Vertex Environmental Inc.

Beneficial Reuse of Soils: Treating Pesticide Impacted Soils In-Situ

October 11, 2017

Bruce Tunnicliffe

Outline

- Background
  - Pesticides
  - Redevelopment of Agricultural Land
- Pesticide Remediation: The Process
- Case Studies
- Questions

Vertex Environmental Inc.

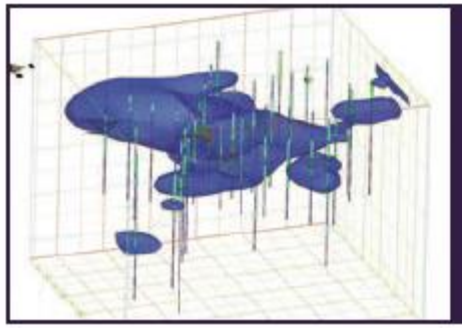
Contracting Company

In-Situ Remediation

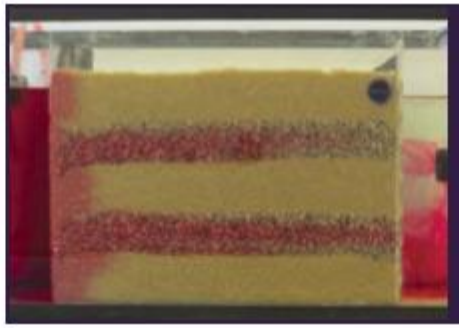
Ex-Situ Remediation

High Resolution Characterization

Treatment Systems



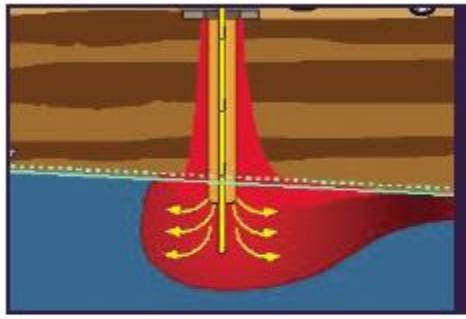
Remedial Design



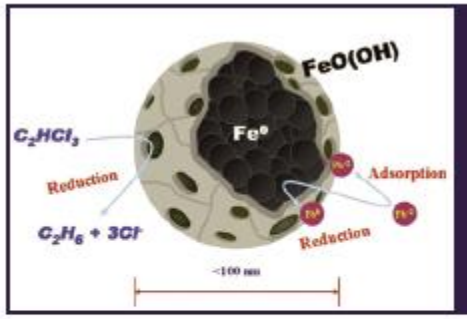
Bench-Scale Testing

Vertex Environmental Inc.

Contracting: In-Situ Remediation

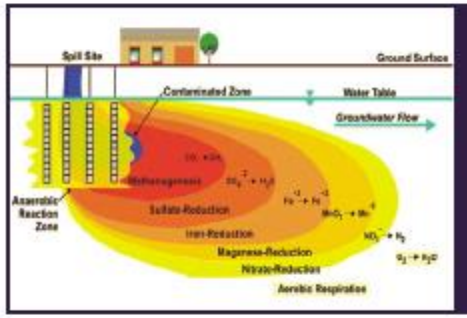


Oxidation



Reduction

Adsorption



Enhanced Bioremediation

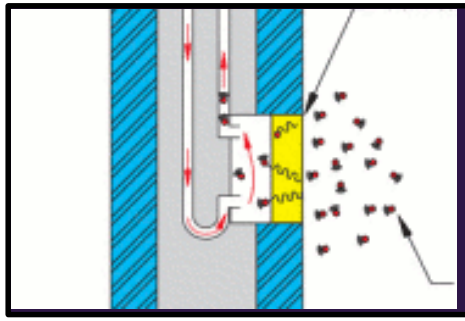
Permeable Reactive Barrier

In-Ground Soil Mixing

Vertex Environmental Inc.

