

## **HALF DAY WORKSHOP**

# **Environmental Chemistry Made Easy A New Perspective on Water, Contaminant Solubility and Sorption, and Introduction to Surfactants in Remediation**

**RemTech 2008  
Remediation Technologies Symposium  
October 15- 17, 2008**

# **Instructor**

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## **Biography**

- ▶ **Mr. Ivey is the President and Senior Remediation Specialist with Ivey International Inc. He has over twenty year's environmental experience, and has worked on more than 1200 projects internationally.**
- ▶ **His background includes: Organic Chemistry, Geological Engineering, and a Master's Certification in Project Management.**

**Among some of his more recent accomplishments include his being awarded:**

- **The 2007 Environmental Business Journal Remediation Bronze Award for Business Achievement;**
- **The 2006 North American Frost & Sullivan Award for Technology Innovation;**
- **The 2006 Environmental Business Journal Remediation Technology Merit Award; and**
- **The 2006 Globe Award for Environmental Innovation & Application.**

**He holds several international patents; continues to conduct applied soil, solid waste, waste water, and groundwater research, and is currently working on several remediation projects around the world.**

## **Course Overview**

- ▶ **Introductions & House Keeping**
- ▶ **Brief History of Surfactants & Uses**
- ▶ **Water (Properties & Characteristics)**
- ▶ **Organics (Properties & Characteristics)**
- ▶ **Sorption & Hydrogeology (Water & Organics)**
- ▶ **Surfactants In Remediation (In-situ & Ex-situ)**
- ▶ **SER, SEB & SEO (Innovative Applications)**

***Class participation is strongly encouraged!  
We will give hands-on and visual demonstrations, and  
Involve you in question and answer along the way...***



## **Workshop Objectives**

- ▶ **To give you a good general understanding of water and organic contaminants;**
- ▶ **An applied understanding of specific water & organic properties and characteristics and their affect within soil and groundwater regimes;**
- ▶ **Importance of Sorption (adsorption and absorption) in remediation system design an application;**
- ▶ **Introduction to Surfactants and how they affect the properties and characteristics of water and organics; and**
- ▶ **Surfactant Application (SER, SEB, & SEO) for In-situ and Ex-situ Remediation (Case Studies and Applied Research).**

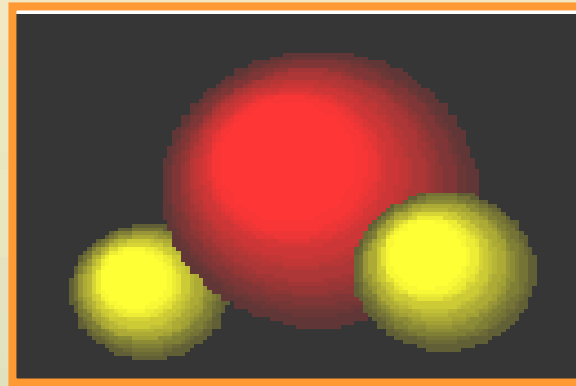
# WATER H<sub>2</sub>O

## *Properties & Characteristic*

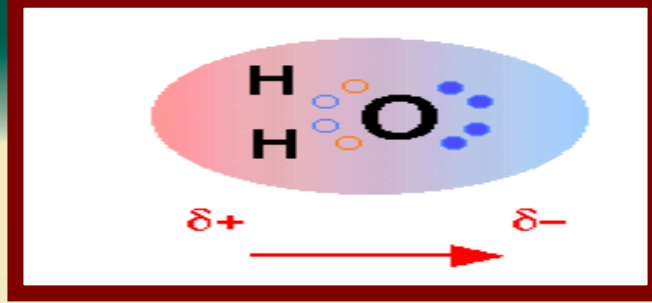


*Is water H<sub>2</sub>O?*

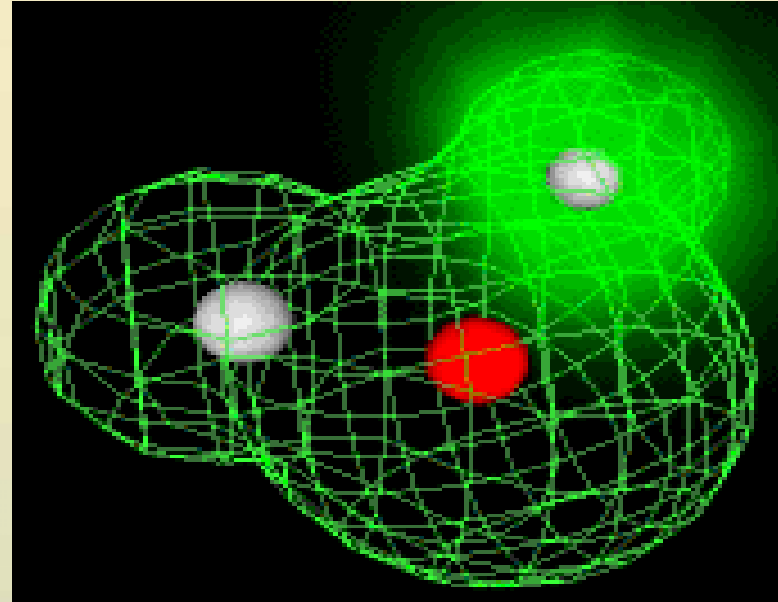
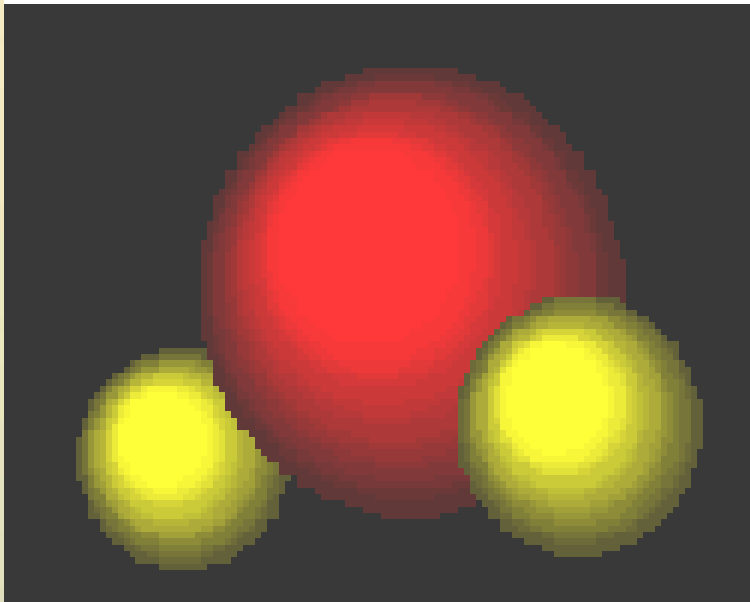
# Introduction to Water Properties and Structure



- ▶ Water has long been known to exhibit many *physical properties that distinguish it from other small molecules of comparable mass.*
- ▶ Chemists refer to these as the "*anomalous*" properties of water, but they are by no means mysterious
- ▶ All are entirely *predictable* consequences of the way the size and nuclear charge of the *oxygen* atom conspire to *distort the electronic charge clouds of the atoms of other elements* when these are chemically bonded to the oxygen.



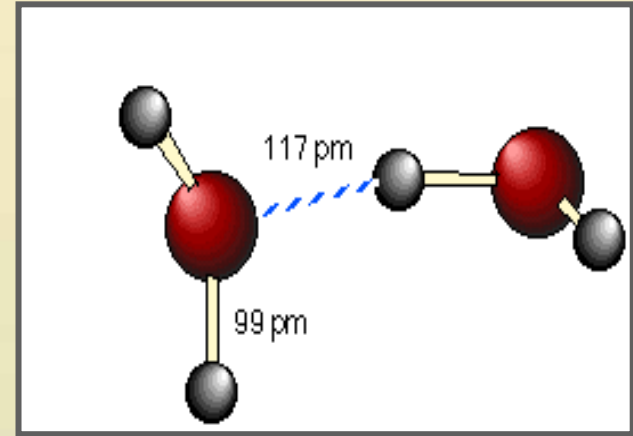
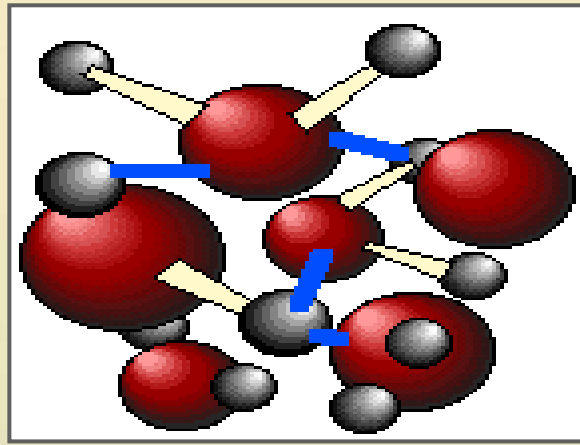
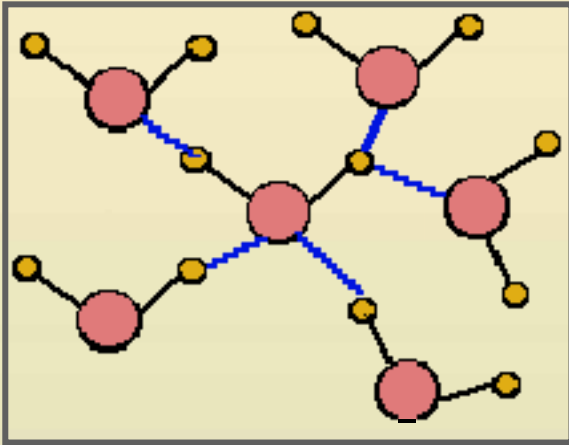
- ▶ A covalent chemical bond consists of two atoms that *share a pair of electrons* between them.
- ▶ In the water molecule H<sub>2</sub>O, the single electron of each H is shared with one of the six outer-shell electrons of the oxygen, leaving *four electrons which are organized into two non-bonding pairs*.
- ▶ Thus the oxygen atom is surrounded by four electron pairs that would ordinarily tend to arrange themselves as far from each other as possible in order to minimize repulsions between these clouds of negative charge.
- ▶ This would ordinarily result in a tetrahedral geometry in which the angle between electron pairs (and therefore the H-O-H bond angle) is 109°.
- ▶ However, because the *two non-bonding pairs remain closer to the oxygen* atom, these exert a stronger repulsion against the two covalent bonding pairs, effectively *pushing the two hydrogen atoms closer together*. The result is a distorted tetrahedral arrangement in which the H—O—H angle is 104.5°.



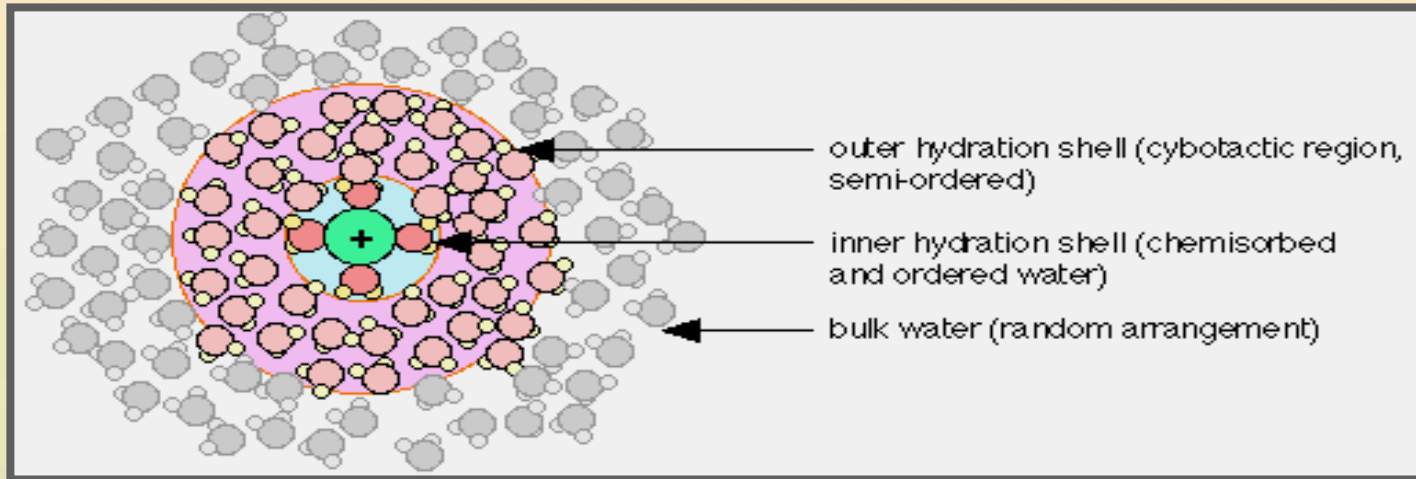
## Water H<sub>2</sub>O Molecule Representations

### Covalent Bond Between Oxygen and Hydrogens

*These two computer-generated images of the H<sub>2</sub>O molecule come from calculations that model the electron density distribution in molecules. The outer envelopes show the effective "surface" of the molecule.*



- ▶ **Hydrogen Bonding (*in-blue*)** Exists Between Neighbouring Polar Water Molecules. The Bonding Exists Between The Oxygen & Hydrogen Atoms *Pulling H<sub>2</sub>O Molecules Together.*
- ▶ They Forming And Break Rapidly (nano-seconds). *Hydrogen Bonding Giving Rise To Waters Surface Tension, Its Physical Properties, And The Insolubility Of Non-Polar NAPL Compounds.*
- ▶ This Property Supports The Hydrophilic (*Water Liking*) Portion Of The Surfactant Molecules that renders NAPL Compounds Miscible In Water.



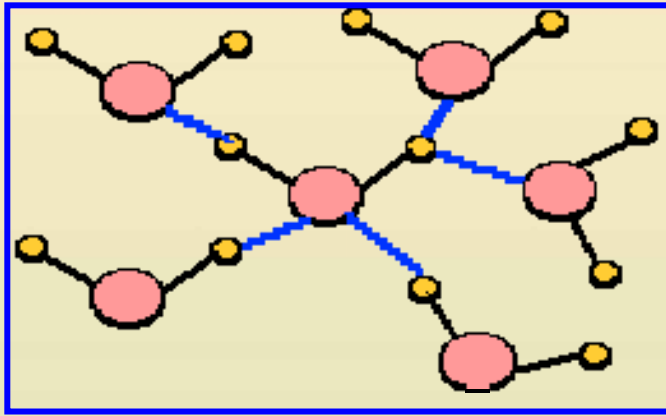
► *Water molecules interact strongly with non-hydrogen bonding species as well. A particularly strong interaction occurs when an ionic substance such as sodium chloride (NaCl, ordinary salt) dissolves in water.*

► Owing to its *high polarity, the H<sub>2</sub>O* molecules closest to the dissolved ion are strongly attached to it, forming what is known as the *primary hydration shell*.

► Positively-charged ions such as *Na<sup>+</sup> attract the negative (oxygen) ends* of the H<sub>2</sub>O molecules, as shown in the diagram below.

► The ordered structure within the *primary shell creates, through hydrogen-bonding, a region in which the surrounding waters are also somewhat ordered*; this is the outer hydration shell, or cybotactic region.

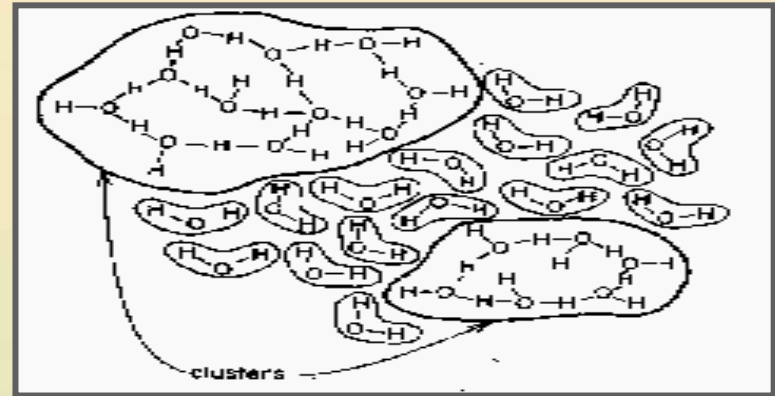
► Water H<sub>2</sub>O Molecule Representations Covalent Bond Between Oxygen and Hydrogens.



Hydrogen Bonding Between Polar Water Molecules (*in-blue*) Pulling Water Together Between Neighbouring H<sub>2</sub>O.

► Hydrogen Bonding Is What Gives Rise To The Insolubility Of Non-Polar NAPL Compounds, And Why the Hydrophilic (*Water Liking*) End Of Surfactant Molecules Are So Effective In Rendering The NAPL Compounds Miscible In Water.

► Clustering of water molecules affects the K (Conductivity) of water in various soil types!



Water Clusters Can Form Form As A Result That Range In Size & Complexity



# Water = Hydrogen Bonding!

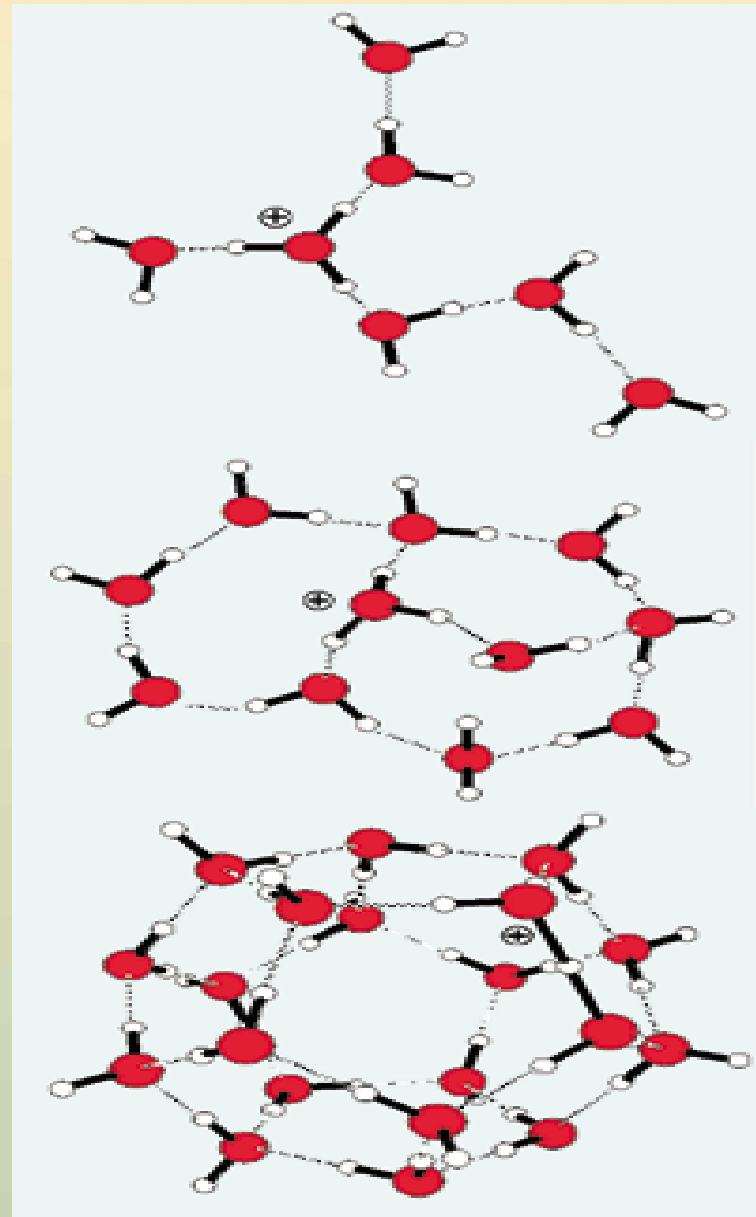
- ▶ When thinking about water and its chemical and physical characteristics, one must understand they are directly the result of Hydrogen Bonding!
- ▶ Hydrogen Bonding dictates water's behavior and how it interacts with other substances including organic chemical contaminants (*i.e.*, LNAPL's & DNAPLs)
- ▶ If the NAPL will or will not dissolve, and/or migrate within soil and/or groundwater plume, and their rate of transport. \_

Formation of  
hydrogen bonds  
between like  
water molecules...

This results in the  
formation of  
Water Clusters  
which can get  
large in size...

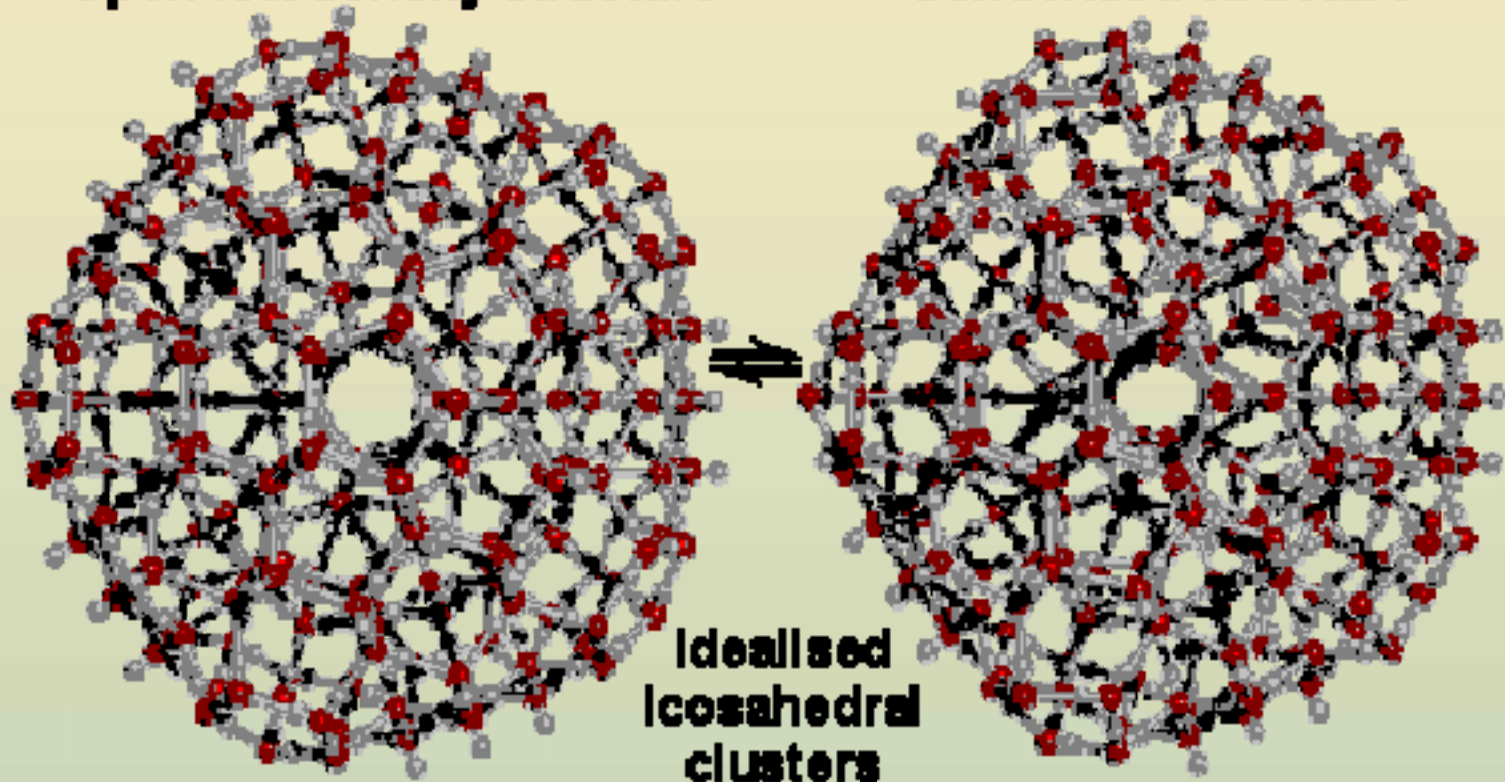
So water is not  
just H<sub>2</sub>O...

So we have to  
change the way  
we think of water  
form a practical  
stand point.



**Open low density structure**

**Condensed structure**



## **This affects many of the chemical and physical properties of water!**

- ▶ **Boiling Point**
- ▶ **Freezing Point**
- ▶ **What will or will not dissolve in water**
- ▶ **Viscosity**
- ▶ **K (Conductivity) in soils**
- ▶ **Surface tension**
- ▶ **Density (Density of Fresh < Salt Water)**
- ▶ **Why some water and soil treatments do not work...**

# Surface Tension

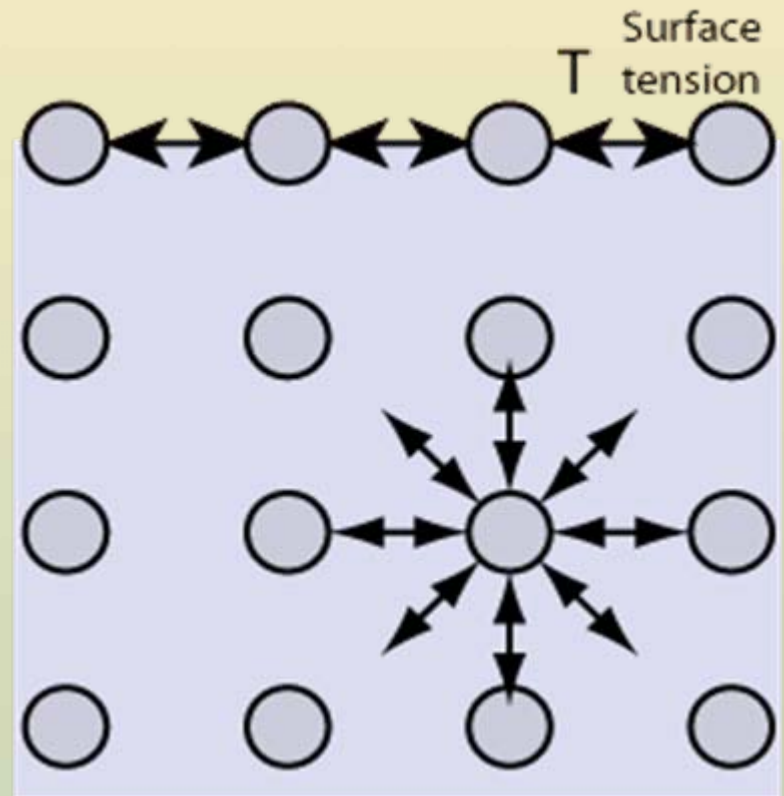
- ▶ The cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension.
- ▶ The molecules at the surface do not have other like molecules on all sides of them and consequently they cohere more strongly to those directly associated with them on the surface. This forms a surface "film" which makes it more difficult to move an object through the surface than to move it when it is completely submerged.
- ▶ Surface tension is typically measured in dynes/cm, the force in dynes required to break a film of length 1 cm. Equivalently, it can be stated as surface energy in ergs per square centimeter.
- ▶ Water at  $20^{\circ}\text{C}$  has a surface tension of  $72.8$  dynes/cm compared to  $22.3$  for ethyl alcohol, and  $465$  for mercury.

# Cohesion and Surface Tension

▶ The cohesive forces between Molecules down into a liquid are shared with all neighboring atoms.

▶ Those on the surface have no neighboring atoms above, and exhibit stronger attractive forces upon their nearest neighbors on the surface.

▶ This enhancement of the intermolecular attractive forces at the surface is called surface tension



# Class Demonstration Exercise I

## *Demonstration #1*

- ▶ **Water Droplets on a Penny (How many?).  
Note: Just water...**
- ▶ **Water Droplets on a Penny (How many?).  
Note: Water with surfactant.**

## *Demonstration #2*

- ▶ **Water droplet on glass, note shape and discuss observations.**
- ▶ **Water with surfactant droplet on glass, note shape and discuss observations.**

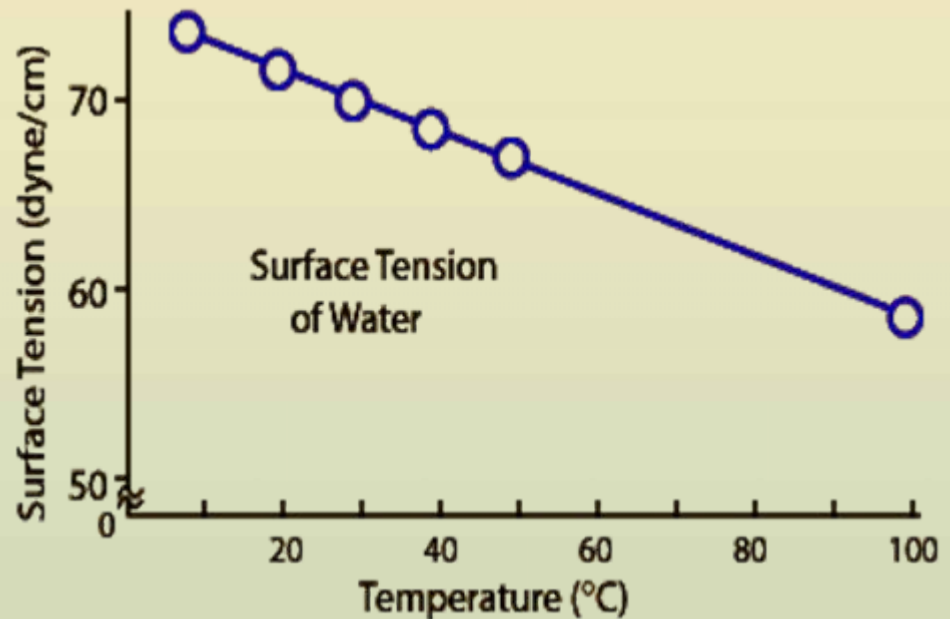
# Cohesion and Adhesion

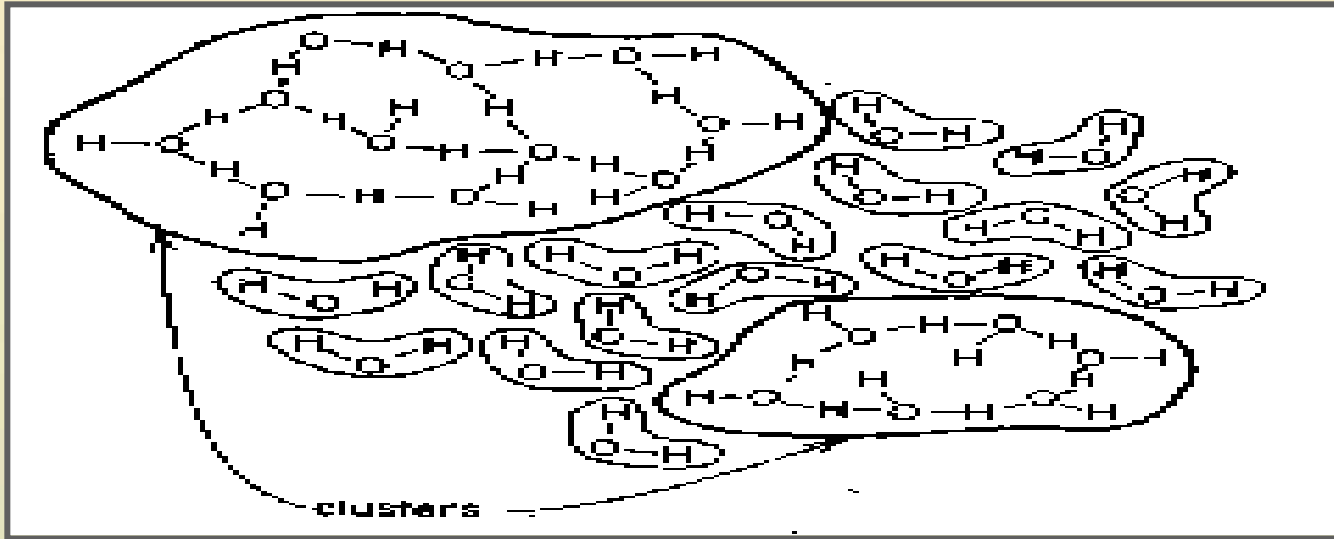
- ▶ Molecules liquid state experience strong intermolecular attractive forces. When those *forces are between like molecules*, they are referred to as *cohesive forces*. For example, the molecules of a water droplet are held together by cohesive forces, and the especially strong cohesive forces at the surface constitute *surface tension*.
- ▶ When the *attractive forces are between unlike molecules*, they are said to be *adhesive forces*. The adhesive forces between water molecules and the walls of a glass tube are stronger than the cohesive forces lead to an upward turning meniscus at the walls of the vessel and contribute to capillary action.
- ▶ The attractive forces between molecules in a liquid can be viewed as residual electrostatic forces and are sometimes called *van der Waals forces or van der Waals bonds*.



# Surface Tension of Water

- ▶ The surface tension of water is 72 dynes/cm at 25°C . It would take a force of 72 dynes to break a surface film of water 1 cm long.
- ▶ The surface tension of water decreases significantly with temperature as shown in the graph. The surface tension
- ▶ Arises from the polar nature of the water molecule. Hot water is a better cleaning agent because the lower surface tension makes it a better "wetting agent" to get into pores and fissures rather than bridging them with surface tension.
- ▶ *Soaps and detergents further lower the surface tension.*

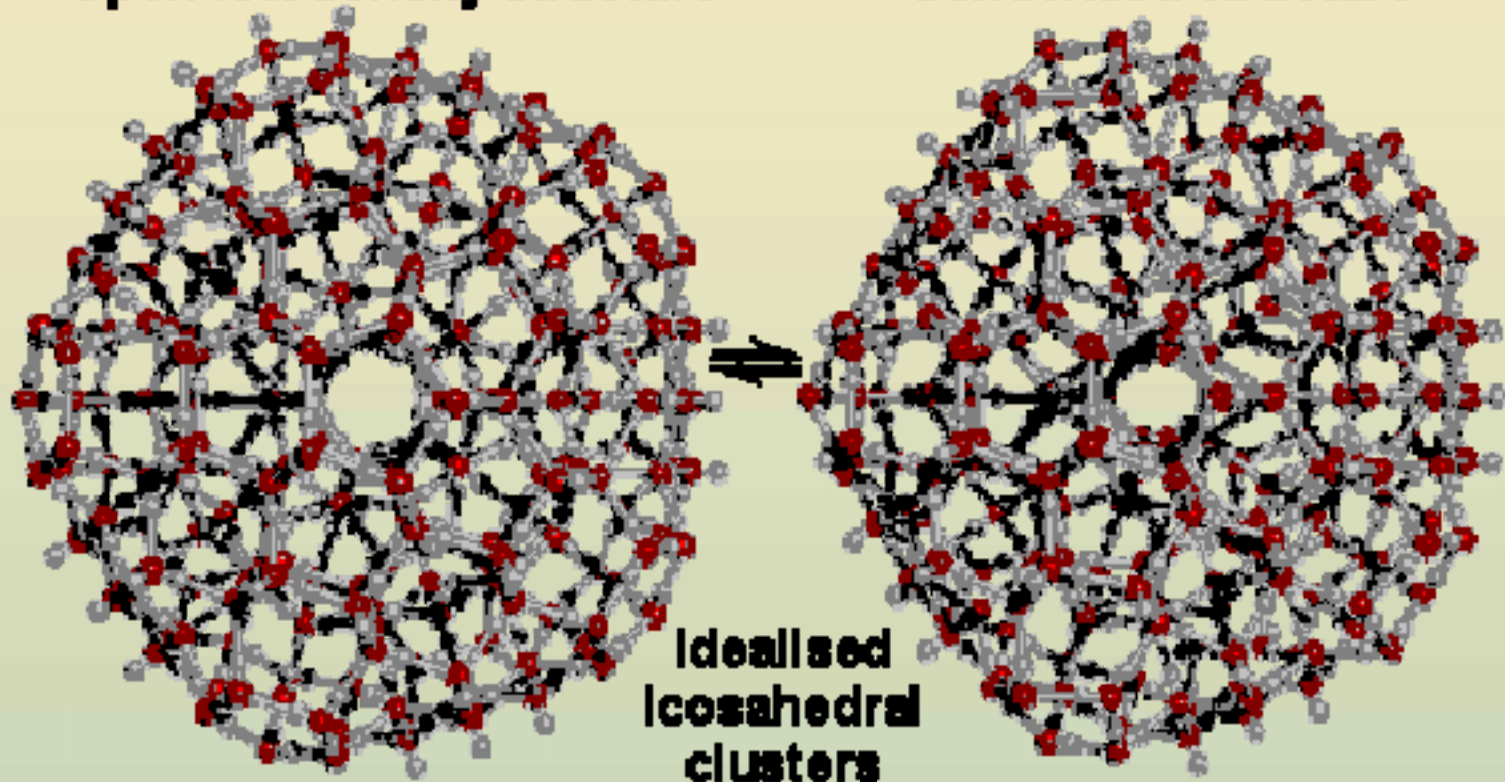




- ▶ The lower the temperature of water, the higher the surface tension (See Graph);
- ▶ The higher the surface tension the greater the formation & size of water clusters (Groundwater is usually between 6-10 °C); and
- ▶ The larger the water clusters, the lower the associated K value in all soil types (Sand  $1 \times 10^{-3}$  cm/sec, Silty-sand  $1 \times 10^{-4}$  cm/sec, Silt  $1 \times 10^{-5}$  cm/sec, Silty Clay  $1 \times 10^{-6}$  cm/sec Clay  $1 \times 10^{-7}$  cm/sec).

