

INVESTIGATION OF A NOVEL MAGNESIUM AND ACIDIFIED ETHANOL SYSTEM
FOR THE DEGRADATION OF PERSISTENT ORGANIC POLLUTANTS

by

PHILLIP RYAN MALONEY
B.S. University of Central Florida 2008

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Major Professor: Cherie L. Yestrebsky

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ABSTRACT

For centuries chemists have sought to improve humankind's quality of life and address many of society's most pressing needs through the development of chemical processes and synthesis of new compounds, often with phenomenal results. Unfortunately, there also are many examples where these chemicals have had unintended, detrimental consequences that are not apparent until years or decades after their initial use. There are numerous halogenated molecules in this category that are globally dispersed, resistant to natural degradation processes, bioaccumulative, and toxic to living organisms. Chemicals such as these are classified as persistent organic pollutants (POPs), and due to their negative environmental and health effects, they require safe, effective, and inexpensive means of remediation.

This research focuses on the development and optimization of a reaction matrix capable of reductively dehalogenating several POPs. Initial experiments determined that powdered magnesium and 1% V/V acetic acid in absolute ethanol was the most effective system for degrading polychlorinated biphenyl (PCB), an extraordinarily recalcitrant environmental contaminant. Further studies showed that this matrix also was capable of degrading polychlorinated dibenzo-*p*-dioxins (PCDDs), polybrominated diphenyl ethers (PBDEs), and four organochlorine pesticides (OCPs); dieldrin, heptachlor, heptachlor epoxide, and chlordane. During this phase of testing, field samples contaminated with chlordane were washed with ethanol and this ethanol/chlordane solution was degraded using the same reaction matrix, thereby demonstrating this technology's potential for "real-world" remediation projects. Finally, a set of experiments designed to provide some insight into the mechanism of dechlorination seems to indicate that two distinct processes are necessary for degradation to occur. First, the passivated

outer layer of the magnesium must be removed in order to expose the zero-valent magnesium core. Next, an electron is transferred from the magnesium to the target molecule, causing the cleavage of the halide bond and the subsequent abstraction of either a hydrogen or proton from a solvent molecule. It is anticipated that an understanding of these fundamental chemical processes will allow this system to be tailored to a wide range of complex environmental media.

To my wife, Rachel
I am so grateful for your support, encouragement, and faith. I love you.

To my daughter, Vanessa
Please never forget the true lesson of learning to hula-hoop.

To my parents
There were times when I don't know how you did it, but thank you from the bottom of my heart.

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LIST OF ACRONYMS/ABBREVIATIONS

ABC	Aerobic bacterial co-metabolism
ARD	Anaerobic reductive dechlorination
ASTDR	Agency for Toxic Substances and Disease Registry
AhR	Aryl hydrocarbon receptor
BFR	Brominated flame-retardants
BHC	Benzene hexachloride
DDE	Dichlorodiphenyltrichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DRE	Destruction removal efficiency
GC	Gas chromatogram
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
ECD	Electron capture detector
K _{ow}	Octanol-water partition coefficient
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MNA	Monitored natural attenuation
NPL	National Priorities List
OCDD	Octachlorinated dibenzo- <i>p</i> -dioxin
OCP	Organochlorine pesticide
PBDE	Polybrominated diphenyl ether

PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxin
PCDF	Polychlorinated dibenzofuran
POP	Persistent organic pollutant
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SPL	Substance Priority List
TCDD	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
TEF	Toxic equivalency factor
TSCA	Toxic Substances Control Act
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
ZVM	Zero-valent metal
ZVMg	Zero-valent magnesium

CHAPTER ONE: INTRODUCTION

Throughout history, as humankind has sought to meet the demands of an ever growing population and its desire for an increasingly higher standard of living, it has been primarily through the development of new and improved technologies that these challenges have been met. The wide ranging and profound influence of these technologies are such that the world today would likely be inconceivable to our counterparts from a century ago. Undoubtedly, a great deal of this progress is a direct result of corresponding advancements in the field of chemistry. It is difficult to imagine an area of our daily lives that has not been affected by advancements in chemistry, from pharmacology and genetics to materials and electronics. Compounds such as those examined in this research were originally developed and used because they did an excellent job of meeting specific, highly beneficial societal needs. In the case of polychlorinated biphenyls (PCBs), their use in electrical transformers was instrumental in increasing people's access to electrical grids. Organochlorine pesticides (OCPs) facilitated increased crop yields and helped curtail the spread of insect-borne diseases in the post-World War II era. And polybrominated diphenyl ethers (PBDEs) are flame-retardants that have saved countless lives and millions of dollars in property damage.

Unfortunately, the obvious initial benefits of newly synthesized chemicals such as these are not always their only consequence. Often the full impacts of these compounds are not realized until a great deal of time has passed and improved analytical processes allow them to be detected at much lower concentrations. In the case of persistent organic pollutants (POPs), the following pattern has been repeated numerous times during the past century:

1. A compound is discovered that has highly desirable properties for a specific industry
2. It is used extensively throughout that industry for many years.
3. The compound is detected (often unexpectedly) in samples that are completely unrelated to its original use.
4. Further testing shows that the compound has spread throughout the environment.
5. Biological studies indicate that the compound may have negative health effects even at low levels.
6. Use of the compound is banned or severely regulated.
7. The search for remediation technologies begins.

The research presented here is an attempt to address the last step in this scenario. This dissertation details the development of a novel technology for the degradation of polychlorinated biphenyl, the application of this technology to other halogenated POPs, its use for the treatment of contaminated environmental media, and a proposed mechanism for the fundamental chemical reaction.

Halogenated Persistent Organic Pollutants

Michael Faraday is generally credited with being the first to synthesize a halogenated persistent organic pollutant for his discovery of benzene hexachloride (BHC) in 1825 (Faraday, 1825). Other significant events occurred in the latter half of the nineteenth century including Zeidler's initial synthesis of dichlorodiphenyltrichloroethane (DDT) in 1873 (Friedman, 1992) and Schmidt and Schultz's synthesis of polychlorinated biphenyl in 1881. However, these

chemicals were not produced on an industrial scale for nearly half a century (Schmidt & Schultz, 1881). Mass production of PCBs began in the 1930s and the insecticidal properties of DDT were not discovered until 1939, a discovery for which Dr. Paul Müller was awarded the 1948 Nobel Prize for medicine (Cairns & Siegmund, 1981; Nobelprize.org).

Once the unique properties of these substances were realized, they were manufactured and utilized in large quantities. Table 1 lists estimated production quantities over given time periods for several halogenated POPs.

Table 1:
Estimated global production during years of major usage or up to the time of publication for selected halogenated POPs

Compound	Years of major production	Amount produced (tonnes)	Reference
PCBs ^a	1930-1980	1,325,810	(Breivik, Sweetman, Pacyna, & Jones, 2007)
DDT ^b	1943-2005	4,500,000	(Li & Macdonald, 2005)
Chlordane ^c	1946-1988	70,000	(Dearth & Hites, 1991)
HCH (hexachlorocyclohexane) ^d	1943-1998	6,000,000	(Li, Bidleman, Barrie, & McConnell, 1998)
PBDEs ^e	1976-2011	1,000,000	(Guo, Shaw, & Kannan, 2011)

The United States Environmental Protection Agency (EPA) and the United Nations Environment Programme (UNEP) identify POPs as carbon-based chemicals that, upon release

into the environment, possess the following characteristics (Secretariat of the Stockholm Convention, 2008c; U.S. EPA, 2002):

- They remain in the environment, chemically unchanged, for long periods due to their inherent resistance to natural degradation processes.
- They are disseminated throughout the environment by natural transport mechanisms.
- Due to their hydrophobicity and lipophilicity, they are bioaccumulative and biomagnified in the food chain.
- They adversely affect the health of the environment and populations in which they are found.

While there are numerous non-halogenated and organometallic compounds that meet these criteria, for the purposes of this dissertation, the term “persistent organic pollutant” will refer only to those compounds that have some degree of halogenation. Moreover, as Figure 1 shows, 56 of the top 100 substances listed on the Agency for Toxic Substances and Disease Registry’s (ASTDR) 2011 Substance Priority List (SPL) are halogenated organic compounds.

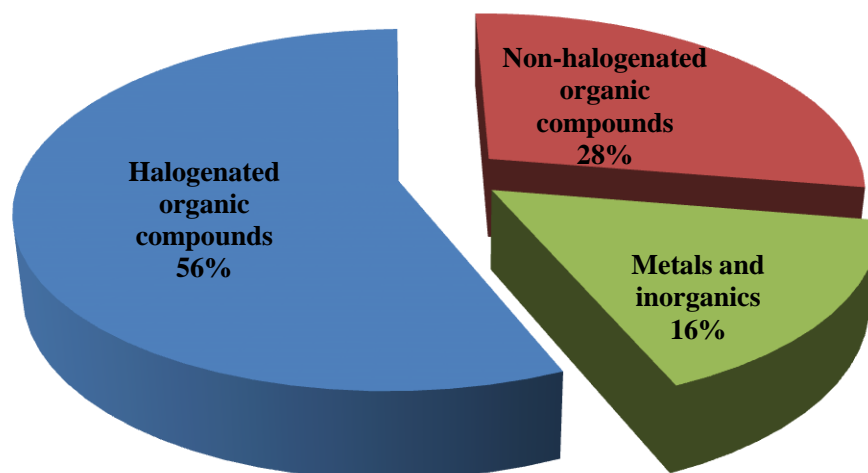


Figure 1: Breakdown by category of the top 100 substances on the ASTDR's Substance Priority List

Although the chemical structures of the halogenated compounds on this list vary greatly (Table 2), their classification as POPs is due largely to a few pertinent physicochemical properties listed in Table 2. POPs tend to have low water solubility, which limit their transport by aqueous systems and increase their residence times in other media (soil, sediment, building material, etc.). Low vapor pressures at relevant atmospheric temperatures retard their dilution via gas phase transport (although, over long periods, this may become a major mode of distribution), resulting in greater persistence in other media. POPs also have high octanol-water partition coefficients (K_{ow}), which can be used as an indicator of their lipophilicity, and hence, their tendency to bioaccumulate. Lastly, due to their inherent chemical stability, POPs exhibit large half-lives in environmental media for which they have an affinity, and for these reasons facilities where contamination occurred over 50 years ago, may still have exceedingly high concentrations.

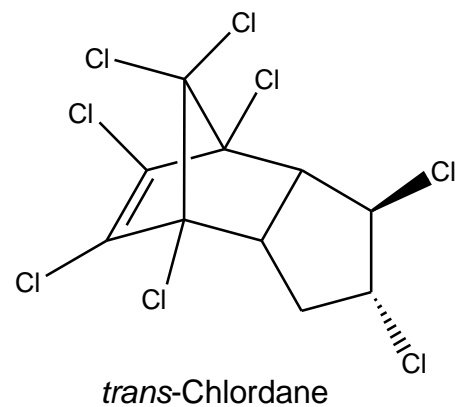
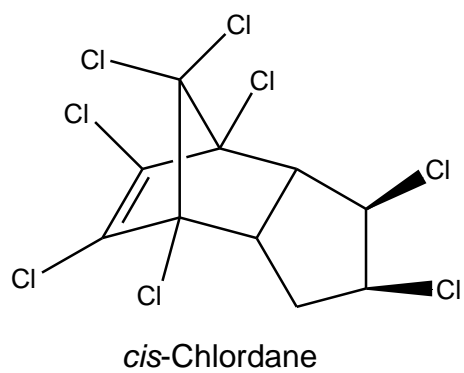
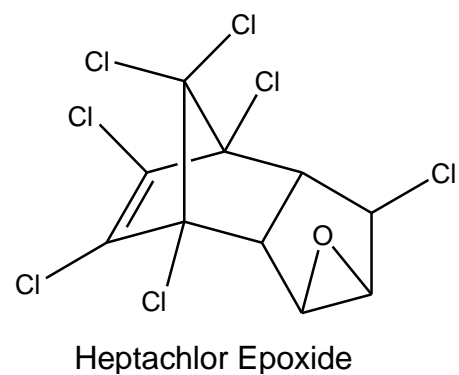
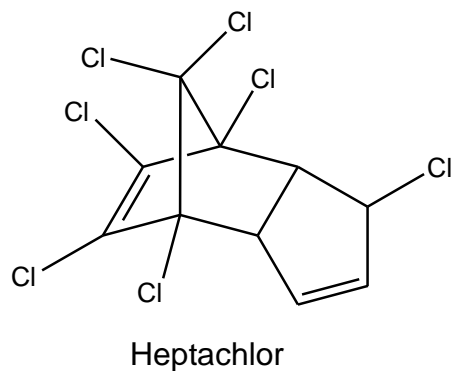
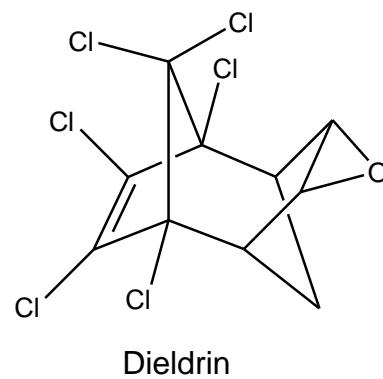
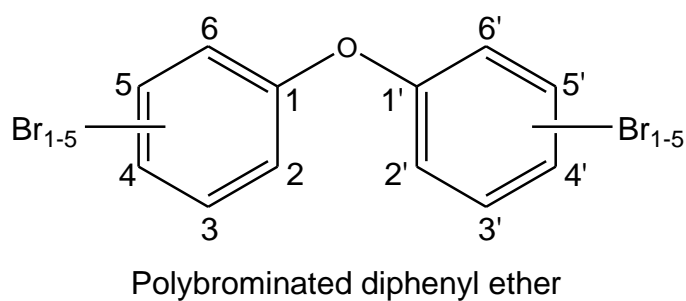
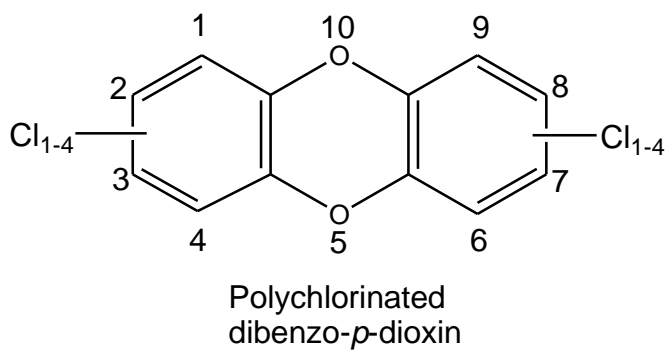
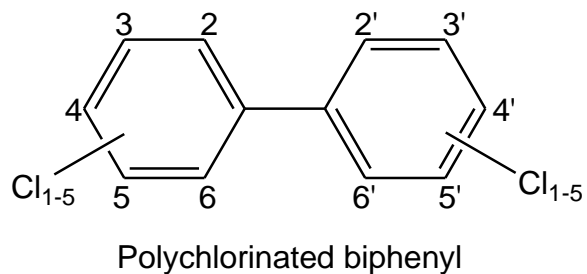


Figure 2: Molecular structures of compounds examined in this work

Table 2:
Key physicochemical properties relevant to the environmental behavior of selected POPs

Compound	Water solubility ($\mu\text{g/L}$)	Vapor pressure (Pa)	log K_{ow}	Exemplar half- life in soil
PCBs	0.9-58	6.5×10^{-2} - 7.7×10^{-5}	6.29-8.7	10d-1.5yr
PCDDs/PCDFs	0.0079-0.317	2.17×10^{-5} - 9.8×10^{-8}	6.64-7.02	10-12yr
Chlordane	56	1.3×10^{-4}	6.0	1yr
Dieldrin	140	2.4×10^{-5}	5.48	5yr
Heptachlor	180	0.04	5.94	≤ 2 yr
Heptachlor epoxide	198	NA	5.42	8.9yr
PBDEs	20-30	3×10^{-3} - 5×10^{-6}	4.8-10	1.6yr*

*Estimated value using EPIWIN estimation software (Palm et al., 2002)

Transport, Exposure, and Toxicity

Within 15 years of its introduction as a pesticide, reports were published indicating some unintended consequences resulting from the wide spread use of DDT, such as unacceptably high soil concentrations ("DDT Residue Persistence High in Some Soils," 1954) and detectable quantities in human populations (Pearce, Mattson, & Hayes Jr., 1952). However, it was Rachel Carson's book, *Silent Spring*, that served as a true clarion call to the scientific community to more closely examine DDT's behavior and eventual fate in the environment (Carson, Darling, & Darling, 1962). Since then, thousands of studies have been undertaken to measure the concentration of virtually every type of POP in biota and environmental media across the world. Table 3 lists some recent review articles that illustrate the extent of global contamination by POPs.

