# Investigation into Total Organic Halogen Formation after Disinfection of Drinking Water by Chlorine

**E Meintjies**

Report to the Water Research Commission
by
Scientific Services
Rand Water

**WRC Report No KV 117/99**

# INVESTIGATION INTO TOTAL ORGANIC HALOGEN FORMATION AFTER DISINFECTION OF DRINKING WATER BY CHLORINE

Report to the

**WATER RESEARCH COMMISSION**

by

E Meintjies

Scientific Services
Rand Water
P O Box 1127
JOHANNESBURG
2000

WRC Report no. : KV 117/99
ISBN : 1 86845 465 7

# TABLE OF CONTENTS

PAGE

Executive Summary . . . . . . . . . . i

Acknowledgements . . . . . . . . . . iv

Definition of Terms . . . . . . . . . . v

List of Tables . . . . . . . . . . vi

List of Figures . . . . . . . . . . x

1. **INTRODUCTION** . . . . . . . . . . 1

2. **LITERATURE SURVEY** . . . . . . . . . . 4

    2.1 INTRODUCTION . . . . . . . . . . 1

    2.2 DISINFECTION BY-PRODUCT FORMATION . . . . . . . . . . 4

    2.3 MUTAGENICITY OF DRINKING WATER AND THE RELATION TO TOTAL ORGANIC HALOGEN . . . . . . . . . . 4

    2.4 CORRELATIONS BETWEEN THMs AND TOX . . . . . . . . . . 5

    2.5 PERFORMANCE OF POX AND NPOX METHODS . . . . . . . . . . 5

    2.6 CONCENTRATIONS OF TOX MEASURED IN DRINKING WATER SUPPLIES . . . . . . . . . . 5

3. **MATERIALS AND METHODS** . . . . . . . . . . 6

    3.1 CHEMICAL ANALYSIS . . . . . . . . . . 6

    3.2 SAMPLING: LOCALITIES AND FREQUENCY . . . . . . . . . . 6

4. **RESULTS AND DISCUSSION OF RESULTS** . . . . . . . . . . 8

    4.1 PHASE I : WATER DESTINED FOR AND LEAVING ZWARTKOPJES BOOSTER STATION . . . . . . . . . . 8

    4.2 PHASE II: WATER DESTINED FOR AND LEAVING PALMIET BOOSTER STATION . . . . . . . . . . 23

    4.3 PHASE III: WATER DESTINED FOR EIKENHOF AND MAPLETON BOOSTER STATIONS . . . . . . . . . . 30

    4.4 SUMMARY OF TTHM, POX AND AOX RESULTS OBTAINED FOR THE FOUR BOOSTER STATIONS . . . . . . . . . . 40

    4.5 PHASE IV: WATER DESTINED FOR THE DISTRIBUTION SYSTEM 43

    4.6 DISSOLVED ORGANIC CARBON CONCENTRATIONS . . . . . . . . 47

PAGE

4.7 NUMBER OF POX, AOX AND TTHM RESULTS EXCEEDING GUIDELINE VALUES . . . . . 47

5. **CONCLUSIONS** . . . . . 49

6. **RECOMMENDATIONS** . . . . . 50

7. **REFERENCES** . . . . . 51

# EXECUTIVE SUMMARY

## INTRODUCTION

Rand Water utilizes chlorination and chloramination as methods of disinfection in order to ensure the microbiological safety of the water which it produces and supplies to more than nine million consumers. The formation of disinfection by-products is one of the major issues facing present-day water treatment technology and drinking water quality control. The by-products of chlorine disinfection are mainly inorganic chlorides but also include both volatile and non-volatile organo-halogen complexes. Although the major inorganic components are well characterized, the specific organic components are largely an unknown factor.

Concern has been expressed over the potential health risks which may be associated with halogenated organic compounds. Although evidence of toxicity is often limited, it is generally accepted that the presence of such compounds in drinking water is undesirable.

The number and diversity of halogenated organic compounds which can be found in water makes their individual measurement a practical impossibility. Despite the diversity of their general properties, halogenated organics have one common property by definition: the presence of at least one halogen atom. This property has been utilised in methods developed to measure organic halogen compounds as a group determinant. The parameters of Purgeable Organic Halogens (POX) and Adsorbable Organic Halogens (AOX) are popular choices.

Trihalomethane (THM) formation, which constitutes part of the volatile organo-halogen complexes formed, has been well-researched and measured by Rand Water. In view of the growing importance of the non-volatile organic compounds produced by the reaction of chlorine with organic substances, a total organic halogen analyzer was purchased by Rand Water to study the range of total organic halogen concentrations in drinking water.

## AIM OF THE PROJECT

The aim of the project was to determine the concentration levels of total organic halogen (Adsorbable Organic Halogen fraction + Purgeable Organic Halogen fraction; TOX = POX + AOX) throughout the Rand Water distribution system.

## RESULTS OBTAINED

The measurement of TTHM, POX and AOX concentrations throughout the distribution system was divided into four phases. Samples were taken at four different sites. These sites were selected to include i) samples which were taken directly after chlorination (twenty minute contact time); ii) samples which had been exposed to free residual chlorine for six hours; iii) samples which were taken directly after chloramination at the Booster Stations; and iv) samples were collected from the distribution system itself (4-36 hours after chloramination).

In general an increase in TTHM, POX and AOX concentrations were observed when comparing samples which had been exposed to free residual chlorine after a 20 minute contact and the samples taken immediately prior to chloramination at the Booster Stations (approximately a six hour contact time). A surprising aspect of the results was that, under conditions soon after the first chlorination, the measured TTHM values were dramatically lower than the measured POX values. No significant increase in TTHM, POX and AOX was measured at the Booster Stations directly after chloramination. A different picture emerged when samples were taken in the distribution system. Results showed no increase in concentrations for the three variables measured in one part of the study, another part of the study showed a dramatic increase in AOX concentration and a third set of analyses showed a significant loss of AOX in the distribution. The AOX/TTHM and AOX/POX ratios appear to have consistent equilibrium values for each group of pipes and sampling points.

Although no guideline value has been set for POX concentrations in potable water, these concentrations can be compared to measured levels of TTHM. The guideline value which Rand Water uses against which to evaluate TTHM results is that of the United States Environmental Protection Agency (TTHM 100 $\mu$g/ℓ). No TTHM results, and therefore by inference no POX concentrations, obtained during this study exceeded this guideline value.

At present Rand Water has not accepted a guideline value against which to evaluate AOX concentrations and the Dutch guideline value of 100 $\mu$g/ℓ was thus used. When compared to this value less than ten percent of the determinations done on samples during this study exceeded an AOX concentration of 100 $\mu$g/ℓ.

The concentration of AOX was found to be up to five times higher than the levels of POX in the chlorinated waters. These findings indicate that the production of AOX is more significant than the production of POX in chlorinated waters.

The results demonstrated that TTHM values cannot be used as a general indication of TOX.

Rand Water, Scientific Services will incorporate POX and AOX measurements of drinking water into their routine monitoring programme.

## RECOMMENDATIONS FOR FUTURE RESEARCH

- Mutagenicity has been linked to an increase in chloroform concentrations. However, an increase in the concentration of AOX has also been measured in this study. Which fraction is causing the mutagenicity? The relationship of levels of POX and AOX to Ames activity should be examined.

- Both POX and AOX determinations should be incorporated into routine drinking water monitoring programmes to give an indication of the volatile and non-volatile fractions which are formed when organics are chlorinated.

- The loss of AOX in the distribution system should be further investigated.
- A comparison of TOX (POX + AOX) produced by chlorinating different qualities of water should be conducted.
- Examination of concentration levels of TOX produced by different purification and disinfection processes *e.g.*, pre-ozonation followed by chlorination, GAC treatment followed by chlorination, chloramination, chlorine dioxide.
- Guideline values for POX and AOX concentrations in drinking water supplies utilizing chlorine disinfection should be set.

## LIST OF PUBLICATIONS ARISING FROM WRC PROJECT NUMBER 8/132

- Total Organic Halogens: Another Step Forward? E Meintjies and M Murphy. International Specialised Conference. "Disinfection of potable water". Kruger National Park South Africa, 13-18 March 1994.
- Disinfection has to be toxic, the by-products must be safe: the Rand Water experience. E Meintjies. IWSA, 20th International water supply congress and exhibition, Durban, 9-15 September 1995.
- Total organic halogens: an extra chemical handle. E Meintjies. WISA biennial conference and exhibition, Port Elizabeth, 20-23 May 1996.

## ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission entitled:

INVESTIGATION INTO TOTAL ORGANIC HALOGEN FORMATION AFTER DISINFECTION OF DRINKING WATER BY CHLORINE

The financing of the project by the Water Research Commission is gratefully acknowledged.

Rand Water provided the necessary infrastructure and additional financial assistance. The author wishes to record sincere thanks to Rand Water and to the following personnel of Scientific Services, Rand Water:

- Mr J Geldenhuys for his contribution and guidance provided throughout the duration of the project
- Mrs M Murphy and Mrs D Haasbroek (nee Wentzel) for technical assistance in performing the analyses
- The Organic Chemistry Section of Scientific Services for the performance of dissolved organic carbon analyses
- Mrs F Nel and personnel at Zwartkopjes Booster Station for taking the many samples requested at the 4 Booster Stations
- Mr T Prins and personnel at Zuikerbosch Booster Station for taking the many samples requested from Zuikerbosch Purification Plant
- Mr S Rafube for collecting the samples requested at Vereeniging Purification Plant
- Mr C Swartz for his willingness to edit the final report

# DEFINITION OF TERMS

## Total Organic Halogen (TOX = POX + AOX)

A general term that, if used, should be used with the understanding when reporting the results of a water analysis that no method completely recovers the organohalides.

## Purgeable Organic Halogen (POX)

The amount of organohalide material able to be purged from the water under defined conditions and measured by microcoulometry after controlled combustion. The POX parameter includes "the volatile lipophilic organic halogen content".

## Adsorbable Organic Halogen (AOX)

The amount of organohalide material left in the water sample after purging under conditions for the determination of POX. The fraction is then trapped onto activated carbon, and measured by microcoulometry after controlled combustion. The organic halogen compounds are adsorbed onto active carbon at low pH. The active carbon is then washed to remove any inorganic chloride. After washing, the carbon is burnt and the amount of adsorbed organic halogen determined. The AOX parameter includes "the lipophilic and weakly hydrophilic organic halogen content".

## Total Trihalomethane (TTHM)

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

Chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$).

$TTHM = CHCl_3 + CHBrCl_2 + CHBr_2Cl + CHBr_3$

## LIST OF TABLES

4.1.1 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the A6 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 8

4.1.2 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A6 Pumping Main . . . . . . . . 10

4.1.3 Ratios of AOX/POX and AOX/TTHM for the A6 Pumping Main . . . . . . . . 10

4.1.4 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the A8 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 11

4.1.5 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A8 Pumping Main . . . . . . . . 11

4.1.6 Ratios of AOX/POX and AOX/TTHM for the A8 Pumping Main . . . . . . . . 12

4.1.7 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the A10 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 13

4.1.8 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A10 Pumping Main . . . . . . . . 13

4.1.9 Ratios of AOX/POX and AOX/TTHM for the A10 Pumping Main . . . . . . . . 14

4.1.10 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the A12 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 14

4.1.11 Ratios of AOX/POX and AOX/TTHM for the A12 Pumping Main . . . . . . . . 14

4.1.12 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the A14 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 15

4.1.13 Ratios of AOX/POX and AOX/TTHM for the A14 Pumping Main . . . . . . . . 15

4.1.14 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the B1 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 16

4.1.15 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B1 Pumping Main . . . . . . . . 16

4.1.16 Ratios of AOX/POX and AOX/TTHM for the B1 Pumping Main . . . . . . . . 17

4.1.17 Measured levels of POX ($\mu g\ Cl^-/\ell$), AOX ($\mu g\ Cl^-/\ell$) and TTHM ($\mu g\ Cl^-/\ell$) in the B2 Pumping Main to Zwartkopjes Booster Station . . . . . . . . 17

4.1.18 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B2 Pumping Main . . . . . . . . . . 18

4.1.19 Ratios of AOX/POX and AOX/TTHM for the B2 Pumping Main . . . . . . . . . . 18

4.1.20 Average measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in Pumping Mains to Zwartkopjes Booster Station . . . . . . . . . . 19

4.1.21 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from Zwartkopjes Booster Station . . . . . . . . . . 20

4.1.22 Ratios of AOX/POX and AOX/TTHM in the Pumping Mains to and from Zwartkopjes Booster Station . . . . . . . . . . 20

4.1.23 Average concentration measured of the components of TTHMs in the Pumping Mains to Zwartkopjes . . . . . . . . . . 21

4.1.24 Summary of AOX/POX and AOX/TTHM ratios obtained for Pumping Mains A6, A8, A10, A12, A14, B1 and B2 (Phase I) . . . . . . . . . . 22

4.2.1 Measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in the B4 Pumping Main to Palmiet Booster Station . . . . . . . . . . 23

4.2.2 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B4 Pumping Main . . . . . . . . . . 23

4.2.3 Ratios of AOX/POX and AOX/TTHM for the B4 Pumping Main . . . . . . . . . . 25

4.2.4 Measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in the B6 Pumping Main to Palmiet Booster Station . . . . . . . . . . 25

4.2.5 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B6 Pumping Main . . . . . . . . . . 26

4.2.6 Ratios of AOX/POX and AOX/TTHM for the B6 Pumping Main . . . . . . . . . . 26

4.2.7 Measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in the B10 Pumping Main to Palmiet Booster Station . . . . . . . . . . 27

4.2.8 Ratios of AOX/POX and AOX/TTHM for the B10 Pumping Main . . . . . . . . . . 27

4.2.9 Average concentration measured of the components of TTHMs in the Pumping Mains to Palmiet . . . . . . . . . . 27

4.2.10 Average measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in Pumping Mains to Palmiet Booster Station . . . . . . . . . . 28

4.2.11 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from Palmiet Booster Station . . . . . . . . . . . . . . . . 28

4.2.12 Ratios of AOX/POX and AOX/TTHM in the Pumping Mains to and from Palmiet Booster Station . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 29

4.2.13 Summary of AOX/POX and AOX/TTHM ratios obtained for Pumping Mains B4, B6, B10 and O1-O4 (Phase II) . . . . . . . . . . . . . . . . . . . . . . . . . . . . 29

4.3.1 Measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in the A19 Pumping Main to Eikenhof Booster Station . . . . . . . . . . . . . . . . . . . . . . . 30

4.3.2 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A19 Pumping Main . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 30

4.3.3 Ratios of AOX/POX and AOX/TTHM for the A19 Pumping Main . . . . . . . . . 33

4.3.4 Measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in the B7 Pumping Main to Eikenhof Booster Station . . . . . . . . . . . . . . . . . . . . . . . 33

4.3.5 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B7 Pumping Main . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34

4.3.6 Ratios of AOX/POX and AOX/TTHM for the B7 Pumping Main . . . . . . . . . . 34

4.3.7 Average measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in Pumping Mains to Eikenhof Booster Station . . . . . . . . . . . . . . . . . . . . . . 35

4.3.8 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from Eikenhof Booster Station . . . . . . . . . . . . . . . 36

4.3.9 Ratios of AOX/POX and AOX/TTHM for the Pumping Mains to and from Eikenhof Booster Station . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 36

4.3.10 Measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in the B8 Pumping Main to Mapleton Booster Station . . . . . . . . . . . . . . . . . . . . . . . 37

