

**IRON-INDUCED REDUCTIVE DECHLORINATION: A SUSTAINABLE REMEDIAL STRATEGY TO
CLEANUP LEGACY DIELDRIN IMPACTED GROUNDWATER**

- A REVIEW

By

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Submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the requirements for the Degree of

Master of Environmental Assessment

Raleigh, North Carolina

2016

Approved by advisory committee:

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ABSTRACT

Fisher, Michael R. Master of Environmental Assessment. Iron-induced Reductive Dechlorination: A Sustainable Remedial Strategy to Cleanup Legacy Dieldrin?-A review

An organo-chlorine compound is typically defined as a chlorinated hydrocarbon with a minimum of one chlorine atom covalently bonded to the structure. Organochlorines include solvents like tetrachloroethene (also known as perchloroethene, or PCE) and trichloroethene (TCE) as well as pesticides such as dichlorodiphenyltrichloroethane (DDT), chlordane, heptachlor, lindane, toxaphene, aldrin, and dieldrin. Organochlorines with more than four chlorine atoms are known as persistent organic pollutants (POPs).

Over a period of nearly 25 years (1950 to 1974), dieldrin, and organochlorine pesticide, was widely applied to crops (cotton, corn and citrus), used to control locusts, mosquitoes and termites, and also used as a wood preservative. Dieldrin is also a degradation product of aldrin, another insecticide. Dieldrin has 6 chlorine atoms, is a known carcinogen, has a relatively high octanol-water partitioning coefficient (K_{ow}) and moderate water solubility. Dieldrin's soil adsorption coefficient, or K_{oc} is log 6.77 (ATSDR) which demonstrates its strong affinity for carbon sorption.

Due to these physico-chemical characteristics, dieldrin sorbs strongly to organic matter, desorbs very slowly, and, thus, naturally attenuates very slowly. Due to its high K_{ow} , (approximately log 6.2, ATSDR) dieldrin will bioaccumulate throughout an ecosystem. Dieldrin's widespread distribution and ecological concentration has led scientists to conclude that the detection of low concentrations of dieldrin in the environment misrepresents the overall toxicological risk (Wurster, 2010).

Research on biotic and abiotic reductive dehalogenation of organochlorine pesticides and chlorinated solvents (PCE and TCE) spans 48 years (Castro and Belser, 1968) and 27 years (Freedman and Gossett, 1989), respectively. First implemented more than two decades ago, reductive dechlorination has become a commonly implemented, successful remedial strategy for cleanup of smaller organochlorine solvents, such as PCE or TCE, in groundwater. This paper addresses the prospect of reductive chlorination cleanup of organochlorine pesticides like dieldrin, specifically for groundwater. Both biotic and abiotic RD processes are considered as well as the reported synergistic effect that occurs between them.

Because pesticides are created for the intended purpose of rendering toxic effects to biological organisms, the success of biotic reductive dechlorination is unpredictable. This paper reviews and discusses the research performed to date regarding the successes and efficacies of various processes for reductive chlorination of dieldrin in groundwater. Special focus is made on the use of iron (Fe) and iron-containing compounds. Additionally, sustainability indicators and applied typical remedial technologies to assess their comparative sustainability. A developed Sustainable Remedial Technology decision graphic tool is presented to assist stakeholders in their evaluation of remedial strategy sustainability.

This paper also offers a relative spatial analysis of dieldrin-impacted sites in the southeastern U.S. This region's history of agricultural (cotton and citrus crops) resulted in a heritage of former manufacturing plants, storage/distribution warehouses, and associated facilities (dumps) impacted by dieldrin. All of these sites are potential targets for application of the remedial strategy of RD. The persistence of dieldrin on agricultural lands, commercial and residential sites, and recreational facilities presents a barrier to redevelopment of these lands and future economic improvement.

BIOGRAPHY

Michael R Fisher is a Senior Project Manager, Senior Scientist, and Registered Professional Geologist with GHD Services, Inc. in West Palm Beach, Florida. Mr. Fisher has over 29 years of experience performing environmental projects throughout the State of Florida and in North Carolina, South Carolina, Georgia, Alabama, and South America.

Mr. Fisher supervised or executed numerous individual or concurrent Phase I and II due diligence environmental site assessments in accordance with the US Environmental Protection Agency's All Appropriate Inquiry rule and American Society of Testing and Materials (ASTM) Standard E-1527, Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process. Mr. Fisher also supervised, or performed, multiple Contamination Assessment Plans (CAPs), Sampling and Assessment Plans (SAPs), Phase III and IV Contamination Assessment Reports (CARs), Site Assessment Reports (SARs), and Remedial Action Plans (RAPs) for a variety of contaminants including petroleum products, solvents, pesticides, metals and Resource Conservation and Recovery Act-listed (RCRA) wastes. Mr. Fisher has written and implemented Groundwater Monitoring Plans and Reports (GWMPs/GWMRs) for remediation sites and landfills, Monitored Natural Attenuation (MNA) plans and reports for remediation sites, project Site Specific and corporate Comprehensive Quality Assurance Plans (SSQAPs and CompQAPs).

Mr. Fisher has conducted compliance audits for commercial and industrial facilities and has participated in landfill, water-use, air quality/emission source, industrial wastewater treatment & discharge, and environmental resource permitting.

Mr. Fisher is a 27-year Florida Registered Professional Geologist with co-registrations in the states of Georgia and Mississippi. Mr. Fisher is also a 22-year Florida licensed Water Well Contractor with deep well geology and drilling experience in the Rocky Mountain district dating back 36 years.

Mr. Fisher has continuously held (renewed) certification for 25 years in the Occupational Health and Safety Administration's (OSHA's) requisite 40-Hour Hazardous Waste Site Operations and Emergency Response (HAZWOPER) training program.

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ACKNOWLEDGEMENTS

I am most grateful to Dr. Elizabeth Nichols for her excellent advice and guidance during the research, planning, and preparation of this paper. I truly appreciated and valued your recommendation to expound upon the topic of sustainability and development of a capstone sustainable remediation decision tree, perhaps the most satisfying and ultimate aspect of my research. You have been both instructional and supportive throughout this effort as well as during my EA program tenure and I look forward to continuing to share our experiences and knowledge going forward .

My thanks too to Dr. Linda Taylor, for tracking me and providing me with timely advice throughout my long-distance involvement these past few years with NCSU's EA program, as well as all of the professors who offered me the privilege of partaking of their instruction, knowledge, and experience. I am also very grateful to have been a part of the EA program and to have studied and worked with so many of the other intensely intelligent program students who brought out the best of academia in me.

Lastly, I would also like to thank and bless my wonderful wife Anna and our little dog, Mooshue, for the love, support, patience, and constant encouragement they provided me each and every day during my quest for my Masters degree.

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INTRODUCTION

Of all the agrochemicals historically applied, organochlorine pesticides (OCPs) remain ubiquitous worldwide due to their slow rates of degradation and tendencies to bioaccumulate in aquatic and terrestrial organisms. Dieldrin (CAS ID #60-57-1), a stand-alone OCP and degradation by-product of aldrin (CAS ID #: 309-00-2). It demonstrates neurotoxic effects and is classified by the U.S. Environmental Protection Agency (EPA) as a probable human carcinogen (ATSDR, 2002). Because of its recalcitrance and toxicity, established regulatory threshold values for dieldrin in soil (by exposure) and water (by ingestion) are in the low range of parts per billion (ppb) to parts per trillion (pet). The Center for Disease Control's Agency for Toxic Substances and Disease Registry ranks dieldrin as 18th (out of 275) on its Priority List of Hazardous Substances, and it is second to DDT as the most critically hazardous pesticides (ATSDR 2015).

Over a period of nearly 25 years (1950 to 1974), dieldrin was widely used to protect crops like cotton, corn and citrus. It was also effective at controlling locusts, mosquitoes and termites. Because it is an effective termiticide, dieldrin was also used to preserve wood and as pre-emptive treatment under foundations. Its use as an exterior-applied termiticide continued until 1987. The estimated combined production of aldrin and dieldrin peaked at almost 20 million pounds per year in the mid-1960s (Jorgenson, 2001). Based on U.S. use data, the aldrin to dieldrin production ratio was about 9:1. In 2001 EPA's Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) program integrated chemical manufacturing data from three references, *SRI Chemical Economics Handbook*, the *Purdue Silver Platter* pesticide CD-ROM, and the *Farm Chemicals Handbook* and identified companies that historically manufactured aldrin and/or dieldrin. Nationwide, 36 manufacturing facilities were identified (Jorgenson, 2001). Sixty-five companies reported manufacturing aldrin and/or dieldrin at one time. More than half of those facilities were located in EPA Region 4 (southeastern USA states with two in Florida, five in Georgia, two in Kentucky, one in Mississippi, five in North Carolina, one in South Carolina, and four in Tennessee FIFRA PGSIS, 2015). **Figure 1** depicts the locations of aldrin and dieldrin manufacturing facilities in the U.S. (Jorgenson, 2001).

Due to the subtropical climate, variety of cultivated crops, the geographic distribution of crops, and the prevalence of pests, the manufacture, distribution, and application of dieldrin more prevalent in southeastern states. Dieldrin's widespread manufacture, use, and disposal in southeastern U.S. states over nearly four decades has resulted in a legacy of toxic impact that poses a threat to prospective changes in land use. Resulting legacy impacts from the historical manufacturing, application, and disposal of dieldrin have temporal and financial implications for Site owners, parties seeking to redevelop impacted land, governments seeking community improvement, regulatory personnel responsible for public health protection, and citizens threatened by probable exposure. Of the forty-five Superfund sites in EPA Region 4 listed for pesticide contamination, fifteen sites have groundwater impacted by dieldrin. **Table 1** lists the fifteen Region 4 sites registered on the EPA's National Priorities List (Superfund program) that demonstrate the legacy of impact left by such manufacturing facilities. All of these sites report dieldrin-impacted groundwater.

In addition to these NPL sites, each Region 4 State has its own inventory of hazardous industrial, commercial, institutional, municipal, agricultural, recreational and even residential sites with dieldrin-impacted groundwater. For example, the Georgia Environmental Protection Division's (EPD) Hazardous Site's Inventory (HSI) list includes 19 waste cleanup sites with dieldrin-impacted groundwater (GADNR). Florida's Department of Environmental Protection (FDEP) Waste Cleanup Site Investigation Section (SIS) list includes multiple sites with dieldrin-impacted groundwater including: the Agrico Chemical Company, the New Warrington & Navy Boulevard Pesticides site, and the highly publicized Country Club Estates

residential neighborhood (FDEP). North Carolina's Department of Environmental Quality (NC DEQ) Inactive Hazardous Site (IHS) database includes the Newland pesticide site (Newland), Terminix Pest Control (Winston-Salem) and Wilson Pest Control (Winston Salem) (NC DEQ; personal conversation with G. Abrams, NC DEQ).

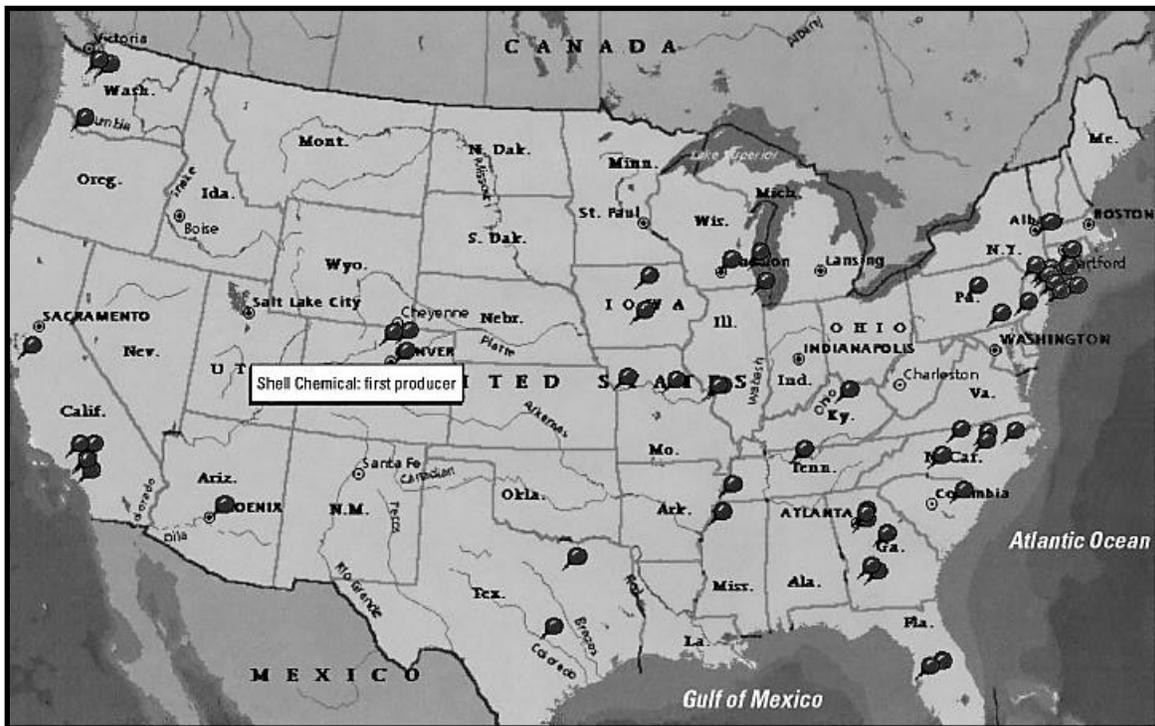


Figure 1 Locations of Historical Chemical Plants in the U.S that Manufactured Aldrin and Dieldrin (courtesy of Jorgenson, 2001)

