CSIR
DIVISION OF WATER TECHNOLOGY

# DISSOLVED AIR FLOTATION FOR THE PRETREATMENT OF EUTROPHIED SURFACE WATER FOR POTABLE USE

by

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# Abstract

The scarcity of water in South Africa has necessitated the not infrequent use of eutrophic impoundments for domestic drinking water sources. These impoundments, in turn, may be eutrophic on account of natural enrichment, or they may be fed by treated sewage which acts as a significant nutrient supplement. One such example is the Hartbeespoort Dam, which receives as much as 80% of its flow during dry periods in the form of treated domestic sewage, and which is the raw water source for the Schoemansville Water Treatment Plant. Eutrophic conditions imply excessive algae growth; blue-green algae (such as *Microcystis aeruginosa*) are frequently naturally buoyant, and are not removed by gravity settling. This creates problems with filtration and also results in high concentrations of halogenated organics following chlorination for disinfection. The halogenated organics of particular concern are the volatile trihalomethanes (THMs), with the major component being chloroform, and bromoform normally as a minor constituent.

This study concerned the optimization of the coagulation, flocculation and dissolved air flotation (DAF) processes for the removal of algae prior to filtration, and mor importantly, for the removal of the trihalomethane precursors (THMP). An extensive literature review indicated that DAF had previously been successfully used for algae removal, but that prior chemical coagulation would be necessary for superior performance, and also for adequate removal of the THMP. Studies had shown that both the algal biomass, as well as extracellular products (ECPs), could be significant precursors. Another major factor was pH, which could affect not only the rate and extent of the THMP reaction with chlorine, but also the efficiency of chemical coagulation.

Water quality parameters of the Hartbeespoort Dam, as they could relate to algal growth as well as THMP concentrations, were evaluated approximately biweekly for 1 year, in order to provide information of seasonal variations, mechanisms related to THM formation, and possible surrogate parameters for THMP/THM measurements. Preliminary DAF tests were conducted on a 6-cylinder batch apparatus; This served to screen the following variables: inorganic coagulant dose, organic polymer choice and dose, bentonite need (to assist with nucleation of the dissolved organics), air-to-

solids ratio, and pH. Jar tests were also done to compare performance with flotation. Pilot DAF tests were then performed with a unit which was installed and tested at the Schoemansville Water Treatment Plant. This pilot plant was operated partly under computer control. Comparisons were made with the performance of the full-scale DAF plant at Schoemansville; this unit was being used primarily to remove tastes and odours, for which purpose powdered activated carbon (PAC) was being applied. Although coagulants were also being added, the plant had not been physically designed for optimum flocculation conditions.

The water quality analyses showed that nutrient levels were high and conducive to vigourous algal activity. This activity was reflected in high values for pH (generally above 9), chlorophyll *a* (average 52,8 µg/ℓ; maximum 158,7 µg/ℓ), and turbidity (average 12,7 NTU). As expected, organohalogen concentrations were also elevated; total organohalogen potential (TOXP) averaged 418 µg/ℓ, and values of THMP as high as 311,6 µg/ℓ were recorded. This latter value far exceeds the Unites States drinking water standard of 100 µg/ℓ. No correlation could be found between TOXP, DOC, or THMP, but an analysis of the influent during pilot plant testing showed good correlations between pH and THMP, and pH and turbidity. Chlorophyll *a* was found to increase with THMP, pH and turbidity. This was felt to provide strong evidence that algal activity was indeed responsible for a major portion of the THMP. High bromide concentrations (average 0,6 mg/ℓ) during much of the study, and in particular before the dam overflowed and algal scum was lost, resulted in abnormally high rations of chloroforms to bromoforms.

Preliminary DAF tests suggested that inorganic coagulant dose (either alum or ferric chloride), polymer dose (cationic), and pH, were the parameters which should be explored during optimization studies. A recycle ration of 10% was suitable, and was not varied during the tests. Bentonite addition had no beneficial effects. Subsequent optimization of the test conditions for the pilot plant, using a factorial experiment design, showed that best performance would be achieved using a ferric chloride dose of 150 mg/ℓ and a depressed pH of around 5. A polymer dose of 0,6 mg/ℓ also appeared to be beneficial, but the statistical significance here was not strong. Under these conditions, the pilot plant was able to achieve in excess of 80% THMP removal, leading to effluent values as low as 30 µg/ℓ. Due to inefficient mixing and flocculation

conditions, as well as the lack of pH control, the same level of performance was not achieved in the full-scale plant, nevertheless a maximum of 65% removal of THMPs was achieved at a ferric chloride dose of 50 mg/ℓ, and no polymer or PAC added.

It is evident, therefore, that DAF, preceded by adequate coagulation conditions (physical as well as chemical) and pH depression to about 5, is capable of removing THMP from eutrophic waters such that the final treated water after chlorination would have a THM concentration below the typical standard of 100 μg/ℓ. Algal activity is clearly responsible for a major component of the THMP pool, as shown by good correlations of THMP with algal concentration parameters, but poor correlation with DOC. The bromoform component of the total THM concentration was higher than in most waters reported in the literature, and its relative concentration increased in the treated water. Since only the toxicity of chloroform has been reasonably well researched, much further work is required concerning the possible harmful health effects of the other components of chlorinated organics.

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Ronald Gehr
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# CHAPTER 1

# INTRODUCTION AND OBJECTIVES OF THE STUDY

## 1.1 Introduction.

Sources of raw water for drinking water supplies to South African cities and towns are frequently contaminated with organic wastes and/or algae (NIWR, 1985). Impoundments, especially, may have as a portion (sometimes even the major portion) of their inflow, rivers with flows supplemented with treated (or even raw) domestic sewage, as well as non-point sources of agricultural runoff containing nutrients (such as nitrogen and phosphorus) from fertilizers and manure. The nutrient-enriched impoundments will readily support a healthy algal population, leading to eutrophic - or even hypertrophic - conditions (Stumm, 1975).

Chlorine is used as the primary disinfectant in the great majority of water treatment plants worldwide. Since the discovery by Rook, and Bellar *et al* (both published in 1974), that the interaction of chlorine with certain organics found in raw waters can result in the production of trihalomethanes (THMs), there has been a certain amount of disquiet regarding the liberal use of chlorine at any convenient location in the water treatment plant and in any mode and duration of contacting. This is because halogenated organics, and in particular the volatile THMs such as chloroform, have been associated with cancers and other disorders in animals (Bull, 1982; Johnson and Jensen, 1986; Pieterse, 1988). Although an analysis of epidemiological studies has shown that THMs *per se* cannot be unequivocally associated with human cancers (Craun, 1988), nevertheless the impetus exists to reduce THM concentrations in delivered drinking water. This may be done either by removing the source organics (presursors, or THMPs), or by removing the formed THMs after chlorination.

As implied above, only certain organics will react with chlorine to form THMs. The precursors originally identified by Rook (1974), Trussell and Umphres (1978) and others were soil-derived fulvic and humic acids. However, it was subsequently shown that organic wastes (including domestic and some industrial sewages; Morris and

Baum, 1978), and algae (Briley *et al*, 1980) could also be significant precursors. The last- mentioned source is of particular interest for the present study.

Over the past decade, many governments and other statutory bodies such as the World Health Organisation, have established guidelines (non- enforceable) or standards (enforceable) for drinking water quality which include maximum desirable or permissible levels for THMs. Concentrations range from 350 µg/ℓ for Canada to as low as 1 µg/ℓ for the Netherlands and Norway (Pieterse, 1988; Sayre, 1988). To date, no standards have been proposed for South Africa (Pieterse, 1989). For the purposes of the present study, the US Primary Regulations maximum contaminant level of 100 µg/ℓ for THMs will be considered as the desirable goal for THM levels in drinking water.

## 1.2 Objectives.

The major aim of this study, as stated in the proposal dated September 19th, 1986, which was submitted to and approved by the Water Research Commission, was to assess the extent to which an optimized Dissolved Air Flotation (DAF)Process could remove trihalomethane precursors from a eutrophied surface water source. DAF has been widely used in the United Kingdom and South Africa for solids separation at drinking water treatment plants (Hyde *et al*, 1977; van Vuuren *et al*, 1985/86). It is particularly attractive when raw waters are rich in algae concentrations, as these may float naturally, and thus may not be removed during sedimentation. The study would involve both a physical optimization of the DAF process, such as by using aeration and air diffusion devices developed at the National Institute for Water Research (NIWR), now the Division of Water Technology (DWT), (Williams and van Vuuren, 1984), and a chemical optimization, such as by the use of polyelectrolytes in addition to the more common inorganic salts used for flocculation (Amy and Chadik, 1983).

Secondary objectives included characterising the chosen eutrophic water supply (Hartbeespoort Dam, at Schoemansville, Transvaal) with respect to its precursor concentrations and parameters which would lead to the formation of these precursors.

It was hoped that surrogate parameters would thus be found which could be used to further elucidate the mechanism of THM production and which might be a less costly indirect means for assessing THMP concentrations.

# CHAPTER 2

# LITERATURE REVIEW

This literature review is intended to cover material specific to the project. Included therefore are dissolved air flotation, trihalomethanes (THM) and their precursors (THMP), and the removal of the precursors from raw waters. However the emphasis will be on dissolved air flotation of algal waters, particularly within the South African context; THM and THMP, especially from aquatic sources; and finally the removal or reduction of precursors, rather than the removal of already formed THM. Analytical methodologies and the toxicity of THM (including carcinogenesis) will not be discussed explicitly.

## 2.1 Dissolved Air Flotation

### 2.1.1 Introduction

Dissolved air flotation (DAF, also known as dissolved air pressure flotation) is the process of causing suspended material in an aqueous matrix to float, by contacting this material with minute air bubbles released from an air-supersaturated recycle stream. Although variations of the process exist, such as dispersed air flotation (where air is introduced by turbulence mechanisms), vacuum flotation (where dissolved air is released under vacuum), and non-recycle pressure flotation, mainly recycle DAF will be covered in this review, on account of its greatest efficiency in terms of bubble supply, and its engineering convenience. The basic theory of DAF will not be discussed here; the reader is referred to articles by Zabel and Hyde (1976), and Hyde *et al* (1977), which cover DAF of waters in potable water processes; Ettelt (1964), Turner (1975), and Gehr and Henry (1980), for DAF in raw sewage and sludge treatment applications, and van Vuuren *et al* (1985/86) for a review of the development and application of DAF technology in South Africa. The application of DAF to algal waters will be discussed in more detail below.

### 2.1.2 DAF of algal waters

One of the earliest publications regarding flotation of algal waters was by van Vuuren *et al* (1965), which involved dispersed air flotation of these waters as part of the program concerned with water reclamation. An early discussion of DAF for algal waters was published by Bare *et al* (1975), and in the 1980's a number of studies appeared concerning DAF of algal and hypertrophic waters in South Africa. In all cases, flotation was considered a desirable process because of the inherent flotability of many algal species, and because conventional sedimentation and even flocculation/sedimentation failed to remove microalgae which would clog filtration units downstream.

During bench-scale testing, Bare *et al* (1975) required 85 mg/ℓ of $Fe_2(SO_4)_3$ or 75 mg/ℓ of alum for treating a predominantly Scenedesmus suspension with a suspended solids concentration (SS) of 100 mg/ℓ. Interestingly, pilot- plant studies yielded scale-up factors of at least 2 in the chemical dosage, possibly due to a change in algal population to Chlorella and Oscillatoria. An air to solids ratio (A:S) of 0.019:1 was required for 96% SS removal, and the hydraulic loading rate was 5.7 m/h.

De Wet (1980) presented design equations and parameters which were considered to be suitable for DAF of algal suspensions. An upflow rate of 60 m/h, downflow rate 7 - 15 m/h, and 7% recirculation at a pressure of 350 kPa were suggested. The need for efficient release of the air bubbles, such as by an abrupt pressure drop across a needle valve, was emphasised. Van Vuuren *et al* (1983), using an integrated DAF and filtration unit (DAFF), found that a recirculation rate of 15% at 350 kPa would be desirable. They also used alum and a polyelectrolyte for improved capture. However, the polyelectrolyte, while improving DAF performance, caused the rate of pressure drop across the filter to increase. Williams *et al* (1985) reported on the use of DAF for upgrading the Schoemansville water treatment plant, which is in fact the plant which was used during the present study. The following operational parameters were reported: hydraulic load 7.8 m/h, A:S 0.12 (considerably higher than for Bare *et al* 1975), 50 mg/ℓ alum, 0.5 mg/ℓ cationic polyelectrolyte, and the use of $H_2SO_4$ to reduce the pH from 9 to 7.2. Recirculated water was supplied from a high-level clear water storage tank to maintain constant pressure, and a patented microbubble nozzle was used for air introduction (see, also, Williams and van Vuuren 1984). Chlorophyll *a* was reduced from 32 to 6 µg/ℓ.

## 2.2 Trihalomethanes

### 2.2.1 Introduction

Trihalomethanes (THMs) may be considered in simplified form to consist of modified methane ($CH_4$) molecules, the modification being a replacement of up to 3 hydrogen atoms by one or more types of halogens. Since chlorine and bromine are the most common halogens encountered in natural aquatic environments, the most common THMs applicable to water treatment are trichloromethane (or chloroform, $CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CBr_2Cl$) and tribromomethane (or bromoform, $CHBr_3$).

In 1974, two articles were published linking the chlorination of natural waters which contained organics to the production of THMs (Rook 1974; Bellar *et al* 1974). Foley & Missingham (1976) have pointed out that chloroform was commonly used as an anaesthetic, as well as flavouring in candy, toothpaste, and cough remedies. However, in 1976 its use as an additive in food or drugs was banned by the US FDA (Trussell & Umphres, 1978b), since these THMs, and especially chloroform, are now known to be carcinogens (see, for example, Tardiff 1977; Cohen 1980; Craun, 1988). Thus, the impetus was initiated to research both the organic precursors and methods for removal of either the precursors (THMPs) or the reactants, ie the THMs. Other areas of research have included finding model compounds or surrogate parameters both to better understand the process of formation and to simplify routine analytical procedures, studying environmetal effects such as pH and temperature on the rate and extent of reaction, and increasing the sophistication of chemical analyses to identify intermediate products as well as other chlorination byproducts which could also pose health problems. Much of this will be covered below.

### 2.2.2 Surveys and regulations.

Hard on the heels of the two pioneering studies of 1974, the (US) National Organics

Survey for Halogenated Organics was published (Symons *et al* 1975). Results from 80 cities surveyed showed mean, median, and range values of THMs to be 68, 41, and non-detectable (ND) - 482 µg/ℓ. Four years later, drinking water regulations were published in the US setting limits on total THM (TTHM) concentrations in finished drinking waters to 100 µg/ℓ (US-EPA 1979). A recent survey showed that as a result of these regulations, US water utilities showed a 40 - 50% reduction in TTHM (McGuire & Meadow 1988). This was achieved largely by changes in clarification and disinfection procedures, including switching from chlorine to chloramines.

Two major surveys of THM concentrations in drinking water have been conducted in Canada. The first involved 13 water treatment plants in Ontario (Foley & Missingham 1976); 3 plants produced water with a THM concentration higher than 100 µg/ℓ (maximum 148 µg/ℓ). A later study covered grab samples from 70 municipalities across Canada, and it also considered the effect of detention time in the distribution system (National Survey..., 1977). The study was subsequently expanded to investigate seasonal effects (Williams *et al* 1980). An interesting point emerged concerning the methodology used to measure THMs; direct aqueous injection resulted in higher values of THMs than gas sparging, due to the conversion of various intermediates to THMs in the heated GC injection port. Thus the range of chloroform measured at the treatment plants was 0 - 77 µg/ℓ for gas sparging, and 0 - 144 µg/ℓ for direct aqueous injection. Maximum values in the distribution system increased to 121 or 150 µg/ℓ respectively. However mean values were below 30 µg/ℓ in all cases, and THMs resulting from ground water sources were about 10% that of river and lake sources. For the single case studied for seasonal effects, levels of chloroform varied from 120 - 160 µg/ℓ (direct aqueous injection) in summer, to only 13 µg/ℓ in January.

No national survey has been conducted in South Africa to date, however a survey of Pretoria's drinking water supplies was published by van Steenderen *et al* in 1983. The range of TTHMs found was 13.9 - 105 µg/ℓ, however it was pointed out by the authors that in many cases there was no chlorine residual (leading to poor bacteriological quality), and that the potential TTHM concentration would be considerably higher. The ratio between maximum actual and potential total organohalogen concentration (TOX), ie volatiles and non-volatiles, was 2.66 . In a report by Thornton and van Steenderen (1984), it was noted that the potential TOX concentration in the river inflows to

Hartbeespoort Dam often exceeded 500 µg/ℓ, and that the TTHM in the drinking water at Schoemansville (which draws its raw water from the dam) was 170 µg/ℓ. Furthermore, TOX levels in the dam itself sometimes ranged between 700 and 2,400 µg/ℓ, indicating that biochemical activity within the dam contributed to the production of TOX (and thus THM). This phenomenon, ie the contribution of algae and their exocellular products as precursors for THMs, will be discussed below.

### 2.2.3 Model compounds and surrogate parameters

Model compounds are those well-defined, usually commercially available chemicals, which will react with chlorine in the same way as natural organics to produce similar concentrations of THMs. They are used in the elucidation of reactions and in the prediction of THM concentrations which would be produced under various conditions. Surrogate parameters are parameters which are closely correlated with THM measurements, and are easier, cheaper, and/or faster to measure than THMs. In some cases, model compounds can act as surrogate parameters for THMPs. Surrogate parameters are useful when assessing optimum conditions for THMP or THM removal, as well as in routine on-site measurements for THMP or THM where sophisticated equipment may not be available.

Rook (1977) was one of the first to point to fulvic acids (FA) as the organic precursors of THMs in naturally coloured waters. These acids are essentially small sized humic acid (HA) molecules which remain in solution at pH 1. Much of his study was concerned with arriving at a satisfactory explanation for the observed THM reaction rate showing an increase with pH. The essential conclusion was that the most reactive sites for the haloform reaction with FA are meta-dihydroxylated benzene moieties. The increased rate at high pH is due to the rapid formation of more phenoxide ions. Excessive chlorination results in an additional degradation pathway which produces more non-volatile products such as chloral.

The significance of non-volatile products will be discussed later in more detail, however in a subsequent paper, Rook (1980) pointed out that the concentration of these non-volatiles may exceed those of THMs by a factor of 5. In a detailed study of HA as precursors, he noted that since HA are essentially benzene and aromatic heterocyclic rings substituted with methoxy- (OMe), hydroxy- (OH), and carboxylic- (COOH) functionalities, the role of these groups should be studied *vis-avis* their promoting of reactions with chlorine. He determined that methylated compounds were unreactive to chlorine at high pH, that methoxy- compounds reacted with bromine to give significantly higher yields of $CHBr_3$ than reactions with chlorine to give $CHCl_3$, and that the principal requirement for incorporation of chlorine into aromatic groups is the presence of the phenolic OH group.

Many other researchers have subsequently pointed to HA and FA as THM precursors. These include Oliver (1980), and Gyunter *et al* (1986). However Fam and Stenstrom (1987) found that the precursors of certain "light" non-volatile chlorinated organics were not classic FA, but smaller, more polar compounds which appeared to be flavones and flavonols.

Thus far, the model compounds discussed are complex organics, often prepared by the individual researchers using extractions from specific soil or aqueous samples. Another class of model compounds are well defined, generally smaller molecules, or at least they are organics which are commercially available. In some cases these compounds are useful as "spiking" materials which serve for quality control during analytical procedures. Stevens *et al* (1976) noted that simple methyl ketones will react through the classical haloform reaction mechanism to form THMs, and that ethanol can be oxidized by hypochlorite to acetaldehyde which in turn will be a THM precursor. More complex materials such as HA will involve a cleavage step prior to the haloform reaction. Acetone could be a precursor at a high pH. Problems with these compounds as precursors were pointed out by Morris & Baum (1978); they noted that although the classic haloform reaction is a base catalyzed series of halogenation and hydrolysis reactions which do occur typically with methyl ketones or other compounds oxidizable to that structure, the reaction, as controlled by the ionization of the methyl ketone, would take almost 1 year to reach completion at pH 7. Thus they suggested that β-diketones (such as 1-3 cyclo-hexanedione, resorcinol, etc), as well as structures with a pyrrole ring (which are important because of their occurrence in chlorophylls, xanthophylls, and heme), as well as acetogenins (which are related to β-ketonic linking, and which are responsible for many natural pigments) may be more likely candidates.

Arguello *et al* (1979) listed phenols, anilines, and meta-and para- dihydroxy-aromatic compounds (such as resorcinol and hydroquinone) as being efficient chloroform producers (0.2 - 0.3 M $CHCl_3$ / M). Resorcinol, also known as 3-5 dihydroxybenzoic acid, has subsequently been used in precursor studies by Dore *et al* (1982), Boyce & Hornig (1983), and Gyunter *et al* (1986). Dore *et al* (1982) and Boyce & Hornig (1983) determined, however, that the maximum yield of $CHCl_3$ for resorcinol occurred at pH 7 - 8, whereas with acetone the maximum yield occurred at pH 11 (Dore *et al*, only). This latter result is more consistent with natural systems (see, for example, Rook (1977) above). On the other hand, the maximum yield of brominated organics derived from resorcinol occurred at pH 10, and with acetone at pH 12.

More recently, other compounds have been proposed as precursors and model compounds for THM formation. Cooper & Kaganowicz (1985) studied α-methylbenzylamine (MBA). Scully *et al* (1985) pointed out that proteins and amino acids are abundant in natural waters suffused with algae, and compared the chlorination reactions of bovine serum albumin (BSA), pepsin, renin, and cytochrome c with HA. All proteins gave similar molar $CHCl_3$ yields of 0.4 - 0.5%, compared with HA at 0.78%, however the rate of THM formation from the proteins was considerably slower than from HA. All compounds showed higher yields at higher pH. Trehy *et al* (1986) also investigated the behaviour of amino acids when reacting with chlorine. Aspartic acid, tyrosine and tryptophan were assessed for yields of $CHCl_3$, as well as the non-volatile products dichloroacetonitrile (DHAN) and chloral hydrate. The former is mutagenic and tumour initiating. Results indicated that the amino acids (ie nitrogenous compounds) would tend to be precursors for the non-volatile compounds, and that HA would be more efficient volatiles (such as $CHCl_3$) precursors.

Welch *et al* (1985) suggested using polymaleic acid (PMA) as a THM precursor, since it was chemically and structurally closely related to the polycarboxylic acid (PCA) fraction of aquatic FA. 1.5% of the organic carbon in PMA reacted to produce $CHCl_3$, compared to 0.2 - 1.6% for natural materials; thus PMA is clearly a vigourous precursor. Significant concentrations of $CHCl_3$, after chlorination of dimedone, resorcin, glucose and 1,3-cyclohexanedione, were measured by Gyunter *et al* (1986). These compounds possessed one or several carbonyl functional groups or phenolic hydroxyls. Hydroquinone, 1-4-cyclohexanediol, acetone, pyrogallol and quinone formed small amounts of $CHCl_3$ only in alkaline media. Thus the authors concluded that the compounds responsible for $CHCl_3$ formation are oxo- compounds with one or several carbonyl groups in the meta or para position, as well as compounds with phenolic hydroxyl groups.

The field of surrogate parameters to replace direct THM measurements has been well covered by Edzwald (1984), Sorrell *et al* (1984), Edzwald *et al* (1985) and Batchelor *et al* (1987), amongst others. Probably the simplest surrogate parameter to measure is UV (254 nm). Edzwald (1984) and Edzwald *et al* (1985) indeed found it to be a suitable one for indirectly measuring THMPs and TOC in river and reservoir waters. In many cases, though, other non-precursor molecules, such as nitrite and bromide, would also absorb UV light; alternatively organic compounds which are not aromatic or which do not have conjugated double bonds would still contain TOC but would not be UV absorbing. Edzwald's studies involved samples from a river and from a reservoir, and in the latter case the THMP were thought to include humic as well as algal material. However neither supply had been subjected to industrial or municipal sewage discharges. Edzwald *et al* (1985) noted that water supplies with humic substances had UV:TOC ratios of 4 -5 $m^{-1}$:mg/ℓ.

Total organic carbon (TOC) is another relatively convenient measurement which has been proposed as a surrogate parameter or has correlated well with THMP removal (Veenstra & Schnoor 1980, Engerholm & Amy 1983, Taylor *et al* 1984, Knocke *et al* 1986). However, Amy *et al* (1987b) found that $UV_{254}$xNPOC (non-purgeable organic carbon) was a more representative surrogate parameter. They suggested that the UV absorbance represents the precursor reactivity, whereas NPOC represents its concentration. Oliver (1980) and Hoehn *et al* (1984) actually found, in contrast, that while THMP levels varied widely during daily or yearly cycles, TOC values remained virtually constant. Oliver & Lawrence (1979) found a better correlation between TOC and TOX for raw water samples, but interestingly not for alum- treated samples.

Sorrell *at el* (1984) assessed purgeable and total organic halide (POX and TOX) for measuring volatile halides in groundwaters. Although costwise similar to THM measurements in their case, (but far more rapid), these authors concluded that more quantitative and qualitative information about specific compounds which would be incorporated into the POX/TOX values would be needed to extract THM readings, hence they were limited in their use as surrogates.

Batchelor *et al* (1987) proposed using iodoform and bromoform formation potentials (IFP and BFP) as indications of THMP. IFP and BFP can be measured by spectrophotometry, thus being much simpler to quantitate than THMP, which requires gas chromatography (GC). Both parameters gave good predictions of THMP, but the yield and the reaction rate were superior for BFP. For routine measurements, however, IFP would be preferable, since measurements are made in the visible range, as opposed to UV for BFP.

### 2.2.4 Molecular weight distribution

The molecular weight distribution (MWD) of THMP has been studied by many researchers, and to a lesser extent the MWD of the THMs as well. A knowledge of the MWD of THMPs enables one to obtain a better understanding of their nature and sources, and can point to suitable engineering options for the removal of both THMP and THM. In many cases, research has focussed on the methodology of obtaining the MWD, however in this review the MWDs themselves will be emphasized. Essentially, the two methods for measuring MWD are gel permeation chromatography (GPC) and ultrafiltration (UF), and Amy *et al* (1987a) conveniently compare the two for characterizing aquatic organic matter. GPC measurements usually require sample preconcentration, which could lead to unwanted interactions, and they are affected by pH and ionic strength. The problems with UF are that the membranes themselves have a range of pore sizes, hence do not have sharp cutoff values. Concentration polarization can interfere with results if certain preventative measures, such as mixing, using low solute concentrations, and using a series of filtration steps, are not taken. Furthermore, the Donan effect (in which the membrane develops an ionic, or charge, potential in order to maintain electroneutrality) can impede the diffusion of solute species which are charged similarly to the membrane. Amy *et al* (1987a) found that GPC generally indicated higher apparent MW than UF, but that a lower pH would cause a shift in the GPC chromatogram to a lower MW.

Trussell and Umphres in their review article (1978b), note that FA have a MW range of 100 - 1,000, whereas the range in MW for HA is 100,000 and higher. Thus HA will precipitate more readily in acid solutions, and will also react with chlorine in a much more active way than FA. However in many cases HA will be present in natural waters at much lower concentrations than FA.

Schnoor *et al* (1979) were amongst the first to study THM yields as a function of precursor MW, agricultural runoff being the major source of THMP in their case. The highest absolute $CHCl_3$ yield occurred in the 3,000 - 6,000 MW fraction (10.9 µg/mg TOC), but since the TOC was itself highly skewed in the lower MW ranges, the highest $CHCl_3$ concentration in terms of TOC occurred in the 1,700 - 3,000 MW range. Interestingly, brominated compounds occurred at their highest concentrations in the 1,000 - 1,700 MW range. Hence the conclusion was that THMs were primarily formed from precursors of MW < 6,000, and that with each bromine atom added, the mean yield decreased and the precursor organics were of lower MW.

Similar conclusions about the range of MWs contributing to THMP were reached subsequently by many other researchers. These include Oliver and Thurman (1983; groundwaters, surface waters, and surface waters draining wetlands), Bruchet *et al* (1984; river), Knocke *et al* (1986; river and reservoir), Collins *et al* (1986; river, reservoir, and aquifer), and El- Rehaili and Weber (1987; Huron River). However some researchers have found significant precursor concentrations at MW <1000 (van Steenderen and Malherbe [1982; activated sludge effluent, DOC measurements only], Bruchet *et al* [1984; reservoir]; Collins *et al* [1986; river, reservoir, aquifer], and Fam and Stenstrom [1987; water hyacynth treatment plant]). Others note major contributions from much higher MW (Glaze *et al* [1980; TOXP evenly spread over 200-31,600, THMP more evident at lower MW; lake], Oliver and Visser [1980; 1,000-10,000 most productive for FA; 10,000 - 20,000 for HA], van Rossum [1984; 1,000-100,000 for inflow - actually effluent from a biological treatment plant - to a water reclamation plant], Collins *et al* [1986; 10,000-30,000 for soil FA], and El-Rehaili and Weber [1987; 3,000- 40,000 for HA]. Thus it appears that waters with higher organic content, as well as HA and FA, tend to contain higher MW precursors.

These MWDs have implications on the choice and effectiveness of treatment processes. In one study, alum proved better for removing the <1,000 THMP fraction, whereas $FeSO_4$ was more effective for the 1,000-10,000 range (Knocke *et al* 1986). Collins *et al* (1986) found that coagulation with alum or lime, followed by filtration, could not remove the dissolved organic matter of MW <1,000, except for one plant which was effective down to MW of 500. Direct filtration could not remove any components! Collins *et al* (1986) pointed out that hydrophobic components were the primary contributors of THMP for most waters, and these are more likely to be removed in flocculation/clarification processes. TOC would often contain significant hydrophilic fractions, leading to a greater % reduction of THMP than TOC. Furthermore, those humic substances with the highest content of acidic functional groups would be the hardest to destabilize by alum coagulation.

The implications of MWD on activated carbon adsorption were addressed by El -Rehaili and Weber (1987). There was a decrease in the extent of adsorption with increasing MW, with the MW fraction > 40,000 being least adsorbable. However, adsorber breakthrough of organics in the intermediate MW range occurred more rapidly than it did for the high and low MW fractions. Alum treatment achieved reasonable removals of low and intermediate range MW fractions, but the dosage had to be increased to affect the highest MW range. The effluent from the low dose alum process was, in turn, harder to adsorb, due to the increased content of high MW organics. However this was considered to be of only minor concern, since the highest MW fractions of the organics contributed only marginally to THMP.

### 2.2.5 Algal precursors

Initial articles on THMs and their precursors pointed to humic material - ie soil derived - as the major source of THMP, and it took about 4 years (to 1978) before articles appeared showing that organics from other sources could also be vigourous precursors. These sources include raw sewage and algae. For the present review, the term "algae" will include blue-green algae or blue-green bacteria. Algae would clearly be of concern in eutrophic or hypertrophic lakes, and the unique aspect of this precursor of THMs is that variations in concentration and/or activity/yield would likely follow diel as well as seasonal patterns, far more so than in the case of the other sources of THMP. Thus the following review will also briefly examine the growth patterns of some relevant algae, and changes in the extracellular products (ECP) which might affect their role as THMP. It should also be noted that halogenated organics (ie not the precursors, but the final products) have been found in a red alga species, Asparagopsis taxiformis (Siuda 1980). This researcher pointed out that over 550 naturally occurring halogenated compounds have been detected in the environment. This is as a result of halogenation in plant and animals being mediated by catalytic proteins called haloperidases, which require hydrogen peroxide as a cosubstrate.

Hoehn *et al* (1978) were amongst the first to notice that algae could produce precursors for THMs. In their study of the Occoquan Reservoir in North Virginia, they noticed a correlation between THM and chlorophyll *a*.

Briley *et al* (1980) assessed Anabaena cylindrica as a THM precursor. THMs resulting from chlorination of ECP as well as from cell mass showed similar patterns, ie an increase in concentration during exponential growth, followed by a slight falling off during the stationary growth phase. The cells themselves produced more THM than ECP. The authors noted that TOC was a poor indicator of THMP, since TOC would continue to increase with increasing culture age. Furthermore, algal biomass was found to react more slowly than ECP to produce THMs.

Although the tests of Hoehn *et al* (1980) were flawed due to the absence of chlorine residuals after many of their experiments, they came to the same conclusions as Briley *et al* (1980), when testing two green and two blue- green algae species. They noted, further, that bacterial activity may alter ECPs to make them more amenable to reaction with chlorine. This observation was confirmed in a subsequent study (Hoehn *et al* 1984), in which it was found that algal ECPs in a lake water were hydrophobic, compared to their more normal hydrophilic character. Thus it was suggested that heterotrophs change the character of the ECPs. Hoehn *et al* (1980) pointed out that due to their faster reaction time, ECPs would probably be more significant precursors than algal biomass during practical water treatment. In addition, the yield of THM for algal ECP, based on TOC, was at least as high as that for FA and HA. In a similarly flawed series of tests (insufficient $Cl_2$ and only 1 h reaction time), Pilkington and van Vuuren (1981) assessed a natural water containing Microcyctis aeruginosa blue-green algae for THMP characteristics. An increase in THM production with pH and with chlorine dose was noted, and filtered samples (containing ECP) actually produced more THMs because there were fewer competing chlorine-demand reactions when chlorine was limiting.

Oliver and Shindler (1980) examined 7 cultured algal strains and 2 natural samples as sources of THMP. The $CHCl_3$ yields differed for different species, with a range of 3.5 - 7.3 $\mu gCHCl_3/mg$ material at pH 7, and 24 - 47 μg/mg at pH 11. Interestingly, the pH effect was far greater than for aquatic humic material. These authors also noted that, given sufficient reaction time, ECPs accounted for only a small fraction (about 20%) of total $CHCl_3$ production, including production from whole cells. Also, algal pigments (such as chlorophyll *a*) were not important as THMP.

The results of pure culture studies were also reported by Scott *et al* (1985) and van Steenderen *et al* (1988), who tested one morphological form of Microcystis aeruginosa: forma flos-aquae. Apparently the death of this alga when phosphorus (P) became limiting resulted in a massive release of TOX (6.7 mg/ℓ). However when P was not limiting, there was only a slow release of TOX as algal growth continued, although even in this case the concentration of excreted TOX after 14 d was >1 mg/ℓ, which is far higher than reported values for other (green) algae or cyanobacteria.

Diel variations in THMs as a result of the characteristics of algal behaviour have been directly analysed in only one study to date (as far as the author is aware), that by Hoehn *et al* (1984). It is perhaps appropriate first to mention the principal conclusions cited in 4 Russian studies which examined the diel variability of ECPs, without actually considering THMs. Kosenko (1974), in an investigation of Anabaena variabilis, discovered that there was a noticeable drop in extracellular carbohydrates when there was a change in lighting conditions. Carbohydrates in the medium were consumed particularly rapidly in the dark, ie when energy requirements from sources other than photosynthesis increase. It was suggested that algae may consume their own extracellular carbohydrates which they had previously released.

Changes in ECPs during different growth phases and light conditions of Microcystis aeruginosa were studied by Sakevich *et al* (1979;1980). In general, the concentration of ECP increases under adverse environmental conditions. These ECPs are composed mainly of polysaccharides, but other components include proteins, amino acids, alcohols, esters, organic acids, carbonyl compounds and amines. Accumulation is more intense in axenic cultures. At the start of growth, the ratio ECP:biomass increases. ECP concentrations range from 17 - 131 mg/ℓ at the start of exponential growth to 259 - 325 mg/ℓ at the end of exponential growth. The ECP:biomass ratio is lowest in old cultures, but with dying cells, there can be posthumous release (in the 1980 report, posthumous release is considered insignificant). Under limiting N or P conditions, the algae may transfer to heterotrophic feeding resulting in a decrease of organic compounds in the medium (in contradiction to the findings of van Steenderen *et al* 1988, above). However, it is possible that this decrease precedes actual death of the cells, and in that event ECPs would again increase (ie posthumous release). On a unit cell mass basis, at the start of the log growth phase, there was a marked increase, then a decrease of soluble organic matter (SOM). However, the SOM was virtually constant at the end of this growth phase. It is suggested that during a time of intensive cell growth, there is a reduction in the content of ECP.

In a natural water body, Sakevich *et al* (1980) observed that SOM was gradually reduced at the start of a light period, then increased by 3 pm (maximum photosynthesis), after which it decreased again. In some cases there was an appreciable SOM increase in the dark, but in others only a slight increase, followed by a reduction and stabilization. The authors pointed out that daily changes in SOM are also affected by the accompanying bacterioflora. It was not clear, though, whether bacteria could affect SOM concentrations, or whether SOMs could contain components which might inhibit bacterial growth.

In a further study of algologically pure cultures of M. aeruginosa and Anabaena variabilis, and axenic cultures of A. variabilis and Nostoc muscorum (Sakevich and Osipov 1983), where $\Delta$ S is algal biomas increase over time, and $\Delta$ P filtered COD increase over time. $\Delta$ S was approximately zero, and $\Delta$ P was high during the lag phase of growth. This phase lasted longer in darkness, and when there was greater mortality, $\Delta$ P was highest (29.8 mg/ℓ-d). During the exponential phase, however, during which there was the most intensive photosynthesis, there was the largest $\Delta S$. For axenic cultures, $\Delta S$ was inversely correlated to $\Delta P$. However this correlation was not always clear in algologically pure cultures, due to the influence of bacteria.

Thus the major conclusion from the above studies with algal ECPs appears to be that they are affected by both growth and light/dark cycles. However the nature of this effect is not clear, and there are sometimes conflicting results, which may, in turn, be due to the influence of bacteria.

Hoehn *et al* (1984) studied THMP variations in a hypertrophic US lake. The predominant algal community during the period of the study (summer) was Microcystis spp, but in the fall, as temperatures dropped, the predominant species changed to Chlamydomonas. The highest THMP was registered in early August, as the algal density was increasing. Diel variations were also observed; they will be discussed in Section 2.6.4 below.

The production of non-volatile organochloro compounds from algal precursors has been the subject of two more recent studies. Oliver (1983) examined the production of dihaloacetonitriles (DHAN), some of which have been found to be mutagenic in bacterial assays. At pH 7, FA produced more DHAN than the algae did, however only 1 - 3% of the organic nitrogen in the FA was converted to DHAN. Anabaena algae produced considerably more DHAN than did Scenedesmus, the latter having a lower organic nitrogen content. The addition of bromide before chlorination was found to greatly increase the production of DHAN. High pH levels were detremental to DHAN production as a result of hydrolysis reactions.

Wachter and Andelman (1985), reacting to previous studies which had shown that non-purgeable (ie non-volatile) chloro-organics had greater mutagenic potentials than their organic precursors, studied 2 green algae and a blue- green algae species for the formation of non-purgeable organohalides (NPOX). The algae were harvested after attaining stationary growth, and were chlorinated during exposure to light. The rate of NPOX formation was most rapid during the first hour, and was not affected by the absence or presence of light. The rate increased with a decrease in pH, and this behaviour was explained by the effect of pH on chlorine speciation; as the pH drops, the total net reactivity of chlorine increases. The majority of organic halides generated from algal ECP was non-purgeable. The filtrate from the blue-green alga produced the most NPOX, compared with the green algae. About 50% of the observed differences among algae species in forming NPOX could be attributed to differences in the respective amounts of ECP excreted. It was also observed that an average of 8.3% of the chlorine demand in algal filtrates was accounted for by NPOX-forming reactions (ie not oxidation reactions); this was apparently higher than previously reported.

### 2.2.6 Environmental effects

#### 2.2.6.1 pH

The effects of pH on THM production are associated with chlorine speciation, with changes in the nature of the precursors (and model compounds) themselves, and, as far as removal is concerned, with affects on the interactions between the organic precursors and coagulants as well as adsorbents.