Table 3:
Literature reviews of global POP contamination

Sampled media	Compounds analyzed	Reference
Human breast milk	DDT	(Smith, 1999)
Human tissues	DDT, DDE	(Jaga & Dharmani, 2003)
Surface soils	PCBs, HCB	(Meijer et al., 2003)
Seafood	PCDD/PCDFs, PCBs	(Domingo & Bocio, 2007)
Air	Endosulfan, PCBs, HCH, chlordanes, heptachlor, heptachlor epoxide, dieldrin, DDE, PBDEs	(Pozo et al., 2008)
Soil/water/sediment	Dieldrin, endrin	(Matsumoto, Kawanaka, Yun, & Oyaizu, 2009)
Birds	PBDEs	(Chen & Hale, 2010)
Human blood	PCDD/PCDFs, PCBs	(Consonni, Sindaco, & Bertazzi, 2012)

The occurrence of worldwide, low-level concentrations of POPs is due to long-range transport processes and their resistance to natural remediation. POPs used in tropical and subtropical regions are gradually redistributed from highly concentrated zones to the rest of the globe via atmospheric and oceanic transport. Atmospheric transport occurs either in the gas phase as these chemicals volatilize from soils and bodies of water or by “hitchhiking” on airborne particulate matter (Valsaraj & Thibodeaux, 2010). Once these substances have entered the air, their redeposition rate and location is largely dependent on specific weather conditions such as prevailing winds, precipitation, air pressure, and temperature, which are subject to seasonal changes. This cycle of deposition and revolatilization may occur numerous times in a

process known as the grasshopper effect. The overall trend is a migration toward the poles where they concentrate due to the “cold trap” effect (Wania & Mackay, 1996).

With POPs as widely dispersed throughout various environmental media as they are, it is not surprising that biota are constantly exposed to these chemicals particularly in the arctic regions. Sijm provides a striking example of the nature of exposure and bioaccumulation:

A polar bear does not drink millions of liters of seawater, but ultimately does receive its concentration of PCBs of ca. 1-10 mg/kg in its fat from water. If the concentration of PCBs in polar seawater is similar as in the Great Lakes, in which the PCB concentration is approximately 0.5 n/L, the bioaccumulation factor for PCBs in polar bears would be around 20,000,000 L/kg! (...) In other words, the polar bear has to extract an equivalent of millions of liters of water to accumulate the PCBs in his fat to such high levels. (...) Its food includes seals exclusively, which in turn prey on fish, which in turn prey on even smaller aquatic species. Whereas the polar bear is not, its food is thus in direct contact with water (Sijm, 2001).

Thus, POPs are transferred from environmental media up the food chain and accumulate in the apex predators of which humans are the foremost. While food consumption is by far the major source of exposure in humans (Domingo & Bocio, 2007), inhalation, incidental ingestion of contaminated material, and dermal absorption also contribute to body burdens (Rostami & Juhasz, 2011).

The POP that receives the most attention based on its toxicity is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, commonly referred to as TCDD. This compound is known to be a human carcinogen (Baan et al., 2009) and has been assigned the highest Toxic Equivalency Factor (TEF). The TEF classification system is a means by which the toxicity of various dioxin congeners and dioxin-like compounds may be quantitatively compared. In addition to being carcinogenic, 2,3,7,8-tetrachloro-*p*-dioxin has been linked to other noncancerous health effects such as: atherosclerosis, hypertension, and diabetes (Marinkovic, Pasalic, Ferencak, Grskovic, &

Rukavina, 2010). While the debate over the toxicity of TCDD has essentially been settled, that is not the case for many other POPs. The problems identified by Eskenazi while reviewing the literature with regards to the toxicity of DDT may be applied to the majority of POPs. The author notes that:

Some studies suggested that DDT exposure may be associated with certain cancers (lung, cancer and lymphomas); however, the lack of control for exposure to other chemicals, small study size, insufficient data on confounding factors (e.g., incomplete information on tobacco use), and short follow-up time for long-latency cancers limited the ability to make any conclusions at that time (IARC) (Eskenazi et al., 2009).

While there remains vigorous debate regarding the toxicity levels of most POPs, perhaps the most relevant position is that of the U.S. EPA since it is the agency's evaluation that determines national regulatory guidelines. Table 4 lists the EPA's current toxicity classification for several POPs, as well as the maximum contaminant level goals (MCLG) and maximum contaminant level (MCL) it has established for drinking water. MCLGs are "*non-enforceable* health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety" while MCLs are *enforceable* standards set as close to the MCLGs as is practical considering available treatment technologies, analytical limitations, public benefit, and cost (U.S. EPA, 2012).

Table 4:
U.S. EPA's National Primary Drinking Water Regulations for selected contaminants (adapted from (U.S. EPA, 2009))

Contaminant	MCL (mg/L)	MCLG (mg/L)	Potential health effects from long term exposure above the MCL	Common sources of contaminant in drinking water
Chlordane	0.002	Zero	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide
Dioxin (2,3,7,8-TCDD)	3.0×10^{-8}	Zero	Reproductive difficulties; increased risk of cancer	Discharge from industrial chemical factories; an impurity of some water treatment chemicals
Heptachlor	0.0004	Zero	Liver damage; increased risk of cancer	Residue of banned termiticide
Heptachlor epoxide	0.0002	Zero	Liver damage; increased risk of cancer	Breakdown of heptachlor
PCBs	0.0005	zero	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer	Runoff from landfills; discharge of waste chemicals

Remediation

As can be seen from Table 4, some of the main causes of POPs contamination in drinking water are their emanation from various point sources, such as agricultural crops in the form of runoff, leaching from landfills, and diffusion via concentration gradient from highly contaminated industrial facilities. Due to the slow rate of environmental transport of POPs discussed in the previous section, these sites may act as contaminant reservoirs for decades or

even centuries if not properly ameliorated (Weber et al., 2008). A great deal of effort has been spent in developing effective technologies to remediate these sites not only to prevent the continued spread of contaminants, but also to make these locations safe for future use. Various types of remediation technologies have been developed and may be generally categorized as destructive or passive and *in situ* or *ex situ*.

Thermal Technologies

Historically, incineration has been one of the most common means of POP remediation. Ideally, incineration is a complete combustion reaction producing only water, CO₂, and other mineralized species. However, strict control over reaction conditions such as temperature, oxygen levels, and residence time are necessary to achieve the target destruction removal efficiency (DRE) of 99.999%. Failure to control these parameters may result in the incomplete oxidation of contaminants. In the case of PCBs, this can lead to the formation of PCDD/PCDFs, a potentially more harmful by-product (Huang & Buekens, 2001). A 2005 study of employees at a Korean incineration facility showed that workers who had been there for more than 100 months had PCDD/PCDF lipid concentrations more than 10 times higher (68.683-78.784 pg I-TEQ/g) than that of a new employee (6.225 pg I-TEQ/g) (B. H. Kim, Lee, Mun, & Chang, 2005). Studies such as this have led to public opposition to the opening and continued use of these facilities.

Vitrification is a process in which a contaminated media such as soil is heated to the point that the soil matrix fuses. This is accomplished by inserting electrodes into the soil and passing an electric current between them causing high-temperature resistive heating. Organic contaminants are either sequestered into the fused soil, pyrolyzed, or combusted in oxygen-rich

zones. Frequently this process is used *in situ*, however, it is not necessarily a destructive process and the energy requirements are quite large.

Passive Technologies

Landfilling is a non-destructive technology often used when the contamination is limited to a relatively shallow depth. In this process, the contaminated material is excavated and sent to a landfill certified to house hazardous waste. For many decades this has been a common practice because of its simplicity, totality, and expense relative to other options. However, landfilling is falling out of favor due to rising disposal costs (Harbottle, Al-Tabbaa, & Evans, 2007) and the increasing realization that POPs are likely to outlast the landfill systems designed to contain them (Weber, Watson, Forter, & Oliaei, 2011).

Monitored natural attenuation (MNA) is the observation of environmental contamination levels and how natural geological, chemical, and biological processes affect them. While this is considered by some to be a “do nothing approach,” it perhaps is more correct to view it as another option based on risk-reward assessments. In the United States, for example, contaminant dispersion is modeled to determine exposure levels for various receptors along the pathway. In scenarios where concentration levels are predicted to decrease as a function of distance from the source and a corresponding decrease in the total mass of the plume is expected to occur either by natural physiochemical processes or by proven bioremediation activity, MNA is seen as a viable option (Ruegner, Finkel, Kaschl, & Bittens, 2006).

Bioremediation

Bioremediation is the process by which living organisms transform contaminants in a way that decreases or eliminates their negative environmental impacts. This occurs either through mineralization of the compound, whereby the organism metabolizes the contaminant and utilizes the energy released by this process, or through co-metabolism, in which the target molecule is consumed in conjunction with a second molecule that functions as the primary carbon and energy source. The products of co-metabolism are partially degraded compounds that in some cases may have higher toxicity than the parent molecule. Several factors may affect the feasibility and rate of bioremediation including: the structure, concentration, and solubility of the target molecule, temperature, and pH.

The fundamental reaction occurring in anaerobic reductive dechlorination (ARD) is the transfer of an electron to the halogenated molecule and a substitution of the halogen with hydrogen. These types of reactions predominate in anoxic environments such as aquatic sediments. The ability of microbes to degrade PCBs via ARD was first discovered when Brown noticed differences between the distribution of PCB congeners in standards of technical mixtures and those retrieved from the Hudson River (Brown et al., 1987). Follow-up studies have confirmed the ARD process (as opposed to natural physiochemical phenomena) by comparing degradation levels in biologically active samples with heat-killed controls (Rysavy, Yan, & Novak, 2005). Some general trends observed with ARD are: Different microbes show different patterns and levels of dehalogenation, the presence of electron donors increases degradation rates and the presence of competing electron receptors decreases rates, and degradation rates increase with the number of exposures to electron acceptors (Field & Sierra-Alvarez, 2008a, 2008b).

Under oxygen-rich conditions destruction of halogenated compounds may proceed via aerobic oxidative degradation. The vast majority of these reactions require co-metabolites such as non-halogenated dibenzofuran or non-halogenated biphenyl, although decomposition of only PCDDs has been observed (Hong, Nam, Murugesan, Kim, & Chang, 2004). It is hypothesized that the inclusion of co-metabolites induces dioxygenase enzymes, which are then responsible for the destruction of the target contaminant (Nojiri & Omori, 2002). Although the proposed mechanisms and pathways vary depending on the species of bacteria and the substitution pattern of the target molecule, chlorinated benzoic acid is the most common product. While anaerobic and aerobic microbial degradation show great promise, there are drawbacks as well. Poor ability to degrade highly chlorinated molecules, limited success in removing *ortho* substituted chlorines, and poor tolerance for less than ideal environmental conditions must all be addressed.

Phytoremediation is the use of higher order plants to remove and/or degrade pollutants from environmental media and is often used as an umbrella term for several distinct processes. Phytoextraction refers to the ability of plants to remove hydrophilic compounds ($\log K_{ow} < 4$) via their root system and/or to sequester airborne hydrophobic compounds in leaf cuticular waxes (Campanella, Bock, & Schroder, 2002). Although plants themselves have a limited capacity to degrade xenobiotics, they have been shown to enhance microbial degradation in the root zone (rhizoremediation) by excreting microbial growth factors, compounds that serve as electron donors for ARD, and other molecules that act as surfactants which make hydrophobic contaminants more accessible to bioremedial processes. Current research is focused on developing transgenic plants that will be capable of degrading contaminants similar to the research which imparted crops with genetic resistance to specific agricultural pests and diseases

(Van Aken, Correa, & Schnoor, 2010). While phytoremediation offers a low cost and environmentally friendly treatment option for contaminated soils and sediments, its inability to chemically degrade most pollutants, slow uptake rates, possible introduction of contaminants into the food chain, and the suitability of plant species to specific types of growth media and climates also must be taken into account.

Oxidative Destruction

Supercritical water, which exists at temperatures above 647.1 K and pressures greater than 220.6 bar, has been shown to oxidatively degrade several water-soluble organic molecules. Researchers seeking to extend this capability to hydrophobic molecules such as PCBs by including methanol as a cosolvent have found that increasing the methanol concentration increases PCB degradation efficiency. Based on this observation, it has been hypothesized that highly reactive methyl radicals are formed and then involved in the oxidation reaction (Anitescu & Tavlarides, 2002). Other reaction parameters that effect degradation rates are temperature, pressure, and residence time in the reactor. Under optimized reaction conditions, PCBs are degraded to CO₂, HCl, and biphenyl (O'Brien, Thies, & Bruce, 2005). However, capital costs and continued energy usage are expected to be high for supercritical water oxidation and it is inherently an *ex situ* process.

Numerous studies have demonstrated the ability of titanium dioxide-based photocatalysts to degrade chlorinated molecules. The degradation process begins when photons of the proper wavelength promote electrons in TiO₂ from the valence band to the conduction band thereby creating a thermodynamically unstable, excited electron/electron hole pair with a reduction potential greater than 3.0 eV. At this potential, compounds adsorbed to the TiO₂ surface are

either directly oxidized, or in the presence of water and oxygen, through reactive intermediates such as O_3^- and HO_2^- (Linsebigler, Lu, & Yates, 1995). Under inert, anaerobic conditions, catalytic reduction may occur where the photocatalytically generated excited electron is transferred to a suitable acceptor such as chlorobenzene (L. F. Zhang, Sawell, Moralejo, & Anderson, 2007). Activity rates of photocatalysts are affected by properties such as surface area, the density of surface lattice defects, and the wavelength of the incident light. TiO_2 is widely used as a photocatalyst due to its low cost and low toxicity, however, it absorbs light in the UV portion of the electromagnetic spectrum, which means artificial light sources are required. Consequently, there is a great deal of research focused on doping TiO_2 with various secondary materials to enable it to absorb light in the visible spectrum allowing for solar activated photocatalysis.

Reductive Destruction

Halogenated pollutants have been degraded via electrochemical reduction either as a sorbed species on an anode (Kulikov, Plekhanov, Tsyganok, Schlimm, & Heitz, 1996; Miyoshi, Kamegaya, & Matsumura, 2004; S. P. Zhang & Rusling, 1995) or through the use of electron transferring, intermediate molecules (Matsunaga & Yasuhara, 2005a, 2005b). The addition of noble metals, which are known to evolve and/or store hydrogen, to electrodes has been shown to improve degradation rates and efficiencies. For these bimetallic electrodes, it is hypothesized that hydrogen is the actual reductant. Of the noble metals tested, palladium achieved the fastest rates of dechlorination which has been attributed to its ability to absorb and maintain a large hydrogen concentration on its surface (Cheng, Fernando, & Korte, 1997).

Zero-valent metals (ZVMs) also have been found to reductively dehalogenate POPs in a manner analogous to the electrodes described above. Dissolving metal reactions, as they are called, have been known for many years and are well documented in the literature, but surprisingly, have scarcely been used for pollutant degradation (Sweeny, 1981; Sweeny & Fischer, 1972). A 1990 study by Reynolds et al. to determine the degree of bias introduced by various materials used for groundwater sampling of halogenated compounds noted “Three metals, including stainless steel, apparently transformed the compounds” (Reynolds, Hoff, & Gillham, 1990). A follow-up study found that zero-valent iron degraded 13 of 14 halogenated aliphatic test compounds. This was attributed to electron transfer from zero-valent iron to molecules in direct contact with the surface (Gillham & Ohannesin, 1994). Aromatic compounds such as PCBs and PCDD/PCDFs have been degraded by zero-valent copper, iron, and zinc (Chuang, Larson, & Wessman, 1995; Hagenmaier, Brunner, Haag, & Kraft, 1987; Wang, Huang, Fennell, & Peng, 2008). However, the use of these metals required non-ambient conditions including elevated temperatures or an inert atmosphere. By adding catalytic amounts (0.05% w/w) of palladium to iron, complete PCB dechlorination was achieved in a matter of minutes (Grittini, Malcomson, Fernando, & Korte, 1995). Magnesium (Agarwal, Al-Abed, & Dionysiou, 2007; Doyle, Miles, Parker, & Cheng, 1998) and aluminum (Yang et al., 2011) also have been used as the bulk metal in palladized bimetal systems with similar degrees of success. It has been proposed that in these systems the bulk ZVM is the electron source, the solvent provides the hydrogen that is then intercalated and stored in the palladium, and the hydrodehalogenation reaction occurs at the interface of the two metals (R. Devor et al., 2009).

Research Objectives

Based on an assessment of the remediation technologies listed above, reduction by zero-valent magnesium (ZVMg) was deemed to have the greatest potential as a viable treatment option. The biggest drawback to this technology is the need to incorporate expensive, perhaps unrecoverable catalytic metals and that the reaction only occurs at the interface of the two metals. The first objective of this research was to create and optimize a PCB degradation system that does not require a secondary metal to take advantage of the reactivity of ZVMg. The second objective was to test this system's applicability to other halogenated compounds and contaminated field samples. The third was to gain an understanding of the fundamental reactions occurring in the system so that it may be tailored to different environmental matrices and conditions.

CHAPTER TWO: DECHLORINATION OF POLYCHLORINATED BIPHENYLS USING MAGNESIUM AND ACIDIFIED ALCOHOLS

Introduction

The term polychlorinated biphenyl (PCB) refers to a group of molecules that have a biphenyl backbone on which one to 10 hydrogens have been replaced by a chlorine atom, in all this encompasses 209 distinct congeners. Physical properties of PCBs include: low water solubility ($(4.0-7.6) \times 10^{-4} \text{ g/m}^3$), low vapor pressure ($(1.1-1.4) \times 10^{-6} \text{ g/m}^3$), low flammability, low electrical conductivity, and high degrees of both chemical and thermal stability (Erickson, 1997). Because of these properties, PCBs, in the form of mixtures of congeners sold under various trade names, were used in a myriad of industrial applications, most notably as dielectric fluids in capacitors and transformers. Unregulated manufacture and disposal of PCBs prior to the passage of the Toxic Substances Control Act (TSCA) (U.S. Congress, October 11, 1976) has led to highly concentrated localized contamination sites around former production and disposal facilities and virtually worldwide background contamination. The numerous studies of PCB concentrations in plants, animals, air, and water, when considered in total, paint a picture of a truly global pollutant. Many studies, dating back to 1936 (Jones & Alden, 1936), have investigated the effects of PCB exposure on humans, however, the multi-congener nature of most occupational and environmental exposures, as well as the presence of other pollutants, has led to conflicting conclusions as to actual PCB toxicity. Presently, the United States Environmental Protection Agency (EPA) classifies PCBs as probable human carcinogens based on predictive studies of other species (EPA, 1996). As such, the need exists for practical PCB remediation technologies.