4.3.11 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B8 Pumping Main . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 37

4.3.12 Ratios of AOX/POX and AOX/TTHM for the B8 Pumping Main . . . . . . . . . . 38

4.3.13 Average concentration measured of the components of TTHMs in the Pumping Mains to Eikenhof . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 38

4.3.14 Summary of AOX/POX and AOX/TTHM ratios obtained for Pumping Mains B7, B8 and S1 (Phase III) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 39

4.4.1 Overall average concentrations of POX ($\mu$g Cl$^-$/$\ell$), AOX ($\mu$g Cl$^-$/$\ell$) and TTHM ($\mu$g Cl$^-$/$\ell$) measured to and from the four Booster Stations for the period January 1994 to December 1995 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 40

4.4.2 Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from the four Booster Stations . . . . . . . . . . . . . . . . 40

4.4.3 Ratios of AOX/POX and AOX/TTHM for the Pumping Mains to and from the four Booster Stations . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 42

4.5.1 Measured levels of POX ($\mu$g Cl$^-$/$\ell$), AOX ($\mu$g Cl$^-$/$\ell$) and TTHM ($\mu$g Cl$^-$/$\ell$) for Distribution sample points . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 43

4.6.1 Dissolved Organic Carbon concentrations measured at Site A . . . . . . . . . . . . . . 47

## LIST OF FIGURES

4.1.1 Results for Zwartkopjes Booster Station . . . . . . . . . . . . . . . . . . . . . . . . . 9

4.2.1 Results for Palmiet Booster Station . . . . . . . . . . . . . . . . . . . . . . . . . . . 24

4.3.1 Results for Eikenhof Booster Station . . . . . . . . . . . . . . . . . . . . . . . . . . . 31

4.3.2 Results for Mapleton Booster Station . . . . . . . . . . . . . . . . . . . . . . . . . . 32

4.4.1 Overall average results obtained per Booster Station . . . . . . . . . . . . . . . . . . 41

4.5.1 Results of selected sampling points in the distribution . . . . . . . . . . . . . . . . . 46

# INTRODUCTION

Rand Water abstracts water from the Vaal Dam and the Vaal River system, a surface water source, for purification purposes. The water is purified in two treatment plants *viz.*, Zuikerbosch and Vereeniging and elevated 375 metres in two stages by primary and booster pumping stations through a 2 500 kilometre network of pipelines to 75 local authorities who supply water to private consumers as well as the mines and industrial undertakings. An area of 17 000 square kilometres is served by Rand Water.

Rand Water employs a conventional purification process of coagulation, flocculation, sedimentation, filtration and chlorination. Chlorine is dosed at a rate of between 1.5 - 2.0 mg/ℓ of chlorine at the purification stations. After being exposed to free residual chlorine for approximately six hours the water is subsequently chloraminated using chlorine and ammonia to produce a monochloramine residual of 0.8 to 1.5 mg/ℓ at four booster stations. The aim is to achieve a residual chlorine concentration of at least 0.3 mg/ℓ at the furtherest end points in the distribution system. This ensures that the microbiological quality is maintained and a chlorine residual is still present at the consumer's tap which could be 150 kilometres from the purification plant. Rand Water supports an extensive routine chemical and biological water quality monitoring programme to ensure that a consistently good quality of potable water is supplied to the consumer.

As mentioned above, Rand Water utilizes chlorination and chloramination as methods of disinfection in order to ensure the microbiological safety of the water which it produces and supplies to more than 9 million consumers. The formation of disinfection by-products is one of the major issues facing present-day water treatment technology and drinking water quality control (Pontius, 1990). The by-products of chlorine disinfection are mainly inorganic chlorides but also include both volatile and non-volatile organo-halogen complexes. Although the major inorganic components are well characterized, the specific organic components are largely an unknown factor.

Concern has been expressed over the potential health risks which may be associated with halogenated organic compounds (Kito *et al.*, 1988). Although evidence of toxicity is often limited, it is generally accepted that the presence of such compounds in drinking water is undesirable.

Chlorine disinfection by-products have a unique chemical handle and thus have been studied to a much greater extent than those from alternative disinfectant candidates. The number and diversity of halogenated organic compounds which can be found in water makes their individual measurement a practical impossibility. For certain important groups such as haloforms, chlorinated pesticides and polychlorinated biphenyls, methods exist which are based on gas-liquid chromatography. However, this technique is limited to compounds which are volatile (or can be made so by chemical means) at the operating temperatures of such instruments (generally up to 350°C). Many of the halogenated compounds which can be found in waters are non-volatile and difficult, if not impossible, to measure by such techniques and alternative methods must thus be applied.

Despite the diversity of their general properties, halogenated organics have one common property by definition: the presence of at least one halogen atom. This property has been utilised in methods developed to measure organic halogen compounds as a group determinand. It is necessary however, to isolate the halo-organics from the sample matrix and because of their wide-ranging properties, no single isolation step is effective in extracting all halo-organics from water. Consequently methods have been developed which measure fractions of the halo-organics, the fraction measured denoted in terms of the isolation technique employed. The parameters of Purgeable Organic Halogens (POX) and Adsorbable Organic Halogens (AOX) are popular choices.

With one and the same sample a POX determination may be followed by an AOX determination, POX + AOX being approximately equal to Total Organic Halogen (TOX). A true TOX will never be achieved because all compounds will not be adsorbed on activated carbon and highly volatile components of the POX fraction may be lost during sampling, sample storage, sample handling and sample preparation.

The results obtained from POX and AOX analyses yields no information about the structure or nature of the organic compounds to which the halogens are bound or about the individual halogens present. These methods are sensitive to organic chloride, bromide and iodide but does not detect fluorinated organics.

The nature of the AOX fraction is largely unknown but is believed to be mainly chlorinated humic acids. Humic substances are amorphous, brown or black, hydrophilic, acidic, polydisperse substances, with molecular weights ranging from several to hundreds of thousands and constitute the major portion of the organic material present in raw waters (Agarwal and Neton, 1989). They have been shown to be the primary trihalomethane precursors, as several different moieties within the humic structure are capable of generating trihalomethanes (Agarwal and Neton, 1989). Besides trihalomethanes, which have been studied the most, numerous non-volatile halogenated and non-halogenated by-products are formed during chlorination of water and humic substances (Agarwal and Neton, 1989). However, very little data regarding their structure and biological effects are available.

Chlorination of humic acid is a highly complex chain of reactions. It is essentially an oxidative, halogenating, degradation method with simultaneous substitution, addition, elimination, rearrangement and hydrolytic reactions taking place, resulting in varied and numerous end products which remain to be fully characterized. This chain of reactions is highly dependent upon level of chlorination, total organic carbon, temperature, time, light and pH.

Trihalomethanes have been chosen to represent volatile organic disinfection by-products which are formed during the disinfection process with chlorine and chloramine. Trihalomethane formation has been well-researched and measured by Rand Water. These trihalomethane results are evaluated against the United States Environment Protection Agency guideline value of 100 $\mu$g/ℓ for total trihalomethanes (TTHM) (USEPA, 1979).

In view of the growing importance of the non-volatile organic compounds produced by the reaction of chlorine with organic substances, a total organic halogen analyzer has been purchased by Rand Water to study the range of Total Organic Halogen (TOX = POX + AOX) concentrations in drinking water.

The aim of this project was to determine the concentration levels of Total Organic Halogen (Adsorbable Organic Halogen fraction + Purgeable Organic Halogen fraction; TOX = AOX + POX) throughout the Rand Water distribution system. The Dutch recommended guideline value of 100 $\mu g/\ell$ for AOX is used against which to evaluate the results obtained in this study (Puyker, 1984).

The measurement of TTHM, POX and AOX concentrations throughout the Distribution was divided into four phases. Although Phase I was conducted prior to the commencement of this project, the results have been included in this report for the sake of completeness.

# LITERATURE SURVEY

## 2.1 Introduction

A Waterlit literature survey was done at the beginning of the project while personal scanning of Journals took place thereafter. A total of 166 publications discussing the concept of total organic halogens in aqueous media were found. Sixty three of these papers dealt with the formation and measurement of chlorinated organic matter in pulp and paper effluents. The remaining publications dealt with a variety of topics including health aspects, method comparisons, formation and measurement of chlorinated organic matter when disinfectants other than chlorine were used, ground water contamination at landfill sites, wastewater composition, organic halides in swimming pool water, removal of organic halide precursors and formation of organic halides in surface waters. Routine monitoring for Total Organic Halogen has not been applied widely in potable water quality control. Few publications were devoted to the measurement of total organic halogens in potable water. The important findings are summarized below.

## 2.2 Disinfection by-product formation

Shukairy and Summers (1992) showed that chloramination produced significantly less organic halides, especially POX, compared to that formed by chlorination or ozonation/chlorination. With both disinfectants, and for both ground and river water sources of organic matter, the nonpurgeable organic halide formation rate was found to be much faster than that of POX. Preozonation significantly decreased the amount of organic halide formed after chlorination, but had no impact on the organic halides formed after chloramination.

Lykins Jr. *et al.*, (1986) showed an average instantaneous TOX by-product formation of 60, 92 and 238 $\mu g/\ell$ for chlorine dioxide, chloramine and chlorine respectively after 30 min contact time with surface water.

## 2.3 Mutagenicity of drinking water and the relation to Total Organic Halogen

Lykins Jr. *et al.*, (1986) demonstrated that chlorination and chloramination of the water consistently caused formation of direct-acting mutagens as measured in the Ames assay. When S-9 enzyme mixture was added to the organic fraction prior to testing in attempts to detect promutagens, the activity decreased.

Kito *et al.*, (1988) did not detect mutagenesis in raw water but found it in the finished water treated with chlorine. The presence of S9 in the assay reduced the level of mutagenicity.
The major objective of an investigation by Agarwal and Neton (1989) was to determine the alkylating and mutagenic activities of chlorinated humic acid and also of its various molecular weight fractions. The respective fractions were analyzed for total organic carbon, total organic halogen, alkylating activity and mutagenicity. They showed that mutagenic responses increased sharply with increasing levels of NPOX (non-purgeable organic halogen)(Agarwal and Neton, 1989).

## 2.4 Correlations between TTHMs and TOX

Singer and Chang (1989) examined the extent to which correlations exist between TTHMs and TOX formation. They found that surface waters treated by conventional coagulation, settling, and filtration at near-neutral pH values, the TOX-to-TTHM ratio in the treated water, including the distribution system, is approximately 3.4:1. On a chlorine-equivalent basis, the TTHMs comprise approximately 26% of the TOX concentration. In waters subjected to precipitative softening at alkaline pH values, the TTHMs on a chlorine-equivalent basis comprised approximately 39% of the TOX concentration. They also showed that, regardless of the source, chloroform comprised approximately 20% of the TOX.

## 2.5 Performance of POX and NPOX methods

Studies by the Drinking Water Research Division of the Municipal Environmental Research Laboratory, US Environmental Protection Agency in Cincinnati have shown that the most accurate TOX results are achieved with disinfected water when an estimation of POX from THM analysis is combined with a separate analysis for nonpurgeable organic halide (NPOX)(Stevens *et al.* 1985). Separate aliquots of the sample must be taken for each analysis. The aliquot taken for NPOX analysis must first be purged free of THMs and can then be analyzed by the carbon adsorption method used for TOX. Purging conditions need not be identical to those of the THM analysis because the THM method compensates for recovery inefficiencies (Stevens *et al.*, 1985). When a direct POX analysis is performed in order to combine the results with those of a direct NPOX analysis on an aliquot of the same sample, purging to obtain the POX result and purging the aliquot free of POX prior to NPOX analysis must be of equivalent efficiency.

Bauman and Stenstrom (1989) examined the effect of dechlorination with sulfites on the total organic halogen content of chlorinated water. The most profound differences were observed between identical samples dechlorinated at low and high pH. TOX levels were lower in all water samples dechlorinated under basic conditions than replicates dechlorinated at $pH<2$.

## 2.6 Concentrations of TOX measured in drinking water supplies

Glaze *et al.*, (1977) measured TOX concentrations at 4 cities in Texas of between 73 and 113 $\mu g/\ell$.

Rook (1980) found that during water chlorination under practical treatment plant conditions, the formation of non-volatile halo-organics exceeded the volatile fraction by three to five times. In a study on US drinking water Krasner *et al.*, (1989) measured quarterly median values for total organic halide concentrations of 150, 180, 170 and 175 $\mu g/\ell$ respectively at 35 water treatment facilities.

In a study on Dutch drinking waters prepared from different source waters, Peters *et al.*, (1991) found AOX concentrations between 2.5 and 104.7 $\mu g/\ell$ for surface water origin. A positive relationship was found for AOX and total haloacetic acid concentration, with the latter accounting for about 15% of the AOX.

## MATERIALS AND METHODS

### 3.1 Chemical Analysis

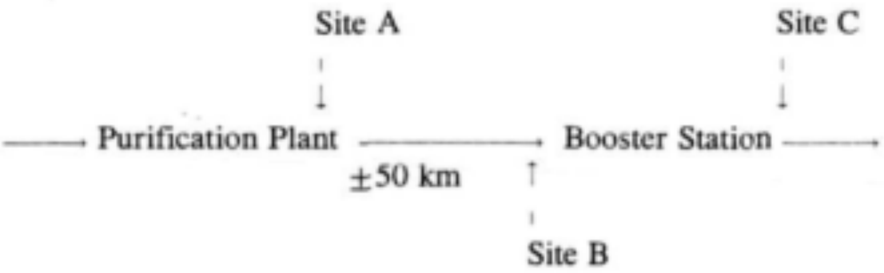
The concentration of POX was determined by purging and microcoulometric measurement using a Euroglas ECS 2000 total organic halogen analyzer. The concentration of AOX in the purged sample was measured by adsorption on activated carbon, combusted and also measured microcoulometrically.

AOX was determined according to the ISO 9562: 1989 method while the proposed standard specification DIN No 38409 Part 25 of the German Institute of Standards was adapted for use in determining the POX fraction.

Trihalomethane analyses were done using a Hewlett Packard 19395A head space sampler coupled to a Hewlett Packard HP5890 gas chromatograph. Total trihalomethane (TTHM) constitutes the sum of the concentrations obtained for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$.

### 3.2 Sampling: Localities and Frequency

For each of the four Booster Stations, references to the sampling point locations are as shown below:



**Phase I: Water destined for and leaving Zwartkopjes Booster Station**

Drinking water grab samples were collected during the period November 1993 to January 1994 from the following sites:

i) from four pumping mains leaving Vereeniging Pumping Station after chlorination (Site A);
ii) from five pumping mains before chloramination at a Booster Station (Site B); and
iii) from four pumping mains after chloramination at Zwartkopjes booster station (Site C).

The samples from Site A were taken after a twenty minute contact time while the samples taken at Site B had been exposed to free residual chlorine for six hours. Samples taken from Site C were taken directly after chloramination.

### Phase II: Water destined for and leaving Palmiet Booster Station

Drinking water samples were collected during the period May 1994 - August 1994 from the following sites:

- i) From three pumping mains leaving Zuikerbosch Pumping Station after chlorination (Site A);
- ii) From two pumping mains before chloramination at Palmiet booster station (Site B); and
- iii) From two pumping mains after chloramination at Palmiet booster station (Site C)

### Phase III: Water destined for and leaving Eikenhof and Mapleton Booster Stations

Drinking water samples were collected during the period
August 1994 - December 1994 from the following sites:

- i) From two pumping mains leaving Zuikerbosch Pumping Station after chlorination (Site A);
  From one pumping main leaving Vereeniging Pumping Station after chlorination (Site A);

- ii) From two pumping mains before chloramination at Eikenhof booster station (Site B);
  From one pumping main before chloramination at Mapleton booster station (Site B);

- iii) From four pumping mains after chloramination at Eikenhof booster station (Site C); and
  From one pumping main after chloramination at Mapleton booster station (Site C).

