Technical Report

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# ABSTRACT

Preozonation has seen widespread use in potable water treatment as a means of reducing the formation of Trihalomethanes (THMs). This is, in part, due to the ability of ozone to oxidize THM precursors. In this laboratory study, the ability of ozone to oxidize Dissolved Organohalide (DOX) precusors in municipal wastewater was investigated. Experiments were conducted on wastewaters collected from municipal plants in Massachusetts between January 1986 and December 1988.

The study of precursor oxidation in wastewater differs from analogous studies in potable water for two principal reasons; (a) different organic material exists in wastewater, and, (b) chloramines predominate in wastewater, whereas in potable water, free chlorine is most important.

Experiments were first performed to assess the effect of chlorine dose and Cl/N ratio on organohalide formation in municipal wastewater effluents. These experiments showed that DOX formation increased with increasing Cl/N ratio and increasing chlorine dose. An especially pronounced increase in DOX formation was observed where the chlorine dose exceeded a Cl/N value of 1.0. Furthermore, with at least one treated wastewater, the DOX formed could be attributed to the reactions of DOX precursors with monochloramine, rather than reactions with a transient free residual.

Subsequent experiments were designed to determine the effect of preozonation on DOX formation. Three municipal wastewater effluents were used in these experiments; one highly nitrified, and two non-nitrified, or slightly nitrified effluents. Three DOX precursor tests (DOXFP) were used which differed with respect to Cl/N ratio and chlorine dose. The DOXFP in the nitrified effluent ($NH_3$-N = 1.00 mg/L) showed a more consistent declining response to preozonation than either of the other two, less nitrified, effluents ($NH_3$-N = 3.86 and 3.95 mg/L). A significant net increase in DOXFP to values nearly six times that of the un-ozonated effluent was observed in one sample which was less nitrified.

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# CHAPTER I: INTRODUCTION

In the interest of public health, most states require assurances that pathogens are adequately removed from municipal wastewater effluents. Pathogen removal is of particular concern when the effluent is discharged to shellfish harvesting areas, recreation areas, or to receiving waters which are sources of water supply for downstream users. Disinfection by chlorine is the most commonly used method of pathogen reduction in such cases. Increasing concern over persistence of chlorine residual and formation of harmful chlorination by-products has encouraged investigation of alternative disinfection methods.

The concentrations of residual chlorine species typically found in chlorinated effluent are toxic to many freshwater fish (Merkens, 1958; Zillich, 1972; Esvelt et al., 1973). In addition, the chlorination of organic matter in wastewater effluent leads to the formation of organically bound chlorine compounds (organohalides) which may have further deleterious effects in the sediments (Coler; 1988). While specific toxic organohalide products have been measured in superchlorinated wastewater (Glaze and Henderson, 1975), the nature of the byproducts formed under less severe conditions is not well understood. A number of researchers have noted an increase in the mutagenicity of municipal effluent following chlorination (Cummings et al., 1980; Fort et al., 1983) but the specific compounds responsible for the mutagenic activity have yet to be isolated despite attempts by investigators (Joley et al., 1983).

Both sulfur dioxide addition and activated carbon treatment have been used to dechlorinate municipal effluents (Metcalf & Eddy, 1979). While sulfur dioxide can remove the total residual chlorine and selected specific chlorination byproducts, it may not be very effective in removing the net dissolved organohalide (DOX) (Croue and Reckhow, 1989). Activated carbon can remove organohalides along with other organic matter but it is expensive and only used in cases where extensive removal of organic matter is desired. Disinfectants other than chlorine, such as chlorine dioxide, ultraviolet light, and ozone have been proposed or used to a limited extent, but these are not usually employed because of their high cost.

Experience with drinking water treatment has found that preozonation leads to a reduction in the amount of chlorine required for final disinfection and a decrease in the amount of organohalide formation (Sander, et al., 1977). Low-level preozonation followed by chlorination is one alternative that has not previously been explored for the disinfection of municipal effluent. It is anticipated that low-level doses of ozone would be more economical than the doses used in wastewater disinfection with ozone alone. Furthermore, certain benefits may accompany the use of ozone, even at low doses. The objective of this research was to evaluate the ability of low-level preozonation to reduce chlorine demand and organohalide formation potential in municipal effluents. The control of chlorination byproducts in Massachusetts wastewater discharges is important for the protection of aquatic life in the Commonwealth.

# CHAPTER II: BACKGROUND

As conceived in this research, low-level preozonation is the addition of a relatively low dose of ozone applied to biologically treated effluent just prior to final disinfection with chlorine. Of interest in this study is how preozonation may effect the formation of organohalide compounds. The interpretation of laboratory results involving the preozonation of wastewater requires that one understand; (a) the chemistry of chlorine in wastewater, (b) the chemistry of aqueous ozone, and, (c) ozonation in wastewater treatment. Each of these topics is addressed in this section.

## A. Chemistry of Chlorine in Wastewater

Chlorine gas applied to water or wastewater rapidly reacts to form hypochlorous acid.

$$Cl_2 + H_2O \text{ ------> } HOCl + Cl^- + H^+ \qquad (1)$$

The dissociation of hypochlorous acid to hypochlorite occurs as follows:

$$HOCl \text{ <-----> } H^+ + OCl^- \qquad pKa = 7.6 \qquad (2)$$

A hypochlorite salt such as sodium hypochlorite or calcium hypochlorite will rapidly form hypochlorous acid also. Through these rapid reactions it can be seen that the same active form of chlorine, $HOCl/OCl^-$, is produced regardless of the form of the applied dose. The concentration of active chlorine in this form is often referred to as free residual chlorine (FRC).

In normal wastewater disinfection practice, FRC is virtually non-existent after only 0.5 seconds under nearly all pH and temperature conditions (Morris & Isaac, 1983). With non-nitrified effluent, the applied chlorine rapidly reacts with ammonia to form Combined Residual Chlorine (CRC) which may consist of chloramines (mono-, di-, and trichloramine) as well as N-chloro-organics. The chlorine residual is often reported as Total Residual Chlorine (TRC) in wastewater treatment practice. TRC is the sum of CRC and FRC (if any is present).

The reactions below describe the formation of three principal inorganic chloramine compounds:

$$NH_3 + HOCl \xrightarrow{k_1} NH_2Cl + H_2O \qquad (3)$$

$$NH_2Cl + HOCl \xrightarrow{k_2} NHCl_2 + H_2O \qquad (4)$$

$$NHCl_2 + HOCl \xrightarrow{k_3} NCl_3 + H_2O \qquad (5)$$

Where at 25°C and neutral pH:

$$k_1 = 4.2 \times 10^6\ M^{-1}s^{-1}$$

$$k_2 = \sim 3.5 \times 10^2\ M^{-1}s^{-1}$$

$$k_3 = 2.1\ M^{-1}s^{-1}$$

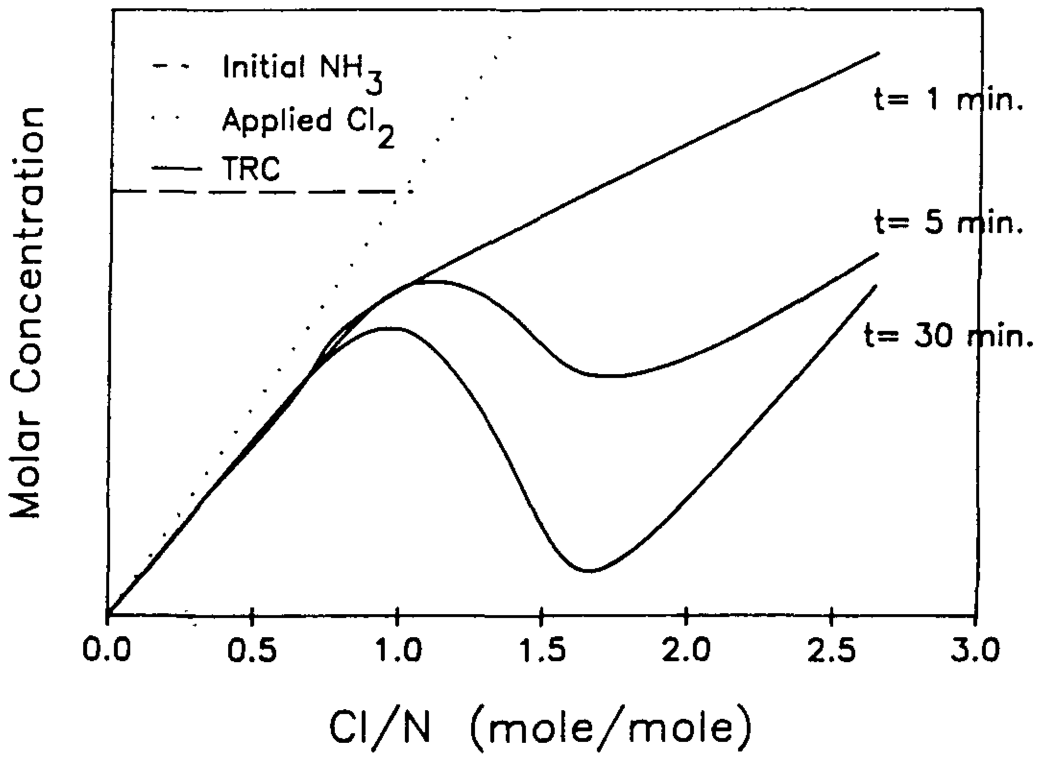
(from Morris and Isaac, 1983)

The predominant chloramine species under typical wastewater chlorination conditions is monochloramine. Chloramines are primarily responsible for disinfection since they are relatively stable and can be maintained for an adequate contact time. The FRC, though a more powerful disinfectant, is too short-lived in pre-breakpoint chlorination to provide adequate disinfection alone.

The response of residual chlorine to increasing chlorine dose can be characterized by the ammonia breakpoint curve. The breakpoint curve is the result of complex reactions between the chlorine, ammonia, and other species present in the water. Figure 1 represents a breakpoint curve derived from the laboratory chlorination of an ammonia solution under

FIGURE 1

IDEALIZED BREAKPOINT CURVES



(From Jafvert, 1985)

standard conditions (pH = 7, 25°C). In an empirical sense, Figure 1 represents an ideal breakpoint curve which occurs without the presence of interfering species which may be present in wastewater. In Figure 1 and in other breakpoint curves presented throughout this study, it is convenient to express the residual chlorine as a function of the molar ratio of applied chlorine to ammonia (Cl/N value). In this manner, the breakpoint characteristics of effluents with different ammonia concentrations can be compared.

In Figure 1, one can see that the formation of the local minimum or breakpoint is not instantaneous. However, after one hour, the reactions contributing to an idealized breakpoint curve generally reach completion.

When the process is allowed to run to completion, the hump and breakpoint of an idealized curve are located near Cl/N values of 1.0 and 1.65, respectively. The hump and breakpoint are important features of the breakpoint curve because they indicate the type of chlorine residual species present at a particular chlorine dose. At doses below Cl/N = 1, the applied chlorine reacts rapidly with ammonia to form monochloramine. In the range of Cl/N values between 1 and 1.65 (between the hump and the breakpoint), the chloramines begin to shift from the predominant monochloramine species to the di- and trichloramine species. The drop in TRC between the hump and the breakpoint reflects the loss of nitrogen [N(- III)] as it is oxidized by chlorine. Beyond the breakpoint, ammonia nitrogen is completely removed and FRC is the dominant chlorine residual species present.

At chlorine doses below Cl/N = 1, the applied chlorine which does not result in the formation of CRC is assumed to have been lost to the broad class of chlorine demand reactions. Reactions of organic and inorganic matter which compete with ammonia for FRC can account for a significant portion of the chlorine demand. In addition, monochloramine can be lost from solution as a result of complex reactions in the presence of bromide and nitrite (Valentine, 1984). At chlorine doses below Cl/N = 1, we will define chlorine demand as:

$$\text{Chlorine Demand} = \text{Applied Chlorine} - \text{TRC} \qquad (6)$$

It is important to note, however, that at chlorine doses greater than Cl/N = 1, under ideal breakpoint conditions, chlorine is consumed by the oxidation of N (-III). Therefore, a general term, "consumed chlorine" will be used here in reference to the applied chlorine minus TRC throughout any region of the breakpoint curve.

As the chlorine to ammonia ratio exceeds one, the oxidizing power of chlorine strips electrons from ammonia nitrogen. Ammonia can be oxidized by chlorine to a number of oxidation products according to specific reactions. For example, the oxidation of ammonia to $N_2$ requires 1.5 moles of chlorine per mole of ammonia.

$$1.5\ HOCl + NH_3 \dashrightarrow 0.5\ N_2 + 1.5\ HCl + 1.5\ H_2O \qquad (7)$$

However, the oxidation of ammonia to nitrate requires 4 moles of chlorine per mole ammonia.

$$4\ HOCl + NH_3 \dashrightarrow NO_3^- + 4\ Cl^- + 5\ H^+ + H_2O \qquad (8)$$

Because the complete removal of ammonia nitrogen occurs at a value of 1.65 under ideal conditions, the principal oxidation product of ammonia would likely be $N_2$. Nitrogen gas has been measured as one of the principal oxidation products of ammonia in chlorinated solutions. Based solely on this end product, the breakpoint should occur at a Cl/N ratio of 1.5 in accordance with Equation (7). However, the formation of small amounts of nitrate or other oxidized nitrogen species explains the commonly observed breakpoint at a Cl/N value of 1.6. Nitrate, for example, has been measured as an ammonia oxidation product in small concentrations (Palin, 1950).

Actual ammonia breakpoint curves are the result of complex interactions between chlorine, ammonia compounds, and the matrix of matter within the wastewater. As might be expected from a medium as complex and varied as municipal wastewater, a breakpoint chlorination curve for a wastewater may differ from the ideal curve presented in Figure 1. One non-ideal condition exists when an excessive chlorine demand reduces active chlorine to chloride in competition with Equation

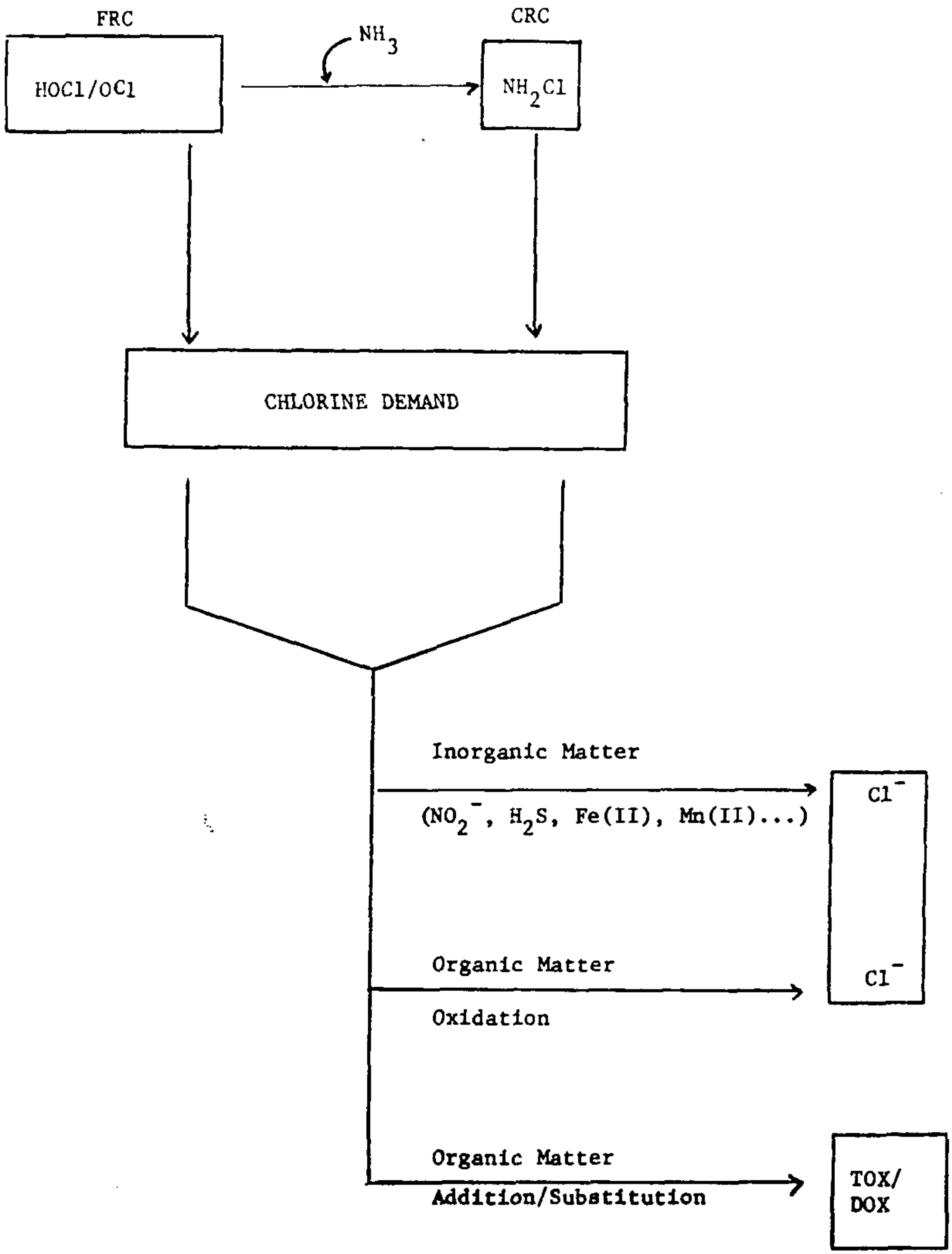
3. A wide variety of species can reduce chlorine to chloride as will be discussed later. In Figure 1, the gap between the applied chlorine line and the TRC gives a relative indication of the amount of reducing agents present. In this ideal case the TRC is only slightly less than the applied chlorine due to the formation of dichloramine. In less ideal cases the gap can be greater indicating that a lower proportion of the applied chlorine is resulting in a residual. Another effect of excessive chlorine demand on the breakpoint curve is a shift of the observed breakpoint to a higher Cl/N value. This is logical because the greater consumption of chlorine will require additional chlorine to be added for the system to reach the ammonia breakpoint.

Another non-ideality in the form of the breakpoint curve can arise from the presence of N-organic compounds. Both FRC and monochloramine can combine with N-organic compounds to form N-chloro-organic compounds (Isaac & Morris, 1980). N-chloro organics are often difficult to distinguish from chloramines using standard analytical methods (DPD titration, APHA et al., 1985). As a result, the breakpoint chlorination curve may indicate the presence of CRC at chlorine doses beyond the actual breakpoint. In addition, the poor disinfecting ability of N-chloro-organics can contribute to an over-estimation of the disinfection achieved in a wastewater (Isaac & Morris, 1981).

The schematic diagram in Figure 2 represents the major categories of reactions for active chlorine in wastewater under a typical chlorine dose. Since the chlorine dose required for disinfection in most wastewaters is less than the ammonia concentration on a molar basis (Cl/N value less than 1.0), a significant portion of the applied chlorine will react rapidly with ammonia to form CRC. The applied chlorine which does not result in CRC is assumed to have been consumed by the chlorine demanding substances. Both free residual and chloramine can be lost to chlorine demand. Here, the discussion of chlorine demand is focused on the demand for FRC. Under chlorine demand, three subclasses of reactions can be defined; (1) the oxidation-reduction reactions with inorganic matter, (2) oxidation-reduction reactions with organic matter, and, (3) addition/substitution reactions with organic matter. The former two groups of reactions result in reduction of the chlorine produced oxidant (FRC or CRC) to chloride. The latter group of reactions results in the formation of a potentially harmful class of compounds known as organohalides.

Many inorganic constituents of wastewater can exert a demand for FRC in competition with Equation 3. These include nitrite, some di-valent metals, sulfide, and sulfite. Monochloramine can also decay in the presence of certain inorganic constituents. Valentine (1984) has shown that monochloramine is degraded in the presence of bromide ion and that small concentrations of nitrite can accelerate this process.

FIGURE 2: FATE OF CHLORINE IN WASTEWATER

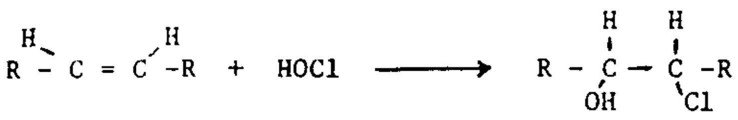


Organic matter can contribute significantly to the overall consumption of free residual chlorine. One study using river water chlorinated with 10 mg/L chlorine as $Cl_2$ showed that the oxidation of organic matter with consequent formation of $CO_2$ accounted for roughly half of the chlorine demand (Helz, et al., 1983). One of the major effects of chlorination upon the organic fraction of wastewater is a significant reduction of molecular size (Grady, et al., 1984). Oxidation-reduction reactions with FRC are thought to account for this molecular size reduction (Jolley et al., 1983). While addition and substitution reactions of FRC with organic matter are to be expected, the reduction-oxidation reactions with organic matter are generally recognized as predominant. Examples of addition and substitution reactions of FRC with organic matter are given in Figure 3. Addition and substitution reactions are also known to occur with organic matter and chloramines (Fleischacker & Randtke, 1983), though little is known about the mechanisms involved.

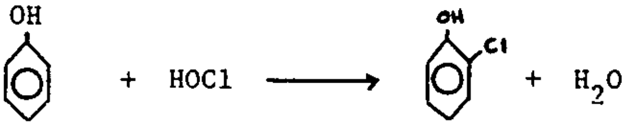
Because of the wide variety of organohalide compounds formed by addition and substitution reactions, the identification of each specific organohalide in a wastewater is very difficult.
Often, a majority of the organohalides are not chromatographable and require complex analytical techniques (Glaze & Henderson, 1975; Jolley, et al., 1983). Since the number of different organohalide compounds in

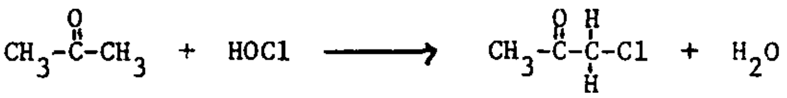
## FIGURE 3: MECHANISMS OF ORGANOHALIDE FORMATION

### Addition to Olefinic Bonds



### Activated Ionic Substitution





$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + HOCl \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-Cl + H_2O$

(From Morris, 1975)

a wastewater is potentially unlimited, Total Organohalide (TOX) or Dissolved Organohalide (DOX) are useful parameters for quantifying the amount of organically bound halide without having to analyze for specific compounds. This method is based on near complete adsorption of organic matter to virgin activated carbon followed by high temperature pyrolysis and microcoulometric detection of the resulting hydrogen halides (APHA et al., 1985). TOX has also been used as a surrogate paramenter for the presence of toxic chlorination by-products. For example, in a study of chlorinated potable waters, TOX gave the strongest correlation to mutagenicity in comparison to other more specific measures of organohalide content (Kool, et al., 1984).

It was stated earlier that both FRC and CRC can react with organic matter to form organohalides. It should be noted that several differences between TOX formation by FRC and CRC have been observed:

(1) Chloramination results in less TOX formation than does free chlorination at an equivalent dose (Fleischacker & Randtke, 1983; (Jensen, et al., 1985).

(2) Chlorination of wastewater effluent with added ammonia reaches completion with respect to TOX formation faster than chlorination without added ammonia (Brown, 1985).

(3) Chloramine-produced TOX may be of larger molecular size and more hydrophilic than free chlorine-produced TOX (Jensen, et al., 1985).

The above observations suggest that the nature of the TOX compounds may be different depending upon whether FRC or CRC is the chlorinating agent. This would also imply that the nature of TOX would be different in a chlorinated wastewater effluent depending upon the location of the system on the ammonia breakpoint curve.

The chlorination of water containing bromide may cause the oxidation of bromide to bromine and initiate a series of reactions which are analogous in some respect to those of HOCl. Bromide, when it is oxidized to bromine, may lead to the formation of bromo-organic compounds which contribute to the TOX in a chlorinated water sample. The oxidation of bromide by chlorine can form bromine:

$$HOCl + 2Br^- \dashrightarrow Br_2 + H_2O + Cl^- \qquad (9)$$

Bromine rapidly hydrolyzes to hypobromous acid:

$$Br_2 + H_2O \dashrightarrow HOBr + H^+ + Br^- \qquad (10)$$

So that the overall reaction can be represented by:

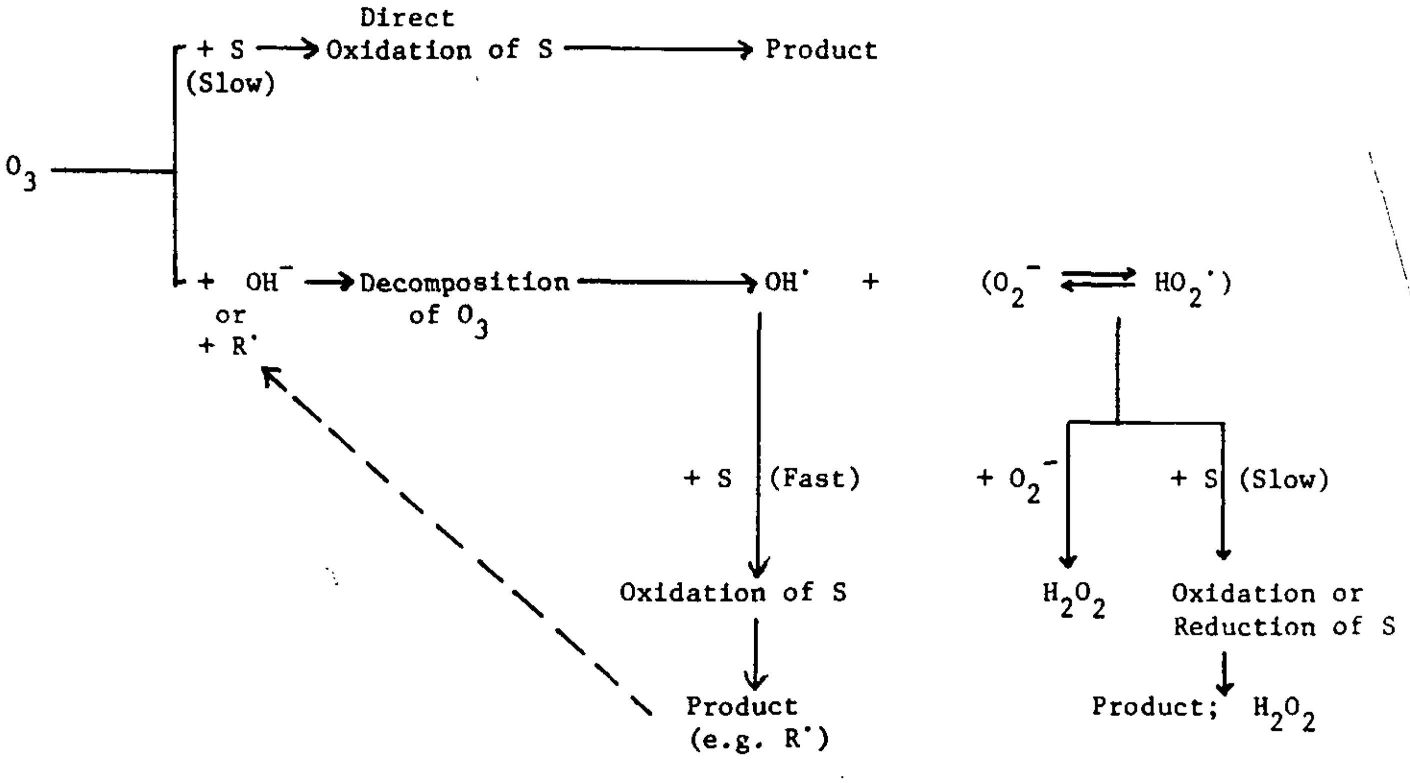
$$HOCl + Br^- \dashrightarrow HOBr + Cl^- \qquad (11)$$

Like hypochlorous acid, hypobromous acid dissociates to a hypohalite ion. The dissociation constant for hypobromous acid, however, is less than that of hypochlorous acid by roughly a factor of ten ($K_a = 2 \times 10^{-9}$ for HOBr as opposed to $3.2 \times 10^{-8}$ for HOCl at 25°C, see Inman and Johnson, 1979). Because of the predominance of HOBr at higher pH values, the disinfection of a wastewater effluent may be enhanced by the presence of bromide.