NC DEQ records include a 2012 report of legacy OCPs, including dieldrin, in private drinking water wells near Academy Road in the Dana community in Henderson County and Bond Road in Wake County, North Carolina. The OCP's in private residential potable wells posed an immediate risk to the community's health prompting response from the NC DEQ, the respective County Departments of Public Health, the U.S. EPA, and the U.S. Department of Health and Human Services (NC DEQ, 2012). The regulatory response included recommended treatment technology involving the installations of granular activated carbon (GAC) filters on individual well-fed potable water systems. Granular activated carbon (GAC) filtration is a demonstrated effective treatment strategy used by Publically Owned Treatment Works (POTWs) to sequester and remove select organic contaminants with high soil partitioning coefficients(K_{oc} s) like VOCs and OCPs (Ninkovic, et al., 2010). The relatively high K_{oc} s of OCPs motivates their affinity to sorb to the carbon. By design, the treatment stage of pump and treat systems installed to remove OCPs from the aqueous matrix must rely on contact with GAC. While individual water system GAC filter mechanisms can provide a measure of protection to the well users, they are not infallible or a permanent solution. GAC has a contaminant-dependent maximum point of sorption saturation. Once the GAC is saturated, contaminant breakthrough occurs and the GAC must be replaced. Regular use (and maintenance) of GAC filtration of potable well water can protect the residents from consuming OCPs but will not reduce or eliminate the OCP impact in the groundwater. In addition, routine long-term use requires regular replacement and disposal or recycling of GAC. Spent GAC must be disposed of because contaminants can desorb and leach to soils and/or groundwater. To avoid this problem of potential contaminant transfer, GAC regeneration is usually favored over disposal. However, the three most

common methods of GAC regeneration, steam, thermal and chemical treatment are energy-intensive processes (US EPA). Due to potentially high cost and energy-dependence, GAC filtration of groundwater is considered a poorly sustainable treatment option.

Table 1
US EPA Region 4 National Priorities List Sites with Reported Dieldrin-Impacted Groundwater

State	Site Name	Site ID	EPA ID	Site Area (size)
AL	T.H. Agriculture & Nutrition Co. (Montgomery Plant)	0404285	ALD007454085	16.4-acres
FL	Helene Chemical Co. (Tampa Plant)	0400674	FLD053502696	8-acres
FL	Kerr-McGee Chemical Corp Jacksonville	0400614	FLD039049101	31-acres
FL	Landia Chemical Co.	0400627	FLD042110841	13-acres
FL	Stauffer Chemical Co. (Tampa)	0400537	FLD004092532	40-acres
GA	Hercules 009 Landfill	0401699	GAD980556906	16.5-acres
GA	T.H. Agriculture & Nutrition Co. (Albany Plant)	0401428	GAD042101261	12-acres
GA	Wolfolk Chemical Works, Inc.	0401315	GAD003269578	31 acres
KY	Brantley Landfill	0402076	KYD980501019	4-acres
MS	Sonford Products	0402405	MSD086556388	6-acres
NC	Aberdeen Contaminated Ground Water	0407447	NCN000407447	~832-acres (co-mingled with Geigy Chemical Corp.-Aberdeen Plant)
NC	Aberdeen Pesticide Dumps	0403099	NCD980843346	37-acres
NC	Geigy Chemical Corp. (Aberdeen Plant)	0404170	NCD981927502	1-acre, (co-mingled with Aberdeen Contaminated Ground Water plume)
NC	North Carolina State University (Lot 86, Farm Unit #1)	0403015	NCD980557656	1.5-acres
SC	Helena Chemical Co. Landfill	0403309	SCD058753971	13.5-acres

The term “sustainability” is a generalized concept with a variety of definitions. The definition relies on the circumstance of application. In 2011, remediation industry representatives working under the Interstate Technology & Regulatory Council (ITRC) coalition defined “sustainable” remediation as, “the site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts, and environmental effects” (Allen et al., 2011)

The ITRC team’s definition is aligned with the typical sustainability indicators that focus on the overall concern for environmental, social, and economic impacts of an activity. **Figure 2** depicts a schematic for sustainability (Allen et al., 2011). The process considers all likely environmental effects of the remedial strategy and integrates options to minimize any potential impact to the environment, the economic

impacts (including community impact and project cost), and social aspects of sustainability in remedial decision making for (Allen et al., 2011). The effort to determine the effect such impacts may have on future generations is a societal consideration known as “stewardship”.

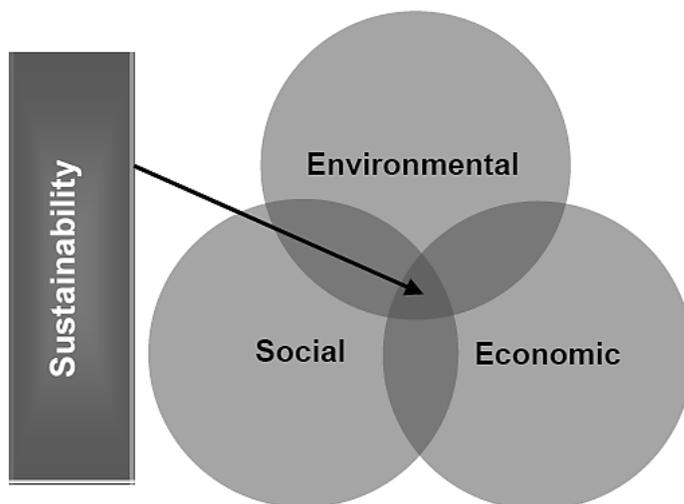


Figure 2 Sustainability Schematic (courtesy of Allen et al., ITRC, 2011).

Sustainable remedial strategies often invoke best management practices (BMPs) or an evaluation of the overall “environmental footprint” (ITRC, 2011). EPA’s key goals for sustainable remedial strategies are 1) reducing the demand on the environment, otherwise called the “footprint” and 2) maximizing the net environmental benefit of remedial actions (OSWER, 2008). Sustainable remediation BMPs help the EPA encourage the stewardship of business and public sectors through their incorporation of environmentally conscious practices. Such BMPs can include advanced methods to:

- Conserve water,
- Improve water quality,
- Increase energy efficiency,
- Manage and minimize toxics and waste, and
- Reduce emission of criteria pollutants and greenhouse gases (GHGs)

(courtesy of U.S. EPA National Center for Environmental Innovation, 2006, per OSWER, 2011).

Incorporation of sustainable remediation design grew out of the recognized performance limitations of routine groundwater treatment technologies like pump and treat. Remediation of groundwater contamination by pump-and-treat systems began in the 1980s. Typically, by design and purpose, pump-and-treat systems are long-term remedies that may operate for many decades (USEPA, 1996). During the period of pump-and-treat remediation, site conditions and/or regulations may change. The initial conceptual site model (CSM) may need to be refined in response to the discovery of new information or the emergence of improved science and technologies (USEPA, 2007). The typical asymptotic performance compared to the material, energy, and labor demands of a pump and treat system’s construction, operations, and maintenance revealed the need for more efficient, less costly, and more environmentally neutral treatment technologies. The 21st century has brought growing demand from the Parties Responsible for Site Restoration (PRSR), and therefore need from the remediation industry, to implement innovative treatment strategies that are faster, more cost-effective, and reduce greenhouse gas (GHG) emissions. The industry trend is a shift away from standardized ex-situ remedial technologies like pump and treat that transfer contaminated media to the surface for subsequent

treatment (Bruton 2015). The typical groundwater remedial strategy of pump-and-treat technology (through granular activated carbon, or GAC) is costly due to equipment, materials, and energy requirements. OCPs, including dieldrin, also respond to bioremediation provided conditions are optimal to support the microbial degraders. Other remedy alternatives include In-Situ Chemical Oxidation (ISCO) and In-Situ Chemical Reduction (ISCR) technologies (US EPA. 1996).

For over two decades, Fe-induced biotic and abiotic RD has been successfully used to treat groundwater impacted by chlorinated compounds like perchloroethylene, trichloroethylene, and dichloroethylene (EPA; Hayes et al., 1997; Lee and Batchelor, 2002 and 2004; Joo and Zhao, 2008; Butler et al., 2009; He et al., 2010; Jeong et al., 2011). During the same period researchers investigated the prospect of using Fe-mediated RD to cleanup polychlorinated biphenyls (PCBs; Royal et al., 2003; Bedard, 2008; Wu et al., 2012; Zanaroli et al., 2012; Long et al., 2014), pentachlorophenols (PCPs: Kao et al., 2004; Dorathi and Kandasamy, 2011), and other OCPs (lindane and DDT/metabolites: Sayles et al., 1997; Fields, 1999; Chiu et al., 2005; Matsumoto et al., 2009; Hara et al., 2009; Cong et al., 2010; and Hara et al., 2009, 2011, and 2012). At least one bench-scale study (conducted by Hara et al., 2009) investigated the prospect of chemical degradation of dieldrin in water using iron.

Based on the successful field-scale implementation for cleanup of other organochlorine compounds, this literature review investigates whether the ISCR process of iron (Fe)-mediated reductive dechlorination (RD) can also effectively attenuate dieldrin in groundwater below the established regulatory levels. This review incorporates the differences between the processes of biotic and abiotic RD of organo-chlorine compounds, the environmental conditions that support them, and the role Fe performs in propagating both biotic and abiotic RD methods. The review focus addresses the decades of research into the mechanisms, conditions, and results from RD of select, recalcitrant organochlorine compounds including chlorinated volatile organic Compounds (ethenes and ethanes), polychlorinated biphenyls (PCBs), and pesticides (DDT, hexachlorocyclohexane (HCH), lindane, chlordane, heptachlor, toxaphene, endosulfan, aldrin, dieldrin, endrin, and methoxychlor. A limited discussion of the structural and physico-chemical properties of these compounds and how their environmental characteristics affect the process of Fe-mediated RD. The review includes a summary of past treatment technologies that have successfully attenuated organochlorine compounds in groundwater for organochlorine RD and the relative sustainability of each approach.

GOALS AND OBJECTIVES

The goal of this paper is to determine whether the process of Fe-induced RD can effectively remediate dieldrin in groundwater and whether the process is sustainable. The objective is to establish why dieldrin is a continued risk to human health and the ecologic community, why it remains a challenge to cleanup, identify the successful remedial technologies applied to clean up dieldrin impacts, why those methodologies are unsustainable, what the process of RD is, how it is sustainably applied to clean up sites impacted by other organo-chlorine compounds, and how the successful prior use and validated research of the treatment of organo-chlorine compounds by Fe-mediated RD points to its potential to sustainably remediate dieldrin-impacted groundwater.

This objective was accomplished by literature review and examination of State and Federal regulatory databases. Literature review focused on research and successful implementation of treatment of dieldrin and other organo-chlorine compounds by RD. Research studies offered information on the process of RD (biotic and abiotic), what aqueous-based organo-chlorine compounds are treatable by Fe-mediated RD, how the RD process works to remediate organo-chlorine compounds, what treatment

options propagate the Fe-mediated RD process, and what chlorinated hydrocarbons (especially OCPs) respond to Fe-mediated RD based on prior research and use. Regulatory databases identified the number of potential sites with dieldrin-impacted groundwater located in the southeastern U.S. Some provided limited record of the applied remedial strategy and the status of the remediation. Additional literature review and analyses of industry and regulatory guidance documents provided reference to the definition of sustainability and the measures employed to assess the value of implementing sustainable practices. Attention was paid to the general indicators by which sustainability is measured. A closer focus was made on the factors used by academics, practicing industry professionals, and regulatory agencies to define the sustainability of various remedial technologies.

METHOD

Research Sources and Topics

Literature, case studies, and regulatory database research sources included academic research, science and industry journals, regulatory (federal and state) records and reports, conference proceedings, and commercial vendor remediation project reports. Research studies were identified through several internet Search engines (Bing, Google, ResearchGate). Electronic copies of relevant studies were obtained from North Carolina State University (NCSU) Library system. **Table 2** presents the record of research conducted for this review.

To compare or contrast the processes and effects, the literature review focused on successful bench-scale, microcosm, and field-scale studies of Fe-mediated RD of organo-chlorine compounds including chlorinated volatile organic compounds (CVOCs) like PCE, TCE, and DCE, Polychlorinated Biphenyls (PCBs), chlorophenols, organo-chlorine herbicides (OCHs), and OCPs, with particular emphasis on studies of Fe-mediated RD of dieldrin. Distinction was made between the biotic and abiotic RD processes to determine whether they work independently or synergistically.