Oliver (1978) was probably the first researcher to show that the total amount of organic chlorine formed was virtually independent of pH, however a shift occurred from non-volatile chloro-organics predominating at low pH to volatile compounds predominating at high pH. He suggested that non- volatile chloro-organics at low pH were in the form of THM intermediates. In a subsequent paper, Oliver (1980) found that $CHCl_3$ intermediates produced at pH 7 were indeed hydrolysed to $CHCl_3$ at pH 11, however the level of $CHCl_3$ produced originally at pH 11 was still higher than that produced by subsequent alkaline reaction of products formed at pH 7. Thus there seemed to be a fundamental change in the reaction at the two pH levels. Miller and Uden (1983) continued along this line of reasoning, and pointed out that the pH at which hypochlorous acid (HOCl) predominates - ie low pH - favours compounds requiring stonger oxidizing conditions, hence the formation of non-volatile compounds (in their case, trichloroacetic acid, TCAA). At high pH, $CHCl_3$, whose formation is base catalyzed, is favoured. Furthermore, in their study, there was a drop in the concentration of chloral hydrate at high pH, due to its instability under alkaline conditions, and the degradation product was $CHCl_3$.

Probably the most comprehensive elucidation of chlorine speciation and its effects on TOX and THM production was presented by Johnson and Jensen (1986). Chlorine can react with naturally occurring organics by oxidation and/or by substitution. Only a small percent of chlorine consumed during water treatment actually substitutes on to organic compounds, and this substitution reaction is slow, compared to oxidation. Chlorine dose affects the mix of substitution/oxidation reactions. At low doses, substitution products predominate, whereas at high doses oxidation and cleavage occur, resulting in THM formation. The chlorination of naturally occurring organics produces 1.5 (at high pH) - 11 times (at low pH) as much NPTOX as $CHCl_3$. Thus although $CHCl_3$ production is increased at high pH, the overall TOX production is actually reduced. Interestingly, chloramines do affect significant substitution reactions, and these lead to the production of TOX. The authors maintain that TOX could be as problematic, from a health point of view, as THM, and that since chloramines have poorer disinfecting abilities than chlorine, their use as disinfectants in place of chlorine is questionable.

In terms of the effect of pH on the precursors themselves, and especially on precursors such as FA and HA, Stevens *et al* (1976) suggest that certain reactive sites on these molecules would react at insignificant rates at lower pH, but are more reactive at higher pH. For example, only 0.7% of the carbon in HA (which was assessed at about 60% C) formed THM at a low pH, whereas this yield was doubled at high pH. Oliver and Lawrence (1979) suggest that humic substances occur as microcolloids, in which particle size is a function of pH. According to Chadik and Amy (1987), the charge density on the phenolic and carboxylic functional groups of HA and FA is proportional to the pH. Thus both size and charge of the THMP molecules is affected by pH. Trussell and Umphres (1978b) suggested that this pH dependence could be utilized in practice by maintaining a low pH during disinfection, then raising the pH once a free chlorine residual was no longer present, ie after $NH_3$ addition. However they caution that additional THM could still be formed in the absence of $Cl_2$ but at a higher pH, due to the hydrolysis of intermediates.

The effect of pH on the reactivity of model compounds was investigated by Morris and Baum (1978) and Dore *et al* (1982). The former researchers found that most substances tested exhibited increased production of $CHCl_3$ at greater pH values, but interestingly, with syringaldehyde, total chlorine demand was less at higher pH values, even though chloroform production was 10 times as high at pH 9.2 as at pH 6.8 . A similar effect was found with nitrogenous compounds, such as those with pyrrolic rings. In some cases, increased yields of $CHCl_3$ were found when the pH was raised after chlorination, even if the solution had been dechlorinated, which suggested that intermediate compounds (such as trichloroacetate) were present which required alkaline conditions for hydrolysis. Morris and Baum (1978) maintained that since most simple chlorinated compounds show about the same level of health risk, one must consider elimination of the total Cl bond level, rather than just $CHCl_3$ removal.

Dore *et al* (1982) found that THM yield for resorcinol passed through a maximum at pH 7, whereas the maximum for pyruvic acid was 12. Thus in terms of behaviour under various pH levels, the latter might be more representative of aquatic precursors, although resorcinol seems to have gained favour as a model - or test - compound by a greater number of researchers.

Coagulation with metal salts is a possible method for removal of THMP. Since it is well known that pH affects the performance of these salts during coagulation for turbidity removal, it is not unexpected that pH would affect THMP coagulation as well. This was indeed found to be the case in a study reported on by Chadik and Amy (1983). They observed that low alkalinity waters needed less coagulant because the coagulant itself (alum or $FeCl_3$) caused the pH to drop, leading to a predominance of positively charged metal complexes. These were more effective THMP coagulants than metal hydroxides at high pH. Knocke *et al* (1986) reached a similar conclusion, and obtained largest THMP reductions at pH 5 for both alum and $FeCl_3$.

### 2.2.6.2 Temperature

Oliver (1980) studied the effect of a wide range of temperatures (2 - 30°C) on the production of THM from FA. This study was prompted by measurements of THM concentrations in Ottawa (Canada) drinking water, which changed from averages of

20 μg/ℓ in winter to 120 μg/ℓ in summer, despite only small changes in TOC. Stevens *et al* (1976) had also noted that temperature differentials alone could easily account for changes in THM production in winter and summer. In Oliver's study, $CHCl_3$ concentrations did increase with temperature, and this increase was found to be as much as 8 times over the temperature range investigated. Similar results were obtained by Knocke *et al* (1986); a specific yield of 60 - 65 μg THM/mg TOC after 7d was obtained at 2°C, vs 140 - 150 μg THM/mg TOC at 22°C.

### 2.2.6.3 Bromide

Sources of bromide in surface and ground waters include geologic sources, sea water, trace impurity in chlorine, sewage and industrial wastes, and rock salt used for de-icing roads (Cooper *et al* 1985). Although typically present in only small amounts in most fresh waters - 4 to 140 μg/ℓ (Ishikawa *et al* 1986) - in many cases bromide concentrations could still be sufficient to significantly affect the total production as well as the chemical species distribution of THMs. The reasons for this are explained below.

Morris (1976), Pierce (1978), Schnoor *et al* (1979), and Ishikawa *et al* (1986), amongst others, have pointed out that the effective reactivity of bromo-compounds (such as hypobromous acid) is greater than the reactivity of the equivalent chlorine species. As an example, Pierce (1978) notes that at pH 8 and 25°C, 90% Br in aqueous solution is present as HOBr, whereas only 19% Cl is present as HOCl (both HOBr and HOCl being amongst the most reactive of their respective species). Furthermore, the addition of chlorine to aqueous solutions containing bromides will result in the following (schematic) chain reaction:

$$Cl_2 + H_2O \text{ -> } HOCl \text{ .....} + Br^- \text{ ->} HOBr + Cl^-$$

Rook (1974) found that the ratio of total Br to total Cl in the THMs of finished water far exceeded their ratio in the raw water; Cooper *et al* (1985) attributed this to chlorine acting preferentially as an oxidant, whereas bromine is a more effective halogen-substituting agent. In their studies on organics from agricultural runoff, Schnoor *et al* (1979) found that with each bromine atom added, the mean yield of THM decreases. Oliver (1980) reached similar conclusions, but due to the faster reaction rate of bromine compounds, found that the yields for $Cl^-$ and $Br^-$ would approach each other after long periods. Dore *et al* (1982) also found that as bromide concentrations increase, both $CHCl_3$ and TTHM will decrease after reactions of chlorine with resorcinol. They also pointed out that on account of the following sequence of redox potentials:

$$Eo_{HOCl} > Eo_{HOBr} > Eo_{HOI} ,$$

hypochlorous acid and the hypochlorites will oxidize bromides to form hypobromides, which results in a competition between the two halogenating agents. This competition is apparently not unbiased: Amy *et al* (1984) report other studies which show that bromine substitution is favoured over chlorine even when chlorine is present in a large excess. In their own studies, TTHM mass concentrations increased with bromine addition, but for some waters molar yields also increased, whereas for others they remained constant but speciation changed. Thus the precursor source and bromide concentration affect bromide incorporation. The greater reactivity of hypobromous acid, compared to hypochlorous acid, was also noted by Welch *et al* (1985) in experiments with the model compound PMA.

The effect of bromide on the production of non-volatile compounds, such as dihaloacetonitriles (DHANs) is similar to its effect on THM; Oliver (1983) obtained an increase in the production of both when bromide was added to green algae prior to chlorination. A recent study of Symons *et al* (1987) used neutron activation analysis in an attempt to obtain a better understanding of the extent of substitution of bromine and chlorine in TOX (ie non-volatile as well as volatile organohalogens) during organics reaction with chlorine in the presence of bromide. The organic precursor was a commercially available humic acid. The pattern of increasing volatile chlorinated trihalomethanes (ie TTHMCl) with increasing pH remained the same whether bromide ion was present or not: The decrease in non-purgeable organo-chlorinated compounds (ie NPOCl) with increasing pH remained the same in the presence or absence of bromide, but suppression of NPOCl occurred in the presence of bromide, especially at the higher pH levels studied (>9) after 3 d and at a Br concentration >= 8.4 µmol/ℓ. TTHMBr also increased with pH, but was suppressed at pH 10.7. The ratio NPOX:TTHMX (ie non-purgeable: purgeable/volatile organics) was unaffected by bromides. It was suggested that NPOX could be greatly reduced by treating water with about 8 µmol Br/ℓ at pH 9 or higher for 3 d; however TTHMX would be slightly increased. Similar conclusions had been reached by others using far less sophisticated and costly methods.

### 2.2.6.4 Seasonal and diurnal/diel effects

In common with many other aqueous pollutants, THMP and THM concentrations have been found to vary on a regular basis. Seasonal effects may be direct and with a low frequency, such as those caused by variations in temperature; diel effects will be observed over 24 h, and may be indirect, such as the influence of the light/dark cycle on the growth of algae and their production of ECPs. In a survey of 14 utilities over 1 year, Arguello *et al* (1979) found large variations in THMs; their concentrations were generally less in winter. Williams *et al* (1980) found variations in the Ottawa/Hull water distribution system ranging from 13 µg/ℓ in January (winter) to 120 - 160 µg/ℓ in the summer months. A more recent survey of 910 utilities in the US (McGuire & Meadow 1988) showed similar though less drastic results, with a median maximum THM concentration in summer of 65 µg/ℓ, and 50 µg/ℓ in winter. In all these cases, temperature would appear to be the dominant and perhaps only cause of the THM variations. Stevens *et al* (1976) have pointed out that temperature could indeed be responsible for the significant changes in THM production between winter and summer.

In some cases, though, temperature itself will not be the only variable, although it may be the cause of changes in other variables which in turn affect THM production. In a study of a single source, the Iowa River, Veenstra and Schnoor (1980) found that an extra peak in the MW distribution of the THMPs (in the > 40,000 range) occurred in the summer and fall. It was believed due to an increase in algal activity as well as runoff. TOC and THMP levels were also highest in the summer and fall months. In contrast, Oliver and Visser (1980), in a study of aquatic humic material, found that the major fraction of THMPs occurred in the 20,000 - 30,000 MW range, and that this component showed very little seasonal change.

Although algae and their ECPs are known to be significant THM precursors, as described in Section 2.5, and although it is well known that their behaviour changes with temperature and light intensity/periodicity, furthermore that different algal species probably have different THM yields, only 1 study to date has examined the diurnal changes in THMP due to the diurnal algae cycle. Hoehn *et al* (1984) found that maximum diel THMP occurred at 8:00, but a significant THMP increase also occurred at night, coincident with a rise in $CO_2$. This indicated significant heterotrophic activity. After the noon hour, THMP decreased, and a number of causes were suggested. These were the intense photorespiratory state of the algae, a downward migration of the algae away from the midday light, oxygen-induced inhibition of bacteria, destruction of low MW compounds or hydrolysis of high MW compounds (ECP) by heterotrophic bacteria, finally, incorporation of precursors into marl ($CaCO_3$) at high pH (since at 14:00 the alkalinity decreased precipitously). Throughout all these changes, dissolved organic carbon (DOC) showed only a slight variation. Welch and van Vliet (1985) interpreted these and similar results to show that ECP from photorespiration has a lower THMP than ECP from photosynthesis.

### 2.2.7 The removal of THMP

The present study is concerned with the removal of THMP from a hypertrophic lake by DAF. The author is unaware of any publications involving the use of DAF in the removal of THMP, although the process, together with PAC, is currently being used at the Schoemansville Plant. Other methods which have been used for removal of THMP will be discussed below. The removal of THM from chlorinated waters will not be covered as a separate section, although many of the techniques used for removal of precursors will also be effective in the removal of THMs. One technique for removal of THMs - aeration - will in general not be suitable for removal of the precursors. Three references on this subject are simply listed here for completeness: Umphres *et al* (1983); Roberts and Levy (1985); Bilello and Singley (1986).

### 2.2.7.1 Coagulation

Coagulation with metal salts and/or polyelectrolytes is probably the most popular and effective method for removing THMP. An early report by Stevens *et al* (1976) already noted that the effectiveness of granular activated carbon (GAC) in removing precursors was relatively short-lived, whereas conventional alum coagulation and sedimentation did remove most precursors from raw waters. Coagulation followed by direct filtration is also effective at removing THMP (Edzwald 1984).

Kavanaugh (1978) reviewed the optimum conditions thus far ascertained for removal of THMP by coagulation. Up to 90% of HA from the Ohio River could be removed with alum or Fe salts whereas only 60 % FA could similarly be removed; this difference was thought to be due to MW effects. Collins *et al* (1986) noted in this context that coagulation would be ineffective at removing organic matter of MW $<$ 500 - 1,000. Optimum pH values for the Ohio river were 5-6 for alum and 3-5 for Fe salts; in a different study (Contra Costa County Water District), optimum pH for alum treatment was slightly lower for TOC than for turbidity removal. In that case study, FA required approximately double the alum dose for 80% removal, compared to the dose needed for HA removal. Collins *et al* (1986) assert that the pH effects are due to the fact that humic substances contain acidic functional groups which impart a pH-related charge density. In their study, alum addition showed an increase in carboxylic acidity - hence higher charge density - in the hydrophobic fractions of the treated water. Furthermore, it appeared that the carboxylic content of humic substances is inversely related to the MW, hence humic substances with the highest content of acidic functional groups will be the most difficult to destabilize by alum coagulation. Hubel and Edzwald (1987) found classical types of coagulation behaviour with the use of alum at different pH levels: At pH 7.2 and 10 mg/ℓ alum dose, removal was by sweep floc effect due to precipitation of $Al(OH)_3$. At pH 5.5, an aluminate/humate precipitate was formed due to charge neutralization, underdose/optimum/overdose behaviour was observed, and the optimum dose was only 3 - 7.5 mg/ℓ. This process was particularly appropriate for low TOC waters; at higher TOC levels, more alum would be needed, leading to $Al(OH)_3$ precipitation.

Oliver and Lawrence (1979) observed that alum treatment was effective in removing 61% TOX, but only 34% TOC. In this case, the humic substances contributing to TOX were thought to occur as microcolloids, hence their efficient removal by alum. The selective removal of THMP from the DOC pool was also noted by Hoehn *et al* (1984) during studies with THMP produced partially by algal sources, by Collins *et al* (1986) when studying various water sources, and by El-Rehaili and Weber (1987) for intermediate and low MW fractions. Collins *et al* (1986) maintained that this selectivity was because hydrophobic compounds are more reactive in forming THM, and are also more likely to be removed in the clarification process. Chadik and Amy (1983) compared the effectiveness of alum and $FeCl_3$ in removing THMP, and found that on an equal dose basis (mg/ℓ), alum was more effective, but there was a higher maximum removal possible with $FeCl_3$ salts. Coagulation at lower pH levels was more effective, due to the presence of positively charged metal complexes. Similar results for pH effects were obtained by Hoehn *et al* (1984) and Knocke *et al* (1986). Interestingly, in Chadik and Amy's study, brominated haloforms were not reduced by coagulation in the same proportion as chloroform.

The effect of temperature on coagulation was investigated by Knocke *et al* (1986). Low temperature adversely effected turbidity removal by alum more than by $FeSO_4$, but TOC removal was more effected with $FeSO_4$ and low temperature. A low pH was still preferable. $FeSO_4$ was superior at removing the 1,000 - 10,000 MW component, whereas alum was more effective with the <1,000 MW fraction. These low MW fractions were the most affected by low temperatures. The authors also noted that at 2°C the specific yield was only 60 - 65 µgTHMP/mgTOC after 7d, compared with 140 - 150 µg/mg at 22°C.

The use of coagulants other than the traditional alum or ferric salts has been investigated by a number of researchers. Thurrott *et al* (1983) used various coagulants in combination with lime softening to remove THMP from a high hardness groundwater. Alum and $FeSO_4$ were similarly effective, but the most promising pilot plant results were obtained with 220 mg/ℓ lime, 5 mg/ℓ bentonite clay, and two different polymers at 20 mg/ℓ and 3.5 mg/ℓ respectively. Taylor *et al* (1984) reported on the use of magnesium carbonate for removing THMP. This process operates at pH >11. Alum was nevertheless found to be superior.

The most popular alternative (or aid) to metal salts is high MW organic polyelectrolytes. Amy and Chadik (1983) reported on the use of cationic polyelectrolytes as primary coagulants for removing THMP. They noted (as did Feige *et al* in 1980) that these polyelectrolytes themselves are THMPs, producing between 0.67 and 4.4 µg/mg. Amy and Chadik found that a maximum of 65% reduction in THMP from natural waters was possible, using 15 mg/ℓ of the polyelectrolyte, however the flocs thus formed were not amenable to settling, and had to be filtered. Hubel and Edzwald (1987) used jar tests to study THMP removal using polyelectrolytes as sole coagulants, as well as in conjunction with alum. Precipitation with polyelectrolytes alone exhibited charge neutralization behaviour. Dosages of between 8 and 150 mg/ℓ were required. When used as a coagulant aid (at 0.1 mg/ℓ), polyelectrolyte addition to alum did not improve organics removal. However when the cationic polymer was the prime coagulant (9 mg/ℓ), and alum the aid (30 mg/ℓ), lower doses of alum were required than when alum was used alone (50 mg/ℓ); furthermore sludge volumes were reduced.

### 2.2.7.2 Activated Carbon Adsorption

Activated carbon adsorption has for many years been the process of choice as a final step in the removal of soluble organics from waters, thus it is an obvious choice for removing THMPs. However, since coagulation is also effective, and usually less costly, activated carbon has more frequently been used to remove THMs themselves, and a review of this particular application will not be covered here.

Hoehn *et al* (1978) reported that powdered activated carbon (PAC) at doses of 20 - 100 mg/ℓ had been applied previous to their studies, and that only 50% THM reductions had been achieved. Their own research showed that 50 mg/ℓ would be the most effective dose, regardless of the point of application (ie the PAC would remove both THMP and THM), however that a far greater precursor reduction (85%) would be achieved by conventional coagulation/settling. The main reason for the low effectiveness of PAC was that the contact time required was far greater than that available during conventional water treatment. They also suggested that PAC probably operated (when applied after chlorination) by removing the residual chlorine, hence the halogenation reaction could not go to completion. They also proposed that prechlorination might still be an effective tool during water treatment, provided that dechlorination was practised after 30 minutes of reaction. This would allow disinfection or algae removal to occur without excessive development of THMs.

Chadik and Amy (1983) used PAC following coagulation of a number of different water sources, and they found a 5 - 33% increase in THMP removal. Similar results were reported by Taylor *et al* (1984). Chadik and Amy (1987) noted that equilibrium was not attained after a 4 hr contact period with PAC, thus leading to questions regarding its practical application. However, they did find that PAC could remove a broader spectrum of MWs than coagulation. They also quoted studies which showed that at lower pH, there was a lower charge on the activated carbon, hence better diffusion, as well as overall more effective adsorption.

The effect of precursor MW on adsorption was studied by El-Rehaili and Weber (1987). They found that there was a decrease in the extent of adsorption of a commercial HA with increasing MW. Since much of the TOC of this HA was of lower MW, at least 70% of the TOC had to be removed by AC to achieve a reduction of 20% of THMP, and these removals would be of the low to intermediate MW fractions. In contrast, with alum treatment, at 53% TOC removal, 85% and 69% of the intermediate and low MW fractions respectively were removed, but organics in the high MW fraction actually increased by 58%. Higher alum doses were needed to remove the high MW fraction, however this removal was really unnecessary since the higher MW fractions contributed very little to THMP concentrations.

#### 2.2.7.3 Ozonation

A study by Yamada *et al* (1986) found that ozone is ineffective at removing THMs by oxidation, although a certain degree of removal by gas stripping would occur. However some precursors could be removed by ozonation. These authors identified 2 groups of precursors. The first, for example HA and some aromatic compounds, had vigorously activating components such as hydroxy- or amino- groups on each molecule. These would consume less chlorine after preozonation. The second group, including citric acid, which contained deactivating or weakly activating components, would actually be converted into more active compounds by ozonation. Thus ozonation would increase their potential as THMP.

### 2.2.8 Non-volatile compounds

Although the emphasis of the present project is on the removal of THMs, which are volatile organics, they actually represent only a small fraction of the total chlorinated by-products (Rook 1980; Bruchet *et al* 1984), especially at lower pH (Miller and Uden 1983). Furthermore, some of the techniques for reducing THMPs or THMs involve the production of correspondingly higher concentrations of non-volatile chlorinated organics, ie (TOX minus THM). Since these non-volatile products may also involve health risks (Bull 1982; Johnson and Jensen 1986), it is appropriate to examine here the interactions between volatile and non-volatile chlorinated compounds.

A number of studies have shown that pH is the major variable influencing the relative concentrations of volatile and non-volatile chlorinated organics. The articles by Oliver (1978), and Miller and Uden (1983) have already been referred to in Section 2.6.1. with respect to pH effects; Wachter and Andelman (1985), included the effects of pH in their investigation of the chlorination of algal ECP (see Section 2.5). All showed that as pH was reduced, there was a shift to non-volatile chlorinated organics. Johnson & Jensen (1986) obtained similar results, but they also found that although higher pH levels favoured the production of $CHCl_3$, the non-purgeable organo-halides (NPTOX) were reduced by even greater amounts. They thus recommended that higher pH levels were preferable. In a recent study which examined the influence of bromide concurrently with pH on the chlorination of HA (Symons *et al* 1987), it was found that non-purgeable organochlorine (NPOCl) decreased with increasing pH to an extent which was dependent on the presence of bromides; suppression of NPOCl in the presence of bromide occurred especially at pH 9.2 and 10.7 after 3d at $Br >= 8.4$ µmol/ℓ. The amount of TOX formed was unaffected by the bromide concentration, but a change in composition occurred, with NPOBr being formed at high Br concentrations. However these compounds were unstable after 1 day.

Glaze *et al* (1980) examined two preconcentration methodologies for determining TOX concentrations: adsorption on to XAD ion exchange resin, or GAC. They found that non-volatile organohalides (ie after chlorination) were unadsorbed by XAD resins. This non-volatile component was thus non- polar, but a reason for this change in polarity could not be given.

MW distribution measurements were also carried out by Glaze *et al* (1980), and the interesting result obtained was that although THMFP increased with decreasing MW (in agreement with other studies previously mentioned), TOXFP was spread evenly through the MW range of (0.2 - 31.6)x$10^3$. In a more recent study, Bruchet *et al* (1984) found that 70% TOX had MW < 1,000, and only 2% >5,000. This higher MW fraction had a low reactivity to chlorine.

In terms of the actual composition of TOX, (and these included some low volatility compounds which were still amenable to GC), Miller and Uden (1983) found chlorophenols, chlorinated saturated and unsaturated aliphatic acids, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), chlorobenzoic acids, and chloral hydrate in their tests on soil derived HA. Both chlorine dose and pH influenced the distribution of these species. Low chlorine doses favoured DCAA and $CHCl_3$, and higher doses - thus more rigorous chlorination/oxidation - favoured TCAA formation. Similarly, higher pH favoured $CHCl_3$, whereas the stronger oxidizing conditions at low pH resulted in TCAA predominance. Chloral hydrate was stable under acidic conditions, but it degraded to $CHCl_3$ at higher pH. In studies with aquatic precursors found at various water treatment plants, Bruchet *et al* (1984) also detected aliphatic molecules (such as carboxylic acids), TCAA in relatively small concentrations, as well as more complex acids or organic chloramines. DCAA and TCAA, together with $\alpha$-chloropropionic acid, were also found by Christman et al (1980) in ether extracts of chlorinated lake- derived HA. Their reactions took place at pH 12, thus indicating that non- volatile products occur even at high pH levels.

Oliver (1983) observed that FA as well as algae could serve as precursors for dihaloacetonitriles (DHANs); at least one of these compounds, dichloro- acetonitrile, is mutagenic in bacterial assays. DHANs would tend to be produced at lower pH levels, due to hydrolysis at pH above neutral, and by algal species with higher N content (such as Anabaena). Relative molar concentrations of DHAN:THM ranged between 2% - 20% . A more recent study by Trehy *et al* (1986) suggested that since the formation potential of $CHCl_3$ was different to that of DHAN, these two compounds might have different precursors, with HA being the precursor for $CHCl_3$, and amino acids or other nitrogenous compounds being precursors for DHAN (as well as chloral).

### 2.2.9 Modelling and prediction

The objective of modelling of environmental processes is to obtain a better global understanding of the process by studying the behaviour and relationships of some of its constitutive parameters. Successful modelling would lead to prediction of the behaviour of the process, given values of the parameters which vary from the values used for calibration. In the case of THMs, successful modelling would yield equations based on surrogate parameters for THMPs as well as various environmental effects such as temperature and pH, and these equations would predict THM concentrations for a range of conditions.

Due to the complexity of the halogenation reactions, as discussed previously in a number of sections, modelling and prediction of THM production is unlikely to be successful, especially if the model is to be applicable over more than one water source, and the literature published to date tends to confirm this. Amy and co-workers have perhaps been the most prolific in terms of publications in this area (Engerholm and Amy, 1983; Morrow and Minear, 1987; Amy, Chadik and Chowdhury, 1987b; Amy, Minear and Cooper, 1987c). The first paper gave a regression equation for the formation of $CHCl_3$ from HA in "synthetic" water; the effects of TOC, Cl- dose, pH, temperature and reaction time were included. The second paper included the effect of bromide. The third paper used 1,090 data points from 9 natural waters to develop a new regression model, and in the process obtained what could be a useful surrogate parameter, UVxNPOC (referred to in Section 2.3). The final paper used 2 data sets from natural waters to calibrate and ascertain the validity of Morrow and Minear's model. In all cases the usefulness of these models would be confined to the conditions under which they were developed, and they would thus have very limited application. It was also clear that even under the specific conditions for each model, single THM values predicted from the measured parameters could be significantly different from the measured (true) values.

Urano *et al* (1983) developed an empirical rate equation for THM formation from HA. This rate was dependent on the log of reaction time, Cl-dose, and $OH^-$ ion concentration, and temperature effects could be described by the Arrhenius equation. Taylor *et al* (1984) developed a regression equation for THM formation after coagulation (and substantial precursor removal) by $MgCO_3$. The effects of the various parameters could be ranked as follows:

TOC > contact time > Cl-dose > Temperature > $OH^-$

Thus in this case, it was found that TOC would have to be reduced to <0.1 mg/ℓ by coagulation in order to meet THM standards in the final water, and ultimately chloramines, GAC filtration, and/or alum coagulation were necessary.

# CHAPTER 3

# ANALYTICAL METHODOLOGY

[Note: Apparatus used for jar tests, and all DAF tests, will be described in the appropriate chapters, ie. Chapters 4 and 5.]

## 3.1 Basic parameters used to characterise Hartbeespoort Dam.

The following parameters were measured according to the methodology given in Standard Methods (APHA *et al*, 1985): Alkalinity (#403), BOD (#507), Bromide (#405), COD (#508 C), SS (#209 C), and Turbidity (#214 A). Chlorophyll *a* was determined by 5-minute extraction of retained material on glass-fibre filters into 96% ethanol at 78°C, followed by spectrophotometric determination of concentration at 665 nm (Sartory, 1982). DOC was measured by UV oxidation of the sample, containing 0,25% $K_2S_2O_8$, in a silica tube, followed by IR analysis of the $CO_2$ gas released (van Steenderen and Lin, 1981). Phosphorus and TKN measurements were performed according to the methodology suggested by Technicon (1975). TOX was analysed by coulometric titration (van Steenderen, 1980). Where appropriate, 0,45$\mu$m filter papers (Nucleopore; 22mm dia; nitro-cellulose membrane) were used, and it was found necessary to rinse these with organic-free water as many as 10 times to remove all traces of organic residues.

## 3.2 Trihalomethane precursors and trihalomethane analyses.

### 3.2.1 Reagents and sample preparation for trihalomethane precursor formation.

Trihalomethane precursors were assessed by chlorinating the samples under standard conditions, then halting the chlorination reaction and analysing for THMs by gas chromatography (see Section 3.2.2).

Note that all sample bottles referred to below, ie. those used for the preparation of reagents as well as sample collection and sample/chlorine interaction, were brown glass. They were thoroughly cleaned with chromic acid, rinsed with organics-free water (either double-distilled or Milli Q (Millipore Corp, Bedford, MA, USA)) then baked at 250°C overnight to remove any traces of organics. Bottle caps contained teflon liners, or were twisted around aluminium-foil which had been placed over the open bottles. All sample reactions (for chlorine residual and THMP analysis) took place in headspace-free bottles.

Preparation of chlorine dosing solution (nominally 10,0 mg/mℓ).

Chlorine solutions (without added stabilizers) were obtained from Klipfontein Organic Products/National Chemical Products (Chloorkop, Tvl). These were nominally 7% solutions, and a volume **x** (calculated by equation 1 below, after a titration with sodium thiosulfate, but typically 35 mℓ), was added to a 230 mℓ bottle to create the chlorine dosing solution.

Titration: Add 1 mℓ chlorine solution to 24 mℓ distilled water
Titrate with 0,1N sodium thiosulfate (according to
Standard Methods Method #408 A) ( = **t1**)

Volume to be added: $\mathbf{x} = (230 \times 10)/(0{,}1 \times 35{,}45 \times \mathbf{t1})$ (1)

The actual strength of this dosing solution was assessed as follows:

Place 5 mℓ of the chlorine dosing solution into a 250 mℓ volumetric flask, and fill with chlorine-demand-free water (water from the Milli Q system was typically used).

Shake.

Take 50 mℓ of this sample, and titrate with 0,025N sodium thiosulfate in similar fashion to that used to obtain equation 1, but use 5 mℓ acetic acid and 1 mℓ starch.

If the titration yields **t2** mℓ, then:

$$\text{Strength} = (0,.025 \times 35,45 \times \mathbf{t2})/50 = \mathbf{S} \qquad (2)$$

<u>Volume of dosing solution used.</u>

The volume of chlorine dosing solution used for THMP analyses was dependent on the chlorine demand of the sample. This was established as follows:

Into a 230 mℓ bottle,
  place 5 mℓ phophate buffer (<u>Standard Methods</u> Method #408 C),
  5 mℓ chlorine dosing solution,
  then fill the remainder with sample.
Close and shake.
Store overnight at 25°C.

Titrate 50mℓ of the sample with 0,025N sodium thiosulfate as above. If the titration yields **t3**, then:

$$\text{Chlorine residual} = (0,025 \times 35,45 \times \mathbf{t3})/50 = \mathbf{R}\ (\text{mg/m}\ell) \qquad (3)$$

and
$$\text{Chlorine demand} = (50 - \mathbf{R} \times 230)/0,230 = \mathbf{C}\ (\text{mg/}\ell) \qquad (4)$$

(expected values would be 30 - 40 mg/ℓ)

Hence, volume of dosing solution, **V**, needed to yield a residual after THM formation of around 1 mg/ℓ would be:

$$\mathbf{V} = (\mathbf{C} \times 5 / \mathbf{D}) + 0,1\ \text{m}\ell \qquad (5)$$

where $\mathbf{D} = 5 \times \mathbf{S} \times 50 / 0,23$

Expected values of **V** would be around 0,8 - 1 mℓ.

Protocol for THMP analysis.

For any series of analyses where the basic character of the raw samples could be expected to remain constant, chlorine demand tests were performed as a preliminary step, and the chlorine dose would then be constant for all samples in this batch. Samples for THMP analysis were then treated as follows:

To a 230 mℓ bottle, add the following:
  5 mℓ phosphate buffer (as above)
  chlorine dosing solution (V from equation 5 above; typically 1 mℓ)
  fill to the top with sample.
Store in the dark for 24 hours at 20°C.

The chlorination reaction was quenched by adding 2 mℓ of sodium sulfite solution (Standard Methods Method #411 A (1985)).

Water blank samples were prepared by filling the bottle with MilliQ water instead of sample, and these served as a control for the overall procedure (the expectation was that no THMs would be detected after chlorination of these samples).

Reagent blanks were prepared as follows:
To a 25 mℓ bottle, add:
  12,5 mℓ chlorine dosing solution
  12,5 mℓ phosphate buffer
Store in the dark for 24 hours at 20°C.

Quench by carefully placing 10 mℓ of this reagent blank solution into a 230 mℓ bottle, then adding 2 mℓ sodium sulfite, and filling to the top with MilliQ water. This dilution process renders an effective reagent volume of 5 mℓ, to be closely similar to the reagent volume in the sample bottles.

The final THM results for any batch of samples were then adjusted by subtracting from them the THM concentrations obtained for the reagent blanks.

As a further check on the THMP preparation and analysis procedure, 3-5 dihydroxybenzoic acid (DHBA, also known as α-Resorcylic acid; MW 154,12; Fluka Cat. # 37600) was used either to spike existing samples, or as a separate sample. This substance is expected to yield approximately 0,7 moles of THM per mole of substrate used at pH 7 (Boyce and Hornig, 1983).

### 3.2.2 Trihalomethane analyses.

The majority of THM analyses were done according to the procedure outlined by van Rensburg *et al* (1978) and van Rensburg and Hassett (1982). The chlorinated organics were concentrated by liquid-liquid extraction into 53% diisopropyl ether and 47% hexane. Gas chromatographic separations occurred in a fused silica capillary column, and detection was by electron capture detector.

In some cases, THM analyses were performed by the laboratories of the Hydrological Research Institute of the Department of Water Affairs, using the purge-and-trap methodology outlined in Standard Methods Method #514 (1985).

# CHAPTER 4

# PRELIMINARY TESTS

## 4.1 Hartbeespoort Dam Water Quality.

The objective of this section is to provide a picture of the overall quality of water in the Hartbeespoort Dam, as it related to the eutrophic level, the algal concentration and species, and the concentration of organics as well as trihalomethane precursors (THMP). Sampling was performed regularly during the initial 1-year period of the study, then only when pilot plant or full-scale DAF experiments were performed.

### 4.1.1 Sampling over the 1-year period, 1986-87.

Samples were taken from Hartbeespoort Dam approximately bi-weekly, from October, 1986 - August, 1987. The station used was located near the inlet to the Schoemansville Water Treatment Plant, and samples were withdrawn 1 m below the water surface.

The following parameters are shown in Table 4.1: alkalinity, BOD, bromide, chlorophyll a, COD (total), DOC, pH, phosphorus (total), SS, TKN, total organohalogen precursors (TOXP) and turbidity. Total trihalomethane precursors (THMP) were not measured at that time because of initial difficulties with the method, the cost of the analysis, and the belief that TOXP was related to THMP. It was determined subsequently that TOXP could not be related to THMP in DAF and other experiments, especially those involved with the removal of THMP. Nevertheless, it is felt that TOXP gives an indication of the highest possible values of THMP in the Dam. These are considerably higher than the de facto standard for THMP in drinking water (0,418 mg/ℓ, compared to the standard of 0,1 mg/ℓ); thus the need for their removal is indicated.

The relatively high values of bromide (average 0,63 mg/ℓ) are responsible for concentrations of brominated-methanes of as much as 15% of the total THM concentrations measured after chlorination. This will be of interest when considering THMP removal strategies, and will be discussed further in Chapter 5.

Table 4.1 Summary Statistics for Hartbeespoort Dam, 1986/87

| Variable: | Alkalinity (mg/L as $CaCO_3$) | BOD (mg/L) | Bromide (mg/L) | Chlorophyll *a*(μ g/L) |
|---|---|---|---|---|
| Sample size | 24 | 9 | 23 | 19 |
| Average | 100,2 | 4,55 | 0,629 | 52,8 |
| Variance | 142,8 | 7,23 | 0,035 | 2 061,4 |
| Minimum | 71 | 1,65 | 0,394 | 6,01 |
| Maximum | 120 | 9 | 1,187 | 158,7 |
| Range | 49 | 7,35 | 0,793 | 152,7 |

| Variable: | COD (total) (mg/L) | DOC (mg/L) | pH | Phosphorus (total) (μ g/L) |
|---|---|---|---|---|
| Sample size | 19 | 17 | 22 | 23 |
| Average | 39,1 | 8,88 | 9,16 | 408 |
| Variance | 310 | 6,94 | 0,249 | 3 030 |
| Minimum | 11,7 | 6,6 | 8,4 | 265 |
| Maximum | 69,5 | 15,2 | 10,3 | 493 |
| Range | 57,8 | 8,6 | 1,9 | 222 |

| Variable: | SS (mg/L) | TKN (mg/L) | TOXP (μ g/L) | Turbidity (NTU) |
|---|---|---|---|---|
| Sample size | 21 | 23 | 12 | 23 |
| Average | 13,5 | 0,868 | 418 | 12,7 |
| Variance | 74,7 | 0,066 | 10,0 | 115,3 |
| Minimum | 4,9 | 0,57 | 238 | 4,3 |
| Maximum | 37,0 | 1,497 | 563 | 40 |
| Range | 32,1 | 0,97 | 325 | 35,7 |

### Table 4.2 Comparison of Water Quality of the Hartbeespoort Dam at Different Periods of the Study

| Parameter | Ave. 1986-87 | Feb. & March 1988 | Apr. 1988 | Feb. & March 1989 |
|---|---|---|---|---|
| Chlorophyll *a* (μ g/L) | 52,8 | 51,6 | 6,23 | 26,02 |
| DOC (mg/L) | 8,88 | 8,04 | 7,47 | 6,80 |
| Dominant algal species | *Microcystis aeruginosa* (+ *Oocystis spp.* in Oct, Nov & Dec) | *Microcystis aeruginosa* | *Microcystis aeruginosa* | *Cryptomonas spp*, Cyclotella meneghiniana |
| pH | 9,1 | 9,7 | 9,2 | 8,7 |
| THMP (μ g/L) | - | 311,6 | 241,6 | 179,7 |
| TKN (μ g/L) | 868 | 726 | 1 114 | 488 |
| Total phos (μ g/L) | 408 | 312 | 271 | 139 |
| TOXP (μ g/L) | 418 | - | - | - |
| Turbidity (NTU) | 12,7 | 11,7 | 2,7 | 3,0 |

The measured pH values are high (generally above 9), and consistent with vigorous algal activity. pH is also of interest because at high pH values, the performance of common coagulants, such as alum and ferric chloride, is somewhat compromised. Furthermore, the reaction rate between chlorine and organics to form THM is increased at elevated pH. Thus the high natural pH is both detrimental to the removal of precursors, and also results in a greater proportion of precursors being converted to THM.

DOC values are an indication of the overall organics concentration of the Dam: a relatively high average value of 8,87 mg/ℓ. It was also expected that there would be correlations between DOC, THMP, and TOHP. In fact, it was found here, as well as in other experiments (Chapter 5, and other trials over 24 hours, not reported herein), that there was little - if any - correlation between DOC, THMP, and/or TOHP. Thus the organics responsible for the formation of THM (ie the THMPs) are very specific, and probably mainly due to algal by-products. This relationship is pursued further in Chapter 5.

The dominant species during most of the year was Microcystis aeruginosa, however Oocystis spp. were also significant in the last three months of 1986. The literature review (Chapter 2) has indicated that Microcystis spp. and their extracellular products are expected to be active as THMP, but there has been no information about the relevant activity of Oocystis.

COD and BOD values (39,1 and 4,5 mg/ℓ respectively) are typical of raw waters with a certain amount of organic pollution. The relatively high ratio of the two (8,7) suggests that the source of much of the organics is biologically treated sewage, where most of the biodegradable component would have been removed. In fact, it is known that during dry months, up to 80% of the inflow to the Dam consists of treated sewage. However, the high concentrations of phosphorus (0,41 mg/ℓ) and TKN (0,86 mg/ℓ) are no doubt more responsible for the hypertrophic nature of the Dam during the period studied. This hypertrophy is well reflected in the high values of chlorophyll *a* concentration (52,8 mg/m$^3$) and turbidity (12,7 NTU).

