Ozonation of Tris-2-Chloroethyl Phosphate (TCEP) in Water

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Abstract

Tris-2-chlorethyl phosphate (TCEP) is a flame retardant and plasticizer that has been detected in drinking water sources and wastewater effluents in many countries. TCEP has been proven to be a recalcitrant compound that is also toxic and carcinogenic. The incomplete removal of TCEP in water and wastewater treatment plants necessitates that treatment processes be identified or developed that will completely remove TCEP from waters. Ozonation has been successfully used as an oxidant to degrade many problematic contaminants in water and wastewater. This research examined the effectiveness of ozone and ozone/hydrogen peroxide oxidation for removing TCEP from water. In laboratory experiments, batch reactions of TCEP solutions were conducted in purified water at different pH conditions and O_3:H_2O_2:TCEP doses. The samples were tested at O_3:TCEP molar ratios of 6:1, 15:1, and 30:1 and with O_3:H_2O_2:TCEP molar ratios of 6:4.2:1, 15:10.5:1and to 30:21:1 respectively. Solution pHs of 4, 7, and 9 were investigated to cover the typical water and wastewater pH range. The Indigo Method was used to measure the starting ozone concentrations in sample water. TCEP concentrations were quantified by liquid-liquid extraction followed by gas chromatography (GC). Greater than 90% reduction of TCEP was achieved at equilibrium conditions with an O_3:H_2O_2:TCEP molar ratio of 30:21:1 at all pH levels examined. Greater than 80% TCEP removal in diluted wastewater was observed at purified water to wastewater dilution of 4:1. The kinetics of oxidation of TCEP with ozone and ozone/hydrogen peroxide were explored in this research. It was found that the reaction rate constants of TCEP are lower than those of other contaminants typically found in water and wastewater.

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Chapter 1: Introduction

Organophosphorous compounds (OPCs) are used as pesticides, plasticizers, flame retardants, hydraulic fluids, solvents, extraction agents, antifoam agents, and coatings for electronic devices [1-3]. OPCs are released to the environment from industrial sources as well as through the disposal of materials that contain these compounds [2]. OPCs are not chemically bonded to the materials that they are used in, and therefore can be released into the environment if manufactured material breaks down. These compounds are produced in high quantities on the order of ten to one-hundred thousand tons annually worldwide [4-7]. OPCs have been found in air [6, 8-10], sludge in wastewater treatment plants (WWTPs) [4, 5, 11-16], in streams, and other source waters that are used for drinking water [1, 3-5, 15-22]. Discovery of OPCs in nature and in treatment waters is a concern because of their high mobility in waters. Chlorinated OPCs are the most difficult to remove in WWTPs and water treatment plants (WTPs) because they are resilient to biological treatments as well as other typical treatments [6, 23, 24]. There are potential health concerns associated with the presence of OPCs in the environment, and in waters used by people for drinking, cooking, cleaning, and recreation, however at this time the health effects are not thoroughly known. Some of these compounds are potentially neurotoxic and carcinogenic, e.g., tri(1,3-dichloro-2-propyl)phosphate (TDCP), tris(2-chloroisopropyl)phosphate (TCPP), and tris(2-chloroethyl)phosphate (TCEP), while others such as tributoxyethel phosphate (TBEP) and triisobutyl phosphate (TiBP) are considered toxic to other parts of the body, mainly internal organs if consumed [2, 7, 25-28].

TCEP is a flame retardant and plasticizer that is used in polyurethane foam. Polyurethane foams are used for packaging, insulation, and many other manufactured products. TCEP has the CAS # 115-96-8 with a linear formula $(ClCH_2CH_2O)_3P(O)$ and a structure that may be seen in Figure

1. TCEP has a molecular weight of 285.49 a density of 1.39 g/mL at 25 degrees Celsius, and solubility in water of 7 g/L at 20 degrees Celsius [29].

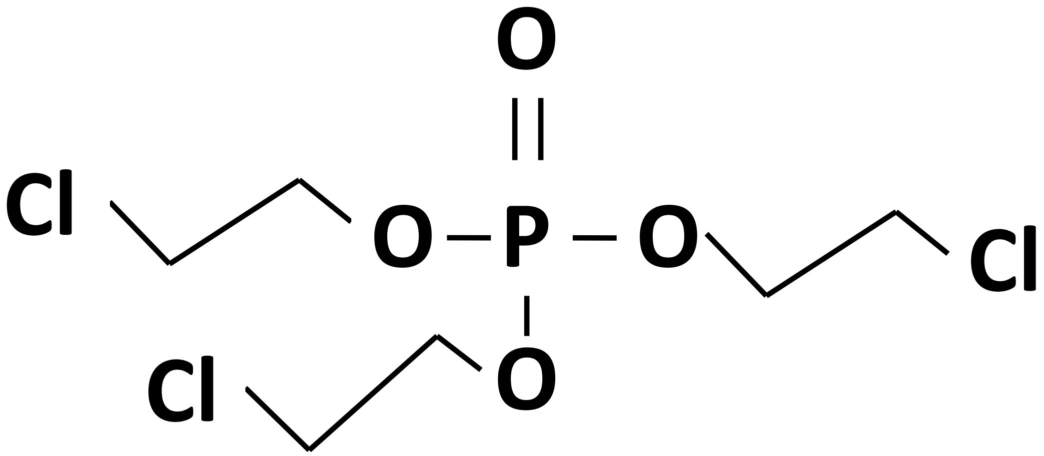

Figure 1: Structure of a TCEP Molecule

TCEP has been frequently found in wastewater effluents, stormwater runoff, groundwater observation wells, reservoirs and other water bodies in North America, Europe, and Asia [1, 4, 5, 9, 10, 14, 17-20, 26, 30]. It has been found to be carcinogenic as well as toxic at maximum contaminant level (MCL) of 3400 ng/L [26, 28]. TCEP has been shown to be genotoxic, neuorotoxic, mutagenic, as well as damaging to liver, kidneys and reproductive systems [2, 21, 28]. TCEP has been placed on the United States Environmental Protection Agency's Final Contaminant Candidate List 3 [31]. It is a bio-recalcitrant compound, and is difficult to remove by biological processes. Therefore it is difficult to remove the contaminant through typical WWTP and WTP operations [7, 10, 14, 16, 21]. TCEP has been found in WWTP effluents, source waters, and WTP finished waters at concentrations of up to 557 ng/L [21], 300 ng/L [25, 27], and 99 ng/L [14], respectively.

In a 2010 study by Guo et al. [22] water samples from three rivers in California were tested for endocrine disrupting compounds and personal care products. The Colorado River, Santa Ana River, and State Project water (Sacremento-San Joaquin River Delta) are all used as drinking water sources, and were the subjects of the 2010 sampling. TCEP was found in all river waters tested. 12 ng/L of TCEP were found in samples from the State Project water and the Colorado River. TCEP at concentrations of 418 ng/L were found in Santa Ana River water samples. In the same study 16 wastewater treatment plant effluents were sampled to try to determine if the effluents were the reason for the personal care products and endocrine disruptors entering river waters. The average concentration of TCEP found in wastewater treatment effluent samples was ≈700 ng/L.

In a 2010 study by Schaider et al. of the Silent Spring Institute [26], 20 wells in the Cape Cod area of Massachusetts were tested for emerging contaminants. Of the 92 contaminants tested for 18 were detected and one of those contaminants was TCEP. TCEP was detected in 3 of the 20 wells with a maximum concentration of 20 ng/L. Other studies have shown TCEP detection in both untreated and finished drinking waters. TCEP concentrations of <500 [5], 110 [32], 260 [33], and 530 [34] ng/L have been found in untreated drinking waters in the U.S. from previous studies. As for treated drinking waters in the U.S. previous research has detected concentrations of 220 [33] and 470 [34] ng/L of TCEP. Many of levels detected are below the regulated concentrations of TCEP; however the presence of TCEP in waters at any concentration raises some concern due to TCEP’s toxic and carcinogenic properties. The recent addition of TCEP to the United States Environmental Protection Agency’s Final Contaminant Candidate List 3 in 2009 shows that TCEP is a compound that needs to be monitored.

Current wastewater and drinking water treatment processes are not able to completely remove TCEP from water. Some experiments to assess alternative water treatment technologies have been conducted. Adsorptive processes, oxidative processes, and membrane processes have been investigated in their use for TCEP removal. Adsorptive processes include the use of metal salt coagulation, lime softening, and powdered active carbon. Oxidative processes include the use of chlorine and ozone to treat waters. In a study conducted in 2005 by Westerhoff et al. it was found that powdered activated carbon was able to remove greater than 80%, chlorine oxidation was able to remove less than 20%, and ozone oxidation was able to remove less than 5% of TCEP in four source waters . Metal salt coagulation and lime softening provided no removal of TCEP in the study [24]. The use of nanofiltration membranes was investigated in a study by Lee et al. [35]. It was concluded that nanofiltration membranes could provide TCEP removal at levels greater than 90% for several water conditions.

Advanced oxidation processes are processes that use highly reactive oxidants that can be used to completely remove contaminants by destruction as opposed to physical removal achieved by membranes and activated carbon. Advanced oxidation processes are used to form free radicals that break down organic contaminants. Some forms of advanced oxidation include Fenton’s reagent, H_2O_2/UV, and O_3/H_2O_2 applications. These advanced oxidation processes have proven to be effective in the removal of many bio-recalcitrant compounds. In a study by Nguyen [36] in 2011, it was found that Fenton’s oxidation was able to remove 100% TCEP in spiked water with a H_2O_2:Fe^{2+}:TCEP molar ratio of 1:150:5 at pH 3.6 +/- 0.1. Greater than 95% removal of TCEP was achieved by H_2O_2/UV advanced oxidation of lake water in a 2008 study by Watts and Linden[37]. Advanced oxidation processes have been used to treat many recalcitrant contaminants including pharmaceuticals, organophosphates, and other manmade chemicals found in water and wastewater treatment [38-40].

Ozone oxidation has been used for disinfection as well as taste and odor control in drinking water. It has also been used for odor control and contaminant destruction in wastewater treatment. Ozone oxidation has been used to degrade many contaminants in water including bio-recalcitrant compounds. In its decomposition, ozone forms free radicals that are very powerful oxidants. The addition of hydrogen peroxide or high pH values can increase the formation of free radicals through ozone's decomposition. In a 2011 study by Pisarenko et al. [41], ozone/hydrogen peroxide oxidation was used to reduce spiked TCEP concentrations in Colorado River water by more than 50%. In the same study TCEP levels in membrane bio reactor filtrate were treated with ozone and ozone/hydrogen peroxide with less than 20% and 35% reductions respectively. A 2007 study by Snyder et al. [16] reported that less than 17% percent removal of TCEP was achieved through ozone and ozone/hydrogen peroxide oxidation in spiked Colorado River water. Ozone oxidation reactions were shown to treat TCEP in several studies, however the percent removals were fairly low. The pH levels of source water were not varied for the ozone and ozone/peroxide experiments performed in the literature. Source waters for the experiments may play a major role in the treatment effectiveness due to the competitive reactions of ozone with other contaminants and the recalcitrant nature of TCEP.

This research investigated the effectiveness of ozone oxidation for treating TCEP contaminated water. It was hypothesized that TCEP can be removed from water by ozone oxidation and that high pH or the addition of hydrogen peroxide enhances the ozone oxidation of TCEP. It was also hypothesized that a higher dose of ozone would achieve greater TCEP removal. Therefore the following objectives were formed:

- Develop a method to perform equilibrium batch reactor ozone oxidation experiments in TCEP spiked water,
- Develop an effective and accurate method to measure TCEP using the Gas Chromatograph (GC) in the Worcester Polytechnic Institute (WPI) Environmental Engineering Lab,
- Determine the effect of ozone dose on the removal of TCEP,
- Determine the effect of hydrogen peroxide addition for the removal of TCEP,
- Study the effect of pH on the removal of TCEP using ozone and ozone/hydrogen peroxide oxidation,
- Investigate the removal of TCEP in waters with other contaminants that may competitively react with ozone and ozone/hydrogen peroxide,
- Examine the kinetics of TCEP destruction in its reaction with ozone and ozone/hydrogen peroxide.

Chapter 2: Ozone Oxidation

Background

The current use of ozone in drinking water and wastewater for various contaminants, as well as its use for disinfection, makes ozonation a very versatile treatment for water/wastewater treatment facilities. Ozone is a very powerful oxidant and a disinfectant that can have very short contact times. Ozone is generated onsite and therefore shipping of harmful chemicals is not required. Ozonation in water creates no harmful residuals that need to be removed because ozone decomposes rapidly unlike chlorine which can create many unwanted compounds that need to be removed from treated waters. Ozone can be added to several different points in a treatment plant; its versatility makes it a great option to help further treat water in existing systems [42]. Figure 2 shows a few of the possible points where ozone treatment or other advanced oxidation processes (AOPs) can be added to existing typical water and wastewater treatment facilities [38].

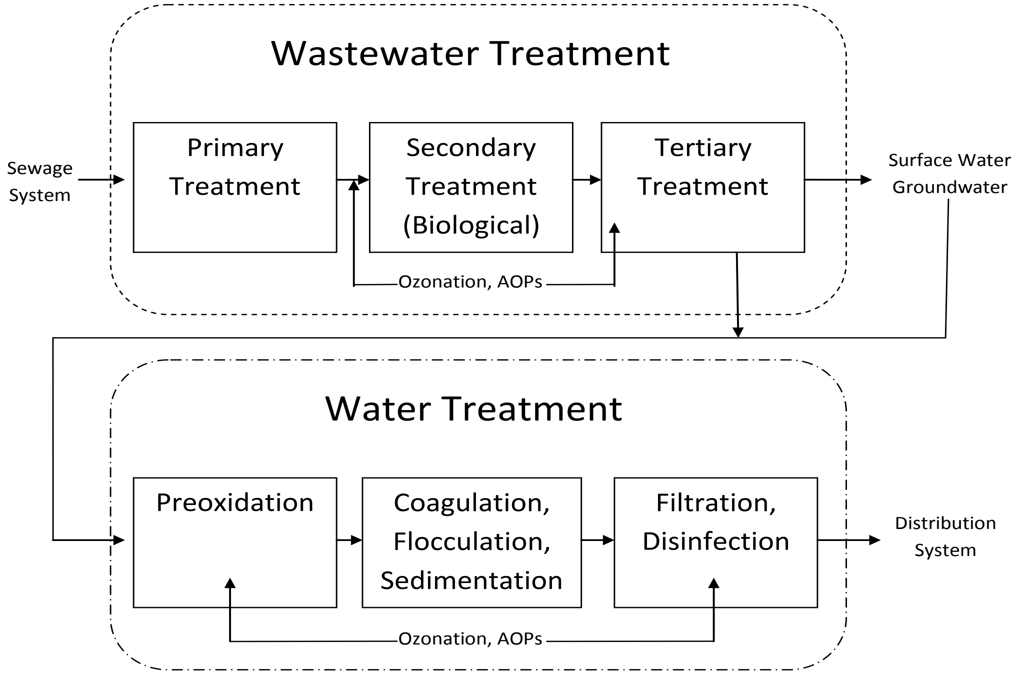

Figure 2: Potential Points to Apply Ozonation to Existing Water or Wastewater Treatment Plants

Ozone (O_3) is a very strong oxidant with an oxidation potential of 2.08 volts (V) which is quite high when compared to permanganate, chlorine dioxide, or oxygen which have oxidation potentials of 1.68 V, 0.9 V, and 1.23 V respectively [43]. With a high rate of reactivity ozone is predominantly used for disinfection and taste and odor control in drinking water treatment, but it has been used to remove other bio-recalcitrant contaminants from water such as endocrine disrupting compounds, organophosphorus compounds, and other organic materials [16, 24, 41, 44, 45]. Due to its instability and high reactivity in air and water, ozone must be generated onsite through an ozone generator.

To produce ozone an ozone generator supplies an electric discharge to separate the oxygen molecule (O_2) into oxygen atoms (O). The free oxygen atom then attaches to an oxygen molecule to form ozone (O_3) as shown in Equations 1 and 2 [46].

Equation 1:

$$O_2 + energy \rightarrow O + O$$

Equation 2**:**

$$O + O_2 \rightarrow O_3$$

The amount of ozone produced by an ozone generator depends on voltage, frequency, and the type and quality of the gas being fed to the generator [47]. The ozone generator may be fed with oxygen or air that passes through a narrow gap. An electrical discharge is created across the gap by alternating current [48]. The voltage cycle created between the gap splits the O_2 molecules into oxygen atoms which then attach to an oxygen molecule forming O_3. The ozone gas produced is passed through a gas dispersion tube for ozone transfer into liquids.

Ozone is very unstable in aqueous solution and reacts with constituents that are in its presence. In aqueous solution ozone goes through spontaneous decomposition. Spontaneous decomposition of ozone is a chain reaction process, usually initiated by hydroxide ions in which several free radicals including superoxide (O_2^-), hydroperoxyl (HO_2), and hydroxyl ($HO^\bullet$) are formed. These radicals have great oxidizing capability, and can be used to further remove unwanted contaminants in water. Hydroxide ions are readily available in high pH waters, but other ways in which spontaneous decomposition may be started is through the addition of H_2O_2, ferrous ions, ultraviolet light, or the presence of natural organic material. The reactions shown in Equations 3-8 illustrate the decomposition of ozone using the hydroxide ion to initiate the sequence [36, 48].

Equation 3:

$$OH^- + O_3 \rightarrow HO_2 + {O_2}^-$$

Equation 4:

$$HO_2 \rightarrow H^+ + {O_2}^-$$

Equation 5:

$${O_2}^- + O_3 \rightarrow O_2 + {O_3}^-$$

Equation 6:

$${O_3}^- + H^+ \rightarrow HO_3$$

Equation 7:

$$HO_3 \rightarrow O_2 + OH$$

Equation 8:

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

Ozone itself is a powerful oxidant, but the advanced oxidation potential of ozone treatment can be achieved through the formation of free radicals during spontaneous decomposition. The hydroxyl radical ($HO^{\bullet}$) is one of the strongest oxidants formed in the spontaneous decomposition of ozone [49]. With an oxidation potential of 2.8 V hydroxyl radicals ($HO^{\bullet}$) react rapidly and non-selectively with most organic compounds [36]. In 1988 Glaze and Kang [50] found that a 0.5 mg to 1 mg dose of hydrogen peroxide to ozone gave the optimum removal of TCE (trichloroethylene) and PCE (tetracholoethylene) due to the high formation of hydroxyl radicals [42]. The advanced oxidation potential associated with ozone makes it a viable treatment for bio-recalcitrant and emerging contaminants.

Materials and Methods

Chemicals. TCEP of 97% purity was purchased from Sigma-Aldrich (St. Louis, MO). Methylene Chloride, Indigo Stock Solution, Hexanes, Hydrogen Peroxide 30% and Methanol were purchased from Fischer Scientific (Pittsburg, PA) and were of ACS reagent grade.

Experiments. All water used was purified with a Barnstead Nanopure water system (Barnstead RO/Nanopure system, Thermo Scientific, Marietta, Ohio). Glassware used was soaked in water and detergent for at least 24 hours, rinsed five times with tap water, and then rinsed three times with purified water.

Indigo Method for Measuring Ozone. The concentration of ozone in water was measured by using the Indigo Method, Standard Methods 4500-O_3 B [51]. Ozone concentration was measured by transferring diluted ozonated water into a 100 mL flask containing 10 mL of indigo reagent II [51], a solution containing indigo stock solution, phosphoric acid, and sodium dihydrogen phosphate (NaH_2PO_4) . The total volume of diluted ozonated water and indigo reagent II was 100 mL. Ozonated water decolorizes the indigo dye. Using a 4.5 cm cell [51] with a 1 cm lightpath (Fisherbrand® Disposable Plastic Cuvette) by Fisher Scientific, the decolorization of the samples were measured with a UV Spectrophotometer (Cary 50 Scan Series Spectrophotometer by Varian Inc., Palo Alto, California) at 600 nm wavelength. The decolorization was determined by measuring the absorbance of a blank sample with no ozonated water and subtracting the absorbance of the diluted ozonated sample water to get a Δ absorbance.

Standard Methods [51] describes in depth the details pertaining to the indigo method. The concentration of ozone is calculated using Equation 9 [51].

Equation 9:

$$\frac{mg\ O_3}{L} = \frac{(V_{total}) \times (\Delta\ Absorbance)}{f \times b \times V}$$

Where:

Δ A = difference in absorbance between blank and sample

b = path length of cell, cm

V = volume of ozonated water, mL

f = 0.42

In order to adjust for dilution the concentration of ozone calculated from Equation 9 was multiplied by an adjustment factor shown in Equation 10.

