THE EVALUATION OF OZONE TECHNOLOGY TO REDUCE THE CONCENTRATION OF POLYCHLORINATED BIPHENYLS (PCBs) IN CONTAMINATED SOIL

By

Shanita Jeewan Moodley

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Supervisor: Professor Milan Carsky

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ABSTRACT

Polychlorinated Biphenyls (PCBs) are hazardous and toxic chemicals to both humans and animals. In the late 1960's PCBs were discovered to be a harmful pollutant which could cause environmental contamination due to its slow degradation and even trace amounts of PCBs were regarded as toxic to both human and animals.

Oil spills are a frequent occurrence at Eskom substations which could contain PCBs. The contaminated sediments which are easily carried away by rain and wind can further contaminate the environment and aquatic bodies. Eskom currently disposes of soil and ballast stones contaminated with PCBs by thermal destruction. This is a costly process as PCBs are regarded as hazardous materials and needs to be safely transported and disposed of at a licensed disposal facility.

Based on literature, ozone has been used on a laboratory scale to treat soil contaminated with PCBs with the addition of chemicals such as hexane and acetone which assist in breaking down PCBs. The objective of this study was to evaluate whether ozone without the addition of chemicals could reduce the levels of PCBs present in contaminated soil. In this study, two soil samples and one ballast stone sample were contaminated with 50 ppm, 200 ppm and 600 ppm of PCBs and then exposed to 0.4, 0.5 and 0.6 l/min of ozone for a period of 60 minutes to examine the effects of increasing ozone flow rates on PCB destruction in soil.

The results of the experimental tests showed that ozone gas reduced the concentration of PCBs in the soil and ballast stone samples for the different total gas flow rates. The literature study identified that the final products of the ozonation of PCBs are carbon dioxide and water and that any products formed after this process could possibly be degraded by the soil natural microorganisms.

Calculations based on the Shin et al. (2004) model proved that ozone was in excess after the ozonation process. The results of the experiments also confirmed this, as the PCB residuals were similar for all three total gas flows, which showed that there was no dependence on the gas flow rates hence, ozone was in excess. The experimental data was then trended with zero, first and second order reaction equations, which showed that the best fit was obtained with the first-order reaction equation. It is recommended that ozone be used for the treatment of PCB contaminated soil at Eskom substations.

DECLARATION

I Shanita Jeewan Moodley student number 205526627 declare that:

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January 2011

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LIST OF SYMBOLS

m_{oil}	The mass of oil
V_{oil}	Volume of oil, litres
ρ_{oil}	Density of transformer oil, kg/m^3
n	Number of moles

DEFINITIONS

Polychlorinated Biphenyls (PCBs)	PCBs are a mixture of 209 chemicals which is toxic to both humans and animals as it is carcinogenic.
PCB Congeners	One of the 209 PCBs or other group of compounds, not necessarily of the same homolog.
Sediment	Non-solid or non-consolidate deposits of solid fragments or particles of material that usually comes from the weathering of rock and are carried and deposited by wind, water or ice.
Ozone	Ozone or trioxygen is a simple triatomic molecule consisting of three oxygen molecules.
Heteroatoms	An atom other than carbon in the structure of a heterocyclic compound.
Free radicals	Radicals (often referred to as free radicals) are atoms, molecules, or ions with unpaired electrons on an open shell configuration.
Reaction Order	In chemical kinetics, the order of reaction with respect to a certain reactant is defined as the power to which its concentration term in the rate equation is raised.

CHAPTER ONE

INTRODUCTION AND BACKGROUND

1.1 INTRODUCTION

The chemical compound Polychlorinated Biphenyls (PCBs) is hazardous and toxic pollutant. In the past, PCBs were added to transformer oil to improve its electrical insulating properties. Hayes (2006) explained that in the late 1960's PCBs were discovered as a pollutant which could cause environmental contamination due to its slow degradation and even trace amounts of PCBs were regarded as toxic to both human and animals. In many countries the use of PCBs on an industrial scale has been prohibited since 1970s, however PCBs are still detected at low levels in certain countries since the contamination of soils and groundwater is of concern due to its toxicity (Shimura et al. 1996).

The Eskom annual report for the year 2009/2010 reported that 950 tons of materials containing PCBs were disposed of (Eskom Annual Report, 2010). Eskom has put a phase out plan in place to remove PCBs from the environment by the year 2025 since South Africa is a party to the Stockholm Convention. Oil spills are a frequent occurrence at Eskom substations which could contain PCBs. These spills mainly occur as a result of a faulty transformer which has oil leaks thus contaminating soil, ballast stones and ground water. The contaminated sediments are easily carried away by rain and wind which could further contaminate the environment and aquatic bodies. Eskom currently disposes of soil and ballast stones contaminated with PCBs by thermal destruction which is an energy intensive process. This is a costly process due to the transportation and thermal destruction of this hazardous material and the disposal of the residues from the thermal destruction process in a licensed facility.

Cassidy et al. (2002) explained that landfilling and incineration are expensive technologies and are the widely used for the disposal for PCB contaminated sediments. Davila et al. (1993) further stated that due to thermal destruction of PCBs many harmful by-products maybe formed.

There is therefore a need to evaluate other non-thermal energy efficient technologies such as ozonation to determine whether such technologies can successfully eliminate or reduce PCBs found in contaminated soil or sediments to an acceptable level. Shin et al. (2004) explained that the by-products produced from the chemical oxidation of soil contaminated with organic material is harmless however high removal efficiencies can be obtained if the process is correctly done. Ozone is a chemical oxidant which has been used in the past to treat waste water, soil and air. Javorska et al. (2009) further substantiated that ozone can be a feasible option for the degradation of organic compounds. The objective of this study is therefore to evaluate whether ozone without the addition of chemicals can reduce the levels of PCBs present in contaminated soil to a safe level.

1.2 BACKGROUND TO THE PROBLEM

Since, oil spills occur frequently at Eskom substations and may contain PCBs, necessary measures need to be put in place in-order to contain the spill and to ensure that further contamination does not occur. Further problems may arise if the oil spill is reported after a long period of time as the contaminants can penetrate further into the soil and could contaminate ground water. The cost and duration for site clean-up, treatment of the contaminated soil and ballast stones and the replacement of soil and ballast stones is considerably high.

1.3 RESEARCH PROBLEM

Research on the ozonation of soil contaminated with PCBs is limited. Cassidy et al. (2002) focused mainly on the destruction of PCBs in soil using ozone and bioremediation techniques. They reported successful results for PCB destruction using both technologies. Javorska et al. (2009) reported on the ozonation of two soil samples spiked with low levels of PCBs for a period of 6 and 36 months and ozonated over different time intervals. Valuable information was extracted from Javorska et al. (2009) study and the results were incorporated into this study.

1.4 THE RESEARCH OBJECTIVE/QUESTION

Section 1.2 discusses the current treatment methods for soil contaminated with PCBs in South Africa. The objective of this study is therefore to establish whether ozone without the addition of chemicals could reduce the concentration of PCBs in soil to an environmentally acceptable level. The aim of this study is to establish a specific methodology for the on-site treatment of oil spills at electrical substations using ozone gas. Based on literature it is expected that PCBs in soil will be reduced to acceptable levels with ozone treatment.

Hayes (2006) reported that when aroclors 1242 was dispersed into Carbon Tetrachloride (CCl_4) it was degraded by ozone within minutes. He also reported that with even under limited supply of ozone, PCBs were still degraded to various extents with some intermediates remaining. A second test was conducted on aroclors 1260 and it was degraded within 40 minutes. This was used as a starting point for this research.

1.5 THE HYPOTHESIS

Ozone gas can be used to reduce the concentration of PCBs in soil and ballast stones.

1.6 THE IMPORTANCE OF THIS STUDY

This study is important to Eskom as it could identify a new method or technique for the treatment of soil and ballast stones contaminated with PCBs at substations. This is in light of the fact that the current treatment cost for soil contaminated with PCBs in South Africa is extremely high. Aronstein et al. (1995) further reported that fentons reagent had the ability to increase the destruction efficiency by over 7 times for soil contaminated with PCBs. Based on literature, ozone has been used on a lab scale to treat soil contaminated with PCBs with the addition of chemicals such as hexane and acetone which assist in breaking down PCBs in soil.

The experimental method for this study was specifically designed for on-site treatment of soil contaminated with PCBs and therefore no chemicals were added during the experimentation due to the possibility of these chemicals reacting with the cables beneath the transformer and also the possibility of leaching. The results of this research are therefore intended to provide Eskom with a new or alternative method to treat soil and ballast stones contaminated with PCBs at electrical substations.

1.7 ORGANISATION OF THE STUDY

This dissertation is organised as follows:

Chapter one presents an introduction to the dissertation and a background to the research problem. The research objective and hypothesis is also included in this chapter. Chapter two presents the review of literature. Chapter three presents the experimental work for this particular study. Chapter four presents the results and discussion. Chapter five concludes the dissertation and makes recommendations for further work.

CHAPTER TWO

LITERATURE REVIEW

Chapter one discussed the impact of oil spills which may contain the chemical compound PCB have at Eskom's electrical substations and the importance for a cost effective solution for the destruction of this harmful compound.

Section 2.1 presents a brief introduction to this study. Section 2.2 discusses the history of PCBs. Section 2.3 reviews the structure and properties of PCBs. Section 2.4 identifies treatment technologies for soil contaminated with PCBs. Section 2.5 discusses ozone technology. Section 2.6 discusses the ozonation of soil. Section 2.7 discusses the breakdown of PCBs in soil. Section 2.8 provides the objectives of this study. Section 2.9 concludes the chapter.

2.1 INTRODUCTION

This chapter begins with the history of PCBs, which is listed as one of the Persistent Organic Pollutants (POPs) identified by the Stockholm Convention and is discussed in detail in section 2.2.1. This chapter further discusses the structure and properties of PCBs, and identifies treatment technologies for soil contaminated with PCBs.

The objective of this research is to establish whether ozone without the addition of chemicals can reduce the concentration of PCB present in contaminated soil and ballast stones. In doing so, this study also identifies studies carried out by other research institutes on soil contaminated with PCBs in order to establish a specific methodology for the testing process.

2.2 HISTORY OF PCBS

Polychlorinated biphenyls were first introduced in 1929. Erickson (1997) reported that the Monsanto Corporation was the major producer of PCB from 1930 to 1977 and PCBs were marketed under the trade name Aroclor®. Aroclors were marketed for use in transformers, capacitors, printing inks, paints, dedusting agents, pesticides and other applications, Erickson (1997). The largest application for PCBs was in the electrical industry and PCBs where mainly used in transformers and capacitors, Wilderding et al. (1990).

PCBs have unique physical properties which make them attractive compounds for industries which are discussed in detail in Table 2-3. Public pressure increased to stop the production and importation of PCBs since it was identified as being toxic to humans (Chemistry of PCB, 2006). PCBs were widely used in many countries thus resulting in the contamination of the environment, Yukselen-Aksoy et al. (2010).

The uses of PCBs can be divided into three categories, (Erickson, 1997);

- Completely closed systems such as capacitors and transformers.
- Nominally closed systems such as hydraulic and heat transfer systems, vacuum pumps.
- Open-ended applications are as following: plasticizers in Polyvinylchloride (PVC), neoprene and other chlorinated rubbers; surface coatings, paints inks, adhesives, pesticide extenders, micro-encapsulation of dyes, carbonless paper. It was also used for the immersion of oils for microscopes, catalysts in the chemical industry, casting waxes, decachlorobiphenyl (decaCB), cutting oils, and lubricating oils.

Aronstein et al. (1995) stated that PCBs is regarded as a pollutant and can have toxic and hazardous effects on the environment. He also stated that due to the low water solubility and strong particle binding tendencies PCBs can remain persistent in the environment for a long period of time. PCBs are resistant to degradation by chemical and biological processes as they are persistent within the environment and have the ability to bioaccumulate thus causing an environmental risk, Javorska et al. (2009).

PCBs are affected by the following: air temperature, wind speed, storm frequency, rainfall rates, (Chemistry of PCB, 2006).

PCBs can be transported around the environment in many ways via air, water, fish, birds, and other routes. PCBs can be deposited into the environment by air from rain, snow, dry fallout, and vapour phase deposition, Erickson (1997). PCBs can also cause environmental contamination from landfill sites, incineration, agricultural lands, industrial discharges and sewage effluents, (Chemistry of PCBs, 2006). Figure 2-1 shows the transport of PCBs via the food chain from the atmosphere into water and then aquatic life and finally to humans.

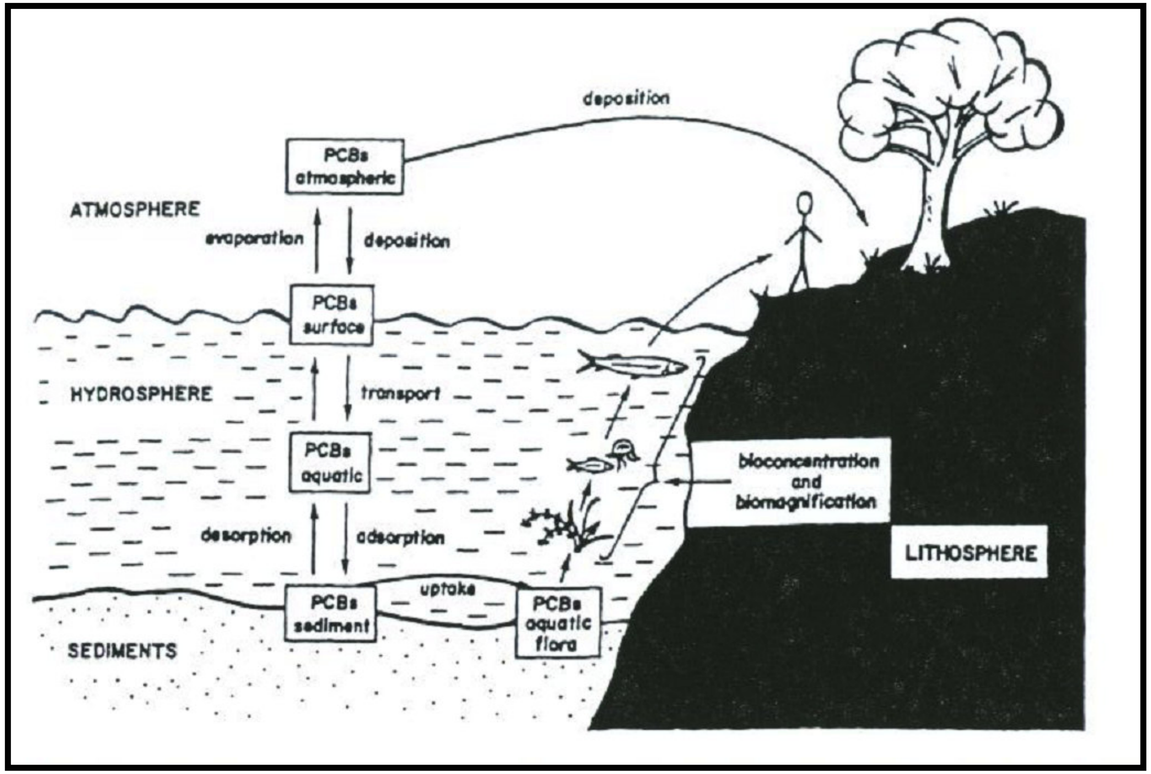

Figure 2- 1 Environmental transport pathways of PCBs (Erickson, 1997)

2.2.1 THE STOCKHOLM CONVENTION

The Stockholm Convention is a global treaty which is intended to protect humans and the environment from the 12 Persistent Organic Pollutants (POPs). PCBs are regarded as a Persistent Organic Pollutant (POPs) by the Stockholm Convention and will need to be eliminated from the environment by the year 2025.

Eskom has put a PCB phase-out plan in place for the removal of PCBs from its environment as partial fulfilment of South Africa's obligation since South Africa is a signatory to the Stockholm Convention. 97 countries and one regional economic integration organization signed the treaty in April 2005, (EPA Reference guide to non-combustion technologies for remediation of POPs in stockpiles and soils, 2010).

The Stockholm Convention states that all countries should be committed to reduce or eliminate the production, use, and release of the 12 POPs which is a major concern globally. Table 2-1 presents the 12 specific POPs identified by the Stockholm Convention of which PCBs is listed as one of them.

Table 2-1 The 12 specific POPs identified by the Stockholm Convention

Pesticides	**Industrial Chemicals or By-Products**
Aldrin	Polychlorinated biphenyls (PCB)
Chlordane	Dioxins
Dieldrin	Furans
Endrin	
Heptachlor	
Hexachlorobenzene (HCB)	
Mirex	
Toxaphene	
Dichlorodiphenyltrichloroethane (DDT)	

2.2.2 THE STRUCTURE AND PROPERTIES OF THE PCB COMPOUND

PCBs consist of a biphenyl (two benzene rings which have a carbon to carbon bond between carbon 1 on one ring and carbon 1 on the second ring) with a varying number of chlorine atoms (Figure 2-2). The chlorine atoms can replace the hydrogen atoms by attaching itself to the carbon, (Environmental Chemistry.com, 2007). The chlorine atom can attached to 10 different positions of the biphenyl which would result in the 209 PCB congeners, Cassidy et al. (2002) which is presented in Table 2-2.

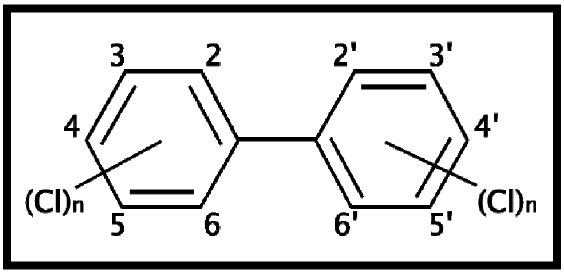

Figure 2- 2 Chemical Structure of PCBs (PCBs, 2007)

Table 2-2 Isomers of PCBs, (Polychlorinated Biphenyls (PCBs) in the environment, 2007)

Chlorine Substitution	**Number of possible Isomers**
Mono-	3
Di-	12
Tri-	24
Tetra-	42
Penta-	46
Hexa-	42
Hepta-	24
Octa-	12
Nona-	3
Deca-	1
Total	**209**

2.3 PROPERTIES OF PCBs

This section discusses the PCB properties (Table 2-3) which includes; phase, colour, viscosity, solubility, biological degradation, electrical insulation, thermal stability and toxicity of PCBs. Soil density, particle size distribution, moisture content, meteorological effects, amount of precipitation, organic carbon content, and the presence of organic colloids affect the mobility of PCBs, (Davila et al. 1993).