### 4.1.2 Data obtained during pilot plant and full-scale testing.

Data on the water quality of the Hartbeespoort Dam, collected during periods of testing of the pilot- and full-scale DAF units, are shown in Table 4.2. Average values taken from Table 4.1 are also shown for comparison. In some cases these parameters were actual measurements of the plant influent (such as DOC, pH, THMP and turbidity), whereas in others the data were collected close to the times of experimentation, but the measurements were part of another project involving the Dam.

In March, 1988, the Dam overflowed, and most of the algal scum was lost. The downward trend of virtually all parameters in Table 4.2 reflects this loss of organic material, and in fact even 1 year later (February and March, 1989), concentrations of organics (such as chlorophyll *a*, DOC, THMP, phosphorus and TKN), as well as turbidity, had not regained their original high values. The dominant algal species had also changed by 1989 (from Microcystis to Cryptomonas and Cyclotella spp). This overall reduction in organics concentrations in the raw water would likely have an effect on the absolute removals of THMPs in the DAF process, however the relative (or percentage) removals may not be as drastically effected, and the statistical analyses performed in Chapter 5 did not (and could not) account for these absolute changes.

## 4.2 Jar Tests.

Jar tests were performed with alum, polymer, and bentonite, in various combinations of dosages, to assess the extent of turbidity and THMP removal by standard settling. This would then act as a comparison to results obtained by DAF.

### 4.2.1 Materials and methods.

The jar test apparatus was the same as that used for the batch DAF tests (see Section 4.3 below), and is shown in Figure 4.1. Six plexiglass jars of 2 ℓ capacity, and 440 mm high, with conical bottoms, were placed beneath a standard Phipps and Bird 6-place stirring apparatus. The experimental protocol was as follows:

Pour raw samples into each cylinder.

Set stirrer at 100 rpm.

Add chemicals in the following order, where appropriate: Bentonite, alum, polymer.

Continue high-speed mixing for 3 min.

Reduce speed to 35 rpm, and maintain for 20 min.

Switch off stirrers, and allow to settle for 30 min.

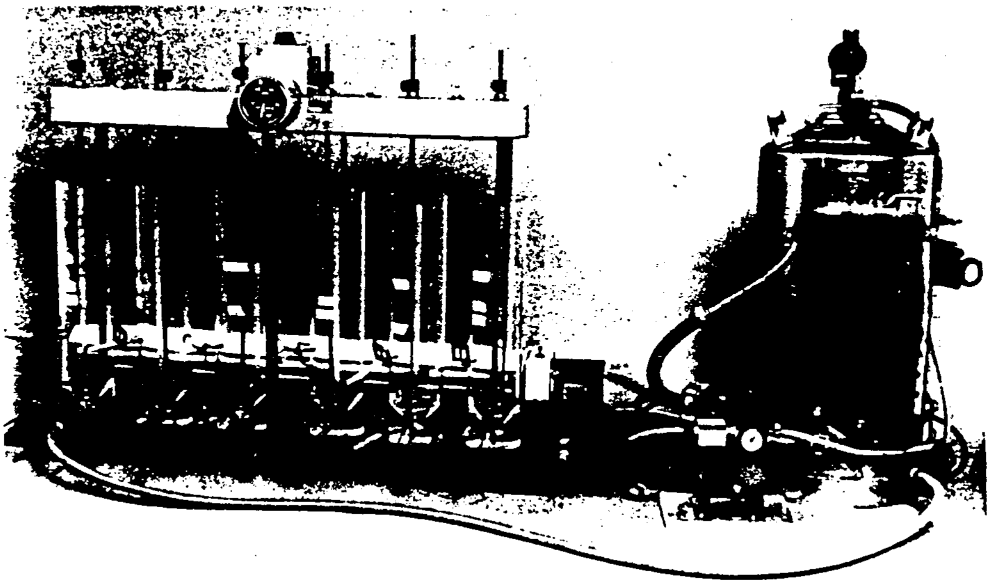


Figure 4.1: Photograph of Jar Test/Batch DAF Apparatus

Alum was industrial grade, with 1 g/ℓ alum powder containing 65 mg/ℓ $Al^{+++}$ and 2,3 mg/ℓ $Fe^{++}$ (and/or $^{+++}$) (measured by atomic absorption spectroscopy). The polymer used was Percol 757, also known as Zetag 57 (Allied Colloids), which is a cationic polyelectrolyte (mainly polyacrylamide), highly charged, and 10-12x$10^6$ molecular weight (MW). It was prepared as a 0.5% stock solution, then diluted ten times further immediately before being added by syringe to the cylinders. Bentonite was technical grade bentonite powder.

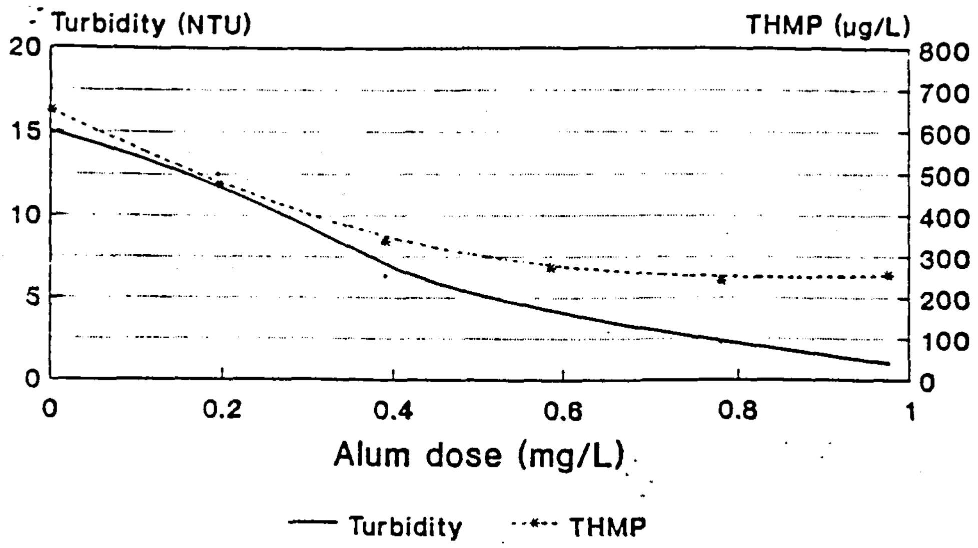
### 4.2.2 Results.

The results of jar tests for alum and polymer separately are shown in Figures 4.2 and 4.3 respectively. They indicate that although polymer alone is effective in reducing turbidity by as much as 81,3 % (at the relatively high - and costly - dose of 4 mg/ℓ), it is ineffective at reducing THMP concentrations. Alum, on the other hand, is effective both for turbidity reduction (maximum 93,8 %), and THM (67,5 %). The optimum dose (as $Al^{+++}$) was 7,8 mg/ℓ for turbidity reduction, and 9,8 mg/ℓ for THMP reduction. A slight overdosing effect for turbidity reduction was observed at the highest alum dose tested.

Using a range of doses about the optimum, a series of tests was done with various combinations of alum, polymer, and bentonite. Results of these are given in Table 4.3 (a - d). The highest removal of turbidity was 98,1 %, ( 0,5 mg/ℓ polymer; 7,3 mg/ℓ alum), while for THMP the highest removal achieved equalled that obtained with alum alone, i.e. 67,5 % . Although within groups of tests, bentonite appeared to improve both turbidity and THMP removal slightly, none of these removals exceeded that achieved when bentonite was omitted. Thus the use of this weighting and/or nucleating agent is not considered worthwhile.

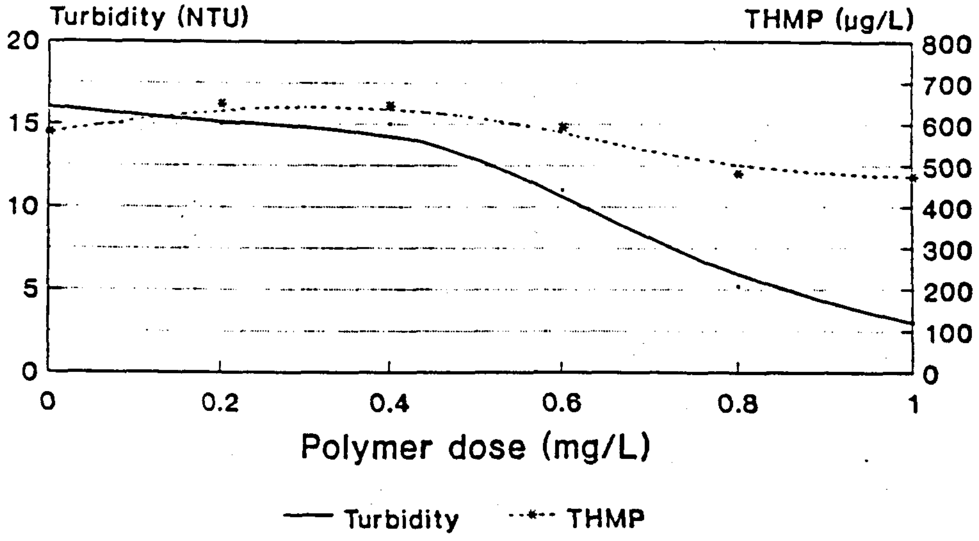
The overall optimum chemical dosages for combined turbidity and THMP removal were 1,0 mg/ℓ polymer and 7,3 mg/ℓ $Al^{+++}$. It should be noted that at this polymer dose, THMP removal was slightly less than without the polymer, and this is possibly due to a small contribution to THMP by the polymer itself.

Figure 4.2 Jar Tests.
Turbidity and THMP removal
for alum dose only.



Raw water pH 9,37; Raw SS 12 mg/L

Figure 4.3 Jar Tests.
Turbidity and THMP removal
for polymer dose only.



Raw water pH 9,37; Raw SS 12 mg/L

## Table 4.3 Summary of Jar Tests

### A) Turbidity removal (%) using alum and polymer

| Polymer dose (mg/L) | Alum dose (mg/L) | | |
|---|---|---|---|
| | 75 | 113 | 150 |
| 0,5 | 83,1 | 98,1 | 96,9 |
| 1,0 | 97,2 | 97,5 | 94,9 |

### B) Turbidity removal (%) using alum, polymer and bentonite

| | Alum dose (mg/L) | | | | | |
|---|---|---|---|---|---|---|
| | 113 | | | 150 | | |
| Polymer dose (mg/L) | Bentonite dose (mg/L) | | | | | |
| | 20 | 40 | 60 | 20 | 40 | 60 |
| 0,5 | 83,1 | 90,8 | 90,0 | Not done | | |
| 0,75 | Not done | | | 92,3 | 94,6 | 95,6 |

C) THMP removal (%) using alum and polymer

| Polymer dose (mg/L) | Alum dose (mg/L) 75 | 113 | 150 |
|---|---|---|---|
| 0,5 | 50,5 | 59,5 | 61,7 |
| 1,0 | 56,7 | 61,4 | 63,0 |

D) THMP removal (%) using alum, polymer and bentonite

| | Alum dose (mg/L) | | | | | |
|---|---|---|---|---|---|---|
| | 113 | | | 150 | | |
| Polymer dose (mg/L) | Bentonite dose (mg/L) | | | | | |
| | 20 | 40 | 60 | 20 | 40 | 60 |
| 0,5 | 56,5 | 57,4 | 57,9 | Not done | | |
| 0,75 | Not done | | | 66,5 | 67,5 | 66,9 |

Jan. 28, 1987

## 4.3 Batch DAF Tests.

The major sets of batch DAF tests, the results of which were employed in selecting the parameters for the pilot plant (Chapter 5), were done using factorial experimental techniques. However, preliminary tests were done to assess individually the effects of alum dose, polymer choice and dose, bentonite dose, and pH.

### 4.3.1 Materials and methods.

As indicated previously, the batch DAF apparatus consisted of six 440 mm high plexiglass cylinders with conical bases, placed below a Phipps & Bird stirring apparatus with lengthened stirrers (see Figure 4.1). Each cylinder had a drain line (closed with hosecock clamps) and a recycle fill line (with rapid disconnect fittings and needle valve) at the base, and a sampling line approximately 150 mm from the base (which was also closed with a hosecock clamp). During a typical experiment, each cylinder would be filled with sample (leaving enough volume at the top for the addition of pressurized liquid) and the appropriate chemical dose. Rapid and slow mix sequences were similar to the jar tests (Section 4.2.1). After wasting a small volume of pressurized liquid via a 7th quick disconnect fitting which lead to a drain, pressurized liquid was then quickly added to each cylinder in turn, by attaching the hose from the pressure vessel to the quick disconnect fitting at the base of each cylinder, and cracking open the needle valve such that bubble production was optimized. Pressure in the pressure vessel (40ℓ capacity and initially filled approximately 2/3 rds full) was maintained at 350 kPa gauge (equivalent to a local absolute pressure of 5 atm) via a pressurized air line. The vessel itself was half filled with 20 mm dia. Raschig rings, randomly scattered, and liquid was recycled continuously via a 0,25 kw pump (not shown in the figure) to maintain a high level of saturation (measured at approximately 80%). A rise time under quiescent conditions of 30 minutes was allowed before samples were taken from the sampling line (a few mℓ of initial sample was wasted).

The alum, bentonite, and polymer Percol 757 used for the DAF tests have been described in Section 4.2.2 above. Two other polymers were assessed: Anionic Percol

156 (also known as Magnafloc 156), which is a high MW (10 - 12 x $10^6$) polyacrylamide, and nonionic Percol 351 (Magnafloc 351), which is also a polyacrylamide of high MW and zero effective charge. The polymers were prepared as described previously.

### 4.3.2 Preliminary tests.

Although in batch tests, the source of pressurized liquid is generally not recycle, but tap water, the term "recycle ratio" will be used here for convenience.

The results of tests to ascertain the recycle ratio to be used are shown in Table 4.4. No chemicals were added at this point, and only turbidity was measured. The results indicate that no effective removals would occur without chemical addition, also that changing recycle ratios had no marked effect. Further tests with constant chemical doses and varying recycle ratios should have been done, but it was decided to use only the 12% recycle henceforth. This was known to be a common level in full-scale tests, even though under the present circumstances, with the low SS concentrations of around 8,0 mg/ℓ (excluding any hydroxide precipitates), the air:solids ratio was approximately 0,9 mg/mg. Furthermore, it would be easier to maintain reproducibility with the slightly higher recycle flows, and it was felt that the 12% level would never be a limiting performance factor.

Tests with the three polymers indicated that only the cationic polymer (Percol 757) would be effective on its own, although it is possible that the anionic or nonionic polymers might be effective as coagulant aids in conjunction with alum. Results for the two discarded polymers are not given herein, but those for alum and Percol 757 (used separately) are shown in Figures 4.4 and 4.5 respectively. It is clear that both are effective at removing turbidity and suspended solids (SS), with optimum doses around 100 mg/ℓ for alum and 0,6 mg/ℓ for Percol 757.

Various doses of bentonite, together with 0,6 mg/ℓ of Percol 757 were tested to determine whether the bentonite would have a positive nucleating effect. The results shown in Table 4.4 indicate that, if anything, the addition of bentonite would have a

## Table 4.4

### Percentage Removals for Various Recycle Ratios and Bentonite Doses

| Recycle Ratios (%) | Turbidity[1] Removal (%) | Bentonite[3] Doses (mg/L) | % Removal[1] Turb. | SS |
|---|---|---|---|---|
| 2 | 0,5 | 0 | 71,3 | 82,5 |
| 4 | -1,5 | 20 | 77,5 | 72,5 |
| 6 | -3,62 | 40 | 78,8 | 70,0 |
| 8 | -1,88 | 60 | 75,0 | 81,3 |
| 10 | -4,13 | 80 | 75,0 | 71,3 |
| 12[2] | -3,63 | 100 | 75,0 | 55,0 |

Notes

1. All values corrected for dilution.
2. A recycle ratio of 12% corresponds approximately to an air:solids ratio of 0,89 mg/mg.
3. Percol 757 dose: 0,6 mg/L.

Figure 4.4

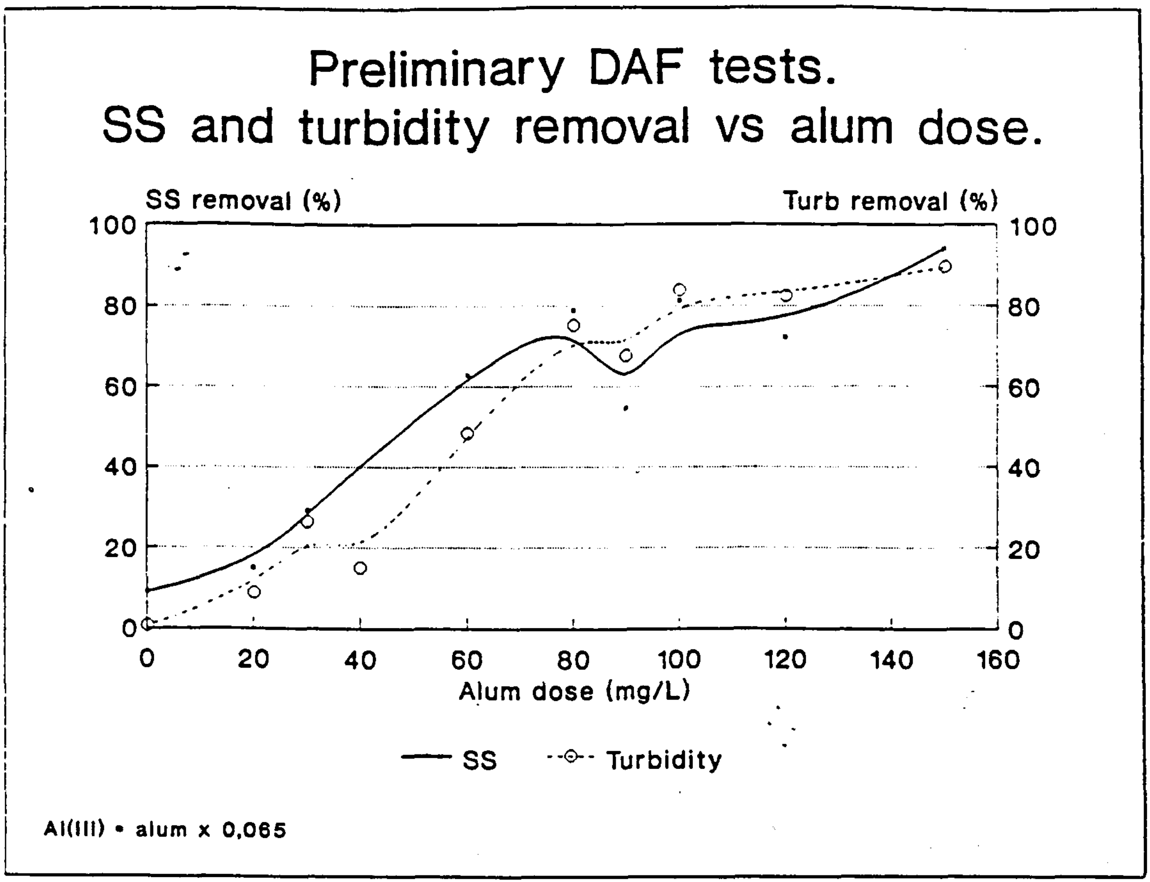
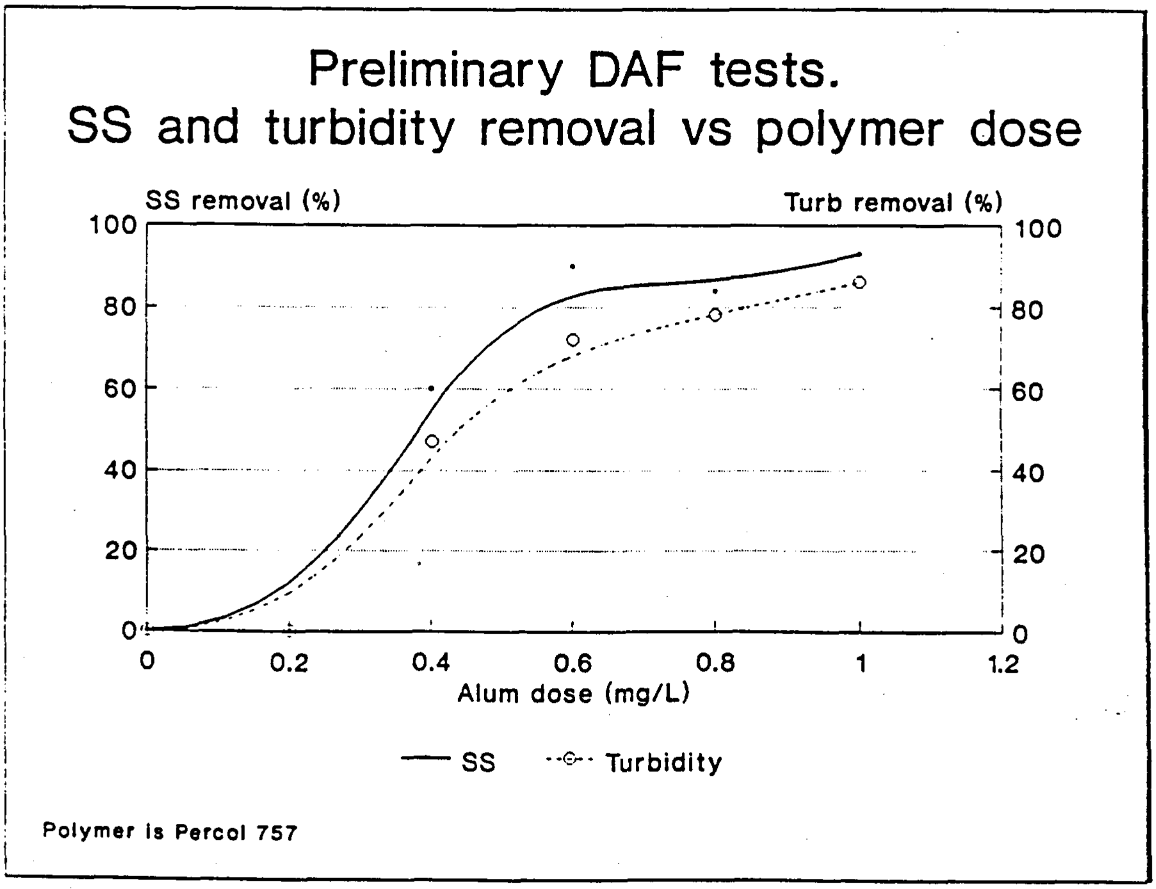


Figure 4.5



negative effect on turbidity and SS removal, and thus likely on THMP removal too.

The final preliminary DAF tests aimed at establishing whether pH might be a significant factor in removal of THMP, as well as the other parameters noted above. Results are given in Table 4.5. It is seen that in virtually every case, a lowering of the pH from about 8,8 to 6,0 would improve THMP removal. Unfortunately, it was only subsequently realised that this pH lowering might effect an improvement in THMP removal not because of any effects during the DAF process, but because of a slower and less extensive reaction rate between chlorine and the precursors at a lower pH. This potential interference in the interpretation of the results was removed by subsequently using the buffering procedure referred to in Section 3.2.1. However it is clear that a reduction in pH also improves turbidity, SS and DOC removal, thus it must have some positive impact on the flocculation process.

An interesting result in Table 4.5 is that the presence of polymer can result in an increase (negative removal) of THMP as well as DOC. This effect has been noted in the literature, and in the case of DOC, is quite to be expected. Thus the polymer itself is shown to be a THM precursor, and its use will have to be well justified.

### 4.3.3. $2^5$ factorial tests.

For these and subsequent $2^n$ factorial experiments, the "Statgraphics" computer package program (STSC, 1988) was used, since it contains a section both for the design and statistical analysis of $2^n$ factorial experiments. These experiments enable one to assess the individual and interactive impact of n variables, each at 2 levels. It is thus equivalent to a screening process.

## Table 4.5

### Percentage Removals for Various pH Values(1)

| | 0,6 mg/L Percol 757 | | | | 0,6 mg/L Percol 757<br>40 mg/L Bentonite | | | | 40 mg/L Alum(3) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Turb | SS | DOC | THMP | Turb | SS | DOC | THMP | Turb | SS | DOC | THMP |
| Natural pH (8,8)(2) | 68,8 | 61,3 | -30,0 | -28,7 | 71,3 | 63,8 | -30,0 | 2,5 | 60,0 | 48,8 | 0 | -3,0 |
| pH 6,0 | 80,0 | 76,3 | -20,0 | 11,0 | 73,0 | 63,8 | -20,0 | 1,3 | 83,8 | 83,8 | 18,5 | 19,8 |

**Notes:**

1. All values corrected for dilution
2. Alum addition would have reduced the "natural" pH slightly
3. Alum dose of 40 mg/ℓ corresponds to 3,6 mg/ℓ as $A1^{+++}$
4. Recycle ratio was 12% (A:S ~ 0,9 mg/mg).

The variables and their levels were chosen as follows:

| | Symbol | Low level | High level |
|---|---|---|---|
| Recycle ratio (%) | a | 6,4 | 12,8 |
| Alum dose (mg/ℓ) | b | 0 | 100 |
| Polymer dose (mg/ℓ) | c | 0 | 0,6 |
| Bentonite dose (mg/ℓ) | d | 0 | 60 |
| pH | e | 6 | ~9(natural) |

The results for these factorial experiments are shown in Table 4.6 and Figure 4.6. The table shows the factor effects for the main effects and all 2-factor interactions, as well as the average value for four of the measured parameters (i.e. SS, turbidity, TOC, and [THMP - chloroform]). Unfortunately, due to analytical errors, reliable chloroform measurements were not available, hence the absence of this component from the THMP result. The values given for the main effects and interactions in Table 4.6 are actually the deviations from the average. In general, therefore, negative deviations for the main effects, and positive deviations for the 2-factor interactions (negative x negative), would be desirable. Only "large" deviations would be of interest, as smaller ones could be due to experimental error and changes in the raw samples over the 4 different days of the experiments. These "large" deviations, i.e. statistically significant ones, are indicated in Figure 4.6 (a-d) as those effects which are clearly offset from the linear cumulative probability plots. (Note that according to the procedure used in the "Statgraphics" program, nonsignificant effects would tend to fall along a straight line passing through the Effects = 0 location.)

The following effects are thus shown to be significant:

- SS : Alum (-8,83); polymer (-6,97); alum x polymer (+7,04)
- Turbidity : Alum (-7,03); polymer (-5,18); alum x polymer (+4.93)
- DOC : Alum (-2,55); polymer (+0,97); recycle x alum x polymer x bentonite (+2,0)

Table 4.6

## Factor effects for $2^5$ factorial batch DAF experiments (main effects and 2-factor interactions only)

| Factor | SS | Turbidity | DOC | THMP(Excluding chloroform) |
|---|---|---|---|---|
| Average | 6.48 | 4.85 | 6.74 | 183 |
| A | 0.442 | -0.408 | 0.088 | 0.25 |
| B | -8.83 | -7.03 | -2.55 | -41.3 |
| AB | 0.906 | 0.683 | -0.636 | -9.38 |
| C | -6.97 | -5.18 | 0.971 | 7 |
| AC | 0.604 | 0.531 | 0.058 | 7.63 |
| BC | 7.04 | 4.93 | 0.607 | 26.9 |
| D | 3.39 | 0.558 | 0.213 | 4.5 |
| AD | -0.051 | 0.996 | -0.019 | 1.38 |
| BD | -3.35 | -0.13 | 0.254 | -19.6 |
| CD | -4.09 | -0.706 | 0.098 | 1.38 |
| E | -1.81 | -0.749 | 0.448 | 40 |
| AE | -1.34 | -0.4 | 0.216 | 23.4 |
| BE | 0.819 | 0.789 | 0.309 | -6.63 |
| CE | 1.69 | 1.17 | -0.179 | -7.88 |
| DE | -2.43 | -0.935 | 0.196 | 8.38 |

Notes: A = recycle ratio
B = alum
C = polymer
D = bentonite
E = pH

Figure 4.6

Normal Probability Plot

a) Suspended solids

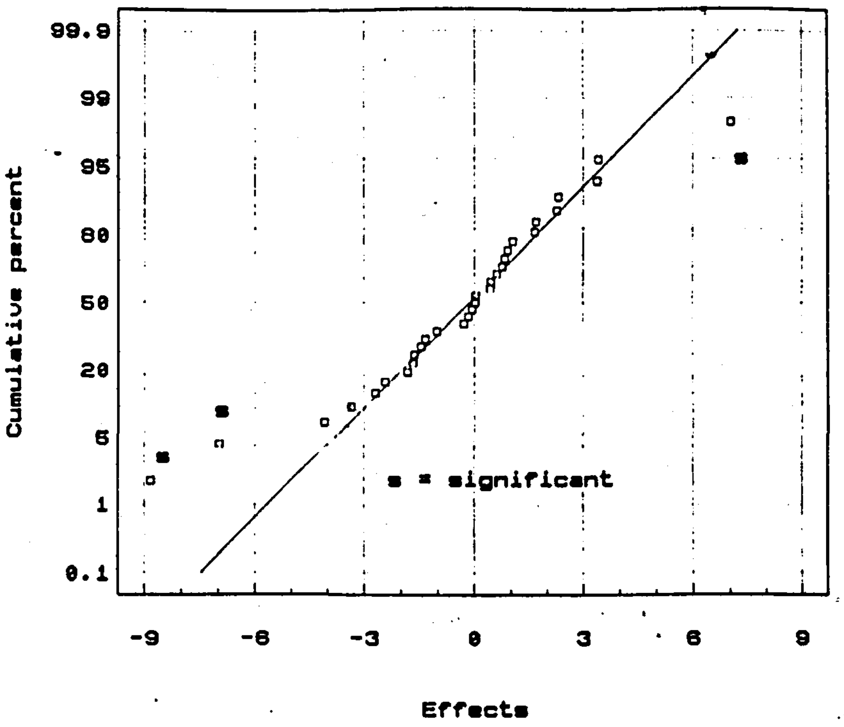


Figure 4.6

Normal Probability Plot

b) Turbidity

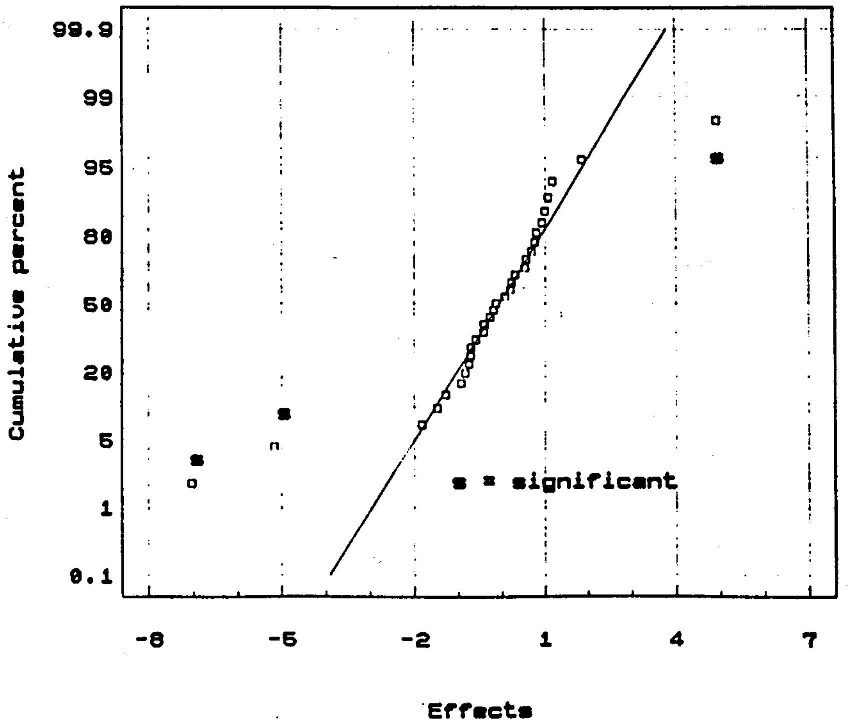


Figure 4.6

Normal Probability Plot

c) DOC

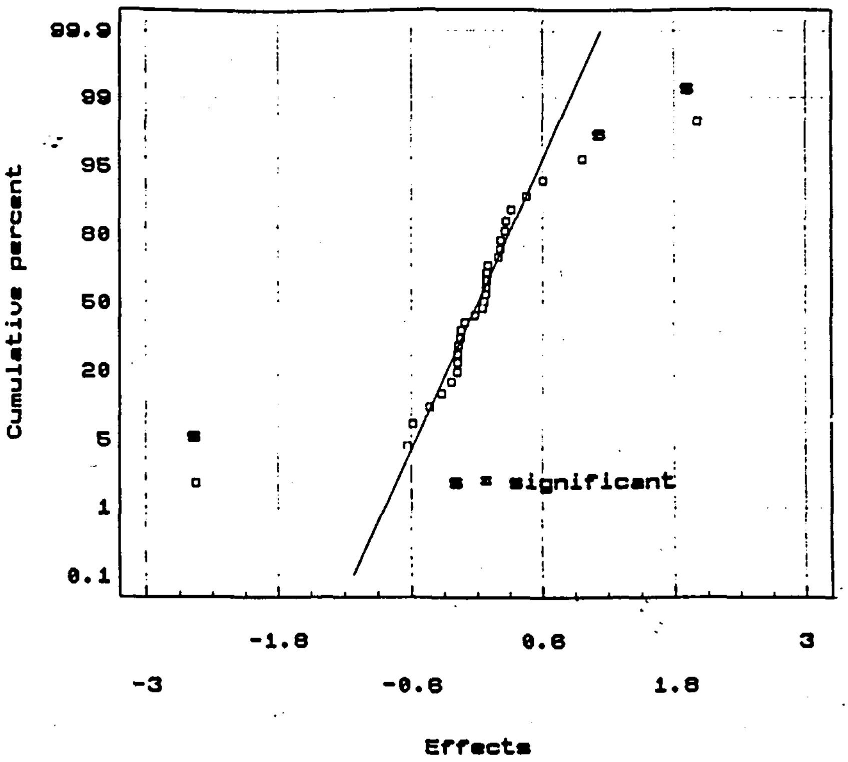
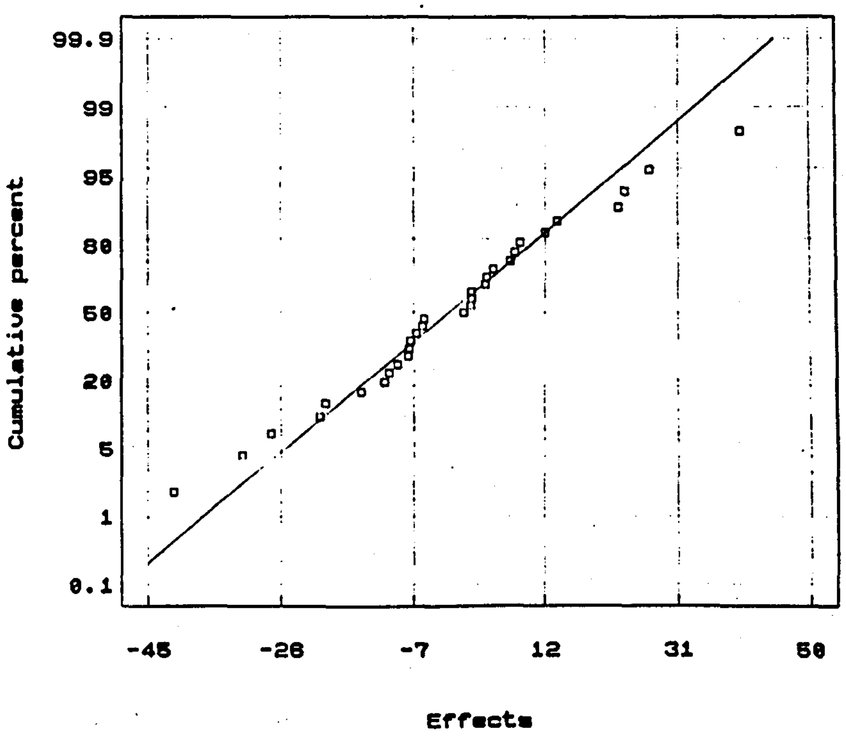


Figure 4.6

Normal Probability Plot

d) THMP



The positive value for the effect of polymer on DOC is undesirable (but in agreement with previous results), and the 4-factor interaction for the DOC is questionable as a real effect and is not shown in Table 4.6. There was no significant effect of any parameter on [THMP-chloroform], but the high negative value for alum (-41,25) and positive value for pH (+40) would indicate the desirability of reducing the pH to a lower value.

Thus, the final conclusions drawn from the $2^5$ factorial experiments are that alum, polymer and pH should be investigated further. Perhaps a range of doses around the highest used thus far for alum and polymer, and around the lowest for pH, should be studied. The resulting set of $3^3$ factorial experiments is described below.

### 4.3.4. $3^3$ factorial tests.

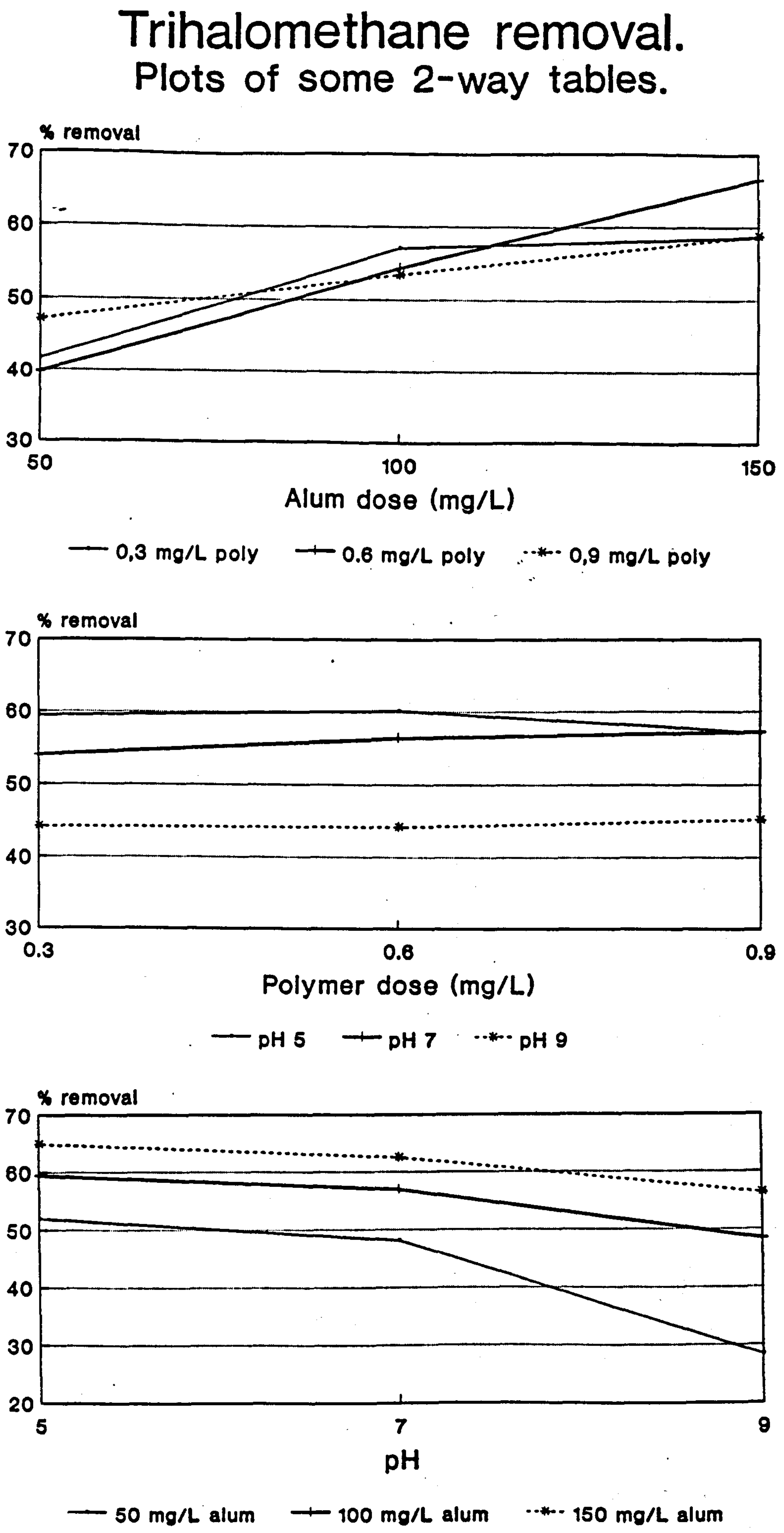
The batch factorial experiments done in this set involved three factors, each at three levels:

| | Low | Medium | High |
|---|---|---|---|
| Alum (mg/ℓ) | 50 | 100 | 150 |
| Polymer (mg/ℓ) | 0,3 | 0,6 | 0,9 |
| pH | 5 | 7 | ~9 (ie. natural pH) |

Computer analysis was not available in this case, and the results are thus presented in Table 4.7 as conventional analysis of variance (ANOVA) for the parameters "Percent Turbidity Removal" and "Percent THMP Removal" (Cochran and Cox, 1957).