## B. CHEMISTRY OF OZONE

Ozone can react via a direct or radical pathway in aqueous solution (Figure 4). In direct reactions, the resonance structure of molecular ozone allows $O_3$ to react as a dipole, an electrophile, or as a nucleophile. The direct reactions are very specific in nature and have an extremely wide range of reaction rate constants with different solutes. In the radical decomposition pathway, secondary oxidants such as $OH^\cdot$ radicals react less selectively with other solute species. Conditions which favor the direct reaction pathway include low pH and the presence of radical scavenging species such as bicarbonate. Ozone decomposition by the radical pathway is favored by high pH, the presence of free radicals, and ultra-violet light (Hoigne and Bader, 1978).

FIGURE 4: PATHWAYS OF OZONE DECOMPOSITION IN WATER



(From Hoigne & Bader, 1976)

Organic matter can react with ozone by either of the two reaction pathways. Several direct reactions of ozone with organic functional groups are illustrated in Figure 5. The ozonation of natural waters can lead to complex reactions because both direct and radical decomposition pathways may operate simultaneously. The organic oxidation products of ozonated waters can vary with the nature of the organic matter initially present. In solutions of unsaturated organic compounds, organic acids can be produced as well as aldehydes, ketoacids, and simple ketones (Baily, 1972).

Over the ozonation doses and times encountered in ozonation systems (~0.5 mg/L, ~10 minutes), it is possible for ozone to oxidize bromide to $OBr^-$ :

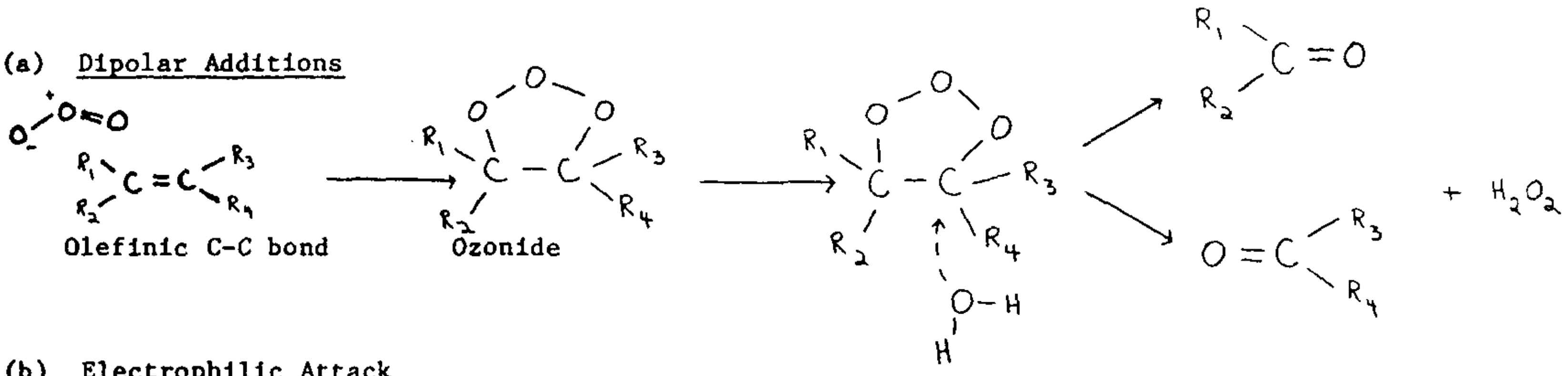
$$O_3 + Br^- \text{----->} O_2 + OBr^- \qquad (13)$$

$$O_3 + OBr^- \text{----->} 2O_2 + Br^- \qquad (14)$$

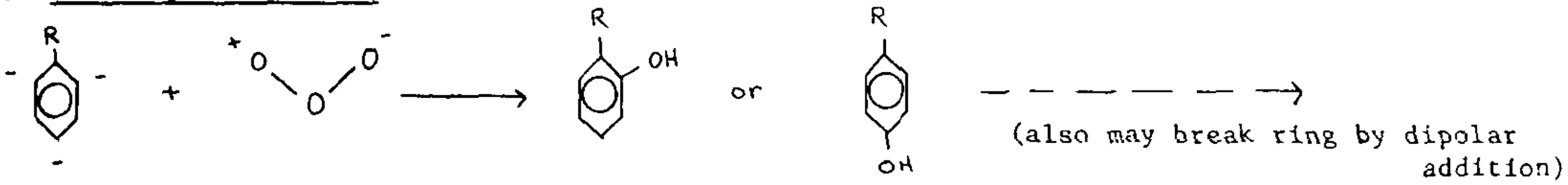
The regeneration of $Br^-$ in Equation 14 indicates that this is a pathway for the catalytic decomposition of ozone. With further ozonation, the $OBr^-$ can be oxidized to $BrO_3^-$, though this would not occur over the dose ranges used in practice (Haag, et al., 1984). Like

FIGURE 5: DIPOLE, ELECTROPHILIC, AND NUCLEOPHILIC REACTIONS OF OZONE

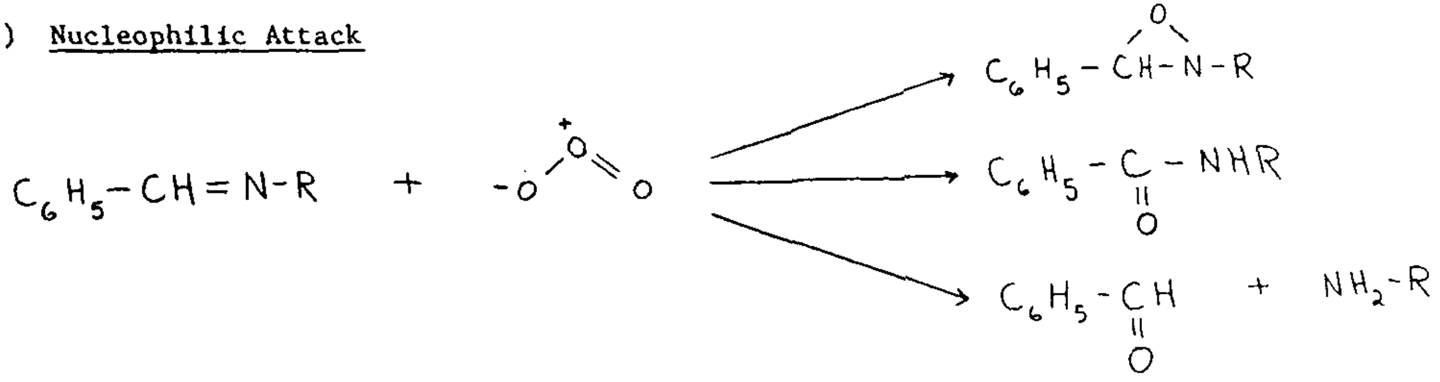
(a) Dipolar Additions



(b) Electrophilic Attack



(c) Nucleophilic Attack



$OCl^-$, $OBr^-$ can be protonated. The pKa for the $HOBr/OBr^-$ system is 8.8 which is greater than that for the $HOCl/OCl^-$ system (pKa = 7.6). The action of HOBr is also similar to HOCl in that HOBr can combine with ammonia and react with organic matter to form organohalide compounds such as bromoform. The presence of bromide in ozonated water can catalytically enhance the removal of ammonia at a rate greater than that possible by ozonation alone (Haag, et al., 1984). This is due to Equations 13 and 14 above and the oxidation of ammonia to nitrate by HOBr. The removal of ammonia by the bromide catalyzed mechanism should not be significant in municipal wastewaters because of the low concentrations (~1 uM) of bromide typically present.

## C. OZONATION IN WASTEWATER TREATMENT

In the U.S., ozonation has been used in wastewater treatment primarily as a disinfectant although several plants have applied ozone for sludge conditioning, for flotation thickening, and for microflocculation of suspended solids (Robson & Rice, 1985). Almost all of the plants using ozone disinfection use some form of extended treatment to remove suspended solids and ammonia before disinfection.

The application of ozone to wastewater can result in alterations in the soluble organic matter. A study by Legube, et al (1986) showed that ozone applied to secondary effluent (activated sludge) over a 15 minute contact time (0.1 - 0.5 mg/L ozone residual) resulted in several effects:

1. A partial or complete elimination of 60 percent of the aromatic compounds.
2. A significant reduction in the concentrations of unsaturated fatty acids.
3. The formation of aldehydes and ketones such as heptanal and nonanal.
4. An increase in the free amino acid concentration.

The observations by Legube are consistent with what would be expected from the direct reaction of ozone with organic matter (see Figure 5).

The effect of ozone on organic matter has bearing on the ability of the organic matter to undergo subsequent addition/substitution reactions upon chlorination. In potable water treatment, it has been shown that ozonation prior to final chlorine disinfection can reduce the concentration of organohalide precursors. Reckhow and Sibony (1986) observed that a dose of 1.0 mg consumed ozone per mg TOC removed 20 to 40 percent of the THMFP in three different fulvic acid solutions. Similar removal in DOXFP was noted as the result of preozonation

(Reckhow, 1984). The direct reactions of ozone with organic matter, as opposed to the secondary oxidants produced by radical decomposition, has been shown to be most effective at precursor removal (Reckhow, et al., 1986).

With potable water, organohalides can continue to form for days after the addition of free chlorine (Stevens et al., 1976; Reckhow, 1984). In contrast, organohalide formation in municipal wastewaters appears to reach completion very quickly (i.e., within several minutes, Brown, 1985). As a result, the DOX precursors (DOXFP) that are active in wastewater must be capable of reacting with the chlorine species very quickly. Since ozone is not maintained as a long-lived residual, it is most effective in destroying compounds which react very rapidly. Because both ozone and chlorine are strong electrophiles, it is likely that both will react quickly with the same type of compounds (i.e., activated aromatics). Compounds which require a slow preliminary activation step cannot be very important in wastewater DOX formation, and are not apt to react significantly with ozone. Thus, it is reasonable to presume that preozonation should be more effective at destroying DOXFP in municipal wastewater than in potable water. In this study, the effect of preozonation on DOXFP in municipal effluents will be investigated.

# CHAPTER III: MATERIALS AND METHODS

## A. EXPERIMENTAL DESIGN

The objective of this study was to determine the effect of low-level preozonation on organohalide formation in municipal wastewater effluents. In order to understand and assess the effects of preozonation it was first necessary to develop a test for DOX precursors in municipal wastewater. This, in turn, required that one understand the principal variables involved with organohalide formation in wastewater. For this reason, four of the five types of experiments performed in this research were concerned with the chemistry of chlorine in wastewater. Only the last set of experiments addressed the effects of preozonation on organohalide formation.

From a review of the literature, two significant questions regarding organohalide formation in wastewaters remained unanswered; (1) It was not certain whether organohalide formation at chlorine doses below Cl/N = 1 was due to reactions with transient free residual or with combined chlorine; (2) While it has been observed that increasing ammonia concentration will decrease organohalide formation (Brown, 1985; Cooper, et al., 1983), a clear relationship between organohalide formation and the ammonia breakpoint curve had not been established. These two questions had bearing on the preozonation experiments because a meaningful procedure for organohalide formation potential had to be established before the effects of preozonation could be properly assessed.

To approach the first question, a set of experiments (Type I) were performed in which a range of HOCl and equivalent molar monochloramine doses were applied to separate aliquots of the same wastewater effluent. From these experiments, the dissolved organohalide formation (DOX) attributable to HOCl could be compared with the DOX from monochloramine (MCA). Of particular interest was the DOX in HOCl-dosed samples below Cl/N = 1 where comparison with the chloraminated samples were most appropriate. Also, since the HOCl doses were chosen to span the breakpoint, observations could be made of the relationship between the breakpoint curve and DOX formation. However, additional trials were conducted to better show the features of the relationship. These comprised the series of experiments labeled Type II.

Although the Type II experiments were designed to investigate the relationship between DOX formation and the breakpoint curve, they cannot shed light on the effects of different CRC concentrations at the same Cl/N ratio. In Experiment Type III, by chlorinating a sample over a range of chlorine doses while holding a constant ratio of Cl:N, observations can be made regarding the sensitivity of DOX formation to the applied concentration of chlorine without a concurrent variation in the Cl/N ratio.

During the course of performing experiment types II and III, it was observed that some wastewater effluents had high chlorine demands which inhibited the formation of combined residual. The problem was severe enough in the case of the Amherst treatment plant to nearly double the required chlorine dose needed to maintain the mandatory minimum residual of 0.5 mg/L. Since the phenomenon occurred so frequently, an investigation into its causes was warranted. Nitrite is one species which reacts with free chlorine at a high enough rate so as to potentially compete with ammonia for free chlorine (Snoeyink and Jenkins, 1980). The effects of nitrite on chlorine demand in Amherst effluent were investigated in Type IV experiments.

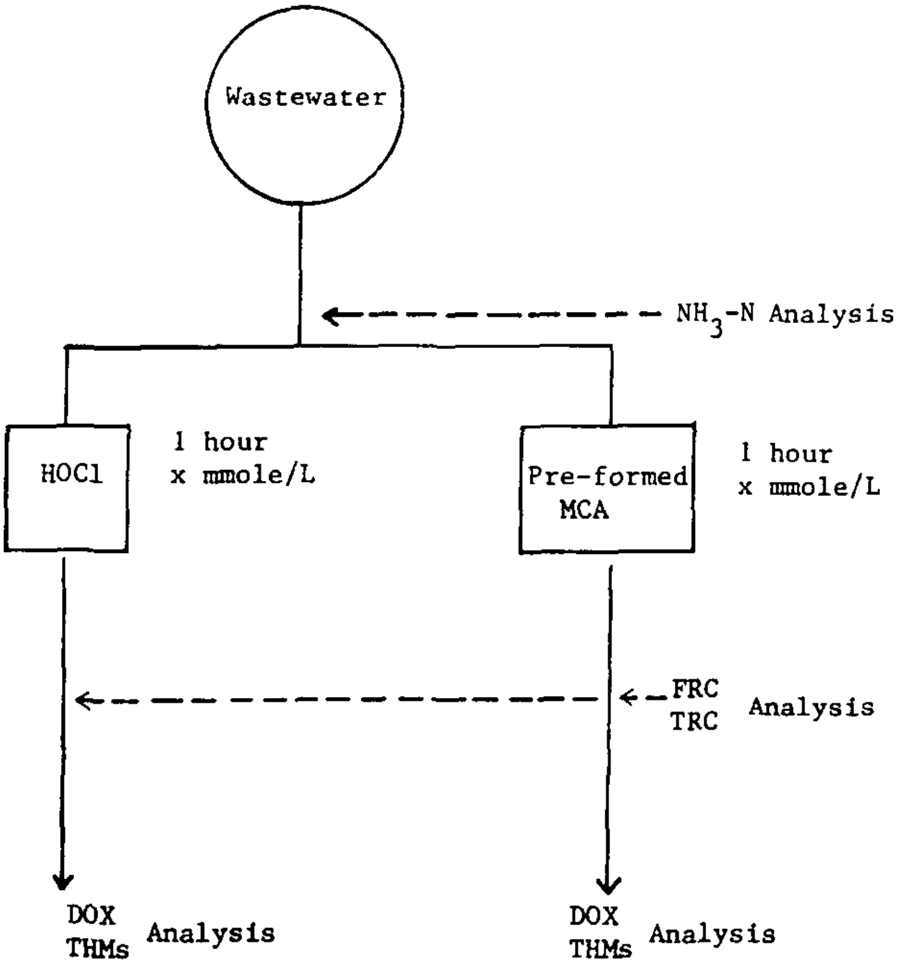
Following the results of the first four experiments types, three tests for dissolved organohalide formation potential (DOXFP) were formulated. These tests were then used as parameters in Type V experiments to examine the effects of low-level preozonation on organohalide formation.

## EXPERIMENT I: Comparison of HOCl- vs MCA-Formed DOX

Figure 6 shows a schematic diagram of experiment Type I. MCA stock was made according to the method of Johnson and Overby (1969). The resulting primary MCA stock yielded an MCA concentration near 73 mM which decayed at a rate of 0.61 mM per hour over the following 53 hours. The final concentration of the MCA stock was 41.2 mM just prior to its

FIGURE 6: DIAGRAM OF EXPERIMENT I

COMPARISON OF HOCl- vs MCA-FORMED DOX



use. HOCl stock was made from laboratory grade 5 % (nominal concentration) sodium hypochlorite solution diluted with RO/DI water (Milli-RO15 Super-Q Water Purifier, Millipore).

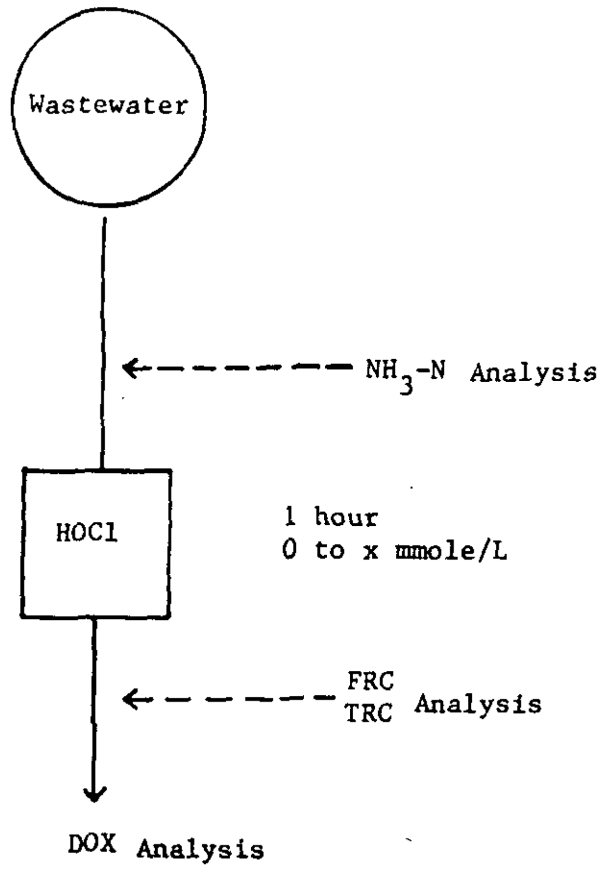
A 20 L sample of effluent was taken from the outfall of the final nutrient lagoon at the Belchertown, MA wastewater treatment plant on 3/26/87. The plant was not chlorinating at this time. The ammonia concentration was measured in the laboratory by means of an ion selective electrode (Orion model 95-10) and aliquots of the sample were removed for subsequent analysis of background TOX, TKN, TOC, and COD by methods outlined in Section C of this chapter. These aliquots were all brought to below pH 2 with sulfuric acid with the exception of the TOX aliquot in which nitric acid was used for pH adjustment. As a supplementary experiment, two breakpoint curves were run on sample aliquots using contact times of 7 and 60 minutes. This was done to ascertain that the chlorine-ammonia reactions were essentially complete by the end of the proposed 2-hour contact time. The sample stock was refrigerated at 5°C when not in use over the following 75 hours. During this time the ammonia concentration dropped from an initial value of 5.1 to 4.2 mg N/L. The loss of $NH_3$ had to be considered when calculating chlorine doses to achieve a specific Cl/N value.

For the main part of the experiment, eight chromic acid-washed BOD bottles were prepared for HOCl doses in a range of Cl/N values from 0.33 to 5.3. A separate set of of six BOD bottles were prepared for MCA doses so that the molar ratio of MCA to $NH_3$ ranged from 0.33 to 2.0. The chlorination procedure outlined in Section C.1a both the HOCl and MCA samples w after which 5 ml of sample was removed for residual chlorine measurement. The remaining sample was quenched with ~100 mg of granular sodium sulfite. The samples were then filtered through washed Whatman 934-AH filters (1.5 μm effective pore size) and refrigerated with the pH brought to below 2 with concentrated nitric acid until TOX analysis could be performed.

## EXPERIMENT II: DOX vs Cl/N

A schematic diagram of this experiment is shown in Figure 7. This experiment was performed twice with two different wastewater samples; one was with Belchertown effluent sampled on 12/22/87 and the other a Northampton effluent sampled on 5/24/88 near the outfall of the secondary clarifier. One difference in the handling of the two experiments is that the Belchertown sample was filtered just prior to TOX analysis whereas the Northampton sample, because of its higher suspended solids content, was filtered prior to chlorination (both samples by Millipore GF/F, 0.7 μM effective pore size). Otherwise, the experimental protocols were the same.

FIGURE 7: DIAGRAM OF EXPERIMENT II
DOX vs Cl/N



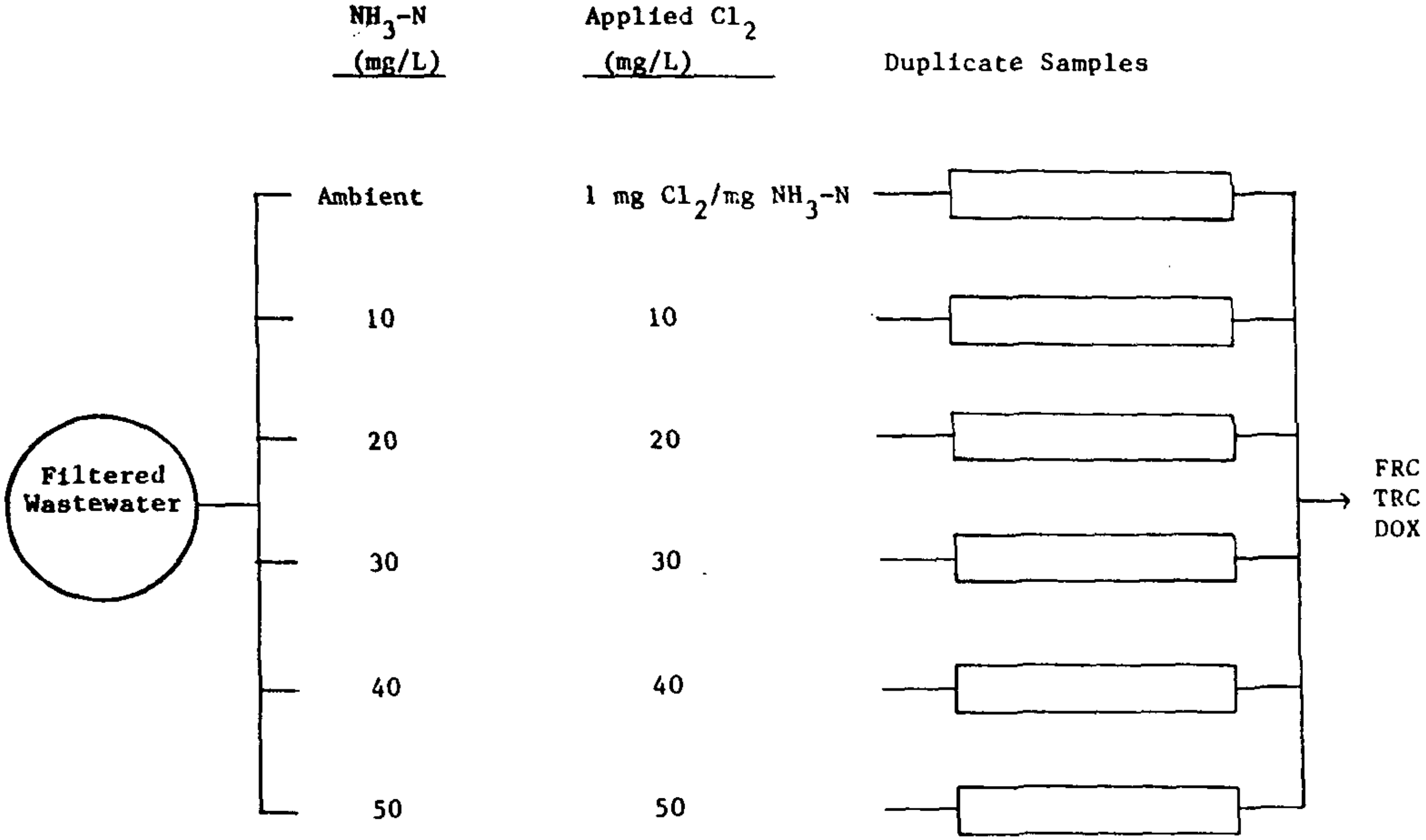
The ammonia concentration was measured in the sample by the phenate method (APHA, et al., 1985) and eleven HOCl doses (diluted from stock NaOCl solution) were calculated so as to give Cl/N values between 0.0 and 2.5. HOCl was applied at 5 minute intervals to aliquots of effluent contained in chromic acid-washed BOD bottles using the chlorination procedure discussed in Section C.1b of this chapter. After a contact time of 1 hour in the dark at room temperature, 100 ml of sample was removed for immediate residual chlorine analysis (FAS Titrimetric Method, APHA, et al., 1985). The 200 ml of remaining sample was quenched with ~100 mg of granular sodium sulfite and refrigerated in the dark at 4°C, headspace-free, with the pH brought to below 2 with concentrated nitric acid until TOX analysis could be performed.