There are several disposal and remediation techniques currently in use including landfilling, incineration, oxidative destruction, and microbial and chemical dechlorination processes. However, each of these processes has certain drawbacks. One area that has shown great potential is the use of zero-valent metals for reductive dechlorination. Chuang et al. (Chuang et al., 1995) demonstrated the ability of zero-valent iron to dechlorinate PCBs at temperatures from 300° to 600° C. In light of certain disadvantages encountered during early research in this area, such as incomplete dechlorination and the need for high reaction temperatures, a great deal of subsequent research focused on identifying a reduction-based technology that produced no toxic by-products and that could be employed under ambient reaction conditions. A process that met these criteria could possibly be used for *in situ* applications. To this end, Boronina et al. (Boronina, Klabunde, & Sergeev, 1995) used zero-valent magnesium, tin, and zinc in place of iron with mixed results and Grittini et al. (Grittini et al., 1995) created a bimetal by depositing small amounts of palladium onto microscale iron particles and observed complete dechlorination of Aroclor 1254 and 1260 on the scale of a few minutes. In an effort to improve the analytical measurement of convoluted PCB mixtures, Doyle et al. used a Mg/Pd bimetal to completely hydrodechlorinate Aroclor 1221 to the extent that biphenyl was the only analyte (Doyle et al., 1998). Using magnesium as the base metal had the advantages of a larger reduction potential (-2.37 V and -0.44 V respectively vs. SHE) and eliminated the need to acid wash the iron prior to palladium deposition. Mg/Pd bimetal has been shown to degrade other halogenated compounds such as 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (dichlorodiphenyltrichloroethane, DDT) (Engelmann, Doyle, & Cheng,

2001), polychlorinated dibenzo-*p*-dioxins and naphthalenes (Hadnagy, Rauch, & Gardner, 2007), and chlorophenols (Patel & Suresh, 2007) in a variety of solvents.

Elucidation of the mechanism, particularly the hydrogen source, of palladium catalyzed hydrodehalogenation on various substrates has been the focus of work by Ukisu and Miyadera (Ukisu & Miyadera, 2003), Agarwal (Agarwal et al., 2007), and DeVor et al. (R. Devor et al., 2009). In each of the proposed mechanisms, the solvent is the hydrogen/hydride donor and the palladium facilitates the reaction by acting as an atomic hydrogen or hydride storage medium and transfer catalyst. DeVor et al. (Robert DeVor et al., 2008) showed that the reaction rate and mechanism change depending on the solvent, and therefore the proton source, being used. Based on this work, the studies presented here were designed to investigate further the source of the hydrogen in the reaction and the effects of various molecular substitutes on the reaction rate.

Methods

Materials and Chemicals

Neat PCB standards were obtained from Accustandard and standard solutions were prepared by diluting the neat standards to the desired concentration with absolute ethanol from Pharmco-AAPER. Micro-scale magnesium (4 μm nominal diameter) was obtained from Hart Metals, Inc. Huot et al. and Soave et al. have shown that the process of ball milling increases the reactivity of magnesium by cracking the passivated hydroxide/oxide surface layer and by changing the microstructure to create more surface defects (Huot, Liang, & Schulz, 2001; Soave, Ferrari, & Pacchioni, 2001). Extensive testing in our lab confirmed these results and determined the optimal ball milling parameters for the dehalogenation of PCBs (Aitken, Geiger, Clausen, &

Quinn, 2006; Coutts et al., 2011). The study shown in Figure 1, comparing ball milled and as received magnesium, illustrates the vastly improved reactivity of the ball milled magnesium. Comparing SEM images of the magnesium powder before and after ball milling does not show a drastic change in particle size or shape. However, as Figure 2 shows, the ball milled particles appear to have a “cleaner” surface, free of irregular outcroppings of metal. The magnesium was ball milled by depositing 85 g of magnesium and 16 stainless steel ball bearings (1.5 cm diameter) into a stainless steel canister (inner dimensions 5.5 cm diameter by 17 cm height) and milling on a Red Devil 5400 series paint mixer for 30 minutes.

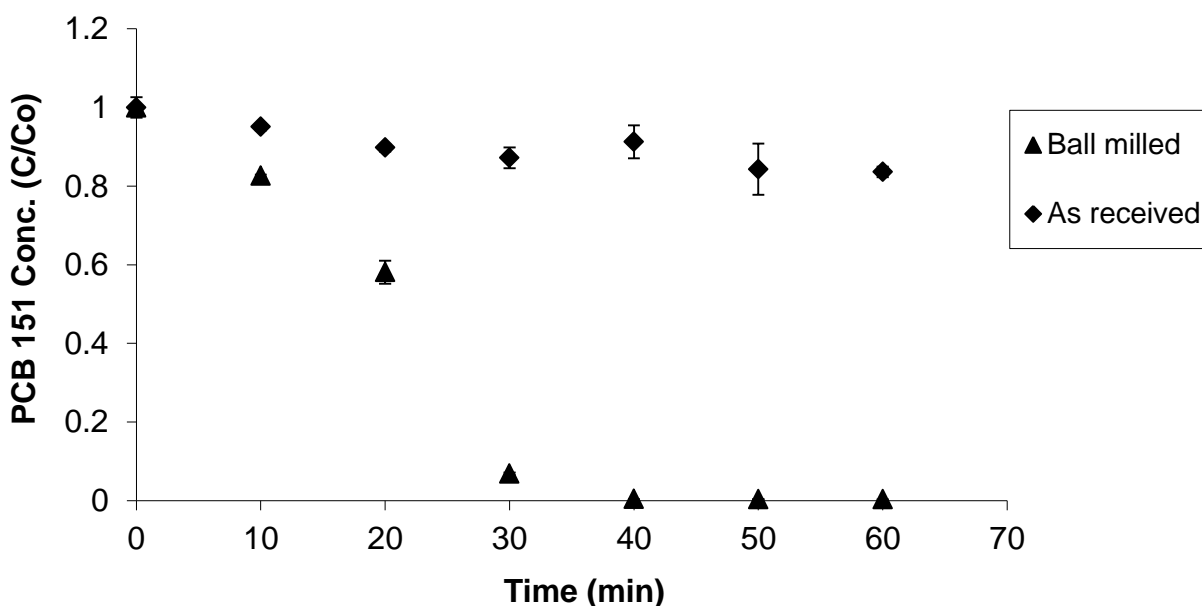


Figure 3: Comparison studies of PCB-151 degradation using ball milled magnesium powder and magnesium powder as received

Methanol, propanol, butanol, octanol, decanol, ascorbic acid, benzoic acid, phosphoric acid, formic acid, acetic acid, propionic acid, butyric acid, and valeric acid were all purchased from Fisher Scientific. All chemicals were used as received unless otherwise noted.

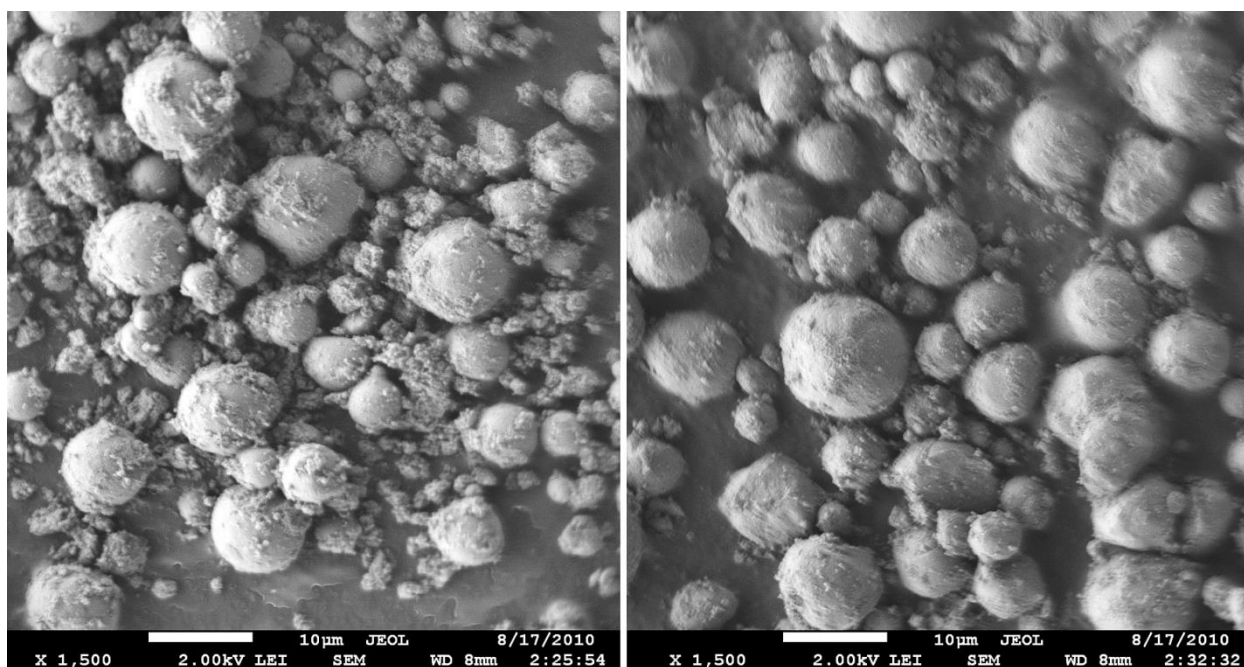


Figure 4: SEM images of magnesium powder before (left) and after (right) ball milling

Experimental Procedure

The following standard experimental procedure was used for all studies described in this paper including the ball milled vs. as received Mg study, the results of which are shown in Figure 3. Modifications to this procedure were made based on the variable being tested in each separate experiment and are described in the corresponding text. Experiments were conducted in 20 mL borosilicate glass vials with PTFE lined caps. Ball milled Mg (0.25 g) and 5 mL of a 10 µg/mL PCB-151 in absolute ethanol solution were added. Next, glacial acetic acid (50 µL) was added and the vials were then placed on a Cole Palmer® EW-51401-06 adjustable shaker table operated at 120 oscillations per minute. Extraction of the PCBs was conducted by adding 5 mL of toluene to the vials and shaking vigorously by hand for two minutes. Of this miscible solution, 4 mL were drawn into a filtered syringe and then deposited in a centrifuge tube. Next, deionized

water (2 mL) was added to induce separation of the ethanol/toluene mixture. Samples were centrifuged for four minutes and the toluene layer then was extracted for further analysis.

Analysis

Sample analysis was performed on a Perkin Elmer AutoSystem XL GC/ECD equipped with a Restek RTX®-5 column (30 m x 0.25 mm i. d., 0.25 µm film thickness) and a temperature ramp from 120° C to 300° C. Degradation was measured by disappearance of the PCB-151 peak and confirmed (as opposed to adsorption to the Mg) by the appearance of lower chlorinated congeners.

Results and Discussion

Choosing a Hydrogen/Proton Donor

Studies were conducted to see if the incorporation of an acid into the reaction matrix would act as a suitable hydrogen/proton source in place of the noble metal in the bimetallic systems currently being used for PCB remediation. Since the acid would be coming into contact with the micro-scale magnesium, acetic acid was initially chosen due to its weak acidity ($pK_a = 4.76$ at 25° C) in order to minimize violent reaction. Initial tests using approximately 1% by volume acetic acid yielded encouraging results. The first chlorine had been removed from an entire 1.0 µg/mL PCB-151 sample in 40 minutes. Further degradation of the resulting lower chlorinated congeners also was seen within the one-hour timeframe of the study, as illustrated in Figure 5. This pattern of by-products was seen in all studies that degradation was observed. The kinetic data for this standard reaction matrix is presented in the following graphs for reference. Tests of the filtered reaction solution (to remove any Mg powder) using wet litmus paper

indicate that upon addition of the acetic acid, the solution is slightly acidic with a pH of 4-5. By one minute, however, the solution pH had risen to 7-8, likely due to the reaction of the acid with the Mg powder. Direct tests of the unfiltered solution also are initially slightly acidic then increase rapidly to a pH > 10 due to the reaction of the Mg with the water on the litmus paper. This result agrees with experiments conducted by Agarwal in aqueous systems using both Mg/Pd bimetal and Mg (Agarwal et al., 2007).

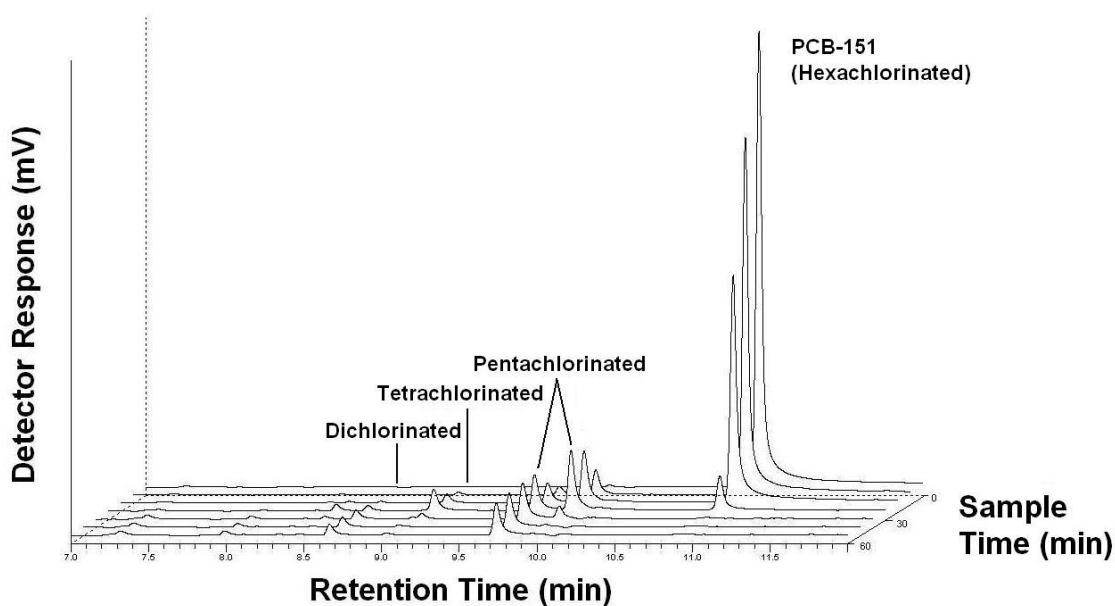


Figure 5: Time resolved PCB-151 degradation GC-ECD chromatograms showing the typically observed dechlorination pattern also seen in these studies

Based on the degradation seen in this first test, experiments were conducted to see if a mineral acid or other organic acids would produce similar results. Phosphoric acid was chosen because it was assumed to be a suitable donor and mineral acids such as phosphoric acid are often used to remove magnesium oxide/hydroxide layers from the bulk material thereby exposing the zero-valent subsurface and activating the metal (Silverman & Rakita, 1996).

Benzoic and ascorbic acids were chosen because their pK_a values are similar to acetic acid (Table 5) and due to their low toxicity. Fifty microliters of concentrated phosphoric acid were added to the sample vials just as acetic is added in the standard reaction procedure and for the studies with ascorbic and benzoic acid, a mass of ethanol was dissolved (i.e. 0.04 g of acid for 5 mL of ethanol). The results of these studies are shown in Figure 6. With each acid, other than acetic, no degradation was observed. This result was unexpected since it was assumed that the availability of a proton was an important factor for the possibility of hydrodehalogenation to occur as well as the rate of that reaction.

