximum	X	Unit
CHC1 ₃	7	21	14	ug/1
CHC1 ₂ Br	1	12	8	ug/l
CHC1Br ₂	0	12	4	ug/1
CHBr ₃	0	4	1	ug/l
Total THM	9	41	26	ug/1
рН	7,9	8,2	8,1	mg/l
DOC	2,5	4,3	3,2	mg/1
Bromide	0,2	3,7	1.0	mg/1
Free chlorine	0,2	0.4	-	mg/1

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CHC1,	13	59	31	ug/1
CHCl ₂ Br	12	30	19	ug/1
CHC1Br ₂	3	20	12	ug/1
CHBr ₃	0	19	5	ug/1
Total THM	47	105	68	ug/1

TABLE 21: THM analysis of sample taken from the distribution system at Kimberley. Source of raw water Vaal River. Treatment process code is 17, obtained from Table B.

(Number of samples taken: 10)

eterminands	Minimum	Maximum	x	Unit
HCl ₃	10	46	28	ug/1
HC1 ₂ Br	2	24	16	ug/l
HC1Br ₂	0	17	8	ug/l
HBr ₃	0	7	2	ug/l
otal THM	31	70	53	ug/l
н	7,2	7,9	7,7	
00	2,9	7.0	5.0	mg/1
romide	0.4	1,1	0,7	mg/1
ree chlorine	ND	ND	ND	mg/1
ree chlorine	ND	ND		ND

CHC13	17	43	29	ug/1
CHC1 ₂ Br	15	32	24	ug/l
CHC1Br ₂	10	23	19	ug/1
CHBr ₃	2	17	8	ug/1
Total THM	53	96	79	ug/l

TABLE 22: THM analysis of sample taken from the distribution system at Prieska. Source of raw water Orange River. Treatment process code is 9 obtained from Table ^B.

(Number of samples taken: 11)

Determinands	Minímum	Maximum	X	Unit
CHC1 ₃	4	46	19	ug/1
CHC1 ₂ Br	2	9	5	ug/1
CHC1Br ₂	0	3	1	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	6	53	24	ug/l
рН	8,0	8,5	8,2	
DOC	2,1	5,8	3.2	mg/l
Bromide	0	1,1	0.5	mg/1
Free chlorine	<0,1	<0,1	-	mg/l

CHC13	12	57	28	ug/l
CHC1 ₂ Br	3	15	10	ug/1
CHC1Br ₂	0	19	4	ug/1
CHBr _a	0	6	1	ug/1
Total THM	15	79	43	ug/l

TABLE 23: THM analysis of sample taken from the distribution system at Douglas. Source of raw water Orange River. Treatment process code is 10, obtained from Table ^B.

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(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	3	12		ug/1
CHC1 ₂ Br	2	6	3	ug/1
CHC1Br ₂	1	3	2	ug/1
CHBr ₃	0	4	1	ug/1
Total THM	10	20	13	ug/1
рH	7,6	8,3	7,8	
DOC	2,1	4,9	3,8	mg/1
Bromide	0.1	2,1	0,6	mg/1
Free chlorine	<0.1	<0,1	-	mg/1
Free chlorine	<0.1	<0,1	-	

CHC13	6	15	10	ug/1
CHC1 ₂ Br	6	12	Э	ug/1
CHC1Br ₂	7	15	12	ug/1
CHBr ₃	5	26	14	ug/l
Total THM	31	62	45	ug/1

TABLE 24: THM analysis of sample taken from the distribution system at Pretoria (Irene). Source of raw water Vaal Dam water. Treatment process code is 11, obtained from Table B.

(Number of samples taken: 13)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	28	71	51	ug/1
CHC1 ₂ Br	14	24	18	ug/l
CHC1Br ₂	2	10	5	ug/l
CHBr ₃	0	0	0	ug/l
Total THM	51	100	74	ug/l
pH	7,ó	8,4	8,1	
DOC	2.8	4,7	4,0	mg/1
Bromide	0,2	0,8	0,5	mg/1
Free chlorine	<0,1	<0.1	-	mg / 1

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CHC13	28	120	65	ug/1
CHC1 ₂ Br	17	80	28	ug/1
CHC1Br ₂	4	10	7	ug/l
CHBr ₃	0	1	0	ug/1
Total THM	55	208	99	ug/l

TABLE 25: THM analysis of sample taken from the distribution system at Pretoria (Montana). Source of raw water Vaal Dam. Treatment process code is 11, obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
	28	77	53	ug/1
CHC1 ₂ Br	14	31	20	ug/l
CHC1Br ₂	2	9	5	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	48	114	78	ug/1
рН	7,6	8,9	8,3	
DOC	3.3	4,2	3,7	mg/1
Bromide	0.3	0,7	0,4	mg / 1
Free chlorine	<0,1	<0,1	<0,1	mg/1

CHC13	- 35	89	60	ug/1
CHC1 ₂ Br	17	35	26	$\mathtt{ug}/1$
CHC1Br ₂	4	13	9	ug/l
CHBr ₃	1	2	1	ug/l
Total THM	57	121	95	ug/1

TABLE 26:THM analysis of sample taken from the distribution system
at Rietvlei (Pretoria). Source of raw water Rietvlei Dam.
Treatment process code is 12 obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	29	29	29	ug/1
CHC1 ₂ Br	16	16	16	ug/l
CHC1Br ₂	4	4	4	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	49	49	49	ug/1
рH	9,0	9,0	9,0	
DOC	7,0	7,0	7.0	mg / 1
Bromide	ND	ND	ND	mg/1
Free chlorine	0,1	0,1	• 0,1	mg/1

Above water chlorinated to a residual of 1 mg/1 free chlorine

CHC13	ND	ND	ND	ug/1
CHC1 ₂ Br	ND	ND	ND	ug/l
CHC1Br ₂	ND	ND	ND	ug/1
CHBr ₃	ND	ND	ND	ug/1
Total THM	ND	ND	ND	ug/1

TABLE 27: THM analysis of sample taken from the distribution system at Durban (Congella). Source of raw water Nagle Dam. Treatment process code is 4, obtained from Table ^B.

