Overview

• What is Causing it?
• Problems with Groundwater Contamination
• Traditional Remediation Techniques
• Zero Valent Iron Emulsion Technology
• Surface Water Remediation Techniques
What is causing all these problems?

- Many pollution events happened decades ago before there was a good understanding of subsurface water.
- Surface pollution: more focus now but our activities (impermeable surfaces) cause run-off to surface waters.
- More people, more of the BIG life, more pollution.
- Necessity (or sometimes regulation) is the Mother of Invention.
**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

**Legend**

1. City
2. Production Wells
3. Water Table
4. Bedrock
5. Sand & Gravel Aquifer
6. Impermeable Layer
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 capital and monitoring costs
• Steam Injection-Volatilizes and mineralizes TCE
• Once contaminant zone is sufficiently heated, in situ boiling of water and contaminant are induced, steam stripping the contaminant from the aqueous phase.
• Injection of steam into subsurface through a series of wells
• Collection and neutralization of gaseous by-product (HCl)
• Difficult to reach all DNAPL areas including pools and ganglia

• High $$$
  - High capitol costs.
  - High cost for constant monitoring during remediation process.
  - Fuel costs to heat water

• Results can reach 90% efficiency
Radio Frequency Heating

- Radio frequency heating and six-phase heating can effectively enhance soil vapor extraction/air sparging (SVE/AS) in cold climates.
- During moderate radio frequency heating, soil temperatures reach 15-40°C.
- Estimated that this system is capable of heating a soil column up to 60 feet in diameter under full-scale application.
- Non-uniform soil temperatures
- High capitol costs
Six-Phase Heating

- High-temperature six-phase heating resulted in soil temperatures that varied with radial distances from the heating electrodes.
- Temperatures of 100°C were reached within an 8- to 10-foot radial distance from the electrodes, while they averaged 85°C (to a depth of 6-16 feet) within a 50-foot diameter soil column.
- High capital costs: machinery and personnel
Chemical Oxidation

- Potassium permanganate
- Injected into the subsurface; mineralizes the contaminant
- $\text{KMnO}_4$ solution primarily moves through areas of least resistance
- Bypasses considerable DNAPL
- Oxidizes surface of DNAPL droplet
- Forms $\text{MnO}_2$ thus protecting remainder of DNAPL
Surfactant Flooding

• Solubilizes or mobilizes DNAPL
• Solubilization occurs in the presence of micelles
• Mobilization occurs by releasing DNAPL ganglia held by capillary forces
• Potential for uncontrolled migration
• Like KMnO$_4$, will travel through the most permeable zones, bypassing much DNAPL
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
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)
Mechanism Not Precisely Known

- Generally Thought To Be Sequential
  \[ \text{C}_2\text{HCl}_3 \rightarrow \text{C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{C}_2\text{H}_4 \]

- Some Studies Suggest Acetylene to be Major Pathway
  \[ \text{C}_2\text{HCl}_3 \rightarrow \text{C}_2\text{HCl} \rightarrow \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_4 \]
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
SEM of Nanoscale Iron

Magnification = 20000X
Water Continuum
Iron particles
Aqueous medium
Hydrophobic membrane

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
Surface Water Remediation

- Phytoremediation
- Membrane Technologies
- Bioaugmentation: Same problems as mentioned earlier.
Phytoremediation

- Phytoremediation is a set of processes that uses plants to clean contamination in ground water and surface waters.
- There are several ways plants can be used for the phytoremediation. These mechanisms include enhanced rhizosphere biodegradation, hydraulic control, phyto-degradation and phyto-volatilization.
• **Enhanced Rhizosphere Biodegradation**

• Enhanced rhizosphere biodegradation takes place in the soil surrounding plant roots. Natural substances released by plant roots supply nutrients to microorganisms, which enhances their ability to biodegrade organic contaminants. Plant roots also loosen the soil and then die, leaving paths for transport of water and aeration. This process tends to pull water to the surface zone and dry the lower saturated zones.
• **Hydraulic Control**

• Depending on the type of trees, climate, and season, trees can act as organic pumps when their roots reach down towards the water table and establish a dense root mass that takes up large quantities of water.

• **Phyto-degradation**

• Phyto-degradation is the metabolism of contaminants within plant tissues. Plants produce enzymes, such as dehalogenase and oxygenase, that help catalyze degradation. Investigations are proceeding to determine if both aromatic and chlorinated aliphatic compounds are amenable to phyto-degradation.
• **Phyto-volatilization**

• Phyto-volatilization occurs as plants take up water containing organic contaminants and release the contaminants into the air through their leaves. Plants can also break down organic contaminants and release breakdown products into air through leaves.
Membranes for Surface Waters

- Certain substances can pass through the membrane, while other substances are caught. Membrane filtration can be used as an alternative for flocculation, sediment purification techniques, adsorption (sand filters and active carbon filters, ion exchangers), extraction and distillation.
There are two factors that determine the affectivity of a membrane filtration process; selectivity and productivity.
What about Removing Salts from Waters?

- When salts need to be removed from water, **nano filtration** and **Reverse Osmosis** are applied. Nano filtration and RO membranes do not work according to the principle of pores; separation takes place by diffusion through the membrane. The pressure that is required to perform nano filtration and Reverse Osmosis is much higher than the pressure required for micro and ultra filtration, while productivity is much lower.
The Group
Thank You

• For your time and attention. Any Questions or Discussion?