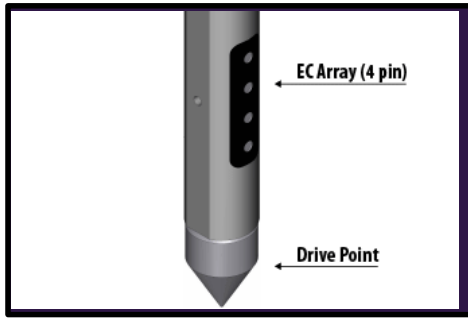
High Resolution Site Characterization

LIF

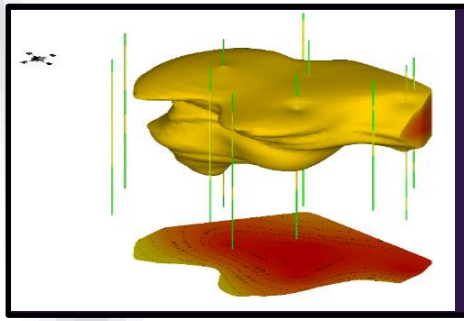


MIP

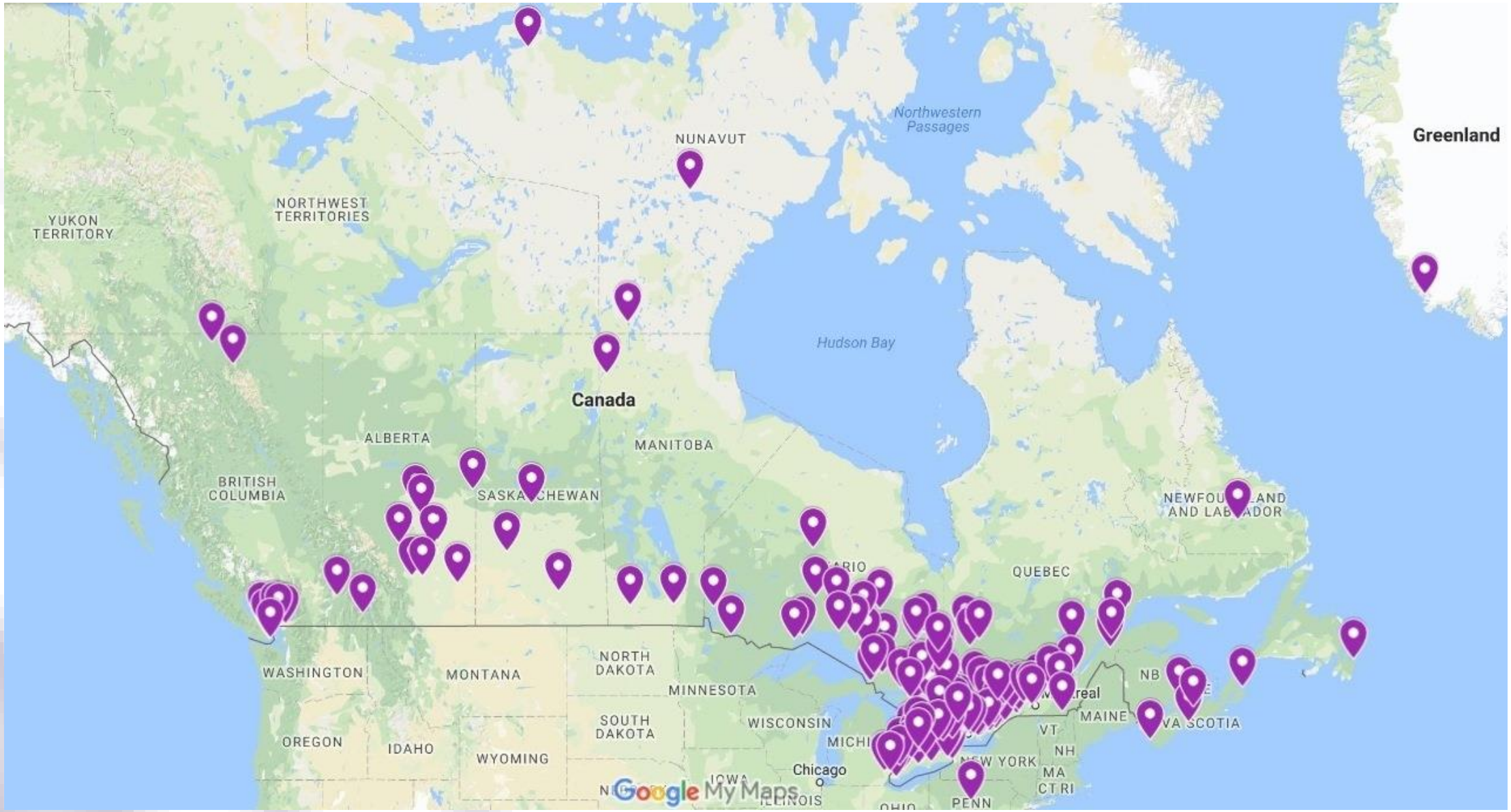
LL-MIP



HPT



Modelling


Northwestern Passages
NUNAVUT
Greenland
NORTHWEST TERRITORIES
YUKON TERRITORY
Hudson Bay
Canada
ALBERTA
MANITOBA
BRITISH COLUMBIA
SASKATCHEWAN
NEWFOUNDLAND AND LABRADOR
QUEBEC
WASHINGTON
MONTANA
NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
OREGON
IDAHO
WYOMING
Chicago
NEW YORK
MAINE
VT
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PENN
NB
NOVA SCOTIA
Google My Maps

Farms & Pesticid

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Development: Calgary Airport