### Phase IV: Water from the Booster Stations destined for the Distribution

Drinking water samples were collected during the period January 1995 to March 1995 from the following sites:

- i) From each of the booster stations *viz.*, Eikenhof, Zwartkopjes, Palmiet, Mapleton (Site C) and thereafter from one or more distribution sampling points emanating from the booster station

  Eikenhof to Randfontein (P1) to Rustenburg (P1): estimated contact time of 24 hours

  Zwartkopjes to Leeupoort: estimated contact time of 4 hours

  Palmiet to Garankuwa: estimated contact time of 24 hours

  Mapleton to Selcourt: estimated contact time of 24 hours

  Selcourt to Secunda: estimated contact time of 36 hours.

# RESULTS AND DISCUSSION OF RESULTS

## 4.1 Phase I: Water destined for and leaving Zwartkopjes Booster Station

The concentrations and ratio comparisons of POX, AOX and TTHM measurements done on water destined for and leaving Zwartkopjes Booster Station are given in Tables 4.1.1 to 4.1.24 and Figure 4.1.1. Separate samples were taken from the C6, C10, C11 and C13 Pumping Mains leaving Zwartkopjes Booster Station for POX, AOX and TTHM analyses. These results have been averaged for the purpose of this exercize and represent the overall quality of the water leaving Zwartkopjes Booster Station at Site C.

**Table 4.1.1: Measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in the A6 Pumping Main to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum ($\mu$g Cl$^-$/ℓ) | Maximum ($\mu$g Cl$^-$/ℓ) | Average ($\mu$g Cl$^-$/ℓ) |
|---|---|---|---|---|---|---|
| A6 | A | TTHM | 2 | 8.96 | 9.20 | 9.08 |
| A6 | B | | 5 | 30.81 | 36.86 | 33.98 |
| C6,10,11,13 | C | | 15 | 32.38 | 37.75 | 34.84 |
| | | | | | | |
| A6 | A | POX | 5 | 6.00 | 61.83 | 32.78 |
| A6 | B | | 5 | 22.92 | 65.8 | 34.09 |
| C6,10,11,13 | C | | 17 | 10.60 | 59.70 | 30.73 |
| | | | | | | |
| A6 | A | AOX | 5 | 57.55 | 135.14 | 92.96 |
| A6 | B | | 5 | 60.88 | 100.23 | 80.36 |
| C6,10,11,13 | C | | 17 | 64.23 | 139.87 | 90.42 |
| | | | | | | |
| A6 | A | TOX | 5 | 98.03 | 145.09 | 125.74 |
| A6 | B | | 5 | 91.07 | 143.60 | 114.25 |
| C6,10,11,13 | C | | 17 | 74.83 | 161.89 | 121.20 |

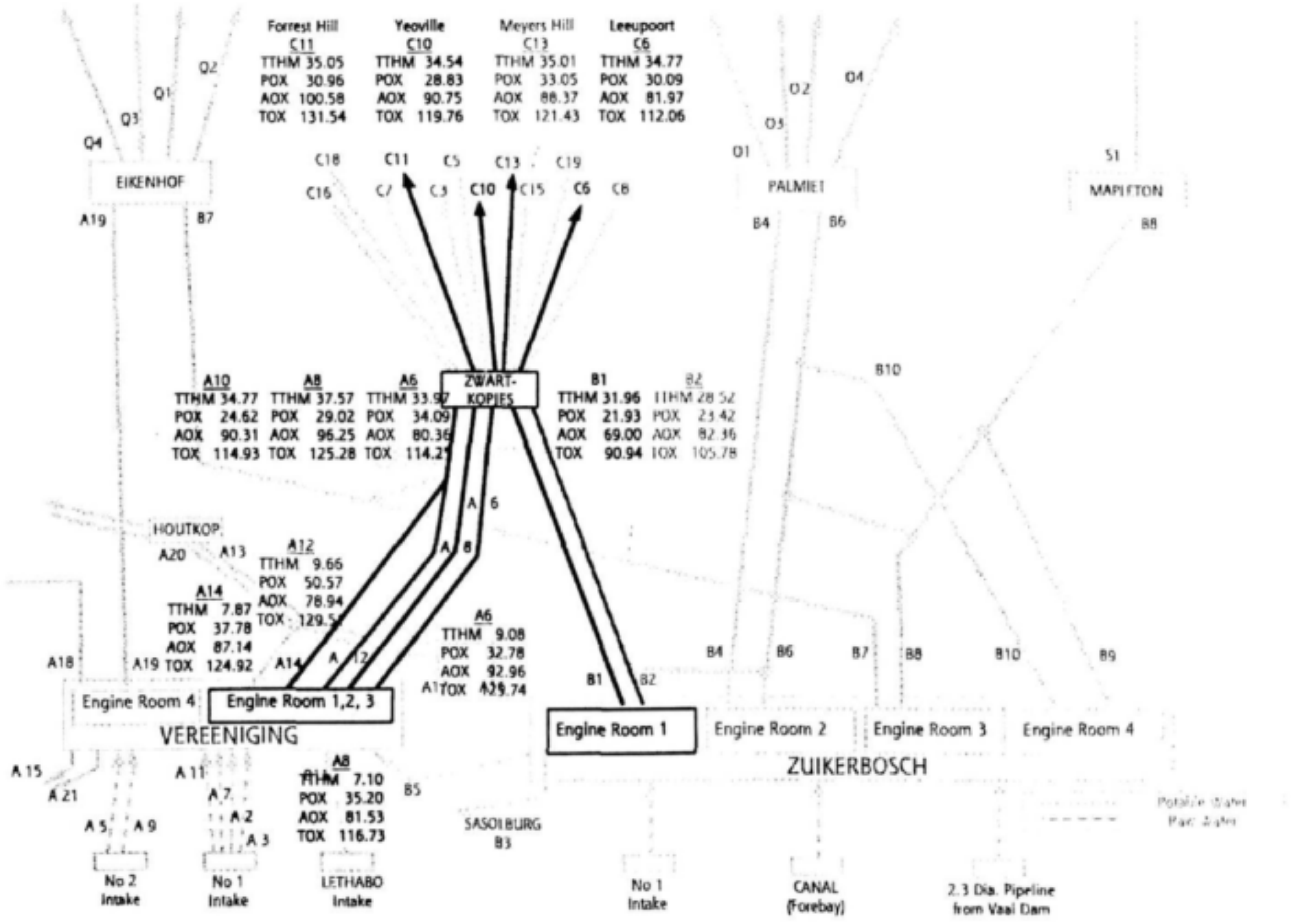


Figure 4.1.1: Results for Zwartkopjes Booster Station. (Summer)

**Table 4.1.2: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A6 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| A6 | TTHM | 9.08/33.98 = 0.27 | 33.98/34.84 = 0.98 |
| | POX | 32.78/34.09 = 0.96 | 34.09/30.73 = 1.11 |
| | AOX | 92.96/80.36 = 1.16 | 80.36/90.42 = 0.89 |
| | TOX | 125.74/114.25 = 1.10 | 114.25/121.20 = 0.94 |

Results show

- a 3.7-fold increase in TTHM from Site A to Site B;
- no increase in TTHM directly after chloramination at Site C;
- no increase in POX between Site A and Site B;
- a small decrease in POX after chloramination at Site C;
- AOX concentration shows a slight decrease between Site A and Site B;
- an increase in AOX directly after chloramination.

**Table 4.1.3: Ratios of AOX/POX and AOX/TTHM for the A6 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| A6 | A | 92.96/32.83 = 2.8 | 92.96/9.08 = 10.2 |
| A6 | B | 80.36/34.06 = 2.3 | 80.36/33.98 = 2.4 |
| C6,10,11, 13 | C | 90.42/30.73 = 2.9 | 90.42/34.84 = 2.6 |

The ratios shown in Table 4.1.3 will be discussed in the summary at the end of this section.

**Table 4.1.4: Measured levels of POX ($\mu$g Cl$^{-}$/$\ell$), AOX ($\mu$g Cl$^{-}$/$\ell$) and TTHM ($\mu$g Cl$^{-}$/$\ell$) in the A8 Pumping Main to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum ($\mu$g Cl$^{-}$/$\ell$) | Maximum ($\mu$g Cl$^{-}$/$\ell$) | Average ($\mu$g Cl$^{-}$/$\ell$) |
|---|---|---|---|---|---|---|
| A8 | A | TTHM | 2 | 6.91 | 7.29 | 7.10 |
| A8 | B | | 5 | 35.05 | 40.18 | 37.57 |
| C6,10,11,13 | C | | 15 | 32.38 | 37.75 | 34.84 |
| | | | | | | |
| A8 | A | POX | 5 | 5.07 | 75.48 | 35.20 |
| A8 | B | | 5 | 25.60 | 31.20 | 29.02 |
| C6,10,11,13 | C | | 17 | 10.6 | 59.70 | 30.73 |
| | | | | | | |
| A8 | A | AOX | 5 | 59.22 | 113.96 | 81.53 |
| A8 | B | | 5 | 67.09 | 118.56 | 96.25 |
| C6,10,11,13 | C | | 17 | 64.23 | 139.89 | 90.42 |
| | | | | | | |
| A8 | A | TOX | 5 | 94.91 | 135.84 | 116.73 |
| A8 | B | | 5 | 98.29 | 135.28 | 125.28 |
| C6,10,11,13 | C | | 17 | 74.83 | 161.89 | 121.20 |

**Table 4.1.5: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A8 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| A8 | TTHM | 7.10/37.57 = 0.19 | 37.57/34.84 = 1.08 |
| | POX | 35.20/29.02 = 1.21 | 29.02/30.73 = 1.06 |
| | AOX | 81.53/96.25 = 0.85 | 96.25/90.42 = 1.06 |
| | TOX | 116.73/125.28 = 0.93 | 125.28/121.20 = 1.03 |

The ratio comparisons in Table 4.1.5 show

- a 5.3-fold increase in TTHM from Site A to Site B;
- no increase in TTHM directly after chloramination at Site C;
- a small decrease in POX between Site A and Site B;
- no increase in POX after chloramination at Site C;
- a 1.2-fold increase in AOX concentration between Site A and Site B;
- a decrease in AOX directly after chloramination.

**Table 4.1.6: Ratios of AOX/POX and AOX/TTHM for the A8 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| A8 | A | 81.53/35.20 = 2.3 | 81.53/7.10 = 11.5 |
| A8 | B | 96.25/29.02 = 3.3 | 96.25/37.57 = 2.6 |
| C6,10,11,13 | C | 90.42/30.73 = 2.9 | 90.42/34.84 = 2.6 |

The ratios shown in Table 4.1.6 will be discussed in the summary at the end of this section.

**Table 4.1.7: Measured levels of POX (μg Cl$^-$/ℓ), AOX (μg Cl$^-$/ℓ) and TTHM (μg Cl$^-$/ℓ) in the A10 Pumping Main to Zwartkopjes Booster Station**

| **Sample origin** | **Site** | **Param** | **n** | **Minimum (μg Cl$^-$/ℓ)** | **Maximum (μg Cl$^-$/ℓ)** | **Average (μg Cl$^-$/ℓ)** |
|---|---|---|---|---|---|---|
| A10 | A | TTHM | | No sample point | | |
| A10 | B | | 5 | 32.62 | 38.13 | 34.77 |
| C6,10,11,13 | C | | 15 | 32.38 | 37.75 | 34.84 |
| | | | | | | |
| A10 | A | POX | | No sample point | | |
| A10 | B | | 5 | 23.10 | 26.00 | 24.62 |
| C6,10,11,13 | C | | 17 | 10.60 | 59.70 | 30.73 |
| | | | | | | |
| A10 | A | AOX | | No sample point | | |
| A10 | B | | 4 | 85.36 | 96.60 | 90.31 |
| C6,10,11,13 | C | | 17 | 64.23 | 139.89 | 90.42 |
| | | | | | | |
| A10 | A | TOX | | No sample point | | |
| A10 | B | | 4 | 108.54 | 119.70 | 114.93 |
| C6,10,11,13 | C | | 17 | 74.83 | 161.89 | 121.20 |

**Table 4.1.8: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A10 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| A10 | TTHM | Not done | 34.77/34.84 = 1.00 |
| | POX | Not done | 24.62/30.73 = 0.80 |
| | AOX | Not done | 90.31/90.42 = 0.99 |
| | TOX | Not done | 114.93/121.20 = 0.95 |

The ratio comparisons in Table 4.1.8 show

- no increase in TTHM directly after chloramination at Site C;

- a 1.2-fold increase in POX after chloramination at Site C;
- no increase in AOX concentration after chloramination.

**Table 4.1.9: Ratios of AOX/POX and AOX/TTHM for the A10 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| A10 | A | Not done | Not done |
| A10 | B | 90.31/24.62 = 3.7 | 90.31/34.77 = 2.6 |
| C6,10,11,13 | C | 90.42/30.73 = 2.9 | 90.42/34.84 = 2.6 |

The ratios shown in Table 4.1.9 will be discussed in the summary at the end of this section.

**Table 4.1.10: Measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in the A12 Pumping Main to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum (μg Cl⁻/ℓ) | Maximum (μg Cl⁻/ℓ) | Average (μg Cl⁻/ℓ) |
|---|---|---|---|---|---|---|
| A12 | A | TTHM | 2 | 7.42 | 11.90 | 9.66 |
| | | POX | 4 | 6.55 | 95.59 | 50.57 |
| | | AOX | 4 | 71.94 | 102.94 | 78.94 |
| | | TOX | 4 | 93.84 | 166.43 | 129.51 |

**Table 4.1.11: Ratios of AOX/POX and AOX/TTHM for the A12 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| A12 | A | 78.94/50.57 = 1.6 | 78.94/9.66 = 8.2 |

The ratios calculated in Table 4.1.11 will be discussed in the summary at the end of this section.

**Table 4.1.12:** **Measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in the A14 Pumping Main to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum ($\mu$g Cl$^-$/ℓ) | Maximum ($\mu$g Cl$^-$/ℓ) | Average ($\mu$g Cl$^-$/ℓ) |
|---|---|---|---|---|---|---|
| A14 | A | TTHM | 2 | 7.42 | 8.30 | 7.86 |
| | | POX | 5 | 7.68 | 76.19 | 37.78 |
| | | AOX | 5 | 65.17 | 119.45 | 87.14 |
| | | TOX | 5 | 105.96 | 141.36 | 124.92 |

**Table 4.1.13:** **Ratios of AOX/POX and AOX/TTHM for the A14 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| A14 | A | 87.14/37.78 = 2.3 | 87.14/7.86 = 11.1 |

The ratios calculated in Table 4.1.13 will be discussed in the summary at the end of this section.

