Cleaning Up the Mess: Using Chemistry to Degrade Persistent Organic Pollutants in the Environment

A Presentation for Café Scientifique

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Overview

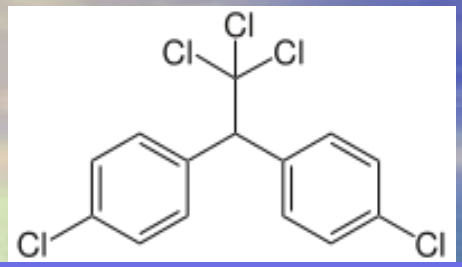
- What are Persistent Organic Pollutants?
- Where do we come in contact with them?
- Challenges in clean-up
- Some new options
- What is the future of environmental remediation?

Persistent Organic Pollutants

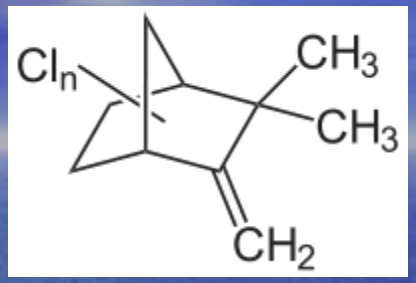
- **Persistent organic pollutants** (**POP**s) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes.

- Because of this, they have been observed to persist in the environment, to be capable of long-range transport, bioaccumulate in human and animal tissue, biomagnify in food chains, and to have potential significant impacts on human health and the environment.

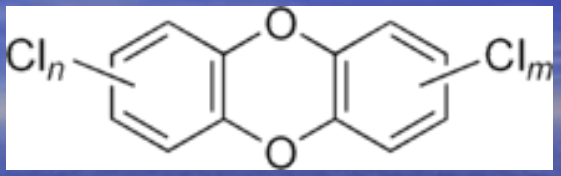
Examples



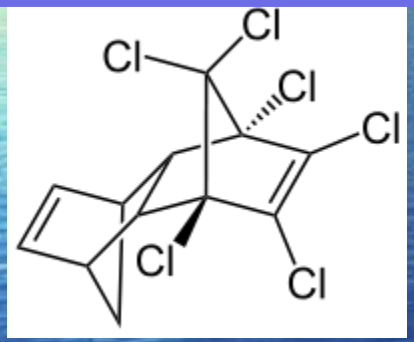
Dichlorodiphenyl trichloroethane DDT



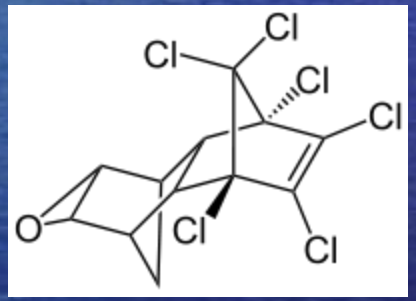
Toxaphene



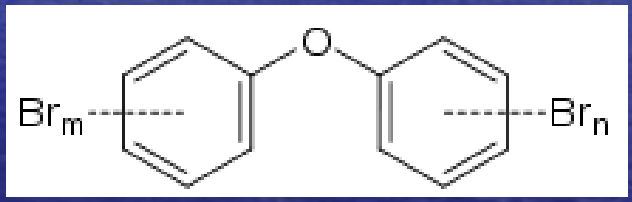
Polychlorinated dibenzodioxi
PCDD



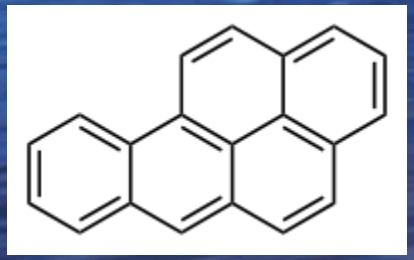
Aldrin



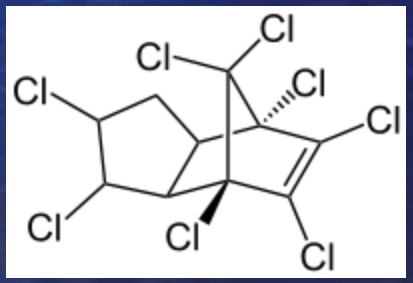
Dieldrin



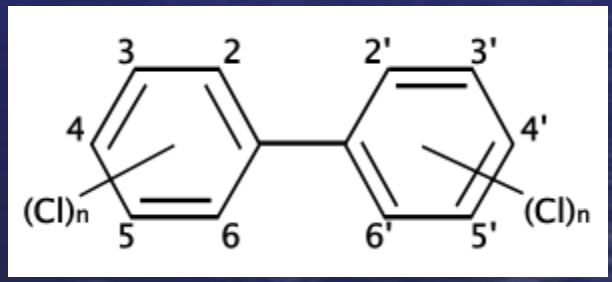
Polybrominated diphenyl ether
PBDE



Benzo(a)Pyrene



Chlordane



Polychlorinated biphenyls
PCB

WHY did we use them?

- Many pollution events happened decades ago before there was a good understanding of behavior of the chemicals.
- Many of these chemical had really GREAT properties! PCBs for example....
- At one time, we wanted our chemicals to have a long half-life.
- More people, more of the BIG life, more pollution.

Another Persistent Problem

- Ground Water contamination!
- Particularly important in Florida

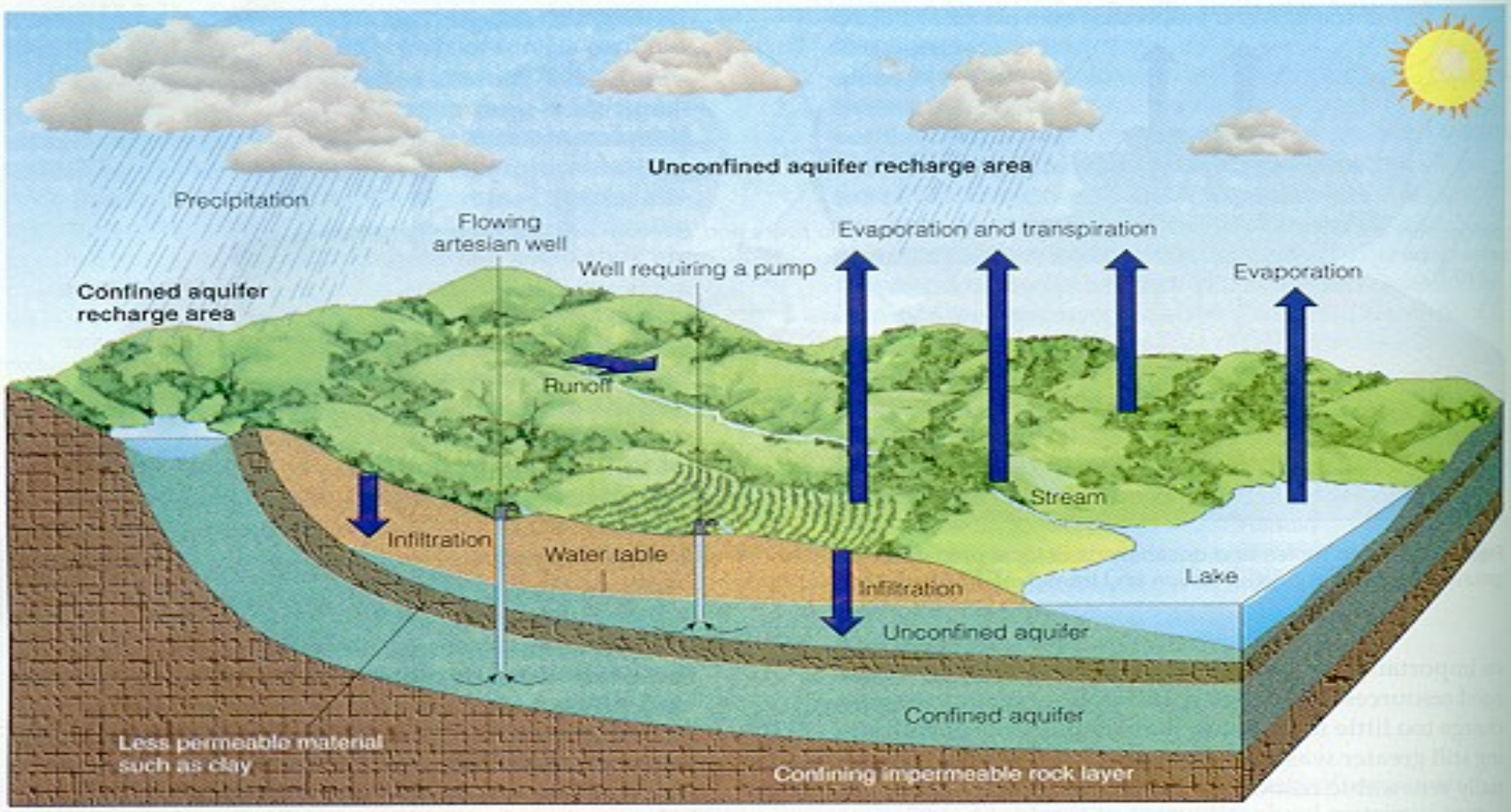


Figure 17-5 The groundwater system. An *unconfined (water table) aquifer* forms when groundwater collects above a layer of rock or compacted clay through which water flows very slowly (low permeability). A *confined aquifer* is sandwiched between layers such as clay or shale that have low permeability. Groundwater in this type of aquifer is confined and under pressure.