Table 2-3 Properties of PCBs

PROPERTIES	**DESCRIPTION OF PROPERTY**
Phase	A large variety of PCB congeners are colourless, odourless crystals (Erickson, 1997).
Colour	Colourless or light yellow. The colour of the oil containing PCBs will be darker with a higher chlorine content (Davila et al.1993).
Viscosity	More highly chlorinated compounds such as Aroclor 1260 are more viscous than Aroclor 1252 with lower chlorine content (Wikipedia, 2007).
Solubility	PCBs have a low solubility in water and can decrease as the chlorine content increases (Polychlorinated Biphenyls (PCBs) in the environment, 2007).
Biological Degradation	The higher the number of chlorines in a PCB molecule, the less the biodegradability (Environmental Chemistry.com, 2007).
Electrical Insulation	PCBs act as insulating medium for transformers thus preventing internal arching which results in extending the lifespan of the transformer (Wikipedia, 2007).
Thermal Stability	PCBs are thermally stable and persistent in the environment, Davila et al. (1993).
Toxicity	PCBs cannot breakdown in the environment and can bioaccumulate in the environment (Environmental Chemistry.com, 2007). PCBs can be toxic to humans and animals as it is a carcinogen.

2.3.1 LIMITS FOR PCBS IN SOILS

South African Bureau of Standards (SABS) together with experts in the field of PCBs from Eskom have compiled the SANS 290 standard which classifies the ranges of PCBs based on contamination (Table 2-4). This document states that articles that contain or come in contact PCBs shall be classified as PCB level 5.

Table 2-4 PCB level classifications of all materials (SANS 290)

PCB content levels mg/kg	**PCB level**	**PCB levels common names**
<1	0	PCB free materials
1-10	1	Non PCB materials
11-20	2	
21-50	3	
51-500	4	PCB contaminated materials
>500	5	PCB materials

2.3.2 HEALTH AND SAFETY WORKING CONDITIONS WITH PCBS

The symptoms of PCB exposure are chloracne, eye irritation, drowsiness, headaches and a sore throat (SANS 290).

"Operative handling of PCB contaminated materials must take the following precautions:

a) Ensure adequate ventilation in the working area. Portable fans at ground should be used in enclosed substations; and
b) wearing of full protective clothing, which shall include the following:
1) one-piece chemical resistant unit
2) chemical resistant gloves;
3) disposal covers for shoes
4) for confined spaces, an approved self–contained breathing apparatus; and
5) a full mask with a type "C" replacement canister can be used for lower level exposure. A respiratory protection device with a full mark and a cartridge or

canister suitable for use with PCBs is required when handling PCB liquids hotter than 55^{0}C, where there is a significant amount of PCB liquid exposed to the air, or where adequate ventilation is not possible. In a fire situation involving PCBs, self-contained breathing apparatus should be used.

Impervious gloves and butyl rubber, neoprene, nitrite rubber, polyvinyl alcohol, viton saranex or teflon (not ordinary rubber) should be worn when handling PCB liquids. Note that PCBs will penetrate most materials, but chemical resistant fluorinated rubbers or elastomers are most suitable and laminated materials offer the best protection against the PCB.

All personal protective equipment shall be disposed of after use. Potentially contaminated protective equipment shall be treated as materials containing PCBs and disposed of accordingly". A Material Safety Data Sheet (MSDS) on PCBs can be seen in Appendix A.

Table 2-5 presents a summary of cleanup levels required under the Environmental Protection Agency (EPA). This summary is based on clean requirements for different categories such as indoor, residential, electrical substations, restricted and non-restricted areas and other.

Table 2-5 A summary of cleanup levels required under the Environmental Protection Agency (EPA) Spill Policy, (Erickson, 1997)

Spill Amount	Use Category	Sample type	Clean requirement
<1 lb PCB	Indoor, residential	Surfaces	10 µg/100cm^2
	Other	Solid Surfaces	Double wash
>1 lb PCB	Electrical substations	Surfaces	100µg/100cm^2
		Soil	25ppm (50ppm with labelling)
	Other resisted access area	High-contact solid surfaces	10 µg/100cm^2
		Low-contact indoor surfaces	
		Low-contact outdoor surfaces	100 µg/100cm^2
		Soil	25ppm
	Non restricted access areas	Furnishings, toys, etc.	Replace
		Indoor and high-contact outdoor solid surfaces	10 µg/100cm^2
		Soil	10ppm

2.4 TREATMENT TECHNOLOGIES FOR SOIL CONTAMINATED WITH PCBS

The previous section reviewed the properties, structure and the safety aspects of PCBs. This section discusses PCB remedial technologies for soil contaminated with PCBs which include; Incineration, Thermal Desorption, Chemical Dehalogenation/Dechlorination, Solvent Extraction, Soil Washing, Solidification/Stabilization, Bioremediation, Vitrification and Land Fill Cap System and Deep Well Injection.

Incineration is a widely used technology in South Africa for the destruction of PCB contaminated materials such as oil, soil etc. Incineration can treat solid and liquid organic contaminants by subjecting them to temperatures greater than 1000^{o}C in the presence of oxygen which causes volatilization, combustion and destruction of compounds, (Davila et al. 1993). 99.9999% destruction efficiencies of PCBs and dioxins can be achieved using incineration. Davila et al. (1993) stated that the off gases and by-products as a result of the incineration process should be treated before it is released into the atmosphere. The cost per ton for the transportation and thermal disposal of contaminated soil sediments is approximately R25 000 per ton.

In-situ Thermal Desorption (ISTD) is an in-situ treatment technology which uses conductive heating elements to directly transfer heat to an environmental media. The ISTD technology can be used to heat soil or sediments in-situ to approximately 538^{o}C and as a result of this it has been used to treat compounds with relatively high boiling points such as such as PCBs, Polycyclic Aromatic Hydrocarbons (PAHs), pesticides and herbicides, (In-Situ Thermal Desorption for Treatment of POPs in Soils and Sediments, 2010). The cost depends on the different types of thermal desorption technologies which range between R618.03 – R839.30 per ton of waste (FRTR Remediation Technologies Screening Matrix and Reference Guide Version 4.0, 2009).

Chemical Dehalogenation can be used for the treatment of halogenated aromatic compounds such as PCBs, Polychlorinated Dibenzodioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), chlorobenzenes, chlorinated phenols, organochlorine pesticides, halogenated herbicide, and certain halogenated aliphatics, (Rahuman et al. 2000). Base Catalysed Decomposition (BCD), Alkaline

Metal Hydroxide (APEG) and Polyethylene Glycol and Potassium Metal Hydroxide (KPEG) are regarded as Chemical Dehalogenation technologies.

The BCD process uses a reagent mixture and a catalyst to treat liquid and solid wastes. As the reagent is heated to 300 ^{O} C, it produces highly reactive atomic hydrogen in order to break down toxic compounds. Carbon and sodium salts residues are produced from the breakdown of heteroatomic anions. The carbon and sodium salts are then liberated during the complete decomposition reactions. The inorganic and carbonaceous solids are separated from the un-reacted oil by gravity or centrifugation after the process and the oil and catalyst can be recovered for re-use for other treatment processes, (Base Catalyzed Decomposition (BCD), 2010).

Chemical Dehalogenation can be used with other technologies such as low-temperature thermal desorption, solvent extraction or biodegradation, (Rahuman et al. 2000). The cost per ton is for treatment is between R1526-R3816 (FRTR Remediation Technologies Screening Matrix and Reference Guide Version 4.0, 2009).

Solvent Extraction is a technology which separates hazardous contaminants from soils and sediments which can then be treated. This technology can be used to treat soils which contain polynuclear aromatic hydrocarbons, petroleum hydrocarbons, pesticide/insecticide, PCBs, dioxins, and pentachlorophenol (PCP) (Rahuman et al. 2000). Treatment cost per ton R839.30-R4120.20 (Management of PCBs in the US, 2007).

Soil washing is an ex-situ technology which uses water to mix, wash and rinse soil to remove its contaminants. This process has two methods to remove the contaminants from soil which is: by dissolving or suspending it in the wash solution which can be treated by other conventional methods or by concentrating the soil into a particle size separation technique, (Davila et al. 1993).

Contaminants which contain more than 40% of silt or clay particles are difficult to remove as they are strongly bonded to these particles. This process can separate the fine clay and silt particles from the coarser sand and gravel particles, (Davila et al. 1993).

The waste stabilization process involves the binding of the waste with binding agents such as Portland cement, cement kiln dust or fly ash which can in turn convert contaminants into a less toxic form. Solidification/Stabilization (S/S) processes can reduce the mobility of PCBs however it cannot destroy or break down the waste. The cost breakdown is as follows: Cost per ton: R381.50-R2365.30 (Management of PCBs in the US, 2007).

Biodegradation or bioremediation refers to the use of microorganisms to breakdown compounds present in soil. This process can be performed in the presence or absence of oxygen. Bioremediation with the addition of chemical processes can be used for the treatment of soils containing PCBs. The cost breakdown is as follows: Cost ton: R419.65- R724.85 (Bioremediation Using DARAMEND® for Treatment of POPs in Soils and Sediments, 2010).

In-situ Vitrification (ISV) is a process which uses heat to melt soil contaminated with organics, inorganics and metal-bearing wastes, (Envirosense, 2007). The vitrification process can be conducted in-situ or ex-situ for the destruction of PCBs. This process can use three different methods to treat waste which is: (In Situ Vitrification, 2010)

1. Waste can be treated in-situ.
2. Different waste can be collected into a waste site and treated.
3. Soils can be mixed with liquids and absorbent and treated in-situ.

The cost per ton varies between R763 – R7630 (Management of Polychlorinated Biphenyls in the United States, 2007).

Land Fill Cap System and Deep Well Injection are technologies which bury contaminated waste to prevent further contamination. Rahuman et al. (2000) stated that persistent wastes should not be buried in a landfill site as this technology only contains the waste and does not destroy the waste. He further stated that constituents from the persistent waste can escape into the environment via leaching into ground water and volatilizing into the air. The cost for disposal of an acre of hazardous material is approximately R1 335 250. He further stated that insufficient information is available regarding the long term impacts of chemicals injected into deep wells.

Incineration, In-situ Thermal Desorption, Chemical Dehalogenation/Dechlorination, Solvent Extraction, Soil Washing, Solidification/Stabilization, Bioremediation, In-situ Vitrification and Land Fill Cap System and Deep Well Injection have been discussed in detail. Solvent Extraction, Soil Washing and Solidification/Stabilization, Bioremediation and Vitrification are not suitable technologies for the treatment of soil contaminated with PCBs. This is further discussed in Table 2-6, which explains the limitations for PCB remedial technologies. Land Fill Cap System and Deep Well Injection are also not suitable technologies as PCB vapours can also escape from landfills.

Incineration is widely used for the treatment of PCB waste in South Africa and due to the high treatment and transportation costs there is a need to investigate other non–thermal PCB destruction technologies which do not release harmful emissions into the environment. Table 2-7 presents commercially available remedial technologies for PCB destruction in the US. PCB Non-combustion remedial technologies can be seen in Appendix C. Figure 2-3 shows a site contaminated with PCBs and treated using incineration and the emissions produced as a result of incineration. This figure also shows a water table and borehole source which is a concern, as PCBs can leach into the water table causing further contamination.

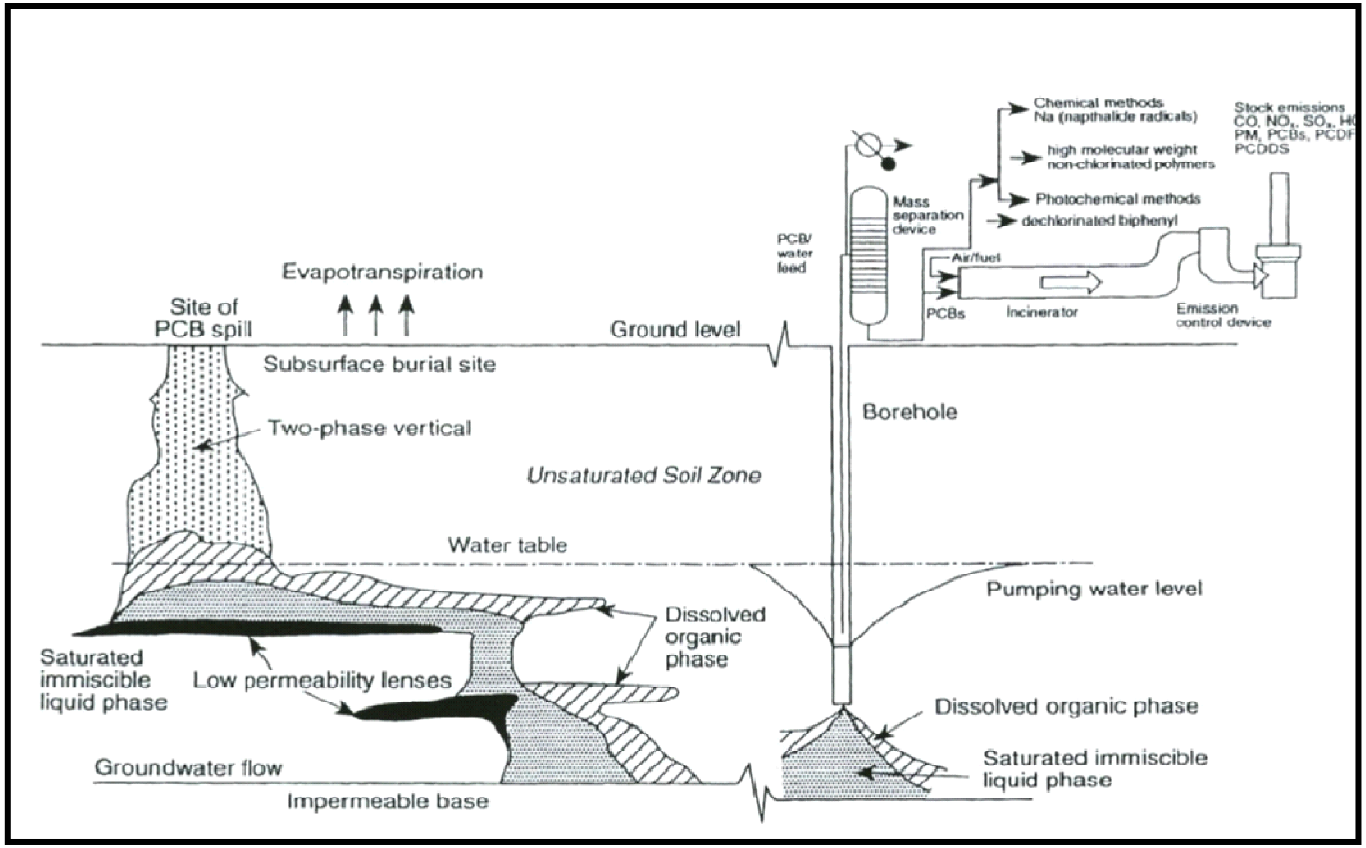

Figure 2-3 A site contaminated with PCBs and the transport of PCBs thus contaminating ground water and treated by incineration (Erickson,1997)

Table 2-6 Limitations of technology alternatives for Remediating PCB contaminated soil and sediment (Management of Polychlorinated Biphenyls in the United States, 2009)

LIMITATIONS OF TECHNOLOGY ALTERNATIVES FOR REMEDIATING PCB CONTAMINATED SOIL AND SEDIMENT								
	Established	Demonstrated				Emerging		
Limitations	Incineration	Thermal Desorption	Chemical Dehalogenation	Solvent Extraction	Soil Washing	Solidification/ Stabilization	Bioremediation	Vitrification
High moisture content adversely affects treatment	X	X	X			X		X
PCBs by-products must be destroyed by another technology		X		X	X			
Produces other residuals that must be treated and/or disposed		X		X	X	X		X
Sensitive to media particle size, clay content, and/or pH		X	X	X	X	X	X	
Not proven to treat all PCB congeners			X			X	X	
Sensitive to contaminants	X		X			X	X	
Off gases must be treated prior to release	X	X	X					X
Often subject to negative public opinion	X	X						X
Volume and/or characteristic changes to treated media					X	X		X
Potentially affected by ambient temperature extremes					X	X	X	
Difficult to measure effectiveness of treatment						X	X	X
Long-term monitoring required for onsite treatment						X	X	

Table 2-7 Commercially available PCB Remedial Technologies in the US (Erickson, 1997)

Technology	**Representative vendors**	**Process name**	**Largest PCB project (U.S)**[a]	**Cost range ($ per ton)**[b]	**Cost per ton**
On-site incineration	Weston Services (PA)	Rotary kiln	20 000^{yd3d}	175-200	R1335.25-R1526
	OHM Remediation Services (OH)	Infrared	18 000 tons		
	Ogden Environmental (NJ)	Circ. bed	120 000 tons		
On-site incineration (oxygen enhanced)	Vesta Technology (FL)	Rotary kiln	1100 tons	N/A[e]	
	Williams Environmental (AL)	Rotary kiln	25 000 tons		
Vitrification (in situ)	Geosafe (WA)		800 tons[f]	N/A	
Chemical dechlorination	Chemical Waste Mgt. (IL)	KGME	Pilot only	N/A	
	GRC Environmental (NY)	APEG-PLUS	Pilot only		
Biodegradation	Non commercially available	-	-		
Solvent Extraction	CF Systems (MA)		Pilot only	NA	
	Resources Conservation (WA)	B.E.S.T	3700 tons[d]		
Soil washing	Biotrol (MN)		N/A	75-150	R572.25-R1144.50
	Waste-Tech Services (CO)		N/A		
	Bergmann USA (CT)		200 tons		
Thermal Desorption	Chemical Waste Mgt. (IL)	X*trax	35 000[d]	125-200	R953.75- R1526
	SoilTech ATP Systems (IN)	Taciuk	40 000 tons		
Solidification/stabilization (in situ)	Int. Waste technologies (KS)		N/A	30-60	R228.90-R457.80
	Geo-Con (PA)		N/A		

[a] GRC Env. And Bergmann USA quantities are for pilot-scale testing.

[b] Cost ranges apply to the generic technology, not to any specific vendor listed. Cost range for S/S is anecdotal, not demonstrated, and does not account for potentially substantial additive costs. Cost range for soil washing is based on European experience.

[c] Representative vendors for large-size transportable units (15-25 tons/h) include AWD Technologies, Inc.; EBASCO Environmental; and International technology Corporation. Project–specific data not obtained.

[d] In progress, total is projected.

[e] N/A = not available

[f] Not a PCB project

Table 2-7 shows that on-site incineration and thermal desorption are widely used in the US to treat soil or sediments contaminated with PCBs. Vitrification, Solvent Extraction and Soil Washing are used on a small scale as treatment technologies. Chemical dechlorination is only used on as a pilot scale while biodegradation and Solidification/Stabilization are not commercially available in the US.