(Number of samples taken: 12)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	27	85	57	ug/1
CHC1 ₂ Br	10	25	20	ug/1
CHC1Br ₂	1	8	5	ug/l
CHBr ₃	0	1	0	ug/1
Total THM	52	116	81	ug/1
рН	7,8	8,9	8,3	
DOC	0.8	3,9	2,1	mg/1
Bromide	0,1	0,7	0,3	mg/1
Free chlorine	<0,1	0,3	-	mg/1

CHC1 ₃	38	101	73	ug/l
CHC1 ₂ Br	13	32	26	ug/1
CHC1Br ₂	1	9	. 7	ug/l
CHBr ₃	1	2	0	ug/1
Total THM	77	136	106	ug/1

TABLE 28: THM analysis of sample taken from the distribution system at Rustenburg. Source of raw water Vaal Dam. Treatment process code is 11 obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
CHC13	39	75	58	ug / 1
CHC1 ₂ Br	11	21	18	ug/1
CHC1Br ₂	, 2	8	5	ug /1
CHBr ₃	0	0	0	ug/1
Total THM	53	92	77	ug/1
рН	7,9	8,2	8,0	
DOC	2,9	5,7	4.4	mg/1
Bromide	0,33	1,4	0,7	mg/l
Free chlorine	<0,1	<0.1	<0,1	mg / 1

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CHC1 ₃	54	80	67	ug/1
CHC1 ₂ Br	14	29	23	ug/1
CHClBr ₂	3	17	9	ug/1
CHBr ₃	0	2	0	ug/1
Total THM	90	116	99	ug/1

TABLE 29: THM analysis of sample taken from the distribution system at Schoemansville. Source of raw water Hartbeespoort Dam. Treatment process code is 13, obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	3	23	11	ug/1
CHC1 ₂ Br	1	15	8	ug/l
CHC1Br ₂	1	10	4	ug/l
CHBr₃	0	4	2	ug/l
Total THM	6	52	25	ug/1
рН	7.1	8,3	7,5	/
DOC	3.8	5,8	4,5	mg/l
Bromide	0,1	0,4	0.3	mg/1
Free chlorine	<0,1	<0.1	_ <i>`</i>	mg/1

CHC1 ₃	7	28	14	ug/l
CHC1 ₂ Br	3	20	9	ug/1
CHC1Br ₂	2	16	8	ug/1
CHBr ₃	1	8	4	ug/l
Total THM	15	68	36	ug/1

TABLE 30: THM analysis of sample taken from the distribution system at Temba (Hammanskraal). Source of raw water Pienaars River. Treatment process code is 1 obtained from Table B.

(Number of samples taken: 2)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	58	62	60	ug/1
CHC1 ₂ Br	53	69	61	ug/1
CHC1Br ₂	37	56	47	ug/1
CHBr ₃	10	18	14	ug/1
Total THM	158	205	182	ug/1
рH	8.0	8,4	8,2	
DOC	7,7	8,3	8,0	mg/1
Bromide	0,5	0,5	0,5	mg/1
Free chlorine	0.2	0,2	0,2	mg/l

CHC1 ₃	-82	82	82	ug/l
CHC1 ₂ Br	87	87	87	ug/l
CHC1Br ₂	67	67	67	ug/1
CHBr₃	20	20	20	ug/1
Total THM	257	257	257	ug/1
TABLE 31:THM analysis of sample taken from the distribution system
at Pietermaritzburg.Source of raw water Midmar Dam.
Treatment process code is 14, obtained from Table B.

(Number of samples taken: 12)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	6	93	34	ug/1
CHC1 ₂ Br	1	17	7	ug/1
CHC1Br ₂	0	7	1	ug/1
CHBr _э	0	0	0	ug/1
Total THM	7	117	43	ug/1
рН	8,1	9,5	9	
DOC	1,4	4,6	2,7	mg/1
Bromide	0	1,8	0.5	mg/1
Free chlorine	<0,1	0,7	-	mg/1

CHC1 ₃	7	142	42	ug/l
CHC1 ₂ Br	1	28	10	ug/1
CHC1Br ₂	0	15	3	ug/l
CHBr ₃	0	0	0	ug/l
Total THM	9	185	59	ug/1

TABLE 32: THM analysis of sample taken from the distribution system at Newcastle. Source of raw water Chelmsford Dam. Treatment process code is 21, obtained from Table ^B.

(Number of samples taken: 10)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	23	53	37	ug/1
CHC1 ₂ Br	9	23	13	ug/1
CHC1Br ₂	1	5	2	ug/l
CHBr ₃	0	. 0	0	ug/1
Total THM	33	69	53	ug/1
pН	8,1	8,9	8,6	
DOC	3,2	4,9	3,7	mg/1
Bromide	0,1	0,9	0,5	mg / 1
Free chlorine	<0,1	<0,1	-	mg / 1

CHC1 ₃	37	61	51	ug/1
CHC1 ₂ Br	16	49	22	ug/1
CHC1Br ₂	4	10	5	ug/1
CHBr ₃	0	2	0	ug/1
Total THM	66	114	78	ug/1

TABLE 33: THM analysis of sample taken from the distribution system at Volksrust. Source of raw water Schuilhoek Dam. Treatment process code is 22, obtained from Table B.