The "blocks" effect indicates the effect of the variation of the raw sample quality on different days; for both parameters this effect was significant (as shown by the "F" ratio higher than "$F_{crit.5\%}$"). This result shows the desirability of statistically removing the (unwanted) effect of day-to-day variations in raw sample quality. Note that this effect was significant even though percentage parameter removals, rather than, say, final turbidity of THMP, were tested.

Figure 4.7


Trihalomethane removal.
Plots of some 2-way tables.
% removal
70
60
50
40
30
50
100
150
Alum dose (mg/L)
0,3 mg/L poly
0.6 mg/L poly
0,9 mg/L poly
% removal
70
60
50
40
30
0.3
0.6
0.9
Polymer dose (mg/L)
pH 5
pH 7
pH 9
% removal
70
60
50
40
30
20
5
7
9
pH
50 mg/L alum
100 mg/L alum
150 mg/L alum

Results from two-way tables for the $3^3$ factorial experiments (for THMP removal only) are plotted in Figure 4.7. The two-way tables show results for the effects of two parameters, averaged over the three experiments when the third factor was at each of its 3 values. The graphs are thus indicative, but do not give statistical information. As shown in Figure 4.7, alum and pH have the major effects, and both higher alum doses and lower pH values are desirable in obtaining high percentage THMP removals. Polymer dose has no clear effect.

The ANOVAs given in Table 4.7 show that only alum was significant for turbidity removal, and that alum and pH were significant for THMP removal. It should be noted that these conclusions apply only to the range of values tested. Thus polymer may still be desirable (as concluded previously), but doses above 0,3 mg/ℓ would not improve matters significantly.

As a result of these and previous batch DAF tests, pilot plant experiments were planned which would allow variation of alum and polymer doses, as well as pH, in the ranges suggested by the batch tests. The pilot plant experiments are discussed in the following chapter.

One further outcome from the $3^3$ factorial batch DAF tests is shown in Table 4.8. This is a correlation matrix for turbidity, % turbidity removal, DOC, TOXP, THMP, and % THMP removal. No useful correlations between these parameters were found. In particular, there was no relationship between THMP, DOC, and TOXP. This is unfortunate, because the analytical costs of DOC and TOXP are considerably lower than those for THMP. The lack of correlation also implies that the precursors for THMP production are complex and specific, and not well explained by general, "global" measures such as DOC or TOXP.

Table 4.7

## $3^3$ Batch DAF Experiments

## Analysis of Variance for Turbidity Removal

| SOURCE | df | SS | MS | F RATIO | $F_{CRIT, 5\%}$ |
|---|---|---|---|---|---|
| Main Effects | | | | | |
| Blocks | 2 | 176,5 | 88,25 | 8,66 | 5,14 |
| Alum | 2 | 198,1 | 99,05 | 9,72 | |
| Polymer | 2 | 13,56 | 6,78 | 0,66 | |
| pH | 2 | 13,87 | 6,94 | 0,68 | |
| Interactions | | | | | |
| Alum/polymer | 4 | 85,74 | 21,43 | 2,10 | 4,53 |
| Alum/pH | 4 | 55,67 | 13,92 | 1,37 | |
| Polymer/pH | 4 | 33,07 | 8,27 | 0,81 | |
| ERROR (BY SUBTRACTION) | 6 | 61,14 | 10,19 | | |
| TOTAL | 26 | 637,65 | | | |

## $3^3$ Batch DAF Experiments

## Analysis of Variance for THMP Removal

| SOURCE | df | SS | MS | F RATIO | $F_{CRIT, 5\%}$ |
|---|---|---|---|---|---|
| Main Effects | | | | | |
| Blocks | 2 | 613,14 | 306,57 | 32,67 | 5,14 |
| Alum | 2 | 1571,05 | 785,53 | 83,72 | |
| Polymer | 2 | 5,027 | 2,51 | 0,267 | |
| pH | 2 | 1032,03 | 516,01 | 54,99 | |
| Interactions | | | | | |
| Alum/polymer | 2 | 222,82 | 55,71 | 5,94 | 4,53 |
| Alum/pH | 4 | 233,28 | 58,32 | 6,22 | |
| Polymer/pH | 4 | 28,35 | 7,09 | 0,756 | |
| ERROR (BY SUBTRACTION) | 6 | 56,30 | | | |
| TOTAL | 26 | 3762 | | | |

Note:

df = degrees of freedom

SS = sum of squares

MS = mean square
= SS/df

F ratio = MS/ERROR MS

## Table 4.8

## Correlation Matrix for $3^3$ Batch DAF Factorial Experiments

| | Turbidity | Turbidity Removal | DOC | TOXP | THMP | THMP Removal |
|---|---|---|---|---|---|---|
| Turbidity | 1,00 | -6,35 | 0,353 | -0,159 | 0,596 | -0,527 |
| Turb. Rem. | -0,635 | 1,00 | -0,436 | -0,212 | -0,496 | 0,653 |
| DOC | 0,353 | -0,436 | 1,00 | 0,237 | 0,267 | -0,355 |
| TOXP | -0,159 | -0,212 | 0,237 | 1,00 | -0,400 | -0,0915 |
| THMP | 0,596 | -0,496 | 0,267 | -0,400 | 1,00 | -8,28 |
| THMP. Rem. | -0,527 | 0,653 | -0,355 | -0,091 | -0,828 | 1,00 |

# CHAPTER 5

# PILOT AND FULL-SCALE TESTS

## 5.1 Introduction.

A dissolved air flotation (DAF) pilot plant from the Division of Water Technology, CSIR, Pretoria, was modified for this trial and set up at the Schoemansville Water Treatment Plant on the banks of the Hartbeespoort Dam. This location was chosen because the full-scale plant itself employed DAF as the solids separation process, ahead of pressure filtration. Thus the two plants could be run in parallel, and various operating conditions compared.

## 5.2 Methods and materials.

### 5.2.1 Pilot plant setup

The pilot plant DAF unit is shown diagrammatically in Figures 5.1 and 5.2, and a photograph of the setup is given in Figure 5.3. The system comprised the following units: A feed pump[1] pumped raw water from the dam into a reservoir, at a rate slightly exceeding the 6,2 ℓ/min chosen for the tests. From this reservoir, a second pump[2] set at 6,2 ℓ/min, pumped the feed to the top of a 6ℓ rapid-mix tank, whence it flowed by gravity through a 40ℓ slow-mix tank, and into the top of the DAF tank itself. The rapid mixer[3] rotated at above 30 rpm, and provided a detention time of ~1 min. The rotation speed of the slow mixer[4] was 6 rpm, and the detention time in this unit was 6,5 min.

The DAF tank consisted of an additional baffled flocculation section, followed by the flotation section of area 0,068 m$^2$. Recycle liquid was pumped[5] at a rate of 0,62 ℓ/min (10% inflow) via a pressure saturation tank half filled with small plastic rings. This tank had an approximate volume of 58 ℓ (but since it was operated at 2/3rds full, this corresponded to a detention time of 5,7 min), and the level was controlled by means of a level controller[6]. At an operating pressure of 400 KPa, the approximate air to solids ratio (A:S), using a value of 76% saturation from previous tests, was 0,33. Downflow velocity in the DAF tank was calculated to be 6.02 m/h, including recycle flow.

**Figure 5.1:** **Schematic of DAF Pilot Plant**

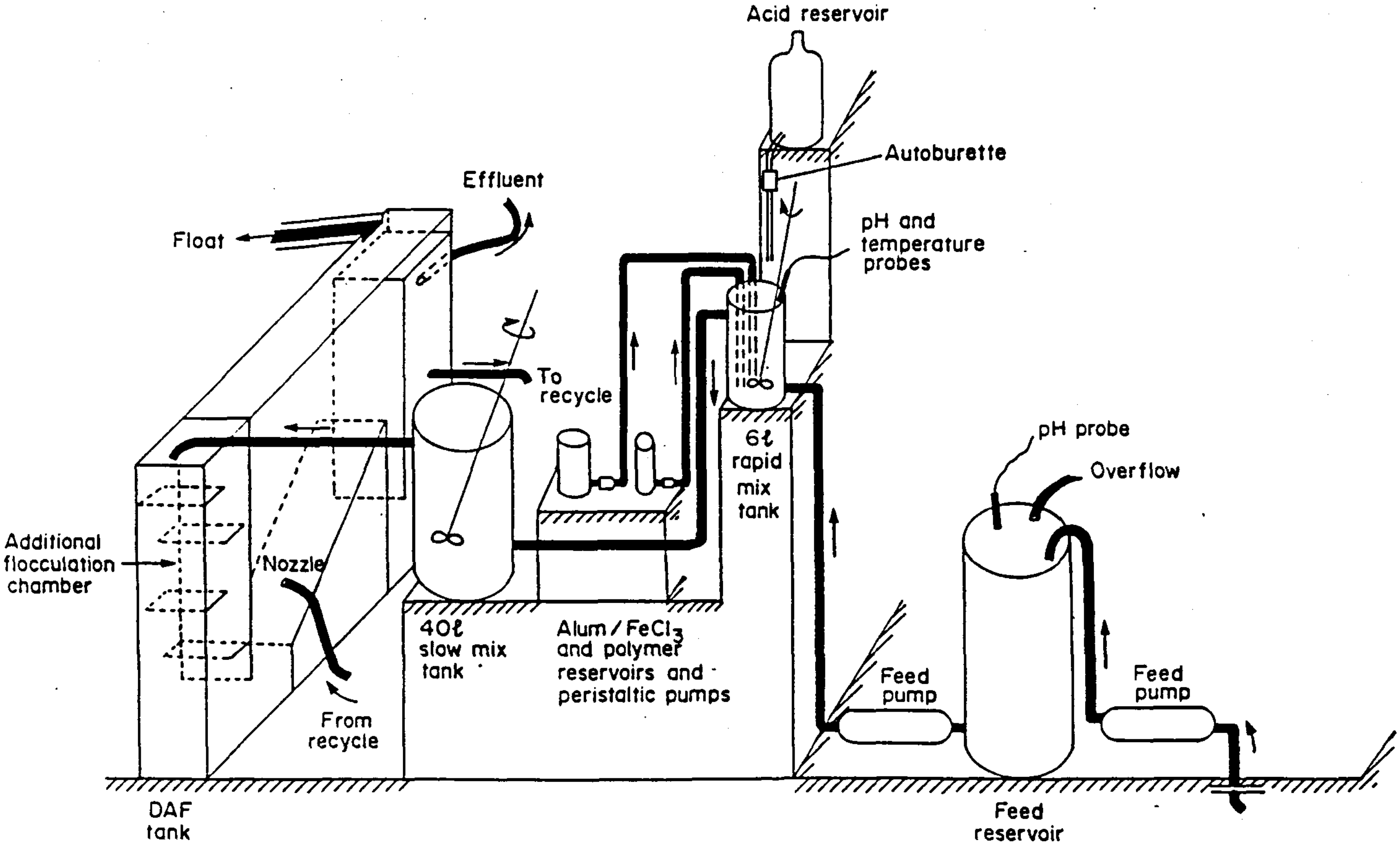
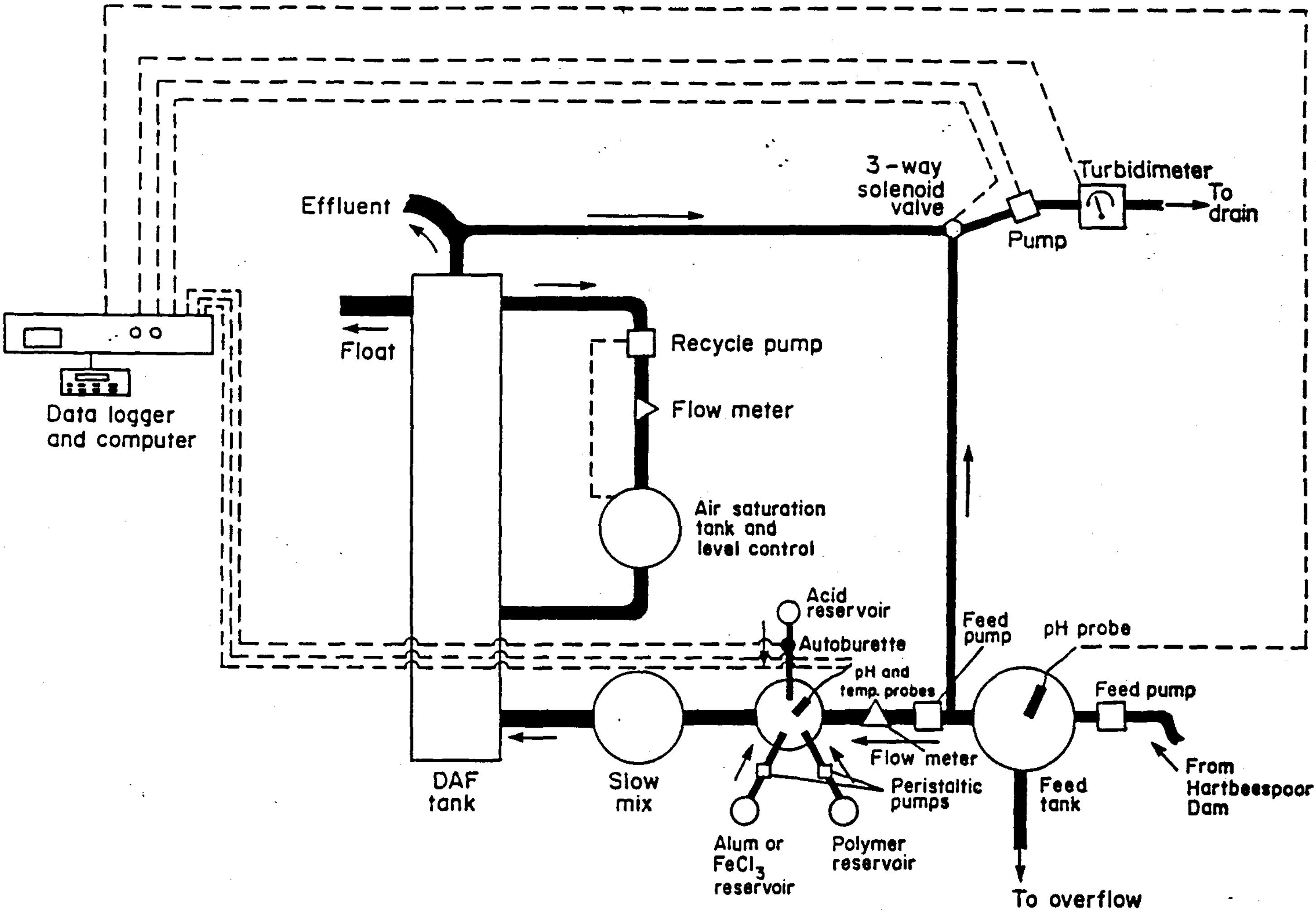


**Figure 5.2:** **Diagram of DAF Pilot Plant showing feed lines and computer control system.**



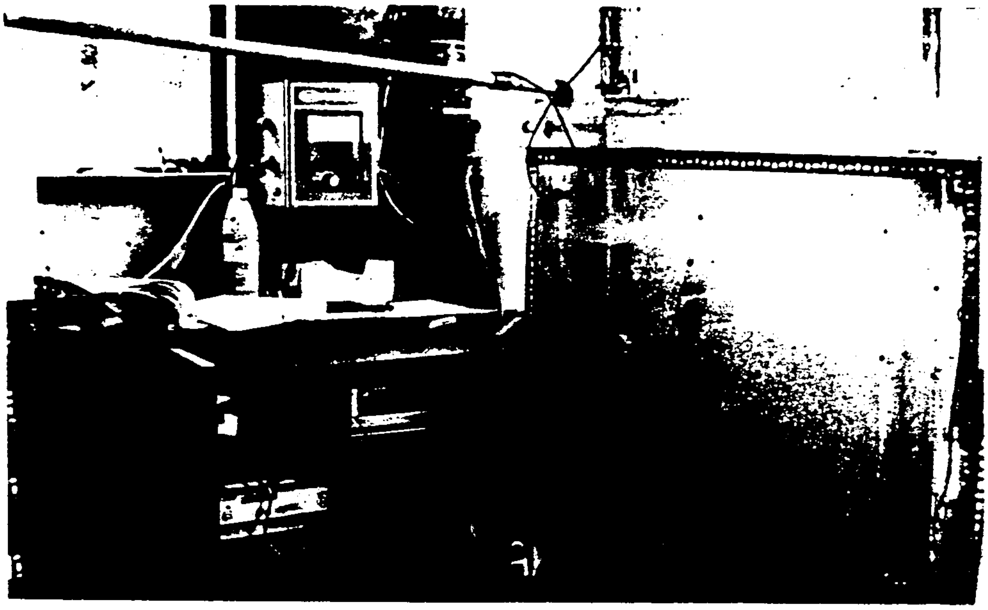


Figure 5.3: DAF Pilot Plant

Chemical addition consisted of alum or ferric chloride ($FeCl_3$), polymer, and sulfuric acid (1 N $H_2SO_4$). Alum was stored at a concentration of 60 g/ℓ, and pumped at a rate of 5,1 or 15,3 mℓ/min[7]. The stock solution and pumping rates of $FeCl_3$ were the same as those for the alum. Polymer (Magnafloc LT24[8]) was prepared at a concentration of 0,6 g/ℓ, and pumped[9] at 6,2 mℓ/min. This polymer was used as a substitute for Percol 757, as the latter was not being made in South Africa, and it's use on full-scale units would be prohibitively expensive. Magnafloc LT24 is a cationic polyacrylamide of molecular weight $> 7x10^6$.

### 5.2.2 Computer control of the pilot plant

A Hewlett-Packard data logger/computer control system was used to control and monitor the DAF plant[10]. A schematic of this system is given in Figure 5.2, and typical programs are given in Appendix A1.

A number of parameters were used for monitoring purposes only. These were influent temperature[11], influent pH[12], and influent and effluent turbidity. The latter was measured by a single turbidimeter[13]; the feed to this instrument was directed from the influent or effluent via a 3- way solenoid valve[14] and a pump[15] operating at approximately 800 mℓ/min. The valve and pump were controlled by the computer such that the turbidity reading would be recorded as applying to the appropriate source.

Computer control was used for controlling the pH of the feed to the DAF unit. To a certain extent, inorganic chemical addition, especially $FeCl_3$, would lower the pH to the desired (low) value, but if necessary, the pH could be further decreased by $H_2SO_4$ addition. This was accomplished via an autoburette[16], controlled by the computer, and dependent on the pH reading[17] in the rapid-mix tank. It was also possible to raise the pH to a desired value by replacing the acid with an appropriate alkaline solution, though in the present study this was done by hand. Final pH measurements in the effluent was also measured by a portable pH meter[18].

### 5.2.3 Full-scale plant setup

A diagram of the full-scale DAF system at Schoemansville is given in Figure 5.4, and a photograph of the overall Water Treatment Plant, including pressure filters, is shown in Figure 5.5.

The coagulation and DAF system comprises first a conical flocculation tank. $FeCl_3$, as well as powdered activated carbon[19] (at 10 mg/ℓ) and polymer (Organofloc[20]) when used, are added to the inflow as it passes over a shallow weir (< 1 m high), and the turbulence at this point is supposed to provide adequate chemical dispersion. Flow of 4,2 $m^3$/min from the outlet of the flocculation tank is directed to the DAF unit, which has an area of 18,6 $m^2$ and a nominal detention time of ~ 9 min. Air saturated recycle water is pumped through an air dissolution system similar to that of the pilot plant, at a pressure of 400 KPa.

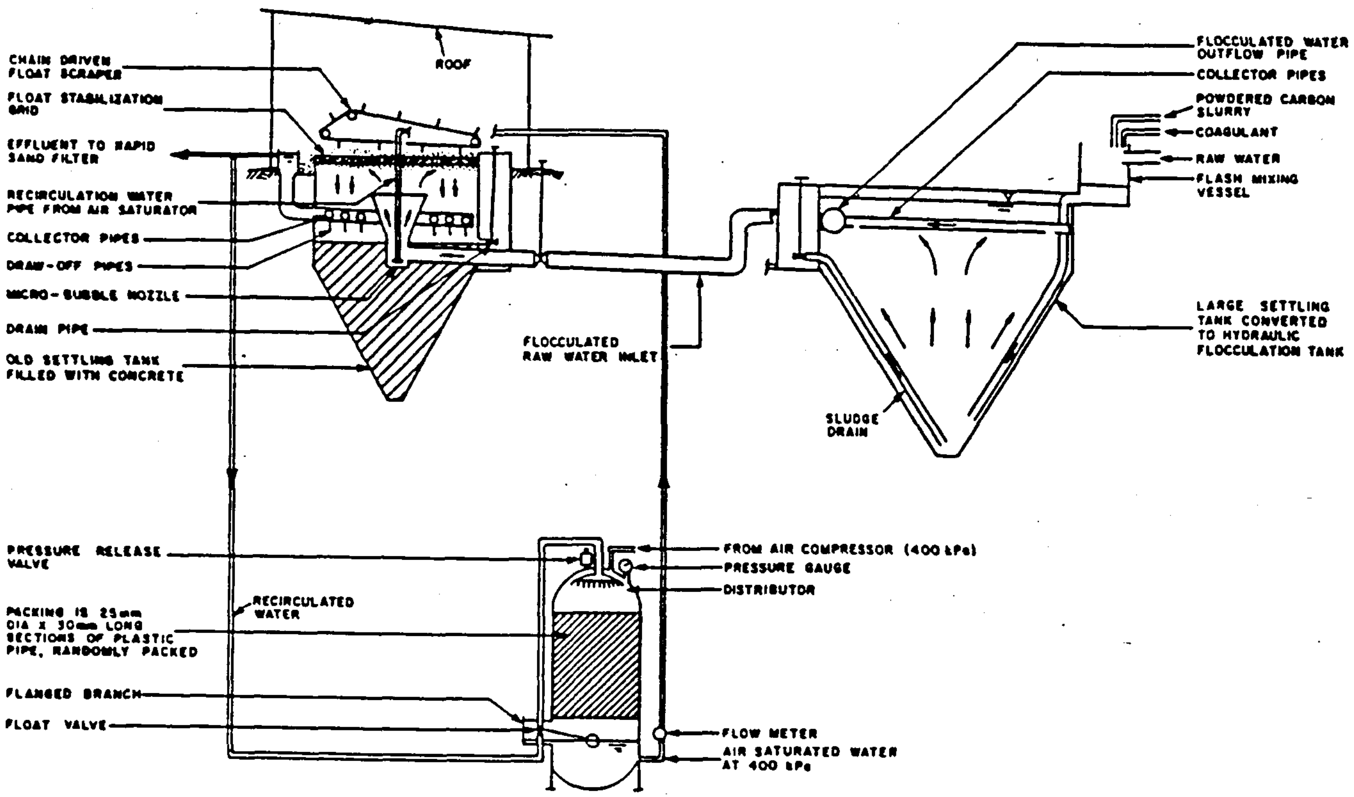
## 5.3 Experimental protocol.

The experimental (factorial) design used for the pilot plant tests was similar to that described in Chapter 4 for the batch DAF tests. A typical design is shown in Table 5.1.

Although the inorganic coagulant tested in the batch DAF tests was alum, both alum and $FeCl_3$ were used in the pilot plant, because only $FeCl_3$ could be used in the full-scale plant. The factorial design employed only $FeCl_3$.

The initial objective was to perform pilot tests under computer control during winter and summer. The effects of temperature - hence different algal populations - could thus be ascertained. However, due to problems experienced with the THMP analyses, the results of the winter tests were unreliable, and could not be used. Furthermore, theft of computer equipment during the winter of 1988 meant that subsequent tests (ie. tests 13 - 17) were done under manual control and measurement.

Figure 5.4 Full-scale DAF system at Schoemansville



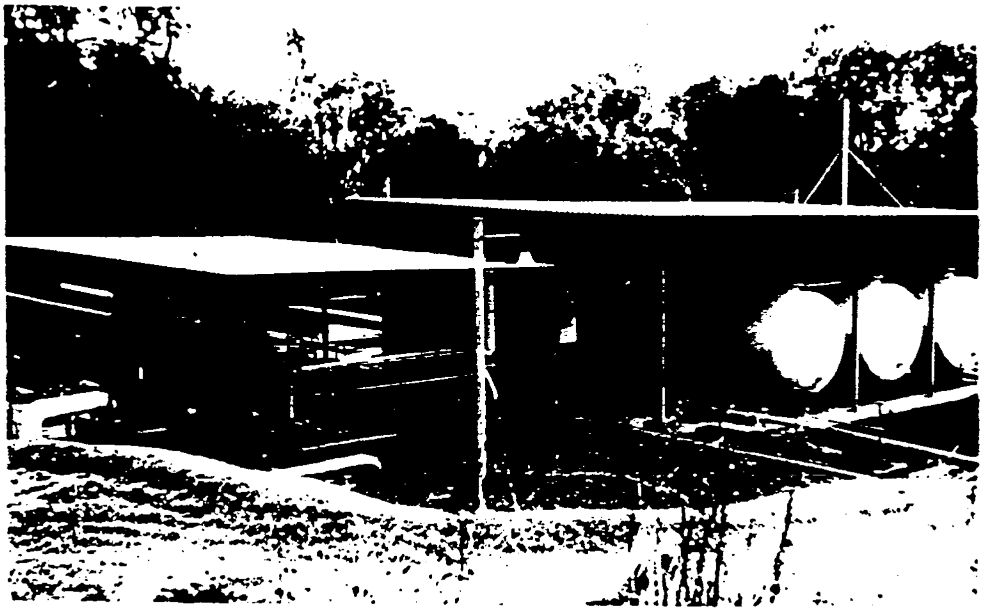


Figure 5.5: Photograph of full-scale DAF system at Schoemansville

## Table 5.1 Pilot Plant Factorial Design

Blocks: 1 Factors: 3 Runs: 8

| Randomized Run Number | Block | Test Parameter Combination A | B | C | Response* |
|---|---|---|---|---|---|
| ( 5) | 1 | - | - | - | 60,3 |
| ( 6) | 1 | + | - | - | 67,5 |
| ( 1) | 1 | - | + | - | 85,1 |
| ( 8) | 1 | + | + | - | 87,8 |
| ( 4) | 1 | - | - | + | 54,0 |
| ( 3) | 1 | + | - | + | 49,1 |
| ( 2) | 1 | - | + | + | 24,6 |
| ( 7) | 1 | + | + | + | 74,6 |

* Example: % removal of total THMP.

## Table 5.2 Codes for Pilot Plant

| CODE | CONDITION |
|---|---|
| A | High $FeCl_3$ dose = 150 mg/L |
| B | High polymer dose = 0,6 mg/L |
| C | High initial pH = 9,0 |
| O | Low parameter condition:<br>$FeCl_3$ = 50 mg/L<br>Polymer dose = 0<br>pH = 5 |
| L | Alum dose at 150 mg/L |

<u>Note</u>: pH values are approximate
Low final pH range 4,78 - 5,97
High final pH range 6,72 - 8,61

It was expected that the algal population in the summer would be dominated by *Microcyctis aeruginosa* (a blue-green cyanobacterium). This had been the case for many years, and was true for the tests conducted in the summer of 1988. However, the dominant species in February, 1989 (Test 13) were *Cryptomonas* (a cryptophyte; unknown species) and *Cyclotella meneghiniana* (of the Chrysophyta division); and in March, 1989 (Tests 14 - 17), the dominant species was *Cryptomonas*. This shift in speciation must have had an effect on the results.

Finally, as noted in Chapter 3, all trihalomethane results were corrected for reagent blanks. These "blank" values were sometimes as high as 109 µg/ℓ for THMP, but were generally in the order of 30 µg/ℓ.

**Equipment used:**

1 Steward Turner
2 Steward Turner
3 Lightning, model F220
4 Framco
5 Mono pump; Rance 22M (75 watts)
6 Electromatic S-System, #SV 110 220
7 Gilson Minipulse 2
8 Allied Colloids, S.A. (Pty) Ltd
9 Gilson Minipulse 2
10 #71B portable computer; #3421 data acquisition and control unit; #9144 disk drive
11 Jenco
12 Metrohm 1026
13 Hach # 1720A
14 FIP plastics
15 Stewart Turner; 210 watts
16 Radiometer
17 Jenco pH transmitter # 692

### 5.4 Results and discussion of pilot plant performance.

Codes for the pilot plant test conditions are shown in Table 5.2, and the raw data, together with summary statistics for the influent, are given in Appendix A2.

Figures 5.6 to 5.13 show test results plotted in test sequence, together with the test codes. These plots give a good visual indication of removals; a statistical analysis of the results will be presented later in this section. It is seen in Figures 5.6 and 5.7 that the highest removals of THMPs occurred under test conditions A, AB, B, L and LB (ie high $FeCl_3$, alone or with polymer, low $FeCl_3$ with polymer, and high alum with or without polymer). The same performance pattern occurred with removal of chloroform (Figures 5.8 and 5.9) and bromodichloroform (Figures 5.9 and 5.10). However DOC (Figure 5.11) and turbidity (Figure 5.12) removals did not always coincide with optimum THMP removals. The implications of the DOC results will be discussed later (Section 5.6); as far as turbidity removals are concerned, it is expected that subsequent filtration would be capable of producing the desired effluent quality. Note that the natural pH condition is a high pH, and the low removals found for test condition C implies that a low pH value is optimum.

Figures 5.14 to 5.18 show some of the more pertinent results plotted according to the date of testing. These plots show a slight downward trend of the influent measured parameters between 1988 and 1989. The gap between the influent and effluent lines indicates the extent of removal, however this form of plotting is misleading due to the unequal spacing between tests. The high removals of THMPs and chloroform which were possible under optimum conditions are shown in Figures 5.14 and 5.15. Bromoform, DOC, and turbidity removals were much lower (Figures 5.16 - 5.18); see, also, Section 5.6.

Before discussing the statistical analysis of the data, it is perhaps instructive to examine the <u>percentage</u> removals of THMP and DOC obtained under the various test conditions. By plotting percentage removals, it is possible to eliminate to a certain extent the variability in the raw water quality. Figure 5.19 shows that, in general, percentage THMP removals are higher than DOC removals, and that values above 80 % may be achieved for the former at high $FeCl_3$ and polymer doses. At high pH, (ie.

C test condition), removals of THMP are, with one exception, lower than at low pH. DOC removals show no such consistent pattern, which is to be expected because of the "global" nature of this parameter.

The discussion thus far has involved a qualitative evaluation of pilot plant performance. A statistical analysis of the results of the 8 factorial experiments (Tests 6, 7, 10, 12, 14, 15, 16 and 17), based on percentage removal results shown in Table 5.3, is given in Table 5.4 and Figures 5.20 - 5.27. In Table 5.4, the first row indicates the average % removal of each parameter for all 8 tests, and subsequent rows show the effects (above or below the average) for the various combinations of test conditions. Points in Figures 5.20 - 5.27 which lie away from the straight line indicate those test conditions which produce a statistically significant improvement (or decrease) in performance from the average. These points are ringed in the figures, and the equivalent values in Table 5.4 are underlined.

The two factors which stand out clearly in this analysis are that a high dosage of $FeCl_3$ (ie. 150 mg/L) and a low pH (around 5,0) are significant for improvements in THMP removal (including chloroform and bromodichloroform) and DOC, and even turbidity removal is significantly affected by pH. The highest % removals occur under conditions B and AB, and reference back to Figure 5.6 shows that effluent THMP values as low as 30 µg/L can then be achieved.

Figure 5.6

Pilot plant total trihalomethanes.
Influent and effluent (in test sequence)

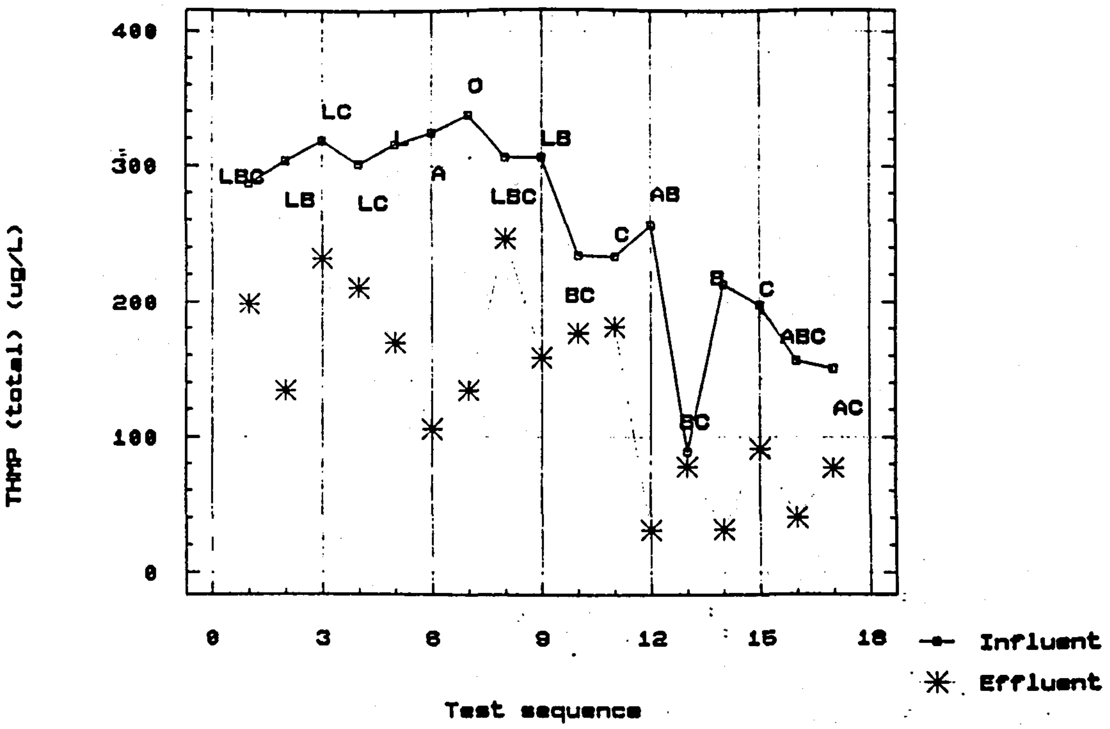


Figure 5.7

Pilot plant filtered trihalomethanes.
Influent and effluent (in test sequence)

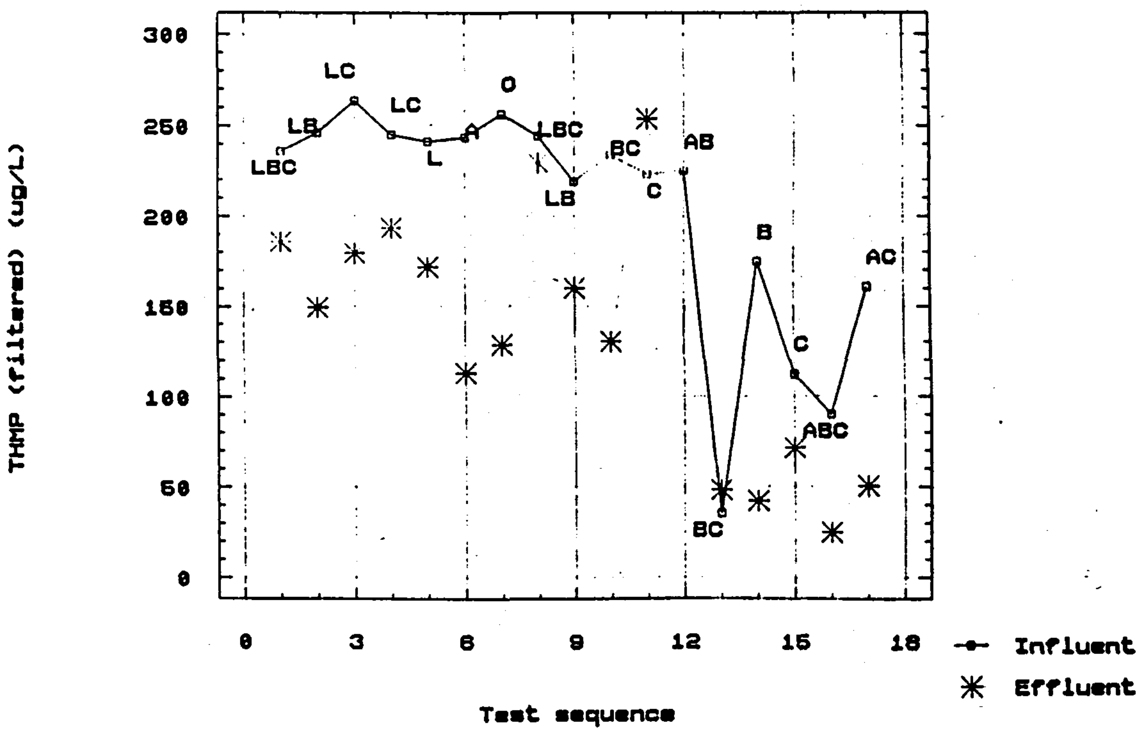


Figure 5.8

Pilot plant total chloroform.

Influent and effluent (in test sequence)

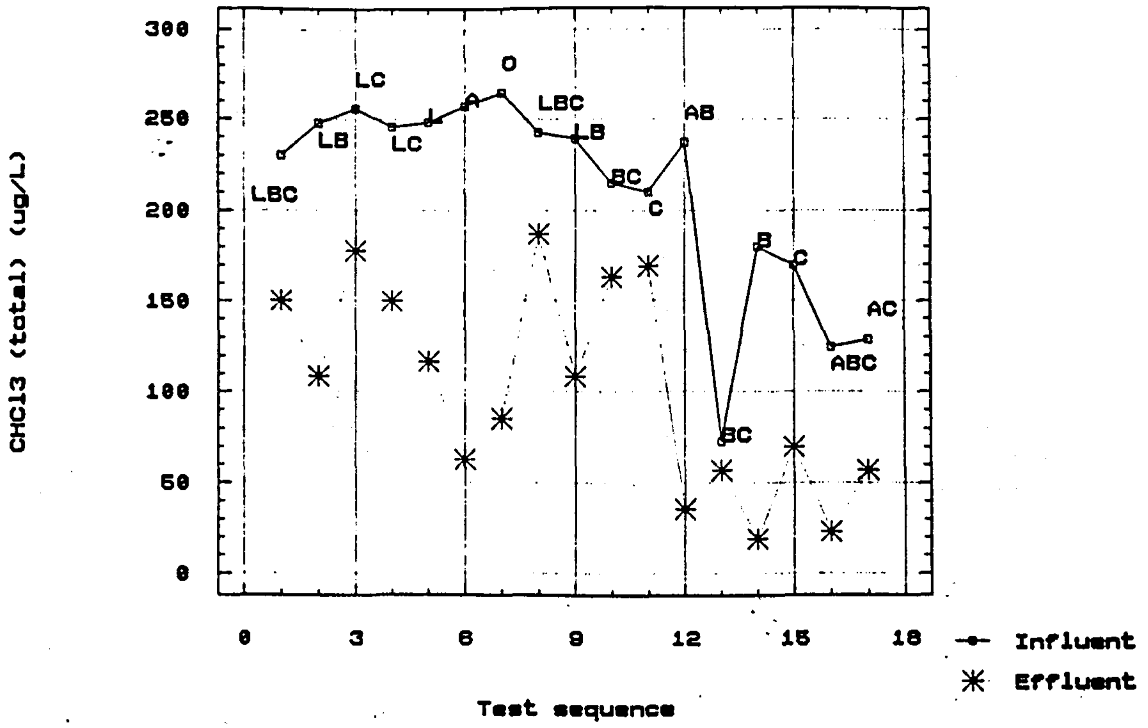


Figure 5. 9.