Equation 10:

$$\frac{mg\ O_3}{L} = \frac{(Calculated\ O_3) \times (Volume\ of\ Ozonated\ Water\ and\ Epure)}{Volume\ of\ Ozonated\ Water}$$

Ozone Oxidation of TCEP: Equilibrium in Purified Water. Ozone oxidation experiments were conducted at room temperature (22+/- 1°C) in 1L glass flasks. Ozone was generated using an oxygen fed L-25 ozone generator from Ozonology Inc. (Northbrook, IL). The ozone generator was set at an airflow of 2 SCFH, at 20 psi, and with an ozone generation of 95-100 V. Ozone passed through a glass dispersion tube (Model 7197-18, Ace Glass, Vineland, New

Jersey) and into a 2 L glass Erlenmeyer flask being stirred with a 1 inch long Teflon^{TM}-coated stir bar mixing rapidly for 0.5-2 hours depending on the ozone concentration desired. Prior to ozonation, purified water was adjusted to pH (4.0, 7.0, and 9.0 +/- 0.1 respectively) using hydrochloric acid (HCl) or sodium hydroxide (NaOH). The pH was monitored after ozonation to ensure that it did not change, and was checked again after all reactions had taken place. The residual ozone was measured using the indigo method to determine the concentration of ozone in the water. The ozonated water was then injected with TCEP to attain an initial concentration of 2 mg/L TCEP. In experiments involving hydrogen peroxide, the addition of hydrogen peroxide of a known concentration, one half of the ozone concentration by mass [42, 50, 52], was injected simultaneously with the TCEP. The reaction was allowed to proceed with a 1 inch long Teflon^{TM}-coated stir bar and magnetic stir plate providing mixing. One day was allowed for reactions to proceed to determine the equilibrium reaction of ozone and ozone/hydrogen peroxide with TCEP. After the 1 day reaction time the ozone oxidation experiments were subjected to liquid/liquid extraction followed by gas chromatography (GC) analysis. Total Organic Carbon (TOC) was measured before and after the reaction with starting conditions of a pH of 7 and a dose of 5 mg/L ozone, 2 mg/L TCEP, and when added 2.5 mg/L hydrogen peroxide.

Ozone Oxidation of TCEP: Equilibrium in Wastewater Effluent. To show the effects of competitive contaminants on the ozone oxidation of TCEP, equilibrium experiments were conducted in a mixture of purified water and wastewater effluent. The wastewater effluent prior to chlorination was obtained from the Upper Blackstone Wastewater Treatment Facility (Millbury, MA) on the morning that experiments were performed (5/1/2013). Ozone oxidation experiments were conducted with the same procedures as in the prior equilibrium experiments in purified water. Prior to ozonation, the purified water and wastewater was adjusted to a pH of 7 +/- 0.1 (the wastewater initial pH was 6.85). The ozonated purified water and a sample of wastewater effluent spiked with TCEP were mixed together at water:wastewater effluent volume ratios of 1:1, 2:1, 4:1 and 1:0. All experimental starting conditions were at a pH of 7, ozone concentration of 5 mg/L, TCEP concentration of 2 mg/L, and when added, 2.5 mg/L hydrogen peroxide. After the 24 hour reaction time the samples were analyzed for TCEP concentration by gas chromatography.

The chemical oxygen demand (COD) of the effluent wastewater was measured using Low Range (5-150 mg/L COD) Mercury Free vials (Bioscience, Inc Environmental Products and Services, Allentown, PA). Standards were made using potassium hydrogen phthalate (KHP) following Standard Methods 5220 B. 3. g. [51]. The COD was also measured at the start and the end of diluted water/wastewater equilibrium reactions. The COD measurements were done to show the reduction of competitive contaminants in wastewater during ozone oxidation.

Ozone Oxidation of TCEP: Kinetics. Kinetic experiments were performed to show the degradation of TCEP over time during ozone oxidation in purified water samples. Experimental starting conditions were at a pH of 7, ozone concentration of 5 mg/L, TCEP concentration of 2 mg/L, and when added, 2.5 mg/L hydrogen peroxide. Reactions were allowed to proceed in a reactor for 0, 30, 60, 120, and 180 minutes with a 1 inch long Teflon^{TM}-coated stir bar and magnetic stir plate providing mixing. Ozone oxidation reactions were quenched using methanol, which was added to achieve a final concentration of approximately 8000 mg/L (10 mL of 100%

Methanol). Tests conducted during this research showed that 10 mL of 100% methanol would completely remove all of the ozone residual in 1 liter of water at a concentration of 10 mg/L ozone. The samples were then analyzed for TCEP concentration by gas chromatography.

Liquid/Liquid Extraction and Gas Chromatography Analysis. Gas chromatography (GC) analyses were performed to determine TCEP concentrations in the samples. Prior to GC analysis all samples were adjusted to pH 7.0 +/- 0.1 using 0.1 normal sodium hydroxide (NaOH) and hydrochloric acid (HCl) (Prior to fully developing the extraction and GC methodology a set of TCEP GC runs were done at varied pH to see if pH would significantly impact the extractions and GC analysis of TCEP. Appendix A shows the data from these runs). A method for liquid/liquid extraction of TCEP from sample water was developed. The following steps were followed to perform the liquid/liquid extraction and GC analysis of TCEP, :

1. Using a separatory funnel two doses of methylene chloride 75 mL were added to 800 mL of sample and were subjected to steps 2 and 3 consecutively.

2. The separatory funnel was the shaken vigorously three times with two minutes in-between shakings, and was settled for 10 minutes.

3. 75 mL of methylene chloride were then drawn out, having been contacted with the sample.

4. The methylene chloride solutions from both 75 mL doses were collected. The 150 ml of solution was then evaporated to dryness in a Rapidvap evaporator from Labconco Corp (Kansas City, Missouri). The temperature was set at 40 Degrees Celcius and the vortex speed was set at 50%. The timer was set to run and the samples were checked periodically until they reached dryness.

5. The dry sample was then reconstituted with 5 ml of hexane. 8 hours was allowed for the hexane to contact the dried sample.

6. 1.5 mL of the eluted hexane solution was transferred to GC vials.

7. The GC vials were placed in an Agilent Technologies (Santa Clara, California) 7683 Series AutoSampler.

8. Agilent ChemStation, a software package, was used to program methods and sequences to run and analyze samples through the GC. See Appendix B for the method settings used to measure TCEP concentrations using the gas chromatograph. See Appendix C for a sample sequence template used to run multiple samples.

9. 1 µL of the samples in each vial were injected into the GC by an Agilent Technologies 7683 Series Injector using an Agilent Gold Standard AutoSampler Syringe.

10. The injected sample was analyzed by a 6890 Series Gas Chromatograph from Agilent Technologies.

The gas chromatography analyses were performed by the 6890 Series GC using an Rtx-5 SIL MS (30 meter length, 0.32 mm inner diameter, 0.5 micrometer film thickness) column by Restek Corporation (Bellefont, Pennsylvania). The electron capture detector (ECD) was used due to its ability to detect chlorinated molecules such as TCEP. The temperature program was adopted from research done by Ollers et al. in 2001 [53] and Nguyen in 2009 [36]. The temperature program was as follows: 1 minute at 90 degrees Celsius, first ramp 15°C/min to 150 degrees Celsius, 15 minutes at 150 degrees Celsius, second ramp 5°C/min to 200 degrees Celsius, 5 minutes at 200 degrees Celsius, third ramp 15°C/min to 290 degrees Celsius, 6 minutes at 290°C. The injector was flushed with hexane in between each sample to avoid cross contamination. Spiked samples of TCEP were included in every set of experimental runs to ensure proper detection of the compound. The limit of detection of TCEP was 10 micrograms (µg) per liter. The retention time of TCEP was determined to be around 29 minutes. See Figure 3 for a chromatogram showing the peak for TCEP.

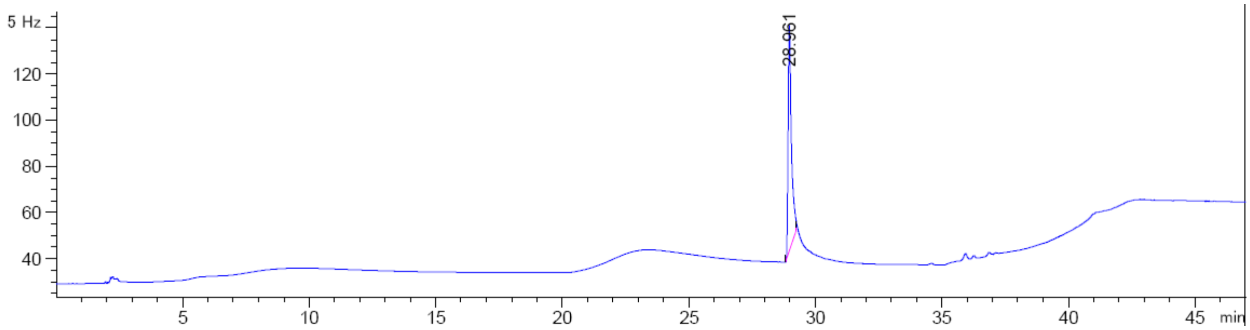

Figure 3: Chromatogram Showing TCEP Peak at ≈ 29 Minutes

After the GC analysis was completed, the unknown concentration remaining after ozone and ozone/hydrogen peroxide oxidation had to be calculated using an equation developed from a standard curve. A standard curve was formed by plotting known TCEP concentrations and the resulting GC peak areas. A line of best fit was determined for the data points. Figure 4 shows the standard curve that was used to determine the concentration of TCEP after the ozone oxidation experiments.

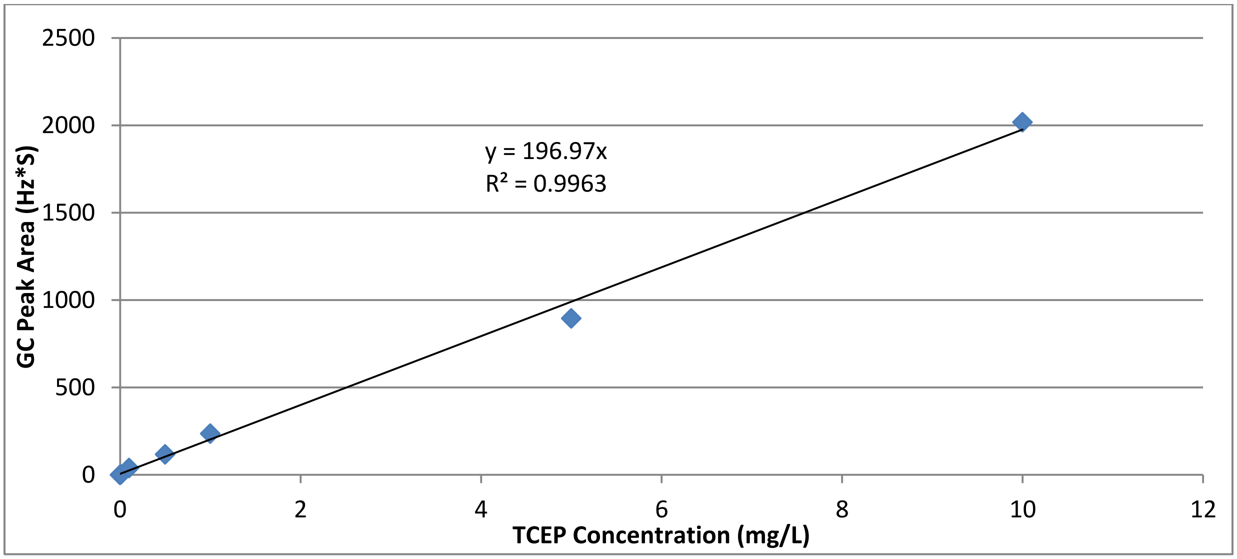

Figure 4: TCEP Standard Curve

From the standard curve Equation 11 was obtained from the line of best fit. This equation was used to develop Equation 12 which was applied to determine unknown concentrations of TCEP.

Equation 11:

$$y = 196.97x$$

This equation was rearranged the give Equation 12

Equation 12

$$x = \frac{y}{196.97}$$

Where:

x = Concentration of TCEP in mg/L

y = GC peak area in Hz*s

The regression fit between the standard curve and the experimental data had an R^2 value of 0.9963 as shown in Figure 4. The method detection limit of TCEP concentration was 10 µg/L. Equation 12 was applied after each set of GC runs to determine the TCEP concentration of the sample after oxidation with ozone or ozone/hydrogen peroxide. TCEP spikes of known concentrations were evaluated each run to ensure that the instrument was running properly for each set of experiments. The data used to develop the standard curve can be found in Appendix D.

Chapter 3: Results and Discussion

Equilibrium Trials in Purified Water. All equilibrium reactions were allowed 24 hours to proceed and started with a TCEP concentration of 2 mg/L. Appendix E shows the mass ratios as well as the molar ratios used for the experiments. Appendix F shows the GC equilibrium experiment results, and Appendix G shows the TCEP spike GC results. Experiments to determine the effect of ozone dose on the removal of TCEP were done at a neutral pH of 7. The ozone doses used were 2, 5, and 10 mg/L. Figure 5 shows the effect of ozone dose on TCEP removal at a neutral pH. All error bars in this research show a 95% confidence interval for multiple experimental runs that may be found in Appendix F.

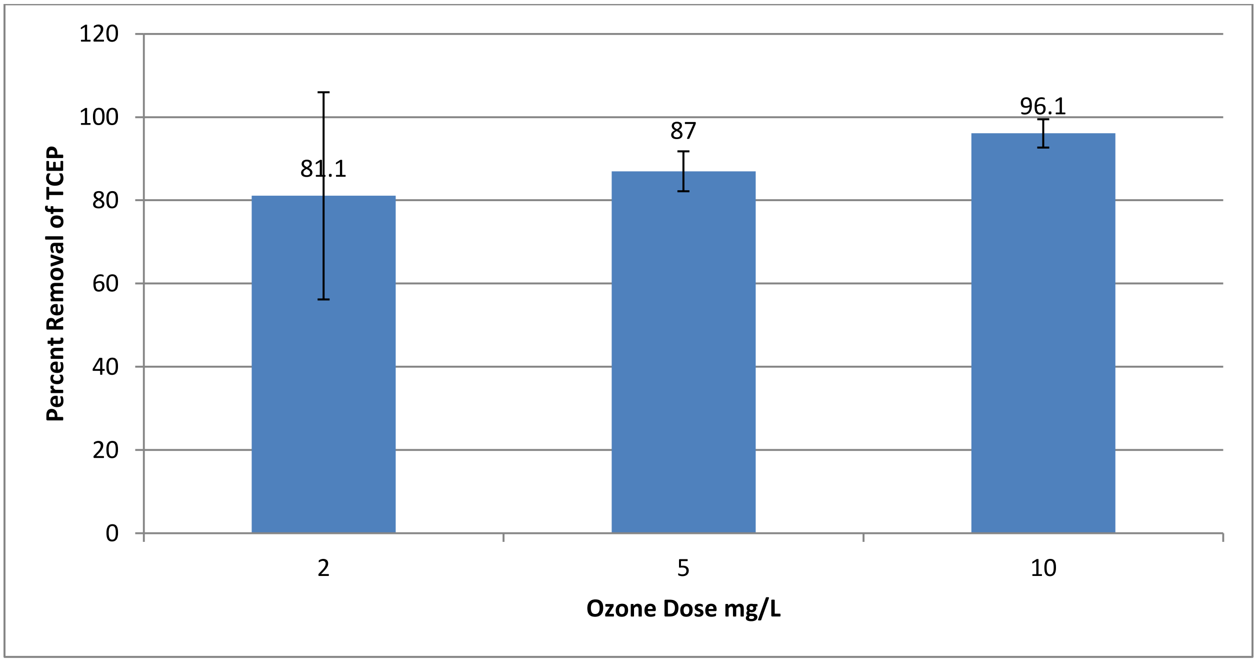

Figure 5: Effect of Ozone Dose on Ozone Oxidation of TCEP at pH 7.
Initial TCEP Concentration = 2 mg/L.

The lowest reduction of TCEP occurred with a dose of 2 mg/L ozone only achieving an 81 percent reduction. The higher doses of 5 and 10 mg/L ozone achieved greater TCEP removal of 87% and 96% respectively. In 2011 Pisarenko et al. reported that as ozone doses ranged from

0.6-10 mg/L the TCEP reduction was 20-50% respectively. The trend of increased ozone dose and increased removal of TCEP in this research is similar to that study although the magnitude of removal is different. It is likely that the differences in the percent removal with the same dose of ozone relates to the water quality parameters of the Colorado river water used for spiked samples in the 2011 study. Table 1 [41] shows the water quality parameters of the sample water from the 2011 study.

Table 1: Water Quality Parameters of Sample Water Used in TCEP Removal Experiments Conducted by Pisarenko et al.

Constituent	**Colorado River Water**
BOD (mg/L)	N/A
COD (mg/L)	N/A
Ammonia (mg-N/L)	N/A
Bromide (mg/L)	0.09
Alkalinity (mg/L as CaCO3)	138
Nitrate (mg-N/L)	0.6
Nitrite (mg-N/L)	<0.05
Silica (mg/L)	7.5
TDS (mg/L)	625
pH	8.1
DOC (mg/L)	2.6
UV254 absorbance (1/cm)	<0.050
Total Coliforms (MPN/100ml)	N/A
Turbidity (NTU)	<0.5

It is likely that some of the constituents in the Colorado River water reacted with ozone, whereas in purified water there is nothing for ozone to react with except for the spiked TCEP. Therefore removals of TCEP in purified water are greater than removals of TCEP in Colorado River Water with the same ozone dose. The same is true for ozone/hydrogen peroxide treatment as seen in Figures 6 and Figure 7 [41].

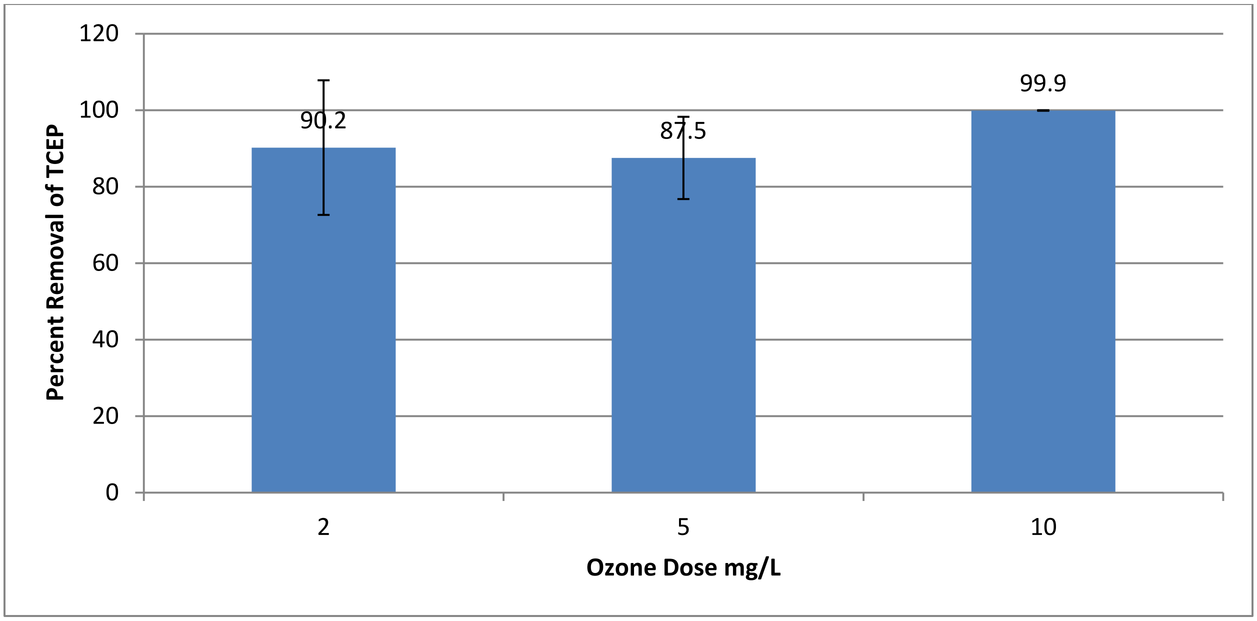

Figure 6: Effect of Ozone Dose on Ozone/Hydrogen Peroxide Oxidation of TCEP at pH 7 (Ratio of H_2O_2:O_3 of 0.5:1 by mass).
Initial TCEP Concentration = 2 mg/L.

