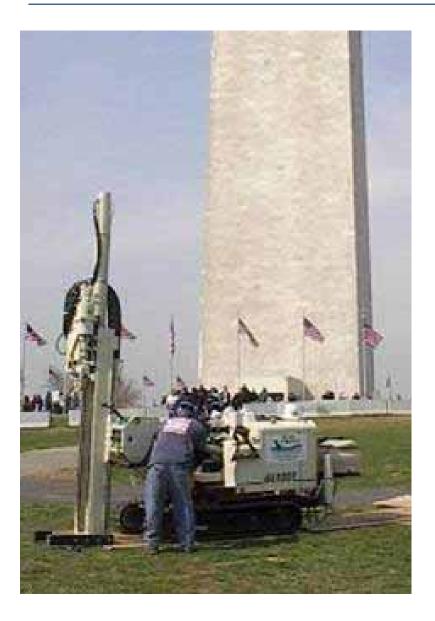
# Accelerating Site Closeout, Improving Performance, and Reducing Costs Through Optimization



"Bringing Chemistry and Contaminants Together To Support Our Consultant Customers"





# Advances in Site Characterization and Investigation Technologies

# Methodology For Integrating The Membrane Interface Probe With In-Situ Remediation Injection Design

Eliot Cooper, <a href="mailto:ecooper@vironex.com">ecooper@vironex.com</a>, 303-277-9773





#### Methodology Overview

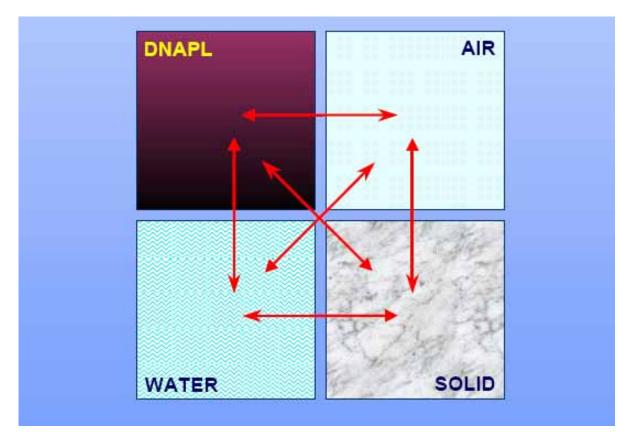
#### To identify contaminant mass in relation to lithology through use of the MIP and confirmation sampling.

To identify target injection intervals and delivery conduit.

- To determine reagent volumes required to meet treatment objectives.
- To select a pumping system to deliver reagent volumes at the design ROI and injection rate.



#### **Contaminant Mass Distribution**



Contaminant mass distribution is based <u>Water-Soil Equilibrium Partition</u> theory....the ability of organic carbon in soil to absorb contamination.



# EPA Difficulty To Treat Matrix

Hydrogeology	Mobile Dissolved (Degrades/ Volatilizes)	Mobile Dissolved	Strongly Sorbed, Dissolved	Strongly Sorbed, Dissolved (Degrades/ Volatilizes)	Separate Phase LNAPL	Separate Phase DNAPL
Homogeneous, Single Layer	1	1-2	2	2-3	2-3	3
Homogeneous, Multiple Layers	1	1-2	2	2-3	2-3	3
Heterogeneous, Single Layer	2	2	3	3	3	4
Heterogeneous, Multiple Layers	2	2	3	3	3	4
Fractured Bedrock	3	3	3	3	4	4