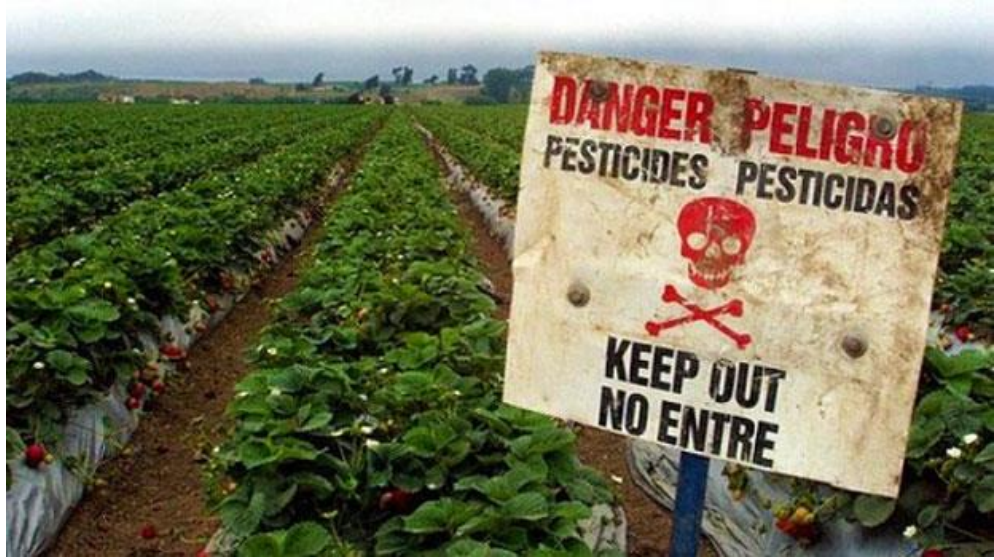
1950

2017

VERTEX

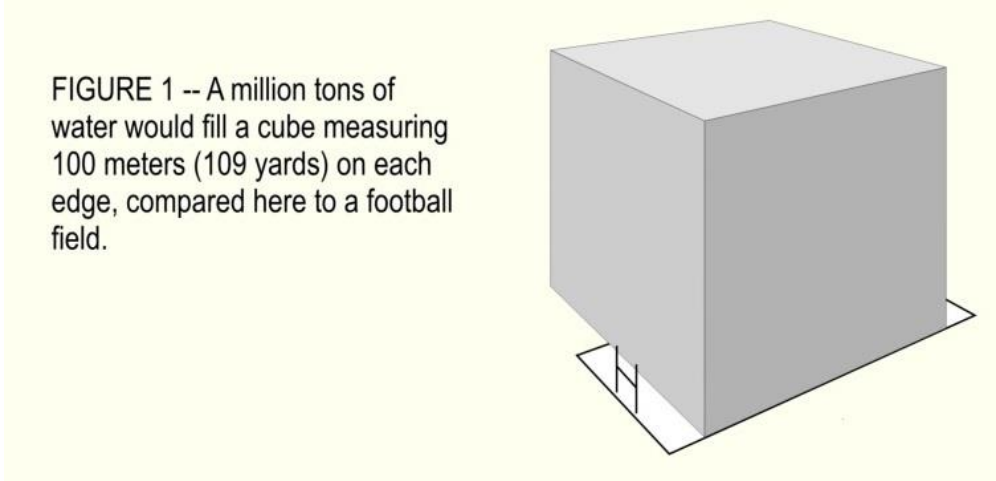
Pesticides

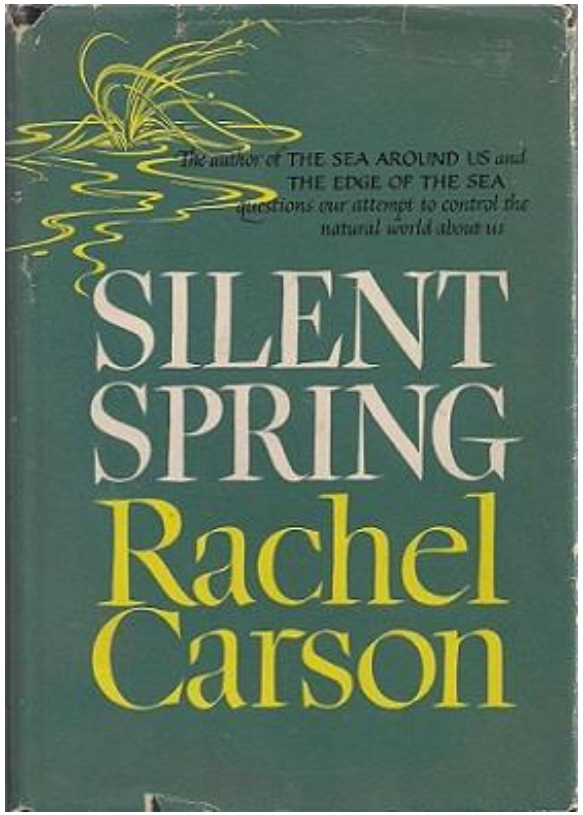
- Agriculture began about 10,000 years ago
  - in the Fertile Crescent of Mesopotamia
  - part of present day Iraq, Turkey, Syria and Jordan
- Coincidentally….
  - farmer's dislike of "pests" began 10,000 yrs ago
- Pesticide use (recorded) dates back over 4,000 yrs
- Pesticides can be natural or synthetic
- Natural
  - Salt Spray
  - Citrus Oil
  - Cayenne Pepper
  - Rosemary, lavender
  - Egg Shells
  - Neem
    - vegetable oil pressed from the fruits and seeds of the neem
    - an evergreen tree
    - banned in the UK
    - neem leaves and neem tea, should not be consumed by pregnant women, women trying to conceive, or children
- Synthetic
  - chemically created
  - DDT, atrazine, etc.



Pesticides

- In 2006 and 2007:
  - the world used approximately 2,400,000 tonnes of pesticides
- > 1,055 active ingredients registered as pesticides
- Over 20,000 pesticide products are marketed in the USA
- Use in countries:
  - 1.0 kg per hectare of arable land in the USA
  - 4.7 kg/ha China
  - 1.3 kg/ha UK
  - 5.9 kg/ha Japan
  - 2.5 kg/ha Italy
- Global market of crop protection products >52 billion US$ in 2019



