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Treatability of Pesticides Using Chemical Oxidants

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Background/Objectives. The presence of pesticides in soil and groundwater can pose a threat to human health and the environment. Pesticide contamination can occur as a result of accidental releases or intentional dumping at formulation and retail sites, misuse during application, or even through normal use. For example, in 1987, over 20 different pesticides were found in the groundwater of 24 states. In situ chemical oxidation (ISCO) has not been used extensively to treat these compounds because the nature of pesticide use commonly involves large, low-level aerial applications for which ISCO is not typically well-suited. However, where such compounds have been released to the environment as point sources or in areas where high concentrations are targeted for remediation, ISCO may be appropriate to consider as a remedial technology. The objectives of this presentation are to discuss the treatability of common pesticides using ISCO and to present data from laboratory evaluations of the treatability of pesticides such as lindane, chlordane, heptachlor, and chlorobenzenes using oxidants such as activated persulfate, catalyzed hydrogen peroxide (CHP), and ozone.

Approach. A review of the use of advanced oxidative processes for the treatment of pesticides will be presented. Substantial work has been conducted in the water/wastewater treatment industries (i.e., ex situ) to evaluate pesticides treatability using oxidants. This work has guided the limited work that has been done in assessing pesticides treatability in soil and groundwater using oxidants, either ex situ or in situ. Results of four treatability studies conducted at Clarkson University will be presented, where different oxidants (CHP, activated persulfate, or ozone) were applied to pesticide-contaminated field soils. The presentation will focus on the site-specific and design factors that influence the success of oxidative treatment of the pesticides lindane, chlordane, heptachlor, and chlorobenzenes. Although limited, intermediate and byproduct data for these studies will be presented as well.

Lessons Learned. Common pesticides are amenable to degradation using oxidants. The extent of degradation depends on site-specific characteristics, such as the degree of sorption onto soils, and the ability to maintain oxidative conditions (i.e., oxidant persistence). Intermediates and byproducts of pesticide oxidation have been observed and should be monitored during and after application of oxidants. While it is evident that pesticides can be degraded by oxidants, the viability of ISCO for treating pesticides sites will depend on the nature of the contamination – the mass distribution; the soil characteristics including particle size, total organic content, and groundwater geochemistry; the site's hydrogeology; and, specifically, the aerial extent and depth of contamination.

Treatability of Pesticides Using Chemical Oxidants

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Pesticides

- Pesticides occurrence
  - Industrial disposal or spill
  - Food crops; lawns and gardens
  - Termite control
  - Runoff
- Properties affecting contamination of soil and groundwater

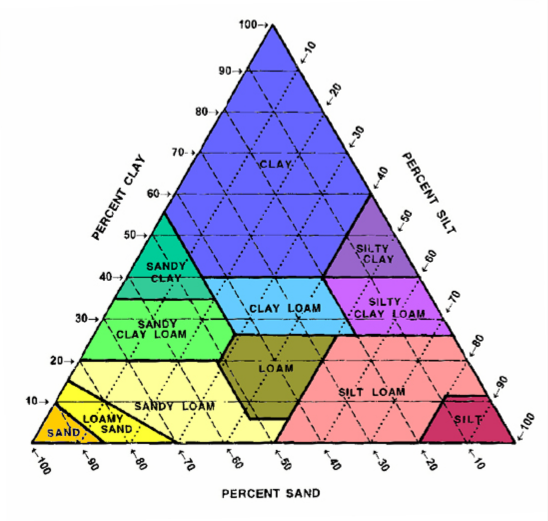
Contamination of Soil and Groundwater

- Properties affecting contamination
  - Pesticides properties

	Chlordane	**Heptachlor**	**Lindane**	**Chloro-benzene**
Solubility (mg/L)	0.056	0.056	7.0	502
Log K_{ow}	5.5	4.4 – 5.5	3.6 – 3.7	2.64
Henry's law constant (atm-m^3/mol)	4.85E-05	2.3E-03	3.5E-06	3.58E-03
EPA MCL (mg/L)	0.002	0.0004	0.0002	0.10

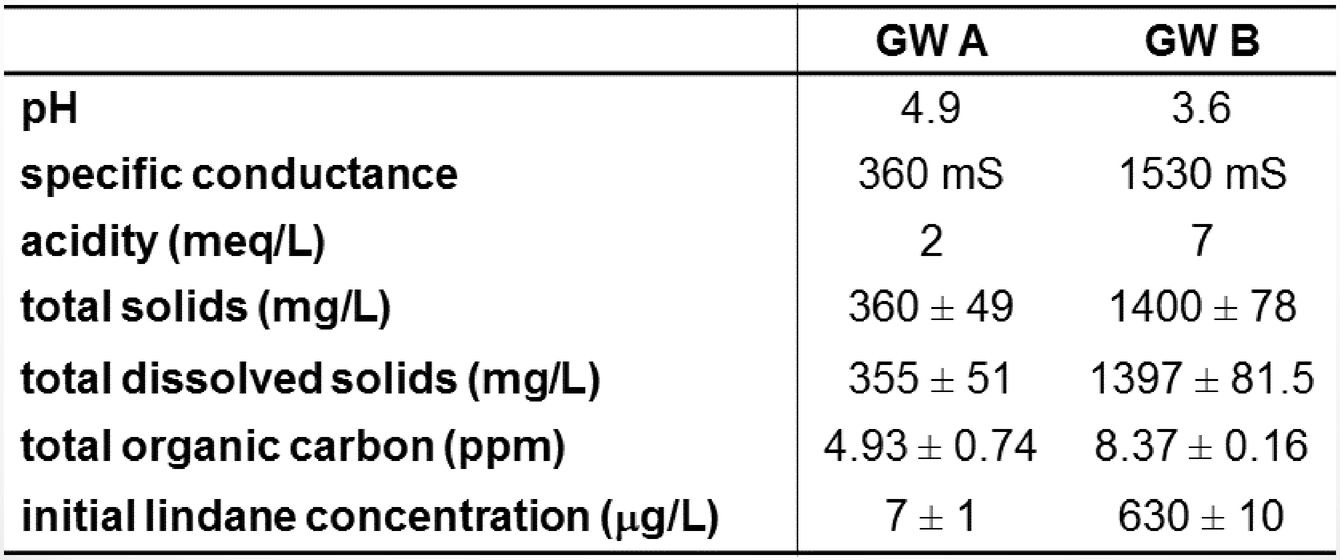
Contamination of Soil and Groundwater

- Properties affecting contamination
  - Soil properties
    - Texture
    - Permeability
    - Organic matter
  - Site characteristics
    - Depth to groundwater
    - Hydrogeology
    - Application method: rate/duration



Study 1

- Evaluate and compare persulfate activation methods for destruction of Lindane and other HCH isomers
- Focus on aqueous phase treatment

