THE USE OF OZONE FOR THE TREATMENT OF LOGYARD RUN-OFF

by

MICHAEL GUY ZENAITIS

B.Eng., McGill University, 1992
M.Eng., McGill University, 1994

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

Department of Chemical and Biological Engineering

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

November 2003

ABSTRACT

This work explored the use of ozone in the treatment of run-off from logyards in an effort to remove its toxicity to aquatic wildlife. In this survey, an EC_{50} range of 1.9%-26.8%, as measured by Microtox, was obtained for samples from a pair of sawmills on the British Columbia coast. Canadian law prohibits toxic discharges into fish-bearing waters; toxicity is defined as a 96-hour rainbow trout LC_{50} less than 100%.

Ozone has been found to be an effective way of reducing the toxicity of logyard run-off. For treatment of run-off at pH 7, the reduction in the levels of COD and BOD was moderate (~35% and 25%, respectively) but reduction in the levels of toxicity and parameters associated with toxicity to aquatic organisms was significant. Acute toxicity as measured by Microtox was reduced by over 85% while DHA (a resin acid toxic to fish at low concentrations) and tannins and lignins were reduced by 100% and 90%, respectively. A decrease in the pH of the treatment from 7 to 5 was found to have a negative effect on the effectiveness of ozone in reducing the levels of the toxicity-related parameters. Although run-off samples had quite different initial COD levels (2380 mg/L-8760 mg/L), the fractional reduction of COD and toxicity-related parameters displayed good consistency when expressed in terms of ozone consumed / initial COD (0.57 mg/mg).

Batch biological treatment of run-off resulted in reductions of BOD, COD, tannins and lignins, and Microtox toxicity of 98%, 80%, 90%, and 96%, respectively. The kinetics of biodegradation are similar to those for a bleached kraft mill effluent.

Ozonation of logyard run-off in conjunction with biological treatment was examined. Ozone treatment of biologically-treated run-off resulted in further reductions of COD (22%) and tannins and lignins (68%); however, these were from quite reduced starting levels of 1130 mg/L

and 105 mg/L, respectively. Microtox toxicity was not improved and BOD increased slightly from a low initial concentration of 94 mg/L.

The ozonation of run-off affected subsequent biological treatment. The BOD of pre-ozonized samples decreased faster than that of non-ozonized samples during biological treatment but the final residual COD at the end of biological treatment was higher for ozonized samples. Although starting from quite different levels (200 mg/L –677 mg/L), the tannin and lignin levels of ozonated and non-ozonated run-off attained similar levels (80 mg/L-105 mg/L) by the end of biological treatment. Toxicity levels (6.8%-23.9% EC_{50}) displayed the same relationship as tannins and lignins (final EC_{50} 55%-60%).

The oxidation of DHA by ozone was examined using Matlab to empirically fit the data. The reaction rate constant between the two compounds was determined to be 1.1×10^2 L/mol·s at 23°C. The reaction was found to consume 3 moles of ozone per mole of DHA consumed, and to also generate 3 moles of hydrogen peroxide per mole of DHA consumed. Radical scavengers were found to have a deleterious effect on the rate of oxidation of DHA by ozone, especially as pH becomes basic.

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Many thanks are owed to the following:

- Dr. Sheldon Duff, my supervisor, for infinite patience
- Dr. Richard Branion, and Dr. Ken Hall, my committee
- the other members of the research group: Maggie, Brihas, Chris, Norm, Christine, Preston, and Steve
- all the PPC staff, especially Tim and Peter for all their help
- the UBC Civil Engineering Department for the loan of the ozone generator
- West Fraser Timber in Prince Rupert for samples
- NSERC and BC Science Council for financial help
- The Sustainable Forest Management Network of Centres of Excellence and BC Hydro for project funding

Special thanks to my wife, Katrina, for unfailing support, and to my daughter Isabella, the apple of my eye.

1. INTRODUCTION

Research over the years has shown that trees produce a wide range of compounds that exhibit either repellency or toxicity to many attacking organisms such as fungi and insects (Werner, 1995; Woodward and Pearce, 1988; Dumas *et al.*, 1983). Usually, these compounds can be found in higher concentration in the bark of the tree and especially at sites where wounds have occurred. The amassing of large numbers of cut trees in one spot is, from the environment's point of view, a highly unnatural occurrence. When trees die or are blown over in the forest, some of the toxic compounds contained therein will be released into the environment; however, this process will occur over a long period and will be subject to the natural attenuation of the forest floor. Logyards, though, are often situated near waterways and contain large numbers of cut logs in a relatively limited space. As a result, a run-off that can be quite toxic to aquatic wildlife will swiftly pass to the adjacent waterways. Canadian law prohibits the release of toxic effluents into fish-bearing waters and this has led sawmill and log sort yard operators to try to find methods to remove the toxicity from the run-off. It was this concern with the toxicity of run-off from logyards and its effect upon marine organisms that prompted this study.

Ozone has seen use in a number of applications where oxidation of undesirable compounds is required. For wood-related uses on an industrial scale, ozone has primarily been used in the bleaching of pulp (Byrd *et al.*, 1992). Previous research involving pulp mill effluent has shown that ozone is able to remove toxicity from this medium (Roy-Arcand and Archibald, 1996a, Ng *et al.*, 1978, Tuhkanen *et al.*, 1997).

This thesis examined the use of ozone to treat run-off in an effort to reduce toxicity to marine wildlife and reduce the levels of some other parameters. Chapter 2 presents a review of the literature dealing with wood chemistry, logyard run-off, ozone chemistry, and the use of

ozone in industrial wastewater treatment. Chapter 3 outlines the objectives of this work and the experimental plan used to reach the objectives. In Chapter 4, the materials and methods used in the work are summarized. In Chapter 5, results on the treatment of run-off samples obtained from two sawmills over the course of a year are presented, examining the extent of removal of various parameters as a function of ozone dose to the sample, and assessing the effect of pH on the treatment. Chapter 6 presents results for the use of ozone both prior to and after biological treatment. In Chapter 7, the reaction between ozone and dehydroabietic acid, a resin acid commonly found in wood, is studied, and a mathematical model developed that permits the determination of the rate constant of the reaction as well as some details of the stoichiometry of the reaction.

2. LITERATURE REVIEW

2.1 Toxicity resulting from wood processing operations

The forest industry continues to play a significant role in the Canadian economy, contributing 12.8% of manufactured shipments and directly employing over 254 000 Canadians. When taking into account indirect employment, over a million jobs in Canada are dependent upon the forest industry (COFI, 2000). As such, the health of the Canadian economy as a whole is still dependent, to a certain extent, on the health of the forest industry and many towns almost exclusively so.

With increased environmental awareness, both in Canada and abroad, has come concern over the impact of industry on the environment. Pressure on industry has come from two main sources: increasingly strict laws limiting the discharge of environmental pollutants, as well as consumers who are willing to pay a premium for goods certified as having been produced in an environmentally responsible manner. For companies, this has meant an increase in the attention paid to environmental issues, as this can have an effect on the demand for their products.

Nationally, the Canadian Environmental Protection Act and the Fisheries Act are the main pieces of legislation that limit the release of potentially toxic materials by industry into the aquatic environment. In particular, the Fisheries Act states in section 36 (3) that "no person shall deposit or permit the deposit of a deleterious substance of any type in water frequented by fish or in any place under any conditions where the deleterious substance or any other deleterious substance that results from the deposit of the deleterious substance may enter any such water".

Historically, the main issue of concern for the forest products industry has been the effluent from pulp mills. The effect of pulp mill effluent on the aquatic wildlife in the receiving

environment was an issue that attracted great attention. The negative effects arose due to a number of causes, which could broadly be classified as follows (Shimp and Owens, 1993):

- Physical effects such as the discharge of colour and suspended solids,
- General organic enrichment of receiving waters,
- Nutrient enrichment,
- Chemical toxicity from both organic and inorganic effluent constituents.

The release of fibers and suspended solids into receiving waters resulted in the loss of stationary benthic organisms and the depletion of feeding and reproductive habitat of mobile organisms. Colour restricted the photosynthesis of light-dependent organisms and limited the visual clues that are needed by some in order to feed or reproduce (Owens, 1991).

The organic and nutrient enrichment caused by pulp mill effluents resulted in eutrophication of the receiving waters and also encouraged the growth of algae that restricted the passage of light to the lower levels of water (Hutchins, 1979).

With the widespread use of chlorine as a bleaching agent in the pulping process, dioxins and furans were present in detectable amounts in the effluent (Muller and Halliburton, 1990). These families of compounds have been found to be carcinogenic, teratogenic, and immunotoxic (Kutz *et al.*, 1990). The bleaching of pulp is now largely done with chlorine dioxide and/or non-chlorine containing oxidizing agents such as hydrogen peroxide or ozone (Albert, 1994; Slinn, 1992). This has resulted in the reduction of dioxin and furan concentrations in pulp mill effluent to below detectable levels.

The acute toxicity of effluents was also found to be a problem. Before 1992, the year that the federal government modified the toxicity regulation for pulp and paper mills, 75% of Canadian bleached pulp mills discharged effluents that exhibited acute toxicity to fish (Canadian Environmental Protection Act, 1991). The revised regulations dictated that the effluents should

be non-toxic (as defined by a 96-h $LC_{50} \geq 100\%$) to rainbow trout (Canadian Fisheries Act, 1992).

Treatment of pulp mill effluents can be divided into three broad categories: primary, secondary and tertiary treatment. In primary treatment, clarification is achieved through a physical process, either sedimentation or flotation. Sedimentation relies on solid particles in the effluent having a density greater than that of water. They will settle to the bottom of the clarifier and be removed. Flotation uses air bubbles to carry suspended solids to the surface; the resulting foam is skimmed off (Hynninen, 1998). This process can be aided by the addition of coagulants and flocculants, which increase the size and rate of settling of flocs.

Secondary treatment involves the use of a biological process to reduce the oxygen demand of the effluent. Activated sludge, aerated lagoons, and anaerobic processes are the techniques used. In addition to decreasing the oxygen demand of the effluent, biological systems are also able to remove many of the wood-derived compounds that are toxic to aquatic wildlife (Leach et al., 1978).

Tertiary treatment, although somewhat limited in use, may become more widespread if regulations governing effluent become more stringent. This category of treatment covers a wide range of options such as membrane processes, chemical oxidation, activated carbon adsorption, freezing, evaporation, stripping and ion exchange (Thompson et al., 2001; Hynninen, 1998).

Between 1996 and 1999, the percentage of mills meeting the legal effluent toxicity limit in tests has improved considerably, from 64% to 81%. In a more recent survey (Kovacs et al., 2002), 96% of surveyed Canadian pulp and paper mills had secondary treatment systems installed. For these mills, over 95% of toxicity tests performed with rainbow trout proved non-toxic while for *Daphnia magna*, the value was 98.5%. With the problem of pulp mill effluent toxicity largely resolved, the attention of environmental authorities has now turned to other

environmental issues in the forestry industry. One of these is the problem of toxicity of logyard run-off.

At a provincial level, the government of British Columbia instituted the Antisapstain Chemical Waste Control Regulation as part of the Waste Management Act in 1990 (B.C. Regulation 300/90, 1990). In addition to a series of requirements that limits the concentration of specific antisapstain chemicals in effluent and stormwater, the regulation also states that "the effluents from operations ... shall not be toxic" with toxicity defined as a rainbow trout 96 hour LC_{50} less than 100%. Many operations with antisapstain treatment have found that in spite of antisapstain chemical concentrations in stormwater being significantly lower than the accepted limits or even non-detectable, they still fall foul of the requirement that the stormwater not be toxic (Finnbogason, 1999). This has obliged companies to search for ways to treat the run-off from these operations.

Before describing the source and nature of the toxic constituents of logyard run-off, it is useful to give a brief overview of wood chemistry.

2.2 Wood chemistry

Trees consist of two components: wood, also called xylem, and bark. The wood serves primarily as a conduit system for nutrients and water from the roots to the crown of the tree where photosynthesis occurs. The bark serves as a protective layer against mechanical damage, attack by insects and fungi, and protects the wood from temperature and humidity variations (Sjöström, 1993).

The main constituents of wood are polysaccharides (cellulose and hemicelluloses), lignin, extractives and water and trace minerals. Very broadly, the function of the first three can be defined as follows. The wood fibers, composed of cellulose and hemicelluloses, give the tree its

structure. Lignin acts as the glue holding these fibers together. Extractives serve a range of purposes, primarily as an energy source and as a defense against insect damage and attack by microorganisms (Alén, 2000).

The main carbohydrates in wood are cellulose and hemicelluloses. The other carbohydrates found in wood, though usually only in minor quantities, are starch and pectic substances (Sjöström, 1993).

Cellulose is the most important of the carbohydrates, constituting approximately 40-45% of the wood mass (Alén, 2000). Wood cellulose is a polymer made of β-D-glucopyranose units with a degree of polymerization of approximately 10 000 in softwoods. The hemicelluloses (~20-30% of wood mass) are heteropolysaccharides, formed of monomeric units of D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, and smaller amounts of other saccharides. Their degree of polymerization is much lower than that of cellulose, around 200 (Sjöström, 1993).

Lignin (26-32% of wood mass in softwoods, 20-25% in hardwoods) is also a polymer; however, its basic unit is phenylpropane (Sjöström, 1993). Unlike the polysaccharides which are concentrated in the secondary wall of wood fibres, a significant fraction of the lignin is found in the middle lamella and primary wall, acting as a binder of wood fibres (Biermann, 1996). The degree of polymerization of softwood milled wood lignin is estimated to be about 75-100 while for hardwoods, it is thought to be slightly lower (Alén, 2000).

Extractives cover a wide range of low molecular weight compounds serving a variety of purposes. They compose between 1-5% of the wood mass in hardwoods and 3-8% in softwoods (Biermann, 1996). Some compounds give the various wood species their characteristic odours, colours, and tastes, others serve as energy sources for the various biological processes in the tree, while many others serve a protective role for the wood. Extractives may be divided into the following broad categories (Alén, 2000):

Terpenes and terpenoids:

- basic unit is isoprene (C_5H_8)
- industrially important as a source of turpentine (mainly monoterpenes)
- serve as defense against wood-boring insects
- e.g., resin acids, juvabiones

Aliphatic extractives:

- source of stored energy for tree
- found in the form of alkanes, fatty alcohols, fatty acids, fats, and waxes
- most fatty acids esterified with glycerol to form triglycerides or with terpenoids

Aromatic extractives:

- fungicidal and insecticidal properties
- main groupings: simple phenols, stilbenes, lignans, hydrolysable tannins, flavonoids (condensed tannins), and isoflavones

Other extractives:

- present in small amounts, sometimes limited to a few species
- e.g., tropolones (cedar); quinones; cyclitols; coumarins; mono-, oligo-, and polysaccharides

The bark of the tree, forming the outer protective layer, is different in both structure and chemical composition from the wood. Chemically, bark is marked by a significantly greater

amount of extractives (20-40% of the dry bark weight), such as pectin and phenolic compounds (Sjöström, 1993).

2.3 Log sort yards

The primary function of log sort yards is to receive cut wood, sort the logs according to species, size and quality, and to facilitate transport of the logs to the appropriate processor. Log sort yards are often associated with a sawmill or pulp mill. Many others are stand-alone operations, so-called dry land sorts. These facilities can range in size from less than a hectare to over 100 hectares, and process wood volumes ranging from a few thousand cubic meters to well over a million cubic meters annually (Orban, 2000). Large quantities of woody debris, from 3-6% by volume of the processed wood, are generated at log sort yards (McWiliams, 1992).

The introduction of water into log sort yards, which can occur through a variety of means (e.g., rainfall, snowmelt, carry-over from logs transported by water, sprinkling of storage areas, equipment cleaning), results in contact between the water and a number of sources of pollutants. As a result, a run-off or leachate contaminated with a range of constituents is generated (AEP, 1996; AFPA, 1999a; NCASI, 1992; Samis *et al.*, 1999). The volume and characteristics of the run-off from a particular site are dictated by a number of factors, including: species and volume of wood processed, climatic considerations (rainfall/snowfall amounts, intensity), characteristics of the site (woodyard surface cover, grade, proximity to water), and practices (sprinkling of wood, equipment cleaning practices, run-off control/treatment measures). Even considering a smaller logyard of 5 hectares and a moderate single rainfall of 10 mm (not uncommon in coastal British Columbia), 500 000 L of run-off are generated. An unpaved yard may reduce this amount by way of seepage into the soil, however, if it becomes saturated with water, seepage will occur to a much lesser extent. The high specific surface area of woody debris found in log yards and the mechanical action of log haulers running over this debris lead to the leaching of extractives from

wood. Contamination of the water resulting from erosion of the storage yard (in unpaved areas), oils and greases from machinery, and metals from machinery and buildings may also occur.

2.4 Toxicity of wood leachate and woodroom effluent

There is little information available specifically concerning the toxicity of logyard run-off. Until recently, the main area of environmental concern for wood processing was the effect of pulp mill effluent on receiving waters. Consequently, a significant body of work exists concerning the toxicity and treatment of pulp mill effluents. However, because of the chemical transformations that take place during the pulping process, either during the pulping or the bleaching stages, it is difficult to extend the results of this research to an analysis of logyard run-off. Because only water and mechanical action is used in its generation, woodroom effluent will probably be the closest surrogate for logyard run-off. Research on a series of softwood debarker effluents by B.C. Research (1974) indicated a very high level of toxicity, elevated BOD_5, and resin acid concentrations significantly greater than the 96-h LC_{50} for rainbow trout. The 96-h rainbow trout LC_{50} of samples was routinely less than 10% and sometimes as low as 0.2%, the BOD_5 of samples from some mills was usually above 500 mg/L and sometimes above 4000 mg/L, and total resin acid concentrations were usually above 10 mg/L and often over 50 mg/L. The lethal concentrations of resin acids are very low, with 96-hr LC_{50} ranging between 0.4-1.1 mg/L using rainbow trout as test organism (Leach and Thakore, 1976). More recently, research specifically involving run-off obtained from sawmills (Bailey *et al.*, 1999) indicated that 42 of 58 samples exhibited toxicity to rainbow trout. In addition, 57% of samples exhibited 100% toxicity at full strength.

Beginning in the early 1970s, research was initiated to better understand and quantify the toxic effects of wood and bark extracts on marine wildlife. Since then, a number of studies have indicated that these extracts, if untreated, exhibit high toxicity. Wood leachate affects marine

organisms by way of two primary mechanisms. Firstly, decomposition of organic compounds in the leachate may reduce the dissolved oxygen levels in receiving waters so as to affect the respiration of fish. Secondly, some of the organic compounds are themselves directly toxic to fish (Liu *et al.*, 1996). Studies that examined the exposure of a wide variety of marine organisms to several wood and bark extracts all indicated a high degree of toxicity. Extracts of Sitka spruce and Western hemlock barks were found to be toxic to pink salmon fry (96-hour LC_{50} of 100-120 mg/L and 56 mg/L, respectively) while the spruce extract was also toxic to adult and larval pink shrimp and larval Dungeness crab (96-hour LC_{50} of 205 mg/L, 415 mg/L and 530 mg/L, respectively) (Buchanan *et al.*, 1976). White pine, balsam fir, and Western hemlock extracts all displayed toxicity to fathead minnows (48-hour LC_{50} of approximately 5%, 20%, and 35%, respectively) as well as *Ceriodaphnia affinis* (48-hour LC_{50} of approximately 10%, 15%, and 30%, respectively) (O'Connor *et al.*, 1992), while leachate from Western red cedar was toxic to coho salmon (median survival time of 18-25 hours) (Peters *et al.*, 1976). Leachate of aspen wood was found to be extremely toxic, exhibiting an LC_{50} of 1-2% for both rainbow trout and *Daphnia magna* and an EC_{50} of 0.3% for Microtox® (Taylor *et al.*, 1996).

2.5 Compounds causing toxicity

Much research has been done which has identified broad families of wood-derived organic compounds that result in the bulk of the direct toxic effect upon aquatic wildlife. Resin and fatty acids (RFAs) have been the subject of greatest study. Previous research has indicated that, in mechanical pulping and wood debarking effluents, RFAs are the main source of acute toxicity to fish, contributing an estimated 60%-90% of the total toxic load (Leach and Thakore, 1976; Leach and Thakore, 1977). Minor amounts of toxicity were contributed by chemically-related alcohols. Fish exposed to resin acids have been shown to suffer from jaundice (Mattsoff and Oikari, 1987) and research into the toxicological mechanism of resin

acids in fish indicates that these compounds increase the rate of red-blood cell hemolysis (Matsoff and Nikinmaa, 1987), decrease the transfer of bilirubin from blood to bile (Matsoff and Nikinmaa, 1988) and affect potassium transport in isolated rainbow trout hepatocytes (Johnsen *et al.*, 1995).

Another family of toxic compounds of lesser importance is the juvabiones, present in firs. These compounds are insect juvenile hormone analogues, which interfere with the maturing of insect larval stages. They also have quite high toxicities, in the range of 1-2 mg/L 96-h LC_{50} for rainbow trout (Leach and Thakore, 1977).

Phenolic compounds have also been implicated in toxicity towards marine life. Lignans are composed of two phenylpropane units and many have fungicidal and insecticidal properties (Samis *et al.*, 1999). Groundwood effluent from western hemlock, which has the lowest amount of resin acids of all western softwood species, was found to have significant toxicity to *Daphnia pulex* (median survival time of 90 minutes). This toxicity was largely attributed to hydroxymatairesinol (Solinas and Tunstall, 1976), a lignan that was present in concentrations approximately 3 times greater than the 48hr LC_{50} of *D. pulex*. In another study, the EC_{50} value by Microtox® of a purified lignan mixture isolated from a mill process water was determined to be 15-40 mg/L (Jørgensen *et al.*, 1995).

Another example of phenolic compounds is bark tannins. Tannins may be either monomers such as catechin, dihydroquercetin, chrysin, or gallic acid, or polymers such as the procyanidins and gallotannins. These compounds compose a significant amount of the bark. Results reported by Field *et al.* (1988) show that extractable tannin yields from bark for a wide range of species average approximately 10% of bark dry weight, although yields as high as 37% have been reported (Hathway, 1962). In addition, tannins constitute up to 50% of the water-soluble COD in bark extracts, the remainder being composed of sugars (35%), non-tannic monomers (10%) and resins (5%) (Field *et al.*, 1988). Bailey *et al.* (1999) showed that, in

sawmill stormwater samples whose toxicity was not explained by the presence of metals, toxicity was correlated with elevated levels of tannins and lignins. Work by Temmink *et al.* (1989) indicated that the bark tannins in the extract from Norway spruce caused the high toxicity seen in carp. Removal of the tannins from the extract resulted in complete survival. Tannins are known to be highly reactive with proteins (Haslam, 1966; Haslam, 1974) and reduce or eliminate the effectiveness of a number of enzymes (Loomis and Battaile, 1966; Daiber, 1975; Tamir and Alumot, 1969; Gupta and Haslam, 1980). Damage to the gills of carp caused by interaction of cell membrane enzymes with oligomeric tannins was hypothesized to be the cause of toxicity (Temmink *et al.*, 1989).

In addition to wood derived organic compounds, metals in run-off have also been found to be a potential source of toxicity to fish. Run-off from roofs has historically been considered a potential source of drinking water, particularly in poorer countries (Gumbs and Dierberg, 1985); however, metal concentrations that are not of immediate concern to human health can be toxic to aquatic life. In an analysis of the run-off from five different roofs of buildings at a Washington state sawmill, copper, lead, and zinc concentrations exceeded water quality criteria in all samples (Good, 1993). Zinc levels were exceptionally high. Samples taken from the roofs of 5 different buildings were taken within 35 minutes of the start of runoff and values of 11 900, 1610, 909, 257, and 82 μg/L were obtained. For three of these samples, the values are more than 10 times the maximum level (86 μg/L) that the EPA deems will not unacceptably affect marine organisms (U.S. EPA, 1986) and in one of those, the value is exceeded by more than 100 times. A rainbow trout acute toxicity assay conducted on the samples registered no survival at 100% concentration in four of the five samples. Even three hours after the start of the rainfall, a sample taken from the roof with a zinc concentration of 1610 μg/L in the runoff registered a dissolved zinc concentration of 1080 μg/L, indicating that zinc was probably being actively leached from the

metal roof. In a study by Bailey *et al.* (1999), the toxicity of stormwater run-off from nine British Columbia sawmills was examined. In three quarters of samples exhibiting toxicity to rainbow trout, this toxicity was associated with divalent cations, particularly zinc. The locations that showed zinc toxicity suggested that the zinc originated from galvanized roofs covering storage areas for logs freshly treated with antisapstain chemicals.

2.6 Toxicity measurement

As previously mentioned, an effluent is legally deemed to be toxic if it has a 96-hour LC_{50} of less than 100% using rainbow trout (*Oncorhynchus mykiss*) as the test organism. In addition, other well-known organisms used for toxicity testing include water fleas (*Daphnia magna* and *Ceriodaphnia dubia*), green algae (*Selenastrum capricornutum*), fathead minnows (*Pimephales promelas*) and mysid shrimp (*Mysidopsis bahia*) (Toussaint *et al.*, 1995). Although widespread usage of the rainbow trout standard has the advantage of consistency across industries, it has some serious drawbacks. The main one is that 4 days elapse before the toxicity level is known. By this time, any opportunity to correct a problem with process conditions and improve effluent quality has passed. Secondly, large amounts of sample (~40 L) are required in order to perform the test. Thirdly, the cost of the test is quite significant, whether performed in-house or at an outside laboratory. These drawbacks have led to the development of a number of rapid-screening toxicity tests designed to greatly accelerate the toxicity testing of wastewater samples. One of the most widespread of these assays is Microtox®. The system is easy to use, requires little space and costs significantly less than a fish or water flea test.

When introducing a novel method of analyzing for toxicity, it is important to determine how well it correlates with the standard assays. Previous research has examined this question but no consistent answer has been reached. Firth and Backman (1990) reported that Microtox® provides a good screening tool for both rainbow trout acute toxicity and *Ceriodaphnia* chronic

toxicity of pulp mill wastewaters. Qureshi *et al.* (1982) reported that the Microtox® assay sensitivity was comparable to rainbow trout and *Daphnia* when measuring the toxicities of organic compounds, pulp and paper mill effluents and oil refinery effluents. Microtox® was generally found to be the most sensitive to industrial effluents and much more so than rainbow trout and *Daphnia* in some cases. Munkittrick *et al.* (1991), in a general review of data comparing Microtox® with *Daphnia*, rainbow trout, and fathead minnow acute toxicity tests, found that Microtox® was generally less sensitive to solutions of pure inorganic compounds and either more, or as sensitive to organic compounds. With effluents of increased complexity, the correlations and sensitivity of Microtox® increased compared to the standard tests. In particular, they stated that Microtox® appears to be suitable for pulp and paper effluents to monitor relative changes in toxicity. Toussaint *et al.* (1995) compared the Microtox® assay to a number of standard acute toxicity tests and found that its sensitivity fell just outside the range represented by the standard tests but determined that it could be used for preliminary screening of chemicals. Further evaluation of complex environmental samples was recommended. Blaise *et al.* (1987), in a study of toxicity responses of Microtox®, rainbow trout, and the alga *Selenastrum capricornutum* to pulp and paper mill effluents, determined that the three tests were in good agreement with each other. On the other hand, for individual compounds found in pulp mill effluents, Springer and Bazarow (1993) found that Microtox® did not correlate well with either fathead minnows or rainbow trout. Finally, Renberg (1992) analyzed data from 20 mill and laboratory experiments from pulp mills and found no correlation between Microtox®, *Ceriodaphnia*, and algal toxicities. However, when samples were limited to particular sources (e.g., mills with similar bleaching sequences), the Microtox® reponse correlated with *Ceriodaphnia*.

Generally, the Microtox® assay seems to be regarded as a useful tool for rapid screening of samples, but correlation of Microtox® with standard toxicity measurements must be done on a case-by-case basis.

2.7 Treatment of logyard run-off

2.7.1 Minimization of leachate generation

Many strategies have been suggested in order to try to minimize the impact of run-off from log processing facilities on the receiving environment (Toews and Brownlee, 1981; Samis *et al.*, 1999; AFPA, 1999b):

- Divert surface drainage around log storage piles
- Perform dry-land handling rather than water handling
- Avoid the violent dumping of logs into water in order to minimize the generation of loose bark and wood debris
- Employ positive bark and wood debris control, collection and disposal methods at log dumps, raft building areas and mill-side handling zones
- Prevent bark and other debris on the land and docks around dump sites from entering the water
- Pave log storage areas in order to reduce the amount of rock and dirt in wood residue and to ensure easier clean-up
- Locate stockpiles of dryland sorting debris as far as possible from the high water mark
- Shape wood residue piles like a cone and minimize the basal area as much as possible to minimize leachate generation
- Grade and/or contour logyard decks to minimize areas of pooled water that are in contact with woody debris

In spite of the implementation of many of these measures, 89% of surveyed logyards in B.C. still generate a leachate (Orban et al., 2002) and, of these, some have significant toxicity towards aquatic life (MacDonald, 1997). Four classes of methods have been suggested for the treatment of logyard run-off (Samis *et al.*, 1999): natural attenuation, recirculation, biological treatment, and physical/chemical treatment. However, very little work has been done in investigating the treatment of logyard run-off with these methods.

2.7.2 Natural attenuation

Natural attenuation occurs as a leachate enters the soil and the concentration of toxic compounds as well as other contaminants is reduced through natural means such as adsorption, ion exchange, precipitation, filtration and biological degradation. When a soil reaches its saturation point, the ability of the soil to attenuate any leachate is drastically reduced (Samis et al., 1999).

2.7.3 Recirculation

Recirculation involves removing leachate from the bottom of a waste pile, returning it to the surface and letting it percolate through. The waste pile can be thought of as a crude biological filter. The pile serves to physically filter out some suspended solids and microorganisms present in the pile oxidize contaminants in the leachate.

As a method of temporary wood preservation at Scandinavian sawmills, water storage is most commonly used (Borga *et al.*, 1996a). With the prohibition of ponding (storage of logs directly in water) in Sweden because of excessive environmental loads (e.g., dissolved organic carbon, phenols, resin acids, inorganics) and oxygen demand, sprinkling of log piles (wet decking) has become quite common. However, even sprinkling can generate leachates with significant loads. Borga *et al.* (1996a, 1996b) examined the effects of closed versus open

leachate recirculation systems as well as the influence of a number of factors on the quality of the leachate from the sprinkling of land-stored softwood timber. Watering intensity, rate of evaporation from the log pile, tree species and radial distribution of extractives in the logs, pH and nutrient level in the inlet water were all found to have an effect on the environmental load of the leachate. The initial amount of microbial growth in the woodpile as well as its rate of increase were found to be key parameters in the initial removal of environmental loads.

2.7.4 Biological treatment

Biological treatment involves the use of microorganisms to oxidize the biodegradable fraction of a waste stream. Biological treatment systems have seen widespread use in the pulp and paper industry because of the high biochemical oxygen demand exerted by pulp mill effluents. A number of alternative biological treatment technologies exist, including activated sludge systems, aerated lagoons, stabilization ponds, anaerobic reactors, trickling filters, rotating biological contactors, and artificial wetlands. Of these, the first two are, by far, the most common.

Recently, work was undertaken to examine the ability of artificial wetlands in both laboratory- and pilot-scale to treat the leachate from a hog fuel pile (Frankowski, 2000). Laboratory results yielded excellent removals of BOD, COD, tannins and lignins, and toxicity (94%, 80%, 80%, and 73%, respectively). Pilot-scale work gave decreased performance for all four variables (26%, 43%, 39%, 49%). Among the possible explanations for the poorer performance were low temperatures, low nutrient levels and insufficient aeration in the pilot system.

2.7.5 Physical/chemical treatment

A large number of potential treatment methods fall under this heading. These include aeration, carbon adsorption, chemical oxidation (e.g., ozone, calcium hypochlorite, hydrogen peroxide, or potassium permanganate), chelation, coagulation/flocculation, ion exchange, neutralization, precipitation, and reverse osmosis (Samis *et al.*, 1999). Although some of these methods have seen use in the pulp and paper industry, they have not been investigated to any significant extent for logyard run-off due to their presumed high operational costs.

An activated carbon system was installed in order to treat the stormwater generated at a former wood-preserving operation in Oklahoma (Bauguss and Weishun, 1999). The flow of run-off generated at the site was directed to a series of ponds where solids settling occurred. Previously, water collected in the ponds was treated and discharged using a portable, trailer-mounted pump-and-treat system that required an operator's presence to be continuous; however, the former sawmill operator wished to automate the treatment system so that only a monthly inspection would be necessary. As a result, a sand and granulated activated carbon system was installed in order to remove the pentachlorophenol and polycyclic aromatic hydrocarbons that were found in the site run-off. The toxicant concentrations were reduced to non-detectable levels. More generally, carbon is also used extensively in municipal water treatment systems for the removal of contaminating organic compounds.

Chemical oxidation in the form of ozone has been used in municipal water systems as a disinfectant and for colour and odour removal since the early 1900s and its use continues to grow around the world (Langlais *et al.*, 1991).

2.8 Ozone chemistry

2.8.1 Ozone in aqueous solution

Historically, ozone initially saw use in the treatment of drinking water. After initial research at the end of the 1880s showed the effectiveness of ozone against bacteria, full-scale use of ozone in drinking water treatment spread in many countries across Europe (e.g., Holland, France, Germany, Russia, Spain) as well as the United States. In addition to the role of ozone in disinfection, the ability of ozone to improve taste and odour was also recognized (Langlais *et al.*, 1991). Because of its strong oxidizing ability, ozone has recently seen increased use in the treatment of industrial wastewaters. Although cost has traditionally been a concern in this application, continuous improvements in its production systems has resulted in a gradual decrease in price (Homer, 2003).

Ozone has been applied to a wide variety of industrial wastewaters. Among these are treatment of marine aquarium wastewaters, removal of cyanide from electroplating wastewaters, recycling of rinse water in electronic chip manufacture, decolorization and surfactant destruction in textile industry wastewaters, oxidation of organics from petroleum refinery effluent, destruction of toxic VOCs in contaminated groundwater and bleaching of pulp in paper mills (Rice, 1997).

The chemistry of ozone in aqueous solution has generated a significant amount of debate within the scientific community over the years. Even as seemingly simple a measurement as the solubility of ozone in water is rendered complex by the instability of ozone in water (Roth and Sullivan, 1981). Examination of the rate of decomposition of ozone in aqueous solutions has been studied in order to better understand the mechanism of ozone reactions. Unfortunately, the rate equations for ozone decomposition determined in many of these papers vary significantly, both in the effect of pH on decomposition and the order of the reaction with respect to ozone concentration. Table 2.1 summarizes some of these published results.

Table 2.1: Published results for pH dependence of ozone breakdown in aqueous solution.

Rate equation	Reference
$k_0[OH^-]^{0.36}[O_3]^2$	Sennewald (1933)
$k_1[OH^-][O_3] + k_2[OH^-]^{0.5}[O_3]^{1.5}$	Weiss (1935)
$k_0[OH^-]^{0.5}[O_3]$	Alder and Hill (1950)
$k_0[OH^-]^{0.75}[O_3]$	Stumm (1954)
$k_0[OH^-]^{0.12}[O_3]$	Sullivan and Roth (1980)
$k_0[OH^-]^{x}[O_3]^{1.5}$, x is pH dependent	Li (1977)
$k_0[OH^-]^{0.88}[O_3]$	Teramoto *et al.* (1981)
$k_0[OH^-]^{0.55}[O_3]^2$	Gurol and Singer (1982)

Gurol and Singer (1982) state that the reasons for these differences can be summarized as: the varying techniques used to measure dissolved ozone concentration, varying ionic compositions and strengths, and impurities in the reagents used.

In addition to determining rate equations of ozone decomposition, some of the papers outlined in Table 2.1 also put forward possible reaction mechanisms for the decomposition of ozone in aqueous solution. Weiss (1935) suggested:

$$O_3 + OH^- \rightarrow \cdot O_2^- + \cdot HO_2$$

$$O_3 + \cdot HO_2 \rightarrow 2O_2 + \cdot OH$$

$$O_3 + \cdot OH \rightarrow O_2 + \cdot HO_2$$

$$2 \cdot HO_2 \rightarrow O_3 + H_2O$$

$$\cdot HO_2 + \cdot OH \rightarrow O_2 + H_2O$$

Alder and Hill (1950) found their data to be consistent with the following mechanism:

$$O_3 + H_2O \rightarrow HO_3^+ + OH^-$$

$$HO_3^+ + OH^- \leftrightarrow 2{\cdot}HO_2$$

$$O_3 + {\cdot}HO_2 \rightarrow {\cdot}OH + 2O_2$$

$${\cdot}OH + {\cdot}HO_2 \rightarrow H_2O + O_2$$

Some important features of ozone decomposition were not captured by these relatively simple models (Virdis *et al.*, 1995). With the advent of more sophisticated analytical techniques such as pulse radiolysis and stopped-flow spectrophotometry, studies involving the actual reaction intermediates themselves were possible, yielding more detailed reaction mechanisms. There are two main reaction mechanisms which have been put forward in order to describe the reactions of ozone in water: one by Staehelin and Hoigné (1985), illustrated in Figure 2.1, and another by Nemes *et al.* (2000a) (Table 2.2) based on the work of Tomiyasu *et al.* (1985). In both models, the decomposition of ozone takes place through a radical chain reaction initiated by hydroxide ion. Propagation of the chain in both models includes a number of free-radical species (e.g., ${\cdot}HO_2$, ${\cdot}O_2^-$, ${\cdot}O_3^-$, ${\cdot}OH$); however, the models differ in the mechanism of hydroxide initiation:

Staehelin and Hoigné (1985): $O_3 + OH^- \rightarrow {\cdot}HO_2 + {\cdot}O_2^-$

Nemes *et al.* (2000a): $O_3 + OH^- \rightarrow HO_2^- + O_2$

Nemes *et al.* (2000a) justify their initiation reaction by stating that theirs involves the transfer of an O atom whereas that of Staehelin and Hoigné (1985) involves the simultaneous transfer of an electron and O atom. Nemes *et al.* (2000a) claim this latter mechanism is unlikely. In addition, the model of Staehelin and Hoigné (1985) is found to predict significantly faster decomposition than is observed for alkaline solutions (Chelkowska *et al.*, 1992). Thus, for neutral-alkaline solutions, the model of Nemes *et al.* (2000a) is preferred.

Figure 2.1: Reactions of ozone in pure water (from Staehelin and Hoigné, 1985).

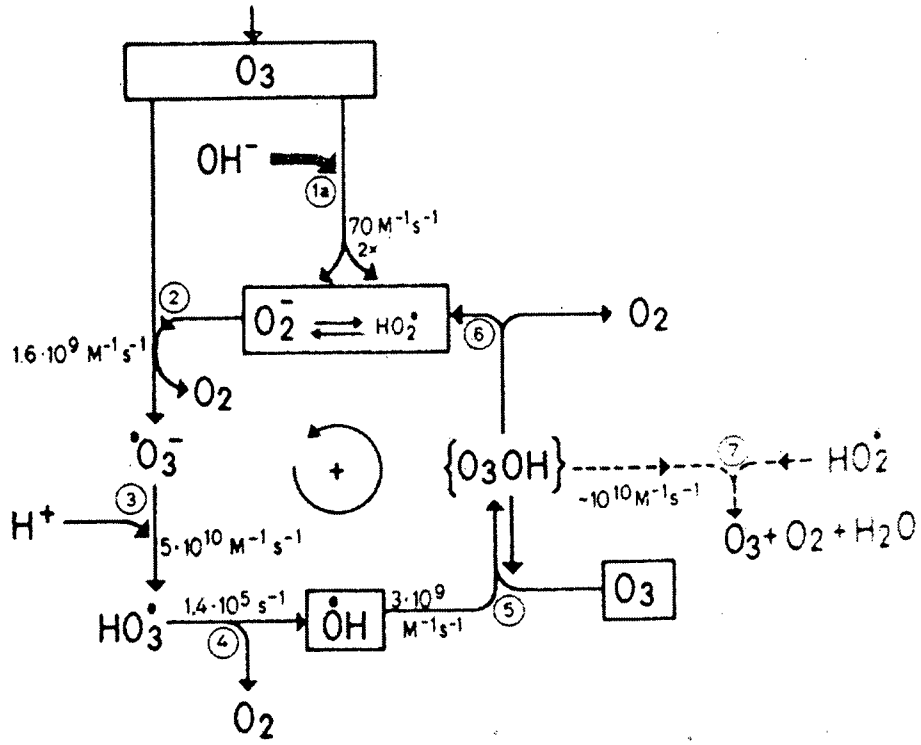


Table 2.2: Reactions and rate constants of the extended TFG model for aqueous ozone decomposition (from Nemes *et al.*, 2000a).

Reaction	Rate constant (L/mol·s) except where noted
$O_3 + OH^- \rightarrow HO_2^- + O_2$	140
$HO_2^- + O_3 \rightarrow \cdot O_3^- + \cdot HO_2$	5.5×10^6
$\cdot O_2^- + O_3 \rightarrow \cdot O_3^- + O_2$	3.0×10^8
$\cdot O_3^- + \cdot OH \rightarrow \cdot O_2^- + \cdot HO_2$	2.0×10^{10}
$\cdot O_3^- + \cdot OH \rightarrow O_3 + OH^-$	8.3×10^9
$\cdot OH + O_3 \rightarrow \cdot HO_2 + O_2$	2.5×10^7
$\cdot O^- + HO_2^- \rightarrow \cdot O_2^- + OH^-$	3.2×10^9
$\cdot O^- + \cdot O_2^- + H_2O \rightarrow O_2 + 2OH^-$	1.8×10^8
$\cdot O_3^- \rightarrow O_2 + \cdot O^-$	5.0×10^3 s^{-1}
$\cdot O^- + O_2 \rightarrow \cdot O_3^-$	2.6×10^9
$\cdot HO_2 + OH^- \rightarrow \cdot O_2^- + H_2O$	1.0×10^{10}
$\cdot O_2^- + H_2O \rightarrow \cdot HO_2 + OH^-$	10 s^{-1}
$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1.0×10^{10}
$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	7.6×10^7 s^{-1}
$\cdot OH + OH^- \rightarrow \cdot O^- + H_2O$	4.0×10^{10}
$\cdot O^- + H_2O \rightarrow \cdot OH + OH^-$	5.4×10^8 s^{-1}
$\cdot HO_3 \rightarrow O_2 + \cdot OH$	1.1×10^5 s^{-1}
$\cdot HO_3 + OH^- \rightarrow \cdot O_3^- + H_2O$	5.2×10^{10}
$\cdot O_3^- + H_2O \rightarrow \cdot HO_3 + OH^-$	3.0×10^2 s^{-1}

When considering the effect of solutes, such as inorganic salts or organic compounds, on ozone decomposition, the reaction system becomes much more complex. Various solutes can act either as initiators of the chain reaction, (reaction with ozone to produce the ozonide ion radical ($\cdot O_3^-$)), propagators (converting the hydroxyl radical to $\cdot O_2^-$), terminators (reaction with a hydroxyl radical to form another radical which is unreactive with ozone), or they can be directly oxidized by ozone. Thus, the stability of ozone in non-pure water is a function of the nature of the impurity. A number of articles have examined the effects of inorganic salts (e.g., phosphate, carbonate, chloride, sulfate) upon aqueous ozone solutions and these have found that several common anions act as radical scavengers. Hoigné and Bader (1976) showed that at pH 10, a level at which ozone decomposes very quickly due to the hydroxyl radicals in the chain reaction, a 2 mM carbonate ion concentration was able to reduce the effect of hydroxyl radicals upon ozone decomposition. This resulted in an increase in the ozone half-life from 20 seconds to 60 seconds. Gurol and Singer (1982) determined that at neutral pH, high phosphate concentrations improve ozone stability because of their hydroxyl radical scavenging ability. Sotelo *et al.* (1989) confirmed these results concerning phosphate as well as the beneficial effect of carbonate and also showed that sulfate serves to stabilize ozone in water. Chloride, which is known to react directly with ozone (Hoigné *et al.*, 1985), accelerates ozone decomposition.

2.8.2 Ozone and hydroxyl radicals

Because of their generation in the decomposition of ozone and also their high reactivity with ozone, hydroxyl radicals play an important role in ozone chemistry. Similarly, hydroxyl radicals can also play a significant part in the ozonation of organic substrates. This becomes apparent when comparing the reaction rates of various organic compounds with either molecular ozone or •OH. For direct oxidation by ozone, rate constants of $1\text{-}10^3$ L/mol·s are typical (Hoigné and Bader, 1983a,b) while for reaction with •OH, constants of $10^8\text{-}10^{10}$ L/mol·s can be expected (Hoigné and Bader, 1976). The pH of the solution is also an important factor in the oxidation rate of organic compounds, particularly dissociable ones. There are two reasons for this. Firstly, because the radical chain reaction leading to the decomposition of ozone into radicals is initiated by hydroxide ions, solutions with high pH quickly decompose the slowly-reacting ozone into the fast-reacting hydroxyl radicals. Secondly, work by Hoigné and Bader (1983b) has shown that for many organic acids and bases, the direct reaction rate with ozone increases considerably with the degree of dissociation of the protonated species (Table 2.3).

Table 2.3: Comparison of reaction rate constants of ozone and non-dissociated (k_{HB}) or dissociated (k_{B^-}) acids (from Hoigné and Bader, 1983b).

Solute	k_{HB} (L/mol·s)	k_{B^-} (L/mol·s)
Glyoxylic acid	0.17	1.9
Malonic acid	<4	7
Formic acid	5	100
Salicylic acid	<500	$2.8 \cdot 10^3$

For some compounds such as phenols, this increase in the rate can attain a factor of 10 per pH unit increase. Hoigné and Bader (1983b) explain this change in reactivity in two ways,

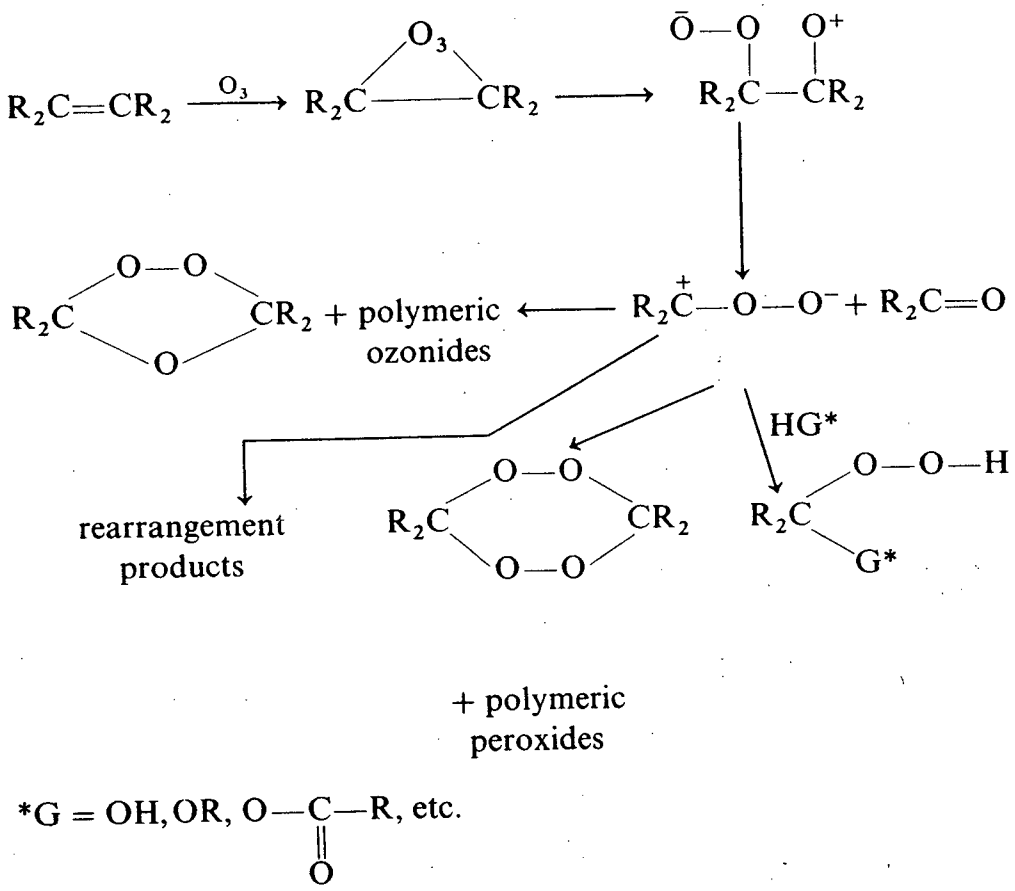
depending upon the nature of the reactant. For carboxylic acids and phenols, they credit the enhanced nucleophilicity of the site of reaction, while for amino compounds, they assume that the reacting group reacts with ozone only when not protonated. As the degree of dissociation approaches 1 at a pH slightly above the pK_a of the acidic form of the compound, a plot of reaction rate versus pH shows a levelling off of the reaction rate constant.

As previously mentioned, radical scavengers have a significant effect on the half-life of ozone in water and, by the same token, the presence of scavengers has a significant effect on the rate of oxidation of organic solutes. Because of the removal of ·OH from solution by the radical scavengers, one would expect the oxidation rates of organic compounds to decrease considerably. Hoigné and Bader (1976) compared the oxidation of propanol and methanol by ozone in both phosphate and carbonate buffers and found that the latter system provided an important degree of protection to the alcohols. At a pH of 10.5, the presence of 20 mM HCO_3^- /CO_3^{2-} resulted in about 50% lower consumption of propanol compared to a sodium phosphate buffer at the same pH with a given amount of ozone added to solution. As well, adjusting the pH of a HCO_3^-/CO_3^{2-} system showed the greater scavenging ability of carbonate compared to bicarbonate ions. Increasing the pH from 9 to 11, the amount of methanol oxidized in a phosphate buffer decreased by about 20% but in a carbonate buffer, it decreased by over 50%.

2.8.3 Oxidation of organic compounds

Our understanding of the reaction of ozone with carbon-carbon double bonds comes largely from the work of Criegee (e.g., Criegee, 1957 & 1975). The Criegee mechanism for ozonolysis is outlined in Figure 2.2. The ozone molecule adds to the double bond through a 1,3-dipolar cycloaddition that results in a 5-membered trioxolane. Through a reverse addition, a zwitterion and either ketone or aldehyde are produced. In water, the zwitterion is expected

Figure 2.2: The Criegee mechanism for ozonolysis of carbon-carbon double bonds (from Bailey, 1978).



to result in a hydroxy hydroperoxide which will then give hydrogen peroxide and an aldehyde or water and a carboxylic acid (Bailey, 1972).

For benzene and substituted benzenes, a similar mechanism is believed to exist, although in competition with the electrophilic addition of ozone. This latter mechanism is expected to be a minor one (Bailey, 1982). The ozonation of aromatic compounds is slow initially; however, once the ring has been broken, the olefinic character of the resulting products means that they react very quickly with ozone. There has been relatively little experimental work done on the ozonation of aromatic compounds other than phenols in aqueous solution. Ozonation of phenols has been the subject of extensive research, primarily due to their recalcitrance in biological treatment systems and their widespread presence in both agricultural and industrial effluents (Benitez et al., 1999a&b; Duguet et al., 1987). Figures 2.3 and 2.4 outline the reaction mechanism of phenol and ozone in water.

Kinetics greatly favour the reaction of ozone with molecules containing double bonds and aromatic groups (Hoigné, 1988). In an extensive examination of reaction rate constants of ozone and various compounds in aqueous solution, the values for alkyl substituted benzenes and unsaturated compounds were generally above 100 L/mol·s (much more so for the latter compounds), whereas for saturated compounds, they are usually below 1 L/mol·s (Hoigné & Bader, 1983a&b). In experiments involving the ozonation of fatty acids, saturated fatty acids were unreactive whereas unsaturated fatty acids were readily consumed (Reynolds et al., 1989).

The nature of the substituents in substituted aromatics and unsaturated compounds also has a significant effect on reaction rates with ozone. Substituents can be classified as activating

Figure 2.3: Products resulting from the ozonation of phenol (from Bailey, 1982).