1= Least Difficult 4 = Most Difficult

Nobel Prize



# Contaminant Mass In Relation To Lithology

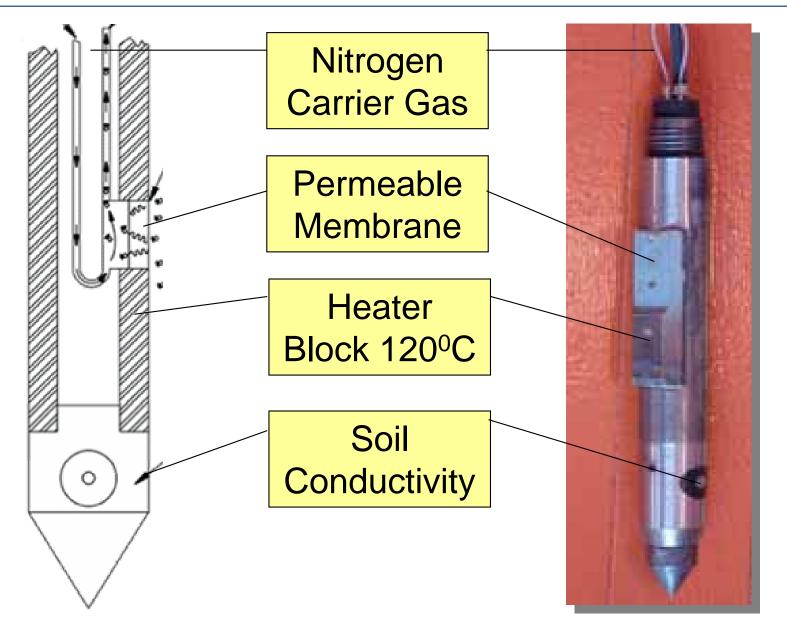
Treatment Zone						
Treatment Interval (Ft to Ft bgs)	Bioremediation and Oxidant Scavengers (ppm)	Natural Oxidant Demand (g/kg)	Dissolved (ppm)	Sorbed (ppm)	Residual NAPL (ppm)	Free Phase NAPL (ppm)
	Treatmer Interval			DNAPI	AIR	
				WATE	R SOLID	

Scavengers – e.g. carbonate ions for peroxide

**Natural Occurring Demand** is the consumption of an oxidant in reactions that are unrelated to degradation of the contaminant of concern



#### Membrane Interface Probe





#### Detectors

	Contaminants	Detection Ranges
PID Photo Ionization	Double-Bonded Compounds (gasoline, BTEX, High level PCE & TCE)	1 - 20,000 ppm Qualitative
FID Flame Ionization	Hydrocarbons (gasoline, BTEX methane, butane, landfill gases)	1 - 100,000 ppm Qualitative
ECD Electron Capture	Halogenated Compounds (Low-Level TCE, PCE, VC)	0.25 – 10 ppm Qualitative
Field Portable GC-MS	Speciated VOCs including MTBE	100 x PID/ECD sensitivity 100% ID of unknowns Quantitative