Pilot plant filtered chloroform.

Influent and effluent (in test sequence)

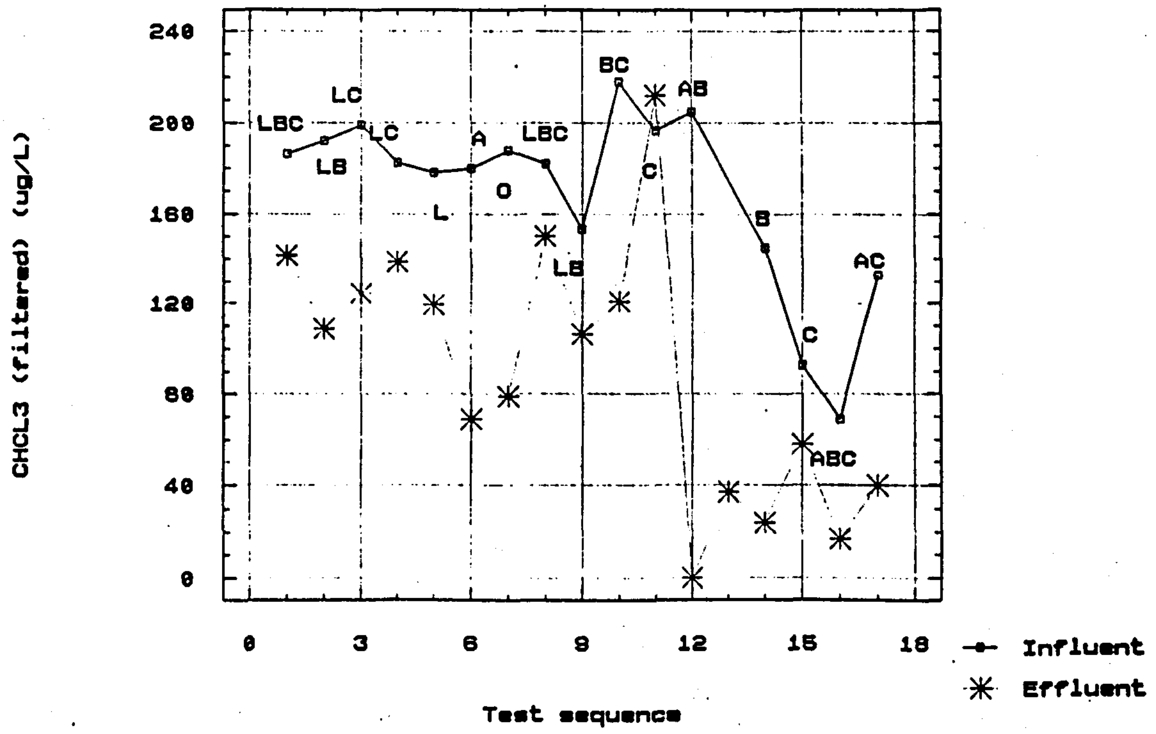


Figure 5.10

Pilot plant total bromodichloroform.
Influent and effluent (in test sequence)

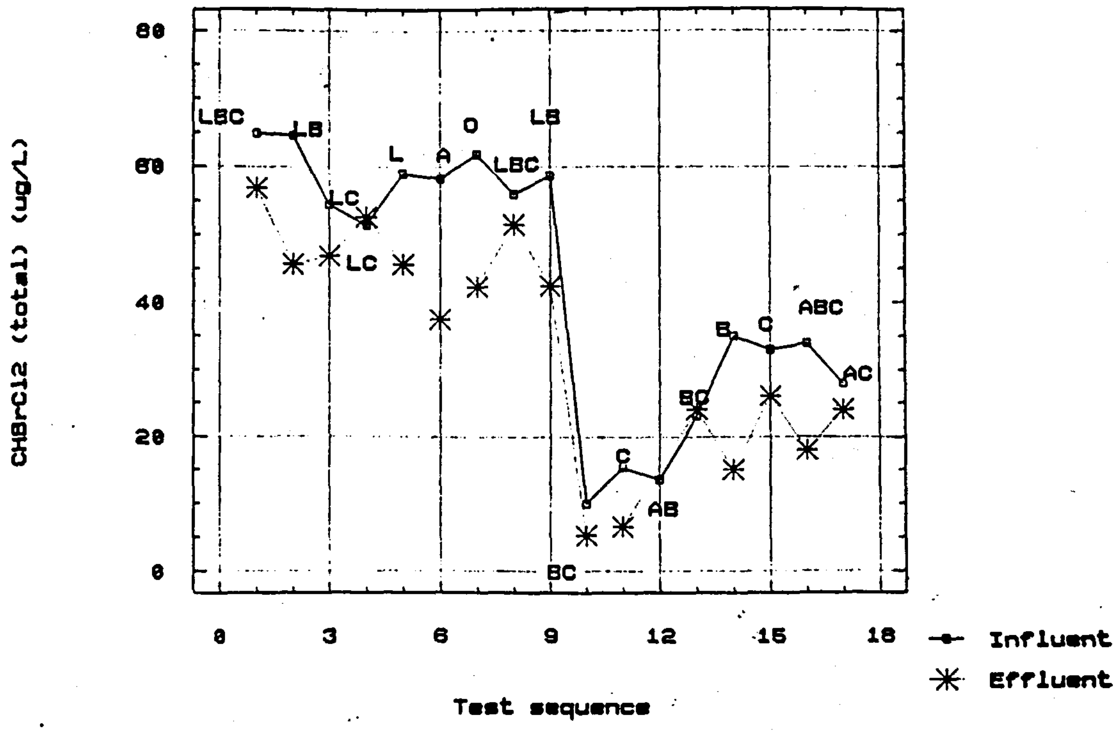


Figure 5.11

Pilot plant filtered bromodichloroform.
Influent and effluent (in test sequence)

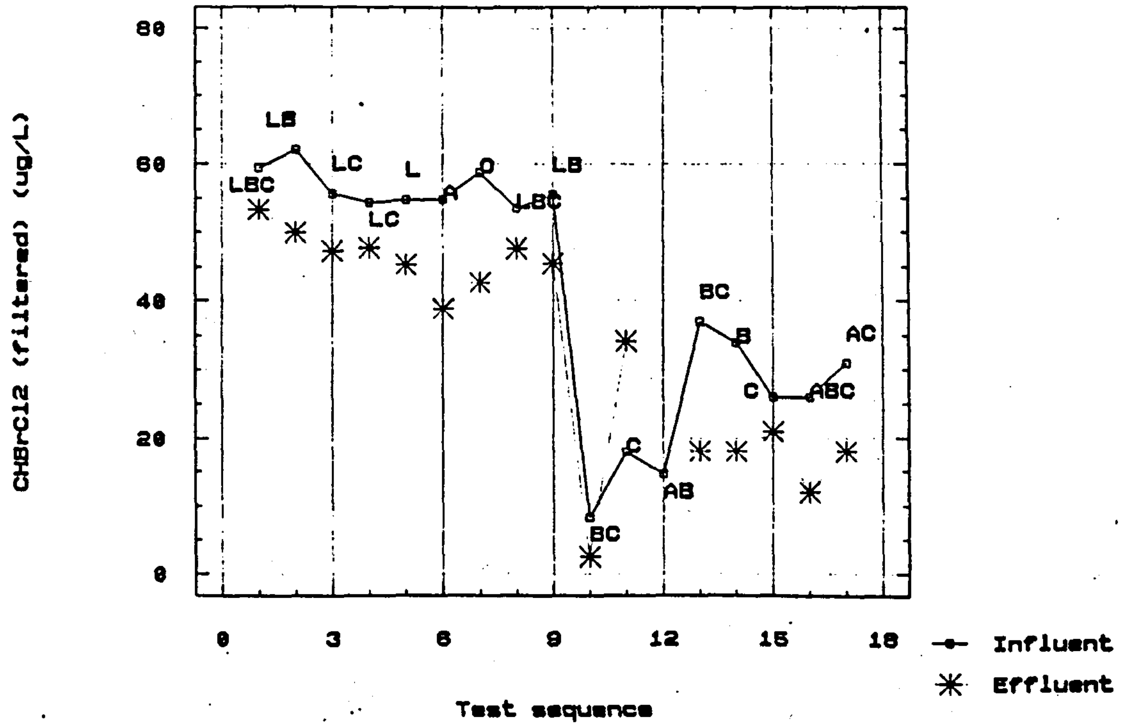


Figure 5.12

Pilot plant total DOC.
Influent and effluent (in test sequence)

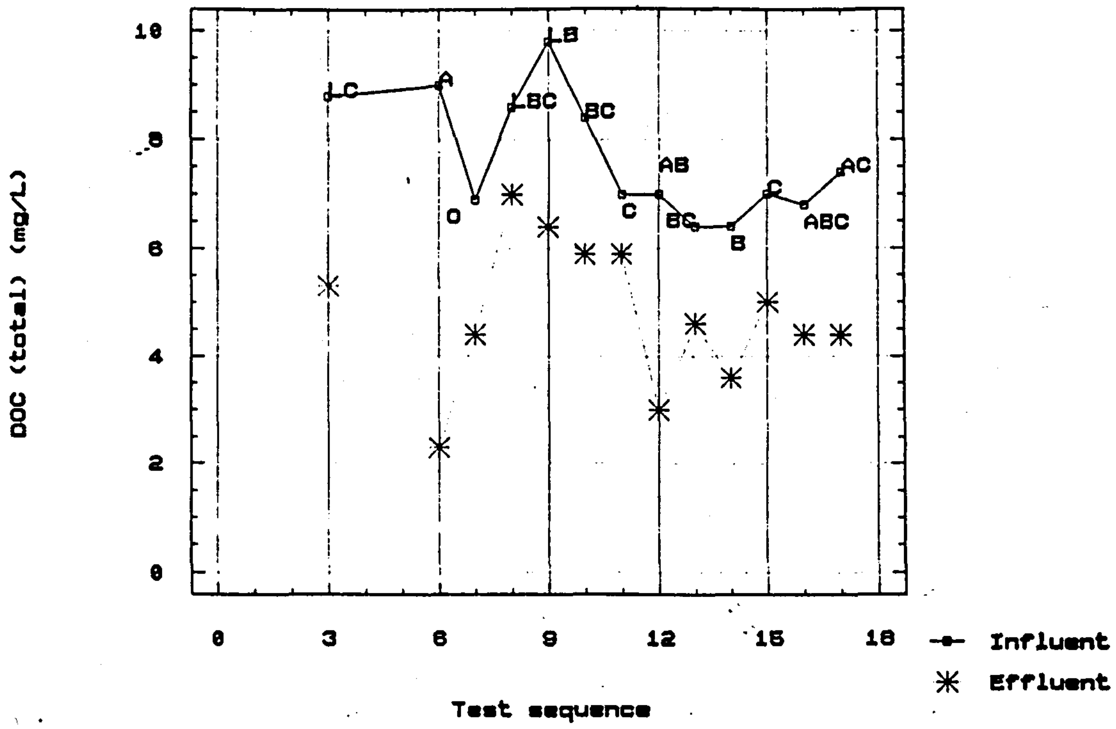


Figure 5.13

Pilot plant turbidity
Influent and effluent (in test sequence)

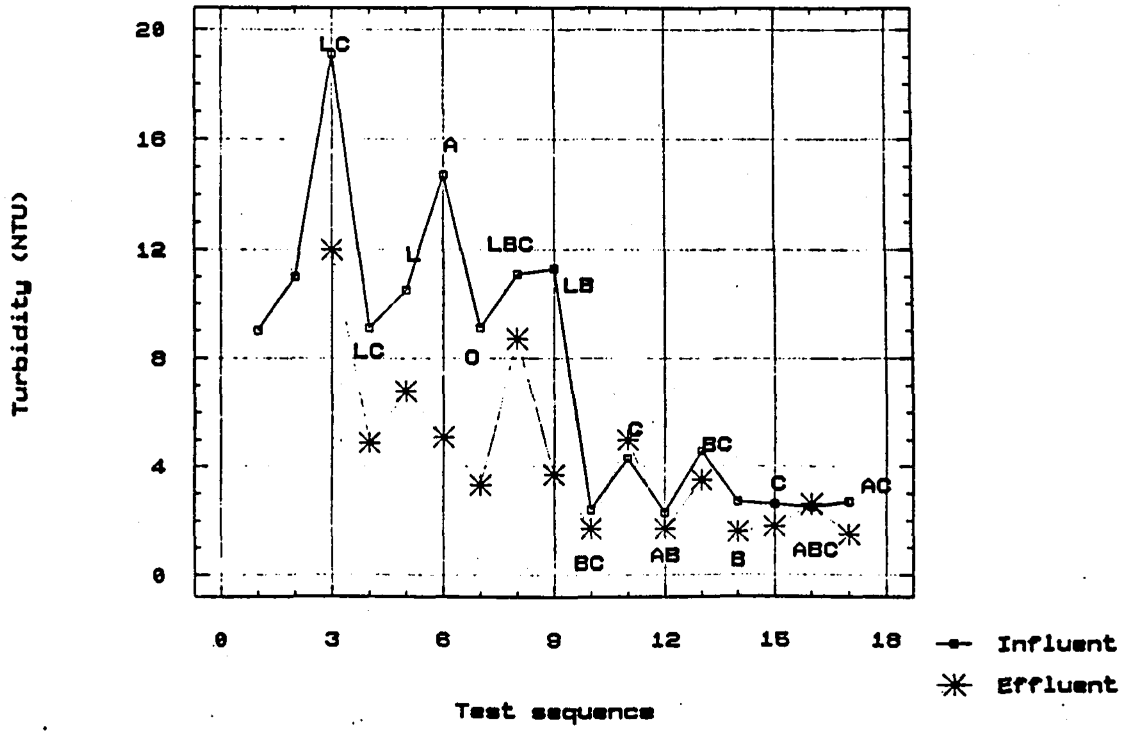


Figure 5.14

Pilot plant total trihalomethanes.
Influent and effluent

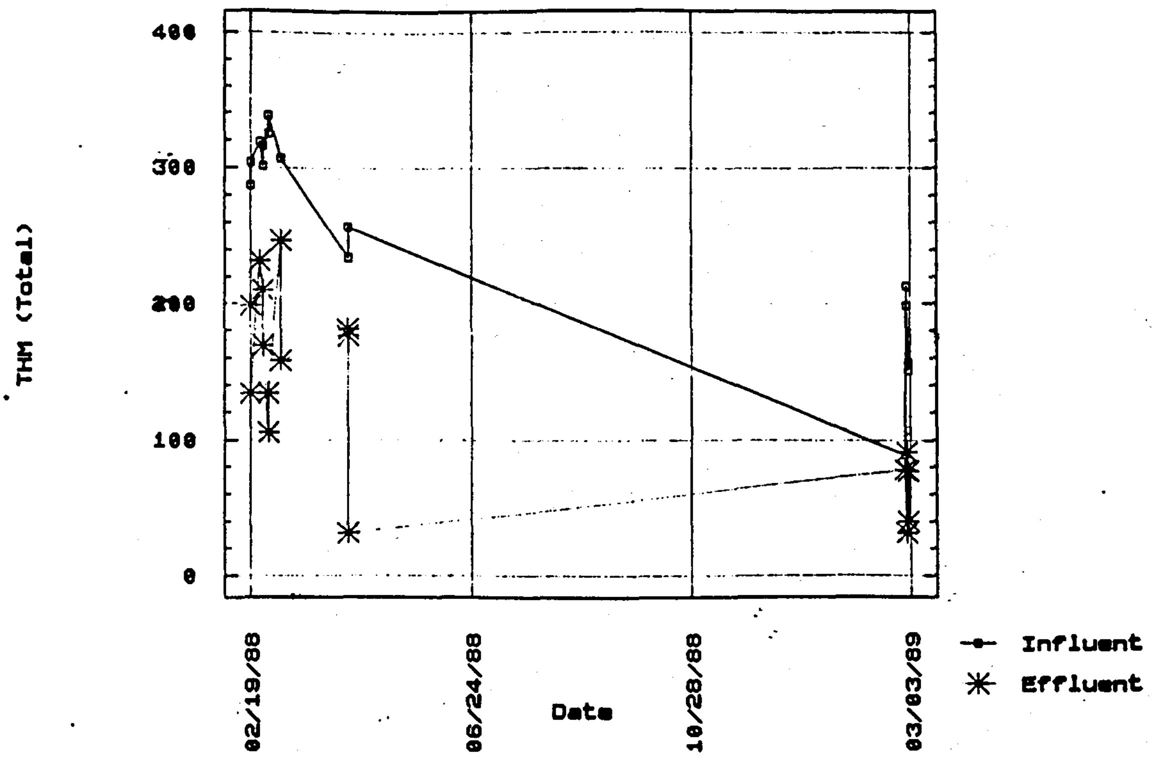


Figure 5.15

Pilot plant filtered chloroform.
Influent and effluent

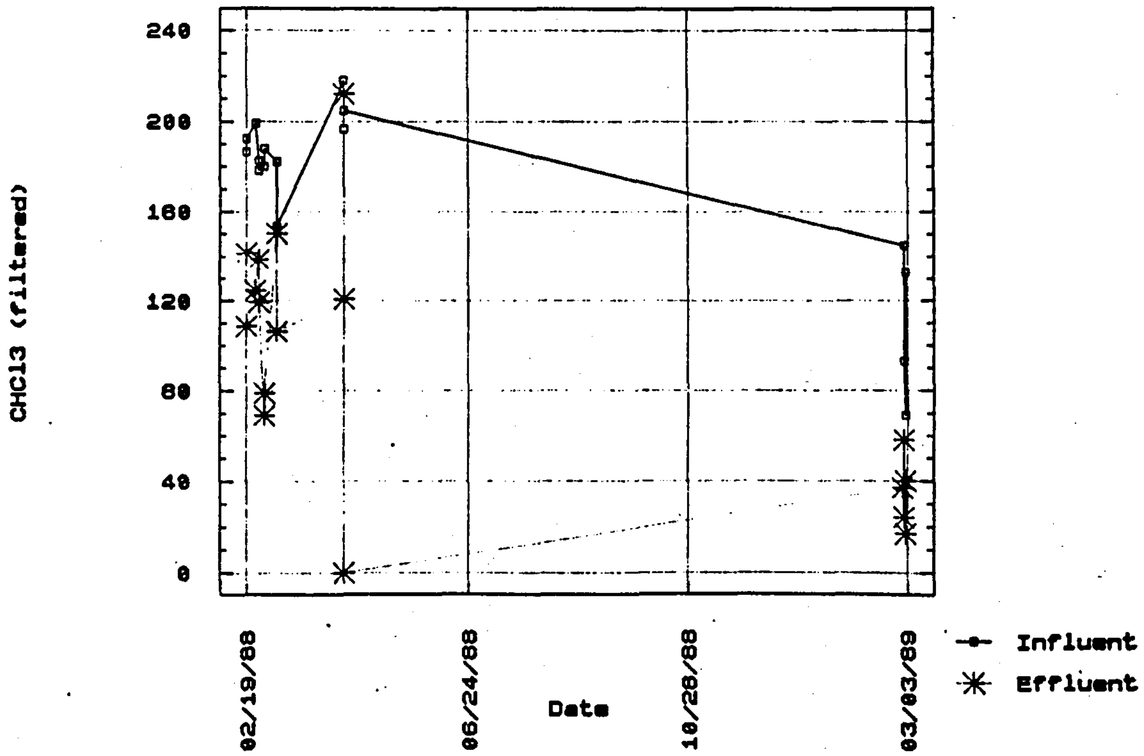


Figure 5.16

Pilot plant total bromodichloroform.
Influent and effluent.

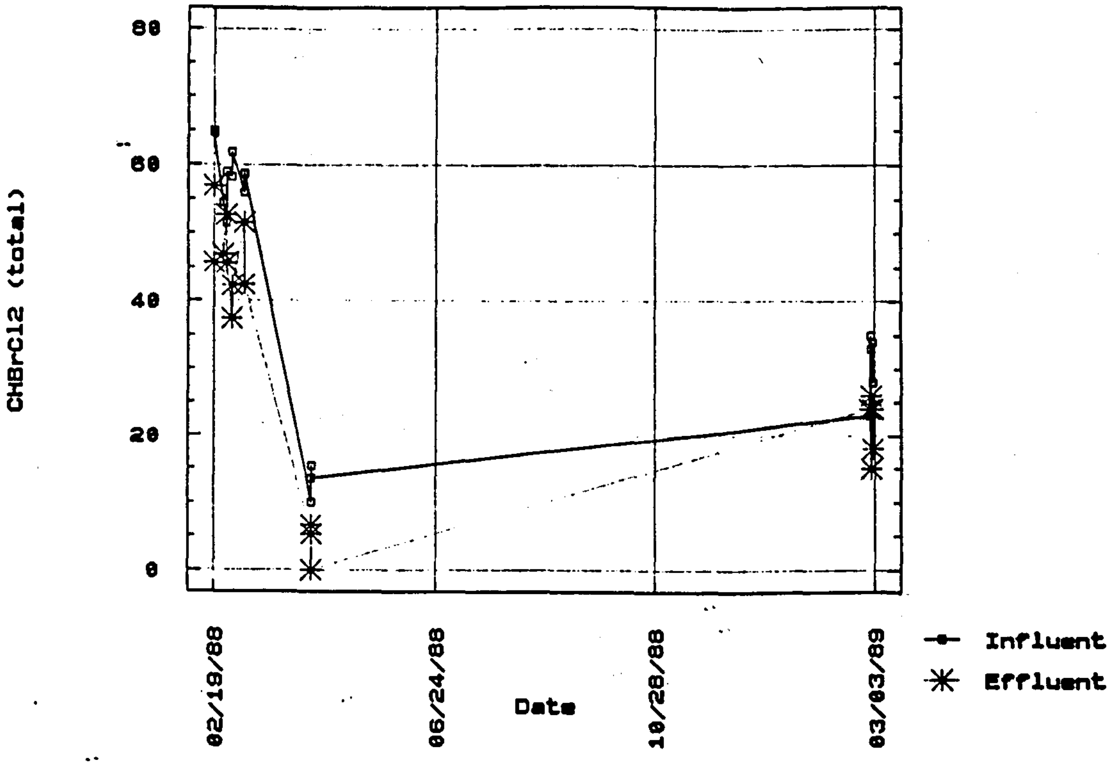


Figure 5.17

Pilot plant total DOC
Influent and effluent

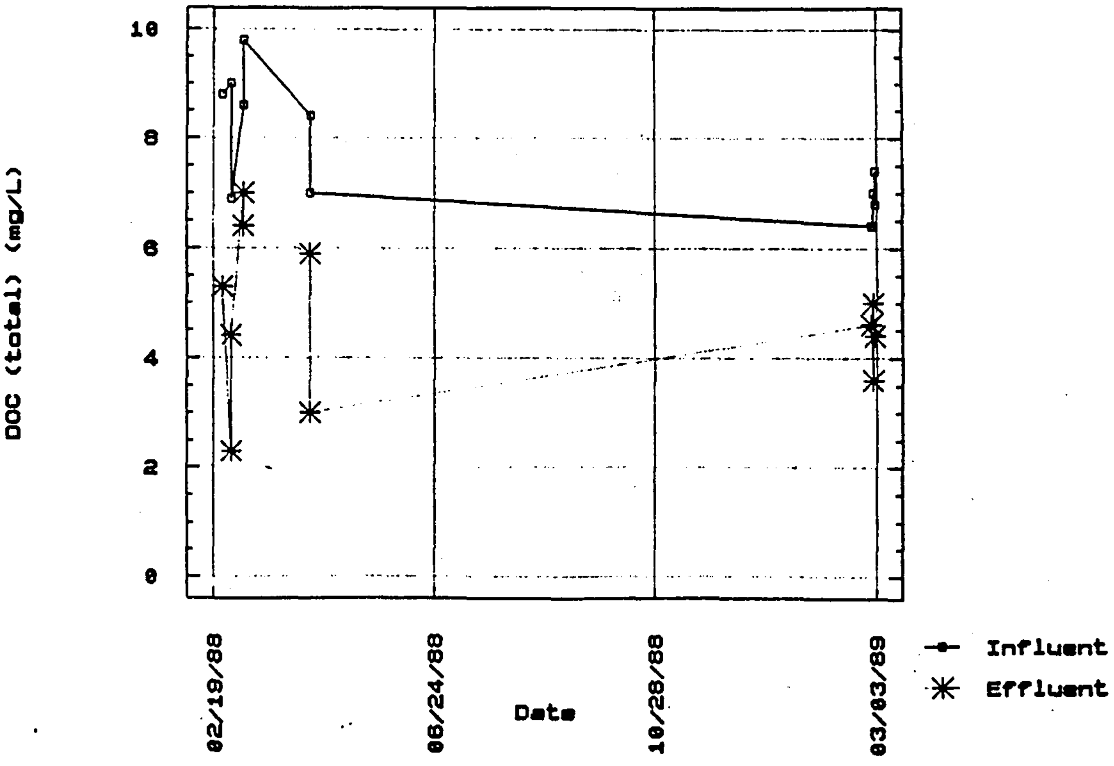


Figure 5.18

Pilot plant turbidity
Influent and effluent

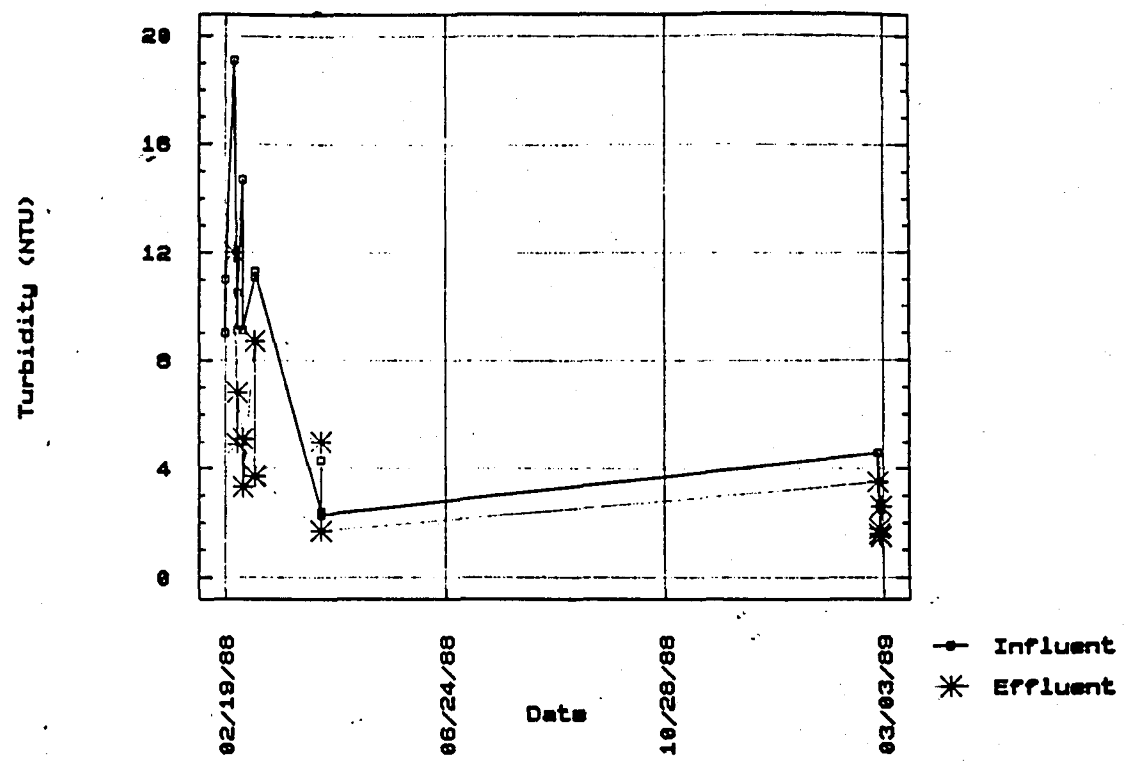
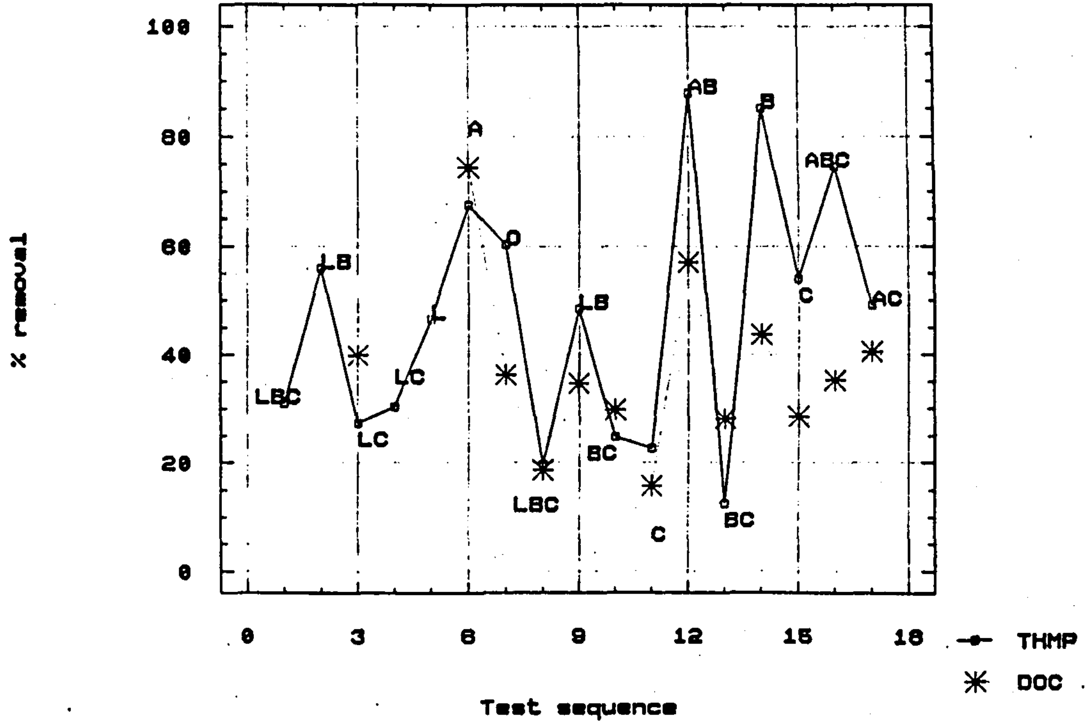


Figure 5.19

Percent removals in the pilot plant.
Total THMP and DOC.



## Table 5.3 Pilot Plant Factorial Experiments: % Removal

| Code | Total THMP | Filtered THMP | Total $CHCl_3$ | Filtered $CHCl_3$ | Total $CHBrCl_2$ | Filtered $CHBrCl_2$ | Total DOC | Filtered DOC | Turbidity |
|---|---|---|---|---|---|---|---|---|---|
| O | 60,3 | 50,0 | 67,9 | 58,0 | 31,7 | 27,4 | 36,2 | 60,4 | 63,7 |
| A | 67,5 | 53,6 | 75,7 | 61,6 | 35,8 | 29,3 | 74,4 | 54,2 | 65,3 |
| B | 85,1 | 75,9 | 89,4 | 83,4 | 57,1 | 47,1 | 43,8 | 50,0 | 40,7 |
| AB | 87,8 | 100,0 | 84,9 | 100,0 | 100,0 | 100,0 | 57,1 | 67,1 | 26,1 |
| C | 54,0 | 36,4 | 58,8 | 37,6 | 21,2 | 19,2 | 28,6 | 44,1 | 30,8 |
| AC | 49,1 | 68,7 | 55,8 | 69,9 | 14,3 | 41,9 | 40,5 | 41,9 | 44,4 |
| BC | 24,6 | 44,4 | 21,9 | 44,5 | 47,0 | 51,4 | 29,0 | 43,8 | 23,9 |
| ABC | 74,6 | 72,5 | 81,6 | 75,4 | 47,1 | 53,8 | 35,3 | 45,5 | -4,0 |

## Table 5.4 Analysis of Pilot Plant $2^3$ Factorial Experiments

| Code | Total THMP | Filt. THMP | Total $CHCl_3$ | Total $CHBrCL_2$ | DOC | Turbidity |
|---|---|---|---|---|---|---|
| Average Removal (%) | 62,9 | 62,7 | 67,0 | 44,3 | 43,1 | 36,4 |
| A | 13,8 | 22,0 | 15,0 | 10,1 | 17,4 | -6,8 |
| B | 10,3 | 21,0 | 4,9 | 37,1 | -3,6 | -29,4 |
| AB | 12,6 | 4,1 | 12,6 | 11,5 | -7,6 | -14,4 |
| C | -24,6 | -14,4 | -25,0 | -23,8 | -19,5 | -25,2 |
| AC | 8,8 | 8,2 | 13,4 | -13,5 | - 8,3 | - 0,3 |
| BC | -12,3 | -15,1 | -10,5 | - 7,8 | 1,2 | 1,7 |
| ABC | 14,9 | - 6,2 | 18,8 | - 8,0 | 4,8 | - 6,3 |

## 5.5 Results and discussion of full-scale plant performance.

Codes for the full-scale plant test conditions are given in Table 5.5, and the raw data are given in Appendix A3

Again, the pertinent results have been plotted according test sequence and with test codes in Figures 5.28 - 5.34, and according to date of experimentation in Figures 5.35 - 5.38. The % removals are shown in Figure 5.39 and tabulated in the Appendix.

It is clear from the figures and Table 5.6 that the full-scale plant performance is generally not as good as the pilot plant. Maximum THMP removals were approximately 65% (compared with over 80% for the pilot plant), and this occurred, interestingly, at low $FeCl_3$ and polymer doses (test code O). High total THMP removal was also experienced under test condition BD (which included powdered activated carbon, PAC), and high filtered THMP removal occurred at condition A (high $FeCl_3$).

It is to be expected that the full-scale plant would give poorer performance than the pilot plant, because the former had no pH control, neither were the flocculation conditions (ie.rapid and slow mix operations) as well controlled. Due to the small number of tests on the full-scale unit, and the fact that the experiments were not designed to be amenable to statistical analysis, it is impossible to specify with confidence the optimum conditions for the plant. It does appear, though, that high doses of polymer are unnecessary (condition BX), and in fact may be detrimental to THMP removal (it is known that the polymer itself could contribute to the THMPs). The single test with PAC yielded an effluent THMP concentration below 100 $\mu g/\ell$, but as shown in Figure 5.28, it is possible to achieve this level simply with $FeCl_3$ and no polymer. Further tests are required, using the optimum conditions from the pilot plant, and especially pH control, to establish the most economical methods for removing THMP.