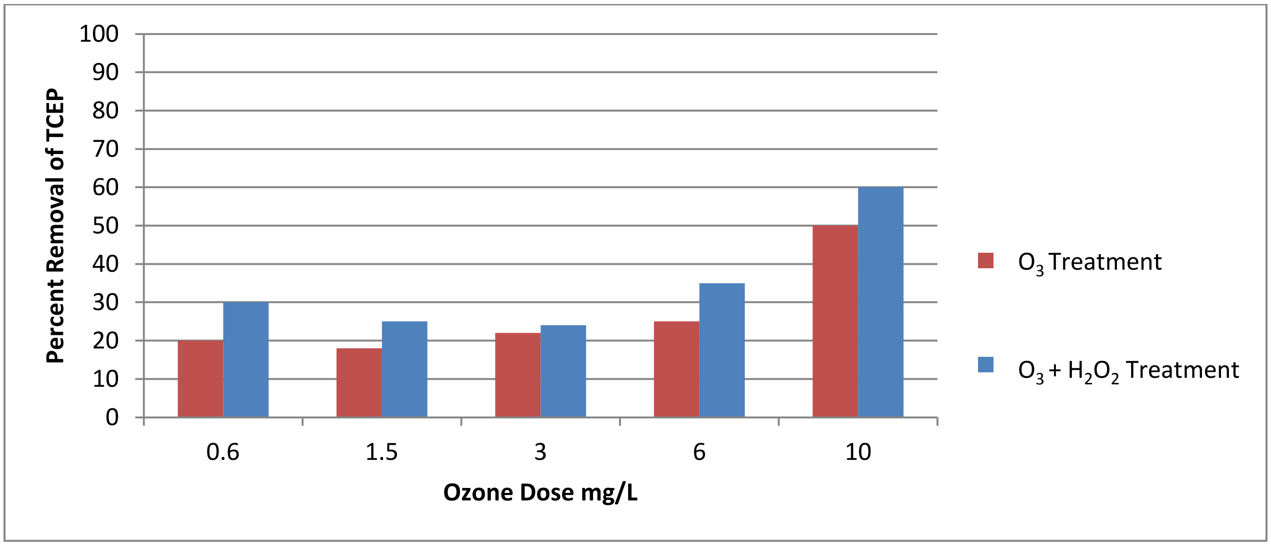

Figure 7: Percent Removal of 5000 ng/L TCEP by O_3 and H_2O_2:O_3 (0.7:1 molar ratio) Oxidation at pH 8.1 (Data from Pisarenko et al. 2011 [41]).

The lowest decrease of TCEP concentration in these experiments occurred during ozone/hydrogen peroxide oxidation with a dose of 5 mg/L ozone and 2.5 mg/L hydrogen peroxide only achieving an 87.5 percent reduction. The highest decrease of TCEP concentration occurred during ozone/hydrogen peroxide oxidation with a dose of 10 mg/L ozone and 5 mg/L hydrogen peroxide achieving a removal of 99.9 percent. The ozone/hydrogen peroxide experiments did show a greater decrease of TCEP with a dose of 2 mg/L ozone than with a dose of 5 mg/L, however the removals were within 3% of each other, 90.2% and 87.5% respectively.

The data from these experiments show a higher removal efficiency of TCEP using ozone/hydrogen peroxide treatment than the data presented by Pisarenko et al. This could be due to the constituents in the Colorado River water reacting with ozone and/or the hydroxyl radicals. Both ozone and hydroxyl radicals are non-selective compounds that react with many constituents in water [54]. This may explain why the TCEP reduction is higher when oxidized by ozone or ozone/hydrogen peroxide in purified water than when in Colorado River water, or any other waters that have oxidizable constituents. The data found in this research on the oxidation of TCEP by ozone and ozone/hydrogen peroxide were investigated in purified water with a pH of 7 while the Colorado River water used in the Pisarenko et al. study was at a pH of 8.1 [41]. Further experiments looking at the effects of varying pH on ozone and ozone/hydrogen peroxide oxidation of TCEP could help to determine the optimum conditions needed for TCEP removal.

To determine the effect of pH on the reduction of TCEP using ozone and ozone/hydrogen peroxide, three pH values were chosen that fit within the parameters of most natural waters and wastewaters. The selected pH values for experiments were 4, 7, and 9. This range was chosen to account for the variations of pH in the environment including rivers, lakes, and typical water/wastewater treatment systems. Figure 8 shows the effect of pH on the removal of TCEP using ozone oxidation with and without hydrogen peroxide addition with an ozone dose of 2 mg/L. Figures 9 and 10 show the same experimental data, but with ozone doses of 5 and 10 mg/L respectively.

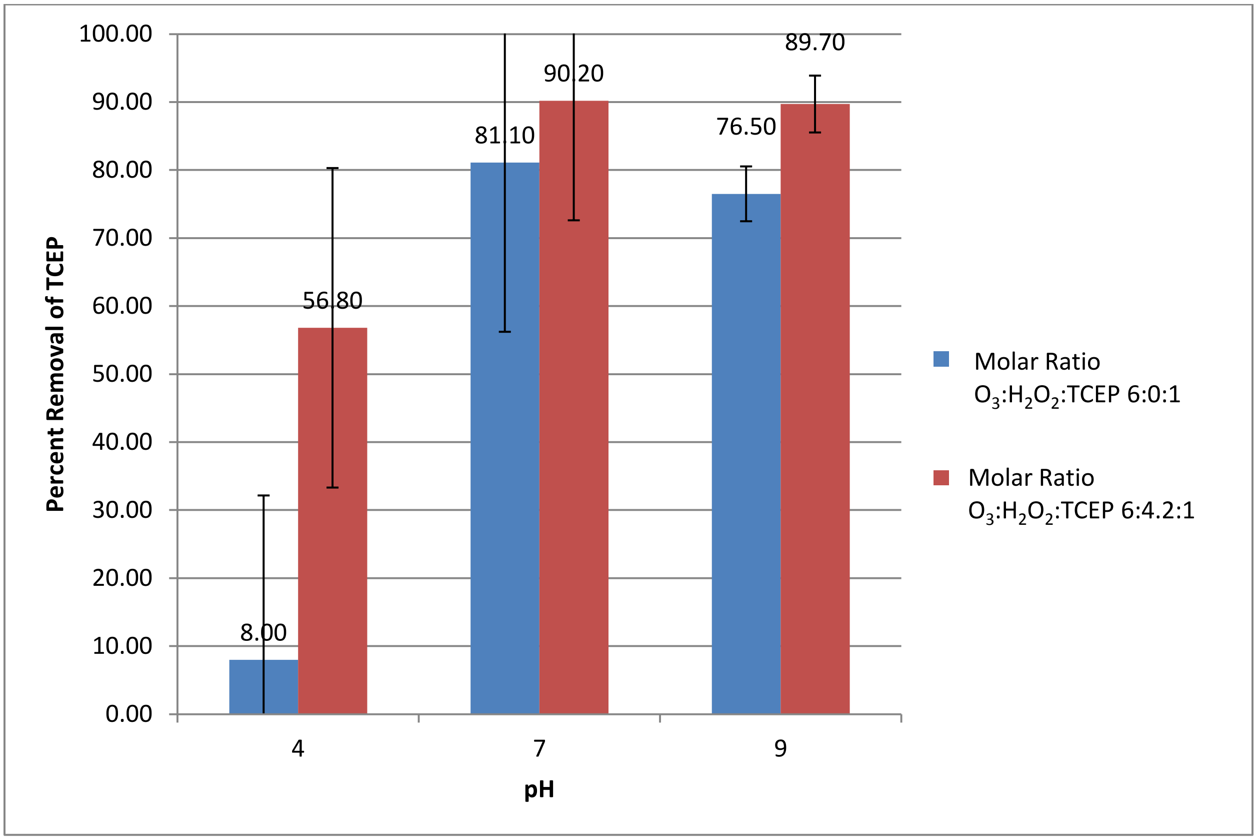

Figure 8: Percent Removal of TCEP for O_3 and H_2O_2/O_3 Treatments at Varied pH (Ozone Dose of 2 mg/L).
Initial TCEP Concentration = 2 mg/L.

As illustrated in Figure 8 the greatest decrease of TCEP concentration with an ozone dose of 2 mg/L occurred at a pH of 7 with a dose of 6:4.2:1 O_3:H_2O_2:TCEP molar ratio. This decrease in TCEP concentration was ≈90%. The greatest decrease of TCEP without hydrogen peroxide addition was ≈81.1% at a pH of 7. The lowest reductions shown in Figure 8 were 8% and ≈57% for O_3 and O_3/H_2O_2 treatments respectively at a pH of 4.

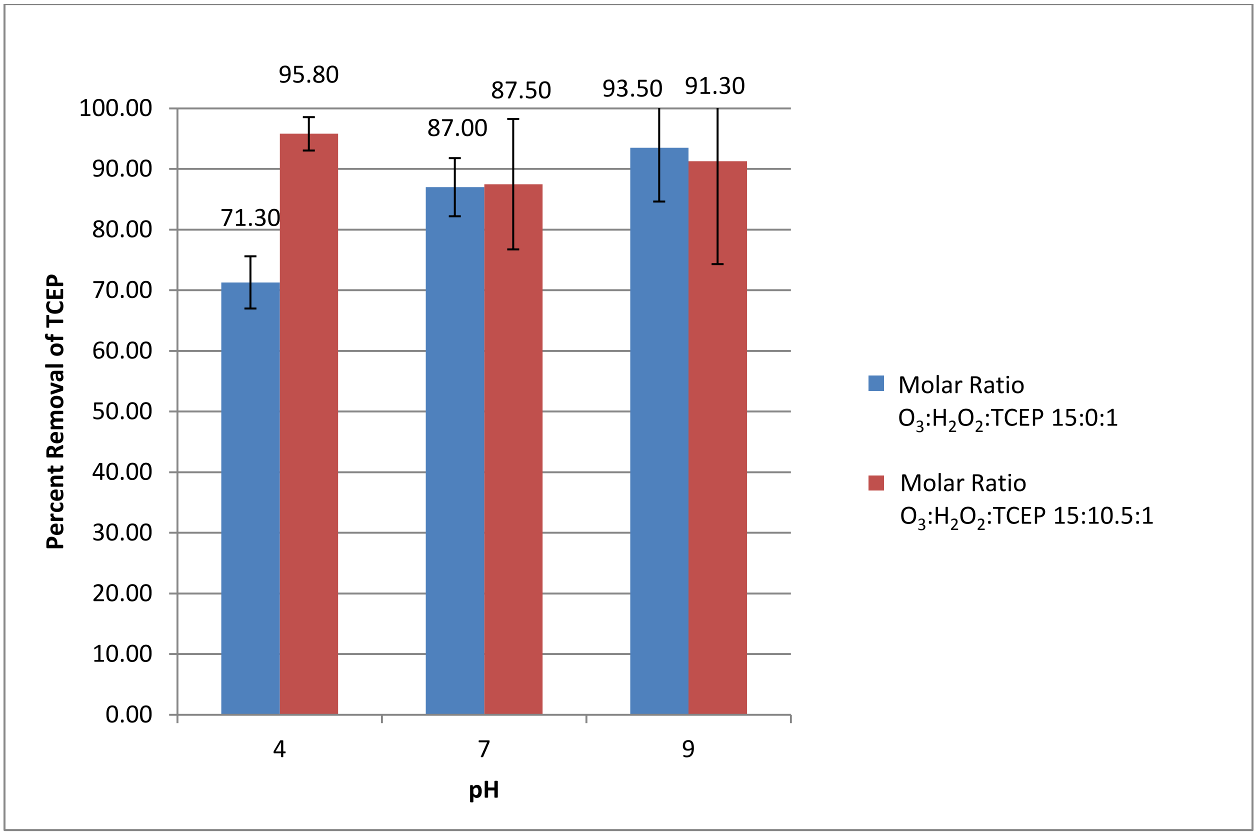

Figure 9: Percent Removal of TCEP for O_3 and H_2O_2/O_3 Treatments at Varied pH (Ozone Dose of 5 mg/L)
Initial TCEP Concentration = 2 mg/L.

Figure 9 shows that 95.8% TCEP removal was achieved at a pH of 4 with an ozone dose of 5 mg/L and a 15:10.5:1 O_3:H_2O_2:TCEP molar ratio. The highest TCEP removal without hydrogen peroxide was 93.5% with a 15:0:1 O_3:H_2O_2:TCEP molar ratio at pH 9. At this dosing of ozone it is apparent that a pH of 9 provided the greatest removal of TCEP concentration without hydrogen peroxide addition. At a dose of 5 mg/L ozone there is a trend that as pH goes up from 4 to 9 the removal efficiency of O_3 treatment efficiency goes up as well.

At increased pH the effectiveness of the addition of hydrogen peroxide seems to become unnecessary to achieve high removals of TCEP. This could be due to competitive kinetics, or a high dose of hydrogen peroxide. Higher pH range waters of 7 to 9 would have more readily available hydroxide ions which could initiate the decomposition ozone creating free radicals [46, 54]. These free radicals could potentially react with hydrogen peroxide instead of a contaminant. The formation of more free radicals may be hindered if radicals react with hydrogen peroxide rather than the contaminant, limiting the treatment efficiency of concerning contaminants such as TCEP. At a low pH of 4 the addition of hydrogen peroxide increased the treatment efficiency of TCEP by more than 20% at an ozone dose of 5 mg/L.

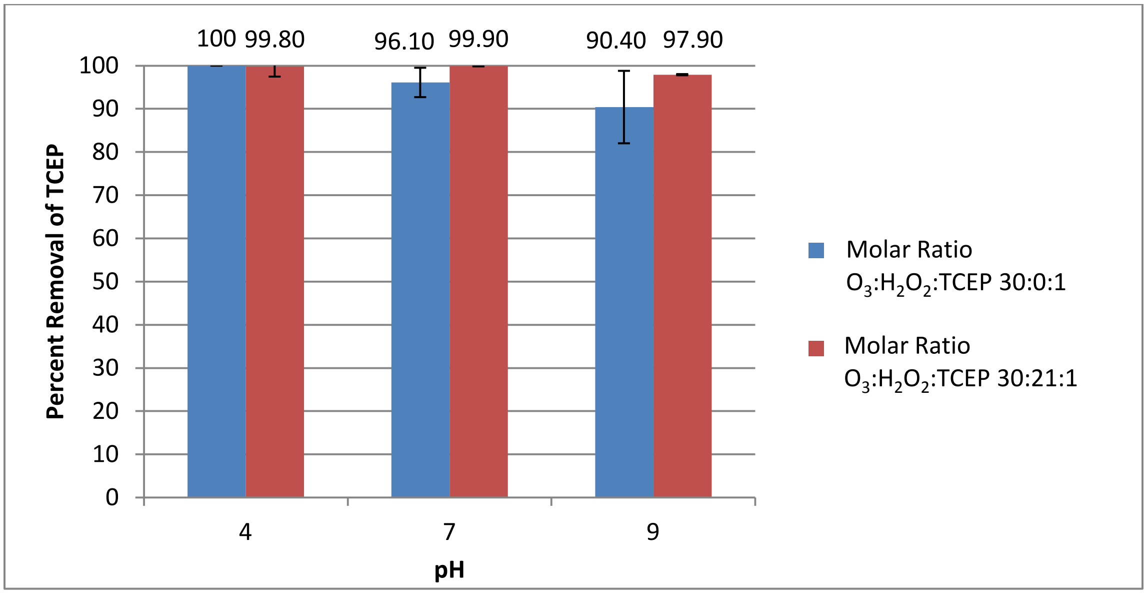

Figure 10: Percent Removal of TCEP for O_3 and H_2O_2/O_3 Treatments at Varied pH (Ozone Dose of 10 mg/L).
Initial TCEP Concentration = 2 mg/L.

An ozone dose of 10 mg/L ozone is portrayed in Figure 10 with 95% confidence interval error bars based on repeat experimental data. With a 30:21:1 O_3:H_2O_2:TCEP molar ratio greater than 95% removal of TCEP was achieved at pH 4, 7, and 9. The greatest removal at this molar ratio occurred at a pH of 7 with 99.9% removal of TCEP. The greatest reduction of TCEP with a

30:0:1 O_3:H_2O_2:TCEP molar ratio was 100% at a pH of 4. The lowest reduction of TCEP, ≈90%, was seen at a pH of 9 and occurred at a 30:0:1 O_3:H_2O_2:TCEP molar ratio. With a dose of 10 mg/L ozone all pH ranges with and without the addition of hydrogen peroxide provided a >90% TCEP removal in purified water spiked with TCEP.

For most doses of ozone, the data in Figures 8, 9, and 10 show that hydrogen peroxide addition enhances the oxidation of TCEP. The data portrayed in Figure 9 show that with a 5 mg/L dose of ozone at pH of 9 hydrogen peroxide addition does not enhance treatment. This may be due to a single experimental run that showed much lower TCEP removals than the three others, this data may be seen in Appendix F. All experiments were run at least three times to ensure repeatability.

The greatest decrease in TCEP concentrations were achieved at an ozone dose of 10 mg/L with hydrogen peroxide addition of 5 mg/L for all pH values. These removals with 30:21:1 O_3:H_2O_2:TCEP molar ratios were all greater than 97%. The greatest decrease of TCEP concentration with ozone oxidation alone occurred at a 30:0:1 O_3:H_2O_2:TCEP molar ratio with a pH of 4 and 7 and at a 15:10.5:1 O_3:H_2O_2:TCEP molar ratio at pH 9 with reductions of 100%, 96.1%, and 93.5% respectively. These high removals of TCEP are in the same range as those found by Watts and Linden [37] and Nguyen [36]. In a 2008 study Watts and Linden achieved >95% removal of 5 mg/L TCEP from lake water using photo-oxidation with $UV_{254\text{ nm}}$ fluence of 6,000 mL/cm^2 in a 50 mg/L hydrogen peroxide solution. In a 2010 study, Nguyen [36] achieved >95% reduction of 100 mg/L TCEP from purified water using Fenton's oxidation with doses between H_2O_2:Fe^{2+}:TCEP molar ratios of 75:2.5:1 and 150:2.5:1.

This research achieved higher removals of TCEP using ozone and ozone/hydrogen peroxide than found in the literature. However this could be due to several of the following factors;

1. **Ozone dose**: The ozone doses used in this research were higher than doses used in other research except for Pisarenko et al. [41]. A 10 mg/L ozone concentration was used to achieve a >50% reduction of TCEP in the 2011 study.

    - Westerhoff et al. [24] used ozone doses of 3-4 mg/L to achieve <5% removal of TCEP.
    - Snyder et al. [16] used ozone doses of 1.25 and 2.5 mg/L to achieve <17% removal of TCEP.

2. **Hydrogen Peroxide Dose:** The hydrogen peroxide dose used in this research was based on the optimum hydroxyl radical producing H_2O_2:O_3 ratio of 0.5:1 by mass [42, 50].

    - Pisarenko et al. [41] used a 0.7:1 molar ratio H_2O_2:O_3 to achieve a >60% removal of TCEP.
    - Westerhoff et al. [24] used a 0.025 mg H_2O_2: 1 mg O_3 dose to achieve <5% removal of TCEP.
    - Snyder et al. [16] used a 0.2 mg H_2O_2: 1 mg O_3 dose to achieve <17% removal of TCEP.

3. **Water Quality Parameters:** The sample water in this research consisted of TCEP spiked purified water. Most other research conducted used surface or waste waters for their TCEP spikes. This lead to differences in pH, dissolved organic matter, and other constituents that could affect the ozone or ozone/hydrogen peroxide oxidation of TCEP.

- Pisarenko et al. [41] used a spiked Colorado River water.
- Westerhoff et al. [24] used a spiked Colorado River water, and three other surface waters.
- Snyder et al. [16] used spiked Colorado River water.

The source water differences could be why the results found in this research gave higher removals of TCEP using ozone and ozone/hydrogen peroxide. However the results presented in this research show that TCEP can be effectively removed by ozone and ozone/hydrogen peroxide in purified water. It would be beneficial to continue research looking into the treatment of TCEP in other waters that may have constituents that could affect the treatment of TCEP using ozone or ozone/hydrogen peroxide.

