PROJECT REPORT
2003-1
FINAL PROJECT REPORT

sustainable
forest
management
network

réseau
sur la
gestion durable
des forêts

Advanced Oxidation for the Treatment of Resin and Fatty Acids

A Network of Centres of Excellence
Un réseau de centres d'excellence

Greg Wright, Daniel W. Smith and Mohamed Gamal El-Din

For copies of this or other SFM publications contact:

Sustainable Forest Management Network
G208 Biological Sciences Building
University of Alberta
Edmonton, Alberta, T6G 2E9
Ph: (780) 492 6659
Fax: (780) 492 8160
http://www.ualberta.ca/sfm

ISBN 1-55261-170-1

Advanced Oxidation for the Treatment of Resin and Fatty Acids

SFM Network Project: Advanced Oxidation Processes for the Removal of Toxic Chemicals from Pulp Mill Effluents

by

Greg Wright, Daniel W. Smith and Mohamed Gamal El-Din

Department of Civil and Environmental Engineering

University of Alberta, Edmonton, Alberta

T6G 2M8

March, 2003

EXECUTIVE SUMMARY

Experiments were conducted to investigate the applicability of advanced oxidation processes (AOPs) to reduce the concentrations of Resin and Fatty Acids (RFAs) found in pulp mill effluents. Toxicity of pulp mill effluents is linked to numerous effluent characteristics. However, the focus of this study is on toxicity due to RFAs, specifically abietic and linoleic acids, respectively. The oxidation kinetics of the reaction between dissolved ozone and either RFA at pH of approximately 7.3 were evaluated using a Continuous Flow Stirred Tank Reactor (CFSTR). The overall kinetics were modeled as a second order, with first order in respect to both ozone and RFA. At 20°C, the overall rate constants for abietic and linoleic acids were predicted to be 3.47×10^3 and 1.31×10^4 $M^{-1}sec^{-1}$, respectively. It was also observed that greater than 85% reduction of 12.0 mg/L linoleic acid and 70% reduction of 4.5 mg/L abietic acid were achieved with ozone doses on the order of 2.5 mg/L. Also, acute toxicity was investigated using Microtox® assays. It was found that treated abietic acid was more toxic than the raw abietic acid sample, whereas the treated linoleic acid showed a decrease in toxicity compared to the raw sample.

ACKNOWLEDGEMENTS

We would like to thank Mrs. Maria Demeter for the countless hours she assisted in the laboratory. Also, thanks to the Sustainable Forest Management (SFM) Network of Centres of Excellence for their financial support in making this research possible.

TABLE OF CONTENTS

1. INTRODUCTION 1

1.1. OBJECTIVES 2

2. RESULTS AND DISCUSSION 2

2.1. SAMPLE PREPARATION 2
2.2. ANALYTICAL PROCEDURES FOR RFA DETERMINATION 3
2.3. CONTINUOUS FLOW STIRRED TANK REACTOR (CFSTR) DESIGN 5
2.4. RESIN AND FATTY ACID DEGRADATION KINETICS 6
2.5. OZONE AUTODECOMPOSITION 8
2.6. KINETICS OF RFA OXIDATION BY OZONE 11
2.6.1. Abietic Acid 11
2.6.2. Linoleic Acid 12
2.7. RFA REMOVAL EFFICIENCY 14
2.7.1. Abietic Acid 14
2.7.2. Linoleic Acid 16
2.8. TOXICITY ANALYSIS 17
2.8.1. Abietic Acid 18
2.8.2. Linoleic Acid 18

3. MANAGEMENT APPLICATIONS 19

4. CONCLUSIONS 20

5. RECOMMENDATIONS 21

5.1. EFFECTS OF OZONE DOSE AND TEMPERATURE ON REMOVAL EFFICIENCY 21
5.2. EFFECT OF OZONE ON TOXICITY OF TREATED EFFLUENT 21

6. REFERENCES 22

APPENDIX A 24

LIST OF TABLES

TABLE 1 RESULTS FROM OZONE OXIDATION OF ABIETIC ACID. 11
TABLE 2 RESULTS FROM OZONE OXIDATION OF LINOLEIC ACID. 13
TABLE 3 ABIETIC ACID RAW DATA FROM OXIDATION EXPERIMENTS. 25
TABLE 4 LINOLEIC ACID RAW DATA FROM OXIDATION EXPERIMENTS. 27
TABLE 5 POOLED RESULTS FROM CFSTR TRACER TESTS ANALYZED BY 2ND ORDER DECAY KINETICS (DATA USED TO PRODUCE FIGURE 6). 29
TABLE 6 MICROTOX® RESULTS FOR ABIETIC ACID (DATA USED TO PRODUCE FIGURE 13). 30
TABLE 7 MICROTOX® RESULTS FOR LINOLEIC ACID (DATA USED TO PRODUCE FIGURES 14) 31

LIST OF FIGURES

FIGURE 1 CALIBRATION CURVE FOR ABIETIC ACID USING GC-FID ANALYSIS. 4
FIGURE 2 CALIBRATION CURVE FOR LINOLEIC ACID USING GC-FID ANALYSIS. 4
FIGURE 3 EXPERIMENTAL SET-UP FOR OXIDATION EXPERIMENTS. 6
FIGURE 4 EXPERIMENTAL AND THEORETICAL KCL CONCENTRATION VERSUS TIME.... 6
FIGURE 5 SCHEMATIC OF THE FLOATING-LID HEADSPACE-FREE REACTOR................ 9
FIGURE 6 POOLED OZONE SPECIFIC DECAY RATE CONSTANTS AT VARIOUS TEMPERATURES. 10
FIGURE 7 POOLED ABIETIC ACID DEGRADATION RATE CONSTANTS. 12
FIGURE 8 POOLED LINOLEIC ACID DEGRADATION RATE CONSTANTS. 13
FIGURE 9 EFFECT OF OZONE DOSE ON THE FRACTION OF ABIETIC ACID REMOVED. . 15
FIGURE 10 EFFECT OF TEMPERATURE ON FRACTION OF ABIETIC ACID REMOVED. 15
FIGURE 11 EFFECT OF OZONE DOSE ON THE FRACTION OF LINOLEIC ACID REMOVED. 16
FIGURE 12 EFFECT OF TEMPERATURE ON FRACTION OF LINOLEIC ACID REMOVED. ... 17
FIGURE 13 MICROTOX ACUTE TOXICITY OF THE ABIETIC ACID SAMPLE TREATED WITH OZONE. 18
FIGURE 14 MICROTOX ACUTE TOXICITY OF THE LINOLEIC ACID SAMPLE TREATED WITH OZONE. 19

1. INTRODUCTION

As with all major industries, the pulp and paper industry has numerous environmental implications. Of greatest concern is the effluent produced and its potential to cause considerable damage to receiving waters. Major environmental problems associated with their effluent arise from one or a combination of: suspended solids, dissolved oxygen demand, toxicity, and color (Poole et al., 1978). Extensive research, testing, and development of wastewater treatment processes have occurred and all of these parameters have been reduced. Toxicity reduction occurs to a greater or a lesser extent depending on the in-plant pulping processes, the type of wood, and the wastewater treatment processes used. The reduction of toxicity is not fully understood as a great deal of materials may be captured in the sludge collected during pulp mill effluent treatment. Studies have shown that toxicity is caused by a number of organic and inorganic compounds. The principle toxicants include (Poole et al., 1978): (1) resin acids; (2) chlorinated lignins; (3) chlorinated resin acids, phenolics and other acidic groups; (4) unsaturated fatty acids; (5) diterpene alcohols; (6) juvabiones; and (7) lignin degradation products. Although much attention has been focused on organochlorines, studies have shown that a significant percentage of effluent toxicity is attributable to resin and fatty acids, and therefore they are of greatest environmental concern (Fahraeus-Van Ree and Payne, 1999).

Resin and fatty acids (RFAs) are organic extractives released from wood fibers during chemical and mechanical pulping. RFAs are lipophilic and have the potential for bioaccumulation in liver, bile, and plasma of freshwater and estuarine fish and in estuarine clams and amphipods (Fahraeus-Van Ree and Payne, 1999). Reported total concentrations of resin and fatty acids range from 0.1 to 80 mg/L in untreated pulp mill effluents, and are acutely toxic to fish at concentrations of the order of 1 mg/L (McLeay, 1987). Therefore, a treatment that provides excellent degradation of toxic compounds is required in order to meet stringent discharge limits.

At present, the majority of pulp mills use activated sludge and aerated lagoons to treat their effluents. The major downfall to biological treatment is that the large organic compounds, such as RFAs, are not fully degraded prior to effluent discharge and therefore pose a threat to the receiving waters. Work by Murray and Richardson (1993) showed that biological degradation of toxic chemicals present in pulp mill effluents can be greatly facilitated by a chemical oxidation pretreatment step. The improvement of effluent biodegradability when using ozone treatment has been reported frequently (Mohammed and Smith, 1992; Roy-Archand and Archibald 1996). Electrophilic attack of ozone breaks lignin and other organics into smaller molecular weight products, which are more susceptible to biological decomposition.

The oxidizing power of ozone can be strengthened further by the use of Advanced Oxidation Processes (AOPs). AOPs generate highly reactive intermediates, including the hydroxyl radical, which is among the strongest oxidants (Sapach and Viraraghavan, 1997). Ozone treatment is classified as an AOP when it is applied at high pH values. Yeber et al. (1999) showed that AOPs could efficiently degrade pulp mill effluents with high organic content, improving their biodegradability and reducing their toxicity.

