Electronic Theses and Dissertations   Theses, Dissertations, and Major Papers

1996

Formation and removal of aldehydes as ozonation by-products in a pilot-scale water treatment plant.

Stephan. Cervi
University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

FORMATION AND REMOVAL OF ALDEHYDES AS OZONATION BY-PRODUCTS IN A PILOT SCALE WATER TREATMENT PLANT

by

Stephan Cervi

A Thesis
Submitted to the Faculty of Graduate Studies and Research
through the Department of Civil and Environmental Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science at the
University of Windsor

Windsor, Ontario, Canada

1996

ABSTRACT

This study investigated the effect of water treatment plant configurations on the formation and removal of aldehydes in a pilot water treatment plant located in Windsor, Ontario, Canada. The plant was operated in non-ozonation, pre-coagulation ozonation, and post-sedimentation ozonation treatment configurations, and ozone dose and flowrate through the anthracite/sand filters were studied to determine the effect on formation and removal of aldehydes in the pilot plant. It was found that formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal were the main aldehyde species formed as a result of ozonation, with formaldehyde usually being found to be formed at the highest concentrations. Aldehyde formation was found to increase as ozone dose was increased.

For removal of aldehydes, it was found that aldehydes were removed marginally in anthracite/sand filtration, and an increase in temperature caused an increase in removal. It was found that low-molecular-mass aldehydes usually decreased, while high-molecular-mass aldehydes only slightly decreased or even increased in anthracite/sand filters, showing that glyoxal and methyl-glyoxal were more difficult to remove in anthracite/sand filtration. Aldehydes consistently showed complete removal in GAC contactors. Finally, at low

flowrates through the anthracite/sand filters, there appeared to be a minimum

level of aldehydes present in the anthracite/sand filters.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AOC = Assimilable organic carbon

AWWARF = American Water Works Association Research Foundation

CGEaux = Compagnie Générale des Eaux

CLSA = Closed loop stripping analysis

D/DBP Rule = Disinfectant/Disinfection By-Product Rule

DOC = Dissolved organic carbon

ECD = Electron capture detector

GAC = Granular activated carbon

GC = Gas chromatography

HAAs = Haloacetic acids

HPLC = High-performance liquid chromatography

LAAW = Los Angeles Aqueduct Water

MCL = Maximum contaminant limit

MOEE = Ontario Ministry of Environment and Energy

NOM = Natural organic matter

PFBHA-HCl = $\underline{O}$ - (2, 3, 4, 5, 6 - pentafluorobenzyl) - hydroxylamine hydrochloride

PFBO = Pentafluorobenzyloxime

PTFE = Polytetrafluorethylene (Teflon)

SOCs = Synthetic organic chemicals

SPW	=	State Project Water
TOC	=	Total organic carbon
USEPA	=	United States Environmental Protection Agency
UV	=	Ultraviolet
WUC	=	Windsor Utilities Commission
WWTP	=	Windsor Water Treatment Plant

Chapter I

INTRODUCTION

1.1. Background

In water treatment, the primary objective is to provide a community with water that is both safe to drink and aesthetically acceptable. In order to provide safe water in most cases, disinfection of the water source must be carried out. Disinfection implies the inactivation or the elimination of harmful or objectionable organisms (pathogens). Since its first continuous use as a primary disinfectant in Middelkerke, Belgium in 1902 (White, 1972), chlorine has been perhaps the most popular disinfectant used in water treatment to this date. However, in addition to reacting with pathogenic microorganisms, chlorine may combine with other compounds in the water to form chlorinated by-products. These by-products may or have been proven to produce harmful health effects in humans. One of the most widely known groups of chlorinated by-products is the trihalomethanes (THMs). THMs consist of four different compounds: chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$). In 1974, Rook (1974) and Bellar & Lichtenberg (1974) reported the possible occurrence of significant amounts of THMs produced in drinking waters as a result of chlorination. A study in the USA by the United States Environmental Protection Agency (USEPA) confirmed this report (Symons

1

et al., 1975), and as a result, in 1979 the USEPA set a maximum contaminant limit (MCL) for total THMs at 100 µg/L based on treatment capabilities (USEPA, 1979). In 1990, the USEPA classified chloroform, bromodichloromethane, and dibromochloromethane as probable human carcinogens (Class B2 cancer group), and classified bromoform as a possible human carcinogen (Class C cancer group) (Pontius, 1990). It is anticipated that new MCLs for total THMs will be set between 80 and 40 µg/L (Pontius, 1993). In Canada, the limit for total THMs in drinking water has been regulated at 350 µg/L (Minister of National Health and Welfare, 1993). It is proposed to apply a maximum limit of 100 µg/L for total THMs in the future (CWWA, 1992). Because of the increased regulation of THMs and other chlorinated by-products such as haloacetic acids (HAAs), new strategies have come into existence in order to minimize chlorinated by-products. One of the more promising options is to replace chlorine with an alternate disinfectant such as ozone.

1.2. Use Of Ozone In Water Treatment

Ozone was first used in drinking water treatment in 1893 in Oudshoorn in the Netherlands. By 1990, there were close to 75 water treatment plants in Canada and the United States with ozonation facilities, and many more plants exist worldwide, especially in Western Europe (AWWARF and CGEaux, 1991). In more recent years, the use of ozonation in drinking water treatment has been steadily increasing in the United States. The replacement of chlorination with

2

ozonation has the attractive advantage of not producing chlorinated by-products such as THMs and HAAs, which is a great concern considering the present and impending strict regulation of these compounds. Ozone is a strong disinfectant, as well as an effective oxidizing agent capable of destroying several taste-and-odor-causing compounds (Ferguson *et al.*, 1991). Its disinfecting strength in comparison to other popular disinfectants is shown in Table 1.1, where the comparisons are made based on C•t values. C•t values express a dosage value required to inactivate an organism where 'C' represents the disinfectant's concentration in the water (usually measured in mg/L) and 't' represents the effective contact time the disinfectant remains in the presence of the organism (usually measured in minutes).

Water treatment plants are and have been considering the switch from chlorine to ozone in recent years. However, ozone may also form several organic and inorganic by-products that are becoming a growing concern, and investigations must be carried out in order to determine ozonation's viability as a safe disinfection or oxidation alternative.

1.3. Ozonation By-Products

Similar to chlorine, ozone reacts with inorganic and organic matter in the source water that is being disinfected to form unwanted and possibly harmful by-products. Relative to the chlorinated by-products, there is still much that is unknown about ozonation by-products with respect to their harmful effects on

Disinfectant

Microorganism	Free chlorine pH 6-7	Preformed chloramine pH 8-9	Chlorine dioxide pH 6-7	Ozone pH 6-7
E. coli	0.034-0.05	95-180	0.4-0.75	0.02
Polio 1	1.1-2.5	770-3700	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3800-6500	0.2-2.1	0.006-0.06
G. lambia cysts	47->150	---	---	0.5-0.6
G. muris cysts	30-630	---	7.2-19	1.8-2.0

Source: Hoff, 1986

Table 1.1 - Summary of C ∗ t value ranges for 99% inactivation of various microorganisms by disinfectants at 5 degrees Celsius.

4

humans. The USEPA has cited ozonation by-products as a generic class of compounds for regulatory consideration because of their suspected potential health effects (USEPA, 1988). The toxicity of aqueous ozonation by-products on mammals has not been greatly studied. The first ozonation by-product that will be regulated as part of the Disinfectant/Disinfection By-Product (D/DBP) Rule in the United States is bromate; proposed to be regulated at a level of 10 µg/L. Bromate is a known animal carcinogen (Kurokawa *et al.*, 1986), and is formed as a result of a series of complex reactions between ozone and bromide ions present in the water being ozonated (Haag & Hoigne, 1983). In Windsor, where this research took place, the level of bromide ions in the water is low enough to not form any significant levels of bromate (Alarcon Herrera, 1994). However, there are other ozonation by-products that are also of concern; these include aldehydes, ketoacids (also known as oxoacids), and carboxylic acids. All of these organic by-products are formed through the reaction of ozone with natural organic matter (NOM) in some way or another. Since all natural drinking water supplies have some level of NOM present, these by-products may occur in many water treatment plants where ozonation is employed. Windsor is such a place where there is sufficient NOM present in the raw water to form significant amounts of ozonation by-products. More will be discussed on ozonation by-products in the following chapter.

5

1.4. Pilot Plant

There is little or no information available regarding levels of ozonation by-products formed as a result of ozonation of Windsor's drinking water source - the Detroit River. Therefore, it was decided that a study of the formation and removal of these by-products would be useful. Since there is an existing pilot plant located inside the Windsor Water Treatment Plant (WWTP) in Windsor, Ontario, Canada (in close proximity to the University of Windsor) there was an opportunity to study ozonation by-products and their behavior in a water treatment plant quite easily. The pilot plant, which is being used to evaluate advanced oxidation processes, such as ozonation, is operated by the Windsor Utilities Commission (WUC) and is sponsored by the Ontario Ministry of Environment and Energy (MOEE). The pilot plant will be discussed in greater detail in Chapter III - Methodology.

1.5. Research Objectives

The specific objectives of this research were to:

- determine the effect of various ozonation treatment configurations on the formation and removal of ozonation by-products, specifically aldehydes, in a pilot plant located in Windsor, Ontario, Canada;

- determine the effect of filtration on the removal of these ozonation by-products;

- determine the effect of ozone dose on the formation and removal of ozonation by-products;

- determine the effect of flowrate through anthracite/sand filters on the formation and removal of ozonation by-products; and

- determine the effect, if any, of pH, temperature, and turbidity on the formation and removal of ozonation by-products.

Chapter II

LITERATURE SURVEY

2.1. Ozone

Ozone is a metastable molecule produced from elemental oxygen, and readily decomposes in most matrices. Because of its rapid decomposition, in order for ozone to be used in any application it must be generated on site. Ozone has been used in full-scale drinking water treatment since 1893 (AWWARF and CGEaux, 1991). Since ozone is a powerful oxidant, it has had many applications in drinking water treatment. These include: disinfection, taste and odor control, oxidation of iron and manganese, color removal, as a coagulant aid in particulate removal, oxidation of phenolic compounds and pesticides, and control of algal growth. Recently, ozone has been found to be practical for the applications of disinfection by-product control, biological stabilization (minimization of the microbiological growth potential of the water), and the control of certain types of organic compounds, mainly synthetic organic chemicals (SOCs). Ozone has become a very popular disinfection and oxidation option for use in drinking water. As of 1990, there were close to 75 water treatment plants in Canada and the United States with ozonation facilities, and many more plants exist worldwide, especially in Western Europe (AWWARF and CGEaux, 1991).

2.2. Production of Ozone

The overall reaction representing the formation of ozone is described by the following endothermic reaction (Masschelein, 1982):

$$3O_2 \rightarrow 2O_3 \quad (\Delta H° \text{ at } 1 \text{ atm} = +285 \text{ kJ/mol})$$
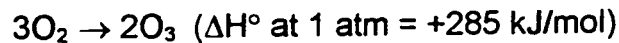
Ozone cannot be produced by adding thermal energy to oxygen; the addition of heat only accelerates the decomposition of ozone. Therefore, ozone must be generated from oxygen by using other forms of energy. These energy sources can consist of electrons or photon quantum energy. Electrons can be used from high-voltage sources in a silent corona discharge, from chemonuclear sources, and from electrolytic processes. Photon quantum energy includes ultraviolet (UV) light of wavelengths lower than 200 nm and gamma-rays (AWWARF and CGEaux, 1991).

In water treatment, ozone must be generated on-site because of its fairly rapid decomposition in a gaseous or liquid matrix. Corona discharge in a dry process gas is presently the most widely used method of generation of ozone for water treatment plants. A silent electrical discharge, frequently described as a corona discharge, is maintained between two electrodes separated by a dielectric material (glass or ceramic) and an air gap by applying a high voltage across the electrodes. At the frequency used, this voltage is held at a value between the threshold at which the oxygen bearing feed gas ionizes, producing ozone, and the value at which the dielectric material will break down - its "dielectric strength". Figure 2.1 shows a typical corona discharge apparatus.
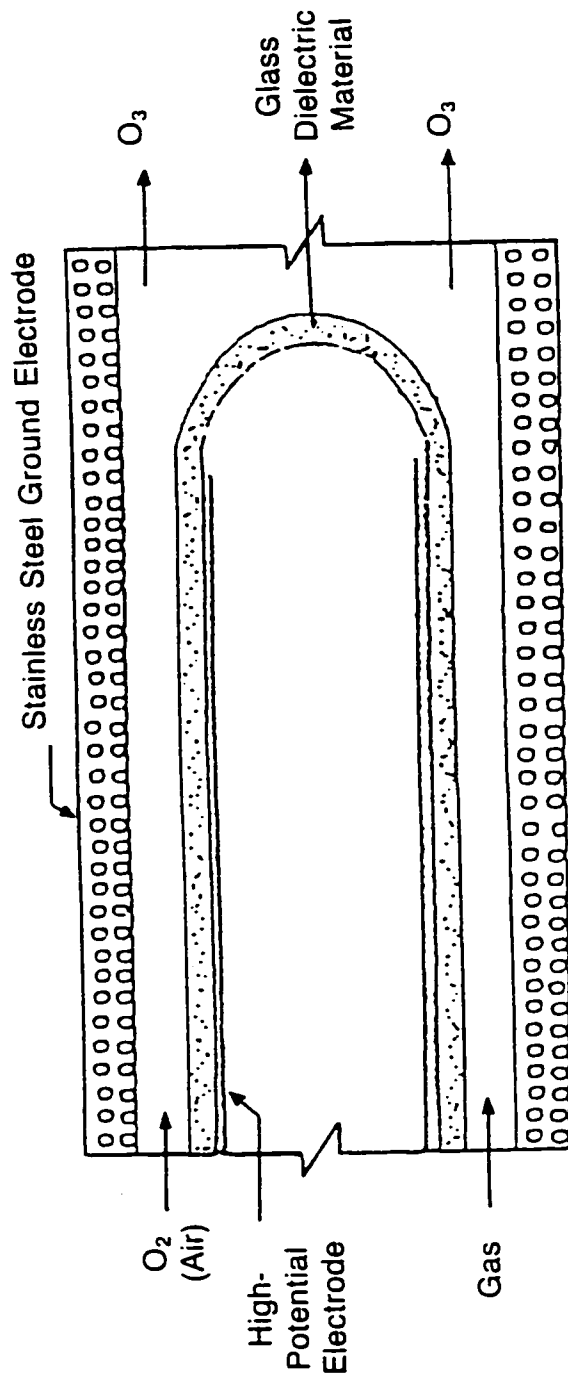
Figure 2.1 - Schematic of corona discharge gap.

Source: AWWARF and CGEaux, 1991

2.3. Ozone Chemistry

Ozone is a powerful oxidant; that is, it is unstable in water according to:

$$O_{3(g)} + 2H^+ + 2e^- \rightarrow H_2O + O_{2(g)} ; \quad e^\circ = +2.076 \text{ V}$$

or $\quad O_{3(g)} + 6H^+ + 6e^- \rightarrow 3H_2O ; \qquad e^\circ = +1.511 \text{ V}$
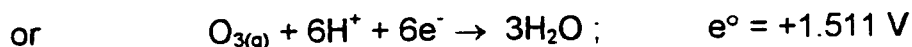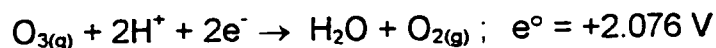
The standard potential (e°) values for these two reactions exceed the one for oxygen ($e^\circ = +1.228$ V). Consequently, ozone exhibits great instability and strong oxidative properties in water. In practice, on-site generation of ozone by an electrical discharge in air or oxygen produces 1 - 2 percent ozone when air is used and 3 - 5 percent ozone when pure oxygen is used. Ozone is moderately soluble in water; 0.494 m^3/m^3 at 0°C. Ozone has a half-life of about 40 minutes in distilled water at pH 7.6 and 14.6°C. At pH 8.5, the half-life is 10 minutes.

In an aqueous solution, ozone may act on various compounds in the following two ways (Hoigne and Bader, 1977):

- by direct reaction with molecular ozone; and

- by indirect reaction with the radical species that are formed when ozone decomposes in water.

Figure 2.2 shows these two basic reactions of ozone in water.

The latter reaction pathway, that is the auto-decomposition of ozone in water, is a very complex combination of a number of phenomena. These may be (Mallevialle, 1982a):

- the transfer of ozone from the gas to the liquid phase;

Figure 2.2 - Reactivity of ozone in aqueous solution.
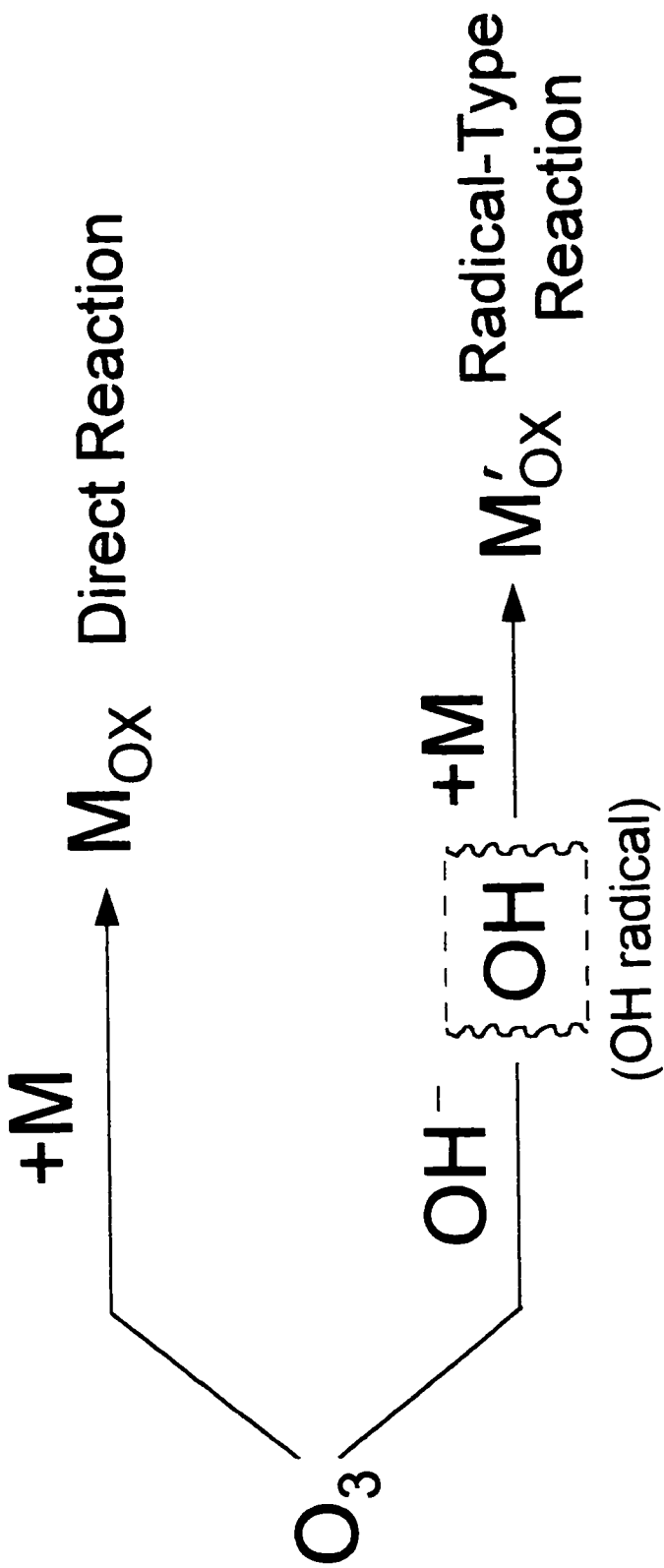
where:

M = any compound

M_{OX} = oxidized compound (direct reaction with ozone)

M'_{OX} = oxidized compound (radical reaction with ozone)

Source: AWWARF and CGEaux, 1991

12

- the relation between the partial pressure of the gaseous ozone and its solubility in aqueous solution;

- the mass transfer of the ozone dissolved to trace impurities present in the water;

- the kinetics of the auto-decomposition of ozone in solution; and

- the kinetics of the oxidation by ozone of the impurities in the water.

Several workers studying the mechanisms of the auto-decomposition of ozone have suggested different intermediate stages in the process. Radical species most often involved are (Mallevialle, 1982a):

$$O_3 + OH^- \rightarrow O_2^- + HO_2$$
$$O_3 + H_2O \rightarrow H_3O^+ + OH^- = 2HO_2$$
$$O_3 + OH^- \rightarrow O^- \cdot O \cdot O \cdot OH$$
$$O_3 + 2OH^- \rightarrow O_2 + 2O^- + H_2O$$
$$O_3 + OH^- \rightarrow O_3^- + OH$$
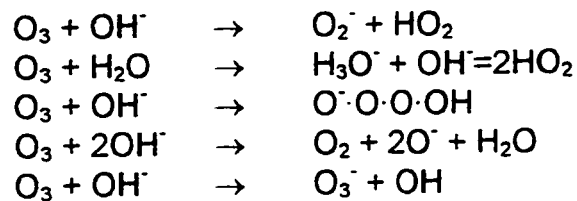
All of these reactions follow various reaction kinetics corresponding to different ranges of temperature and pH. It should be noted that of all the intermediate species formed in the decomposition of ozone, the OH radical is the most significant radical intermediate formed, and therefore plays a substantial role in reactions with ozonation by-product precursors in water (Hoigne, 1988).

2.4. Ozonation By-Products

Both of ozone's reaction pathways (the direct, molecular ozone pathway, and the free radical pathway, resulting from the complex decomposition of

ozone) are likely to play a role in the formation of ozonation by-products in natural waters. Ozone can form by-products by reacting with both organic and inorganic contaminants in drinking water. This research work only investigates one of the most prevalent group of organic ozonation by-products (aldehydes), and thus inorganic ozonation by-products will not be discussed.

2.4.1. Organic Ozonation By-Products

Molecular ozone can react directly with organic compounds through reactions that are highly selective, having second-order rate constants ranging over 12 orders of magnitude. Hoigne and Bader (1983a, 1983b) have investigated many of these reactions and compiled a list of second-order rate constants for a variety of organic compounds. In general, in drinking water treatment, activated aromatic compounds, olefins, and simple amines would be expected to react quickly with the molecular form of ozone.

Ozone can also react with organic compounds indirectly through decomposition, producing free radical species which oxidize the organic contaminants. These indirect radical-type reactions tend to be very fast and nonselective, with second-order rate constants varying over two to three orders of magnitude. Organic compounds slow to react with molecular ozone, such as aliphatic acids, aldehydes, ketones, and less highly activated aromatics, are more likely to react via this pathway (Singer, 1990).

In the ozonation of natural waters, it is difficult to determine which of ozone's two reaction pathways dominates in a particular situation, although it appears most likely that the radical pathway plays a dominant role in most oxidation reactions involving ozone in natural waters (Glaze, 1986a).

Many studies have been conducted involving the oxidation of model organic compounds by ozone (Bailey, 1978, 1982; Eisenhauer, 1968; Hoigne and Bader, 1983a, 1983b; Yamamoto, 1979). Much of these have been performed in nonaqueous solvents, so it is difficult to find information on reaction mechanisms, pathways, and by-product identification in aqueous solutions. However, some studies have been performed in aqueous solutions with natural organic matter, which serves as the major precursor material for production of ozonation by-products in natural waters.

Natural organic matter (NOM) consists mainly of humic substances, which come from naturally occurring plant and animal decay products or any other carbon source. Aquatic humic substances are found naturally in all aquatic environments and consist mainly of humic and fulvic acids, the structures of which are generally not well defined. The composition and distribution of aquatic humic substances varies greatly in natural waters and thus characterization and concentration can only be studied for specific waters. Because NOM can be found in any source water, is the dominant fraction of total organic carbon (TOC) in most waters, and will always react with ozone used

during water treatment, it is important that the reaction of ozone and NOM be studied.

Several researchers have attempted to identify ozonation by-products of isolated samples of humic acid and fulvic acid, and some have oxidized the entire mix of organics in natural waters (Lawrence *et al.*, 1980; Mallevialle *et al.*, 1978; Shevchenko and Taran, 1966; Sievers *et al.*, 1977). In a review of these studies, Glaze (1986a) has indicated that the ozone molecule can directly attack the humic material at three types of sites: carbon-carbon double bonds, aromatic rings that are activated with phenolic groups, and sites containing complexed metals. In addition, humic substances can act as initiators to generate radical intermediates from ozone that may then participate in nonselective oxidation reactions. The products from these reactions would most likely be formed from reactions with the hydroxyl radical and would include hydroxylation reactions of benzene rings that would otherwise be nonreactive to molecular ozone. These rings would then be more prone to further oxidation, and the principal end products would be low-molecular-mass acids and aldehydes, which are relatively unreactive toward ozone (Glaze, 1986a). In summary, the reaction of ozone with humic substances proceeds through reactions that involve both the direct and indirect pathways.

In water treatment plants, smaller amounts of ozone are used than would be necessary to fully mineralize complex humic and fulvic precursor substances. A typical ozone to carbon ratio is about 1.2 mg O_3/mg C (AWWARF and

CGEaux, 1991). At this level, complete ozonation of humic and fulvic substances is not achieved, but a change does occur. Ozonated humic substances are different than the raw humic substances, in that more lower-molecular-mass, polar compounds exist than before, and high-molecular-mass compounds are decreased. This is due to the conversion of high-molecular-mass compounds to lower-molecular-mass compounds by oxidation with ozone. Since it has been difficult to quantify and identify these lower-molecular-mass compounds, the resources for understanding ozonation by-products are relatively limited.

2.4.2. Health Effects

The USEPA has cited ozonation by-products as a generic class of compounds for regulatory consideration because of their believed potential health effects (USEPA, 1988). The toxicity of aqueous ozonation by-products on mammals has not been greatly studied. In one study of ozonated and ozonated/chlorinated humic acids toxicity on Sprague-Dawley rats, minor toxicological effects were observed, including increased serum calcium, phosphate and glucose levels, as well as changes in liver mass and thyroid lesions (Daniel *et al.*, 1991). However, it was concluded that no definitive statement regarding the relative toxicity of ozonated versus chlorinated humics could be made.