**Open low density structure**

**Condensed structure**



## WATER CLUSTERS

- ▶ Theoretical models suggest that the average cluster may encompass as many as **90** H<sub>2</sub>O molecules at 0°C, so that very cold water can be thought of as a collection of ever-changing ice-like structures.
- ▶ At 70° C, the average cluster size is probably no greater than about **25**.
- ▶ Groundwater is between 6 to 10°C, so moderate to large clusters.
- ▶ So water clusters are a reality in soil and ground water remediation, and have a direct affect on K

# WATER & ORGANICS

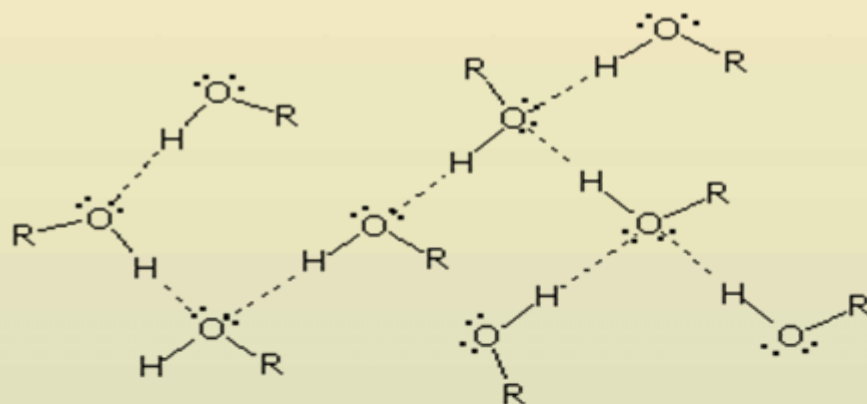
Intermolecular Forces  
Physical Properties  
Hydrogen Bonding  
Boiling Point  
Freezing Point  
Solubility in Water



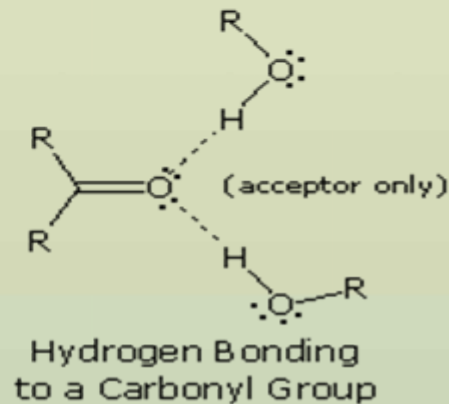
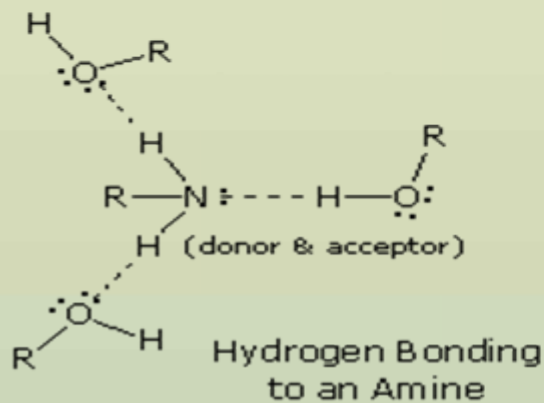
## Solubility in Water

- ▶ Water has been referred to as the "*universal solvent*", and its widespread distribution on this planet and essential role in life make it the benchmark for discussions of solubility.
- ▶ Water *dissolves many ionic salts* thanks to its high dielectric constant and ability to solvate ions. The former reduces the attraction between oppositely charged ions and the latter *stabilizes the ions* by binding to them and delocalizing charge density.
- ▶ *Many organic compounds, especially alkanes and other hydrocarbons, are nearly insoluble in water. Organic compounds that are water soluble, generally have hydrogen bond acceptor and donor groups.* The least soluble of the listed compounds is diethyl ether, which can serve only as a hydrogen bond acceptor and is 75% hydrocarbon in nature.
- ▶ Even so, diethyl ether is about two hundred times more soluble in water than is pentane.

# Organic Molecules & Hydrogen Bonding



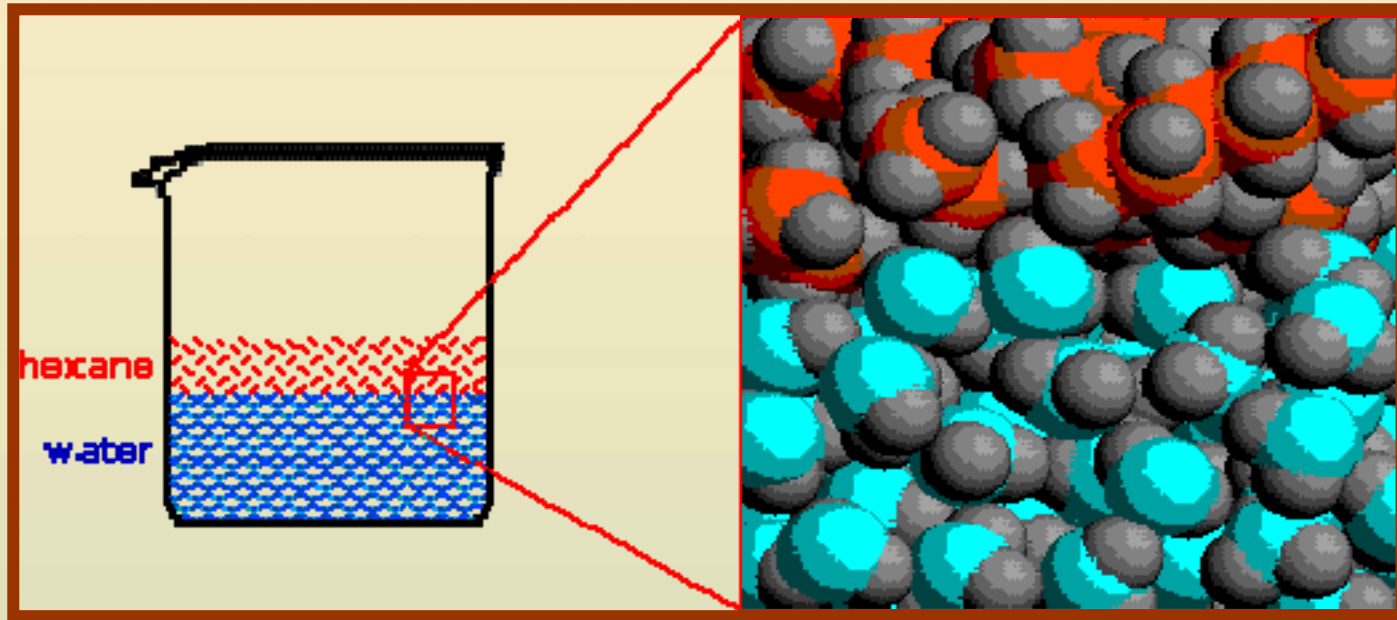
Hydrogen Bonding  
in Alcohols and  
Water (R=H)





- ▶ The *chief characteristic of water that influences these solubilities is the extensive hydrogen bonded association of its molecules with each other.*
- ▶ This *hydrogen bonded network is stabilized by the sum of all the hydrogen bond energies*, and if non-polar molecules such as hexane were inserted into the network they would destroy local structure without contributing any hydrogen bonds of their own.
- ▶ Of course, hexane molecules experience significant van der Waals attraction to neighboring molecules, but these attractive forces are much weaker than the hydrogen bond.
- ▶ *Consequently, when hexane or other non-polar compounds are mixed with water, the strong association forces of the water network exclude the non-polar molecules, which must then exist in a separate phase.* This is shown in the following illustration, and since hexane is less dense than water, the hexane phase floats on the water phase.





- ▶ It is important to remember this *tendency of water to exclude non-polar molecules* and groups, since it is a factor in the structure and behavior of many complex molecular systems.
- ▶ A common nomenclature used to describe molecules and regions within molecules is *hydrophilic* for polar, hydrogen bonding moieties and *hydrophobic* for non-polar species.

# Intermolecular Forces & Physical Properties

- ▶ The *attractive forces that exist between molecules* are responsible for many of the bulk physical properties exhibited by substances.
- ▶ Some compounds are gases, some are liquids, and others are solids.
- ▶ The *melting and boiling points of pure substances reflect these intermolecular forces, and are commonly used for identification. Of these two, boiling point is considered the most representative measure of general inter-molecular attractions.*
- ▶ Thus, a *melting point reflects the thermal energy needed to convert the highly ordered array of molecules in a crystal lattice to the randomness of a liquid.*

# Intermolecular Forces & Physical Properties

## *Continued*

- ▶ *Molecular size is important, but shape is also critical, since individual molecules need to fit together cooperatively for the attractive lattice forces to be large.*
- ▶ *Spherically shaped molecules generally have relatively high melting points, which in some cases approach the boiling point, reflecting the fact that spheres can pack together more closely than other shapes.*
- ▶ *Thus, structure or shape sensitivity is one of the reasons that melting points are widely used to identify specific compounds.*
- ▶ *Boiling points, on the other hand, essentially reflect the kinetic energy needed to release a molecule from the cooperative attractions of the liquid state so that it becomes an unincumbered and relative independent gaseous state species.*

# Intermolecular Forces & Physical Properties

## *Continued*

- ▶ All atoms and molecules have a *weak attraction for one another*, known as *van der Waals attraction*.
- ▶ This *attractive force* has its origin in the *electrostatic attraction of the electrons of one molecule or atom for the nuclei of another*, and has been called *London dispersion force*.
- ▶ *In general, larger molecules have higher boiling points than smaller molecules of the 'same' kind*, indicating that dispersion forces increase with mass, number of electrons, number of atoms or some combination thereof.

▶ The following table lists the boiling points of an assortment of elements and covalent compounds composed of molecules lacking a permanent dipole.

▶ The *number of electrons* in each species is noted in the first column, and the *mass of each is given* as a superscript number preceding the formula.

# Electrons	Molecules & boiling points °C
10	<sup>20</sup> Ne -246 ; <sup>16</sup> CH <sub>4</sub> -162
18	<sup>40</sup> Ar -186 ; <sup>32</sup> SiH <sub>4</sub> -112 ; <sup>30</sup> C <sub>2</sub> H <sub>6</sub> -89 ; <sup>38</sup> F <sub>2</sub> -187
34-44	<sup>84</sup> Kr -152 ; <sup>58</sup> C <sub>4</sub> H <sub>10</sub> -0.5 ; <sup>72</sup> (CH <sub>3</sub> ) <sub>4</sub> C 10 ; <sup>71</sup> Cl <sub>2</sub> -35 ; <sup>88</sup> CF <sub>4</sub> -130
66-76	<sup>114</sup> [(CH <sub>3</sub> ) <sub>3</sub> C] <sub>2</sub> 106 ; <sup>126</sup> (CH <sub>2</sub> ) <sub>9</sub> 174 ; <sup>160</sup> Br <sub>2</sub> 59 ; <sup>154</sup> CCl <sub>4</sub> 77 ; <sup>138</sup> C <sub>2</sub> F <sub>6</sub> -78

▶ Two ten electron molecules are shown in the first row. Neon is heavier than methane, but it boils 84° lower. Methane is composed of five atoms, and the additional nuclei may provide greater opportunity for induced dipole formation as other molecules approach.

▶ The ease with which the electrons of a molecule, atom or ion are displaced by a neighboring charge is called **polarizability**, so we may conclude that *methane is more polarizable than neon*.

▶ In the second row, four eighteen electron molecules are listed. Most of their boiling points are higher than the ten electron compounds neon and methane, but fluorine is an exception, boiling 25° below methane. The remaining examples in the table conform to the correlation of boiling point with total electrons and number of nuclei, but fluorine containing molecules remain an exception.

▶ The anomalous behavior of fluorine may be attributed to its very high electronegativity. The *fluorine nucleus exerts such a strong attraction for its electrons that they are much less polarizable than the electrons of most other atoms*

# Electrons	Molecules & boiling points °C
10	<sup>20</sup> Ne -246 ; <sup>16</sup> CH <sub>4</sub> -162
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- ▶ Of course, *boiling point relationships* may be dominated by even stronger attractive forces, such as involving *electrostatic attraction* between oppositely charged ionic species, and between the *partial charge separations* of molecular dipoles.
- ▶ *Molecules having a permanent dipole moment* should therefore have higher boiling points than equivalent non-polar compounds, as illustrated by the data in the following table.

# Electrons	Molecules & boiling points °C
14-18	$^{30}\text{C}_2\text{H}_6$ -89 ; $^{28}\text{H}_2\text{C}=\text{CH}_2$ -104 ; $^{26}\text{HC}\equiv\text{CH}$ -84 ; $^{30}\text{H}_2\text{C}=\text{O}$ -21 ; $^{27}\text{HC}\equiv\text{N}$ 26 ; $^{34}\text{CH}_3\text{-F}$ -78
22-26	$^{42}\text{CH}_3\text{CH}=\text{CH}_2$ -48 ; $^{40}\text{CH}_3\text{C}\equiv\text{CH}$ -23 ; $^{44}\text{CH}_3\text{CH}=\text{O}$ 21 ; $^{41}\text{CH}_3\text{C}\equiv\text{N}$ 81 ; $^{46}(\text{CH}_3)_2\text{O}$ -24 ; $^{50.5}\text{CH}_3\text{-Cl}$ -24 ; $^{52}\text{CH}_2\text{F}_2$ -52
32-44	$^{58}(\text{CH}_3)_3\text{CH}$ -12 ; $^{56}(\text{CH}_3)_2\text{C}=\text{CH}_2$ -7 ; $^{58}(\text{CH}_3)_2\text{C}=\text{O}$ 56 ; $^{59}(\text{CH}_3)_3\text{N}$ 3 ; $^{95}\text{CH}_3\text{-Br}$ 45 ; $^{85}\text{CH}_2\text{Cl}_2$ 40 ; $^{70}\text{CHF}_3$ -84



- ▶ In the first row of compounds, ethane, ethene and ethyne have *no molecular dipole*, and serve as useful references for single, double and triple bonded derivatives that do.
- ▶ Formaldehyde and hydrogen cyanide clearly show the enhanced intermolecular attraction resulting from a *permanent dipole*. Methyl fluoride is anomalous, as are most organo-fluorine compounds.
- ▶ In the *second and third rows*, all the compounds have *permanent dipoles*, but those associated with the hydrocarbons (first two compounds in each case) are very small. Large molecular dipoles come chiefly from bonds to high-electronegative atoms (relative to carbon and hydrogen), especially if they are double or triple bonds.
- ▶ Thus, *aldehydes, ketones and nitriles tend to be higher boiling than equivalently sized hydrocarbons and alkyl halides*.
- ▶ The atypical behavior of fluorine compounds is unexpected in view of the large electronegativity difference between carbon and fluorine.

# Electrons	Molecules & boiling points °C
14-18	$^{30}\text{C}_2\text{H}_6$ -89 ; $^{28}\text{H}_2\text{C}=\text{CH}_2$ -104 ; $^{26}\text{HC}\equiv\text{CH}$ -84 ; $^{30}\text{H}_2\text{C}=\text{O}$ -21 ; $^{27}\text{HC}\equiv\text{N}$ 26 ; $^{34}\text{CH}_3\text{-F}$ -78
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## Hydrogen Bonding

- ▶ Most of the simple hydrides of group IV, V, VI & VII elements display the expected rise in boiling point with number of electrons and molecular mass, but the hydrides of the *most electronegative elements (nitrogen, oxygen and fluorine)* have abnormally high boiling points, and also listed on the right.
- ▶ The exceptionally *strong dipole-dipole attractions that are responsible for this behavior are called hydrogen bonds*.
- ▶ When a *hydrogen atom is part of a polar covalent bond to a more electronegative atom such as oxygen, its small size allows the positive end of the bond dipole (the hydrogen) to approach neighboring nucleophilic or basic sites more closely than can components of other polar bonds*. Coulombic forces are inversely proportional to the sixth power of the other polar bonds.

Group	Molecules & boiling points °C
VII	HF 19 ; HCl -85 ; HBr -67 ; HI -36
VI	H <sub>2</sub> O 100 ; H <sub>2</sub> S -60 ; H <sub>2</sub> Se -41 ; H <sub>2</sub> Te -2
V	NH <sub>3</sub> -33 ; PH <sub>3</sub> -88 ; AsH <sub>3</sub> -62 ; SbH <sub>3</sub> -18

- ▶ The table of data above provides *convincing evidence for hydrogen bonding*. In each row the first compound listed has the *fewest total electrons and lowest mass, yet its boiling point is the highest due to hydrogen bonding*.
- ▶ Other compounds in each row have *molecular dipoles, the interactions of which might be called hydrogen bonding, but the attractions are clearly much weaker*.
- ▶ The first two hydrides of group IV elements, methane and silane, are listed in the first table above, and do not display any significant hydrogen bonding.

- Organic compounds incorporating O-H and N-H bonds will also exhibit enhanced intermolecular attraction due to hydrogen bonding. Some examples are given below.

Class	Molecules & Boiling Points °C	
Oxygen Compounds	$C_2H_5OH$ 78 ; ethanol $(CH_3)_2O$ -24 ; dimethyl ether $(CH_2)_2O$ 11 ; ethylene oxide	$(CH_2)_3CHOH$ 124 & cyclobutanol $(CH_2)_4O$ 66 ; tetrahydrofuran
Nitrogen Compounds	$C_3H_7NH_2$ 50 ; propyl amine $C_2H_5NH(CH_3)$ 37 ; ethyl methyl amine $(CH_3)_3N$ 3 ; trimethyl amine	$(CH_2)_4CHNH_2$ 107 & cyclopentyl amine $(CH_2)_4NCH_3$ 80 ; N-methylpyrrolidine
Complex Functions	$C_2H_5CO_2H$ 141 & propanoic acid $CH_3CO_2CH_3$ 57 ; methyl acetate	$C_3H_7CONH_2$ 218 & butyramide $CH_3CON(CH_3)_2$ 165 ; N,N-dimethylacetamide

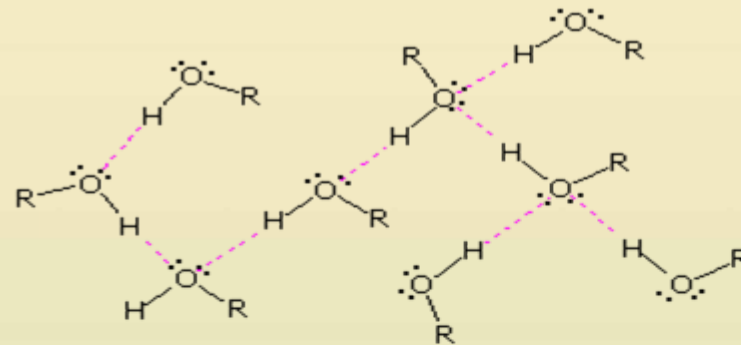
## Water Solubility

- ▶ Water is the single most abundant and important liquid on this planet.
- ▶ The miscibility of other liquids in water, and the solubility of solids in water, must be considered when isolating and purifying compounds.
- ▶ To this end, the *following table lists the water miscibility (or solubility) of an assortment of low molecular weight organic compounds.*
- ▶ *The influence of the important hydrogen bonding atoms, oxygen and nitrogen is immediately apparent.* The first row lists a few hydrocarbon and chlorinated solvents. Without exception these are all immiscible with water, although it is interesting to note that the  $\pi$ -electrons of benzene and the nonbonding valence electrons of chlorine act to slightly increase their solubility relative to the saturated hydrocarbons.
- ▶ *When compared with hydrocarbons, the oxygen and nitrogen compounds listed in the second, third and fourth rows are over a hundred times more soluble in water, and many are completely miscible with water.*

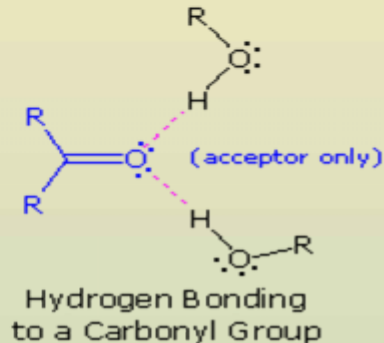
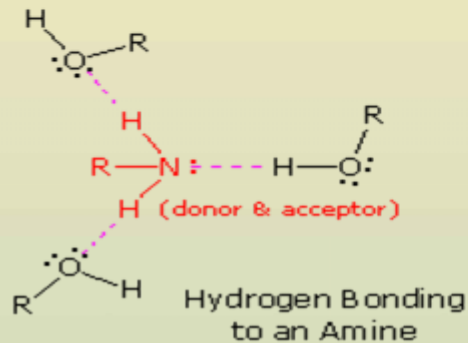
## Water Solubility of Characteristic Compounds

Compound Type	Specific Compounds	Grams/100mL	Moles/Liter		Specific Compounds	Grams/100mL	Moles/Liter
Hydrocarbons & Alkyl Halides	butane	0.007	0.0012		benzene	0.07	0.009
	hexane	0.0009	0.0001		methylene chloride	1.50	0.180
	cyclohexane	0.006	0.0007		chloroform	0.8	0.07
Compounds Having One Oxygen	1-butanol	9.0	1.2		ethyl ether	6.0	0.80
	tert-butanol	complete	complete		THF	<i>complete</i>	<i>complete</i>
	cyclohexanol	3.6	0.36		furan	1.0	0.15
	phenol	8.7	0.90		anisole	1.0	0.09
Compounds Having Two Oxygens	1,3-propanediol	<i>complete</i>	<i>complete</i>		1,2-dimethoxyethane	<i>complete</i>	<i>complete</i>
	2-butoxyethanol	<i>complete</i>	<i>complete</i>		1,4-dioxane	<i>complete</i>	<i>complete</i>
	butanoic acid	<i>complete</i>	<i>complete</i>		ethyl acetate	8.0	0.91
	benzoic acid	<i>complete</i>	<i>complete</i>		γ-butyrolactone	complete	complete
Nitrogen Containing Compounds	1-aminobutane	<i>complete</i>	<i>complete</i>		triethylamine	5.5	0.54
	cyclohexylamine	<i>complete</i>	<i>complete</i>		pyridine	<i>complete</i>	<i>complete</i>
	aniline	3.4	0.37		propionitrile	10.3	2.0
	pyrrolidine	<i>complete</i>	<i>complete</i>		1-nitropropane	1.5	0.17
	pyrrole	6.0	0.9		DMF	<i>complete</i>	<i>complete</i>

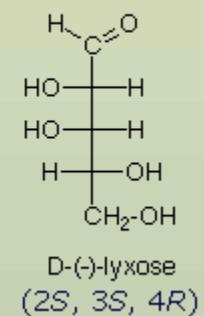
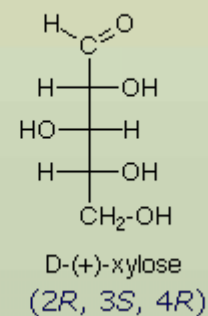
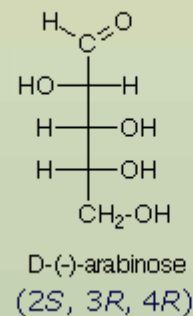
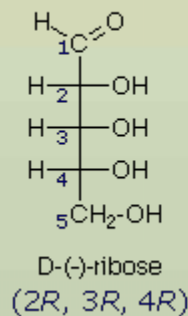
- ▶ Some general trends are worth noting from the data above. First, *alcohols* (second row left column) *are usually more soluble than equivalently sized ethers* (second row right column). This reflects the fact that the hydroxyl group may function as both a hydrogen bond donor and acceptor; whereas, an ether oxygen may serve only as an acceptor.
- ▶ The increased solubility of phenol relative to cyclohexanol may be due to its greater acidity as well as the pi-electron effect noted in the first row.
- ▶ The *cyclic ether THF (tetrahydrofuran) is more soluble than its open chain analog, possibly because the oxygen atom is more accessible for hydrogen bonding to water molecules.*
- ▶ Due to the decreased basicity of the oxygen in the aromatic compound furan, it is much less soluble. The oxygen atom in anisole is likewise deactivated by conjugation with the benzene ring (note, it activates the ring in electrophilic substitution reactions).
- ▶ *A second oxygen atom dramatically increases water solubility, as demonstrated by the compounds listed in the third row. Again hydroxyl compounds are listed on the left. Nitrogen exerts a solubilizing influence similar to oxygen, as shown by the compounds in the fourth row. The primary and secondary amines listed in the left hand column may function as both hydrogen bond donors and acceptors.*
- ▶ Aromaticity decreases the basicity of pyrrole, but increases its acidity. The compounds in the right column are only capable of an acceptor role. The low solubility of the nitro compound is surprising.



Hydrogen Bonding  
in Alcohols and  
Water (R=H)



### Four Diastereomeric C<sub>5</sub>H<sub>10</sub>O<sub>5</sub> Aldopentoses





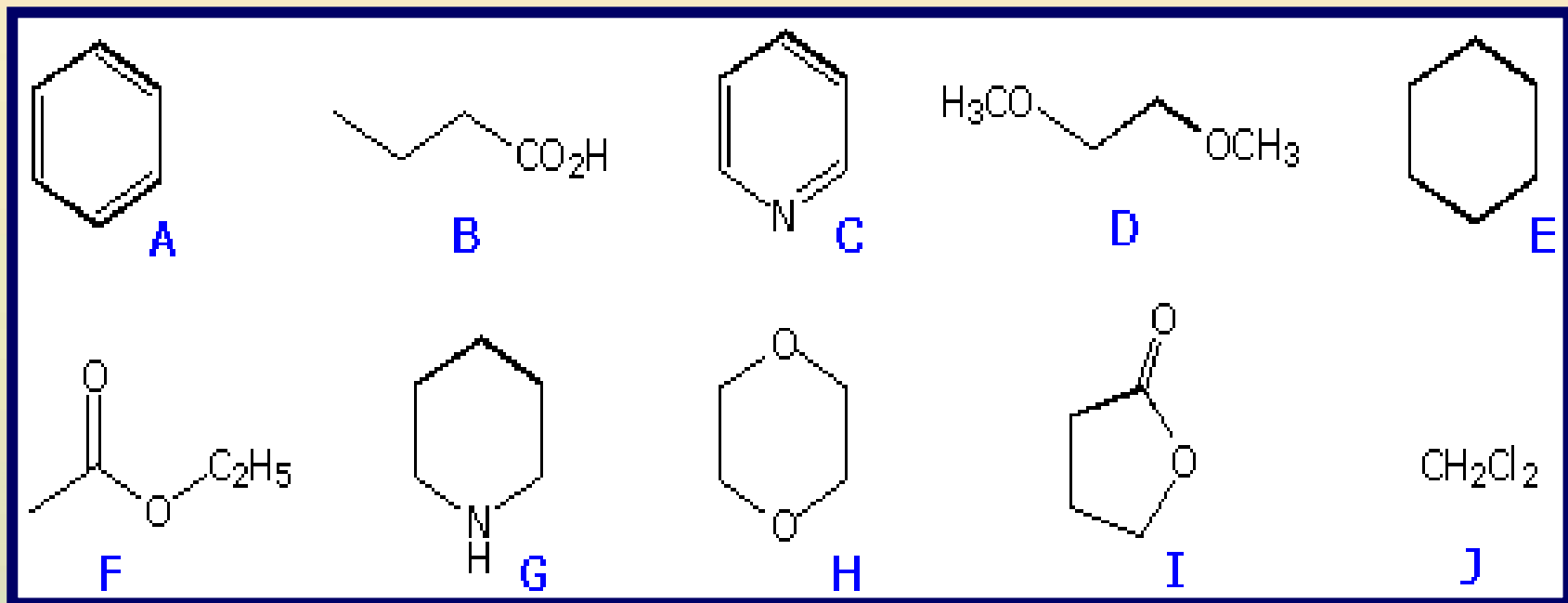
## **Class Exercise II** *(Individual or Group)*

- i) Rank Compounds **A** through **J** from most to least soluble;**
- ii) List all compounds which have potential for Hydrogen Bonding, and which one you feel has most and least;**
- iii) Rank compounds from highest to lowest boiling point.**
- iv) Be prepared to explain your answers...**

*No answers are wrong, this is to get you thinking and using some of the basic principle described earlier.*

*You will need a CRC Handbook to confirm your answers.*





- i) Solubility (Greatest to least) ?
- ii) Hydrogen bonding (Highest to lowest) ?
- iii) Boiling point (Highest to lowest) ?
- iv) Why for the greatest/highest and least/lowest ?

# *Organic Compounds Properties & Characteristic*



## ORGANIC CHEMISTRY

► Organic Chemistry is a specific discipline within chemistry which involves the scientific study of the structure, properties, composition, reactions, and preparation (by synthesis or by other means) of chemical compounds consisting of primarily carbon and hydrogen, which may contain any number of other elements, including nitrogen, oxygen, halogens as well as phosphorus, silicon and sulfur.

► The original definition of organic chemistry came from the misperception that these compounds were always related to life processes, but it has been shown that this is not the case.

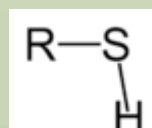
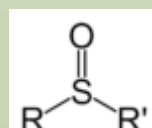
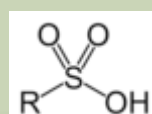
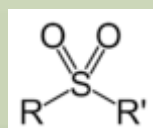
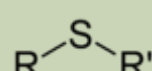
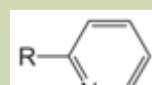
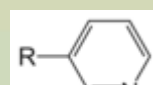
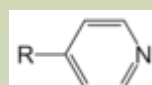
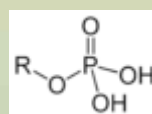
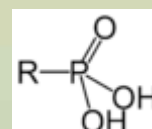
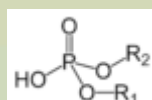
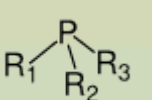
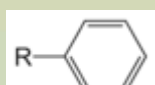
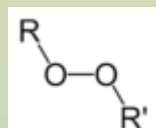
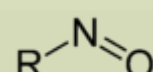
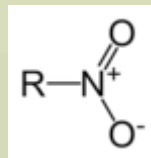
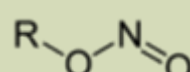
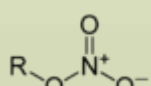
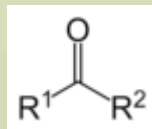
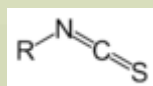
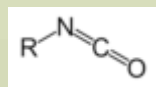
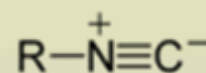
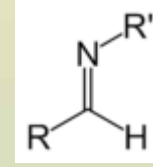
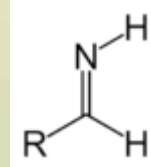
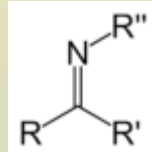
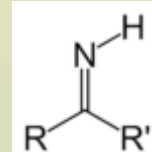
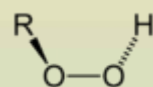
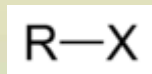
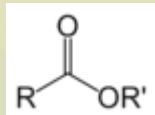
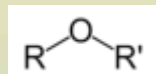
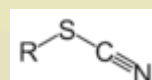
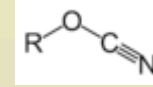
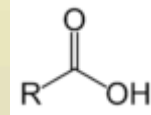
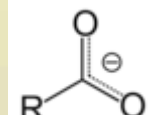
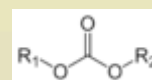
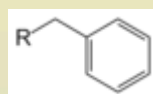
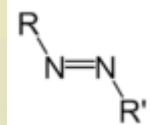
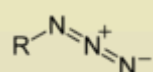
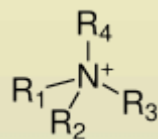
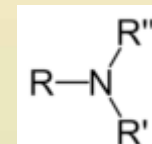
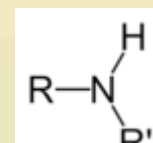
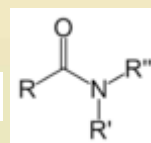
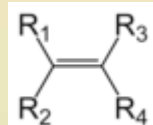
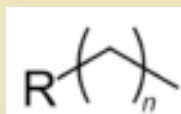
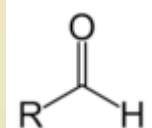
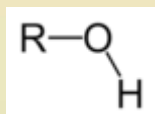
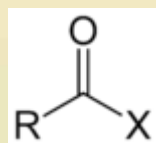
► Compounds that are related to life processes are dealt with in the branch of chemistry which is called biochemistry.

- ▶ Because of their unique properties, multi-carbon compounds exhibit extremely large variety and the range of application of organic compounds is enormous.
- ▶ They form the basis of, or are important constituents of many products (paints, plastics, food, explosives, drugs, petrochemicals, and many others) and of course (apart from a very few exceptions) they form the basis of all life processes.
- ▶ The different shapes and chemical reactivities of organic molecules provide an astonishing variety of functions, like those of enzyme catalysts in biochemical reactions of live systems.
- ▶ The autopropagating nature of these organic chemicals is what life is all about.

## Functional Groups In Organic Chemistry

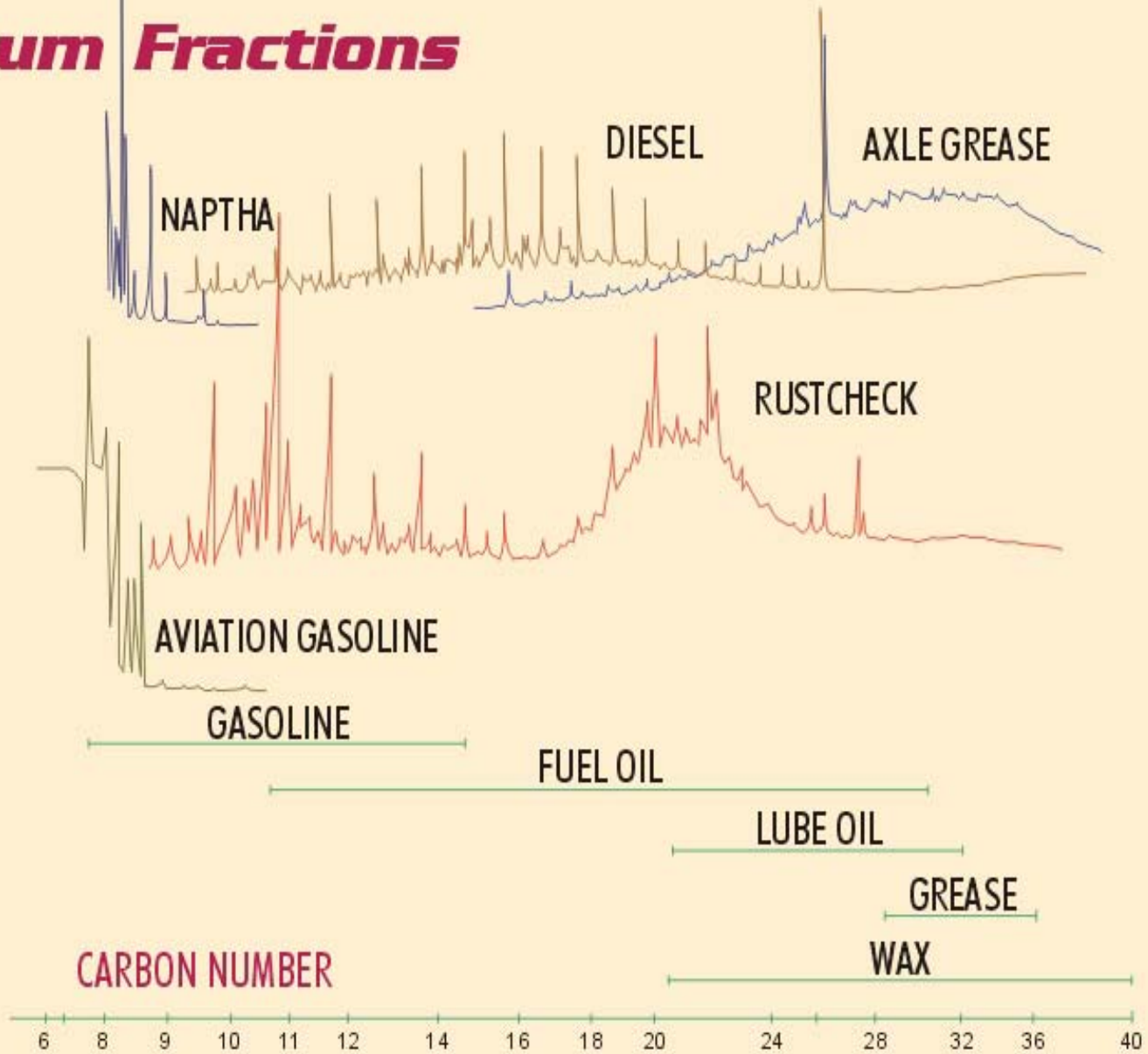
- ▶ In organic chemistry, functional groups are specific groups of atoms within molecules, that are responsible for the characteristic chemical reactions of those molecules. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule it is a part of.
- ▶ The following is a list of common functional groups. In the formulas, the symbols R and R' usually denotes an attached hydrogen, or a hydrocarbon side chain of any length, but may sometimes refer to any group of atoms. Combining the names of functional groups with the names of the parent alkanes generates a powerful systematic nomenclature for naming organic compounds.

# Functional Groups In organic Chemistry





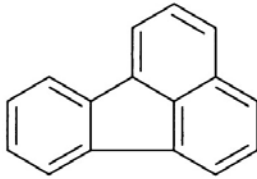
# Petroleum Fractions



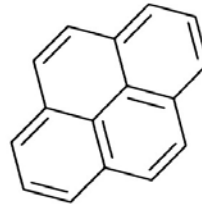
## Functional Groups In Organic Chemistry *Continued*

- ▶ The non-hydrogen atoms of functional groups are always associated with each other and with the rest of the molecule by covalent bonds.
- ▶ When the group of atoms is associated with the rest of the molecule primarily by ionic forces, the group is referred to more properly as a polyatomic ion or complex ion. And all of these are called radicals, by a meaning of the term *radical* that predates the free radical.
- ▶ The first carbon after the carbon that attaches to the functional group is called the alpha carbon. Functional groups are attached to the carbon backbone of organic molecules.
- ▶ They determine the characteristics and chemical reactivity of molecules. Functional groups are far less stable than the carbon backbone and are likely to participate in chemical reactions. Six common biological functional groups are hydrogen, hydroxyl, carboxyl, amino, phosphate, and methyl.

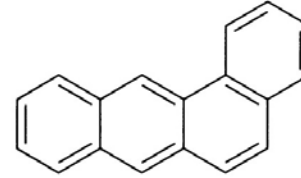




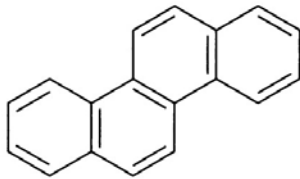
Fluoranthene



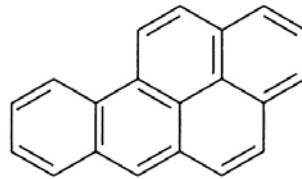
Pyrene



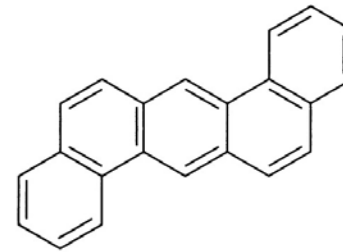
Benz[a]anthracene



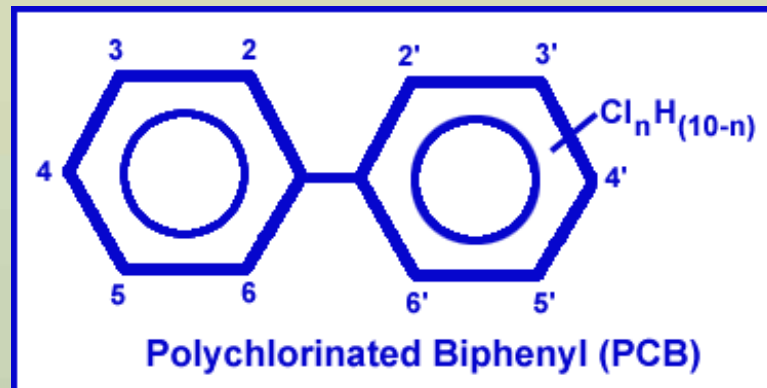
Chrysene



Benzo[a]pyrene



Dibenz[a,h]anthracene



## Methods of Describing Molecules with Increasing Refinement Composition

- ▶ **Composition:** The number and kinds of atoms that make up a molecule. This information is supplied by a molecular formula. **eg. CH<sub>4</sub> methane gas**
- ▶ **Constitution:** The bonding pattern of the atoms of a molecule (ie. which atoms are connected to which other atoms and by what kind of bonds). Different bonding constitutions are interconverted only by breaking and reforming covalent bonds.  
**eg. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> Butane and CH<sub>3</sub>-CH<sub>2</sub>=CH<sub>2</sub>-CH<sub>3</sub> Butene**
- ▶ **Configuration:** The permanent spatial relationship of the atoms of a molecule to each other. Different configurations are interconverted only by breaking and reforming covalent bonds. This information is given in a stereo-formula, and is also provided by a prefix to the IUPAC name (eg. cis & trans).
- ▶ **Conformation:** The variable spatial orientation of the atoms of a molecule to each other that occurs by rotation or twisting of bonds. Different conformations are interconverted without breaking covalent bonds. This information is supplied by conformational formulas, and also by nomenclature terms (eg. gauche & anti).