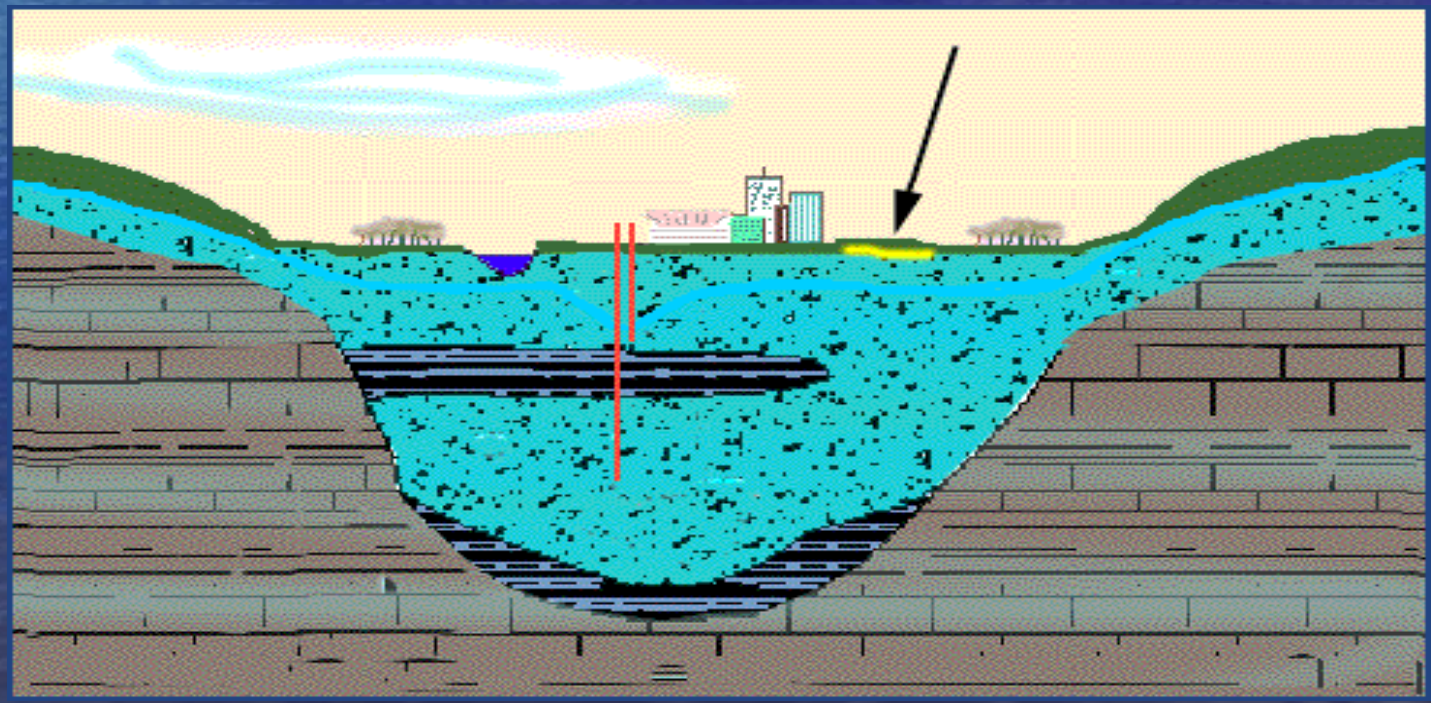
DNAPL Groundwater Contamination

Dense NonAqueous Phase Liquids

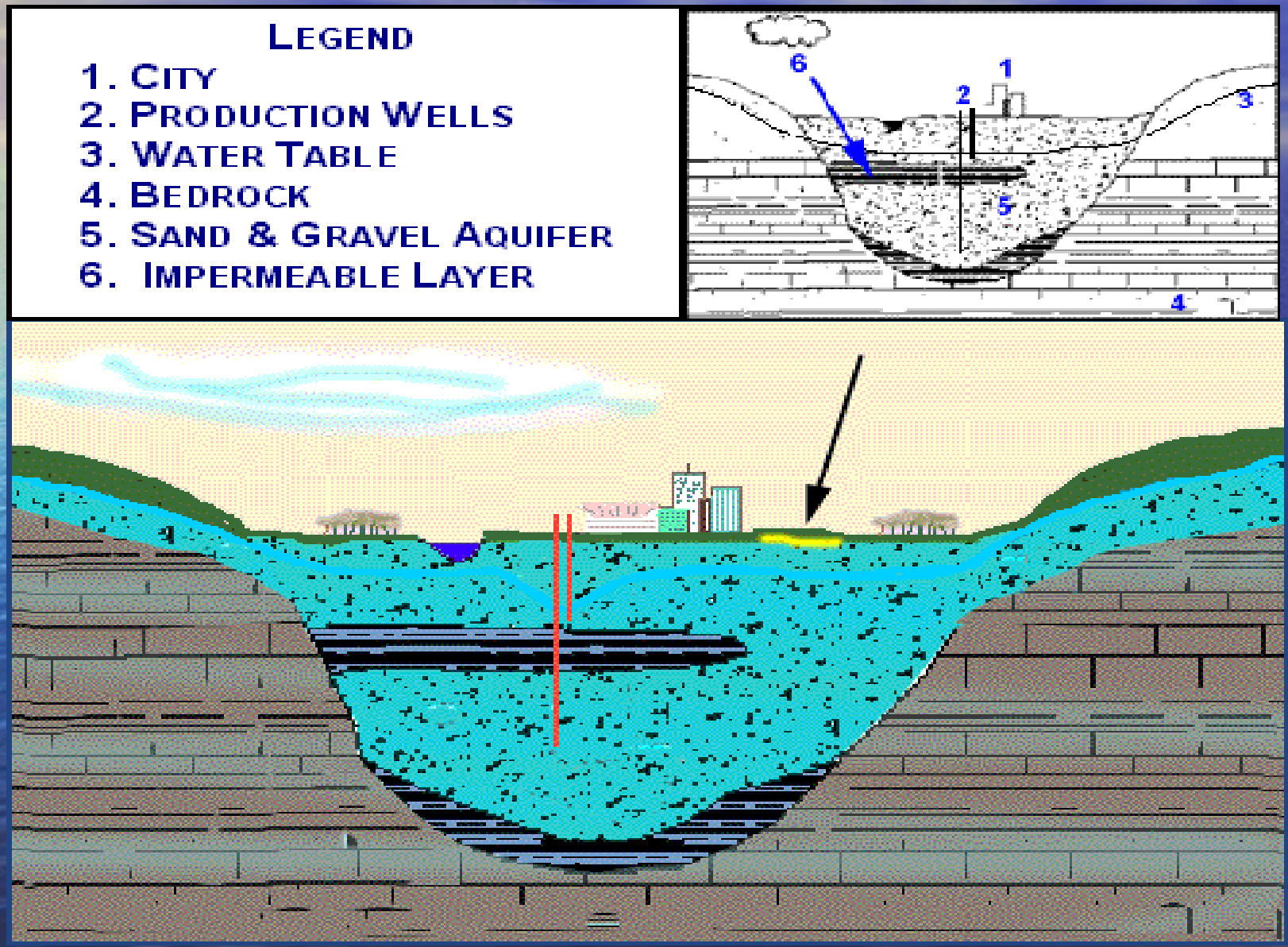
More dense than water so they sink

TCE trichloroethene

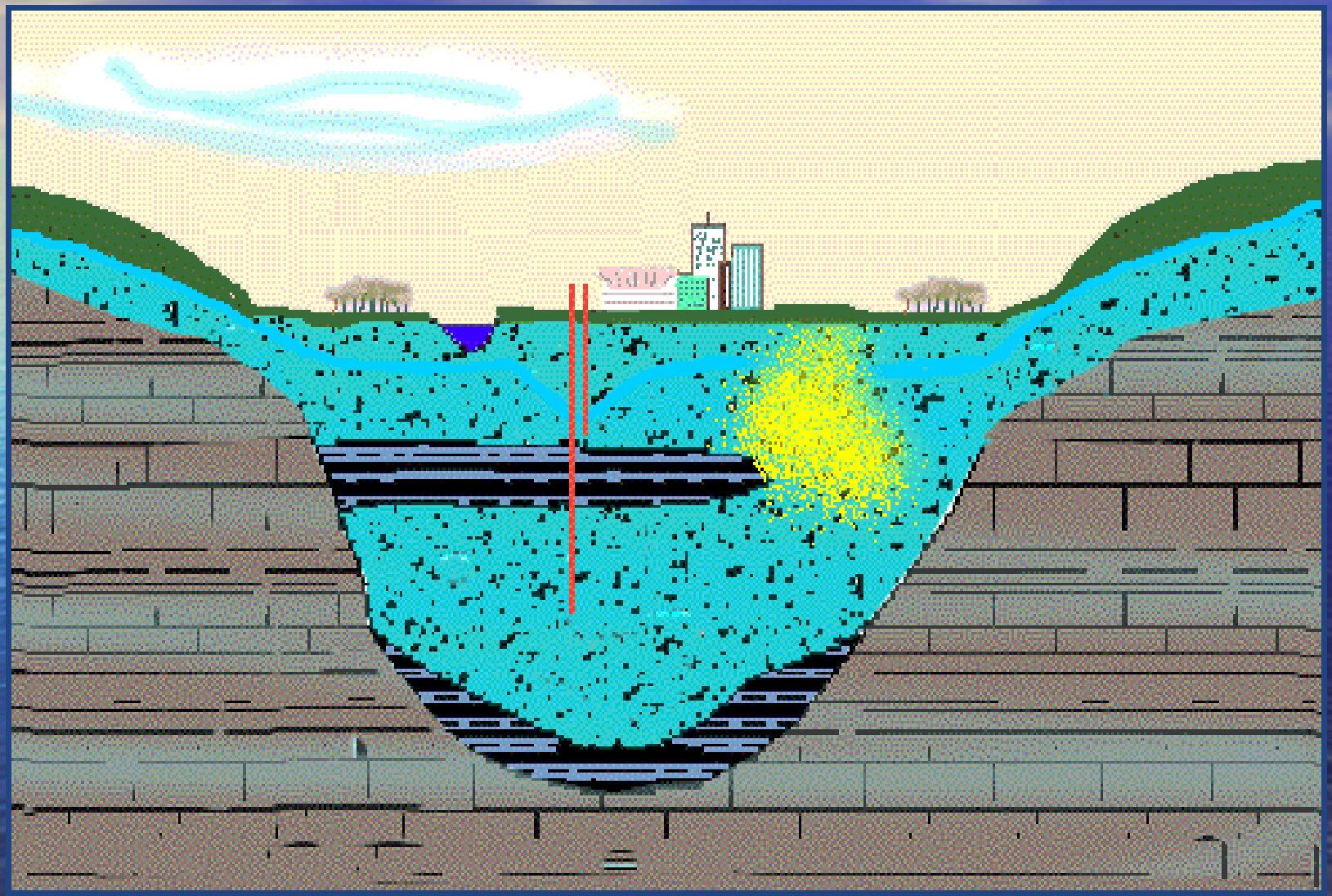
- **Pools**
- **Ganglia**
- **Sorbed**
- **Gaseous**



