Example Petroleum Release Training Materials

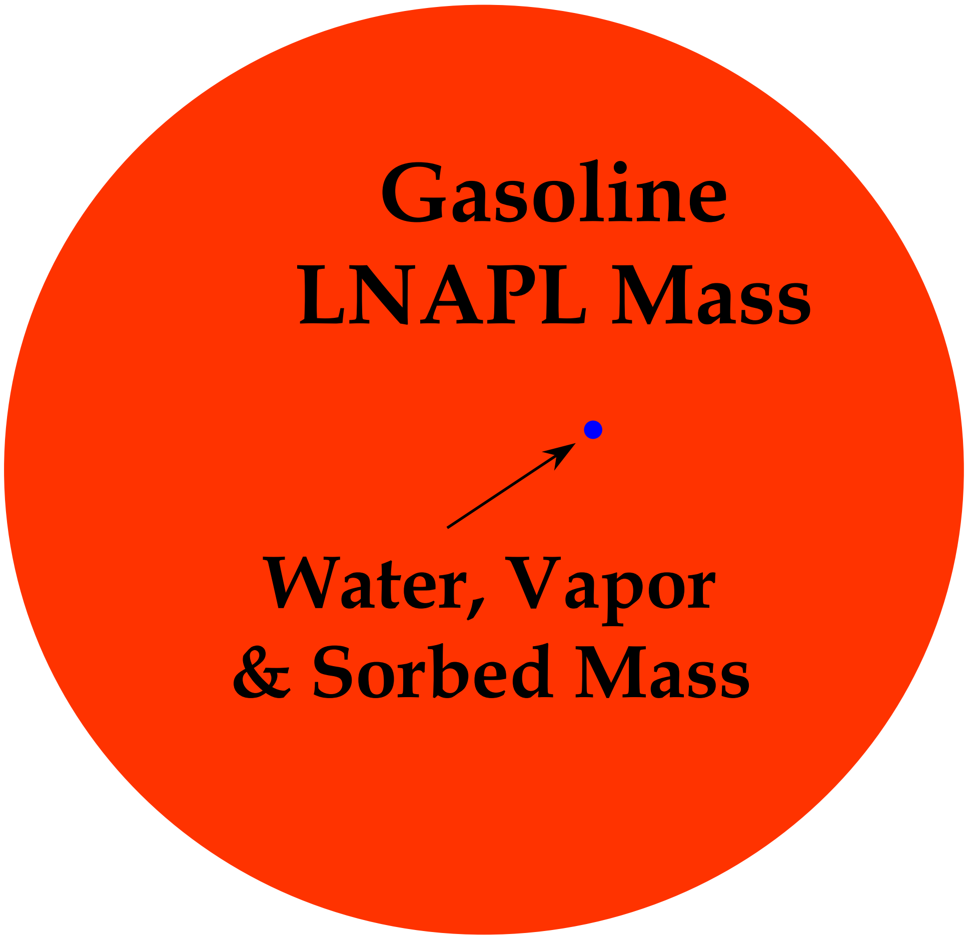
Presented to:
Hawaii Department of Health & Interested Parties

October 10-11, 2017
G.D. Beckett, PG, CHG
AQUI-VER, INC.

© AQUI-VER, INC.

LNAPL is the Mass & Source of Impacts

(and will generally linger awhile)

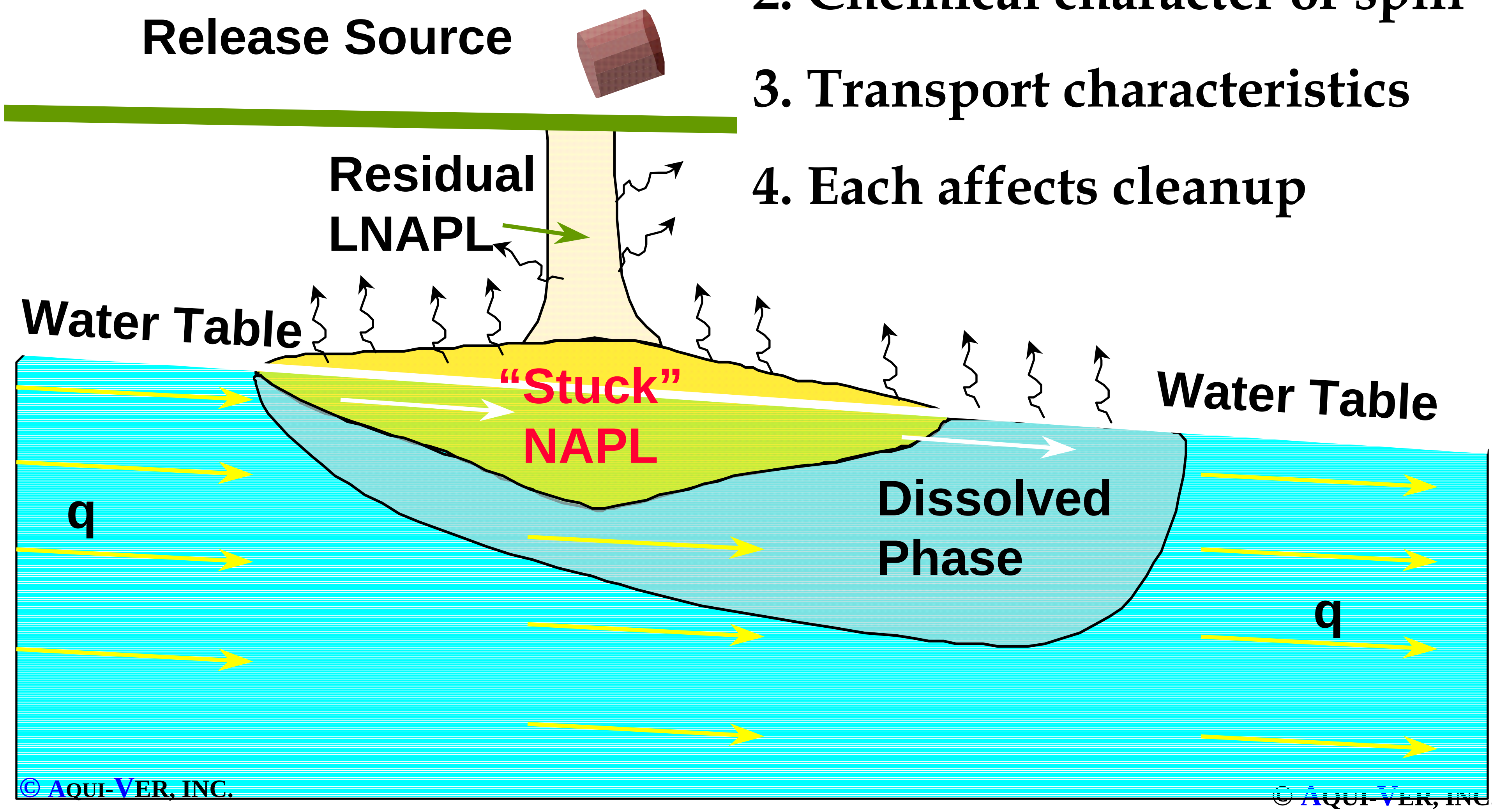


- Risk depends on:
  - Concentration (dose)
  - Receptors
  - Toxicology
  - Exposure duration
- Longevity depends on:
  - Source strength
  - Fluxes from source

© AQUI-VER, INC.

Chemical impacts depend on the LNAPL

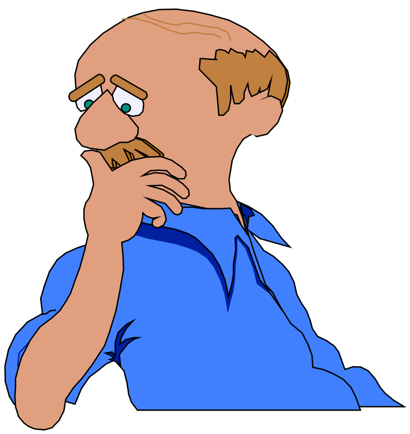
1. Distribution of spill
2. Chemical character of spill
3. Transport characteristics
4. Each affects cleanup



© AQUI-VER, INC.

© AQUI-VER, INC.

Quite Obvious Why We Try to Cleanup NAPL..

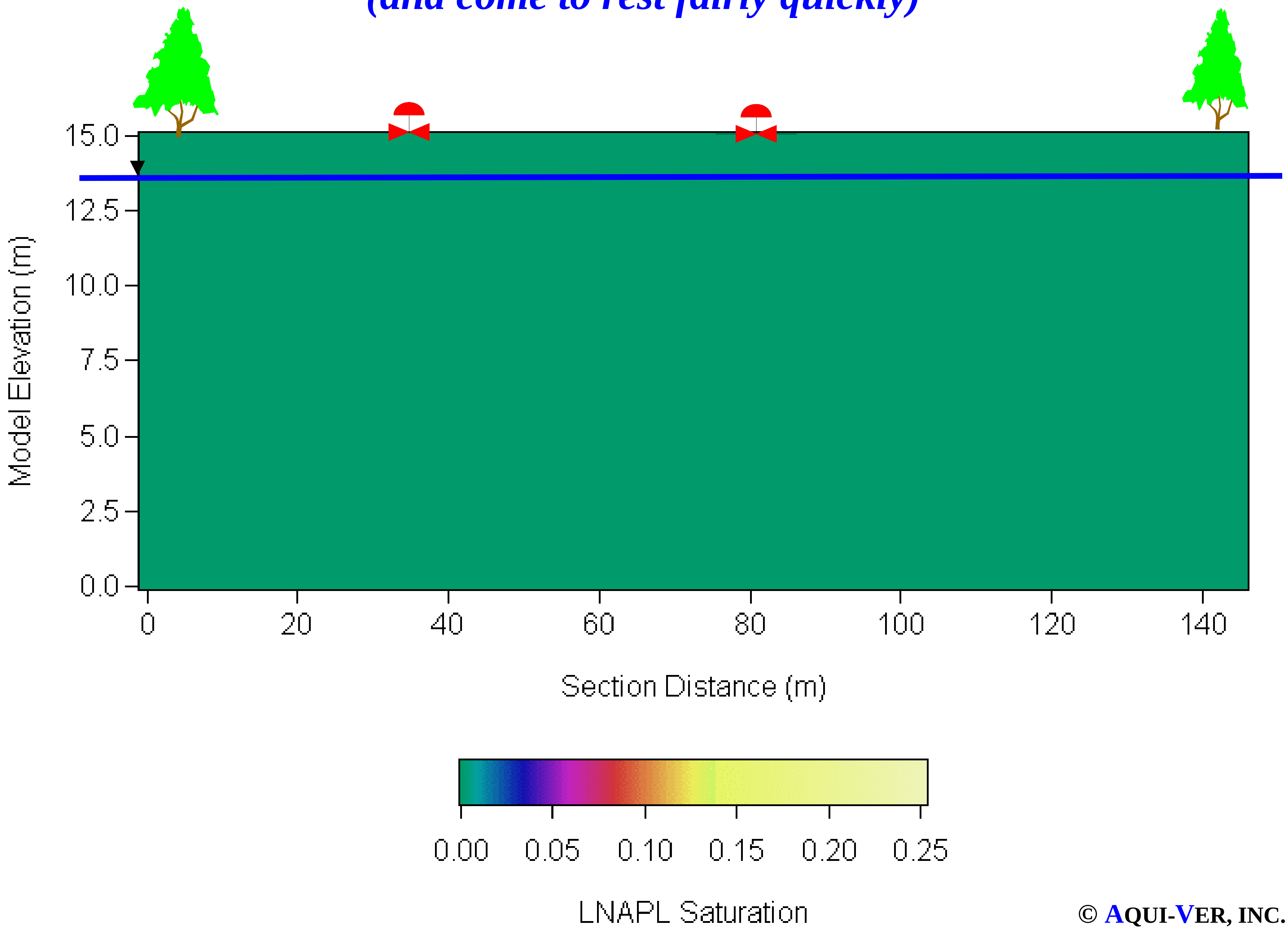


- NAPL is a concentrated source of potential risk
  – Get rid of the source, get rid of the risk
- But what if..
  – 100% NAPL recovery is infeasible?
  – No risk exists under ambient conditions?
  – No risk exists, but long-lived plumes?
  – Significant risk exists and NAPL recovery does not mitigate key pathways to receptors?
- Many folks are wrestling with these issues

© AQUI-VER, INC.

LNAL Release Are Highly Transient

(and come to rest fairly quickly)



© AQUI-VER, INC.

Factors Controlling LNAPL Releases

Migration & eventual stabilization

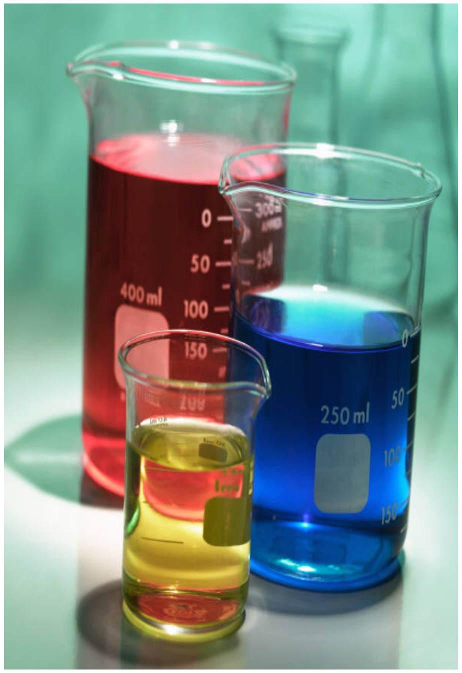
© AQUI-VER, INC.

Key Release Concepts

- Fluids share the pore space in varying percentages
  - Controlled by gradients, capillary & soil/fluid properties
- Relative phase mobility depends on several factors
  - Phase saturation - key control
  - Intrinsic permeability
  - Fluid viscosity & density – varies widely with product type
- Saturation and relative permeability are transient
  - Exponential relationships
  - High parameter sensitivity
  - Yep, that means thoughtful interpretation needed

© AQUI-VER, INC.

Oil Products Vary Widely in Physical Character

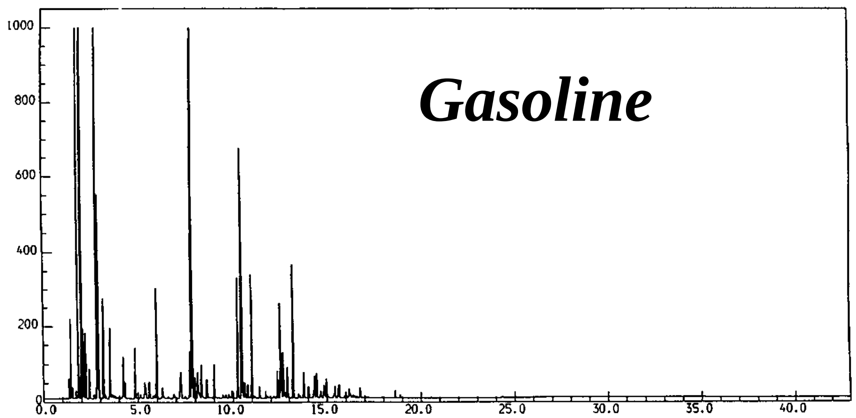


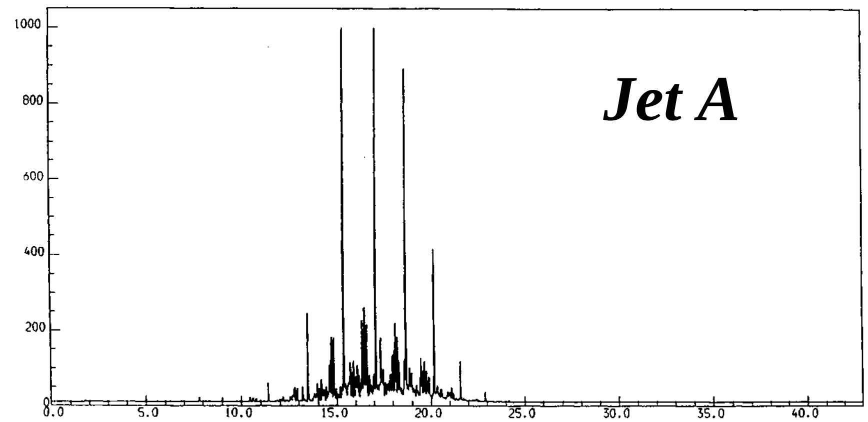
Light Oils

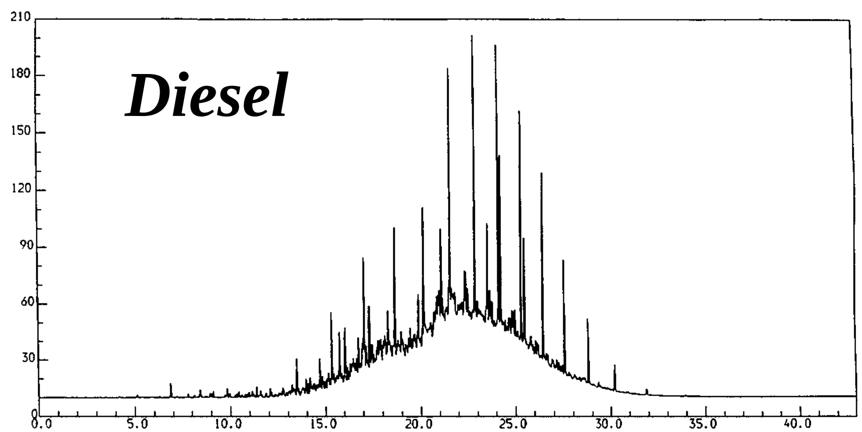
Heavy Fuel & Crude Oils

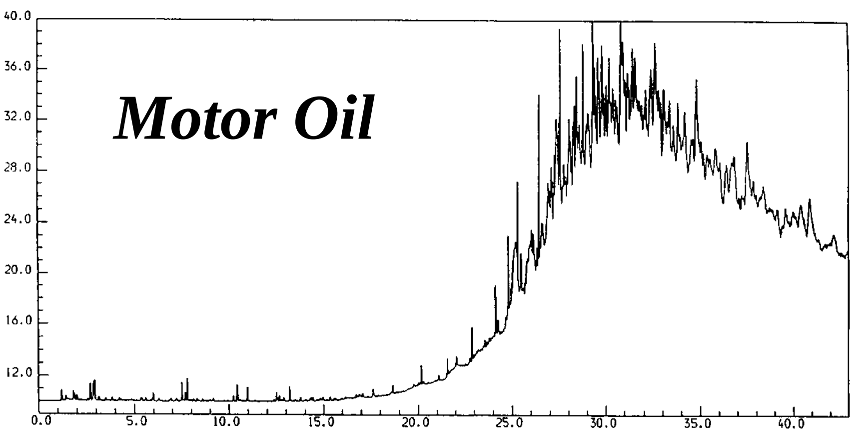
© AQUI-VER, INC.

Each Has Significantly Differing Chemistry





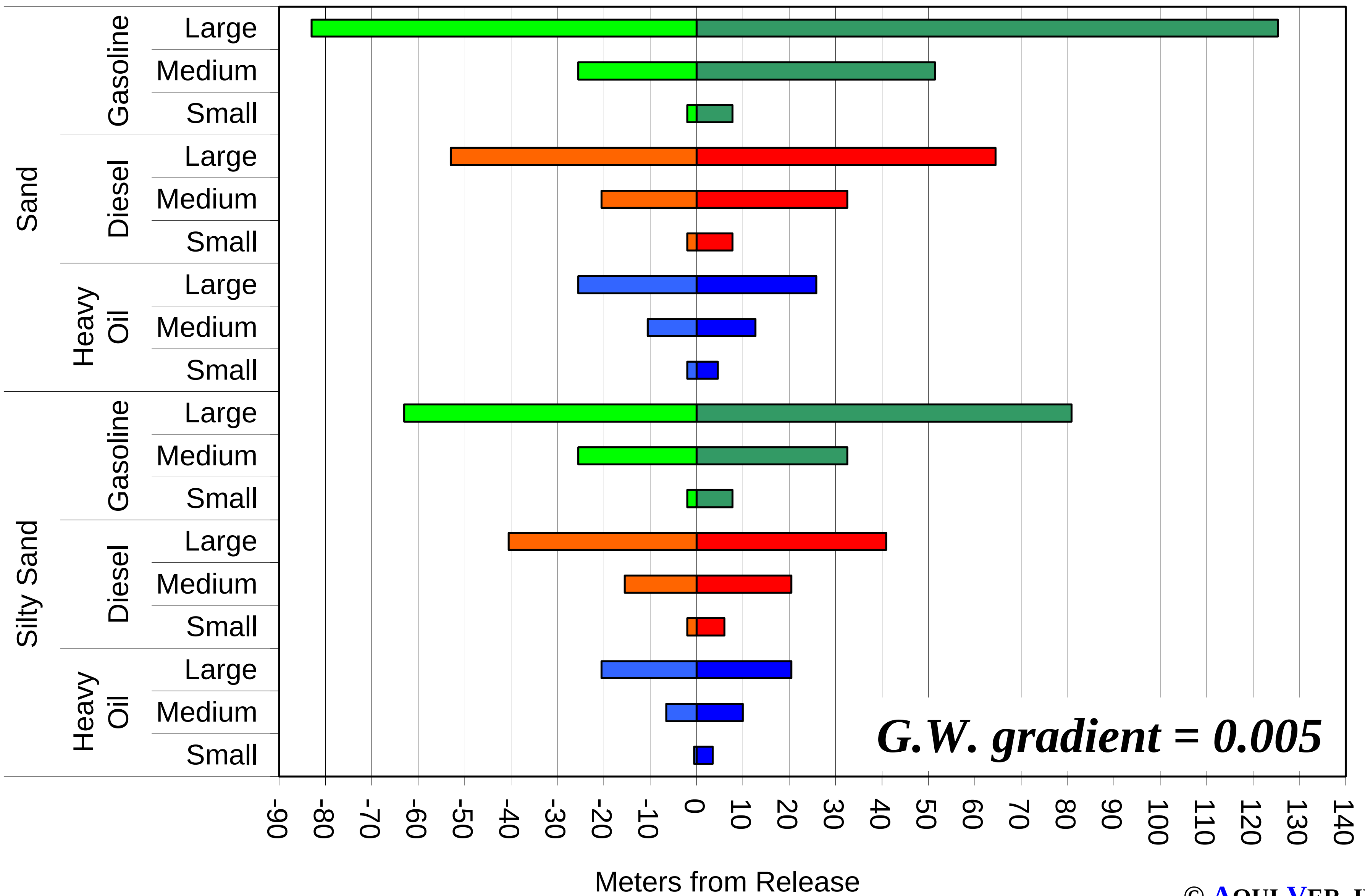




© AQUI-VER, INC.

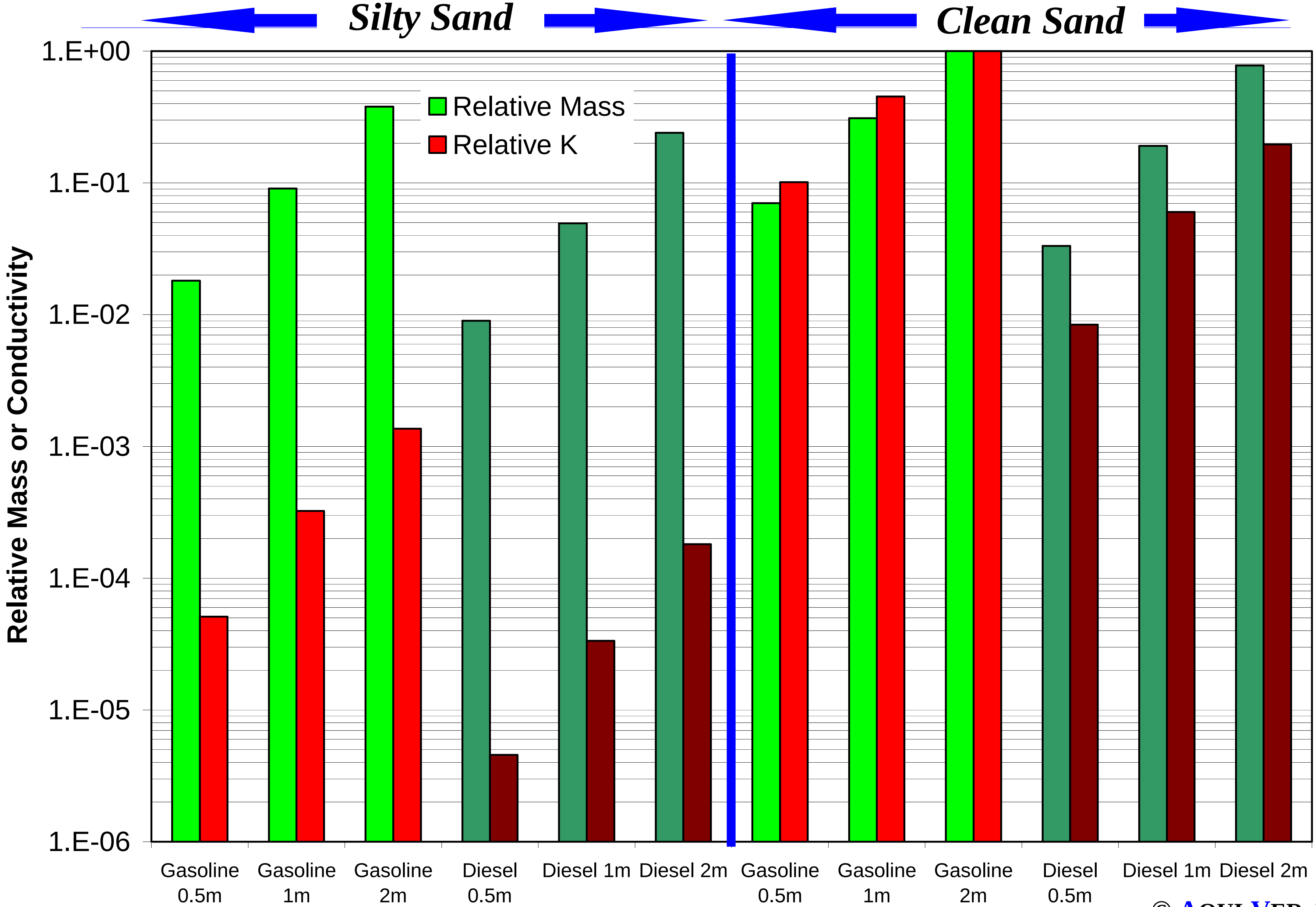
Comparative Lateral LNAPL Migration

(converse is true for vertical migration)



© AQUI-VER, INC.

Relative Mobility & Mass Comparison



© AQUI-VER, INC.

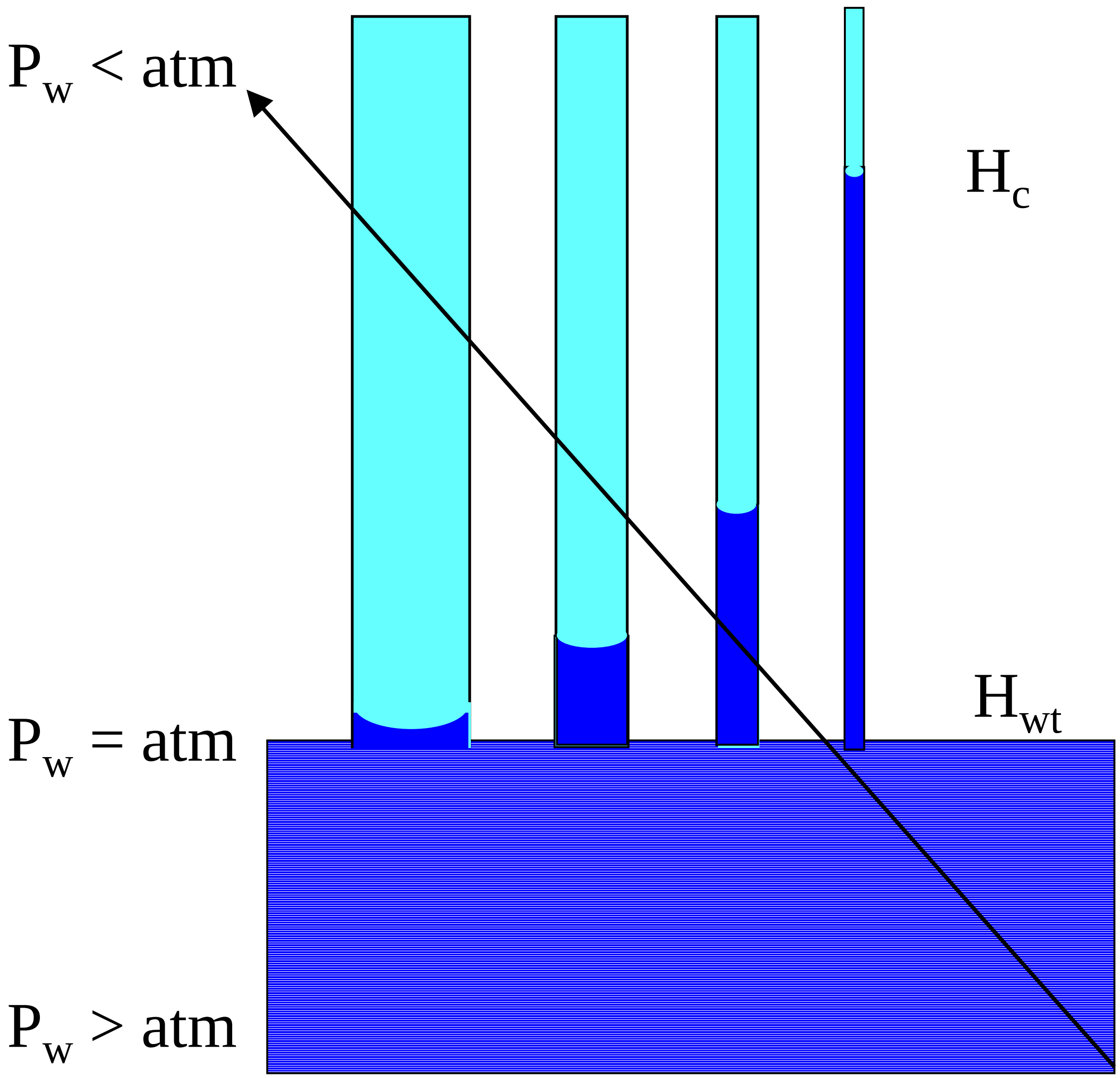
The Bottom Line:

When all is said & done, it is the NAPL you leave *behind* & its chemistry that defines the benefit of any remediation strategy. There is almost always mass left behind..

© AQUI-VER, INC.

THE MYSTERY OF CAPILLARITY

© AQUI-VER, INC.



As pore size gets smaller, capillary rise gets bigger. At equilibrium:

$$P_c = P_{nw} - P_w$$

$$H_c = H_{wt}$$

&

$$H = Z + P/\gamma_w$$

$$Z_c = 2\sigma_{aw}/\gamma_w r$$

© AQUI-VER, INC.

Wetting Phase Importance

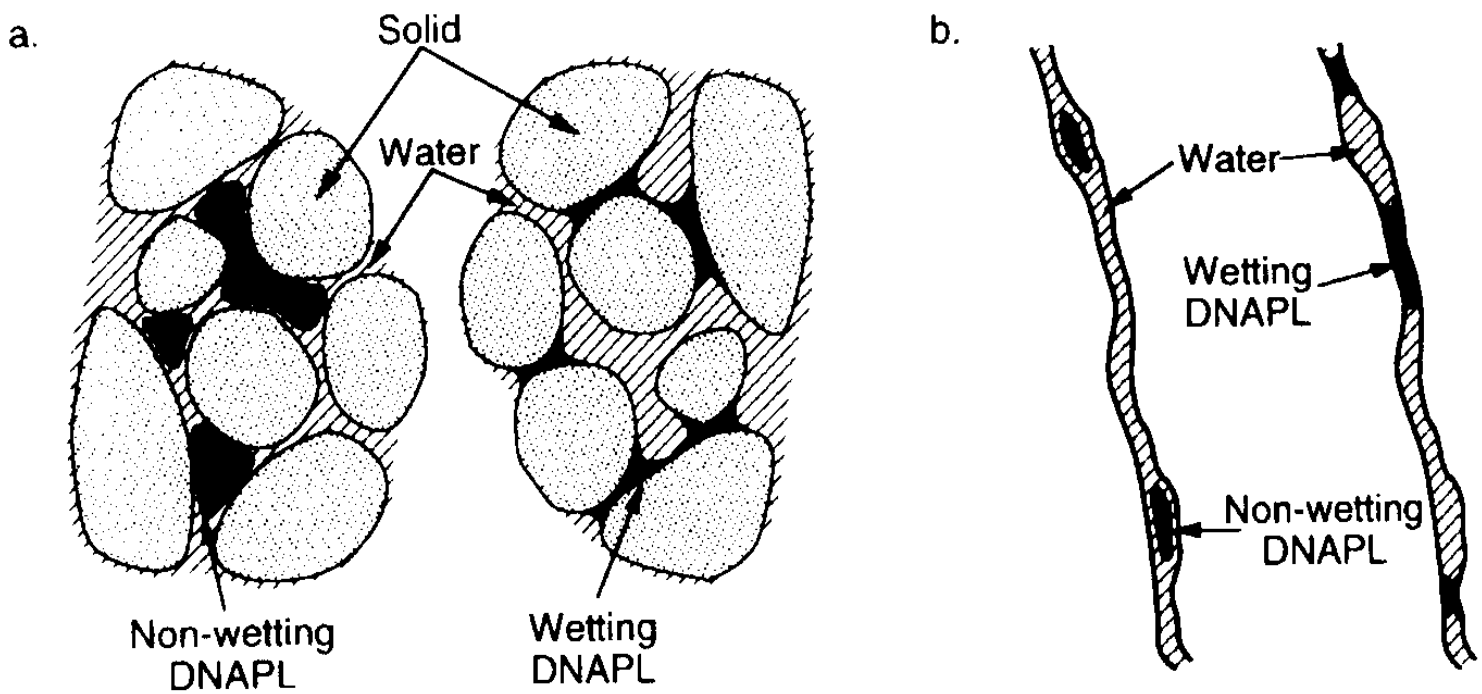
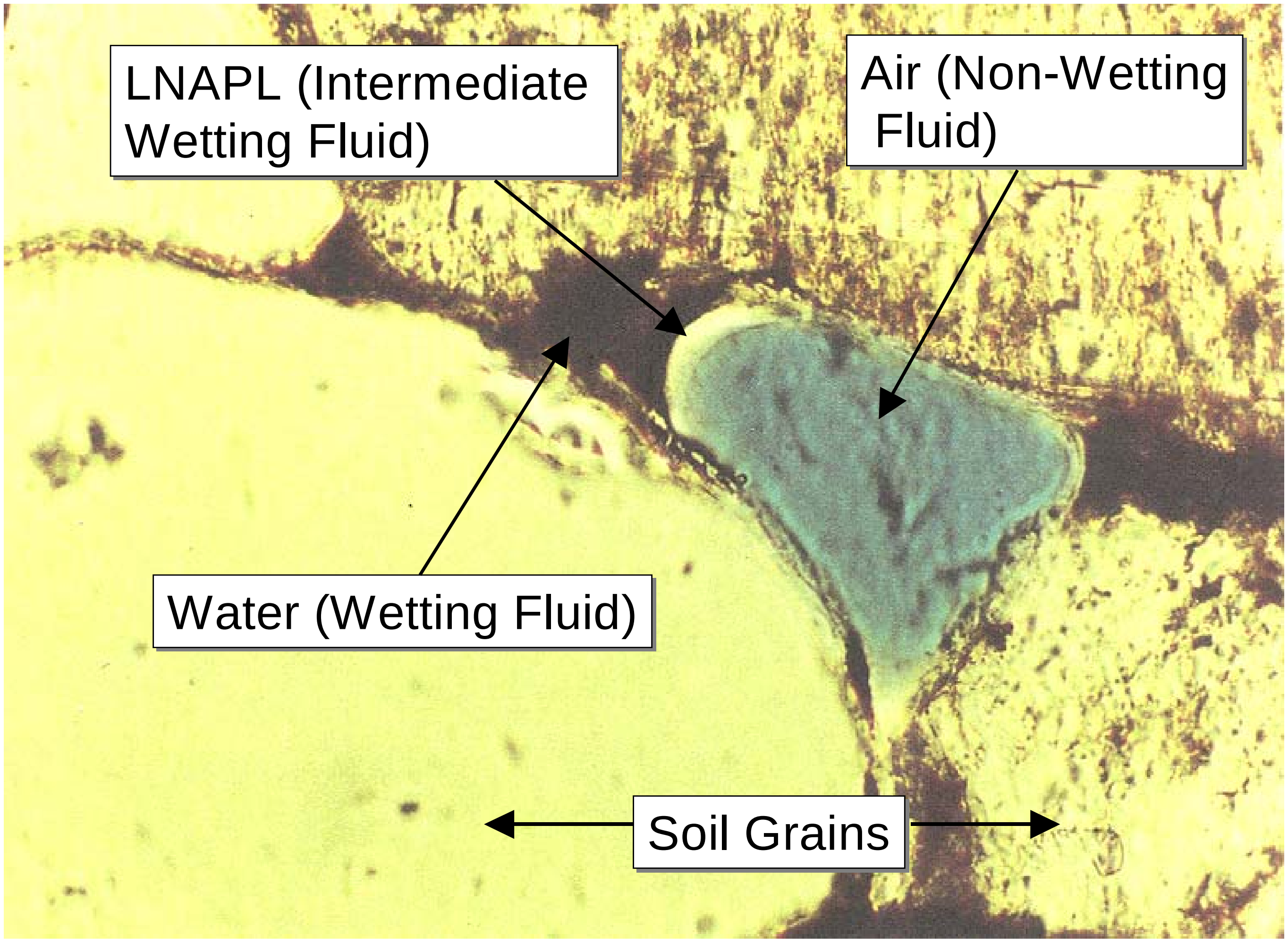


Figure 2.3 Pore-scale representation of non-wetting and wetting DNAPL residual in: a) water-saturated sand; and b) a fracture.

after Pankow & Cherry, 1996

© AQUI-VER, INC.

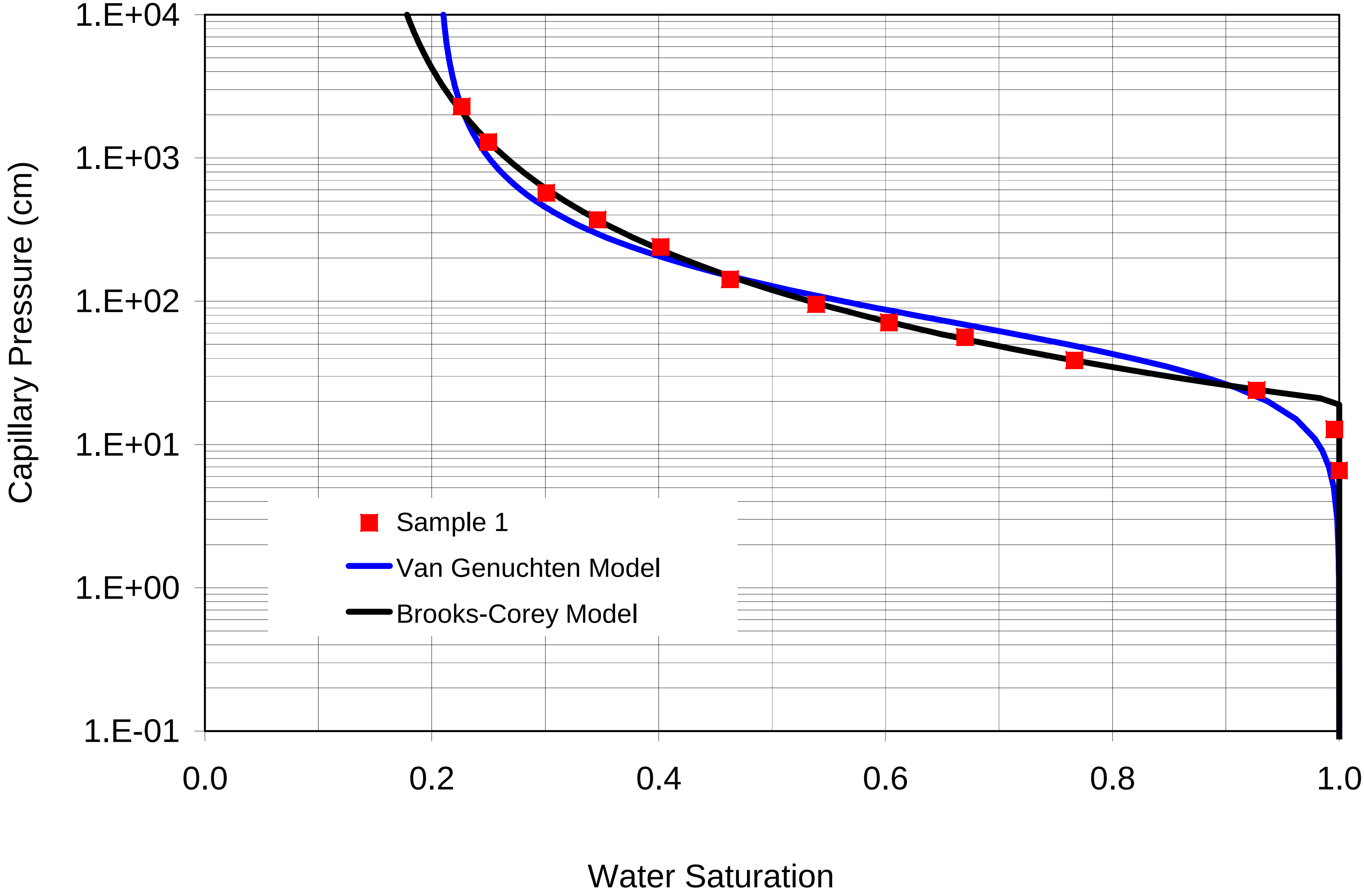
How Does Capillarity Translate in Soil?



After John L. Wilson, 1990; NMT

© AQUI-VER, INC.

Example Capillary Curve: Lab Data & Fits

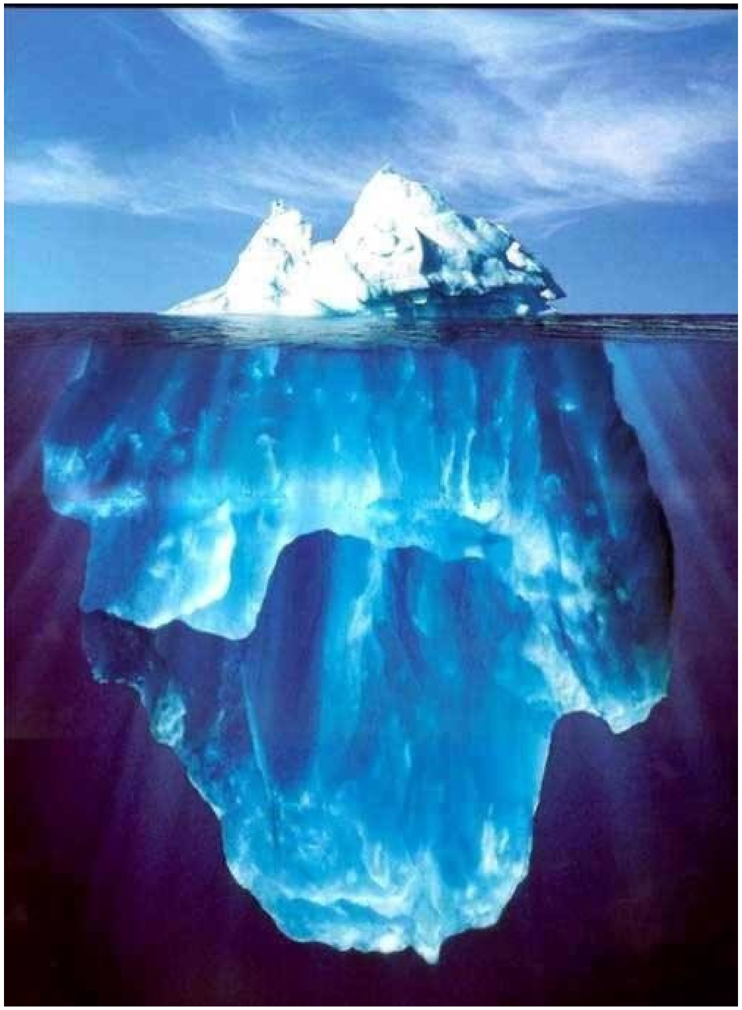


© AQUI-VER, INC.

© AQUI-VER, INC.

Under Hydrostatic Conditions: Free-Phase LNAPL is like an Iceberg

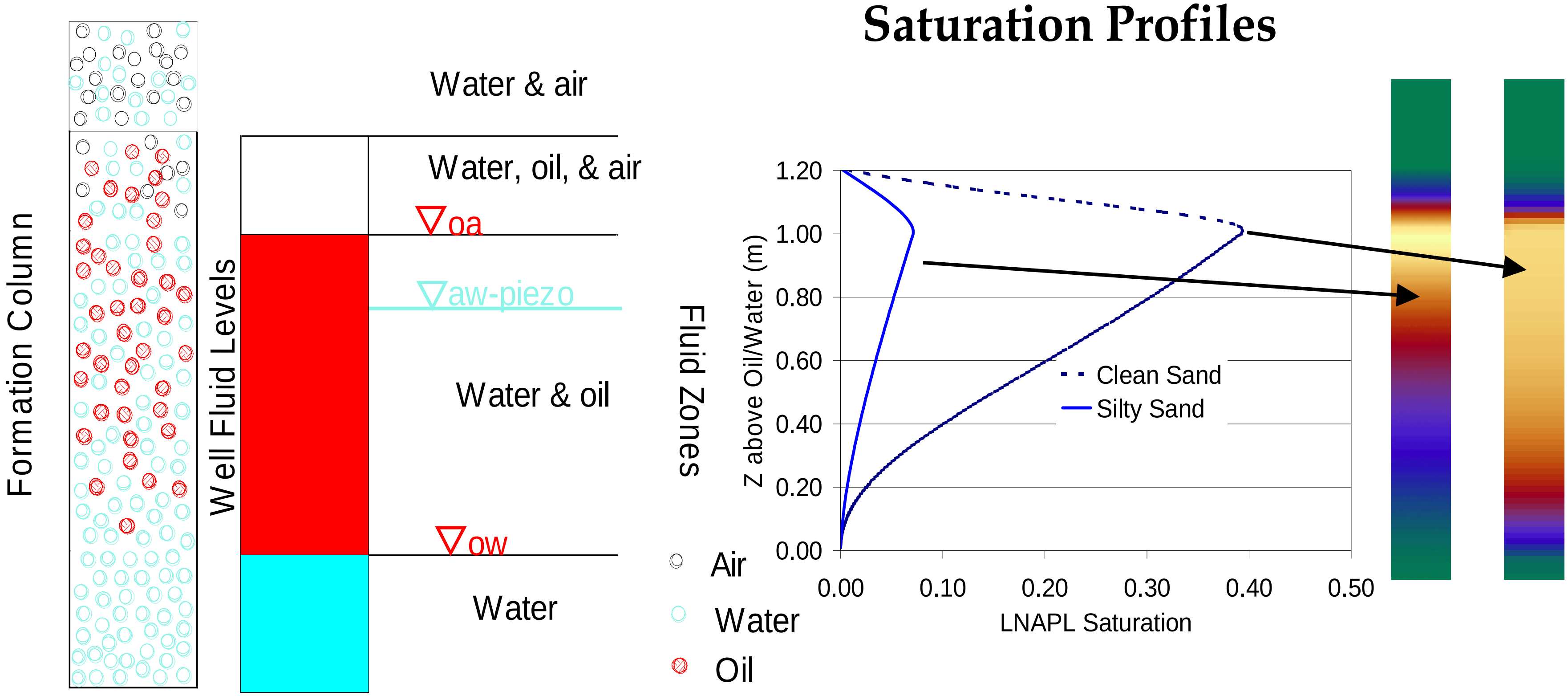
- Water is displaced until forces equalize
- An iceberg does not float on top of "water table"
- LNAPL "sinks" into the aquifer
  - Perching is possible
  - Transient aspects are important
- Oil infiltrates largest pores first
  - Increasing head, more infiltration
  - No thickness exaggeration
  - Volume exaggeration of oil



© AQUI-VER, INC.

LNAPL Distribution at Vertical Equilibrium

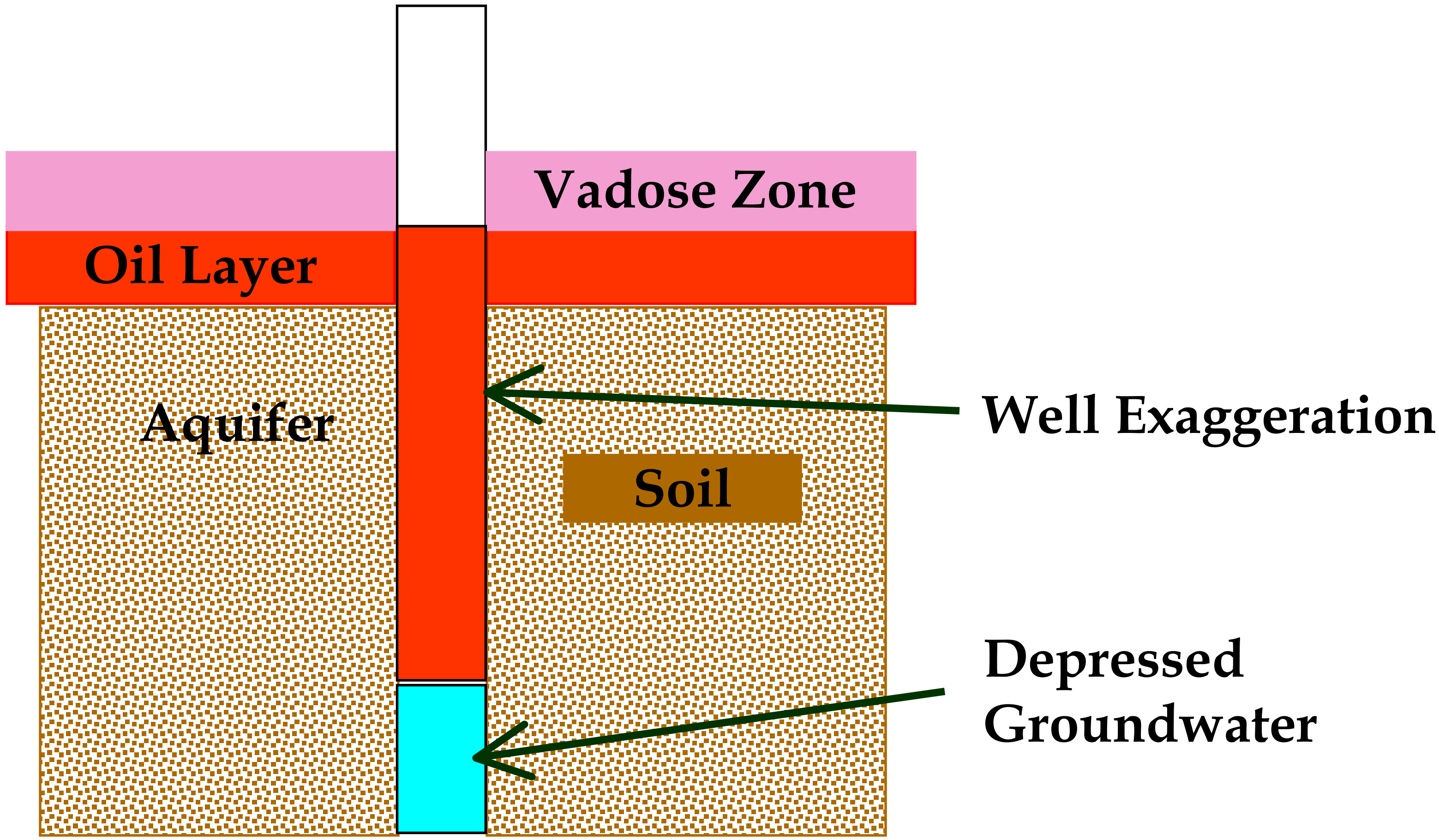
Example Vertical Saturation Profiles



© AQUI-VER, INC.