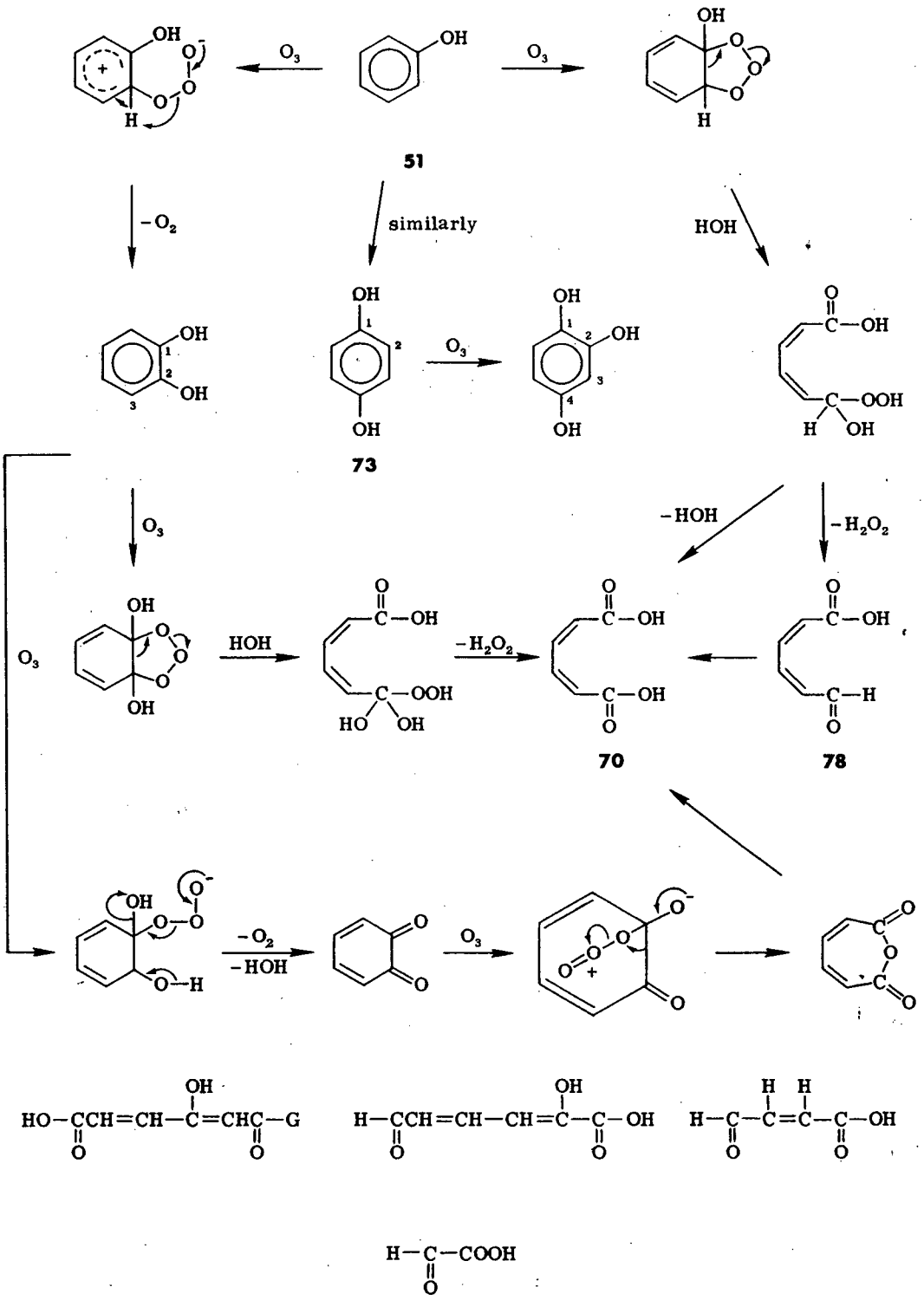
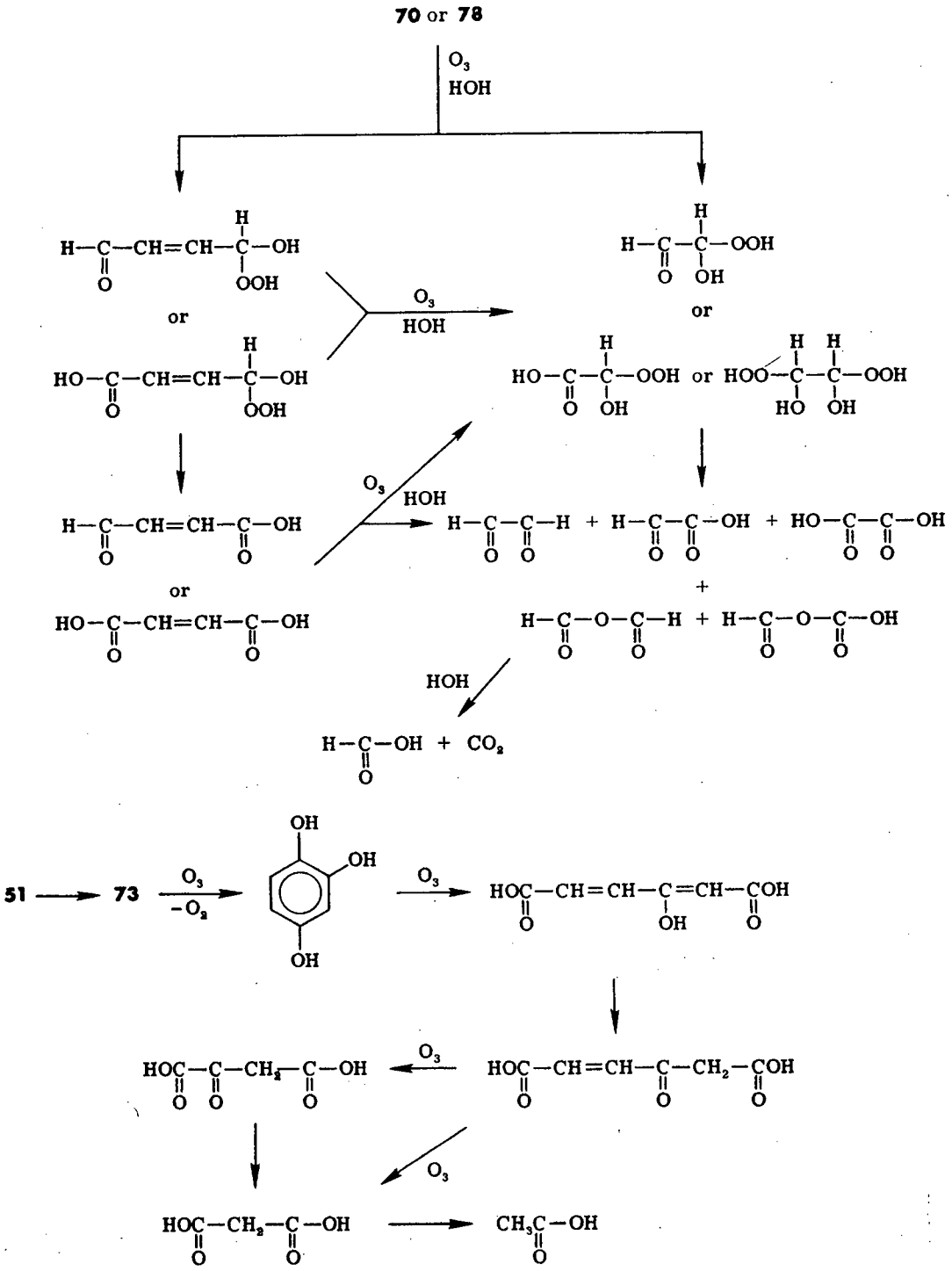


Figure 2.4: Further products resulting from the ozonation of phenol (from Bailey, 1982).



or deactivating, depending on whether they accelerate or retard the rate of reaction of the parent molecule with another reagent. Activating groups such as alkyl, alkoxy, hydroxy, and amino substituents greatly accelerate the ozone reaction rate whereas deactivating groups such as halogens, nitro, and carboxyl groups lower it. Table 2.4 illustrates these trends.

Table 2.4: Effect of substituents on reaction rate constant of ozone and substituted benzenes (Hoigné & Bader, 1983a).

Compound	Rate constant (L/mol·s)
Benzene	2
Nitrobenzene	0.09
Chlorobenzene	0.75
Benzoate ion	1.2
Benzaldehyde	2.5
Toluene	14
o-xylene	90
Anisole	290
Phenol	1300
Benzylamine	6.3×10^4

In modeling the ozone/DHA system, there are some unknowns to deal with. Firstly, the number of ozone molecules consumed per mole of DHA must be determined. As previously described, after the aromatic ring of a molecule is opened, the remaining double bonds of the diene should be rapidly cleaved. This would result in an expected ozone:DHA stoichiometric

ratio of 3:1, the first ozone molecule consumed in opening the ring, then two more to react with the two double bonds of the resulting diene. If, however, an electrophilic addition of ozone also takes place, this would result in a ratio of 4:1. Previous research involving ozonolysis of various phenols has yielded a ratio of 3:1 (Bernatek & Frengen, 1961; Bernatek *et al.*, 1961; Wibaut and Sixma, 1952; Kuo and Huang, 1995), and ozonation of various aromatic compounds gave a ratio of 2.5:1 (Hoigné and Bader, 1983a).

Another unknown is the extent of production of hydrogen peroxide from ozonolysis, about which relatively little has been published. Some make qualitative statements regarding H_2O_2 generation from ozonolysis (i.e., H_2O_2 is determined to be a reaction product but no concentration determined) (Gilbert, 1978; Bernatek *et al.*, 1961, Cotruvo *et al.*, 1977). Others have reported quantitative results for H_2O_2 production from ozonation (Gauducheau *et al.*, 1986; Legube *et al.*, 1983), however, no research has been found that has thoroughly examined this issue. In those papers that do report H_2O_2 production, there exists a significant amount of variation in terms of the quantity of H_2O_2 produced. Ozonation of styrene and naphthalene yielded an almost equimolar amount of H_2O_2. Ozonation of benzaldehyde yielded less than half the number of moles of H_2O_2 as benzaldehyde reacted (Legube et al., 1983). No explanation was given for this difference.

2.9 Ozone in pulp and paper effluent treatment

Although no literature has been found dealing specifically with ozonation of logyard run-off, there does exist a body of work concerning the treatment of pulp and paper mill effluents with ozone. Table 2.5 outlines some of the results obtained. Certain general patterns emerge upon examination of the results obtained by various researchers. COD removal by ozone is relatively limited, not exceeding 20% removal for ozone doses of 100 mg/L. On the other hand,

Table 2.5: Results of previous research on the ozonation of pulp mill and woodroom effluents.

Authors	Effluent type	Ozone dose (mg/L)	COD_0 (mg/L)	COD(%red.)	BOD_0 (mg/L)	BOD(%red)	AOX_0 (mg/L)	AOX(%red)
Dorica and Wong (1979)	Linerboard	78	356-613	5.0-20.0	177-273	-20 - -25		
Zhou and Smith (1997)	Secondary treatment Kraft mill	120	485	20			7.77	50
Tuhkanen *et al.* (1997)	Bleach plant Birch feed	0.4 mg/mg COD	720	~40	225	~0		
	Bleach plant Pine feed	0.4 mg/mg COD	2820	~20	750	~ -40		
Roy-Arcand *et al.* (1996)	CTMP	30	1434	2.9	613	8.2		
		100	1434	8.2	613	17.5		
	Woodroom	30						
		100						
Roy-Arcand and Archibald (1996a)	Mechanical	100	1300	~15	350			
Roy-Arcand and Archibald (1996b)	Kraft	100	615-1410	15-20	281-383	3.4 – 21.4	5-20	20-30
Laari *et al.* (1999)	TMP filtrate	500-800						
Hostachy *et al.* (1997)	Kraft mill effluent	550	700	50				

Table 2.5 (cont.): Results of previous research on the ozonation of pulp mill and woodroom effluents.

Authors	Effluent type	Ozone dose (mg/L)	DHA_0 (mg/L)	DHA(%red)	Toxicity(%red.) (Microtox®)
Dorica and Wong (1979)	Linerboard	78			
Zhou and Smith (1997)	Secondary treatment Kraft mill	120			
Tuhkanen *et al.* (1997)	Bleach plant Birch feed	0.4 mg/mg COD	~ 1	91	
	Bleach plant Pine feed	0.4 mg/mg COD	~ 1	99	
Roy-Arcand *et al.* (1996)	CTMP	30		42 (RFA+JB)	62
		100		75 (RFA+JB)	100
	Woodroom	30			~55
		100			~95
Roy-Arcand and Archibald (1996a)	Mechanical	100		~50	~85
Roy-Arcand and Archibald (1996b)	Kraft	100	50 - 200	60-90(RFA+JB)	~70
Laari *et al.* (1999)	TMP filtrate	500-800	53(Lipophilic wood extractives)	90 (Lipophilic wood extractives)	
Hostachy *et al.* (1997)	Kraft mill effluent	550			

treatment with ozone results in a significantly greater oxidation of resin and fatty acids and juvabiones, though it was not determined whether these compounds were completely or only partially oxidized (Dorica and Wong, 1979; Roy-Arcand and Archibald, 1996a; Laari *et al.*, 1999). For BOD, the effect of ozone is much more variable. Roy-Arcand *et al.* (1996) showed that in treatment of CTMP effluent, BOD undergoes a slight reduction. Dorica and Wong (1979), on the other hand, show an increase in BOD levels of about 25% during ozone treatment of linerboard effluent. Bauman and Lutz (1974) report that ozonation of the secondary effluent from a kraft pulp mill resulted in an increase of BOD of 100%, albeit from a very low starting point of <10 mg/L. Mohamed and Smith (1992) show variable results for kraft mill effluent. Some ozonated samples had higher BOD_5 (secondary effluent), while others experienced a slight decrease (bleach plant and primary effluents). As a rule of thumb, high BOD samples will see their BOD decrease slightly with ozone treatment while low BOD samples will see an increase. The general explanation given for this result is that, in high BOD solutions, ozone will react with both simple biodegradable compounds and high molecular weight non-biodegradable compounds. As the ozonation proceeds, the high molecular weight compounds are broken into smaller fragments; the simpler compounds are further broken down and mineralized. The net effect is a slight decrease in BOD. In low BOD_5 samples, the ozone will primarily react with the more complex compounds, resulting in more small fragments, thus increasing BOD.

Another pattern that was noticed was the diminishing reduction in measured parameters as ozonation proceeded. For example, quite small ozone additions of 10 mg/L resulted in significant reductions in pulp mill effluent resin acid concentrations (~30%) and toxicity (~55%). An extra 90 mg/L did reduce the parameters further but not by the same degree (~75% total resin acid removal and ~80% total toxicity removal) (Roy-Arcand and Archibald, 1996b). The same trend was evident in the levels of colour and AOX (Zhou and Smith, 1997; Bauman and Lutz, 1974; Roy-Arcand and Archibald, 1996a&b). All papers investigating toxicity reduction in mill

effluents report significant toxicity reductions by ozone. Roy-Arcand and Archibald (1996a), in the treatment of CTMP effluent, achieved toxicity reductions of ~70% for ozone doses of 100 mg/L. For woodroom effluent, they obtained similarly significant toxicity reductions.

Although they deal with somewhat differing substrates (TMP, CTMP, Kraft and woodroom effluents), the general conclusions reached by the authors follow a similar pattern: low ozone doses result in small COD decreases, variable BOD reductions, and quite significant extractive and toxicity reductions (when measured on a percentage basis).

2.10 Treatment combining ozone and biological processes

The use of biological systems in the wood processing industry is well established. Pulp and paper mills are now virtually all equipped with some type of biological treatment, mainly aerated stabilization basins or activated sludge units. These biological systems consume organic compounds and thereby reduce the significant oxygen demand of these compounds in receiving waters. Often, biological treatment is the least expensive and most effective method for removing organic pollutants from wastewater streams (Gottschalk *et al.*, 2000); however, not all organic compounds are amenable to biodegradation. In such cases, the inclusion of a chemical oxidation step in series with the biological treatment system can be of use in improving the biodegradability of the waste stream.

Scott and Ollis (1995) have reviewed the literature and outlined four situations where combined biological/chemical oxidation may be of use: (1) waste streams containing only biologically recalcitrant compounds may be chemically oxidized to more biologically amenable forms; (2) waste streams may have significant biodegradability; however, one or more recalcitrant compounds may remain after biological treatment. In such cases, chemical oxidation after biological treatment may be used; (3) compounds that are inhibitory to biological treatment may exist in a wastewater. In such cases, an initial chemical oxidation step may be of use,

although the economics of the situation may not justify the expense; (4) biological treatment of a waste compound may lead to a so-called dead-end compound, one that cannot be biologically degraded. Chemical oxidation followed by further biological treatment may be considered.

Full-scale systems using both biological treatment and ozonation have been outlined in Gottschalk *et al.* (2000). These systems are primarily used to treat landfill leachates and textile effluents, streams that can contain high concentrations of biologically recalcitrant material. Also, a sequential bio-ozone system is reportedly in use for treatment of pulp and paper mill effluent, however, details are not provided. In addition, research has been published recently that examines the use of ozone and biological systems in treating much more complex systems such as municipal wastewater (Beltrán *et al.*, 1997), wine distillery wastewater (Beltrán *et al.*, 1999a,b), black olive wastewater (Beltrán *et al.*, 2000) and pulp mill effluents (Roy-Arcand *et al.*, 1996). These have found that an ozonation step can improve the biodegradability of the wastewater although varying results are found for the resulting biological kinetic parameters. For the wine distillery wastewater, pre-ozonation leads to an improved μ_{max} for the microorganisms during subsequent biological treatment and a removal of inhibitory effects (Beltrán *et al.*, 1999b). For municipal wastewater, pre-ozonation results in a similar improvement in biodegradability; however, a lag phase in biological treatment becomes apparent.

3. OBJECTIVES AND EXPERIMENTAL PLAN

3.1 Initial assessment of potential treatment technologies

In the process of selecting a technology for further study, an initial screening process was undertaken to narrow the range of candidates. As a guide to the potential methods that could be used in the treatment of logyard run-off, the broad treatment classifications of Samis *et al.* (1999) were considered. These are:

- Natural attenuation
- Recirculation
- Biological treatment
- Physical/chemical treatment

Natural attenuation was not deemed promising for future work. The two sawmills used as sources of run-off in this study are both limited in terms of area available for dispersal of run-off on unpaved ground and are situated beside fish-bearing waters. The sawmills are situated on the coast of British Columbia and can receive sufficient rainfall during a given storm event to easily overcome the saturation capacity of the soil. Saturation of the soil and proximity to fish-bearing waters could result in numerous instances of toxic leachate release. Previous laboratory trials have shown that natural attenuation of wood-residue leachate in soil ranged from very limited to ineffective, while field studies have similarly shown attenuation to not be effective or practicable (Samis *et al.*, 1999).

Recirculation was not considered for experimentation due to concerns about rainfall levels. As previously stated, at one of the sawmills used as a source of run-off, one centimetre of

rainfall results in an estimated 500 000 litres of run-off. It is simply unrealistic to expect that a recirculation system could deal with this amount of run-off, let alone the amounts created by a larger storm event. At the north coast location where logyard run-off was sampled, the average number of days with elevated precipitation can be considerable (Figure 3.1).

Biological treatment systems are in widespread use in the pulp and paper industry as a method of removing the BOD exerted from effluents (O'Connor and Voss, 1998). In order for biological systems to function properly, they require stability, particularly in flow rate, organic loading, temperature, pH and nutrient content. For logyard run-off, however, certain difficulties would be encountered in employing a biological treatment system. Firstly, the large variations in run-off flow rates would cause significant problems. Coastal British Columbia experiences large swings in average rainfall. For the mill on the North Coast, the average monthly precipitation ranges from about 110 mm in July to 380 mm in October and an average number of days with precipitation of 16 in July to 25 in October. For the mill on Vancouver Island, average monthly precipitation goes from 30 mm in July to 200 mm in December and the average number of days of precipitation range from 8 in July and August to 20 in December (Meteorological Service of Canada, http://www.msc.ec.gc.ca/climate/climate_normals_1990). Naturally, these averages hide variations from year to year with some wetter months and others much drier (Figure 3.1). Especially during the summer months, there are liable to be periods when no rain may fall for several weeks in succession. As a result, with no run-off to treat, a biological system would have three options:

- shut down,
- a synthetic effluent would need to be created and used to maintain the biological system until such time as run-off would be generated,
- previous run-off could be stored and used during periods of no rainfall.

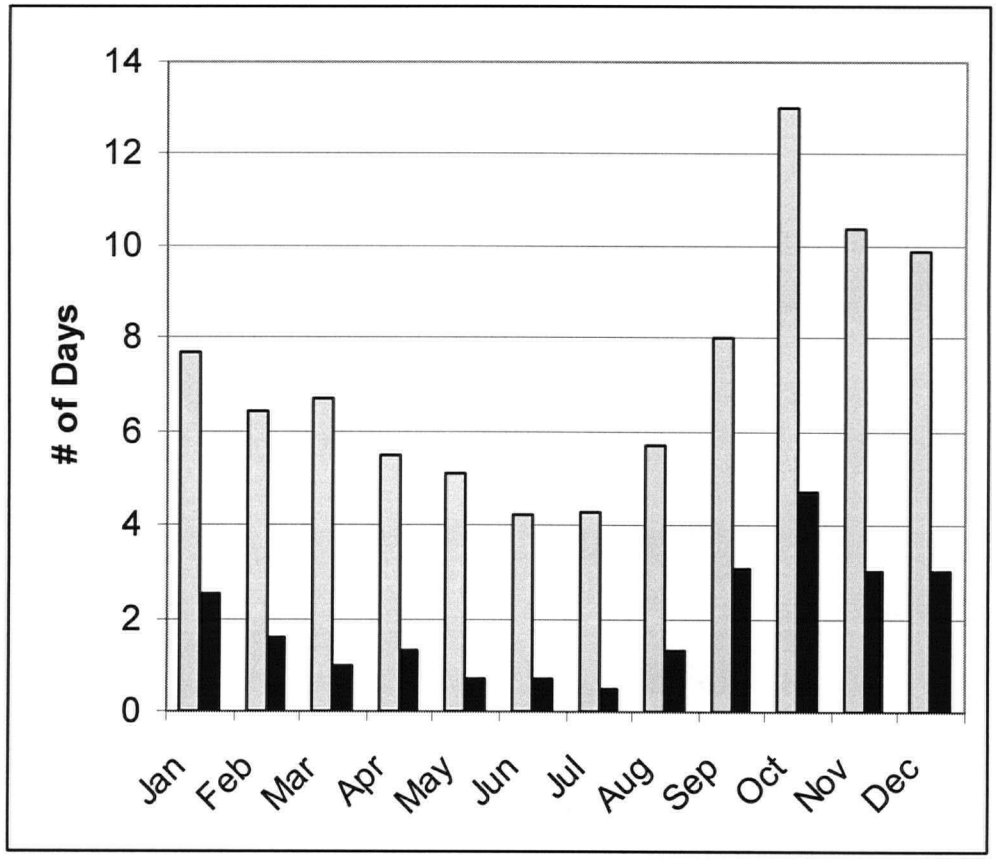


Figure 3.1: Number of days per month with rainfall greater than 10 mm (▒) and 25 mm (▉) at north coast sampling site. (Meteorological Service of Canada, http://www.msc-smc.ec.gc.ca/climate/climate_normals).

Another problem is variation in temperature. During the winter, when the rate of precipitation is highest and efficiency of treatment is at its most critical, the temperature of the run-off will be at its lowest. Ideally, biological treatment is operated at approximately 35°C in order to obtain maximum rate of oxidation. During summer months, the average temperature on the North Coast of British Columbia is about 15°C while on Vancouver Island it is 22°C. However, during the winter months, when greatest efficiency is needed because of the high rate of precipitation, the temperature is about 5°C. Because of the lower temperatures in winter, either the system would have to be sized to accommodate a significantly slower rate of treatment or the run-off would have to be pre-heated, a potentially appreciable expense. These factors combine to make biological treatment a less than ideal option.

3.2 Project objectives

Although logyard run-off has been identified as a source of toxic discharge into waterways in some instances, and some reports have been produced that outline best management practices for the reduction of the run-off volumes (e.g., G3 Consulting Ltd., 2003; Samis *et al.*, 1999; AFPA 1999b), no published papers have been found detailing the results of treatment methods to reduce the toxicity levels in logyard run-off. Given this dearth of information, an investigation of possible treatment methods was warranted.

A preliminary survey of a number of potential treatment technologies (Appendix A) indicated that the use of ozone to reduce toxicity levels merited further study. Thus, the first objective of this project was to determine the effectiveness of ozone in the treatment of logyard run-off.

The widespread use of biological treatment systems in pulp mills means that there is a wealth of information on the subject of the effectiveness of this method in treating various kinds of mill effluent; however, nothing is known to have been published concerning treatment of

logyard run-off. With previous work indicating that a combination of ozonation and biological treatment of certain substrates can achieve better performance than either method separately, this prompted the second objective of this study, namely, an examination of ozonation and biological treatment used in sequence on logyard run-off.

In an effort to better understand the reactions involved in a complex system, it is a common method to simplify the problem by simulating the system using a single compound of interest. Logyard run-off is a very complex system containing various wood-derived chemicals, a number of which have been found to exhibit toxicity to aquatic wildlife. The final objective of this work was to study the reaction between ozone and one of these toxic compounds, the resin acid DHA.

3.3 Ozonation of logyard run-off

The ability of ozone to reduce the toxicity as well as other parameters of logyard run-off was determined by obtaining samples from two sawmills during rain events over a period of one year. The mills used different wood species, thus allowing one to see whether this factor would result in significant variations in treatability. The leachate as obtained was always mildly acidic. In order to determine whether the pH at which ozonation was performed had an effect on the treatment, samples were treated at a pH of both 5 and 7. The variables that were analyzed were COD, BOD, tannins and lignins, DHA, and Microtox toxicity.

3.4 Biological treatment of logyard run-off

Although biological treatment of logyard run-off has been previously discussed as a less-than-ideal solution to the problem of run-off toxicity, there are times when this method may be of interest. For example, pulp mills often maintain large supplies of wood chips as feedstock and rain on these piles can generate a leachate. Since virtually all Canadian pulp mills now have a

biological treatment system on site, it would be interesting to know whether such a system would be able to deal with wood leachate and, if so, if the kinetics of the biodegradation are very much different from those of pulp mill effluent. To this end, a sample of run-off was obtained and biologically-treated in a batch reactor system. Parameters that were followed over the course of the treatment were COD, BOD, tannins and lignins, and Microtox toxicity. The kinetics of degradation were also determined in order to form a basis for comparison with previous research involving bleached kraft mill effluent.

3.5 Biological treatment in conjunction with ozone

Ozone as both pre- and post-treatment to a biological method was examined for a run-off sample. In the case of biological treatment followed by ozonation, part of the sample obtained after biological treatment was then ozonated. COD, BOD, tannins and lignins, and Microtox toxicity were analysed over the course of ozonation to determine whether any reductions in these parameters were obtained over and above what was achieved with biological treatment.

In the case of ozonation followed by biological treatment, it was of interest to determine how varying degrees of ozonation would affect subsequent biological treatment. Three levels of ozonation of a run-off sample were obtained (no ozonation, 10 minutes, 30 minutes, representing 0 mg/L, 250 mg/L, and 720 mg/L ozone dose, respectively) and these were then subjected to biological treatment. Samples were taken periodically to determine how the parameters of COD, BOD, tannins and lignins, and Microtox toxicity varied over the course of the biological treatment.

3.6 Oxidation of DHA by ozone in aqueous solution

Some very preliminary work involving the oxidation of an aqueous solution of DHA in the lab reactor used for logyard run-off ozonation experiments was performed. It was soon realized, however, that questions of ozone mass transfer and surface chemistry between DHA and ozone/oxygen bubbles would complicate any attempt to yield meaningful results from this experimental set-up. In order to eliminate issues arising from the transfer of ozone to the aqueous phase, a method that utilized addition of an aqueous ozone solution to the DHA had to be used. The method that was used is essentially the one used by Hoigné and Bader (1983a&b) in their compilation of reaction rate constants between ozone and many organic molecules. A UV spectrophotometer cuvette was used as a reactor. The DHA solution was first added to it, followed by the ozone solution. The addition of the ozone solution just beneath the surface of the DHA solution allowed for excellent mixing in the cuvette while at the same time eliminating the mass transfer issues that plagued the large-scale reactor.

Issues that were of interest in studying the ozonation of DHA were the effect of the presence of radical scavengers on the oxidation of DHA as well as the effect of pH. A full factorial design was used with three levels of radical scavenging (no scavenger, 6.4 mM HCO_3^- /CO_3^{2-}, and 6.4 mM t-BuOH) and three pH levels (6.5, 8.1, 9.7) chosen to perform experiments. The ratio of moles of ozone consumed per mole of DHA reacted and the ratio of moles of hydrogen peroxide produced per mole of DHA reacted were the response variables examined. From the results obtained in these experiments, a mathematical model of the ozone/DHA system was formulated.

3.7 Modeling of the ozonation of DHA

Using a mathematical technique to obtain the concentrations of DHA and ozone in solution over time from some of the spectrophotometric results, an attempt was made to determine the reaction rate of ozone and DHA as well as establish the stoichiometry of the reaction. A computer model of the reaction was devised from current knowledge about ozone chemistry in aqueous solution as well as reactions of ozone with organic compounds. Because the stoichiometry of the reaction was not certain, both with respect to ozone consumed and hydrogen peroxide produced per unit DHA reacted, a number of variations of the model were run (4:1, 3:1 O_3:DHA ratio, each with either 3:1, 2:1, 1:1, or 0:1 H_2O_2:DHA ratio).

In addition to the reaction of molecular ozone with DHA, the influence of radicals on the various reaction systems depending on the level of radical scavenging was also examined in the model in order to better understand the results obtained from the ozonation of DHA.

4. MATERIALS AND METHODS

4.1 Logyard run-off

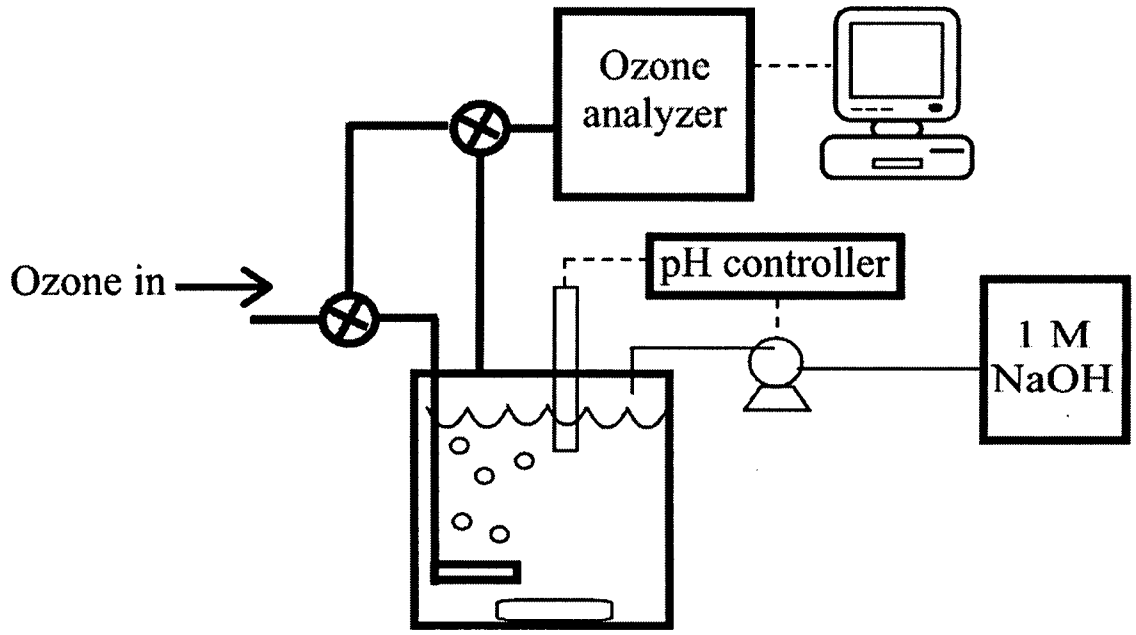
Samples of run-off were obtained during periods of rainfall from two British Columbia sawmills, one on the north coast of the province (Mill A), the other on Vancouver Island (Mill B). A total of 7 samples were collected during the period of June 2000 through March 2001. Samples were collected in 20-L plastic containers and stored in the dark at 4°C upon receipt. All samples were used within one week of receipt. Mill A processes 200 000 m^3/year of balsam fir, western hemlock, Sitka spruce, and western red cedar. Mill B processes 500 000 m^3/yr, primarily Douglas fir and western hemlock, and sees significant variation in the composition of its feedstock, sometimes going through a complete species change in the space of 24 hours.

4.2 Batch ozonation treatment

The main ozonation experiments were performed in a 3 L total volume (11.25 cm diameter, 25.25 cm height) jacketed glass reactor equipped with ports for sampling, ozone inlet and outlet, pH measurement, and pH adjustment (Canadian Scientific Glassblowing, Richmond, BC) (Figure 4.1). A magnetic stir plate and stir bar were used for mixing. An ozone gas analyzer (Ozometer™, Model HA-100GTP, Hankin Atlas, Scarborough, ON) was used to measure ozone concentration both in the inlet and outlet of the reactor, allowing the calculation of ozone consumed in the reactor. Prior to treatment, the run-off sample was centrifuged at 2000 rpm (~650g) for 20 minutes to remove solids.

To carry out the ozone treatment, 2.5 L of the supernatant resulting from the centrifugation was added to the reactor and the pH adjusted to either 5 or 7 using 3 M H_2SO_4 or NaOH as necessary. The sample was maintained at 25 °C using a water bath (VWR Scientific, Model 1162). Stirring was effected by a magnetic stirrer (Fisher Scientific) at maximum speed. Ozone was produced using a Grace Davison Model LG-2-L1 ozone generator with oxygen feed of 1 L/min. The oxygen/ozone stream was fed to the reactor through a sintered glass dispersion tube and the off-gas ozone concentration was measured by the ozone analyzer. Using Collect/W software (Labtronics Inc., Guelph, ON), the off-gas ozone concentration values were relayed to a computer and stored in a spreadsheet every 15 seconds. Because of the gradual acidification of the reaction mixture during the ozonation, the pH of the system was maintained within 0.1 pH units of the desired value by the addition of 1 M NaOH using a Cole-Parmer pH controller (Model 57000-00).

Figure 4.1: Diagram of the reactor system used for ozonation of logyard run-off.



4.3 Batch aerobic biological treatment

Batch biological treatability studies were carried out under the operating conditions listed in Table 4.1. The experimental program was carried out in a 15 L (10.4 L working volume) cylindrical jacketed Plexiglas reactor. Seed was obtained from the recycle line of the UNOX® system at Western Pulp's 800 air dried tons/d (adtpd) Squamish mill. Reactor temperature was maintained at 35°C by circulating water from a constant temperature bath (VWR Scientific, Model 1131) through the annular Plexiglas jacket encasing the reactor. A temperature of 35°C was selected because biological treatment of logyard run-off would most likely occur at a facility such as a pulp mill effluent treatment plant. Operating temperatures at such plants are typically around 35°C. Samples were collected from the sampling port at the bottom of the reactor. The reactor was aerated through a sintered glass stone at a rate of approximately 1 volume/volume reactor·min using building air. The concentration of DO was monitored to maintain the level above 5 mg/L. This was to ensure that DO would not be a limiting reagent.

Effluent samples were centrifuged at 2000 rpm (~650 g) and the supernatant was acidified to pH 2 or less with concentrated H_2SO_4. The resulting samples were stored at 4°C with minimal headspace prior to analysis.

Table 4.1: Summary of experimental conditions for batch treatability study.

Raw Wastewater Volume (L)	8
Seed Volume (L)	2.4
Seed Concentration (mg SS/L)	10600
Initial MLSS (mg/L)	2800
Run time (h)	48
Temperature (°C)	35
pH	7
$MgSO_4 \cdot 7H_20$ added (mg/L)	25
$CaCl_2$ added (mg/L)	30
$FeCl_3$ added (mg/L)	0.3

4.4 Determination of kinetic parameters for biological degradation

Microbial substrate uptake kinetics were determined in duplicate using a respirometric method developed by Cech *et al.* (1984). The oxygen uptake rate (OUR) values were divided by the mass of oxygen consumed (OC) per mass of substrate (BOD) metabolized (i.e., OC/S) to obtain substrate uptake rates (SUR). The values were divided by the MLSS concentration in the respirometer in order to obtain specific ΔOUR (SOUR). This method was chosen due to the accuracy with which DO may be measured, and because it was relatively easy to carry out.

The respirometer (Figure 4.2, Canadian Scientific Glassblowing Company Ltd., Richmond, B.C.) consisted of a jacketed 180 mL glass vessel equipped with ports for DO measurement, aeration and sample injection. Vessel temperature was maintained at 35°C by circulating water from a constant temperature bath (VWR Scientific, Model 1131) through the annular jacket encasing the respirometer. Mixing was provided by the DO probe (YSI Inc., Model 5905) as well as a magnetic stir plate (Fisher Scientific) and stir bar. An aquarium pump (Rolf C. Hagen Inc., Optima Model) provided the necessary aeration.

For respirometry, biomass obtained from the recycle line of the UNOX® system at Western Pulp's 800 adtpd Squamish mill was diluted to a concentration of 700-800 mg/L mixed liquor suspended solids (MLSS); the exact concentration was measured at the end of the test and used in subsequent calculations. This diluted mixed liquor was added to the respirometer and aerated for 30 minutes in order to degrade any substrate present. After this aeration period, aeration was stopped and the DO probe was inserted into the respirometer. Prior to sample addition, the probe was allowed to stabilize for approximately two minutes and the endogenous respiration rate was measured for at least two minutes. A known amount of substrate, adjusted to pH 7 with concentrated NaOH, was added through an injection port using Becton-Dickinson syringes and the change in respiration rate, as reflected by DO concentration changes, was monitored. Upon injection, the OUR immediately increased and then slowly returned to the

initial endogenous rate. In order to ensure that the complete OUR profile (Figure 4.3) was captured, data were collected for 2-3 minutes after sample injection. At the end of the test, data collection was terminated, and the DO probe was removed from the respirometer. Before another sample was injected, the mixed liquor was aerated until the DO value reached 6-8 mg/L.

Figure 4.2: Respirometer used for kinetic parameter determination.

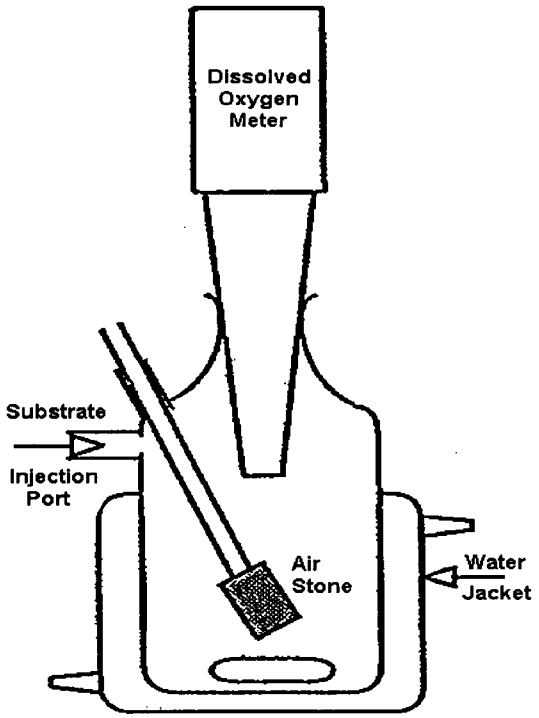
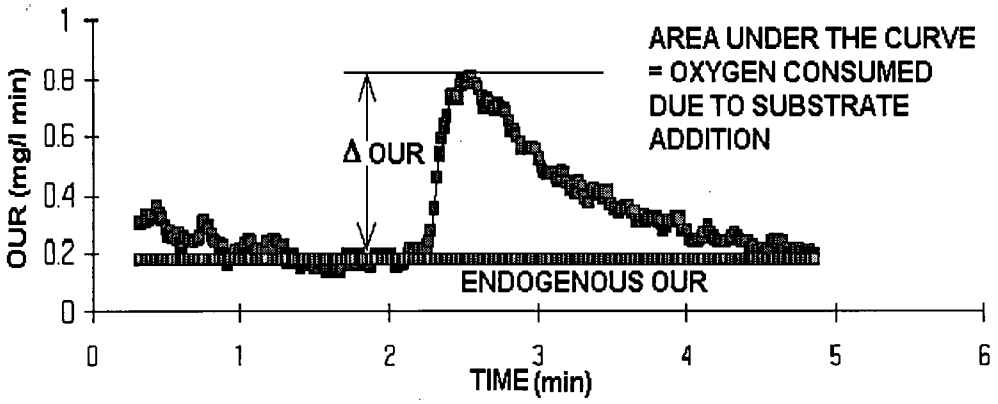


Figure 4.3: Sample of data from respirometric determination of biodegradation kinetics.



The data from the DO meter (YSI Inc., Model 59) were imported into a spreadsheet using Collect/W (Labtronics Inc., Guelph, Canada). The DO, percent saturation, and temperature were recorded every second. Using a macro, the ΔOUR and oxygen consumed (OC) were determined for each substrate injection.

The microbial growth or specific substrate uptake rate can be described using Monod kinetics, which can be expressed in terms of substrate uptake rate as follows:

$$\text{Monod:} \qquad q = \frac{q_{max} S}{S + K_s} \qquad (1)$$

where: q is the substrate uptake rate

q_{max} is the maximum substrate uptake rate

S is the substrate (BOD) concentration

K_s is a constant

Monod kinetic parameters, q_{max} and K_s, were estimated by plotting a Lineweaver-Burk plot.

4.5 Sequential biological treatment/ozonation

Biologically-treated effluent was collected from the batch reactor after 48 hours. It was centrifuged at 2000 rpm (~650g) for 20 min to remove solids and treated with ozone. Ozonation was carried out in the same manner as described in the "Batch Ozonation Treatment" section above.

4.6 Sequential ozonation/biological treatment

The run-off sample was centrifuged at 2000 rpm (~650g) for 20 minutes. Part of the sample was set aside in order to compare biological treatment of ozonated and unozonated samples. Two 2.5 L samples were then treated with ozone as described above, one for 10 minutes, the other for 30 minutes. Nitrogen and phosphorus were added in the form of NH_4Cl and NaH_2PO_4 in order to ensure a BOD:N:P ratio of 100:5:1. To these samples, activated sludge was added to obtain a MLSS concentration of 2500 mg/L. A series of 100 mL aliquots of each sample were added to 250 mL Erlenmeyer flasks and incubated in a shaker at 35°C and 150 rpm. At 2, 4, 8, 12, 24, and 33 hours following the start of biological treatment, duplicates of each sample were removed and centrifuged at 2000 rpm (~650 g) for 20 minutes. The resulting supernatant was acidified to pH 2 or less with concentrated H_2SO_4 and stored at 4°C with minimal headspace prior to analysis.

4.7 General analyses

BOD_5 was measured in 300 mL BOD bottles using standard methods (APHA, 1995). Seed was obtained from the recycle line of the full-scale UNOX® activated sludge treatment system at Western Pulp's 800 adtpd kraft pulp mill near Squamish, B.C.

COD was measured using the standard colorimetric dichromate closed reflux method (APHA, 1995).

Tannins and lignins were measured using the standard colorimetric method (APHA, 1995). Folin phenol reagent (a solution of phosphomolybdic and phosphotungstic acids) and a sodium carbonate/sodium tartrate reagent are added to the sample and allowed to stand for 30

minutes. The absorbance of the solution is measured at 700 nm. Tannic acid was used as reference and all results are reported as mg/L of tannic acid.

Acute toxicity of run-off samples was measured using a Microtox® 500 analyzer and the basic test protocol supplied by Microbics Corporation (Carlsbad, CA). The Microtox® system uses *Vibrio fischeri,* a marine bioluminescent bacterium, as test organism. The generation of light, which arises from the action of the enzyme luciferase, is an integral part of the cellular electron transport system. Thus, any change in the metabolic activity of the bacteria will be reflected in the intensity of light that is emitted (Ribo and Kaiser, 1987). Prior to testing, samples were centrifuged for 10 minutes at 10,000 rpm (10,300 g) in a microcentrifuge in order to remove any remaining suspended solids. Five minute EC_{50} values and 95% confidence intervals were calculated by the Toxcalc software provided with the Microtox® system.

Daphnia magna toxicity measurements were performed at BC Research laboratories according to the method set out by Environment Canada (Environment Canada, 1990). Prior to testing, the 250 mL beakers to be used were first rinsed using a 10% HCl solution, then thoroughly rinsed with distilled water and left to dry overnight. For each sample to be tested, a logarithmic set of dilutions (100%, 56%, 32%, 18%, and 10%) was made with a moderately-hard reconstituted water (deionized water with 105.6 mg/L $NaHCO_3$, 66.0 mg/L $CaSO_4$, 57.2 mg/L $MgSO_4$, 4.4 mg/L KCl, 2 μg/L vitamin B_{12}, and 2 μg/L SeO_2) used for dilution water. Temperature, pH, dissolved oxygen, and conductivity were measured for each beaker. Ten neonate daphnids were then added to each beaker and the beakers were placed on a shelf, covered with a Plexiglas sheet. After 48 hours, the number of surviving daphnids in each beaker was determined and final measurements of dissolved oxygen, pH, and temperature were taken.

LC_{50} values for the samples were determined using the trimmed Spearman-Karber method (Hamilton et al., 1977).

Dehydroabietic acid (DHA) was measured by gas chromatography (GC) based on published methods (Örså and Holmbom, 1994). Briefly, after adjusting the pH to approximately 9, 50 mL of sample was extracted twice with an equal amount of methyl t-butyl ether. The resulting organic phase was then concentrated in a rotary evaporator, transferred to a glass vial, and dried under a stream of nitrogen. The sample was derivatized using bis(trimethylsilyl) trifluoroacetamide. O-methyl podocarpic acid (Helix Biotech Scientific, Richmond, BC) and heneicosanoic acid (Aldrich Chemical, Milwaukee, WI) were used as recovery and internal standard, respectively. The GC analyses were performed on a Hewlett-Packard 5890A system using a HP-5, 30m x 0.32mm x 0.25μm fused silica capillary column and flame ionization detector. Helium was the carrier gas and a split/splitless insert used with a 50:1 split. The injector and detector were set to 260°C and 290°C, respectively. The oven temperature was programmed as follows: 150°C for 1 minute, ramp at 4°C/min to 265°C, maintain for 3 minutes, ramp at 12.5°C/min to 290°C.

4.8 Ozone oxidation of DHA

In order to further examine the oxidation of a particular toxic compound, oxidation of a solution of pure DHA was examined. As previously mentioned, ozone undergoes a decomposition reaction in water that is accelerated by the presence of hydroxide ions. One of the products of this reaction is hydroxyl radicals. Hydroxyl radicals are known for their very high rates of reaction with organic molecules and can therefore interfere with measurements of rates of reaction of ozone. For this reason, studies involving the oxidation of solutes by molecular ozone in water are usually performed in acidic solutions (pH approximately 2-3) along with a hydroxyl

radical scavenger (e.g., t-butanol). One of the main difficulties encountered was the extremely low solubility of DHA in water at low pH. Nyren and Back (1958) examined the issue of DHA and abietic acid solubility in aqueous solution. According to their results, the solubility of DHA at a pH of 6.5 is approximately 10 mg/L. Bouffard (1998) obtained a similar result. Below the pH of 6.5, the starting solubility and, hence, the optical absorbance of the DHA will be lower, giving a smaller range of possible ozone additions. Because of this, a pH of 6.5 was selected as the lowest pH at which experiments on ozonation of DHA would be performed.

Initially, a DHA solution in a phosphate buffer at pH values of 6.5, 8.1 and 9.7 was studied. In addition, the effect of radical scavengers (t-butanol and sodium bicarbonate) on the reaction was studied.

In preparation for the experiments, all glassware was fully cleaned and then left to soak for an hour in an aqueous ozone solution ($[O_3]\approx 15$ mg/L). It was then left to dry overnight. All water used in the reactions was first ozonated and left for a minimum of one hour in order to remove any oxidizable material and subsequently boiled for one hour to remove any residual ozone.

Phosphate buffers were made by adding NaH_2PO_4 and $Na_2HPO_4 \cdot 7H_2O$ in such proportion as to give a 0.05 M phosphate solution of the desired pH. For those experiments involving radical scavengers, t-butanol or $NaHCO_3$ was added in appropriate amounts to the phosphate buffer solution in order to obtain the desired concentration.

A DHA stock solution was made by dissolving approximately 10 mg of DHA in 100 mL of a 0.01 M NaOH solution. The DHA solution for the reaction was made by dissolving 5 mL of the DHA stock solution with sufficient buffer to make 50 mL of solution. To a quartz cuvette was added 2.5 mL of DHA solution followed by 1.0 mL of ozonated water (initially $\approx$ 15 mg/L). Concentration of ozone in the water was determined by the indigo trisulfonate method (Bader and Hoigné, 1981). The cuvette was then placed in a diode array spectrophotometer (Hewlett-

Packard model 8452A) and readings taken at appropriate intervals. The ozonated water was then diluted and another oxidation of DHA performed. This was repeated to obtain a series of oxidations at six different ozone concentrations.

4.9 Calculation of DHA and ozone concentrations during ozonation

After the aqueous solution of ozone was added to the DHA solution in the quartz cuvette, the absorbance of the mixture was followed over time. In order to estimate the concentrations of DHA and ozone in the mixture over the course of the reaction, the absorbance values at 222 nm and 260 nm were used to perform the calculations. The value of 222 nm was used because of the presence of a shoulder in the UV spectrum of DHA and good linearity as a function of concentration at this value (Figure 4.4). A value of 208 nm was initially tried because of the maximum absorbance of DHA at this wavelength; however, it was found to be unsatisfactory in subsequent calculations. A value of 260 nm was used because of the absorbance maximum of ozone (Figure 4.5).

The absorbance value at 222 nm at any given instant is the result of three components: DHA, ozone and absorbance of whatever reaction products are formed by the reaction of ozone and DHA. The absorbance at 260 nm is similarly composed. This can be expressed in the following manner:

$$\text{Abs } 222 = \text{Abs } 222_{DHA} + \text{Abs } 222_{O3} + \text{Abs } 222_{Prod.} \quad (1)$$

$$\text{Abs } 260 = \text{Abs } 260_{DHA} + \text{Abs } 260_{O3} + \text{Abs } 260_{Prod.} \quad (2)$$

By measuring the absorbance spectrum of both DHA and ozone at a series of concentrations, it was calculated that the absorbance of DHA at 260 nm is 0.06883 of the value at 222 nm while for ozone, the absorbance at 222 nm is 0.2626 the value at 260 nm. Thus,

$$\text{Abs } 222 = \text{Abs } 222_{DHA} + 0.2626\text{Abs } 260_{O3} + \text{Abs } 222_{Prod.} \quad (3)$$

$$\text{Abs } 260 = 0.06883\text{Abs } 222_{DHA} + \text{Abs } 260_{O3} + \text{Abs } 260_{Prod.} \quad (4)$$

Figure 4.4: Specific absorbance of DHA as a function of wavelength (■) and linearity of absorbance measurements of DHA up to 10 mg/L (◆).

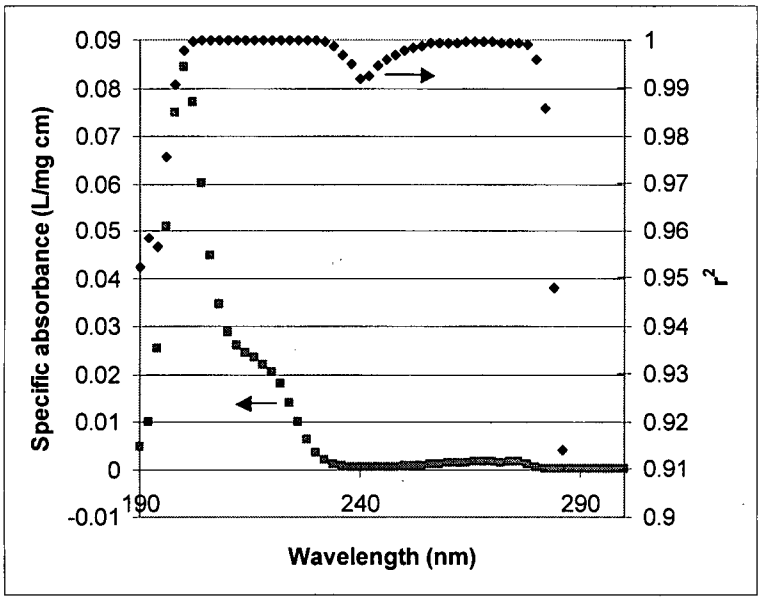
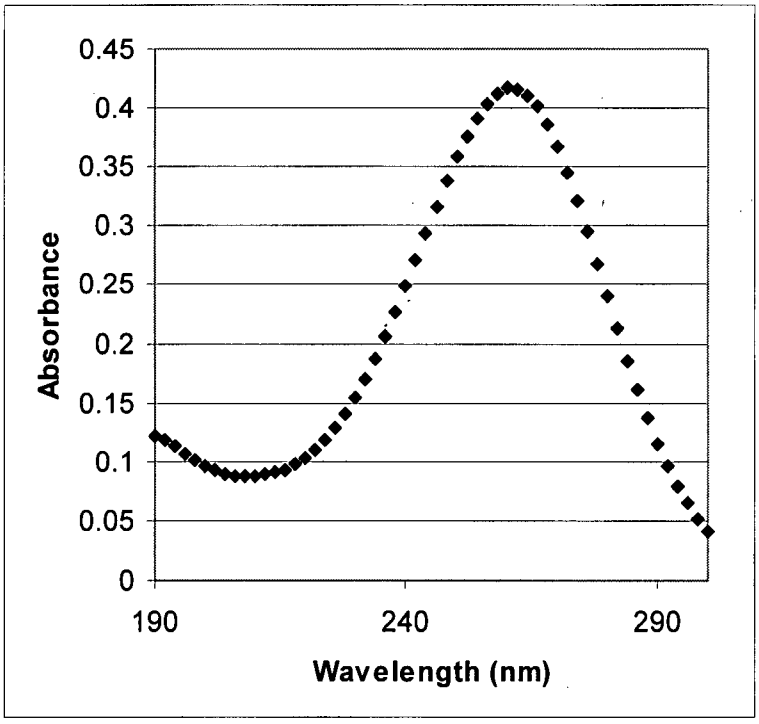


Figure 4.5: UV absorbance spectrum of ozone.



The absorbance of DHA at 222 nm can be replaced by Abs_0222_{DHA}, the absorbance of the initial concentration of DHA, multiplied by a factor X, the fraction of original DHA remaining. For the product terms, these are assumed to be proportional to the amount of DHA reacted. The equations will then be:

$$\text{Abs } 222 = Abs_0222_{DHA}\cdot X + 0.2626\text{Abs } 260_{O3} + Abs_0222_{DHA}\cdot (1\text{-}X)\cdot PAF_{222} \quad (5)$$

$$\text{Abs } 260 = 0.06883Abs_0222_{DHA}\cdot X + \text{Abs } 260_{O3} + Abs_0222_{DHA}\cdot(1\text{-}X)\cdot PAF_{260} \quad (6)$$

where PAF represents what is termed a product absorbance factor. If the amount of product produced is proportional to the amount of DHA oxidized, then the absorbance of the products at a given wavelength will be proportional to the absorbance of DHA removed. Rearranging the equations, one obtains:

$$\text{Abs } 222 - Abs_0222_{DHA}\cdot PAF_{222} = (Abs_0222_{DHA} - Abs_0222_{DHA}\cdot PAF_{222})\cdot X + 0.2626\text{Abs } 260_{O3} \quad (7)$$

$$\text{Abs } 260 - Abs_0222_{DHA}\cdot PAF_{260} = (0.06883Abs_0222_{DHA} - Abs_0222_{DHA}\cdot PAF_{260})\cdot X + \text{Abs } 260_{O3} \quad (8)$$

For each pH and scavenger combination, a series of gradually more dilute ozone solutions were added to the DHA solution. After the reaction was completed, the final DHA concentration was measured by GC. Knowing the final amount of DHA (and hence X, by dividing by the initial amount of DHA) and the absorbances at 222 and 260 nm, one is able to calculate the PAF for each wavelength and the values for a series of ozone additions can be averaged to obtain the value used in subsequent calculations. In this way, the above equations become a system of two equations and two unknowns that can easily be solved for each sample point by matrix multiplication. The use of matrices for multi-component analysis in spectroscopy has been previously outlined (Maddams, 1999).