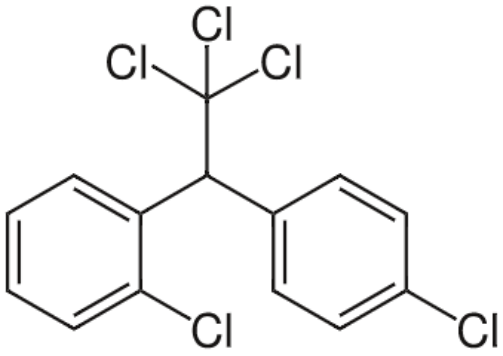


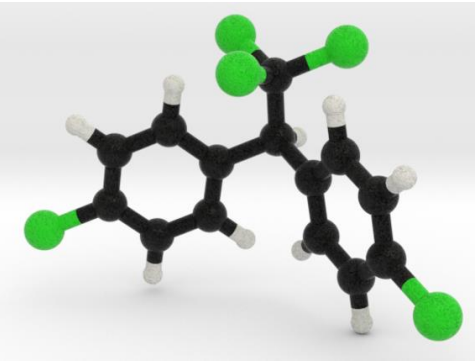
1962

Concern: DDT

Pesticides

Famous Pesticide: DDT



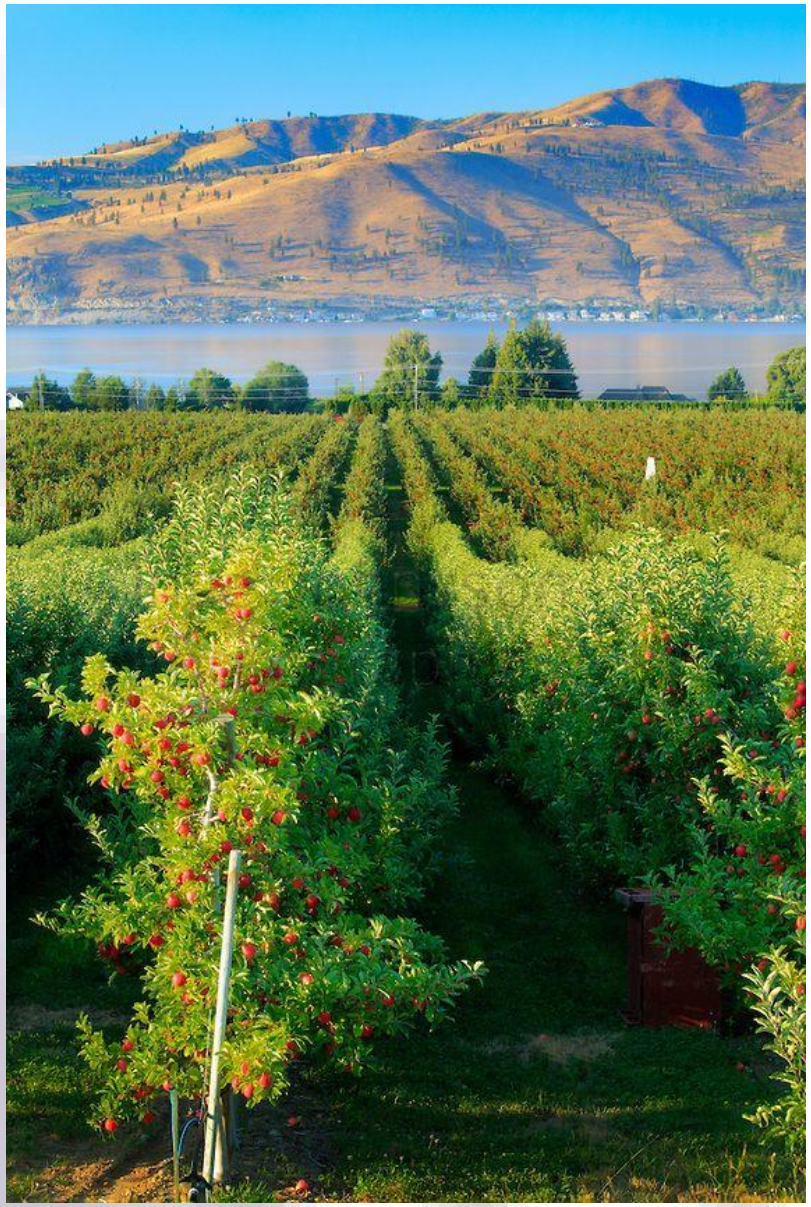


Dichlorodiphenyltrichloroethane (DDT)

History of DDT

- 1874: First synthesized in 1874
- 1939: DDT's insecticidal benefits discovered
- 1943: used in the second half of World War II
  - to control malaria and diseases among civilians and troops
- 1948: was awarded the Nobel Prize:
  - Müller awarded Nobel Prize in Physiology or Medicine
  - "for his discovery of the high efficiency of DDT as a contact poison against several arthropods“
- 1962: Silent Spring book
- 1972: DDT banned
  - Stockholm Convention on Persistent Organic Pollutants

Pesticides and Redevelopment of Agricultural Land



- **Why Is This Important?**
- Cities are expanding
- People do not want to live on contaminated land
- Pesticides are “contamination”
- Excess Soil Regulations
  - Making movement of soil difficult

Pesticides and Redevelopment of Agricultural Land

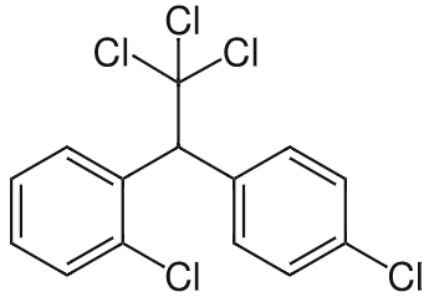
- **Possible Volume of Pesticide-Soil?**
- Pesticides can migrate into soil 0.6 m to 0.9 m
- 1 hectare = 10,000 m2
- 6,000 m3/ha

- **Cost of Traditional Remediation?**
- 10,800 MT
- about 500 truck loads of soil
- Say it's $50/MT disposal & trucking
- $500,000 per hectare cost
  - No backfill

How To Clean Up?

Remediating Pesticides

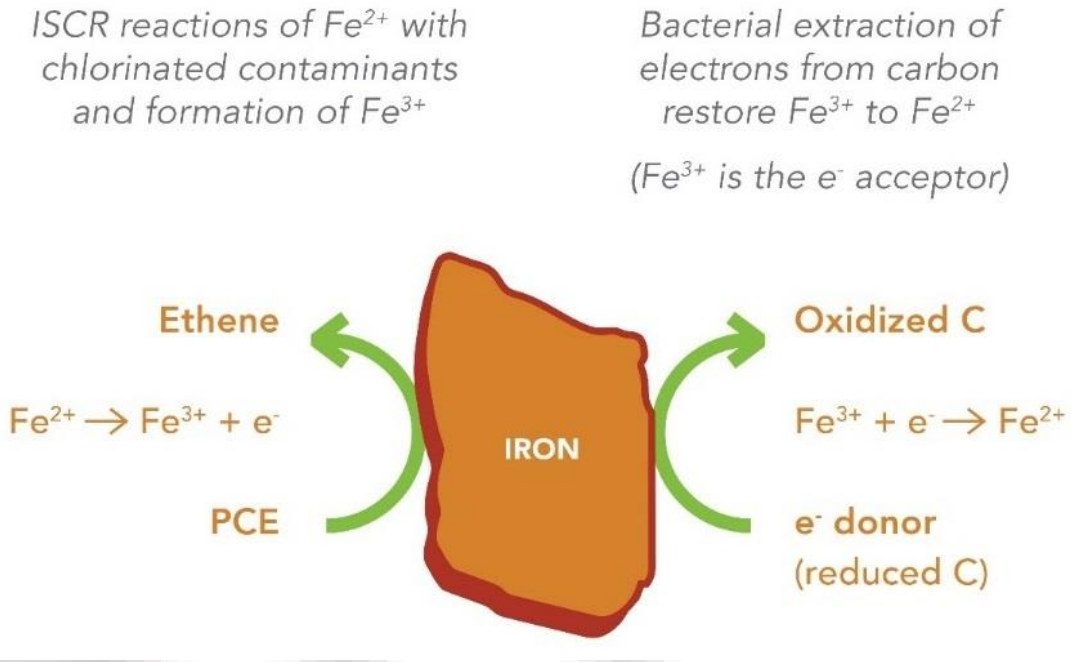
- Pesticides are recalcitrant (resist bio)
- Need to break the molecule
  - electron transfer / biodegradation
- How?

