



Wet air oxidation of sediments contaminated with polychlorinated biphenyls (PCBs)  
by Justin Michael Ray

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
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**Abstract:**

Wet air oxidation is a process that utilizes the dissolved oxygen in water with elevated temperatures and pressures to oxidize most organic compounds to carbon dioxide, water, and low-molecular weight acids. This process is thought to occur via a generally accepted radical chain mechanism initiated by thermally induced reactions between oxygen and the organic substrate. Wet air oxidation could be a very attractive process for the remediation of sediments contaminated with polychlorinated biphenyls (PCBs). Thus far, only partial degradation of PCBs has been attained with conventional WAO. PCBs probably do not react directly with oxygen at the conditions of conventional WAO, but are known to react with active radical species, specifically hydroxyl radicals, which have been generated in other oxidation technologies. Additions of catalysts, hydrogen peroxide, or easily oxidizable organic matter have enhanced wet air oxidation rates of some compounds recalcitrant to oxidation through different contributions to the radical chain mechanism. Experiments applying these enhancements to a batch wet air oxidation system were conducted and the effects observed to gain insight into the governing factor(s) for WAO of PCBs on sediments.

A high pressure, temperature controlled reactor with connections for pressurization, pressure measurement, temperature measurement, and chemical addition was used to wet oxidize sediment/water slurries contaminated with known quantities of PCBs. Congener specific analysis of remaining PCBs in sediment, water, and vapor phases and on reactor surfaces was performed after each experiment using gas chromatography with electron capture detection.

Results of these experiments indicate that oxidation of organic matter naturally associated with sediments is not the source of radical species causing PCB degradation by wet air oxidation. In addition, solution phase radical species do not appear to react with PCBs sorbed to sediments. Surfaces of either sediment particles or the reactor may be catalyzing the reaction. The contribution of pH is probably significant.

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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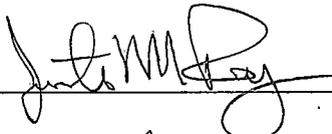
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## ABSTRACT

Wet air oxidation is a process that utilizes the dissolved oxygen in water with elevated temperatures and pressures to oxidize most organic compounds to carbon dioxide, water, and low-molecular weight acids. This process is thought to occur via a generally accepted radical chain mechanism initiated by thermally induced reactions between oxygen and the organic substrate. Wet air oxidation could be a very attractive process for the remediation of sediments contaminated with polychlorinated biphenyls (PCBs). Thus far, only partial degradation of PCBs has been attained with conventional WAO. PCBs probably do not react directly with oxygen at the conditions of conventional WAO, but are known to react with active radical species, specifically hydroxyl radicals, which have been generated in other oxidation technologies. Additions of catalysts, hydrogen peroxide, or easily oxidizable organic matter have enhanced wet air oxidation rates of some compounds recalcitrant to oxidation through different contributions to the radical chain mechanism. Experiments applying these enhancements to a batch wet air oxidation system were conducted and the effects observed to gain insight into the governing factor(s) for WAO of PCBs on sediments.

A high pressure, temperature controlled reactor with connections for pressurization, pressure measurement, temperature measurement, and chemical addition was used to wet oxidize sediment/water slurries contaminated with known quantities of PCBs. Congener specific analysis of remaining PCBs in sediment, water, and vapor phases and on reactor surfaces was performed after each experiment using gas chromatography with electron capture detection.

Results of these experiments indicate that oxidation of organic matter naturally associated with sediments is not the source of radical species causing PCB degradation by wet air oxidation. In addition, solution phase radical species do not appear to react with PCBs sorbed to sediments. Surfaces of either sediment particles or the reactor may be catalyzing the reaction. The contribution of pH is probably significant.

## CHAPTER ONE

## INTRODUCTION

Banned from production in 1976, polychlorinated biphenyls (PCBs) have proven to be one of the most persistent and widespread environmental contaminants to date. The inertness, fire resistance, and thermal stability of PCBs made them highly attractive for use as hydraulic and heat transfer fluids. PCBs also found use in lubricants, waterproofing coatings, inks, plasticizers, and adhesives (1). Appreciable quantities of PCBs have been discovered in nearly every component of the global ecosystem including soil, water, air, foodstuffs, and human adipose tissue (2). River, lake, and marine sediment contamination pose a special problem in that these media provide a link to the human food chain through the contamination of aquatic organisms. Extremely slow metabolism of PCBs results in bioaccumulation that when carried up the food chain can cause consumption of large quantities by humans (3,4,5). PCBs have been implicated in causing liver, thyroid, dermal and ocular changes, immunological alterations, reduced birth weight, reproductive toxicity, and cancer (6). The probability is good that PCBs hinder neurobiological development in children (7).

