

REMOVAL OF DOX AND DOX PRECURSORS  
IN MUNICIPAL WASTEWATER TREATMENT PLANTS

A Master's Project Presented

By

Christopher Simmons Hull

9/89 3

Submitted to the Department of Civil Engineering of  
the University of Massachusetts in partial fulfillment  
of the requirements for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

September 1989

Department of Civil Engineering

REMOVAL OF DOX AND DOX PRECURSORS  
IN MUNICIPAL WASTEWATER TREATMENT PLANTS

A Master's Project

By

Christopher Simmons Hull

Approved as to style and content by:

---

Dr. David A. Reckhow, Chairperson

---

Dr. James K. Edzwald, Member

---

Dr. John E. Tobiason, Member

---

Dr. William H. Hightler, Department Head



UNIVERSITY OF MASSACHUSETTS  
AT AMHERST

Department of Civil Engineering

Marston Hall  
Amherst, MA 01003  
(413) 545-2508

28 June 1989

John J. Jonasch  
R&D Program Manager  
Massachusetts Division of Water Pollution Control  
Technical Services Branch  
Westview Bldg., Lyman School  
Westborough, MA 01581

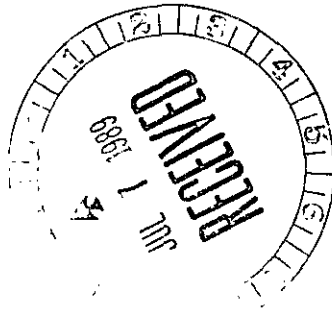
Dear John:

Enclosed is a copy of Chris Hull's MS Project, "Removal of DOX and DOX Precursors in Municipal Wastewater Treatment Plants." This work was supported partly under the "Halogens" project and partly under the "Ozone" project. We are considering the possibility of preparing a manuscript for publication in JWPCF based on this work. If we decide to do this, I will send you a draft copy for your comment.

Sincerely,

David A. Reckhow  
Assistant Professor

cc: A. Screpetis  
R. Isaac  
M. Switzenbaum



## ACKNOWLEDGEMENTS

Thanks must go to many people without whom this study would never have been possible. Special thanks go to my parents, for instilling the love for learning in me. I wish to thank Karina Santos for all the love and support.

Many people helped me in the lab, and thanks go to all of them. I wish to thank especially Jim Malley and Bob Hickey for always having had a moment to answer a question. A great deal of late night lab work was done with the aid of the music of Frank Zappa. I also appreciate my landlord Yves Lieou for providing an inexpensive pleasant place to live for three years.

Most of all I wish to thank my advisor David Reckhow whose insight, patience, and knowledge helped make this project succeed. This work was funded by a grant provided by the Massachusetts Division of Water Pollution Control.

This work is dedicated to the loving memory of Peter Stanley Hull.

## ABSTRACT

This study focused on the removal of chlorinated organic compounds and their precursors in municipal wastewater treatment processes. Concern has arisen over the potentially toxic nature of disinfection by-products in wastewater treatment plant effluents. While some of the toxicity may be due to the presence of residual chloramines, there are indications that chlorinated organic compounds may also be responsible. The objectives of this study were: (1) to evaluate dissolved organic halide (DOX) concentrations in raw and treated wastewaters, and (2) to determine the removals of DOX and precursor organics by wastewater treatment processes. As part of this study, seven municipal wastewater treatment plants were evaluated for the removal of chlorinated organic compounds and their precursors in primary and secondary treatment. A procedure to measure dissolved organic halide formation potential (DOXFP) using monochloramine as the oxidant was developed. DOX and DOXFP analyses were performed using a modified total organic halide (TOX) procedure.

Results showed removal of DOXFP generally paralleled decreases in DOC and COD. DOXFP decreased through each plant in almost all cases. DOX was observed to increase within some plants. This increase is presumed to be the result of large temporal variations in influent DOX concentration.

Removal of DOX and DOXFP was small within primary and secondary settling basins. Biological treatment removed the largest percentage of organic halides and precursors. Biological treatment proved more

effective at removing DOC than DOX or DOX precursors. The ratio DOXFP/DOC was observed to increase following biological treatment in all plants studied. A survey of 10 Massachusetts facilities was performed and effluent discharges of DOX were found to range from 56 to 1527  $\mu\text{g}$  Cl/L.

## TABLE OF CONTENTS

Acknowledgements .....	iii
Abstract.....	iv
List of Figures.....	viii
List of Tables.....	x

<u>Section</u>	<u>Title</u>	<u>Page</u>
I.	Introduction.....	1
II.	Background.....	3
III.	Materials and Methods.....	10
	A. Sample Collection and Preservation.....	11
	B. Filtration.....	12
	C. DOXFP Procedure .....	12
	D. Standard Analytical Procedures.....	15
	1. Residual Chlorine .....	15
	2. Chemical Oxygen Demand .....	15
	3. Ammonia Nitrogen .....	16
	4. Total Kjeldahl Nitrogen.....	16
	5. Dissolved Organic Carbon .....	16
	6. Dissolved Organic Halide .....	17
IV.	Experimental Results .....	19
	A. Removal of DOX, DOXFP Through Municipal Wastewater Treatment.....	19
	1. Amherst Wastewater Treatment Plant (January Sampling).....	19
	2. Amherst Wastewater Treatment Plant (June Sampling).....	22
	3. Belchertown Wastewater Treatment Plant.....	22
	4. Greenfield Wastewater Treatment Plant.....	25
	5. Hatfield Wastewater Treatment Plant .....	30
	6. Northampton Wastewater Treatment Plant .....	30
	7. Sunderland Wastewater Treatment Plant .....	35
	B. Discharge of DOX from Municipal Wastewater Plants.....	35
V.	Discussion of Results.....	39
	A. Raw Wastewater Quality and Plant Performance.....	39
	B. Removal of DOX and DOXFP.....	40

C.	Correlations Among Organic Parameters.....	43
D.	DOXFP/DOC Ratio.....	50
E.	DOX Loadings to Natural Waters.....	56
VI.	Conclusions.....	58
VIII.	Recommendations for Future Research.....	60
	References.....	61
	Appendix	
	Raw Data.....	68



LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1.	Analytical Protocol for Determination of DOXFP .....	14
2.	Amherst Wastewater Treatment Plant Schematic (January Sampling) .....	20
3.	Amherst WWTP (January) Organics Removal vs. Location .....	21
4.	Amherst WWTP (June) DOX, DOXFP Removal vs. Location .....	21
5.	Amherst Wastewater Treatment Plant Schematic (June Sampling) .....	23
6.	Amherst WWTP (June) Organics Removal vs. Location .....	24
7.	Amherst WWTP (June) DOX, DOXFP Removal vs. Location .....	24
8.	Belchertown Wastewater Treatment Plant Schematic .....	26
9.	Belchertown WWTP Organics Removal vs. Location .....	27
10.	Belchertown WWTP DOX, DOXFP Removal vs. Location .....	27
11.	Greenfield Wastewater Treatment Plant Schematic .....	28
12.	Greenfield WWTP Organics Removal vs. Location .....	29
13.	Greenfield WWTP DOX, DOXFP Removal vs. Location.....	29
14.	Hatfield Wastewater Treatment Plant Schematic .....	31
15.	Hatfield WWTP Organics Removal vs. Location .....	32
16.	Hatfield WWTP DOX, DOXFP Removal vs. Location .....	32
17.	Northampton Wastewater Treatment Plant Schematic .....	33
18.	Northampton WWTP Organics Removal vs. Location .....	34
19.	Northampton DOX, DOXFP Removal vs. Location .....	34
20.	Sunderland Wastewater Treatment Plant Schematic .....	36
21.	Sunderland WWTP Organics Removal vs. Location .....	37
22.	Sunderland WWTP DOX, DOXFP Removal vs. Location .....	37

23.	Correlation of DOX, DOC .....	45
24.	Correlation of COD, DOC .....	46
25.	Correlation of DOX, DOXFP .....	46
26.	Correlation of DOXFP, DOC .....	47
27.	Correlation of COD, DOX .....	47
28.	Correlation of Combined Cl <sub>2</sub> Demand, DOC .....	48
29.	Correlation of DOXFP, Combined Cl <sub>2</sub> Demand .....	48
30.	Correlation of Combined Cl <sub>2</sub> Demand, COD .....	49
31.	Correlation of COD, DOXFP .....	49
32.	Amherst WWTP (January) DOXFP/DOC vs. Location .....	52
33.	Amherst WWTP (June) DOXFP/DOC vs. Location .....	52
34.	Belchertown WWTP DOXFP/DOC vs. Location .....	53
35.	Greenfield WWTP DOXFP/DOC vs. Location .....	53
36.	Hatfield WWTP DOXFP/DOC vs. Location .....	54
37.	Northampton WWTP DOXFP/DOC vs. Location .....	54
38.	Sunderland WWTP DOXFP/DOC vs. Location .....	55

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1.	Amherst Wastewater Treatment Plant Data (January Sampling) .....	20
2.	Amherst Wastewater Treatment Plant Data (June Sampling) .....	23
3.	Belchertown Wastewater Treatment Plant Data .....	26
4.	Greenfield Wastewater Treatment Plant Data .....	28
5.	Hatfield Wastewater Treatment Plant Data .....	31
6.	Northampton Wastewater Treatment Plant Data .....	33
7.	Sunderland Wastewater Treatment Plant Data .....	36
8.	Effluent DOX Survey.....	38
9.	DOX, DOXFP: Plant Influent and Unchlorinated Effluent .....	39
10.	DOX, DOXFP Removal: Primary Settling .....	41
11.	DOX, DOXFP Removal: Secondary Settling .....	41
12.	DOX, DOXFP Removal: Biological Treatment.....	43
13.	Literature Values For Wastewater DOX.....	57

CHAPTER I  
INTRODUCTION

Wastewater disinfection is routinely practiced in the United States to reduce pathogen levels in municipal effluent (White, 1972). Reasons frequently cited for disinfection include: minimization of risks to downstream water users; reduction in pathogen loadings to downstream drinking water plants; and reduction of disruption to downstream aquatic life. The Clean Water Act of 1972 (PL92-500) established regulations limiting the discharge of fecal coliforms to receiving waters, with chlorination often serving as the most cost effective means of compliance. Recent concern regarding the toxicity of chlorinated effluents to aquatic life has led to a re-examination of the policy of wastewater disinfection. Although much of the concern has focused on inorganic chloramines, organic chlorine compounds formed during disinfection may also contribute significantly to toxicity. A recent study at the University of Massachusetts has suggested that long term toxicity to macroinvertebrates is associated with the dissolved organic halide (DOX) and not inorganic chloramine (Coler, 1988).

The objectives of this investigation were (1) to determine the removal of dissolved organic halide and organic precursors to dissolved organic halide through the various stages of municipal wastewater treatment; and (2) to assess the organohalide loading from municipal wastewater treatment plants to receiving waters in Massachusetts. Samples were collected and analyzed for DOX and dissolved organic halide formation potential (DOXFP) upstream and downstream of the primary

settling, biological treatment, and secondary settling processes in seven municipal wastewater treatment plants. The more conventional parameters of dissolved organic carbon (DOC) and soluble chemical oxygen demand (COD) were also measured for the purpose of comparison with DOX and DOXFP. In addition, ten treatment plants were surveyed to determine the DOX concentration and DOX loading in chlorinated municipal wastewater treatment plant effluents.

## CHAPTER II

### BACKGROUND

In the past fifteen years much research has been devoted to the examination of disinfection by-products in drinking water. Elevated levels of chlorinated compounds in drinking water were first reported in 1974 in New Orleans where there was an increased incidence of cancer in the population (Morris, 1975). Several studies have demonstrated significant mutagenicity associated with the non-volatile fraction of chlorination by-products (Cheh et al., 1980; Meier, Lingg, and Bull, 1983). As a result of this work and other related findings, strict regulations have been promulgated limiting levels of chlorination by-products in drinking water.

Wastewater disinfection is also routinely practiced in this country. Although disinfection by-products have not been regulated for wastewater, concern has grown over the potentially toxic nature of chlorinated effluents. Since the volatile by-products are believed to be minor and may ultimately discharge to the atmosphere, the few studies that have been conducted on wastewater chlorination by-products have focused on the non-volatile fraction. In contrast, toxic effects of chloramine residuals, their formation, and persistence have been studied extensively (e.g., Zillich, 1972; Paller et al., 1983).

Concentrations of specific chemical byproducts produced from the chlorination of wastewaters have been documented by several researchers. Jolley et al. (1975) reported concentrations of some of the compounds formed upon addition of 2.5 and 6.0 mg/L of chlorine. Glaze and

Henderson (1975) added chlorine doses of greater than 1000 mg/L chlorine and quantified the chlorinated compounds produced. A wide variety of chlorinated species were found at the microgram per liter level.

Chlorinated compounds present at a concentration ranging from 1 to 50  $\mu\text{g/L}$  included chlorinated alcohols, ketones, dichlorobenzenes, and other chlorinated aromatics. Chlorinated aromatics predominated in number, which is expected due to the generally greater rates of reaction of aromatic compounds with electrophiles such as hypochlorous acid. One compound found at substantially higher concentrations was 3-chloro-2-methyl but-1-ene, with a typical concentration of 285  $\mu\text{g/L}$ . These compounds would not necessarily be representative of those found in municipal treatment due to the large doses used.

More recently, Fam and Stenstrom (1987) chlorinated wastewater effluents and measured the chlorination products by GC/MS. The products were shown to be derived from lower molecular weight precursors, and approximately fifty compounds were tentatively identified. Compounds included chlorinated aliphatics, ketones, phenols, carboxylic acids, and many unidentified aromatics. The concentrations of these compounds ranged from less than 0.5  $\mu\text{g/L}$  to 30  $\mu\text{g/L}$ .

Not all halogenated compounds present in municipal wastewater effluents are produced as a result of chlorination. Non-biodegradable or slowly biodegradable halogenated compounds present in the raw wastewater may be only partially removed by treatment. Chlorinated organic compounds are presumed to be present in wastewater due to drinking water disposal, home disposal of chlorinated solvents, and industrial sources. Researchers have related the removal of specific

pollutants to the removal of more commonly measured parameters such as COD and TOC. Removal of compounds designated by the EPA as priority pollutants has been assessed in municipal treatment plants (Petrasek et al., 1983) with an average decrease of 97% reported for toxic compounds introduced into a pilot wastewater treatment plant. The overall reduction of COD and TOC was 89% and 90%, respectively, in the pilot treatment plant studies. A study of six wastewater treatment processes (Hannah et al., 1986) demonstrated that activated sludge caused the largest removal of both conventional and toxic priority pollutants. Volatile and semi-volatile compounds were analyzed, and volatiles were reduced an average of 84% during activated sludge treatment, with a concomitant 69% reduction of soluble COD. High rate trickling filter treatment reduced the volatiles by an average of 48%, and was accompanied by a 26% reduction in soluble COD. The average removal of semivolatile organics was 35% for the trickling filter and 85% for the activated sludge treatment.

The removal of chlorinated compounds in wastewater treatment processes appeared to be strongly correlated to volatility in the data of Hannah, et al. (1986). More volatile compounds averaged higher removals. No clear trend indicating higher removals for unchlorinated compounds was observed. In this study, the removal of the semivolatile organic compounds phenol, 2-4 dichlorophenol, and pentachlorophenol was assessed. Phenol was removed the least compared to the chlorinated derivatives in activated sludge and aerated lagoon systems. In contrast, trickling filters effected greater removal of the unchlorinated phenol. A similar evaluation of wastewater treatment



processes by Petrasek, et al. (1983) demonstrated that removal of chlorinated compounds in activated sludge systems often appeared to be less as compared to removal of unchlorinated compounds. In this study, a 95% decrease in phenol concentration was found compared to a 9 % decrease in pentachlorophenol concentration.

Removal of chlorinated organic compounds during the treatment of pulp mill wastewater has been studied more extensively. For this reason, it is useful to review these findings here. Leuenberger et al., (1985) demonstrated removals of 13% to 54% for chlorinated phenols in an activated sludge treatment plant treating pulp wastewater. Removal of chlorinated C<sub>1</sub> and C<sub>2</sub> hydrocarbons ranged from 17% for 1,1,1 trichloroethane to 93% for carbon tetrachloride. For this plant, the COD and DOC removal was approximately 50%. Data seem to indicate poorer removals, in general, for chlorinated compounds except for the highly volatile compounds lost during aeration. Halogenation has been implicated in resistance to biodegradation, especially in aerobic environments. (e.g., Pitter, 1976; Haller, 1978 Kobayashi and Rittman, 1982;).

Analysis of non-volatile chlorination by-products of drinking water by GC/MS has demonstrated that only approximately 50% to 60% of the organic-bound chlorine can be attributed to specific by-products (Miller and Uden, 1983). Efforts to identify specific by-products of chloramination have been even less successful (Jensen, 1983). For this reason, the total organic halide (TOX) parameter is useful as a means of estimating the sum of the organically bound chlorine.

One of the initial studies reporting organochlorine formation was

conducted by Bellar who detected significant increases in specific compounds following chlorination (Bellar et al., 1974). Following the development of the pyrolysis-microcoulometric method, the more general parameter of DOX was measured (Takahashi et al., 1980). A number of studies have documented increases in TOX following wastewater chlorination (McCahill, 1980; Chow and Roberts, 1981; Brown, 1985). These studies indicate that chlorination increases the TOX concentration from less than 100  $\mu\text{g/L}$  in the effluent prior to chlorination to 200 to 300  $\mu\text{g/L}$  following chlorination.

The influence of effluent ammonia concentrations on the formation of chlorinated organic compounds from wastewater chlorination is thought to be significant (Chow and Roberts, 1981). In the presence of ammonia, less TOX is produced due to the very rapid reaction of aqueous chlorine ( $\text{HOCl}$ ) with ammonia, producing chloramines. Chloramines are not as reactive as free chlorine, and thus do not produce as great a concentration of chlorinated by-products compared to free chlorine. The type of inorganic chloramine and the concentrations formed depend on the chlorine to ammonia ratio. This ratio is also important because it determines the lifetime of the transient free chlorine residual that exists during the course of monochloramine formation. The transient free residual may play an important role in DOX formation.

Some classes of chemical compounds present in wastewaters are more susceptible to chlorine attack than others. A secondary treatment plant effluent was analyzed (Manka et al., 1974) and was estimated to be comprised of 40% to 50% humic material, 1% to 2% tannins, 15% to 20% anionic detergents, 5% to 10% carbohydrates, 20% to 25% proteins, and

10% to 20% ether extractables (e.g., fatty acids, hydrocarbons, and aromatics). As proteins, carbohydrates, and fatty acids have been shown to be poor trihalomethane (THM) and TOX precursors (Morris, 1975), the humic material is thought to be the dominant precursor of chlorinated by-products.

Recently, Suzuki and Nakanishi (1987) measured DOXFP as a surrogate measurement of organic matter. The chlorine dose in their formation potential procedure was much larger than that required for breakpoint chlorination. Therefore these authors were measuring chlorination formation potentials rather than chloramination formation potentials. These researchers investigated the reduction of DOXFP in specific wastewater treatment processes. Their results showed a reduction of 1% and 6% for DOC and DOXFP, respectively, from influent values following primary treatment. Reductions of 79% and 80% for DOC and DOXFP, respectively, were observed following primary and activated sludge treatment consecutively.

Research conducted at Japanese wastewater treatment plants (Yamada and Somiya, 1984, 1985 a,b; Suzuki and Nakanishi, 1987) has shown a significant change in the ratio of DOXFP to DOC from influent to effluent. This ratio is a measure of the susceptibility of the organic matter to chlorine substitution/addition on a per carbon atom basis. Following activated sludge treatment, Suzuki and Nakanishi (1987) found that the DOXFP/DOC increased significantly for unfiltered samples. An increase, however, was not observed in the DOXFP/DOC ratio for the filtered samples. A contact oxidation biological filtration process was also evaluated (Yamada and Somiya, 1985 b) and was found not to increase

the DOXFP/DOC ratio.

A study of chlorine incorporation potential using radioactive NaOCl (Koczwar et al., 1983) was performed to assess effects of changes in the chemical nature of secondary effluent on the formation of organic chlorine compounds. Since many of the soluble organic compounds in treatment plant effluents are produced by microorganisms (Grady et al., 1972, Parkin and McCarty, 1981a,b), the metabolic and ecological state of the microorganisms may be important to the chlorine incorporation potential. Koczwar et al. (1983) chose to examine the effect of the operational variables of pH and dissolved oxygen (DO) to determine their effect on the chlorine incorporation potential (CIP) of the model treatment plant effluent. Dissolved oxygen was found to be the only variable causing a significant change in CIP, and reactors operating at high DO levels generally produced effluents less susceptible to attack by active chlorine (i.e., lower CIP).