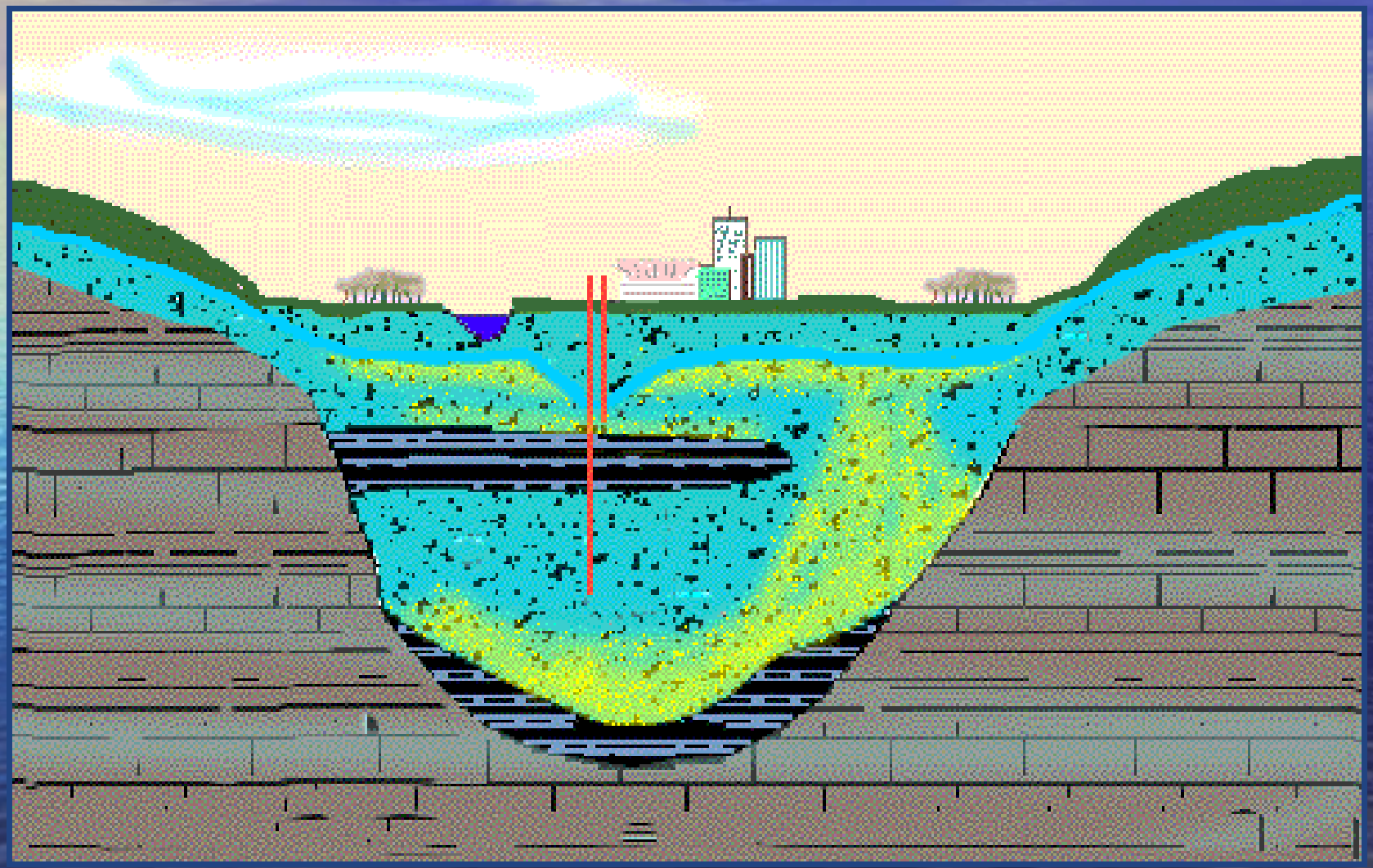
Groundwater Contamination: Step 1



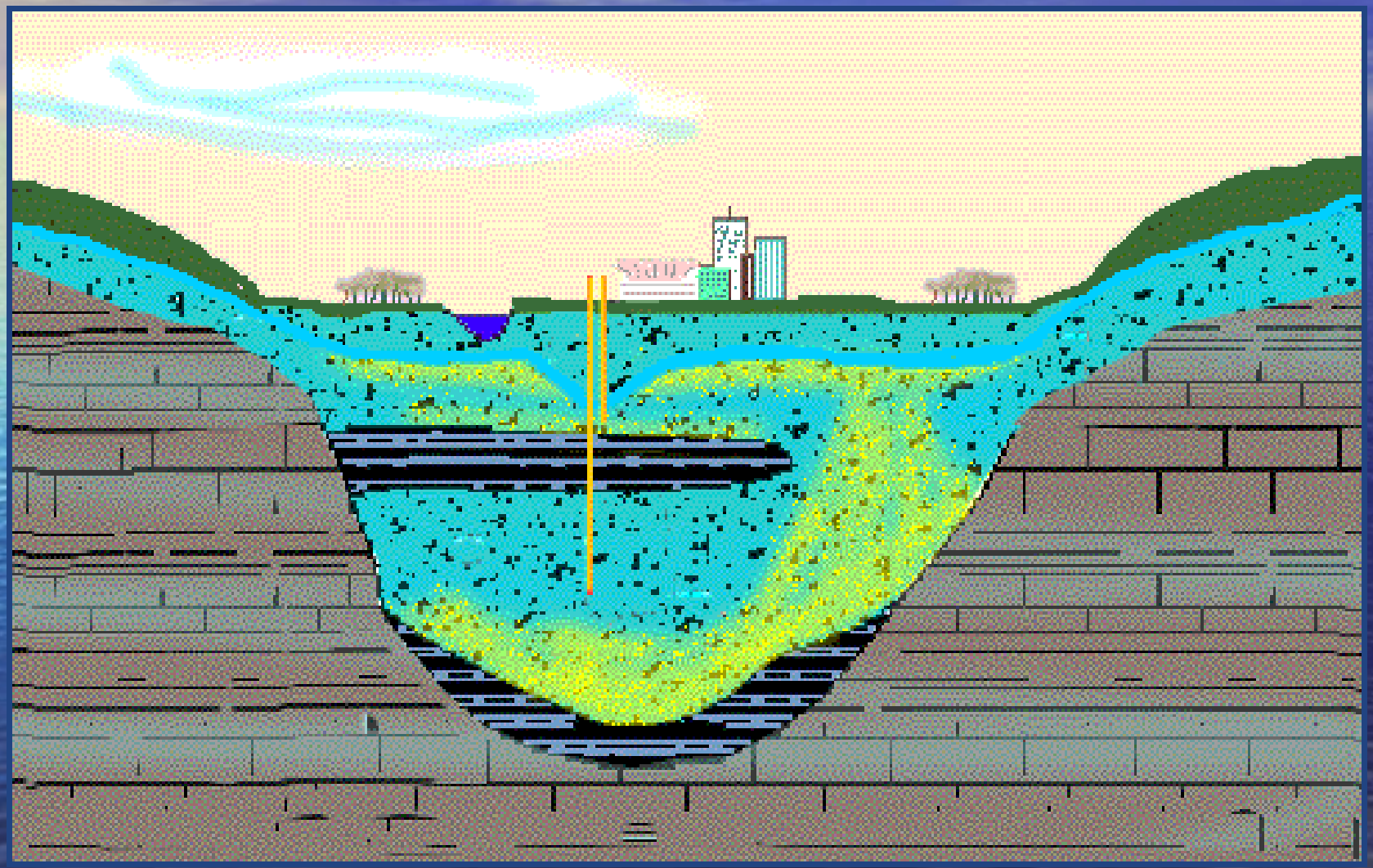
Groundwater Contamination: Step 2



Groundwater Contamination: Step 3



Groundwater Contamination: Step 4



Traditional DNAPL Remediation Techniques

- Excavation
- Used primarily for contamination of heavy metals or nonvolatile compounds (ex. polychlorinated biphenyls)
- High cost and liability issues

- Pump and Treat
- Treats only dissolved phase compounds
- Would have to treat for decades
- High capitol and monitoring costs

Bioremediation/Bioaugmentation