1.1. Objectives

The overall objective of this study is to investigate the degradation kinetics of toxic chemicals (RFAs) from pulp mills effluents by the advanced oxidation processes (AOPs). The specific objectives of this study include:

1. To further our fundamental understanding of chemical oxidation of resin and fatty acids present in pulp mill effluents by AOPs. RFAs selected for this research are abietic acid (resin acid) and linoleic acid (fatty acid);

2. To determine the effect of important parameters such as ozone dose, pH, and temperature on the removal of these RFAs;

3. To utilize bioassay toxicity tests in order to evaluate the removal of toxicity as a result of applying advanced oxidation processes; and

4. To establish the degradation kinetics of the selected RFAs.

2. RESULTS AND DISCUSSION

2.1. Sample Preparation

Based on literature, it was determined to use abietic acid to represent the resin acids found in pulp mill effluents, and linoleic acid to represent the fatty acids. Both abietic acid and linoleic acid sample preparations involved; first preparing a stock solution, and next a working solution. The abietic acid stock solution was prepared by dissolving 240 mg of abietic acid in 4 mL of 95% Ethanol and applying heat. The working solution was then prepared by adding 2 mL of the concentrated stock solution to 12 L of pH 8 phosphate buffer. The linoleic acid stock solution was prepared by dissolving adding 133 μL of 0.9 g/mL linoleic acid in 250 mL of pH 11 buffer. The 250 mL stock solution was then transferred into 12 L of pH 8 buffer to make the working sample. The phosphate buffer solution was prepared using sodium phosphate monobasic, potassium phosphate, de-ionized water, and pH regulated using a 5N NaOH solution. The recipe for 2 L of pH 8 phosphate buffer is as follows: combine 14.196 grams of $Na_2HPO_4*7H_2O$ with 0.852 grams of KH_2PO_4 and fill to volume (2L) with ozone demand free water. Working RFAs samples were prepared within 48 hours of experiments and stored at 4 ºC. Dissolved ozone solutions were prepared immediately prior to ozonation experiments by applying ozone gas to a pH 7 phosphate buffer solution. An ozone generator model C2P-9C-4 by PCI Ozone Corp. was utilized to produce ozone gas using extra dry, high purity oxygen.

2.2. Analytical Procedures for RFA determination

The analytical procedure for the determination of RFAs concentrations is based on the work by Voss and Rapsomatiotis (1985). The first step was the extraction phase, which involved mixing 15 mL of the quenched ozonated samples (and blanks) with 5 mL of methyl *tert*-butyl ether (MTBE) and removing the solvent extract using a 200 mL separatory funnel. Next, the solvent extract was placed in a 50 mL round-bottom flask and concentrated to less that 0.3 mL (nearly dry) using a vacuum rotary evaporator (model Rotavapor-R by Buchi) at 40 ºC. The remaining solution was then methylated by adding 900 μL of diazomethane solution to the nearly dry flask. The diazomethane solution was prepared using the method outlined in *Standard Methods for the Examination of Water and Wastewater* (1992). Using a diazomethane generator, 600 μL of a 5N NaOH solution was added to 66 mg of 1-methyl-3-nitro-1-nitrosoguanidine, and the off-gas was collected in 6 mL of diethyl ether. The solution was then transferred to GC vials and allowed to stabilize overnight at 4ºC. The samples were then analyzed using GC-FID.

Chromatographic analyses were made using a Hewlett-Packard Model 5890A gas chromatograph, equipped with FID. The column used was a 30 m x 0.25 mm I.D. fused silica capillary column (Supelco) wall coated with poly(20% diphenyl/80% dimethylsiloxane) (SPB-20 type) phase of 0.25 μm film thickness. The GC conditions were as follows: (1) the column temperature was held at 170 ºC for 2 minutes then programmed to increase to 280 ºC at a rate of 6 ºC/min and then it was held constant at 280 ºC for 20 minutes; (2) the injector temperature was set at 250 ºC; (3) the detector temperature was set at 280 ºC; and (4) helium was used as the carrier gas at 140 kPa. RFAs concentrations were determined based on standard curves obtained using electronically-integrated GC peaks of known RFAs concentrations. The standard curves for abietic and linoleic acids are shown in Figures 1 and 2, respectively.

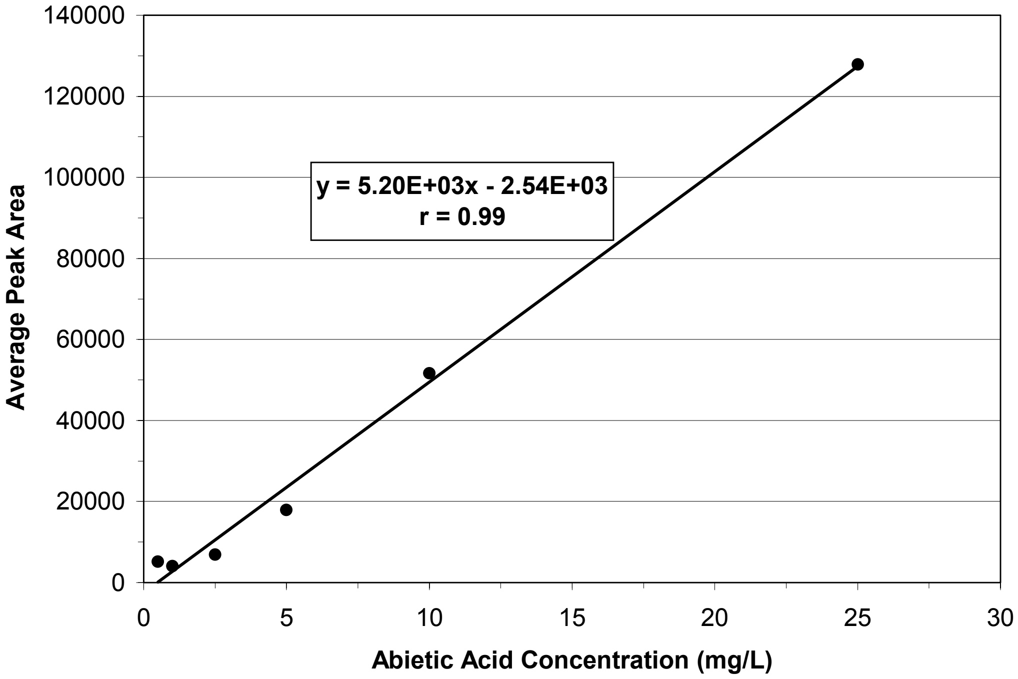

Figure 1 Calibration curve for abietic acid using GC-FID analysis.

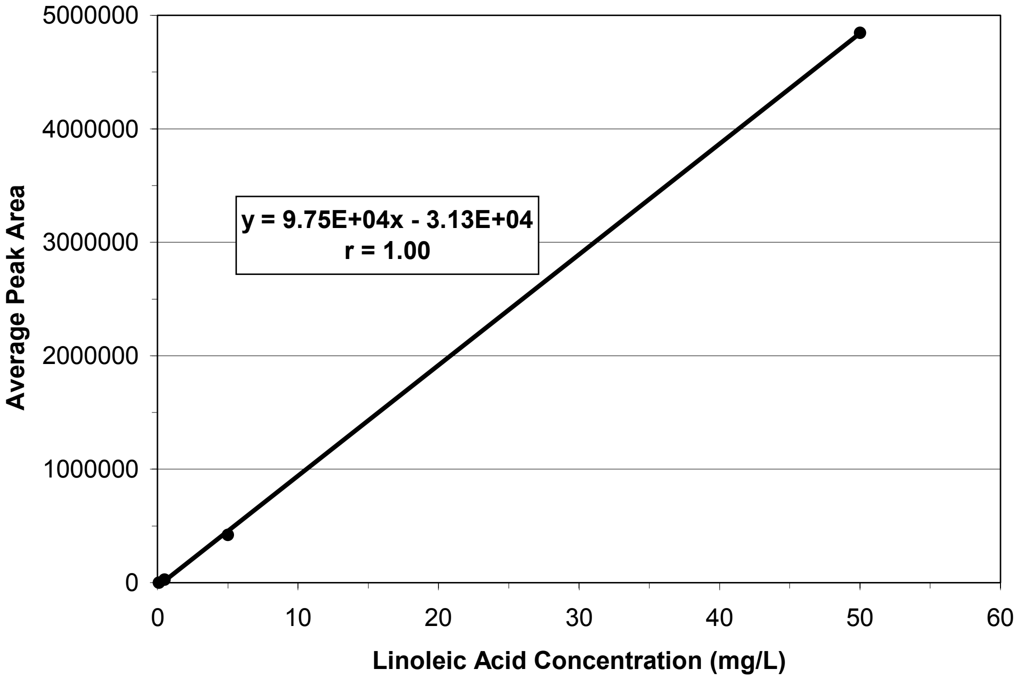

Figure 2 Calibration curve for linoleic acid using GC-FID analysis.

2.3. Continuous Flow Stirred Tank Reactor (CFSTR) Design

All oxidation experiments between ozone and either linoleic or abietic acid were conducted in a continuous flow stirred tank reactor (CFSTR). As shown in Figure 3, the experimental set-up includes: (1) CFSTR with two inlets and one outlet fitted with an adjustable valve calibrated for a flow rate of 430 mL per minute; (2) one 25 L glass bottle containing a know concentration of either linoleic or abietic acid; (3) one 25 L glass bottle containing ozonated buffer solution; (4) ice bath; (5) two peristaltic pumps each calibrated to deliver 215 mL/min to the CFSTR; and (6) a port to sample for dissolved ozone concentration being added to the reactor.