Of course, the use of an average PAF value for determining the ozone and DHA concentrations in solution presumes that the set of PAF values obtained with the series of ozone additions at increasing dilutions is constant. In order to determine whether this was the case, a linear regression was performed for each set of PAF values versus the initial ozone concentration using Microsoft Excel 2000. If a slope of 0 was within the range of the 95% confidence interval of the slope of the line, then the PAF value was considered to remain constant over the course of the reaction. For some of the conditions, a single ozone addition (usually, the final one with the lowest concentration of ozone) would yield a PAF value very different from the values generated by the other ozone additions. In this case, the method in Himmelblau (1980) for detection and removal of outliers was used. If the PAF value was determined to be an outlier, then that value was not utilized in the calculation of the average PAF value. It is believed that this problem at low ozone doses emerges because of the method used to calculate the PAF. The equation to calculate the PAF value at a wavelength of 222 nm is

$$PAF_{222} = \frac{Abs\,222 - Abs_0\,222_{DHA}}{Abs_0\,222_{DHA}(1-X)}$$

The denominator contains the term (1-X), which is the fraction of DHA consumed during the reaction. For some of the low ozone doses, the fraction of ozone consumed was about 0.02. Thus, due to the nature of division, a very small error in the measurement would result in a very large error in the calculated PAF value. The same problem occurs for the calculation of PAF_{260}.

This method of determining the ozone and DHA concentrations over the course of the reaction worked for the reactions in phosphate buffer at the pH of 6.5 and 8.1 as well as those with t-butanol as radical scavenger at a pH of 6.5. It did not work for those experiments where a carbonate/bicarbonate system was used as radical scavenger, the higher pH values when using t-butanol as radical scavenger, or with no scavenger at pH 9.7. For all the cases in which the method was deemed not to work, the reason was the variation of the PAF value with changing

initial ozone concentration (a listing of all the calculated product absorbance factors is found in Appendix C). The matrix multiplication method assumes a consistent value for the PAF over the course of the reaction. Possible explanations for this will be discussed in section 7.5.

4.10 Computer modeling of ozone/DHA reaction

The chemistry of ozone in water is quite complex with many radical species present in aqueous solution. In addition to reacting with DHA, ozone also reacts with hydroxide ions to initiate a radical chain reaction that results in the decomposition of ozone. In an attempt to determine the rate of reaction of ozone with DHA, the NFG kinetic model for ozone decomposition (Nemes et al., 2000a) was used with additional terms representing oxidation of DHA. In adding these terms, some assumptions were made:

Assumption 1: Reaction between molecular ozone and DHA occurs solely at the aromatic group. As previously mentioned, the rate of reaction of ozone with aromatic groups is at least 2 orders of magnitude greater than that of ozone with saturated compounds. Therefore, reaction of ozone at a site other than an aromatic one in DHA is considered to be negligible.

Assumption 2: After the ring opening by ozone, the resulting diene is oxidized very quickly relative to the ring opening. Previous work involving the ozonation of phenols suggests that the primary products resulting from the ozonation are themselves oxidized much faster than the original phenols (Bernatek et al, 1961). Other researchers have also stated that rapid cleavage of the diene occurs after opening of the ring (Bell & Gravestock, 1970). A comparison of reaction rates of ozone with aromatic compounds and alkenes shows that the latter react several orders of magnitude faster than the former (Neta et al., 1988).

Assumption 3: The reaction between DHA and ozone is assumed to be first order with respect to each reagent. In previous work involving a wide range of compounds (Hoigné and

Bader, 1983a&b), both olefinic and aromatic, all reactions with ozone were found to be first order with respect to each reagent. Reactions between DHA and hydroxyl and phosphate radicals were also assumed to be of the same order

Assumption 4: The rate of reaction of the various phosphate radicals with DHA is not known. In order to simplify the calculations involving the reactions of these species with DHA, the rate of reaction of phosphate radicals with benzene and substituted benzenes was examined. Table 4.2 shows some of these values. In all cases, $\cdot H_2PO_4$ reacts approximately one order of magnitude faster than does either $\cdot HPO_4^-$ or $\cdot PO_4^{2-}$. As an approximation of the reaction of the phosphate radicals with DHA, $\cdot H_2PO_4$ was assumed to react at 10 times the rate of either $\cdot HPO_4^-$ or $\cdot PO_4^{2-}$.

Table 4.2: Reaction rate constants (L/mol·s) for selected aromatics and phosphate radicals (Rosso et al., 1998).

	$\cdot H_2PO_4$	$\cdot HPO_4^-$	$\cdot PO_4^{2-}$
Benzene	$8.9 \cdot 10^7$	$1.7 \cdot 10^7$	$4.3 \cdot 10^6$
Toluene	$5.2 \cdot 10^8$	$1.4 \cdot 10^7$	$1.4 \cdot 10^7$
p-xylene	$8.8 \cdot 10^8$	$3.8 \cdot 10^7$	$4.6 \cdot 10^7$

Assumption 5: Hydroxyl radicals will react not only with DHA and the other radicals occurring as a result of ozone breakdown but also with the oxidation products of the DHA. For this reason, throughout the reaction period, hydroxyl radicals are assumed to react with a concentration of organic compounds equivalent to the original DHA concentration.

Assumption 6: DHA that reacts with hydroxyl radicals will result in hydrogen abstraction rather than ring opening. Past work with the reaction of hydroxyl radicals and lignin model compounds has found negligible amounts of ring opening products (Gierer *et al.*, 1992).

As a result, ring opening of the DHA radical by molecular ozone is still possible and is considered to proceed at the same rate as for DHA. As with DHA, the resulting diene resulting from the ring opening is considered to be oxidized instantaneously by ozone.

There is an additional limitation in the model regarding the radical chemistry. Reaction rate constants between phosphate and carbonate radicals are not known; however, including a reaction term between the two species did not have any significant effect on the final DHA concentrations.

Table 4.3 lists the various reactions used in order to generate the model. The model consists of a series of differential equations, one for each species in the reaction mixture. The rate of change of concentration of each species consists of the sum of all the reactions involving that species. Reactions that generate a compound contribute a positive term to the differential equation; reactions that consume a compound contribute a negative term to the differential equation. As an example, we shall consider the term for hydrogen peroxide. The following lists all reactions from Table 4.3 involving H_2O_2 with associated rate constants in L/mol·s:

Reaction	Rate constant (L/mol·s except as stated)	
$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	$1.0 \cdot 10^{10}$	(9)
$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	$7.6 \cdot 10^7\ s^{-1}$	(10)
$\cdot OH + \cdot OH \rightarrow H_2O_2$	$4.2 \cdot 10^9$	(11)
$\cdot OH + H_2O_2 \rightarrow \cdot HO_2 + H_2O$	$2.7 \cdot 10^7$	(12)
$\cdot CO_3^- + H_2O_2 \rightarrow HCO_3^- + \cdot HO_2$	$7.6 \cdot 10^8$	(13)
$\cdot H_2PO_4 + H_2O_2 \rightarrow H_2PO_4^- + \cdot HO_2 + H^+$	$5.5 \cdot 10^7$	(14)
$\cdot HPO_4^- + H_2O_2 \rightarrow HPO_4^{2-} + 2H^+ + \cdot O_2^-$	$2.7 \cdot 10^7$	(15)
$DHA + xO_3 \rightarrow Products + yH_2O_2$	$k_{O3/DHA}$	(16)
$\cdot DHA + xO_3 \rightarrow Products + yH_2O_2$	$k_{O3/DHA}$	(17)

where x and y represent the stoichiometric ratios of ozone consumed to DHA oxidized and hydrogen peroxide produced to DHA oxidized, respectively.

Combining all of the terms, one forms a differential equation that describes the rate of change of $[H_2O_2]$ over time:

$$d[H_2O_2]/dt = -1.0\cdot10^{10}[H_2O_2][OH^-] + 7.6\cdot10^{7}[HO_2^-] + 4.2\cdot10^{9}[\cdot OH]^2 - 2.7\cdot10^{7}[\cdot OH][H_2O_2] - 7.6\cdot10^{8}[\cdot CO_3^-][H_2O_2] - 5.5\cdot10^{7}[\cdot H_2PO_4][H_2O_2] - 2.7\cdot10^{7}[\cdot HPO_4^-][H_2O_2] + y\cdot k_{O3/DHA}[DHA][O_3] + y\cdot k_{O3/DHA}[\cdot DHA][O_3]$$

For each species, a similar process was followed to generate a differential equation. The computer program MATLAB was used to solve the resulting system of differential equations using the initial concentrations of ozone and DHA and an initial value of 0 mol/L for all the radical species. The ode15s solver was used to perform this task with a step interval of 0.04 second. The actual MATLAB program with all differential equations used is included in Appendix B.

The comparison of the modeled curves with the experimental ones in the process of determining the reaction rate constant of the ozone/DHA reaction was done by difference of squares and the best model was determined by minimization of the difference of squares. Because of the highly non-linear nature of this reaction system, it was not possible to linearize the resulting concentration curves of ozone and DHA and thereby obtain a confidence interval for the reaction rate constant.

Table 4.3: Reaction mechanism used for modeling of DHA ozonation.

Reaction	Rate Constant (L/mol·s except as stated)	Reference
$O_3 + OH^- \rightarrow HO_2^- + O_2$	140	Nemes et al (2000a)
$HO_2^- + O_3 \rightarrow \cdot O_3^- + \cdot HO_2$	5.5×10^6	"
$\cdot O_2^- + O_3 \rightarrow \cdot O_3^- + O_2$	3.0×10^8	"
$\cdot O_3^- + \cdot OH \rightarrow \cdot O_2^- + \cdot HO_2$	2.0×10^{10}	"
$\cdot O_3^- + \cdot OH \rightarrow O_3 + OH^-$	8.3×10^9	"
$\cdot OH + O_3 \rightarrow \cdot HO_2 + O_2$	2.5×10^7	"
$\cdot O^- + HO_2^- \rightarrow \cdot O_2^- + OH^-$	3.2×10^9	"
$\cdot O^- + \cdot O_2^- + H_2O \rightarrow O_2 + 2OH^-$	1.8×10^8	"
$\cdot O_3^- \rightarrow O_2 + \cdot O^-$	5.0×10^3 s^{-1}	"
$\cdot O^- + O_2 \rightarrow \cdot O_3^-$	2.6×10^9	"
$\cdot HO_2 + OH^- \rightarrow \cdot O_2^- + H_2O$	1.0×10^{10}	"
$\cdot O_2^- + H_2O \rightarrow \cdot HO_2 + OH^-$	10 s^{-1}	"
$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1.0×10^{10}	"
$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	7.6×10^7 s^{-1}	"
$\cdot OH + OH^- \rightarrow \cdot O^- + H_2O$	4.0×10^{10}	"
$\cdot O^- + H_2O \rightarrow \cdot OH + OH^-$	5.4×10^8 s^{-1}	"
$\cdot HO_3 \rightarrow O_2 + \cdot OH$	1.1×10^5 s^{-1}	"
$\cdot HO_3 + OH^- \rightarrow \cdot O_3^- + H_2O$	5.2×10^{10}	"
$\cdot O_3^- + H_2O \rightarrow \cdot HO_3 + OH^-$	3.0×10^2 s^{-1}	"
$\cdot OH + \cdot O_2^- \rightarrow O_2 + OH^-$	1×10^{10}	Elliot & Buxton (1992)

$\cdot OH + \cdot OH \rightarrow H_2O_2$	4.2×10^9	Elliot et al (1990)
$\cdot OH + H_2O_2 \rightarrow \cdot HO_2 + H_2O$	2.7×10^7	Buxton et al (1988)
$\cdot OH + HO_2^- \rightarrow \cdot O_2^- + H_2O$	7.5×10^9	Christensen et al (1982)
$\cdot OH + \cdot HO_2 \rightarrow O_2 + H_2O$	1×10^{10}	Elliot & Buxton (1992)
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$	5.0×10^9	Nemes et al (2000b)
$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$	$1.7 \times 10^6\ s^{-1}$	"
$CO_3^{2-} + \cdot OH \rightarrow \cdot CO_3^- + OH^-$	1.0×10^8	"
$\cdot CO_3^- + \cdot O_3^- \rightarrow CO_3^{2-} + O_3$	5.5×10^7	"
$CO_3^{2-} + \cdot O^- + H_2O \rightarrow \cdot CO_3^- + 2OH^-$	1.0×10^7	"
$HCO_3^- + \cdot OH \rightarrow \cdot CO_3^- + H_2O$	2×10^7	"
$HCO_3^- + \cdot O_2^- \rightarrow \cdot CO_3^- + HO_2^-$	4.0×10^6	"
$\cdot CO_3^- + \cdot O_2^- \rightarrow CO_3^{2-} + O_2$	8.7×10^7	"
$\cdot CO_3^- + H_2O_2 \rightarrow HCO_3^- + \cdot HO_2$	7.6×10^8	"
$\cdot CO_3^- + HO_2^- \rightarrow CO_3^{2-} + \cdot HO_2$	1.0×10^8	"
$\cdot H_2PO_4 + H_2O_2 \rightarrow H_2PO_4^- + \cdot HO_2 + H^+$	5.5×10^7	Nakashima & Hayon (1970)
$\cdot HPO_4^- + H_2O_2 \rightarrow HPO_4^{2-} + 2H^+ + \cdot O_2^-$	2.7×10^7	"
$H_2PO_4^- + \cdot OH \rightarrow \cdot H_2PO_4 + OH^-$	2×10^4	Maruthamuthu & Neta (1978)
$HPO_4^{2-} + \cdot OH \rightarrow \cdot HPO_4^- + OH^-$	1.5×10^5	"
$\cdot H_2PO_4 + OH^- \leftrightarrow \cdot HPO_4^- + H_2O$	$\rightarrow 1 \times 10^{10}$ $\leftarrow 50$	"
$\cdot HPO_4^- + OH^- \leftrightarrow \cdot PO_4^{2-} + H_2O$	$\rightarrow 1 \times 10^{10}$ $\leftarrow 7.9 \times 10^4$	"
$\cdot H_2PO_4 + \cdot H_2PO_4 \rightarrow H_2P_2O_8^{2-} + 2H^+$	1×10^9	Grabner et al (1973)
$\cdot HPO_4^- + \cdot HPO_4^- \rightarrow P_2O_8^{4-} + 2H^+$	1.5×10^8	"
$\cdot PO_4^{2-} + \cdot PO_4^{2-} \rightarrow P_2O_8^{4-}$	3.9×10^7	"
$\cdot H_2PO_4 + \text{t-BuOH} \rightarrow H_3PO_4 + \cdot \text{t-BuOH}$	3.9×10^6	Maruthamuthu & Neta (1977)

$\cdot HPO_4^- + t\text{-BuOH} \rightarrow H_2PO_4^- + \cdot t\text{-BuOH}$	4.5×10^5	"
$\cdot PO_4^{2-} + t\text{-BuOH} \rightarrow HPO_4^{2-} + \cdot t\text{-BuOH}$	4.2×10^5	"
$\cdot OH + t\text{-BuOH} \rightarrow H_2O + \cdot t\text{-BuOH}$	6×10^8	Buxton et al (1988)
$\cdot t\text{-BuOH} + \cdot t\text{-BuOH} \rightarrow$ Products	6×10^8	Von Piechowski et al (1992)
$\cdot CO_3^- + \cdot CO_3^- \rightarrow$ Products	2×10^7	Czapski et al (1994)
$O_3 + t\text{-BuOH} \rightarrow$ Products	0.003	Hoigné & Bader (1983a)
DHA + $xO_3 \rightarrow$ Products + yH_2O_2 (x and y are varied in the model)	$k_{O3/DHA}$	
DHA + OH $\rightarrow \cdot$DHA + H_2O	$k_{\cdot OH/DHA}$	
$\cdot$DHA + $xO_3 \rightarrow$ Products + yH_2O_2 (x and y as for DHA/O_3 reaction)	$k_{O3/DHA}$	
$\cdot OH$ + Products $\rightarrow$ Products	$k_{\cdot OH/DHA}$	
DHA + $\cdot PO_4^{2-} \rightarrow$ Products DHA + $\cdot HPO_4^- \rightarrow$ Products	$k_{\cdot PO4/DHA}$	
DHA + $\cdot H_2PO_4 \rightarrow$ Products	$10 \cdot k_{\cdot PO4/DHA}$	

RESULTS AND DISCUSSION

5 OZONATION OF LOGYARD RUN-OFF

5.1 Characterization of run-off samples

Run-off quality, as measured by COD, BOD, tannins and lignins, DHA and acute toxicity, was highly variable (Table 5.1), as evidenced by the high values for the coefficients of variation (standard deviation/average) of the parameters (soluble COD: 0.79, soluble BOD: 0.86, tannins and lignins: 0.75, DHA: 0.69, Microtox toxicity: 1.03). Dehydroabietic acid (DHA) was present in all samples at concentrations greater than the reported 96h-LC_{50} for rainbow trout (~1.2 mg/L) (Leach and Thakore, 1976). Approximately half of the COD was associated with suspended solids and about 25% of the soluble material was measured as BOD_5.

5.2 Effect of ozonation on oxidation of COD

The treatment of logyard run-off with ozone at pH 7 resulted in a dose-dependent decrease in COD concentration (Figure 5.1). Up to 35% of COD was removed during the treatment trials. Although the initial COD concentrations of the various samples cover a wide range of values, when results are expressed in terms of the fractional removal of COD, COD oxidation is independent of initial COD concentration as well as the logyard of origin of the run-off and, by extension, the species that are found in the yard at the time of the creation of the run-off (Figure 5.2). Of particular concern in any industrial installation is whether, and how easily, the system is able to deal with variations in input. These results suggest that the system is indeed able to deal with a range of run-offs and that COD removal efficiency, as measured by fraction

Table 5.1: Characteristics of run-off samples used in the study.

Note: Mill symbols refer to figures.

†: H – Western hemlock, F – Douglas fir
*: Composition of Mill A logyard varies little. 35% Balsam fir, 35% Western hemlock, 25% Sitka spruce, 5% Western red cedar

Date	00/06/05	00/09/06	00/10/17	00/11/30	01/01/04	01/02/02	01/03/28	Avg.± Std. Dev.
Mill	B (×)	A (◆)	B (■)	B (▲)	B (●)	A (+)	B (–)	
Logyard Species Composition†	50% H 50% F	*	100% H	100% H	40% H 60% F	*	50% H 50% F	
Tannins & lignins (mg/L)	2470	770	510	640	1030	160	1550	1020±770
Total COD (mg/L)	8760	3740	2470	2380	4590	2970	8050	4710±2650
Soluble COD (mg/L)	5970	1610	1150	1560	2480	310	3550	2380±1890
Soluble:Total COD	0.682	0.430	0.466	0.655	0.540	0.104	0.441	0.474±0.192
BOD_5 (mg/L)	1900	920	300	370	920	190	1250	660±650
Soluble BOD_5 (mg/L)	1480	290	260	320	590	80	970	570±490
Soluble:Total BOD_5	0.779	0.315	0.867	0.865	0.641	0.421	0.779	0.667±0.220
Sol BOD_5: Sol COD	0.248	0.180	0.226	0.205	0.238	0.258	0.273	0.233±0.032
DHA (mg/L)	2.38	2.60	2.38	3.81	N/A	1.82	8.42	3.57±2.47
Toxicity (EC_{50})	1.9	9.5	16.1	7.8	7.4	26.8	7.6	6.2 (3.1 - >100)
pH	5.9	5.0	6.5	5.6	5.9	6.5	5.8	5.9±0.5

Figure 5.1: Effect of ozone on COD (soluble) of logyard run-off (treatment at pH 7).

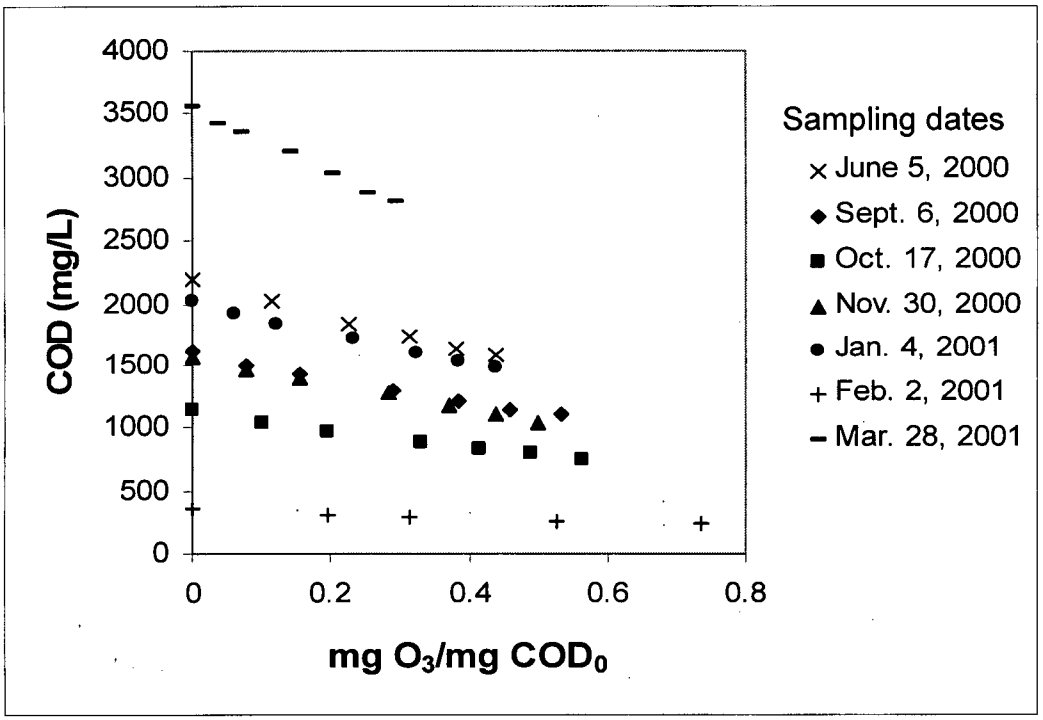
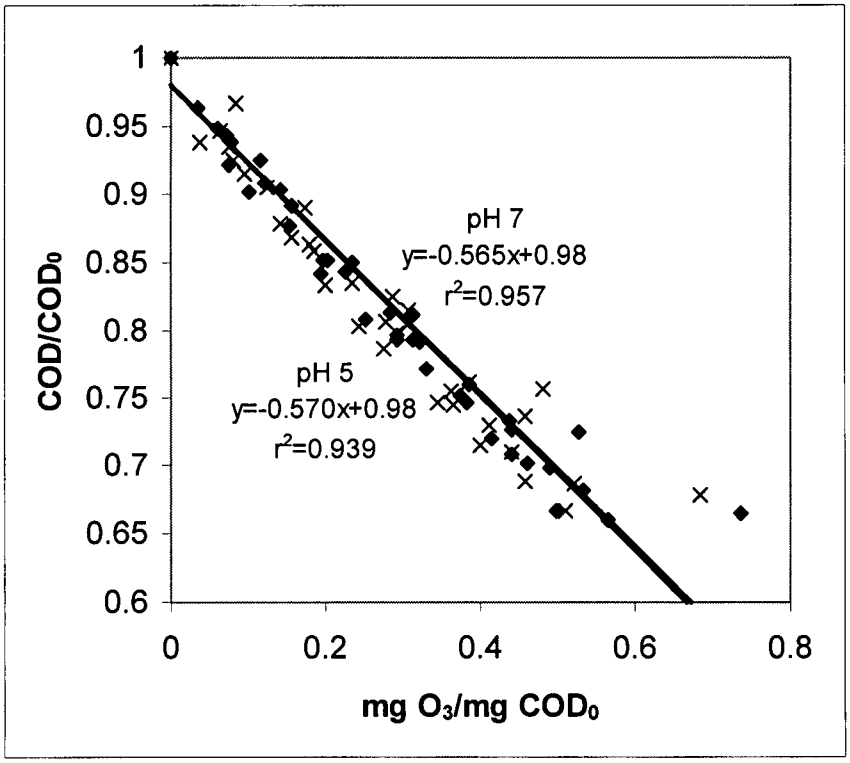


Figure 5.2: Data of Figure 5.1 replotted in terms of fractional removal of original COD. pH 5 (×), pH 7 (◆).



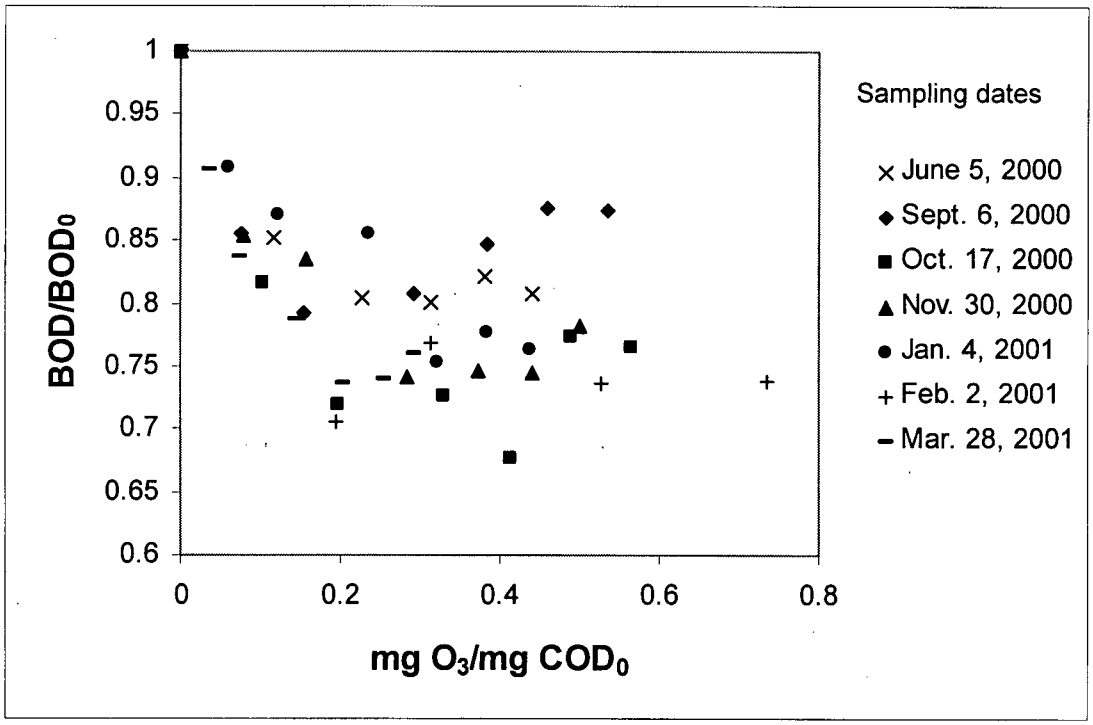
of original COD, would be consistent across different sites. This consistency would mean that ozone dosage could be adjusted as a function of the COD content of the run-off. Site-to-site variation in the species of wood processed would be irrelevant and would make adjustment of an ozone dosage system much simpler than one that required different dosing as the wood present in the logyard changed. The slope of the line in Figure 5.2 yields units of amount of COD oxidized per unit ozone consumed, a measure of the ozone utilization efficiency. Linear regression of all samples treated at pH 7 as a group yielded a value of 0.57 mg COD/mg ozone consumed (95% C.I. 0.53-0.60). This value is in good accord with results obtained by other researchers using ozone to oxidize other substrates such as landfill leachates and pulp mill effluents (Steensen, 1997; Kaptijn, 1997; Baig *et al.*, 1999; Hostachy *et al.*, 1997). Steensen (1997) reports a range of values of COD removal for ozonation of landfill leachates from 0.45-0.83 mg COD/mg ozone consumed. The others report values in the range 0.52-0.64 mg COD/mg ozone consumed.

The pH of the run-off samples obtained varied from 5 to 6.5 upon receipt. In an effort to determine whether the pH affects the oxidation rate, samples were treated at a pH of 7 and 5. As observed in Figure 5.2, pH over this range yielded no significant difference in ozone utilization efficiency for COD removal. Linear regression yielded a value of 0.57 mg COD/mg O_3 (95% C.I. 0.52-0.62).

5.3 Effect of ozonation on BOD concentration

Treatment with ozone had a limited effect on the BOD of the run-off samples (Figure 5.3). Where COD continuously decreased over the course of treatment, the BOD decreased at the beginning of treatment (experiments at pH 7: 25.5%±4.9%, experiments at pH 5: 24.2%±3.2%) before leveling off at a constant value. This is a result of two competing reactions. First, ozone will cause the breakdown of high molecular weight (HMW), non-biodegradable compounds in

Figure 5.3: Effect of ozonation on BOD of logyard run-off. Results for pH 7.



the run-off into lower molecular weight (LMW), biodegradable compounds. At the same time, LMW compounds already present, along with those being formed, will be mineralized by the ozone. Once the rate of conversion of HMW to LMW compounds becomes equal to the rate of mineralization of LMW compounds, the BOD of the mixture remains constant. Such an explanation has been put forward to explain similar results obtained in research involving ozonation of pulp mill effluents (Baumann and Lutz, 1974; Nebel *et al.*, 1974; Roy-Arcand and Archibald, 1996b).

5.4 Effect of ozonation on tannin and lignin concentration

Oxidation of tannins and lignins (TL) occurred at low ozone doses and over 90% removal was readily achieved (Figure 5.4). As with COD oxidation, the fraction removal of TL was independent of initial concentration and species content of the logyard. Since TL are characterized by phenolic groups, which are favored reaction sites for ozone compared to aliphatic groups (Hoigné, 1988; Rice and Browning, 1981), a given amount of ozone will oxidize a greater fraction of TL than of COD. The initial fractional reduction of TL levels is between 3.3-7.6/(mg O_3/mg initial COD), significantly greater than the value of 0.56 for COD. As the TL concentration decreases, the rate of TL oxidation decreases. By expressing the TL removal as first order with respect to ozone dose (mg O_3/mg initial COD) (i.e., $TL=TL_0e^{-kx}$, where x is the ozone dose), values can be obtained for the oxidation coefficient, k, which can be used to compare the extent of reaction per unit O_3 consumed. Figure 5.5 shows the results of TL oxidation plotted as $\ln(TL/TL_0)$ vs. the ozone dose. The slope of the resulting line is the oxidation coefficient. Ozonation at pH 7 resulted in a slightly, but statistically significant, higher rate of oxidation of TL compared to pH 5 (Table 5.2).

Table 5.2. k (mg COD_0/mg O_3) values for measured parameters in ozonated logyard run-off.

	pH 5	pH 7
Tannins & Lignins	4.4 (4.1-4.7)	5.2 (4.9-5.5)
DHA	6.0 (5.6-6.4)	8.7 (8.2-9.3)
Toxicity	5.2 (4.7-5.6)	6.1 (5.7-6.5)

Note: Values in brackets represent 95% confidence interval of k.

Figure 5.4: Effect of ozonation on tannin and lignin concentration of logyard run-off. Results for pH 7.

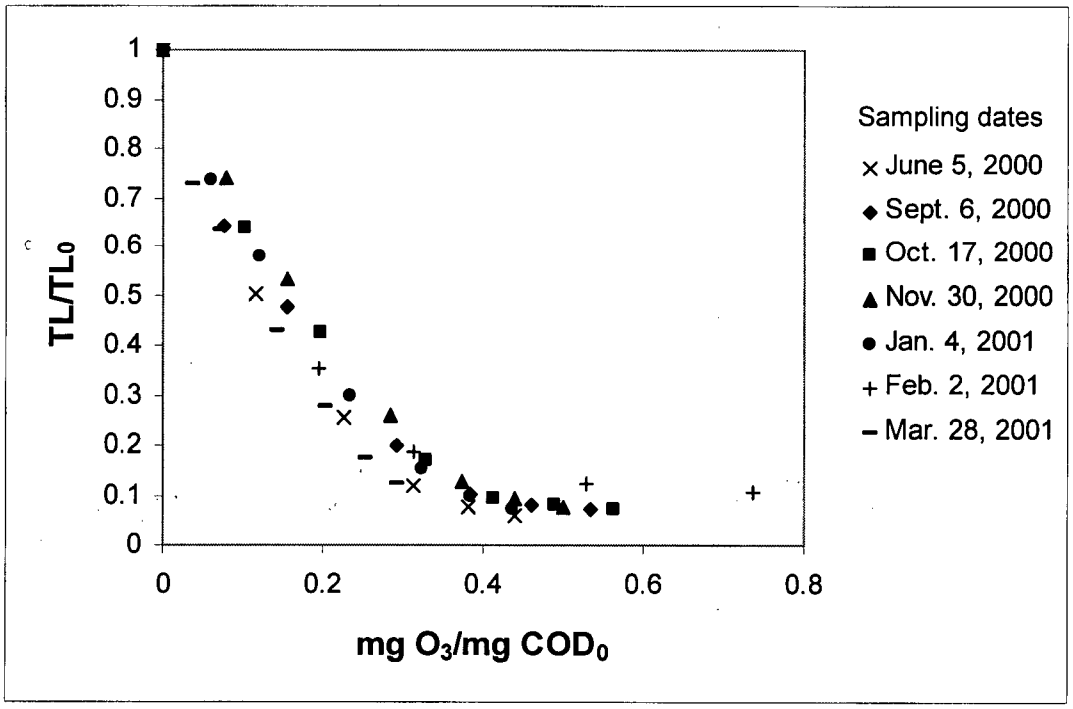
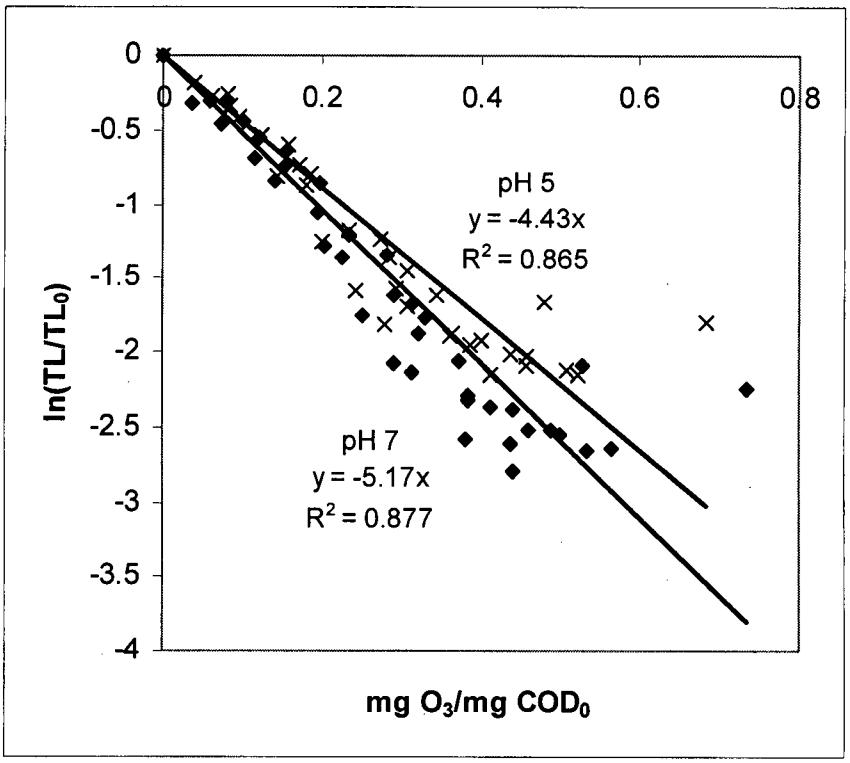


Figure 5.5: Effect of ozonation on tannin and lignin concentration of logyard run-off. Replotted as first order with respect to ozone dose. pH 5: (×), pH 7: (◆).



5.5 Effect of ozonation on DHA concentration

DHA is readily oxidized by ozone (Figure 5.6). In all samples bar one treated at pH 7, complete DHA oxidation was achieved (and the one exception had a removal of 92%). Of all the parameters measured, ozone was most effective at removing DHA (Table 5.2). Initial fractional reduction of DHA levels is between 4.2–9.2/(mg O_3/mg COD) at pH 7. One of the common criticisms leveled against ozone as a water treatment method is its indiscriminate oxidation of organic compounds. The results presented here would suggest that ozone shows a greater selectivity toward oxidation of resin acids compared to other organic compounds and are consistent with previous results with pulp mill effluent (Roy-Arcand and Archibald, 1996a).

DHA oxidation during treatment at pH 7 is much faster than at pH 5 (Figure 5.7). This increase in oxidation rate with pH agrees with previous work involving the ozonation of pure, ionizable compounds in water (Hoigné and Bader, 1983b). In addition, as the pH of the system increases, the increased presence of hydroxyl radicals, which are more reactive than molecular ozone, should lead to increased rates of reaction (Hoigné and Bader, 1976). The surface chemistry of the system is another possible factor in the change of oxidation rate as seen by the more pronounced foaming of the reaction mixture at the beginning of the treatment at pH 5 compared to pH 7. The pKa of DHA is 5.7 (Nyren and Back, 1958). The pH range of 5-7 therefore sees a fundamental shift in the nature of DHA from the un-ionized to ionized forms. The surface-active nature of DHA (Werker *et al.*, 1996), the changing solubility of DHA over the pH range 5-7, and the differing degrees of ionization, combined with the complexity of the run-off chemistry make it difficult to accurately determine the nature of the DHA in solution. It is possible that the greater solubility of DHA at the higher pH results in it being more accessible to oxidation by dissolved ozone, resulting in the faster oxidation at the higher pH.

Figure 5.6: Effect of ozonation on DHA concentration of logyard run-off. Results for pH 7.

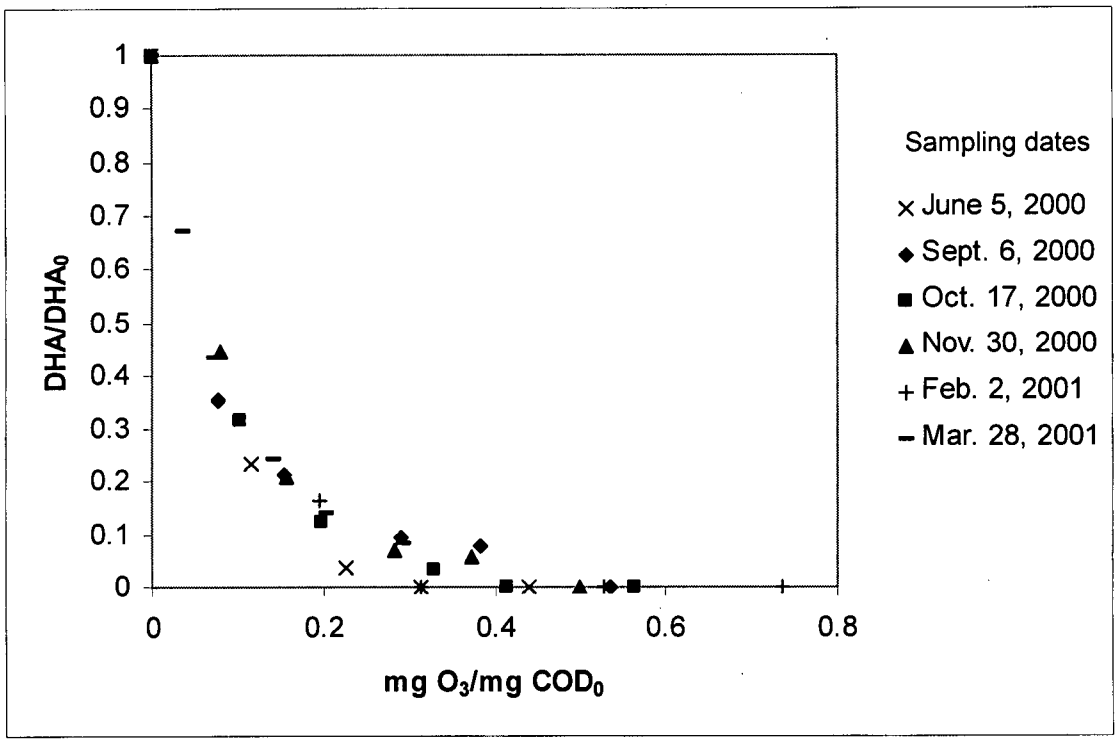
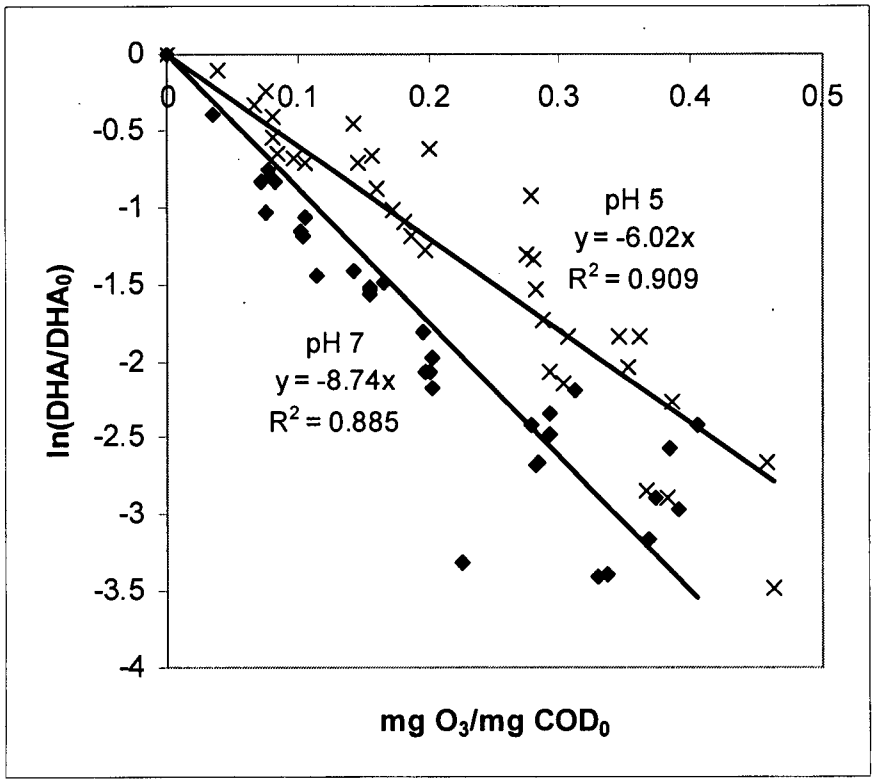


Figure 5.7: Effect of ozonation on DHA concentration of logyard run-off. Replotted as first order with respect to ozone dose. pH 5: (×), pH 7: (◆)



5.6 Effect of ozonation on toxicity levels

Removal of acute toxicity (Microtox) ranged between 80-90% (Figures 5.8 and 5.9) for treatment of the run-off at a pH of 7. Once more, that this removal was achieved regardless of the tree species contained in the yards demonstrates the wide-ranging potential of this treatment method. Toxicity removal was also affected by pH in the same way as TL and DHA, namely increased removal at a higher pH value. Since the pH of the run-off is acidic, it would have to be determined whether the increased rate of detoxification obtained at a greater pH would warrant the additional cost required for pH adjustment. At a pH of both 5 and 7, the rapid toxicity removal only occurred until an ozone consumption of about 0.35 mg O_3/mg COD was achieved. After this point, the rate of toxicity removal decreased, as seen by the decreased slope in Figure 5.9. The improved toxicity removal obtained at higher pH is in agreement with the research of Roy-Arcand and Archibald (1996a) involving ozonation of a CTMP primary clarifier effluent but runs counter to the results of Hostachy et al. (1997), who found that ozonation of pulp mill bleach plant effluent gave poorer toxicity removals as pH increased. The difference in the latter case could be ascribed to the very different nature of the effluent treated, since it came from the bleach plant (chlorine dioxide bleaching) of a kraft mill.

As previously discussed, the source of the toxicity in wood processing effluents has been variously attributed to resin acids, phenolic compounds, and metal ions. Figures 5.10 and 5.11 compare the toxicity reduction during ozone treatment with the reduction in TL and DHA concentrations. The closer the correlation between the reduction in toxicity and that of another parameter, the closer the slope of the plot will be to 1. In this case, the correlation between Microtox® toxicity and TL is stronger with a slope of 0.98 (r^2=0.90) versus 0.86 (r^2=0.94) for the correlation with DHA. One cannot conclude from this that the tannins and lignins are the cause

of the toxicity, but it does show that their removal from solution could be used as a surrogate for toxicity removal.

Although DHA removal did follow the trend of toxicity removal, previous work involving measurement of the toxicity of DHA and abietic acid on Microtox has shown that the toxicity of these two resin acids to *Vibrio fischeri*, the organism used in the Microtox test, is quite low (Patoine et al., 1997). A mixture of 50 mg/L each of DHA and abietic acid registered a 15 min EC_{50} of 11%. Even assuming that all the toxicity was accounted for by DHA, the EC_{50} of a 2.5 mg/L DHA solution (the highest concentration of DHA treated in the ozonation runs) would be 220%. This shows the difficulty in measuring the toxicity of specific compounds since the value may be very different depending upon the test species used (the 96-h LC_{50} of DHA to rainbow trout is about 1 mg/L).

Figure 5.8: Effect of ozone on acute toxicity (Microtox) of logyard run-off. Result for pH 7.

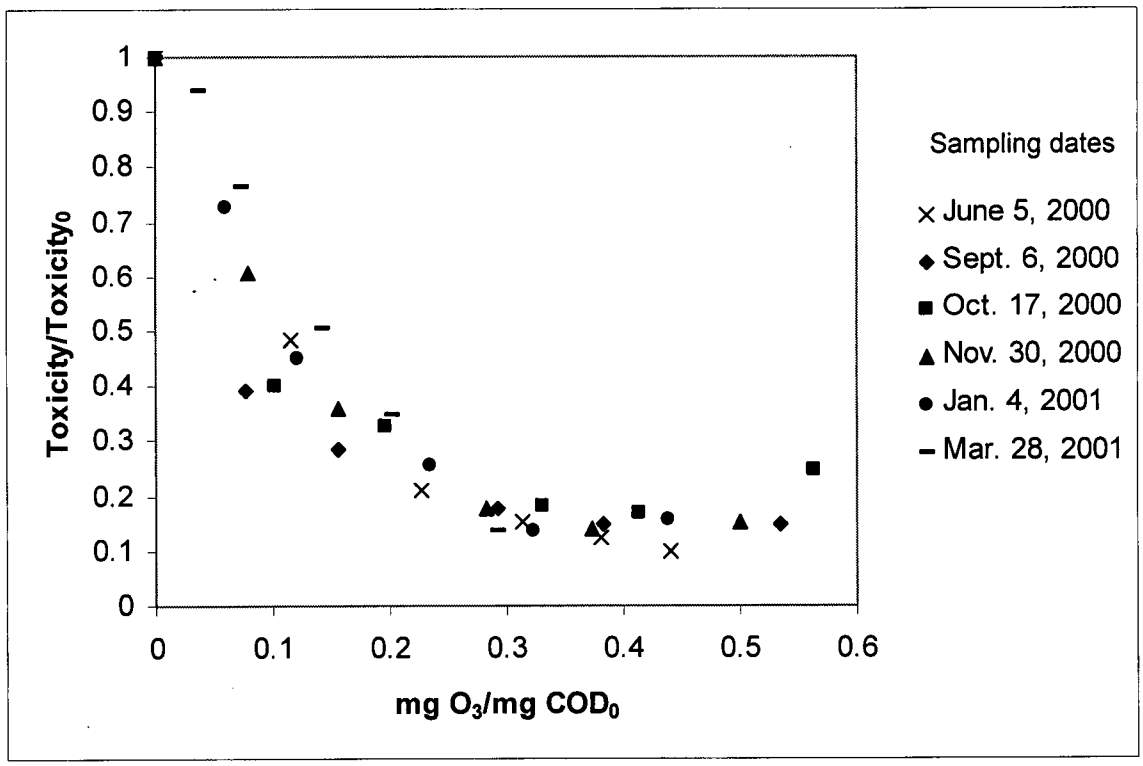


Figure 5.9: Effect of ozonation on acute toxicity (Microtox) of logyard run-off. Replotted as first order with respect to ozone dose. pH 5: (×), pH 7: (◆). Linear regression on results up to 0.35 mg O_3/mg COD_0.

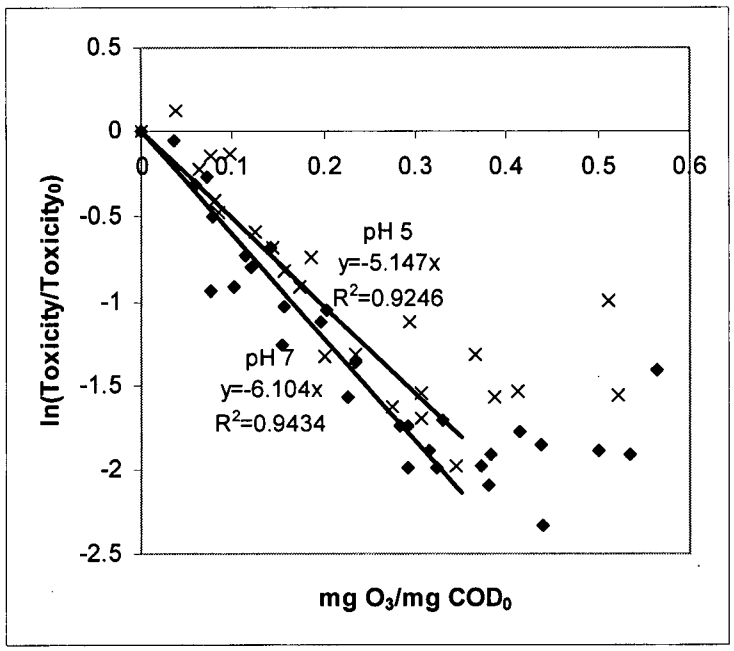


Figure 5.10: Comparison of toxicity removal vs. tannin and lignin removal during ozonation of logyard run-off. Experiments performed at pH 5 (×) and pH 7 (◆). Regression line for combined results.

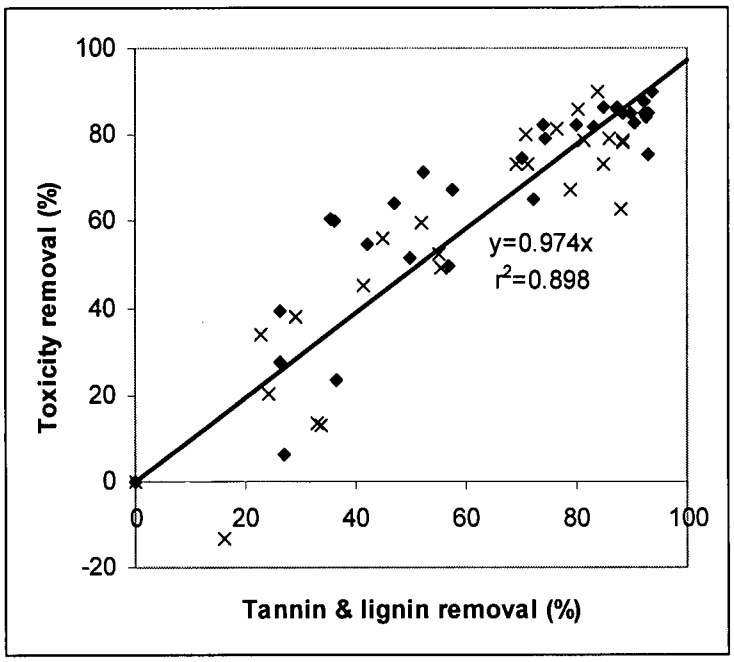
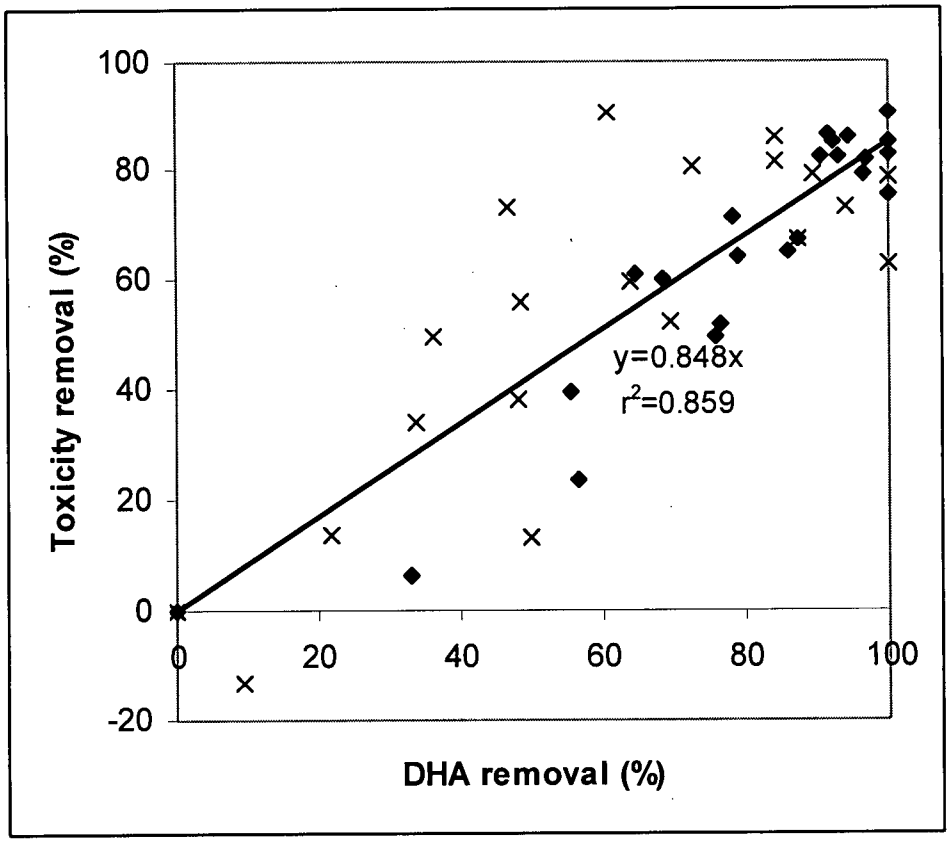


Figure 5.11: Comparison of toxicity removal vs. DHA removal during ozonation of logyard run-off. Experiments performed at pH 5 (×) and pH 7 (◆). Regression line for combined results.