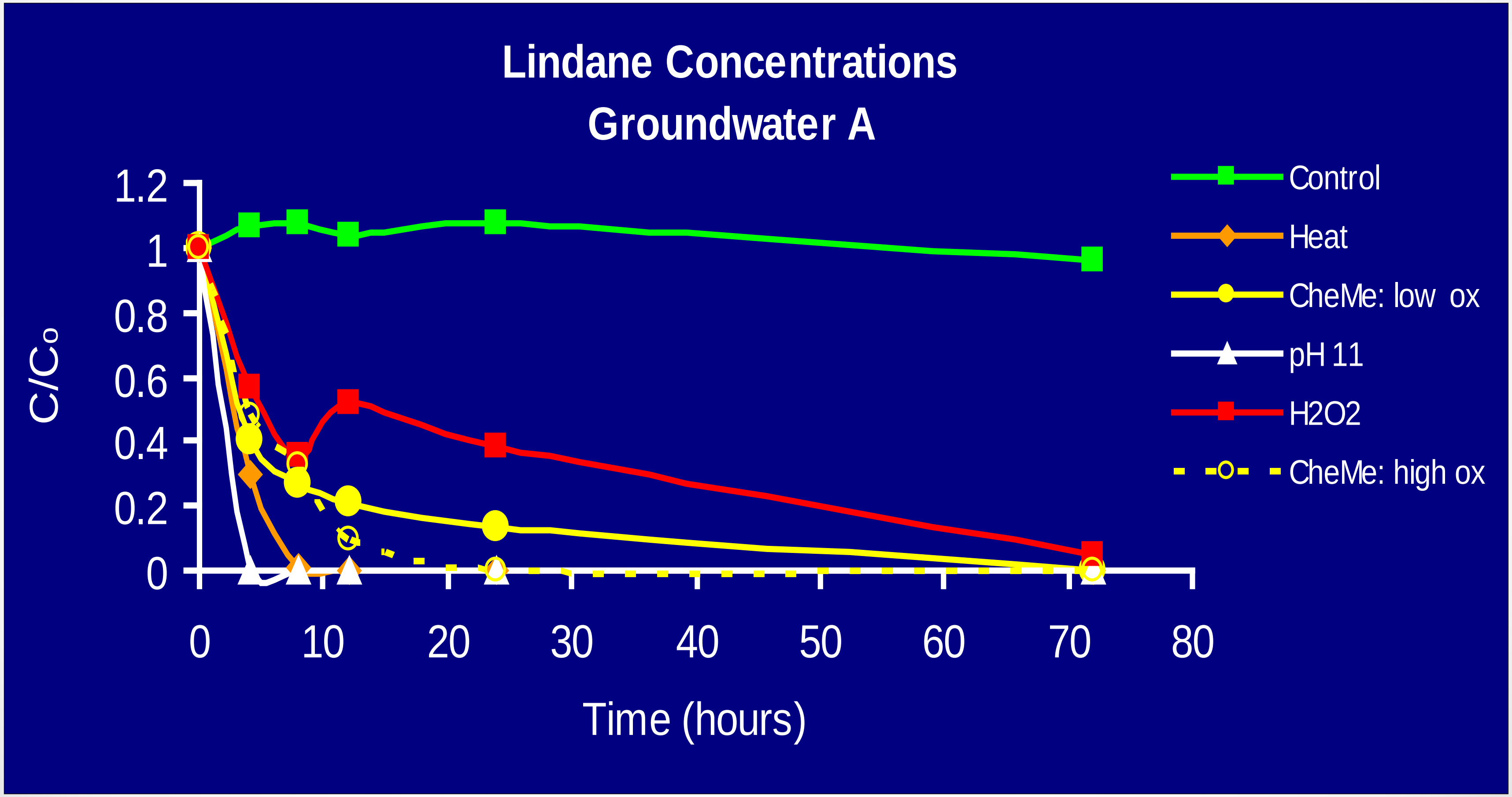


	GW A	GW B
pH	4.9	3.6
specific conductance	360 mS	1530 mS
acidity (meq/L)	2	7
total solids (mg/L)	360 ± 49	1400 ± 78
total dissolved solids (mg/L)	355 ± 51	1397 ± 81.5
total organic carbon (ppm)	4.93 ± 0.74	8.37 ± 0.16
initial lindane concentration (μg/L)	7 ± 1	630 ± 10

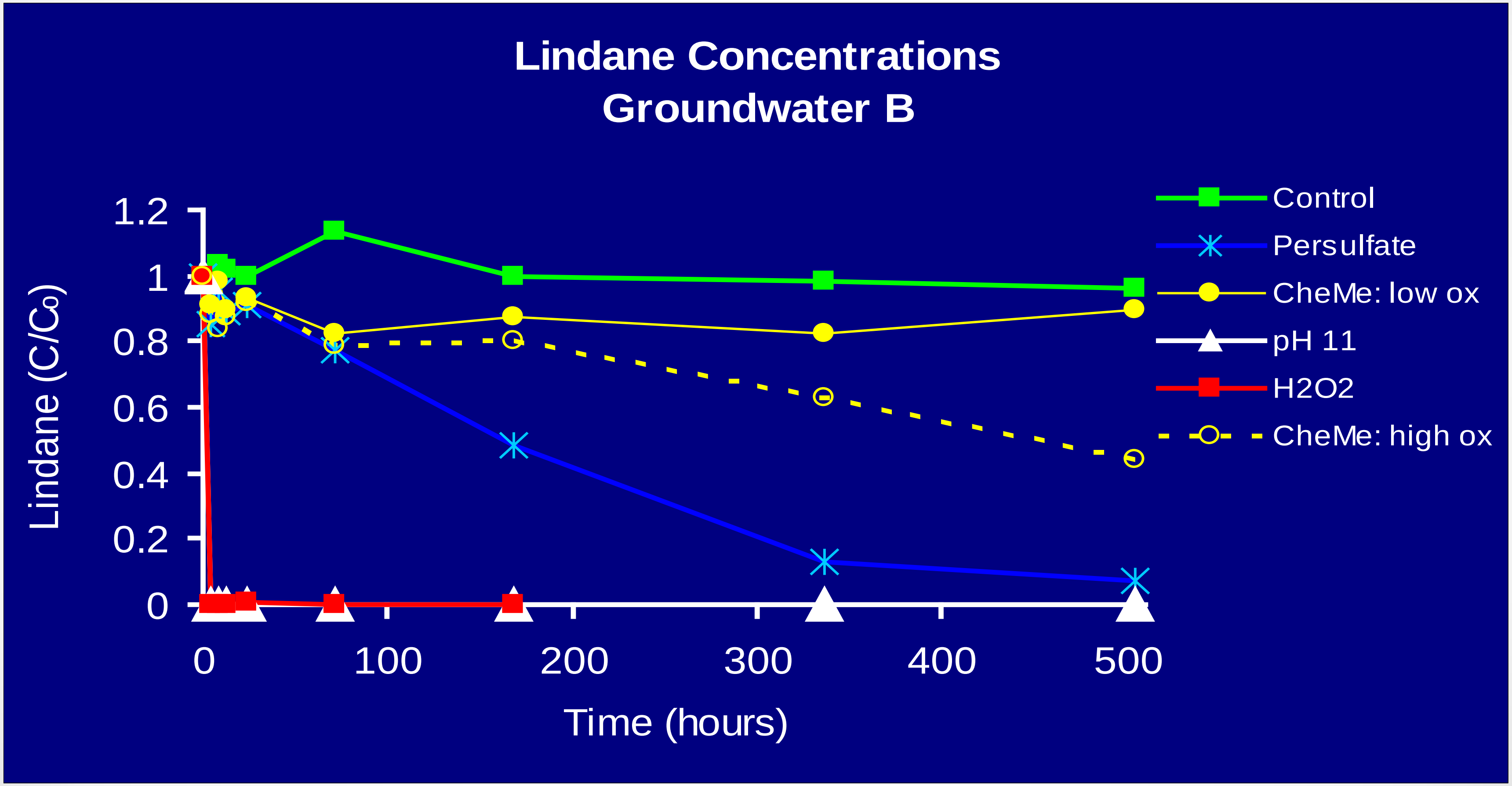
Study 1

Run ID	Persulfate Conc. (g/L)	Activation Method	Temp
1	0	0	room temp
2	15	0	room temp
3	15	heat	40C
4	15	*Fe-EDTA	room temp
5	15	*Alkaline	room temp
6	15	*peroxide (10:1)	room temp
7	30	*Fe-EDTA	room temp

Study 1

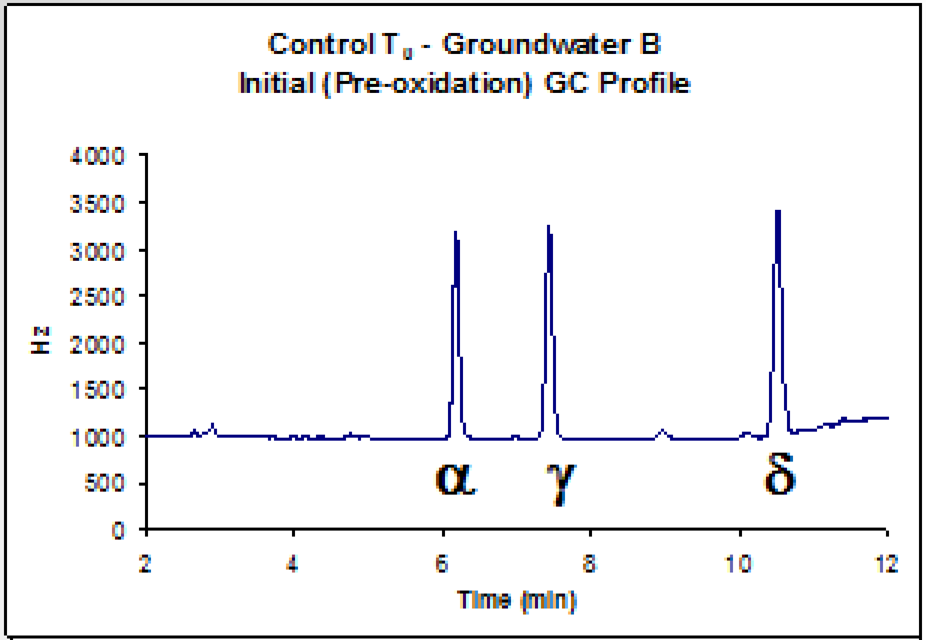

Lindane Concentrations
Groundwater A
C/Co
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
70
80
Time (hours)
Control
Heat
CheMe: low ox
pH 11
H2O2
CheMe: high ox