The "Exaggeration" Thickness Model

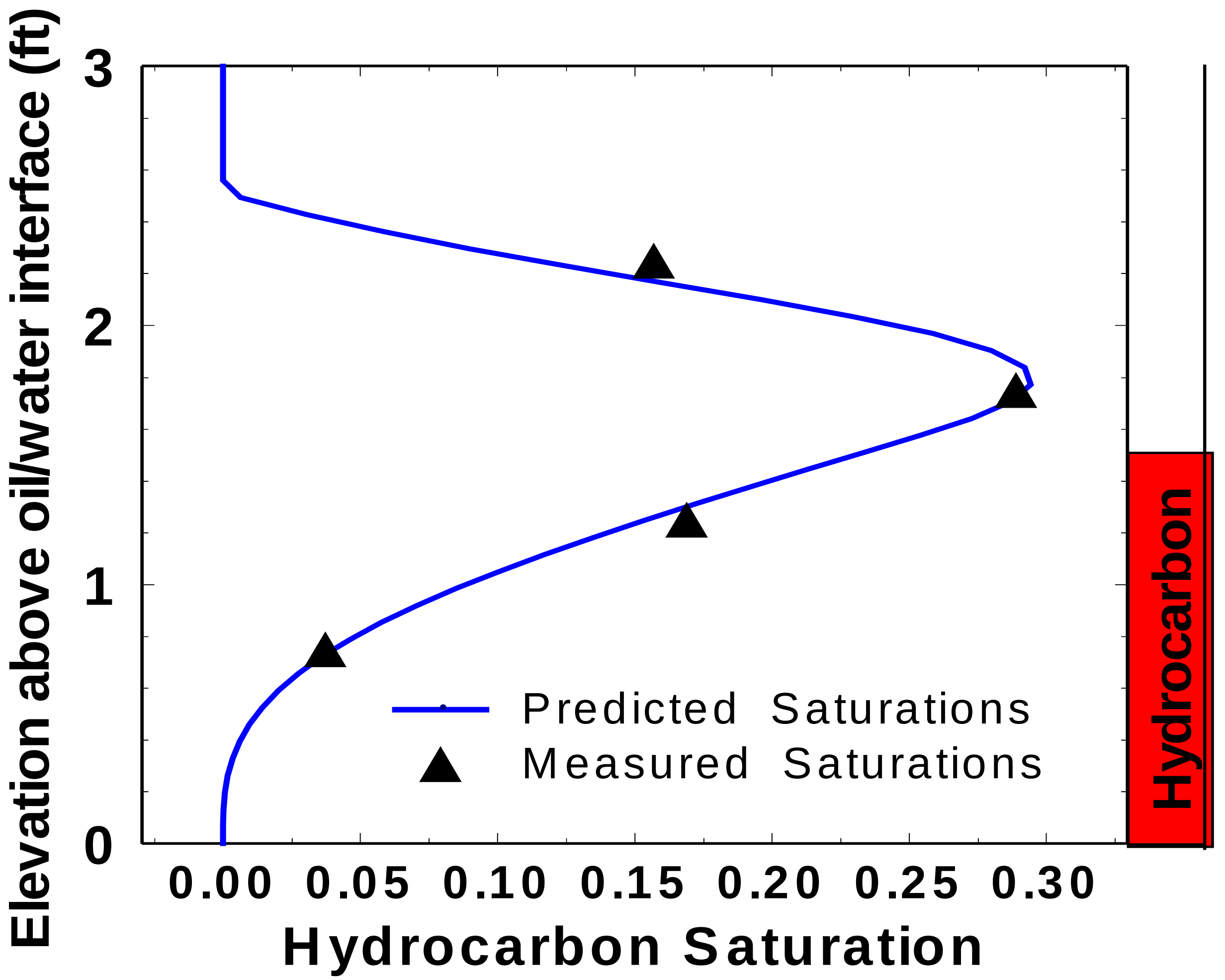
(no physical basis except perching; i.e., not correct)



© AQUI-VER, INC.

VEQ Works Under Ideal Conditions

(Field Measured Equilibrium LNAPL Saturation)



After Huntley, 1995

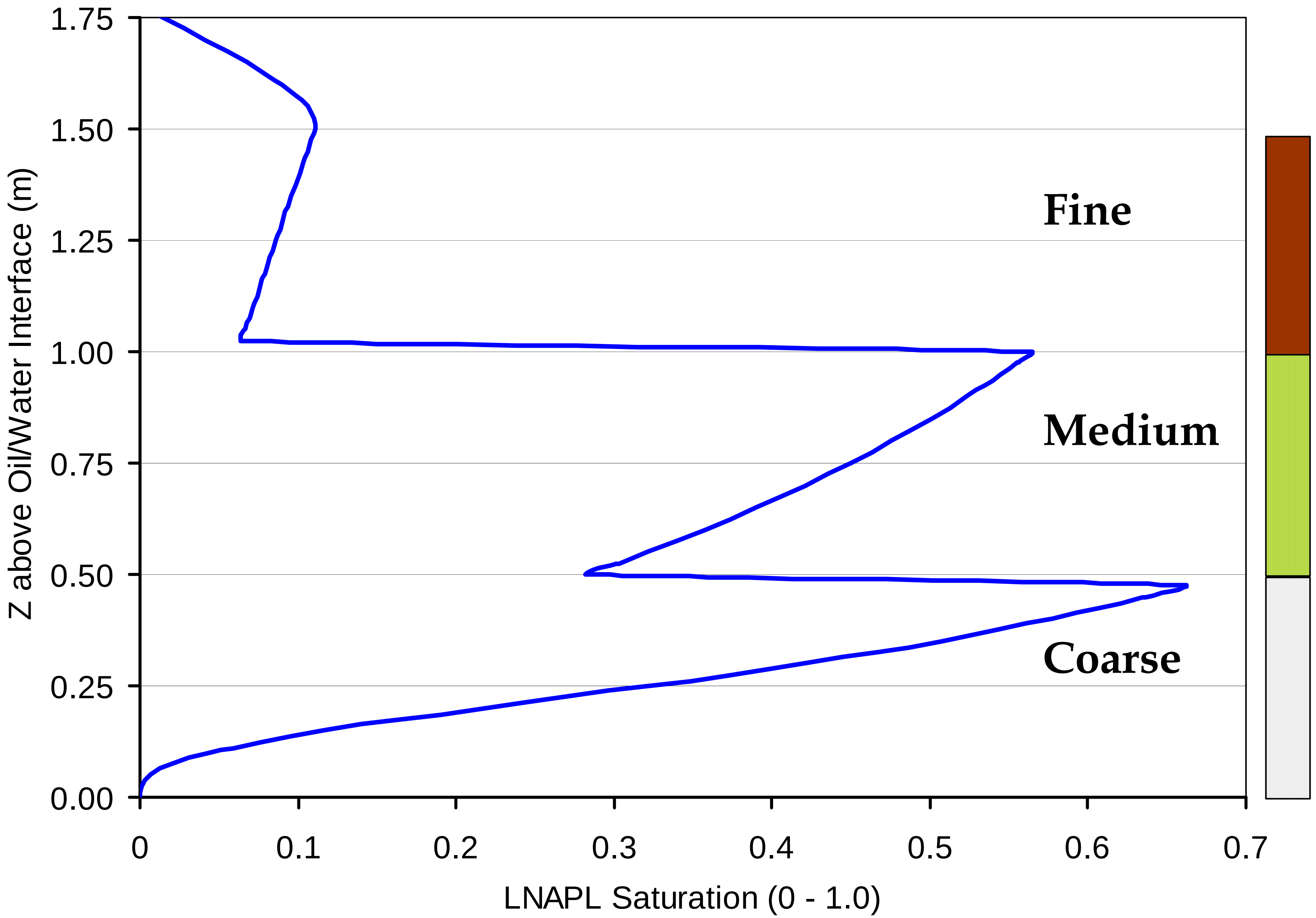
© AQUI-VER, INC.

What about Stratified Conditions?

Well, Equilibrium is Still Equilibrium..

© AQUI-VER, INC.

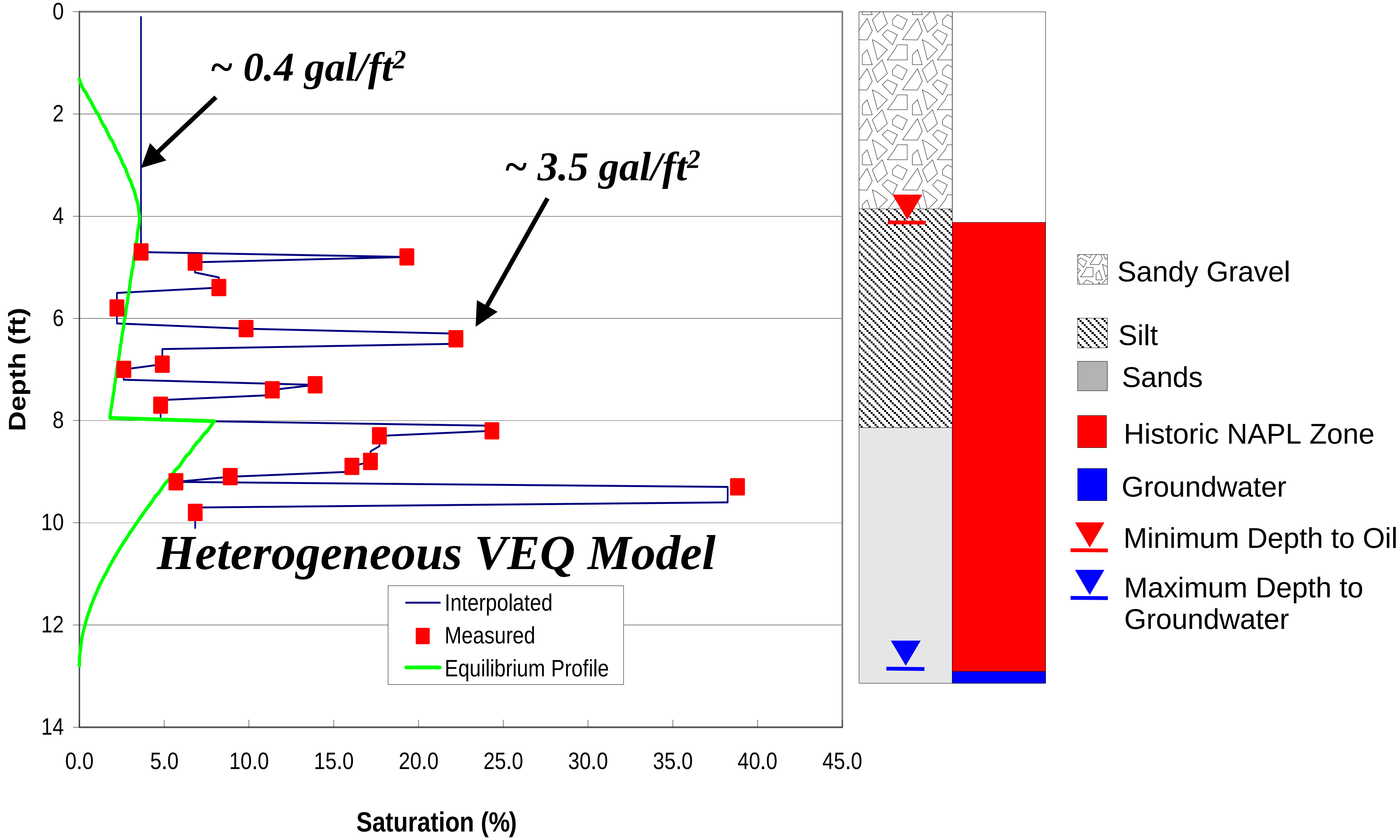
Heterogeneous Lithology: LNAPL at VEQ



© AQUI-VER, INC.
© AQUI-VER, INC.

VEQ Often Doesn’t Match the Real-World

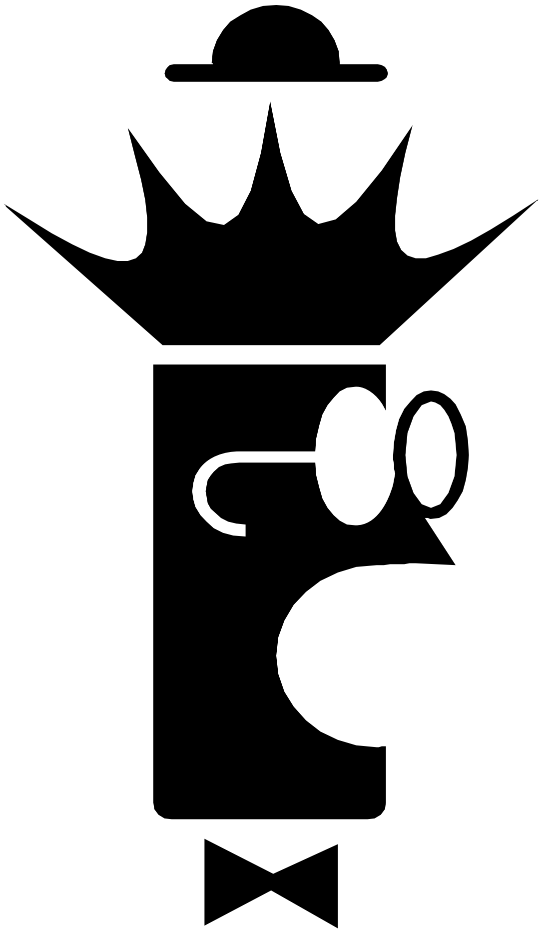
(not at all unusual; can you think of reasons?)



© AQUI-VER, INC.

VEQ Poorly Represents Many Situations

(because sites are often complex; limitations are not met)



- When simple VEQ does not apply, we're often in need of other data *(if the answer is important enough, otherwise its back to interpretation)*
- It's why volume, mobility, recoverability, flux and risk components can't be estimated by well thickness for most cases
- VEQ does not account for residual
  - Residual is often the dominant mass
- BUT, VEQ can lead our thinking in good directions
  - As long as it is properly applied

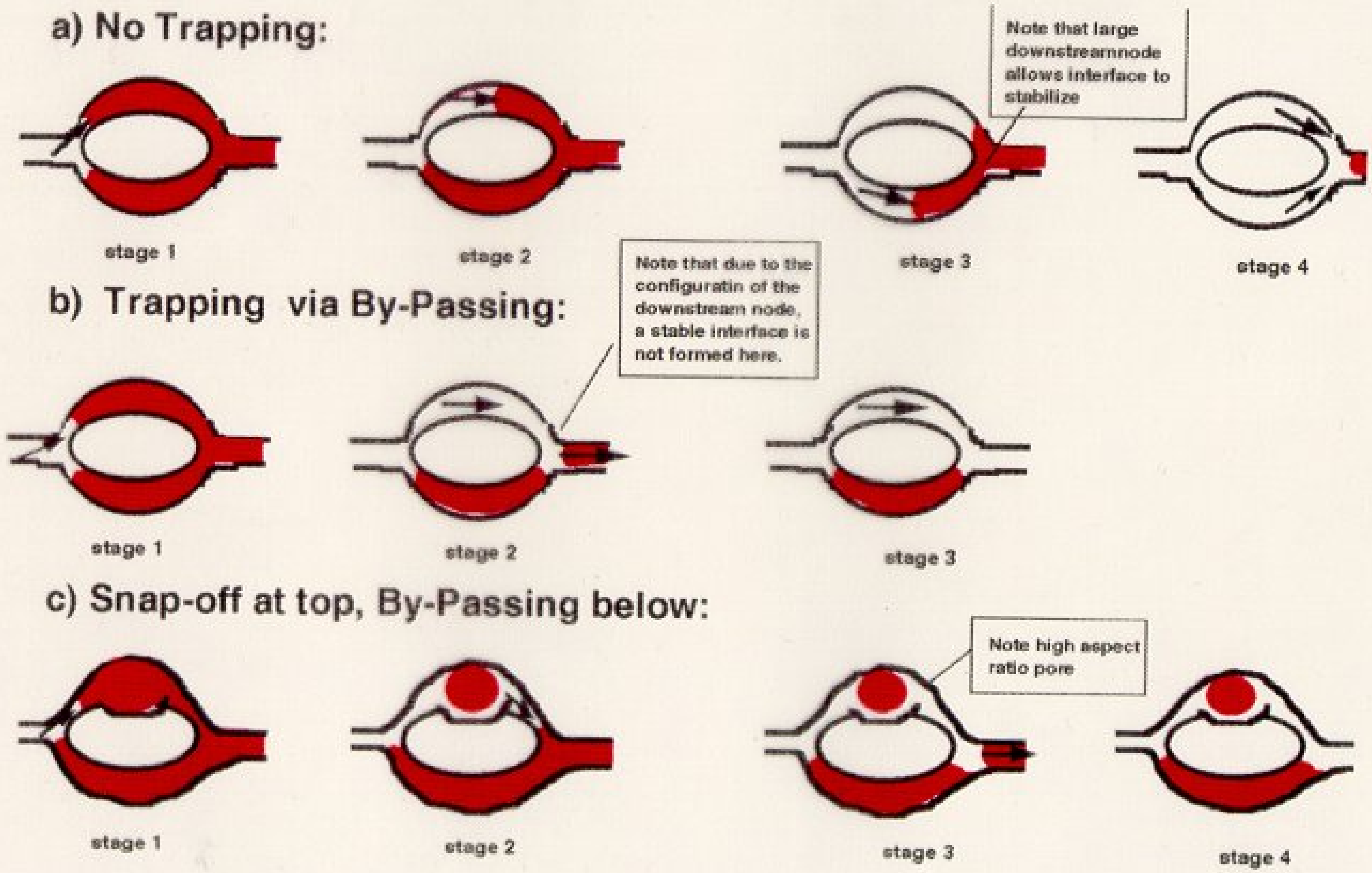
© AQUI-VER, INC.

What is Residual Saturation?

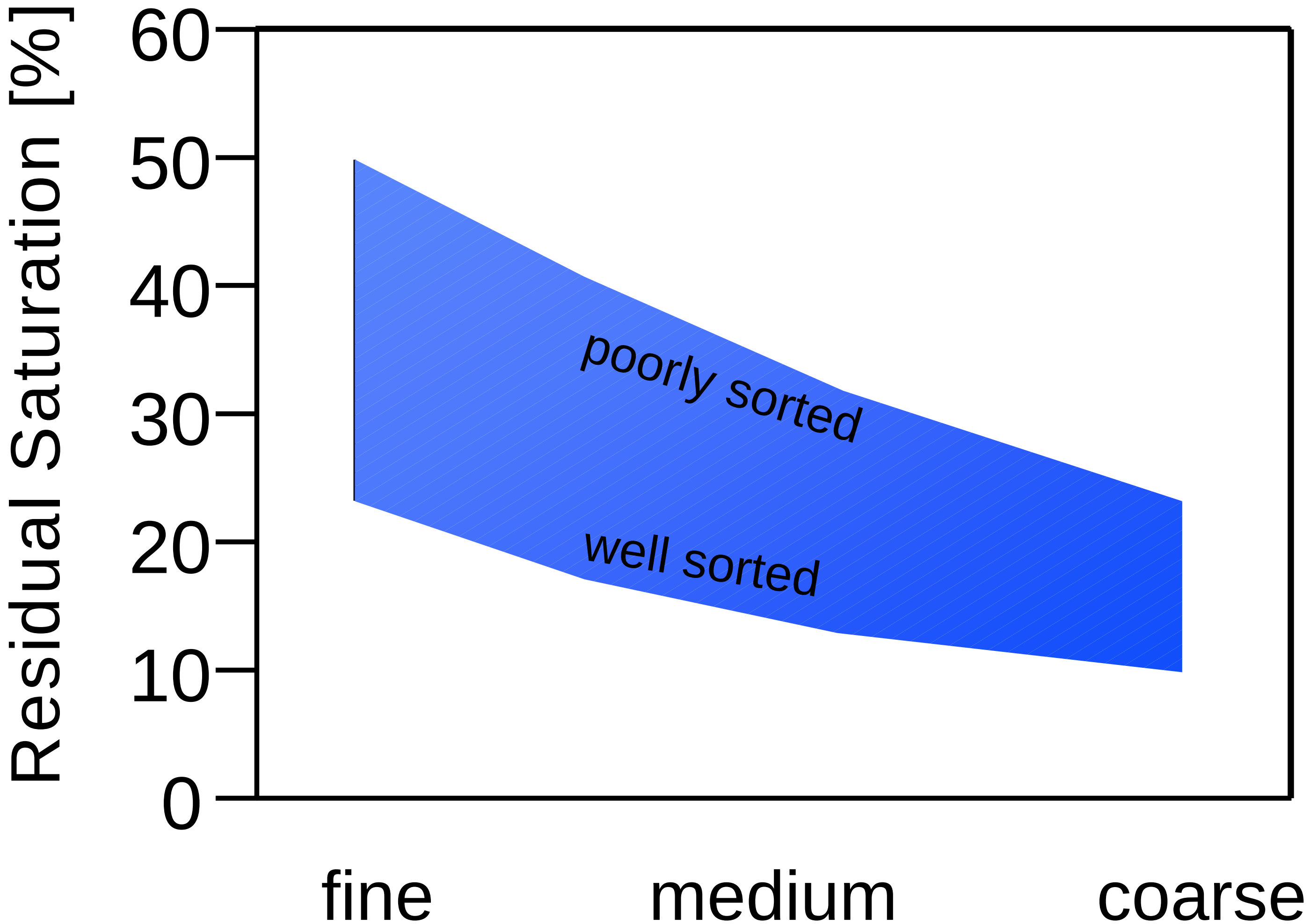
It is the amount of any fluid in the pore network that is hydraulically trapped. This important factor is complex, and affected by release & gradient history.

© AQUI-VER, INC.

Sketches Illustrating Trapping Mechanisms Using the Pore Doublet Model (after Chatzis et al., 1983)



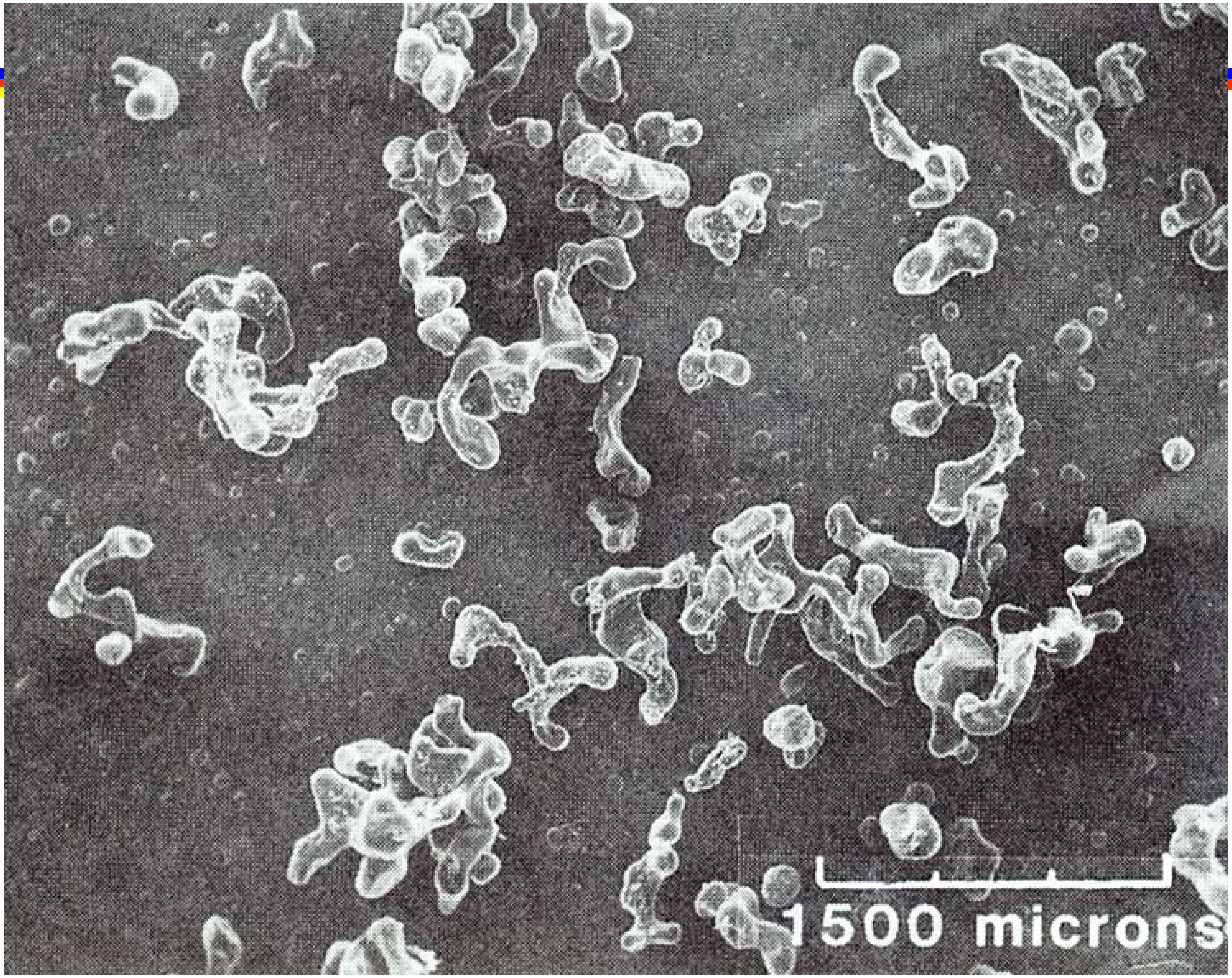
2-Phase Residual Saturation Range in Sands



Beckett & Lundegard, 1997

© AQUI-VER, INC.

MICROGRAPH OF RESIDUAL NAPL GANGLIA

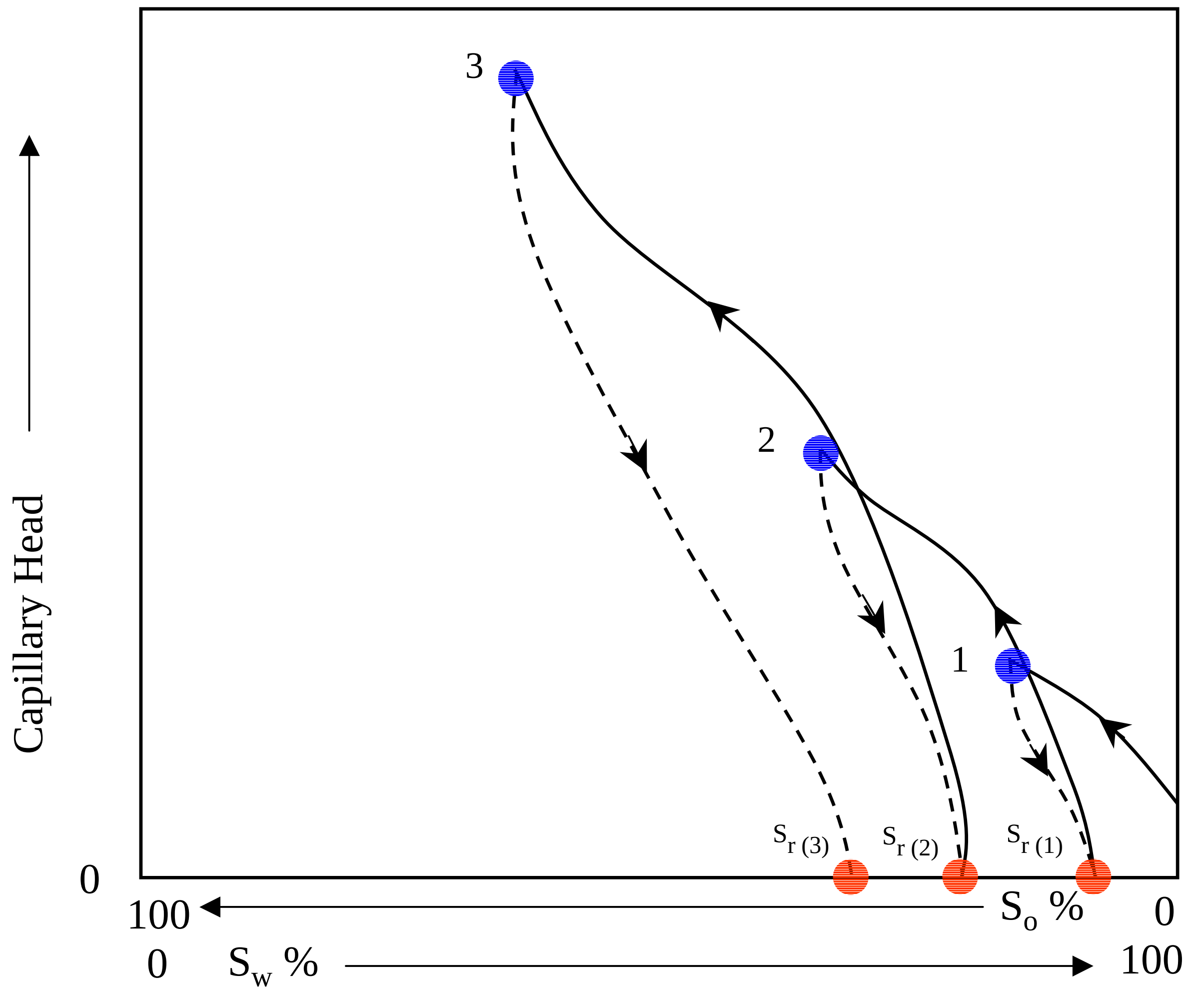


John L. Wilson, 1990; NMT

© AQUI-VER, INC.

Residual is Not a Constant

(rather, it varies with saturation history)



(After Pickell et al. 1966; modified by Adamski,2005)

© AQUI-VER, INC.

Initial vs. Residual Saturation Relationship

(for these specific study soils & oils)

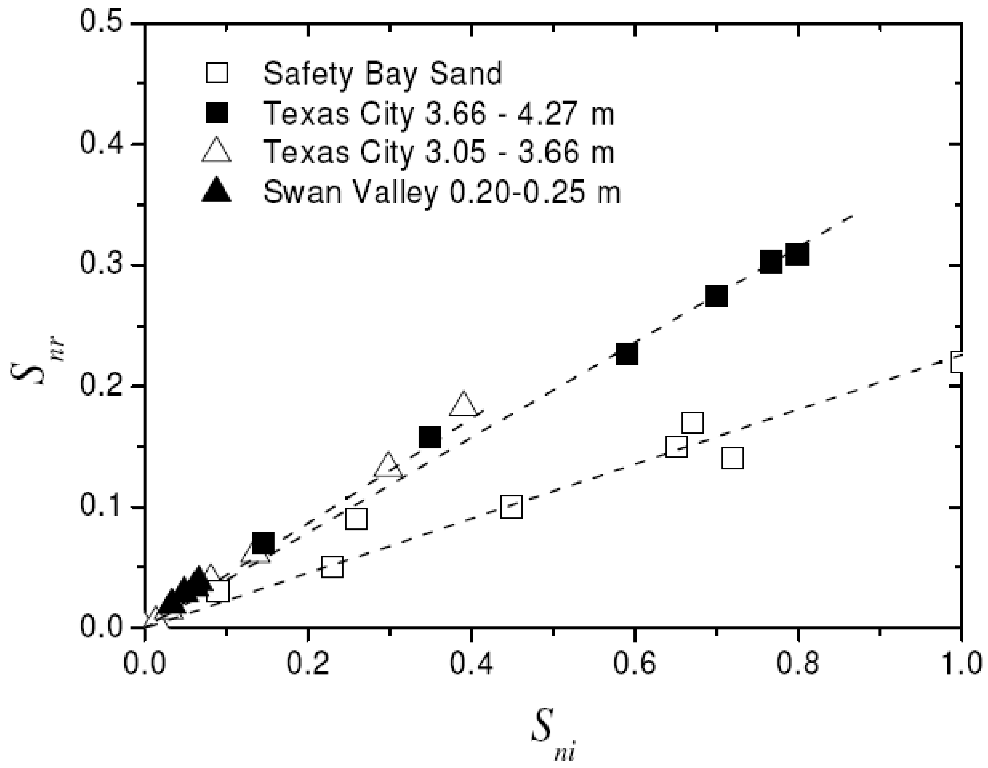


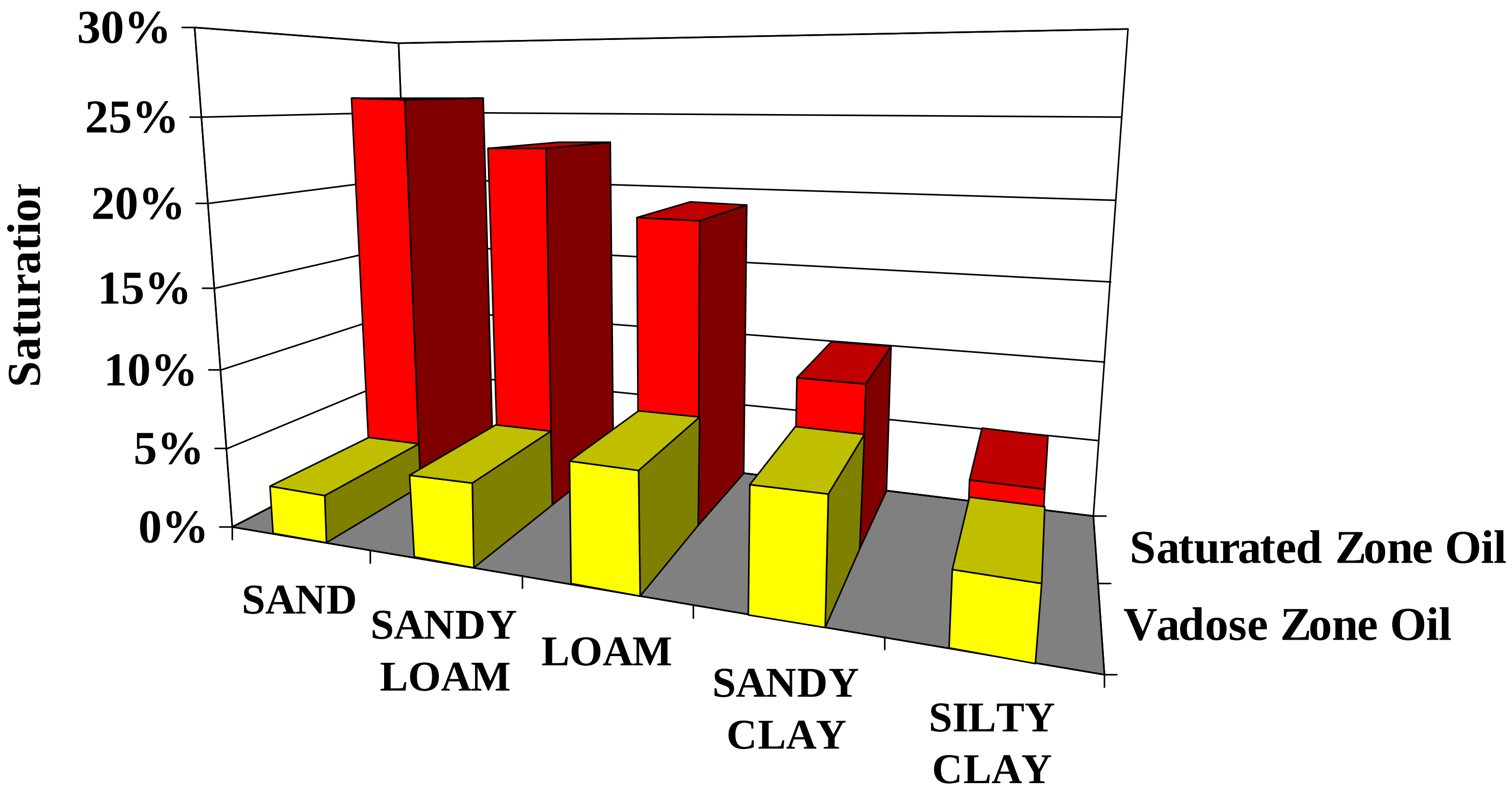
Fig. 4. Residual NAPL saturation, S_{nr}, as a function of initial NAPL saturation, S_{ni}, for the samples of the present study and for the Safety Bay Sand of Steffy *et al.* 1997. Symbols show measured values and lines show the fitted linear regression $S_{nr} = bS_{ni}$.

(From Johnston, C., & Adamski, M., 2005)

© AQUI-VER, INC.

2-Phase Vs. 3-Phase Residual Saturation

(3-phase is usually much smaller than 2-phase)



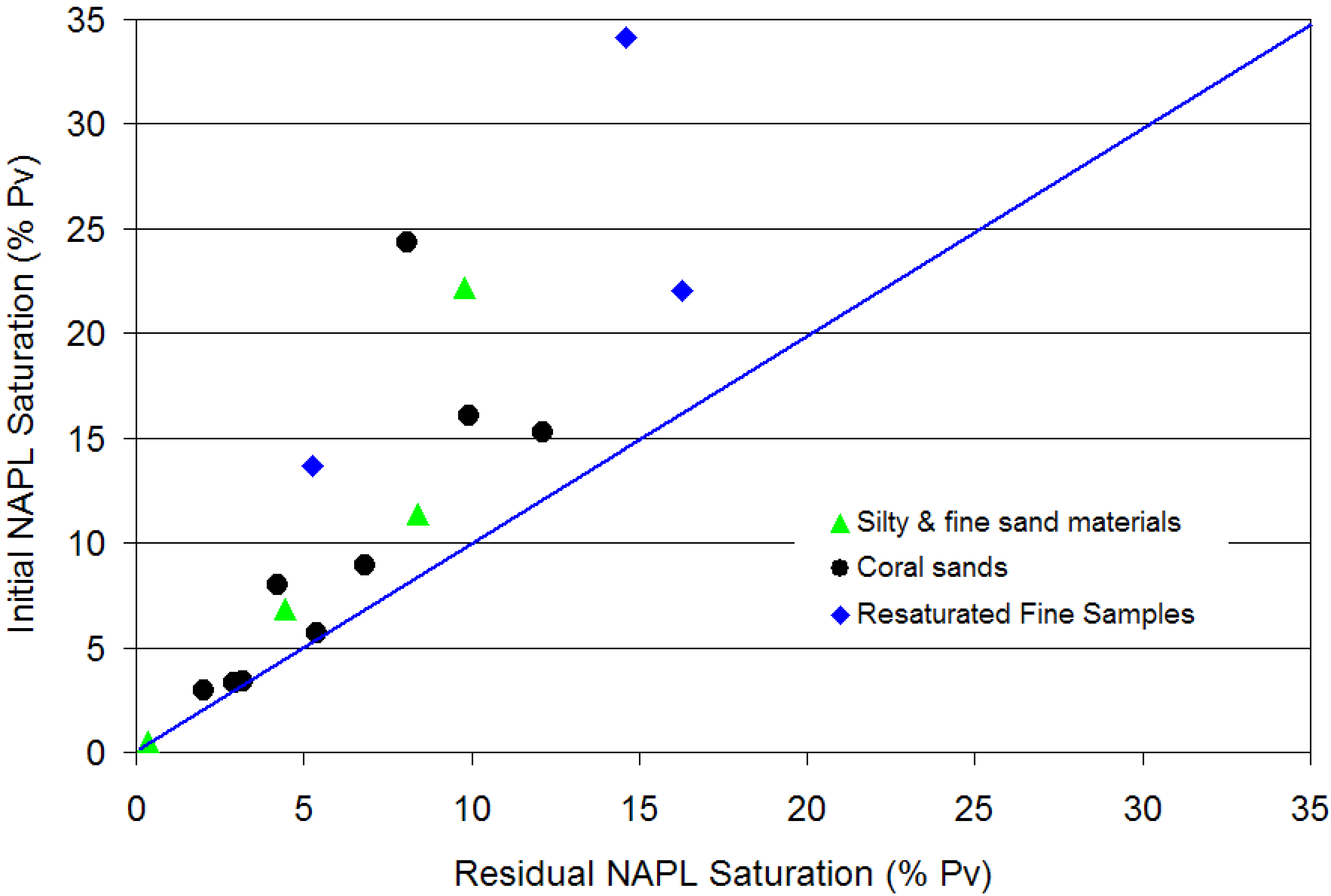
after, J. Parker, 1994

…but not much in fine textured soil

Courtesy of T. Peargin, Chevron ETC

© AQUI-VER, INC.
© AQUI-VER, INC.

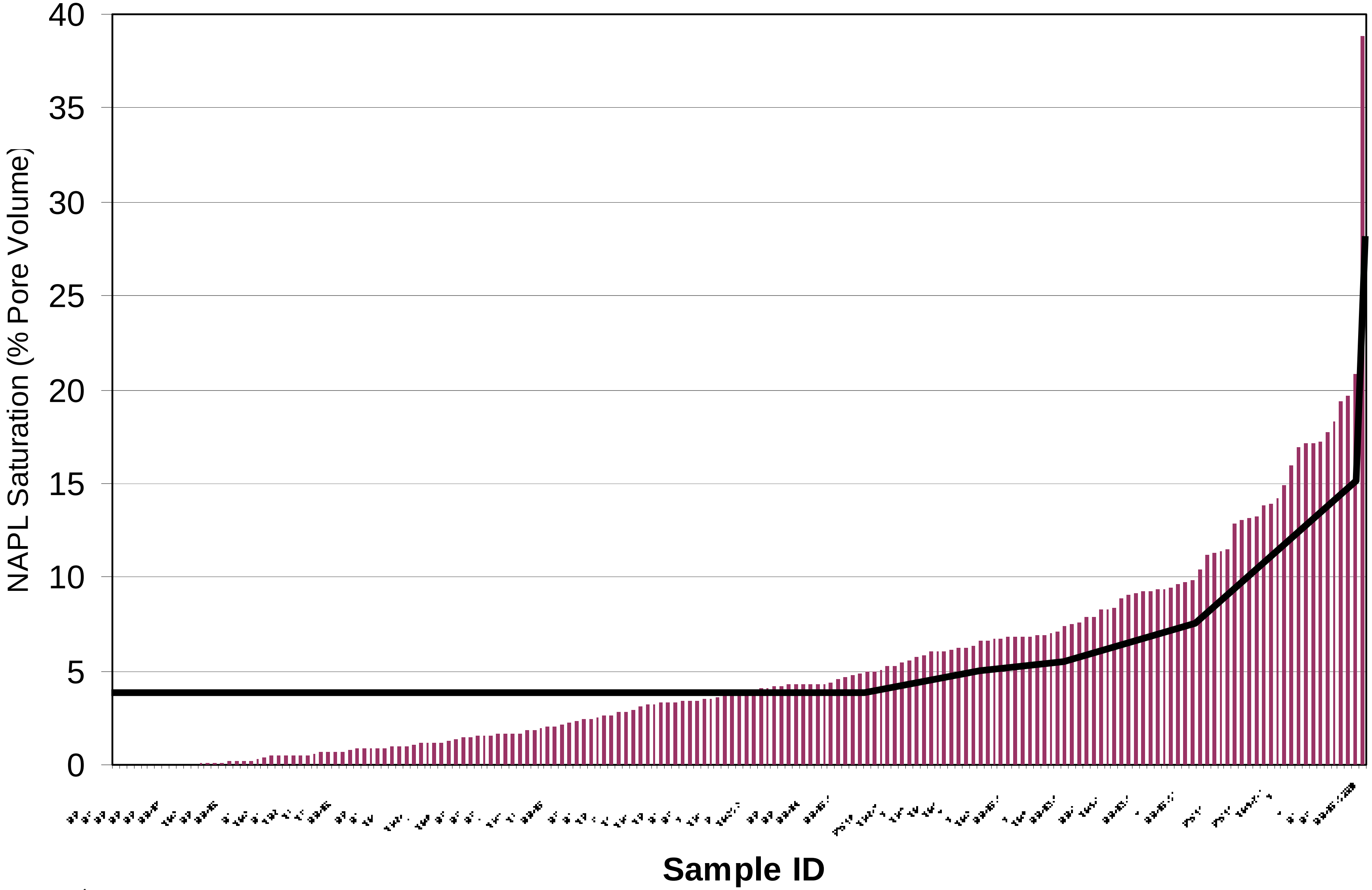
Example 3-Phase Residual LNAPL Saturation



© AQUI-VER, INC.

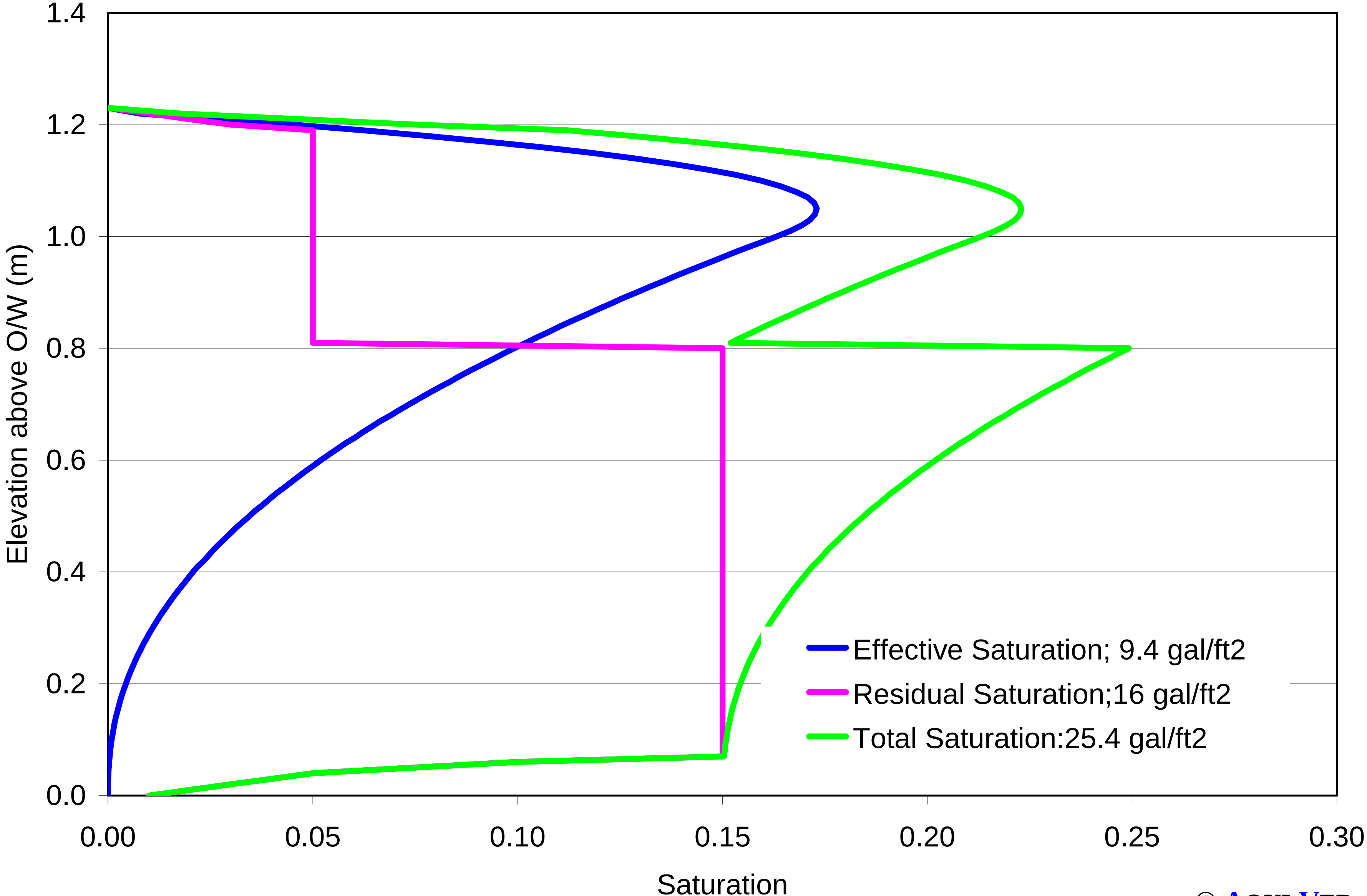
Native Vs. Residual NAPL Saturation

2005 3-phase Residual Tests are Basis



© AQUI-VER, INC.

Effective Vs. Total Saturation Profiles



© AQUI-VER, INC.

NAPL Properties vs. C_{sat} & C_{res}

Name	$C_{res\text{-}soil}$ mg/kg	$C_{sat\text{-}soil}$ mg/kg	ρ_{liquid} g/cm^3	MW g/gmole	S mg/L	P_{vap} mm Hg
TCE	70,000	**1,045**	1.5	131	1,100	75
Benzene	53,000	**444**	0.9	78	1,750	95
O-xylene	2,000	**143**	0.9	106	178	7
Gasoline	3,400 to 80,000	**106**	0. 8	99	164	102
Diesel	7,700 to 34,000	**18**	0.9	207	4	0.8
Fuel Oil	17,000 to 50,000	**18**	0.9	207	4	0.8
Mineral Oil	20,000 to 150,000	**3**	0.8	244	0.4	0.04

after Brost & DeVaull, 1998

© AQUI-VER, INC.

Will Residual "Blobs" Move?