Eg. The 3-Demensional flexing, twisting and rotation of molecule and or functional groups on the molecule (Benzene - Chain and Saddle Positions, not Planar)

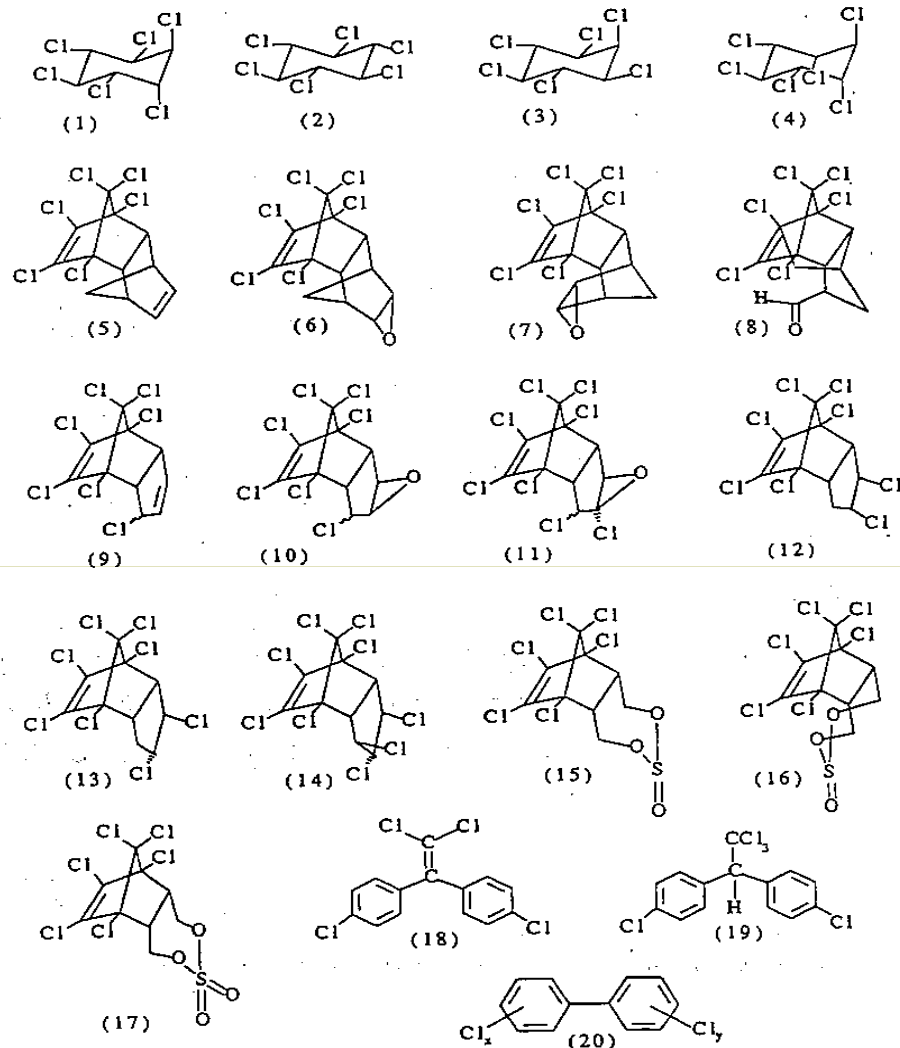


FIGURE 1. Compounds studied: (1)  $\alpha$ -hexachlorocyclohexane (a-BHC); (2)  $\beta$ -hexachlorocyclohexane (b-BHC); (3)  $\delta$ -hexachlorocyclohexane (d-BHC); (4)  $\gamma$ -hexachlorocyclohexane or lindane (g-BHC); (5) aldrin; (6) dieldrin; (7) endrin; (8) endrin aldehyde (endrin acid); (9) heptachlor; (10) heptachlor epoxide (hepta epox); (11) oxychlordan; (12)  $\alpha$ -chlordane (a-chlordane); (13)  $\gamma$ -chlordane (g-chlordane); (14) *trans*-nonachlor (t-nonachlor); (15) endosulfan I (endo I); (16) endosulfan II (endo II); (17) endosulfan sulfate (endo sulfate); (18) *p,p'*-DDE; (19) *p,p'*-DDT; (20) general structure of polychlorinated biphenyls (PCBs).

## Summary Comments

- ▶ Simply put, Organic compounds are essentially comprised of *Carbon (C) and Hydrogen (H)* atoms.
- ▶ Added to this, the organic molecules *may contain* other atoms or groups with Oxygen (*O*), Nitrogen (*N*), Sulphur (*S*), Chloride (*CL*), Bromide (*Br*), etc.
- ▶ The chemical *structure and composition* (What's on the molecule) will give rise to its bulk *physical and chemical characteristics*.
- ▶ *If the organic will dissolve in water*, and/or sorb to soil/solids will be largely a *function of hydrogen (HB)* bonding. If HB can occur it will dissolve, if not, it will not dissolve and most likely *sorb onto soil surfaces*.

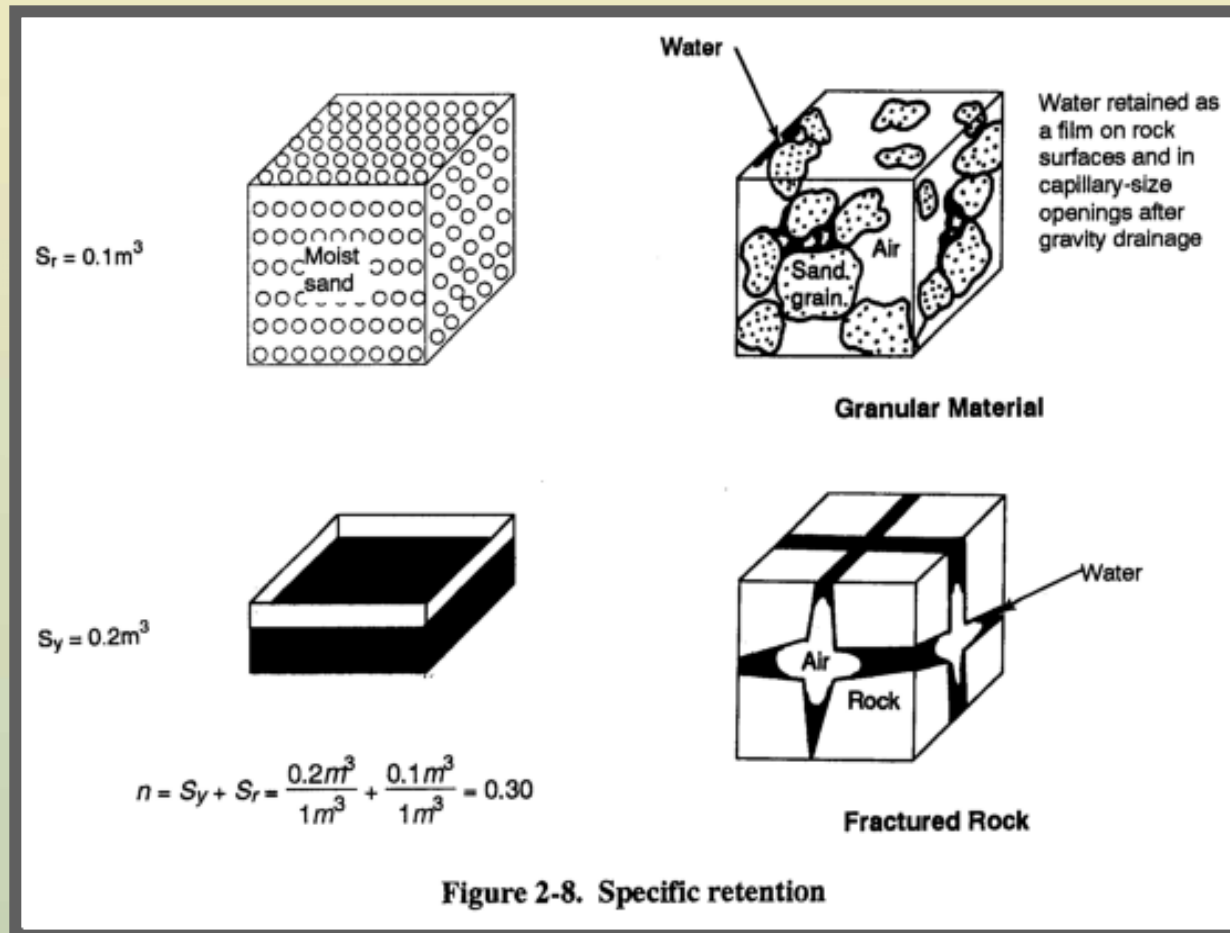
## **Class Exercise III** *(Group Discussion)*

- i) What affects may the chemical composition of an organic contaminant have on its water solubility?**
- ii) What affects may the chemical composition of an organic contaminant have on its sorption in soils?**
- iii) Will chemical composition of an organic affect its hydraulic extraction? If yes, explain. If no, explain.**
- iii) What affects could the 'Physical 3-Demensional' structure & make-up of a molecule have on its rate of movement through a soil? Explain.**

# SORPTION

## Adsorption and Absorption

### Properties and Characteristics



## **FACT**

**90 to 95 % of All Contaminants Are  
Absorbed To Particles In  
Soil, Bed Rock and Groundwater**

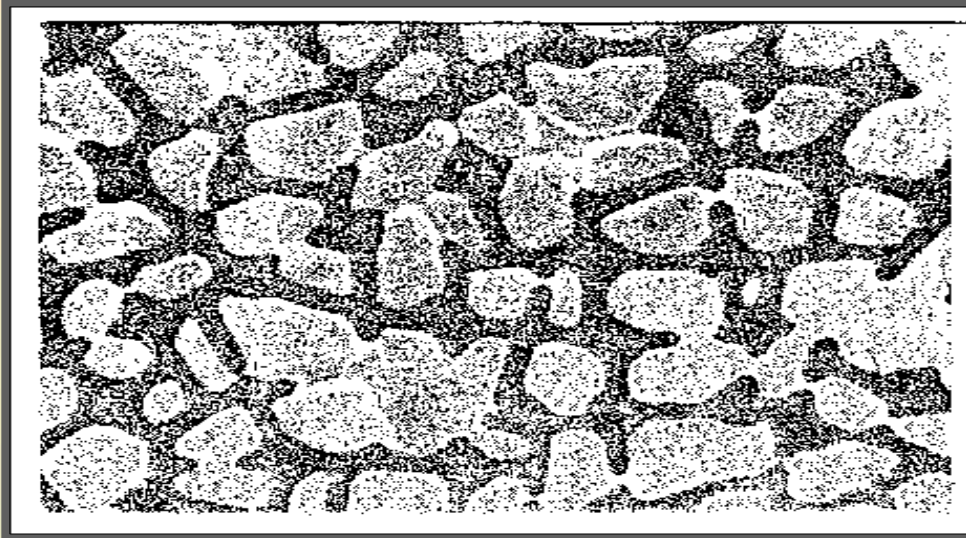


**Contaminant Sorption  
Limits Availability of Contaminants For  
Remediation**



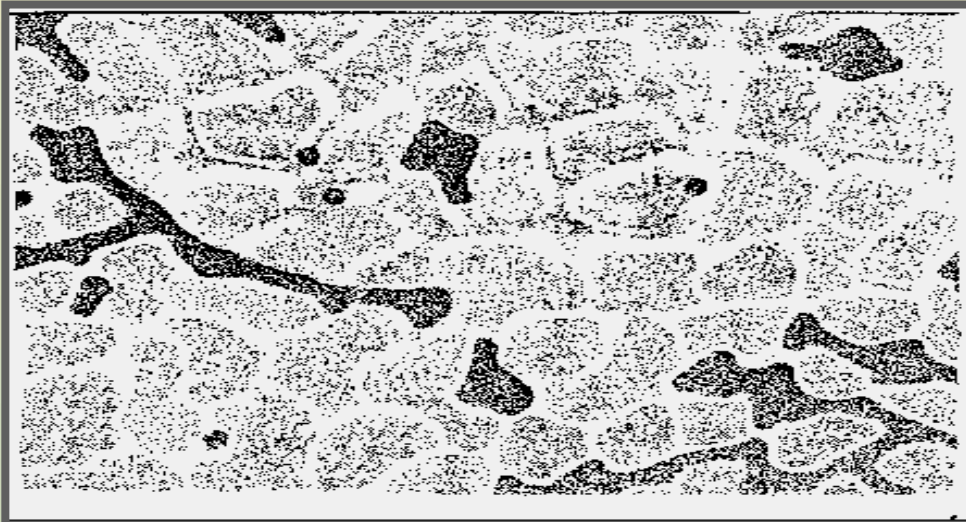
**Sorption is the #1 Reason Why Many In-situ  
and Ex-situ Remediation Project are  
Slow, Costly and/or Fail.**





▶ **Contaminants Sorbed (Adsorbed and or absorbed).**

▶ **Note partial and or fully blocking the pores and hydraulic pathways.**





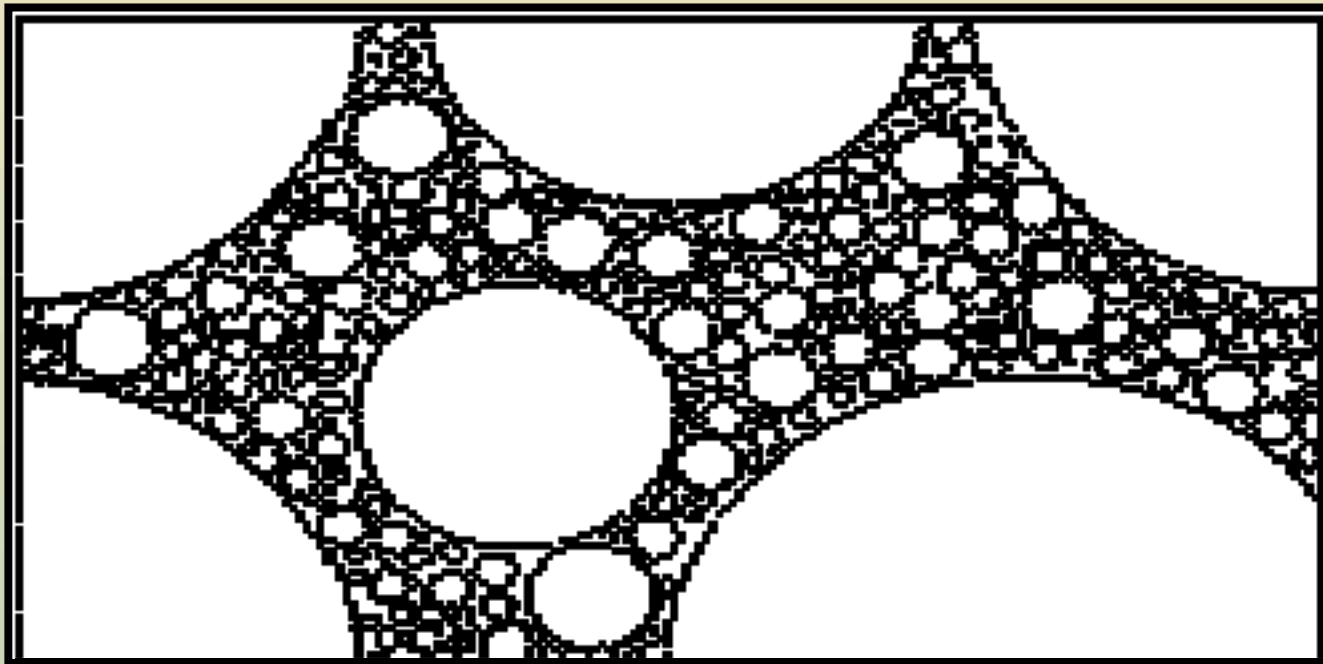
### *Sorption and Partitioning (Kd):*

- *Sorption* refers to the property of a solute to either *attach* to the *surface* of a solid (**adsorption**) and/or then *penetrate* the solid (**absorption**).
- Sorption results in a reaction between the concentration of solute in the aqueous phase, and the concentration on or in the solid. At equilibrium, the partitioning of solutes between liquid and solid phases in the porous medium can be described by an equilibrium constant, **Kd**
- partitioning causes a *retardation* in the contaminant front. Because solutes are almost always slower than the groundwater, they are said to be *retarded*. Exceptions: halogens - chloride, iodide, fluoride

- ▶ The *sorption of a contaminant* is one of the significant processes that *can hinder the remediation of a soil and ground water* aquifer system.
- ▶ Sorption is defined as being the *attraction of an aqueous species to the surface of a solid*.(Alley, 1993).
- ▶ In ground water the sorbing species , usually an *organic compound*, is called the *sorbate*, and the solid media, usually *soil*, to which the sorbate is attracted is known as the *sorbent*.
- ▶ The underlying principle behind this attraction results from some form of bonding between the contaminant and adsorption receptor sites on the solid.
- ▶ The *amount of sorption* that occurs *in soil and or groundwater* is *dependent on particular characteristics of the sorbate and sorbent*. The amount of sorption that takes place on organic matter also follows various isotherms or kinetic rates.
- ▶ *Sorption tends to cause contaminants to move more slowly than the groundwater*, therefore the effects must be taken into consideration when calculating how far the contaminant has traveled in a given time period.

## Sorption (Absorption and Adsorption) of Contamination in Soil Matrix

Soil & Water Remediation Must Address This To Be Successful.





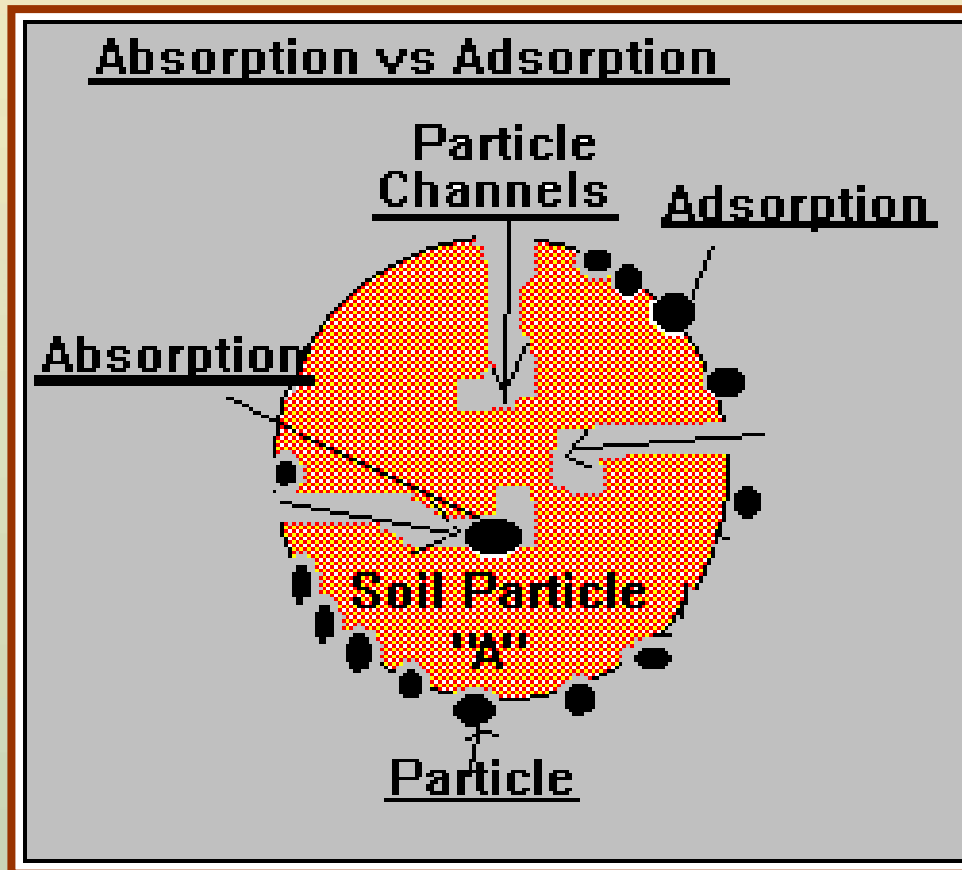
**Ivey-sol • SPTT**



## **Adsorption vs. Absorption**

- ▶ Sorption reactions generally occur over a short period of time, however if the adsorbed contaminant begins to be incorporated into the structure of the sorbent, a slow occurring reaction, known as absorption, begins to take place.
- ▶ To be more precise, the difference between adsorption and absorption is that adsorption is the attraction between the outer surface of a solid particle and a contaminant, whereas absorption is the uptake of the contaminant into the physical structure of the solid.
- ▶ This figure shows the primary differences between intra-particle absorption versus surface adsorption.
- ▶ The main difference being that some contaminant particles are attracted to the outer surface of the soil particle, while another has been actually incorporated into the particle's structure.

## Adsorption vs. Absorption



# **Class Exercise IV**

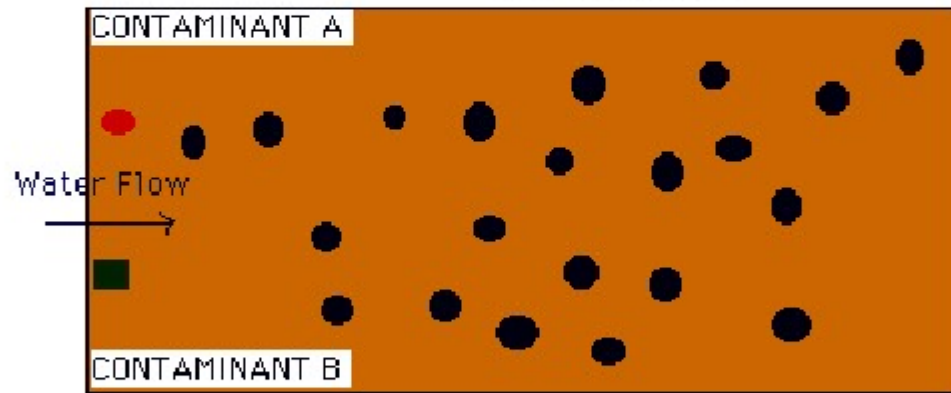
## **Sorption Demonstration**

*(Animation)*

**The following animation sequence displays how sorption can affect two separate particles' velocity.**

**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.**

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





# Key Properties of Contaminants:

- ▶ **Water Solubility**
- ▶ **Polarity of the Compound**
- ▶ **Kow (Octanol Water Partition Coefficient)**

## Solubility & Polarity

- ▶ **Solubility** is defined as the maximum amount of a contaminant that can be dissolved in water at a specified temperature. The solubility of a compound tends to be inversely proportional to the amount of sorption that the contaminant can undergo.
- ▶ The **Polarity** of a compound plays a major role in the mobility of the compound. Polar substances tend to dissolve more readily in water than nonpolar substances and, therefore adsorb to soil particles less.
- ▶ Benzene, toluene, and xylene are **non-polar** constituents of gasoline that dissolve uniquely well in water. Interestingly, benzene is considered a carcinogen to humans, therefore great care must be taken to insure the safety of drinking water in the area of gasoline spills.
- ▶ Many of the **polar** contaminants found in soils are metabolites of pesticides and phenols.

## Partition Coefficient

- ▶ The *Kow*, or Octanol - Water partition coefficient, *is simply a measure of the hydrophobicity (water repulsing) of an organic compound. The more hydrophobic a compound, the less soluble it is, therefore the more likely it will adsorb to soil particles (Bedient 1994).*
- ▶ **Kow can be determined by adding a known amount of contaminant to a bottle consisting of equal volumes of Octanol and water.**
- ▶ *The coefficient is determined by calculating the concentration in the Octanol phase compared to the concentration in the water phase.*
- ▶ **The Kow of a compound can also be used to find the Koc of a particular contaminant. Koc is the partition coefficient of the contaminant in the organic fraction of the soil.**
- ▶ *Koc depends on the physico-chemical properties of the contaminant, not the percent of organic matter in the soil. One such relationship between Kow of aromatic compounds and Koc is:*

$$\text{Log Koc} = 1.00 (\text{Log Kow}) - 0.21$$

*A separate equation is used for every class of compound to determine the organic partitioning coefficient from the octanol-water partitioning coefficient of the compound.*

## **Characteristics of the Soil and Fluid:**

- ▶ **Texture**
- ▶ **Organic Carbon Content**
- ▶ **Surface Charge**
- ▶ **pH of the Fluid**

- ▶ The **texture** of a soil is extremely important in the sorption process. If a soil is made up of mostly clay and organic matter a significant amount of sorption will take place.
- ▶ *Clay especially intermixed with organic particles, by far adsorbs the most out of the three main soil textures (clay, silt, and sand) because of its small particle size, high surface area, and high surface charge.*
- ▶ The *pH of the fluid can affect sorption* considerably because it can affect the solubility of a compound. Certain compounds dissolve better in fluids under certain pH's, for example *organic acids tend to adsorb better under acidic conditions and amino compounds adsorb better under alkaline conditions* (Cantor et al. 1985).

## **Pesticide Sorption Coefficients** *Common Pesticides*

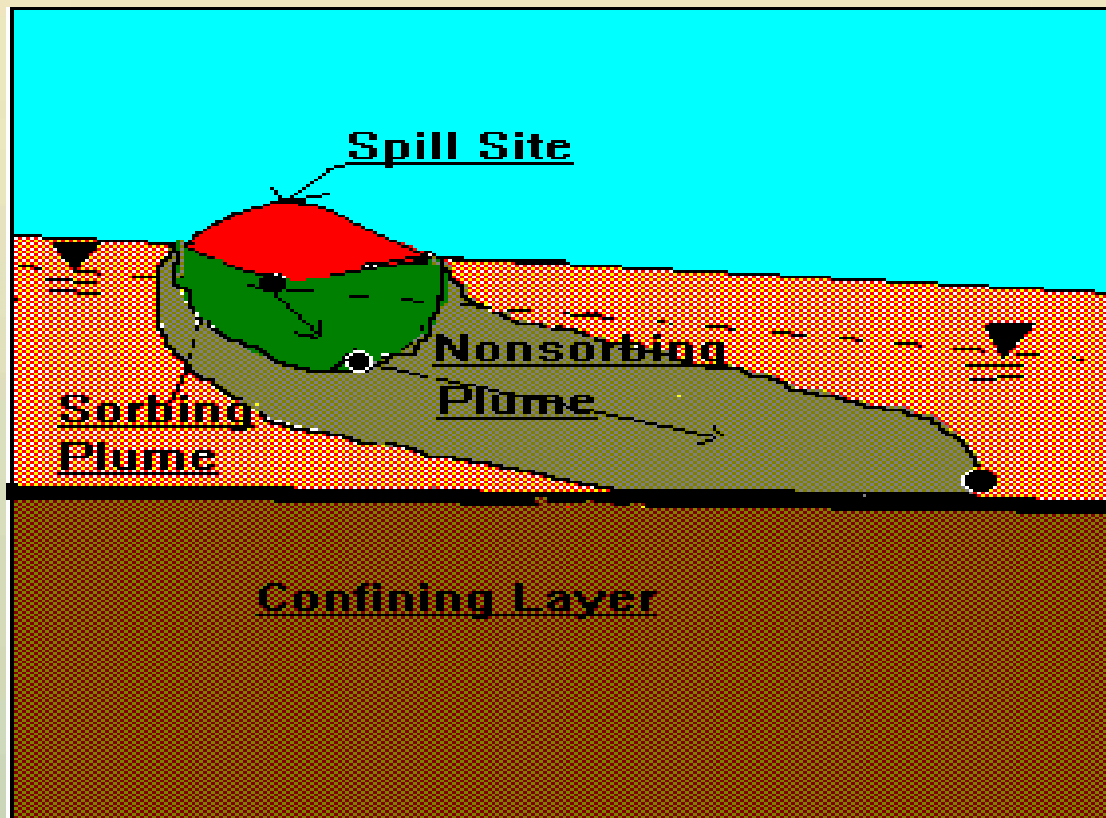
<b>Pesticide Name</b>	<b>Molecular Weight (g/mol)</b>	<b>Water Solubility (mg/L)</b>	<b>Sorption Coefficient, Koc (ml/g)</b>
<b>Atrazine (Herbicide)</b>	<b>215.69</b>	<b>33</b>	<b>163</b>
<b>Diazanon (Insecticide)</b>	<b>304.3</b>	<b>40</b>	<b>1000E</b>
<b>DDT (Insecticide)</b>	<b>354.5</b>	<b>0.001-0.004</b>	<b>24000</b>
<b>Carbofuran (Insecticide)</b>	<b>221.25</b>	<b>700</b>	<b>29</b>
<b>Cyanazine (Herbicide)</b>	<b>240.7</b>	<b>420</b>	<b>10000E</b>

## Retardation Factors in Ground Water

- ▶ A *correction factor known as a retardation factor ( $R_f$ )* takes into account how much a contaminant's velocity is affected by sorption in the ground water system. The overall correction factor is a measure of the bulk density of the media, the porosity, and the distribution coefficient ( $K_d$ ).
- ▶ The retardation factor in ground water has been measured quite often by using nonsorbing tracers and highly sorbing contaminants in on site experiments. In one such experiment a chloride tracer, along with *carbon tetrachloride (CTET)* and *tetrachloroethylene (PCE)* were added to ground water.
- ▶ After a two year monitoring period the distance that the two organic contaminant plumes had traveled were measured against the distance that the chloride tracer had traveled and the difference in distances were used to calculate the retardation factor.
- ▶ It turned out that in the two year period the chloride tracer had moved 60 meters and the PCE had only traveled a distance of 10 meters (Masters 1991). The retardation factor figures into the advection - dispersion equation by dividing average linear velocity and any dispersion coefficients through by this retardation factor.



This image displays how a **retardation factor** can hinder the movement of a **spill** in the ground water: **Effect of  $R_f$  Value on Dispersion**



*Adapted from Bennett and Zheng*

## *Sorption and Partitioning ( $K_d$ ) (cont.):*

- **Retardation Factor,  $R_f$** , refers to the velocity of the plume front relative to the velocity of the flowing groundwater.

$$R = \frac{\bar{v}}{\bar{v}_c} = 1 + \left( \frac{\rho_b}{n} \right) K_d$$

where

$\bar{v}$  = average linear velocity

$\bar{v}_c$  = velocity of the mid-point of the plume front, where  $C/C_o = 0.5$  point

$\rho_b$  = bulk mass density of the porous medium (usually  $1800 \text{ kg/m}^3$ )

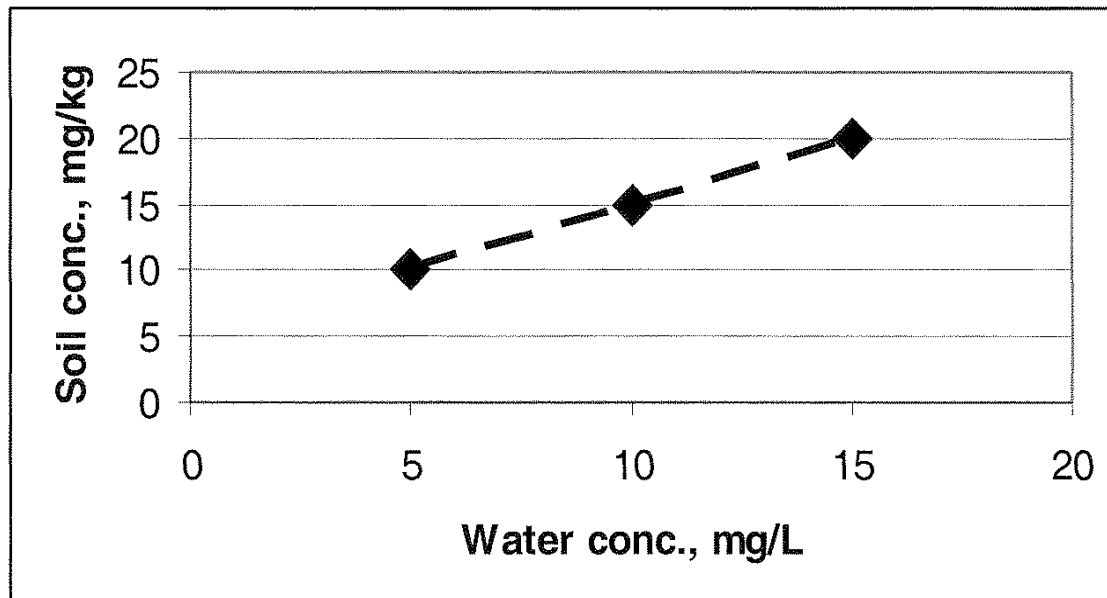
$n$  = porosity of the porous medium

$R_f$  = retardation factor

## *Sorption and Partitioning ( $K_d$ ) (cont.):*

$K_d$  generally ranges from near 0 mL/g to  $10^3$  mL/g, but may be much greater for highly sorbed chemicals such as PCBs.