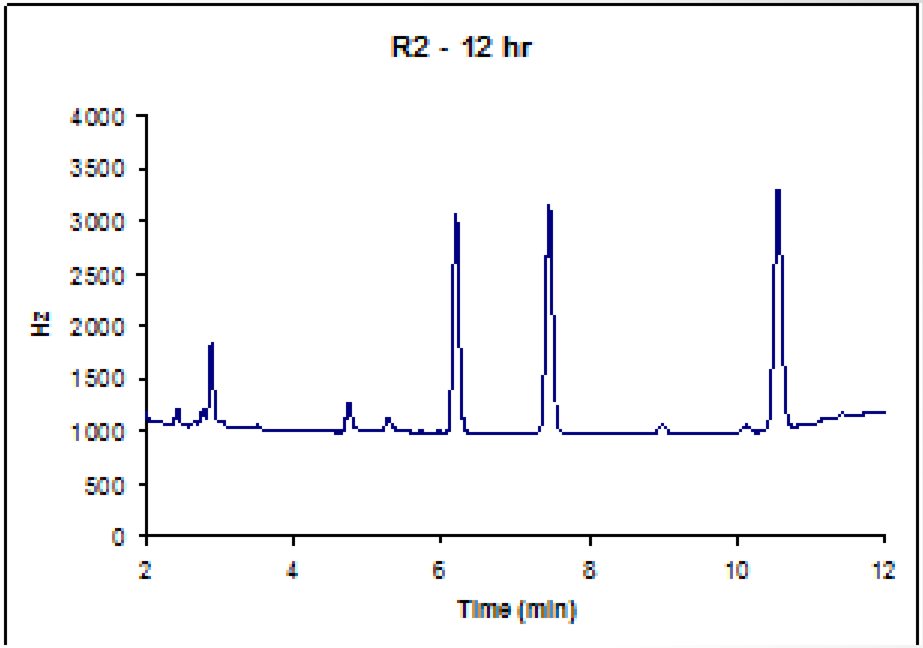
Study 1

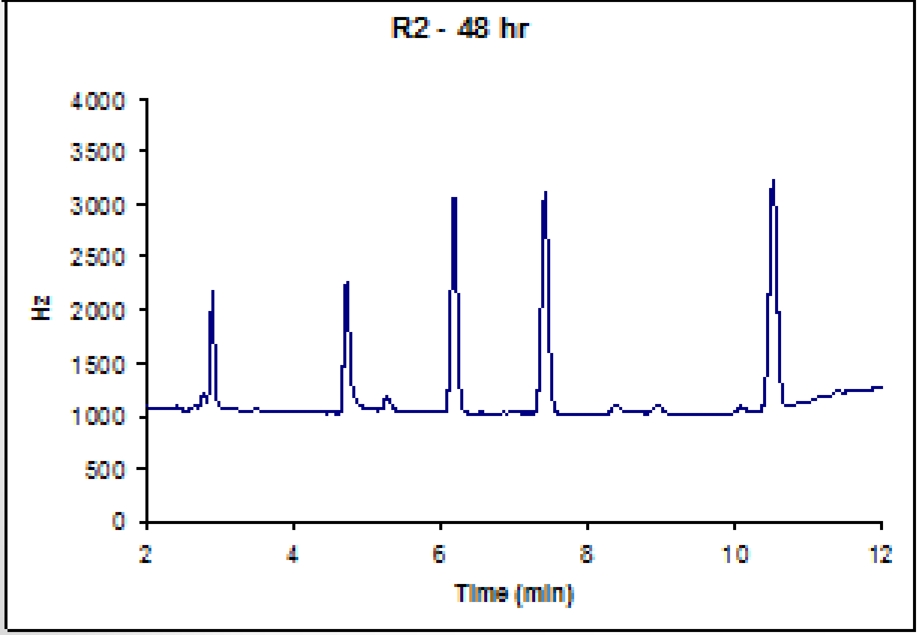

Lindane Concentrations
Groundwater B
Lindane (C/C0)
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
Time (hours)
Control
Persulfate
CheMe: low ox
pH 11
H2O2
CheMe: high ox

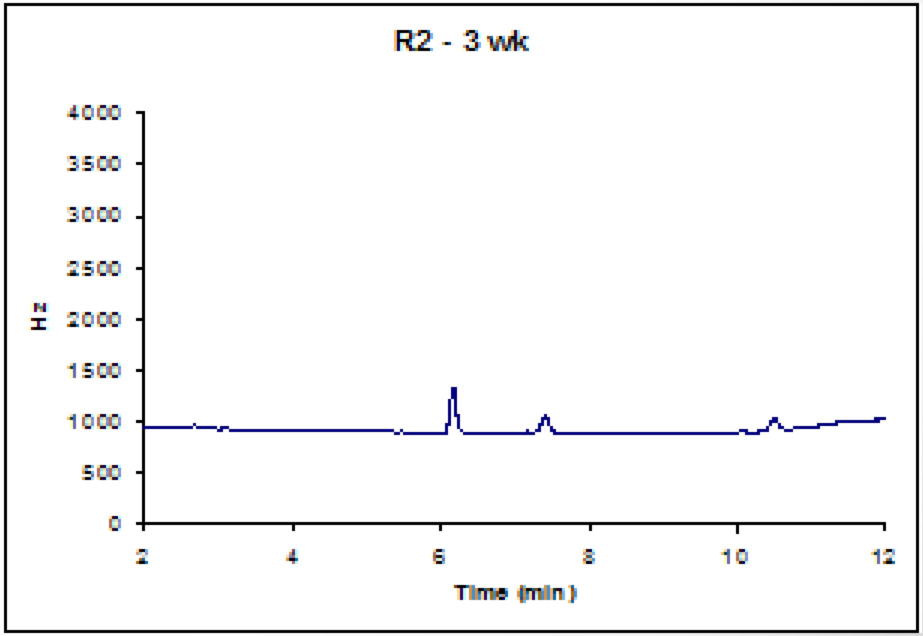
Study 1

- Lessons learned
  - Treatment
    - Dependent on groundwater geochemistry
  - Reaction intermediates
    - None observed for all conditions evaluated with Groundwater A
    - None observed in fast Lindane degradation systems with Groundwater B, but intermediates observed in slower Lindane degradation systems