Table 5:
 pK_a values and masses of acids tested in these experiments

Acid	pK_a	Amount used/5 mL EtOH
Acetic	4.75	53 mg
Phosphoric	2.12	84 mg of 85% H_3PO_4
Ascorbic	4.10	39 mg
Benzoic	4.19	39 mg
Formic	3.75	61 mg
Propionic	4.87	50 mg
Butyric	4.81	48 mg
Valeric	4.82	47 mg

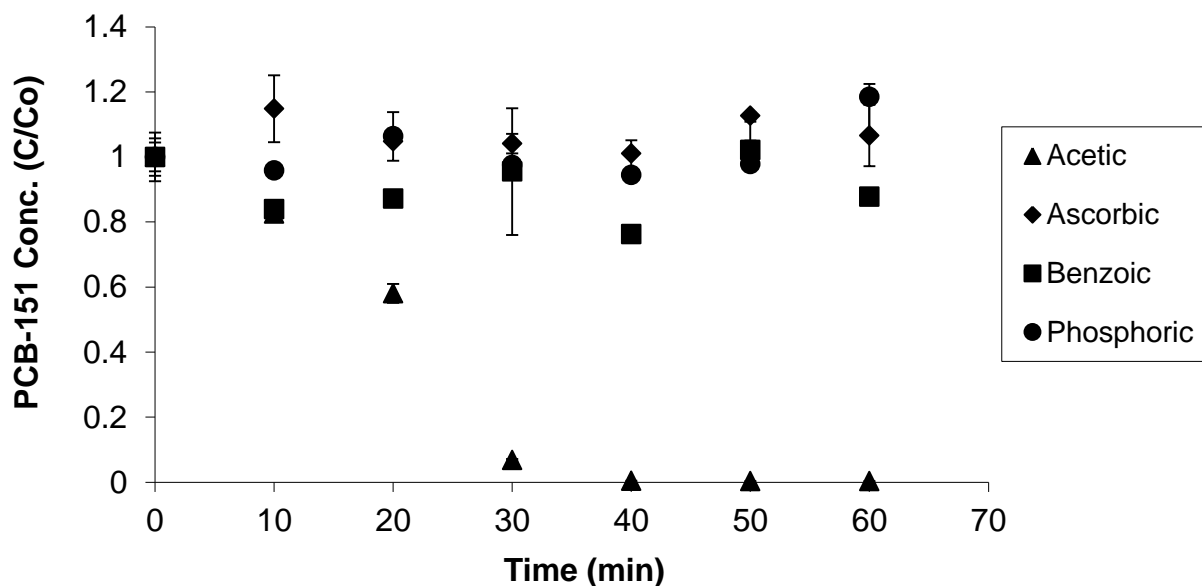


Figure 6: Comparison of PCB-151 degradation using acids with similar pK_a values to acetic acid and phosphoric acid

Because experiments using a mineral acid with a much lower pK_a (phosphoric acid) and organic acids with similar pK_a values (ascorbic and benzoic) showed no degradation, pK_a appeared to either not be the determining or not the only determining property for an acid to produce the desired reaction matrix. In the next set of experiments, a series of structurally similar carboxylic acids was tested. Over the one-hour time period of this study no degradation was observed with any acid other than acetic (Figure 7). It is worth noting that in an extended study (96 hours) formic and propionic acid were able to degrade PCB-151 over a longer period of time with formic acid degrading 80% of the starting concentration of PCB-151 by day four and propionic acid degrading 100% by day three. As in the one-hour study, no degradation was seen using either butyric or valeric acid over this extended time period. These results seem to invalidate the hypothesis that pK_a is correlated to reactivity. Paoprasert *et al.* have reported that

in carboxylate-metal complexes methylene groups act as insulators against electron transfer, which may explain the decreased reactivity observed in the longer chain carboxylic acids (Paoprasert et al., 2010).

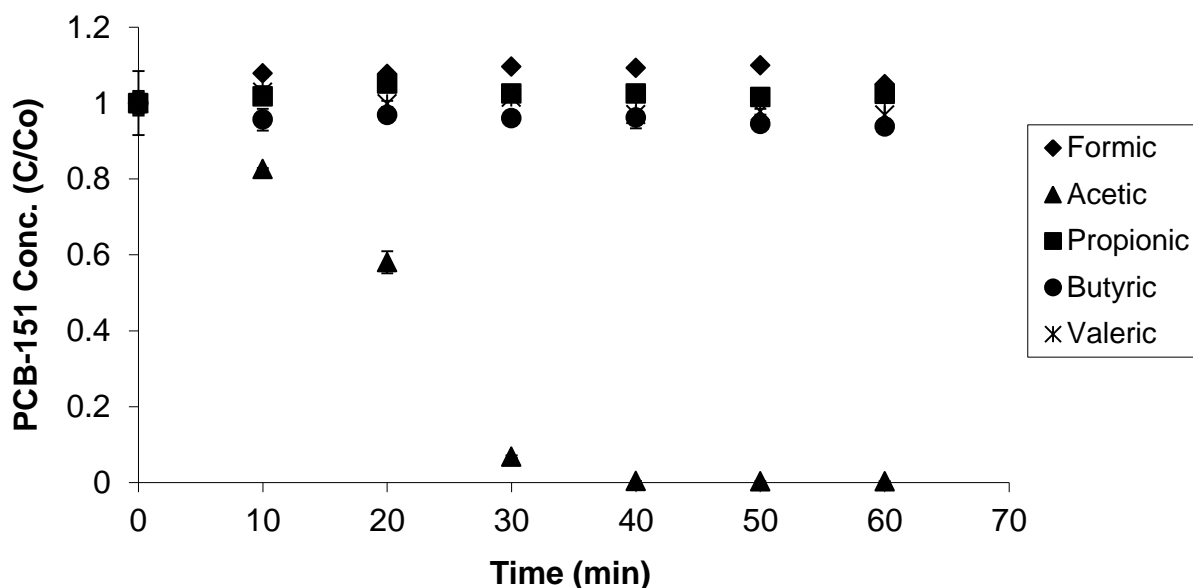


Figure 7: Comparison of PCB-151 degradation using various, straight-chain carboxylic acids

Effect of Mg Loading on PCB Degradation

In the next study, the effect of varying the amount of Mg was observed. Previous work conducted in our lab had shown that in Mg/Pd bimetallic systems, as the amount of palladium present in the reaction matrix was increased, the reaction rates increased as well. The following study was designed to see if the same trend would be seen in matrices using only Mg. To determine this, Mg loadings of 0.05, 0.10, 0.15, 0.20, and 0.25 g were used. As can be seen from Figure 8, virtually complete degradation of PCB-151 was achieved in 60 minutes in loadings as small as 0.05 g. While this may not be a surprising result based on molar amounts of the

reactants in the 0.05 g study ($Mg \approx 2 \times 10^{-3}$ mol, $PCB-151 \approx 1 \times 10^{-8}$ mol, and acetic acid $\approx 9 \times 10^{-4}$ mol), the amount of reactive Mg actually available for reaction is most likely limited by surface area and the extent of oxidation. While this paper does not attempt to quantify either of these factors, it can be said that at loadings down to 0.10 g of magnesium, neither appears to have an effect on the reaction rate.

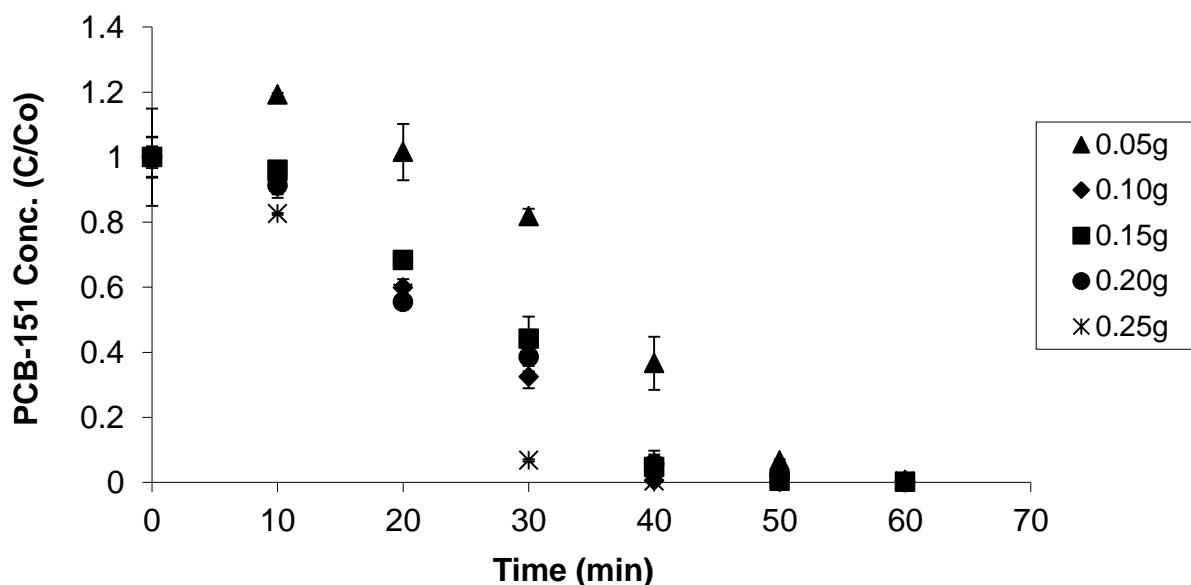


Figure 8: Comparison of PCB-151 degradation using various loadings of Mg

Effect of Varying Acetic Acid Concentration on PCB Degradation

This study attempted to determine the effect of acetic acid concentration on the rate of PCB-151 dechlorination. Volumes of 0.5, 5.0, 25, and 50 μL (approximately 0.01, 0.1, 0.5, and 1.0% by volume respectively) were added to the reaction matrix. Over the standard one-hour time period of the studies presented thus far, degradation was observed only in the samples with 50 μL of acetic acid. However, the graph in Figure 9 has been extended to 12 hours to show that

the samples containing 25 μL of acetic acid showed 95% PCB-151 degradation by the fourth hour. Over the entire 96-hour time period of this study, virtually no degradation was seen in the samples containing 0.5 or 5.0 μL of acetic acid. This demonstrates a clear dependence of the reaction rate on the volume of acetic acid present in the reaction matrix. It may be the case that at these lower volumes there is not enough acid present to neutralize the $\text{Mg}(\text{OH})_2$ layer and allow access to the reactive Mg^0 .

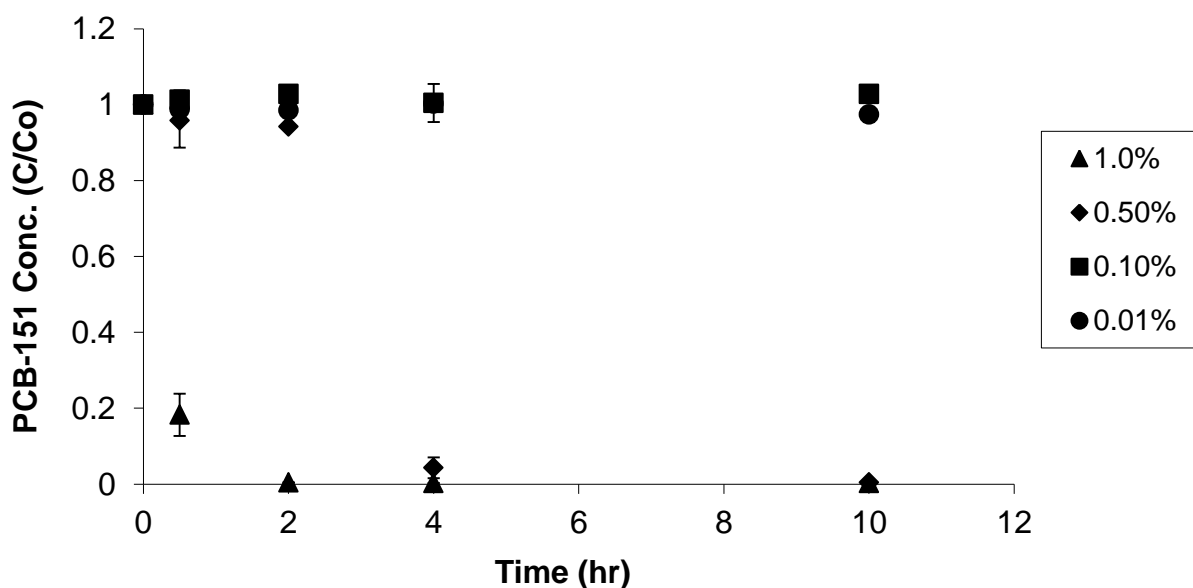


Figure 9: Comparison of PCB-151 degradation with various volumes of acetic acid

Effect of PCB Concentration on Degradation

In the fourth study, the concentration of PCB-151 was varied to see what effect this may have on the rate of degradation and to see if there is an upper limit to how much PCB-151 is capable of being degraded with the standard amount of other reagents. As indicated by the data in Figure 10, the standard acidified ethanol matrix is capable of degrading PCB-151 at least to

the highest experimental concentration of 50 $\mu\text{g}/\text{mL}$ with relatively little change on the rate of degradation.

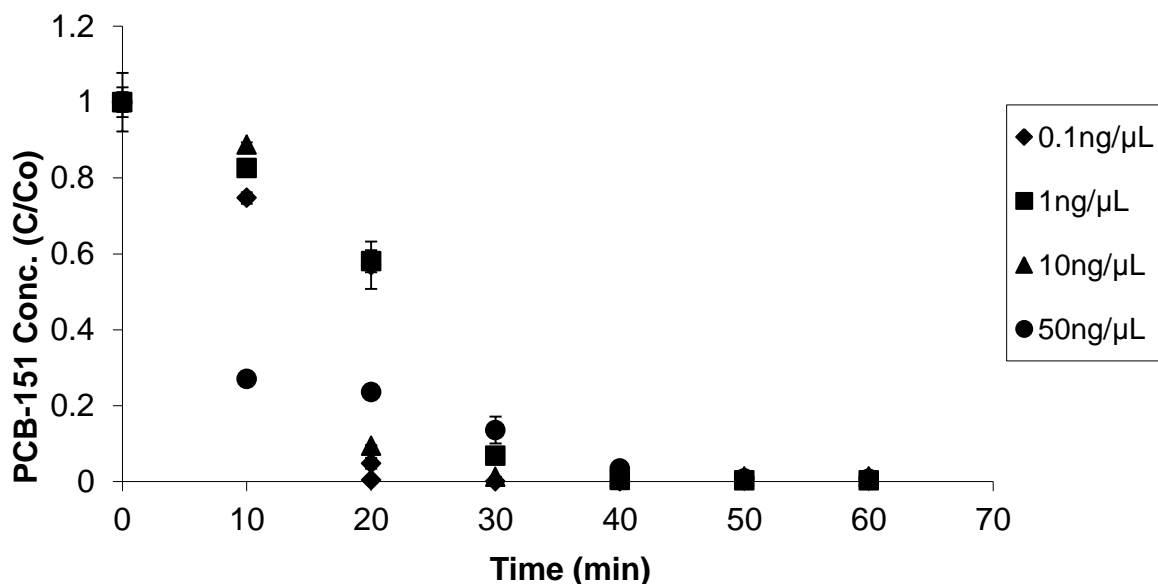


Figure 10: Comparison of PCB-151 degradation using various initial concentrations of PCB-151

Effect of Various Straight Chain Alcohol Solvents on PCB Degradation

Previous studies have indicated that the solvent was the hydrogen/hydride source in the reduction of PCBs. Based on our working hypothesis that the acid was now the hydrogen source, a study was designed to determine what, if any, effect the solvent would have on the reaction rate. In order to make comparisons to ethanol as close as possible, several straight-chain alcohols were substituted as reaction solvents. Matrices using methanol, ethanol, propanol, *n*-butanol, *n*-octanol, and *n*-decanol as the solvent were all tested at 60 minutes. As Figure 11 shows, only the samples with ethanol and methanol solvents showed significant degradation during the 60-minute time period of the study. Therefore, in order to have a more detailed

picture of the reaction rates in these two solvents, a second study was conducted with samples being taken at 20-minute intervals. PCB-151 was degraded by 73% from its initial concentration in the methanol solvent and, as seen in previous studies using ethanol, the PCB-151 concentration is below the detection limit by 40 minutes. Interestingly, in the 60-minute studies using *n*-propanol, *n*-butanol, *n*-octanol, and *n*-decanol, it was decanol that showed the greatest reduction in PCB-151 concentration and was the only one of these solvents in which lower chlorinated by-products were detected. A linear size/degradation rate relationship is not apparent.

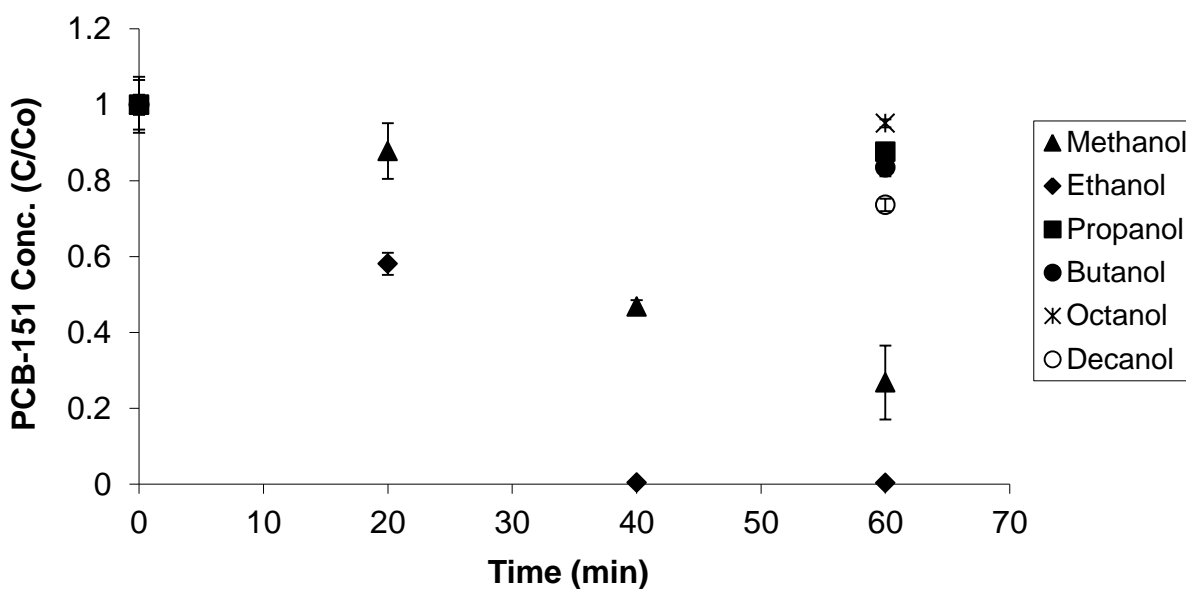


Figure 11: Comparison of PCB-151 degradation using various straight-chain alcohols

Conclusion

This paper describes a magnesium, acetic acid, and ethanol matrix that is, to the best of our knowledge, a novel reaction matrix for the hydrodechlorination of PCBs. No appreciable

decrease in the rates of degradation was seen in studies using as little as 0.05 g of Mg or PCB-151 concentrations as high as 50 $\mu\text{g/mL}$. However, the rate of reaction showed a strong dependence on the type and amount of acid used as well as the choice of solvent. In these experiments, it was found that a volume of 50 μL of acetic acid in 5 mL ethanol solution yielded the best results. Neither phosphoric acid, which has been used to activate magnesium, nor organic acids with similar $\text{p}K_{\text{a}}$ values were suitable substitutes for acetic acid. Steric effects were then considered since the ascorbic and benzoic acids used in the first study with formic acid, which has both a lower $\text{p}K_{\text{a}}$ and is a smaller molecule, showed a slower rate of degradation as well. Additionally, the rate of reaction showed a strong dependence on which solvents were used, with methanol and propanol yielding much lower reaction rates than ethanol. Currently, the exact roles of the acid and the solvent in the reaction are not fully understood.