## CHAPTER III

### MATERIALS AND METHODS

The objectives of this research were to measure levels of organic halides and their precursors in wastewater treatment plants, and to use this information to assess organohalide loadings to receiving waters in Massachusetts. This chapter presents the detailed experimental protocol used to measure various parameters in the wastewater treatment plants. Six municipal treatment plants were surveyed for the removal of dissolved organic halide and precursors to dissolved organic halide. The six plants chosen represent a cross section of the plants found in western Massachusetts. The biological treatment processes employed were activated sludge, rotating biological contactors, and trickling filters. The plants surveyed differed significantly in their flows and service communities. One plant was investigated twice to assess temporal changes in the results.

The plants were sampled for the various parameters immediately upstream and downstream of each of the major unit processes, thus determining the net change across the unit process. The plant grab samples were analyzed for chemical oxygen demand (COD) and dissolved organic carbon (DOC) as measures of the organic matter in the sample. The samples were also analyzed for total kjeldahl nitrogen and ammonia in order to define the chemical environment prior to chlorination. Dissolved organic halide and precursors (DOXFP) were measured upstream and downstream of the unit processes to evaluate the change in

concentration of these parameters in the treatment process employed. The DOXFP procedure was adopted specifically for this study. Monochloramine was chosen as the oxidant for the DOXFP procedure because most plants in Massachusetts are not practicing breakpoint chlorination.

A survey of Massachusetts municipal treatment plant effluents was performed to assess DOX concentrations in plant effluents. A total of ten plants were evaluated. For these measurements, effluent grab samples were quenched with sodium sulfite at the plant following plant chlorination and were analyzed for DOX. The ten plants represented a variety of communities in western Massachusetts ranging from small towns to small cities with a larger industrial base.

#### A. Sample Collection and Preservation

Samples were collected immediately upstream and downstream of primary sedimentation, secondary treatment, secondary sedimentation, and tertiary treatment at each of the wastewater treatment plants. Samples were always collected at highly turbulent locations, where adequate mixing was assured. Existing plant sample collection devices were used and were rinsed several times at the sample location with the wastewater at the site. Samples were stored headspace free in glass bottles and were immediately packed in ice. Chlorinated effluent samples for the plant effluent survey were immediately quenched with excess sodium sulfite and packed in ice. These samples were stored at 4°C in a refrigerator upon return to the laboratory.

## B. Filtration

Grab samples were filtered within eight hours of sample collection. They were first prefiltered through Whatman 934 AH glass fiber filters (Whatman International Ltd., Maidstone, England) that had been rinsed with at least 300 mL of deionized, reverse osmosis (Super Q System, Millipore Corp., Bedford, MA.) water (DIRO). The prefiltered samples were then immediately re-filtered through Whatman GF/F glass fiber filters (effective retention size = 0.7  $\mu\text{m}$ ) that had been pre-rinsed with at least 300 mL of DIRO water. The only exceptions to this procedure were the first four samples collected for the effluent DOX survey.

## C. DOXFP Procedure

The DOXFP procedure developed for this study utilized monochloramine as the oxidant. In order to obtain comparable results from one plant to another, each sample must be exposed to an identical oxidizing environment (i.e., same concentrations of active chlorine species for the same period of time). For this reason, a uniform chlorine dose and chlorine to ammonia nitrogen ratio were adopted for the DOXFP test. This required that the  $\text{NH}_3\text{-N}$  concentration be constant also. Due to the inability to remove ammonia selectively from the samples without altering other constituents, it was decided that the ammonia nitrogen concentration should be elevated in all samples to some high arbitrary level. For this test, a uniform concentration of 40.0

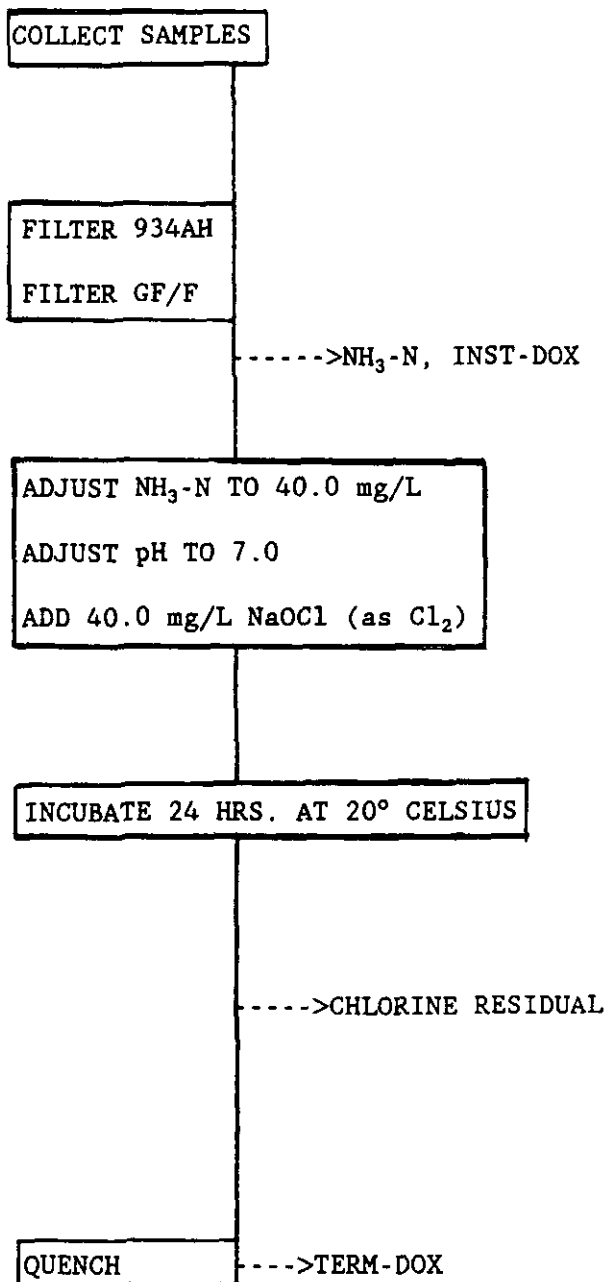
mg/L was chosen. Ammonia concentrations in the unaltered samples typically ranged from 3 to 20 mg NH<sub>3</sub>-N/L, with none exceeding 40 mg/L. A chlorine to ammonia mass ratio of 1 was chosen for this test because this mass ratio is typical of that used in practice with non-nitrified effluents. Accordingly, a chlorine dose of 40.0 mg/L was applied to each sample. This chlorine to ammonia ratio results in the rapid formation of monochloramine, with little di- and tri-chloramine, though some N-chloro-organics may result from the presence of organic amines (Morris, 1967). Massachusetts discharge permits stipulate that the maximum allowable total chlorine residual in treatment plant effluents is 1.5 mg/L as Cl<sub>2</sub> (WPCF, 1987), and this, in combination with the ammonia concentrations often seen in effluents, generally fixes monochloramine as the principal form of residual chlorine in non-nitrified plant effluents.

The specific procedures used for the DOXFP test are shown in Figure 1. Plant grab samples were analyzed for ammonia immediately after filtration. The ammonia concentration was then adjusted for each 500 mL filtered sample to 40 mg/L as N using aliquots of a 3500 mg N/L NH<sub>4</sub>Cl solution. The pH was adjusted to 7.0 using dilute NaOH or H<sub>2</sub>SO<sub>4</sub>, and 20 mg NaOCl (as Cl<sub>2</sub>) was added from an NaOCl stock solution (approximately 10,000 mg/L) with rapid mixing. The pH was readjusted to 7.0, and the chlorinated sample was poured into a BOD bottle, stoppered headspace free, and incubated at 20°C in the absence of light for 24 hours. At the end of the incubation period, aliquots of 10 mL to 50 mL were removed for the determination of combined residual chlorine. Samples were then quenched with excess sodium sulfite, adjusted to pH



FIGURE 1

ANALYTICAL PROTOCOL FOR DETERMINATION OF DOXFP



DOXFP= (TERM-DOX) - (INST-DOX)

less than 2 with concentrated  $H_2SO_4$ , and stored at  $4^\circ C$  for future analysis of DOX. Each plant grab sample was filtered, adjusted to the correct ammonia concentration, and chlorinated before proceeding to the next sample. The DOXFP was defined to be the difference between the terminal DOX measured at the end of the incubation period and the instantaneous DOX in the unchlorinated sample.

#### D. Standard Analytical Procedures

##### 1. Residual Chlorine

Residual chlorine was measured using the DPD ferrous titrimetric method (APHA, 1985, Method 408D). All samples were performed in duplicate, and the strength of the FAS titrant was checked bi-weekly. All chlorine residual measurements were performed in chromic acid washed chlorine demand free glassware.

##### 2. Chemical Oxygen Demand

Chemical oxygen demand (COD) was determined on filtered samples (Whatman GF/F) using the Hach micro-COD (Hach Co., Loveland, CO.) method (APHA, 1985, Method 508). Sample volumes of 2.0 mL were used. Residual dichromate was measured spectrophotometrically using a Bausch and Lomb Spec 70 spectrophotometer at a wavelength of 600 nm.

### 3. Ammonia Nitrogen

Ammonia concentrations were determined on filtered samples (Whatman GF/F) by the double known addition modification of the ammonia selective electrode method (APHA, 1985, Method 417F). Additions of 1 mL and 10 mL of a 1000 mg N/L  $\text{NH}_4\text{Cl}$  solution were used. Standard solutions were always used to check proper electrode response.

### 4. Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen was measured on filtered samples (Whatman GF/F) using Method 420B of Standard Methods (APHA, 1985). The ammonia resulting from the digestion was measured with the ammonia selective electrode using double known addition. Sample volumes of 50 mL to 100 mL were typically used in the digestions, and NaI was used to eliminate complexation of the ammonia by the mercury digestion catalyst.

### 5. Dissolved Organic Carbon

Dissolved organic carbon (DOC) was measured on filtered samples (Whatman GF/F) using a Beckman Model 915 Total Organic Analyzer (Beckman Instruments, Fullerton, CA). Fifty microliters of sample were injected and peak heights were compared to peak heights for 10, 50, and 100 mg C/L standards of potassium acid phthalate.

## 6. Dissolved Organic Halide

Since TOX procedures utilizing carbon adsorption are only appropriate for the analysis of dissolved compounds, all samples were filtered through rinsed Whatman GF/F glass fiber filters. No special care was taken to avoid loss of volatile organohalides at this point. The term DOX for dissolved organic halide will be used to describe the results of this study, since all samples measured were filtered prior to analysis. In addition, the name for the analytical procedure is being changed for the upcoming 17th edition of Standard Methods from TOX to DOX. This reflects the fact that the adsorption/pyrolysis procedure is only applicable to soluble species.

Dissolved organic halide measurements were performed with a Dohrmann DC-20 total organic halide analyzer (Rosemont Analytical, Xertex Corp., Santa Clara, CA). The standard carbon adsorption/pyrolysis/microcoulometry procedure (APHA, 1985, Method 506) was used with minor modifications for the untreated and post primary settled wastewater samples. It was found that a simple once through passage using two 40 mg carbon columns was insufficient to remove greater than 95 percent of the DOX with these samples. This may be a result of the high concentrations of organic matter in raw and primary wastewater. Also, monochloramine attack of the humic matter present may make the organic matter less susceptible to adsorption to the activated carbon. Others have noted the poor adsorption properties of wastewater organic halides (Jensen, 1982). For this reason effluent from the first two carbon columns was routinely recycled through a third column. In

addition, the volume of nitrate wash reagent was increased from 2 to 3 mL, to ensure removal of inorganic chloride. The pyrolysis and microcoulometric analysis was performed in accordance with Method 506. Standards of NaCl and trichlorophenol or trichloroacetic acid were analyzed on a daily basis to assess analyte recovery.

CHAPTER IV  
EXPERIMENTAL RESULTS

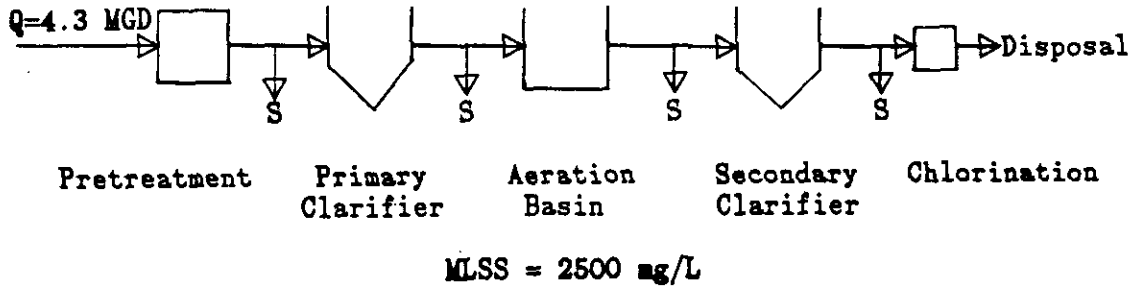
The results for the seven wastewater treatment plant experiments as well as the plant effluent survey are presented in this chapter. The wastewater characteristics, process configuration, flow train, and chemical parameters measured are presented for each plant. The parameters that reflect the organic content of the water are displayed in figures for specified locations in the plant, and are also listed in tables. The combined chlorine demand is also presented in the tables. Chlorine demand is defined as the difference between the applied and residual combined chlorine. Included in the DOX and DOXFP vs. location figures are error bars for one standard deviation as calculated from standards analyses (5% for DOX, 10% for DOXFP). The results of the effluent survey are summarized at the end of the chapter in Table 8.

A. Removal of DOX and DOXFP through Municipal Wastewater Treatment

1. Amherst Wastewater Treatment Plant: January Sampling

The Amherst Wastewater Treatment Plant is a well operated completely mixed activated sludge plant which consistently produces high quality effluent. This plant serves a town of approximately 35,000 people, with little heavy industry. The process schematic for the Amherst Wastewater Treatment Plant is displayed in Figure 2. Results of the analyses for DOX, DOXFP, COD, DOC, and chlorine demand are presented

Figure 2: AMHERST WWTB SCHEMATIC: January Sampling Period



S - Sample collection points (Samples collected 1/20/88, 2:00 p.m.)

Table 1: Amherst Wastewater Treatment Plant Data (January Sampling)

<u>Wastewater Characteristics</u>					
<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>			
BOD mg/L	150	4			
SS mg/L	170	4			
	<u>Detention Time (hrs.)</u>	<u>Overflow Rate (GPD/ft.)</u>			
Primary Clarifier	3.1	710			
Aeration Basin	3.5	---			
Secondary Clarifier	6.6	410			
<u>Sample Location</u>	<u>COD</u> <u>mg O<sub>2</sub>/L</u>	<u>DOC</u> <u>mg C/L</u>	<u>DOX</u> <u>µg Cl/L</u>	<u>DOXFP</u> <u>µg Cl/L</u>	<u>Cl<sub>2</sub> DEMAND</u> <u>mg as Cl<sub>2</sub>/L</u>
Raw	150	44	198	614	17.9
Post Primary	130	41	188	580	22.1
Post Aeration	25	7.8	98.9	338	22.3
Post Secondary	25	7.8	88.8	228	22.7

FIGURE 3: ORGANICS, % RAW vs. LOCATION

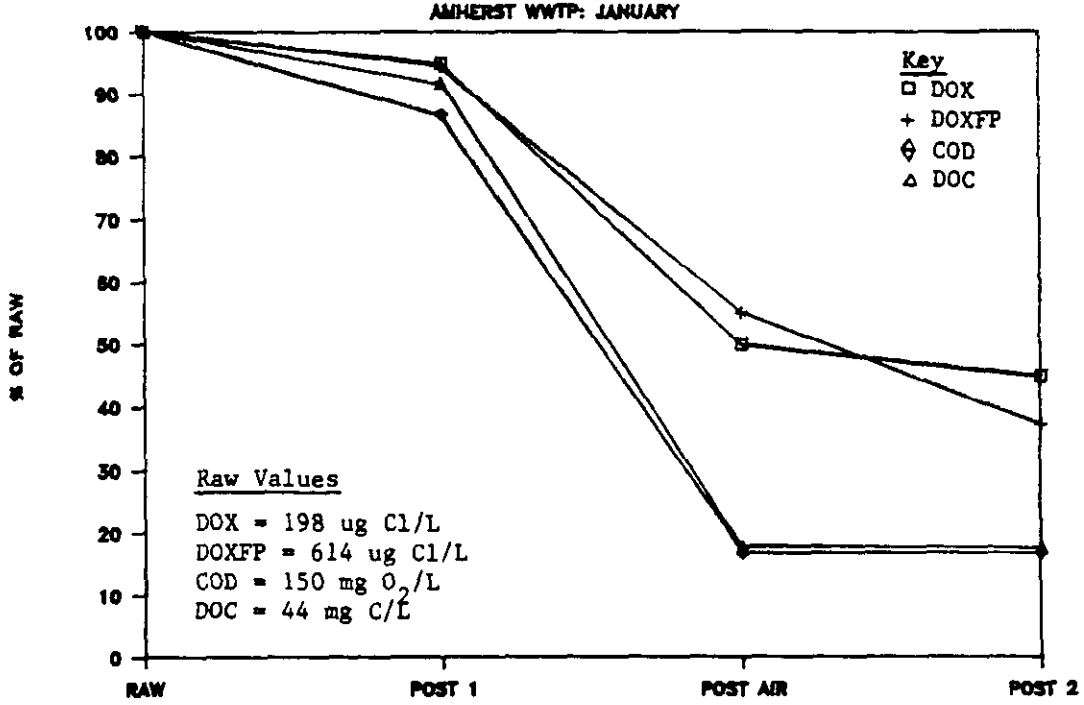
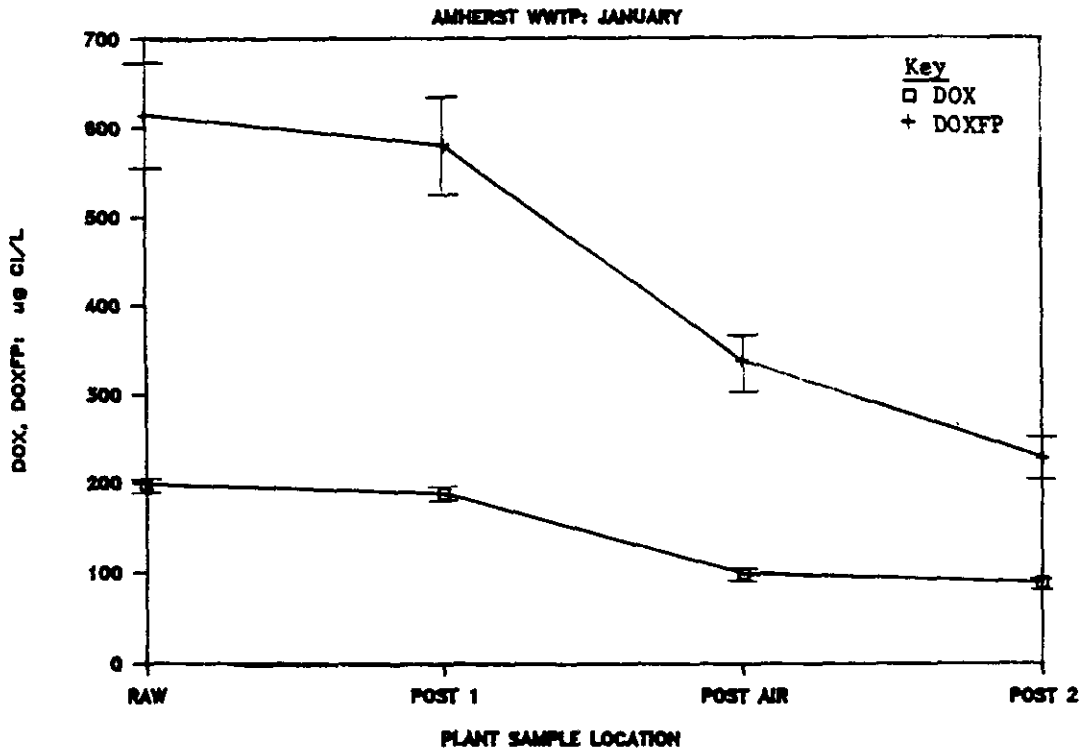


FIGURE 4: DOX, DOXFP vs. LOCATION





in Table 1. The removal of organic material during treatment is shown in Figures 3 and 4. Organic matter as measured by the soluble COD and DOC is decreased to 80% of influent values, and is removed to a greater extent than DOX and DOXFP. Removal of DOX and DOXFP parallels the removal of COD and DOC.