$K_d$  usually measured in a laboratory using batch tests to develop a *linear isotherm*:



***Sorption and Partitioning ( $K_d$ ) (cont.):***

Recall that for organics,  $K_{oc}$  is related to  $K_d$ :

$$K_d = K_{oc} (f_{oc})$$

where

$K_{oc}$  = partition coefficient between soil organic carbon and water

$f_{oc}$  = fraction of organic carbon (usually 0.01% to 1 %)

## Soil Type Retardation Factors

**Table 2-2. Specific yield and retention percentages  
(values in percent by volume)**

<b>Material</b>	<b>Porosity</b>	<b>Specific Yield</b>	<b>Specific Retention</b>
Soil	55	40	15
Clay	50	2	48
Sand	25	22	3
Gravel	20	19	1
Limestone	20	18	2
Sandstone (semiconsolidated)	11	6	5
Granite	0.1	0.09	0.01
Basalt (young)	11	8	3

*The finer the soil, the more retardation.*

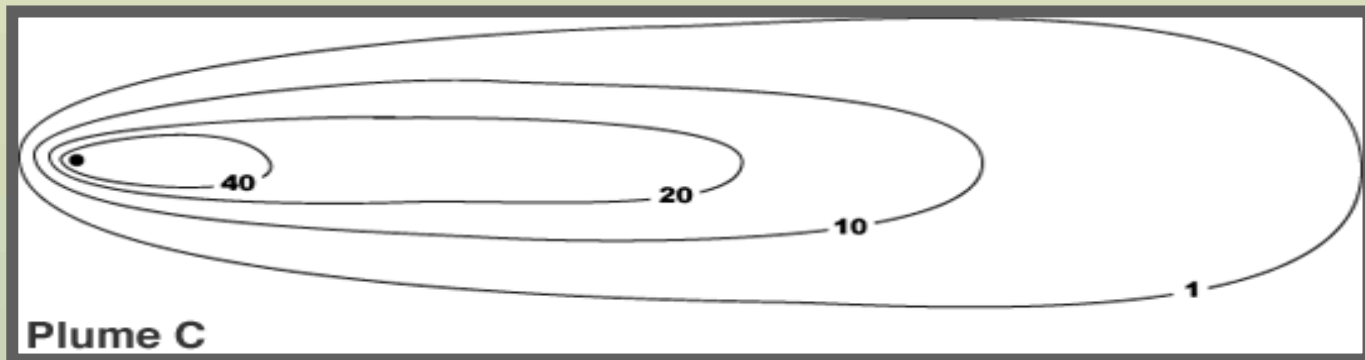
# Organic Plumes

## Hydrogeological Consideration

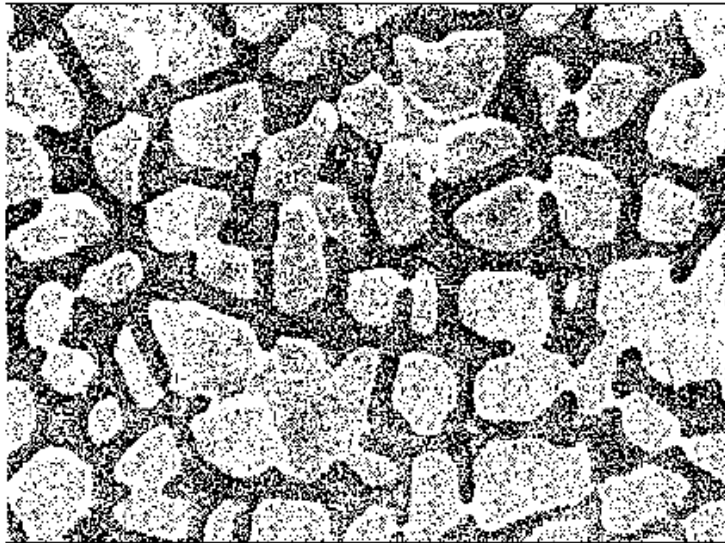
As a Function of:

**Sorption • Geology • Retardation  
Water & Contaminant Chemistry**

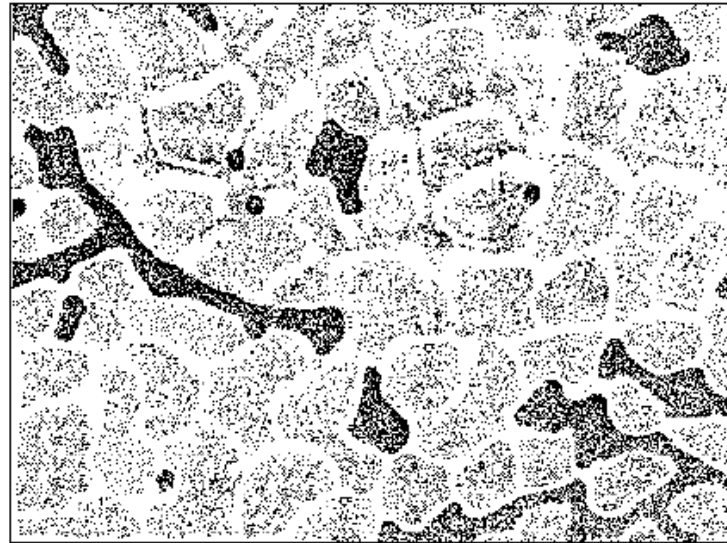
*The Bowl of Contaminant Soup*



# *NAPL and Water*



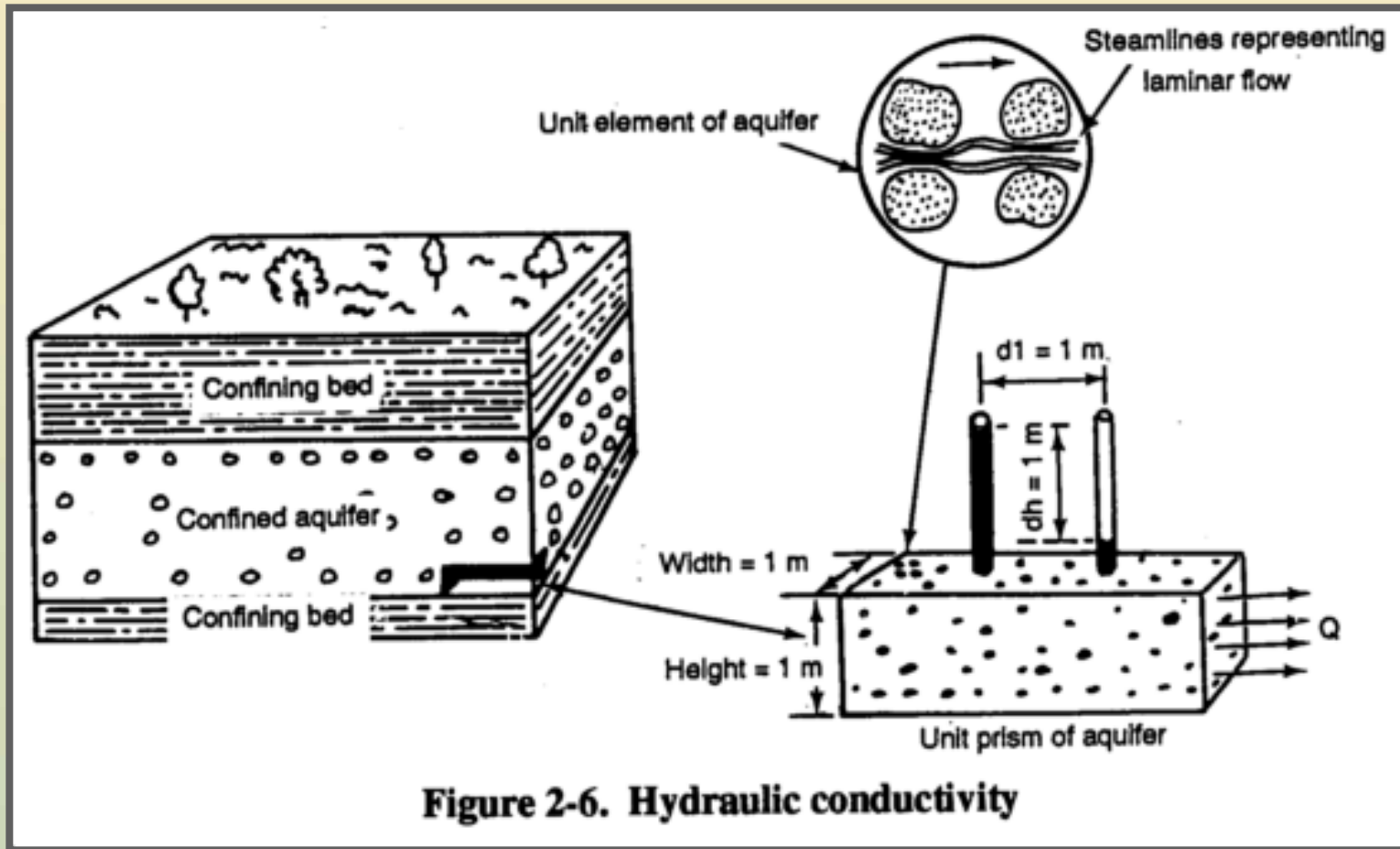
a



b

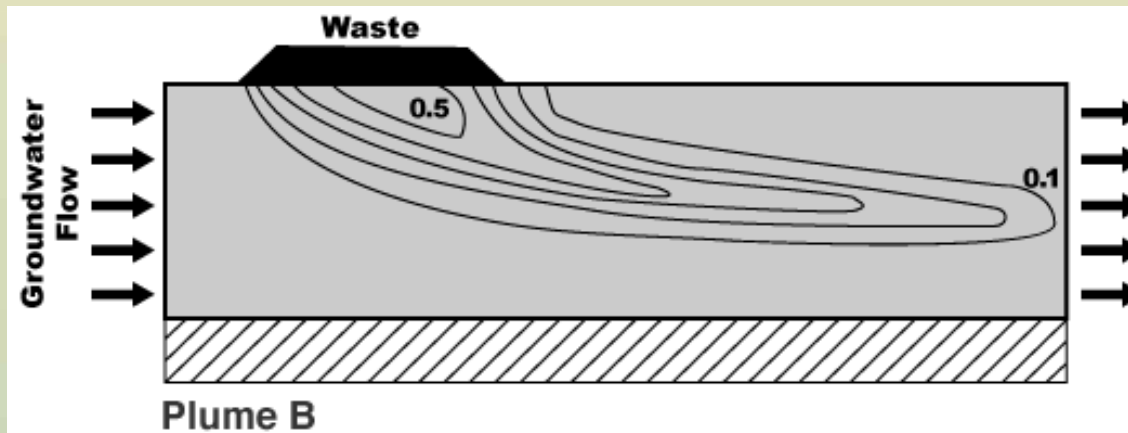
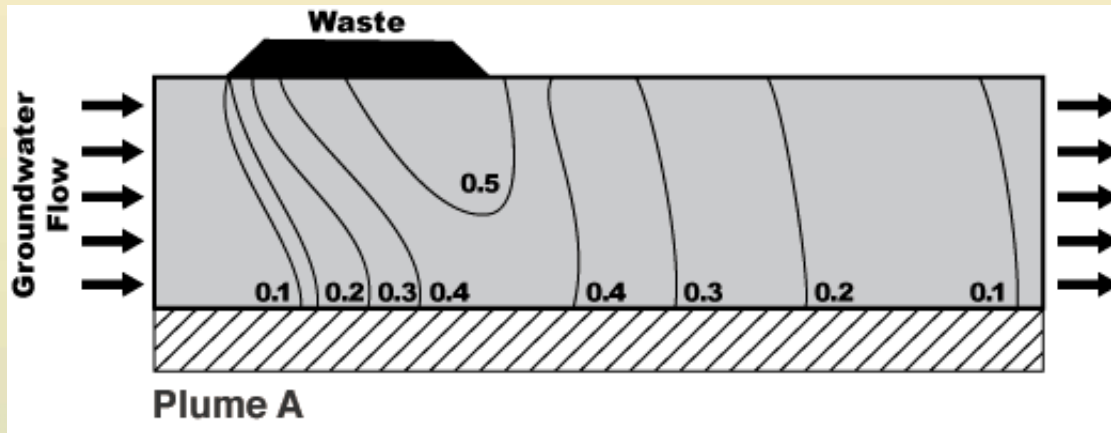
**Figure 8.** Dark NAPL (Soltrol) and water in a homogenous micromodel after (a) the displacement of water by NAPL and then (b) the displacement of NAPL by water, with NAPL at residual saturation (Wilson et al., 1990).





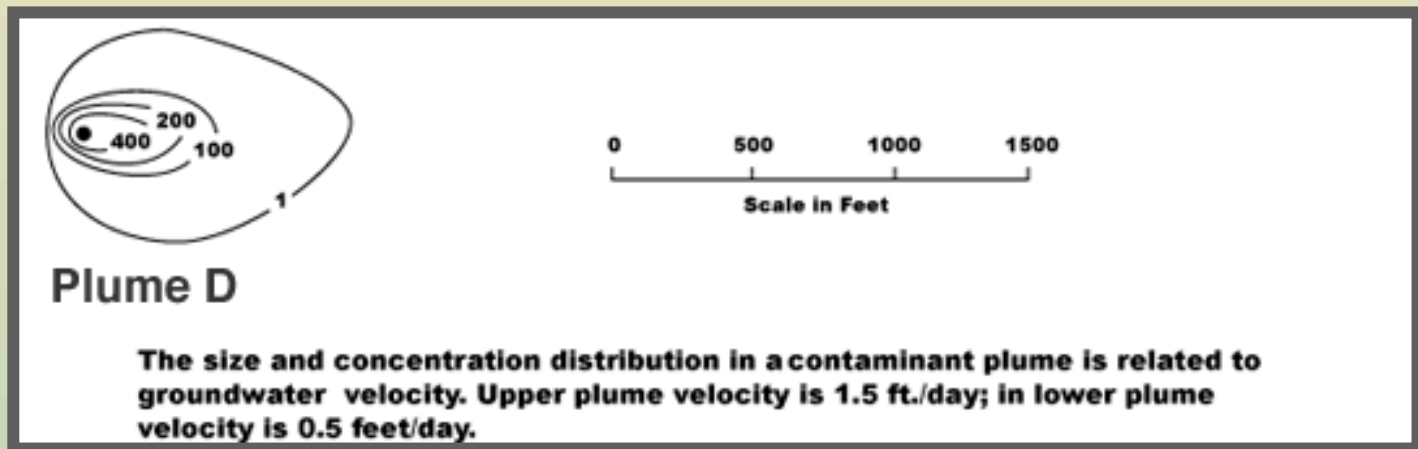
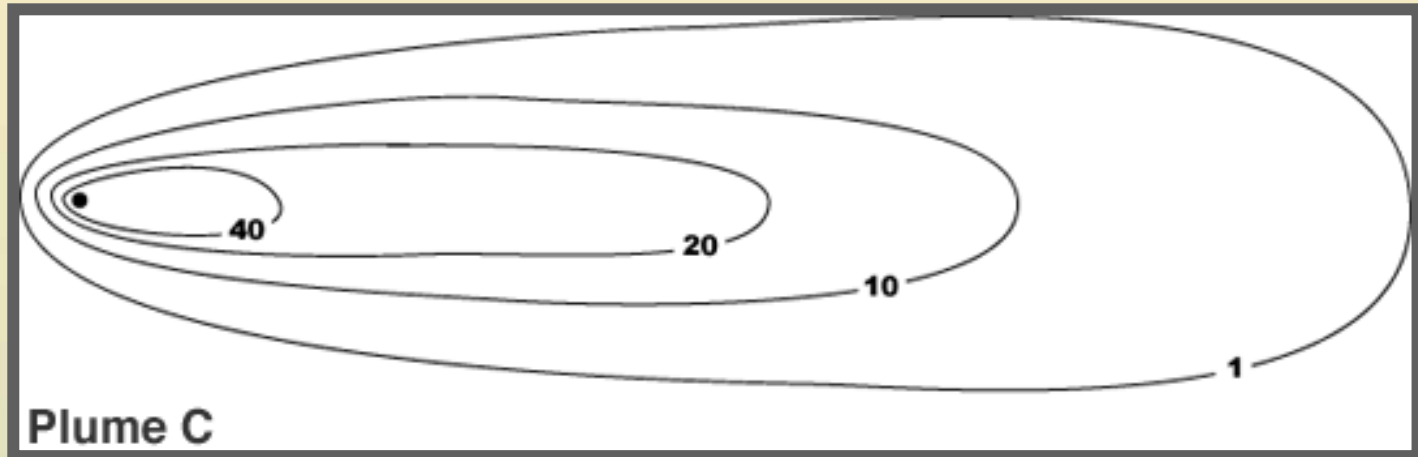
**Figure 2-6. Hydraulic conductivity**

# Contamination Plumes



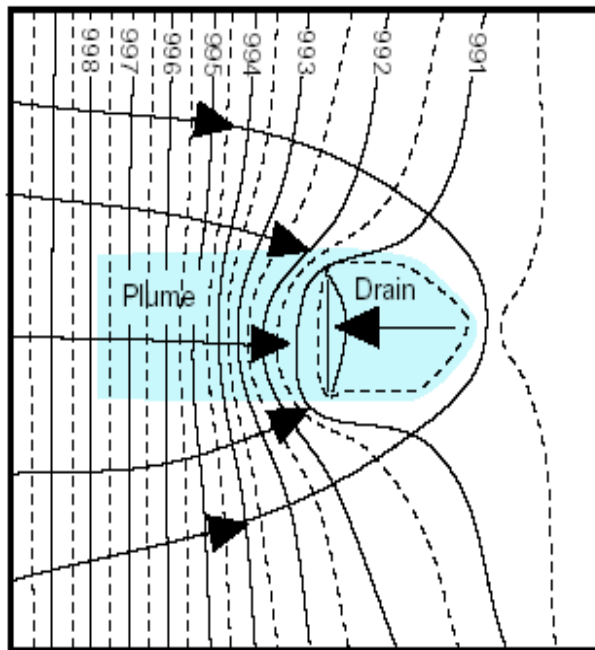
Plume diagrams from the Handbook of Chemical Hazard Analysis Procedures, published by the U.S. Federal Emergency Management Agency, Department Of Transportation, and Environmental Protection Agency.

# Contamination Plumes

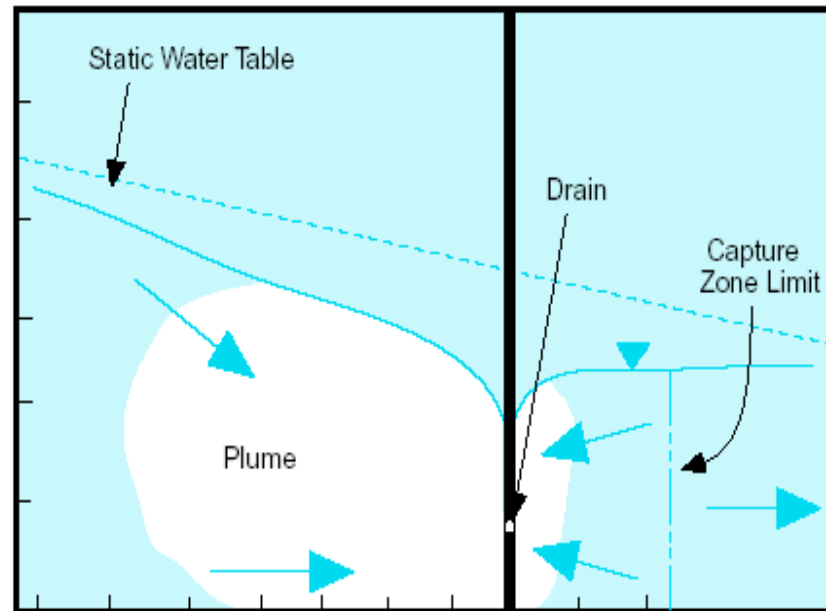


Plume diagrams from the Handbook of Chemical Hazard Analysis Procedures, published by the U.S. Federal Emergency Management Agency, Department Of Transportation, and Environmental Protection Agency.

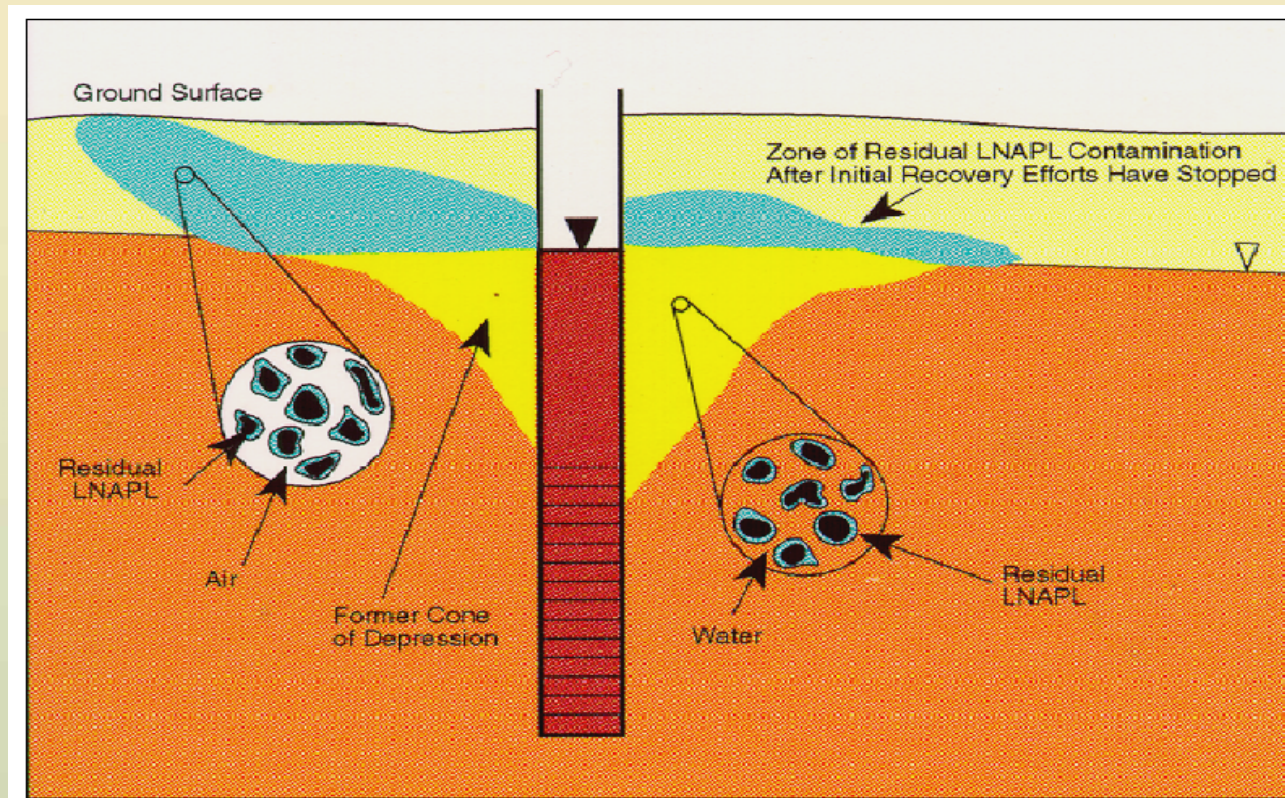
# Pump and Treat



(b)



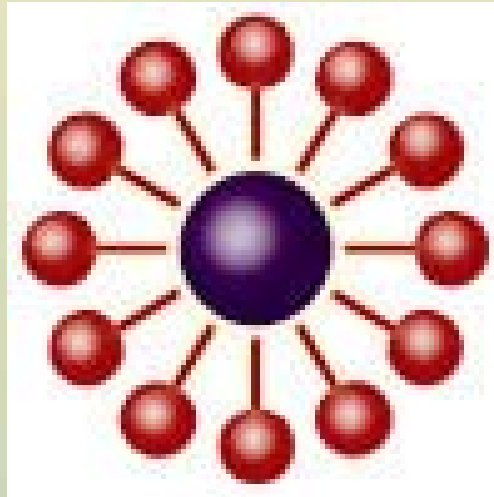
## Residual Sorbed LNAPL in Soil Groundwater Matrix



**Figure 16.** Zone of residuals created in former cone of depression after cessation of LNAPL recovery system (Gorelick et al., 1993).

# SURFACTANTS

## *Properties & Characteristic*



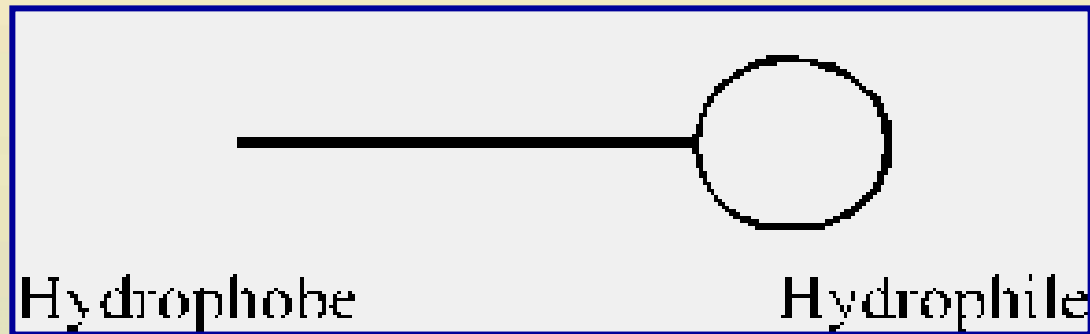


## **Class Exercise III** ***(Individual or Group)***

- i) How many types of surfactants (Classes) are there?**
- ii) What is the definition of surfactant?**
- iii) How long have people been using surfactants?**
- iv) When was the term first coined?**
- v) Name common products surfactants are used in?**
- vi) List various commercial, industrial, oil and gas application that use surfactants**



## Structure & Definition



**Surface Active Agent (SAA), i.e., Hydrophilic (water loving) and Hydrophobic (oil-liking) Groupings Shown.**

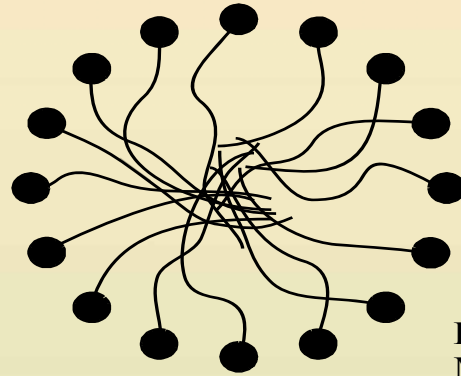


Fig. 2  
Model of a micelle.

A real micelle is raspberry shaped rather than spherical.  
The tails inside are random rather than straight.

- ▶ Critical micelle concentration (CMC) is a measure of surfactant efficiency. A lower CMC indicates less surfactant is needed to saturate interfaces and form micelles.
- ▶ Typical CMC values are less than 1% by weight. To obtain optimal cleaning performance, concentrations of 1-5% are common. This concentration is higher than that needed to achieve micelle formation; therefore, providing a reservoir of additional surfactant molecules to form micelles.
- ▶ A new class of ‘Selective’ non-ionic surfactants are capable of working well below the CMC, having many application benefits.

## Definition

- ▶ The term *surfactant* is a blend of *surface active agent*.
- ▶ Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads").
- ▶ Therefore, they are soluble in both organic solvents and water. A surfactant is a molecule that, when added to a liquid at low concentration, changes the properties of that liquid at a surface or interface.
- ▶ The term surfactant was coined by *Antara Products in 1950*.
- ▶ The *surface tension of water is 72 dyne/cm*; a *surfactant can reduce this to a value in the range of 30-50 dyne/cm*.
- ▶ **Surface-Active:** (Of a substance) tending to *reduce the surface tension of a liquid in which it is dissolved*.

## 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*.

**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 (PAH's), dichloroethane (DCE), trichloroethane (TCE), perchloroethylene (PCE) and other similar petroleum products.

**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*.

## Application & Uses

### Surfactants are used in cleaners and detergents to:

- ▶ Improve wetting / spreading
- ▶ Provide detergency by solubilizing & suspending soil (*particulate, oily*)
- ▶ Produce, modify or control foam
- ▶ Emulsify / disperse (e.g., silicone, wax)
- ▶ Couple or compatibilize formulation components
- ▶ Modify viscosity

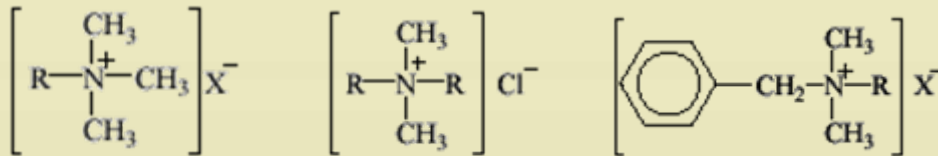
### Other commercial and industrial uses included:

- Vapour and odour suppression (including fire fighting);
- Storage tank and parts cleaning;
- Off-shore dispersants, and shoreline spill clean-up;
- In-situ Surfactant Enhanced Aquifer Remediation (SEAR);
- In-situ and Ex-situ Surfactant Enhanced Bioremediation (SEB);
- In-situ and Ex-situ Surfactant Enhanced Oxidation (SEO);
- Oil recovery from oil sand and oil-shale;
- Treating drilling mud and drilling cuttings; and
- Improving oil recovery from oil production fields.

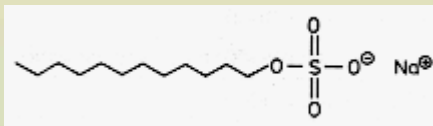
<u>Preservative</u>	<u>Suspending/Surfactant</u>	<u>Emulsifying Surfactant</u>
Alcohol (20% or more) <b>Ophthalmic:</b> Benzalkonium Chloride Benzethonium Chloride Chlorobutanol Phenylmercuric Acetate Phenylmercuric Nitrate Thimerisol/Thimerosal Benzoic Acid Boric Acid Chlorocresol Creosol Phenol Alcohol Quaternium 1-121 Chlorhexidine Methylparaben Propylparaben Phenylmercuric Nitrate Polymyxin B Sulfate (active ingredient for otic) <b>Quats:</b> Benzethonium Chloride Myristalkonium Chloride Cetylpyridinium Chloride Myrtrimonium Bromide <b>Formaldehyde Releasing:</b> Imidazolidinyl Urea Diazolidinyl Urea DMDM Hydantoin <b>Emit Cl or NO<sub>x</sub>:</b> Chloroacetamide Chlorhexidine Di... <b>Work same way as ethanol:</b> p-Chloro-m-cresol 2-Bromo-2-nitropropane-1,3-diol Phenoxyethanol Phenethyl Alcohol <b>Isothiazolinone:</b> Methylchloroisothiazolinone Methylisothiazolinone <b>Azolidine:</b> 7-ethyl-bicycloazolidine Dimethylloxazolidine <b>Other:</b> Butylhydroxyanisole (BHA) Butylated Hydroxyl Toluene (BHT) Sorbic, Boric, Salicylic, Propionic, & Dehydroacetic Acid Ethyl Vanillin Alkyl p-Hydrobenzoate	Polyoxyl-40-stearate <b>Cationic:</b> Benzalkonium Chloride Quaternium 1-120 <b>Anionic:</b> Sodium Lauryl Sulfate Alkyl Sulfonates <b>Neutral:</b> Tweens (Polysorbate) Spans (Sorbitan) Brij's (Polyoxyethylene Ethers) Myrj's (Esters) Arlacel 20-85 <b>Celluloses:</b> Methylcellulose Carboxymethylcellulose (CMC) Ethylcellulose Hydroxypropylmethylcellulose (HPMC) <b>Gums &amp; Mucilages:</b> Xanthan Acacia Alginic Acid Tragacanth (Hog) Starch Gelatin? <b>Others:</b> Bentonite (Magma) Veegum (Magma) Carbopol/Carbomer (Carboxypolymethylene) Polyvinylpyrrolidone (PVP) Kaolin Pectin <b>Saponifying:</b> Triethanolamine Lime Water (CaOH <sub>2</sub> ) Sodium Baborate (Borax)	<b>Anionic:</b> (form O/W emulsions) Sodium Stearate Sodium Borate Sodium Dodecyl Sulfate Sodium Dodecyl Benzene Sulfonate Sodium Cholate Potassium Laurate Potassium Stearate Sodium Octane Sulfonate Sodium Decane Sulfonate Sodium Dodecane Sulfonate Docusate Sodium <b>Cationic:</b> Hexadecyltrimethyl Ammonium Br. Dodecylpyridinium Chloride Decyltrimethyl Ammonium Br. Tetradecyltrimethyl Ammonium Br. Tetradecyltrimethyl Ammonium Cl. Dodecyl Ammonium Chloride <b>Neutral:</b> Heptaoxyethylene Monohexadecyl <b>Fatty Acid:</b> Caproic Acid Caprylic Acid Palmitic Acid Stearic Acid Lauric Acid <b>Co-Surfactant:</b> Cetyl Alcohol (anything w/ Alcohol next to it) <b>Amphoteric:</b> (form O/W emulsions) Lethicin Lauryl Betaine, Sultaine, Sulfobetaine Myristoamphoacetate Sodium Lauriminodipropionate <b>Emollient:</b> Beeswax Petrolatum Cholesterol Lanolin
<u>Vehicle/Solvent</u>	<u>Flavoring</u>	<u>Humectant</u>
Alcohol (<20%) Purified Water Rose Water Lime Water (CaOH <sub>2</sub> ) Syrup USP <b>Otic:</b> Glycerin (Glycerol) Mineral Oil Propylene Glycol (common solvent in oral meds)	Sodium Saccharin Aspartame Rose Water Cinnamon Water Peppermint Water Syrup USP Orange Oil Ethyl Vanillin Glycyrrhiza Fructose	Glycerin (Glycerol) 2-10% Propylene Glycol 4-10% 70% Sorbitol Solution 4-10% Glycerol Monostearate

# Surfactants Chemical Structure

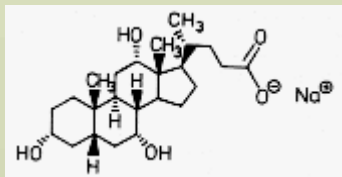
## ► Structures of common cationic surfactants:



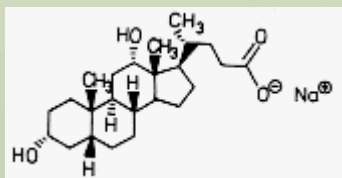
## ► Structures of common surfactants used in biochemistry:



*Sodium dodecylsulfate (SDS)*

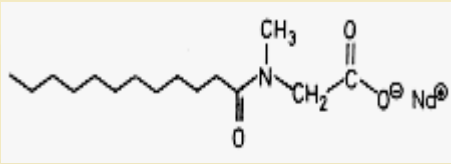


*Sodium cholate*

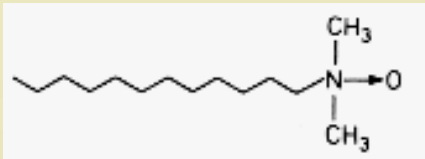


*Sodium deoxycholate (DOC)*

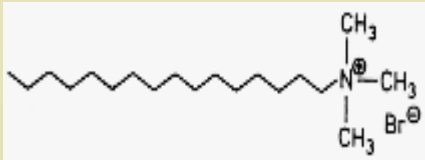




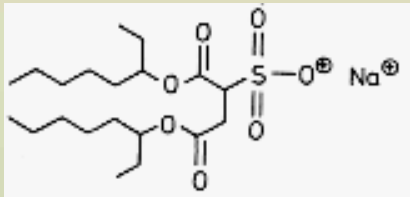
**N-Lauroylsarcosine Sodium salt**



**Lauryldimethylamine-oxide (LDAO)**



**Cetyltrimethylammoniumbromide (CTAB)**

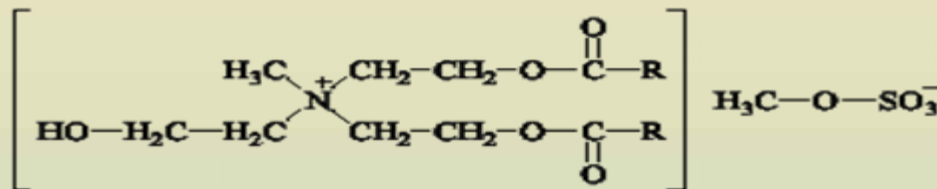


**Bis(2-ethylhexyl)sulfosuccinate Sodium salt**

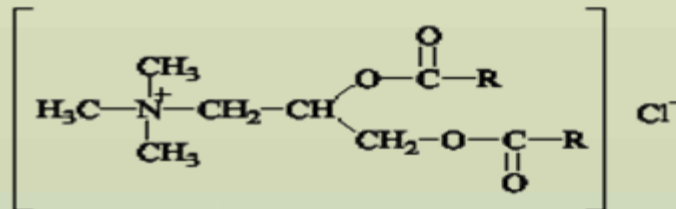
# Structures of alkyl ester ammonium salts

- ▶ These structures are examples, understanding there are hundreds to thousands of forms in use today.
- ▶ *Applications may include:* Thickening of water to change density even in the presence of inorganic salts such as sodium chloride (NaCl). Used in oils and gas industry for down-hole applications.
- ▶ Some types are used by drycleaners to clean soiled fabrics.

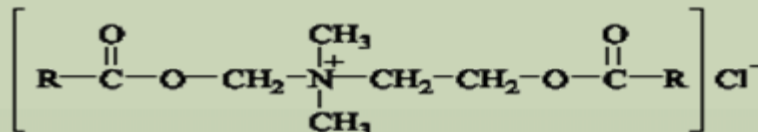
Esterquat (EQ)



Diesterquat (DEQ)



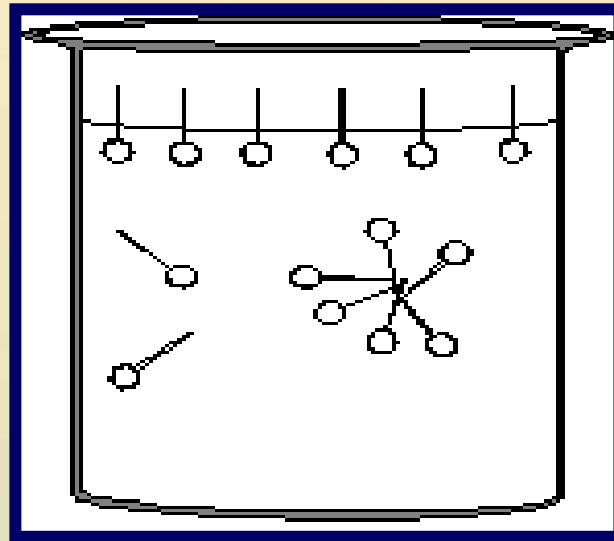
DEEDMAC



# Ivey-sol • SPTT

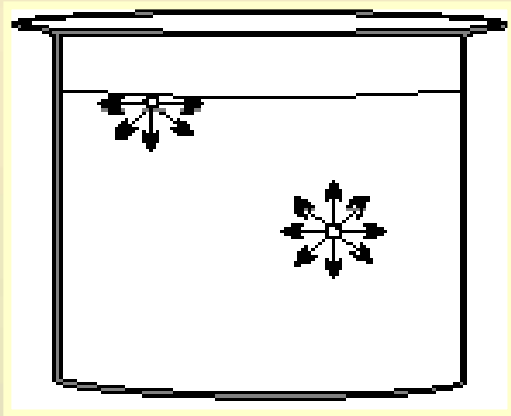
	Name/Structure	Type*	HLB
(a)	<p>Ethylene glycol distearate</p> $\begin{array}{c} \text{H} \quad \quad \quad \text{O} \\   \quad \quad \quad    \\ \text{H}-\text{C}-\text{O}-\text{C}-(\text{CH}_2)_{16}-\text{CH}_3 \\   \\ \text{H}-\text{C}-\text{O}-\text{C}-(\text{CH}_2)_{16}-\text{CH}_3 \\   \quad \quad \quad    \\ \text{H} \quad \quad \quad \text{O} \end{array}$	N	1.3
(b)	<p>Propylene glycol monostearate</p> $\begin{array}{c} \text{H} \quad \quad \quad \text{O} \quad \quad \quad \text{H} \quad \quad \quad \text{H} \\   \quad \quad \quad    \quad \quad \quad   \quad \quad \quad   \\ \text{H}-\text{C}-\text{O}-\text{C}-(\text{C})_{16}-\text{C}-\text{H} \\   \quad \quad \quad \quad \quad \quad \quad   \quad \quad \quad   \\ \text{H}-\text{C}-\text{O}-\text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	N	3.5
(c)	<p>N, N dimethyl stearamide</p> $\begin{array}{c} \text{H} \quad \quad \quad \text{O} \\   \quad \quad \quad    \\ \text{H}-\text{C}-\text{H} \quad \quad \quad \text{C}-(\text{CH}_2)_{16}-\text{C}-\text{H} \\ \quad \quad \quad \quad \quad \quad \quad   \\ \quad \quad \quad \quad \quad \quad \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad   \\ \quad \quad \quad \quad \quad \quad \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad   \\ \quad \quad \quad \quad \quad \quad \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad   \\ \quad \quad \quad \quad \quad \quad \quad \text{H} \end{array}$	N	7
(d)	<p>4-Cetyl-phenyl sulfonate</p> $\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$	A	~11+
(e)	<p>Tertiary (poly oxyethylene) amine</p> $\begin{array}{l} \text{N} \begin{cases} (\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-\text{CH}_2-\text{OH} \\ (\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-\text{CH}_2-\text{OH} \\ (\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-\text{CH}_2-\text{OH} \end{cases} \end{array}$ <p>(where n = 6 to 16)</p>	C	~14
(f)	<p>Potassium oleate</p> $\text{K} \begin{array}{c} (+) \quad (-) \\   \quad \quad   \\ \text{O} \quad \quad \quad \text{O} \\    \quad \quad \quad    \\ \text{C}-(\text{CH}_2)_7-\text{C}=\text{C}-(\text{CH}_2)_7-\text{C}-\text{H} \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$	A	20

\* N nonionic  
A anionic  
C cationic

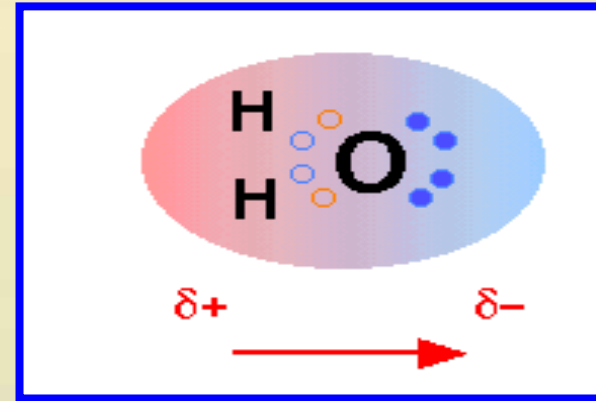


**Alignment At Surface & Squeezed In Water**

**The Hydrophobic & Hydrophilic Characteristics  
Of The Surfactant Molecules  
Dictate Their Behaviour In Water**

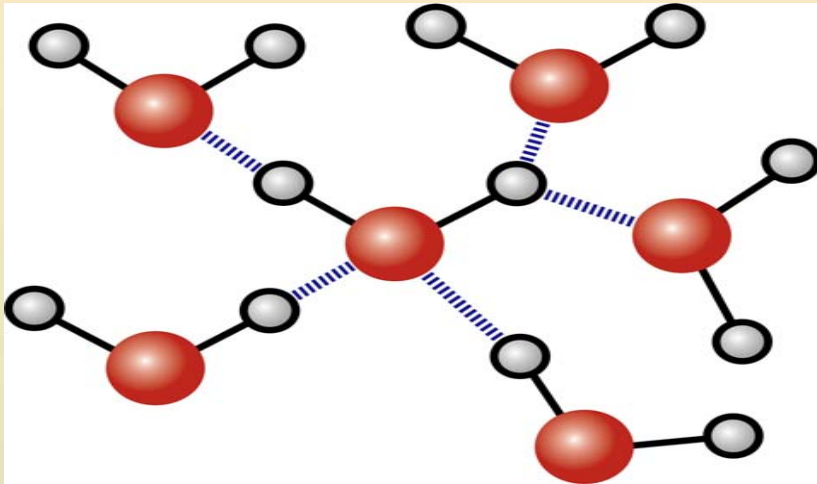


**Surface Tension Forces Shown  
Pulling Water Together**

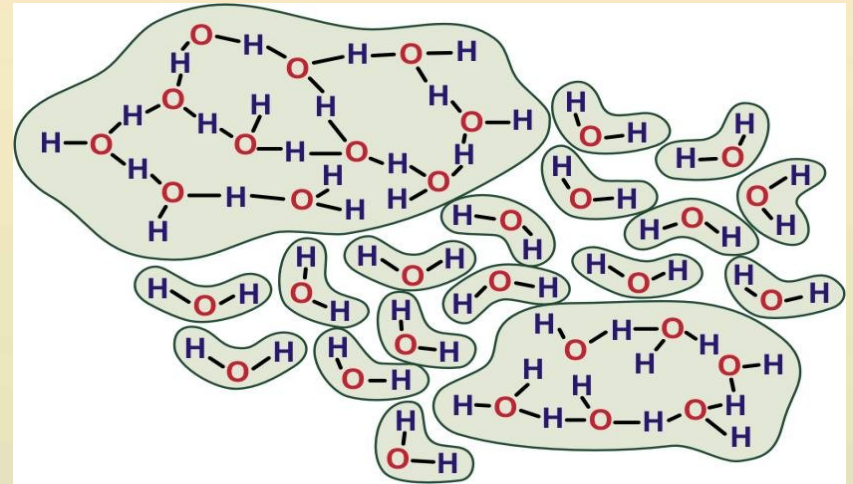


**Polar Water Molecule  
{Oxygen ( $\zeta-$ ) Hydrogen ( $\zeta+$ )}**

**Surface Tension In Water Is Caused By The Attractive Forces Between Neighbouring H<sub>2</sub>O molecules. The oxygen (-) in one water molecule is attracted to the hydrogen (+) atoms in the neighbouring water molecules. Forming “Hydrogen-Bonding”**



Hydrogen Bonding Between Polar Water Molecules (*in-blue*) Pulling Water Together Between Neighbouring H<sub>2</sub>O.