### EXPERIMENT III: DOX at Constant Cl/N

A diagram of this experiment type is outlined in Figure 8. This experiment was performed twice, once using Belchertown effluent sampled on 3/11/88 and again using Belchertown effluent sampled on 5/3/88. The latter sample was filtered through washed Millipore GF/F filters (E.S. - 0.7 μm) prior to treatment. After measuring the ammonia in the stock wastewater using the phenate method, six aliquots were brought to the ammonia concentrations shown in Figure 8 with ammonium chloride. From Figure 8, note that the ratio of $Cl_2$ to $NH_3$-N were maintained at 1 mg/mg. This corresponds to a constant Cl/N value of 0.2. The six

FIGURE 8: DIAGRAM OF EXPERIMENT III

DOX at Constant Cl/N



aliquots of wastewater with added ammonia were each split into two replicates and chlorinated according to the procedure in Section C.1a of this chapter over a contact time of 24 hours. Residual chlorine and DOX were measured in the same manner as in Experiment Type II.

### EXPERIMENT IV: Effect of Nitrite on Chlorine Demand

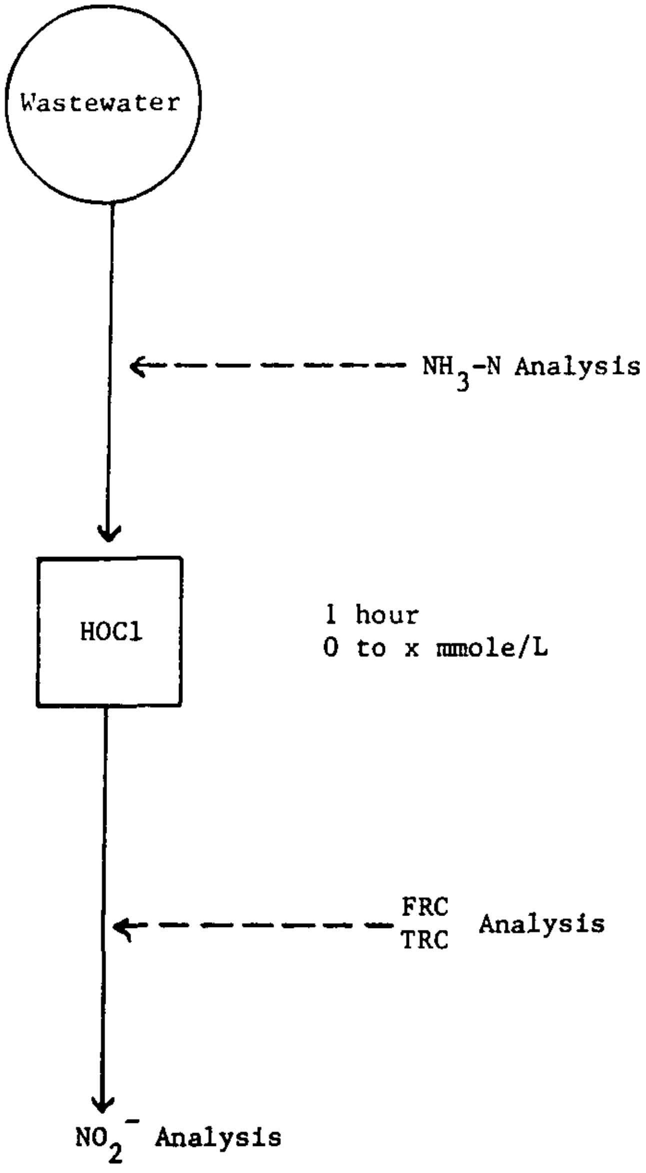
Nitrite is one possible species which reacts with free chlorine at a high enough rate so as to potentially compete with ammonia for free chlorine (Snoeyink and Jenkins, 1980). Nitrite has also been implicated as having a role in accelerating monochloramine decay in the presence of bromide (Valentine, 1984). The Amherst plant routinely produces nitrified effluent, especially in warmer months. A logical step in tracing the problem of high chlorine demand was to measure the concentration of nitrate, if any, and observe the trends of nitrite concentration across a series of chlorine doses spanning the ammonia breakpoint. A diagram of Experiment Type IV is given in Figure 9.

### EXPERIMENT V: Effect of Low-level preozonation on Organohalide Formation

In potable water treatment, THM precursor concentration is estimated by means of the trihalomethane formation potential (THMFP) test. This requires that a sample be chlorinated to produce a free residual over a contact time of 3 to 7 days. The THM concentration measured at the end

FIGURE 9: DIAGRAM OF EXPERIMENT IV

EFFECTS OF $NO_2^-$



of this contact period is the THMFP. Similar procedures are used for the assessment of DOX precursors (DOXFP) in potable water. An analogous test for DOXFP is desired in experiment Type V to assess the effect of low-level preozonation. However, in wastewater, where the concentration of $NH_3$ may vary substantially, a fixed dose of chlorine may yield different Cl/N ratios resulting in a substantially different environment for DOX formation. Because of the importance of chlorine-ammonia chemistry, three different DOXFP tests were used.

The first DOXFP test, referred to as DOXFP1, requires that the ammonia concentration of all the samples be elevated to 40 mg/L by addition of ammonium chloride. The samples are then chlorinated at a dose of 40 mg/L to give an Cl/N value of 0.2. This gives a standardized precursor test, where nearly the same residual chlorine environment exists regardless of the original sample chemistry. For this reason, it is the best of the three tests for comparing the reactivity of organic matter. The second and third test protocols are better suited for estimating the actual DOX concentrations expected during wastewater disinfection. These do not require fortification with ammonia. Instead, they make use of the ambient ammonia, and chlorine doses that give Cl/N values of 0.2 and 1.4. Thus, the DOXFP2 includes precursors that are active on the leading slope of the breakpoint curve (before the CRC maximum), and the DOXFP3 covers the precursors that are active when chlorinating between the CRC maximum and the breakpoint. The three DOXFP protocols are summarized in Table 1.

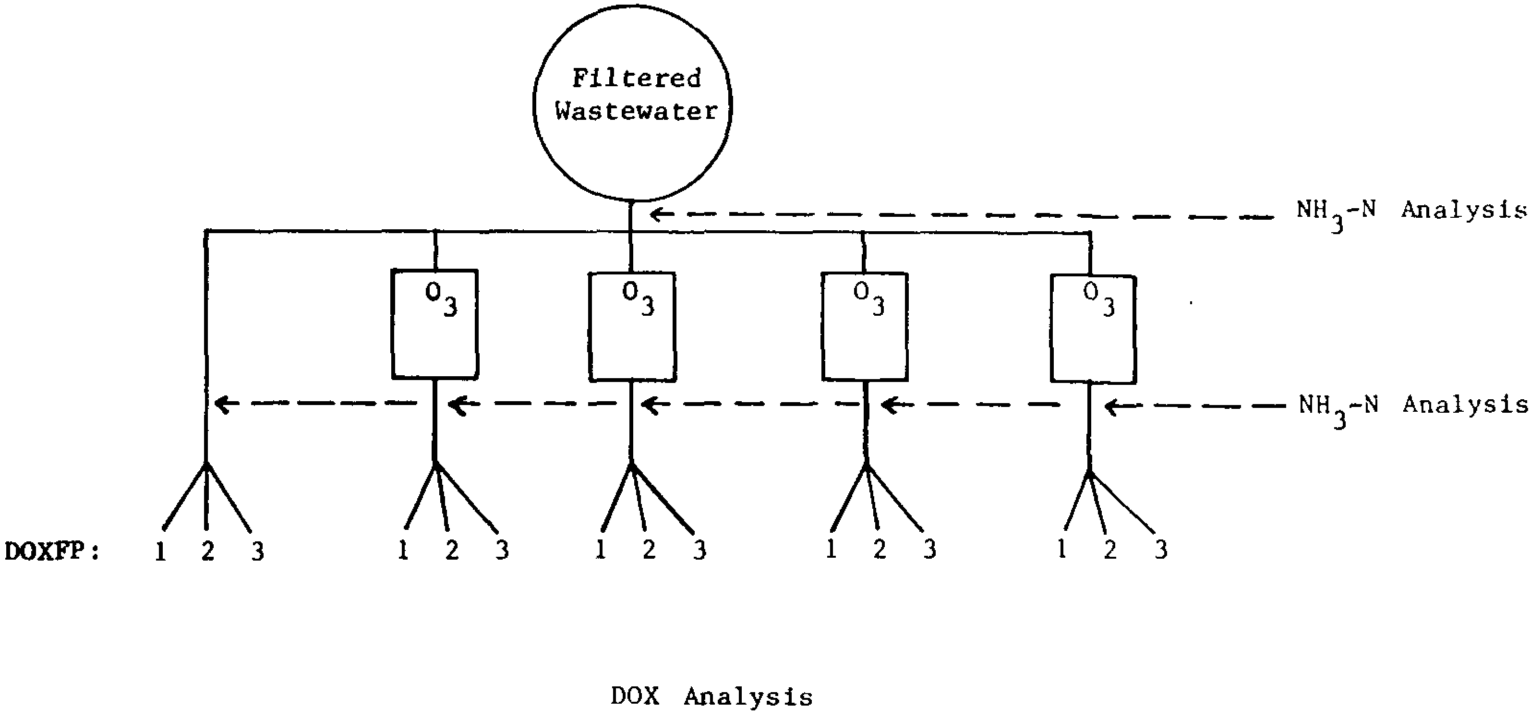
TABLE 1: DOXFP Protocols

| Type | $NH_3$-N (mg/L) | Cl/N | Contact Time |
|---|---|---|---|
| DOXFP1 | 40 | 0.2 | 24 hrs. |
| DOXFP2 | Ambient | 0.2 | 1 hr. |
| DOXFP3 | Ambient | 1.4 | 1 hr. |

A diagram of the Type V experiment is given in Figure 10. preozonation was performed according to the procedure outlined in Section C.4 of this chapter. Following preozonation, the samples were stored at 5°C for nearly 20 hours after which time the three DOXFP tests were performed on each preozonated aliquot. Detailed DOXFP protocols are discussed in Section C2 of this chapter.

**FIGURE 10:** DIAGRAM OF EXPERIMENT V

DOXFP vs PREOZONATION DOSE



## B. SAMPLE COLLECTION AND HANDLING

A 20 liter Nalgene plastic carboy, equipped with a screw-cap and spigot, was used to collect wastewater samples from municipal treatment plants. The carboy was acid washed with 10 % HCl after each use and rinsed 3 times with effluent before obtaining a sample. Many of the municipal wastewater treatment plants in the Connecticut River watershed practice seasonal chlorination. When a plant was not chlorinating, samples were taken from a point as close as practical to the outfall. The absence of chlorine was verified in the lab by FAS titration (APHA, et al., 1985). During periods of chlorination, samples were obtained from the effluent of the secondary settling basin. In the case of the Belchertown treatment plant, samples were taken from the outlet of the final nutrient lagoon.

Schematic diagrams of the principal treatment processes for each of the sampled plants are given in Figures 11, 12, and 13. The retention times and overflow rates (where applicable) for the conditions existing at the times of sampling are given in Tables 2, 3, and 4.

FIGURE 11: NORTHAMPTON WASTEWATER TREATMENT PLANT SCHEMATIC

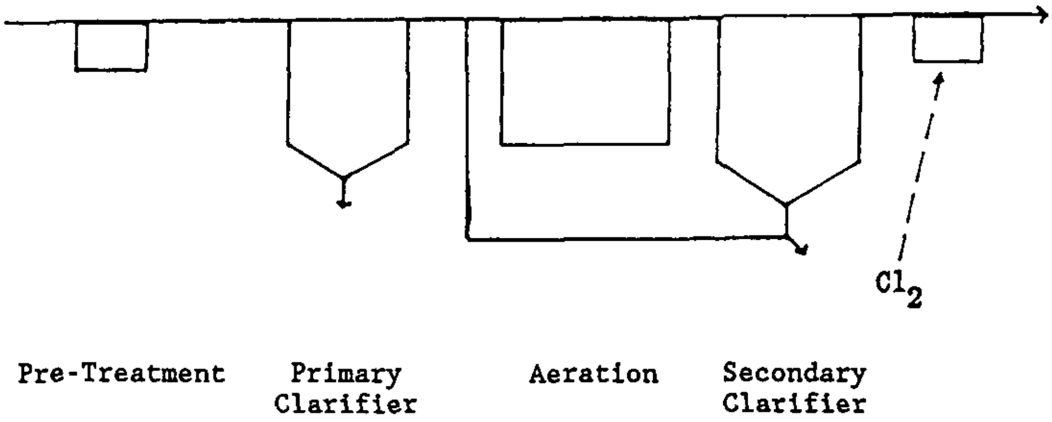


TABLE 2a: NORTHAMPTON WASTEWATER TREATMENT PLANT DATA - 5/24/88

| | Retention Time (hrs) | Surface Overflow Rate (gpd/ft$^2$) |
|---|---|---|
| Primary Clarifier | 2.6 | 690 |
| Aeration | 8.2 | -- |
| Secondary Clarifier | 5.4 | 400 |
| | 16.2 | |

TABLE 2b: NORTHAMPTON WASTEWATER TREATMENT PLANT DATA - 8/1/88

| | Retention Time (hrs) | Surface Overflow Rate (gpd/ft$^2$) |
|---|---|---|
| Primary Clarifier | 2.7 | 650 |
| Aeration | 8.6 | -- |
| Secondary Clarifier | 3.8 | 565 |
| | 15.1 | |

FIGURE 12: AMHERST WASTEWATER TREATMENT PLANT SCHEMATIC

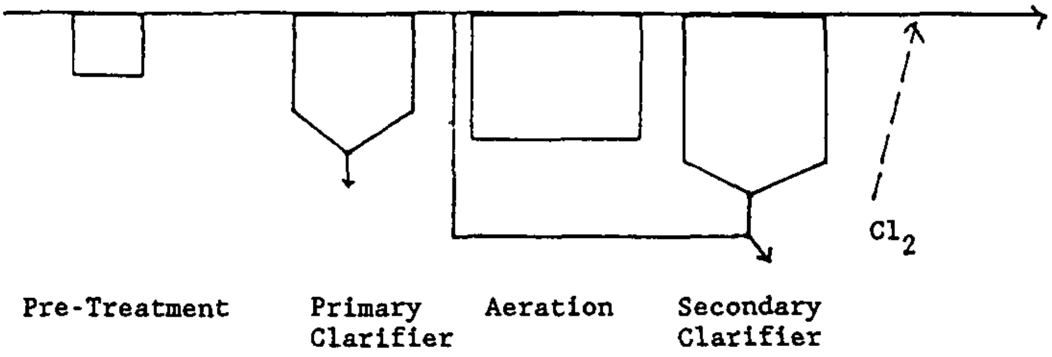


TABLE 3a: AMHERST WASTEWATER TREATMENT PLANT DATA - 3/22/88

| | Retention Time (hrs.) | Surface Overflow Rate (gpd/ft$^2$) |
|---|---|---|
| Primary Clarifier | 3.6 | 500 |
| Aeration | 7.9 | -- |
| Secondary Clarifier | 8.1 | 360 |
| | 19.6 | |

TABLE 3b: AMHERST WASTEWATER TREATMENT PLANT DATA - 3/24/88

| | Retention Time (hrs.) | Surface Overflow Rate (gpd/ft$^2$) |
|---|---|---|
| Primary Clarifier | 3.8 | 470 |
| Aeration | 8.4 | -- |
| Secondary Clarifier | 8.6 | 340 |
| | 20.8 | |

TABLE 3c: AMHERST WASTEWATER TREATMENT PLANT DATA - 6/28/88

| | Retention Time (hrs.) | Surface Overflow Rate (gpd/ft$^2$) |
|---|---|---|
| Primary Clarifier | 2.5 | 800 |
| Aeration | 7.4 | --- |
| Secondary Clarifier | 9.8 | 290 |
| | 19.7 | |

FIGURE 13: BELCHERTOWN WASTEWATER TREATMENT PLANT SCHEMATIC

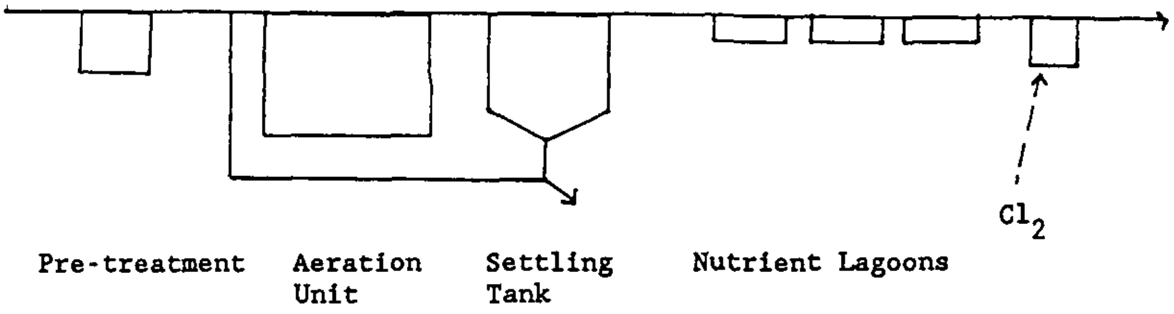


Table 4a: BELCHERTOWN WASTEWATER TREATMENT PLANT DATA - 3/26/87

| | Retention Time (hrs.) | Surface Overflow Rate (gpd/ft$^2$) |
|---|---|---|
| Aeration Unit | 4.4 | --- |
| Settling Tank | 2.1 | 679 |
| Nutrient Lagoons: | | |
| Pond 1 | 29.5 | --- |
| Pond 2 | 29.5 | --- |
| Pond 3 | 29.5 | --- |
| | 65.5 | |

TABLE 4b: BELCHERTOWN WASTEWATER TREATMENT PLANT DATA - 12/22/87

| | Retention Time (hrs.) | Surface Overflow Rate ($gpd/ft^2$) |
|---|---|---|
| Aeration Unit | 6.8 | --- |
| Settling Tank | 3.2 | 440 |
| Nutrient Lagoons: | | |
| Pond 1 | 45.5 | --- |
| Pond 2 | 45.5 | --- |
| Pond 3 | 45.5 | --- |
| | 146.5 | |

TABLE 4c: BELCHERTOWN WASTEWATER TREATMENT PLANT DATA - 5/30/88

| | Retention Time (hrs.) | Surface Overflow Rate ($gpd/ft^2$) |
|---|---|---|
| Aeration Unit | 5.1 | --- |
| Settling Tank | 2.4 | 586 |
| Nutrient Lagoons: | | |
| Pond 1 | 34.2 | --- |
| Pond 2 | 34.2 | --- |
| Pond 3 | 34.2 | --- |
| | 110.1 | |

TABLE 4d: BELCHERTOWN WASTEWATER TREATMENT PLANT DATA - 6/13/88

| | Retention Time (hrs.) | Surface Overflow Rate ($gpd/ft^2$) |
|---|---|---|
| Aeration Unit | 8.1 | --- |
| Settling Tank | 3.9 | 365 |
| Nutrient Lagoons: | | |
| Pond 1 | 54.9 | --- |
| Pond 2 | 54.9 | --- |
| Pond 3 | 54.9 | --- |
| | 176.7 | |

## C. DETAILED EXPERIMENTAL PROCEDURE

### 1. Chlorination Procedure

The aliquots to be chlorinated were removed from the 20 liter carboy of sample stock by means of a spigot mounted at the base of the carboy. An impeller introduced through the top of the carboy was used to gently stir the sample stock while aliquots were removed. If the sample stock was not to be immediately used, it was refrigerated at 4°C in the dark to minimize any biochemical decomposition. The ammonia concentration of sample stock at room temperature was measured (Ion Selective Electrode or Phenate Method; APHA, et al., 1985) just prior to chlorination so that an accurate molar ratio of chlorine to ammonia could be obtained. Under no circumstances was a sample stock held for longer than three days.

Aliquots for chlorination were collected in chromic acid-washed BOD bottles. The chlorine (or monochloramine) was applied from a stock solution by means of a Pyrex glass pipette which was soaked in dilute sodium hypochlorite solution and rinsed with RO/DI water just prior to use. A dilution factor was included in subsequent calculations if the volume of required chlorine stock was greater than 1.0 % of the sample volume. Chlorination was carried out under either one of two mixing conditions:

(a) Chlorine (or MCA) was slowly pipeted into a BOD bottle filled 9/10 full of sample while stirring at constant speed with a Teflon-coated magnetic stir bar. After addition of the chlorine, the BOD bottle was brought to full headspace-free volume with sample and allowed to sit in the dark at room temperature for the required contact time. The pH was measured before chlorination and after the required contact time.

(b) Chlorine was rapidly pipeted into a BOD bottle filled 9/10 full of sample. After addition of chlorine, the BOD bottle was brought to full headspace-free volume, capped, and slowly inverted three times. The conditions for chlorine contact were the same as in (a) above.

Results of Fleischacker and Randtke (1983), Brown (1985), and this study (data not included), indicate that there is no measurable effect of mixing on organohalide formation under the laboratory conditions used. This does not preclude the importance of hydraulic dead spaces or short circuiting in full-scale treatment plants.

### 2. <u>DOXFP Procedure</u>

#### (a) <u>DOXFP1</u>

The ammonia concentration was measured in the sample stock (Phenate Method, APHA et al., 1985). An aliquot of sample was then brought to a total $NH_3$-N concentration of 40 mg/L with ammonium chloride (stock concentration of 5000 mg/L as N) in a 1000 ml volumetric flask. An aliquot from the volumetric flask was then dosed with 40 mg/L chlorine as in 1(b) above.

(b) DOXFP2

The ammonia concentration in the sample stock was used to calculate the chlorine dose necessary to provide a molar ratio of chlorine to ammonia of 0.2. This chlorine dose was applied to an aliquot of sample by the method of item 1(b) above.

(c) DOXFP3

A procedure similar to that of DOXFP2 was performed except that the applied chlorine dose was provided to yield an Cl/N value of 1.4.

Chlorination reactions for all three DOXFP tests were conducted according to the procedure in Section C.1.b of this chapter. Residual chlorine was measured in the same manner as in Experiment II. DOX was measured according to the method described in Section C4 of this chapter.

### 3. Ozonation Procedure

Preozonation was performed on 2100 ml aliquots of filtered (Whatman GF/F, 0.7 μm E.S.) effluent using a semi-continuous apparatus. The overall gas transfer coefficient ($K_La$) for this system with ozone was 0.0175 $min^{-1}$ at 25°C as reported in Lehan (1989). A flow of 40 ml/min of ozone enriched oxygen was carried by Teflon tubing to the reaction vessel of nominal 2 L volume. The ozone reaction vessel was composed of pyrex glass and was equipped with a Teflon encased magnetic stir bar rotated at a fixed speed throughout all ozonation runs. The inflow of ozone was released 1 cm above the rotating stir bar by a vertical glass tube with a 2 mm diameter at the outlet. Off-gas was routed to a 500 ml gas washing bottle containing 2 % KI solution for determination of effluent ozone concentration (iodometric method. APHA et al., 1985). Headspace in the reaction vessel was no greater than 50 ml between the sample and the off-gas trap. The concentration of applied ozone was measured by routing the 40 ml/minute gas flow to a separate KI gas trap over timed intervals both before and after an ozonation run. The pH was measured in samples both before and after the ozonation period.

Since oxygen feed gas was used for the ozone generator (Welsbach model T-408), a single oxygen blank was run for each effluent sample. This was prepared exactly as the sample receiving the highest ozone dose, except that the ozone generator was shut off. Titrations of samples for residual ozone by the KI method performed 10 minutes after the end of the longest ozonation period showed no measurable ozone residual. After ozonation, samples were stored at 4°C until the following day when chlorination procedures were performed.

### 4. DOX Analysis

A Dohrmann DX-20 TOX analyzer was used to determine dissolved organohalide concentrations by the adsorption-pyrolysis-titration method (APHA et al., 1985). Samples were analyzed in duplicate for the preozonation experiments with an error estimated as the standard deviation between the two duplicate samples or 5 percent, whichever was greater. For the adsorption step, 100/200 mesh granular activated carbon (GAC) was purchased from Dohrmann-Xertex, Inc. In this study and in others (Brown,1985), THM formation was low in wastewaters chlorinated below the breakpoint. In general, the non-volatile fraction of organohalides has been found to be much greater than the volatile fraction in chlorinated humic materials (Rook, 1980), in potable waters (Reckhow, 1984), and in wastewater (Brown, 1985). This is especially true of systems dominated by chloramines (Brown, 1985; Stevens et al., 1986). In preozonation experiments (Type V), the effluent was filtered prior to chlorination so that no further filtration was required before TOX analysis. This minimizes the loss of volatile organohalides. Distinction between purgable and non-purgable organohalides was neglected in this study.

### 5. Trihalomethanes (THMs)

THMs were analyzed roughly in accordance with EPA Method 501.1 (Federal Register, 1979) in which an aqueous sample is extracted with pentane and injected in 1 microlitre volumes into a Varian 3300 gas chromatograph equipped with an electron capture detector. The 6-ft by 4 mm glass column was packed with 3 % SP-1000, 100/120 mesh Supelcoport packing material. Column, injector, and detector temperatures were set at 75, 120, and 200°C, respectively.

## 6. Standard Analytical Methods

(a) Ammonia - Ammonia nitrogen was measured using the method of known additions with an ion selective electrode (Orion Corp.) or by the phenate method (APHA et al., 1985).

(b) Residual Chlorine - Residual chlorine was measured by the DPD Ferrous titrimetric method . A dichromate standard was used to calibrate the normality of the ferric ammonium sulfate titrant (APHA et al., 1985).

(c) Nitrite - Nitrite nitrogen was measured by the NED dihydrochloride method (APHA et al., 1985).

(d) Total Kjeldahl Nitrogen - TKN was analyzed by the Macro-Kjeldahl method using an ammonia-selective electrode in the final measurement (APHA et al., 1985).

(e) Total Organic Carbon - TOC was measured using a Beckman 915 TOC analyzer set at 950°C with the oxygen carrier gas flow at 125 ml/min at 4 psig. Samples were analyzed in triplicate after acidification to below pH 2 with nitric acid and purging of $CO_2$ with 99.99 % nitrogen (APHA et al., 1985).

(f) Chemical Oxygen Demand - COD was measured using a Hach Micro-COD analysis kit in which color formed by the reduction of dichromate is related to the oxidation of organic matter. The color formation, as measured spectrophotometrically (Perkin-Elmer model Lamda 3A) is related by Beer's law to the quantity of oxidizable matter.