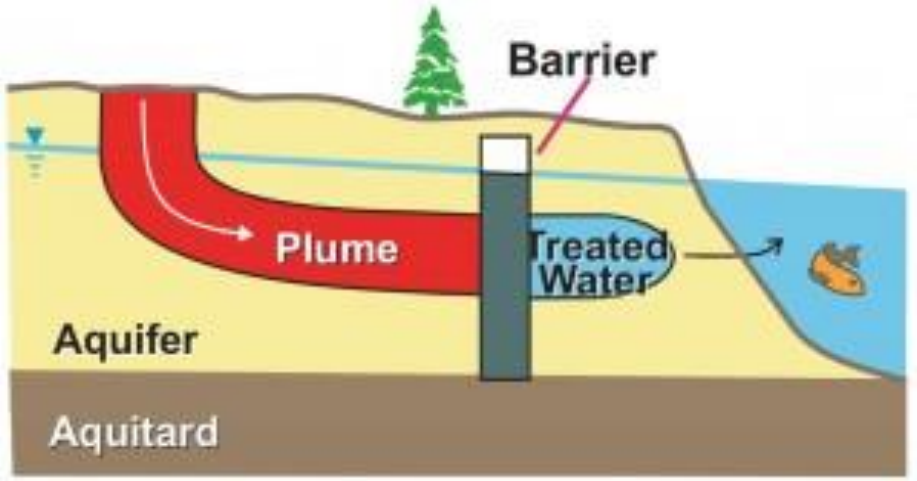


Dichlorodiphenyltrichloroethane (DDT)

Remediating Pesticides

- In-situ Chemical Reduction (ISCR)
- Transfer of electrons from reduced metals (i.e. ZVI) to contaminants
  - Permeable Reactive Barriers (PRBs) constructed using ZVI = example of simple ISCR
- Advanced ISCR: combining ZVI & carbon reagents



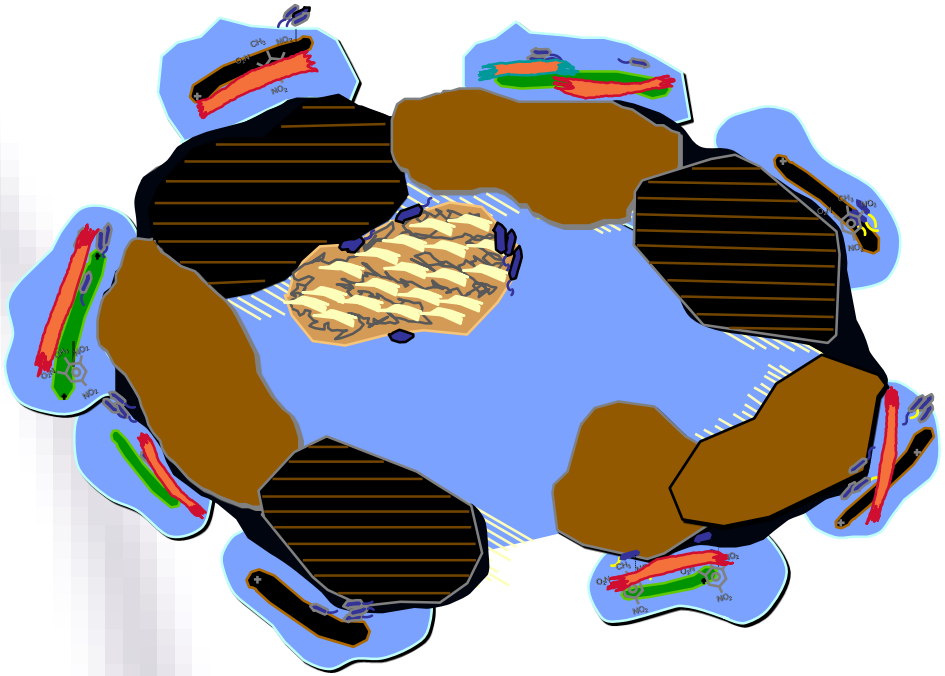


Permeable Reactive Barrier (PRB)

Source - PeroxyChem

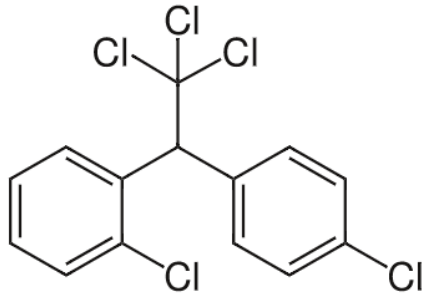
Remediating Pesticides

- ISCR using ZVI
  - excellent for treatment of cVOCs, including PCE, TCE
- ZVI is ineffective on some pesticides, such as DDT
  - However, degradation of DDT is possible
  - Strongly anaerobic environment & reductive degradation reactions
- DARAMEND® uses ZVI and enhanced bioremediation
  - Daramend® composed of micro-scale zero valent iron (ca. 40% w/w) + solid organic carbon (ca. 60% w/w)