(concept of trapping numbers)

- Recall residual "mechanism" graphic
- If "blobs" are trapped by pore throats & corners
  - Is it possible to "push/pull" them out; overcome that block?
- Why do we care about this?
  - Can transient events cause the plume to remobilize?
  - Can hydraulics or physical techniques get the oil out?
- So, what can we say about trapping numbers?
  - If we know capillarity, IFT, viscosity, etc.
  - We can figure out what we might expect
  - Through correlation/comparison to empirical data

© AQUI-VER, INC.

Capillary, Bond & Trapping Numbers

(higher numbers => more potential mobility)

Capillary Number

$$N_{ca} = \frac{kk_{ri}}{\sigma}\frac{\Delta\Phi}{L}$$

Bond Number

$$N_B = \frac{kk_{ri}}{\sigma}\Delta\rho\, g$$

$$N_t = \sqrt{N_{ca}^2 + N_B^2 - 2N_{ca}N_B\, Sin\,\alpha}$$

For horizontal flow $N_t = \sqrt{N_{ca}^2 + N_B^2}$

Courtesy of Dr. Richard Jackson, Interra, 1998

© AQUI-VER, INC.

Threshold Ranges for NAPL Mobilization

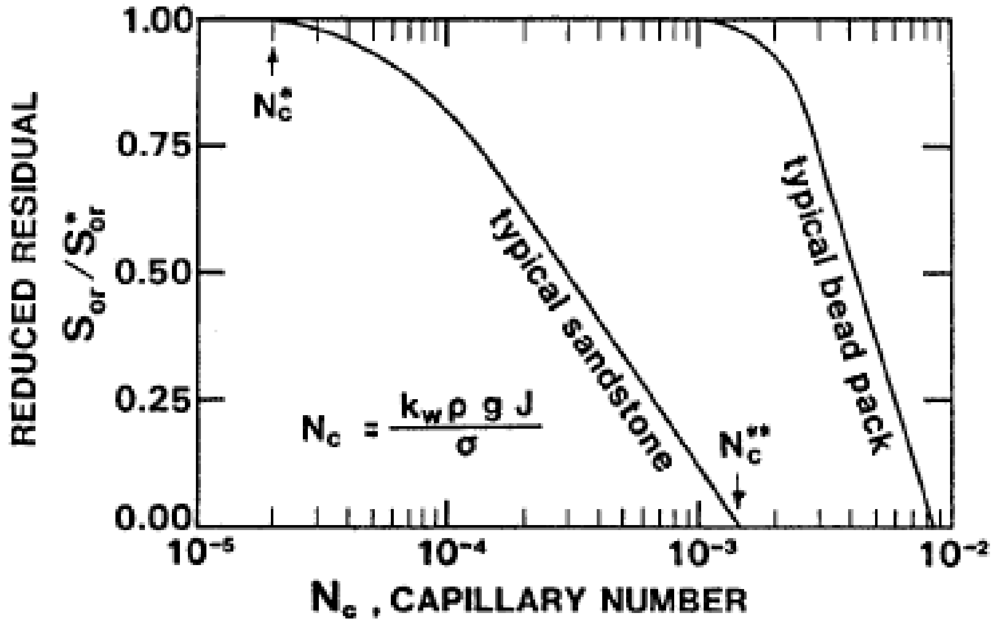


FIG. 7 Residual hydrocarbon saturation ratio, relating final residual saturation S_{or} to initial residual S^*_{or}, as a function of capillary number, N_c. The critical capillary number N^*_c represents initiation of blob motion, while N^{**}_c represents complete removal of blobs. The sandstone curve is from Chatzis & Morrow (1981); the bead-pack curve is based on the work reported in Morrow & Chatzis (1982).

From Wilson & Conrad, NMT, 1984

© AQUI-VER, INC.

Ranges of Capillary Numbers for Honolulu Site

Material	Description	K (ft/day)	Permeability (cm^2)	S_o	k_{rw}	i	IFT	N_c
Silt	Highest K	7	2.52E-08	5.20%	5.10E-02	0.0036	25.1	1.84E-13
	Low K	0.25	9.00E-10	5.20%	5.10E-02	0.0036	25.1	6.58E-15
	Median K	0.56	2.02E-09	5.20%	5.10E-02	0.0036	25.1	1.47E-14
	Lab perm high	0.253	9.11E-10	5.20%	5.10E-02	0.0036	25.1	6.66E-15
Coral Sand	Highest K	70	2.52E-07	8.30%	2.80E-01	0.0036	25.1	1.01E-11
	Low K	2.5	9.00E-09	8.30%	2.80E-01	0.0036	25.1	3.61E-13
	Median K	5.6	2.02E-08	8.30%	2.80E-01	0.0036	25.1	8.10E-13
	Lab perm high	0.57	2.05E-09	8.30%	2.80E-01	0.0036	25.1	8.24E-14

- These example N_c values are very low
- Well below typical thresholds of potential mobilization
- Well below reasonable induced gradient changes

© AQUI-VER, INC.

Key Implications of Capillarity & Saturation

- Thickness in wells is complex
  - Particularly for heterogeneous settings
  - Well thickness can be difficult to interpret
- Wells do not exaggerate LNAPL thickness
  - What you see is the free-phase zone
  - It is not an "apparent" thickness, it is the thickness
- Much more oil in coarse soil for same pressures
- All materials trap residual oil
  - Typically more in fine-grained materials
  - Usually more in poorly sorted/angular soils
  - 2-phase > 3-phase residual values
- Saturation drives relative mobility
  - Higher saturation => higher mobility

© AQUI-VER, INC.

Phase Mobility Details – But Not All…

© AQUI-VER, INC.

Multiphase Flow Background

Darcy's Law and the Continuity Equation

Easy Darcy

$$q = -Ki \quad \& \quad v_p = -Ki/\theta_e$$

Multiphase Darcy

$$q_{p_j} = -\frac{k_{ij}k_r}{\mu_p}\left[\frac{\partial P_p}{\partial \chi_j} + \rho_p g \frac{\partial Z}{\partial \chi_j}\right]$$

Continuity Eqn

$$\frac{\partial \theta}{\partial t} + \lambda = \frac{\partial}{\partial x}[q_x] + \frac{\partial}{\partial y}[q_y] + \frac{\partial}{\partial z}[q_z]$$

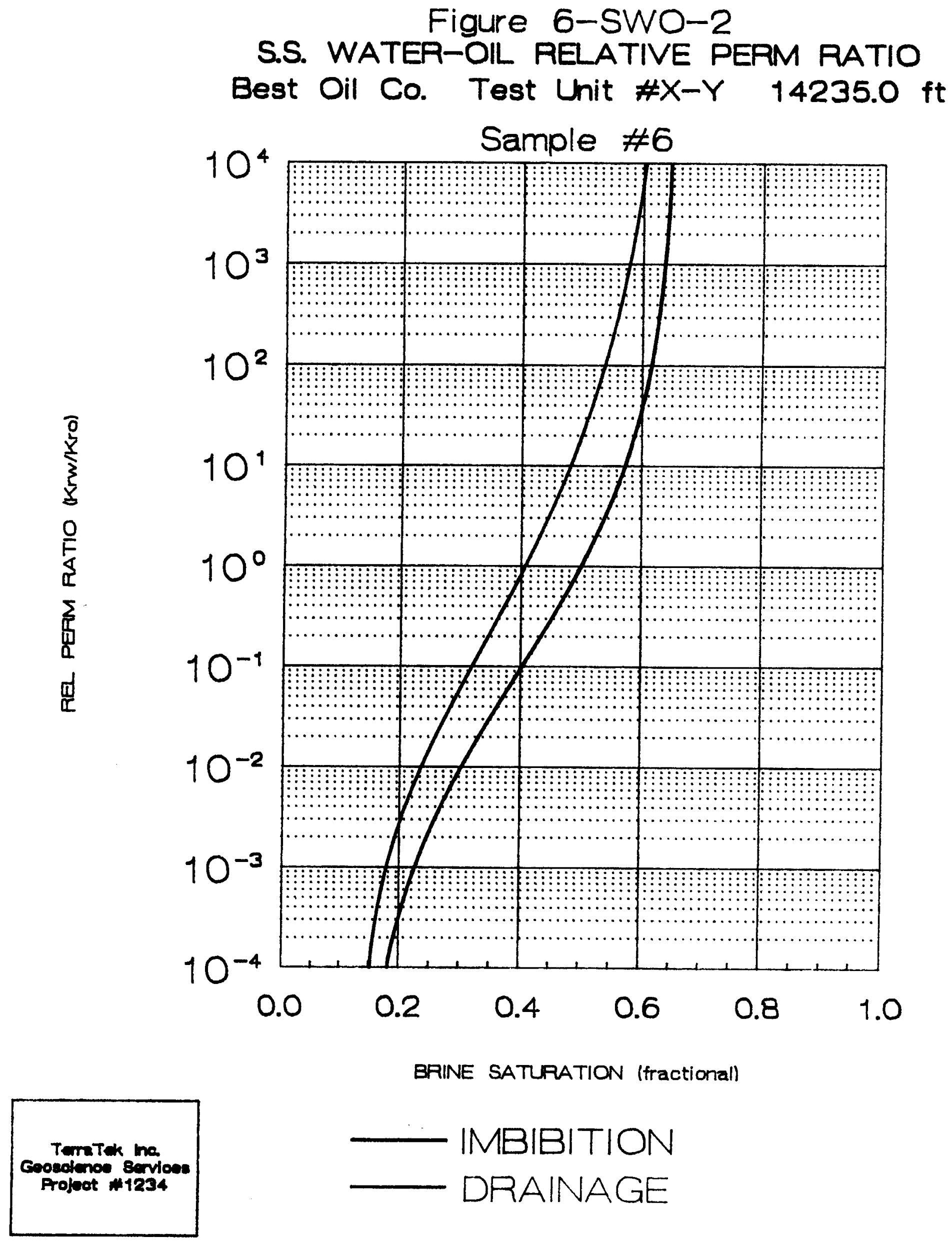
Multiphase Transmissivity

$$T_p = K_p b_p = \frac{\rho_p g}{\mu_p}\int k_{ij}k_r \partial z$$

A factor of key interest is the relative permeability, a scalar that varies exponentially as a function of phase saturation, which varies with capillary pressure, etc.

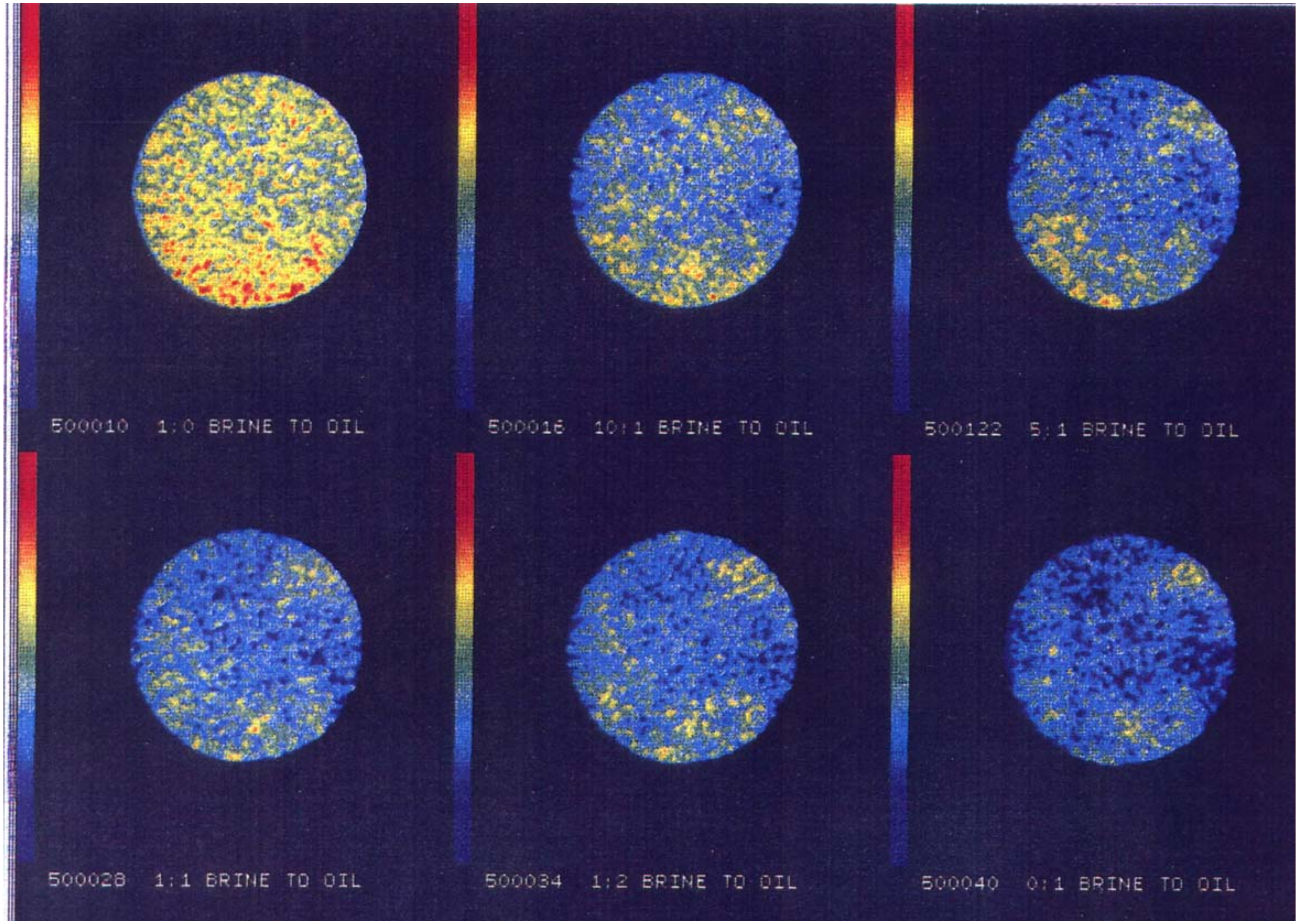
© AQUI-VER, INC.

What Does Lab Data Say?



Courtesy of Terra Tek, Salt Lake City, UT

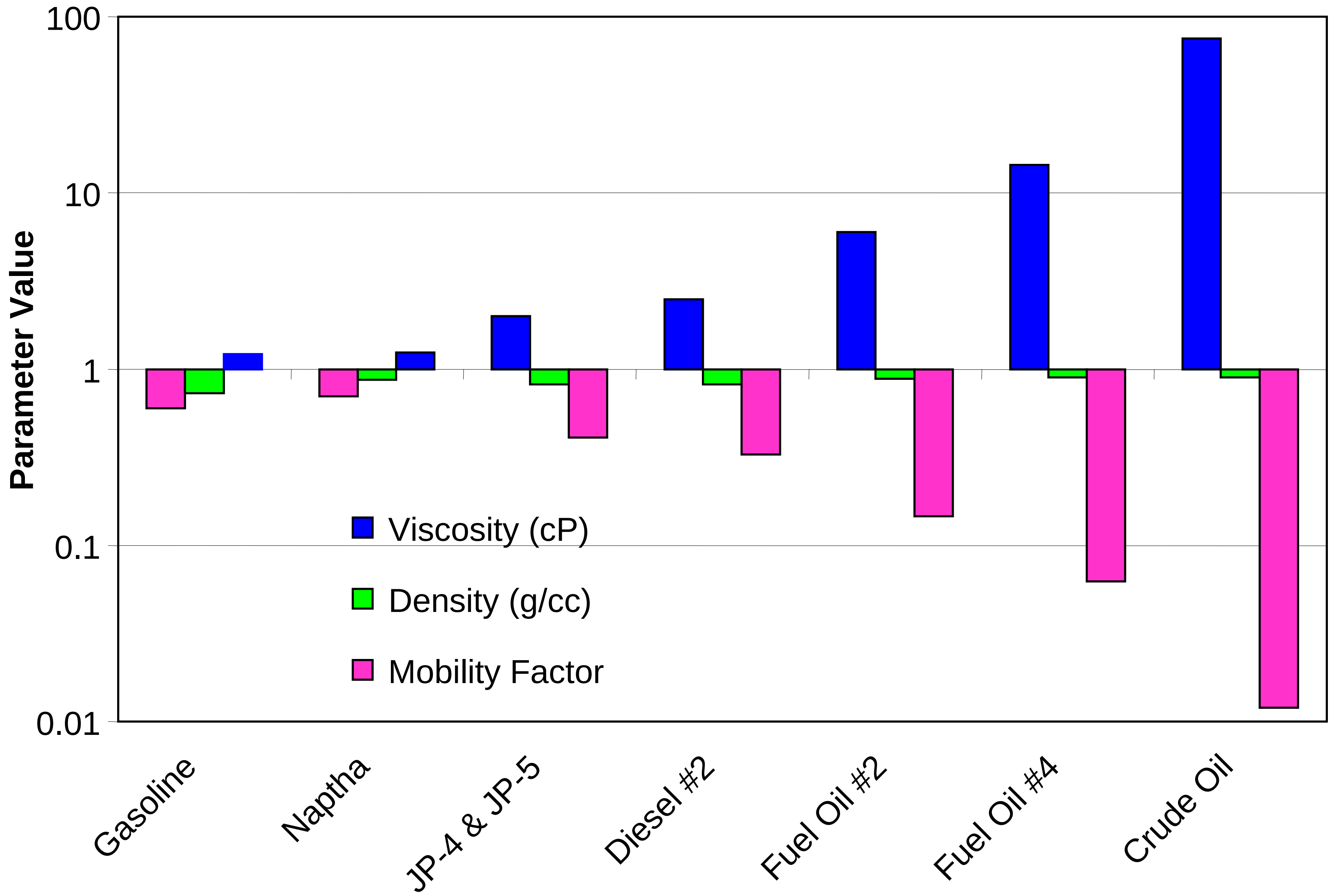
A Visual of That Relative Mobility (cool!)



Courtesy of Terra Tek, Salt Lake City, UT

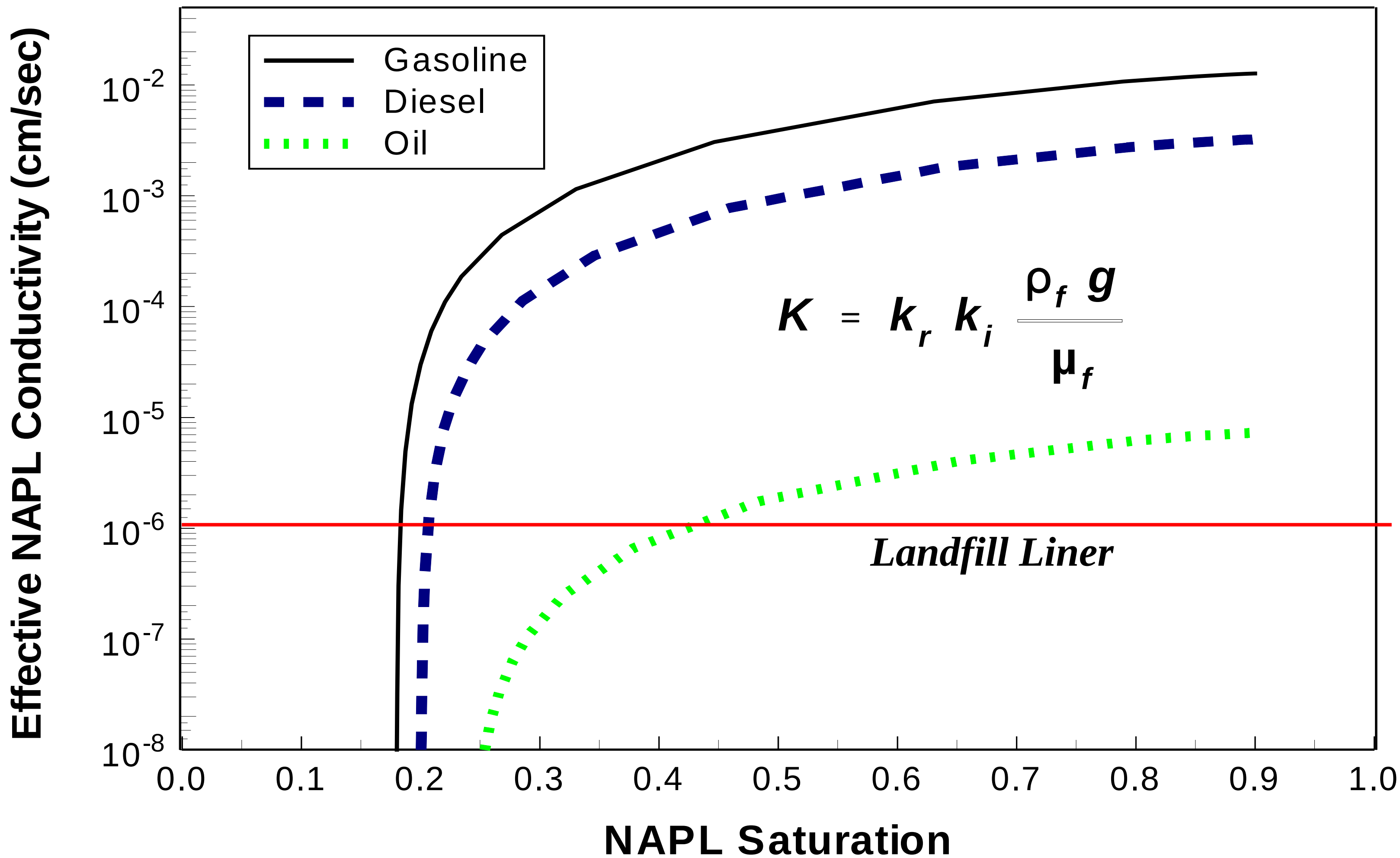
© AQUI-VER, INC.

Relative Mobility of Different Products



© AQUI-VER, INC.

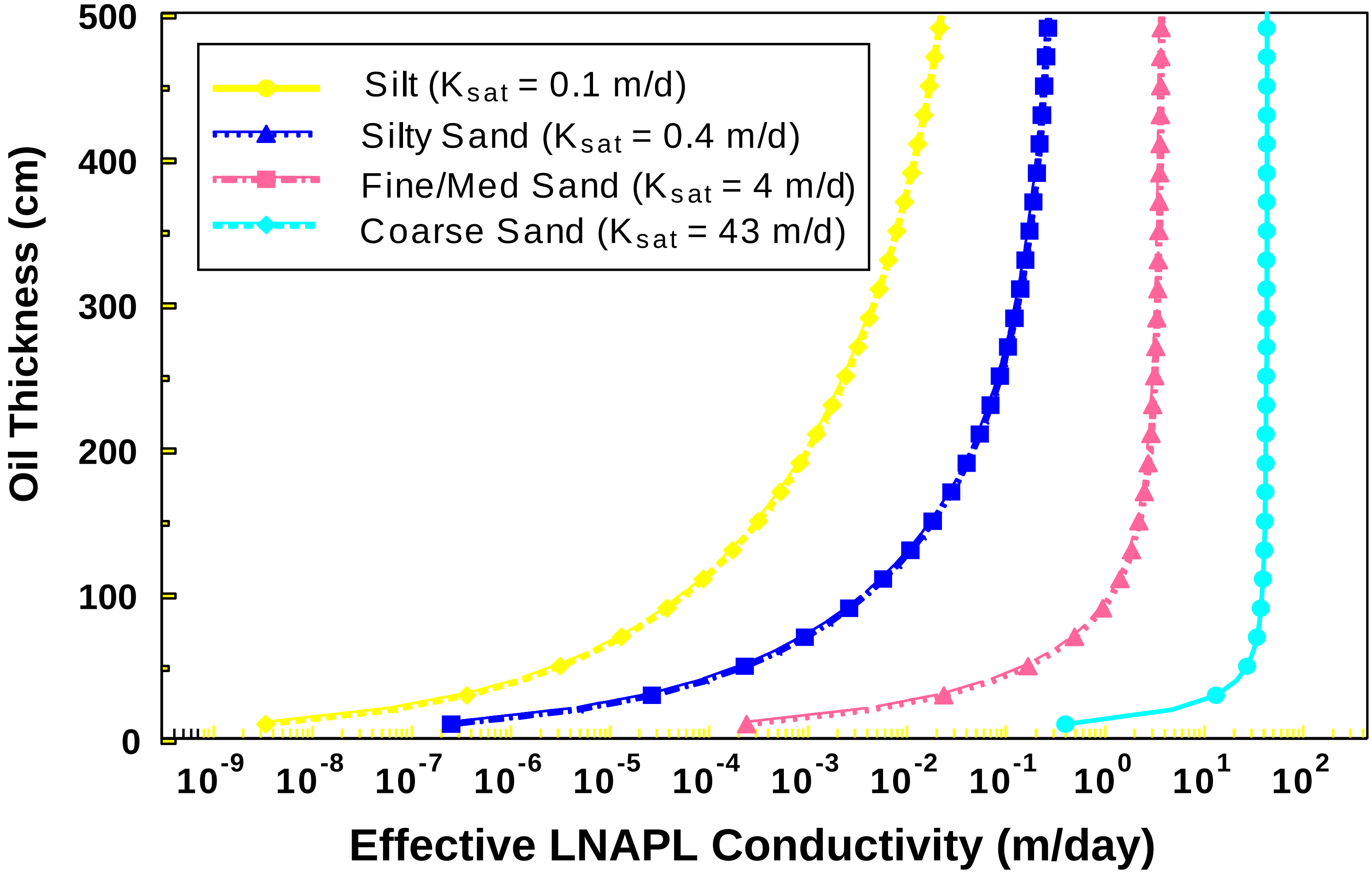
Effective NAPL Conductivity



© AQUI-VER, INC.

Effect of Soil & VEQ Thickness on K_{oil}

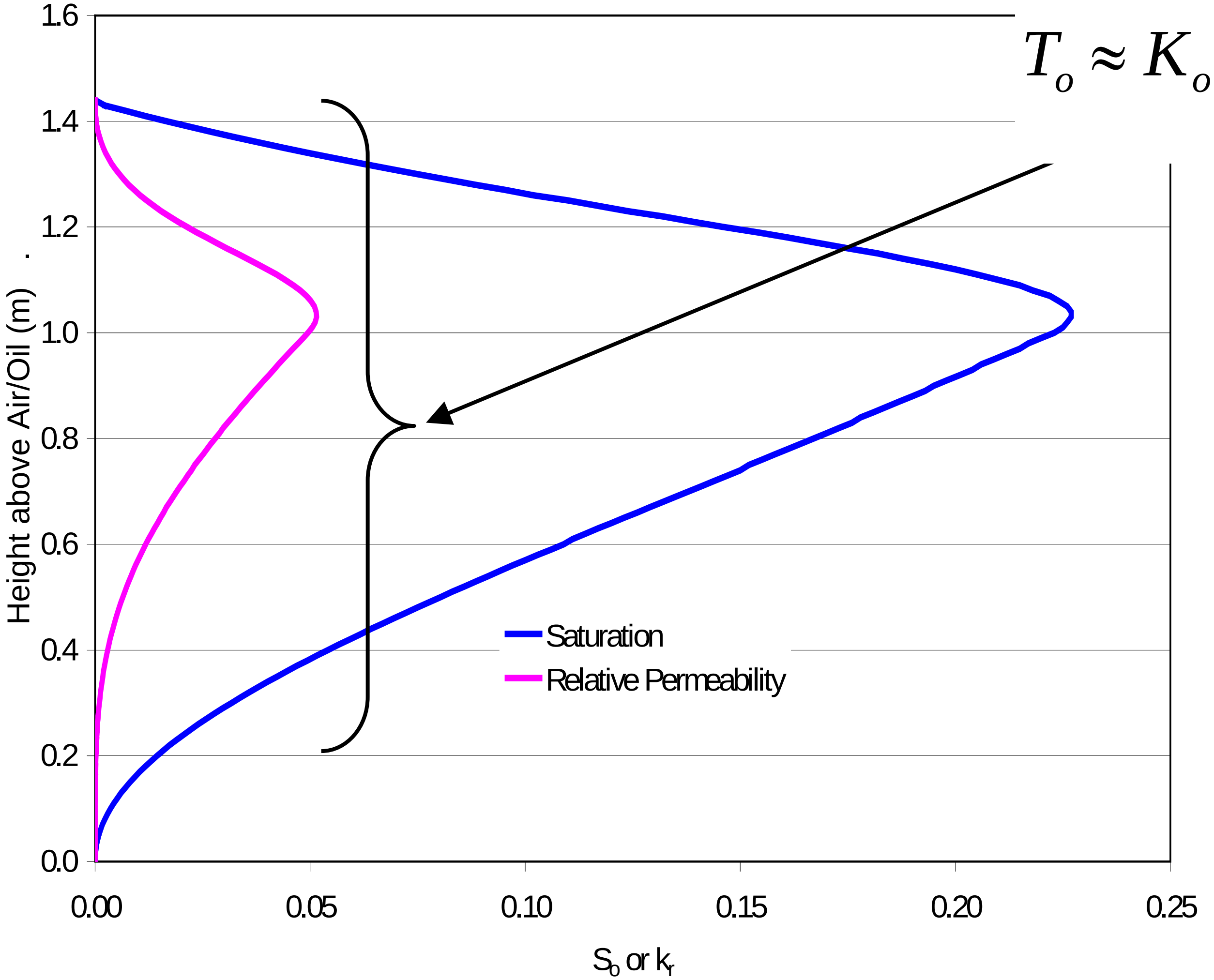
(but recall our "problem" with VEQ)



© AQUI-VER, INC.

What is NAPL Transmissivity?

$$T_o \approx K_o b_o = \frac{\rho_o g}{\mu_p} \int k_{ij} k_{ro} \partial z_o$$

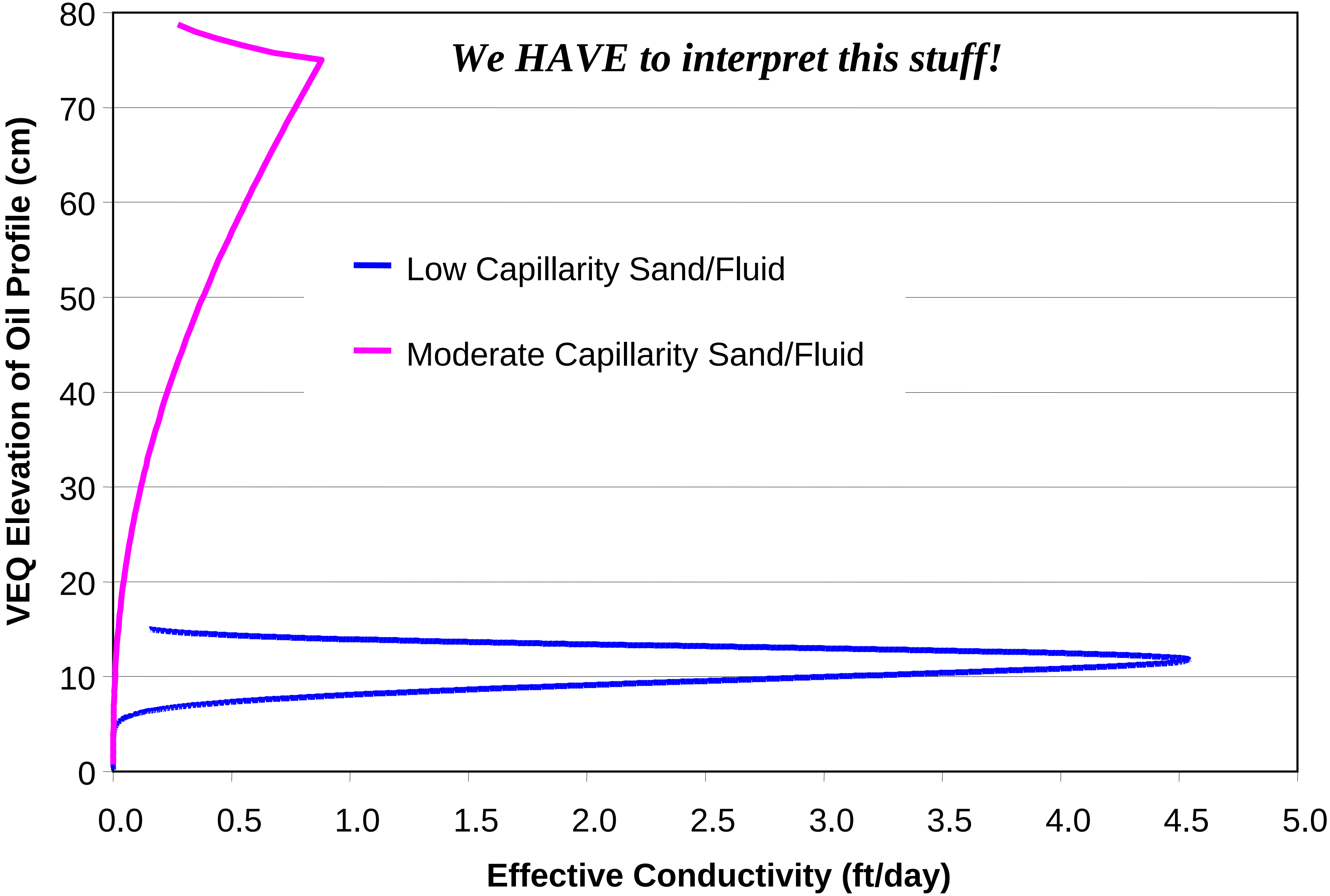


It has similar meaning, but is a much different beast than g.w. transmissivity.

© AQUI-VER, INC.

Two Sands with ***Same*** Oil Transmissivity

(but much different oil conductivity & mobility)



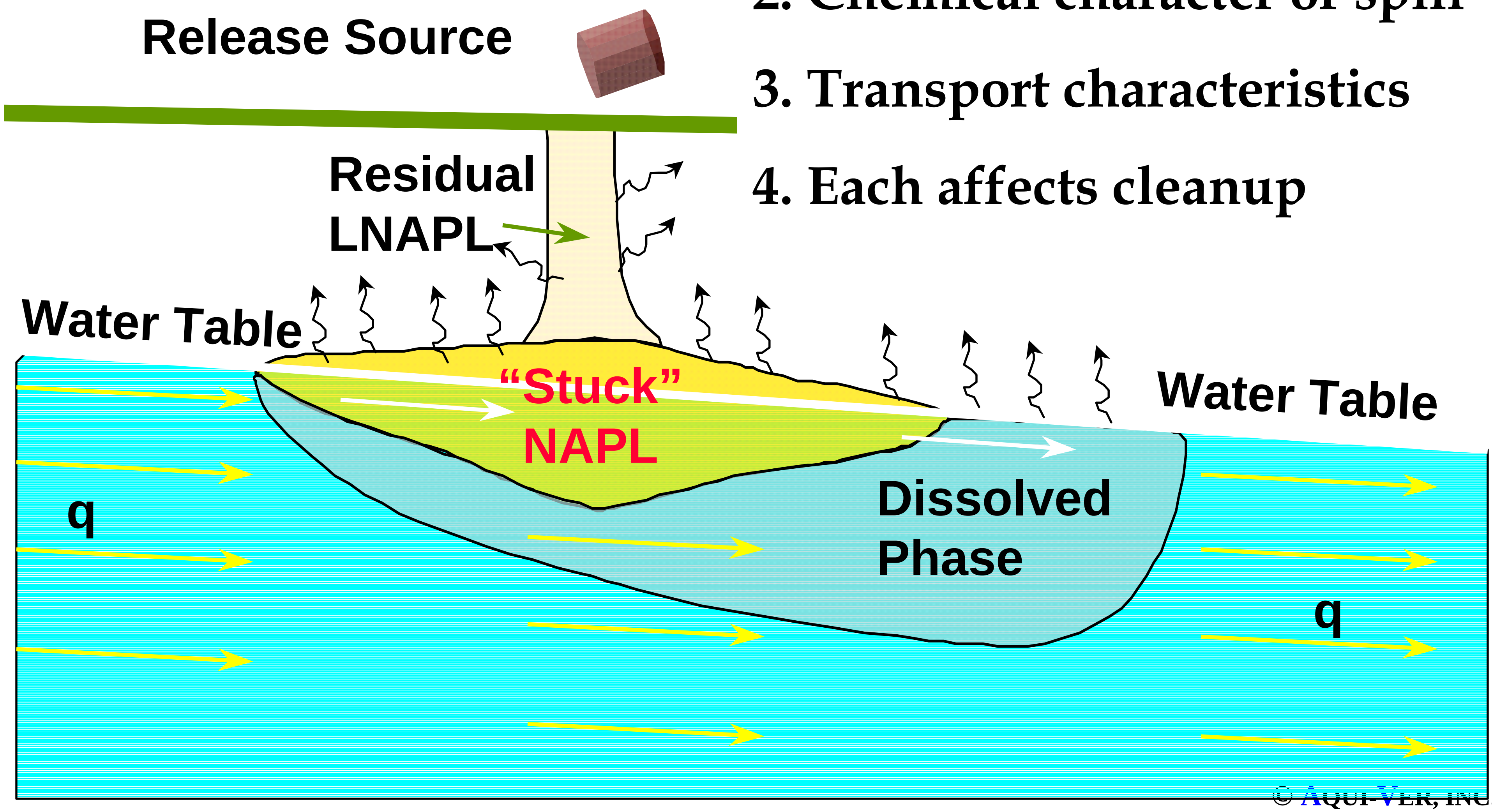
© AQUI-VER, INC.

How About Some Chemistry?

© AQUI-VER, INC.

Chemical impacts depend on the LNAPL

1. Distribution of spill
2. Chemical character of spill
3. Transport characteristics
4. Each affects cleanup



© AQUI-VER, INC.

Effective Solubility

(Analog of Raoult's Law)

$$C_{eff_m} = X_m \; C_{sat_m}$$

X_m = Mole Fraction of Component m.

C_{sat_m} = Pure Phase Solubility of Phase m.

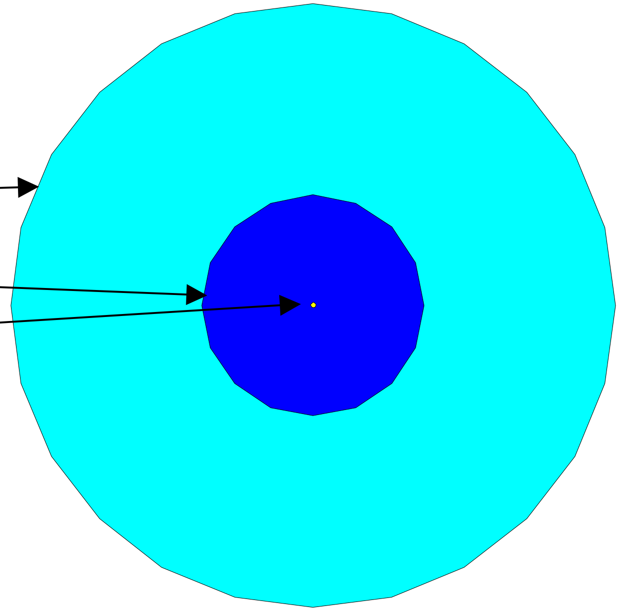
$$\text{Flux} = \int C_{effm} \bullet q_r$$

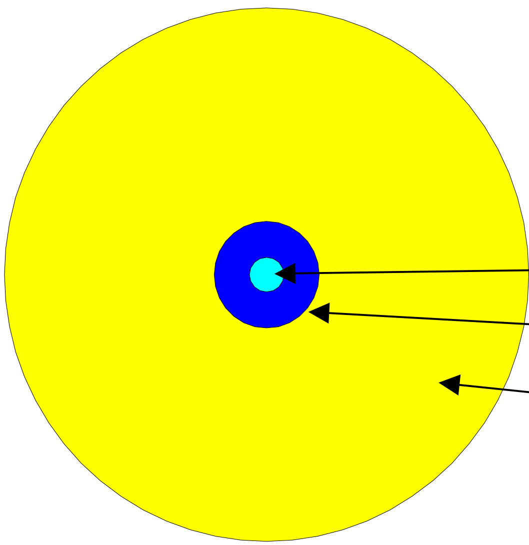
© AQUI-VER, INC.

Geology Can Greatly Affect Flux & Longevity

Relative Fluxes:

Coarse-grained soil (SW)
Fine-medium soil (SM)
Fine-grained material





Relative Time to De Minimis:

Coarse-grained soil (SW)
Fine-medium soil (SM)
Fine-grained material

© AQUI-VER, INC.

Chemistry Affects Flux Magnitude

(for same LNAPL & geologic conditions)

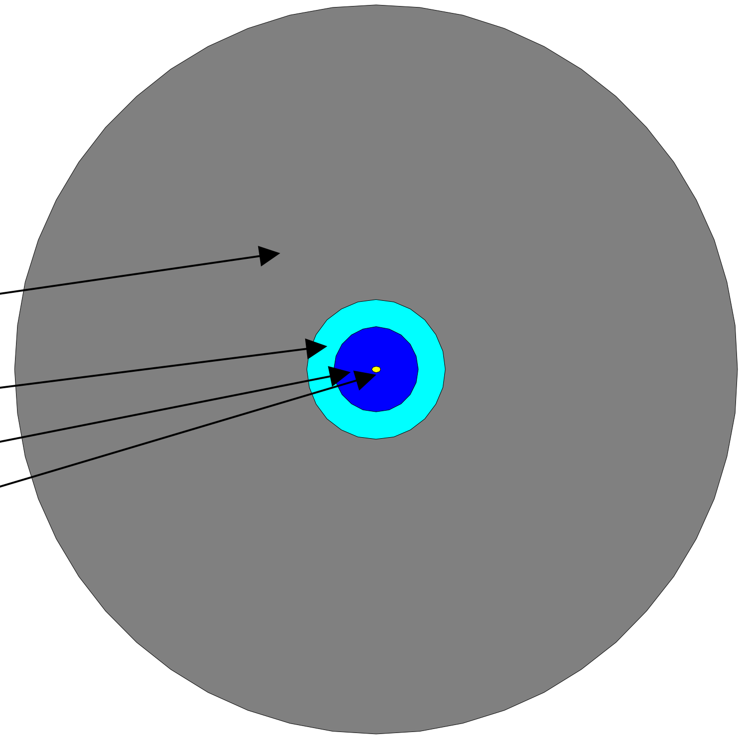
<u>Chemical Compound:</u>

MTBE @ 2%

Benzene @ 2%

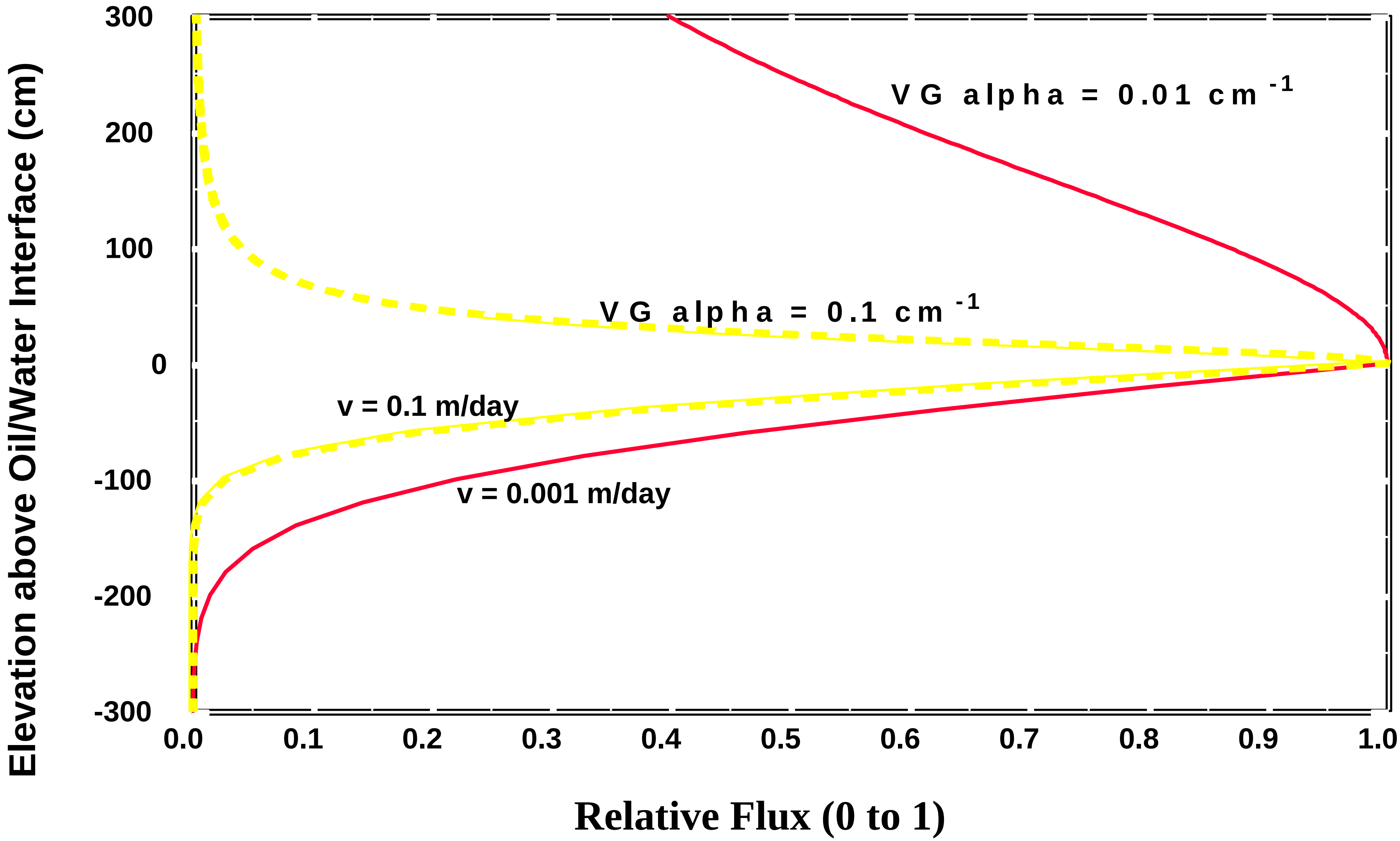
Xylenes @ 7.5%

Fluorenes @ 2%



© AQUI-VER, INC.

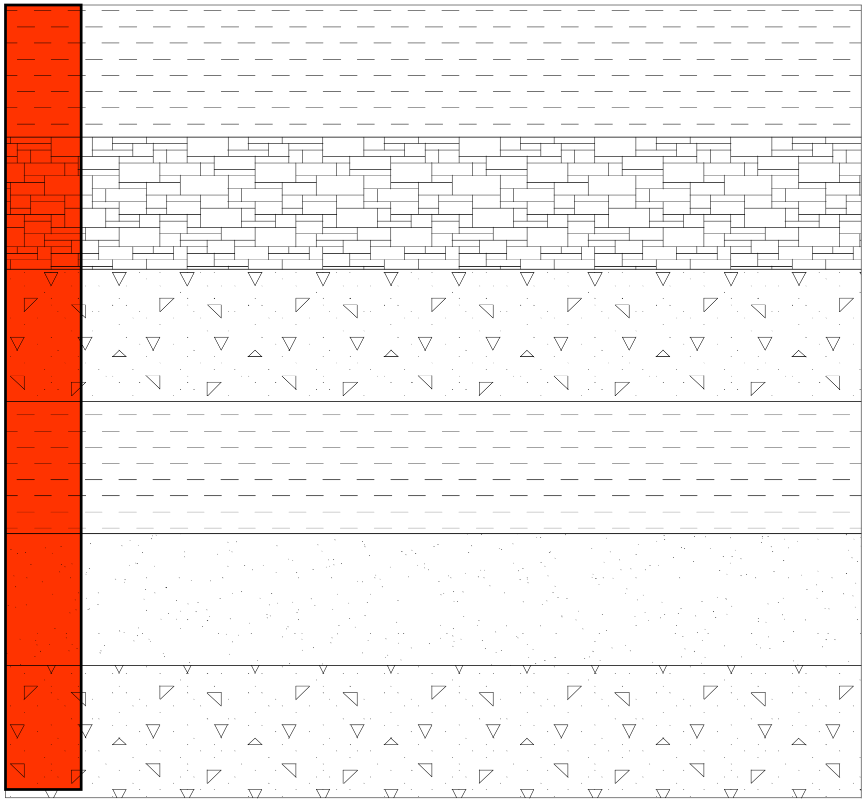
Relative Mass Flux Through NAPL Zone



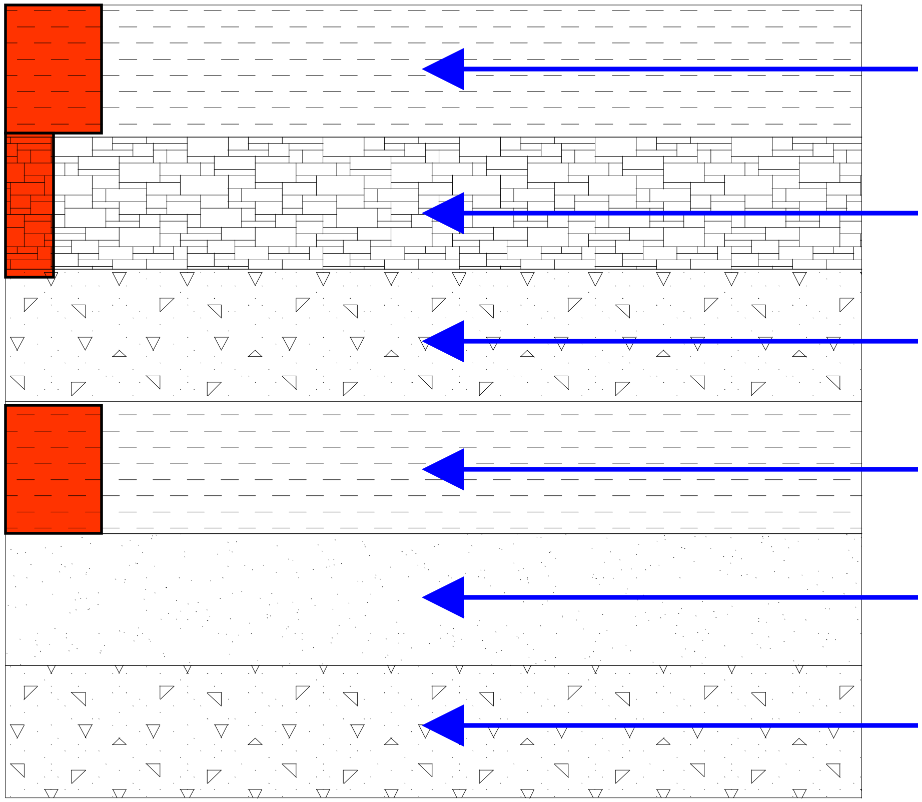
after Huntely & Beckett, 2002; J of Cont. Hydro

© AQUI-VER, INC.

