Surfactant Enhanced HVDPE Remediation of Petroleum Contaminated Soil, Bedrock, and Groundwater Northern California, USA

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WATERtech 2011
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Recap

What really affect remediation…water, soil and contamination…

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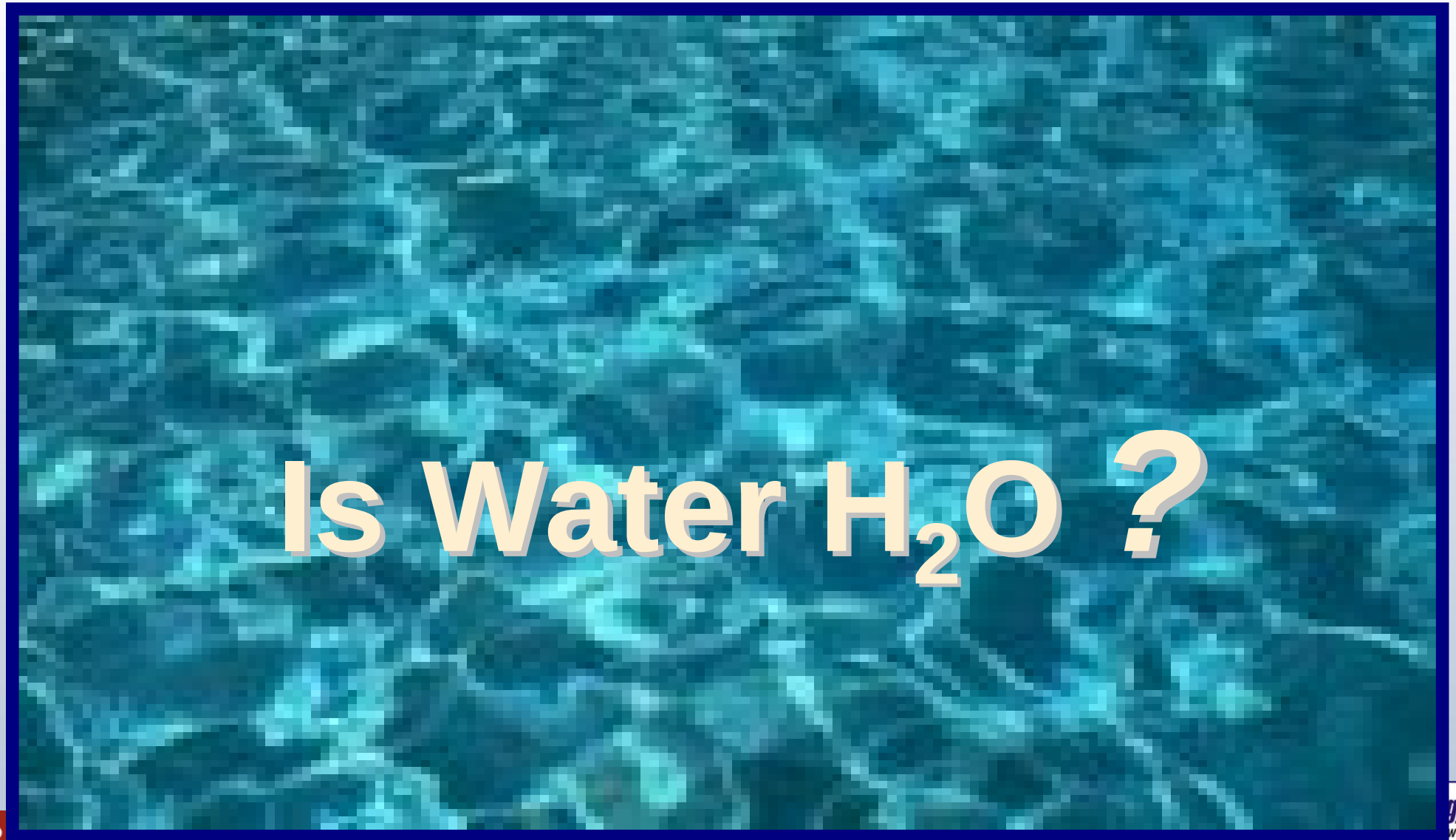
Water H_2O
Properties and Characteristics



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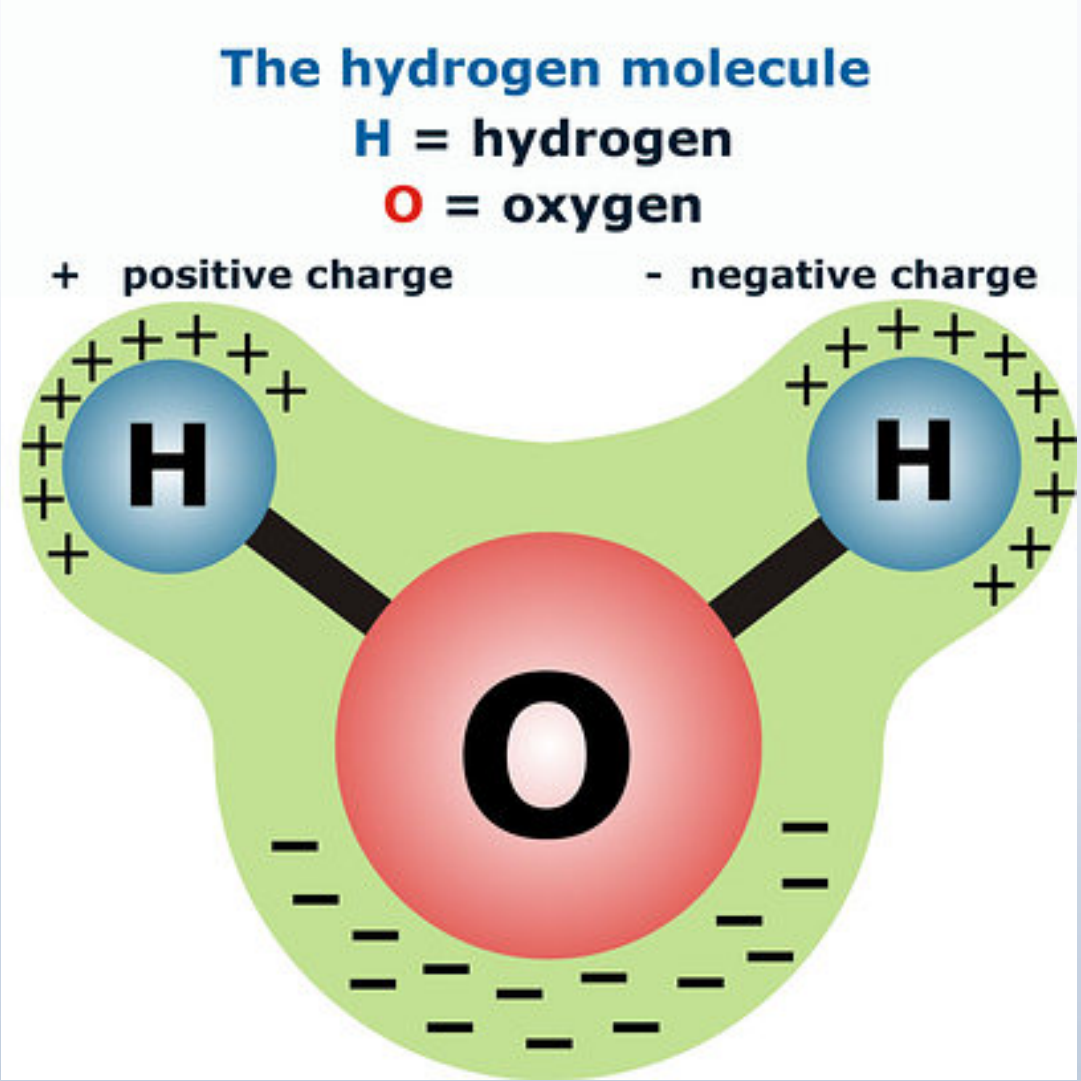
Polarity of Water



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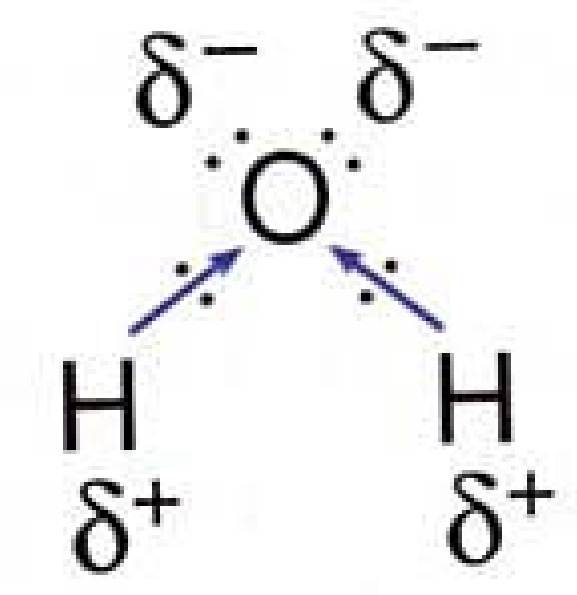
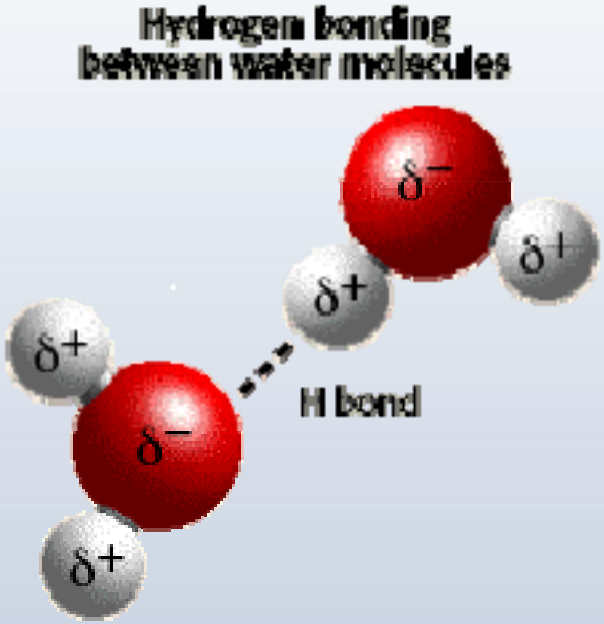
Hydrogen Bonding



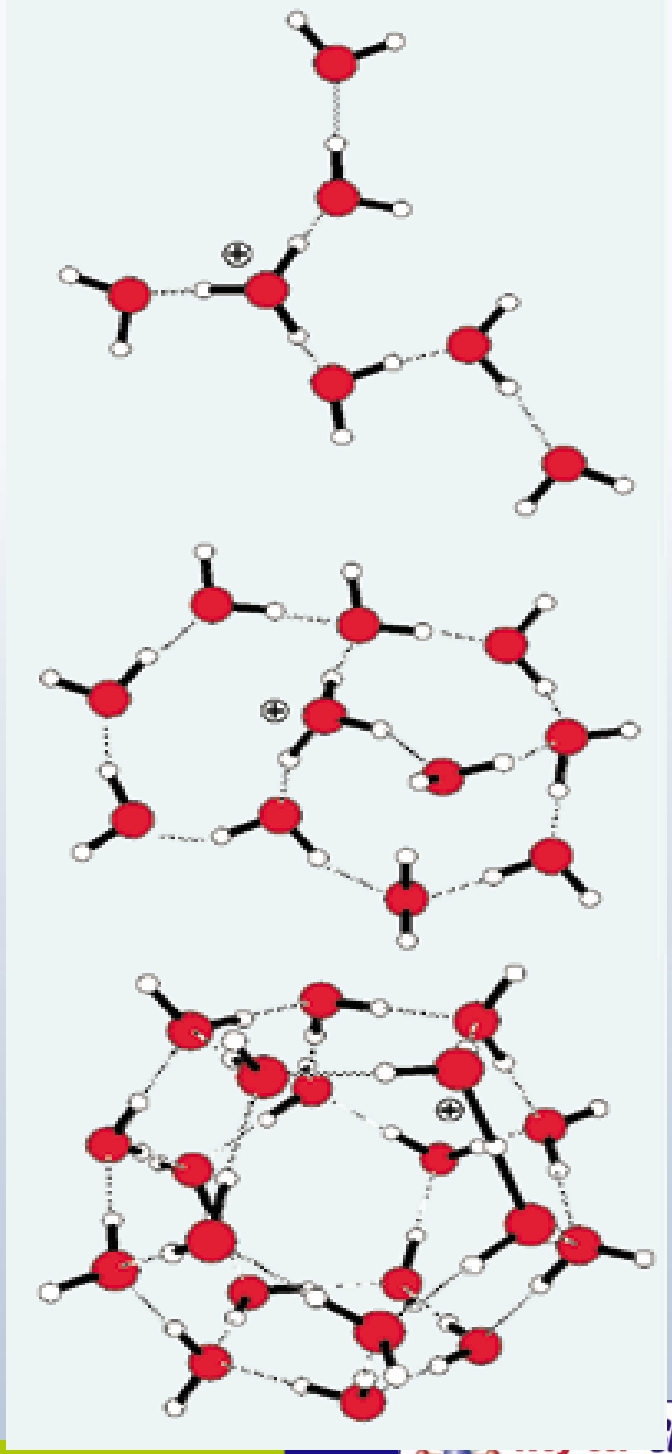


Formation of hydrogen bonds between like water molecules…

This results in the formation of water clusters which can get large in size…

So water is not just H_2O…

So we have to change the way we think about water from a practical stand point.



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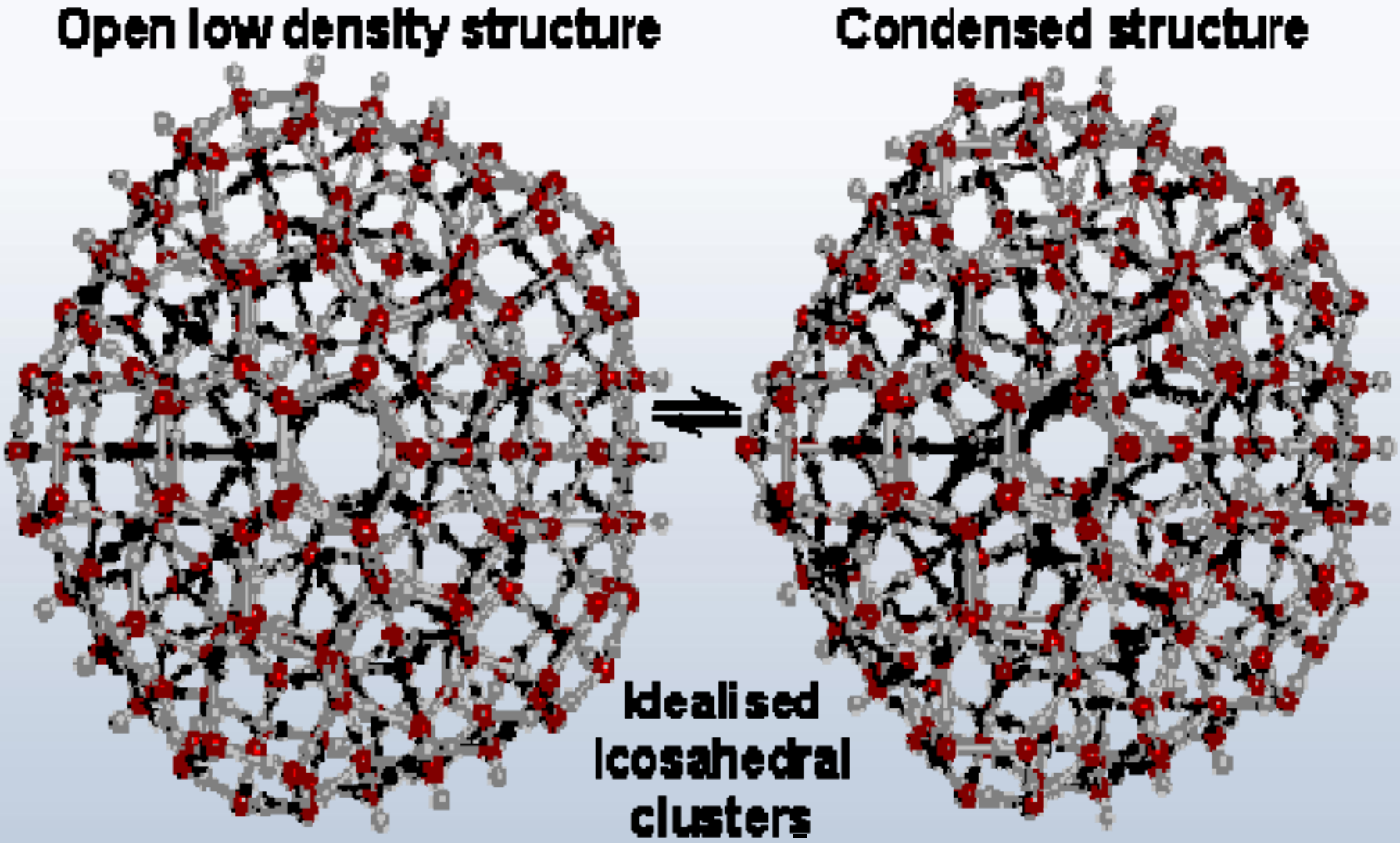

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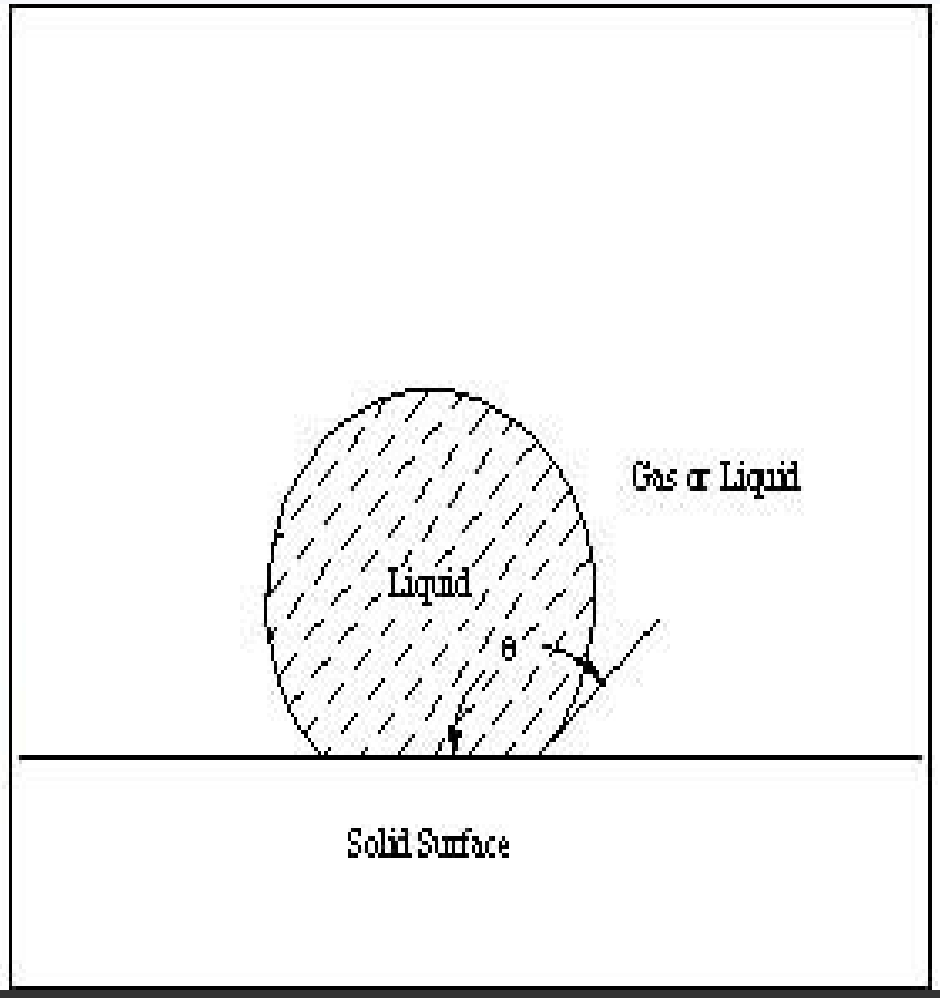
Water Beads - Surface Tension -Water Clustering



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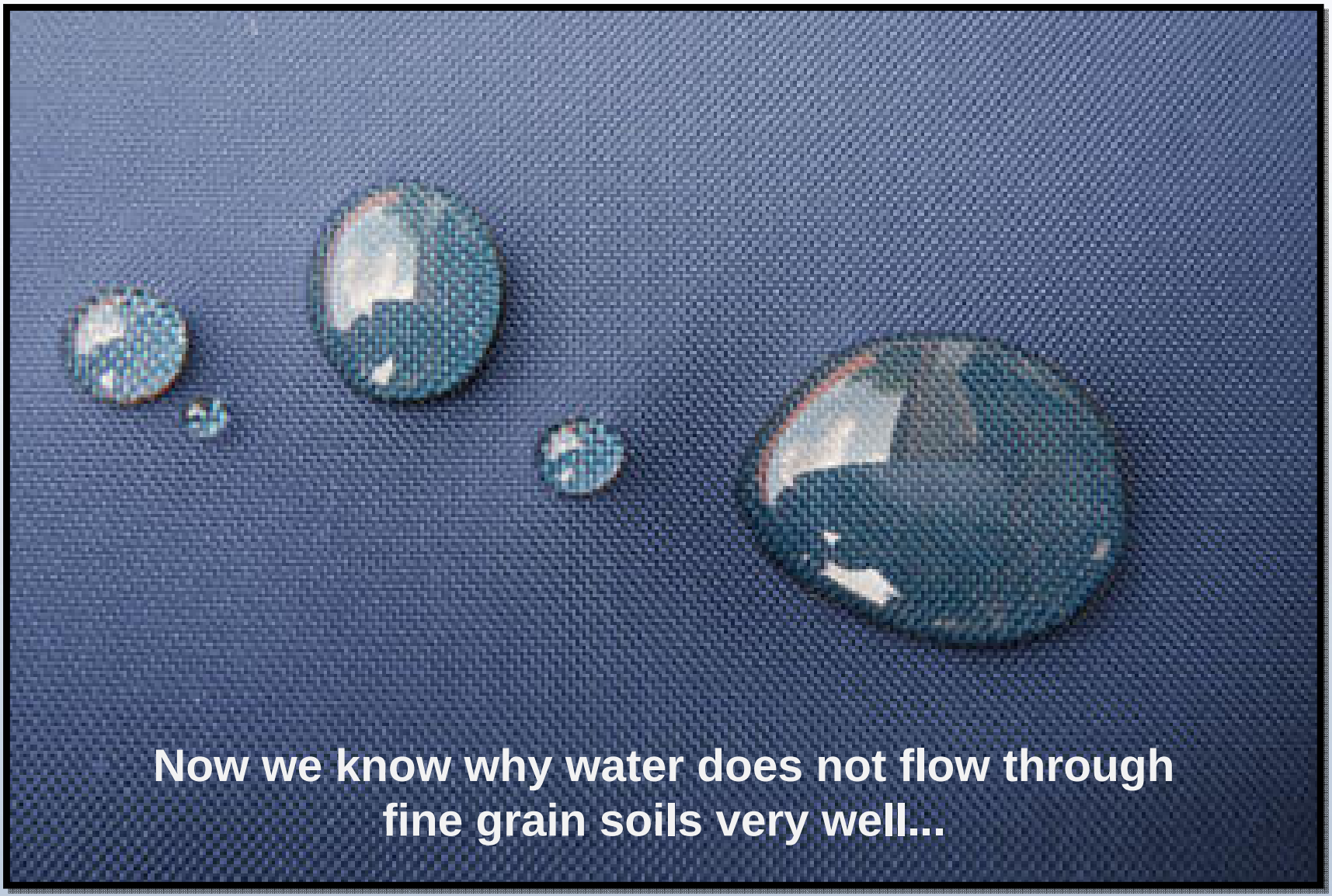
Water Beading On Gortex



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Question

What would happen if you did a bell flop into a pool of Water, or Ethanol , or Mercury?