Table 2
Research Sources and Identified Data

Databases Searched	Literature Found
ResearchGate NCSU Library Google Scholar (search engine) NCSU Library Science Journals (search engine) NCSU Library (Web of Science)	<ul style="list-style-type: none"> • 133 Research Studies
Colorado School of Mines	<ul style="list-style-type: none"> • 1 reference (Sustainability)
Remediation Vendors	<ul style="list-style-type: none"> • 8 OCP remediation by RD case studies (3-Ontario, CN, 3 –Florida, 1- Alabama, 1- South Carolina)

Databases Searched	Literature Found
EPA Office of Solid Waste and Emergency Response	<ul style="list-style-type: none"> • 5 references (1- RD, 1- POP Remedies, 1- P&T Optimization, 2 – Superfund Site P&T Cost and Performance Reports)
EPA Cleanup Technology, CLU-IN	<ul style="list-style-type: none"> • 9 references (1 – Contaminants Sites Guide, 1- Contaminant-based Remedial Options Guide, 1- ISCR Guide, 2-OCP Bioremediation Reports –NC & AZ, 1- RD/Bioremediation Report – NC, 1- Technology Demonstration Report – FL, 1- Costs Analysis Guide: P&T versus PRB, 1- Green Remediation/Sustainable Practices Guide)
EPA Office of Research and Development	<ul style="list-style-type: none"> • 1 reference (P & T Decision Guide)
CDC Agency for Toxic Substances and Disease Registry	<ul style="list-style-type: none"> • 3-references (1- ToxGuide. 1 – ToxFAQ, 1- Hazardous Substances Priority List Data, 1- Aldrin/Dieldrin-Manufacturing, Use, and Disposal Report)
USDA	<ul style="list-style-type: none"> • 6 references (1-Sustainable Remediation of Chlorinated Organic Compounds, 5-Crop Profiles for Cotton – AL, FL, GA. MS, and NC)
USGS	<ul style="list-style-type: none"> • 6- references (1- Pesticide National Synthesis Project report, 1- statistical table of pesticides in urban wells, 1- statistical table of pesticides in undeveloped wells, 1- statistical table of pesticides in mixed land use wells, 1 report of Land Use change in eastern US states, 1- report of DNAPL removal to accelerate remediation)
The Interstate Technology & Regulatory Council	<ul style="list-style-type: none"> • 3 references (1-Technology Overview of Sustainable Remediation, 1-Technology Guide for Sustainable Remediation, Technology Guide for Permeable Reactive Barriers)
EPA Superfund	<ul style="list-style-type: none"> • Region 4 Superfund sites with pesticide CoCs: 183 Total Sites-45 sites impacted by pesticides, 15 impacted by dieldrin
Florida Dept. of Environmental Protection	<ul style="list-style-type: none"> • Site Investigation Sites (SIS) List: 246 Total Sites Kerr-McGee Superfund Site-Jacksonville • Country Club Estates subdivision, Ground Water Investigation – DeLand
Georgia Department of Natural Resources	<ul style="list-style-type: none"> • Hazardous Site Investigations List: 552 Total Sites
Kentucky Dept. for Environmental Protection	<ul style="list-style-type: none"> • Licensed Chemical Facilities List: 112 Total sites • Allen Chemical (Dump) Site • Amfine Chemical Corp

Databases Searched	Literature Found
Mississippi's Department of Environmental Quality	<ul style="list-style-type: none"> • CERCLA Uncontrolled Sites List: 1,998 Total sites • Hercules, Inc. Superfund Site (CVOCs) • Red Panther Chemical Co. Superfund Site (OCPs) • Agricultural Chemical Groundwater Monitoring Program: 2012 and 2014 Annual Summaries
North Carolina Dept. of Environmental Quality	<ul style="list-style-type: none"> • Inactive Hazardous Sites (HIS) List: 1,878 sites • Academy Road Water Well Investigation • Bond Street Water Well Investigation • Terminex Pest Control • Newland Residential Site
South Carolina Dept. of Health and Environmental Control	<ul style="list-style-type: none"> • SC Superfund and equivalent sites list: 56 Total sites • Public Records List (of Facilities): 520 Total sites • Adams (Pete) Hasell Site • W.R. Grace Ag Chemical Group Site
Massachusetts Dept. of Environmental Protection	<ul style="list-style-type: none"> • MA DEP Spills List
California Environmental Protection Agency	<ul style="list-style-type: none"> • Bioremediation of OCPs at Borello Property (Northern CA)
New Jersey Dept. of Environmental Protection	<ul style="list-style-type: none"> • 1 reference (NJDEP-Findings and Recommendations for the Remediation of Historic Pesticide Contamination)

Regulatory Records

To create a catalog of geographic and site-specific contamination assessment and cleanup activities data, the regulatory records review concentrated on listed OCP-impacted Superfund and State waste cleanup sites. Sites with confirmed dieldrin-impacted groundwater were targeted especially historical chemical/pesticide/OCP manufacturing facilities, landfills, and agricultural sites deemed the likeliest to harbor legacy impact. Regulatory agency sources included EPA Superfund-National Priorities List (NPL), USGS, and USDA; ADEM, FDEP, GDNR, KDEP, MDEQ, NC DEQ, SCDHEC, and TDEC; and NJ DEP.

Data Analysis

The literature review began with appraisal of abstracts for published research papers relevant to the topic of RD with attention on the process of Fe-mediated biotic and abiotic treatment of OCPs and other organochlorine compounds in an aqueous medium. If the abstract revealed relevance, a more advanced review was conducted. The detailed review included the background, goals, objectives, findings (for results), discussions (for interpretations), and conclusions (for summary and determinations). Key details of the core content that contributed to the study's conclusions were annotated for reference.

Beyond the target research studies, reviewed journal articles, texts, conference presentations, and remediation vendor reference projects produced data and references directly ascribed to Fe-mediated RD of OCPs and other organochlorine compounds in water. Collectively, more than 175 research papers related to studies of reductive dechlorination and 43 regulatory guidance documents were reviewed resulting in fifty-seven (57) cited references. Regulatory database listings of 5,075 facilities were

reviewed yielding the referenced 42 sites with reported groundwater impacted by dieldrin. Citations of the research papers, journal articles, texts, conference presentations, and remediation vendor projects are listed in the References section at the end of this paper.

Data for OCP-impacted sites obtained from federal and State regulatory agency records was analyzed for the existing OCP or suite of OCPs, impacted media, status of cleanup, proposed or implemented remedial strategy, the effectiveness of the treatment strategy, problematic or accommodating Site conditions or characteristics, and how problematic or accommodating Site conditions or characteristics affected the RD treatment process. Records review identified 14 Superfund sites in EPA region 4, and multiple waste cleanup sites in EPA region 4 states with reported dieldrin-impacted groundwater. Sources of regulatory records are listed in the Introduction section earlier in the text.

REDUCTIVE DECHLORINATION

The chemical structures of organo-chlorine compounds are variable and diverse. Their human and ecotoxicity characteristics have historically prompted experts to evaluate whether they degrade in the natural systems. The answer depends on many factors including the physical, chemical and microbiological characteristics of the environment where the release occurred, and the structure of the substrate (Neilson, 1996). Reductive dechlorination (RD) is a process of degradation of chlorinated organic compounds by the release, or *reduction*, of inorganic chloride ions (Butler et al., 2009).

As early as 1967, Hill and McCarty noted that OCPs including gamma-hexachlorocyclohexane, (γ -HCH or lindane), heptachlor, endrin, DDT, DDD and aldrin degraded in anaerobic sewage sludge (Macalady et al., 1986). In 1978, EPA research and development into the internal processes by which living organisms degrade pesticides recognized RD as a natural mechanism of OCP degradation (Matsumura, 1978). Alkyl dehalogenation, the process by which chloride is replaced with hydrogen, occurs in organisms, sediments, sewage sludge, and reduced iron porphyrin model systems. By 1986, RD was already a prime focus of the research into the degradation of halogenated hydrocarbons (Macalady, 1986).

RD occurs biotically (by microbial mediation) or abiotically (by chemical mediation). Macalady et al. pointed out the potential ambiguity of the term "abiotic" and chose to define it as term that referenced many chemically-mediated degradation processes typically resulting from biological activity. However, abiotic RD does not usually involve any direct mediation by microbes (Macalady et al., 1986). As revealed Hill and McCarty, RD typically occurs under anaerobic, conditions.

A majority of the global hydrosphere consists of anaerobic regimes: fresh water bodies below the photic zone, most sediments and muds, many groundwater systems, agricultural operations that require flood conditions (ISS. e. rice paddies), and natural waste treatment systems (Macalady et al., 1986). Macalady et al. also identified the term "anaerobic" as yet another possibly vague concept. Literally, anaerobic is defined (by the Oxford Dictionary) as "relating to, involving, or requiring an absence of free oxygen". In the field of environmental research, anaerobic literally refers to environments absent measurable free oxygen. More specifically, according to Singleton and Sainsbury (1978) it is peer-recognized as those environments unable to support the aerobic microorganisms that use oxygen as an electron acceptor. However, the term fails to differentiate a considerable range of chemical conditions which exist in such environments (Macalady et al., 1986). Macalady's group noted that systemic evaluations of in-situ chemical reduction (ISCR) do not typically distinguish between the biotic and abiotic processes; that synergistic transitions apparently occur between the processes under aerobic and anaerobic conditions. The realized limitations of anaerobic biodegradation and recognition of the interactions between biotic

and abiotic processes prompted subsequent work (Lee et. al., 2002) focused on characterizing natural reductants responsible for abiotic RD.

The best demonstration of the process of RD occurring in natural systems under anaerobic conditions is the unassisted degradation of lindane and PCBs in flooded rice paddies that occupy Mekong River delta sediments (Macalady, 1986; Hara et. al., 2012). Peijnenburg et al. (1992) evaluated the RD of halogenated aromatics in saturated pond sediments under induced anaerobic conditions. Results from their manipulated microcosm experiments revealed the degradation products to be generally less toxic, less bioaccumulative, and, therefore, more prone to further degradation (Peijnenburg et al. 1992, Cong et al., 2010).

In a 2009 study of RD of CVOCs in anaerobic environments, Butler et. al. reported that the biotic and abiotic processes are not mutually exclusive and can potentially occur simultaneously. The 2009 study concluded that the abiotic pathway of PCE and TCE reduction occurred by β -elimination while the biotic pathway occurred by hydrogenolysis, each course leading to different degradation products; the comparative abundance of by-products potentially indicates the main RD process (Butler, et al., 2009).

Biotic RD reportedly occurs by three pathways (Neilson, 1996):

(1) **Hydrolytic displacement** is the process by which aliphatic chlorinated hydrocarbons (and carboxylic acids) generally degrade; less typically for aromatic organochlorine compounds.

(2) **Elimination of HCl** results in the development of alkenes (Wedemeyer, 1967) and cycloalkane creation (Ohisa et al., 1982). The microbial degradation of hexachlorocyclohexane (HCH) causes a series of such eliminations (Nagata et al., 1994).

(3) **Reductive displacement** predominates the process of degradation of many organochlorine aromatic under anaerobic conditions (Van Dort & Bedard, 1991).

Abiotic β -elimination involves the formation of an additional carbon-carbon bond by concurrent removal of two chlorine atoms (dehalogenation) or simultaneous H and Cl removals (dehydrohalogenation). The process of hydrogenolysis results in the release of chlorine from the molecule to solution (as chloride, Cl⁻). The chlorine is concurrently replaced on the molecule by a hydrogen atom, resulting in a net input of one proton and two electrons (He et. al., 2011, Bruton et. al., 2015). A net transfer of two electrons occurs for both reactions (Hara, 2012). **Table 3** provides the chemical classifications of example organochlorine compounds. **Figure 3** depicts the anaerobic dehalogenation mechanisms for aromatic and non-aromatic organochlorine compounds (Sims et al., 1991).

Thus, the process of RD offers two effective pathways for the in-situ treatment of organochlorine compounds. At times these processes are competitive, often they co-operate depending upon the specific environmental conditions. Nonetheless, the process of β -elimination is likely to dominate over hydrogenolysis during the abiotic reduction of CVOCs involving mediation by zero-valent iron (Bruton, 2015).

By 2011 significant effort had been made to develop innovative, effective alternative strategies to treat various media contaminated by chlorinated organics by studying their steps and processes (Che 2011). Recognition of Hill and McCarty's (1967) discovery of OCP degradation by alkyl dehalogenation in anaerobic sewage sludge and Matsumura's (1978) findings of similar processes performed by living organisms intensified the research into the biotic and abiotic pathways of RD of more common halogenated hydrocarbons.