Distributed "Equilibrium"



$C/C_m = 1.0$

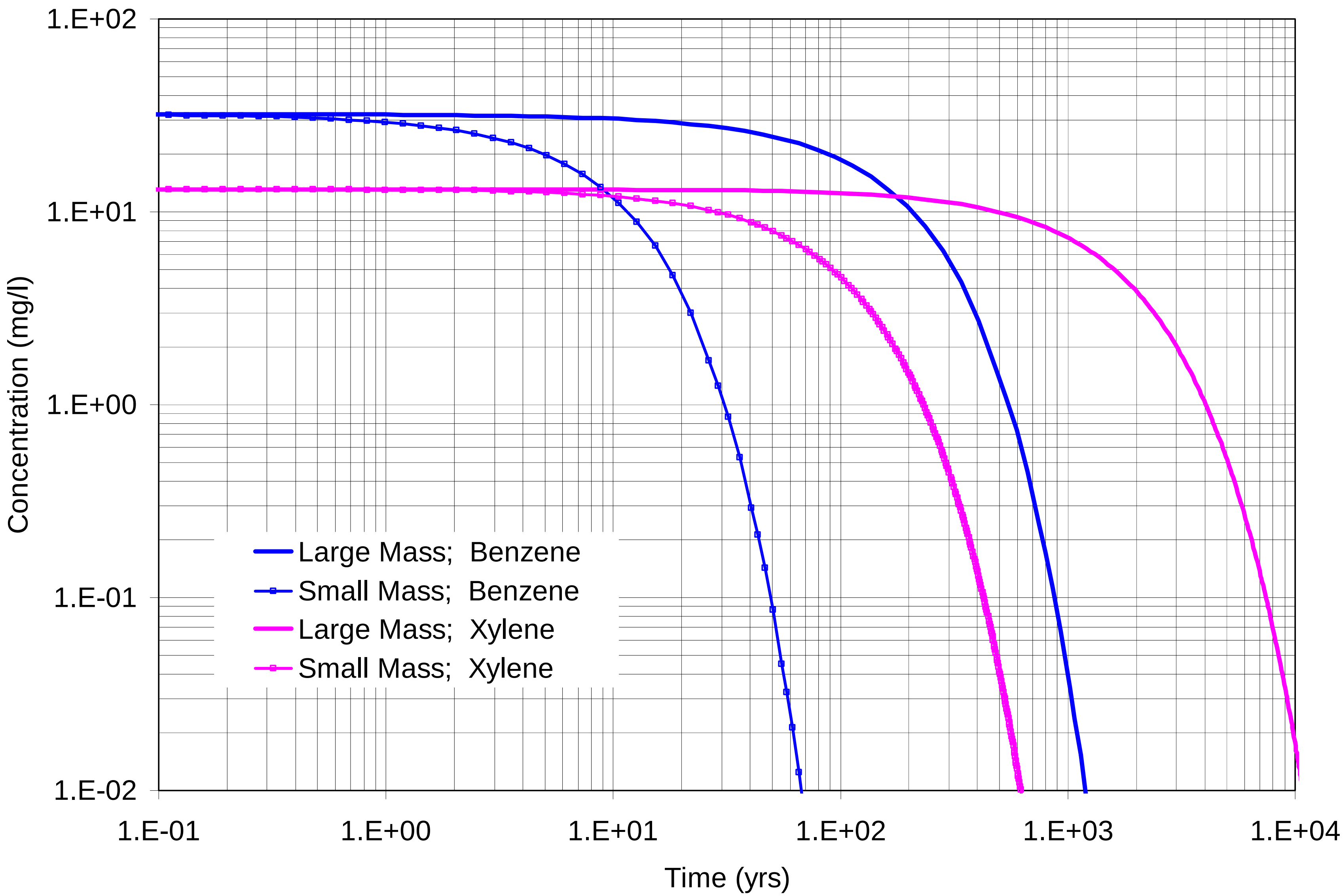


$C/C_m = 0.5$

© AQUI-VER, INC.
© AQUI-VER, INC.

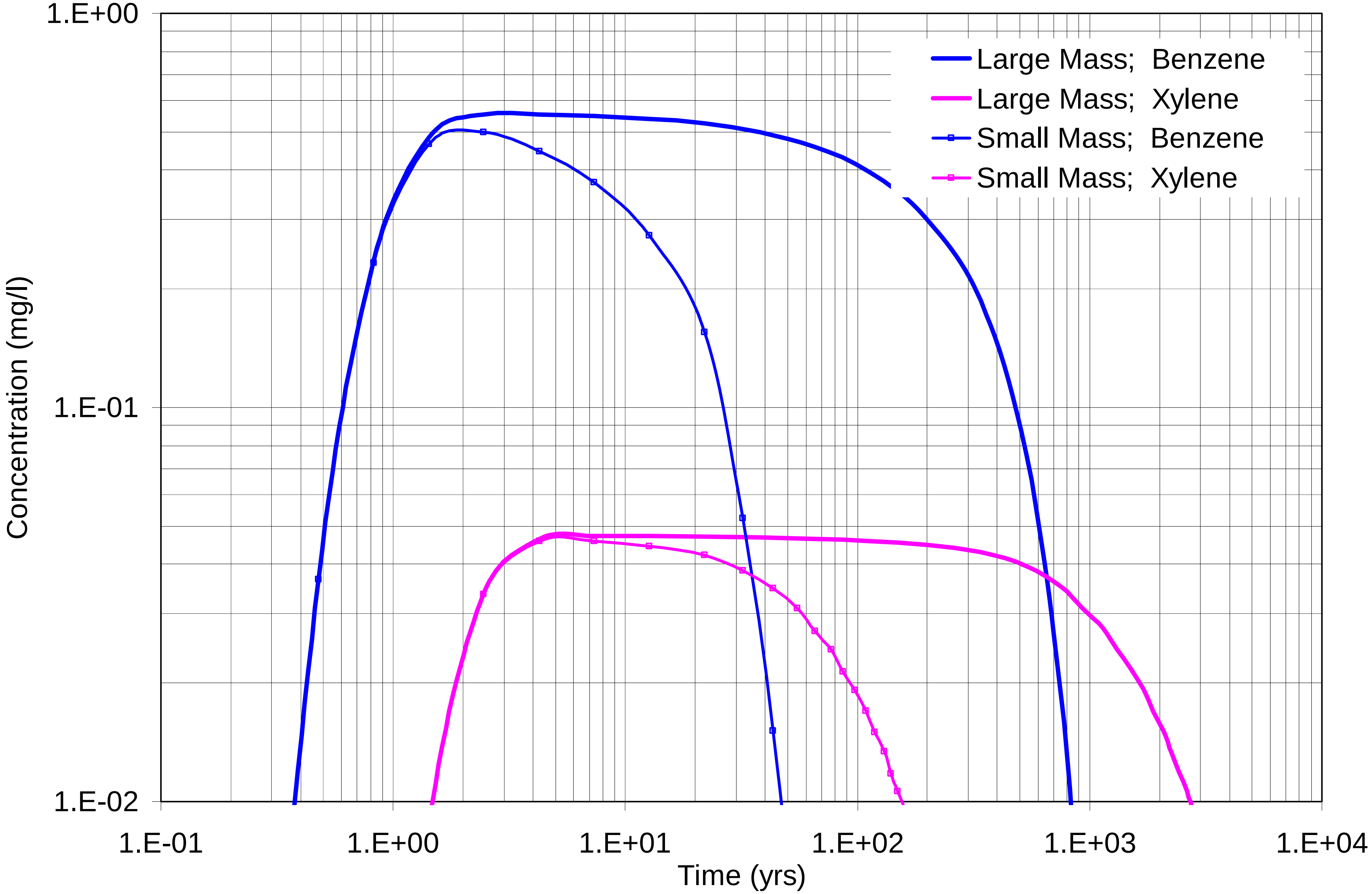
Different Styles of Plume Source Strength

(accounts for source term depletion)



© AQUI-VER, INC.

Breakthrough Form Depends on Source Strength



© AQUI-VER, INC.

What Can We Draw From All Those Things?

- If mass is finite, it has to deplete through time
  - And, site g.w. data can be used to show that
  - Different compounds flux at different rates
  - Heterogeneity affects the form of the mass losses
- Plume conditions generally improve through time
  - Exception; new &/or ongoing releases
  - Or when transport conditions bring impacts to receptors
  - These things “show up” in the trend evaluations
- Certain chemicals are short-lived, others longer-lived
- We often have a lot of groundwater monitoring data
  - It should reflect the exponential forms of the plume
  - Those “forms” are an amalgam of the underlying processes

© AQUI-VER, INC.

Part II: Implication of LNAPL Mechanics

See list in TGM & Companion Guides

© AQUI-VER, INC.

General Key Implications

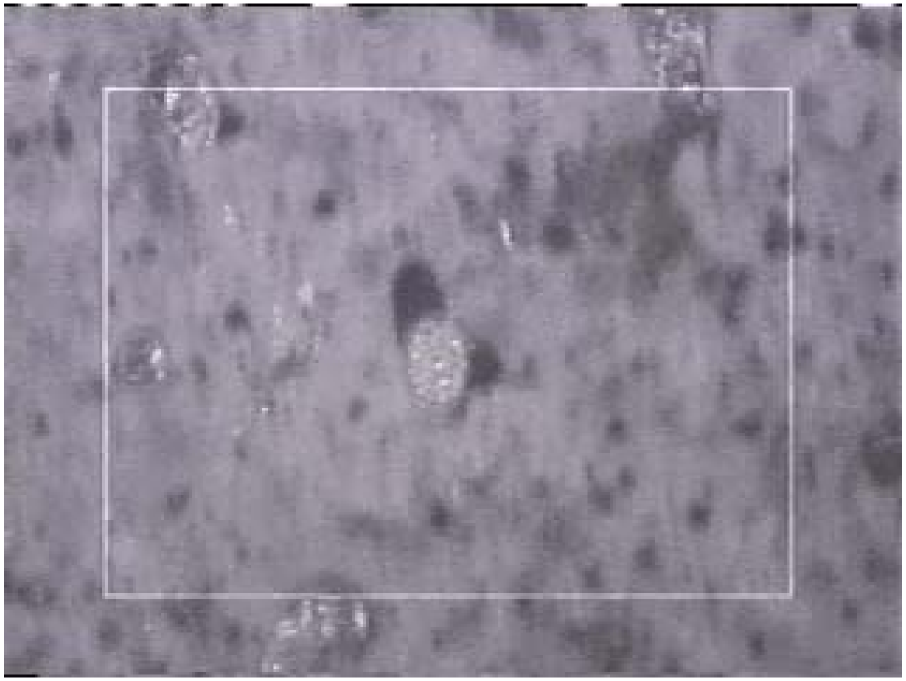
(just a few of oh so many.. and not always so)

- Finite LNAPL release stabilize relatively quickly
  - So, old plumes are typically stable plumes
- Fractured rock on the Islands can present high mobility
- Stabilization processes also limit recoverability
- Persistent dissolved-phase plumes are LNAPL-sourced
  - And can be used to interpret LNAPL conditions
- LNAPL in wells represents free-phase
  - The total mass (free + residual) controls longevity
  - Free-phase mass is usually a small fraction of the whole
- LNAPL hydrogeologic parameters are transient
- LNAPL will find its way to the deepest water levels
  - Over the history of the release; LNAPL will be submerged

© AQUI-VER, INC.

And As We'll Find, It Can Be Complex

(an example source term, viewed in the ground)



Courtesy of the U.S. Navy SCAPS Team; Len Sinfield, Steve Lieberman
(now decommissioned in the infinite wisdom of Uncle Sam)

© AQUI-VER, INC.

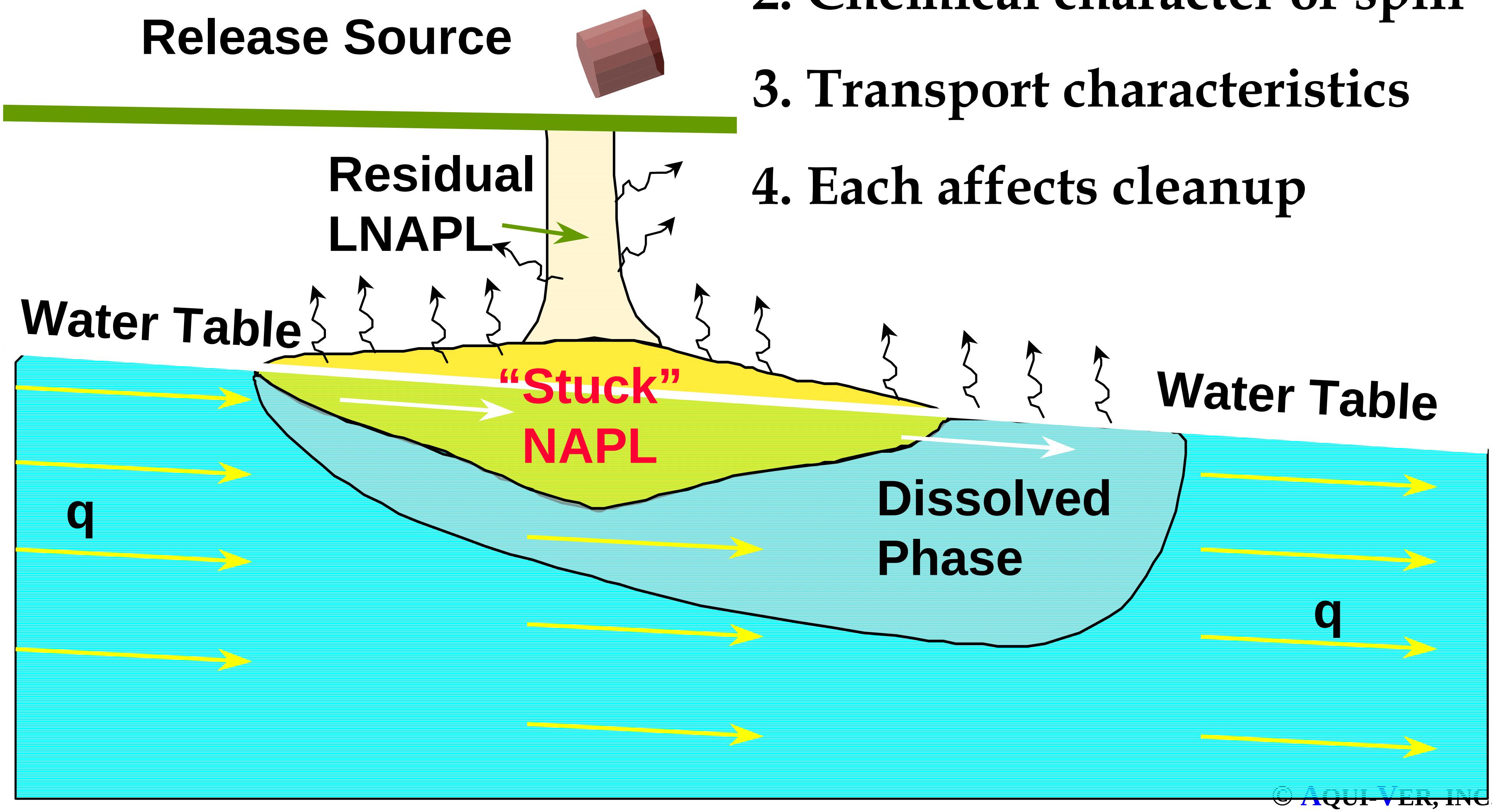
Examples of Using Typical Site Data

To Determine Plume Distribution

© AQUI-VER, INC.

Chemical impacts depend on the LNAPL

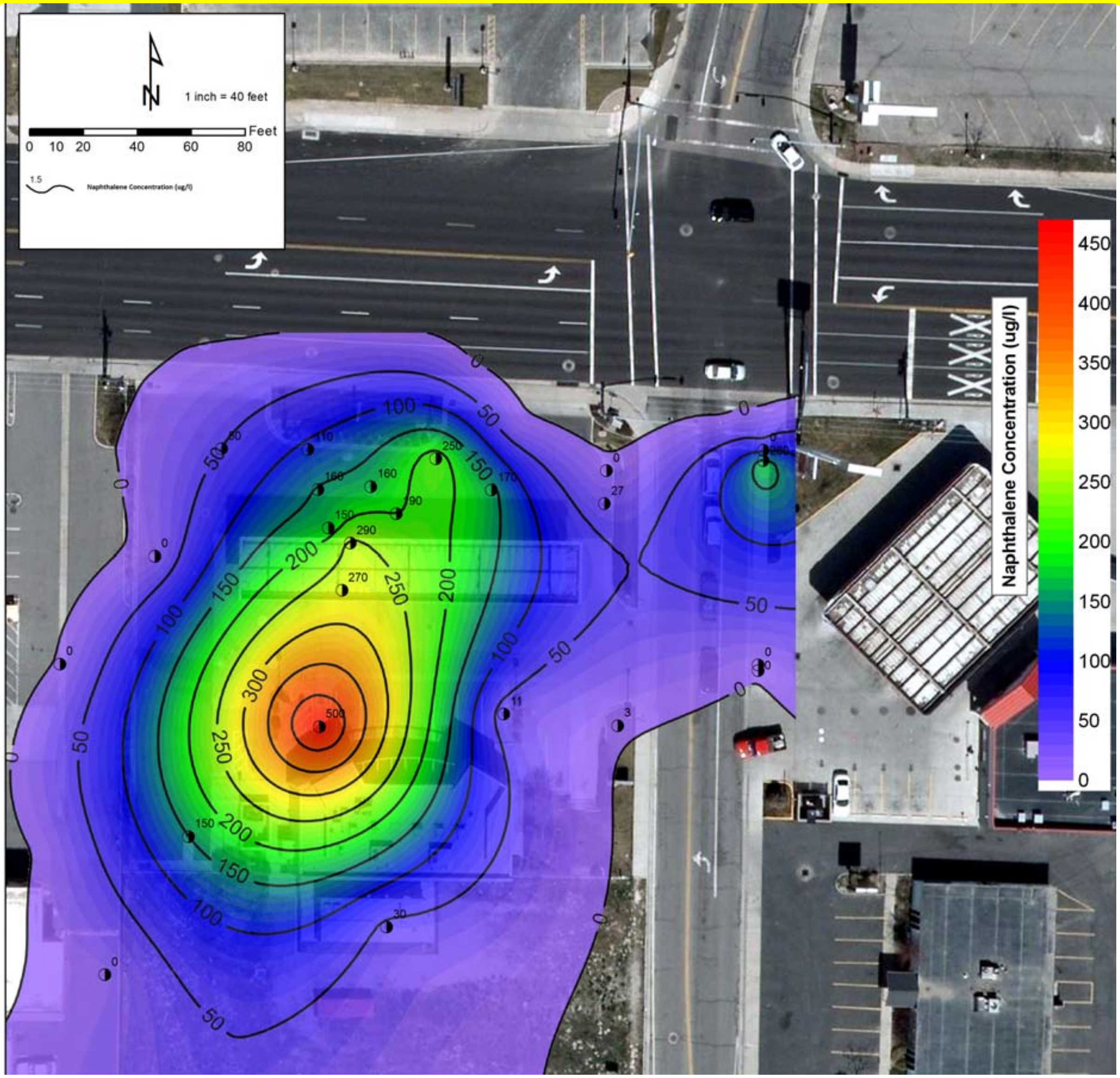
1. Distribution of spill
2. Chemical character of spill
3. Transport characteristics
4. Each affects cleanup



© Aqui-Ver, Inc.

Example Naphthalene Distribution

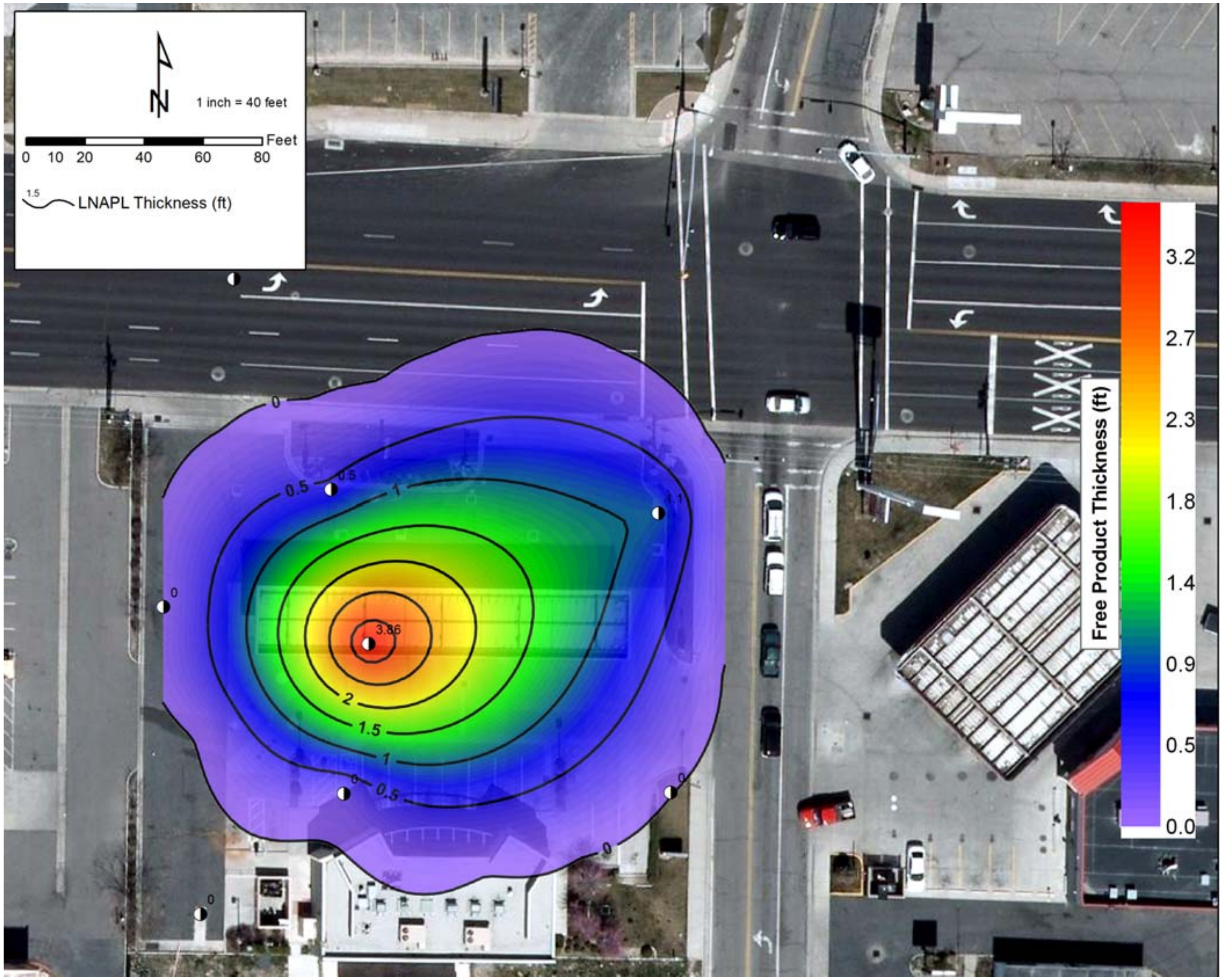
(low mobility compound, what is expected?)



© AQUI-VER, INC.

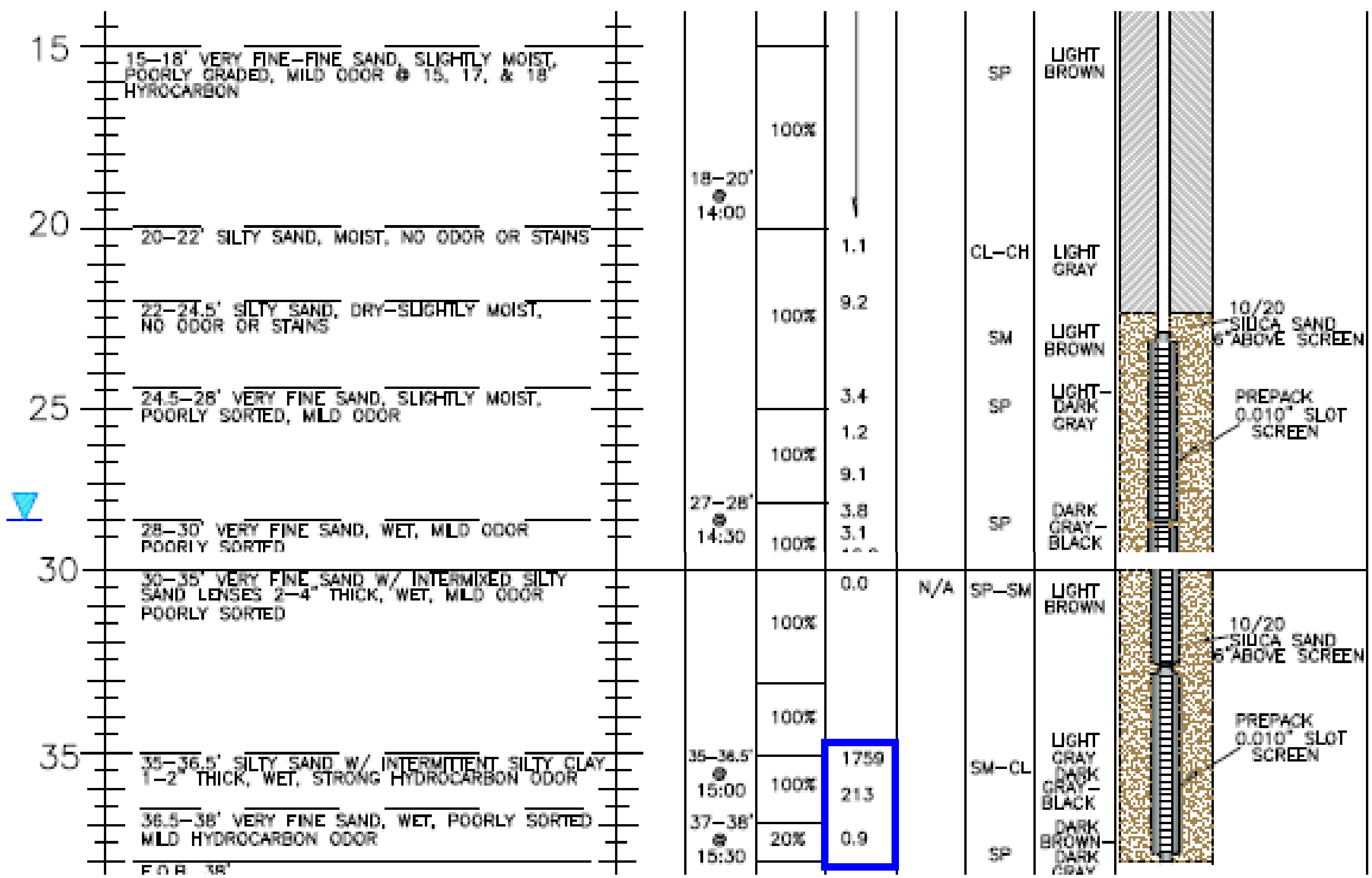
Maximum LNAPL Thickness & Extent

(for all time – why?)



© AQUI-VER, INC.

Look at Boring Logs If Available



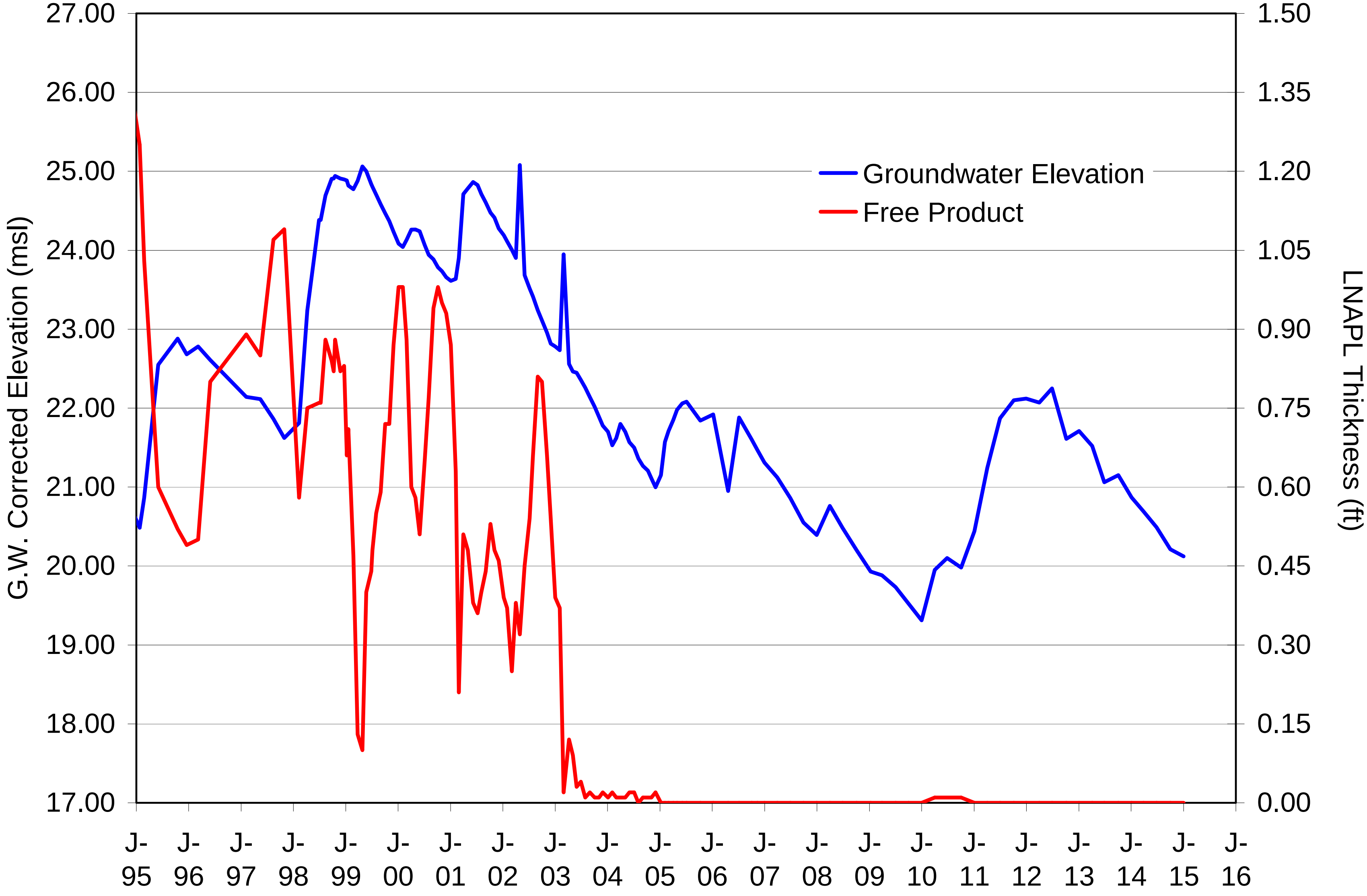
© AQUI-VER, INC.

Look At Available Analytic Data

Location No.	Sample Depth (feet bgs)	Soil Concentrations (mg/kg)							
		Benzene	Ethyl Benzene	MTBE	Naph-thalene	Toluene	Total Xylenes	TPH-GRO	TPH-DRO
B-1	17.5'-19'	0.00217	0.00182	<0.00100	<0.00500	<0.00500	<0.00300	<0.500	<4.00
	25'-27'	<0.248	19.2 J3,J6	<0.248	11.3 J6	2.190	**162**	1360	219 J6
	28'-29'	0.00112	0.00142	<0.00100	<0.00500	<0.00500	0.00488	<0.500	<4.00
	37'-38'	<0.00100	0.00147	<0.00100	<0.00500	<0.00500	0.00684	<0.500	<4.00
B-2	18'-20'	0.00222	0.00300	<0.00100	<0.00500	0.00824	0.0120	<0.500	<4.00
	27'-28'	<0.00100	<0.00100	<0.00100	<0.00500	<0.00500	<0.00300	<0.500	<4.00
	35'-36.5'	0.0604	0.0577	<0.00100	0.0358	0.150	0.372	8.16	4.81
	37'-38'	0.00140	0.00105	<0.00100	<0.00500	<0.00500	0.00526	0.511	<4.00
B-3	8'-10'	<0.00100	<0.00100	<0.00100	<0.00500	<0.00500	0.00533	102	39.4
	20'-22'	0.537	**59.3**	<0.248	15.8	13.7	**294**	**2820**	228
	25'-27.5'	0.00127	<0.00100	<0.00100	0.00662	<0.00500	0.00665	<0.500	<4.00
	27.5'-30'	<0.194	10.6	<0.194	4.10	13.1	81.2	636	79.1
	32.5'-34'	<0.245	7.53	<0.245	7.03	2.52	64.2	407	49.5
B-4	14'-16.5'	<0.00100	<0.00100	<0.00100	<0.00500	<0.00500	<0.00300	<0.500	<4.00
	22.5'-24'	0.00122	0.00161	<0.00100	<0.00500	<0.00500	0.00527	<0.500	<4.00
	34'-36'	0.00173	0.00182	<0.00100	<0.00500	<0.00500	0.00301	<0.500	<4.00
B-5	17.5'-20'	0.00180	0.00175	<0.00100	<0.00500	<0.00500	0.00693	<0.500	<4.00
	22.5'-25'	0.00156	0.00183	<0.00100	<0.00500	<0.00500	0.00655	<0.500	<4.00
	34'-35'	0.00265	0.00263	<0.00100	<0.00500	<0.00500	0.00308	<0.500	<4.00

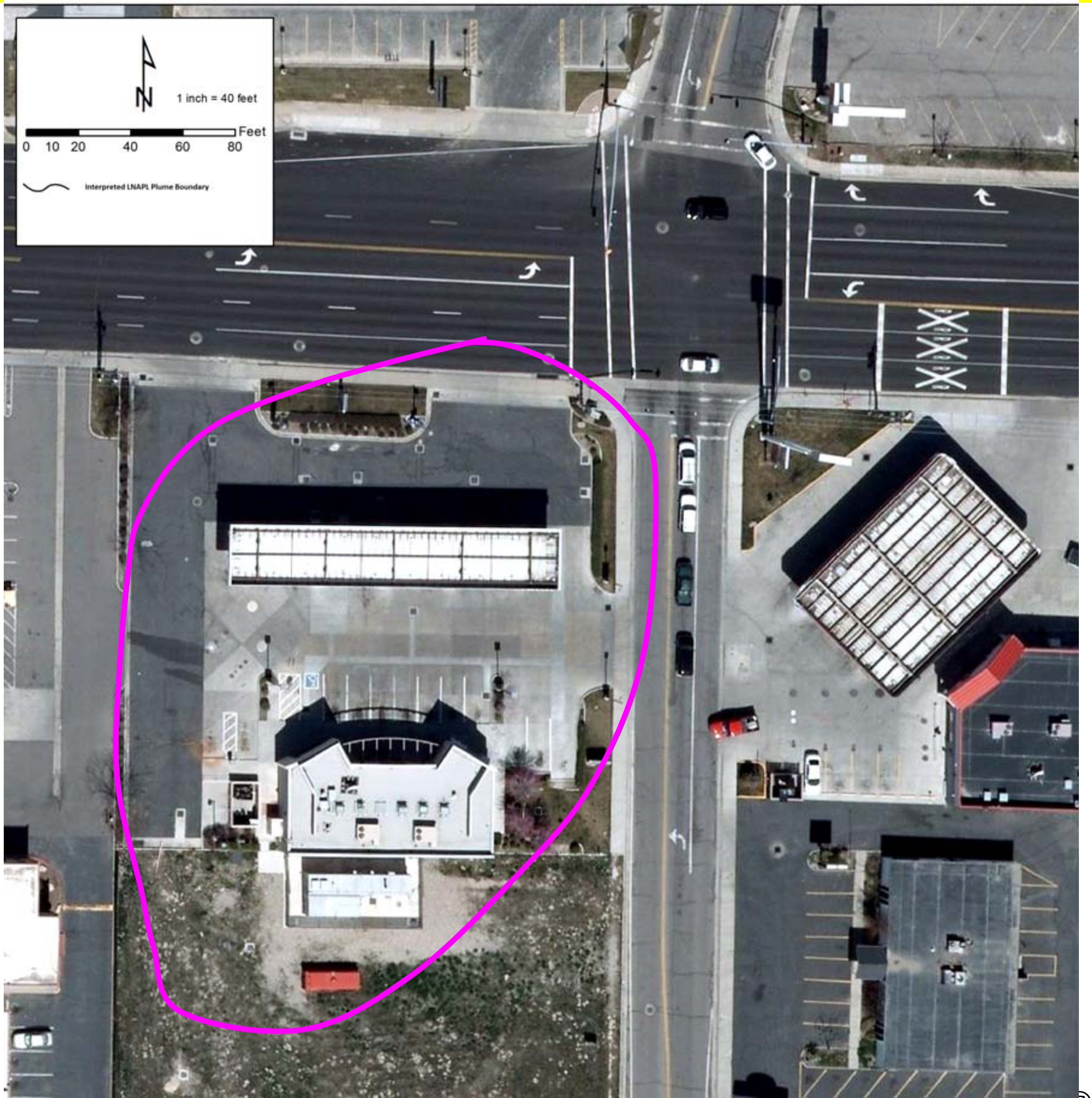
© AQUI-VER, INC.

Periphery Hydrographs with LNAPL



© AQUI-VER, INC.

Resulting in The Estimated LNAPL Extent



© AQUI-VER, INC.

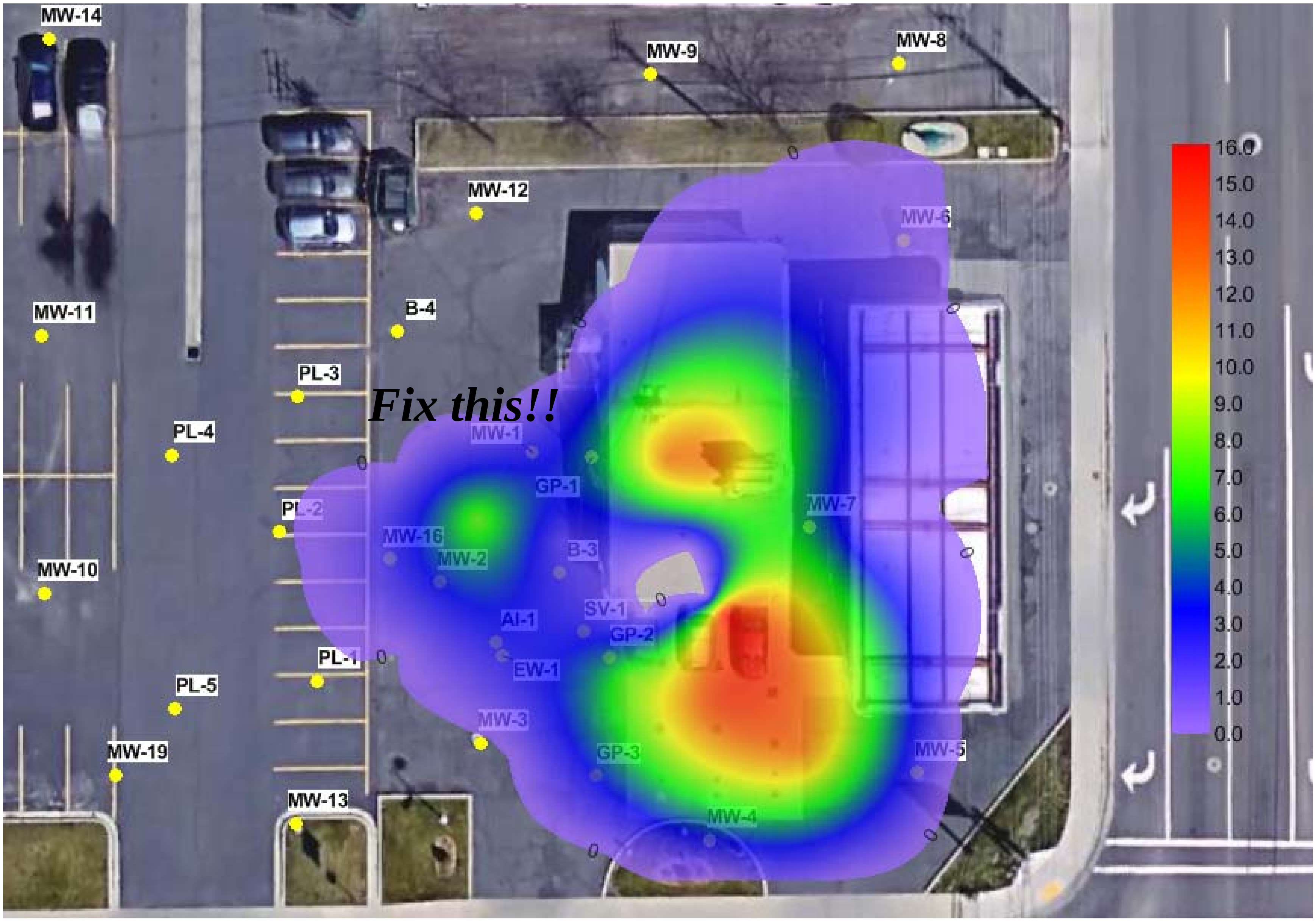
Easy Enough to Estimate LNAPL Smear Zone

(analytic data + boring log reviews)

Well	X-ft	Y-ft	Z-ft	SMZ-thick	Top Smear Zone-ft	Bottom Smear Zone-ft	enzene Conc Soil-mg/	PH-G Conc Soil-mg/
GP-1	255.038	123.464	100	12.56	94	90	4.96	2140
GP-2	258.471	84.749	100	15.7	95	90	0.245	616
GP-3	255.846	61.908	100	14.13	95.5	91	1.56	3000
MW-1	243.5207	124.4933	99.95	12.56	93.95	89.95	6.55	3410
MW-2	225.5762	99.37104	99.6	1.57	91.1	90.6	14.4	3060
MW-3	233.471	68.285	99.25	7.85	92.25	89.75	11.6	3910
MW-4	277.8264	49.54866	100	12.56	91	87		
MW-5	318.0432	62.53204	99.54	0	-	-	0.0053	2.46
MW-6	315.2987	165.449	99.57	0	-	-	0.599	44.8
MW-7	297.064	110.016	99.81	0	-	-	1.89	846
MW-8	314.4543	199.6491	99.02	0	-	-	0	0
MW-9	266.2152	197.538	99.66	0	-	-	0	0
MW-10	149.2593	97.25993	98.49	0	-	-	0	0
MW-11	148.626	146.9768	98.16	0	-	-	0.0104	0
MW-12	232.5429	170.6213	99.39	0	-	-	0	0.0706
MW-13	197.745	52.651	99.88	0	-	-	0	0.665
MW-14	150.012	204.451	98.32	0	-	-	0.00521	0.072
MW-15	183.6611	215.8249	98.42	0	-	-	0	0
MW-16	216.0762	103.8044	99.65	1.57	90.65	90.15	14.2	4170
MW-17	55.087	147.306	98.57	0	-	-	0	0
MW-18	54.593	204.55	98.27	0	-	-	0	0
MW-19	162.796	62.066	98.38	0	-	-	0	0.149

© AQUI-VER, INC.

Interpreted LNAPL Smear Zone Distribution



© AQUI-VER, INC.

Summary of Site Data Use

- We often have a lot of data
  - And it often cost a lot of $$ to acquire
- We can use common data to figure:
  - LNAPL plume distribution/boundary
  - LNAPL impacts & mass
  - How dissolved-plumes reflect LNAPL
  - LNAPL mobility/stability
- So for many Tier I sites
  - We don’t need additional data
  - Need to work more with what we have

© AQUI-VER, INC.

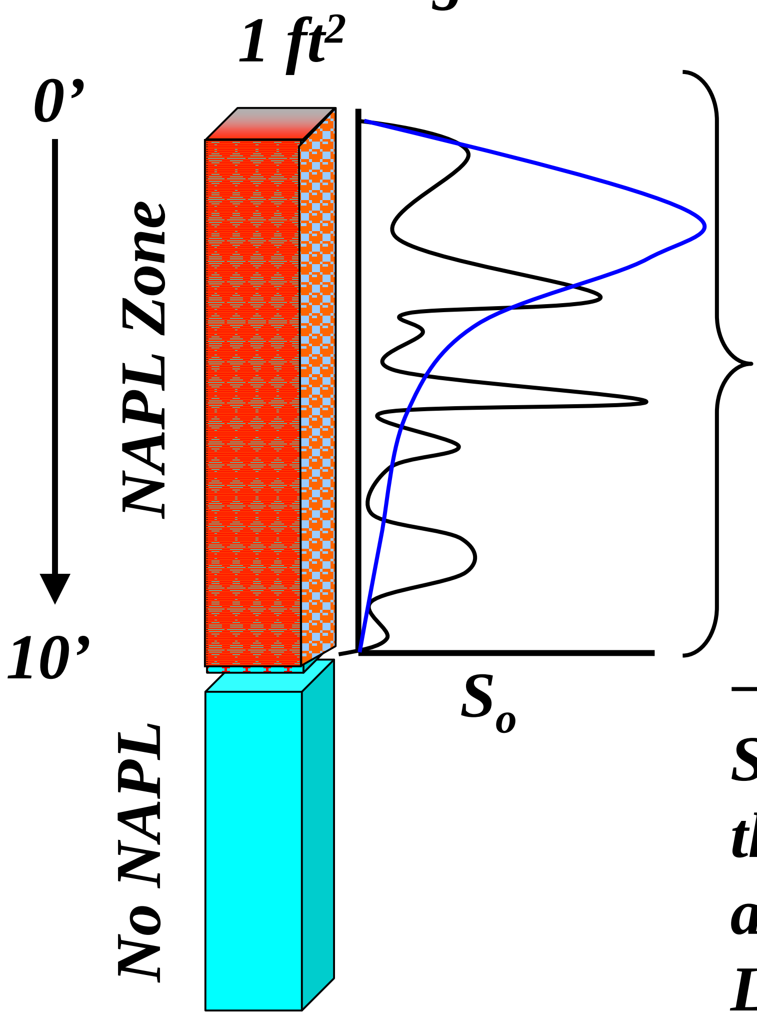
Lets Use Capillary Theory to Estimate Formation LNAPL Volume

We'll use a real site as an example, & we'll also see from it what can go wrong…

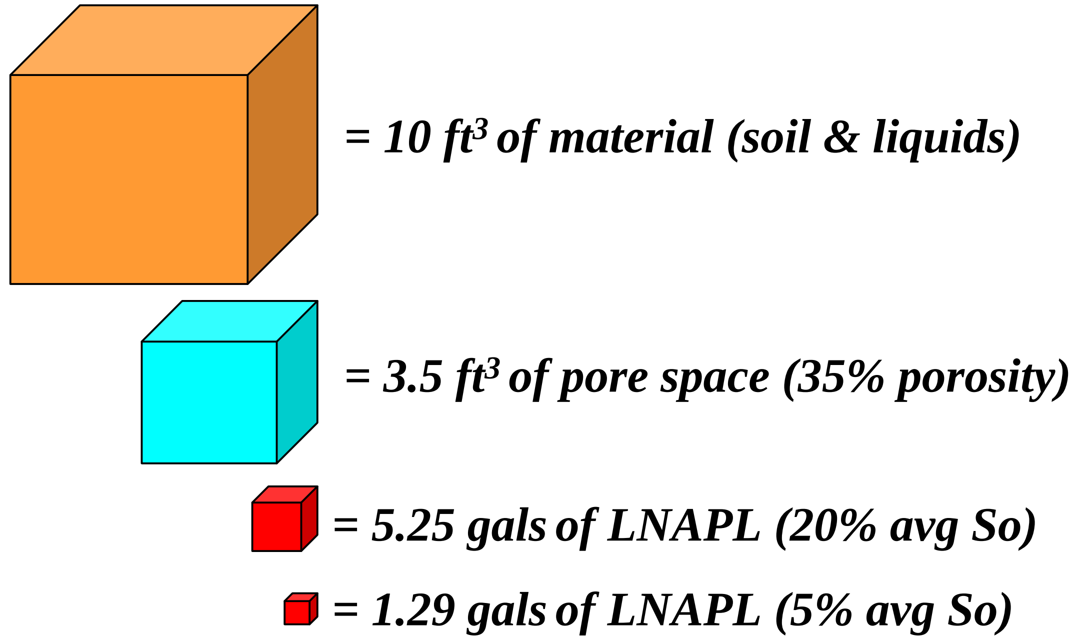
© AQUI-VER, INC.

First: Definition of Specific Volume

Schematic Boring Location



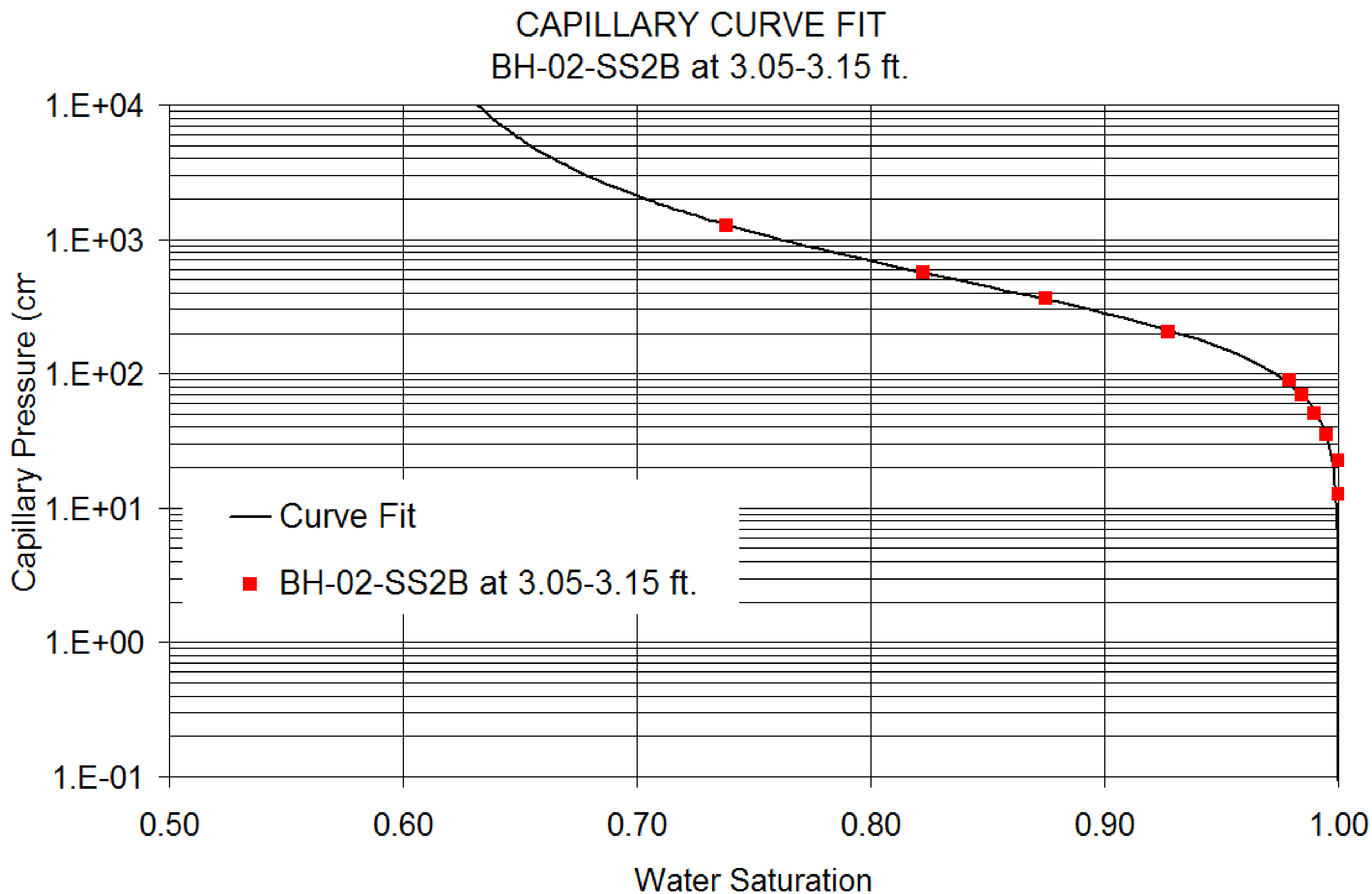
What's in that 10-ft Column?