(Number of samples taken: 1)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	31	31	31	ug/l
CHC1 ₂ Br	4	4	4	ug/l
CHC1Br ₂	0	0	0	ug/1
CHBr ₃	0	0	0	ug/l
Total THM	35	35	35	ug/l
рН	8.0	8,0	8,0	
DOC	2,1	2,1	2,1	mg/1
Bromide	0,4	0,4	0,4	mg/1
Free chlorine	ND	ND	ND	mg/l

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CHC1 ₃	44	44	44	ug/1
CHC1 ₂ Br	б	6	6	ug/1
CHC1Br ₂	1	1	1	ug/l
CHBr ₃	0	0	0	ug/1
Total THM	51	51	51	ug/1

TABLE 34: THM analysis of sample taken from the distribution system at Port Elizabeth. Source of raw water, Churchill and Elandsjagt works. Treatment process code is 19, obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	7	57	43	ug/1
CHC1 ₂ Br	15	34	28	ug/1
CHC1Br ₂	13	39	27	ug/1
CHBr ₃	б	30	18	ug/l
Total THM	91	150	119	ug/1
рН	8,1	8,8	8,4	
DOC	3.4	6.3	4,6	mg/1
Bromide	0,1	1,1	0,6	mg/l
Free chlorine	<0.1	<0,1	-	mg/1

CHC1 3	20	63	46	ug/1
CHC1 ₂ Br	2ь	46	35	ug/1
CHC1Br ₂	32	57	46	ug/1
CHBra	27	45	37	ug/1
Total THM	. 142	195	168	ug/l

TABLE 35: THM analysis of sample taken from the distribution system at Port Elizabeth. Source of raw water Loerie Works. Treatment process code is 19, obtained from Table B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit
CHCl ₃	23	82	57	ug/1
CHC1 ₂ Br	21	33	28	ug/l
CHC1Br ₂	8	28	19	ug/l
CHBr ₃	2	23	7	ug/l
Total THM	79	138	112	ug/1
рН	7,8	9,1	8,5	
DOC	1.0	6.3	3,5	mg/1
Bromide	0,1	1,7	0,7	mg/1
Free chlorine	<0,1	<0,1		mg / 1

CHC13	-31	91	71	ug/l
CHC1 ₂ Br	27	45	37	ug/1
CHC1Br ₂	19	43	28	ug/1
CHBr ₃	4	32	11	ug/1
Total THM	109	183	147	ug/1
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TABLE 36: THM analysis of sample taken from the distribution system at George. Source of raw water Swart River Dam and Tuin Roete Dam. Treatment process code is 4 obtained from Table B.

(Number of samples taken: 9)

Determinands	Minimum	Maximum	x	Unit
CHC1 ₃	12	57	30	ug/1
CHC1 ₂ Br	2	12	8	ug/1
CHC1Br ₂	0	4	1	ug/1
CHBr ₃	0	0	0	ug/1
Total THM	17	72	39	ug/1
pH	7,9	8,8	8,5	
DOC	1	4,3	3,1	mg / 1
Bromide	0,1	1,6	0,6	mg / 1
Free chlorine	<0,1	<0.1	-	mg/1

CHC1 ₃	22	100	56	ug/l
CHC1 ₂ Br	4	27	16	ug/l
CHC1Br ₂	1	13	4	ug/1
CHBr ₃	0	0	0	ug/l
Total THM	27	139	76	ug/l

TABLE 37: THM analysis of sample taken from the distribution system at East London. Source of raw water Bridle Drift Dam. Treatment process code is 7, obtained from Table ^B.

(Number of samples taken: 8)

Determinands	Minimum	Maximum	x	Unit	
CHC1 ₃	2	14	10	ug/1	
CHCl ₂ Br	2	8	6	ug/1	
CHC1Br ₂	1	2	1	ug/1	
CHBr₃	0	2	1	ug/1	
Total THM	5	29	18	ug/1	
рH	8,1	8,6	8,3		
DOC	3.4	5,5	4,3	mg/1	
Bromide	0,1	2,4	1,2	mg/1	
Free chlorine	<0,1	<0.1	· –	mg / 1	

CHC13	12	21	15	ug/l
CHC1₂Br	9	15	13	ug/l
CHC1Br ₂	5	21	15	ug/l
CHBr ₃	2	25	13	u g/1
Total THM	28	73	57	ug/l

TABLE 38: THM analysis of sample taken from the distribution system at King William's Town. Source of raw water Laing Dam. Treatment process code is 15 obtained from Table ^B.

(Number of samples taken: 3)

Determinands	Minimum	Maximum	X	Unit	
CHCl ₃	17	22	20	ug/1	
CHC1 ₂ Br	12	19	15	ug/1	
CHC1Br ₂	7	13	11	ug/l	
CHBr ₃	1	3	3	ug/1	
Total THM	43	57	48	ug/1	
рН	8,0	8,2	8,1		
DOC	0,9	2,1	1,7	mg/1	
Bromide	0,3	0.8	0,5	mg/1	
Free chlorine	<0,1	<0,1	_	mg / 1	

CHC13	32	47	29	ug/l
CHC1 ₂ Br	12	19	15	ug/1
CHC1Br ₂	7	13	11	ug/l
CHBr ₃	1	3	3	ug/l
Total THM	74	122	91	ug/l

TABLE 39: THM analysis of sample taken from the distribution system at Beestekraal (Western Transvaal). Source of raw water Vaalkop Dam. Treatment process code is 20, obtained from Table B.

(Number of samples taken: 7)

Determinands	Minimum	Maximum	x	Unit	
CHC1 ₃	42	111	69	ug/1	
CHC1 ₂ Br	3	23	15	ug/1	
CHC1Br ₂	0	6	. 4	ug/1	
CHBr ₃	0	0	0	ug/l	
Total THM	56	137	88	ug/1	
pH	7.9	9.0	8.6		
DOC	1.7	4.6	2,9	mg/1	
Bromide	0,3	1,1	0,6	mg / 1	
Free chlorine	0,8	1,0	. –	mg/1	

CHC1 ₃	62	184	118	ug/1
CHCl2Br	14	25	21	ug/l
CHC1Br ₂	2	13	7	ug/l
CHBr ₃	1	1	0	ug/l
Total THM	95	200	146	ug/1

TABLE 40: THM analysis of sample taken from the distribution system at Brits. Source of raw water Crocodile River. Treatment process code is 16, obtained from Table B.