2. 5 OZONE TECHNOLOGY

The previous section discussed PCB remedial technologies for the treatment of soil contaminated with PCBs. This section discusses the chemistry and formation of ozone using corona discharge, Ultra Violet (UV) and cold plasma, the health effects of using ozone, the reaction of ozone on soil and the breakdown of PCBs in soil using ozone gas.

2.5.1 BACKGROUND OF OZONE

Ozone was discovered in 1840 by Christian Friedrich Schönbein and named after the greek word ozein, (Wikipedia, 2009). Ozone occurs naturally in the atmosphere and has many important functions on earth, (The Application of Ozone Technology for Public Health and Industry, 2005).

2.5.2 THE CHEMISTRY OF OZONE

Ozone consists of three oxygen atoms bonded together and is unstable, (Innovative Technology Group, 2005) as indicated in Figure 2-4.

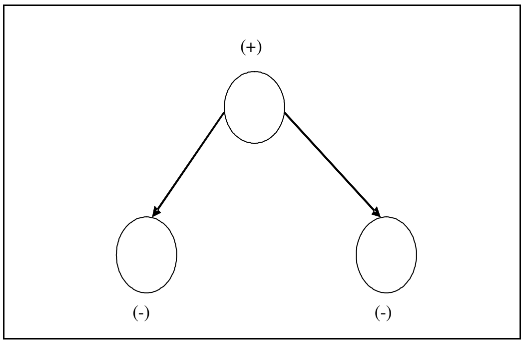

Figure 2-4 Ozone molecule – (re-drawn, Wikipedia 2007)

Ozone levels at 20% can be explosive mixtures, (GE Infrastructure Water and Process Technologies, 2006). Ozone is capable of dissolving in water and is 13 times soluble than oxygen, Cassidy et al. (2002). Kilham et al. (1999) further reported that ozone can replace chlorine as a disinfection method due to health issues associated with the use of chlorine and the effectiveness of chlorine against pathogens. These properties make ozone an ideal candidate for sparging contaminated sediment. Ozone sparging has proven to be effective in oxidising PAHs in sediments.

Ozone is a more powerful oxidizing agent than oxygen. It is also unstable at high concentrations and can decay to ordinary diatomic oxygen (reaction 2-1). Ozone has a half-life of half an hour.

$$2\ O_3 \rightarrow 3\ O_2 \qquad (2\text{-}1)$$

Reaction 2-1 proceeds more rapidly with increasing temperature and increased pressure. Basic chemistry research (Piper Environmental Group, 2007) indicated that ozone decomposes quite quickly during the water treatment process.

Ozone has the ability to react with metals. Lim et al. (2002) stated that the decomposition of ozone on metal (MO) oxides i.e. iron (Fe), Manganese (Mn) and Titanium (Ti) oxides has been investigated. Some of the chemical reactions (see equations 2-2 to 2-11) that occur with ozone (Wikipedia, 2009) are,

Ozone can oxidize metals with the exception of gold, platinum and iridium;

$$2\ Cu^{+} + 2\ H_3O^{+} + O_3 \rightarrow 2\ Cu^{2+} + 3\ H_2O + O_2 \qquad (2\text{-}2)$$

Oxidation of nitric oxide to nitrogen dioxide using ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2\text{-}3)$$

Ozone can oxidize ammonia to ammonium nitrate:

$$2\ NH_3 + 4\ O_3 \rightarrow NH_4NO_3 + 4\ O_2 + H_2O \qquad (2\text{-}4)$$

Ozone can react with carbon to form carbon dioxide:

$$C + 2\ O_3 \rightarrow CO_2 + 2\ O_2 \qquad (2\text{-}5)$$

Ozone can oxidize sulfides to sulfates where Lead(II) sulfide can be oxidised to lead(II) sulfate:

$$PbS + 4\ O_3 \rightarrow PbSO_4 + 4\ O_2 \qquad (2\text{-}6)$$

Ozone can produce Sulfuric acid:

$$S + H_2O + O_3 \rightarrow H_2SO_4 \qquad (2\text{-}7)$$

$$3SO_2 + 3\ H_2O + O_3 \rightarrow 3\ H_2SO_4 \qquad (2\text{-}8)$$

Ozone can react with hydrogen sulfide in its gas phase to form sulfur dioxide:

$$H_2S + O_3 \rightarrow SO_2 + H_2O \qquad (2\text{-}9)$$

Ozone can prodce elemental suplhur and sulphuric acid together in the aqueous phase:

$$H_2S + O_3 \rightarrow S + O_2 + H_2O \qquad (2\text{-}10)$$

$$3H_2S + 4\ O_3 \rightarrow 3\ H_2SO_4 \qquad (2\text{-}11)$$

2.5.3 GENERATION OF OZONE

Ozone can be generated by Corona Discharge, Ultraviolet (UV) and Cold plasma. Ozone generated by corona discharge passes a flow of either oxygen or air containing oxygen through an electrical discharge. Large scale ozone production is generated using corona discharge. Ozone for on-site remediation is produced using electrical ozone generators. Shin et al. (2004) stated that ozone is effective for unsaturated, partially or fully saturated soil which can be delivered as a gas mixture. He then explained that gaseous ozone has a short history in terms of its use as an oxidising agent for soil remediation.

An electrical discharge (a spark) splits an oxygen molecule into two oxygen atoms. This electrical discharge is also referred to as corona discharge (Figure 2-5). The unstable oxygen atoms then combine with other oxygen molecules to form ozone. Medical and industrial grade ozone generators also use corona discharge tube to generate ozone. Corona discharge for ozone production is cost effective and does not require an oxygen source other than the ambient air (Wikipedia, 2009).

UV ozone generators or Vacuum-Ultraviolet (VUV) ozone generators use a light source to generate a narrow band ultraviolet light. Standard UV ozone generators produce ozone with a concentration 0.5% or lower. This method allows the oxygen to be exposed to the UV source for a longer time thus making it impractical for rapidly moving air or water streams (in-duct air sterilization), (Wikipedia, 2009).

In the cold plasma method pure oxygen gas is exposed to a plasma which is created by a dielectric barrier discharge. This method produces higher ozone concentrations compared to ultraviolet ozone generators however the units are expensive, (Wikipedia, 2009).

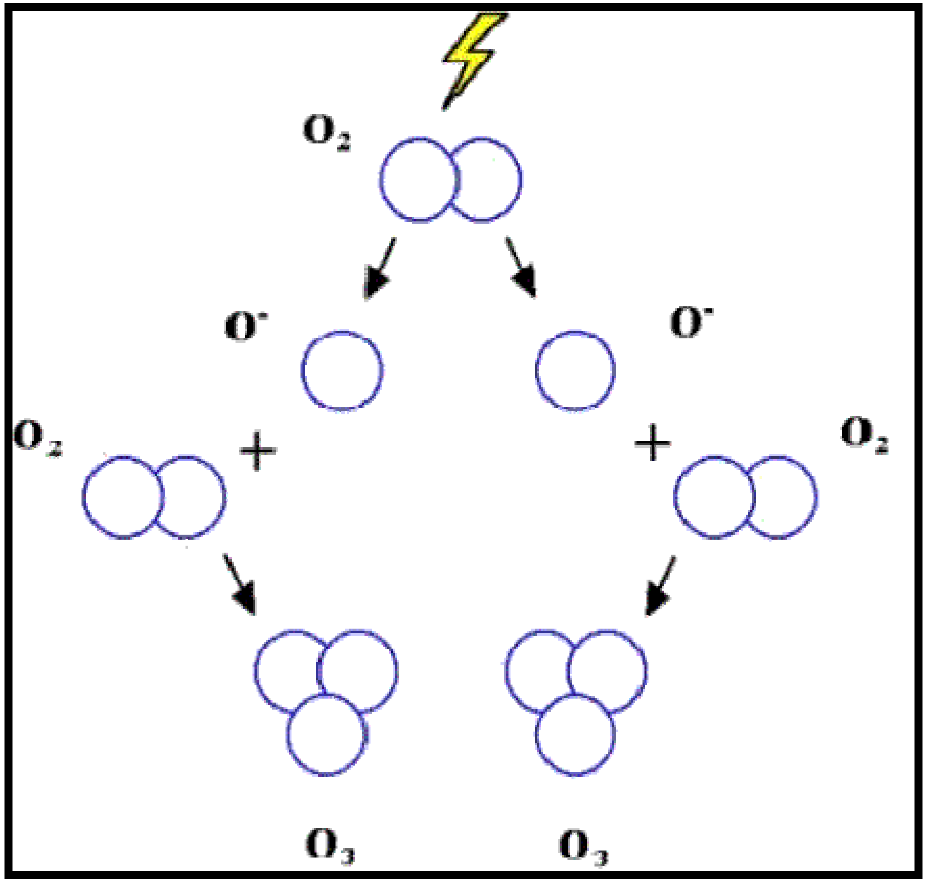

Figure 2-5 Ozone formation using Corona Discharge (Lenntech Water Treatment Solutions, 2007)

2.5.4 PHYSICAL AND CHEMICAL PROPERTIES OF OZONE

Ozone is the trivalent, excited state of oxygen. The two distinctive physical properties of ozone are its smell and colour, (Innovative Technology Group, 2005). Ozone can be smelt in air after lightning storms and has a light blue colour. The physical constants of ozone are presented in Table 2-8. Ozone has a density of 2.144 g/l and a boiling point of -111.9 °C.

Table 2-8 Physical constants of Ozone (Purfresh, 2007)

Physical constants of Ozone	
Molecular weight, g/g-mol	48.0
Boiling point, °C	-111.9
Melting point, °C	-193.0
Gas density, °C grams/litre	2.144
Critical temperature, °C	-12.1
Critical pressure, atm	54.6
Critical volume, cc/mol	147.1

Ozone exists as a colourless gas with a pungent odour readily detectable at concentrations as low as 0.02 to 0.05 parts per million (ppm). Ozone is a powerful oxidising agent, which has an oxidation potential of 2.07 compared to 1.36 of chlorine and 1.78 of hydrogen peroxide volts (Table 2-9). Ozone can oxidise organic and inorganic materials, (Purfresh, 2007).

At high concentrations ozone gas is highly corrosive and toxic. Shin et al. (2004) explained that since the hydroxyl radical is a very strong oxidant with redox potentials, E^o of 2.07 and 3.06 V, ozone was capable of oxidising organic chemicals.

Table 2-9 Comparative Oxidising Properties (Purfresh, 2007)

Reagents	**Redox Potential (Volts)**
Fluorine (F$_2$)	2.87
Ozone (O$_3$)	2.07
Hydrogen Peroxide(H$_2$O$_2$)	1.78
Potassium Permanganate (KMnO$_4$)	1.70
Hyprobromous Acid (HOBr)	1.59
Hypochlorous Acid (HOCl)	1.49
Chlorine (Cl$_2$)	1.36
Chlorine dioxide (ClO$_2$)	1.27
Oxygen (O$_2$)	1.23
Chromic Acid (H$_2$CrO$_4$)	1.21
Bromine (Br$_2$)	1.09
Nitric Acid (HNO$_3$)	0.94
Iodine (I$_2$)	0.54

2.5.5 ADVANTAGES AND DISADVANTAGES OF OZONE TECHNOLOGY

Ozone can be manufactured on-site using both air and oxygen for the treatment of soil contaminated with PCBs.

2.5.5.1 Advantages of the Ozone technology:

- Ozone has low capital equipment and operating costs.
- No vapours are produced during ozonation as the contaminants are destroyed.

2.5.5.2 The disadvantages of Ozone Technology, (The Application of Ozone Technology for Public Health and Industry, 2005)

- High levels of ozone exposure can cause coughing, irritation of the throat or uncomfortable sensations in the chest. Ozone concentrations should be carefully monitored to prevent fatalities. This is further discussed in section 2.5.5.3.
- Ozone has a half life of 25 minutes at ambient temperature (The Ozone, 2008).

2.5.5.3 Health Regulations of using Ozone

The United Stated (US) Occupational Health and Safety Act (OHSA) has established a Permissible Exposure Limit (PEL) of 0.1 ppm calculated as an 8 hour time weighted average to protect workers from high levels of ozone exposure. The National Institute for Occupational Safety and Health (NIOSH) has indicated an Immediately Dangerous to Life and Health Limit (IDLH) of 5 ppm of ozone exposure, (Wikipedia, 2007). All working enviroments should have good air circulation and ventiliation.

Table 2-10 discusses the health effects of using ozone for on-site treatment of PCBs at substations. Appendix B contains a Material Safety Data Sheet (MSDS) for ozone.

Table 2-10 Health effects of Ozone (EPA, 2009)

HEALTH EFFECTS	RISK FACTORS	HEALTH STANDARDS
Decrease in lung function	Increase in ozone air concentration	The Food and Drug Administration (FDA) requires ozone output of indoor medical devices to be no more than 0.05 ppm.
Aggravation of asthma	Greater duration of exposure for some health effects	The Occupational Safety and Health Administration (OHSA) requires that workers not be exposed to an average concentration of more than 0.10 ppm for 8 hours.
Throat irritation and cough	Activates the breathing rate	The National Institute of Occupational Safety and Health (NIOSH) recommends an upper limit of 0.10 ppm, not to be exceeded at any time.
Chest pain and shortness of breath Inflammation of lung tissue. Higher susceptibility to respiratory function.	Certain pre-existing diseases (e.g., asthma)	EPA’s National Ambient Air Quality standard for ozone is a maximum 8 hour average outdoor concentration of 0.08 ppm.

2.5.5.4 Applications of Ozone in Industry

Ozone has been used for the treatment of industrial wastewater as is readily soluble in water and is a strong oxidizer. When treated with ozone the wastewater is not only disinfected but the organic contaminants are oxidised in the water, (Innovative Technology Group, 2005). Table 2-11 presents the applications of ozone in industry.

Table 2-11 Applications of Ozone in Industry (Ozone generator applications, 2007)

Industry	**Applications**
Aquaculture	Ozone is used in aquaculture water treatment for the removal of the following: Removal of fine and colloidal solids Removal of dissolved organic compounds Removal of Nitrite Used for disinfection purposes
Bottled Water	Ozone is used as a disinfectant for bottled water.
Cooling Towers	Ozone is used in cooling towers to control and prevent the formation of legionella.
Food processing	In the food processing industry ozone is used to disinfect stored food.
Industrial Processes	Ozone is used as an oxidant in industrial processes due to its high oxidative potential.
Pharmaceutical	In the pharmaceutical industry it is difficult to maintain low levels of microbial contamination in nutrient waters. Ozone has been proven to sanitise, stored and distributed pure and ultra water.
Potable water disinfection	Ozone is used for disinfection of drinking water.
Soil remediation	Ozone has been used to clean up sites containing a variety of soil contaminants and is used for the breakdown compounds which are not biodegradable over a long period of time. Ozone has been used in lab scale as well as industry to treat PCBs in soil with the addition of reagents to break down the PCBs.
Waste water treatment	Ozone is used effectively in the processing of water laden with concentrations of industrial by-products. Pesticides, organics, Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are treated effectively using ozone.
Wineries	Ozone is used to maintain and improve the microbial health of oak barrels which store wine. Ozone is also used for winery sanitation since; it is a fast, effective, environmentally friendly treatment method and has no residue.

2.6 OZONATION OF SOIL

The previous section discussed the generation of ozone, physical and chemical properties and health effects of using ozone and the applications of ozone in industry. This section discusses the reaction of ozone with soil and the break down of PCBs using ozone.

Shin et al. (2004) stated that ozone gas can be used for the treatment of soil contaminated with hazardous waste as it has been identified as a promising method of treatment. Ozone can be used to destroy hazardous organic pollutants and successful treatment can be achieved within a few months, Nelson (2002). Ozone has been used for the treatment of industrial wastewater because it is readily soluble in water and is a strong oxidizer. Due to the unstability nature of ozone it has to be produced on site, (Innovative Technology Group, 2005). This study was therefore initiated to establish whether ozone could effectively break down soil contaminated with PCBs.

Air sparging is a technology which has lead to the in-situ ozonation of soil. Nelson (2002) mentioned that a well designed air sparging system can be used for the in-situ ozonation of soil. In-situ ozonation systems need to work effectively to break down present PCBs in soil as Soil contains Organic Matter (SOM) which is comprised of microorganisms and humus. Lim et al. (2002) stated that SOM and metal oxides can increase the reaction of ozone with soil. He further stated that ozone can be delievered as a dissolved or gas phase. Ozone can be consumed in the soil by following ways: including “empty-column self-decomposition in the gas phase and at the surfaces of the system, catalytic decomposition through interaction with soil particles and reaction with Soil Organic Matter (SOM) and Soil Inorganic Matter (SIM)”, Shin et al. (2004).

Figure 2-6 shows the catalytic reaction of ozone on the soil surface and the removal of organics. Step 1 shows the radical generation of ozone which is followed by the non-radical generation. Step 3, 4 and 5 shows the oxidation of the radical and formation of carbon dioxide. Step 6, 7 and 8 shows the oxidation of ozone and the formation of carbon dioxide. A higher destruction efficiency can be expected as Lim et al. (2002) concluded that “field soil has a high soil SOM and metal content”.