So, specific volume is the volume of oil that would exist within a boring 1 ft^2 in area over the full vertical interval of LNAPL presence (units = vol/area).

© AQUI-VER, INC.

Example Capillary Curve For This Site



© AQUI-VER, INC.

After Huntley, 2006

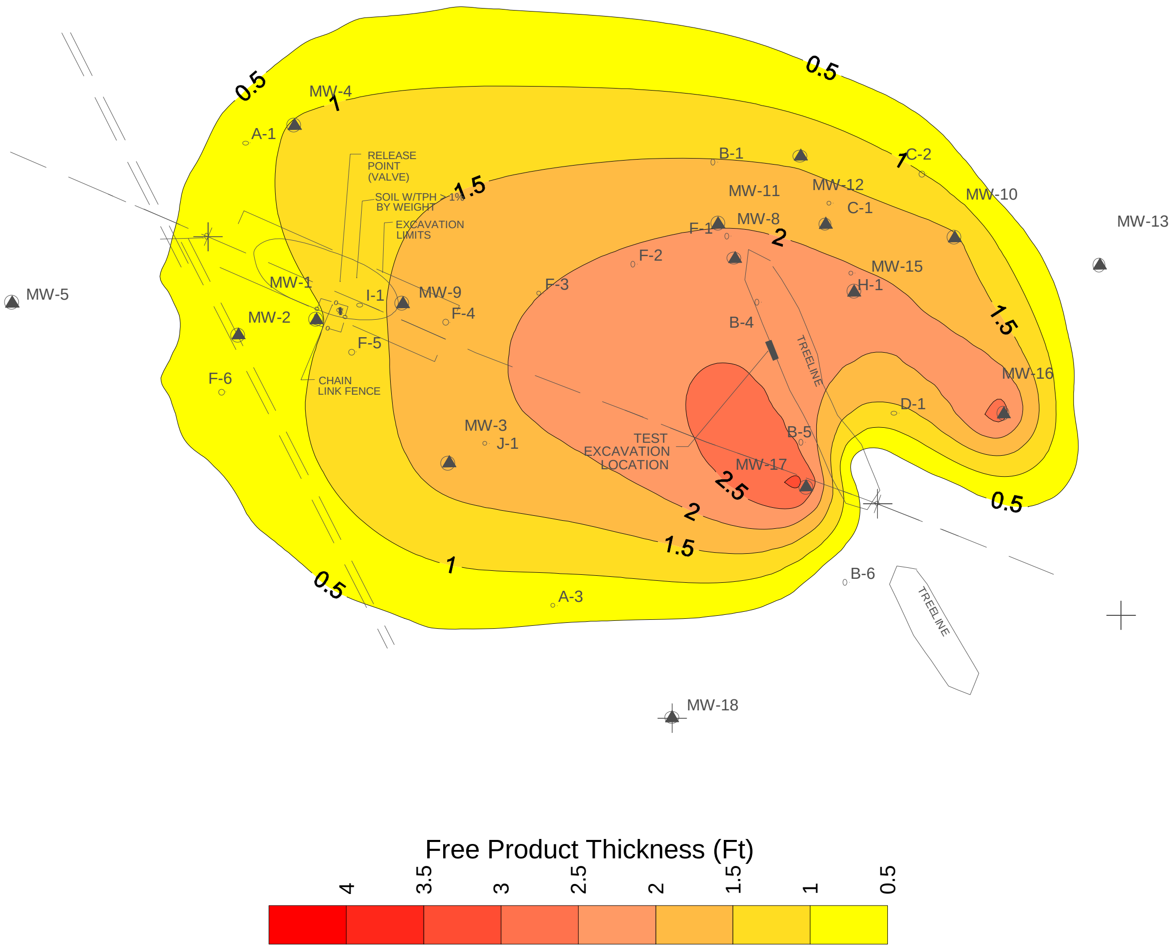
Fluid Properties (Lab)

SAMPLE ID	MATRIX	TEMP., (°F)	SPECIFIC GRAVITY	DENSITY (g/cc)	VISCOSITY (centistokes)	VISCOSITY (centipoise)
BH-1	NAPL	60	0.8392	0.8384		
		70		0.8327	5.56	4.63
		100		0.8210	3.78	3.11
		130		0.8090	2.75	2.23
BH-2	NAPL	60	0.8411	0.8403		
		70		0.8346	5.81	4.85
		100		0.8226	3.98	3.28
		130		0.8099	2.93	2.37
BH-3	NAPL	60	0.8381	0.8373		
		70		0.8318	5.36	4.46
		100		0.8201	3.63	2.97
		130		0.8070	2.73	2.20

PHASE PAIR SAMPLE ID / PHASE	PHASE PAIR SAMPLE ID / PHASE	TEMP., (°F)	INTERFACIAL TENSION, (Dynes/centimeter)
MW-2 (WATER)	AIR	74	73.0
MW-2 (WATER)	MW-8 (NAPL)	74	25.4
MW-2 (NAPL)	AIR	74	26.4
MW-4 (WATER)	AIR	72	72.6
MW-4 (WATER)	MW-9 (NAPL)	73	17.6
MW-4 (NAPL)	AIR	73	27.3
MW-6 (WATER)	AIR	71	74.0
MW-6 (WATER)	MW-10 (NAPL)	71	25.9
MW-6 (NAPL)	AIR	71	26.3

© AQUI-VER, INC.

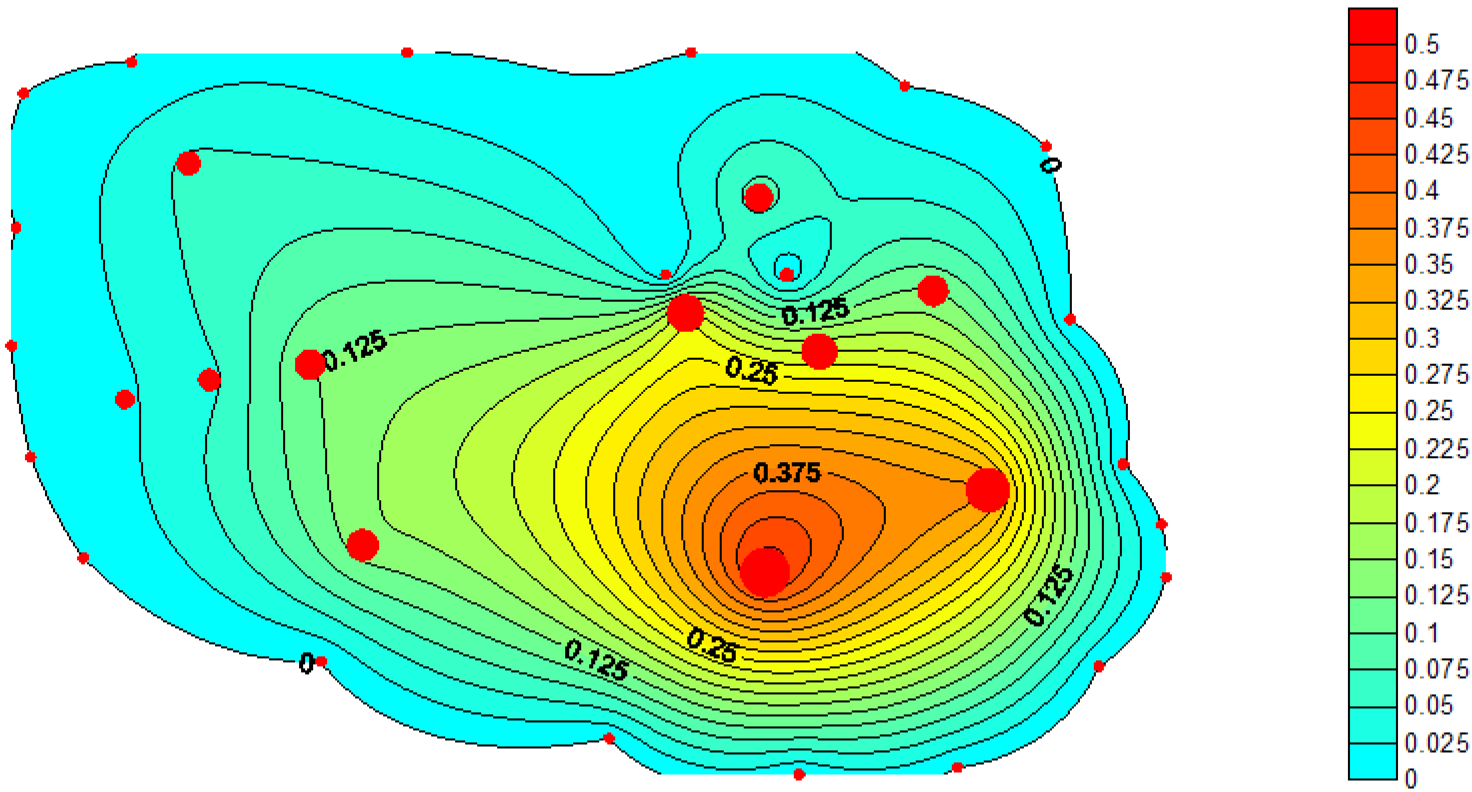
Observed Well Thickness Map



© AQUI-VER, INC.

Resulting Volume Integration Map

(total volume ~ 62,000 gallons)



Neat stuff, eh?

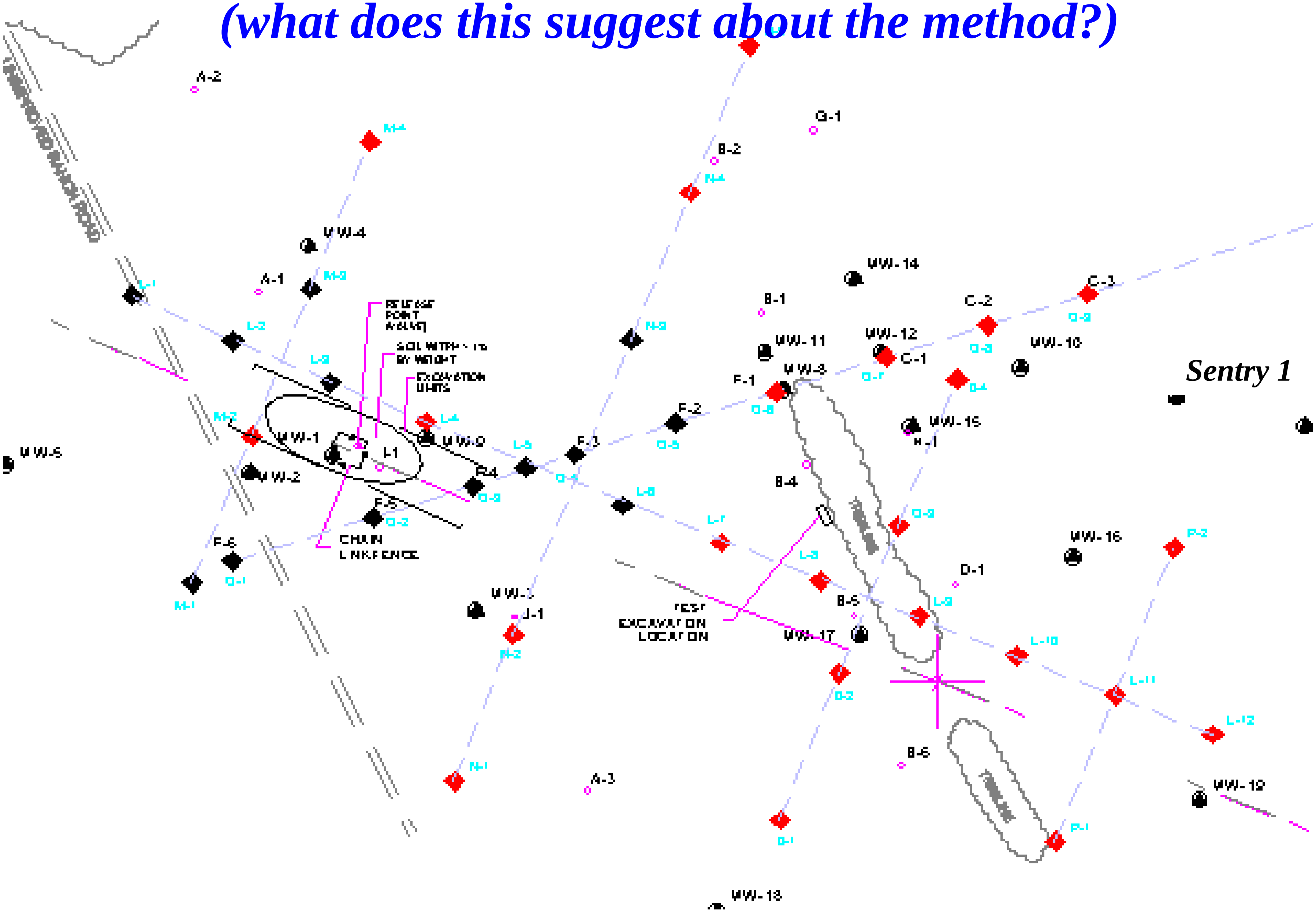
BUT, is that a realistic plume volume?

(sorry we had to ask)

© AQUI-VER, INC.

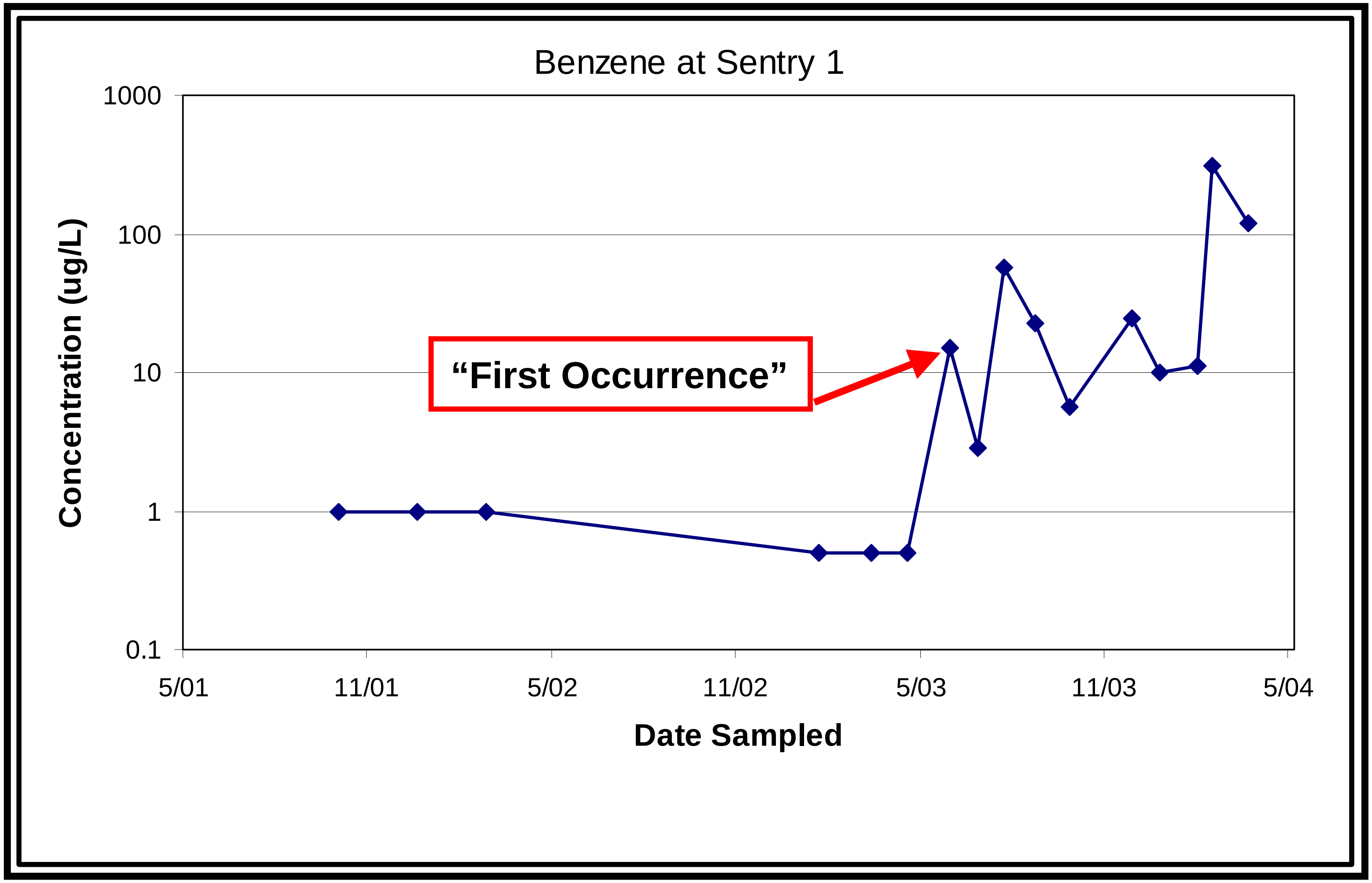
Oil Plume Footprint Through Time

(what does this suggest about the method?)



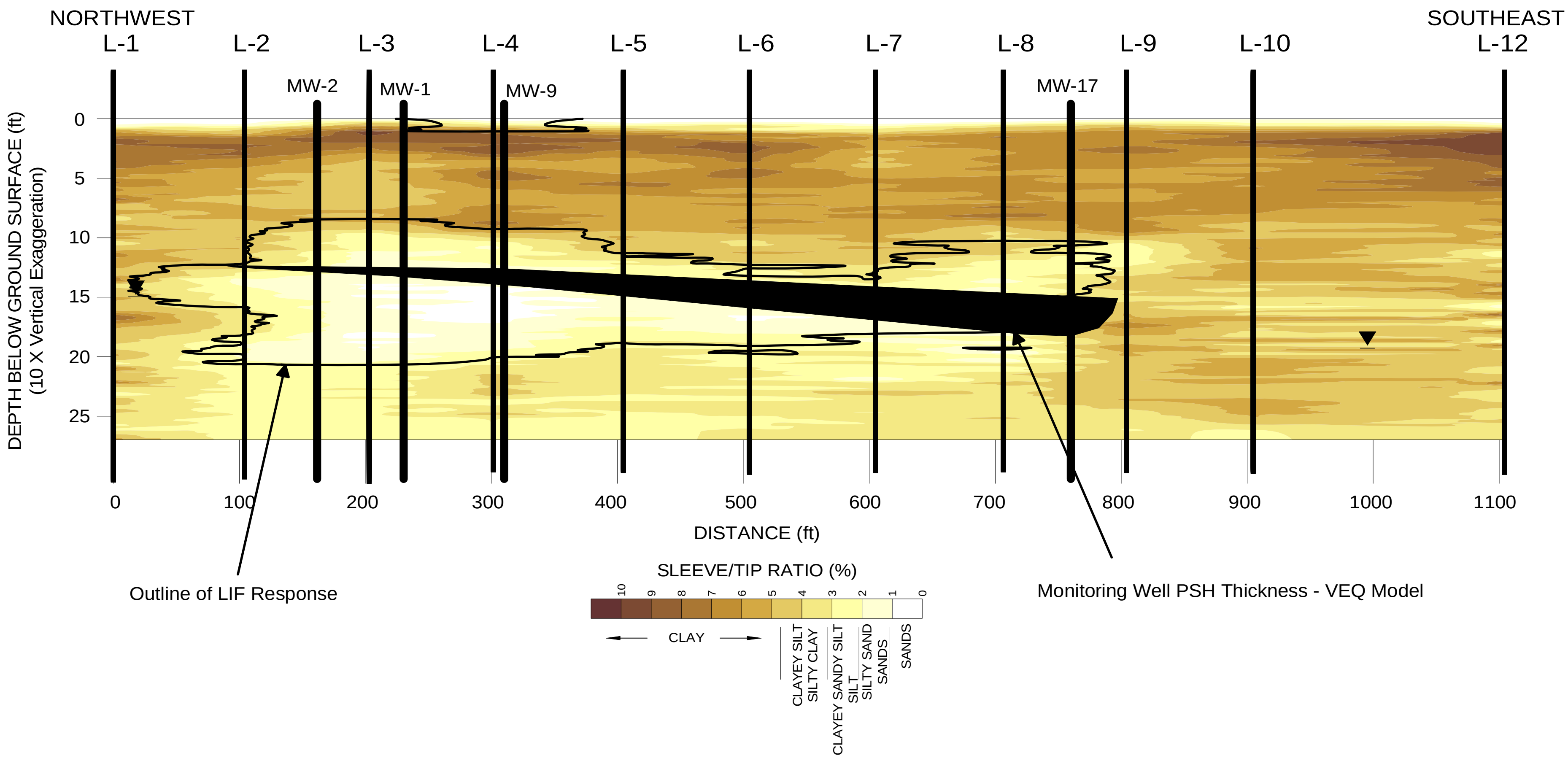
© AQUI-VER, INC.

Dissolved Benzene Record For Sentry 1



© AQUI-VER, INC.

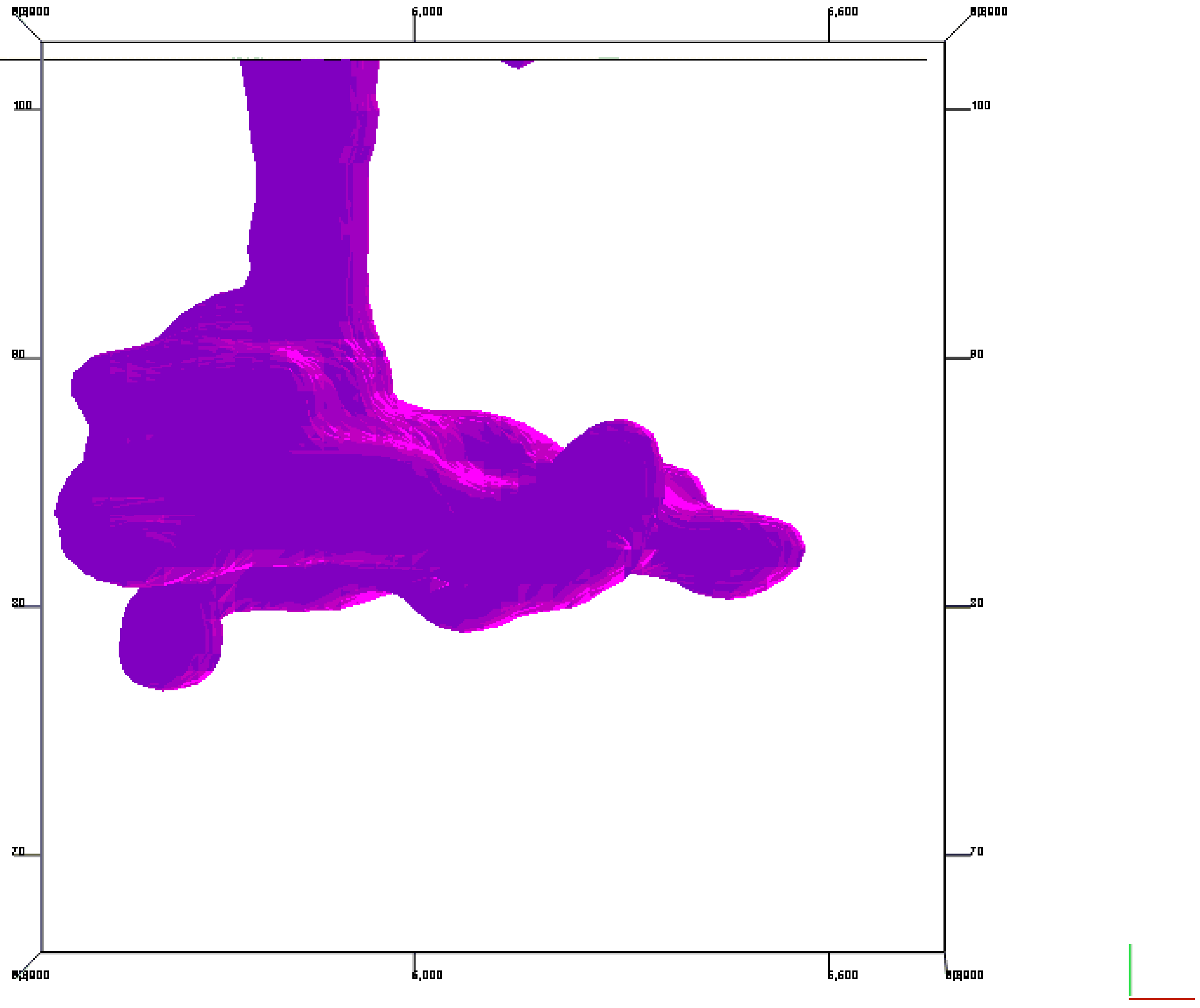
LNAPL Distribution Vs. VEQ Model



© AQUI-VER, INC.

3D Animation of a Smear Zone – Side View

(actual LNAPL volume ~ 750k gallons)



© AQUI-VER, INC.

Total Volume is Vastly Underestimated

(because VEQ estimates only the free-phase fraction)

- Remember, the 1st premise is that of VEQ conditions
  - All LNAPL would have to be in communication with wells
  - Residual is not in communication with the well
- For this example, free-phase is less than 10% of total
  - And the plume is only a few years old at that time
- So for an older, heterogeneous plume
  - VEQ even less likely to be representative
- Homogenous & stable conditions are needed for VEQ
  - Still can have challenges; recall NAPL cross-section
  - Need to account for residual zones
  - TOTAL mass controls risk & longevity
- In short, well thickness is NOT a good proxy for total mass

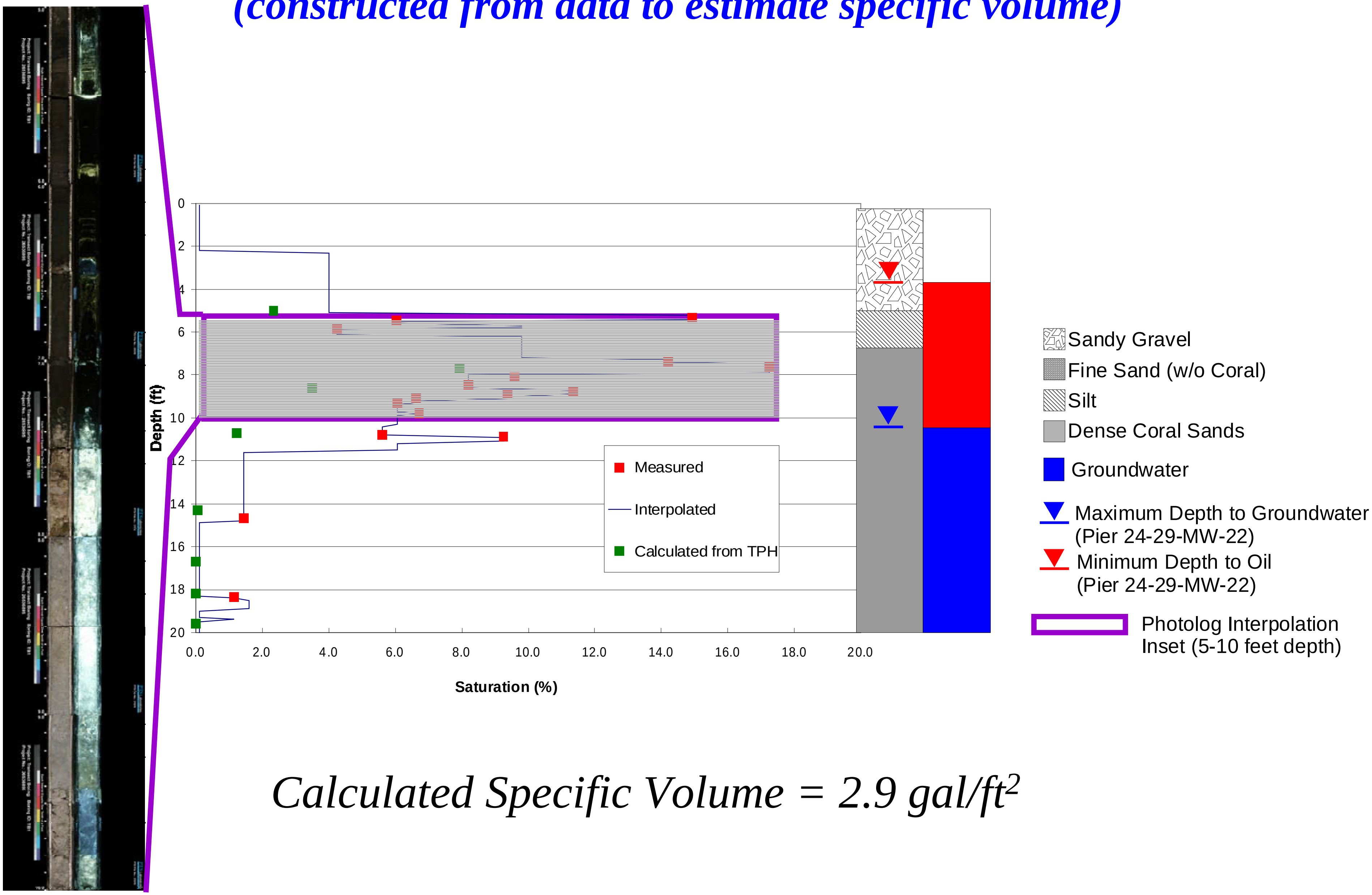
© AQUI-VER, INC.

Let's Use Boring Saturation Data to Estimate LNAPL Volume

Same goal, but different path...

Site Specific Saturation Profile: TB-1

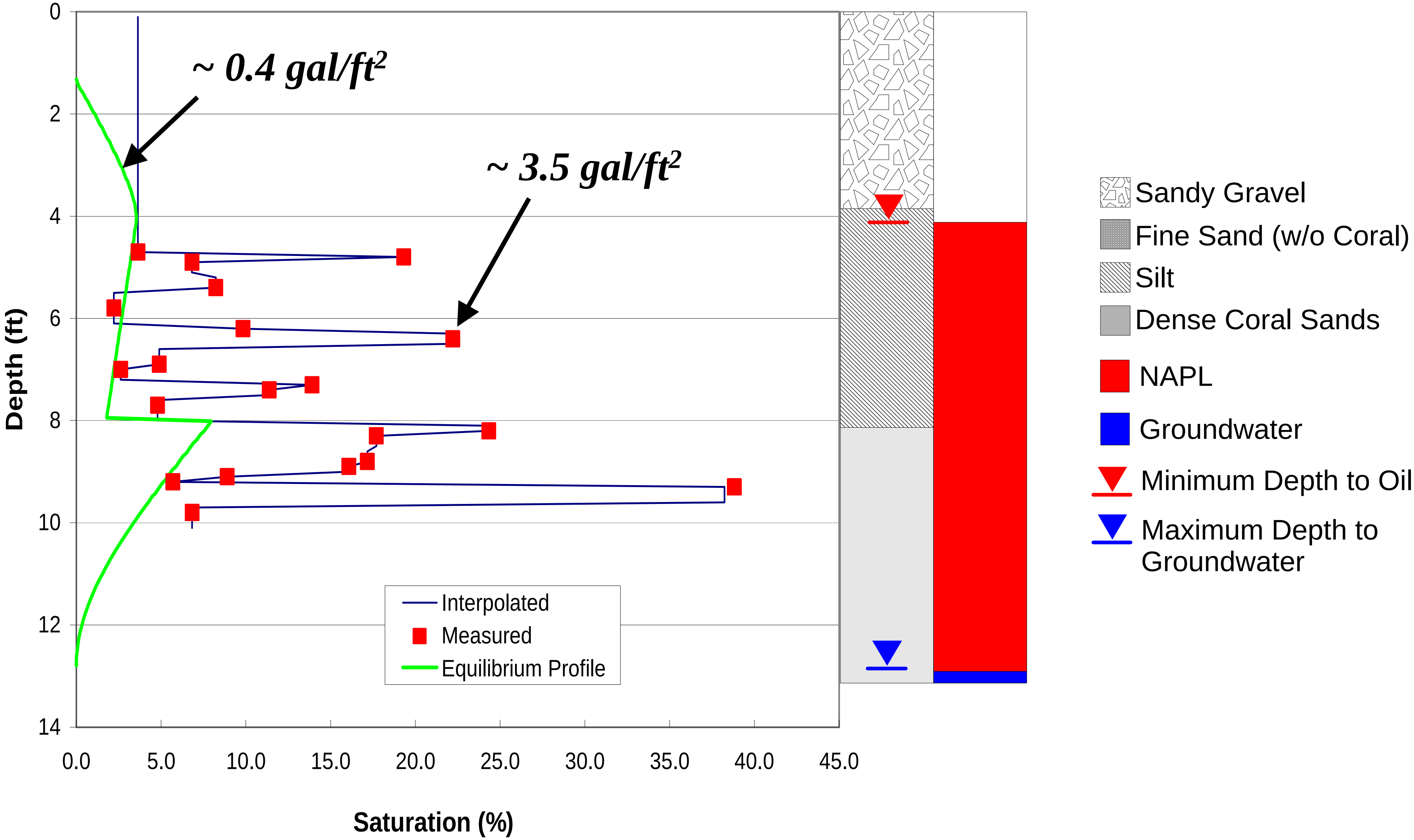
(constructed from data to estimate specific volume)



Calculated Specific Volume = 2.9 gal/ft²

AQUI-VER, INC.

Would Equilibrium Theory Work? No.
BH-07/Pier 24-29-MW-19

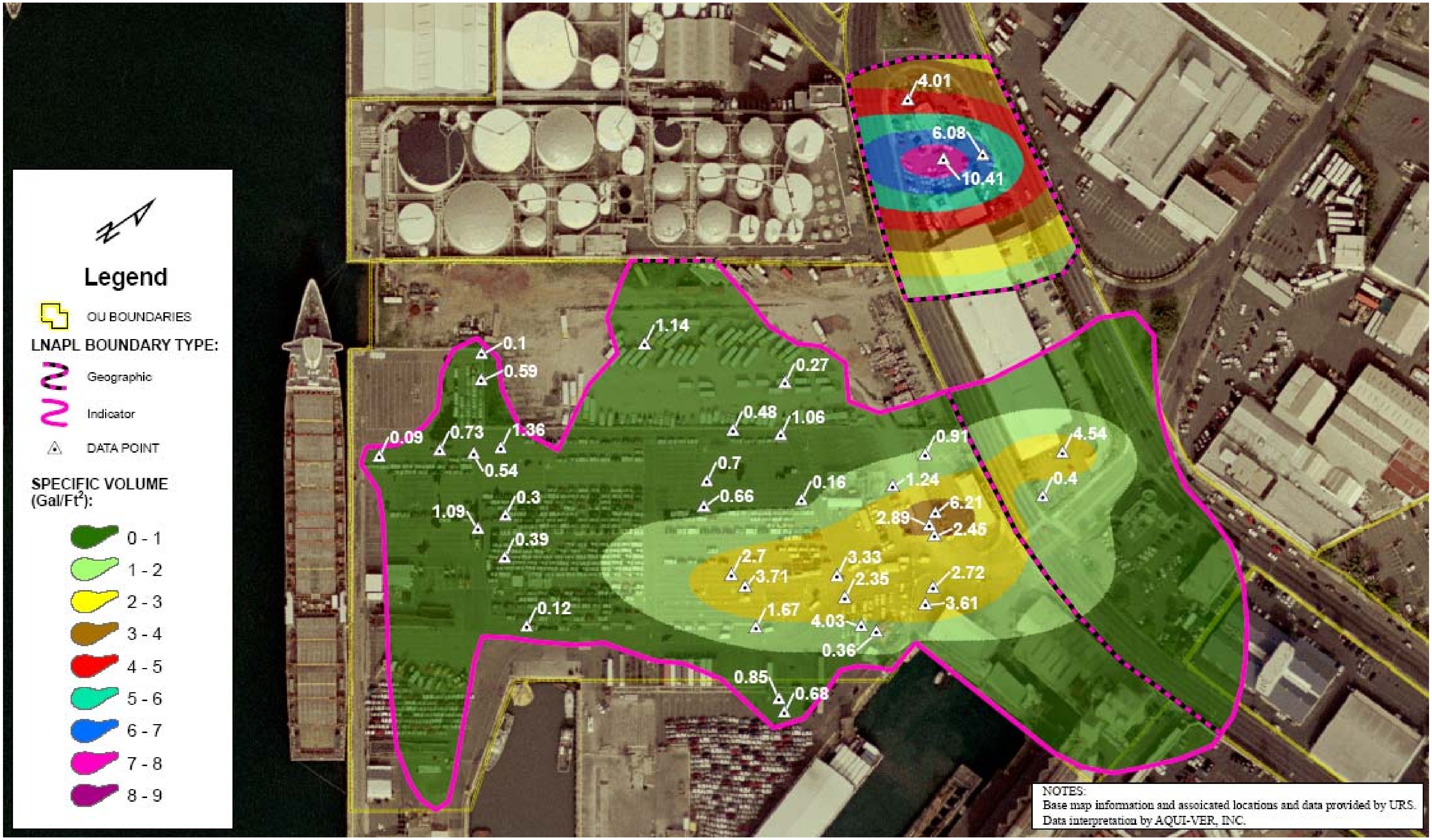


Base profile after Huntley, 2006

© AQUI-VER, INC.

Example of an LNAPL Volume Estimate

(kriging with geomean porosity by soil type)



© AQUI-VER, INC.

Mobility & Well Free Product Observations

What we see in a well has meaning, but it's not simple in many cases (like at Honolulu Harbor)

© AQUI-VER, INC.

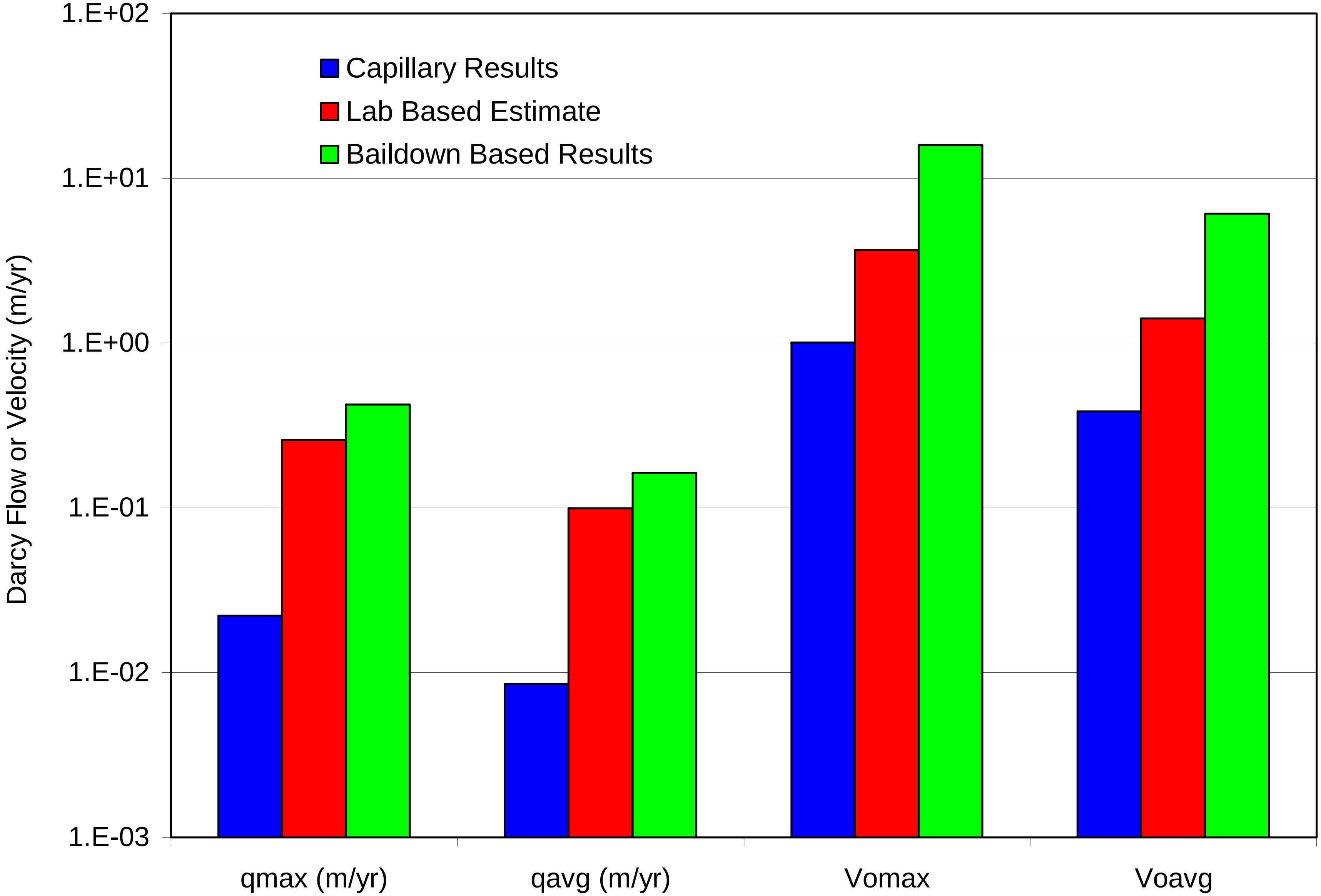
Screening Mobility Evaluation

- Need to estimate oil K and combine with oil gradient
  - K can be estimated by several general methods
    - Through oil slug testing
    - Through pump testing
    - Through lab core analysis
      - Saturation & relative permeability estimated by capillarity
      - Field saturation values taken directly
- Oil gradient is simply the top of oil at atmospheric
  - Exactly analogous to how a water table surface is estimated
  - The oil gradient was likely originally radial
  - Eventually the oil gradient collapses to groundwater
- All combined for a “now” estimate of spreading potential

© AQUI-VER, INC.

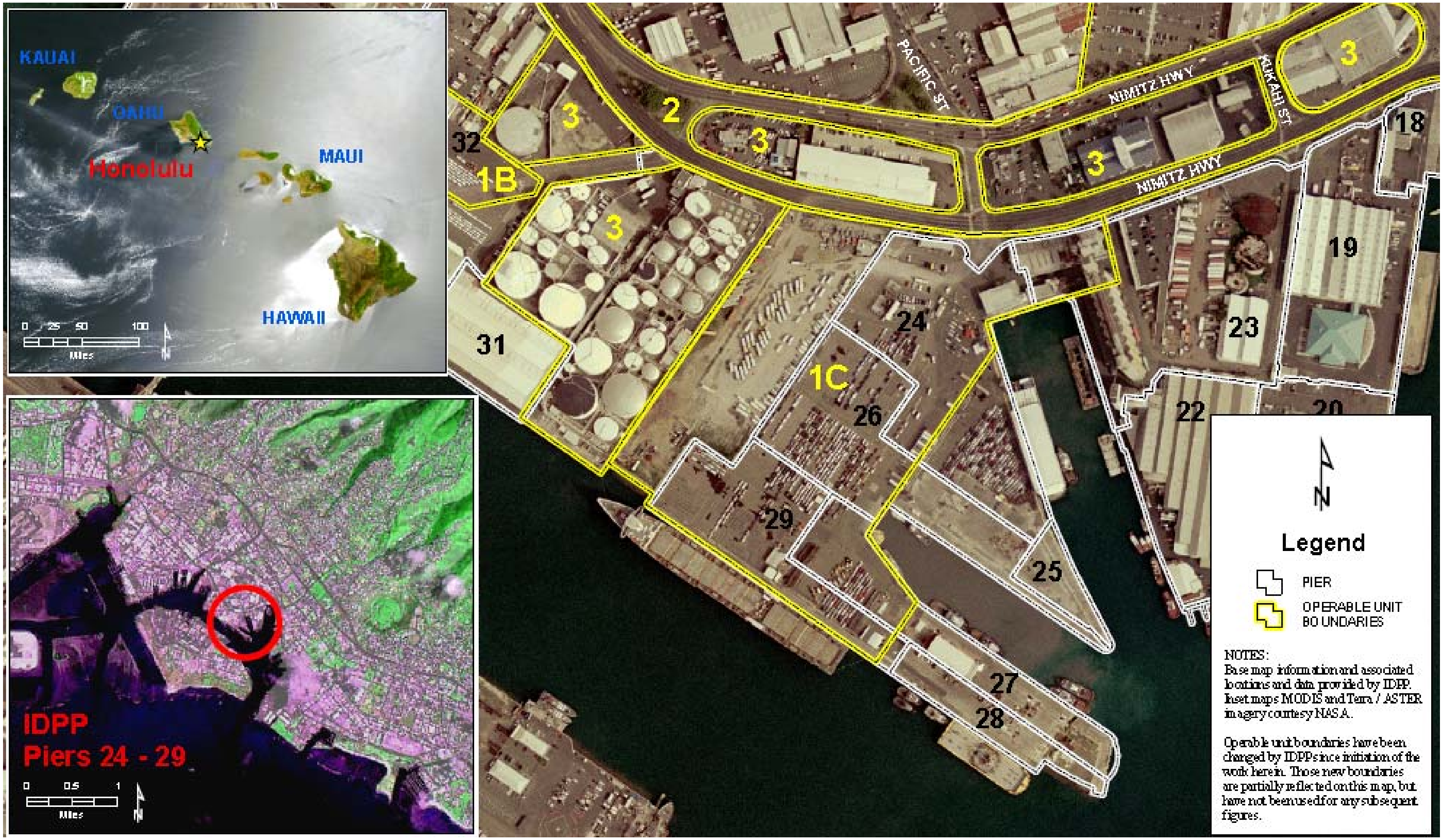
Darcy & Pore Velocity Potential For Oil

(calculated to represent current & worst-case future conditions)



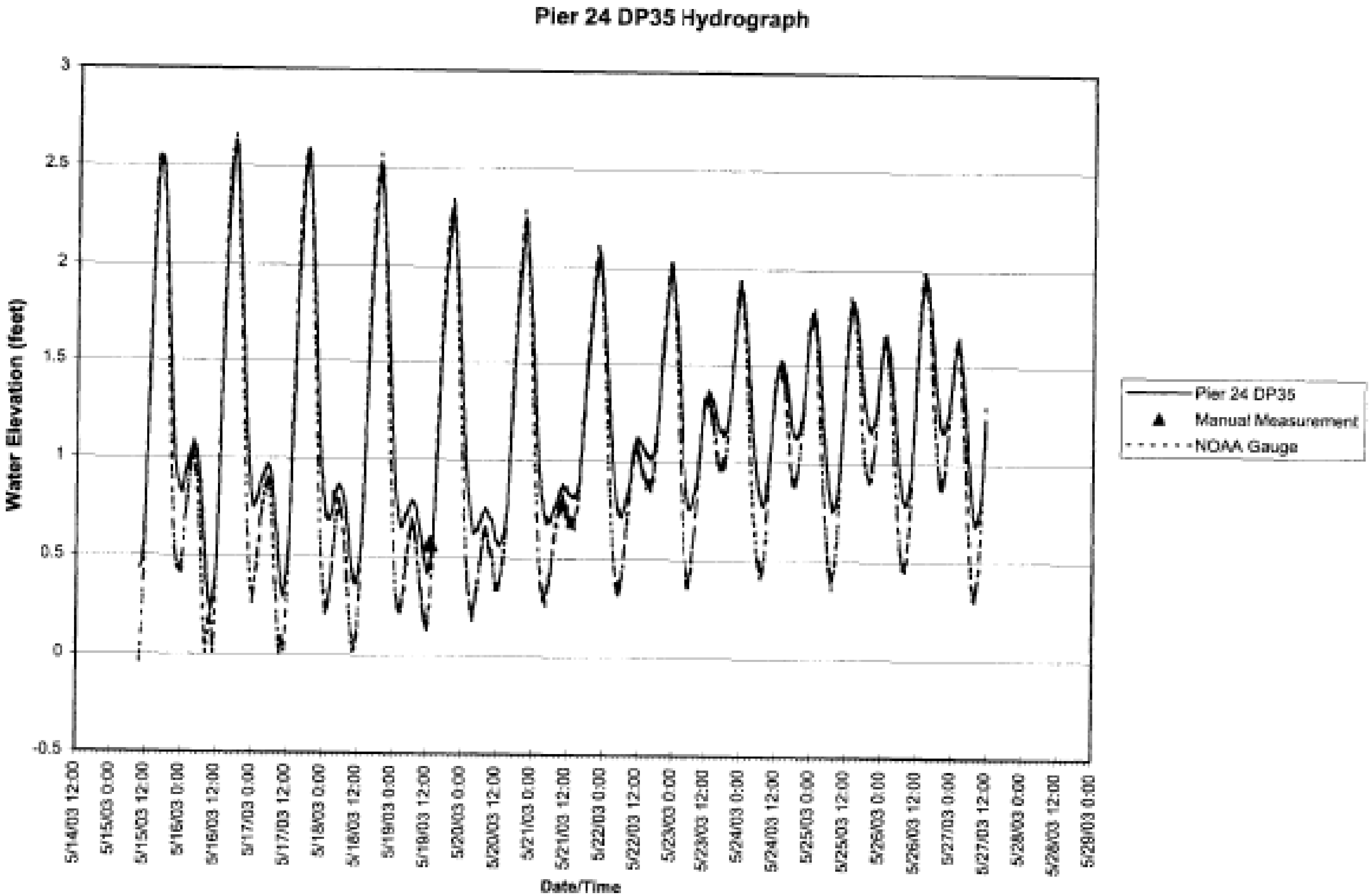
© AQUI-VER, INC.
© AQUI-VER, INC.