17

Researchers have examined the ozonation of humic acids, fulvic acids, and other organics and reported that mutagenicity was sometimes found and sometimes not (Kowbel *et al.*, 1982, 1984; Kamei *et al.*, 1985; Somiya and Yamada, 1987; Yamada and Somiya, 1989). Matsuda *et al.* (1992) ozonated the components of humic substances and found that aldehydes such as formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal contributed to the mutagenicity of ozonated humic substances.

Glaze (1986a) has noted that three classes of organic ozonation by-products are of special interest because of their potential health effects, such as carcinogenicity or toxicity to certain organs. These are organic peroxides, unsaturated aldehydes, and epoxides. Organic peroxides can be formed when ozone reacts with olefins and aromatic species. Unsaturated aldehydes, which are known to be severe hepatotoxins (toxic to the liver), are expected to be formed from the cleavage of polyunsaturated alkyl or aromatic compounds by ozone (Glaze, 1986a). Epoxides, which are potential carcinogens, have been commonly identified in ozonation reactions with unsaturated organic compounds in nonaqueous solvents, but few reports of their occurrence in water have been verified (Glaze, 1986a).

Finally, there have been studies in which low-and-moderate-molecular-mass carbonyl compounds, primarily formaldehyde, have been detected in ozonated surface waters (Yamada and Somiya, 1989; Glaze *et al.*, 1989a; Jacangelo *et al.*, 1989; and Glaze *et al.*, 1989b). The public health significance

18

of these low concentrations of aldehydes is not yet clear, and further study is recommended (Singer, 1990).

In conclusion, the question of health effects of ozonation by-products is a very serious issue. Knowledge of ozone chemistry and reaction pathways with various organic species suggest that reaction compounds would include compounds such as aldehydes, ketones, carboxylic acids, and other aliphatic and hydroxylated aromatic forms (Singer, 1990). With the exception of the aldehydes, most of these do not appear to be very detrimental to human health at the concentrations found in ozonated waters. It should also be noted that in the analysis of many of these ozonation by-products, a preconcentration step is usually involved that may cause unstable by-products to decompose. This would result in a lower response and an underestimate of the actual health effect.

There has been much conflict over whether or not ozonation by-products are more hazardous than chlorinated by-products. THMs are the chlorinated by-products of greatest concern. In 1990, the USEPA classified chloroform, bromodichloromethane, and dibromochloromethane as probable human carcinogens (Class B2 cancer group), and classified bromoform as a possible human carcinogen (Class C cancer group) (Pontius, 1990). Another group of chlorinated by-products of concern to human health, the HAAs, are also suspected of carcinogenic potential. Because of these concerns, both the THMs and HAAs are becoming subject to increased regulation by the D/DBP Rule in

the United States (Means III and Krasner, 1993). The general consensus is that ozonation by-products are less hazardous than chlorinated by-products such as THMs. However, it is also agreed that because of the complexity of ozone's reactions with compounds present in natural waters, much more research should be performed in order to determine the health effects of known ozonation by-products.

2.5. Aldehydes

Ozone has long been known to produce aldehydes as by-products from a wide variety of unsaturated organic compounds via the Creigee mechanism (Figure 2.3). In 1982, Mallevialle (1982b) made a summary list of identified reaction products produced from ozonation, and aldehydes were found to be produced from many organic compounds. Table 2.1 displays a list of these precursors to aldehydes which Mallevialle documented.

2.5.1. Formation of Aldehydes

Many studies have been conducted where aldehydes were found to be produced as a result of ozonation of natural waters. The concentrations of C_1 through C_7 aldehydes have been found to increase upon ozonation of natural water with many different source waters including: two surface water sources in California (Los Angeles Aqueduct Water [LAAW] and State Project Water [SPW]) (Glaze et al., 1989b); a treatment plant in Turin, Italy (Gilli et al., 1989);

20

STAGE 1: 1-3 dipolar cyclo addition of ozone on unsaturated bonds
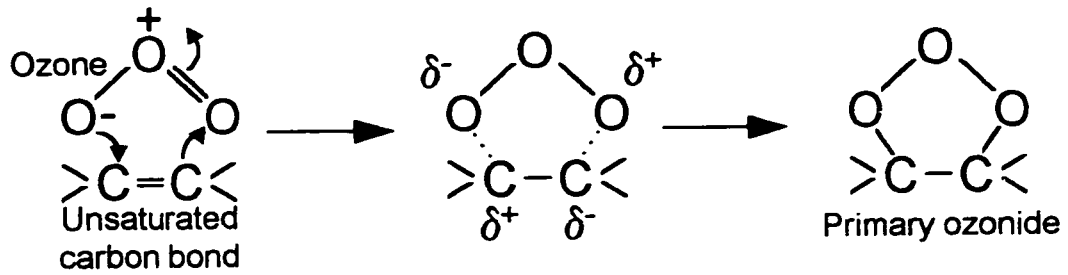
STAGE 2: Decomposition of primary ozonide in water

Carbonyl compound plus hydrogen peroxide
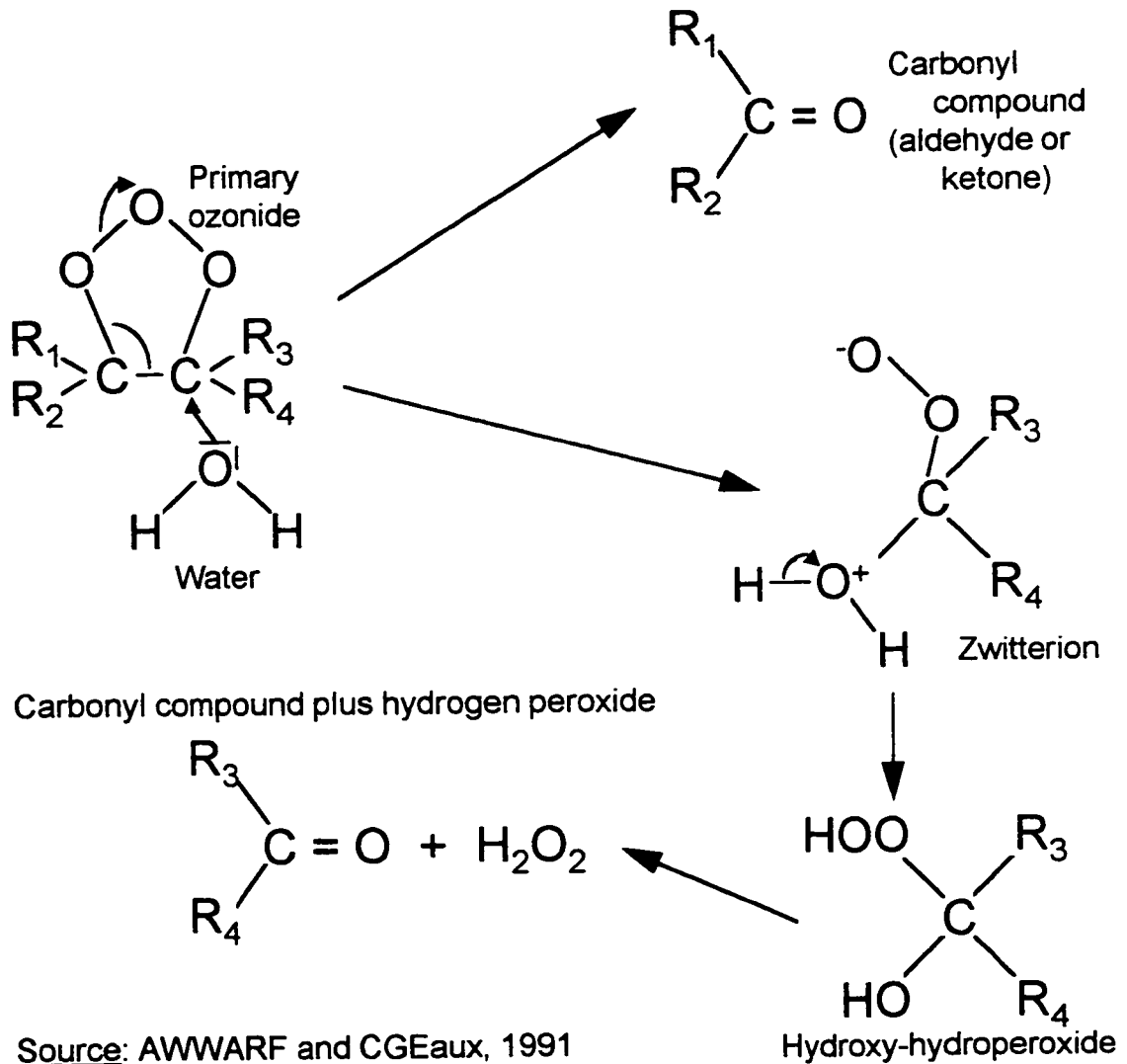
Figure 2.3 - The Criegee mechanism (cyclo addition).

COMPOUND (C)	ALDEHYDE(S) PRODUCED BY OZONATION OF (C)
Acetone	Formaldehyde
Aliphatic alcohols	Aldehydes
Alkenes	Aldehydes
Alkylbenzene sulfonic acid	Formaldehyde, Alkyl glyoxal
Benzene	Glyoxal
Benzofuran	Salicylic aldehyde
4-chloro-o-cresol	Methyl glyoxal
o-, m-, p-chlorophenol	Glyoxal
Crotonaldehyde	Acetaldehyde, Glyoxal
Decylbenzene sulfonic acid	Formaldehyde, Nonyl glyoxal
Ethylic alcohol	Acetaldehyde
Fulvic acids	Benzaldehyde
Humic acids	Aldehydes
Linolenic	Acetaldehyde, Propionaldehyde
Linoleic acid	Hexanaldehyde, Propionaldehyde
Mesitylene	Methyl glyoxal
Methyllinoleic acid	Malonic aldehyde
Naphthalene	Phtalic aldehyde
Naphthalene-2-7-disulfonic acid	Glyoxal
Nonylbenzene sulfonic acid	Formaldehyde, Nonyl glyoxal
Olefins (unsaturated)	Aldehydes
Phenol	Glyoxal, Formaldehyde, Muconaldehyde
Styrene	Benzaldehyde, Formaldehyde

Source: Mallevialle, 1982b

Table 2.1 - Known organic precursors to aldehydes produced by ozonation.

four utilities in Southern California (Jacangelo *et al.*, 1989; Krasner *et al.*, 1993; Weinberg *et al.*, 1993); Ohio River water (Miltner *et al.*, 1992); source waters for the communities of Hackensack, NJ, Palm Beach County, FL, and Myrtle Beach, SC (Schechter and Singer, 1995); and the Sacramento River in Northern California (Najm and Krasner, 1995).

The degree of increase in aldehydes depends on the ozone dose, with some intermediate dose giving a maximum formation, after which increased ozone doses bring about a decrease in aldehydes (Glaze *et al.*, 1988). Perhaps, at higher ozone doses aldehydes are oxidized further to corresponding carboxylic acids (Miltner *et al.*, 1992). It has also been shown that an increase in dissolved organic carbon levels in the water being ozonated causes an increase in aldehyde levels (Najm and Krasner, 1995). However, Glaze *et al.* (1989a, 1989b) found that the nature of the background organic matter and not just the dissolved organic carbon (DOC) level is critical in determining the distribution and concentration of aldehydes formed. Andrews and Huck (1994) found that fulvic acids may be major precursors to aldehydes.

The pH of ozonation has also been found to affect aldehyde formation, with low pH values (e.g. 5.5) tending to produce more aldehydes than higher pH values (e.g. 8.5) (Andrews and Huck, 1994; Schechter and Singer, 1995). Changes in bromide ions have been studied to determine their effect on aldehydes, if any, and have been found to have no effect on aldehyde production (Schechter and Singer, 1995; Najm and Krasner, 1995). Inorganic

23

carbon concentrations also appear to have no effect on aldehyde production (Schechter and Singer, 1995).

Formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal are the most ubiquitous aldehydes reported in most of the studies mentioned earlier. Formaldehyde is generally reported as having the highest concentration of all the aldehydes. One study by Glaze et al. (1989b), named heptanal as having the highest concentration compared to other aldehydes.

2.5.2. Detection of Aldehydes

A brief history of the methods of detecting aldehydes is discussed here. A detailed description of the method used in this thesis is discussed in Chapter IV - Experimental Procedures.

In 1978, Schalekamp (1978) used closed loop stripping analysis (CLSA) and found increases of C_6 through C_{13} aldehydes in the nanogram-per-liter range. Glaze et al. (1989b) also used this CLSA to investigate the presence of aldehydes in ozonated water.

In 1985, Van Hoof et al. (1985) used a derivatization/pentane extraction/high-performance liquid chromatography (HPLC)/UV method to examine the formation of C_1 through C_7 aldehydes at a detection level of about 1 $\mu g/L$. In 1989, Yamada and Somiya (1989) described a new method that employed aqueous derivatization, hexane extraction, and gas chromatography (GC), allowing for quantitation of simple aldehydes at microgram-per-liter levels.

24

This method was later improved in 1989 by Glaze *et al.* (1989a) and also modified in 1990 by Sclimenti *et al.* (1990). The Yamada and Somiya method is the basis for most of the methods used in aldehyde studies from 1990 to present.

2.5.3. Risks Associated With Aldehydes

Aldehydes are of concern for three main reasons. First, there is the concern of adverse health effects, especially potential carcinogenicity. Toxicological data on some of the aldehydes, including formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal, show that they are mutagenic (producing mutations in animals) or carcinogenic (producing cancer in animals) (Bull and Kopfler, 1991). Formaldehyde and acetaldehyde, which are relatively volatile, have produced respiratory tumors in animals (formaldehyde has produced tumors in humans as well after inhalation exposure) (Alceon Corp., 1993). In the case of ingestion of formaldehyde, animal cancer bioassays have produced conflicting data (Alceon Corp., 1993). Glyoxal, however, has been shown to promote stomach tumors after administration of a known initiator (Alceon Corp., 1993). There is still uncertainty as to the health effects of ingestion or inhalation (such as during a shower) of aldehydes at levels that are found after ozonation of drinking water. However, aldehydes may be viewed as surrogates for a large number of polar organics that are formed at low levels when ozone is used in treatment of natural waters. These compounds may

include as yet unidentified species such as peroxides and epoxides, which have been discussed earlier and may have more serious health effects than aldehydes.

Secondly, when aldehydes react with chlorine in a typical treatment plant, halogenated by-products such as cyanogen chloride and chloral hydrate can increase (McKnight and Reckhow, 1992). There is concern due to the adverse health effects of these halogenated aldehydes.

Finally, polar ozonation by-products, especially aldehydes are more biodegradable than their precursors. If aldehydes were present in distributed drinking water as assimilable organic carbon (AOC), the potential for increase in bacterial populations would be great, and consumers would be at higher risk of diseases caused by microbial regrowth.

2.5.4. Removal of Aldehydes

Due to concerns with aldehydes in distributed drinking waters, studies have been conducted to investigate ways of reducing aldehyde levels. Van Hoof et al. (1985) showed that precursor removal resulted in reduced aldehyde formation. Glaze et al. (1989a) speculated that secondary reactions between aldehydes and other constituents may lead to the disappearance or transformation of some of these ozonation by-products.

Glaze et al. (1989b) stated that the treatment steps following ozonation in the plant in their study (flocculation, filtration, and chlorination) removed a

substantial number of ozonation by-products. Other studies have been more specific and found that biologically activated filtration can be an effective way of removing aldehydes. Since aldehydes are easily biodegradable, biologically activated filters have been studied as a means of removing them from drinking water (Miltner et al., 1992; Weinberg et al., 1993; Krasner et al., 1993). Researchers have found that biotreatment reduces aldehyde concentrations to less than the concentration in the raw water, even when there is a significant increase in aldehydes formed by ozonation (Miltner et al., 1992; Weinberg et al., 1993; Krasner et al., 1993). Both Krasner et al. (1993) and Weinberg et al. (1993) found that anthracite filters were not as effective as granular activated carbon (GAC) filters in reducing aldehydes. Weinberg et al. (1993) concluded that aldehydes were removed by filters that possessed an active biomass and that filtration rate and history of the filters might have an effect on removal. Biomass must be present for effective aldehyde removal. It was found that in plants where a disinfectant was applied either upstream of or directly on to the filters, thus removing the biomass, there was minimal removal of aldehydes, and in some cases there appeared to be additional aldehyde formation on the filter bed (Weinberg et al., 1993). This additional aldehyde formation was possibly due to an ozone residual persisting on the filter or the shedding of previously adsorbed by-products. Finally, it was also found that the dialdehydes (glyoxal and methyl-glyoxal) appeared to be more difficult to remove through biological mediation than either formaldehyde or acetaldehyde.

27

Chapter III

METHODOLOGY

The research presented in this thesis examined the formation and removal of ozonation by-products, specifically aldehydes, in a pilot plant operated by the Windsor Utilities Commission (WUC). The source water that this pilot plant treats is obtained from the Detroit River. This chapter discusses the pilot plant, the scope of the research, and quality assurance aspects.

3.1. Pilot Plant

The pilot plant used to obtain samples for this research is located inside the Windsor Water Treatment Plant (WWTP) in Windsor, Ontario, Canada, and is operated and sponsored by the Ontario Ministry of Environment and Energy (MOEE) and the WUC. Figure 3.1 shows its location within the City of Windsor, as well as the raw water intake for the plant. Raw water is obtained from the Detroit River, which is a connecting channel between Lake St. Clair and Lake Erie. The pilot plant commenced operation in January of 1993 and is part of the Environmental Technology Program initiated to stimulate the development of new environmental technologies in Ontario (Alarcon Herrera, 1994). The original layout and design of the plant was accomplished by Mr. W.B. Anderson and Dr. P.M. Huck of the University of Waterloo.
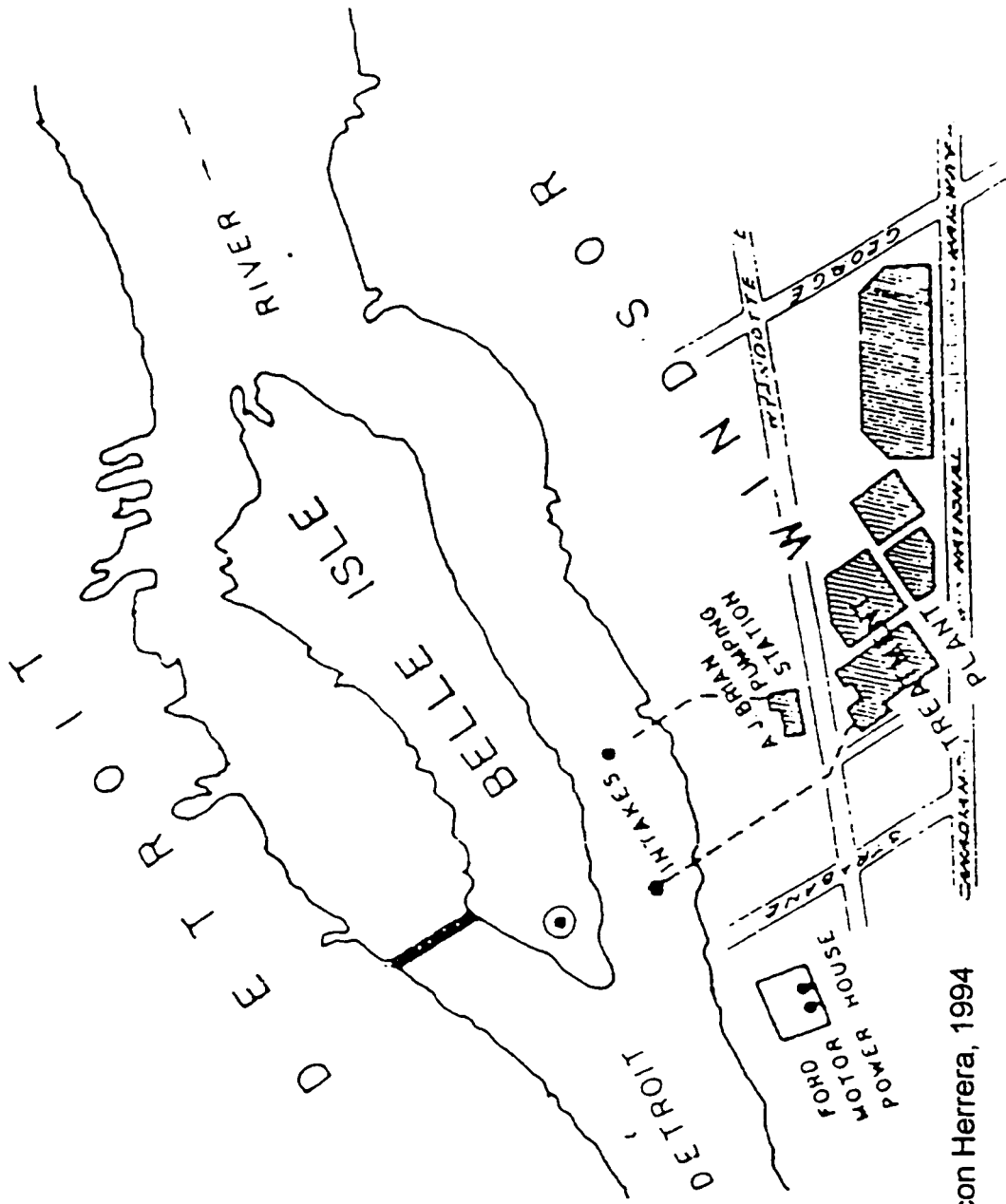
Figure 3.1 - Location of WUC Pilot Plant.

29

The pilot plant follows many of the basic units in operation at the full-scale Windsor Water Treatment Plant. In the main conventional plant, alum and polyelectrolytes are added at the head of the plant to the raw water in rapid mix units as part of the coagulation process. After this, the water flows to flocculation tanks. The water is then sent through a sedimentation process with incline plate settling tanks. Clarified water from the sedimentation tanks is filtered through dual-media (anthracite/sand) filter beds. All treatment steps are the same in the pilot plant. In the conventional treatment plant chlorine is added after filtration, whereas in the pilot plant no chlorine is added anywhere during treatment.

The pilot plant is equipped with two separate treatment trains which can be configured with a number of different treatment options. During this research, there were three different modes in which the pilot plant was operated. These consisted of: A) non-ozonation treatment versus pre-coagulation ozonation treatment with varying ozone dose and constant flowrate, B) non-ozonation treatment versus pre-coagulation ozonation treatment with constant ozone dose and varying flowrate, and C) pre-coagulation ozonation treatment versus post-sedimentation ozonation treatment with constant ozone dose and varying flowrate. Changes in flowrate referred to throughout this research refer to change in flowrate through the anthracite/sand filters only. Flowrates through all other components of the plant remained constant throughout the entire research

period. Figure 3.2 shows the pilot plant configuration for options A and B and Figure 3.3 shows the pilot plant configuration for option C.

The pilot plant was constructed of stainless steel, glass and inert fluorocarbons. These materials were also used for sealing purposes and in all tanks, pumps, piping, mixers, columns and water contacting surfaces of on-line instrumentation associated with the pilot plant. This was done to eliminate organic contamination which can be associated with other construction materials.

For all configurations of the plant, raw water was pumped to a constant head tank. From the constant head tank, the flow was split between two identical process trains at a flowrate of 13.0 L/min per side. Each side shared identical physical characteristics to allow direct comparisons between the two sides of the plant with a common raw water quality.