TCEP Oxidation Products and Total Organic Carbon Analysis. In a 2008 study by Watts and Linden [37] it was found that with increasing OH• oxidation of TCEP solutions there was an increase in Cl^- and H^+ concentrations. It is likely that the oxidation of TCEP breaks the bonds between carbon and Cl,$^-$ as well as the bonds between carbon and H^+. Observations of 100% release of Cl^- and a 20% mineralization of TOC with a 96% UV/H_2O_2 oxidation of TCEP in solution were made by Watts and Linden. They also stated that a portion of TCEP oxidation products would become an available carbon source for bacterial growth in further treatment or distribution in water systems.

Another study by Ruan et al. [55] took place in 2012 and aimed at determining the effectiveness of degrading TCEP by UV/H_2O_2. Photo oxidation was found to be an effective treatment method, and the products of TCEP from oxidation were found by GC/MS (Mass Spectrometry) analysis during the study. It was found that hydroxyl radicals formed by the addition of hydrogen peroxide attacked TCEP. The TCEP was degraded to monochloroacetic acid, monochloacealdehyde, formic acid, acetic acid and some small molecular organics. At this point PO_4^{3-} ions were released and the chlorinated small organic chemicals were further degraded to Cl^-, formic acid, and acetic acid. Eventually all of the intermediates were mineralized to carbon dioxide and water. The reactions of TCEP by UV/H_2O_2 oxidation are likely similar to the reactions that would take place in the ozone or ozone/hydrogen peroxide oxidation of TCEP.

Total organic carbon analyses were performed in a Shimazdu TOC-5000A (Shimazdu, Columbia, Maryland) carbon analyzer following standard methods 5310B. The starting conditions of the samples were as follows; solution pH of 7, 2 mg/L TCEP, 0.518 mg/L TOC, 5 mg/L ozone, and when added 2.5 mg/L hydrogen peroxide. TOC after ozone and ozone/hydrogen peroxide treatment were 0.463 mg/L and 0.452 mg/L respectively. The TOC analyses showed that 10.62% and 12.74% destructions of TOC were achieved by ozone and ozone/hydrogen peroxide oxidation respectively. Watts and Linden [37] found a 20% mineralization of TOC with a 96% oxidation of TCEP (5 mg/L starting concentration) by UV/H_2O_2. The data found in this research as well as the research conducted by Watts and

Linden shows that some TCEP was mineralized to carbon dioxide and water during ozone and ozone/hydrogen peroxide oxidation. For the same starting conditions TCEP removals were 87% and 87.5% for ozone and ozone/hydrogen peroxide treatments. The higher removals of TCEP than TOC indicates that TCEP intermediates were formed. These products were likely monochloroacetic acid, monochloacealdehyde, formic acid, acetic acid, Cl^-, H^+, and PO_4^{3-} as indicated in previous research of the photo-oxidation of TCEP [55]. Watts and Linden [37] found that for low levels of TCEP, ozone oxidation would not be expected to effect the pH concentration. The solution pH after oxidation in this research was typically lower than starting pH by 0.01 to 3 pH units. The lowest pH values were achieved with the highest removals of TCEP. This may be due to the release of H^+ during the oxidation of TCEP. During photo oxidation Watts and Linden [37] found that for a 95% oxidation of TCEP the solution pH dropped from 7 to 4.25. Based on the literature and TOC results from this research it is likely that TCEP was partially mineralized by ozone and ozone/hydrogen peroxide oxidation. Higher doses of ozone may be able to more completely mineralize TCEP and should be investigated in future research.

Equilibrium Trials in Wastewater Effluent. All equilibrium reactions were allowed 24 hours to proceed and started with a TCEP concentration of 2 mg/L in spiked wastewater. Appendix F shows the GC equilibrium experiment results and Appendix G shows the TCEP spike GC results. Experiments to determine the effect of ozone dose on the removal of TCEP were done at a neutral pH of 7 in wastewater (starting pH 6.85 adjusted to pH 7.0 +/- 0.1) from the Upper Blackstone Wastewater Treatment Facility in Worcester, MA diluted with purified water. Table

2 shows the starting conditions for wastewater equilibrium experiments conducted in this research.

Table 2: Starting Conditions for Wastewater Equilibrium Experiments

pH	7
TCEP Conc.	2 mg/L
Ozone Conc.	5 mg/L
Hydrogen Peroxide Conc.	0 or 2.5 mg/L
Water:Wastewater Ratio	1:1, 2:1, 4:1, or 1:0

Figure 11 shows the TCEP removal by ozone and ozone/hydrogen peroxide oxidation at a neutral pH in diluted wastewater.

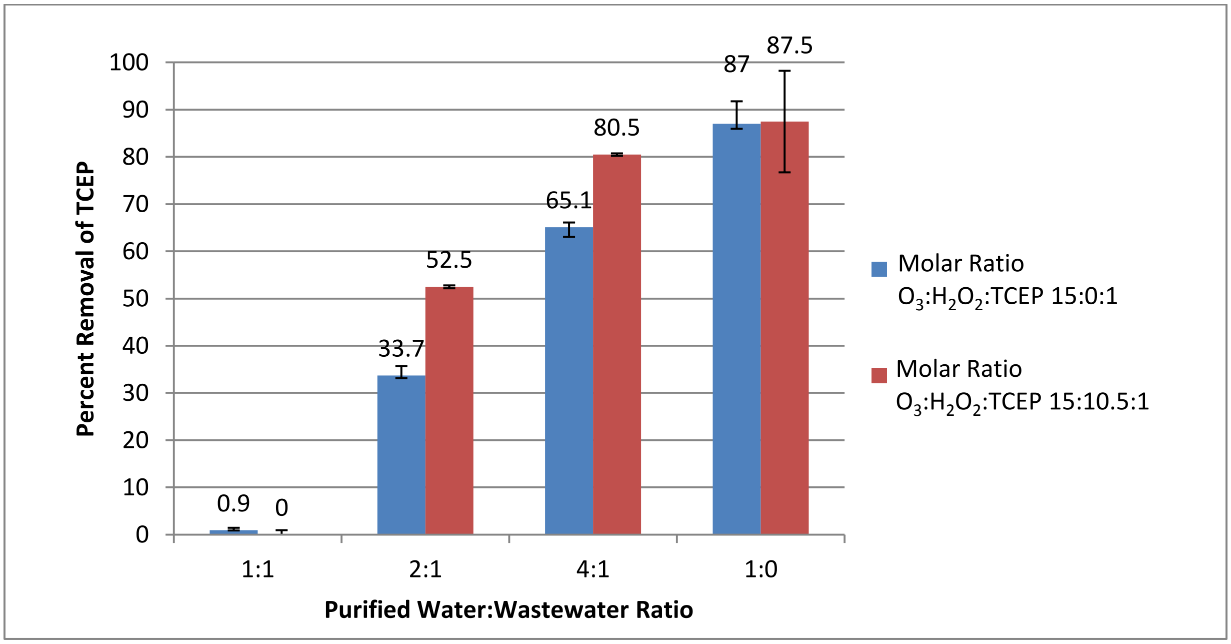

Figure 11: Percent Removal of TCEP for O_3 and H_2O_2/O_3 Treatments in Diluted Wastewater at pH 7 (Ozone Dose of 5 mg/L).
Initial TCEP Concentration = 2 mg/L.

Purified water without wastewater addition achieved the greatest TCEP removals as expected. Figure 11 shows that an 80.5% TCEP removal was achieved at a pH of 7 with an ozone dose of 5 mg/L and a 15:10.5:1 O_3:H_2O_2:TCEP molar ratio in a 4:1 water:wastewater dilution. The highest TCEP removal without hydrogen peroxide was 65.1% with a 15:0:1 O_3:H_2O_2:TCEP molar ratio in a 4:1 volumetric ratio of purified water and wastewater. The lowest reductions of TCEP with and without hydrogen peroxide addition occurred in a 1:1 water:wastewater dilution with TCEP removals of 0.9% and 0% respectively. The 2:1 water:wastewater dilution showed a 33.7% and a 52.5% reduction of TCEP with ozone and ozone/hydrogen peroxide treatment respectively. These data show that the removal of TCEP from wastewater effluent prior to chlorination is difficult using ozone and ozone/hydrogen peroxide. The TCEP removal in 1:1 water:wastewater volumetric ratio at a pH of 7 with an ozone dose of 5 mg/L (15:0:1 and 15:10.5:1 O_3:H_2O_2:TCEP molar ratio) was in the same range as results reported by Westerhoff et al.[24] <5%, and Snyder et al.[16] <17% reduction of TCEP in Colorado River water using ozone and ozone/hydrogen peroxide. The reason for the low removals of TCEP is likely due to competitive kinetics. The reaction between ozone and TCEP, or ozone/hydrogen peroxide and TCEP is hindered due to other contaminants in the sample water. Both ozone and hydroxyl radicals are non-selective compounds and may react with constituents other than TCEP. Therefore the additional constituents in wastewater require that water be diluted to allow TCEP removal to take place. Increasing the contact time or dose of ozone with wastewater may allow for more efficient treatment. TCEP concentration can be decreased in diluted wastewater, but only at high dilutions of water:wastewater . Further testing looking at higher doses and contact times of ozone and ozone peroxide could be useful to determine if higher removals of TCEP can be achieved in wastewater.

The chemical oxygen demand (COD) levels were tested before and after the ozone and ozone/hydrogen peroxide reactions with TCEP spiked diluted wastewaters. Table 3 shows the results of the COD testing.

Table 3: COD Before and After Wastewater Equilibrium Trials

Purified Water: Wastewater Volumetric Ratio	1:1	1:1	2:1	2:1	4:1	4:1
Treatment	O_3	O_3+H_2O_2	O_3	O_3+H_2O_2	O_3	O_3+H_2O_2
COD mg/L at Start	12.167	12.167	8.44	8.44	4.55	4.55
COD mg/L at End	0	0	0	0	0	0

COD Wastewater Effluent Prior to Chlorination: ≈25 mg/L

The results show that all COD levels were reduced to zero in all experiments. The data shows that the experiments that started with a lower COD had higher TCEP removal efficiencies. The competitive contaminants that inhibit TCEP reduction could be associated with the presence of COD in the wastewater.

Kinetic Trials. The degradation of TCEP at O_3:H_2O_2:TCEP molar ratios of 15:0:1 and 15:10.5:1 over time are shown in Figure 12. The degradation of TCEP using ozone and ozone/hydrogen peroxide oxidation occurred most rapidly in the first hour. The 24 hour degradation of TCEP at molar ratio doses of 15:0:1 and 15:10.5:1 were 87% and 87.5% respectively.

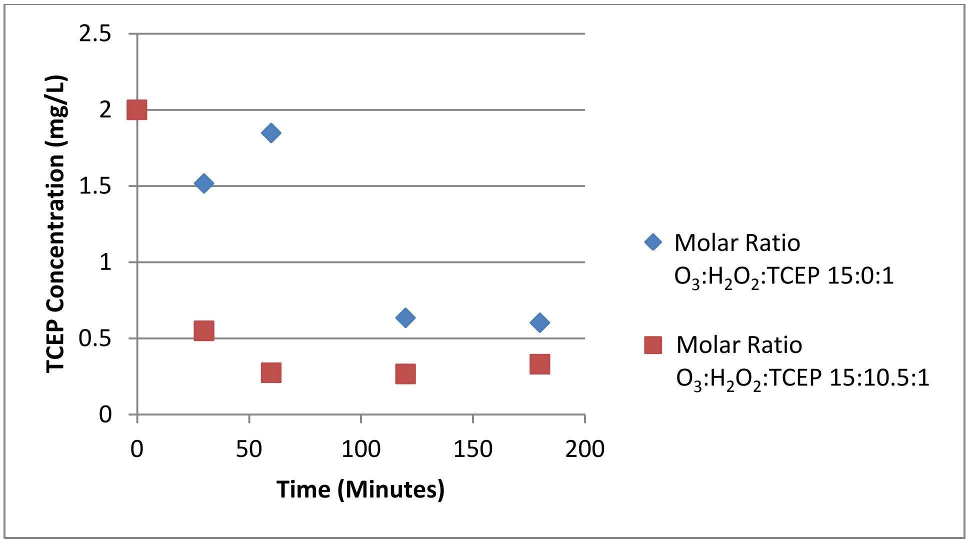

Figure 12: Kinetics Experimental Data for O_3 and O_3/H_2O_2 Oxidation of TCEP
(pH = 7, Initial TCEP =2 mg/L, Ozone Dose = 5 mg/L, and Hydrogen Peroxide Dose = 2.5)

The data portrayed in Figure 12 shows that TCEP degradation is slower when compared to other ozone and ozone/hydrogen peroxide oxidation studies. In a study by Rosario-Ortiz et al. [52] all dissolved ozone residual was consumed down to levels < 0.1 mg/L within 10 minutes in the three tertiary treated wastewaters studied. Therefore the contaminants in wastewater were reacting very quickly with ozone. In a 2006 study determining the kinetics of ozone with progesterone Barron et al. [56] found progesterone to have a second order rate constant of 480 +/- 30 M^{-1} *min^{-1} and reactions were completed in less than 10 minutes. In a wastewater study by Janex et al. 2000 [57] it was shown that in three wastewaters there was an immediate ozone demand that ranged from 4.5-5.5 mg/L ozone. The instantaneous demand shows that the reaction rates of contaminants in wastewater with ozone is very fast, much faster than the kinetic results found between TCEP and ozone in this research. 4 chlorophenol, benzoic acid, and hydroxyl benzoic acid were oxidized by ozone fully within 60, 15, and 30 minutes respectively in a study done by Boncz in 2002 [13]. In a study of the removal of 32 pharmaceutical compounds using ozone with and without hydrogen peroxide treatment by Rosal et al. [58]. It was found that most compounds were removed by >99% after five minutes of treatment. These examples show that TCEP degrades much slower than many other organics when oxidized by ozone. Watts and Linden [37] showed that TCEP intermediates retain the recalcitrant properties of TCEP, this explains the slow decrease in TCEP concentration in oxidative processes.

TCEP's slow degradation could be due to the phosphorus in the compound. It has been shown that phosphates (PO_4^{-3}) can inhibit the formation of hydroxide radicals, which are a major component of ozone and ozone/hydrogen peroxide oxidation [38, 59]. Ruan et al. [55] showed that the formation of PO_4^{-3} ions was the rate limiting step in the degradation of TCEP. The phosphorus-oxygen bonds and the carbon oxygen bond in TCEP are the strongest chemical bonds in the compound. The bond dissociation energies for the phosphorus-oxygen bond, the phosphorus-oxygen double bond, and the carbon-oxygen bond are 335 KJ/mole, 544 KJ/mole and 358 KJ/mole respectively [62]. These strong bonds may contribute to the slow reaction between TCEP and ozone or ozone/hydrogen peroxide.

The reaction describing TCEP degradation with ozone or ozone/hydrogen peroxide oxidation is shown by Equations 13 and 14.

Equation 13:

$$TCEP + O_3 \rightarrow Products$$

Equation 14:

$$TCEP + OH^{\bullet} \rightarrow Products$$

The rate equations for TCEP are shown in Equations 15 and 16.

Equation 15:

$$K_{TCEP} = -\frac{dc_{TCEP}}{dt} \div (C_{TCEP} \times C_{O_3})$$

Equation 16:

$$K_{TCEP} = -\frac{dc_{TCEP}}{dt} \div (C_{TCEP} \times C_{OH^{\bullet}})$$

Where C_{TCEP} is the concentration of TCEP, C_{O3} is the concentration of ozone, $C_{OH\bullet}$ is the concentration of hydroxyl radicals, and K_{TCEP} is the reaction rate constant of TCEP.

To simplify kinetic analysis for the first order reaction rate O_3 and $OH^{\bullet}$ concentrations were assumed to be constant and Equations 15 and 16 were simplified and integrated to Equation 17.

Equation 17:

$$C_{TCEP} = C_{TCEP,0} \times \, e^{-k_{TCEP} \times t}$$

$C_{TCEP,\,0}$ is the initial concentration of TCEP, t is time in minutes.

To ensure a thorough investigation a simplified 2nd order rate constant equation was developed to try to model the data as well shown as Equation 18.

Equation 18:

$$C_{TCEP} = \frac{1}{(K_{TCEP} \times t) + (\frac{1}{C_{TCEP,0}})}$$

Linear regressions were applied to the data (Appendix H) to obtain the TCEP degradation rate constants for Equations 17 and 18. Several K_{TCEP} values were found and are summarized in Table 4.

Table 4: K_{TCEP} Values for O_3 and O_3/H_2O_2 Reactions with First and Second Order Regressions

Reaction Rate Constant	First Order Regression (1/min)	Second Order Regression (M^{-1}*min^{-1})
K_{TCEP} (O_3)	.0108	2.59*10^{-8}
K_{TCEP}(O_3/H_2O_2)	.0477	1.8*10^{-7}

The kinetic models based on these reaction rate constants are plotted in Figures 13 and 14 with the experimental TCEP data for the molar ratio O_3:H_2O_2:TCEP doses of 15:0:1 and 15:10.5:1

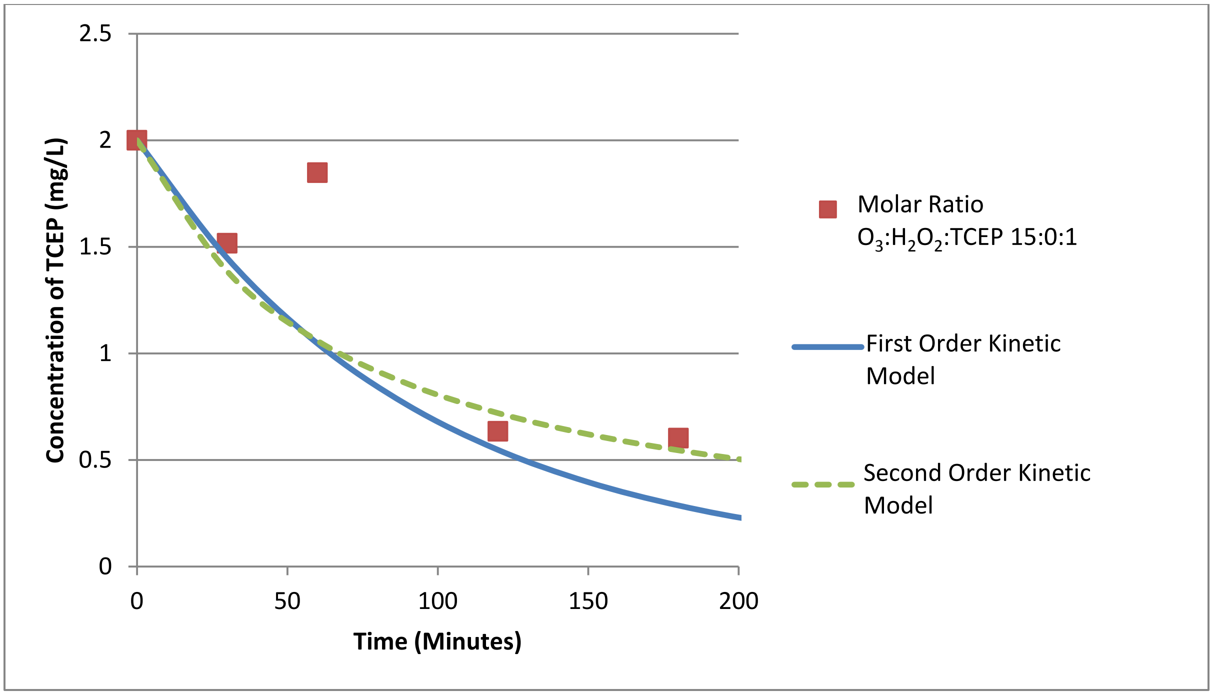

Figure 13: Measured and Kinetic Model Values of TCEP Concentration with Ozone Treatment. (Initial Conditions: TCEP = 2 mg/L, Ozone = 5 mg/L, Hydrogen Peroxide = 0 mg/L, pH = 7 O_3:H_2O_2:TCEP Molar Ratio of 15:0:1).