Control T$_0$ - Groundwater B
Initial (Pre-oxidation) GC Profile


R2 - 12 hr

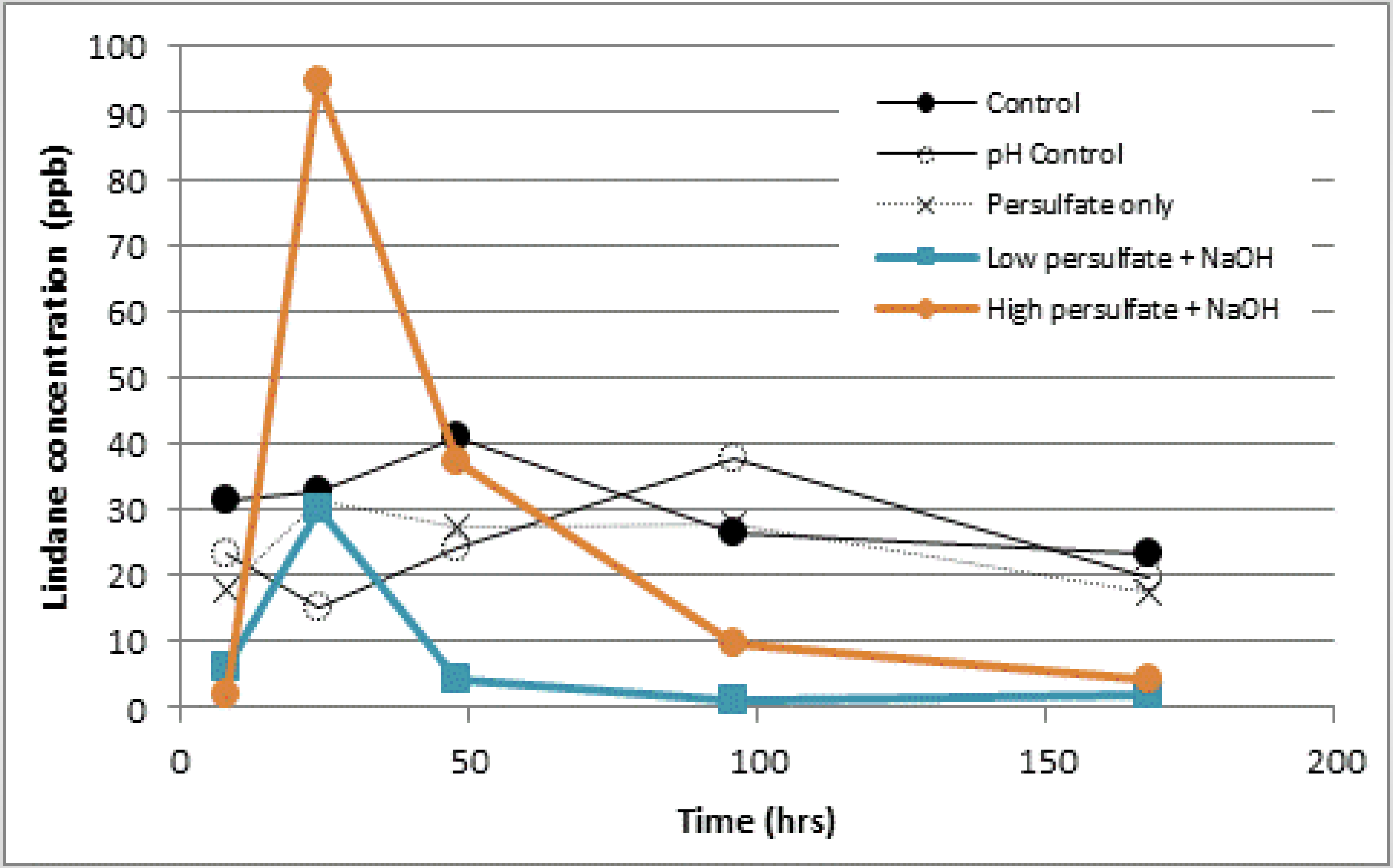

R2 - 48 hr


R2 - 3 wk

Study 2

- Evaluate alkaline activated persulfate for treatment of Lindane in soil and groundwater

Run ID	Persulf Conc (g/L)	Activation Method	Note
1	0	None	Control
2	0	Alkaline pH	pH control
3	15	None	Reagent control
4	15	Alkaline pH	
5	30	Alkaline pH	


Lindane concentration (ppb)
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
Time (hrs)
Control
pH Control
Persulfate only
Low persulfate + NaOH
High persulfate + NaOH

Study 2

- Lessons learned
  - It is possible that altering soil organic carbon can increase total contaminant mass destruction

Study 3

- Compare ozone and persulfate for chlordane and heptachlor treatment in soil and groundwater

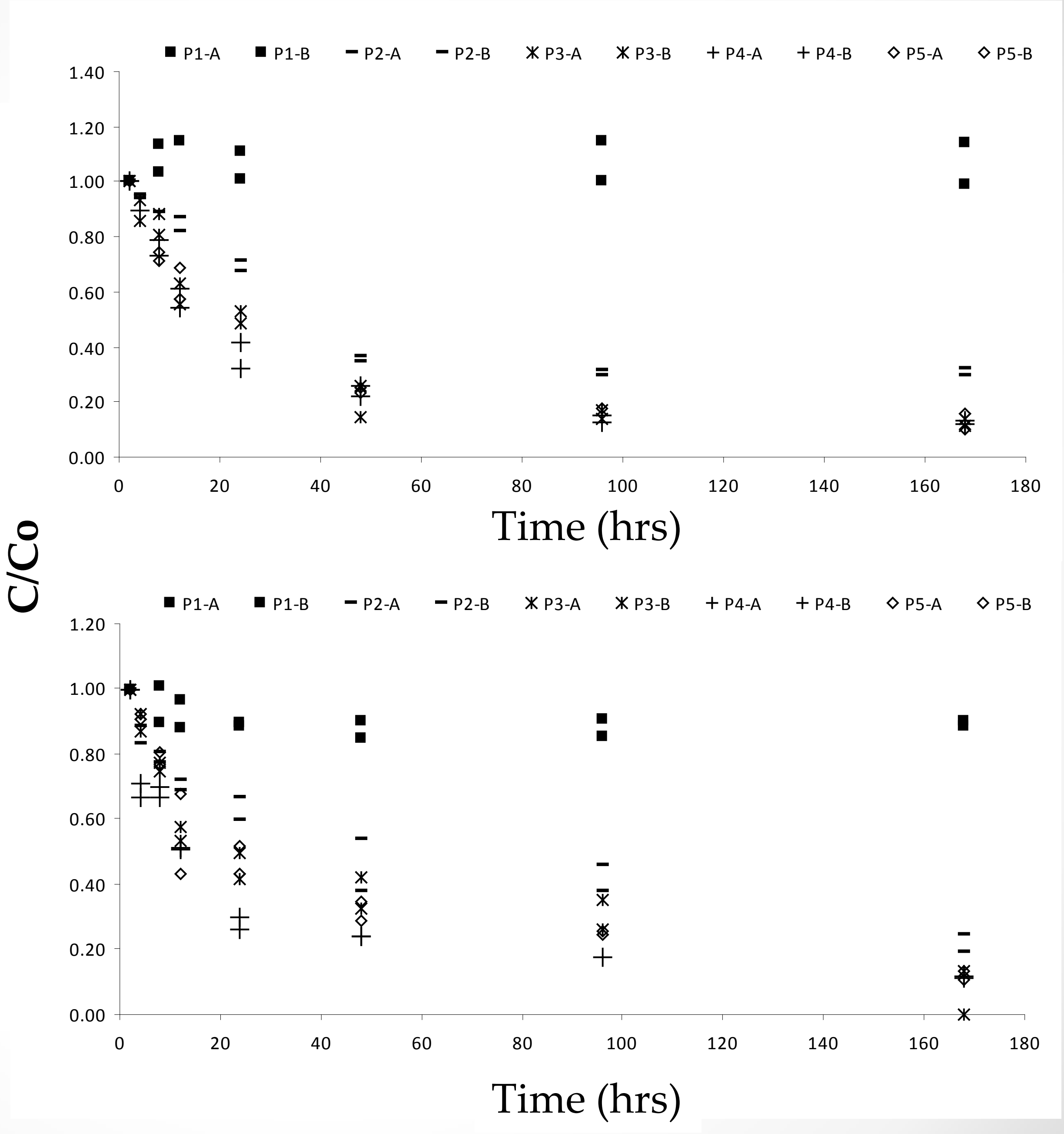
	Chlordane (alpha)		Chlordane (gamma)		Heptachlor		Heptachlor epoxide	
	Soil (µg/kg)	GW (µg/L)	Soil (µg/kg)	GW (µg/L)	Soil (µg/kg)	GW (µg/L)	Soil (µg/kg)	GW (µg/L)
GW A	1053	8.4	2573	19.1	15	BDL	159	3.7
	849	9.1	1995	20.5	12	BDL	116	3.8
	874	8.9	2025	19.9	12	BDL	115	3.8
GW B	2118	BDL	4886	1.4	360	BDL	1634	BDL
	1941	BDL	3989	1.1	149	BDL	1564	BDL
	1993	BDL	4828	1.2	167	BDL	1614	BDL

Study 3

ID	Persulf. Conc. (g/L)	Activation Approach	NOTES
P1	---	---	Control
P2	30		Persulfate only
P3	30	NaOH pH 11	FMC NaOH procedure
P4	30	Hydrogen peroxide	3% peroxide
P5	30	Iron	3300 ppm

ID	Ozone Application Rate (mg/min)	NOTES	Operation Period	Operating Time and Intervals
O1	---	Control	---	---
O2	0.6	Low dose	0-12 hrs	Applied 15 min/hr
			12-96 hrs	Applied 30 min 2x/day
O3	30	Medium	0-12 hrs	Applied 15 min/hr
			12-96 hrs	Applied 30 min 2x/day
O4	230	High	0-12 hrs	Applied 15 min/hr
			12-96 hrs	Applied 30 min 2x/day