(g) Bromide - Bromide was measured using a bromide-selective electrode in filtered samples (APHA et al., 1985).

(h) pH - was measured using a combination Micro-pH probe (Fisher 13-639-94) in conjunction with an Orion 940 Expandable Ion Analyzer. A two-point calibration of the pH at sample temperature was done before each run.

## D. PRECISION OF MEASUREMENTS

As a result of replicate analyses performed throughout this study, Table 5 was developed to summarize the precision of each of the analytical methods. In Table 5, the 90 percent confidence interval is expressed as a percent of the measured value.

TABLE 5: Precision of Measurements

| Parameter | Percent Recovery of Standards | Standard Conc. | 90 % Confidence Interval (Expressed as percent of Measured Value) |
|---|---|---|---|
| pH | - | - | (accurate within 0.05 pH unit) |
| Temp. | - | - | (accurate within 0.5°C) |
| $NH_3$-N (phenate) | | - | ± 9 % |
| $NH_3$-N (electrode) | | - | ± 17 % |
| $NO_2$-N | - | - | ± 1 % |
| TKN | 93 | 20 mg/L | ± 28 % |
| TOC | - | - | ± 7 % |
| COD | - | - | ± 54 % |
| THMs ($CHCl_3$) | - | - | ± 4 % |
| DOX | 68 - 115 | 250 - 100 (μg/L) | * |

* Uncertainty in measurement was estimated as the standard deviation of replicate analyses or 5% of the replicate average, whichever was greater. Error bars in figures are adjusted accordingly.

# CHAPTER IV: RESULTS AND DISCUSSION

The discussion of data is broken into three main headings according to the class of reactions being considered. In Part A, the chemistry of chlorine and ammonia as observed in the wastewater systems is discussed. This is discussed first because of the importance of residual chlorine in DOX formation. In Part B, the discussion turns to the nature of organohalide formation in the effluents and how it is related to the chemistry of chlorine and ammonia. Finally, in Part C, experiments on the effects of preozonation are discussed with respect to the first two classes of reactions.

## A. REACTIONS OF CHLORINE AND AMMONIA

### A.1 Breakpoint Chlorination Curves

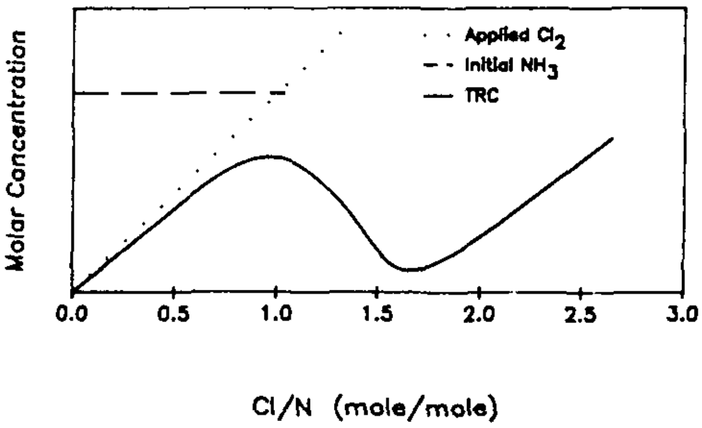
Breakpoint chlorination experiments were performed on nine separate effluent samples used in this study. These are grouped according to the wastewater treatment plants from which they were sampled. For convenience, idealized breakpoint chlorination characteristics are shown in Figure 14 for the 1-hour contact times used in the chlorination experiments. Figures 15, 16, and 17 show data for the Northampton, Amherst, and Belchertown wastewater treatment plants, respectively. In Figure 18, the general features of all nine breakpoint curves are summarized by plotting the molar ratio of total residual chlorine to ammonia versus the Cl/N value. In this manner, both the chlorine dose and the chlorine residual are normalized to the ammonia concentration.

The numbers in parentheses in Figure 18 indicate the initial $NH_3$-N concentration of each sample. In Tables 6 and 7, a partial characterization of the wastewater samples used for experiments is presented.

Of the nine effluents sampled, five showed idealized breakpoint characteristics. These include one of the Northampton samples (Figure 15, upper graph), one of the Amherst samples (Figure 16, bottom graph), and all three of the Belchertown samples (Figure 17). These five samples exhibited the characteristics of an ideal breakpoint curve having the CRC maximum near a value of Cl/N = 1 and the appearance of free residual at the breakpoint between Cl/N values of 1.5 and 2.0. Ideal breakpoint characteristics were observed in samples having a wide range of ammonia concentrations. For example, the Belchertown effluent of 12/22/87 and the Northampton effluent of 5/24/88 both exhibited ideal characteristics though their ammonia concentrations were 1.5 and 15 mg N/L, respectively. The remaining four samples showed an inhibition of residual chlorine formation as indicated by the lower yield of TRC obtained from an applied dose of chlorine. In these non-ideal samples, it was evident that higher chlorine doses (Cl/N values) were required to reach the CRC maximum and breakpoint. In the samples obtained for this study, it was observed that only non-nitrified effluents exhibited ideal breakpoint characteristics. Inspection of Figure 18 indicates that only effluents with ammonia concentrations greater than 100 $\mu$M (1.4 mg N/L) exhibited idealized breakpoint characteristics while those with ammonia concentrations of 100 $\mu$M or less exhibited non-ideal characteristics.

FIGURE 14

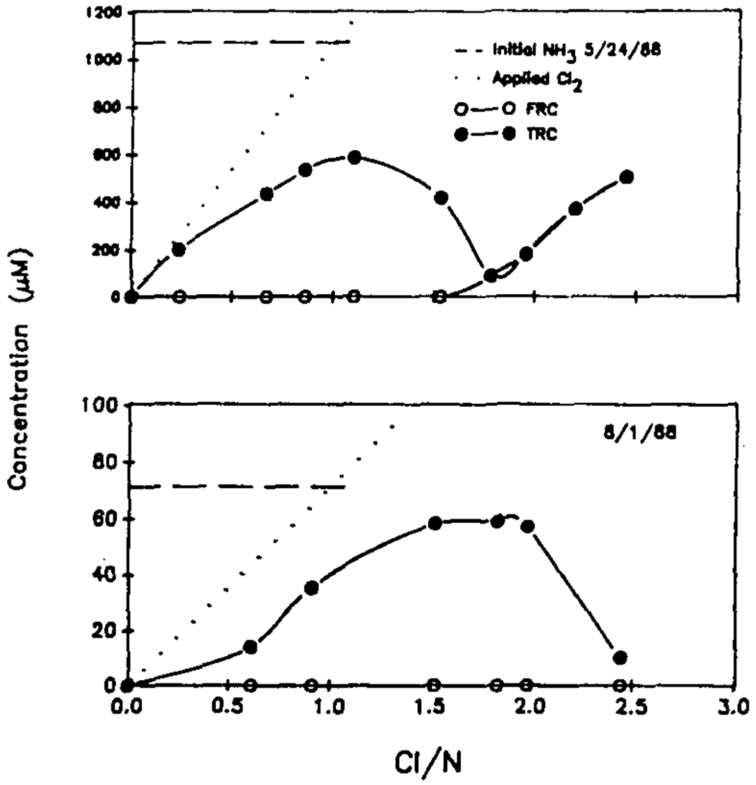
IDEALIZED BREAKPOINT CURVE



(From Jafvert, 1985)

FIGURE 15

BREAKPOINT CHLORINATION CHARACTERISTICS
OF NORTHAMPTON EFFLUENT



## FIGURE 16

### BREAKPOINT CHLORINATION CHARACTERISTICS OF AMHERST EFFLUENT

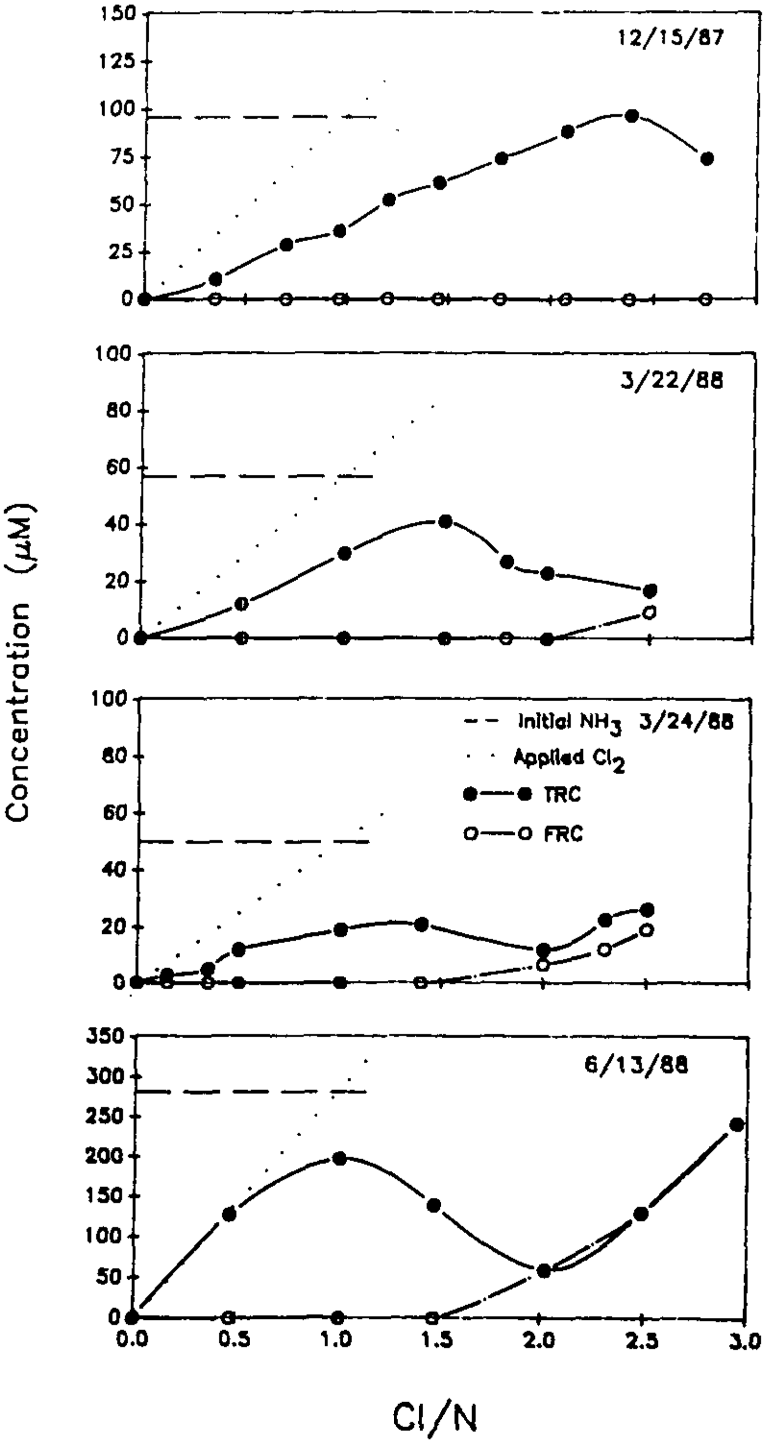


FIGURE 17

BREAKPOINT CHLORINATION CHARACTERISTICS
OF BELCHERTOWN EFFLUENT

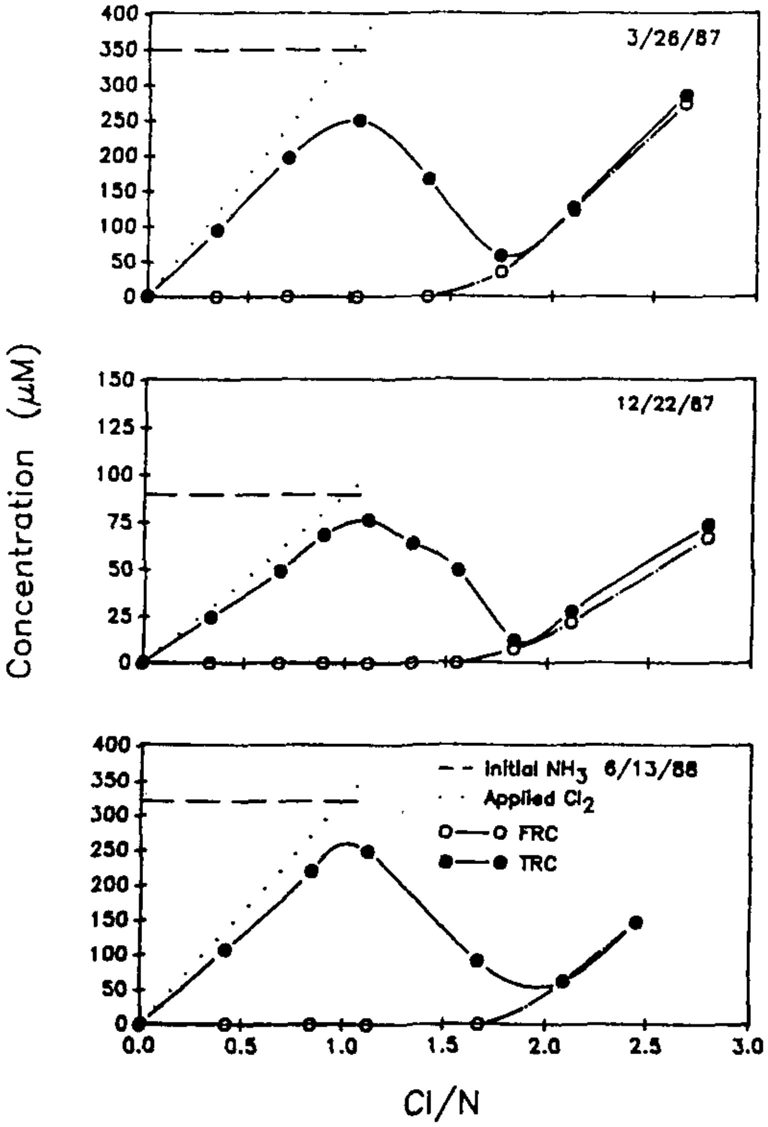
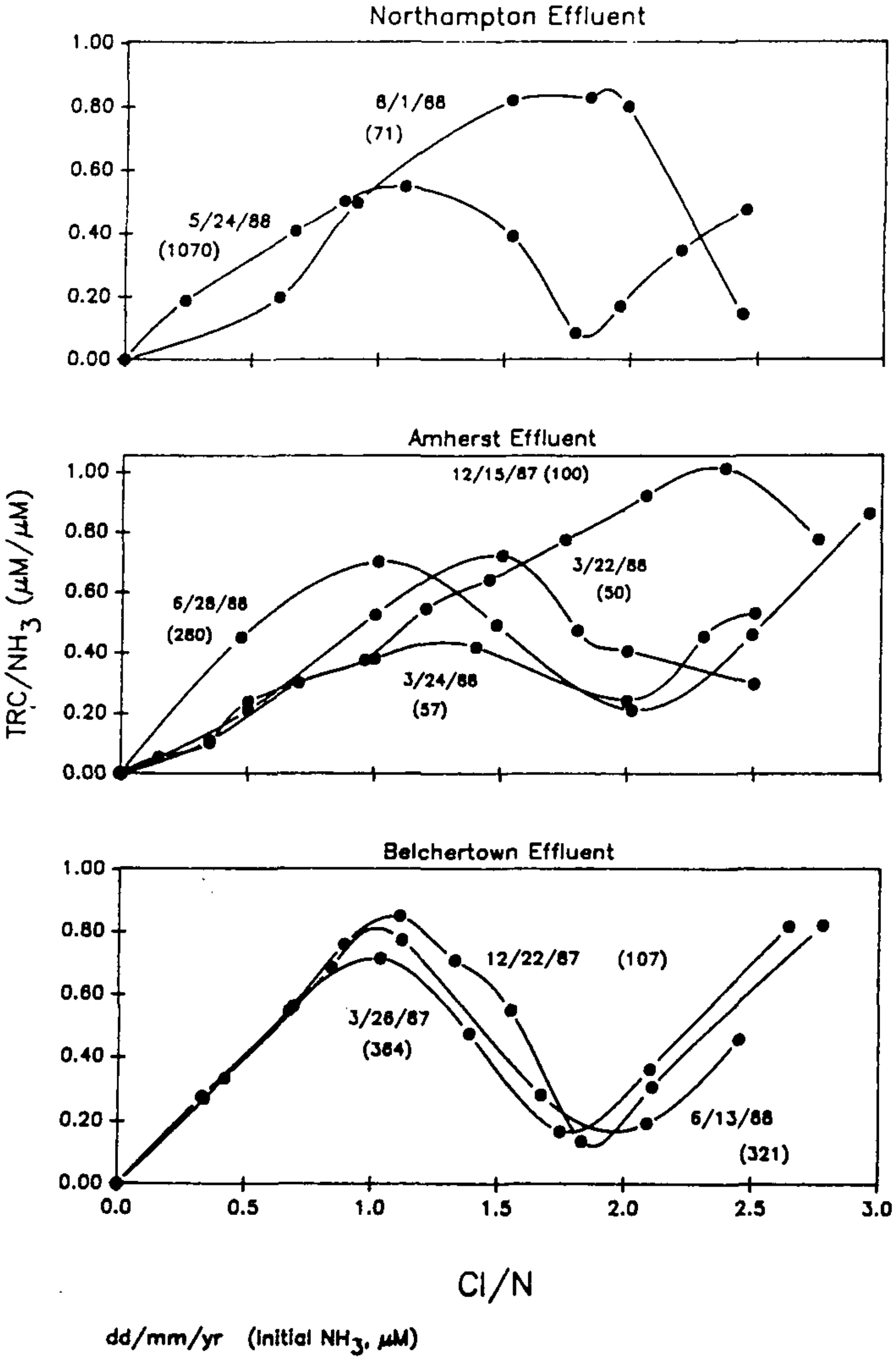


FIGURE 18

SUMMARY OF BREAKPOINT CHLORINATION CHARACTERISTICS



## TABLE 6: PARTIAL CHARACTERIZATION OF MUNICIPAL WASTEWATER EFFLUENTS USED IN EXPERIMENTS I - IV

| | AMHERST................. | | | BELCHERTOWN............. | | | NORTHAMPTON |
|---|---|---|---|---|---|---|---|
| PARAMETER | 12/15/87 | 3/22/88 | 3/24/88 | 3/26/87 | 12/22/87 | 5/30/88 | 5/24/88.... |
| pH | 6.9 | 6.3 | 6.1 | 7.2 | 7.0 | 7.5 | 7.7 |
| Temp. ( C) | 23 | 12 | 12 | 19 | 19 | 15 | 15 |
| Plant $BOD_5$ (mg/L) | -- | ~4.0 | ~4.0 | -- | 9.1 | -- | 16.0 |
| Suspend Solids (mg/L) | -- | -- | -- | 4.7 | 1.3 | -- | 8.0 |
| $NH_3$-N (mg/L) | 1.4 | 0.8 | 0.7 | 5.1 | 1.5 | 3.0 | 15 |
| $NO_2$-N (mg/L) | -- | 0.14 | 0.19 | -- | -- | -- | -- |
| TKN (mg/L) | -- | -- | -- | 7.8 | -- | 4.3 | -- |
| TOC (mg/L) | -- | -- | -- | 31 | -- | -- | -- |
| COD (mg/L) | -- | -- | -- | 58 | 30 | 37 | 44 |
| DOX (µg/L) | 86<br>(Filt. 0.7 µm prior to TOX) | -- | -- | 30<br>(not filt.) | 59<br>(Filt. 0.7 µm prior to TOX) | 25<br>(Filt. 0.7 µm prior to $Cl_2$ add'n) | 88<br>(Filt. 0.7 µm prior to TOX) |

TABLE 7: PARTIAL CHARACTERIZATION OF MUNICIPAL WASTEWATER EFFLUENTS USED IN OZONATION EXPERIMENTS

| PARAMETER | AMHERST 6/28/88 | BELCHERTOWN 6/13/88 | NORTHAMPTON 8/1/88 |
|---|---|---|---|
| pH | 7.5 | 7.45 | 6.87 |
| Temp. (°C) | 19 | 15 | 15 |
| Plant $BOD_5$ (mg/L) | ~2.5 | 11.9 | ~4 |
| $NH_3$-N (mg/L) | 3.95 | 3.86 | 1.00 |
| $NO_2$-N (mg/L) | -- | -- | 0.32 |
| TKN (mg/L) | 4.3 | -- | 1.2 |
| DOC (mg/L) | 9.4 | 9.6 | 8.6 |
| COD (mg/L) | 31 | 54 | -- |
| Dissolved Bromide (mg/L) | 2.3 | 2.3 | 2.1 |
| Absorbance @ 254 nm (1 cm cell) | -- | -- | 0.157 |
| DOX (µg/L) | 86 | 56 | 79 |
| DOXFP1 (µg/L) | 74 | 218 | 137 |
| [µM] | [2.1] | [6.15] | [3.86] |
| DOXFP2 (µg/L) | 46 | 32 | 37 |
| [µM] | [1.3] | [0.90] | [1.0] |
| DOXFP3 (µg/L) | 158 | 154 | 117 |
| [µM] | [4.46] | [4.34] | [3.30] |

NOTE: All characteristics are for effluent filtered through glass fiber filters (0.7 µm effective pore size) prior to ozonation.

## A.2 Investigation of High Chlorine Demand

Because it was necessary to understand the primary reactions of chlorine before the wastewater system could be characterized with respect to DOX formation, a brief study of the potential causes of the non-ideal behavior was undertaken. Nitrite is one species that may exist in nitrified effluent and is known to consume free chlorine very rapidly near neutral pH:

$$NO_2^- + HOCl + H_2O \dashrightarrow NO_3^- + H_3O^+ + Cl^- \qquad (15)$$

The consumption of chlorine in the presence of nitrite has been observed in municipal effluent by several researchers along with an associated loss of disinfection power (Dhaliwal and Baker, 1983; Gordon, 1985; Gasser, 1984). The loss of combined residual (monochloramine) in the presence of nitrite is commonly attributed to Equation 15, above, reacting in direct competition with monochloramine formation (Snoeyink and Jenkins, 1980). Work by Valentine et al. (1981) and Valentine (1984) suggests that the loss of monochloramine under certain conditions may be due to a complex mechanism of decay. Several important observations of the stability of chloramines in the presence of nitrite have been made by Valentine and co-workers:

(1) Monochloramine can be degraded in the presence of bromide via a mechanism involving monochlorammonium ion ($NH_3Cl^+$) and bromide.

(2) Monochloramine degradation in the presence of bromide occurs at a slower rate in organic-rich solutions than in pure $NH_2Cl$ /$Br^-$ solution.

(3) The disappearance of monochloramine can be greatly accelerated by the presence of nitrite.

The rate expression developed by Valentine et al. (1981) for the decay of monochloramine in 0.25 M phosphate buffer at 25°C is:

$$-d[NH_2Cl]/dt = k_1 [H^+][Br^-][NH_2Cl] + k_2 [H^+][NO_2^-][NH_2Cl] \qquad (16)$$

Where: $k_1 = 5.46 + 0.25 \times 10^7\ M^{-2}min^{-1}$

$k_2 = 1.8 + 0.1 \times 10^9\ M^{-2}min^{-1}$

In the breakpoint curves developed for this study, the conditions differ from Valentine's chloramine decay experiments because free chlorine was added to samples directly rather than pre-formed monochloramine. In addition to the complex mechanisms investigated by Valentine, the chlorine may have reacted directly with nitrite as in equation 15 and precluded the formation of chloramine. The contribution by both of these factors may contribute to an overall high chlorine demand in an effluent. The breakpoint chlorination curves of nitrified Amherst effluent of 3/22/88 and 3/24/88 are shown in Figure 19. Nitrite was measured in the samples prior to chlorination and after the 1-hour contact time with each successive chlorine dose. As would be expected, the nitrite is removed by the chlorine. While it is generally recognized that the oxidation of nitrite by HOCl is a faster reaction than the formation of monochloramine (Jafvert, 1985; Valentine,1985; Morris, 1975), the reaction rate for this process at neutral pH has not been reported.

If one assumes that Equation 15 predominates in the wastewater system, there would be a 1:1 mole ratio of chlorine consumed for nitrite oxidized. By this approach, the CRC concentration which would have existed in the absence of nitrite can be approximated as the TRC plus the molar amount of removed nitrite. For example, Figure 20 shows the portions of the breakpoint curves at doses below the CRC maximum. In this region, the term "chlorine demand" applies to all the reactions of chlorine which do not contribute to the formation of CRC. For the March 22 effluent, the oxidation of nitrite appears to account for about half of the chlorine demand (i.e., half of the difference between the applied HOCl and the TRC). In the March 24 effluent, nitrite oxidation appears to account for nearly all of the chlorine demand.