(Number of samples taken: 6)

Determinands	Minimum	Maximum	x	Unit	
CHC1 ₃	47	82	61	ug/1	
CHC1 ₂ Br	41	51	47	ug/1	
CHC1Br ₂	25	48	35	ug/1	
CHBr ₃	4	7	5	ug/1	
Total THM	131	165	148	ug/1	
рН	7,7	7,7	7,7		
DOC	4,5	5.9	5,1	mg/1	
Bromide	0,3	1,1	0,7	mg/1	
Free chlorine	<0,1	0.2	-	mg/l	

	99	71	ug/l
40	55	46	ug/1
26	49	37	ug/I
4	9	6	ug/1
144	187	160	ug/1
	26 4	26 49 4 9	26 49 37 4 9 6



Concentration range of determinand ----->

Table 41. Statistical calculations on average DOC results from 37 sample sites.

(Sample	site)	DOC

Statistical calculations

Sample size	37
Average	3.52162
Median	3.2
Mode	3.2
Geometric mean	3.27512
Variance	2.03285
Standard deviation	1.42578
Standard error	0.234397
Minimum	1.8
Maximum	8
Range	6.4
Lower quartile	2.7
Upper quartile	4.1
Interquartile range	1.4
Skewness	1.2987
Standardized skewness	3.22503
Kurtosis	2.27938
Standardized kurtosis	2.83016
	Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Upper quartile Interquartile range Skewness Standardized skewness Kurtosis



DOC=dissolved organic carbon

Table⁴². Statistical calculations on average THM results from 37 sample sites.

(Sample site) THM Statistical calculations

i)	56	(19)	53	(37)	148	Sample size	37
2)	47	(20)	24			Average	53.4324
3)	45	(21)	13			Median	47
4)	52	(22)	74			Mode	48
5)	43	(23)	78			Geometric mean	42.8706
ε;	29	(24)	81			Variance	1440.2
75	ç	(25)	77			Standard deviation	37.9499
8)	15	(26)	25			Standard error	6,23893
95	20	(27)	182			Minimum	9
10)	33	(28)	43			Maximum	182
1)	21	(29)	53			Range	173
12)	21	(30)	35			Lower quartile	26
13)	34	(31)	119			Upper quartile	74
14)	5÷	(32)				Interguartile range	48
15)	74	(33)	39			Skewness	1,65458
16)	32	(34)	13			Standardized skewness	4,10878
17)	51	(35)	48			Kurtosis	3.11447
-	26	(36)	83			Standardized kurtosis	3.86704

THM=CHC13+CHC1Br2+CHC12Br+CHBr3

Box-and-Whisker Flot



Table 43.Statistical calculations on average THMC results from 37 sample sites.

(Sample site) 1	HMC	Statistical calc	ulations	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Sample size Hverage Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Interquartile range Skewness	37 22.8108 75 45 72.3962 2255.94 47.4967 7.80841 32 257 225 46 93 53 1.69424	Ect-and-Whisker Plot $ \begin{array}{c} $
+16) 50 (34) 57 (17) 70 (35) 91 (18) 68 (36) 146		Standardized skewness Kurtosis Standardized kurtosis	4.20727 3.81283 4.73416	THMC ug/1

THMC=CHC13+CHC1Br2+CHC12Br+CHBr3 chlorinated

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Table 44. Statistical calculations on average Br results from 37 sample sites.

Box-and-Whisker Plot

0.2 0.6 1 0.4 0.8 1.2

Br mg/1

¢

(Sample	site) Br	Statistical cal	culations
	(19) 0.7 (37	0.7 Sample size	37
(2)0.2		Average	0.489189
(3) 0.7	(21) 0.5	Median	0.5
4 0.4	(22) 0.5	Mode	0.3
: 5) 0.3	(23) 0.4	Geometric mean	0.447596
(6) 0.7	(24) 0.3	Variance	0.040991
(7)0.7	(25) 0.7	Standard deviation	0.202462
(E) 0.4	(26) 0.3	Standard error	0.0332846
9) 0.6	(27) 0.5	Minimum	0.1
(10) 0.5	(28) 0.5	Max i mum	1.2
(11) 0.3	(29) 0.5	Range	1.1
(12) 0.3	(30) 0.4	Lower quartile	0.3
(13) 0.3	(31) 0.6	Upper quartile	0.5
·14) 0.3	(32) 0.7	Interquartile range	0.3
(15) 0.5	(33) 0.6		1.00456
16) 0.4	(34) 1.2	Standardized skewnes	s 2.49459
(17) 0.3	(35) 0.5	Kurtosis	2.81993
13) 0.1	(36) 0.6	Standardized kurtosi	s 3.50134

Br=bromide

Table 45. Statistical calculations on average Br3Br2 results from 37 sample sites.

(Samp	les	ite)	Br3Br2	Statistical calcu	lations	
5 1) 5 2)		13) 1 20) -	0 (37)40 1	Sample size Average	37 6.97297	Box-and-bhisker Plot
(3)	-	21)	3	Median	4	
(4)		22)	5	Mode	1	
- 51			5	Geometric mean	0	
			5	Variance	196.138	
			5	Standard deviation	14.0049	
(B)	1 (26)	6	Standard error	2.3024	
(9)	1 (27) 6:	1	Minimum	0	
(10)	2 (28)	1	Maximum	61	
(11)	1 (29) (2	Range	61	
(12)	1 <	30) ()	Lower quartile	1	
(13)	1 (31) 4	5	Upper quartile	8	<u> </u>
(14)	8 (32) 2(5	Interquartile range	7	0 20 40 60 80
(15)	2.(33) 1	L	Skewness	2.456	Br3Br2 ug/1
(16)	1 (34) 3	2	Standardized skewness	6.09892	_
(17)	8 (35) 14	£ ·	Kurtosis	5.67305	
(18)	5 (36) 4	ł	Standardized kurtosis	7.04387	
					من ذار مع و معناد ا	

Br3Br2=CHC1Br2+CHBr3

Table 46.Statistical calculations on average Br3Br2C results from 37 sample sites.