There are no efficient, cost effective technologies for removal of PCBs from sediments. Combustion in special incinerators with long residence times was the only method specifically approved when the regulations for disposal of PCBs were outlined in promulgation of the Toxic Substances Control Act. However, incineration is not cost effective for sediments that are laden with moisture. Other methods include vitrification,

solvent extraction, thermal desorption, and landfilling. All of these alternatives have drawbacks when applied to sediments. Wet air oxidation (WAO), a process used to remediate aqueous waste streams containing organic compounds, might avoid these disadvantages.

Wet air oxidation systems utilize dissolved oxygen in water at elevated temperatures and pressures to oxidize most organic compounds to carbon dioxide, water, and low-molecular weight acids. Temperatures ranging from 150-325°C and pressures ranging from 300-3000 psi are commonly used (8,9). Wet oxidation has been referred to as "flameless combustion" and "underwater incineration".

Unfortunately, while WAO satisfactorily degrades most organics including polyaromatic hydrocarbons (PAHs), it is less successful with organic compounds consisting of halogenated benzene rings lacking other functional groups like PCBs (10). A bench-scale treatability study was conducted using Zimpro's Wet Air Oxidation Process on contaminated sediments from the Grand Calumet River containing PAHs and PCBs (11). The process effectively treated the sediment for PAHs by removing nearly 99% of the contaminant. However, the treatment efficiency for PCBs was much lower, removing only 29%.

Enhancement of conventional wet air oxidation technology with respect to PCBs would increase its viability. The capability of treating such a common and enduring environmental contaminant would add to the attractiveness of a technology that has many advantages over alternative treatment methods. If the causes of the partial removal of PCBs in conventional wet air oxidation were understood, these factors could presumably

be manipulated to achieve more extensive or even complete oxidation of PCBs. This requires an analysis of some of the elemental principles of wet air oxidation.

The most widely accepted theoretical mechanism for WAO consists of a series of reactions involving radicals, which is based on a mechanism proposed by Emanuel et al. (12). Triggered by thermal energy, oxygen reacts with the weakest C-H or O-H bond of organic compounds present to abstract hydrogen and generate an organic radical. This organic radical propagates the radical chain sequence by reacting with other organic molecules to generate peroxy radical species that eventually decompose to form hydroxyl radicals.

Hydroxyl radicals are extremely powerful oxidizers and will react with most organics, PCBs included, at rates that are very close to being diffusion limited (13). A review of the literature indicates that dissolved PCB molecules do not react directly with oxygen at an appreciable rate at temperatures utilized for conventional wet air oxidation. In the heterogeneous sediment/water system, the partial removal of PCBs may be the result of reactions with hydroxyl radicals produced in side reactions of organic matter (OM) naturally associated with the sediment or the result of reactions catalyzed by the sediment surfaces.

This thesis attempts to determine the role played by OM and sediment surfaces in PCB destruction and explores possibilities for enhancement of PCB oxidation rates.

## General Hypothesis

The destruction of PCBs from sediment is dependant on the generation of radical species, specifically hydroxyl radicals, either in solution or at the sediment/water interface.

### Hypothesis One

Destruction of PCBs occurs in the dissolved state. Both organic matter (OM) and PCBs desorb from the sediment surface at the elevated temperature. Active radical species generated in solution during the oxidation of OM indiscriminately react with both OM and PCBs leading to partial removal of PCBs.

### Hypothesis Two

Destruction of PCBs occurs in the sorbed state. Active radical species produced at the sediment/water interface during the oxidation of sorbed organic matter result in partial removal of PCBs.

### Hypothesis Three

Sediment surfaces may directly catalyze PCB oxidation via hydrogen abstraction or indirectly catalyze destruction via generation of active radical species.

This thesis has been formatted to provide a literature review in Chapter 2 summarizing a variety of background issues pertinent to PCBs, wet air oxidation, and issues surrounding remediation of PCB contaminated sediment with WAO. Chapters 3 and 4 are a treatment of the research endeavor in the form of a professional publication covering experimental methods, results, and discussion. Conclusions, an overview of work completed, and suggestions for future research are included in Chapter 5. All supporting material, including detailed experimental methods and data tables are located in the Appendices.

