



REMOVAL OF ORGANICS FROM  
COLOURED WATER. OVERVIEW.

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**REMOVAL OF ORGANICS FROM COLOURED WATER.**

**OVERVIEW.**

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## SUMMARY

### I OBJECTIVES

To investigate the production of disinfection (by chlorination) by-products (DBPs), including trihalomethanes (THMs) during the treatment of coloured water and to define suitable, cost effective, methods for their removal or control with due regard to other water quality determinands, such as colour, iron, manganese and aluminium.

### II REASONS

The presence of DBPs in drinking water derived from coloured sources may pose a health risk to the consumer and exceed regulated water quality criteria. Dissolved air flotation and 2 stage filtration is the most likely process to be used for treatment of upland coloured water; this process requires investigation and optimisation with respect to the control of the trace organics of concern.

### III CONCLUSIONS

- (i) DBPs can be minimised by operating under coagulation conditions (dose and pH, iron or aluminium) that reduce final water colour to a minimum. Using chlorinated copperas or the polyelectrolyte LT31 as primary coagulant results in increased concentrations of DBPs.
- (ii) Pre-chlorination increases DBPs in the final water. Pre-ozonation has little effect on final water THMs, but reduces other DBPs, including those giving rise to mutagenic activity. Increasing inter-filtration chlorine dose to supplement disinfection capacity results in an increase in DBPs.
- (iii) Inter-filtration ozonation reduces DBPs, but can oxidise manganese to a colloidal form that is difficult to remove. Post-ozonation reduces DBPs.

- (iv) Granular activated carbon (GAC) reduces disinfection by-products by removing precursors, effective bed life is proportional to empty bed content time. The use of ozone prior to GAC reduces the load of DBP precursors and thereby increases bed life. Coal based GAC performs better than peat based GAC, which performs better than wood based GAC, for the reduction of DBPs.

#### **IV RECOMMENDATIONS TO MINIMISE CHLORINATION BY-PRODUCTS**

Pre-chlorination should not be used unless considered necessary to the treatment process (e.g. algal removal); ozone can be considered as a replacement for chlorine.

Coagulation conditions should be selected to produce minimum final water colour (rather than acceptable final water colour).

The interfiltration chlorine dose for manganese removal should be kept as low as possible; the secondary filters should not be used to provide residence time for disinfection.

Ozone can be considered for use after primary filtration, or as a post treatment. The potential effects of ozone on manganese removal need to be considered on a site specific basis, and attention must be given to the removal of any biodegradable ozonation by-products.

GAC can be used to reduce DBPs, and coal based GAC appears to be the most effective GAC for this function. Effective bed life is primarily determined by contact time and can be extended by the use of ozone prior to GAC.

#### **V RESUME**

A series of tests investigating 3-stage treatment and additional treatment options has been conducted over a 3-year period. A summary of the work and an overview of the results and conclusions are presented.

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## SECTION 1 - INTRODUCTION

Upland surface water accounts for approximately one third of the UK potable water supply and, prior to treatment, contains a wide range of organic compounds. The presence of some of these compounds can be directly attributed to the activities of the land user (pesticides, road run off etc) but for the majority of supplies the compounds are all of natural origin. These natural compounds are classified as humic and fulvic acids and give upland water its characteristic brown colour and an acidic pH; they enter the water from decaying vegetation, in particular peaty deposits. The acidity of the water also leads to the dissolution of metals such as iron, aluminium and manganese from the rocks that characterise much of upland Britain.

Historically such waters have only been given basic treatment with, typically, a single stage of coagulation/filtration or two stages of coagulation/clarification and filtration. It is now recognised that to meet standards relating to colour, aluminium, iron and manganese, three stages of treatment are required. New treatment plants typically now consist of:

- (1) Chemical dosing with coagulant and alkali;
- (2) Flocculation at pH 4.5 - 5.5;
- (3) Dissolved air flotation (DAF) or upflow clarification;
- (4) Rapid sand filtration at pH 6.0 - 7.0;
- (5) Rapid sand filtration at pH 8.0 - 9.0 with oxidation by chlorine.

- \* The first stage, at pH 4.5 - 5.5, removes the organic colour and dissolved iron;
- \* The second stage, at pH 6.0 - 7.0, removes aluminium and coagulant carryover;
- \* The third stage, at pH 8.0 - 9.0, removes manganese.

In addition to the removal of organic and inorganic material, one of the primary objectives for water treatment is to produce a water that is microbiologically safe, i.e. disinfected. In the UK the recommended agent that should be used to achieve disinfection is chlorine; this is because it is an effective microbiocide, inexpensive and relatively easy to produce, simple to apply and control, and is stable enough to persist within the distribution network.

Historically, treatment plant operators have often applied chlorine at multiple points within the treatment stream. Pre-chlorination has been common on the basis that by maintaining a free chlorine residual through the plant it is possible to increase the total disinfection contact time, and prevent biofouling of the equipment. Chlorine is also used to assist in the removal of manganese in the filtration stages; the presence of a free chlorine residual will usually guarantee the removal of manganese and may enable its removal at a lower pH (as in, for example, the first filtration stage).

Chlorine, however, reacts not only with inorganic compounds such as manganese, but also with the organic colour. The reaction often results in a decrease in colour and "super chlorination" is a recognised process for treating coloured waters. However, the by-products of these reactions include identified and unidentified compounds which may pose a quantifiable health risk to the consumer.

Trihalomethanes (THMs, e.g. chloroform) are subject to a prescribed concentration of 100µg/l by the Water Supply (Water Quality) Regulations (1989), principally because chloroform has been shown in tests to be carcinogenic (although not at concentrations found in water). There is, however, a large number of other chlorination by-products that are not identified, but still give rise to concern. Epidemiological studies are usually unable to demonstrate clear links between the health of a population and water quality (other than water borne diseases). One study in the United States<sup>(1)</sup> found a small positive relationship between the incidence of bladder cancer and the level of exposure to chlorinated surface water but a review of the evidence by Fawell and Horth<sup>(2)</sup> concluded that recent tests provided reassurance with respect to the risk to health from long term consumption of chlorinated water. In view of the requirements to meet THM regulations and the concern with respect to other by-products it has been considered prudent to investigate ways of reducing chlorination by-products.

In 1986 a three year study of the control of chlorination by-products during the treatment of lowland surface water was begun by WRc. The work examined the use of ozone, activated carbon, coagulation conditions, and slow sand filtration. The results of the work<sup>(3)</sup> produced a number of recommendations, foremost of

which was that chlorine should continue to be used as the primary disinfectant but that the use of chlorine within the treatment process should be kept to a minimum. The work also concluded that ozone could be used to reduce the consumption of chlorine and that although GAC was effective, it has a limited ability to remove by-products. Although these recommendations could probably be applied to upland water it was recognised that the presence of higher levels of colour and the need to remove metals such as manganese may introduce confounding factors.

The work reported herein in many respects parallels the work on lowland surface water and was undertaken over 3 years. Its objective was to determine how best a 3-stage (DAF based) treatment process could be operated to meet current Water Quality Regulations whilst minimising chlorination by-products but continuing to use chlorine as the primary disinfectant. The details of this work, and the results, can be found in a series of reports<sup>(4,5,6,7)</sup>. This report seeks to present a summary of the three years work and an overview of the results and conclusions.

## SECTION 2 - EXPERIMENTAL

### 2.1 EXPERIMENTAL PARAMETERS

The objective of the work was to define cost effective methods of operating 3 stage (DAF + 2 stage rapid gravity filtration) water treatment plant to minimise disinfection by-products. Table 1 is a matrix showing the main parameters for the operation of a three stage water treatment plant.

**Table 1 - Parameters for 3 stage water treatment**

| STAGE                              | CHEMICAL                               | PHYSICAL   |
|------------------------------------|--|--|
| Pretreatment                       | Ozone Dose<br>Chlorine Dose            |  |
| Coagulation                        | pH<br>Coagulant Type<br>Coagulant Dose |  |
| Flocculation                       | Floc Aid Type<br>Floc Aid Dose         | Paddle Speed<br>Retention Time   |
| Dissolved Air Flotation            |  | Upflow Rate<br>Recycle Rate<br>Saturation Pressure                                     |
| Primary Rapid Gravity Filtration   | pH                                     | Sand/Carbon<br>Carbon Type<br>Carbon Contact Time<br>Filtration Rate                   |
| Secondary Rapid Gravity Filtration | pH<br>Chlorine Dose<br>Ozone Dose      | Sand/Carbon<br>Sand Condition<br>Carbon Type<br>Carbon Contact Time<br>Filtration Rate |
| Post Treatment                     | Ozone Dose                             | Carbon Type<br>Carbon Contact Time   |

The pilot plant and experimental programme were designed to investigate the effect of the parameters shown in Table 1 on the production of disinfection by-products.

## 2.2 PILOT PLANT DESCRIPTION

### 2.2.1 Location and raw water quality

The pilot plant was located at North West Water's Clough Bottom water treatment works, between Rawtenstall and Burnley in the Lancashire Pennines (OS Ref. SD 845267). The pilot plant was supplied with raw water from the Clough Bottom reservoir. The site was selected on the basis of providing a typical upland raw water, high in colour, low in turbidity and of low conductivity. Although the colour in the raw water was lower than anticipated, the raw water treated during the experimental programme was typical of many upland raw waters. Table 2 shows the raw water quality between August 1990 and March 1991, and is representative of the water quality for the duration of the work (from December 1988 to March 1991).

Table 2 - Raw water quality

|            | COLOUR (°H) |      | pH  | TURB<br>NTU | Fe<br>mg/l | Mn<br>mg/l | Al<br>mg/l | TOC<br>mg/l | TOTAL<br>THMs*<br>ug/l | AOX*<br>ug/l |
|------------|-------------|------|-----|-------------|------------|------------|------------|-------------|------------------------|--------------|
|            | APPAR       | TRUE |     |             |            |            |            |             |                        |              |
| Mean       | 38          | 22   | 5.2 | 2.5         | 0.46       | 0.17       | 0.30       | 5.25        | 21.8                   | 74.4         |
| Std. Dev.  | 11          | 5    | 0.4 | 0.8         | 0.08       | 0.01       | 0.15       | 1.48        | 5.2                    | 15.4         |
| No. Points | 147         | 147  | 147 | 147         | 29         | 29         | 26         | 28          | 31                     | 16           |
| Maximum    | 51          | 32   | 6.1 | 4.2         | 0.62       | 0.20       | 0.52       | 7.80        | 33.0                   | 107.9        |
| Minimum    | 18          | 12   | 4.6 | 0.9         | 0.31       | 0.15       | 0.03       | 2.54        | 10.3                   | 50.5         |

\* After 30 minutes hand chlorination (see Section 2.4 below).

### 2.2.2 Pilot plant details

The pilot plant was situated in two transport containers; one 30' long, the other 20' long. Each container rested on its own concrete pad; the concrete pads were laid to provide a 1.00m head between the two

containers. Each container was provided with a heater, and the pipes between the two containers were lagged.

The majority of the process pipework was constructed from 316 stainless steel. Drains and the raw water line were constructed from PVC pipe. All process tanks, except for the final water tanks, were constructed out of 304 stainless steel. The final water tanks were constructed out of PVC.

The pilot plant was designed so that the flow through a given stage could be varied independently of previous or subsequent stages. Points were provided to permit sampling before or after each stage of the process.

Raw water from the treatment works main entered the top container, where it was split into two streams. From this point on, the pilot plant consisted of two identical streams. The detailed flowsheet for one stream is shown in Figure 1, and a description follows.

The first stage in the process was normally chemical dosing, although provision was provided for ozonation prior to chemical dosing. There were three in-line dosing points, and two in-line mixers. The first two dosing points, caustic (sodium hydroxide) and chlorine (sodium hypochlorite), lay upstream of both in-line mixers, whilst the third dosing point, coagulant, lay in between the two in-line mixers. The caustic dose was automatically controlled between set points by a signal from a pH probe placed in the first flocculator. Coagulant dose was controlled either manually, or automatically by a streaming current detector and controller. Chlorine dose was set manually according to the needs of a particular test. The use of ozone or chlorine at this point is referred to as "pre-oxidation".

Flocculation was achieved in a two stage flocculator, the dimensions of which are given in Table 3. Each stage was stirred by a paddle with a variable speed drive. Polyelectrolyte could be dosed directly into the first flocculation tank.

Flocculated water flowed on into the dissolved air flotation (DAF) unit or to drain via a graduated V-notch. The flow over the V-notch could be varied from 0-100% of total flow by adjusting its height. This allowed flocculation time and DAF throughput to be varied independently.

**Table 3 - Flocculator details (per stage)**

|                               |                                    |
|-------------------------------|------------------------------------|
| Dimensions (l*w*h) (mm)       | 1400*700*1000                      |
| Nominal throughput (l/hour)   | 3500                               |
| Nominal residence time (mins) | 15                                 |
| Paddle speed (rpm)            | 0-200                              |
| Paddle size (w*h) (mm)        | 4 blades -<br>60*600 on a 330mm od |

The DAF unit is shown schematically in Figure 2. Details of the DAF unit and the saturator are given in Table 4. Water flowing from the flocculator was directed down by a vertical baffle (which could be placed in one of three positions). At the bottom of this baffle recycle water from the saturator was introduced via a WRC nozzle, and the aerated water then flowed up a second baffle. The baffle was inclined at 60 degrees from horizontal and could be placed in one of three positions. The water then flowed down the length of the DAF tank and flocculated solids attached to the air bubbles rose to the surface of the water where they formed a float; this was removed by a scraper to drain. The speed of the float scraper could be varied and it could run continuously or intermittently.

Table 4 - DAF and saturator details

|                               | DAF          | SATURATOR    |
|-------------------------------|--------------|--------------|
| Dimensions (l*w*h) (mm)       | 2150*25*1220 | 1300*300 dia |
| Nominal flowrate (l/hour)     | 3000         | 300          |
| Nominal residence time (mins) | 10           | -            |
| Downflow rate (m/hour)        | 8            | 4.2          |
| Packing depth (mm)            | -            | 850          |
| Float scraper speed (mm/s)    | 0-80         | -            |

Clarified water rose up behind a baffle and into the treated water trough. The required volume of DAF treated water flowed by gravity to the filtration stages, excess water passed to drain.

Up to 15% of the treated water could be recycled through the saturator. In the saturator, water was distributed on to the top of ceramic ring packing. The water flowed down through the packing, coming into contact with pressurised air. Oil free air was fed into the base of the saturator from a compressor. The pressure within the saturator was regulated by a valve just before the saturator inlet. The saturator was equipped with a pressure relief valve, which was normally set at 450 kPa (65 psi).

The flows into and out of the saturator were indicated by rotameters. The flow out of the saturator was controlled only by the air pressure within the saturator and the size of one of the holes in the nozzle in the DAF tank. The flow into the saturator was controlled by a variable speed mono pump, a throttle valve and a parallel solenoid valve. By appropriate adjustment of the feed pump rate and the throttle valve, the flow into the saturator could be set just greater than the flow out of the saturator when the solenoid valve was open, and just less when the solenoid valve was closed. Two probes positioned below the packing in the saturator detected the water level. When the level was at the top



probe the solenoid was shut, and when the level was at the bottom probe the solenoid opened. In this way the packing did not become flooded which would have reduced the efficiency of the saturator, and air was prevented from flowing direct to the nozzle.

Clarified water flowed by gravity into the primary rapid gravity filter (1° RGF). Caustic was dosed before the 1° filter to raise the water pH to 6.5 for aluminium residual and coagulant removal. Water from the 1° filter flowed into a tank from where it either flowed to drain, or was pumped to the secondary rapid gravity filter (2° RGF). Before entering the 2° filter, water was first dosed with caustic to raise the pH to 9.0 and then dosed with chlorine to oxidise for manganese removal; the dose rates were set manually. Alternatively, water could be passed through one or more of three ozone contactors prior to the 2° filter. The application of chlorine, or ozone, at this stage is referred to as "inter-filtration oxidation".

After secondary filtration, the water could be pumped to a post adsorber, either directly or via one or more of three ozone contactors. The post adsorbers were closed to atmosphere, thus acting as pressure filters, with flow control on the outlet. Although provision was made for manual backwashing, this was never carried out. The application of ozone and or GAC, at this stage is referred to as "post-ozonation" or "post-treatment".

The rapid gravity filters were operated as constant flow, variable head filters. Backwashing was initiated when the water level rose to 1.4m above the top surface of the sand, total filtration head available was 1.0m. The backwash sequence was controlled by a programmable logic controller which was set to give one minute air scour followed by 15 minutes backwash using treated water from the Clough Bottom treatment plant. If a filter had not backwashed for a pre-set period then an override automatically initiated the backwash sequence. Throughout most of the experimental programme, 1° filters were operated with automatic 12 hourly backwashing, (which prevented samples being taken immediately after backwashing); 2° filters were operated with 48 hour backwashing. Details of the filters are given in Table 5.

Table 5 - Details of rapid gravity filters and post adsorbers

|                                     | PRIMARY  | SECONDARY                              | POST ADSORBER  |
|-------------------------------------|--|--|----------------|
| Dimensions (mm)                     | 2350*400 dia   | 2350*200 dia                           | 3000 x 150 dia |
| Nominal flowrate (l/hour)           | 750  | 350                                    | 75             |
| Nominal downflow rate (m/hour)      | 6  | 11                                     | 4.3            |
| Mesh size (BSS410) media (depth mm) | 10/18, sand (100)<br>16/30, sand (600)<br>or GAC (630) | 10/18, sand (700)<br>-<br>or GAC (630) | GAC (710)      |
| Air scour rate (m/h)                | 20   | 20                                     | -              |
| Backwash rate (m/h)                 | 30   | 20                                     | -              |

The ozone generating and contacting equipment consisted of an Ozobloc OC2 generator, capable of generating up to 38g/hr of ozone, and three ozone contactors. Each contactor consisted of an identical base section, including diffuser and viewing window, under a 4m section of 4", 6" or 8" pipe. Ozone from the generator could be passed to any one contactor, or any combination of two contactors, thus, enabling the selection of a wide range of contact times. A proportion of the ozonated air from the generator could be diverted to a thermal ozone destructor, allowing the dosing of very low ozone doses without requiring excessive turndown of the generator. Figure 3 shows the ozone flowsheet.