**Table 4.1.14:** **Measured levels of POX ($\mu$g Cl$^-$/$\ell$), AOX ($\mu$g Cl$^-$/$\ell$) and TTHM ($\mu$g Cl$^-$/$\ell$) in the B1 Pumping Main to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum ($\mu$g Cl$^-$/$\ell$) | Maximum ($\mu$g Cl$^-$/$\ell$) | Average ($\mu$g Cl$^-$/$\ell$) |
|---|---|---|---|---|---|---|
| B1 | A | TTHM | | Not done | | |
| B1 | B | | 5 | 28.40 | 36.86 | 31.96 |
| C6,10,11,13 | C | | 15 | 32.38 | 37.75 | 34.84 |
| | | | | | | |
| B1 | A | POX | | Not done | | |
| B1 | B | | 4 | 18.00 | 25.35 | 21.93 |
| C6,10,11,13 | C | | 17 | 10.60 | 59.70 | 30.73 |
| | | | | | | |
| B1 | A | AOX | | Not done | | |
| B1 | B | | 4 | 56.45 | 82.81 | 69.00 |
| C6,10,11,13 | C | | 17 | 64.23 | 139.87 | 90.42 |
| | | | | | | |
| B1 | A | TOX | | Not done | | |
| B1 | B | | 4 | 78.65 | 100.81 | 90.94 |
| C6,10,11,13 | C | | 17 | 74.83 | 161.89 | 121.20 |

**Table 4.1.15:** **Ratios of increase of POX, AOX amd TTHM from Site A/Site B and Site B/Site C for the B1 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| B1 | TTHM | Not done | 31.96/34.84 = 0.92 |
| | POX | Not done | 21.93/30.73 = 0.71 |
| | AOX | Not done | 69.00/90.42 = 0.76 |
| | TOX | Not done | 90.94/121.20 = 0.75 |

The ratio comparisons in Table 4.1.15 show

- a 1.1-fold increase in TTHM from Site B to Site C;

- a 1.4-fold increase in POX between Site A and Site B;
- a 1.3-fold increase in AOX after chloramination at Site C;

**Table 4.1.16:** **Ratios of AOX/POX and AOX/TTHM for the B1 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| B1 | A | Not done | Not done |
|  | B | 69.00/21.93 = 3.1 | 69.00/31.96 = 2.1 |
|  | C | 90.42/30.73 = 2.9 | 90.42/34.84 = 2.6 |

The ratios calculated in Table 4.1.16 will be discussed in the summary at the end of this section.

**Table 4.1.17:** **Measured levels of POX (μg Cl$^{-}$/ℓ), AOX (μg Cl$^{-}$/ℓ) and TTHM (μg Cl$^{-}$/ℓ) in the B2 Pumping Mains to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum (μg Cl$^{-}$/ℓ) | Maximum (μg Cl$^{-}$/ℓ) | Average (μg Cl$^{-}$/ℓ) |
|---|---|---|---|---|---|---|
| B2 | A | TTHM |  | Not done |  |  |
| B2 | B |  | 5 | 26.35 | 30.30 | 28.52 |
| C6,10,11,13 | C |  | 15 | 32.38 | 37.75 | 34.84 |
|  |  |  |  |  |  |  |
| B2 | A | POX |  | Not done |  |  |
| B2 | B |  | 4 | 17.00 | 35.70 | 23.42 |
| C6,10,11,13 | C |  | 17 | 10.60 | 59.70 | 30.73 |
|  |  |  |  |  |  |  |
| B2 | A | AOX |  | Not done |  |  |
| B2 | B |  | 4 | 77.25 | 88.10 | 82.36 |
| C6,10,11,13 | C |  | 17 | 64.23 | 139.87 | 90.42 |
|  |  |  |  |  |  |  |
| B2 | A | TOX |  | Not done |  |  |
| B2 | B |  | 4 | 97.05 | 123.80 | 105.78 |
| C6,10,11,13 | C |  | 17 | 74.83 | 161.89 | 121.20 |

**Table 4.1.18:** **Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B2 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| B2 | TTHM | Not done | 28.52/34.84 = 0.82 |
| | POX | | 23.42/30.73 = 0.76 |
| | AOX | | 82.36/90.42 = 0.91 |
| | TOX | | 105.78/121.20 = 0.87 |

The ratio comparisons in Table 4.1.18 show

* a decrease in TTHM directly after chloramination at Site C;
* a 1.3-fold increase in POX directly after chloramination;
* a 1.1-fold increase in AOX concentration after chloramination.

**Table 4.1.19:** **Ratios of AOX/POX and AOX/TTHM for the B2 Pumping Main**

| **Sample origin** | **Site** | **AOX/POX** | **AOX/TTHM** |
|---|---|---|---|
| B2 | A | Not done | Not done |
| | B | 82.36/23.42 = 3.5 | 82.36/28.52 = 2.9 |
| | C | 90.42/30.72 = 2.9 | 90.42/34.84 = 2.6 |

The ratios calculated in Table 4.1.19 will be discussed at the end of this section.

Tables 4.1.20 to 4.1.22 is a summary of the above averages in order to compress the above data.

**Table 4.1.20:** **Average measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in Pumping Mains to Zwartkopjes Booster Station**

| Sample origin | Site | Param | n | Minimum ($\mu$g Cl$^-$/ℓ) | Maximum ($\mu$g Cl$^-$/ℓ) | Average ($\mu$g Cl$^-$/ℓ) |
|---|---|---|---|---|---|---|
| A6,8,12,14 | A | TTHM | 8 | 6.91 | 11.90 | 8.43 |
| A6,8,10 | B | | 25 | 26.35 | 40.18 | 33.36 |
| C6,10,11,13 | C | | 15 | 32.38 | 37.75 | 34.84 |
| | | | | | | |
| A6,8,12,14 | A | POX | 19 | 5.07 | 95.59 | 39.08 |
| A6,8,10 | B | | 23 | 17.00 | 65.80 | 26.62 |
| C6,10,11,13 | C | | 17 | 10.60 | 59.70 | 30.73 |
| | | | | | | |
| A6,8,12,14 | A | AOX | 19 | 57.55 | 102.94 | 85.14 |
| A6,8, 10 | B | | 23 | 56.45 | 118.56 | 83.66 |
| C6,10,11,13 | C | | 17 | 64.23 | 139.87 | 90.42 |
| | | | | | | |
| A6,8,12,14 | A | TOX | 19 | 94.91 | 135.84 | 121.24 |
| A6,8,10 | B | | 23 | 78.65 | 143.60 | 110.24 |
| C6,10,11,13 | C | | 17 | 74.83 | 161.89 | 121.20 |

**Table 4.1.21:** **Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from Swartkopjes Booster Station**

| Parameter | Site A/Site B | Site B/Site C |
|---|---|---|
| TTHM | 8.43/33.36 = 0.25 | 33.36/34.84 = 0.96 |
| POX | 39.08/26.62 = 1.47 | 26.62/30.73 = 0.87 |
| AOX | 85.15/83.66 = 1.02 | 83.66/90.42 = 0.93 |
| TOX | 121.24/110.24 = 1.10 | 110.24/121.20 = 0.91 |

The ratio comparisons in Table 4.1.21 show

- a 4-fold increase in TTHM directly after chlorination at Site B;
- no increase in TTHM directly after chloramination at Site C;
- a decrease in POX from Site A to Site B;
- a 1.1-fold increase in POX directly after chloramination;
- no increase in AOX from Site A to Site B;
- a 1.1-fold increase in AOX concentration after chloramination.

**Table 4.1.22:** **Ratios of AOX/POX and AOX/POX in the Pumping Mains to and from Zwartkopjes Booster Station**

| **Site** | **AOX/POX** | **AOX/TTHM** |
|---|---|---|
| A | 85.14/39.08 = 2.2 | 85.14/8.43 = 10.1 |
| B | 83.66/26.62 = 3.1 | 83.66/33.36 = 2.5 |
| C | 90.42/30.73 = 2.9 | 90.42/34.84 = 2.6 |

Table 4.1.22 shows that the concentration of AOX is 2.2 times (Site A), 3.2 times (Site B) and 2.9 times (Site C) higher than POX concentrations. The concentration of AOX is 10.1 times (Site A), 2.5 times (Site B) and 2.6 times greater than TTHM concentrations.

**Table 4.1.23:** **Average concentration measured of the components of TTHMs in the pumping mains to Swartkopjes: $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ ($\mu g\ Cl^-/\ell$)**

| Sample origin | Site | n | $CHCl_3$ | $CHCl_2Br$ | $CHClBr_2$ | $CHBr_3$ | TTHM |
|---|---|---|---|---|---|---|---|
| A6 | A | 2 | 5.79 | 2.72 | 1.02 | n.d.* | 9.08 |
| A6 | B | 5 | 22.99 | 8.44 | 2.55 | n.d. | 33.98 |
| C6,10,11,13 | C | 15 | 25.06 | 8.78 | 2.79 | n.d. | 34.87 |
| | | | | | | | |
| A8 | A | 2 | 4.90 | 1.62 | 0.58 | n.d. | 7.10 |
| A8 | B | 5 | 24.95 | 9.87 | 2.76 | n.d. | 37.57 |
| C6,10,11,13 | | | | | | | |
| A10 | B | 5 | 23.52 | 8.70 | 2.55 | n.d. | 34.77 |
| | | | | | | | |
| A12 | A | 2 | 5.79 | 2.60 | 1.28 | n.d. | 9.66 |
| | | | | | | | |
| A14 | A | 2 | 4.90 | 1.95 | 1.02 | n.d. | 7.87 |
| | | | | | | | |
| B1 | B | 5 | 21.38 | 7.92 | 2.65 | n.d. | 31.96 |
| | | | | | | | |
| B2 | B | 5 | 19.96 | 6.62 | 1.94 | n.d. | 28.52 |

* n.d. = not detected

Chloroform is the dominant species of TTHM at all three sites.
The concentration of $CHCl_3 > CHCl_2Br > CHClBr_2 > CHBr_3$ The concentration of bromoform was below the detection limit in all cases.

**Summary of results obtained for Zwartkopjes Booster Station**

In the early development of the method, the TOX concentration was estimated by converting the data on trihalomethanes to units of $Cl^-$ and adding the value to the AOX fraction (Stevens *et al.*, 1985; Heller-Grossman *et al.*, 1993). The newer development of using POX is still to be ratified as a standard method. The values obtained by the POX method have been reported in the literature to be as much as 20 percent lower than those found by the TTHM method (Stevens *et al.*, 1985; Heller-Grossman *et al.*, 1993). The results obtained in this study for sampling points B and C show this trend. However, an anomaly appears at sampling point A.

Site C is an average of the results of outlets as the water is mixed at this point, and no large variations were encountered here. The chloramination process has no significant effect on either the TTHM, POX or AOX concentrations.

The choice of AOX as the normalizing point gives very consistent and reproducible comparison values. The intermediate tables drawn up previously are now summarized here and serve to highlight the results from Site A (Table 4.1.24). The relative amount of TTHM after chlorination increases and stabilizes after six hours contact time. As this is the first such study, the exact nature of the anomaly has to be further investigated.

**Table 4.1.24: Summary of AOX/POX and AOX/TTHM ratios obtained for Pumping Mains A6, A8, A10, A12, A14, B1 and B2 (Phase I)**

| **Sample origin** | **AOX/POX** | **AOX/TTHM** | **Sample origin** | **AOX/POX** | **AOX/TTHM** |
|---|---|---|---|---|---|
| A6/A | 2.8 | 10.2 | A8/A | 2.3 | 11.3 |
| A6/B | 2.3 | 2.4 | A8/B | 3.3 | 2.6 |
| C6,10,11, 13 | 2.9 | 2.6 | C6,10,11, 13 | 2.9 | 2.6 |
| | | | | | |
| A12/A | 1.6 | 8.2 | A14/A | 2.3 | 11.1 |
| A12/B | - | - | A14/B | - | - |
| A12/C | - | - | A14/C | - | - |
| | | | | | |
| A10/A | - | - | B1/A | - | - |
| A10/B | 3.7 | 2.6 | B1/B | 3.1 | 2.1 |
| C6,10,11, 13 | 2.9 | 2.6 | C6,10,11, 13 | 2.9 | 2.6 |
| | | | | | |
| B2/A | - | - | | | |
| B2/B | 3.5 | 2.9 | | | |
| C6,10,11, 13 | 2.9 | 2.6 | | | |

## 4.2 Phase II: Water destined for and leaving Palmiet Booster Station

The concentrations of POX, AOX and TTHM measurements done on water destined for and leaving Palmiet Booster Station are given in Tables 4.2.1 to 4.2.13 and Figure 4.2.1.

**Table 4.2.1: Measured levels of POX (µg Cl$^-$/ℓ), AOX (µg Cl$^-$/ℓ) and TTHM (µg Cl$^-$/ℓ) in the B4 Pumping Main to Palmiet Booster Station**

| Sample origin | Site | Param | n | Minimum (µg Cl$^-$/ℓ) | Maximum (µg Cl$^-$/ℓ) | Average (µg Cl$^-$/ℓ) |
|---|---|---|---|---|---|---|
| B4 | A | TTHM | 14 | 5.61 | 12.09 | 9.21 |
| B4 | B | | 13 | 38.33 | 54.01 | 44.01 |
| O2+O4 | C | | 14 | 36.99 | 54.03 | 45.41 |
| | | | | | | |
| B4 | A | POX | 15 | 4.64 | 20.58 | 11.48 |
| B4 | B | | 12 | 20.96 | 41.92 | 33.65 |
| O2+O4 | C | | 14 | 21.67 | 46.99 | 35.92 |
| | | | | | | |
| B4 | A | AOX | 15 | 35.33 | 93.69 | 55,81 |
| B4 | B | | 12 | 70.93 | 111.31 | 83.82 |
| O2+O4 | C | | 14 | 70.82 | 119.13 | 90.90 |
| | | | | | | |
| B4 | A | TOX | 15 | 44.20 | 106.87 | 67.28 |
| B4 | B | | 12 | 92.55 | 151.56 | 117.47 |
| O2+O4 | C | | 14 | 92.49 | 156.40 | 126.82 |

**Table 4.2.2: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B4 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| B4 | TTHM | 9.21/44.01 = 0.21 | 44.01/45.41 = 0.97 |
| | POX | 11.48/33.65 = 0.34 | 33.65/35.92 = 0.94 |
| | AOX | 55.81/83.82 = 0.66 | 83.82/90.90 = 0.92 |
| | TOX | 67.28/117.47 = 0.57 | 117.47/126.82 = 0.93 |