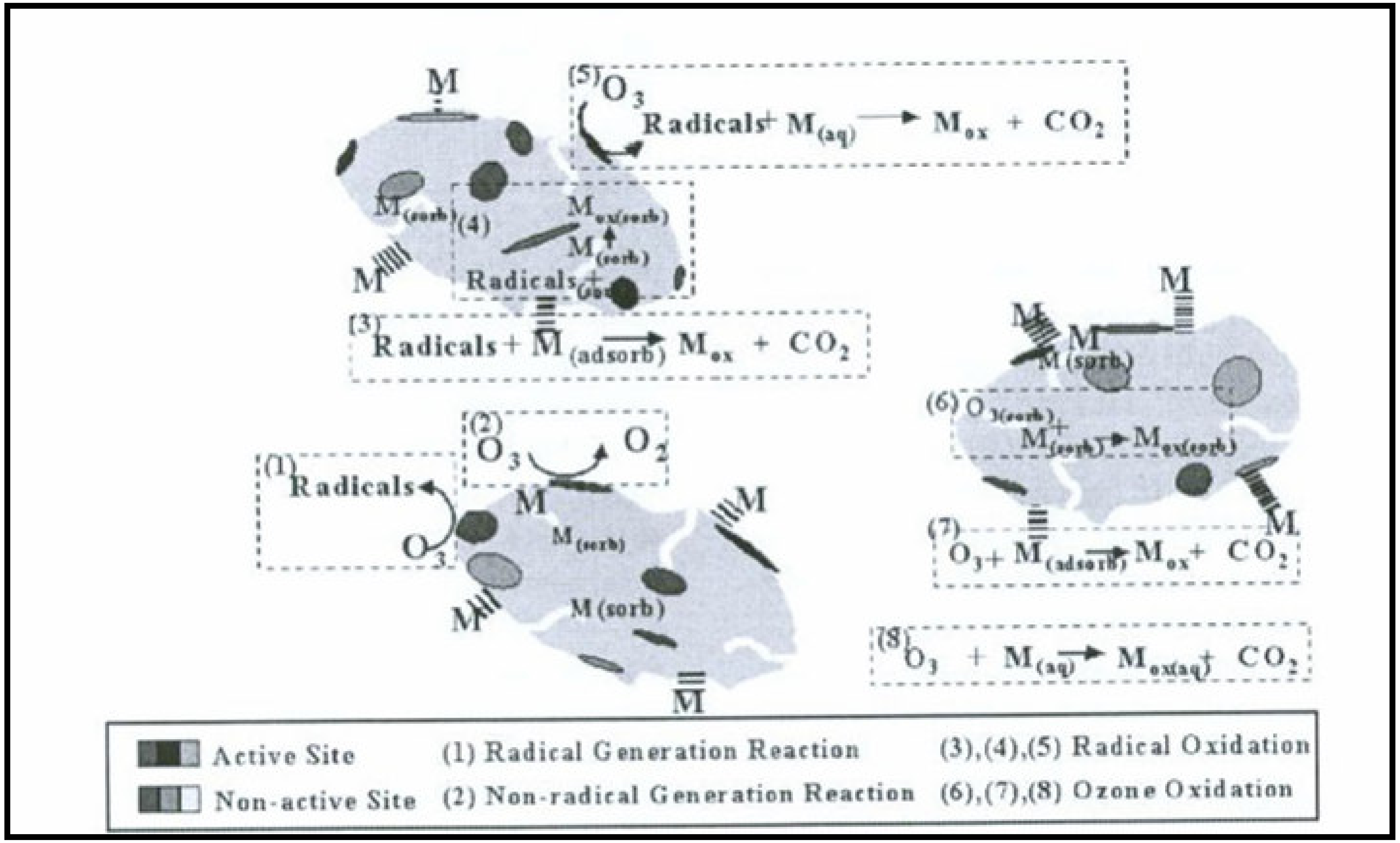

Figure 2-6 Catalytic reaction of ozone on the soil surface and the removal of organics, (Lim et al. 2002)

2.7 BREAKDOWN OF PCBS IN SOIL

Hayes (2006) concluded that Polychlorinated Phenols (PCP) and Benzoic Acids (BA) are formed when ozone reacts with PCBs. Benzoic acid is a white crystalline compound present in some plant resins and is used as a food preservative. The products are further reacted with ozone to produce quinones which is a class of compounds containing benzoquinone isomers.

Quinones then further react with the ozone to produce acid and ketone intermediates which are known to be biodegradable to low molecular weight dicarboxylic acids, carbon dioxide and water. Dicarboxylic acids are organic compounds which are substituted with two carboxylic acid functional groups. The final products of the ozonation process was carbon dioxide and water (Figure 2-7).

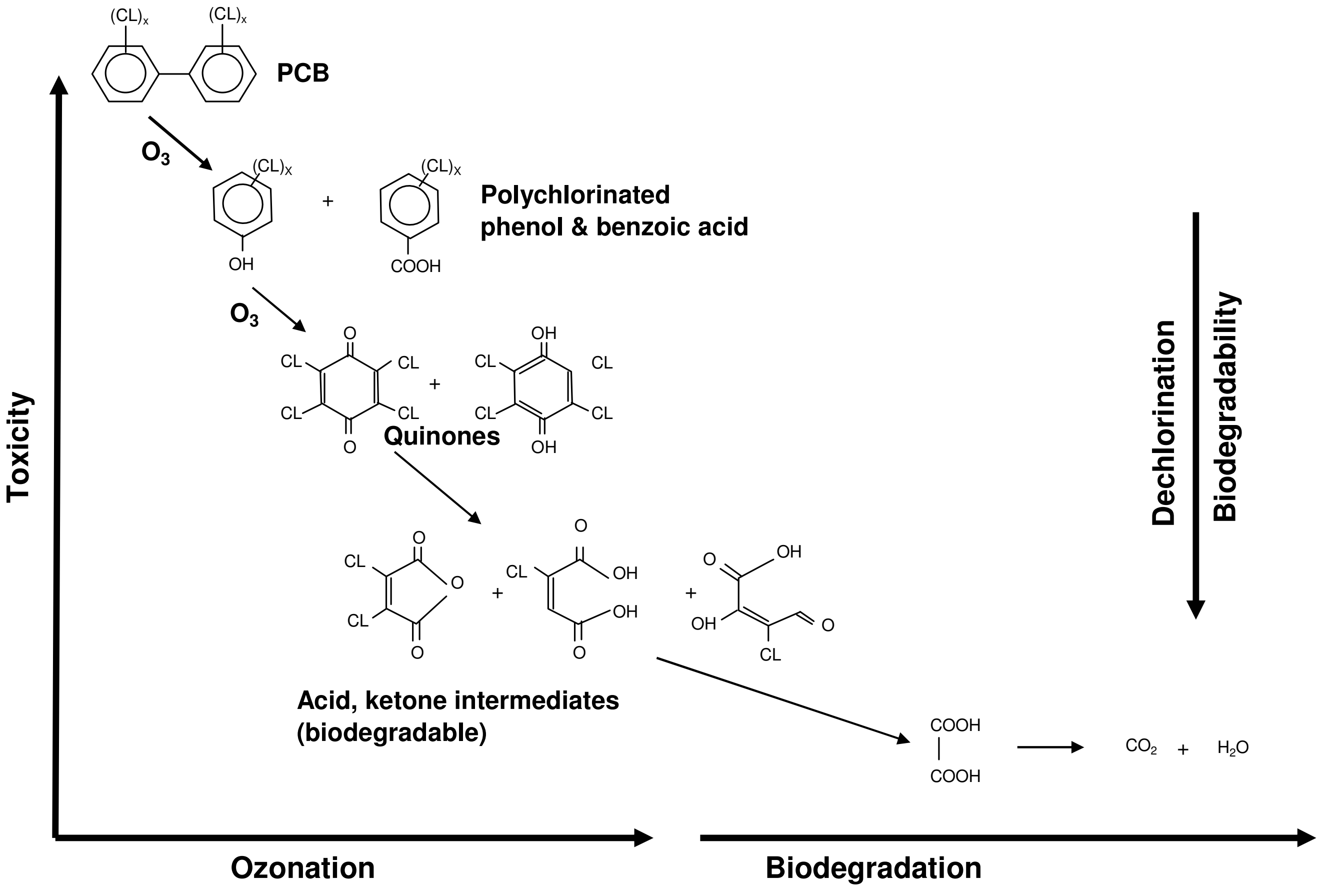

Figure 2-7 PCB Degradation using Ozone, (re-drawn Hayes, 2006)

Important factors which affect the degradation of PCBs are contact time, agitation and pH, Hayes (2006).

Cassidy et al. (2002) concluded that the major oxidation products produced from the ozonation of soil contaminated with PCBs is benzoic acids. This resulted in the splitting of one of the PCB molecules from the biphenyl ring thus allowing the chlorine atoms on the uncleaved ring to be replaced with hydroxyl (OH). He then reported that the chlorine atoms from PCBs were removed as a result of the ozonation. He further substantiated that in his study no attempt was made to identify the presence of alcohols, aldehydes and ketones as previous studies had showed that the formation of these products during the ozonation of soil containing PCBs were minute.

Hayes (2006) concluded that during the ozonation of soil contaminated PCBs other reactions may occur however, the by-products produced during this reaction would be non-hazardous. He further concluded that carbon dioxide and water are the final products of this process. During the ozonation of soil contaminated with PCBs Cassidy et al. (2002) concluded that the residual carbon formed was degraded by microorganisms present in the system.

2.8 CONCLUSION

- PCB is a toxic molecule and according to the Stockholm convention needs to be removed from the environment the year 2025.
- Oil spills are a frequent occurrence at Eskom substations which could contain PCBs and the contaminated sediments are easily carried away by rain which could further contaminate the environment and aquatic bodies.
- The incomplete combustion of PCBs can result in the formation of dioxins and furans.
- The two most common disposal methods for PCB contaminated sediments are landfilling and incineration which poses tremendous problems and is very expensive.
- Incineration is an established technology that has been used to treat soil contaminated with PCBs in South Africa and world-wide. Currently this is a very expensive option and the only option available in South Africa for the destruction of PCBs and therefore there was a need to investigate other technologies such as ozone.
- Ozone (O_3) has been used together with bioremediation for the treatment of soil contaminated with PCBs and has provided successful results.
- The health aspects of using ozone was discussed in detail and will be taken into consideration during the experimentation process for this study as the side effects of using ozone can be detrimental and therefore a well ventilated area is required during testing.
- Ozone can be consumed in the soil by following ways: including "empty-column self-decomposition in the gas phase and at the surfaces of the system, catalytic decomposition through interaction with soil particles and reaction with Soil Organic Matter (SOM) and Soil Inorganic Matter (SIM)", Shin et al. (2004).
- PCBs can be broken down into less harmful by-products such as carbon dioxide and water using ozone gas.
- Cassidy et al. (2002) concluded that the major oxidation products produced from the ozonation of soil contaminated with PCBs is benzoic acids.

- The literature study identified that the final products of the ozonation of PCBs are carbon dioxide and water and that any products formed after this process could possibly be degraded by the soil's natural microorganisms.
- This chapter also revealed that very little research has been conducted on soil contaminated with PCBs.

CHAPTER THREE

EXPERIMENTAL OZONATION TESTS

The previous chapter discussed the literature review which included the structure and properties of PCBs, the description of ozone technology and the destruction of PCBs in soil using ozone. This chapter discusses the experimental ozonation tests. In these tests PCB contaminated samples were exposed to different flow rates of ozone gas.

Section 3.1 presents a brief introduction to this chapter. Section 3.2 shows the sampling of oil containing PCB and the preparation of soil and ballast stone samples. This section also discusses the soil composition characteristics and the experimental equipment used in the study. Section 3.3 presents a summary of the test methodology. Section 3.4 concludes chapter three.

3.1 INTRODUCTION TO THE EXPERIMENTAL INVESTIGATION

Based on a study conducted by Hong (2006) 1.4 millimole (mM) of PCBs (Aroclor 1260) was dispersed into a solution of Carbon Tetrachloride (CCl_4) and ozonated using a concentration of 65 mg/l of ozone. PCBs were completely degraded within 40 minutes. It was therefore decided to ozonate the contaminated soil and ballast stones samples for a period of one hour using an ozone concentration of 65 mg/l. The objective of this research is to establish whether ozone without the addition of chemicals can reduce the concentration of PCBs present in contaminated soil to an acceptable level, while still maintaining safe operating conditions. The test samples were exposed to ozone at three different flow rates. In this study ozone was produced from air. The experimental reactor for the testing process was operated as an open flow system.

3.2 SAMPLING OF PCB OIL AND SOIL

3.2.1 PCB OIL AND SOIL PREPARATION

Samples were pumped from 210 litre drums (transformer oil containing PCBs) using a paraffin pump and stored in vials. Each sample was taken in duplicate and analysed for the following PCB ranges: 50 ppm, 200 ppm and 600 ppm by the Eskom PCB laboratory. Figure 3-1 shows a PCB oil sample being measured in a vial.

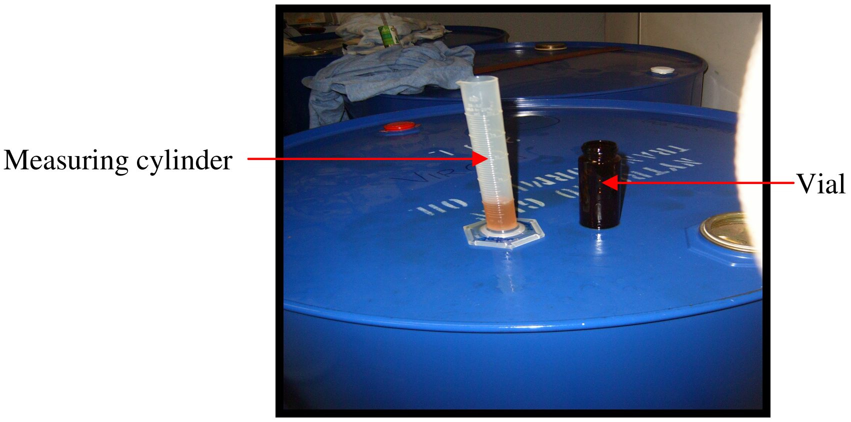

Figure 3-1 A PCB oil sample being measured in a vial

3.2.2 DETERMINATION OF THE AMOUNT OF OIL TO BE MIXED WITH SOIL

Based on the contamination level from previous spillage sites a mixture ratio of 0.0042 kg oil per kg of soil was used for the ozone experimentation. The mass and the volume of oil was calculated according to equations 3-1 and 3-2 respectively, where m_{soil} is a mass of uncontaminated soil.

$$\begin{aligned} m_{oil} &= 0.0042 m_{soil} \\ &= 0.0042\,\text{kg} \end{aligned} \qquad (3\text{-}1)$$

$$V_{oil} = \frac{m_{oil}}{\rho_{oil}} = \frac{0.0042\ \text{kg}}{840\ \text{kg}/\text{m}^3} = 0.000005\ \text{m}^3 = 0.005\ \text{L} = 5\,\text{ml} \qquad (3\text{-}2)$$

5 ml of PCBs in transformer oil (Figure 3-6) was sampled using a measuring cylinder and poured into a vial. Each PCB sample was vigorously shaken and used to contaminate the soil sample.

3.2.3 SOIL AND BALLAST STONE PREPARATION

Two types of soil and one ballast stone samples were used in the experimentation. The soil samples were sieved using a 200 mm sieve with an aperture size of 3350 µm to remove any stones and vegetation from the soil (Figure 3-2). The sieved soil (1kg) was mixed with oil and then placed into the reactor for ozonation. The height of the soil sample was maintained at approximately 5 mm to ensure that the ozone gas was able to reach the particles at the base of the sample tray. The soil samples were then thoroughly mixed before the testing process. Hayes (2006) stated that due to the hydrophobic nature of PCBs, it needs to be adequately mixed with the soil in order for the contaminants to effectively react with the soil.

Figure 3-2 Sieving of soil

3.2.4 ANALYSIS OF SOIL SAMPLES

The two soil samples (Figure 3-3 and Figure 3-4) and the one ballast stone sample (Figure 3-5) were analysed by the Agricultural Research Institute. Table 3-1 shows the soil characteristics and Table 3-2 shows the mineral composition of the ballast stones.

Figure 3-3 Soil Sample A

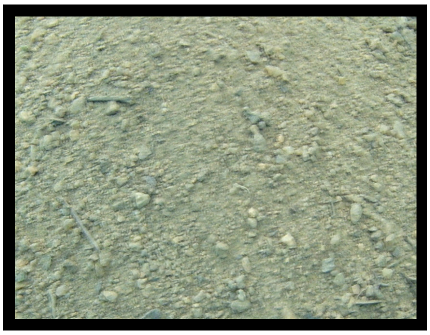

Figure 3-4 Soil Sample B

Figure 3-5 Weighed Ballast Stones

Figure 3-6 Labelled vials containing different ranges of PCBs

Table 3-1 presents the soil characteristics for Soil A and B. Soil A was dark brown in colour (Figure 3-3) and contained a moisture content of 0.19 % compared to 0.02 % of Soil B. Soil B was light brown in colour and more sandy than soil A (Figure 3-4).

The pH for soil sample A and B was 7.76 and 6.50. Vollmuth et al. (1995) reported that the pH had no influence on the degradation of Polyaromatic Hydrocarbon (PAH) and Chlorinated Phenols (CP).

Particle size distribution percentages for soil sample A and soil sample B can be seen in table 3-1.

Table 3-1 Soil Characteristics

Soil Type	Particle-size distribution (%)			pH	Moisture (%)	Exchange acidity cmol(+)/kg
	Silt <0.002mm %	Sand (0.05-0.002mm)%	Clay (2-0.05mm)%			
Soil A	18	50	32	7.76	0.19	0
Soil B	26.38	59.62	14	6.5	0.02	0.162

Table 3-1 shows that soil sample B had a higher percentage of sand compared to soil sample A.

Table 3-2 Mineral composition of ballast stones

Minerals	**Composition (%)**
Quartz	74
Mica	6
Feldspar	18
Smectite	1
Kaolinite	1

3.3 OZONE ANALYSER

A portable Murco detector was hired from Ozone Service Industries to ensure a safe working environment during the experimentation.

3.4 EXPERIMENTAL EQUIPMENT

The experimental reactor was operated as an open flow system. The ozonation tests were conducted outdoors to ensure that there was good air circulation in order to maintain a safe working environment. The ozone generator has a capability of producing ozone from either air or oxygen**.** For this study, air was used to produce ozone as the quantities of oxygen required for on-site treatment would not be cost effective to transport to site.

Javorska et al. (2009) reported that ozone gas has been reported as a promising technique to remove contaminants such as hydrocarbons, polyaromatic hydrocarbons, diesel fuels, pesticides and chlorinated solvents from soil even with a presence of geological material in soil. Ozone gas was produced by the generator and was piped (teflon piping) to a stainless steel manifold with three outlets (Figure 3-7). The manifold ensured an even distribution of ozone gas onto the contaminated soil samples. A PVC pipe was fitted onto the top of the hood to allow excess ozone and any by-products which may have formed during the ozonation process to exit safely into the atmosphere. The ozone levels were carefully monitored and the importance of monitoring the ambient ozone concentration and a safe working environment was discussed in chapter two of this study. One sample could only be ozonated at a time due to the size of the experimental equipment. The sample was placed on a tray and covered with the hood to ensure maximum contact of ozone with the PCB containing sample. The ozonated samples were carefully bagged for further analysis (Figure 3-9 and Figure 3-10). Figure 3-8 shows a schematic of the experimental ozone equipment.