A system using magnesium, acetic acid, and ethanol has the potential to significantly reduce material expenses in comparison to similar systems using costly secondary metals such as palladium, platinum, gold, or silver. Additionally, the exclusion of a heavy metal eliminates recovery and regulation considerations for any *in situ* remediation techniques.

CHAPTER THREE: DEGRADATION OF VARIOUS HALOGENATED POLLUTANTS BY MICROSCALE MAGNESIUM AND ACIDIFIED ETHANOL: PROOF OF CONCEPT FOR FIELD APPLICATIONS

Introduction

The Stockholm Convention on Persistent Organic Pollutants is a global treaty intended to codify international regulations regarding the production and use of chemicals that have been found to be widely dispersed, resistant to degradation, bioaccumulative, and detrimental to the environment. Based on these criteria, 12 substances, known as the dirty dozen, were listed by the first convention in 2001, nine more were added to the list in 2009, and at the 2011 meeting one more compound was included (Table 6). While the production and use of these chemicals has either been severely restricted or outright banned, many countries are searching for effective methods of disposing of existing inventories and remediating contaminated sites. In addition to the shared environmental and biological behaviors listed above, a chemical characteristic common to each of these molecules is that they all have some degree of halogenation. It is therefore reasonable that a chemical degradation process that proceeds via dehalogenation may be applicable to several of these compounds.

Table 6:
Substances currently listed under the Stockholm Convention*

Added in 2001	Original use	Halogen moieties	Added in 2009/2011†	Original use	Halogen moieties
Aldrin	Pesticide	Cl - 6	Chlordecone	Pesticide	Cl - 6
Chlordane	Pesticide	Cl - 8	Alpha hexachlorocyclohexane	Pesticide, by-product	Cl - 6
DDT	Pesticide	Cl - 5	Beta hexachlorocyclohexane	Pesticide, by-product	Cl - 6

Added in 2001	Original use	Halogen moieties	Added in 2009/2011†	Original use	Halogen moieties
Dieldrin	Pesticide	Cl - 6	Lindane	Pesticide	Cl - 6
Endrin	Pesticide	Cl - 6	Pentachlorobenzene	Pesticide, industrial chemical, by-product	Cl - 5
Heptachlor	Pesticide	Cl - 7	Hexabromobiphenyl	Industrial chemical	Br - 6
Hexachlorobenzene	Pesticide, industrial chemical, by-product	Cl - 6	Hexa/heptabromodiphenyl ether	Industrial chemical	Br - 6/7
Mirex	Pesticide	Cl - 12	Perfluorooctane sulfonic acid/perfluorooctane sulfonyl fluoride	Industrial chemical	F - 17/18
Toxaphene	Pesticide	Cl - 5-12	Tetra/pentabromodiphenyl ether	Industrial chemical	Br - 4/5
PCBs	Industrial chemical, by-product	Cl - 1-10	Endosulfan and related isomers†	Pesticide	Cl - 6
PCDD	By-product	Cl - 1-8			
PCDF	By-product	Cl - 1-8			

*Adapted from (Secretariat of the Stockholm Convention, 2008b)

It has been shown previously that a reaction matrix consisting of powdered magnesium, ethanol and acetic acid is able to rapidly degrade polychlorinated biphenyls (PCBs) via hydrodechlorination (Maloney et al., 2011). The purpose of this work is to determine if the same reaction matrix also is capable of degrading polychlorinated dibenzo-*p*-dioxin (PCDD), polybrominated diphenyl ether (PBDE), and four organochlorine pesticides (OCPs) and if it can be successfully applied to contaminated environmental media.

The generic term dioxin is commonly used to refer to any of the 75 distinct polychlorinated dibenzo-*p*-dioxin congeners. They have never been produced or used intentionally, but are by-products of other industrial activities such as waste incineration, paper bleaching, metal smelting, and production of other chlorinated compounds (Kulkarni, Crespo, & Afonso, 2008). Of the 75 possible congeners, seven are considered highly toxic with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) being the most toxic. Because of their lipophilicity, the primary source of human exposure is through the ingestion of foods with high fat content. Once inside an organism, dioxins interact with the aryl hydrocarbon receptor (AhR), which may adversely affect gene expression, hormone signaling, reproduction, and development (Mandal, 2005).

Polybrominated diphenyl ethers are a class of 209 congeners in which any of the 10 hydrogens in diphenyl ether have been replaced by bromine. They are flame-retardants, which are commonly added to a wide range of consumer products such as; upholstery, carpet pads, plastics, and electronics. Unlike most other POPs, since PBDEs are added to household items they are primarily indoor pollutants (Lam & Loganathan, 2012). With the exception of those congeners banned by the Stockholm Convention, PBDEs still are being manufactured and environmental monitoring studies show that after decades of sharp increases, levels since the mid 2000's appear to have plateaued (de Wit, Alaee, & Muir, 2006; Wu et al., 2012).

As Table 6 shows, 15 of the 22 chemicals listed under the Stockholm convention are chlorinated pesticides. The origin of organochlorine pesticides can be traced back to 1939 when Dr. Paul Müller notice the insecticidal properties of dichlorodiphenyltrichloroethane (1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane, DDT). A United States patent for DDT was granted in

1943 and it was soon used on an industrial scale for the protection of agricultural crops and to control the spread of various insect-borne diseases (Cremlyn, 1978). As a result of the unprecedented success of DDT, the period from 1945 to 1955 saw the synthesis of numerous new OCPs collectively referred to as second-generation pesticides. During this period, there was little to no regulation on their use and pesticides were deployed indiscriminately with little concern for their eventual fate in the environment (Lehman & Pimentel, 1993). By the mid-1950s scientific studies were published indicating these pesticides' long-term persistence in soils ("DDT Residue Persistence High in Some Soils," 1954), the ability of pests to develop resistance toward them (Kitaoka, 1952), and their presence in human populations through non-occupational exposure (Pearce et al., 1952). However, it was not until 1962, with the publication of Rachel Carson's *Silent Spring* (Carson et al., 1962), that some of the unintended environmental side effects of OCPs were brought to the general public's attention. In response to growing public concern, the federal government began to explore the possibility of establishing guidance for their application and disposal (Greenberg, 1963). Thus began a decades-long process of increasing federal regulation of OCPs. With respect to the pesticides included in this research, they are dieldrin, restricted in 1969 and voluntarily discontinued in 1987; heptachlor and heptachlor epoxide, restricted in 1978 and voluntarily discontinued in 2000; chlordane, restricted in 1978 and banned in 1988 (U.S. EPA, 2002).

Although these OCPs have not been used in decades, due to their inherent chemical stability and tendency to strongly bind to soils, they remain contaminants of concern (Navarro, Vela, & Navarro, 2007). As of February 2013, there are dozens of sites listed on the United

States Environmental Protection Agency's (EPA) National Priorities List (NPL) contaminated with each of the four OCPs included in this research.

Methods

Materials and Chemicals

Stock solutions were prepared by dissolving neat octachlorinated dibenzo-*p*-dioxin (OCDD), decabrominated diphenyl ether (DBDE), and OCP standards, purchased from Accustandard, in absolute ethanol (Pharmco-AAPER). Micro-scale magnesium powder with a nominal diameter of 4 μm was obtained from Hart Metals Inc. Prior to use, this magnesium was ball milled in a stainless steel canister with 16 stainless steel ball bearings on a Red Devil 5400 series paint mixer for 30 minutes. This process has been shown to increase the reactivity of the metal in hydrodehalogenation reactions (Maloney et al., 2011). Glacial acetic acid was purchased from Fischer Scientific and used as received. Soil samples received by our lab had been analyzed by an independent laboratory prior to our receipt, and were found to have a chlordane contamination level of 72 mg/kg. Analysis performed in our lab determined the concentration to be 81 mg/kg.

Experimental Procedure

All experiments were conducted in 20 mL borosilicate glass vials with PTFE lined caps. The reaction matrix consisted of 0.25 g of ball milled Mg, 5 mL of absolute ethanol, 50 μL of glacial acetic acid, and concentrations of 50 ng/ μL for OCDD, deca-BDE, dieldrin, heptachlor, and heptachlor epoxide, and 100 ng/ μL for the chlordane technical mixture. Sample vials were

placed on a Cole Palmer EW-51401-06 adjustable reciprocating shaker table operating at 120 oscillations per minute for the duration of the experiment.

During the OCDD and deca-BDE experiments, samples were taken at 0, 0.5, 1.0, 24, and 72 hours in duplicate. In the first OCP experiment, samples were taken in duplicate at 24 and 48 hours, however, by the 24-hour time point all samples were below the limit of detection (less than 1 ng/ μ L). A second set of OCP experiments was setup under the same experimental parameters, with adjustments made to the duration of the experiment and the sampling times, which were decreased to one hour and 10 minutes respectively. A third experiment was performed on the chlordane-contaminated soil. The chlordane was extracted from the soil by combining 10 mL of absolute ethanol per 1.0 g of soil in a 20 mL vial and subjecting this mixture to ultrasonication for 90 minutes. The ethanol/chlordane solution then was decanted and filtered using a syringe equipped with a Millipore 25 mm nylon filter disc (0.45 μ m pore size). This solution then was reacted in a matrix identical to that of the first two experiments, except that the reagent quantities were all cut by 20% (i.e., 4 mL of chlordane/ethanol solution, 0.20 g Mg and 40 μ L of glacial acetic acid). For samples to be analyzed by ECD, a solvent/solvent extraction was performed by adding an equal volume of toluene to the reaction vial and shaking vigorously by hand for two minutes. A filtered syringe then was used to draw 4 mL of this miscible solution and deposit it into a centrifuge tube. Next, 2 mL of deionized water were added to the centrifuge tube to facilitate the separation of the ethanol/toluene solution. Samples then were centrifuged for four minutes and the toluene layer was collected for analysis.

Analysis

Samples from the OCDD and PBDE studies were analyzed on an Agilent 6850 Series II gas chromatograph coupled with an Agilent 5975 mass selective detector equipped with a DB-5 capillary column (DB-5MS 30 m x 0.25 mm i.d., 0.25 μ m film thickness). OCP analysis was performed on a Perkin Elmer Autosystem XL GC/ECD and a Thermo-Finnigan Trace DSQ GC/MS, both equipped with a Restek RTX-5 column (30 m, 0.25 mm i.d., 0.25 μ m film thickness). Degradation was quantified by the disappearance of the reactant peak and confirmed (as opposed to adsorption to the Mg) by the subsequent appearance of less halogenated product peaks.

Results and Discussion

Dioxin Degradation

Figure 12 illustrates that the magnesium and acidified ethanol matrix rapidly dehalogenated OCDD during the first hour of the experiment. Mass spectra were used to assign degrees of chlorination to the peaks in the chromatograms. Due to the symmetry of the OCDD molecule, there are only two possible heptachlorinated products, both of which were formed during this study. This indicates that both longitudinal (1, 4, 6, 9) and lateral (2, 3, 7, 8) chlorines can be removed. The peaks of four of the 10 possible hexachlorinated isomers are clearly distinguishable in the 0.5- and 1.0-hour chromatograms, which may indicate that not all of the possible products are formed. However, since analytical standards of all of the hexachlorinated dioxins were not available for comparison, the possibility that multiple congeners are coeluting cannot be ruled out. As Table 7 shows, there are numerous penta-,

tetra-, and trichlorinated isomers, which coincide with the many peaks seen in the chromatograms for those groups.

Table 7

Distribution of PCDD and PBDE congeners based on degree of halogenation

Degree of PCDD chlorination	Number of constitutional isomers	Degree of PBDE bromination	Number of constitutional isomers
Mono	2	Mono	3
Di	10	Di	12
Tri	14	Tri	24
Tetra	22	Tetra	42
Penta	14	Penta	46
Hexa	10	Hexa	42
Hepta	2	Hepta	24
Octa	1	Octa	12
		Nona	3
		Deca	1
Total	75		209

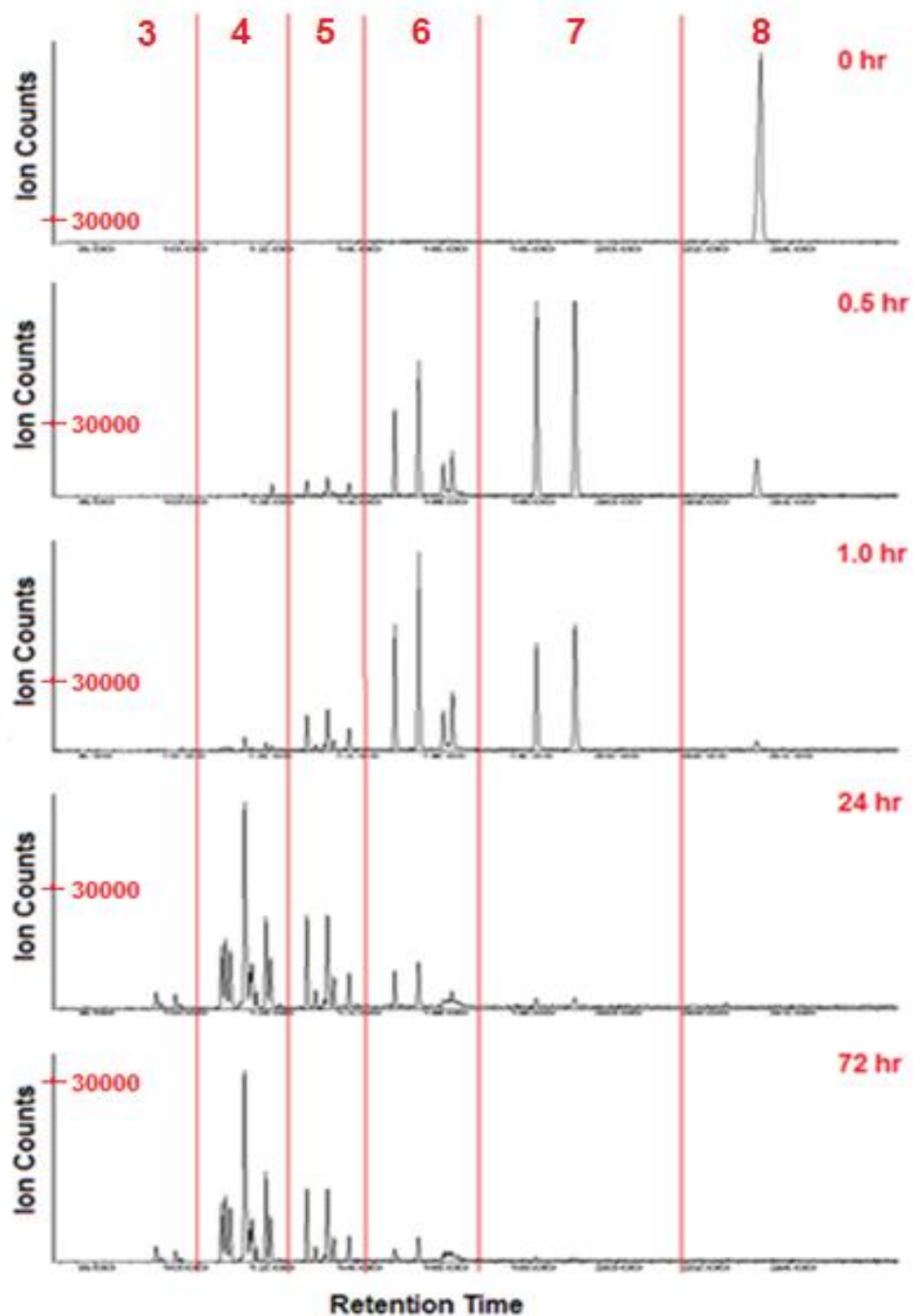


Figure 12: Chromatograms showing the degradation pattern of OCDD. Although no attempt was made to identify specific product congeners, mass spectrum information allows them to be identified by their degree of chlorination. Please note the Y-axis is not set to a uniform scale among the chromatograms.