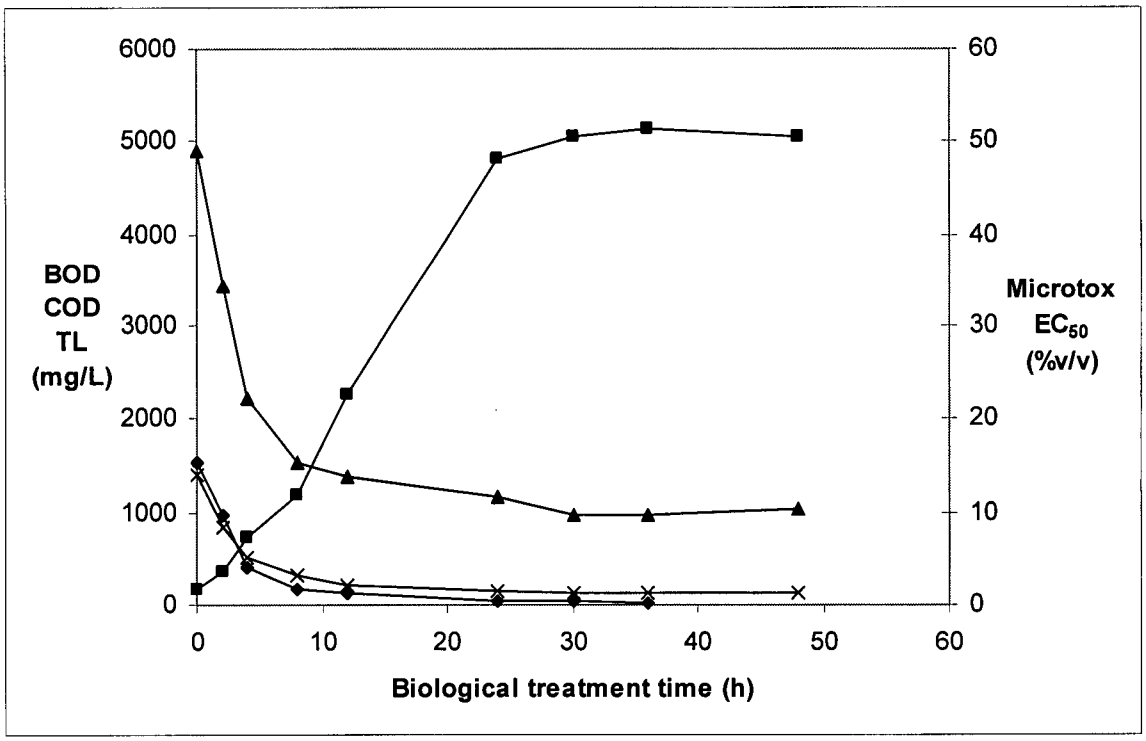
6. OZONE AND BIOLOGICAL TREATMENT OF LOGYARD RUN-OFF

6.1 Batch biological treatment of run-off

Given that previous research has indicated that the use of biological treatment and ozonation together can result in improved removal of the organic load of a wastewater (Scott and Ollis, 1995; Roy-Arcand et al., 1996; Beltrán et al., 1999b; Beltrán et al., 2000; Beltrán-Heredia et al., 2000; Zeng et al., 2000), it was decided to examine the effectiveness of this combination in the treatment of logyard run-off. The effectiveness of ozonation as a polishing step after the biological treatment was studied, as well as ozonation prior to biological treatment, in order to ascertain if ozonation of the sample would result in improved biodegradability. Before this was done, however, biological treatment alone was studied.

Biological treatment of the log yard run-off was effective in reducing the concentration of most parameters of concern. Batch biological treatment of log yard run-off reduced BOD, COD and TL concentration by 98%, 80%, and 90%, respectively (Figure 6.1). Final values of BOD_5, COD and TL were 30, 1045 and 130 mg/L, respectively. Acute toxicity (Microtox) was decreased over the treatment, from an initial EC_{50} of 1.8% to a value of 50% after 48 hours, for a 96% reduction in toxicity (as calculated based on toxic units). There is no known previous work involving the biological treatment of logyard run-off. A point of comparison could be made with the treatment of pulp mill (especially TMP) wastewater. Koning et al. (1994) outline the use of activated sludge to treat a mechanical pulp effluent. The BOD load was decreased by 97% with a 6h HRT and a MLSS of 3000 mg/L. Lo et al. (1994) investigated the use of activated sludge to treat TMP effluent in two mills. BOD removals were usually above 90%, the main exceptions occurring at the lower tested HRT value of 8 hours. Toxicity as measured by both 96-h rainbow

Figure 6.1: Removal of BOD (◆), COD (▲), TL (×), and acute toxicity (■) during batch biological treatment of logyard run-off.



trout LC_{50} and 48-h *D. magna* LC_{50} was consistently greater than 100% in the treated effluent. This was improved from an influent 96-h LC_{50} of 5-15%. Resin and fatty acid removals were also consistently greater than 90% and usually greater than 95%. Shere and Daly (1982) investigated the biological treatment of another TMP wastewater stream with a laboratory activated sludge system that attempted to simulate the conditions in a Deep Shaft treatment system. Beginning with COD and BOD values of approximately 2650 mg/L and 1000 mg/L, respectively, BOD removals of 95% and COD removals of 78% were achieved with a HRT of 4 hours and a MLSS of approximately 5000 mg/L. Acute toxicity was also removed, dropping from a $LC_{50} < 10\%$ to $LC_{50} > 100\%$ as measured by rainbow trout. The scale of the parameter reductions obtained by biological treatment of logyard run-off are, therefore, quite similar to those obtained by treatment of pulp mill effluent.

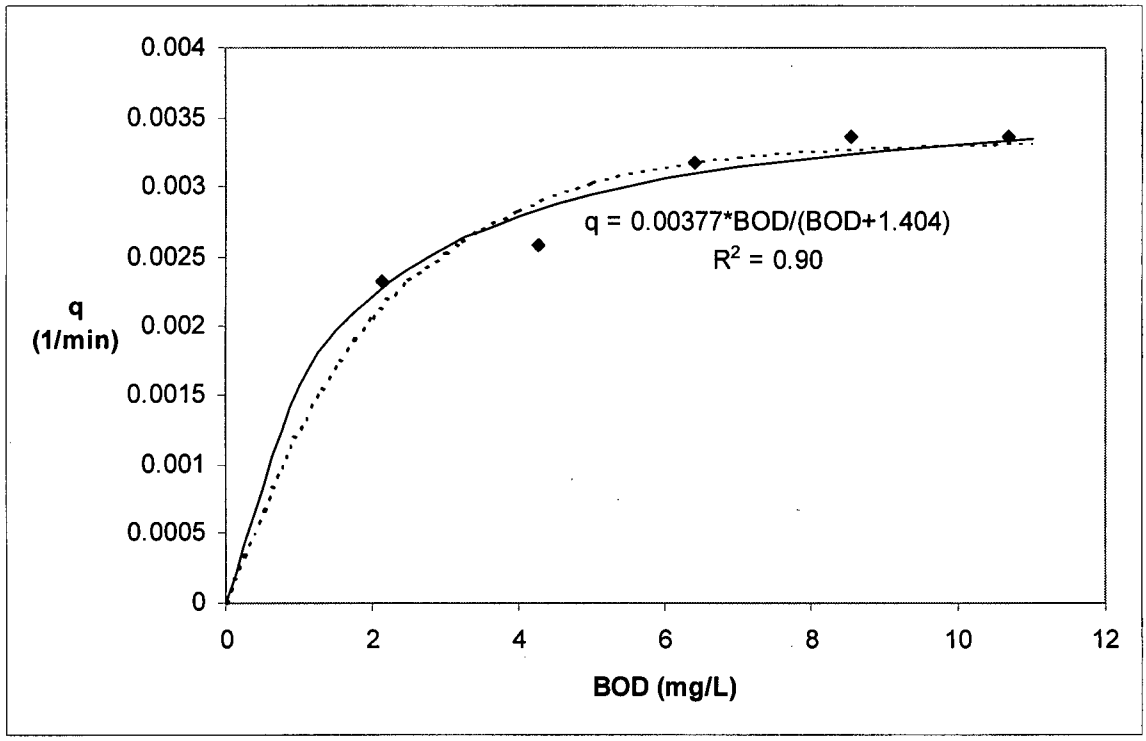
In order to design a biological treatment process for run-off, it is important to determine the kinetics of degradation. For this reason, a respirometric technique was used to determine the kinetics of degradation of the log yard run-off. The experimental data were fit to the Monod model (Figure 6.2). The maximum specific substrate uptake rate and the K_s value were found to be 0.0038 mg BOD/mg VSS·min and 1.4 mg/L, respectively. Since the microbial seed used had not been acclimated to substrate over a long time period, these values can be considered to be conservative. The values determined for maximum specific substrate uptake rate (q_{max}) and the K_s are comparable to values for kraft pulp mill effluents determined using this technique (q_{max}=0.0038 mg BOD/mg VSS·min, K_s=0.774 mg/L)(Helle, 1999).

During respirometry, the value of the oxygen consumed/BOD added (OC/S) can be considered to be the portion of the oxygen uptake that went directly into substrate oxidation (Čech *et al.*, 1984). Based on this, 1-OC/S can be used as an estimate of the growth yield, or the fraction of substrate that was not directly oxidized. In this study, the growth yield constant was approximately 0.77 mg VSS/mg BOD.

6.2 Combined biological treatment/ozonation

The potential of ozone for water and wastewater treatment has received increasing attention in recent years (Rice, 1997). Ozone has a number of advantages over conventional technologies, including potential for mineralisation of wastewater constituents of concern, rapid reaction rates, and applicability to intermittent flows. However, ozone application to wastewater has been limited due to the high ozone demand for wastewater treatment and higher capital and operating costs of ozone generation systems (Mohammed and Smith, 1992). For this reason, it was desirable to examine the efficacy of ozone as a polishing treatment on biologically-treated effluent.

Figure 6.2: Substrate uptake rate data as fitted by the Monod model.



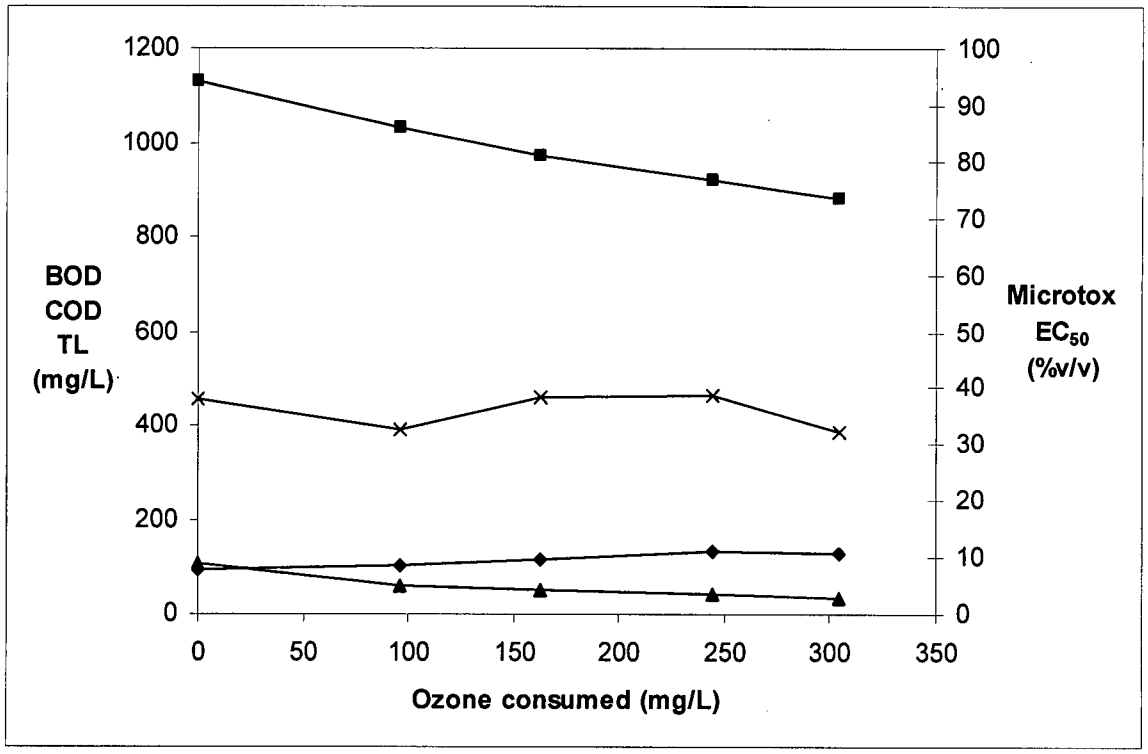
Prior to ozonation, the biologically-treated effluent began with a COD of 1130 mg/L, BOD_5 of 95 mg/L, TL concentration of 105 mg/L and Microtox® EC_{50} of 38%. After thirty minutes of ozone treatment (304 mg/L ozone consumed), COD and TL concentration were reduced by 22% and 68%, respectively (Figure 6.3). The ozone utilization efficiency as measured by COD oxidation per unit of ozone consumed is much higher in the biologically-treated effluent compared to untreated effluent (0.81 mg COD/mg O_3 vs. 0.57 mg COD/mg O_3). This is most likely due to biological treatment removing compounds such as sugars, which are not easily oxidizable by ozone, and leaving more complex compounds such as polyphenolics, which, with their aromatic groups, are more easily oxidizable by ozone. In the case of TL, a k value of 4.4 mg COD_0/mg O_3 is obtained, slightly lower than the value obtained with untreated run-off. The BOD concentration increased after 30 minutes of ozonation, similar to results in previous research where a wastewater with low initial BOD was ozonated (Bauman and Lutz,

1974; Dorica and Wong, 1979). This increase in BOD was most likely due to the conversion of a portion of the high molecular weight COD to lower molecular weight compounds capable of exerting a BOD.

Ozonation did not improve acute toxicity (Microtox) over that achieved with biological treatment alone. In making this conclusion, it should be noted that there is a large amount of variability in Microtox measurements made on samples with low toxicity. It is also possible that residual toxicity is due to compounds not affected by ozone treatment (for example, metals).

It does not appear that ozonation provides much benefit to biologically-treated logyard run-off. For such a high consumption of ozone (304 mg/L), BOD is increased, COD and TL are only decreased by a slight extra amount (5% of the sample COD and TL prior to biological treatment), and Microtox toxicity is not improved.

Figure 6.3: Removal of BOD (◆), COD (■), TL (▲) and acute toxicity (×) during ozonation of biologically-treated logyard run-off.



6.3 Combined ozonation/biological treatment

In an effort to determine whether pre-ozonation of logyard run-off would have a positive effect on subsequent biological treatment, samples were ozonated for 10 and 30 minutes and then inoculated with activated sludge. Ozonation had only a slight effect on the COD and BOD levels of the run-off (30 minute sample COD and BOD reduced by 10% and 3%, respectively) and the biological treatment resulted in similar parameter trends as in the batch treatment of non-ozonated run-off. Interesting results emerge, though, when comparing BOD (Figure 6.4) and COD results (Figure 6.5) for the various ozonation times. During the initial stages of the biological treatment, the ozonated samples underwent a more rapid reduction in BOD; however, by 8 hours of biological treatment, this initial difference had largely been eliminated. Although the BOD of the ozonated and unozonated samples is reduced by approximately the same amount at the end of the entire biological treatment, the COD reduction is quite different. The COD of the unozonated sample is reduced by 2120 mg/L to 510 mg/L while the COD of the sample ozonated for 30 minutes is reduced by 1400 mg/L to 980 mg/L. There was a greater biologically inert fraction in the ozonated sample. This was initially puzzling as the ozonated samples were expected to have a lower final COD value because molecular breakdown caused by the ozone would generate smaller, more easily biodegradable products. A few possible explanations for this result exist. The activated sludge may release less biodegradable metabolites into the solution during biological treatment of ozonated samples. Previous work investigating the cell wall of various bacteria has found that during exponential growth, wall polymers are lost from cells (De Boer *et al.*, 1981; Frehel and Ryter, 1979; Glaser and Lindsay, 1977; Wong *et al.*, 1974). Certain changes in growth medium can result in changes in cell wall composition. For example, De Boer *et al.* (1981) showed that *Bacillus subtilis* grown under phosphate-limited conditions contained a different anionic polymer in its cell wall compared to the same bacterium grown in a phosphate-containing medium. Potentially, the ozonation of the run-off might lead to

Figure 6.4: Removal of BOD during biological treatment of ozonated logyard run-off. ◆: No ozonation, ■: 250 mg/L ozonation, ▲: 720 mg/L ozonation.

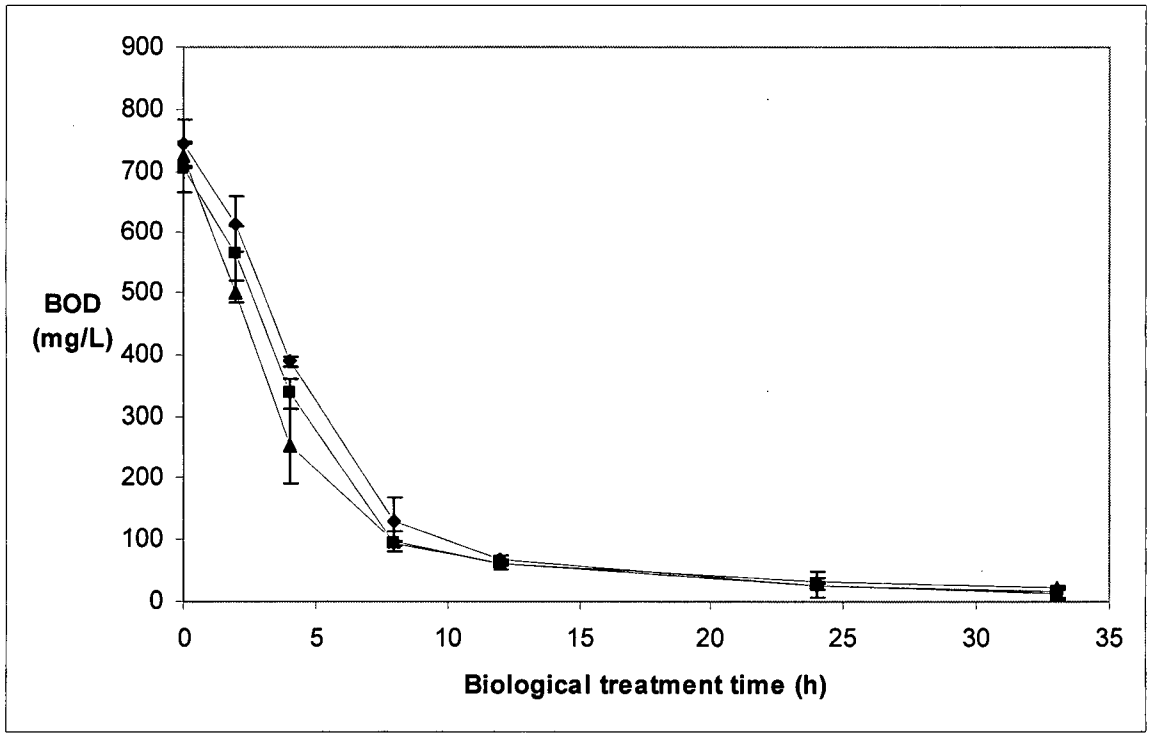
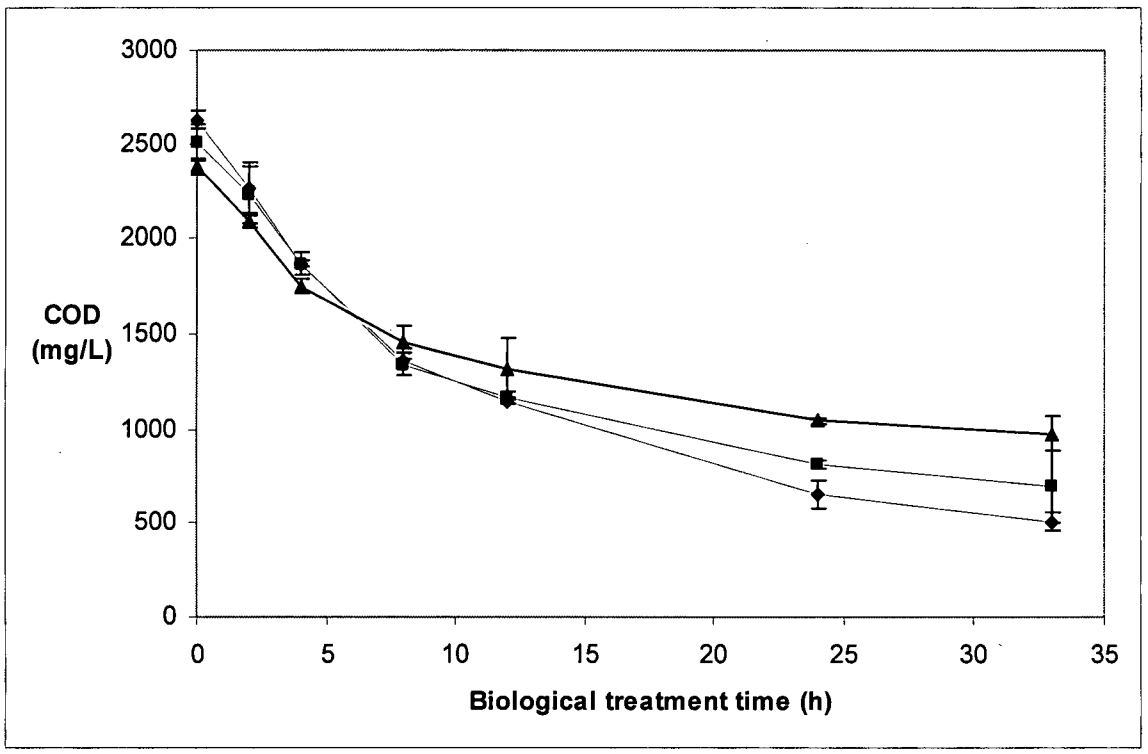


Figure 6.5: Removal of COD during biological treatment of ozonated logyard run-off. ◆: No ozonation, ■: 250 mg/L ozonation, ▲: 720 mg/L ozonation.



a change in the composition of the cell wall and, therefore, a change in the composition of the cell wall polymers that are released, polymers that are more resistant to subsequent biological breakdown. Another possibility is that ozonation of the sample may yield non-biodegradable compounds through polymerization of organic compounds into larger molecules. Ozonation of bleach plant effluent from a pulp mill has shown that high- and low-molecular weight compounds increase in concentration but the concentration of medium-sized molecules decreases (Beulker and Jekel, 1993). This result can be explained by the differing mechanisms of ozone and hydroxyl radicals. Work involving the reaction of lignin model compounds and hydroxyl radicals has shown that polymerization occurs to a significantly greater degree than does ring opening (Gierer et al, 1992). Molecular ozone, though, reacts primarily by attacking at double bonds and aromatic groups, leading to breaks and ring opening, respectively (Rice and Browning, 1981). Thus, the results of the ozone/biodegradation experiments can be explained as follows: the increase in lower molecular weight compounds caused by the action of molecular ozone results in the improved biodegradability of the run-off as shown by the improved initial BOD removal rate for ozonated samples. Conversely, the action of hydroxyl radicals, which result in a larger fraction of higher molecular weight non-biodegradable compounds, leads to a greater biologically inert organic fraction and thus, a greater final COD value for the ozonated run-off samples that are subsequently ozonated.

On an industrial scale, this could have repercussions on the design of a treatment system combining ozone with biological treatment. An improved BOD removal rate results from pre-ozonation of the run-off, thus leading to a smaller biological treatment system being needed. The resulting greater final COD could be a problem, though, if this parameter is subject to limitations on its release into receiving waters.

When considering tannin and lignin levels, the use of a pre-ozonation step offers a marked improvement over a solely biological system. The initial ozonation step achieves a large initial reduction in TL that is then continued by the biological treatment (Figure 6.6). Approximately 15 hours of biological treatment of the unozonated sample were required in order to achieve the 70% reduction in TL obtained by 30 minutes of pre-ozonation. By the end of the biological treatment period for both unozonated and ozonated samples, though, the same final TL level was achieved. Likewise, the removal of toxicity followed a very similar trend, albeit with a somewhat quicker reduction of toxicity in the unozonated sample when compared to TL removal (Figure 6.7). After a rapid detoxification (71% removal after 30 minutes) by ozonation, further biological treatment results in only a small further improvement. Biological treatment of the unozonated sample eventually results in toxicity levels similar to those obtained by treatment of the ozonated sample. Although not proof of a causal link, the strong similarity between the plots of TL and Microtox® toxicity suggests that TL, or a compound that co-varies with TL, could be an important determinant of the toxicity of the logyard run-off. It also reconfirms the good correlation between TL concentration and Microtox® obtained during the ozonation of logyard run-off and recalls the work of Bailey et al. (1999) that also showed that toxicity in sawmill stormwater was often associated with elevated TL levels.

Figure 6.6: Removal of tannins and lignins during biological treatment of ozonated logyard run-off. ◆: No ozonation, ■: 250 mg/L ozonation, ▲: 720 mg/L ozonation.

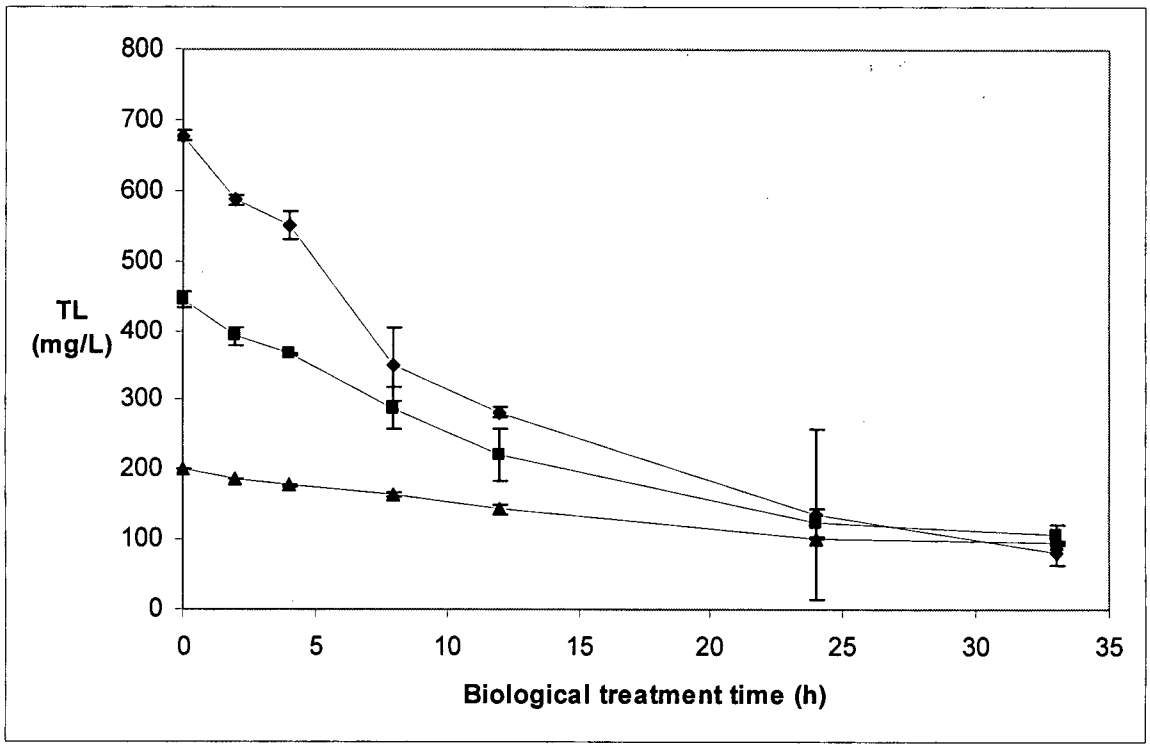
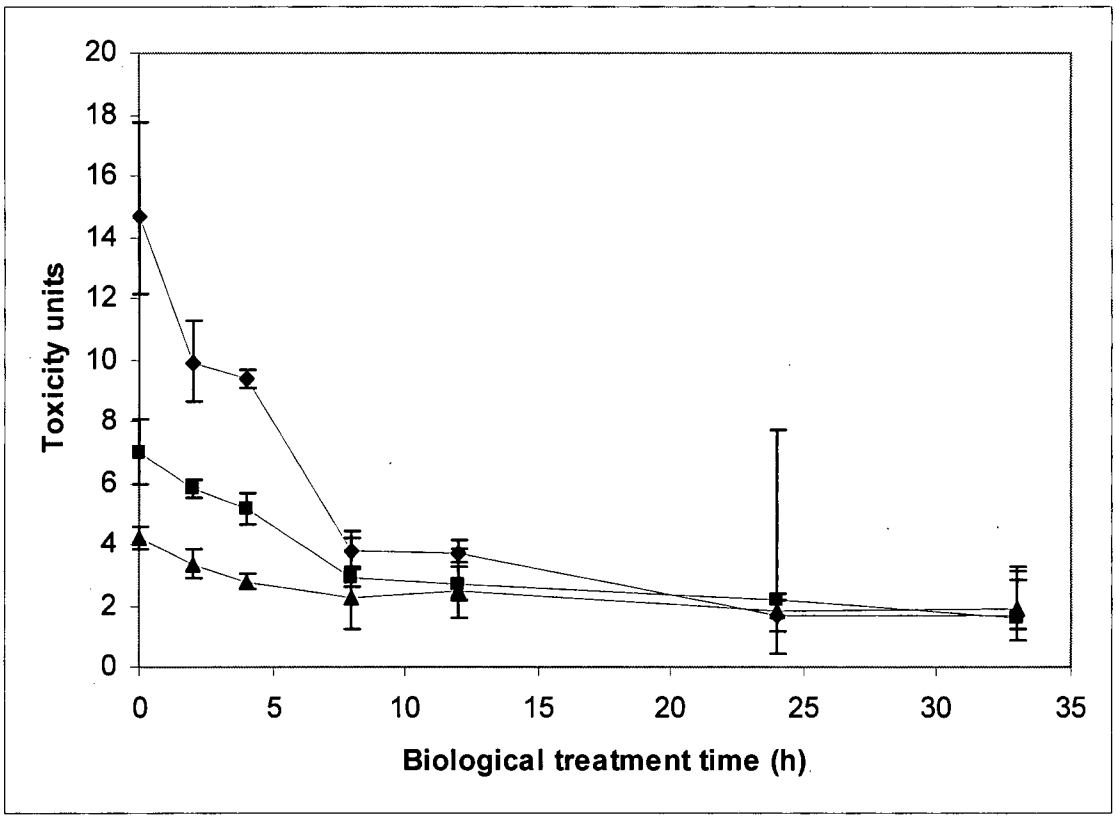


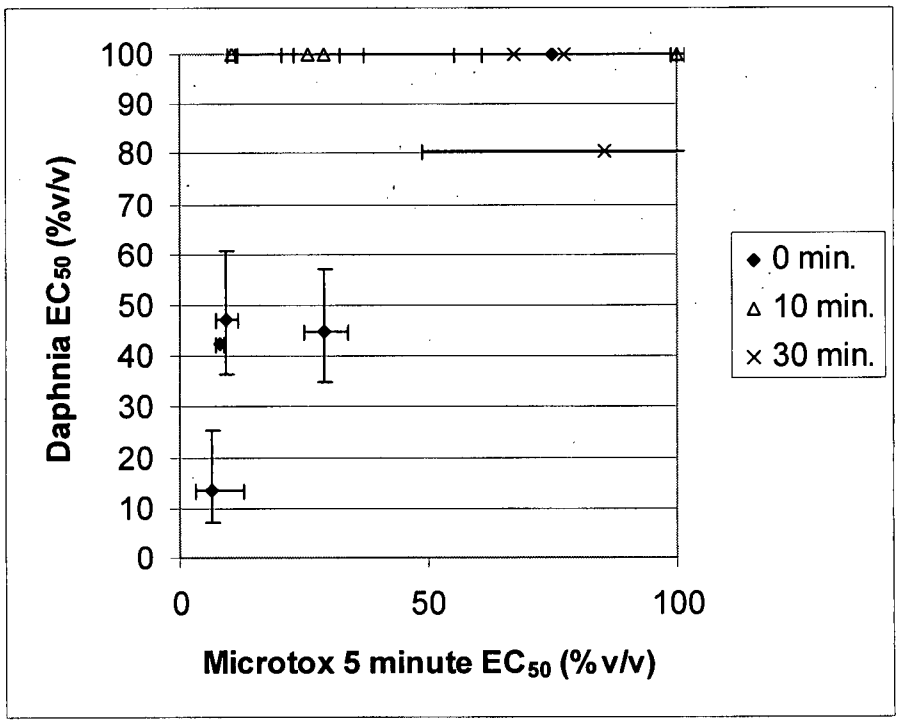
Figure 6.7: Removal of Microtox toxicity during biological treatment of ozonated logyard run-off. ◆: No ozonation, ■: 250 mg/L ozonation, ▲: 720 mg/L ozonation.



6.4 Comparison of Microtox® and *Daphnia* toxicity tests

A number of the run-off samples obtained from the sawmills were subjected to ozonation for a period of 10 and 30 minutes, and the toxicities of the resulting treated samples were determined using both *Daphnia* and Microtox toxicity assays (Figure 6.8). The Microtox assay was more sensitive than *Daphnia* (with only one exception and a large portion of the 95% confidence interval of that measurement is in the area of the graph where Microtox is more sensitive than Daphnia). For the unozonated samples, significant toxicity was apparent using both measurements, and for those that underwent ozonation for 30 minutes there was a large decrease in toxicity for both *D. magna* and Microtox. For those samples ozonated for 10 minutes though, there is a significant discrepancy between the results. In all the samples the *D. magna* EC_{50} values were greater than 100%, whereas for Microtox their EC_{50} values ranged between 10.5 and 29.2%. Given the complexity of the run-off, it is impossible to give a rationale for why the sensitivity of the Microtox test is significantly greater at this time. The overall trend for both tests is similar, a decrease in toxicity as ozonation progresses. The results presented here are similar to those in the review by Munkittrick et al. (1991). They state that the sensitivity of Microtox to complex organic systems is greater than that for higher level organisms, and that for pulp and paper wastes, Microtox was found to be suitable for monitoring relative changes in toxicity. For both treated and untreated logyard run-off, the sensitivity of Microtox was found to be greater than that of *D. magna* and can therefore provide a lower limit for EC_{50} values measured by *D. magna*. Establishing a correlation between *Daphnia* and Microtox toxicity readings is hampered by the dearth of samples with *Daphnia* EC_{50} below 40%. More samples need to be analyzed in this range before any firm conclusion can be made.

Figure 6.8: Comparison of *Daphnia magna* and Microtox EC_{50} values after various ozonation times. Daphnia EC_{50} values of 100% are actually >100% since extrapolation beyond this point is not possible.



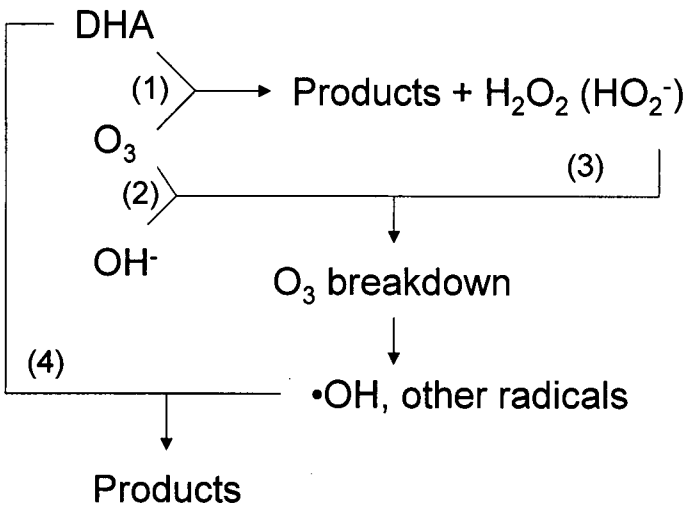
7. MODELING OF THE OZONE/DHA REACTION

7.1 The reaction rate constant of DHA and molecular ozone

In any attempt to model a complex reaction system such as the ozonation of logyard run-off, it is necessary to first know some fundamental parameters of the constituents of the system. One of the most important of these parameters that can be determined is the reaction rate constant. Knowledge of this value is essential if one wishes to predict reagent concentrations as a function of time. As an initial step in modeling the ozonation of logyard run-off, it was decided to investigate one of the resin acids, a family of compounds well known for their toxicity to marine wildlife. Of all the resin acids, DHA is one of the most persistent as well as one of the most plentiful (Brownlee *et al.*, 1977; Fox, 1977; Oikari *et al.*, 1980). Because of this, an examination of the reaction of DHA and ozone was selected for further work.

The reaction between DHA and ozone is more complex than would normally be expected from a system with just two initial reagents. Figure 7.1 illustrates why this is so. The main reaction of interest is that between DHA and ozone (1). An oxidized DHA product will result, along with hydrogen peroxide. In addition to reacting with DHA, ozone can also react with OH^- (2) and the ionized form of hydrogen peroxide (3) to produce radical breakdown products, one of which is ·OH. This radical can, in turn, react with DHA (4), as well as with ozone and H_2O_2/HO_2^-. Thus, the pH and the extent to which hydrogen peroxide is produced from the oxidation of DHA will affect to what degree ozone is broken down before it is able to react with DHA.

Figure 7.1: Reaction of DHA and ozone in aqueous solution



. The variables in the model are:

- pH
- ratio of ozone consumed:DHA oxidized (x)
- ratio of H_2O_2 produced:DHA oxidized (y)
- rate of reaction between ozone and DHA ($k_{O3/DHA}$)
- rate of reaction between ·OH and DHA ($k_{\cdot OH/DHA}$)
- rate of reaction between phosphate radicals and DHA ($k_{\cdot PO4/DHA}$)

The associated reactions and rate constants for variables involving DHA are as follows:

$DHA + xO_3 \rightarrow Products + yH_2O_2$	$k_{O3/DHA}$
$DHA + \cdot OH \rightarrow \cdot DHA + H_2O$	$k_{\cdot OH/DHA}$
$\cdot DHA + xO_3 \rightarrow Products + yH_2O_2$	$k_{O3/DHA}$
$\cdot OH + Products \rightarrow Products$	$k_{\cdot OH/DHA}$
$DHA + PO_4^{2-} \rightarrow Products$	$k_{\cdot PO4/DHA}$
$DHA + HPO_4^- \rightarrow Products$	$k_{\cdot PO4/DHA}$
$DHA + H_2PO_4 \rightarrow Products$	$10 \cdot k_{\cdot PO4/DHA}$

In order to determine the reaction rate constant between ozone and DHA, the experimental results obtained at a pH of 6.5 and with t-butanol as a radical scavenger will be considered. Under these conditions, ·OH generation is the lowest of all conditions examined. The effect of ·OH on the measurements will be analyzed after discussion of the determination of the reaction rate constant.

As part of this determination, the ratios of O_3 consumed and H_2O_2 produced per molecule of DHA oxidized were varied and the resulting plots of DHA and O_3 over time compared to the experimental results. The combination of O_3 consumed:DHA oxidized, H_2O_2 produced:DHA oxidized, and reaction rate constant in the model that gives the closest fit to the experimental results will be considered the appropriate set of values to use in subsequent modelling and calculations.

The ratios of ozone added to DHA reacted for the experiment done at pH 6.5 and t-butanol as radical scavenger are listed in Table 7.1. An initial examination of the ratios would suggest a value of either 4:1 or 3:1. For the first modeling attempt, a ratio of 4:1 was tried.

Table 7.1: Ratio of O_3 added:DHA oxidized (pH 6.5, radical scavenger: t-butanol)

$[O_3]_0$ (mM)	Ratio O_3 added:DHA oxidized
.1066	4.89
.0629	3.92
.0411	3.47
.0242	3.41
.0150	3.43
.0093	4.38

A Matlab model was run using reaction rate constant values between 50 L/mol·s and 200 L/mol·s, ozone consumed:DHA reacted ratio of 4:1, and a hydrogen peroxide produced:DHA reacted ratio of 3:1 (Figure 7.2). Clearly, although the ozone concentration plot can be approximated by a reaction rate constant between 50 L/mol·s and 100 L/mol·s (Figure 7.2 e-h), the results for the DHA concentration consistently overestimate the final DHA concentration remaining in the mixture after all the ozone has reacted (Figure 7.2 a-d). This suggests that the combination of ratios used in the model is incorrect. The value of the H_2O_2 produced:DHA consumed ratio was then varied and plots at values of 2:1, 1:1, and 0:1 were generated (Figures 7.3-7.5), although this latter value would be extremely unlikely given previous work with ozonation of aromatic and olefinic compounds (Trapido et al, 1997; Rice & Browning, 1981). As with a H_2O_2:DHA ratio of 3:1, the ozone traces for all the lower H_2O_2:DHA ratios suggest a reaction rate constant between 50 L/mol·s and 100 L/mol·s (Figures 7.3-7.5, e-h); however, the DHA concentrations predicted by the model are consistently greater than the measured final DHA concentrations (Figures 7.3-7.5, a-d). The inability of the model to generate final DHA concentrations as low as the measured values would indicate that the ratio of 4:1 being used for the O_3 reacted:DHA oxidized ratio is too high. A lower ratio would result in a greater amount of ozone left to react with residual DHA, leading to a lower final DHA value.

Since modeling of an ozone:DHA ratio of 4:1 did not fit the experimental data, a model using a value of 3:1 was attempted. In this case, a much better fit of the experimental data was obtained. Once again, the model was run at the same H_2O_2 produced:DHA reacted ratios as before. For both the 3:1 and 2:1 ratios of H_2O_2:DHA, a good fit was obtained for a reaction rate constant of approximately 100 L/mol·s (Figures 7.6-7.7). The model runs for a 1:1 ratio of H_2O_2:DHA do not give a good fit. The O_3 plots (Figure 7.8 e-h) yield an adequate fit for a reaction rate constant of approximately 100 L/mol·s; however, the DHA models consistently yield lower values than those obtained experimentally (Figure 7.8 a-d). In the case of a model

with no H_2O_2 production, the model runs for DHA deviate greatly from experimental results (Figure 7.9 a-d).

The possibility of a 2:1 ratio of ozone consumed:DHA reacted, although remote, was also examined; however, the models bore no resemblance to experimental results (Figure 7.10).

Since the 3:1 and 2:1 H_2O_2:DHA ratios with a 3:1 O_3:DHA ratio both gave good visual fits with the experimental results, these were then further examined to determine the reaction rate constant value that yielded the best fit with experimental data. The best fit was determined by running the model with a range of reaction rate constants, calculating the sum of squares for each one and then narrowing the search until the rate constants yielding least squares for the DHA and ozone plots were found. In obtaining the best value of k by minimization of squares, the 3:1 H_2O_2:DHA model gave consistently lower least squares values than the 2:1 H_2O_2:DHA model. Also, the reaction rate constants that were calculated from the ozone and DHA plots separately were closer together with the 3:1 H_2O_2:DHA model. These calculated best fit rate constants for each plot are listed in Table 7.2. Since both the minimization of squares and the comparison of k values obtained from the ozone and DHA plots indicate that a 3:1 H_2O_2:DHA model gives a superior fit of the data, this was the model that was used in subsequent calculations (further weight for this argument will be provided in an ensuing section). Grubbs' test for the detection of outliers was then applied to the k values obtained with the 3:1 H_2O_2:DHA ratio. With 95% confidence, the value of 177 L/mol·s is an outlier. By averaging the remaining optimum values of k obtained for each injection, an average of 1.1×10^2 L/mol·s was calculated for the ozone/DHA reaction rate constant at the reaction temperature of 23°C.

A comparison of this reaction rate constant with those obtained for other substituted benzenes is of interest (Table 7.3). The value of 1.1×10^2 L/mol·s obtained for DHA is certainly a reasonable estimate given the similar order of magnitude of the value compared to other doubly- and triply-substituted benzenes. It should be noted that the values calculated by Hoigné and

Table 7.2: Best fit values for the O_3/DHA reaction rate constants.

$[O_3]_0$ ($x10^{-5}$ M)	Experimental k (L/mol·s) using 3:1 H_2O_2:DHA model		Experimental k (L/mol·s) using 2:1 H_2O_2:DHA model		Differences between best fit values for DHA and O_3 plots	
	DHA plot	O_3 plot	DHA plot	O_3 plot	3:1 H_2O_2:DHA model	2:1 H_2O_2:DHA model
10.66	113	117	105	159	4	54
6.29	109	109	102	122	0	20
4.11	101	102	98	107	1	9
2.42	110	126	107	129	16	22
1.50	119	177	116	178	58	62
Avg.±95%C.I.	112±6*		122±20			

*: Calculation does not include the value of 177 L/mol·s as it is considered an outlier by Grubbs' test.

Table 7.3: Assorted values of reaction rate constants of substituted benzenes with ozone in aqueous solution (from Hoigné and Bader, 1983a)

Compound	Reaction Rate Constant (L/mol·s)	Reaction Rate Constant (L/mol·s) Assuming 3:1 O_3:DHA Ratio
Cumene	11	3.7
o-xylene	90	30
m-xylene	94	31.3
p-xylene	140	47
1,2,3-trimethylbenzene	400	130
1,3,5-trimethylbenzene	700	230

Bader (1983a) do not take into account the stoichiometry of the reaction of aromatic compounds with ozone in their calculations. If, as determined here, a further two molecules of ozone are quickly consumed after the initial ring opening, then the values quoted in the original paper should be divided by 3 to compare with the value of $1.1 \cdot 10^2$ L/mol·s determined for DHA. Indeed, taking the triply substituted benzenes as somewhat similar compounds to DHA, dividing their rate constants by 3 yields values quite close to that of DHA calculated here. Another comparison of interest would be the reaction of ozone with 1,2,3,4-tetrahydronaphthalene (because of the juxtaposition of an aromatic ring with a non-aromatic ring); however, a search of the literature does not show that the reaction rate of this compound with ozone has been determined.

Figure 7.11 shows the experimental results and the modeled results with $k = 1.1 \cdot 10^2$ L/mol·s. As noted before, the reaction rate constant derived from the ozone plot of the last addition is considered an outlier. Comparing the modeled and experimental results, a significant discrepancy is observed in the initial ozone concentration (Figure 7.11j). This effect is especially prevalent in the additions with low initial ozone concentrations. This arises because the absorbance at 260 nm is very low from the beginning of the addition and the matrix multiplication method used to determine the experimental DHA and ozone concentrations is subject to larger errors as a fraction of initial values as initial concentrations decrease.

For the O_3:DHA molar ratio, only integer values have been considered; however, additional side reactions might result in a higher, non-integer, molar ratio being more appropriate for the model. For each injection, the model was run with a molar ratio between 2.8 and 3.2 at intervals of 0.1 (the injection with $[O_3]_0=1.5 \cdot 10^{-5}$ M was not considered as the reaction rate constant from the ozone plot is considered an outlier). For each molar ratio, the O_3/DHA reaction rate constant was varied to obtain the values that provided the best fit with the ozone data and the DHA data. These results were then plotted and are presented in Figure 7.12. Since

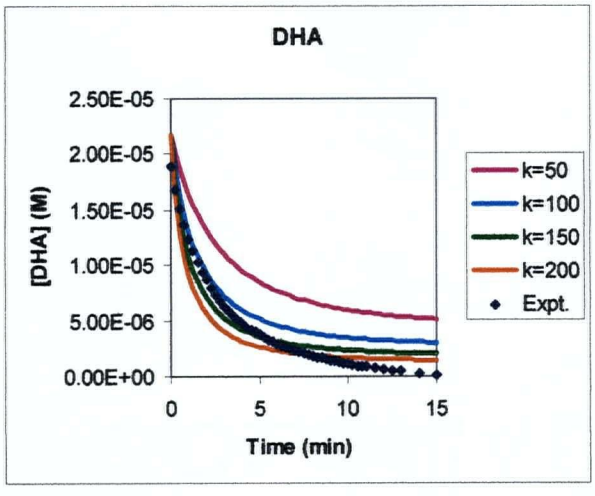
the reaction rate constant determined from the DHA and ozone curves should theoretically be the same, where the lines intersect indicates the reaction rate constant as well as the stoichiometric ratio of the reaction. The values for the O_3:DHA ratio obtained in the figures are 3.05, 3, 2.98, and 3.14, averaging 3.04. Thus, the value of 3:1 for the O_3:DHA ratio is appropriate.

An issue that has not been mentioned until now in the calculations concerns potential radical reactions with DHA. The point of using a radical scavenger and an acidic (albeit only slightly) pH was to keep ·OH generation to a minimum and thereby maximize the oxidation of DHA by molecular ozone. The model was run with a number of combinations of reaction rates for both hydroxyl and phosphate radicals in order to determine the extent of radical reactions with DHA. Phosphate radical reaction rates with DHA up to 10^{10} L/mol·s (approximately the value where reactions become diffusion-controlled rather than kinetically-controlled (Nemes *et al.*, 2000a), and also much higher than typical phosphate radical reaction rates (see p. 62)) made no perceptible difference in the trials (at most, 0.01% of total reacted DHA would have reacted with phosphate radicals). The reaction of ·OH and DHA only marginally affects the results. For example, comparing model results between no ·OH reaction and a reaction rate of 10^{10} L/mol·s results in a change of less than 2% in DHA consumed and does not materially affect the conclusions reached concerning the ozone:DHA reaction rate calculated at pH 6.5.