Oxidation experiments were conducted by pumping the sample solution (either linoleic or abietic acid) and the dissolved ozone solution, both at 215 mL/min for a total reactor flow rate of 430 mL/min, into the reactor. It was assumed that the solutions were instantaneously and completely mixed upon entering the reactor. Ozone doses entering the reactor were determined by potassium iodide titration analysis (APHA-AWWA-WEF, 1992) of samples taken from the ozone line sampling port. Residual ozone and RFA concentrations were determined by analysis of samples taken from the outlet of the CFSTR. In order to validate the assumption that the reactor performs as an ideal CFSTR, tracer tests were conducted by injecting a potassium chloride (KCl) tracer at the reactor inlet and measuring the KCl concentration eluting from the CFSTR outlet. Figure 4 illustrates the measured and theoretical concentrations of the KCl tracer versus time, i.e., the measured and theoretical residence time distribution (RTD) curves. Based on the comparison between the measured and theoretical RTDs, it is safe to assume that the reactor can be modeled as a CFSTR.

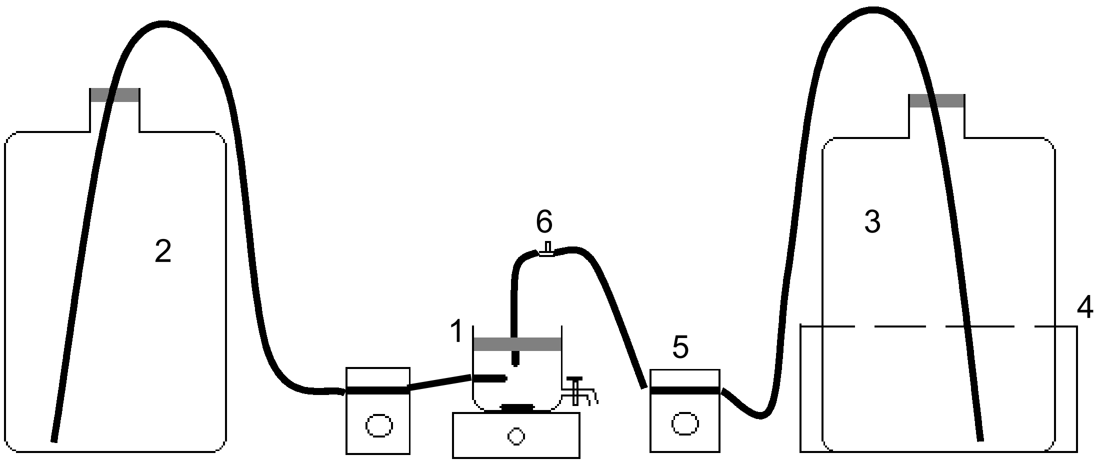

Figure 3 Experimental set-up for oxidation experiments.

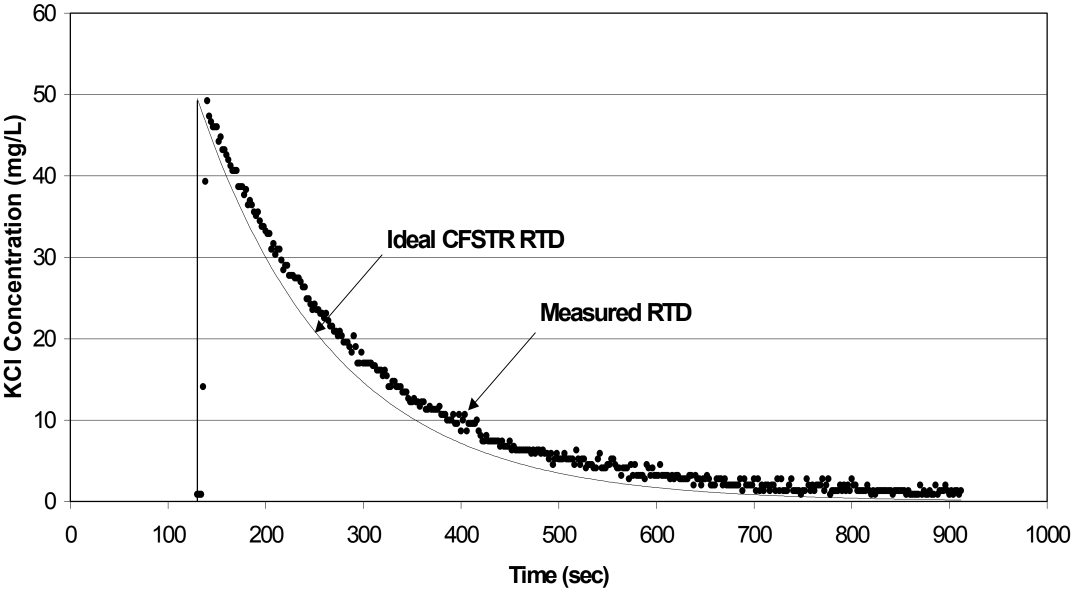

Figure 4 Experimental and theoretical KCl concentration versus time.

2.4. Resin and Fatty Acid Degradation Kinetics

Using the CFSTR system, experiments were conducted to evaluate the degradation kinetics of linoleic and abietic acids when oxidized with dissolved ozone. Preliminary studies showed that the reaction between ozone and either RFA is pH dependent. It was found that no reaction takes place at low pH (below 4) and a rapid reaction takes place at pH 8. The pH dependency suggests that the hydroxyl radical may be the oxidant, and therefore, AOPs are well suited for RFAs degradation. At high pHs, the dissolved ozone is rapidly converted to hydroxyl radical which is among the most powerful oxidants. The overall reaction between either linoleic acid or abietic acid and ozone can be expressed as:

$$aO_3^{n1} + bRFA^{n2} \rightarrow \text{Products}$$

According to the above reaction, "a" moles of ozone react with “b” moles of either RFA. n_1 is the reaction order with respect to ozone while n_2 is the reaction order with respect to either RFA. Analysis to determine the kinetics was based on mass balance of the reactor system with respect to both RFA and ozone. The mass balance through the reactor with respect to ozone and either RFA are, respectively:

$$QC_{ozone,in} - QC_{ozone,out} - k_w C_{ozone,out}^{2} V - ak_{oa} C_{ozone,out}^{n1} C_{acid,out}^{n2} V = 0 \tag{1}$$

$$QC_{acid,in} - QC_{acid,out} - bk_{oa} C_{ozone,out}^{n1} C_{acid,out}^{n2} V = 0 \tag{2}$$

where: Q is the total flow rate through the reactor (430 mL/min); C_{ozone} is the concentration of dissolved ozone entering ("in") or exiting("out") the reactor; C_{acid} is the concentration of either RFA entering (“in”) or exiting (“out”) the reactor; a and b are the stoichiometric coefficients of ozone and RFA, respectively; k_w is the ozone specific utilization rate constant; k_{oa} is the RFA degradation rate constant; n_1 and n_2 are the reaction order with respect to ozone and RFA (both assumed to equal 1); and V is the volume of the reactor (1 L). Since all parameters, in Equations 1 and 2, are known, except k_{oa}, Equations 1 and 2 can be simplified to:

$$\text{Constant}_1 = ak_{oa} C_{ozone,out}^{n1} C_{acid,out}^{n2} \tag{3}$$

$$\text{Constant}_2 = bk_{oa} C_{ozone,out}^{n1} C_{acid,out}^{n2} \tag{4}$$

where:

$$\text{Constant}_1 = QC_{\text{ozone,in}} - QC_{\text{ozone,out}} - k_w C^2_{\text{ozone,out}} V \quad (5)$$

$$\text{Constant}_2 = QC_{\text{acid,in}} - QC_{\text{acid,out}} \quad (6)$$

Finally the RFA degradation rate constant can be calculated by combining Equations 3 and 4, to generate:

$$k_{oa} = \frac{\text{Constant}_1 + \text{Constant}_2}{(a+b)(C^{n1}_{\text{ozone,out}} C^{n2}_{\text{acid,out}})} \quad (7)$$

Therefore, the RFA degradation rate constant k_{oa} can be determined using the above equations by measuring the influent and residual concentrations of ozone and RFAs.

2.5. Ozone Autodecomposition

In order to evaluate the overall RFA degradation rate constant, the rate at which ozone is lost due to autodecomposition must be determined. Experiments were conducted using a 1200 mL floating lid head space free reactor (See Figure 5). The design of the experimental set-up and the experimental procedure were adapted from the study of Oke et al. (1998). Detailed description of the experimental methods can be found in Oke et al. (1998). In this study, experiments were conducted by combining 500 mL of buffer solution pH 8 with 500 mL dissolved ozone buffer solution pH 7 to give a mixed pH of 7.34 (solutions prepared as outlined in Section 2.1). The kinetics study was conducted over a range of solution temperatures in order to investigate its effect on the ozone autodecomposition kinetics. The water temperatures in this study ranged from 5.5 to 22.0 °C.