What would you tell About the Experience afterwards?

Hints:

- In each pool the liquid is 20°C
- Water has a surface tension of 72.8 dynes/cm
- Ethanol (In Beer and Wine) has a surface tension 22.3 dynes/cm
- Mercury has a surface tension of 465 dynes/cm.

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CONTAMINANTS OF CONCERN (COC)

Solubility and Sorption of Contaminants Is A Function of Hydrogen Bonding

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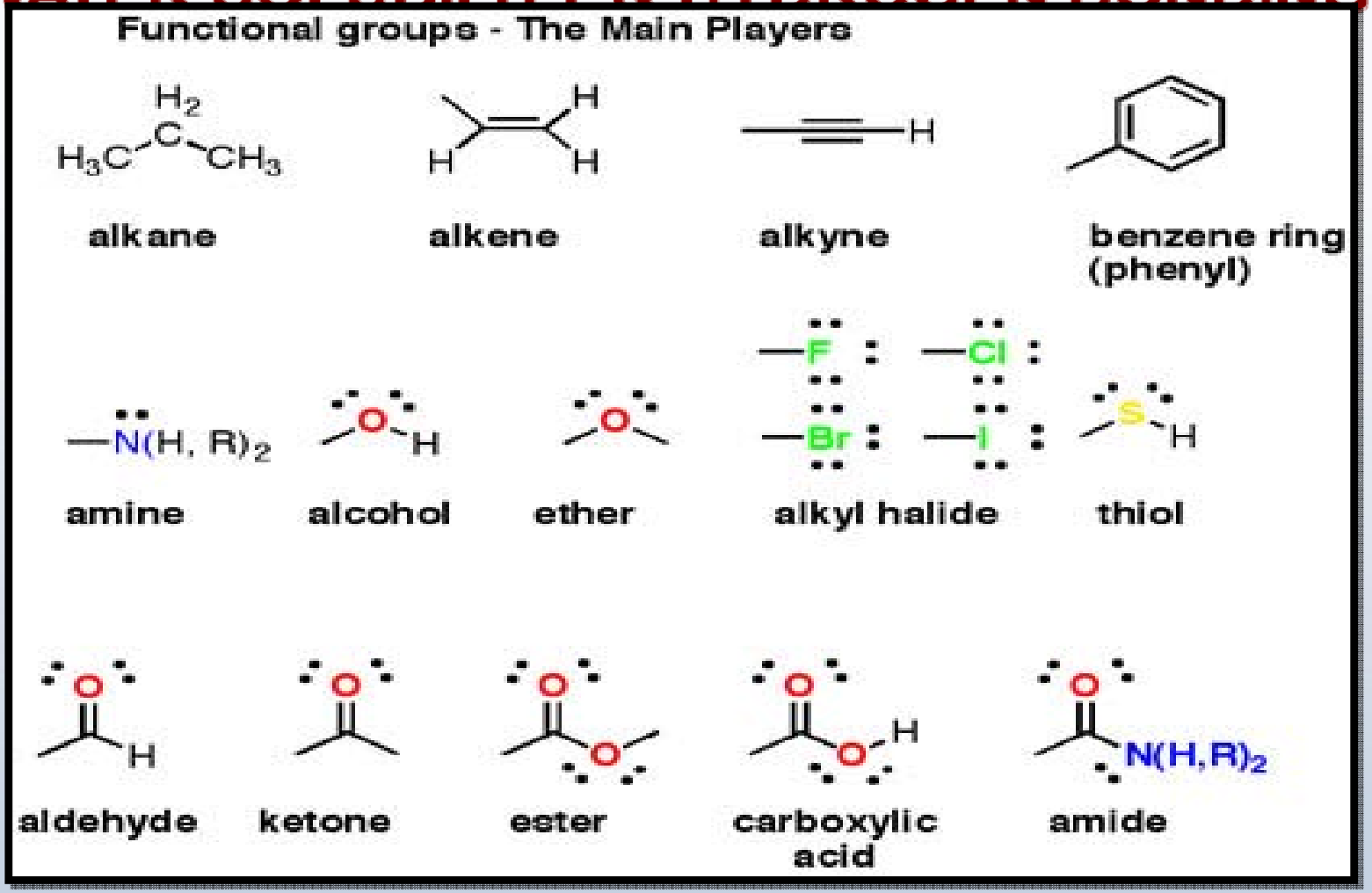
FUNCTIONAL GROUPS

WATER SOLUBILITY & HYDROGEN BONDING



Electronegative atoms in the structure give rise to local polarity and hydrogen bonding opportunities...and increased solubility.

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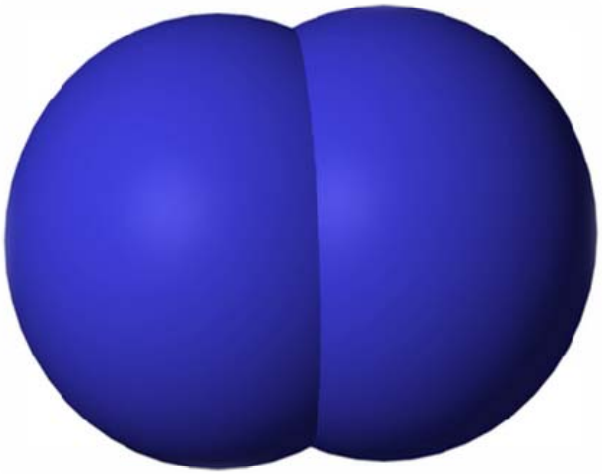
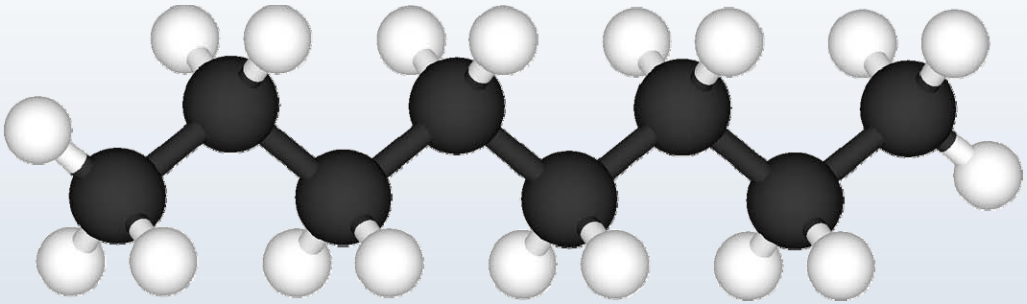
CHEMICAL HAVE THREE (3) CHOICES BE:

NEUTRAL – POLAR – IONIC

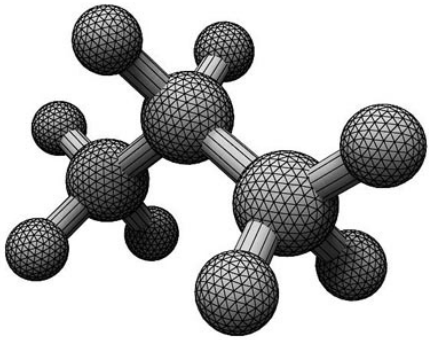
(Attitude & Behaviour)



N_2 Nitrogen



C_8H_{18} Octane



C_3H_8 Propane

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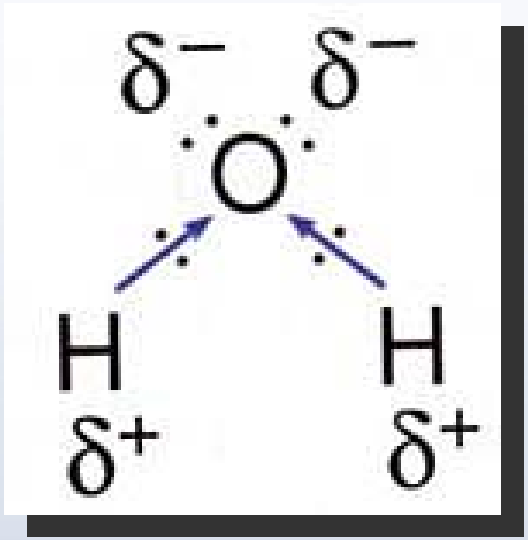
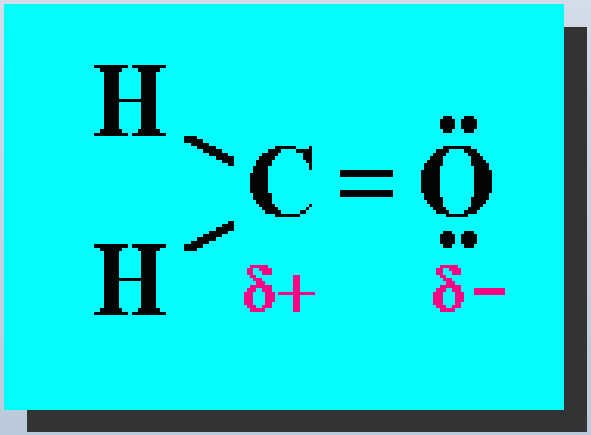
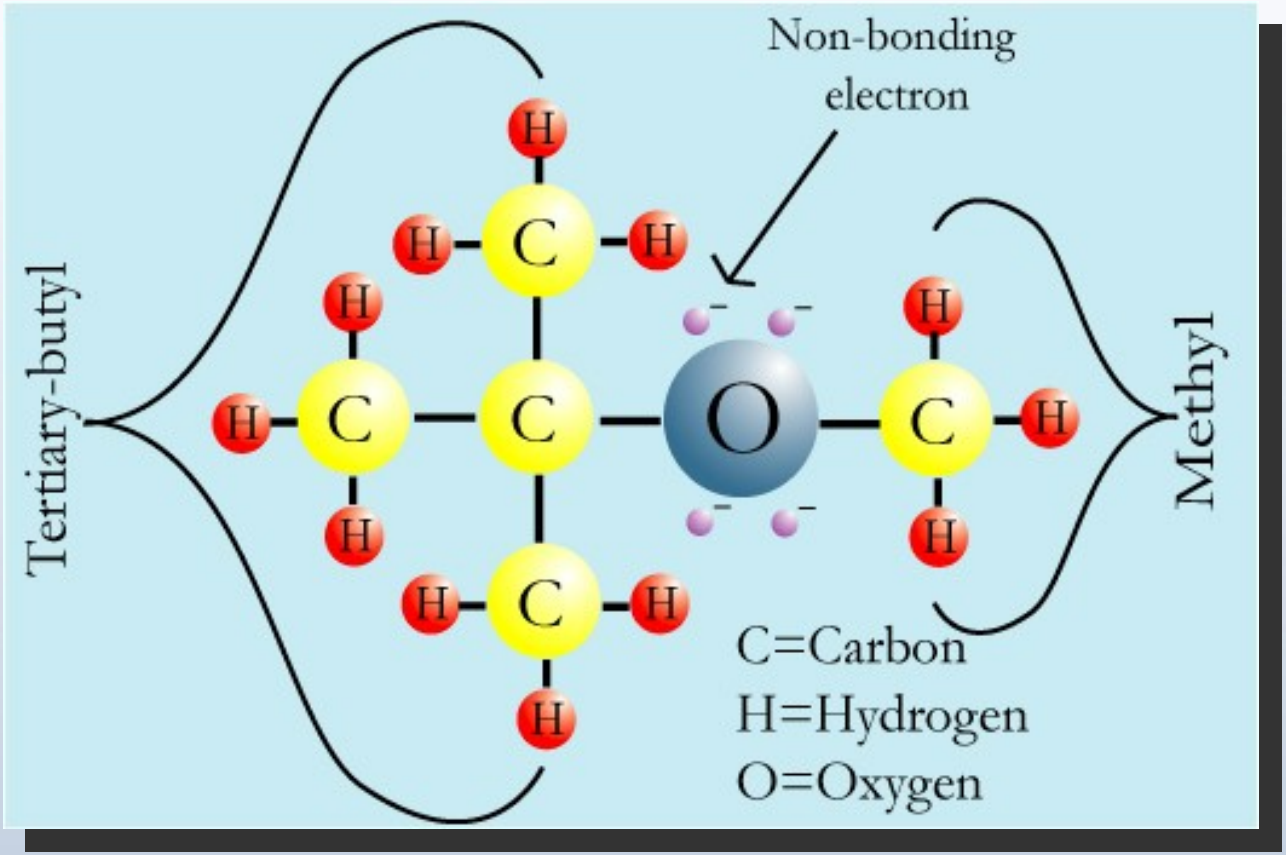
POLAR TO POLAR LIKE



Water



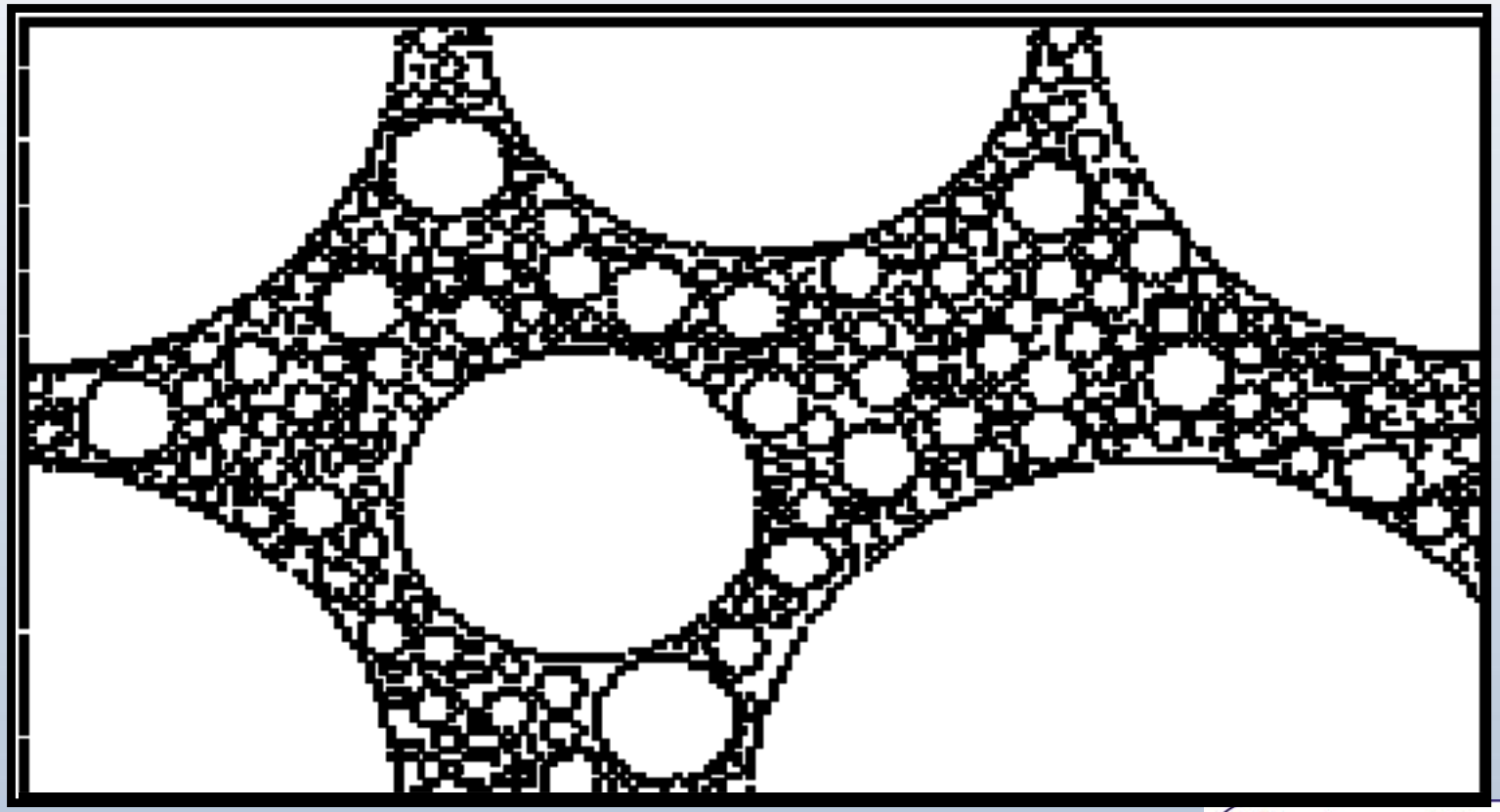
Formaldehyde



MTBE

Sorption (Absorption and Adsorption) of Contamination in Soil Matrix

Soil and water remediation must address this to be successful.



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FACT

>90 to 95 % of all organic contaminants are sorbed to particles in soil, sediment, bedrock and groundwater regimes

•

Contaminant sorption limits '*availability*' of contaminants for Remediation and reclamation

•

Sorption is the #1 reason why many in-situ and ex-situ remediation and reclamation projects are slow, costly, or fail.

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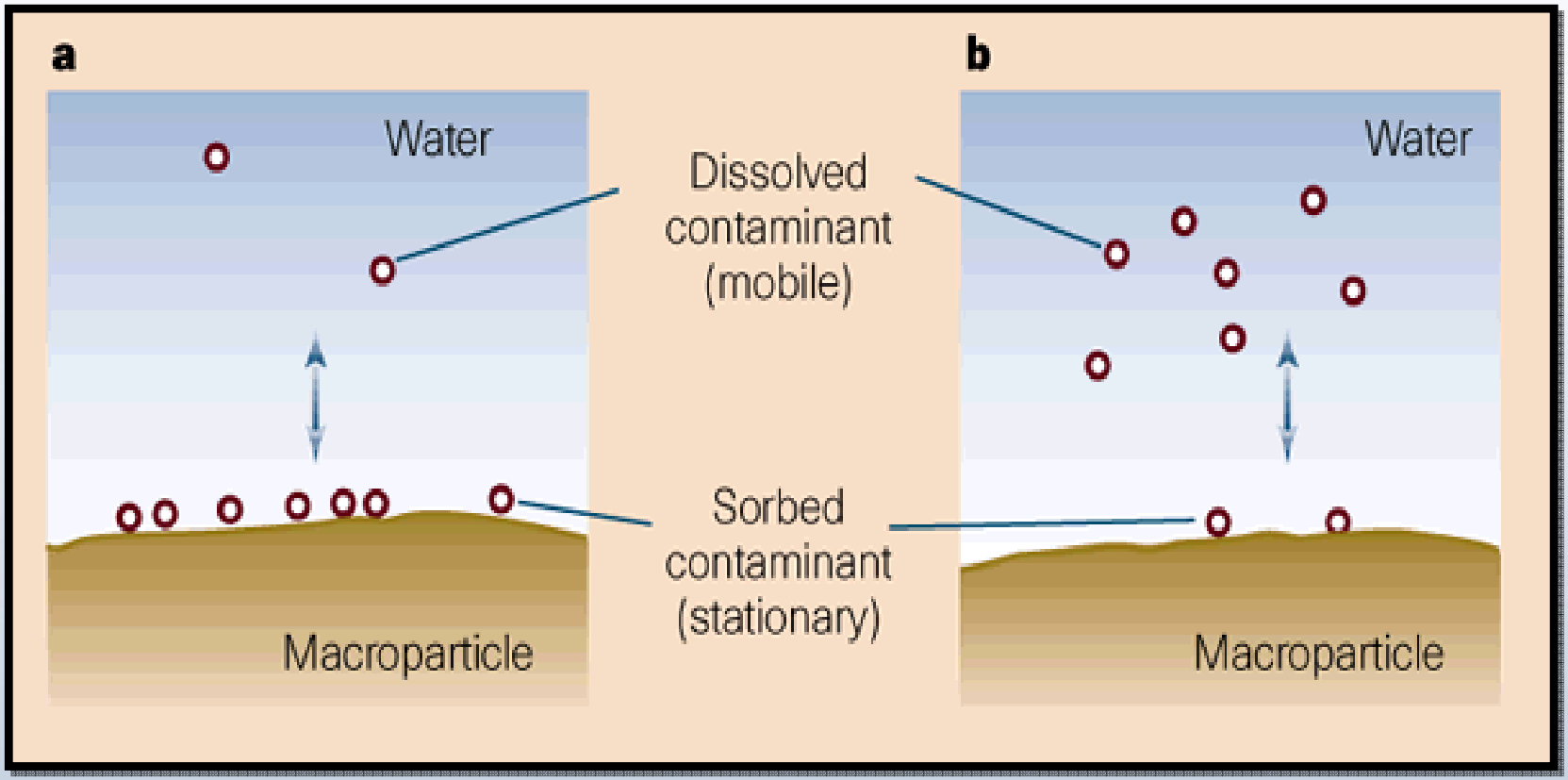
Sorption A Function of Solubility



The lower the Solubility the Greater the Sorption of the Contaminant! This also affects soil and groundwater contaminant transport and associated Plume Dynamics.