Table 3
Chemical Classifications of Organochlorine Compounds

Aromatics

PCBs
 PCDD (dioxins);
 PCDF (furans);
 Chlorobenzene;
 1,2-, 1,3-, and 1,4-Dichlorobenzenes;
 1,2,3-, 1,2,4- & 1,3,5-Trichlorobenzenes;
 Penta- and Hexachlorobenzenes;
 1,2,3,4-, 1,2,3,5-, & 1,2,4,5-Tetrachlorobenzene;
 2- and 4-Chlorophenols;
 2,4-and 2,6-Dichlorophenol;
 2,4,6- and 2,4,5-Trichlorophenol;
 2,3,4,6-Tetrachlorophenol;
 DDT;
 α -, β -, δ - Hexachlorocyclohexane (HCH), and γ -HCH (lindane);
 Methoxychlor;
 Pentachlorophenol

Aliphatics

Di-, Tri-, and Tetrachloroethylenes;
 1,1,2-Di-, 1,1,2,2-Tetra-, and Hexachloroethanes;
 Chloromethanes;
 1,2-Dichloropropane;
 Hexachlorobutadiene

Cyclodienes

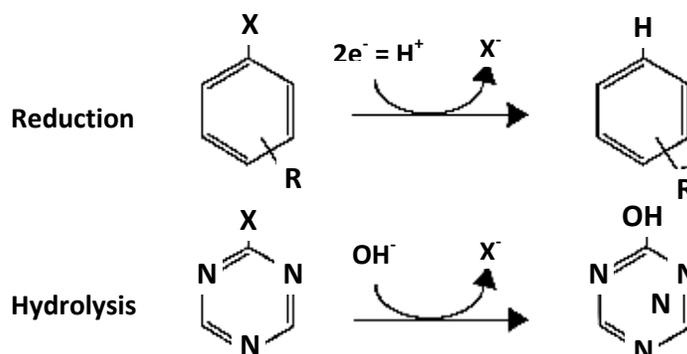
Aldrin (HHDN), dieldrin (HEOD), endrin, and isodrin;
 Bromo- and Chlorbicyclen;
 Chlordane;
 Chlordecone;
 Dilor;
 Endosulfan and γ -Endosulfan;
 Heptachlor & Heptachlor Epoxide;
 Isobenzan;
 Kelevan;
 Mirex

FE-MEDIATED REDUCTIVE DECHLORINATION

Glass (1972) initiated the research into the possible effect reduced iron (Fe^{2+}) had on the redox state in flooded soil and the observed transformation of DDT. Macalady's team found that in naturally anaerobic environments speciation, activity, and the catalytic capabilities of organic and metallic reductants controlled the abiotic reduction of organic chemicals (Macalady et al., 1986). Subsequent work concluded that Fe-rich soil was more likely to stimulate microbial iron reduction rather than the process of RD of OCPs (Kazumi et al., 1995b).

Anaerobic Dehalogenation Mechanisms

Aromatic Compounds



Non-aromatic Compounds

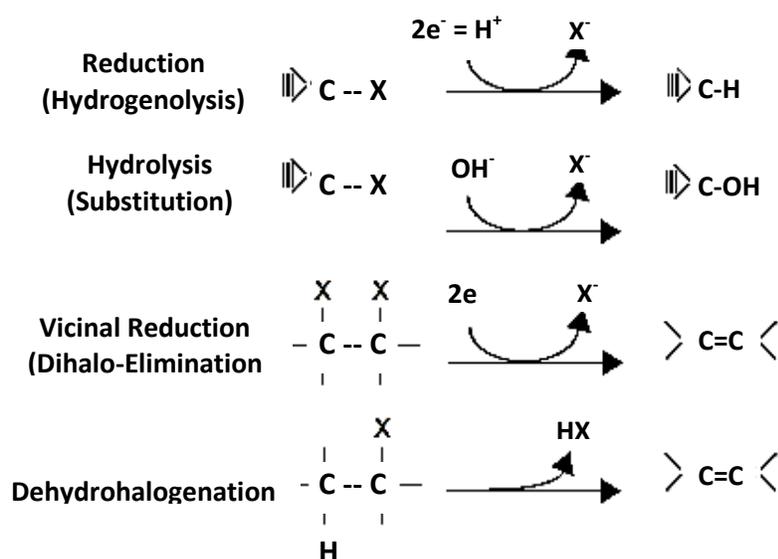


Figure 3 Mechanisms of Anaerobic Dehalogenation of Organochlorine Compound Classes
(courtesy of US EPA, Superfund Technology Support Center for Ground Water)

Liu et al. (2003 and 2008) and Cao et al. (2010) described solid or aqueous-based reductants like ZVI (Fe^0) or naturally occurring Fe^{2+} as the strategic drivers of the abiotic process of reductive dechlorination (Chen et al., 2014). As expected, Fe -mediated RD is abiotic and, therefore, proceeds by the process of β -elimination.

In the aqueous environment, Weathers et. al. (1997) and Lee et. al. (2001) reported that oxidation (corrosion) of ZVI resulted in the continuous generation of cathodic hydrogen (H^+), the requisite energy source required for anaerobe halo-respiration. Subsequently, Wang et. al. (2008) and Karachalios and Scalzi (2013) described the synergistic relationship between ZVI and anaerobes responsible for RD; ZVI creates the highly reducing conditions in which dechlorinating microbes thrive (Bruton 2015).

Permeable reactive barriers (PRBs) containing ZVI are often the in-situ remediation technology applied to anaerobically reduce chlorinated ethenes and ethanes in soil and groundwater (Hara, 2012). El-Temsah et al. noted Fe -mediated reduction of the contaminants in soils was typically inferior to RD of

aqueous-based contaminants. The root cause is believed to be the reduction of contaminant availability in the soil matrix due to physical characteristics versus conditions in aqueous media (El-Temsah et al., 2016).

The research of Gillham and O'Hannesin (1994) Powell et al. (1995), Baker et al. (1997); Benner et al. (1997); Lo et al. (2005), and Lai et al. (2006) confirmed that ZVI installed in a PRB exerts the various processes of precipitation, sorption, chemical-, and biological-mediated reduction to treat dissolved chlorinated aliphatics in an aquifer. These in-situ processes can result in groundwater downgradient of the PRB at or below target remediation or regulated concentrations (Lai and Lo, 2006). Fogler (1992), Powell et al. (1998), Su and Puls (1999), and Lai and Lo (2002) reported that ZVI reactivity in full-scale PRBs is influenced by such factors as seasonal changes in groundwater temperature and velocity because these parameters potentially affect the rate of electron transfer between ZVI and chlorinated aliphatics and mass transfer of chlorinated aliphatics to the ZVI surface. Lai and Lo's subsequent bench-scale (column) studies showed that groundwater chemistry, including the levels of hardness and Total Alkalinity (as CaCO_3), and concentrations of Fe^{2+} , SO_4^{2-} , Cl^- , and chlorinated aliphatics, did not significantly affect the RD process (Lai and Lo, 2006).

From the date of their initial implementation in the mid 1990's through 2001 more than 65% of ZVI-packed PRBs were installed to treat groundwater contaminated with chlorinated aliphatics (USEPA 2002; Lee and Batchelor 2002). Subsequently, Eggen and Majcherczyk (2006) and Yang et al. (2010) reported achieving limited success degrading DDT in water and soil by applying ZVI (El-Temsah et al., 2016). It has been reported that ZVI-packed PRBs can have a treatment lifespan of up to thirty (30) years.

REDUCTIVE DECHLORINATION OF ORGANO-CHLORINE COMPOUNDS CVOCs

Chlorinated solvents are volatile organic compounds. Except perhaps for the widespread presence of petroleum compounds, chlorinated solvents were some of the most prevalent chemicals generated and released during the post-industrialization technological revolution. CVOCs like tetrachloroethylene (PCE) and trichloroethylene (TCE) are frequently detected in ground water at industrial sites and are the most common contaminants found at Superfund sites (Lee, 2002, Wang and Tseng, 2008, Butler 2009, Che 2011). Additionally, dichloroethane (DCA) and vinyl chloride (VC) are often detected in extensive areas of soil and ground water surrounding chemical factories that produced OCPs and chlorinated herbicides (Kastanek et al., 2007).

This frequent detection in the soil and groundwater at Superfund, industrial, and commercial sites, and recalcitrant response to standard remedial technologies (i.e., pump and treat) prompted research to focus on the prospect of biodegradation of chlorinated solvents. Because chlorine atoms are electronegative in nature, carbon-carbon bonds in CVOC molecules are not typically thermodynamically amenable to oxidative degradation by aerobes. This led to the discovery that CVOCs, serving as an electron acceptor for microbial dehalorespirers, are reductively dechlorinated under anaerobic conditions, (Newell et. al, 1994).

As opposed to the β -elimination reaction endemic to the Fe-mediated RD, biotic RD occurs via the process of hydrogenolysis. RD by hydrogenolysis allows for the sequential dechlorination of higher chlorinated ethenes like PCE and TCE to DCE, VC, and ethene. The process hydrogenolysis occurs in stepwise manner because the higher chlorinated ethenes are the preferred substrates (Bruton, 2015). This process of stepwise transformations was originally determined by Vogel et al. (1987) who observed that RD of aliphatic compounds depended on their individual standard redox potential; a value that

correlated with the number of replacement halogens (substituents). **Figure 4** is a conceptual representation of a release of chlorinated compounds. CVOCs sink and dissolve into groundwater. The low redox potential in deeper, anaerobic aquifer promotes degradation by RD. Vogel et al. also found that the rate of RD varied in accordance with the surrogacy of chlorine on the compounds carbon atoms; the more chlorine atoms replaced the faster the RD process occurred. (Li et al., 2010).

Since aquifer conditions where most CVOC contaminated groundwater exists is typically anaerobic (or mildly aerobic), RD-stimulated bioremediation of halogenated compounds is a demonstrated viable alternate treatment strategy. Because anaerobes utilize chlorinated hydrocarbons as electron acceptors to metabolize energy for growth, organochlorine-reducing microbes are the probable major mechanism of RD in anaerobic environments. Yet, early bench-scale studies and in situ observations by Maymó-gatell et. al. (1995), Magnuson et. al. (1998) and Holliger et. al. (1999) found that that most halo-respiring microbes only reduced PCE and TCE to cis-dichloroethylene (cis-DCE) and vinyl chloride (VC) as terminal products. VC is the most toxic of the four CVOCs and, therefore, an undesirable degradation product. Only a few microbes can completely dechlorinate PCE and TCE to less toxic ethene or ethane rendering anaerobic RD an incomplete treatment strategy. Yager et al. (1997) observed that the dechlorination rates of the cometabolic processes are much slower than halo-respiration, and the observed contributions of enzyme-mediated processes to dehalogenation in natural environments are negligible (Wang et. al., 2008).

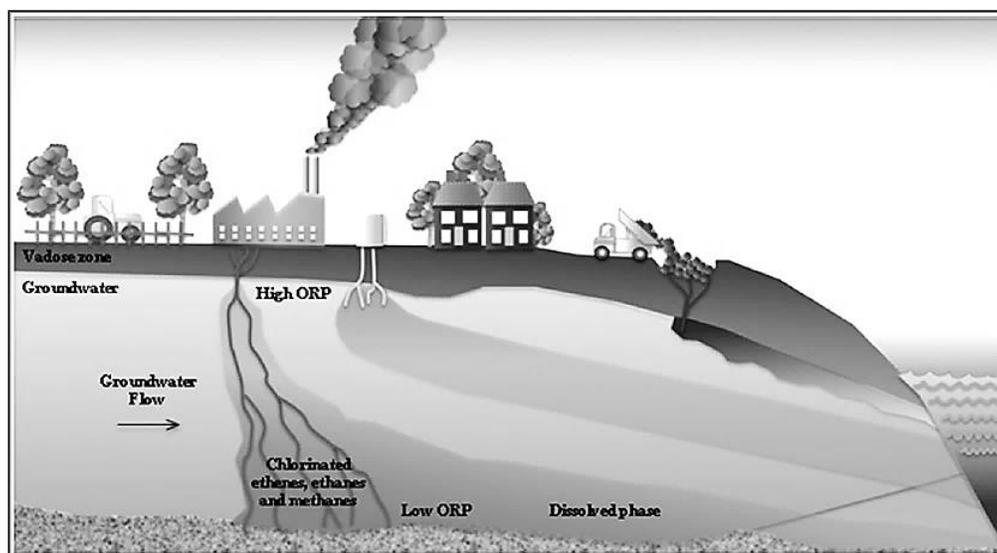


Figure 4 Conceptual Model of CVOC Release and Diffusion in Groundwater (Koenig et al., 20015)

Studies by Amonette et al. (2000) and Shinet al. (2007) respectively discovered the capability of dissimilatory iron-reducing bacteria (DIRB) to reduce chlorinated compounds like carbon tetrachloride (CT) and trichloroethylene (TCE). Their research revealed that the enzymatic (metabolic) activity of DIRB yielded the same reduced species of iron, Fe^{2+} , that effectively catalyzed the reduction of chlorinated aliphatic hydrocarbons under anaerobic conditions (Li et al., 2010).