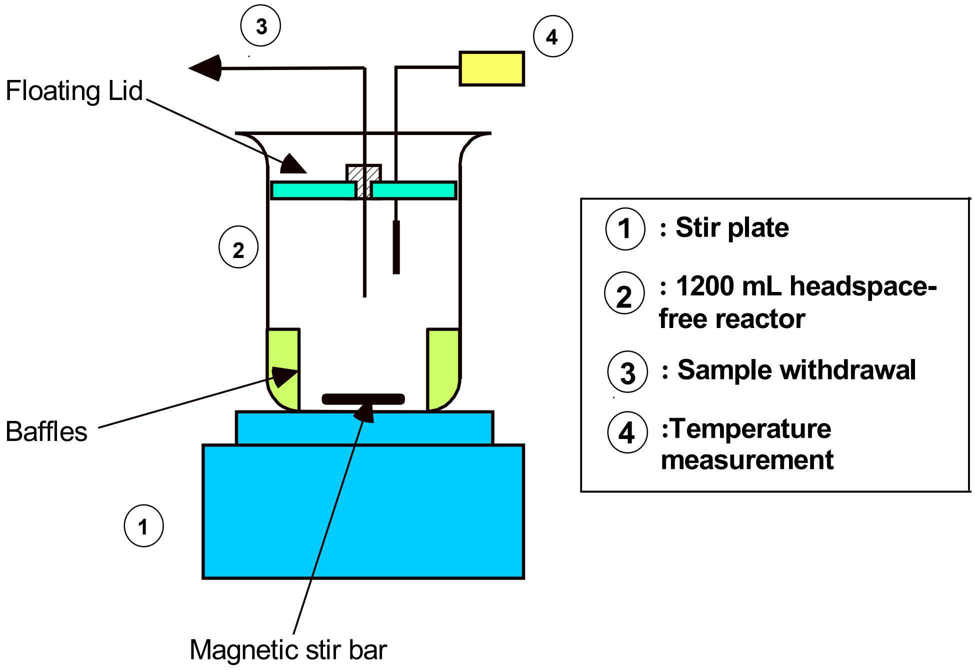

Figure 5 Schematic of the floating-lid headspace-free reactor.

The ozone autodecomposition was found to follow second order decay kinetics as follows:

$$\frac{dC}{dt} = -k_w C^2 \qquad (8)$$

where C is the dissolved ozone concentration at time "t" (mg/L), k_w is the ozone specific utilization rate constant (L/mg.s), and t is the reaction time (s). The data from each run was plotted based on the following linear equation:

$$\frac{1}{C} = \frac{1}{C_o} + k_w t \qquad (9)$$

The assumption that ozone autodecomposition can be represented by second order kinetics was valid if the plotted experimental data, following Equation 9, could be represented by a straight line. The plots of 1/C versus the reaction time were well described by a straight lines and the linear regression analyses produced correlation coefficients $0.99 \geq (r's) \geq 0.59$. For the tests that had the same initial water temperature and different initial dissolved ozone concentrations, similar decay rate constants (k_w's) were obtained suggesting that there was no effect of the initial ozone concentration on the decay rate constant of the ozone autodecomposition kinetics The individual k_w's were then pooled together and analyzed using a linear regression technique to determine the effect of solution temperature (T) on the ozone specific utilization rate constant. The kinetics temperature dependency was assumed to follow the Van't Hoff-Arrhenius relationship as follows:

$$\ln(k_w|_{T^\circ C}) = \ln(k_w|_{20^\circ C}) + (T-20)\ln\theta \tag{10}$$

where θ is the temperature correction factor. The linear regression technique was applied to obtain θ and $k_w|_{20^\circ C}$, as shown in Figure 6.

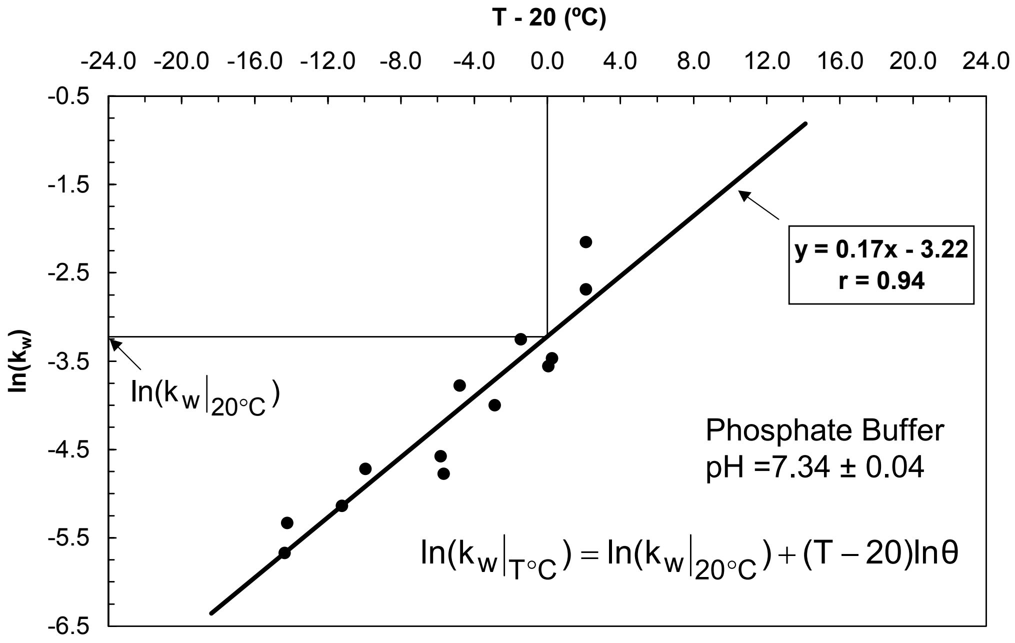

Figure 6 Pooled ozone specific decay rate constants at various temperatures.

From the linear regression, the solution temperature correction factor (θ) and $k_w|_{20^\circ C}$ were predicted to be 1.19 and 3.99×10^{-2} L/mg.s, respectively. The correlation coefficient of the pooled k_w's is 0.94, which validates the assumption that the ozone autodecomposition kinetics can be represented by a second order. These results were applied to the CFSTR mass balance equations, and thus the RFA degradation rate constants were calculated.

2.6. Kinetics of RFA Oxidation by Ozone

Oxidation experiments were conducted using the CFSTR operated by mixing dissolved ozone with either a linoleic acid or abietic acid sample solution. The experiments were conducted at various temperatures in order to determine the effect of temperature on the oxidation reaction of ozone with the RFAs. The results from individual oxidation experiments were analyzed using the mass balance principles outlined in section 2.4, to produce predicted values for the RFA degradation rate constant. Much like in the determination of the ozone specific utilization rate constant, the rate constant results from the individual runs were pooled together and analyzed using linear regression techniques to determine the overall RFA degradation rate constant as a function of sample temperature (T °C) following Van't Hoff Arrhenius equation. The overall degradation kinetics were modeled as a second order, with first order in respect to both ozone and RFA.

2.6.1. Abietic Acid

Oxidation experiments were conducted using ozone doses on the order of 2.5 mg/L and abietic acid sample concentration of approximately 4.5 mg/L. Results from the runs are outlined in Table 1.

Table 1 Results from ozone oxidation of abietic acid.

Run	**Temperature**	**Abietic Acid Concentration**	**Ozone Dose**	**2nd order rate constant**
	^oC	**mg/L**	**mg/L**	**$k_{oa} = M^{-1}s^{-1}$**
15	14.6	3.17	1.57	1.52E+03
5	15.5	5.32	3.89	1.33E+03
11	16.0	3.55	1.87	1.62E+03
3	16.6	4.37	2.73	1.35E+03
13	18.6	3.71	1.68	2.38E+03
4	19.1	5.76	2.76	2.29E+03
9	21.4	5.94	2.97	6.05E+03
8	22.5	5.17	2.42	5.85E+03

Upon investigation of the 2nd order rate constants shown in Table 1, it can be noted that there is a general trend indicating an increase in the magnitude of the rate constant with increasing temperature. This suggests that abietic acid is more easily degraded by ozone in warmer conditions. Figure 7 illustrates the pooled results from abietic acid ozonation studies analyzed using the Van't Hoff-Arrhenius linear relationship.

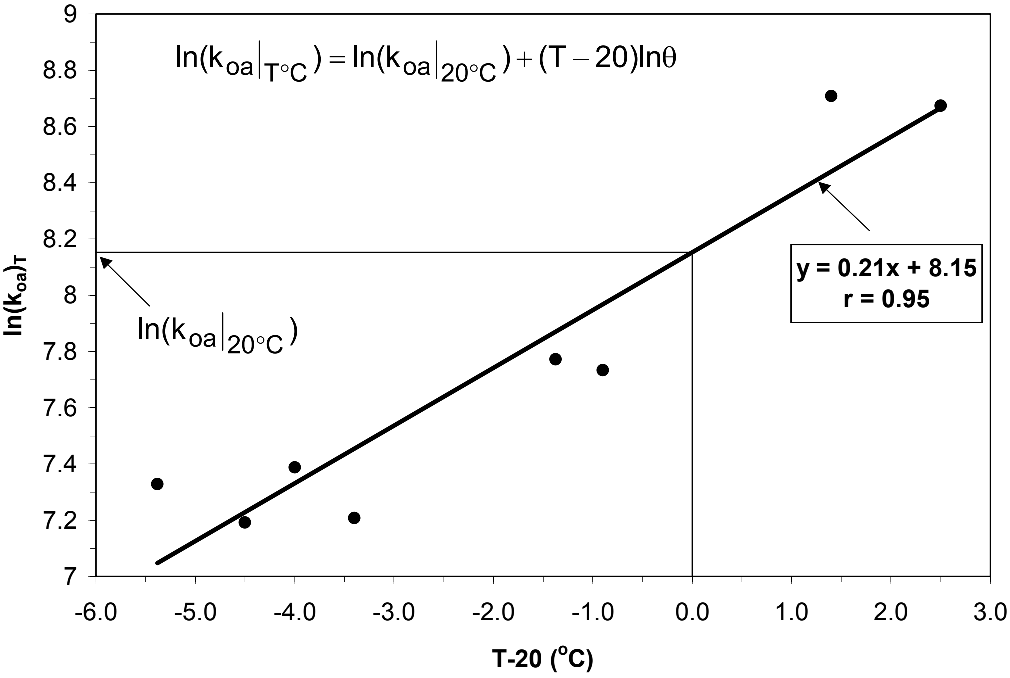

Figure 7 Pooled abietic acid degradation rate constants.