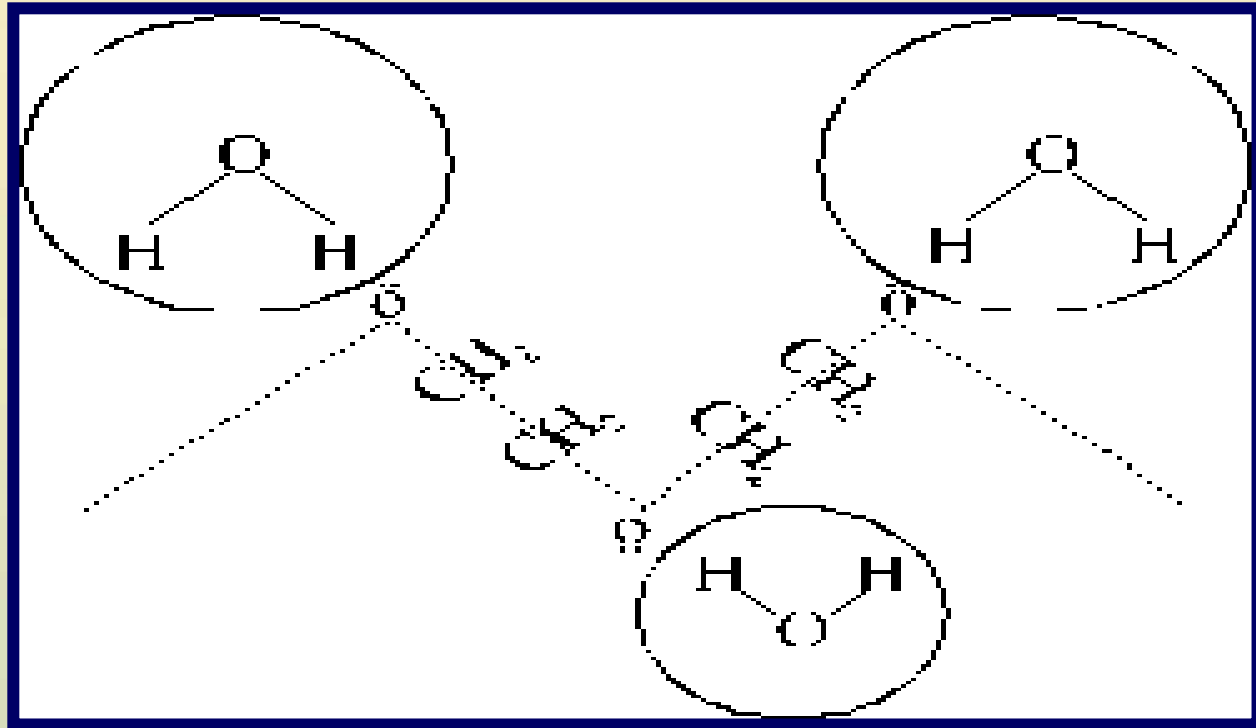


Water Clusters Can Form Form As A Result That Range In Size & Complexity

**Hydrogen Bonding** Is What Gives Rise To The Insolubility Of Non-Polar NAPL Compounds, And Why the Hydrophilic (*Water Liking*) End Of The Ivey-sol Molecules Are So Effective In Rendering The NAPL Compounds Miscible In Water.

- ▶ The ability of surfactants to reduce the surface tension of water to a low value is a fundamental characteristic that results in highly efficient and effective performance in a wide range of applications.
- ▶ *Surfactants change* the surface tension of water by breaking up *the forces holding the water molecules together* at the interface.
- ▶ Surface tension is usually expressed dynes/cm or mN/m. Two surface tension measurements commonly performed provide two different types of data.

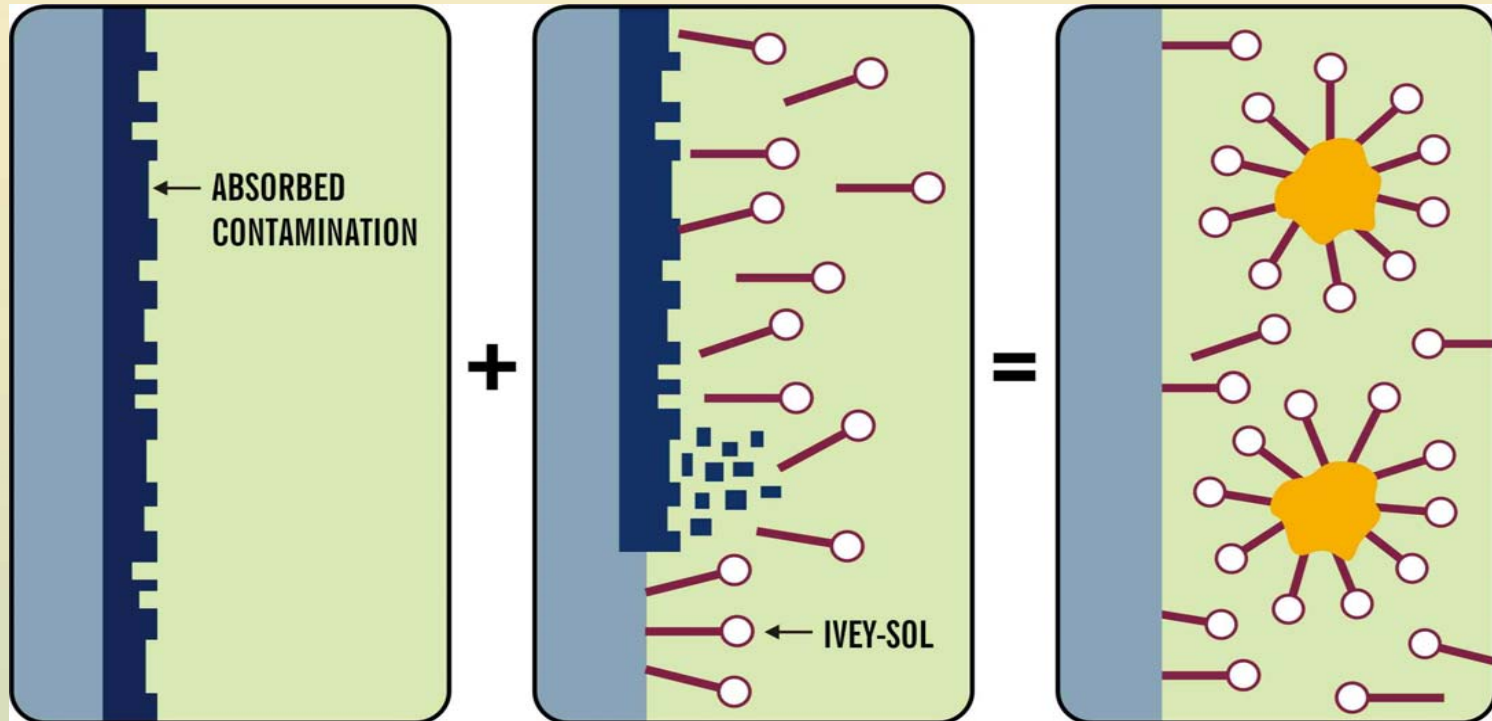




Surfactant Hydrophilic Interaction With Water ( $H_2O$ ) Utilizes Hydrogen Bonding Effects To Aid Dissolving Contaminants in Water and Disrupt the forces of Hydrogen Bonding Hydrophobic end attached to organic contaminant.

# **Surfactants Lower The Surface Tension of Water From 72 Dynes to <50 dynes**

**This increases the wetting ability of the water  
when present, makes surfactant application  
possible in fine grain soils improving  
Water Permeability (K).**



**Surfactant Interaction With Organic (NAPL) On A Surface With Partial Micelle Encapsulated of Oil Droplet (Some Surfactants Are Effective Below CMC)**



## **How To Choose The Best Surfactant**

- ▶ Several surfactants may be appropriate in a given application. Final surfactant selection will depend on your specific requirements, end-use application, and what properties are most important in your application.**
- ▶ Surfactants can serve many functions in a formulation, but rarely can a single surfactant fulfill all these roles.**
- ▶ To facilitate correct selection, decide what role the surfactant plays (e.g., provide foam, emulsification, wetting, detergency, stabilization) in an application, and select the surfactants that most closely match your requirements.**
- ▶ Other factors that will affect your choices will be the effectiveness, toxicity and cost of the surfactants you are choosing from. In terms of a large scale project, you will have to evaluate the cost benefit ratio for your given application.**

## **What Is Hydrophilic-Lipophilic Balance (HLB)**

- ▶ How Is It Applied To Formulate Emulsions
- ▶ HLB (Hydrophile-Lipophile Balance) is an empirical expression for the relationship of the hydrophilic (water-loving) and hydrophobic (water-hating) groups of a surfactant.
- ▶ The higher the HLB value, the more water-soluble the surfactant.
- ▶ Water-in-oil emulsions (w/o) require low HLB surfactants.
- ▶ Oil-in-water (o/w) emulsions often require higher HLB surfactants.

***< 10 HLB 'oil' Soluble : > 10 HLB 'water' Soluble***

## **FACT**

**90 to 95 % of All Contaminants Are  
Absorbed To Particles In  
Soil, Bed Rock and Groundwater  
Aquifers**



**Contaminant Absorption  
Limits Availability of Contaminants For  
Remediation**

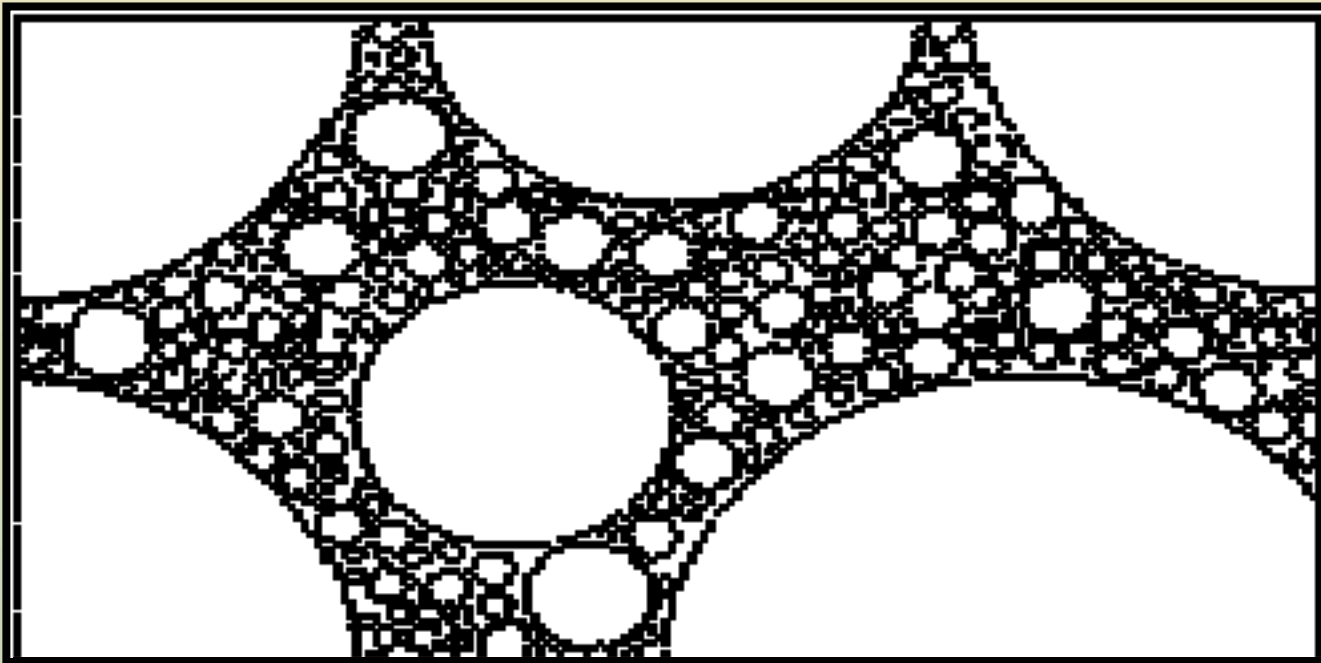


**Sorption is the #1 Reason Why Many In-situ  
and Ex-situ Remediation Project are  
Slow, Costly or Fail.**



## **Sorption (Absorption and Adsorption) of Contamination in Soil Matrix**

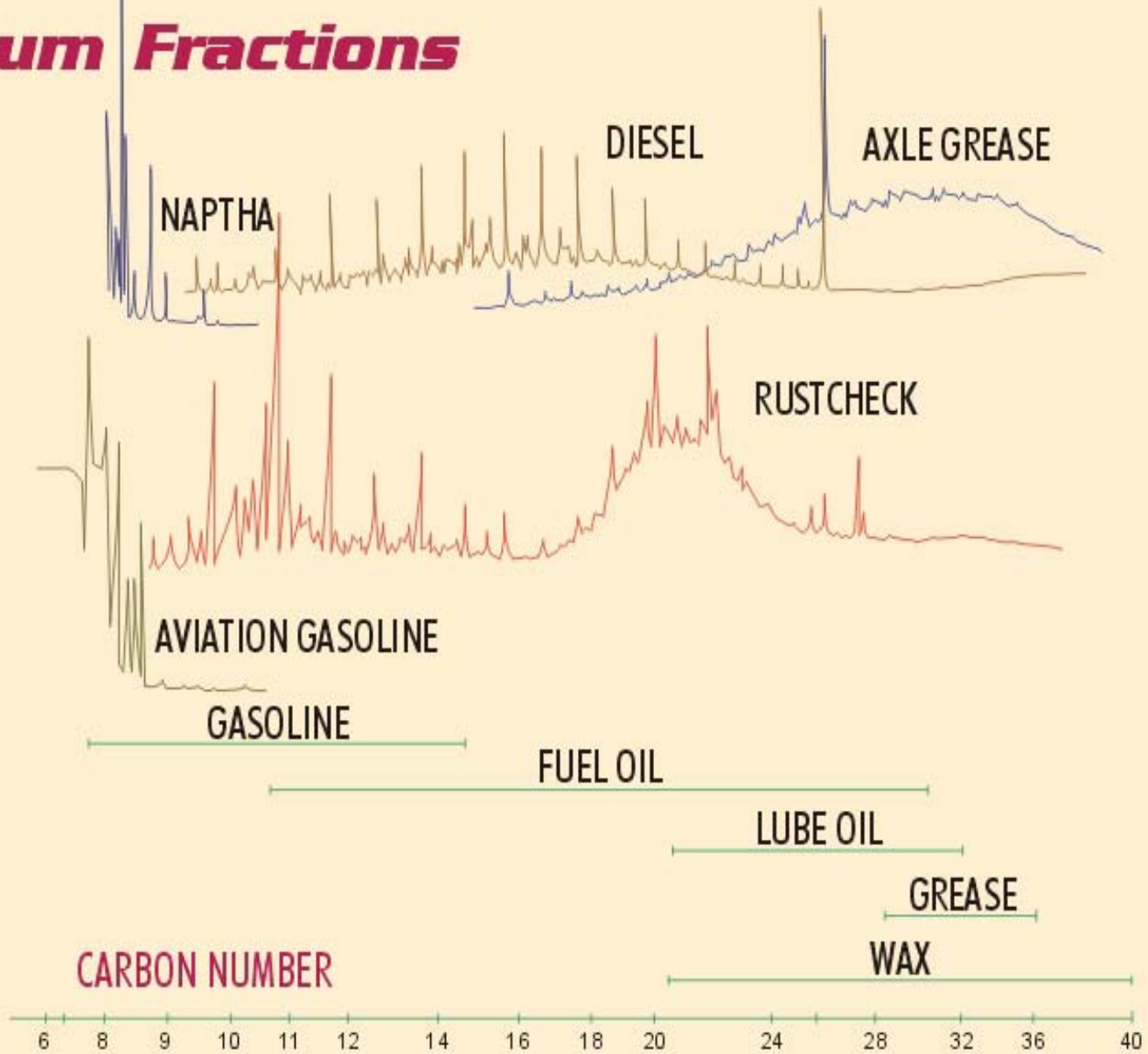
**Soil & Water Remediation Must Address This To Be Successful.**



**Ivey-sol • SPTT**

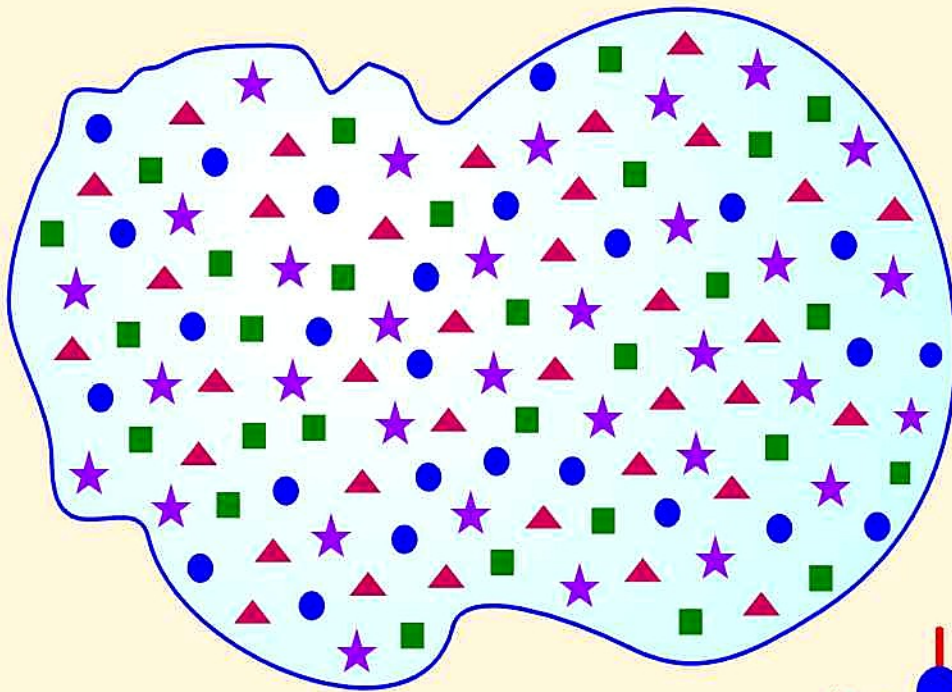


# Petroleum Fractions





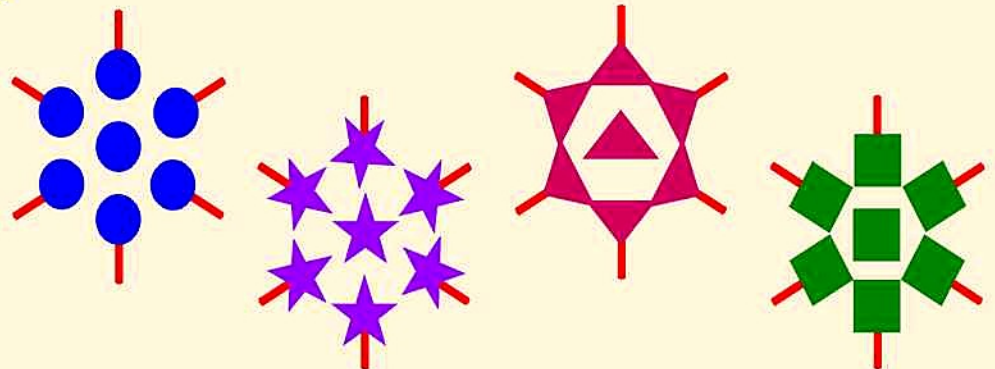
# Selective Micelle Encapsulation of Contamination



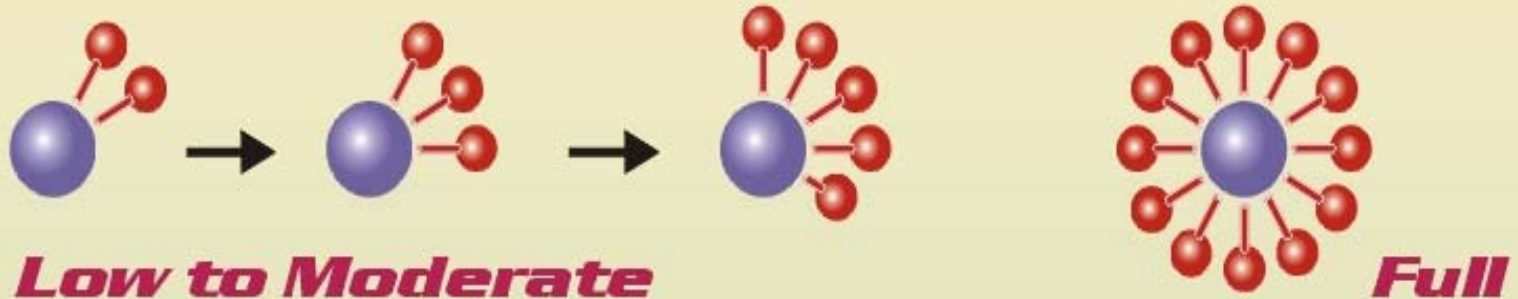
Legend:

- |             |                  |
|-------------|------------------|
| ● Aromatics | ■ Cyclic Alkanes |
| ★ Alkanes   | ▲ PAHs           |

- ☞ Selective Micelle Formation
- ☞ Encapsulation and increased solubility
- ☞ Applicable for full LNAPL and PAH range
- ☞ Ivey-sol mixture is tailored to type/range of contamination being treated



## Encapsulation Effects



Liberation of contamination can be effected with low to moderate encapsulation. Hence, low SPTT concentrations are effective.



As partial encapsulation is predominant due to injection concentrations, no negative effects are realized at the treatment system (e.g., GAC, Air Stripping, Bio-Reactors, Membrane Separation, etc.)

## **APPLICATION RANGE**

### **LNAPL**

**Full LNAPL (F1,F2, F3, and F4) Range Including: BTEX, Gasoline, Diesel, Motor-Oil, Bunker-C, MTBE, PAH's, etc.**

### **DNAPL**

**25 Fold (+) Increase In Solubility & Recovery Rate. This includes Compounds Like: PCE, PCB, TCE, TCA, CTC, TCM, PCP, & Various other Cl / Br Solvents**

### **Heavy Metals**

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



***Ivey-sol • SPTT***



**Fuel-oil - Bunker-C - Gasoline  
Dissolved In Water With Ivey-sol**



## PAH Soil Remediation

Parameters	Baseline	Ivey-sol 106	% Reduction
<b>PAH'S</b>	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>
1-Methylnaphthalene	130	5	96.1%
2-Methylnaphthalene	220	6	97.3%
Acenaphthene	46	6.1	86.7%
Acenaphthylene	140	6.4	95.4%
Anthracene	190	19	90.0%
Benzo(a)anthracene	100	14	86.0%
Benzo(a)pyrene	74	9	87.8%
Benzo(b)fluoranthene	54	6.3	88.3%
Benzo(ghi)perylene	21	3.3	84.3%
Benzo(k)fluoranthene	54	6.3	88.3%
Chrysene	100	13	87.0%
Dibenzo(a,h)anthracene	9.6	1.2	87.5%
Fluoranthene	230	26	88.7%
Fluorene	190	12	93.7%
Indeno(1,2,3-cd)pyrene	35	4.5	87.1%
Naphthalene	560	9.7	98.3%
Perylene	20	1.6	92.0%
Phenanthrene	420	37	91.2%
Pyrene	170	19	88.8%

## Treatment of Chlorinated Contaminated Fine Grain Soil

<b>Chlorinated Compounds</b>	<b>Baseline Mg/kg</b>	<b>Treatment No. 1</b>	<b>Reduction (%)</b>	<b>Treatment No. 2</b>	<b>Reduction (%)</b>	<b>Total Reduction</b>
<b>1,2-Dichlorobenzene</b>	<b>8,300,000</b>	<b>490,000</b>	<b>94%</b>	<b>56000</b>	<b>89%</b>	<b>99.33%</b>
<b>1,3-Dichlorobenzene</b>	<b>1,100,000</b>	<b>45,000</b>	<b>96%</b>	<b>8100</b>	<b>82%</b>	<b>99.26%</b>
<b>1,4-Dichlorobenzene</b>	<b>2,900,000</b>	<b>110,000</b>	<b>96%</b>	<b>14000</b>	<b>87%</b>	<b>99.52%</b>
<b>Chlorobenzene</b>	<b>170,000</b>	<b>12,000</b>	<b>93%</b>	<b>150</b>	<b>98.80%</b>	<b>99.91%</b>
<b>Styrene</b>	<b>1200</b>	<b>74</b>	<b>94%</b>	<b>ND</b>	<b>&gt;99.99%</b>	<b>&gt;99.99%</b>
<b>TCE</b>	<b>590</b>	<b>41</b>	<b>93%</b>	<b>ND</b>	<b>&gt;99.99%</b>	<b>&gt;99.99%</b>

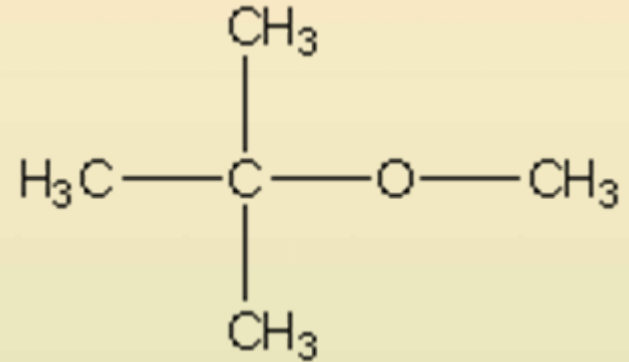


**Common name: Methyl Tertiary Butyl Ether**

**Molecular Formula: C<sub>5</sub>H<sub>12</sub>O**

**Chemical name: 2-Methoxy-2-methyl-propane**

**Solubility: In water, 51.26 g/L @ 25°C**



**Usage:** Introduced as an octane replacement for tetraethyl lead in the 1970s, used as an oxygenating agent added to ~30% of U.S. gasoline supply to reduce carbon monoxide emissions of automobiles and meet air quality standards. Almost the entire production of MTBE (9.1 billion pounds in 1992 by 27 companies in the United States) is used as a gasoline additive.

In 1999, it was estimated that between 5 and 10% of community drinking water supplies in high MTBE use areas had detectable MTBE levels; as many as 9000 community water supply wells in 31 states may be affected.

MTBE is considered a potential human carcinogen.

**Ref: USEPA et. al**

## ***MTBE***

- i) MTBE is the third greatest contaminator of groundwater in the USA.**
- ii) It is xenibiotic & relatively recalcitrant to biodegradation.**
- iii) EPA is currently examining the formation of toxic “by-products” that result from technologies that modify the chemical structure of contaminants.**
- iii) Ivey-sol Technology (Using SAA) selectively aids the controlled solubility of MTBE without modification of its chemical structure.**
- iv) *Ivey-sol* Increases The Recovery of MTBE from Groundwater By >740%.**

**Recent Research Has Confirmed**  
*Ivey-sol* **Increases**  
**The Controlled Solubility and**  
**Rate of *MTBE* Recovery**  
**From Soils, Bed Rock, and Groundwater**  
**By >740%**

*Reference: Dr. Davis Craft, University of Alberta (2004)*

# PCB's

**Ivey-sol Increases The Solubility  
of PCB's by > 900%**

*Based on Research and Development Work*

*Completed in 2005 by*

*Dr. David Craft (NRC) & George Ivey (Ivey International)*



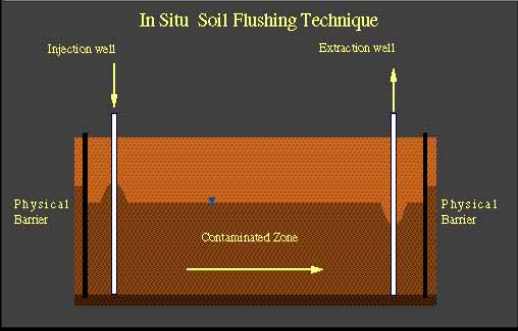
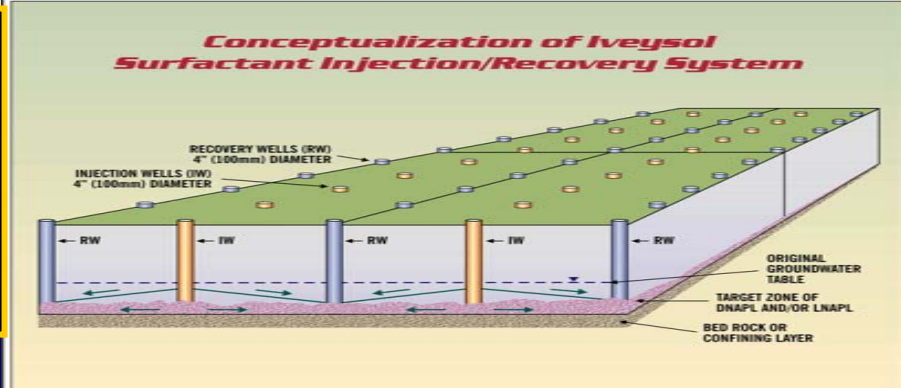
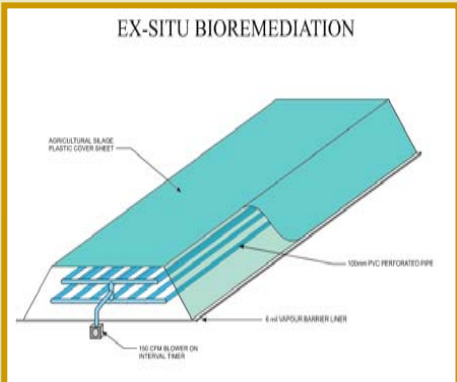
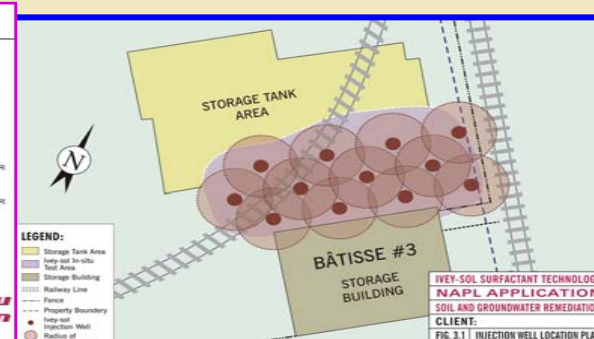
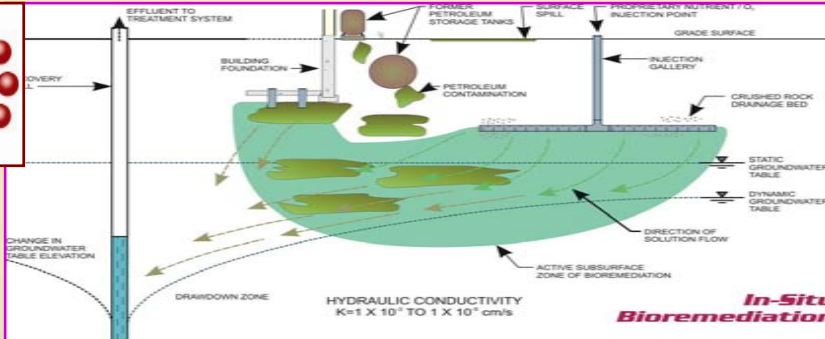
## **Range Of Applications**

- ▶ **Surfactant Enhanced Remediation (SER)**
- ▶ **Surfactant Enhanced Bioremediation (SEB)**
- ▶ **Surfactant Enhanced Oxidation (SEO)**
- ▶ **Off-shore Oil-spill Dispersant**

### **Other Application:**

- ▶ ***Oil Recovery (From Oil-Sands)***
- ▶ ***Tank Cleaning***
- ▶ ***NORM Treatment***
- ▶ ***Oil Stain Removal (Parking Areas)***
- ▶ ***Degreaser***

# Surfactant Remediation SER SEB SEO



# **SER<sup>®</sup>**

**The application and use of Surfactants for soil  
and groundwater remediation Is Known As**

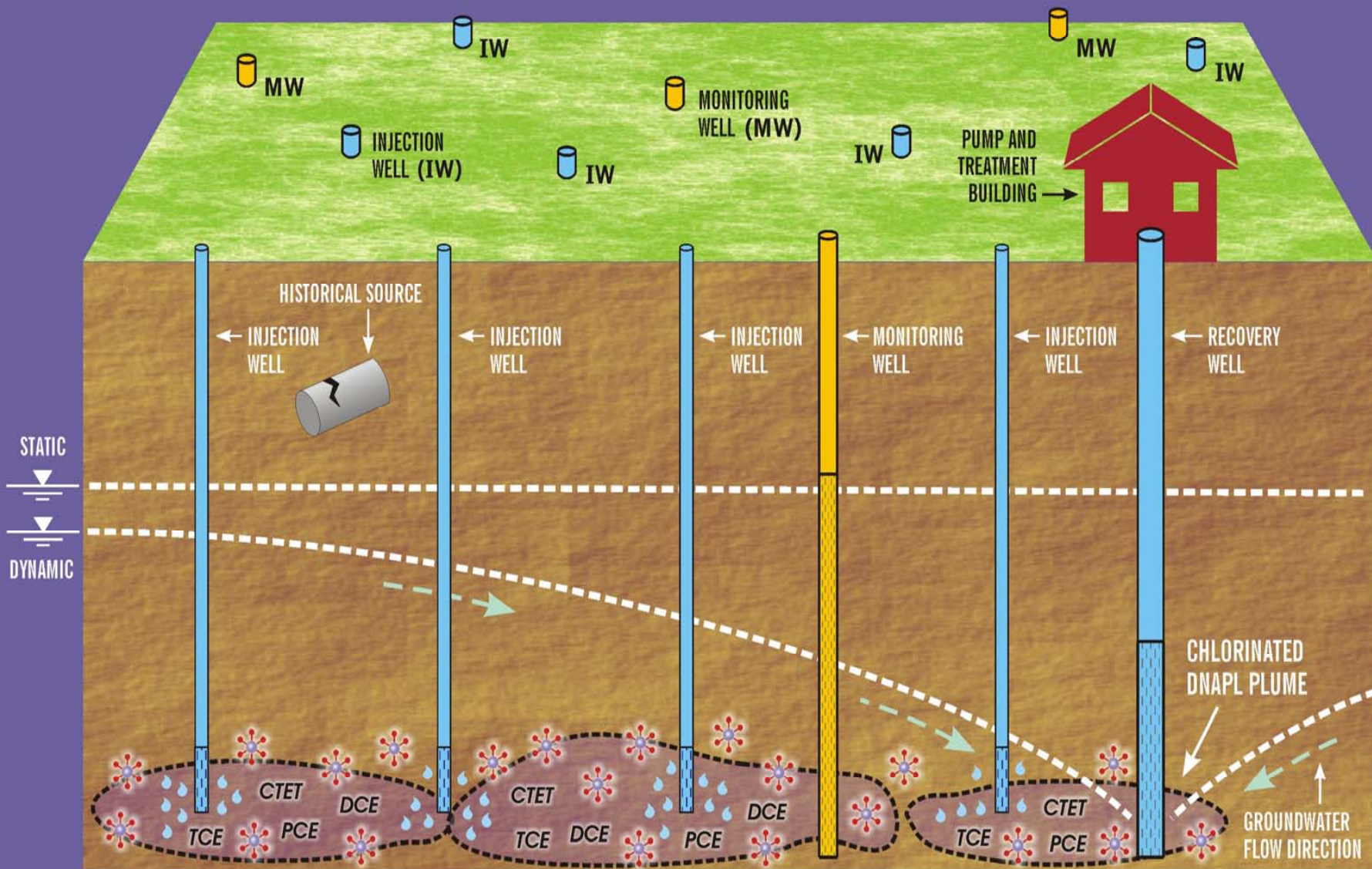
**SER - Surfactant Enhanced Remediation**