While the pilot plant compared one treatment process with another, some basic treatment units were identical on both sides of the plant. On each side of the plant, metering pumps injected treatment chemicals (Alum, which is a coagulant, and Percol, which is a coagulant-aid) into the feed water line. The water then traveled from the feed water line into a rapid mix tank before entering the flocculation tank. Flocculated water was passed through an inclined plate sedimentation tank, which had an automated sludge withdrawal system using a programmable control valve operating on a timer sequence.
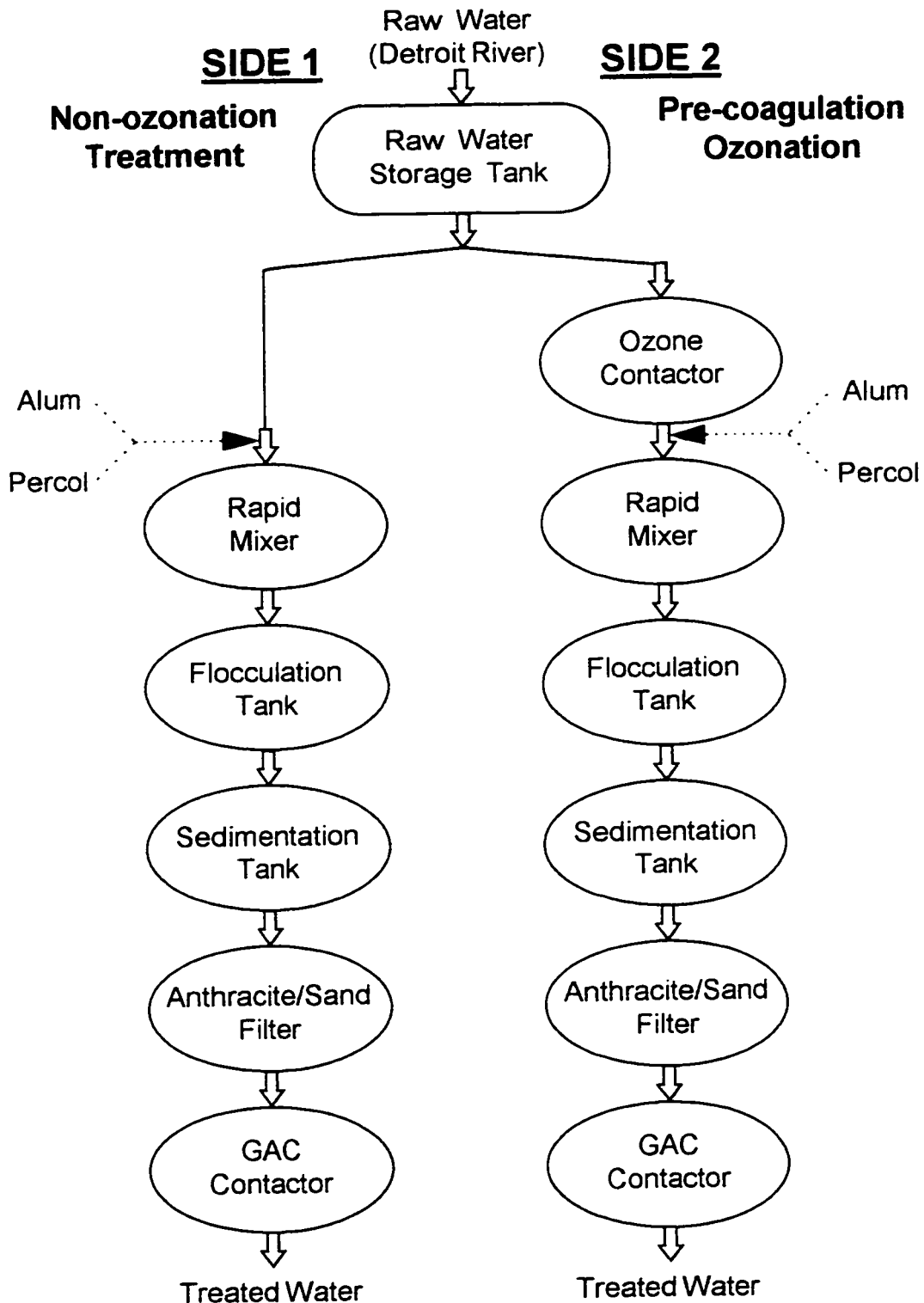
Figure 3.2 - WUC Pilot Plant configuration: Non-ozonation treatment versus pre-coagulation ozonation.
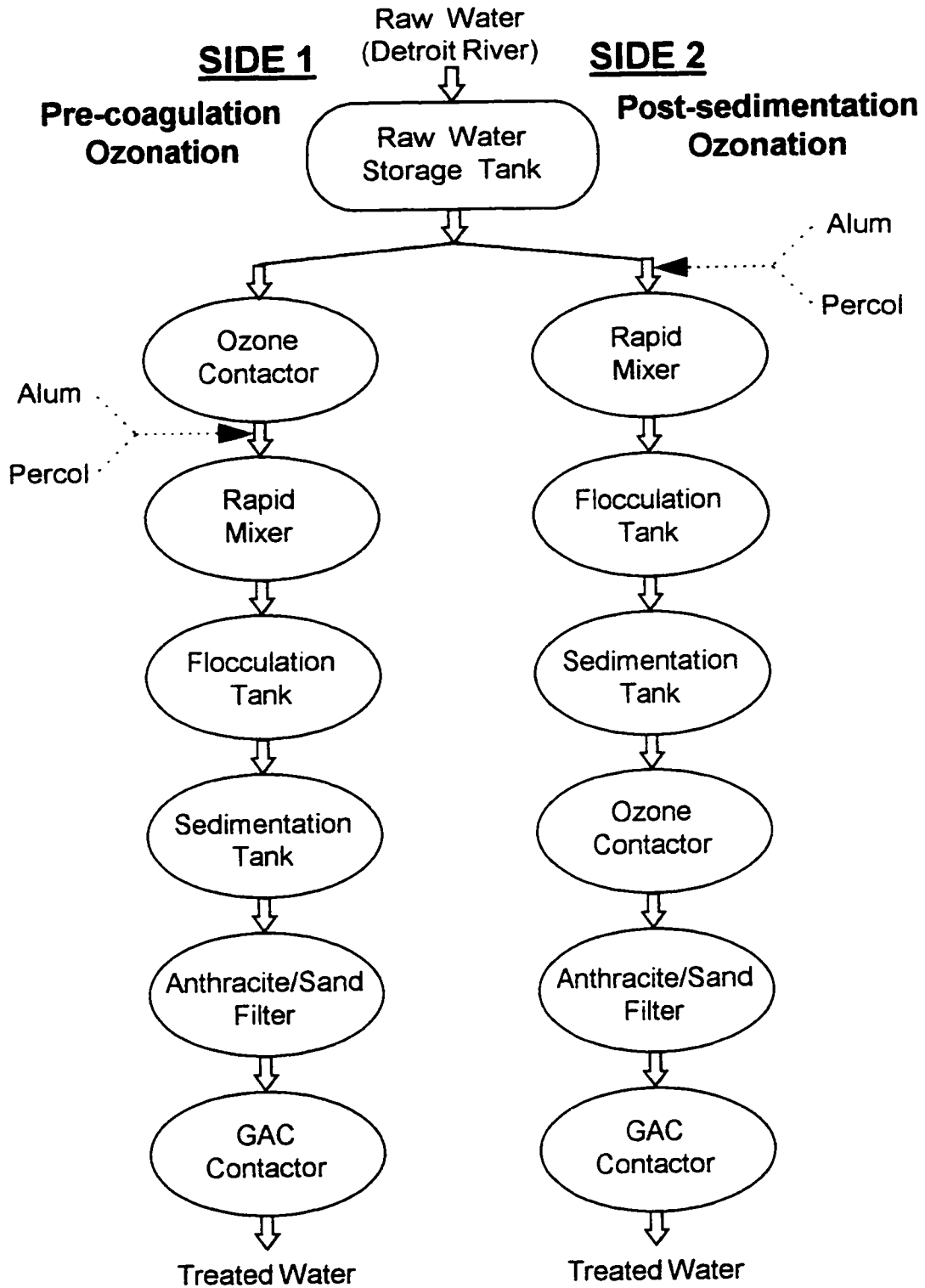
Figure 3.3 - WUC Pilot Plant configuration: Pre-coagulation ozonation versus post-sedimentation ozonation.

33

Settled water was collected in a water storage tank where it was fed to a dual media filter (anthracite/sand). Filtrate from the dual media filter was then directed to a granular activated carbon (GAC) contactor, after which it was considered to have received final treatment. Filtrate from the dual media filter was collected in a backwash tank with dedicated storage cells. Water for backwashing was then pumped from the dedicated cell back to the filter on the side of the plant from which it was collected. This was done to avoid backwashing a unit with water containing a disinfectant which the unit did not usually use. An air compressor and injection port allowed for air-scour to enhance filter backwashing.

The pilot plant was equipped with computer-assisted process and instrumentation control and on- and off-line data collection and storage capability. The pilot plant computers could be remotely accessed and controlled.

When ozone was used on either side of the pilot plant, it was generated using a PCI Ozone & Control Systems, Inc. GL-1 Laboratory Ozone Generator. Ambient air concentrations were monitored using a PCI LC-12 ozone monitor while generator output and contactor off-gas ozone levels were measured using a PCI HC-12 ozone monitor.

Ozone was generated from dry air using a Compressed Air Purifier/Dryer unit (Peak Scientific Model AP-03). The prepared air dew point was checked using an Alnor Model 7200 (Alnor Instrument Co., distributed by Cole-Parmer

Instrument Company). Ozone gas not consumed in the contactor was destroyed using a PCI OD-2 ozone destruction unit equipped with a preheater.

3.2. Scope

For this research, there were thirteen (13) sets of samples collected and analyzed for aldehydes. Samples were collected at the following locations in the Windsor pilot plant: at the raw water distribution well, after the sedimentation tanks on each side of the plant, after the dual media anthracite/sand filters on each side of the plant and after the GAC contactors on each side of the plant. The seven (7) sampling points throughout the pilot plant are shown on Figure 3.4.

Samples were collected throughout the year of 1995 in three batches corresponding to the three configuration setups in the pilot plant as previously mentioned. These samples were gathered during March 1995, May/June 1995, and September/October 1995 respectively for each of the three batches. The times of the year in which samples were collected were not intentionally set, but because of seasonal changes in water quality, were expected to have some effect on the results of the study. Table 3.1 summarizes the sampling dates and the plant configurations during each sample batch. It should be noted that each time the ozone dose or flowrate was changed in the pilot plant during this research, the plant was allowed to stabilize for at least one week before a sample was collected.

Raw Water
(Detroit River)

Raw Water
Storage Tank

SIDE 1

SIDE 2

Sample
RAW

Ozone
Contactor

Alum

Percol

Alum

Percol

Rapid
Mixer

Rapid
Mixer

Flocculation
Tank

Flocculation
Tank

Sedimentation
Tank

Sedimentation
Tank

Sample
S1

Sample
S2

(ozone added
after sample)

Anthracite/Sand
Filter

Anthracite/Sand
Filter

Sample
F1

Sample
F2

GAC
Contactor

GAC
Contactor

Sample
C1-3

Sample
C2-3

Treated Water

Treated Water

Figure 3.4 - Name and location of sampling points at
the WUC Pilot Plant.

Plant Configuration	Sampling Date	Flowrate Through Anthracite/Sand Filters (L/min)	Transferred Ozone Dose (mg/L)
Non-Ozonation vs. Pre-Coagulation Ozonation	March 1, 1995	3.25	0.27
	March 8, 1995	3.25	0.50
	March 17, 1995	3.25	1.0
	March 22, 1995	3.25	1.5
	March 28, 1995	3.25	2.0
Non-Ozonation vs. Pre-Coagulation Ozonation	May 16, 1995	3.25	0.75
	May 26, 1995	3.5	0.75
	June 6, 1995	4.2	0.75
Pre-Coagulation Ozonation vs. Post-Sedimentation Ozonation	September 8, 1995	3.0	1.2
	September 15, 1995	3.0	1.2
	September 22, 1995	4.2	1.2
	September 29, 1995	4.8	1.2
	October 6, 1995	4.2	1.2

Table 3.1 - Summary of WUC Pilot Plant configuration, sampling dates, and plant conditions.

In addition to analyzing for aldehydes, which was the primary scope of this research, additional parameters were measured by the WUC at the pilot plant concurrently with the aldehyde samples. These parameters were: pH, temperature, turbidity, and filter run time for the anthracite/sand filters. The significance of these parameters will be discussed in Chapter V - Results and Discussion.

3.3. Quality Assurance

All samples were collected and analyzed in duplicate, and an average of the levels found in each of the duplicate samples was reported. With each set of samples, method blanks and check standards were prepared and analyzed in duplicate. These blanks were always freshly prepared immediately prior to the collection of samples. The method blanks consisted of organic-free water containing only the reagents used for preservation and derivatization in the method. These blanks were used to determine the background levels of aldehydes in the method during the entire procedure, and final levels of aldehydes in the collected samples were adjusted for this background level in the final calculations. The check standard consisted of organic-free water spiked with 50 μg/L of mixed aldehyde standard solution, as well as the reagents used during the method. This check was run to view the recovery of each different aldehyde in the method. All blanks were analyzed in the exact manner that all samples were treated throughout the entire experimental procedure.

Chapter IV

EXPERIMENTAL PROCEDURES

4.1. Introduction

Ozonation by-products that are formed during ozonation are usually oxygenated and polar in nature, and some are relatively biodegradable. Analysis of these compounds in the past had proven difficult because of their chemical nature. The basic method of analysis for aldehydes and carbonyl compounds was first described by Yamada and Somiya (1989), was later improved by Glaze et al. (1989a) and also modified by Sclimenti et al. (1990). The method used during this research at the University of Windsor was based on the same analysis procedure performed at the University of Waterloo, with slight modifications. Both the University of Waterloo and the University of Windsor procedures were primarily based on Sclimenti et al.'s modified procedure for analyzing aldehydes. A flowchart of the complete procedure used at the University of Windsor is shown in Figure 4.1.

The basic method of analysis of aldehydes uses $\underline{O}$ - (2, 3, 4, 5, 6 - pentafluorobenzyl) - hydroxylamine hydrochloride [PFBHA-HCl] as a derivatizing agent. The specific aldehydes that can be quantitatively recovered by this method of analysis are low-molecular-mass, mono-aliphatic C_1 to C_{10} aldehydes (formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, heptanal,

40-mL vial containing:
32.5-mg $HgCl_2$
32.5-mg NH_4Cl
2-mL of 6-mg/mL PFBHA-HCl

Retrieve headspace-free sample

Store sample at 4°C for >24 hr

Add to 20-mL aliquot:
4 drops conc. H_2SO_4
4-mL hexane containing
100-μg/L 1,2-dibromopropane

Shake 10 minutes
Allow to stand 15 minutes
for phase separation

Aqueous layer:
Discard

Organic layer:
Wash with 10-mL 0.1 M H_2SO_4

Shake 10 minutes
Allow to stand 15 minutes
for phase separation

Aqueous layer:
Discard

Organic layer:
Transfer to 2-mL GC Vial
containing 20-mg Na_2SO_4

GC/ECD analysis

Figure 4.1 - Method used for analysis of aldehydes
at the University of Windsor.

40

octanal, nonanal, and decanal), dialdehydes (glyoxal and methyl-glyoxal), and an aromatic aldehyde (benzaldehyde). The analysis technique employed a direct aqueous derivatization with PFBHA-HCl, which reacted with the aqueous aldehydes to form corresponding oximes (where PFBO is pentafluorobenzyloxime) (Sclimenti *et al.*, 1990). Figure 4.2 shows a diagram of this derivatization reaction. With most of the aldehydes, two geometric isomers were formed (E-PFBO and Z-PFBO), except for formaldehyde, which is symmetrical. Methyl-glyoxal also produced only one prominent isomer, which may be due to some steric hindrance constraint.

After derivitization reached completion, the derivatives were extracted into hexane where they were separated by gas chromatography and detected with an electron capture detector. The aldehyde isomers that were able to be detected by the method of analysis utilized by the University of Windsor and their approximate GC retention times are listed in Table 4.1. A detailed description of the experimental procedures is given below.

4.2. General

All glassware used for this research was cleaned according to Method No. 1070 in *Standard Methods* (APHA-AWWA-WPCF, 1989) prior to use in the laboratory. Reagents were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI, USA except for mercuric chloride, ammonium chloride, and sodium sulfate, which were obtained from Chemical Stores at the University of

Figure 4.2 - Aldehyde derivatization reaction pathway.

Source: Sclimenti et al., 1990

42

ALDEHYDE NAME	APPROXIMATE GC RETENTION TIME (min.)
Formaldehyde	11.36
E-Acetaldehyde	13.28
Z-Acetaldehyde	13.46
E-Propanal	14.82
Z-Propanal	14.95
E-Butanal	16.29
Z-Butanal	16.39
E-Pentanal	17.72
Z-Pentanal	17.81
E-Hexanal	19.11
Z-Hexanal	19.17
Heptanal	20.43
Octanal	21.69
Benzaldehyde	21.94
Nonanal	22.90
E-Glyoxal	24.82
Z-Glyoxal	24.98
Methyl-glyoxal	25.39

Table 4.1 - Aldehyde isomers detected at the University of Windsor and their GC retention times.

Windsor. The hexane and methanol used were both of HPLC-grade and all reagents were reagent-grade chemicals.

Organic-free water was required for preparing all aqueous solutions and for the method blank. This water was generated using a Milli-Q Plus water purification system (Millipore Corp., Bedford, MA, USA). The water was generated as needed and used immediately, so storage was not required.

4.3. Analysis

The analysis of aldehydes at the University of Windsor consisted of three main parts:

- sample preparation and acquisition,

- sample derivitization and extraction, and

- sample quantification by gas chromatography.

The following section describes the steps taken during each of these stages of analysis.

4.3.1. Sample Preparation and Acquisition

Samples were collected from the pilot plant in clean 40 mL glass vials sealed with polypropylene caps with PTFE-faced silicone septa (Chromatographic Specialties Inc.). Approximately two to three hours prior to sample collection, the sampling vials were prepared at the University of Windsor's laboratory by adding preservatives and the PFBHA-HCl derivatizing

44

agent. Samples were preserved with mercuric chloride [HgCl$_2$] to prevent any formation of additional aldehydes after collection, and ammonium chloride [NH$_4$Cl] to prevent any biodegradation of aldehydes present during collection. Approximately 32.5 mg of each preservative was added to each sampling vial. Approximately 40 mL of a 6 mg/mL solution of PFBHA-HCl in organic-free water was freshly prepared for each set of samples, and each sampling vial in the set was dosed with 2 mL of the PFBHA-HCl solution using an automatic micropipette (Eppendorf).

Samples were then collected at the pilot plant. Each sampling line was allowed to flush for a sufficient volume before sampling. It was also ensured that there was no headspace in each sample vial by inverting the vial and visually inspecting it for the presence of air bubbles. After sampling, the vials were immediately returned to the University of Windsor and stored at 4°C for at least 24 hours to allow the derivatization reaction to reach completion. No special refrigeration was used during transport from the pilot plant to the University of Windsor since the approximate travel time was 10 - 15 minutes.

4.3.2. Sample Derivatization and Extraction

After the 24 hour storage period, a 20 mL aliquot was taken from each sample vial. The sample was acidified with 4 drops of concentrated sulfuric acid [H$_2$SO$_4$], and 4 mL of hexane containing 100 µg/L of 1,2-dibromopropane internal standard was added using an autodispenser. The sample was then shaken in a

mechanical wrist action shaker (Burrell Scientific, Pittsburgh, PA., USA) for 10 minutes, and allowed to stand for 15 minutes for phase separation. Where separation of the hexane layer took longer than 15 minutes, the hexane layer was dried by passing an appropriate amount of sodium sulfate [Na_2SO_4] through it. The hexane layer in each vial was then transferred by clean micropipette to a corresponding clean 40 mL vial containing 10 mL of 0.1 M sulfuric acid. This was done in order to wash the hexane extract. The sample was shaken again in the mechanical shaker for 10 minutes and then allowed to settle for 15 minutes for phase separation. The hexane layer was then transferred by clean micropipette to a 2 mL LoVial GC vial with silicone septa (Kimble - Division of Owens-Illinois) containing approximately 20 mg of sodium sulfate. The sodium sulfate was used as a moisture trap to ensure that no traces of moisture entered the gas chromatograph.

4.3.3. Sample Quantification By Gas Chromatography

For quantification analysis, each sample was injected in duplicate into a gas chromatograph (GC), using a Hewlett Packard 7673A automatic injector. After every sample injection, the syringe was rinsed six times with GC-grade ethanol to prevent contamination between samples. The GC system consisted of a Hewlett Packard 5890 gas chromatograph with a Phase DB-1 capillary column (J & W Scientific, 30 m X 0.25 mm I.D., Film Thickness 0.25 μm), and an electron capture detector (ECD) for compound detection. The signal from the

46

detector was integrated on a Hewlett Packard 3396A integrator and the entire system was controlled by a Hewlett Packard 7673A controller. The carrier gas was argon containing 5 percent methane with a flowrate of 1 mL/min (50°C). The injector temperature was 300°C and the detector temperature was 300°C. The GC oven was temperature programmed from 50°C (held for 5 minutes) to 295°C at 10°C/min and held at the maximum temperature (295°C) for 5 minutes. The sample injection volume for each sample was 2 μL, split 1 : 5. To ensure constant optimal operation of the GC, the injection port septa was changed and the injection port liner was cleaned and the glass wool insert changed approximately every 100 injections.

The HP-3396A integrator was used for peak integration and displaying area counts. A sample chromatogram from the integrator is shown in Figure 4.3 and the corresponding area counts for each peak are shown in Figure 4.4.

The integrated peaks and area counts were translated to aldehyde levels by using external calibration curves. Calibration curves were produced by analyzing calibration standards prepared by spiking standard aldehyde solutions into organic-free water using the exact method by which all samples were analyzed. The standard aldehyde solutions were prepared gravimetrically in methanol from pure aldehyde compounds as needed. Calibration was performed by plotting an 8 point standard calibration curve from 0.1 to 200 μg/L for each aldehyde studied. The calibration curve was plotted as a

FORMALDEHYDE

E-ACETALDEHYDE
Z-ACETALDEHYDE

E-PROPANAL
Z-PROPANAL

E-BUTANAL
Z-BUTANAL

E-PENTANAL
Z-PENTANAL

E-HEXANAL
Z-HEXANAL

HEPTANAL

OCTANAL   BENZALDEHYDE

NONANAL

E-GLYOXAL   Z-GLYOXAL

METHYL-GLYOXAL
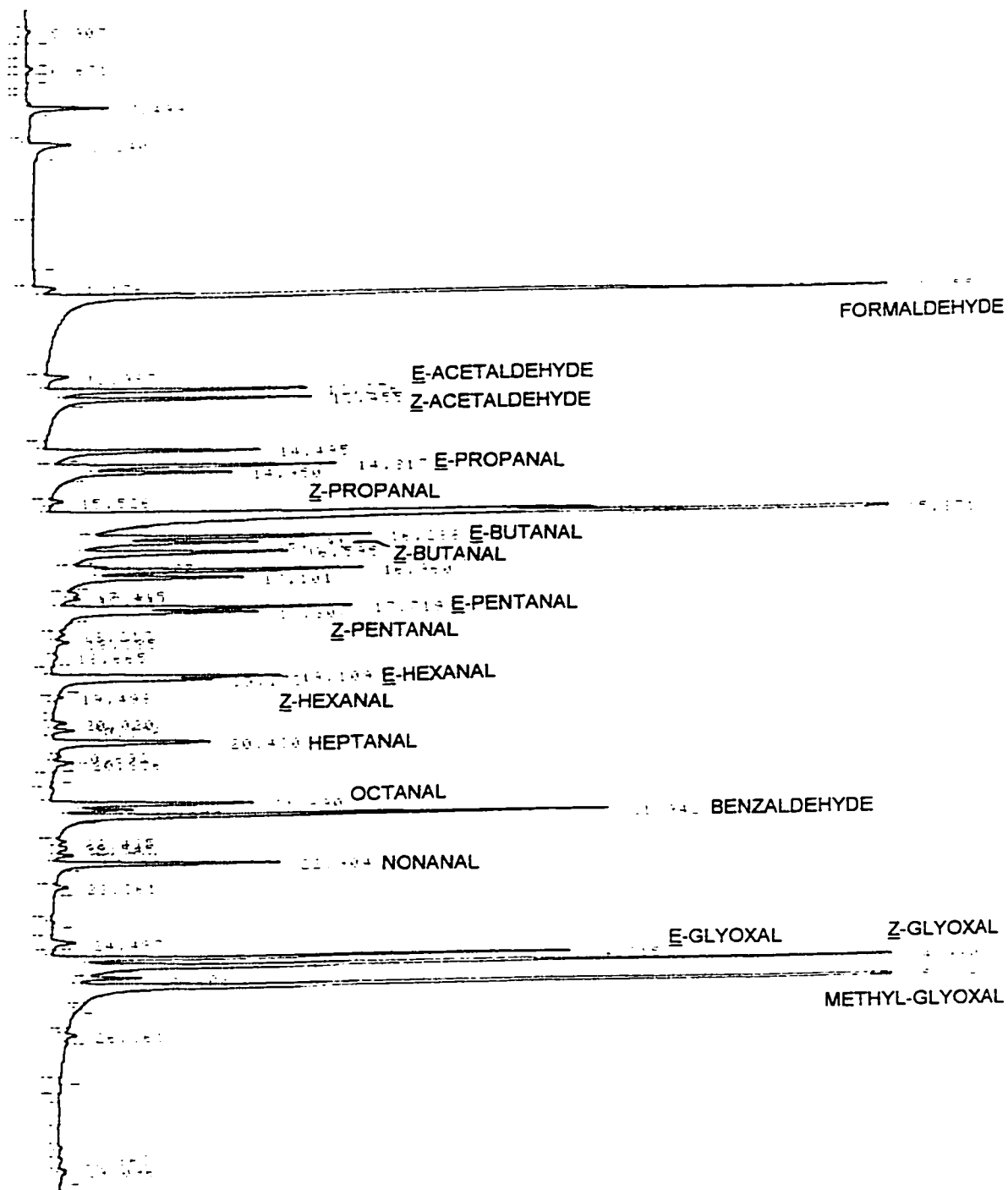
Figure 4.3 - Sample chromatogram of 50-μg/L mixed aldehyde
standard solution.

48

RT	AREA	TYPE	WIDTH	AREA%	
1.107	2364	BV	.105	.14204	
1.127	8015	VV	.106	.50191	
2.501	13159	VV	.119	1.09599	
3.017	45770	VV	.095	2.36625	
3.946	7221	VV	.113	.45246	
3.962	2136	VB	.037	.13439	
4.297	2004	VV	.067	.79000	
7.459	11173	PB	.061	.59629	
8.240	3522	PB	.100	.15993	
11.175	2553	PP	.067	.15993	
11.255	163390	PB	.045	10.16951	FORMALDEHYDE
11.457	4133	PP	.071	.25392	
11.576	34126	PV	.053	2.13707	E-ACETALDEHYDE
13.455	32515	VB	.056	2.03613	Z-ACETALDEHYDE
14.495	34507	PB	.073	2.16093	
14.517	37967	PV	.060	2.37760	E-PROPANAL
14.550	27772	VB	.071	1.73916	Z-PROPANAL
15.526	1349	BV	.060	.11579	
15.706	59035	PV	.049	3.69694	
15.971	184738	VB	.077	11.56981	E-BUTANAL
16.198	35136	BV	.056	2.20345	Z-BUTANAL
16.391	24716	VV	.065	1.54779	
16.595	33899	VB	.073	2.12235	
16.877	2952	BV	.039	.17360	
16.960	43992	VV	.067	2.74864	
17.101	29638	VB	.075	1.85682	
17.415	2002	BV	.073	.12537	
17.511	2408	VP	.066	.15080	
17.713	39292	PV	.060	2.45395	E-PENTANAL
17.907	28479	VB	.065	1.78297	Z-PENTANAL
19.035	1784	PP	.063	.11172	
19.109	31524	PV	.061	1.97412	E-HEXANAL
19.172	22294	VB	.062	1.39549	Z-HEXANAL
20.020	2205	PV	.065	.13909	
20.176	3086	VP	.061	.19325	
20.430	32575	PV	.090	2.03994	HEPTANAL
20.692	1596	VV	.099	.09992	
20.906	2267	VB	.069	.20459	
21.690	32052	PV	.071	2.00719	OCTANAL
21.909	3920	VV	.054	.55922	
21.941	68219	VB	.056	4.27327	BENZALDEHYDE
22.425	1124	BV	.055	.07039	
22.545	2447	VV	.043	.15024	
22.711	2272	VP	.056	.14024	
22.904	20640	PB	.060	1.91395	NONANAL
23.161	2143	PB	.065	.13409	
24.467	1937	PB	.075	.24141	
24.915	51999	PV	.047	1.11989	E-GLYOXAL
24.990	139025	VB	.047	9.70676	Z-GLYOXAL
25.105	5605	BP	.045	.15100	
25.136	139327	PB	.044	12.16950	METHYL-GLYOXAL
26.161	1557	BC	.062	.09759	
26.741	1060	PP	.061	.06615	

TOTAL AREA=1596162
MUL FACTOR=1.0000E-00

concentration-versus-area counts plot using a best fit polynomial. Standard calibration curves for each aldehyde are found in Appendix A.