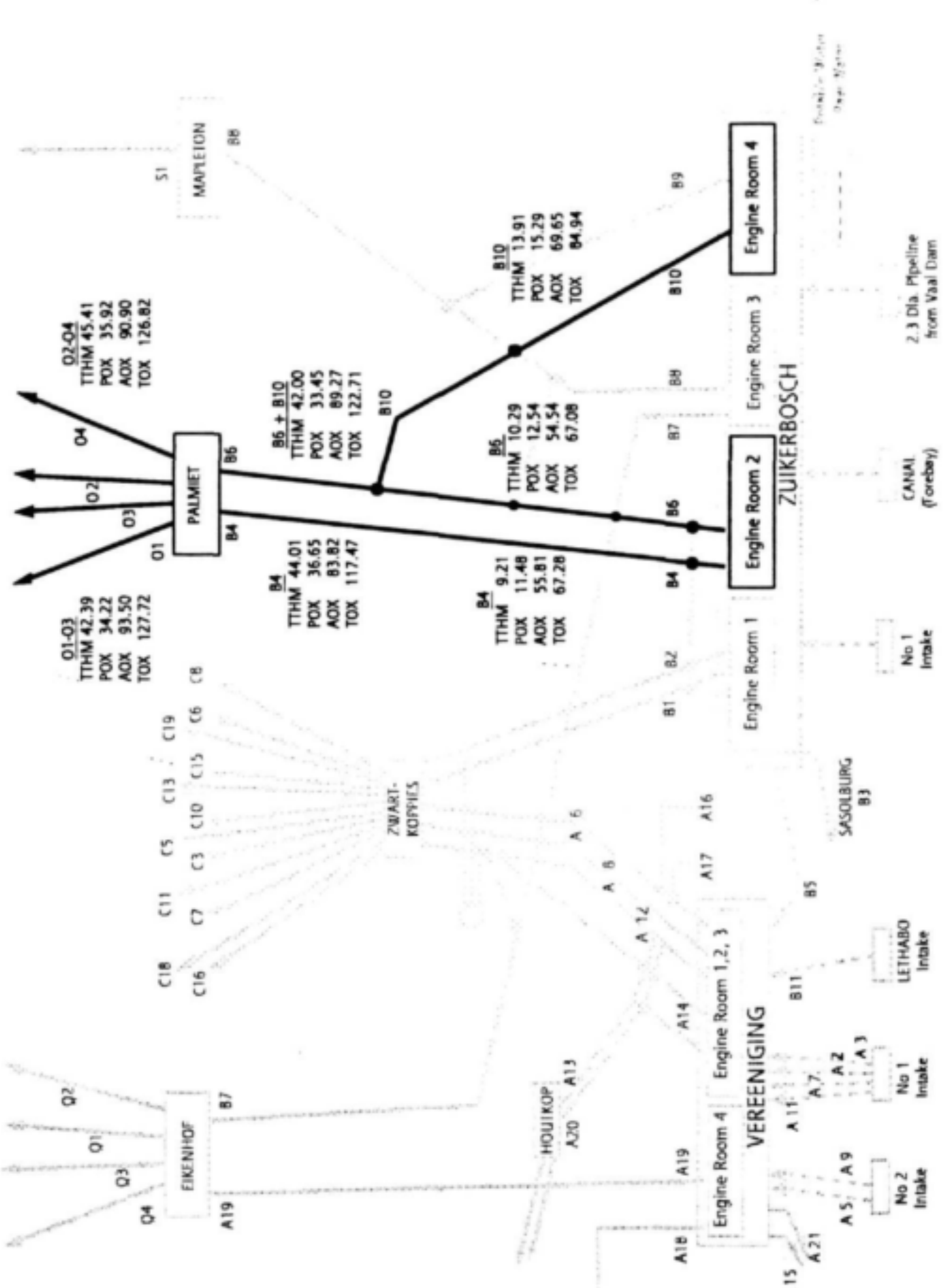


Figure 4.2.1: Results for Palmiet Booster Station. (Autumn/Winter)

Results show

- a 4.8-fold increase in TTHM from Site A to Site B;
- no increase in TTHM is observed directly after chloramination at Site C;
- a 2.9-fold increase in POX from Site A to Site B;
- a 1.1-fold increase in POX directly after chloramination;
- a 1.5-fold increase in AOX from Site A to Site B;
- a 1.1-fold increase in AOX directly after chloramination.

**Table 4.2.3: Ratios of AOX/POX and AOX/TTHM for the B4 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| B4 | A | 55.81/11.48 = 4.9 | 55.81/9.21 = 6.0 |
| B4 | B | 83.82/33.65 = 2.5 | 83.82/44.01 = 1.9 |
| O2+O4 | C | 90.90/35.92 = 2.5 | 90.90/45.41 = 2.0 |

The ratios calculated in Table 4.2.3 will be discussed in the summary at the end of this section.

**Table 4.2.4: Measured levels of POX (μg $Cl^-$/ℓ), AOX (μg $Cl^-$/ℓ) and TTHM (μg $Cl^-$/ℓ) in the B6 Pumping Main to Palmiet Booster Station**

| Sample origin | Site | Param | n | Minimum (μg $Cl^-$/ℓ) | Maximum (μg $Cl^-$/ℓ) | Average (μg $Cl^-$/ℓ) |
|---|---|---|---|---|---|---|
| B6 | A | TTHM | 15 | 4.50 | 16.73 | 10.29 |
| B6 | B | | 13 | 35.29 | 48.95 | 42.00 |
| O1+O3 | C | | 14 | 32.51 | 51.24 | 42.39 |
| B6 | A | POX | 15 | 6.06 | 22.11 | 12.54 |
| B6 | B | | 13 | 20.42 | 43.79 | 33.45 |
| O1+O3 | C | | 14 | 20.74 | 46.69 | 34.22 |
| B6 | A | AOX | 15 | 31.85 | 76.91 | 54.54 |
| B6 | B | | 13 | 76.38 | 113.30 | 89.27 |
| O1+O3 | C | | 14 | 60.13 | 128.06 | 93.50 |
| B6 | A | TOX | 15 | 39.15 | 90.49 | 67.08 |
| B6 | B | | 13 | 98.75 | 155.49 | 122.71 |
| O1+O3 | C | | 14 | 92.04 | 174.76 | 127.72 |

**Table 4.2.5: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B6 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| B6 | TTHM | 10.29/42.00 = 0.25 | 42.00/42.39 = 0.99 |
| | POX | 12.54/33.45 = 0.37 | 33.45/34.22 = 0.98 |
| | AOX | 54.54/89.27 = 0.61 | 89.27/93.50 = 0.95 |
| | TOX | 67.08/122.71 = 0.55 | 122.71/127.72 = 0.96 |

Results show

- a four-fold increase in TTHM from Site A to Site B;
- no increase in TTHM is observed directly after chloramination at Site C;
- a 2.7-fold and a 1.6-fold increase in POX and AOX was observed respectively between Site A and Site B;
- no increase in concentration of these parameters was observed directly after chloramination.

**Table 4.2.6: Ratios of AOX/POX and AOX/TTHM for the B6 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| **B6** | A | 54.54/12.54 = 4.3 | 54.54/10.29 = 5.3 |
| | B | 89.27/33.45 = 2.7 | 89.27/42.00 = 2.1 |
| | C | 93.50/34.22 = 2.7 | 93.50/42.39 = 2.2 |

The ratios shown in Table 4.2.6 will be discussed in the summary at the end of this section.

**Table 4.2.7: Measured levels of POX (µg Cl⁻/ℓ), AOX (µg Cl⁻/ℓ) and TTHM (µg Cl⁻/ℓ) in the B10 Pumping Main to Palmiet Booster Station**

| Sample origin | Site | Param | n | Minimum (µg Cl⁻/ℓ) | Maximum (µg Cl⁻/ℓ) | Average (µg Cl⁻/ℓ) |
|---|---|---|---|---|---|---|
| B10 | A | TTHM | 13 | 10.66 | 16.47 | 13.91 |
| | | POX | 13 | 9.21 | 20.25 | 15.29 |
| | | AOX | 13 | 52.54 | 108.10 | 69.65 |
| | | TOX | 13 | 67.11 | 125.13 | 84.94 |

The comparison of Site A/Site B and Site B/Site C is not relevant as B10 has a connection with B6 approximately two-thirds of the way to Palmiet booster station.

**Table 4.2.8: Ratios of AOX/POX and AOX/TTHM for the B10 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| B10 | A | 69.65/15.29 = 4.5 | 69.65/13.91 = 5.0 |

The concentration of AOX is 4.5 times greater than POX and 5.0 times greater than TTHM concentrations. These ratios will be discussed in the summary at the end of this section.

**Table 4.2.9: Average concentration measured of the components of TTHMs in the pumping mains to Palmiet; $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ (µg Cl⁻/ℓ)**

| Sample origin | Site | N | $CHCl_3$ | $CHCl_2Br$ | $CHClBr_2$ | $CHBr_3$ | TTHM |
|---|---|---|---|---|---|---|---|
| B4 | A | 14 | 6.66 | 2.27 | 0.28 | n.d.* | 9.21 |
| B4 | B | 13 | 31.92 | 10.38 | 1.71 | n.d. | 44.01 |
| O2+O4 | C | 14 | 33.05 | 10.60 | 1.76 | n.d. | 45.41 |
| B6 | A | 15 | 7.43 | 2.56 | 0.31 | n.d. | 10.30 |
| B6 | B | 13 | 29.60 | 10.68 | 1.73 | n.d. | 42.01 |
| O1+O3 | C | 14 | 30.16 | 10.50 | 1.74 | n.d. | 42.40 |
| B10 | A | 13 | 9.33 | 3.95 | 0.62 | n.d. | 13.90 |

* n.d. = not detected

Chloroform is the dominant species of TTHM at all three sites. The concentration of $CHCl_3$ > $CHCl_2Br$ > $CHClBr_2$ > $CHBr_3$. The concentration of bromoform was below the detection limit in all cases.

**Table 4.2.10:** **Average measured levels of POX (μg Cl⁻/ℓ), AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) in Pumping Mains to Palmiet Booster Station**

| Sample origin | Site | Parameter | n | Minimum | Maximum | Average |
|---|---|---|---|---|---|---|
| B4,6,10 | A | TTHM | 42 | 4.50 | 16.73 | 11.14 |
| B4,6,10 | B | | 26 | 35.29 | 54.01 | 43.00 |
| O1-O4 | C | | 28 | 32.51 | 51.24 | 43.90 |
| | | | | | | |
| B4,6,10 | A | POX | 43 | 4.64 | 22.11 | 13.10 |
| B4,6,10 | B | | 25 | 20.42 | 41.92 | 33.55 |
| O1-O4 | C | | 28 | 20.74 | 46.49 | 35.07 |
| | | | | | | |
| B4,6,10 | A | AOX | 43 | 31.85 | 108.10 | 59.32 |
| B4,6,10 | B | | 25 | 70.93 | 119.13 | 86.55 |
| O1-O4 | C | | 28 | 60.13 | 128.06 | 92.20 |
| | | | | | | |
| B4,6,10 | A | TOX | 43 | 39.15 | 125.13 | 73.10 |
| B4,6,10 | B | | 25 | 92.55 | 155.49 | 120.09 |
| O1-O4 | C | | 28 | 92.04 | 156.40 | 127.27 |

**Table 4.2.11:** **Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from Palmiet Booster Station**

| Parameter | Site A/Site B | Site B/Site C |
|---|---|---|
| TTHM | 11.14/43.00 = 0.26 | 43.00/43.90 = 0.98 |
| POX | 13.10/33.55 = 0.39 | 33.55/35.07 = 0.96 |
| AOX | 59.32/86.55 = 0.69 | 86.55/92.20 = 0.94 |
| TOX | 73.10/120.09 = 0.61 | 120.09/127.27 = 0.94 |

Results show

- a 3.9-fold increase in TTHM from Site A to Site B;
- no increase in TTHM directly after chloramination at Site C;
- a 2.6-fold increase in POX between Site A and Site B;
- no increase in POX after chloramination at Site C;
- a 1.5-fold increase in AOX concentration between Site A and Site B;
- a 1.1-fold increase in AOX directly after chloramination.

**Table 4.2.12: Ratios of AOX/POX and AOX/TTHM in the Pumping Mains to and from Palmiet Booster Station**

| Sample Origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| B4,6,10 | A | 59.32/13.10 = 4.5 | 59.32/11.14 = 5.3 |
| B4,6,10 | B | 86.55/33.55 = 2.6 | 86.55/43.00 = 2.0 |
| O1-O4 | C | 92.20/35.07 = 2.6 | 92.20/43.90 = 2.1 |

The ratios shown in Table 4.2.12 will be discussed in the summary at the end of this section.

**Summary of Results obtained for Palmiet Booster Station**

While not as dramatic as the results from Phase 1, the anomaly of the TTHM being lower (increased AOX/TTHM ratio) is clearly apparent, and confirms the trends seen in Phase 1.

**Table 4.2.13: Summary of AOX/POX and AOX/TTHM ratios obtained for Pumping Mains B4, B6, B10 and O1-O4 (Phase II)**

| Sample origin | AOX/POX | AOX/TTHM | Sample origin | AOX/POX | AOX/TTHM |
|---|---|---|---|---|---|
| B4/A | 4.9 | 6.0 | B6/A | 4.3 | 5.3 |
| B4/B | 2.5 | 1.9 | B6/B | 2.7 | 2.1 |
| O2+O4 | 2.5 | 2.0 | O1+O3 | 2.7 | 2.2 |
| | | | | | |
| B10/A | 4.5 | 5.0 | | | |
| B10/B | - | - | | | |
| B10/C | - | - | | | |

## 4.3 Phase III: Water destined for Eikenhof and Mapleton Booster Stations

The concentrations of POX, AOX and TTHM measurements done on water destined for and leaving Eikenhof and Palmiet Booster Stations are given in Tables 4.3.1 to 4.3.14 and Figures 4.3.1 and 4.3.2. Separate samples were taken from the Q1, Q2, Q3 and Q4 Pumping Mains leaving Eikenof Booster Station for POX, AOX and TTHM analyses. These results have been averaged for the purpose of this exercize and represent the overall quality of the water leaving Eikenhof Booster Station at Site C.

**Table 4.3.1: Measured levels of POX (µg $Cl^-$/ℓ), AOX (µg $Cl^-$/ℓ) and TTHM (µg $Cl^-$/ℓ) in the A19 Pumping Main to Eikenhof Booster Station**

| Sample origin | Site | Param | n | Minimum (µg $Cl^-$/ℓ) | Maximum (µg $Cl^-$/ℓ) | Average (µg $Cl^-$/ℓ) |
|---|---|---|---|---|---|---|
| A19 | A | TTHM | 18 | 11.47 | 35.05 | 22.51 |
| A19 | B | | 17 | 34.53 | 97.85 | 55.18 |
| Q1-Q4 | C | | 64 | 36.43 | 97.95 | 58.86 |
| | | | | | | |
| A19 | A | POX | 16 | 17.09 | 49.11 | 24.94 |
| A19 | B | | 164 | 14.45 | 43.98 | 31.64 |
| Q1-Q4 | C | | 64 | 18.99 | 52.44 | 34.67 |
| | | | | | | |
| A19 | A | AOX | 16 | 62.18 | 139.25 | 83.17 |
| A19 | B | | 16 | 55.62 | 126.65 | 88.59 |
| Q1-Q4 | C | | 64 | 69.32 | 161.63 | 98.36 |
| | | | | | | |
| A19 | A | TOX | 16 | 81.48 | 188.36 | 108.10 |
| A19 | B | | 16 | 70.07 | 170.63 | 120.23 |
| A1-Q4 | C | | 64 | 88.51 | 207.02 | 133.02 |

**Table 4.3.2: Ratios increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the A19 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| A19 | TTHM | 22.51/55.18 = 0.41 | 55.18/58.86 = 0.94 |
| | POX | 24.94/31.64 = 0.79 | 31.64/34.67 = 0.91 |
| | AOX | 83.17/88.59 = 0.94 | 88.59/98.36 = 0.90 |
| | TOX | 108.10/120.23=0.90 | 120.23/133.02=0.90 |