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## CHAPTER TWO

## LITERATURE REVIEW

Description of PCBs

Polychlorinated biphenyls (PCBs) are a group of 209 different chemicals that differ from each other in the number and arrangement of chlorines attached to two aromatic rings. Groups of PCBs that have the same number of chlorines attached are homologues. Differences in positions of chlorine constituents separate congeners. A typical congener is shown in Figure 1. The congeners are identified by a system delineated in 1980 by Ballschmiter and Zell whereby congeners are numbered in order of increasing chlorine constituent numbers (1). For this reason, the congener numbers are often referred to as BZ numbers. After slight revision by Schulte and Malisch (2), the system currently conforms to the IUPAC (International Union of Pure and Applied Chemistry) naming system.

PCBs were first produced commercially in 1929 to fulfill a need in the electrical industry for an improved dielectric fluid to replace mineral oil in transformers and capacitors. Inertness, fire resistance, and thermal stability made PCBs highly attractive for use as hydraulic and heat transfer fluids. PCBs were also used in lubricants, waterproofing coatings, inks, plasticizers, and adhesives (3).

Typically, PCBs were manufactured by reacting chlorine gas with molten biphenyl. With this method, chlorination of the rings is governed thermodynamically,

giving rise to preferential chlorination patterns and congener concentrations. Mixtures of PCBs were sold under the tradenames Aroclor, Clophen, Fenclor, and Kanechlor. The Aroclor mixtures accounted for almost all of the PCBs distributed in the United States. A four-digit number identifies an Aroclor mixture, where the first two digits (usually 12) refer to the 12 carbons in a PCB molecule and the second two digits indicate the approximate percentage of chlorine by weight in the mixture. For example, Aroclor 1242 would be a mixture of different congeners that consists of approximately 42% chlorine. The exception is Aroclor 1016, which has a 41% chlorine content.

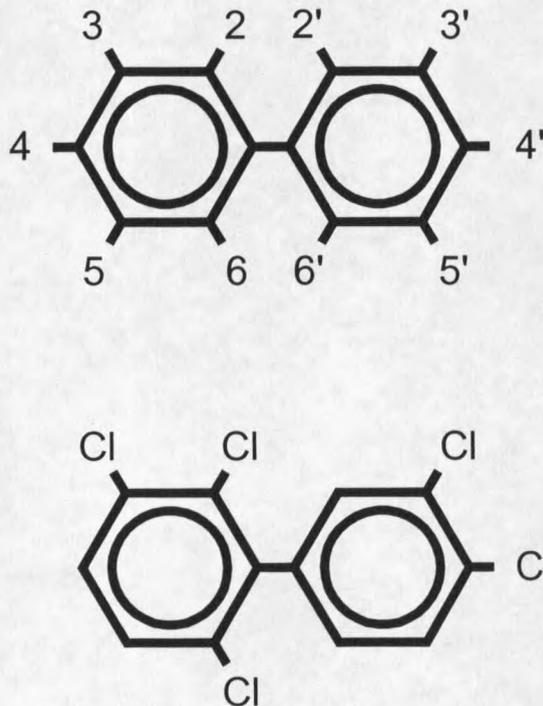


Figure 1. Example of PCB congener.  
Chlorine substitution positions and numbering are shown at top.  
Congener #110 – 2,3,3',4',6-pentachlorobiphenyl is shown at bottom.

### Environmental Issues

The first indication that PCBs were a potential environmental problem occurred in the late 1960s when interference peaks in DDT analysis of fish were identified as PCBs (4). Evidence began quickly mounting that PCBs were accumulating in the environment. As there are no known natural sources of PCBs, all environmental occurrences are considered to be caused by man. Federal legislation passed in 1976 (Toxic Substances Control Act) restricting the use and application of PCBs resulted in the termination of production in the United States (5). Promulgation of TSCA resulted in discontinuance of use and directions for handling and disposal (6,7).

Unfortunately, by the time production ceased numerous sites had been contaminated with PCBs. It is estimated that over 1.5 million pounds of PCBs have been released into the environment (8). Large amounts have been discarded in landfills as components of products or equipment that contained PCBs. Partial volatility at ambient temperatures provides transport through the air. Redistribution can occur in rain or through dry deposition (9). Detectable quantities of PCBs (parts per billion) have been discovered in nearly every component of the global ecosystem including soil, water, air, foodstuffs, and human adipose tissue (10,11). The average person is contaminated with approximately 1 milligram of PCBs per kilogram of fatty tissue. Of special concern are sites with high PCB concentration where spilling or dumping occurred. The scale of the problem is growing as additional contaminated sites are continually discovered. In 1989, 216 of 1177 hazardous waste sites on the National Priorities List indicated PCB contamination. By 1999, this number had grown to 500 of 1598 sites.