As was postulated based on the results in Table 1, the relationship between the rate constant and temperature is well described by a straight line and the linear regression analysis produced a correlation coefficient (r) of 0.95 (see Figure 7). From the linear regression of the pooled results, the solution temperature correction factor (θ) was predicted to be 1.23 and the overall degradation rate constant at 20°C was predicted to be 3.47×10^3 $M^{-1}s^{-1}$.

2.6.2. Linoleic Acid

Ozone oxidation experiments were conducted using ozone doses on the order of 2.8 mg/L and linoleic acid sample concentration of approximately 12.0 mg/L. Results from the runs are outlined in Table 2.

Table 2 Results from ozone oxidation of linoleic acid.

Run	Temperature	Linoleic Acid Concentration	Ozone Dose	2nd order rate constant
	°C	mg/L	mg/L	$k_{oa} = M^{-1}s^{-1}$
11	8.1	9.80	4.13	1.25E+03
10	13.4	16.01	2.56	4.81E+03
9	14.0	15.14	3.12	7.21E+03
8	15.2	16.45	2.93	1.25E+03
4	21.9	10.44	3.03	8.14E+03
5	22.0	8.94	2.60	3.99E+04
6	23.3	8.61	1.82	3.84E+04

With the exception of run 8, it can be noted from Table 2 that the degradation rate constant increased with increasing temperature. This suggests that the oxidation reaction is facilitated in warmer conditions, as was observed with abietic acid. The above results were then pooled and analyzed based on Van't Hoff-Arrhenius linear principles (Figure 8).

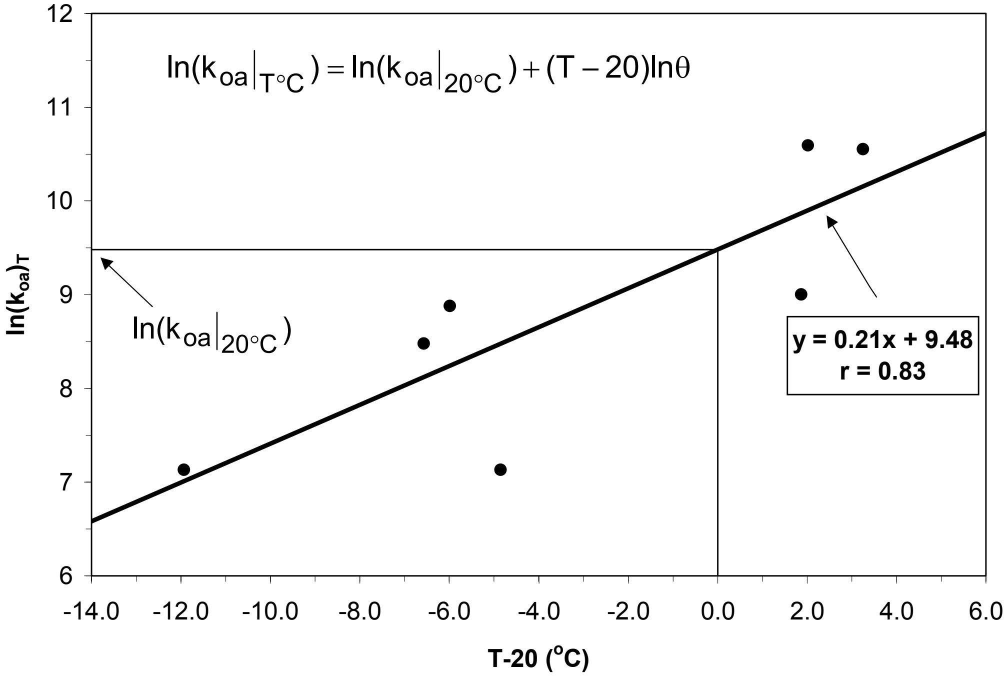

Figure 8 Pooled linoleic acid degradation rate constants.

The experimental results produced a modest linear fit, with a linear correlation coefficient of 0.83. Linear regression of the results produced a solution temperature correction factor (θ) of 1.23 and a degradation rate constant at 20°C of $1.31 \times 10^4\ M^{-1}s^{-1}$.

2.7. RFA Removal Efficiency

The results from the CFSTR oxidation experiments were also used to determine the effect of ozone dose and temperature on RFA removal. The removal efficiency can be calculated by Equation 11:

$$\eta(\%) = \frac{C_{acid,in} - C_{acid,out}}{C_{acid,in}} \times 100 \qquad (11)$$

where: η is the removal efficiency (%), and $C_{acid,in}$ and $C_{acid,out}$ are the raw and residual acid concentrations, respectively. The purpose of evaluating the results for removal efficiency with respect to either temperature or ozone dose, is to determine the optimum conditions to operate the CFSTR system. In general, removal efficiency increases to a certain point, after which the effect of improving ozone dose or temperature has minimal effect. Therefore, if the optimum values can be determined, the CFSTR can be operated at such conditions continuously and thus the desired removal efficiency can be achieved.

2.7.1. Abietic Acid

Results from the oxidation experiments with ozone and abietic are shown in Table 3 (refer to Appendix A). It can be noted from the raw data that the removal efficiency ranged from 12% to 84% with ozone doses ranging from 1.5 to 3.9 mg/L. Figure 9 illustrates the effect of ozone dose on the removal efficiency of abietic acid.

Although the removal efficiency never reaches 90%, it can be noted that there is a modest trend indicating an increase in removal efficiency with increasing ozone dose. This is in agreement to what one might speculate, since it stands to reason that a higher ozone dose would have the potential to degrade a larger amount of abietic acid. It can also be observed that over the range of ozone doses used in this study, there is no apparent optimum dose. Therefore, perhaps experiments conducted using higher ozone doses would provide conditions necessary to achieve optimal removal efficiency.

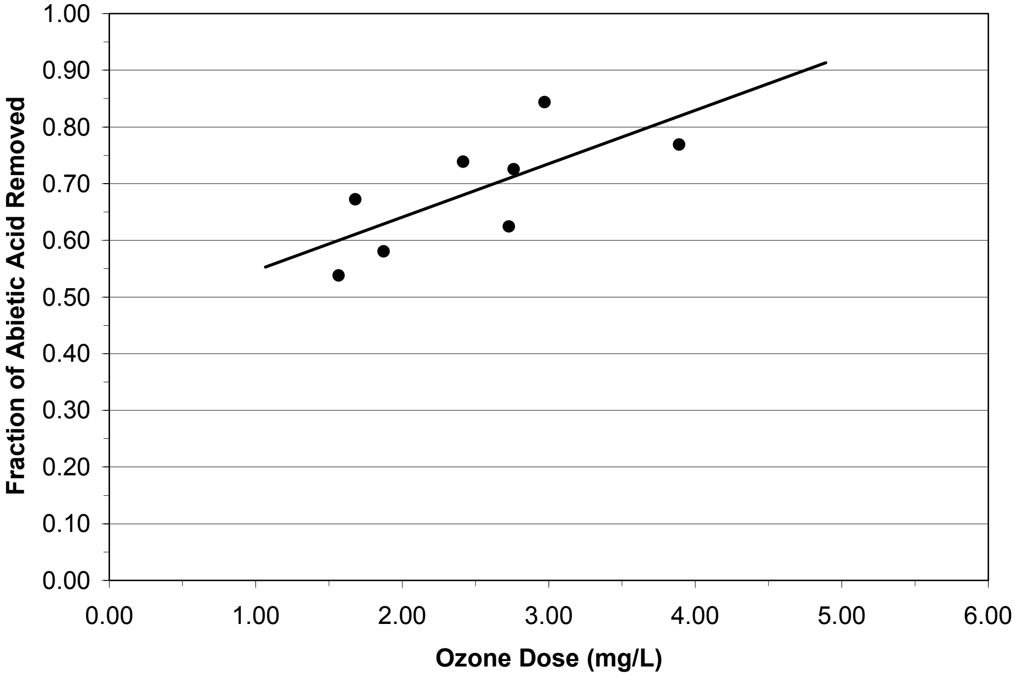

Figure 9 Effect of ozone dose on the fraction of abietic acid removed.

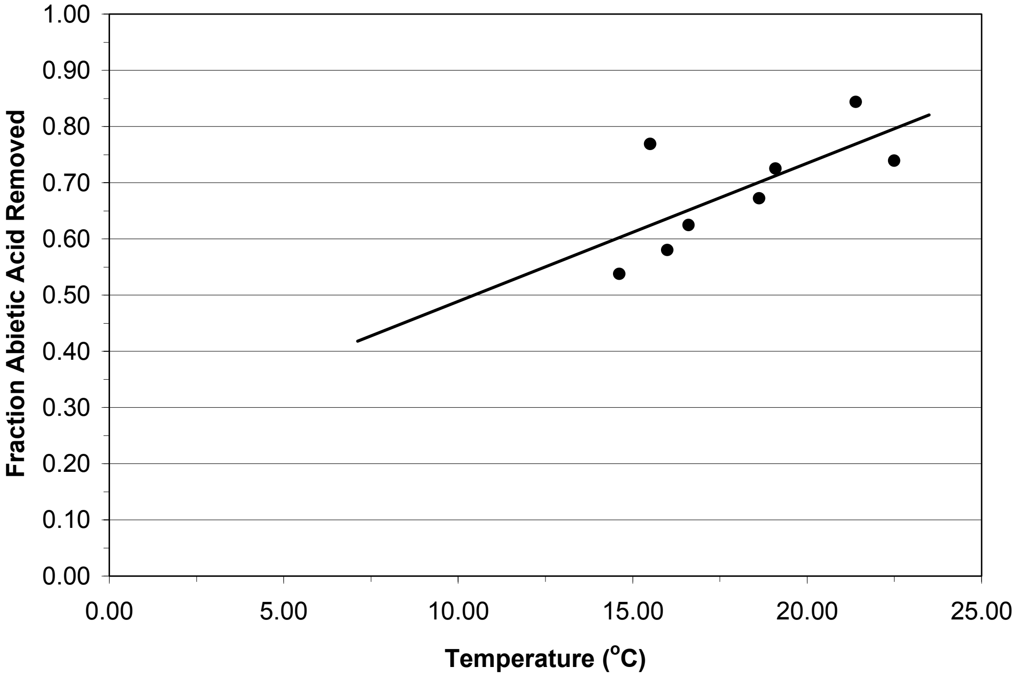

Figure 10 Effect of temperature on fraction of abietic acid removed.