- Initiating a population of chlorinated solvent-consuming microbes or increasing the population of such a native species
- Initiating a new population is very difficult to sustain
- Bioaugmentation is more attainable. Problem can be similar to $KMnO_4$ and surfactants
- Good use as a ‘polishing’ technique

Zero Valent Iron Technology

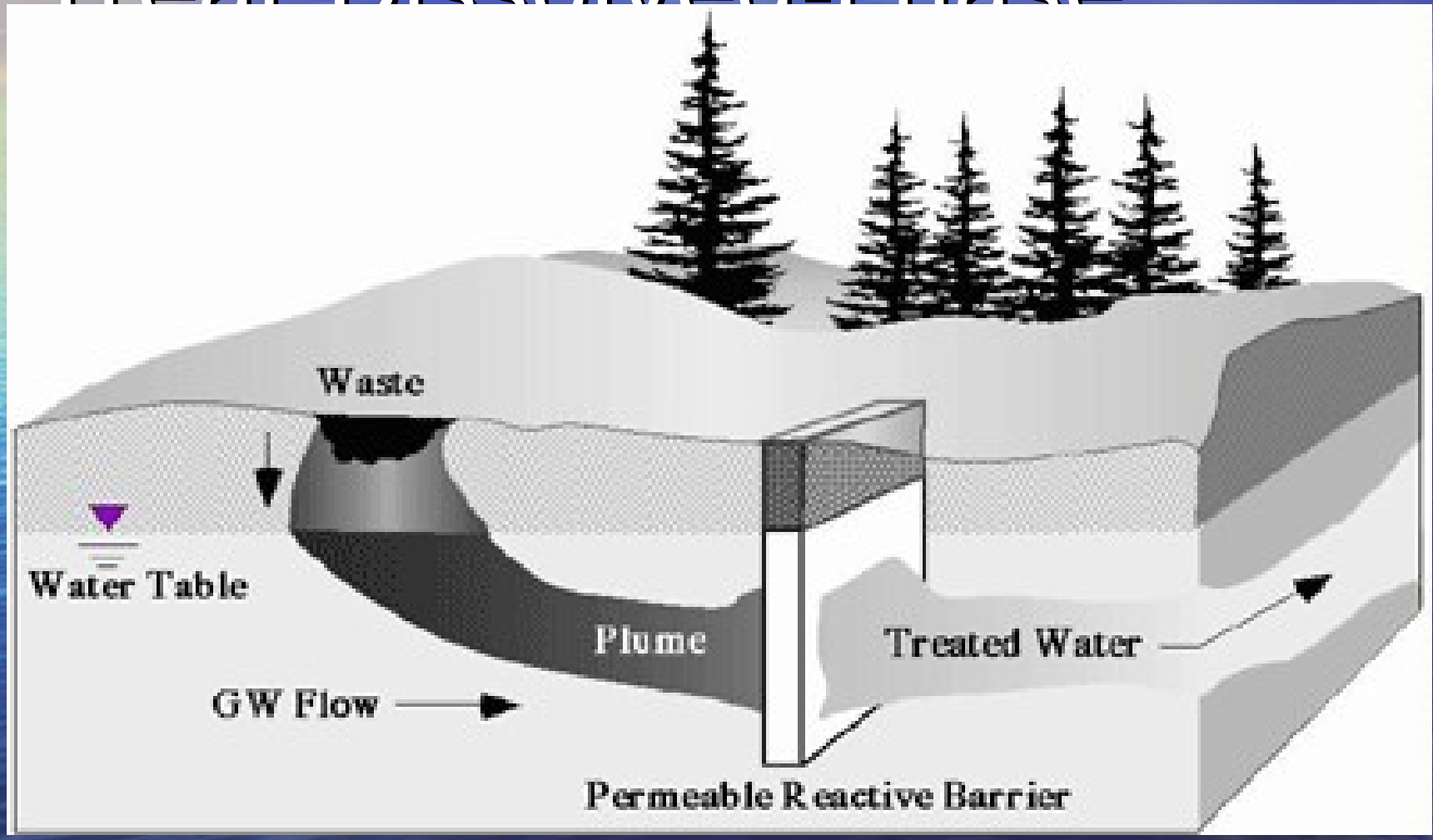
- Zero Valent Iron
  - In Permeable Reactive Barriers
  - Treats Dissolved Phase TCE
- Reaction of Elemental Iron With Chlorinated Aliphatic:

$$RCl + Fe + H^{+} \Rightarrow RH + Cl^{-} + Fe^{+2}$$

- Iron Alone Will Not Degrade DNAPL
  - Fe is Hydrophilic (water loving)
  - DNAPL is Hydrophobic (water hating)