Figure 7.2: Additions of O_3 to DHA, modeled with O_3:DHA of 4:1, H_2O_2:DHA of 3:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)



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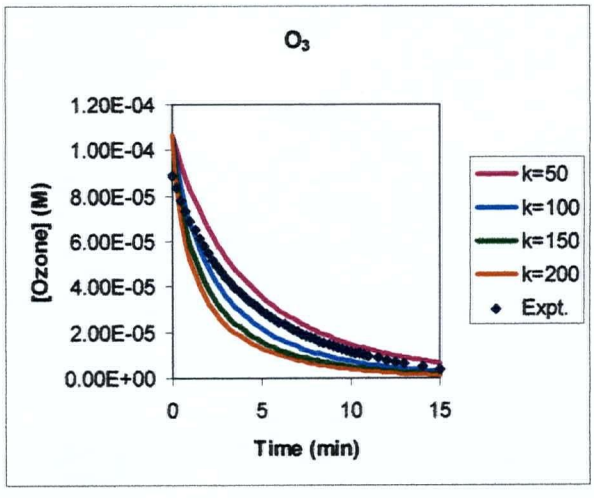
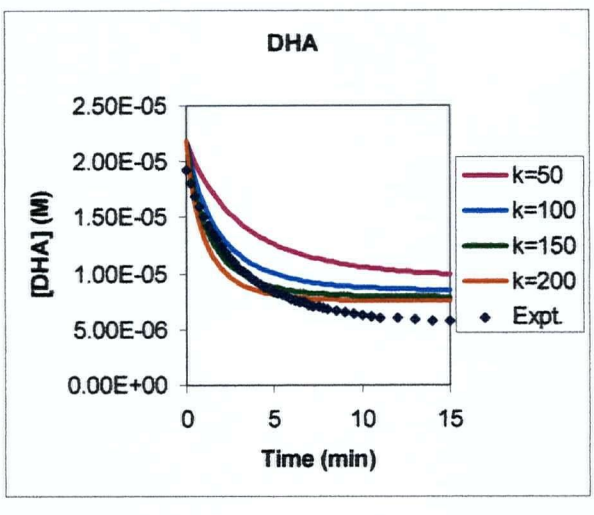
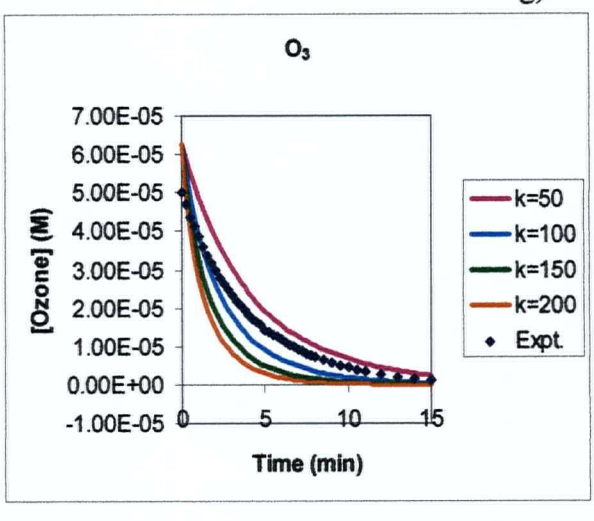


$[O_3]_0 = 0.0629$ mM

b)

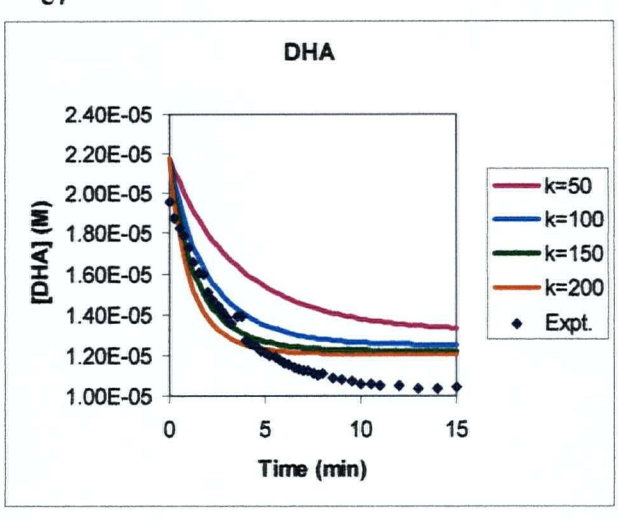


g)

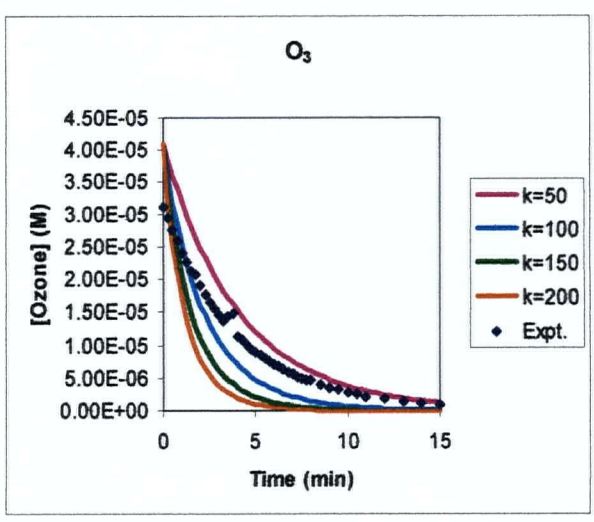


$[O_3]_0 = 0.0411$ mM

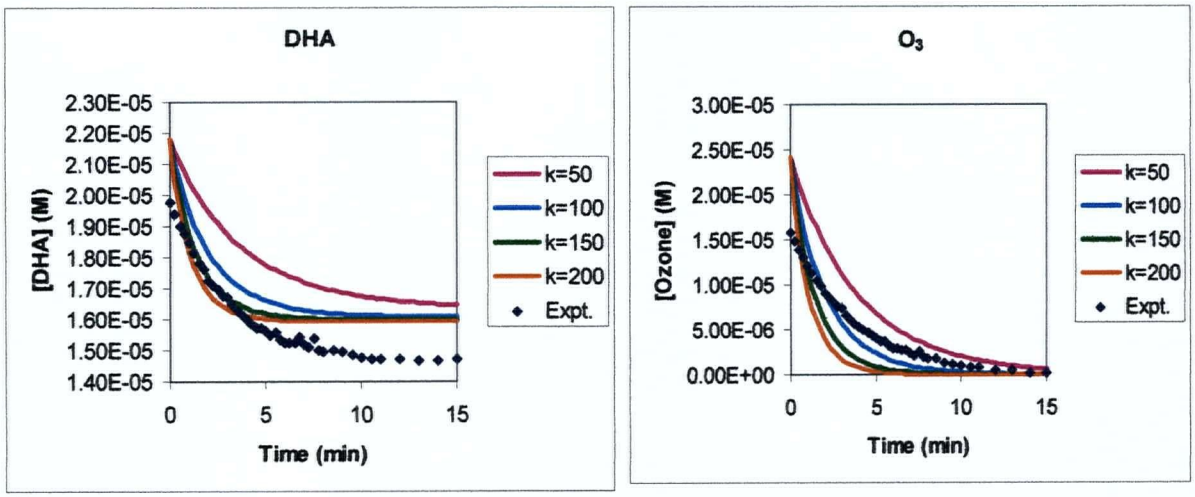
c)



h)



d) $[O_3]_0 = 0.0242$ mM i)



e) $[O_3]_0 = 0.0150$ mM j)

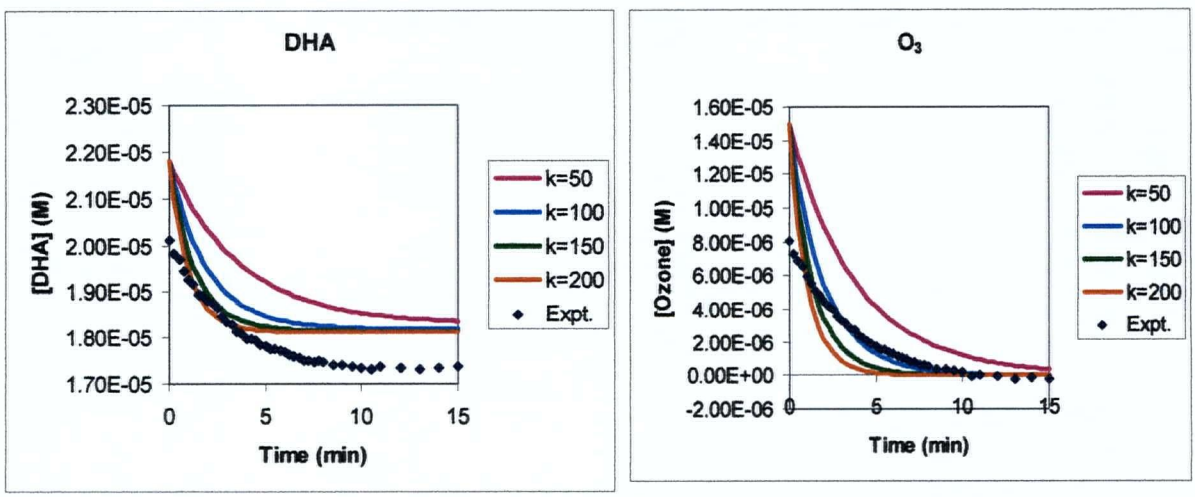
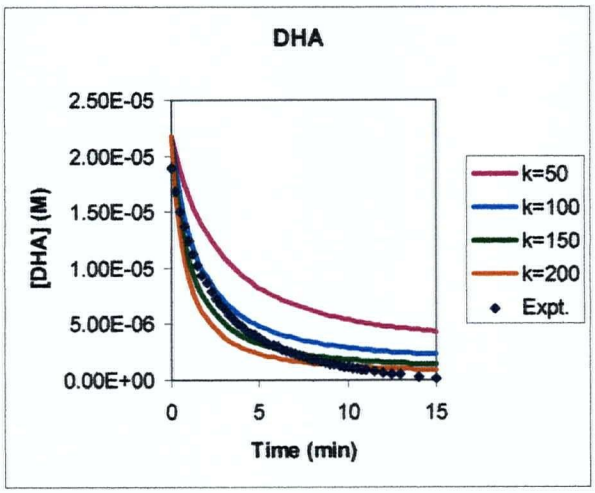


Figure 7.3: Additions of O_3 to DHA, modeled with O_3:DHA of 4:1, H_2O_2:DHA of 2:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)



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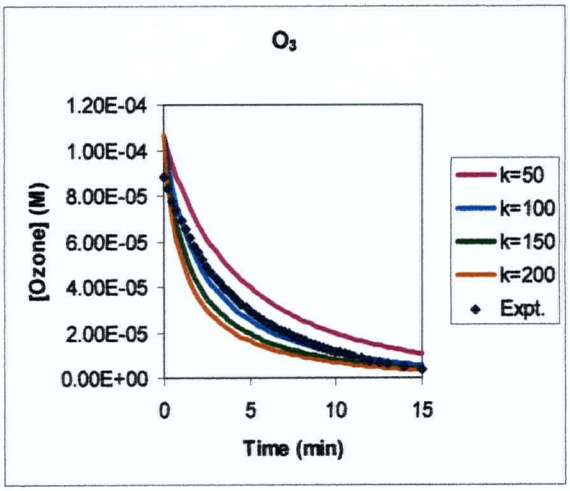
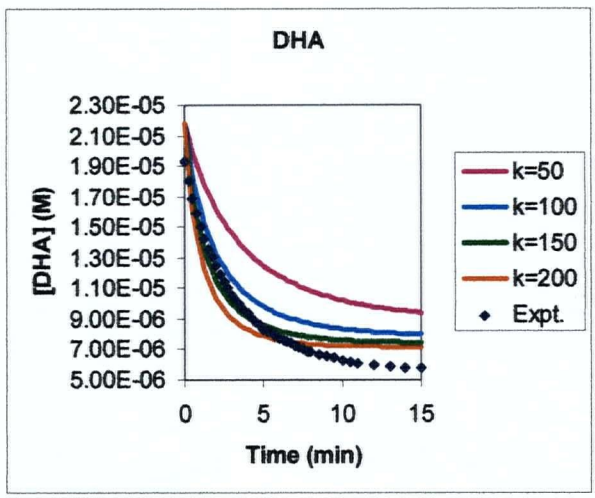
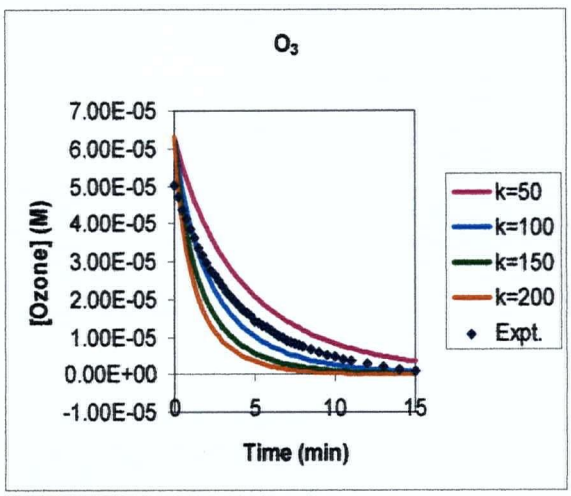


$[O_3]_0 = 0.0629$ mM

b)

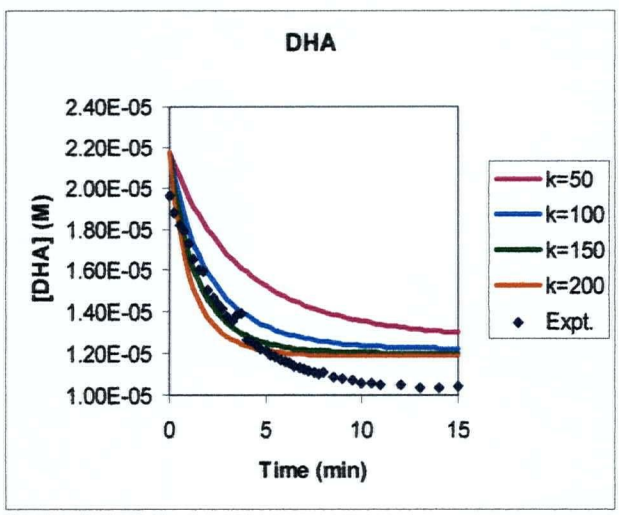


g)

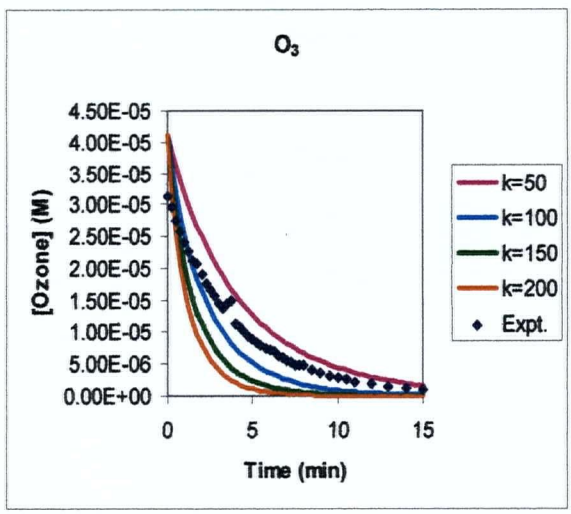


$[O_3]_0 = 0.0411$ mM

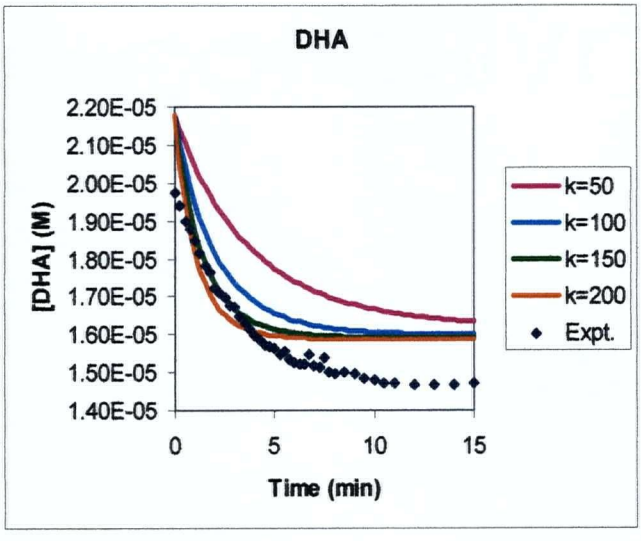
c)

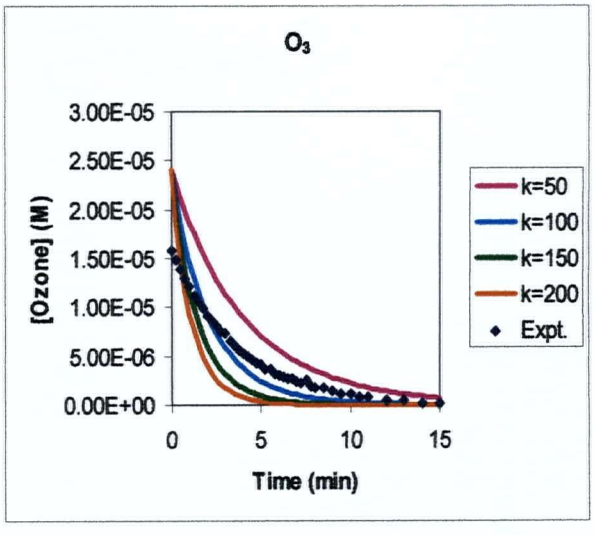


h)

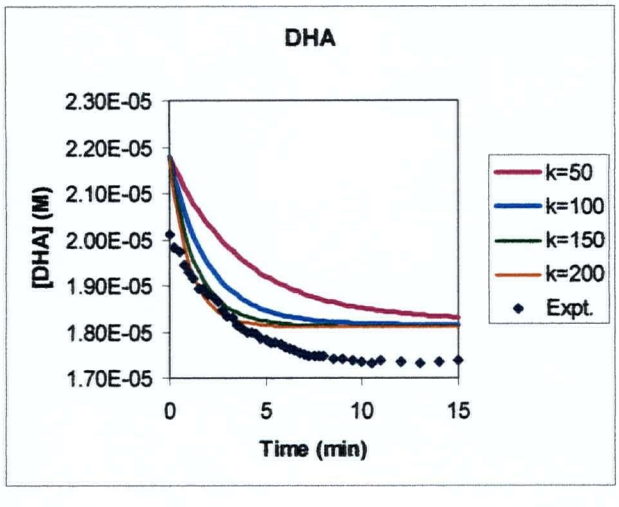


d) $[O_3]_0 = 0.0242$ mM i)





e) $[O_3]_0 = 0.0150$ mM j)



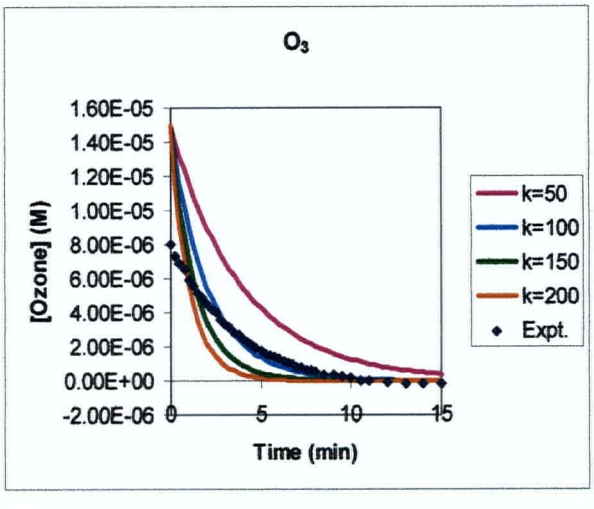
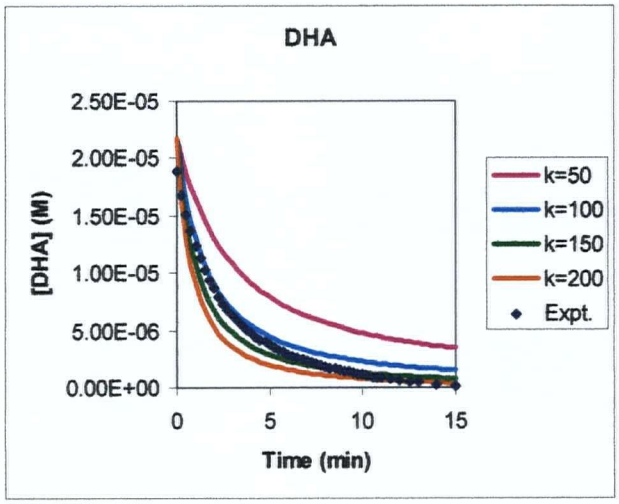


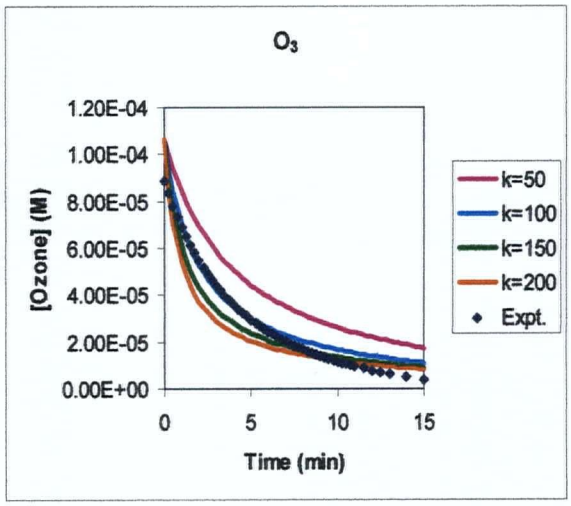
Figure 7.4: Additions of O_3 to DHA, modeled with O_3:DHA of 4:1, H_2O_2:DHA of 1:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)

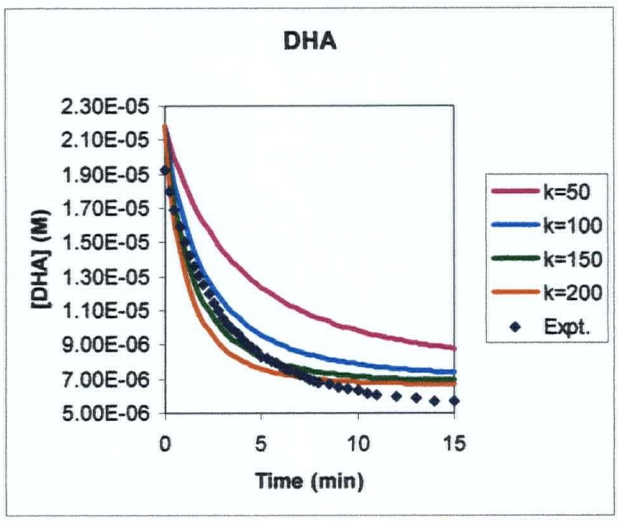


f)

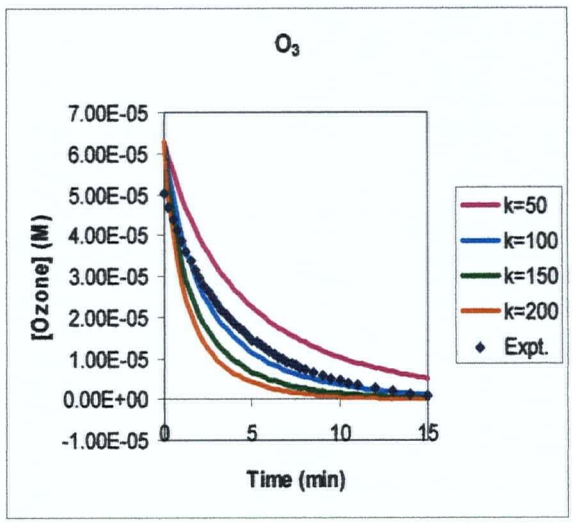


$[O_3]_0 = 0.0629$ mM

b)

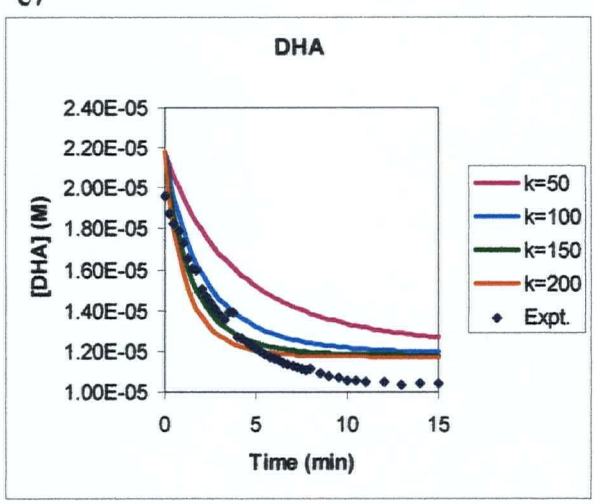


g)

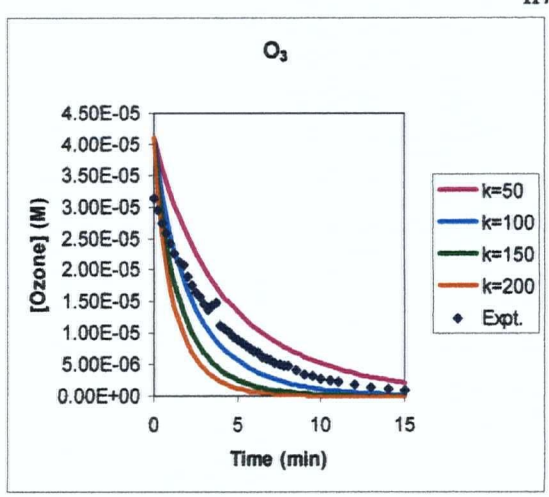


$[O_3]_0 = 0.0411$ mM

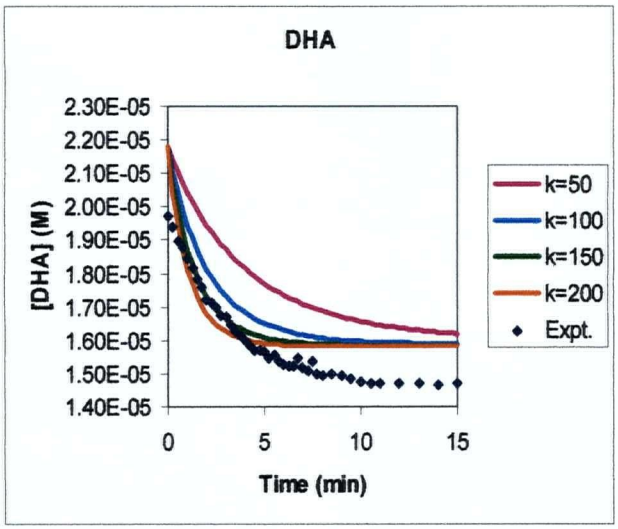
c)

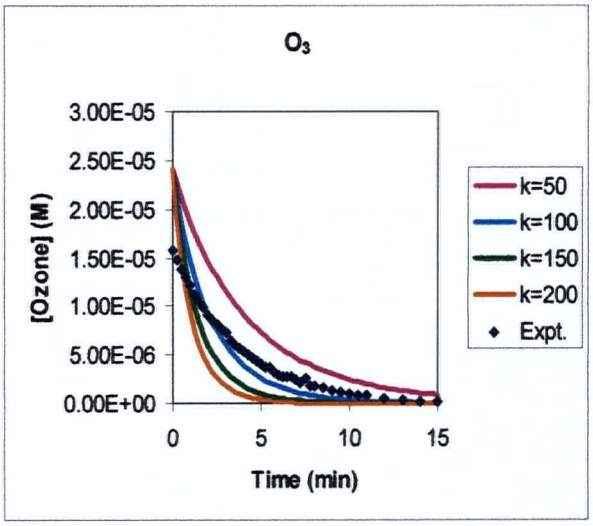


h)

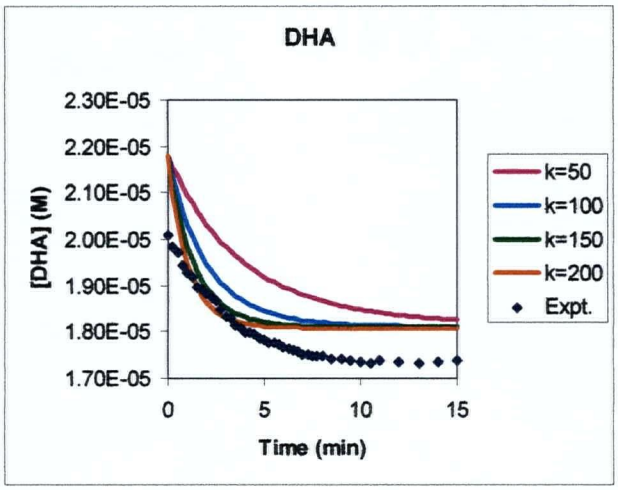


d) $[O_3]_0 = 0.0242$ mM i)





e) $[O_3]_0 = 0.0150$ mM j)



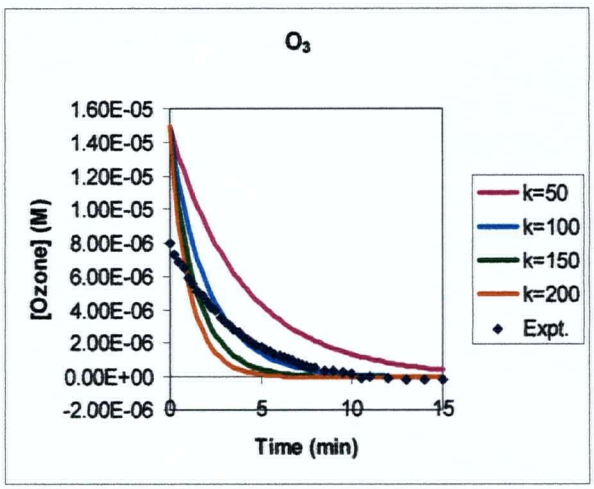
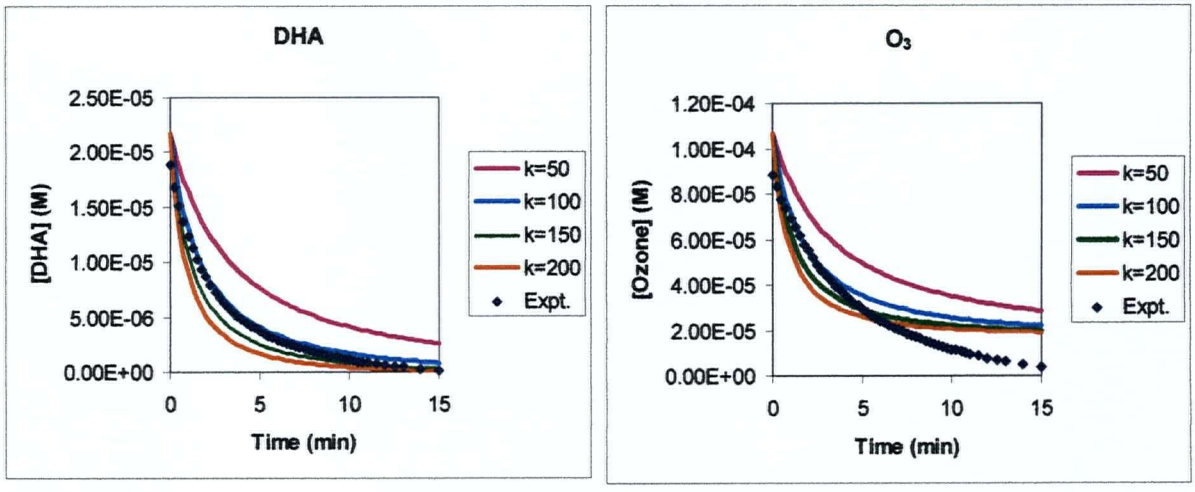


Figure 7.5: Additions of O_3 to DHA, modeled with O_3:DHA of 4:1, H_2O_2:DHA of 0:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

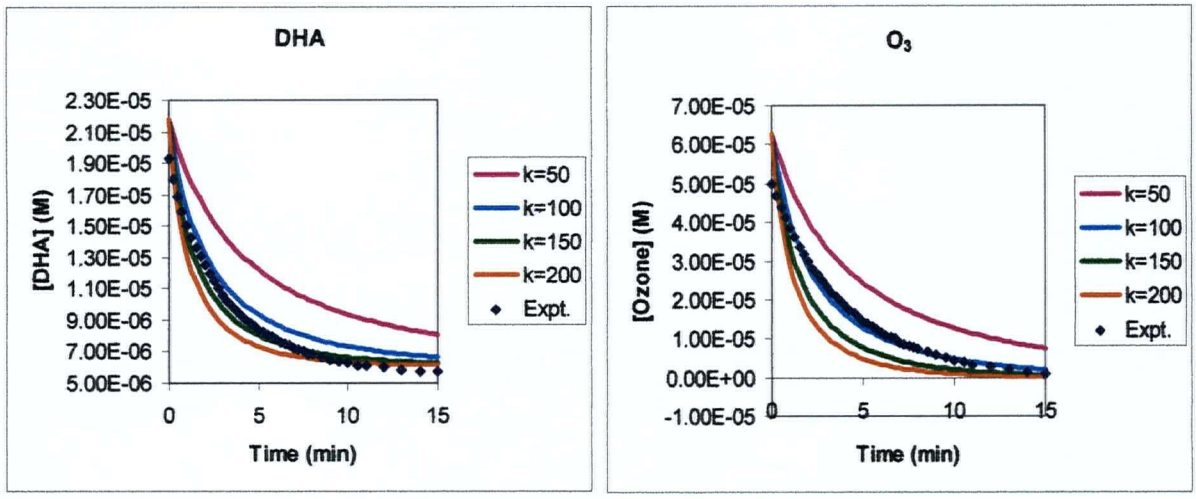
$[O_3]_0 = 0.107$ mM

a) f)



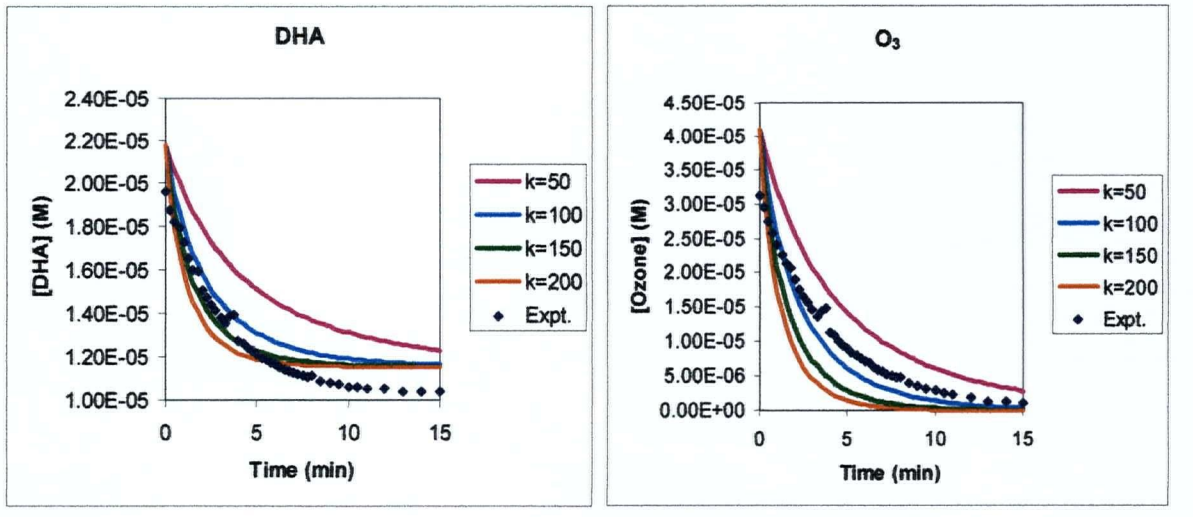
$[O_3]_0 = 0.0629$ mM

b) g)

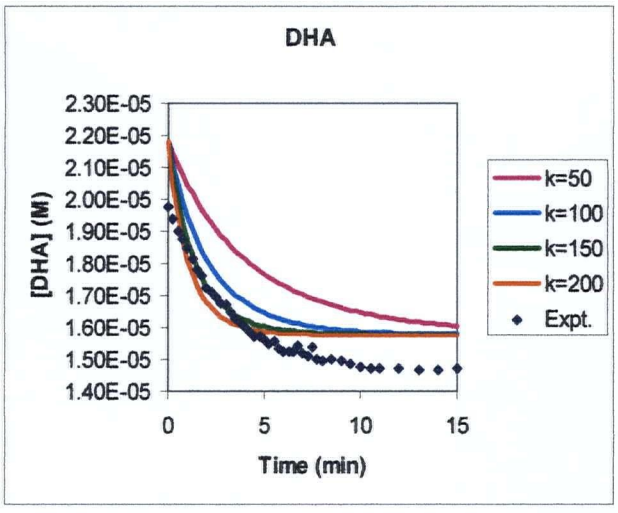


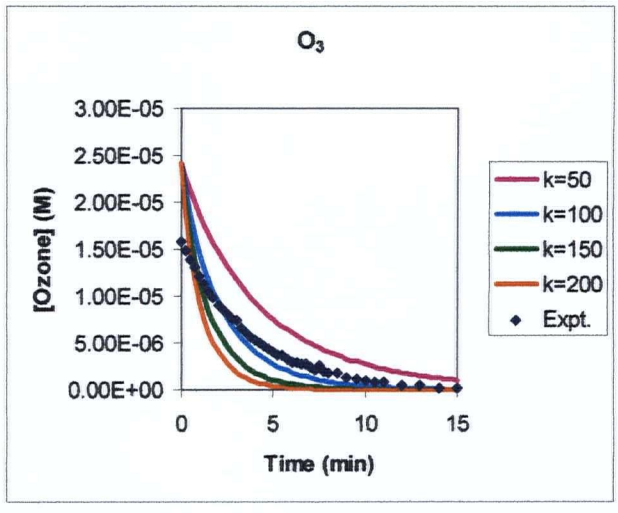
$[O_3]_0 = 0.0411$ mM

c) h)

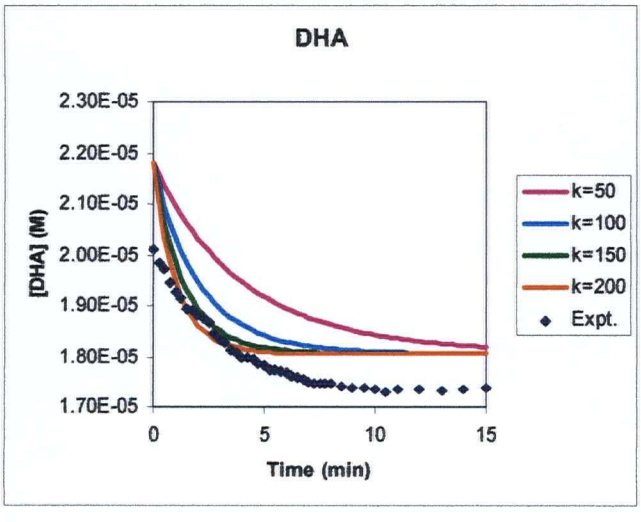


d) $[O_3]_0 = 0.0242$ mM i)





e) $[O_3]_0 = 0.0150$ mM j)



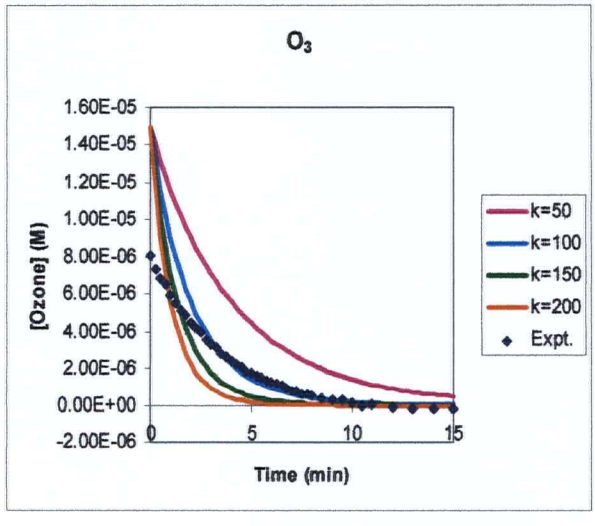
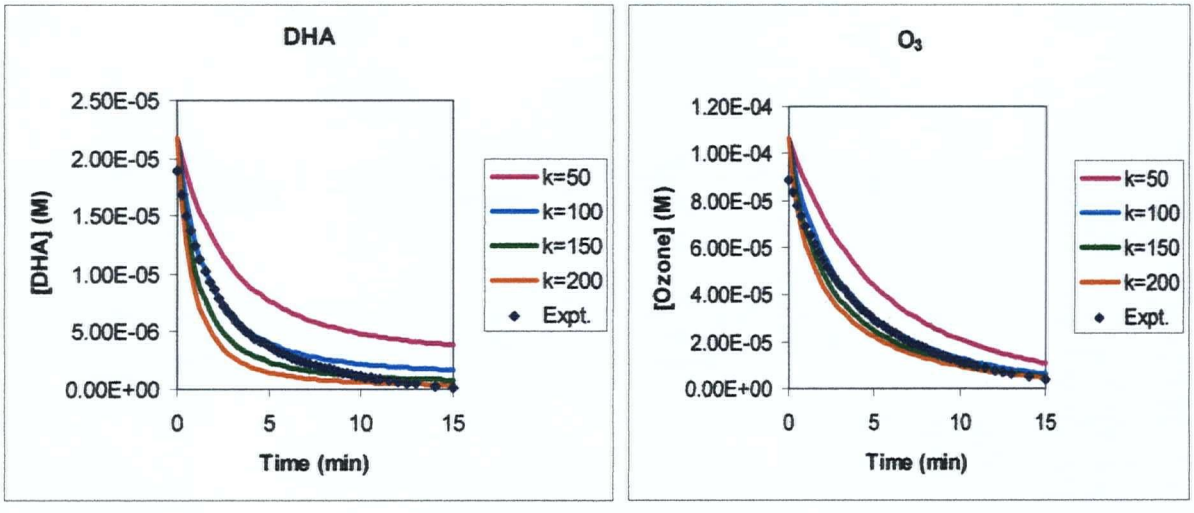
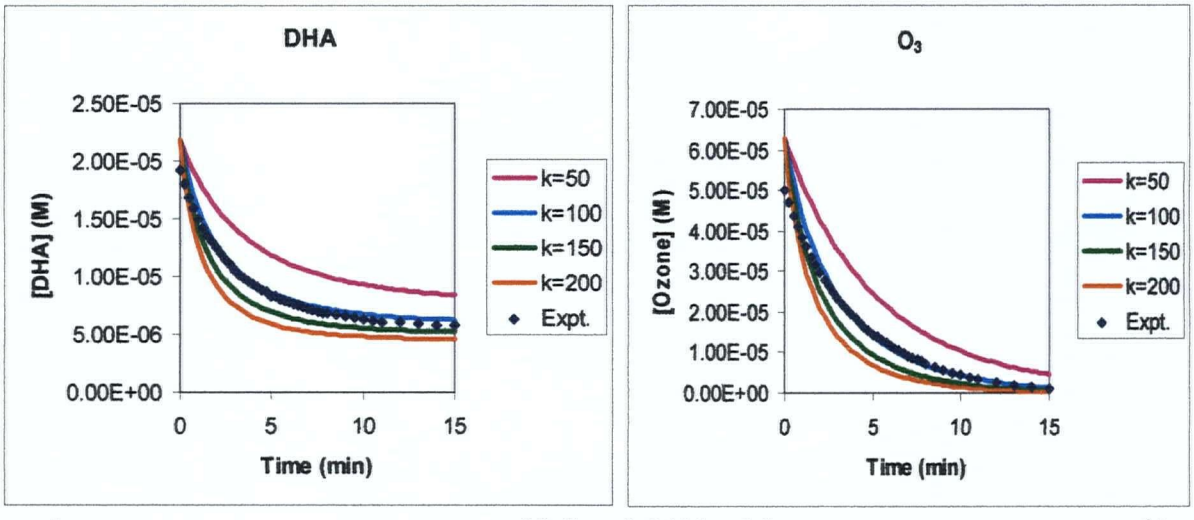


Figure 7.6: Additions of O_3 to DHA, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

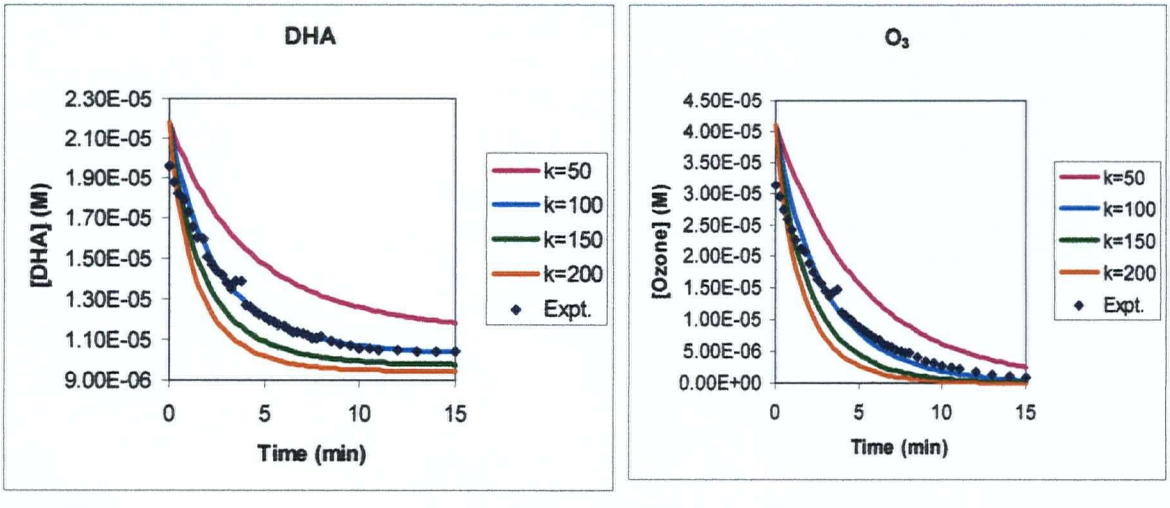
a) $[O_3]_0 = 0.107$ mM f)



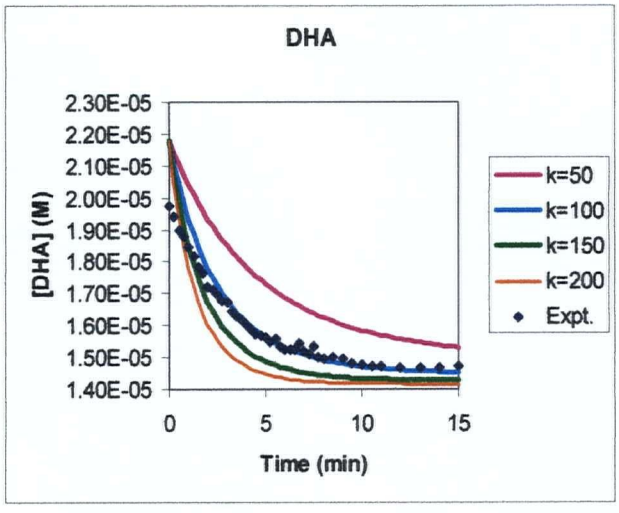
b) $[O_3]_0 = 0.0629$ mM g)

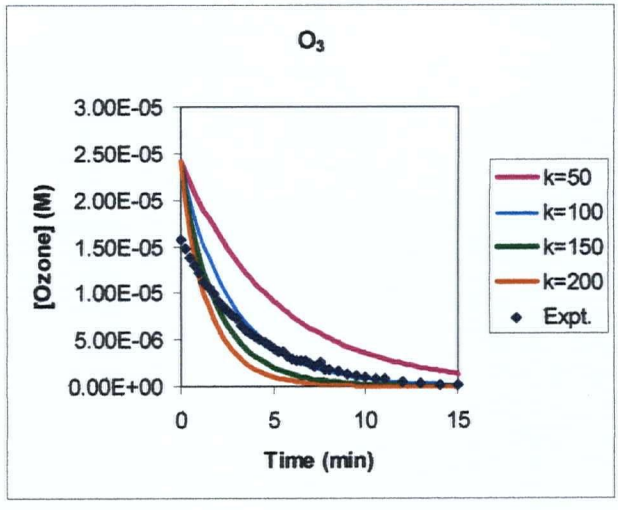


c) $[O_3]_0 = 0.0411$ mM h)

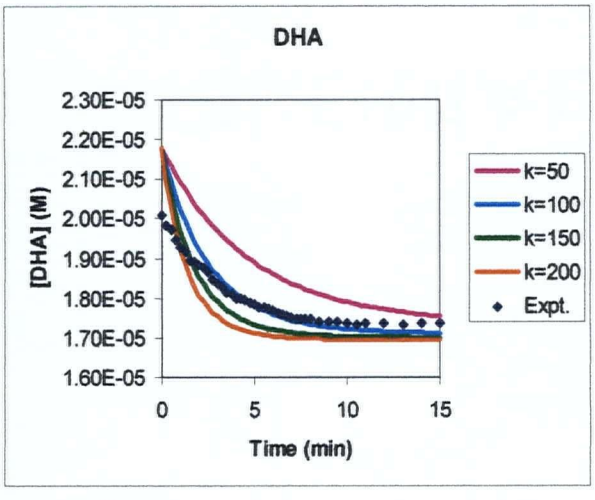


d) $[O_3]_0 = 0.0242$ mM i)





e) $[O_3]_0 = 0.0150$ mM j)



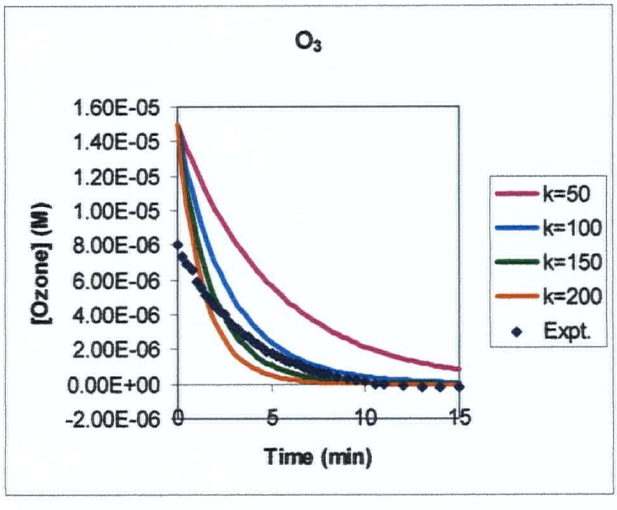
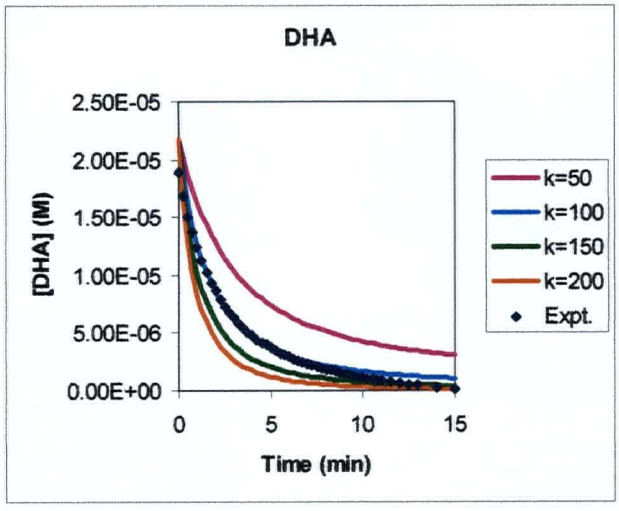


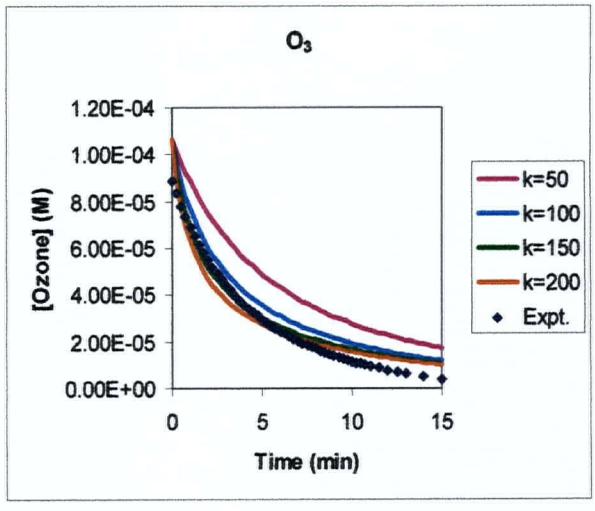
Figure 7.7: Additions of O_3 to DHA, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 2:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)

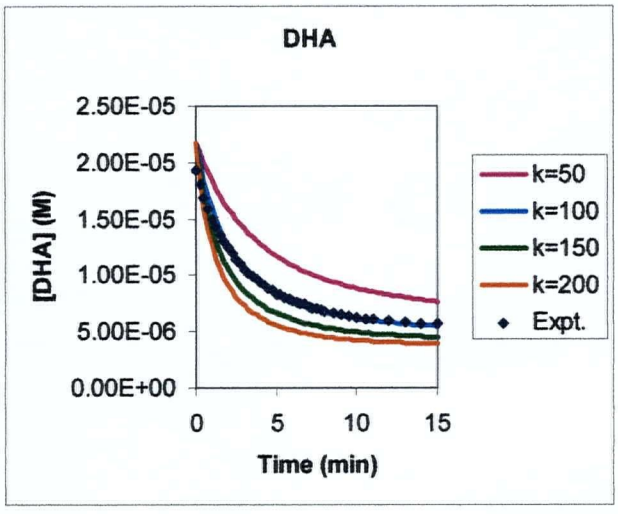


f)

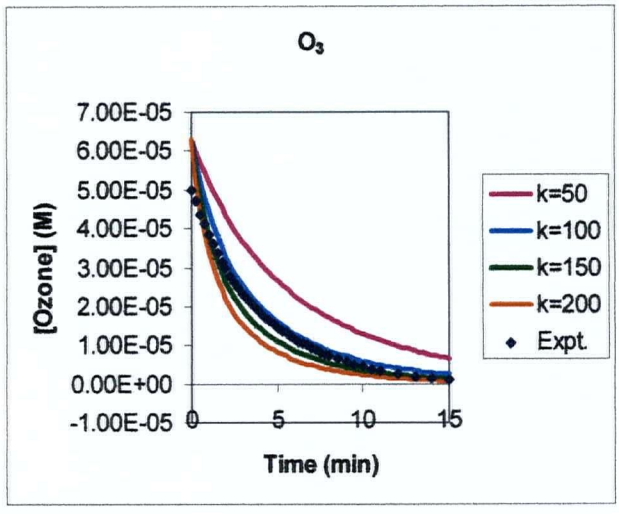


$[O_3]_0 = 0.0629$ mM

b)

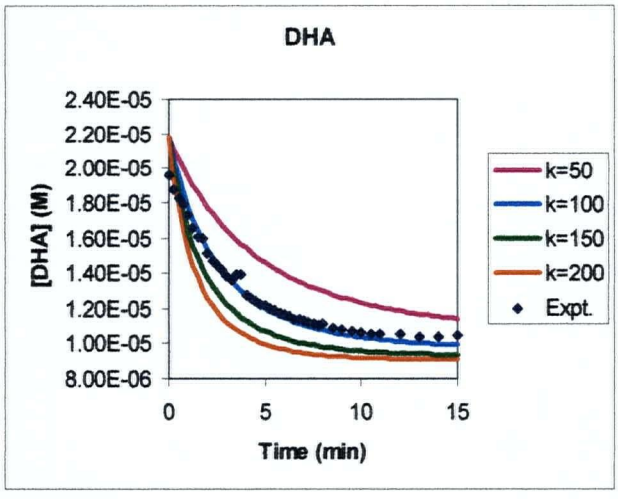


g)

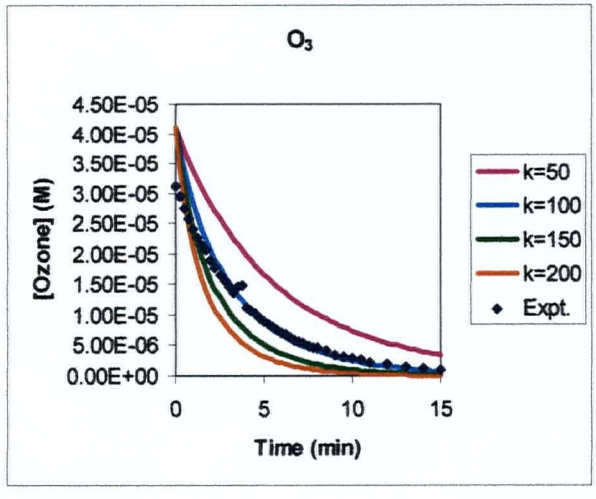


$[O_3]_0 = 0.0411$ mM

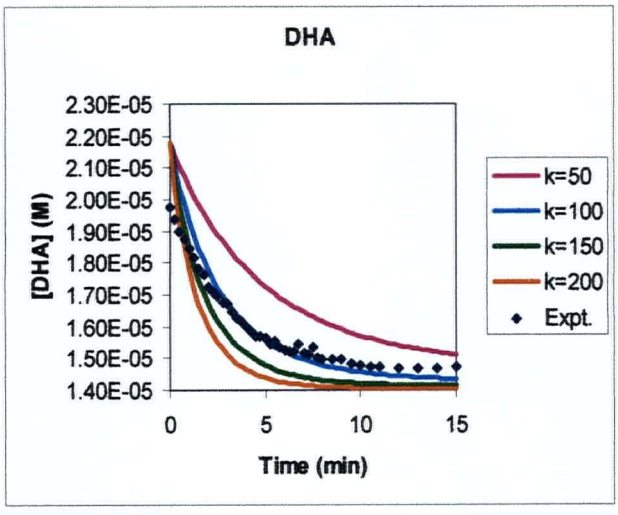
c)

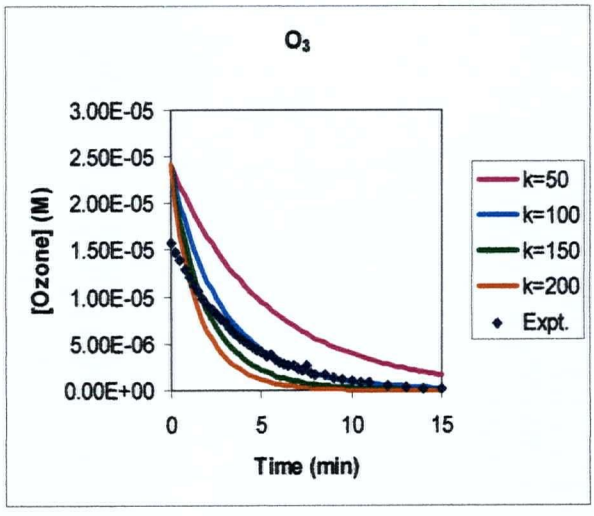


h)

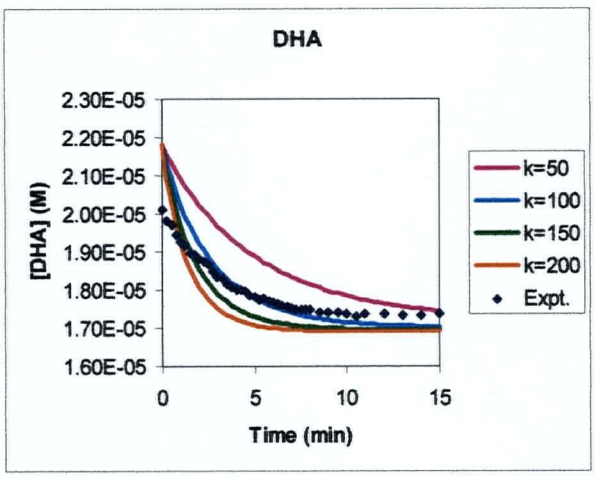


d) $[O_3]_0 = 0.0242$ mM i)





e) $[O_3]_0 = 0.0150$ mM j)