Method detection limits (MDLs) were also calculated for each aldehyde according to Method No. 1030E in *Standard Methods* (APHA-AWWA-WPCF, 1989). A set of seven aldehyde standard solutions at a level of approximately 1.0 μg/L of each aldehyde were prepared and analyzed in the same way as all other samples, and the standard deviation of the seven replicate measurements was calculated for each aldehyde. Along with these standards, organic-free water blanks were analyzed. The MDL for each aldehyde was determined using the following formula:

$$MDL = t\,(s) + b$$

where: t = 3.143   (student t - value for 6 degrees of freedom
and 99 percent confidence level)

s = standard deviation of seven replicate analyses

b = mean value of organic - free water blanks

The MDLs for each aldehyde are listed in Table 4.2.

ALDEHYDE NAME	METHOD DETECTION LIMIT (microgram/L)
Formaldehyde	2.0
Acetaldehyde	1.9
Propanal	1.6
Butanal	1.2
Pentanal	3.4
Hexanal	0.7
Heptanal	0.6
Octanal	1.2
Benzaldehyde	0.3
Nonanal	3.1
Glyoxal	0.3
Methyl-glyoxal	1.6

Table 4.2 - Aldehyde method detection limits (MDLs) calculated at the University of Windsor.

Chapter V

RESULTS AND DISCUSSION

5.1. General

Aldehydes were analyzed and quantified as ozonation by-products at the WUC pilot plant located in Windsor, Ontario, Canada. All aldehyde samples were collected and analyzed according to the experimental procedures described in Chapter IV. As previously stated in Chapter III, samples were collected throughout the year of 1995 in three different phases to allow different plant configuration comparisons. The results will thus be discussed in terms of these three phases.

5.2. Phase One Results

Phase one consisted of comparing non-ozonation treatment (side one of the pilot plant) with pre-coagulation ozonation treatment (side two of the pilot plant). In this phase, the ozone dose was increased from a level of 0.27 mg/L of ozone transferred to a level of 2.0 mg/L of ozone transferred. The flowrate through the anthracite/sand filters was kept constant at 3.25 L/min on each side of the plant. Five sets of samples were collected throughout the month of March, 1995.

Figure 5.1 shows the level of total aldehydes detected on the non-ozonation treatment side of the plant (side 1) and Figure 5.2 shows the level of total aldehydes detected on the pre-coagulation ozonation treatment side of the plant (side 2) during phase one. No aldehydes were detected on the non-ozonation treatment side of the plant. On the pre-coagulation ozonated side, there was a general linear increase in total aldehydes seen in the sedimentation tank (S2) as the ozone dose was increased from 0.27 to 2.0 mg/L. It is reported in the literature that aldehyde levels increase as the ozone dose is increased, with some intermediate dose giving a maximum formation, after which increased ozone doses bring about a decrease in aldehydes (Glaze et al., 1988). A suggested reason for this is that at higher ozone doses aldehydes are oxidized further to corresponding carboxylic acids (Miltner et al., 1992). In this research, total aldehyde levels increased up to the maximum dose of 2.0 mg/L as shown in Figure 5.2. Since no decrease in aldehydes was seen, it can be concluded that the ozone dose required for peak aldehyde formation is higher than 2.0 mg/L. It should be noted also at this time that even at the highest ozone dose used in this research (2.0 mg/L), the maximum total level of aldehydes produced was less than 40 µg/L.

Figure 5.3 shows the percentage removals of total aldehydes in the anthracite/sand filters and the GAC contactors on side two of the plant for phase one. In general, it can be seen that aldehydes were removed slightly, if at all, in the anthracite/sand filters (F2) and aldehydes were removed completely in the

Phase 1, Side 1: Non-Ozonation Treatment

Figure 5.1 - Total aldehyde levels detected during non-ozonation treatment - Phase 1.

	3/1/95	3/8/95	3/17/95	3/22/95	3/28/95
Sampling Date					
Ozone Dose (mg/L)	0.27	0.50	1.0	1.5	2.0
Flowrate (L/min)	3.25	3.25	3.25	3.25	3.25

Legend:
- □ RAW
- ▤ S1
- ▥ F1
- ■ C1-3

Total Aldehydes (µg/L)

Figure 5.2 - Total aldehyde levels detected during pre-coagulation ozonation treatment - Phase 1.
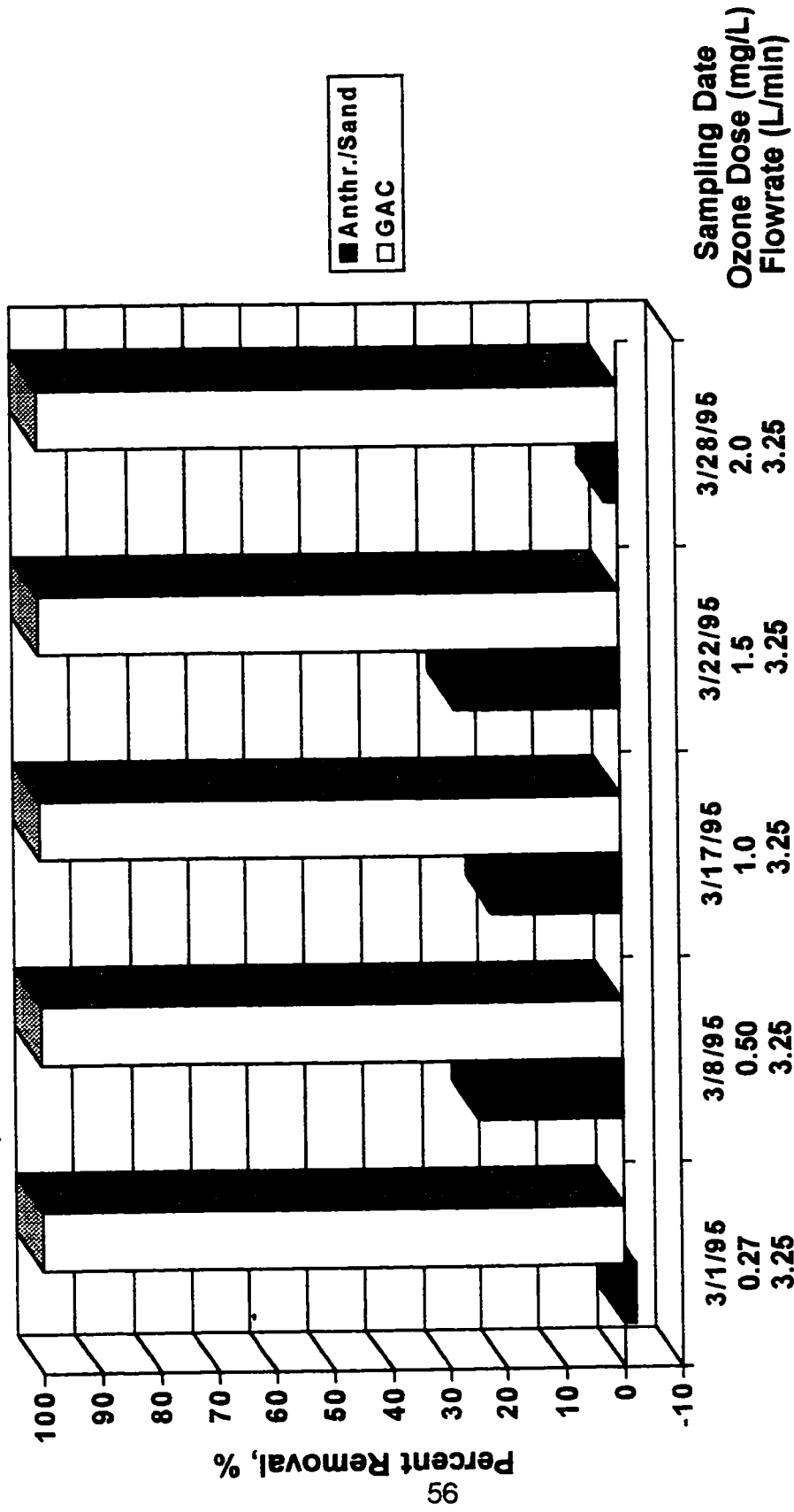
Figure 5.3 - Percent removals of total aldehydes in anthracite/sand filters and GAC contactors - Phase 1.

GAC contactors (C2-3). Krasner *et al.* (1993) and Weinberg *et al.* (1993), had observed similar results. It was also noted that the low-molecular-mass aldehydes (formaldehyde, acetaldehyde and propanal) decreased in the anthracite/sand filters, while the high-molecular-mass dialdehydes (glyoxal and methyl-glyoxal) actually increased in the anthracite/sand filters. From the literature, it is known that glyoxals are more difficult to remove than other aldehydes (Weinberg *et al.*, 1993). Also, where there is no biomass present on the filters, there appears to be additional aldehyde formation on the filter bed (Weinberg *et al.*, 1993). This has been attributed possibly to the shedding of previously adsorbed by-products. Although it is unknown why the increase in dialdehydes occurred in this research, it may be speculated that since the samples were taken in March, a biomass was not present to aid in removing the dialdehydes due to low temperatures. This combined with the reasons cited in the literature earlier may explain why the dialdehydes increased. The increase in dialdehydes can be seen in Table 5.1.

Table 5.1 shows the individual levels of aldehydes throughout the pilot plant for only the raw water (RAW), the settled water (S2) and the anthracite/sand filtered water (F2) on side two of the plant. At all other sample locations, aldehydes were either below method detection limits or not detected. A complete comprehensive report of aldehydes detected on each date of sampling as well as check standards for the entire duration of this research is shown in Appendix B. As can be seen from Table 5.1, the major aldehydes

Concentrations of Aldehydes Present (μg/L)

ALDEHYDE	3/1/1995 O₃ Dose = 0.27 mg/L Flowrate = 3.25 L/min			3/8/1995 O₃ Dose = 0.50 mg/L Flowrate = 3.25 L/min			3/17/1995 O₃ Dose = 1.0 mg/L Flowrate = 3.25 L/min			3/22/1995 O₃ Dose = 1.5 mg/L Flowrate = 3.25 L/min			3/28/1995 O₃ Dose = 2.0 mg/L Flowrate = 3.25 L/min		
	RAW	S2	F2	RAW	S2	F2	RAW	S2	F2	RAW	S2	F2	RAW	S2	F2
Formaldehyde	-	5.6	5.0	-	7.8	7.5	-	9.8	8.4	-	19.9	10.1	-	15.7	15.0
Acetaldehyde	-	-	-	-	2.9	-	-	2.6	-	-	4.2	3.7	2.0	7.2	6.2
Propanal	-	2.0	-	-	5.8	3.9	-	1.9	-	-	-	-	-	3.1	1.8
Heptanal	-	-	-	-	2.4	-	-	-	-	-	-	-	-	-	-
Glyoxal	-	2.8	3.6	-	5.1	5.7	-	5.2	5.8	-	4.6	5.2	-	7.1	8.4
Methyl Glyoxal	-	-	2.0	-	2.8	3.1	-	3.4	3.7	-	3.4	4.0	-	5.2	6.1
TOTAL	-	10.4	10.6	-	26.8	20.2	-	22.9	17.9	-	32.1	23.0	2.0	38.3	37.5

Table 5.1 - Individual concentrations of aldehydes present during pre-coagulation ozonation treatment - Phase 1

consistently detected were: formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal. Formaldehyde was noted as the aldehyde that was present at the highest concentration throughout this phase. These findings are consistent with many other researchers' findings with completely different sources of water. (Miltner et al.,1992; Krasner et al., 1993; Weinberg et al., 1993; Schechter and Singer, 1994; and Najm and Krasner, 1995).

5.3. Phase Two Results

Phase two consisted of comparing non-ozonation treatment (side one of the pilot plant) with pre-coagulation ozonation treatment (side two of the pilot plant). In this phase, the ozone dose was kept constant at a transferred dose of 0.75 mg/L, while the flowrate through the anthracite/sand filters was increased from 3.25 L/min to 4.2 L/min on both sides of the plant. This increase in flowrate was made in order to determine if increased hydraulic loading of the filters would have an effect on aldehyde removals. Three sets of samples were collected throughout the months of May and June, 1995.

Figure 5.4 shows the levels of total aldehydes detected on the non-ozonation treatment side of the plant (side 1) and Figure 5.5 shows the levels of total aldehydes detected on the pre-coagulation ozonation treatment side of the plant (side 2) during phase two. As was found in phase one, no aldehydes were detected on the non-ozonation treatment side of the plant. On the pre-coagulation ozonated side, total aldehydes seen in the sedimentation tank (S2)

Phase 2, Side 1: Non-Ozonation Treatment

Total Aldehydes (µg/L)

40 35 30 25 20 15 10 5 0

Legend:
☐ RAW
▥ S1
▦ F1
■ C1-3

Sampling Date
Ozone Dose (mg/L)
Flowrate (L/min)
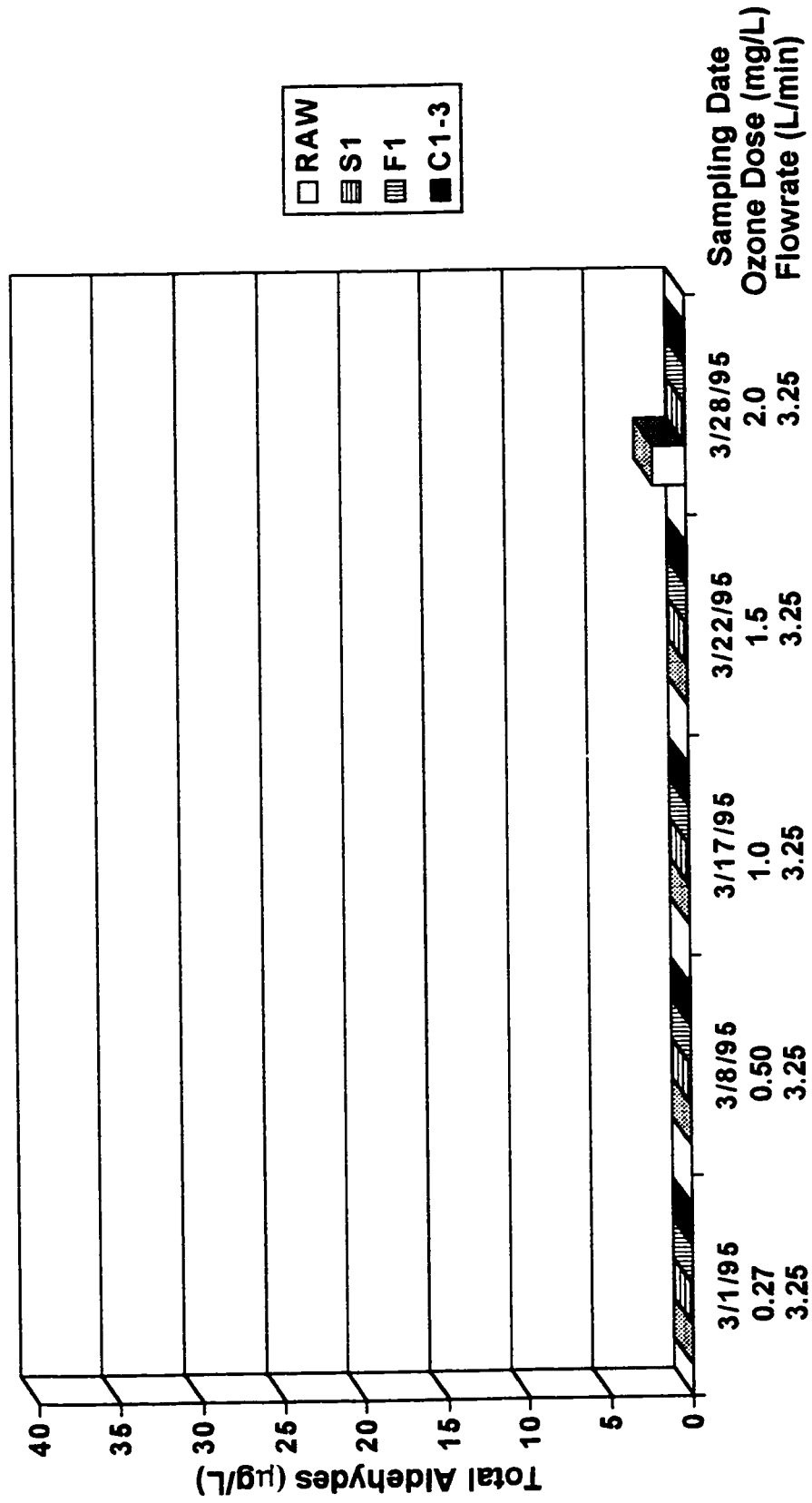
5/16/95
0.75
3.25

5/26/95
0.75
3.5

6/6/95
0.75
4.2
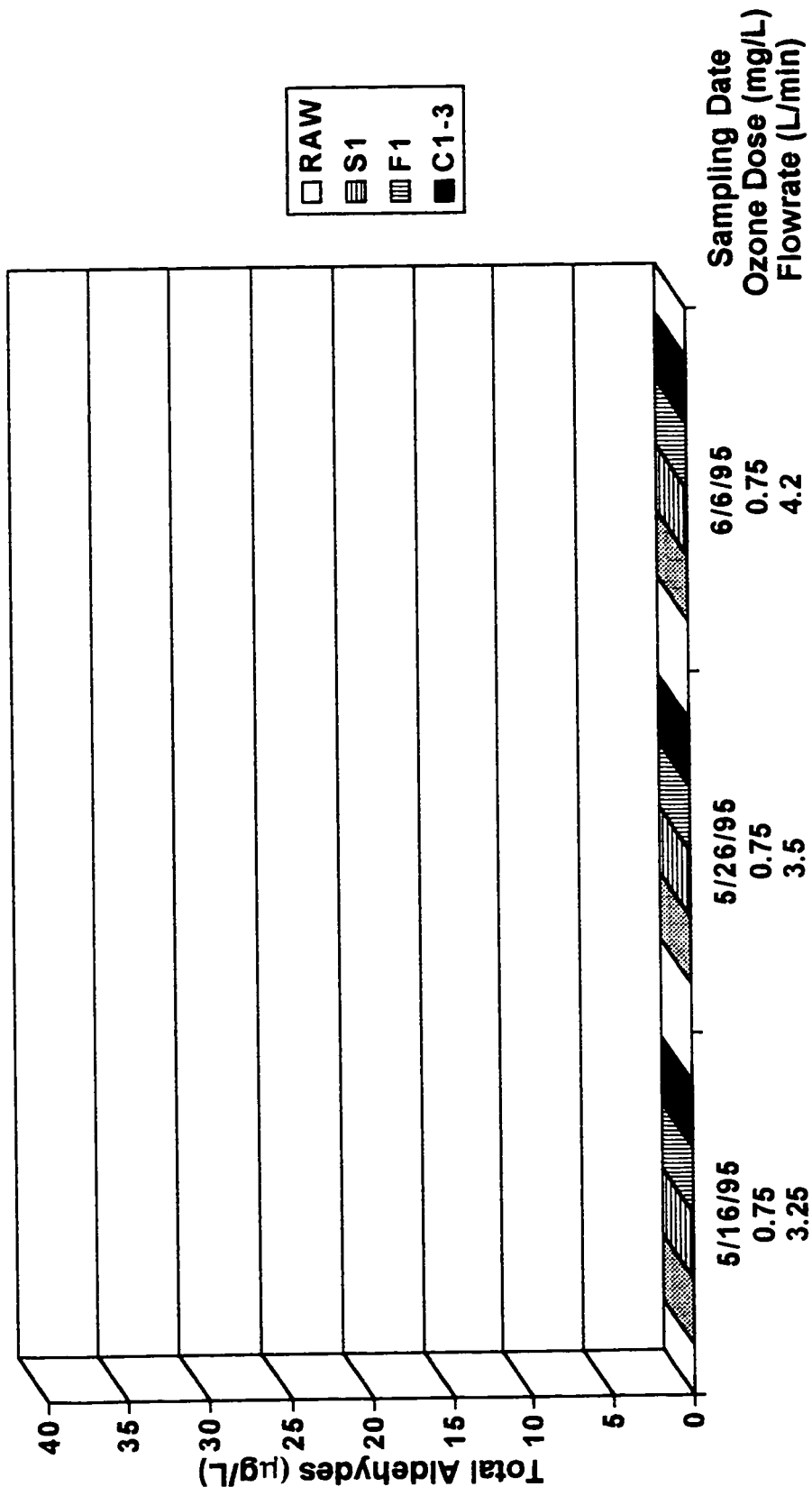
Figure 5.4 - Total aldehyde levels detected during non-ozonation treatment - Phase 2.
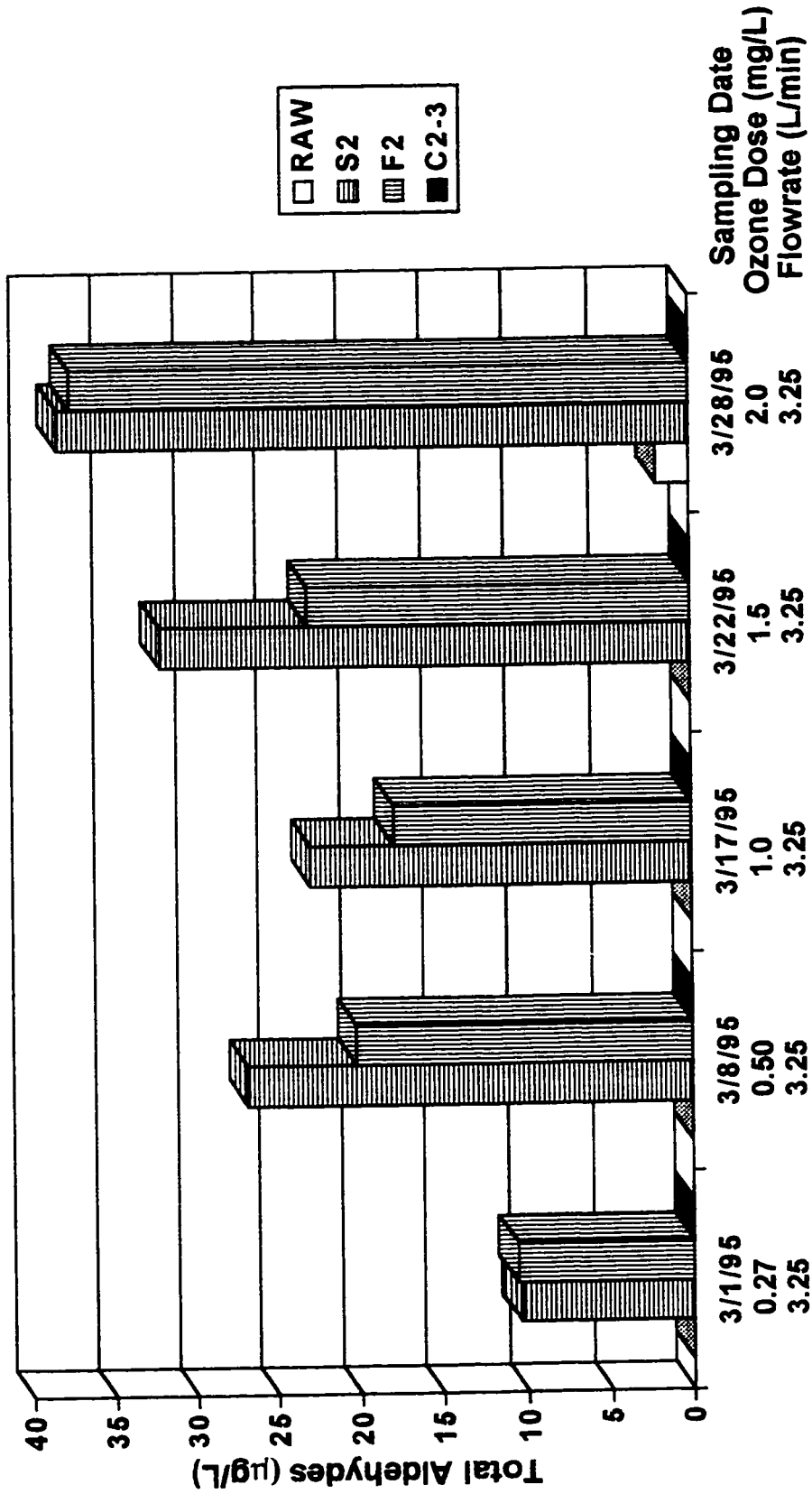
60

Phase 2, Side 2: Pre-Coagulation Ozonation Treatment

Total Aldehydes (µg/L)

Sampling Date	5/16/95	5/26/95	6/6/95
Ozone Dose (mg/L)	0.75	0.75	0.75
Flowrate (L/min)	3.25	3.5	4.2

Legend: RAW, S2, F2, C2-3
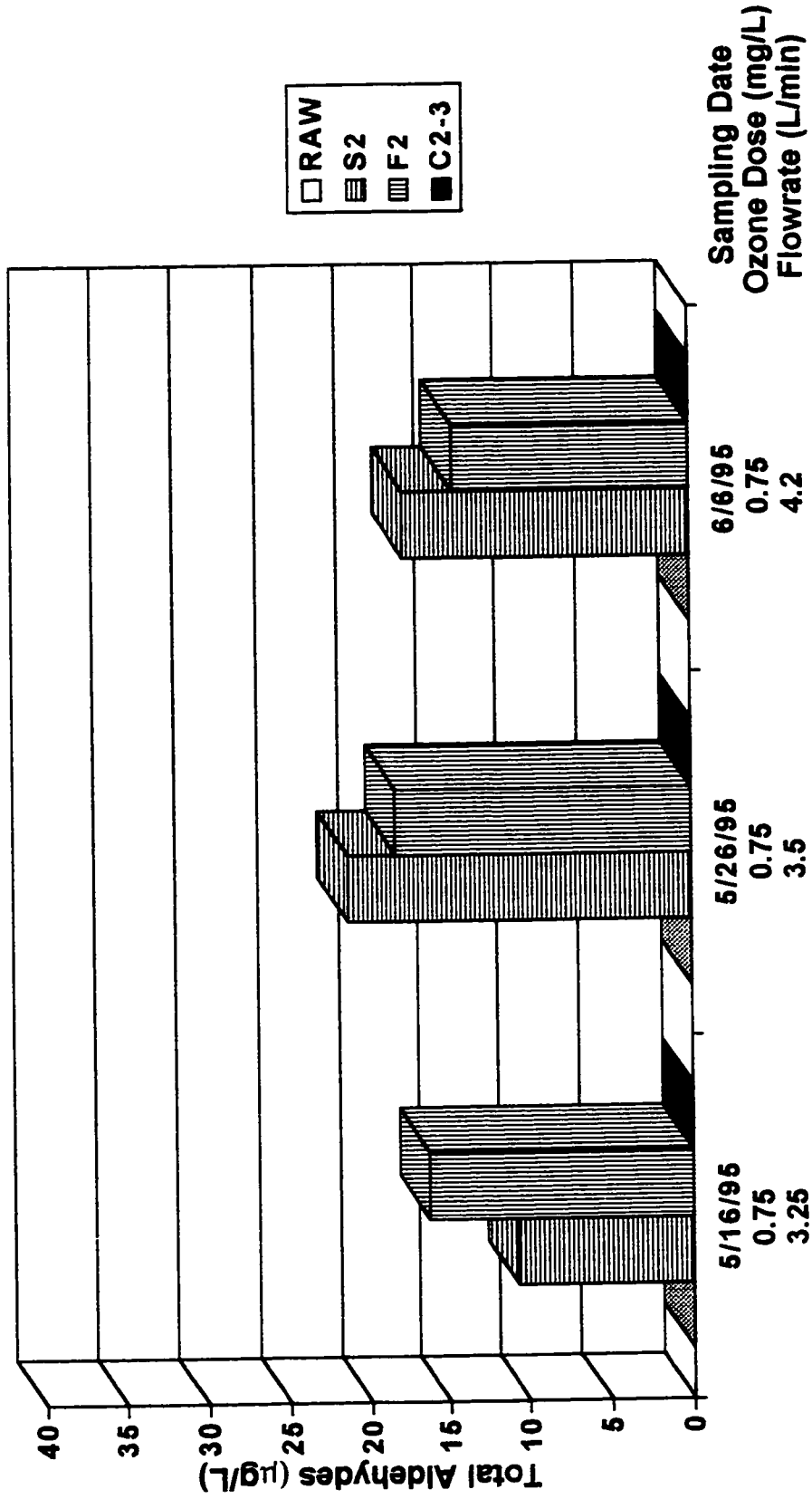
Figure 5.5 - Total aldehyde levels detected during pre-coagulation ozonation treatment - Phase 2.

varied from slightly above 10 µg/L to slightly above 20 µg/L, even though the ozone dose remained constant at 0.75 mg/L of transferred ozone. This variation is most likely due to slight changes in raw water quality and other minor variations.