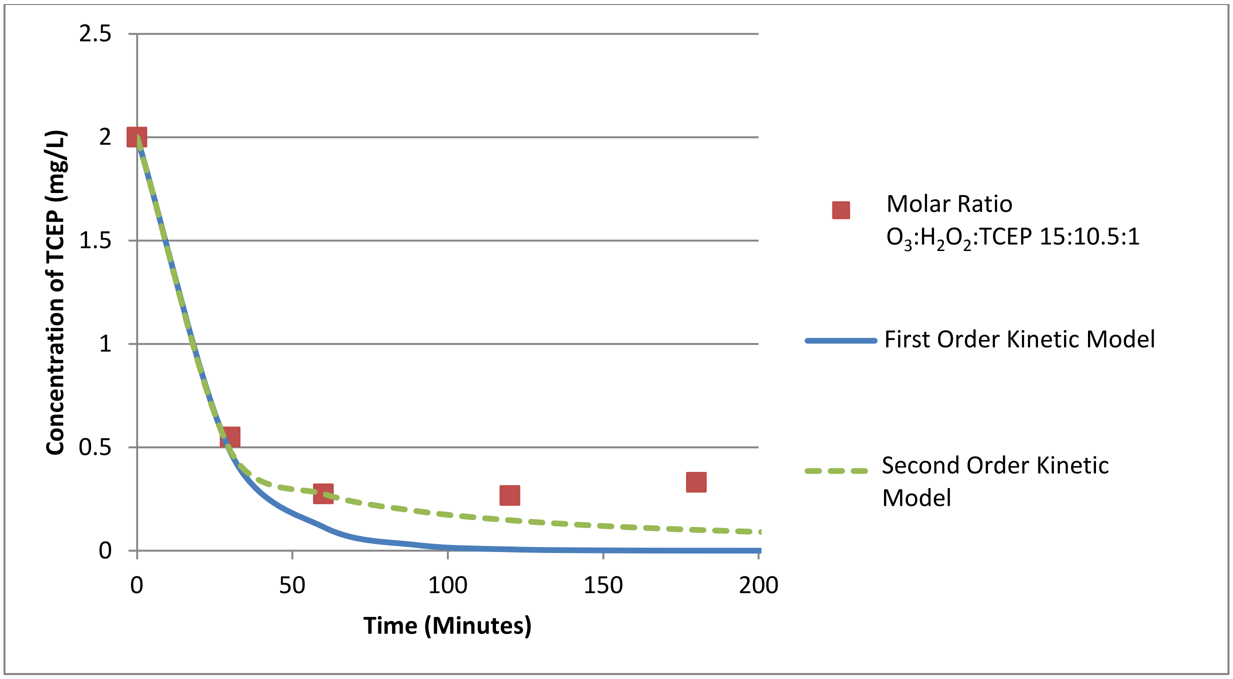

Figure 14: Measured and Kinetic Model Values of TCEP Concentration with Ozone/Hydrogen Peroxide Treatment.
(Initial Conditions: TCEP = 2 mg/L, Ozone = 5 mg/L, Hydrogen Peroxide = 2.5 mg/L, pH = 7 O_3:H_2O_2:TCEP Molar Ratio of 15:10.5:1).

Figures 13 and 14 show that the dose of ozone used did not completely remove TCEP. It can be seen that at a TCEP concentration of approximately 0.25 mg/L the reaction seems to be completed. The models shown in the figures show the first and second order kinetic models so that the rate constants, first and second order, may be compared to the rate constants of other constituents found in treatment waters.

The rate constants found in this study show that the TCEP reaction rates with ozone and ozone/hydrogen peroxide are much lower than that of many other contaminants in wastewaters. Table 5 shows a table of other contaminants reaction rates with ozone.

Table 5: Ozone Reaction Rates of Contaminants Found in Water

Contaminant	**Second Order Reaction Rate (M^{-1}*min^{-1}) K_{O3}**	**Second Order Reaction Rate (M^{-1}*min^{-1}) $K_{OH\cdot}$**
Progesterone [56]	-	480
Atrazine [52]	-	6
Atenolol [52]	-	$1.7*10^3$
TCE [49, 60]	0.1	$4.0*10^9$
PCE [49, 60]	17	$2.8*10^9$
Carbonate [60, 61]	-	$4.2*10^8$
Bicarbonate [60, 61]	-	$1.5*10^7$

As seen in the Table 5 the reaction rates of other contaminants oxidized by ozone and ozone/hydrogen peroxide are much higher than the reaction rate constants found for TCEP. Several compounds in the study by Rosario-Ortiz et al.2008 [52] have much higher reaction rate constants with ozone such as atrazine (k=6 $M^{-1}min^{-1}$) and atenolol (k=$1.7*10^3$ $M^{-1}min^{-1}$). In the 2000 study by Janex et al. [57] the wastewaters studied showed reaction rate constants of 0.20

min^{-1} with ozone after an initial demand of ≈5 mg/L of ozone. These other contaminants may explain why TCEP removal by ozone oxidation in wastewater proved to be ineffective.

The rate constants found in this study were similar to the constant found by Nguyen in a 2011 study [36] using Fenton's reagent to degrade TCEP. In her study the rate constant found was $5.2*10^{-3}$ min^{-1}. Echigo et al. [30] found reaction rates of 0.1, 0.1, 0.92, and 0.52 min^{-1} for TCEP removal using O_3/UV, O_3/H_2O_2, UV, and UV/H_2O_2 treatments respectively. These values are slightly higher than those found in this research but that may be due to the fact that Echigo et al. calculated the rate constants in the first five minutes of the reactions. They found that after five minutes the degradation of OPCs becomes slower probably due to the consumption of hydroxyl radicals by the products of the initial reactions. Westerhoff et al. [24] were unable to degrade TCEP with ozonation. This may be due to highly competitive contaminants in the sample waters used for the experiments. The contaminants in the wastewater used likely reacted with ozone rather than TCEP reacting with ozone due to TCEP's slow reaction rate. Other reasons for the slow reaction rates could be due to phosphates inhibiting the formation of free radicals in the oxidation process as mentioned earlier.

Chapter 4: Conclusions and Future Work

Conclusions

Tris-2-chloroethyl phosphate (TCEP) is a compound that has been found to be neurotoxic and carcinogenic. The compound is used as a flame retardant and a plasticizer for many manufactured foam products and predominantly in rigid foams used for insulation. TCEP has been detected in wastewater treatment plant effluents, source waters, and water treatment plant finished waters. Past research has shown that ozone oxidation and ozone/hydrogen peroxide oxidation are effective treatments for removing pharmaceutical, endocrine disrupting, organophosphorus and other bio-recalcitrant compounds from water [16, 24, 41, 44, 45]. The intent of this research was to determine the effectiveness of ozone and ozone/hydrogen peroxide oxidation of water contaminated with TCEP, as well as to determine optimum pH conditions for the treatment of TCEP.

Ozone and ozone/hydrogen peroxide oxidation were found to be an effective treatment method for the removal of TCEP from purified water. Ozone oxidation treatment gave a >85% removal of TCEP (2 mg/L) with a 30:0:1, 30:21:1, 15:0:1 and a 15:10.5:1 O_3:H_2O_2:TCEP molar ratio at all pH values examined (4,7,and 9) except for the 15:0:1 molar ratio at pH 4 which gave ≈71% removal. Ozone and ozone/hydrogen peroxide treatment showed TCEP reductions of >95% for doses 30:21:1 and 30:0:1 O_3:H_2O_2:TCEP molar ratio at pH 4 and 7. For most of the doses and pH values the addition of hydrogen peroxide did enhance the oxidation of TCEP. A reduction of TCEP occurred with all doses at all pH values with ozone and ozone/hydrogen peroxide oxidation in purified water.

Ozone and ozone/hydrogen peroxide oxidation of TCEP in diluted wastewater effluent were found to be effective at purified water to wastewater volumetric ratios of 4:1. At a 4:1 water to wastewater dilution with a pH of 7, an ozone dose of 5 mg/L, and a 15:10.5:1 O_3:H_2O_2:TCEP molar ratio an 80.5% reduction of TCEP was achieved. A 65.1% removal of TCEP was attained with a 15:0:1 O_3:H_2O_2:TCEP molar ratio in a 4:1 volumetric ratio of purified water and wastewater at pH 7. It was more difficult to remove TCEP from lower dilutions of water/wastewater. <50% and <1% reductions of TCEP occurred at 2:1 and 1:1 purified water to wastewater dilutions respectively.

Chemical oxygen demand (COD) tests showed that all COD was removed in all experiments, however the COD was greater in the lower water/wastewater dilutions initially. A trend was observed that the oxidation experiments with higher COD achieved a lower reduction of TCEP concentration.

The first order kinetic rate constants for ozone and ozone/hydrogen peroxide oxidation of TCEP were found to be .0108 and .0477 min^{-1} respectively. These first order constants were found by applying linear regression to experimental data with 84% and 97% fit for ozone and ozone/hydrogen peroxide first order reaction rates. Second order kinetic rate constants for TCEP oxidation were also investigated. For ozone treatment a rate constant of $2.59*10^{-8}$ $M^{-1}*min^{-1}$ was found with a linear regression fit of 86% to the data found, while ozone/hydrogen peroxide had a rate constant of $1.8*10^{-7}$ $M^{-1}*min^{-1}$ with a 99% regression line fit to the data.

The ozone and ozone/hydrogen peroxide oxidation TCEP kinetic rate constants found were significantly lower than treatment rate constants of other contaminants typically found in wastewaters and source waters. This may be the reason why TCEP oxidation by ozone and ozone/hydrogen peroxide is effective in purified water, but ineffective in wastewater and diluted wastewater. The instantaneous oxidant demand of wastewater may explain the ineffective degradation of TCEP in wastewaters, and may be why previous research showed low removals of TCEP using ozone and ozone/hydrogen peroxide. The use of ozone and ozone/hydrogen peroxide could be used to remove TCEP from water, however pretreatment or higher doses/contact times with the oxidants may be required for complete removals.

Engineering Implications and Future Research

Ozone and ozone/hydrogen peroxide oxidation of TCEP in purified water is effective at lab bench scale. Gas chromatography and total organic carbon analyses indicated that some TCEP and its products were mineralized. However, the products formed that were not mineralized during ozone oxidation of TCEP should be investigated in the future. It would be beneficial to know what products are being created in the ozone treatment of TCEP to ensure that while fixing one problem another is not created. Future research should be aimed at determining the products created in the ozone oxidation of TCEP.

Past research has shown that ozone oxidation of TCEP in source waters has its limitations due to the competitive kinetics of ozone and the hydroxyl radicals formed during ozone's spontaneous decomposition. Future research should consider the effectiveness of ozone and ozone/hydrogen peroxide oxidation of TCEP in other water matrices (i.e. surface water, finished drinking water, wastewater effluent…). By using higher doses of ozone it may be found that TCEP can be removed from any water source. An issue seen in past research may be that a low dose of ozone is used up reacting with other non-target constituents leaving no residual to react with recalcitrant compounds such as TCEP. Higher doses of ozone mean higher operating costs, but research needs to be done to determine at what dose all competing constituents in water will be oxidized. When no competing contaminants are present TCEP will be oxidized more fully. Future research should investigate the feasibility of ozone oxidation of TCEP in several waters.

Lower doses of TCEP should also be investigated. Using the method developed for this research one could look at increasingly smaller concentrations of TCEP by using a larger sample volume and separatory funnel. Removal of TCEP could be difficult at lower concentrations due to potential effects of the kinetics of TCEP oxidation at lower doses. With advanced equipment and techniques low TCEP concentration treatment should be investigated in the future.

Other ways to remove TCEP may exist and should be investigated. Solution pH seemed to have little effect for treatment at doses >2 mg/L of ozone. However at the lower dose of 2 mg/L ozone the optimum ozone/hydrogen peroxide oxidation and optimum ozone oxidation occurs at pH 7 or 9 for TCEP. Depending on the characteristics of the contaminated water pre and post treatment costs may be incurred for pH adjustment. Ozone generation is also a major energy cost. Watts and Linden [37] were able to remove 95% TCEP using UV/H_2O_2 treatment. Nguyen [36] was able to remove 95% TCEP using Fenton's oxidation. Energy consumption, pH adjustment, hazards, and ease of operation should all factor into choosing a treatment methods. Cost considerations should be evaluated for the use of ozone oxidation, Fenton's oxidation, and photo-oxidation of TCEP in future research. Looking at other advanced oxidation processes such as O_3/UV and UV/TiO_2 would also be useful to determine their effectiveness at TCEP removal, and then evaluated for cost considerations.

A batch system bench scale reactor was used in this research. However other reactor types should be considered for future bench scale studies, or pilot scale implementation. Continuous stirred tank reactors (CSTRs) or plug flow reactors (PFRs) offer continuous flow operation. CSTRs offer good mixing for chemical addition and stabilize pH, temperature, and concentration of substances rapidly. PFRs offer the opportunity for multiple dosing, or continuous dosing throughout the reactor. PFRs also have no moving parts therefore maintenance and operational costs are typically low. There are other configurations of these reactors such as CSTR in series reactors that may offer advanced removal efficiency. Other reactor types should be considered in the future research on TCEP removal.

Other organophosphorus compounds of concern should be investigated using ozone and ozone/hydrogen peroxide oxidation. Tri(1,3-dichloro-2-propyl)phosphate (TDCP), tris(2-chloroisopropyl)phosphate (TCPP), tributoxyethel phosphate (TBEP) and triisobutyl phosphate (TiBP) are a few of many organophosphate compounds with known health concerns. Being organophosphates they all have a similar chemical structure. These contaminants should be evaluated by health risk, and future research should aim at the removal of these contaminants as well as other emerging contaminants from water and waste water. Oxidation of the chemicals would completely eliminate them from water; therefore the removal of these contaminants should be investigated. Ozone oxidation, Fenton’s oxidation, photo-oxidation or other forms of advanced oxidation could prove to be useful in eliminating current and emerging contaminants from water. These treatments should be investigated for removal of different compounds in future research.

There are several concerns that would need to be addressed prior to implementing an ozone or ozone/hydrogen peroxide treatment method to TCEP contaminated water. These concerns include but are not limited to;

1. Removal of TCEP Required
2. Reactor Design (type, size/contact time, material, cost, number of reactors…)
3. Contaminated Water Characteristics (pH, interfering chemicals, organic matter…)
4. Pretreatment (filtration, pH adjust, …)
5. Ozone/Hydrogen Peroxide Addition (dose, location in reactor, continuous or pulse…)
6. Post Treatment (pH adjust, bi-products)
7. Costs (economic, environmental, safety)

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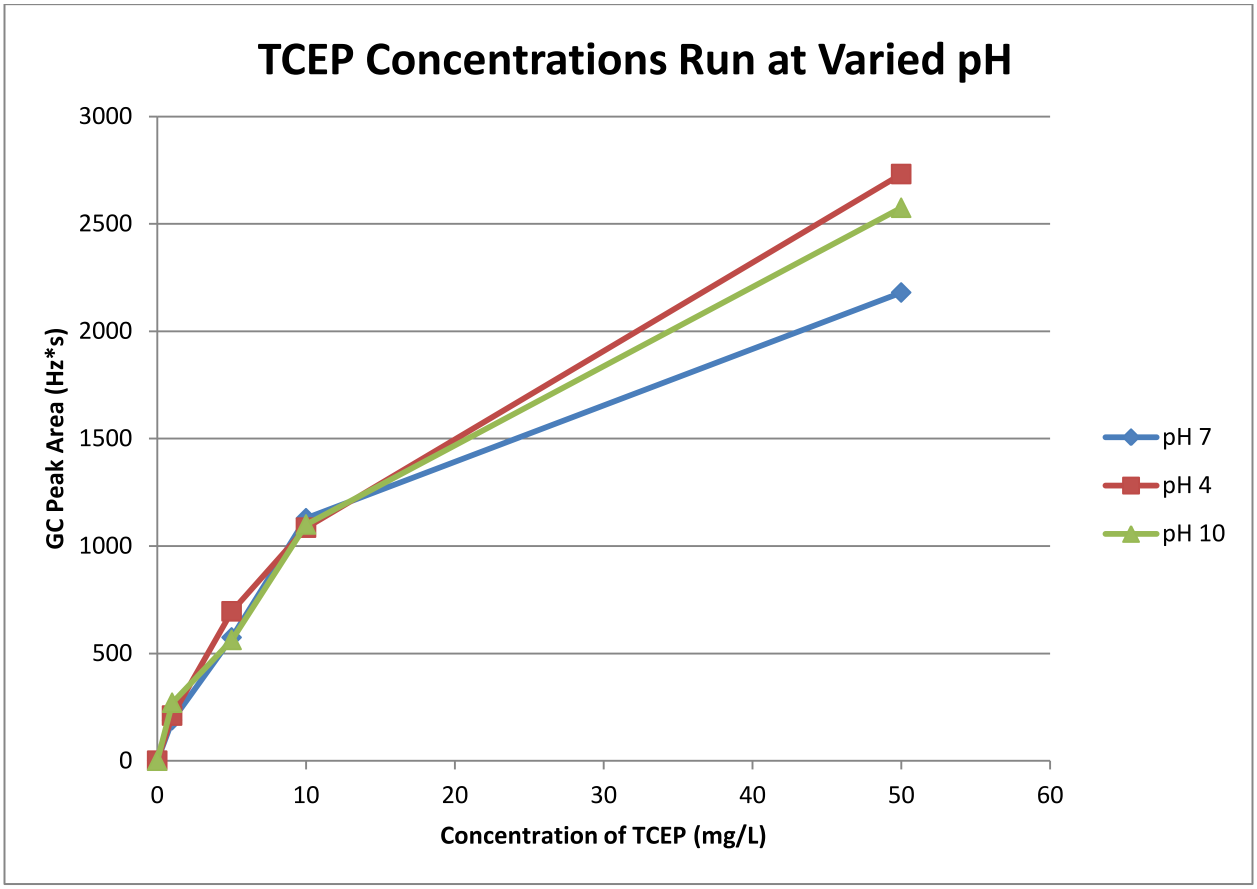
Appendix A: GC Analysis of TCEP at Varied pH



The graph shows that concentrations less than 10 mg/L of TCEP are not significantly affected by varying pH. In order to ensure the accuracy of GC analysis all samples were adjusted to pH 7.0 +/- 0.1 prior to liquid/liquid extraction. Note that this data was collected using a slightly different extraction method in which 500 mL samples were extracted using 75 mL of methylene chloride. All other steps were the same, but that explains the significantly lower GC peak areas for corresponding TCEP concentrations when compared to the standard curve used for the rest of analysis.