# IN-SITU REMEDICATION

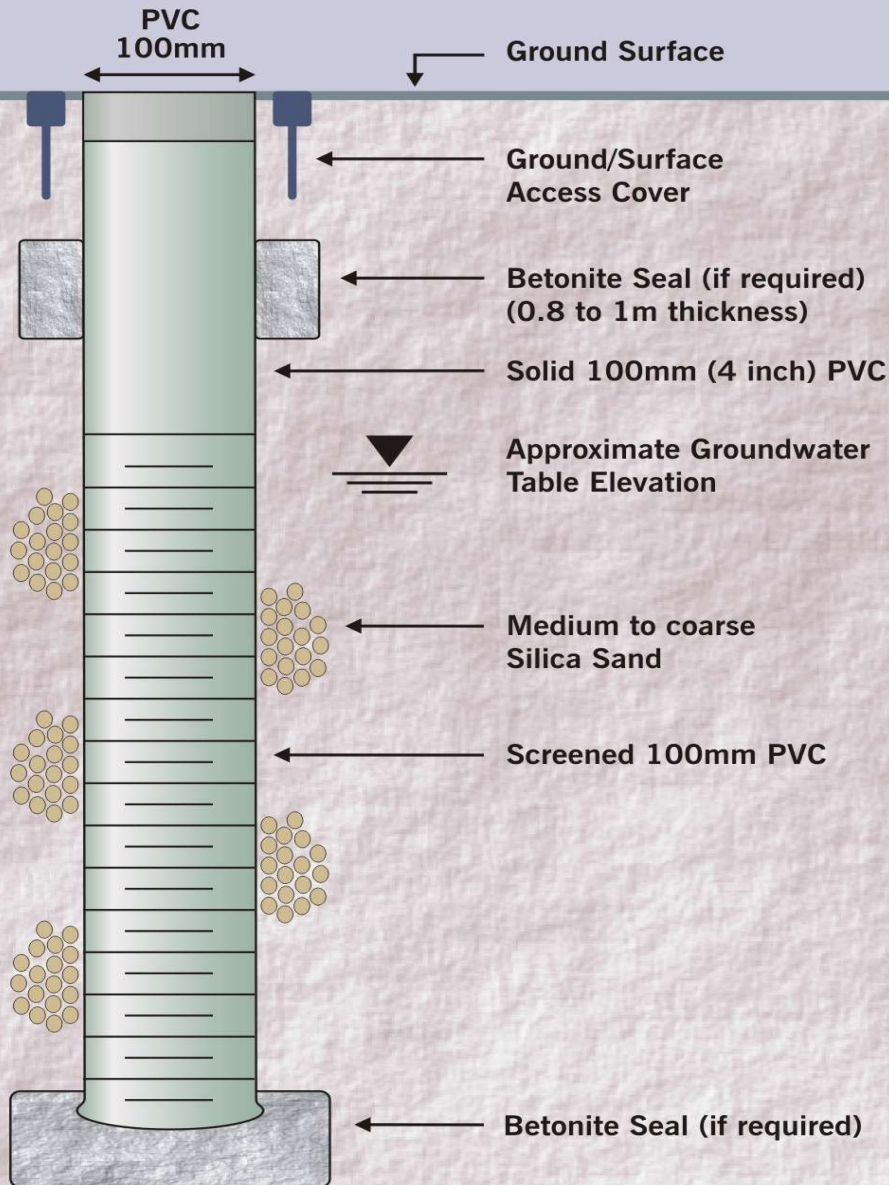
*To design a good 'Remediation Action Plan' you need a good quality Phase II Site Investigation.*



# Ivey-sol • SPTT



# Injection Well Design

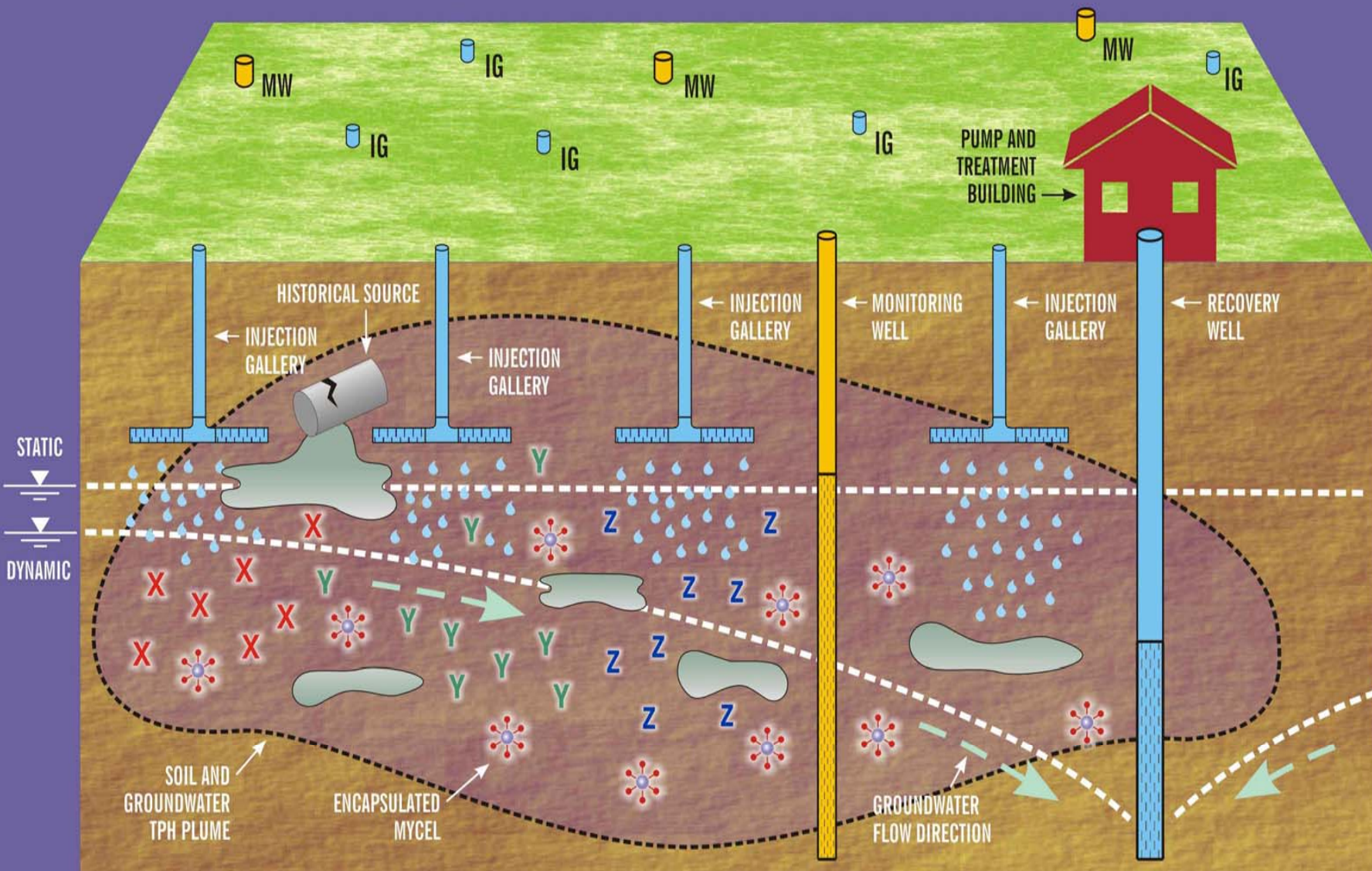


Not To Scale

## Standard Injection Well (IW) Design

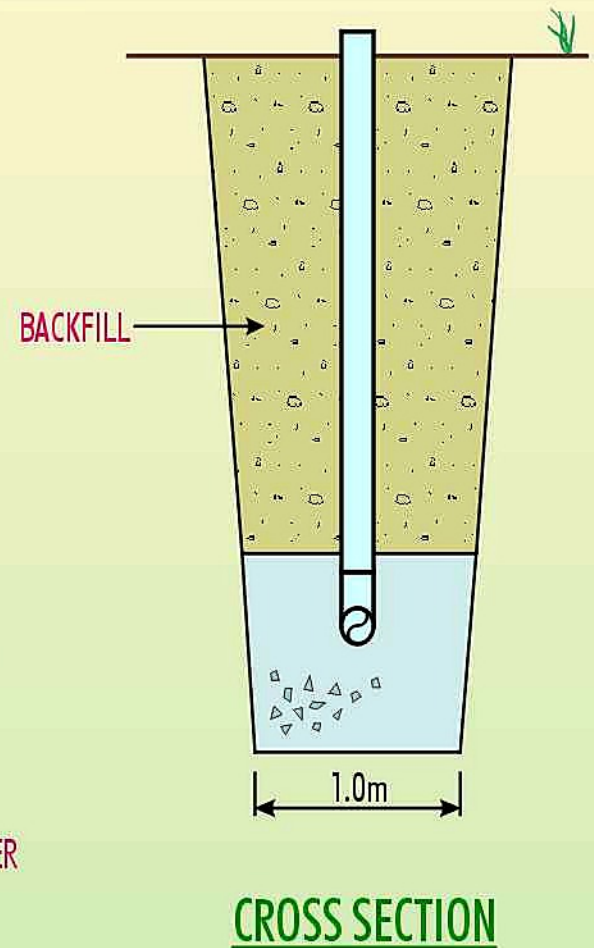
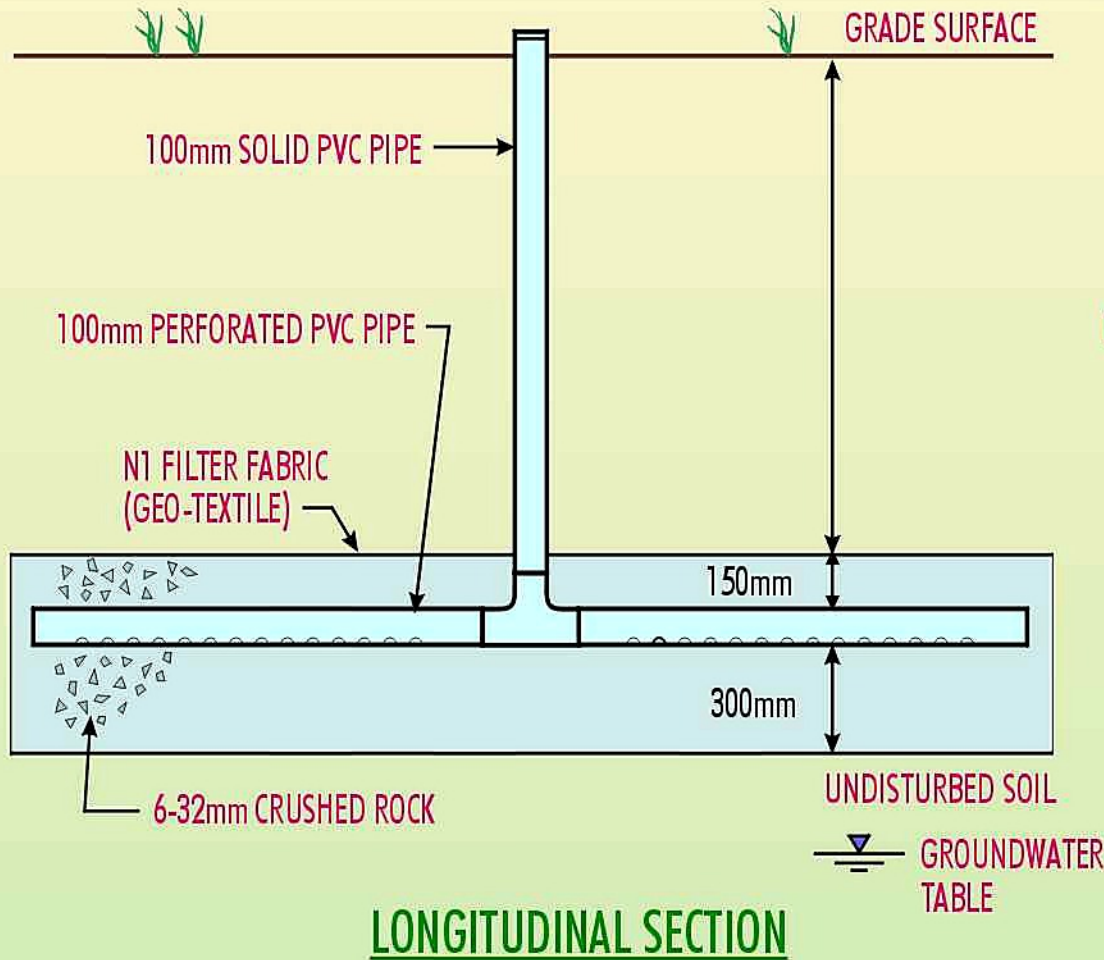


# Ivey-sol • SPTT

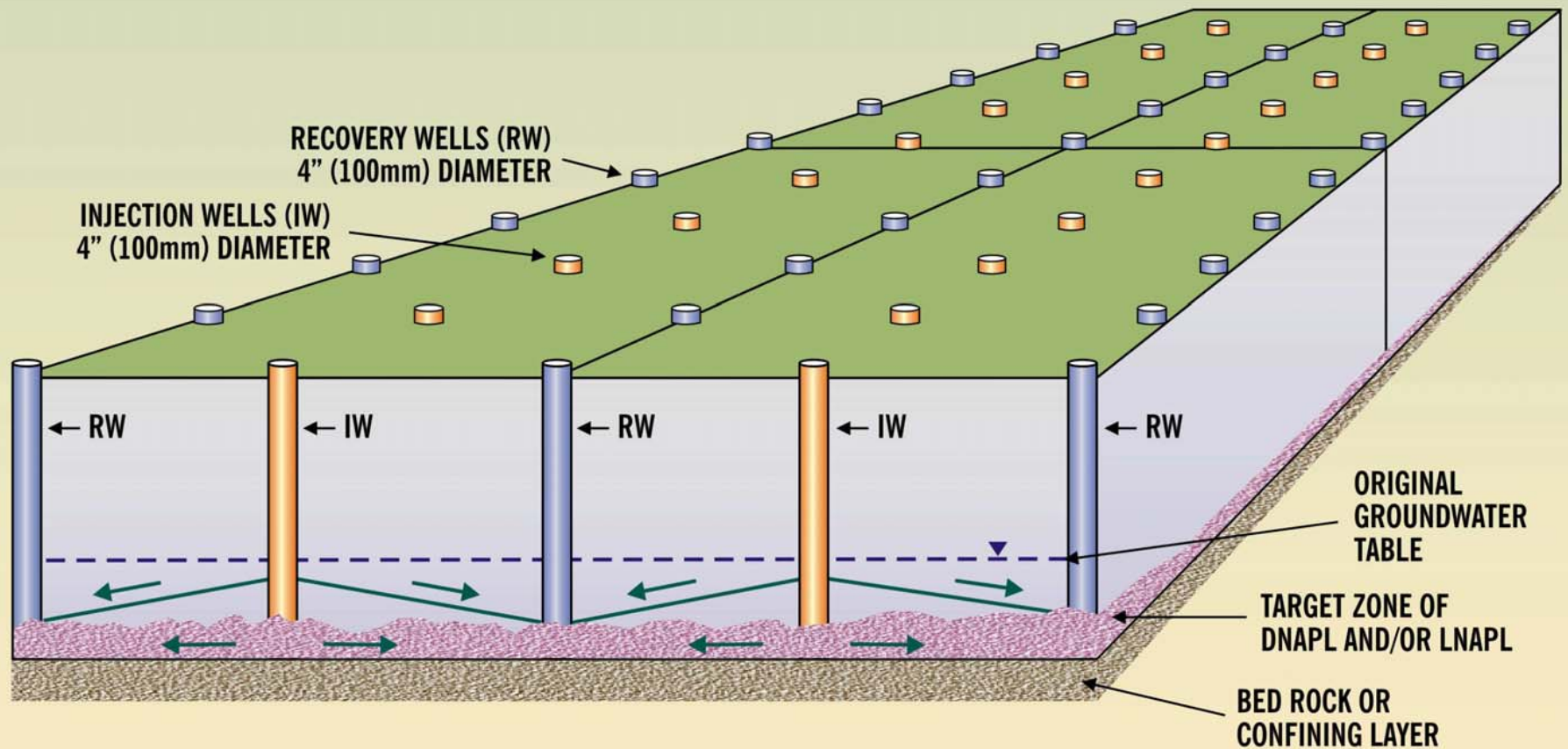




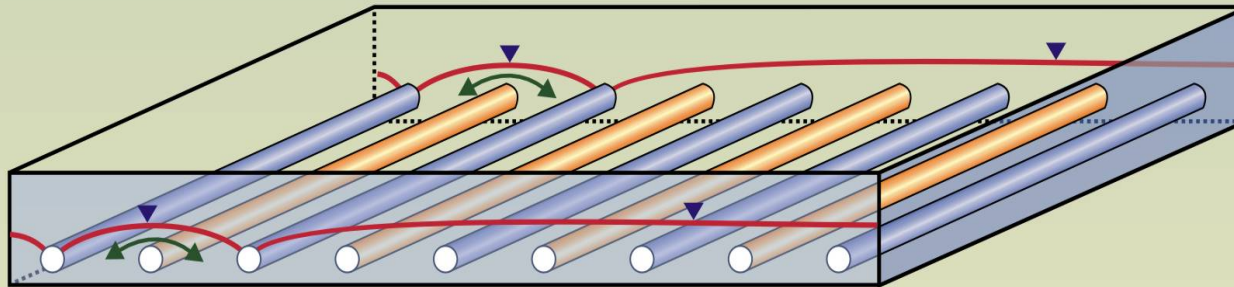
# Injection Gallery (Basic Design)



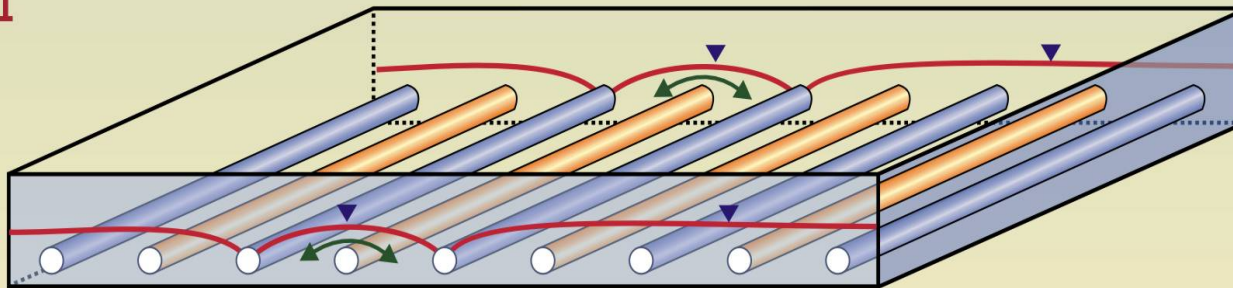
# *Conceptualization of Iveysol Surfactant Injection/Recovery System*



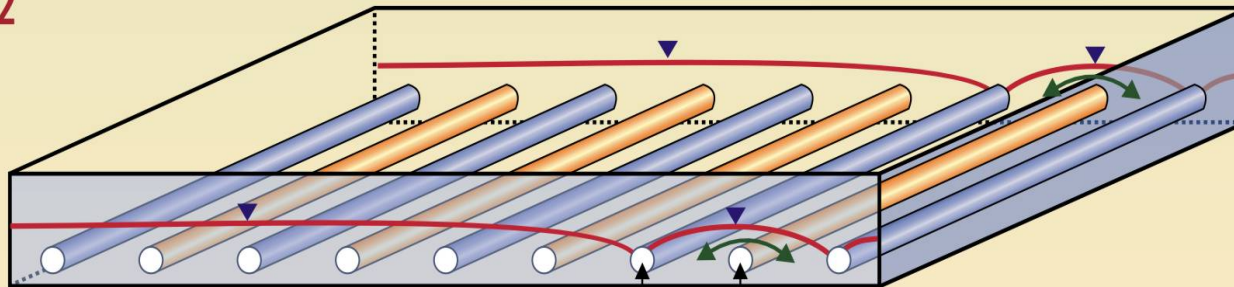
# *Conceptualization of a Phased Modular Implementation Approach (Ivey-sol)*



**PHASE 1**



**PHASE 2**



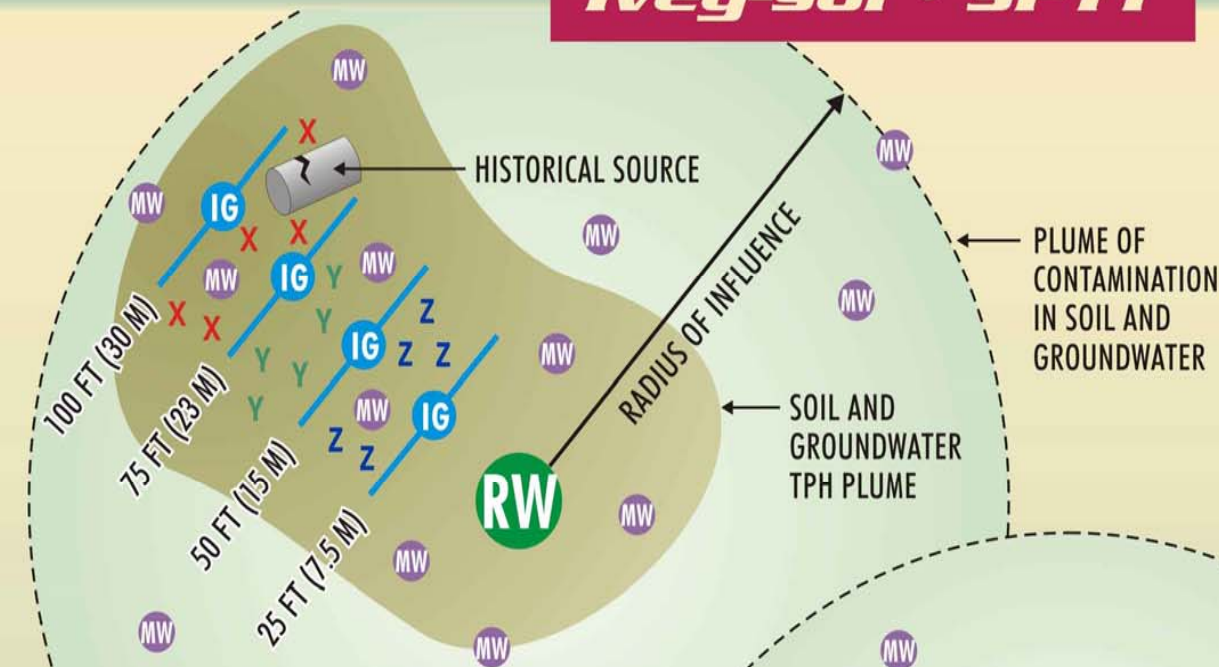
**PHASE 3**

RECOVERY  
DRAINLINE

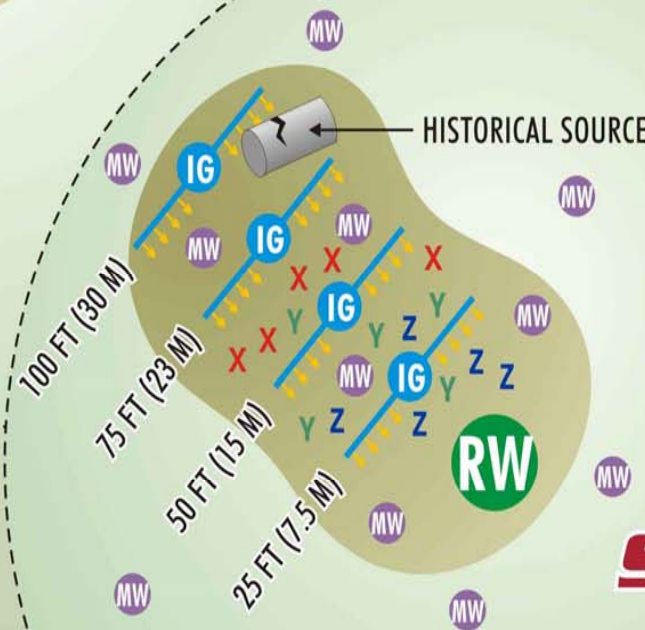
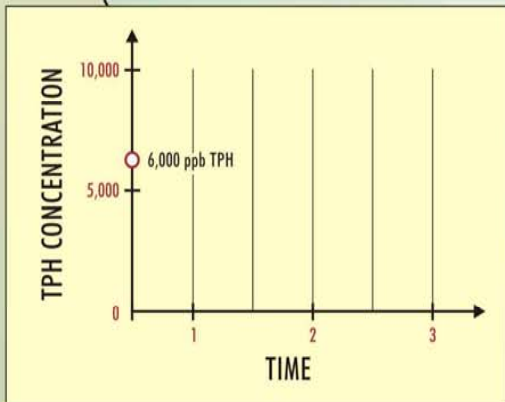
INJECTION  
DRAINLINE



# Ivey-sol • SPTT



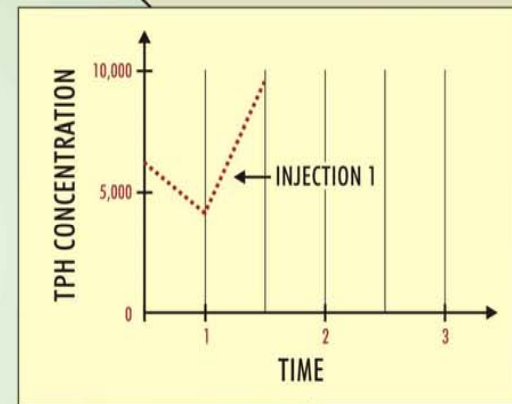
## Baseline



## SPTT Phase I

### LEGEND:

- MW** MONITORING WELL
  - IG** IN-SITU SPTT INJECTION GALLERY
  - X** 1500 ppb TPH
  - Y** 2500 ppb TPH
  - Z** 4000 ppb TPH
  - RW** RECOVERY WELL = 6000 ppb TPH
- BASELINE CONDITION TIME = 0**



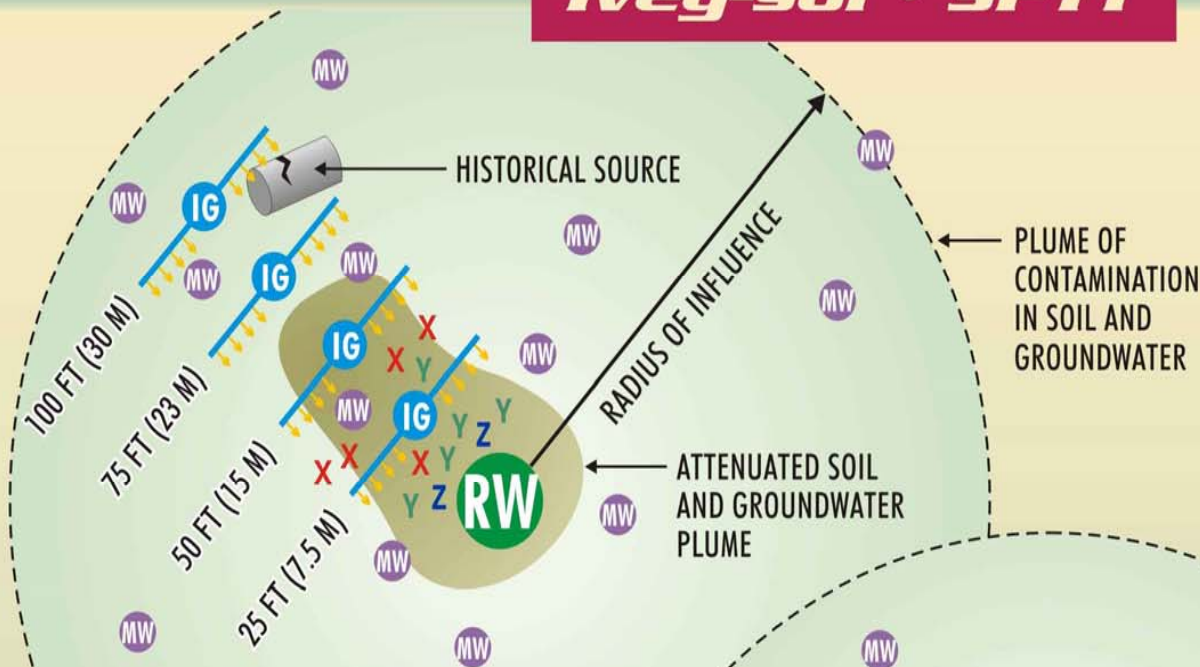
**Conducting an Ivey-sol Injection at an Injection Wells on a hydrocarbon contaminated site.**

**Introduced 4-5 Gal. of mixture followed by 40-50 Gal. of water for subject application.**





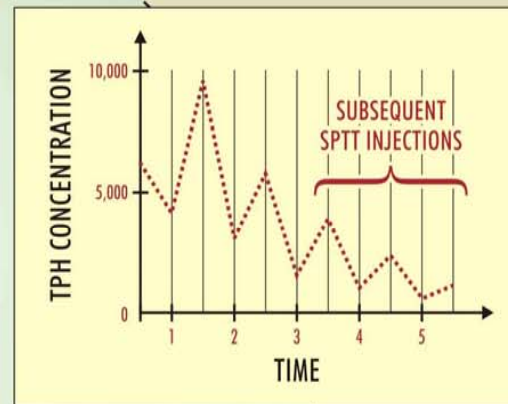
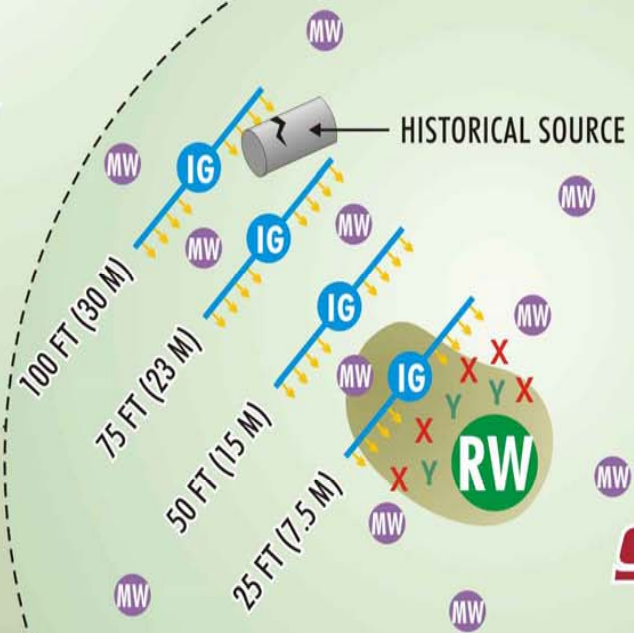
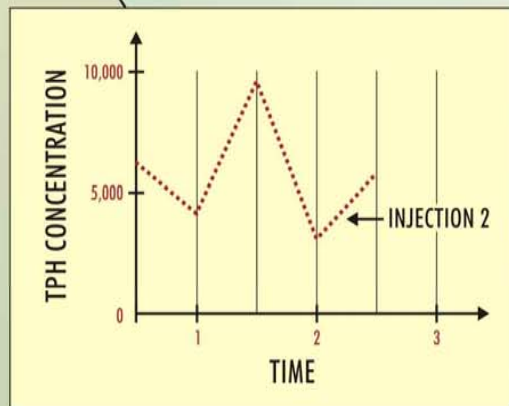
# Ivey-sol • SPTT



## LEGEND:

- MONITORING WELL
  - IN-SITU SPTT INJECTION GALLERY
  - 1500 ppb TPH
  - 2500 ppb TPH
  - 4000 ppb TPH
  - RECOVERY WELL = 6000 ppb TPH
- BASELINE CONDITION TIME = 0

## SPTT Phase II

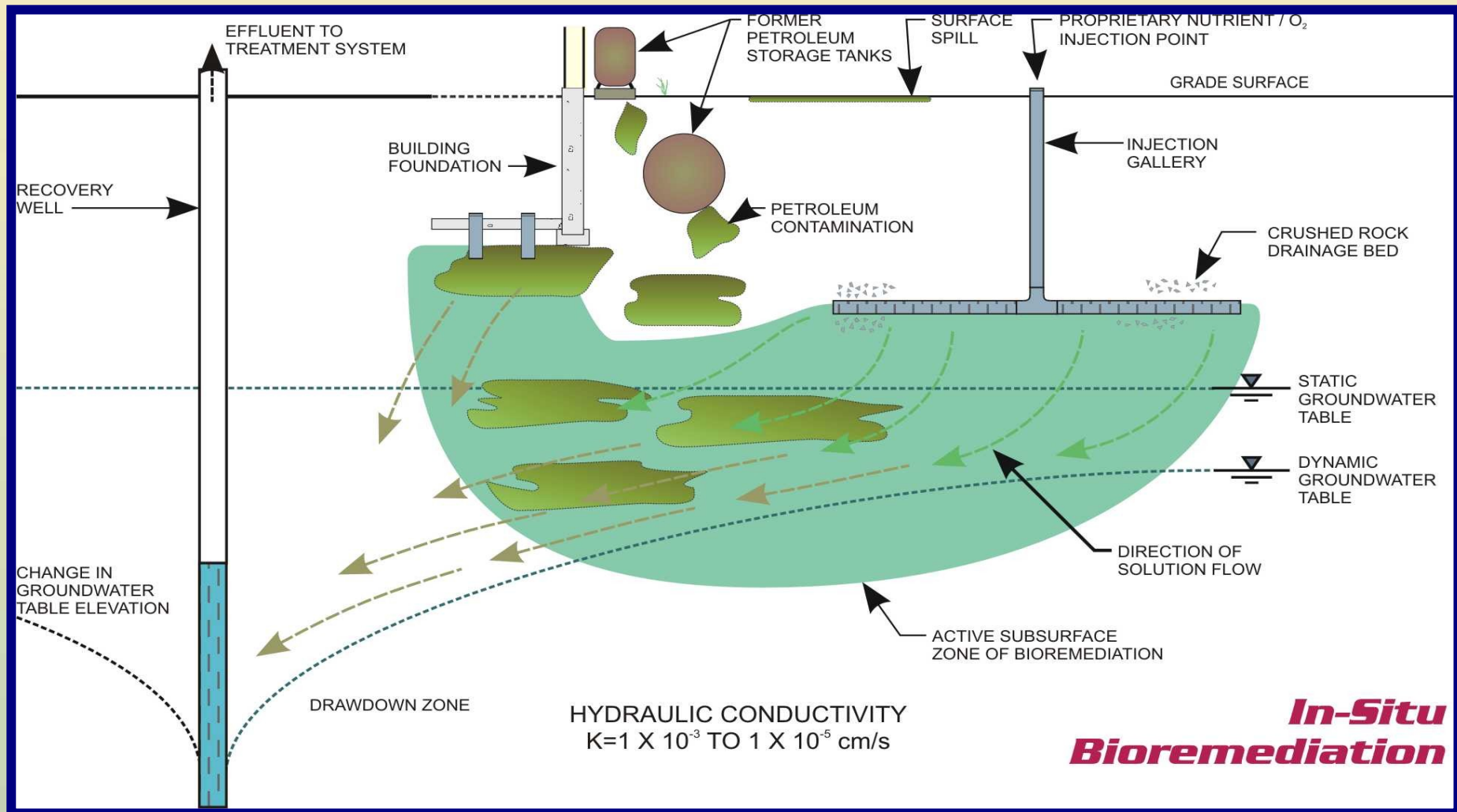


## SPTT Phase III



# In-Situ SEB

## Surfactant Enhanced Bioremediation



# EX-SITU REMEDICATION

***Ivey-sol • SPTT***



## **Ex-Situ Soil Treatment Unit**

**Small To Large Scale LNAPL & DNAPL**

**Soil Remediation**

**(Mobile 3 to 35 cubic yards units)**











**Refinery Site - Soil Contamination**  
**Clean-up Objective: < 3% Mineral Oil & Grease**



## Alberta Canada Oil Refinery Site (>5000 Tons)

Contaminated soil with a baseline concentration of 40,000 ppm (4%). Ex-situ Ivey-sol Soil Washing SER Process achieved applicable soil remediation site objectives. Project data set provided below showing pre and post soil washing remediation results with time based sample analysis.