The effect of temperature on the removal efficiency was also investigated (Figure 10). It can be noted from Figure 10 that a modest correlation between temperature and removal efficiency is present. Figure 10 also illustrates the effect of temperature to facilitate the oxidation reaction of abietic acid and ozone. Over the range of conditions used in this study, there are no indications to the optimal temperature.

2.7.2. Linoleic Acid

Results from the oxidation experiments with linoleic acid and dissolved ozone are provided in Table 4 (refer to Appendix A). Removal efficiencies ranged from 58% to 93% for ozone doses between 1.8 and 4.1 mg/L. Figure 11 illustrates the effect of ozone dose on the linoleic acid removal efficiency.

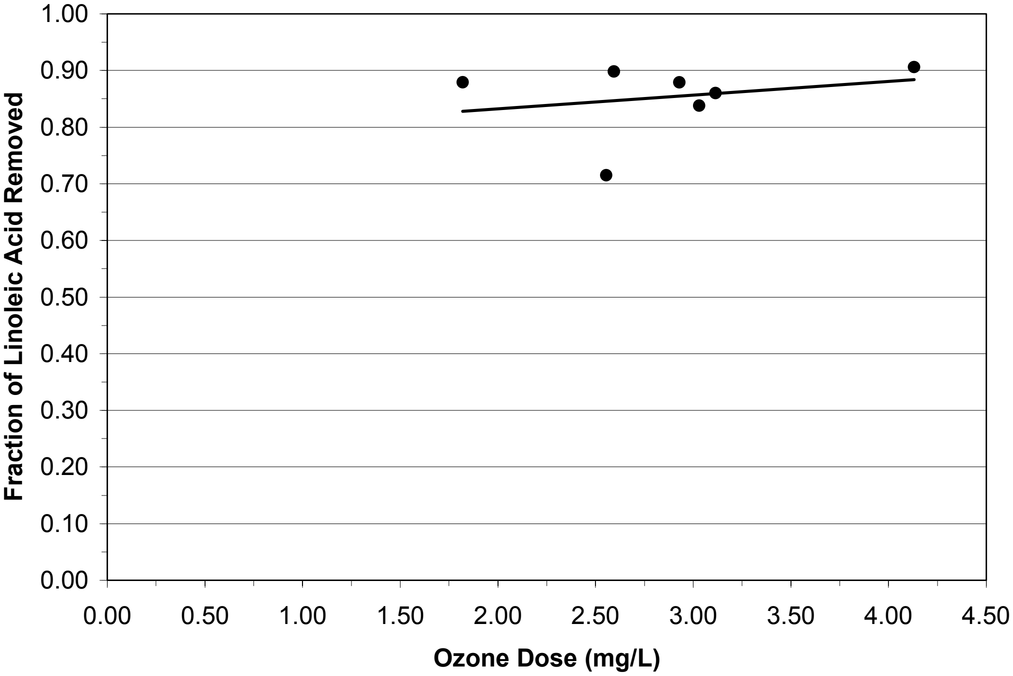

Figure 11 Effect of ozone dose on the fraction of linoleic acid removed.

It can be noted from Figure 11 that over the range of ozone doses used in this study the removal efficiency is almost at a plateau. This would suggest that the ozone doses used were at or above the optimum value. Also, the fact that the removal efficiency is between 85 and 90 percent would support the prediction that experiments were conducted at or above the optimum ozone doses. Therefore, studies using slightly lower ozone doses may shed light on the optimum ozone dose for linoleic acid degradation.

The effect of temperature on the linoleic acid removal efficiency was also investigated (Figure 12). Figure 12 shows that the effect of temperature on the removal efficiency is almost at a plateau. This is likely the result of experiments being conducted at or above the optimum conditions.

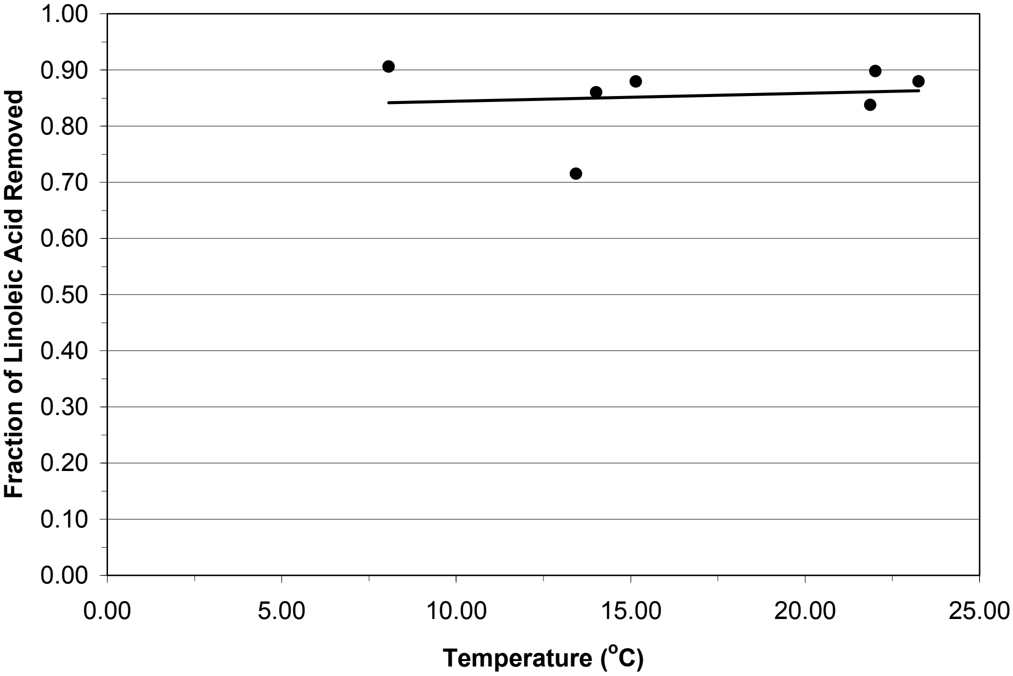

Figure 12 Effect of temperature on fraction of linoleic acid removed.

2.8. Toxicity Analysis

Toxicity was estimated using the Microtox® luminescence assay. This assay uses a phosphorescent marine bacterium *Photobacterium phosphoreum* to assess the EC_{50} values of liquid samples. The assay measures a decrease in light intensity in response to the presence of substances that interfere with the normal cell operation of the bacterium. The EC_{50} represents the concentration of sample in dilution water (%V/V) at which the bioluminescence is reduced by 50 percent. The results generated from the tests are expressed as percent light inhibition, and are measure at 5, 15 and 30 minutes. The EC_{50} values were obtained using linear and nonlinear regression of the results. Toxicity is reported as toxicity units ($TU = 100/EC_{50}$), measured at 15 minutes.

2.8.1. Abietic Acid

Raw and residual abietic acid samples from ozone oxidation experiments were tested using Microtox® to evaluate the toxicity reduction (Figure 13)

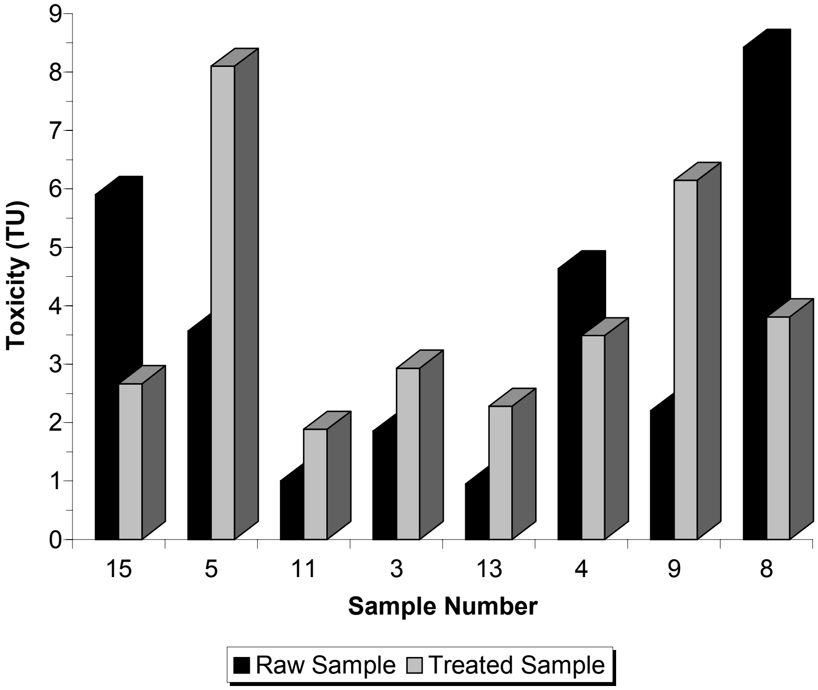

Figure 13 Microtox acute toxicity of the abietic acid sample treated with ozone.