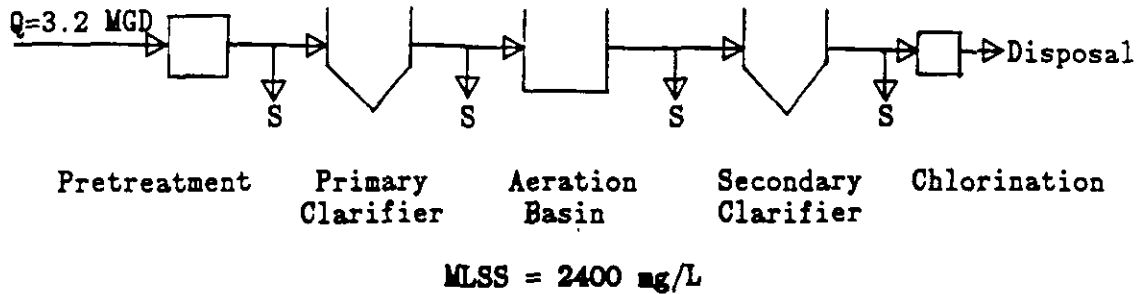
## 2. Amherst Wastewater Treatment Plant: June Sampling

Results for the June sampling of the same treatment plant demonstrate similar trends to the January sampling results, and are listed in Table 2. The process configuration is shown in Figure 5, and is the same as for the January sampling except for the slightly decreased flow in June. A notable exception to the similarities with the January sampling is the slight increase in DOXFP seen in primary and secondary settling (Figures 6 and 7). The slight increases seen, 8% and 5% of the raw levels for primary and secondary settling, respectively, may not be significant considering the standard deviation of the measurement, 10%. It is unlikely that precursor formation would be occurring in the settling basins.

## 3. Belchertown Wastewater Treatment Plant

The Belchertown Wastewater Treatment Plant serves the town of Belchertown and the Belchertown State School, with few significant industrial discharges to the plant. The plant is notable for its lack of primary settling, its extended aeration process, and the presence of

Figure 5: AMHERST WTP SCHEMATIC: June Sampling Period



S - Sample collection points (Samples collected 6/16/88, 3:30 p.m.)

Table 2: Amherst Wastewater Treatment Plant Data (June Sampling)

<u>Wastewater Characteristics</u>		
<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>
BOD mg/L	140	3
SS mg/L	160	2

	<u>Detention Time (hrs.)</u>	<u>Overflow Rate (GPD/ft )</u>
Primary Clarifier	2.1	1050
Aeration Basin	3.1	---
Secondary Clarifier	8.9	300

<u>Sample Location</u>	<u>COD</u> mg O <sub>2</sub> /L	<u>DOC</u> mg C/L	<u>DOX</u> mg Cl/L	<u>DOXFP</u> mg Cl/L	<u>Cl<sub>2</sub> DEMAND</u> mg as Cl <sub>2</sub> /L
Raw	166	60	170	467	23.1
Post Primary	143	58	141	504	15.6
Post Aeration	30	13	84.4	162	11.3
Post Secondary	30	13	69.5	187	16.6

FIGURE 6: ORGANICS, % RAW vs. LOCATION

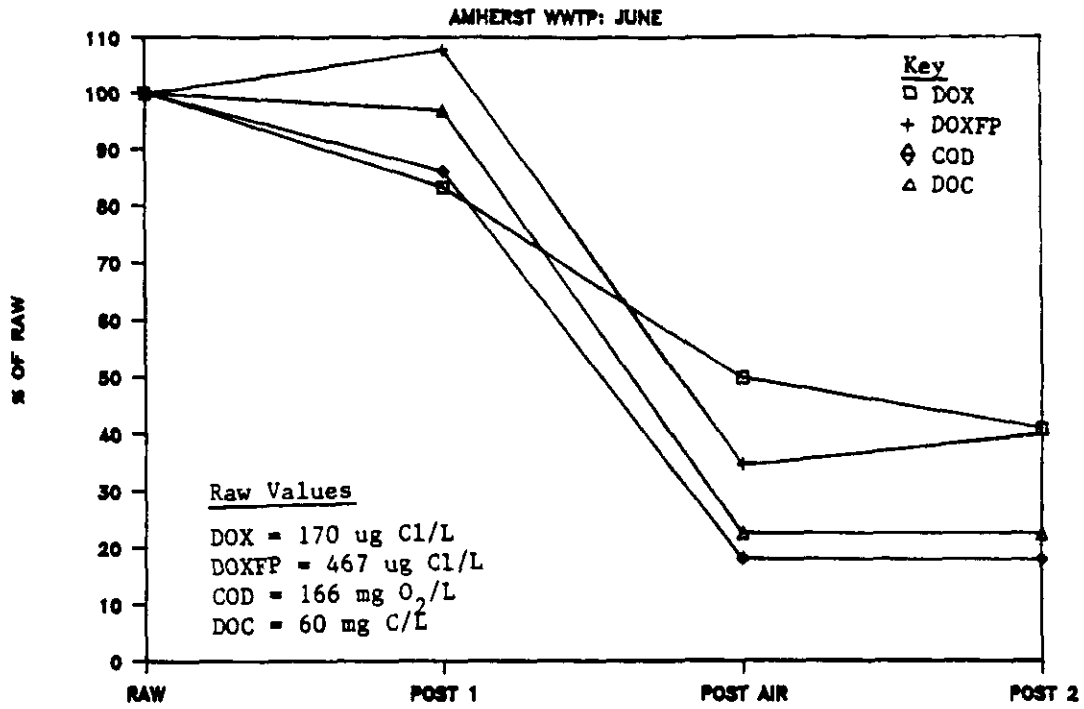
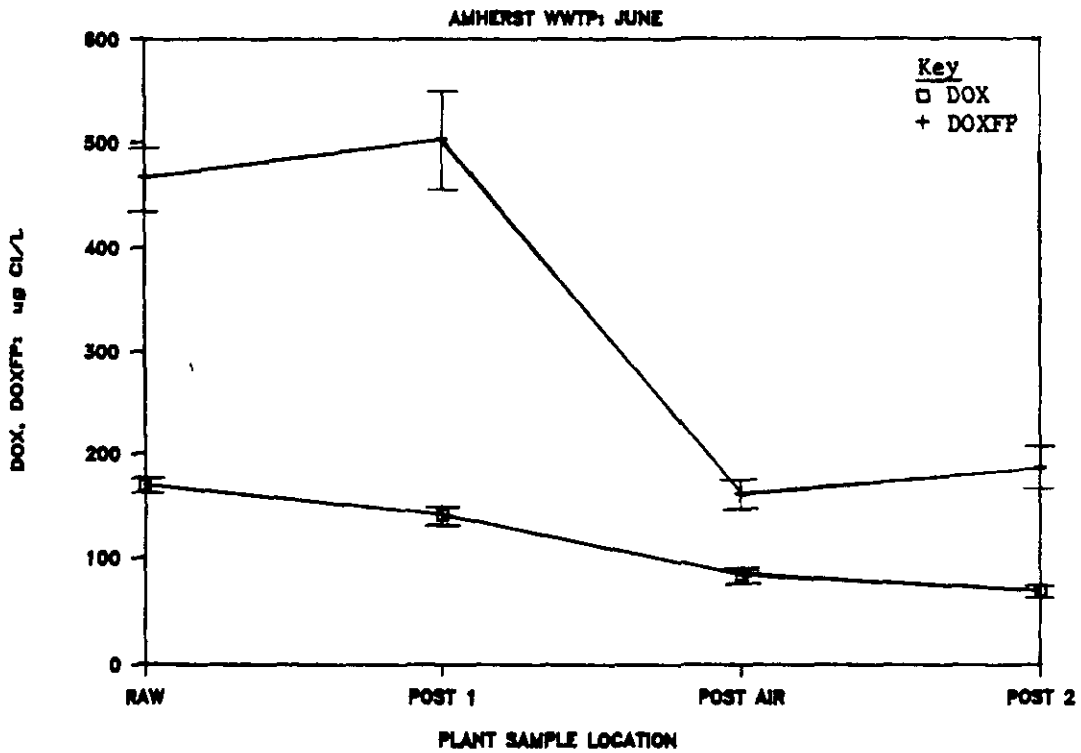


FIGURE 7: DOX, DOXFP vs. LOCATION

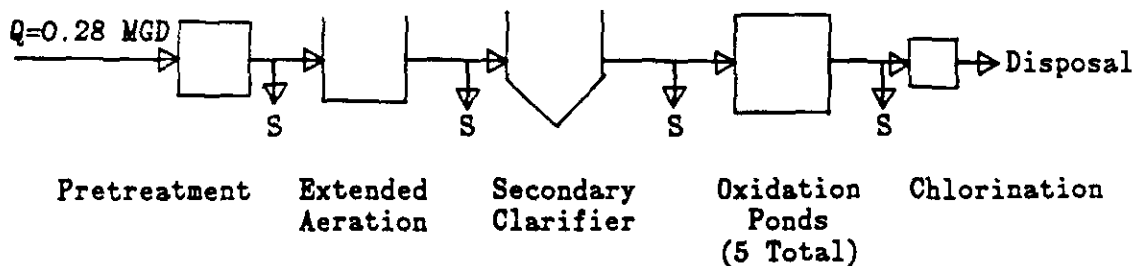


finishing ponds (Figure 8). Removal of DOX, DOXFP, DOC, and COD in the extended aeration process was greater than 60% for all parameters, but a high COD value was observed following secondary settling and after the finishing ponds (Figures 9 and 10). This is the only parameter to increase significantly, and is presumed to be due to sample contamination. DOX and DOXFP concentrations decreased monotonically through the plant. The finishing ponds did not seem to have a significant effect upon treatment efficiency, despite their long hydraulic residence time (Table 3).

#### 4. Greenfield Wastewater Treatment Plant

The Greenfield Wastewater Treatment Plant uses trickling filters with characteristic poor quality effluent (Figure 11). Plant flow frequently exceeds the design flow and the effluent barely meets its discharge limits (Table 4). Organics removal across the secondary settling basin was not evaluated at this plant because the secondary settling basin was serving a dual function as a chlorine contact tank. Chemical oxygen demand, DOC, and DOXFP removals were quite similar, but a greater concentration of DOX was observed following primary settling than was present in the influent (Figures 12 and 13). This is presumed to be due to a spike of DOX moving through the plant rather than organohalide production in the primary settling basin.

Figure 8: BELCHERTOWN WASTEWATER TREATMENT PLANT SCHEMATIC



MLSS = 2800 mg/L

S - Sample collection points (Samples collected 1/12/88, 3:30 p.m.)

Table 3: Belchertown Wastewater Treatment Plant Data

<u>Wastewater Characteristics</u>					
<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>			
BOD mg/L	135	7			
SS mg/L	122	1			
		<u>Detention Time (hrs.)</u>	<u>Overflow Rate (GPD/ft )</u>		
Aeration Basin		24	---		
Secondary Clarifier		3.6	400		
Oxidation Pond (each)		58	12.3		
Oxidation Ponds (total)		291	---		
<u>Sample Location</u>	<u>COD</u> mg O <sub>2</sub> /L	<u>DOC</u> mg C/L	<u>DOX</u> µg Cl/L	<u>DOXFP</u> µg Cl/L	<u>Cl<sub>2</sub> DEMAND</u> mg as Cl <sub>2</sub> /L
Raw	270	61	130	900	22.1
Post Aeration	68	6.6	51.3	281	5.7
Post Secondary	255	7.8	52.1	166	1.3
Post Ponds	162	8.4	45.9	146	3.8

FIGURE 9: ORGANICS, % RAW vs. LOCATION

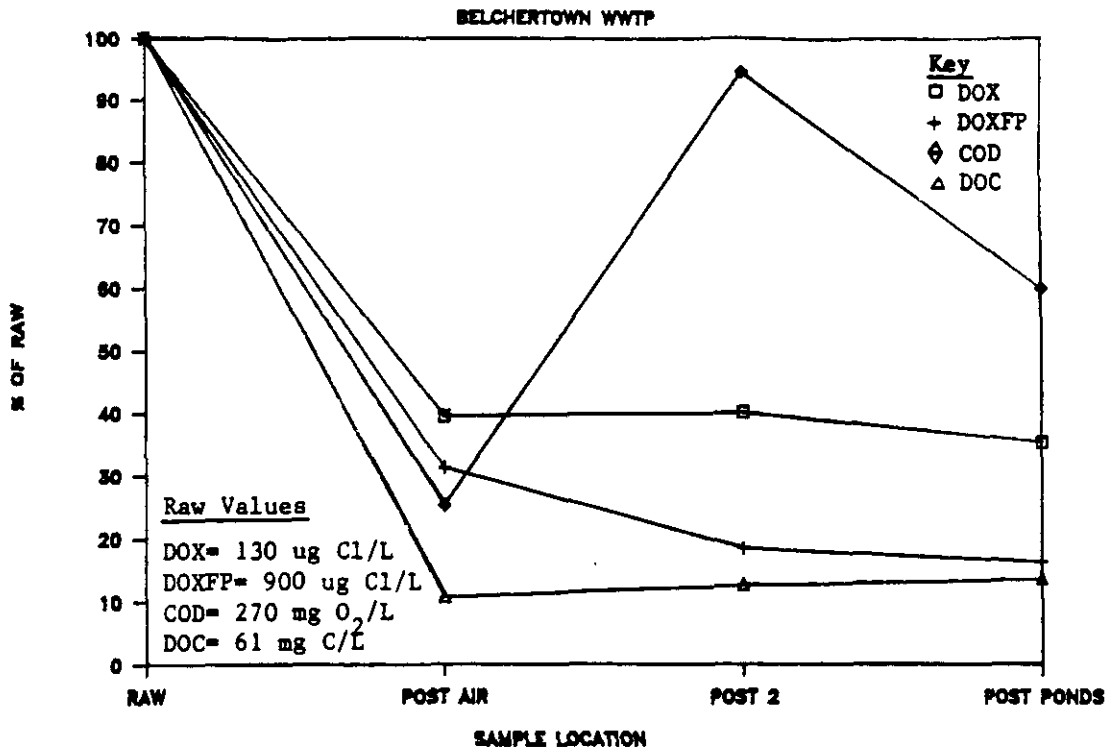


FIGURE 10: DOX, DOXFP vs. LOCATION

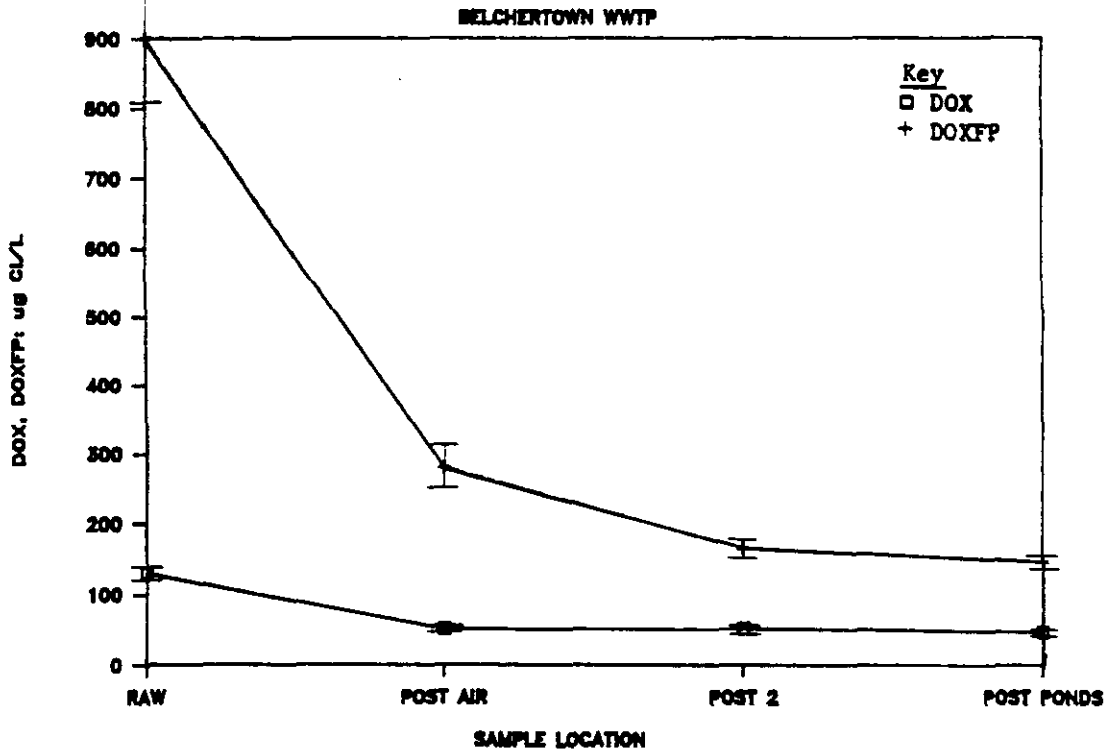
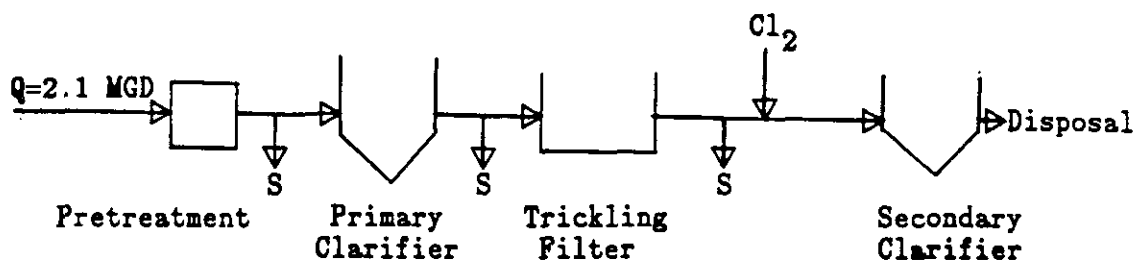


Figure 11: GREENFIELD WASTEWATER TREATMENT PLANT SCHEMATIC



S - Sample collection points (Samples collected 6/20/88, 1:00 p.m.)