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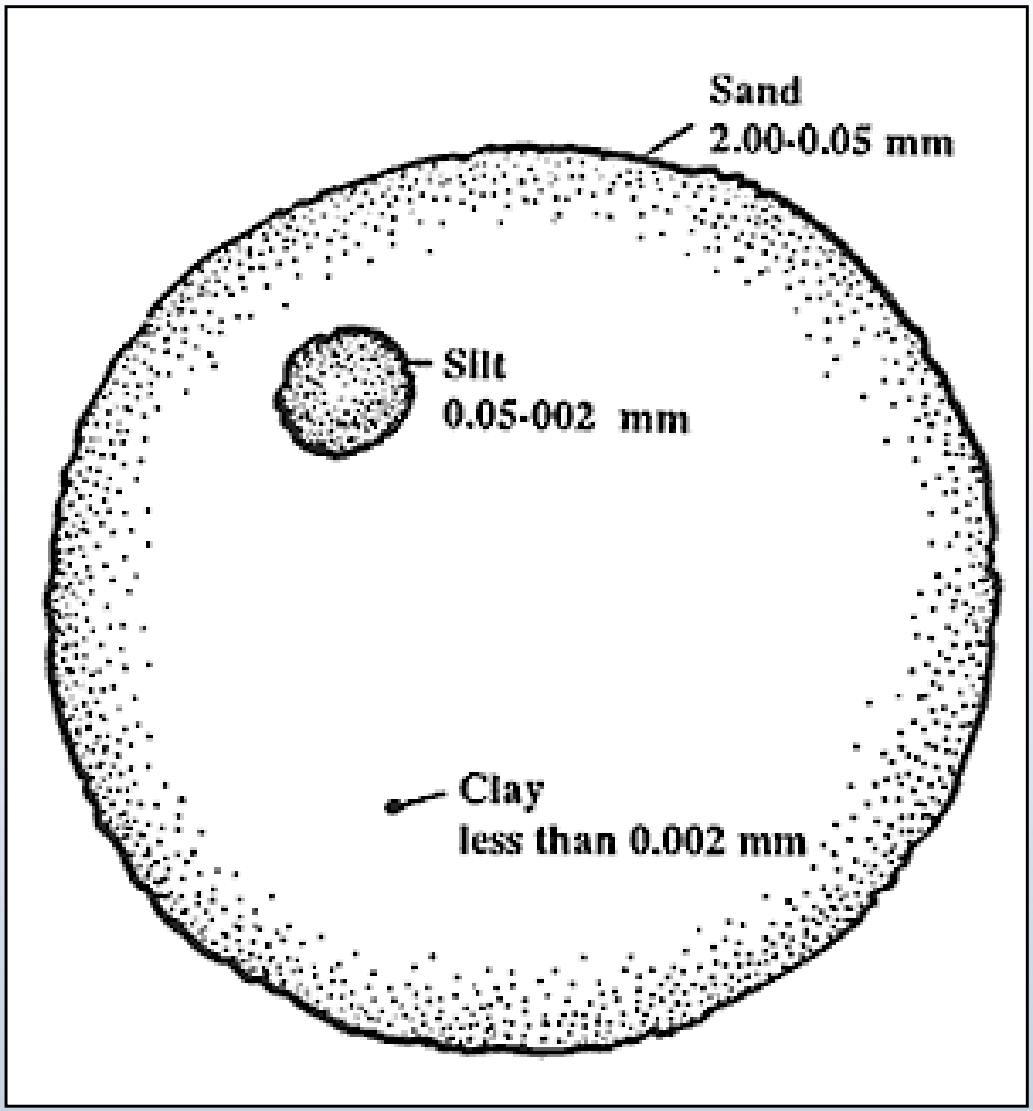

Did You Know ???

Surface Area For Sorption

Coarse Sand = 3 m²

V. Fine Sand = 2.5 NHL Rinks

Coarse Clay = > CFL Football Field!

Finer soils have greater sorption potential!!!

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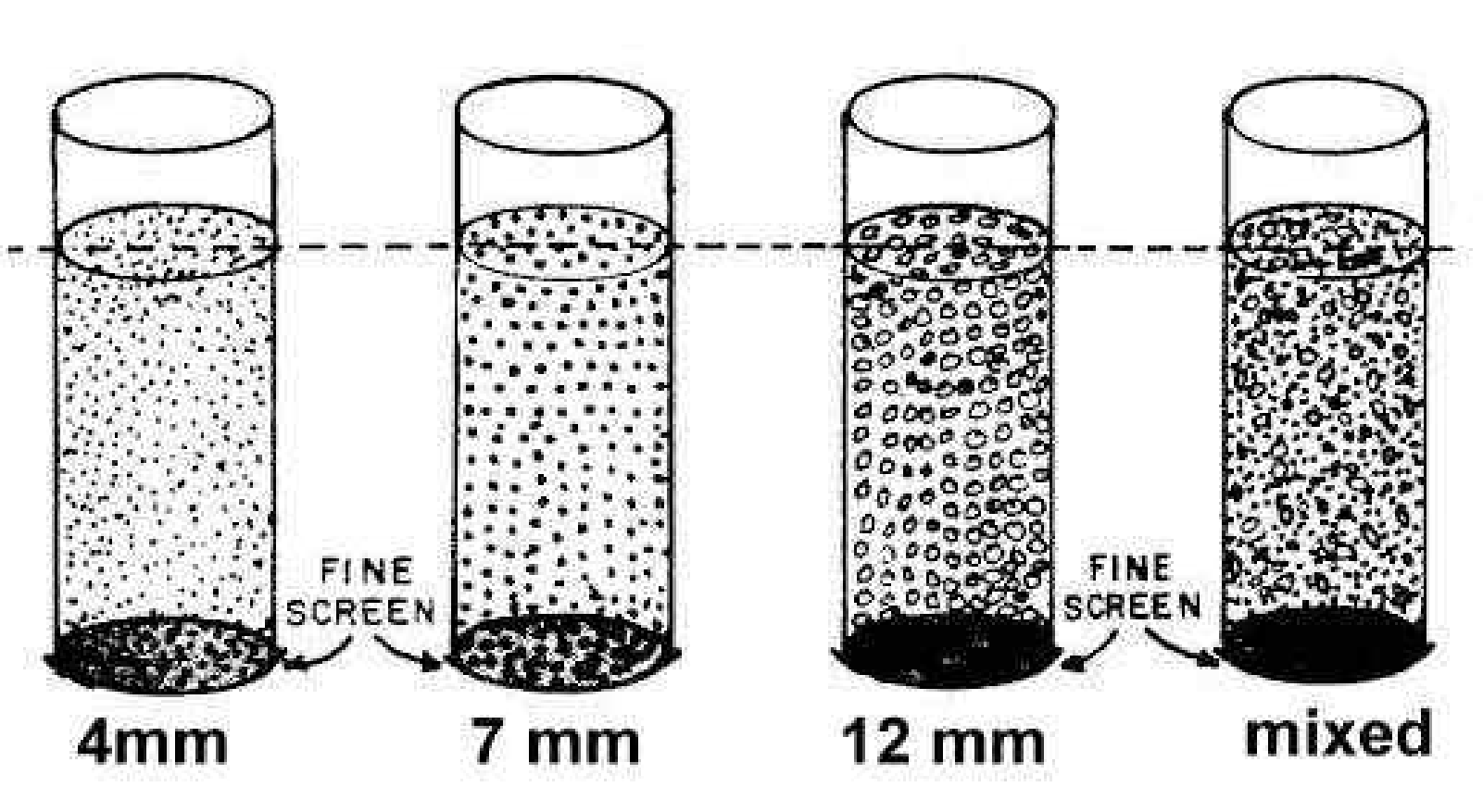
SOIL TEXTURE & SURFACE AREA



- Which soil has the greatest surface area? Why?
- Does this have any significance for sorption?

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Finer grain soils have more surface area for contaminant sorption

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Sorption Demonstration
(Animation)

The following animation sequence displays how sorption can affect two separate particles' velocity over an 18 month period.

Basically, the animation shows a vertical cut from a soil column, interspersed particles of organic matter, and two contaminants that are moving Through the soil matrix.

Discuss why each particle (A & B) behave as they do, and how this affects contaminant transport, and strategies for remediation and reclamation.

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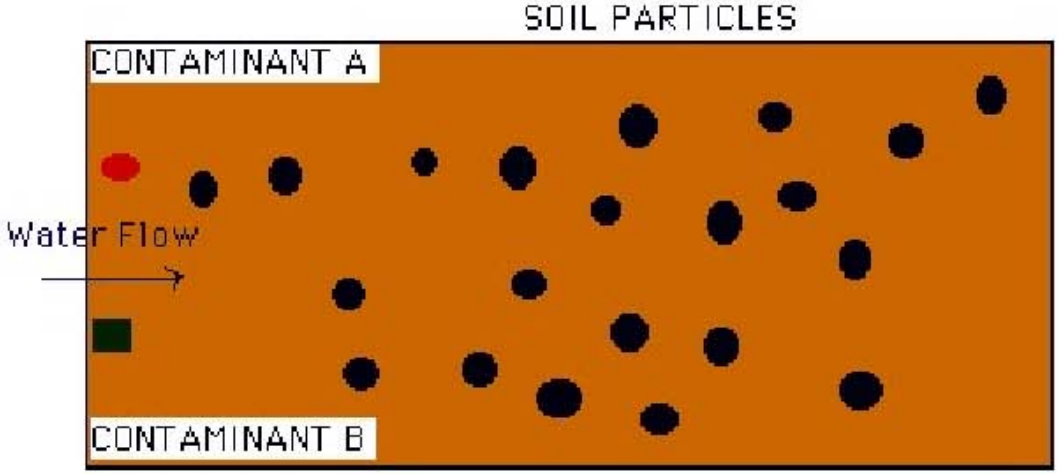
THE VELOCITIES OF TWO CONTAMINANTS
ONE IS SORBING---ONE IS NOT



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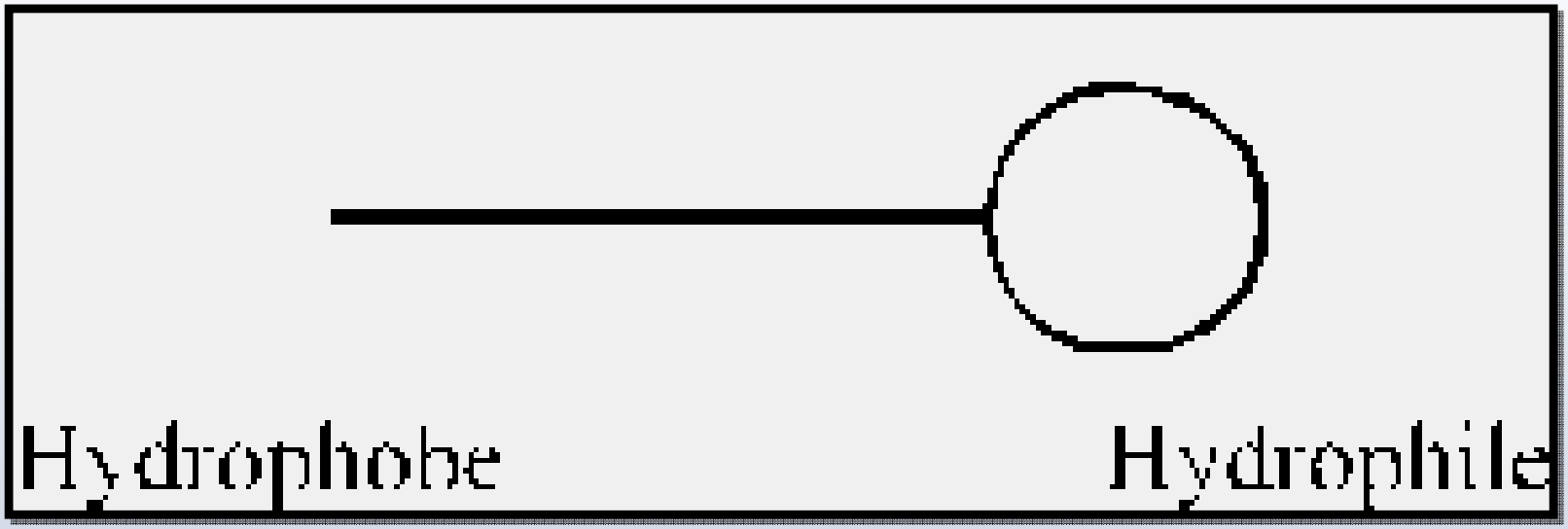
Structure and Definition



Surface Active Agent (SAA), i.e., Hydrophilic (water loving) and Hydrophobic (oil-liking) groupings shown.

Classes Of Surfactants

Anionic: They have one or more negatively charged groupings. They have very Good detergent ability and are commonly used as ***laundry detergent***.

Cationic: They have one or more positively charged groupings. They typically have poor detergency, but are well suited for use as ***germicides, fabric softeners, and emulsifiers***.

Amphoteric: They contain both anionic and cationic groupings and have the characteristics of both anionic and cationic SAA. They work well at neutral pH and are found in products such as ***hair shampoo, skin cleaners, and carpet shampoo***.

Non-ionic: **As** their name implies, they have no ionic constituents or groupings. **They are the largest single group of SAA and have a correspondingly wide range of chemical characteristics and application.** SPTT mixtures, which have the unique ability to selectively dissolve LNAPL, DNAPL, polycyclic aromatic hydrocarbons (PAHs), dichloroethane (DCE), trichloroethane (TCE), perchloroethylene (PCE) and other similar petroleum products.

The first three classes are collectively know as Ionic Surfactants.

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Surfactants Lower the Surface Tension of Water from 72 Dynes to <30 dynes

This increases the wetting ability of the water when present, making surfactant application possible in fine grain soils improving water permeability (K).

Can make the water clusters smaller!

Recall Exercise I at beginning of the class.

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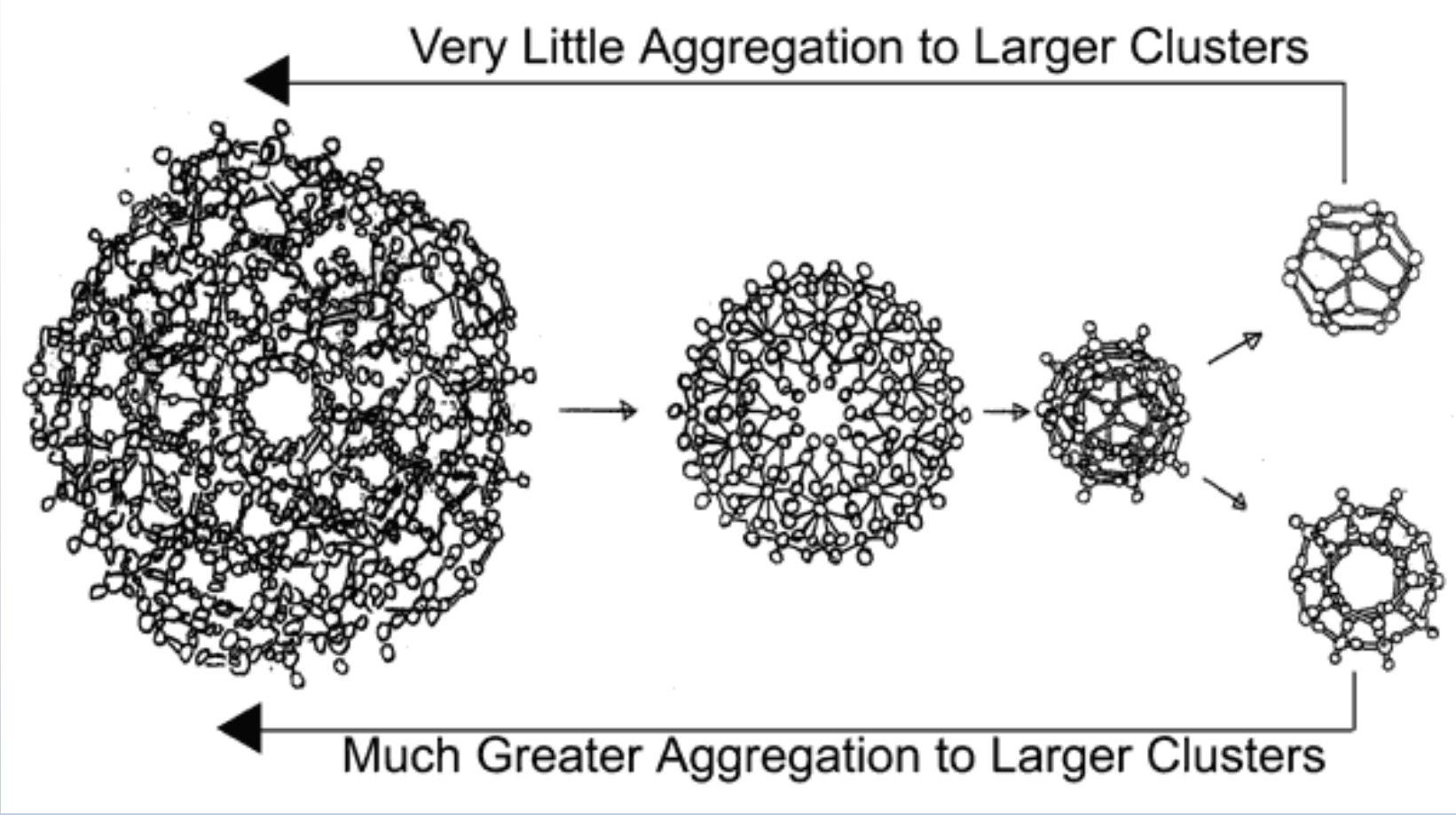
WATER CLUSETR AGGREGATION



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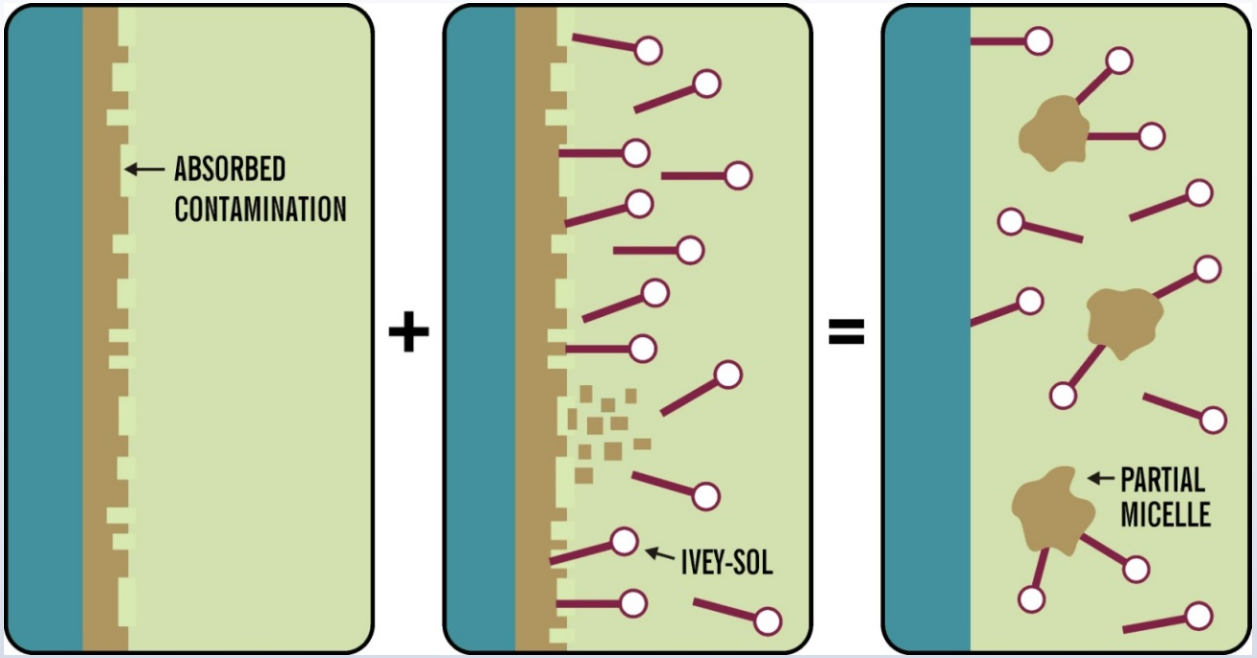
MECHANISM



Surfactant Interaction with Organic (NAPL) on a Surface with Partial Micelle Encapsulated of Oil Droplet (some surfactants are effective below CMC)

The NAPL is now more '*Available*' for remediation!