<u>Soil Parameter</u>	<u>Base Line</u>	<u>5 Minutes</u>	<u>7 minutes</u>	<u>Reductions</u>
CCME F1 C6-10	72 ppm	< 1 ppm	< 1ppm	100%
CCME F1 BTEX	71 ppm	< 1 ppm	< 1ppm	100%
CCME F2 C10-16	417 ppm	35 ppm	21 ppm	95%
CCME F3 C16-34	13, 600 ppm	1,600 ppm	826 ppm	94%
CCME F4 C34-50	5,060 ppm	512 ppm	259 ppm	95%
CCME F4 C34-50+	13,000 ppm	571 ppm	290 ppm	98%

**Note:** *CCME = Canadian Council of Ministers for the Environment.  
From CCME Soil and Water Clean-up Guideline Parameters.*



**Pre and Post Ivey-sol Treatment  
Effective Removal of Heavy-end Hydrocarbons.**

# Ex-Situ Soil Treatment Sydney Australia





**Ivey-sol • SPTT**

## Ex-situ Soil Treatment SEO & SEB



***Ivey-sol • SPTT***



**Tank Cleaning Applications  
Before & After Ivey-sol® Cleaning**



**Stream and Shoreline  
Spill Clean-up With  
(Ivey-sol ®).**

**Application via high-  
pressure spray to  
liberate hydrocarbons  
from stream-bed sand,  
rock and vegetation.**

**Removal of dissolved  
wastes from localized  
area via Vacuum  
suction hose.**





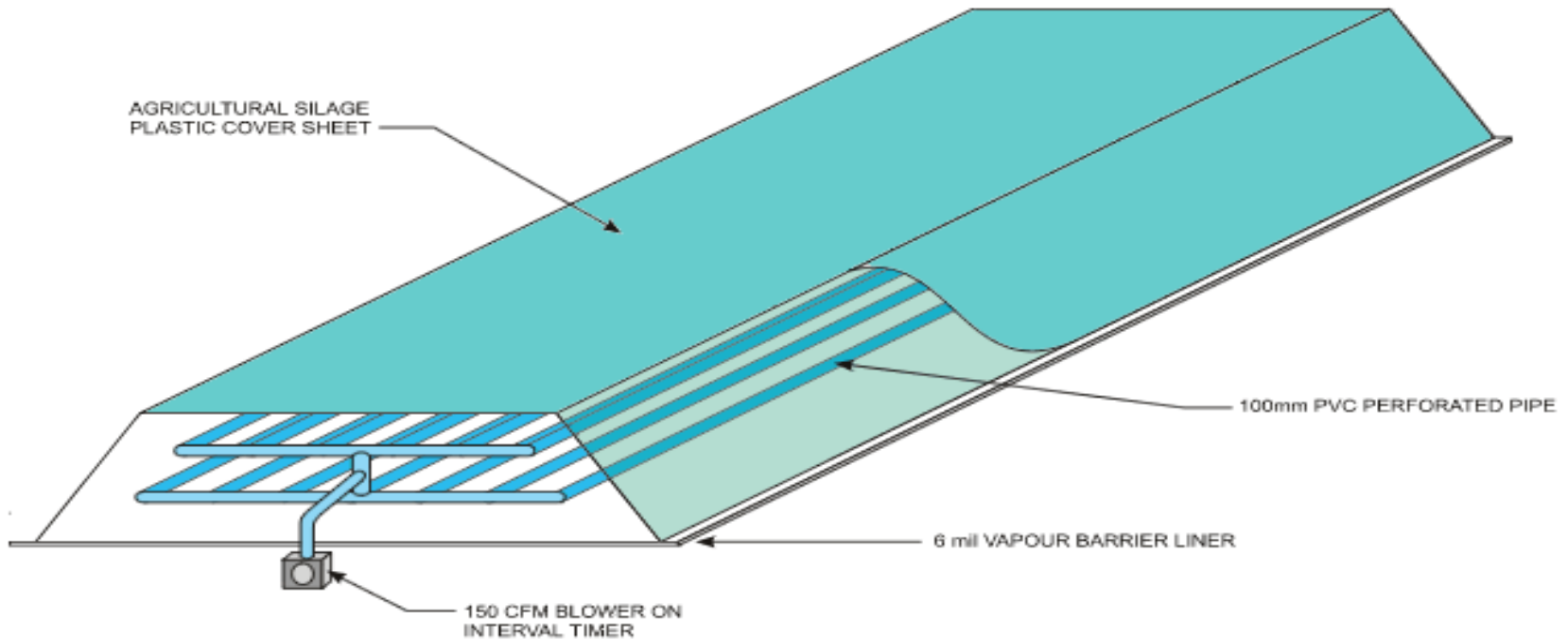
**Oil & Gas Well  
Frac-Sand Waste  
Treatment (Ivey-sol®)**

**Sample From Alberta,  
Western Canada**



# Ex-Situ SEB Surfactant Enhanced Bioremediation (F3 &F4)

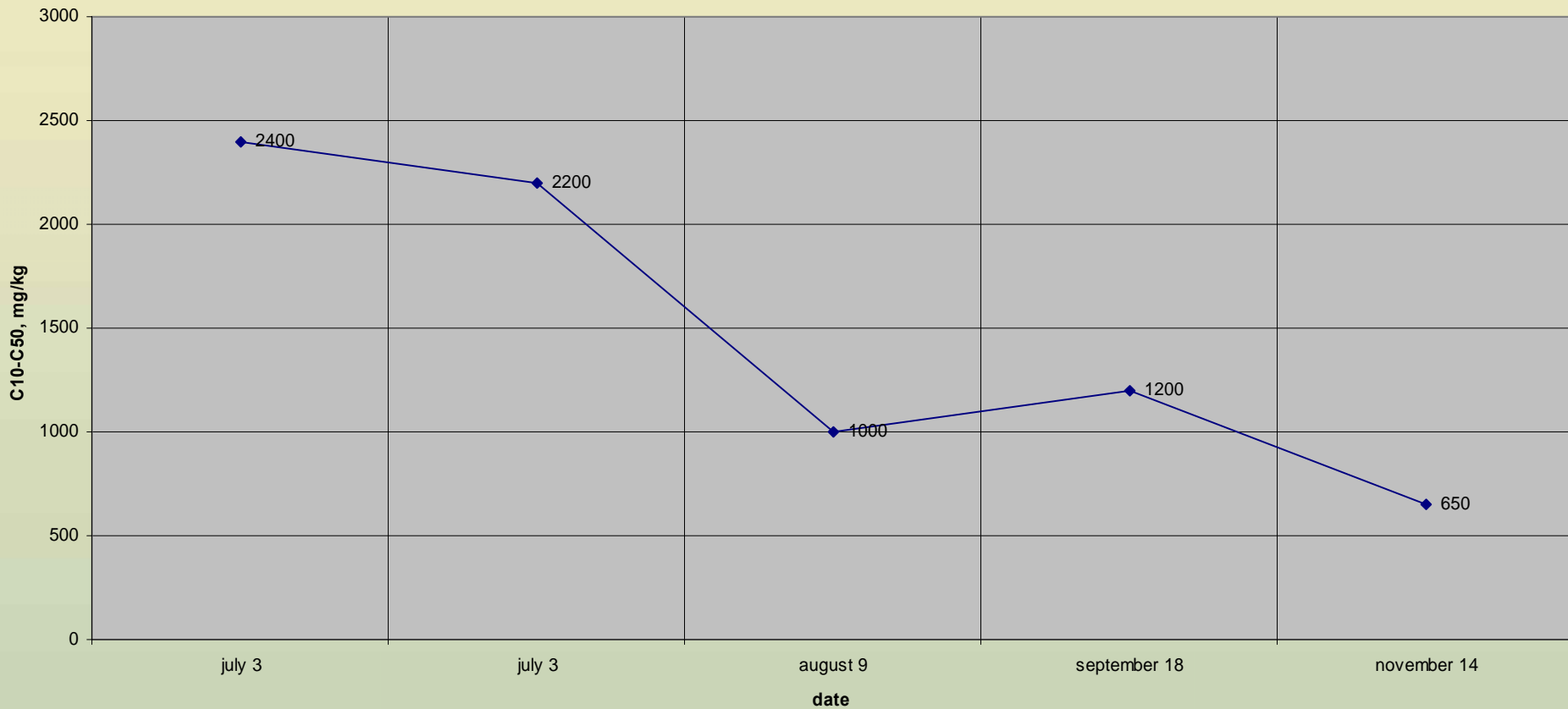
## EX-SITU BIOREMEDIATION



SEB Diesel Contaminated Soil  
SEB Ex-situ Soil Remediation Project

Quebec, Canada

Andain A-1



***Ivey-sol • SPTT***

## **SEB Fine Grain F3 & F4 Remediation**

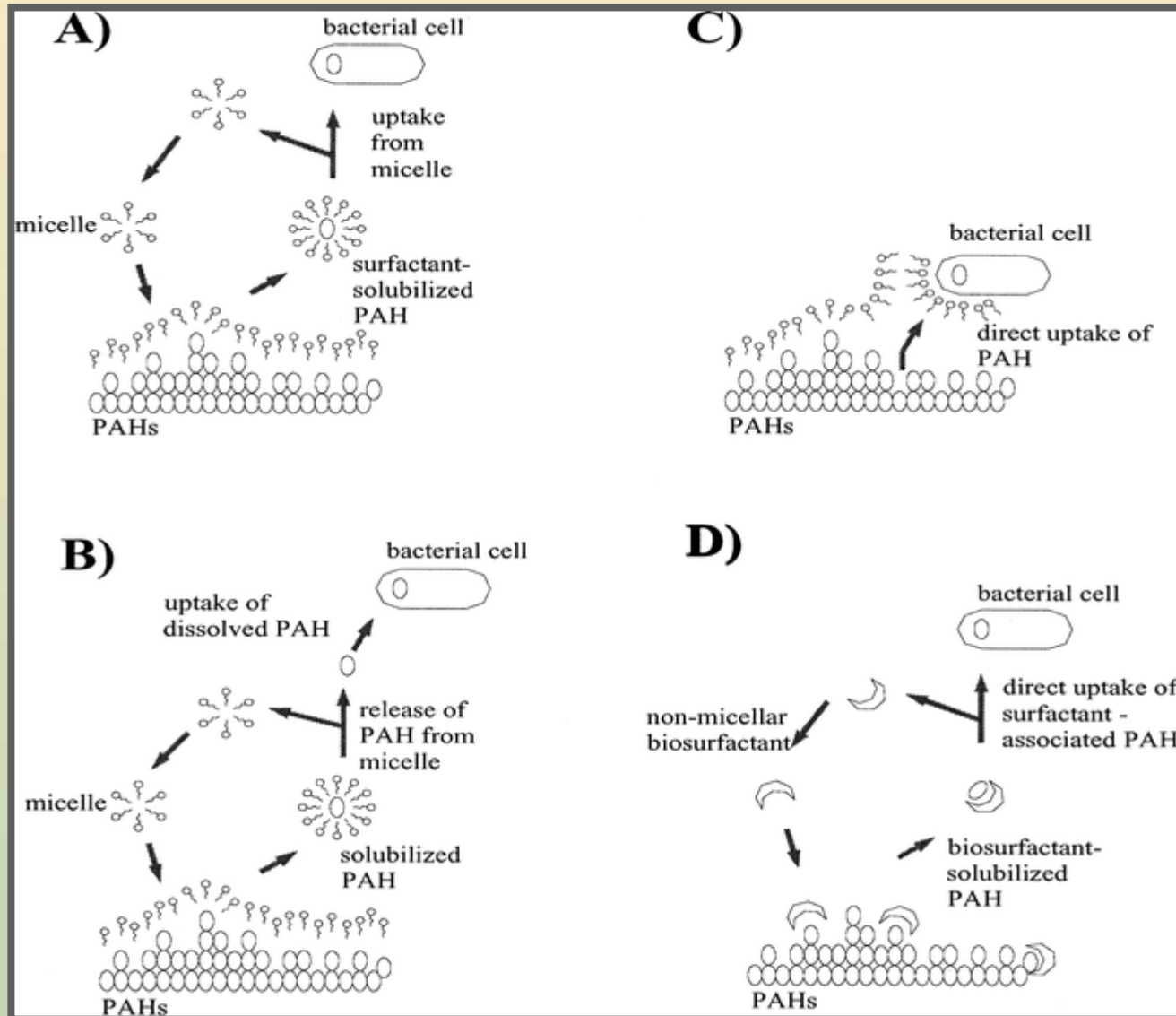




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# SEB Mechanism For PAH's





## **Surfactant Enhanced Oxidation (SEO)**

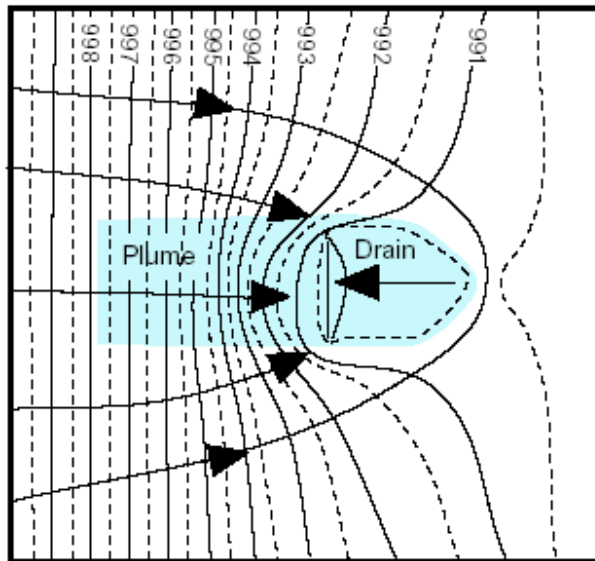
- **Ivey-sol Surfactants are applied to PCB contaminated soils to desorb PCBs**
- **Following de-sorption of PCB's a water soluble oxidizing chemical (Agent) is applied.**
- **PCB levels reduced to clean-up standards with some samples coming back Non-Detectable.**
- **When oxidizers are used alone, efficiency was < 35%.**

***Reference: 2005 & 2007 Project Collaborations***

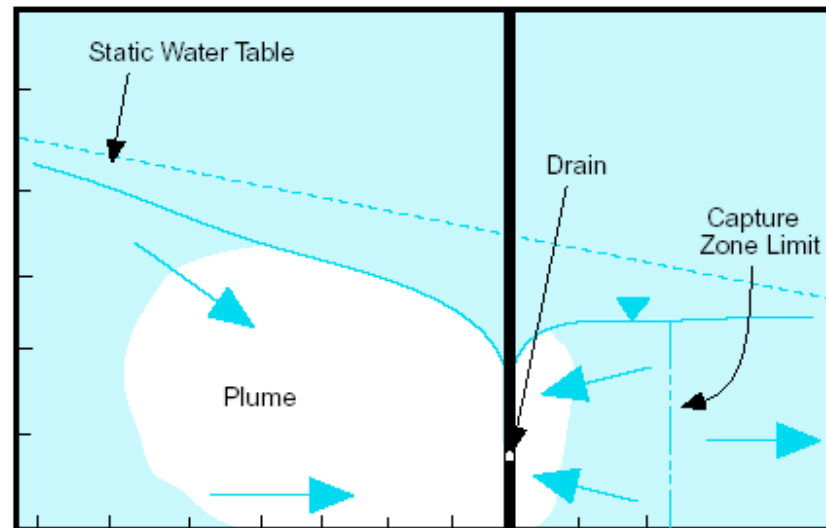
# Surfactant Application Design Considerations

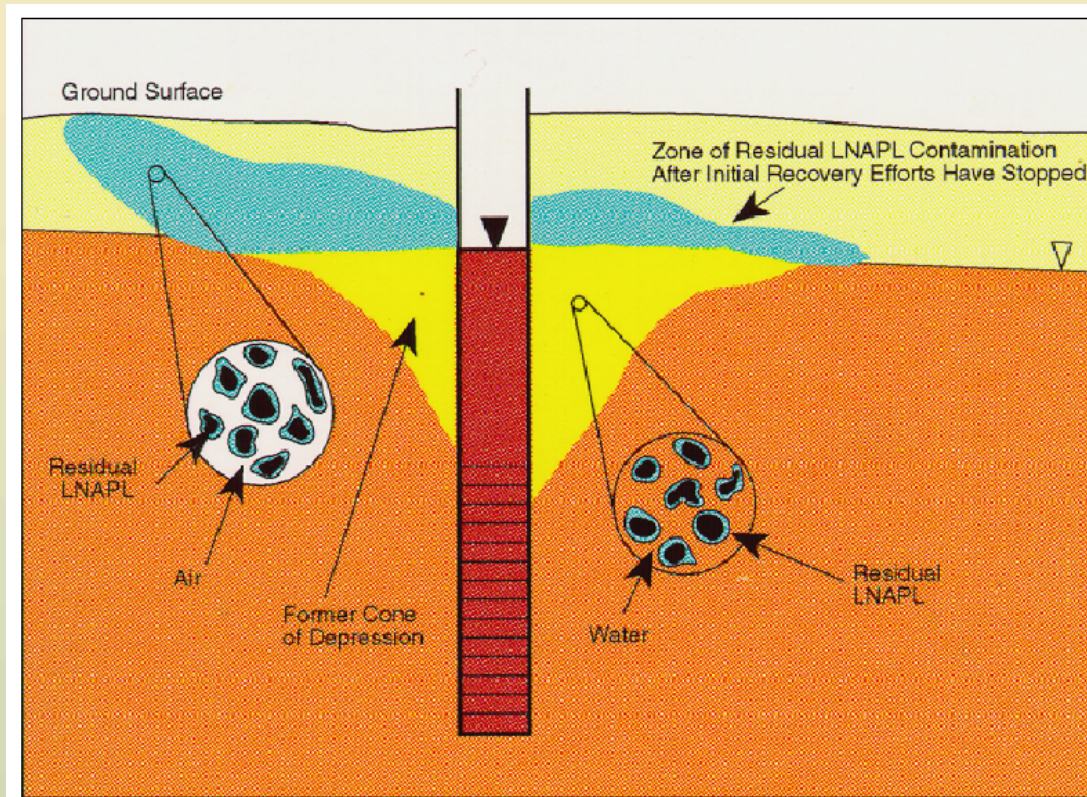
- ▶ For pump and treatment (In-situ SER & SEB)
- ▶ Injection well design options, considerations...
- ▶

# Pump and Treat

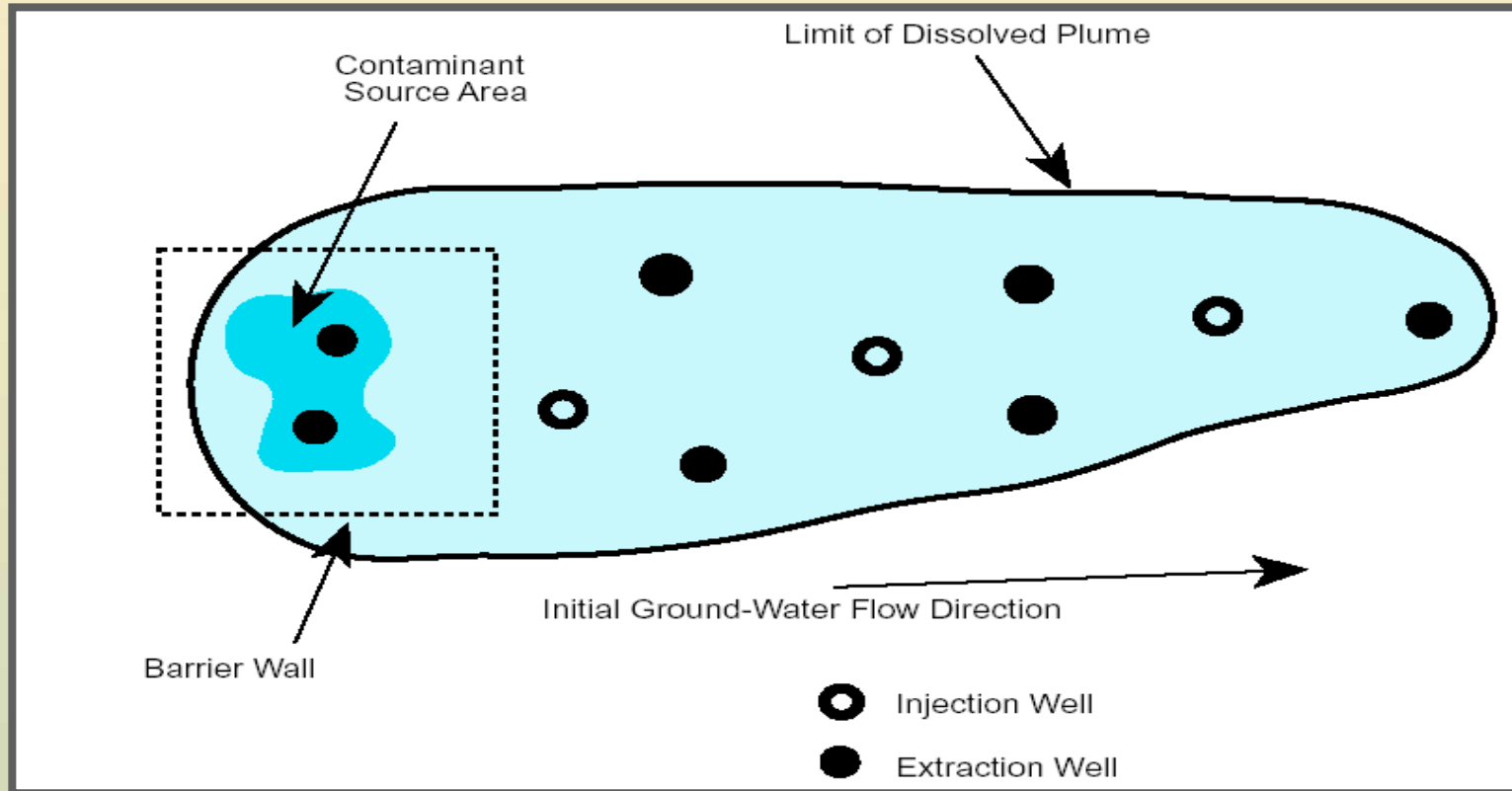


(b)



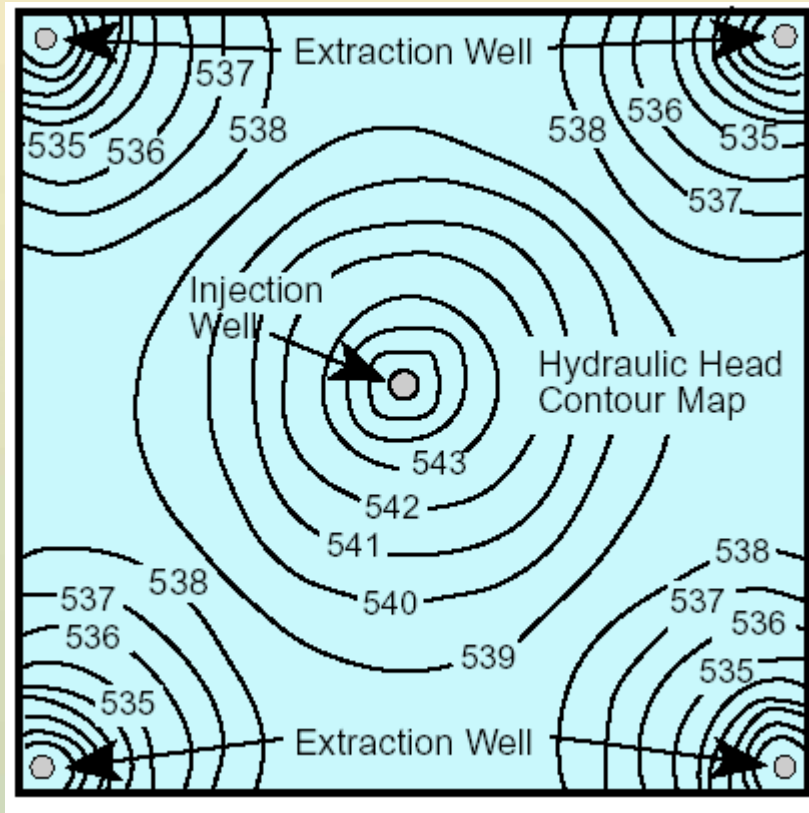


**Figure 16.** Zone of residuals created in former cone of depression after cessation of LNAPL recovery system (Gorelick et al., 1993).

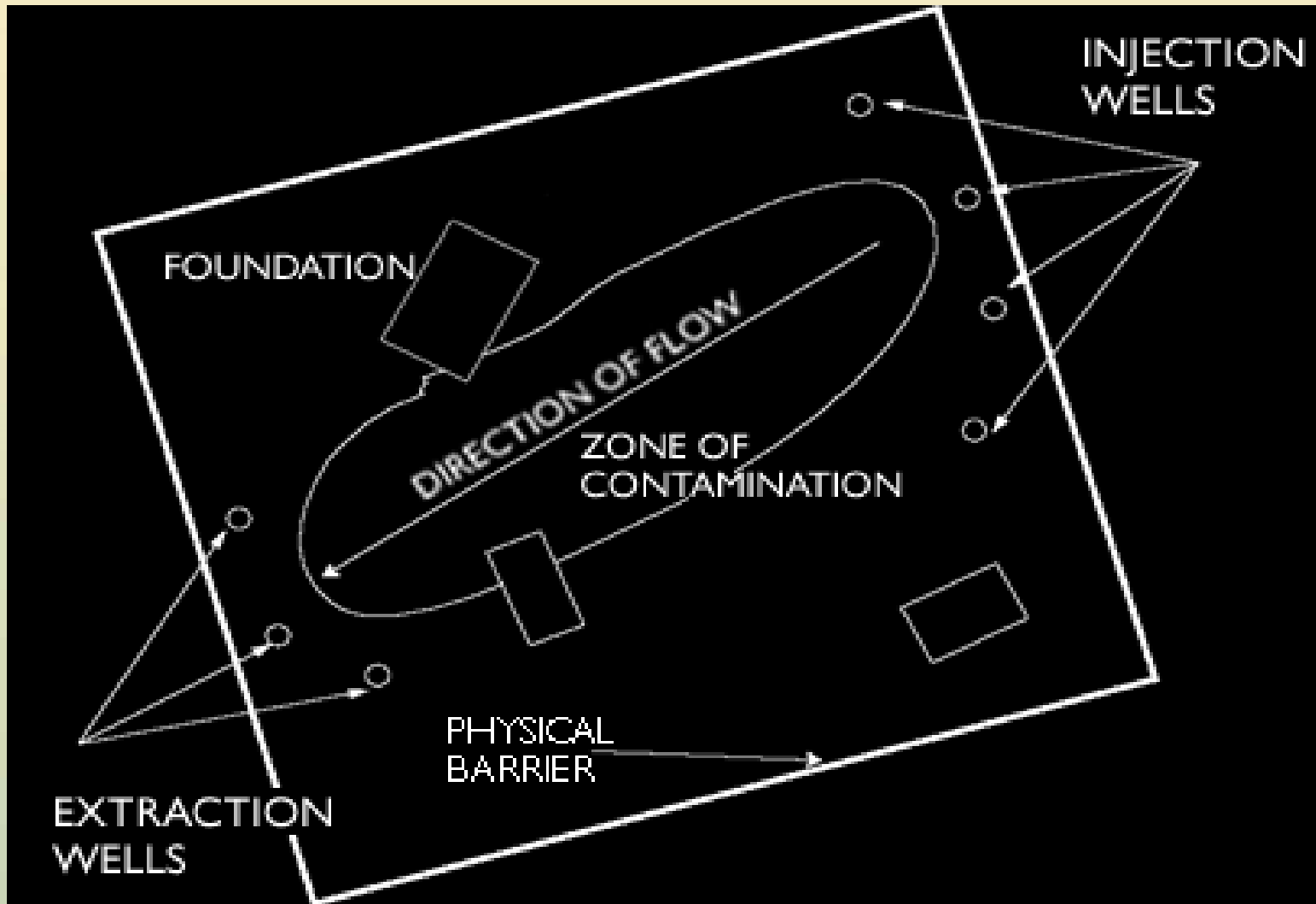


Plan view of a mixed containment-restoration strategy. A pump-and-treat system is used with barrier walls to contain the ground-water contamination source areas (e.g., where NAPL or waste may be present) and then collect and treat the dissolved contaminant plume (Cohen et al., 1994).

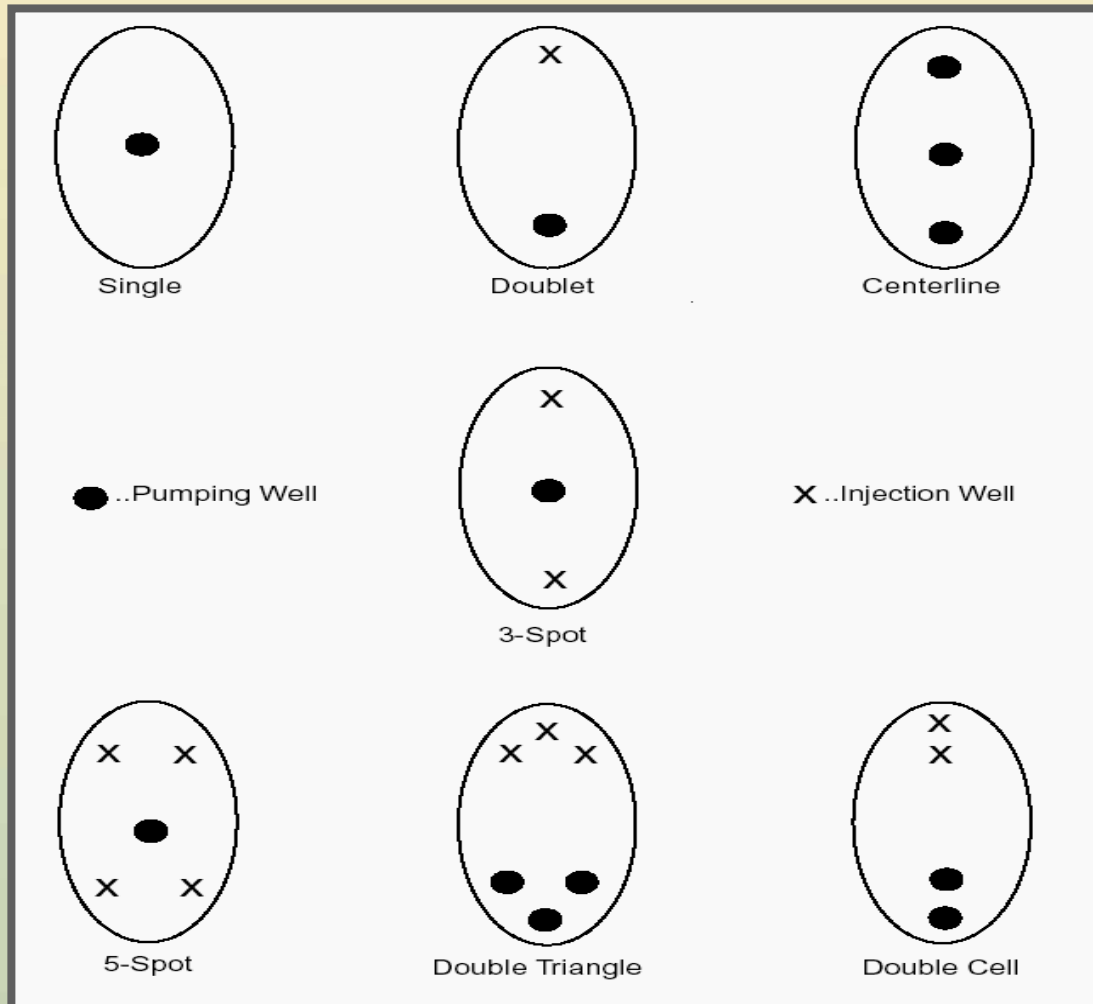




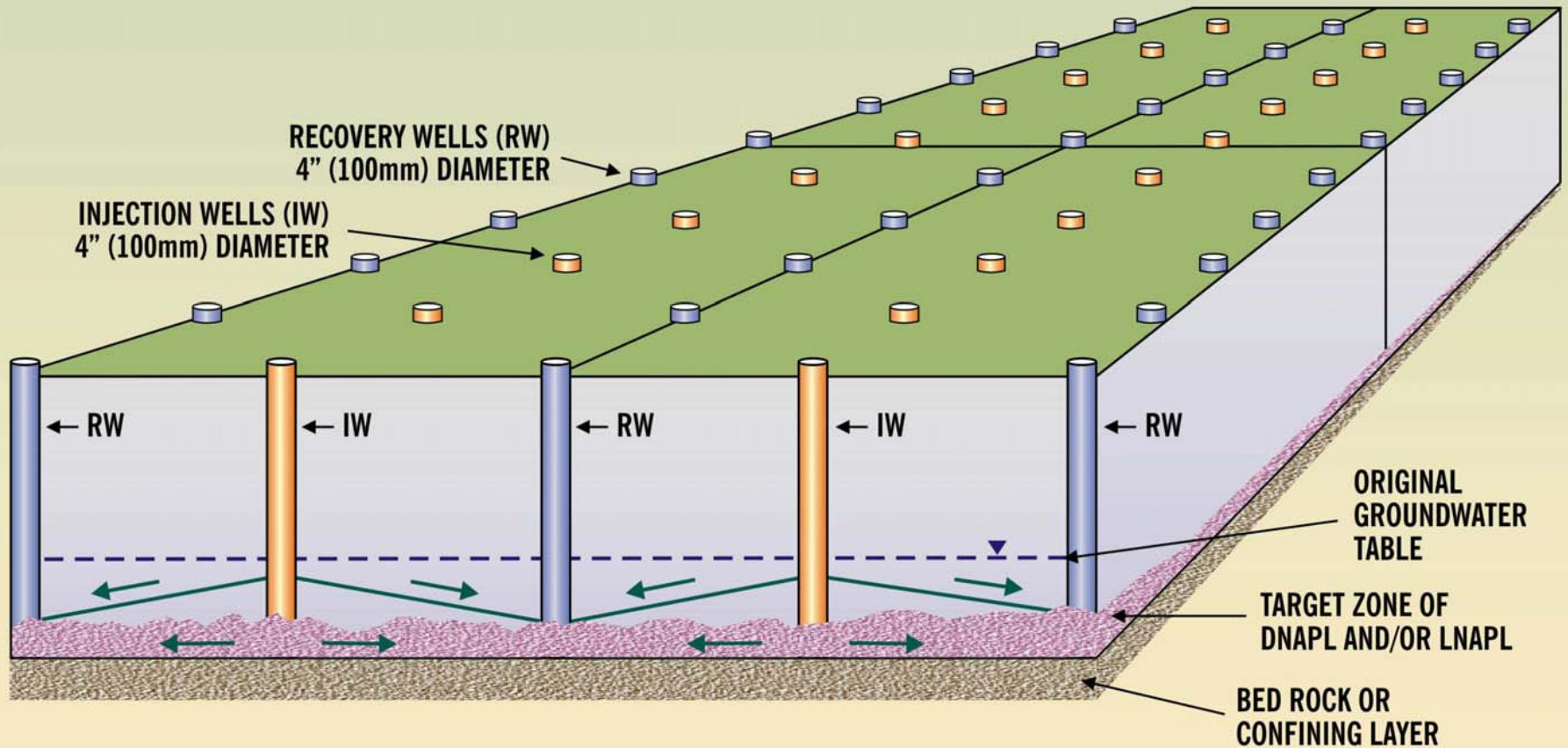
Examples of stagnation zones (shaded where ground-water velocity is less than 4 L/T): (a) single pumping well and (b) four extraction wells with an injection well in the center (Cohen et al., 1994).

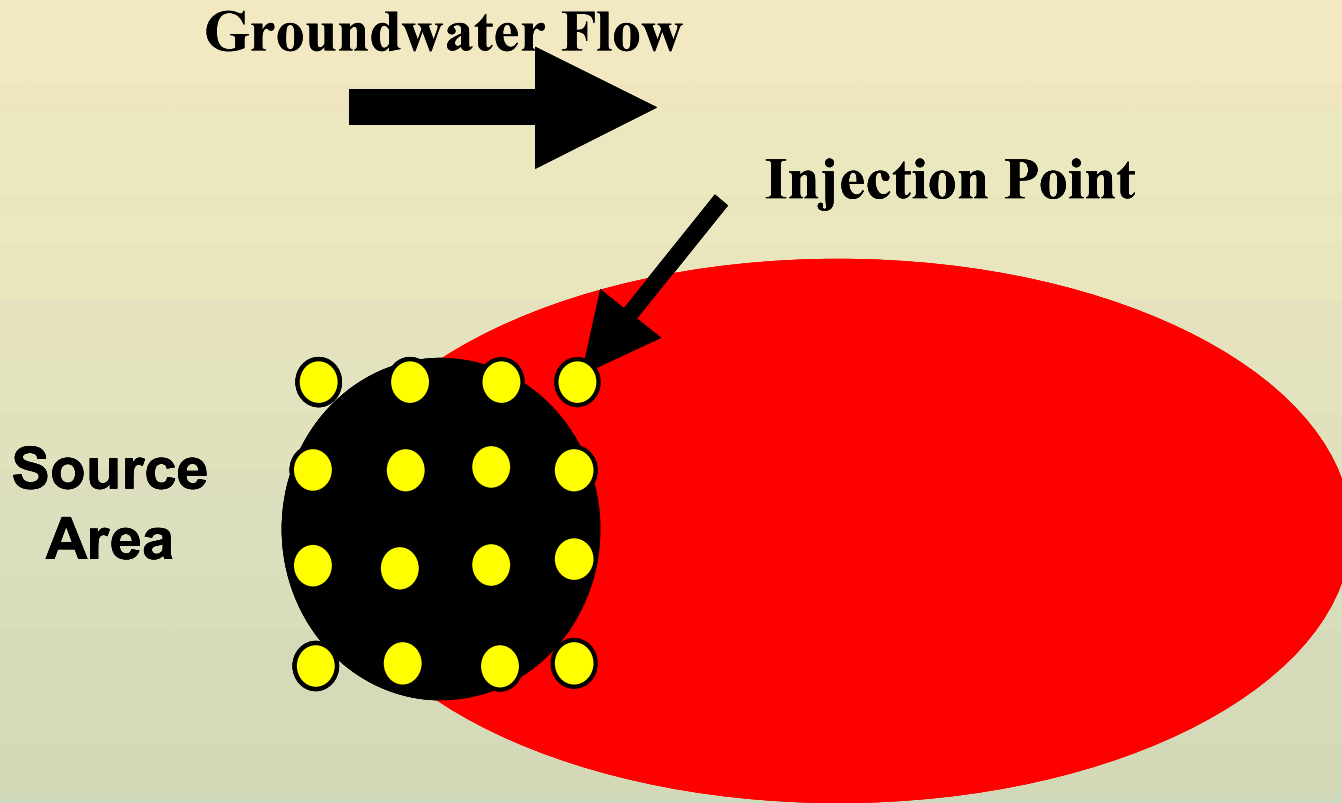


# Pumping Injection Well Patterns



# *Conceptualization of Iveysol Surfactant Injection/Recovery System*







## “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 removal NAPLs from Soil.

***Ivey-sol • SPTT***

*Ivey-sol • SPTT*

# **CASE STUDIES**

**In-situ & Ex-situ**

*Ivey-sol • SPTT*

# ***Case Study***

***Monroe, Connecticut, USA***










PRESENTED BY:

***George A. Ivey***

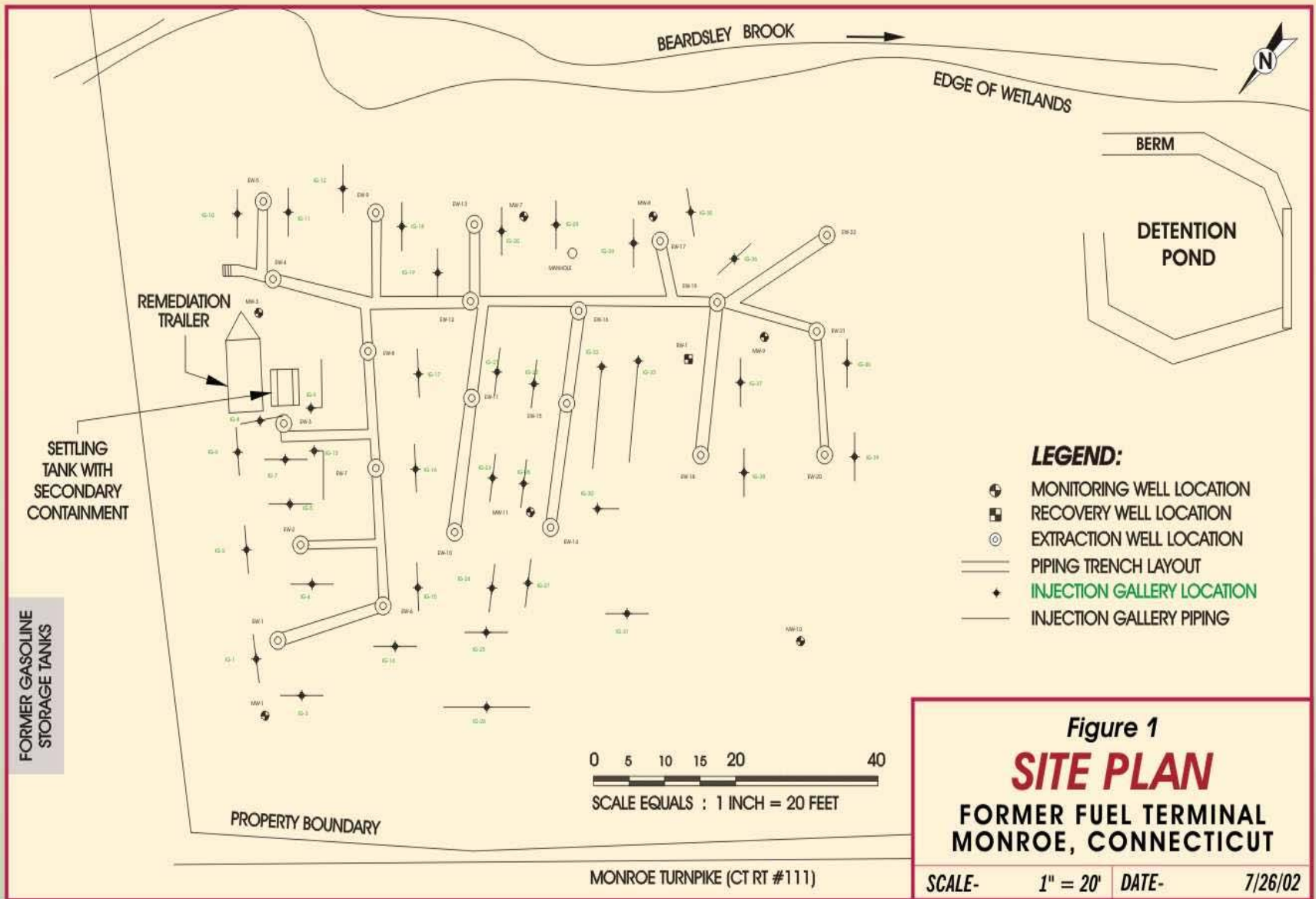
SENIOR ENVIRONMENTAL SCIENTIST,  
IVEY INTERNATIONAL INC.