Permeable Reactive Barriers

Treat Dissolved-Phase

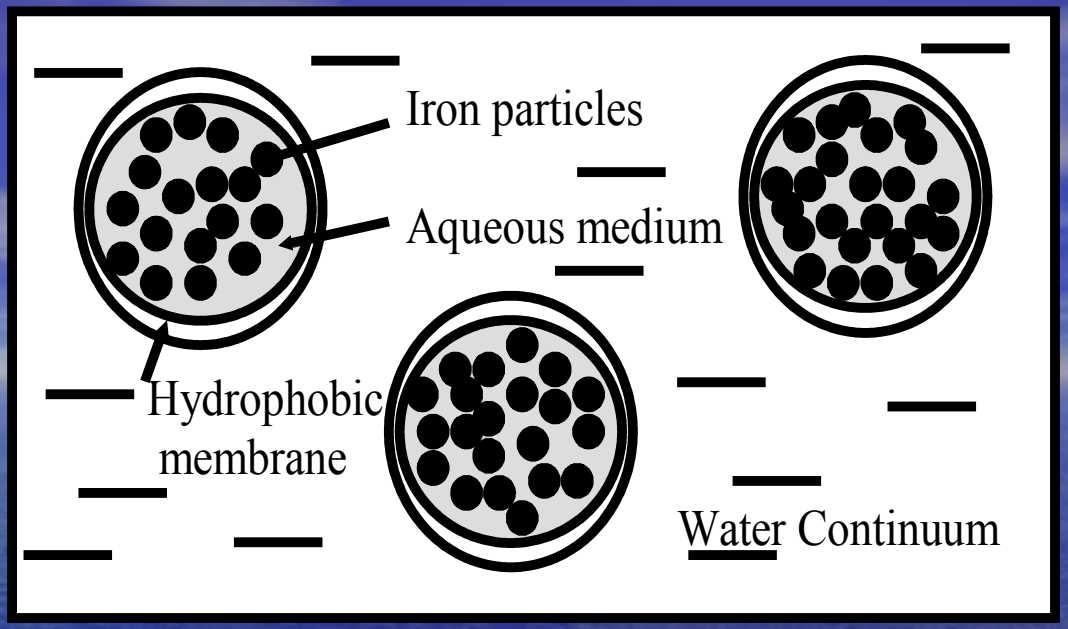


http://www.powellassociates.com/sciserv/3dflow.html

Zero Valent Iron Emulsion Technology

- Emulsified Zero Valent Iron (EZVI)
  - Surfactant-stabilized, Biodegradable O/W Emulsion
  - Contains Nanoscale or Microscale Iron Particles Within Emulsion Droplet
  - Reductively Dehalogenates Chlorinated DNAPLs
    - Draws DNAPL Through Hydrophobic Oil Membrane
    - Reductive Dehalogenation Occurs on the Surface of the Iron Particle

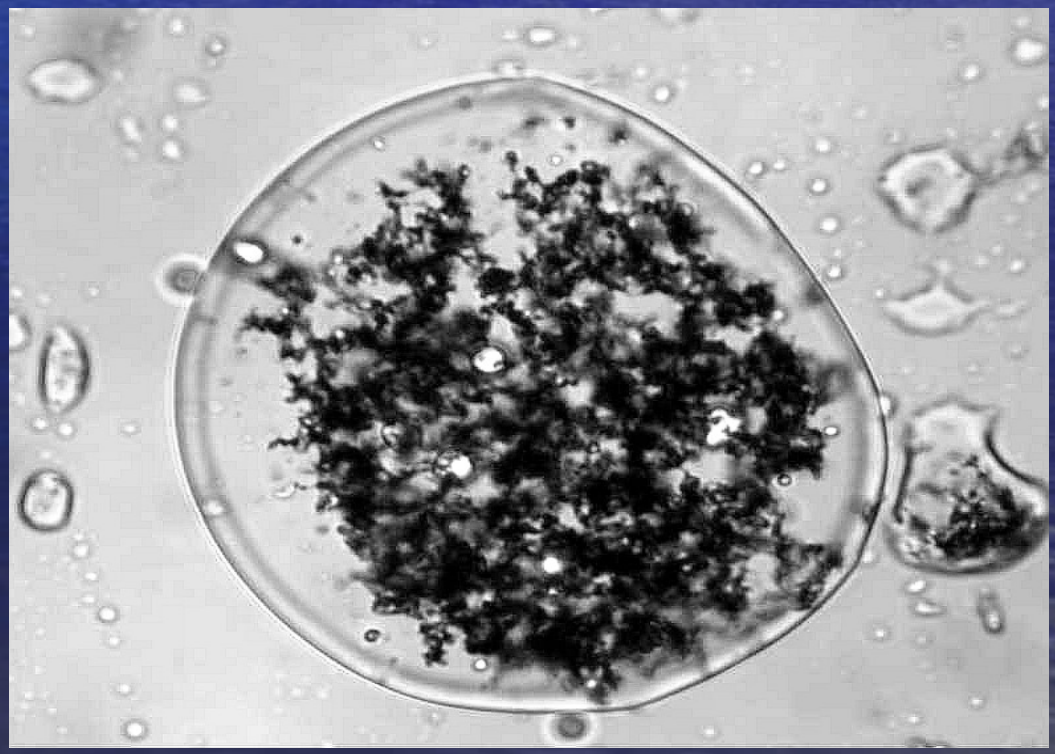
Drawing Depicting What We Envisioned Before Research Began →



Emulsion Composition:

-corn or vegetable oil
-food grade surfactant
-iron particles

Micrograph of Nanoscale Iron Emulsion Droplet (Approximately 12 microns in Diameter) →



Visual Studies

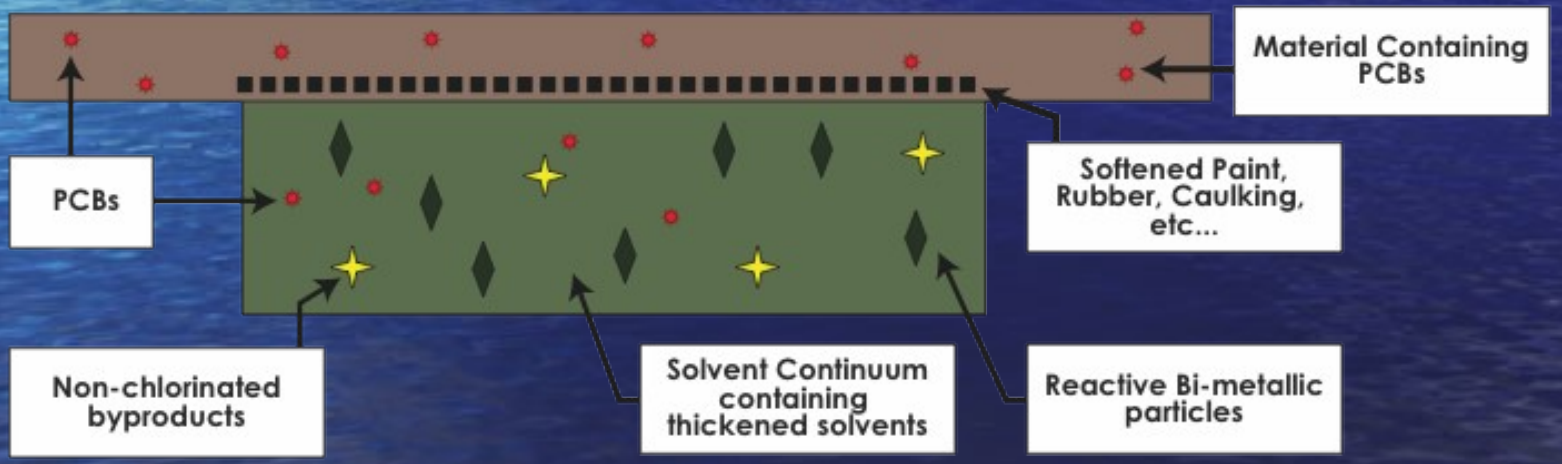
Control **Free Phase Iron** **Emulsion**

Success!!

- Thus far, the EZVI technology has won seven national and international awards, several more regional awards.
- It has been used in over twenty states and four countries. It has cleaned dozens of sites to below regulatory levels.