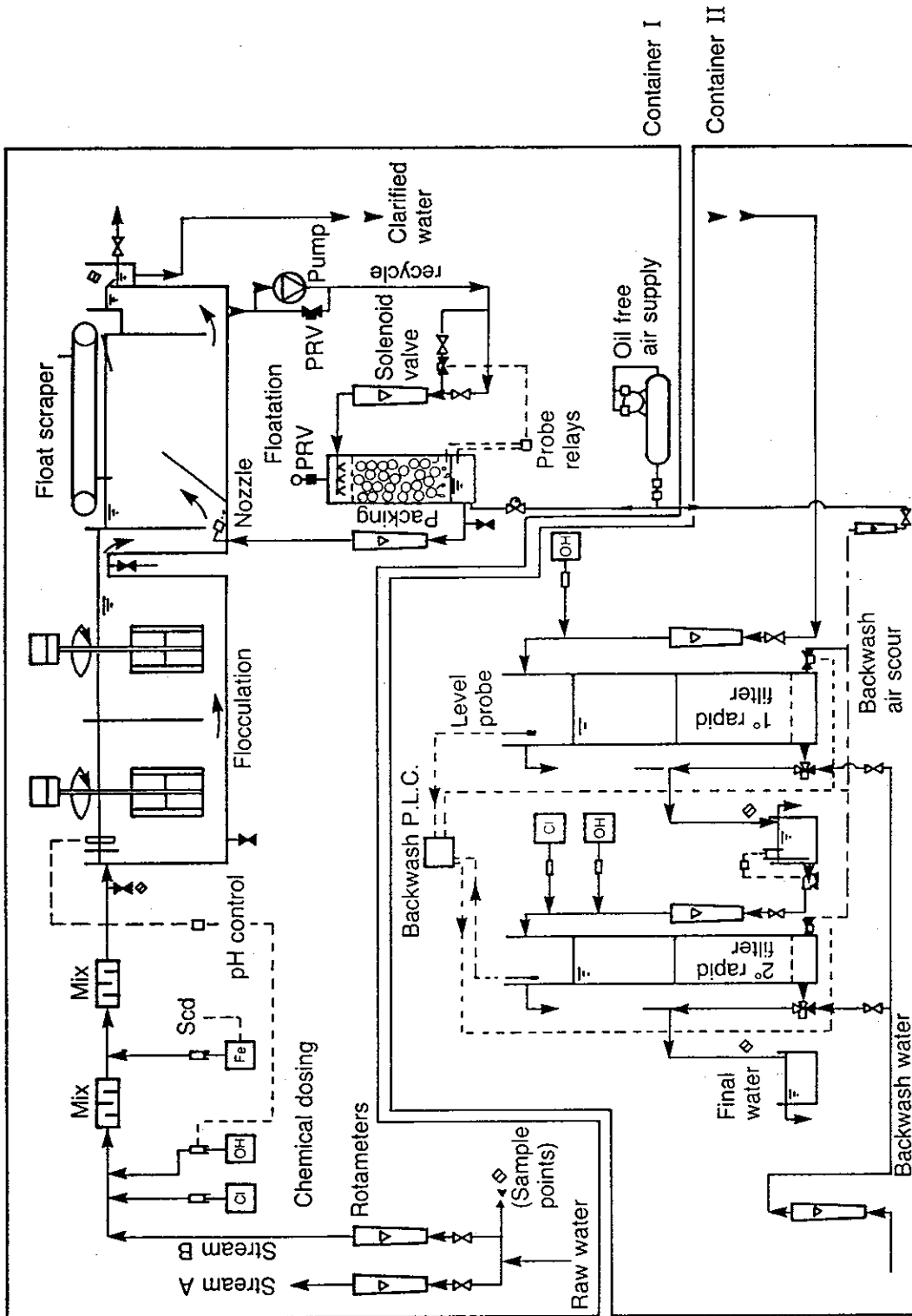


Figure 1 Detailed Flow Sheet DAF and RGFs

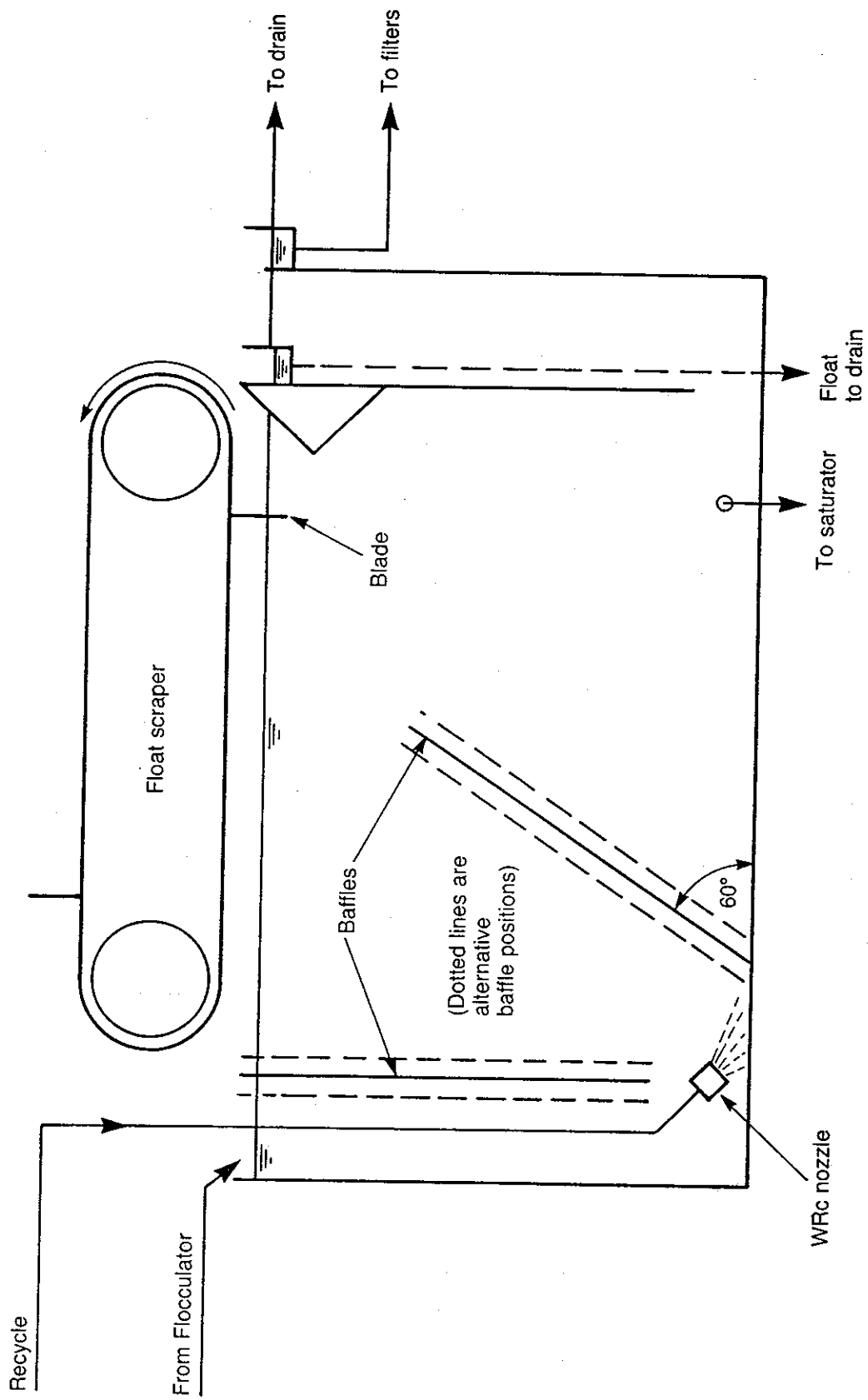


Figure 2 Dissolved Air Flotation Unit

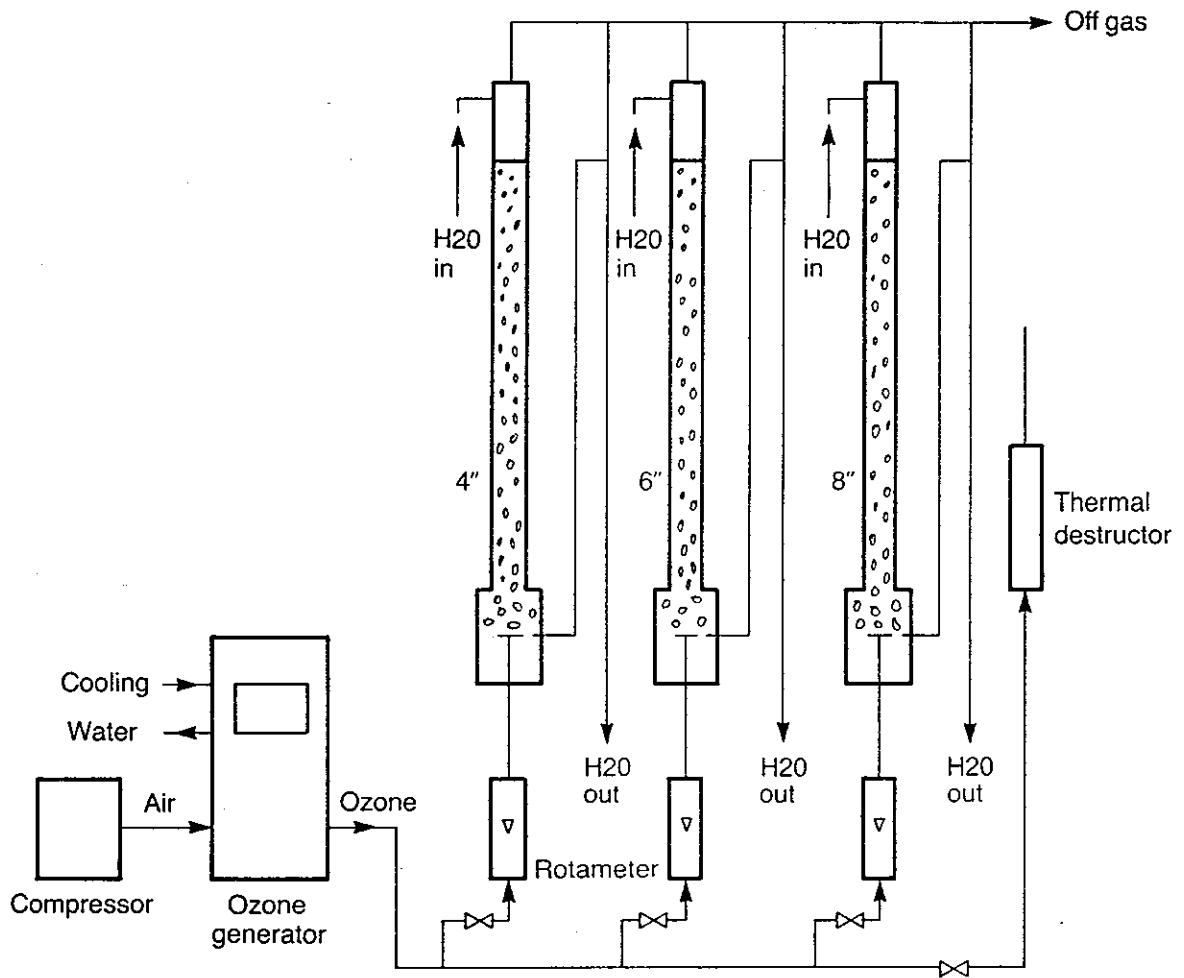


Figure 3 Ozone Flowsheet

## 2.3 EXPERIMENTAL PROGRAMME

Because of variations in the raw water quality, the pilot plant was always run with parallel trial and control streams. The operation of each stream was identical, except for the parameter under investigation.

The experimental work was divided up into a commissioning programme and three experimental phases. The scope of each stage of the work is outlined below.

### 2.3.1 Commissioning programme

During commissioning, the physical parameters of flocculation and flotation were optimised with respect to colour and turbidity in the floated water. The optimum conditions thus determined were applied throughout all three phases of the experimental programme. Since the physical performance of the DAF stage was not under investigation, the optimum conditions were taken as being those at which solid-liquid separation in the DAF was not limited by any of the physical parameters shown in Table 1.

### 2.3.2 Phase 1

During this phase, coagulation and flocculation chemistry were investigated. Two coagulants (ferric sulphate and aluminium sulphate) were investigated in detail, with the effect of coagulant dose and pH being investigated for each coagulant. In addition, chlorinated copperas and Allied Colloid's polyelectrolyte LT31 were briefly investigated as alternative coagulants.

During this phase, the 1° filtration pH was fixed at 6.5, the 2° filtration pH was fixed at 9.0, and the inter-filtration chlorine dose was fixed to give a free residual of 0.1mg/l after the 2° filter. Neither activated carbon nor pre-oxidation were used. The pilot plant was run as shown in Figure 4, but without pretreatment oxidant.

### 2.3.3 Phase 2

During this phase, the use of pre-treatment by ozone or chlorination, and the use of inter-filtration oxidation by ozone or chlorine were investigated. Pre-chlorination was only investigated briefly. Pre-ozonation was investigated at a range of ozone doses, in addition to ozonation of the raw water without further treatment. Inter-filtration oxidation was investigated at a number of chlorine and ozone doses, and in addition, two stage ozonation, (pre-oxidation and inter-filtration oxidation), was investigated with different doses at each point.

During this phase, only ferric was used as a coagulant, and the ferric dose was adjusted by the operator as required by the raw water conditions. The chemical conditions for filtration were fixed as in Phase 1, except where the trial stream conditions were altered to investigate inter-filtration oxidation.

In order to investigate pre-treatment and dual point ozonation, the pilot plant was operated as shown in Figure 4, and in order to investigate inter-filtration oxidation, the pilot plant was operated as in Figure 5.

### 2.3.4 Phase 3

During phase 3, the use of activated carbon and post-ozonation were investigated. The effect of empty bed contact time (EBCT) and use at different points in the treatment stream were investigated using a coal based carbon (Chemviron Filtrasorb F400). A comparison was made between coal based (F400) and peat based (Norit PK) carbons, by using the same feed to each carbon at equal EBCTs. In addition to investigating the effects of ozonation as a post treatment, the combined effect of ozone and GAC, using a coal based (F400) and a wood based (Pica Biol) carbon was investigated.

The chemical conditions for filtration were fixed as in phase 1, except for the final 4 weeks of operation, when the effects of reducing the 2° filtration pH, and removing the inter-filtration chlorine dose were