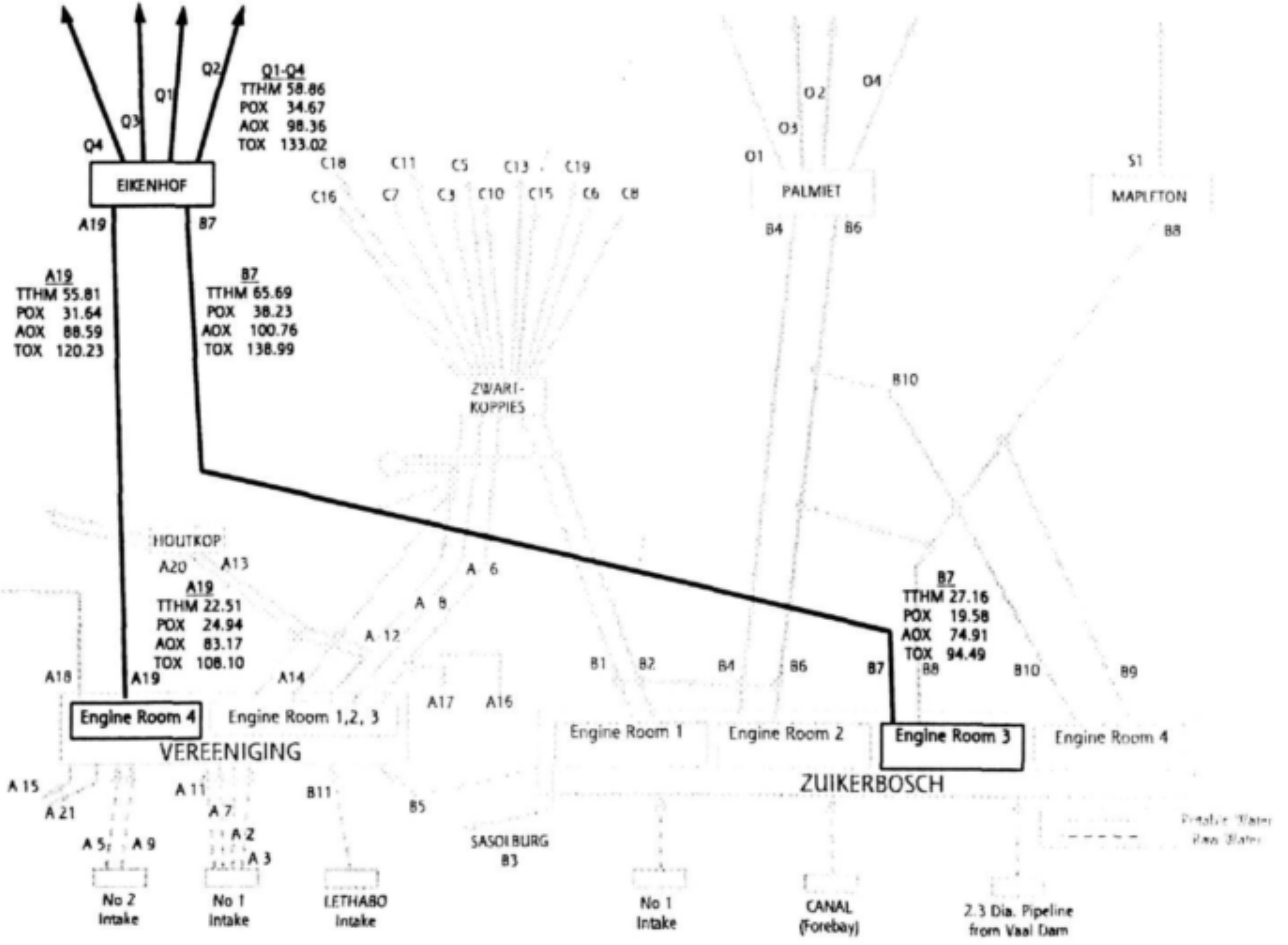


Figure 4.3.1: Results for Eikenhof Booster Station. (Spring/Summer)

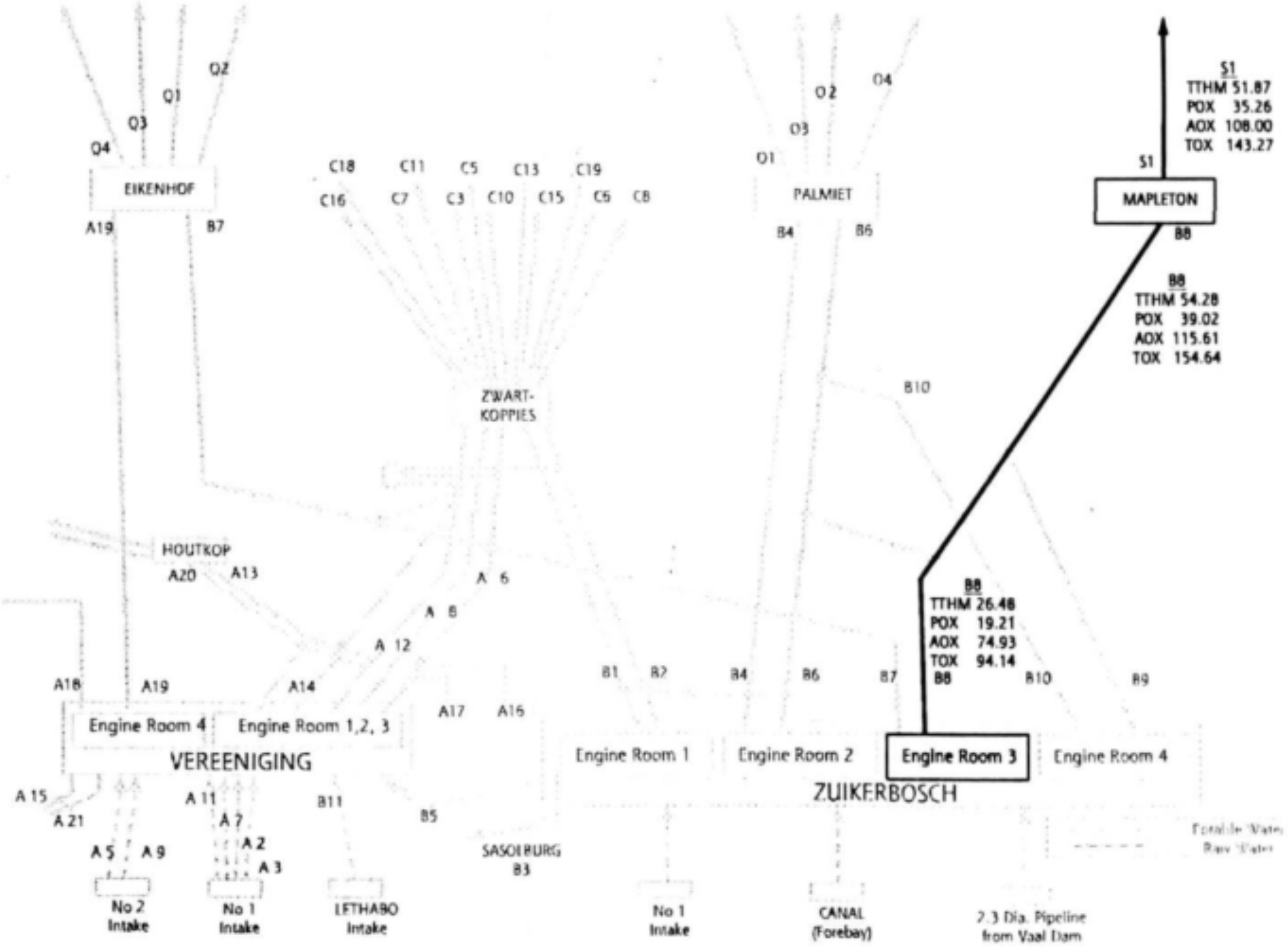


Figure 4.3.2: Results for Mapleton Booster Station. (Spring/Summer)

Results show

- a 2.4-fold increase in TTHM from Site A to Site B;
- no increase in TTHM directly after chloramination at Site C;
- a 1.3-fold increase in POX between Site A and Site B;
- a 1.1-fold increase in POX after chloramination at Site C;
- a 1.1-fold increase in AOX concentration between Site A and Site B;
- a 1.1-fold increase in AOX directly after chloramination.

**Table 4.3.3: Ratios of AOX/POX and AOX/TTHM for the A19 Pumping Main**

| **Sample origin** | **Site** | **AOX/POX** | **AOX/TTHM** |
|---|---|---|---|
| A19 | A | 83.17/24.98 = 3.3 | 83.17/22.51 = 3.7 |
| A19 | B | 88.59/31.64 = 2.8 | 88.59/55.18 = 1.6 |
| Q1-Q4 | C | 98.36/34.67 = 2.8 | 98.36/58.86 = 1.7 |

The ratios calculated in Table 4.3.3 will be discussed in the summary at the end of this section.

**Table 4.3.4: Measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in the B7 Pumping Main to Eikenhof Booster Station**

| **Sample origin** | **Site** | **Param** | **n** | **Minimum ($\mu$g Cl$^-$/ℓ)** | **Maximum ($\mu$g Cl$^-$/ℓ)** | **Average ($\mu$g Cl$^-$/ℓ)** |
|---|---|---|---|---|---|---|
| B7 | A | TTHM | 16 | 4.82 | 44.08 | 27.16 |
| B7 | B | | 12 | 36.12 | 102.01 | 65.69 |
| Q1-Q4 | C | | 64 | 36.43 | 97.95 | 58.86 |
| | | | | | | |
| B7 | A | POX | 15 | 5.48 | 27.39 | 19.58 |
| B7 | B | | 12 | 25.34 | 50.18 | 38.23 |
| Q1-Q4 | C | | 64 | 18.99 | 52.44 | 34.67 |
| | | | | | | |
| B7 | A | AOX | 15 | 24.18 | 100.97 | 74.91 |
| B7 | B | | 12 | 70.54 | 134.10 | 100.76 |
| Q1-Q4 | C | | 64 | 69.32 | 161.63 | 98.36 |
| B7 | A | TOX | 15 | 29.66 | 125.81 | 94.49 |
| B7 | B | | 12 | 102.21 | 181.83 | 138.99 |
| Q1-Q4 | C | | 64 | 88.51 | 207.02 | 133.02 |

**Table 4.3.5: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B7 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| B7 | TTHM | 27.16/65.59 = 0.41 | 65.69/58.86 = 1.12 |
| | POX | 19.58/38.23 = 0.51 | 38.23/34.67 = 1.10 |
| | AOX | 74.91/100.76 = 0.74 | 100.76/98.36= 1.02 |
| | TOX | 94.49/138.99 = 0.68 | 138.99/133.02=1.04 |

Results show

- a 2.4-fold increase in TTHM from Site A to Site B;
- a decrease in TTHM directly after chloramination at Site C;
- a 1.9-fold increase in POX between Site A and Site B;
- a decrease in POX after chloramination at Site C;
- a 1.3-fold increase in AOX concentration between Site A and Site B;
- no increase in AOX directly after chloramination.

**Table 4.3.6: Ratios of AOX/POX and AOX/TTHM for the B7 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| B7 | A | 74.91/19.58 = 3.8 | 74.91/22.96 = 3.3 |
| | B | 100.76/38.23 = 2.6 | 100.76/65.69 = 1.5 |
| | C | 98.36/34.67 = 2.8 | 98.36/58.86 = 1.7 |

The ratios calculated in Table 4.3.6 will be discussed in the summary at the end of this section.

**Table 4.3.7: Average measured levels of POX ($\mu$g Cl$^-$/ℓ), AOX ($\mu$g Cl$^-$/ℓ) and TTHM ($\mu$g Cl$^-$/ℓ) in Pumping Mains to Eikenhof Booster Station**

| Sample origin | Site | Parameter | n | Minimum | Maximum | Average |
|---|---|---|---|---|---|---|
| A19, B7 | A | TTHM | 34 | 4,82 | 44.08 | 24.84 |
| A19, B7 | B | | 29 | 34.53 | 102.01 | 60.44 |
| Average Q1-Q4 | C | | 64 | 36.43 | 97.95 | 58.86 |
| | | | | | | |
| A19, B7 | A | POX | 31 | 5.48 | 49.11 | 22.26 |
| A19, B7 | B | | 28 | 14.45 | 50.18 | 34.94 |
| Average Q1-Q4 | C | | 64 | 18.99 | 52.44 | 34.67 |
| | | | | | | |
| A19, B7 | A | AOX | 31 | 24.18 | 139.25 | 79.04 |
| A19, B7 | B | | 28 | 55.62 | 134.10 | 94.68 |
| Average Q1-Q4 | C | | 64 | 69.32 | 161.63 | 98.36 |
| | | | | | | |
| A19, B7 | A | TOX | 31 | 29.66 | 188.36 | 101.30 |
| A19, B7 | B | | 28 | 70.07 | 181.83 | 129.61 |
| Average Q1-Q4 | C | | 64 | 88.51 | 207.02 | 133.02 |

**Table 4.3.8: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from Eikenhof Booster Station**

| Parameter | Site A/Site B | Site B/Site C |
|---|---|---|
| TTHM | 24.84/60.44 = 0.41 | 60.44/58.86 = 1.03 |
| POX | 22.26/34.94 = 0.64 | 34.94/34.67 = 1.01 |
| AOX | 79.04/94.68 = 0.83 | 94.68/98.36 = 0.96 |
| TOX | 101.30/129.61 = 0.78 | 129.61/133.02 = 0.97 |

Results show

- a 2.4-fold increase in TTHM from Site A to Site B;
- no increase in TTHM directly after chloramination at Site C;
- a 1.6-fold increase in POX between Site A and Site B;
- no increase in POX after chloramination at Site C;
- a 1.2-fold increase in AOX concentration;
- a 1.04-fold increase in AOX directly after chloramination.

**Table 4.3.9: Ratios of AOX/POX and AOX/TTHM for the Pumping Mains to and from Eikenhof Booster Station**

| Site | AOX/POX | AOX/TTHM |
|---|---|---|
| A | 79.04/22.26 = 3.5 | 79.04/24.84 = 3.2 |
| B | 94.68/34.94 = 2.7 | 94.68/60.44 = 1.6 |
| C | 98.36/34.67 = 2.8 | 98.36/58.86 = 1.7 |

The ratios shown in Table 4.3.9 will be discussed in the summary at the end of this section.

**Table 4.3.10:** **Measured levels of POX (μg $Cl^-/\ell$), AOX (μg $Cl^-/\ell$) and TTHM (μg $Cl^-/\ell$) in the B8 Pumping Main to Mapleton Booster Station**

| Sample origin | Site | Param | n | Minimum (μg $Cl^-/\ell$) | Maximum (μg $Cl^-/\ell$) | Average (μg $Cl^-/\ell$) |
|---|---|---|---|---|---|---|
| B8 | A | TTHM | 16 | 14.75 | 38.95 | 26.48 |
| B8 | B | | 6 | 33.64 | 79.86 | 54.28 |
| S1 | C | | 6 | 27.91 | 85.18 | 51.87 |
| | | | | | | |
| B8 | A | POX | 15 | 13.96 | 24.08 | 19.21 |
| B8 | B | | 5 | 27.07 | 54.13 | 39.02 |
| S1 | C | | 5 | 19.09 | 48.99 | 35.26 |
| | | | | | | |
| B8 | A | AOX | 15 | 57.09 | 102.20 | 74.93 |
| B8 | B | | 5 | 93.40 | 129.87 | 115.61 |
| S1 | C | | 5 | 96.10 | 118.00 | 108.00 |
| | | | | | | |
| B8 | A | TOX | 15 | 75.29 | 126.26 | 94.14 |
| B8 | B | | 5 | 137.71 | 164.79 | 154.64 |
| S1 | C | | 5 | 134.76 | 148.48 | 143.27 |

**Table 4.3.11:** **Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the B8 Pumping Main**

| Sample origin | Parameter | Site A/Site B | Site B/Site C |
|---|---|---|---|
| B8 | TTHM | 26.48/54.28 = 0.49 | 54.28/51.87 = 1.05 |
| | POX | 19.21/39.02 = 0.49 | 39.02/35.26 = 1.11 |
| | AOX | 74.93/115.61=0.65 0,65 | 115.61/108.00=1.07 |
| | TOX | 94.14/154.64 =0.61 0,61 | 154.64/143.27=1.08 |

Results show

- a 2.0-fold increase in TTHM from Site A to Site B;
- a decrease in TTHM directly after chloramination at Site C;
- a 2-fold increase in POX between Site A and Site B;
- a decrease in POX after chloramination at Site C;
- a 1.5-fold increase in AOX concentration between Site A and Site B;
- a decrease in AOX directly after chloramination.