To assess the comparative influence of abiotic and biotic processes to the RD of PCE and TCE, Butler et al. created “well defined” microcosms with natural aquifer materials collected from three locations. Electron donors and terminal electron acceptors were added to each microcosm to simultaneously stimulate microbial activity and to generate reactive minerals via microbial iron and sulfate reduction. The relative contribution of each process to the RD was gauged by analysis of reaction products,

reaction kinetics, and fractionation of stable carbon isotopes (C-12/C-13). Butler's team made several key findings and identified differences between the biotic and abiotic RD processes at a microcosm scale. Their findings and variations included:

- Chlorinated ethenes (PCE and TCE) are susceptible to RD by dechlorinating microorganisms and abiotic RD by reduced minerals (such as FeS);
- The predominant transformation pathway in most of the microcosms was microbial-mediated RD;
- The rates of abiotic transformation were similar in magnitude to those for microbial transformations only in the microcosms purposely prepared with slightly higher pH (pH 8.2 versus 7.2). This ambient condition was believed to have inhibited the dechlorinating bacteria;
- Biotic RD was typically faster than the abiotic process.

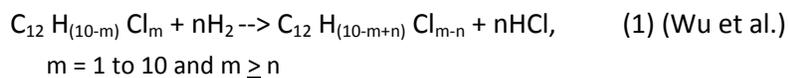
Based on their findings from the microcosm studies, the researchers concluded that though microbial-mediated RD can potentially degrade PCE and TCE rapidly, abiotic RD also contributes to the degradation. Abiotic RD is more likely to occur under conditions where the implemented remedial technology is: 1) designed to purposely generate high masses of reactive minerals, 2) where dechlorinating microbe activity is nominal, and/or 3) where biotic RD cannot completely degrade PCE or TCE to ethane. Further, the researchers concluded that while faster biotic RD often results in the generation of toxic intermediates such as cis-DCE and VC that resist further degradation, slower mineral-mediated abiotic RD typically results in complete degradation to preferred non-toxic products like acetylene (Butler 2009).

Polychlorinated Biphenyls (PCBs)

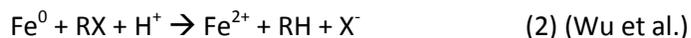
Studies have shown that oxic and anoxic bioremediation of PCBs is a difficult process. Early research by Bedard et al. (1986) found that aerobic biodegradation of PCB species diminished as the number of chlorine atoms increased. In fact, the degradation of PCB species with five or more Cl- atoms by aerobic microbes rarely occurred (Long, et al., 2013). Sudell et al. confirmed that PCB's present in oxygenated media persist because they do not biodegrade (Sudell et al., 1994). Jacobus et al. (1995) subsequently observed that naturally occurring anaerobic microbes capable of degrading PCBs grow very slowly (Long, et al., 2013). The inhibited reproduction of the anaerobes thus limits their functional ability to degrade PCBs. Further confirming the findings of their predecessors, Wu et al. determined that despite its considered status as a sustainable treatment strategy, the relatively slow process of bioremediating PCBs limits its application as a cleanup strategy (Wu et al., 2012). The concurrent research of Zanaroli et al. identified the slow growing species Dehalococcoides and Chloroflexi as the biotic-mediators of the RD process since they use hydrogen and PCBs as electron acceptors (Zanaroli et al., 2012). More recently, a study conducted by Long, et al. discovered that despite the resistance, RD of PCBs by microbes, even higher chlorinated congeners, can still occur if the environment conditions are suitable (Long, et al., 2013).

RD by catalytic hydrodechlorination emerged as the preferred, more efficient remedial technology to treat PCBs because it required less energy and did not result in the formation of PCDD/F. The process of catalytic hydrodechlorination of PCBs involves the successive removal of chlorine atoms. The process, by which one H⁺ atom is added to a chlorine-atom-attached to carbon on a PCB, yields a reactive intermediate, an arenium ion (a univalent cyclohexadienyl cation). When a second H⁺ atom is combined with the chlorine atom, it forms HCl resulting in dechlorination of the PCB (Wu et al., 2012).

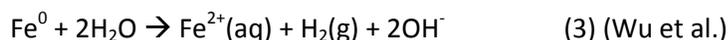
The conventional degradation equation for catalytic hydrodechlorination of PCBs is:



RD of PCBs by the process of catalytic hydrodechlorination typically involves the use of a transition metal like Fe (Wu et al., 2012). The work of Matheson and Tratnyek (1994) yielded three proposed mechanisms of PCB dechlorination (Wu et al., 2012). The first involves iron reduction by the direct transfer of two electrons from Fe⁰ (ZVI) to the adsorbed alkyl halide:

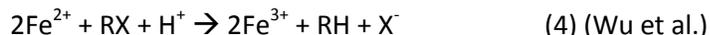


The second and third mechanisms involved ZVI corrosion in anaerobic water:



The resulting H₂ is also a donor reductant that can dehalogenate RX ($RX + H_2 \rightarrow RH + H^+ + X^-$). However, dechlorination by this process is deficient in the absence of effective catalysts.

Fe²⁺ produced by corrosion can also dehalogenate RX directly:



Rysavy et al. (2005), Kirschling et al. and Xiu et al. (2010), and Zanaroli et al. (2012) successively demonstrated that the addition of ZVI to sediments yields H⁺. The cathodic hydrogen stimulates microbes thereby reducing the lag in PCB dechlorination previously reported by Bedard, Sudell and Wu (Long, et al., 2013). Winchell and Novak (2008) proved ZVI to be a more efficient promoter of PCB bio-dechlorination in sediment than other substrates. The H₂-producing capability of ZVI helped reduce the loss of the electron donor consumed by other hydrogen-utilizing microbes (Wu et al., 2012). Recent work by Long, et al (2013) confirmed that the key to successful RD of PCBs is adequate and suitable electron-donating substrates. The independent studies of Son et al (2006) and Yu et al. (2006) determined that reductants like molecular hydrogen (H₂) act as electron donors to microbial dechlorinators (Long et al., 2013). So, ZVI has become the preferred reactant to stimulate RD of PCBs because it is easily produced, stable (Long, et al., 2013) and is a longer-lasting H₂ donor than fermentable substrates (Zanaroli et al., 2012).

Reporting on the environmental conditions that best support Fe-mediated RD, Schreier and Reinhard (1994) achieved dechlorination of an alkyl halide (RX) using Fe powder in anaerobic and (pH) neutralized PCB in water at 323° K (Wu et al., 2012). At the same time Sudell et al. observed the degradation of dilute PCBs in aqueous solutions under anaerobic conditions at neutral pH and a temperature of 20° C, typical of groundwater (Sudell et al., 1994). The research of Chuang et al. (1995) reported dechlorination of PCBs with ZVI at 473–873° (Wu et al., 2012). Both Yu et al.'s 2006 study and Srinivasa et al.'s 2011 research demonstrated that a neutral to slightly alkaline pH environment and sufficient supply of H₂ in ZVI-amended sediments would sustain the population of the dehalorespiring anaerobes, Dehalococcoides (Long, et al., 2013).

Studying ZVI's contribution to the RD of PCBs in various media, Wang and Zhang (1997) reported nearly 90% degradation of PCBs in aqueous solution. A decade later, similar work by Varanasi et al. (2007) resulted in a much lower 38% degradation of PCBs in soils. The projected difference in degradation rates between the media is thought to be the result of weaker diffusion of PCB from soil particles to the ZVI particle surfaces. (El-Temsah et al., 2016). Hara identified likely proof of this effect under natural environmental conditions. While PCBs, DDT, HCH, and endosulfan are all present in Vietnam's Mekong

River Delta sediment and biota, concentrations in the corresponding aquatic environment are less than the values reported in other regions of Vietnam and Asia (Hara J, 2012). The regional soil regime in the Mekong Delta is acidic with a widespread manifestation of metallic sulfides. Natural ferric sulfide exists in the aquatic environment. The presence of ferric sulfide, a demonstrated contributor to the process of RD, led the researcher to conclude that the Delta's natural environment promotes PCB degradation.

OCPs

In 1966, Sanitary Engineers David Hill and Perry McCarty conducted experiments in wastewater sludge to evaluate and compare the degradation of OCPs under aerobic versus anaerobic conditions. At the time, conventional science assumed that if a compound resisted degradation under aerobic conditions then degradation under anaerobic conditions was improbable. Their targeted pesticides included DDT, lindane, heptachlor, aldrin, dieldrin, and endrin. Structural differences between the cyclodiene OCPs (aldrin, heptachlor, dieldrin, and endrin) were noted; aldrin and heptachlor are unsaturated while dieldrin, and endrin are epoxidized (containing a triangulated ether). The molecular structures of common OCPs are depicted in **Figure 5**.

Hill and McCarty observed that all of the OCPs degraded to some degree under anaerobic conditions. Except for the epoxidized (drin structure) compounds, all exhibited superior degradation under anaerobic conditions than under corresponding aerobic conditions. Some of the key findings from this early research included:

- As the biological activity increased, the anaerobic degradation of lindane improved and was generally more rapid in the anaerobic environment than in the corresponding aerobic environment;
- Aerobic conditions (i.e., several milligrams per liter of dissolved oxygen) impeded the degradation of DDT while it quickly degraded to DDD under anaerobic conditions;
- Anaerobic degradation of heptachlor converted it to daughter products more persistent than the primary compound (i.e., heptachlor epoxide);
- Under anaerobic conditions endrin formed similar extractable degradation products; and
- Dieldrin was most resistant to degradation under anaerobic conditions.

Based on the results of their work, the researchers ranked the OCPs and their resulting degradation products for their demonstrated persistence under anaerobic conditions as follows: 1) lindane, 2) heptachlor, 3) endrin, 4) DDT, 5) DDD, 6) aldrin, 7) heptachlor epoxide, and 8) dieldrin (Hill and McCarty, 1967). The cyclodienes and epoxides exhibited the strongest resistance to anaerobic degradation. The study acknowledges the biologic activity in anaerobic environments and the apparent role it plays in the degradation of OCPs. However, the research makes no reference to RD, biotic or abiotic, as the process involved in the target pesticide degradations.

A few years after Hill and McCarty, Castro and Yoshida (1971) observed that DDT tended to disappear from flooded soil and suggested that it resulted from biotic (microbial) degradation rather than abiotic (chemically-mediated) processes. Aislabie et al. (1997) claimed that indigenous organisms were not effective degraders of DDT and that the biotic degradation of DDT only contributed a small fraction to the reduction of DDT in the natural environment (Li et al., 2010). A couple of years later, contrary to the claim by Aislabie's research team, Löffler et al. (1999) found that dehalorespiring bacteria in anaerobic soil played a significant role in the biotic dechlorination of OCPs for processes that involved an electron acceptor during energy metabolism (Chen et al., 2014).

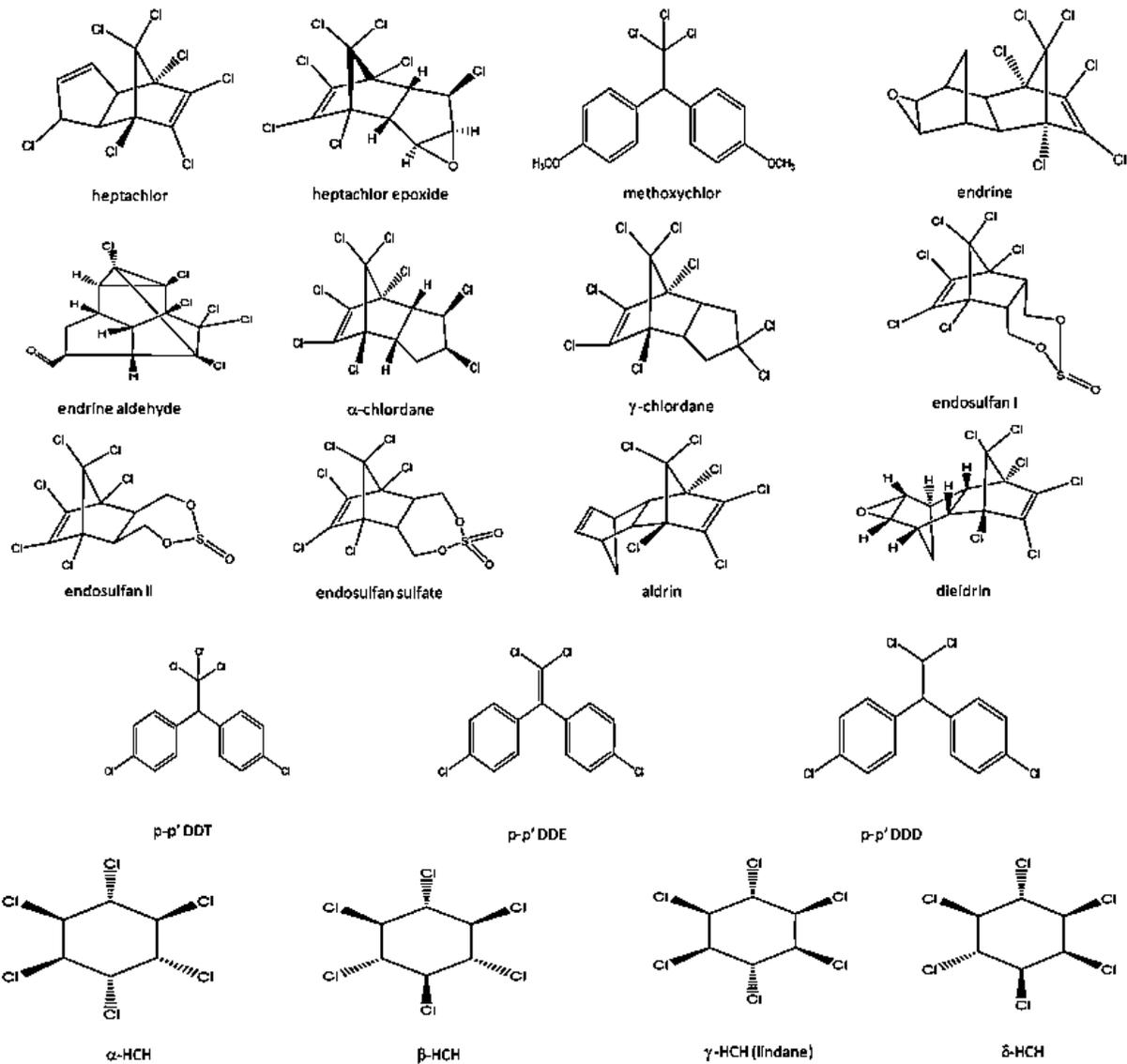


Figure 5 Molecular Structures of Example OCPs (courtesy of Panseri, et al., 2013)