Appendix B: GC Method and Settings

Method Information

Method: C:\CHEM32\2\METHODS\MJV TCEPECD.M

Modified: 1/25/2013 at 8:10:58 AM

Method Audit Trail

Operator : Michael J Votruba

Date : 1/25/2013 8:10:57 AM

Change Info: This method was created at 1/25/2013 8:10:57 AM and based on method C:\Chem32\2\METHODS\MJV TCEPECD.M

Operator : Michael J. Votruba

Date : 1/25/2013 8:10:58 AM

Change Info: Method saved. User comment: ""

Run Time Checklist

Pre-Run Cmd/Macro: off

Data Acquisition: on

Standard Data Analysis: on

Customized Data Analysis: off

Save GLP Data: off

Post-Run Cmd/Macro: off

Save Method with Data: off

```
                  Injection Source and Location


    Injection Source:   GC Injector


    Injection Location: Back
================================================================================
========
                         6890 GC METHOD
================================================================================
========


OVEN
   Initial temp:  90 'C (On)              Maximum temp:  290 'C
   Initial time:  1.00 min               Equilibration time:  3.00 min
   Ramps:
      #  Rate  Final temp  Final time
      1 15.00      150       15.00
      2  5.00      200        5.00
      3 15.00      290        6.00
      4   0.0(Off)
   Post temp:  50 'C
   Post time:  0.00 min
   Run time:  47.00 min
```

FRONT INLET (SPLIT/SPLITLESS)

Mode: Split
Initial temp: 50 'C (Off)
Pressure: 0.00 psi (Off)
Total flow: 45.0 mL/min
Gas saver: Off
Gas type: Nitrogen

BACK INLET (SPLIT/SPLITLESS)

Mode: Splitless
Initial temp: 250 'C (On)
Pressure: 9.04 psi (On)
Purge flow: 0.0 mL/min
Purge time: 0.00 min
Total flow: 100.1 mL/min
Gas saver: Off
Gas type: Nitrogen

COLUMN 1

Capillary Column
Model Number: J&W 123-1334
DB-624
Max temperature: 260 'C
Nominal length: 30.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 1.80 um
Mode: constant pressure
Pressure: 9.03 psi
Nominal initial flow: 1.6 mL/min
Average velocity: 31 cm/sec
Inlet: Back Inlet
Outlet: Back Detector

COLUMN 2

Packed Column
Mode: (see column 1)
Pressure: 9.03 psi
Inlet: Back Inlet
Outlet: Back Detector
Outlet pressure: ambient

Outlet pressure: ambient

FRONT DETECTOR (FID)	BACK DETECTOR (ECD)
Temperature: 250 'C (Off)	Temperature: 250 'C (On)
Hydrogen flow: 40.0 mL/min (Off)	Anode purge flow: 6.0 mL/min (On)
Air flow: 450.0 mL/min (Off)	Mode: Constant makeup flow
Mode: Constant makeup flow	Makeup flow: 40.0 mL/min (On)
Makeup flow: 45.0 mL/min (Off)	Makeup Gas Type: Nitrogen
Makeup Gas Type: Nitrogen	Adjust offset: 60.00
Flame: Off	Electrometer: On
Electrometer: Off	
Lit offset: 2.0	

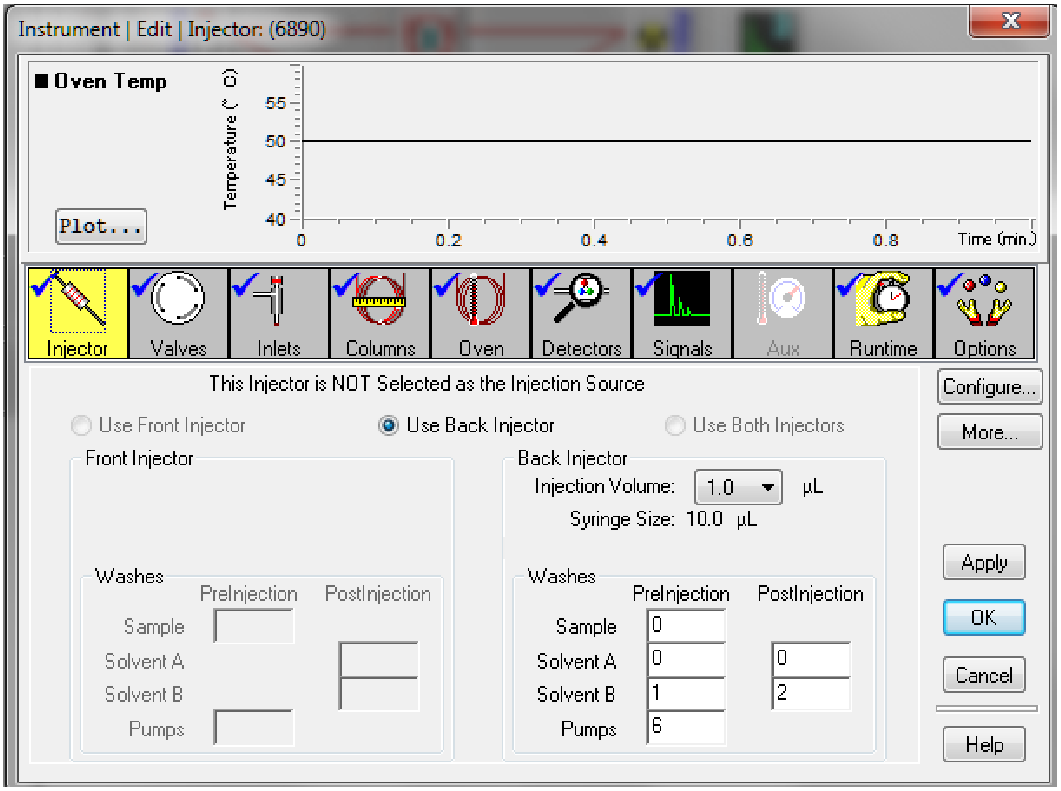
SIGNAL 1	SIGNAL 2
Data rate: 20 Hz	Data rate: 20 Hz
Type: back detector	Type: back detector
Save Data: On	Save Data: On
Zero: 0.0 (Off)	Zero: 0.0 (Off)
Range: 0	Range: 0
Fast Peaks: Off	Fast Peaks: Off
Attenuation: 0	Attenuation: 0

COLUMN COMP 1	COLUMN COMP 2
Derive from back detector	Derive from back detector

```
                    POST RUN

                     Post Time: 0.00 min


TIME TABLE

  Time     Specifier            Parameter & Setpoint



                 GC Injector



  Front Injector:

No parameters specified



  Back Injector:

    Sample Washes            0

    Sample Pumps             6

    Injection Volume        1.00 microliters

    Syringe Size          10.0 microliters

    PreInj Solvent A Washes    0

    PreInj Solvent B Washes    1

    PostInj Solvent A Washes    0

    PostInj Solvent B Washes    2

    Viscosity Delay          0 seconds

    Plunger Speed          Fast

    PreInjection Dwell      0.00 minutes

    PostInjection Dwell     0.00 minutes
```

```
The Acq. Method's Instrument Parameters for the Run were :


Data File  : C:\Chem32\2\DATA\MJV TCEP SPIKE BACK INJECTOR 2013-05-03 08-22-
47\030B0101.D

Acq. Method: MJV TCEPECD.M


The Acq. Method's Instrument Parameters for the Run were :

=====================================================================

                         Column(s)

=====================================================================

Column Description :  DB-624

Inventory#        :  AB001

Model#            :  123-1334         Manufacturer: J&W

Diameter          : 320.00 µm         Length :   30.0 m

Film thickness     :  1.80 µm        Void time :    1.603 min

Maximum Temperature:    0.0 °C

Comment           :


Column Description :

Inventory#        :  12739

Model#            : 530399                   Manufacturer: Restek

Diameter          :  0.32µm         Length :    30 m

Film thickness     :  0.5 µm        Void time :    0.000 min

Maximum Temperature:    350 °C

Comment           :
```

Method Name: MJV TCEPECD



Instrument | Edit | Injector: (6890)

This Injector is NOT Selected as the Injection Source

○ Use Front Injector ● Use Back Injector ○ Use Both Injectors

Front Injector

Washes

	PreInjection	PostInjection
Sample		
Solvent A		
Solvent B		
Pumps		

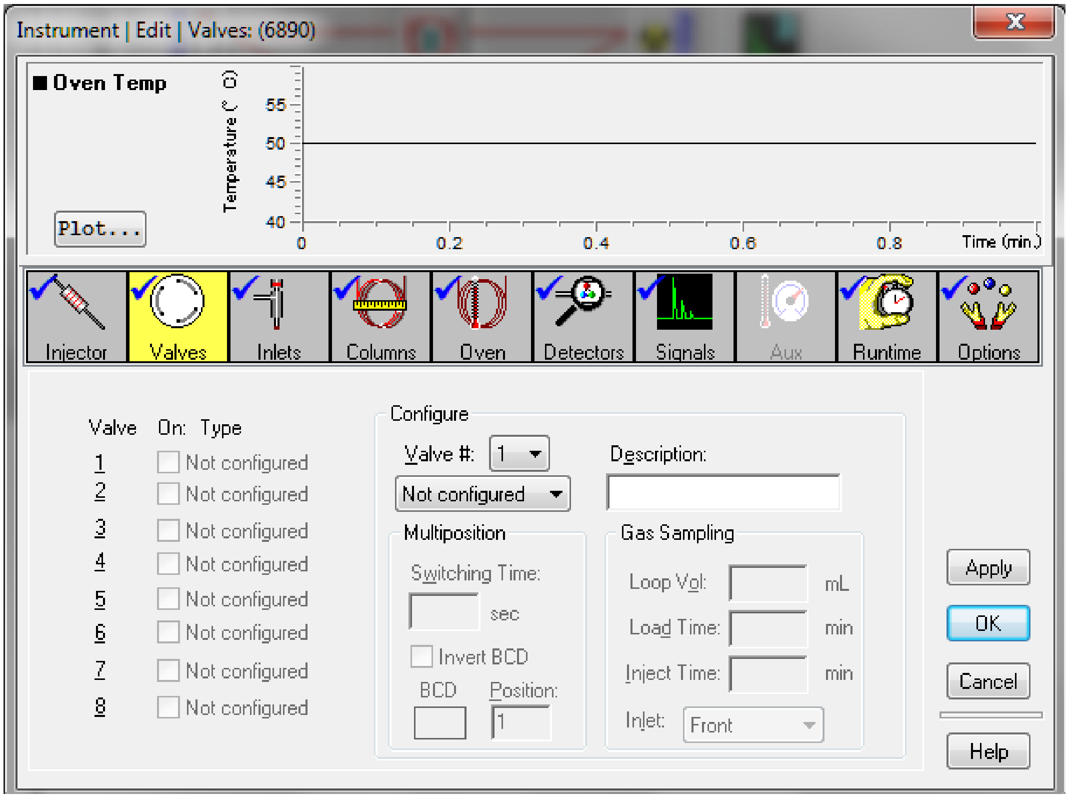
Back Injector

Injection Volume: 1.0 µL

Syringe Size: 10.0 µL

Washes

	PreInjection	PostInjection
Sample	0	
Solvent A	0	0
Solvent B	1	2
Pumps	6	



Instrument | Edit | Valves: (6890)

Valve	On:	Type
1	☐	Not configured
2	☐	Not configured
3	☐	Not configured
4	☐	Not configured
5	☐	Not configured
6	☐	Not configured
7	☐	Not configured
8	☐	Not configured

Configure

Valve #: 1

Not configured

Description:

Multiposition

Switching Time: sec

☐ Invert BCD

BCD

Position: 1

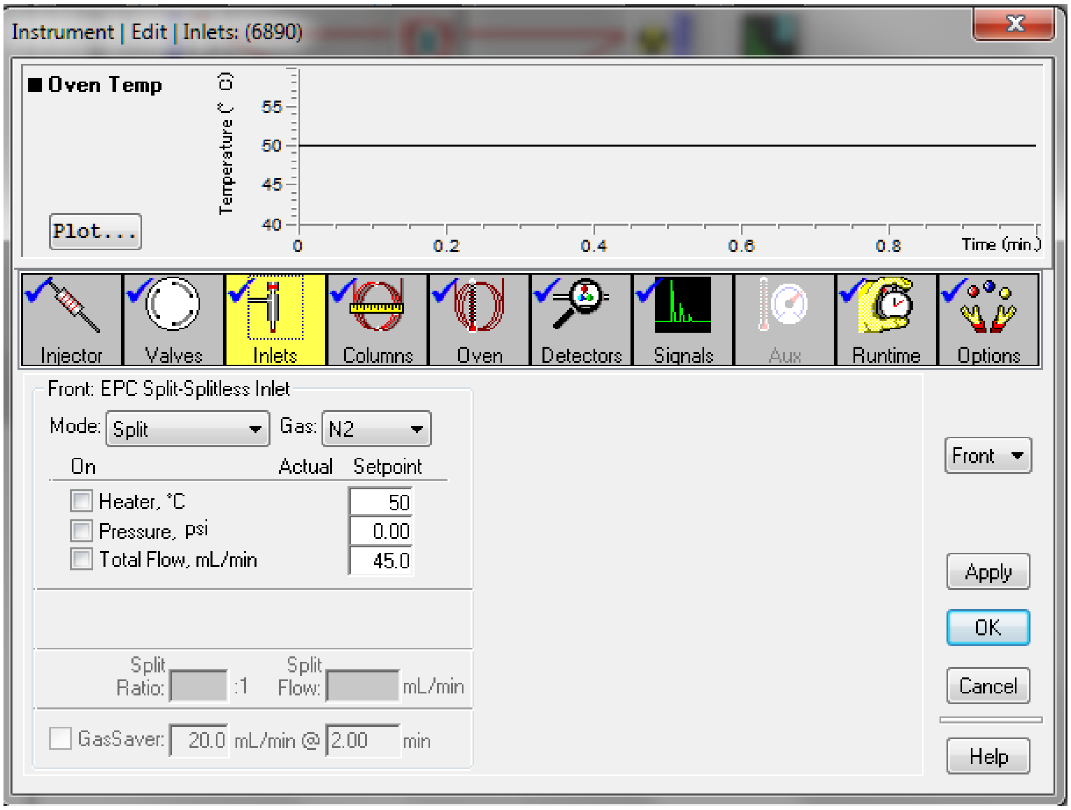
Gas Sampling

Loop Vol: mL

Load Time: min

Inject Time: min

Inlet: Front



Front: EPC Split-Splitless Inlet

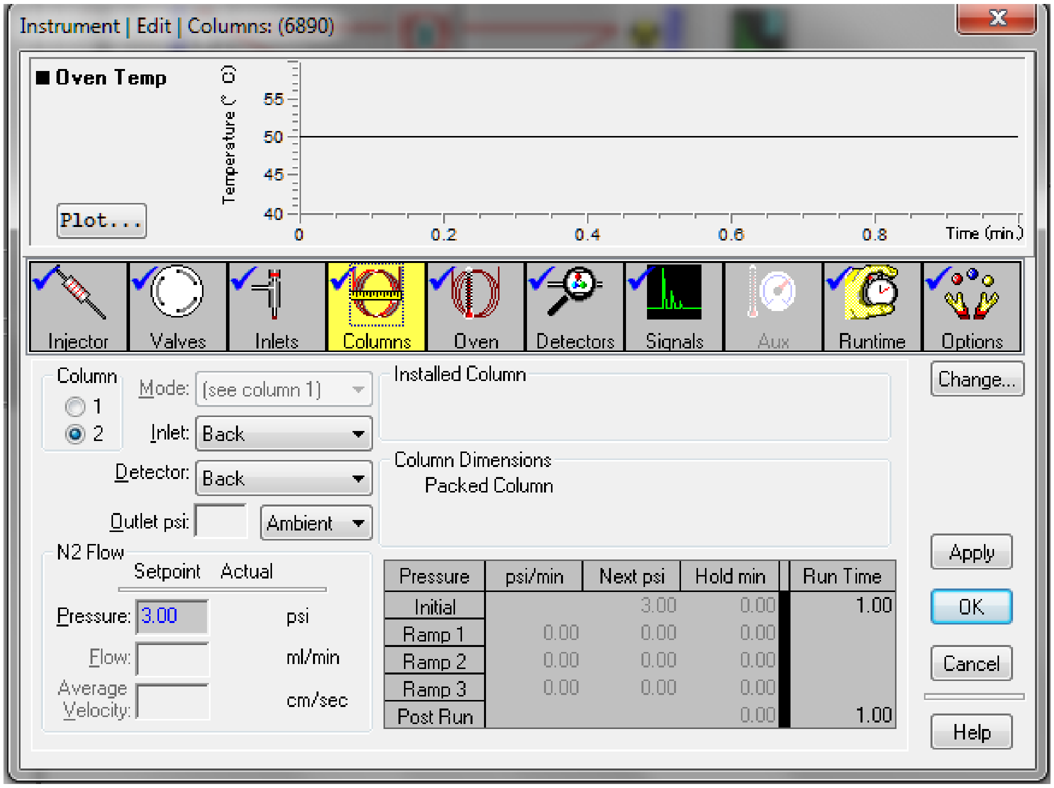
Mode: Split

Gas: N2

On	Actual	Setpoint
☐ Heater, °C		50
☐ Pressure, psi		0.00
☐ Total Flow, mL/min		45.0

Split Ratio: :1 Split Flow: mL/min

☐ GasSaver: 20.0 mL/min @ 2.00 min



Column ○ 1 ● 2

Mode: (see column 1)

Inlet: Back

Detector: Back

Outlet psi: Ambient

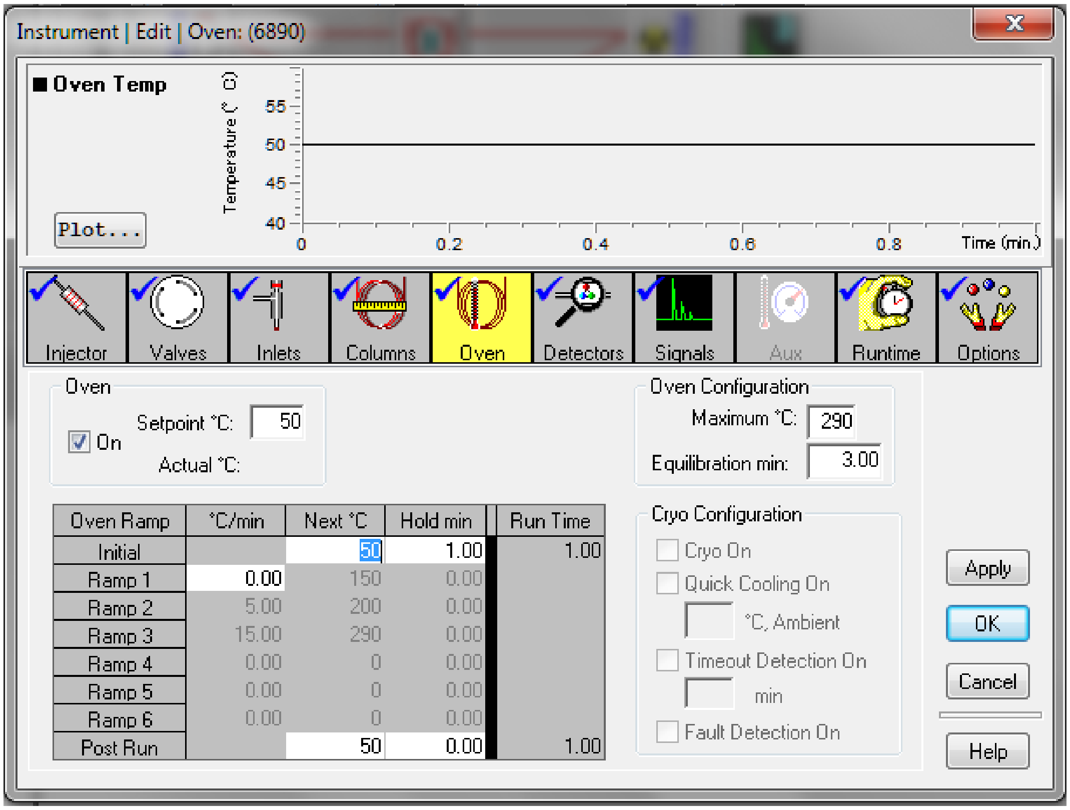
Installed Column

Column Dimensions
Packed Column

N2 Flow

	Setpoint	Actual	
Pressure:	3.00		psi
Flow:			ml/min
Average Velocity:			cm/sec

Pressure	psi/min	Next psi	Hold min	Run Time
Initial		3.00	0.00	1.00
Ramp 1	0.00	0.00	0.00	
Ramp 2	0.00	0.00	0.00	
Ramp 3	0.00	0.00	0.00	
Post Run			0.00	1.00



Instrument | Edit | Oven: (6890)

Oven

☑ On

Setpoint °C: 50

Actual °C:

Oven Configuration

Maximum °C: 290

Equilibration min: 3.00

Oven Ramp	°C/min	Next °C	Hold min	Run Time
Initial		50	1.00	1.00
Ramp 1	0.00	150	0.00	
Ramp 2	5.00	200	0.00	
Ramp 3	15.00	290	0.00	
Ramp 4	0.00	0	0.00	
Ramp 5	0.00	0	0.00	
Ramp 6	0.00	0	0.00	
Post Run		50	0.00	1.00

Cryo Configuration

☐ Cryo On

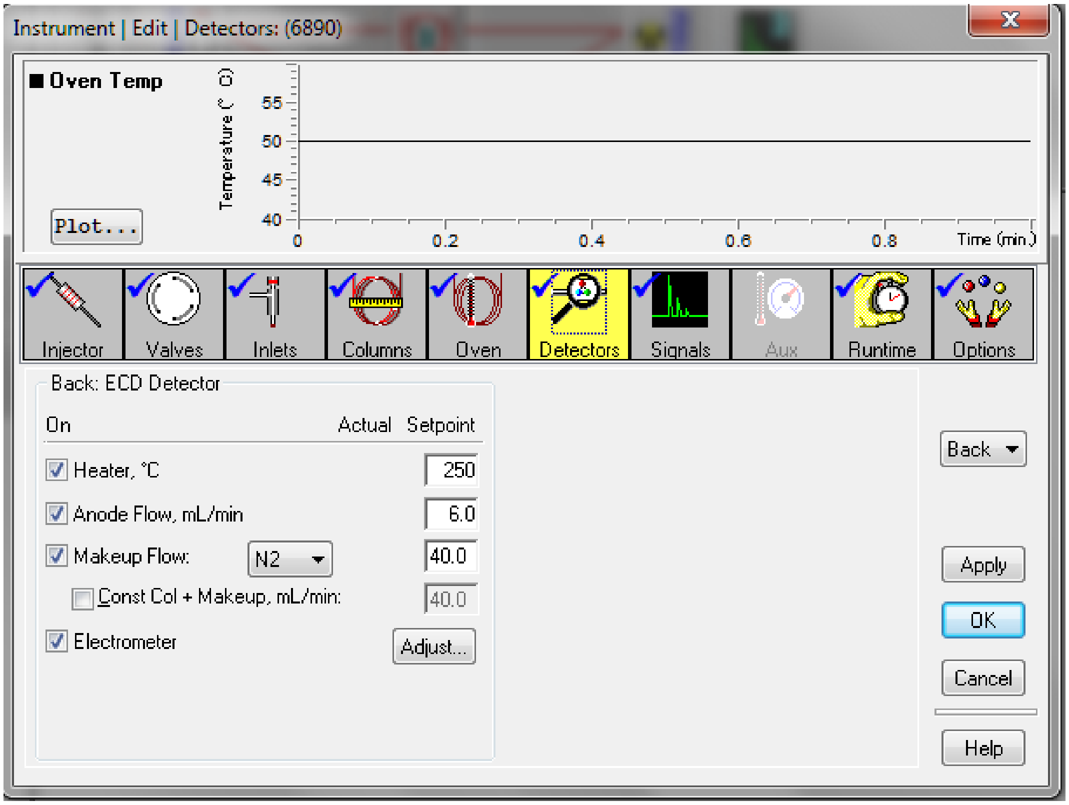
☐ Quick Cooling On

°C, Ambient

☐ Timeout Detection On

min

☐ Fault Detection On



Instrument | Edit | Detectors: (6890)