Figure 5.6 shows the percentage removals of total aldehydes in the anthracite/sand filters and the GAC contactors on side two of the plant for phase two. It was noted that at the plant's lowest flow (3.25 L/min), the amount of total aldehydes found after the anthracite/sand filters (F2) was about 50 percent higher than the total aldehydes entering the filters. However, at the following higher flows, aldehydes were found to be slightly removed through anthracite/sand filtration. This observation could also be seen in the previous phase of sampling. In examining Figure 5.2 from phase one of sampling once more, which maintained a constant flowrate of 3.25 L/min, it can be seen that the total aldehydes found after the anthracite/sand filters for the first set of samples (March 1, 1995), were also slightly higher than the aldehydes formed. In examining Figure 5.5, it can be seen that the level of total aldehydes found just after the anthracite/sand filters remains fairly constant throughout the phase. It can be speculated that there was perhaps a certain base level of aldehydes present in the anthracite/sand filters, causing a constant minimum level to be detected after the filters at lower flowrates. Thus, where it was seen in Figure 5.6 that aldehyde levels increased by 50 percent in the anthracite/sand filters it can be concluded that the amount of aldehydes initially formed was small in
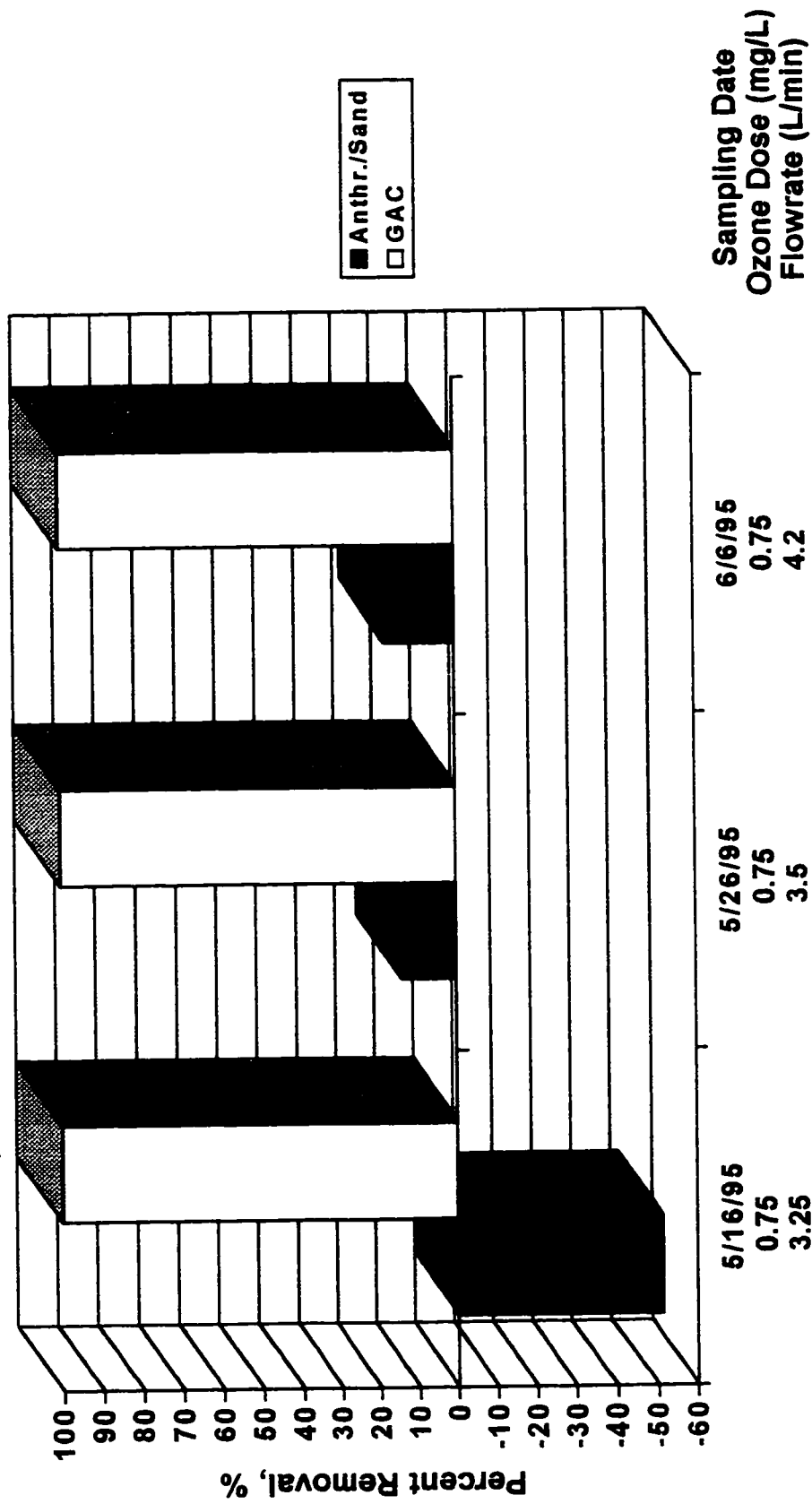
Figure 5.6 - Percent removals of total aldehydes in anthracite/sand filters and GAC contactors - Phase 2.

comparison to the base level of aldehydes already present on the filters, showing an increase in levels. Again, the GAC contactors (C2-3) were found to remove 100 percent of the aldehydes all of the time.

Also noted in this phase was the fact that the low-molecular-mass aldehydes (formaldehyde, acetaldehyde and propanal) actually increased some times instead of decreasing in the anthracite/sand filters, while the high-molecular-mass dialdehydes (glyoxal and methyl-glyoxal) both increased and decreased in the anthracite/sand filters. Again, according to the literature, when there is little or no biomass present on the filters, there appears to be additional aldehyde formation on the filter bed (Weinberg et al., 1993). This has been attributed to the shedding of previously adsorbed by-products. This reason is a possible explanation for the findings in this research. However, it is unknown why this change from phase one was found in phase two. The changes in aldehyde/dialdehyde levels can be seen in Table 5.2.

Table 5.2 shows the individual levels of aldehydes throughout the pilot plant for only the raw water (RAW), the settled water (S2) and the anthracite/sand filtered water (F2) on side two of the plant. At all other sample locations, aldehydes were either below method detection limits or not detected. As can be seen from Table 5.2, the major aldehydes consistently detected were: formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal. This is consistent with the findings in phase one. Also consistent with the findings in phase one was the fact that formaldehyde was present at the highest concentration throughout

64

Concentrations of Aldehydes Present (μg/L)

ALDEHYDE	5/16/1995 O_3 Dose = 0.75 mg/L Flowrate = 3.25 L/min			5/26/1995 O_3 Dose = 0.75 mg/L Flowrate = 3.5 L/min			6/6/1995 O_3 Dose = 0.75 mg/L Flowrate = 4.2 L/min		
	RAW	S2	F2	RAW	S2	F2	RAW	S2	F2
Formaldehyde	-	5.3	7.1	-	7.2	5.2	-	5.9	7.4
Acetaldehyde	-	4.2	5.0	-	7.2	4.1	-	5.2	4.0
Propanal	-	-	2.8	-	-	1.7	-	-	-
Glyoxal	-	1.2	1.3	-	3.5	4.2	-	3.4	3.1
Methyl Glyoxal	-	-	-	-	3.4	3.1	-	3.2	-
TOTAL	-	10.7	16.2	-	21.3	18.3	-	17.7	14.5

Table 5.2 - Individual concentrations of aldehydes present during pre-coagulation ozonation treatment - Phase 2

65

phase two. Again, these findings are consistent with many other researchers' findings with completely different sources of water. (Miltner et al.,1992; Krasner et al., 1993; Weinberg et al., 1993; Schechter and Singer, 1994; and Najm and Krasner, 1995).

5.4. Phase Three Results

Phase three consisted of comparing pre-coagulation ozonation treatment (side one of the pilot plant) with post-sedimentation ozonation treatment (side two of the pilot plant). In this phase, the ozone dose was kept constant for both sides at a transferred dose of 1.2 mg/L. The flowrate through the anthracite/sand filters was varied from 3.0 L/min to 4.8 L/min on both sides of the plant. Five sets of samples were collected throughout the months of September and October, 1995.

Figure 5.7 shows the level of total aldehydes detected on the pre-coagulation ozonation treatment side of the plant (side 1) and Figure 5.8 shows the level of total aldehydes detected on the post-sedimentation ozonation treatment side of the plant (side 2) during phase three. On the pre-coagulation ozonated side, total aldehydes seen in the sedimentation tank (S1) maintained a fairly constant formation level of about 22 μg/L. This was to be expected since the ozone dose remained constant throughout the phase. It was not possible to know aldehyde formation levels for the post-sedimentation ozonated side, since
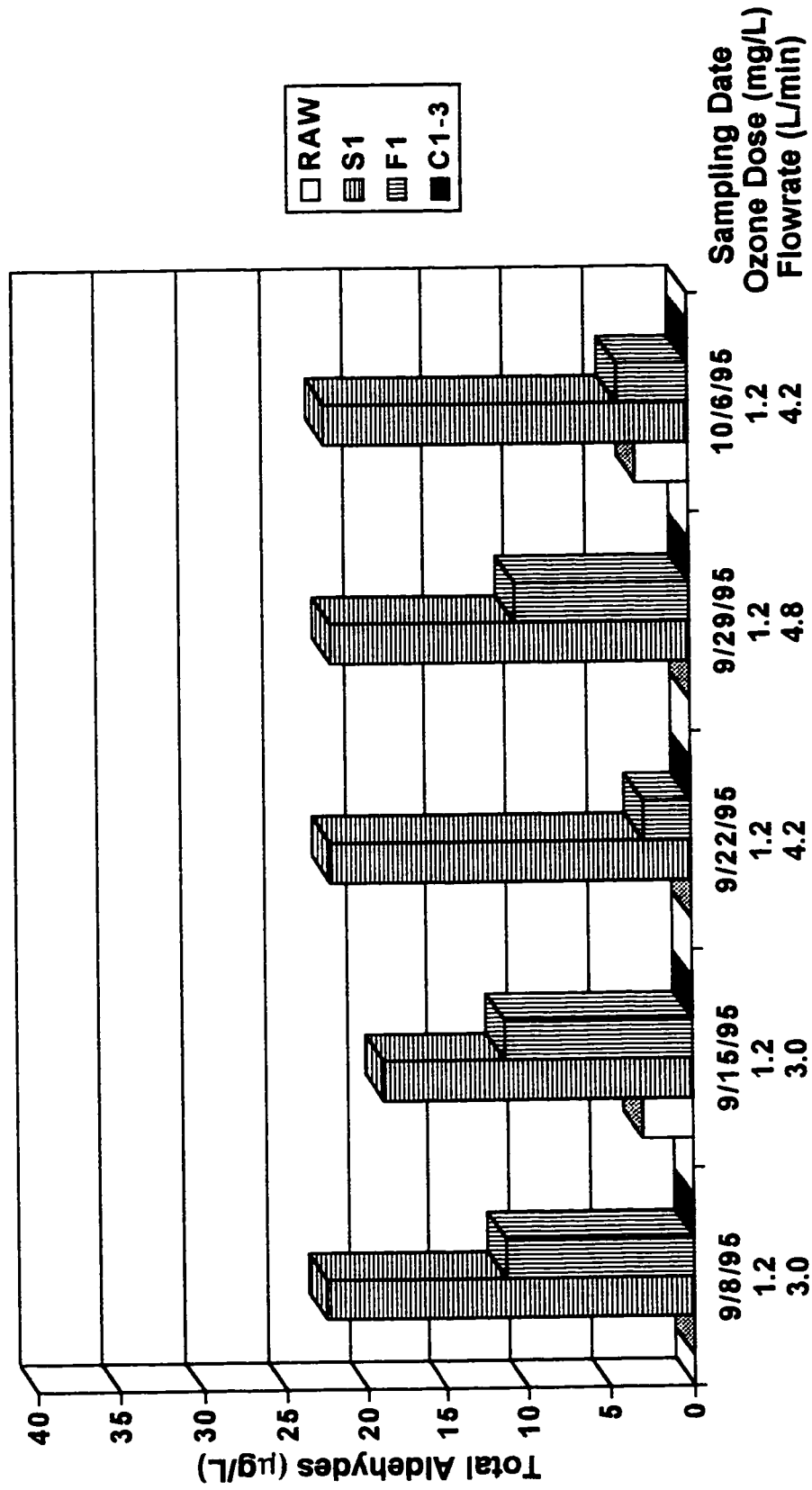
Figure 5.7 - Total aldehyde levels detected during pre-coagulation ozonation treatment - Phase 3.

Figure 5.8 – Total aldehyde levels detected during post-sedimentation ozonation treatment - Phase 3.

68

the sampling point in the pilot plant was before ozone was added to the settled water.

Examining aldehyde removals in Figure 5.7, pre-coagulation ozonation treatment, it can be seen that levels in the anthracite/sand filters remained at about 10 or 11 μg/L for all flowrates excepting the flowrate of 4.2 L/min. It is seen that there is a much higher removal rate at this flowrate. Perhaps at the higher flowrate (4.8 L/min) there is some residence time effect so that, if the filters are biologically active, there is not enough time for the organisms to degrade the aldehydes, and at the lower flowrate (3.0 L/min), there is actually some adsorption effect that keeps a constant level of aldehydes on the anthracite/sand filters. In one study (Weinberg et al., 1993), it was found that low flowrates increased aldehyde removals. However, these conclusions were drawn from many different plants operating at different flowrates, not one plant altering the flowrate. It is difficult to compare this study with the research in this thesis, since different flowrates were not compared at one plant. Regardless, there seems to be some improvement of removal of aldehydes in pre-coagulation ozonation at a flowrate of 4.2 L/min in this research. On the post-sedimentation ozonation treatment side, it is difficult to draw any conclusions since it is not known how much of the aldehydes produced were removed. However, it can be seen that the levels found after the anthracite/sand filters on this side are approximately the same or slightly higher than those found on side one, except for one sample on September 15, 1995. It seems that there is not a

very significant difference between the two plant configurations in this respect in terms of aldehyde levels present after the anthracite/sand filters.

Figure 5.9 shows the percentage removals of total aldehydes in the anthracite/sand filters and the GAC contactors on side one of the plant for phase three. It can be seen that at the flowrates of 3.0 and 4.8 L/min, there is a removal of between 40 to 50 percent of total aldehydes after the anthracite/sand filters (F2). At the flowrate of 4.2 L/min, however, the removal rate is between 80 and 85 percent. The flowrate of 4.2 L/min significantly improves aldehyde removals and has been discussed in the preceding paragraph. There is a noticeably higher removal rate in the anthracite/sand filters in this phase than in the previous two phases. The most likely cause of this is that since the water temperature had risen significantly since the other two phases, as can be seen in Table 5.3, the filters had developed significantly more biological activity and were subsequently able to remove more aldehydes. Finally, as with the rest of this research, the GAC contactors on both sides of the plant (C1-3 and C2-3) removed 100 percent of the aldehydes at all times. For side two, since the only removal that could be quantified was the GAC contactor, the removals are not shown here. The removals are again 100 percent in the GAC contactors.

It is also noted that the low-molecular-mass aldehydes (formaldehyde, acetaldehyde and butanal) decreased consistently in the anthracite/sand filters, while the high-molecular-mass dialdehydes (glyoxal and methyl-glyoxal) also

70
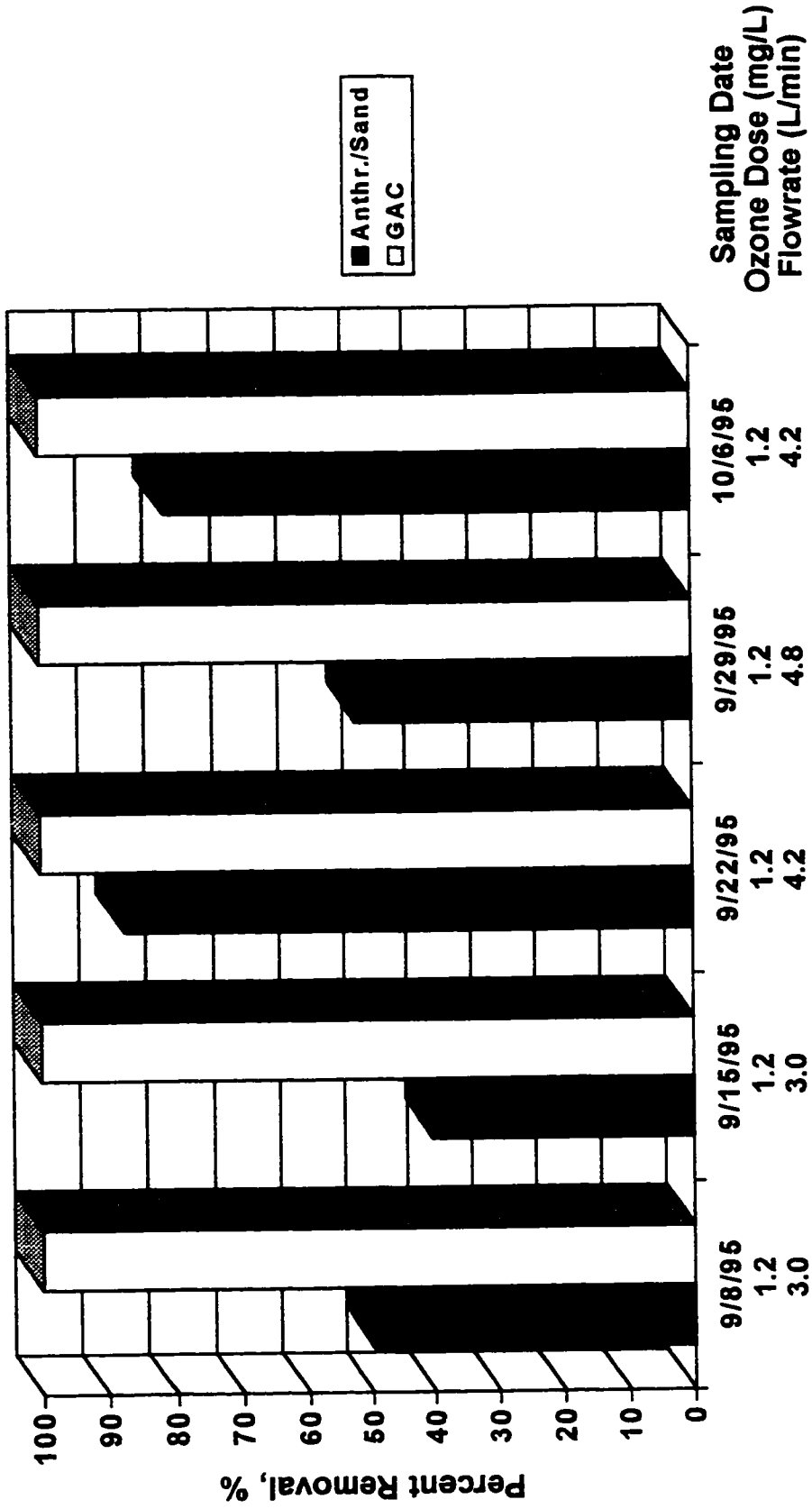
Figure 5.9 - Percent removals of total aldehydes in anthracite/sand filters and GAC contactors - Phase 3.

Phase	Sampling Date	Temperature (°C)
One	March 1, 1995	1.6
	March 8, 1995	1.7
	March 17, 1995	4.7
	March 22, 1995	4.8
	March 28, 1995	6.5
Three	September 8, 1995	22.0
	September 15, 1995	21.1
	September 22, 1995	17.9
	September 29, 1995	17.7
	October 6, 1995	16.6

Table 5.3 - Change in raw water temperature during research at the WUC Pilot Plant.

decreased consistently in the anthracite/sand filters but to a lesser extent. Once more, it appears that the dialdehydes are more difficult to remove than the aldehydes, and this is consistent with other researcher's findings (Weinberg *et al.*, 1993). The changes in aldehyde/dialdehyde levels can be seen in Table 5.4 and Table 5.5.

Table 5.4 shows the levels of various types of aldehydes throughout the pilot plant for only the raw water (RAW), the settled water (S1) and the anthracite/sand filtered water (F1) on side one of the plant. Table 5.5 shows these individual levels of aldehydes in the pilot plant for only the raw water (RAW) and the anthracite/sand filtered water (F2) on side two of the plant. At all other sample locations, aldehydes were either below method detection limits or not detected. As can be seen from Tables 5.4 and 5.5, the major species of aldehydes consistently detected were: formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal. This is consistent with the findings in both phase one and phase two. Formaldehyde was the aldehyde that was present at the highest concentration for most of the samples in phases one and two. However, in this phase acetaldehyde was sometimes the aldehyde that was present at the highest concentration for some of the samples, instead of formaldehyde. This may be due to the differences in raw water quality because of seasonal variations. Unfortunately, no TOC or DOC values were measured during this research to correlate with these observations.

Concentrations of Aldehydes Present (µg/L)

ALDEHYDE	9/8/1995 O₃ Dose = 1.2 mg/L Flowrate = 3.0 L/min			9/15/1995 O₃ Dose = 1.2 mg/L Flowrate = 3.0 L/min			9/22/1995 O₃ Dose = 1.2 mg/L Flowrate = 4.2 L/min			9/29/1995 O₃ Dose = 1.2 mg/L Flowrate = 4.8 L/min			10/6/1995 O₃ Dose = 1.2 mg/L Flowrate = 4.2 L/min		
	RAW	S1	F1	RAW	S1	F1	RAW	S1	F1	RAW	S1	F1	RAW	S1	F1
Formaldehyde	-	6.8	3.3	3.0	5.8	3.6	-	9.3	-	-	7.9	3.2	-	10.5	-
Acetaldehyde	-	7.7	2.8	-	10.2	7.2	-	5.8	-	-	6.7	2.8	-	1.9	-
Butanal	-	-	-	-	-	-	-	-	-	-	1.4	-	3.1	-	-
Glyoxal	-	4.0	3.3	-	0.8	0.5	-	4.0	2.8	-	3.2	2.8	-	5.8	4.2
Methyl Glyoxal	-	4.0	1.9	-	2.1	-	-	3.0	-	-	2.8	1.7	-	4.1	-
TOTAL	-	22.5	11.3	3.0	18.9	11.3	-	22.1	2.8	-	22.0	10.5	3.1	22.3	4.2

Table 5.4 - Individual concentrations of aldehydes present during pre-coagulation ozonation treatment - Phase 3

Concentrations of Aldehydes Present (μg/L)

ALDEHYDE	9/8/1995 O_3 Dose = 1.2 mg/L Flowrate = 3.0 L/min		9/15/1995 O_3 Dose = 1.2 mg/L Flowrate = 3.0 L/min		9/22/1995 O_3 Dose = 1.2 mg/L Flowrate = 4.2 L/min		9/29/1995 O_3 Dose = 1.2 mg/L Flowrate = 4.8 L/min		10/6/1995 O_3 Dose = 1.2 mg/L Flowrate = 4.2 L/min	
	RAW	F2	RAW	F2	RAW	F2	RAW	F2	RAW	F2
Formaldehyde	-	4.5	3.0	-	-	-	-	1.6	-	3.4
Acetaldehyde	-	4.9	-	-	-	-	-	4.0	-	2.4
Butanal	-	-	-	-	-	-	-	-	3.1	-
Glyoxal	-	2.5	-	-	-	2.5	-	2.5	-	3.5
Methyl Glyoxal	-	2.0	-	-	-	1.7	-	1.9	-	2.0
TOTAL	-	13.9	3.0	-	-	4.2	-	10.0	3.1	11.3

Table 5.5 - Individual concentrations of aldehydes present during post-sedimentation ozonation treatment - Phase 3

5.5. Other Characteristics

Throughout the three phases involved in this research, certain raw water characteristics were measured to determine if they would have any effect on aldehyde formation or removal. These characteristics were: pH, temperature, and turbidity. Table 5.6 outlines the measurements of these characteristics taken throughout the entire research.

It can be seen that pH varied between 8.17 and 8.74 throughout the research. Although it has been found in the literature that aldehyde levels increased when the pH levels are relatively lower (Andrews and Huck, 1994; Schechter and Singer, 1995), a drop of 0.6 pH units does not constitute a significant enough change to increase aldehyde levels noticeably. In the literature, the relative difference between high and low pH was 2 or 3 pH units.