Sediment containing PCBs can contaminate aquatic organisms, which can be subsequently consumed by humans. Fish and shellfish are a major source of PCB contamination in the diet of humans (12). As metabolism of PCBs is exceedingly slow in mammals, bioaccumulation is inevitable (13,14). This accumulation causes a magnification up the food chain (15). For instance, consuming contaminated fish also means consuming any PCBs that have accumulated over the lifetime of the fish.

### Health Risks

There have been few well-documented cases of human contamination at high enough concentrations to cause acute effects. However, of greater importance are the effects of long-term low-level exposure. Some information on health effects of PCBs in humans is available from studies of people exposed occupationally, by consumption of contaminated fish and other food products of animal origin, and via general environmental exposures. There are large differences in toxicity of congeners with twelve of the 209 congeners considered to be "very toxic" (16). These are the "coplanar" or flat congeners with chlorine substitution at the meta- and para- positions that have a similarity in structure to 2,3,7,8-tetrachlorodibenzo-p-dioxin, a highly toxic substance. From animal studies, generally with rats and Rhesus monkeys, PCBs are reasonably anticipated to be a human carcinogen (17,18). Contamination affects the body in several areas (19). PCBs have been implicated in altering thyroid, hepatic, and digestive systems and their enzymatic production. Inhibitions of the immunological system have been

reported as caused by PCBs. Changes in eyes, skin, and liver have been assigned to PCBs. Reduced birth weight and gestational times have been noted in women with higher than average PCB concentrations in their body. Evidence is also growing that PCBs hinder neurobiological development in children especially if present in the mother during times of gestation and breastfeeding (20).

### Current Treatment Methods

A need exists for an effective, economically feasible means of removing PCBs from sediment. Alternative treatment methods include landfilling, incineration, solvent extraction, thermal desorption, and vitrification (21). Landfilling is not considered to be a permanent solution and may be additionally curtailed as a temporary solution by leaching to groundwater and loss of PCBs by volatilization (22). PCBs can be destroyed by combustion at temperatures in excess of 1100°C using incinerators with long residence times. Incineration and thermal desorption are expensive for sediment high in moisture content and incineration has the added disadvantage of being perceived by the public as a technology that emits toxins and dust to the air. Solvent extraction produces an organic PCB laden solvent that must still be treated. Vitrification is a process that does not destroy contaminants, but utilizes electric currents to melt soils in place, in effect immobilizing them. This technology produces off-gases that must be treated and is not generally applicable to sediments in river and lake bottoms. Several aerobic and anaerobic biological processes are currently being studied. This technology generally

suffers from extended treatment timescales that may not be ideal and it has been most effective only on the least chlorinated congeners. Modification of a process in use with other organic contaminants, wet air oxidation (WAO), may be a solution that avoids the problematic issues of other methods.

### Conventional Wet Air Oxidation

Wet air oxidation systems utilize the dissolved oxygen in water at elevated temperatures and pressures to oxidize most organic compounds to carbon dioxide, water, and low-molecular weight acids. WAO systems are enclosed and have a very low interaction with the environment. Temperature ranges from 150-325°C and pressures from 300-3000 psi are commonly used (23,24,25,26). The high temperatures are necessary to initiate thermal reactions between oxygen and organics. High pressure facilitates oxygen transfer and ensures the presence of an aqueous phase, as virtually zero oxidation will occur in the vapor phase (27). Wet oxidation has been referred to as "flameless combustion" and "underwater incineration". If chemical oxygen demand (COD) is high enough, the process can be autothermal and excess energy can be recovered.

Wet air oxidation (WAO) was originally developed for recovering vanillin from spent pulping liquors (28,29,30). Subsequently, the process was applied as a method of conditioning municipal sewage sludge (31,32,33,34,35) and regeneration of activated carbon catalysts (36,37). The process is increasingly being applied to the removal of

organic compounds from aqueous waste streams that may be either too dilute for incineration or too concentrated for biological treatment (38,39).