Site Index and Area Map



© AQUI-VER, INC.

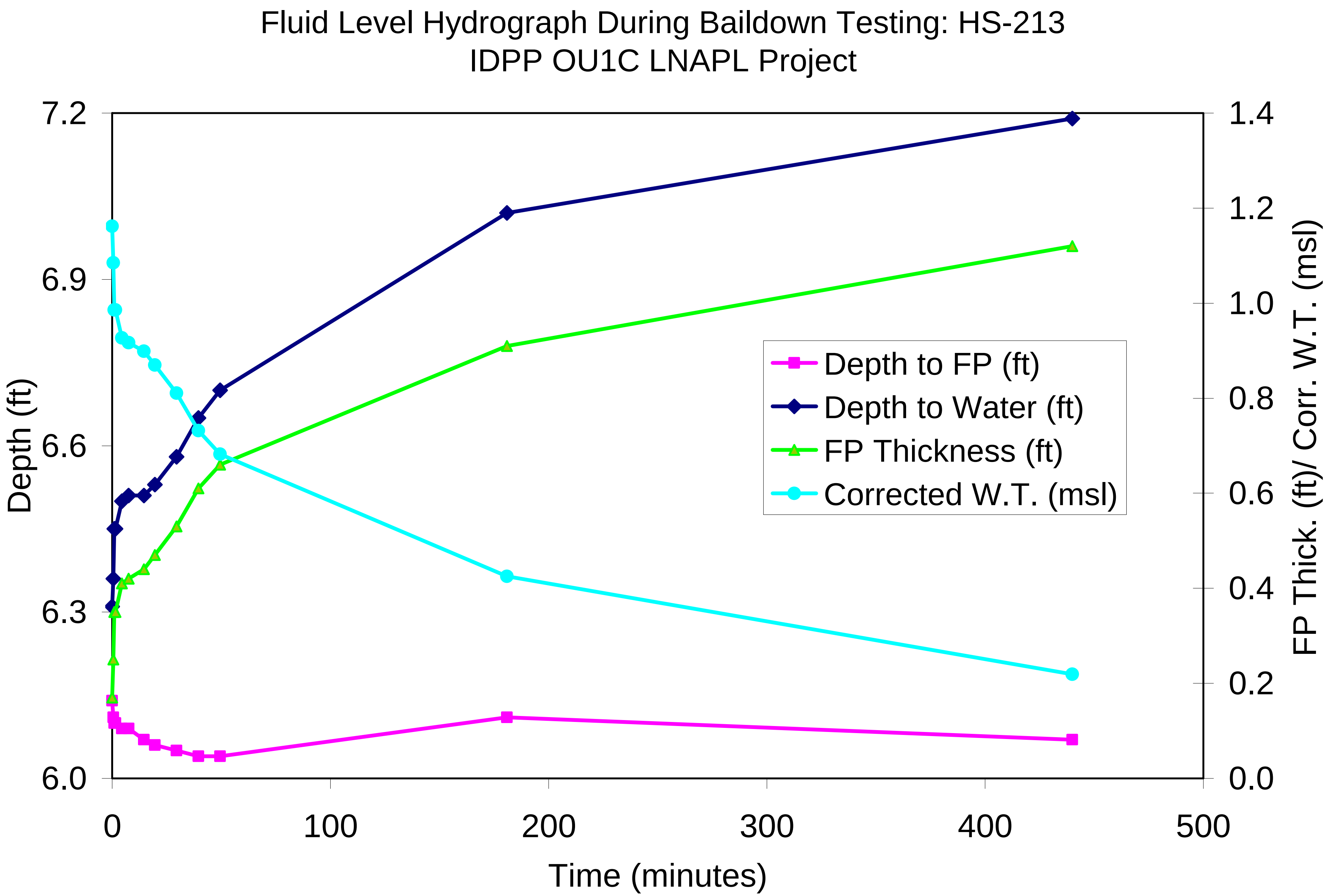
Example: Tidal Response in Onsite Wells



C.

Example LNAPL Baildown Test

Falling Water Table (tide) Influenced Results



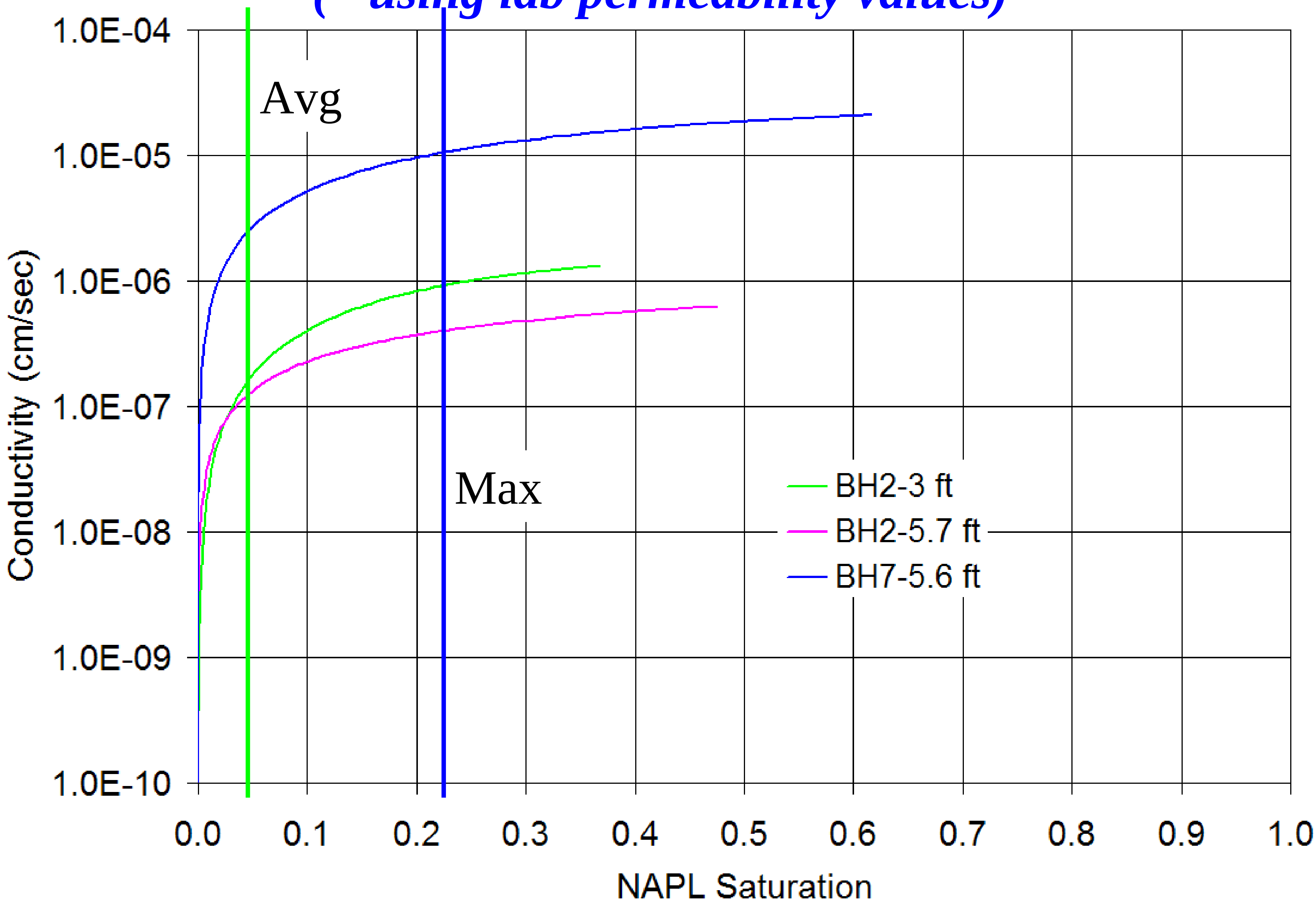
LNAPL Physical Properties

Sample LOCATION	Gravity (60 F) (g/ml)	Density (104 F) (gm/cc)	Viscosity (104 F) (cSt)	Viscosity (104 F) (cP)	IFT (oil/water) (dynes per cm)
MW-10	0.8606	0.8597	4.53	3.89	--
MW-14	0.8861	0.8853	5.87	5.20	--
MW-15	0.8791	0.8782	4.38	3.85	--
DP-66 (MW-13)	0.8784	0.8775	4.72	4.14	--
DP-19 (MW-19)	0.9091	0.9082	23.79	21.61	--
DP-34	0.9096	0.9087	11.05	10.04	--
HS-213	0.9038	0.9029	12.12	10.94	24
HS-214	0.8873	0.8864	8.22	7.29	--
HS-205	0.8841	0.8832	5.17	4.57	24
DP-46	0.8328	0.832	1.75	1.46	--
DP-42	0.8554	0.8546	2.64	2.26	25
DP-7	0.7847	0.7839	0.87	0.68	8
MW-17	0.7889	0.7881	0.86	0.68	--
MW-18	0.798	0.7972	1.00	0.80	--
MW-32	0.8941	0.8932	13.21	11.80	28
MW-31	0.9002	0.8993	16.30	14.66	27
MW-22	0.8734	0.8725	6.53	5.70	23
DP-38	0.888	0.8871	7.71	6.84	--
MW-7	0.8259	0.8251	1.52	1.25	--

© AQUI-VER, INC.

Effective LNAPL Conductivity; Silt Soils

(* using lab permeability values)

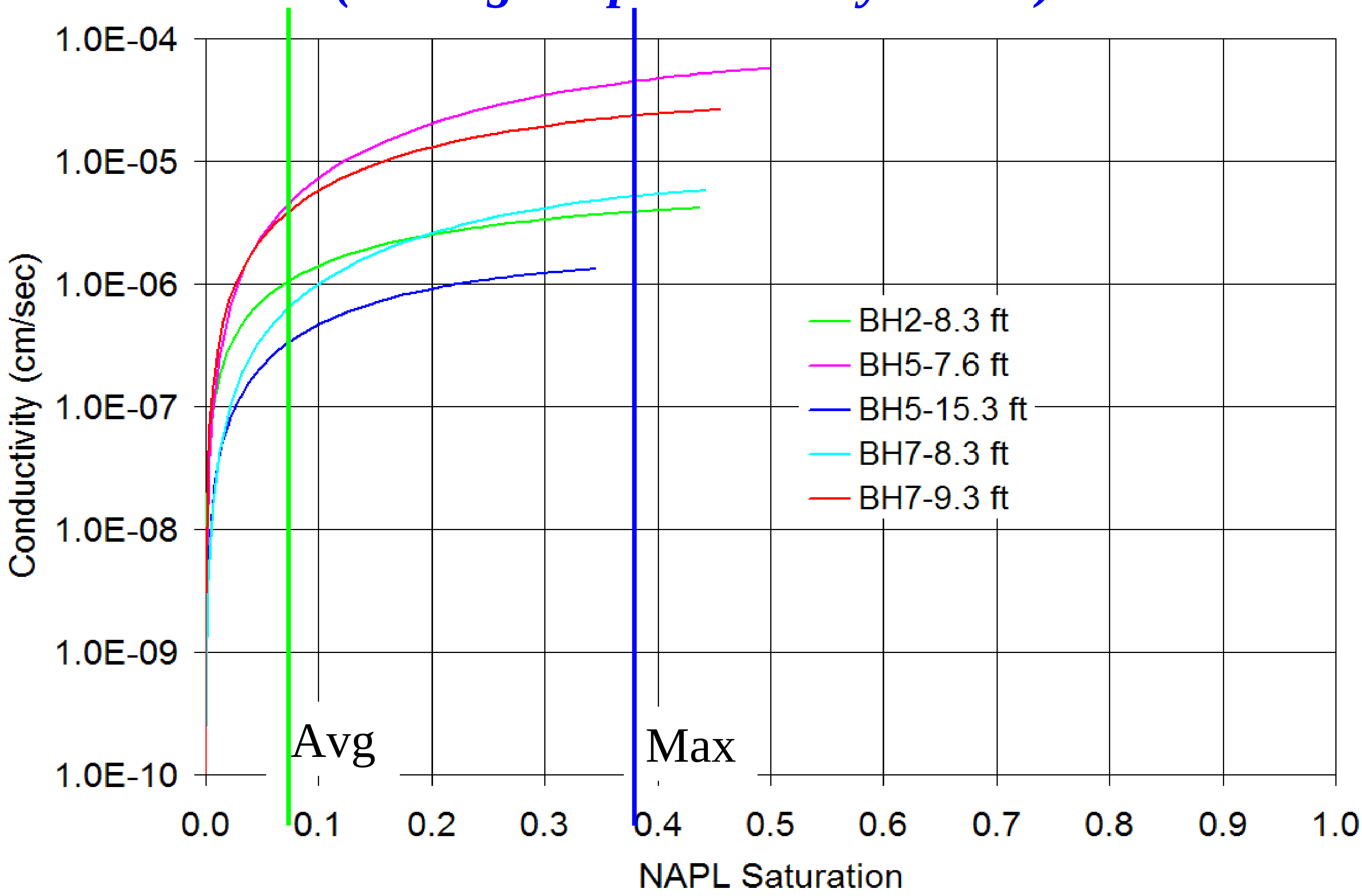


After Huntley, 2006

© AQUI-VER, INC.

Effective LNAPL Conductivity; Coral Sands

(* using lab permeability values)



© AQUI-VER, INC.

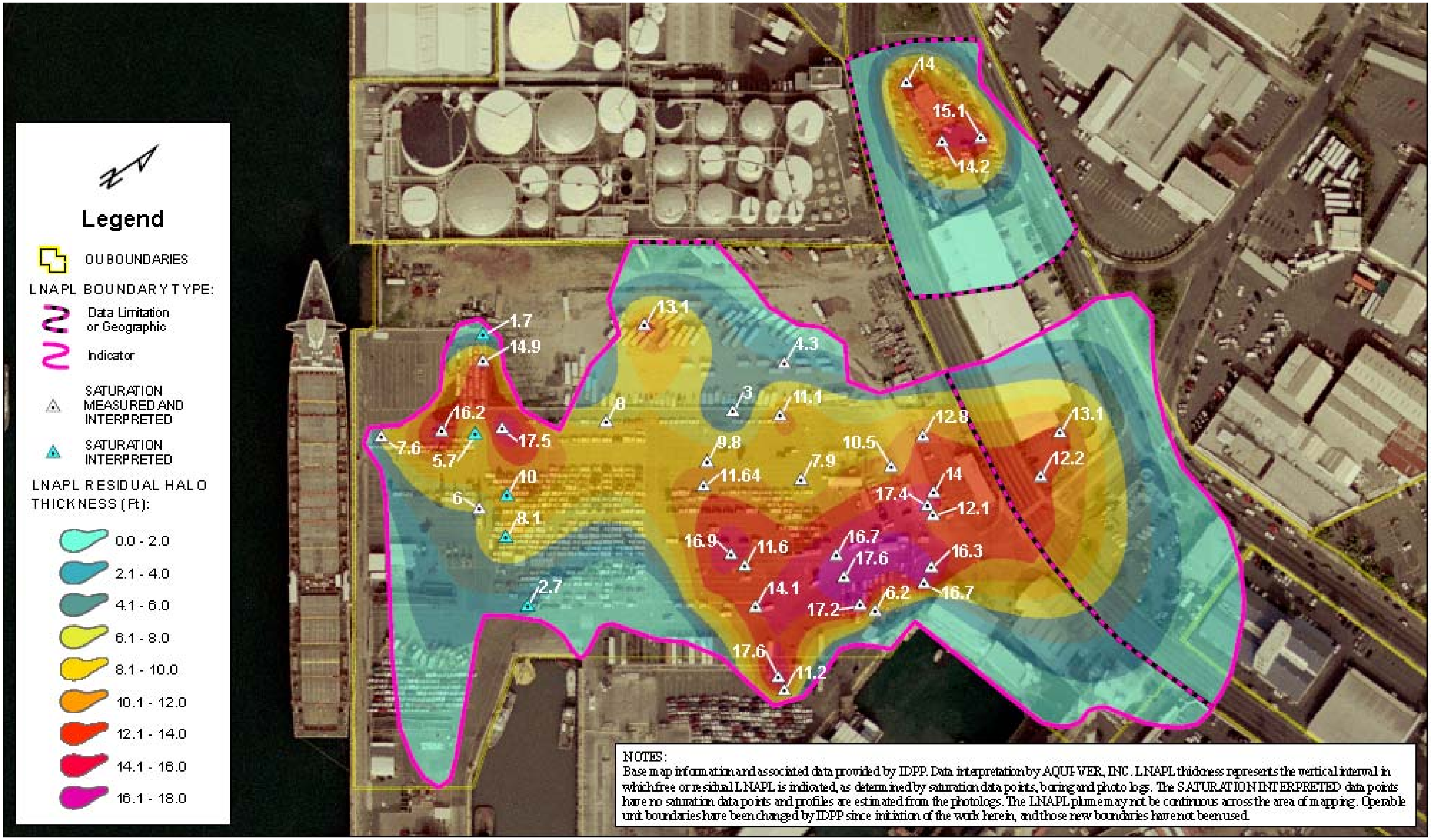
NAPL Indicator Mapping to Define the Boundary

(volume would otherwise be greatly overestimated)

© AQUI-VER, INC.

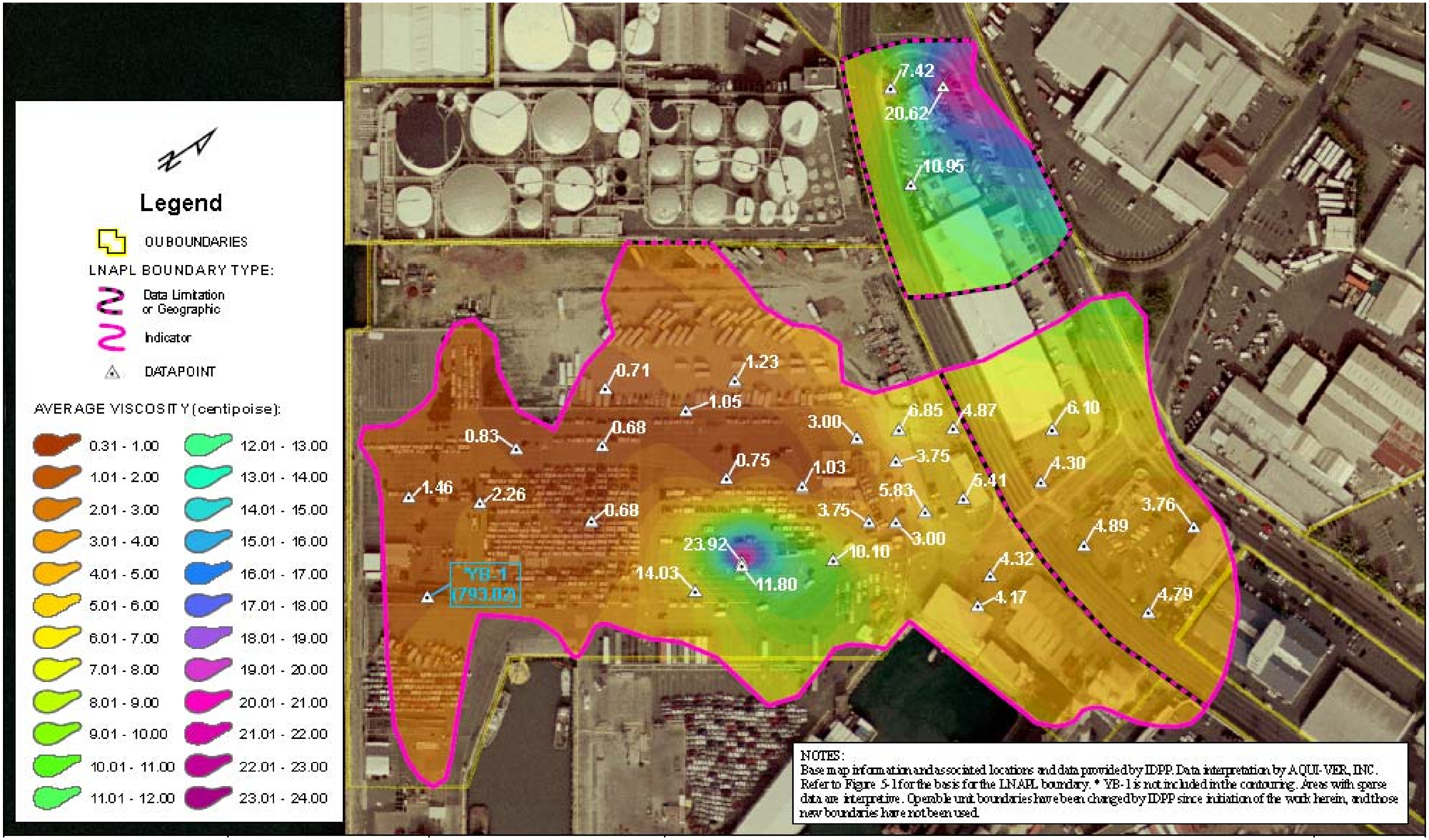
Total Thickness of LNAPL Impacts – Not Free Product

(Residual forms Top & Bottom; we can easily see source areas)



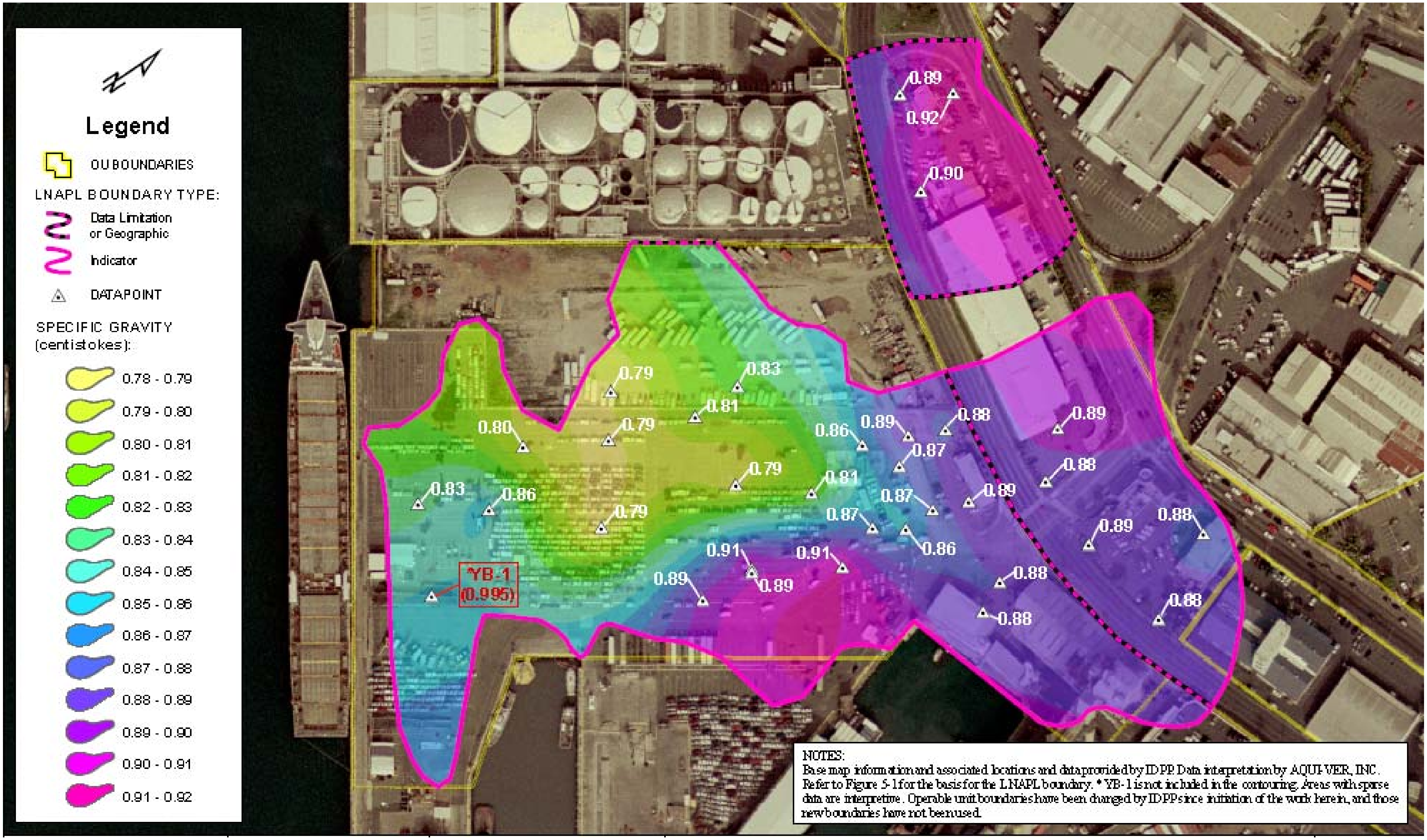
© AQUI-VER, INC.

LNAPL Viscosity



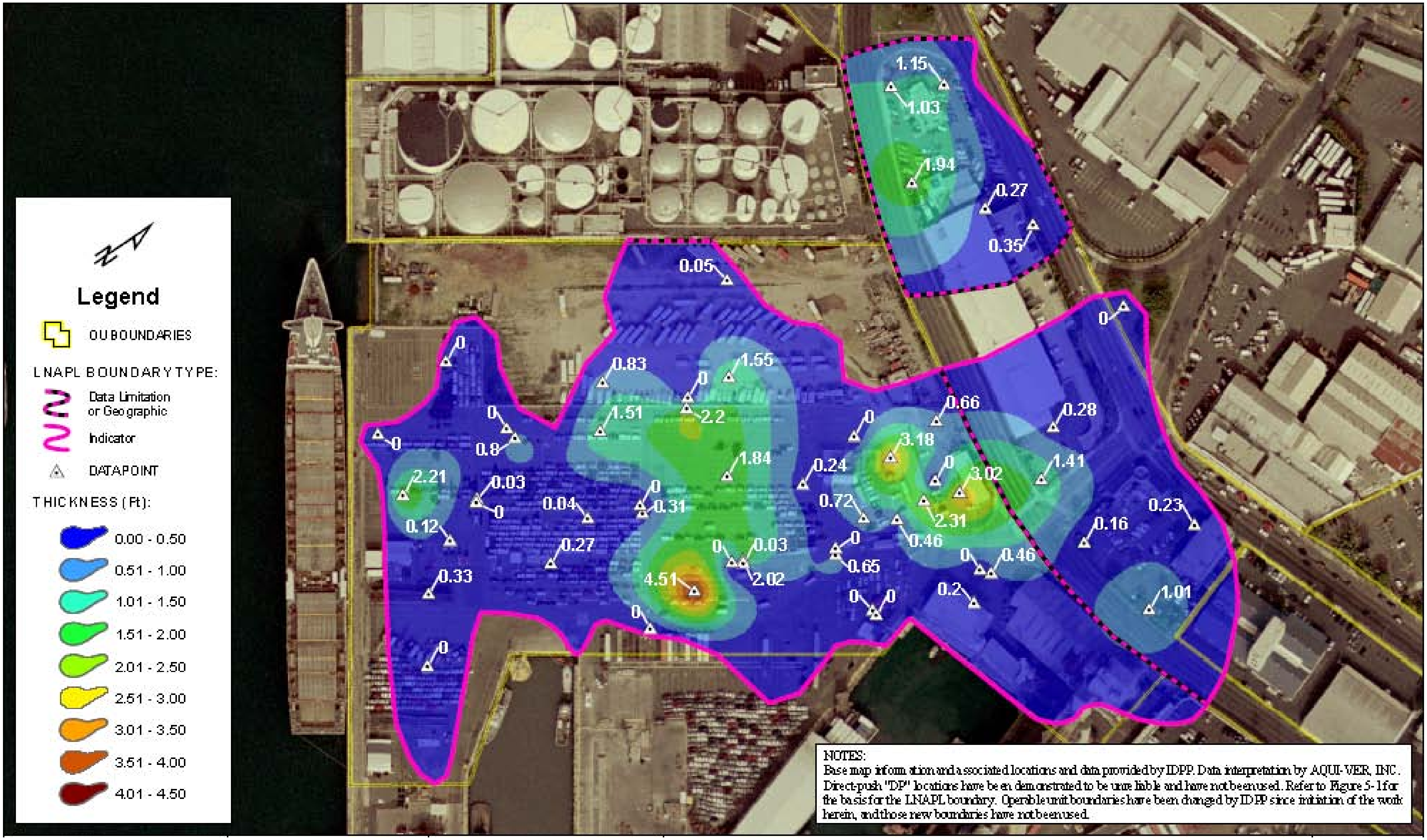
© AQUI-VER, INC.

LNAPL Specific Gravity



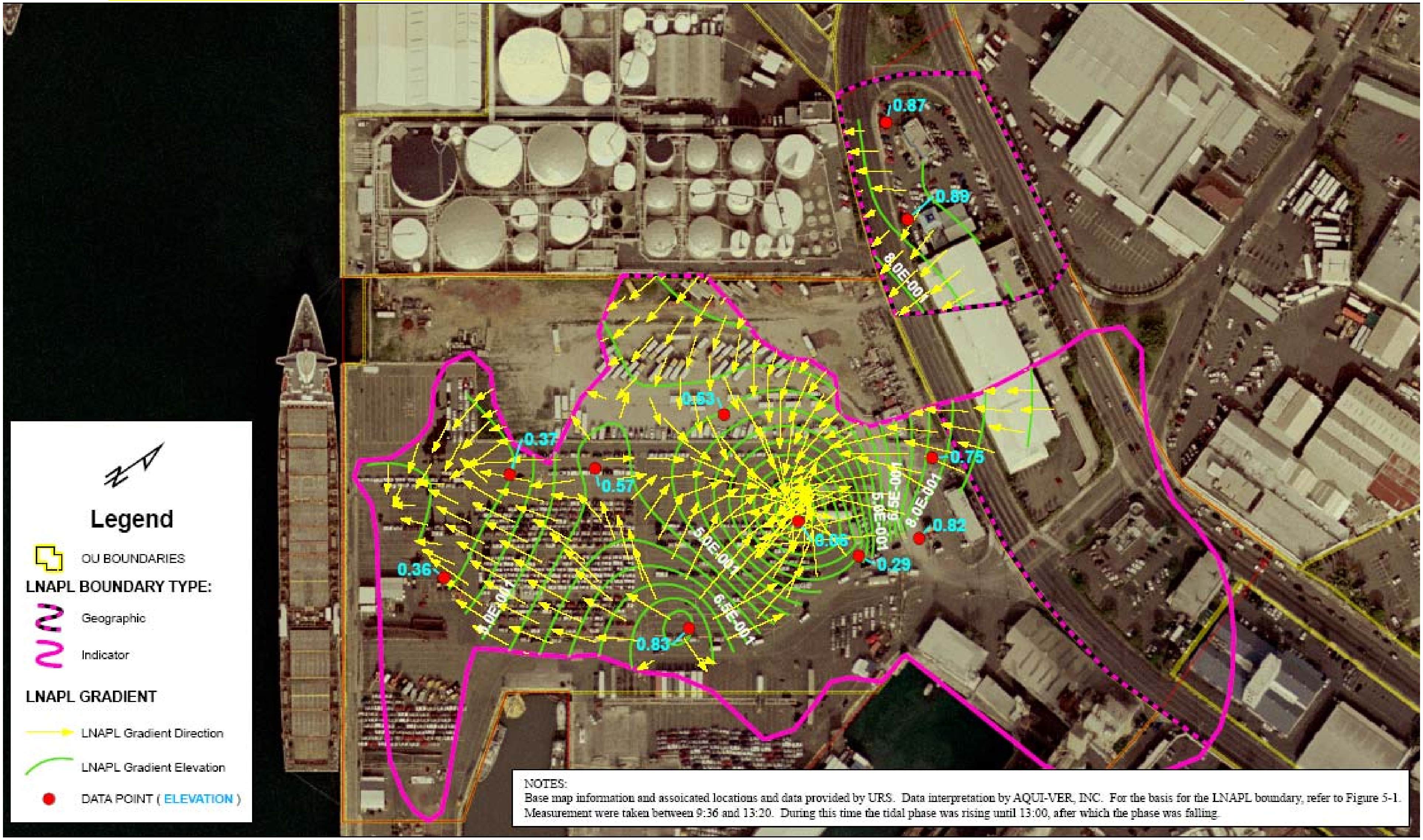
© AQUI-VER, INC.

Maximum LNAPL Thickness in Wells - 2007



© AQUI-VER, INC.

LNAPL Gradient; March 8, 2006



© AQUI-VER, INC.

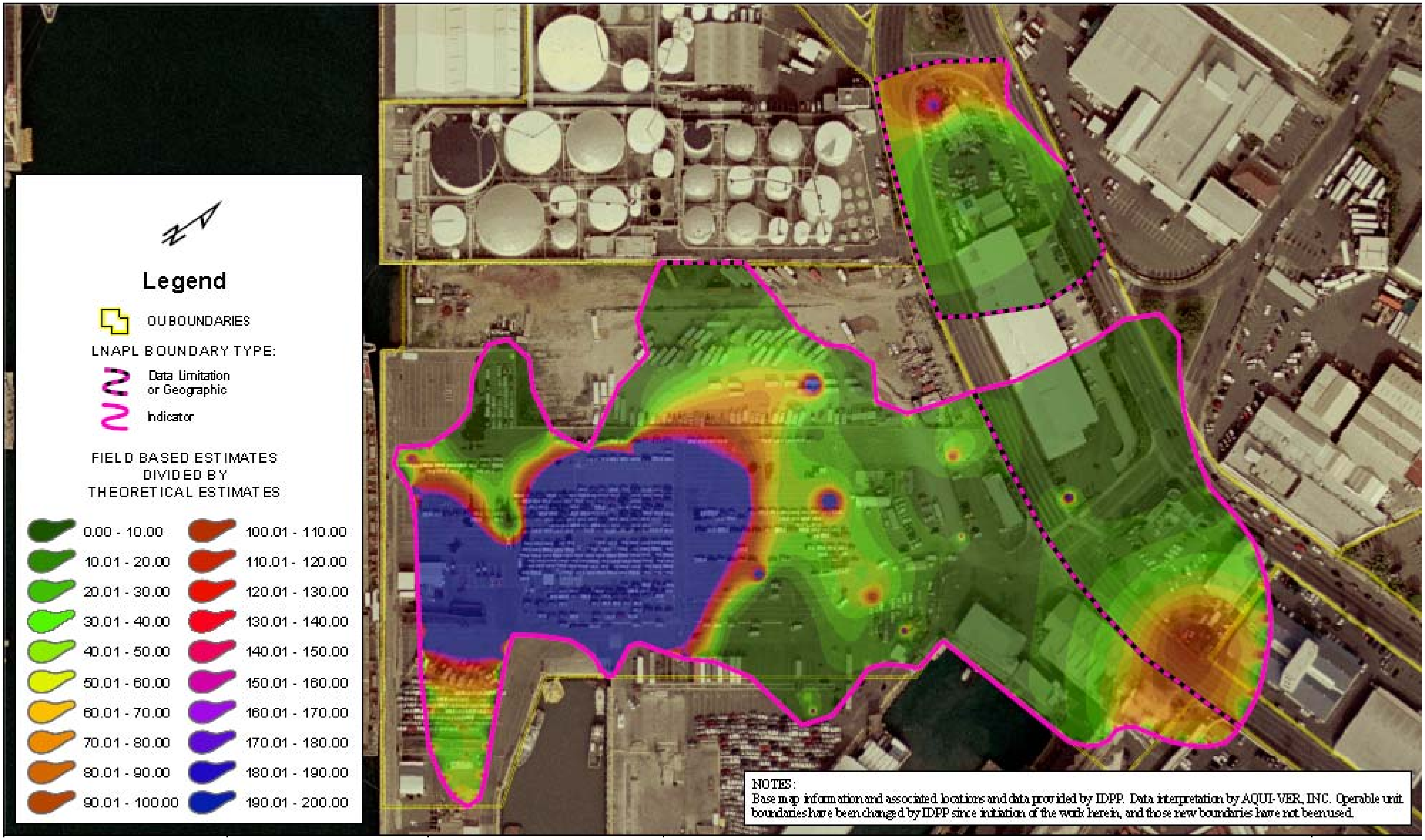
Combining That: Velocity Potential Mapping (ft/yr)

(high S_n & mass in 3-phase zone are keys)

© AQUI-VER, INC.

Lab vs. Field Based LNAPL Transmissivity

(majority of lab-based are lower, indicating potential bias)



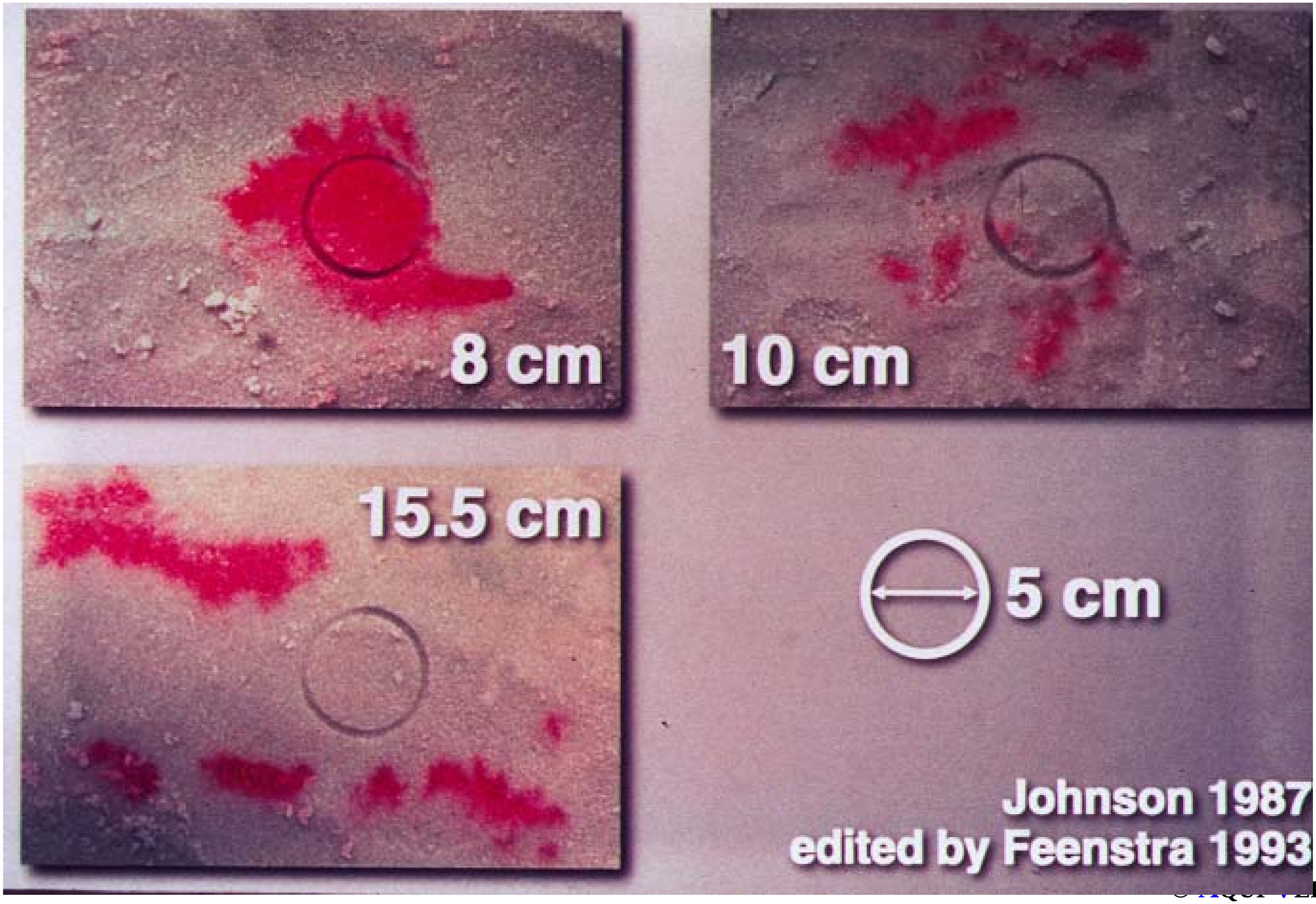
© AQUI-VER, INC.

A Few Quirks & Pitfalls

There are so many.. we'd need weeks and a keg of something just to make it through! And then I'd forget & have to start over... that's just me

Oil In Soil: What do Samples Mean?

(yes, it is a measurement, but of what representative volume?)



© AQUI-VER, INC.

LNAPL Thickness with Changing Water Levels

1

LNAPL enters and floats at the top of the water table.

2

Water table drops with LNAPL creating smear zone in soil.

3

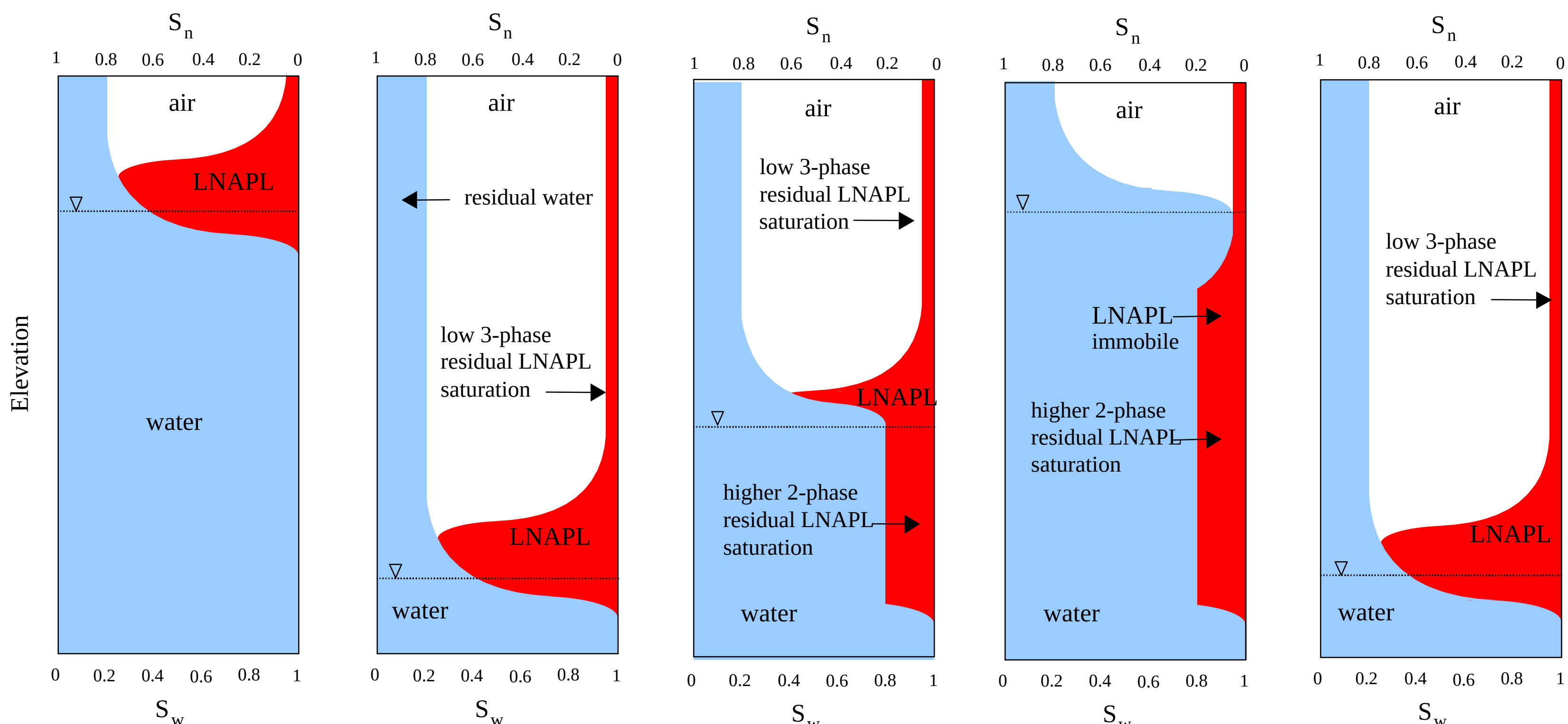
Water table rises, entrapping LNAPL in the soil.

4

At water table maximum, LNAPL may be entirely entrapped.

5

As water table declines, LNAPL drains from soil.

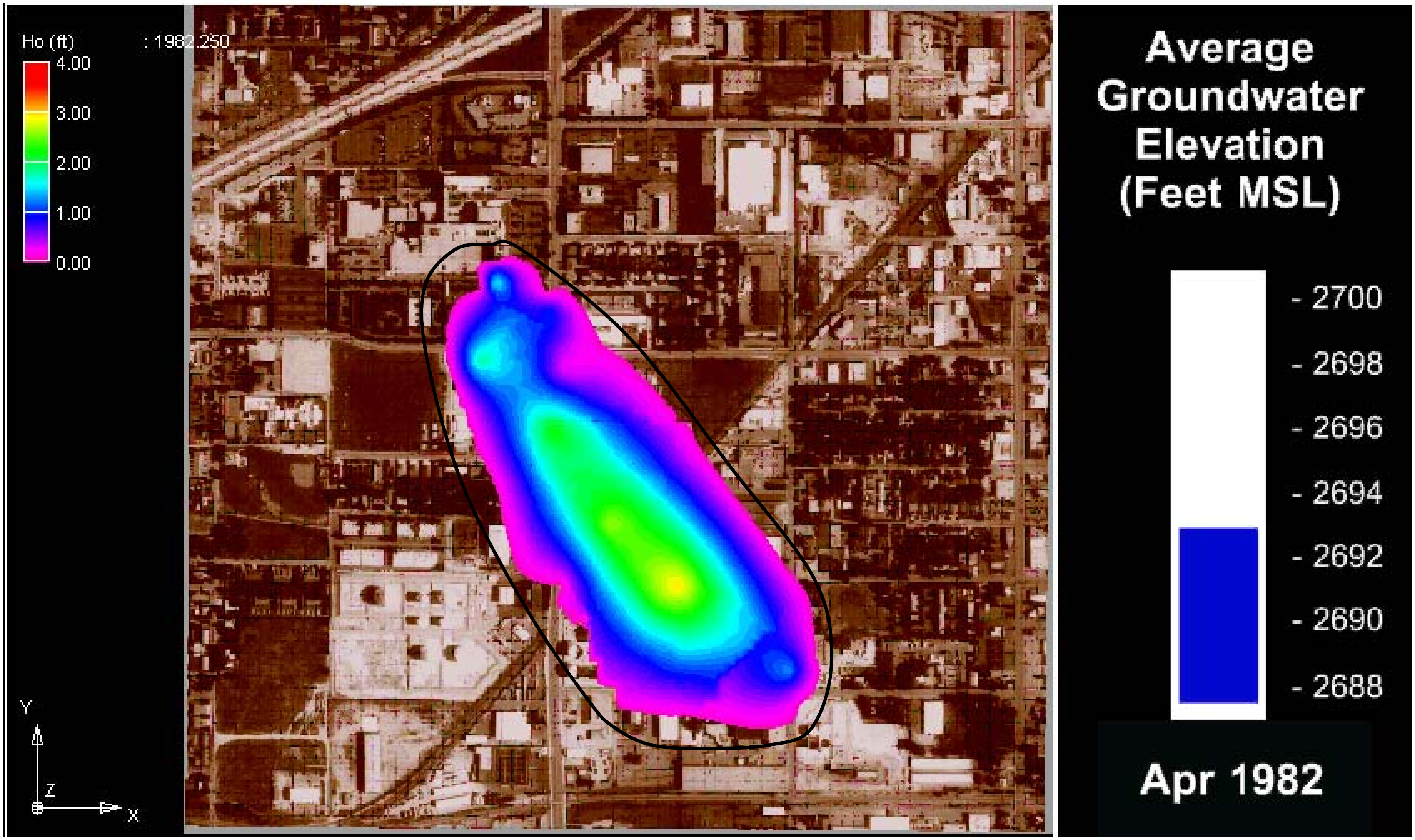


after Richard Jackson, 2000

Note: S_w = Saturation of water, S_n = Saturation of LNAPL

© AQUI-VER, INC.

And What Happens When Water Tables Vary

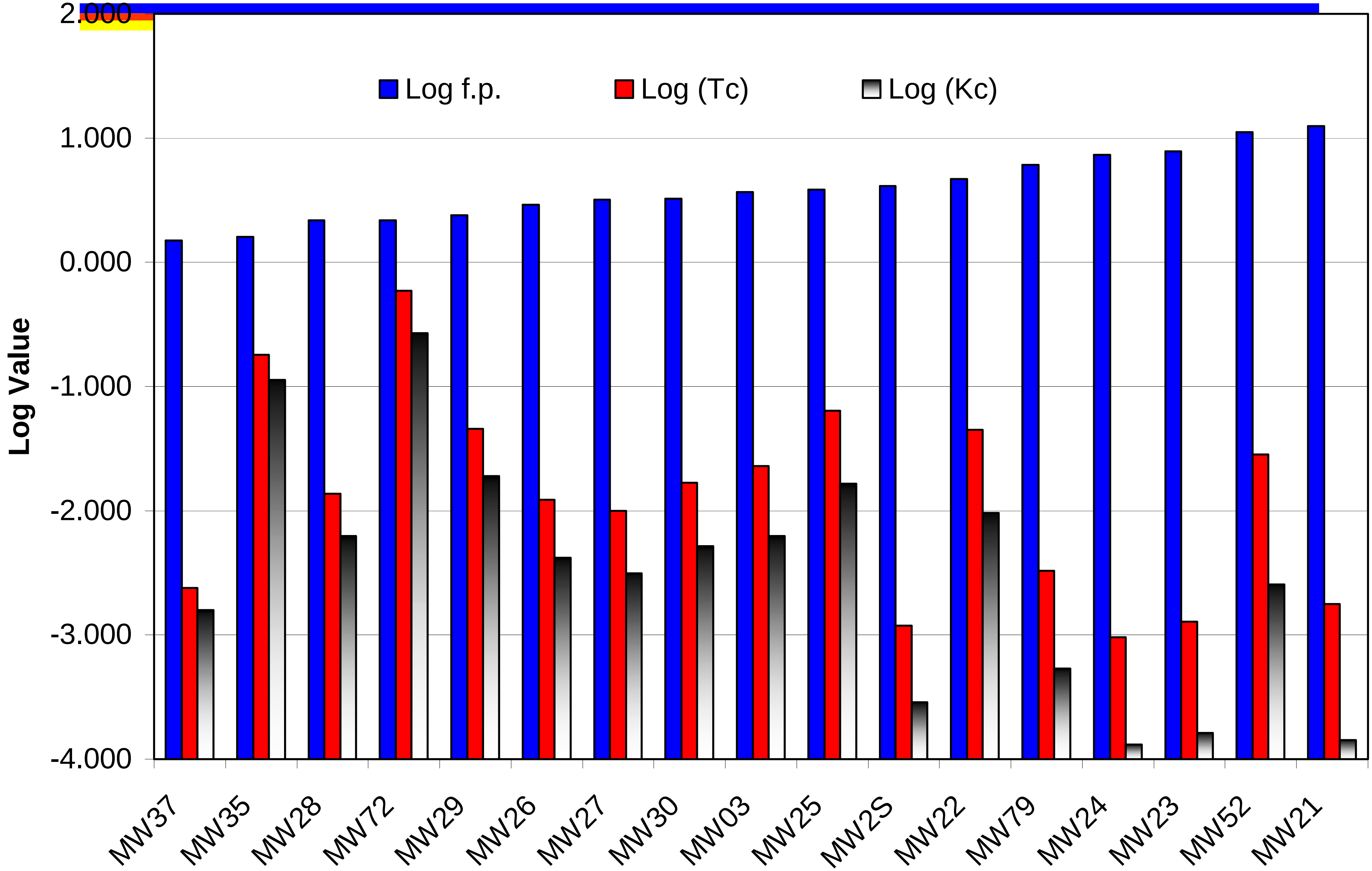


Source: API Interactive LNAPL Guide, 2004

© AQUI-VER, INC.