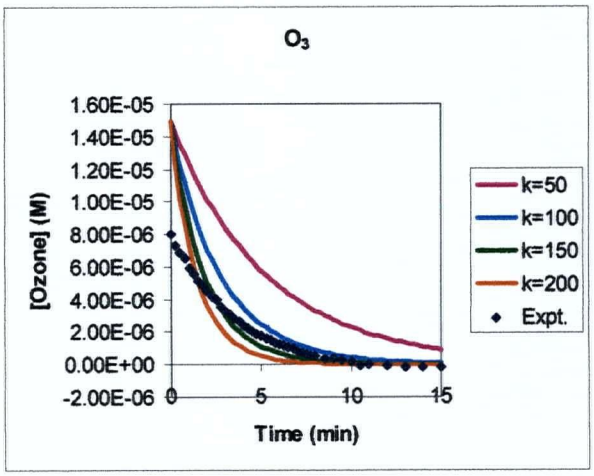
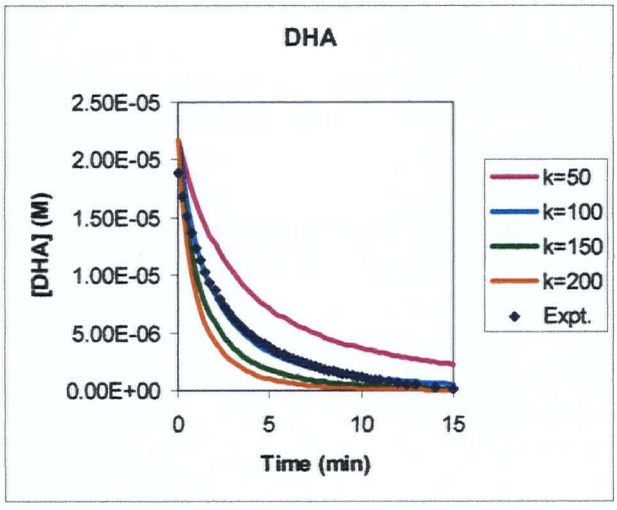


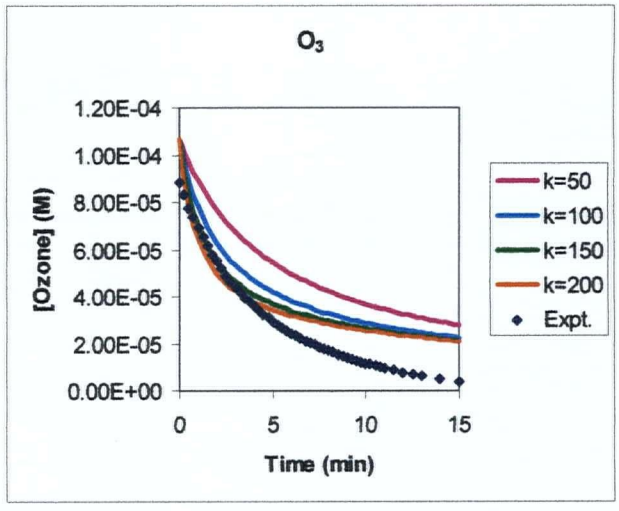
Figure 7.8: Additions of O_3 to DHA, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 1:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)

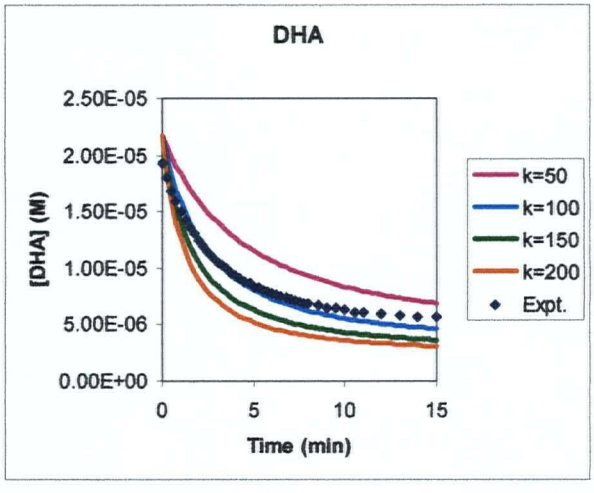


f)

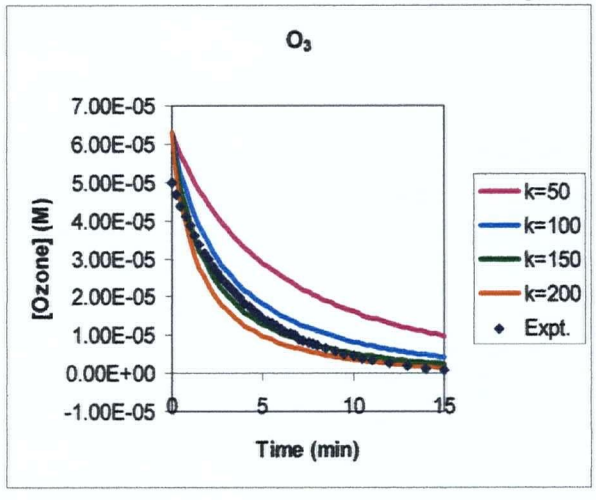


$[O_3]_0 = 0.0629$ mM

b)

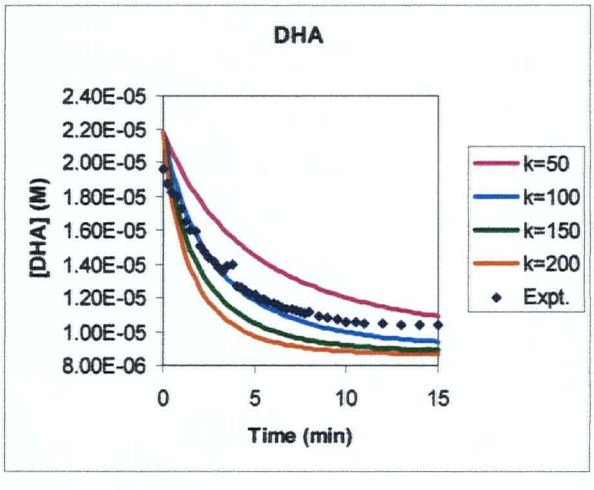


g)

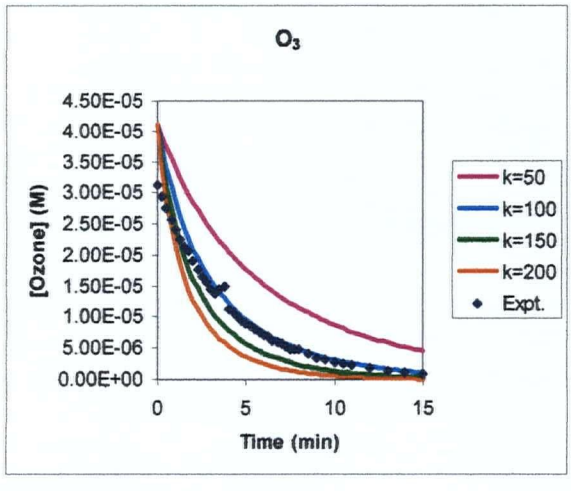


$[O_3]_0 = 0.0411$ mM

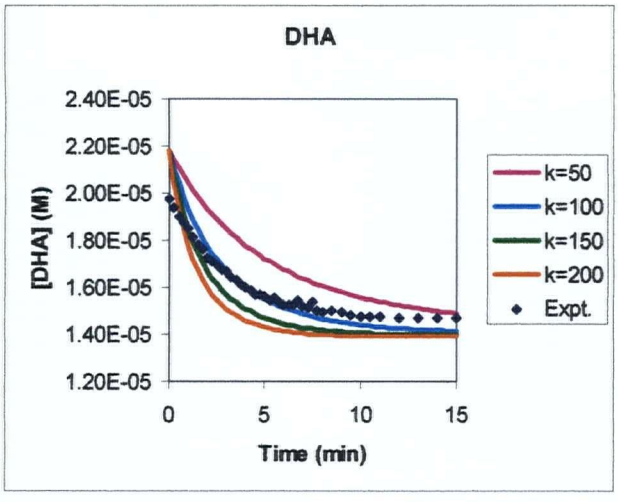
c)

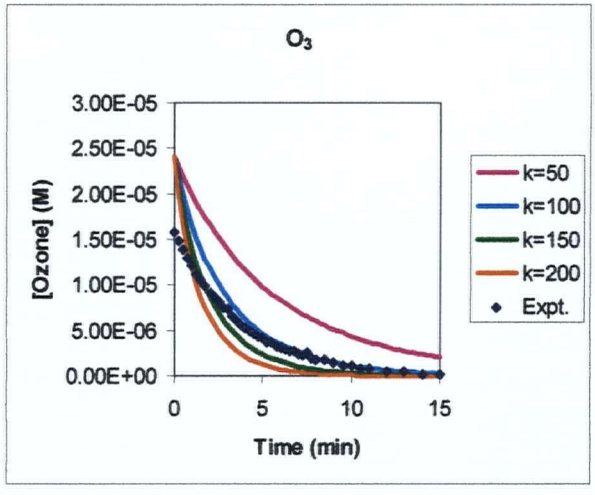


h)

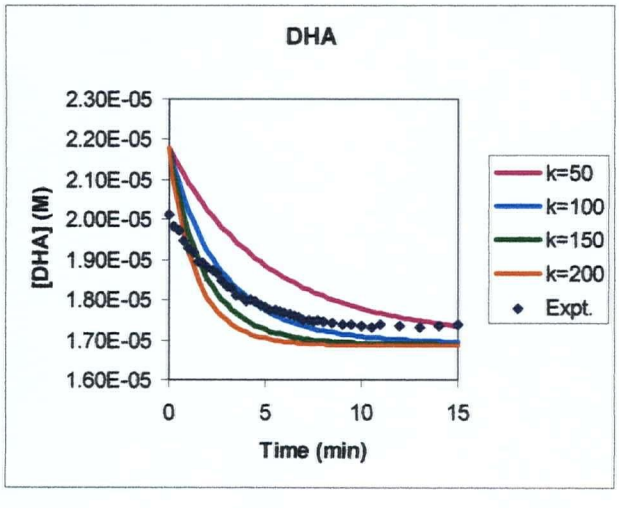


d) $[O_3]_0 = 0.0242$ mM i)





e) $[O_3]_0 = 0.0150$ mM j)



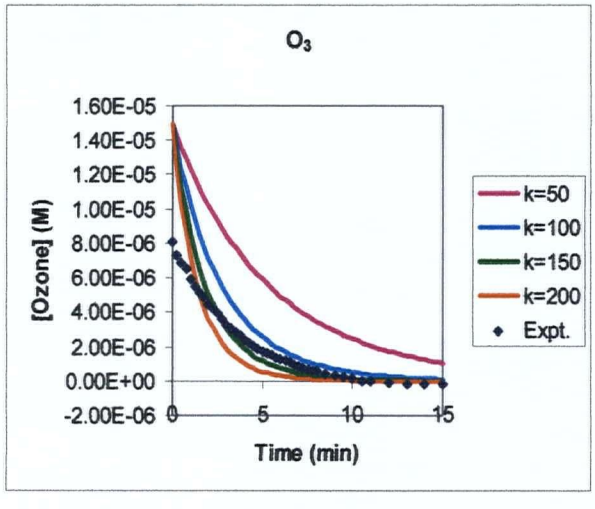
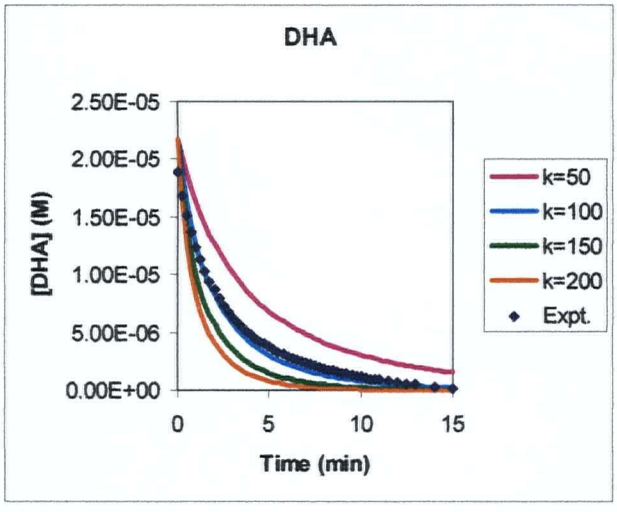


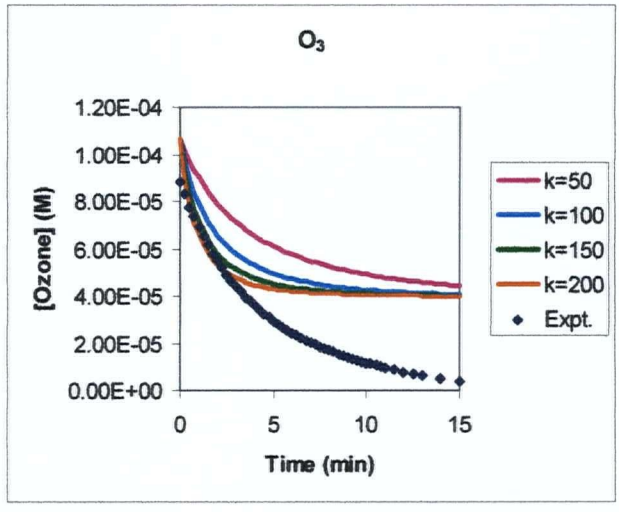
Figure 7.9: Additions of O_3 to DHA, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 0:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)

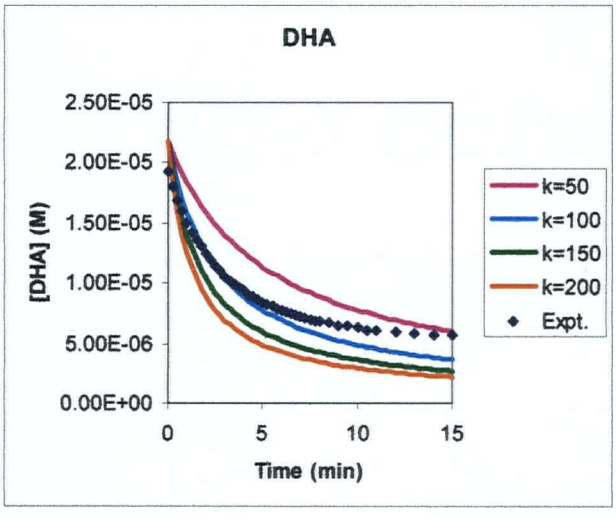


f)

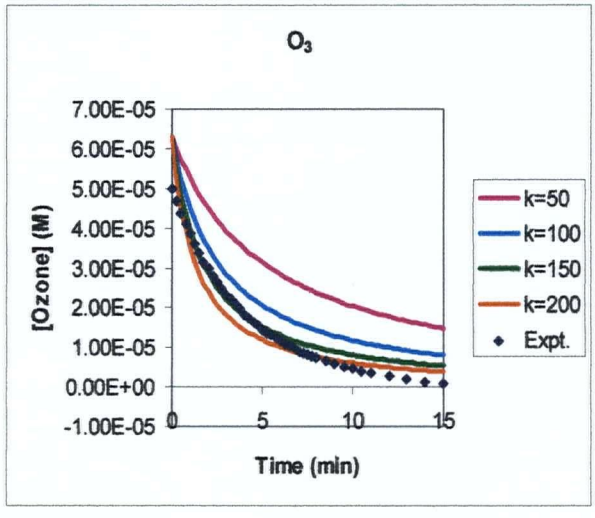


$[O_3]_0 = 0.0629$ mM

b)

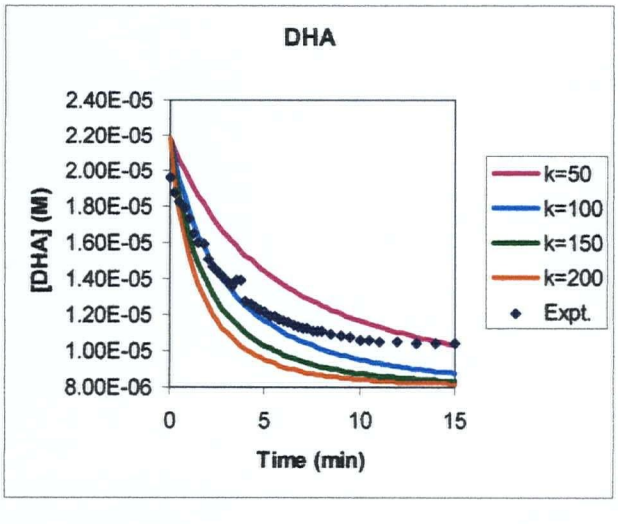


g)

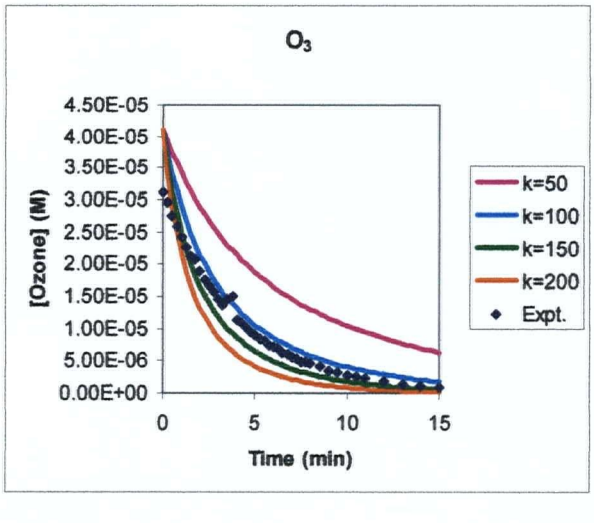


$[O_3]_0 = 0.0411$ mM

c)

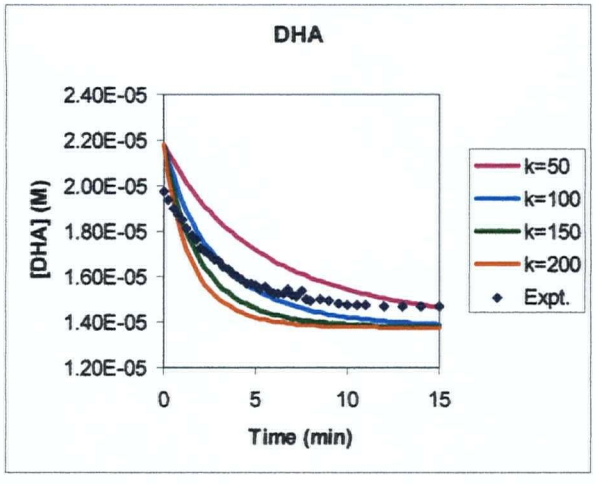


h)

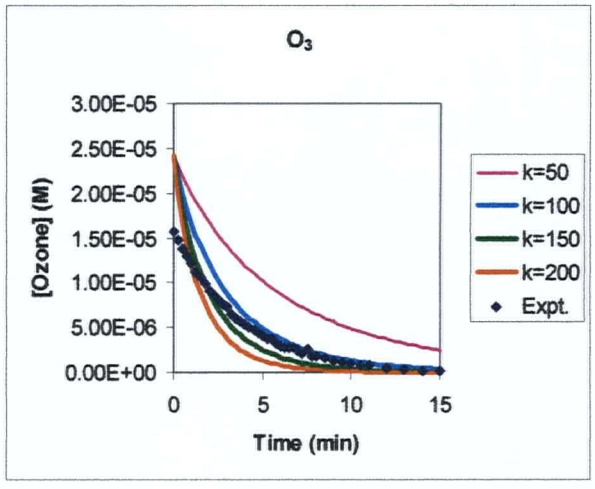


$[O_3]_0 = 0.0242$ mM

d)

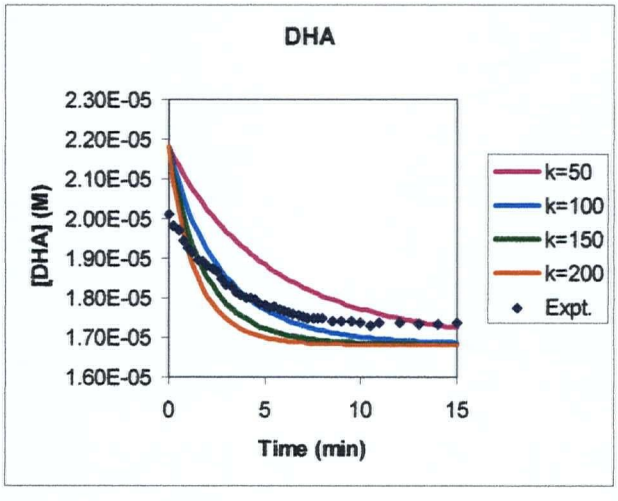


i)



$[O_3]_0 = 0.0150$ mM

e)



j)

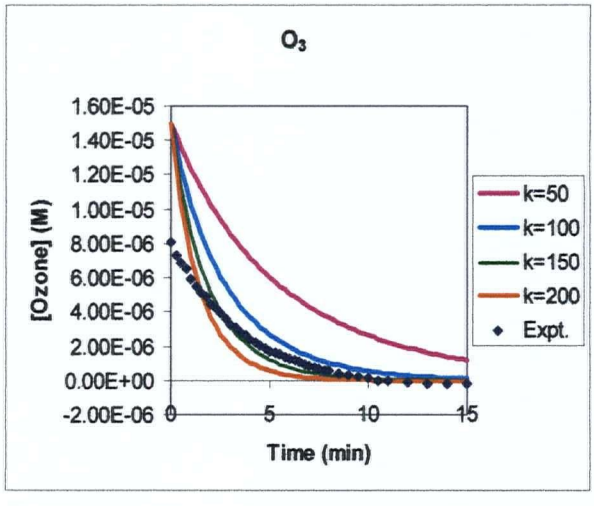
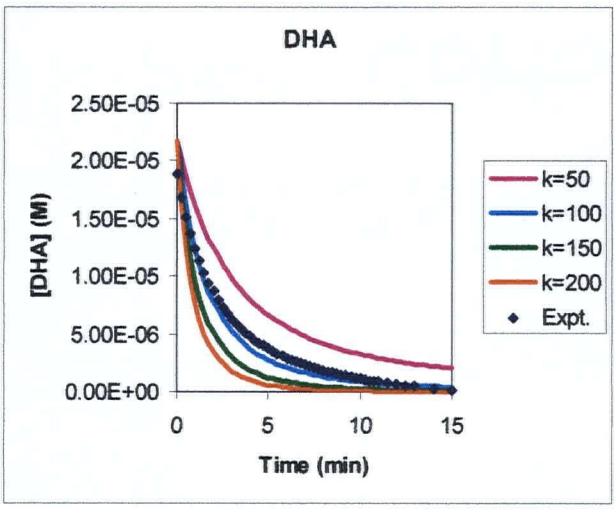


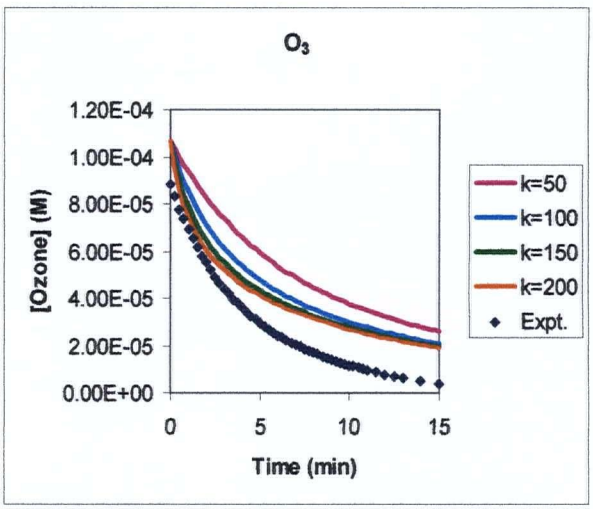
Figure 7.10: Additions of O_3 to DHA, modeled with O_3:DHA of 2:1, H_2O_2:DHA of 2:1. 6.41 mM t-butanol radical scavenger, pH 6.5.

$[O_3]_0 = 0.107$ mM

a)

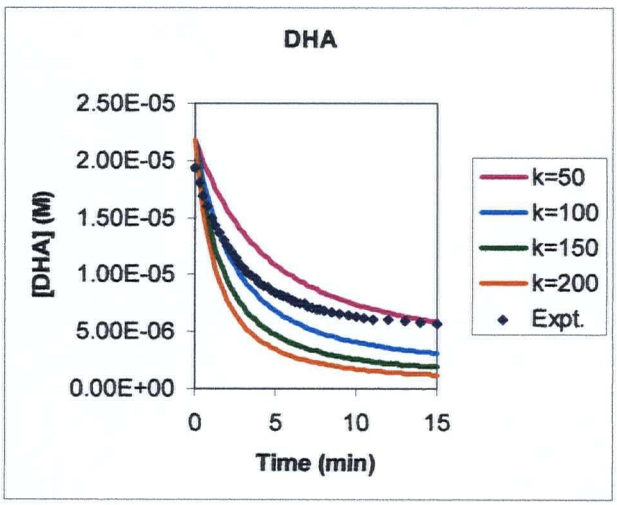


f)

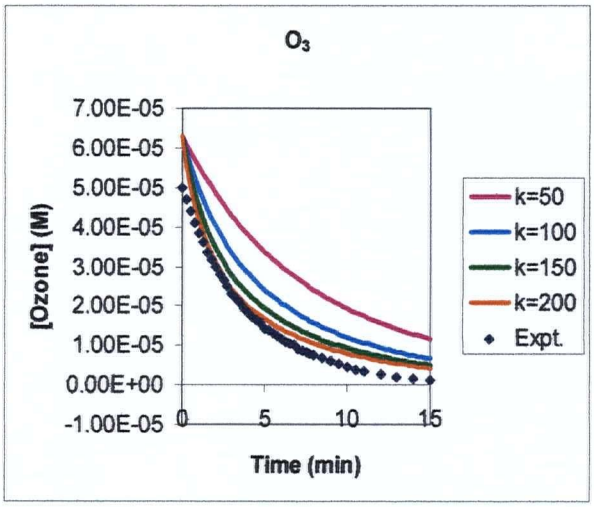


$[O_3]_0 = 0.0629$ mM

b)

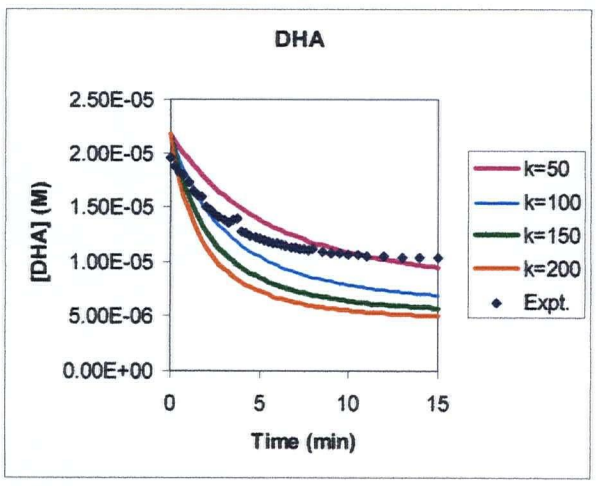


g)

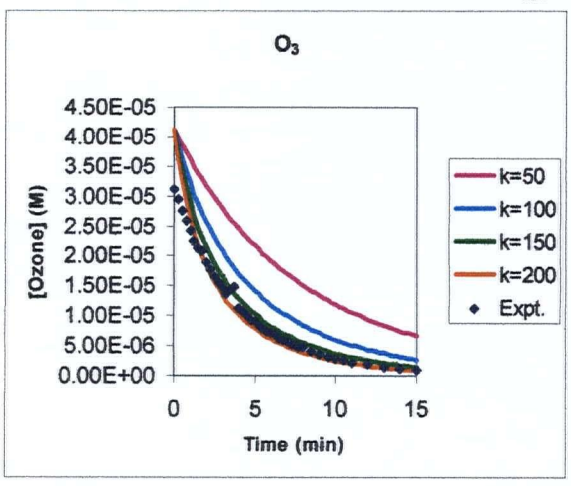


$[O_3]_0 = 0.0411$ mM

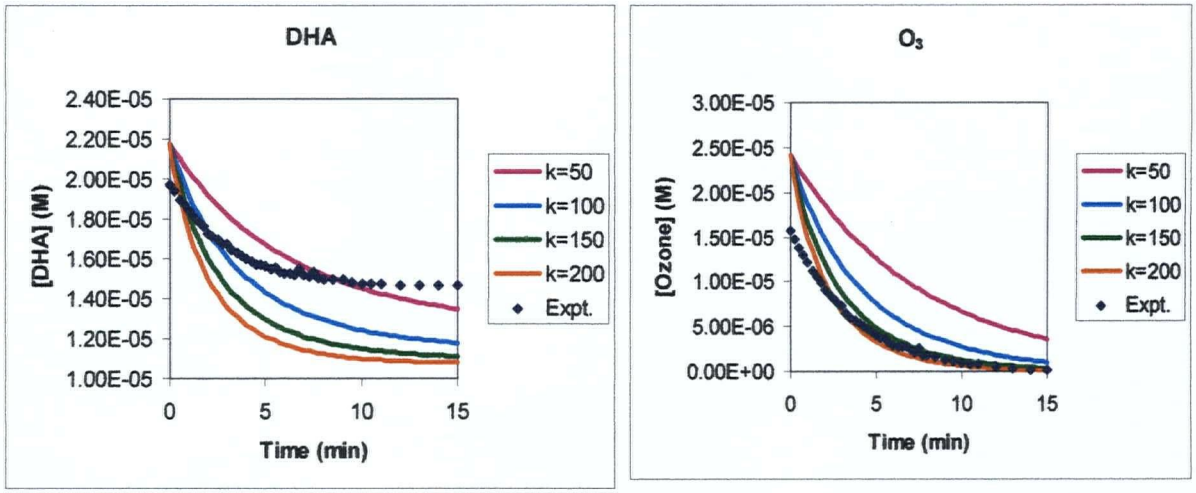
c)



h)



d) $[O_3]_0 = 0.0242$ mM i)



e) $[O_3]_0 = 0.0150$ mM j)

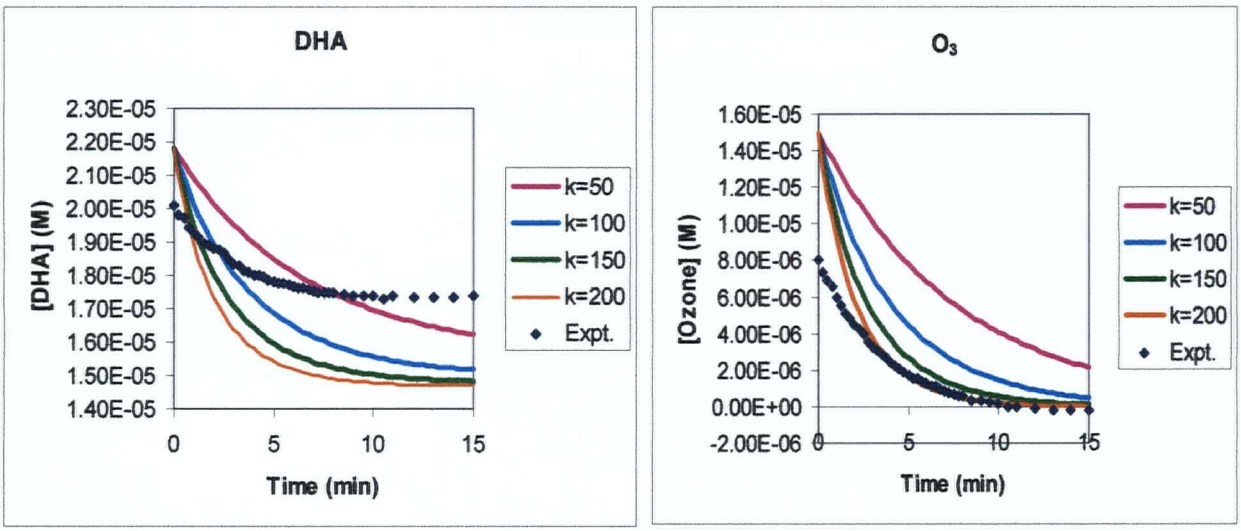
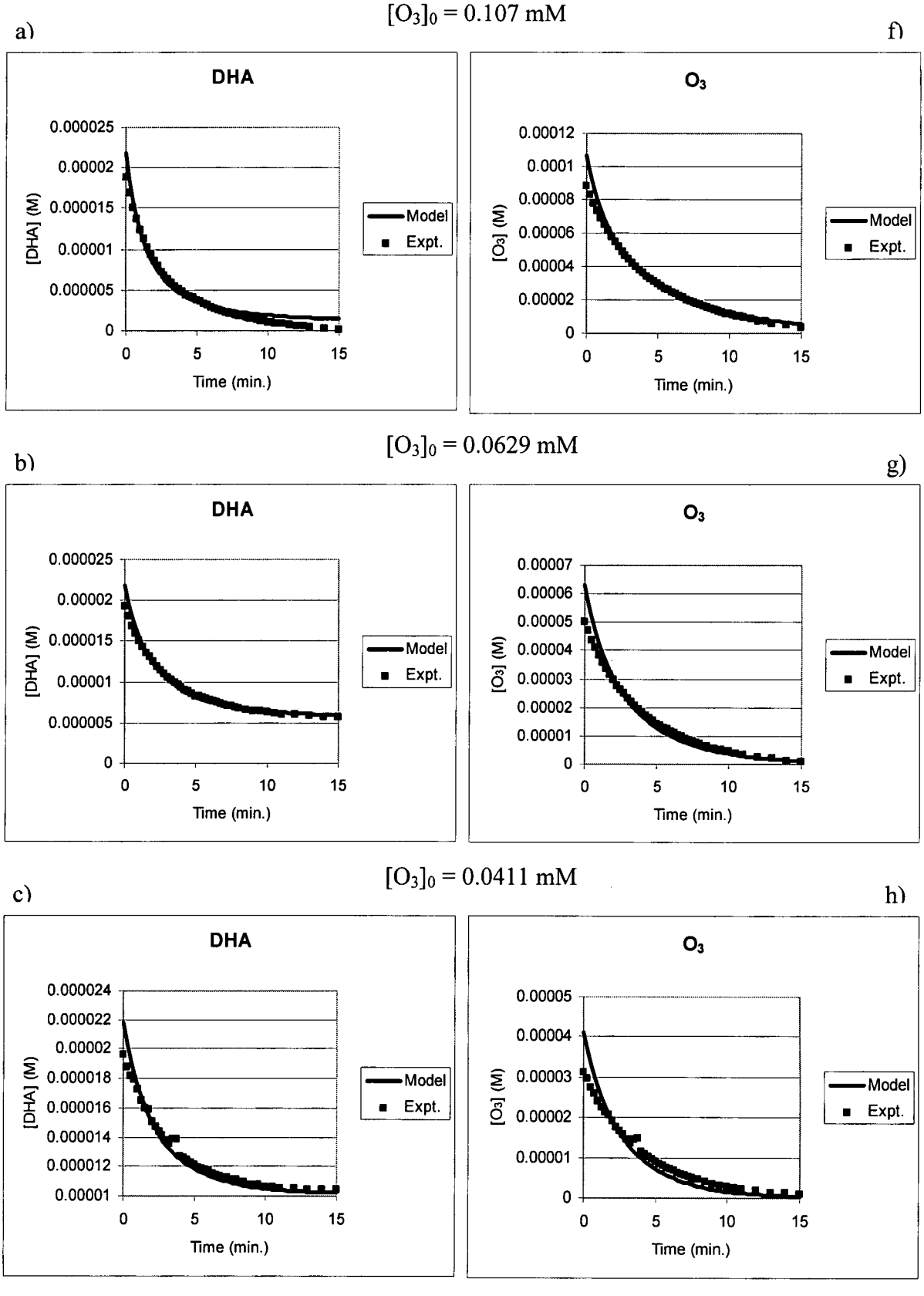
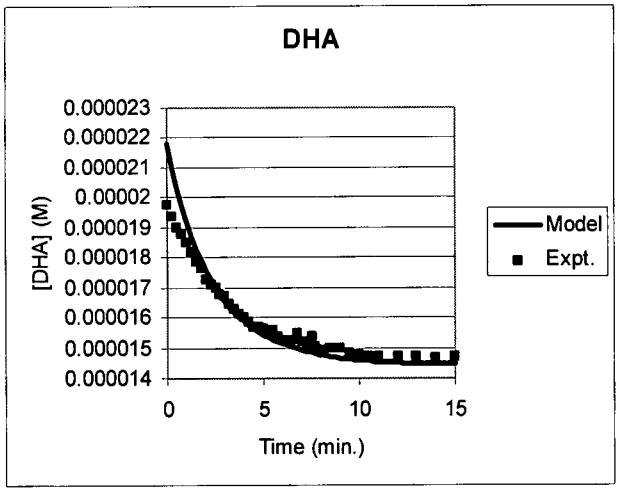


Figure 7.11: Comparison of experimental and modeled ($k=1.1\cdot10^2$ L/mol·s) results for additions of O_3 to DHA, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1. 6.41 mM t-BuOH radical scavenger, pH 6.5.

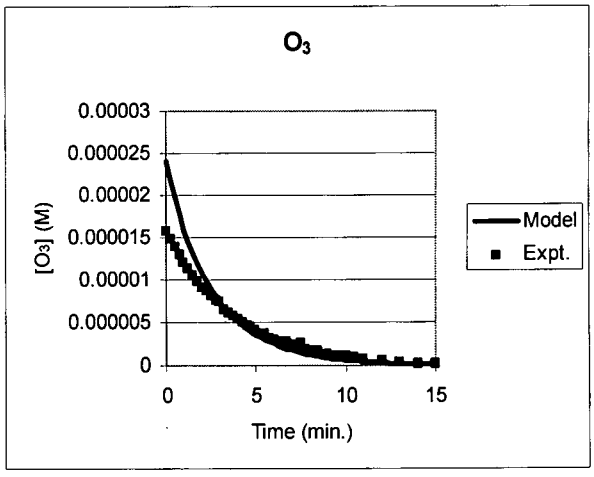


$[O_3]_0 = 0.0242$ mM

d)

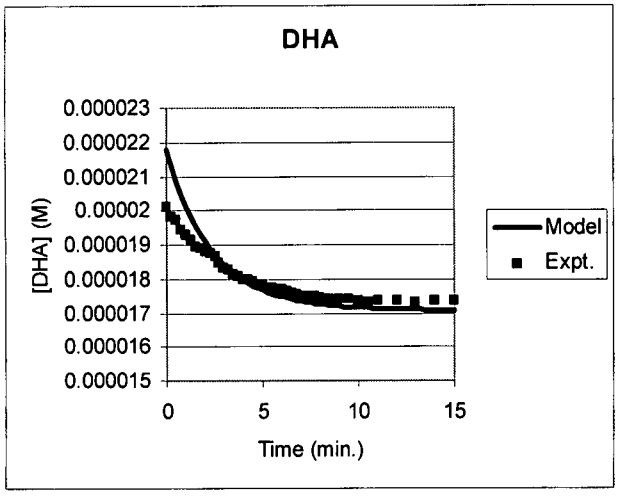


i)



$[O_3]_0 = 0.0150$ mM

e)



j)

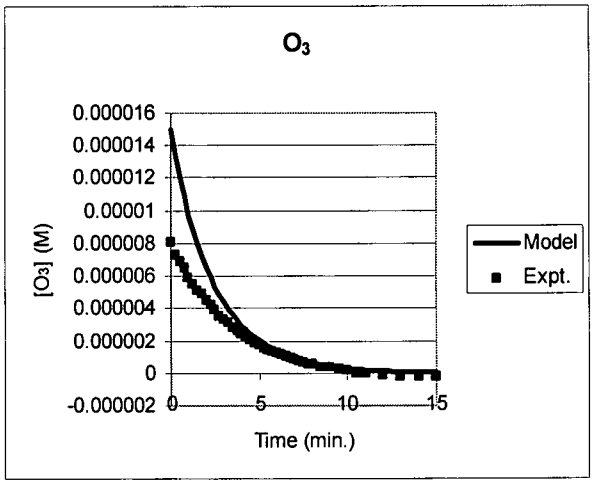
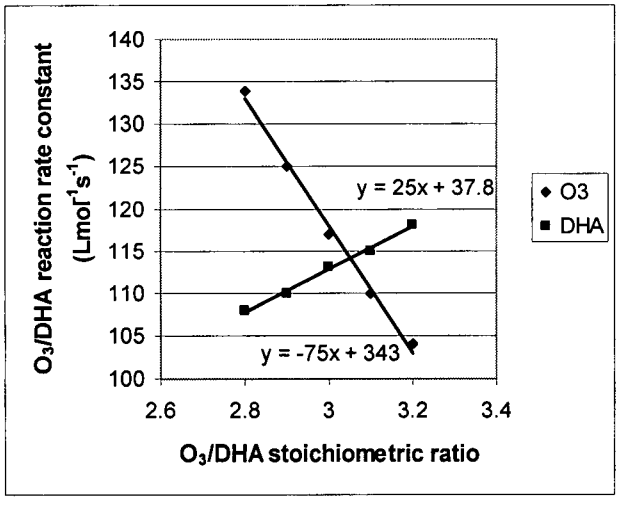
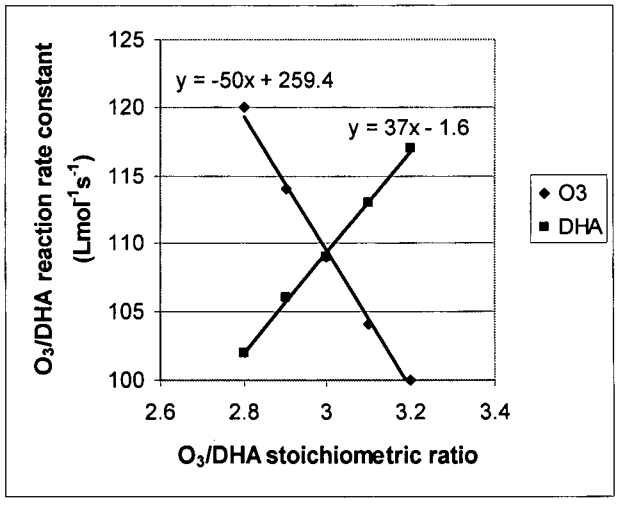


Figure 7.12: Reaction rate constants yielding best fit values for DHA and O_3 plots, as a function of the O_3:DHA ratio used in the model.

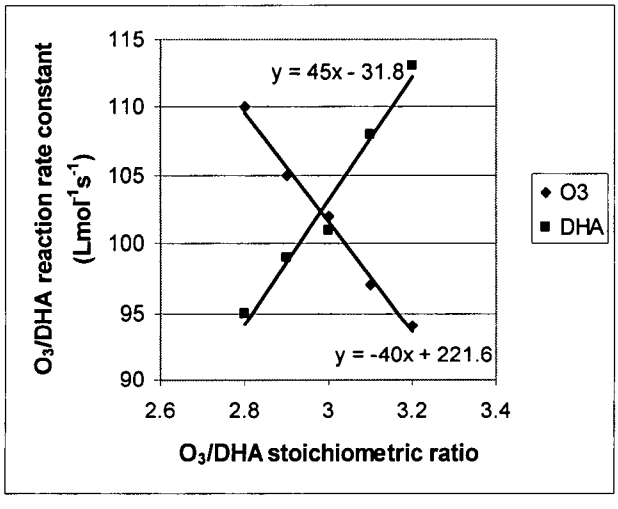
a) $[O3]_0 = 0.107$ M



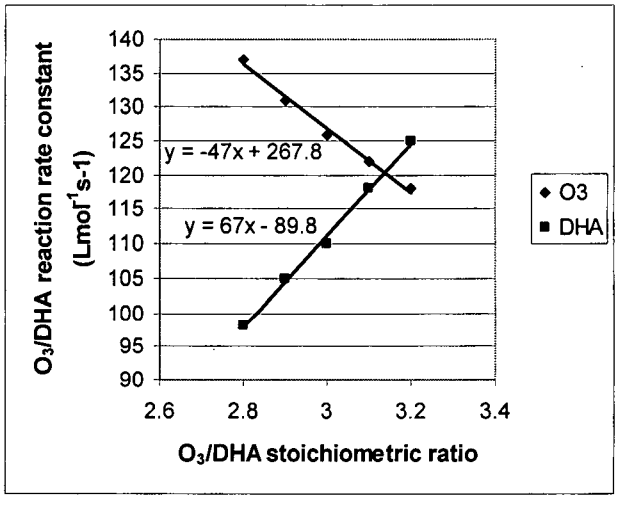
b) $[O3]_0 = 0.0629$ M



c) $[O3]_0 = 0.0411$ M



d) $[O3]_0 = 0.0242$ M



7.2 Influence of increased radical production at basic pH

The experiments at pH 6.5 indicated a ratio of 3:1 for ozone:DHA consumed. For the value of moles H_2O_2 produced per mole DHA consumed, both 2:1 and 3:1 provide an adequate fit to the data. The 3:1 ratio is favoured because of lower least squares values compared to the 2:1 ratio and the closer values for the reaction rate constant measured separately from the ozone and DHA plots. The next series of experiments were carried out at a pH of 8.1 with t-butanol as radical scavenger. For the runs done at pH 8.1, modeling was performed for both ratios in order to determine if one of the ratios provided a better fit with the experimental results. Since the value for the product absorbance factor for this set of experiments was found not to be constant, the experimental curves seen from the experiments at pH 6.5 are not calculated here, because they would not give accurate representations of the DHA and ozone concentrations over time. As a result, the comparison of the ability of the two models to fit the experimental data is limited to examining the measured final DHA values.

The DHA results show important differences between the two models using the different hydrogen peroxide:DHA ratios (Figures 7.13 & 7.14). This results from the interaction of ozone with the ionized form of hydrogen peroxide, HO_2^- and a resulting breakdown product, O_2^-. The predominant reactions in the system are:

(1) $DHA + 3\ O_3 \rightarrow Products + (3 \text{ or } 2)\ H_2O_2$

(2) $H_2O_2 \leftrightarrow H^+ + HO_2^-$

(3) $O_3 + HO_2^- \rightarrow \cdot O_3^- + \cdot HO_2$

(4) $\cdot HO_2 \leftrightarrow H^+ + \cdot O_2^-$

(5) $O_3 + \cdot O_2^- \rightarrow \cdot O_3^- + O_2$

The hydrogen peroxide that is produced by the oxidation of DHA (1) is subject to the equilibrium of (2). The pk_a of H_2O_2 is 11.62 (Weast, 1990). At the pH of 8.1, the equilibrium is

Figure 7.13: Measured and modeled final DHA concentrations for additions of O_3 to DHA, pH 8, 6.41mM t-butanol, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

Note: Legend values are the reaction rate constants DHA/O_3, DHA/·OH.

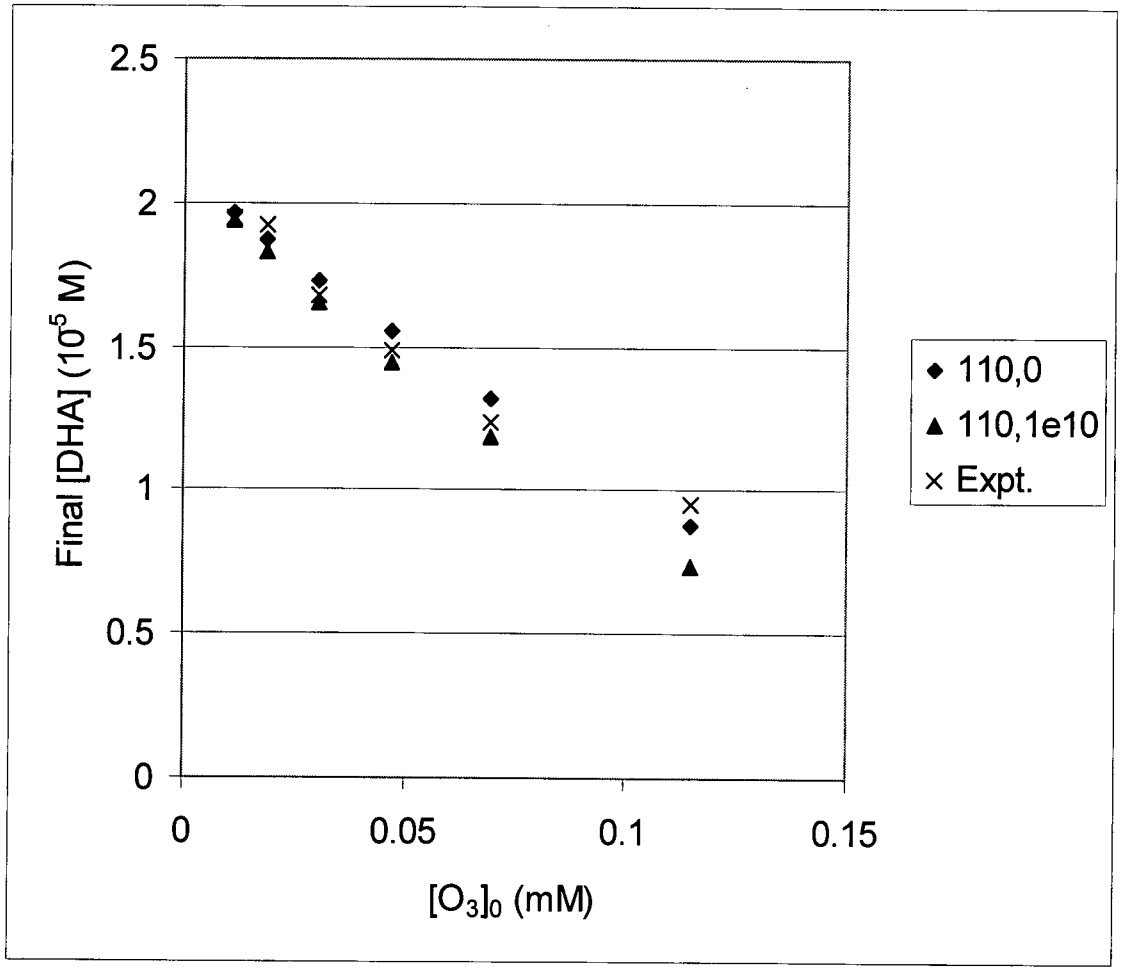
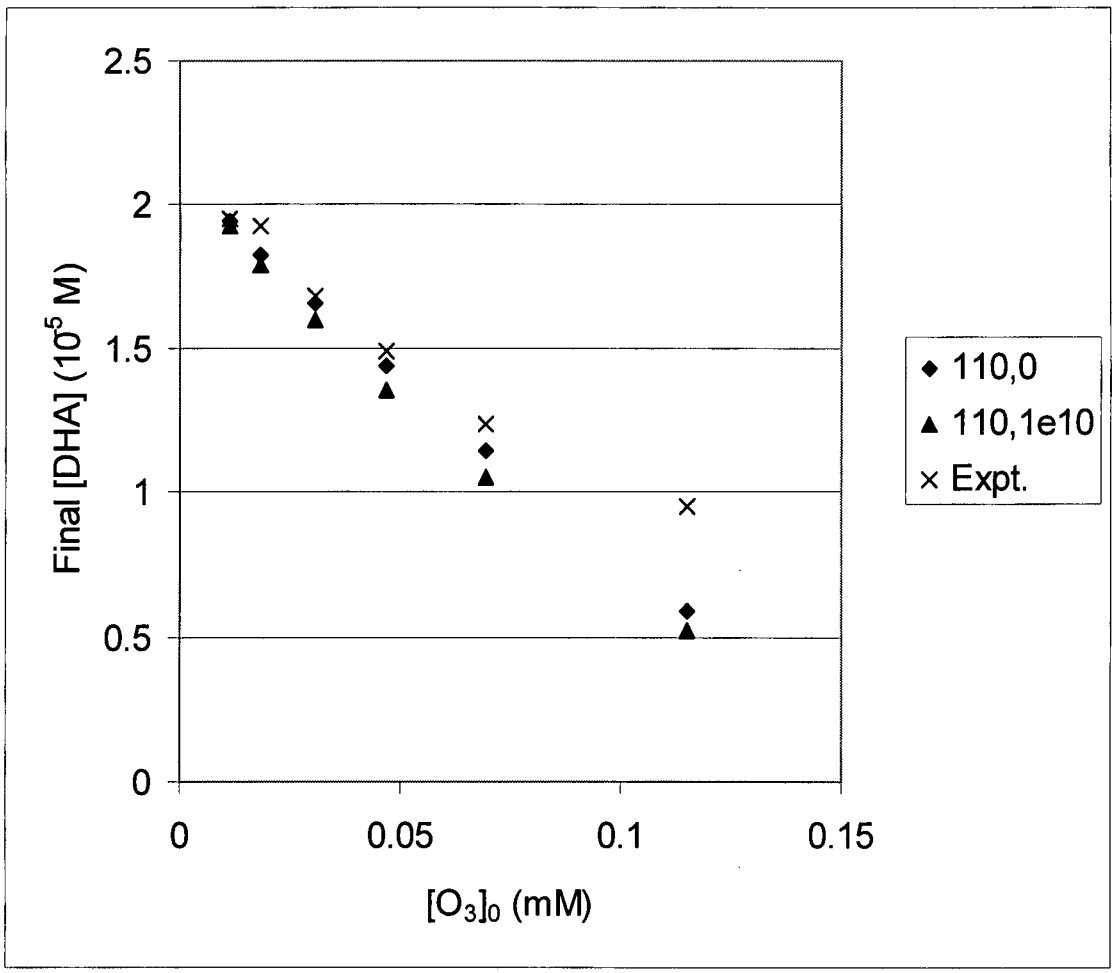


Figure 7.14: Measured and modeled final DHA concentrations for additions of O_3 to DHA, pH 8, 6.41mM t-butanol, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 2:1.