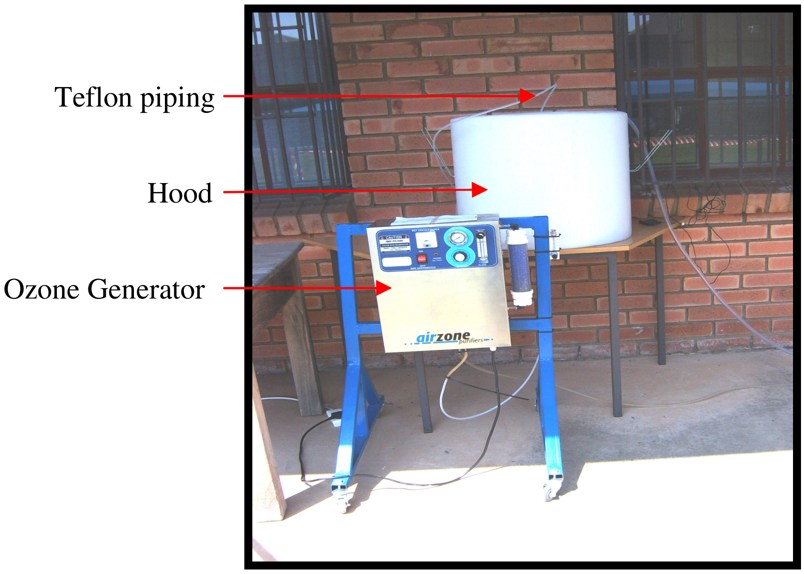

Figure 3-7 Ozone unit and hood used for testing

3.4.1 Ozone Generator Set-up

The ozone unit was calibrated by the supplier to produce total gas flow rates of 0.4, 0.5 and 0.6 l/min while the ozone concentration of 65 mg/l was maintained (according to the supplier of the ozone generator unit) for a period of 60 minutes.

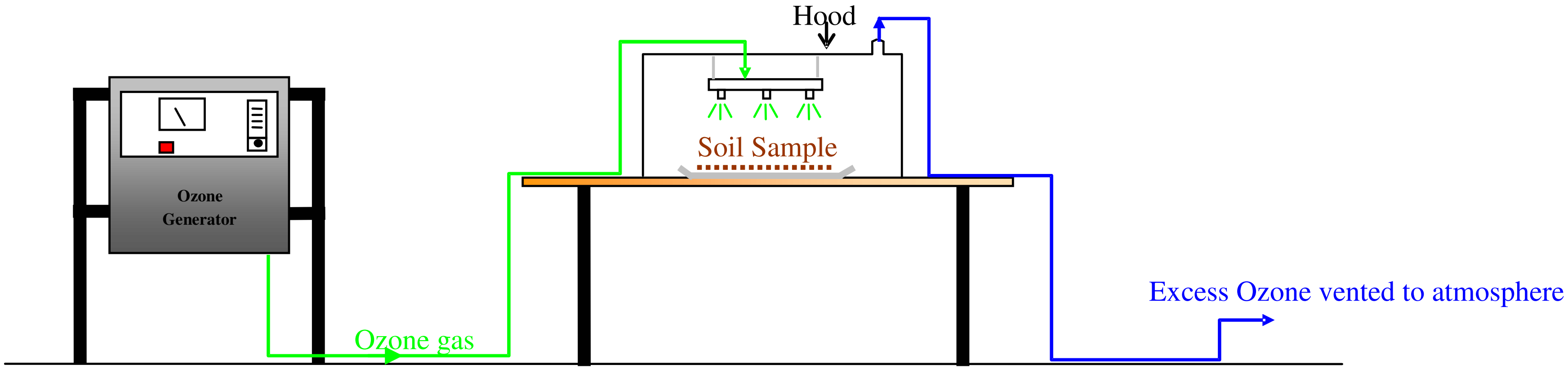

Figure 3-8 Experimental ozone equipment

3.5 SUMMARY OF TEST METHODOLOGY

The method and technique for the experimental process was developed specifically for this particular research and is as follows:

- The soil samples were sieved using a 200 mm diameter sieve. The large stones and vegetation were removed from the soil.
- The soil and ballast stones was weighed into 1kg samples and placed into a tray.
- 5 ml of transformer oil with a PCB concentration was mixed with soil and ballast stone samples to ensure an even distribution of the sample.
- The samples were left in the laboratory over night for the PCBs in soil to be absorbed into the soil.
- Before testing, samples were again mixed and placed into the test unit and the ozone unit was switched on for testing.
- Samples were ozonated for a period of 60 minutes using total gas flow rates of 0.4, 0.5 and 0.6 l/min.
- After testing the unit was switched off and the sample remained in the hood for a period of 20 minutes to ensure that the atmosphere around the test unit was safe.
- A portable ozone analyser was used to monitor the ozone concentration escaping from the test unit and was closely monitored.
- After approximately 1 hour and 20 minutes the sample was removed from the hood and each sample was mixed thoroughly.
- Cassidy et al. (2002) concluded that the major oxidation products produced from the ozonation of soil contaminated with PCBs is benzoic acids. He further substantiated that in his study no attempt was made to identify the presence of alcohols, aldehydes and ketones as previous studies had showed that the formation of these products during the ozonation of soil containing PCBs.
- Hayes (2006) concluded that during the ozonation of soil contaminated PCBs other reactions may occur however, the by-products produced during this reaction would benon-hazardous. He further concluded that carbon dioxide and water are the final products of this process.
- The processed samples were labelled and analysed using Gas Chromatography Electron Capture Detection (GC-ECD).

3.6 GAS CHROMATOGRAM ELECTRON CAPTURE DETECTION (GC-ECD) ANALYSIS

Samples were analysed using a GC-ECD by the South African Bureau of Standards (SABS). SABS is an accredited laboratory by SANAS ISO 17025 and uses the Association of Analytical Communities (AOAC) official method 970.52M, 1995 (Amended) for PCB analysis.

The GC-MS has been widely known as a gold standard for forensic substance identification because it is used to perform a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample. The PCBs were quantified by comparing the peak areas of selected peaks in the sample chromatograms with that of the same peaks in the standard chromatograms.

Gas chromatography makes use of capillary column i.e. length, diameter and film thickness as well as the phase properties. The molecules with different retension times passes from the gas chromatograph which allows the mass spectrometer tocapture, ionise, accelerate, deflect and detect the all ionized molecules separately.

The presence of PCBs was confirmed when the mass spectra peaks in the standard was compared with the peaks in the sample thus establishing, the PCB concentrations in each samples. The limit of quantification was 0.01 mg/kg with a recovery range of 93-100%.

Figure 3-9 Soil samples after ozonation

Figure 3- 10 Ballast stone samples after ozonation

3.7 CONCLUSION

This chapter discussed the sampling for soil, oil and ballast stones for the experimentation process which lead to the following:

- A special method or technique for the experimentation was developed for this particular study.
- All safety aspects were taken into consideration during the experimentation.
- A test unit was designed and built for the testing process to ensure that ozone made sufficient contact with the PCBs in 1 kg of soil (height of soil was approximately 5 mm).
- This chapter was concluded with the analysis of samples using GC-ECD to detect PCBs residuals in the soil and ballast stones after ozonation.

CHAPTER FOUR

ANALYSIS AND DISCUSSION OF RESULTS

The previous chapter discussed the sampling preparation, experimentation process and the test methodology which was developed for this particular study. The objective of this chapter is to analyse, interpret and discuss the experimental results for this study and also includes calculations for ozone self decomposition and the determination of the kinetic mechanism of the ozonation process. Two soil and one ballast stone sample were contaminated with three different concentrations of PCBs and exposed to three different ozone gas flow rates. In a study conducted by Javorska et al. (2009), it was identified that the soils Chernozem and Fluisol were of similar soil characteristics to the Eskom Soil A and B samples. The Chernozem and Fluisol soils which contained a PCB concentration of 0.7 ppm were incubated for 6 and 36 months. The results of this study were therefore used together with Javorska et al. (2009) results to determine the kinetic mechanism.

Section 4.1 addresses the self decomposition of ozone using the Shin et al. (2001) model. Section 4.2 discusses the stoichiometric requirement of PCBs. Section 4.3 investigates the kinetic mechanism of the ozonation process. Section 4.4 calculates the order of reaction for the ozonation process.

4.1 CALCULATION OF OZONE SELF DECOMPOSITION

This section examines ozone self decomposition using the Shin model. Shin et al. (2004) explained that ozone can be consumed in the following manner for batch experiments: “empty column self decomposition in the gas phase and at the surfaces of the system, catalytic decomposition through interaction with soil particles and interactions with moisture, Soil Organic Matter (SOM) and Soil Inorganic Matter (SIM)”. He then explained that these effects were “expressed by the kinetic rate for empty-column ozone self-decomposition and catalytic decomposition which was promoted by the surface of soil particles and interactions of ozone with SOM and SIM”, Shin et al. (2004).

Shin et al. (2004) during his experimentation established the self decomposition of ozone and stated “ozone in an empty-column cycling batch experiment decreased with time which resulted in ozone self decomposition, catalytic reactions at the surfaces of the system and reacts with the moisture at the system”.

The ozone concentration after self decomposition was therefore calculated based on the first-order decay reaction determined by Shin et al. (2004).

$$\frac{d[O_3]}{dt} = -k_1[O_3] \qquad (4\text{-}1)$$

where k_1 is the self decomposition rate constant (s^{-1}) equal to 7.7 X 10^{-6} s^{-1}. Initial ozone concentration $[O_3]_0$ is 65 mg/l. Integration of Equation 4-1 from t=0 $[O_3]$ = $[O_3]_0$ to t equal to the reaction time which results in expression (4-2).

$$-\ln\left(\frac{[O_3]}{[O_3]_o}\right) = k_1 t \qquad (4\text{-}2)$$

With the soil in the system Shin et al. (2004) further reported that ozone in small quantities was consumed quite quickly resulting in the self decomposition of ozone. This statement further supports that ozone decomposed before and after it reacted with the soil thus resulting in ozone self decomposition. In the equation 4-3, W_s is regarded as the weight of 1 kilogram (kg) of soil. The Available Concentration of Soil Organic Matter (AOM) is 140 µg/g of soil. AOM is a fixed value for the ozone degradation rate; k_3 is the apparent ozone-SOM interaction rate constant(s^{-1}). k_1, k_2, the average of k_3, and the AOM value were extracted from the Shin et al. (2004). Table 4-1 summarises the data used in the calculation of ozone self decomposition.

Table 4-1 Data used in the ozone self decomposition calculation

W_s (kg)	Tank Volume (m^3)	k_1 (s^{-1})	k_2 (m^3/kg/s)	k_3 (m^3/kg/s)	AOM (kg/kg)	Reaction t (s)
1	0.0981748	0.0000077	0.000000719	0.181	0.00014	3600

Expression 4-3 resulted from Shin et al. (2004) for the catalytic decomposition of ozone in soil:

$$-\ln(\frac{[O_3]}{[O_3]_0}) = (k + k_2\frac{W_s}{V} + k_3\frac{W_s}{V}[AOM]) \tag{4-3}$$

Expression 4-3 shows that ozone self decomposed from 65 mg/l to 24.31 mg/l after it reacted with the contaminated soil for a period of 60 minutes. This further concludes that the self decomposition of ozone and the reaction of ozone with the soil occurred simultaneously.

4.2 STOICHMETRIC REQUIREMENT FOR PCBS

In order to calculate whether ozone was in excess after the experimentation the total number of moles of ozone required to completely destroy PCBs was calculated. Hayes (2006) showed that 2 moles of ozone was required to break down 1 mole of PCB based on the stoichiometric requirement. The number of moles of PCBs in the soil sample was calculated as follows:

By using oil with the highest PCB content of 600 ppm (the most conservative case), the initial mass of PCBs per 1 kg of soil is:

$$m_{PCBs} = 600\,\text{ppm X } 5\,\text{ml X } 0.84\,\text{g oil/ml X}10^{-6} = 0.00252\,\text{g} \tag{4-4}$$

$$n_{PCBs} = \frac{\text{Initial PCB Concentration in 1kg soil}}{\text{Average molar mass of PCBs}} \tag{4 - 5}$$

$$= \frac{0.00252\,\text{g}}{331.99\,\text{g/mol}} = 7.59\,\text{x}\,10^{-6}\ \text{moles}$$

The number of PCBs calculated was $7.59\,\text{x}\,10^{-6}$ moles therefore the number of moles of ozone required to degrade 1 mole of PCB based on the stoichiometric ozone requirement was $1.52\text{x}10^{-5}$ moles. The number of moles of ozone available after self decomposition during an experimental test for a period of 60 minutes was calculated as follows:

$$\begin{aligned} n_{\text{ozoneexperiment}} &= \frac{\text{Airflow X Ozone concentration after experiment X Time}}{\text{molar mass of ozone (M)}} \\ &= \frac{0.4\ \text{l/min X } 0.024315\ \text{g/l X } 60\ \text{minutes}}{48\ \text{g/mol}} \qquad (4\text{-}6) \\ &= 0.012158\ \text{moles} \end{aligned}$$

The above expression (4-6) proves that ozone is well in excess of the stoichiometric requirements for the destruction of PCB's in soil (by 79983.79%) and its concentration does not have to be considered in the kinetic model.

4.3 THE INVESTIGATION OF THE KINETIC MECHANISM OF THE OZONATION PROCESS

In section 4.2, it was proven that ozone is in excess after it reacts with the PCBs in the soil. This section investigates the kinetic mechanism of the ozonation process. The PCBs residuals results after the ozonation process are shown in Table 4-2 and Figure 4-1. Samples were ozonated for a period of 60 minutes with total gas flow rates of 0.4 l/min, 0.5 l/min and 0.6 l/min for Soil A, B, and Ballast Stones.

Table 4-2 PCB residual in soil in ppm after ozonation for a period of 60 minutes

Sample Name	Ozone Flow rates		
	0.4 l/min	0.5 l/min	0.6 l/min
Soil A 50 ppm	0.01	0	0.9
Soil A 200 ppm	0.82	1.03	0.99
Soil A 600 ppm	0.97	1.07	0.07
Soil B 50 ppm	0.05	0.09	0
Soil B 200 ppm	1.26	0.62	0.63
Soil B 600 ppm	0.58	0.66	0.43
Ballast Stones 50 ppm	0	0.03	0.03
Ballast Stones 200 ppm	0.45	0.68	0.99
Ballast Stones 600 ppm	0.92	0.82	0.87

The PCB residuals in the soil and ballast stones samples showed that as the ozone flow rates increased from 0.4-0.6 l/min, the PCB residuals were within the same range for all three total gas flow rates; this indicates that the destruction of PCBs showed no dependence on the increasing total gas flow rates as ozone was in excess. The PCB residuals are similar with some exceptions i.e. for soil A at 50 ppm and 200 ppm with a total gas flow rate of 0.6 l/min and soil B at 0.4 l/min, this was as a result of an experimental error with a maximum deviation of 0.5 ppm but the deviations are normally between 0.1ppm and 0.2 ppm.

Soil B showed a higher PCB removal compared to Soil A. This could be due to the fact the Soil B had a higher portion of fine particles which may have increased the surface area available for the reaction. Soil A and Chernozem had a higher clay content compared to Soil B and Fluvisol which had a higher sand content. Soil B showed a higher PCB removal compared to Soil A. Javorska et al. (2009) further reported that since Fluvisols have larger pore sizes compared to clay soils such as Chernozem, a higher level of PCB7 removal was reported in Fluvisol.

The PCB concentration for all the soil samples decreased significantly within a period of 60 minutes of ozonation. The ballast stones results could not be compared to both Soil A and B, Chernozem and Fluvisol due to different soil and mineral compositions.

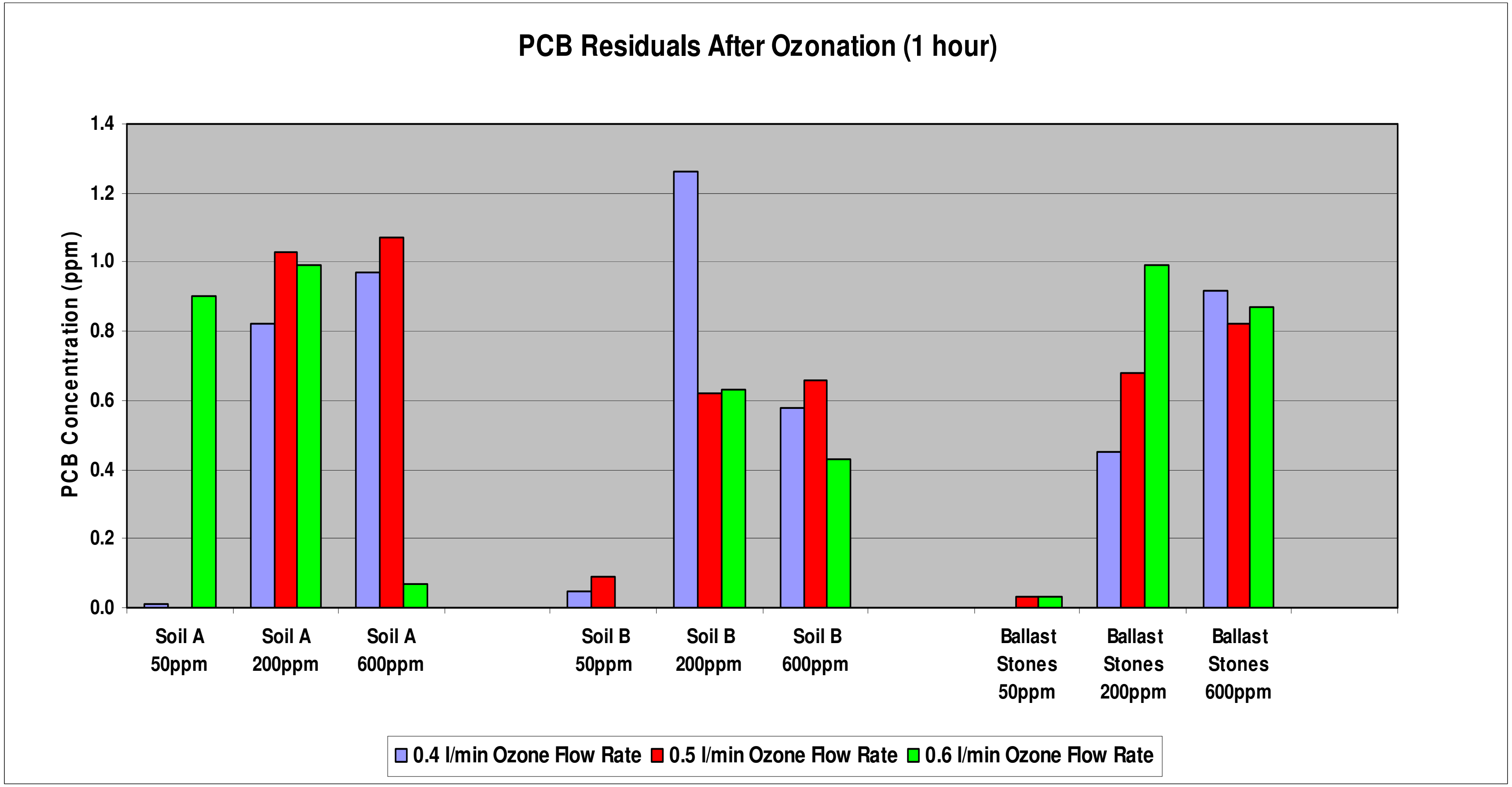

Figure 4-1 PCB residuals (ppm) after ozonation in soil and ballast stones

4.4 CALCULATION FOR THE ORDER REACTION

For the determination of the kinetic mechanism for the reaction of PCBs with ozone, data from Javorska et al. (2009) was used together with results from this study based on the following observations:

1. Similar soils were used in Javorska et al. (2009), i.e. Chernozerm and Fluvisol had similar soil characteristics to Soil A and B (Table 4-3).
2. The gas flow rate used was 0.45 l/min which was similar to our study i.e. 0.4, 0.5 and 0.6 l/min.
3. The initial PCB concentration was 700 ug/kg for Chernozem and Fluvisol, compared initial PCB concentration of 845 ug/kg for soil A and B.