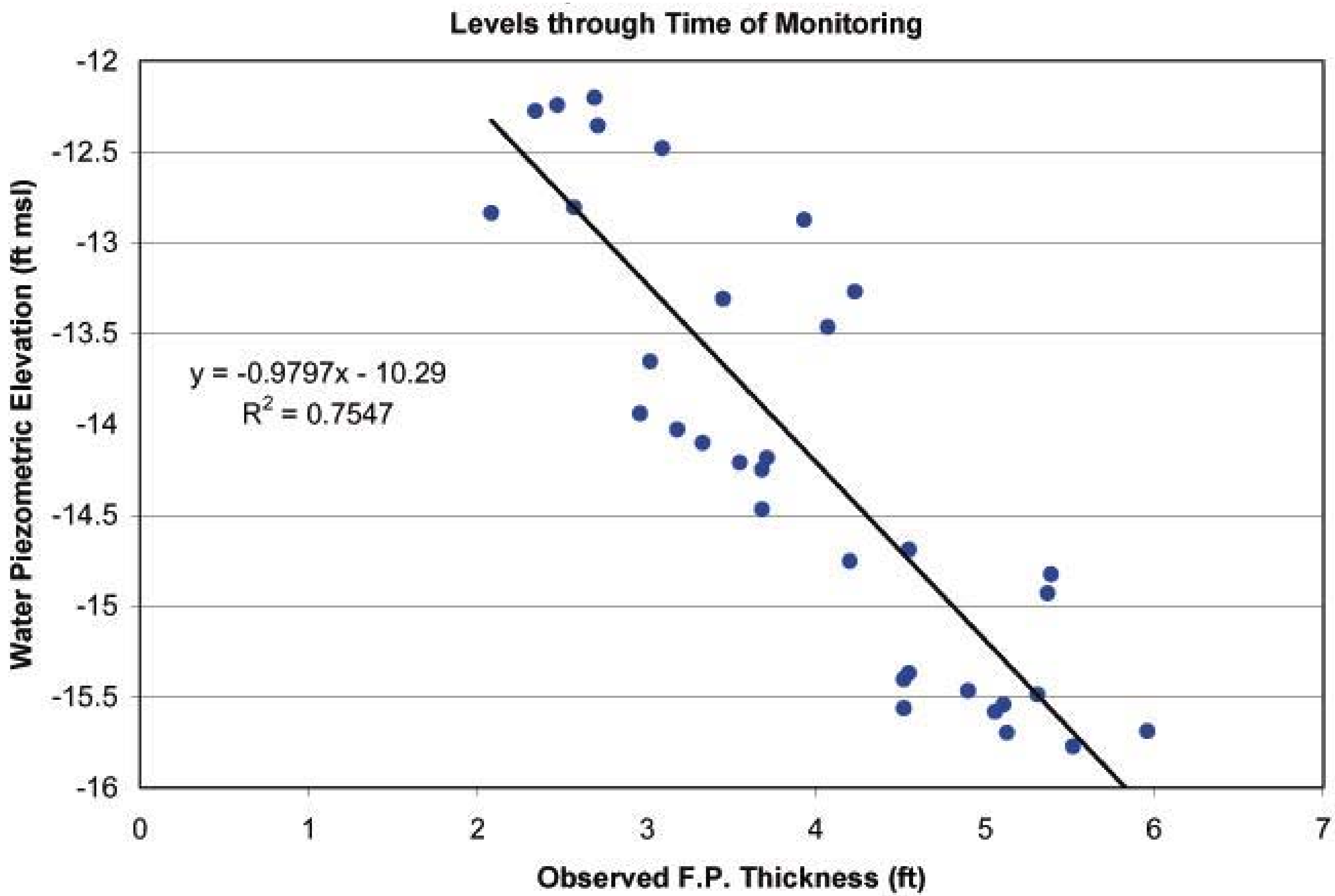
Natural T/K Variability in Contrast to Theory

(Nothing Wrong, Just Geology Again)



© AQUI-VER, INC.
© AQUI-VER, INC.

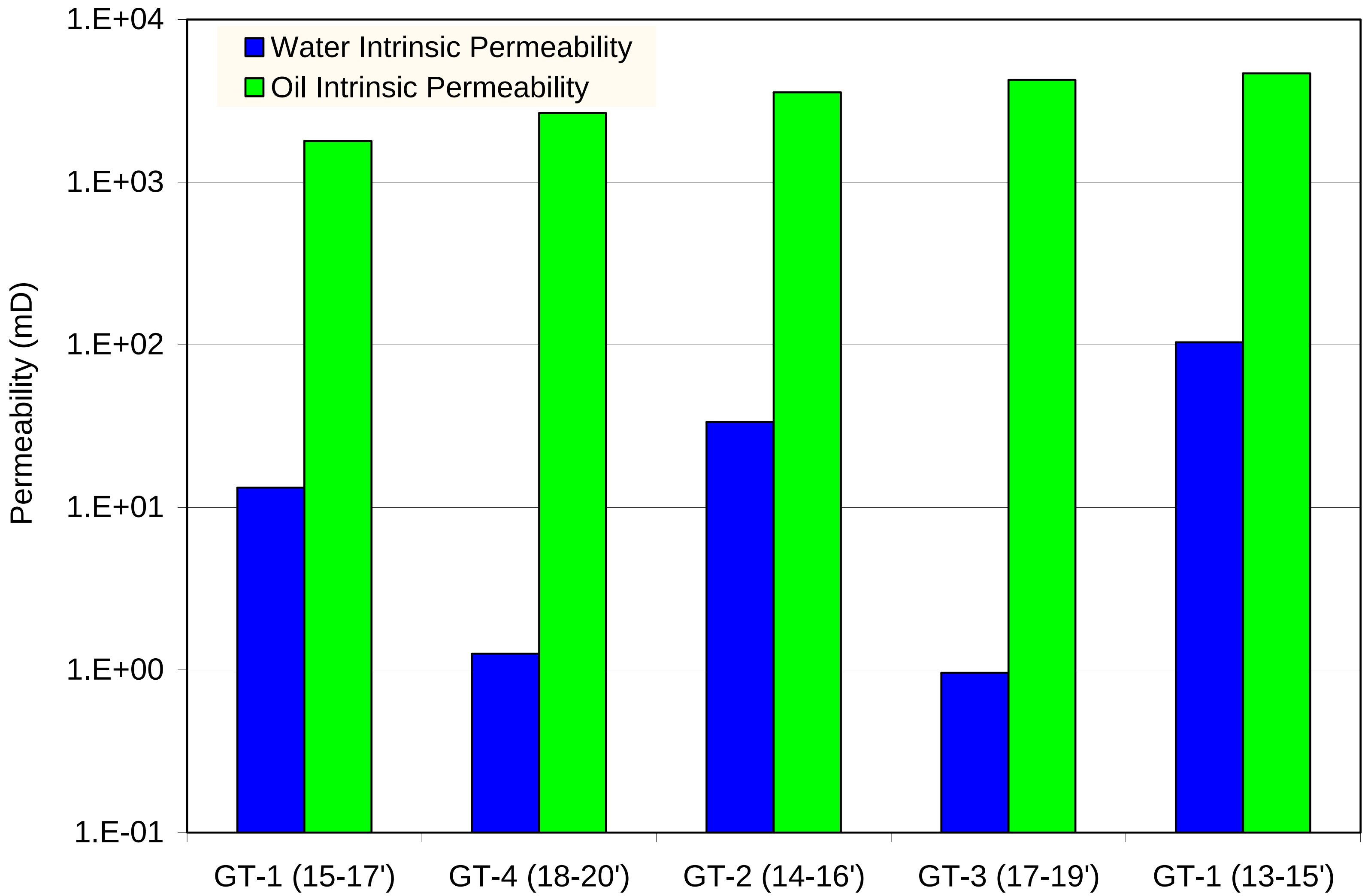
Refinery Site, L.A. Basin



© AQUI-VER, INC.

Lab Results – Intrinsic K: Oil vs. Water

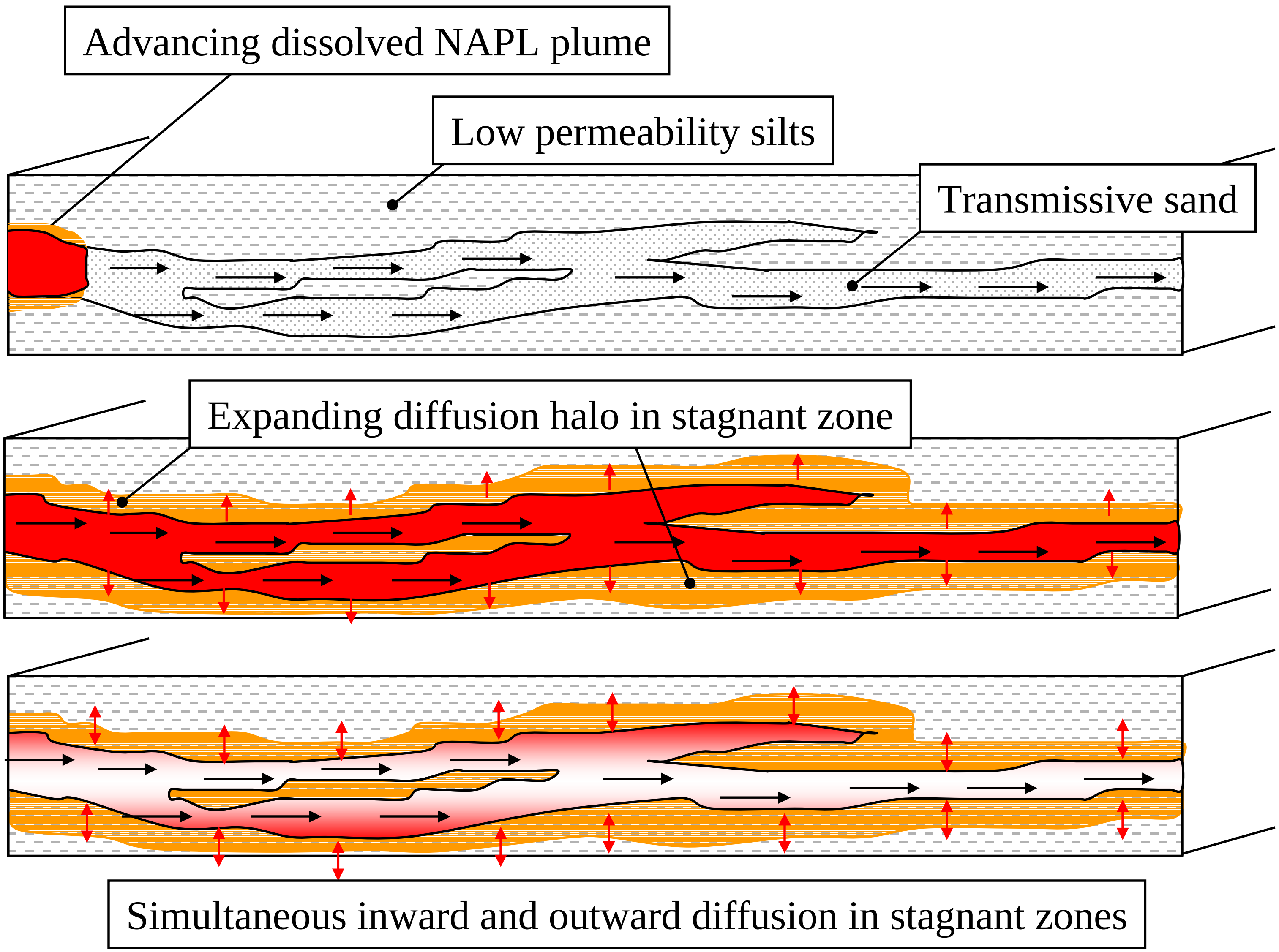
(shouldn't they be the same??)



© AQUI-VER, INC.

Mass Partitioning by Matrix Diffusion

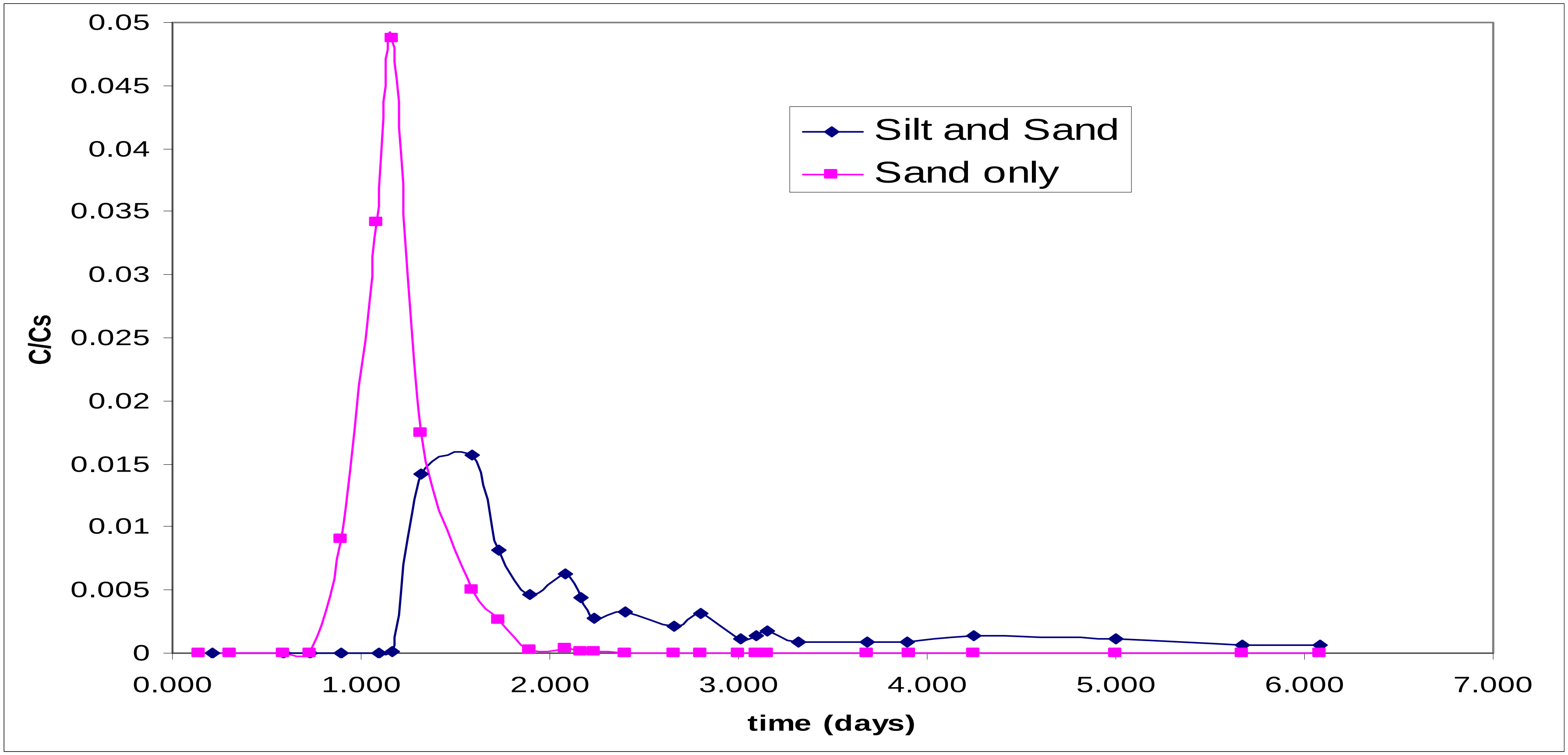
(e.g. after Parker and Cherry; data from Tom Sale, CSU)



© AQUI-VER, INC.

MTBE Tank Experimental Results

(Layered System (diffusive) vs. Homogeneous)

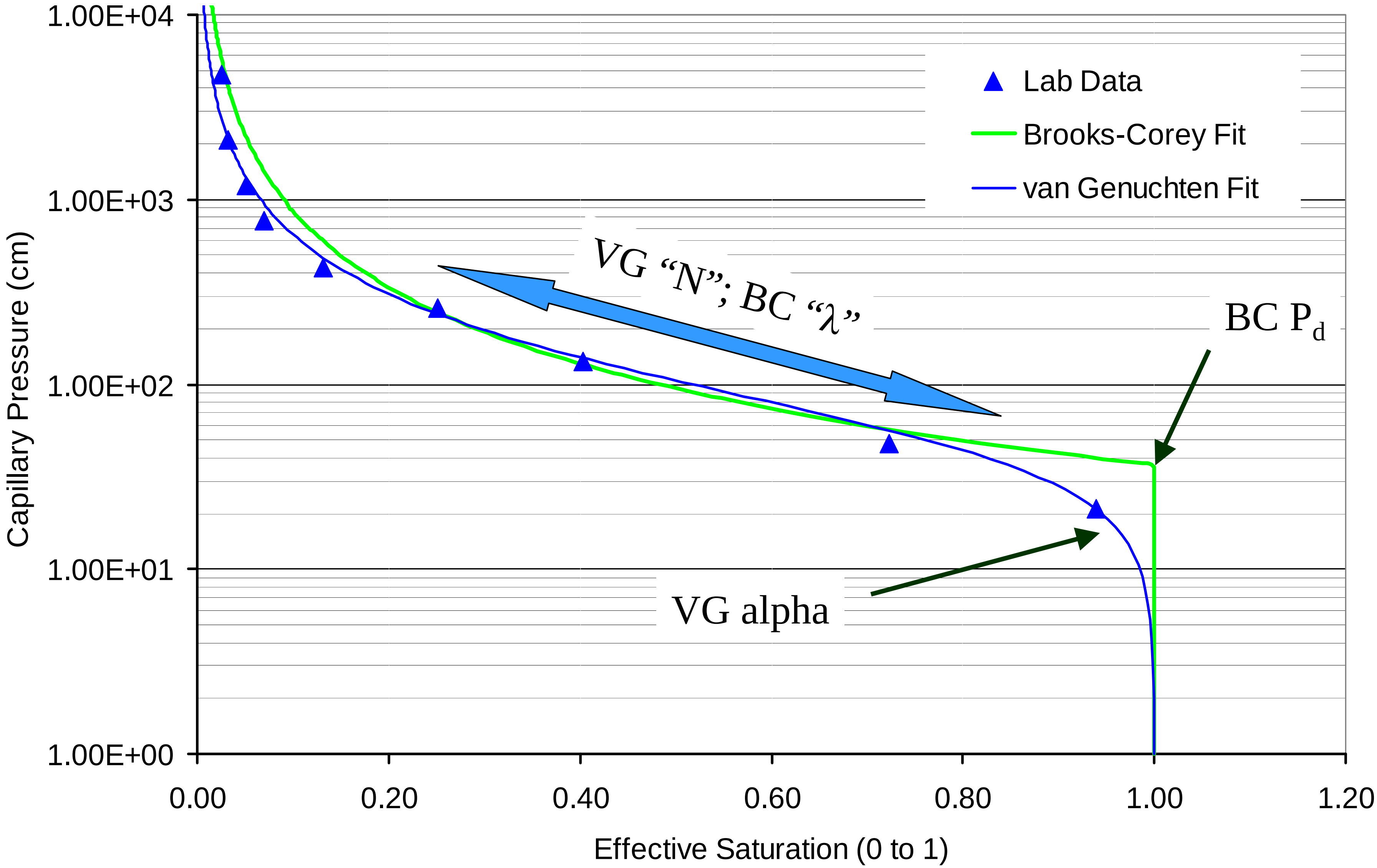


(courtesy of Tom Sale, CSU)

© AQUI-VER, INC.

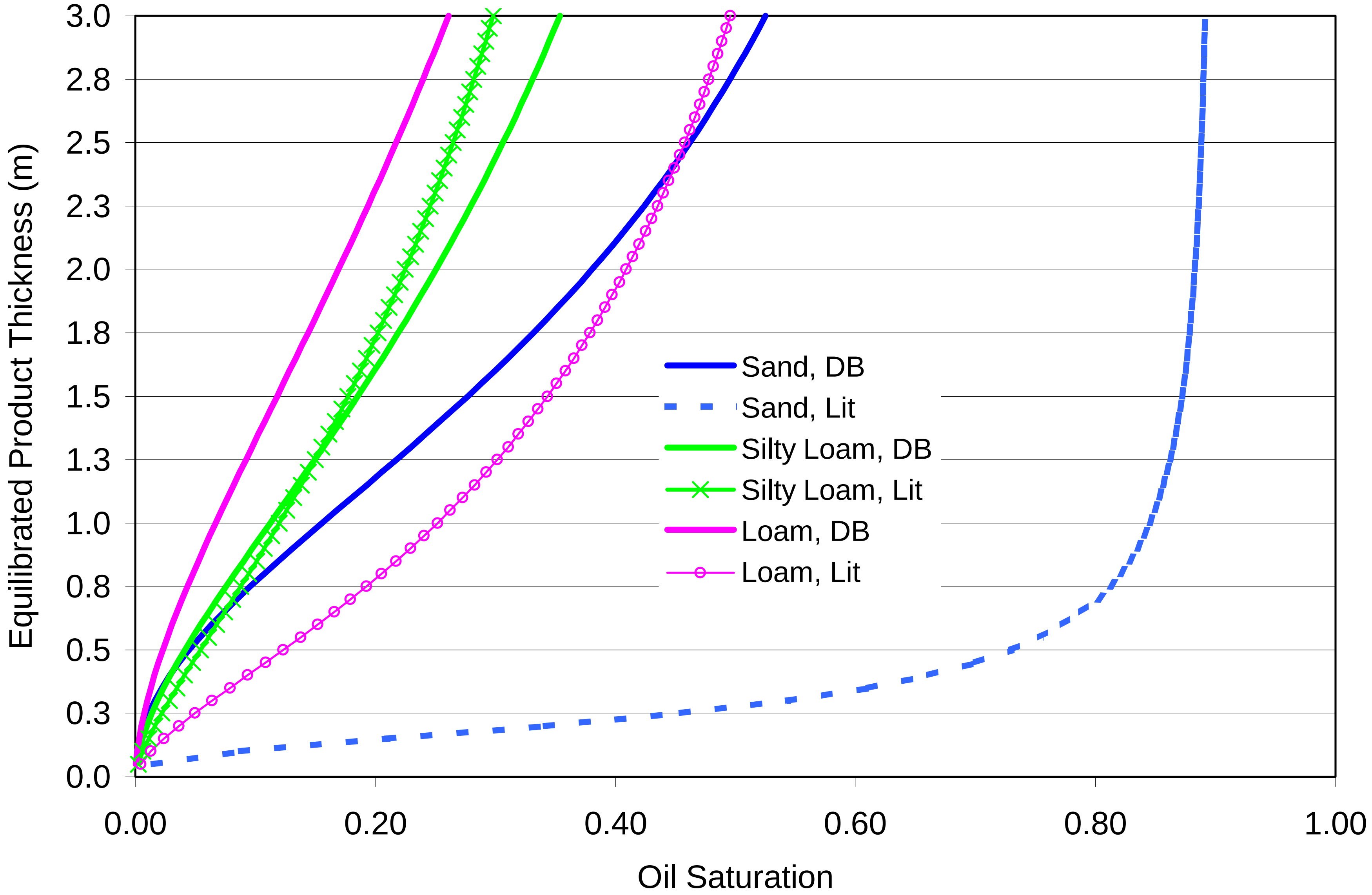
Capillary Curve Examples

(measured capillary relationships)



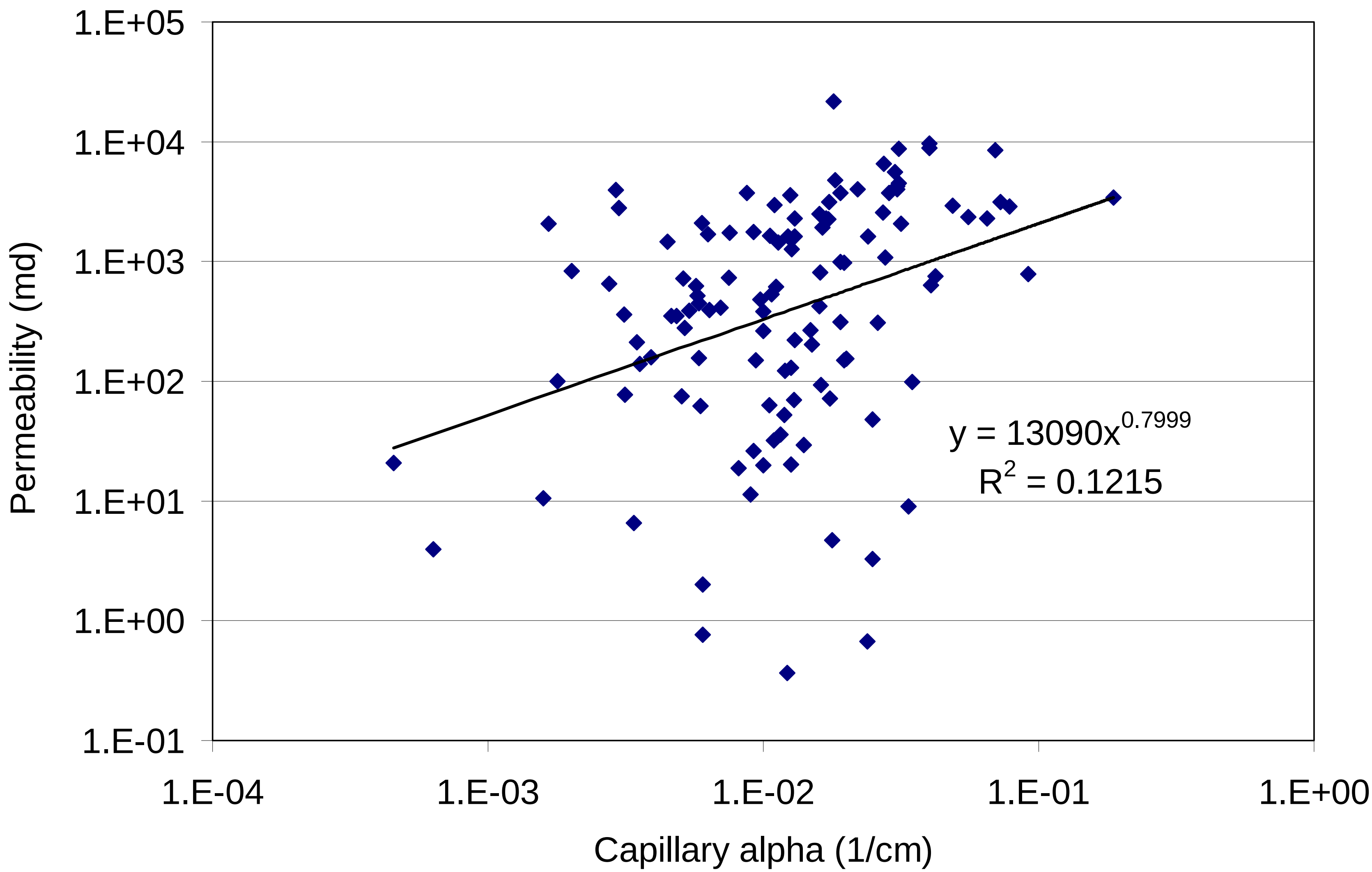
© AQUI-VER, INC.

Parameter Contrast Results for Saturation



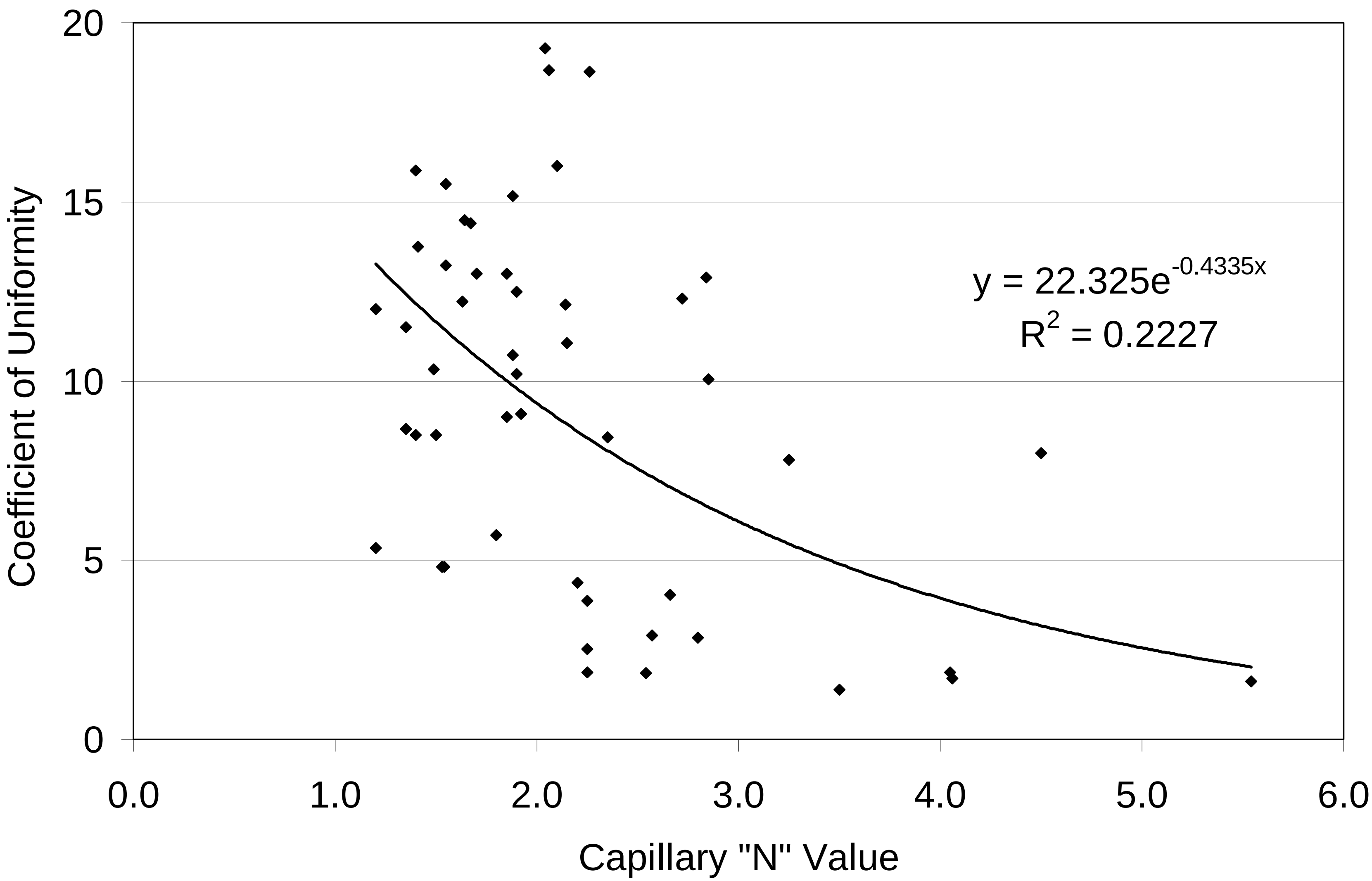
© AQUI-VER, INC.

Intrinsic Permeability Versus Capillary Alpha



© AQUI-VER, INC.

Grain-Size Vs. Capillary Uniformity



© AQUI-VER, INC.

What Did We Learn?

(Shoot, I'm never quite sure..)

- Things are complicated with NAPLs
  - Have to be discerning in evaluations
- But, we have a lot of existing site data
  - Can we use more of it in context?
- What's important?
  - Protecting people, environment and resources
  - New releases are the greatest threat
  - Let's pay attention to likelihood's
- Removing mass for its own sake?
  - It will reduce plume longevity
  - But enough to make it worthwhile?
- Ideally, we'd like to remove every ounce
  - But, is that feasible?

© AQUI-VER, INC.

LNAPL REMEDIATION

Hydraulic recovery & other commonly applied methods

© AQUI-VER, INC.

Important Mace et al. Finding:
Can the Duration and Status of Plumes be Predicted?

While remediation efforts may be effective at individual sites, the persistence of plumes in phases II (stable) and III (declining) do not appear predictable solely on the basis of remediation.

Short English:

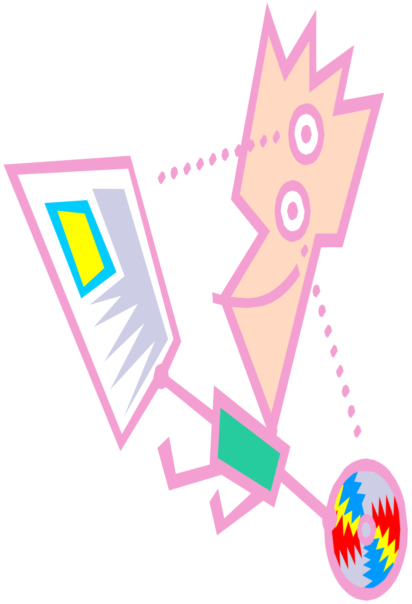
Remediation efforts have caused no statistical change in plume observations when using industry standard cleanup methods.

Our Lesson Here:

That isn't really a surprise given the state of learning that initiated our field actions across the board.

© AQUI-VER, INC.

Design As We Might.. Cleanup Is Limited

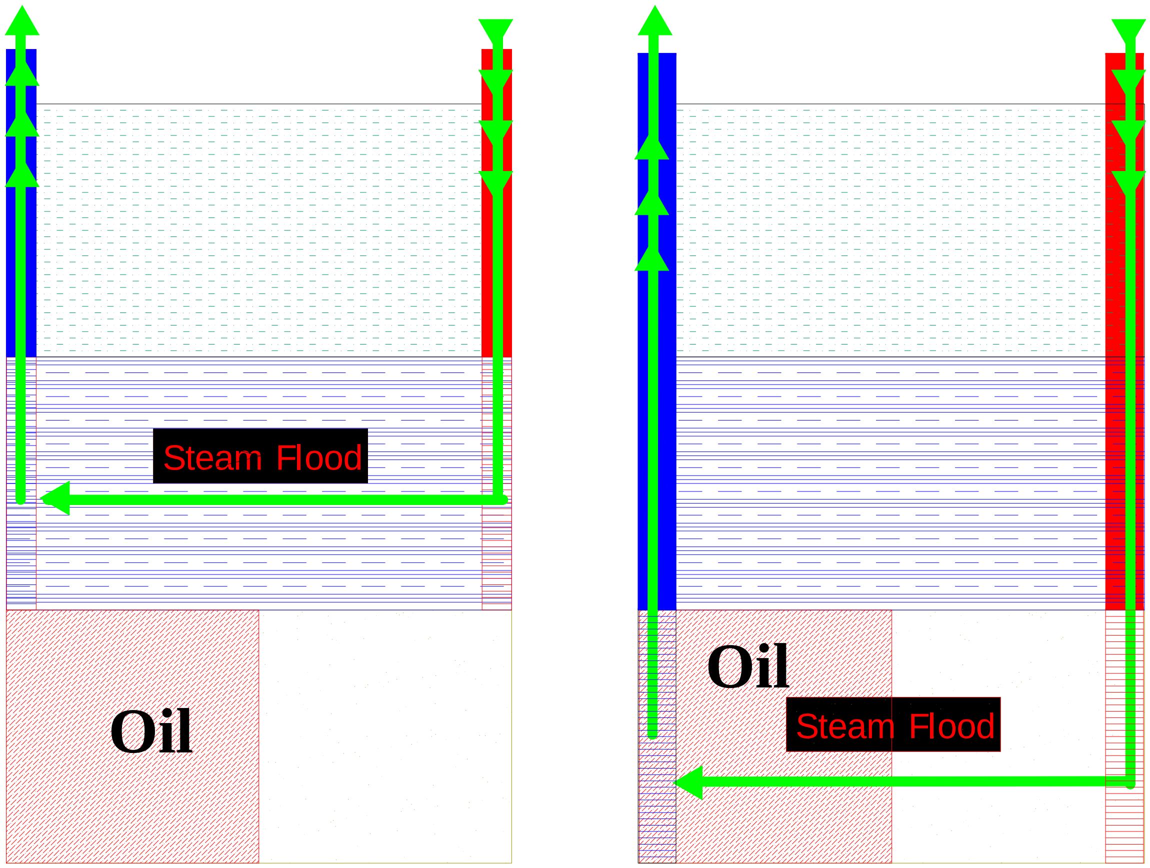


- Low flow conditions
  - Geologic barriers to flow
  - Small phase hydraulic conductivity
  - Heterogeneous parametric distributions
- Chemical limitations
  - Low solubility/volatility fuels
  - Slow chemical delivery mechanisms
  - Diffusion is generally a slow process
  - Phase transfer is often key
- The endpoint of cleanup defines:
  - Residual risk and risk residence time
  - Whether management actions change

© AQUI-VER, INC.

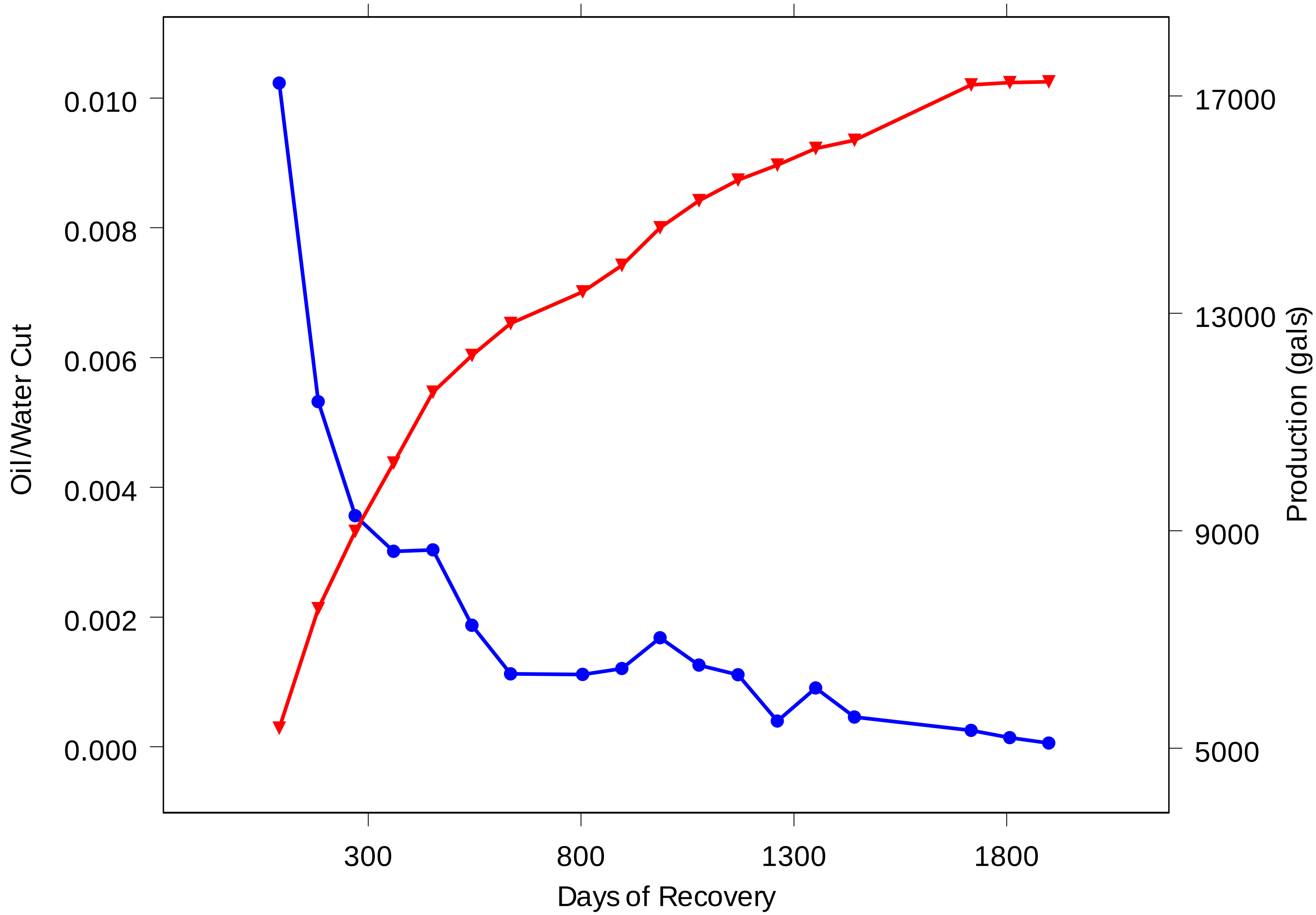
Which Scenario Works Best?

(targeting is critical; can't hit what we can't see)



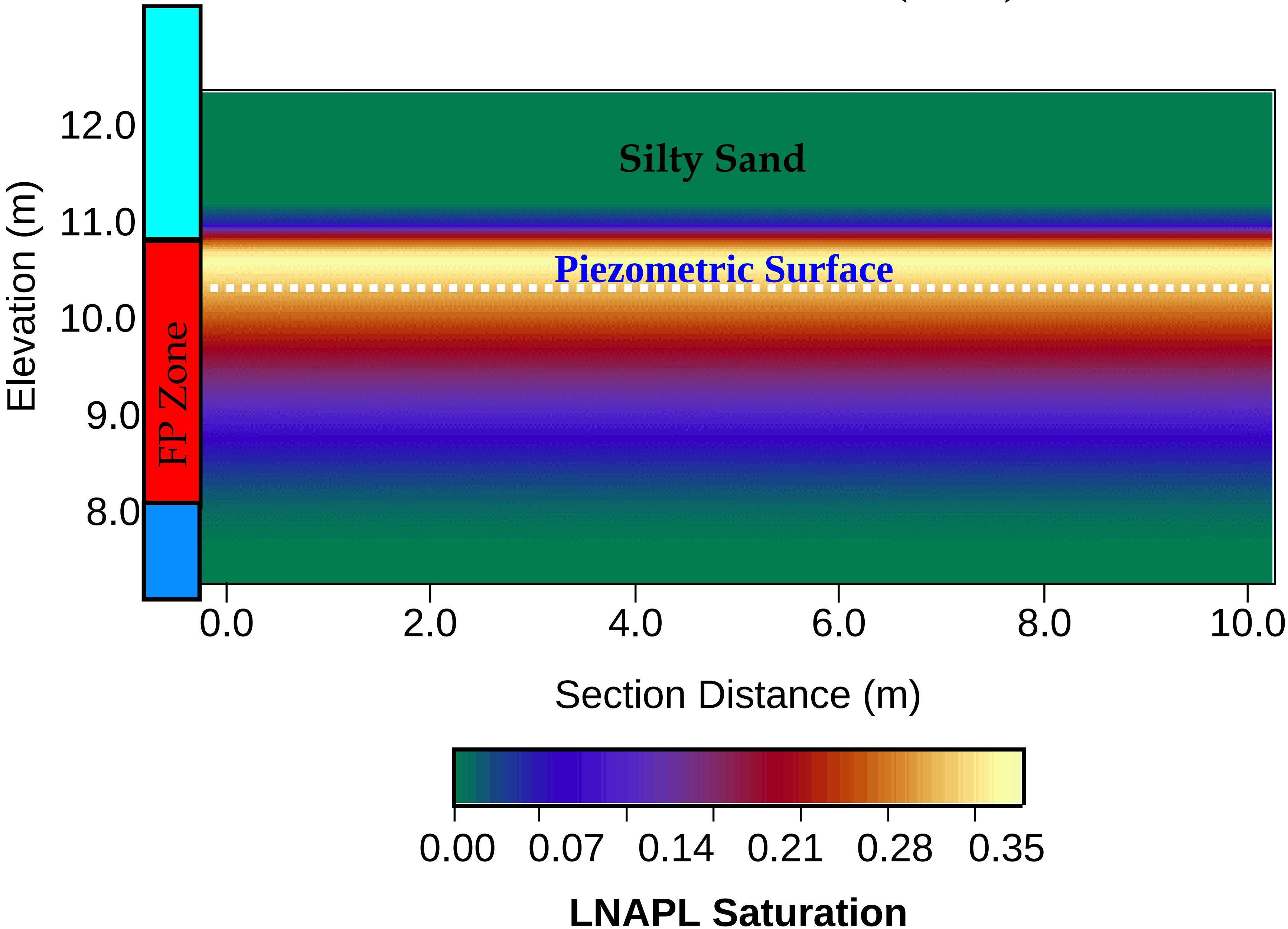
© AQUI-VER, INC.

LNAPL Production & Cut Through Time



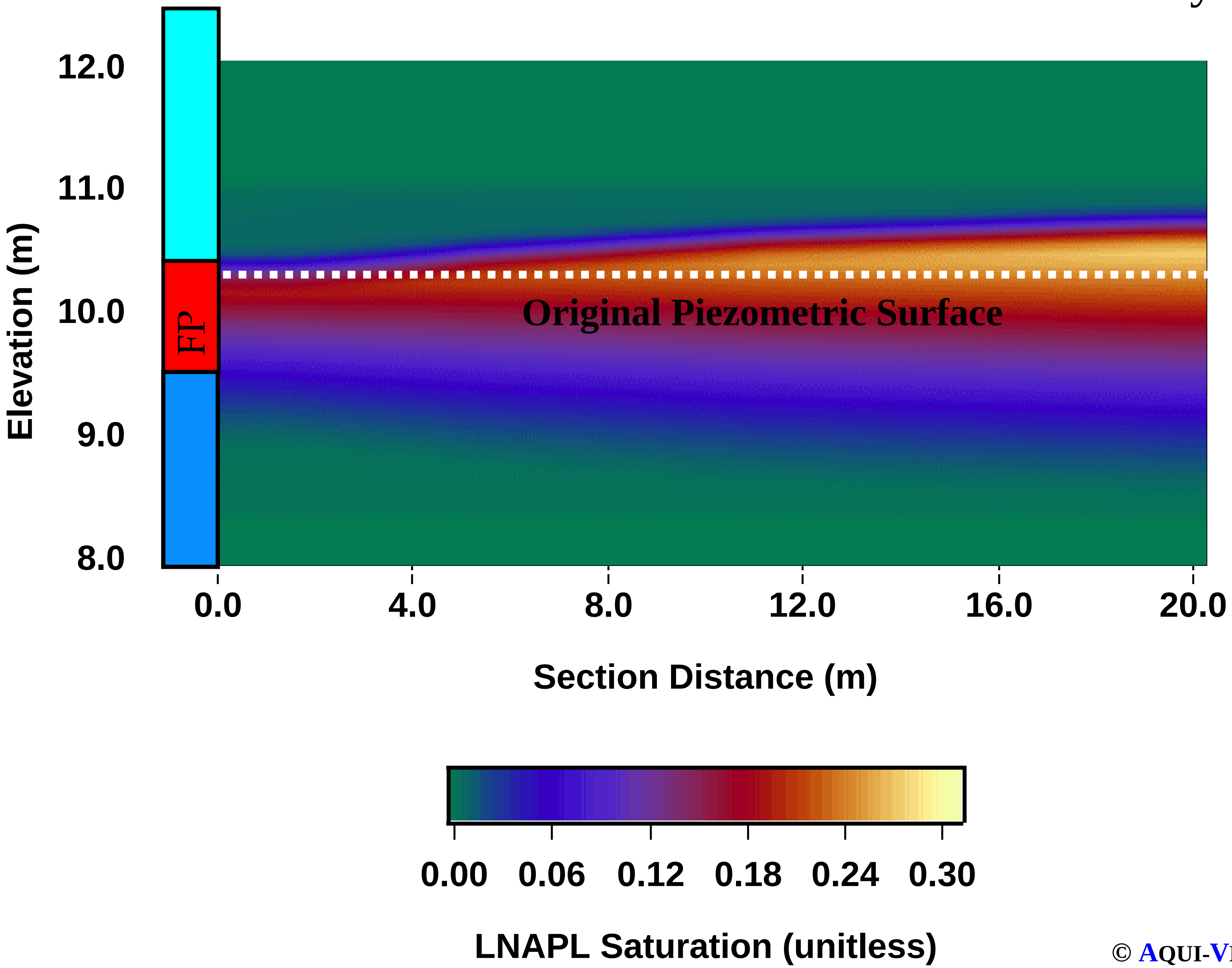
© AQUI-VER, INC.

Initial LNAPL Saturation with 3 m (10 ft) Free Product



© AQUI-VER, INC.