The temperature of the raw water increased during the time of this research and slowly decreased after September 8, 1995. This change in temperature can be a factor in increasing the biological activity of the anthracite/sand filters and the subsequent greater removal of aldehydes in these filters during warmer months.

Finally, it can be seen that the turbidity levels fluctuated from as low as 1.5 NTU to as high as 59.4 NTU as the research progressed. Since the turbidity levels varied so greatly while other known factors were kept constant with consistent results, it can be assumed that there is no correlation between turbidity levels and the formation and removal of aldehydes.

Phase	Sampling Date	pH	Temperature (°C)	Turbidity (NTU)
One	March 1, 1995	8.46	1.6	1.5
	March 8, 1995	8.74	1.7	6.4
	March 17, 1995	8.38	4.7	11.5
	March 22, 1995	8.17	4.8	5.8
	March 28, 1995	8.17	6.5	12.6
Two	May 16, 1995	-	-	4.0
	May 26, 1995	-	-	7.1
	June 6, 1995	-	-	-
Three	September 8, 1995	8.42	22.0	28.1
	September 15, 1995	8.36	21.1	8.7
	September 22, 1995	8.25	17.9	12.2
	September 29, 1995	8.54	17.7	2.9
	October 6, 1995	8.17	16.6	59.4

Table 5.6 – Summary of raw water physical characteristics during research at the WUC Pilot Plant.

Chapter VI

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The following conclusions may be drawn from this research:

- conventional water treatment processes do not produce aldehydes;

- aldehyde production is increased as transferred ozone dose is increased;

- major aldehyde species consistently formed as a result of ozonation of Detroit River water are: formaldehyde, acetaldehyde, glyoxal, and methyl-glyoxal; with formaldehyde usually being found at the highest concentration;

- aldehydes are removed marginally, if at all, in anthracite/sand filtration and an increase in temperature causes an increase in removal, most likely due to the increased biological activity in the filters;

- aldehydes are consistently removed completely in GAC contactors;

- low-molecular-mass aldehydes usually decrease, while high-molecular-mass aldehydes only slightly decrease or even increase in anthracite/sand filters, showing that glyoxal and methyl-glyoxal

are more difficult to remove in anthracite/sand filtration;

- at low flowrates, there appears to be a minimum level of aldehydes present in the anthracite/sand filters;

- at a flowrate of 4.2 L/min through the anthracite/sand filters, there is a much higher removal of aldehydes than at lower or higher flowrates; perhaps due to a residence time effect at higher flowrates and an adsorption effect at lower flowrates which keeps a constant level of aldehydes on the anthracite/sand filters;

- pH variations in the raw water are not significant enough to affect aldehyde levels, and turbidity levels appear to have no effect on the formation or removal of aldehydes.

6.2. Recommendations

The determination of the maximum level of aldehydes should be performed by increasing the ozone dose to the highest required dose, and further study should be made into the effects of biological activated filtration on the removal of specific species of aldehydes. The bioactivity of the filters should be measured while aldehyde samples are being measured. The background organic matter content and composition should be more closely studied by measuring TOC and DOC while aldehydes are measured.

Also, other ozonation by-products such as oxoacids and carboxylic acids should be studied and the determination of the negative health effects of

ozonation by-products at the levels found in drinking water treatment should be more closely examined.

Finally, where GAC contactors are used to remove aldehydes produced during ozonation, breakthrough curves should be determined to ensure safe operation.

REFERENCES

ALARCON HERRERA, M.T., "Removal of Trihalomethane Precursors In Drinking Water Treatment Processes", *Ph. D. Dissertation*, University of Windsor, (1994).

ALCEON CORP., *An Overview of Available Information on the Toxicity of Drinking Water Disinfectants and Their By-Products*, Cambridge, MA., (1993).

AMERICAN WATER WORKS ASSOCIATION, *Water Chlorination Principles and Practices*, AWWA Manual M20, AWWA, New York, (1973).

AMERICAN WATER WORKS ASSOCIATION RESEARCH FOUNDATION (AWWARF) and COMPAGNIE GÉNÉRALE DES EAUX (CGEAUX), *Ozone in Water Treatment: Application and Engineering*, Langlais, B.; Reckhow, D.A.; and Brink, D.R. (eds.), Lewis Publishers, Chelsea, MI, (1991).

ANDREWS, S.A., *Ph. D. Dissertation*, University of Alberta, (1993).

ANDREWS, S.A. AND HUCK, P.M., "Using Fractionated Natural Organic Matter to Quantitate Organic By-Products of Ozonation", *Ozone Sci. & Engrg.*, v.16, pp.1-12, (1994).

APHA-AWWA-WPCF, *Standard Methods for the Examination of Water and Wastewater*, Clesceri, L.S.; Greenberg, A.E.; and Trussell, R.R. (eds.), 17th ed., (1989).

BAILEY, P.S., *Ozonation in Organic Chemistry, Vol. 1, Olefinic Compounds.*, Academic Press, New York, (1978).

BAILEY, P.S., *Ozonation in Organic Chemistry, Vol. 2, Non-Olefinic Compounds.*, Academic Press, New York, (1982).

BELLAR, T.A. AND LICHTENBERG, J.J., "Determining Volatile Organics at Micrograms Per Liter Levels By Gas Chromatography", *J. Am. Water Works Assoc.*, v.66, no.12, pp.739-744, (1974).

BULL, R.J. AND KOPFLER, F.C., "Health Effects of Disinfectants and Disinfection By-Products", *AWWARF Report*, Denver, CO., (1991).

CANADIAN WATER AND WASTEWATER ASSOCIATION (CWWA), "Trihalomethane Forum - September 13, 1992.", *CWWA Bulletin*, ISSN 0836-0278, (1992).

DANIEL, F.B. ET AL., "Subchronic Toxicity Study of Ozonated and Ozonated/Chlorinated Humic Acids in Sprague-Dawley Rats: A Model System for Drinking Water Disinfection", *Envir. Sci. & Technol.*, v.25, no.1, pp.93-98, (1991).

EISENHAUER, H.R., "The Ozonation of Phenolic Wastes", *Jour. WPCF*, v.40, pp.1887, (1968).

FAUST, S.D. AND ALY, O.M., *Chemistry of Water Treatment*, Butterworth Publishers, Woburn, MA, (1983).

FERGUSON, D.W.; GRAMITH, J.T.; AND MCGUIRE, M., "Applying Ozone for Organics Control and Disinfection: A Utility Perspective", *J. Am. Water Works Assoc.*, v.83, no.5, pp.32, (1991).

GILLI, G. ET AL., "Water Disinfection: A Relationship Between Ozone and Aldehyde Production", *Ozone Sci. & Engrg.*, v.11, no.10, pp.231-241, (1989).

GLAZE, W.H., "Chemistry of Ozone, By-Products and Their Health Effects", *Ozonation: Recent Advances and Research Needs.*, AWWARF, Denver, CO., (1986a).

GLAZE, W.H., "Reaction Products of Ozone: A Review", *Envir. Health Perspectives*, v.69, pp.151-157, (1986b).

GLAZE, W.H. ET AL., "Application of Closed Loop Stripping and XAD Resin Adsorption for the Determination of Ozone By-Products from Natural Water", *Biohazards of Drinking Water Treatment*, Larson, R.A. (ed.), Lewis Publishers, Inc., Chelsea, MI, p.201, (1988).

GLAZE, W.H. ET AL., "Ozonation By-Products. 2. Improvement of an Aqueous-Phase Derivitization Method for the Detection of Formaldehyde and Other Carbonyl Compounds Formed by the Ozonation of Drinking Water", *Envir. Sci. & Technol.*, v.23, no.7, pp.838-847, (1989a).

GLAZE, W.H. ET AL., "Evaluation of Ozonation By-Products From Two California Surface Waters", *J. Am. Water Works Assoc.*, v.81, no.8, pp.66-73, (1989b).

HAAG, W.R. AND HOIGNE, J., "Ozonation of Bromide-Containing Water: Kinetics of Formation of Hypobromous Acid and Bromate", *Envir. Sci. & Technol.*, v.17, pp.261, (1983).

HENRY, J.G. AND HEINKE, G.W., *Environmental Science and Engineering*, Prentice-Hall Inc., Englewood Cliffs, NJ, (1989).

HOFF, J.C., *Inactivation of Microbial Agents by Chemical Disinfectants*, p.5, EPA/600/S2-86/067, USEPA, Washington D.C., (1986).

HOIGNE, J., "The Chemistry of Ozone in Water", *Process Technologies for Water Treatment*, Plenum Publishing Corp., New York, (1988).

HOIGNE, J. AND BADER, H., "Ozonation of Water: Selectivity and Rate of Oxidation of Solutes", *3rd International Ozone Association (IOA) Congress Proceedings*, Paris, France, (1977).

HOIGNE, J. AND BADER, H., "Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water I. Non-Dissociating Organic Compounds", *Water Res.*, v.17, pp.173-183, (1983a).

HOIGNE, J. AND BADER, H., "Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water II. Dissociating Organic Compounds", *Water Res.*, v.17, pp.185-194, (1983b).

JACANGELO, J.G. ET AL., "Ozonation: Assessing Its Role in the Formation and Control of Disinfection By-products", *J. Am. Water Works Assoc.*, v.81, no.8, pp.74-84, (1989).

JOHNSON, J.D. (ed.), *Disinfection: Water and Wastewater*, Ann Arbor Science, Ann Arbor, MI, (1975).

JOLLEY, C. ET AL. (eds.), *Water Chlorination: Chemistry, Environmental Impact, and Health Effects*, v.6, Lewis Publishers, Inc., Chelsea, MI, (1990).

KAMEI, T.; TANPO, N.; AND TAMURA, S., "Environmental Mutagenicity of Compounds From Aquatic Humic Substances by Chlorination or Ozonation", *J. Jpn. Water Works Assoc.*, v.54, pp.25-33, (1985).

KOWBEL, D.J. ET AL., "Determination of Mutagenic Activity in Salmonella of Residual Fulvic Acids After Ozonation", *Water Res.*, v.16, pp.1537-1538, (1982).

KOWBEL, D.J. ET AL., "Chlorination of Ozonated Soil Fulvic Acids: Mutagenicity Studies in Salmonella", *Sci. Total Environ.*, v.37, pp.171-176, (1984).

KRASNER, S.W.; SCLIMENTI, M.J.; AND COFFEY, B.M., "Testing Biologically Active Filters for Removing Aldehydes Formed During Ozonation", *J. Am. Water Works Assoc.*, v.85, no.5, pp.62-71, (1993).

KUROKAWA, Y. ET AL., "Dose-Response Studies in the Carcinogenicity of Potassium Bromate in F344 Rats After Long-Term Oral Administration", *J. Natl. Cancer Inst.*, v.77, pp.977, (1986).

LAWRENCE, J. ET AL., "The Ozonation of Natural Waters: Product Identification", *Ozone Sci. & Engrg.*, v.2, pp.55-64, (1980).

MALLEVIALLE, J.; LAVAL, Y.; AND LEFEBVRE, M., "The Degradation of Humic Substances in Water By Various Oxidation Agents (Ozone, Chlorine, Chlorine Dioxide)", *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*, Rice, R.G. (ed.), pp.189-199, Ozone Press International, Cleveland, OH, (1978).

MALLEVIALLE, J., "Identified Reaction Products in Ozonization", *Ozonization Manual for Water and Wastewater Treatment*, Masschelein, W.J. (ed.), pp.105-125, John Wiley & Sons, New York, (1982b).

MASSCHELEIN, W.J., "Thermodynamic Aspects of the Formation of Ozone and Secondary Products of Electrical Discharge", *Ozonization Manual for Water and Wastewater Treatment*, Masschelein, W.J. (ed.), pp.9-12, John Wiley & Sons, New York, (1982).

MATSUDA, H. ET AL., "Aldehydes as Mutagens Formed By Ozonation of Humic Substances", *The Science of the Total Environment*, v.114, pp.205-213, (1992).

McKNIGHT, A. AND RECKHOW, D.A., "Reactions of Ozonation By-Products With Chlorine and Chloramines", *AWWA Annual Conference Proceedings*, Vancouver, B.C., (1992).

MEANS III, E.G. AND KRASNER, S.W., "D-DBP Regulation: Issues and Ramifications", *J. Am. Water Works Assoc.*, v.85, no.2, pp.68-73, (1993).

MILTNER, R.J.; SHUKAIRY, H.M.; AND SUMMERS, R.S., "Disinfection By-Product Formation and Control By Ozonation and Biotreatment", *J. Am. Water Works Assoc.*, v.84, no.11, pp.53-62, (1992).

MINISTER OF NATIONAL HEALTH AND WELFARE, *Guidelines for Canadian Drinking Water Quality*, 5th ed., p.18, Federal-Provincial Subcommittee on Drinking Water of the Federal-Provincial Advisory Committee on Environmental and Occupational Health, Ottawa, (1993).

NAJM, I.N. AND KRASNER, S.W., "Effects of Bromide and NOM on By-Product Formation", *J. Am. Water Works Assoc.*, v.87, no.1, pp.106-115, (1995).

PONTIUS, F.W., "Toxicology and Drinking Water Regulations", *J. Am. Water Works Assoc.*, v.82, no.10, pp.14-17, 90, (1990).

PONTIUS, F.W., "Reg-Neg Process Draws To A Close", *J. Am. Water Works Assoc.*, v.85, no.9, pp.18-19, (1993).

RICE, R.G.; PICHET, P.; AND VINCENT, M.A.(eds.), *Proceedings of The Second International Symposium On Ozone Technology*, International Ozone Institute, Syracuse, NY, (1976).

ROOK, J.J., "Formation of Haloforms During Chlorination of Natural Waters", *Water Treatment and Examination*, v.23, no.3, pp.234-243, (1974).

SCHALEKAMP, M., "Experiences with Ozone in Switzerland with Special Respect to the Changes in Hygienically Questionable Materials", *Ozonews*, International Ozone Association, (1978).

SCHECHTER, D.S. AND SINGER, P.C., "Formation of Aldehydes During Ozonation", *Ozone Sci. & Engrg.*, v.17, pp.53-69, (1995).

SCLIMENTI, M.J. ET AL., "Ozone Disinfection By-Products: Optimization of the PFBHA Derivatization Method for the Analysis of Aldehydes", *AWWA Water Quality Technology Conference (WTQC) Proceedings*, San Diego, CA, (1990).

SHEVCHENKO, M.A. AND TARAN, P.N., "Investigation of the Ozonolysis Products of Humus Materials", *Ukrain. Khim. Zh.*, v.32, pp.408-410, (1966).
SIEVERS, R.E. ET AL., "Environmental Trace Analysis of Organics in Water", *J. Chromatogr.*, v.142, pp.745-754, (1977).

SINGER, P.C., "Assessing Ozonation Research Needs in Water Treatment", *J. Am. Water Works Assoc.*, v.82, no.10, pp.78-88, (1990).

SOMIYA, I., AND YAMADA, H., "Products Formed During Ozonation of Organic Compounds in Aqueous Solutions", *Eisei Kagaku*, v.33, pp.365-384, (1987).

SYMONS, J.M.; BELLAR, T.A.; CARSWELL, J.K. ET AL., "National Organics Reconnaissance Survey For Halogenated Organics", *J. Am. Water Works Assoc.*, v.67, no.11, pp.634-647, (1975).

USEPA, *Federal Register*, 44:68670, (1979).

USEPA, *Federal Register*, 53:14:1892, (1988).

VAN HOOF, F. ET AL., "Determination of Aliphatic Aldehydes in Waters by High-Performance Liquid Chromatography", *Anal. Chim. Acta*, v.169, pp.419-424, (1985).

VIESSMAN, W.J. AND HAMMER M.J., *Water Supply and Pollution Control*, 5th ed., Harper Collins College Publishers, New York, (1993).

WEINBERG, H.S. ET AL., "Formation and Removal of Aldehydes in Plants That Use Ozonation", *J. Am. Water Works Assoc.*, v.85, no.5, pp.72-85, (1993).

WHITE, G.C., *Handbook of Chlorination*, Van Nostrand Reinhold Co., New York, (1972).

WORLD HEALTH ORGANIZATION, *Guidelines for Drinking Water Quality, vol.1 - Recommendations*, 2nd ed., WHO, Geneva, (1993).

YAMADA, H. AND SOMIYA, I., "The Determination of Carbonyl Compounds in Ozonated Water by the PFBOA Method", *Ozone Sci. & Engrg.*, v.11, no.2, pp.127-141, (1989).

YAMAMOTO, Y. ET AL., "Ozonation of Organic Compounds. 2. Ozonation of Phenol in Water", *Jour. Organic Chem.*, v.44, pp.2137, (1979).

Appendix A

STANDARD CALIBRATION CURVES
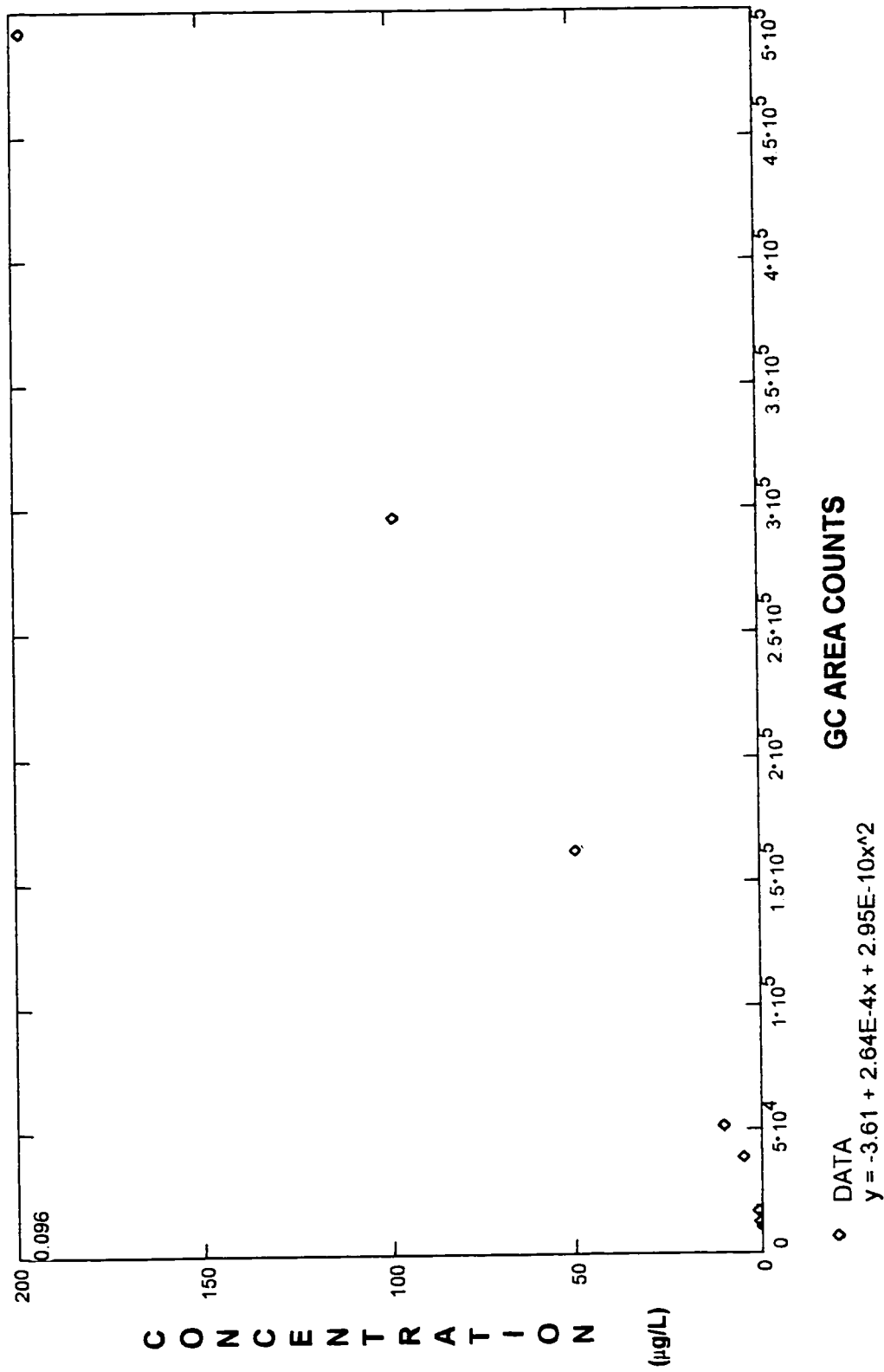
Figure A.1. - Standard Calibration Curve - Formaldehyde.

$y = -3.61 + 2.64E\text{-}4x + 2.95E\text{-}10x^2$

GC AREA COUNTS

CONCENTRATION (µg/L)
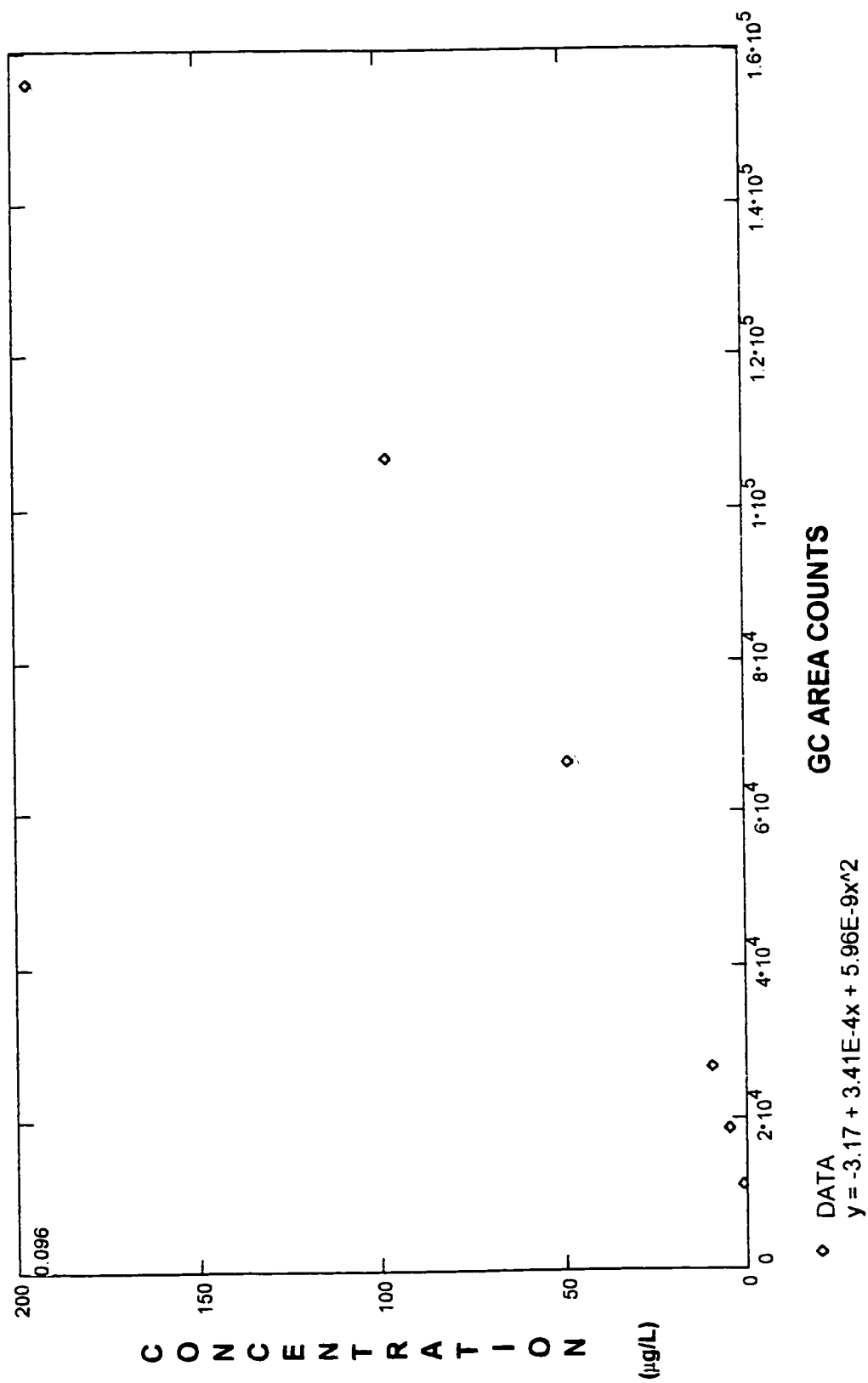
Figure A.2. - Standard Calibration Curve - Acetaldehyde.