Figure 5.20

Total THMP; % removal in pilot plant.
Normal prob. plot of factorial design

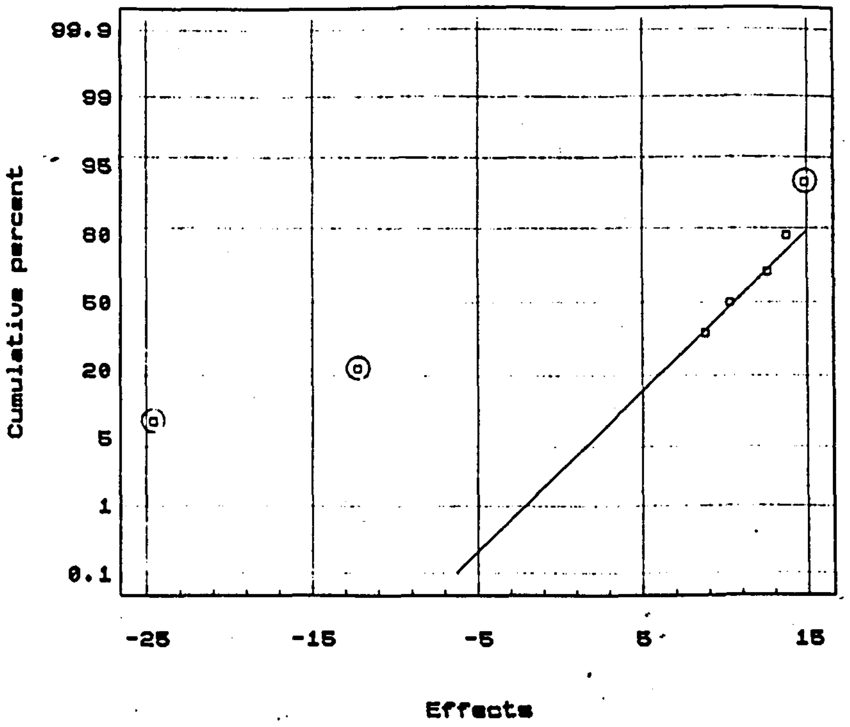


Figure 5.21

Filt. THMP; % removal in pilot plant.
Normal prob. plot of factorial design

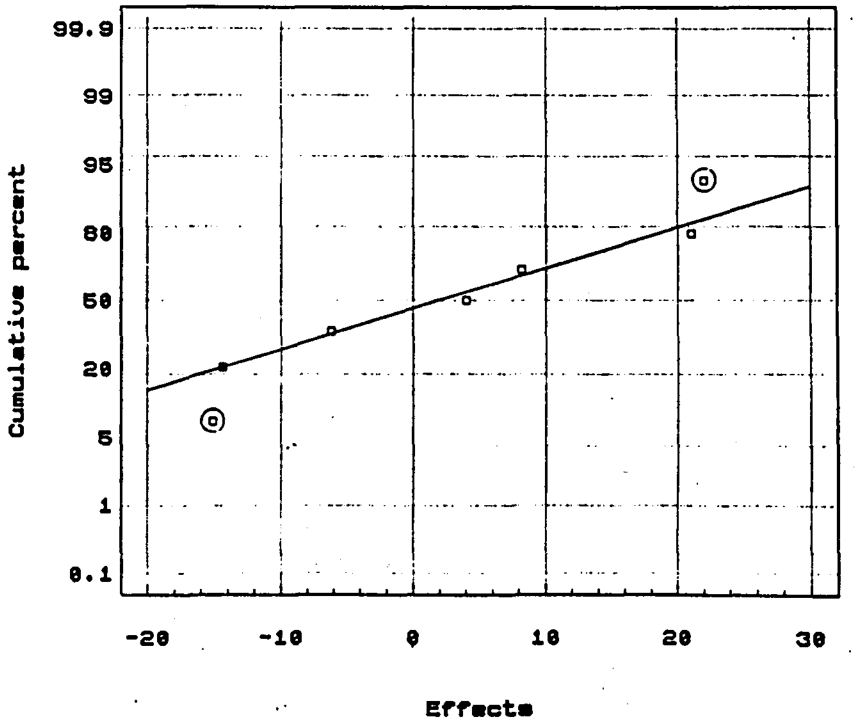


Figure 5.22

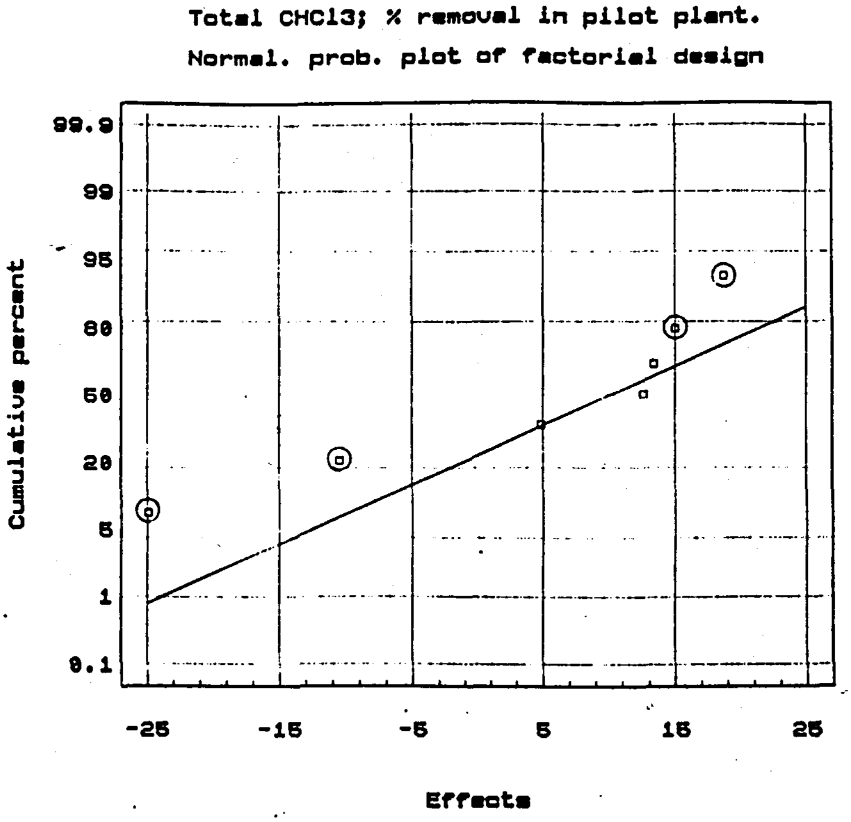


Figure 5.23

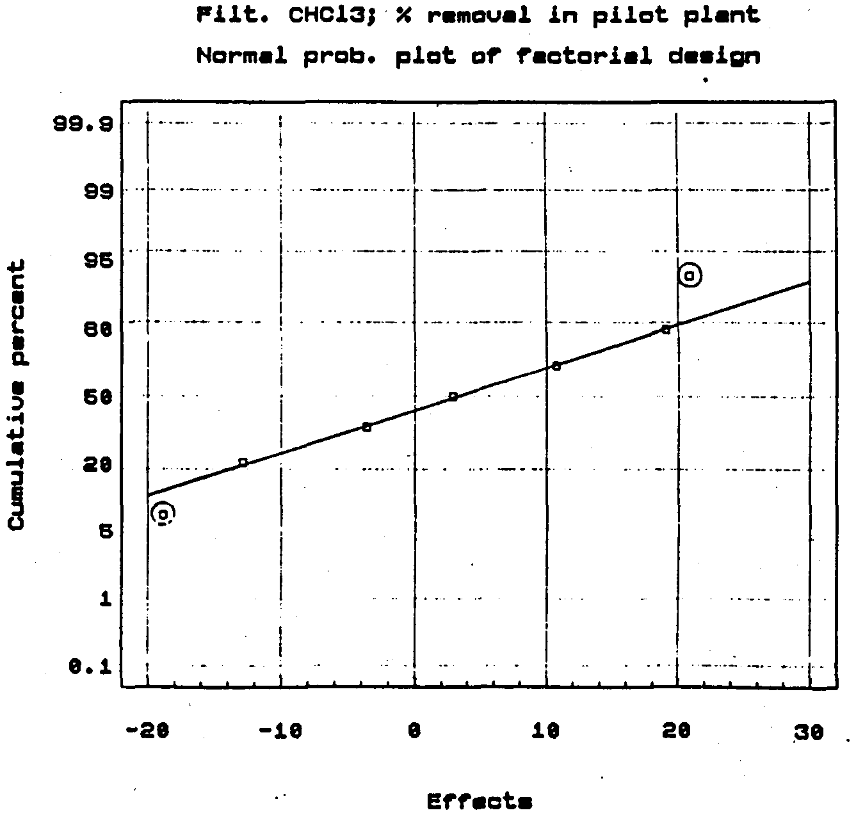


Figure 5.24

Total CHBrCl2; % removal in pilot plant
Normal prob. plot of factorial design

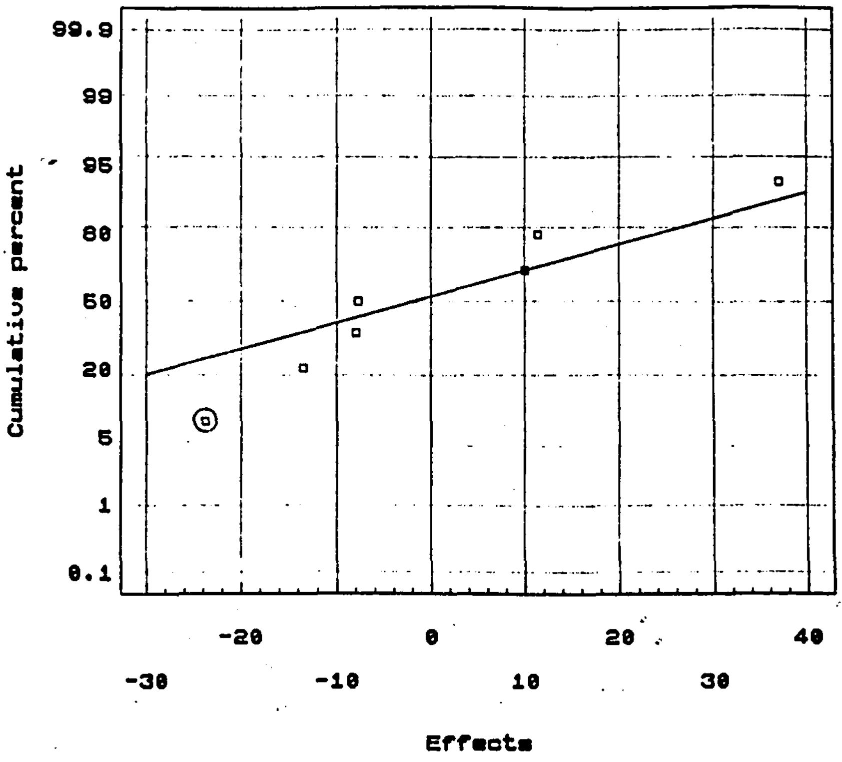


Figure 5.25

Filt. CHBrCl2; % removal in pilot plant.
Normal prob. plot of factorial design

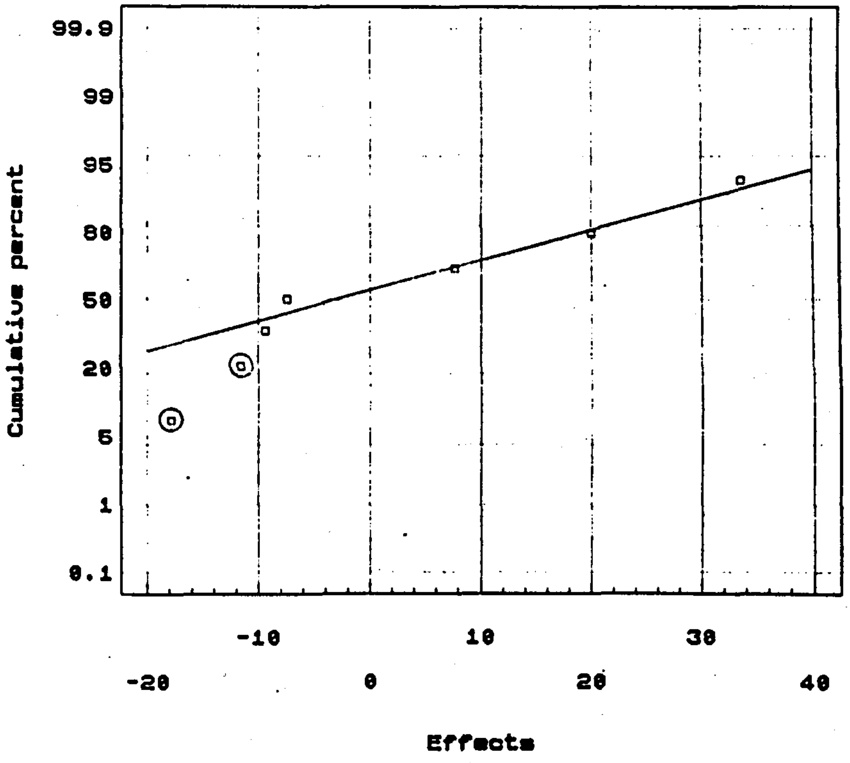


Figure 5.26

Total DOC; % removal in pilot plant.
Normal prob. plot of factorial design

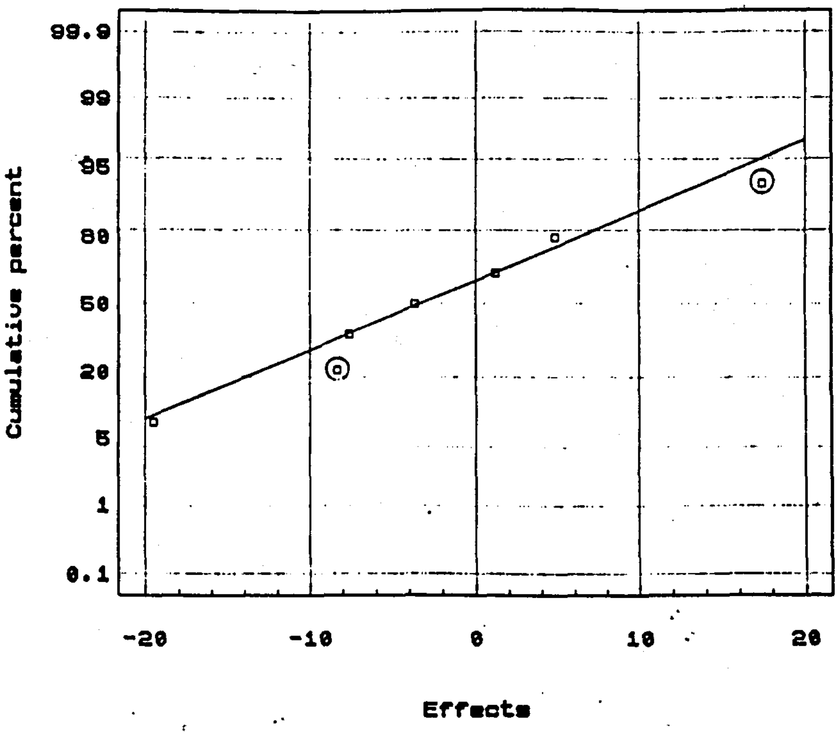
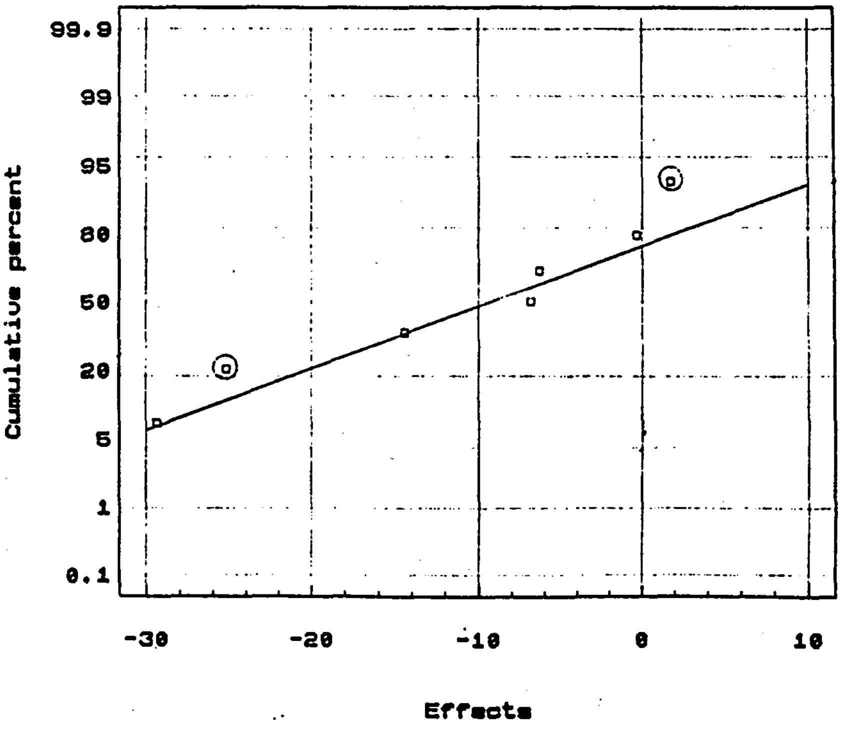


Figure 5.27

Turbidity; % removal in pilot plant.
Normal prob. plot of factorial design



## Table 5.5 Codes for Full-Scale Plant

| CODE | CONDITION |
|---|---|
| A | High $FeCl_3$ dose = 100 mg/L |
| B | Polymer dose = 0,6 mg/L |
| BX | Polymer dose = 6,0 mg/L |
| D | PAC dose = 10 mg/L |
| O | Low parameter condition:<br>$FeCl_3$ = 50 mg/L<br>Polymer dose = 0<br>PAC dose = 0 |

Figure 5.28

Full-scale plant total trihalomethanes.
Influent and effluent (in test sequence)

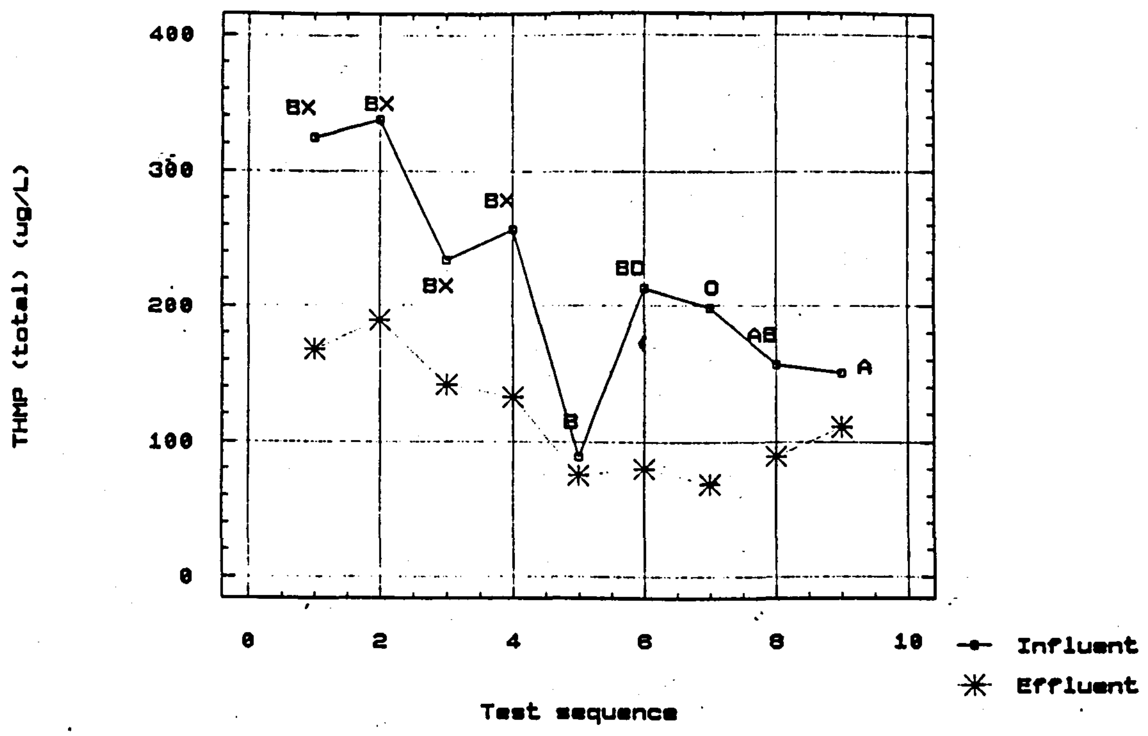


Figure 5.29

Full-scale plant filtered THMP.
Influent and effluent (in test sequence)

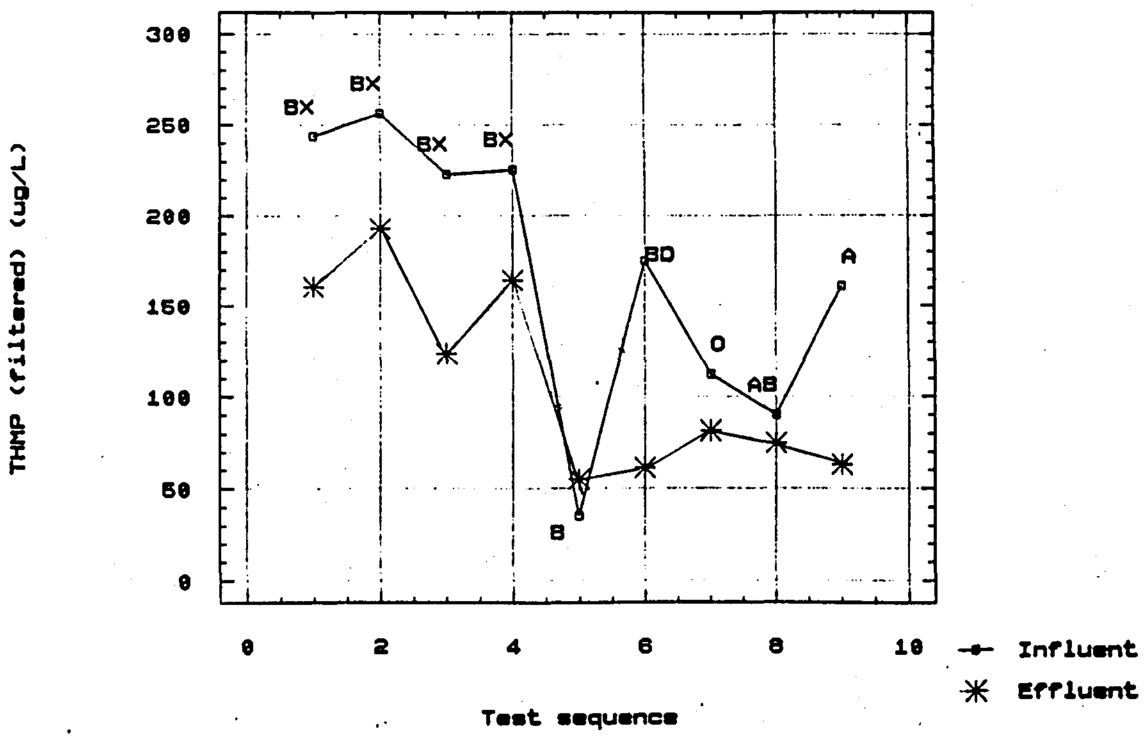


Figure 5.30

Full-scale plant total chloroform.
Influent and effluent (in test sequence)

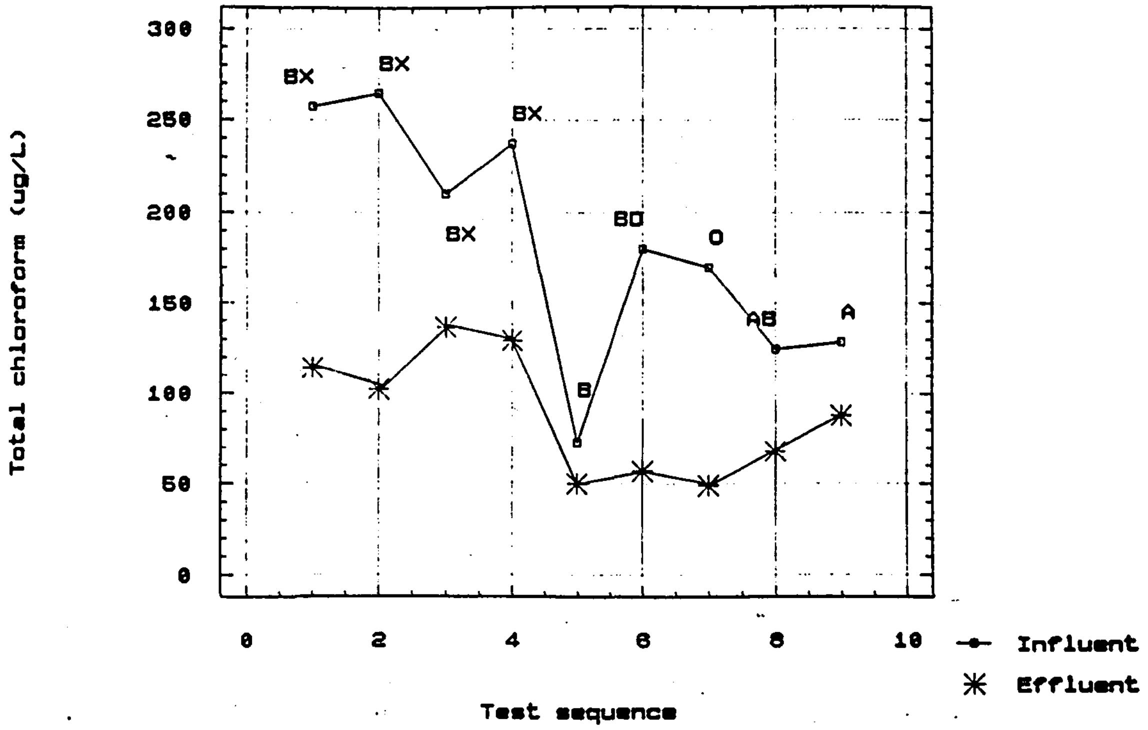


Figure 5.31
Full-scale plant filtered chloroform.

Influent and effluent (in test sequence)

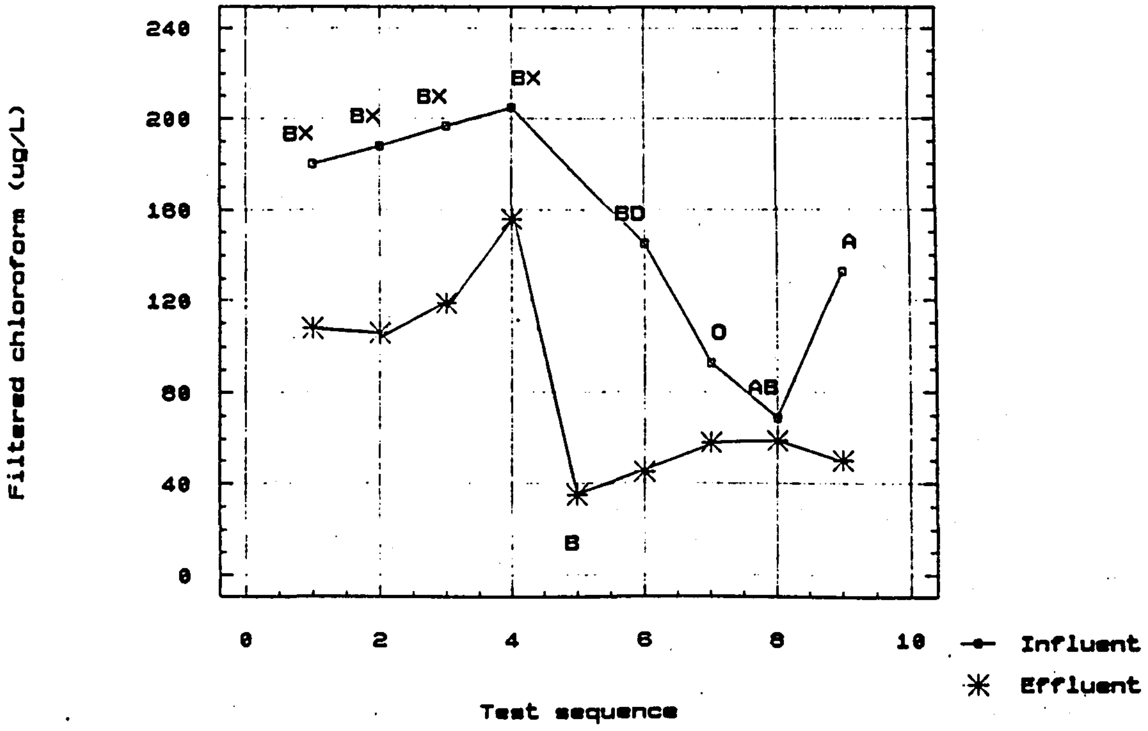


Figure 5.32

Full-scale plant tot. bromodichloroform
Influent and effluent (in test sequence)

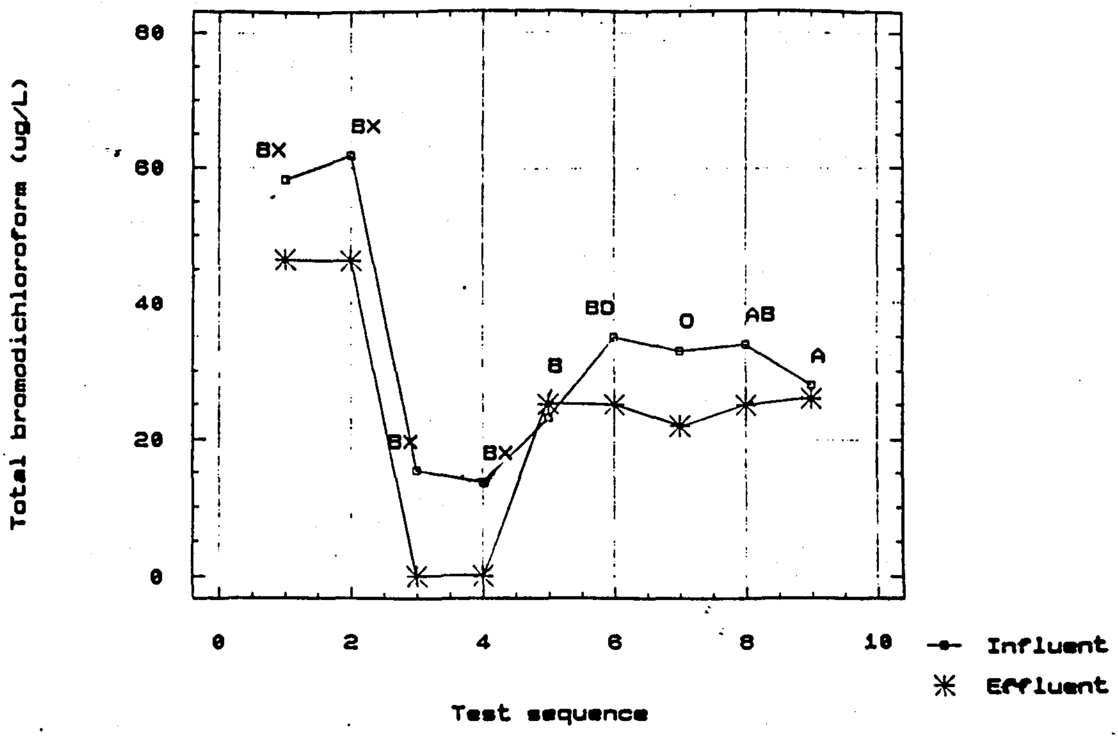


Figure 5.33

Full-scale plant filt. bromodichloroform
Influent and effluent (in test sequence)

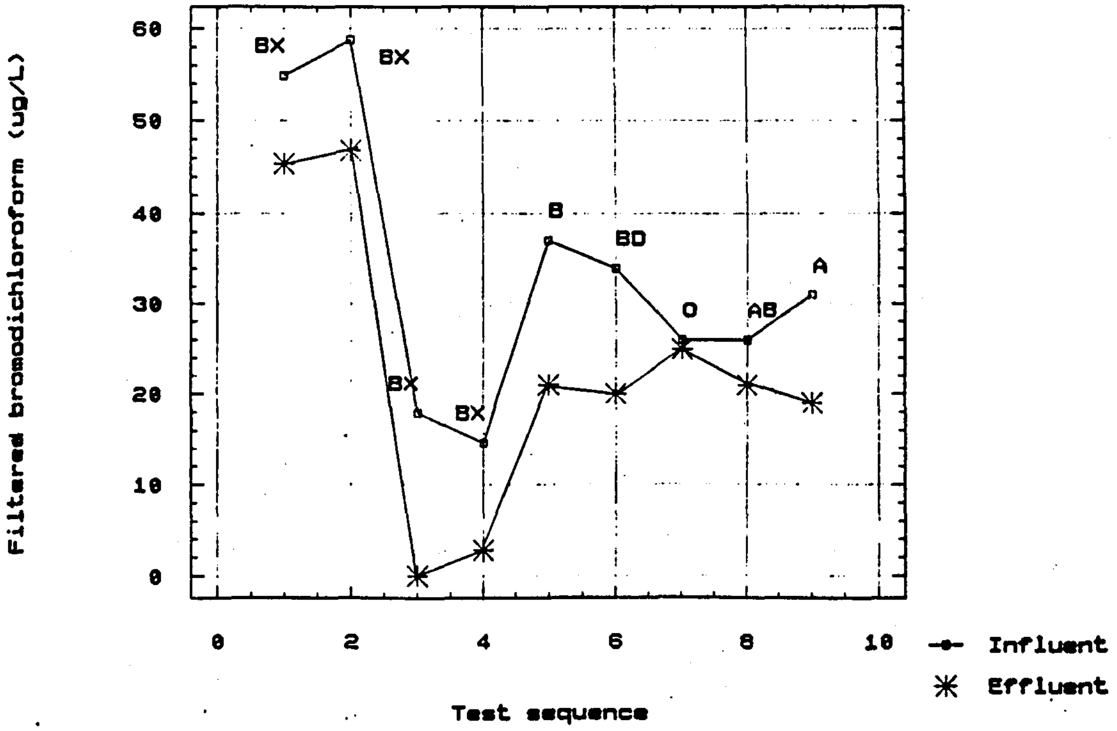


Figure 5.34

Full-scale plant total DOC.
Influent and effluent (in test sequence)

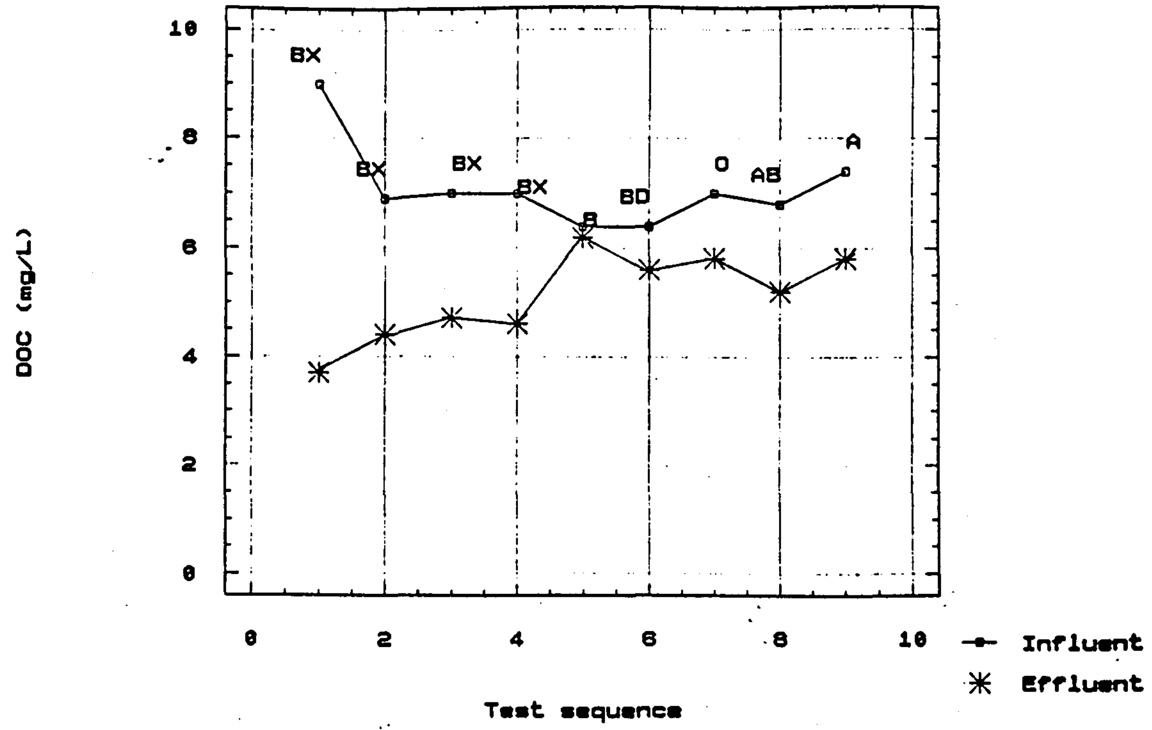


Figure 5.35

Full-scale total THMP.
Influent and effluent.

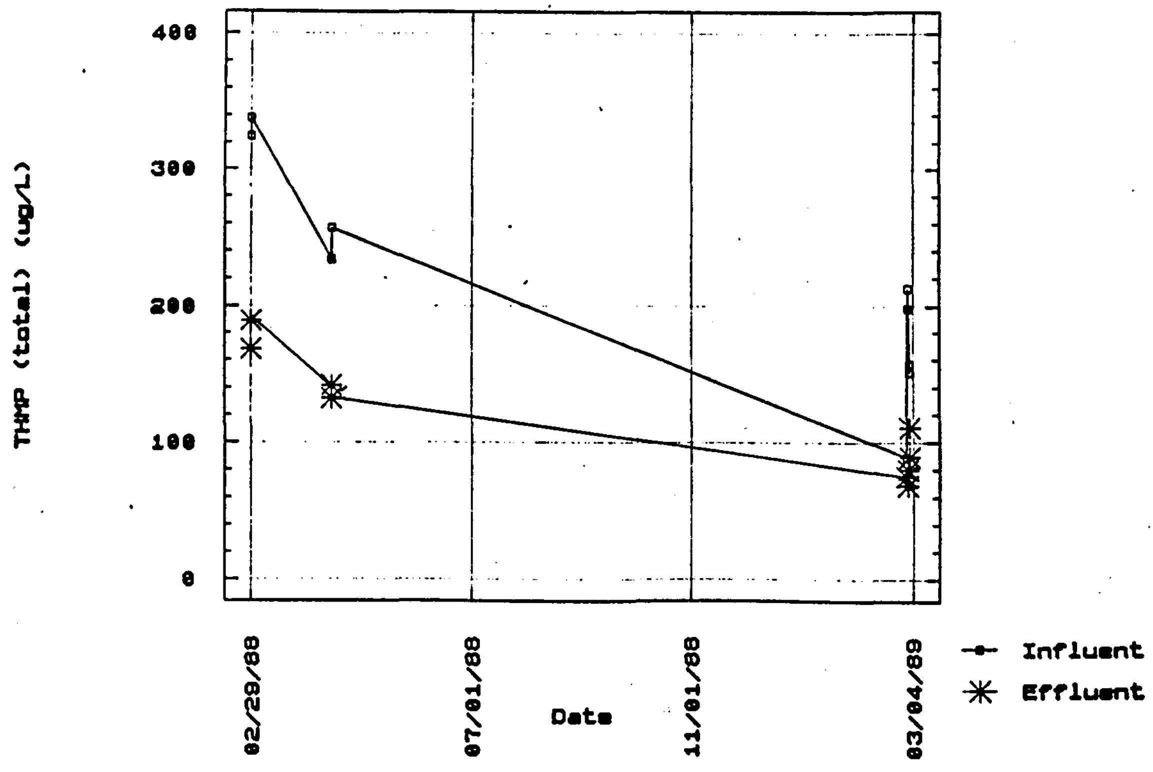


Figure 5.36

Full-scale filtered chloroform
Influent and effluent

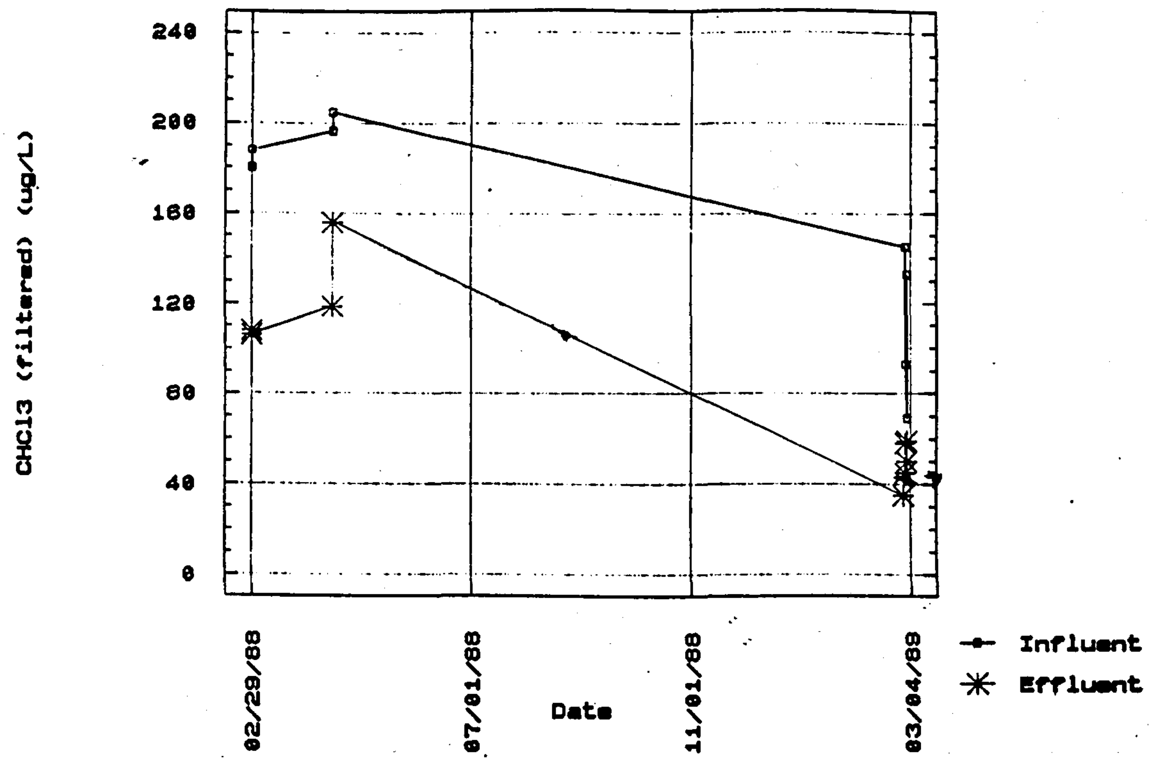


Figure 5.37

Full-scale total bromodichloroform.
Influent and effluent.