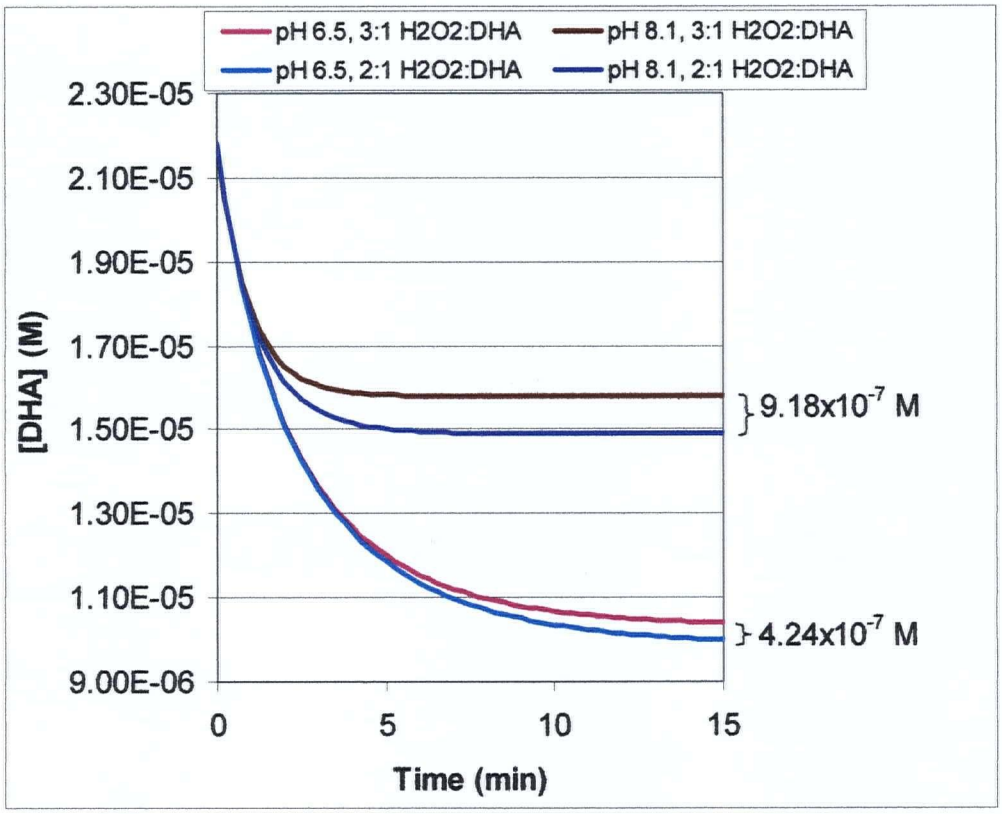
Note: Legend values are the reaction rate constants DHA/O_3, DHA/·OH.



still heavily weighted to the un-ionized form ($[HO_2^-]/[H_2O_2]=3\cdot10^{-4}$). Due to the rapid reaction rate between ozone and HO_2^- ($k=5.5\cdot10^6$ L/mol·s), though, the small amounts of the ionized form that are produced lead to an important amount of ozone being consumed by HO_2^- according to reaction (3), and generating a $\cdot HO_2$ radical. The pKa of the HO_2/O_2^- system is 4.8 (4) (Staehelin & Hoigné, 1985); thus, for all pH values at which experiments were performed, the equilibrium is such that any HO_2 generated can be considered to immediately ionize to O_2^-. The O_2^- then reacts with another ozone molecule. The model with a 3:1 H_2O_2:DHA ratio results in an increased consumption of ozone by radical byproducts compared to the model with a 2:1 ratio and leads to an increased residual DHA. This difference between the two models can be used in determining which of the two H_2O_2:DHA ratios provides a better fit for the experimental results. As previously mentioned, the results for the two ratios at a pH of 6.5 are close enough that it is difficult to confidently state which one should be chosen. But at a pH of 8.1, the shift in the equilibrium of the H_2O_2/HO_2^- system is sufficient to result in a greater consumption of ozone by reactions (3) and (5) for an additional H_2O_2 molecule produced. This greater consumption of ozone will lead to a greater difference between final DHA values at a pH of 8.1 than at 6.5. For example, Figure 7.15 shows the plot of DHA concentration vs. time for a series of modeled runs at varying pH values and H_2O_2:DHA ratios. It is clear that a greater difference exists for the model run at a pH of 8.1.

This difference in the model is useful in determining the correct H_2O_2:DHA ratio. All of the additions modeled with a 2:1 H_2O_2:DHA ratio underestimate the final DHA value as measured by GC (Figure 7.14), even a model with no reaction between DHA and ·OH. Given the high reactivity of ·OH with organic compounds, this is quite unrealistic. On the other hand, the model with a 3:1 H_2O_2:DHA ratio (Figure 7.13) provides a much better fit with the experimental results. For 4 of the 6 additions, the final concentration of DHA as measured by GC fits the value obtained by the 3:1 H_2O_2:DHA model with a DHA/·OH reaction rate constant

Figure 7.15: Effect of change of pH on the difference between modeled runs with different H_2O_2:DHA ratios. Reaction rates used: DHA/O_3 = 110 L/mol·s, DHA/·OH = $5 \cdot 10^9$ L/mol·s, DHA/·PO_4 = 0 L/mol·s.



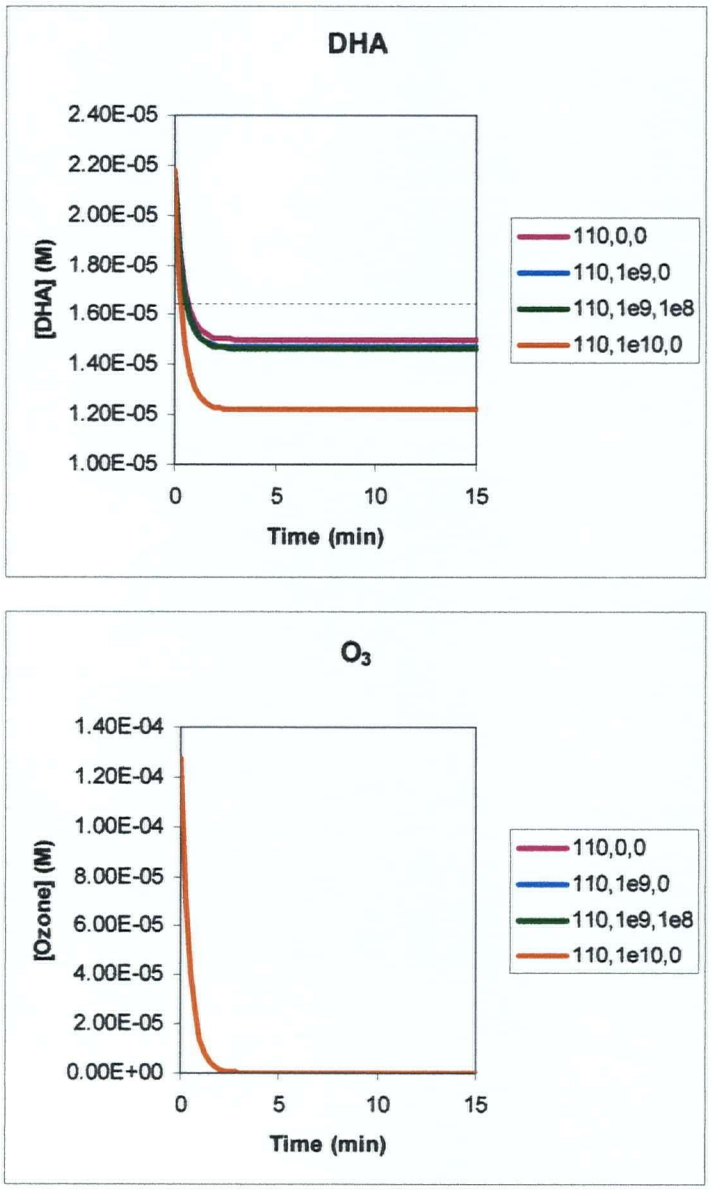
between $1 \cdot 10^9$ and $1 \cdot 10^{10}$ L/mol·s (specifically, the values calculated are $6 \cdot 10^9$, $6 \cdot 10^9$, $6 \cdot 10^9$, and $9 \cdot 10^9$ L/mol·s). The values were obtained by running the model with a DHA/O_3 reaction rate constant of 110 L/mol·s and varying the DHA/·OH reaction rate constant until the model yielded a final DHA concentration value equal to the measured value. Table 7.4 lists a brief selection of reaction rates of cyclic and aromatic compounds with hydroxyl radicals. These compounds were selected because of their structural similarities with certain sections of the DHA molecule. All of the compounds listed have a reaction rate constant with ·OH greater than $5 \cdot 10^9$ L/mol·s. For the addition with the highest initial ozone concentration, although both models calculate a lower final DHA concentration than was experimentally measured, the model with a 3:1 H_2O_2:DHA ratio is much closer to the value. The same argument holds for the second lowest ozone concentration . This lends further support for the use of the 3:1 H_2O_2:DHA ratio in the model.

Experiments were also performed with a DHA solution at a pH of 9.7; however, the fast rate of decomposition of the ozone at this elevated pH means that it is impossible to accurately model the oxidation of the DHA using the spectrophotometric method used. Figure 7.16 is a typical example of the plots obtained for this experiment. The final concentration of the DHA, as determined by the model, consistently underestimated the value obtained experimentally, even when using a model with no DHA/·OH reaction. The reaction takes under a minute to be completed, even at the highest ozone concentration. Localized effects during the addition of the aqueous ozone solution to the DHA solution can make a significant difference when compared to the model, which assumes perfect instantaneous mixing of the two solutions.

Table 7.4: Rate constants for reaction between ·OH and selected aromatic and cyclic compounds

Compound	k (L/mol·s)
Toluene	5.1×10^9
Ethylbenzene	7.5×10^9
Cumene (Isopropylbenzene)	7.5×10^9
o-Xylene	6.7×10^9
m-Xylene	7.5×10^9
1,2,3-Trimethylbenzene	7.0×10^9
Cyclohexane	6.1×10^9
Cyclohexanecarboxylate ion	5.5×10^9

Figure 7.16: Addition of O_3 to DHA, pH 9.7, 6.41mM t-butanol, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1, $[O_3]_0 = 0.127$ mM.



7.3 Use of HCO_3^-/CO_3^{2-} as radical scavenger

Since bicarbonate/carbonate can be found in natural waters, a set of DHA oxidation experiments was performed with a bicarbonate/carbonate buffer system. In addition to acting as buffers, HCO_3^- and, to a greater extent, CO_3^{2-} are radical scavengers that will serve to slow the rate of oxidation of DHA by ·OH (Hoigné and Bader, 1976). According to the model of Nemes et al. (2000b), the reaction rate constants of ·OH with HCO_3^- and CO_3^{2-} are $1 \cdot 10^7$ L/mol·s and $1 \cdot 10^8$ L/mol·s, respectively. Over the pH range studied in the HCO_3^-/CO_3^{2-} experiments, however, HCO_3^- is the main scavenging species. Even at the highest pH of 9.2 which was studied, the ratio of $[CO_3^{2-}]/[HCO_3^-]$ is approximately 0.046, leading to approximately 30% of the ·OH scavenging being done by CO_3^{2-}.

Since the concentration of DHA and ozone could not be followed over the course of the reaction, the fit of the reaction model can only be determined by comparing the final DHA concentrations as determined by the model with the experimentally-determined DHA concentrations. The experiments at all three pH levels that were examined (Figures 7.17-7.19) confirm that a model with: O_3/DHA reaction rate constant of $1.1 \cdot 10^2$ L/mol·s, 3:1 O_3/DHA ratio, 3:1 H_2O_2/DHA ratio and a ·OH/DHA constant in the range of $1 \cdot 10^9$ to $1 \cdot 10^{10}$ L/mol·s is able to properly fit the ozone/DHA reaction. Running the model, assuming no phosphate radical/DHA reactions, the ·OH/DHA rate constant values that resulted in the measured final DHA values clustered around a value of $2 \cdot 10^9$ L/mols. In order to determine whether phosphate radical reactions have an important effect on the reaction, the model was re-run, decreasing the ·OH/DHA constant while increasing the phosphate radical/DHA constant, in order to achieve the same final measured DHA value. Since previous work involving the reaction of phosphate radicals with aromatic compounds has shown that the rate constants for $\cdot HPO_4^-$ and $\cdot PO_4^{2-}$ are generally $\leq 10^8$ L/mol·s, and for $\cdot H_2PO_4$ they are $\leq 10^9$ L/mol·s, these values were taken as the

Figure 7.17: Measured and modeled final DHA concentrations for additions of O_3 to DHA, pH 6.5, 6.41mM HCO_3^-/CO_3^{2-}, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

Note: Legend values are the reaction rate constants DHA/O_3, DHA/·OH.

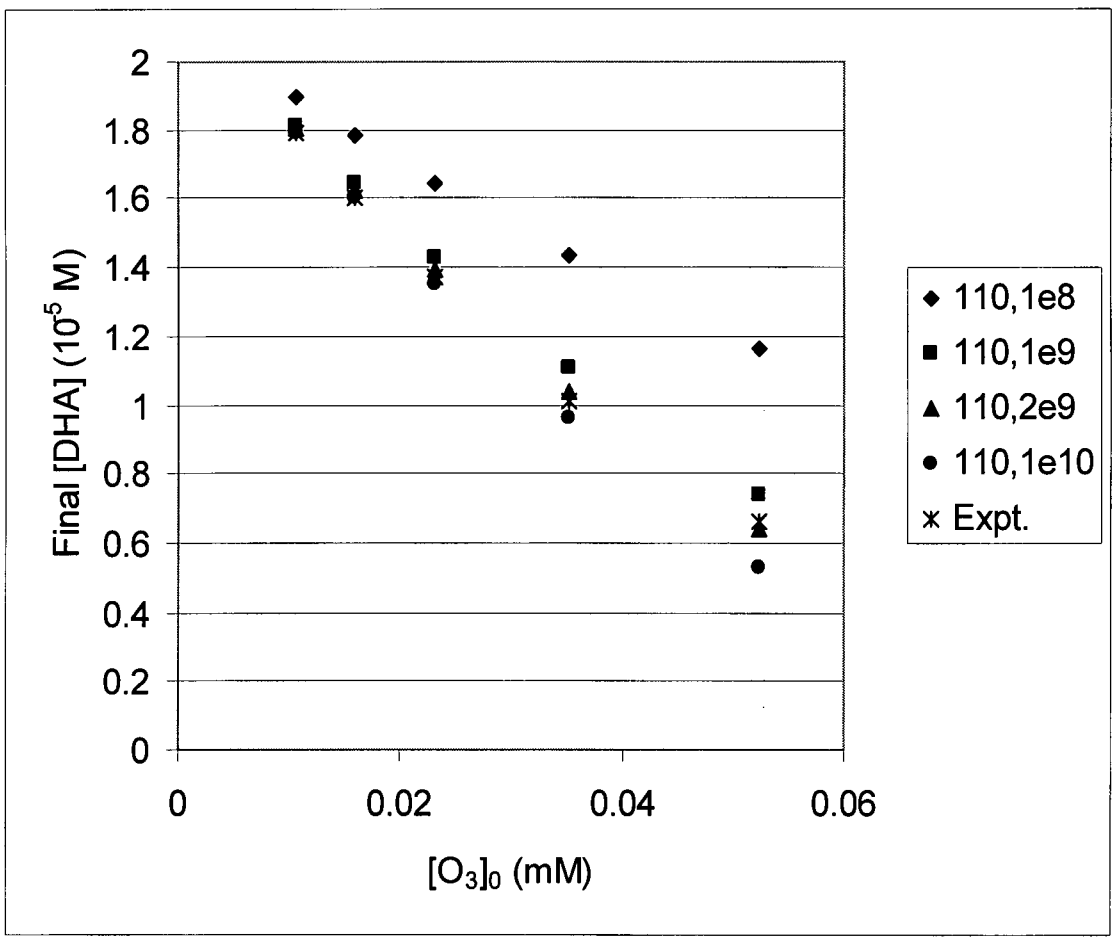


Figure 7.18: Measured and modeled final DHA concentrations for additions of O_3 to DHA, pH 8.1, 6.41mM HCO_3^-/CO_3^{2-}, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

Note: Legend values are the reaction rate constants DHA/O_3, DHA/·OH.

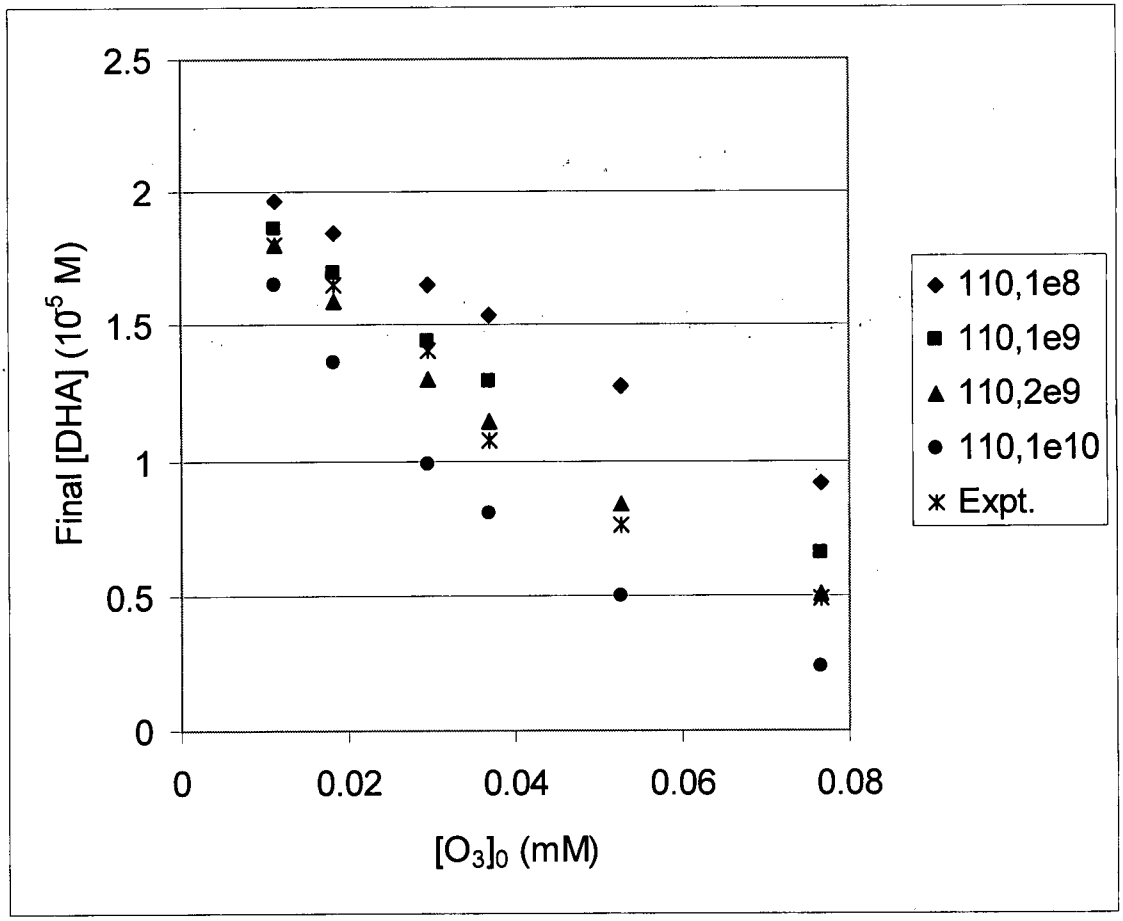
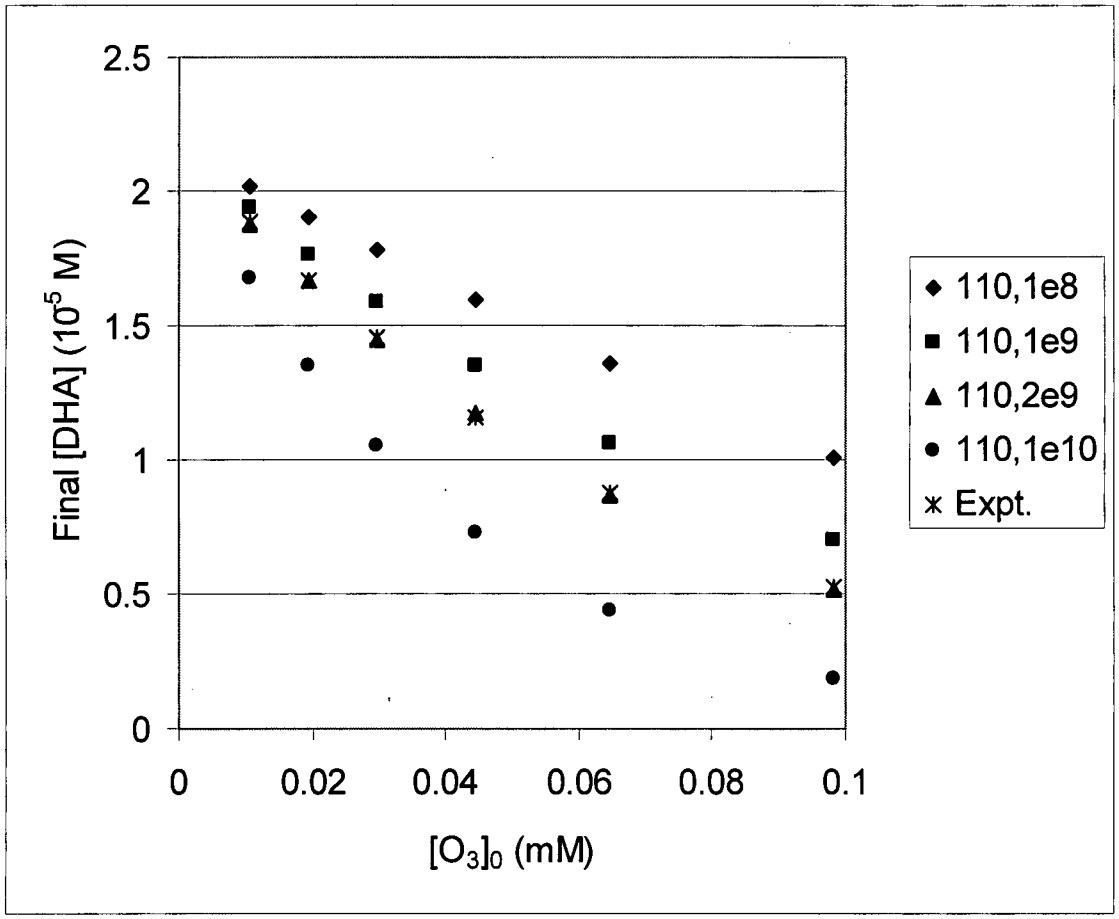


Figure 7.19: Measured and modeled final DHA concentrations for additions of O_3 to DHA, pH 9.2, 6.41mM HCO_3^-/CO_3^{2-}, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

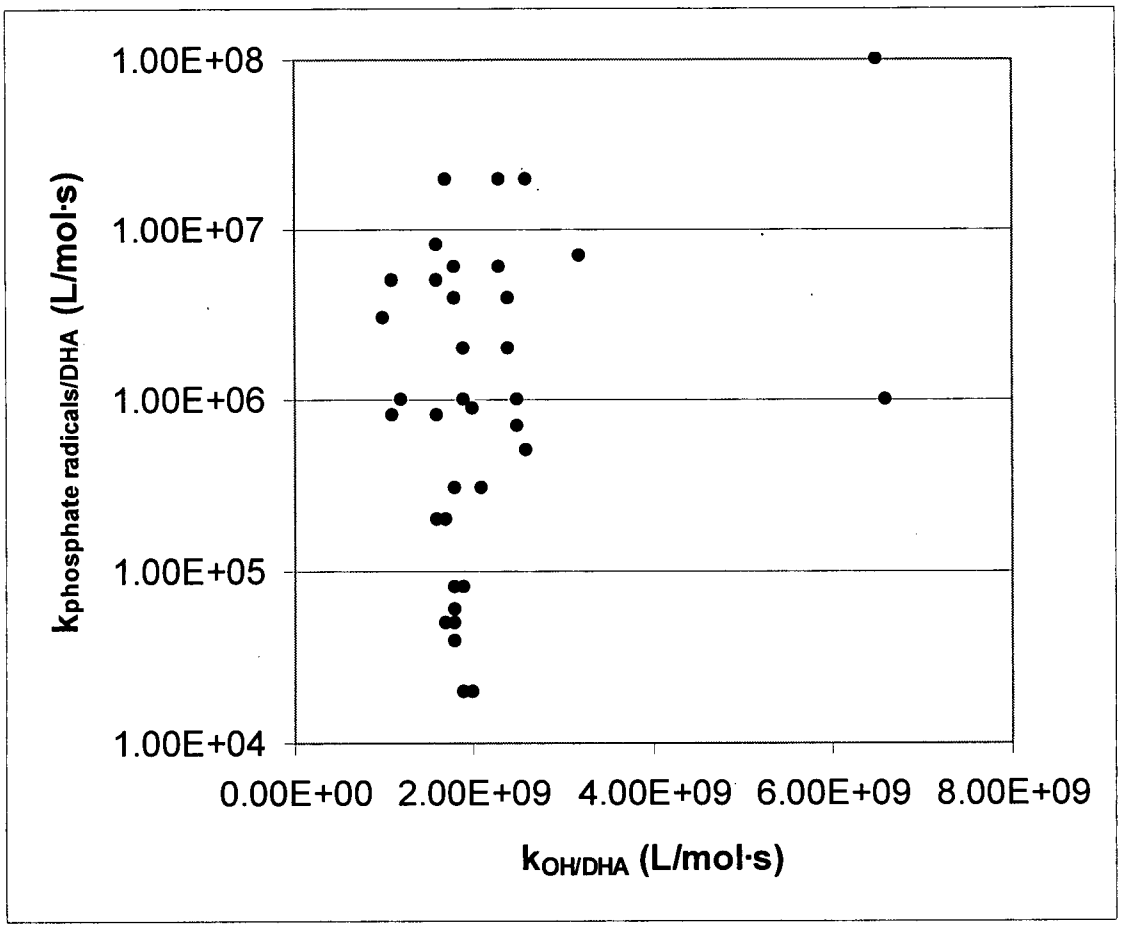
Note: Legend values are the reaction rate constants DHA/O_3, DHA/·OH.



upper limits for the reaction rates with DHA. Figure 7.20 illustrates the results obtained for all experiments run with HCO_3^-/CO_3^{2-} as radical scavenger. Varying the phosphate radical/DHA rate constant between 0 and 10^8 L/mol·s had an effect of, at most, $0.4 \cdot 10^9$ L/mol·s on the calculated ·OH/DHA rate constant. Given that important differences in reaction rates are usually given in terms of orders of magnitude, this is quite a modest difference.

By far, the most common techniques used to obtain accurate values for reaction rates of free radicals are pulse radiolysis and flash photolysis combined with optical detection (Buxton, 1999), rather than an indirect mathematical method as used here. The value of $2 \cdot 10^9$ L/mol·s for the ·OH/DHA rate constant as presented here must be considered only an estimate of the actual value. The calculations made in this work are subject to a number of uncertainties concerning the radical chemistry of the system that make it impossible to directly and accurately calculate the ·OH/DHA rate constant. As mentioned in the Materials and Methods section (p. 63), a number of assumptions were made regarding the chemistry of the system, in order to either simplify the model or because the required data are not known. With t-butanol as radical scavenger, free radicals are removed to such an extent that their effect on the reaction system can be reduced to insignificant levels. In this way, DHA is oxidized almost exclusively by ozone, as previously discussed. The scavenging ability of HCO_3^-/CO_3^{2-} ($k_{\cdot OH/bicarbonate} = 10^7$ L/mol·s, $k_{\cdot OH/carbonate} = 10^8$ L/mol·s) is much lower compared to t-butanol ($k_{\cdot OH/t\text{-}butanol} = 6 \cdot 10^8$ L/mol·s) however. Because of this, the effect of ·OH and other free radicals is much more prevalent in the HCO_3^-/CO_3^{2-} system than in the t-butanol one. For example, at a pH of 6.5, the model estimates that approximately 25% of the oxidation of DHA is done by hydroxyl radicals, unlike in the t-butanol system where a maximum value of 2% was calculated. As the pH increases, so does the effect of ·OH. At a pH of 8.1, about half of the DHA is oxidized by hydroxyl radicals, and at a pH of 9.2, the fraction increases to about 55%. Because of the increased importance of hydroxyl radicals in the oxidation of DHA, they consequently have a much greater importance in the

Figure 7.20: Effect of phosphate radical reactions on ·OH/DHA reaction rate constant determination, 3:1 H_2O_2:DHA ratio, HCO_3^-/CO_3^{2-} as radical scavenger



model. Uncertainties in certain aspects of the radical chemistry mean that hydroxyl radical concentrations cannot be calculated accurately; thus, the ·OH/DHA reaction rate constant cannot be determined accurately. At best, the value of $2 \cdot 10^9$ L/mol·s derived from Figures 7.17-7.19 can be used in the model, as presently conceived, to predict the final DHA value for a given pH and ozone addition.

7.4 Modeling of Solutions Containing No Radical Scavengers

In a final set of experiments, no radical scavengers were used, and the only reactant involved besides ozone and DHA was the phosphate buffer. Figures 7.21 – 7.23 outline the results obtained in these experiments. For the additions of ozone at a pH of 6.5, the various modeled results for each ozone plot show very little differentiation one from the other, as shown by the almost entirely overlapping curves (Figure 7.21, f-j). That having been said, the modeled curves do fit reasonably well over the experimental ones and again support the use of the O_3/DHA rate constant of $1.1 \cdot 10^2$ L/mol·s and an elevated (i.e., $>10^9$ L/mols) ·OH/DHA rate constant.

Looking at the DHA curves (Figure 7.21, a-e), they initially show good agreement with the previous results, indicating an elevated ·OH/DHA rate constant (Figure 7.21, a-c); however, the last two ozone additions (Figure 7.21, d-e) do not, particularly as judged by the final DHA concentration. Given that the O_3/DHA rate constant is a good estimate and that a ·OH/DHA constant $>10^9$ L/mol·s appears eminently reasonable given previous research work involving the reaction of ·OH and organic molecules, the reason for the deviation of the two last additions from the modeled results is not clear.

Results from additions at pH 8 are similar except in regards to the ·OH/DHA rate constant as implied by the DHA curves. The ozone results as calculated by the models with various ·OH/DHA and phosphate radical/DHA rate constants are virtually identical (Figure 7.22,

f-j). For example, comparing the models with ·OH/DHA rate constants of 10^8 and 10^{10} L/mol·s, the greatest difference between the two occurs during the first minute, and amounts to, at most, 8% of the initial concentration of ozone. Subsequently, the difference quickly narrows. From the DHA models, the ·OH/DHA rate constant suggested by these plots is much lower than an expected value of $>10^9$ L/mol·s. Assuming no reaction of phosphate radicals with DHA, the range for the ·OH/DHA rate constant is determined from the second through fifth additions of ozone (Figure 7.22, a-d) to be in the range of $1.4 - 4.0 \cdot 10^8$ L/mol·s. The results obtained from the final addition (Figure 7.22, e,j) cannot be explained in the context of the model as presented, since a model with no radical/DHA reactions results in a final DHA value lower than the value that was measured.

The reaction of ozone and radicals with DHA at a pH of 9.7 occurred too quickly to make any statements concerning the models and their relationship with the experimental results. As can be seen for all the additions (Figure 7.23), the reaction was completed in approximately 15 seconds. The addition of the ozonated water to the DHA mixture is not instantaneous (addition of the ozonated water took approximately 5 seconds). When a reaction takes place over the course of 15 minutes, the effect of a 5 second addition and mixing period will be minimal; however, when the reaction is completed in 15 seconds, the 5 second period to complete addition of ozone and mixing becomes important. The results that are obtained from an assumption of instantaneous complete mixing cannot be taken to be accurate.

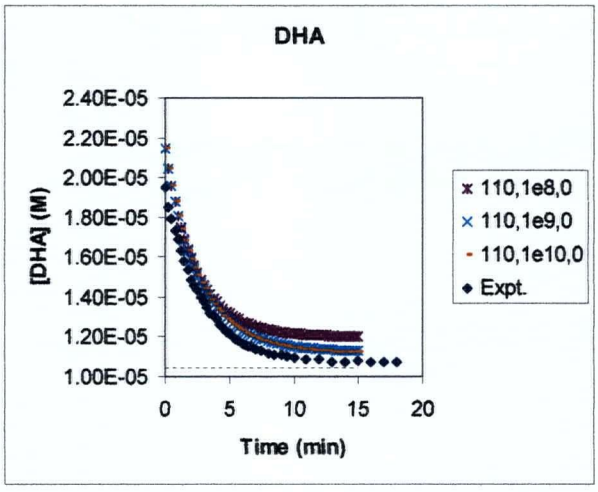
7.5 A note about the product absorbance factors

As previously mentioned (p. 60), the product absorbance factors that were calculated for each combination of pH and radical scavenger conditions were not always constant over the series of different initial ozone concentrations. Two main explanations can be provided for this.

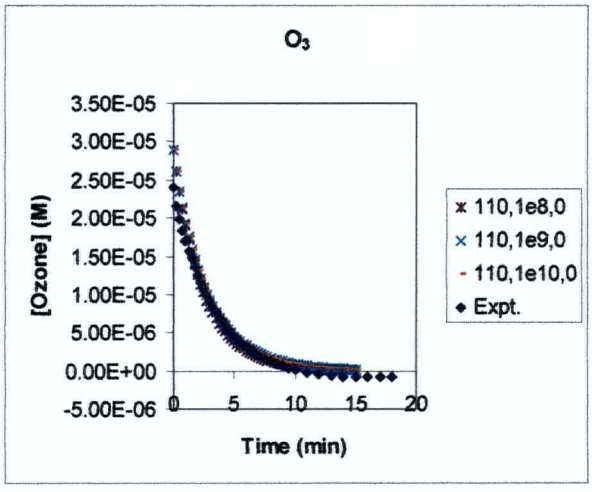
Figure 7.21: Addition of ozone to DHA, pH 6.5, no radical scavenger, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

[O3] = 0.0289 mM

a)

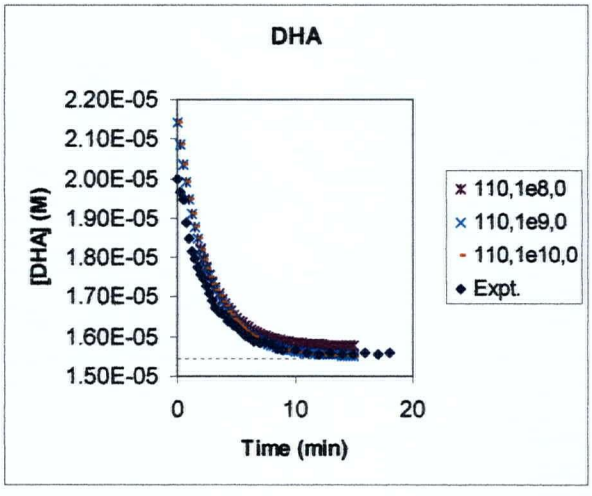


f)

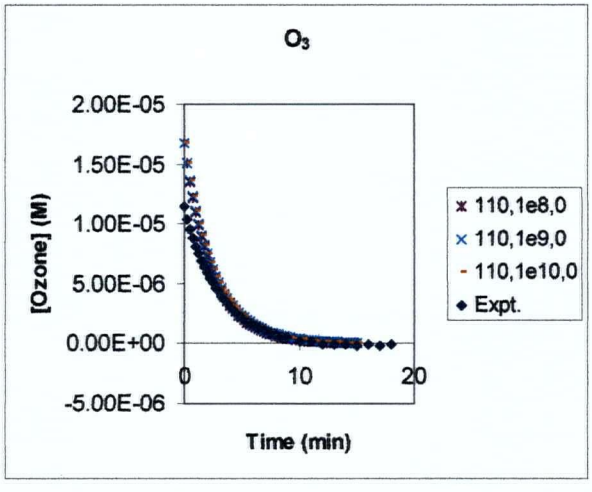


[O3] = 0.0167 mM

b)

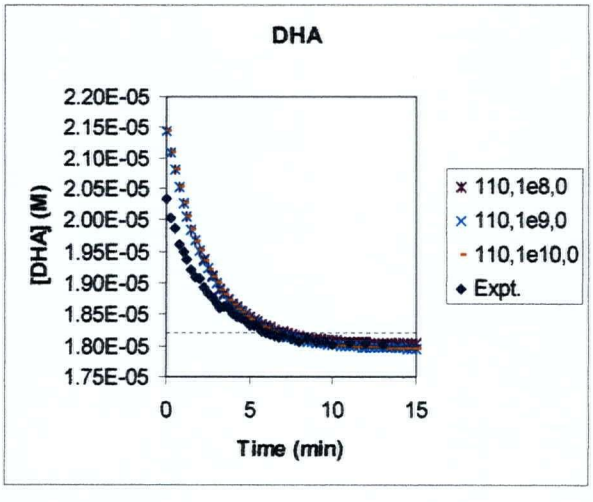


g)

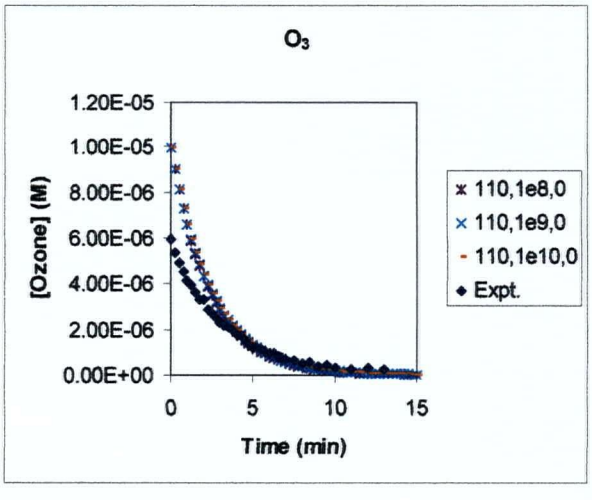


[O3] = 0.0100 mM

c)

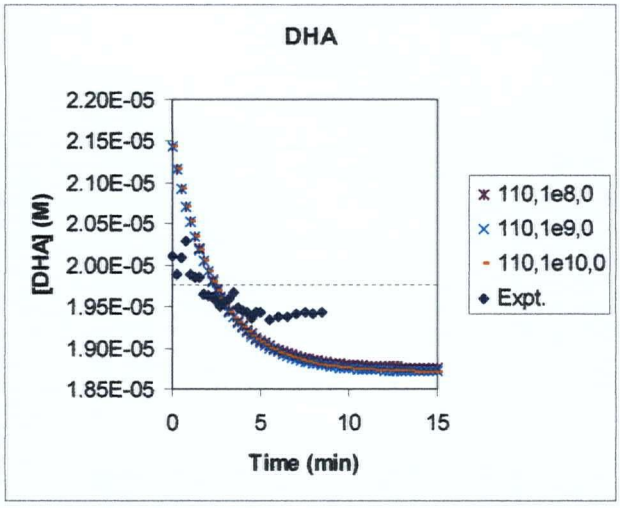


h)

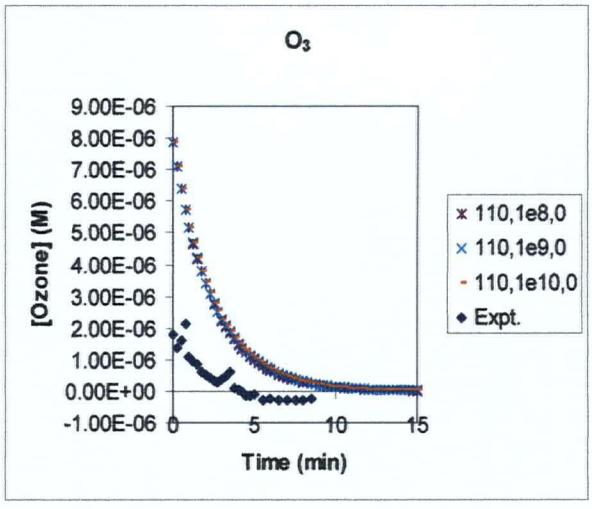


[O3] = 0.0079 mM

d)

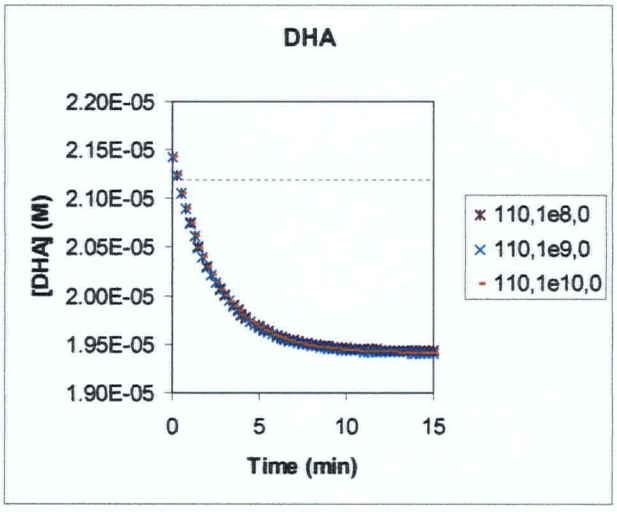


i)



[O3] = 0.0059 mM

e)



j)

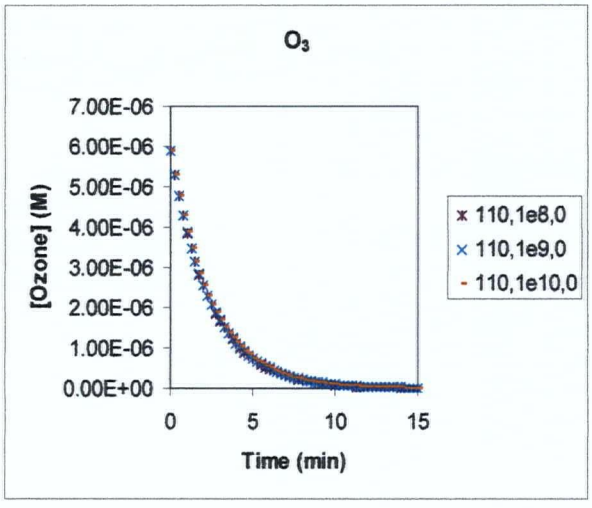
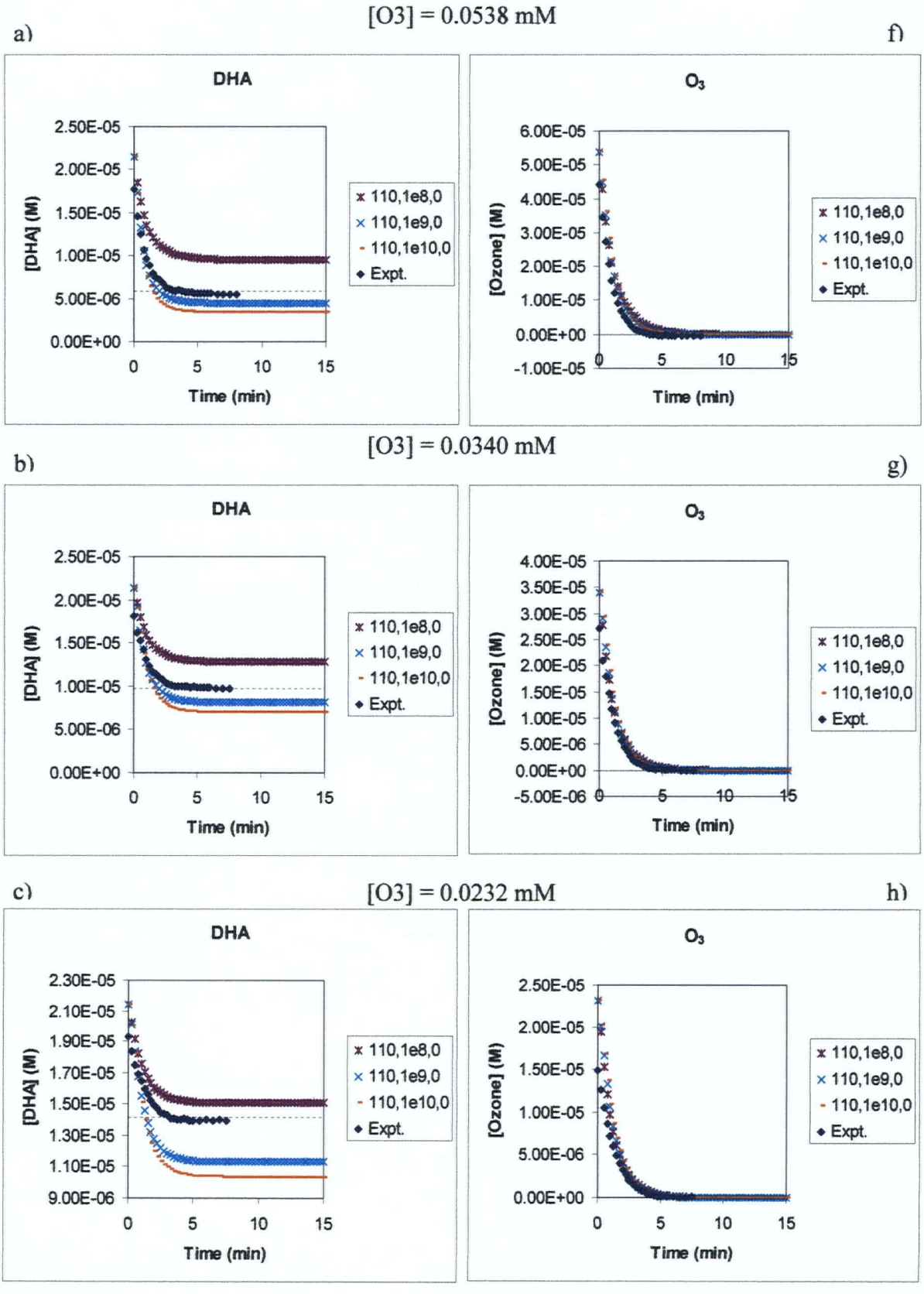
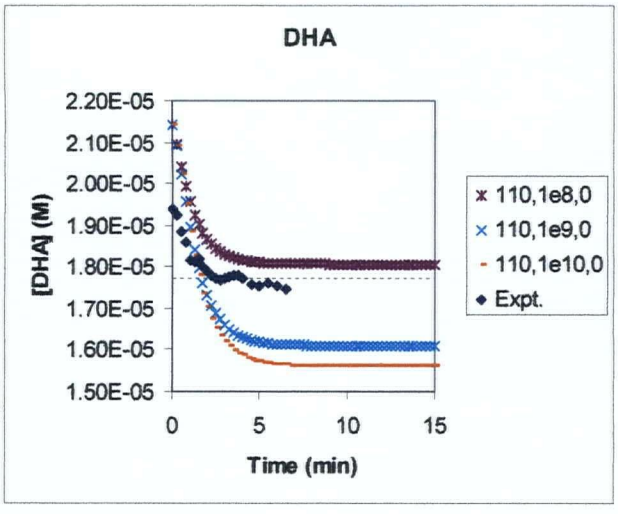


Figure 7.22: Addition of ozone to DHA, pH 8.1, no radical scavenger, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

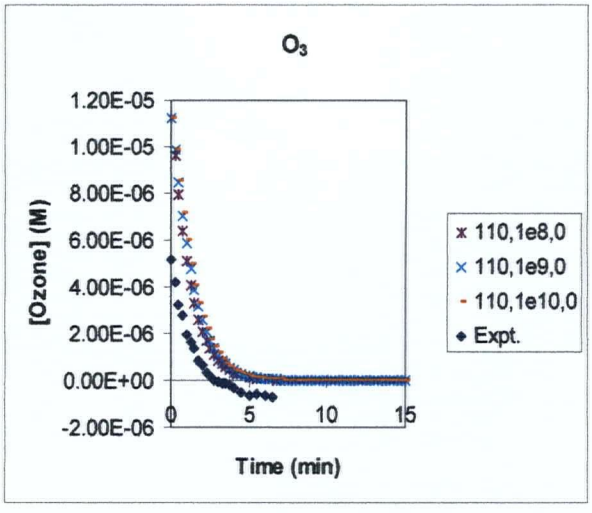


[O3] = 0.0112 mM

d)

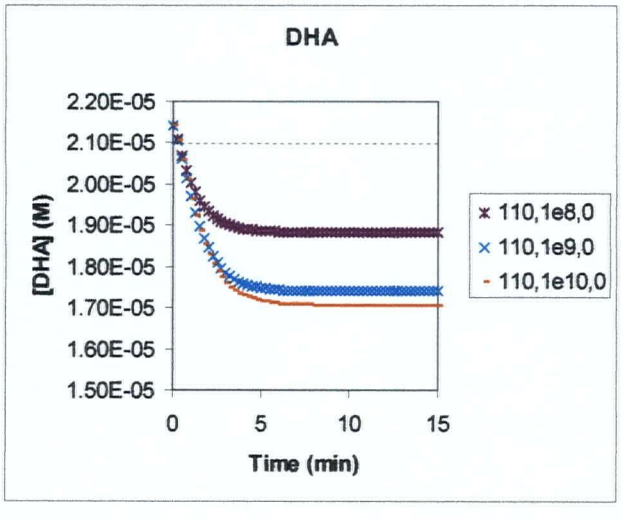


i)



[O3] = 0.0085 mM

e)



j)

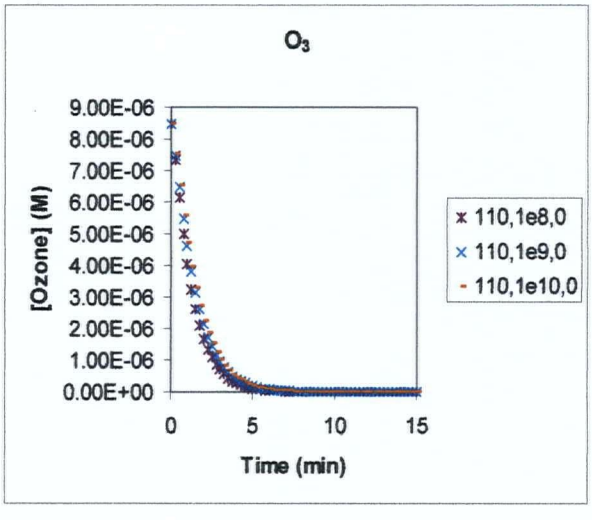
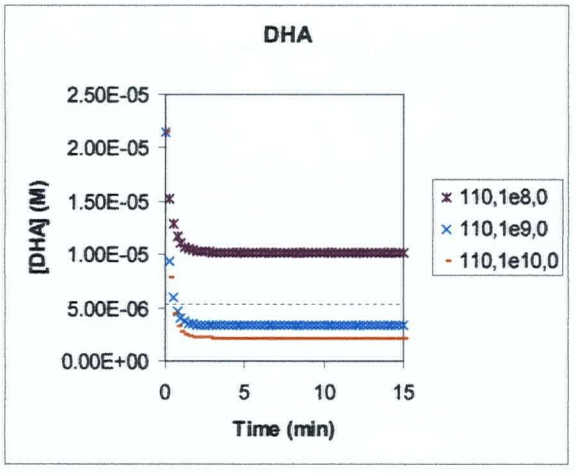


Figure 7.23: Addition of ozone to DHA, pH 9.7, no radical scavenger, modeled with O_3:DHA of 3:1, H_2O_2:DHA of 3:1.