PCBs
Technical Approach

- BTS consists of elemental magnesium coated with a small amount of palladium in a solvent solution capable of hydrogen donation



(Schematic of BTS)

BTS has two functions:

- Extract PCBs from weathered coating or other material such as paint
- Rapidly degrade the extracted PCBs via abiotic reduction in the presence of zero valent Mg or Mg/Pd

Paste Formulation

- Must be viscous enough to stay on vertical surface
- Components:
  - **Ethanol**- *hydrogen donor solvent*
  - **Limonene**- *paint softener*
  - **Calcium stearate, polyethylene glycol-** *stabilizers, thickeners*
  - **Sodium polyacrylate-** *absorbent (delays evaporation)*
  - **Glycerin**- *thickener*
  - *Mg or Mg/Pd- active particles*
  - *Acetic Acid-activator*

Sealant

- Unsuccessful Sealants
  - Aluminum foil - *labor intensive, susceptible to leaks*
  - Water-based latex paint - *cracks when dry*
  - Organic-based paint - *not able to retain moisture*
- Successful Sealants
  - Silicon seal
  - Vinyl truck bedliner
  - *Plastic wrap*

Field Demonstration 1

Vertical Integration Building (VIB), Cape Canaveral Air Force Station

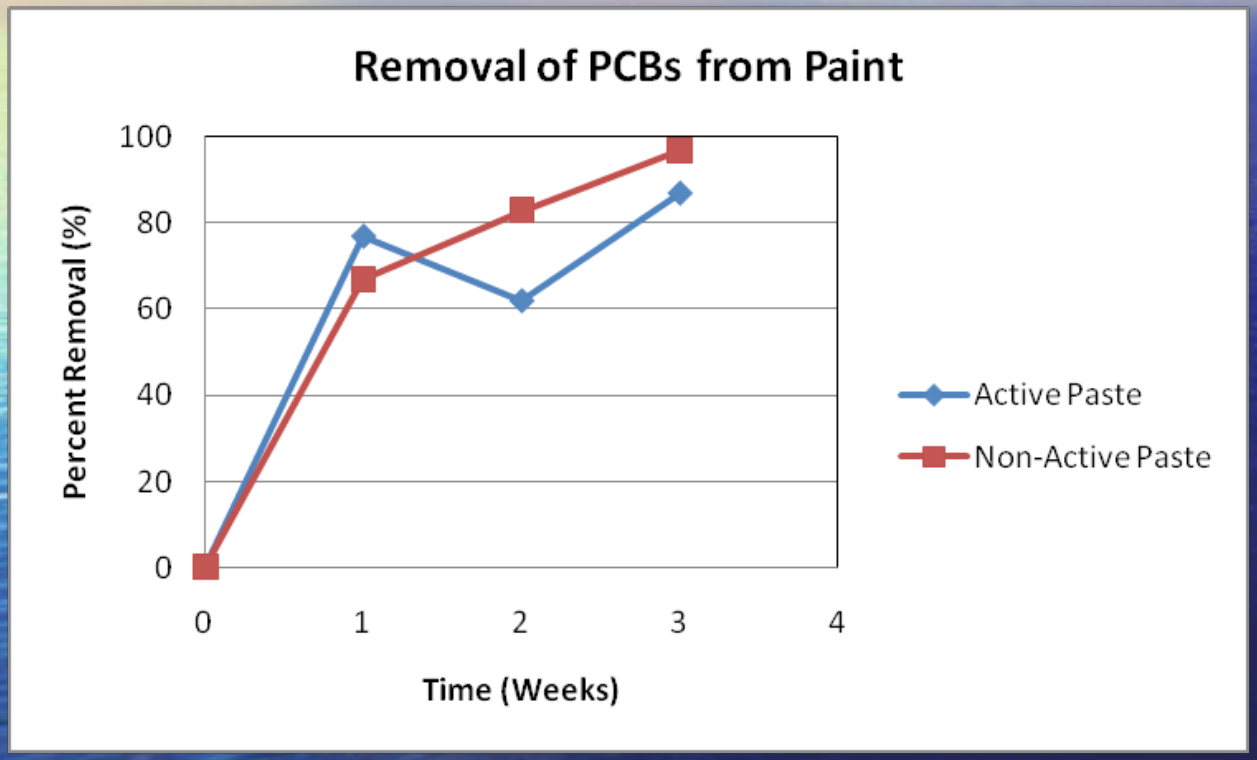
- The Vertical Integration Building (VIB) was scheduled for demolition when chosen for Demo in order to determine the presence, distribution, and concentrations of the PCB-containing paints, paint samples were collected from various structures within the VIB and sent to be analyzed.
- Concentrations of PCBs in the VIB test panels used in the demonstration ranged from ~10 to ~100 mg PCB/kg paint.

Material Tested at VIB

Application of BTS to VIB samples using pressurized sprayer

Manual application of BTS to VIB samples.

Results: Field Demonstration 1



- Performance Objective Met, PCBs removed from paint to below 50 mg/kg

Average of samples (2 samples at 1 week and 2 weeks and between10 and 20 samples at week 3)

Field Demonstration 2

- **Badger Munitions Depot, WI:** Initial Pretreatment Sampling: 56 samples were collected including painted concrete, wood and metal
- PCB concentrations from paint samples taken from structures range from 30 to 55,000 mg/kg

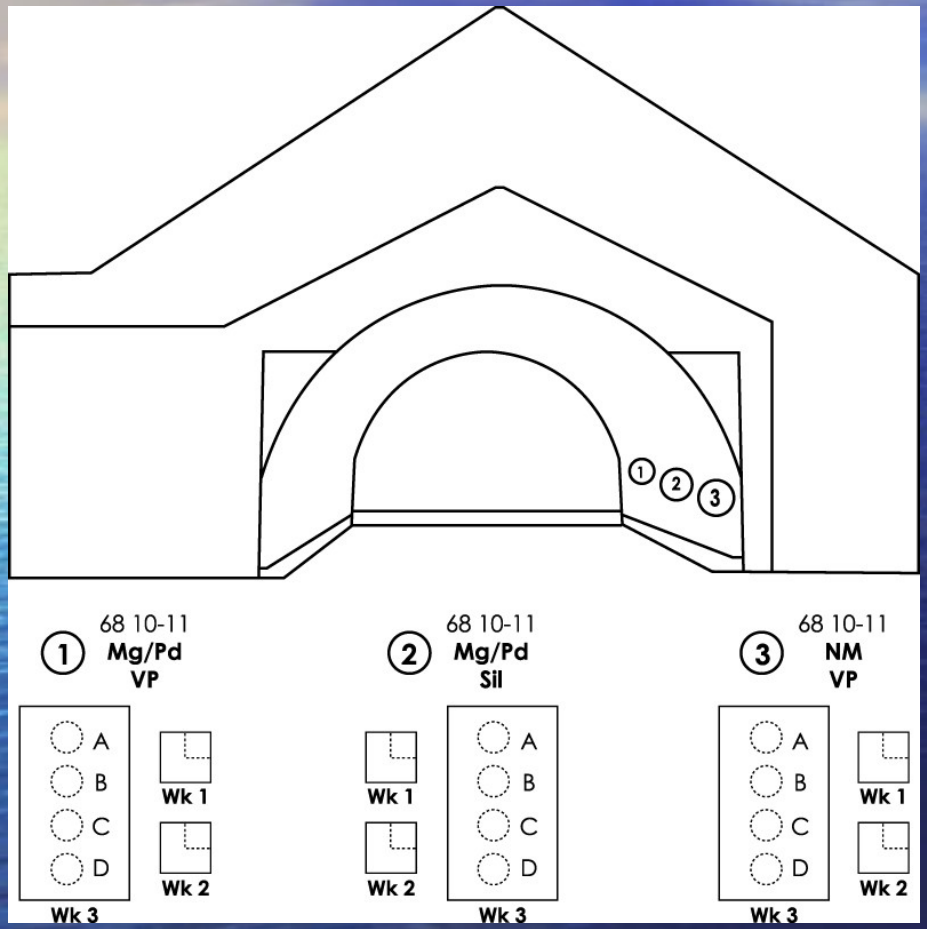
Application

- Paste applied by hand using a trowel and on some of the treatment surfaces using a spray gun (paint sprayer)
- Four locations were treated: Two concrete bunkers, metal tanks in a nitrating facility, and propellant presses in a staging area