### Mechanism

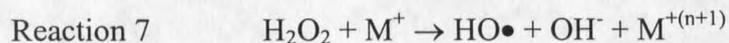
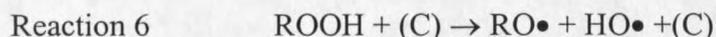
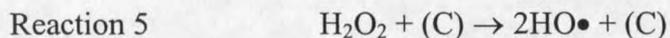
The most widely accepted theoretical mechanism for WAO consists of a series of reactions involving radicals. Based on the mechanism proposed by Emanuel et al. (40), a general form of the mechanism has been elucidated over the years. Day et. al. suggested that high conversion of propionic acid to carbon dioxide was indicative of a free radical oxidation (41). Hydrogen abstraction as a propagating step was proposed by Imamura et. al. in the oxidation of water-soluble polymers (42). After an exhaustive study of reaction intermediates and carbon dioxide formation, Devlin and Harris put forward a complete reaction pathway for phenol that allowed for decarboxylation to carbon dioxide from the beginning of the reaction to completion (43). Nikolaou further clarified the model in experiments with valeric acid (44). Finally, a general model was developed by Li et. al. that can be applied to a variety of organic molecules (45).

Triggered by thermal energy, oxygen reacts with the weakest C-H or O-H bond of organic compounds present to abstract hydrogen in the initiation step. This step could also involve reactions with carbon/carbon double bonds. For oxidation of single organic compounds, this step is rate-limiting. The resulting free radical reacts with O<sub>2</sub> to form peroxy radicals that can further abstract hydrogen from additional organic molecules to

form new peroxy radicals, or abstract hydrogen from  $-\text{COOH}$  groups to produce  $\text{CO}_2$  after decarboxylation.



Hydrogen peroxide and organic hydroperoxides generated in the above reactions can decompose at high temperatures by the following reactions to produce hydroxyl radicals.



The collision partner (C) in Reaction 5 and Reaction 6 could be water molecules, sediment in the reactor, or the walls of the reactor (46,47). The relative importance of homogenous reactions with water molecules compared with heterogeneous reactions on surfaces depends on the ratio of surface area to fluid volume, the chemical and physical characteristics of the sediment and reactor, and the temperature. The metal denoted by  $\text{M}^+$  in Reaction 7 is a transition metal such as iron, copper, chromium, and cobalt. A

Fenton's reagent reaction using hydrogen peroxide and ferrous iron is a commonly known example of this type of reaction. The addition of homogenous catalysts may also function in this fashion to enhance degradation of organic contaminants.

Hydroxyl radicals are extremely vigorous oxidizers, the strongest oxidants of the oxy-radical family, surpassed in oxidative power only by the fluorine radical (48). The rate of reactions between hydroxyl radicals and most organics, including PCBs, are reported to be close to being diffusion limited (49). Peroxyl radicals, while not as oxidative as hydroxyl radicals, probably contribute to much of the oxidative degradation of organic matter in WAO (50,51).

### Methods to Enhance WAO Rates

#### Temperature

Supply of energy and oxygen are important aspects of WAO. Small variations of the partial pressure of oxygen have almost no effect when oxygen is supplied in 3-4 times theoretical oxygen demand. Therefore, temperature is the key factor controlling the reaction rate (52). Reaction rates and temperature are linked in a typical Arrhenius relationship whereby an increase in temperature produces a corresponding increase in reaction rate of the initial, rate-limiting reaction of the organic molecule with oxygen (Reaction 1).

### Hydrogen Peroxide Addition

Wet peroxide oxidation (WPO) is performed by the addition of hydrogen peroxide to a wet air oxidation system either in place of oxygen as the oxidizing agent or combined with oxygen as a free radical initiator (53). At elevated temperatures, hydrogen peroxide instantaneously decomposes into hydroxyl radicals. Addition of hydrogen peroxide increases the concentration of reactant in Reaction 5. This serves to greatly increase the population of strongly oxidizing hydroxyl radicals within the reactor. Temperatures typically are lower than that of conventional wet air oxidation and as a result will offer a substantial reduction in capital expenditures. However, hydrogen peroxide tends to be quite costly and therefore increases operational costs. WPO has been shown to be effective in the treatment of PCBs sorbed to sediment (54). Removal efficiencies can be very high depending on the amount of hydrogen peroxide added. Careful consideration of total cost must occur before application of hydrogen peroxide to WAO.

### Catalyst Addition

Application of heterogeneous and homogeneous catalysts to the WAO has been attempted. Both have been found to be effective. Obviously, in a thermal process such as WAO, similar results from milder conditions or better results in similar conditions would prove to be quite valuable in reducing capital and operating costs. While metal ions will act to form radical species from peroxides (Reaction 7), this does not provide the rate enhancing function, since these radicals are easily decomposed by severe reaction conditions and by collisions with the reactor and sediment surfaces. Instead, catalysts

















































































































