Well before this research debate arose over the contribution and predominance of biotic vs. abiotic degradation processes, Glass (1972) noted an apparent connection between low reductive/oxidative (redox) potential (Eh) and the rapid degradation of DDT. Fifteen years after Glass' findings, Vogel et al. (1987) also observed the RD of aliphatic compounds depended on redox potential. Decades later, Li et al. pointed out that the stability of DDT is due to the chlorinated aliphatic and aromatic structures that make up the molecule. Glass' observation of impact of redox potential on DDT degradation prompted the theory that the presence of reduced iron (Fe^{2+}) strategically influenced the redox state and the transformation of DDT in inundated soil (Li et al., 2010).

Shortly after Glass' proposed model, Wade and Castro (1973) suggested Fe^{2+} porphyrins (a pigment with an aromatic ring of linked heterocyclic groups surrounding a metal atom) as the mediator of RD of alkyl halides (a functional group with the formula R-X where X is a halogen, like chlorine). Khalifa et al conducted a subsequent study on the effect of Fe^{2+} porphyrins on the degradation of toxaphene in pH

neutral aqueous solution and found that roughly one-half of the compound's C-Cl bonds were split resulting in the formation of lighter, dechlorinated degradation compounds (Khalifa et al, 1976). More than two decades after Khalifa's work, Grittini's study of toxaphene treatment with Fe²⁺ porphyrins identified the apparent combined contribution of two distinct RD processes, dehydrochlorination and β-elimination. The research also established one key required condition for the RD process, the presence of water. Grittini concluded that since water was required for the RD reactions to transpire, that the chlorinated compounds must be in aqueous solution. Further, the RD reactions take place at ambient temperature and pressure, and are over within a matter of minutes (Grittini, 1997).

Cong et al. pursued experiments to show an apparent connection between RD of OCPs in soil, Grittini's contention of the importance of water to the process, and Dombeck et al.'s (2001) demonstration of the following RD reaction between iron and organochlorine compounds in the water solution:



Using soils collected from former pesticide-manufacturing facility, the 2010 experiments proved the ability of zero-valent iron (Fe⁰) to reductively dechlorinate lindane and DDT. Based on the results, the scientists concluded that the rate of RD of the target OCPs was mainly limited by the rate of dissolution from the sorbed to the aqueous phase (Cong et al., 2010).

In their study of the dechlorinating effects of acetate amendments on TCE, Wei and Finneran (2011) found that it is possible for simultaneous RD and Fe reduction to occur in soils. Though they were focused on the RD of TCE, their findings led them to declare that despite an intricate relationship, the RD of OCPs and Fe reduction is a cooperative sequence that can happen in anaerobic soils. This opinion stemmed from cited evidence that the redox potentials for the RD of OCPs and Fe reduction notably overlapped (Chen et al., 2014).

REDUCTIVE DECHLORINATION OF DIELDRIN

Beginning in the late 1960s, studies of biodegradation of OCPs revealed that most, especially dieldrin, tended to persist in aerobic environments. Studies by Wedemeyer (1968), Matsumura et al. (1968 and 1970), Bixby et al. (1971), Jagnow and Haider (1972), and Pati et al. (1972) revealed dieldrin's transformation under aerobic conditions to intermediate metabolites and microbial mineralization to CO₂. Chiu et al. noted that under aerobic conditions, microbes or mammals are capable of enzymatically metabolizing aldrin to epoxidized dieldrin (Chiu et al., 2005).

The succession of sanitary engineering research into the methods and conditions that supported the RD of CVOCs, like TCE, and OCPs, like lindane and DDT, led to the conclusion that by comparison to CVOCs and most other OCPs, the structure and chemical complexity of dieldrin rendered it less responsive to RD under anaerobic conditions (Hara, 2012). Yet investigations of aerobic bioremediation conducted by Georgacakis and Khan (1971) revealed that the degradation intermediate photo-dieldrin was more toxic than the parent compound (Matsumoto et al, 2009).

Over a thirty-five year period that began in 1980, a variety of methods for in-situ remediation of dieldrin were studied. Treatment strategies included combined ultraviolet (UV)/Fenton reagent, combined UV/chemical reaction, Palladium/Carbon (Pd/C) catalysis, solar photo-catalysis, and bioremediation. The research of Books (1980), Dureja et al. (1987), Maule et al. (1987), Bandala et al.(2002), Baczynski et al. (2004), Kusvuran and Erbatur (2004), Chiu et al. (2005), and Zinovyev et al.(2005) all resulted in the incomplete degradation of dieldrin. As with the earlier studies of aerobic biodegradation, dieldrin was

again transformed to mono- or di-dechlorinated intermediates with dual-ring (drin) structures by the other in-situ treatment methods (Hara, 2009, 2010, and 2012).

By contrast, the research of Miles et al. (1971), Siddarame et al. (1977), Maule et al. (1987), and Sutherland et al. (2000) respectively reported anaerobically degrading heptachlor, endrin, aldrin, dieldrin, and endosulfan (Chiu et al., 2005 and Matsumoto et al., 2009). Microbial RD is the predominant anaerobic degradation process attributed with the elimination of the chlorine atom from the cyclodiene structure. However, the process of degradation of dieldrin under anaerobic conditions was difficult to achieve and identify. Maule et al. reported that a consortium of anaerobes could transform dieldrin to its end products, syn- and anti-mono-dechloro-dieldrin, by the removal of a chlorine atom from the methylene bridge. But, the transformation of dieldrin to aldrin by epoxide removal had yet to be observed in the natural environment. Almost two decades after Maule et al., Chiu et al. identified a mixed culture of anaerobic microorganisms in riverbed sediments that degraded dieldrin to aldrin by the previously unseen mechanism of epoxide ring cleavage (Chiu et al., 2005).

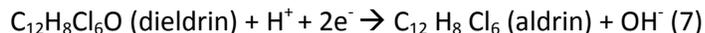
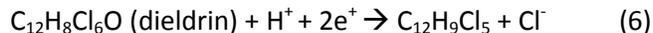
Investigating the potential of microbial mediation of dieldrin and endrin Matsumoto et al. noted that anaerobes capable of degrading cyclodiene OCPs like dieldrin, endrin, aldrin, and heptachlor had unique morphological and physiological characteristics (Matsumoto et al., 2009). Though Chiu et al. reported discovering a consortium of anaerobes capable of degrading the epoxides to less toxic products, Matsumoto's group reported no evidence of successful in-situ degradation of dieldrin or endrin in soil or sediment. The study team concluded that optimal in-situ anaerobic biodegradation of the cyclodiene OCPs, including epoxides, to low toxicity or non-toxic metabolic products could occur at contaminated sites if suitable environmental conditions were present (Matsumoto et al., 2009).

A comparative study by Ghadiri et al. (1995) of microbial degradation of aldrin and dieldrin in soil under controlled laboratory conditions versus outdoor environment noted significantly faster transformation rates in the controlled environment. Degradation rates in the laboratory ranged from 28 to 42 weeks while rates for the soil stored outdoors were prolonged 5 to 6 years. The researchers reported that dieldrin degraded faster than aldrin in both controlled environment and outdoor conditions; relevant because the typical degradation pathway is aldrin to dieldrin.

Ghadiri's team identified temperature and water content as notable factors influencing the degradation process (Ghadiri et al., 1995). Chiu et al. reported yet another key environmental factor affecting the transformation of dieldrin, redox potential. The researchers observed that dieldrin degraded faster under conditions of lower redox potential (Chiu et al., 2005). Contrasting the degradation capabilities of ferric iron (Fe^{3+}) versus ferric sulfide (Fe_2S_3), Hara et al. (2009) noted that varying environmental conditions including organic content, soil chemical composition, competing oxidants, and co-solvents interfered with the transformation process (Hara et al., 2009).

In 1972, Glass conceived that reduced iron (Fe^{2+}) potentially influenced redox and the transformation of DDT in inundated soil. Succeeding work established how the corrosion of iron produced donor cathodic hydrogen that served in different capacities in biotic and abiotic RD. Beginning in 2009, Hara et al. began a series of investigations into the influence variously charged Fe and iron sulfide play in the process of RD of dieldrin. Pyrite, a naturally-occurring, mineralized form of iron sulfide (Fe_2S_3), was obtained from a mine and pulverized in the laboratory to serve as the Hara's experimental reductant.

Initially, Hara's team determined that Fe^{3+} (ferric) was well capable of dechlorinating dieldrin, but resulted in partial dechlorination, mainly degrading to aldrin, and subsequently to unacceptable toxic intermediates according to one or more of the following chemical reactions:



Treatment with the Fe_2S_3 yielded superior results, transforming the dieldrin to water-soluble intermediates via oxidative degradation under anaerobic condition. Though Fe_2S_3 initially provided a faster rate of degradation than Fe^{3+} , acidification by the sulfate ion was recognized as the cause of the slower degradation rate. Conversely, the degradation rate was accelerated by Fe^{3+} .

Introduction of aerobic conditions also caused a decline in the reactivity of the pyrite due to oxidation of the surface layer. Under low redox potential, the cycle of pyrite oxidation proceeds, but the conversion of ferrous state iron (Fe^{2+}) to ferric state (Fe^{3+}) and sulfur monoxide (SO) to sulfate (SO_4^{2-}) lapses. Considering the kinetics of the process of dieldrin dechlorination under anaerobic and low redox conditions, O_2 was assumed to be the primary controlling factor affecting the surface of the pyrite. Based on their bench-scale results, the researchers concluded that ferric sulfide was capable of thoroughly degrading dieldrin. However, the process had yet to be induced under field conditions (Hara et al., 2009).

Citing Hashimoto's (2005) observation of dieldrin's regular detection on agricultural land as cause to develop RD for in-situ treatment, Hara pursued further research into the degradation capability of Fe_2S_3 . The research found that oxygen (O_2) concentration controlled the generation of reaction products and, thus, dieldrin's rate of degradation. Under anaerobic conditions, increasing O_2 caused the degradation rate to decrease while a nominal amount of oxygen (10 μ mol) accelerated the dechlorination of dieldrin. The results led the team to suggest that the presence of pyrite in natural systems induces the reduction of drin specie OCPs (Hara, 2011).

Continuing his study of Fe-mediated RD as a viable technology for in-situ treatment of chlorinated compounds, Hara noted how earlier work revealed similar capabilities between Fe^0 (ZVI) and Fe_2S_3 (pyrite) to dechlorinate dieldrin. Despite considerably different reaction processes, each resulted in a better than 90% reduction after 29 days. **Figure 6** graphically depicts Hara's comparative degradation profiles of dieldrin treated with pyrite and ZVI under aerobic conditions. (Hara, 2012).