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'Surfactant Flushing Research to Remove Organic Liquids from Aquifers', Groundwater Currents, March 1994. EPA 542-N-92-002

► Soil column experiments were conducted to test the ability of a non-ionic surfactant to recover entrapped dodecane.

► ***After injecting a 4% surfactant solution, the concentration of the dodecane exiting the column increased by 100,000 times.***

► *Removal of the 10% of the residual dodecane required 0.7 litres of surfactant solution, while comparable recovery without surfactant would have required 130,000 L of water*. Numerical models were developed to explore the optimal surfactant strategies based on the flow rate, flushing time, and volume of surfactant required to remove NAPLs from soil.

Think about P&T Sites That Take 7 to 10 Years!
With Ivey-sol it often takes only 7 to 10 months!

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Surfactant Enhanced Remediation (SER)

Implications For Contaminated Site Remediation & Reclamation

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APPLICATION RANGE

LNAPL

Full LNAPL (F_1,F_2, F_3, and F_4) range including: BTEX, gasoline, diesel, motor oil, Bunker-C, MTBE, PAHs, etc.

DNAPL

25 Fold (+) increase in solubility and recovery rate. This includes compounds like: PCE, PCB, TCE, TCA, CTC, TCM, PCP, and various other Cl / Br solvents

Heavy Metals

Transition metals, including organo-metallic complexes, and radio-active metals associated with NORMS.

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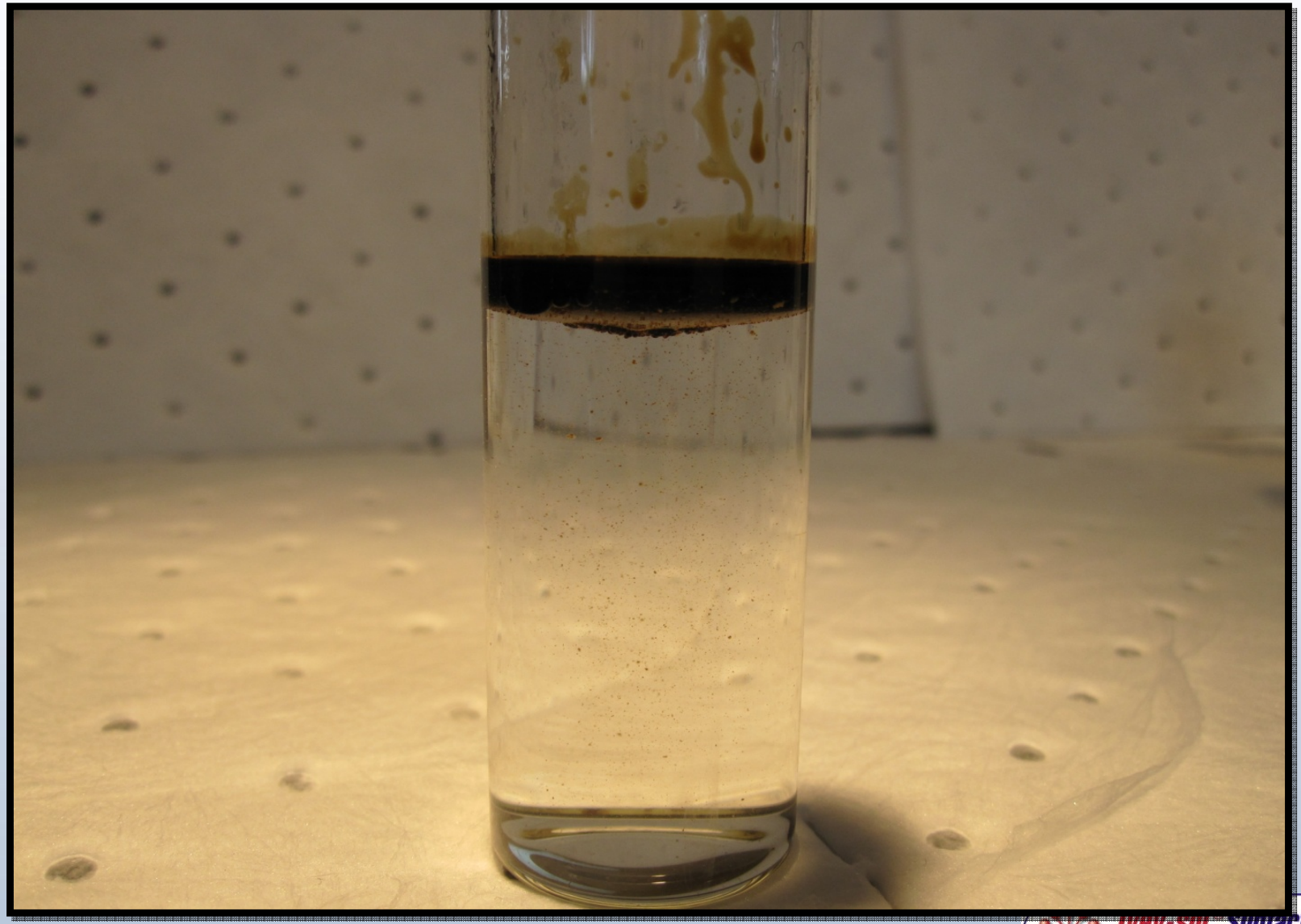
CRUDE OIL



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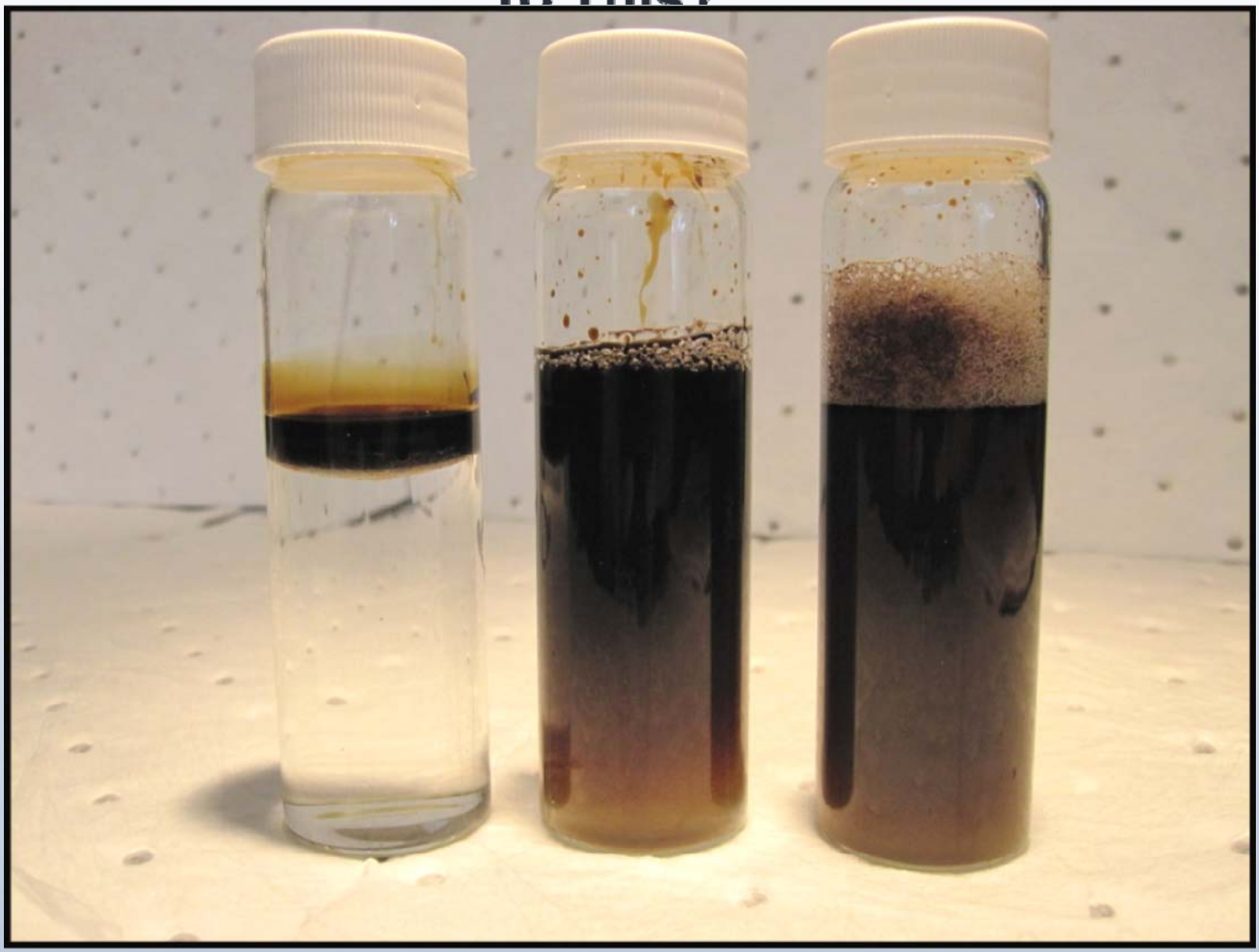
To This?



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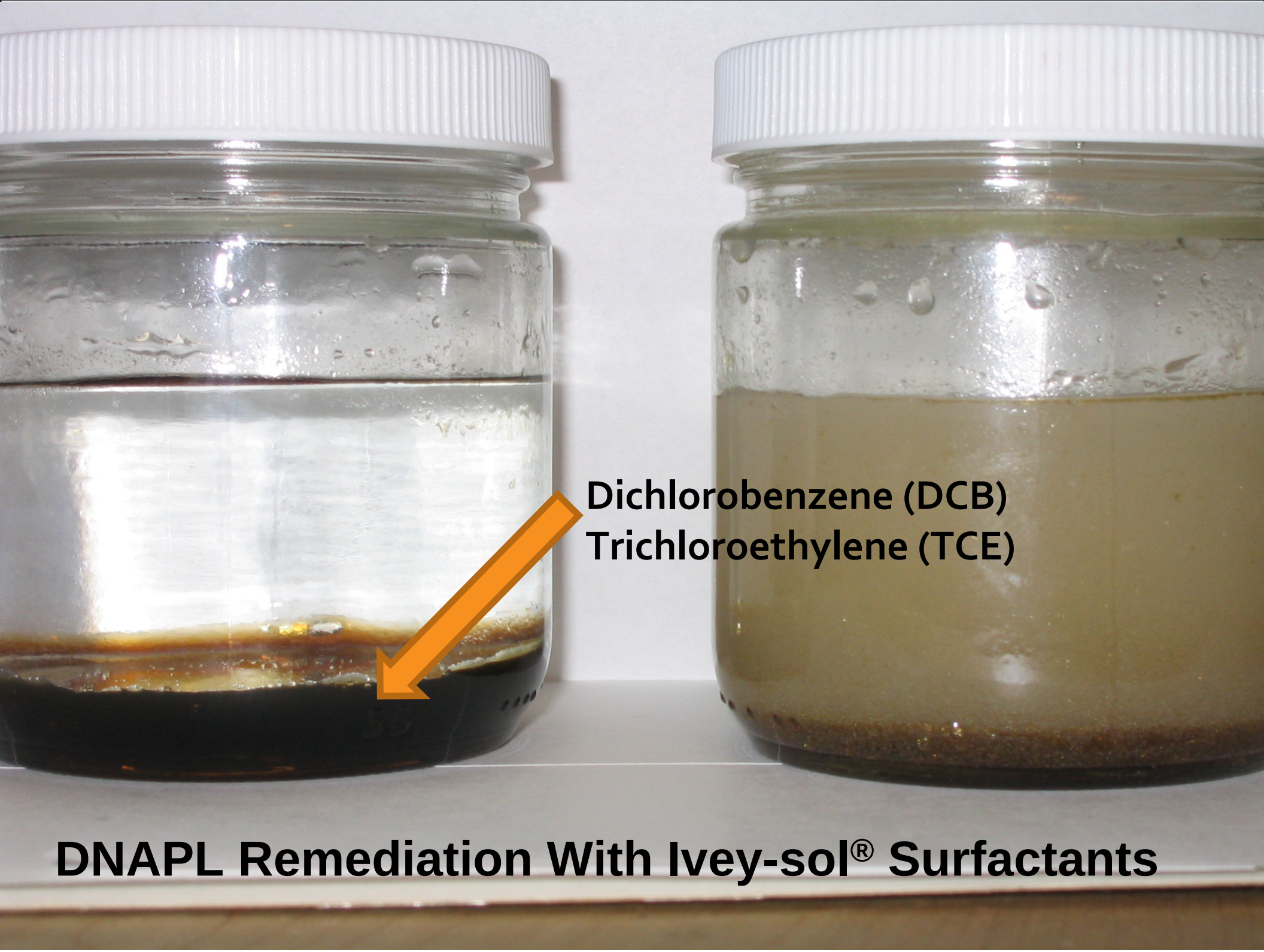

DNAPL Remediation With Ivey-sol® Surfactants

Presentation Outline

- High Vacuum Dual Phase Extraction
- Surfactant Chemistry
- Site Conditions & Pilot Test Approach
- Pilot Test Results
- Questions

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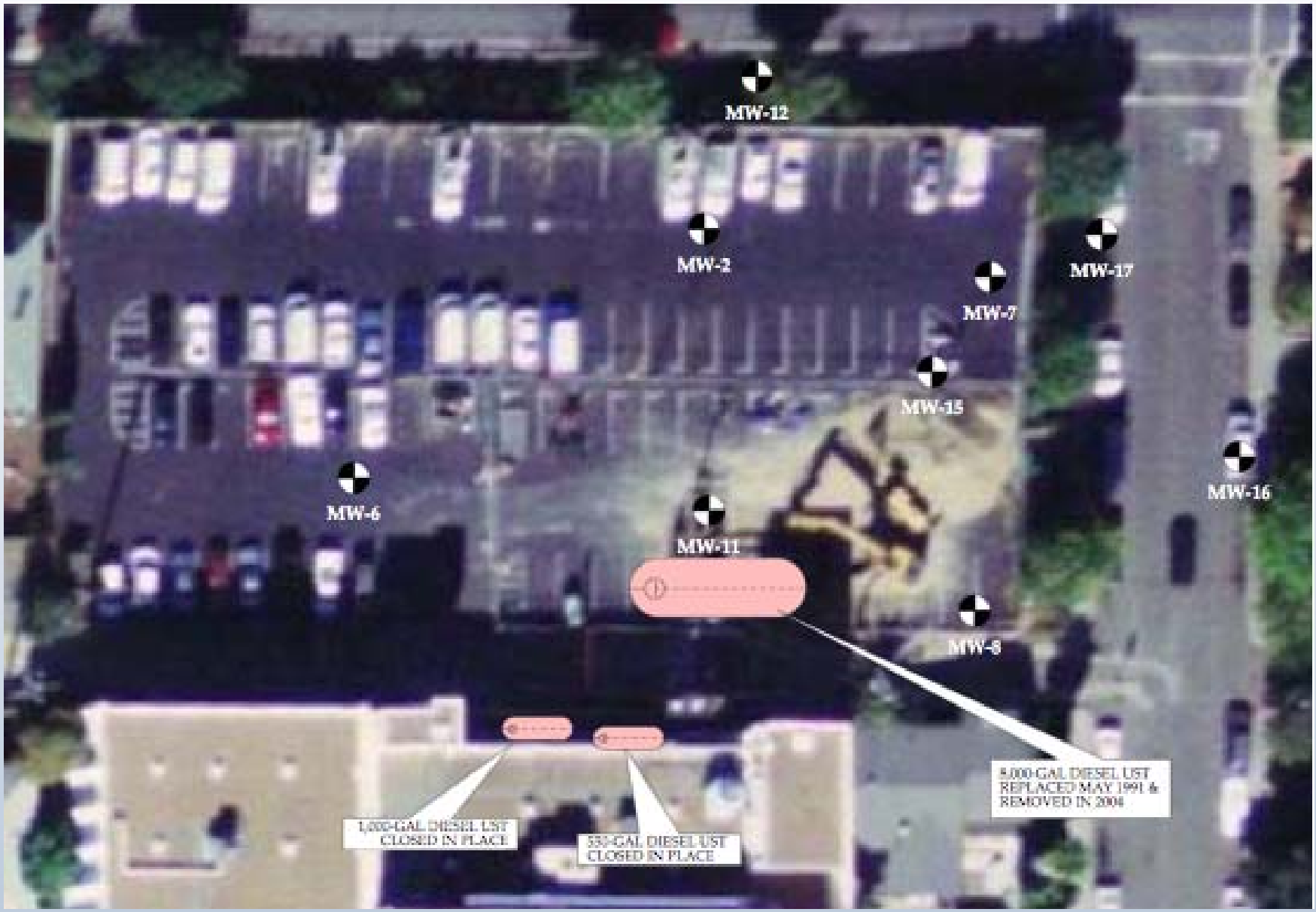
The Site



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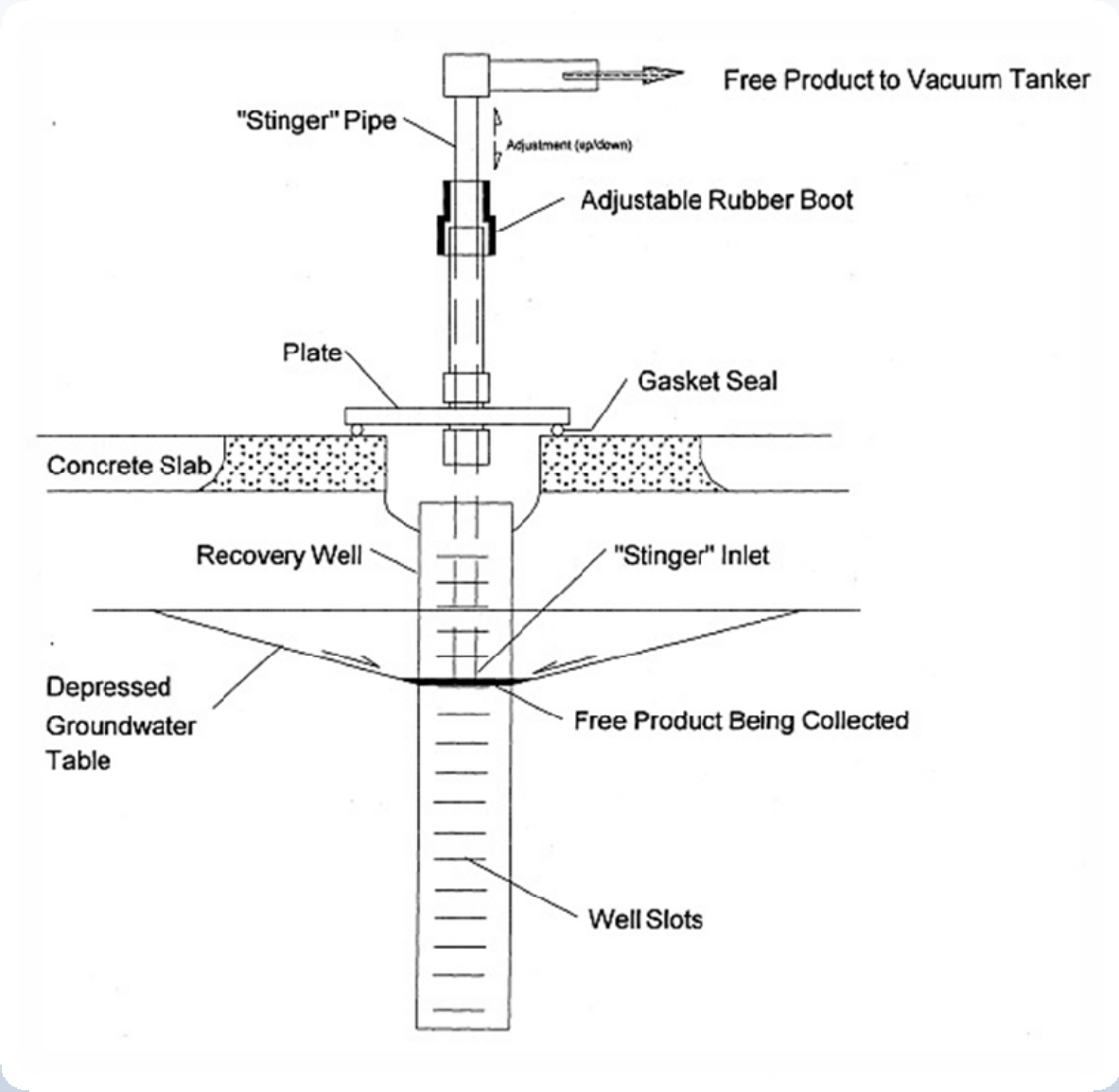