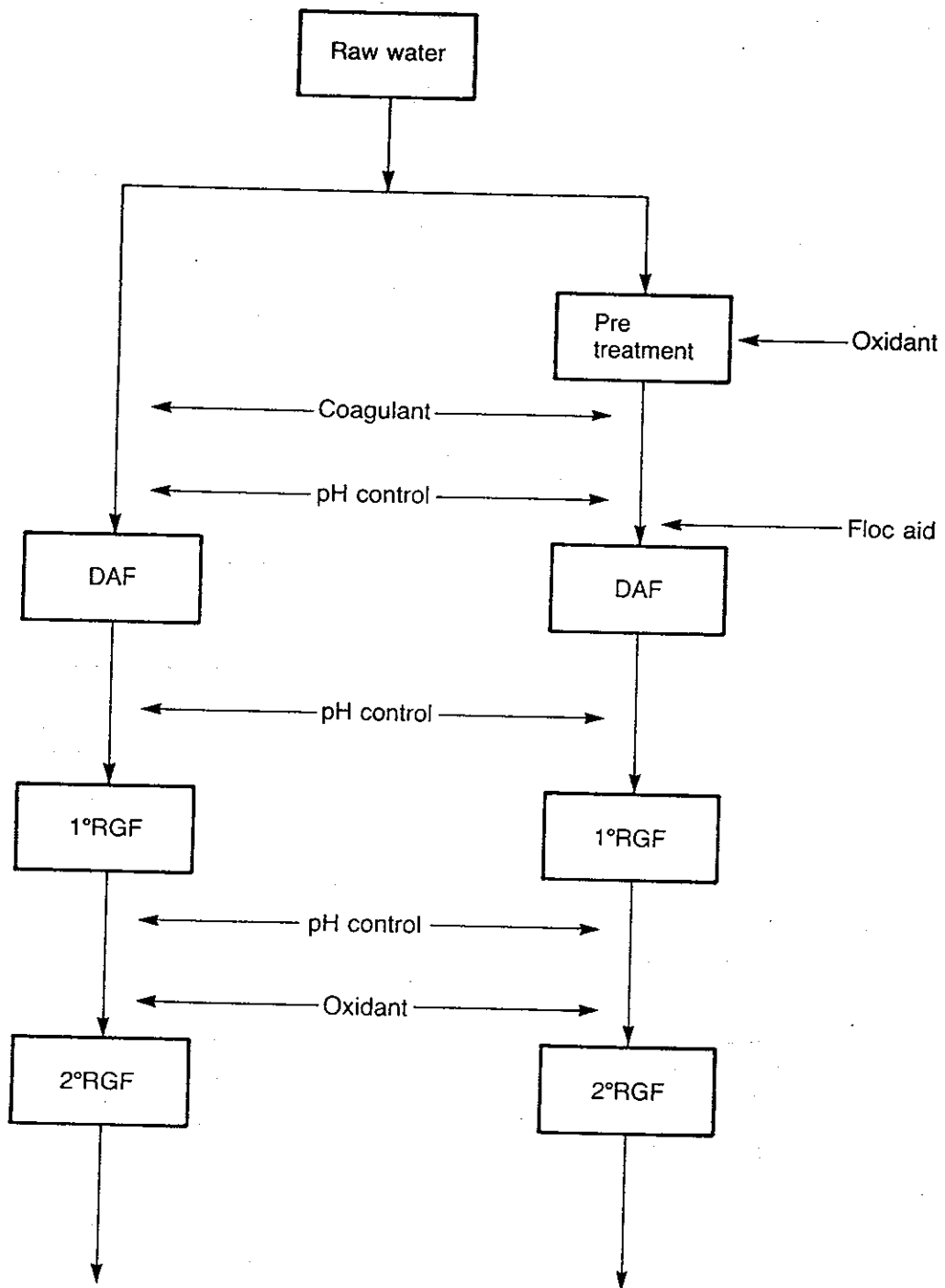


Figure 4 Pilot Plant Flowsheet A



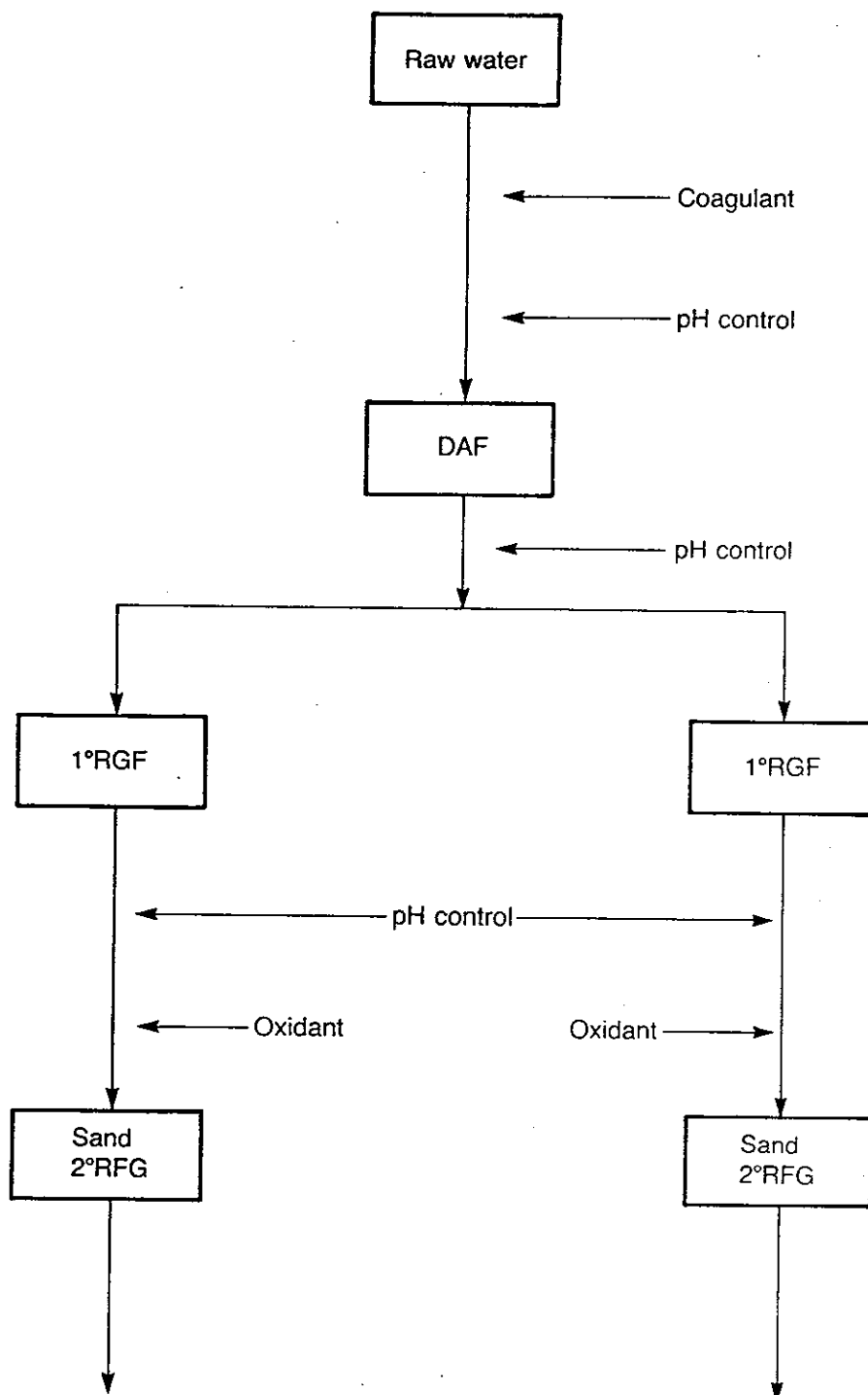


Figure 5 Pilot Plant Flowsheet B

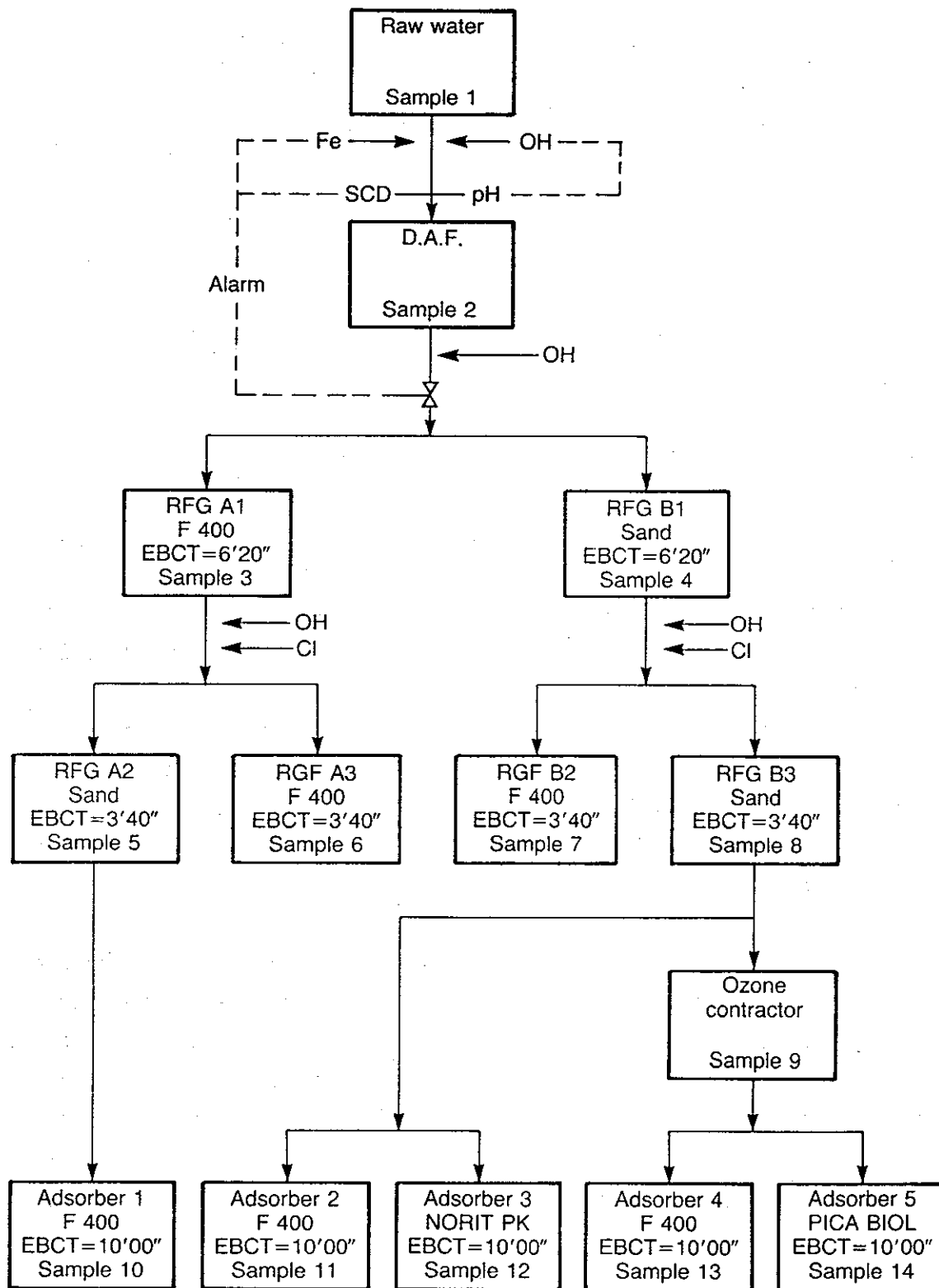


Figure 6 Pilot Plant Flowsheet C

investigated. Only one DAF unit was operated, using ferric as the coagulant; the dose was controlled automatically by an Aztec streaming current detector. The pilot plant was operated as in Figure 6.

## 2.4 ANALYTICAL

### 2.4.1 Standard assays

Each sample was analysed daily for pH, colour, turbidity, UV absorbance at 254nm, and where appropriate, chlorine residual. In addition, a more rigorous analysis of each sample was carried out, on a weekly basis, for most of the determinands in Table 6, AOX and mutagenic activity were analysed at less frequent intervals (2-4 weeks).

The samples submitted for THM, mutagenic activity and AOX analysis had been subjected to 30 minutes of hand chlorination prior to sampling. During this procedure, the water collected from a sample point had its pH adjusted to 9.0 and was then dosed with chlorine (sodium hypochlorite), gently stirred for 30 minutes, and then analysed for free chlorine: if the free residual were  $0.5\text{mg/l} \pm 0.05\text{mg/l}$ , the sample was quenched with sodium thiosulphate, and sent for analysis. However, if the free residual lay outside the required range, the hand chlorination procedure was repeated on a fresh sample of water using a suitably altered dose of sodium hypochlorite.

This technique was used as a standardised method for comparing the potential of water from alternative treatment strategies to form THMs. The concentration of THMs generated during the 30 minutes contact will be lower than the concentration that could be generated by longer contact times and higher doses (such as experienced at many treatment works and within distribution networks), but reaction however reflects a reduction in longer term potential<sup>(7)</sup>.

Table 6 - Analytical determinands

| DETERMINAND             | METHOD   | UNITS                    |
|-------------------------|--|--------------------------|
| Colour*                 | Absorbance at 400nm in 20mm light path   | Absorbance/m or °Hazen** |
| UV*                     | Absorbance at 254nm in 20mm light path   | Absorbance/m             |
| Turbidity               | Ratio Turbidimeter - colour compensated nephelometer   | NTU                      |
| Temperature             | Mercury thermometer  | °C                       |
| pH                      | Colorimetric for site laboratory use, Russel CETL probe for in-line monitoring (recommended by WW) | pH units                 |
| Metals Fe, Al, Mn       | Colorimetric for site laboratory use, atomic absorption off site                                   | mg/l                     |
| TOC (organic carbon)    | TOC monitor (UV based)   | mg/l                     |
| THM***                  | Gas chromatography   | µg/l                     |
| AOX*** (organic halide) | Adsorption onto activated carbon followed by pyrolysis and assay for halides                       | µg/l                     |
| Colony counts***        | Pour plate at 22° and 37°C   | CFU/ml                   |
| Coliforms***            | Membrane   | CFU/100ml                |
| Mutagenic activity      | See Section 2.4.2  | Slope value              |

\* Expressed as "apparent" on whole sample, "true" on 0.45 µ filtered sample

\*\* °Hazen = (Absorbance/m)\*11 (based on NWW standard of 50°Hazen)

\*\*\* Sample bottles used for THM, AOX and bacterial assay have sodium thiosulphate present to quench the free chlorine.

#### 2.4.2 Mutagenicity assays

This can be separated into sample preparation and mutagen assessment.

(i) **Sample preparation:**

The pH of a 20 l sample is adjusted to 7.0 - 7.5 and is then passed through a column of XAD resin at a rate of 1 bed volume per minute and the eluate is collected. The eluate pH is then adjusted to 2.0 - 2.2 using H<sub>2</sub>SO<sub>4</sub> and is passed through a second column of XAD resin. The adsorbed organic material is subsequently eluted from each of the XAD columns using acetone which is then reduced in volume under nitrogen. The overall concentration factor is 2000. Each 20 l sample produces two concentrates: one containing material which has been extracted at pH 7 and another which has been extracted at pH 2. The compounds extractable at pH 2 are more polar at neutral pH than those extractable at pH 7.

(ii) **Assessment of mutagenic activity:**

This is a development of the Ames test<sup>(8)</sup> and uses a specially selected bacterium, *Salmonella typhimurium*. When placed in the prescribed growth medium the bacterium can only proliferate if it first mutates. A culture of the bacterium is exposed to a range of doses of sample concentrate; the number of mutations is then assessed for each dose. If the material is mutagenic then there will be a positive relationship between dose and the number of mutations. This relationship can be expressed as a slope value, the greater the value then the more potent is the concentrate. The potency is not necessarily a direct measure of the concentration of mutagenic material.

Two strains of the bacterium are used, TA 100 and TA 98, and thus each sample can be represented by 4 slope values (TA100 pH7, TA100 pH2, TA98 pH7 and TA98 pH2) although the pH7 and pH2 values can be combined to give a "total" activity for a given strain.

A positive response with TA 98 and TA 100 gives a measure of two different types of mutagenic compound.

Mutagenicity assays are widely used to assess the potential of a compound, or mixture of compounds, to induce cancer, a carcinogen is usually also mutagenic but the converse is less so. The mutagenic potency of drinking water is extremely low, as indicated by the need to concentrate by a factor of 2000 to get a measurable response in the test, and the health concern relates to long term consumption (in conjunction with many other materials) during a consumers lifetime. To date epidemiological studies have been unable to show a clear link between the occurrence of any specific types of cancer and the quality of drinking water.

## SECTION 3 - RESULTS

### 3.1 METALS

Figures 7 to 9 show average iron, manganese and aluminium concentrations respectively at the different stages of three stage treatment in the control stream. For each figure two bar charts are shown: one when alum was used as the coagulant and one when ferric was used. Results are from Phase I, without automatic dose control.

#### 3.1.1 Iron (Figure 7)

When alum was used as the coagulant, there was some removal of iron by the DAF, and there was further removal of iron by the 1° RGF. When ferric was used as the coagulant, there was increased iron concentration after the DAF due to coagulant carryover, but this was removed by the 1° RGF. There was no further removal of iron by the 2° RGF, irrespective of coagulant.

#### 3.1.2 Aluminium (Figure 8)

When alum was used as the coagulant, there was increased aluminium concentration after the DAF due to coagulant carryover, but this was removed by the 1° RGF. When ferric was used as the coagulant, most of the aluminium was removed by the DAF, with further removal by the 1° RGF. There was very little aluminium removal in the 2° RGF with either coagulant.

#### 3.1.3 Manganese (Figure 9)

There was no manganese removal, with either coagulant, by the DAF or the 1° RGF. Virtually all of the manganese was removed by the 2° RGF.

Figure 10 plots manganese concentration in the 2° RGF filtrate as a function of pH, filter media, and the use of interfiltration chlorination. At a pH greater than 8.5, manganese was removed on both

GAC and sand, with or without inter-filtration chlorine being dosed. Manganese could be removed on sand at any pH between 6.4 and 9, as long as a measurable free residual of chlorine in the 2° filtrate was maintained; without inter-filtration chlorination, manganese could only be removed if pH were greater than 7.5. Manganese could be removed on GAC at a pH greater than 7.0 with inter-filtration chlorination or at a pH greater than 8.5 without inter-filtration chlorination.



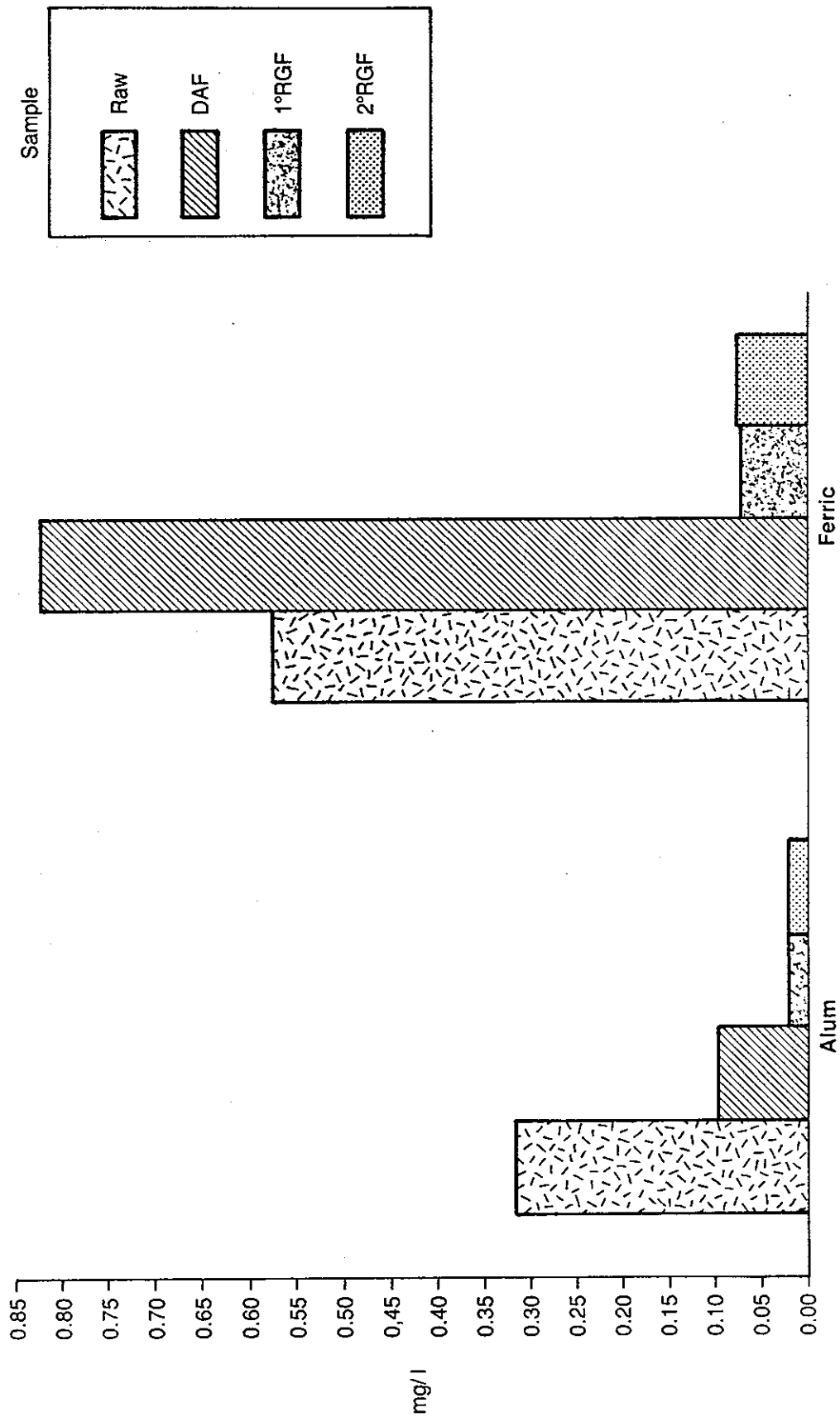


Figure 7 Average Iron at Different Treatment Stages Using Alum or Ferric as Coagulant