# ***Fuel Terminal***

***Monroe, Connecticut, USA***

-  Former heating oil terminal from the mid-1950's to the late 1970's
-  No. 2 fuel oil was stored at the site
-  Multiple releases occurred over time
-  Site and surrounding area are wetlands, with the former terminal area elevated with fill material for commercial use
-  Irregular fill consisting of sand, silt, gravel and boulders with some timbers and metal buried throughout the site
-  Sensitive receptors are adjacent stream and down-gradient potable wells
-  High vacuum (dual phase) extraction system in use at the site since late 1999
-  Selective Phase Transfer Technology (SPTT) system installed in May 2002
-  Monthly SPTT injections commenced in May 2002





**Ivey-sol • SPTT**

# ***Fuel Terminal***

***Monroe, Connecticut, USA***

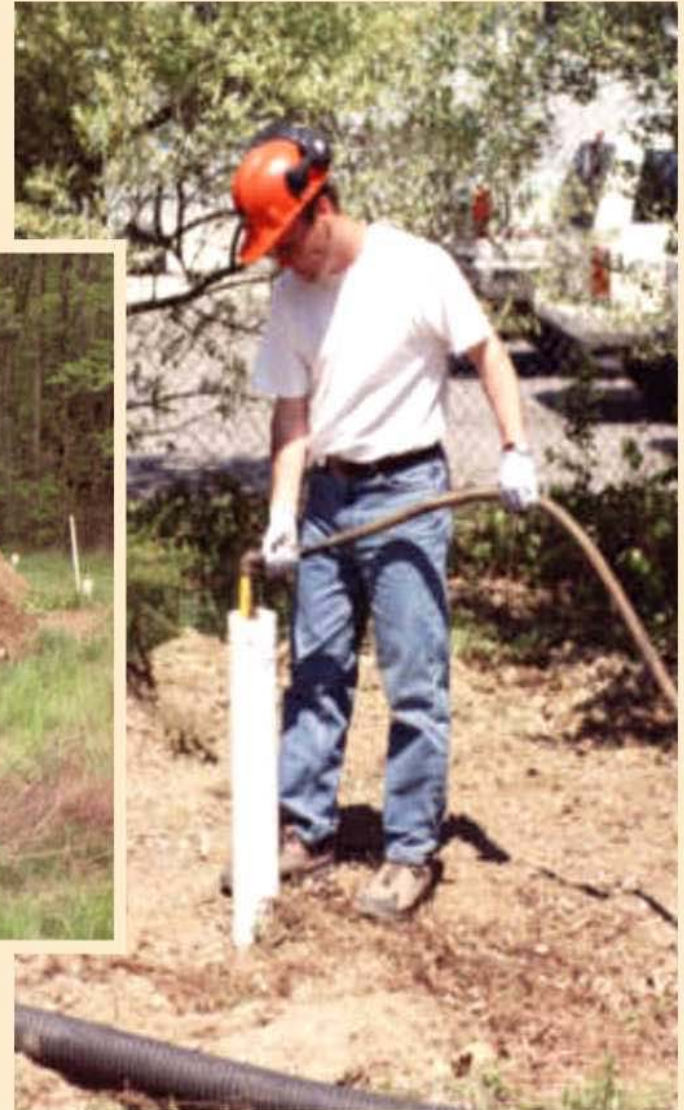




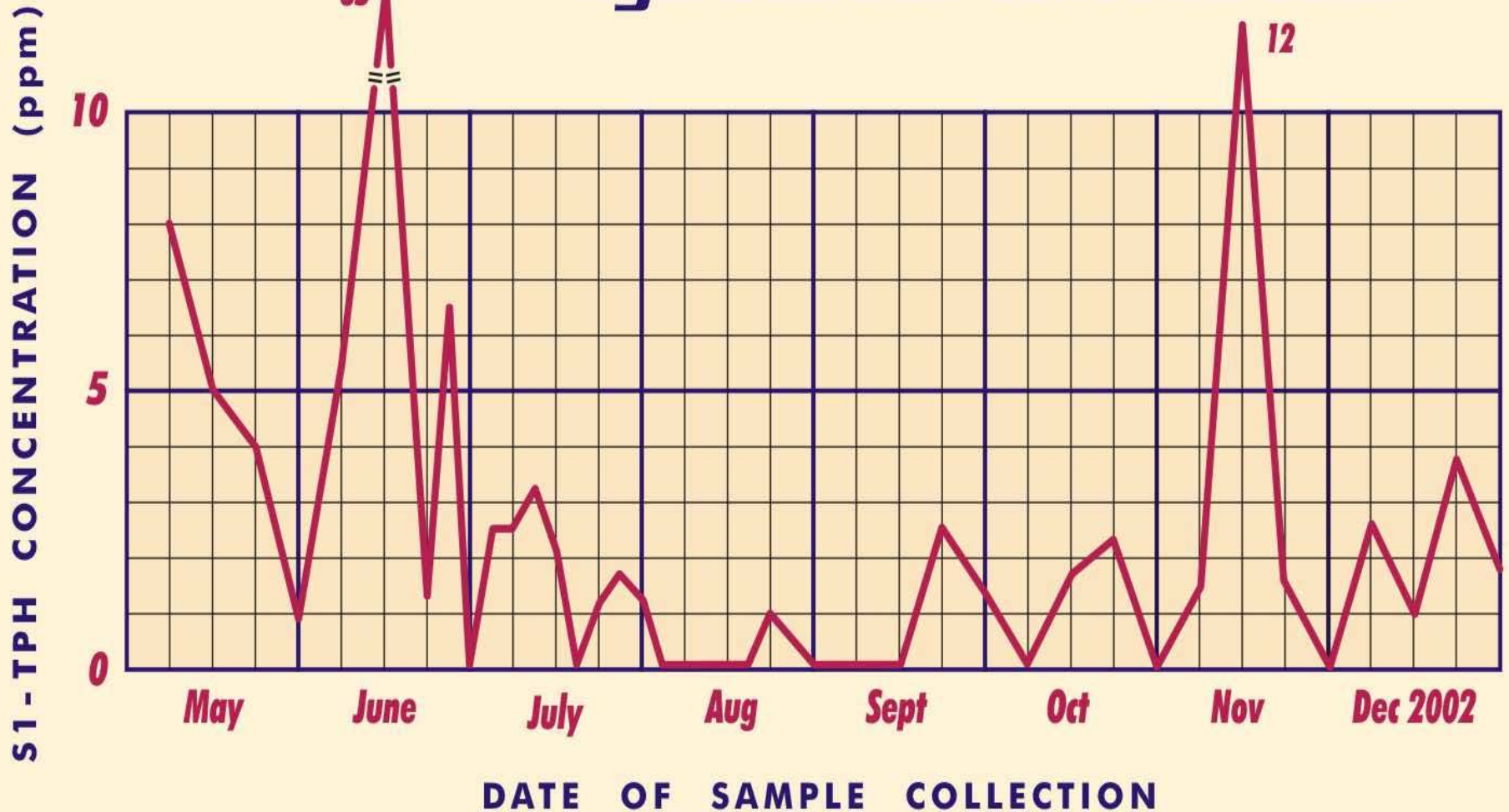
***Ivey-sol • SPTT***

# ***Fuel Terminal***

***Monroe, Connecticut, USA***











## Influent Total Petroleum Hydrocarbon Concentration





# ***Fuel Terminal***

***Monroe, Connecticut, USA***

-  **Mass Recovery = Flow Rate x Concentration**
-  **Mass Recovery (pounds per day) =  
gallons per minute (gpm) x mg/l X 0.012**
-  **3.785 l/gal x 1 lb/454,000 mg x 1440 minutes/day = 0.012**
-  **Mass Recovery prior to the injection period is based on an  
average influent concentration of 0.75 mg/l**
-  **8 gpm x .075 mg/l x 0.012 = 0.072 lbs/day =  $3.269 \times 10^4$  mg/day  
(prior to SPTT use)**
-  **Mass Recovery during the injection period is based on a concentration  
average calculated using the post injection peak concentrations of 3.07 mg/l**
-  **8 gpm x 3.07 mg/l x 0.012 = 0.29472 lbs/day =  $13.38 \times 10^4$  mg/day  
(during SPTT use)**
-  **Pre vs. post injection mass removal rates show an increase of 409.3%**



## **Project Concluded In 11 Months**

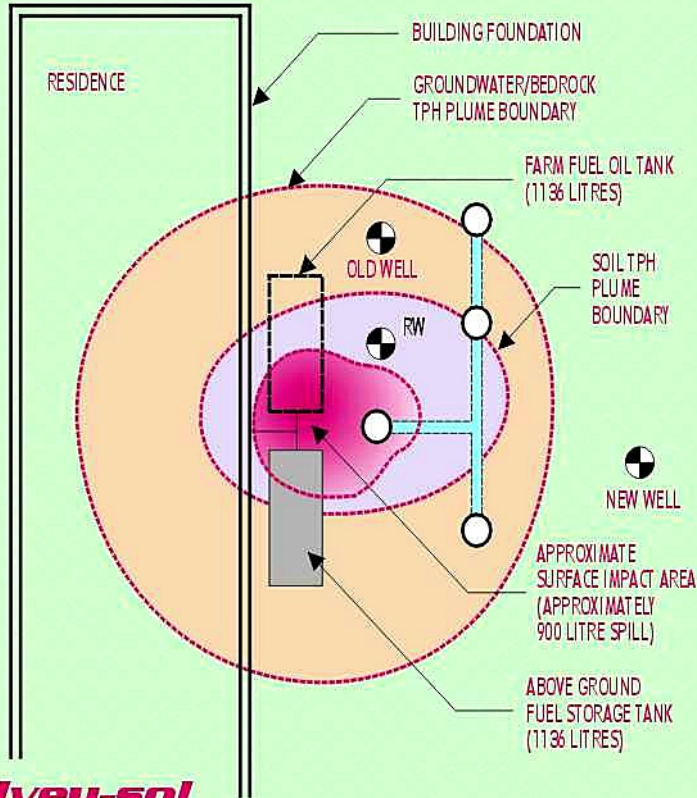


*“We accomplished more with \$50,000 of Ivey-sol than we did with the first \$500,000 we spent on the site over the previous 4 years”*

*“Ivey-sol Increased our rate of contaminant recovery by >400%”*

**Reference: Dan Smith, Senior Project Manager  
Connecticut, United States**

**PROJECT NO. 93-156**



**Ivey-sol  
Phase Transfer  
Site Remediation**

(Air, Soil & Groundwater)

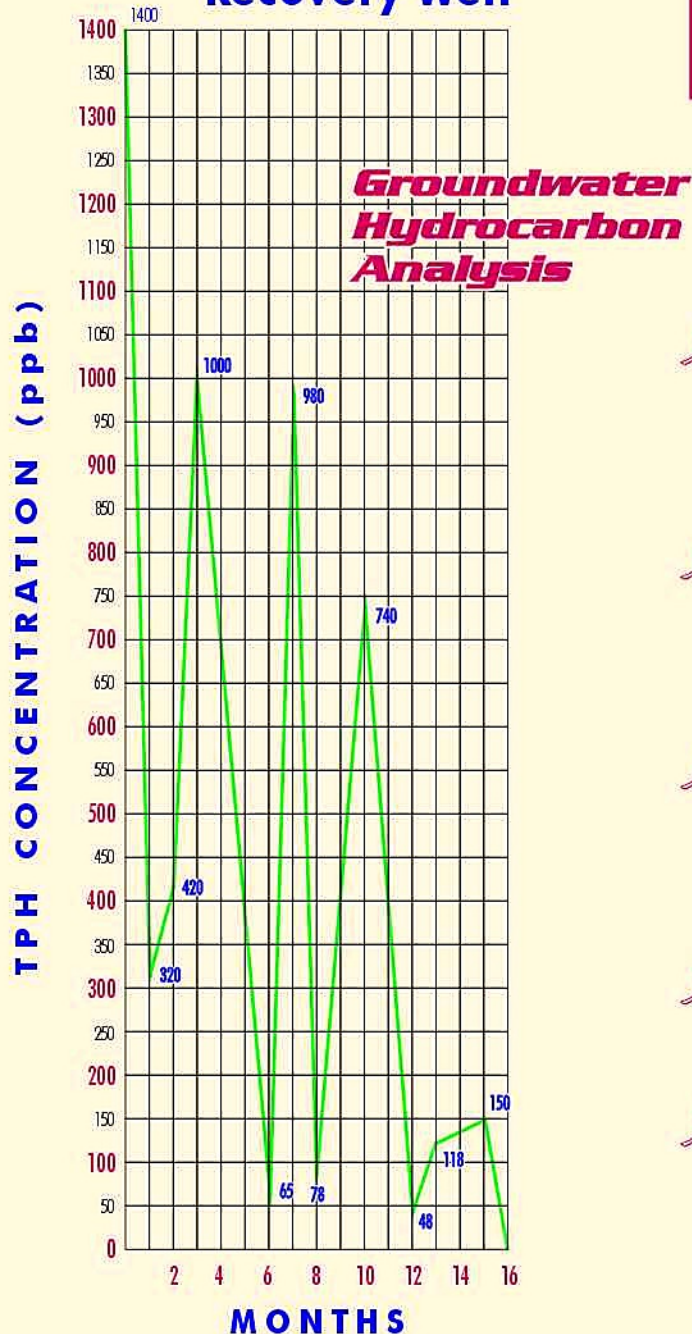
(NOT TO SCALE)

LEGEND:	
	MONITORING WELL
	RECOVERY WELL
	INJECTION GALLERY

# **Case Study I**

- Approximately 900 L (200 gal) fuel oil spill at the above ground storage tank
- Drinking water well and bedrock-aquifer were contaminated at 1400 ppb TPH
- Classified as a Sensitive Site by the Department of Environment with a 10 ppb TPH groundwater clean-up objective

### Recovery Well



Ivey Environmental Services installed a pump & treat system at the recovery well



Several Ivey-sol injection galleries were designed and installed



The site was successfully cleaned up to under 10 ppb in less than 18 months



The client estimates the savings at > \$50,000



The Department of the Environment decommissioned the site

## **Project Concluded In 17 Months**

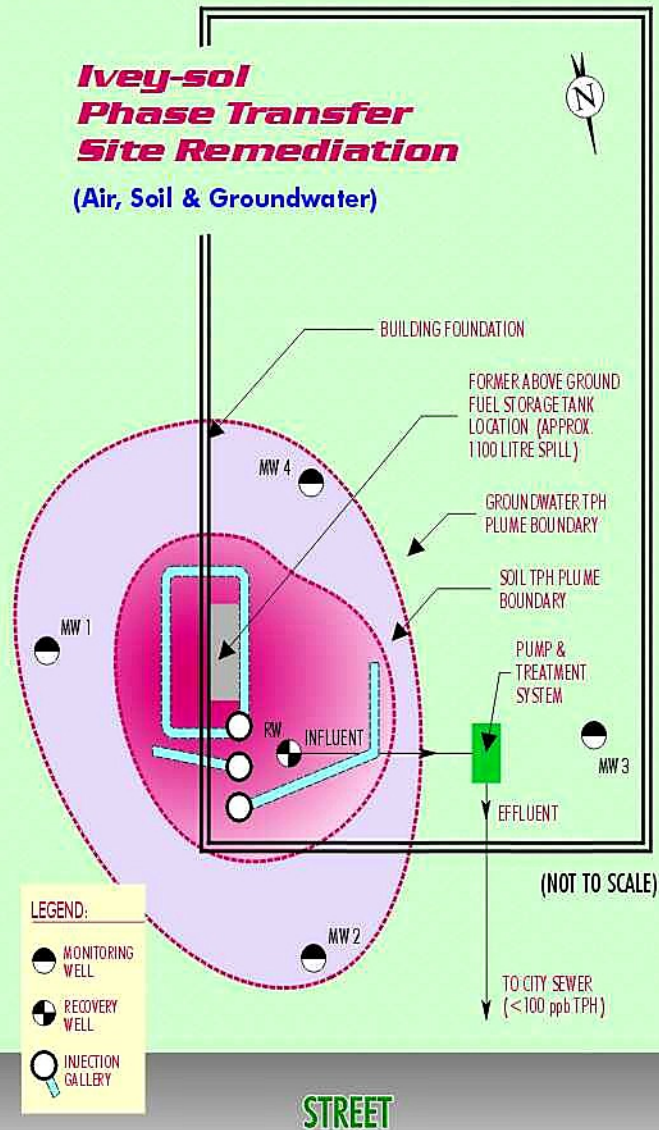


***“We saved over >\$100,00 using Ivey-sol compared to  
the other options we considered”***

**Reference: Peter L. Clark, President Clark Oil Co.  
(Ultramar) Eastern, Canada**



## PROJECT NO. 98-271



## Case Study II

- Approximately 1100 L (240 gal) fuel oil spill from an above ground storage tank
- The water table was contaminated at 9500 ppb TPH; the soil under the building was saturated with free product
- Classified as a Non-sensitive Site by the Department of Environment, with clean-up objectives of 1000 ppb TPH for groundwater and 100 ppm TPH for soil

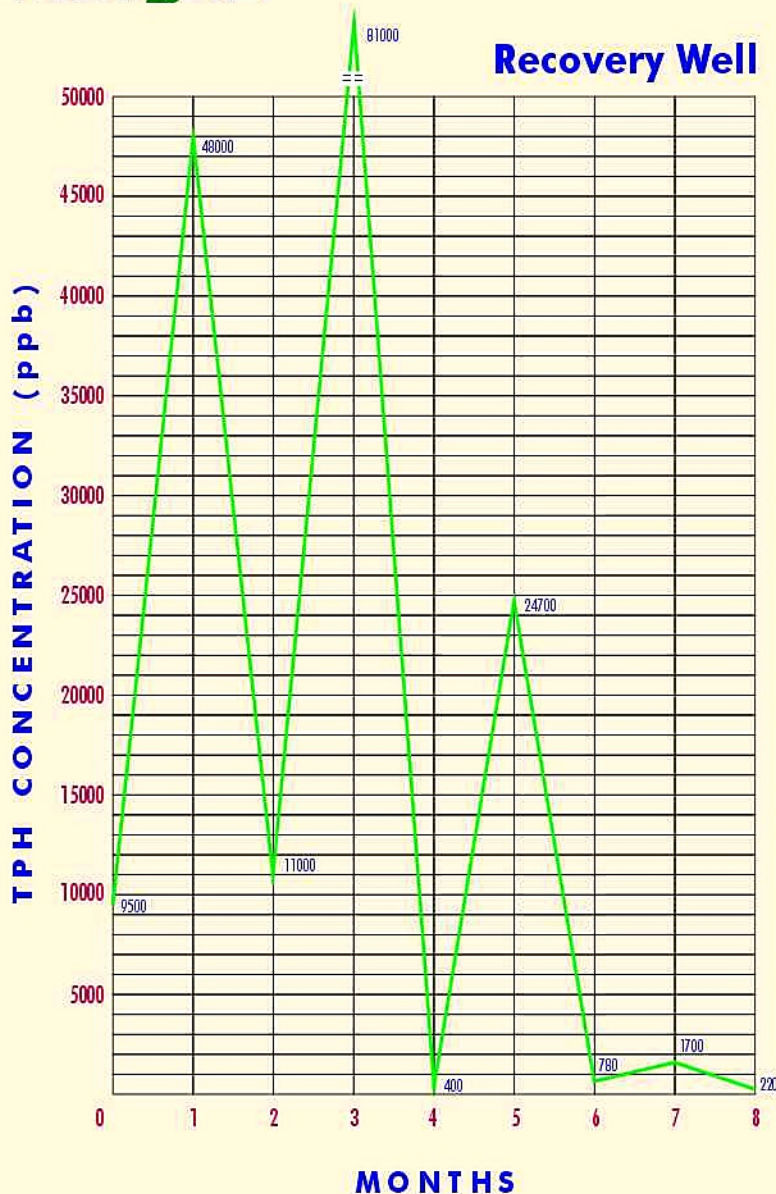


# Groundwater Hydrocarbon Analysis

Ivey-sol

## Case Study II

Recovery Well



Ivey Environmental Services designed and installed a recovery well and a pump & treat system within the building basement



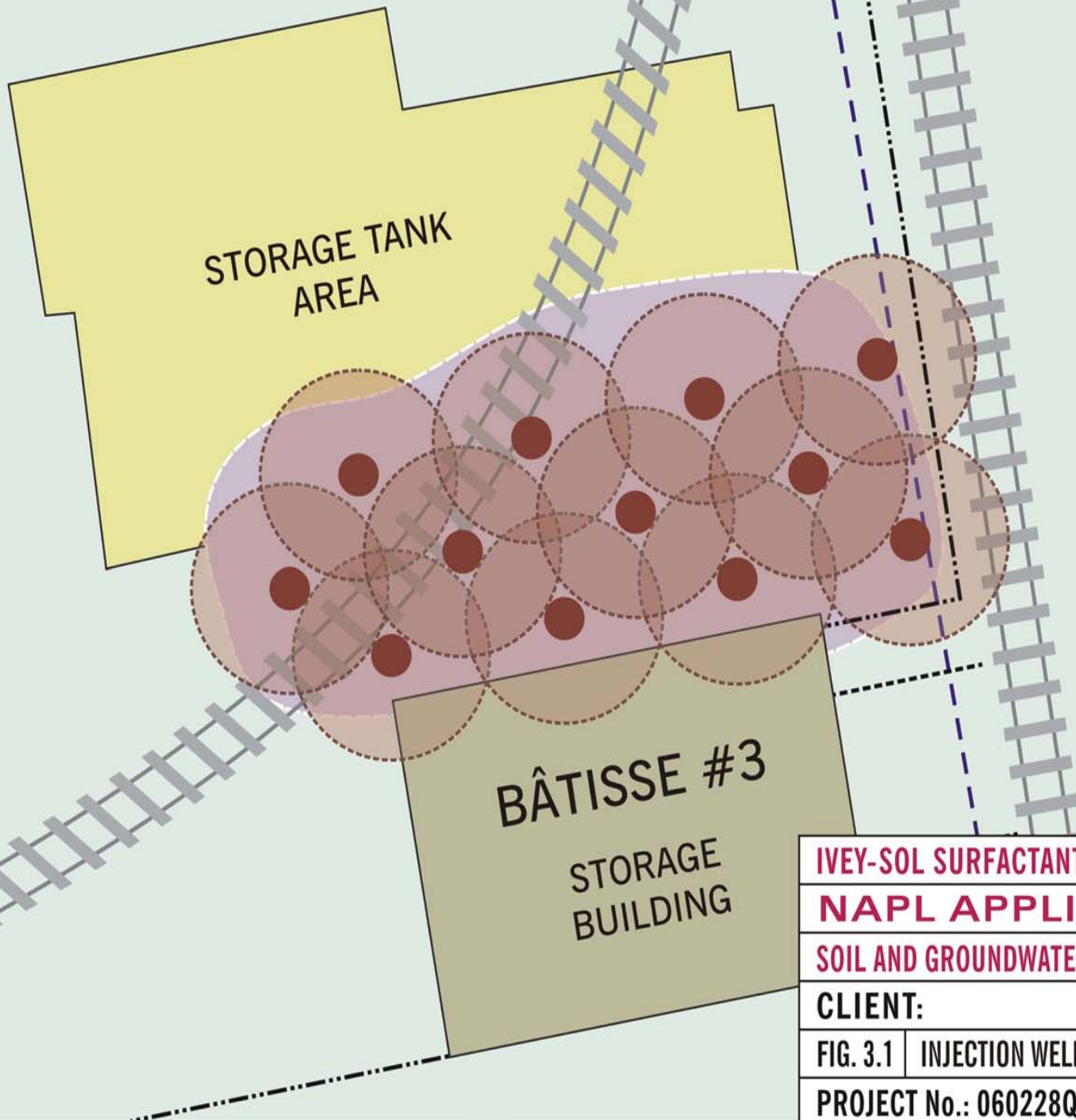
Several Ivey-sol injection galleries were designed and installed in the vicinity of structurally sensitive foundation footings











The site was successfully cleaned up to 220 ppb in eight months



The Department of the Environment decommissioned the site



**LEGEND:**

-  Storage Tank Area
-  Ivey-sol In-situ Test Area
-  Storage Building
-  Railway Line
-  Fence
-  Property Boundary
-  Ivey-sol Injection Well
-  Radius of Contaminant Influence (80%)

**IVEY-SOL SURFACTANT TECHNOLOGY  
NAPL APPLICATION  
SOIL AND GROUNDWATER REMEDIATION**

**CLIENT:**

**FIG. 3.1 | INJECTION WELL LOCATION PLAN**

**PROJECT No.: 060228QE | SCALE: NTS**

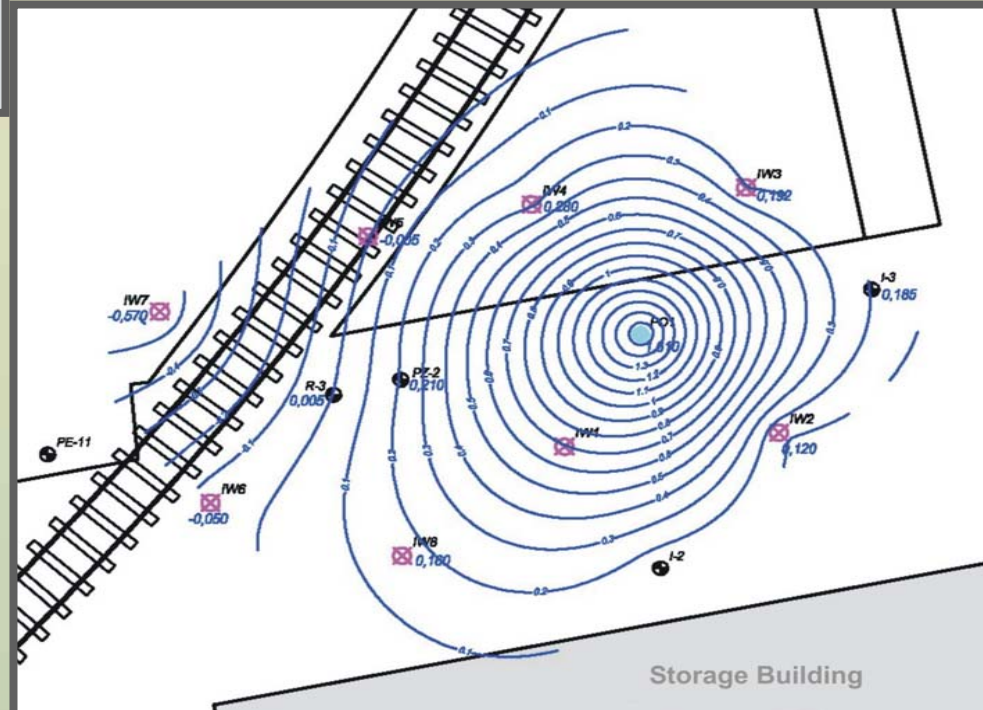
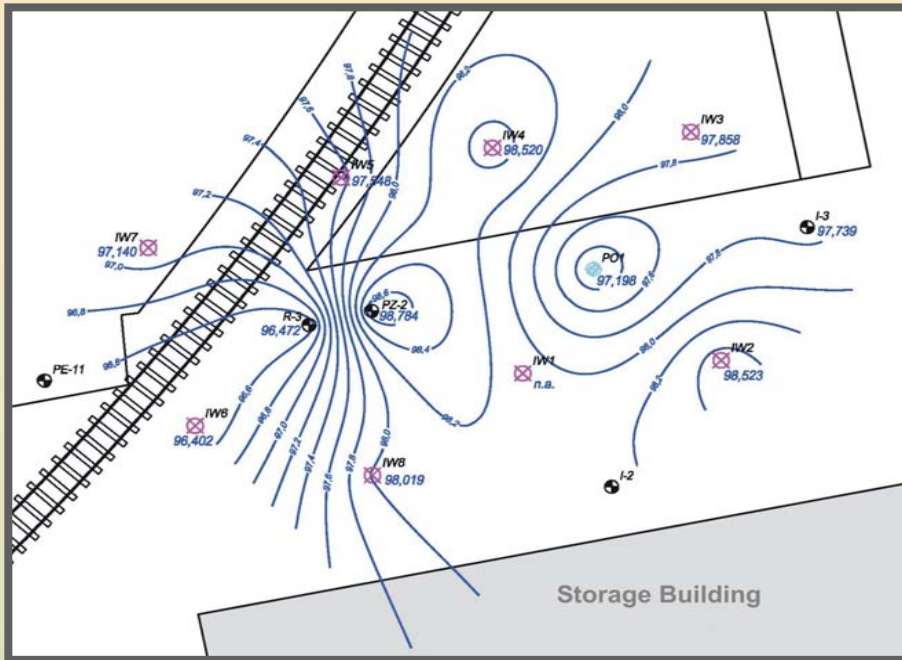


# Ivey-sol • SPTT





## Pre-Injection Hydraulic Containment Conditions Static Ground Water Gradient

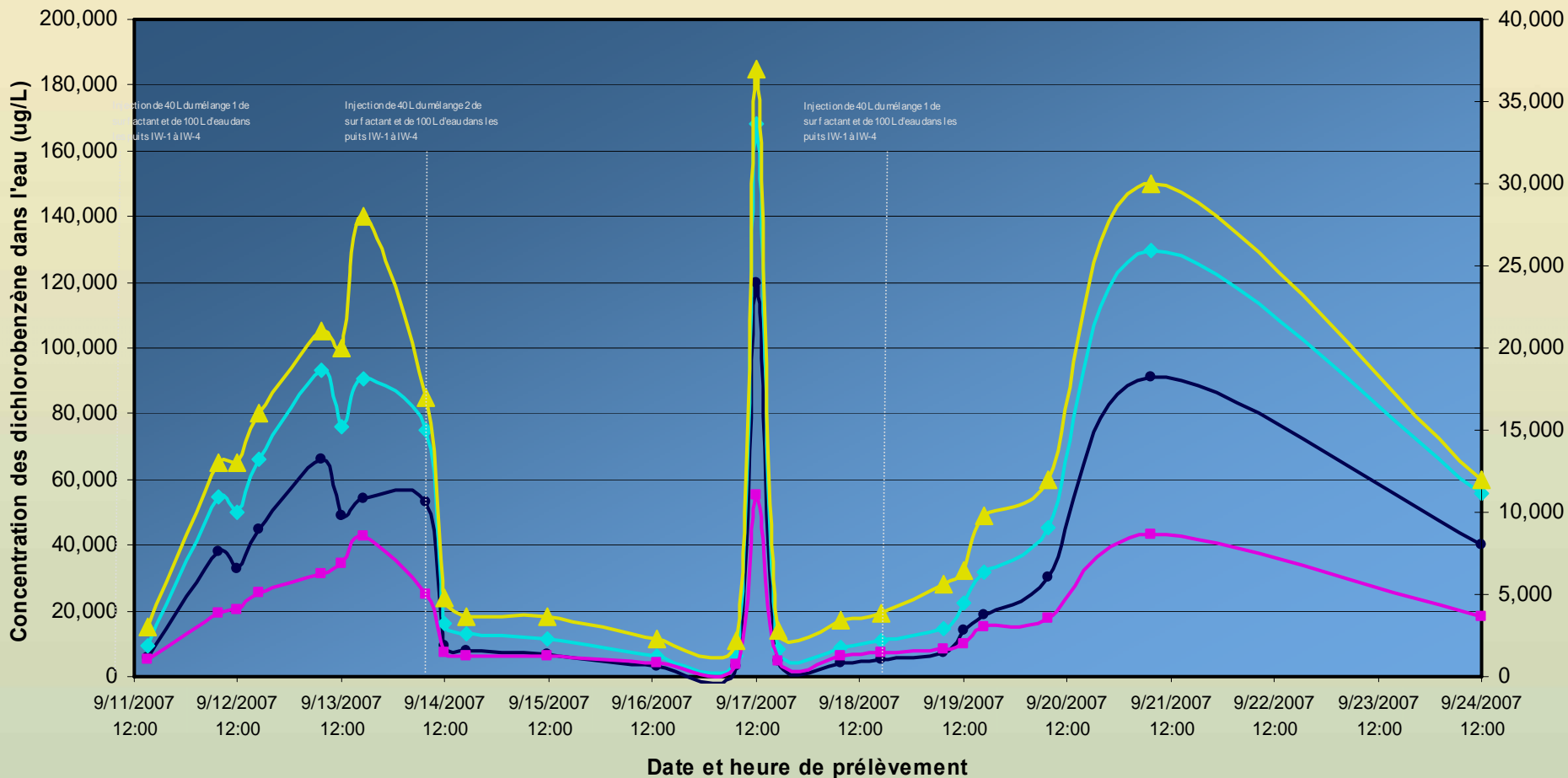


## Pre-Injection Hydraulic Conditions Post Vacuum Extraction System Hydraulic Stabilization





Variation de la concentration des dichlorobenzènes en fonction du temps au puits PO-1



● Dichloro-1,2 benzène (m) (échelle de gauche)

◆ Somme des Dichlorobenzène (échelle de gauche)

■ Dichloro-1,3 benzène (o) (échelle de droite)

▲ Dichloro-1,4 benzène (p) (échelle de droite)

## **Pilot Scale Project Test Results**

- ▶ **The In-situ Ivey-sol Surfactant Application Significantly increased the rate of DCB recovery;**
- ▶ **Increased DNAPL (DCB = Dichlorobenzene) recovery by 800-1200%;**
- ▶ **Recovered kg(s) of DCB over a three (3) injection pilot Scale Application in one-week;**
- ▶ **Client was pleased as all three previous remediation techniques applied failed at a significant cost to the client; and**
- ▶ **Client has awarded the environmental consultant the contract to proceed with full scale application.**

## **Project Concluded In 8 Months**



*“We had to evacuate the building after the spill, it was a mess. Ivey-sol cleaned up the site up rapidly. It improved the air, soil and groundwater quality”*

**Reference: John Vidditto, Developer/Owner**

**Dispersants tend to reduce the long term impacts of an Oil Spills.**



***By dispersing and lessening the concentration of oil in the water column can make the oil more available for natural biodegradation***



***Surfactant Enhanced Biodegradation***



Department of Transportation & Communications  
HEADQUARTERS PHILIPPINE COAST GUARD  
(PUNONG HIMPILAN TANOD BAYBAYIN NG PILIPINAS)  
139 25<sup>th</sup> Street, Port Area 1018 Manila



## Accreditation Certificate

PCG-07-06-038

NUMBER

This Certificate is issued to

**Silahis Marketing Corporation**

manufacturer/distributor of

**IVEY-SOL OIL DISPERSANT**

with business address at

**3<sup>RD</sup> Flr. LPL Bldg., 215 Sen Gil Puyat Ave., Makati City**

Upon completion of all requirements for

**Accreditation for Oil Spill Dispersant**


Issued this 20<sup>th</sup> day of June 2007

Pursuant to Republic Act 5173, PD 600 as amended by PD 979 and MARPOL related regulations

**HPCG Memo Circular No 04-2005 dated 14 October 2005**

This certificate unless cancelled, suspended, or revoked shall continue to be in effect until

**19 June 2010**

  
**DAMIAN L. CARLOS**  
ADM                      PCG  
Commandant,            PCG

NOT VALID WITHOUT OFFICIAL SEAL



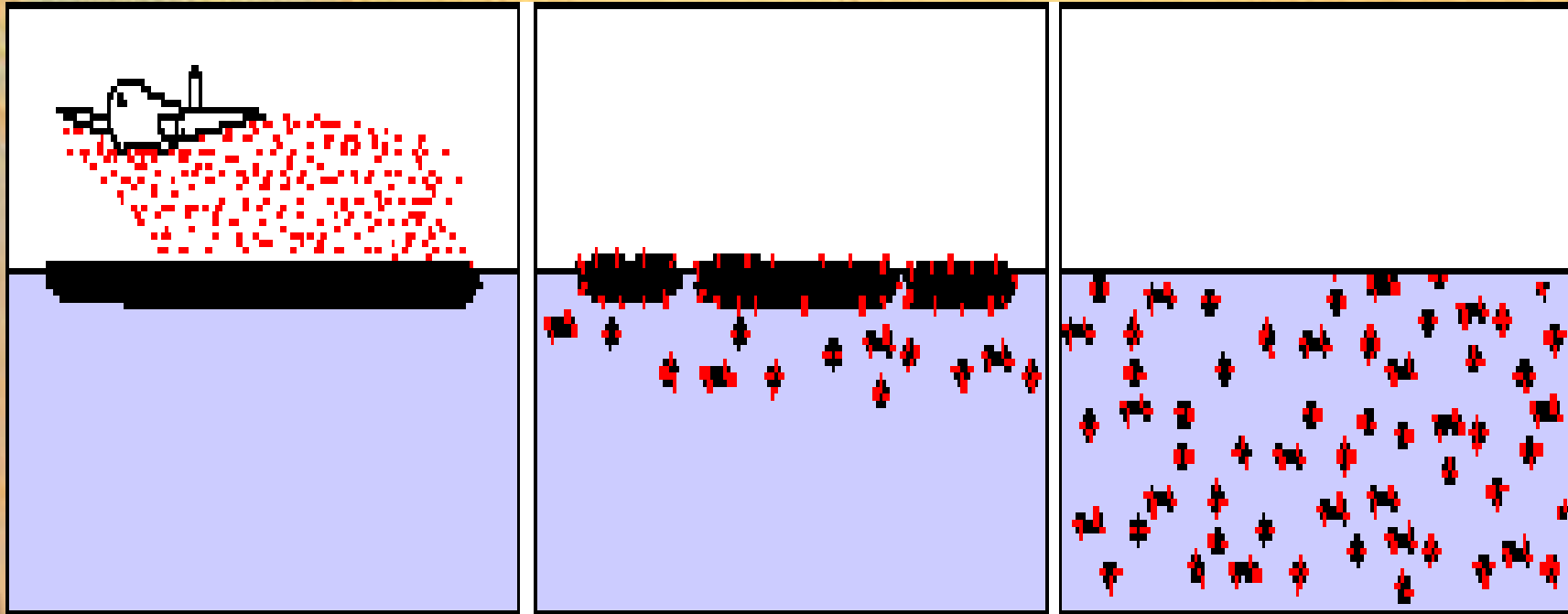
# Oil Spill As Viewed From The Air



# Dispersant Applications



# Mechanism Aerial Dispersion





**To Be Effective, dispersants must be applied within a short 'Window of Opportunity' following a spill.**



**Taken From Plane  
1- Day After Dispersant  
Application (*Very Effective*)**

**Taken From Plane Just  
After Dispersant  
Application (*Time Zero*)**



## Before and After Dispersant Shore Line Clean-up



**1989 - Exxon Valdez**  
**40,000 tons of oil spilled**





***Ivey-sol • SPTT***

**Learn More About Ivey International Inc.  
Ivey-sol<sup>®</sup> Surfactant Technology  
or  
Arrange Corporate Presentations**

**Contact:**

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Ivey International Inc.**

**250 923 6326 (Direct)**

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**[www.iveyinternational.com](http://www.iveyinternational.com)**