Aqueous phase Chlordane (alpha)



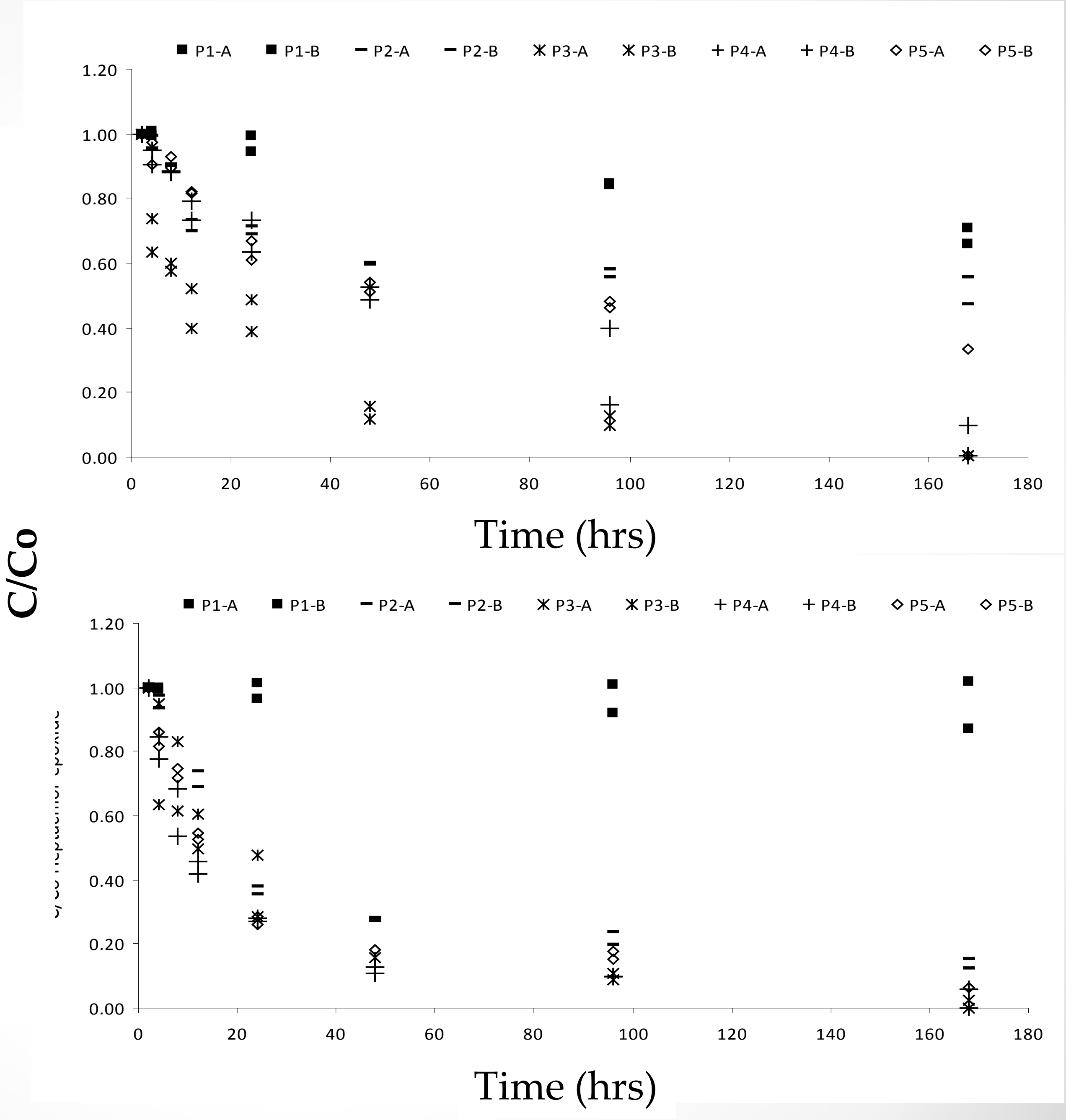
Persulfate

Aqueous phase Heptachlor epoxide

A

B

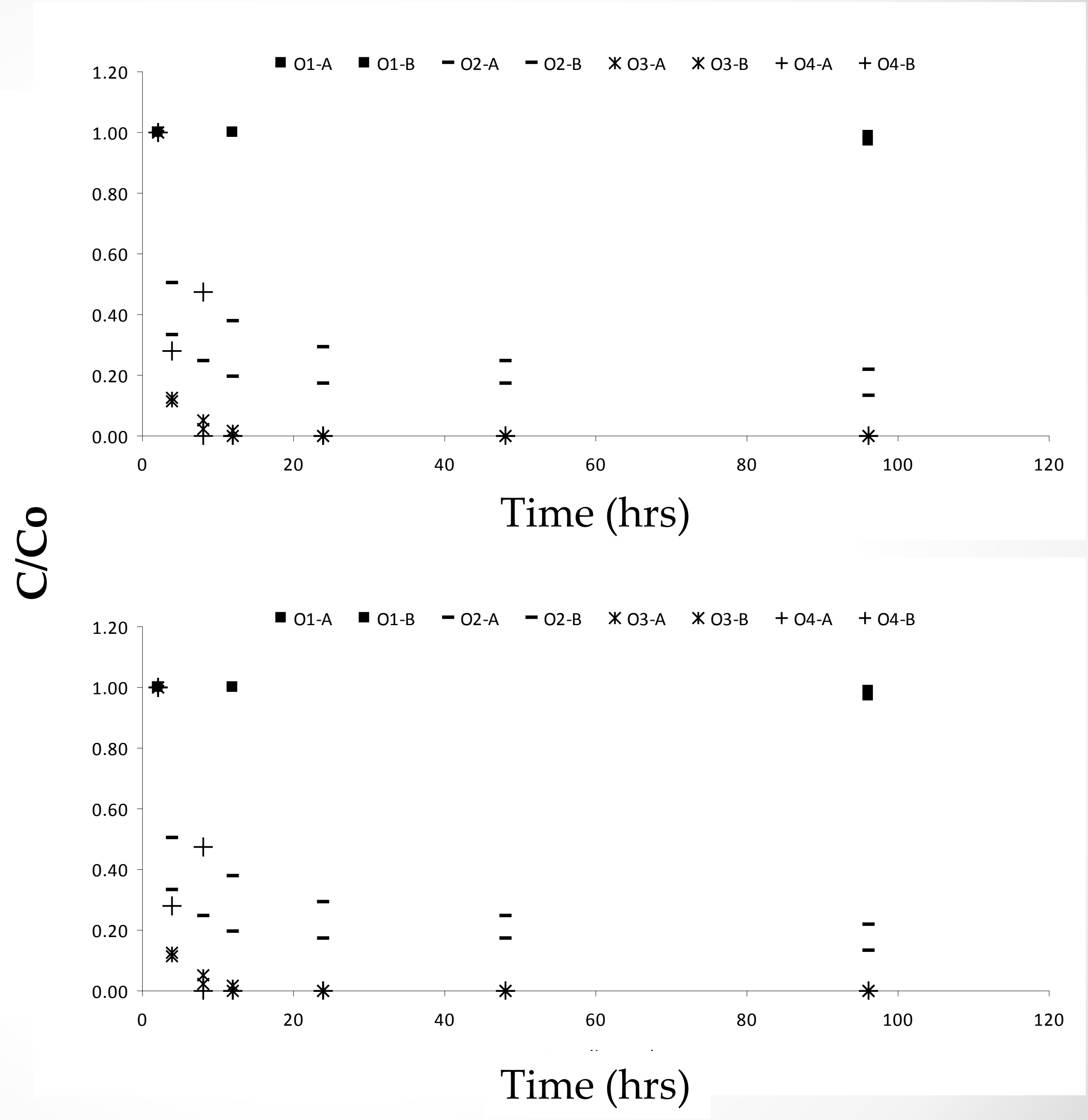
Persulfate



Aqueous phase Chlordane (alpha)