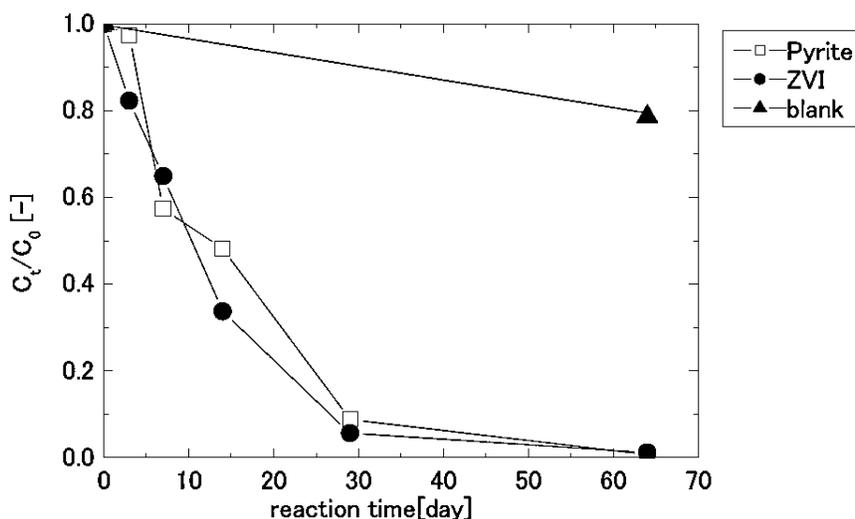


Figure 6 Anaerobic degradation profile of dieldrin using ZVI and pyrite (Fe_2S_3) (Hara, 2012)

Under anaerobic and aerobic conditions, the path for dechlorination of dieldrin occurs mostly by the process of oxidative degradation. Oxidative ability does not depend upon O₂ content. This is proved by the generation of the reductant species under either aerobic or anaerobic condition by the reactions of pyrite with either H₂O or O₂. While degradation under aerobic conditions produces a variety of weak organic acids, the reductive pathway under anaerobic (or micro-aerobic) conditions, primarily driven by the degradation of the epoxide ring, characteristically results in just two organic acids: formic and malonic (Hara, 2012).

Like the result for Fe³⁺, ZVI reductively dechlorinates dieldrin to mono-dechlorinated intermediates products and aldrin. Whereas Fe₂S₃ oxidatively degrades dieldrin to water-soluble compounds, the cathodic hydrogen and electron generated by ZVI oxidation leading the RD process impedes the pathway to complete dechlorination (Hara, 2012).

SUSTAINABILITY OF REDUCTIVE DECHLORINATION

Matheson and Tratnyek (1994) Burris et. al. (1995) Orth and Gillham (1996), Roberts et. al. (1996), Wüst et al. (1999), Choe et. al. (2001), and Cervini et. al. (2002) all noted that the densities and low water solubilities of chlorinated solvents that cause them to exist as DNAPLs inhibit the remediation of these compounds in groundwater by pump-and-treat method (Wang and Tseng, 2008). Tailing, or tail-off, and rebound are phenomena that often result at pump-and-treat sites. Tailing refers to the sequential decline in the rate of contaminant reduction that tends to routinely occur with pump-and-treat system operations. Rebound is the frequently observed sudden jump in the concentrations of dissolved contaminants that occurs after the pump is turned off. Rebound often results in stabilized, slightly lower concentrations (USEPA, 1996). These factors are some of the key reasons why pump and treat technology ends up as a long-term remedy. The escalation of cost to operate and maintain this technology during the extended period of geometric decline in the treatment efficiency is a key indicator of its unsustainable character.

An example of the extreme cost of implementing pump-and-treat technology is the remedial design for the Baird and McGuire Superfund Site in Holbrook, Massachusetts. Baird and McGuire, Inc. had a 71 year history of chemical mixing operations on the site. In late 1982, a plume of VOCs and SVOCs identified in the site's groundwater, including dieldrin, posed an immediate risk to public health. Shortly thereafter, the former manufacturing facility was listed as a NPL site. Reflecting the health threat, cleanup goals were established for benzene, toluene, ethylbenzene, xylene, 2,4-dimethyl phenol, naphthalene, acenaphthene, dieldrin, chlordane, arsenic, and lead (US EPA 1998).

To address groundwater impact, a pumping system consisting of six extraction wells and treatment system were designed and installed. Surface treatment included equalization and removal of light non-aqueous phase liquid (LNAPL), two-stage chemical treatment, flocculation/clarification, aeration, filtration, and pre-discharge carbon adsorption polishing. Despite successfully removing 2,100 pounds of organic contaminants from the groundwater, after three years of operation (1994 through 1997) the ex-situ system had not met the established cleanup goals. The reported cost for design, construction, operations, and maintenance of the pump-and-treat system was \$22.7MM. **Table 4** is a breakdown of the capital and O&M expense with comparative unit costs incurred by the treatment technology.

Table 4

Baird and McGuire Superfund Site Groundwater Pump and Treat Remedial System Cost Breakdown (courtesy of USEPA, 1998).

Cost Item	Cost
Capital equipment	\$15,000,00
Operations and Maintenance(O&M) activities	\$7,800,00
Designed O&M costs (\$/month)	\$58,000
Actual Monthly O&M costs (\$/month)	\$240,000
Unit treatment cost per 1,000 gallons of groundwater extracted (\$/1,000-gallons)	\$284
Unit treatment cost per pound of contaminant removed (\$/pound)	\$10,822

Given that a sanitary engineering study of degradation of OCPs anaerobic sewage sludge initiated the subsequent pursuit of research of RD as an in-situ treatment technology, it seems appropriate to review the sustainability factors considered in the evaluation of wastewater treatment technology. In their evaluation, Muga and Mihelcic acknowledged the three primary sustainability evaluation indicators: economic, environmental, and societal. Looking beyond cost and performance factors, the researchers found that sustainability varies by degrees according to the selection and operation of a specific treatment technology. Their work revealed an inherent difficulty in selecting a technology that satisfies all factors, especially certain societal indicators (Muga and Mihelcic, 2008). The researchers acknowledged that the best outcome of the process is an acceptable balance between all indicators weighted towards the best interest of the affected community.

The EPA's guidance document "*Incorporating Sustainable Environmental Practices into Remediation of Contaminated Sites*" notes that sustainable remediation should focus on capitalizing the net environmental benefit while maintaining the effectiveness of the remedy. EPA's Office of Solid Waste and Emergency Response (OSWER) identifies six core elements of sustainable remediation:

- Energy requirements of the treatment system;
- Air emissions;
- Water requirements and impacts on water resources;
- Land and ecosystem impacts;
- Material consumption and waste generation; and
- Long-term stewardship actions

These six core elements are measured against the triad of sustainability indicators: economic, environmental, and societal impacts (OSWER, 2008). **Figure 7** depicts the relationship of the core elements of sustainable remediation.

Two routinely implemented RD treatment processes, bioremediation and ISCR, are in-situ strategies with demonstrably lower costs and significantly less environmental and societal impacts than long-term capital and energy intensive ex-situ treatment technologies like pump and treat. Permeable reactive barrier (PRB) technology using zero-valent iron (Fe⁰) as reactive media has received a great attention because of its cost-effective, minimal impact approach for *in situ* groundwater remediation (Scherer et

al. 2000; USEPA 2002). It has been reported that after the initial activity and cost of implementation, ZVI PRBs can treat contaminated groundwater up to 30 years after installation. Unlike pump and treat technology, this long-term treatment strategy has little, if any, maintenance requirements. **Table 5** compares the capital cost and operating cost for the implementation of pump and treat remedial technology at 32 USEPA-regulated cleanup sites versus the cost for installation of PRBs at 16 cleanup sites (USEPA, 2001).

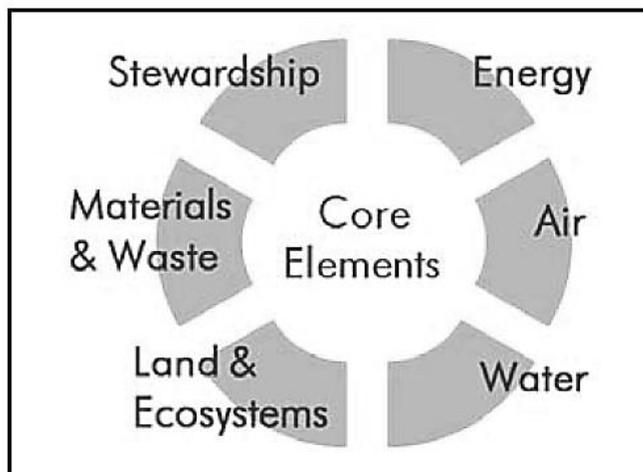


Figure 7 –Relationship of Sustainable Remediation Core Elements (courtesy of OSWER, 2008)

While in-situ RD strategies are associated with key sustainability evaluation factors like lower cost and GHG footprint, other factors (like efficacy) and uncertainties linked to each potential treatment technology should also be considered. **Table 6** is a tabulation of cost-related uncertainties associated with various groundwater treatment remedial strategies (USEPA, 1996).

While the uncertainties for each of the remedial technologies listed in **Table 6** are specifically cost-related, they are a good indicator of the complexity of evaluating the sustainability of treatment strategies. All of the listed treatment technologies share the six listed general uncertainties (duration, regulatory changes, changing site conditions, technology improvements, temporal cost increases, and down-time losses). Despite probable attempts to define aquifer characteristics and hydrologic dynamics, all of the technologies share an uncertainty about the measured versus actual radius of influence of injection and/or extraction processes. That uncertainty leads to the question of the technology’s ability to access the target contaminants. In turn, that leads to the uncertainty of rates of predicted versus real mass transfer and contaminant reduction. The ultimate uncertainties are then the efficacy of the treatment technology and the associated timeframe to achieve the goal of the remedial strategy.

Based on capital and operating cost alone, in-situ treatment technologies certainly appear to be more sustainable than ex-situ treatment technologies. Yet, the multiple of uncertainties manifested by in-situ technologies outnumber those for the common pump and treat technology. Thus, like the sustainability evaluation of wastewater treatment technology, it is advisable to evaluate all of the indicators to find the best, sustainable strategy to treat aqueous-phase dieldrin. Though the uncertainties presented in **Table 6** are primarily cost-related they also present implications of probable effects to the environmental and social indicators of sustainability. A true example is the potential environmental

Table 5

Summary of Remedial Cost and Unit Cost Data for Forty-eight Remediation Sites
(Pump & Treat versus Permeable Reactive Barrier)
(courtesy of US EPA, OSWER, 2001)

Cost Category	<u>Pump & Treat Sites</u>				<u>Permeable Reactive Barrier Sites</u>			
	25 th Percentile	Median	75 th Percentile	Average	25 th Percentile	Median	75 th Percentile	Average
Years of system operations (with data available)	4	5	3	6	NC	NC	NC	NC
Average volume of groundwater treated per year (1,000 gallons/year)	7,000	30,000	100,000	120,000	NC	NC	NC	NC
Total Capital Cost	1,700,00	2,000,000	5,900,00	4,900,00	440,000	630,000	1,000,000	730,000
Average operating cost (\$/year)	180,000	260,000	730,000	770,000	NC	NC	NC	NC
Capital cost per volume of groundwater treated per year (\$/1,000 gallons/year)	23	78	350	280	NC	NC	NC	NC
Average annual operating cost per volume of groundwater treated per year (\$/1,000 gallons/year)	5	16	41	32	NC	NC	NC	NC

degradation posed by the potential generation of daughter products with greater toxicity than parent contaminant as a result of enhanced bioremediation. Another example is the possible environmental and/or social consequences of changing the oxidative state of an impacted aquifer as a result of the implementation of air sparging or ISCO technologies. **Figure 8** presents a conceptual Remedial Strategy Sustainability Decision Tree that evaluates sustainability of ex-situ (pump and treat) versus in-situ (ISCR-RD) groundwater remedial strategies based on the cost-related uncertainties associated with the treatment technologies provided in **Table 6**. The basis for the decision about the remedial strategy's sustainability is a comparative ranking of the technology's uncertainties to OSWER's six core elements of sustainable remediation. For the Decision Tree ranking, the six core elements are merged into three key criteria:

- Demand (Energy, Water, and Materials);
- Impacts (Emissions, Water Resources, Land/Ecosystem, Waste); and
- Benefits (Stewardship).

Table 6

Typical Cost-related Uncertainties Associated with Common Groundwater Remedies
(courtesy of US EPA, OSWER, 2007)

Remedial Technology	Typical Uncertainties
Pump and Treat	<ul style="list-style-type: none">• Mass removal rate and loading to treatment system over time• Area of influence and capture provided by extraction wells
In-situ Chemical Oxidation (ISCO)	<ul style="list-style-type: none">• Radius of influence of injection points• Amount of oxidant lost to dispersion or naturally occurring organic matter• Ability to access targeted contaminant mass• Unexpected consequences of changing the aquifer's oxidative state (e.g. fouling of existing monitoring or extraction wells)• Number of applications/injections• Ability to reach Maximum Contaminant Levels (MCLs) or target contaminant concentration
Enhanced In-situ Bioremediation	<ul style="list-style-type: none">• Radius of influence of injection points• Amount of chemicals required to achieve targeted rate of biodegradation• Number of applications/injections• Ability to provide complete degradation of site contaminants and reach MCLs or target contaminant concentration• Potential to foul existing pump & treat system (if present)• Release of arsenic or other naturally occurring contaminants due to a change in the aquifer's oxidative state• Generation of daughter products with greater toxicity than parent contaminant
Air Sparging and Soil Vapor Extraction (AS/SVE)	<ul style="list-style-type: none">• Radius of influence of sparge points and vapor extraction wells• Influence of site soil regime and stratigraphy on sparge zone• Relative role of volatilization in mass removal versus contaminant degradation through addition of oxidation• Potential to foul existing pump & treat system (if present)• Ability to address all targeted contaminants• Potential channeling or short-circuiting of sparged air• Influent concentration to SVE system over time• Mass transfer of contaminants from one phase to another requiring dual stage treatment• Contaminant migration due to improperly controlled/balanced sparging and extraction processes
General	<ul style="list-style-type: none">• Remedy duration• Changes in regulatory environment• Changes in site conditions• Changes in available and practical remedial technologies• Changes in discount rate (including effects of inflation)• Potential failures in protection and costs for appropriate redundancy

Key criteria are ranked (+1 or -1) based on the anticipated positive or negative effect the uncertainty will have on the remedial technology's sustainability. Key criteria ranking may be subjective as it will be based on the evaluator's knowledge, experience and known (or unknown) Site conditions. Ranked key criteria are collectively tallied into a final decision score for each of the remedial technologies. Final decision scores for each remedial technology are compared to determine which represents the more sustainable technology.