Table 4: Greenfield Wastewater Treatment Plant Data

<u>Wastewater Characteristics</u>		
<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>
BOD mg/L	190	30
SS mg/L	200	24

	<u>Detention Time (hrs.)</u>	<u>Overflow Rate (GPD/ft )</u>
Primary Clarifier	3.9	460
Trickling Filters	0.5	---
Secondary Clarifier	4.8	370

<u>Sample Location</u>	<u>COD</u> mg O <sub>2</sub> /L	<u>DOC</u> mg C/L	<u>DOX</u> μg Cl/L	<u>DOXFP</u> μg Cl/L	<u>Cl<sub>2</sub> DEMAND</u> mg as Cl <sub>2</sub> /L
Raw	186	89	119	925	23.3
Post Primary	160	65	192	783	15.2
Post Trickling Filter	80	35	127	499	18.0

FIGURE 12: ORGANICS, % RAW vs. LOCATION

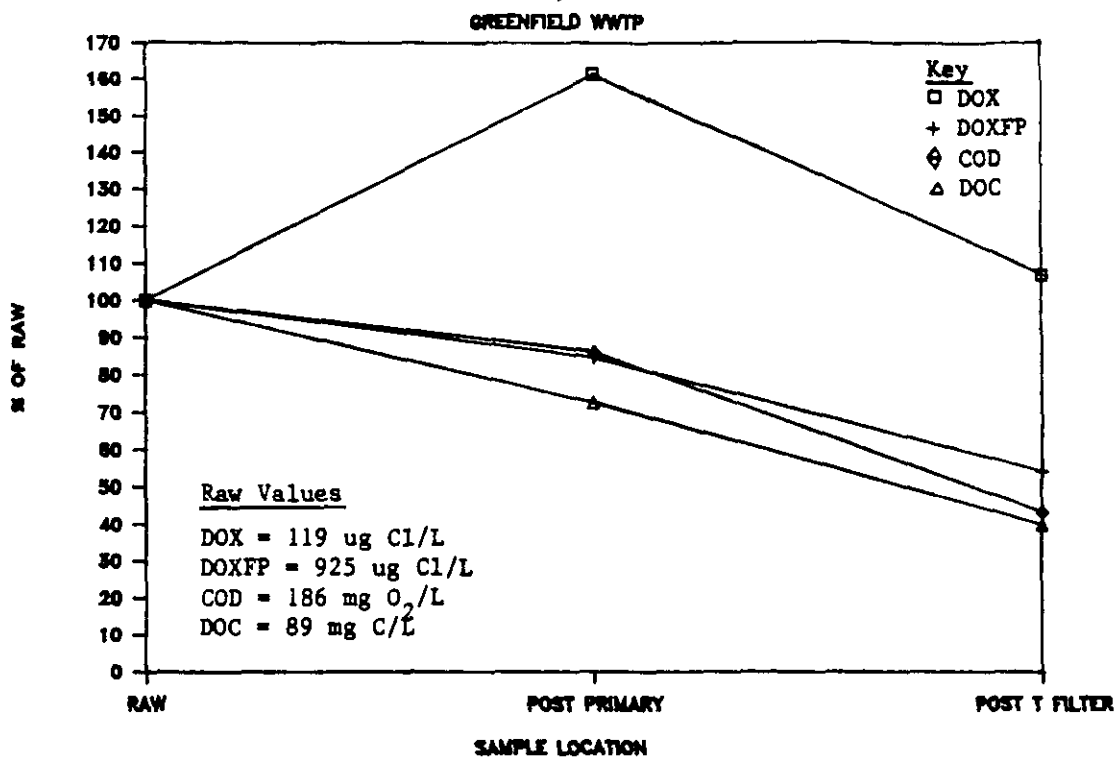
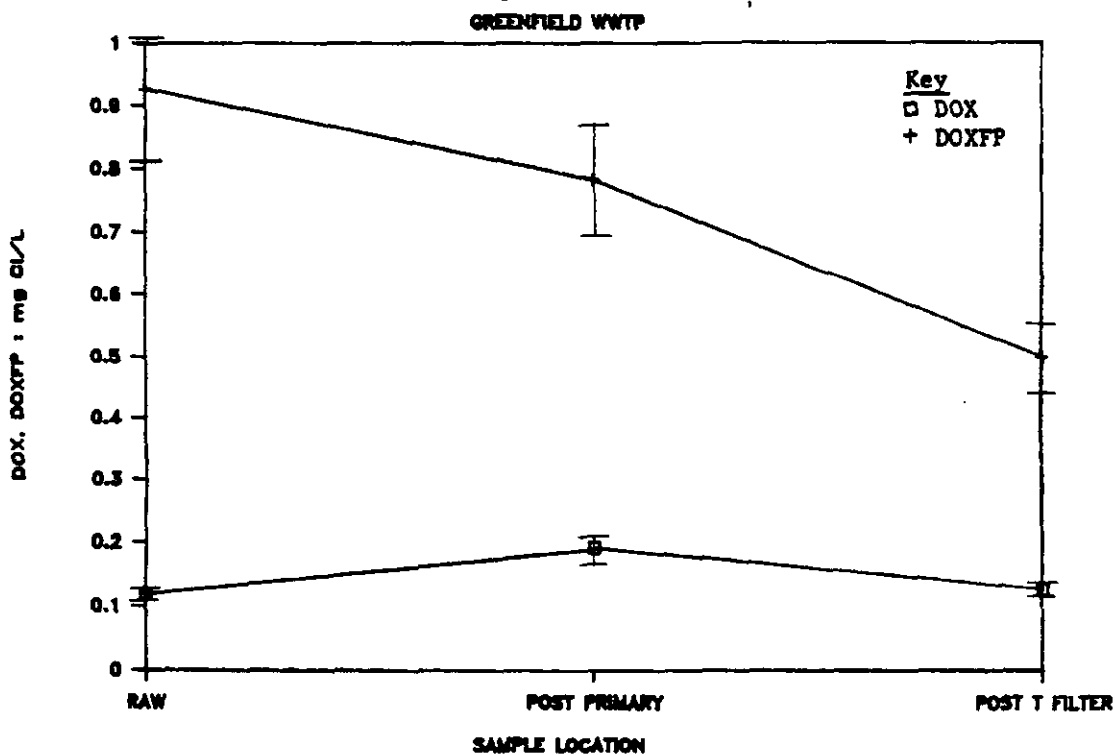


FIGURE 13: DOX, DOXFP vs. LOCATION





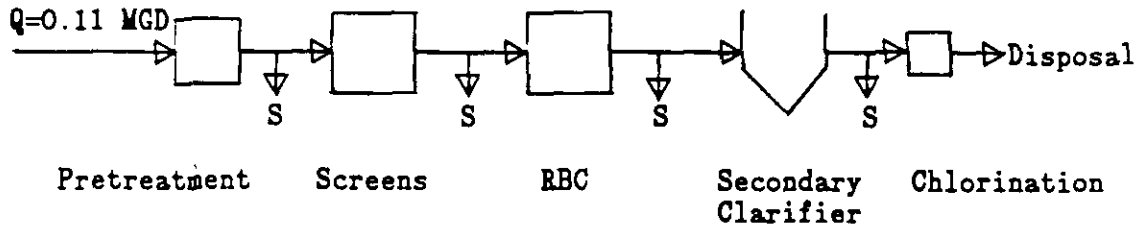
#### 5. Hatfield Wastewater Treatment Plant

The town of Hatfield is a small farm community with little industry. The Hatfield Wastewater Treatment Plant is the only plant surveyed that utilizes rotating biological contactors. Microscreens with openings of 0.06 inches are used rather than primary settling basins following pretreatment (Figure 14). All organic parameters decreased monotonically across the plant with the exception of the DOC following secondary settling (Figures 15 and 16). The reason for the increase in DOC is unknown, and it is not accompanied by an increase in any of the other organic parameters. As seen in Table 5, the effluent was of a poorer than average quality.

#### 6. Northampton Wastewater Treatment Plant

Northampton is a small city with a significant industrial base. The Northampton Wastewater Treatment Plant is a conventional activated sludge plant with prechlorination for odor control (Figure 17; Table 6). The organic parameters shown in Figures 18 and 19 depict similar removal efficiencies across the unit processes. As with other plants, the largest decrease in organics occurs across the biological treatment process, ranging from 50% for DOX to 77% for DOC. The primary clarifier influent did not show a significant difference in DOX concentration due to prechlorination in comparison to other plants not practicing prechlorination. Chlorine demand provided a reasonably accurate surrogate for other organic parameters in this case (see data; Table 6).

Figure 14: HATFIELD WASTEWATER TREATMENT PLANT SCHEMATIC



S - Sample collection points (Samples collected 6/21/88, 2:00 p.m.)

Table 5: Hatfield Wastewater Treatment Plant Data

		<u>Wastewater Characteristics</u>			
		<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>	
	BOD	mg/L	160	17	
	SS	mg/L	180	10	
		<u>Detention Time (hrs.)</u>		<u>Overflow Rate (GPD/ft.)</u>	
RBC		3.2		---	
Secondary Clarifier		9.8		160	
<u>Sample Location</u>	<u>COD</u>	<u>DOC</u>	<u>DOX</u>	<u>DOXFP</u>	<u>Cl<sub>2</sub> DEMAND</u>
	<u>mg O<sub>2</sub>/L</u>	<u>mg C/L</u>	<u>µg Cl/L</u>	<u>µg Cl/L</u>	<u>mg as Cl<sub>2</sub>/L</u>
Raw	54	35	193	584	17.0
Post Screens	50	33	143	572	19.2
Post RBC	50	15	114	411	16.3
Post Secondary	30	22	79.6	296	10.3

FIGURE 15: ORGANICS, % RAW vs. LOCATION

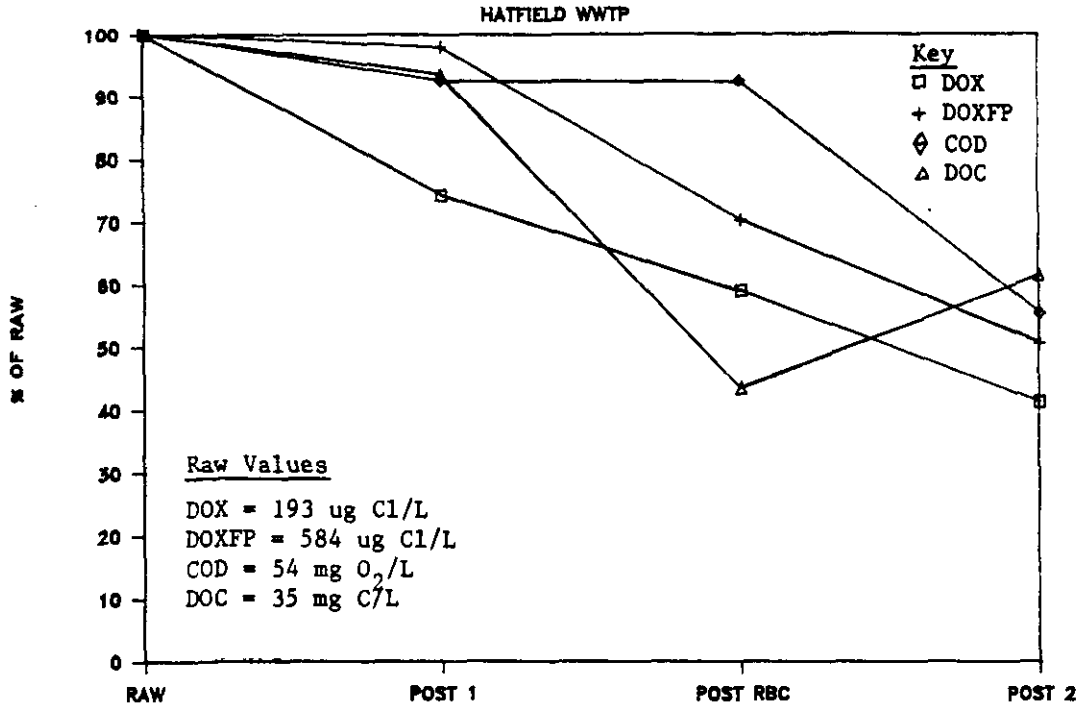


FIGURE 16: DOX, DOXFP vs. LOCATION

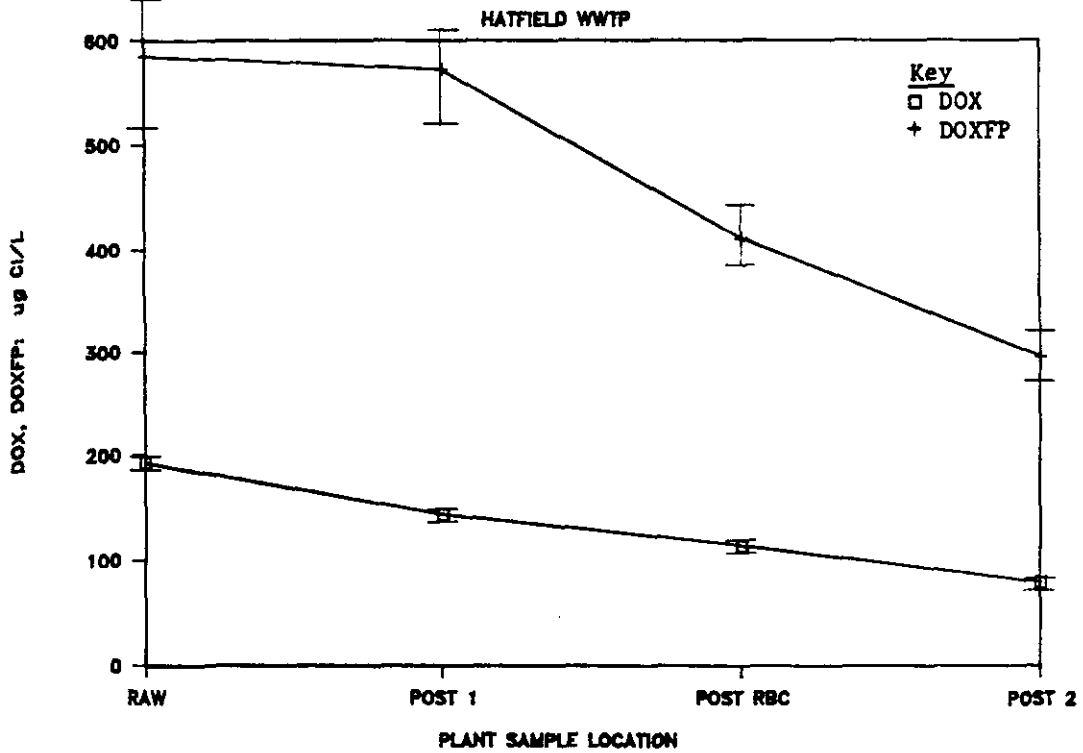
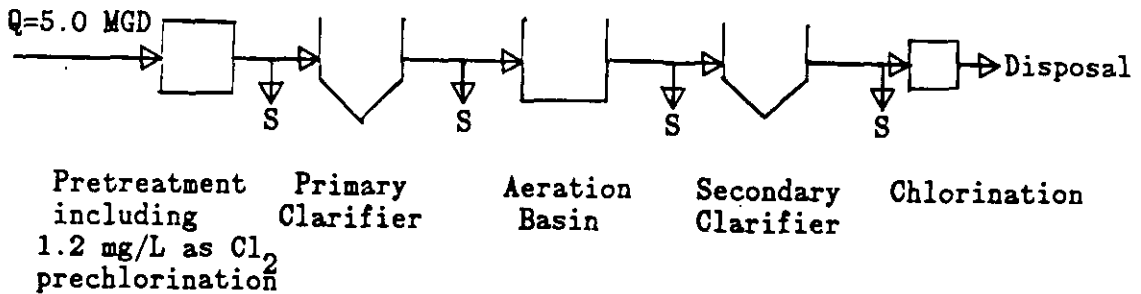


Figure 17: NORTHAMPTON WASTEWATER TREATMENT PLANT SCHEMATIC



MLSS = 1900 mg/L

S = Sample collection points (Samples collected 6/8/88, 2:00 p.m.)

Table 6: Northampton Wastewater Treatment Plant Data

<u>Wastewater Characteristics</u>					
<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>			
BOD mg/L	300	10			
SS mg/L	210	10			
	<u>Detention Time (hrs.)</u>		<u>Overflow Rate (GPD/ft )</u>		
Primary Clarifier	3.8		570		
Aeration Basin	8.6		---		
Secondary Clarifier	5.0		430		
<u>Sample Location</u>	<u>COD</u> <u>mg O<sub>2</sub>/L</u>	<u>DOC</u> <u>mg C/L</u>	<u>DOX</u> <u>µg Cl/L</u>	<u>DOXFP</u> <u>µg Cl/L</u>	<u>Cl<sub>2</sub> DEMAND</u> <u>mg as Cl<sub>2</sub>/L</u>
Raw	214	66	196	638	27.8
Post Primary	162	63	179	554	19.2
Post Aeration	50	12	78.8	173	9.0
Post Secondary	50	9.9	72.2	172	9.8

FIGURE 18: ORGANICS, % RAW vs. LOCATION

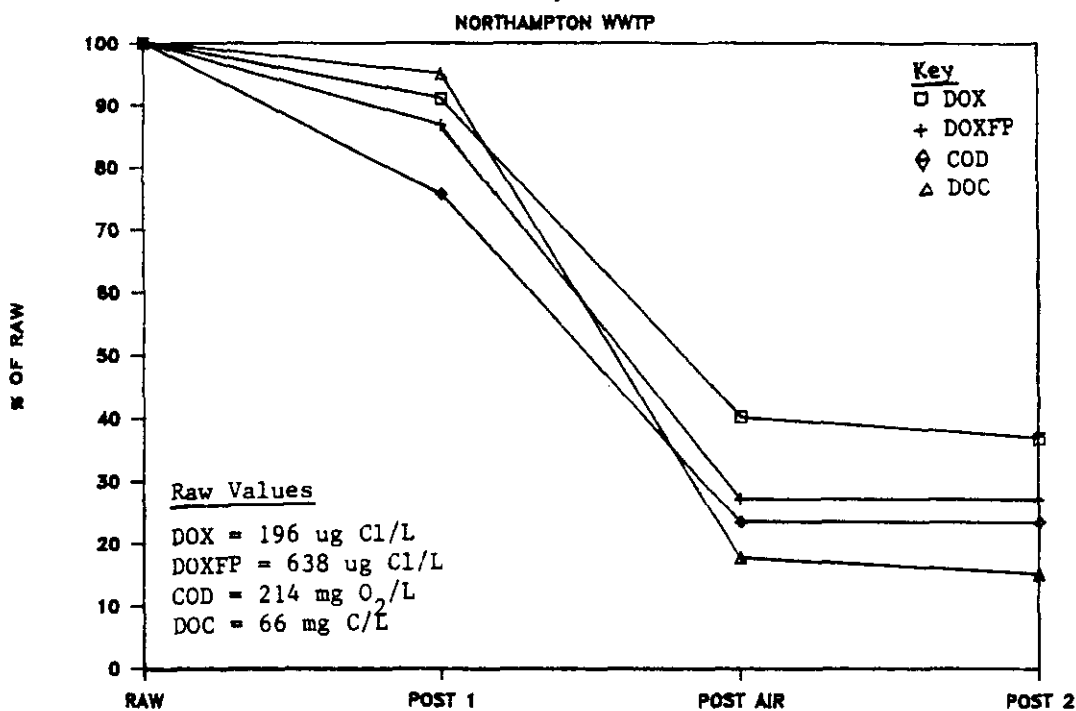
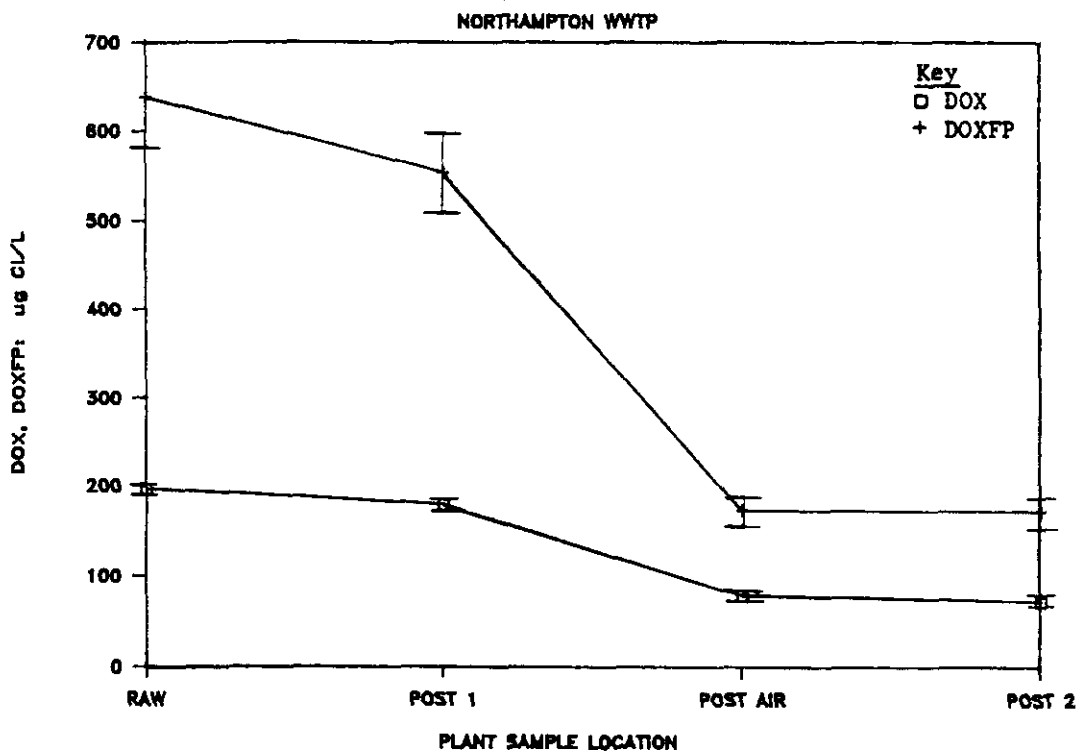


FIGURE 19: DOX, DOXFP vs. LOCATION



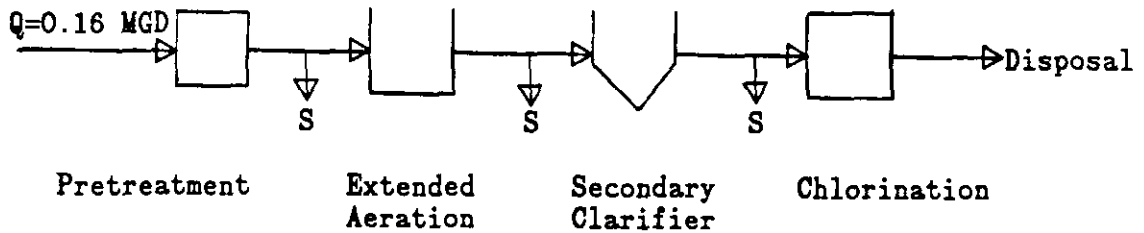
## 7. Sunderland Wastewater Treatment Plant

Sunderland is a small farm community on the Connecticut River with little industry. The Sunderland Wastewater Treatment Plant is a small extended aeration activated sludge facility without primary sedimentation (Figure 20). The detention time for the aeration basin on the day surveyed was greater than 24 hours (Table 7). Removals of greater than 50% were observed for DOC, COD, and DOXFP, but an increase in DOX concentration was observed following the aeration basin (Figures 21 and 22). This is presumed to be due to a spike of DOX moving through the treatment plant, as was noted in the Greenfield plant. Note the unusually low raw DOX concentration.