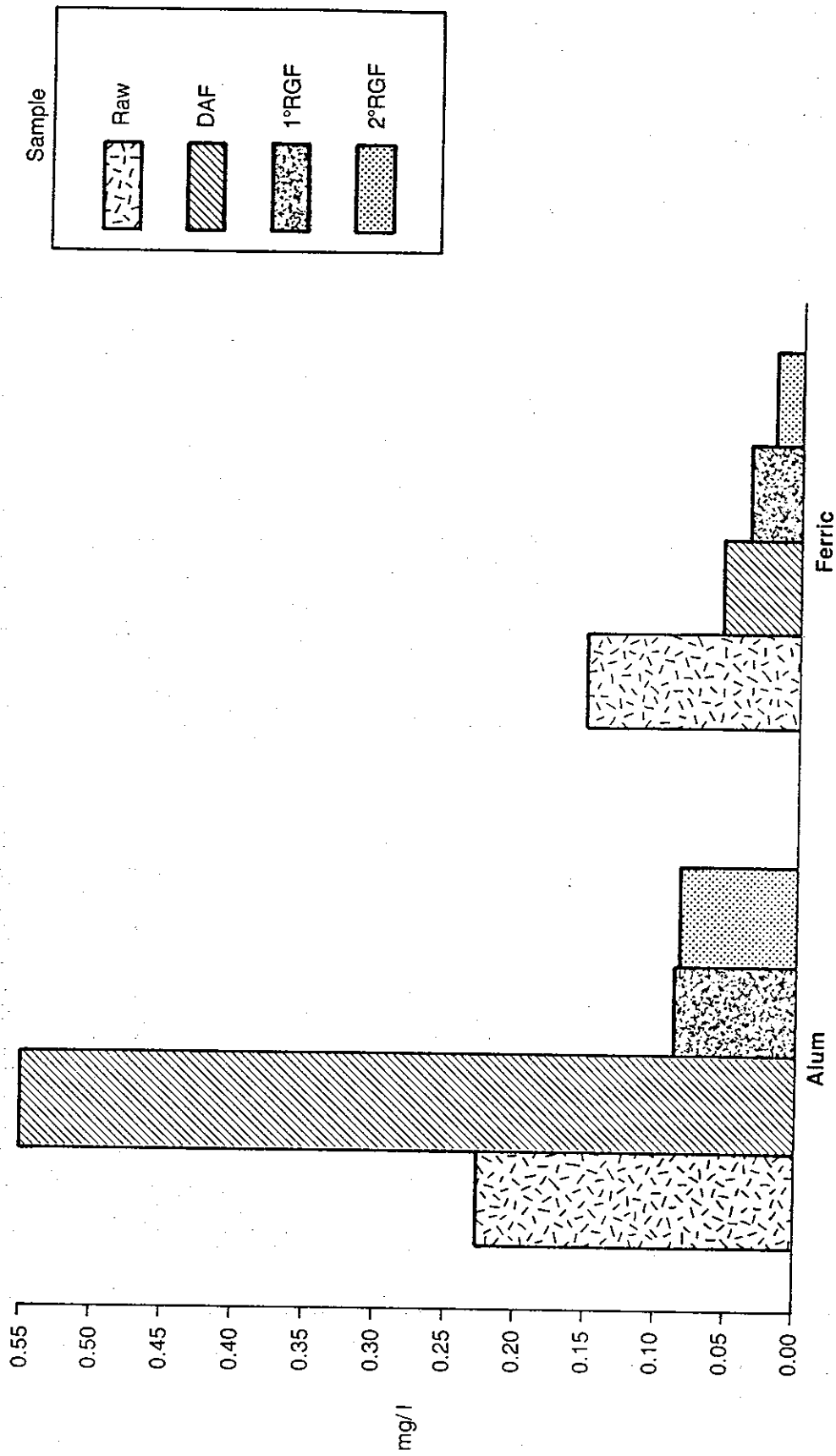


Figure 8 Average Aluminium at Different Stages using Alum or Ferric as Coagulant

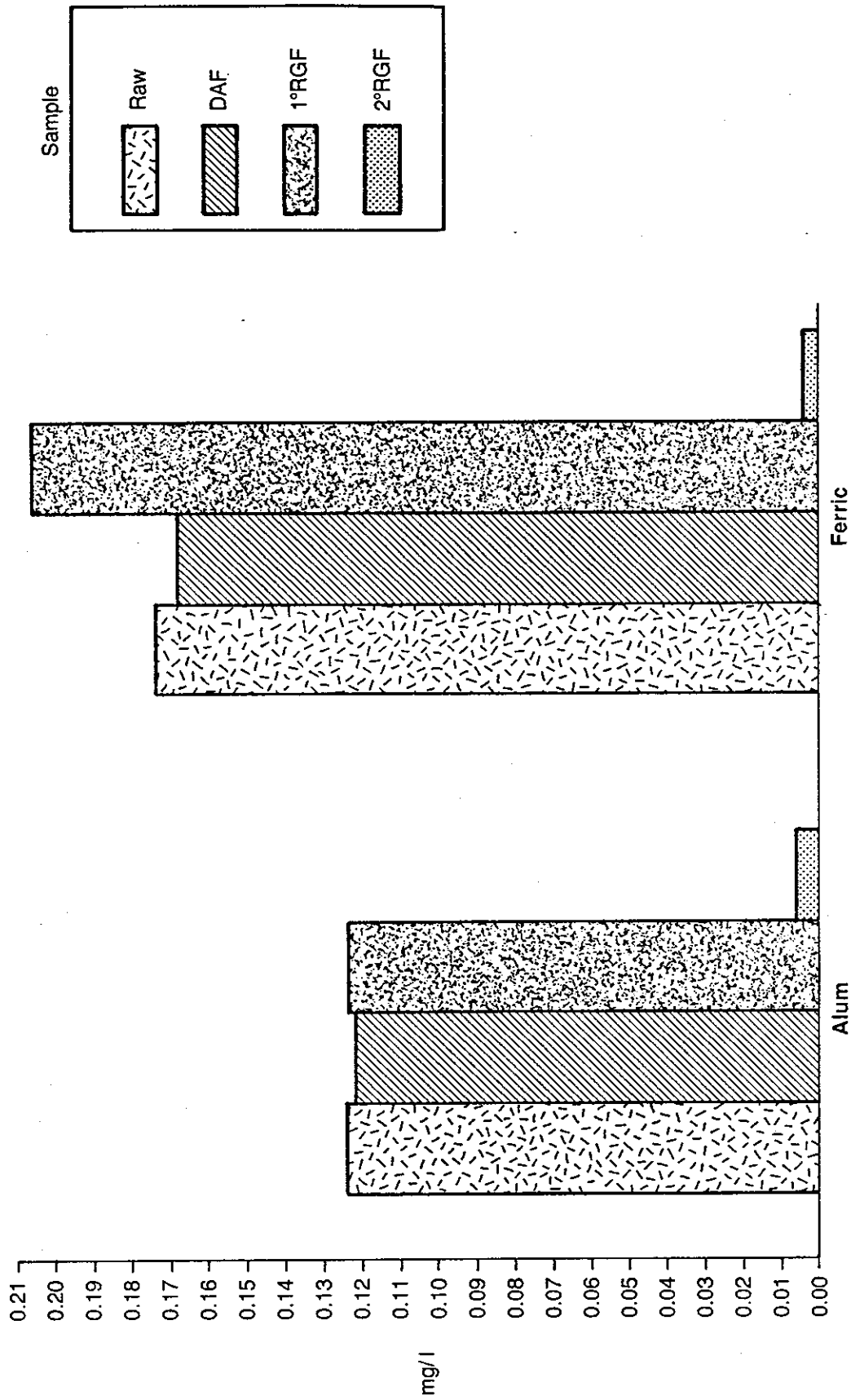


Figure 9 Average Manganese at Different Treatment Stages Using Alum or Ferric as Coagulant

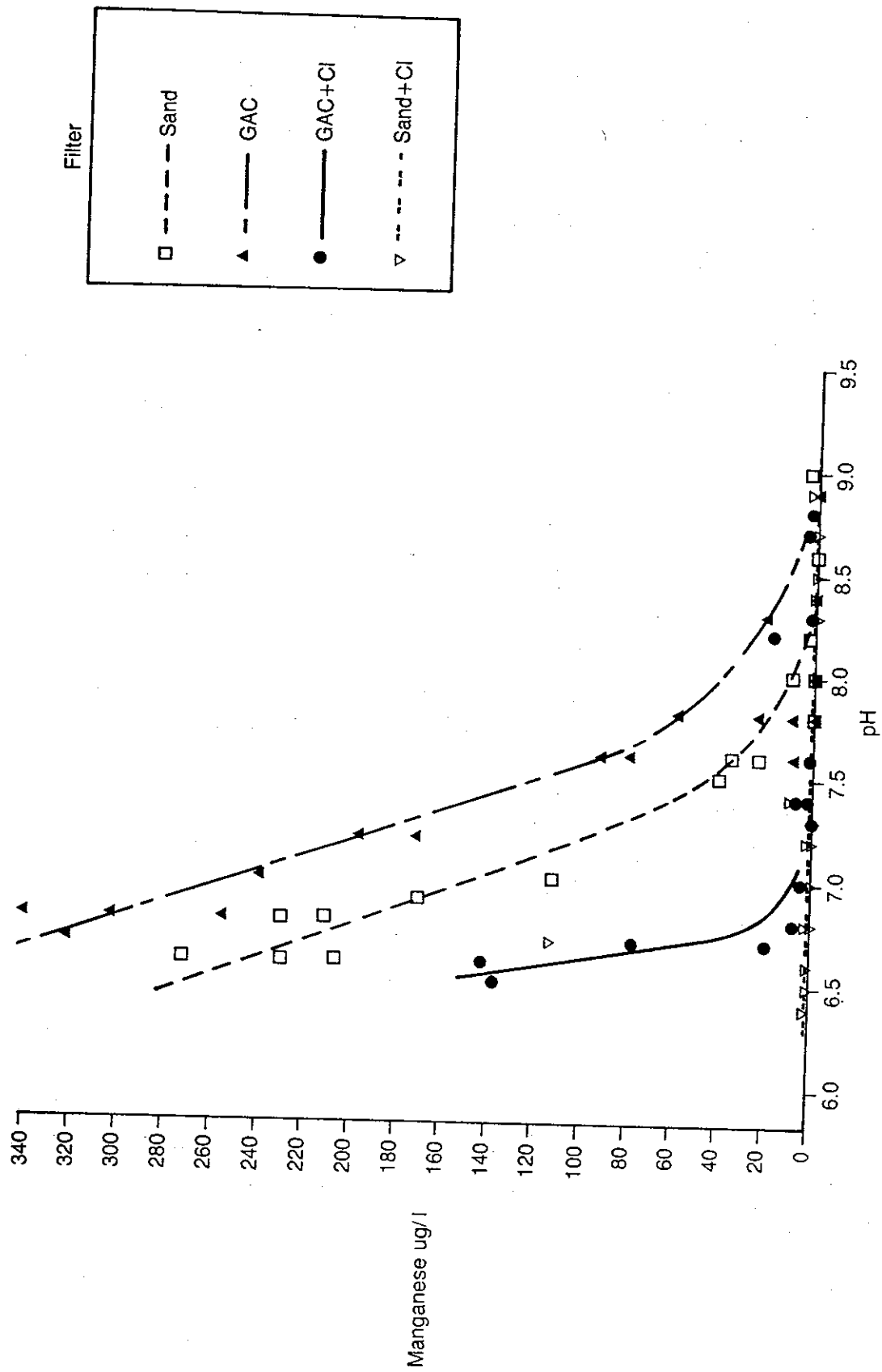


Figure 10 Manganese vs. Secondary RGF pH

## 3.2 ORGANICS

### 3.2.1 Coagulation conditions

Figures 11 to 13 plot final water colour, TOC, or total THMs (formed after 30 minutes of hand chlorination) against coagulation pH when using alum or ferric as the coagulant. There was a similar trend for each determinand, with an optimum pH of 4.6 when ferric was used, and an optimum pH of 5.5 when alum was used.

Figures 14 to 16 plot final water colour, TOC, or total THMs (formed after 30 minutes of hand chlorination) against coagulant dose when using alum (at pH 5.4) or ferric (at pH 4.6) as the coagulant. Increasing coagulant dose resulted in decreases in all three determinands, but after 2-4mg/l, further increases in coagulant dose resulted in little, or no further, decrease in any of the determinands.

Table 7 compares the performance of different coagulants and flocculation aids with respect to the removal of a number of organic determinands.

When comparing ferric with alum, doses were equimolar, and the coagulation pH was 5.4 for alum and 4.6 for the ferric.

When comparing copperas and ferric, doses were equal in terms of iron, and the coagulation pHs were the same.

LT31 was used alone as a coagulant, at a dose and pH (4.7) decided by jar tests.

With both LT25 and LT22, the ferric dose and coagulation pH in the trial and control streams were equal, and the floc aid was dosed into the inlet of the trial stream flocculator.

Table 7 - Effect of coagulant type and floc aids

|           | DOSE<br>mg/l | COLOUR<br>HAZEN | TOC<br>mg/l | THMs<br>ug/l | AOX<br>ug/l | MUTAGENICITY   |                 |
|-----------|--------------|-----------------|-------------|--------------|-------------|----------------|-----------------|
|           |              |                 |             |              |             | TA 98<br>Slope | TA 100<br>Slope |
| Alum      | 1.9          | 3               | 3.3         | 14           | 27          | 28             | 12              |
| Ferric    | 3.9          | 2               | 2.9         | 9            | 20          | 23             | 9               |
| Copperas  | 3.9+3.6Cl    | 2               | 3.4         | 62           | 41          | 27             | 8               |
| Ferric    | 4.0          | 2               | 3.1         | 38           | 32          | 17             | 7               |
| LT31      | 5.1          | 4               | 3.6         | 34           | 43          | 40             | 7               |
| Ferric    | 4.0          | 3               | 2.6         | 20           | 25          | 27             | 6               |
| Fe + LT25 | 3.5+0.3      | 4               | 2.6         | 17           | 25          | 23             | 5               |
| Ferric    | 3.8          | 4               | 2.5         | 17           | 27          | 21             | 7               |
| Fe + LT22 | 2.9+0.4      | 4               | 2.1         | 14           | 22          | 21             | 5               |
| Ferric    | 3.2          | 4               | 2.2         | 14           | 26          | 20             | 5               |

From the table, it can be seen that ferric produced slightly better quality water in terms of all 6 determinands than alum. Chlorinated copperas produced final water of equal colour, and similar TOC to ferric, but produced much greater disinfection by-products. LT31 produced worse quality water than ferric in terms of all 6 determinands. Neither of the floc aids appeared to produce a change in water quality compared to ferric in terms of any of the 6 determinands but the float produced by the DAF was visibly thicker.