Table 4-3 Percentage composition of Soil A, B, Chernozem and Fluvisol

Soil	**Silt**	**Sand**	**Clay**
Soil A	18	50	32
Soil B	26.38	59.62	14
Chernozem	29	37.5	33.5
Fluvisol	6	83	11

The percentage soil characteristics for Chernozem and Fluvisol were averaged as both incubation times of 6 and 36 months were included in this study. The values in Table 4-4 presents the initial PCB concentration before it was added into soil samples (Soil A, B, Chernozerm and Fluvisol). For the determination of the order of reaction the PCB concentrations were re-calculated to the same base of initial PCB concentrations (Table 4-5). Soil A and B were exposed to ozone flow rates of 0.5 l/min for a period of 60 minutes. Chernozerm and Fluvisol were incubated for a period of 6 and 36 months and were exposed to an ozone flow rate of 0.45 l/min for 2.5, 4 and 6 hour periods, Javorska et al. (2009).

Table 4-4 Initial PCB Concentration for Soil A, B, Chernozem and Fluvisol

Soil Samples	Mass of oil in soil (g)	Volume of oil (l)	Initial PCB Concentration (µg/kg soil)	Initial PCB Concentration (ppm)
Soil A	4.225	0.005	845	200
Soil B	4.225	0.005	845	200
Chernozem			700	0.7
Fluvisol			700	0.7

The PCB residual results (Table 4-5) for Chernozerm and Fluvisol for periods 1, 2.5, 4 and 6 hours were combined and averaged for the calculation of the kinetic mechanism of the ozonation process in order to determine the order of reaction.

Table 4-5 The PCB residual in soil samples for Soil A, B, Chernozem and Fluvisol

Sample	1 hour (µg/kg)	2.5 hours (µg/kg)	4 hours (µg/kg)	6 hours (µg/kg)
Soil A	819			
Soil B	624			
Chernozem		560	560	525
Fluvisol		577.50	451.5	343

The reaction order of a batch reactor can be determined by the differential, integral or the least squares method (Fogler, 1993). Based on the calculation of the kinetic mechanism the reaction order can be zero, first or second order. The reaction proceeds with A which was regarded as PCBs and B regarded as Ozone.

$$A + B \rightarrow \text{Products}$$

In expression 4-7 both the reactants and products is used to calculate the order of reaction

$$-r_A = -kC_A{}^{\alpha}C_B{}^{\beta} \qquad (4\text{-}7)$$

Where, C_A is the concentration of PCBs and C_B is the concentration of ozone. It was proven in section 4-2 (Expression 4-6) that C_B is in excess after the ozonation process. The change in concentration of C_B is minimal during the reaction, therefore C_B is assumed to be constant thus expression 4-7 can be simplified to expression (4-8);

$$r_A = -k_2 C_A{}^{\alpha} \tag{4-8}$$

For the determination of the first-order chemical reaction expression 4-8 can be simplified to expression 4-9.

$$-\frac{dC_A}{dt} = kC_A \tag{4-9}$$

Expression 4-9 is integrated which results in expression 4-10.

$$\ln C_A = \ln C_{A_o} - k_2 t \tag{4-10}$$

where C_{A_o} is the initial concentration of PCBs. Figure 4-2 shows a plot of experimental values of logarithm of residual PCBs concentration versus time. The plot is a straight line which indicates that the order of reaction is 1.

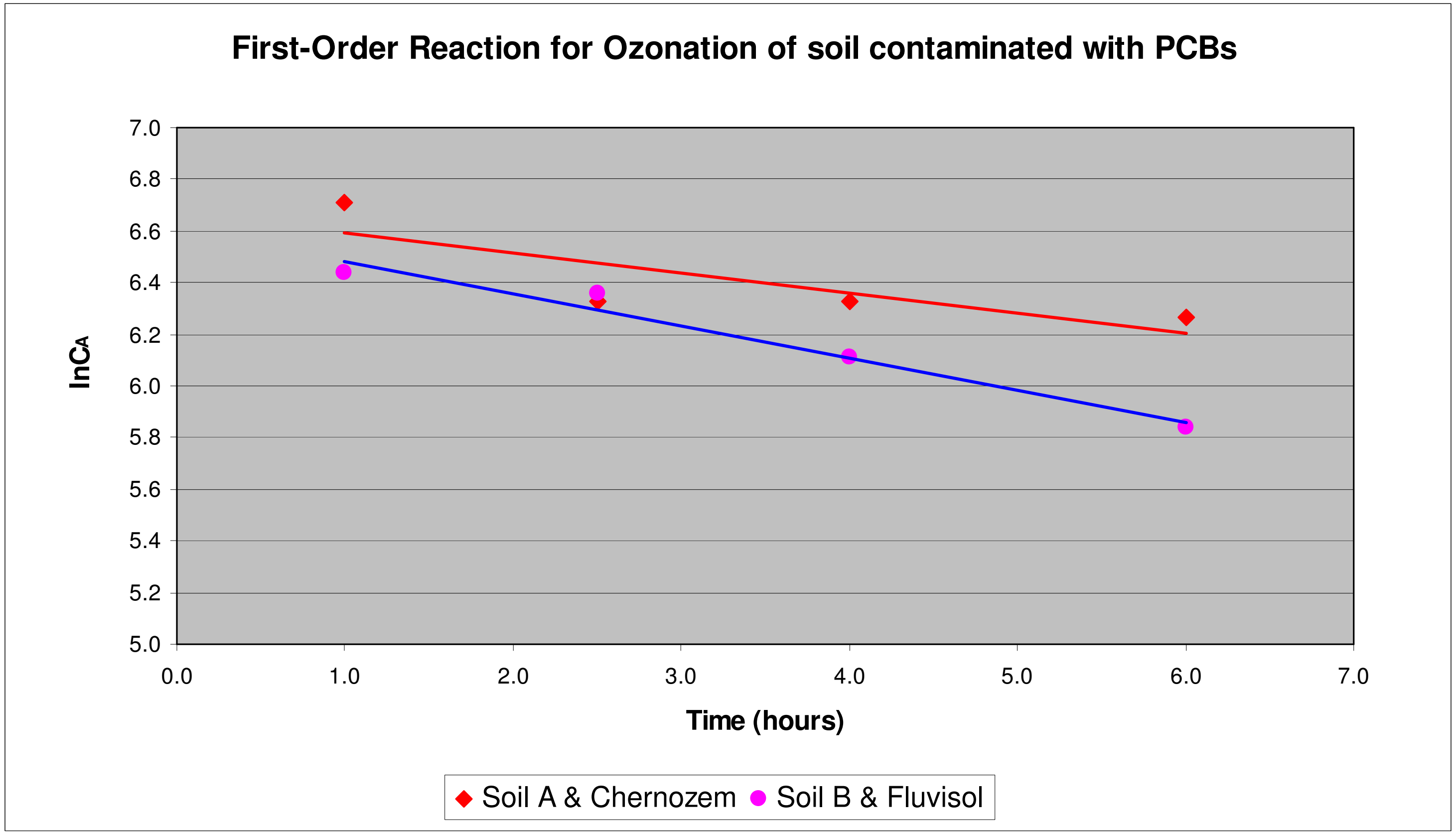

Figure 4-2 First-Order Reaction of Soil A & Chernozem and Soil B & Fluvisol

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

The previous chapter analysed, interpreted and discussed the results for this study. This chapter provides the conclusions and recommendations. The objective of this study was to establish whether ozone without the addition of chemicals, could effectively destroy PCBs present in soil and ballast stones samples while exposed to ozone at three different flow rates. In this study ozone was produced from air. The literature study identified that incineration is widely used in South Africa and world-wide for the treatment soil contaminated with PCBs. In this study, a new methodology for the testing process was developed. Safe conditions were exercised according to the Food and Drug Administration (FDA) on the use of ozone gas.

The results of this study show that ozone can reduce the concentration of PCBs in soil and ballast stones with the total gas flow rates of 0.4, 0.5 and 0.6 l/min. The results of this study were used together with the results of a study conducted by Javorska et al. (2009). The ozone self decomposition based on the first-order decay reaction by Shin et al. (2004) was taken into consideration.

5.1 LIMITATION OF THIS STUDY

The main limiting factor for this study was budgetary constraints, and as a result of this only a limited number of tests could be conducted during the experimentation process. However, valuable results were obtained from this study. A second limiting factor was the cost for hiring an online ozone analyser from Ozone Services Industries for the entire experimentation process; this unit was hired for set-up of the testing process for the different ozone flow rates and could not be used for the entire testing process.

5.2 CONCLUSIONS

- The results obtained from this study show that ozone without the addition of chemicals can reduce the concentration of PCBs present in soil and ballast stones to an acceptable level. The PCB concentration for all the soil samples decreased significantly within a period of 60 minutes of ozonation. A method was developed for the treatment of soil contaminated with three ranges of PCBs (50, 200, 600 ppm) for a period of 60 minutes using total gas flow rates of 0.4, 0.5 and 0.6 l/min.
- The PCB residuals in the soil and ballast stones samples showed that as the ozone flow rates increased from 0.4-0.6 l/min, the PCB residuals were within the same range for all three total gas flow rates; this indicates that the destruction of PCBs showed no dependence on the increasing total gas flow rates as ozone was in excess. The PCB residuals are similar with some exceptions i.e. for soil A at 50 ppm and 200 ppm with a total gas flow rate of 0.6 l/min and soil B at 0.4 l/min, this was as a result of an experimental error with a maximum deviation of 0.5 ppm but the deviations are normally between 0.1ppm and 0.2 ppm.
- Residual concentrations decreased for all total gas flow rates and for all initial PCBs concentrations with some exceptions which was caused by an experimental error.
- Soil A and B had similar soil characteristics when compared to Chernozem and Fluvisol. Soil A and Chernozem had a higher clay content compared to Soil B and Fluvisol which had a higher sand content. Soil B showed a higher PCB removal compared to Soil A. Javorska et al. (2009) further reported that since Fluvisols have larger pore sizes compared to clay soils such as Chernozem, a higher level of PCB7 removal was reported in Fluvisol.
- The ballast stones results could not be compared to both Soil A and B, Chernozem and Fluvisol due to different soil and mineral compositions.
- It was concluded that before ozone reacts with the soil, it self decomposes. The self decomposition of ozone and the reaction of ozone with the soil occurred simultaneously. The ozone self decomposition was therefore calculated based on the first-order decay reaction obtained from Shin et al. (2004). Ozone self decomposed from the initial ozone concentration of 65 mg/l to 24.31 mg/l after it reacted with the contaminated soil for a period of 60 minutes thus proving that ozone was in excess. The self decomposition takes place in the space ahead of the layer of soil in the reactor.
- The data was then trended with zero, first and second reaction order equations, which showed that the best fit was obtained with the first-order reaction equation.

- The literature study identified that the final products of the ozonation of PCBs are carbon dioxide and water and that any products formed after this process could possibly be degraded by the soil natural microorganisms.

5.3 RECOMMENDATIONS

Based on this research, the following are recommended:

- It is recommended that ozone be used for the treatment of PCB contaminated soil at Eskom substations. A larger mobile test unit must be designed and fabricated with ozone monitors. An on-site analyser is required to determine PCB concentrations after ozonation.
- It is also recommended that further research be conducted with enzymes and micro-organisms to reduce the PCB residual concentration after the ozonation process.

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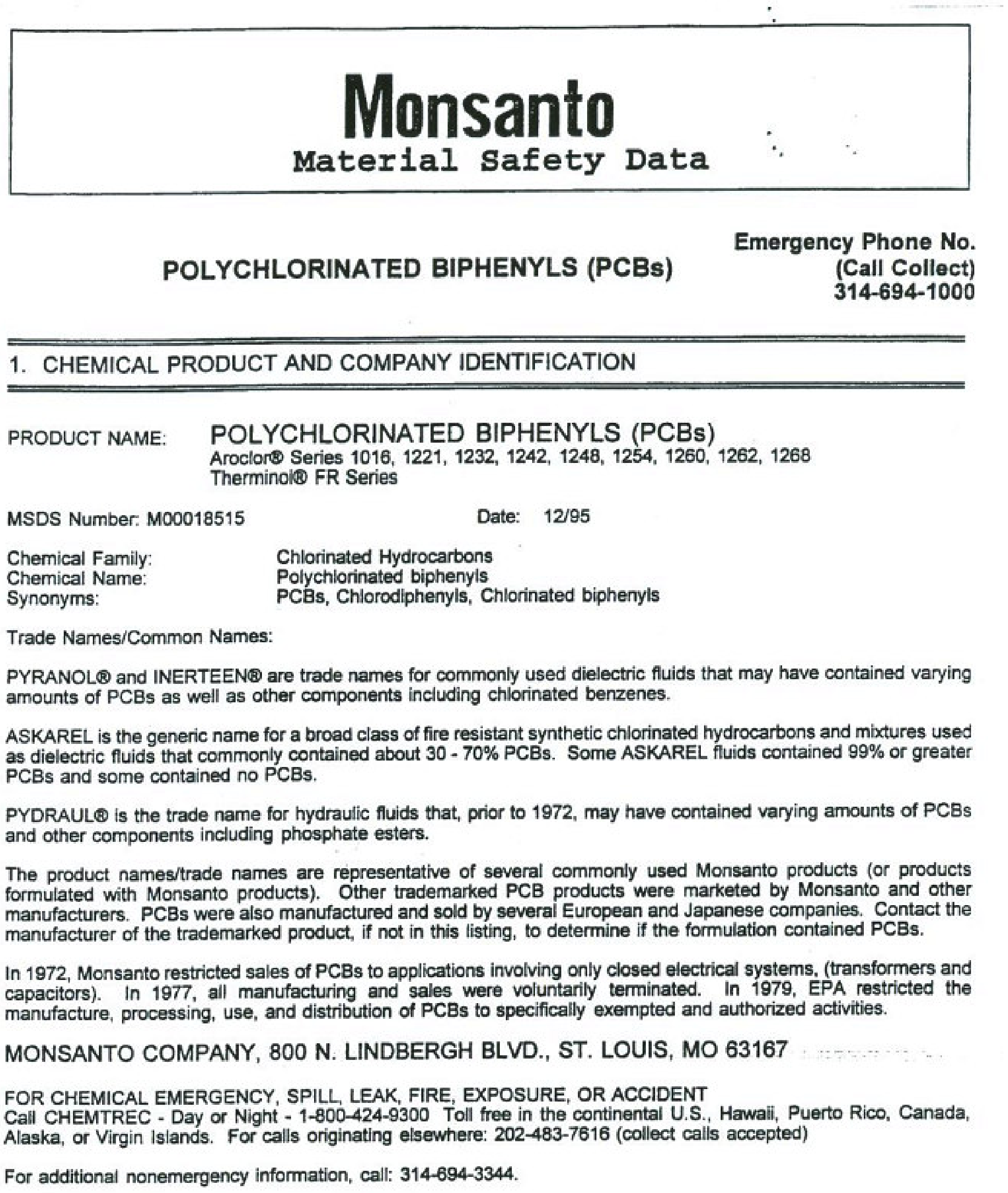
APPENDICES

APPENDIX A - PCB MATERIAL SAFETY DATA SHEET (MSDS)



Monsanto

Material Safety Data

POLYCHLORINATED BIPHENYLS (PCBs)

Emergency Phone No.
(Call Collect)
314-694-1000

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: **POLYCHLORINATED BIPHENYLS (PCBs)**
Aroclor® Series 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268
Therminol® FR Series

MSDS Number: M00018515 Date: 12/95

Chemical Family:	Chlorinated Hydrocarbons
Chemical Name:	Polychlorinated biphenyls
Synonyms:	PCBs, Chlorodiphenyls, Chlorinated biphenyls

Trade Names/Common Names:

PYRANOL® and INERTEEN® are trade names for commonly used dielectric fluids that may have contained varying amounts of PCBs as well as other components including chlorinated benzenes.

ASKAREL is the generic name for a broad class of fire resistant synthetic chlorinated hydrocarbons and mixtures used as dielectric fluids that commonly contained about 30 - 70% PCBs. Some ASKAREL fluids contained 99% or greater PCBs and some contained no PCBs.

PYDRAUL® is the trade name for hydraulic fluids that, prior to 1972, may have contained varying amounts of PCBs and other components including phosphate esters.

The product names/trade names are representative of several commonly used Monsanto products (or products formulated with Monsanto products). Other trademarked PCB products were marketed by Monsanto and other manufacturers. PCBs were also manufactured and sold by several European and Japanese companies. Contact the manufacturer of the trademarked product, if not in this listing, to determine if the formulation contained PCBs.

In 1972, Monsanto restricted sales of PCBs to applications involving only closed electrical systems, (transformers and capacitors). In 1977, all manufacturing and sales were voluntarily terminated. In 1979, EPA restricted the manufacture, processing, use, and distribution of PCBs to specifically exempted and authorized activities.

MONSANTO COMPANY, 800 N. LINDBERGH BLVD., ST. LOUIS, MO 63167

FOR CHEMICAL EMERGENCY, SPILL, LEAK, FIRE, EXPOSURE, OR ACCIDENT
Call CHEMTREC - Day or Night - 1-800-424-9300 Toll free in the continental U.S., Hawaii, Puerto Rico, Canada, Alaska, or Virgin Islands. For calls originating elsewhere: 202-483-7616 (collect calls accepted)

For additional nonemergency information, call: 314-694-3344.

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemically, commercial PCBs are defined as a series of technical mixtures, consisting of many isomers and compounds that vary from mobile, oily liquids to white crystalline solids and hard noncrystalline resins. Technical products vary in composition, in the degree of chlorination, and possibly according to batch.

The mixtures generally used contain an average of 3 atoms of chlorine per molecule (42% chlorine) to 5 atoms of chlorine per module (54% chlorine). They were used as components of dielectric fluids in transformers and capacitors. Prior to 1972, PCB applications included heat transfer media, hydraulic, and other industrial fluids, plasticizers, carbonless copy paper, paints, inks, and adhesives.