A

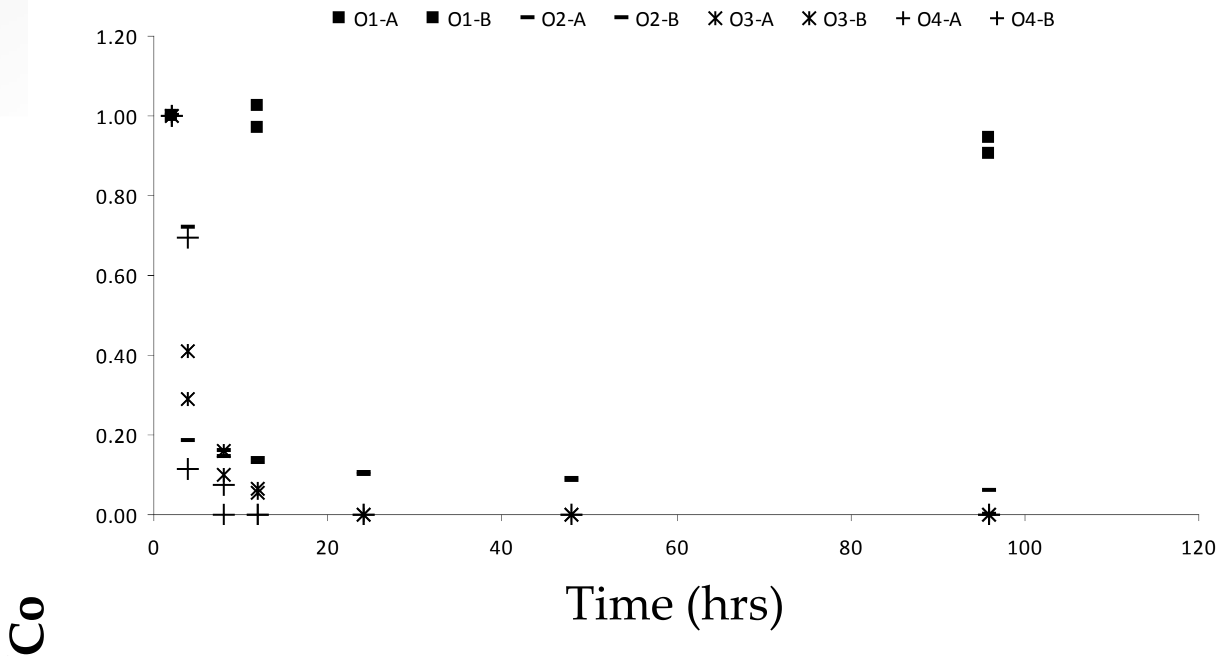
B



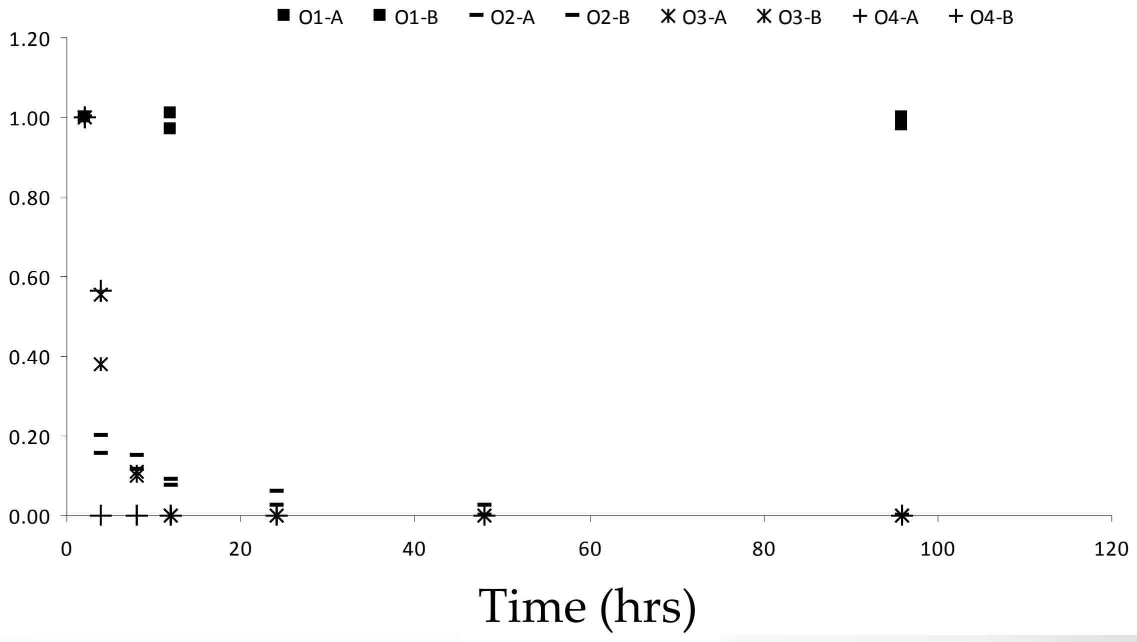
Ozone

Aqueous phase
Heptachlor epoxide

A



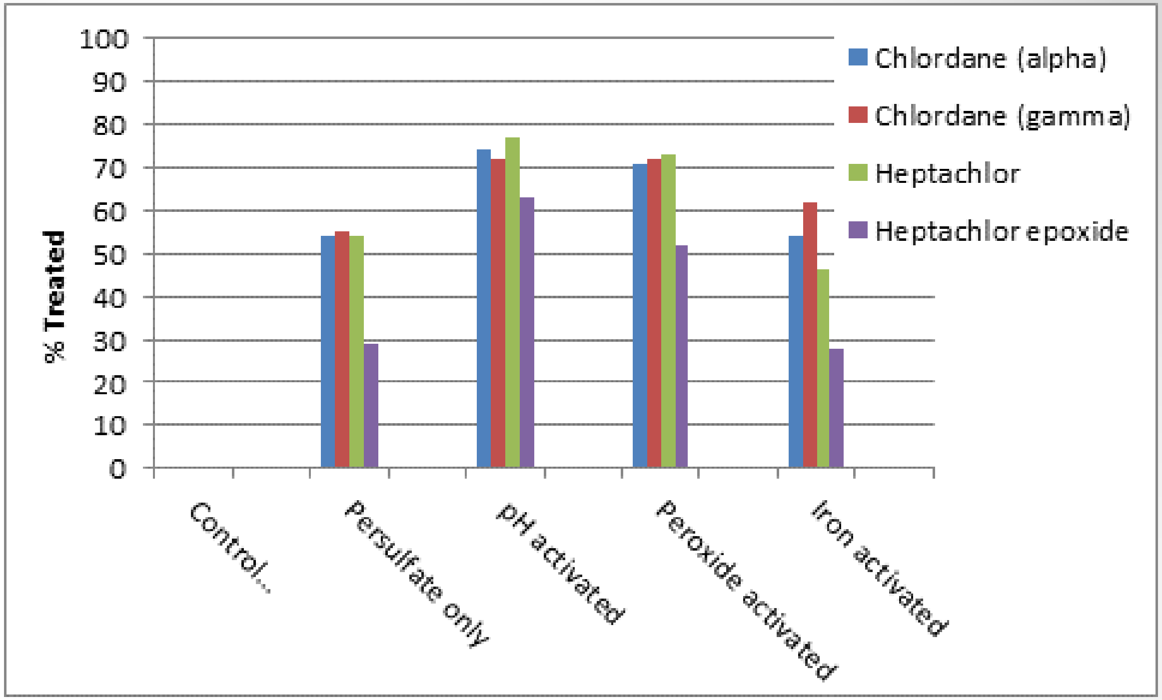
B



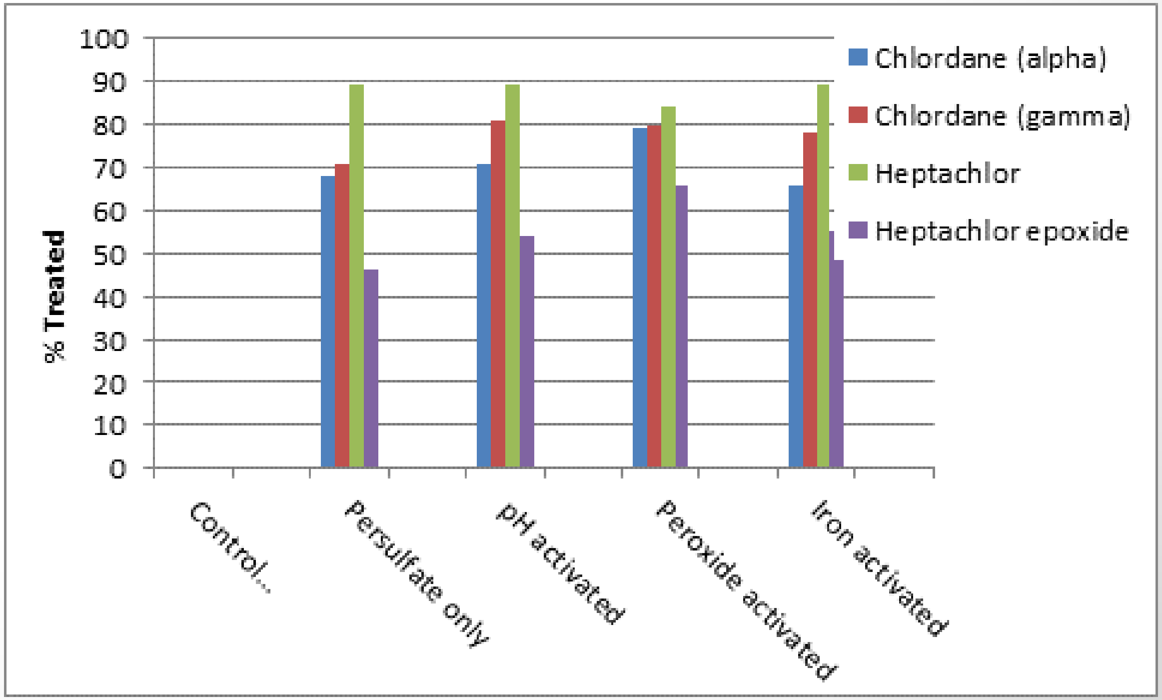
Ozone

Total Mass Destroyed

A



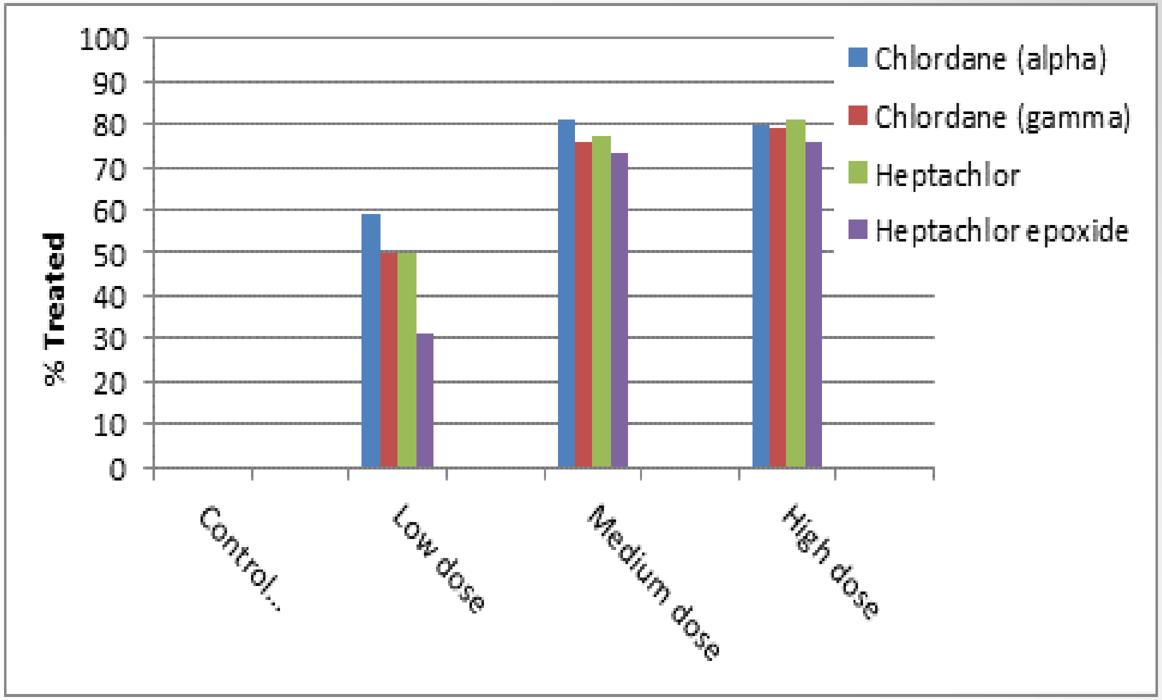
B