(Sample	site)Br3Br2C	Statistical calc	ulations	
(1) 1 (2) 3 (3) 2 (4) 7 (5) 3 (6) 76 (7) 17 (8) 4 (9) 2 (10) 2	(19) 27 (37) 43 (20) 5 (21) 26 (22) 7 (23) 10 (24) 7 (25) 9 (26) 12 (27) 87 (28) 3	Sample size Average Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum	37 17.7568 7 3 8.47027 542.023 23.2814 3.82743 1 87	Box-and-Whisker Flot
<pre>(11) 2 (12) 3 (13) 3 (14) 25 (15) 56 (16) 4 17) 13 (16) 17</pre>	(29) 5 (30) 1 (31) 83 (32) 39 (33) 4 (33) 4 (34) 25 (35) 14 (36) 7	Range Lower quartile Upper quartile Interguartile range Skewness Standardized skewness Kurtosis Standardized kurtosis	86 3 23 22 1.53644 4.80872 3.0173 3.7464	0 20 40 60 80 100 Br3Br2C ug/I

Br3Br2C=CHC1Br2+CHBr3 chlorinated

Table 47. Statistical calculations on average Cl3Cl2 results from 37 sample sites.

(San	<u>iple</u>	<u>sit</u>	e)C1	3012	Statistical calcu	lations	=
(<u>San</u> (<u>1</u>) (<u>2</u>) (<u>3</u>) (<u>3</u>) (<u>3</u>) (<u>5</u>) (<u>5</u>) (<u>5</u>) (<u>5</u>) (<u>5</u>) (<u>5</u>) (<u>10</u>) (<u>11</u>) (<u>12</u>) (<u>11</u>) (<u>12</u>) (<u>13</u>) (<u>15</u>) (<u>15</u>) (<u>15</u>) (<u>15</u>)	ap <u>le</u> 54419599392654521 132654521	sit (19) (20) (21) (22) (23) (24) (25) (26) (27) (26) (27) (28) (29) (30) (31) (32) (33) (34)	44 24 63 73 75 19	<u>3C12</u> (37) 108	Statistical calcu Sample size Average Median Mode Geometric mean Variance Standard deviation Standard error Minimum Maximum Range Lower quartile Upper quartile Interquartile range Skewness Standardized skewness	37 45.5405 41 9 37.3304 758.255 27.5364 4.52696 9 121 112 25 69 44 0.83159 2.18923	= Pox-and-Whisker Plot
(17) (12)	31 43 22	(34) (35) (36)	35 84		Standardized skewness Kurtosis Standardized kurtosis	2.18523 0.447336 0.55543	C13C12 ug/1

C13C12 = CHC13 + CHC12Br

Table ⁴⁸.Statistical calculations on average Cl3Cl2C results from 37 sample sites.

(Sam	ple	site)01	<u>3C12C</u>	Statistical calcu	lations	
(1) (2) (3)	75 56 32	(19) (20) (21)	53 38 19	(27) 117	Sample size Average Median	37 65.1351 56	Bex-and-Whisker Plot
(4)	77	(22)	93 -		Mode	44	
5)	61	(23)	86		Geometric mean	55.1163	
(6)	10	(24)	99		Variance	1314.62	
. 7)	18	(25)	90		Standard deviation	36.2577	
(3	33	(26)	23		Standard error	5.96073	┝━━━┥╎╎┝━━━┥
(9)	30	(27)	169		Minimum	10	
(10)	44	(28)	52		Maximum	169	المسمعات ا
(11)	44	(29)	73		Range	159	
(12)	35	(30)	50		Lower quartile	38	
(13)	87	(31)	81		Upper quartile	87	<u></u>
(14)	120	(32)	108		Interquartile range	49	30 90 15 0
(15)	101	(33)	72		Skewness	0.832532	0 60 120 16
115)	4 -	(34)	28		Standardized skewness	2.06741	C13C12C ug/1
17)	57	(35)	44		Kurtosis	0.533066	
18)	5 0	(35)	139		Standardized kurtosis	0.661875	

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Cl3Cl2C=CHCl3+CHCl2Br chlorinated

Table 49. Correlation regression of THM on DOC.

Regression Analysis - Linear model: Y = a+bX

Dependent variable:		THM	Independent	t variable:	DOC
Parameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	15.6549 10.7273	15.6138 4.11751	1.00263	0.322922	

Analysis of Variance

Source Model Error	Sum of Squares 8421.5237 43425.557	Df 1 35	Mean Square 8421.5237 1240.730	F-Ratio 6.7876	Prob. Level .01339
Total (Corr.)	51847.081	36			

Correlation Coefficient = 0.403026 Stnd. Error of Est. = 35.224 R-squared = 16.24 percent



Confidence limits: 95% Prediction limits: 95%

THM=CHC13+CHC1Br2+CHC12Br+CHBr3

Table 50. Correlation regression of THMC on DOC.

Jependent v	ariable:	THMC	Independen	t variable:	DOC
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept	30.2218	19.0871	1.58336	0.122334	
Slope	14.9332	5.03343	2.9668	5.39426E-3	

Fegression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	Prob. Level
Hodel	16319.759	1	16319.759	8.802	.00539
Error	64893.917	35	1854.112		·
Total (Corr.)	81213.676	36	<u> </u>		
Correlation Coef	ficient = 0.448273		R-squared =	20.09 pe	rcent



Confidence limits: 95% Prediction limits: 95%

THMC=CHC13+CHC1Br2+CHC12Br+CHBr3 chlorinated

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Table 51. Correlation regression of Br3Br2 on Br.

Regression Analysis - Linear model: Y = a+bX

Dependent variable:		BR3BR2	Independen	t variable:	BF
Farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	0.987363	6.00356 11.3621	0.164463	·0.870313 0.159678	

Analysis of Variance

Source Model Error	Sum of Squares 393.23616 6667.7368	Df 1 35	Mean Square 393.23616 190.5068	F-Ratio 2.06416	Prob. Level .15968
Total (Corr.)	7060.9730	36			

Correlation Coefficient = 0.23599 Stnd. Errcr of Est. = 13.8024 R-squared = 5.57 percent



Confidence limits: 95% Prediction limits: 95%

Br3Br2 = CHC1Br2 + CHBr3

Table 52. Correlation regression of Br3Br2C on Br.