Back: ECD Detector

On Actual Setpoint

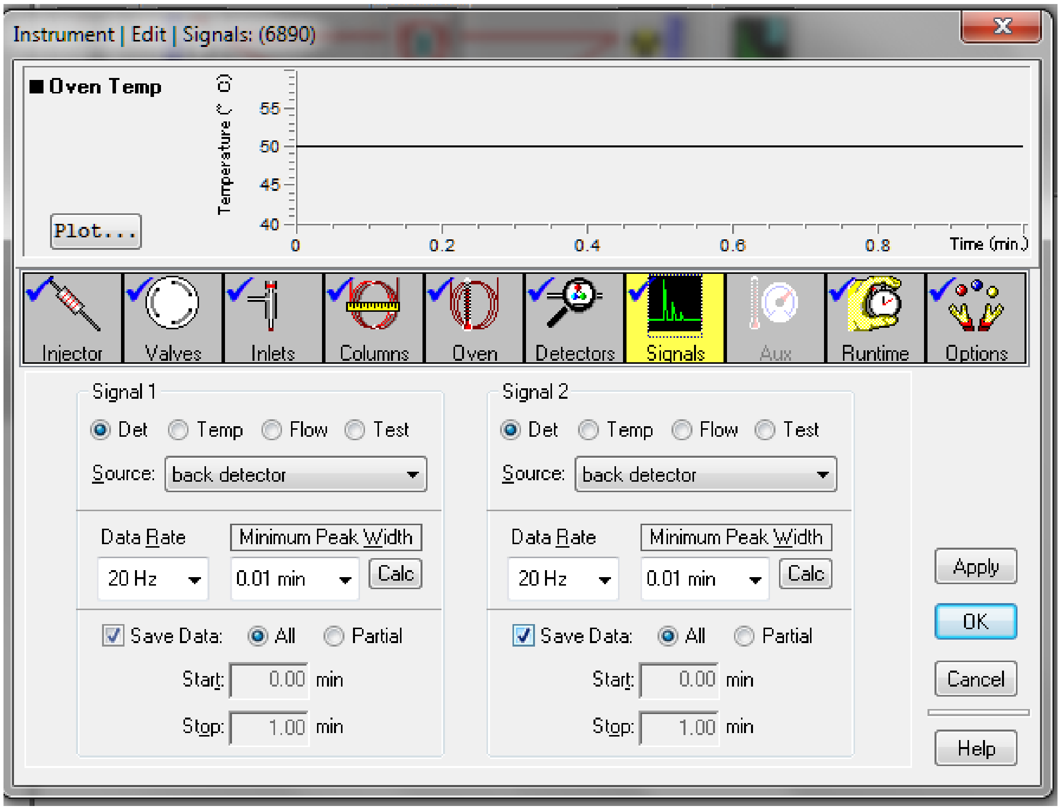
☑ Heater, °C 250

☑ Anode Flow, mL/min 6.0

☑ Makeup Flow: N2 40.0

☐ Const Col + Makeup, mL/min: 40.0

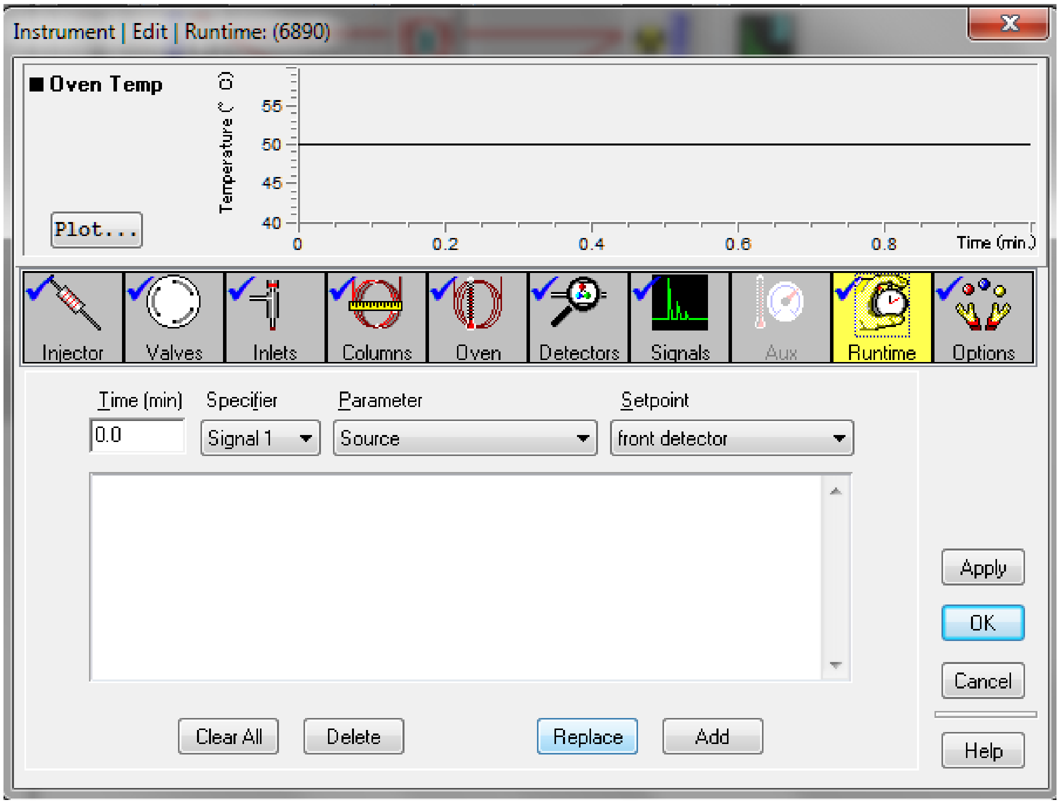
☑ Electrometer Adjust...



Instrument | Edit | Signals: (6890)

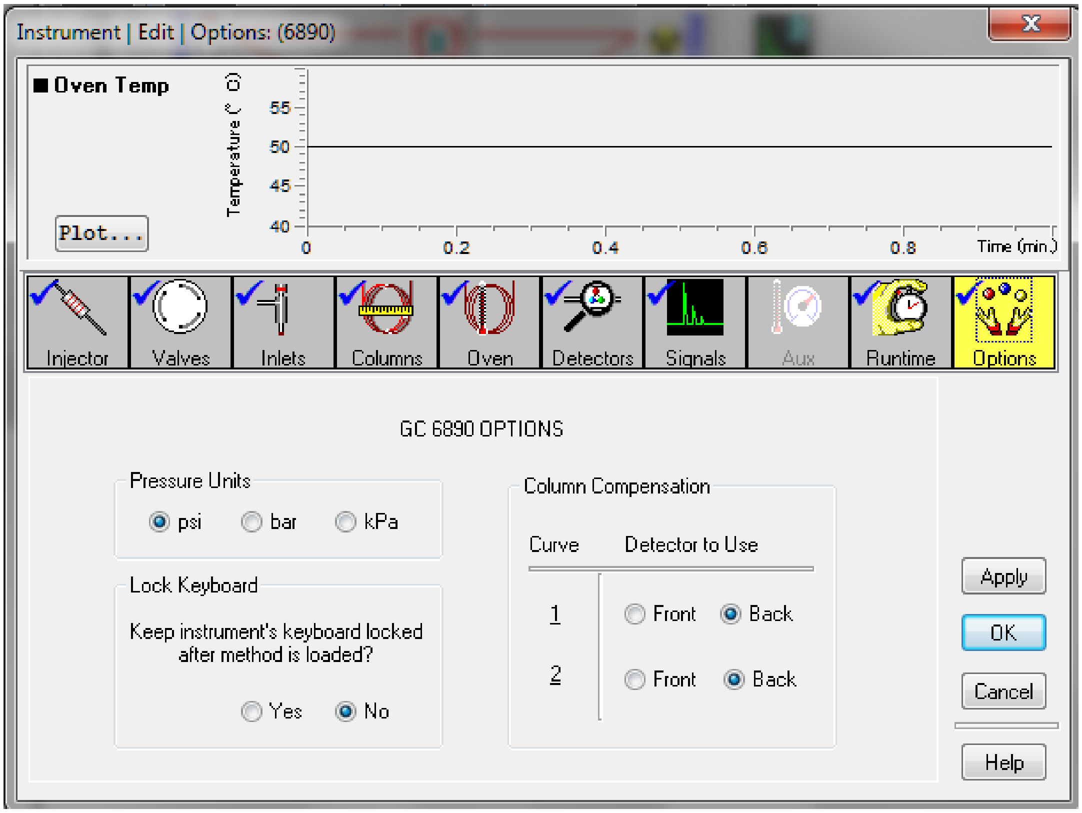
Signal 1
● Det ○ Temp ○ Flow ○ Test
Source: back detector
Data Rate: 20 Hz
Minimum Peak Width: 0.01 min
☑ Save Data: ● All ○ Partial
Start: 0.00 min
Stop: 1.00 min

Signal 2
● Det ○ Temp ○ Flow ○ Test
Source: back detector
Data Rate: 20 Hz
Minimum Peak Width: 0.01 min
☑ Save Data: ● All ○ Partial
Start: 0.00 min
Stop: 1.00 min



Instrument | Edit | Runtime: (6890)

Time (min)	Specifier	Parameter	Setpoint
0.0	Signal 1	Source	front detector



GC 6890 OPTIONS

Pressure Units

● psi ○ bar ○ kPa

Lock Keyboard

Keep instrument's keyboard locked after method is loaded?

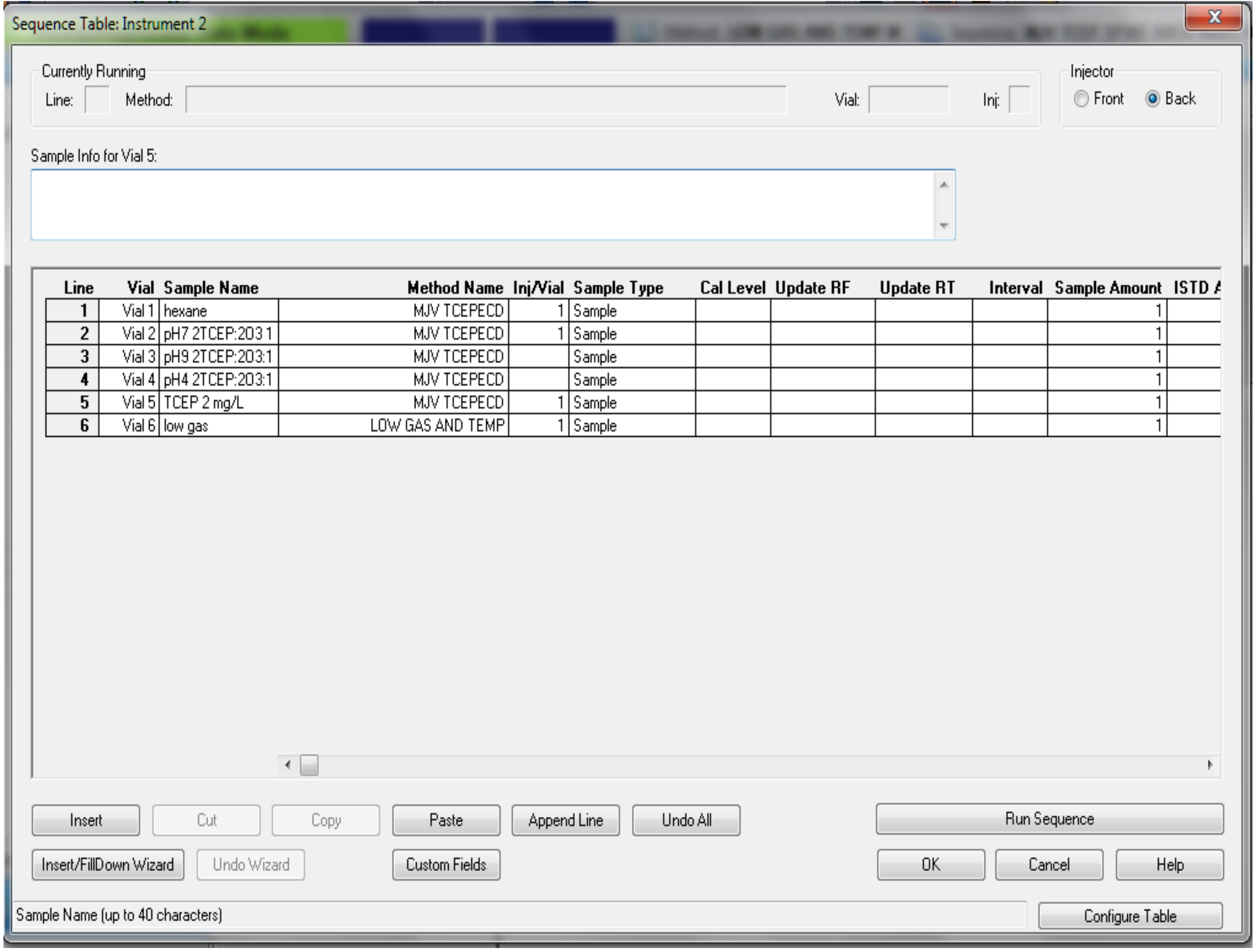
○ Yes ● No

Column Compensation

Curve	Detector to Use
1	○ Front ● Back
2	○ Front ● Back

Appendix C: GC Sequence Template

Sequence Name: MJV TCEP SPIKE BACK INJECTOR



Sample Info for Vial 5:

Line	Vial	Sample Name	Method Name	Inj/Vial	Sample Type	Cal Level	Update RF	Update RT	Interval	Sample Amount	ISTD
1	Vial 1	hexane	MJV TCEPECD	1	Sample					1	
2	Vial 2	pH7 2TCEP:203 1	MJV TCEPECD	1	Sample					1	
3	Vial 3	pH9 2TCEP:203:1	MJV TCEPECD		Sample					1	
4	Vial 4	pH4 2TCEP:203:1	MJV TCEPECD		Sample					1	
5	Vial 5	TCEP 2 mg/L	MJV TCEPECD	1	Sample					1	
6	Vial 6	low gas	LOW GAS AND TEMP	1	Sample					1	

Sample Name (up to 40 characters)

Appendix D: Standard Curve Data

TCEP Concentration		GC Peak Area (Hz*s)			
mg/L	µg/L	Run 1	Run 2	Run 3	Average
0	0	0	0	0	0.0
0.01	10	2.35	2.48	2.37	2.4
0.1	100	35.07	39.97	42.69	39.2
0.5	500	122.48	115.5	113.63	117.2
1	1000	232	240.5	235.19	235.9
5	5000	892.17	898.36	895.97	895.5
10	10000	2050.66	1975.32	2028.01	2018.0

All samples were adjusted to pH 7 prior to liquid/liquid Extraction.

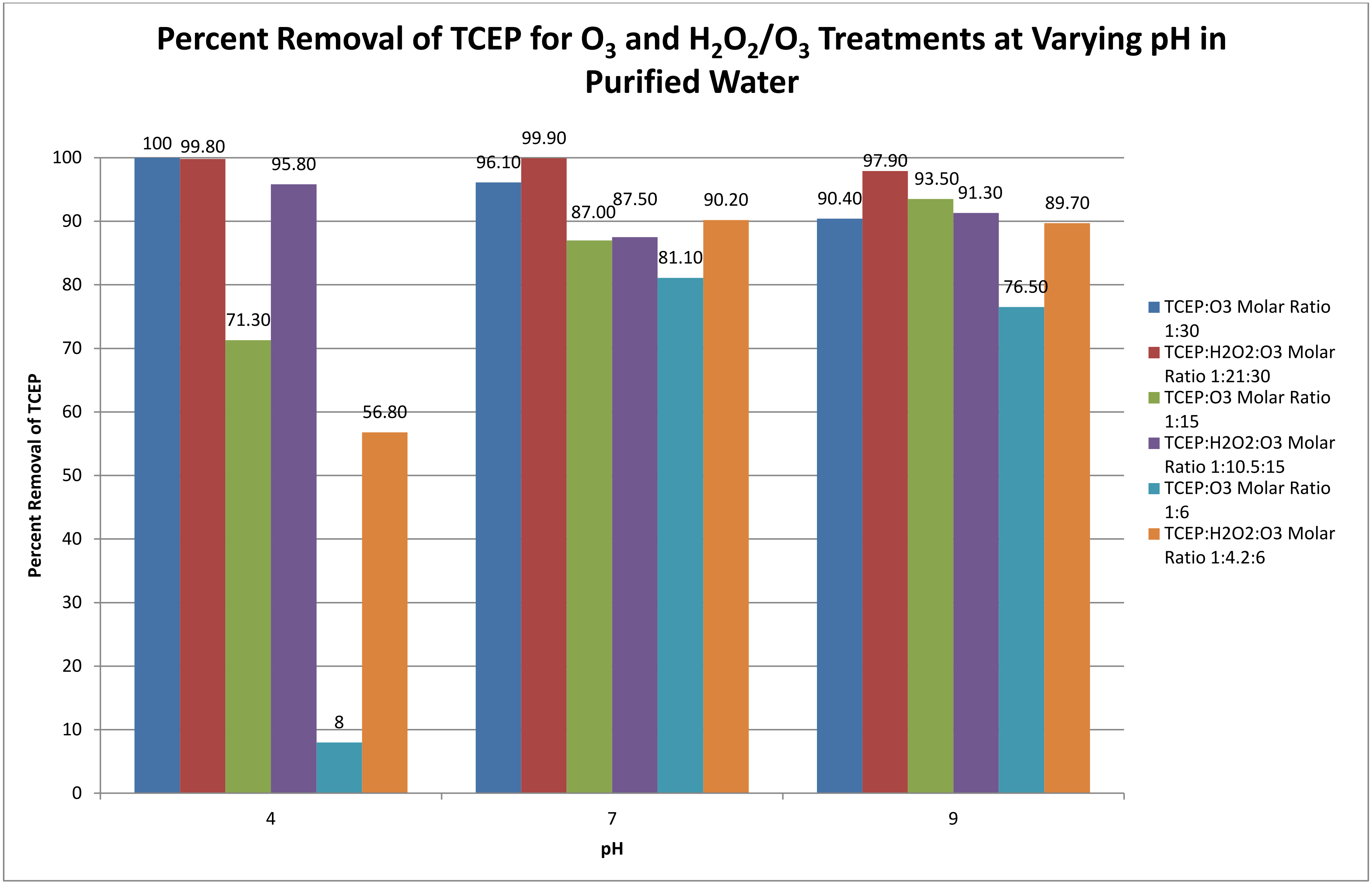
All peak retention times were ≈ 29 minutes

Appendix E: Gas Chromatography (GC) Experimental Molar Ratio Calculations

Molar Ratio Calculations

Compound Details		Mass Ratio; 2mg:5mg:10mg		Mass Ratio; 2mg:2.5mg:5mg		Mass Ratio; 2mg:1mg:2mg	
Compound	**MW (g)**	**g compound/MW of compound**	**Molar Ratio TCEP:H_2O_2:O_3**	**g compound/MW of compound**	**Molar Ratio TCEP:H_2O_2:O_3**	**g compound/MW of compound**	**Molar Ratio TCEP:H_2O_2:O_3**
TCEP	285.49	7.0055E-06	1	7.0055E-06	1	7.0055E-06	1
H_2O_2	34.0147	0.000146995	20.98283977	7.34976E-05	10.49141989	2.93991E-05	4.196567954
O_3	48	0.000208333	29.73854167	0.000104167	14.86927083	4.16667E-05	5.947708333