**Table 4.3.12: Ratios of AOX/POX and AOX/TTHM for the B8 Pumping Main**

| Sample origin | Site | AOX/POX | AOX/TTHM |
|---|---|---|---|
| B8 | A | 74.93/19.21 = 3.9 | 74.93/26.48 = 2.8 |
| | B | 115.61/39.02 = 3.0 | 115.61/54.28 = 2.1 |
| | C | 108.00/35.26 = 3.1 | 108.00/51.87 = 2.1 |

The ratios calculated in Table 4.3.12 will be discussed in the summary at the end of the section.

**Table 4.3.13: Average concentration measured of the components of TTHMs in the Pumping Mains to Eikenhof: $CHCl_3$ ($\mu$g $Cl^-/\ell$), $CHCl_2Br$ ($\mu$g $Cl^-/\ell$), $CHClBr_2$ ($\mu$g $Cl^-/\ell$) and $CHBr_3$ ($\mu$g $Cl^-/\ell$)**

| Sample origin | Site | n | $CHCl_3$ | $CHCl_2Br$ | $CHClBr_2$ | $CHBr_3$ | TTHMs |
|---|---|---|---|---|---|---|---|
| A19 | A | 16 | 15.84 | 5.66 | 0.97 | 0.04 | 22.51 |
| A19 | B | 16 | 39.25 | 13.64 | 2.24 | 0.04 | 55.18 |
| Q1-Q4 | C | 16 | 41.98 | 14.41 | 2.43 | 0.05 | 58.86 |
| | | | | | | | |
| B7 | A | 16 | 19.42 | 6.57 | 1.13 | 0.05 | 27.16 |
| B7 | B | 12 | 46.38 | 16.32 | 2.90 | 0.09 | 65.69 |
| Q1-Q4 | C | 16 | 41.98 | 14.41 | 2.43 | 0.05 | 58.86 |
| | | | | | | | |
| B8 | A | 16 | 18.98 | 6.38 | 1.08 | 0.04 | 26.48 |
| B8 | B | 6 | 39.22 | 12.98 | 2.08 | 0.00 | 54.28 |
| S1 | C | 6 | 38.59 | 11.37 | 1.91 | 0.01 | 51.87 |

**Summary of results obtained for Eikenhof and Mapleton Booster Stations**

Similar to Phases I and II, the TTHM values are still low or about equal to the POX values at sample point A (Table 4.3.14).

**Table 4.3.14:** **Summary of AOX/POX and AOX/TTHM ratios obtained for Pumping Mains B7, B8 and S1 (Phase III)**

| Sample origin | AOX/POX | AOX/POX | Sample origin | | AOX/TTHM |
|---|---|---|---|---|---|
| A19/A | 3.3 | 3.7 | B7/A | 3.8 | 2.8 |
| A19/B | 2.8 | 1.6 | B7/B | 2.6 | 1.5 |
| Q1-Q4 | 2.8 | 1.7 | Q1-Q4 | 2.8 | 1.7 |
| | | | | | |
| B8/A | 3.9 | 2.8 | | | |
| B8/B | 3.0 | 2.1 | | | |
| S1/C | 3.1 | 2.1 | | | |

## 4.4 Summary of TTHM, POX and AOX results obtained for the four Booster Stations

The overall average concentrations of POX, AOX and TTHM measurements done on water destined for and leaving the four Booster Stations are given in Figure 4.4.1. These results have been pooled to give an estimate of the overall quality of the water over a one-year period.

**Table 4.4.1: Overall average concentrations of POX (μg Cl⁻/ℓ) AOX (μg Cl⁻/ℓ) and TTHM (μg Cl⁻/ℓ) measured to and from the four Booster Stations for the period January 1994 to December 1995**

| Site | Param | n | Minimum (μg Cl⁻/ℓ) | Maximum (μg Cl⁻/ℓ) | Average (μg Cl⁻/ℓ) |
|---|---|---|---|---|---|
| A | TTHM | 100 | 8.43 | 26.48 | 17.70 |
| A | POX | 108 | 13.10 | 39.08 | 23.41 |
| A | AOX | 108 | 59.32 | 115.61 | 84.78 |
| A | TOX | 108 | 73.10 | 154.64 | 112.57 |
| | | | | | |
| B | TTHM | 86 | 33.36 | 60.44 | 47.17 |
| B | POX | 81 | 26.62 | 35.26 | 31.59 |
| B | AOX | 81 | 83.66 | 108.00 | 93.22 |
| B | TOX | 81 | 110.24 | 143.27 | 125.80 |
| | | | | | |
| C | TTHM | 113 | 34.84 | 58.86 | 45.87 |
| C | POX | 114 | 30.73 | 35.07 | 33.49 |
| C | AOX | 114 | 90.42 | 98.36 | 93.66 |
| C | TOX | 114 | 121.20 | 133.02 | 127.16 |

**Table 4.4.2: Ratios of increase of POX, AOX and TTHM from Site A/Site B and Site B/Site C for the Pumping Mains to and from the four Booster Stations**

| Parameter | Site A/Site B | Site B/Site C |
|---|---|---|
| TTHM | 17.70/47.17 = 0.37 | 47.17/45.87 = 1.03 |
| POX | 23.41/31.59 = 0.74 | 31.59/33.49 = 0.95 |
| AOX | 84.78/93.22 = 0.91 | 93.22/93.66 = 1.00 |
| TOX | 112.57/125.80 = 0.89 0.8 | 125.80/127.16 = 0.99 |

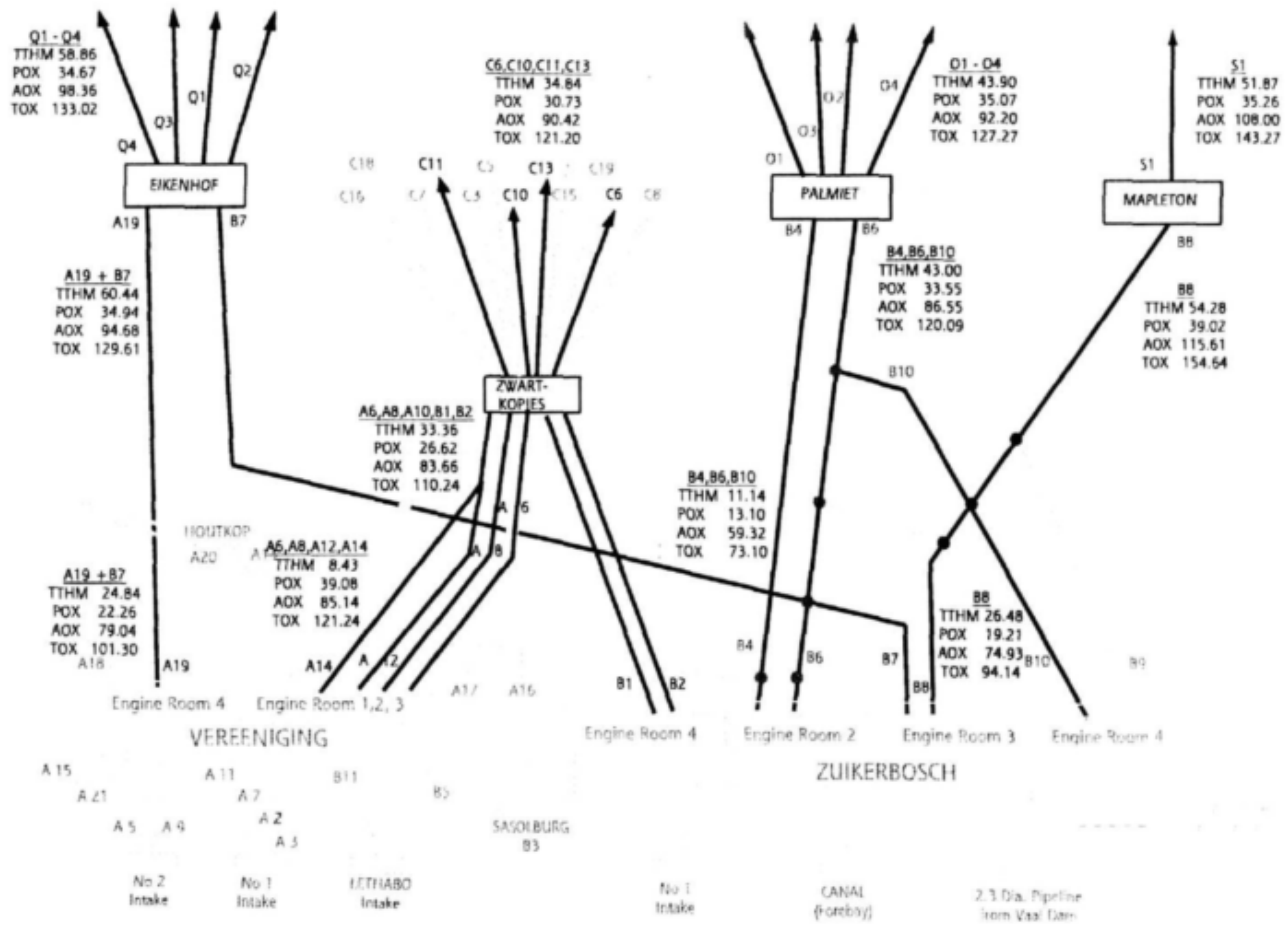


Figure 4.4.1: Overall Average results obtained per Booster Station.

Results show

- a 2.7-fold increase in TTHM from Site A to Site B;
- no increase in TTHM directly after chloramination at Site C;
- a 1.4-fold increase in POX between Site A and Site B;
- a 1.1-fold increase in POX after chloramination at Site C;
- a 1.1-fold increase in AOX concentration between Site A and Site B;
- no increase in AOX directly after chloramination.

**Table 4.4.3: Ratios of AOX/POX and AOX/TTHM for the Pumping Mains to and from the four Booster Stations**

| Site | AOX/POX | AOX/TTHM |
|---|---|---|
| A | 84.78/23.41 = 3.6 | 84.78/17.70 = 4.8 |
| B | 93.22/31.59 = 3.0 | 93.22/47.17 = 2.0 |
| C | 93.66/33.49 = 2.8 | 93.66/45.87 = 2.0 |

The concentration of AOX exceeded the concentration of POX by three to four times in the chlorinated waters while the concentrations of AOX were two to five times higher than the THM concentration (Table 4.3.3). Thus, it seems that the production of AOX is more significant than that of the TTHM in chlorinated drinking water.

The chloramination process has no significant effect on either of the TTHM, POX or AOX concentrations (Table 4.4.2). However, the formation of TTHM, given approximately six hours contact time after chlorination, is much faster than the formation of POX. Similarly, the formation of POX proceeds at a faster rate than the formation of AOX.

## 4.5 Phase IV: Water destined for the Distribution

The concentrations of POX, AOX and TTHM measurements done on water from each Booster Station destined for the Distribution are given in Table 4.5.1 and Figure 4.5.1.

**Table 4.5.1: Measured levels of POX (µg Cl$^-$/ℓ), AOX (µg Cl$^-$/ℓ) and TTHM (µg Cl$^-$/ℓ) for Distribution sample points**

| Sample origin | Param | n | Minimum (µg Cl$^-$/ℓ) | Maximum (µg Cl$^-$/ℓ) | Average (µg Cl$^-$/ℓ) |
|---|---|---|---|---|---|
| Q2 Eikenhof | TTHM | 6 | 27.12 | 47.74 | 40.29 |
| P1 Randfontein | | 4 | 30.14 | 46.37 | 39.63 |
| P1 Rustenburg | | 7 | 29.59 | 47.06 | 39.76 |
| | | | | | |
| C6 Zwartkopjes | | 7 | 24.93 | 40.48 | 32.47 |
| C6 Leeupoort Depot | | 7 | 27.14 | 41.80 | 34.36 |
| | | | | | |
| O2 Palmiet | | 7 | 24.12 | 35.50 | 31.14 |
| H23 Garankuwa | | 8 | 25.49 | 39.63 | 33.45 |
| | | | | | |
| S1 Mapleton | | 4 | 28.67 | 46.02 | 36.37 |
| N4 Selcourt | | 5 | 30.59 | 39.72 | 35.36 |
| M2 Heidelberg | | 6 | 15.24 | 45.29 | 32.98 |
| Devon | | 1 | | | 35.16 |
| Secunda | | 8 | 30.95 | 41.94 | 37.22 |
| | | | | | |
| Q2 Eikenhof | POX | 6 | 21.92 | 34.28 | 26.48 |
| P1 Randfontein | | 3 | 27.53 | 39.66 | 32.16 |
| P1 Rustenburg | | 8 | 19.30 | 36.21 | 31.47 |
| | | | | | |
| C6 Zwartkopjes | | 8 | 12.70 | 30.41 | 23.48 |
| C6 Leeupoort Depot | | 8 | 15.04 | 27.14 | 20.45 |
| | | | | | |
| O2 Palmiet | | 6 | 13.66 | 28.34 | 20.83 |
| H23 Garankuwa | | 8 | 11.55 | 26.70 | 21.83 |

| | | | | | |
|---|---|---|---|---|---|
| S1 Mapleton | | 3 | 19.86 | 25.22 | 22.38 |
| N4 Selcourt | | 5 | 12.34 | 26.14 | 19.59 |
| M2 Heidelberg | | 4 | 16.25 | 24.24 | 21.84 |
| Devon | | 1 | | | 26.69 |
| Secunda | | 7 | 11.48 | 24.40 | 20.00 |
| | | | | | |
| Q2 Eikenhof | AOX | 6 | 42.59 | 69.41 | 56.52 |
| P1 Randfontein | | 3 | 83.78 | 97.95 | 88.78 |
| P1 Rustenburg | | 8 | 51.53 | 120.31 | 93.77 |
| | | | | | |
| C6 Zwartkopjes | | 8 | 45.14 | 63.37 | 54.04 |
| C6 Leeupoort Depot | | 8 | 42.44 | 74.05 | 52.57 |
| | | | | | |
| O2 Palmiet | | 6 | 12.72 | 71.81 | 47.80 |
| H23 Garankuwa | | 8 | 35.36 | 63.63 | 51.74 |
| | | | | | |
| S1 Mapleton | | 3 | 59.68 | 72.96 | 65.27 |
| N4 Selcourt | | 5 | 47.99 | 66.29 | 57.58 |
| M2 Heidelberg | | 4 | 49.11 | 63.98 | 58.64 |
| Devon | | 1 | | | 53.55 |
| Secunda | | 7 | 36.69 | 60.63 | 45.81 |
| | | | | | |
| Q1 Eikenhof | TOX | 6 | 55.70 | 93.65 | 83.00 |
| P1 Randfontein | | 3 | 120.94 | 127.14 | 120.94 |
| P1 Rustenburg | | 8 | 70.83 | 140.78 | 125.24 |
| | | | | | |
| C6 Zwartkopjes | | 8 | 57.84 | 90.52 | 77.53 |
| C6 Leeupoort Depot | | 8 | 56.37 | 97.22 | 73.02 |
| | | | | | |
| O2 Palmiet | | 6 | 35.14 | 100.15 | 68.82 |
| H23 Garankuwa | | 8 | 46.06 | 90.02 | 73.95 |

| | | | | | |
|---|---|---|---|---|---|
| S1 Mapleton | | 3 | 81.74 | 92.82 | 87.65 |
| N4 Selcourt | | 5 | 60.69 | 88.43 | 77.16 |
| M2 Heidelberg | | 4 | 73.35 | 85.77 | 80.48 |
| Devon | | 1 | | | 80.23 |
| Secunda | | 7 | 52.27 | 84.65 | 65.8 |

The results on distribution end points were obtained in the period January to March 1995. A comparison of the results obtained on water emanating from Mapleton Booster Station shows that the POX and TTHM concentrations essentially remain unchanged at the selected end points. A different picture emerges for AOX in that there appears to be a progressive loss of AOX in the distribution (Table 4.5.1 and Figure 4.5.1). The reason for this loss has not been established. A loss in AOX is welcome news in terms of process control but will require further investigation to obtain an understanding of the mechanism.