### B. Discharge of DOX from Municipal Wastewater Treatment Plants

The results of the effluent survey of the wastewater treatment plants located in western Massachusetts are presented in Table 8. The DOX concentrations in the wastewater effluents ranged from 56 to 1527  $\mu\text{g}$  as Cl/L. Small towns, small and medium sized cities, as well as several types of treatment processes were surveyed, and these plants represent a cross section of the Massachusetts wastewater treatment plants. The samples that were not filtered with the GF/F filter were sampled before the protocol utilizing GF/F filters was established. The North Brookfield sample was collected during a time in which chlorination was not being performed.

Figure 20: SUNDERLAND WASTEWATER TREATMENT PLANT SCHEMATIC



MLSS = 2400 mg/L

S - Sample collection points (Samples collected 5/26/88, 11:00 A.M.)

Table 7: Sunderland Wastewater Treatment Plant Data

<u>Wastewater Characteristics</u>					
<u>Parameter</u>	<u>Influent</u>	<u>Effluent</u>			
BOD mg/L	147	13			
SS mg/L	89	2			
	<u>Detention Time (hrs.)</u>	<u>Overflow Rate (GPD/ft )</u>			
Extended Aeration	36	---			
Secondary Clarifier	12.5	122			
<u>Sample Location</u>	<u>COD</u> mg O <sub>2</sub> /L	<u>DOC</u> mg C/L	<u>DOX</u> μg Cl/L	<u>DOXFP</u> μg Cl/L	<u>Cl<sub>2</sub> DEMAND</u> mg as Cl <sub>2</sub> /L
Raw	102	33	42.2	554	16.4
Post Aeration	54	12	50.7	261	33.6
Post Secondary	58	14	44.8	212	14.6

FIGURE 21: ORGANICS, % RAW vs. LOCATION

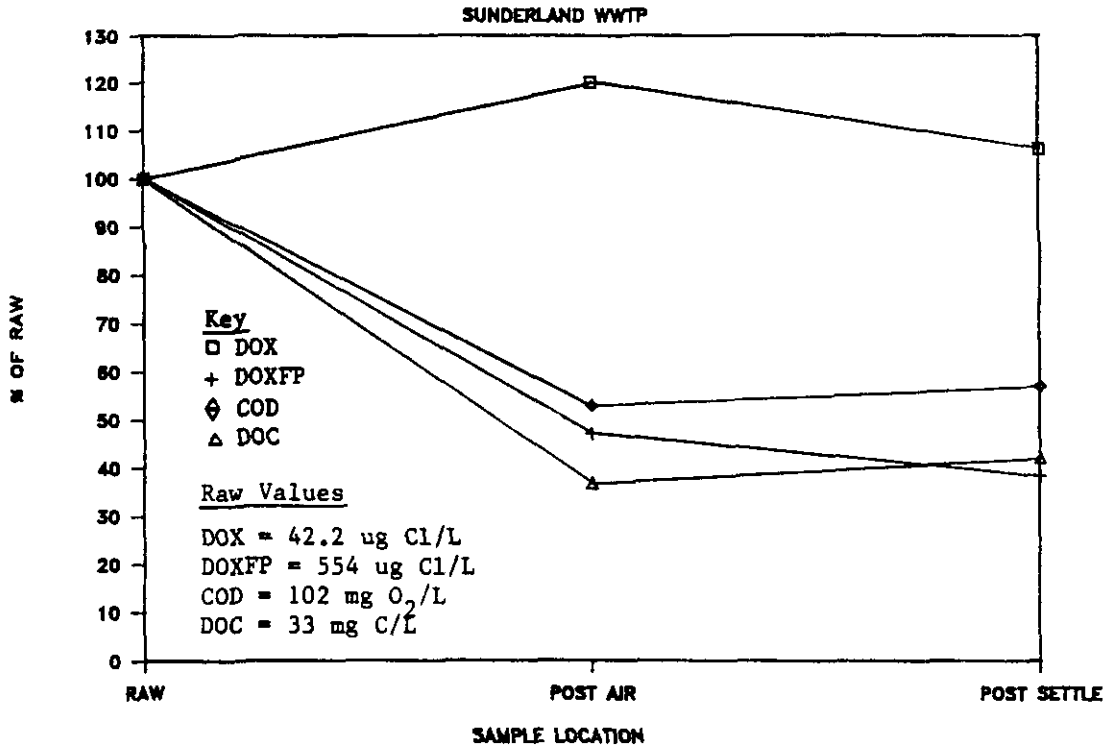


FIGURE 22: DOX, DOXFP vs. LOCATION

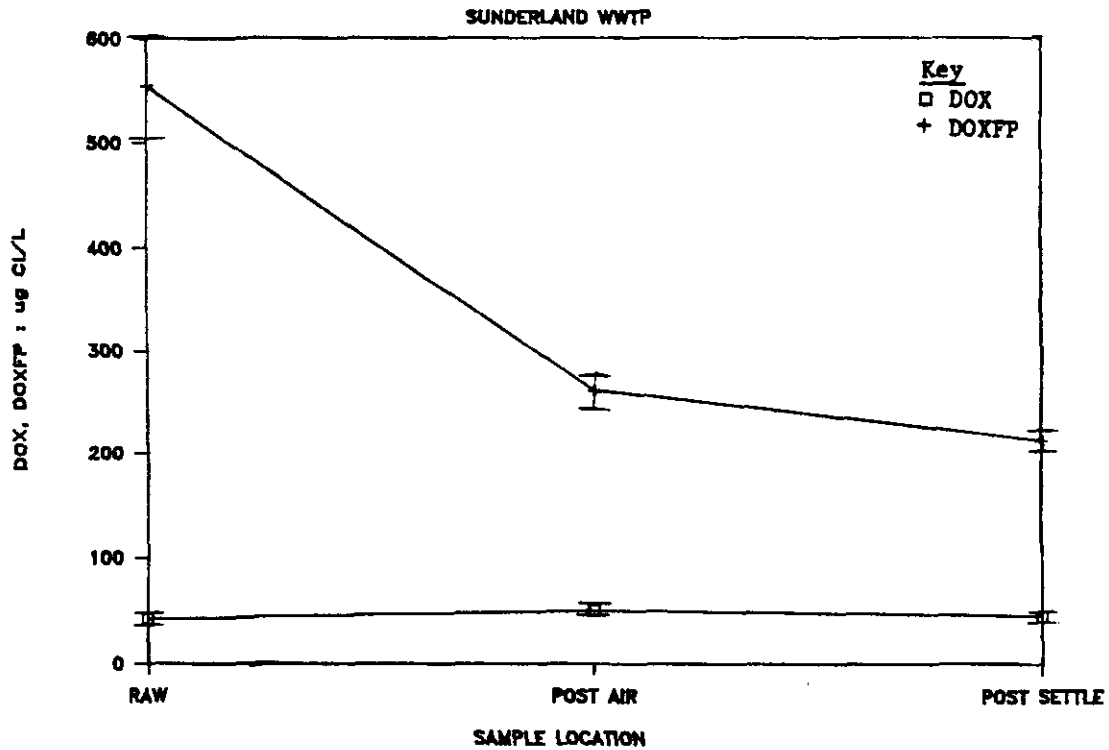




Table 8: EFFLUENT DOX SURVEY

<u>PLANT LOCATION</u>	<u>DOX (<math>\mu\text{g Cl/L}</math>)</u>	<u>FILTER USED</u>	<u>CHLORINATED</u>	<u>DATE</u>
Fernald School, Templeton, Ma.	194	unfiltered	yes	11/20/86
North Brookfield Ma.	56	unfiltered	no	1/19/87
Erving, Ma.	1527	GF/C, membrane	yes	6/15/87
Belchertown, Ma.	66	unfiltered	yes	7/23/87
Northampton, Ma.	151	GF/F	yes	6/28/88
Montague, Ma.	110	GF/F	yes	6/28/88
Sunderland, Ma.	88	GF/F	yes	6/28/88
Holyoke, Ma.	598	GF/F	yes	6/28/88
Hatfield, Ma.	108	GF/F	yes	6/21/88
Greenfield, Ma.	209	GF/F	yes	6/20/88

CHAPTER V  
DISCUSSION OF RESULTS

A. Raw Wastewater Quality and Plant Performance

The wastewater treatment plants surveyed showed removals of organic matter on the order of 80% for DOC and COD, with the exception of the Greenfield and Hatfield Wastewater Treatment Plants. Note that these are the only two plants intensively surveyed that did not utilize activated sludge. Influent DOX values for the six plants ranged from 50 to 200  $\mu\text{g/L}$  with an average of 150  $\mu\text{g/L}$ . Effluent concentrations of DOX prior to chlorination ranged from 40 to 140  $\mu\text{g/L}$ , with an average of 75  $\mu\text{g/L}$ . Influent DOXFP ranged from 500 to 900  $\mu\text{g/L}$ , with an average of 670  $\mu\text{g/L}$ . Effluent DOXFP concentrations ranged from 140 to 500  $\mu\text{g/L}$ , with an average of 250  $\mu\text{g/L}$ . Results are summarized in Table 9.

Table 9: DOX, DOXFP IN PLANT INFLUENT, UNCHLORINATED EFFLUENT

<u>PLANT</u>	<u>INFLUENT (<math>\mu\text{g Cl/L}</math>)</u>		<u>EFFLUENT (<math>\mu\text{g Cl/L}</math>)</u>	
	DOX	DOXFP	DOX	DOXFP
Amherst (January)	198	614	89	228
Amherst (June)	170	467	70	187
Belchertown	130	900	46	146
Greenfield	119	925	127	499
Hatfield	193	584	80	296
Northampton	196	638	72	172
Sunderland	42	554	45	212
Mean +/- S.D.	150+/- 57	669+/-175	76+/-28	249+/-120
Median	130	614	72	212

Rotating biological contactors and trickling filters generally showed poorer removals of DOX and DOXFP than activated sludge.

The results agree with reported values in the literature for the removal of organics in wastewater treatment plants (e.g., Petrasek et al., 1983; Leuenberger, et al., 1985; Hannah et al., 1986; Suzuki and Nakanishi, 1987). The study conducted by Suzuki and Nakanishi (1987) demonstrated similar plant removals of DOXFP with primary and secondary treatment, although aeration and secondary settling were not evaluated separately in their study.

B. Removal of DOX and DOXFP

1. Settling

Removal efficiencies of DOX and DOXFP in primary and secondary settling basins are shown in Tables 10 and 11. As some means were skewed significantly by one or two values, the median was calculated also. In a few circumstances, concentrations increased following settling. The large uncertainty in the mean for DOX removal in primary settling is due to the large relative increase seen in the Greenfield plant. The median values presented in the tables in conjunction with the similar decreases observed for COD and DOC suggests that slight decreases in DOX and DOXFP are perhaps occurring in the settling basins. Influent concentration variations may be affecting the results. The two main mechanisms believed to be responsible for removal of DOX in settling basins are biodegradation and sorption to settleable particles. As biodegradation of chlorinated compounds and dehalogenation are normally associated with anaerobic environments, significant biodegradation is not expected. The detention time and potential for an anoxic environment, however, may lead to some biodegradation. Another

possible cause of DOX and DOXFP reduction is that the microorganisms alter the organic matter in such a way as to decrease the adsorption to activated carbon in the DOX procedure. While this is possible, it is not thought to be responsible due to the concomitant reductions seen in DOC and COD. Volatilization is not thought to be responsible for removal of DOX as such extremely volatile compounds are lost during the vacuum filtration step of DOX analysis.

Table 10: DOX, DOXFP REMOVAL IN PRIMARY SETTLING BASINS

<u>PLANT</u>	<u>% RAW DOX REMOVED</u>	<u>% RAW DOXFP REMOVED</u>
Amherst (January)	5.1	5.5
Amherst (June)	16.6	-7.9
Greenfield	-61.3	15.4
Hatfield (Screens)	25.8	2.1
Northampton	9.0	13.2
Mean +/- Std. Dev.	-1.0% +/- 35%	5.7% +/- 9.0%
Median	9.0	5.5

Table 11: DOX, DOXFP REMOVAL IN SECONDARY SETTLING BASINS

<u>PLANT</u>	<u>% RAW DOX REMOVED</u>	<u>% RAW DOXFP REMOVED</u>
Amherst (January)	5.1	17.9
Amherst (June)	8.8	-5.3
Belchertown	-0.6	12.8
Hatfield	17.7	19.7
Northampton	3.4	0.1
Sunderland	14.0	8.8
Mean +/- Std. Dev.	8.1% +/- 6.8%	7.3% +/- 10.0%
Median	5.1/8.8	12.8/8.8

## 2. Biological Treatment

Reduction in organohalides and organohalide precursors was greatest across biological treatment (not including secondary settling). Decreases of more than 50% of raw DOX and DOXFP were observed in many of the treatment plants surveyed. Table 12 lists removal percentages for all plants. The decrease in DOX and DOXFP was generally greater at the activated sludge plants compared to the trickling filter and RBC plants, again paralleling the results seen in other organic parameters. The hydraulic detention time in hours is listed in parentheses after the plant. Removal of DOX and DOXFP does not appear to be related to hydraulic detention time at the different plants. This may be expected due to the different process details at each plant. The possibility exists for a relation between the solids residence time and the decrease in the removal of DOX and DOXFP, but it was not possible to keep influent conditions constant at the plant resulting in a constant solids residence time. Influent variations in wastewater quality and flow would also make such a relation between solids residence time and removal efficiencies difficult to establish.

The results shown in Table 11 demonstrate that in many of the cases DOXFP removal percentages were greater than DOX removal percentages. A review of Figures 2 through 22 confirms that in most cases, percentage of DOX in the effluent was greater than the percentages for the other parameters. The limited potential for dechlorination in aerobic environments is believed to play a role in this phenomenon. Any conclusions regarding the exact mechanism for

removal are speculative and were not addressed in this study. It can only be stated in the most general case that DOXFP was removed to a greater extent than DOX.

Table 12: DOX, DOXFP REMOVAL IN BIOLOGICAL TREATMENT

<u>PLANT(RET. TIME, HR)</u>	<u>TYPE</u>	<u>% RAW DOX REMOVED</u>	<u>% RAW DOXFP REMOVED</u>
Amherst (January) (3.5)	CMAS	45	39
Amherst (June) (3.1)	CMAS	34	73
Belchertown (24)	EAAS	61	69
Greenfield (0.5)	TF	54	31
Hatfield (3.2)	RBC	15	27
Northampton (8.6)	CMAS	51	60
Sunderland (36)	EAAS	-20	53
Activated Sludge Mean +/- S.D.		34% +/- 32%	59% +/- 14%
Activated Sludge Median		45	60

\* EAAS= Extended Aeration Activated Sludge TF= Trickling Filter  
 RBC= Rotating Biological Contactor CMAS= Completely Mixed Activated Sludge

### C. Correlations Among Organic Parameters

The objective of this section is to present correlations among the various organic parameters measured. This is desired because the DOX and DOXFP tests involved in this study are time consuming, and surrogate parameters are desired for DOX and DOXFP. Surrogate relations allow the prediction of plant performance through the measurement of a different parameter. The validity of the surrogates can be assessed by examining the Figures 23 through 31.

Correlations between the various organic parameters are shown in Figures 23 through 31. These figures include the complete set of plant data (six plants, three or four samples per plant). As shown in Figure 23, there is a correlation between the pair DOX and DOC, with  $r^2$  equal to 0.52. The high degree of scatter and the positive y-intercept suggests the independent behavior of these two parameters and confirms the greater removability of the DOC seen previously. Chemical oxygen demand and DOC correlation is shown in Figure 24. The outliers in Figure 24 (upper left hand corner) are the pair of points for the Belchertown plant having a high COD with a low DOC. This figure supports the hypothesis that these points are due to sample contamination. These points were not included in regression analyses. The correlations between the pairs DOX, DOXFP and DOXFP, DOC are shown in Figures 25 and 26. The weak correlation between DOX and DOXFP is expected, ( $r^2 = 0.48$ ) as DOX concentrations were seen to be less well correlated to other organic parameters. In addition, one would not, a priori, expect a strong correlation between ambient levels of DOX and other organic parameters. This is seen in Figure 27, with no correlation observed between COD and DOX.

As shown in Figures 28, 29, and 30, chlorine demand is not correlated with any of the other organic parameters. Reviewing Tables 1 through 7, there were no instances where the chlorine demand paralleled the other organic parameters consistently. The lack of correlation with chlorine demand is thought to be due to the interferences frequently encountered in measuring chlorine residuals in wastewater. For the free chlorination of humic materials, DOX formation is strongly correlated