HVDPE Extraction Well

Diagram shows radius of influence and potential LNAPL collection

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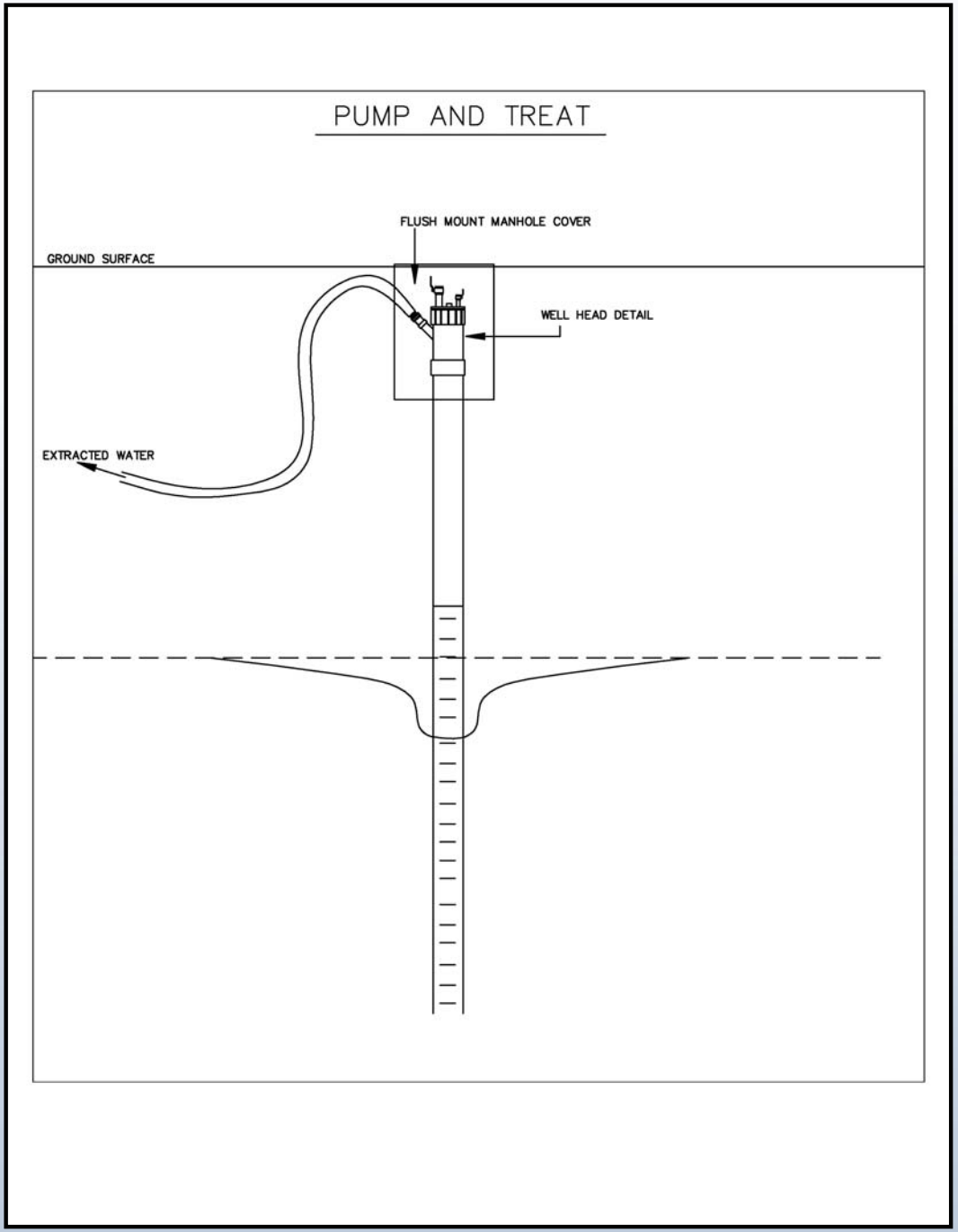
Standard Pump & Treatment drawdown.

Creates an unsaturated zone.

Often requires higher pumping rates to affect and maintain ROI.

The unsaturated zone can be a source of contaminant rebound.



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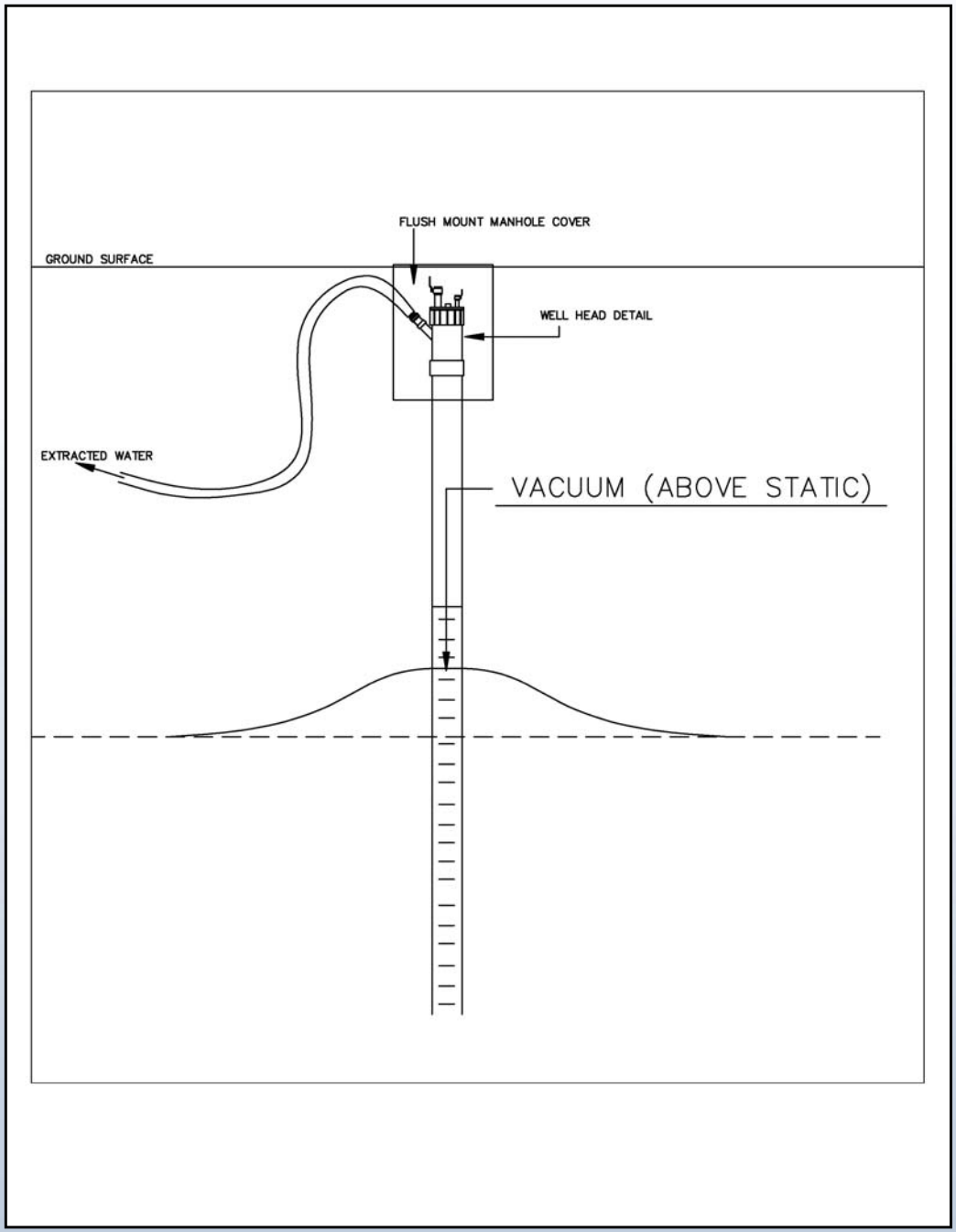
HVDPE
(Multi-Phase Extraction)

This targets the contaminants in both the saturated and unsaturated zone (flexible).

The ROI is controlled by the distribution of vacuum.

ROIcan be achieved with low flow rates.



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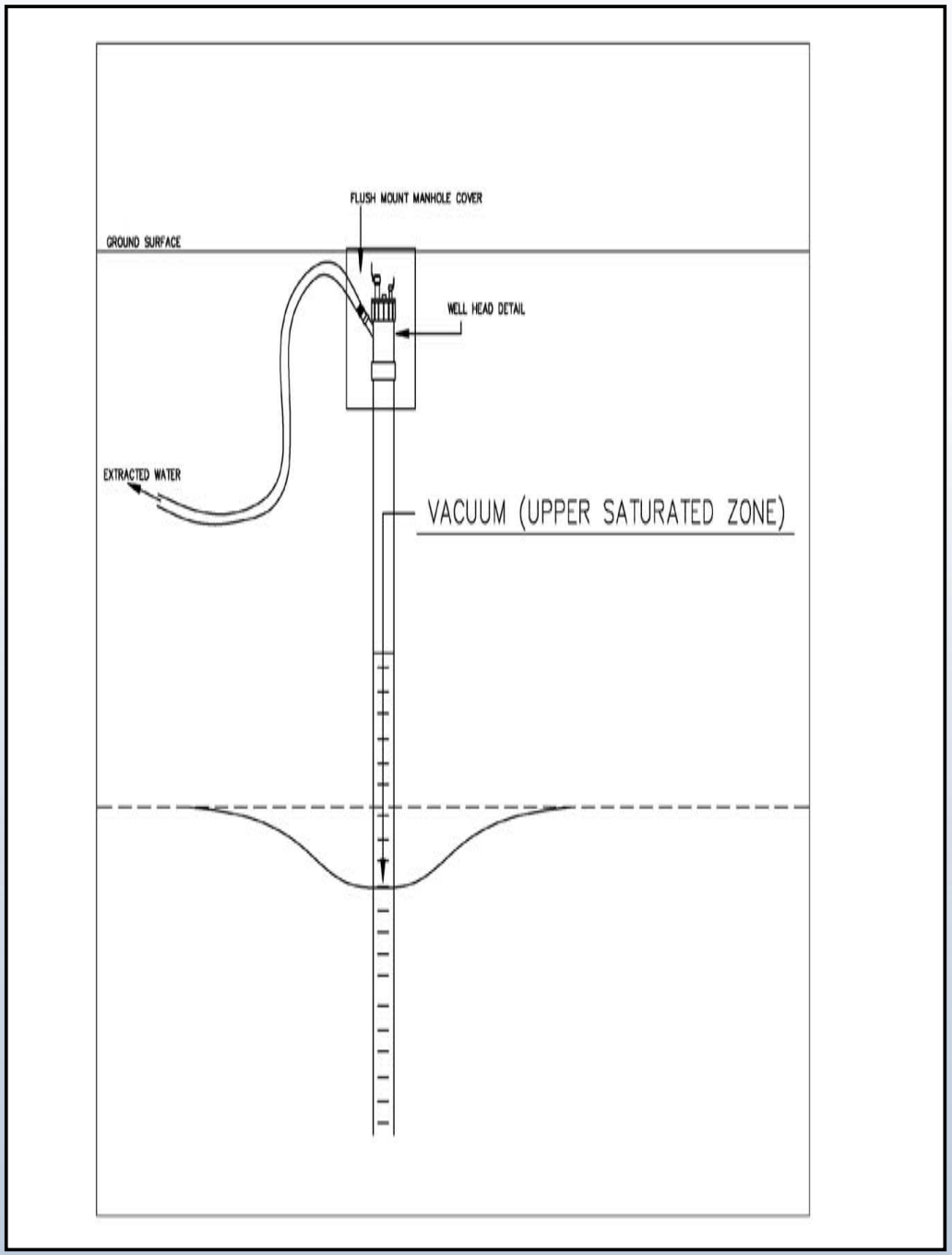
This represent HVDPE conditions.

ROI is well maintained with low pumping rates.

HVDPE vacuum position allows flexibility in ensuring a saturated zone condition for Ivey-sol surfactant application.

The Ivey-sol® surfactants desorb the sorbed phase under these condition for enhanced mass recovery.

This also resolved rebound issues.



Practical Vacuum Effect on GW Extraction

- Static Groundwater Level = 45 ft (13.7 m) MSL
- Dynamic Groundwater Level under pumping conditions = 50 ft (15.24 m) MSL
- Vacuum Effect on Groundwater Extraction raised water table approx. 5ft (1.52 m) in MW-6 and approx. 10 ft (3.05 m) in MW-7
- Flow rate kept 0.24 gpm (0.91 lpm) throughout the pilot test

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On-site Photos

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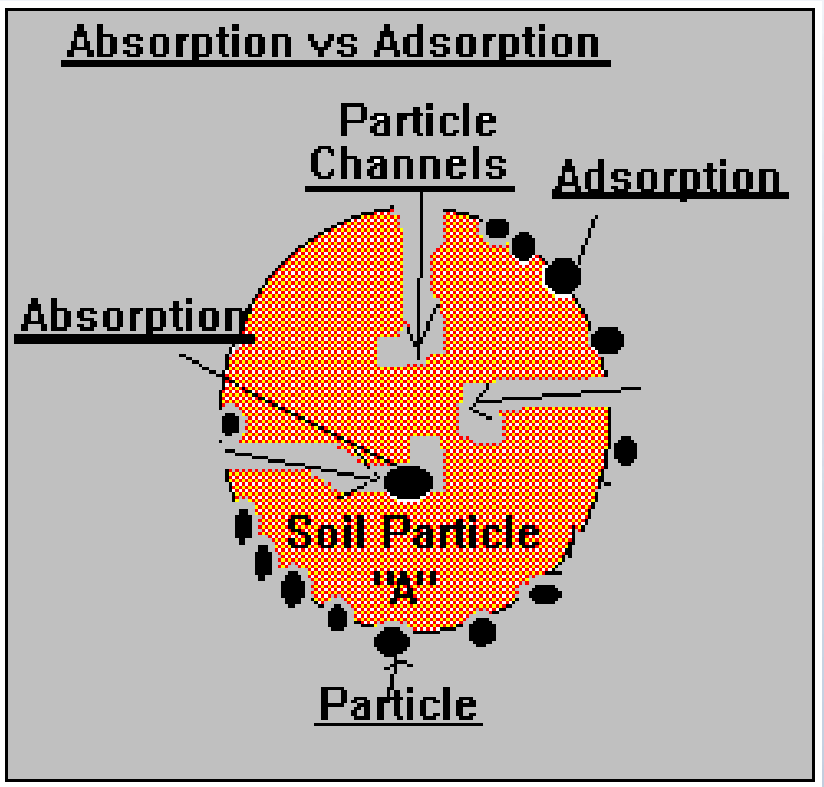
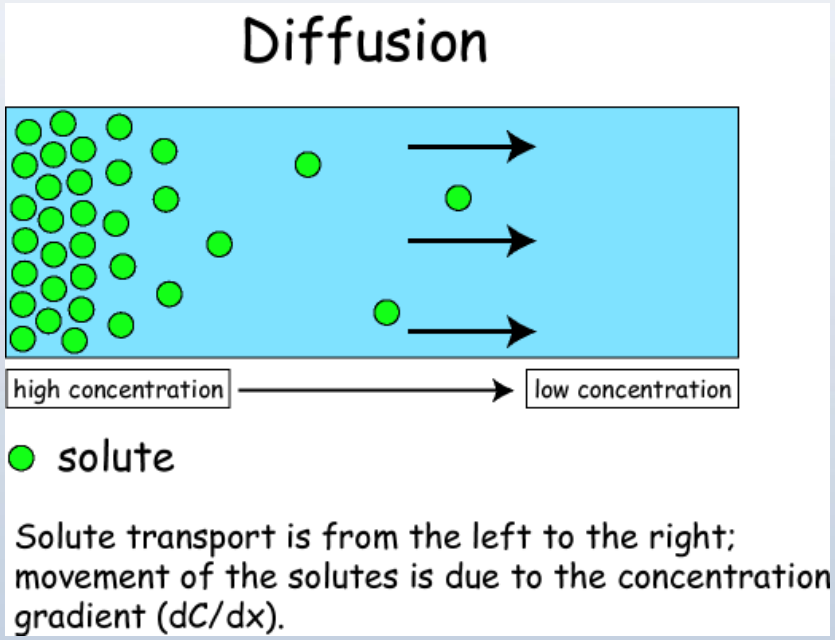
Remediation Challenge

Sorption >>>

>>Desorption or Diffusion





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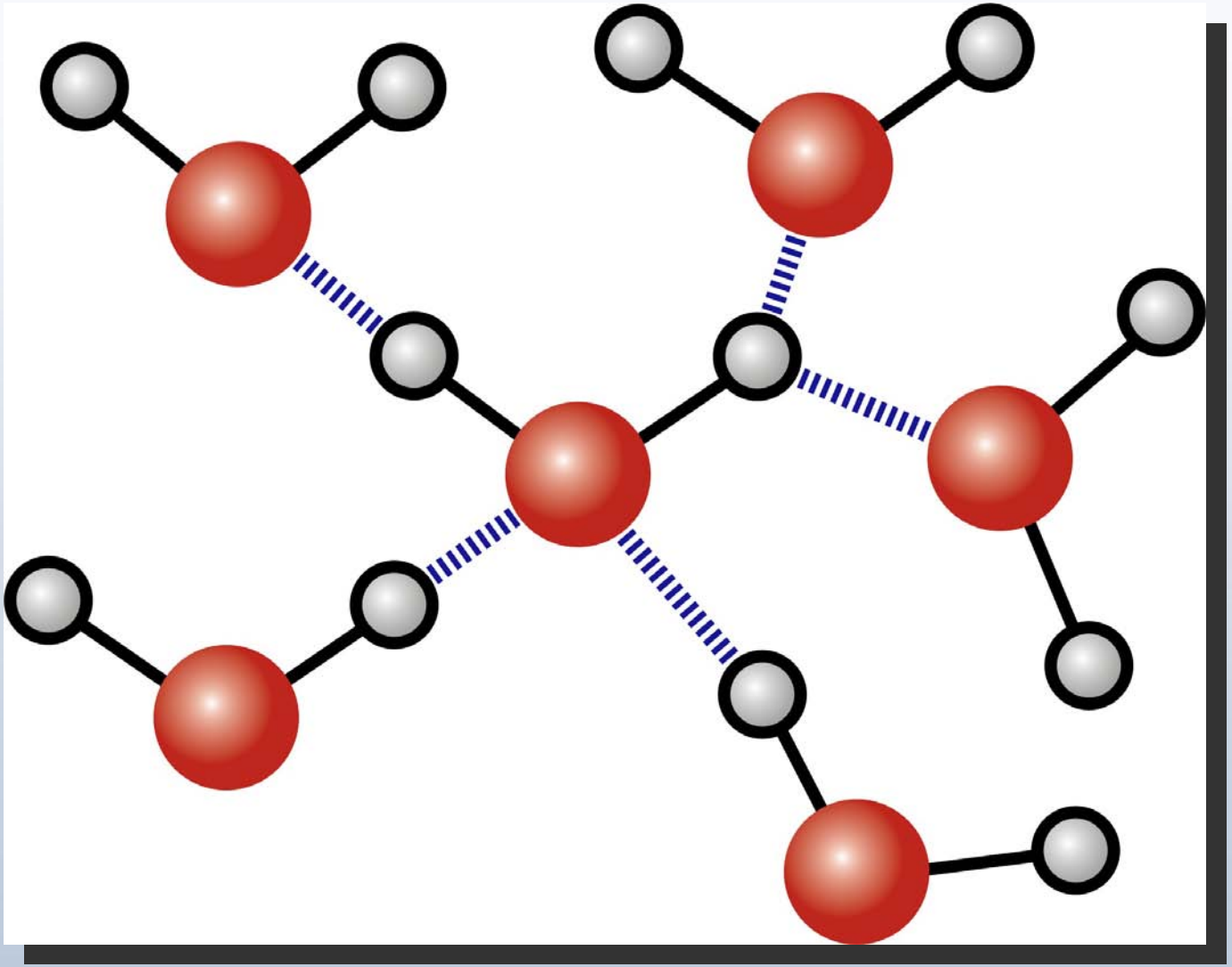
Did You Know ???
Water Is Not H_2O



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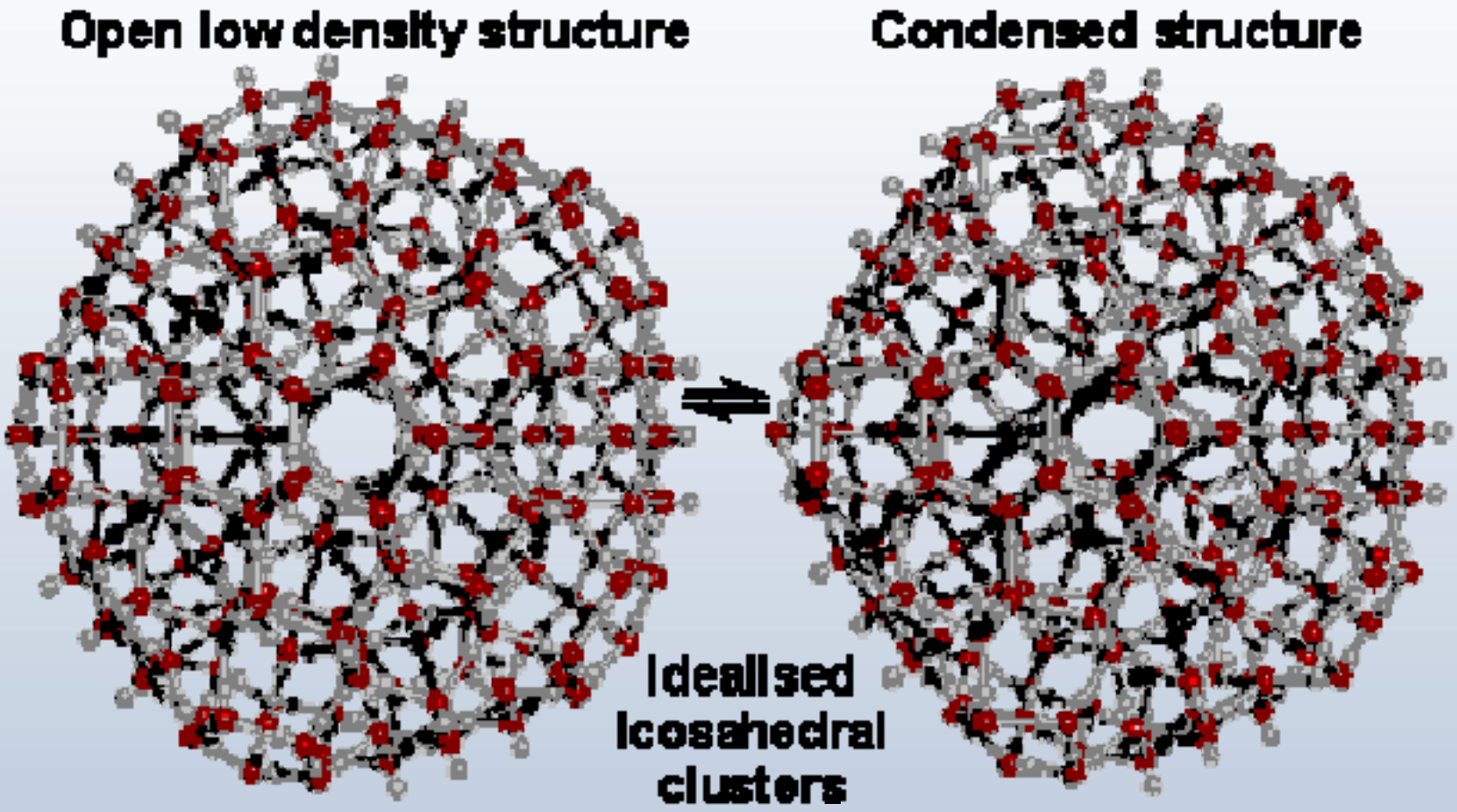
Water Is Actually a Three Dimensional Cluster



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Why a Surfactant?