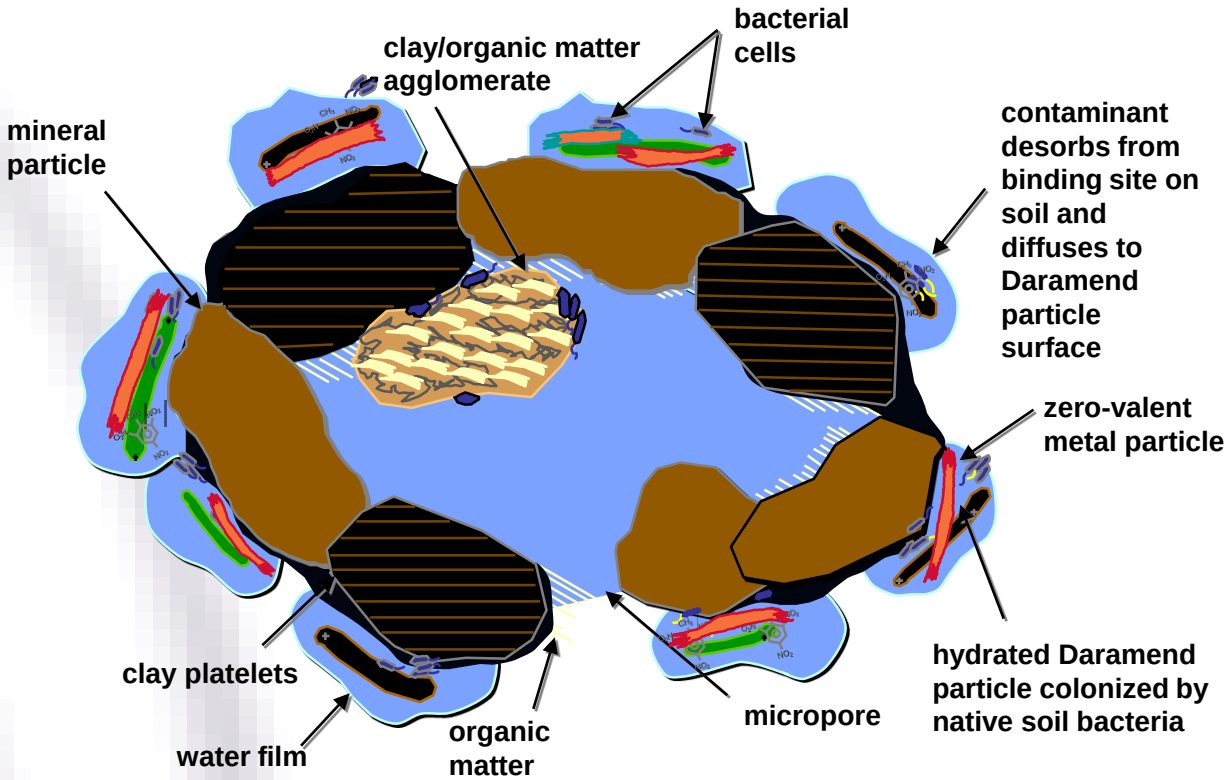


Source - PeroxyChem

Remediating Pesticides



- ZVI: promotes dehalogenation (removal of Cl^- ions)
- Organic carbon + nutrients: >microbial growth & oxygen consumption
- Together: create a highly reduced state (i.e. strongly negative E_h)
- The thermodynamics become favorable for the reductive dechlorination of pesticides
  - Contaminants that are persistent and resistant can now be degraded



Source - PeroxyChem

The Process

Remediating Pesticides

Remediating Pesticides

Remediating Pesticides

Case Studies

Project Cambridge

CIBA Geigy, Cambridge ON, Canada
1996

Source - PeroxyChem

Project Cambridge

Table 2 - Metolachlor Concentrations (mg/kg) [3]

Area	Initial	Day 2	Day 7	Day 28	Day 208	Day 306	Day 454	Day 565
Main Treatment cell[1]	67	72	65	53	27	14	3.1	ND
HM cell[2]	170	140	140	110	78	57	42	38
Static Control cell	37	NS	49	87	63	57	66	56

- Static Control Cell – no significant change
- Metolachlor® was reduced by >99% in the main treatment area from 67 mg/kg to <0.5 mg/kg
- Removal efficiency was lower in the high Metolachlor ® area (only 78% from 170 mg/kg to 38 mg/kg

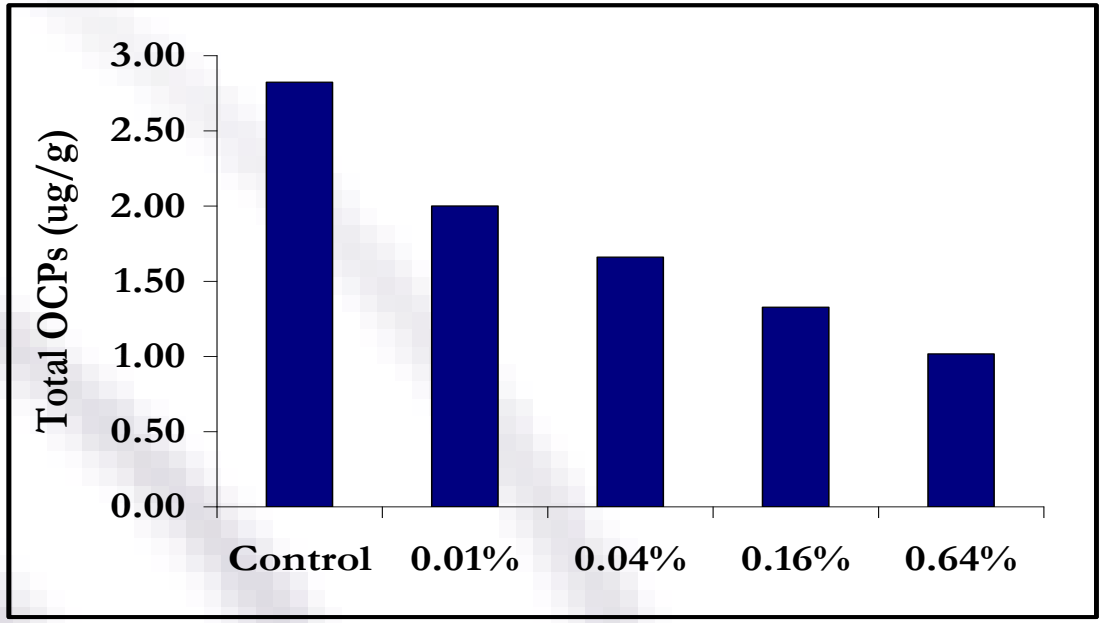
Source - PeroxyChem

Project FL

Confidential Agricultural Site
Palm Beach County FL

Project FL

Bench-scale Dosage Evaluation



Mean value of triplicate samples; eight cycles

Field-scale Performance Data

Compound	Concentration (µg/kg)		RDE (%)[1]
	Initial	Final	
Dieldrin	48.4	11.6	**76**
α-Chlordane	8.5	4.1	**51**
γ-Chlordane	13.9	4.1	**71**
Total	**70.8**	**19.8**	**72**