FIGURE 23: CORRELATION OF DOX, DOC

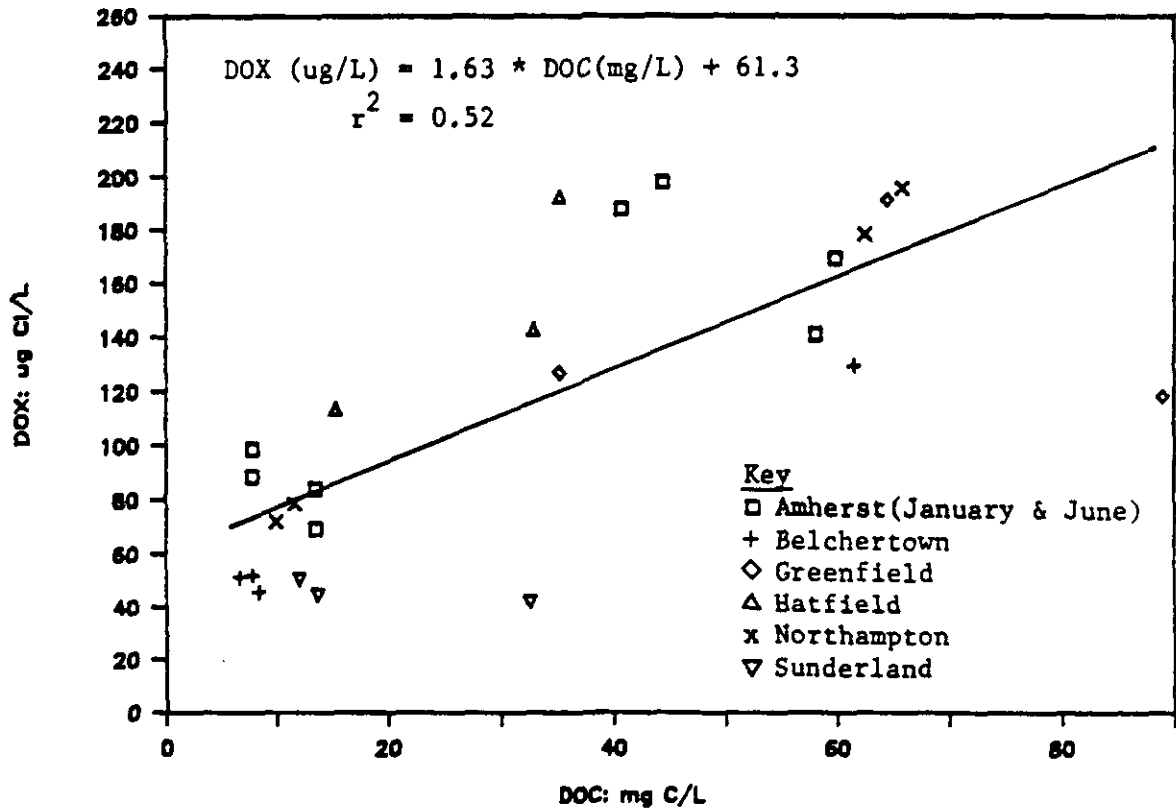




FIGURE 24: CORRELATION OF COD, DOC

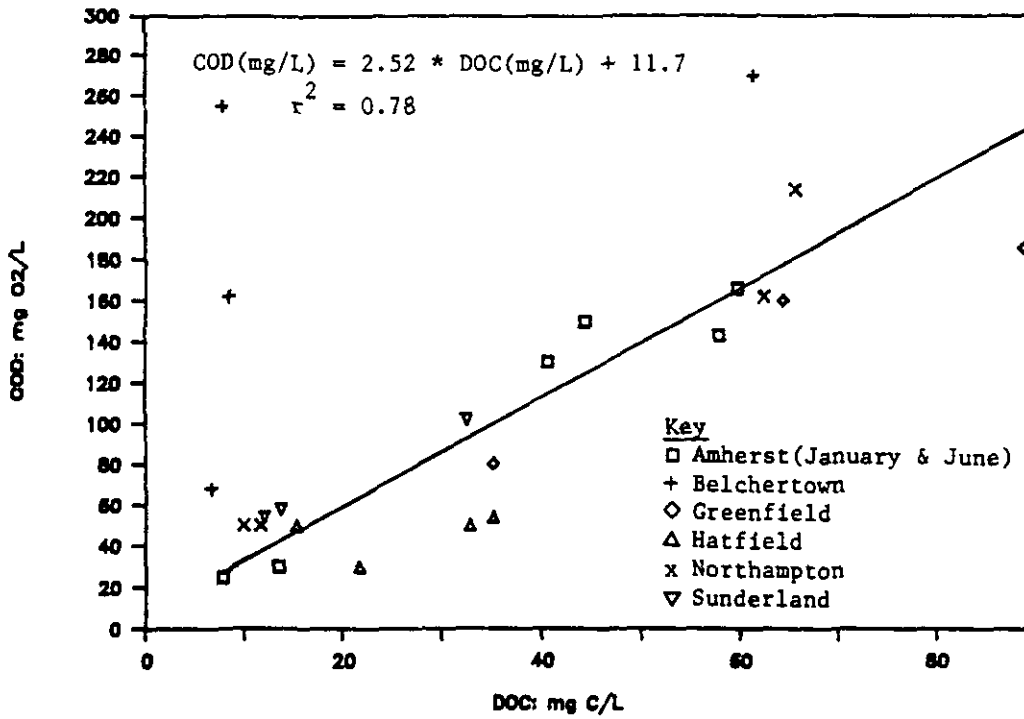


FIGURE 25: CORRELATION OF DOX, DOXFP

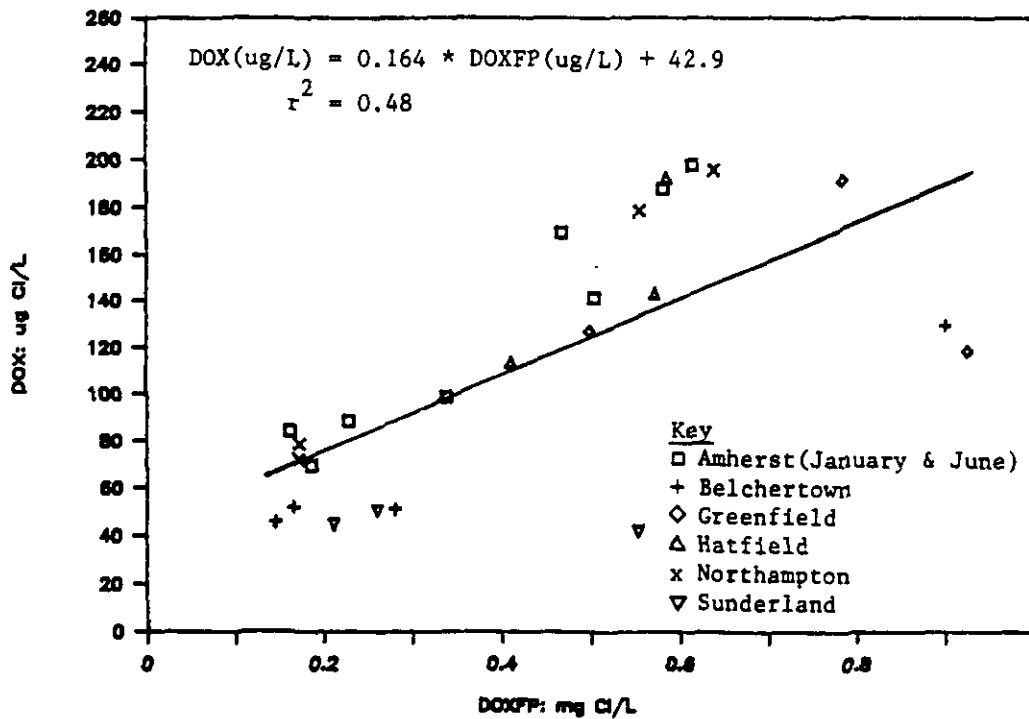


FIGURE 26: CORRELATION OF DOXFP, DOC

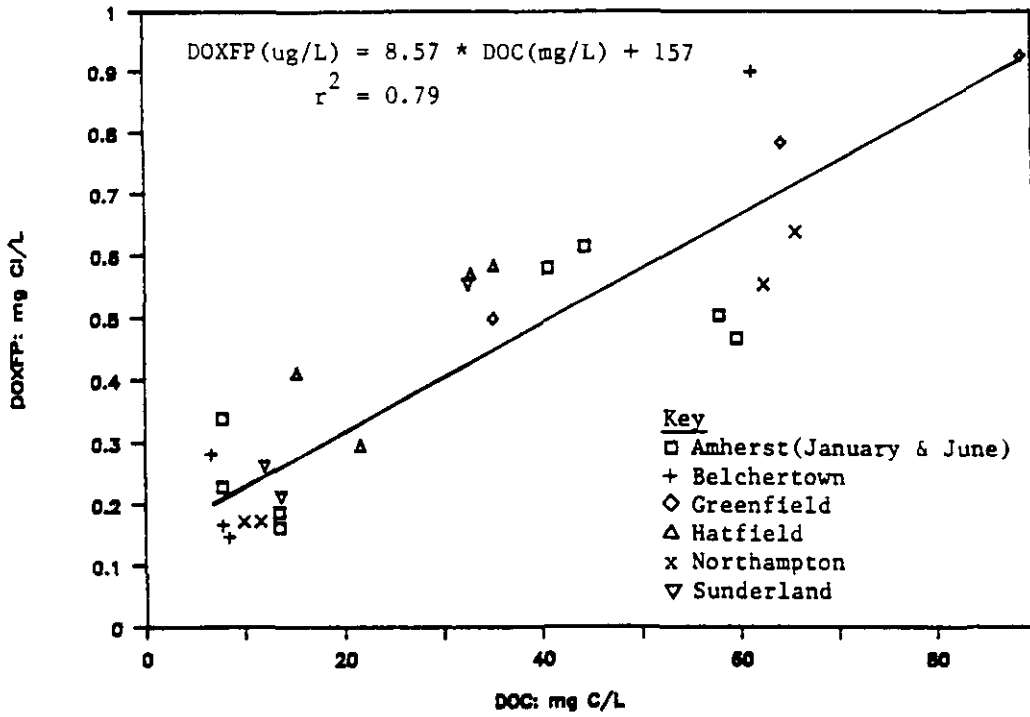


FIGURE 27: CORRELATION OF COD, DOX

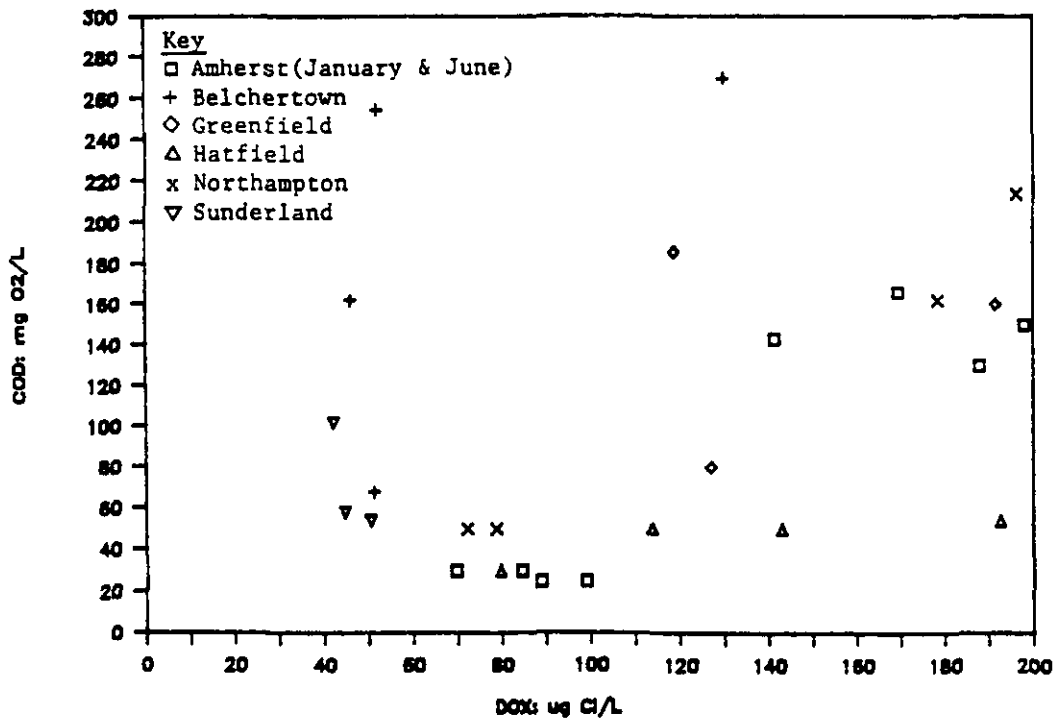


FIGURE 28: CORRELATION:  $Cl_2$  DEMAND, DOC

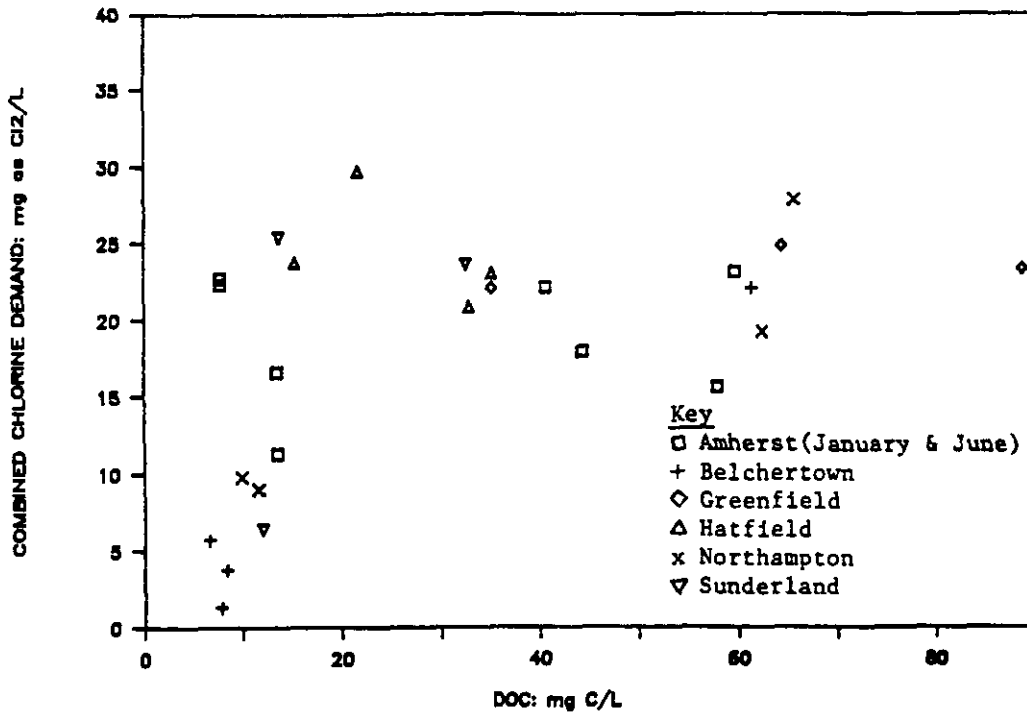


FIGURE 29: CORRELATION DOXFP,  $Cl_2$  DEMAND

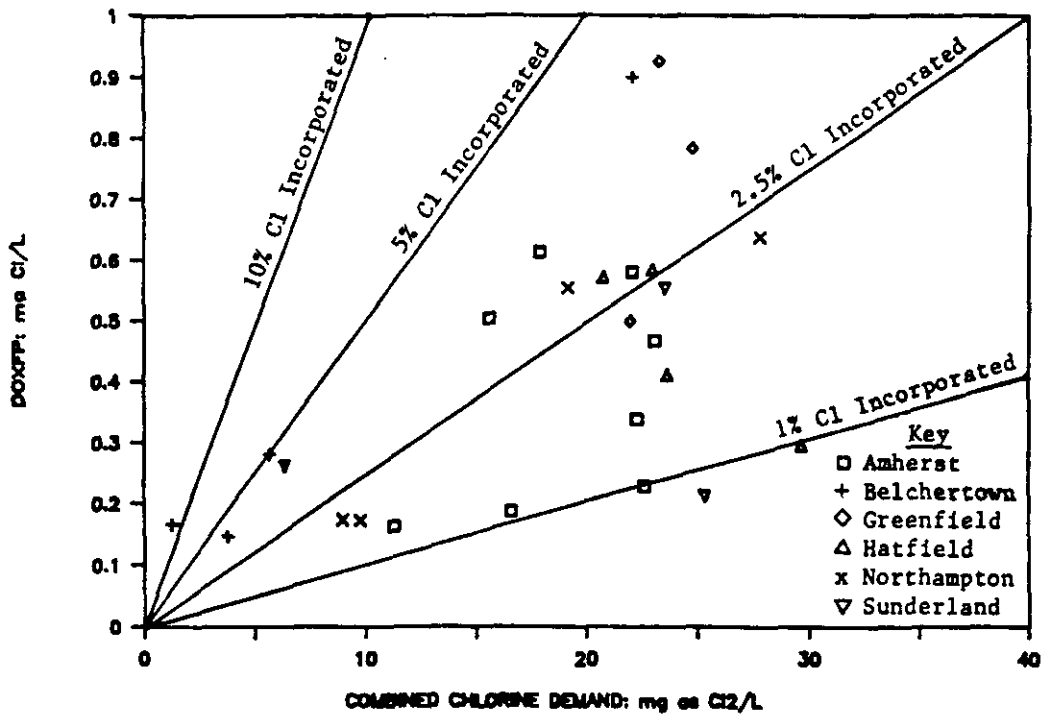


FIGURE 30: CORRELATION:  $Cl_2$  DEMAND, COD

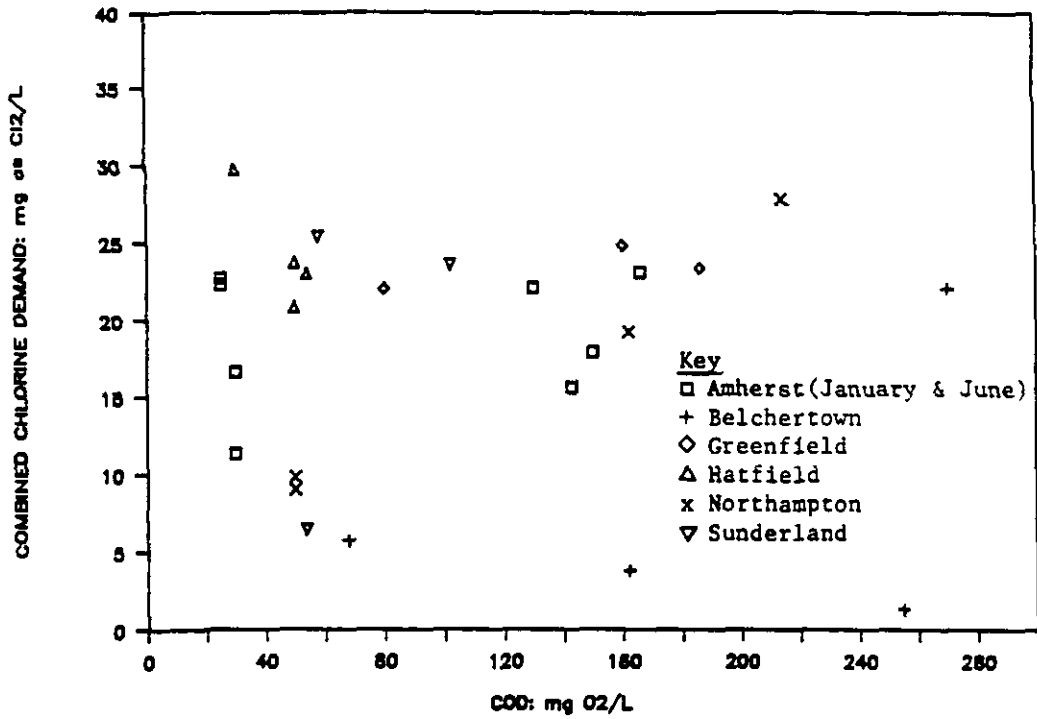
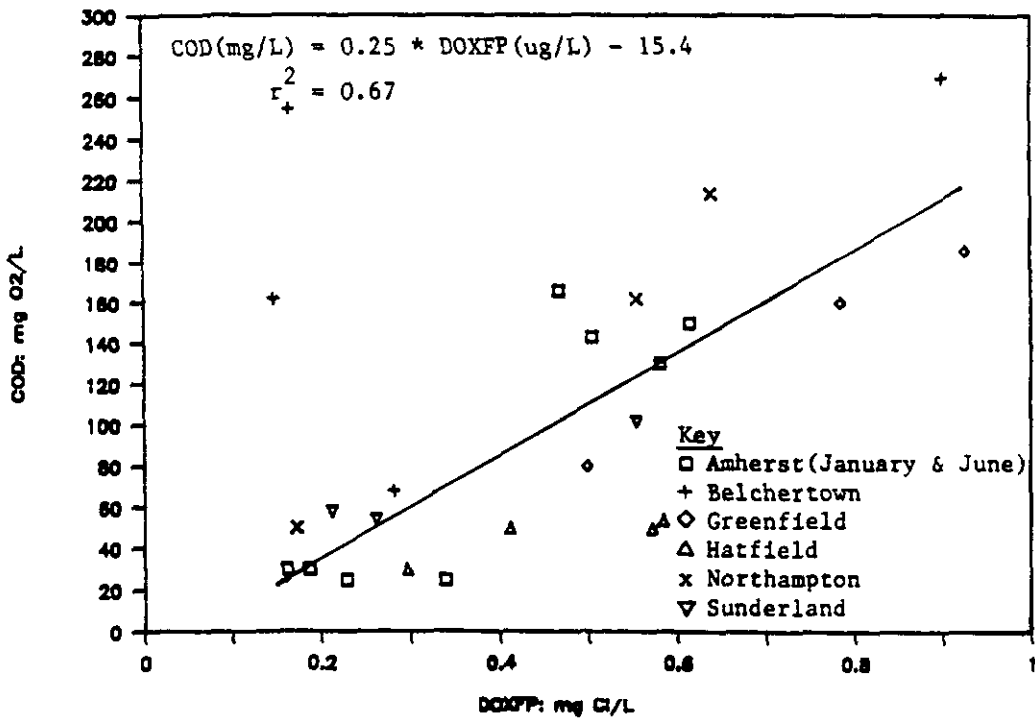


FIGURE 31: CORRELATION OF COD, DOXFP



with chlorine demand (Reckhow, 1984). Several studies have documented the difficulties in measuring active chlorine in wastewater, notably due to the presence of organic nitrogen moieties (Strupler, 1978), though other ions are also known to interfere with the measurement of residuals using the DPD ferrous titrimetric method (APHA, 1985). The percent incorporated lines displayed in Figure 29 represent the fraction of chlorine consumed that was incorporated into DOXFP, and most points fall between 1% and 5% chlorine incorporated. This is typical of wastewater chlorination and has been borne out previously. Lastly, a significant positive correlation is seen between COD and DOXFP in Figure 31. The two erratic points from the Belchertown plant were discarded for the regression analysis.

As shown in this series of figures, the most accurate surrogate parameter for DOXFP is DOC. Chemical oxygen demand can also be used but the association is not as strong as for DOC. Neither COD nor DOC were seen to be an accurate reflection of DOX values. Lastly, chlorine demand is not well correlated with any of the other parameters measured.

#### D. DOXFP/DOC Ratio

Several recent studies in Japan have described changes in the ratio of DOXFP to DOC following biological treatment (Yamada and Somiya, 1984, 1985a,b; Itoh, 1985; Suzuki and Nakanishi, 1987). The ratio of DOXFP/DOC may be thought of as a measure of the susceptibility of the organic matter to become covalently bonded with chlorine under conditions typical of wastewater disinfection. Thus changes in this

ratio reflect a change in reactivity.

Figures 32 through 38 show DOXFP/DOC ratios as a function of location for the seven treatment plants surveyed. In all cases, a noticeable increase in DOXFP/DOC was observed following biological treatment. In some cases, the ratio of DOXFP to DOC continued to increase across the secondary clarifier basin while in others, the ratio decreased. This suggests that the effluent organic material from biological treatment is, on the average, more reactive with respect to DOX formation than the influent organics. Given that this biological treatment effluent has been determined to be composed largely of soluble metabolic products (SMP), it may be that SMP are more reactive toward monochloramine than the biological substrate that is removed. It has been shown (Hoehn et al., 1980) that algal extracellular material is highly susceptible to the formation of organic halides upon chlorination. On the other hand, the increased DOXFP/DOC following biological treatment may be the result of preferential removal of DOC that is less reactive to monochloramine. Some treatment processes may remove certain less reactive constituents of organic matter, leaving a residue of the more reactive compounds. Examples of unreactive DOC would include sugars, carbohydrates, and proteins.