- **Improves desorption of target contaminants** from soil
- **Lowers the surface tension of water** improving both its wetting and associated permeability (K) properties
- Effective as a stand alone technology for soil washing
- Effective to improve other remediation techniques (i.e., P&T, Bioremediation, Chemical Oxidation, etc.)

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It's all about contact…with the contaminant

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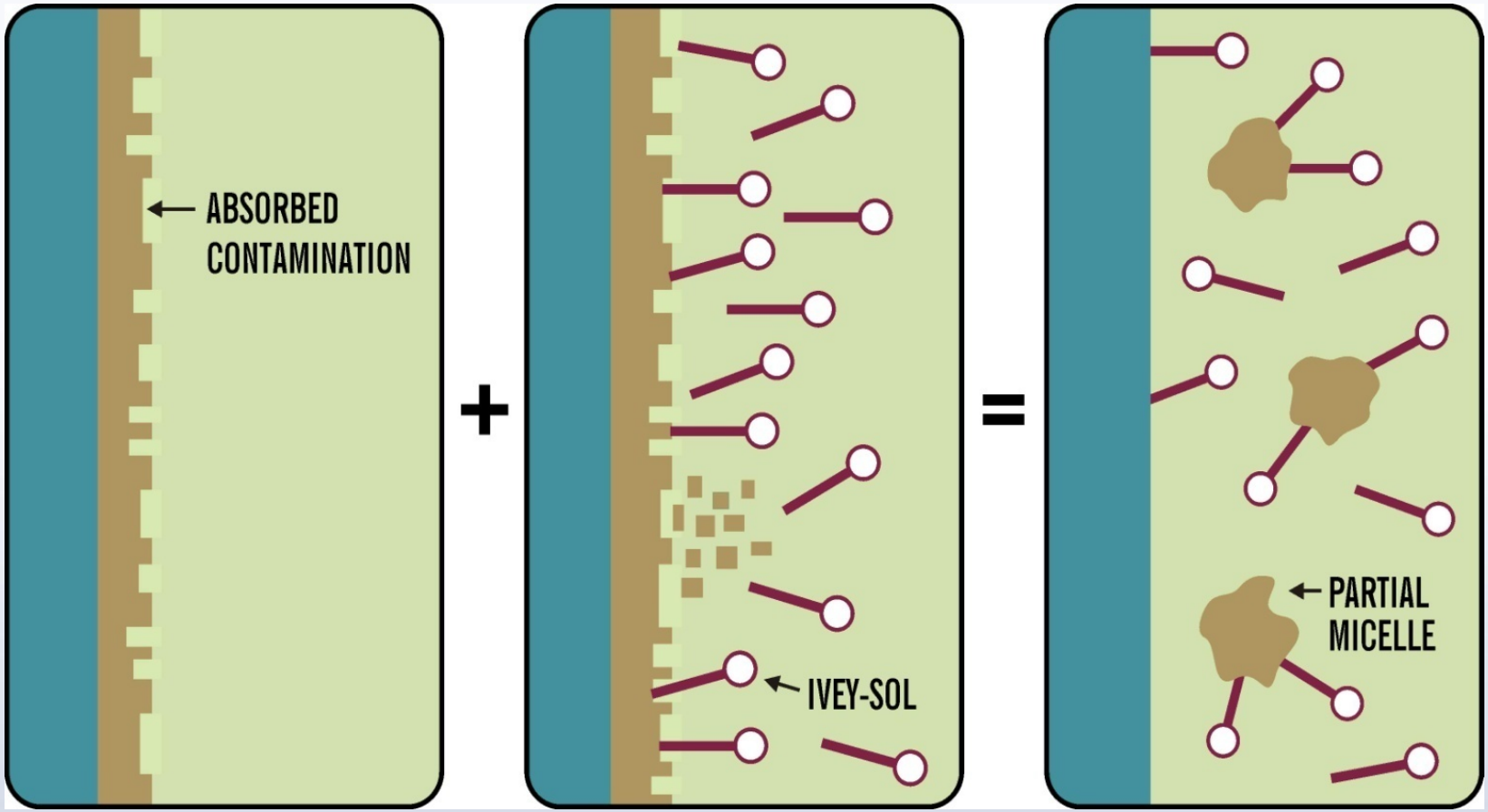

Surfactant Interaction with DNAPL. Helps dissolve DNAPL into pore space.

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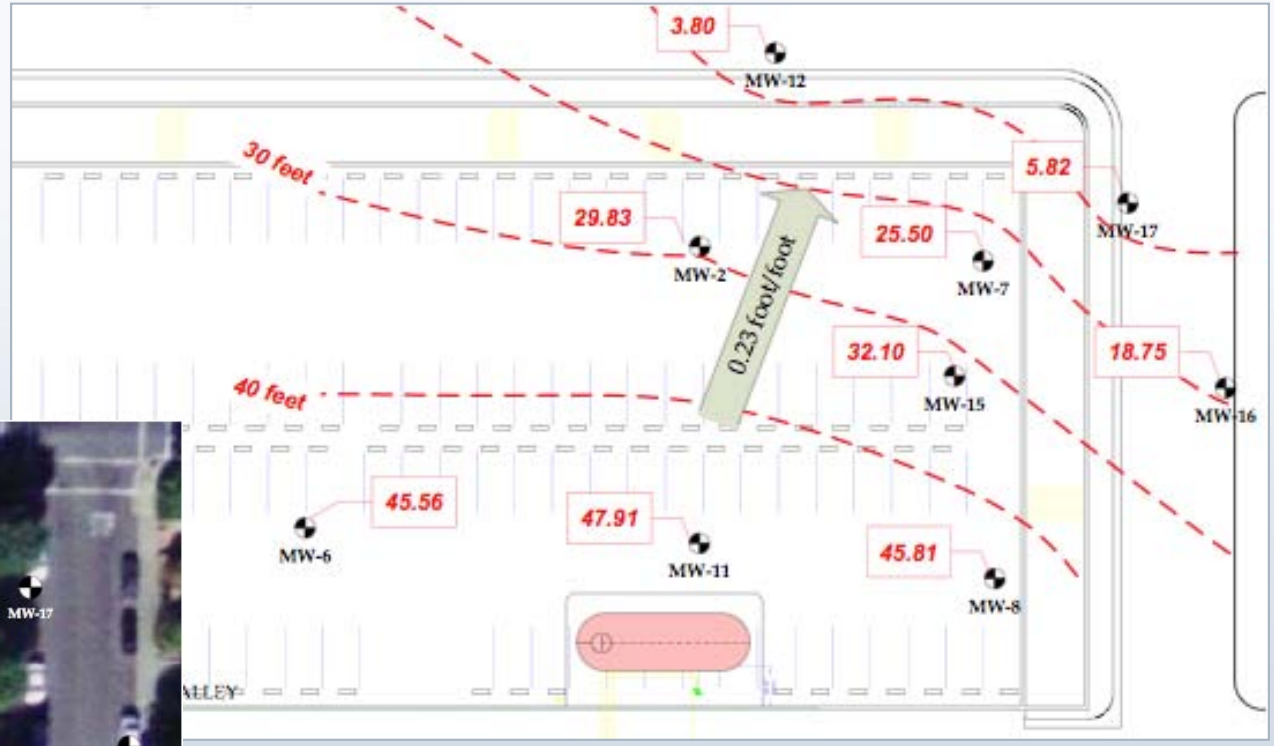
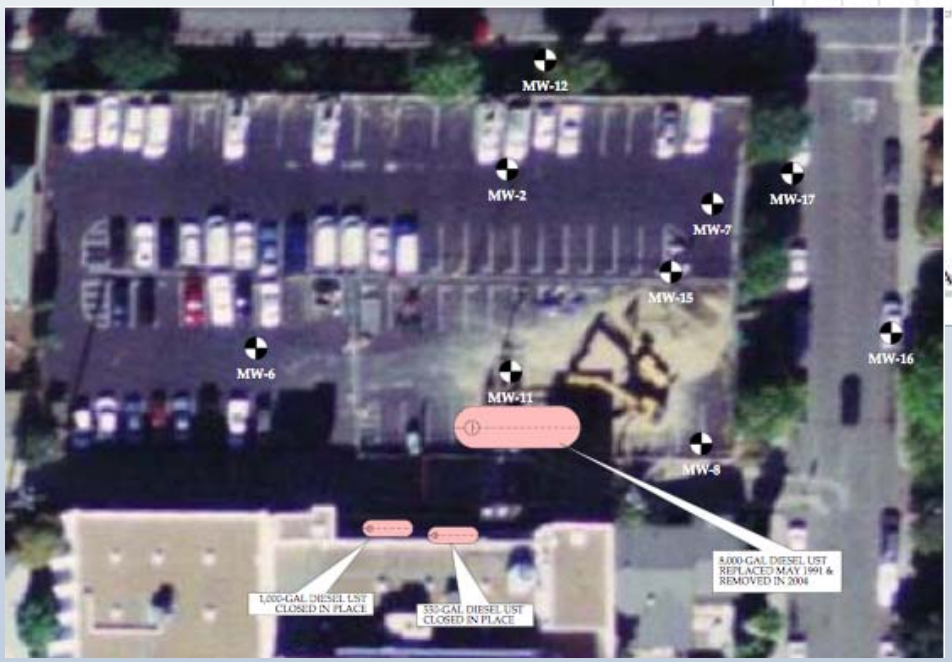
Site GW Gradient





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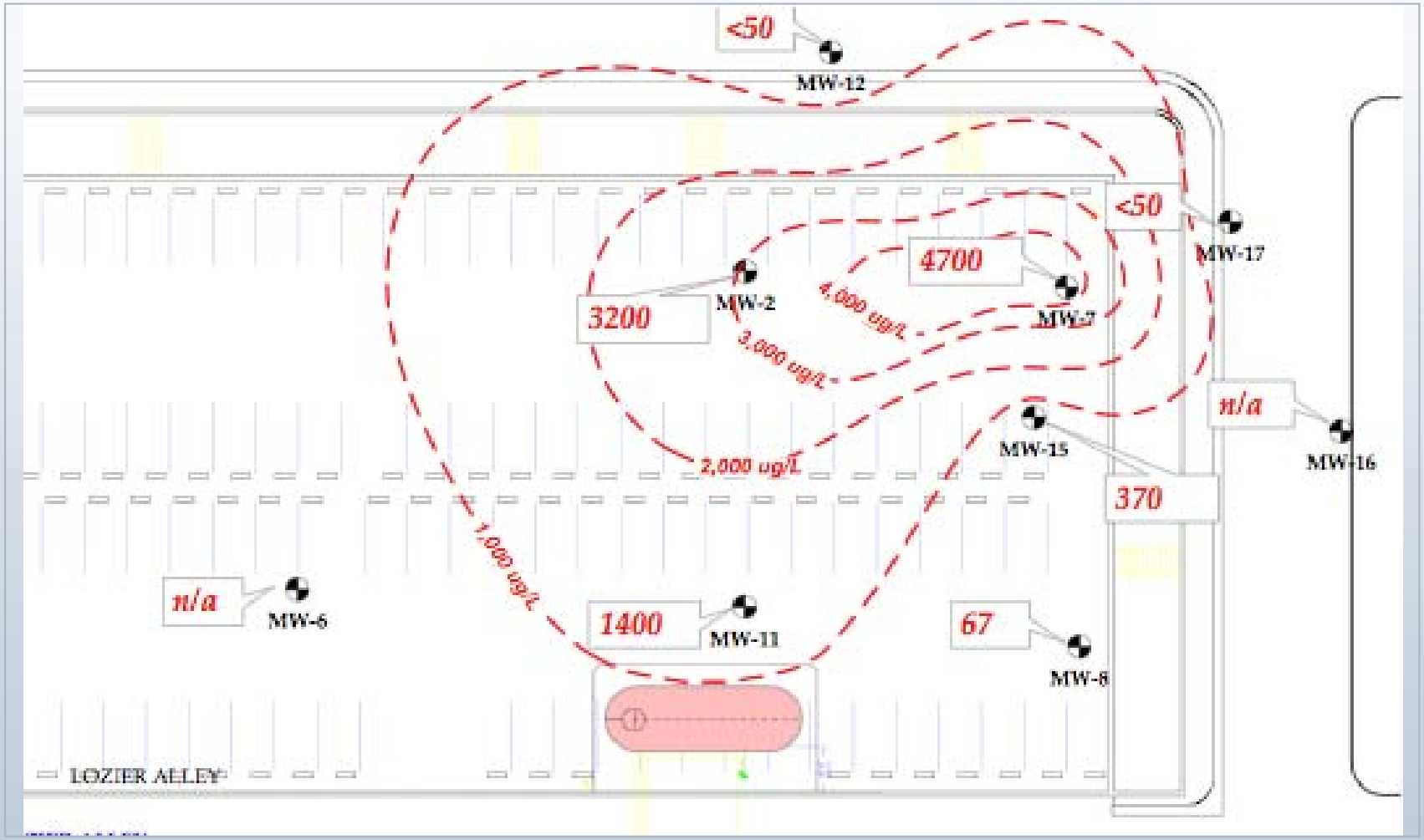
TPH-dIso concentration map



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Site Conditions

- Clayey shale with sandstone interbeds
- Depth to groundwater at approximately 50-70 feet below ground surface
- Impacted with diesel range petroleum hydrocarbons
- Former private use diesel fuel underground tanks for emergency generator
- Property owner operated HVDPE for multiple years without satisfactory results… at considerable cost

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Pilot Test Objectives

- Maintain hydraulic control
- Achieve effective injection radius of influence
- Improve LNAPL recovery
- Assess potential mass recovery for full scale design

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Pilot Test Approach

- Ivey-sol® 103 pilot scale injection program undertaken over 120 hours (5-days) in July 2009
- Four injection events with one injection well
- Five surrounding recovery and monitoring wells
- Mobile HVDPE system capable of 28 inch Hg vacuum and 800 SCFM; and

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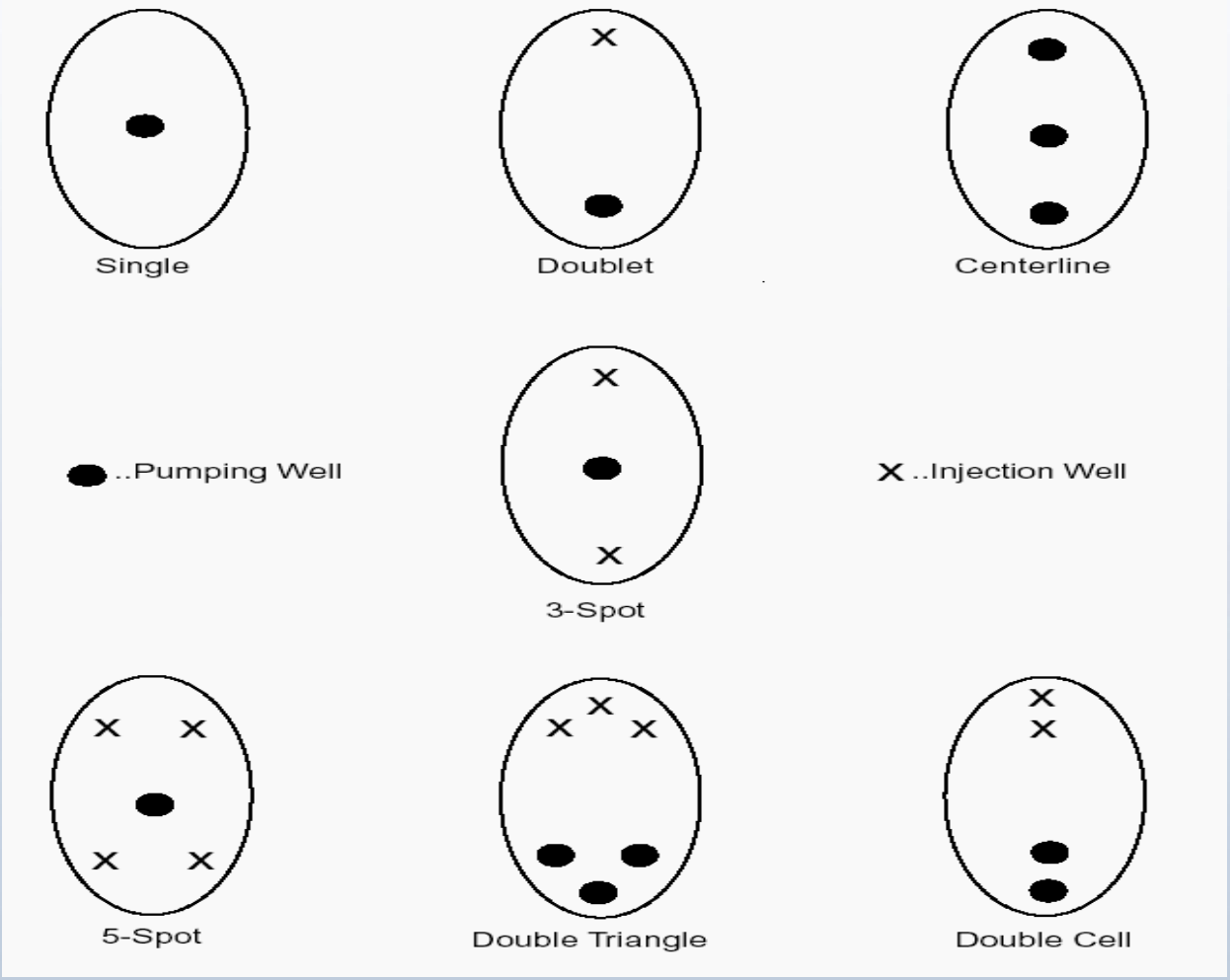
Five and Single Spot Pattern Used



5 Spot Common Application

Major types of pumping/injection well patterns (Satkin and Bedient, 1988).