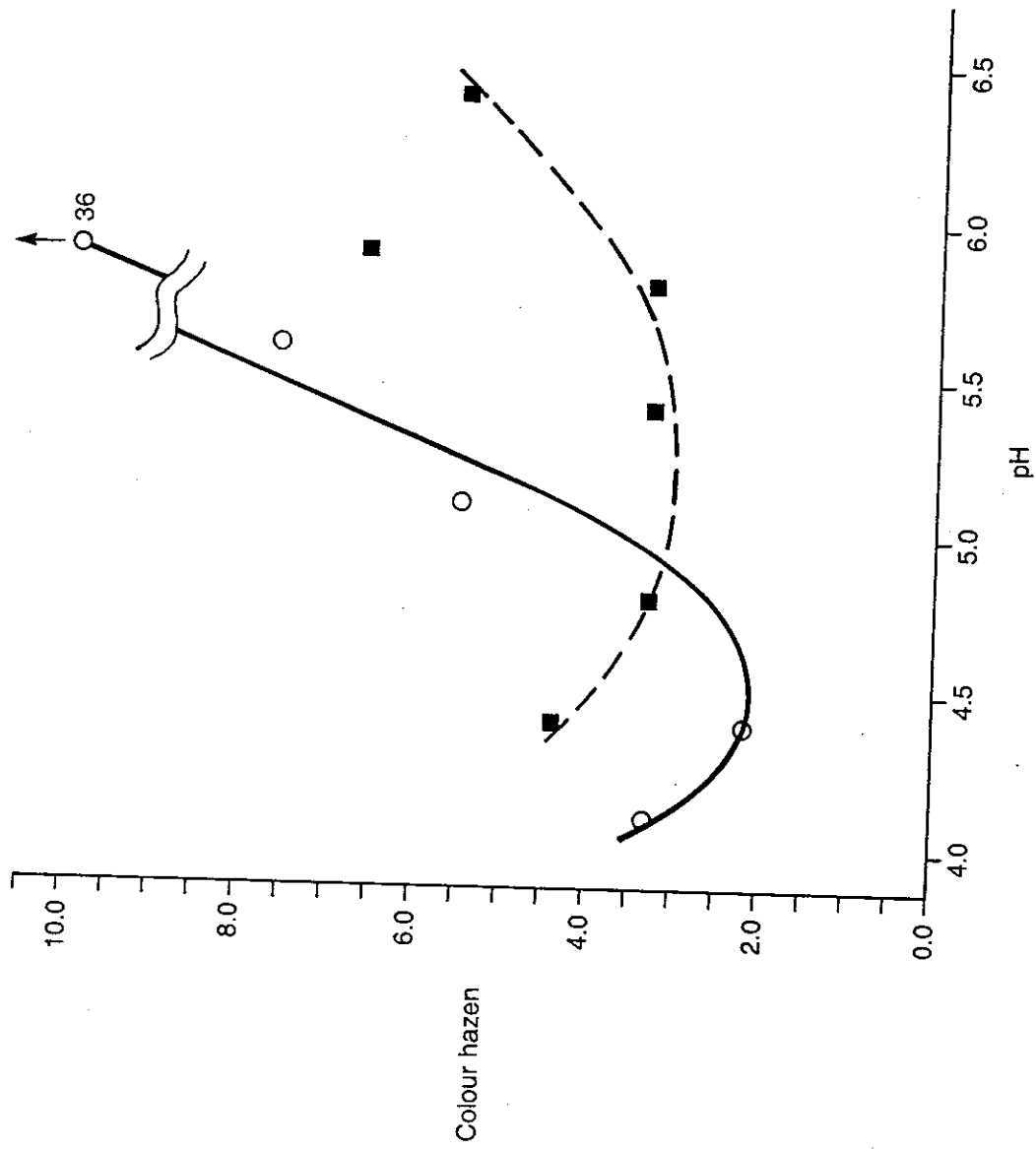


Figure 11 Effect of Coagulation pH on Final Water Colour

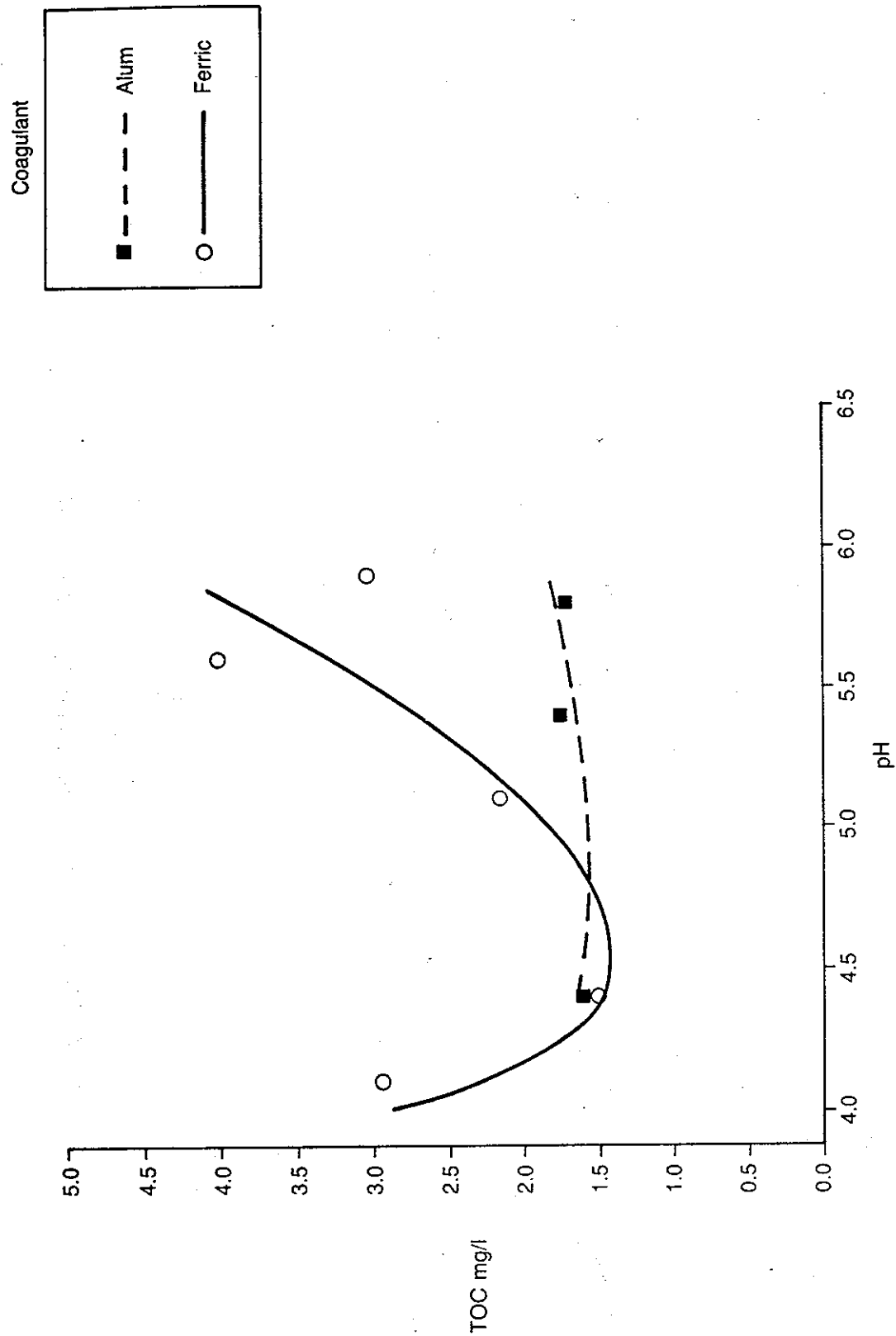


Figure 12 Effect of Coagulation pH on Final Water TOC



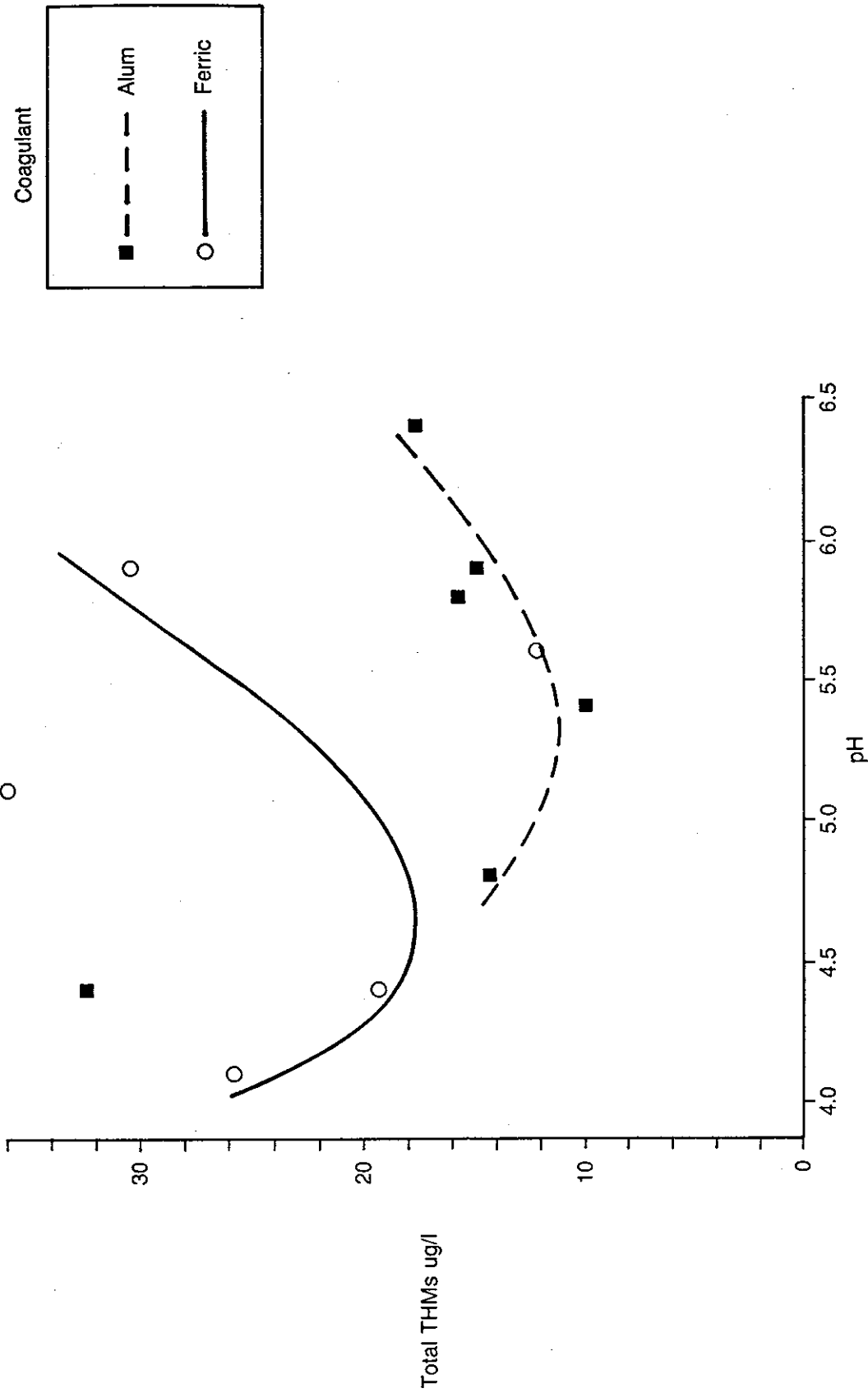


Figure 13 Effect of Coagulation pH on Final Water Total THMs

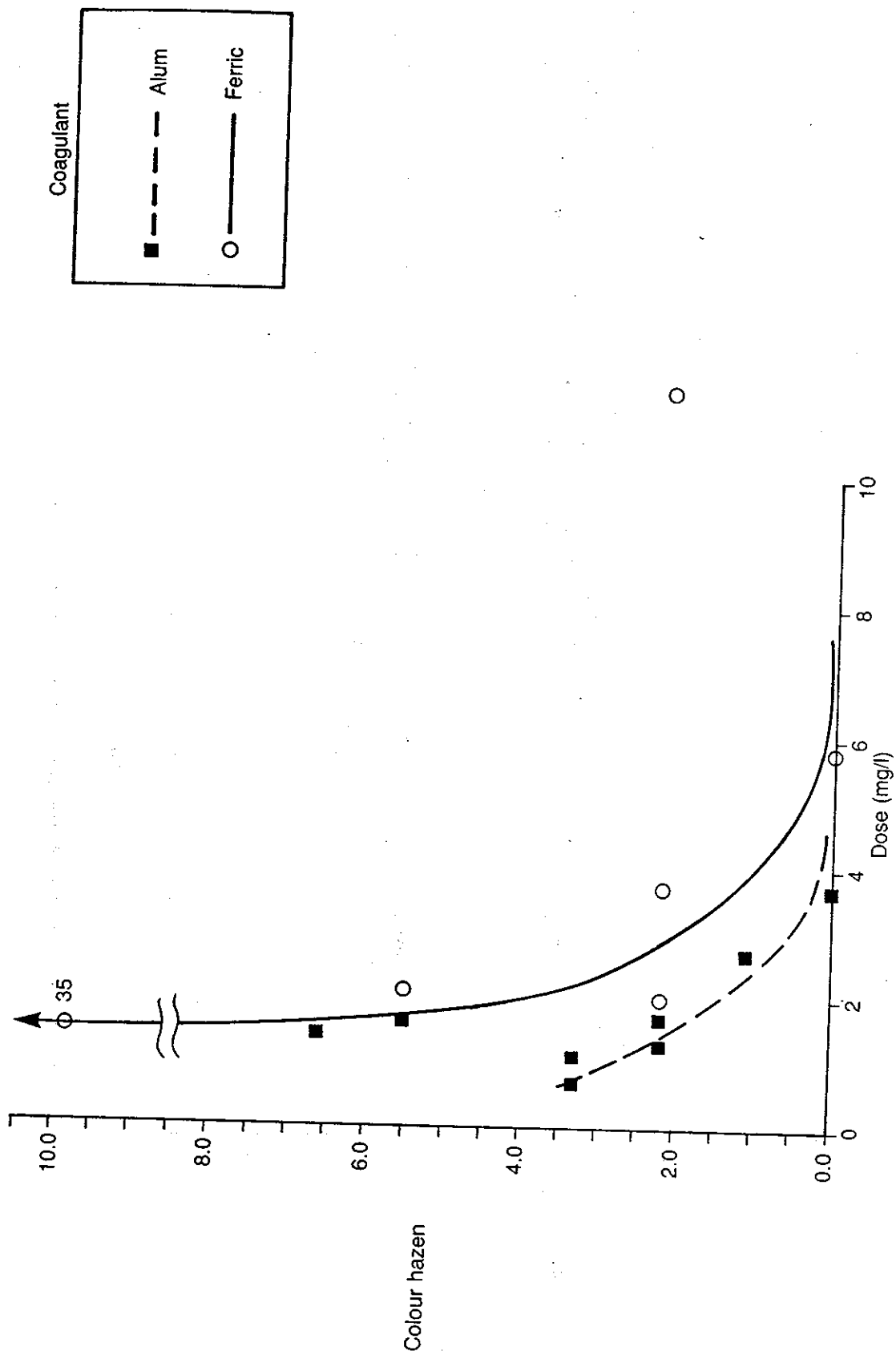


Figure 14 Effect of Coagulant Dose on Final Water Colour

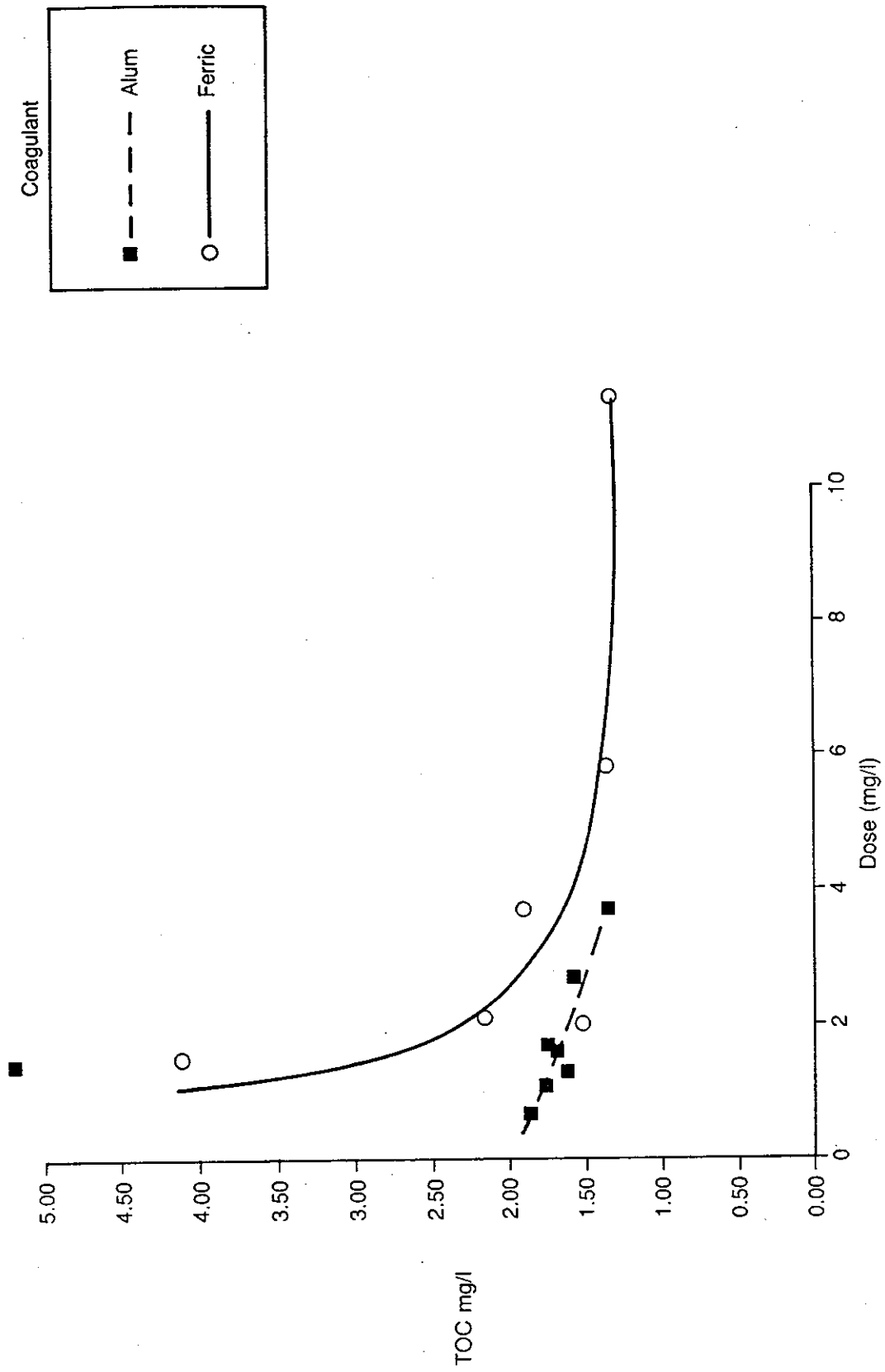


Figure 15 Effect of Coagulant Dose on Final Water TOC

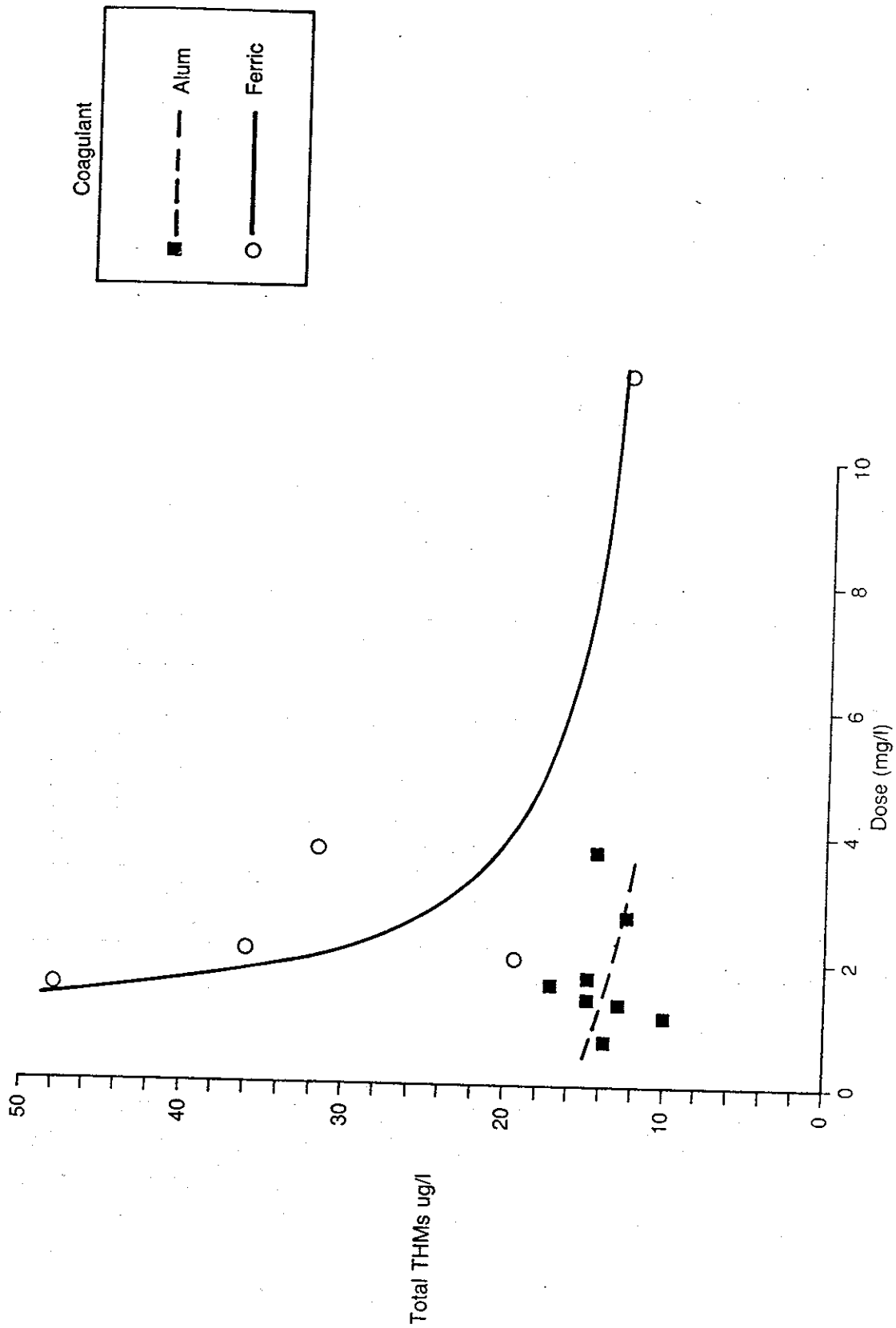


Figure 16 Effect of Coagulant Dose on Final Water Total THMs

### 3.2.2 Use of oxidants

Table 8 shows the effect of using ozone or chlorine at different stages of the treatment process. The table shows the percentage change in organic determinands in the oxidised stream compared to the control stream (thus positive numbers indicate that the use of an oxidant resulted in a deterioration in water quality); the average concentrations in the control stream during phase 3 are given for comparison. On occasions some TA98 mutagenic activity was measured in the raw water, prior to any chlorination, but this was less than 30% of the total TA98 after chlorination. Other mutagenic activity was absent from the raw water.

**Table 8 - Mean percentage change in organic determinands in final, hand chlorinated, water**

| OXIDANT POSITION AND TYPE | COLOUR         | TOC           | THMs          | AOX            | MUTAGENICITY   |                 |
|---------------------------|----------------|---------------|---------------|----------------|----------------|-----------------|
|                           |                |               |               |                | TA 98          | TA 100          |
| Pre Cl2                   | 0              | -7            | +125          | +40            | +40            | +70             |
| Pre O3                    | -10            | -2            | +5            | -28            | -54            | -24             |
| Inter Cl2                 | -2             | +1            | +25           | +13            | nd             | nd              |
| Inter O3                  | +236           | -9            | -52           | -57            | -76            | -61             |
| Post O3                   | -77            | -3            | -31           | -56            | -80            | -61             |
| (control)                 | (2.2)<br>Hazen | (2.6)<br>mg/l | (8.3)<br>ug/l | (33.0)<br>ug/l | (6.7)<br>Slope | (22.8)<br>Slope |

nd - not determined

#### (a) Preoxidation

Neither pre-chlorination nor pre-ozonation had much effect on final water colour or TOC. Pre-chlorination resulted in greatly increased THMs, and increased AOX and mutagenic activity, due principally to the production of by-products during the treatment process.

Although there was only a small effect of pre-ozonation on final water colour, its effect was very much dependent on dose (Figure 17). Low pre-ozonation doses (up to 2mg/l) resulted in a reduction in final water colour, but high pre-ozonation doses (over 4mg/l) resulted in a deterioration in final water quality. Pre-ozonation had very little effect on THMs (at any ozone dose, see Figure 18) but reduced AOX and mutagenic activity.

(b) **Inter-filtration oxidation**

Inter-filtration chlorination had very little effect on colour or TOC, but it did result in increased THMs and slightly increased AOX. This increase is shown in Figure 19 where the concentration of THMs formed during hand chlorination (to a 30 minute 0.5mg/l free Cl residual) of a 1° RGF filtrate is compared to that formed during 2° RGF filtration (at different free chlorine residual concentrations) and subsequent hand chlorination (to a 30 minute 0.5mg/l free Cl residual). The greater the free residual in the 2° RGF filtrate, the lower was the chlorine dose required during hand chlorination of the 2° RGF filtrates to provide the 30 minute residual of 0.5mg/l. The results are plotted as a percentage increase in THMs against free chlorine concentration in the 2° RGF filtrate. The results indicate that increasing the chlorine dose applied to the 2° RGF leads to higher levels of THMs.