CONCLUSIONS

This literature review was undertaken to determine if the body of research conducted to date supported the prospect of utilizing Fe-mediated RD to treat groundwater impacted by dieldrin. The basis for this review was the suspected impact to groundwater by dieldrin in states located in the southeastern U.S. due to the climate and agricultural history. The recent demographic shift of population to the southeastern states has put pressure on communities to expand. The ensuing land use change requires development, and in some cases, redevelopment to support the communities improvement goals. The recalcitrance and resistance of dieldrin to treatment applies adverse economic pressures to those pursuing land use changes and to the regulatory agencies charged with the protection of public health. The goal was to identify whether the proposed in-situ remedial method was an appropriately effectual and sustainable technology to clean up known and yet to be discovered sites with dieldrin-impacted groundwater.

Focusing on regulatory records of sites in southeastern U.S. states contiguous with the US EPA's Region 4 identified at least twenty (20) known facilities that reportedly manufactured aldrin and/or dieldrin at one time. The record of fifteen (15) Region 4 Superfund sites with reported legacy dieldrin-impacted groundwater is predominated by such manufacturing facilities and affiliated pesticide dumps. Though an exhaustive search of State regulatory records was beyond the scope of this review, the subtropical climate, variety of cultivated crops, their wide geographic distribution, and the prevalence of pests in southeastern states provoked suspicion of a ubiquitous presence of dieldrin throughout the region. Reviewed State records confirmed a significant number of sites with reported impact to groundwater by dieldrin over and above the NPL-listed facilities. It is anticipated that further research of State regulatory records would manifest even more such sites. Thus, an inventory of sites with dieldrin-impacted groundwater located just within the southeastern U.S. region establishes a probable need for a sustainable in-situ remediation strategy like Fe-mediated RD.

The literature review revealed nearly 50 years of research into the process of RD. The studies date back to the original work of two sanitary engineers evaluating the process of degradation of organochlorine compounds in anaerobic wastewater sludge. The ensuing progression of research that followed identified, and named, the process of reductive dehalogenation/dechlorination, the distinction of biotic (microbial-mediated) and abiotic (chemically-mediated) methods, the differences and synergies in the distinctive chemical transformations produced by each method, environmental conditions and factors that stimulate or inhibit the RD processes, resulting degradation products, the best degradation method for each organo-chlorine compound, and whether the success from the laboratory-scale experiments were applicable at the environmental scale. The successful implementation of field-scale RD to cleanup chlorinated solvents sites that began in the mid-1990's is a testimony to the success and transition of the research work performed up to that time. Based on the successful implementation of the RD technology, the studies that followed sought to improve and expand the treatment protocols to cleanup other, much more resistant organochlorine compounds like PCBs, Dioxins, Furans, and OCPs.

Remedial Strategy Sustainability Decision Tree

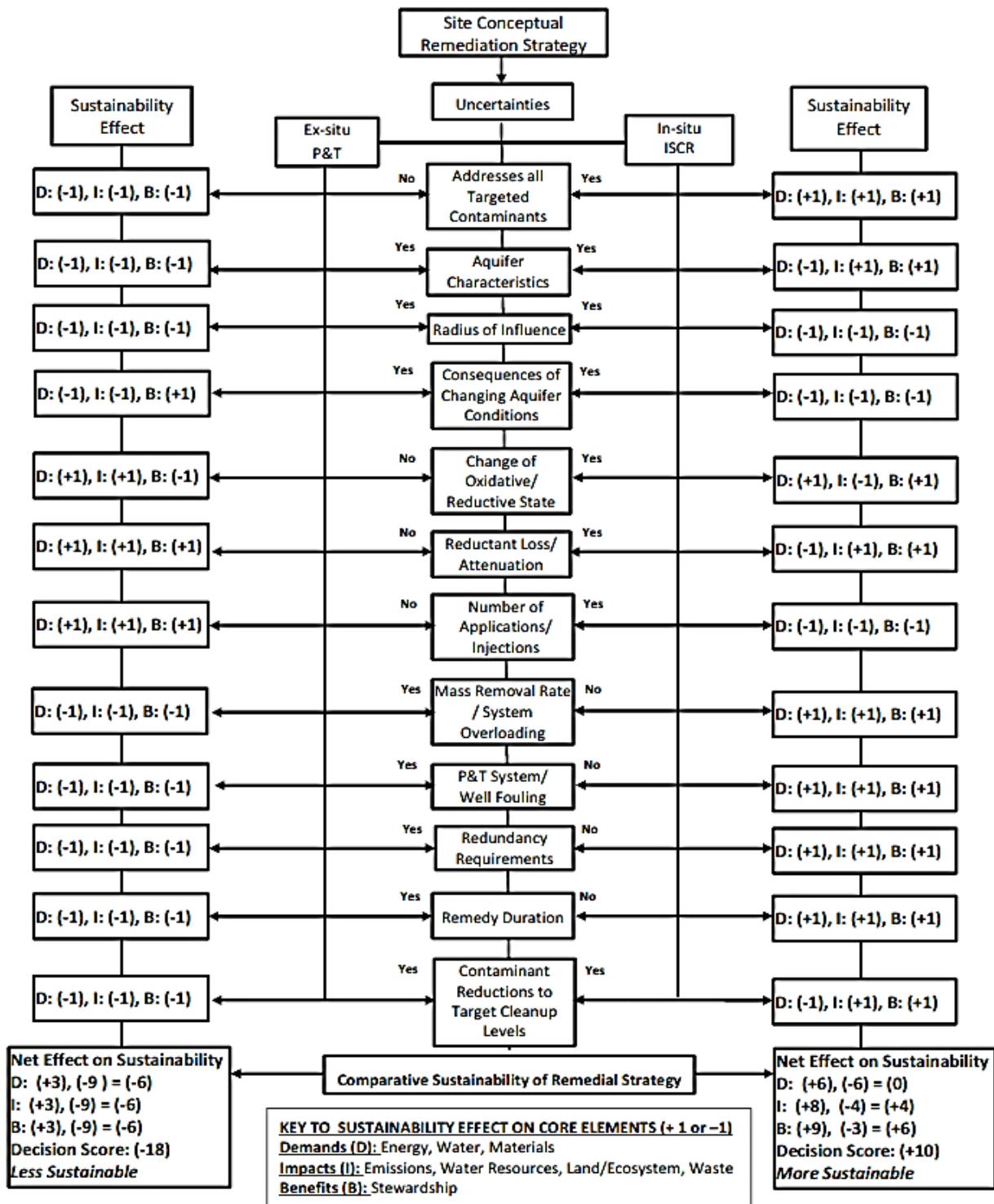


Figure 8 Remedial Strategy Sustainability Decision Tree

Early on during the research, scientists noted that despite known activities that resulted in the surficial application or release of organochlorine compounds, that concentrations of these compounds in iron-rich natural systems were much lower than expected. This prompted studies of the role iron played in the degradation of chlorinated compounds. These efforts revealed the contribution of iron to the biotic and abiotic RD processes. Consequently, this led to the discoveries that various species of iron could be used or generated by microbes (resulting in dechlorination) or the iron could react directly with the contaminants (propagating RD). The success of the research again translated to field scale with the first installations of PRBs packed with ZVISS.

Studies of RD of OCPs initially revealed that the molecular structure and the number of chlorine atoms significantly influenced the degradation process. Aromatics like DDT and lindane are more easily degraded by RD than cyclodienes like heptachlor, toxaphene, chlordane, and aldrin. Epoxidized cyclodienes like heptachlor epoxide and dieldrin are most resistant to the RD process. However, the successful degradation of DDT motivated further research to identify the best way to reductively dechlorinate the persistent epoxide OCPs.

Specific research into the RD of dieldrin found that RD by a consortium of anaerobic microbes was achievable but inconsistent in natural environments. The study concluded that optimal in-situ anaerobic biodegradation of the cyclodienes, including epoxides, to low toxicity or non-toxic metabolic products would only proceed under unspecified suitable environmental conditions. A test of the difference in the degradation of dieldrin in controlled (laboratory) versus outdoor (microcosm) environments identified temperature and water content as critical environmental factors. Another study revealed that dieldrin degraded faster under conditions of lower redox potential. Low redox potential in anaerobic aquifers has been cited as the ideal condition for RD of CVOCs. Low redox typically signifies anaerobic status.

Contrasting the degradation capabilities of ferric iron (Fe^{3+}) versus ferric sulfide (Fe_2S_3), researchers found that Fe^{3+} was well capable of dechlorinating dieldrin, but resulted in partial dechlorination, mainly degrading to aldrin, and subsequently to unacceptable toxic intermediates. Treatment with the Fe_2S_3 under anaerobic conditions yielded superior results, transforming the dieldrin to water-soluble intermediates via oxidative degradation. Though Fe_2S_3 initially provided a faster rate of degradation than Fe^{3+} , acidification by the sulfate ion slowed the degradation rate. Conversely, the degradation rate was accelerated by Fe^3

Aerobic conditions cause a decline in the reactivity of naturally-occurring Fe_2S_3 (pyrite) due to oxidation of the surface layer. Under low redox potential, the cycle of pyrite oxidation proceeds, but the conversion of ferrous state iron (Fe^{2+}) to ferric state (Fe^{3+}) and sulfur monoxide (SO) to sulfate (SO_4^{2-}) lapses. Under anaerobic and low redox conditions, O_2 wields the greatest influence as it affects the surface of the pyrite. The same research team reported that varying environmental conditions including organic content, soil chemical composition, competing oxidants, and co-solvents interfered with the RD process.

In 2007, Shaw Environment and Infrastructure (Shaw) completed a successful groundwater treatability study using ZVI for the Kerr-McGee Superfund site in Jacksonville, Florida. Historically, the chemical plant on that Site blended and produced OCPs including dieldrin. In 2014, based on Shaw's bench-scale results, AECOM proposed treating the groundwater with ZVI to promote in-situ RD (AECOM, 2014). As of 2015, it appears that Site's OCP impacts remained untreated. If implemented, the proposed remedial strategy may be the first application of iron-mediated RD to cleanup dieldrin-impacted groundwater. No decision approving that proposed RD remedial strategy was available at the time of this literature and regulatory record review.

Increased global recognition of the economic, environmental, and social impacts of contaminated site cleanup activities is driving the focus of industry and regulatory entities toward designing and implementing more sustainable remedial strategies. The movement is prompting the discovery and application of new technologies that no longer involve costly, high energy demand, waste-generating ex-situ processes. Advanced, in-situ technologies are designed to promote and stimulate the natural system processes of the impacted environment. This is achieved by reducing the demand for materials, energy and water resources, minimizing impacts from emissions and generated wastes, and demonstrating stewardship towards future generations by reducing the foot print (i.e., greenhouse gases) and environmental degradation contribution of the remediation process. A conceptual Remedial Strategy Sustainability Decision Tree is presented as a possible tool to rank and compare the sustainability of potential remedial technologies.

This literature review revealed that fifty years of RD research has yielded the successful implementation of field-scalable in-situ treatment technologies that resulted in the reductions of a host of dissolved-phase chlorinated compounds including CVOCs, PCBs, and OCPs. The progress of research into the RD of dieldrin under anaerobic conditions has yielded limited success in the laboratory. Both ferric iron and ferric sulfide have been identified as suitable reductants to promote in-situ degradation of dieldrin. Ferric sulfide appears to provide the best result by transforming dieldrin to less-toxic, water-soluble intermediates. The apparent key to the successful field-scale implementation of ferric sulfide is suitable environmental conditions. Ideally, these include low oxygen content manifested by low redox potential and few if any competing electron acceptors. An extended field-scale pilot study at a site with groundwater predominantly impacted by cyclodienes would be an excellent extension of the research conducted to date. A comprehensive evaluation of the aquifer conditions should be conducted as a prelude to the pilot study.

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