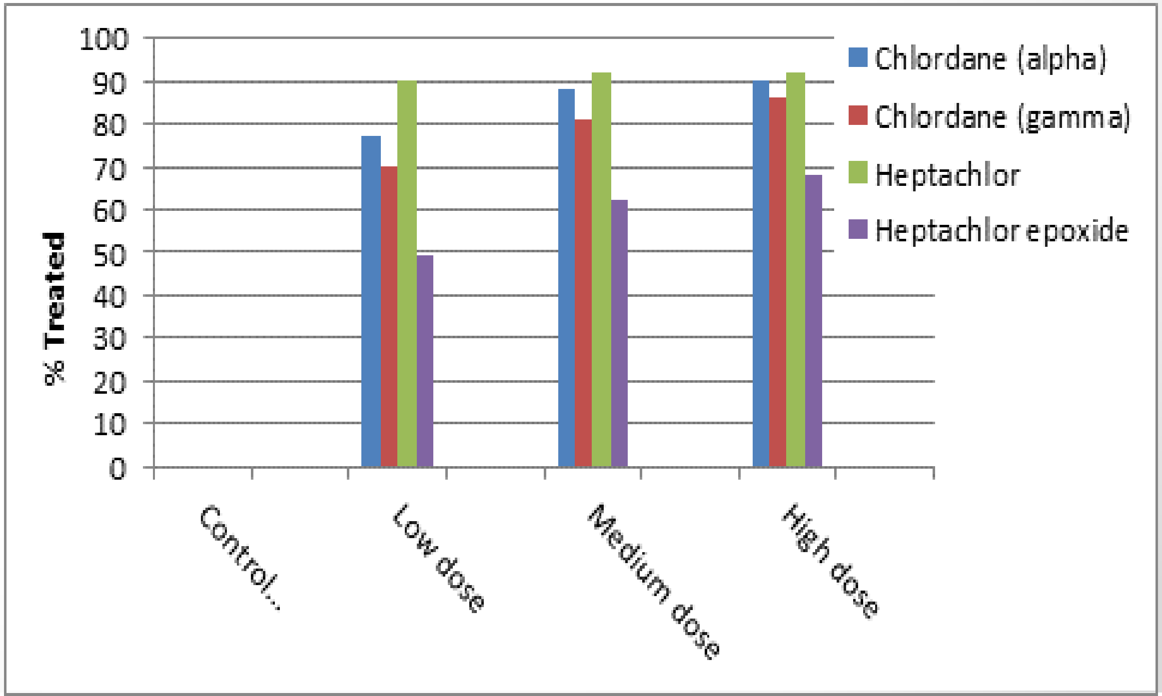
Persulfate

Total Mass Destroyed

A



B



Ozone

Study 3

- Lessons learned
  - Treatment effectiveness varies with groundwater and soil properties
  - Oxidants can treat chlordane and heptachlor in the aqueous phase
    - Significant mass associated with the solids remains untreated