Inter-filtration ozonation resulted in reductions in disinfection by-products, with little effect on TOC, but greatly increased colour. The colour was not organic colour but was associated with manganese which appeared to be oxidised by ozone into a colloidal form that was not removed by the 2° filters (nor by a 0.45µm acetate membrane filter). The results summarised in Table 8 were obtained from inter-filtration ozone doses varying from 0.3mg/l to 5.0mg.l but there appeared to be little extra benefit, in terms of THMs, from doses greater than 2mg/l.

(c) **Post-ozonation**

Post-ozonation resulted in reductions of colour, AOX, mutagenic activity, and THMs (formed after 30 minutes of hand chlorination) but had little or no effect on TOC. The ozone dose was kept constant at about 2mg/l.

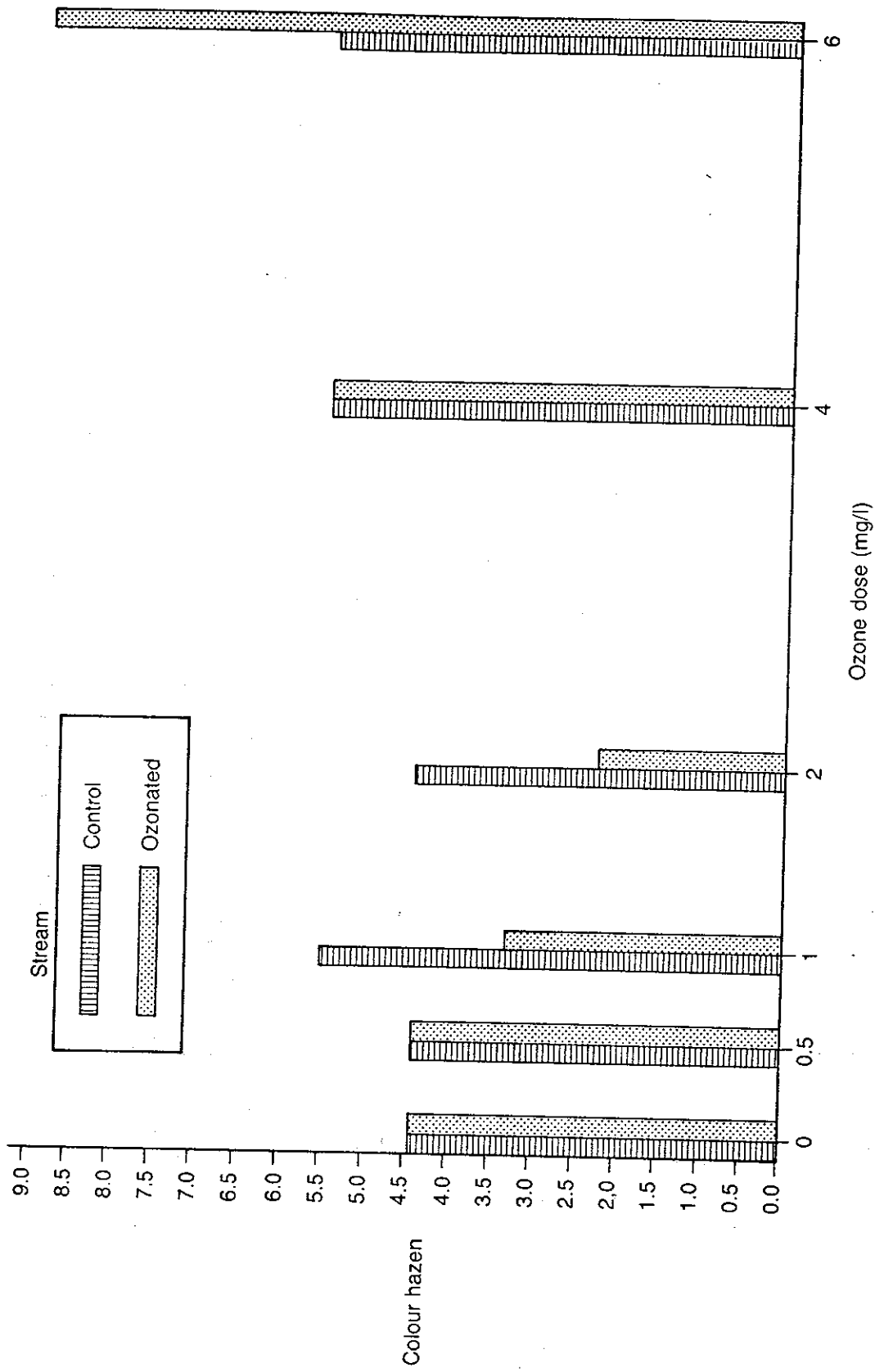


Figure 17 Final Water Colour vs. Raw Water Ozone Dose



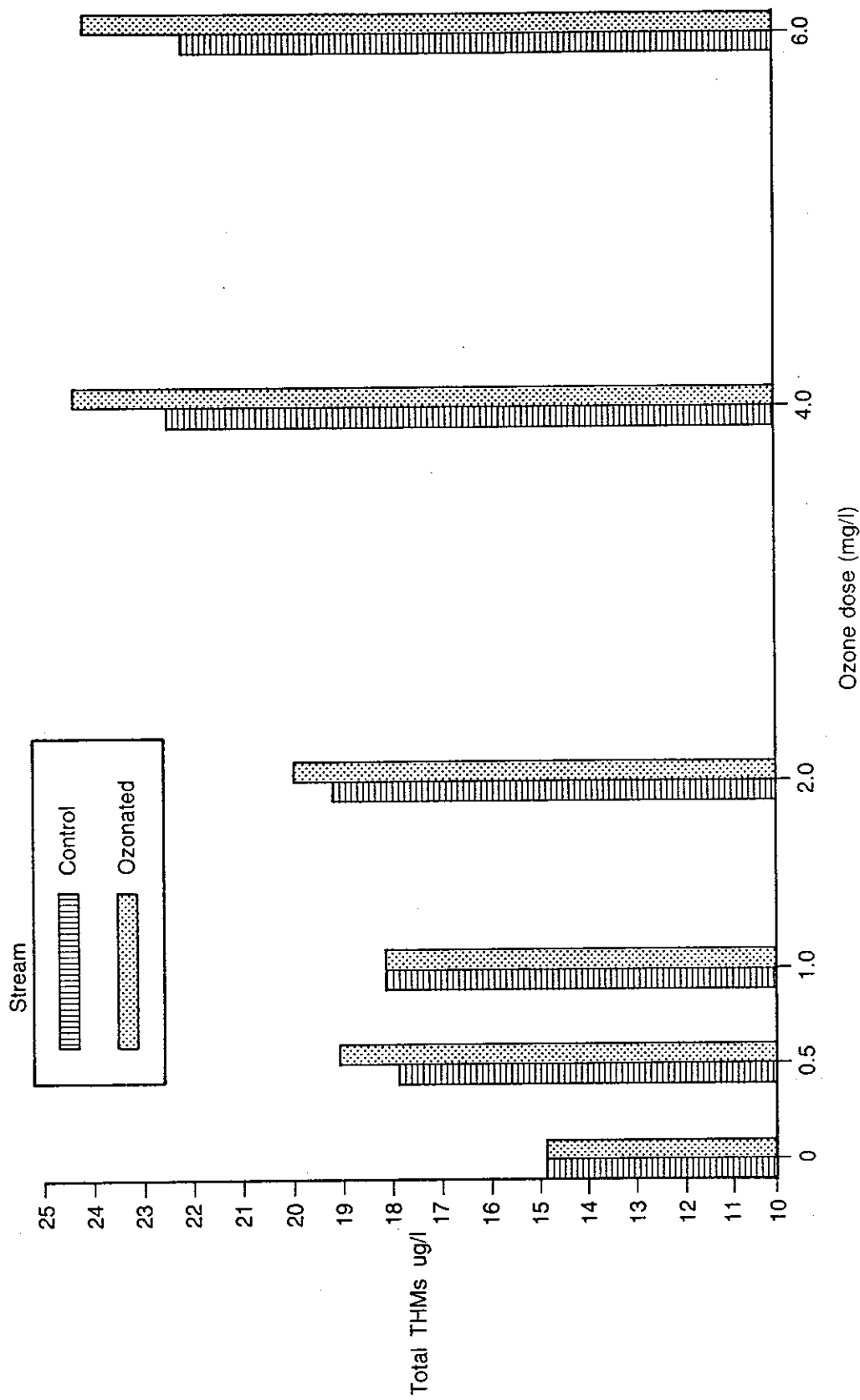


Figure 18 Final Water THMs vs. Raw Water Ozone

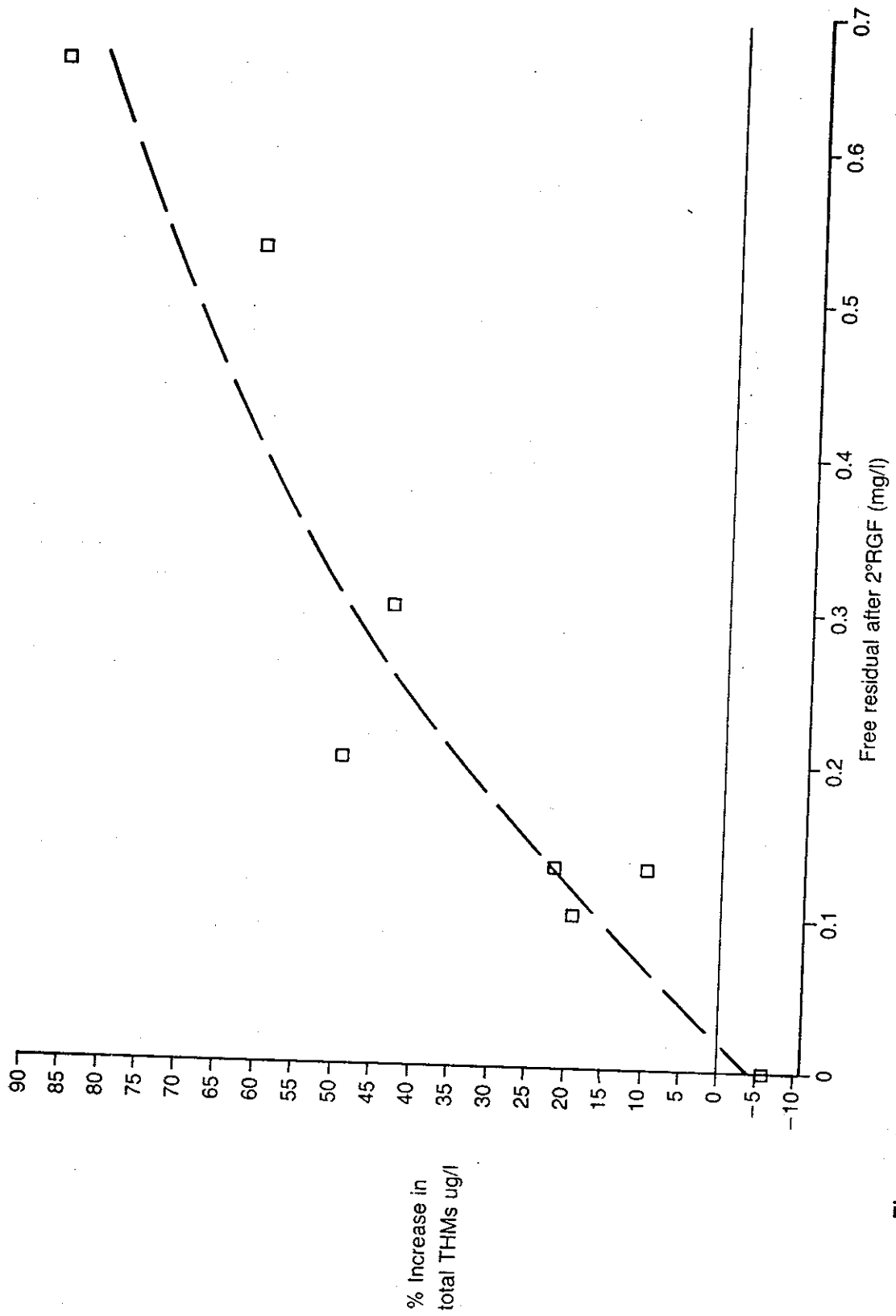


Figure 19 % Increase in THMs Between 2°RGF and 1°RGF vs. Free Residual After 2°RGF

### 3.2.3 Use of granular activated carbon

#### (a) EBCT/location

Figures 20 to 25 show the effect of empty bed contact time (EBCT) on the reduction in organic determinands. In each case, the GAC used was coal based (Chemviron Filtrasorb F400) and the different EBCTs represent different locations within the process stream. The plots for colour and TOC show cumulative removal and those for THMs, AOX and Mutagenicity show breakthrough curves. All of the plots shows that increasing EBCT resulted in proportionately extended bed life. This is quantified by Figure 26 which plots the run length at which 50% breakthrough of UV absorbance occurred, against EBCT. For an EBCT greater than 6 minutes, run length was directly proportional to EBCT. Location had little effect on performance as indicated by the F400 post adsorber, with an EBCT of 10 minutes, which performed almost identically to the combined 1° + 2° RGFs F400 (which combined also had an EBCT of 10 minutes).

#### (b) GAC type

Table 9 shows mean reductions (relative to the sand filtered water) over a 240 day run in organic determinands for different types of GAC treatment. All of the GACs had an EBCT of 10 minutes.

The coal based GAC (F400) performed better than peat based GAC (Norit PK).

(c) **Ozonation**

Ozonation prior to GAC resulted in greater removal of organics than GAC alone. However, the reduction obtained with ozone and GAC appeared to be no greater than would be expected from the sum of the reductions from the two individual processes (i.e. there was no synergistic effect from the combination).

In addition, Table 9 shows that after ozone, coal based GAC (F400) performed much better than wood based GAC (Pica Biol) for organics removal.

**Table 9 - % reduction in organic determinands for different GAC treatments**

| GAC TREATMENT     | COLOUR         | TOC           | THMs          | AOX            | MUTAGENICITY   |                 |
|-------------------|----------------|---------------|---------------|----------------|----------------|-----------------|
|                   |                |               |               |                | TA 98          | TA 100          |
| 1'+2' RGF F400    | 45             | 26            | 60            | 47             | 69             | 50              |
| Post F400         | 55             | 24            | 63            | 40             | 78             | 58              |
| Post Norit PK     | 27             | 1             | 39            | 16             | 55             | 33              |
| 03+Post F400      | 91             | 34            | 75            | 73             | 91             | 80              |
| 03+Post Pica Biol | 77             | 4             | 40            | 61             | 87             | 65              |
| 03 only           | 77             | 3             | 31            | 56             | 80             | 61              |
| (control)         | (2.2)<br>Hazen | (2.6)<br>mg/l | (8.3)<br>ug/l | (33.0)<br>ug/l | (6.7)<br>Slope | (22.8)<br>Slope |