With the exception of samples 8, 4 and 15, there was actually an increase in toxicity as a result of ozone oxidation. In most cases the toxicity increased by 50%. This indicates that rather than reducing the toxicity, the oxidation reaction produces byproducts that are more toxic than the untreated abietic acid. But at the same time, the two samples that had toxicity reductions (8 and 15) showed improvements in toxicity greater than 50%.

2.8.2. Linoleic Acid

Linoleic acid samples from ozone oxidation experiments were also investigated using Microtox® assays. Figure 14 illustrates the results from these tests. It was observed that the acute toxicity was reduced in all linoleic acid samples. The greatest improvement was sample 10 where approximately 95% of the toxicity was eliminated, whereas sample 4 and 5 showed improvements of less than 5%.

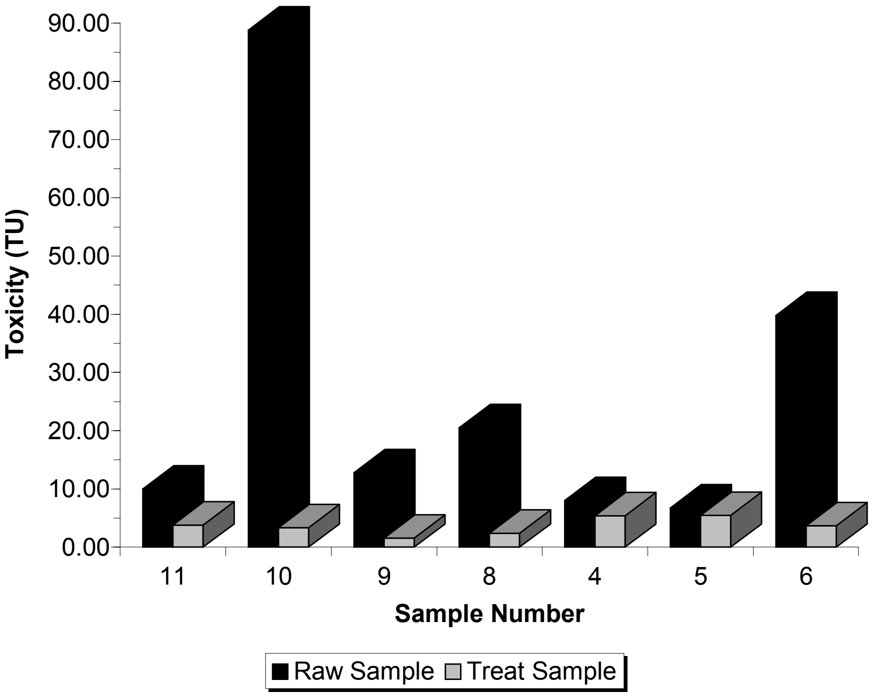

Figure 14 Microtox acute toxicity of the linoleic acid sample treated with ozone.

3. MANAGEMENT APPLICATIONS

This project involved the evaluation of the treatability of resin and fatty acids (RFAs), found in pulp mill effluents, using advanced oxidation (particularly, ozonation). This treatment has the potential to improve the quality of pulp mill effluents through the toxicity reduction in these effluents. Especially, when treating pulp mill effluents containing fatty acids (such as linoleic acid). The knowledge of the mechanisms and kinetics of the reactions between ozone and RFAS will lead to accurate design of ozone treatment systems for reducing the toxicity of pulp mill effluents.

As a result of achieving higher treatment levels of pulp mill effluents, the ecological integrity of the boreal forest waterways can be well maintained. Thus, this can lead to the preservation and improvement of the Canadian public and environmental health.

With the standards, that are used to regulate wastewater effluent discharges into the receiving environment, becoming more stringent, the need for effective treatment processes such as ozonation will become a necessity for many industries in order to comply with the stringent wastewater effluent quality standards.

4. CONCLUSIONS

The overall goal of this study was to evaluate the treatability of resin and fatty acids with advanced oxidation processes, and to establish degradation kinetics of RFAs under such conditions. The oxidation reaction between dissolved ozone and either abietic or linoleic acid showed a dependency on pH, with no reaction occurring at pH 3 and a rapid reaction taking place at pH 7.3. The dependency of a high pH suggests that the hydroxyl radical may be the oxidant, and therefore, AOPs are well suited for RFAs degradation.

A continuous flow stirred tank reactor was selected as the device to carry out the oxidation reactions. The removal efficiency of 4.5 mg/L abietic acid and 12.0 mg/L linoleic acid for ozone doses above 2.5 mg/L were found to be greater than 70% and 85%, respectively. It was also found that ozone dose and temperature greatly affected the removal efficiency of abietic acid, where either an increase in ozone dose or temperature lead to an increase in abietic acid removal efficiency. The effect of ozone dose and temperature on the removal efficiency of linoleic acid was also positive, however the magnitude of the effect was significantly lower than that on abietic acid removal. This might suggest that the oxidation experiments with ozone and linoleic acid were operating at or near optimum ozone dose or temperature levels. Whereas the levels were below optimum for the experiments with abietic acid, based on the fact that no plateau for removal efficiency was reach.

Based on a mass balance of the CFSTR system, the degradation kinetics of abietic and linoleic acids were calculated. The overall kinetics were modeled as a second order, with first order in respect to both ozone and RFA. At 20^{o}C, the overall rate constants for abietic and linoleic acids, were predicted to be $3.47\text{x}10^{3}$ and $1.31\text{x}10^{4}$ $M^{-1}sec^{-1}$, respectively.

Toxicity evaluation of the RFA oxidation was achieved using Microtox® assays. Results from the toxicity testing showed an increase in toxicity for abietic acid oxidation, but a decrease in toxicity for linoleic acid oxidation. A possible reason for the increase in toxicity with abietic acid oxidation is the formation of toxic byproducts that were not oxidized as a result of ozone doses being too low.

5. RECOMMENDATIONS

5.1. Effects of Ozone Dose and Temperature on Removal Efficiency

The conditions used in this study provided some insight to the effect of ozone dose and temperature on the removal efficiency of both abietic and linoleic acid. Not only were the ranges of ozone doses and experimental temperatures not broad enough, there was no way to accurately quantify the effect of each individual parameter. It is recommended that further studies be conducted where-by experiments are directed based on factorial design principles. This implies running experiments at three or more ozone doses and three or more temperatures, with triplicate runs at each parameter value, and evaluating the removal efficiency for each set of conditions.

5.2. Effect of Ozone on Toxicity of Treated Effluent

Although some insight to the effect of ozone on RFA toxicity was gained, no definate conclusions can be drawn. Therefore, it is suggested that more toxicity assays be performed to evaluate the exact effect of ozone on RFA toxicity. It can be anticipated that further toxicity testing will prove whether or not higher ozone doses can fully degrade toxic byproducts of the abietic acid oxidation. Also, it is suggested that further studies using actual pulp mill effluent be conducted to evaluate the toxicity removal of "real life" samples.

6. REFERENCES

1 APHA-AWWA-WEF, Standard methods for the examination of water and wastewater. 18th Ed. American Public Health Association, American Water Works Association, and Water Environment Federation (Washington, DC, USA: American Public Health Association, 1992).

2 Fahraeus-Van Ree, G.E. and Payne, J.F., “Enzyme Cytochemical Responses of Mussels (Mytilus edulis) to Resin Acid Constituents of Pulp Mill Effluents”, Bull. Environ. Contam. Toxicol., 63(4), 430-437 (1999).

3 McLeay, D., “Aquatic Toxicity of Pulp and Paper Mill Eflluent: A Review”, Report EPS 4/PF/1, Environment Canada, Canada (1987).

4 Mohammed, A. and Smith, D.W., “Effects of Ozone On Kraft Process Pulp Mill Effluent”, Ozone: Sci. & Eng., 14, 461-485 (1992).

5 Murray, W. and Richardson, M., “Development of biological and process technologies for the reduction and degradation of pulp mill wastes that pose threat to human health”, Crit. Rev. Environ. Sci. and Technol., 23(2), 157-194 (1993).

6 Oke, N. J., Smith, D. W. and Zhou, H, "An Experimental Analysis of Ozone Decay Kinetics in Natural Waters", Ozone: Sci. & Eng., 20,361-379 (1998).

7 Poole, N.J., Wildish, D.J. and Kristmanson, D.D., “The Effects of the Pulp and Paper Industry on the Aquatic Environment”, Crit. Rev. Environ. Control, 8(2), 153-185 (1978).

8 Roy-Arcand, L. and Archibald, F.S., “Ozonation as a Treatment for Mechanical and Chemical Pulp Mill Effluents”, Ozone: Sci. & Eng., 18, 363-384 (1996).

9 Sapach, R. and Viraraghavan, T., “An Introduction to the Use of Hydrogen Peroxide and Ultraviolet Radiation: An Advanced Oxidation Process”, J. Environ. Sci. Health, A32(8), 2355-2366 (1997).

10 Voss, R.H. and Rapsomatiotis, A., “An Improved Solvent-Extraction Based Procedure for the Gas Chromatographic Analysis of Resin and Fatty Acids in Pulp Mill Effluents”, J. Chromatogr., 346, 205-214 (1985).

11 Yeber, M.C., Rodriguez, J., Baeza, J., Freer, J., Zaror, C., Duran, N. and Mansilla, H.D., “Toxicity Abatement and Biodegradability Enhancement of Pulp Mill Bleaching Effluent by Advanced Chemical Oxidation”, Wat. Sci. Tech., 40(11-12), 337-342 (1999).