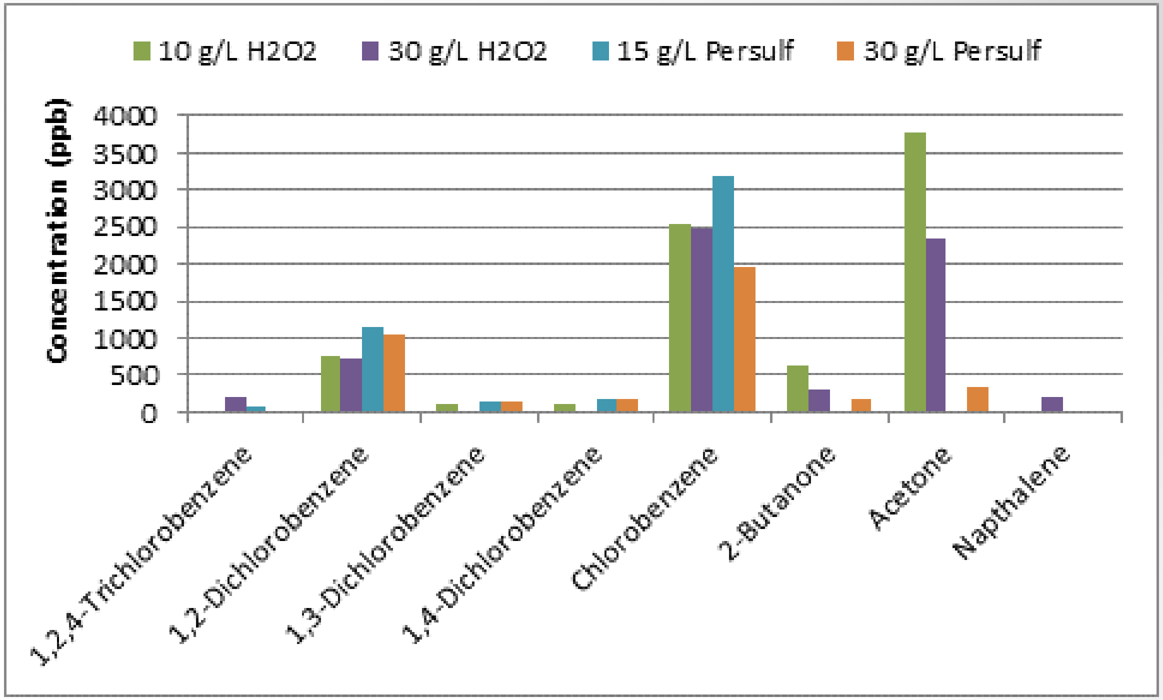
Study 4

- Compare the effectiveness of catalyzed hydrogen peroxide and iron-activated sodium persulfate for treatment of chlorobenzenes in soil and groundwater

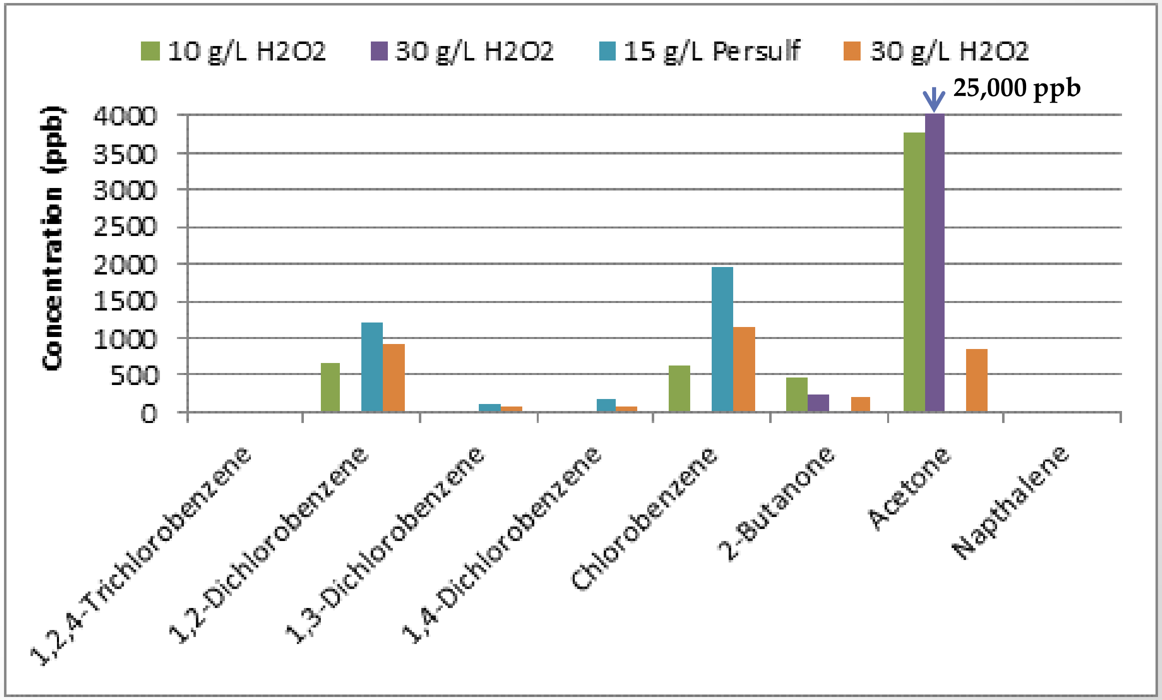
		Soil	GW
pH		7.8	6.6
ORP		-49.2 mV	22 mV
COD		34.45 g/kg	373 mg/L
Contaminants	1,2,4-trichlorobenzene	4560 mg/kg	1850 µg/L
	1,2-dichlorobenzene	nondetect	15400 µg/L
	1,3-dichlorobenzene	nondetect	2720 µg/L
	1-4-dichlorobenzene	nondetect	3210 µg/L
	chlorobenzene	nondetect	58100 µg/L

ID	Oxidant	Oxidant Conc. (g/L)	Note
A	None	0	Control
B	CHP	10	Iron to oxidant ratio = 1:10
C	CHP	30	
D	Persulfate	15	
E	Persulfate	30	

2 Applications



4 Applications



Study 4

- Lessons Learned
  - Reaction intermediates/byproducts can accumulate
  - Multiple injections can improve mass destruction

Oxidation of Pesticides

- Chemical oxidants
  - Focus on water/wastewater treatment
    - Oxidants
      - Heterogeneous TiO_2 photocatalysis
      - Ozonation
      - Photo-Fenton's
    - Approach: complete destruction or transformation to more biodegradable products

Chiron S, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo (2000). Pesticide Chemical Oxidation: State-of-the-Art. *Wat. Res.* 34(2):366-377.

Oxidation of Pesticides

- Chemical oxidants
  - Focus on water/wastewater treatment
    - Lessons learned
      - Oxidation efficiency dependent on pesticides concentrations and concentrations of other constituents in solution
      - Byproduct generation with oxidative treatment is common
      - It is appropriate to couple oxidative and biodegradation techniques to treat pesticides

Chiron S, A. Fernandez-Alba, An Rodriguez, E. Garcia-Calvo (2000). Pesticide Chemical Oxidation: State-of-the-Art. *Wat. Res.* 34(2):366-377.

Oxidation of Pesticides

- Chemical oxidants

Oxidant	Pesticides	Notes	Reference(s)
Catalyzed hydrogen peroxide	2,4-D and 2,4,5-T	Chlorophenol intermediates released; Not all contaminant was mineralized to CO_2	Pignatello, 1992; Pignatello and Baehr,1994; Tarr et al., 2002; Chu et al., 2004
Persulfate	Lindane; Atrazine	Extent of destruction depended on activation method and site-specific characteristics	Crimi, 2005; Anipsitakis and Dionysiou, 2003
Ozone	Atrazine; Trifluralin and Aniline	Intermediates accumulated with Atrazine degradation; Extensive complete mineralization achieved for Trifluralin and Aniline degradation, with some intermediates	Adams and Randtke,1992; Pierpoint et al., 2003

Oxidation of Pesticides

- Lessons learned
  - Treatment effectiveness varies with groundwater and soil properties, as well as oxidation chemistry
  - Reaction intermediates/byproducts can accumulate

Oxidation of Pesticides

- Lessons learned
  - Significant mass associated with the solids remains untreated

Pignatello JJ and M Day. 1996. Mineralization of Methyl Parathion Insecticide in Soil by Hydrogen Peroxide Activated with Iron(III)-NTA or –HEIDA Complexes. *Haz. Waste & Haz. Mat*. 13(2):1996.

Watts RJ, AP Jones, P-H Chen, A. Kenny. 1997. Mineral-catalyzed Fenton-like oxidation of sorbed chlorobenzenes. *Water Env. Res.*, 69(3):269-275.

Quan HN, A.L. Teel, R.J. Watts. 2003. Effect of contaminant hydrophobicity on hydrogen peroxide dosage requirements in the Fenton-like treatment of soils. *J. Haz. Mat.*, B102:277-289.

Limitations of Oxidation for Treatment of Pesticides

- Generation of intermediates and/or byproducts
  - Approaches to overcome
    - Multiple applications
    - Couple with post-oxidation bioprocesses

Limitations of Oxidation for Treatment of Pesticides

- Sorption of hydrophobic pesticides onto soils limits extent of oxidation
  - Approaches to overcome
    - Thermal
    - Surfactants/cosolvents
    - Alter/destroy organic matter

Conclusions

- Oxidation is a viable approach for treating pesticides contamination in soil and groundwater
  - Effectiveness, rate, and extent dependent on soil and groundwater properties
- Limitations
  - Sorption
  - Intermediates/byproducts

Acknowledgments

- ARCADIS
- R&M Technologies
- FMC
- Research assistants

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