Regression Analysis - Linear model: Y = a+bX

Dependent variable:		BR3BR2C	Independer	nt variable:	BR
farameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	-1.27234 38.8993	9.66474 18.2911	-0.131548 2.12667	0.896017 0.0405728	

Analysis of Variance

Source Model Error	Sum of Squares 2232.9231 17279.888	D{ 1 35	Mean Square 2232.9231 493.711	F-Ratio 4.5227	Frob. Level .04057
Total (Corr.)	19512.811	36	. 		

Correlation Coefficient = 0.338281 Stnd. Error of Est. = 22.2196 R-squared = 11.44 percent



Confidence limits: 95% Prediction limits: 95%



Table 53. Correlation regression of Cl3Cl2 on Br.

Pegression Analysis - Linear model: Y = a+bX

Dependent va	riable:	CL3CL2 Independent variabl		nt variable:	BR
Parameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	41.9881 7.2619	12.1299 22.9567	3.46152 0.31633	1.43362E-3 0.753631	

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	Frob. Level
Model	77.820142	1	77.820142	.100065	,75363
Error	27219.369	35	777.696		
Total (Corr.)	27297.189	36			

Correlation Coefficient = 0.0533933 Stnd. Error of Est. = 27.8872 R-squared = .29 percent



Confidence limits: 95.00 Prediction limits: 95.00

Cl3Cl2 = CFCl3 + CHCl2Br

Table 54. Correlation regression of C13C12C on Br.

Dependent variable:		CL3CL2C	Independer	nt variable:	BR
Parameter	Estimate	Standard Error	T Value	Prob. Level	
Intercept Slope	72.0456 -14.1264	15.9447 30.1763	4.51847 -0.468127	6,81231E-5 0.642596	

Regression Analysis - Linear model: Y = a+bX

Analysis of Variance

Source So Model Error	um of Squares 294.47762 47031.847	Df 1 35	Mean Square 294.47762 1343.767	F-Ratio .21914	Prob. Level .64260	
Total (Corr.)	47326.324	36	· .		,	
Correlation Coeffici.	ant = -0 0788814	,	Permanad	= 62	nercent	

Correlation Coefficient = -0.0788814 Stnd. Error of Est. = 36.6574 R-squared = .62 percent



Confidence limits: 95% Prediction limits: 95%

Cl3Cl2C=CHCl3+CHCl2Br chlorinated

DIVISION OF WATER TECHNOLOGY

CSIR

DEVELOPMENT OF A PORTABLE TOXICITY DETECTOR FOR WATER

FINAL REPORT

Contract Report for the Water Research Commission

by

WSG MORGAN and PC KÜHN

File No : W5/205/4/1/1

Project No : 670 2906 6

ACKNOWLEDGEMENT

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DEVELOPMENT OF A PORTABLE TOXICITY DETECTOR FOR WATER

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

Dr M J Pieterse Mrs E Bailey Dr W H J Hattingh Dr P L Kempster Mr F S Viviers

Dr W S G Morgan Mr P C Kühn Water Research Commission (Chairman) C S I R (Secretary) Water Research Commission Department of Water Affairs Department of National Health and Population Development C S I R C S I R

The financing of the project by the Water Research Commission and the contributions by the members of the Steering Committee are acknowledged gratefully.

EXECUTIVE SUMMARY

The technology described in this report was developed to satisfy the need for a low-cost, portable instrument for the measurement and processing of extremely low light levels emitted by certain bioluminescent compounds. The instrument is to be employed to detect hazardous materials in surface and drinking water supplies in the laboratory and/or field rapidly, simply and cost effectively.

Bioluminescent reactions, which are adversely affected by hazardous toxic compounds, have proved viable for the detection of such compounds in water. However, the instrumentation utilized thus far to detect the low light outputs of such biochemical reactions, depending as it does on the use of photomultipliers, is energy demanding, fragile and expensive. Such instrumentation is not suitable for use in the field.

Experimental development work carried out at the DWT and the Industrial Electronics division of Production Technology resulted in a prototype, single channel detector (LUCID 1) which was capable of providing reliable detection of these biochemical light emissions.

Subsequently an optimized, dual channel instrument incorporating a microcomputer which could be programmed to provide automatic indication of toxic hazard in water samples, was fabricated (LUCID 2). The development was funded by the Water Research Commission.

The instrument comprises a detector cell having two identical lighttight chambers and two channels for measuring the extremely low light levels emitted by the biological or biochemical samples contained in two small vials inserted therein. Temperature control is affected by circulating water from a temperature controlled bath through the detector cell.

Unique analogue electronic circuitry provided sufficient sensitivity, resolution and signal-to-noise ratio to achieve a meaningful correlation between the LUCID 2 instrument and a standard laboratory luminometer.

Ν

A dedicated microcomputer unit measures the processed light signals from both channels and displays the light output from both channels on a 16 character Liquid Crystal display panel.

The instrument is interfaced with a dot matrix printer which depicts peak height and peak area for the light output from each sample. The presence of hazardous substances is evaluated using a software expansion capability which compares the light output of a test and control sample.

The instrument is self-contained, battery operated with built-in battery charger and of a size and weight suitable for field use.

Laboratory simulation experiments investigating the effects of six toxicants upon the bioluminescent output of the bacterium <u>Photo-</u> <u>bacterium phosphoreum</u> have indicated that the instrument is capable of detecting, within 15 minutes, levels of toxicity equivalent to those of the standard 96-h fish bioassay.

LUCID 2, therefore, detects toxic effects successfully and its level of sensitivity compares well with standard bioassays presently being employed.

INTRODUCTION

Several biological tests have been developed for determining toxicity in aquatic environments using fish, protozoa, algae and other freshwater and marine organisms. However, most of these tests are relatively long and expensive and often require the time-consuming propagation of test organisms. As a result there is a general need to develop rapid, inexpensive and, at the same time, sensitive tests to determine and monitor the toxicity of an ever-increasing number of complex chemicals being discharged to aquatic environments. A study of the literature indicates that no adequate instrumentation is available nationally, and probably internationally, for use in the field to establish toxic hazard in aquatic ecosystems simply, rapidly and by unsophisticated technologists in Third World situations which prevail in many parts of Southern Africa.