PBDE Degradation

A PBDE degradation study was performed using the same experimental procedures as the OCDD study above. The resulting chromatograms are shown in Figure 12. Debromination of the 50 ng/ μ L starting concentration of deca-BDE was quite fast, as evidenced by the appearance of octabrominated isomers in the zero hour samples. All zero hour samples are shaken for 15 seconds to facilitate complete mixing of the reactants and the extraction procedure takes approximately two minutes. Therefore, although they are labeled as zero hour samples, the reactants actually are in contact for a little over two minutes, which may explain the appearance of product peaks. Increased reactivity of bromine relative to chlorine in other zero-valent metal systems has been reported (Hutchins, Suchismita, Zipkin, & Taffer, 1989; Mitoma et al., 2001). By 0.5 hours, deca-BDE and octa-BDEs are no longer evident, and the highest remaining brominated isomers are hexa-BDE. There are numerous tri- to octa-BDE isomers (Table 7) and individual identification was not attempted. As in the OCDD study, mass spectra were used to identify chromatogram peaks only in terms of their level of bromination. No significant change was seen in the 24-hour and 72-hour chromatograms suggesting that the magnesium was no longer reactive.

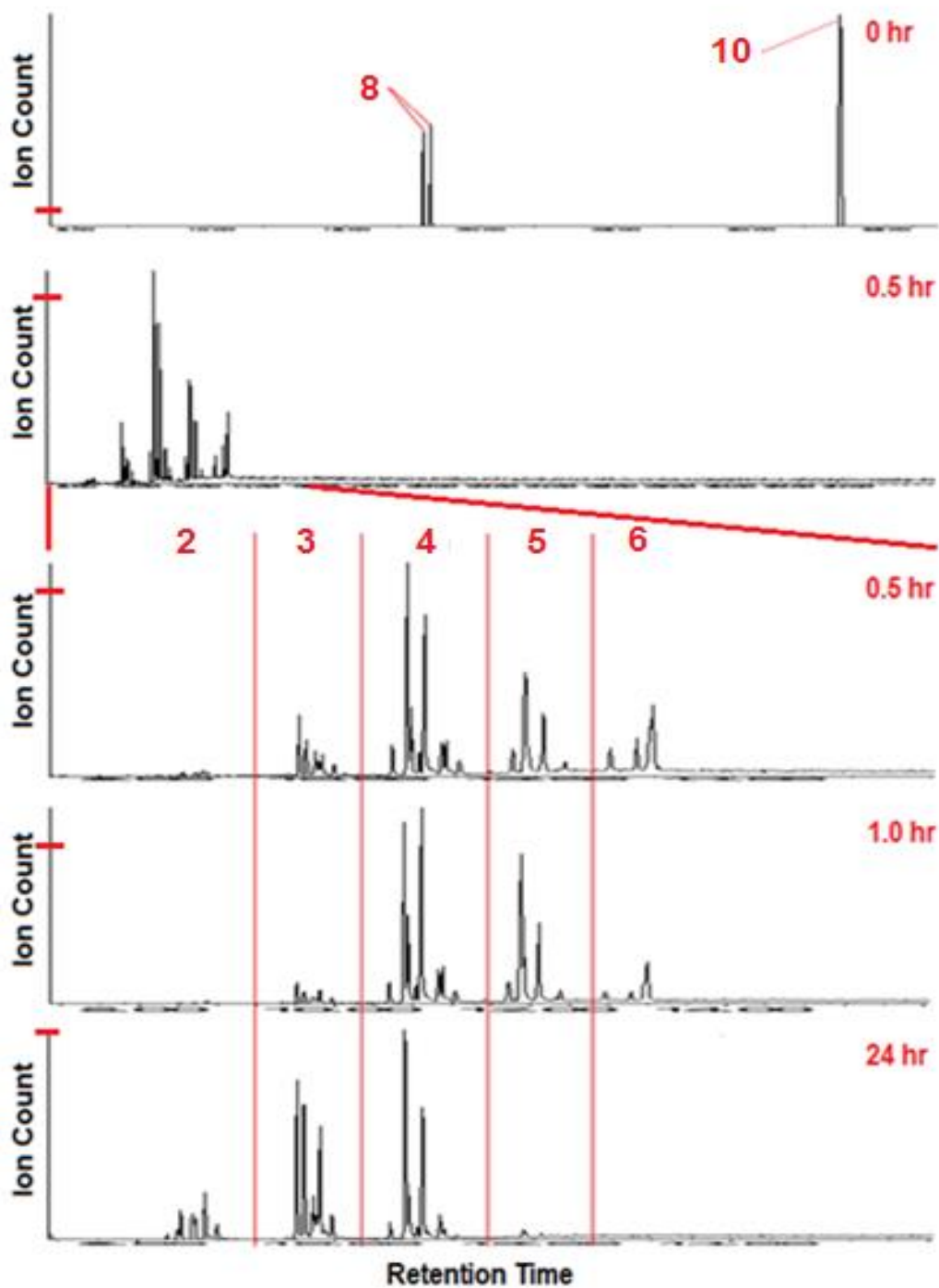


Figure 13: Chromatograms showing the degradation of samples of 50 ng/ μ l deca-BDE. The expansion shows the grouping of retention times of lower brominated products. Please note, the y-axis is not set to a uniform scale among the chromatograms.

24-Hour OCP Studies

The first group of studies was designed to determine if the magnesium/ethanol reaction matrix described above was capable of degrading any of the selected OCPs. The four experiments were each to last one week with samples taken once per day. However, analysis of the first day's samples indicated that none of the parent compound remained. Furthermore, no highly chlorinated by-products, which one would expect to detect by ECD, were present either. This outcome seemed to indicate that either the reaction proceeded to such an extent that there were no reaction products with enough remaining chlorines to be detected by ECD or that the OCPs had sorbed to the magnesium and were not recoverable by our extraction process.

One-Hour OCP Studies

The second set of experiments was setup to provide more detail on what was happening to the parent OCP molecule during the first hour of the reaction. These studies indicated that the disappearance of the parent compound was not due to sorption since lower chlorinated molecules are clearly being formed as the parent OCP is degraded. These experiments also revealed that the majority of the degradation occurred during the first hour of the reaction, as illustrated below in Figure 14. Heptachlor, heptachlor epoxide, and chlordane were degraded to below instrumental detection limits (i.e. > 99% degradation) by the 60-minute time point. The reaction rate of dieldrin was somewhat slower, with 71% of the 50 ng/ μ L starting concentration degraded over the same period.

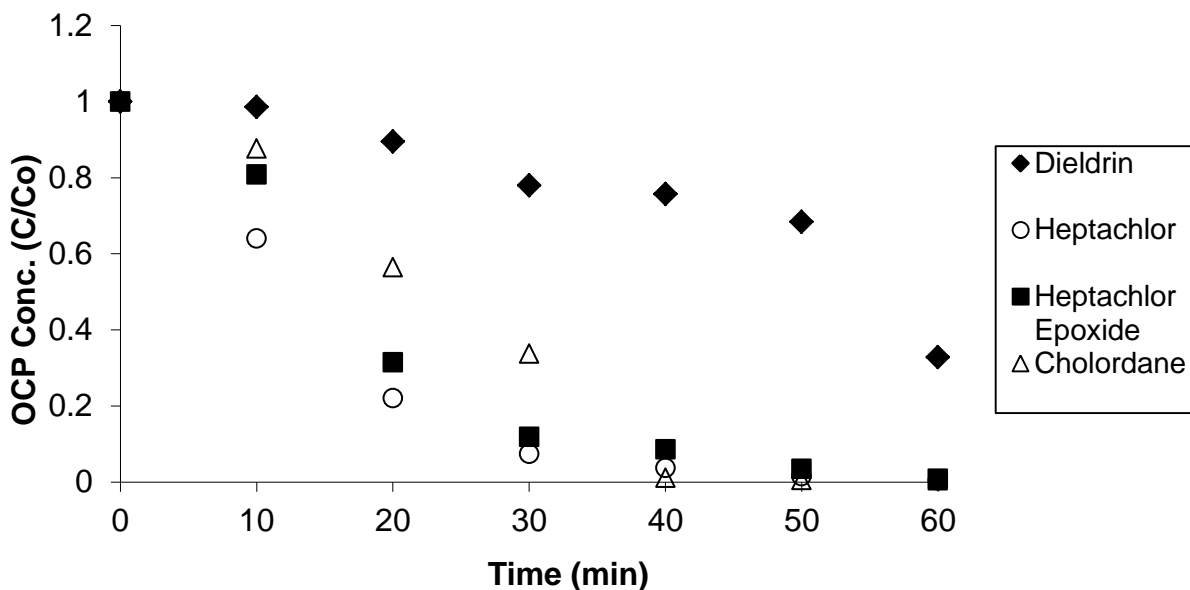


Figure 14: Comparison of the degradation rates of four representative organochlorine pesticides

In each of the four OCP studies, multiple products with one less chlorine were detected indicating that the first hydrodechlorination reaction was able to occur at several different chlorine sites per molecule, i.e., there are multiple simultaneous degradation pathways. In two separate studies, Zhuang and Kim reported similar concerted pathways when using palladized zero-valent iron to debrominate polybrominated diphenyl ethers (PBDE) and PCBs respectively (Y. H. Kim, Shin, & Ko, 2004; Zhuang et al., 2011). The abundance of by-products is illustrated in Figure 15, which shows a time-resolved set of ECD chromatograms for the degradation of heptachlor epoxide. Here the reaction products are shown to increase as the heptachlor epoxide parent peak decreases. These two experiments demonstrated that the acidified ethanol system is capable of rapidly degrading a variety of OCPs.

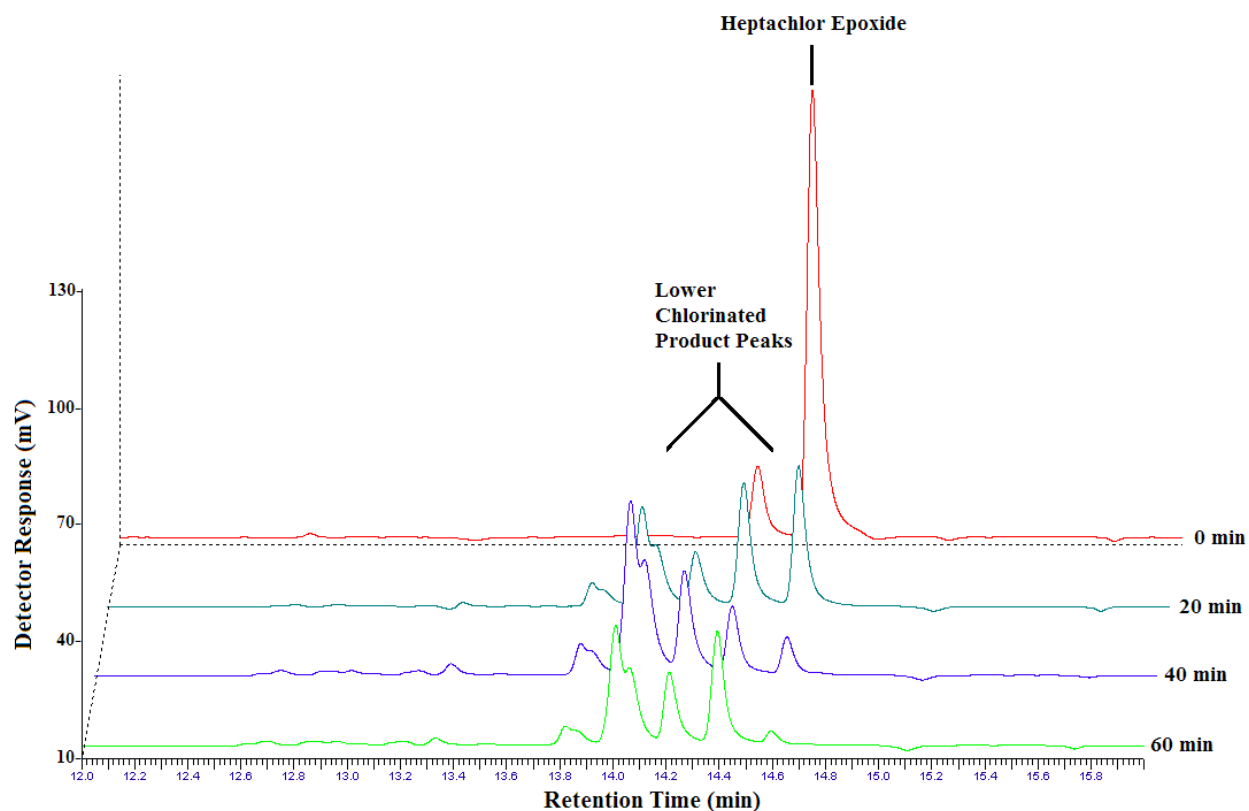


Figure 15: Time resolved heptachlor epoxide GC-ECD chromatograms from the one-hour degradation study

Remediation of Chlordane Contaminated Soil

The purpose of the third experiment was to determine if this system was capable of degrading OCPs found in soil matrices. Our lab received field samples with a chlordane concentration of 72 mg/kg for the purpose of testing the remediation technique described above. The soil appeared to be a sandy loam with a small amount of gravel and plant matter. Prior to our analysis and treatment, the soil was filtered through a number 16 mesh sieve to remove any larger material. Interaction between soils and OCPs, such as sorption to organic material or sequestration to micropores inaccessible to chemical reactants, may hinder or prevent reactions that readily occur under simplified laboratory conditions (Gevao, Semple, & Jones, 2000).

Therefore, in order to minimize possible effects of these interferences, the chlordane was extracted into absolute ethanol prior to adding the other reactants. Solvent washing is an established technique for transferring contaminants from soil to a medium more amenable to the treatment process and ethanol in particular has been shown to be effective for removing chlorinated molecules (Jonsson, Lind, Lundstedt, Haglund, & Tysklind, 2010; Khodadoust, Suidan, Acheson, & Brenner, 1999; Koustas & Fischer, 1998; Thangavadivel et al., 2011). This was accomplished by placing the ethanol/soil slurry in an ultrasonic bath for 90 minutes. Calculations based on the resulting chlordane in the soil were 81 mg/kg, 9 mg/kg higher than the determination made by an independent analytical laboratory prior to our receipt of the samples. Based on this result, we felt confident that the solvent extraction process was removing an acceptable level of chlordane from the soil.

Once the ethanol had been decanted and filtered, the Mg powder and acetic acid were added to begin the degradation reaction. The results of the degradation study show that approximately 90% of the starting concentration of the chlordane was degraded by the final two-hour sample point as shown in the chromatograms in Figure 16. Analysis was complicated somewhat by the fact that the chlordane profile from the soil did not match our technical grade standard, most likely due to preferential volatilization of certain components in the mixture, and other processes (Eitzer, Iannucci-Berger, & Mattina, 2003). As a result, two of the largest five peaks in the chlordane standard were not present in the soil samples. Therefore, the remaining three peaks were used for correlation between the calibration curve and the soil samples and the reported degradation percentages are based on this calculation.

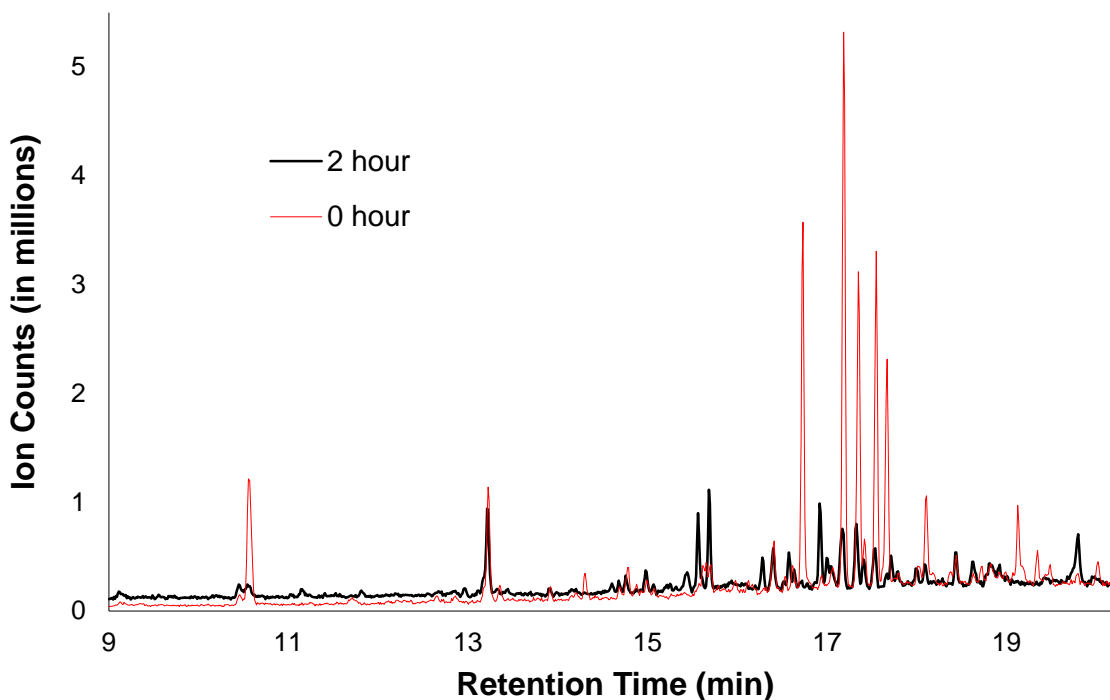


Figure 16: GC-MS chromatograms showing degradation of chlordane extracted from the soil sample

Conclusion

These experiments demonstrate the magnesium/acidified ethanol matrix is capable of degrading numerous halogenated contaminants. Starting concentrations of 50 ng/ μ L OCDD and DBDE were both dehalogenated within the one-hour resulting in numerous lower halogenated products. The data from the initial 48-hour OCP experiments indicate that the concentrations of all OCPs tested had decreased to below detectable limits within the first 24 hours, which equated to > 99% degradation. The results of the one-hour follow-up study showed that the heptachlor, heptachlor epoxide, and chlordane were each degraded to below 1% of their initial concentration by the end of the study. The kinetics of the dieldrin degradation were somewhat slower with an

approximately 71% decrease in the initial concentration over one hour. For remediation of the contaminated soil, the solvent extraction into ethanol proved to be effective for the removal of chlordane from the soil and the following degradation study showed that by two-hour the concentration of chlordane in the ethanol had fallen by 90%.