$y = -3.17 + 3.41E-4x + 5.96E-9x^2$

GC AREA COUNTS

CONCENTRATION (µg/L)

89
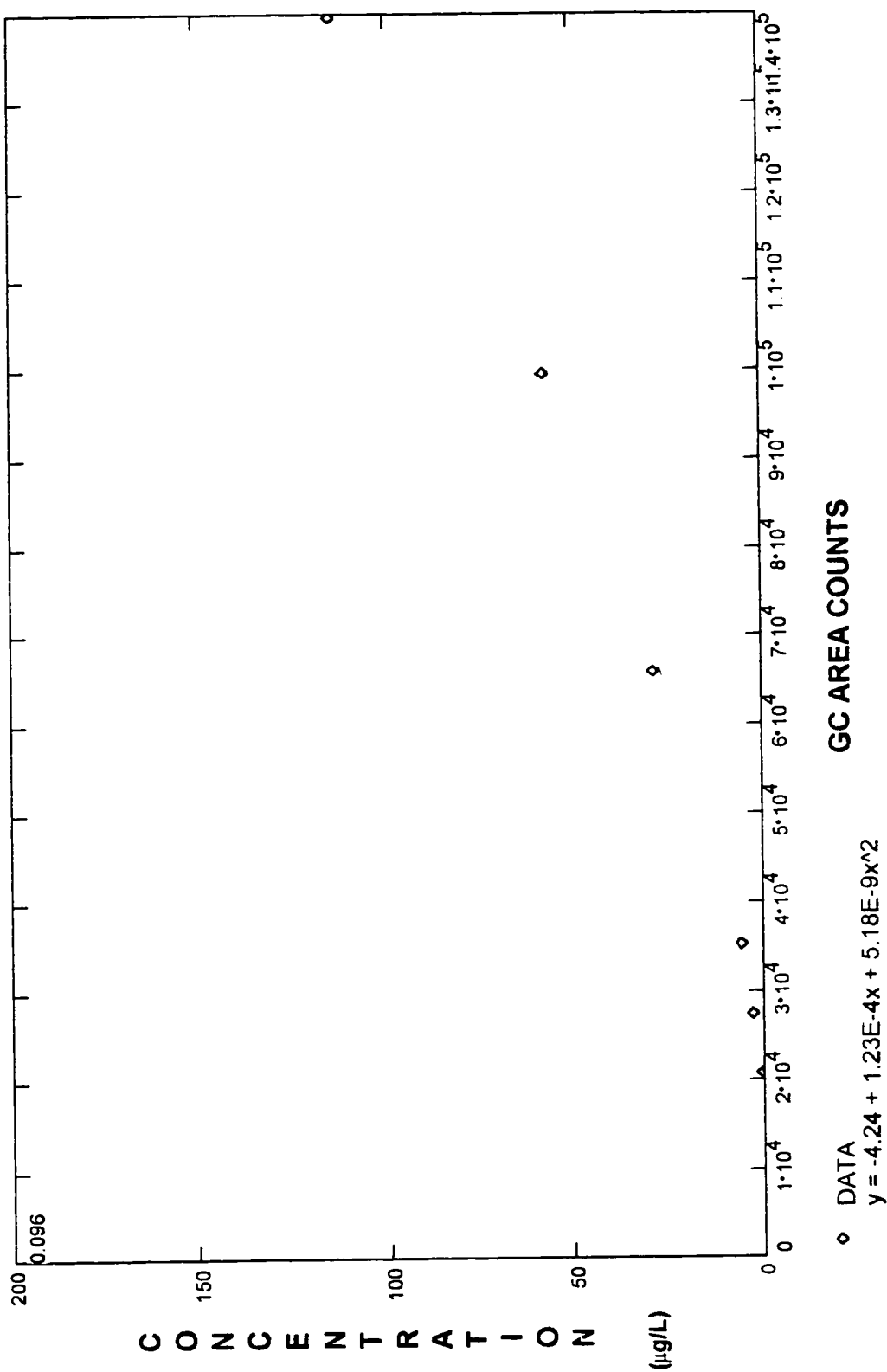
Figure A.3. - Standard Calibration Curve - Propanal.

$y = -4.24 + 1.23E\text{-}4x + 5.18E\text{-}9x^2$

DATA

GC AREA COUNTS

CONCENTRATION (µg/L)

$y = -3.22 + 4.46E\text{-}4x + 5.81E\text{-}9x^2$
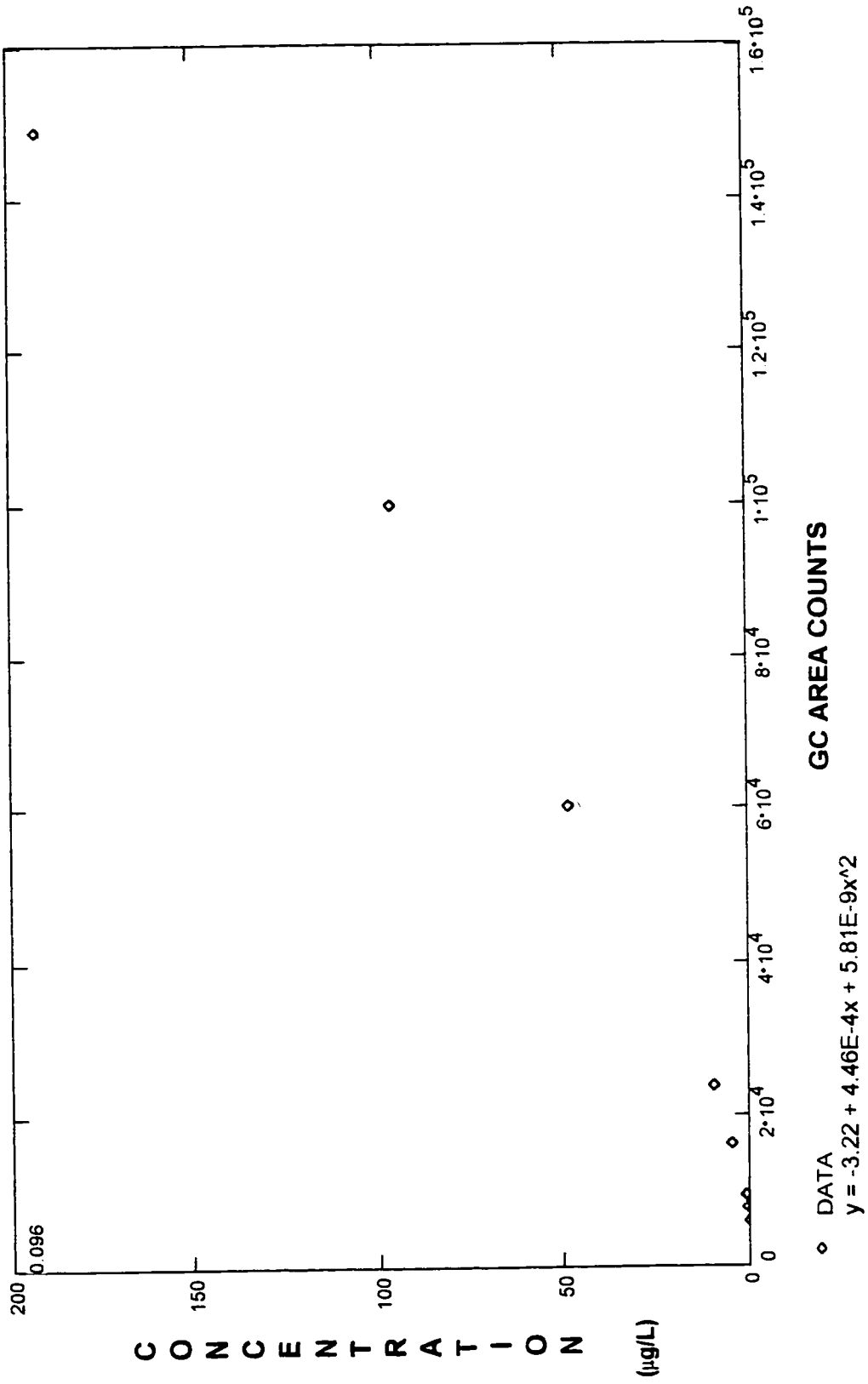
◇ DATA

Figure A.4. - Standard Calibration Curve - Butanal.

91

CONCENTRATION (µg/L)
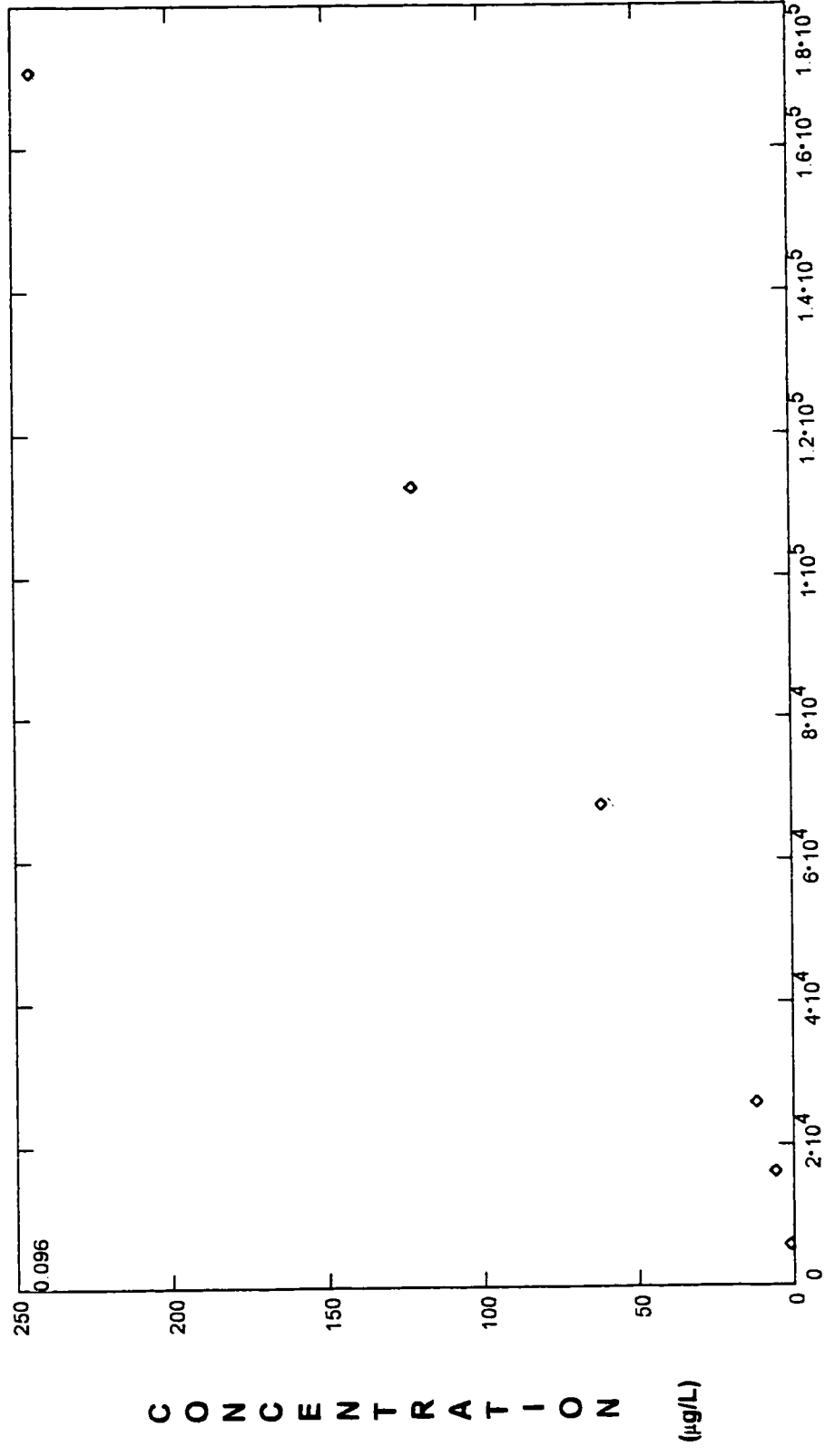
GC AREA COUNTS

◇ DATA
$y = -3.05 + 5.37E-4x + 5.31E-9x^2$

Figure A.5. - Standard Calibration Curve - Pentanal.

92
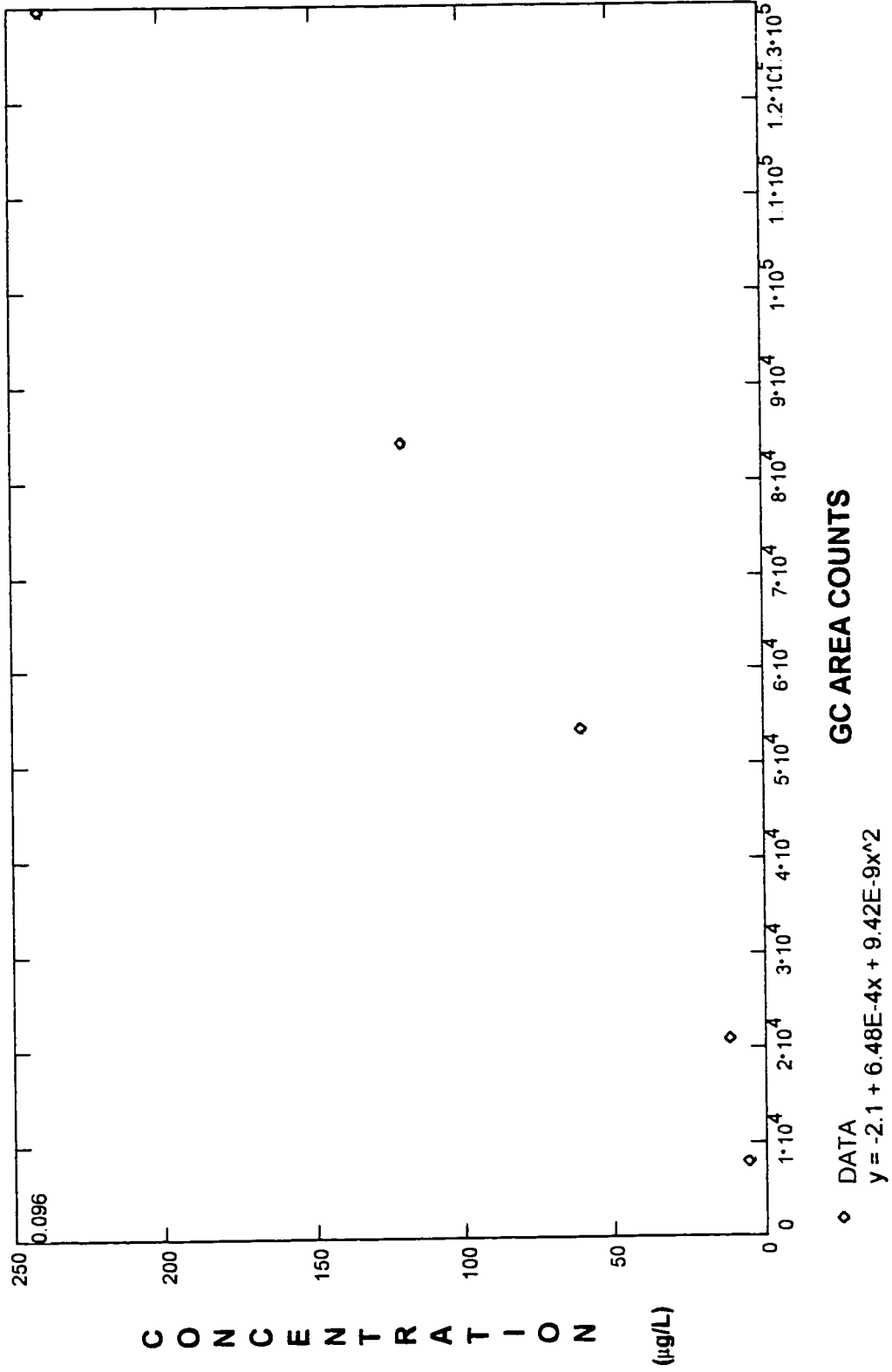
Figure A.6. - Standard Calibration Curve - Hexanal.

DATA
$y = -2.1 + 6.48E\text{-}4x + 9.42E\text{-}9x^{\wedge}2$

GC AREA COUNTS

CONCENTRATION (µg/L)

93
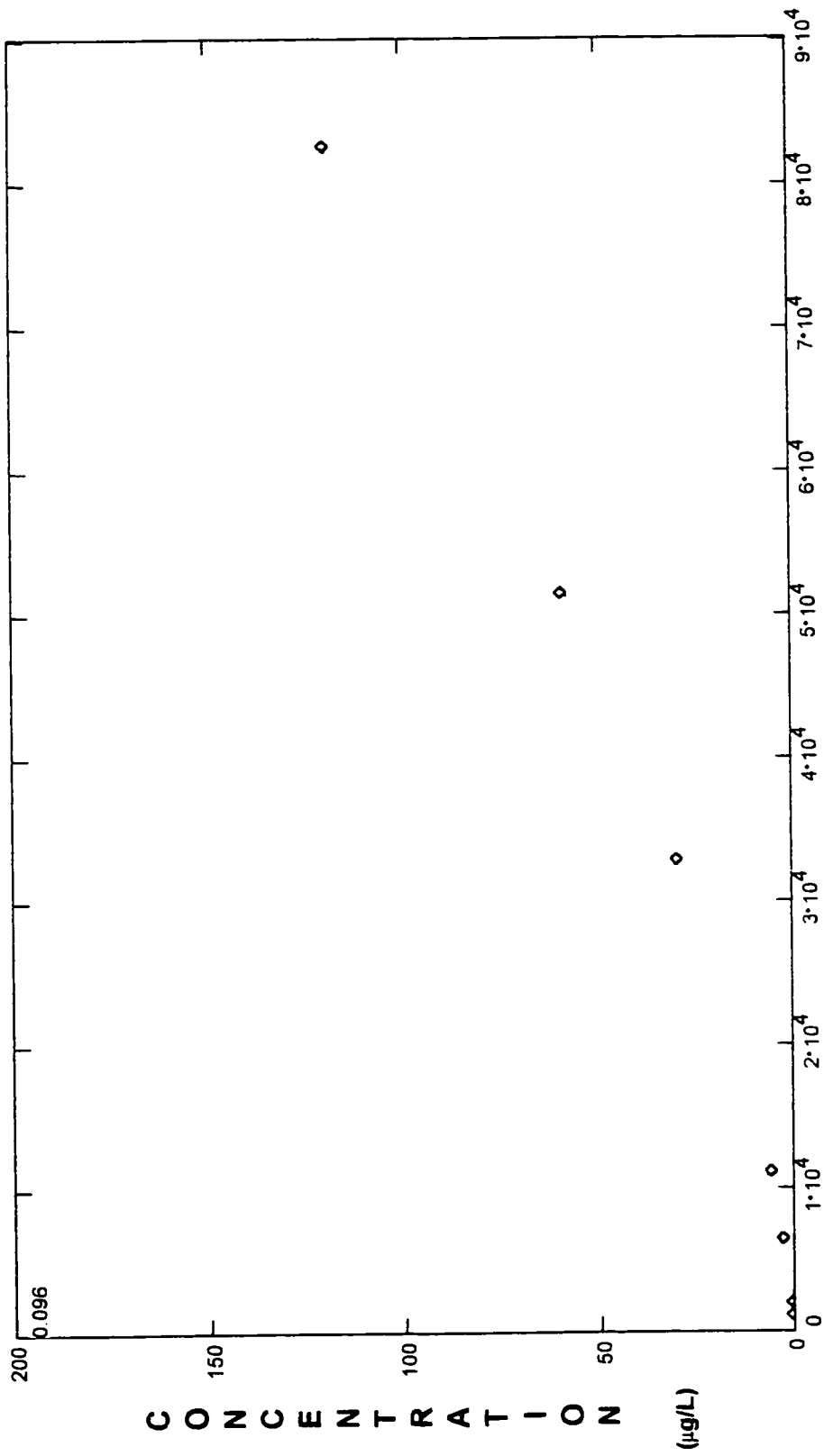
Figure A.7. - Standard Calibration Curve - Heptanal.

◇ DATA
y = -1.27 + 6.48E-4x + 9.94E-9x^2

GC AREA COUNTS

CONCENTRATION
(µg/L)

94
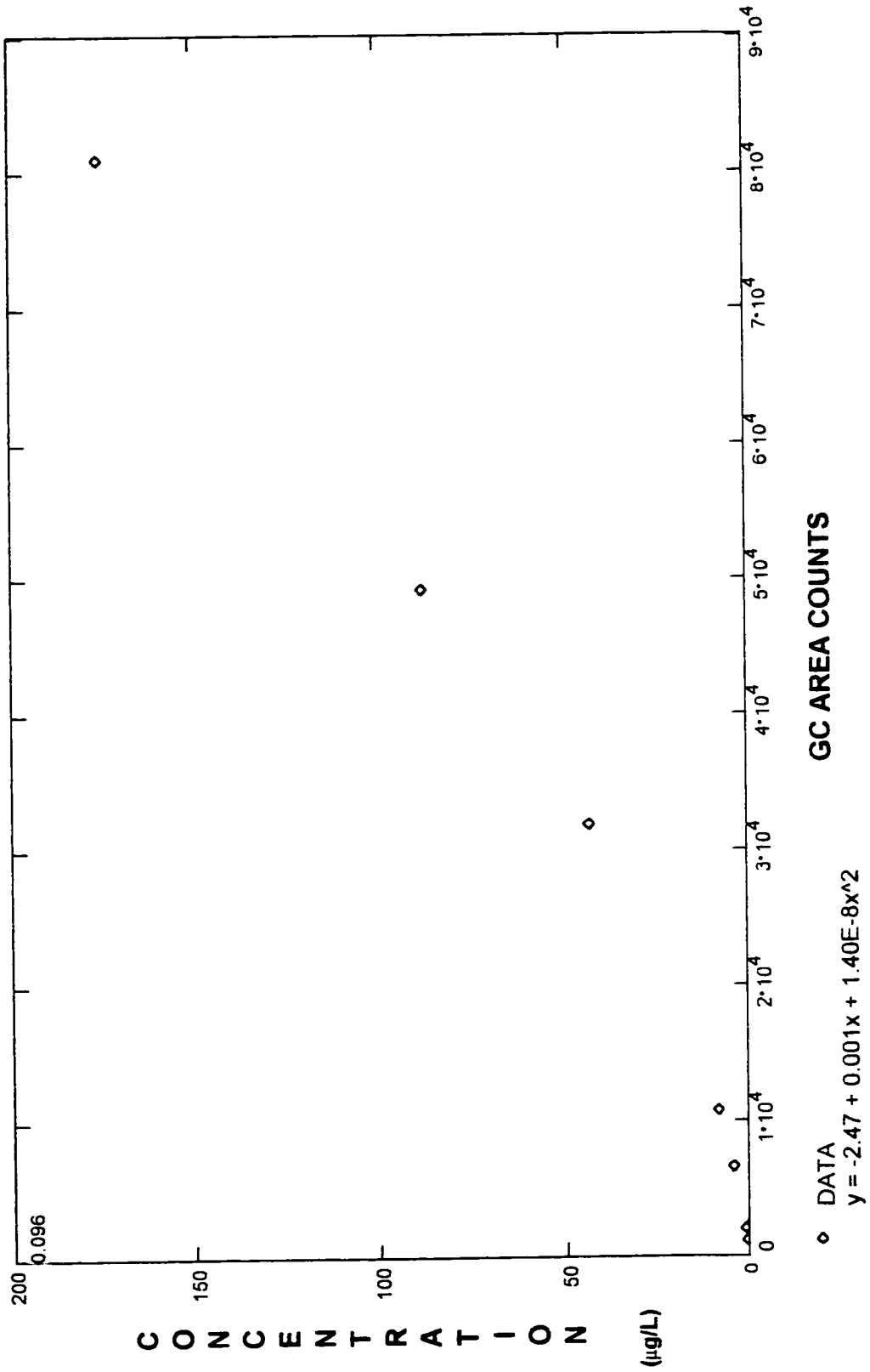
Figure A.8. - Standard Calibration Curve - Octanal.

DATA
y = -2.47 + 0.001x + 1.40E-8x^2

95
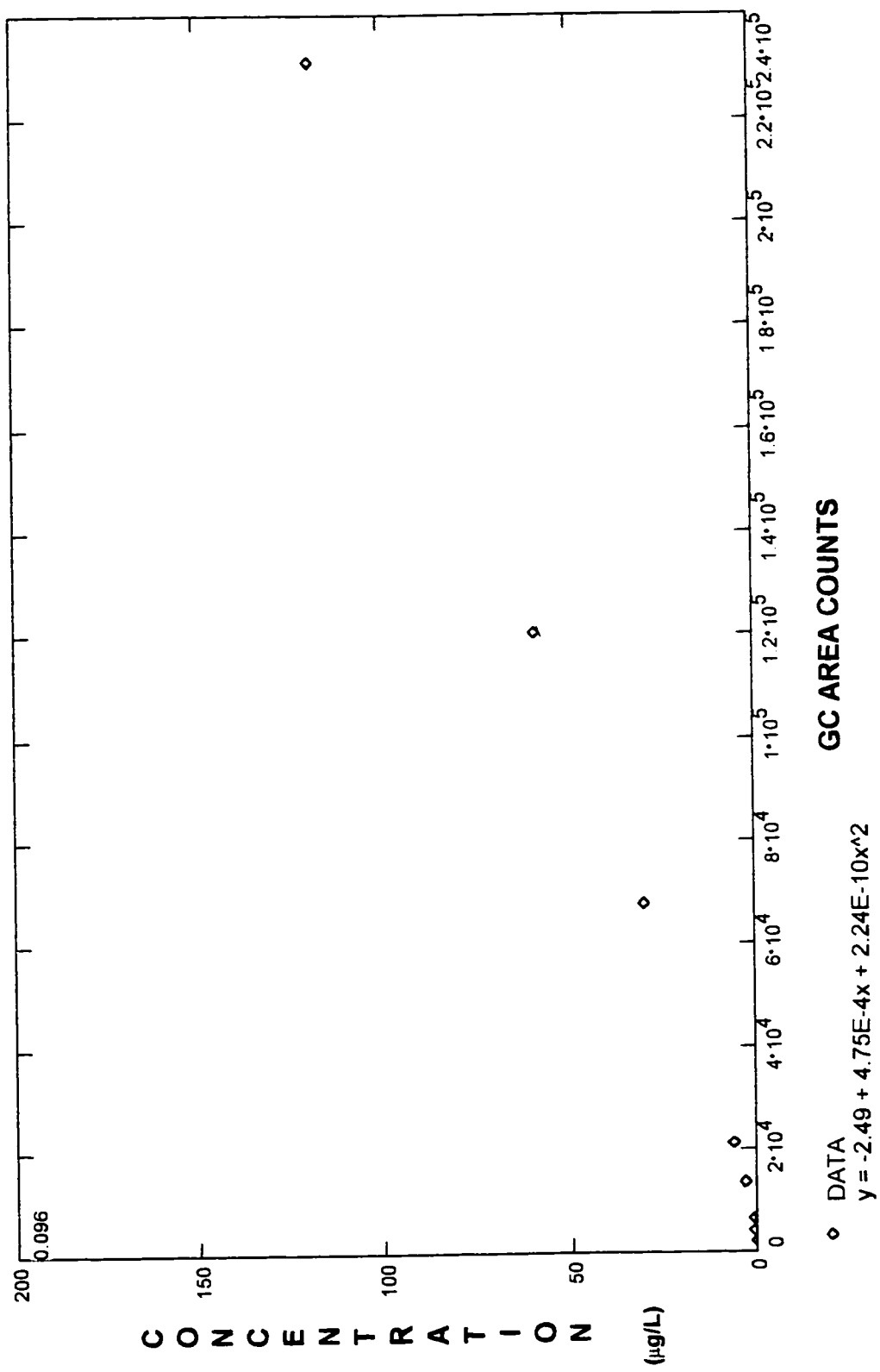
Figure A.9. - Standard Calibration Curve - Benzaldehyde.