[O3] = 0.0703 mM

a)



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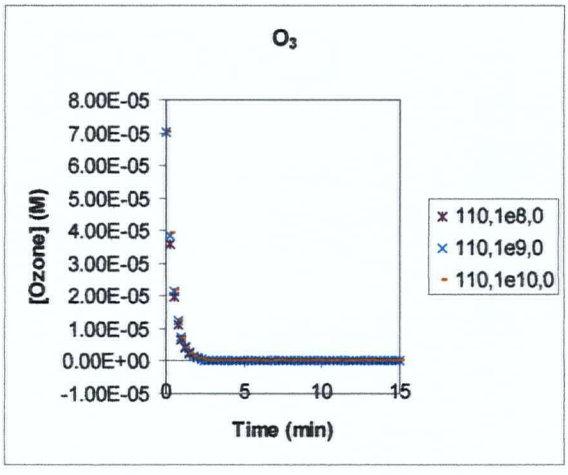
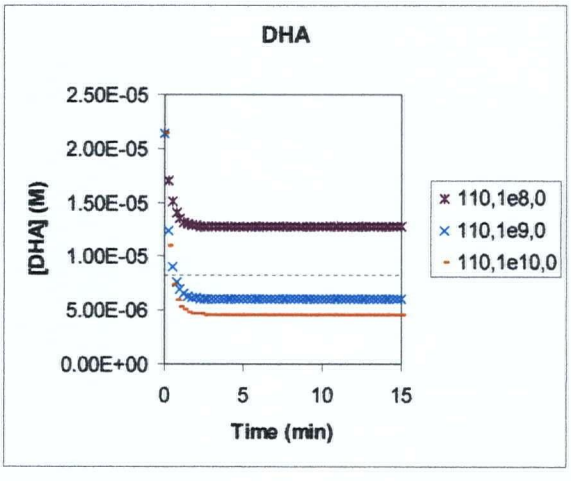
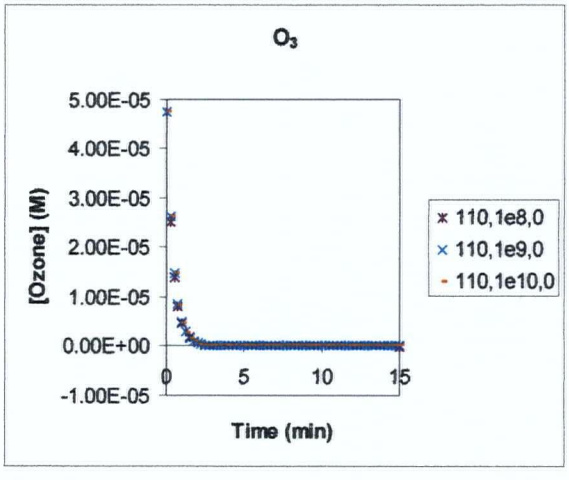


[O3] = 0.0473 mM

b)

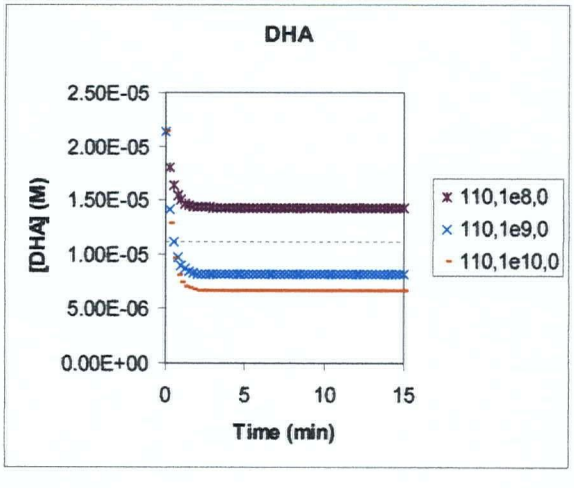


g)



[O3] = 0.0362 mM

c)



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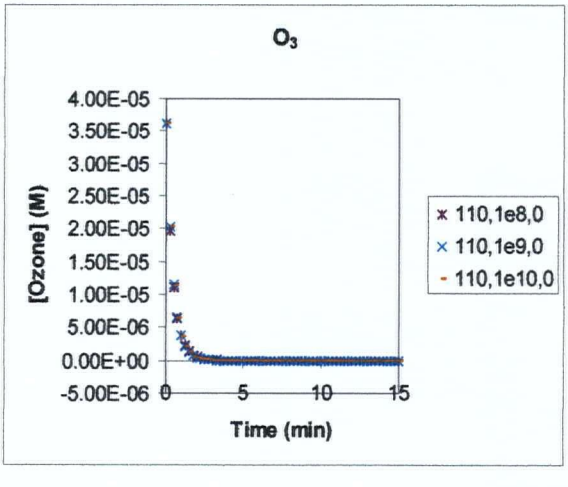
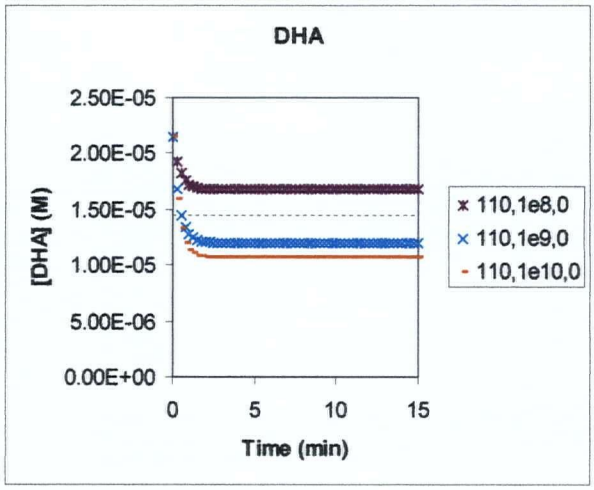
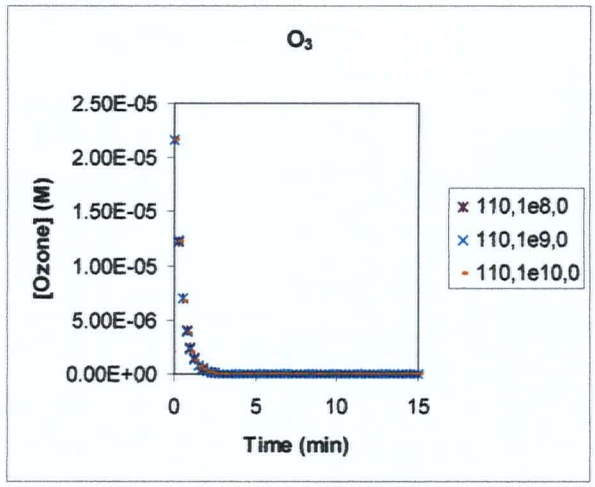
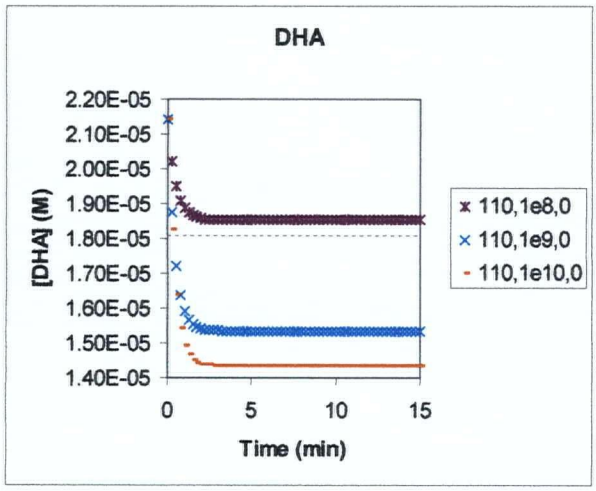


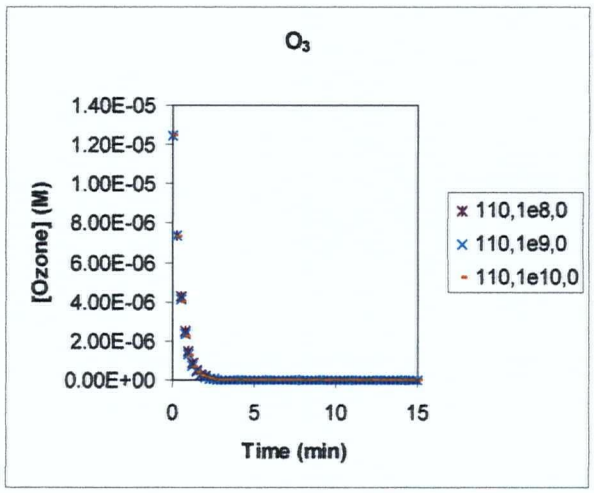
d) [O3] = 0.0216 mM i)





e) [O3] = 0.0125 mM j)





Firstly, for certain conditions, the fraction of DHA oxidized by ozone compared to that oxidized by radicals changes dramatically over the range of initial ozone doses used. For example, with the HCO_3^-/CO_3^{2-} system at pH 6.5, it is estimated that 74% of the DHA will be oxidized by ozone at the highest $[O_3]_0$ whereas at the lowest $[O_3]_0$, 91.5% will be oxidized by ozone. Because the nature of the products from ozone and free radical reactions are so different (ring opening in the case of ozone versus electron abstraction, hydrogen abstraction, addition/elimination, as well as polymerization of resulting organic radicals for radical reactions), the change in the ratio of oxidation products as a function of the initial ozone dose will most likely result in a changing UV spectrum and consequently, changing PAF values. Secondly, the radical reactions themselves will produce a whole spectrum of products, depending on whether they are initially reacting with DHA, a ring-opened product of a DHA/O_3 reaction, a previously polymerized DHA-DHA molecule. Whether it is a hydroxyl or phosphate radical that is reacting will also make a difference since their mechanisms of reaction differ. Hydroxyl radicals largely react with organic molecules through hydrogen abstraction and addition while phosphate radicals also react through electron abstraction (Rosso et al., 1998). Given this complexity in radical reactions, it is perhaps not surprising that different extents of oxidation of DHA will result in different kinds of oxidation products and PAF values.

7.6 Efficiency of Ozone Use

In examining the efficiency of ozone use as measured by the ratio of ozone added to DHA consumed, the lack of a radical scavenger results in superior efficiency compared to samples containing a radical scavenger, especially when performing the reaction at a higher pH. At a pH of 9.7 with t-butanol as radical scavenger, the ratio of mol O_3 added/mol DHA oxidized

was approximately 22 (Figure 7.24a); however, with no scavenger, the ratio varied between 3 and 5 (Figure 7.24b), a marked improvement in ozone utilization efficiency. The reason for this is the presence of hydroxyl radicals. When the radical scavenger is present, a large fraction of the hydroxyl radicals (approximately 97% as calculated by the model) will be scavenged, leaving the DHA to react primarily with the ozone. If no scavenger is present, however, the resulting hydroxyl radicals will react only to a very minor extent with residual ozone (1-2%), somewhat more with phosphate ions (~4%), but mainly with the DHA and its breakdown products in solution (~95%). The model was run with various scenarios of reaction rate constants to provide an estimate of the fraction of the DHA oxidized by each reactive species. In the case of t-butanol as radical scavenger at a pH of 9.7, a O_3/DHA rate constant of $1.1 \cdot 10^2$ L/mol·s and a ·OH/DHA rate constant of $5 \cdot 10^9$ L/mol·s, the model estimates about 77% of the DHA will be oxidized by ozone while 23% will be oxidized by ·OH. With no scavenger, however, about 5 times more DHA will be oxidized and, of that, about 9% will react with ozone compared to over 90% with hydroxyl and phosphate radicals. With the bicarbonate/carbonate system, the slight scavenging effect of these ions leads to results intermediate to those of t-butanol and no radical scavenger, 25% of DHA oxidized by ozone and 75% by ·OH. This leads to the results shown in Figure 7.24a, where ozone utilization efficiency is greatest with no scavenger. As removal of ·OH increases through removal by radical scavengers, the efficiency decreases.

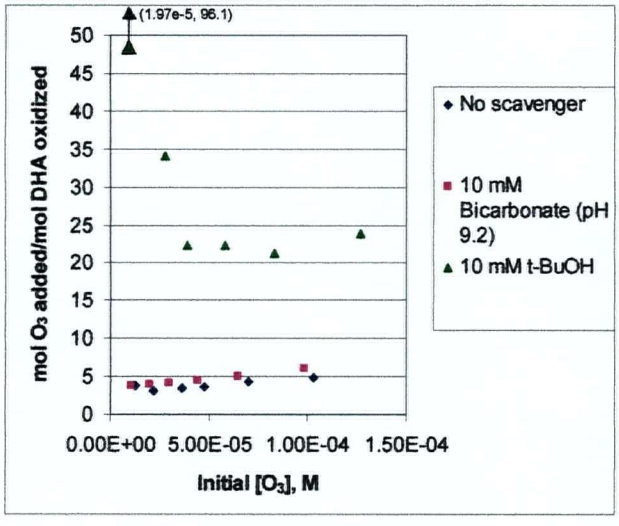
As the pH of the system decreases, the effect of radical scavengers on the ozone utilization efficiency also decreases (Figure 7.24c&d). This occurs primarily because the rate of the initiation step of the ozone breakdown (i.e., $O_3 + OH^- \rightarrow HO_2^- + O_2$) is proportional to the hydroxide ion concentration. As the pH decreases, the rate of this step, which leads through a series of radical generating reactions to a hydroxyl radical, decreases as well. Thus at a pH of 6.5, the rate at which hydroxyl radicals are generated by the initiation step is much lower than in basic solutions (2.3% of the rate at pH 8.1, 0.06% of the rate at pH 9.7). This results in most of

the oxidation of DHA being done by ozone. With t-butanol as radical scavenger, there will be some wasting of oxidative potential through scavenging of hydroxyl radicals (seen by the t-butanol system oxidizing approximately 85% of the DHA oxidized by a system with no scavenger, as calculated by the model); however, this is nowhere near the 5 times difference seen at higher pH. Figure 7.24d illustrates this with an ozone utilization efficiency that is slightly worse for the t-butanol system, but much better than at the pH of 9.7 (Figure 7.24a).

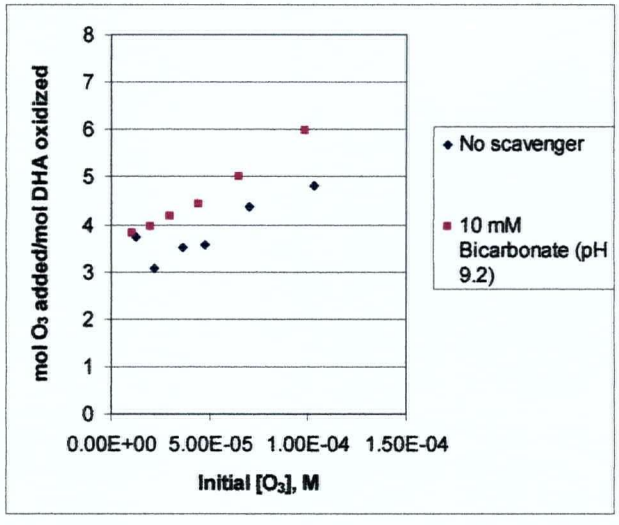
For systems with HCO_3^-/CO_3^{2-}, the change in pH affects the equilibrium of the ions and, therefore, the scavenging ability of the pair since their reaction rate constants with ·OH differ by a factor of 10. At a pH of 6.5, with the equilibrium firmly weighted towards the HCO_3^- ion and its lesser scavenging ability, there is no apparent difference between the ozonation efficiency of the HCO_3^-/CO_3^{2-} system and one with no scavenger (Figure 7.24d). As the pH increases, the gradually increasing presence of CO_3^{2-} results in increasing radical scavenging. At the experiments done at pH over 9, (Figure 7.24b), the effect on the ozone utilization efficiency is clearly seen. Approximately 25% more ozone is consumed per unit of DHA oxidized. Bearing in mind that the HCO_3^-/CO_3^{2-} experiment was performed at pH 9.2 while the one with no scavenger was done at pH 9.7, the model was run for the HCO_3^-/CO_3^{2-} at a pH of 9.7. It is estimated that at this pH, only 80% of the DHA oxidized at a pH of 9.2 will be oxidized; thus, if oxidation efficiency at a pH of 9.7 is compared, it is estimated that the HCO_3^-/CO_3^{2-} system will consume 50% more ozone per unit DHA oxidized than if no radical scavenger is used.

Figure 7.24: Dependence of ozone utilization efficiency on presence of radical scavenger and pH.

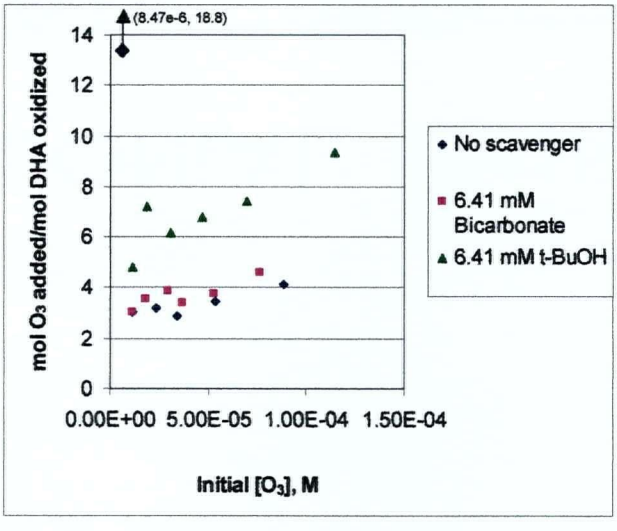
a) pH 9.7



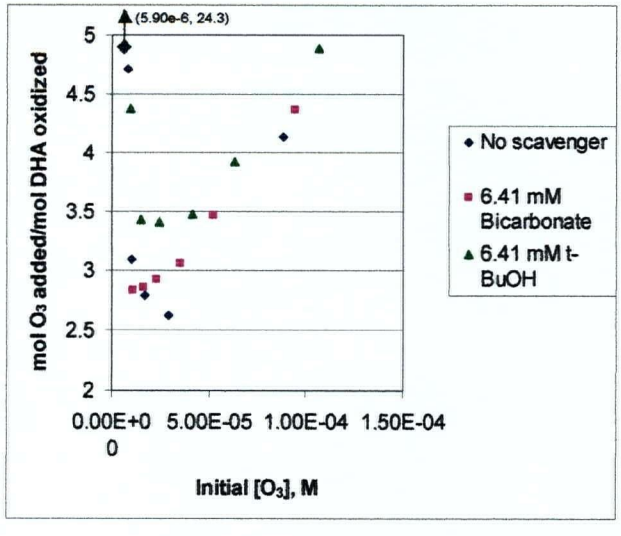
b) pH 9.7 (different scale)



c) pH 8.1



d) pH 6.5



8. CONCLUSIONS

This work summarizes the results of an investigation into the treatment of logyard run-off with the goal of eliminating the acute toxicity to aquatic life that such run-off often contains.

Use of ozone to treat logyard run-off resulted in the reduction of many parameters associated with water pollution and aquatic toxicity. The initial concentrations of the various parameters saw a great degree of variability from sample to sample, as evidenced by the high coefficients of variation (tannins and lignins: 0.75, soluble COD: 0.79, soluble BOD: 0.86, DHA: 0.69, Microtox toxicity: 1.03). COD, tannins and lignins, DHA concentration, and acute toxicity (measured using both Microtox™ and *Daphnia magna*) all saw reductions in their levels after treatment using ozone. For COD, reductions of 0.56 mg COD/ mg O_3 consumed were achieved. This is in line with results obtained by other researchers. The concentrations of tannins and lignins, DHA, and toxicity, decreased exponentially when measured with respect to ozone consumption per unit COD. The exponential constant was used to compare the degree of oxidation per unit ozone consumed. DHA underwent the most ozone-efficient oxidation of all parameters measured (k=8.74). In most trials, complete DHA elimination was obtained. Tannins and lignins (k=5.17) also saw reductions of over 90%, while Microtox™ toxicity levels (k=6.29) were reduced approximately 85%. Microtox™ toxicity decreased until an ozone dose of approximately 0.35 mg O_3/mg COD_0 was reached. Thereafter, little change in toxicity levels was seen. Using *Daphnia magna* as a toxicity test organism, complete detoxification of the run-off was obtained at a much earlier point than with Microtox, showing the greater sensitivity of the Microtox test. BOD concentrations initially decreased approximately 25% and then remained around that level for the remainder of the treatment.

The effect of pH was examined by performing ozonation runs at a pH of 5 and 7. Changing the pH of the solution in the acidic/neutral region did not have a significant effect on COD oxidation. Tannins and lignins, DHA, and toxicity were all oxidizied to a greater extent with increased pH. This is most likely a result of two factors. The reactivity of ionizable compounds with ozone is greater for the basic than for the acidic form. As well, at higher pH, the greater concentration of hydroxide ions increases the rate of decomposition of ozone, leading to an increased concentration of the very reactive hydroxyl radicals.

A comparison of toxicity results as measured by both Microtox™ and *Daphnia magna* showed that toxicity as measured by both assays follow similar trends during the ozonation of samples. Microtox™ showed greater sensitivity to run-off than *D. magna*, particularly in the ozone treated samples.

Batch biological treatment of logyard run-off reduced BOD, COD, and tannin and lignin concentrations by 99, 80, and 90%, respectively. Microtox™ toxicity was reduced from an initial EC_{50} of 1.83% to 50.4% after 48 hours, a reduction of 96%. The kinetics of biodegradation are similar to those for a bleached kraft mill effluent (q_{max}=0.0038 mg BOD/mg VSS·min and K_s=1.4 mg/L for run-off versus q_{max}=0.0038 mg BOD/mg VSS·min and K_s=0.774 mg/L for BKME).

Ozonation as both polishing and pre-treatment step for biological treatment of run-off was also examined. As a polishing treatment, COD and tannins and lignins were reduced by a further 22% and 68% from already much reduced levels (1130 mg/L and 105 mg/L, respectively). No improvement was observed in Microtox™ toxicity and the BOD increased 38% from a very low concentration (95 mg/L). Used as a pre-treatment, ozonation had an effect on the subsequent biological treatment. The BOD of pre-ozonized samples decreased faster than that of non-ozonized samples during biological treatment; however, the final residual COD after biological treatment was greater for the ozonized samples. Ozonation served to remove tannins

and lignins much faster than biological treatment (30 minutes of ozonation reduced tannin and lignin levels by the same amount as 24 hours of biological treatment); however, in subsequent biological treatment, residual tannins and lignins of ozonized samples were reduced much more slowly than in unozonized samples (after 33 hours of biological treatment, a 105 mg/L reduction for the sample pre-ozonized for 30 minutes compared to 600 mg/L for the unozonized sample). As a result, biological treatment of the two samples eventually resulted in similar final tannin and lignin concentrations of 80-90 mg/L. For toxicity measurements, biological treatment of ozonized and unozonized run-off samples resulted in similar low final toxicity levels (50%-70% EC_{50} as measured by Mircrotox); however, biological treatment of 8 hours was required to reduce toxicity to the same level as one half hour of ozonation.

The rate of reaction between ozone and DHA, one of the main resin acids found in wood, was determined to be 1.1×10^2 L/mol·s at 23°C. This rate is for the opening of the aromatic ring in DHA. Subsequently, the resulting diene is rapidly cleaved as shown by the apparent 3:1 molar ratio of ozone consumed per unit DHA oxidized. Production of hydrogen peroxide as a result of the ozonation of DHA was also shown through an examination of the UV spectrum of a DHA/ozone reaction mixture in combination with a mathematical model. A ratio of 3:1 H_2O_2 produced:DHA oxidized was determined to have the best fit with experimentally-derived results.

Ozone utilization efficiency decreased in the presence of radical scavengers, particularly as pH was increased into the basic range. At a pH of 9.7, removal of the free radicals by t-butanol resulted in only one fifth of the DHA being oxidized compared to when no radical scavenger is present. The HCO_3^-/CO_3^{2-} system makes very little difference at a pH of 6.5 as the radical scavenging ability of HCO_3^- (the dominant species of the two at this pH) is one tenth that of CO_3^{2-}. At higher pH, the greater scavenging ability of CO_3^{2-} results in poorer use of ozone for oxidation of DHA (almost 50% greater ozone usage per unit DHA oxidized at pH 9.7).

9. ENGINEERING SIGNIFICANCE

The collection of large numbers of felled trees in sawmill storage yards open to the elements can, during periods of rainfall, result in significant amounts of toxic run-off being generated and released into adjacent waterways. A treatment method for this run-off would be desirable.

Because of the relatively small footprint that an ozonation system has compared to that of a typical biological treatment system, and the proven ability of ozone to reduce the toxicity of logyard run-off, ozonation as a treament method for logyard run-off is certainly of potential interest to sawmills and log sort yards where run-off volume and toxicity have been identified as detrimental to aquatic wildlife. Technically, it is able to treat run-off in an on-demand fashion, avoiding the problem of biological systems running out of feed during prolonged periods with no precipitation. Unlike biological systems, activated carbon, or other physical/chemical methods, ozone produces no solid residue that requires subsequent disposal.

The decision as to whether ozone is economically feasible as a method of treatment for logyard run-off will need to be done on a case-by-case basis as there are numerous variables involved in the choice. Peak rainfall amounts, annual rainfall amounts, run-off quality, logyard area, extent of ozone treatment, and electricity costs will all factor into the cost of ozone treatment. A preliminary calculation for the north coast sampling site gives an indication of the costs involved. Taking estimates from Air Liquide (Homer, 2003), the cost of an ozone production system including installation with a capacity of 50 kg O_3/h (sufficient to deal with a rainfall of about 35 mm over a 24 hour period) is $170 000. The cost for the initial system is dependent on the maximum capacity that one wishes to be able to treat. The system as described above, would not be able to fully treat all storm events since about 10 times per year, daily rainfalls greater than 35 mm are recorded. Usually, 1 or 2 daily rainfalls of over 80 mm are

recorded annually. To deal with this scale of rainfall would require a system costing close to $300 000. Assuming average annual rainfall of 250 cm (north coast of British Columbia average), 500 000 L of run-off / cm of precipitation (surface area of 50 000 m^2), initial soluble COD of 2400 mg/L, ozone treatment of 0.3 mg O_3/mg COD, power consumption of 15 kWh/kg O_3 and cost of $0.05/kWh, power costs for the ozone production amount to $67 500/yr. For annual oxygen costs, 430 t/yr at $225/t amounts to about $100 000/yr. These numbers are for the north coast of British Columbia, known for its high annual rainfall. Other areas with less annual rainfall would have proportionately lower annual operation costs; however, the initial costs for the system would not necessarily be markedly lower because rain events further south can sometimes be as large as those of the north coast, although not as frequent. It should be noted that this cost estimate does not include any costs associated with run-off collection, piping installation, or ozone/run-off reactor system. As well, the work presented in this thesis deals with run-off that has had suspended solids removed. Suspended solids are expected to have a significant effect on the amount of ozone required to remove toxicity from the run-off. On a large scale, this would require the installation of a system for solids removal.

Determination of the reaction rate constant of DHA with ozone represents a very first step in being able to fully model an aqueous system containing this compound. The presence of radical scavengers in solution has been shown to be detrimental to the effective use of ozone in the oxidation of DHA, particularly as the pH increases into the basic pH region.

10. RECOMMENDATIONS FOR FUTURE WORK

The following areas of study are suggested for future work on this project.

1. This study examined run-off from sawmills working with softwoods. Chemically, hardwoods are different than softwoods. Work on run-off from sawmills or sort yards containing hardwoods would be useful in extending the applicability of ozone as a treatment method.

2. Confirmation of the amount of H_2O_2 produced by the O_3/DHA reaction is possible through the direct measurement of H_2O_2 in water by way of ASTM method D6363-98. This method is used to detect the very low levels of hydrogen peroxide found in rainwater samples (the range expected to be found in this work) and requires a fluorometer. After addition of ozone to a DHA solution, the resulting concentration of H_2O_2 in solution as measured with this method could be compared to H_2O_2 values calculated by the model.

3. Examination of the products obtained from the ozonation of DHA would allow one to better understand the reaction mechanism, particularly in regards to the effect of free radicals on the reaction. This would require the development of extraction methods to concentrate the products so that they could be measured by GC/MS. The extent to which polymerization occurs as a result of free radical reactions is of interest in view of the results obtained during biological treatment of ozonized run-off (higher residual COD after biological treatment of ozonated run-off compared to non-ozonated run-off).

4. In order to better simulate the ozonation of DHA in run-off, ozonation of DHA solutions with an added tannin model compound would be of interest. Because of the high concentration of tannins and lignins in the run-off, it is important to understand how tannins and lignins affect the ozonation of DHA (e.g., whether changing pH affects the

ratio of O_3/tannins oxidized, how do different structures of tannins affect the oxidation of DHA).

5. In order to be able to properly select and design a solids removal system, the nature of the particles in the run-off must be characterized. Work should be done to examine how particle characteristics in the run-off change with changing climatic conditions, wood species present in the logyard, and vehicular traffic.
6. The effect of residual solids on treatability by ozone should be studied. How do the amount of suspended solids and particle size distribution affect the ozonation of logyard run-off? How are the COD removal efficiency and k values for tannin and lignin, DHA, and toxicity removal affected?
7. Mass transfer of ozone to logyard run-off should be studied in order to be able to properly design an ozone/run-off contactor system. Issues surrounding k_La, its enhancement due to rapid consumption of ozone in solution, and the change in the enhancement over the course of ozonation due to the changing nature of the run-off must be addressed.

NOMENCLATURE

Abbreviation	Explanation
AOX	Adsorbable organic halogens
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CTMP	Chemi-thermomechanical pulp
DHA	Dehydroabietic acid
DO	Dissolved oxygen
EC_{50}	50% effective concentration. Concentration at which 50% of Microtox luminescence is extinguished
GC	Gas chromatography
HMW	High molecular weight
HRT	Hydraulic retention time
K_s	Monod half saturation coefficient
LC_{50}	50% lethal concentration. Concentration at which 50% of toxicity test organisms are killed
LMW	Low molecular weight
MLSS	Mixed liquor suspended solids
μ_{max}	Maximum specific biomass growth rate
OC	Oxygen consumed
OUR	Oxygen uptake rate
PAF	Product absorbance factor
q	Substrate uptake rate
q_{max}	Maximum substrate uptake rate
RFA	Resin and fatty acids
SOUR	Specific oxygen uptake rate
SUR	Substrate uptake rate
TL	Tannins and lignins
TMP	Thermomechanical pulp
VOC	Volatile organic compounds
VSS	Volatile suspended solids

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APPENDICES

APPENDIX A. INITIAL SCREENING

A.1 Treatment by coagulation/flocculation

Prior to the work on ozonation of logyard run-off, a set of experiments was performed in order to test the feasibility of potential methods of treating the run-off.

The coagulant, Callaway 4000, and the flocculent, Callaway 4340, are known to be a highly effective combination in the treatment of pulp mill effluent (Hofer, 2003). These were therefore chosen for the screening procedure for the logyard run-off treatment. Samples of 100 mL of run-off obtained from a sawmill on the north coast of British Columbia were used. To a series of flasks, coagulant was added in a concentration of 0 to 100 ppm (w/v) in 10 ppm intervals. These were mixed at medium speed on a magnetic mixer for three minutes. To each of these flasks 10 ppm of flocculent was added. The mixture was then stirred for a further three minutes at medium speed and stirred for another three minutes at half the previous speed. The flasks were removed from the stirrer and allowed to settle. The samples were centrifuged at 2500 rpm (~1100g) for 20 minutes to remove any remaining particulates and then analyzed for total organic carbon (TOC) and Microtox toxicity.

A.2 Treatment by tailored minerals

One tailored mineral called Ogilvie with two different particle sizes (2-2.4 mm and <180 μm) were used. This mineral is a heulandite, a hydrated calcium sodium aluminum silicate (Polar Powders and Technologies, Calgary). Both samples had previously been treated with hexadecyltrimethylammonium cations at a dose of 100% of the external cation exchange capacity. The minerals were added to samples of 7.5 mL of run-off in concentrations of 5 and 20

mg/mL. The samples were mixed for 24 hours, using a Lab Quake mixer in order to ensure equilibrium. After the 24-hour period, the samples were centrifuged at 2500 rpm (~1100g) for 20 minutes to remove the minerals.

A.3 Treatment by activated carbon

Initial treatment of run-off samples with activated carbon was performed with three types of carbon: Norit RO 0.8 pellets, Darco KB 12-20 Mesh and Darco KB –100 Mesh (BDH, Toronto,Ont.). Three concentrations of carbon were used: 1.0, 2.5, and 4.0 mg/mL. As with the tailored mineral treatment, activated carbon was added to samples of 7.5 mL of run-off. These were then mixed for 24 hours in a Lab Quake mixer to ensure equilibrium. The samples were centrifuged at 2500 rpm (~1100g) for 20 minutes to remove the activated carbon.

A.4 Treatment by ozone

In a preliminary trial of ozonation as a treatment method, two samples were used. One was an extract of Sitka spruce bark. A sample of 60 g of Sitka spruce bark chips (obtained from the North Coast mill) was added to 2 L of tap water and the mixture was blended using a Braun hand held mixer for 5 minutes. The resulting extract was centrifuged for 20 minutes at 2500 rpm (~1100g) to remove suspended solids. The sample was divided into two equal portions. One was left as-is, at its pH of 6.0; the other was adjusted to a pH of 2.0 with concentrated H_2SO_4. The other sample that was used was leachate obtained from a sawmill in the Lower Mainland (species present at time of sampling were Douglas fir and Western hemlock in roughly equal amounts). It was treated at its original pH of 5.5 and also at a pH of 3 (adjusted with concentrated H_2SO_4).

The reactor system was as illustrated in Figure A.1. The reactor was a simple glass column (total volume ≈ 1.5 L, working volume 1.25 L) with no water jacket for temperature

control and no ports for pH control or measurement. Compressed air at a flow rate of 1 L/min was used as a feed gas.

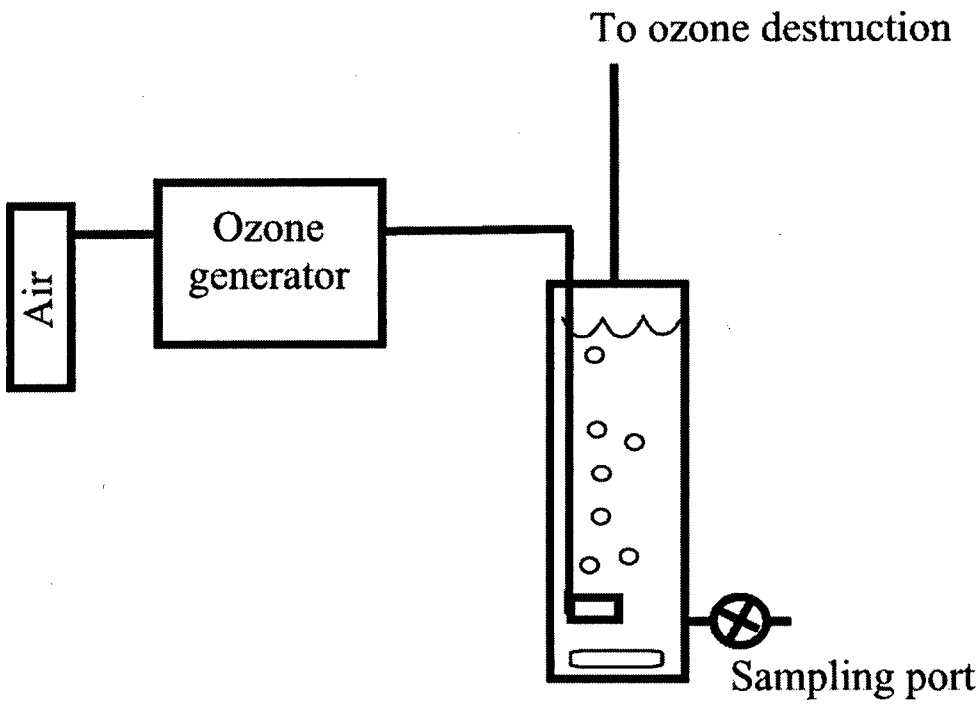


Figure A.1: Diagram of the reactor system used for preliminary tests of ozonation of logyard run-off.

A.5 Comparison of potential methods for run-off treatment

As an initial screening procedure for toxicity removal from logyard run-off, four methods were examined: coagulation/flocculation (Figure A.2), adsorption by tailored minerals and activated carbon (Table A.1), and oxidation by ozone (Table A.2).

Toxicity removal by coagulation/flocculation and tailored minerals was poor, with a maximum value of 17.2% for the former and 30.6% for the latter. The TOC removals were marginally better in both cases, between 16.7% and 26.7% for the coagulation/flocculation test and 35.4% for the best tailored mineral run, which used the more finely ground sample of mineral. Tests using the coarser variety resulted in the toxicity of the sample increasing. The

Figure A.2: Toxicity and TOC removal by coagulation/flocculation.

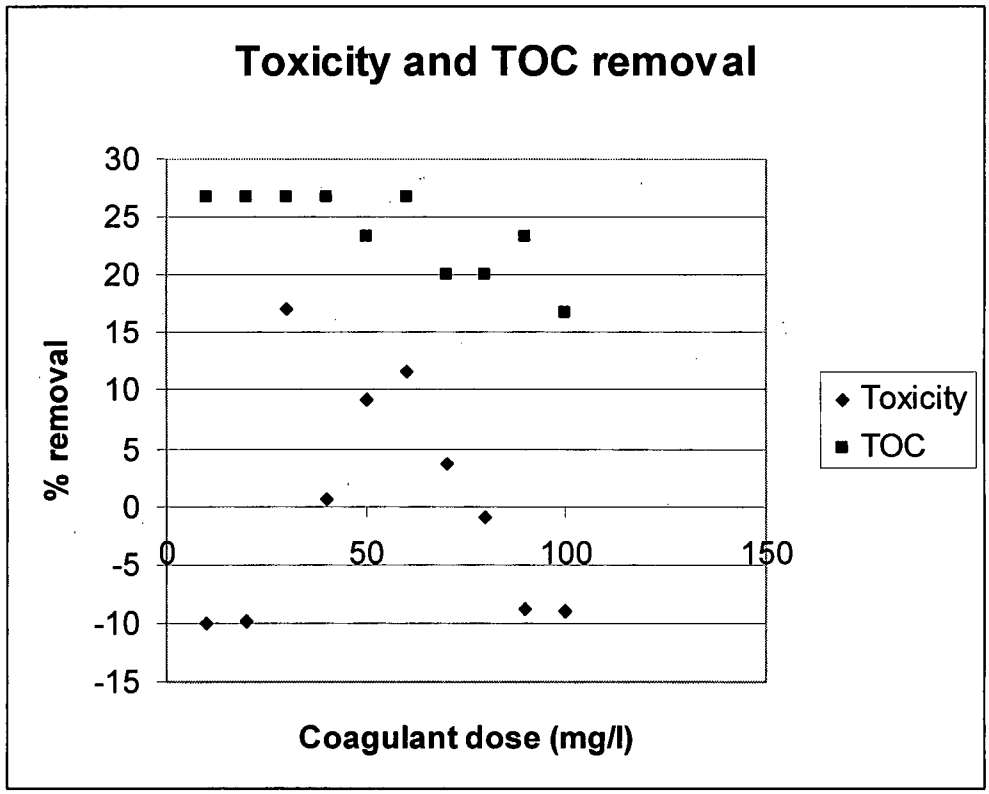


Table A.1: Toxicity and TOC removal from logyard run-off by organically-tailored minerals and activated carbon.

Type	Concentration (mg/ml)	% Toxicity Removal	% TOC Removal
Tailored Mineral			
2-2.4 mm Ogilvie 100% ECEC	5	-5.5	8.3
	20	-7.0	20.8
<180 Ogilvie 100% ECEC	5	n/a	10.4
	20	30.6	35.4
Activated Carbon			
Norit RO 0.8 (pellets)	1	68.4	33.3
	2.5	71.5	50.0
	4	74.0	54.2
Darco 12-20 Mesh (granulated)	1	61.1	29.2
	2.5	83.0	50.0
	4	92.2	65.0
Darco KB -100 Mesh (powder)	1	100.0	80.0
	2.5	100.0	87.5
	4	100.0	89.2

Table A.2: Maximum toxicity removals from screening samples achieved by ozonation.

Sample	Initial pH	Maximum toxicity removal (%)
Sitka spruce extract	6	>85
Sitka spruce extract	2	>90
Lower Mainland sawmill	5.5	71
Lower Mainland sawmill	3	53

reason for this is not known. The most likely explanation is that some of the tailoring compound (hexadecyltrimethyl ammonium) is released into solution and results in added Microtox® toxicity.

Tests were performed on the ability of 3 different kinds of activated carbon to remove toxicity from a logyard run-off sample. All three activated carbons tested gave significantly better results than coagulation/flocculation and tailored minerals. At the concentrations tested, the maximum toxicity reductions for the Norit RO 0.8, Darco 12-20 Mesh, and Darco KB -100 Mesh were 74.0%, 92.2%, and 100%, respectively. However, the activated carbon concentrations tested were significantly higher than the 20-200 mg/L normally used in industrial applications (Metcalf & Eddy Inc., 1991). TOC removals were also superior. The much smaller particle size of the Darco KB -100 Mesh resulted in a much larger surface area per unit mass and, therefore, a greater ability to remove organic compounds. This resulted in a superior toxicity and TOC removal for this activated carbon.

Preliminary trials of ozonation of bark leachate and logyard run-off are presented in Figures A.3 and A.4. The toxicity removals that were achieved were good considering that these were the first attempts. Table A.2 lists the maximum toxicity removals attained for each trial. In all cases, significant toxicity removal was achieved.

Figure A.3: Toxicity removal by ozonation from Sitka spruce bark extract.

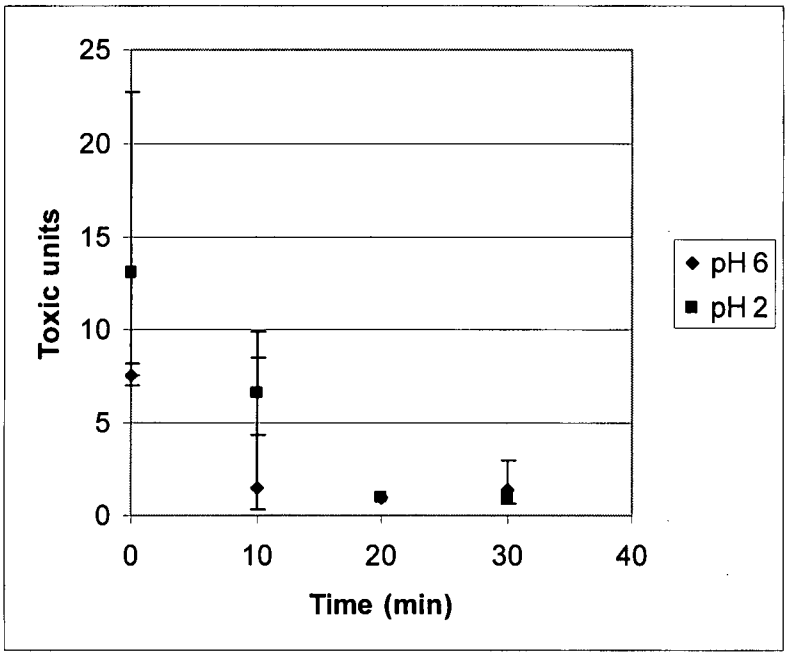
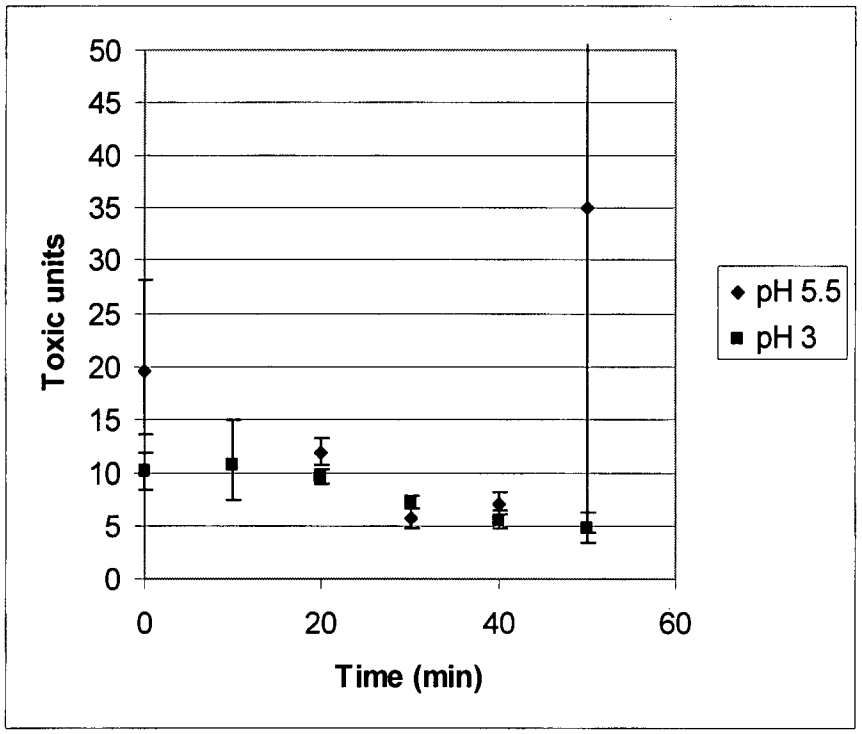


Figure A.4: Toxicity removal by ozonation from Lower Mainland sawmill run-off.



Although the trials of the tailored minerals and the coagulation/flocculation procedures removed some toxicity, at most they removed 30%. In addition, treatment with either of these two methods leaves the issue of how to treat the resulting contaminated mineral or sludge. Although the powder form of activated carbon rendered the run-off non-toxic according to Microtox (albeit at concentrations significantly higher than is normal in industrial practice), the resulting carbon requires subsequent treatment. This can take the form of either off-site disposal or on-site regeneration. Ozone treatment, on the other hand, requires minimal attention. It does not generate a solid waste that needs further processing. The only two streams created are the ozonized run-off and the off-gas, which may need to be treated to remove any residual ozone (although any industrial system would be designed to ensure the maximum utilization of ozone). Additionally, because the ozone would be added as part of a stream of oxygen, the dissolved oxygen level in the run-off would be increased significantly, thus helping to counteract the effect of any residual BOD in the run-off. Because of the ability of ozone to significantly reduce toxicity levels in logyard run-off, as well as its ease of use, it was decided to select ozone for further investigation.

APPENDIX B. MATLAB MODEL FOR CALCULATION OF SPECIES CONCENTRATIONS DURING OXIDATION OF DHA

B.1 Main program

```
format short e;
pH=input('pH?');
carb=input('carbonate?');
but=input('butanol?');
k1=input('O3/DHA rate constant?');
k2=input('OH/DHA rate constant?');
but=but*6.4286e-4;

switch pH
case 6.5
  h2po=0.026852;
  hpo=0.0052907;
  switch carb
  case 0
    hco=0;
    co=0;
  case 10
    hco=3.7575e-3;
    co=5.5736e-7;
  end

case 8
  pH=8.13;
  h2po=0.00341788;
  hpo=0.0287241;
  switch carb
  case 0
    hco=0;
    co=0;
  case 10
    hco=6.284128e-3;
    co=3.975621e-5;
  end

case 9
  switch carb
  case 0
    pH=9.67;
    h2po=0.0001098;
    hpo=0.0320001;
    hco=0;
    co=0;
```

```
  case 10
    pH=9.19;
    h2po=0.0003296;
    hpo=0.0318024;
    hco=5.98514e-3;
    co=0.434747e-3;
  end

end

y=[0 2.8938e-5 0 0 0 0 0 0 0 0 2.1798e-5 hco co 0 0 0 0 0 0 0 0 0 0];
y(1,2)=input('O3 init. ');
k3=input('Phosphate rad./DHA rate ');
d=0;
r=1;
b=zeros(60,2);
a=zeros(60,1);
b(1,1)=y(1,2);
b(1,2)=y(1,11);
f0=[y(1,2) y(1,3) y(1,4) y(1,5) y(1,6) y(1,7) y(1,8) y(1,9) y(1,10) y(1,11) y(1,12) y(1,13) y(1,14)
y(1,15) y(1,16) y(1,17) y(1,18) y(1,19) y(1,20) y(1,21) y(1,22) y(1,23)];
for i=1:60
  for j=1:15
  tspan=[d:0.04:d+1];
    [t,f]=ode15s('tfgphosphate',tspan,f0,[],pH,but,k1,k2,h2po,hpo,k3);
  d=d+1;
  for l=1:22
    f0(1,l)=f(26,l);
  end
  end
  r=r+1;
    y(r,1)=t(26,1);
  for z=2:23
    y(r,z)=f(26,z-1);
  end
  a(r)=t(26,1);
  b(r,1)=f(26,1);
  b(r,2)=f(26,10);
end
plot(a,b);
dlmwrite('attempt',b,'\t');
```

B.2 Differential equation subroutine 'tfgphosphate'

```
function dy=tfgphosphate(t,y,flag,q1,q2,q3,q4,q7,q8,q9)
dy=zeros(22,1);
dy(1)=-140*y(1)*10^(q1-14)-3e8*y(1)*y(6)-5.5e6*y(1)*y(2)+8.3e9*y(3)*y(4)-2.5e7*y(1)*y(4)-
3*q3*y(1)*y(10)-0.003*y(1)*q2+5.5e7*y(13)*y(3)-3*q3*y(1)*y(21);
dy(2)=140*y(1)*10^(q1-14)-5.5e6*y(1)*y(2)-3.2e9*y(2)*y(7)+1e10*y(9)*10^(q1-14)-
7.6e7*y(2)+4e6*y(11)*y(6)-3e7*y(13)*y(2)-7.5e9*y(4)*y(2);
dy(3)=5.5e6*y(1)*y(2)+3e8*y(1)*y(6)-2e10*y(3)*y(4)-8.3e9*y(3)*y(4)-
5e3*y(3)+2.5e9*y(7)*3.43e-4+5.2e10*y(8)*10^(q1-14)-300*y(3)-5.5e7*y(13)*y(3);
dy(4)=-q4*2.1798e-5*y(4)-2e10*y(3)*y(4)-8.3e9*y(3)*y(4)-2.5e7*y(1)*y(4)+1.1e5*y(8)-
4e10*y(4)*10^(q1-14)+5.4e8*y(7)-2e4*y(4)*q7-1.5e5*y(4)*q8-6e8*y(4)*q2-1e8*y(12)*y(4)-
1e7*y(11)*y(4)-2.7e7*y(4)*y(9)-1e10*y(4)*y(6)-8.4e9*y(4)^2-7.5e9*y(4)*y(2)-
1e10*y(4)*y(5);
dy(5)=5.5e6*y(1)*y(2)+2e10*y(3)*y(4)+2.5e7*y(1)*y(4)-1e10*y(5)*10^(q1-
14)+10*y(6)+7.6e8*y(13)*y(9)+3e7*y(13)*y(2)+5.5e7*y(14)*y(9)+2.7e7*y(4)*y(9)-
1e10*y(4)*y(5);
dy(6)=-3e8*y(1)*y(6)+2e10*y(3)*y(4)+3.2e9*y(2)*y(7)-1.8e8*y(6)*y(7)+1e10*y(5)*10^(q1-
14)-10*y(6)-4e6*y(11)*y(6)-8.7e7*y(13)*y(6)+2.7e7*y(15)*y(9)-
1e10*y(4)*y(6)+7.5e9*y(4)*y(2);
dy(7)=-3.2e9*y(2)*y(7)-1.8e8*y(6)*y(7)+5e3*y(3)-2.5e9*y(7)*3.43e-4+4e10*y(4)*10^(q1-14)-
5.4e8*y(7)-1e7*y(12)*y(7);
dy(8)=-1.1e5*y(8)-5.2e10*y(8)*10^(q1-14)+300*y(3);
dy(9)=-1e10*y(9)*10^(q1-14)+7.6e7*y(2)-7.6e8*y(13)*y(9)+3*q3*y(1)*y(10)-
5.5e7*y(9)*y(14)-2.7e7*y(15)*y(9)-2.7e7*y(4)*y(9)+4.2e9*y(4)^2+3*q3*y(1)*y(21);
dy(10)=-q3*y(1)*y(10)-q4*y(4)*y(10)-10*q9*y(14)*y(10)-q9*y(15)*y(10)-q9*y(16)*y(10);
dy(11)=-5e9*y(11)*10^(q1-14)+1.7e6*y(12)-1e7*y(11)*y(4)-
4e6*y(11)*y(6)+7.6e8*y(13)*y(9);
dy(12)=5e9*y(11)*10^(q1-14)-1.7e6*y(12)-1e8*y(12)*y(4)+5.5e7*y(13)*y(3)-
1e7*y(12)*y(7)+8.7e7*y(13)*y(6)+3e7*y(13)*y(2);
dy(13)=1e8*y(12)*y(4)-5.5e7*y(13)*y(3)+1e7*y(12)*y(7)+1e7*y(11)*y(4)+4e6*y(11)*y(6)-
8.7e7*y(13)*y(6)-7.6e8*y(13)*y(9)-3e7*y(13)*y(2)-2e7*y(13)^2;
dy(14)=2e4*y(4)*q7-5.5e7*y(14)*y(9)-1e10*y(14)*10^(q1-14)+50*y(15)-
10*q9*y(14)*2.1798e-5-2e9*y(14)^2-3.9e6*q2*y(14);
dy(15)=1.5e5*y(4)*q8-2.7e7*y(15)*y(9)-1e10*y(15)*10^(q1-14)+7.9e4*y(16)-
q9*y(15)*2.1798e-5+1e10*y(14)*10^(q1-14)-50*y(15)-3e8*y(15)^2-4.5e5*q2*y(15);
dy(16)=1e10*y(15)*10^(q1-14)-7.9e4*y(16)-7.8e7*y(16)^2-4.2e5*q2*y(16)-q9*y(16)*2.1798e-
5;
dy(17)=-1.2e9*y(17)^2+3.9e6*q2*y(14)+4.5e5*q2*y(15)+4.2e5*q2*y(16)+6e8*y(4)*q2;
dy(18)=q3*y(1)*y(10);
dy(19)=q4*y(4)*y(10);
dy(20)=10*q9*y(14)*y(10)+q9*y(15)*y(10)+q9*y(16)*y(10);
dy(21)=q4*y(4)*y(10)-q3*y(1)*y(21);

% 1:ozone
% 2:HO2-
% 3:.O3-
```

% 4:.OH
% 5:.HO2
% 6:.O2-
% 7:.O-
% 8:.HO3
% 9:H2O2
%10:DHA
%11:HCO3-
%12:CO3--
%13:.CO3-
%14:.H2PO4
%15:.HPO4-
%16:.PO4--
%17:.t-BuOH
%18:DHA reacted with ozone
%19:DHA reacted with .OH
%20:DHA reacted with .PO4s
%21:DHA aromatic radicals

APPENDIX C. COMPLETE LIST OF PRODUCT ABSORBANCE FACTORS FOR OZONATION OF DHA

Table C.1: Product absorbance factors for ozonation of DHA

Scavenger	pH							
t-butanol	6.5	$[O_3]_0$ ($x10^{-5}$ M)	10.66	6.29	4.11	2.42	1.50	0.93
		222 nm	0.4597	0.4754	0.5062	0.4862	0.4657	0.2742
		260 nm	0.2086	0.2616	0.2799	0.2819	0.2602	0.1574
	8.1	$[O_3]_0$ ($x10^{-5}$ M)	11.47	6.96	4.70	3.06	1.85	1.13
		222 nm	0.5388	0.5939	0.6176	0.6114	0.6836	0.8045
		260 nm	0.3357	0.3333	0.3563	0.3569	0.4148	0.2697
	9.7	$[O_3]_0$ ($x10^{-5}$ M)	12.72	8.33	5.84	3.88	2.74	1.97
		222 nm	0.7055	0.6810	0.5912	0.5483	0.0511	-2.2740
		260 nm	0.4223	0.4118	0.4007	0.3845	0.4792	0.4944
HCO_3^-/CO_3^{2-}	6.5	$[O_3]_0$ ($x10^{-5}$ M)	9.44	5.23	3.53	2.31	1.60	1.07
		222 nm	0.7265	0.7826	1.0455	0.9856	0.9513	0.9064
		260 nm	0.3136	0.3765	0.4566	0.4197	0.4188	0.3467
	8.1	$[O_3]_0$ ($x10^{-5}$ M)	7.67	5.28	3.68	2.96	1.83	1.12
		222 nm	0.6808	0.6864	0.6375	0.9645	0.9286	1.1772
		260 nm	0.3854	0.3721	0.3492	0.4905	0.4582	0.5664
	9.2	$[O_3]_0$ ($x10^{-5}$ M)	9.82	6.47	4.44	2.97	1.96	1.07
		222 nm	0.7233	0.7256	0.6941	1.1104	1.1382	1.6273
		260 nm	0.4123	0.4201	0.3952	0.5527	0.5057	0.7830
No scavenger	6.5	$[O_3]_0$ ($x10^{-5}$ M)	8.85	2.89	1.67	1.00	0.79	0.59
		222 nm	0.4805	0.6113	0.6126	0.5959	0.4995	-1.1095
		260 nm	0.2318	0.3181	0.3388	0.4026	0.3614	0.5538
	8.1	$[O_3]_0$ ($x10^{-5}$ M)	8.84	5.38	3.40	2.32	1.12	0.85
		222 nm	0.6466	0.6798	0.7002	0.6850	0.6883	-0.7389
		260 nm	0.3195	0.3597	0.3680	0.3842	0.3350	0.8584
	9.7	$[O_3]_0$ ($x10^{-5}$ M)	10.30	7.03	4.73	3.62	2.16	1.25
		222 nm	0.7516	0.7749	0.8195	0.8320	0.8475	0.9034
		260 nm	0.3540	0.4240	0.4231	0.4281	0.4344	0.4571