Component	CAS No.
chlorinated biphenyl	1336-36-3
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1262	37324-23-5
Aroclor 1268	11100-14-4

There are also CAS Numbers for individual PCB congeners and for mixtures of Aroclor® products.

PCBs are identified as hazardous chemicals under criteria of the OSHA Hazard Communication Standard (29 CFR Part 1910.1200). PCBs have been listed in the International Agency for Research on Cancer (IARC) Monographs (1987)-Group 2A and in the National Toxicology Program (NTP) Annual Report on Carcinogens (Seventh).

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

Appearance and Odor: PCB mixtures range in form and color from clear to amber liquids to white crystalline solids. They have a mild, distinctive odor and are not volatile at room temperature. Refer to Section 9 for details.

WARNING!
CAUSES EYE IRRITATION
MAY CAUSE SKIN IRRITATION

PROCESSING AT ELEVATED TEMPERATURES MAY RELEASE VAPORS OR FUMES WHICH MAY CAUSE RESPIRATORY TRACT IRRITATION

POTENTIAL HEALTH EFFECTS

Likely Routes of Exposure:	Skin contact and inhalation of heated vapors
Eye Contact:	Causes moderate irritation based on worker experience.
Skin Contact:	Prolonged or repeated contact may result in redness, dry skin and defatting based on human experience. A potential exists for developing chloracne. PCBs can be absorbed through intact skin.
Inhalation:	Due to the low volatility of PCBs, exposure to this material in ambient conditions is not expected to produce adverse health effects. However, at elevated processing temperatures, PCBs may produce a vapor that may cause respiratory tract irritation if inhaled based on human experience.
Ingestion:	No more than slightly toxic based on acute animal toxicity studies. Coughing, choking and shortness of breath may occur if liquid material is accidentally drawn into the lungs during swallowing or vomiting.

Other: Numerous epidemiological studies of humans, both occupationally exposed and nonworker environmentally exposed populations, have not demonstrated any causal relationship between PCB exposure and chronic human illnesses such as cancer or neurological or cardiovascular effects. PCBs at high dosage can cause skin symptoms; however, these subside upon removal of the exposure source.

Refer to Section 11 for toxicological information.

4. FIRST AID MEASURES

IF IN EYES, immediately flush with plenty of water for at least 15 minutes. If easy to do, remove any contact lenses. Get medical attention. Remove material from skin and clothing.

IF ON SKIN, immediately flush the area with plenty of water. Wash skin gently with soap as soon as it is available. Get medical attention if irritation persists.

IF INHALED, remove person to fresh air. If breathing is difficult, get medical attention.

IF SWALLOWED, do NOT induce vomiting. Rinse mouth with water. Get medical attention. Contact a Poison Control Center. NEVER GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON.

NOTE TO PHYSICIANS: Hot PCBs may cause thermal burn. If electrical equipment arcs between conductors, PCBs or other chlorinated hydrocarbon dielectric fluids may decompose to produce hydrochloric acid (HCl), a respiratory irritant. If large amounts are swallowed, gastric lavage may be considered.

5. FIRE FIGHTING MEASURES

Flash Point: 284 degrees F (140 degrees C) or higher depending on the chlorination level of the Aroclor product

Fire Point: 349 degrees F (176 degrees C) or higher depending on the chlorination level of the Aroclor product

NOTE: Refer to Section 9 for individual flash points and fire points.

Extinguishing Media: Extinguish fire using agent suitable for surrounding fire. Use dry chemical, foam, carbon dioxide or water spray. Water may be ineffective. Use water spray to keep fire-exposed containers or transformer cool.

PCBs are fire-resistant compounds. They may decompose to form CO, CO2, HCl, phenolics, aldehydes, and other toxic combustion products under severe conditions such as exposure to flame or hot surfaces.

Dielectric fluids having PCBs and chlorinated benzenes as components have been reported to produce polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs) during fire situations involving electrical equipment. At temperatures in the range of 600-650 degrees C in the presence of excess oxygen, PCBs may form polychlorinated dibenzofurans (PCDFs). Laboratory studies under similar conditions have demonstrated that PCBs do not produce polychlorinated dibenzo-p-dioxins (PCDDs).

Federal regulations require all PCB transformers to be registered with fire response personnel.

If a PCB transformer is involved in a fire-related incident, the owner of the transformer may be required to report the incident. Consult and follow appropriate federal, state and local regulations.

Fire Fighting Equipment: Fire fighters and others exposed to products of combustion should wear self-contained breathing apparatus. Equipment should be thoroughly decontaminated after use.

6. ACCIDENTAL RELEASE MEASURES

Cleanup and disposal of liquid PCBs and other PCB items are strictly regulated by the federal government. The regulations are found at 40 CFR Part 761. Consult these regulations as well as applicable state and local regulations prior to any cleanup or disposal of PCBs, PCB items, or PCB contaminated items.

If PCBs leak or are spilled, the following steps should be taken immediately:

All nonessential personnel should leave the leak or spill area.

The area should be adequately ventilated to prevent the accumulation of vapors.

The spill/leak should be contained. Loss to sewer systems, navigable waterways, and streams should be prevented. Spills/leaks should be removed promptly by means of absorptive material, such as sawdust, vermiculite, dry sand, clay, dirt or other similar materials, or trapped and removed by pumping or other suitable means (traps, drip-pans, trays, etc.).

Personnel entering the spill or leak area should be furnished with appropriate personal protective equipment and clothing as needed. Refer to Section 8 for personal protection equipment and clothing.

Personnel trained in emergency procedures and protected against attendant hazards should shut off sources of PCBs, clean up spills, control and repair leaks, and fight fires in PCB areas.

Refer to Section 13 for disposal information and Sections 14 and 15 for information regarding reportable quantity, and Section 7 for marking information.

7. HANDLING AND STORAGE

Care should be taken to prevent entry into the environment through spills, leakage, use vaporization, or disposal of liquid or containers. Avoid prolonged breathing of vapors or mists. Avoid contact with eyes or prolonged contact with skin. If skin contact occurs, remove by washing with soap and water. Following eye contact, flush with water. In case of spillage onto clothing, the clothing should be removed as soon as practical, skin washed, and clothing laundered. Comply with all federal, state, and local regulations.

Federal regulations under the Toxic Substances Control Act require PCBs, PCB items, storage areas, transformer vaults, and transport vehicles to be marked (check regulations, 40 CFR 761, for details).

CAUTION
CONTAINS
PCBs
(Polychlorinated Biphenyls)

A toxic environmental contaminant requiring special handling and disposal in accordance with U.S. Environmental Protection Agency Regulations 40 CFR 761 For Disposal Information contact the nearest U.S. E.P.A. Office

In case of accident or spill, call toll free the U.S. Coast Guard National Response Center
800-424-8802

Also Contact ______
Tel. No. ______

CAUTION —
CONTAINS
PCBs
(Polychlorinated Biphenyls)
FOR PROPER DISPOSAL INFORMATION
CONTACT U.S. ENVIRONMENTAL
PROTECTION AGENCY

Storage: The storage of PCB items or equipment (those containing 50 ppm or greater PCBs) and PCB waste is strictly regulated by 40 CFR Part 761. The storage time is limited, the storage area must meet physical requirements, and the area must be labeled.

Avoid contact with eyes.
Wash thoroughly after handling.
Avoid breathing processing fumes or vapors.
Process using adequate ventilation.

MSDS #: M00018515

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Eye Protection: Wear chemical splash goggles and have eye baths available where there is significant potential for eye contact.

Skin Protection: Wear appropriate protective clothing and chemical resistant gloves to prevent skin contact. Consult glove manufacturer to determine the appropriate type glove for a given application. Wear chemical goggles, face shield, and chemical resistant clothing such as a rubber apron when splashing is likely. Wash immediately if skin is contacted. Remove contaminated clothing promptly and launder before reuse. Clean protective equipment before reuse. Provide a safety shower at any location where skin contact can occur. Wash thoroughly after handling.

ATTENTION! Repeated or prolonged skin contact may cause chloracne in some people.

Respiratory Protection: Avoid breathing vapor, mist, or dust. Use NIOSH/MSHA approved equipment when airborne exposure limits are exceeded. Full facepiece equipment is recommended when airborne exposure limits are exceeded and, if used, replaces the need for face shield and/or chemical splash goggles. Consult respirator manufacturer to determine the type of equipment for a given application. The respirator use limitations specified by NIOSH/MSHA or the manufacturer must be observed. High airborne concentrations may require use of self-contained breathing apparatus or supplied air respirator. Respiratory protection programs must be in compliance with 29 CFR Part 1910.134.

ATTENTION! Repeated or prolonged inhalation may cause chloracne in some people.

Ventilation: Provide natural or mechanical ventilation to control exposure levels below airborne exposure limits (see below). If practical, use local mechanical exhaust ventilation at sources of vapor or mist, such as open process equipment.

Airborne Exposure Limits:

Product: Chlorodiphenyl (42% chlorine)

OSHA PEL: 1 mg/m^3 8-hour time-weighted average - Skin*
ACGIH TLV: 1 mg/m^3 8-hour time-weighted average - Skin*

Product: Chlorodiphenyl (54% chlorine)

OSHA PEL: 0.5 mg/m^3 8-hour time-weighted average - Skin*
ACGIH TLV: 0.5 mg/m^3 8-hour time-weighted average - Skin*

*For Skin notation see Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, American Conference of Government Industrial Hygienists, 1995-1996.

9. PHYSICAL AND CHEMICAL PROPERTIES

PROPERTIES OF SELECTED AROCLORS[1]

PROPERTY	1016	1221	1232	1242	1248	1254	1260
Color (APHA)	40	100	100	100	100	100	150
Physical state	mobile oil	mobile oil	mobile oil	mobile oil	mobile oil	viscous liquid	sticky resin
Stability	inert	inert	inert	inert	inert	inert	inert
Density (lb/gal 25°C)	11.40	9.85	10.55	11.50	12.04	12.82	13.50
Specific gravity x/15.5°C	1.36-1.37 x-25°	1.18-1.19 x-25°	1.27-1.28 x-25°	1.30-1.39 x-25°	1.40-1.41 x-65°	1.49-1.50 x-65°	1.55-1.56 x-90°
Distillation range (°C)	323-356	275-320	290-325	325-366	340-375	365-390	385-420
Acidity mg KOH/g, maximum	.010	.014	.014	.015	.010	.010	.014
Fire point (°C)	none to boiling point	176	238	none to boiling point	none to boiling point	none to boiling point	none to boiling point
Flash point (°C)	170	141-150	152-154	176-180	193-196	none	none
Vapor pressure (mm Hg @ 100°F)	NA	NA	0.005	0.001	0.00037	0.00006	NA
Viscosity (Saybolt Univ. Sec. @ 100°F) (centistokes)	71-81 13-16	38-41 3.6-4.6	44-51 5.5-7.7	82-92 16-19	185-240 42-52	1800-2500 390-540	— —

[1]NA—*Not Available*

NOTE: These physical data are typical values based on material tested but may vary from sample to sample. Typical values should not be construed as a guaranteed analysis of any specific lot or as specifications for the product.

10. STABILITY AND REACTIVITY

Stability: PCBs are very stable, fire-resistant compounds.
Materials to Avoid: None
Hazardous Decomposition
Products: PCBs may decompose to form CO, CO_2, HCl, phenolics, aldehydes, and other toxic combustion products under severe conditions such as exposure to flame or hot surface.
Hazardous Polymerization: Does not occur.

11. TOXICOLOGICAL INFORMATION

Data from laboratory studies conducted by Monsanto and from the available scientific literature are summarized below.
Single exposure (acute) studies indicate:
Oral - Slightly Toxic (Rat LD50 - 8.65 g/kg for 42% chlorinated; 11.9 g/kg for 54% chlorinated)

The liquid products and their vapors are moderately irritating to eye tissues. Animal experiments of varying duration and at different air concentrations show that for similar exposure conditions, the 54% chlorinated material produces more liver injury than the 42% chlorinated material.

There are literature reports that PCBs can impair reproductive functions in monkeys. The National Cancer Institute (NCI) performed a study in 1977 using Aroclor 1254 with both sexes of rats. NCI stated that the PCB, Aroclor 1254, was not carcinogenic under the conditions of their bioassay. There is sufficient evidence in the scientific literature to conclude that Aroclor 1260 can cause liver cancer when fed to rodents at high doses. Similar experiments with less chlorinated PCB products have produced negative or equivocal results.

The consistent finding in animal studies is that PCBs produce liver injury following prolonged and repeated exposure by any route, if the exposure is of sufficient degree and duration. Liver injury is produced first, and by exposures that are less than those reported to cause cancer in rodents. Therefore, exposure by all routes should be kept sufficiently low to prevent liver injury.

Numerous epidemiological studies of humans, both occupationally exposed and nonworker environmentally exposed population, have not demonstrated any causal relationship between PCB exposure and chronic human illnesses such as cancer or neurological or cardiovascular effects. PCBs at high dosage can cause skin symptoms; however, these subside upon removal of the exposure source.

PCBs have been listed in the International Agency for Research on Cancer (IARC) Monographs (1987)-Group 2A and in the National Toxicology Program (NTP) Seventh Annual Report on Carcinogens.

12. ECOLOGICAL INFORMATION

Care should be taken to prevent entry of PCBs into the environment through spills, leakage, use, vaporization or disposal of liquid or solids. PCBs can accumulate in the environment and can adversely affect some animals and aquatic life. In general, PCBs have low solubility in water, are strongly bound to soils and sediments, and are slowly degraded by natural processes in the environment.

13. DISPOSAL CONSIDERATIONS

The disposal of PCB items or equipment (those containing 50 ppm or greater PCBs) and PCB wastes is strictly regulated by 40 CFR Part 761. For example, all wastes and residues containing PCBs (wiping cloths, absorbent material, used disposable protective gloves and clothing, etc.) should be collected, placed in proper containers, marked and disposed of in the manner prescribed by EPA regulations (40 CFR Part 761) and applicable state and local regulations.

14. TRANSPORT INFORMATION

The data provided in this section are for information only. Please apply the appropriate regulations to properly classify a shipment for transportation.

DOT Classification:	IF WEIGHT OF PCBs TO BE SHIPPED IS OVER ONE POUND, THE FOLLOWING CLASSIFICATION AND LABEL APPLY.	
DOT Label:	LIQUID:	Environmentally Hazardous Substance, liquid, n.o.s. (Contains PCB), 9, UN 3082, III
	SOLID:	Environmentally Hazardous Substance, solid, n.o.s. (Contains PCB), 9, UN 3077, III
DOT Label:	Class: 9	
DOT Reportable Quantity:	One Pound	
IMO Classification:	Polychlorinated Biphenyls, IMO Class 9, UN 2315, II IMO Page 9034, EMS 6.1-02	
IATA/ICAO Classification:	Polychlorinated Biphenyls, 9, UN2315, II	

15. REGULATORY INFORMATION

For regulatory purposes, under the Toxic Substances Control Act, the term "PCBs" refers to a chemical substance limited to the biphenyl molecule that has been chlorinated to varying degrees or any combination of substances which contain such a substance (40 CFR Part 761).

TSCA Inventory: not listed.

Hazard Categories Under Criteria of SARA Title III Rules (40 CFR Part 370): Immediate, Delayed.
SARA Section 313 Toxic Chemical(s): Listed-1993 (De Minimis concentration 0.1%.)

Reportable Quantity (RQ) under DOT (49 CFR) and CERCLA Regulations: 1 lb. (polychlorinated biphenyls) PCBs.

Release of more than 1 (one) pound of PCBs to the environment requires notification to the National Response Center (800-424-8802 or 202-426-2675).

Various state and local regulations may require immediate reporting of PCB spills and may also define spill cleanup levels. Consult your attorney or appropriate regulatory officials for information relating to spill reporting and spill cleanup.

16. OTHER INFORMATION

Reason for revision: Conversion to the 16 section format. Supersedes MSDS dated 10/88.

Therminol®, Aroclor® and Pydraul® are registered trademarks of Monsanto Company
Pyranol® is a registered trademark of General Electric Company
Inerteen® is a registered trademark of Westinghouse Electric Corporation

FOR ADDITIONAL NONEMERGENCY INFORMATION, CONTACT:

Gary W. Mappes
Manager, Product & Environmental Safety

Robert G. Kaley, II
Director, Environmental Affairs

Monsanto Company
800 North Lindbergh Boulevard
St. Louis, MO 63167
(314) 694-3344

APPENDIX B - OZONE SAFETY DATA SHEET (MSDS)

AFROX

MATERIAL SAFETY DATA SHEET

OZONE

DATE: April 2001

1 PRODUCT AND COMPANY IDENTIFICATION

PRODUCT IDENTIFICATION

Product Name	OZONE
Chemical Formula	O3
Trade name	Ozone
Company Identification	African Oxygen Limited 23 Webber Street Johannesburg, 2001 Tel. No: (011) 490-0400 Fax No: (011) 490-0506

2 COMPOSITION/INFORMATION ON INGREDIENTS

Chemical Name	Ozone
Chemical Family	Oxidant
CAS No.	10028-15-6
UN No.	3139
Hazchem Code:	2 SE
Hazchem Warning	Oxidising substance

3 HAZARDS IDENTIFICATION

Main Hazards	Ozone is a non-flammable, but highly unstable gas which decomposes slowly at room temperature to liberate oxygen. The readiness of ozone to decompose makes it a powerful oxidising agent, which is capable of touching off several violent reactions. Never permit oil, grease or other readily combustible substance to come into contact with high concentrations of ozone.
Adverse Health effects	Ozone is a highly toxic, irritant gas on both short-term and long-term exposure. It causes inflammation and congestion of the respiratory tract and, in the event of severe exposure, it produces pulmonary oedema, haemorrhage and death.
Chemical hazards	Under the action of heat, in the presence of catalysts such as hydrogen, iron, copper and chromium, ozone is subject to explosive decomposition, almost spontaneously. Liquid and solid ozone are especially unstable and capable of causing violent explosions. Unsaturated organic compounds react with ozone to produce ozonides which are subject to sudden decomposition.
Biological Hazards	Symptoms of acute ozone toxicity appear at a concentration of about 1 ppm by volume. The type and severity of symptoms depend on the concentration and duration of exposure. In mild cases or in the early phases of severe cases, symptoms will include one or more of the following: irritation or burning of the eyes, nose, or throat; lassitude; frontal headache; sensation of substernal pressure, constriction or oppression; acid in mouth; and anorexia.