BTS applied at Badger




Application Matrix: Concrete Bunker



Ammunition storage bunker

LEGEND

Wk 1 Week 1 sample area

Wk 2 Week 2 sample area

Wk 3 Week 3 sample area

VP Vinyl polymer truck bed liner sealant

Sil Silicon roof sealant

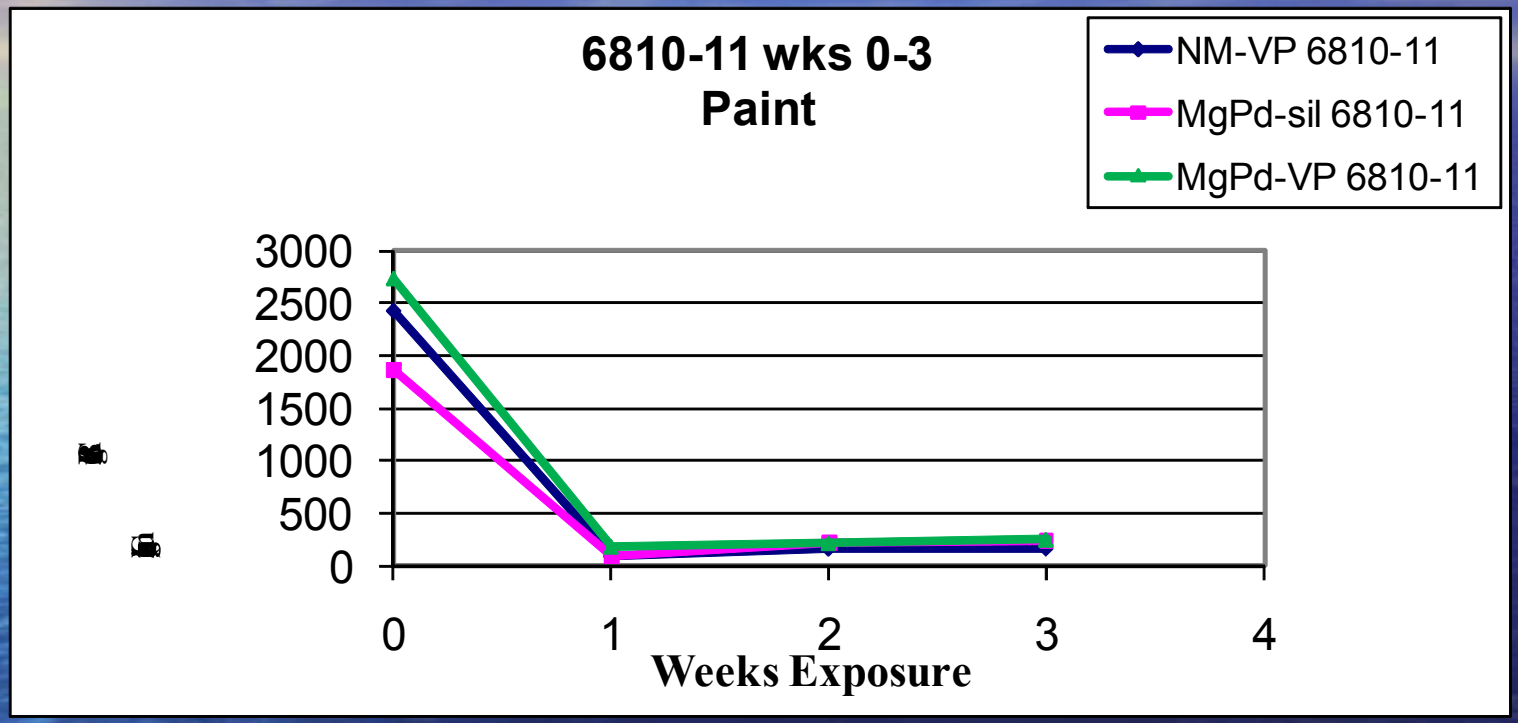
Mg/Pd Magnesium palladium, active paste

NM No metal, inactive paste

Results from Badger

- PCB concentrations in paint in concrete bunkers were between ~ 1800 mg/kg to as high as 3880 mg/kg
- Significant reduction in PCB concentration after one week
- Post treatment concentration in paint after three weeks of treatment was between 96 mg/kg and 200 mg/kg
- Laboratory studies have demonstrated that a second application of fresh paste can get PCB levels below 50 mg/kg

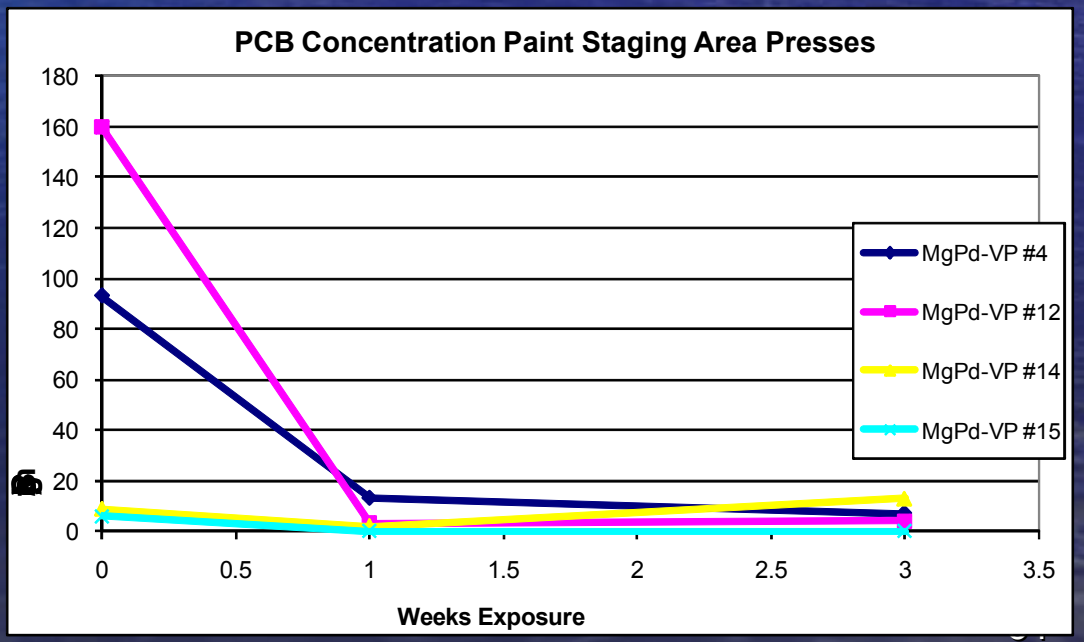
Results: Paint on Concrete Bunkers



Concentrations in paint after 1, 2 and 3 weeks exposure to BTS on concrete bunker