The absolute values of DOXFP/DOC were significantly different in the Japanese studies compared to the results presented here, because of the different strength of the oxidants utilized. Suzuki and Nakanishi (1987) used two different free chlorine doses to evaluate DOXFP, one a relatively low dose and the other significantly higher. In both cases a significant free residual of chlorine was maintained throughout the

FIGURE 32: DOXFP/DOC vs. LOCATION  
AMHERST WWTP, JANUARY

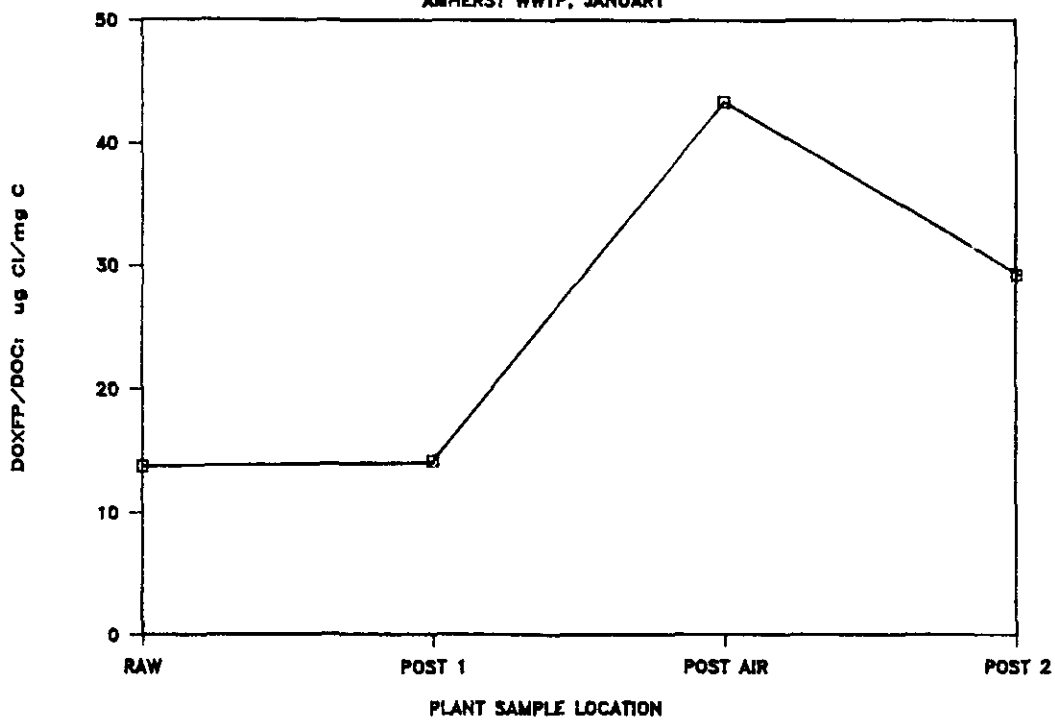


FIGURE 33: DOXFP/DOC vs. LOCATION  
AMHERST WWTP, JUNE

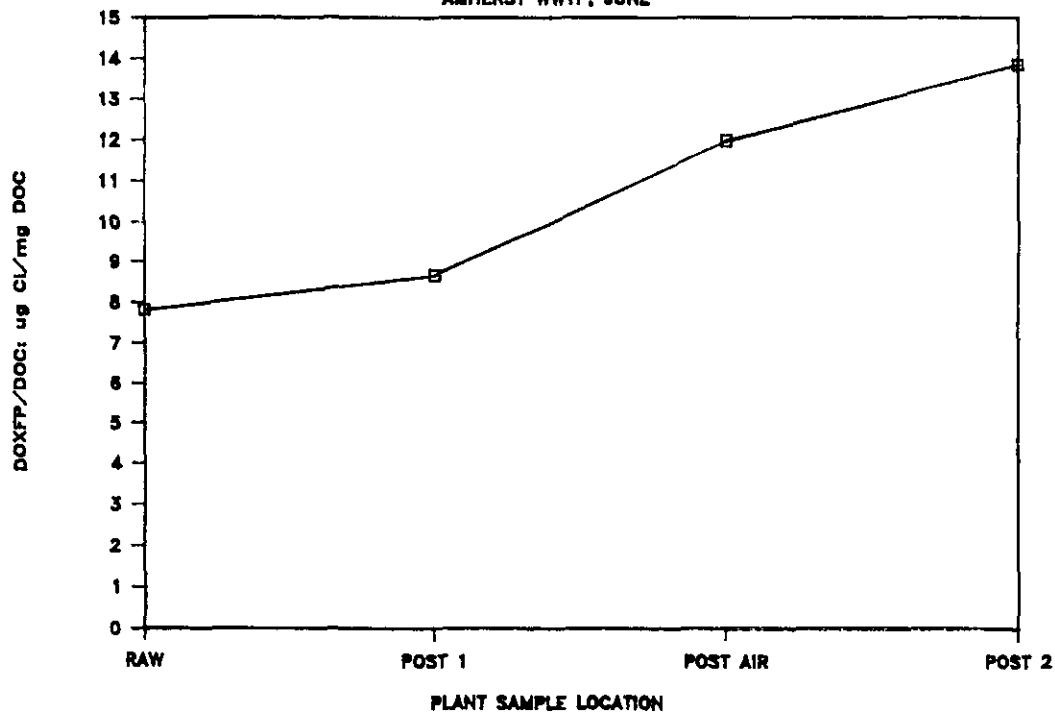


FIGURE 34: DOXFP/DOC vs. LOCATION

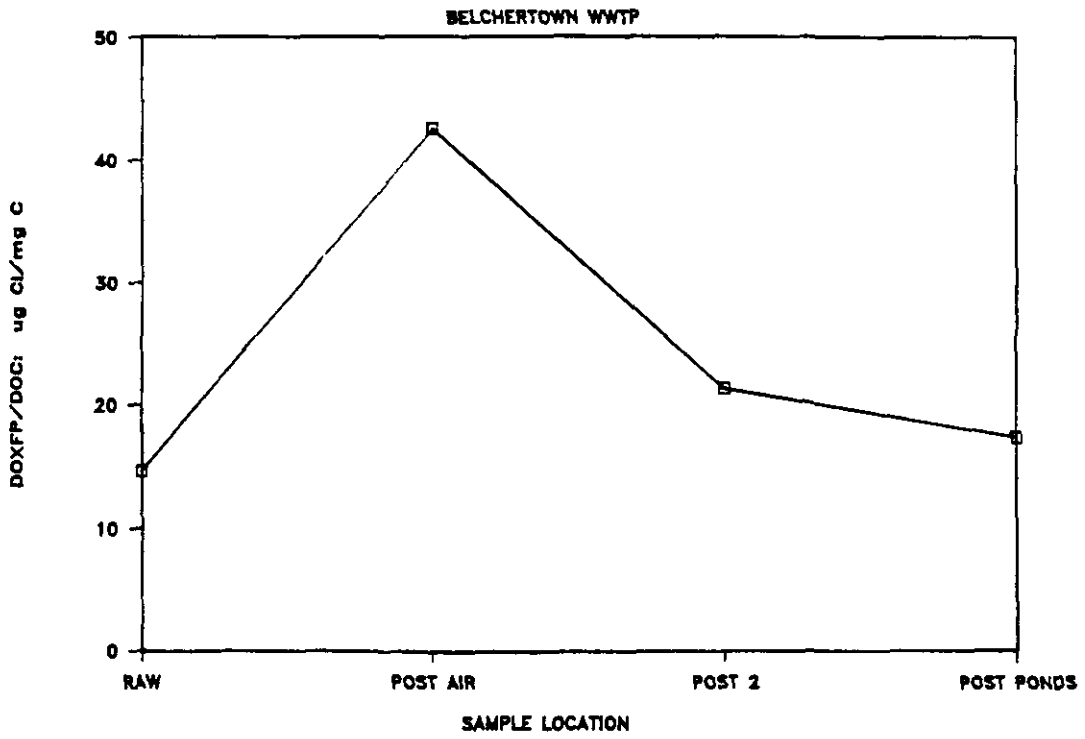


FIGURE 35: DOXFP/DOC vs. LOCATION

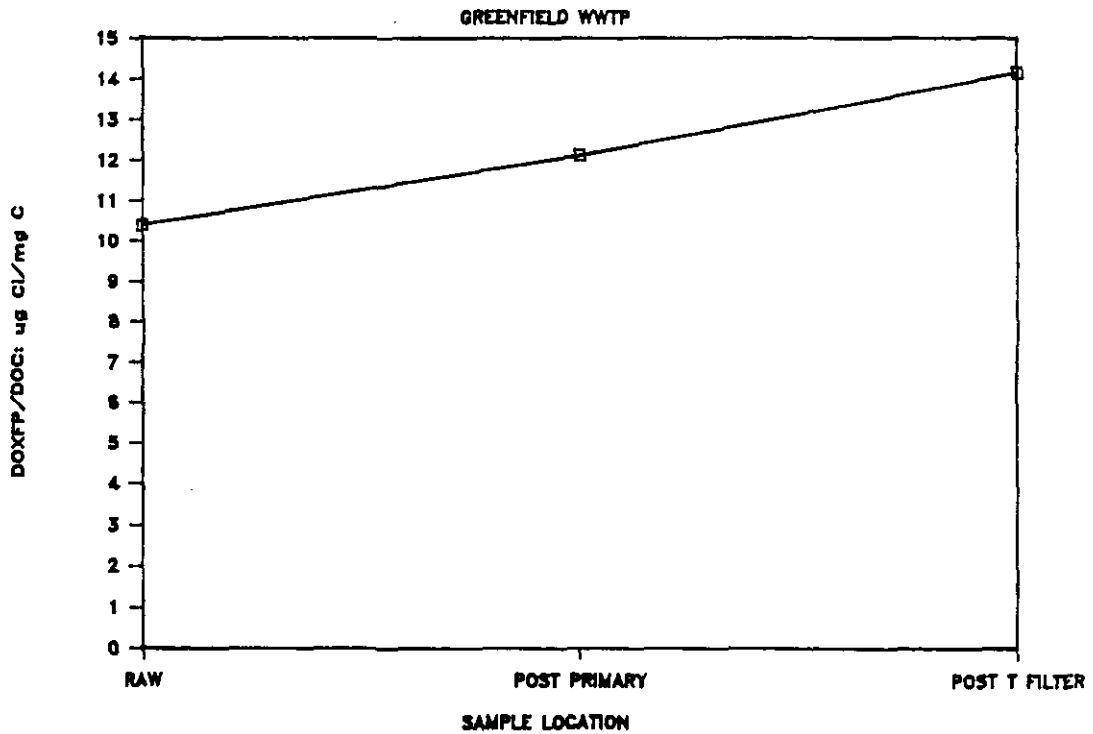




FIGURE 36: DOXFP/DOC vs. LOCATION

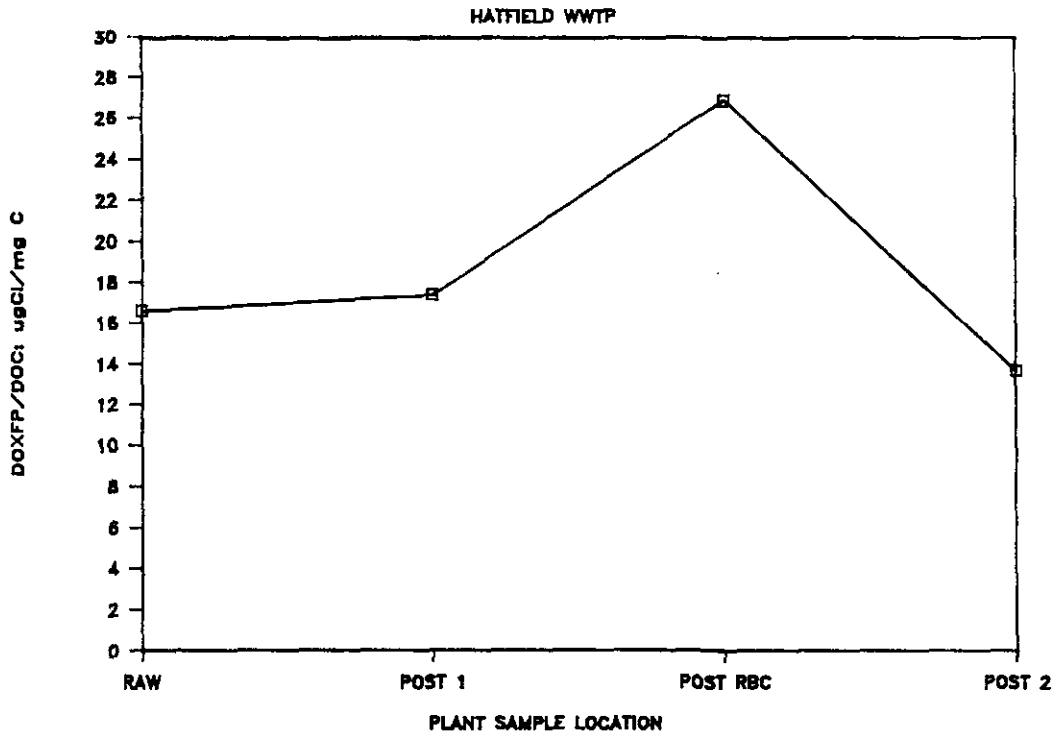


FIGURE 37: DOXFP/DOC vs. LOCATION

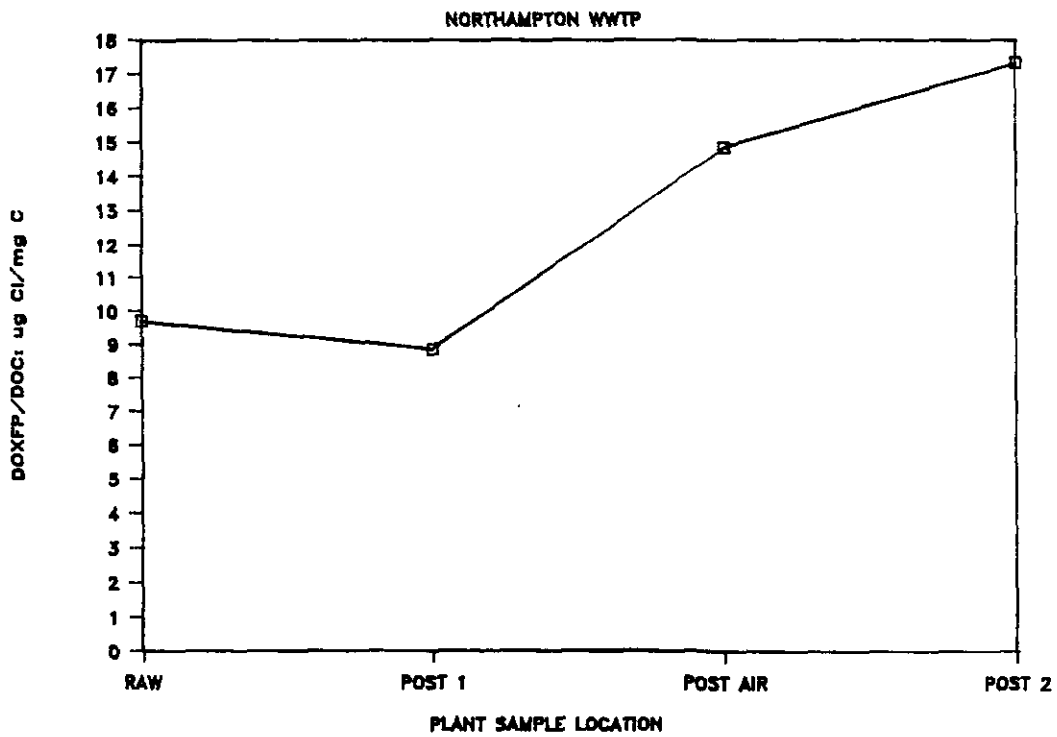
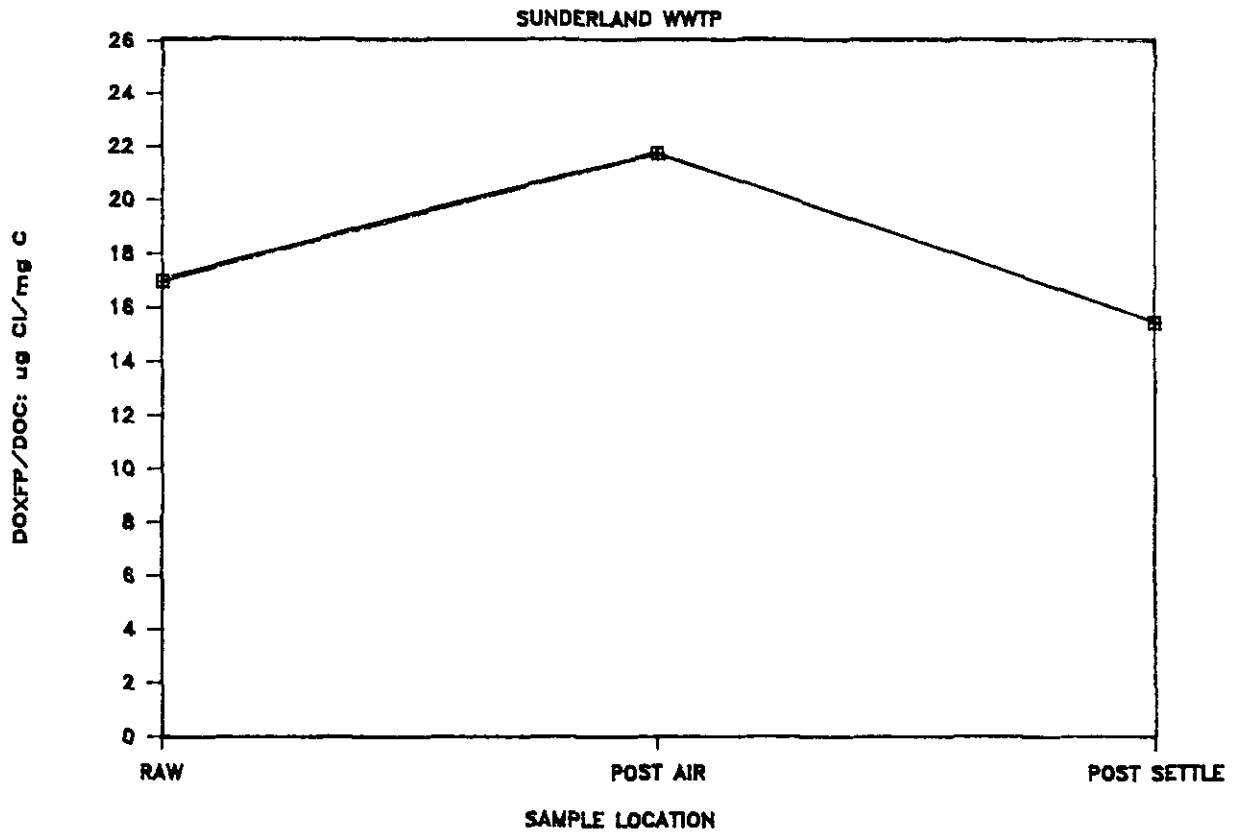


FIGURE 38: DOXFP/DOC vs. LOCATION



reaction period. Their experiments showed a DOXFP/DOC ratio of 96 to 180  $\mu\text{g Cl/mg C}$  in filtered treatment plant samples. The values in this study ranged from 10 to 50  $\mu\text{g Cl/mg C}$ , where monochloramine was used as the oxidant.

The effluent DOXFP/DOC was 1.4 times the influent DOXFP/DOC for the high DOXFP chlorine dose in the plant surveyed in Japan by Suzuki and Nakanishi (1987) (unfiltered samples). Similar results were observed in this study using filtered samples, though the effluent DOXFP/DOC ratio was close to the influent in several plants (Figures 32 to 38).

#### E. DOX Loadings To Natural Waters

The effluent survey demonstrated that several plants discharge high concentrations of DOX. The values ranged from 56 to 1527  $\mu\text{g/L}$ , with an average value of 330  $\mu\text{g/L}$  for chlorinated effluents. This average is skewed somewhat by the large values for the Erving and Holyoke sites. The Erving plant is a special case, as 95% of the flow is derived from an industrial source. The other extreme value is from the Holyoke plant. The city of Holyoke has a significant amount of industry, and this is presumed to be responsible for the high effluent DOX. Chlorinated solvents or halogenated bleaching by-products are among the compounds likely to be discharged by industrial sources to the municipal treatment plant. Many of these may not be effectively removed by primary settling and biological treatment.