- Strong positive relationship between Daramend dosage and pesticide destruction
- Pesticide reductions were greater in sampling areas where lower Eh conditions were achieved
- Initial levels were treated to very low remedial standards (15 µg/kg for Dieldrin)
- High organic matter in this soil did not appear to inhibit degradation/shield pesticides

Source - PeroxyChem

Project X

Confidential Site

Project X

	Contaminated Cells	Clean Cells	Total Cells Sampled	% Failing
Prior to Treatment	112	0	112	100%

Project X

	Contaminated Cells	Clean Cells	Total Cells Sampled	% Failing
Prior to Treatment	112	0	112	100%
After Cycle 1	90	22	112	80%

Project X

	Contaminated Cells	Clean Cells	Total Cells Sampled	% Failing
Prior to Treatment	112	0	112	100%
After Cycle 1	90	22	112	80%
After Cycle 2	75	37	112	67%

Project X

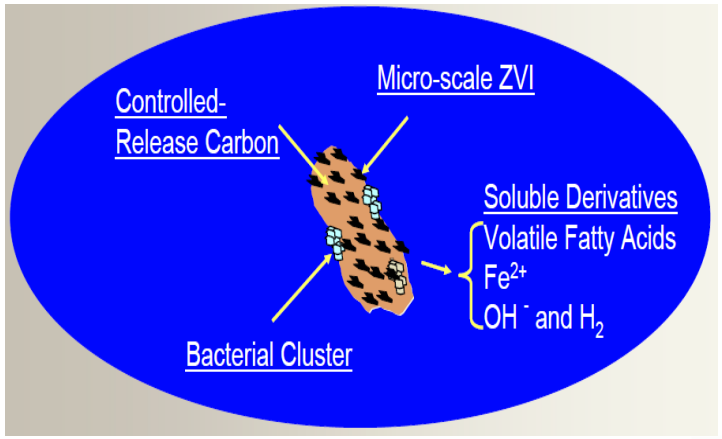
	Contaminated Cells	Clean Cells	Total Cells Sampled	% Failing
Prior to Treatment	112	0	112	100%
After Cycle 1	90	22	112	80%
After Cycle 2	75	37	112	67%
After Cycle 3	22	42	64	34%

Brownfield Site

- Recall: $500,000/ha – soil removal & disposal (@ only $50/MT)

Project Elmira

Uniroyal, Elmira ON, Canada
1997



Source - PeroxyChem

Project Elmira

Figure 1. Influence of DARAMEND treatment on 2,4-D concentration.

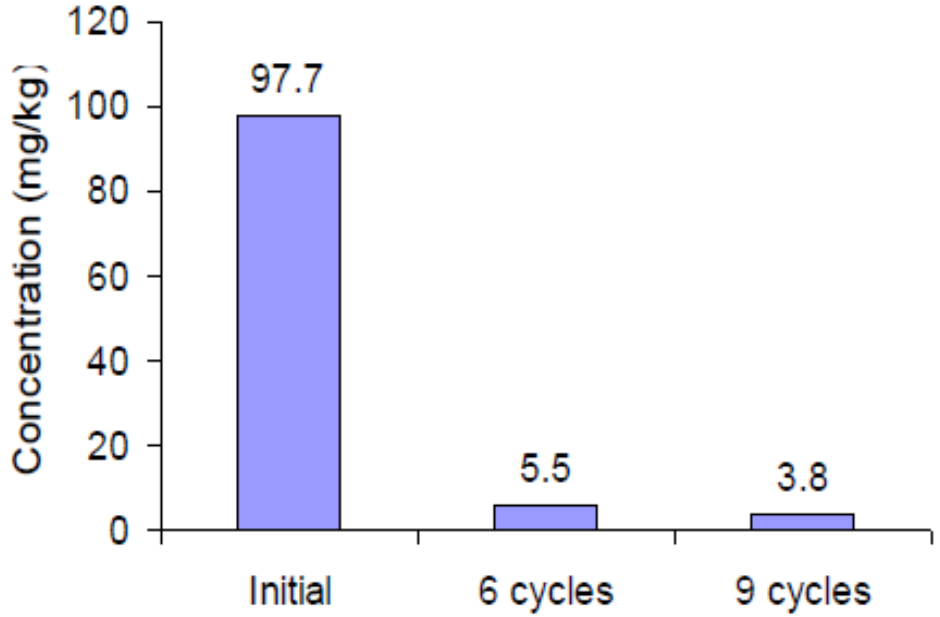
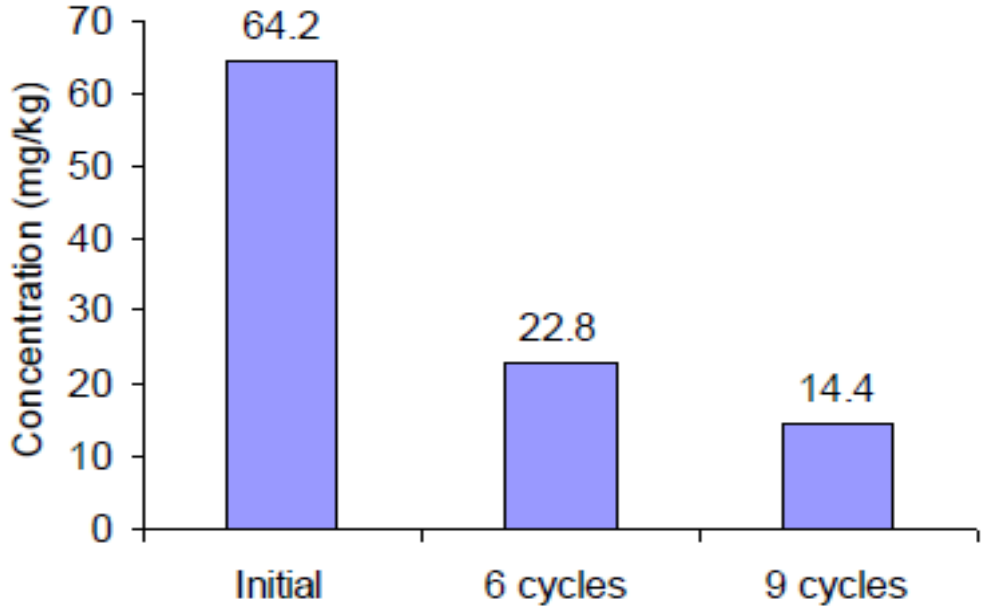