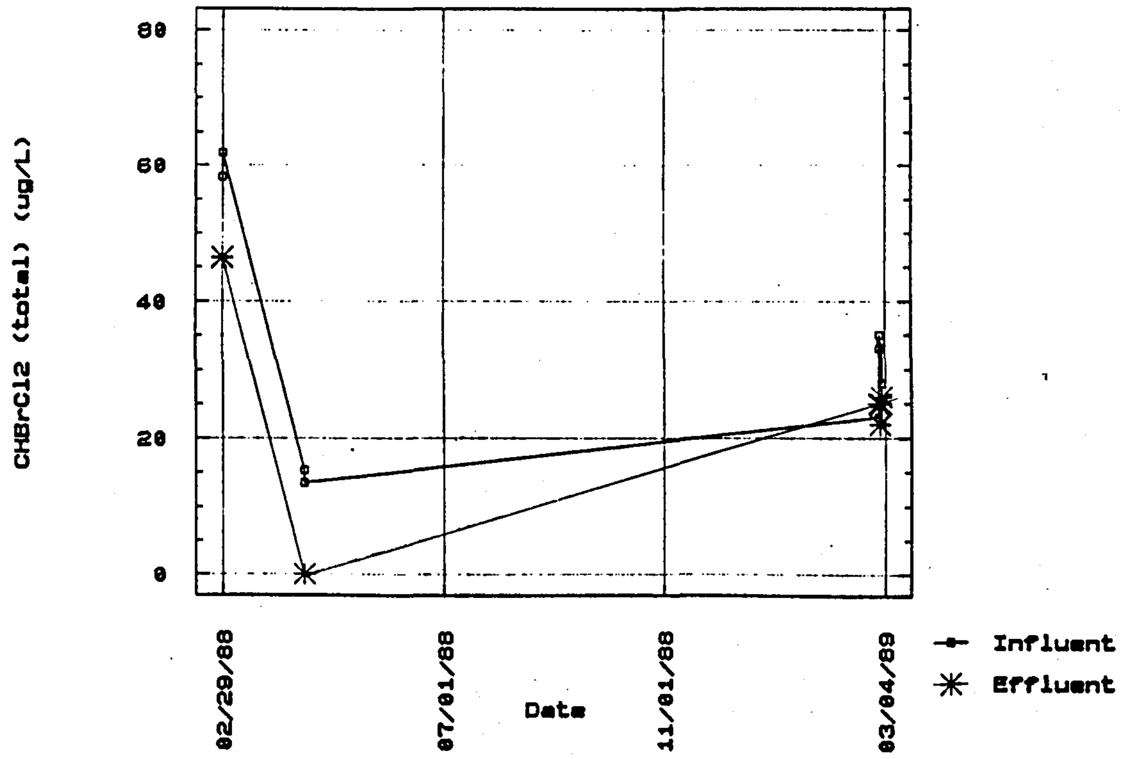


Figure 5.38

Full-scale total DOC

Influent and effluent

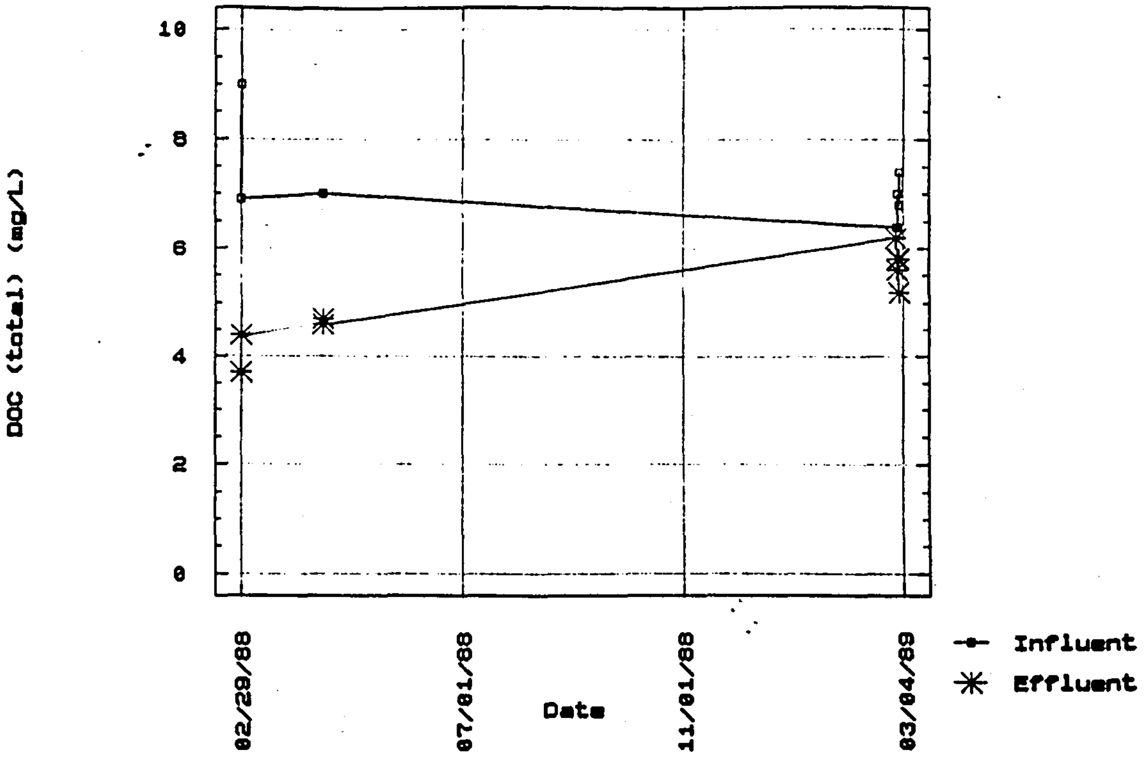
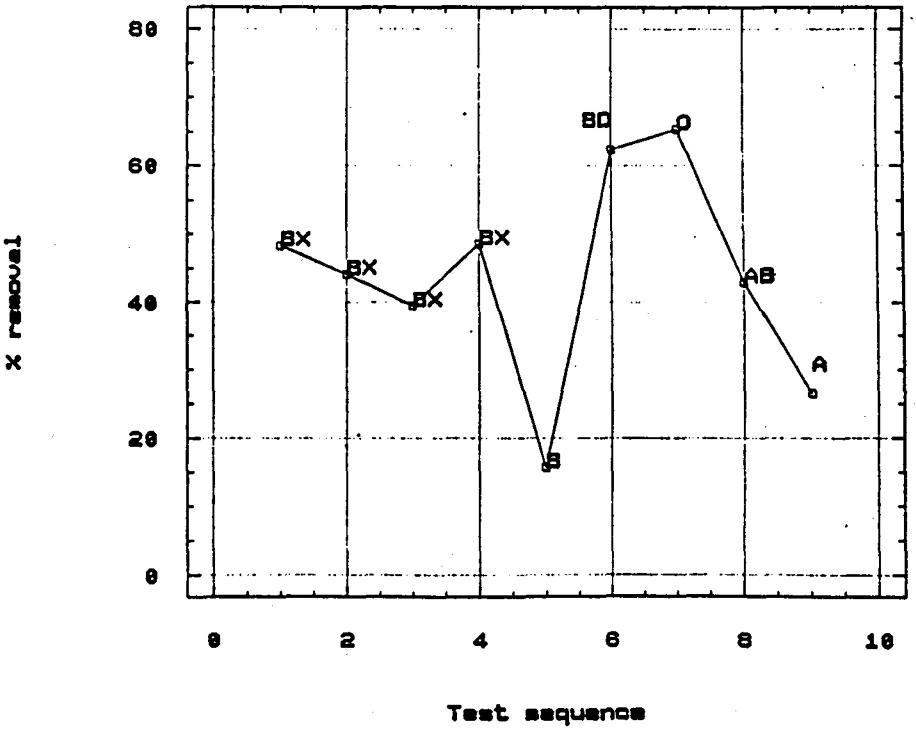


Figure 5.39

Percent removal in the full-scale plant.

Total THMP.



## 5.6 General parameter correlations, and ratios between chloroform and bromodichloroform.

Correlation analyses for all the measured variables (influent, effluent, and combined data) for the pilot and full-scale plants are given in Appendix A4, and some of the more interesting regressions with high correlation coefficients are plotted in Figures 5.40 - 5.43 (influent and effluent variables), and Figures 5.44 - 5.46 for chlorophyll *a*.

Figure 5.40 shows a strong correlation between influent THMP and pH for the pilot plant (R = 0,904; the full-scale plant had the same influent, but it was sampled on fewer occasions, and R = 0,868). This result points to the contribution of high algal activity - yielding a corresponding high pH - also being responsible for high THMP production. A similar correlation with pH is evident for turbidity (Figure 5.41), and this is consistent with the high algal activity/growth being responsible for high pH.

Interestingly, regression coefficients between influent THMP and DOC were low, which implies that only a portion of the dissolved organics are responsible for THMP. However, the relationship with DOC is further complicated when examining plant effluents. A reasonably high positive correlation coefficient (R = 0,775; Figure 5.42) was found between effluent total $CHCl_3$ and total DOC for the pilot plant, however for the full-scale plant, the value of this coefficient was high but negative (R = -0,871; Figure 5.43). It is difficult to find a rational explanation for this behaviour, and one must conclude simply that DOC is a poor indicator of THMP, either in terms of raw water quality, or removal.

Regressions of THMP, pH and turbidity on chlorophyll a are shown in Figures 5.44 - 5.46 respectively. Although the regression coefficients are not particularly high (the R value for turbidity being the highest at 0,80), the figures do show that chlorophyll *a* will increase with each parameter. Since algae are well known as being responsible for increases in turbidity, pH and chlorophyll *a*, it is reasonable to conclude from these graphs that they will also cause the increase in THMP. Also, since chlorophyll *a* and other parameters associated with measuring algal production and influence are known to be problematic, correlations such as 0,664 for Figure 5.44 are meaningful. Thus, given the above evidence, albeit circumstantial, algae and their exocellular products

Figure 5.40

Regression of pilot plant influent total THMP on pH.

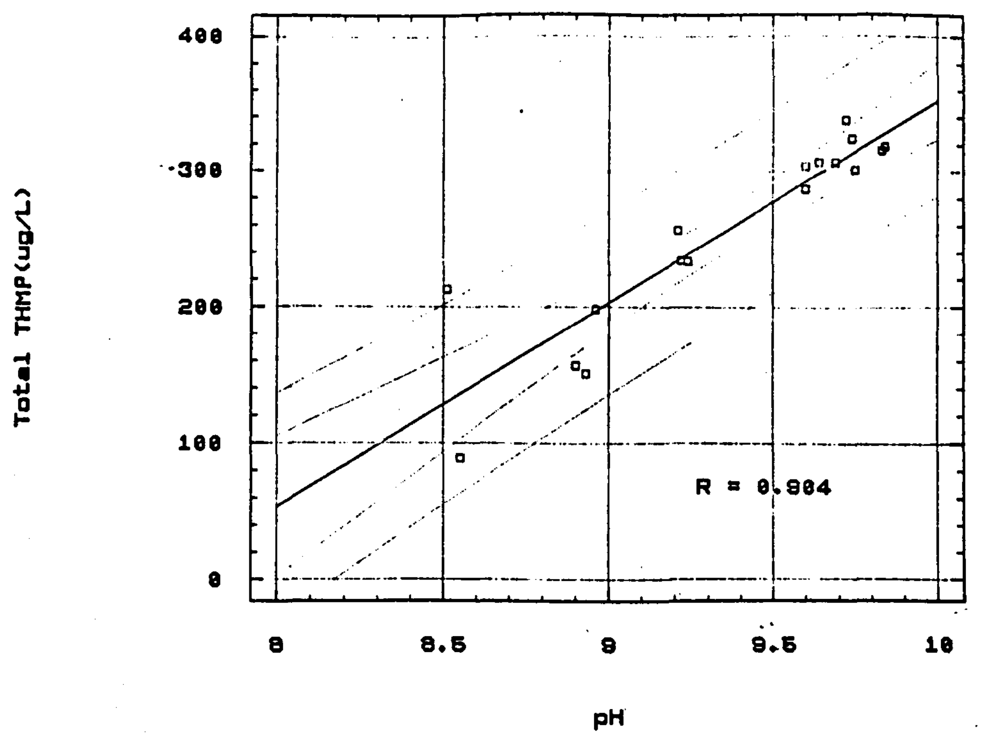


Figure 5.41

Regression of pilot plant influent turbidity on pH

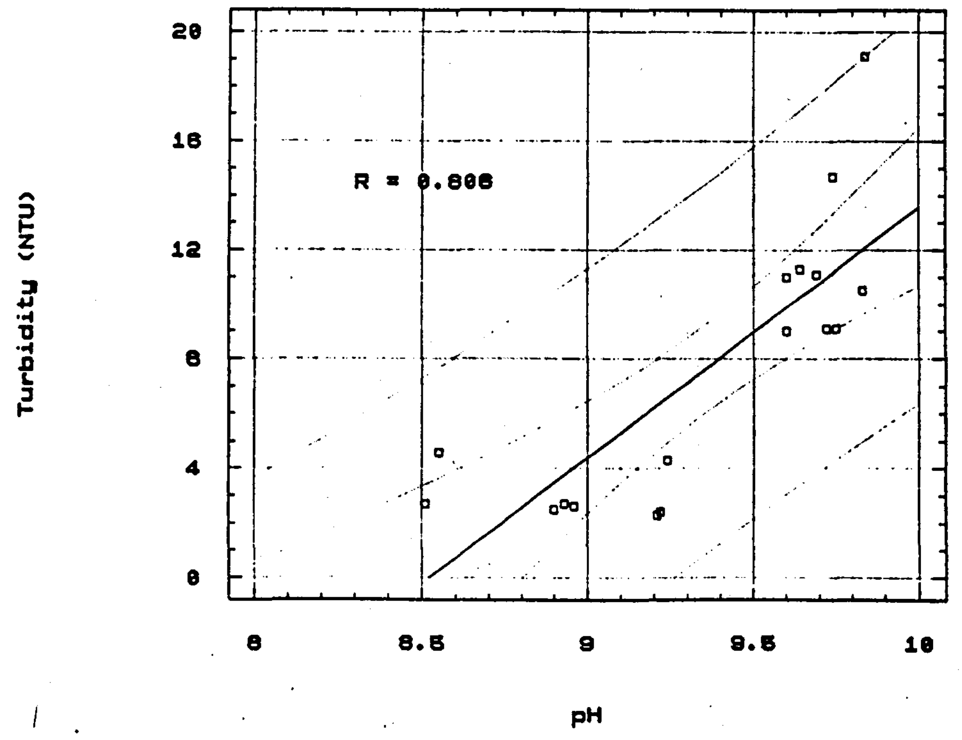


Figure 5.42

Regression of pilot plant effluent.
Total CHCl3 on total DOC

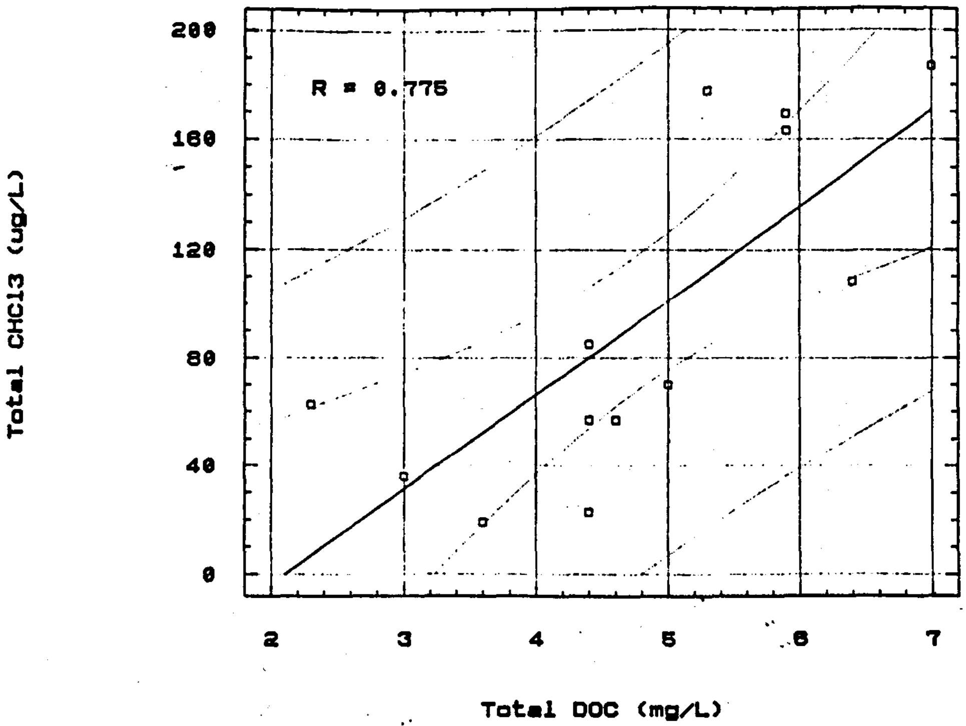


Figure 5.43

Regression of full-scale effluent
Total THMP on total DOC

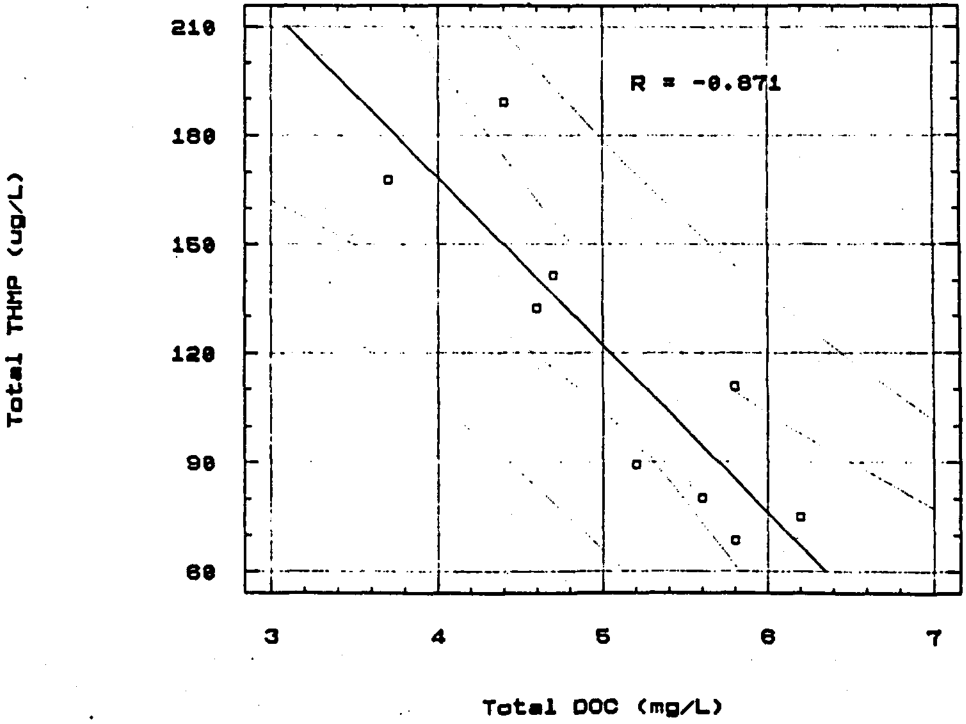


Figure 5.44

Regression of total THMP on chlorophyll

Pilot plant influent

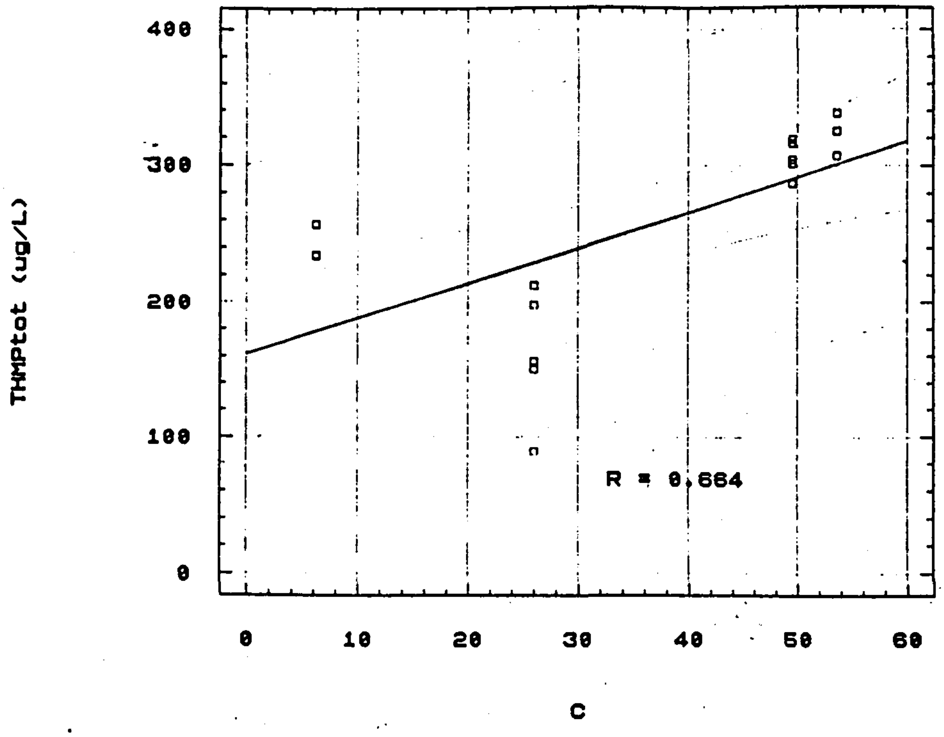


Figure 5.45

Regression of pH on chlorophyll a

Pilot plant influent

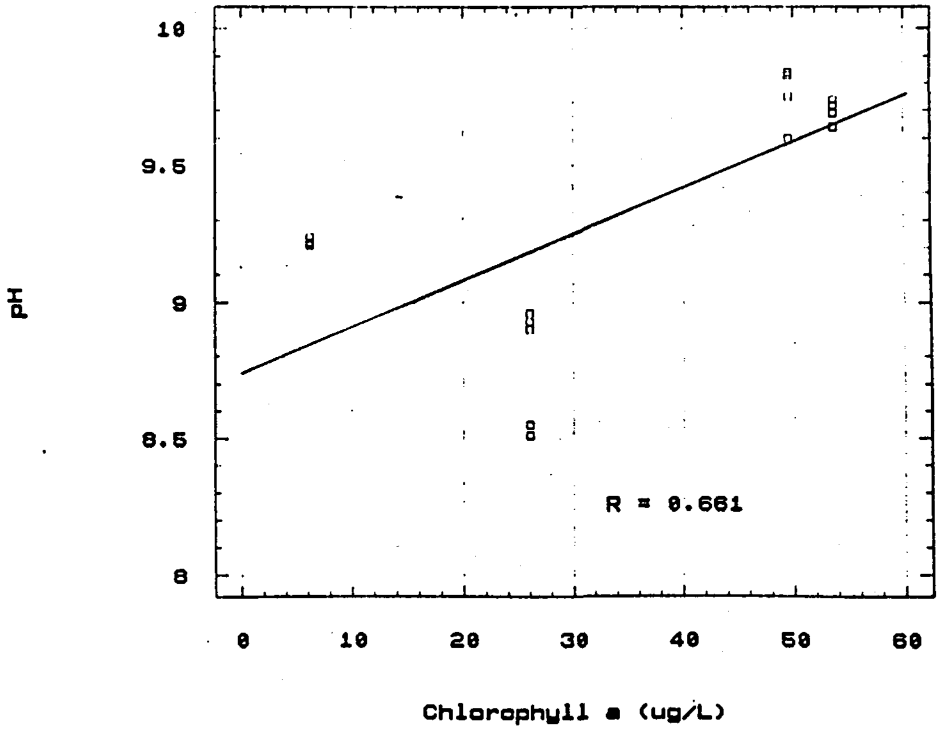
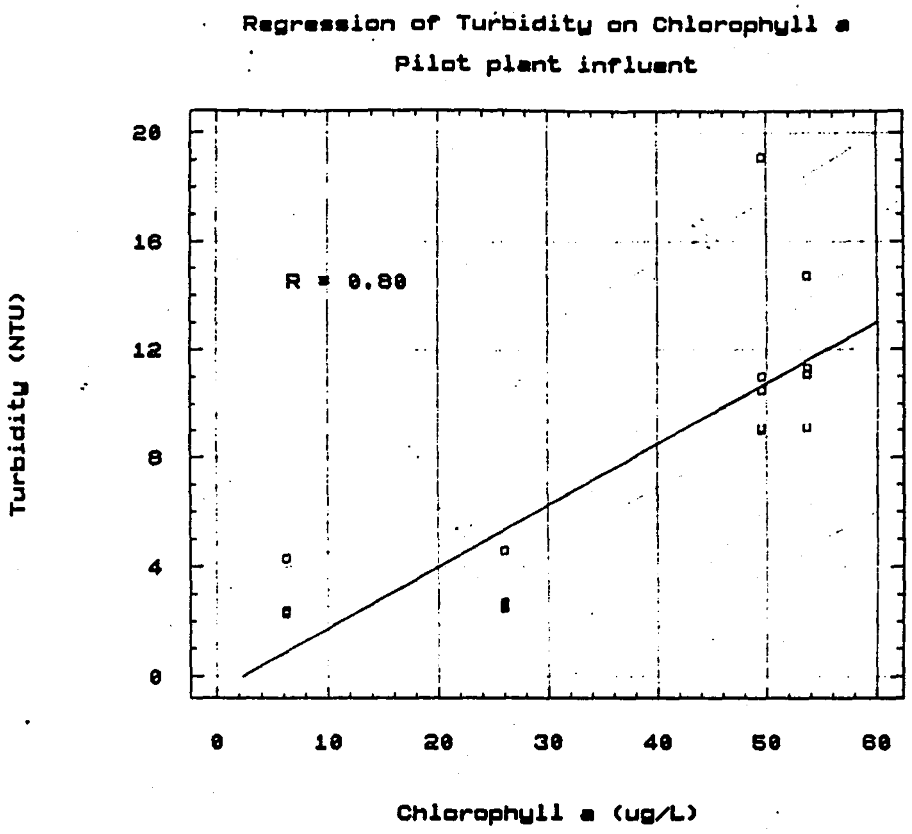


Figure 5.46


Regression of Turbidity on Chlorophyll a
Pilot plant influent
R = 0.80
Turbidity (NTU)
0
4
8
12
16
20
0
10
20
30
40
50
60
Chlorophyll a (ug/L)

can be considered to have a major impact on the THMP concentration.

An examination of the relative concentrations of chloroform and bromoforms in the influent and effluent is of interest due to the relatively high concentration of bromide in Hartbeespoort Dam (about 0,6 mg/ℓ) - hence a higher than normal concentration of these bromoforms in chlorinated effluents - and the fact that pH modification could change the reactivity of chlorine to bromide and hence alter the distribution of trihalomethane species in the effluent. Analysis actually showed that there was only very weak correlation between the ratios of the two haloforms (ie. $CHCl_3$:$CHBrCl_2$) and pH. However other interesting trends emerged. The first is that the above ratio for total, filtered, influent and effluent samples remained more or less constant over the entire series of tests, except for those done on April 14, 1988. Shortly before this date, Hartbeespoort Dam overflowed, and it can be seen in Figures 5.47 - 5.50 that the ratio increased severalfold. This implies that bromoform concentrations were much lower than usual, compared with chloroform. Unfortunately, raw water bromide measurements were not taken at this time, but it is probable that the loss of algal biomass was accompanied by reductions in bromide concentrations.

The second point to emerge is that the ratio for the filtered sample is consistently lower than for the total sample, in both the influent (Figure 5.42) and the effluent (Figure 5.43), except for the April 14th case, but for the effluent the difference is smaller. Figures 5.44 and 5.45 also show that, apart from the April 14th anomaly, the ratios for the influent are consistently higher than for the effluent, for both filtered and unfiltered samples. The probable explanation here is that during chlorination of the samples in the laboratory to convert the precursors into the various trihalomethane species, the bromine reactants formed by chlorination of the bromide (such as HOBr) are more reactive than the chlorine species (such as HOCl). Thus bromoforms would be formed more rapidly, and chloroform would be formed from the remaining organics. Since the DAF process will remove much of the organics, and of these especially the "insoluble" component, greater reductions in halogenated species will be observed for chloroform than for bromoform. The result is thus more an artifact of the chemical reactions following precursor removal than any selection of precursor components during removal itself.

Figure 5.47

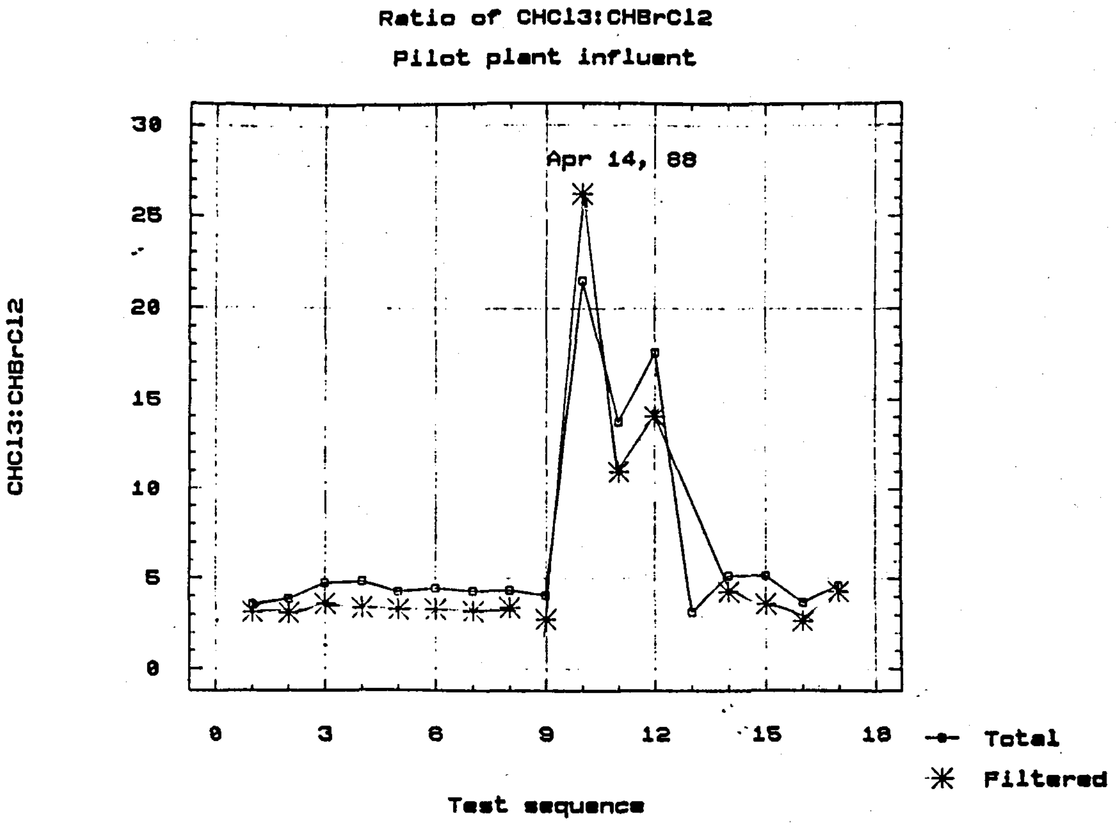


Figure 5.48

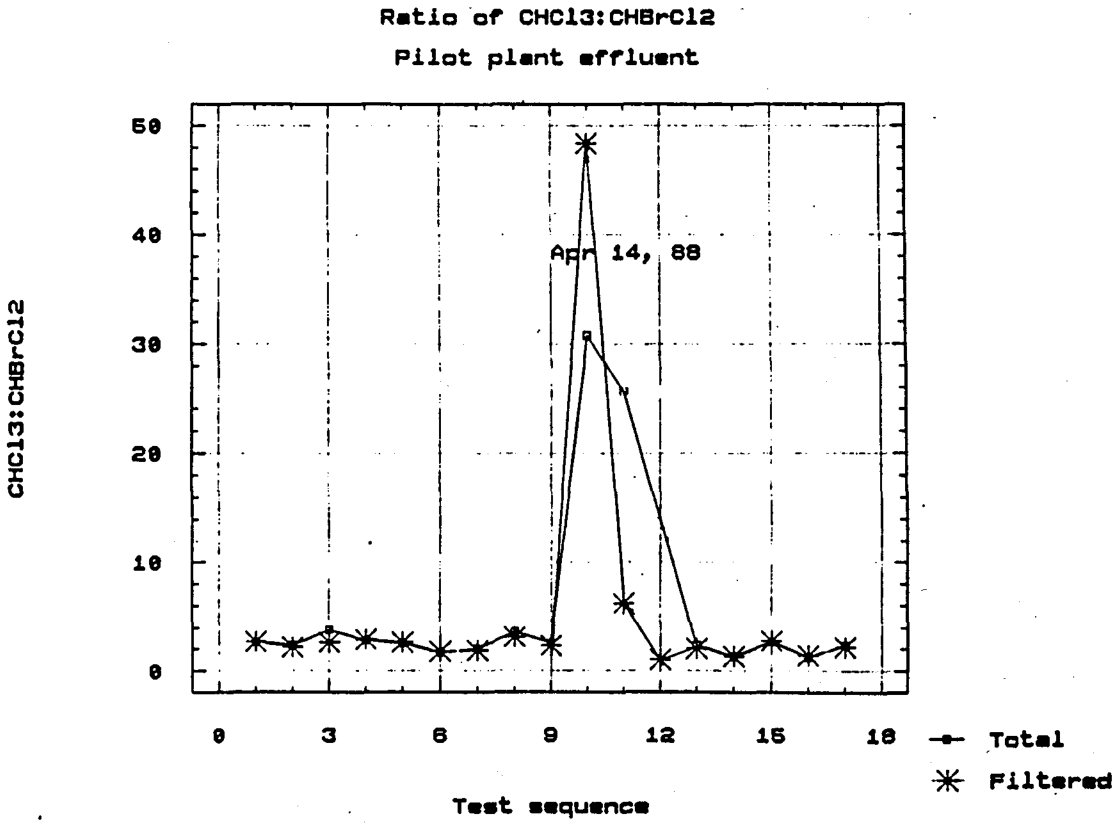


Figure 5.49

Ratio of total $CHCl_3:CHBrCl_2$.
Pilot Plant

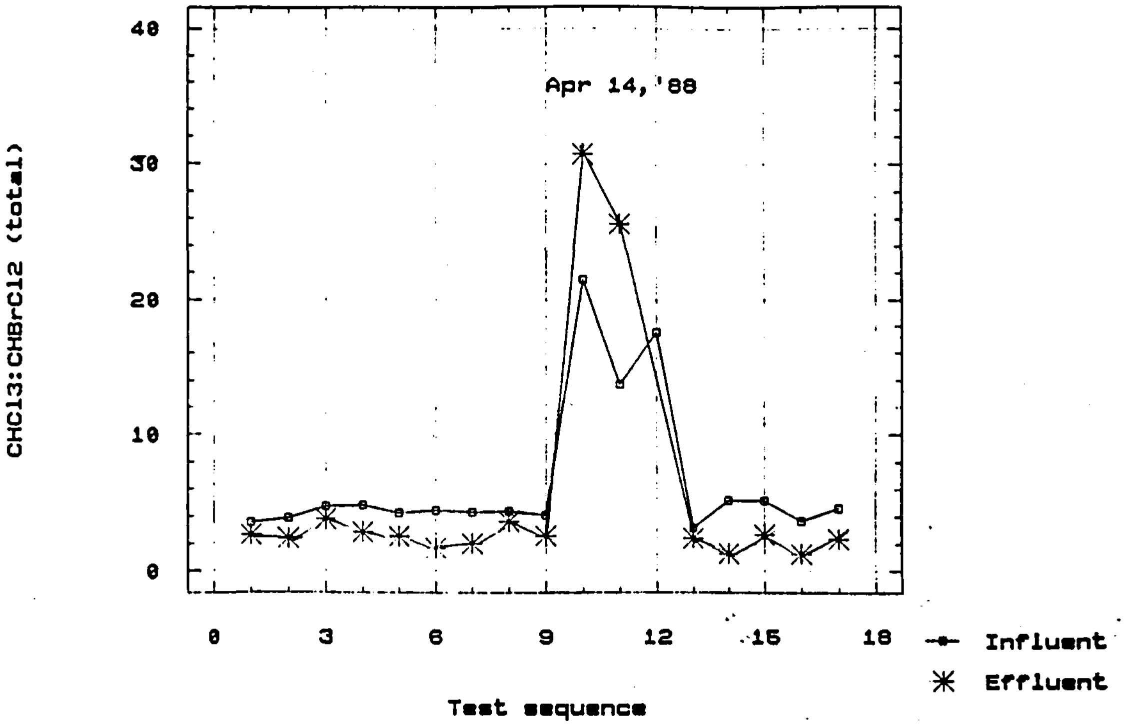
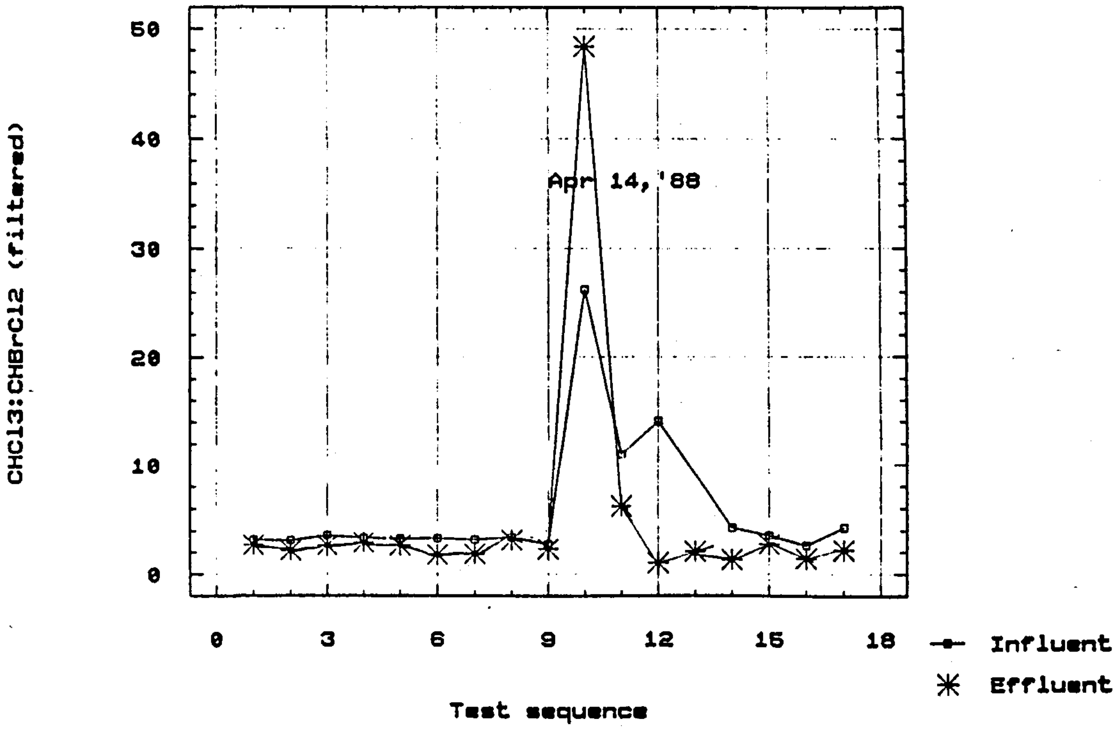


Figure 5.50

Ratio of filtered $CHCl_3:CHBrCl_2$.
Pilot plant



# CHAPTER 6

# SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

## 6.1 Summary.

In preparation for pilot and full-scale tests which investigated the use of dissolved air flotation (DAF) for the removal of trihalomethane precursors (THMP) from eutrophic waters, a number of preliminary tests were done. Hartbeespoort Dam was chosen as the source of raw water, as it was well known as a eutrophic - if not hypertrophic - water body. Furthermore, a full-scale DAF plant was already operational as part of the drinking water treatment process for the town of Schoemansville, on the banks of Hartbeespoort dam. A summary and discussion of pertinent water quality parameters of the dam is included in Chapter 4. Microcystis aeruginosa is the dominant algal species for much of the year, but other significant species include Oocystis, Cryptomonas, and Cyclotella. Other parameters of specific interest to the study include the high pH (typically above 9), high bromide concentrations (average 0,63 mg/ℓ), and THMPs of the raw water sometimes exceeding 300 µg/ℓ. High DOC values (average around 7 mg/ℓ) and chlorophyll a values as high as 159 µg/ℓ are indeed indicative of hypertrophic conditions.

Chapter 4 also includes the results of 2 additional sets of preliminary experiments: jar tests and batch DAF tests. Jar tests investigated the effects of alum, polymer, and bentonite on turbidity and THMP removal. The overall optimum doses for both turbidity and THMP removal (98,1% and 59,5% respectively) were 113 mg/ℓ alum and 0,5 mg/ℓ polymer. Slightly higher removals were possible at much higher doses of alum and polymer, while bentonite addition yielded only small improvements in THMP removal, but was detrimental to turbidity removal. Batch DAF tests involved preliminary tests to choose useful ranges for the various parameters, followed by 2 sets of factorial tests ($2^5$ and $3^3$) to eventually determine the optimum values of these parameters. Bentonite was eliminated after the first factorial set, and the optimum recycle ratio was also fixed after analysis of this first set. The second set indicated that high alum (150 mg/ℓ) and low pH (5) would be most beneficial in THMP removal, but there was no clear effect due to polymer addition (0,3; 0,6; or 0,9 mg/ℓ). Finally, correlation analyses performed on data from the $3^3$ factorial experiments showed no relationship between THMP, DOC, or total organohalogen precursors (TOHP).

The results of pilot and full-scale tests are given in Chapter 5. The pilot plant consisted of rapid- and slow-mix tanks for coagulant addition (alum or $FeCl_3$, and polymer), a reservoir for acid or base addition, and a flotation tank/air dissolution system. A computerized data acquisition and control system could take temperature, pH and turbidity measurements, and control the pH. A $2^3$ factorial set of tests was performed to assess the impact of $FeCl_3$ and polymer doses, as well as pH control. The full-scale system included a flocculation tank, preceded by chemical addition ($FeCl_3$, polymer, and powdered activated carbon (PAC)) to a small influent box, and a flotation tank/air disssolution system. There was no pH adjustment or computer control.