It appears from Figure 20 that nitrite competes with ammonia for free chlorine. Presuming that Equation 15 and the formation of monochloramine from free chlorine (Equation 3) are both first order with respect to chlorine and that the two reactions operate in parallel, it is possible to estimate the relative rate of reaction for Equation 15 and Equation 3. The removal of $NH_3$ and $NO_2^-$ can be expressed:

# FIGURE 19
# NITRITE REMOVAL DURING BREAKPOINT CHLORINATION

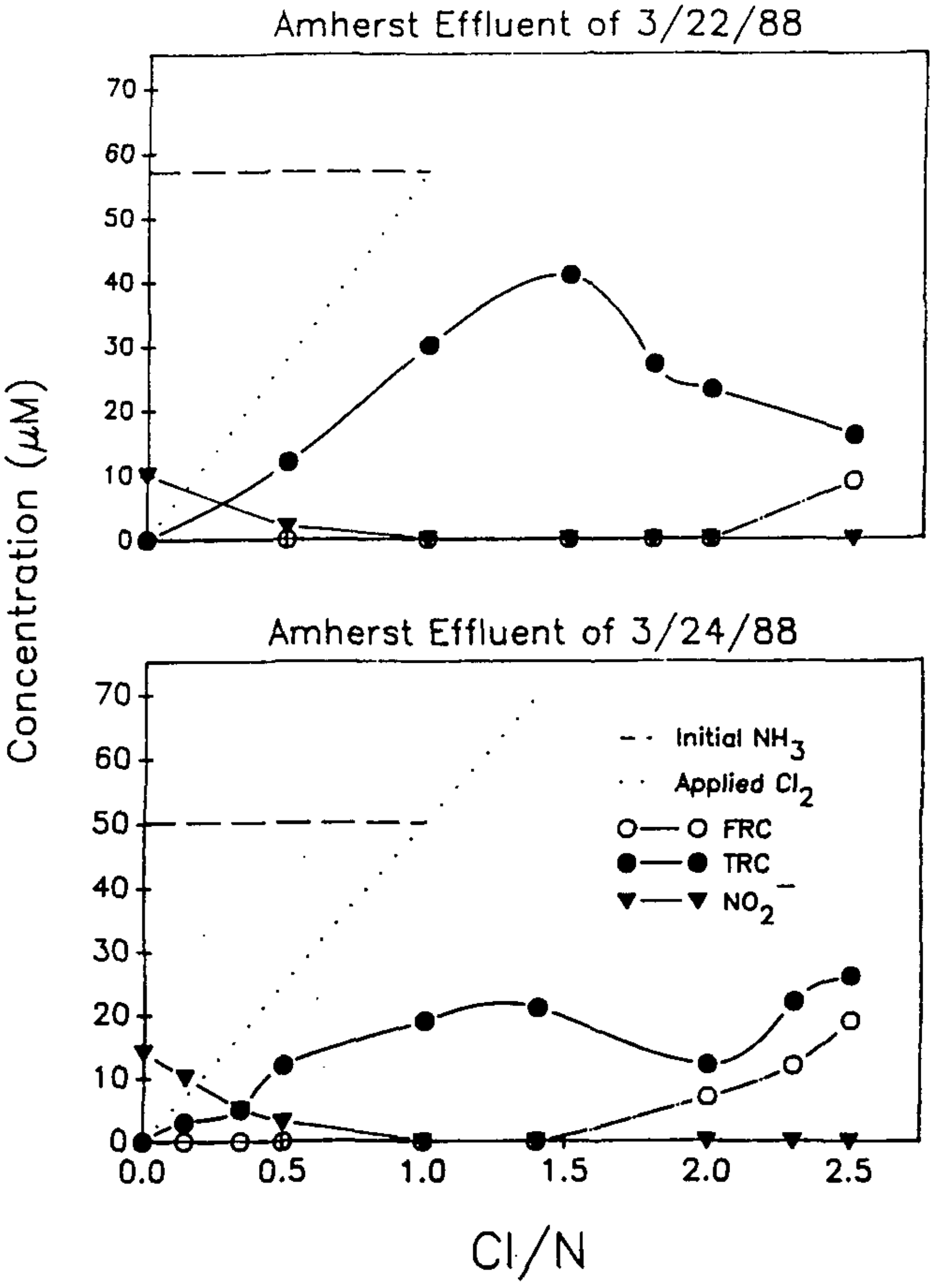
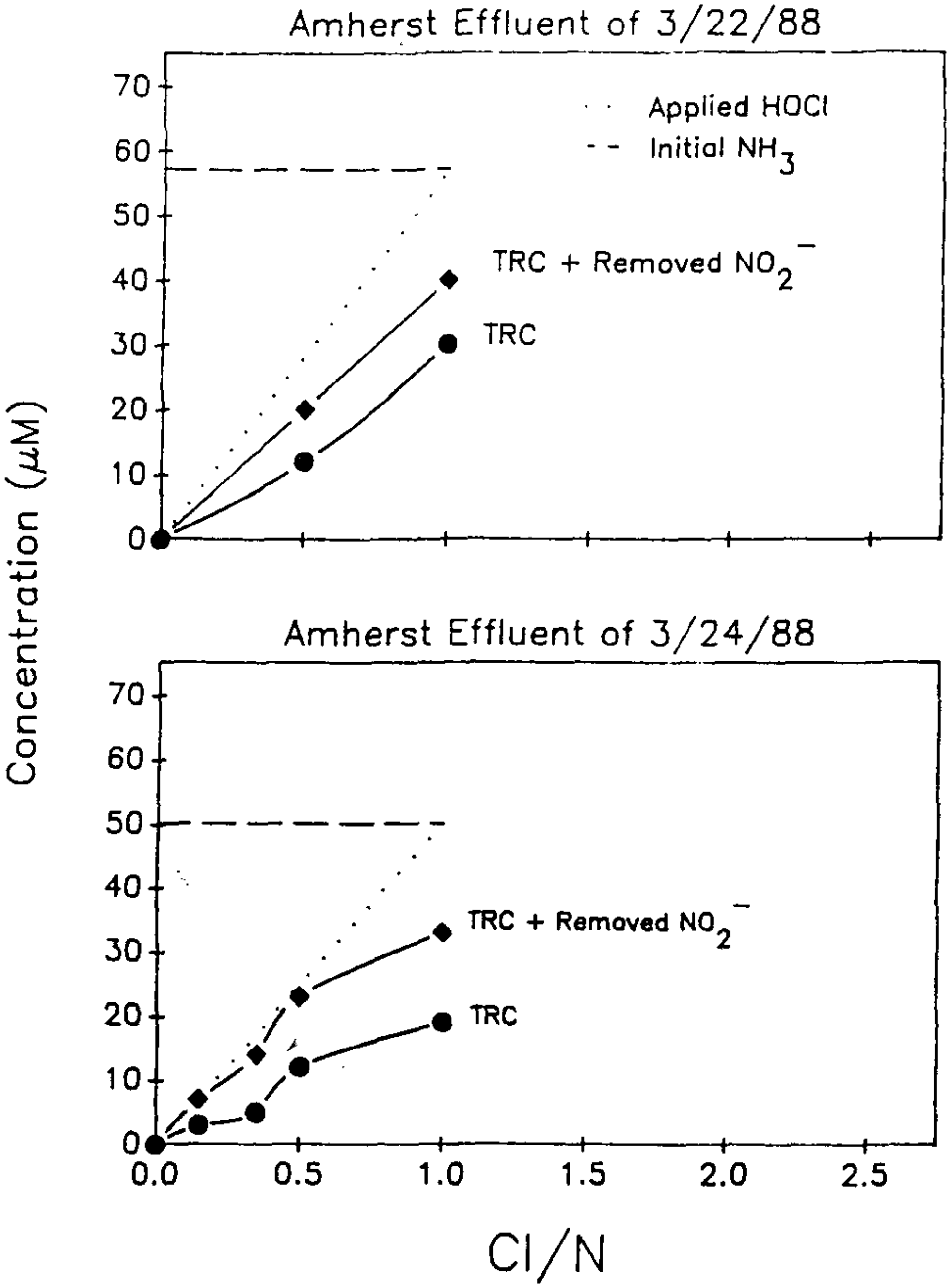


FIGURE 20

CHLORINE DEMAND BY $NO_2^-$ IN WASTEWATER



$$- d[NH_3]/dt = k_1[NH_3]\ [HOCl] \qquad (17)$$

$$- d[NO_2^-]/dt = k_2[NO_2^-]\ [HOCl] \qquad (18)$$

Dividing Equation 17 by Equation 18 causes the HOCl term to drop out:

$$\frac{d\ [NH_3]}{d\ [NO_2^-]} = \frac{k_1[NH_3]}{k_2\ [NO_2^-]} \qquad (19)$$

Integrating Equation 19, one gets a practical expression for the relative reaction rate, $k_1/k_2$.

$$\frac{k_1}{k_2} = \frac{\ln\{\ [NH_3]_{final}/\ [NH_3]_{initial}\}}{\ln\{\ [NO_2^-]_{final}/\ [NO_2^-]_{initial}\}} \qquad (20)$$

Table 8 shows the results of applying Equation 20 to the data in Figure 19. Only data where measurable amounts of TRC and nitrite were present could be used in Equation 20 with any degree of accuracy. Because the chlorine doses occurred at low Cl/N values, the oxidation of ammonia nitrogen would be minor and the TRC would consist almost entirely of monochloramine thus justifying Equation 3 as the principal TRC-forming reaction. While ammonia was not measured directly after the 1-hour contact time with chlorine, it was assumed that the final concentration of ammonia was equal to the initial ammonia minus the TRC. The result of the relative rate calculation in Table 8 indicates that the overall rate of MCA formation was 0.15 times the rate of nitrite oxidation, or in other words, the rate of nitrite oxidation is ~ 7 times the rate of MCA formation. Based on a rate constant for monochloramine formation of $1.5 \times 10^{10}\ M^{-1}\ hr^{-1}$ derived by Morris and Isaac (1983), a rate of nitrite oxidation near $10 \times 10^{10}\ M^{-1}\ hr^{-1}$ could be proposed for these conditions (pH 6.1, 15°C). It is important to note, however, that an alternative interpretation exists. It is possible that monochloramine formed quantitatively prior to significant oxidation of nitrite. Then, the monochloramine slowly reacted with the nitrite directly, or through hydrolysis to FRC. Unfortunately, without further experimentation, the validity of this latter hypothesis cannot be assessed.

### A.3 Practical Significance

Discussion with the operators of the Amherst treatment plant revealed that difficulties in maintaining the minimum required chlorine residual of 0.5 mg/L are not uncommon particularly in the summer months. On occasion, the operators must add more than twice the amount of chlorine than would otherwise be required to maintain the minimum residual. Interestingly, the only sample of Amherst effluent which did not exhibit an unusually high chlorine demand was taken 15 days after the mechanical failure of one of three aeration units which reduced the average hydraulic retention time of aeration from 10 to 6.5 hours. The practical significance of this observation is that the problem of high

## TABLE 8: CALCULATION OF RELATIVE RATE OF REACTION

(a) Amherst Effluent of 3/24/88

Initial $NH_3$ = 0.05 mM     Initial $NO_2^-$ = 0.014 mM

| Cl/N | Applied HOCl (mM) | Final $NH_3$ (mM) | Final* $NO_2^-$ (mM) | $\ln \frac{[NH_3]_f}{[NH_3]_i}$ | $\ln \frac{[NO_2^-]_f}{[NO_2^-]_i}$ | $k_1/k_2$ |
|---|---|---|---|---|---|---|
| 0.14 | 0.007 | 0.047 | 0.010 | -0.06187 | -0.33647 | 0.184 |
| 0.34 | 0.017 | 0.045 | 0.005 | -0.10536 | -1.02961 | 0.102 |
| 0.50 | 0.025 | 0.038 | 0.003 | -0.27443 | -1.54044 | 0.178 |

(b) Amherst Effluent of 2/22/88

Initial $NH_3$ = 0.057 mM     Initial $NO_2^-$ = 0.010

| Cl/N | Applied HOCl (mM) | Final $NH_3$ (mM) | Final* $NO_2^-$ (mM) | $\ln \frac{[NH_3]_f}{[NH_3]_i}$ | $\ln \frac{[NO_2^-]_f}{[NO_2^-]_i}$ | $k_1/k_2$ |
|---|---|---|---|---|---|---|
| 0.5 | 0.028 | 0.045 | 0.002 | -0.23638 | -1.60943 | 0.147 |

Average Relative Rate = 0.15
Standard Deviation = 0.04

* Final $NH_3$ approximated as initial $[NH_3]$ - final [CRC]

chlorine demand was apparently eliminated by the reduction in retention time. A plant experiencing an unusually high chlorine demand due to nitrite may wish to consider reducing the retention time of aeration, thereby saving a portion of the cost of operating the aeration units and possibly saving the cost of the excess chlorine.

## B. DOX FORMATION IN WASTEWATER

### B.1 DOX and THM Formation vs Cl/N Ratio

The results of Experiment Type I showed the formation of DOX and THMs in HOCl- and MCA-dosed effluent. In Figure 21, the formation of DOX and THMs are plotted as a function of Cl/N for the HOCl-dosed samples. Two observations can be made;

(1) THMs are not formed significantly below a chlorine-ammonia ratio of 1.

(2) Bromine substituted THMs are formed which indicate the presence of bromide in the effluent.

The first observation above is consistent with observations of Brown (1985) and Fleischacker and Randtke (1983). Since one would expect that monochloramine is the principal chloramine species at chlorine-ammonia ratios less than one, the lack of THM formation is in agreement with observations that few THMs are formed as the result of reactions between monochloramine and organic matter (Stevens, et al., 1976; Fleischacker and Randtke, 1983). The second observation above is also not very surprising. Analysis for bromide at all three wastewater treatment plants in this study yielded bromide concentrations near 2 mg Br/L. The same effluent was dosed with monochloramine across a range of doses as will be discussed in the next section. No THMs were detected in the chloraminated samples.

In Experiment Type II, a greater number of chlorine doses (ten to twelve data points) across a range of Cl/N values between 0 and 2.8 allowed a closer inspection of the relation between DOX formation and the breakpoint curve. Figure 22 shows Type II experiments on a Belchertown effluent (sampled 12/22/87) with an initial ammonia concentration of 1.5 mg N/L and a Northampton effluent (sampled 5/24/88) with an initial ammonia concentration of 15 mg N/L. It was noted in Part A of this chapter that both these effluents exhibited ideal breakpoint characteristics. A comparison of the DOX formation curves in Figure 22 shows a remarkable similarity in shape, with a shallow slope of DOX formation at doses below the CRC maximum followed by a steep increase up to the breakpoint with another slight increase of DOX past the breakpoint. Given that DOX formation is greater as a result of free residual chlorine, the shape of the DOX curves are consistent with the predominant chlorine species present throughout the regions of the breakpoint curve.

FIGURE 21

DOX AND THM FORMATION AS A FUNCTION OF Cl/N
(2 hours contact at 20°C)

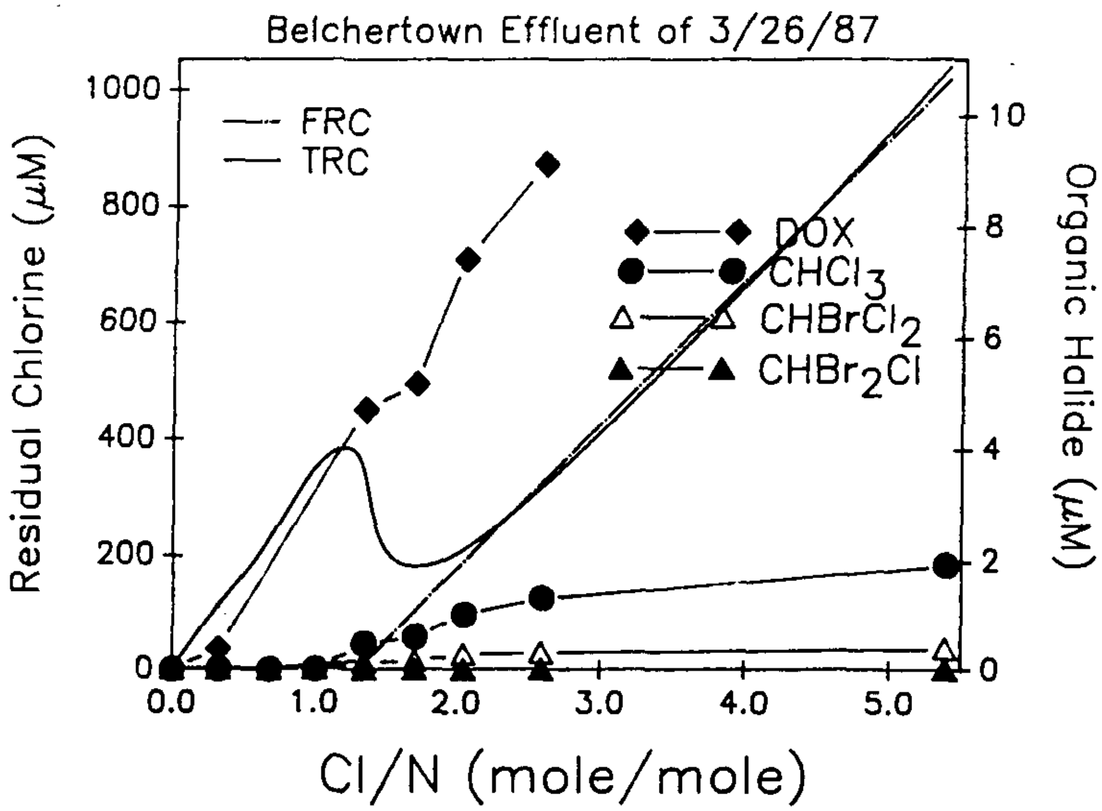
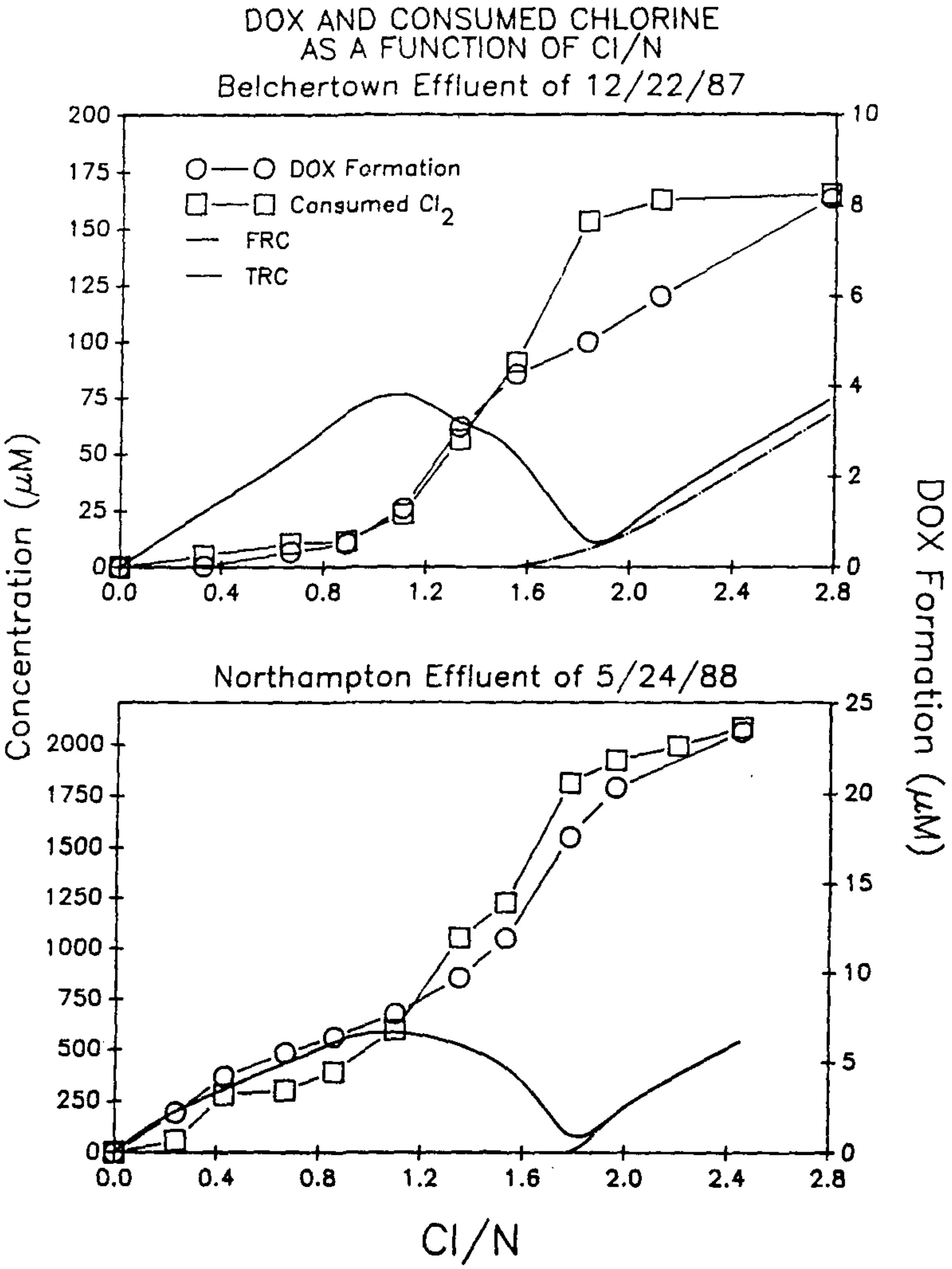


Figure 22

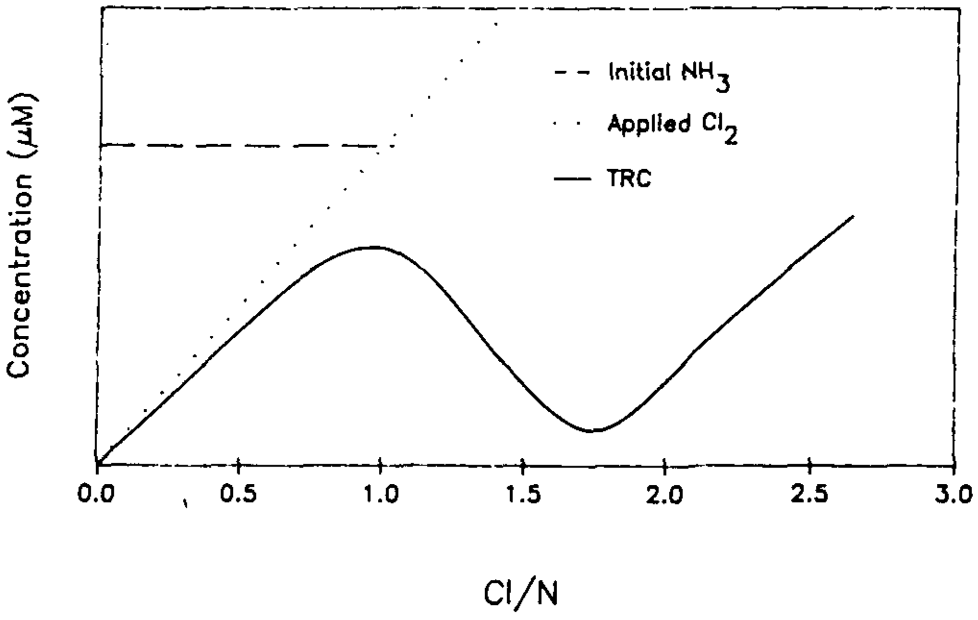

DOX AND CONSUMED CHLORINE
AS A FUNCTION OF Cl/N
Belchertown Effluent of 12/22/87
DOX Formation
Consumed $Cl_2$
FRC
TRC
200
175
150
125
100
75
50
25
0
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
10
8
6
4
2
0
Northampton Effluent of 5/24/88
2000
1750
1500
1250
1000
750
500
250
0
25
20
15
10
5
Concentration (μM)
DOX Formation (μM)
Cl/N

In Figure 22, it is notable that the shape of the DOX formation curves are similar to the curves for chlorine consumption. The similarity in shape of these curves may be due to the dominance of chlorine-ammonia chemistry in the wastewater system rather than any direct relationship between chlorine consumption and DOX formation. According to the scheme of principal reactants proposed in Figure 23, DOX formation increases greatly in the region between the CRC maximum and the breakpoint because of an increasing presence of transient FRC. On the other hand, chlorine consumption - defined as applied chlorine minus TRC - increases sharply in the same region because of the loss of TRC. The reasons for the sharper increases of DOX formation and chlorine consumption are different, yet both relate to the loss of ammonia.