The technology described in this report, the development of which was funded by the Water Research Commission, is aimed at correcting this . lack of appropriate means of toxic hazard detection.

BACKGROUND INFORMATION

One of the most important mechanisms of toxic action within living material is the poisoning of enzyme systems. The inhibition of enzyme activity by waterborne toxicants adversely affects natural metabolic processes in biological organisms the detection of which forms the basis for a number of systems evolved to assess the degree of aquatic pollution.

One rapid screening technique that has recently received attention is the bacterial assay (described Microtox) developed by Beckman Instruments Inc., which measures the decrease in natural light emission from the luminescent bacteria *Photobacterium phosphoreum* in response to a toxic effect upon the enzyme luciferase. The decrease in light output is expressed as a 5-minute median effective concentration (EC 50), that is the concentration that effects a 50

percent reduction in light output. Data obtained thus far demonstrates that the luminescent bacteria test provides an extremely rapid, simple test of toxicity with a precision equal to or greater than traditional fish toxicity tests (Curtis *et al*, 1982; Qureshi <u>et</u> <u>al</u>., 1982).

A measurable result of nearly all influences which affect the primary processes of photosynthesis is a change of the fluorescent light emission of a plant. This change of the fluorescence emission due to toxicants which affect or block the enzyme controlled photosynthetic pathways has been utilized to detect various levels of aquatic pollution. The fluorescent light emission test, due to the optical characteristics of photosynthetic pigments (chlorophyll fluorescence >660 nm), allows the measurement of the fluorescence of algae. The time from the dosage of a toxicant to a clear reduction in fluorescent light output from algae is very short (5 minutes) and the sensitivity of the test compares favourably with standard assays.

Techniques, therefore, based upon bioluminescence and algal fluorescence, have proved viable for the universal detection of toxic hazard in water. However, the instrumentation utilized thus far to monitor light output of such biochemical reactions, depending, as it does, on the use of photomultipliers and photo-electric cells, is both energy demanding and expensive, the Beckman Microtox instrumentation retailing at approximately R80 000 and 50c per test. Such instrumentation is not suitable for use in the field.

A new concept involving modern solid state electronic technology to detect light emissions has, therefore, been employed to solve this problem.

TECHNOLOGICAL DESCRIPTION

In order to utilize the enzyme inhibition effects, described above, it was required to measure accurately the extremely low light levels emitted and to detect fluctuations therein. Various photosensors,

normally used in applications such as this (including photomultipliers), were considered and rejected as unsuitable for portable field use because of their size, cost, fragile nature and their requirement for bulky, high voltage power supplies.

After experimenting with a number of solid-state photo-sensors, an OSI-5k type PIN photo-dibde with integral transconductive amplifier was selected. Evaluation criteria included cost, size, supply voltage requirements, responsitivity and NEP (noise equivalent power).

A mechanical structure was devised (hereafter referred to as the detector cell), containing the photo-sensor (Figure 1, a) and a means of holding the liquid sample (b) in a light tight enclosure. Α slotted disc (c), driven by a special low noise servomoter, chops the light emitted by the sample before it reaches the detector. This principle facilitates the processing of the extremely small resultant signal and improves the noise rejection characteristics. As can be seen in the accompanying function diagram, the signal is first amplified by a factor of approximately 10 000 employing two low noise stages (d). Next the signal plus noise is passed through a highly selective digital bandpass filter (e), which automatically tracks the signal within the noise. This is achieved through the use of a reference frequency extracted from the spinning chopper disc by means a second photosensor (f) located in the cell. Referring to the of functional diagram this reference frequency is passed through a pulse shaped circuit before being multiplied one hundredfold using a phaselocked frequency multiplier (h). The multiplier output serves as a clock signal for the digital filter thus continuously adjusting the filter's centre frequency to that of the chopped signal. The signal is filtered once more (i) and finally converted to a d.c. voltage proportional to its true R.M.S. value on a scale of 0 to 200 millivolts representing the intensity of the light emitted by the This concludes the description of the detector and cell sample. proper.

The detector's analogue output was connected to a multi-channel data acquisition unit incorporating a microcomputer which had been previously constructed for use in other experiments. Being programmable in BASIC language it was possible to configure the unit to continuously log the detector output and provide an automatic printout of the varying light intensity. Certain checks and operator prompts were incorporated so as to ensure a high degree of repeatability in the measurements. The accompanying flowchart shows the main programme features (Figure 2).

Laboratory tests showed the detector to have excellent sensitivity and noise characteristics (typical signal to noise ratio = 40dB) One serious which were in fact beyond expectations. problem remained, however. This had to do with static charge build-up on the window of the photo-sensor due to the rotating chopper disc. This had the effect of causing a spurious signal far in excess of the legitimate one and thus masking it to a large degree. This was most effectively by depositing a micro-layer of solved gold (thickness less than 1 micron) onto the photo-sensor window by means of a sputtering process in our Integrated Circuit production facility. The window remained transparent and showed negligible attenuation of the incoming light, while the low surface resistance of the gold layer completely prevented any static build-up.

LABORATORY SIMULATION TESTING

A prototype light emission detector unit (LUCID 1) was fabricated and interfaced to a data acquisition and control module in order to evaluate the concept under laboratory conditions and to compare its efficacy with that of a standard laboratory luminometer (LKB - WALLAC 1250).