The results obtained on water samples originating from Palmiet and Zwartkopjes Booster Stations showed that the concentrations of TTHM, POX, AOX and TOX essentially remain unchanged.

A totally different picture emerges for water from Eikenhof Booster Station. The TTHM concentrations remain the same from Eikenhof Booster Station to Randfontein and finally Rustenburg. A small increase in POX concentration is measured between Eikenhof Booster Station and Randfontein with no further increase at Rustenburg end point. However, a substantial increase in measured AOX is observed from Eikenhof to Randfontein (from 57 to 89 $\mu$g $Cl^-/\ell$). A small increase in AOX was measured subsequently between Randfontein and Rustenburg.

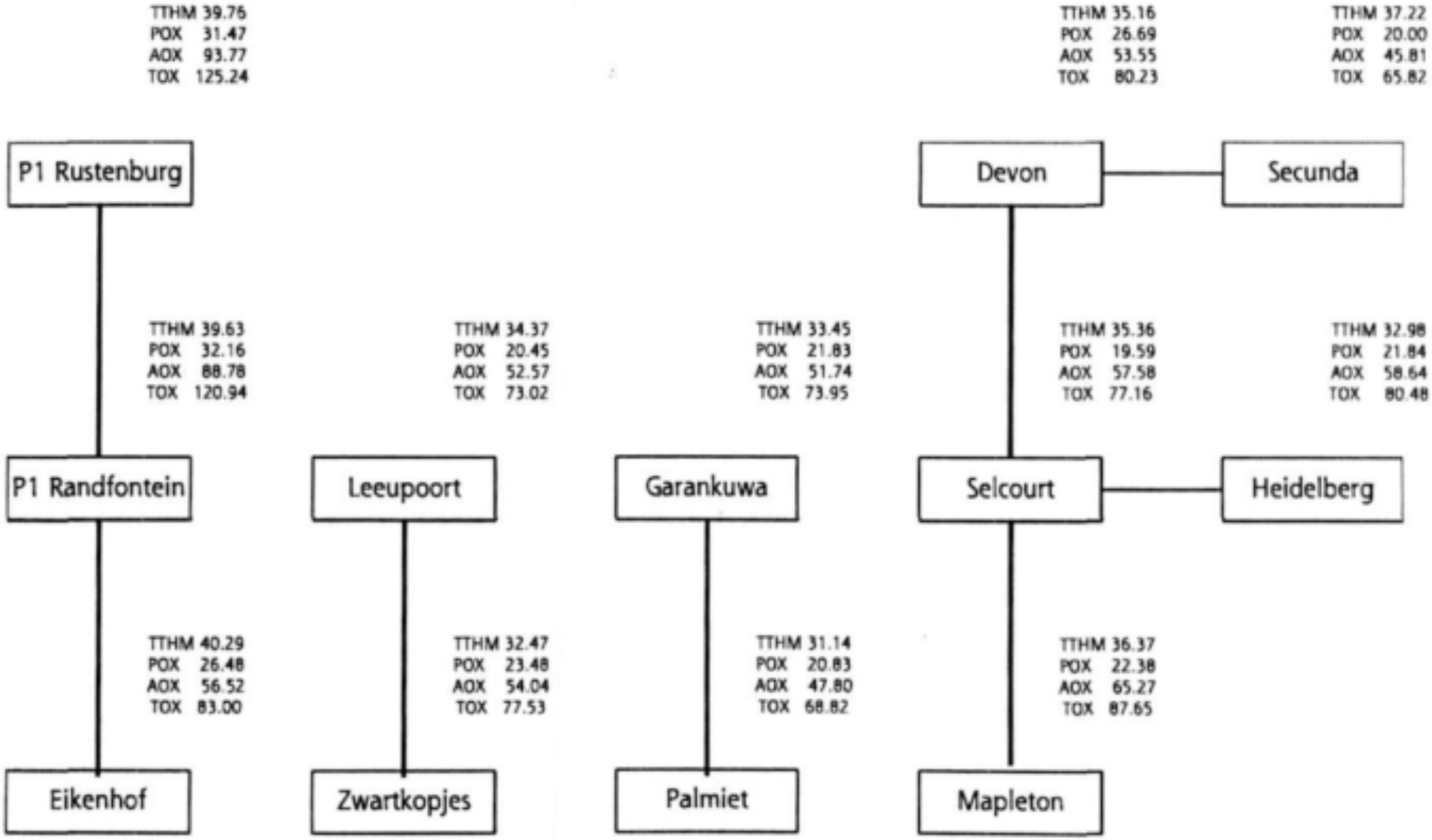


Figure 4.5.1: Results of selected sampling points in the distribution

## 4.6 Dissolved Organic Carbon Concentrations

It has been well documented that no relationship can be obtained between Dissolved Organic Carbon concentrations and TTHM concentrations. However, it is possible to calculate a yield of organic chloride ($\mu$g $Cl^-$) per unit of organic carbon present in the water (mg C).

Dissolved Organic Carbon concentrations for Site A were available (Table 4.6.1) and it has been assumed for the purpose of this excercise that the organic carbon content of the water generally remains unchanged during distribution.

**Table 4.6.1: Dissolved Organic Carbon concentrations (mg C/ℓ) measured at Site A**

| **Sample Point** | **A6** | **A8** | **A12** | **A14** | **A19** | **B1** | **B2** |
|---|---|---|---|---|---|---|---|
| No. of results | 17 | 17 | 17 | 17 | 17 | 16 | 16 |
| Minimum* | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Maximum | 2.9 | 2.6 | 3.1 | 2.7 | 3.6 | 3.1 | 3.1 |

* It was not possible to use results that were less than the minimum detection limit for statistical information. Thus where a result was less than the minimum detection limit a value of half the minimum detection limit was used as input data.

Taking the average of Dissolved Organic Carbon to be 3 mg C/ℓ and the overall TOX concentrations (Table 4.4.1), yields of 38 $\mu$g $Cl^-$/mg C (Site A), 42 $\mu$g $Cl^-$/mg C (Site B) and 42 $\mu$g $Cl^-$/mg C (Site C) are obtained respectively.

## 4.7 Number of POX, AOX and TTHM results exceeding guideline values

Although no guideline value has been set for POX concentrations in potable water, these concentrations can be compared to measured levels of TTHM. The guideline value which Rand Water uses against which to evaluate TTHM results is that of the United States Environmental Protection Agency (TTHM 100 $\mu$g/ℓ). No TTHM results obtained during this study exceeded this guideline value.

At present Rand Water has not accepted a guideline value against which to evaluate AOX. The Dutch association of water producing companies has drawn up a proposal for drinking water standards with regard to organic halogen compounds (Puyker, 1984). Their proposal is for a maximum AOX content of drinking water after chlorination of 100 $\mu$g/ℓ. When compared to this stringent proposed standard then 4 percent (14/370) of the determinations done on samples from Site A, 5 percent (17/370) of samples from Site B and 8 percent (29/370) of samples from Site C exceeded a concentration of 100 $\mu$g/ℓ. The levels of AOX obtained during this study compares favourably with those measured in potable water samples in the United States (Krasner, 1989).

The concentration of AOX is up to five times higher than the levels of POX in the chlorinated waters. These finding indicate that the production of AOX is more significant than that of the production of POX in chlorinated waters. The nature of AOX is still unknown but is believed to be mainly chlorinated humic acids.

Studies undertaken at Rand Water have shown that higher mutagenic activity occurs in water one hour after break-point chlorination than directly after break-point chlorination (Site A)(Louw, 1993). Mutagenic activity then increases until the Booster Station before chloramination (Site B). The addition of S9 metabolic activating enzyme decreased the observed mutagenicity. Indications are that the liver enzymes present in the human body decrease or destroy the mutagenicity of possible mutagens in drinking water. No increase in mutagenic activity was observed after chloramination (Site C) and it can thus be concluded that chloramination does not contribute to the observed mutagenicity.

## CONCLUSIONS

The aim of this project was to determine the concentration levels of Total Organic Halogen (Adsorbable Organic Halogen fraction + Purgeable Organic Halogen fraction; TOX = AOX + POX) throughout the Rand Water distribution system. This aim was achieved.

The TOX measurement is an inexpensive and useful method: for screening large numbers of samples before specific (and more complex) analyses; for monitoring the breakthrough of some synthetic organic compounds in water treatment process; and for estimating the level of formation of chlorinated organic by-products after disinfection with chlorine.

For the analysis of volatile disinfection by-products, headspace gas chromatography is prefered over a POX measurement because GC analysis provides significantly more information, namely, the identities and concentrations of specific compounds. The draw-back is that the sample will still require purging to remove the POX component in order to determine the AOX fraction.

TOX measurements are a sum of results and also of any associated errors, so, for comparison purposes, the AOX measurements provide a better base from which to calculate. Normalizing to the AOX values produces some very consistent and easily discernible trends.

The difference between TTHM and POX values has been reported in the literature, as have some attempts at correlating these values to AOX measurements. However, what has been unexpected in this study is that, under conditions soon after the first chlorination, the measured TTHM values are dramatically lower than the measured POX values. The AOX/TTHM and AOX/POX ratios appear to have consistent "equilibrium" values for each group of pipes and sampling points. This demonstrates that TTHM values cannot be used as a general indication of TOX; the results show a well-marked relationship to AOX, but it is site specific. This has a serious impact on evaluating toxicity tests when only TTHM measurements are available.

A further crucial point is that not all the organics in the water react with the chlorine. After chloramination at the Booster Stations, no further increase in AOX is discernable. This implies that the extra chlorine dosage is fully available to maintain its disinfection function without increasing the risk of further by-products formation. The lower limit of measuring Dissolved Organic Carbon was limited to 2 000 micrograms and as the treated water is often below this value, the above statement cannot, at this stage, be quantified with a AOX/DOC ratio for the Rand Water supply system.

# RECOMMENDATIONS

1. Mutagenicity has been linked to an increase in chloroform. However an increase in the concentration of AOX has also been measured in this study. Which fraction is causing the mutagenicity? The relationship of levels of POX and AOX to Ames activity should be examined.

2. Mutagenicity studies have been conducted on the Rustenburg pipeline which showed an increase in AOX concentrations. A similar study should be conducted on the water destined for Secunda where a reduction in AOX concentration has been measured.

3. The loss of AOX in the distribution should be further investigated.

4. The improvements in sensitivity of the TOC analyzer which has been purchased by Rand Water may enable us to give a meaningful quantitation to the ratio of AOX/TOC.

5. Both POX and AOX should be incorporated into routine drinking water monitoring programmes to give an indication of the volatile and non-volatile fractions which are formed when organics are chlorinated.

6. A comparison of TOX (POX + AOX) produced by chlorinating different qualities of water should be conducted.

7. Examination of concentration levels of TOX produced by different purification and disinfection processes *e.g.*, pre-ozonation followed by chlorination, GAC treatment followed by chlorination, chloramination, chlorine dioxide *etc.*, *etc.*

8. Guideline values for POX and AOX concentrations in drinking water supplies utilizing chlorine disinfection should be set.

## REFERENCES

AGARWAL, S.C. AND NETON, J. 1989. Mutagenicity and alkylating activity of the aqueous chlorination products of humic acid and their molecular wieght fractions. *The Science of the Total Environment*, 79, 69-83.

BAUMAN, L. and STENSTROM M.K. 1989. Observations of the reaction between organohalides and sulfite. *Environ. Sci. Technol.* 23, 232-236.

GLAZE, W.H., PEYTON, G.R. and RAWLEY, R. 1977. Total organic halogen as water quality parameter: adsorption/microcoulometric method. *Environ. Sci. Technol.* 11(7), 685-690.

Heller-Grossman, L, J Manka, B Limoni-Relis and M Rebhun. 1993. Formation and distribution of haloacetic acids, THM and TOX in chlorination of bromide-rich lake water. *Wat. Res.*, 27(8), 1323-1331.

KITO, K., OTSUKI, T.,SUZUKI, N. and NAKANISHI, J. 1988. Mutagenicity of drinking water and the relation to total organic halogen. *Chemosphere*, 17(11), 2219-2232.

KRASNER, S.W., McGUIRE, M.J., JACANGELO, J.G., PATANIA, N.L., REAGAN, K.M. and AIETA, E.M. 1989. The occurrence of disinfection by-products in US drinking water. *Journal AWWA*, 41-53.

LOUW, B. 1993. Die mutagenisiteit in drinkwater geproduseer met verskillende behandelingsmetodes uit oppervlakwaterbronne. WNK verslag no 360/1/93.

LYKINS JR., B.W., KOFFSKEY W.E. and MILLER, R.G. 1986. Chemical products and toxicologic effects of disinfection. *Journal AWWA*, 66-75.

PETERS, R.J.B., ERKELENS, C., DE LEER, ED W.B. and DE GALAN, L. 1991. The analysis of halogenated acetic acids in Dutch drinking water. *Wat. Res.* 25(4) 473-477.

PONTIUS F.W. 1990. Complying with the new drinking water regulations. *Journal American Water Works Association*, 82, 32-35.

Purgeable organic halogens. Proposed standard specification Din No 38409 Part 25, of the Germain Institute of Standards, Berlin.

PUYKER, L.M., JANSEN, H.M.J. and KEMPERT, H.G.A. 1984. *$H_2O$*, 17(15).

SHUKAIRY, H.M. and SUMMERS, R.S. 1992. The impact of preozonation and biodegradation on disinfection by-product formation. *Wat. Res.*, 26(9), 1217-1227.

SINGER, P.C. and CHANG, S.D. 1989. Correlations between trihalomethanes and total organic halides formed during water treatment. *Journal AWWA*, 61-65.

STEVENS, A.A., DRESSMAN, R.C., SORRELL R.K. and BRASS H.J. 1985. Organic halogen measurements: Current uses and future prospects. *Journal American Water Works Association*, 146-154.

U.S. Environmental Protection Agency 1979. National interim primary drinking water regulations: Control of trihalomethanes in drinking water; Final Rule. *Federal Register, 44*, 68624-68707.

Water quality - Determination of adsorbable organic halogens (AOX). *International Standard, ISO 9562*, First edition, 1989-09-01.

WHO 1984 *Guidelines for drinking water quality*. Volume 2: Health criteria and other supporting information. World Health Organization, Geneva.