Appendix F: Gas Chromatography (GC) Experimental Results



Date of Runs: **4/1/2013-4/2/2013 and 4/26/2013** Molar Ratio O_3:H_2O_2:TCEP 30:0:1 or 30:21:1

Sample	pH	Starting Dose TCEP (mg/L)	O_3 Dose (mg/L)	H_2O_2 Dose (mg/L)	Peak Area	Conc TCEP (mg/L)	AVG Conc TCEP	Percent TCEP Removal
TCEP + O_3 + H_2O_2	4	2	10	5	7.092	0.009445093	0.004181974	99.8
					7.40149	0.011016348		
					6.14365	0.004630401		
					0	0		
					0	0		
					0	0		
TCEP + O_3	4	2	10	0	0	0	0	100.0
					0	0		
					0	0		
TCEP + O_3 + H_2O_2	7	2	10	5	6.06874	0.004250089	0.001045455	99.9
					5.63	0.002022643		
					3.69	0		
					0	0		
					0	0		
					0	0		
TCEP + O_3	7	2	10	0	34.3899	0.148034218	0.077530927	96.1
					36.3304	0.157885972		
					36.6021	0.15926537		
					0	0		
					0	0		
					0	0		
TCEP + O_3 + H_2O_2	9	2	10	5	14.2471	0.04577093	0.041482798	97.9
					13.1529	0.040215769		
					12.8074	0.038461695		
					14.2471	0.04577093		
					13.1529	0.040215769		
					12.8074	0.038461695		
TCEP + O_3	9	2	10	0	0	0	0.191407152	90.4
					0	0		
					0	0		
					81.8389	0.388928771		
					79.1974	0.375518099		
					80.8673	0.38399604		

Date of Runs: **4/11/2013-4/30/2013**

Molar Ratio O_3:H_2O_2:TCEP 15:0:1 or 15:10.5:1

Sample	pH	Starting Dose TCEP (mg/L)	O_3 Dose (mg/L)	H_2O_2 Dose (mg/L)	Peak Area	Conc TCEP (mg/L)	AVG Conc TCEP	Percent TCEP Removal
TCEP + O_3 + H_2O_2	4	2	5	2.5	0	0	0.083341753	95.8
					29.2396	0.121886582		
					26.8777	0.109895416		
					25.2408	0.101585013		
TCEP + O_3	4	2	5	0	92.257633	0.441823797	0.573469606	71.3
					125.886	0.612552165		
					126.913	0.617766157		
					127.695	0.621736305		
TCEP + O_3 + H_2O_2	7	2	5	2.5	119.143	0.578318526	0.250668376	87.5
					30.34	0.127473219		
					38.99	0.171388536		
					29.95	0.125493222		
TCEP + O_3	7	2	5	0	30.239767	0.126964343	0.260820514	87.0
					76.568	0.362168858		
					60.1959	0.279049094		
					59.418	0.275099761		
TCEP + O_3 + H_2O_2	9	2	5	2.5	141.819	0.693442656	0.173360664	91.3
					1.1907	0		
					1.12787	0		
					1.29453	0		
TCEP + O_3	9	2	5	0	84.1521	0.400672691	0.129635985	93.5
					11.6881	0.032779103		
					15.3273	0.051255013		
					11.8965	0.033837133		

Date of Runs: **4/14/2013-4/30/2013** Molar Ratio O_3:H_2O_2:TCEP 6:0:1 or 6:4.2:1

Sample	**pH**	**Starting Dose TCEP (mg/L)**	**O_3 Dose (mg/L)**	**H_2O_2 Dose (mg/L)**	**Peak Area**	**Conc TCEP (mg/L)**	**AVG Conc TCEP**	**Percent TCEP Removal**
TCEP + O_3 + H_2O_2	4	2	2	1	33.8204	0.145142915	0.864224247	56.8
					222.48	1.102951719		
					223.851	1.109912169		
					221.68	1.098890186		
TCEP + O_3	4	2	2	0	205.028	1.014349393	1.839327816	8.0
					423.331	2.122655227		
					407.432	2.041937351		
					434.305	2.178369295		
TCEP + O_3 + H_2O_2	7	2	2	1	149.77353	0.733827148	0.195189792	90.2
					9.4	0.021162614		
					7.5	0.011516475		
					8.039	0.014252932		
TCEP + O_3	7	2	2	0	229.677	1.139490278	0.377663223	81.1
					30.0633	0.126068437		
					29.3064	0.12222572		
					29.433	0.122868457		
TCEP + O_3 + H_2O_2	9	2	2	1	71.0016	0.333908717	0.206131771	89.7
					38.1562	0.167155404		
					37.9517	0.166117175		
					36.224	0.157345789		
TCEP + O_3	9	2	2	0	73.442933	0.34630316	0.469587416	76.5
					105.244	0.50775448		
					105.431	0.508703864		
					106.787	0.515588161		

Wastewater Trials

Date of Runs: **5/1/2013-5/5/2013**

Molar Ratio O_3:H_2O_2:TCEP 15:0:1 or 15:10.5:1

Water: Wastewater Volumetric Ratio	**pH**	**Starting Dose TCEP (mg/L)**	**O_3 Dose (mg/L)**	**H_2O_2 Dose (mg/L)**	**Peak Area**	**Conc TCEP (mg/L)**	**AVG Conc TCEP**	**Percent TCEP Removal**
1:1	7	2	5	2.5	404.887	2.029016602	2.048	0.0
					407.447	2.042013505		
					413.318	2.071820074		
1:1	7	2	5	0	397.348	1.990741737	1.981	0.9
					396.539	1.986634513		
					392.578	1.966524852		
2:1	7	2	5	2.5	190.651	0.941358583	0.949	52.5
					193.043	0.953502564		
					193.05	0.953538102		
2:1	7	2	5	0	265.675	1.322249073	1.325	33.7
					275.697	1.373129918		
					257.553	1.281014368		
4:1	7	2	5	2.5	81.7442	0.388447987	0.390	80.5
					83.3345	0.396521805		
					81.0045	0.384692593		
4:1	7	2	5	0	143.16	0.7002508	0.698	65.1
					147.227	0.720898614		
					138.022	0.674165609		
0:1	7	2	0	0	400.821	2.008373864	2.030	N/A
					412.859	2.06948977		
					401.83	2.013496472		
0:1	7	0	0	0	No Detect	0	0.000	N/A
					No Detect	0		
					No Detect	0		

Appendix G: Gas Chromatography (GC) Spiked TCEP Samples

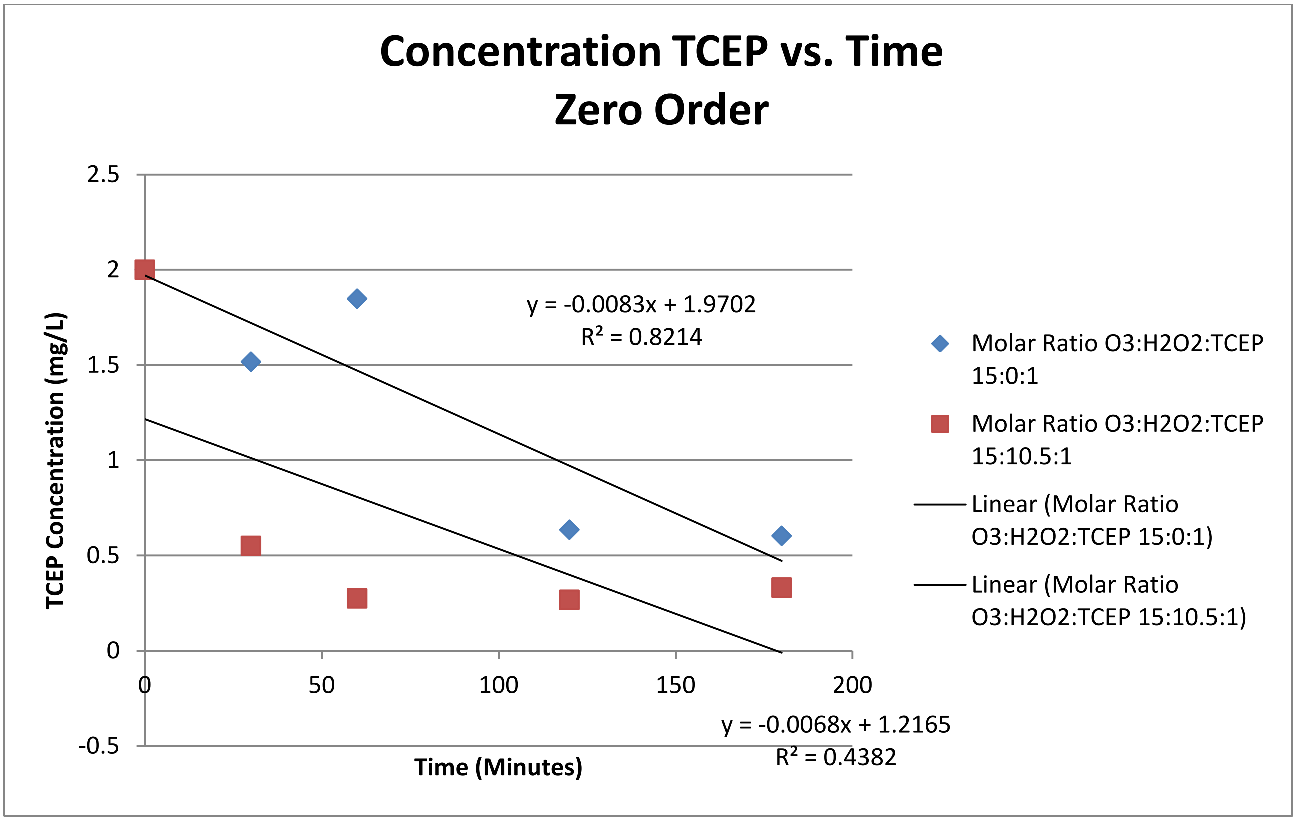
Date	Sample	pH	Peak Area	Concentration of TCEP (mg/L)	Percent error
4/1/2013	TCEP Spike 2 mg/L	7	416.984	2.09	4.33
4/1/2013	TCEP Spike 2 mg/L	7	402.764	2.02	0.90
4/2/2013	TCEP Spike 2 mg/L	7	399.865	2.00	0.18
4/11/2013	TCEP Spike 2 mg/L	7	403.299	2.02	1.04
4/12/2013	TCEP Spike 2 mg/L	7	399.271	2.00	0.03
4/14/2013	TCEP Spike 2 mg/L	7	408.845	2.05	2.40
4/15/2013	TCEP Spike 2 mg/L	7	401.563	2.01	0.60
4/16/2013	TCEP Spike 2 mg/L	7	398.567	2.00	0.15
4/25/2013	TCEP Spike 2 mg/L	7	399.202	2.00	0.01
4/30/2013	TCEP Spike 2 mg/L	7	402.781	2.02	0.91
5/1/2013	TCEP Spike 2 mg/L	7	395.446	1.98	0.95
5/3/2013	TCEP Spike 2 mg/L	7	414.181	2.08	3.67
5/5/2013	TCEP Spike 2 mg/L	7	398.057	1.99	0.28
5/8/2013	TCEP Spike 2 mg/L	7	400.476	2.08	0.33
5/10/2013	TCEP Spike 2 mg/L	7	404.038	1.99	1.22

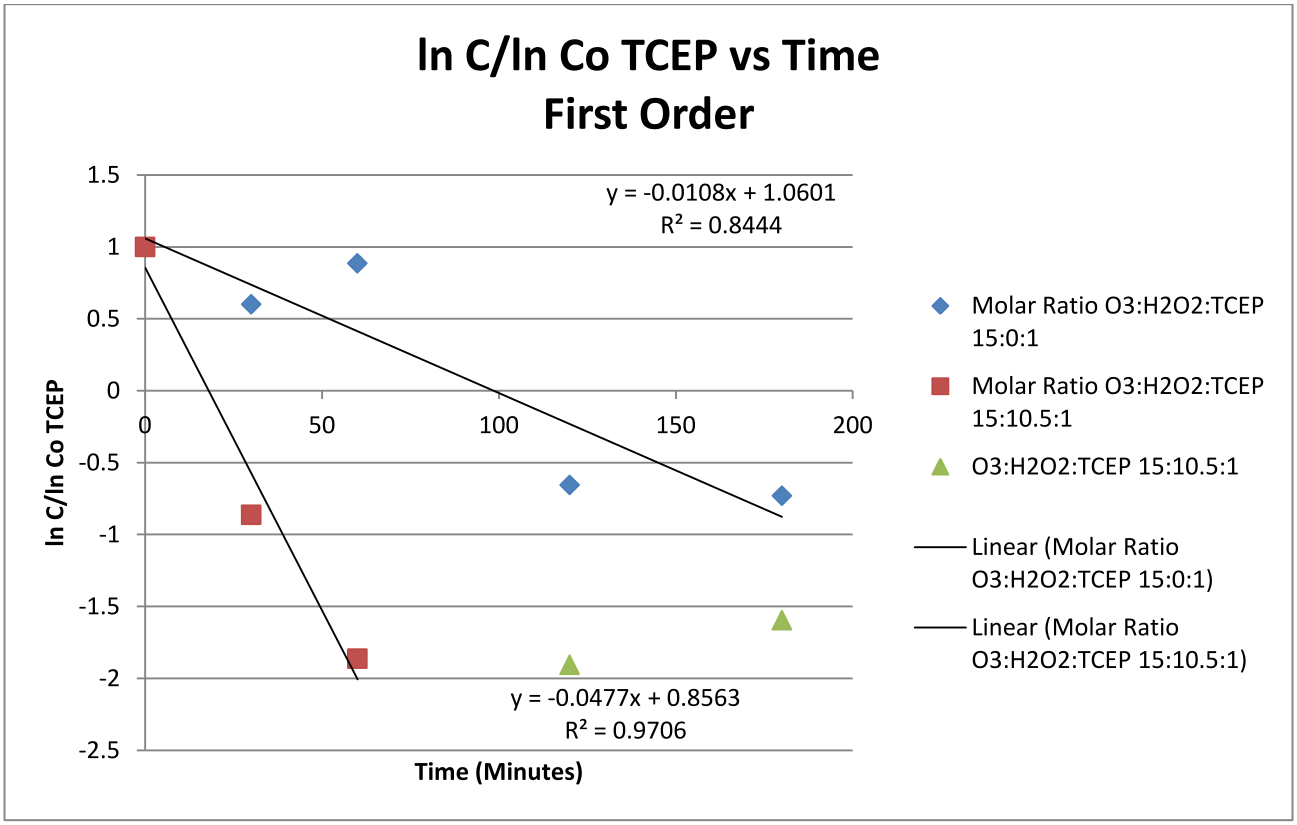
The spiked samples were run to ensure that the GC was running properly. Spikes were at the beginning and end of each set of experimental runs. The data shows that the GC analyses of spiked samples were accurate. This shows that the GC was giving consistent readings of TCEP samples.

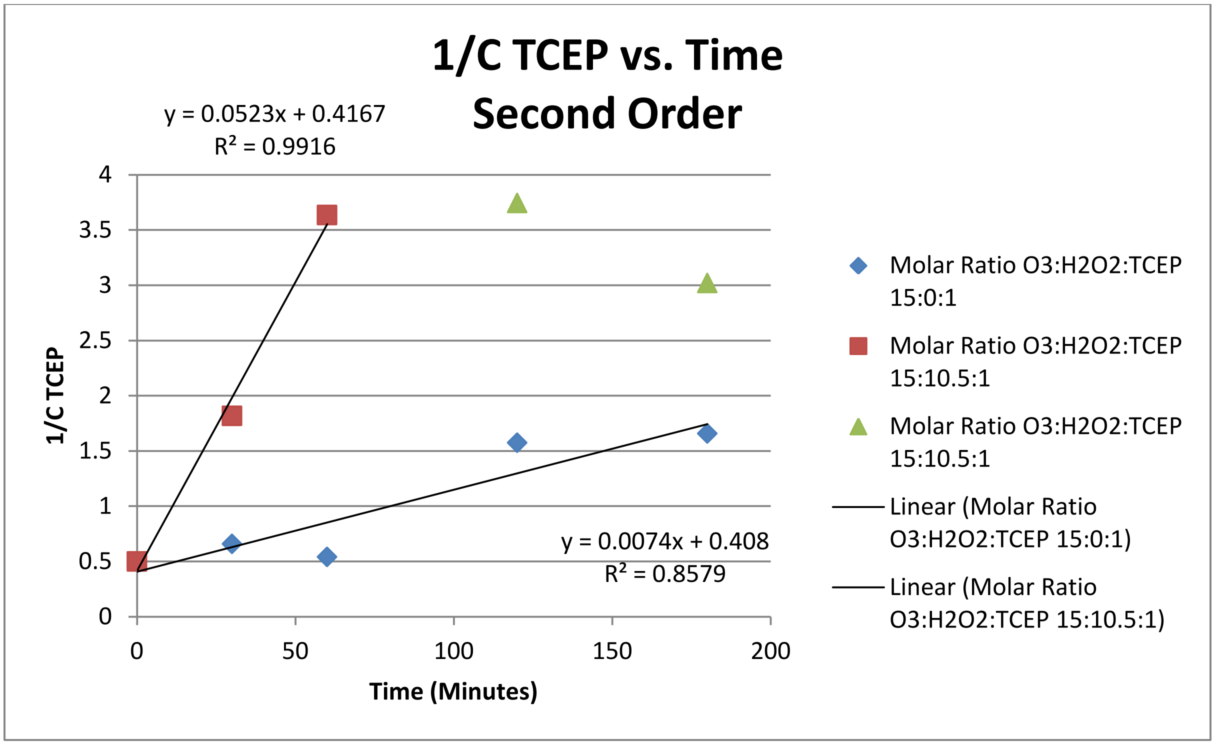
Appendix H: Kinetics Data and Analysis

Date of Runs:	**5/9/2013-5/10/2013**	Molar Ratio O_3:H_2O_2:TCEP	15:0:1 or 15:10.5:1

Reaction Time (min)	pH	Starting Dose TCEP (mg/L)	O_3 Dose (mg/L)	H_2O_2 Dose (mg/L)	Peak Area	Conc TCEP	Percent TCEP Removal
0	7	2	5	0 and 2.5	0	2.000	NA
30	7	2	5	2.5	113.609	0.550	72.5
30	7	2	5	0	304.0466667	1.517	24.1
60	7	2	5	2.5	59.3022	0.275	86.3
60	7	2	5	0	369.2653333	1.848	7.6
120	7	2	5	2.5	57.8143	0.267	86.7
120	7	2	5	0	130.2433333	0.635	68.3
180	7	2	5	2.5	70.42953333	0.331	83.4
180	7	2	5	0	123.9643333	0.603	69.9


Concentration TCEP vs. Time
Zero Order
TCEP Concentration (mg/L)
2.5
2
1.5
1
0.5
0
-0.5
0
50
100
150
200
Time (Minutes)
y = -0.0083x + 1.9702
R² = 0.8214
y = -0.0068x + 1.2165
R² = 0.4382
Molar Ratio O3:H2O2:TCEP 15:0:1
Molar Ratio O3:H2O2:TCEP 15:10.5:1
Linear (Molar Ratio O3:H2O2:TCEP 15:0:1)
Linear (Molar Ratio O3:H2O2:TCEP 15:10.5:1)


ln C/ln Co TCEP vs Time
First Order
ln C/ln Co TCEP
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
0
50
100
150
200
Time (Minutes)
y = -0.0108x + 1.0601
R² = 0.8444
y = -0.0477x + 0.8563
R² = 0.9706
Molar Ratio O3:H2O2:TCEP 15:0:1
Molar Ratio O3:H2O2:TCEP 15:10.5:1
O3:H2O2:TCEP 15:10.5:1
Linear (Molar Ratio O3:H2O2:TCEP 15:0:1)
Linear (Molar Ratio O3:H2O2:TCEP 15:10.5:1)


1/C TCEP vs. Time
Second Order
y = 0.0523x + 0.4167
R² = 0.9916
y = 0.0074x + 0.408
R² = 0.8579
1/C TCEP
Time (Minutes)
0
0.5
1
1.5
2
2.5
3
3.5
4
0
50
100
150
200
Molar Ratio O3:H2O2:TCEP 15:0:1
Molar Ratio O3:H2O2:TCEP 15:10.5:1
Molar Ratio O3:H2O2:TCEP 15:10.5:1
Linear (Molar Ratio O3:H2O2:TCEP 15:0:1)
Linear (Molar Ratio O3:H2O2:TCEP 15:10.5:1)