The results presented here demonstrate that (1) the magnesium/acidified ethanol matrix rapidly and completely degrades several different halogenated compounds and (2) this technology combined with a simple solvent washing step, has proven effective for remediation of pesticide contaminated soil. Continuing research will be focused on testing this system's applicability to additional types of environmental media, identifying reaction products and achieving a mass balance, and understanding the fundamental chemical processes at work in order to optimize its effectiveness.

CHAPTER FOUR: MECHANISTIC ASPECTS OF THE HYDRODEHALOGENATION OF POLYCHLORINATED BIPHENYL BY ZERO-VALENT MAGNESIUM IN ACIDIFIED ETHANOL

Introduction

The term persistent organic pollutant (POP) refers to a wide range of chemicals that are ubiquitous in the environment, highly resistant to degradation, bioaccumulative and harmful to living organisms. Many chemicals that fit into this category were originally used because they possessed some industrially valuable property. After decades of essentially unregulated use, however, concern over the long-term effects and eventual fate of these substances began to emerge. Corresponding advances in analytical instrumentation and techniques showed that these chemicals were not consumed at their initial point of use but were in fact extremely persistent in the environment. Furthermore, research showed that these compounds were being dispersed to virtually every part of the globe via atmospheric and oceanic transport processes. In response to the global problem of POP contamination, the United Nations drafted the Stockholm Convention on Persistent Organic Pollutants. The 12 compounds identified in this treaty have come to be known as the “dirty dozen” (Secretariat of the Stockholm Convention, 2008a).

One member of this group that has been the focus of a tremendous amount of research is polychlorinated biphenyl (PCB). PCBs are a class of molecules that have a biphenyl backbone with chlorines substituted in place of any or all of the hydrogens. There are 209 distinct PCB congeners that are identified as BZ-1 to BZ-209 according BZ nomenclature system (Ballschmiter & Zell, 1980). They were manufactured on an industrial scale through the reaction of biphenyl with chlorine gas, a process that created technical mixtures of numerous individual congeners. Monsanto, the major U.S. manufacturer of PCBs, sold these mixtures under the trade

name Aroclor 12XX, where the number 12 refers to the 12 carbons in biphenyl and the number represented by XX denotes the mass percentage of chlorine that was added in the reaction.

These PCB mixtures had numerous applications, but their main use was in electrical components due to their low electrical conductivity and flammability and chemical inertness. Ironically, the same high degree of stability that made PCBs so well suited for industrial use also has made them extremely vexing environmental contaminants. Because of their high octanol-water partition coefficients (K_{ow}) and low aqueous solubility, PCBs tend to concentrate in fatty tissues and are not readily eliminated by normal metabolic processes. As a result PCBs are biomagnified in apex predators, particularly those with seafood-based diets such as harbor seals (Cullon et al., 2012) and brown pelicans (Vander Pol, Anderson, Jodice, & Stuckey, 2012).

Over the last twenty years, zero-valent metals have been used extensively to degrade halogenated compounds. The majority of this work has focused on the use of iron as a reductant either alone or in combination with a second, catalytic metal. Early studies showed that zero-valent iron was capable of degrading several chlorinated aliphatic POPs. However, in most cases, degradation efficiency was proportionate to the degree of chlorination and iron was not always capable of completely dechlorinating the target molecule under mild experimental conditions (Elliott, Lien, & Zhang, 2009; Gillham & Ohannesin, 1994; Matheson & Tratnyek, 1994; Orth & Gillham, 1996; Scherer, Balko, Gallagher, & Tratnyek, 1998). Halogenated aromatic compounds proved to be more difficult to degrade and required modified reaction parameters such as elevated temperatures (Chuang et al., 1995; Kluyev, Cheleptchikov, Brodsky, Soyfer, & Zhilnikov, 2002), increased pressures (Yak, Wenclawiak, Cheng, Doyle, & Wai,

1999), or the inclusion of secondary metal (Grittini et al., 1995; Wang, Huang, Peng, & Fennell, 2010).

In an effort to simplify analysis of complex Aroclor mixtures, Doyle et al. sought to convert of the constituent PCBs to biphenyl using Fe/Pd and Mg/Pd. Based on mechanisms that had been proposed, Fe and Fe/Pd systems, they hypothesized that magnesium's more negative electrode potential relative to iron (Mg = 2.37 V, Fe = 0.44 V) would make it a suitable reductant as well. Although both systems achieved complete dechlorination, comparisons of kinetic data were not reported (Doyle et al., 1998). Subsequently, others have used Mg/Pd bimetals to degrade many halogenated pollutants under various experimental conditions (Agarwal et al., 2007; Robert DeVor et al., 2008; Hadnagy et al., 2007).

Methods

Materials and Chemicals

Neat PCB-151 standards were purchased from Accustandard and stock solutions were prepared by dissolving the neat standards into absolute ethanol purchased from Pharmco-AAPER. Micro-scale magnesium was purchased from Hart Metals Inc. and was ball milled prior to use. The ball milling procedure consisted of placing 85 g of Mg powder and 16 1.5 cm diameter stainless steel balls into a stainless steel canister (inner dimensions; 5.5 cm diameter x 17 cm height) and milling on a Red Devil 5400 series paint shaker for 30 minutes. Glacial acetic acid was purchased from Fisher Scientific and used as received.

Experimental Procedure

Experiments were conducted in 20 mL borosilicate glass vials with PTFE lined caps. Ball milled Mg (0.25 g) and 5 mL of 1 ng/ μ L PCB-151 stock solution were added to the vials, followed by 50 μ L of glacial acetic acid. The vials were then placed on a Cole Palmer EW-51401-06 adjustable shaker table operating at 120 oscillations per minute. Sample extractions were performed by drawing 2 mL of solution into a syringe equipped with a Millipore 25 mm (0.45 μ m pore size) nylon syringe filter.

Analysis

Samples were analyzed using a Varian 3800 GC/ECD equipped with a Restek RTX-5 capillary column (30 m x 0.25 mm i. d., 0.25 μ m film thickness). Degradation was confirmed by the disappearance of the PCB-151 peak and corresponding appearance of lower chlorinated congeners. Images were taken using a JEOL JSM-7500F scanning electron microscope equipped with a Thermo NORAN System Six energy-dispersive X-ray spectrometer.

Results and Discussion

Previously we have shown that a reaction matrix consisting of microscale zero-valent magnesium and an acetic acid/ethanol solution (1.0 V/V %) is capable of completely and rapidly degrading an exemplar PCB congener, PCB-151, to lower chlorinated products (Maloney et al., 2011). As Figure 17 shows, plotting PCB-151 concentration vs. time yields a distinctly sigmoidal curve. However, if one ignores the starting plateau and evaluates the reaction kinetics over the time period of active degradation (Figure 18), it is pseudo zero-order with respect to PCB-151. Kinetic data such as these are well known for surface area mediated reactions and are

attributed to the saturation of active sites suggests that in this reaction PCB degradation may be operating under similar constraints (House, 2007).

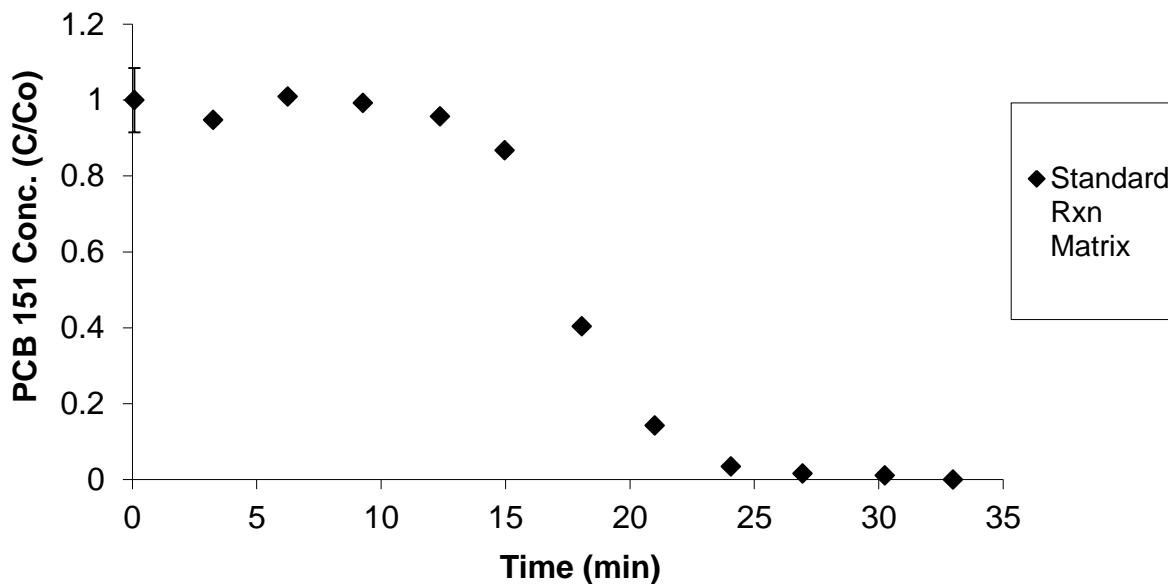


Figure 17: Concentration vs. time plot for the standard reaction matrix showing a sigmoidal shape.

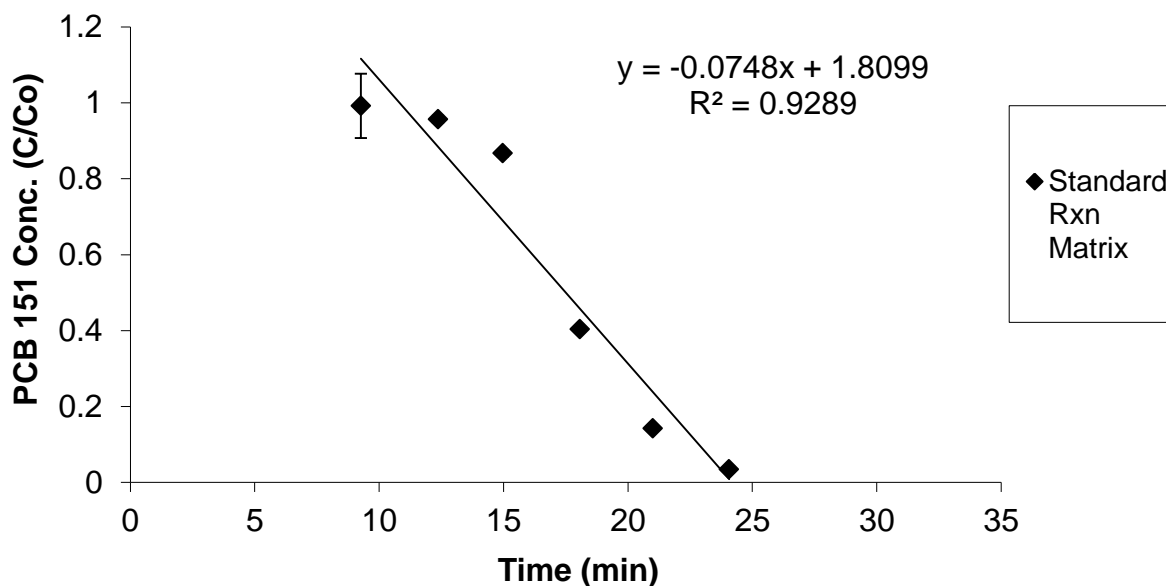
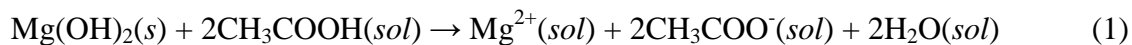
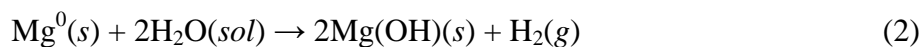


Figure 18: A zero-order rate plot using truncated data points from Figure 17.

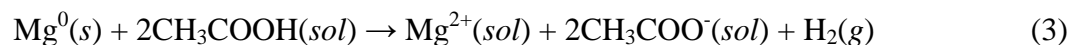
Magnesium is considered a reactive metal; however, under normal atmospheric conditions (humidity, oxygen and carbon dioxide levels, etc.) this reactivity causes the formation of a passivated $\text{Mg}(\text{OH})_2$ surface film (Abreu et al., 1998). The plateau seen during the first 10 minutes of the reaction in Figure 17 may be attributed to the time necessary for the acetic acid to react with the passivated hydroxide layer of the magnesium via the following reaction:



The water formed in this reaction then will react with the newly exposed Mg^0 according to the following well characterized reaction (Song & Atrens, 1999):



Combining equations 1 and 2 yields



Which is merely the digestion of a metal by an acid. However, it is the cancelled $\text{Mg}(\text{OH})_2$ terms that are of interest to the overall degradation process. The combination of $\text{Mg}(\text{OH})_2$ and protons to produce water (Equation 2) and rapid reverse reaction and precipitation of the very insoluble ($K_{\text{sp}} = 2.06 \times 10^{-13}$) $\text{Mg}(\text{OH})_2$ salt, allows it to be translocated thereby exposing the zero-valent magnesium active sites. Further evidence for this hypothesis is provided by examining the effect of agitation upon the system. A study was conducted according to the standard experimental procedure with the lone exception that the reaction vials were placed on a bench top instead of a shaker table. Samples that were not shaken showed a marked decrease in degradation as shown in Figure 19. For reactions in which the rate is chemically controlled increased mixing should have no effect, but in reactions that are diffusion controlled agitation should increase the reaction rate (Compton, 1989). In most heterogeneous reactions, the purpose of mixing is to bring the dissolved reactant into contact with the surface catalyst/reactant. In this case, however, it is necessary to remove the dissolved products from equation 1 and prevent equation 2 from occurring on the surface so that the PCBs may come in contact with the zero-valent magnesium.

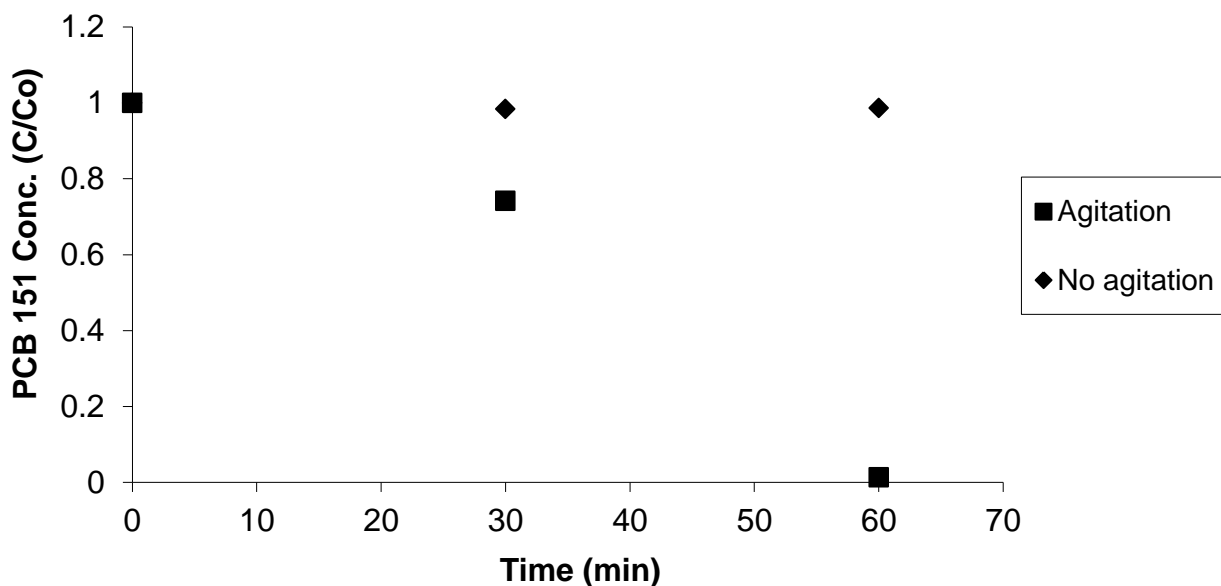


Figure 19: This graph, which compares the amount of degradation achieved in an agitated vs. non-agitated system, clearly illustrates the dependence of degradation upon mixing of the reaction matrix.