HAPSITE - March, 2004



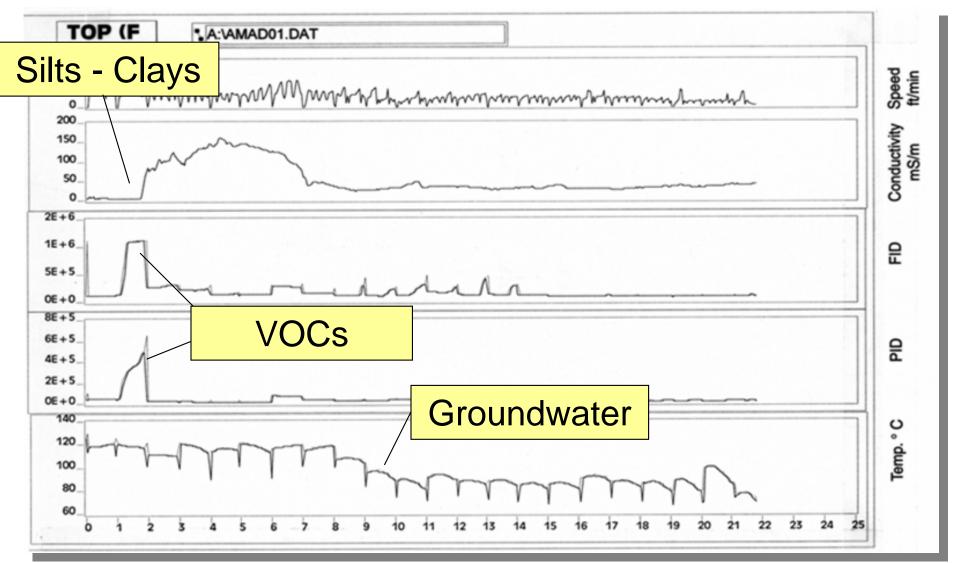
#### Membrane Interface Probe

# **MIP** Equipment





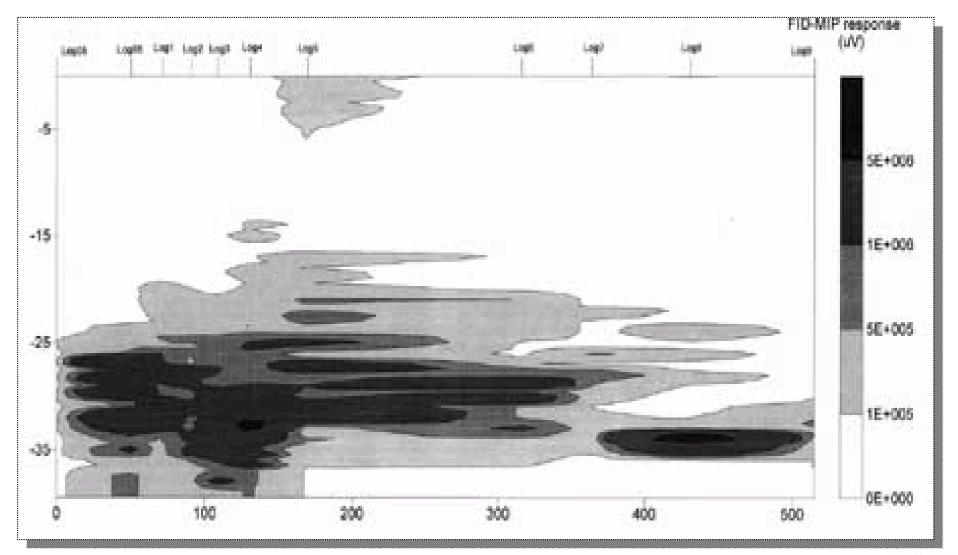
# MIP Real Time Data Display





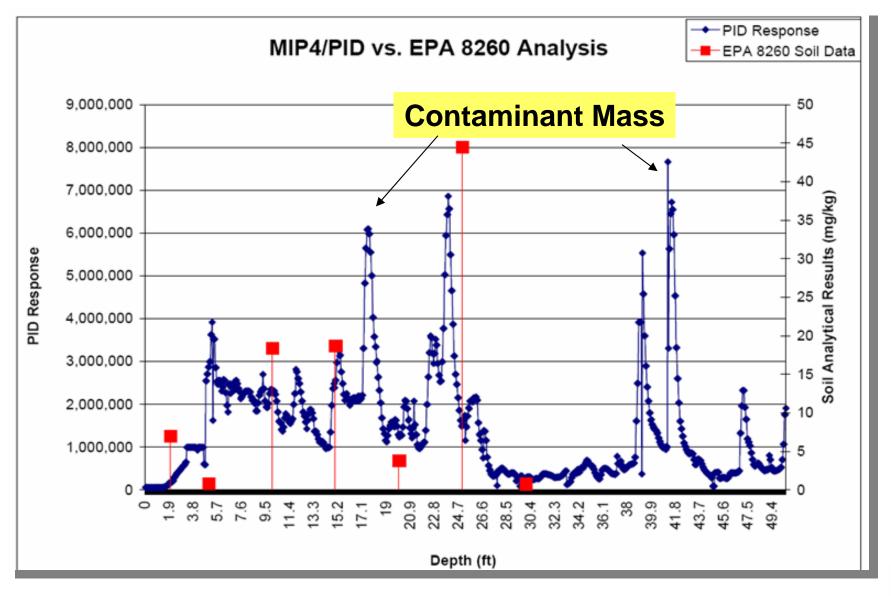
#### **Membrane Interface Probe**

# Contaminant Mass Identification – FID