DATA
y = -2.49 + 4.75E-4x + 2.24E-10x^2

96
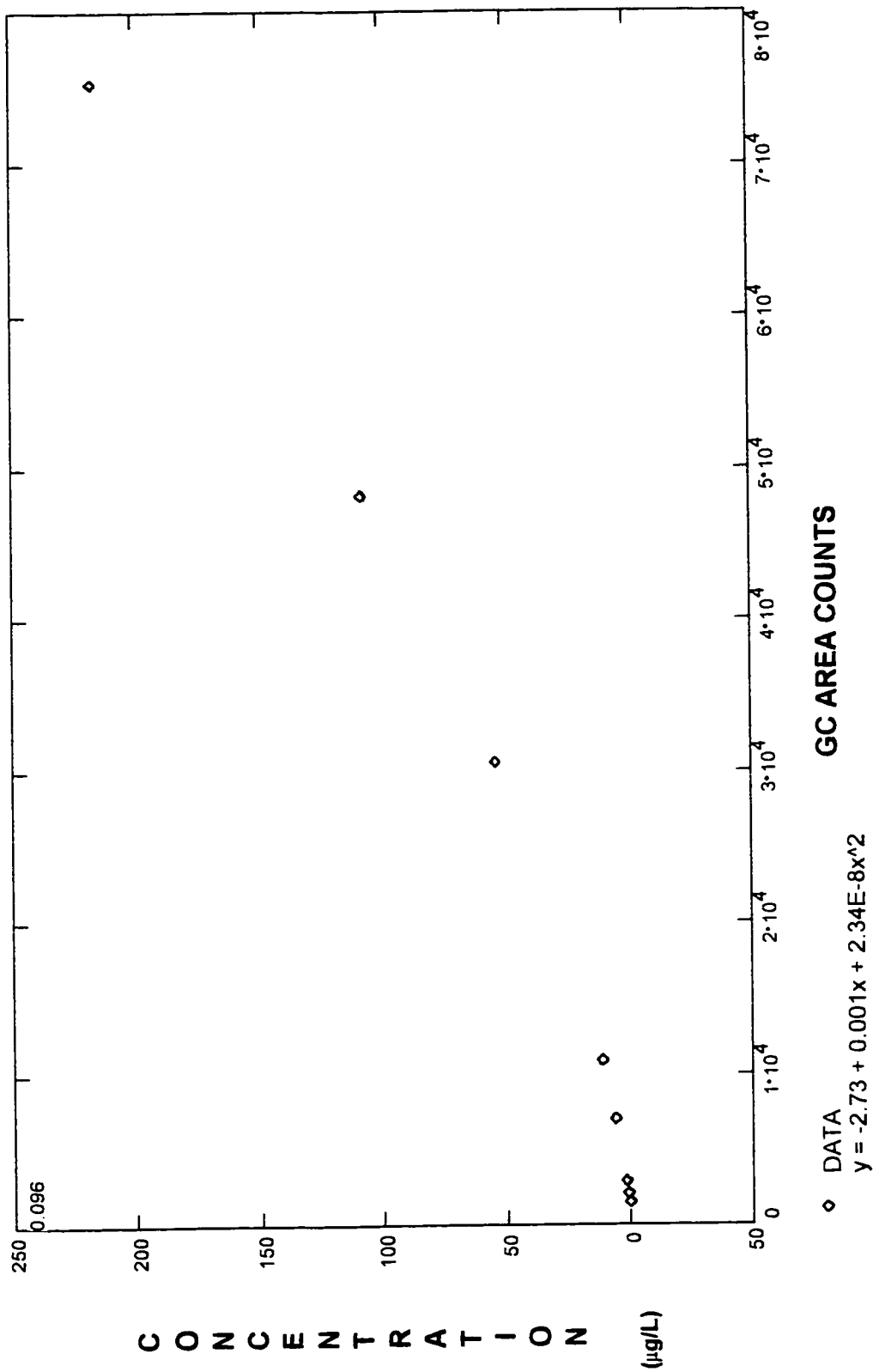
Figure A.10. - Standard Calibration Curve - Nonanal.

97

Figure A.11. - Standard Calibration Curve - Glyoxal.
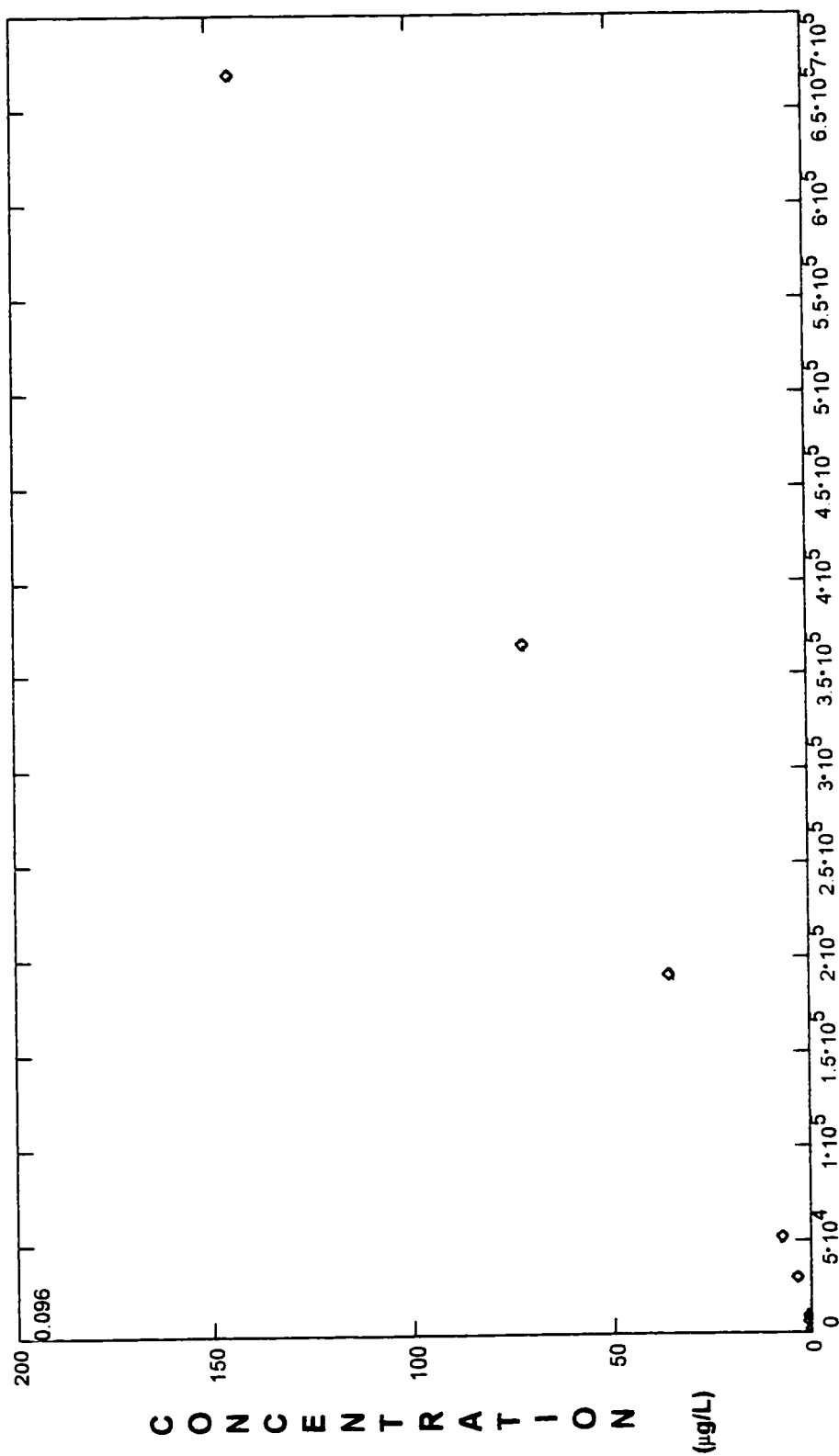
DATA
$y = -1.03 + 1.80\text{E-}4x + 5.53\text{E-}11x^2$

GC AREA COUNTS

CONCENTRATION (μg/L)

98
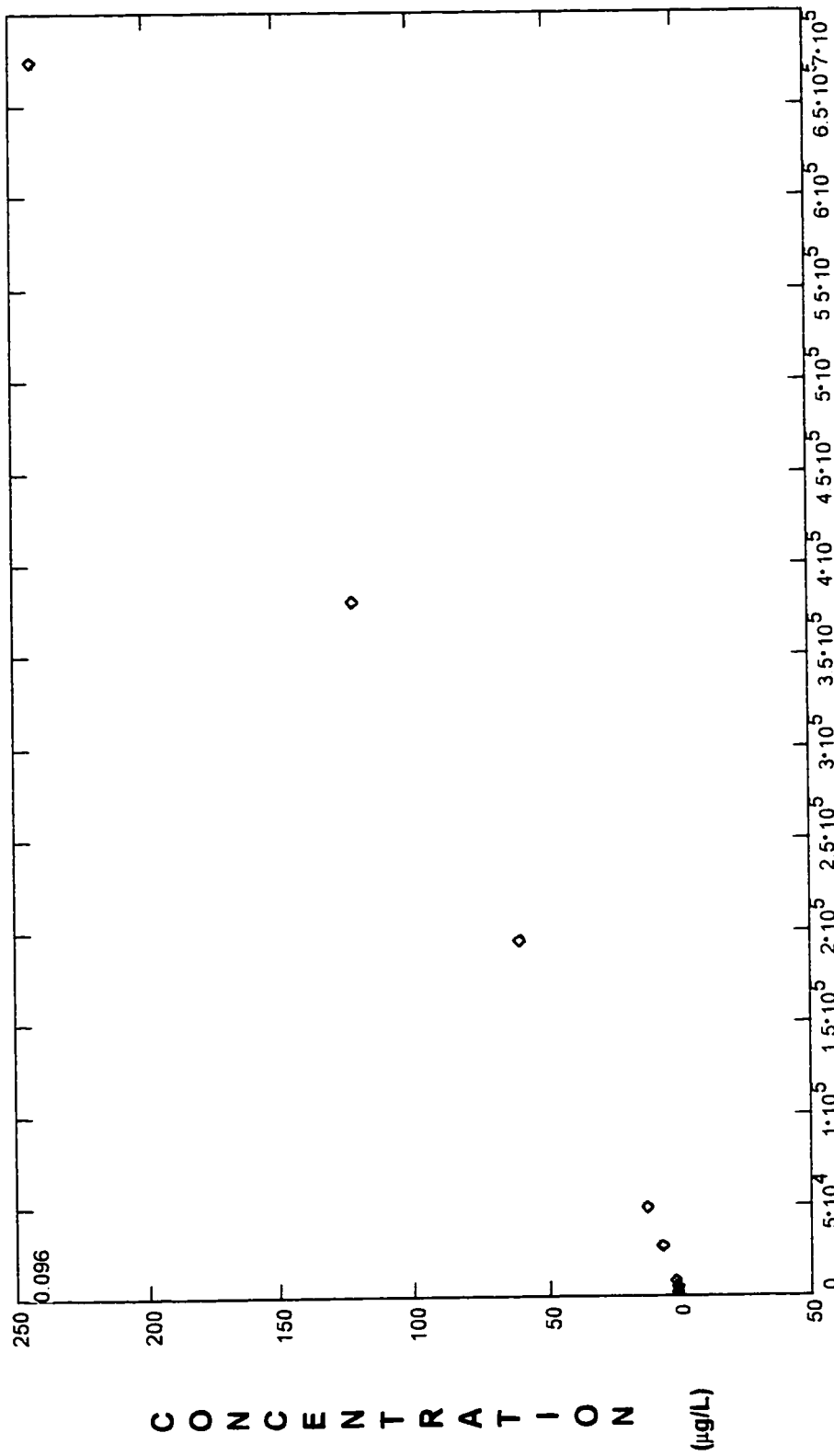
Figure A.12. - Standard Calibration Curve - Methyl-glyoxal.

◇ DATA
y = -0.99 + 2.82E-4x + 1.17E-10x^2

GC AREA COUNTS

CONCENTRATION (μg/L)

99

Appendix B

ALDEHYDE REPORT SHEETS

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: March 1, 1995

Approximate Ozone Concentration = 0.27 mg/L

Flowrate = 3.25 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
S1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	ND
S2	5.6	BDL	2.0	BDL	BDL	BDL	BDL	ND	ND	BDL	2.8	BDL
F2	5.0	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	BDL	3.6	2.0
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	BDL
Check Standard	49.0	50.1	30.0	49.2	65.8	71.9	34.5	51.6	31.8	61.7	43.7	71.6
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: March 3, 1995   Date of GC/ECD Analysis: March 10, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.1. - Aldehyde Report Sheet, March 1, 1995.

101

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: March 8, 1995

Approximate Ozone Concentration = 0.50 mg/L

Flowrate = 3.25 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
S1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	ND
S2	7.8	2.9	5.8	BDL	BDL	BDL	2.4	ND	ND	BDL	5.1	2.8
F2	7.5	BDL	3.9	BDL	BDL	BDL	BDL	ND	ND	BDL	5.7	3.1
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
Check Standard	44.8	49.8	33.8	48.8	65.4	69.4	34.2	49.2	30.0	57.3	37.7	61.8
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	BDL	ND	BDL	BDL

Date Extracted: March 9, 1995   Date of GC/ECD Analysis: March 11, 1995

NOTES: All values represent a duplicate mean

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.2. - Aldehyde Report Sheet, March 8, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: March 17, 1995

Approximate Ozone Concentration = 1.0 mg/L

Flowrate = 3.25 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
S1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	ND
S2	9.8	2.8	1.9	BDL	BDL	BDL	BDL	ND	ND	BDL	5.2	3.4
F2	8.4	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	BDL	5.8	3.7
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
Check Standard	45.3	50.7	41.2	51.2	70.6	72.9	33.8	45.2	28.1	50.4	34.9	55.0
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: March 18, 1995   Date of GC/ECD Analysis: March 18, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.3. - Aldehyde Report Sheet, March 17, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: March 22, 1995

Approximate Ozone Concentration = 1.5 mg/L

Flowrate = 3.25 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
S1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	ND
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	19.9	4.2	BDL	BDL	BDL	BDL	BDL	ND	ND	BDL	4.6	3.4
F2	10.1	3.7	BDL	BDL	BDL	BDL	BDL	ND	ND	BDL	5.2	4.0
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
Check Standard	45.8	52.8	47.4	52.3	71.9	75.8	33.4	45.4	27.5	52.7	34.4	55.1
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	ND

Date Extracted: March 23, 1995   Date of GC/ECD Analysis: March 23, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.4. - Aldehyde Report Sheet, March 22, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: March 28, 1995

Approximate Ozone Concentration = 2.0 mg/L

Flowrate = 3.25 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	2.0	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
S1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	15.7	7.2	3.1	BDL	BDL	BDL	BDL	ND	ND	ND	7.1	5.2
F2	15.0	6.2	1.8	BDL	BDL	BDL	BDL	ND	ND	ND	8.4	6.1
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
Check Standard	45.2	52.2	45.5	57.0	72.6	78.2	34.6	50.4	29.6	59.1	33.4	56.4
Spike Sample (S2)	65.7	53.6	44.0	46.1	51.3	25.7	14.6	19.8	15.7	21.2	29.3	49.8
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: March 30, 1995   Date of GC/ECD Analysis: March 30, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.5. - Aldehyde Report Sheet, March 28, 1995.

105

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: May 16, 1995

Approximate Ozone Concentration = 0.75 mg/L

Flowrate = 3.25 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	5.3	4.2	BDL	BDL	BDL	BDL	ND	ND	ND	ND	1.2	BDL
F2	7.1	5.0	2.8	BDL	BDL	BDL	ND	ND	ND	ND	1.3	BDL
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
Check Standard	39.2	61.1	51.0	45.9	69.6	70.2	34.0	36.3	22.1	46.9	23.8	33.7
Spike Sample (S2)	53.0	64.4	50.0	45.6	58.7	32.5	25.2	23.9	19.4	32.3	17.6	28.6
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: May 18, 1995   Date of GC/ECD Analysis: May 19, 1995

NOTES: All values represent a duplicate mean
The method blank contribution to the samples has been accounted for in the calculations.
ND: Aldehyde/dialdehyde not detected
BDL: Aldehyde/dialdehyde level below detection limit

Table B.6. - Aldehyde Report Sheet, May 16, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: May 26, 1995

Approximate Ozone Concentration = 0.75 mg/L

Flowrate = 3.5 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
S1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
F1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
S2	7.2	7.2	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	3.5	3.4
F2	5.2	4.1	1.7	BDL	BDL	BDL	BDL	BDL	ND	BDL	4.2	3.1
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
Check Standard	38.5	46.2	41.4	42.7	62.6	61.8	28.4	36.9	21.1	47.5	27.3	39.9
Spike Sample (S2)	52.6	49.4	40.8	49.3	61.3	55.1	25.9	32.5	17.7	41.3	23.3	37.0
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: May 27, 1995   Date of GC/ECD Analysis: May 29, 1995

NOTES: All values represent a duplicate mean

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.7. - Aldehyde Report Sheet, May 26, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date. June 6, 1995

Approximate Ozone Concentration = 0.75 mg/L

Flowrate = 4.2 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND
S1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND
F1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND
S2	5.9	5.2	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	3.4	3.2
F2	7.4	4.0	BDL	BDL	BDL	BDL	ND	BDL	ND	ND	3.1	BDL
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND	BDL	ND
Check Standard	33.2	43.3	36.0	38.2	59.7	55.2	26.8	34.0	19.2	45.8	24.7	34.3
Spike Sample (S2)	51.6	52.0	40.6	49.4	61.7	59.8	32.7	32.7	17.0	42.6	22.1	34.4
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	BDL	ND	ND	ND	ND

Date Extracted: June 7, 1995   Date of GC/ECD Analysis: June 7, 1995

NOTES: All values represent a duplicate mean

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL. Aldehyde/dialdehyde level below detection limit

Table B.8. - Aldehyde Report Sheet, June 6, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: September 8, 1995

Approximate Ozone Concentration = 1.2 mg/L

Flowrate = 3.0 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S1	6.8	7.7	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	4.0	4.0
F1	3.3	2.8	BDL	BDL	BDL	BDL	ND	ND	ND	ND	3.3	1.9
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
F2	4.5	4.9	BDL	BDL	BDL	BDL	ND	ND	ND	ND	2.5	2.0
C2-3	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND
Check Standard	35.6	47.4	36.7	37.3	52.8	27.9	27.9	27.0	19.5	35.1	17.4	30.7
Spike Sample (S1)	61.1	57.5	39.2	36.8	47.2	46.3	19.9	18.8	16.9	24.0	16.4	30.8
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: Sept. 9, 1995   Date of GC/ECD Analysis: Sept. 10, 1995

NOTES: All values represent a duplicate mean

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.9. - Aldehyde Report Sheet, September 8, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: September 15, 1995

Approximate Ozone Concentration = 1.2 mg/L

Flowrate = 3.0 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	3.0	BDL	BDL	BDL	BDL	ND	ND	BDL	ND	ND	ND	ND
S1	5.8	10.2	BDL	BDL	ND	BDL	ND	ND	ND	ND	0.8	2.1
F1	3.6	7.2	BDL	BDL	BDL	ND	ND	ND	ND	ND	0.5	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND
S2	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND
F2	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND
C2-3	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND
Check Standard	34.2	46.5	35.1	46.3	53.1	25.6	27.6	25.7	19.5	31.4	10.5	21.1
Spike Sample (S1)	48.5	47.0	32.8	33.7	46.2	42.8	21.0	20.4	15.0	25.5	9.4	20.1
Method Blank	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND	ND

Date Extracted: Sept. 16, 1995   Date of GC/ECD Analysis: Sept. 17, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.10. - Aldehyde Report Sheet, September 15, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: September 22, 1995

Approximate Ozone Concentration = 1.2 mg/L

Flowrate = 4.2 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S1	9.3	5.8	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	4.0	3.0
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	2.8	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F2	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	2.5	1.7
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
Check Standard	35.6	41.3	32.0	41.5	55.4	48.0	25.9	29.0	20.0	34.6	19.7	33.0
Spike Sample (S1)	46.5	46.4	27.9	35.2	46.7	48.8	18.4	20.8	13.0	25.2	14.4	24.4
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: Sept. 23, 1995   Date of GC/ECD Analysis: Sept. 26, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.11. - Aldehyde Report Sheet, September 22, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: September 29, 1995

Approximate Ozone Concentration = 1.2 mg/L

Flowrate = 4.8 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	BDL
S1	7.9	6.7	BDL	1.4	BDL	BDL	BDL	ND	ND	ND	3.2	2.8
F1	3.2	2.8	BDL	BDL	BDL	BDL	ND	ND	ND	BDL	2.8	1.7
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	ND
F2	1.6	4.0	BDL	BDL	BDL	BDL	ND	ND	ND	ND	2.5	1.9
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
Check Standard	34.1	38.3	30.1	37.8	53.1	44.4	20.1	29.2	18.9	33.9	24.0	35.7
Spike Sample (S1)	44.7	41.6	26.7	41.9	46.9	39.0	16.6	24.9	12.6	27.0	20.4	32.6
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted. Sept. 30, 1995   Date of GC/ECD Analysis: Oct. 1, 1995

NOTES: All values represent a duplicate mean

The method blank contribution to the samples has been accounted for in the calculations.

ND. Aldehyde/dialdehyde not detected

BDL. Aldehyde/dialdehyde level below detection limit

Table B.12. - Aldehyde Report Sheet, September 29, 1995.

Windsor Water Treatment Pilot Plant Aldehyde and Dialdehyde Analysis Results

Sampling Date: October 6, 1995

Approximate Ozone Concentration = 1.2 mg/L

Flowrate = 4.2 L/min

All results shown in p.p.b. (microgram/L)

SAMPLE LOCATION	Formaldehyde	Acetaldehyde	Propanal	Butanal	Pentanal	Hexanal	Heptanal	Octanal	Benzaldehyde	Nonanal	Glyoxal	Methyl-glyoxal
Raw Water	BDL	BDL	BDL	3.1	BDL	BDL	ND	ND	ND	BDL	BDL	BDL
S1	10.5	1.9	BDL	BDL	BDL	BDL	BDL	ND	ND	BDL	5.8	4.1
F1	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	4.2	BDL
C1-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
S2	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	BDL	BDL
F2	3.4	2.4	BDL	BDL	BDL	BDL	ND	ND	ND	ND	3.5	2.0
C2-3	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND
Check Standard	42.3	43.1	32.5	48.4	70.5	58.0	28.8	36.0	23.2	38.7	32.5	46.2
Spike Sample (S1)	68.3	45.7	28.3	55.9	72.8	52.3	26.7	31.6	18.0	33.0	29.7	43.8
Method Blank	BDL	BDL	BDL	BDL	BDL	BDL	ND	ND	ND	ND	ND	ND

Date Extracted: Oct. 7, 1995   Date of GC/ECD Analysis: Oct. 8, 1995

NOTES: All values represent a duplicate mean.

The method blank contribution to the samples has been accounted for in the calculations.

ND: Aldehyde/dialdehyde not detected

BDL: Aldehyde/dialdehyde level below detection limit

Table B.13. - Aldehyde Report Sheet, October 6, 1995.

VITA AUCTORIS

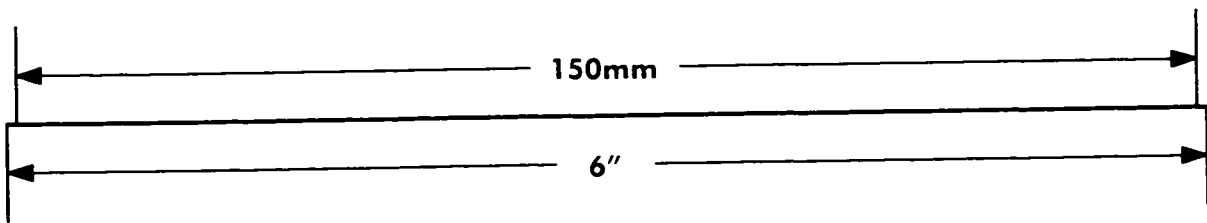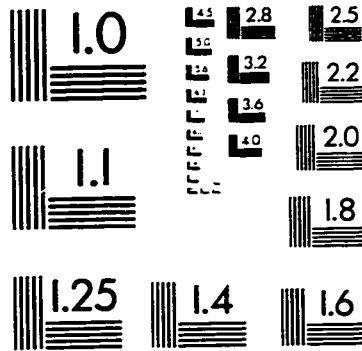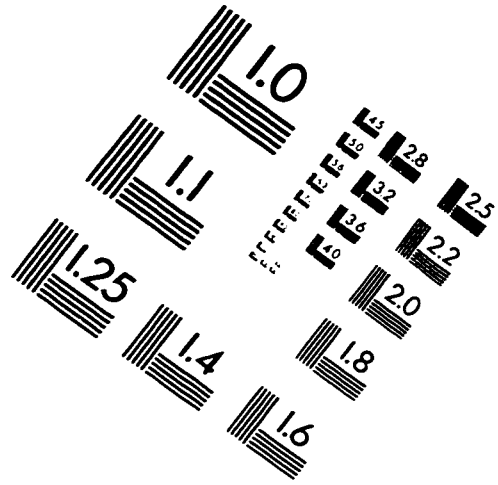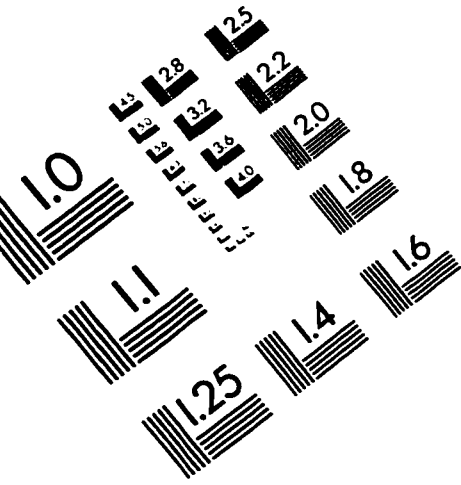|	
NAME:	Stephan Cervi
PLACE OF BIRTH:	Windsor, Ontario.
DATE OF BIRTH:	July 4, 1971
EDUCATION:	F.J. Brennan Secondary School, Windsor, Ontario 1984 - 1989
	University of Windsor, Windsor, Ontario 1989 - 1993 B.A.Sc.
	University of Windsor, Windsor, Ontario 1994 - 1996 M.A.Sc.

IMAGE EVALUATION
TEST TARGET (QA-3)

150mm

6"