Relatively high removal of THMP was possible in the pilot plant - over 80%, with effluent THMPs as low as 30 µg/ℓ - but turbidity removals were only 40 - 60%. The statistical analysis showed that a high $FeCl_3$ dose of 150 mg/ℓ, together with a low pH of around 5, were significant in obtaining optimum removals. Polyelectrolyte addition was not as important. Poorer performance was experienced in the full-scale plant: only 65% THMP reduction. This was achieved at low $FeCl_3$ doses (50 mg/ℓ) and zero polymer addition, but also at high $FeCl_3$ dose (100 mg/ℓ), as well as at 50 mg/ℓ $FeCl_3$, 10 mg/ℓ PAC, and 0,6 mg/ℓ polymer.

Both influent THMP and influent turbidity correlated well with pH, which is indicative of a high algal activity being responsible for much of the precursors. Overall, DOC correlated poorly with THMPs. The ratio of chloroform ($CHCl_3$) to bromodichloroform ($CHBrCl_2$) changed dramatically immediately following overflow of the Hartbeespoort Dam in March, 1988. There was a reduction in $CHCl_3$:$CHBrCl_2$ from influent to effluent, which confirms the higher reactivity of bromine to the organics.

## 6.2 Conclusions.

The study has shown that dissolved air flotation, preceded by the addition of coagulants, as well as pH control, is capable of reducing trihalomethane precursor concentrations from above 300 μg/ℓ to below the 100 μg/ℓ level which is a reasonable standard for drinking water. This is best accomplished at adjusted influent pH 5,0 and $FeCl_3$ addition of 150 mg/ℓ. In many cases it will be unnecessary to acidify the influent, as the $FeCl_3$ itself will reduce the pH to the required level. The need for polymer (polyelectrolyte) as a coagulant aid is questionable, and powdered activated carbon addition is unnecessary (although it may be desirable for taste and odour control).

There is little doubt that algae in the dam, either as biomass or as producers of extracellular material, are responsible for a major component of the precursors. This shown by the strong correlation of THMP and turbidity with pH, which in turn is elevated due to high algal activity. Correlations between chlorophyll *a*, and THMP, pH and turbidity, were also positive. The poor correlation of THMP with DOC indicates that many of the organics not associated with algae are not effective THM precursors. Bromide concentrations in the dam are responsible for higher than normal ratios of bromoforms to chloroforms, and it appears that a sudden loss of algae due to dam overflow will reduce bromide as well as bromoform concentrations. While it is known that bromines are more reactive than chlorines to organics, and that chloroform concentrations might be reduced by increasing bromide concentrations and hence bromoforms, this is not recommended as a control strategy in view of the unknown toxicities of bromoforms to humans.

## 6.3 Recommendations.

1). The role of algae in THMP formation should be studied explicitly. This is best accomplished by a number of subsidiary studies, including pure culture studies, laboratory assessment of the effects of light and dark cycles on THMP production, and continuing studies on-site at various locations and times of the year. The influence of algal growth on bromine, and the resulting impact on THM concentrations, should also be investigated.

2). Work should be continued at the full-scale DAF plant at Schoemansville, to optimize conditions for THMP removal. Chemical addition and flocculation must be improved to provide adequate rapid mixing, as well as slow mixing and detention for optimum floc growth. PAC could be eliminated if possible, due to its high costs, and provided that it is not needed for taste and odour control. Computer control should be employed to improve operation and data collection. The Schoemansville Plant is already a unique facility; it should be converted into an excellent full-scale research operation investigating many aspects of the interaction of hypertrophic water sources with various water treatment modes.

3). A knowledge of the molecular mass distribution (MMD) of THMPs, as well as of any remaining THMs after chlorination, is important to the understanding of THM production, and the removal of THMPs or THMs, should basic coagulation and separation processes be insufficient. The MMD of the materials to be removed will dictate which of various adsorbents will be suitable, or whether it is necessary to employ reverse osmosis. Further studies regarding MMD of organics in eutrophic water bodies, as well as the resulting halogenated products, are needed.

4). The need for establishing surrogate parameters to assess THMP levels more rapidly and cheaply is imperative. Total organohalogen measurements (TOX) have been studied briefly for the present project, and these results have not been encouraging. However TOX will continue to be an important parameter when considering the non-volatile components of chlorination. Iodoform and bromoform measurements are possible indirect measures of THM, and their use should be explored.

5). The analytical capabilities of local laboratories measuring THMs as well as other chlorinated organics will have to be improved. In particular, automated purge-and-trap facilities, ideally coupled with a mass selective detector, will be required if large numbers of tests on chlorinated organics are to be done.

6). Long-term plans should include wide ranging studies into the toxicity of all possible chlorinated organics. Since chlorination of drinking water is ubiquitous worldwide, and since there is concern that chlorinated products other than the THMs could also be detrimental to health, South Africa should plug into the international research community, and provide its contribution in giving a realistic perspective regarding the dangers - or otherwise - of chlorination of drinking water. Epidemiologic studies in South Africa and neighbouring countries is an urgent priority, as is the setting of limits, in drinking water standards, on THMs and other chlorinated organics. In the short term, although there is disagreement regarding the appropriate absolute level for a THM standard (the range is 1 - 350 µg/ℓ), it is strongly recommended that an interim, legally mandated standard be set for South Africa immediately, so that excessively high values in domestic drinking water can be avoided. The 100 µg/ℓ value currently being used in the United States would seem to strike a good balance beween what is practical to achieve (and measure) and what might be ultimately desired.

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# APPENDIX A1

# PROGRAMS FOR COMPUTER CONTROL OF THE PILOT PLANT

```
10 ! ***"TURBCAL"***
20 ! PROGRAM FOR CALIBRATING TURBIDIMETER
30 ! USING CHANNEL 2
40 DISP "THE VALUES OBTAINED" @ WAIT 3
50 DISP "FOR INTERCEPT AND SLOPE" @ WAIT 3
60 DISP "SHOULD BE ENTERED MANUALLY" @ WAIT 3
70 DISP "IN THE 'CONVERT' PROGRAM" @ WAIT 5
80 OPTION BASE 1
100 DESTROY ALL
110 DISP "TURBIDITY CALIBRATION" @ WAIT 5
120 DISP "PRESS'CONT'TO CONTINUE" @ PAUSE
130 DISP "5 POINT CALIBRATION" @ WAIT 5
140 DIM P(30)
150 STAT T(2)
160 CLSTAT
170 FOR I=1 TO 5
180 K=0
190 DISP "POINT ";I @ WAIT 5
200 INPUT "ENTER'R'WHEN STABLE ";R$
210 IF R$="R" THEN GOTO 220
220 OUTPUT ;1 ;"DCV2-2"
230 FOR J=1 TO 30
240 ENTER :1 ;P(J)
250 K=K+P(J)
260 NEXT J
270 A=K/30
280 INPUT "ACTUAL TURBIDITY?";B
290 ADD A,B
300 NEXT I
310 DISP "CORRELATION" @ DISP CORR(1,2) @ WAIT 5
320 LR 1,2,C,M
330 DISP "INTERCEPT= ";C @ WAIT 5
340 DISP "SLOPE= ";M
350 ASSIGN #3 TO DATATURB
360 PRINT #3;C,M
370 ASSIGN #3 TO *
380 END
```

```
10 ! ***CONVERT***
20 ! FILE CONTAINING CONVERSION/CALIBRATION SUBPROGRAMS
30 ! FOR DATA LOGGER SETUP PROGRAMS ("DAFPH5" & "DAFPH7")
40 !
50 ! CONVERSION PROGRAM FOR TURBIDITY MEASUREMENTS.
60 ! CALIBRATION PROGRAM ITSELF IS "TURBCAL"
70 SUB CALIBRAT(R( ),N)
80 ASSIGN #3 TO DATATURB
90 RESTORE #3
100 READ #3;C,M
120 FOR I=1 TO N
130 R(I)=(R(I)-C)/M
140 NEXT I
150 END SUB
160 !
170 ! CONVERSION PROGRAM FOR REMOTE pH
180 ! USING pH TRANSMITTER AND
190 ! CALIBRATION PROGRAM "REMPHCAL"
200 SUB CALIBPHR(R( ),N)
205 ASSIGN #1 TO DATAPHR
210 RESTORE #1
220 READ #1;M,C
230 FOR I=1 TO N
240 R(I)=C+M*R(I)
250 NEXT I
260 END SUB
270 !
280 ! CONVERSION PROGRAM FOR DIRECT pH MEASUREMENTS
290 ! USING METROHM ELECTRODE DIRECTLY INTO CHANNEL 3
300 ! CALIBRATION PROGRAM IS "PHCALIB"
310 SUB CALIBPH(R( ),N)
315 ASSIGN #2 TO DATAPH
320 RESTORE #2
330 READ #2;A1,T,C1
340 FOR I=1 TO N
350 R(I)=(R(I)-A1)*5039.08/(273+T)*C1+7
360 NEXT I
370 END SUB
380 !
390 ! CONVERSION PROGRAM FOR STRIP CHART
400 ! RECORDING OF METROHM pH
410 SUB CALIBMET(S)
415 ASSIGN #2 TO DATAPH
420 RESTORE #2
430 READ #2;A1,T,C1
440 S=(S-A1)*5039.08/(273+T)*C1+7
450 END SUB
460 !
470 ! CONVERSION PROGRAM FOR STRIP CHART
480 ! RECORDING OF pH AMPLIFIER
490 SUB CALIBAMP(S)
495 ASSIGN #1 TO DATAPHR
500 RESTORE #1
510 READ #1;M,C
520 S=C+M*S
530 END SUB
540 !
550 ! CONVERSION PROGRAM FOR STRIP CHART
560 ! RECORDING OF TURBIDITY
570 SUB CALTURB(S)
580 ASSIGN #3 TO DATATURB
590 RESTORE #3
```

```
10 ! ***"REMPHCAL"***
20 ! PROGRAM FOR CALIBRATING pH VIA
30 ! pH TRANSMITTER (1-5 VOLT SIGNAL)
40 ! USING CHANNEL 4
50 DESTROY ALL
60 OPTION BASE 1
70 DIM H1(30),H2(30)
80 DISP "REMOTE pH CALIB" @ WAIT 5
90 DISP "USE HIGHER BUFFER FIRST" @ WAIT 5
100 DISP "PRESS'CONT'TO CONTINUE" @ PAUSE
110 DISP "PROBE IN CHANNEL 04" @ WAIT 5
120 INPUT "ENTER BUFFER#1 pH  ";B1
130 ! FIRST BUFFER
140 INPUT "ENTER'R'WHEN READY  ";R$
150 IF R$="R" THEN GOTO 160
160 OUTPUT :1 ;"DCV4-4"
170 FOR J=1 TO 30
180 ENTER :1 ;H1(J)
190 K1=K1+H1(J)
200 NEXT J
210 A1=K1/30
220 ! SECOND BUFFER
230 INPUT "ENTER BUFFER#2 pH  ";B2
240 INPUT "ENTER'R'WHEN READY ";Q$
250 IF Q$="R" THEN GOTO 260
260 OUTPUT :1 ;"DCV4-4"
270 FOR I=1 TO 30
280 ENTER :1 ;H2(I)
290 K2=K2+H2(I)
300 NEXT I
310 A2=K2/30
320 M=(B2-B1)/(A2-A1)
330 C=B1-M*A1
340 DISP "CALIB EQUATION IS..." @ WAIT 5
350 DISP "pH = ";M;"*V + ";C
370 ! THE FOLLOWING STATEMENTS ARE TO ALLOW
390 ! THE DATA LOGGER TO USE CALIBRATION EQUATION IN
390 ! FILE "CONVERT", SUBPROGRAM "CALIBPHR"
400 ASSIGN #1 TO DATAPHR
410 PRINT #1;M,C
420 ASSIGN #1 TO *
430 END
```

```
10 ! ***PHCALIB***
20 ! PROGRAM FOR CALIBRATING
30 ! pH PROBE DIRECTLY USING CHANNEL 3.
40 DIM H1(30),H2(30)
50 OPTION BASE 1
60 DISP "pH CALIBRATION" @ WAIT 5
70 DISP "PRESS'CONT'TO CONTINUE" @ PAUSE
80 K1=0 @ K2=0 @ A1=0 @ A2=0 @ T=0
90 DISP "NOTE: USE THIS PROBE" @ WAIT 5
100 DISP "(IN CHANNEL 3)" @ WAIT 5
110 DISP "FOR THE INFLUENT" @ WAIT 5
120 DISP "FIRST BUFFER MUST BE pH 7" @ WAIT 5
130 DISP "AND TEMP OF BUFFER AND" @ WAIT 5
140 DISP "INFLUENT SHOULD BE EQUAL." @ WAIT 5
150 ! LATER, COULD PERHAPS PROGRAM
160 ! TEMPERATURE READING FROM PROBE IN CHANNEL 5
170 !
180 ! FIRST BUFFER
190 INPUT "ENTER BUFFER#1 pH ";B1
200 INPUT "ENTER TEMP ";T
210 INPUT "ENTER'R'WHEN READY ";R$
220 IF R$="R" THEN GOTO 230
230 OUTPUT :1 ;"DCV3-3"
240 FOR J1=1 TO 30
250 ENTER :1 ;H1(J1)
260 K1=K1+H1(J1)
270 NEXT J1
280 A1=K1/30
290 ! SECOND BUFFER
300 INPUT "ENTER BUFFER#2 pH ";B2
310 INPUT "ENTER'R'WHEN READY ";Q$
320 IF Q$="R" THEN GOTO 330
330 OUTPUT :1 ;"DCV3-3"
340 FOR J2=1 TO 30
350 ENTER :1 ;H2(J2)
360 K2=K2+H2(J2)
370 NEXT J2
380 A2=K2/30
390 ! SENSITIVITY CALCULATION
400 ! IDEAL CONDITIONS
410 E1=(B1-B2)*(273+T)/5039.08
420 ! ACTUAL CONDITIONS
430 C1=(A1-A2)/E1
440 DISP "SENSITIVITY = ";C1 @ WAIT 10
450 ! THE FOLLOWING STATEMENTS ARE TO ALLOW
460 ! THE DATA LOGGER TO USE CALIBRATION EQUATION IN
470 ! FILE "CONVERT", SUBPROGRAM "CALIBPH"
480 ASSIGN #2 TO DATAPH
490 PRINT #2:A1,T,C1
500 END
```

```
10 ! ***PHCONTRL***
20 ! LIMIT PROGRAM FOR pH CONTROL
30 ! USING MAGNETIC VALVE SWITCHED BY CHANNEL 10
40 ! AND pH PROBE (VIA AMPLIFIER) IN CHANNEL 04
50 !
60 SUB MGV5(R1)
70 ! SUBPROGRAM FOR MAINTAINING pH 5
90 OPTION BASE 1
120 GOTO 160
130 IF R1<=5.1 THEN GOTO 'EXIT'
140 CLOSE 10 @ WAIT 3
150 OPEN 10 @ WAIT 30
160 CALL READPH(R1)
170 GOTO 130
180 'EXIT': DISP "EXIT" @ END SUB
190 !
200 ! SUBPROGRAM FOR READING pH IN
210 ! CHANNEL 4, AND CONVERTING mV TO pH,
220 ! FOLLOWING 1 SECOND OF ACID ADDITION.
230 SUB READPH(R1)
235 DIM H1(31)
240 OUTPUT :1 ;"DCV4-4"
250 FOR J=1 TO 30
260 ENTER :1 ;H1(J)
270 K1=K1+H1(J)
280 NEXT J
290 A1=K1/30
300 ASSIGN #1 TO DATAPHR
310 RESTORE #1
320 READ #1;M,C
330 R1=C+M*A1 @ DISP R1
340 END SUB
350 !
360 ! SUBPROGRAM FOR MAINTAINING pH 7
370 SUB MGV7(R1)
390 OPTION BASE 1
420 GOTO 460
430 IF R1<=7.1 THEN GOTO 'EXIT'
440 CLOSE 10 @ WAIT 1
450 OPEN 10 @ WAIT 30
460 CALL READPH(R1)
470 GOTO 430
480 'EXIT': DISP "EXIT" @ END SUB
500 !
510 ! SUBPROGRAM TO CAUSE WAITING PERIOD OF 6 MINUTES (MINIMUM)
520 SUB HOLD(P)
525 DISP "WAITING..."
530 WAIT 360
535 DISP "COULDN'T WAIT NO MORE"
540 END SUB
```

# APPENDIX A2

# PILOT PLANT DATA

Table A 1 . Summary statistics
for the pilot plant influent.

| Variable: | THMPtot | THMPfilt | CHCl3tot |
|---|---|---|---|
| Sample size | 17 | 17 | 17 |
| Average | 255.112 | 203.041 | 210.135 |
| Geometric mean | 242.338 | 185.34 | 200.484 |
| Variance | 5278.67 | 4364.16 | 3108.61 |
| Standard deviation | 72.6545 | 66.0618 | 55.755 |
| Minimum | 89 | 35.4 | 73 |
| Maximum | 338 | 263.7 | 264.9 |
| Range | 249 | 228.3 | 191.9 |

| Variable: | CHCl3filt | CHBrCl2tot | CHBrCl2fil |
|---|---|---|---|
| Sample size | 16 | 17 | 17 |
| Average | 168.813 | 42.4235 | 41.4118 |
| Geometric mean | 162.563 | 36.8712 | 36.3412 |
| Variance | 1664.74 | 375.272 | 322.556 |
| Standard deviation | 40.8012 | 19.3719 | 17.9598 |
| Minimum | 69 | 10 | 8.3 |
| Maximum | 217.8 | 64.9 | 62.1 |
| Range | 148.8 | 54.9 | 53.8 |

| Variable: | DOCtot | DOCfilt | pH |
|---|---|---|---|
| Sample size | 13 | 13 | 17 |
| Average | 7.65385 | 7.35385 | 9.34882 |
| Geometric mean | 7.58171 | 7.28979 | 9.33865 |
| Variance | 1.24769 | 1.06769 | 0.198086 |
| Standard deviation | 1.117 | 1.03329 | 0.445069 |
| Minimum | 6.4 | 6.2 | 8.51 |
| Maximum | 9.8 | 9.1 | 9.84 |
| Range | 3.4 | 2.9 | 1.33 |

| Variable: | Turbidity |
|---|---|
| Sample size | 17 |
| Average | 7.58824 |
| Geometric mean | 5.97316 |
| Variance | 25.5674 |
| Standard deviation | 5.05642 |
| Minimum | 2.3 |
| Maximum | 19.1 |
| Range | 16.8 |

Table A2. Raw Data; Pilot Plant

| ow | Date | Number | Code | THMPtot | THMPfilt | CHCl3tot | CHCl3filt | CHBrCl2tot | CHBrCl2fil | DOCtot | DOCfilt | pH | Turbidity | Chlorophyl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2/19/88 | 0 | I | 287.2 | 236.1 | 230.3 | 186.5 | 64.9 | 59.4 | 6.6 | 6.4 | 9.60 | 9.0 | 49.52 |
| 2 | 2/19/88 | 0 | LBC | 198.3 | 185.8 | 149.8 | 141.6 | 56.9 | 53.3 |  |  | 7.30 |  |  |
| 3 | 2/19/88 | 0 | I | 304.1 | 246.3 | 247.6 | 192.2 | 64.6 | 62.1 | 6.6 | 6.4 | 9.60 | 11.0 | 49.52 |
| 4 | 2/19/88 | 0 | LB | 134.1 | 149.5 | 108.4 | 108.7 | 45.7 | 50.0 |  |  | 5.00 |  |  |
| 5 | 2/24/88 | 1 | I | 318.9 | 263.7 | 256.1 | 199.0 | 54.5 | 55.7 | 8.8 | 6.5 | 9.84 | 19.1 | 49.52 |
| 6 | 2/24/88 | 1 | LC | 231.9 | 179.4 | 177.5 | 124.5 | 46.9 | 47.3 | 5.3 | 4.8 |  | 12.0 |  |
| 7 | 2/26/88 | 1R | I | 301.5 | 245.1 | 245.9 | 182.4 | 51.5 | 54.4 |  |  | 9.75 | 9.1 | 49.52 |
| 8 | 2/26/88 | 1R | LC | 210.1 | 193.4 | 149.7 | 138.7 | 52.7 | 47.8 |  |  |  | 4.9 |  |
| 9 | 2/26/88 | 2 | I | 315.9 | 241.3 | 248.4 | 178.2 | 59.0 | 54.8 |  |  | 9.83 | 10.5 | 49.52 |
| 10 | 2/26/88 | 2 | L | 169.0 | 171.5 | 116.6 | 119.3 | 45.6 | 45.4 |  |  | 5.05 | 6.8 |  |
| 11 | 2/29/88 | 3 | I | 324.6 | 243.6 | 257.5 | 180.0 | 58.3 | 54.9 | 9.0 | 7.2 | 9.74 | 14.7 | 53.61 |
| 12 | 2/29/88 | 3 | A | 105.5 | 113.0 | 62.6 | 69.1 | 37.4 | 38.8 | 2.3 | 3.3 | 4.95 | 5.1 |  |
| 13 | 2/29/88 | 4 | I | 338.0 | 256.4 | 264.9 | 187.9 | 61.9 | 58.8 | 6.9 | 9.1 | 9.72 | 9.1 | 53.61 |
| 14 | 2/29/88 | 4 | O | 134.2 | 128.3 | 85.1 | 79.0 | 42.3 | 42.7 | 4.4 | 3.6 | 5.97 | 3.3 |  |
| 15 | 3/07/88 | 5 | I | 307.0 | 244.4 | 242.6 | 182.1 | 56.0 | 53.6 | 8.6 | 8.6 | 9.69 | 11.1 | 53.61 |
| 16 | 3/07/88 | 5 | LBC | 246.8 | 229.4 | 186.9 | 150.2 | 51.5 | 47.7 | 7.0 | 7.8 | 8.04 | 8.7 |  |
| 17 | 3/07/88 | 6 | I | 307.0 | 218.8 | 239.4 | 153.5 | 58.7 | 55.5 | 9.8 | 9.0 | 9.64 | 11.3 | 53.61 |
| 18 | 3/07/88 | 6 | LB | 158.3 | 159.9 | 108.5 | 106.3 | 42.4 | 45.5 | 6.4 | 6.6 | 4.78 | 3.7 |  |
| 19 | 4/14/88 | 7R | I | 234.3 | 234.2 | 215.1 | 217.8 | 10.0 | 8.3 | 8.4 | 8.2 | 9.22 | 2.4 | 6.23 |
| 20 | 4/14/88 | 7R | BC | 176.3 | 130.1 | 163.1 | 120.9 | 5.3 | 2.5 | 5.9 | 6.2 | 7.24 | 1.7 |  |
| 21 | 4/14/88 | 9 | I | 233.8 | 223.0 | 210.2 | 196.6 | 15.3 | 17.9 | 7.0 | 7.3 | 9.24 | 4.3 | 6.23 |
| 22 | 4/14/88 | 9 | C | 180.9 | 253.9 | 169.3 | 212.1 | 6.6 | 34.2 | 5.9 | 5.6 | 7.36 | 5.0 |  |
| 23 | 4/14/88 | 10 | I | 256.8 | 225.2 | 237.3 | 204.8 | 13.5 | 14.6 | 7.0 | 7.3 | 9.21 | 2.3 | 6.23 |
| 24 | 4/14/88 | 10 | AB | 31.3 | 0.0 | 35.8 | 0.0 | 0.0 | 0.0 | 3.0 | 2.4 | 5.48 | 1.7 |  |
| 25 | 2/28/89 | 16 | I | 89.0 | 35.4 | 73.0 |  | 23.0 | 37.0 | 6.4 | 6.4 | 8.55 | 4.6 |  |
| 26 | 2/28/89 | 16 | BC | 77.9 | 48.2 | 57.0 | 37.0 | 24.0 | 18.0 | 4.6 | 3.6 | 6.72 | 3.5 |  |
| 27 | 3/01/89 | 18 | I | 212.9 | 174.8 | 180.0 | 145.0 | 35.0 | 34.0 | 6.4 | 6.4 | 8.51 | 2.7 |  |
| 28 | 3/01/89 | 18 | B | 31.7 | 42.1 | 19.0 | 24.0 | 15.0 | 18.0 | 3.6 | 3.2 | 5.70 | 1.6 |  |
| 29 | 3/01/89 | 20 | I | 198.2 | 112.5 | 170.0 | 93.0 | 33.0 | 26.0 | 7.0 | 6.8 | 8.96 | 2.6 |  |
| 30 | 3/01/89 | 20 | C | 91.2 | 71.5 | 70.0 | 58.0 | 26.0 | 21.0 | 5.0 | 3.8 | 7.27 | 1.8 |  |
| 31 | 3/02/89 | 17 | I | 156.8 | 90.1 | 125.0 | 69.0 | 34.0 | 26.0 | 6.8 | 6.6 | 8.90 | 2.5 |  |
| 32 | 3/02/89 | 17 | ABC | 39.9 | 24.8 | 23.0 | 17.0 | 18.0 | 12.0 | 4.4 | 3.6 | 8.55 | 2.6 |  |
| 33 | 3/02/89 | 19 | I | 150.9 | 160.8 | 129.0 | 133.0 | 28.0 | 31.0 | 7.4 | 6.2 | 8.93 | 2.7 |  |
| 34 | 3/02/89 | 19 | AC | 76.8 | 50.4 | 57.0 | 40.0 | 24.0 | 18.0 | 4.4 | 3.6 | 8.61 | 1.5 | 1.00 |

Note: I = Influent
For other codes, see Table 5.2

Table A3. Percentage Removals in the Pilot Plant.

| row | THMPtot | THMPfilt | CHCl3tot | CHCl3filt | CHBrCl2tot | CHBrCl2fil | DOCtot | DOCfilt | Turbidity | Cod |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 30.9540 | 21.3045 | 34.9544 | 24.07506 | 12.32665 | 10.2693 | | | | LBC |
| 2 | 55.9026 | 39.3016 | 56.2197 | 43.44432 | 29.25696 | 19.4847 | | | | LB |
| 3 | 27.2812 | 31.9681 | 30.6911 | 37.43718 | 13.94495 | 15.0807 | 39.7727 | 26.15384 | 37.1727 | LC |
| 4 | 30.3150 | 21.0934 | 39.1215 | 23.95833 | -2.33009 | 12.1323 | | | 46.1538 | LC |
| 5 | 46.5020 | 28.9266 | 53.0595 | 33.05275 | 22.71186 | 17.1532 | | | 35.2381 | L |
| 6 | 67.4984 | 53.6124 | 75.6893 | 61.61111 | 35.84905 | 29.3260 | 74.4444 | 54.16666 | 65.3061 | A |
| 7 | 60.2958 | 49.9610 | 67.8746 | 57.95636 | 31.66397 | 27.3809 | 36.2318 | 60.43956 | 63.7362 | O |
| 8 | 19.6091 | 6.1374 | 22.9596 | 17.51784 | 8.03571 | 11.0074 | 18.6046 | 9.30232 | 21.6216 | LBC |
| 9 | 48.4364 | 26.9195 | 54.6783 | 30.74918 | 27.76831 | 18.0180 | 34.6938 | 26.66666 | 67.2566 | LB |
| 10 | 24.7545 | 44.4491 | 24.1748 | 44.49035 | 47.00000 | 69.8795 | 29.7619 | 24.39024 | 29.1666 | BC |
| 11 | 22.6261 | -13.8565 | 19.4576 | -7.88402 | 56.86274 | -91.0614 | 15.7142 | 23.28767 | -16.2790 | C |
| 12 | 87.8115 | | 84.9136 | | | | 57.1428 | 67.12328 | 26.0869 | AB |
| 13 | 12.4719 | -36.1581 | 21.9178 | | -4.34782 | 51.3513 | 28.1250 | 43.75000 | 23.9130 | BC |
| 14 | 85.1103 | 75.9153 | 89.4444 | 83.44827 | 57.14285 | 47.0588 | 43.7500 | 50.00000 | 40.7407 | B |
| 15 | 53.9858 | 36.4444 | 58.8235 | 37.63440 | 21.21212 | 19.2307 | 28.5714 | 44.11764 | 30.7692 | C |
| 16 | 74.5535 | 72.4750 | 81.6000 | 75.36231 | 47.05882 | 53.8461 | 35.2941 | 45.45454 | -4.0000 | ABC |
| 17 | 49.1053 | 68.6567 | 55.8139 | 69.92481 | 14.28571 | 41.9354 | 40.5405 | 41.93548 | 44.4444 | AC |

Note: For Codes, see Table 5.2.

## Table A5 Percentage Removals in the Pilot Plant

| Code | Date | Total THMP | Filtered THMP | Total $CHCl_3$ | Filtered $CHCl_3$ | Total $CHBrCl_2$ | Filtered $CHBrCl_2$ | Total DOC | Filtered DOC |
|---|---|---|---|---|---|---|---|---|---|
| BX | 2/29/88 | 48,3 | 34,0 | 55,7 | 40,1 | 20,4 | 17,3 | 58,9 | 51,4 |
| BX | 2/29/88 | 44,1 | 24,8 | 61,4 | 43,6 | 25,2 | 20,4 | 36,2 | 51,6 |
| BX | 4/14/88 | 39,5 | 44,5 | 35,0 | 39,6 | 100,0 | 100,0 | 32,9 | 32,9 |
| BX | 4/14/88 | 48,5 | 27,2 | 45,4 | 24,0 | 100,0 | 80,8 | 34,3 | 39,7 |
| B | 2/28/89 | 15,7 | -55,1 | 31,5 |  | -8,7 | 43,2 | 3,1 | 18,8 |
| BD | 3/ 1/89 | 62,4 | 65,0 | 68,3 | 69,0 | 28,6 | 41,2 | 12,5 | 15,6 |
| O | 3/ 1/89 | 65,4 | 27,4 | 71,2 | 37,6 | 33,3 | 3,8 | 17,1 | 20,6 |
| AB | 3/ 2/89 | 43,0 | 16,9 | 45,6 | 14,5 | 26,5 | 19,2 | 23,5 | 30,3 |
| A | 3/ 2/89 | 26,6 | 60,8 | 31,8 | 62,4 | 7,1 | 38,7 | 21,6 | 12,9 |

# APPENDIX A3

# FULL-SCALE PLANT DATA

Table A4. Raw Data; Full-scale Plant.

| Row | Date | Number | Code | THMPtot | THMPfilt | CHCl3tot | CHCl3filt | CHBrCl2tot | CHBrCl2fil | DOCtot | DOCfilt | pH | Turbidity | Chlorophyl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2/29/88 | 3 | I | 324.6 | 243.6 | 257.5 | 180.0 | 58.3 | 54.9 | 9.0 | 7.2 | 9.74 | 14.7 | 53.61 |
| 2 | 2/29/88 | 3 | BX | 167.9 | 160.7 | 114.0 | 107.8 | 46.4 | 45.4 | 3.7 | 3.5 | | | |
| 3 | 2/29/88 | 4 | I | 338.0 | 256.4 | 264.9 | 187.9 | 61.9 | 58.8 | 6.9 | 9.1 | 9.72 | 9.1 | 53.61 |
| 4 | 2/29/88 | 4 | BX | 188.9 | 192.8 | 102.2 | 105.9 | 46.3 | 46.8 | 4.4 | 4.4 | | | |
| 5 | 4/14/88 | 9 | I | 233.8 | 223.0 | 210.2 | 196.6 | 15.3 | 17.9 | 7.0 | 7.3 | 9.24 | 4.3 | 6.22 |
| 6 | 4/14/88 | 9 | BX | 141.5 | 123.7 | 136.7 | 118.7 | 0.0 | 0.0 | 4.7 | 4.9 | | | |
| 7 | 4/14/88 | 10 | I | 256.8 | 225.5 | 237.3 | 204.8 | 13.5 | 14.6 | 7.0 | 7.3 | 9.21 | 2.3 | 6.22 |
| 8 | 4/14/88 | 10 | BX | 132.2 | 164.2 | 129.6 | 155.7 | 0.0 | 2.8 | 4.6 | 4.4 | | | |
| 9 | 2/28/89 | 16 | I | 89.0 | 35.4 | 73.0 | | 23.0 | 37.0 | 6.4 | 6.4 | 8.55 | 4.6 | |
| 10 | 2/28/89 | 16 | B | 75.0 | 54.9 | 50.0 | 35.0 | 25.0 | 21.0 | 6.2 | 5.2 | | | |
| 11 | 3/01/89 | 18 | I | 212.9 | 174.8 | 180.0 | 145.0 | 35.0 | 34.0 | 6.4 | 6.4 | 8.51 | 2.7 | |
| 12 | 3/01/89 | 18 | BD | 80.1 | 61.2 | 57.0 | 45.0 | 25.0 | 20.0 | 5.6 | 5.4 | | | |
| 13 | 3/01/89 | 20 | I | 198.2 | 112.5 | 170.0 | 93.0 | 33.0 | 26.0 | 7.0 | 6.8 | 8.96 | 2.6 | |
| 14 | 3/01/89 | 20 | O | 68.5 | 81.7 | 49.0 | 58.0 | 22.0 | 25.0 | 5.8 | 5.4 | | | |
| 15 | 3/02/89 | 17 | I | 156.8 | 90.1 | 125.0 | 69.0 | 34.0 | 26.0 | 6.8 | 6.6 | 8.90 | 2.5 | |
| 16 | 3/02/89 | 17 | AB | 89.3 | 74.9 | 68.0 | 59.0 | 25.0 | 21.0 | 5.2 | 4.6 | | | |
| 17 | 3/02/89 | 19 | I | 150.9 | 160.8 | 129.0 | 133.0 | 28.0 | 31.0 | 7.4 | 6.2 | 8.93 | 2.7 | |
| 18 | 3/02/89 | 19 | A | 110.8 | 63.0 | 88.0 | 50.0 | 26.0 | 19.0 | 5.8 | 5.4 | 20.00 | 20.0 | 20.00 |

Note: I = Influent
For other codes, see Table 5.5.

# APPENDIX A4

# CORRELATION ANALYSES

## Table A 6 . Correlations
## for pilot plant influent.

```
                            Sample Correlations
---------------------------------------------------------------------------
                    THMPtot    CHCl3tot CHBrCl2tot     DOCtot        pH  Turbidity
THMPtot              1.0000      .9786      .6612      .6440     .9036     .7184
                   (    13)  (    13)  (    13)  (    13)  (    13)  (    13)
                      .0000      .0000      .0139      .0175     .0000     .0057

CHCl3tot              .9786     1.0000      .4957      .5971     .8608     .6128
                   (    13)  (    13)  (    13)  (    13)  (    13)  (    13)
                      .0000      .0000      .0849      .0312     .0002     .0260

CHBrCl2tot            .6612      .4957     1.0000      .5198     .6541     .7906
                   (    13)  (    13)  (    13)  (    13)  (    13)  (    13)
                      .0139      .0849      .0000      .0686     .0153     .0013

DOCtot                .6440      .5971      .5198     1.0000     .7547     .7094
                   (    13)  (    13)  (    13)  (    13)  (    13)  (    13)
                      .0175      .0312      .0686      .0000     .0029     .0066

pH                    .9036      .8608      .6541      .7547    1.0000     .8064
                   (    13)  (    13)  (    13)  (    13)  (    13)  (    13)
                      .0000      .0002      .0153      .0029     .0000     .0009

Turbidity             .7184      .6128      .7906      .7094     .8064    1.0000
                   (    13)  (    13)  (    13)  (    13)  (    13)  (    13)
                      .0057      .0260      .0013      .0066     .0009     .0000

---------------------------------------------------------------------------
                Coefficient  (sample size)  significance level
```

Table A7 . Correlations
for pilot plant effluent.

```
                                  Sample Correlations
--------------------------------------------------------------------------------
                    THMPtot   CHCl3tot CHBrCl2tot      DOCtot          pH  Turbidity
THMPtot              1.0000      .9663      .3356       .7440       .0253      .7075
                   (    11)  (    11)  (    11)   (    11)   (    11)   (    11)
                      .0000      .0000      .3130       .0087       .9411      .0149

CHCl3tot              .9663     1.0000      .0869       .7748       .1377      .5924
                   (    11)  (    11)  (    11)   (    11)   (    11)   (    11)
                      .0000      .0000      .7994       .0051       .6865      .0548

CHBrCl2tot            .3356      .0869     1.0000       .0990     -.3026      .5834
                   (    11)  (    11)  (    11)   (    11)   (    11)   (    11)
                      .3130      .7994      .0000       .7721       .3657      .0596

DOCtot                .7440      .7748      .0990      1.0000       .3070      .3672
                   (    11)  (    11)  (    11)   (    11)   (    11)   (    11)
                      .0087      .0051      .7721       .0000       .3584      .2666

pH                    .0253      .1377     -.3026       .3070      1.0000     -.0210
                   (    11)  (    11)  (    11)   (    11)   (    11)   (    11)
                      .9411      .6865      .3657       .3584       .0000      .9512

Turbidity             .7075      .5924      .5834       .3672      -.0210     1.0000
                   (    11)  (    11)  (    11)   (    11)   (    11)   (    11)
                      .0149      .0548      .0596       .2666       .9512      .0000

--------------------------------------------------------------------------------
            Coefficient  (sample size)  significance level
```

Table A8 . Correlations
for full-scale plant effluent.

```
                          Sample Correlations
--------------------------------------------------------------------------------
                  THMPtot   CHCl3tot CHBrCl2tot      DOCtot
THMPtot            1.0000      .7951      .3119      -.8708
                  (     9)  (     9)  (     9)   (     9)
                    .0000      .0104      .4139       .0022

CHCl3tot            .7951     1.0000     -.2852      -.7795
                  (     9)  (     9)  (     9)   (     9)
                    .0104      .0000      .4570       .0133

CHBrCl2tot          .3119     -.2852     1.0000      -.2209
                  (     9)  (     9)  (     9)   (     9)
                    .4139      .4570      .0000       .5679

DOCtot             -.8708     -.7795     -.2209      1.0000
                  (     9)  (     9)  (     9)   (     9)
                    .0022      .0133      .5679       .0000

--------------------------------------------------------------------------------
              Coefficient  (sample size)  significance level
```

Table A9. Correlations Including Chloroform/Bromoform Ratios.

```
                          Sample Correlations
--------------------------------------------------------------------------------------------------
              THMPtot    THMPfilt      DOCtot          pH  Turbidity Chlorophyl    RatioCBr  RatioCBrf
THMPtot        1.0000       .8495       .5851       .8826      .8046      .6639      -.1104     -.1281
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .0000       .0005       .0457       .0001      .0016      .0186       .7328      .6916

THMPfilt        .8495      1.0000       .5145       .7637      .6332      .3293       .2495      .2375
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .0005       .0000       .0870       .0038      .0271      .2959       .4342      .4573

DOCtot          .5851       .5145      1.0000       .7172      .7152      .5517      -.0983     -.0135
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .0457       .0870       .0000       .0087      .0089      .0630       .7612      .9667

pH              .8826       .7637       .7172      1.0000      .8498      .6609      -.1304     -.1292
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .0001       .0038       .0087       .0000      .0005      .0193       .6862      .6889

Turbidity       .8046       .6332       .7152       .8498     1.0000      .8043      -.4322     -.4086
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .0016       .0271       .0089       .0005      .0000      .0016       .1605      .1872

Chlorophyl      .6639       .3293       .5517       .6609      .8043     1.0000      -.7748     -.7084
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .0186       .2959       .0630       .0193      .0016      .0000       .0031      .0099

RatioCBr       -.1104       .2495      -.0983      -.1304     -.4322     -.7748      1.0000      .9644
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .7328       .4342       .7612       .6862      .1605      .0031       .0000      .0000

RatioCBrf      -.1281       .2375      -.0135      -.1292     -.4086     -.7084       .9644     1.0000
              (   12)     (   12)     (   12)     (   12)    (   12)    (   12)    (   12)    (   12)
                .6916       .4573       .9667       .6889      .1872      .0099       .0000      .0000

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                   Coefficient  (sample size)  significance level
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