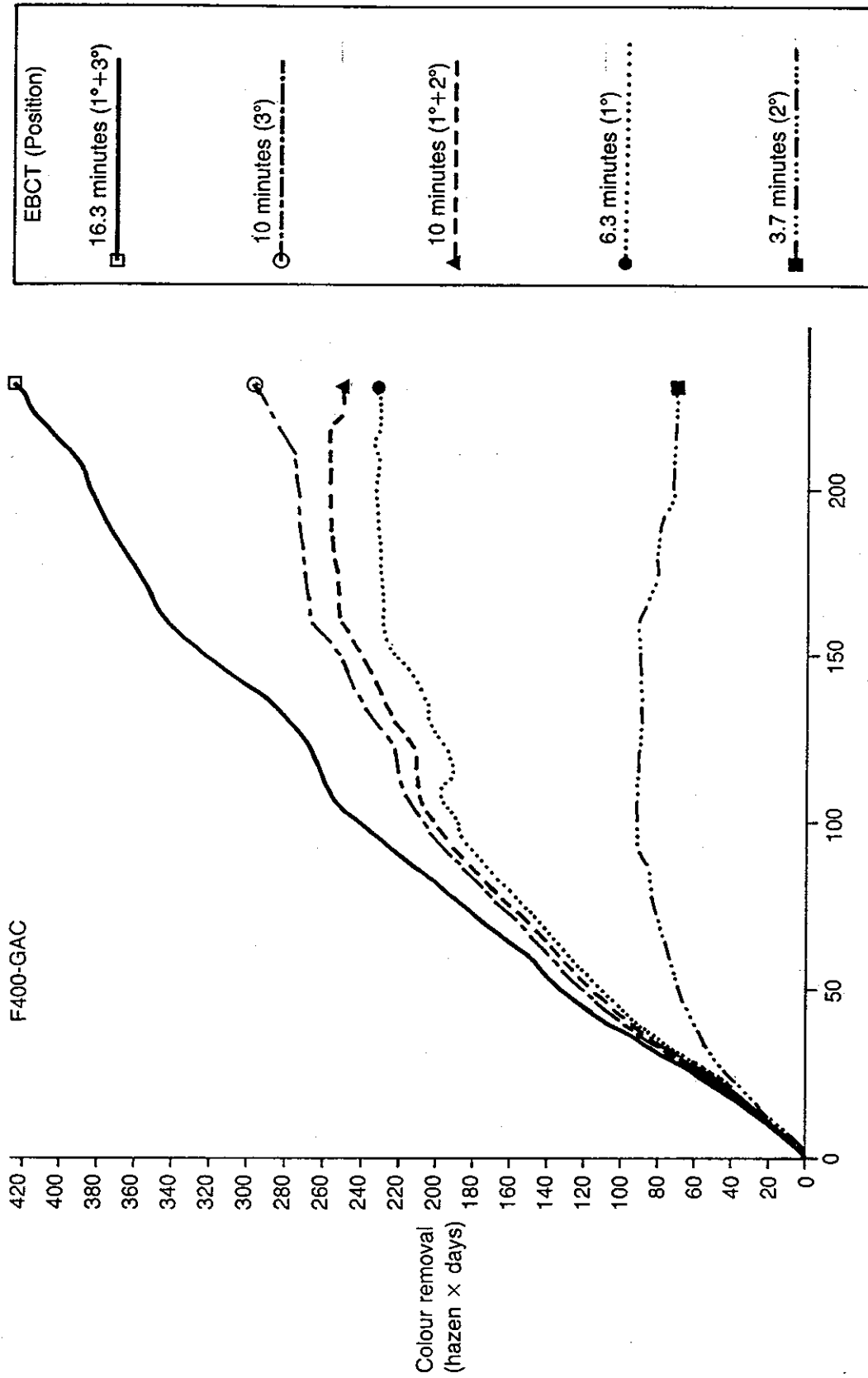


Figure 20 Effect of Empty Bed Contact Time on Cumulative Colour Removal

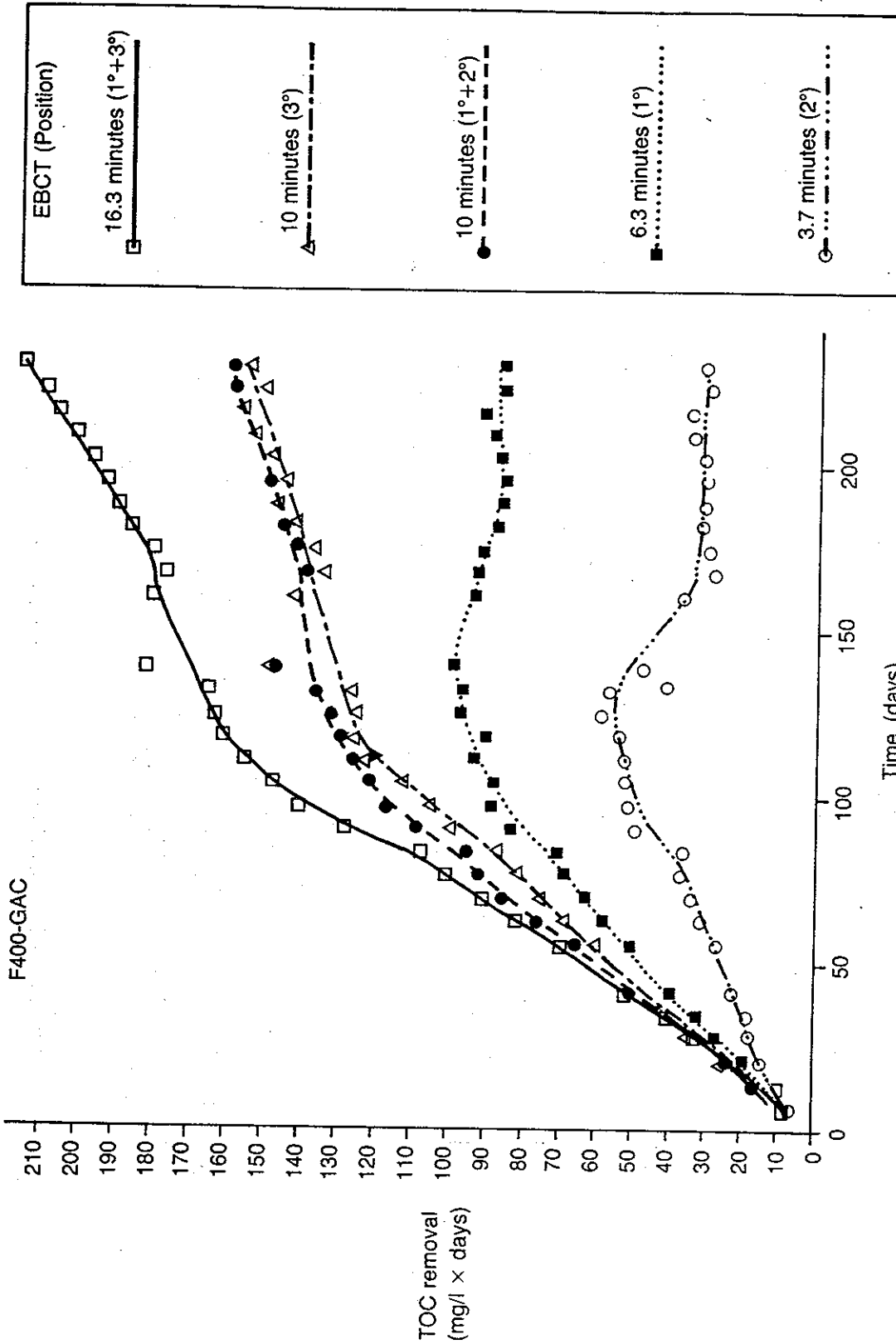


Figure 21 Effect of Empty Bed Contact Time on Cumulative TOC Removal

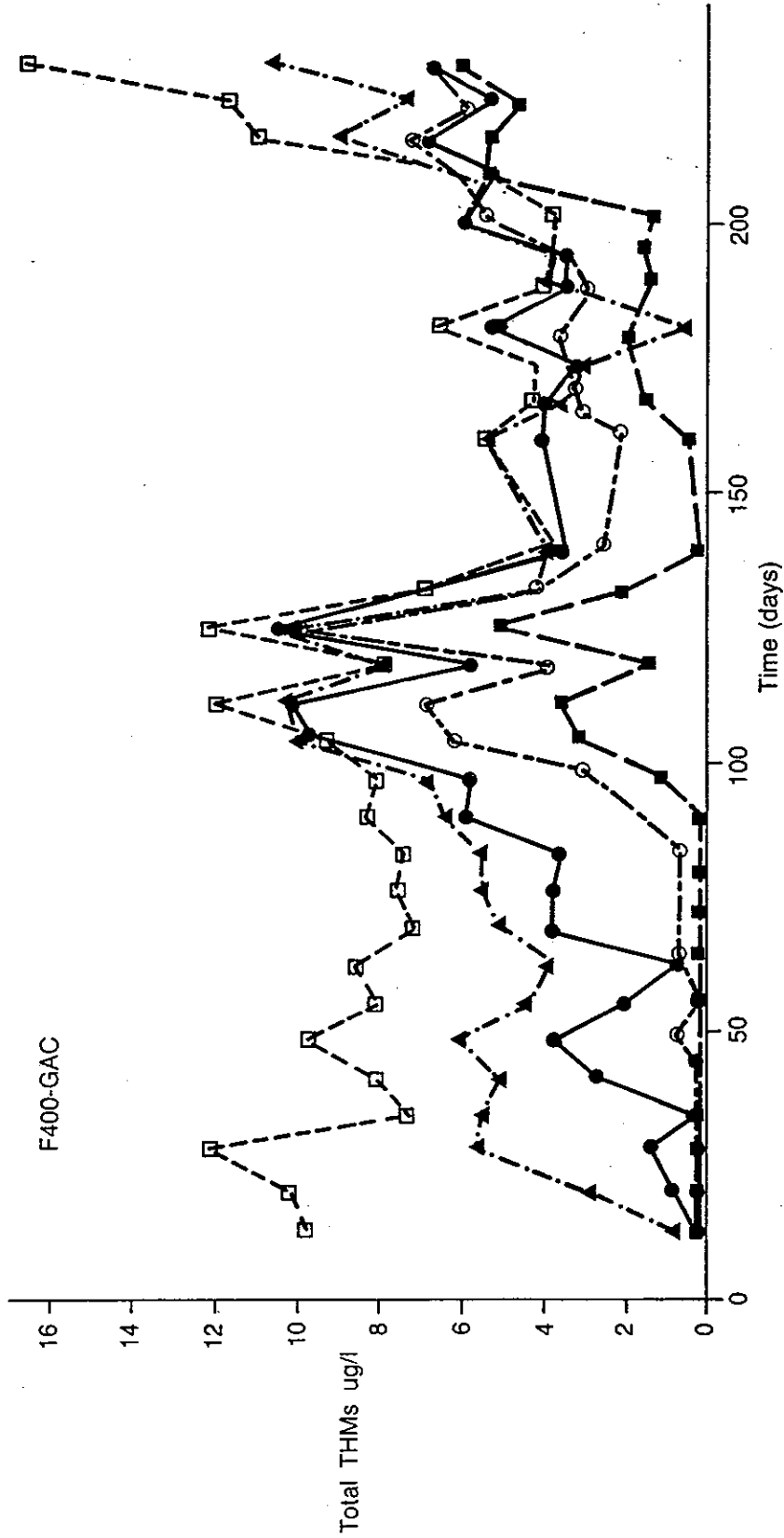
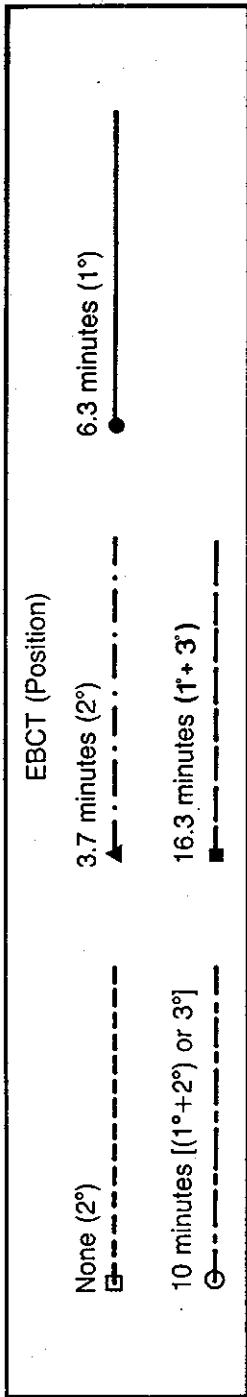