LNAPL Formation Saturation at the End of Recovery

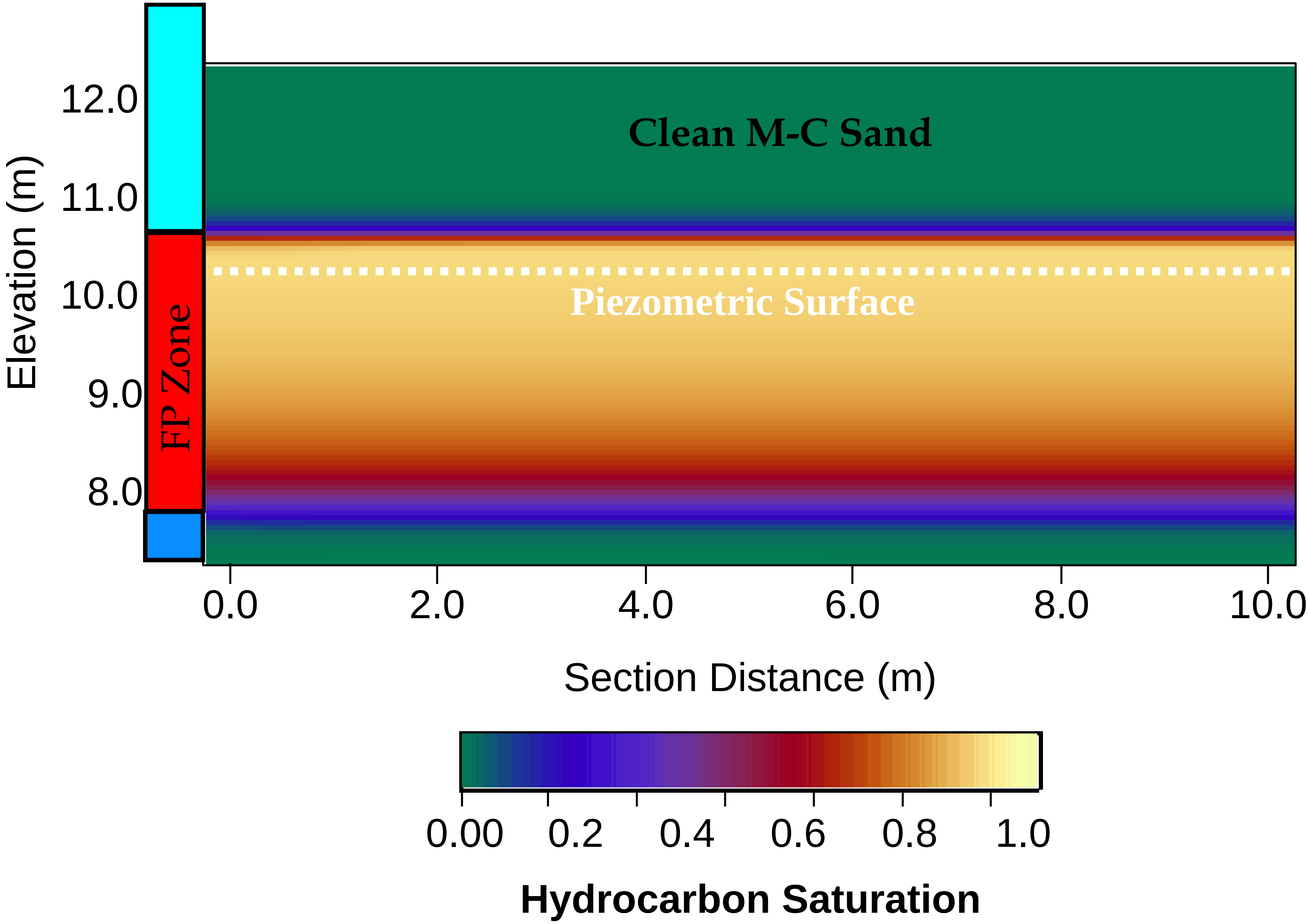


© AQUI-VER, INC.

Let’s Contrast That ..

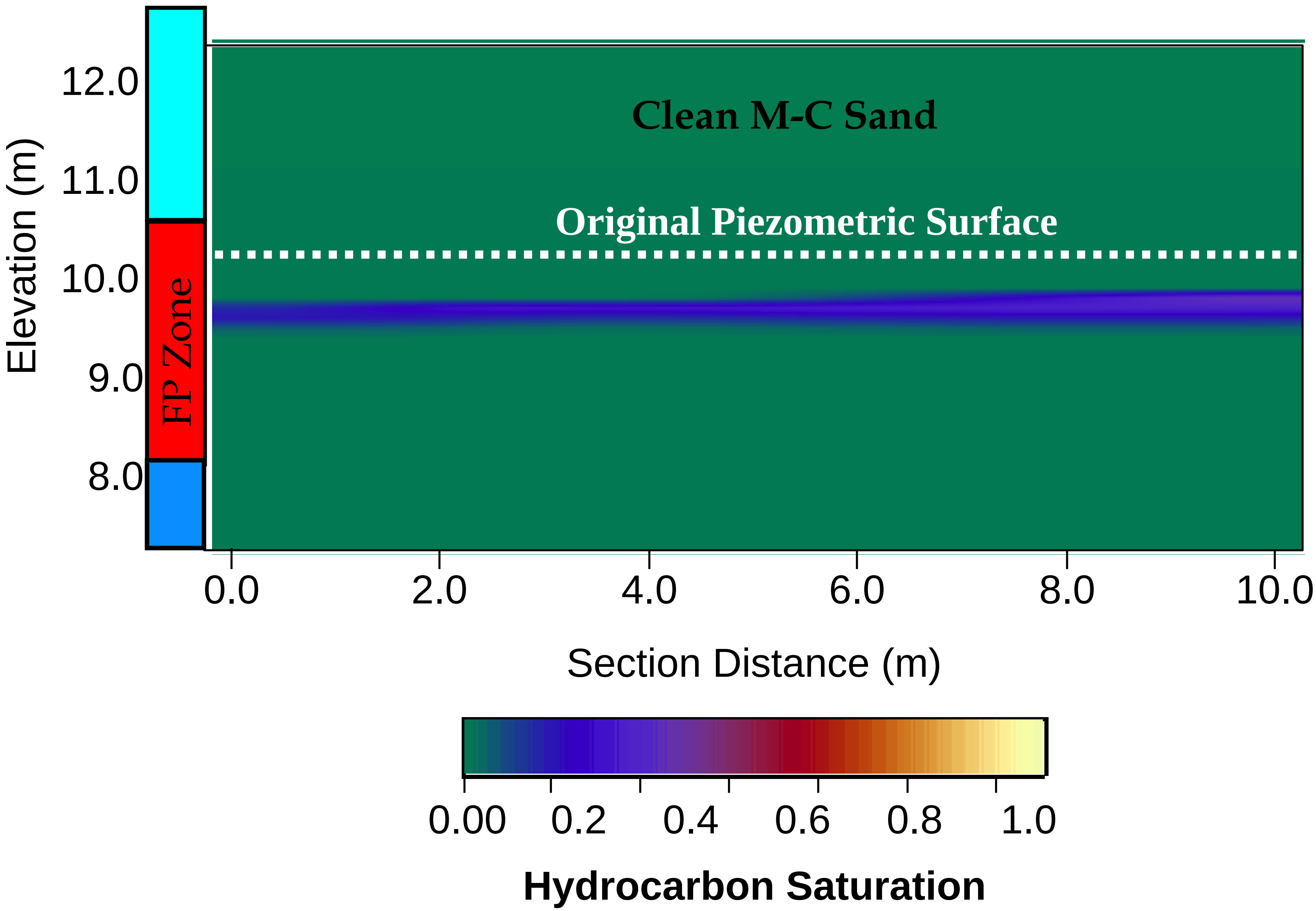
© AQUI-VER, INC.

Static Hydrocarbon Saturation with 3 m (10 ft) Free Product



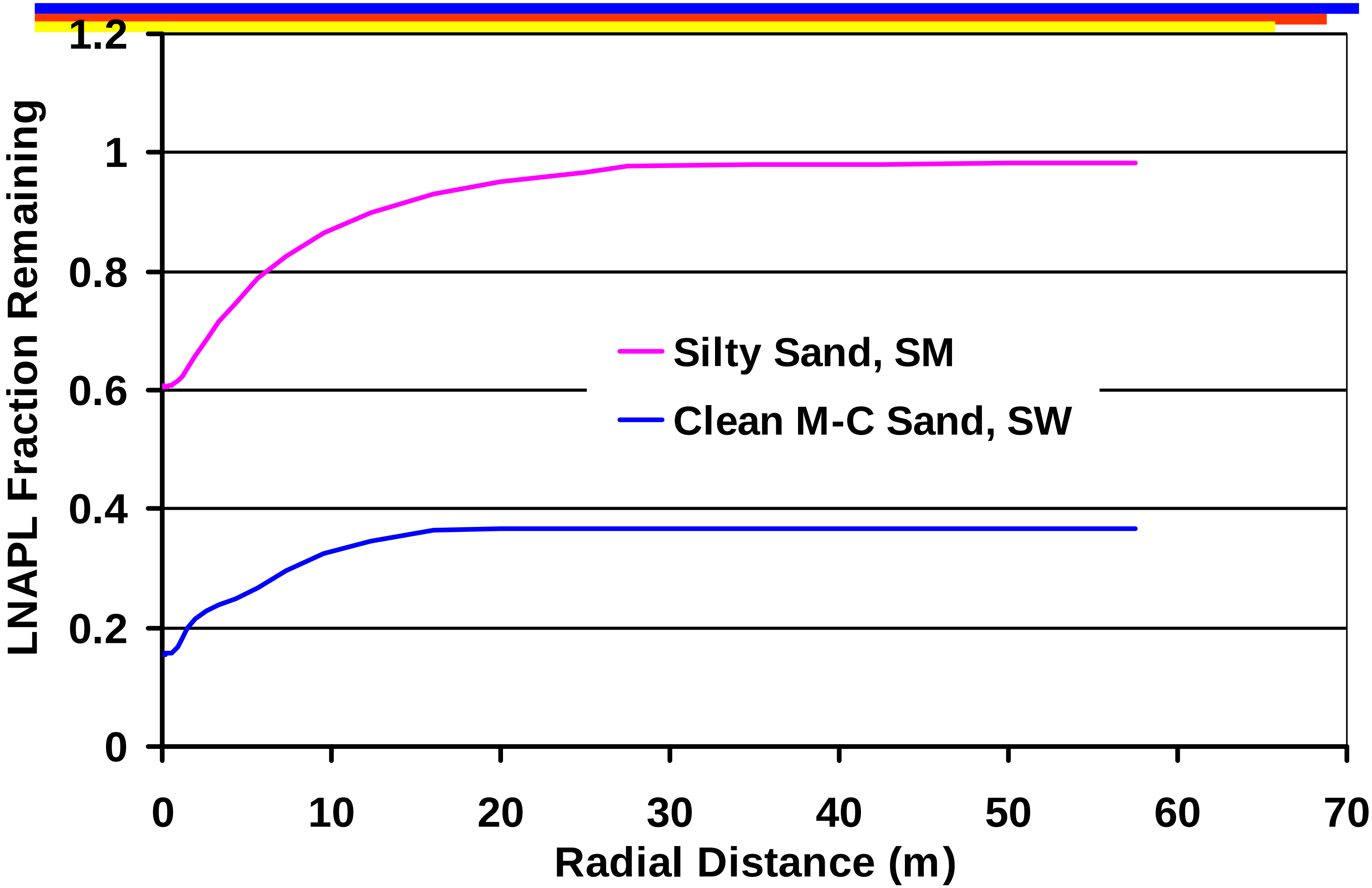
© AQUI-VER, INC.

LNAPL Formation Saturation after 3.2 Yrs Fluid Recovery



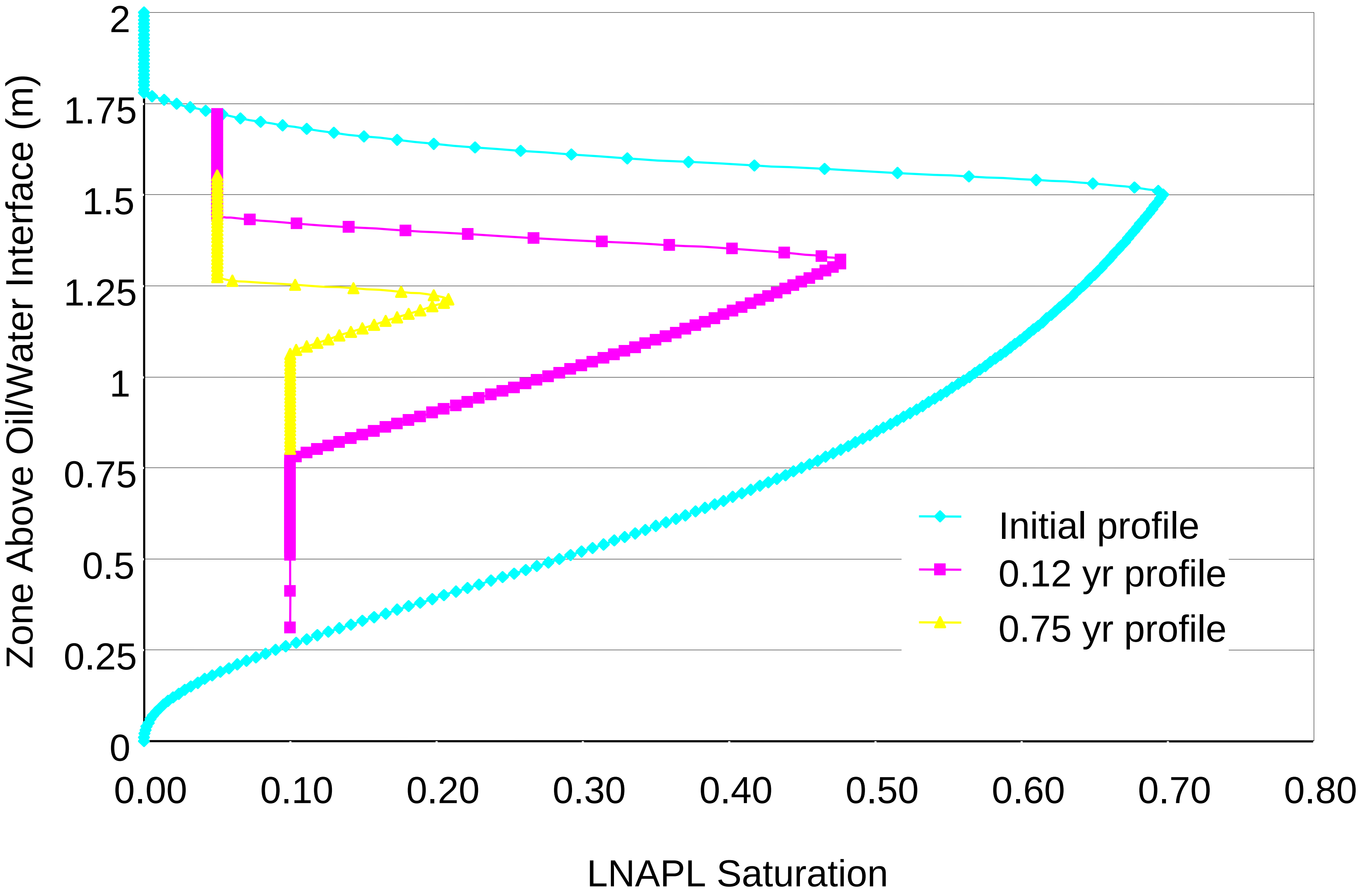
© AQUI-VER, INC.

Gasoline Fraction Remaining Vs. Distance



© AQUI-VER, INC.

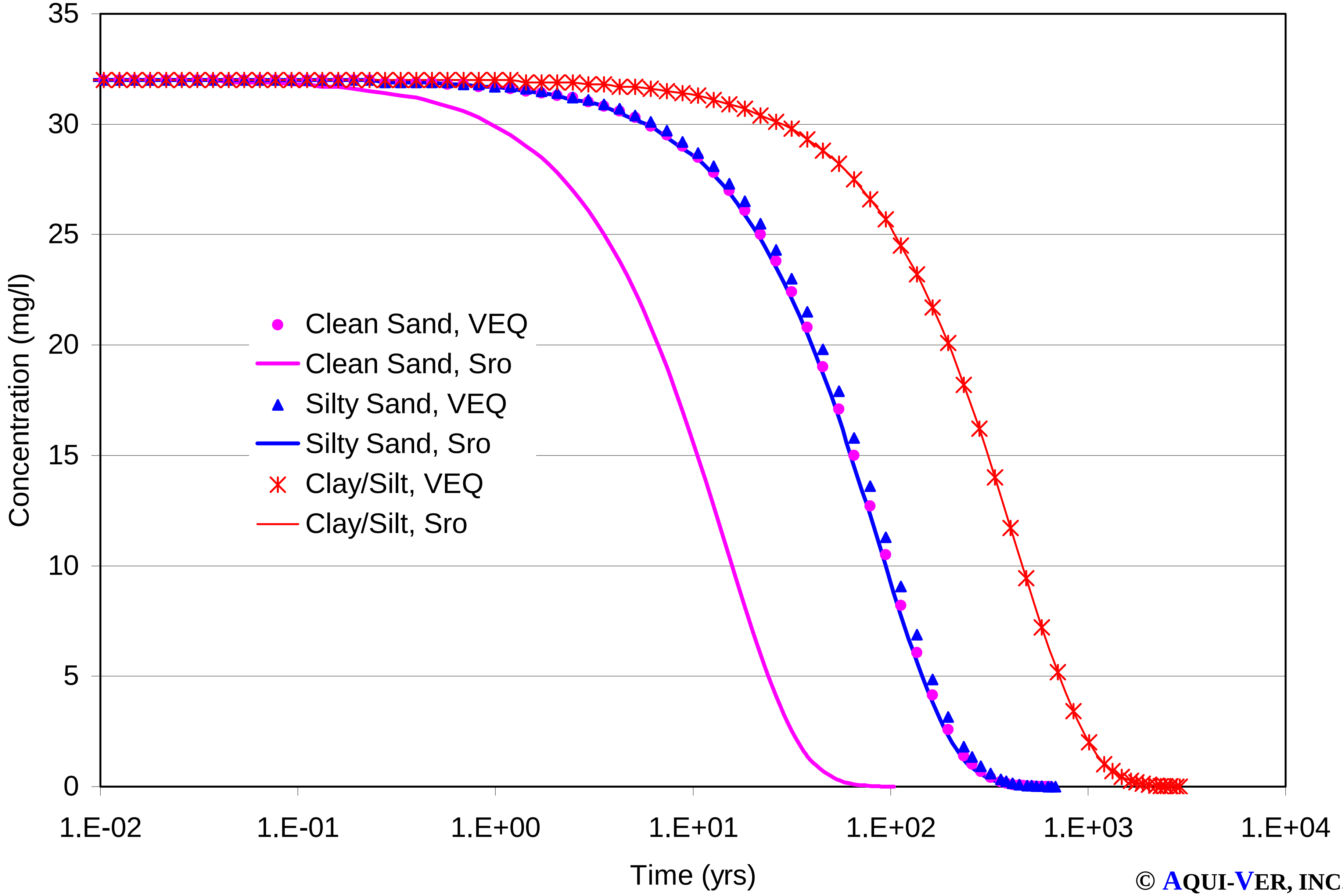
LNAPL Drainage Profiles through Time



© AQUI-VER, INC.

Benzene Longevity for Prior Examples; 1m FP

(clay/ silt, silty sand, clean sand)



© AQUI-VER, INC.

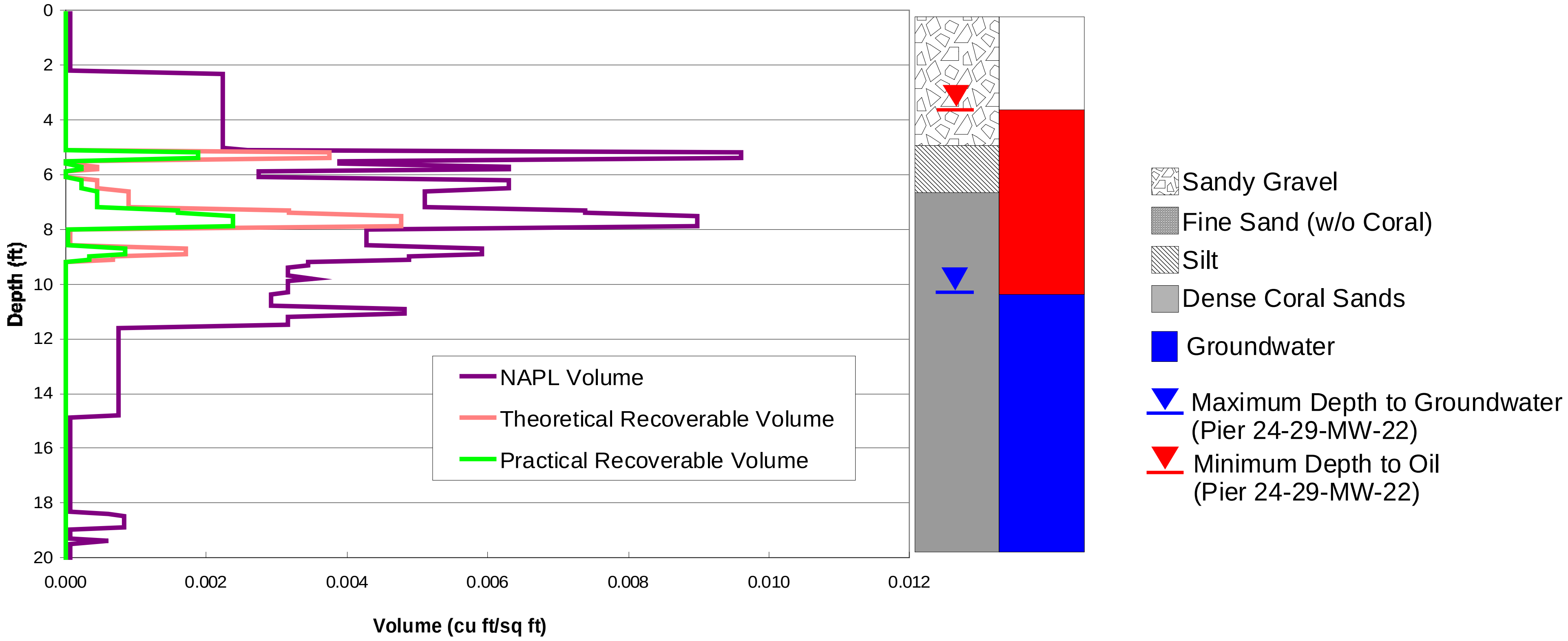
How Can We Define Practicable Limits?

(that mystery factor between theory, reality & hope)

- Look at saturation changes as function of applied pressure
  - We can achieve certain in situ pressure drops
  - Lab can give us this range on coral sands
    - Existing residual are all at high pressure endpoints
- Look at recovery decay away from well
  - Recovery falls off with radial distance
- Consider drawdown/water production limits
  - We can only expose a fraction of the LNAPL zone
  - The remainder is not hydraulically recoverable
- Other limitations
  - Wellfield interference
  - Operational efficiencies, etc.

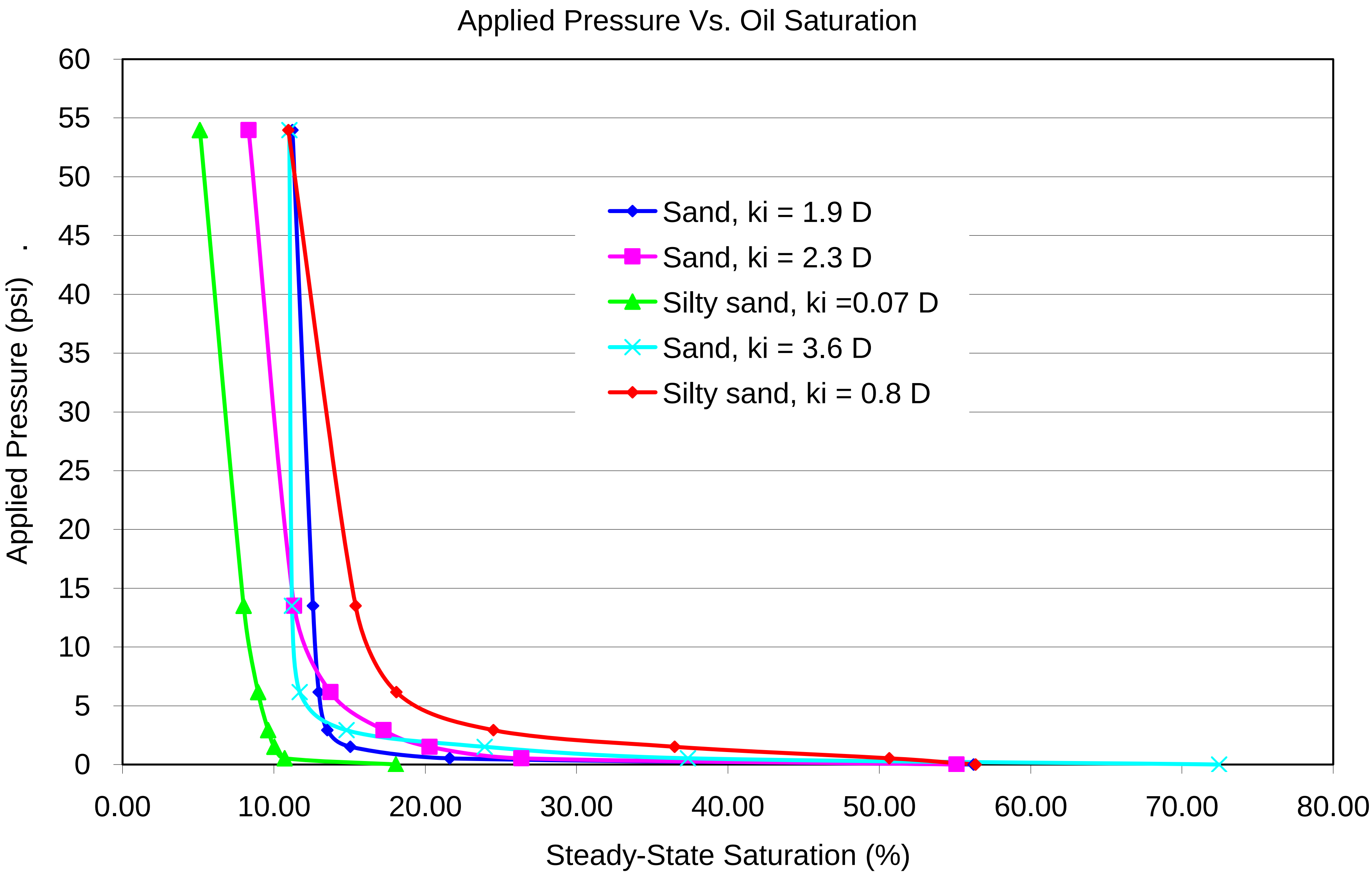
© AQUI-VER, INC.

Recoverable Profile Example



© AQUI-VER, INC.

Example of Applied Pressure Vs. Saturation



© AQUI-VER, INC.

Other Remediation Methods

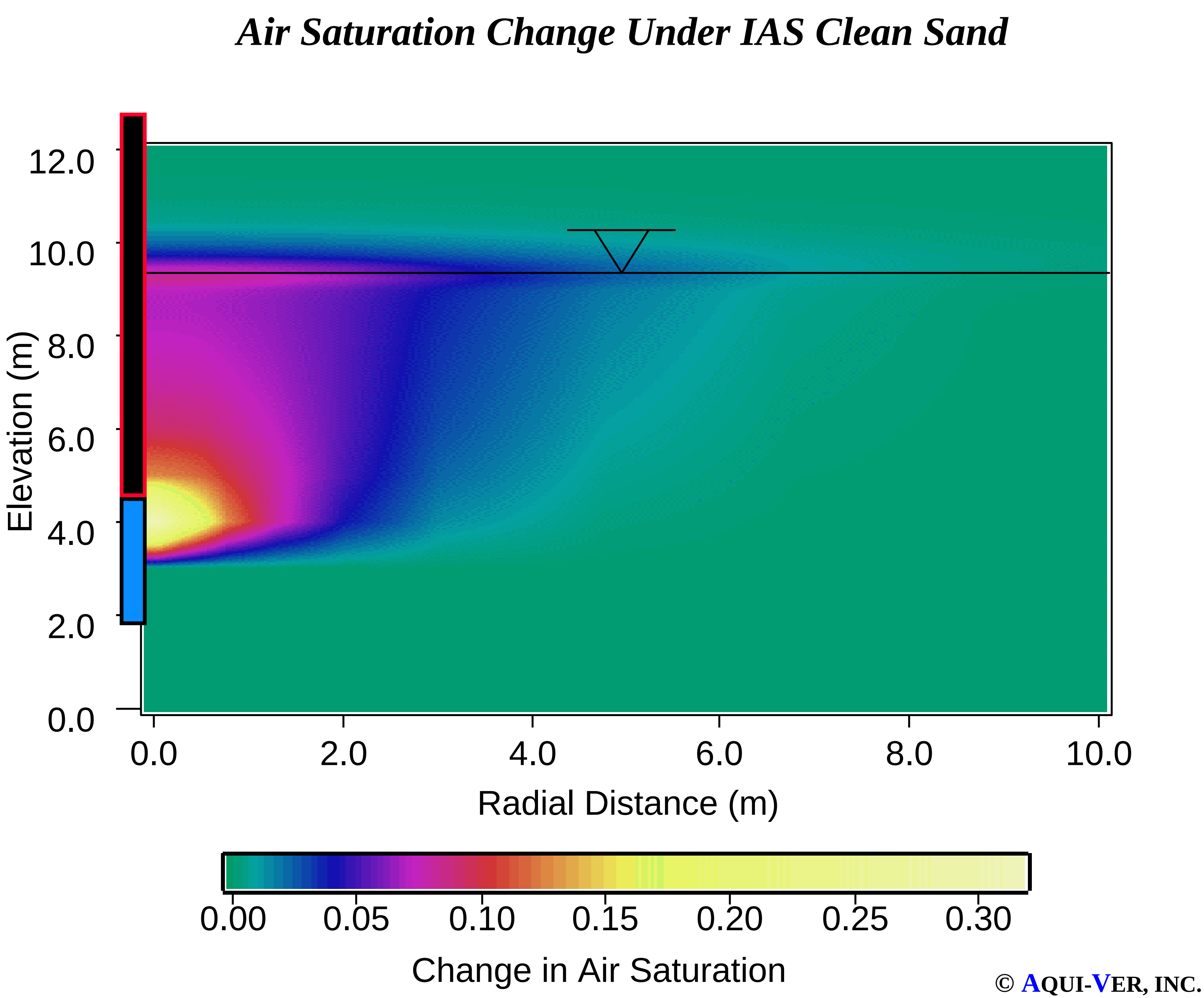
Air-based methods as Example

© AQUI-VER, INC.

Aeration

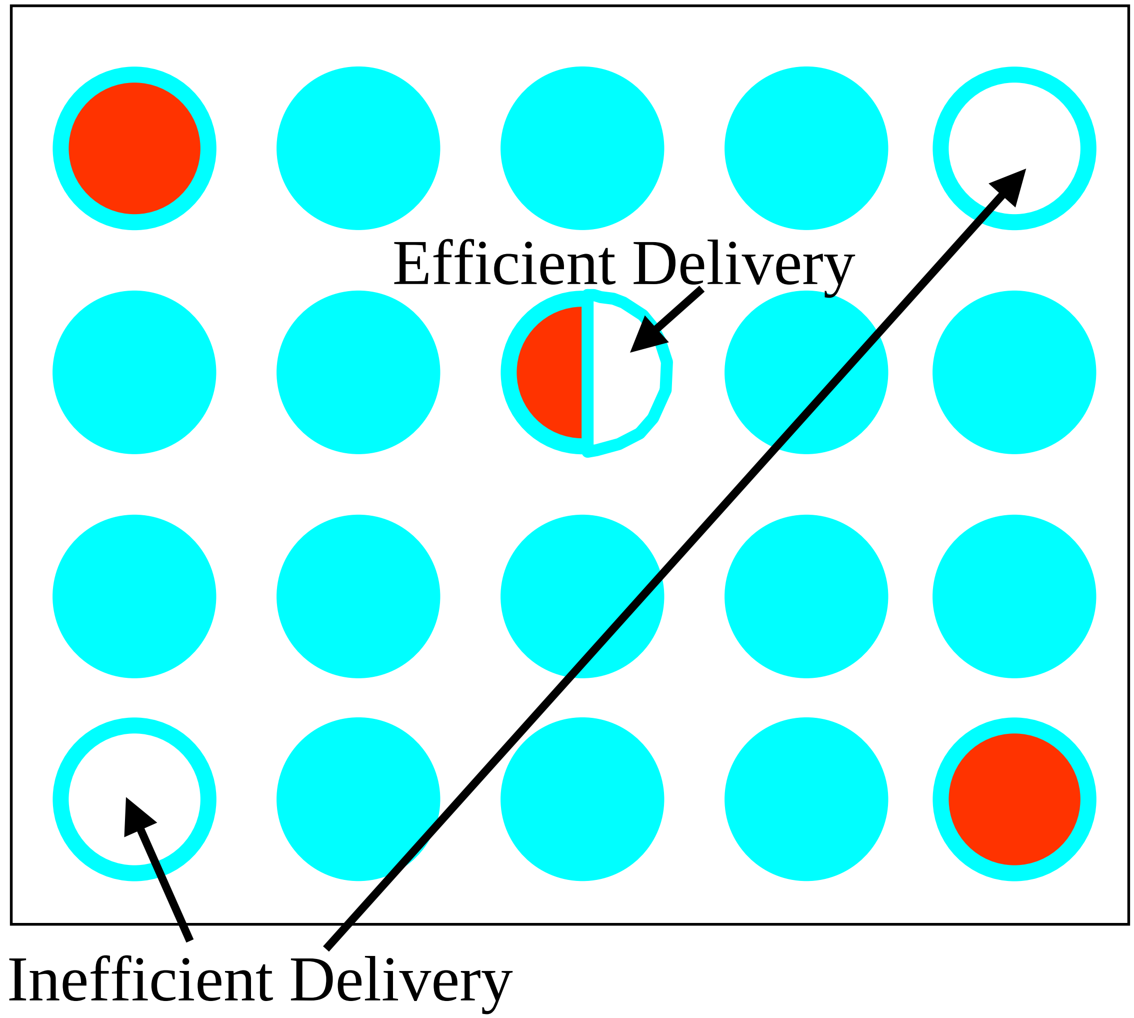
- Works preferentially based on volatilization
  - IE, specific chemicals partition differently
- Also some biologic component from O_2 additions
- So, while mass recovery methods remove everything
  - Aeration & similar methods preferentially strip chemicals
- How do those different mechanisms affect cleanup
  - With regard to rate
  - Effectiveness & residual longevity of chemicals remaining

© AQUI-VER, INC.


Air Saturation Change Under IAS Clean Sand
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Elevation (m)
0.0
2.0
4.0
6.0
8.0
10.0
Radial Distance (m)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Change in Air Saturation
© AQUI-VER, INC.

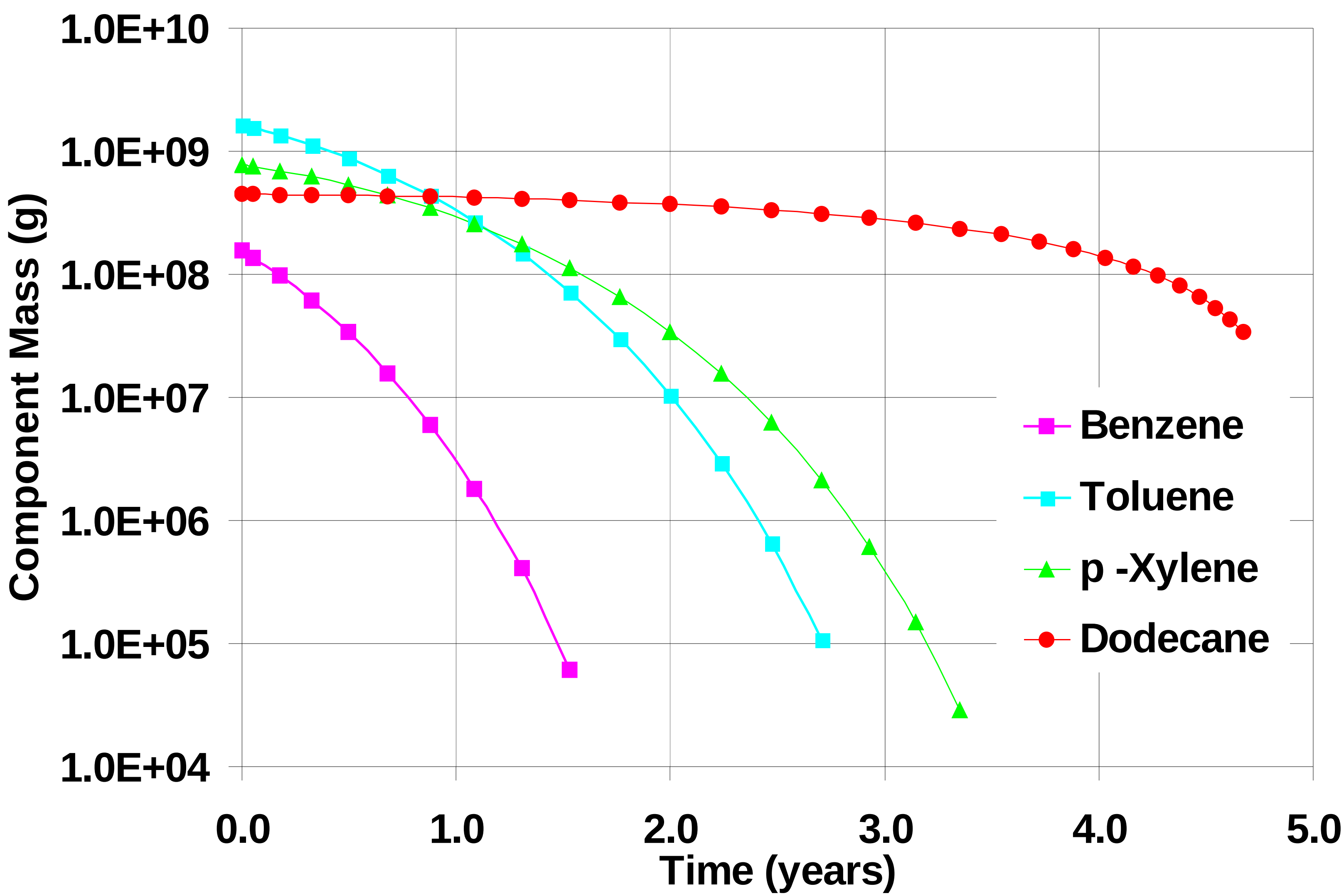
IAS Pore Field Deliver Efficiency

Multiphase Delivery Can Be Complex



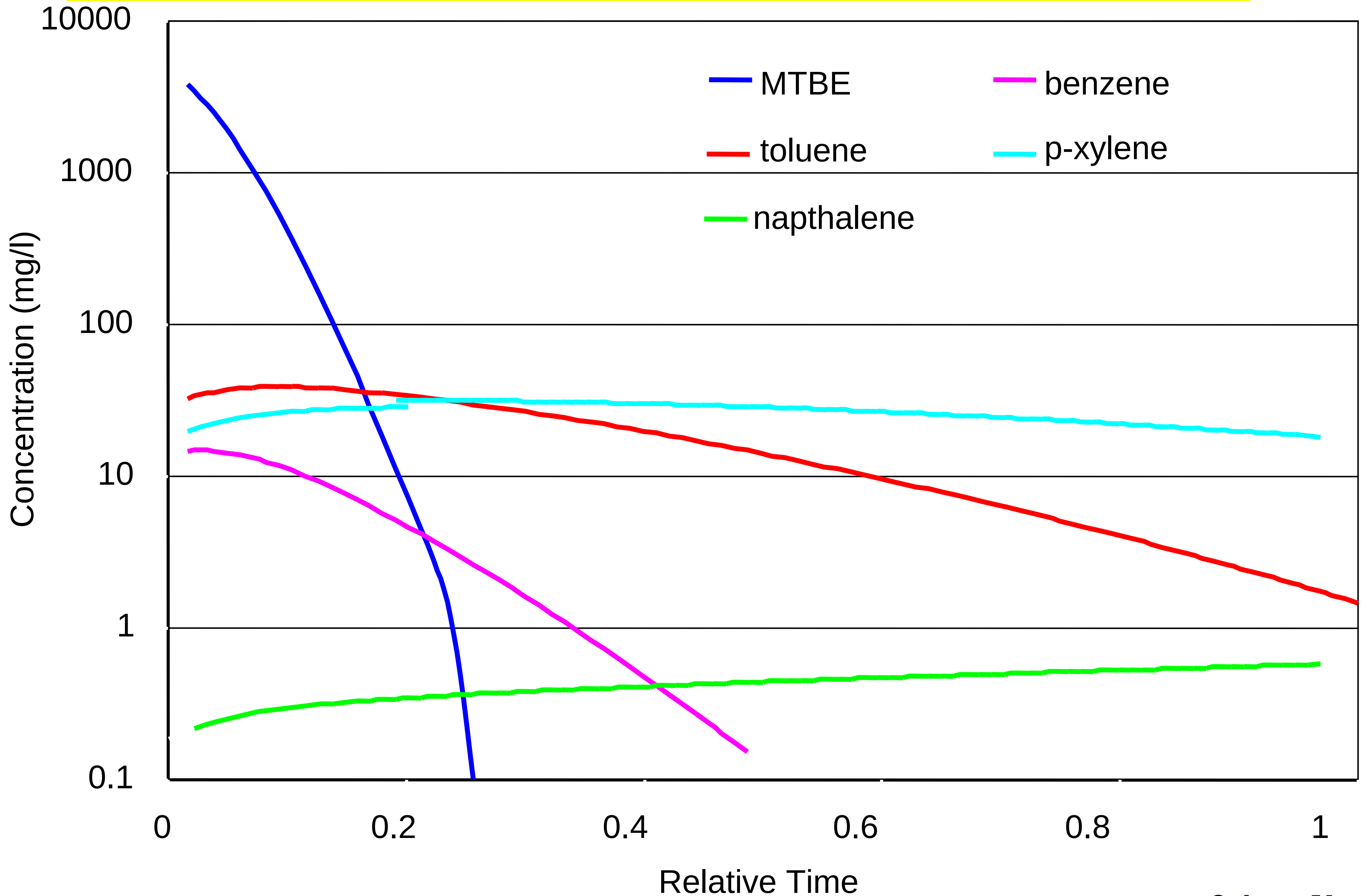
© AQUI-VER, INC.
© AQUI-VER, INC.

Component Stripping By SVE & IAS



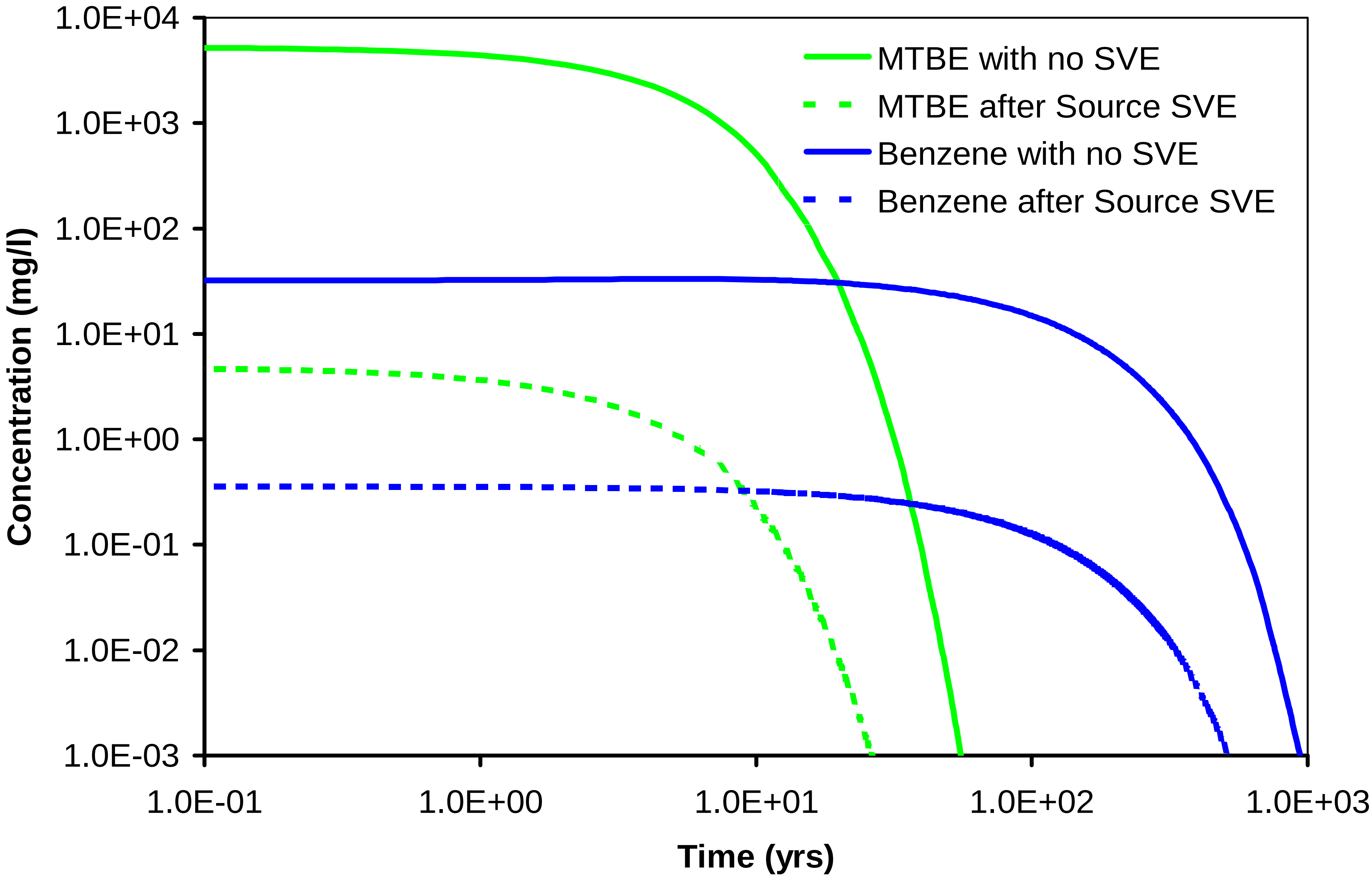
© AQUI-VER, INC.

Water Concentration Change Due to Stripping



© AQUI-VER, INC.

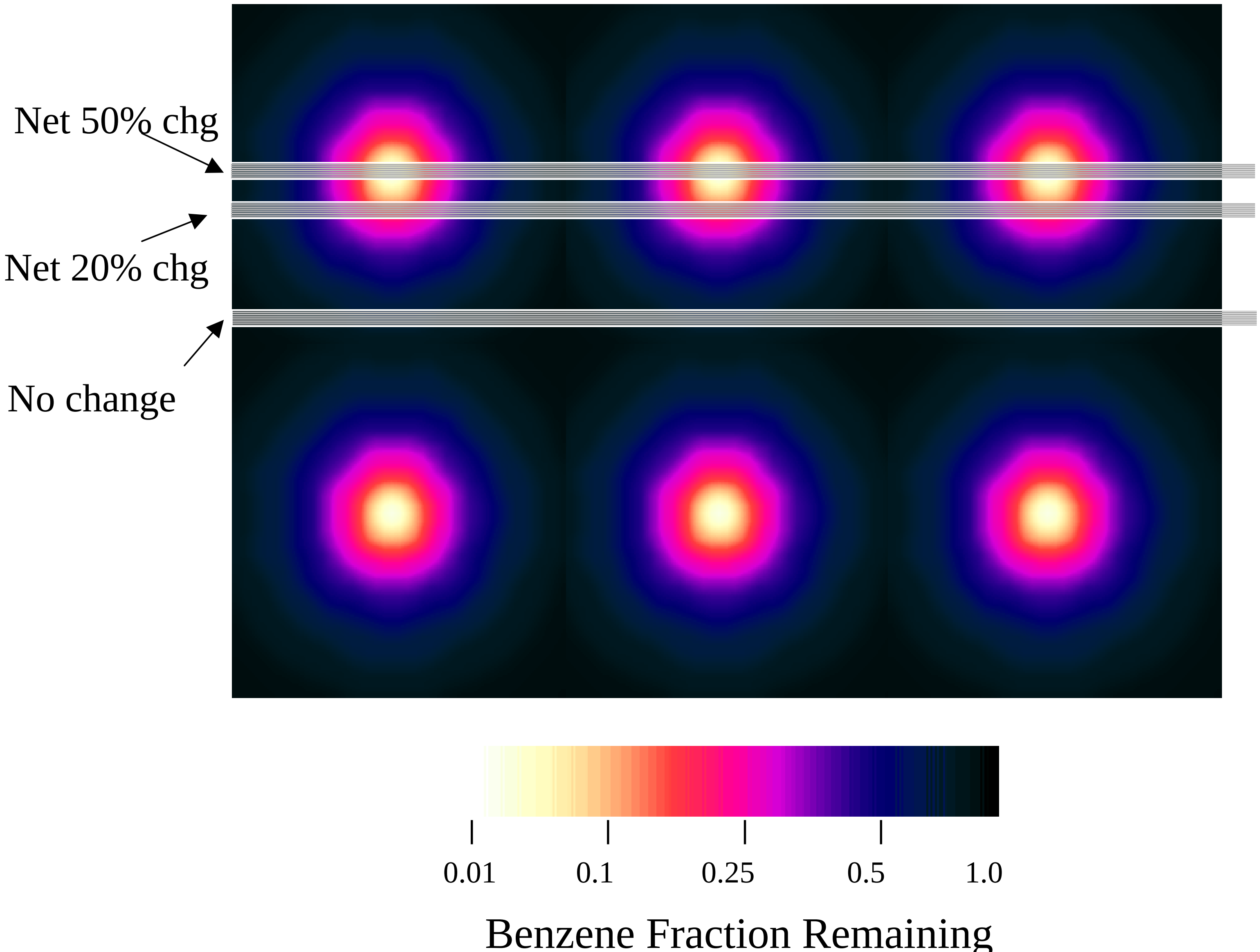
Effect of Stripping on Gasoline Source



© AQUI-VER, INC.

Different "Risk" Paths Through Cleanup Field

(as always, cleanup delivery is key issue)



© AQUI-VER, INC.

What Did We Learn?

(Shoot, I'm never quite sure..)

- All cleanups leave LNAPL mass in-place
  - Exceptions ***might*** be total excavation
- The mass left behind defines the benefit
  - If majority of mass remains, little benefit
  - If little remains, what is residual quality?
    - If it tastes bad, it still requires treatment
- Most remediation ROTs are not relevant
  - Real measurements, but not predictive
  - Radius of influence is a key ROT
    - Real, but useless in targeting
- All remediation ends in asymptotic behavior
  - Both efficient and failed systems
  - All it says is that its done, not that cleanup is done

© AQUI-VER, INC.