Qualitative





#### PID Soil Confirmation Samples – Vadose Zone





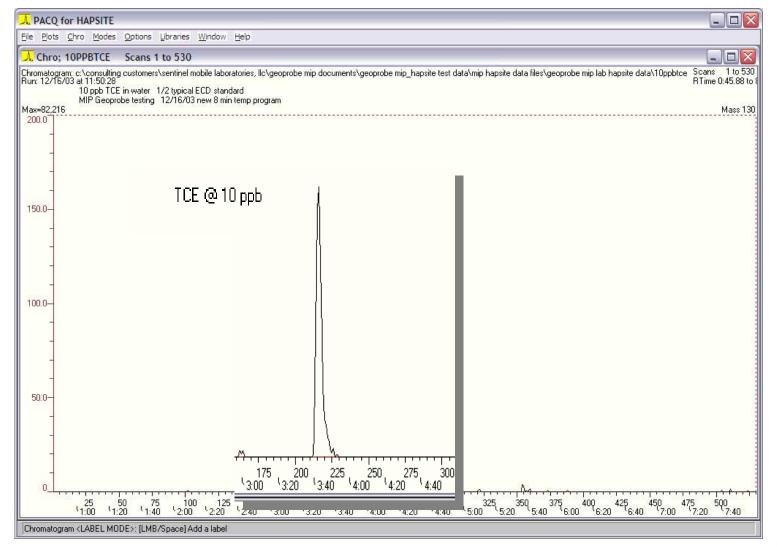
# HAPSITE Portable GC-MS & Headspace Sampling System







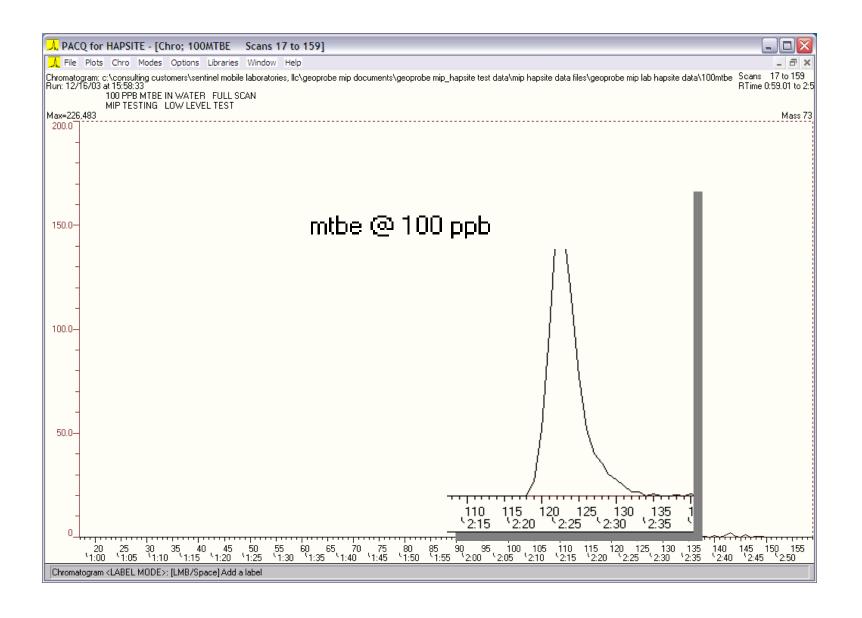
# X 100 Increase in Sensitivity Membrane Interface Probe with HAPSITE Integrated MIP System