Figure 22 Effect of Empty Bed Contact Time on Total THM Precursors

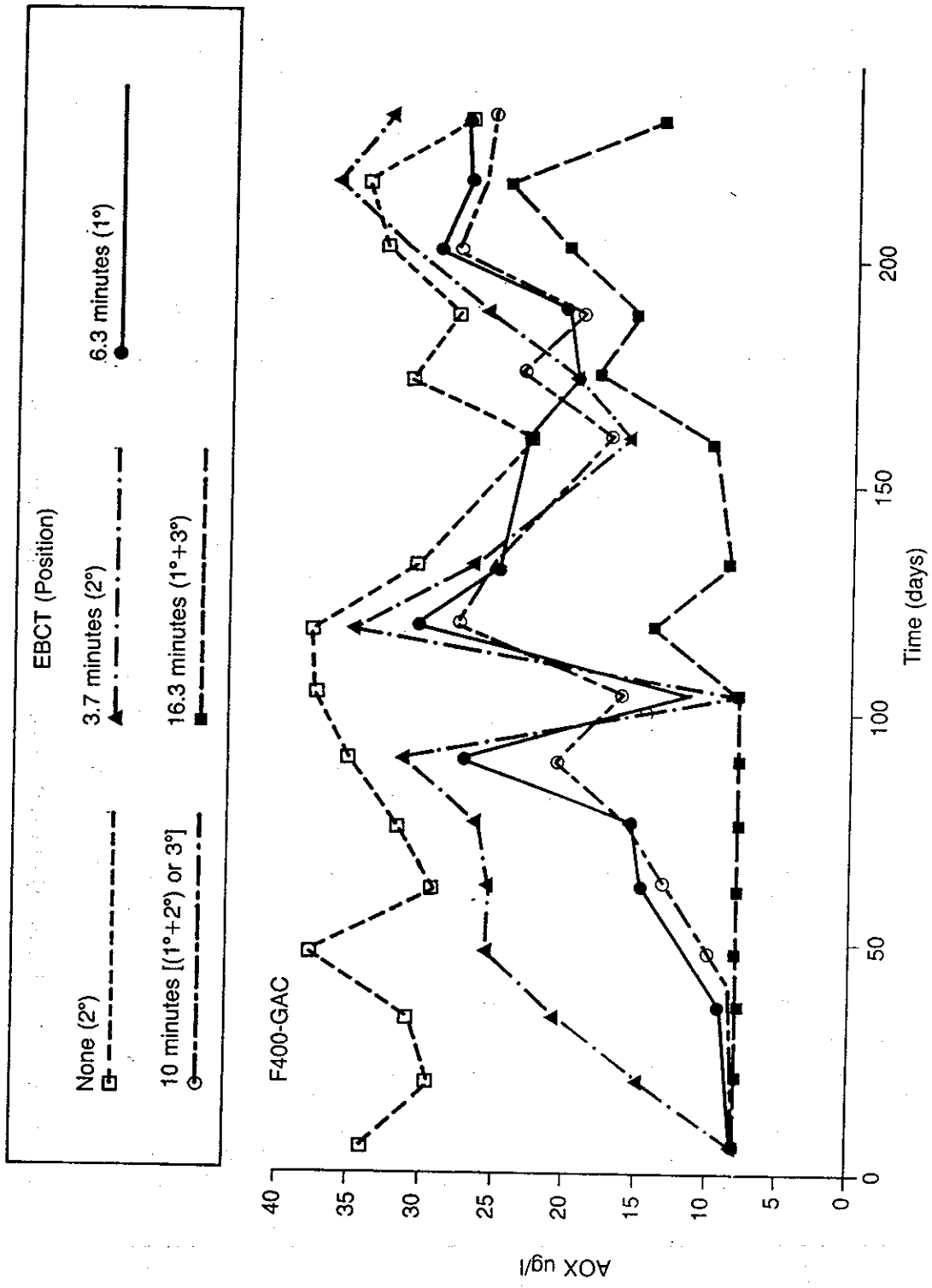


Figure 23 Effect of Empty Bed Contact Time on AOX



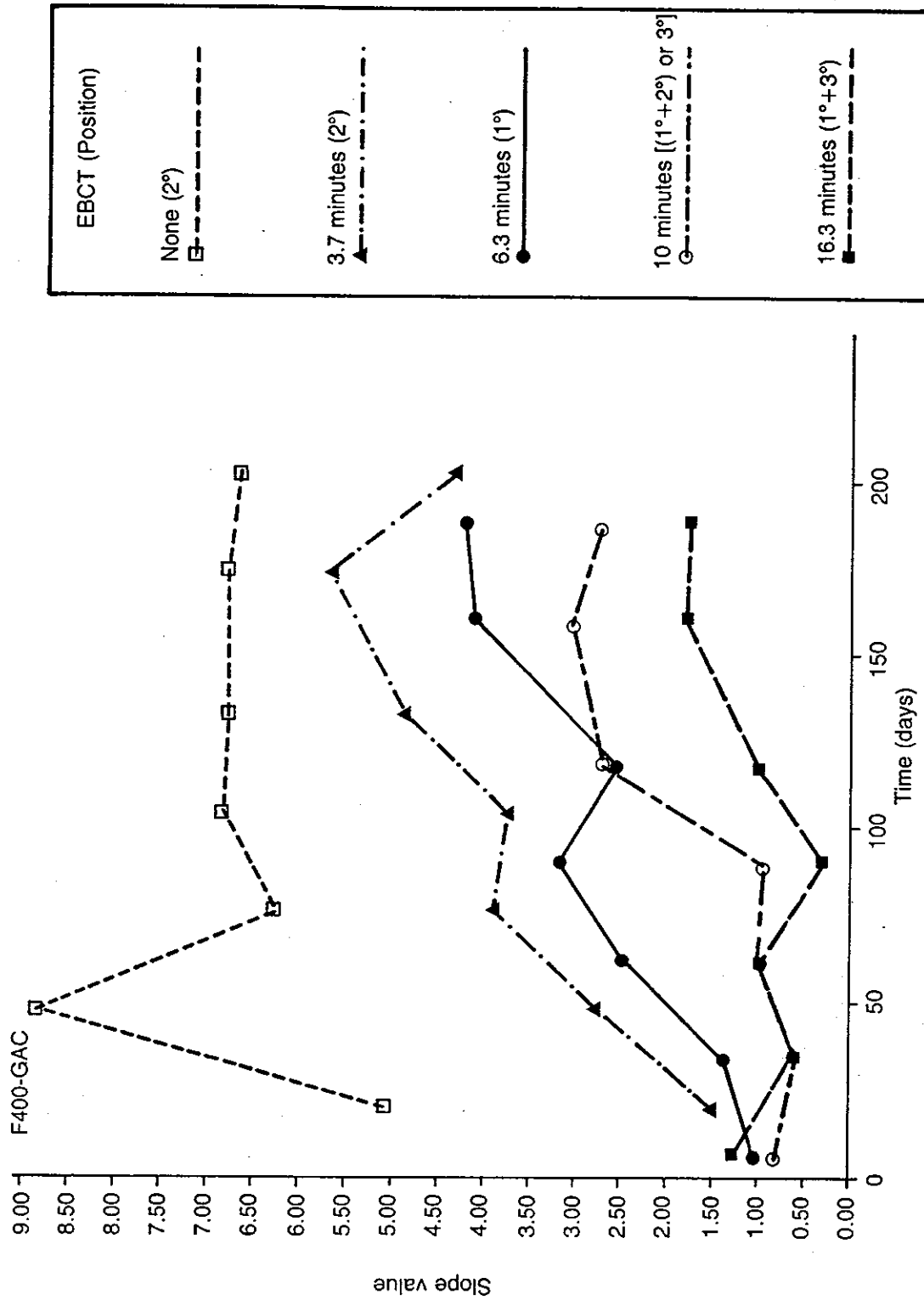


Figure 24 Effect of Empty Bed Contact Time on Total TA 98 Mutagenic Activity

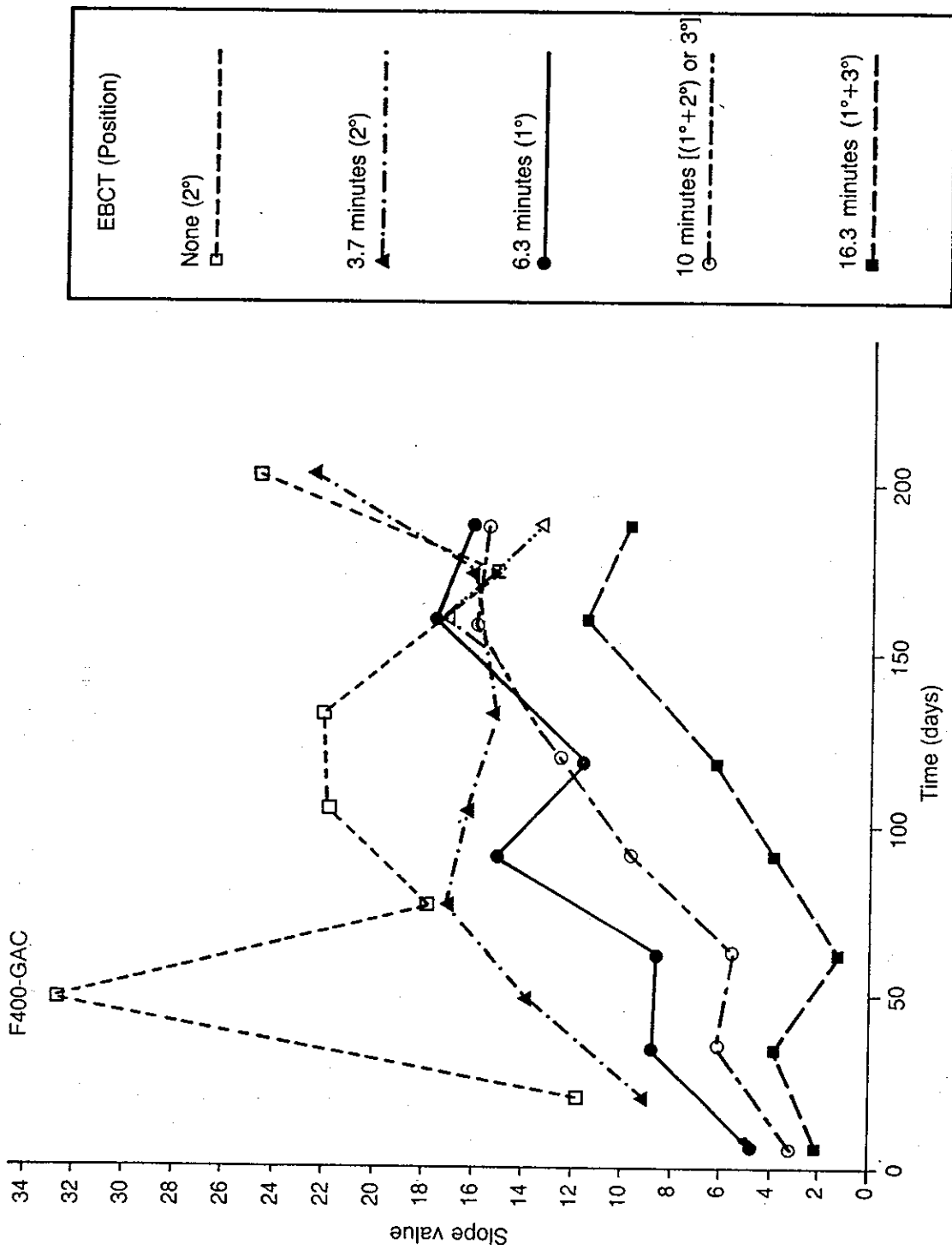


Figure 25 Effect of Empty Bed Contact Time on Total TA 100 Mutagenic Activity

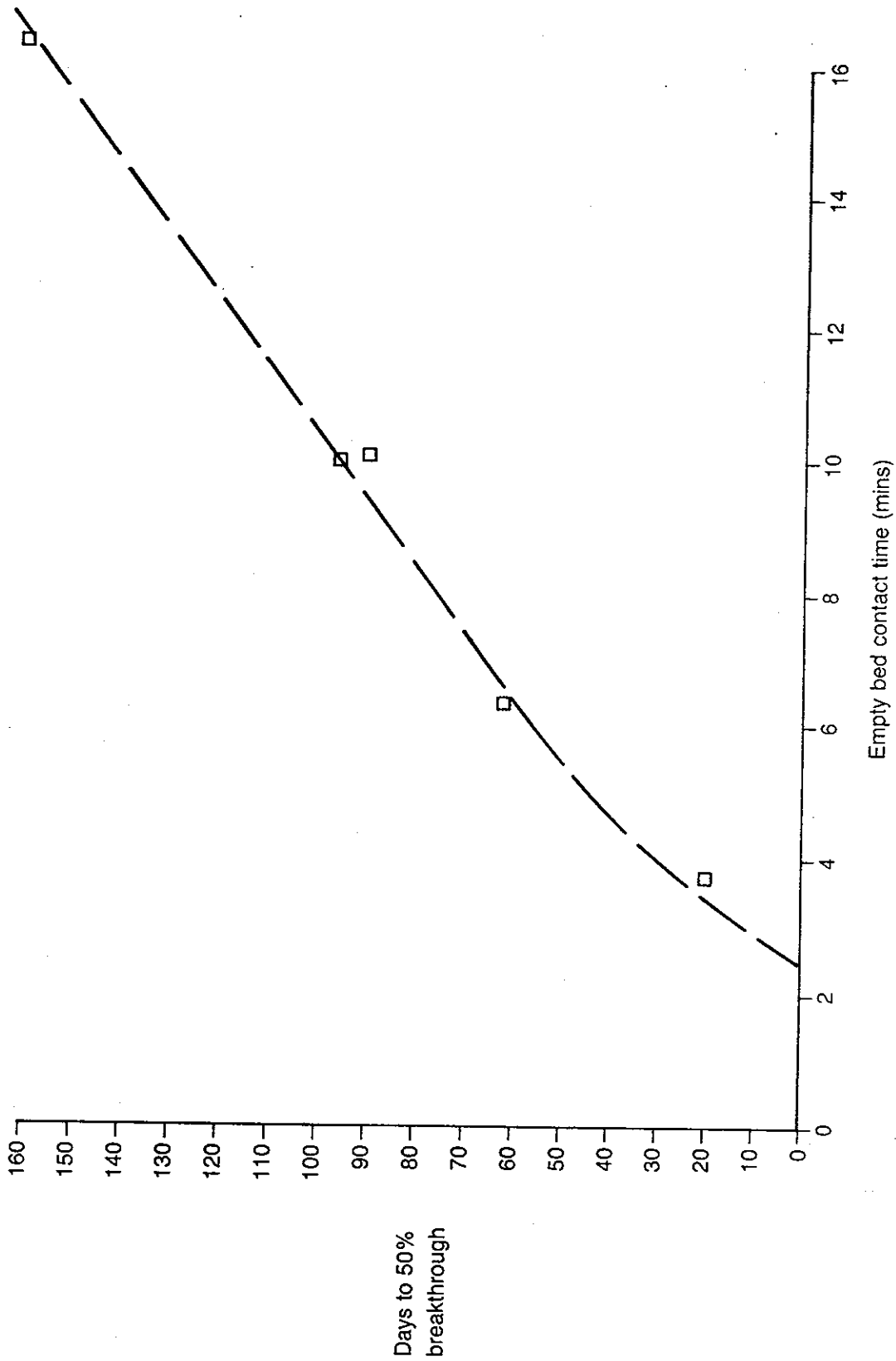


Figure 26 Effect of EBCT on Bed Life for Removal of uv Absorbance

## SECTION 4 - DISCUSSION

### 4.1 METALS REMOVAL

Provided that three stage treatment is used and good control of coagulation and filtration conditions is maintained, there should be no difficulty in reducing iron, aluminium and manganese to below the concentration prescribed by the Water Quality Regulations (0.2mg/l, for iron and aluminium, and 0.05mg/l for manganese) or even to the EC guide levels (0.05mg/l for iron and aluminium, 0.02mg/l for manganese). It is worth noting that in Figures 7 to 9 the average final water aluminium concentration with alum as coagulant, and the average final water iron concentration with ferric as coagulant did exceed the EC guide levels because control was not always maintained. With more sophisticated control systems the risk of exceeding the water quality regulations can be minimised but it is clear that when alum is used as a coagulant there is the potential to fail on aluminium, and when ferric is used as a coagulant there is the potential to fail on iron.

When the filter media at either filtration stage was replaced with granular activated carbon, the EC guide levels for iron, aluminium and manganese could still be met. However, the conditions for manganese removal by GAC were different to those required for removal by sand (a higher chlorine dose and/or pH). Thus, where manganese removal by sand currently requires large chlorine doses and high pH, it is likely that it would not be possible to remove manganese on carbon. Although the removal of iron, aluminium and turbidity at the 1° filtration stage was not greatly affected by choice of the filter media, sand or carbon, there was some evidence to suggest that sand was better. If sand is to be replaced by GAC then attention must be given to adjustment of backwash flowrates because of the relatively low density of GAC.

## 4.2 ORGANICS REMOVAL

### 4.2.1 Coagulation conditions

Variations in coagulant dose and coagulation pH produced similar trends in colour, TOC and total THMs (formed after 30 minutes of hand chlorination) in the final water. It can therefore be assumed that in order to optimise coagulation conditions for TOC and THMs, the coagulation conditions should be optimised for colour. However, the results shown in Figures 11 to 16 indicate that although optimising coagulation conditions can result in almost complete removal of colour, it is not possible to remove all TOC and THM precursors by coagulation alone. It can therefore be concluded that a proportion of the organic material making up the TOC and THM precursors in a water is not organic colour and may not be readily removed by coagulation.

At many works, the coagulant dose is chosen to give a specified colour in the final water (typically 5° Hazen), in order to produce acceptable final water colour at minimum coagulant costs. Since this practise means that the minimum achievable final water colour may not be attained, the concentration of THMs in the final water could potentially be reduced further by increasing the coagulant dose to produce a final water colour closer to the minimum. This may be one of the simplest and cheapest measures which could be implemented in order to reduce disinfection by-products.

Another disadvantage of running a works at minimum dose (to achieve a specified final water colour) is that if the coagulant dose control mechanism's response to sudden changes in raw water quality is slow (e.g. colour is measured manually once or twice a day and coagulant dose is manually altered by the operator), then temporarily very poor final water quality could result. This should not be a problem where there is automatic coagulant dose control, but it could be avoided by running at the coagulant dose which produces the minimum final water colour, or (where extreme variations are experienced), at an "overdose".

Selection of coagulation conditions can be based on jar tests, first determining the pH for minimum coagulant residual and then a coagulant dose to provide maximum colour removal. A matrix approach to jar tests used by Jackson<sup>(9)</sup> reached the same conclusions.

The use of LT31 alone as a coagulant resulted in poor water quality in terms of organics and disinfection by-products particularly THMs, and the use of chlorinated copperas resulted in high levels of disinfection by-products. Thus neither LT31 nor chlorinated copperas are recommended as replacement coagulants.

The use of LT22 and LT25 as floc aids did not affect the final water quality, and would therefore not normally be recommended as their use is not necessary for the separation of floc by DAF. However, since they did not produce any deterioration in water quality, there would appear to be no reason why LT22 or LT25 should not be used with floc blanket clarifiers, where polyelectrolytes are much more important to provide increased floc density and cohesion.

During the comparison of ferric and alum it was demonstrated that at equimolar doses, ferric produced better quality water in terms of colour, TOC and THMs (formed after 30 minutes of hand chlorination). This was probably a result of the lower pH which was used with ferric, since colour removal by coagulation is more effective at a lower pH. The difference in final water quality when comparing alum with ferric would probably have been removed by increasing the alum dose and, therefore, the choice of coagulant could be based solely on economic considerations unless alum is deemed to be unacceptable for other reasons.

#### 4.2.2 Use of chlorine and ozone

The use of prechlorination results in great increases in chlorination by-products, and should be avoided or reduced wherever there are identified problems with meeting by-products standards.

Small pre-ozonation doses (up to 2mg/l) do not affect THM formation, but reduce AOX, mutagens and colour. Thus where pre-oxidation is essential (e.g. for algal control), the use of low pre-ozonation doses could be used instead of chlorine to prevent problems with the formation of chlorination by-products. The colour removed during pre-ozonation may also allow for a small saving in coagulant dose. Large pre-ozonation doses (greater than 4mg/l) can interfere with the coagulation/flocculation chemistry and result in very poor quality final water in terms of coagulant residual and colour. Pre-ozonation alone is therefore unlikely to be of great benefit in reducing regulated chlorination by-products.

Inter-filtration chlorination results in increased disinfection by-products in the final water, but may be necessary for manganese oxidation. Increasing the chlorine dose above that required for manganese removal, for disinfection purposes, further increases disinfection by-products in the final water. This increase may be due not only to the small increase in contact time but also to a catalytic action of the manganese dioxide coating on the filter media. Thus, if disinfection by-products are a problem, the 2° filtration stage should not be used to provide contact time for disinfection, and the chlorine residual in the 2° RGF filtrate should be maintained at the minimum required to obtain complete manganese removal. With some waters, it may be possible to remove manganese on the 2° filter using high pH alone, with no chlorine dose (although a chlorine dose may be needed to activate the media surface initially). This method of operation should result in the lowest potential levels of disinfection by-products in the final water, and, although the contribution to total THMs from the 2° filter is not thought to be very great, it may be important in borderline cases.

Inter-filtration ozonation reduces disinfection by-products both in its own right, and by replacing inter-filtration chlorination. However it was shown to cause problems with manganese and, therefore, if inter-filtration ozonation is considered desirable, site specific trials should be carried out to ensure that manganese removal with ozone can be

achieved. Experience elsewhere of ozonation of coloured water, of low alkalinity, has also indicated that manganese may not be removed. In France<sup>(10)</sup> it is claimed that the remineralization, or hardening, of the water using CO<sub>2</sub> or lime will overcome the problems. More work is required in this area to define the conditions for the successful oxidation of manganese by ozone.

Post-ozonation reduces disinfection by-products in the final water, without the potentially adverse consequences of ozonating water containing manganese. However, post ozonation (and also inter-filtration ozonation) is likely to increase the assimilable organic carbon (AOC) in the final water, and could lead to problems of bacteriological growth in the distribution system.

#### **4.2.3 Use of granular activated carbon**

GAC reduces the production of disinfection by-products for a length of time that is dependent on the quality of the water fed to the carbon, and is proportional to the EBCT used; increasing the EBCT of the carbon increases the bed life, and increasing the concentration of organics in the feed to the carbon reduces the bed life.

The performance of carbon does not seem to be significantly affected either by the deposition of solids and frequent backwashing at the 1<sup>o</sup> filtration stage, or by the deposition of manganese at the 2<sup>o</sup> filtration stage. Nor does there appear to be a difference between the performance of carbon at pH 6.5 and 9.0. It can therefore be concluded that the location of GAC in the treatment scheme after coagulation/clarification is not important but the available EBCT of the carbon is important.

Of the carbons investigated, coal based carbon performed better than peat based carbon and wood based carbon for the removal of organics that lead to the production of THMs, AOX, and mutagenic activity.

Using ozone prior to GAC reduces the precursor load going onto the carbon, and the carbon has the potential to reduce the AOC generated by



ozonation. This, therefore, makes the greatest use of the benefits of ozone, and results in prolonged carbon bed life.

Coal based carbon performed considerably better after ozone than did wood based carbon for the removal of colour and disinfection by-product precursors. There was little evidence that the wood based carbon was removing organic material by biological activity but AOC was not measured. It could be concluded that any biological removal was limited to a very small fraction of the total organic material.

## SECTION 5 - CONCLUSIONS

### 5.1 COAGULATION

- (i) Three stage treatment is capable of producing water of very high quality.
- (ii) There is an optimum coagulation pH for colour removal. This is 4.6 when the coagulant is ferric and 5.5 when the coagulant is alum.
- (iii) There is an optimum coagulant dose, which is dependent on raw water colour. The optimum ferric dose is approximately twice the optimum alum dose (in terms of mg/l of metal).
- (iv) The optimum coagulation pH and coagulant dose for colour removal appear to be the optimum coagulation pH and coagulant dose for reducing the formation of disinfection by-products.
- (v) For equimolar alum and ferric doses, ferric produced water with lower levels of colour, TOC, and disinfection by-products.
- (vi) Chlorinated copperas produced water with equal levels of colour and TOC when compared to water produced by ferric. However, the water had higher levels of disinfection by-products due to the reaction of chlorine with raw water.
- (vii) The organic coagulant, LT31, produced worse quality water than ferric in terms of colour, TOC and disinfection by-products.
- (viii) The use of flocculation aids with the optimum primary coagulant dose made no difference to the quality of the final water.

## 5.2 OXIDATION

- (i) Some mutagenic activity (TA 98) was present in raw water but chlorination was responsible for the production of most activity.
- (ii) When ozonating waters containing manganese, colloidal manganese may be formed which cannot be removed by subsequent filtration. Site specific investigations into this effect are therefore necessary if ozone is to be used.
- (iii) Prechlorination increases disinfection by-products.
- (iv) Pre-ozonation does not reduce THM formation during final chlorination , but can reduce AOX and mutagenic activity.
- (v) Small pre-ozonation doses (up to 2mg/l) may allow a small reduction in coagulant dose but large pre-ozonation doses (greater than 4mg/l) appear to disrupt the coagulation/flocculation process, resulting in poor quality final water.
- (vi) If pre-oxidation is considered necessary (i.e. when there are algal problems) then ozone at low doses should be considered instead of chlorine to maintain low levels of disinfection by-products.
- (vii) Increasing inter-filtration chlorine dose allows a reduction in the final disinfection chlorine dose but results in increased overall chlorine consumption and THMs.
- (viii) Continued inter-filtration chlorination may not be necessary for manganese removal on matured filters, if pH control is good. However, chlorination will compensate for the effects of poor pH control.

- (ix) Inter-filtration ozonation reduces disinfection by-products (but not chlorine consumption) and, for the quality of water encountered in this study, only a short ozone contact time is required.
- (x) Post-ozonation had no effect on TOC concentrations but reduced total THM precursors by approximately 30%, and also resulted in reductions in colour (77%), AOX (56%) and mutagenic activity (70%).
- (xi) For AOX and THM reduction, only a small ozone dose is required (about 0.3mg/l) but for UV absorbance and mutagenic activity reduction, the optimum ozone dose is greater (about 2mg/l).
- (xii) The overall effect of dual point ozonation is the sum of the effects of the individual ozonations.

### 5.3 ADSORPTION

- (i) Solids, iron and aluminium carried over from the clarification stage can be removed just as well by filtration through GAC as by filtration through sand.
- (ii) The removal of solids, iron and aluminium carried over from the clarification stage does not adversely affect the performance of GAC for organics removal.
- (iii) Given the correct conditions, manganese can be removed on GAC.
- (iv) The removal of manganese on GAC does not adversely affect the performance of the GAC for organics removal.
- (v) The removal of organics by carbon was the same at pH 6.5 and at pH 9.
- (vi) The carbon bed life is dependent on the empty bed contact time: doubling the empty bed contact time of carbon doubles the bed life.

- (vii) Coal based carbon (F400) performed better than peat based carbon (Norit PK) for TOC, colour, THMs, AOX and mutagenic activity reduction.
- (viii) F400 after ozonation performed much better than wood based Pica Biol after ozonation for TOC, THMs, AOX and mutagenic activity reduction.
- (ix) There was no synergistic effect from using ozone and GAC, but the improvement in water quality from ozonation resulted in extended bed life of the subsequent carbon adsorber.
- (x) During the 8 months of the trial there were very few indications of bacteriological activity within the carbon bed.

## SECTION 6 - RECOMMENDATIONS FOR REDUCING DISINFECTION BY-PRODUCTS

1. Prechlorination should not be used unless it can be shown to be of importance in achieving effective treatment of the water. Its use in conjunction with copperas is not recommended as alternative coagulants such as aluminium sulphate or ferric sulphate are equally effective. If pre-oxidation is used to combat seasonal algal problems then the use of ozone should be considered.
2. The coagulation process should be operated to maximise colour removal. This requires that the coagulation pH and coagulant dose are correctly selected and controlled; operating at minimum coagulant dose without reliable, rapid process control is undesirable particularly where raw water quality can change quickly. In the absence of good control the coagulant dose should be set greater than the minimum to provide a buffer against sudden changes.
3. Where interfiltration chlorine is added to oxidise manganese, the dose should be controlled to give the minimum free chlorine residual needed. Adding high doses of chlorine to supplement disinfection capacity should be avoided unless this would compromise disinfection.
4. Ozone should be considered as an addition to the treatment process where problems with chlorination by-products can not be solved by application of recommendations 1-3. Ozone can be applied as a pre-treatment stage at low doses; high doses should be avoided as this can result in disruption of the coagulation process. Ozone is best applied after coagulation but should not be the final stage of treatment unless it can be demonstrated (by pilot trials for example) that levels of AOC will not result in problems within the distribution network. For example where ozone is used to oxidise high levels of colour it should always be followed by a filtration stage that allows the development of biological activity, such as GAC or slow sand filtration.

When manganese is present at problem levels the use of ozone should always be examined at pilot scale. Oxidation of manganese by ozone is likely to be dependent on inorganic water quality parameters and may need to be modified by use of lime or carbonate addition to prevent the formation of colloidal manganese. More research is needed to identify the conditions under which ozone can be used for manganese oxidation.

5. Activated carbon can be used to reduce disinfection by-products by removing precursor molecules. The most effective carbon is likely to be coal based. It can be used as a media replacement in primary or secondary filters but its effective bed life will be dependent on the available contact time. Economic evaluation will be needed to decide on the best location. Bed life can be increased by using the GAC in conjunction with ozone.

If GAC is to be used to replace sand in a 2° filter that is currently being used to remove manganese in conjunction with chlorine then facilities to operate at a higher pH should be considered; the higher the pH used the less will be the need for chlorine. It will not be possible to use GAC at high pH in 1° filters as this would result in the resolubilisation of coagulant carry over.

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