LIGHT DETECTION

Enzymes are proteins which catalize specific chemical reactions under mild conditions. In certain cases the products of such reactions are

relatively easily identified, for example, firefly luciferase produces light by a bioluminescent reaction as follows:

 $\mathbf{E} + \mathbf{L}\mathbf{H}_2 + \mathbf{A}\mathbf{T}\mathbf{P} = \mathbf{E} \cdot \mathbf{L}\mathbf{H}_2\mathbf{A}\mathbf{M}\mathbf{P} = \mathbf{P}\mathbf{P}\mathbf{i} \tag{1}$

 $LH_2AMP + 0_2 = E.P. + AMP + C0_2 + light$ (2)

where	E	=	Luciferase	PPi	=	pyrophosphate
	LH2	~	D(-) luciferin	ATP	=	adenosine triphosphate
	Р	2	Oxyluciferin	AMP	Ħ	adenosine monophosphate

The amount of light produced is directly proportional to the concentration of substrate ATP.

The light detection capability of LUCID 1 was assessed utilizing an ATP Monitoring kit commercially available.

Picozyme F (United Technologies Packard) is an example of a highly purified firefly luciferase-luciferin mixture supplied in freezedried form, together with Trios-Mg buffer components and serum albumin. It is reconstituted by adding distilled water according to the manufacturers instructions. A pH of 7,7 is attained which is the optimum for luciferase.

In order to establish substrate dilution curves for ATP using Picozyme F, the latter was reconstituted in 100μ d of distilled water and allowed to incubate at room temperature for 30 minutes. At the end of the 30 minute period, ATP in the range 10^{-6} to 10^{-5} M was rapidly added and the light output measured in a luminometer. Duplicate tests were performed on both a standard laboratory - model luminometer (LKB Wallac 1250) and on LUCID 1 (Figure 3).

Initial experiments showed that LUCID 1 was limited by a maximum output of 200 mV (Figure 4). This has been increased to 5000 mV (Figure 5) by a desentitization of the light recording device (such

that saturation is reached at 3,5 - fold higher light intensity) and the introduction of a scaling factor of 7 upon data output. This gives a final output (in millivolts) approximately equivalent to the LKB Wallac 1250 luminometer. Figure 5 indicates that the baseline output (electronic noise plus background light) and resolution have also automatically increased. Neither of the latter are significant, however, as the resolution is acceptable (0,5% of maximum output) and the baseline is easily corrected to zero upon data output.

The primary reason for the abovementioned change is an extension of the portable luminometers range. This will dictate using sufficient light - generating reagent to produce a suitably large light output, but will ensure a reduced error in detecting differences between control and inhibited enzyme - catalyzed reactions. Although every test for inhibition must be related to a matched control, LUCID 1 provides a system where the light output for the control is at least 1000 mV. In this way, even 10% inhibition of the reaction will give an output reduction of one to several hundred millivolts.

The light detection capability of LUCID 1 is, therefore, more than adequate for toxicity assessment and compares favourably with commercial luminometry systems.

TOXICANT ASSESSMENT

Bioassays were conducted by measuring the decrease in luminescence of the bacterium *Photobacterium phosphoreum* in response to a toxicant. Because the reaction is almost immediate, thus precluding the mixture of reacting substances outside the detector cell, a simple injection device was designed for LUCID 1. It involved sinking a threaded recess into the cap of the instrument. This recess communicates with the reaction vessel (cuvette) below, and with the outside (through a smaller cap) via fine-bore holes designed to take the needle of a syringe. A constant rate, semi-automatic syringe (Hamilton CR-700-200) was acquired for this purpose. It is sturdy, of medium weight and designed to delivery 10 - 200 μ 1. The syringe needle is pierced

through a silincone rubber septum (gas chromatography type) which lies in the abovementioned recess. In this way light is excluded from the recording chamber, but the reaction can be started and reagents rapidly mixed by injection of one or more of the substrates. The tests were conducted by injecting a set volume of bacterial culture into either a test or control solution whilst the data acquisition unit continuously logged the detector output printing results every 2 seconds. Six toxicants have been tested; Copper, Mercury, Cyanide, Arsenic, Phenol and Kelthane. The bacterial suspension (0,01 ml) was injected into either the test or control adjusted to a salinity equivalent الم adjusted to a salinity equivalent to 2% NaCl). At least four concentrations of each toxicant were employed and the concentration effecting a 50% decrease in light output after 5 minutes exposure calculated by interpolation. The effect of various concentrations of Arsenic (as Arsenate) upon bacterial light output is represented in Figure 6. The results obtained from these tests were compared with those using a Microtox toxicity analyzer system. (Curtis et al., 1982; Qureshi et al., 1982). The results expressed in Table 1 indicate that LUCID 1 performed better in this respect being more sensitive than the Microtox system, probably because the Microtox system employed reconstituted lypholized luminescent bacteria whereas we used fresh cultures in our tests.

LUCID 1, therefore, detects toxic effects successfully and its level of sensitivity compares well with standard bioassays presently being employed.

Toxicant	Compound	Test Results LUCID 1	EC 50 MICROTOX (mg/1)	
	1. 10 The summer of	(mg/1)		
Copper	CuSO ₄ . 5H ₂ O	0,05	0,07	
Mercury	MgCl ₂	0,05	0,08	
Arsenate	Na ₂ H.AsO ₄ .H ₂ O	0,09	0,04	
Cyanide	KCN	0,01	0,01	
Phenol	CeHaOH	0,11	0,22	
Kelthane		0,26	0,45	

TABLE 1: EC 50 results of the bioassays compared with Microtox tests

Initial results with LUCID 1 were, therefore, promising and proved the viability of the concept. A pre-production field testing unit has consequently been designed and fabricated and is fully described as Appendix 1.

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Figure 1. FUNCTION DIAGRAM OF DETECTOR CELL AND SIGNAL PROCESSING CIRCUITRY.



Figure 2. BASIC PROGRAM STRUCTURE







Figure 4. Comparison of LUCID 1 maximum output before and after modification



Figure 5. Comparison of LUCID 1 baseline output (electronic noise and background) before and after modification

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Figure 6 The effect of different concentrations of arsenate upon light output of Photobacterium phospheoreum

Light output (mV)



APPENDIX 1

The development of electronic hardware and software for a low cost luminometer system for the detection of hazardous toxic substances in water.

For information on the electronic hardware and software contact Dr W S G Morgan, Division of Water Technology, CSIR, P O Box 395, Pretoria, 0001