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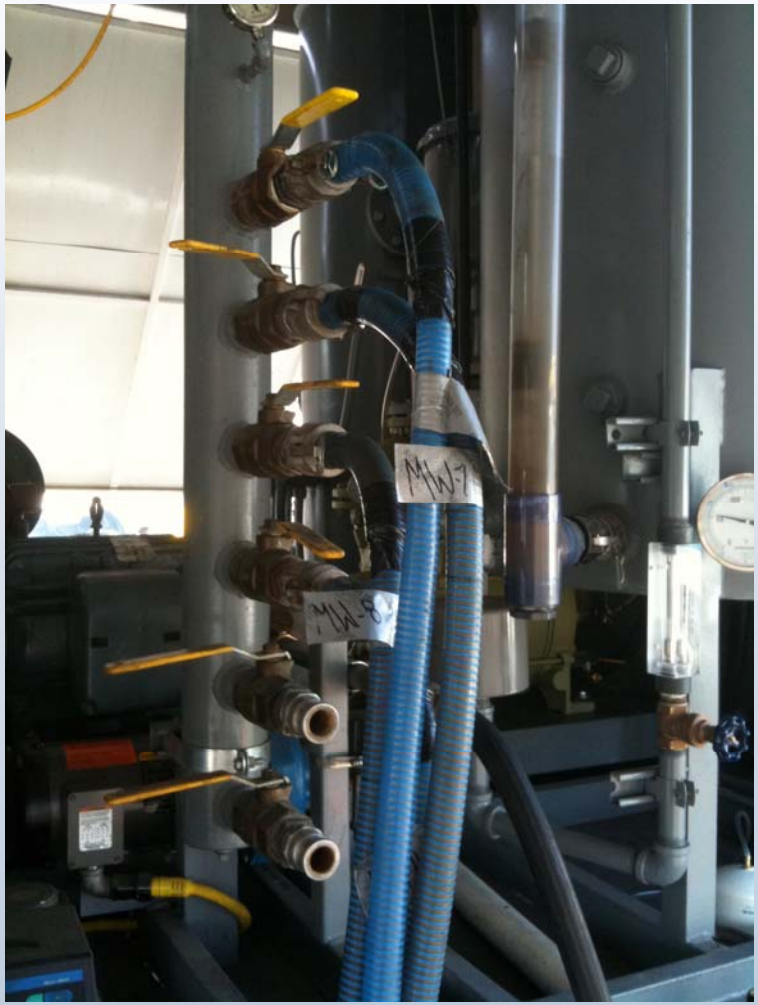
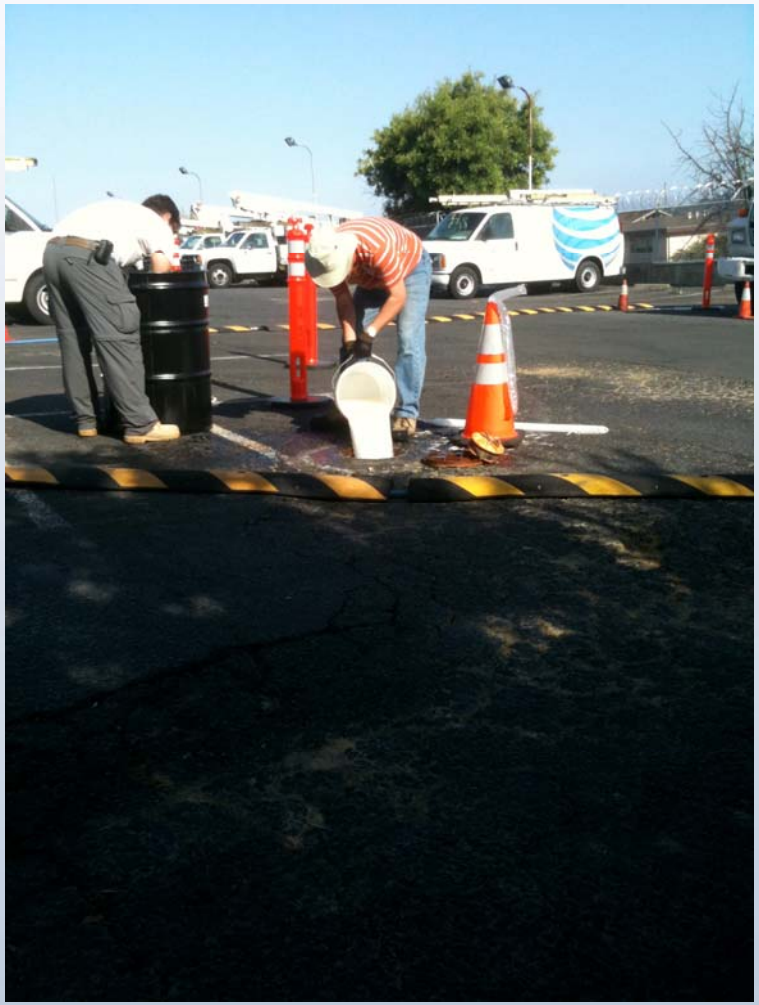
On-site Photos





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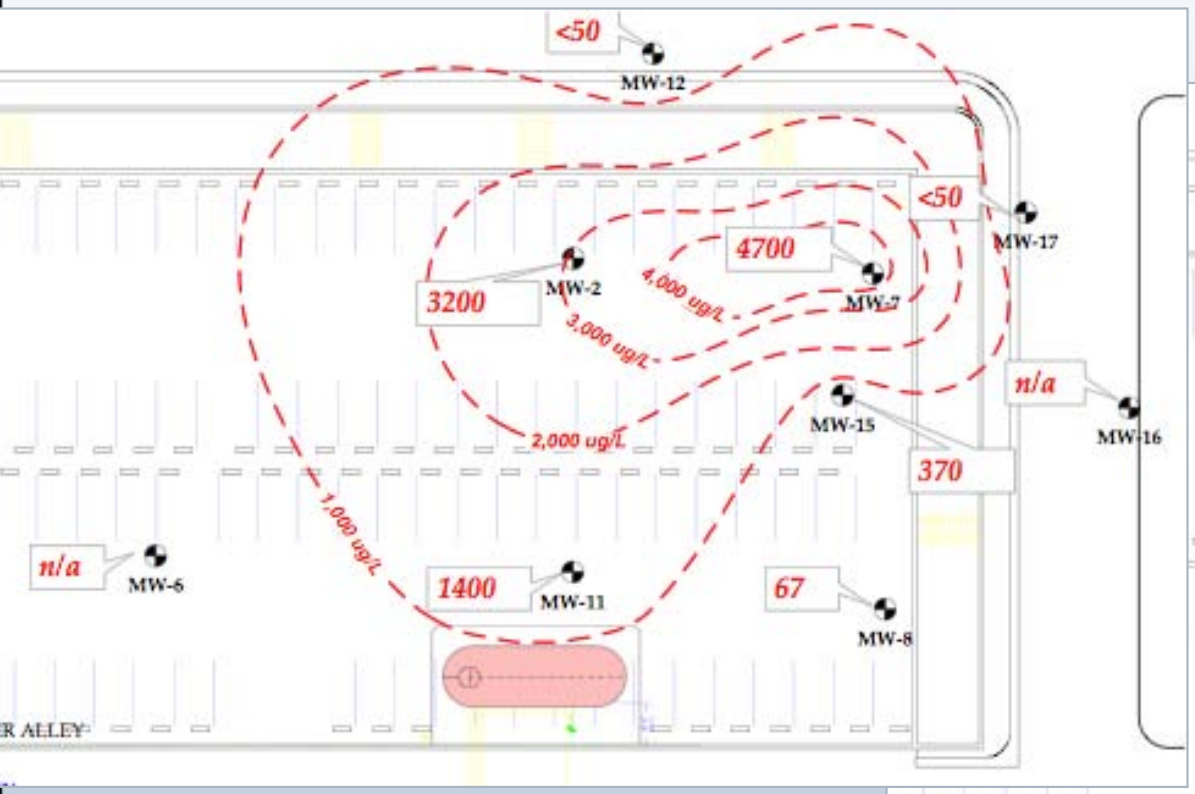
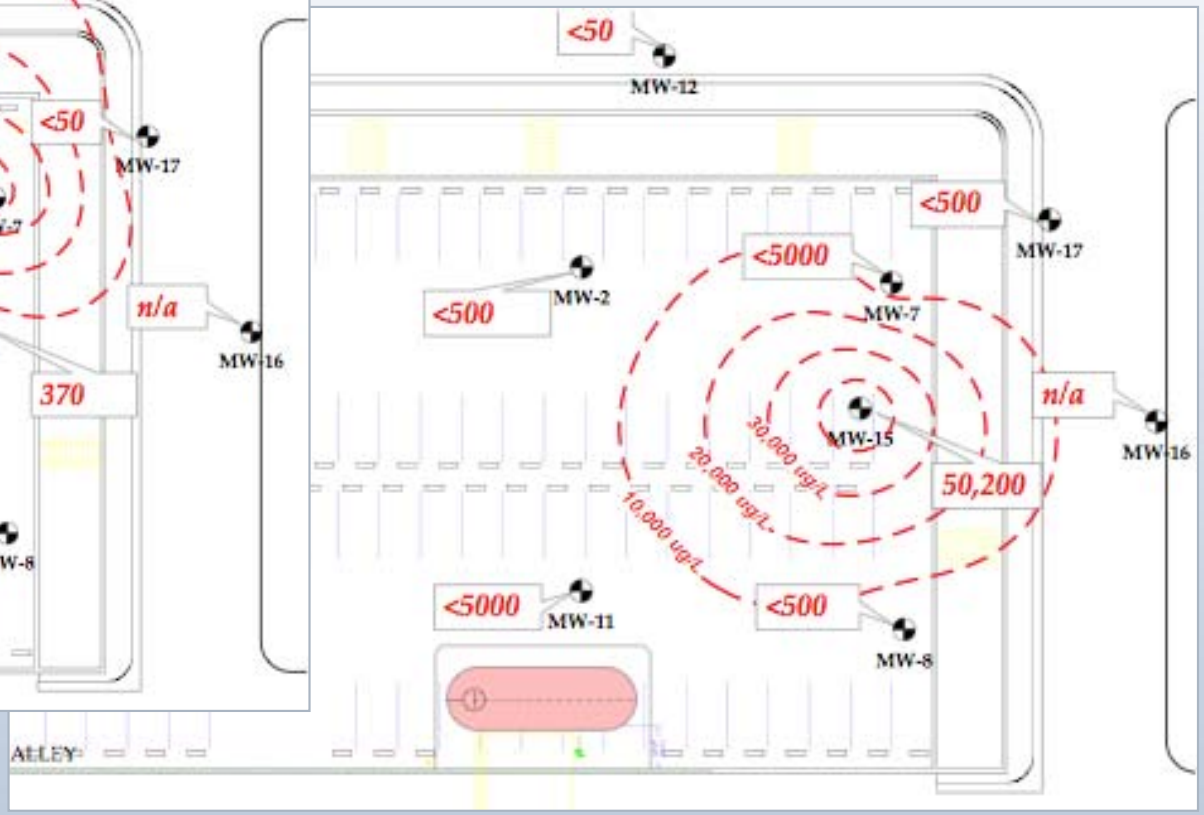
Before and During Test

TPH-dIsocon Map before Pilot Test



TPH-dIsocon Map 2 hrs after Pilot Test



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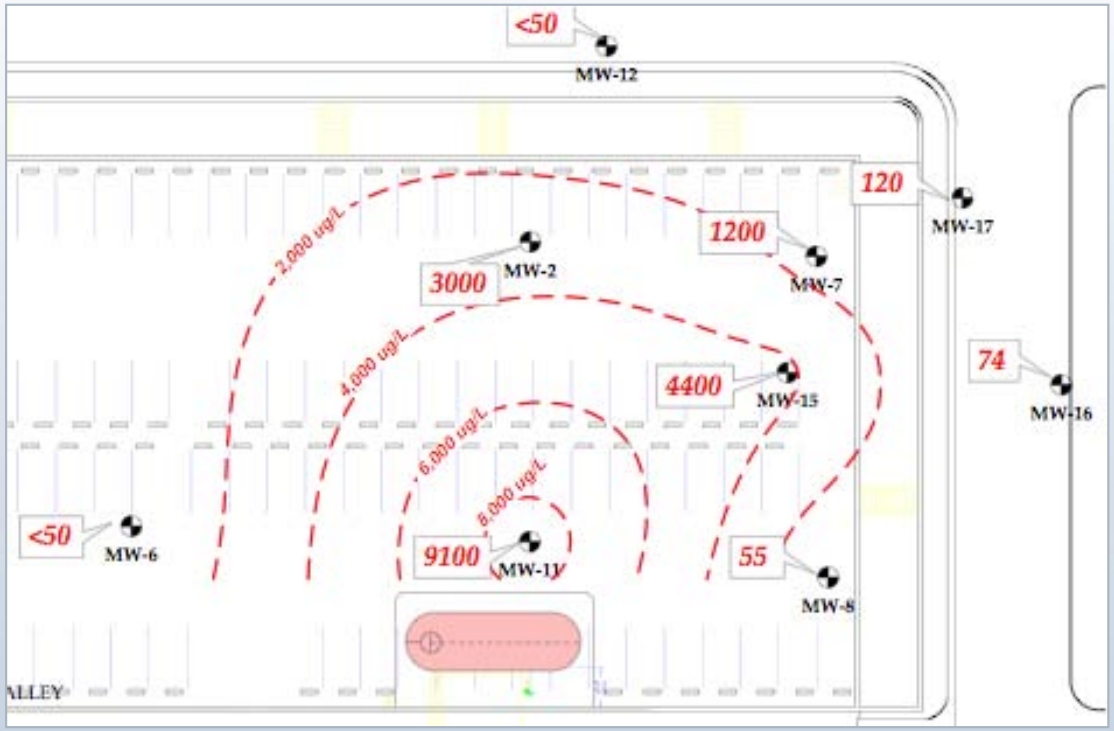
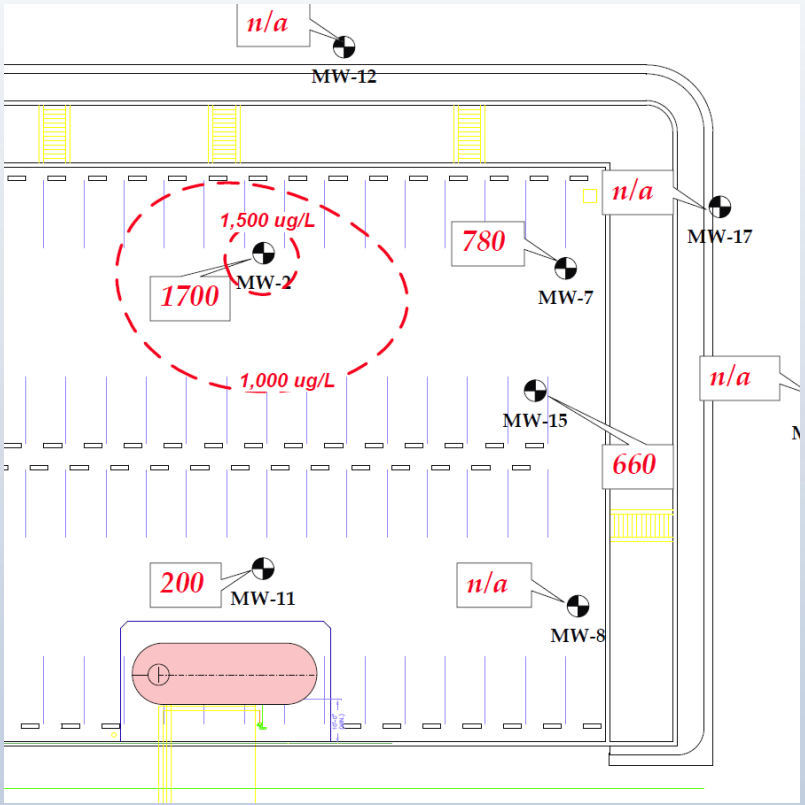
Post Pilot Test Results

TPH-d Isocon Map
1 Month after Pilot Test



TPH-d Isocon Map
3 months after Pilot Test



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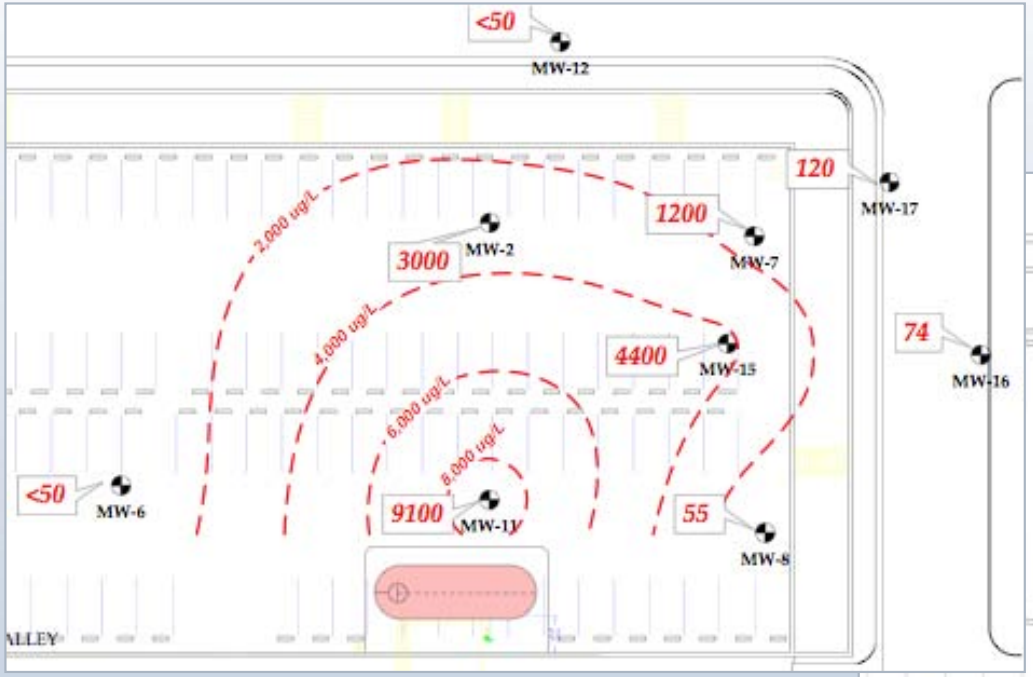
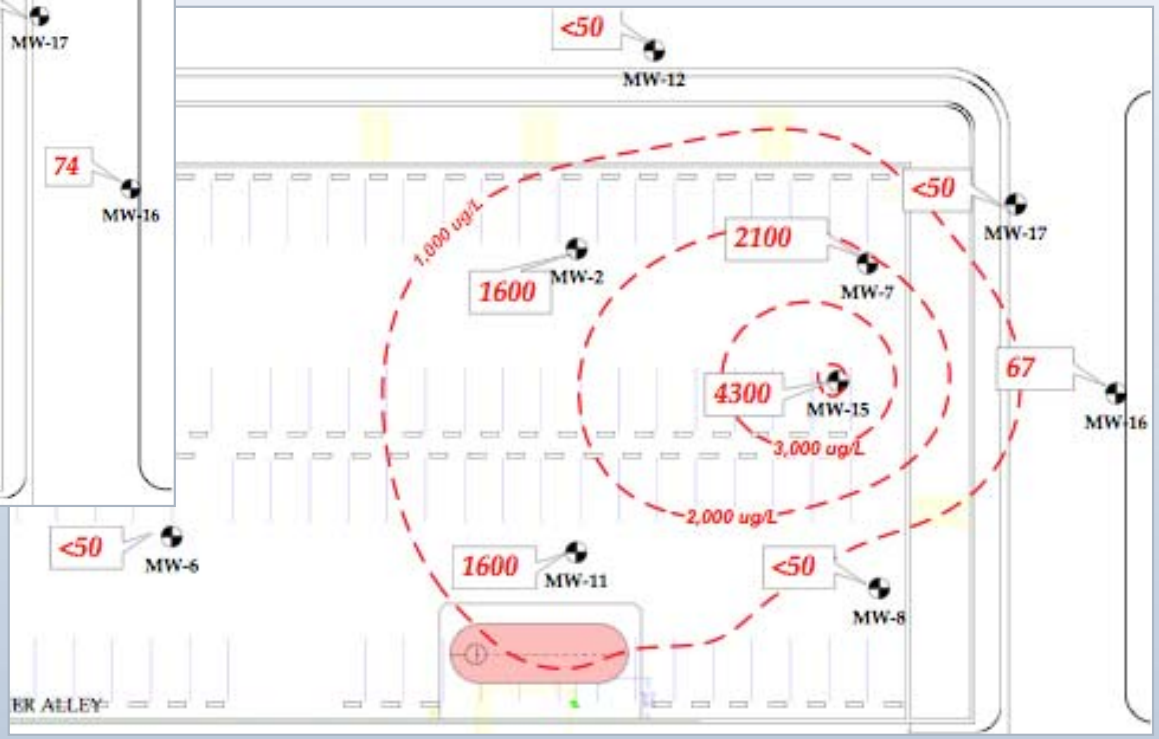
Post Pilot Test Results

TPH-d Isocon Map
1 Month after Pilot Test



TPH-d Isocon Map
7 months after Pilot Test



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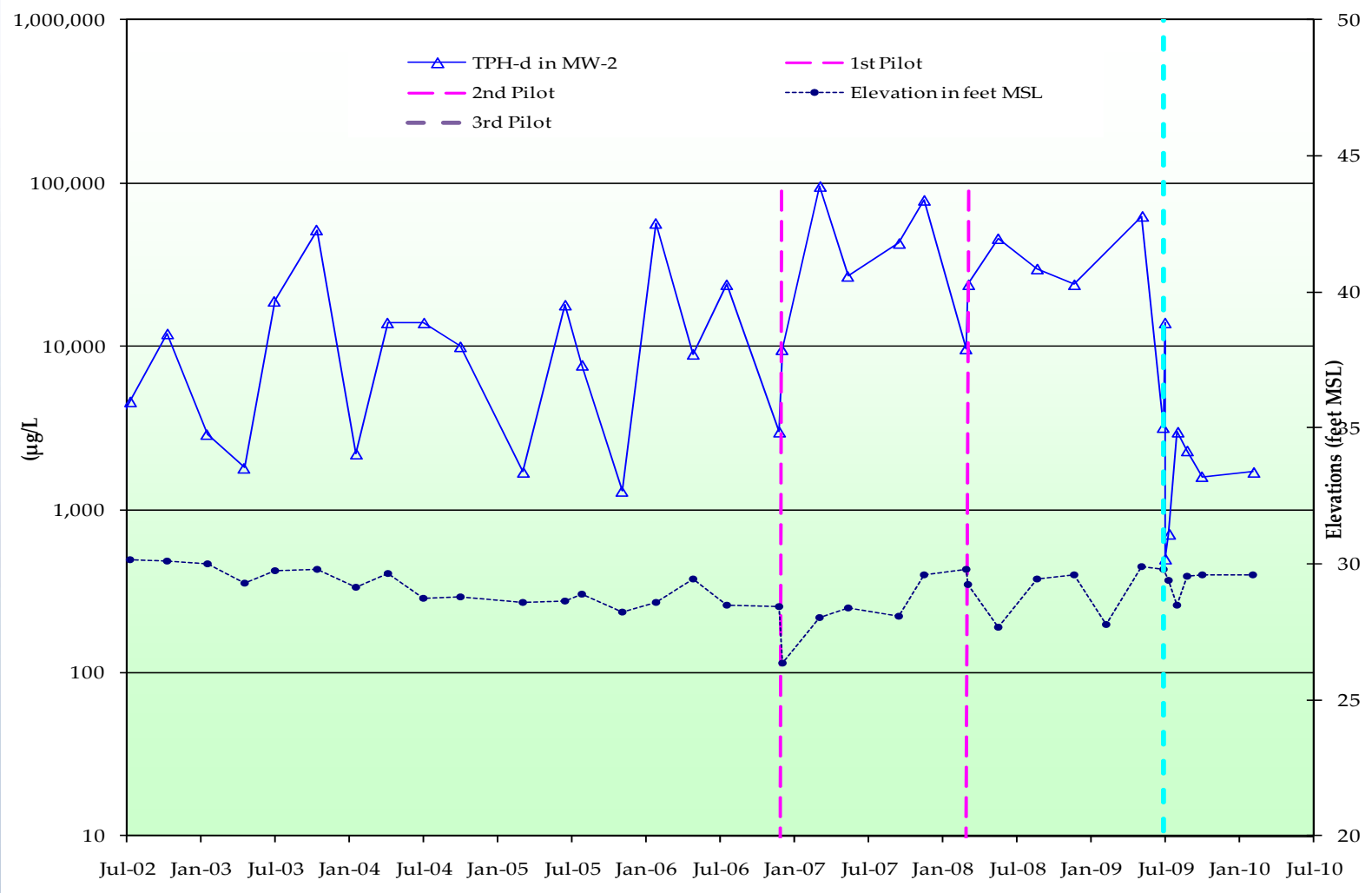
MW -2