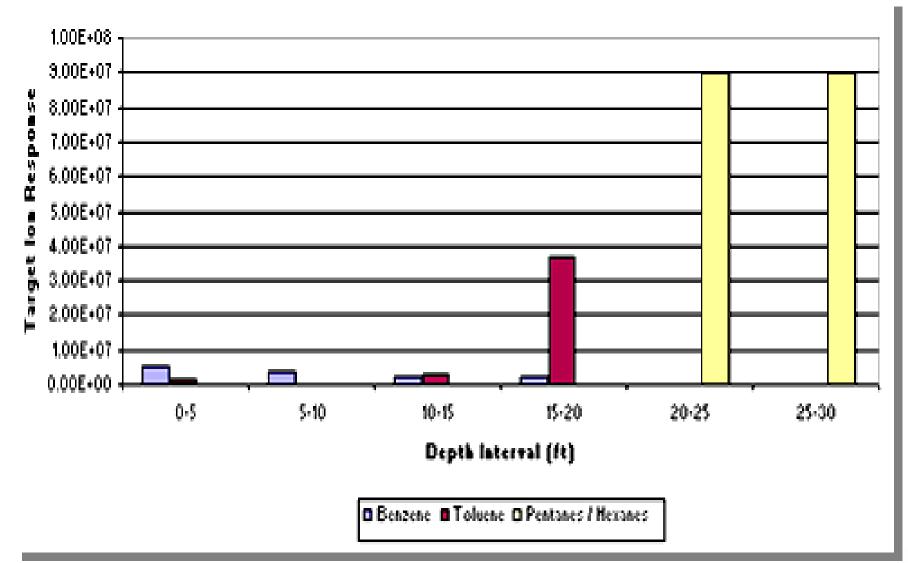
#### **Membrane Interface Probe**

### Ability to Detect MTBE





#### **MIP HAPSITE** - Quantitative



Vironex

# Confirmation Sampling and Modeling (NAPLANAL)

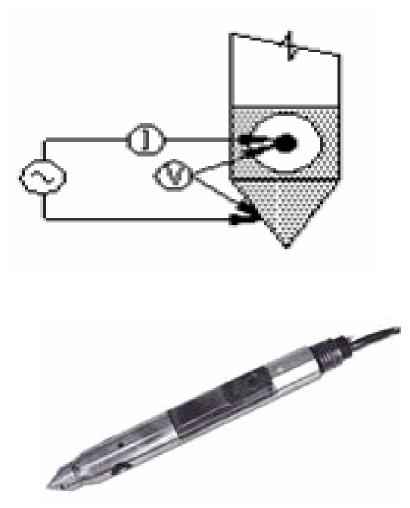
	Sample Name Identification: Model used: Porosity (Volume Frac.): Fraction organic carbon (f <sub>oc</sub> ): NAPLANAL ANALYSIS RESU			0.3 0.001	15 urated & po	prosity know	wn		
	Name	Total Mass (mg/kg)*	Mass in Water (mg/kg)*	Mass in Soil (mg/kg)*	Mass in NAPL (mg/kg)*	Conc. in Water (mg/L)	Sorbed in Soil (mg/kg)^	Conc. in NAPL (kg/L)	Mole Fraction in NAPL
	c-DCE	4.89	0.4335	0.245 4.2115 3.3227 0.2858 0.0005 0.0					0.0005
	PCE	0.28	0.0006	0.0014	0.2781	0.0043	0.0016	0	0.0000
	TCE	12345	180.571	149.561	12014.9	1384.2	174.41	1.4594	0.9995
	t-DCE	0.1	0.0059	0.0023	0.0918	0.0454	0.0027	0	0.0000
	(mg/kg)*	= mg per k	g of soil sa	mple (wet	soil)				
	(mg/kg)^	= mg per k	g of solid (	dry soil)					
Water Volume Frac. (L/L)				0.28219	Bulk (	Density (kg	/L) 2.16	32	
	NAPL Vo	lume Frac.	(L/L)	0.01781 NAPL Density (kg/L) 1.4599					
	Soil Volu	me Frac. (l	_/L)	0.7					
	Porosity (	Volume Fr	ac.)	0.3	NAPL	Saturation	n(%) 5.93	64	

Mariner, Jin & Jackson, An algorithm for the estimation of NAPL saturation and composition from typical soil chemical analyses. Ground Water Monitoring & Remediation Spring 1997, pp. 122-129.