As well as pointing out the similarities in the DOX formation curves of the Belchertown and Northampton effluents in Figure 22, it is important to note the differences. Because the ammonia concentrations were 1.5 and 15 mg N/L for the Belchertown and Northampton samples, respectively, the chlorine doses for the Northampton effluent were ten times those in the Belchertown effluent at the same values of Cl/N. The nature of the organic matter in the two effluents is certainly different. When the DOX formation and TRC are normalized to the applied chlorine as in Figure 24, the DOX yields as a percent of applied chlorine are seen to be very different for the two effluents. Since chlorine was applied in proportion to the ammonia, the yield of chlorine residual is similar. The differences in DOX yields in Figure 24 are attributable, in part, to the ratio of chlorine to organic

Figure 23

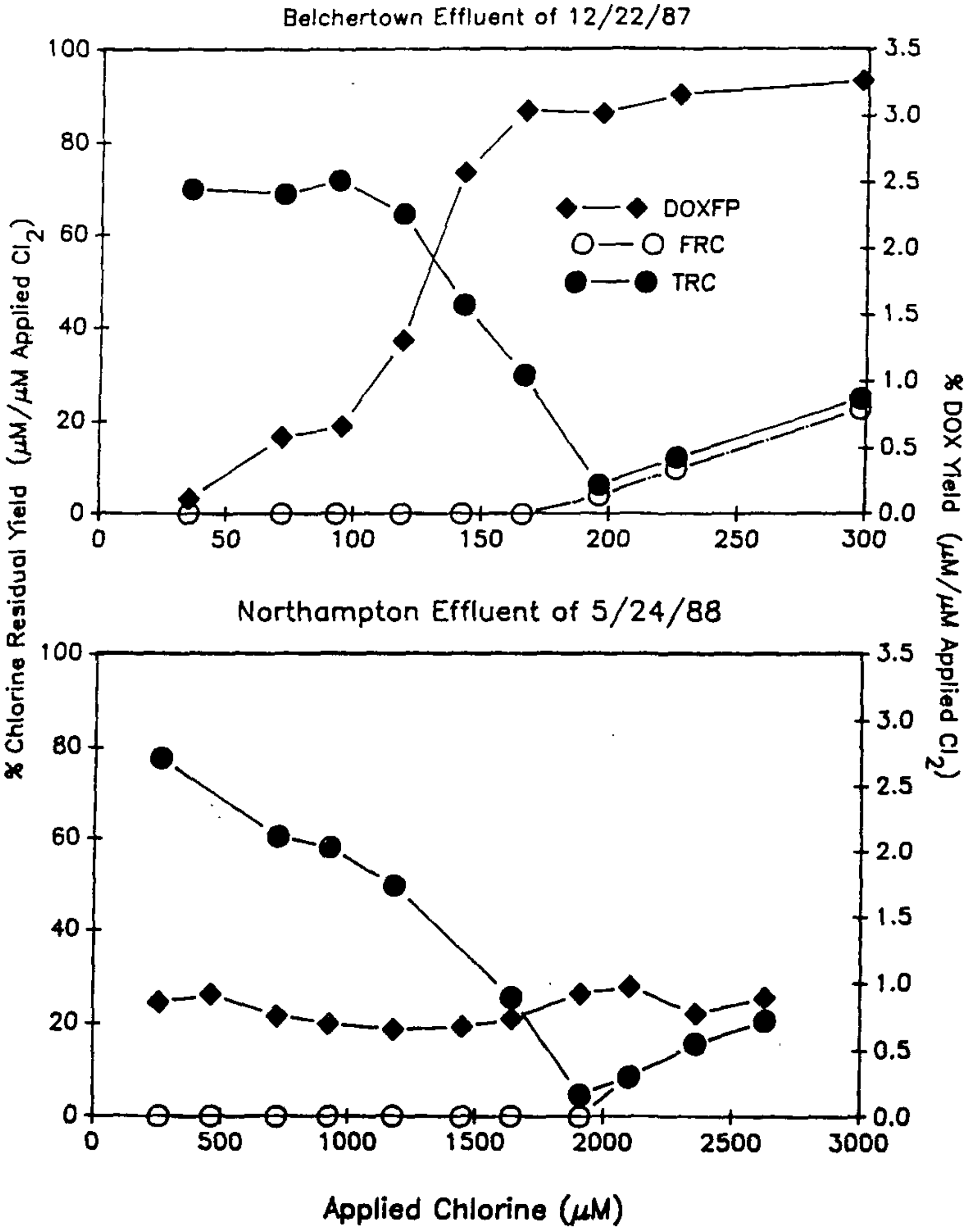
IDEALIZED BREAKPOINT CURVE AND PRINCIPAL REACTANTS



| | | | |
|---|---|---|---|
| Principal TRC Species | $NH_2Cl$ | $NHCl_2$<br>$NH_2Cl$ | $HOCl/OCl^-$ |
| CHLORINE CONSUMING SPECIES | Inorganic Reducing Agents<br>Oxidation of Organics | Inogranic Reducing Agents<br>Oxidation of Organics<br>Oxidation of $NH_3$ | Inorganic Reducing Agents<br>Oxidation of Organics<br>Oxidation of $NH_3$ |
| DOX-PRODUCING AGENT | $NH_2Cl$<br>(Transient FRC ?) | $NH_2Cl$<br>Transient FRC | FRC |

Figure 24

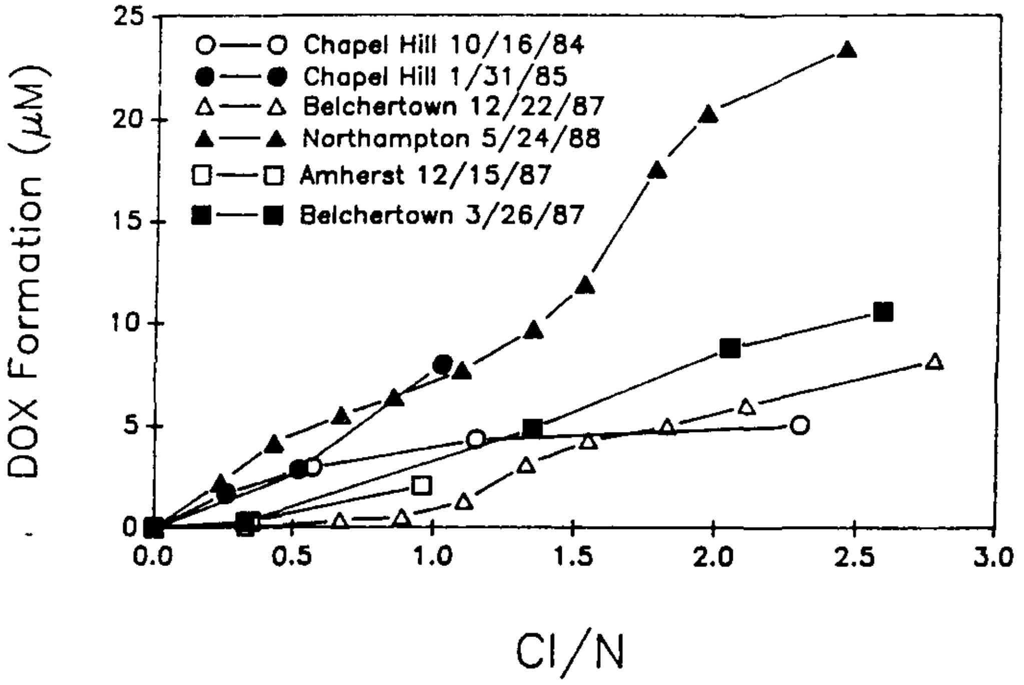
YIELD OF DOX AND TRC AS PERCENT OF APPLIED CHLORINE



matter. This ratio is small for the Belchertown effluent and large for the Northampton effluent. In reactions involving organic matter and chlorine it is possible that one or the other could limit the formation of DOX. Without speculating as to the nature of the organic matter in the two effluents, it may be inferred that low applied chlorine doses limited the DOX formation in the Belchertown effluent while the concentration of organic precursors limited DOX formation in the Northampton effluent.

In Figure 25, values for DOX formation are plotted against Cl/N for several effluent samples. The data from Brown (1985) was collected at the Chapel Hill wastewater treatment plant, a conventional activated sludge treatment system serving mixed domestic and industrial users. Note that the DOX formation obtained by Brown (1985) was from effluents with unknown breakpoint chlorination characteristics. In this case, it is uncertain whether the given Cl/N values actually attained the ammonia breakpoint. Though generally higher concentrations of DOX formed in the Northampton effluent and relatively low concentration of DOX formed in the Belchertown effluent, the DOX formation of the five effluent samples range within an order of magnitude for a given chlorine-ammonia ratio and generally increase with increasing Cl/N.

Figure 25



DOX vs Cl/N: Comparison with Literature Values

(Chapel Hill data from Brown, 1985; all other data from this study)

### B.2 DOX Formed by CRC vs Transient FRC

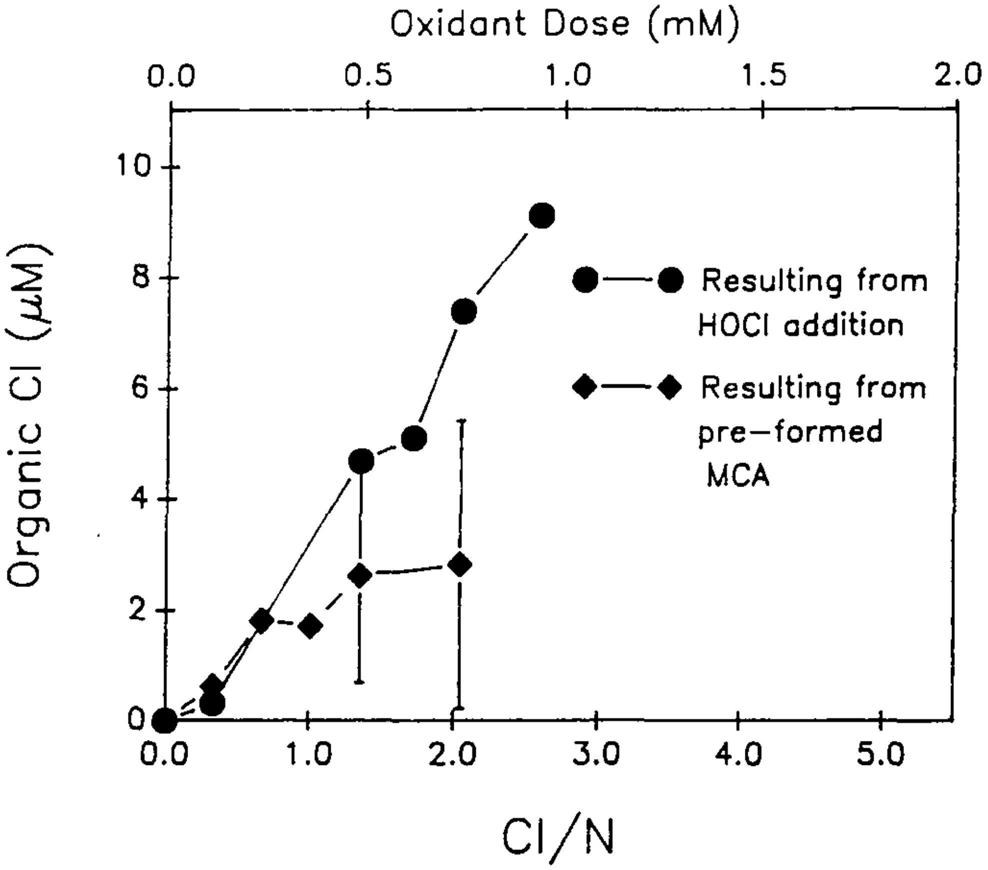
A comparison of the DOX formed by HOCl and MCA is presented in Figure 26. The data show higher DOX formation by chlorination, particularly above chlorine-ammonia ratios of 1.0. Interestingly, the quantity of DOX formed below oxidant-ammonia ratios of 1.0 appears to be similar. This would suggest that the formation of organohalides in this effluent, at least between Cl/N values of 0 and 0.5, is largely a result of reactions with MCA. It can also be noted from Figure 26 that a large degree of error in DOX measurement is associated with the two highest MCA doses. The measurement of DOX showed unusually poor precision in these samples which was attributed to poor adsorption characteristics during TOX analysis. Studies by Jensen et al. (1984) have shown that fulvic acid treated with MCA may be less amenable to adsorption by GAC than a fulvic acid treated with an equivalent dose of free chlorine. Jensen and co-workers attributed the poor adsorption characteristics to a larger molecular size and greater hydrophilicity associated with MCA treated fulvic acid. In any case, it is evident from Figure 26 that the quantity of DOX produced by HOCl and MCA begins to diverge near oxidant-ammonia ratios of 1.0.

Because MCA and FRC are the two principal forms of chlorine which exist in wastewater and both are capable of producing organohalides, it is logical that two principal pathways of DOX formation exist. A diagram of the MCA and FRC pathways for DOX formation is shown in Figure 27. At chlorine doses beyond the breakpoint, DOX formation by FRC would predominate. At chlorine doses less than the CRC maximum, in the range

Figure 26

COMPARISON OF DOX FORMATION RESULTING FROM CHLORINATION AND CHLORAMINATION

Belchertown Effluent of 3/26/87

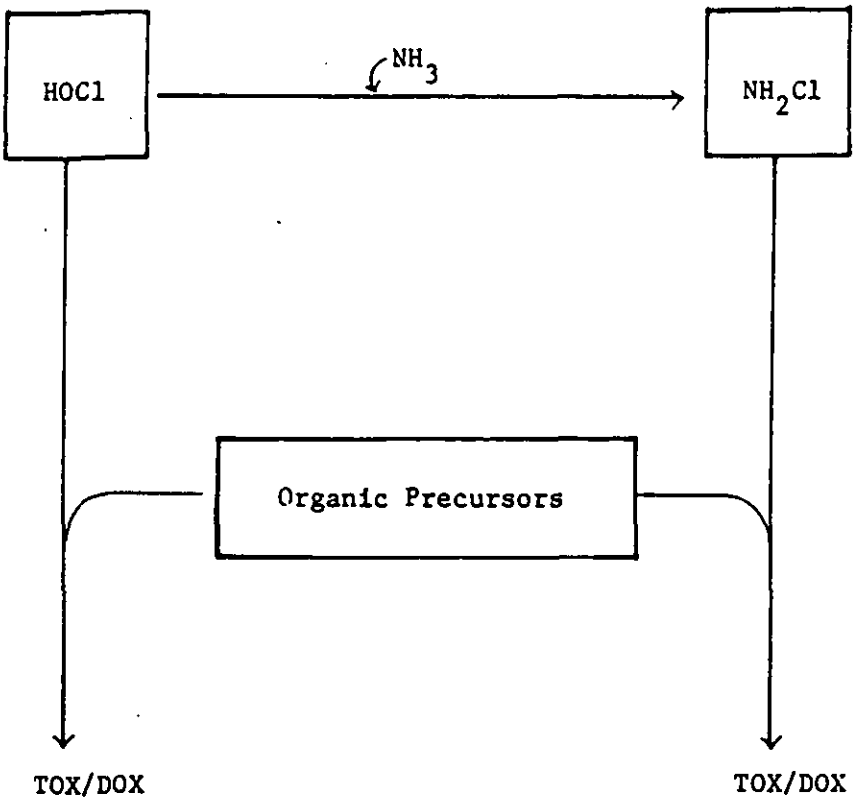


of chlorine doses most commonly applied in wastewater disinfection practice, DOX formation by MCA would likely be the predominant pathway. However, it is conceivable that a portion of the transient FRC could react with organic matter to form DOX before combining with ammonia. The effect of a transient free residual at low chlorine doses would likely depend on the reactivity of the organic matter to addition and substitution reactions with FRC. Since the qualities of organic matter can vary widely, the propensity of DOX formation to occur via a transient free residual at low chlorine doses may vary with different effluents. Also of interest is the DOX formation in the range of chlorine doses between the CRC maximum and the breakpoint. In this transition region, ammonia is increasingly oxidized by chlorine. One can propose that the organic precursors may better compete for free chlorine with the relatively slow reactions of di- and trichloramine formation (Equations 4 and 5).

### B.2 DOX Formation vs Chlorine Dose

In order to separate the effects of chlorine dose from the effects of chlorine-ammonia ratio, Experiment Type III was performed. Increasing chlorine doses were added to a series of duplicate effluent aliquots with ammonia added prior to chlorination so as to maintain a constant ratio. The results are shown in Figure 28. Although there is an unusual amount of scatter in the data, Figure 28 (upper graph) shows that the DOX formation increases with applied chlorine dose as one would expect. However, with respect to the amount of chlorine added, the increase in DOX is small. Between the lowest and highest chlorine

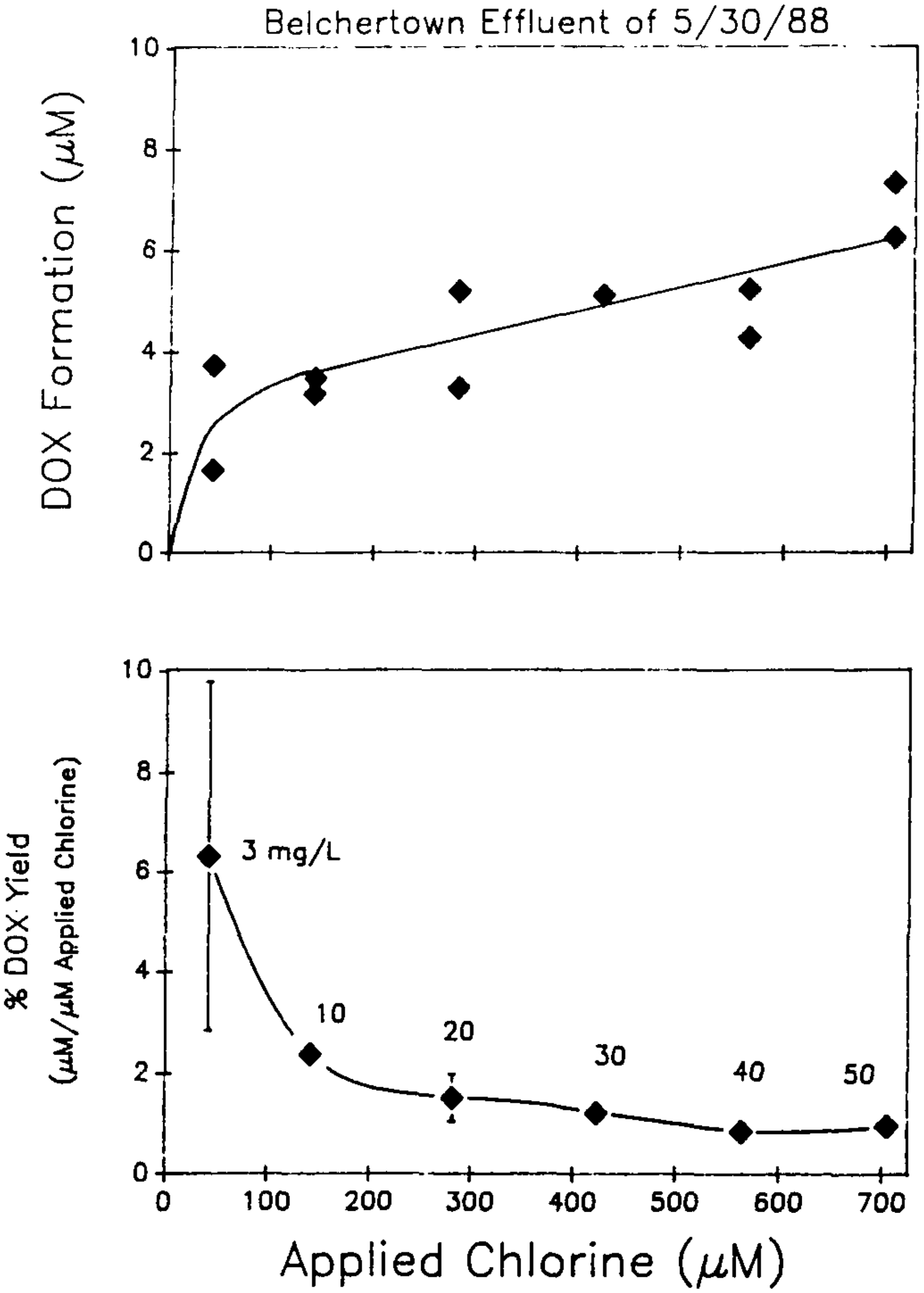
FIGURE 27: Pathways for DOX Formation in Wastewater



doses, the DOX increased by a factor of about 2 while the applied chlorine increased by a factor of nearly 17. Therefore, the sensitivity of DOX formation to chlorine dose is low as long as the ratio of chlorine to ammonia (Cl/N) is held constant. In Figure 28 (lower graph), it can be seen that the percent yield of DOX is greater at lower doses. This has also been observed in the free chlorination of raw drinking waters (Malley et al., 1986) and fulvic acid solutions (Fleischacker and Randtke, 1983).

The goal of Experiments I through IV was to better understand the conditions which effect DOX formation in wastewater. The most important reactions of the system are the chlorine-ammonia reactions as indicated in the ammonia breakpoint curve. With respect to DOX formation, the chlorine-ammonia ratio will determine the principal oxidant species (Figure 27). Since free chlorine is substantially more reactive than combined chlorine, the shift in chlorine residual from chloramines to free residual has a significant positive effect on DOX formation. When plotted with an ideal breakpoint curve, DOX increases with chlorine dose in a sigmoid or 'S' shaped curve having critical changes of slope near the CRC maximum and the breakpoint.

FIGURE 28
CHLORINATION OF BELCHERTOWN EFFLUENT
AT CONSTANT Cl/N (Cl/N = 0.2)
(24 Hours Contact @ 20°C)



## C. EFFECTS OF PREOZONATION

### C.1 Introduction

To determine the effects of preozonation on organohalide formation, three DOX formation potential (DOXFP) protocols were developed and applied to aliquots of effluent ozonated over a range of low ozone doses (0 - 2.7 mg absorbed $O_3$/L). The DOXFP protocols were discussed in Chapter III, and are presented here again for reference:

DOXFP Protocols

| Type | $NH_3$-N (mg/L) | Cl/N | Contact Time |
|---|---|---|---|
| DOXFP1 | 40 | 0.2 | 24 hrs. |
| DOXFP2 | Ambient | 0.2 | 1 hr. |
| DOXFP3 | Ambient | 1.4 | 1 hr. |

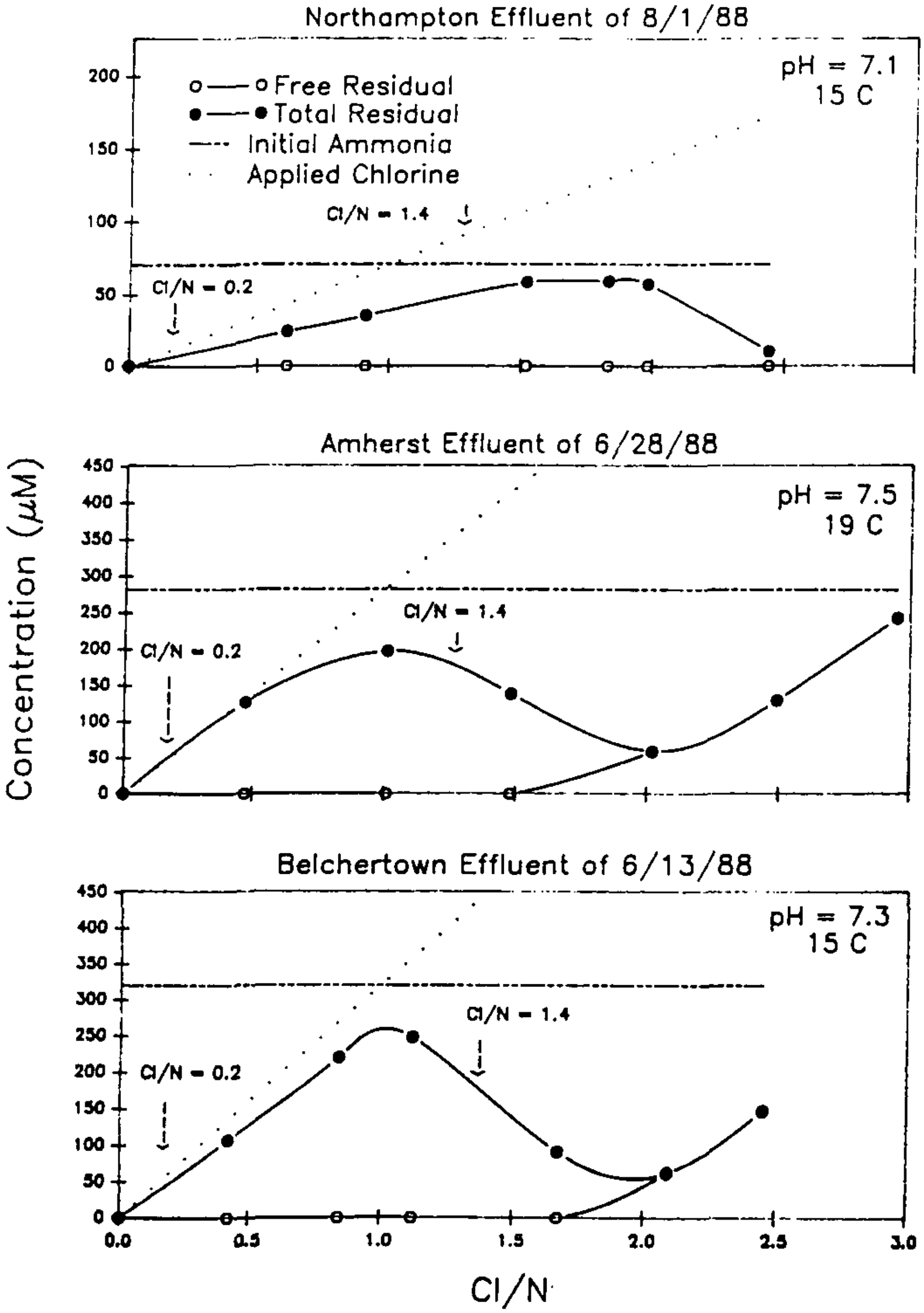
Three wastewater effluents were sampled and treated with a range of preozonation doses. DOX formation potentials were then measured for each of these ozonated wastewaters. A partial characterization of the three effluents used in preozonation experiments was presented in Table 7 along with the non-ozonated values of DOXFP1, DOXFP2, and DOXFP3. Though the three effluents have similar dissolved organic carbon (DOC) concentrations after filtration, the nature and reactivity of the organic matter is certainly different. Both the Amherst and Northampton plants use conventional activated sludge treatment, however, at the time of this sampling, the Northampton effluent was largely nitrified and the

Amherst effluent was not. The Belchertown plant is different from either of the other two plants because of the extremely long hydraulic retention time provided by three nutrient stabilizing ponds which act as a form of tertiary treatment. Thus, the three effluents have been influenced by different microbial ecosystems.

Breakpoint chlorination curves were run in order to establish the relationship between Cl/N ratios with respect to the breakpoint curve. These were first presented in Figures 14 through 17, and they are again presented here, in Figure 29, along with markers indicating the TRC at the Cl/N = 0.2 and Cl/N = 1.4 chlorine doses. Recall that these are the doses used for the DOXFP2 and DOXFP3 protocols. The Amherst and Belchertown effluents exhibited ideal breakpoint characteristics while the Northampton effluent on this date was nitrified, showing the presence of 0.32 mg/L $NO_2$-N and exhibiting significant rapid chlorine demand typical of nitrified effluent. The intent of DOXFP2 and DOXFP3 was to test for precursors both before and after the CRC maximum ("hump") of the breakpoint curve. DOXFP2 is conducted under conditions where MCA dominates, and DOXFP3 coresponds to DCA domination under ideal conditions. Note that this intent is not realized in the nitrified Northampton effluent because of the shift of the CRC maximum to the right. Instead, both the Cl/N = 0.2 and Cl/N = 1.4 doses fall before the CRC maximum in the Northampton effluent.

FIGURE 29

BREAKPOINT CHLORINATION OF THREE UN-OZONATED WASTEWATERS



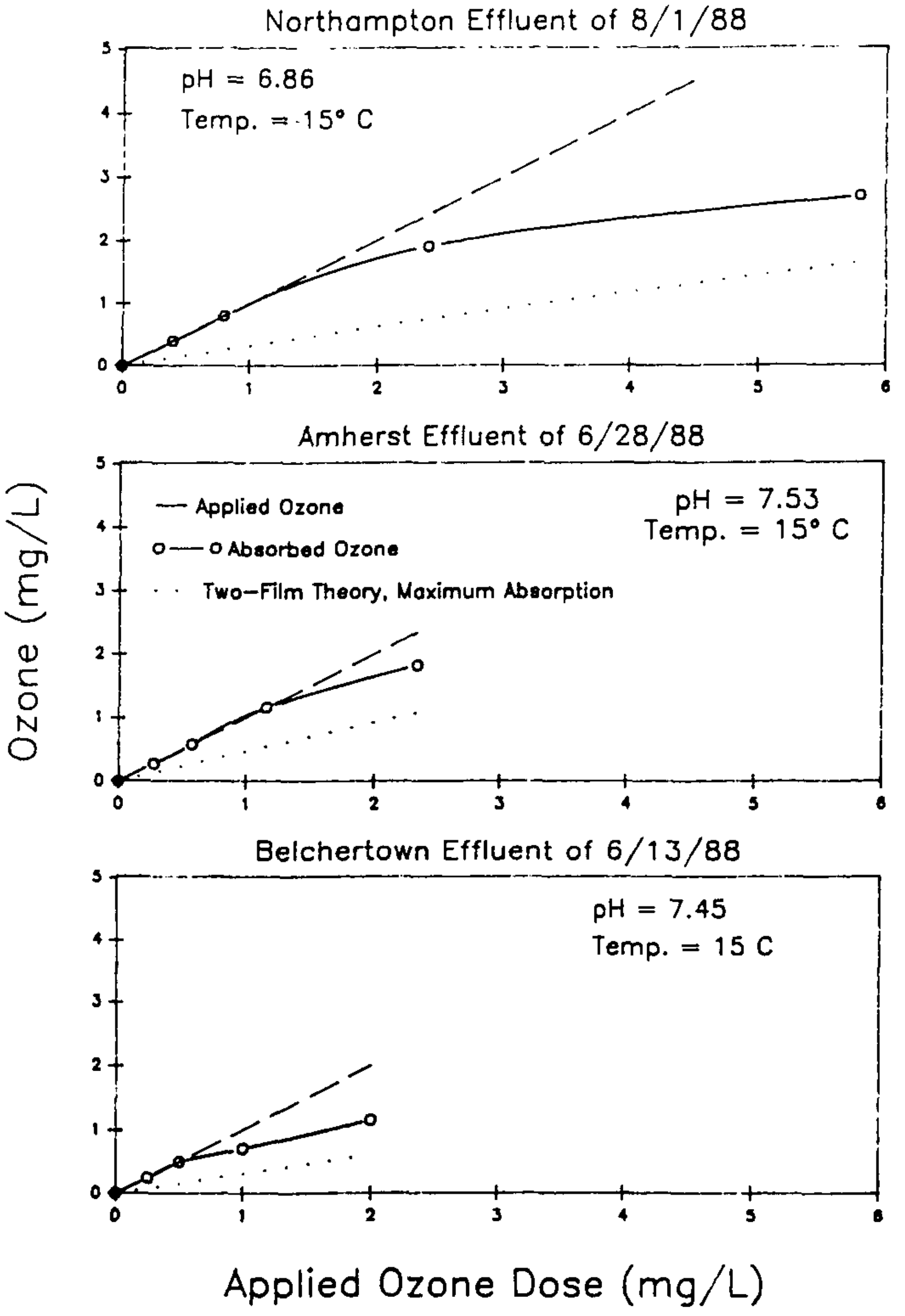
## C.2 Ozone Transfer

Figure 30 shows the results of the ozone mass balance observed during ozone contacting. The applied ozone dose is plotted against itself as a reference to the absorbed ozone and the maximum ozone absorption predicted by classical two-film theory. Under the two-film theory of gas transfer kinetics, the ozone is assumed to remain unreactive in the liquid film. Lehan (1989) describes how the overall gas transfer coefficient ($k_La$) was calculated for the type of ozone reaction vessel used in this study. The fact that the actual absorbed ozone falls above this line suggests that the early demand was extremely rapid. Such observations have been explained within the context of the two-film theory as being due to ozone consumption within the liquid film. In addition, residual ozone could not be detected after the end of the ozonation runs. Therefore, the consumption of ozone was quite rapid and limited by gas transfer rather than reaction kinetics.