[9.169 x 10^3mg/day÷1.5551 x 10^3mg/day] x 100% = 590 %



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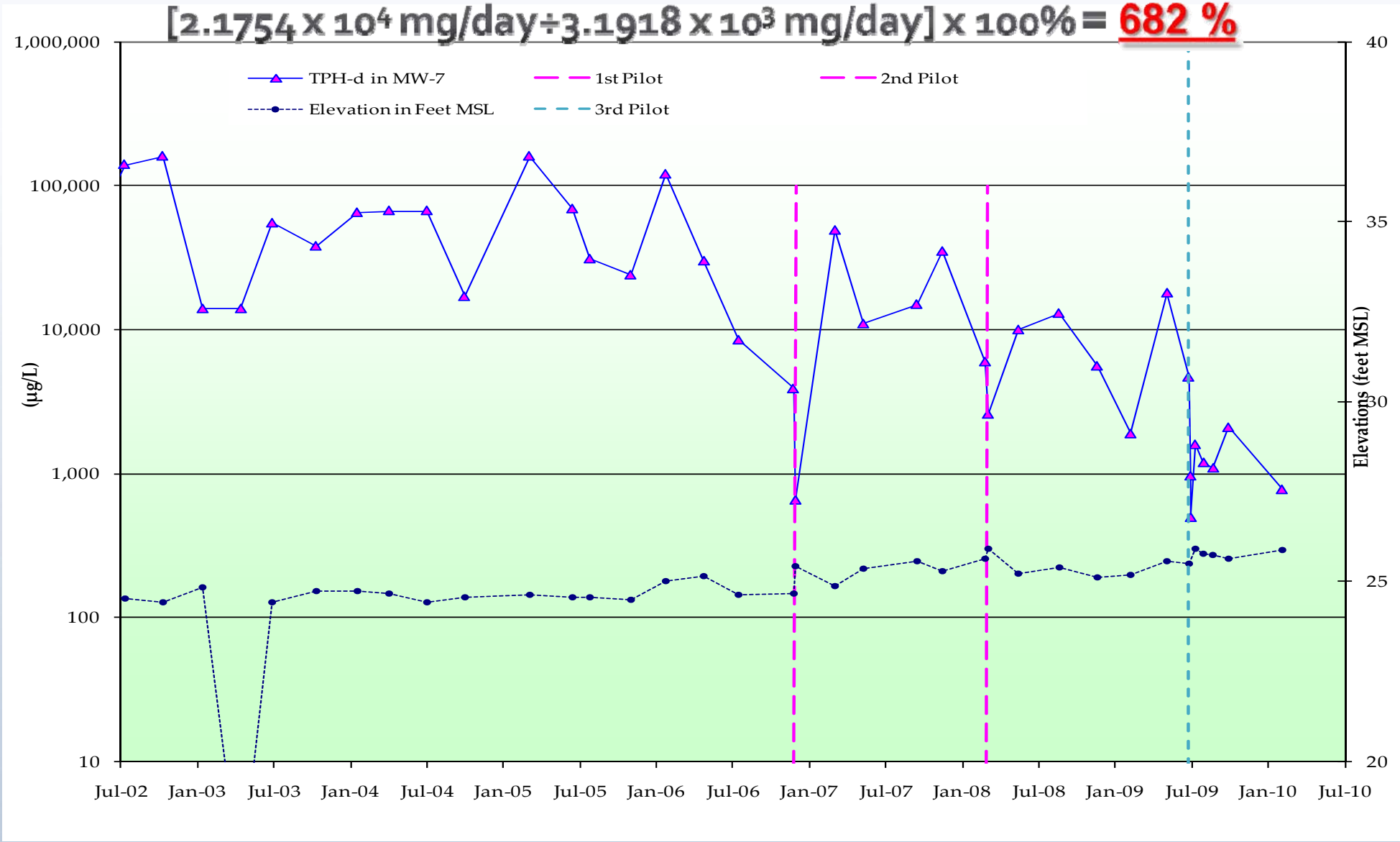
MW -7

$[2.1754 \times 10^4 \text{ mg/day} \div 3.1918 \times 10^3 \text{ mg/day}] \times 100\% = 682\ \%$



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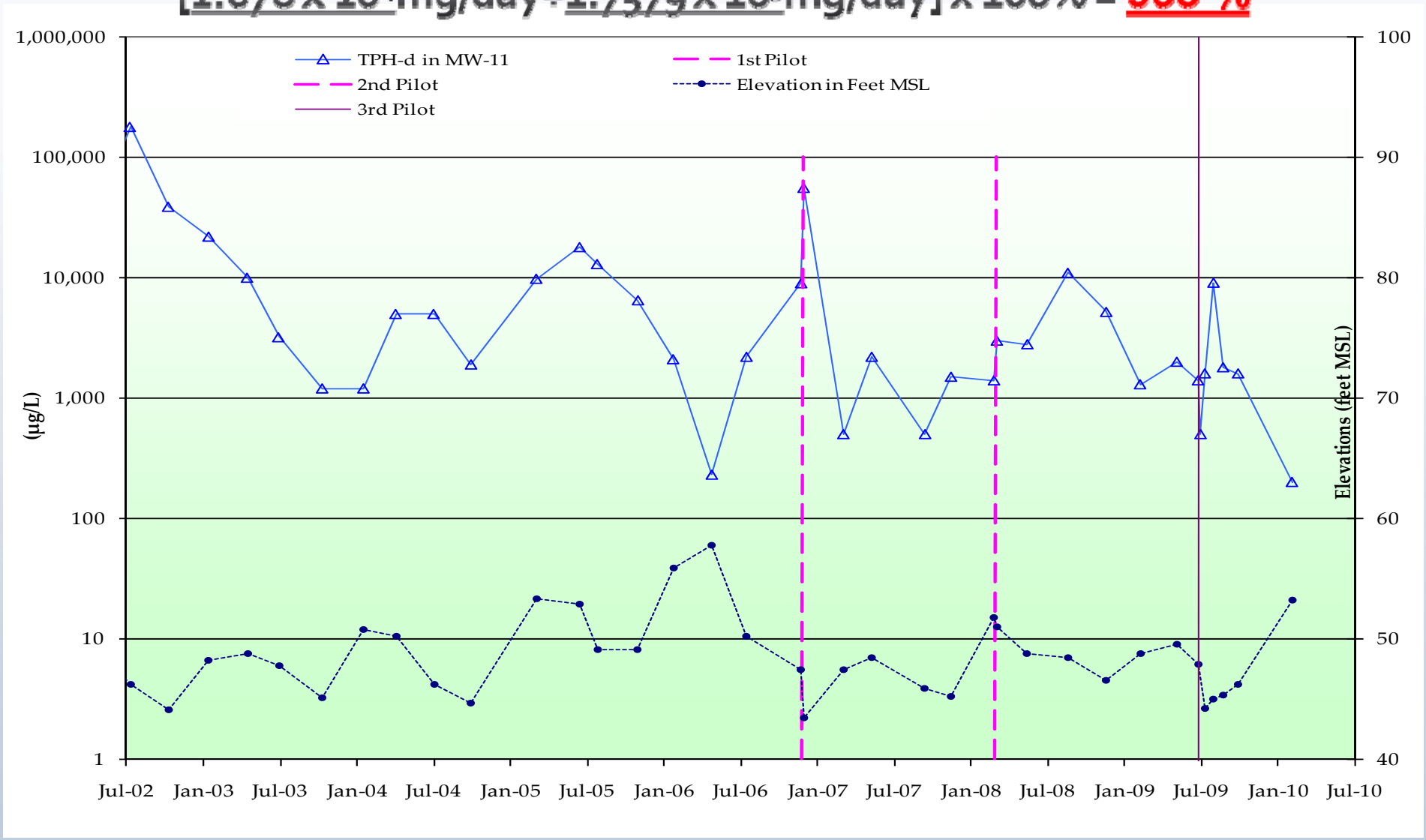
MW -11

$[1.678 \times 10^4 mg/day \div 1.7579 \times 10^3 mg/day] \times 100\% = \underline{955\ \%}$



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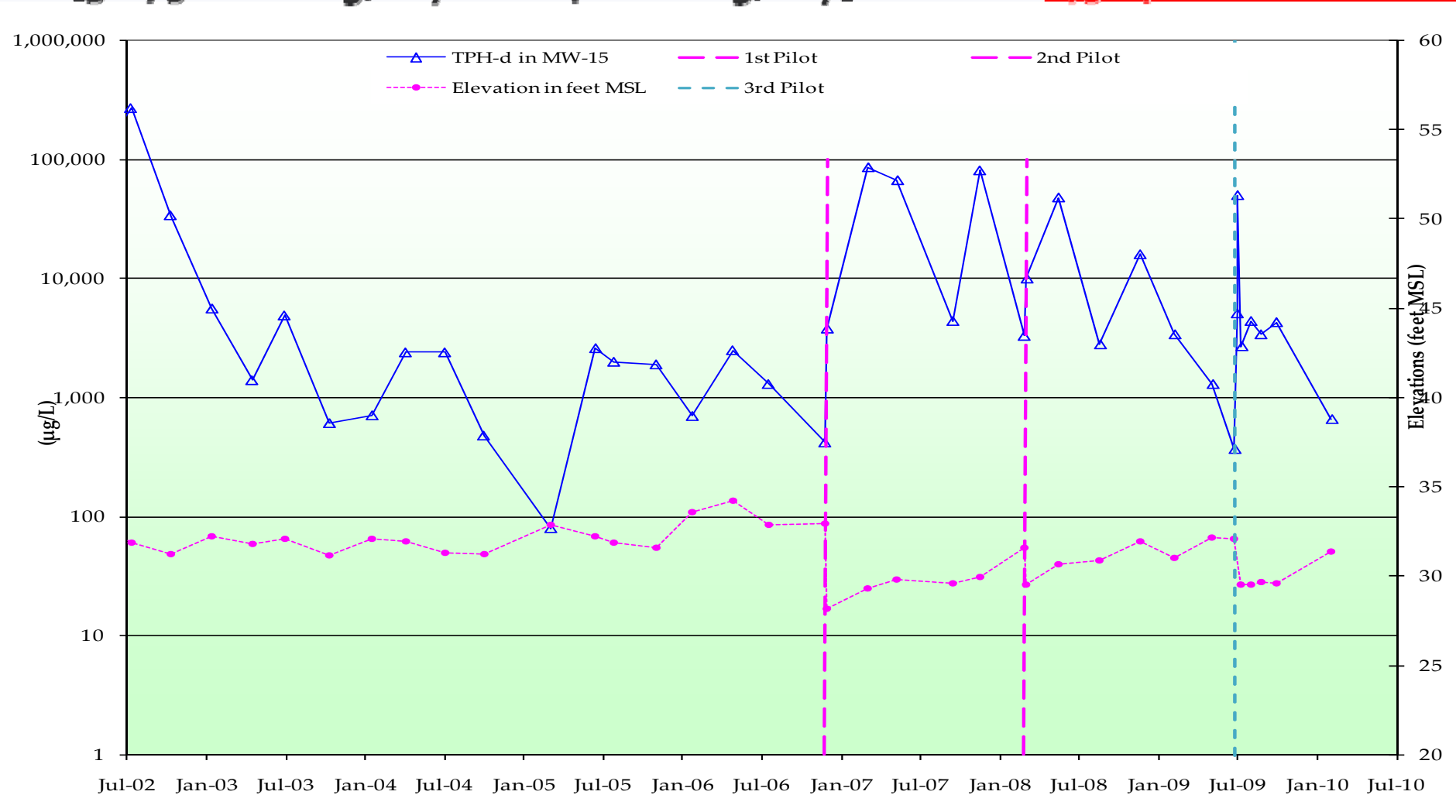
MW -15

$[4.4107 \times 10^4 \text{ mg/day} \div 2.7603 \times 10^3 \text{ mg/day}] \times 100\% =$ **1,598 %** **Standard Pilot**

$[3.875 \times 10^4 \text{ mg/day} \div 2.014 \times 10^3 \text{ mg/day}] \times 100\% =$ **1,924 %** **Push-Pull**



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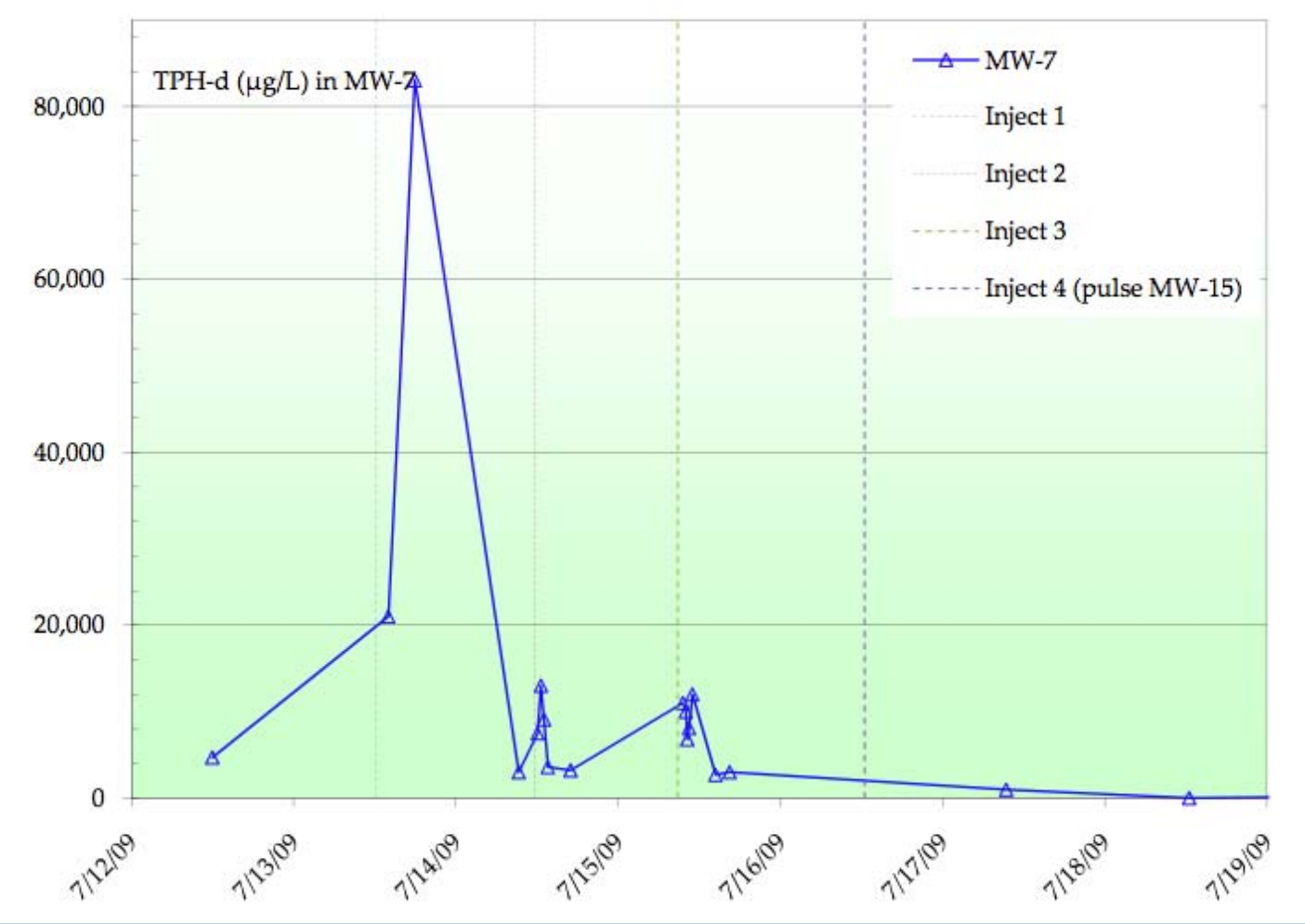
Radius of Influence

Response in MW-7 from injections in MW-15



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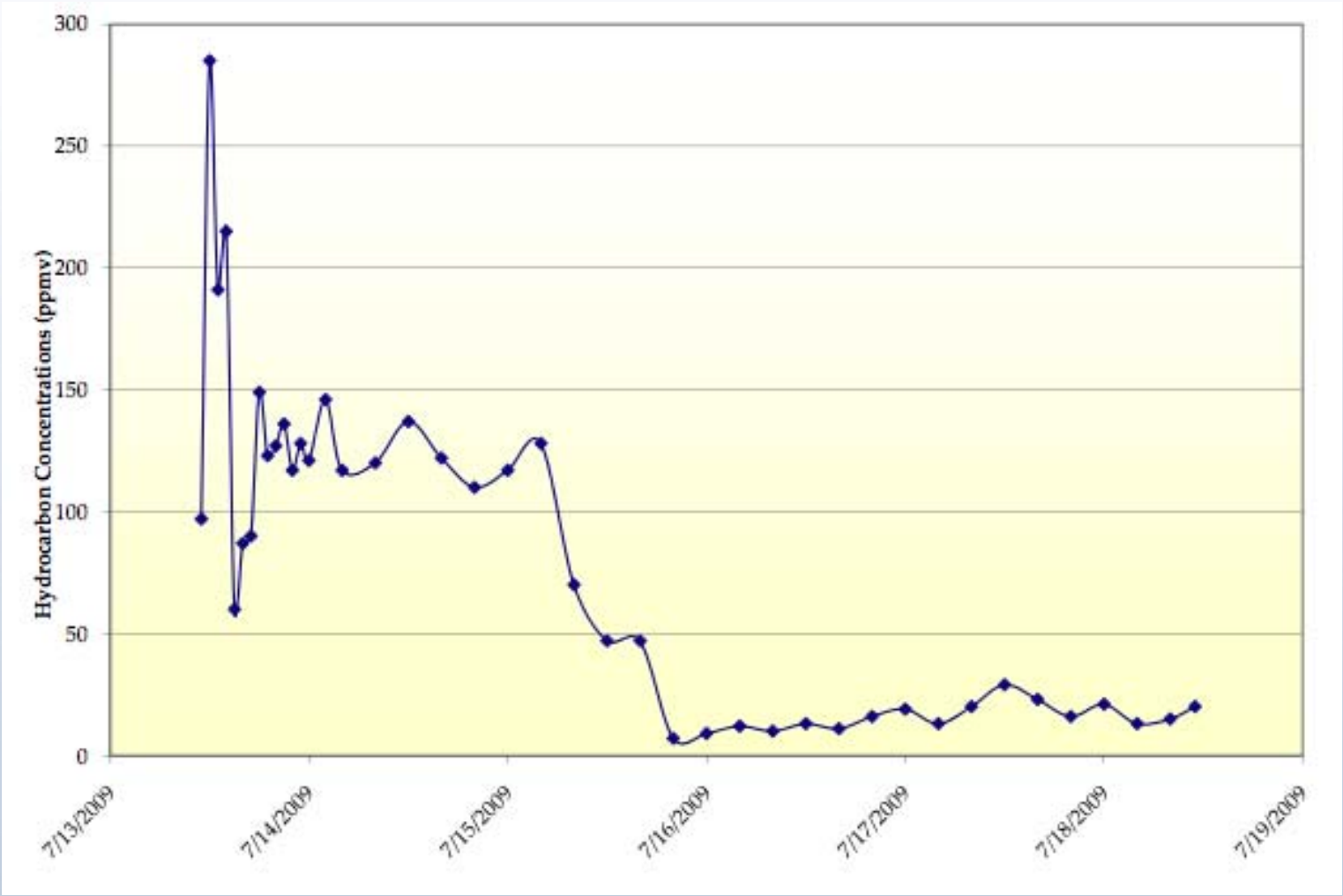
HVDPE Vapour Concentrations



RMT

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Pilot Test Results Summary

- Hydraulic Control Achieve (< 1 L/min)
- Limited water to manage to achieve remediation of soil and groundwater
- Increased TPH_d Recovery 590 to 924%!
  - **MW2 590%**
  - **MW7 682%**
  - **MW11 955%**
  - **MW15 1,598 to 1,924%**
- Obtained information for full-scale design

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