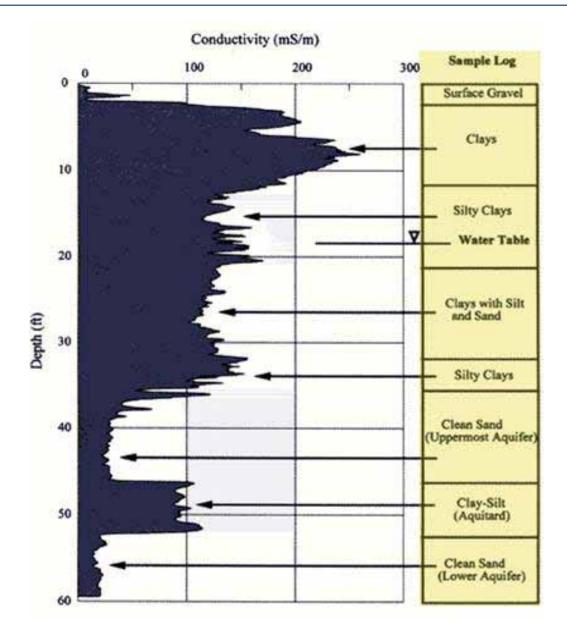
# Soil Conductivity

- The soil Ec uses a dipole measurement arrangement
- Alternating current is passed from the center of the probe to the probe body
- The voltage response of the soil to current is measured across the same two points
- Lower conductivities indicate sands, while higher conductivities indicate silts and clay