Decolorization of the Belchertown effluent was apparent to the naked eye at the highest ozone dose though not at any lower doses. This is somewhat surprising because the highest absorbed ozone dose in this effluent was 1.2 mg/L which is lower than the maximum doses for the other two effluents. No other samples showed this degree of decolorization. This is another example of the wide differences in reactivity of the organic matter in the three effluents.

FIGURE 30

OZONE TRANSFER IN THREE MUNICIPAL WASTEWATERS

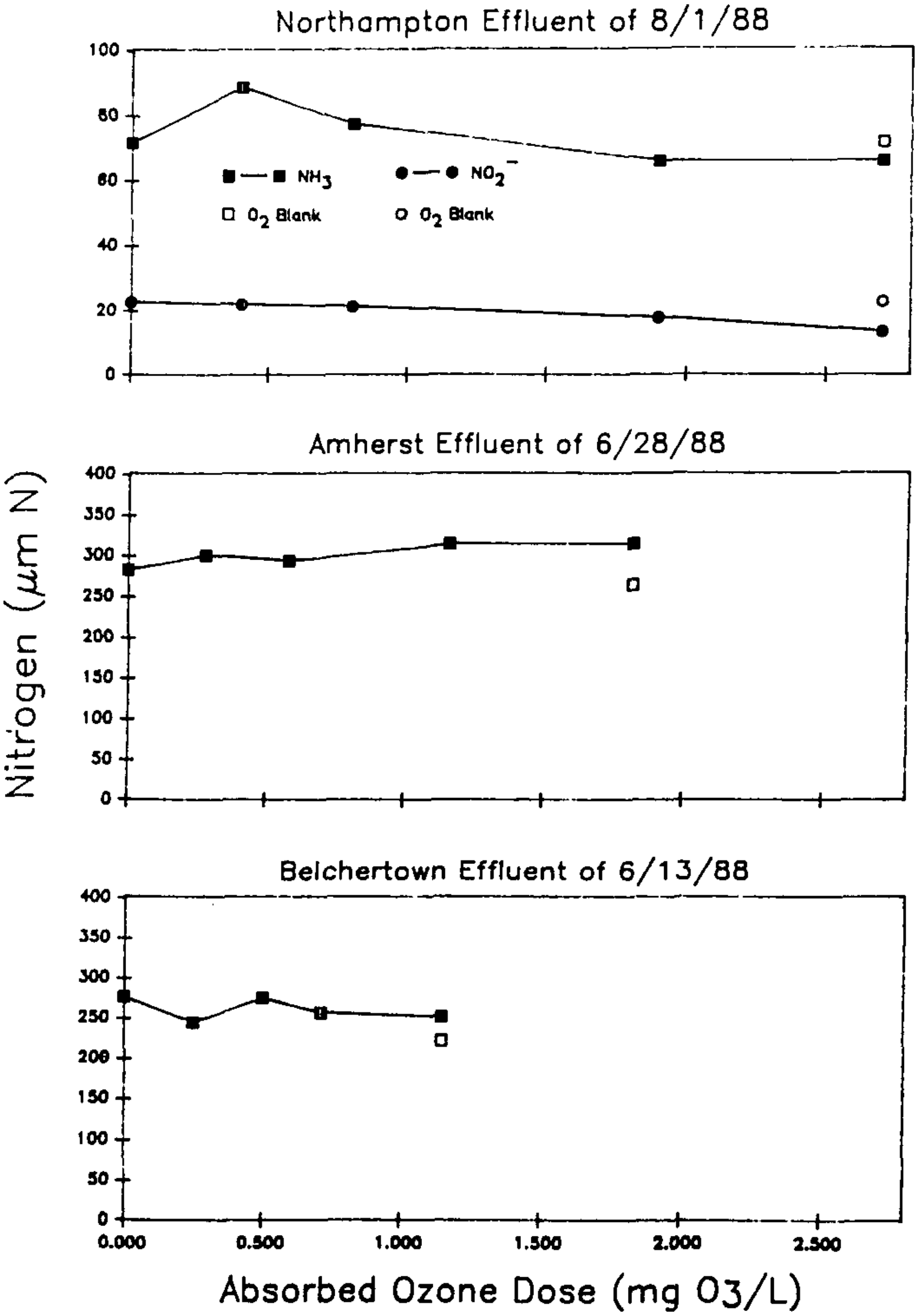


## C.3 Effect of Ozonation on Ammonia and Nitrite

The effect of ozonation on the ammonia concentration can be seen in Figure 31. The ammonia concentration is important for the DOXFP2 and DOXFP3 protocols used in this study which depend on chlorine doses applied at a consistent ratio to the ambient ammonia concentration. The ammonia concentrations in Figure 30 were measured 24 hours after ozonation with the ozonated samples held at 5°C until measurements could be made. It was also of concern to separate the chemical effects of ozone from the physical and chemical effects of the oxygen carrier gas. For this purpose, a single sample of effluent was run under the same conditions as the highest ozone dose (i.e., the longest contact period) except with the ozonator power off. While some ammonia was lost in the oxygen blanks, the concentration remained within 20 percent of the initial ammonia concentration. Based on the measured $K_La$ of the reactor, the longest time of ozonation, and the wastewater pH, less than 1 percent of the ammonia would be lost due to stripping without gas-phase resistance. The actual amount lost to stripping, considering gas phase resistance, should be less. After ozonation, some small increases in ammonia concentration were observed. This may be due to the decomposition of amino acids or other organically bound amino groups. Ammonia oxidation by molecular ozone is quite slow with a second order reaction rate near 20 $M^{-1}s^{-1}$(Hoigne & Bader, 1978). Ammonia oxidation by ozone has been shown to proceed more rapidly in the presence of bromide (Haag, et al., 1984). However, the quantity of ozone required to achieve this effect is far greater than the doses applied here.

## FIGURE 31

## EFFECT OF OZONATION ON INORGANIC NITROGEN



Northampton Effluent of 8/1/88

Amherst Effluent of 6/28/88

Belchertown Effluent of 6/13/88

The nitrite measured in the partially nitrified Northampton effluent was removed as a result of ozonation from an initial concentration of 0.32 mg N/L (22.9 μM) to a final concentration of 0.19 mg N/L (13.3 μM). Hoigne et al., (1985) derived a rate constant for the removal of nitrite by ozone which was nearly $3.7 \times 10^5$ $M^{-1}s^{-1}$. The equivalent steady state concentration of ozone required for the observed removal of nitrite is 0.13 ng/L $O_3$. The absorbed ozone dose of 2.7 mg/L in the semi-continuous ozone reaction vessel, over the 500 second ozonation time, is several orders of magnitude higher. Apparently, the ozone demand by other species in the wastewater was high enough to significantly suppress the pseudo steady-state aqueous ozone concentration.

## C.4 Effects of Ozonation on DOX Precursors

Since the chlorination conditions are the same for all effluent samples in the DOXFP1 protocol (i.e., 40 mg/L $Cl_2$, 40 mg/L $NH_3$-N), this is the most suitable of the DOXFP tests for the comparison of preozonation effects between different effluents. After each DOXFP test, the DOX analysis was run in duplicate. The uncertainty in measurement was taken to be the standard deviation of the two duplicate samples or 5 percent of the average DOX, whichever was greater. Where no error bars appear in Figures 32 through 36, the uncertainty of measurement was calculated to be smaller than the size of the data point symbol.

Figure 32 shows the effect of preozonation on DOXFP1 and chlorine consumption. The Northampton effluent shows similar trends in DOXFP1 and consumed chlorine with ozone dose where both tend to decrease slightly with increasing dose. Under this protocol the Northampton effluent showed a reduction of DOXFP by as much as 70 percent. Though the response of DOXFP1 versus ozone dose in the Belchertown effluent was somewhat erratic, all pre-ozonated samples showed lower DOXFP1 values than the un-ozonated sample. The maximum removal of DOXFP1 of near 35 percent was observed in both the lowest and highest doses in the Belchertown sample. The Amherst sample was unique in that DOXFP1 increased to nearly six times the un-ozonated value. The data are not artifactual as the oxygen blank and the non-ozonated samples gave nearly identical DOXFP1 values with good repeatability.

The effects of preozonation on DOXFP and chlorine demand under the DOXFP2 protocol can be seen in Figure 33. The term "chlorine demand" is appropriate for the DOXFP2 protocol since the chlorine doses (Cl/N = 0.2, 24 hrs contact) are well below those required to give a CRC maximum. This means that very little chlorine is consumed in the oxidation of ammonia nitrogen. The low chlorine doses produced less organohalides than either of the other two chlorination protocols. As a result, the changes in DOXFP2 brought about by preozonation were often insignificant when compared to the precision of the DOX measurements. This is true for both the Amherst and Belchertown effluents under the DOXFP2 protocol. The Northampton effluent yielded good replicate values in duplicate DOX measurements. For the Northampton effluent, DOXFP2 reductions of near 50 percent were observed at the highest ozone dose.

FIGURE 32

DOXFP1 and Chlorine Demand as a Function of Ozone Dose
(Chlorination Protocol: 40 mg $Cl_2$/40 mg $NH_3$–N)

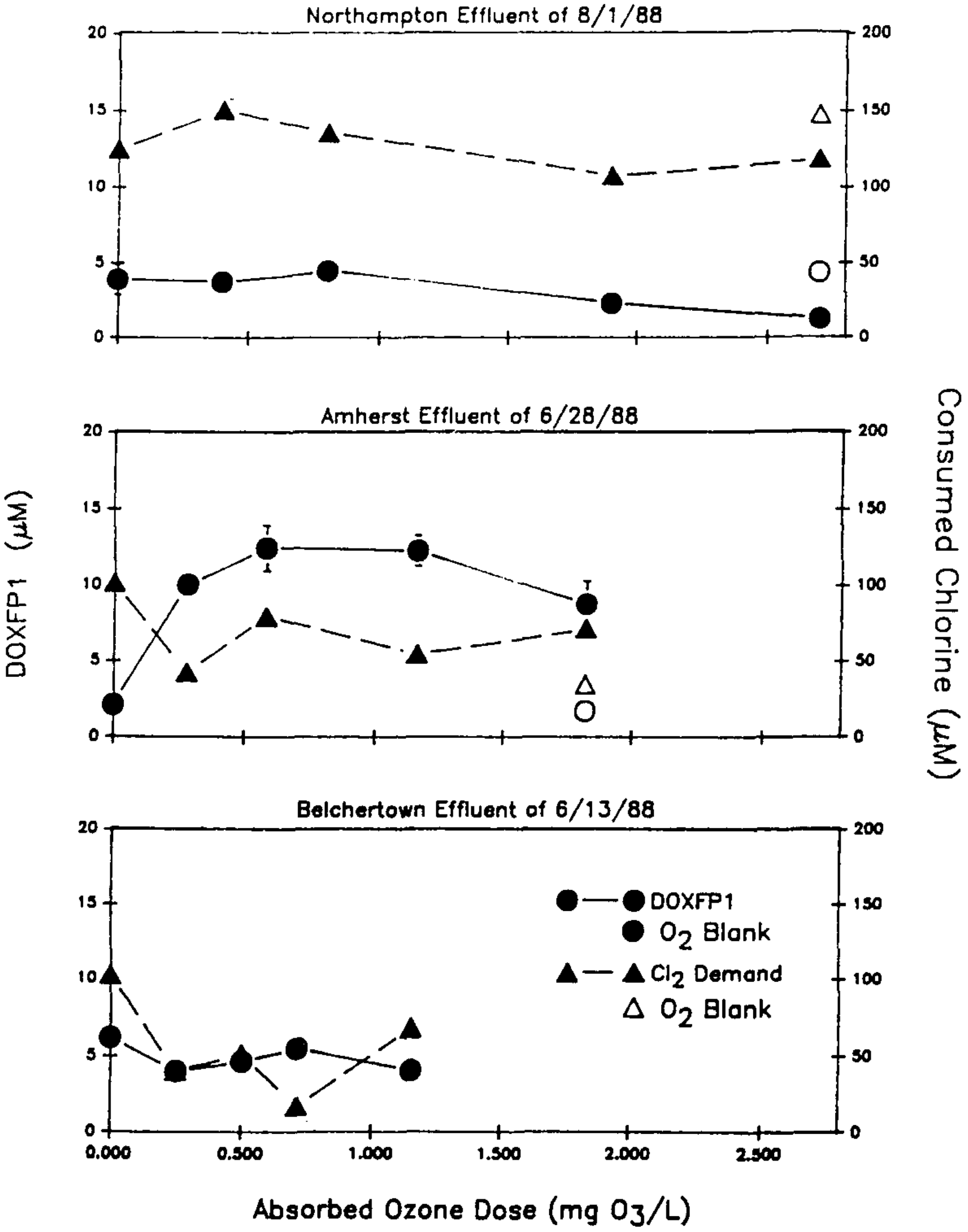


FIGURE 33

DOXFP2 and Chlorine Demand as a Function of Ozone Dose

(Chlorination Protocol: Cl/N = 0.2; 1 hr. Contact)

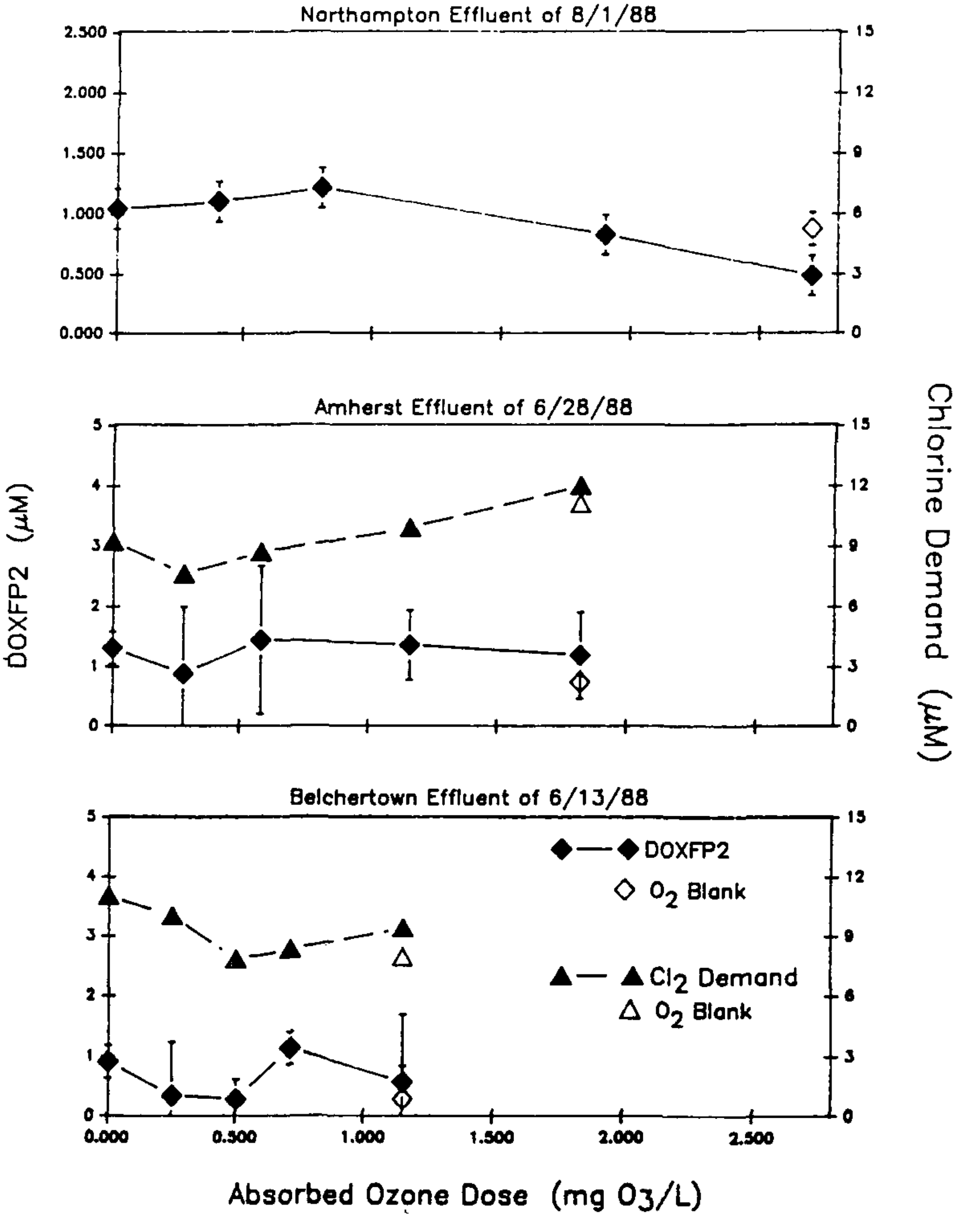


Figure 34 shows the effect of preozonation on effluents chlorinated under the DOXFP3 protocol. The error in measurement was smaller than in Figure 33 so that significant changes can be observed for all three wastewaters. The loss of chlorine consumption seemed to mirror the lossof DOXFP3 in the Northampton effluent. No such similarity was observed in the Amherst or Belchertown samples. Preozonation generally caused an increase in the DOXFP3 and chlorine consumption of the Amherst effluent. The maximum reductions in DOXFP3 for the Northampton and Belchertown effluents were near 35 and 15 percent, respectively.

Figures 35 and 36 show the relative change of DOXFP and consumed chlorine with preozonation dose. These figures allow more direct comparisons between the different DOXFP protocols in each effluent. Care should be taken in interpreting the DOXFP2 results because of the large relative errors in these data.

Studies of aquatic humic materials have shown that percent DOXFP removals by preozonation are similar to the accompanying removals of THM precursors (Reckhow and Singer, 1984). A comparison of the observations made in experiments with THMFP removal by prozonation would be appropriate here. The net formation of THM precursors has been observed when small doses of ozone are applied to model organic compounds (Dore et al., 1978; Yamada et al., 1986) and humic materials (Riley et al., 1978; Reckhow et al., 1986). The precursors referenced here are those that react with free chlorine to give THMs. These studies generally showed that the application of higher preozonation doses decreased the THMFP. Similarly, the Northampton effluent showed a slight increase or no net change in DOXFP precursors at low ozone doses which was followed

FIGURE 34

DOXFP3 and Consumed Chlorine as a Function of Ozone Dose

(Chlorination Protocol: Cl/N = 1.4; 1 hr. Contact)