Eye contact	Gas	No known effect
	Liquid	Will cause severe cryogenic burns
Skin contact	Gas	No known effect
	Liquid	Will cause severe cryogenic burns
Ingestion	Liquid	Will cause severe cryogenic burns

4 FIRST AID MEASURES

Prompt medical attention is mandatory in all cases of overexposure to ozone. Rescue personnel should be cognisant of extreme fire hazard associated with oxygen-rich atmospheres. After removal from exposure, the victim should be at rest. Treatment with supplemental oxygen is useful for other than minor irritant effects. Vital signs (pulse, blood pressure, respirations) should be monitored. Because the possibility of delayed pulmonary oedema with other than minor irritant effects should receive medical evaluation. Treatment with a bronchodilator, such as albuterol, or an anticholinergic inhalant, such as Atrovent, administered by responding emergency medical team personnel, may be useful if there are chest symptoms.

Eye contact	If high concentrations of ozone contact the eyes, they should be thoroughly irrigated with large amounts of water for at least 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all exposed tissues. Two or three drops of a 0.5% pontocaine solution may be instilled in the eyes to prevent eyelid spasm and facilitated irrigation. An ophthalmologist should be consulted at once.
Skin contact	Liquid. Remove all contaminated clothing under an emergency shower. Wash the affected skin areas under running water with soap for at least 15 minutes. Subsequent medical treatment is the same for the thermal burns.
Ingestion	Liquid. Allow damaged areas to warm gently. Seek medical attention.

5 FIRE FIGHTING MEASURES

Extinguishing media	As ozone is non-flammable but strongly supports combustion, the correct type of extinguishant should be used depending on the combustible material involved.
Specific hazards	Ozone (O_3) is an unstable, bluish, strongly oxidant gas which is potentially explosive. Materials that would not normally burn in air could combust vigorously in atmospheres having high concentrations of ozone.
Emergency actions	If possible, shut off the source of escaping ozone. Evacuate area. CONTACT THE NEAREST AFROX BRANCH.
Protective clothing	Since ozone is toxic, self-contained breathing apparatus must be used when in the vicinity of leaking ozone.
Environmental precautions	Ozone is a very strong oxidant and particular precautions should be taken to prevent contact with grease, oil or other combustible materials. It is recommended that ozone be handled in a hood to prevent it from getting into the surrounding atmosphere in case of leaks.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions	An effective educational, training and industrial hygiene program should be instituted for the benefit of all persons working with, or in the vicinity of ozone. The program should include the following: (1) The nature and hazards of the gas; (2) Proper handling and usage procedures; (3) First aid measures to be followed in the event of an exposure; (4) Emergency procedures. Personal protective equipment should include the following: (1) A minimum of industrial safety glasses meeting ANSI Z87.1 requirements; (2) Long sleeves and trousers must be worn; (3) Leather or other insulating gloves should be utilised. Open shoes or sandals should be prohibited. Self-contained breathing apparatus should be available and persons must be trained in their proper usage and oxygen inhalation equipment, and persons qualified in administering oxygen must be readily available for inhalation emergencies.
Environmental precautions	Because of its oxidising nature, all ozone containers or generators, associated equipment and piping must be kept free of oil, grease or dirt and must not be handled with oily hands, oily gloves or greasy equipment. Although not flammable, ozone supports combustion. Therefore, proper fire precautions must be taken. Always keep away from flammable or combustible materials by a distance of more than 6 meters, or by a non-combustible barrier at least 2 meters high with a fire resistance rating of at least one-half hour. Rooms and buildings should be provided with portable fire extinguishers.
Small spills	Evacuate area. Shut off the source of excess ozone. Ventilate the area. Low concentrations of ozone may be readily destroyed by passing through a bed of granulated charcoal or by reaction with potassium iodine solution.
Large spills	Evacuate the area. Shut off the source of the spill if this can be done without risk. High concentrations of ozone can be neutralised by passing through a bed of molecular sieves. Ventilate the area using forced draught if necessary. Do not re-enter the area until it has been shown that it is safe to do so.

7 HANDLING AND STORAGE

Requirements for room or building construction, windows, fire doors, explosion venting, etc. must be given careful consideration with regard to applicable NFPA Codes, local and OSHA regulations, and insurance company requirements. Never use copper, copper alloys or rubber as construction materials in a system containing ozone. Keep out of reach of children.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational exposure hazards	Ozone is a gas in normal atmosphere conditions (15°C, 101,325 kPa). It is a toxic gas and a powerful oxidising agent. It exists in the atmosphere in very low concentrations. At ground level, it is present in a concentration of 0,025 to 0,045 ppm by volume. The initial effects of exposure are subjective in that the gas can usually be detected by its odour at concentrations as low as 0,05ppm. At concentrations above 0,1 ppm, there is dryness and irritation of the throat and upper respiratory tract; at 1 ppm and above, exposures lasting more than 0,5 h result in headache and malaise. Measurable changes in the vital capacity of the lungs occur in man following exposure to concentrations of 1,5 ppm and above lasting a few hours. Incapacitating pulmonary congestion may be caused by daily, intermittent exposures above 5 ppm (arc welders).
Engineering control measures	Engineering control measures are preferred to reduce exposure to ozone-enriched atmospheres. General methods include forced-draught ventilation, separate from other exhaust ventilation systems. Ensure that sufficient fresh air

enters at, or near, floor level. Careful consideration must be given to the products of ozonolysis (ozonides), many of which are explosive. Low temperatures and reactions carried out in solution have been employed to counteract this hazard. It is recommended that ozone be used only in a well-designed local exhaust system.

Personal protection	Personal protective equipment should include the following: (1) a minimum of industrial safety glasses meeting ANSI Z87.1 requirements; (2) long sleeves and trousers must be worn; (3) leather or other insulating gloves should be utilised.	
Skin	Gas	No known effect

9 PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL DATA

Chemical Symbol	O_3
Molecular Weight	47,998
Relative density (air = 1)	1,66
Colour	None (bluish in high concentrations)
Taste	None
Odour	Sharp, pungent

10 STABILITY AND REACTIVITY

Conditions to avoid At room temperature, 50% of the ozone is decomposed in a few days. The principal safety hazard posed by high concentration of O_3 is its explosive and fire potential. It reacts with unsaturated organic compounds such as aniline, benzene, diethyl ether, ethylene, and organic matter.

Incompatible materials The use of copper and copper alloys should be avoided because these materials act as a catalyst to promote decomposition. Rubber or any composition thereof is unsuitable. Extreme precaution should be taken to avoid contact with oil, grease or other readily combustible substances. The following metals react more easily with ozone than with oxygen: alkali metals, alkaline-earth metals, silver and mercury. The action of ozone on other metals is comparable to that of oxygen.

Hazardous Decomposition Products Ozonolysis has been extensively used in the laboratory for structural analysis and has also found commercial application for the production of aldehydes and acids. The application of this method has been limited to some extent by the fact that many ozonides are explosive.

11 TOXICOLOGICAL INFORMATION

Acute Toxicity: Symptoms of acute ozone toxicity appear at a concentration of about 1 ppm by volume. The type and severity of symptoms depend on exposure concentration and duration. The safe level for short exposures to ozone concentrations in excess of 0.1 ppm (TLV) is not known with certainty. Probably 2 ppm is safe for several minutes, provided no respiratory infection is present. The atmospheric concentration immediately hazardous to life is also not known, but inhalation of 50 ppm for 30 minutes would probably be lethal. The ACGIH 1987-88 TLV for ozone is 0.1 ppm with a STEL of 0.3 ppm.

Skin & eye contact: Gas No known effect.

Chronic Toxicity: The role of long-term, low level exposure to O_3 in the causation of chronic pulmonary disease in man is unclear. Studies assessing the health effects of air pollution must consider the contribution of other pollutants as well (Sulphur dioxide, carbon monoxide, nitrogen dioxide, peroxyacyl nitrates (PAN), particulates). Certainly, air pollutants (including O_3) exacerbate pre-existing pulmonary disorders.

Carcinogenicity: Chronic exposure appears to lead to relative increased in Type I collagen content in the lung and may be progressive even after exposure ceases (Last, 1984). Elevated Type I collagen is associated with chronic lung fibrosis in humans.

Mutagenicity: The chromosomal and mutational effects of ozone are controversial (Menzel, 1984). Ozone's potential to elicit reactive free radicals in tissue suggests it may be a genetic hazard.

Reproductive Hazards: Human clinical or epidemiological studies regarding reproductive or carcinogenic effects are lacking.

12 ECOLOGICAL INFORMATION

At room temperature 50% of ozone decomposes in a few days, yielding oxygen. It can act as a disinfectant for both air and water by virtue of the oxidising power.

13 DISPOSAL CONSIDERATIONS

Disposal Methods Low concentrations of ozone may be readily destroyed by passing through a bed of granulated charcoal or by reaction with potassium iodide solution. High concentrations of ozone can be neutralised by passing through a bed of molecular sieves.

14 TRANSPORT INFORMATION

Road transportation	
UN No.	3139
Hazchem code	2 SE
Hazchem warning	Oxidising substance
Sea & air transportation	Not applicable

15 REGULATORY INFORMATION

EEC Hazard class	Oxidising, toxic
Risk phrases	R4 Forms very sensitive, explosive metallic compounds R9 Explosive when mixed with combustible material R26 Very toxic by inhalation R33 Danger of cumulative effects R37 Irritating to respiratory system R40 Possible risks of irreversible effects R49 May cause cancer by inhalation R50 Very toxic to aquatic organisms R54 Toxic to flora R55 Toxic to fauna R56 Toxic to soil organisms R57 Toxic to bees
Safety phrases	S2 Keep out of reach of children S4 Keep away from living quarters S17 Keep away from combustible material S21 When using, do not smoke S23 Do not breathe gas S27 Take off immediately all contaminated clothing S36 Wear suitable protective clothing S38 In case of insufficient ventilation, wear suitable respiratory equipment S44 If you feel unwell, seek medical advice S51 Use only in well ventilated areas S57 Use appropriate containment to avoid environmental contamination S58 To be disposed of as hazardous waste
National legislation.	None

Refer to SABS 0265 for explanation of the above

16 OTHER INFORMATION

Bibliography

Compressed Gas Association, Arlington, Virginia

Handbook of Compressed Gases - 3rd Edition

Matheson, Matheson Gas Data Book - 6th Edition

Matheson Gas products

Effects of Exposure to Toxic Gases

First Aid & Medical Treatment

L'Air Liquide

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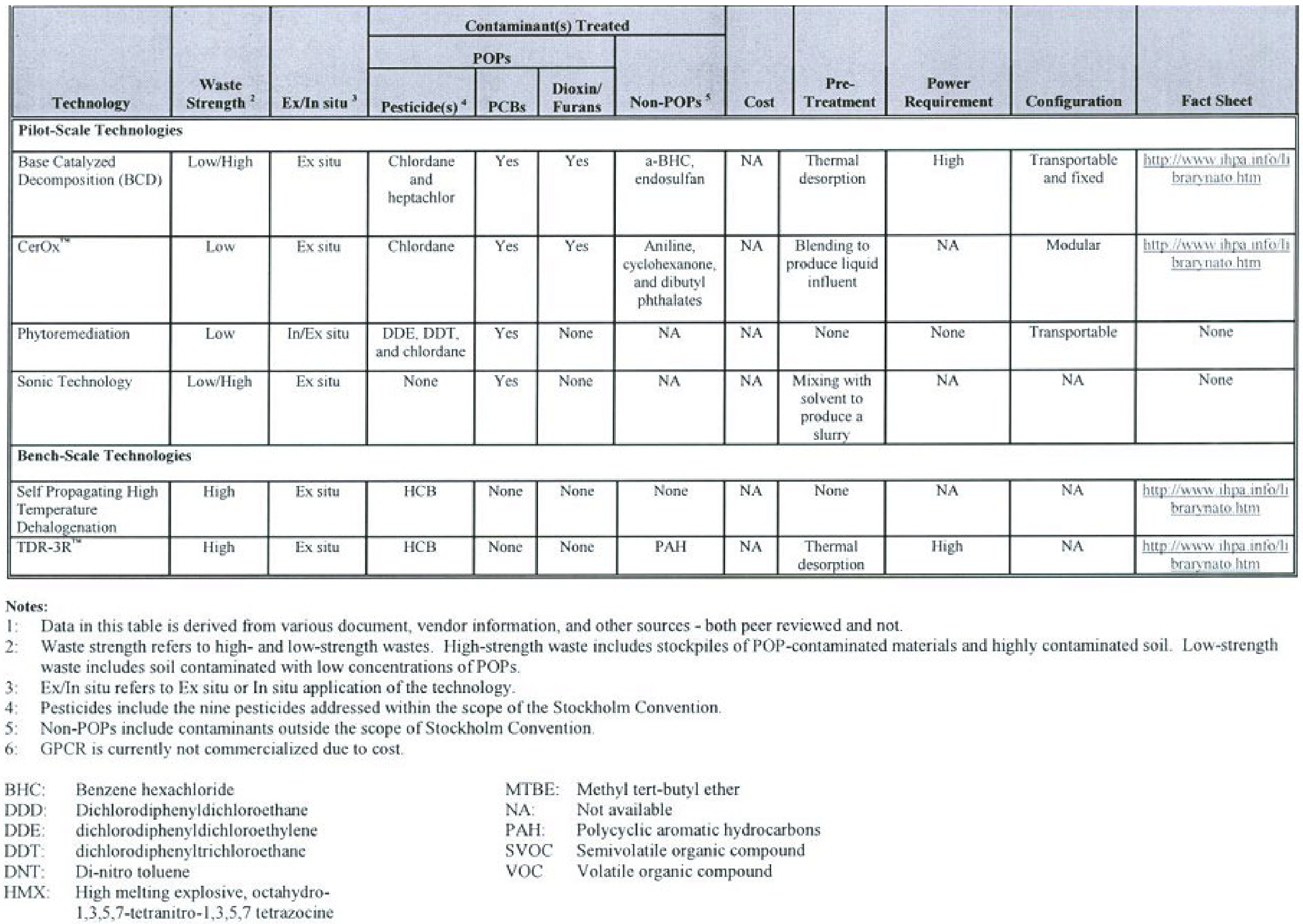
17 EXCLUSION OF LIABILITY

Although reasonable care has been taken in the preparation of this document, we extend no warranties and make no representations as to the accuracy or completeness of the information herein, and assume no responsibility regarding the suitability of this information for the user's intended purposes or for the consequences of its use. Each individual should make a determination as to the suitability of the information for their particular purpose(s).

APPENDIX C - NON COMBUSTION REMEDIAL TECHNOLOGIES



Technology	Waste Strength [2]	Ex/In situ [3]	Contaminant(s) Treated				Cost	Pre-Treatment	Power Requirement	Configuration	Fact Sheet
			POPs								
			Pesticide(s) [4]	PCBs	Dioxin/ Furans	Non-POPs [5]					
Pilot-Scale Technologies											
Base Catalyzed Decomposition (BCD)	Low/High	Ex situ	Chlordane and heptachlor	Yes	Yes	a-BHC, endosulfan	NA	Thermal desorption	High	Transportable and fixed	http://www.ihpa.info/librarynato.htm
CerOx™	Low	Ex situ	Chlordane	Yes	Yes	Aniline, cyclohexanone, and dibutyl phthalates	NA	Blending to produce liquid influent	NA	Modular	http://www.ihpa.info/librarynato.htm
Phytoremediation	Low	In/Ex situ	DDE, DDT, and chlordane	Yes	None	NA	NA	None	None	Transportable	None
Sonic Technology	Low/High	Ex situ	None	Yes	None	NA	NA	Mixing with solvent to produce a slurry	NA	NA	None
Bench-Scale Technologies											
Self Propagating High Temperature Dehalogenation	High	Ex situ	HCB	None	None	None	NA	None	NA	NA	http://www.ihpa.info/librarynato.htm
TDR-3R™	High	Ex situ	HCB	None	None	PAH	NA	Thermal desorption	High	NA	http://www.ihpa.info/librarynato.htm

Notes:

1: Data in this table is derived from various document, vendor information, and other sources - both peer reviewed and not.
2: Waste strength refers to high- and low-strength wastes. High-strength waste includes stockpiles of POP-contaminated materials and highly contaminated soil. Low-strength waste includes soil contaminated with low concentrations of POPs.
3: Ex/In situ refers to Ex situ or In situ application of the technology.
4: Pesticides include the nine pesticides addressed within the scope of the Stockholm Convention.
5: Non-POPs include contaminants outside the scope of Stockholm Convention.
6: GPCR is currently not commercialized due to cost.

BHC:	Benzene hexachloride
DDD:	Dichlorodiphenyldichloroethane
DDE:	dichlorodiphenyldichloroethylene
DDT:	dichlorodiphenyltrichloroethane
DNT:	Di-nitro toluene
HMX:	High melting explosive, octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine
MTBE:	Methyl tert-butyl ether
NA:	Not available
PAH:	Polycyclic aromatic hydrocarbons
SVOC	Semivolatile organic compound
VOC	Volatile organic compound

			Contaminant(s) Treated								
			POPs								
Technology	**Waste Strength** [2]	**Ex/In situ** [3]	**Pesticide(s)** [4]	**PCBs**	**Dioxin/ Furans**	**Non-POPs** [5]	**Cost**	**Pre-Treatment**	**Power Requirement**	**Configuration**	**Fact Sheet**
Full-Scale Technologies											
Anaerobic bioremediation using blood meal for the treatment of toxaphene in soil and sediment	Low	Ex situ	Toxaphene	None	None	None	$98 to $296 per cubic yard (in 2004)	None	None	Transportable	Appendix A
DARAMEND®	Low	Ex/In situ	Toxaphene and DDT	None	None	DDD, DDE, RDX, HMX, DNT, and TNT	$55 per cubic yard (in 2004)	None	None	Transportable	Appendix B
Gas Phase Chemical Reduction (GPCR™)[6]	High	Ex situ	DDT and HCB	Yes	Yes	PAH, chlorobenzene	NA	Thermal desorption	High	Fixed and transportable	http://www.ihpa.info/librarynato.htm
GeoMelt™	Low/High	In/Ex situ	DDT, chlordane, dieldrin and HCB	Yes	Yes	Metals and radioactive waste	NA	None	High	Fixed and transportable	http://www.ihpa.info/librarynato.htm
In-Situ Thermal Desorption (ISTD)	Low/High	In situ	NA	Yes	Yes	VOCs, SVOCs, oils, creosote, coal tar, gasoline, MTBE, volatile metals	$200 to $600 per cubic yard (from 1996 to 2005)	None	High	Transportable	Appendix C
Mechanochemical Dehalogenation (MCD™)	High	Ex situ	Aldrin, dieldrin and DDT	None	None	Lindane, DDD, and DDE	NA	None	NA	NA	http://www.ihpa.info/librarynato.htm
Xenorem™	Low	Ex situ	Chlordane, DDT, dieldrin, and toxaphene	None	None	Molinate	$132 per cubic yard (in 2000)	None	NA	Transportable	None