Results: Staging Area

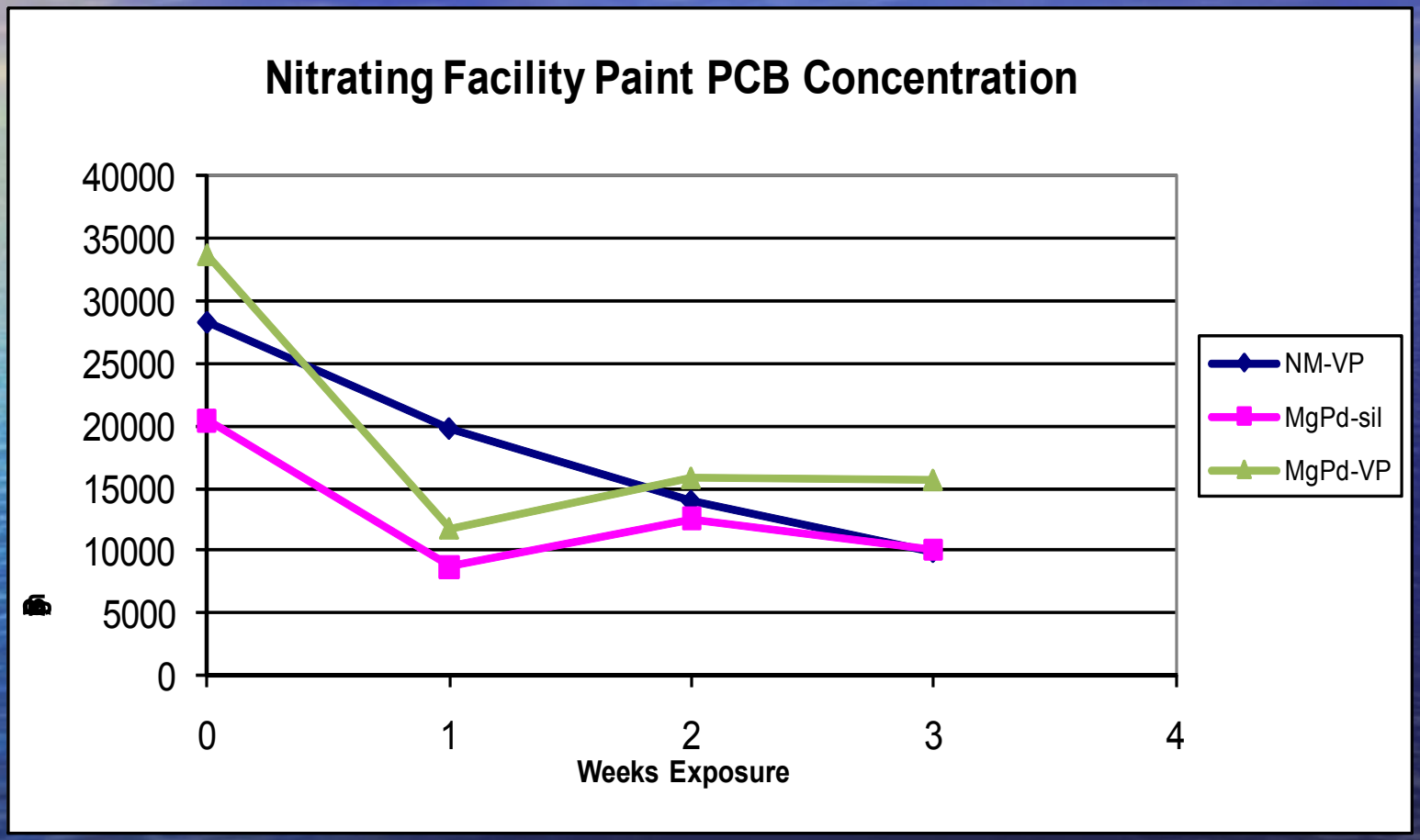
- PCB concentrations in paint on the metals in the staging area were much lower ~ 3 mg/kg to as high as 170 mg/kg
- After treatment, the concentration in the paint was between ND and 17 mg/kg. BTS was successful at extracting PCBs to below 50 mg/kg after one week



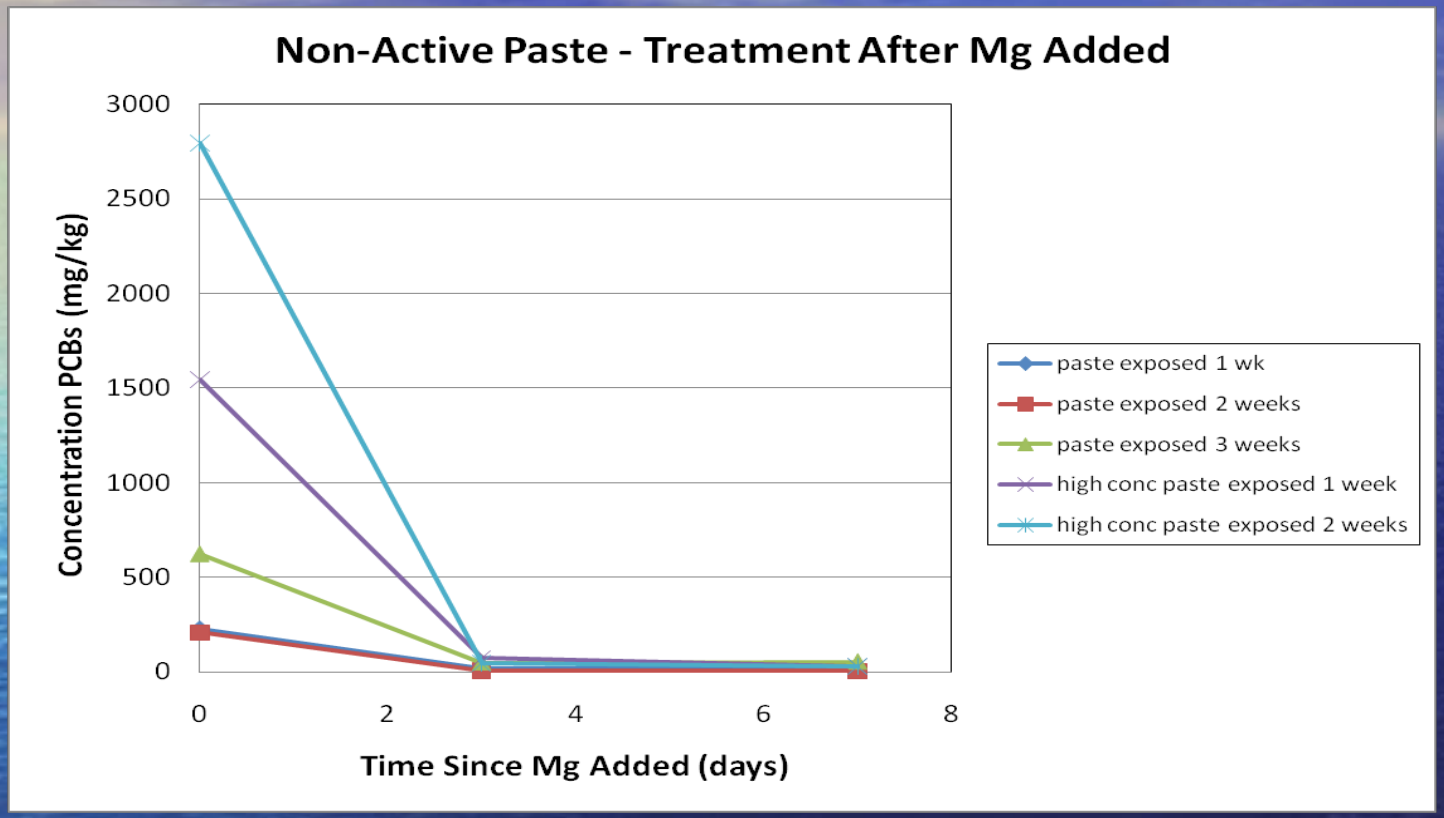
Nitrating Facility Results

- PCB concentrations in paint on the metals in building 6657-02 were much higher ~10,000 mg/kg to as high as 53,000 mg/kg
- Post treatment concentration in paint was between 6,600 mg/kg and 20,000 mg/kg
- BTS successful at extracting PCBs but need multiple applications of BTS to treat such high starting concentrations in multiple layers of paint.

Paint Concentrations: Nitrating Tank Before and After Treatment



Non-Active Paste: Treatment after Addition of Mg

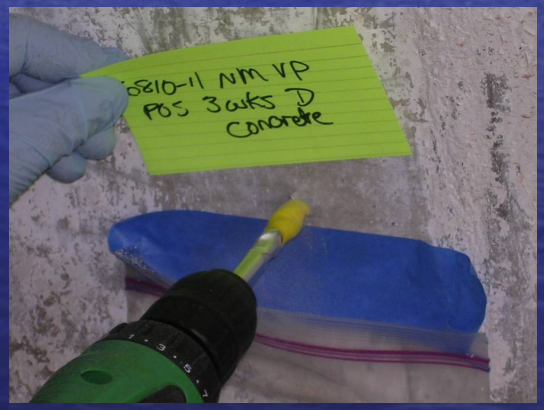


- 10 % of activated Mg added to paste after removed from painted structures and successful treatment to below 50 mg/kg even with high starting concentrations

BTS and Effect on PCB Transport

- Concrete samples taken to evaluate whether solvent in BTS could take PCBs from the paint into the concrete
- Samples taken prior to BTS application and after three weeks of BTS application at five locations

Sample ID	PRE-TR Conc. (mg/kg)	PRE-TR Average (mg/kg)	Post-Conc. (mg/kg)	Post-TR Average (mg/kg)
MgPd Sil 1wk concrete	85	139	17	18
	110		16	
	183		23	
	178		17	
MgPd VP Concrete	50	59	10	20
	60		37	
	43		16	
	39		15	
	75		28	
	84		14	



- BTS did not transfer PCBs into the concrete from the paint but actually pulled some PCBs from the concrete and treated them.

Acknowledgements: Thanks to ESTCP for funding this projec

Questions?

The Group