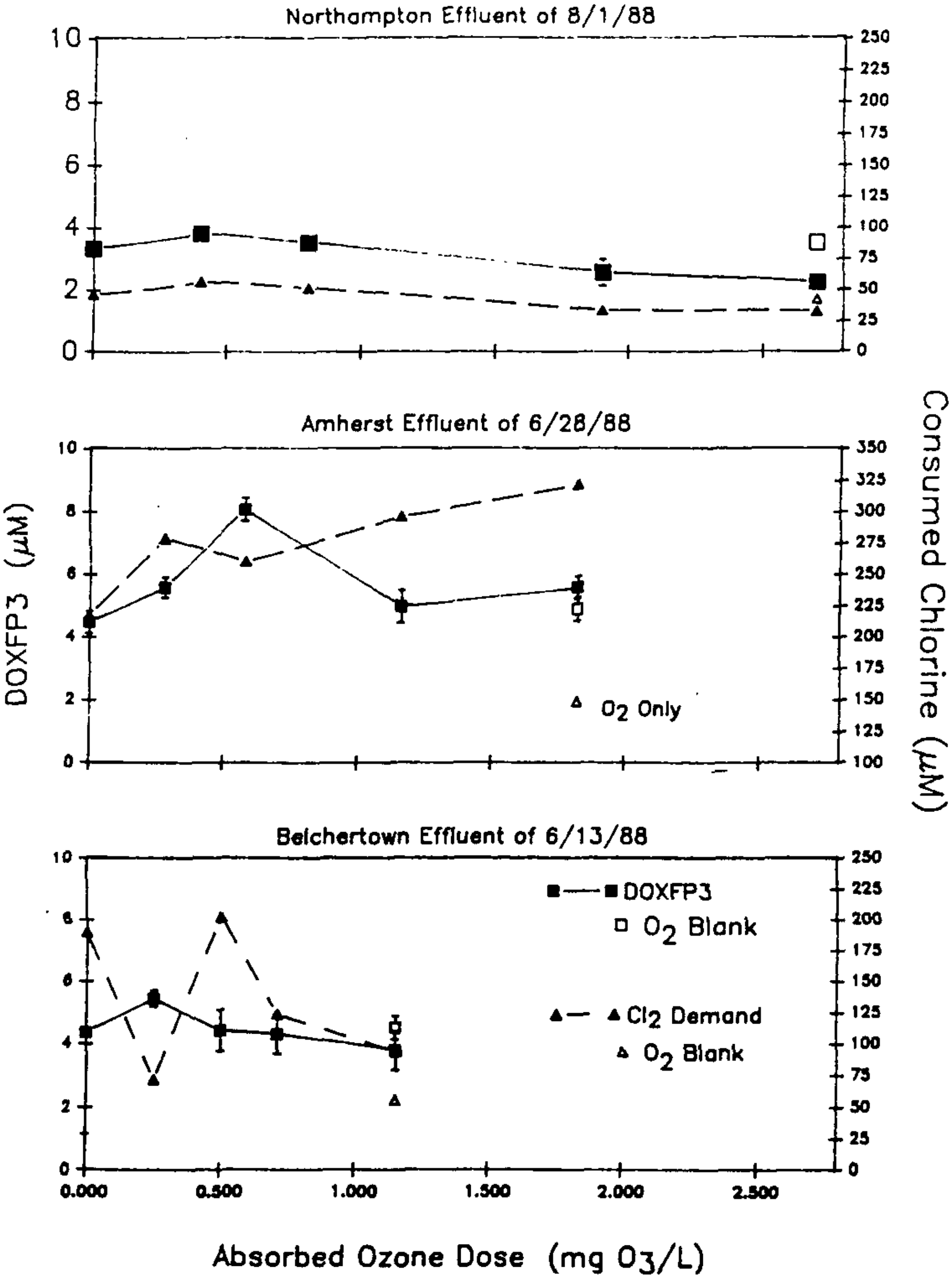


FIGURE 35

RELATIVE CHANGE IN DOXFP WITH OZONE DOSE

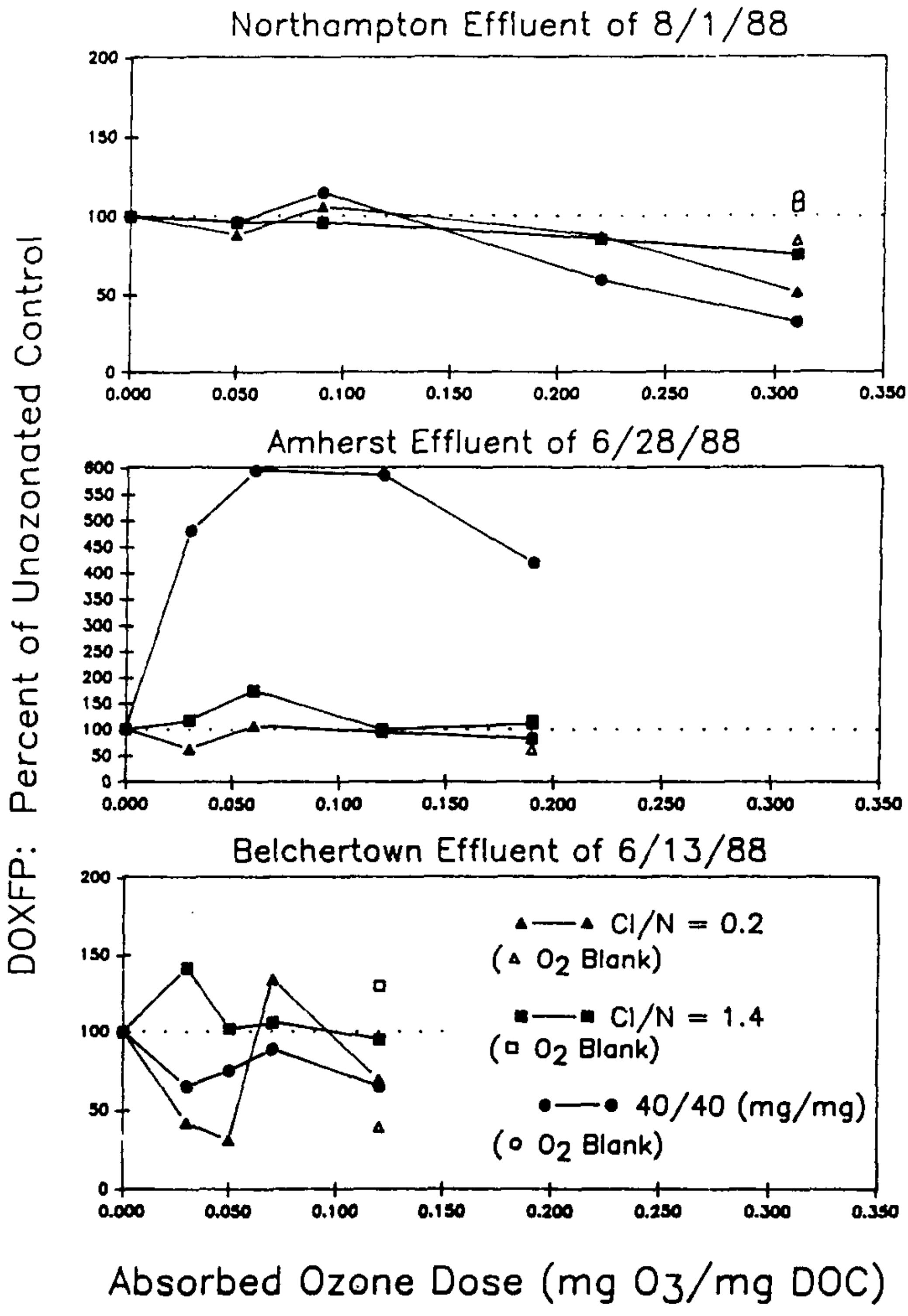
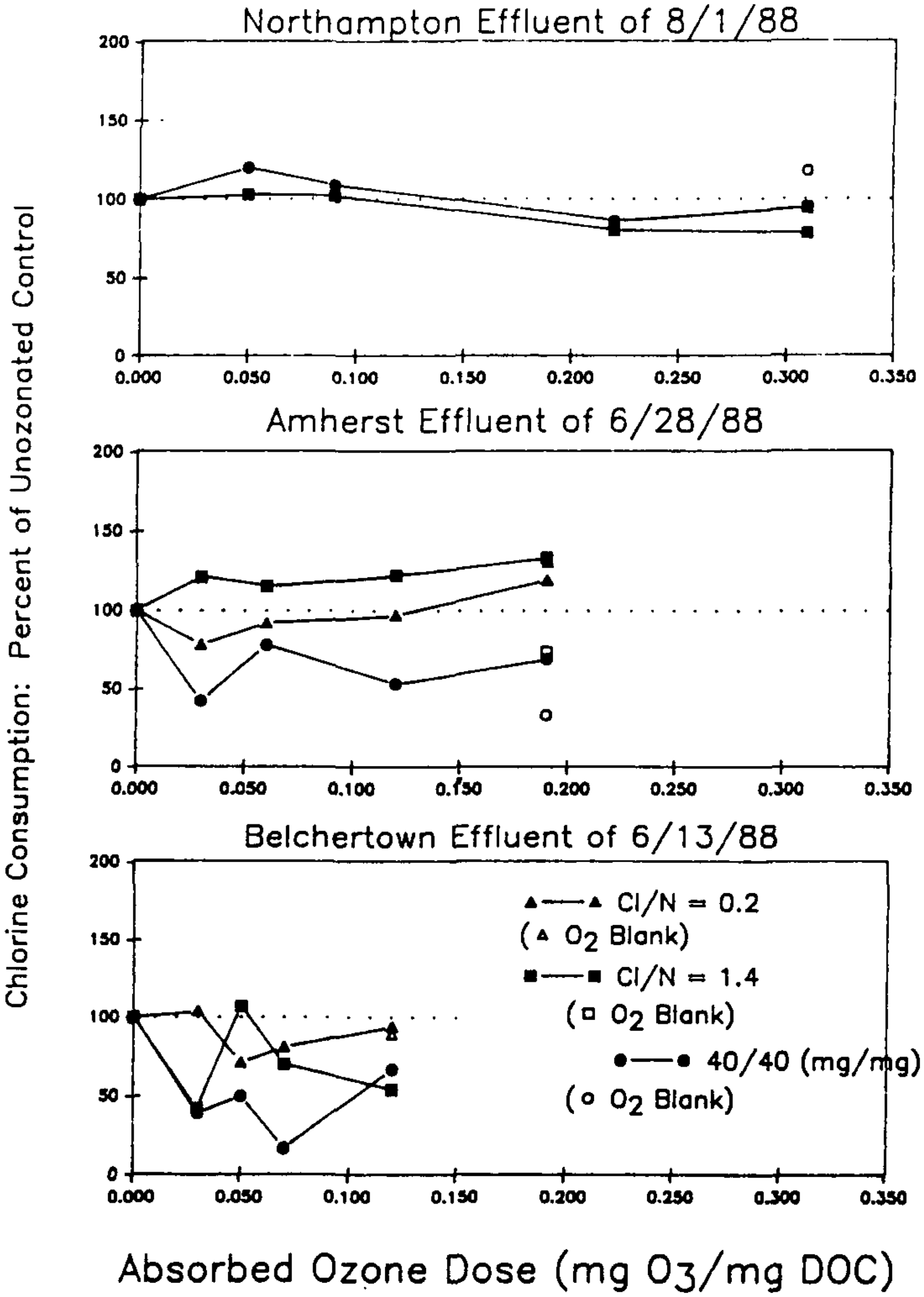


FIGURE 36
RELATIVE CHANGE IN CONSUMED CHLORINE
WITH OZONE DOSE



Northampton Effluent of 8/1/88

Amherst Effluent of 6/28/88

Belchertown Effluent of 6/13/88

by a decrease in DOXFP precursors at higher ozone doses for all three precursor tests. The loss of DOXFP in the Northampton effluent was on the order of 50 % for an absorbed ozone dose of about 3 mg/L (0.3 mg/mg-C). This represents a greater removal than is commonly seen in the ozone-induced loss of THMFP in drinking water and humic materials subject to free chlorination. On the average, a 0.3 mg/mg-C dose with these studies gives about 10 % THMFP reduction, whereas, doses up to 2 mg/mg-C would be required to obtain a 50 % reduction. Belchertown effluent showed a more modest reduction of DOXFP with removals near 35 and 10 % for DOXFP1 and DOXFP3 at the highest absorbed dose of 1.2 mg/L. The Amherst effluent, on the other hand, showed an increase in DOXFP over the entire range of preozonation doses.

Alkalinity is one water quality variable which may effect the ability of preozonation to destroy organohalide precursors. In a study by Reckhow et al. (1986), it was shown that increasing bicarbonate concentrations in the range 0.1 to 10 mM improved the ability of preozonation to remove organohalide precursors. Because many natural waters, including wastewaters, have alkalinities in the lower end of this range, it would be expected that alkalinity is a factor. For example, Amherst plant data for June 1988 shows an average alkalinity value of 0.4 mM (data is not available for the other plants). The mechanism by which bicarbonate operates to improve precursor removal is described generally in Figure 4 where the decomposition of ozone by the radical chain pathway can be slowed by the presence of a radical scavenger such as bicarbonate. The improved stability of molecular ozone can result in a predominance of the direct reactions of ozone with organic matter which are more effective in the removal of precursors. Recent work by Legube et al (1989), has shown that fulvic acids extracted from raw water sources can act as both initiators and enhancers of ozone decay by the radical chain pathway. This suggests that organic matter as well as alkalinity may have a role in determining the reaction pathway of ozone.

Although the Northampton effluent did not have the lowest unozonated DOXFP1, which is the most comparitive test, the nitrified Northampton effluent sample exhibited a relatively steady decline in all three DOXFPs with preozonation dose. The greater removal of DOXFP in the Northampton effluent is possibly due to the higher degree of nitrification in this effluent as compared to the other two. In a study by Koczwara et al (1983), the distribution of radiolabeled $^{36}Cl$ was followed in laboratory activated sludge effluents subject to breakpoint chlorination. The study concluded that a high level of dissolved oxygen maintained in the reactor (near 7.0 mg/L Dissolved $O_2$) had a significant effect in reducing the incorporation of chlorine into organic matter. The study suggests that the nature of the organic matter is important in its reactivity with chlorine and that more oxidized matter, such as would be present in nitrified effluent, would have less reactivity with chlorine.

## C.5 Discussion of Process Application

The process of preozonation as conceived in this study can now be reviewed with respect to the data. First, one must consider whether the required preozonation dose for DOXFP removal in an effluent may alone achieve sufficient disinfection and render further disinfection by chlorination unnecessary. In this case, the process is simply one of ozone disinfection, of which much has been written (see for example, Robson and Rice, 1985; Stover et al., 1981). Disinfection efficiency is commonly measured in terms of removal of fecal coliform. The effects of preozonation on disinfection efficiency were not measured in this study. However, based on empirical values from pilot-scale studies, a rough approximation of the transferred (absorbed) ozone dose required for a given level of disinfection can be calculated:

$$\text{Log}\ (N/N_o) = n\ \text{Log}\ (T/q) \qquad (21)$$

Where: $N$ = final fecal coliform per 100 ml

$N_o$ = initial fecal coliform per 100 ml

$n = -4.7$ = slope [Log $(N/N_o)$ / mg $O_3$/L]

$q = 1.8$ = x-axis intercept (mg $O_3$/L)

$T$ = Transfered Ozone Dose (mg $O_3$/L)

(n and q are average values for 7 pilot plant studies, see Rakness, 1985)

From the above relationship and knowledge of the initial concentration of fecal coliform, the approximate absorbed ozone dose needed to obtain a desired effluent quality can be calculated. For example, based on data collected by Robson and Rice (1985), a target fecal coliform concentration of 200 per 100 mL and a range of typical initial concentrations from $10^3$ to $10^5$ per 100 ml would require an absorbed ozone dose of 2.5 to 7.0 mg/L

Secondly, the concentration of absorbed ozone required for significant DOXFP removal - approximately 0.3 mg $O_3$/TOC obtained from this study in filtered nitrified effluent - must be corrected for the additional demand of suspended solids present in the effluent. Preozonation, as conceived in this report, may be economical if the ozone dose required for DOXFP removal is substantially lower than the ozone dose required for disinfection. The limited data available through this study suggests that an absorbed ozone dose near 0.3 mg $O_3$/mg DOC is required for significant DOXFP removal. This amount may be above the concentration required for disinfection by ozone alone in some effluents.

# CHAPTER V: CONCLUSIONS

The data obtained from chlorination experiments on the effects of ammonia and chlorine dose on DOX formation show relatively clear trends. The effects of ozonation on the three filtered wastewater effluents are more difficult to interpret. While several consistent trends can be observed in the ozonation experiments, the lack of a consistent response to preozonation is equally as interesting. Several conclusions may be drawn from this study:

1. Oxidation of nitrite can account for 50 - 100 % of the chlorine demand observed in nitrified Amherst wastewater chlorinated at a molar ratio, Cl/N, less than 1. Thus, the high chlorine demands often reported by treatment plant operators in Western Massachusetts at certain times of the year may be attributable to nitrite.
2. If nitrite oxidation and monochloramine formation are assumed to compete for free chlorine, the oxidation of nitrite by chlorine in the Amherst wastewater appears to be 7 times as fast as the formation of monochloramine. Presuming second order kinetics and no unusual catalytic reactions, the rate constant of nitrite oxidation by chlorine at 15°C and pH 6.1 was estimated to be $1 \times 10^{11}\ M^{-1}hr^{-1}$.
3. DOX is readily formed when wastewaters are chlorinated. The amount of DOX formation increases with increasing Cl/N. This increase is

especially pronounced near a Cl/N ratio of 1.0 in wastewaters exhibiting idealized breakpoint chlorination characteristics.

4. At chlorine-ammonia mole ratios less than 1, the formation of DOX apparently resulted from reactions of organic precursors with monochloramine rather than with a transient free chlorine residual in one effluent tested.
5. The ratio of DOX to consumed chlorine remained roughly constant in wastewater effluents which where chlorinated over a range of Cl/N values from 0.2 to 1.6.
6. Low-level preozonation doses in the range 0 to 3 mg/L (0 to 0.3 mg absorbed $O_3$/mg DOC) caused changes in the DOXFP of the three filtered effluents studied. In one nitrified effluent, DOXFP was reduced by as much as 50% at ozone doses of 0.3 mg/mg DOC. However, the effect of preozonation may be unpredictable. A six-fold increase in DOXFP was observed in another effluent as the result of preozonation at a dose of 0.06 mg absorbed $O_3$/mg DOC.

# CHAPTER VI: RECOMMENDATIONS FOR FUTURE RESEARCH

Several recommendations for future research are listed below. These are based on the experience gained by the authors in this current research, along with their judgement on the types of investigations most likely to give useful results.

1. Evaluate the effect of preozonation on the toxicity of chlorinated municipal effluents. One of the impediments to properly assessing the benefits of preozonation is the lack of knowledge on the long-term impacts of municipal effluents. Data from both chemical studies and bioassays are needed to make an intelligent decision regarding innovative treatments such as ozonation.

2. Determine the effects of premixing chloramines on DOX formation. Data presented here suggests that pre-mixed chloramines may not give fewer byproducts than in-situ formed chloramines. This is a relatively simple and inexpensive alternative. Therefore, it should be carefully evaluated.

3. Better characterize the DOX formed from chlorination of wastewater. More must be learned regarding the nature of DOX in municipal effluents before its environmental impact can be intelligently addressed. It would be especially valuable if specific coumpounds could be identified.

# REFERENCES

APHA, AWWA, and WPCF, 1985. Standard Methods for the Examination of Water and Wastewater, 16th Ed., American Public Health Association, Washington.

Baily, P. S., "Organic Grouping Reactive Towards Ozone, Mechanisms in Aqueous Media," In Ozone in Water and Wastewater Treatment, F. L. Evans, III, ed., p. 25 - 29, Ann Arbor Science Publishers, Inc., Ann Arbor MI, 1972

Brown, R. A., "Formation of Halogenated Organics During Wastewater Chlorination" Masters Thesis, Department of Environmental Science and Engineering, University of North Carolina, Chapel Hill, 1985

Coler, R. A., 1988. personal communication

Cooper, W. J., J. T. Villate, E. M. Ott, R. A. Slifker, F. Z. Parsons, and G. A. Graves, "Formation of Organohalogen Compounds in Chlorinated Secondary Wastewater Effluent," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 1, p. 483, R. L. Jolley, et al., editors, Ann Arbor Science Publishers, Ann Arbor, MI 1983

Cooper, W. J., G. L. Amy, C. J. Moore, and R. G. Zika, "Bromoform Formation in Groundwater Containing Bromide and Humic Substances," Ozone: Science and Engineering, 8(1) 1986

Croue, J-P, and D. A. Reckhow. 1989. "Destruction of Chlorination Byproducts with Sulfite," Envrion. Sci. Technol., 23:11:1412-1419.

Cumming, R. B., N. E. Lee, L. R. Lewis, J. E. Thomson, and R. L. Jolley, "Relationship of Disinfection to Mutagenicity in Wastewater Effluents," In, Water Chlorination: Environmental Impacts and Health Effects, Vol. 3, p. 881, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor MI, 1980

Dhaliwal, B. S. and R. A. Baker, 1983. "Role of Ammonia-N in Secondary Effluent Chlorination," Journal WPCF 55:5:

Esvelt, L. A., W. J. Kaufman, and R. E. Selleck. 1973. "Toxicity Assessment of Treated Municipal Wastewaters," J. Wat. Poll. Contr. Fed. 45:7:1558.

Federal Register. 1979. National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water; Final Rule. 44(231):68624 (Nov. 29, 1979).

Fort, C. L., et al., 1983. "Evaluation of the Quality of Wastewater Treatment Effluent Following Chlorination or Ozonation," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 2, p. 1261, R. L. Jolley, et al., editors, Ann Arbor Science Publishers, Ann Arbor, MI.

Fleischacker, S. J. & S. J. Randtke, 1983, "Formation of Organic Chlorine in Public Water Supplies," Journal AWWA, 75:3.

Gasser, J. A., 1984. "Disinfection of Nitrified Effluents," Communication in Journal WPCF 56:4.

Glaze, W. H. & J. E. Henderson IV , "Formation of Organochlorine Compounds From the Chlorination of Municipal Secondary Effluent," Journal Water Pollution Control Federation, 47:10: 2511 (1973)

Grady, C. P. L., E. J. Kirsch, M. K. Koczwara, B. Trgovich, and R. D. Watt, 1984. "Molecular Weight Distributions in Activated Sludge Effluents," Water Res., 18:2:239-246.

Gordon, J. H., 1985. "The Effect of Ammonia in Effluent Chlorination," Communication in Journal WPCF 57:1.

Haag, W. R. & J. Hoigné, 1983. "Ozonation of Bromide Containing Waters: Kinetics of Formation of Hypobromous Acis and Bromate," Environ. Sci. Technol., 17:5.

Haag, W. R., J. Hoigné, and H. Bader, 1984. "Improved Ammonia Oxidation by Ozone In the Presence of Bromide Ion During Water Treatment," Water Res., 18:9.

Helz, G. R., D. A. Dotson, and A. C. Siglio, 1983. "Chlorine Demand: Studies Concerning its Chemical Basis," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 1, p. 181, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor, MI.

Hoigne, J., and H. Bader, 1978. "Ozone Initiated Oxidations of Solutes in Water: A reaction Kinetic Approach," Envir. Sci. Technol. 12:79.

Hoigne, J., and H. Bader, 1976. "The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions," Water Res., 10:377-386.

Hoigne, J., H. Bader, W.R. Haag, and J. Staehelin. 1985. "Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water-III. Inorganic Compounds and Radicals," Wat. Res., 19:8:993-1004.

Inman, G. W., and J. D. Johnson, 1979. "The Kinetics of Hypobromous Acid Formation in Chlorinated Sea Water," Div. Environ. Chem., Am. Chem. Soc. 19:2:68-71.

Isaac, R. A. and J. C. Morris, 1980. "Rates of Transfer of Active Chlorine Between Nitrogenous Substrates," In Water Chlorination: Environmental Impact and Health Effects, Vol. 3, p. 183, R. L. Jolley, W. A. Brungs, and R. B. Cumming, Eds. (Ann Arbor Science Publishers, Inc., Ann Arbor MI.

Isaac, R. A. and J. C. Morris, 1981. "Modeling of Reactions Between Aqueous Chlorine and Nirtogenous Compounds," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 1, p. 63, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor, MI.

Jafvert, C. T., 1985. "A Unified Chlorine-Ammonia Speciation and Fate Model," Ph.D. Dissertation, University of Iowa.

Jensen, J. N., et al., 1984. "Characterization of the Reactions Between Monochloramine and Isolated Aquatic Fulvic Acid," In Water Chlorination: Chemistry, Environmental Impacts, and Health Effects, Vol. 5, p. 939, R. L. Jolley, et al., ed., Lewis Publishers, Inc, Chelsea, MI.

Johnson, J.D. and R. Overby. 1969. "Stabilized Neutral Orthotolidine, SNORT, Colorimetric Method for Chlorine," Anal. Chem., 41:13:1744.

Jolley, R. L., et al., 1983. "Nonvolatile Organics in Disinfected Wastewater Effluents: Chemical Characterization," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 1, p. 499, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor, MI.

Jolley, R. L., and J. H. Carpenter, 1983. "A Review of the Chemistry and Environmental Fate of Reactive Oxidant Species in Chlorinated Water," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 1, p. 3, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor, MI.

Koczwara, M. K., E. J. Kirsch, and C. P. L. Grady, 1983. "Formation of Organic Chlorine in Activated Sludge Effluents," Water Res., 17:12:1863-1869.

Kool H. J., C. F. Van Kreijl, and H. Van Oers 1984. "Mutagenic Activity in Drinking Water in the Netherlands: A Survey and Correlation Study," Toxic. Envir. Chem. 7:111-129.

Legube, B., J-P Croue, and D. A. Reckhow, "Ozonation of Organic Precursors Effects of Bicarbonate and Bromide," The Role of Ozone In Water and Wastewater Treatment, R. Perry & A. E. McIntyre, ed., Selper Ltd, London

Legube, B., F. Xiong and M. Dore, 1989. "Enhancement of Radial Chain Reactions of Ozone in Water in the Presence of Aquatic Fulvic Acids," in Ozone In Water Treatment, Vol. 1, Proceedings, Ninth Ozone World Congress, New York, June 1989, L. Joseph Bollyky, Ed. p.15.

Lehan, E.R. 1989, M.S. Project, University of Massachusetts, Department of Civil Engineering, Environmental Engineering Program; Amherst, MA.

Malley, J. P., J. K. Edzwald and N. M. Ram, 1986, "Preoxidant Effects on Organohalide Formation and Granular Activated Carbon Adsorption of Organic Halide Precursors," Presented at the AWWA Annual Conference, Denver, CO, June 1986

Meier, J. R., and R. J. Bull, 1984. "Mutagenic Properties of Drinking Water Disinfectants and By-Products," In Water Chlorination: Environmental Impacts and Health Effects, Vol. 5, p. 207, R. L. Jolley, et al., editors, Lewis Publishers, Inc, Chelsea, MI.

Merkens, J. C., 1958. Water & Waste Treat. J. 7:150.

Metcalf & Eddy, Inc., 1979. Wastewater Engineering, McGraw-Hill Book Company, p.297.

Morris, J. C., 1975, Formation of Halogenated Organics by Chlorination of Water Supplies, US EPA 600 1-75-02, Washington, D.C.

Morris, J. C. and R. A. Isaac, 1983. "A Critical Review of Kinetic and Thermodynamic Constants for the Aqueous Chlorine-Ammonia System," In Water Chlorination: Environmental Impacts and Health Effects, Volume 4, Book 1, p. 49, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor, MI.

Palin, A. T., 1950. "A Study of the Chloro Derivatives of Ammonia and Related Compounds, with Special Reference to their Formation in the Chlorination of Natural and Polluted Waters," Water and Water Engineering, 54:151-159, 189-200, 248-256.

Reckhow, D. A., 1984. "Organic Halide Formation and the Use of Pre-Ozonation and Alum Coagulation to Control Organic Halide Precursors," Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC.

Reckhow, D.A. and P.C. Singer, 1985. "Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications with Respect to Pre-ozonation", in Water Chlorination: Environmental Impact and Health Effects Vol. 5, pp. 1229-1257, Lewis Publishers, Inc., Chelsea, MI.

Reckhow, D. A. and J. Sibony, 1986. "Several Approaches to Minimizing the Formation of THM's and Other Hazardous Chlorination Byproducts," Presented at the G.R.U.T.T.E.E. Seminar, Rennes, France.

Reckhow, D. A., B. Legube, P. C. Singer, 1986. "The Ozonation of Organohalide Precursors: Effect of Bicarbonate," Water Resources, 20: 8:987-998.

Rice, R. G., Evison, L. M., and Robson, C. M., 1981. "Ozone Disinfection of Municipal Wastewater -- Current State-of-the-Art," Ozone: Science and Engineering, 3.

Riley, T.L., K.H. Mancy, and E.A. Boettner, 1978. "The Effect of Preozonation on Chloroform Production in the Chlorine Disinfection Process," In *Water Chlorination: Environmental Impact and Health Effects*, Vol. 2, R.L. Jolley, H. Gorchev, and D.H. Hamilton, Eds, Ann Arbor Science Publishers, Inc., Ann Arbor MI., pp.593-603.

Robson, C.M. and R.G. Rice, 1985. "Wastewater Ozonation in the USA - History and Current Status," In *The Role of Ozone in Water and Wastewater Treatment*, R. Perry & A.E. McIntyre, Eds., Selper Ltd., London, pp.230-246.

Rook, J.J. 1980. "Possible Pathways for the Formation of Chlorinated Degradation Products During Chlorination of Humic Acids and Resorcinol," In *Water Chlorination: Environmental Impact and Health Effects*, Vol. 3, R. L. Jolley, W. A. Brungs, and R. B. Cumming, Eds., Ann Arbor Science Publishers, Inc., Ann Arbor MI. pp.85-98.

Sander, V.R., W. Kuhn, and H. Sontheimer, 1977. "Untersuchungen zur Umsetzung von Chlor mit Huminsubstanzen," *Z. f. Wasser-und Abwasser-Forschung*, 10:5:155-160.

Siuda, J. F., 1980. "Natural Production of Organohalogens," In *Water Chlorination: Environmental Impact and Health Effects*, Vol. 3, R. L. Jolley, W. A. Brungs, and R. B. Cumming, Eds., Ann Arbor Science Publishers, Inc., Ann Arbor MI.

Snoeyink, V.L. and D. Jenkins, 1980. *Water Chemistry*, John Wiley & Sons, Inc., New York.

Stevens, A. A., C. J. Slocum, D. R. Seeger, and G. G. Robeck. 1976. "Chlorination of Organics in Drinking Water," *J. AWWA* 68:11:615-620.

Stover, E. L., R. N. Jarnis, and J. P. Long, 1981. "Ozone for High Level Wastewater Disinfection," *Ozone: Sci. and Engineering*, 3:3-18.

Suzuki, N., and Nakanishi, J., 1987. "Total Organic Halogen (TOX) Formation Potentials In Activated Sludge Treatment and Small Rivers," *Journal WPCF*, 59:8.

Trgovich, B., E. J. Kirsch, and C. P. L. Grady, 1983. "Characteristics of Activated Sludge Effluents Before and After Breakpoint Chlorination," *J. Water Pollution Control Fed.*, 55:7:966-976.

Valentine, R. L. and R. E. Selleck, 1981. "Effect of Bromide and Nitrite on the Degradation of Monochloramine," In *Water Chlorination: Environmental Impacts and Health Effects*, Volume 4, Book 1, p. 125, R. L. Jolley, et al., ed., Ann Arbor Science Publishers, Ann Arbor, MI.

Valentine, R. L., 1984. "Disappearance of Monochloramine in the Presence of Nitrite," In *Water Chlorination: Environmental Impacts and Health Effects*, Vol. 5, p. 975, R. L. Jolley, et al., editors, Lewis Publishers, Inc, Chelsea, MI.

Yamada, H., I. Somiya, and F. Inanami, 1986. "The Effect of Preozonation on the Control of Trihalomethane Formation," Ozone: Sci. & Engineering, 8:129-150.

Zillich, J. A., 1972. "Toxicity of Combined Chlorine Residuals to Freshwater Fish," Journal Water Pollution Control Federation, 44:2:212.