APPENDIX A

Table 3 Abietic acid raw data from oxidation experiments.

Run		**Temperature**	**2nd order rate constant**	**Reaction order**	**Reaction Stoichiometric Coefficient**		**[Abietic]$_{in}$**	**[Abietic]$_{out}$**
#	**date**	**^{o}C**	**k_{oa}, $M^{-1}min^{-1}$**	**$n_1 = n_2 = 1$**	**w.r.t. O_3, a**	**w.r.t. abietic acid, b**	**mg/L**	**mg/L**
1	19/04/02	18.9	7.51E+04	1.0	2.35	1.0	7.13	1.73
2	23/04/02	19.1	-3.57E+03	1.0	2.27	1.0	7.45	1.86
3	30A/04/02	16.6	8.10E+04	1.0	6.29	1.0	4.37	1.64
4	02A/05/02	19.1	1.37E+05	1.0	4.17	1.0	5.76	1.58
5	02B/05/02	15.5	7.98E+04	1.0	5.99	1.0	5.32	1.23
6	28A/05/02	22.6	3.38E+04	1.0	19.91	1.0	2.07	1.37
7	28B/05/02	26.6	1.17E+05	1.0	11.38	1.0	2.75	1.25
8	04A/06/02	22.5	3.51E+05	1.0	3.99	1.0	5.17	1.35
9	04B/06/02	21.4	3.63E+05	1.0	3.73	1.0	5.94	0.93
10	19A/06/02	17.6	3.73E+05	1.0	3.07	1.0	4.88	1.46
11	19B/06/02	16.0	9.70E+04	1.0	5.73	1.0	3.55	1.49
12	19C/06/02	12.8	6.14E+03	1.0	76.49	1.0	1.38	1.22
13	26A/06/02	18.6	1.43E+05	1.0	4.88	1.0	3.71	1.54
14	26B/06/02	18.1	7.51E+04	1.0	8.80	1.0	2.94	1.67
15	26C/06/02	14.6	9.14E+04	1.0	5.79	1.0	3.17	1.47

Table 3 cont.

$[\text{Ozone}]_{in}$	$[\text{Ozone}]_{out}$	Percent Abietic Acid Removed	Ozone dose
mg/L	mg/L	%	mg/L
2.49	0.48	75.73	2.01
2.79	0.77	75.04	2.02
3.07	0.35	62.47	2.73
3.08	0.32	72.54	2.76
4.51	0.62	76.87	3.89
2.41	0.23	34.04	2.18
2.88	0.17	54.72	2.72
2.56	0.15	73.89	2.42
3.22	0.25	84.40	2.97
1.78	0.12	70.00	1.67
2.12	0.25	58.02	1.87
2.42	0.38	12.16	2.04
1.92	0.24	58.49	1.68
2.00	0.23	43.15	1.77
1.80	0.23	53.78	1.57

Table 4 Linoleic acid raw data from oxidation experiments.

Run		Temperature	2nd order rate constant	Reaction order	Reaction Stoichiometric Coefficient		[Linoleic]$_{in}$	[Linoleic]$_{out}$
#	date	°C	k_{oa}, $M^{-1}min^{-1}$	$n_1 = n_2 = 1$	w.r.t. O_3, a	w.r.t. linoleic acid, b	mg/L	mg/L
1	26A/07/02	12.5	4.56E+05	1.0	7.34	1.0	2.83	0.41
2	26B/07/02	16.3	0.00E+00	1.0	0.00	1.0	0.00	0.00
3	26C/07/02	16.1	2.64E-01	1.0	33.78	1.0	0.84	0.41
4	16A/08/02	21.9	4.89E+05	1.0	2.02	1.0	10.44	1.69
5	16B/08/02	22.0	2.40E+06	1.0	1.89	1.0	8.94	0.91
6	16C/08/02	23.3	2.30E+06	1.0	1.40	1.0	8.61	1.04
7	13A/09/02	15.7	9.47E+04	1.0	3.28	1.0	8.91	3.74
8	13B/09/02	15.2	7.51E+04	1.0	1.18	1.0	16.45	1.99
9	13C/09/02	14.0	4.32E+05	1.0	1.40	1.0	15.14	2.12
10	13D/09/02	13.4	2.88E+05	1.0	1.30	1.0	16.01	4.56
11	17A/09/02	8.1	7.51E+04	1.0	2.72	1.0	9.80	0.92
12	17B/09/02	7.9	7.79E+05	1.0	2.03	1.0	11.50	1.56

Table 4 cont.

$[Ozone]_{in}$	$[Ozone]_{out}$	Percent linoleic acid removed	Ozone Dose
mg/L	mg/L	%	mg/L
3.28	0.24	85.42	3.04
3.24	0.19	-	3.05
2.55	0.11	50.55	2.44
3.22	0.19	83.81	3.03
2.67	0.07	89.82	2.60
1.88	0.06	87.92	1.82
3.17	0.27	58.00	2.90
3.27	0.34	87.91	2.93
3.38	0.27	86.00	3.12
2.72	0.17	71.50	2.56
4.58	0.45	90.60	4.13
3.60	0.16	93.20	3.44

Table 5 Pooled results from CFSTR tracer tests analyzed by 2nd order decay kinetics (data used to produce figure 6).

Tracer Test #	**pH**	**T(°C)**	**k_w (s^{-1})**
5	7.37	5.6	3.43E-03
4	7.38	5.8	4.84E-03
3	7.38	8.8	5.88E-03
6	7.32	10.1	8.91E-03
8	7.34	14.2	1.03E-02
7	7.31	14.3	8.42E-03
9	7.33	15.2	2.29E-02
10	7.32	17.1	1.83E-02
11	7.32	18.6	3.87E-02
13	7.31	20.1	2.85E-02
12	7.33	20.3	3.12E-02
2	7.34	22.1	1.16E-01
1	7.34	22.1	6.81E-02

average = 7.34

Table 6 Microtox® results for abietic acid (data used to produce Figure 13).

Run		**Temperature**	**Sample ID**	**[Abietic]**	**Toxicity Unit**
#	**date**	**(°C)**		**(mg/L)**	**(TU50, 95% confidence range)**
15	26C/06/02	14.62	Raw	3.17	5.905 (2.796 to 12.470)
			Residual 2	1.14	2.354 (1.230 to 4.506)
			Residual 3	1.21	2.975
5	02B/05/02	15.50	Raw	5.32	3.569 (1.593 to 7.994)
			Residual 1	0.97	6.939 (5.246 to 9.178)
			Residual 3	1.23	9.258 (8.798 to 9.743)
11	19B/06/02	16.00	Raw	3.55	0.984 (0.775 to 1.250)
			Residual 2	1.21	1.747
			Residual 3	1.63	2.021 (0.878 to 4.649)
3	30A/04/02	16.60	Raw	4.91	1.854 (0.561 to 6.120)
			Residual 1	1.57	1.303
			Residual 2	1.32	4.864 (3.068 to 7.711)
13	26A/06/02	18.63	Raw	7.42	0.954 (0.386 to 2.359)
			Residual 1	1.54	3.063 (2.565 to 3.658)
			Residual 2	1.57	1.498 (0.720 to 3.117)
4	02A/05/02	19.10	Raw	5.76	4.631 (2.783 to 7.706)
			Residual 1	1.41	5.017 (2.812 to 8.953)
			Residual 3	1.62	1.959 (1.569 to 2.446)
9	04B/06/02	21.40	Raw	6.69	2.204 (1.106 to 4.389)
			Residual 1	0.93	6.147 (4.721 to 8.004)
8	04A/06/02	22.50	Raw	5.17	8.425 (6.726 to 10.550)
			Residual 1	1.42	3.401 (2.494 to 4.637)
			Residual 2	1.28	4.221 (3.911 to 4.554)

Table 7 Microtox® results for linoleic acid (data used to produce Figures 14).

Run		Temperature	Sample ID	[Linoleic Acid]	Toxicity Unit
#	Date	°C		(mg/L)	(TU50, 95% confidence range)
11	17A/09/02	8.1	Raw	19.60	9.978 (7.170 to 13.890)
			Residual 2	0.61	3.564 (2.125 to 5.976)
			Residual 3	0.70	3.983 (3.878 to 4.090)
10	13D/09/02	13.4	Raw	32.02	88.780 (32.290 to 244.000)
			Residual 1	7.07	2.487
			Residual 3	4.14	4.250 (3.140 to 5.753)
9	13C/09/02	14.0	Raw	30.28	12.780 (11.270 to 14.480)
			Residual 2	2.61	0.988 (0.234 to 4.170)
			Residual 3	1.63	2.184 (1.274 to 3.745)
8	13B/09/02	15.2	Raw	32.90	20.530 (13.390 to 31.470)
			Residual 2	2.09	2.627
			Residual 3	2.24	2.167
4	16A/08/02	21.9	Raw	20.88	7.995 (5.702 to 11.210)
			Residual 1	1.69	4.773 (3.569 to 6.384)
			Residual 2	0.00	6.043 (5.317 to 6.868)
5	16B/08/02	22.0	Raw	17.88	6.719 (5.499 to 8.210)
			Residual 1	0.91	6.372 (5.032 to 8.069)
			Residual 2	0.91	4.601 (4.298 to 4.926)
6	16C/08/02	23.3	Raw	17.22	39.830 (18.220 to 87.080)
			Residual1	0.95	4.332 (3.591 to 5.226)
			Residual 3	0.88	3.027 (2.873 to 3.190)