The Hatfield and Greenfield effluent samples were collected on the

same day as the intra plant samples were taken. A DOX increase from 127 to 209  $\mu\text{g/L}$  was observed across the chlorine contact tank at the Greenfield plant due to plant chlorination. The Hatfield plant chlorination increased the DOX from 80 to 108  $\mu\text{g/L}$ . In comparison, the DOXFP was 499 and 296  $\mu\text{g/L}$  at the Greenfield and Hatfield plants, respectively. The significantly different values are due in part to the longer contact time for the DOXFP test. These results are similar to other values found in the literature, as shown in Table 13. For example, Brown (1985) found a net DOX increase of 50 to 150  $\mu\text{g/L}$  resulting from plant chlorination.

Table 13  
Literature Values For Wastewater DOX

<u>RAW</u> ( $\mu\text{g/L}$ )	<u>EFFLUENT RANGE</u> ( $\mu\text{g/L}$ )	<u>AVG</u>	<u>AUTHOR</u>
85	100 - 325	210	McCahill <u>et al.</u> (1980)
-	220 - 340	280	Jekel and Roberts(1980)
22	164	-	Glaze <u>et al.</u> (1975)
87 - 230	189 - 280	240	Brown (1985)
42 - 198	56 - 1527	330	this study

CHAPTER VI  
CONCLUSIONS

Based on the results of this study, the following conclusions are made:

1. In all cases DOX and DOXFP were observed to decrease as a result of wastewater treatment.
2. The average raw wastewater DOX was 150  $\mu\text{g/L}$ , and the DOXFP average was 669  $\mu\text{g/L}$ .
3. Percent removal of DOXFP was generally correlated with the percent removal of COD and DOC.
4. Removal of DOX correlated reasonably well with DOC, but pre-formed DOX present in raw wastewater was removed less effectively than bulk organic matter as measured by DOC and COD.
5. In all cases, settling basins contributed slightly to removal of DOX and DOXFP, and activated sludge treatment removed the greatest portion of DOX and DOXFP, 45% and 60% respectively.
6. DOC was found to be an accurate surrogate parameter for DOXFP. Neither DOC nor COD were satisfactory as general surrogate parameters for DOX.
7. Chlorine demand was not seen to be an accurate surrogate for organic parameters in wastewaters.
8. Increases in DOXFP/DOC following biological treatment were found to occur when DOXFP resulted from chloramination.
9. Activated sludge effected better removal of DOX and DOX precursors than the trickling filter and rotating biological contactor

studied.

10. The effluent from the 10 wastewater treatment plants surveyed had an average DOX concentration of 330  $\mu\text{g/L}$ , and a range of 56 to 1527  $\mu\text{g/L}$ .

11. High DOX values seemed to be associated with high levels of industrial activity.

## CHAPTER VII

### RECOMMENDATIONS FOR FURTHER RESEARCH

#### 1. Particulate DOX

A systematic study needs to be performed to assess the flux of DOX associated with particulates in chlorinated effluents. The fate of the DOX adsorbed to particulate matter also needs to be studied.

#### 2. DOXFP: Monochloramine versus Free Chlorine

Two separate procedures for evaluating DOXFP have been proposed. A study needs to be made to determine the correlation between the two procedures.

#### 3. Removal Mechanisms for DOX and DOXFP

Various possibilities exist for removal mechanisms of DOX and DOXFP. A study needs to assess the relative importance of adsorption, biodegradation, volatilization in removal of DOX and DOXFP.

#### 4. DOXFP/DOC

The occurrence of the increase in DOXFP/DOC following biological treatment needs to be studied, particularly with regards to the changes occurring following secondary settling. Research needs to be performed to examine the changes over time in DOXFP/DOC following biological treatment.

## REFERENCES

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater, 16th Edition, American Public Health Association, Washington, D.C., 1985.

Bellar, T. A., et al., "The Occurrence of Organohalides in Chlorinated Drinking Water," Journal American Water Works Association, 66:12:703 (1975).

Brown, R. A., "Formation of Halogenated Organics During Wastewater Chlorination," Master's Thesis, University of North Carolina at Chapel Hill, 1985.

Cheh, A.M. et al. "Nonvolatile Mutagens in Drinking Water: Production by Chlorination and Destruction by Sulfite." Science, 207:1:90-92 (1980).

Chow, B.M. and Roberts, P.V., "Halogenated Byproduct Formation by Chlorine Dioxide and Chlorine." Journal of the Environmental Engineering Division, ASCE, 107:EE4:609 (1981).

Coler, R.A., Personal Communication, 1988.



Fam, Sami and Stenstrom, M.K., "Precursors of Non-volatile Chlorination By-products." Journal Water Pollution Control Federation, 55:11:969 (1987).

Fleischacker, S.J. and Randtke, S.J., "Formation of Organic Chlorine in Public Water Supplies." Journal American Water Works Association, 75:3:132 (1983).

Glaze, W. H., and Henderson, J. E., "Formation of Organochlorine Compounds from the Chlorination of Municipal Effluent," Journal Water Pollution Control Federation, 47:10:2511 (1975).

Grady, C.P.L. Jr., et al., "Effects of Growth Rate and Influent Substrate Concentration on Effluent Quality From Chemostats Containing Bacteria In Pure and Mixed Culture," Biotechnol. Bioengng., 14:391(1972).

Haller, H.D., "Degradation of Mono-Substituted Benzoates and Phenols By Wastewater," Journal Water Pollution Control Federation, 50:2771(1978).

Hannah, S.A. et al., "Comparative Removal of Toxic Pollutants By Six Wastewater Treatment Processes," Journal Water Pollution Control Federation, 58:27(1986).

Hoehn, R.C., et al., "Algae as Sources of THM Precursors," Journal Water Pollution Control Federation, 72:344(1980).

Itoh, S., et al., "Acetoacetic Acid as a Potential Trihalomethane Precursor in the Biodegradation Intermediates Produced by Sewage Bacteria," Water Research, 19:1305 (1985).

Jekel, M.R., and Roberts, P.V., "Total Organic Halogen as a Parameter for the Characterization of Reclaimed Waters: Measurement, Occurrence, Formation, and Removal." Environmental Science and Technology, 14:8:970 (1980).

Jensen, J.N., "Characterization of the Reaction Between Monochloramine and Isolated Fulvic Acid," Master's Thesis, University of North Carolina at Chapel Hill, 1983.

Jolley, R. L., et al., "Chlorine containing organic constituents in Chlorinated Effluents," Journal Water Pollution Control Federation, 47:3:601 (1975).

Kobayashi, H. and Rittman, B.E., "Microbial Removal of Hazardous Organic Compounds," Environmental Science and Technology, 16:170A(1982).

Koczvara, M.K. et al., "Formation of Organic Chlorine in Activated Sludge Effluents," Water Research, 17:1863 (1983).

Leuenberger, et al., "Persistent Chemicals in Pulp Mill Effluents." Water Research, 19:7:885 (1985).

Manka, J., et al., "Characterization of Organics in Secondary Effluents," Environmental Science and Technology, 8:12:1017 (1974).

McCahill, M.P. et al. "Determination of Organically Combined Chlorine in High Molecular Weight Organics." Environmental Science and Technology, 14:2:201 (1980).

Meier, J.R., Lingg, R.D., and Bull, R.J., "Formation of Mutagens Following Chlorination of Humic Acid- A Model for Mutagen Formation During Drinking Water Treatment." Mutation Research, 118:25- 41 (1983).

Miller, J. W., and Uden, P. C., "Characterization of the Non-volatile Aqueous Chlorination Products of Humic Substances," Environmental Science & Technology, 17:10:625 (1983).

Morris, J., "Formation of Halogenated Organics by Chlorination of Water Supplies: A Review," United States Environmental Protection Agency, EPA-600/1-75-002.

Morris, J., "Kinetics of Reactions Between Aqueous Chlorine

and Nitrogen Compounds," Principles and Applications of Water Chemistry, (S.D. Faust and J.V. Hunter, Editors), John Wiley and Sons, N.Y., N.Y. (1967).

Paller, M.H. et al. "Effects of Ammonia and Chlorine on Fish in Streams Receiving Secondary Discharges." Journal Water Pollution Control Federation, 55:8:1087 (1983).

Parkin, G.F. and McCarty, P.L., "Sources Of Soluble Organic Nitrogen in Activated Sludge Effluents," Journal Water Pollution Control Federation, 53:89(1981).

Parkin, G.F. and McCarty, P.L., "Production Of Soluble Organic Nitrogen During Activated Sludge Treatment," Journal Water Pollution Control Federation, 53:99(1981).

Petrasek, A., et al., "Fate of Toxic Organic compounds in Wastewater Treatment Plants." Journal Water Pollution Control Federation, 55:10:1286 (1983).

Pitter, P., "Determination of Biological Degradability of Organic Substances," Water Research, 10:231 (1976).

Reckhow, D.A., "Organic Halide Formation and the Use of Pre-Ozonation and Alum Coagulation To Control Organic Halide Precursors," PhD Dissertation, University of North Carolina at Chapel Hill, (1984).

Strupler, N. "A Study of Interferences in the Measurement of Free and Combined Chlorine in Water By the DPD and Syringaldazine Methods." Proceedings of the AWWA Water Quality Technology Conference, Louisville, Kentucky(1978).

Suzuki, N. and Nakanishi, J., "Total Organic Halogen Formation Potentials in Activated Sludge Treatment and Small Rivers." Journal Water Pollution Control Federation, 59:8:767 (1987).

Takahashi, Y., et al. "The Measurement of Total Organic Halides (TOX) and Purgeable Organic Halides (POX) in Water Using Carbon Adsorption and Microcoulometric Titration." Presented before the Division of Environmental Chemistry at the 1980 Conference of the American Chemical Society, March 23-28, Houston, TX.(1980).

White, G.C., Handbook of Chlorination. VanNostrand-Reinhold Co., New York, N.Y. (1972).

WPCF Disinfection Committee, "Disinfection Case Studies," Journal Water Pollution Control Federation, 59:860(1987).

Yamada, H. and Somiya, I., "Evaluation of Precursors of Halogenated Organics and Volatile Halogenated Organics in a Municipal Wastewater Treatment." Japanese Journal Water Pollution Research, 7:4:239 (1984).

Yamada, H. and Somiya, I., "Evaluation of Organic Halide Precursor Produced with the Activated Sludge." Japanese Journal Water Pollution Research, 8:4:223 (1985).

Yamada, H. and Somiya, I. "Evaluation of Organic Chloride Precursor Produced through Contact Oxidation-Biological Filtration Process." Japanese Journal Water Pollution Research, 8:4:239 (1985).

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

APPENDIX

RAW DATA

APPENDIX: AMHERST DATA: JANUARY

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O <sub>2</sub> /L	DOC mg C/L	NH <sub>3</sub> -N mg N/L	TKN mg N/L
RAW	7.3	150	44.4	14.80	29.00
POST 1	7.3	130	40.7	20.60	26.20
POST AIR	7.0	25	7.8	9.00	11.00
POST 2	6.9	25	7.8	7.50	8.40

ORGANIC N mg N/L	DOX ug Cl <sub>2</sub> /L	TERMINAL DOX ug Cl <sub>2</sub> /L	DOXFP ug Cl <sub>2</sub> /L	COMBIN. Cl <sub>2</sub> RES ug Cl <sub>2</sub> /L
14.20	198.0	812	614	22.1
5.60	188.0	768	580	17.9
2.00	98.9	437	338	17.7
0.90	88.8	317	228	17.3

Cl <sub>2</sub> DEMAND ug Cl <sub>2</sub> /L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFP (PROCESS)	DELTA % COD (PROCESS)
17.9	3.4	-	-	-
22.1	2.6	5.1	5.5	13.3
22.3	1.5	45.0	39.4	70.0
22.7	1.0	5.1	17.9	0.0

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFP OF RAW	% COD OF RAW	% DOC OF RAW	ORG N/DOC mg/mg
-	100.0	100.0	100.0	100.0	0.32
8.3	94.9	94.5	86.7	91.7	0.14
74.1	49.9	55.0	16.7	17.6	0.26
0.0	44.8	37.1	16.7	17.6	0.12

DOXFP/DOC  
ug Cl/mg DOC

=====  
13.8  
14.3  
43.3  
29.2



AMHERST DATA: JUNE

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O <sub>2</sub> /L	DOC mg C/L	NH <sub>3</sub> -N mg N/L	TKN mg N/L
RAW	6.9	166.0	59.8	16.5	19.1
POST 1	6.8	143.0	58.0	16.4	19.7
POST AIR	6.8	30.0	13.5	6.2	7.0
POST 2	6.6	30.0	13.5	3.0	3.8

ORGANIC N mg N/L	DOX ug C12/L	TERMINAL DOX ug C12/L	DOXFP ug C12/L	COMBIN. C12 RES mg C12/L
2.6	169.6	637.0	467.4	16.9
1.3	141.4	645.5	504.1	24.4
0.8	84.4	246.5	162.1	28.7
0.8	69.5	256.6	187.1	23.4

C12 DEMAND mg C12/L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFP (PROCESS)	DELTA % COD (PROCESS)
23.1	2.0	0.0	0.0	0.0
15.6	3.2	16.6	-7.9	13.9
11.3	1.4	33.6	73.2	68.1
16.6	1.1	8.8	-5.3	0.0

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFP OF RAW	% COD OF RAW	% DOC OF RAW	ORG N/DOC mg/mg
0.0	100.0	100.0	100.0	100.0	0.044
3.0	83.4	107.9	86.1	97.0	0.022
74.4	49.8	34.7	18.1	22.6	0.059
0.0	41.0	40.0	18.1	22.6	0.059

DOXFP/DOC  
ug C1/mg

7.8
8.7
12.0
13.9

BELCHERTOWN DATA

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O <sub>2</sub> /L	DOC mg C/L	NH <sub>3</sub> -N mg N/L	TKN mg N/L
RAW	7.4	270	61.5	13.30	21.70
POST AIR	6.8	68	6.6	0.19	1.38
POST 2	6.7	255	7.8	0.09	1.31
POST PONDS	7.0	162	8.4	1.30	2.44

ORGANIC N mg N/L	DOX ug Cl <sub>2</sub> /L	TERMINAL DOX ug Cl <sub>2</sub> /L	DOXFP ug Cl <sub>2</sub> /L	COMBINED Cl <sub>2</sub> ug Cl <sub>2</sub> /L
8.40	130.0	1030	900	17.9
1.19	51.3	332	281	34.3
1.22	52.1	218	166	38.7
1.14	45.9	192	146	36.2

Cl <sub>2</sub> DEMAND ug Cl <sub>2</sub> /L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFP (PROCESS)	DELTA % COD (PROCESS)
22.1	4.1	-	-	-
5.7	4.9	60.5	68.8	74.8
1.3	12.8	-0.6	12.8	-69.3
3.8	3.8	4.8	2.2	34.4

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFP OF RAW	% COD OF RAW	% DOC OF RAW	ORG-N/DOC mg/mg
-	100.0	100.0	100.0	100.0	0.137
89.3	39.5	31.2	25.2	10.7	0.180
-2.0	40.1	18.4	94.4	12.7	0.156
-1.0	35.3	16.2	60.0	13.7	0.136

DOXFP/DOC  
ug Cl/mg

=====  
14.6  
42.6  
21.3  
17.4

GREENFIELD DATA

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O2/L	DOC mg C/L	NH3-N mg N/L	TKN mg N/L
RAW	7.1	186	89.0	15.2	18.6
POST PRIMARY	7.2	160	64.5	19.9	27.0
POST T FILTER	7.6	80	35.2	20.5	23.2

ORGANIC N mg N/L	DOX ug C12/L	TERMINAL DOX ug C12/L	DOXFP ug C12/L	COMBINED C12 ug C12/L
3.5	118.8	1044.0	925	16.7
7.1	191.6	974.5	783	15.2
2.7	127.1	625.6	499	18.0

C12 DEMAND ug C12/L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFP (PROCESS)	DELTA % COD (PROCESS)
23.3	4.0	-	-	-
24.8	3.2	-61.3	15.4	14.0
22.0	2.3	54.3	30.7	43.0

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFP OF RAW	% COD OF RAW	% DOC OF RAW	ORG-N/DOC mg/mg
-	100.0	100.0	100.0	100.0	0.039
27.5	161.3	84.6	86.0	72.5	0.110
32.9	107.0	53.9	43.0	39.6	0.077

DOXFP/DOC ug C1/mg
10.4
12.1
14.2

HATFIELD DATA

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O2/L	DOC mg C/L	NH3-N mg N/L	TKN mg N/L
RAW	7.1	54.0	35.2	11.3	12.80
POST 1	7.2	50.0	32.9	11.4	12.60
POST RBC	7.1	50.0	15.3	3.5	3.80
POST 2	7.2	30.0	21.7	2.0	2.20

ORGANIC N mg N/L	DOX ug Cl2/L	TERMINAL DOX ug Cl2/L	DOXFP ug Cl2/L	COMBIN. Cl2 RES mg Cl2/L
1.50	192.8	776.9	584.1	17.0
1.20	143.1	714.7	571.6	19.2
0.30	113.8	524.8	411.0	16.3
0.20	79.6	375.3	295.7	10.3

Cl2 DEMAND mg Cl2/L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFP (PROCESS)	DELTA % COD (PROCESS)
23.0	2.5	-	-	-
20.8	2.7	25.6	2.1	7.4
23.7	1.7	15.2	27.5	0.0
29.7	1.0	17.7	19.7	37.0

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFP OF RAW	% COD OF RAW	% DOC OF RAW	ORG N/DOC mg/mg
-	100.0	100.0	100.0	100.0	0.043
6.3	74.2	97.9	92.6	93.5	0.036
50.0	59.0	70.4	92.6	43.5	0.020
-18.2	41.3	50.6	55.6	61.6	0.009

DOXFP/DOC  
ug Cl/mg

16.6
17.4
26.9
13.6

NORTHAMPTON DATA

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O2/L	DOC mg C/L	NH3-N mg N/L	TKN mg N/L
RAW	6.8	214	65.8	20.5	22.4
POST 1	6.7	162	62.5	19.5	20.4
POST AIR	6.9	50	11.6	17.7	20.2
POST 2	6.8	50	9.9	16.0	18.4

ORGANIC N mg N/L	DOX ug C12/L	TERMINAL DOX ug C12/L	DOXFP ug C12/L	COMBIN. C12 RES mg C12/L
1.9	196.2	834.4	638.2	12.2
0.9	178.6	732.4	553.8	20.8
2.5	78.8	251.4	172.6	31.0
2.4	72.2	244.0	171.8	30.2

C12 DEMAND mg C12/L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFP (PROCESS)	DELTA % COD (PROCESS)
27.8	2.3	-	-	-
19.2	2.9	9.0	13.2	24.3
9.0	1.9	50.9	59.7	52.3
9.8	1.8	3.4	0.1	0.0

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFP OF RAW	% COD OF RAW	% DOC OF RAW	ORG N/DOC mg/mg
0.0	100.0	100.0	100.0	100.0	0.03
5.0	91.0	86.8	75.7	95.0	0.01
77.4	40.2	27.0	23.4	17.6	0.22
2.6	36.8	26.9	23.4	15.0	0.24

DOXFP/DOC  
ug C1/mg

9.7
8.9
14.9
17.4

SUNDERLAND DATA

GRAB SAMPLE LOCATION	FILTERED pH	COD mg O <sub>2</sub> /L	DOC mg C/L	NH <sub>3</sub> -N mg N/L	TKN mg N/L
RAW	7.5	102	32.6	30.10	27.20
POST AIR	6.6	54	12	0.59	2.18
POST SETTLE	6.9	58	13.7	0.81	3.86

ORGANIC N mg N/L	DOX ug C12/L	TERMINAL DOX ug C12/L	DOXFF ug C12/L	COMBINED C12 ug C12/L
0.00	42.2	596	554	16.4
1.59	50.7	312	261	33.6
3.05	44.8	257	212	14.6

C12 DEMAND ug C12/L	% CHLORINE INCORPORATED	DELTA % DOX (PROCESS)	DELTA % DOXFF (PROCESS)	DELTA % COD (PROCESS)
23.6	2.3	-	-	-
6.4	4.1	-20.1	52.9	47.1
25.4	0.8	14.0	8.8	-3.9

DELTA % DOC (PROCESS)	% DOX OF RAW	% DOXFF OF RAW	% COD OF RAW	% DOC OF RAW	ORG-N/TOC mg/mg
-	100.0	100.0	100.0	100.0	0.000
63.2	120.1	47.1	52.9	36.8	0.133
-5.2	106.2	38.3	56.9	42.0	0.223

DOXFF/DOC  
ug C1/mg

17.0
21.8
15.5