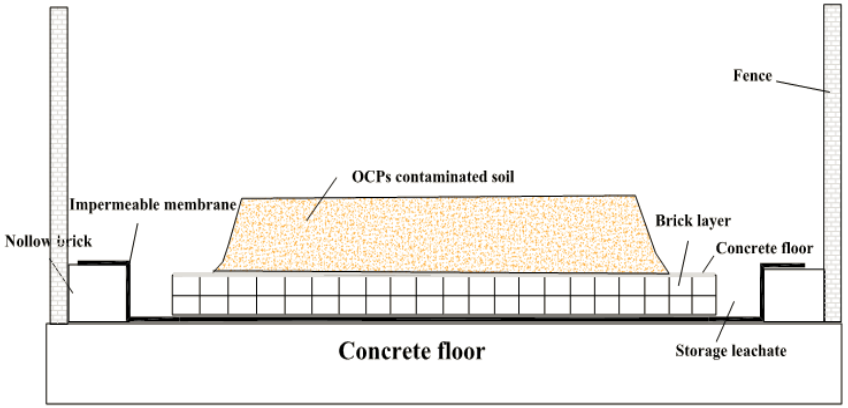
Figure 3. Influence of DARAMEND treatment on DDX concentration.



Source - PeroxyChem

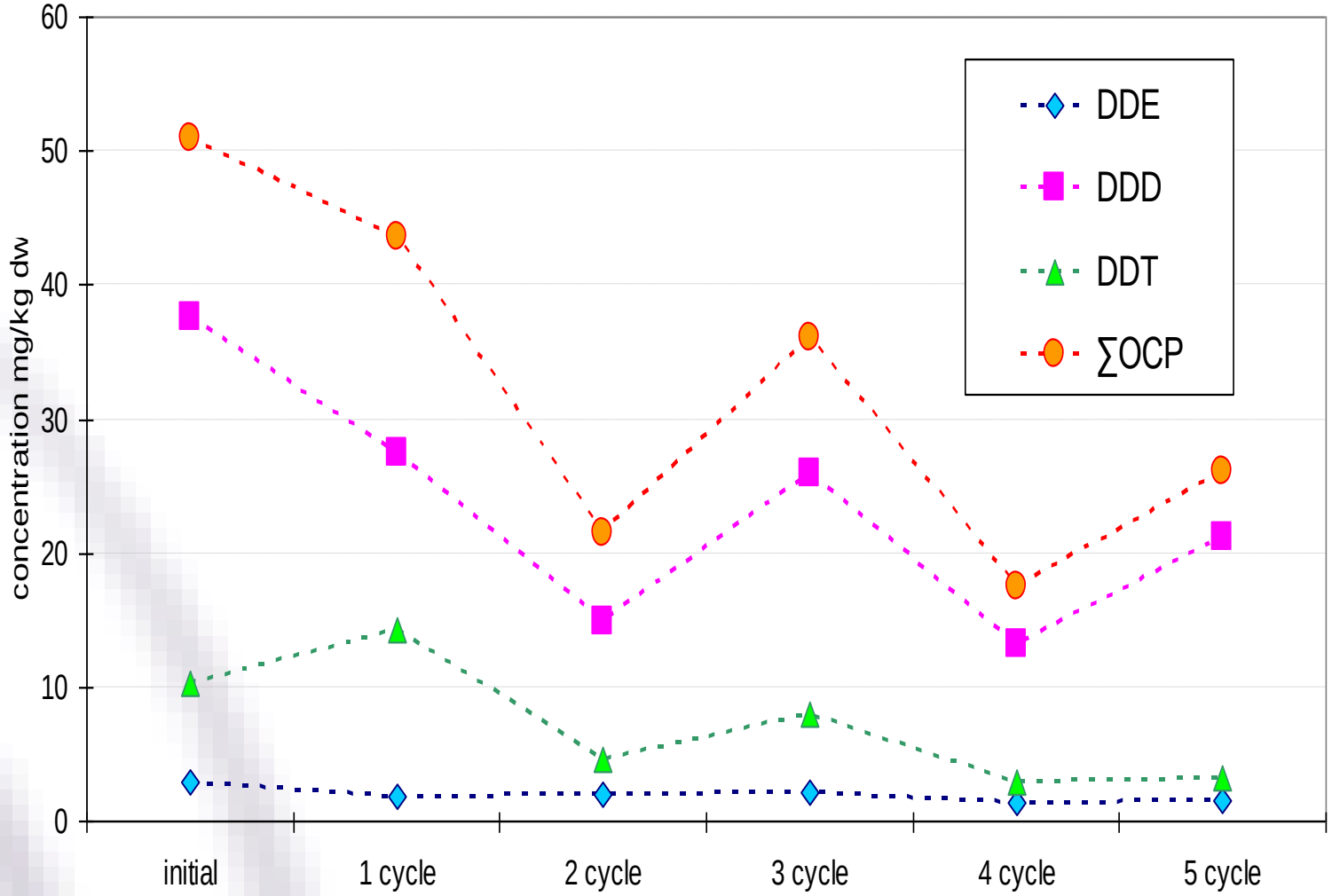
Project China

Confidential Pesticide Manufacturing Site
Hangzhou, Zhejiang China
2012



Source - PeroxyChem

Project China



Source - PeroxyChem

Pesticide Remediation

Conclusions

- Cities are moving into Agricultural lands around the World
- Soil criteria becoming more robust, analytical detections lower
- Pesticides are “contamination”
- Excess Soil Regulations will “find” contamination
- Treating soil on-site may become desirable
- It will be expensive to excavate and dispose of pesticide-contaminated soil (due to volume)
- On-Site ISCR (highly reducing conditions) is proven
  - ZVI & organics
- On-Site ISCR can be a fraction of the cost
  - Compared to excavation and landfill disposal

Questions?

Thank You for
Your Time

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