Qualitatively, the contents of the shaken vials remain a dark grey slurry for the duration of the reaction period whereas in the unshaken vials, after some initial mixing caused by the addition of the reactants, the Mg powder quickly settles. By 20 minutes a grey-white precipitate forms on top of the metal and at this point, despite vigorous shaking by hand, the metal remains quite strongly affixed to the bottom of the reaction vial. Figure 20 shows SEM images of magnesium before (left) and after (right) use in the reaction matrix. Images of the used magnesium show a secondary material that binds numerous granules together thereby drastically reducing the amount of surface area available for reaction.

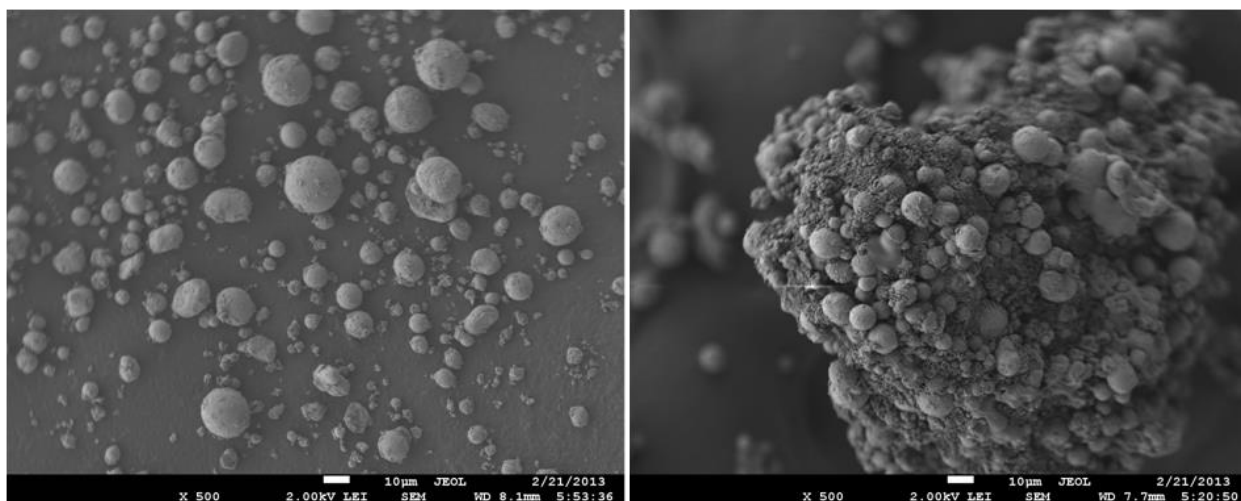


Figure 20: SEM images of magnesium powder before (left) and after (right) use in a typical degradation study

EDS analysis of this precipitate indicates that it is higher in carbon and oxygen content relative to the magnesium powder around which it has agglomerated (Figure 21). Since the only sources of carbon in the system are acetic acid and ethanol, it is most likely either magnesium acetate or magnesium ethoxide. The solubility of magnesium acetate in methanol is reported to be 5.25 g/ 100 mL (Weast & Astle, 1982) and it is expected that its solubility in ethanol would be similar. This equates to 0.263 g/ 5 mL when scaled down to the reaction conditions of this study. Assuming the entire volume of acetic acid is converted to magnesium acetate, this would produce 0.0622 g of magnesium acetate, less than one quarter of its solubility limit. Coupled with the fact that ethanol comprises just over 99% of the total solvent volume in the system, it may reasonably be assumed that the precipitate is magnesium ethoxide with a small contribution of magnesium hydroxide produced from the reactions shown in equations 1 and 2.

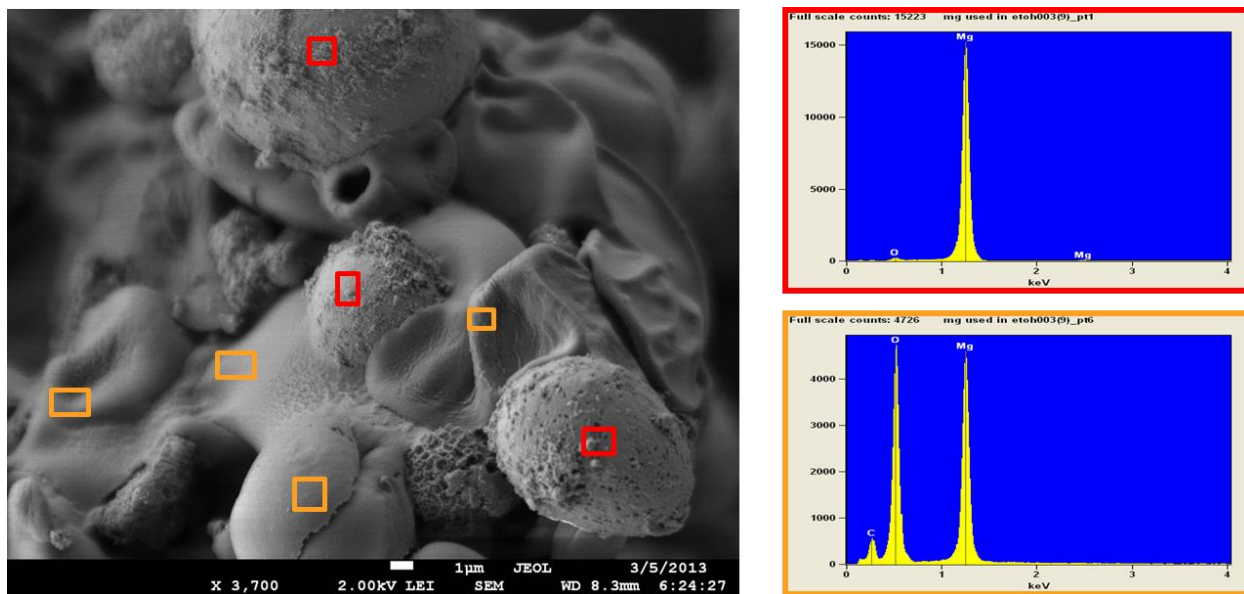


Figure 21: SEM image and EDS analysis of a magnesium and precipitate cluster similar to the one shown in the image on the right in Figure 20. The top EDS spectrum is typical of sampling points on the magnesium powder that are outlined in red. The bottom EDS spectrum is typical of the precipitate sample sites that are outlined in orange. The precipitate clearly shows a relative increase in carbon and oxygen content.

The used magnesium also shows signs of corrosion (Figure 22), a process that may be enhanced by the presence of chloride ions formed during PCB degradation due to the conversion of highly insoluble $\text{Mg}(\text{OH})_2$ to the more soluble $\text{Mg}(\text{OH})\text{Cl}$ (Bryce-Smith, Wakefield, & Blues, 1963; Kahlenberg, 1903; Taub, Roberts, LaGambina, & Kustin, 2002).

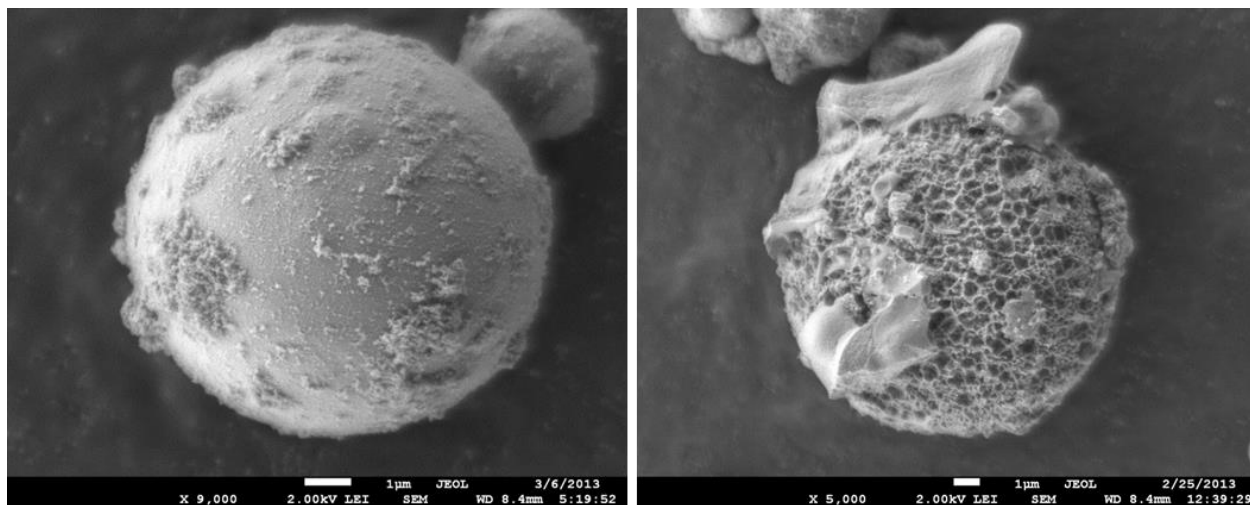


Figure 22: SEM image showing an individual sphere of magnesium before (left) and after (right) use in the acidified ethanol matrix. Corroded particles such as the one on the right are only found in magnesium samples once they have been used

Studies alternating the order in which PCBs and acetic acid were added to the reaction matrix were performed to test the effective reaction time of the exposed zero-valent metal. In the normal experimental procedure, PCBs are added to the reaction vial prior to the acetic acid, which generates degradation data such as those graphed in Figure 17. In the study where the acetic acid was added prior to the PCBs, practically no degradation occurred over the same reaction period. Two conclusions may be drawn from this result. First, because the PCBs were added within a minute of the acetic acid, the effective reaction time of the exposed zero-valent magnesium is quite short. This most likely is due to the extremely low solubility of $Mg(OH)_2$, which will precipitate as quickly as it is formed and re-passivate the zero-valent magnesium. The second conclusion is that, in order for degradation to occur, PCBs must be present at the active sites as they are formed. Several studies, both theoretical (Balzani, 2001) and practical (Hernandez, Zappi, & Kuo, 2004; Matheson & Tratnyek, 1994) have noted the dependence of reaction feasibility with sorption of the oxidizing species to the metal surface.

Once the $\text{Mg}(\text{OH})_2$ layer has been breached and the zero-valent magnesium is exposed, PCBs may react with the metal according to the following generalized scheme, which has been established through electrochemical experiments (Andrieux, Blocman, Dumasbouchiat, & Saveant, 1979)



The neutral aryl radical, Ar^{\cdot} , reacts further by adding a hydrogen to yield ArH . The pH measurements taken during standard degradation experiments show that the solution turns basic ($\text{pH} \geq 10$) within minutes of the addition of the acid due to the reactions shown in equations 1 and 2 and the solubility, albeit slight, of $\text{Mg}(\text{OH})_2$. Therefore the hydrogen that replaces the halogen must come from the solvent that is the only remaining hydrogen source in the matrix. Two mechanisms for the abstraction of hydrogen from a solvent donor have been proposed (Mhalla, Pinson, & Saveant, 1980). Scheme 1 involves the abstraction of a hydrogen atom from a solvent molecule (SH) that then forms a salt with Mg^0 .

Scheme 1



In scheme 2, Mg further reduces the neutral aryl radical before abstracting a proton from a solvent molecule.

Scheme 2

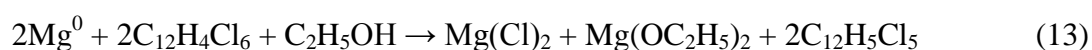




Irrespective of the exact mechanism of the hydrogen abstraction mechanism, the overall reaction equation is



Which in terms of reaction matrix used here would be:



Conclusion

Degradation in the magnesium/acidified ethanol system appears to be the result of two separate but necessary processes. First, the passivating surface layer of $\text{Mg}(\text{OH})_2$ that is spontaneously formed when magnesium is exposed to air must be removed. In this system, the acetic acid is used to etch this passivated layer thereby exposing the reactive zero-valent magnesium. The second process is the actual series of chemical reactions that result in the hydrodechlorination of the PCB molecule. It begins with the transfer of an electron from the magnesium to a PCB in close enough proximity. This forms an aryl halide anion that then expels a halide anion leaving an aryl radical. This highly nucleophilic species then is able to abstract a hydrogen from an ethanol molecule thereby completing the hydrodehalogenation process.

CHAPTER FIVE: CONCLUSION

Recently, it has been shown that both the mechanism and efficiency of PCB hydrodehalogenation using Mg/Pd bimetals is strongly dependent on the source of the hydrogen in the reaction. In these systems, it has been hypothesized that the magnesium acts as the reducing agent and palladium abstracts hydrogens from the solvent and stores it as a reactive species at or near its surface. In order to investigate the role of the hydrogen source further, a series of experiments were performed to see if an organic or mineral acid, acting as a proton donor, can obviate the need for palladium in the matrix.

Acetic acid was chosen first since it is a weak acid and has low toxicity. Initial tests showed that magnesium powder was able to degrade a PCB-151 in an acetic acid/ethanol (1.0 V/V %) solution to below detection limits within one hour. Based on the success of these tests other acids with similar pK_a values also were studied, but only formic and propionic acid were capable of any degradation, albeit over a much longer time period. Further tests were performed to evaluate the solvent's role in the matrix. A series of experiments using straight chain alcohol solvents show that the highest reaction rate was achieved with ethanol, although some degradation was seen using methanol and propanol. With ethanol and acetic acid shown to produce the highest degradation rates, studies were performed to determine the minimum amount of Mg and acetic acid necessary for the reaction to proceed. These tests showed that reaction rates are not appreciably affected using Mg loading as small as 0.10 g/ 5 mL of solvent. However, reducing the acetic acid concentration by half (0.5 V/V%) delayed the onset of degradation by four hours. A final experiment was performed to test the degradation capacity of the matrix. At the highest PCB concentration of 50 ng/ μ L no decrease in the reaction rate was

observed. These experiments show that a novel reaction matrix, consisting of three inexpensive reactants with low toxicity, is able to rapidly dehalogenated PCBs at normal pressures and temperatures.

Based on the Mg/acidified ethanol matrix's success in degrading PCBs, a series of experiments were conducted to see if the system could achieve similar results with other persistent organic pollutants. The first compound tested was octachloro dibenzo-*p*-dioxin. Like the PCB experiments, the parent congener was completely converted to lower chlorinated products within the first hour. Mass spectrum analysis of samples shows that stepwise dechlorination is occurring up to the last sample time of 72 hours. By this point, the products are a range of tri- to hexachlorinated isomers. An experiment using decabrominated diphenyl ether produced similar results. Here, the initial debromination occurs very rapidly leading to the occurrence of octabrominated products within the first three minutes. By the final reported sampling time of 24 hours, the remaining products are a mix of di- to pentabrominated isomers. Up to this point, the system only had been tested on aromatic halides, so the next four experiments were conducted using aliphatic, chlorinated compounds. Initially the experiments were set up with samples to be taken every 24 hours, but by the first sampling time, neither the parent molecule nor any chlorinated products were detected. Consequently, a second set of experiments was setup with samples taken every 10 minutes in order to track the reaction's progress. These studies showed that heptachlor, heptachlor epoxide and chlordane all were degraded to below the detection limit and only 29% of the initial concentration of dieldrin remained by the end of the first hour.

The ultimate purpose of developing this technology is so that it may eventually be used as the basis for “real-world” remediation applications. Soil samples from a chlordane-contaminated site were sent to our lab to test the effectiveness of the magnesium/acidified ethanol system toward this media. Chlordane was extracted from the soil by adding ethanol and sonicating the resulting slurry for 90 minutes. The chlordane ethanol solution was decanted from the soil and subjected to the standard degradation procedure. Results show that the chlordane was indeed degraded in a similar fashion to the neat experiments, which demonstrates that this technique may be used to treat contaminated environmental media.

A final set of experiments was performed with the goal of understanding the fundamental chemical processes occurring in this system. A plot of PCB-151 vs. concentration vs. time reveals two distinct functions. Initially, the PCB concentration remains unchanged, and it is hypothesized that this period of inactivity corresponds to the amount of time it takes for the acetic acid to react with the passivated surface layer of the magnesium powder. However, studies show that a reaction between the acid and Mg(OH)_2 is not the only process necessary for the PCB degradation to occur. Agitation must be applied to the system to facilitate mass transport of Mg^{2+} and HO^- away from the newly exposed zero-valent magnesium surface before they reform Mg(OH)_2 and precipitate back out of solution. Studies, both theoretical and practical, have reported that oxidants, which in this reaction are the PCBs, in close proximity to zero-valent magnesium are then subject to reduction via direct electron transfer. A chloride then is expelled from the aryl halide anion leaving a highly reactive aryl radical. Next, the aryl radical abstracts a hydrogen from a solvent molecule by one of two possible reaction schemes. The overall result of this process is the hydrodehalogenation of the PCB molecule.

A paper by Laine states that an appropriate treatment process for pollution abatement must possess four qualities (Laine & Cheng, 2007). It should be highly effective at degrading the target pollutant, any reaction products should be environmentally benign, the process should proceed under mild reaction conditions, and starting materials should be non-toxic, inexpensive, and easily stored and handled. The magnesium/acidified ethanol matrix described in this paper certainly meets the first, third and fourth of these requirements. Further research is necessary to identify lower chlorinated reaction products so that their toxicity may be evaluated. Ultimately, it is hoped that by better understanding the fundamental chemical reactions, this method may be optimized to completely dehalogenate a wide range of pollutants found in various environmental media.

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