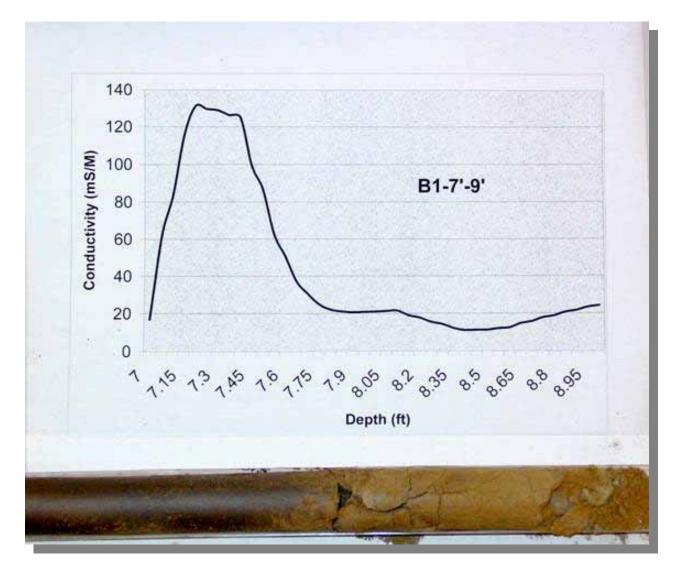


### Soil Ec Log Explanation





### Soil Conductivity Confirmation





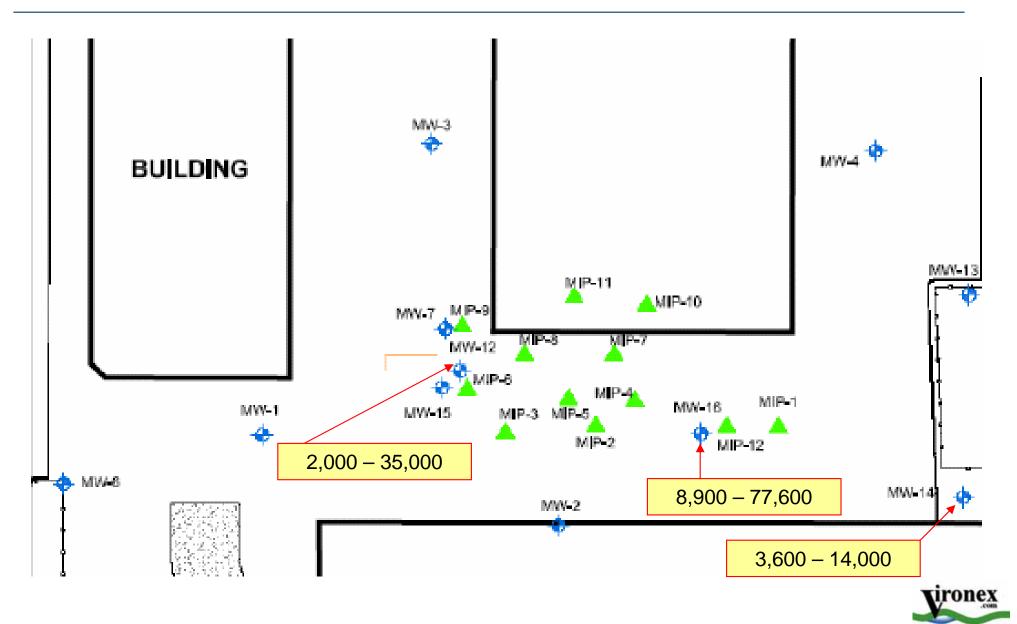
# MIP Case Study - Background

 Southern California industrial site where high TCE concentrations were indicated an upgradient unidentified DNAPL source zone

- Target saturated zone 14' to 33' bgs
- Primarily silts and clays
- Overriding concern was not to puncture aquitard at 33' bgs



# Groundwater Monitoring Well and MIP Locations



**Membrane Interface Probe** 

#### MIP PID and SC Results Summary

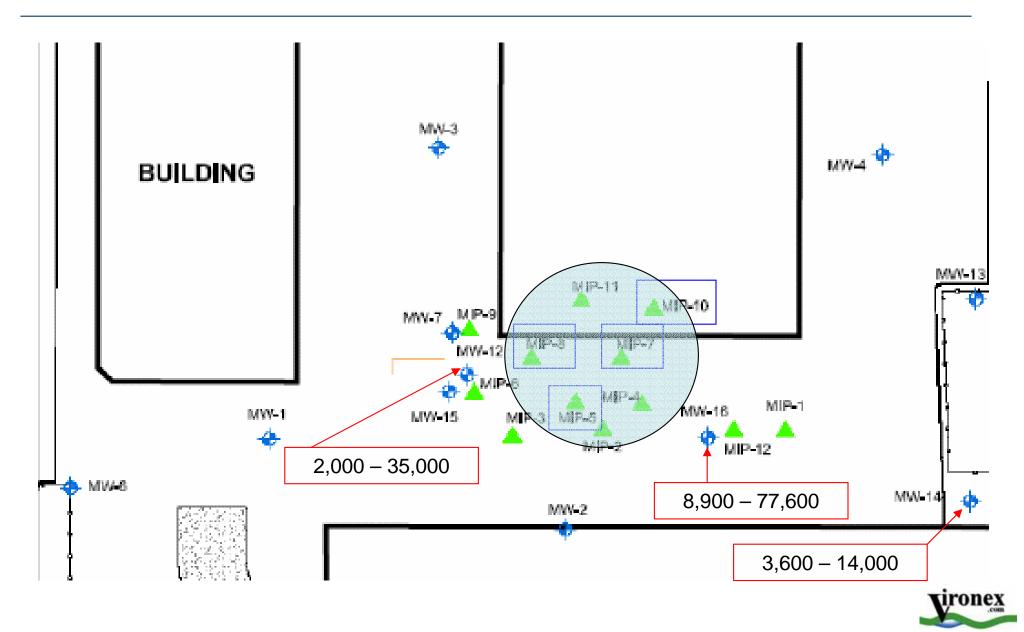
MIP Boring	Max PID Response X 10 <sup>6</sup>	Maximum PID Response Ft-bgs	Response Interval Ft-Ft	Soil Conductivity Max Response*
1	1	31.5	22 - 31	250
2	0.25	24	19-32	150
3	0.1	26	23-30	200
4	0.8	30	23-31	250
S	2	28	23-31	275
6	0.5	33	25-33	200
7	7.8	23	20-28	400
8	4	26	21-29	200
9 9	0.25	27	25-29	100
10	3.2	23	21-26	150
11	0.65	20	19-24	150
12	0.12	23	20-32	200

* Soil Type							
0-50	Clean Sand						
50-100	Clay-Silt						
100-200	Silty-Clays						
200 +	Clay						

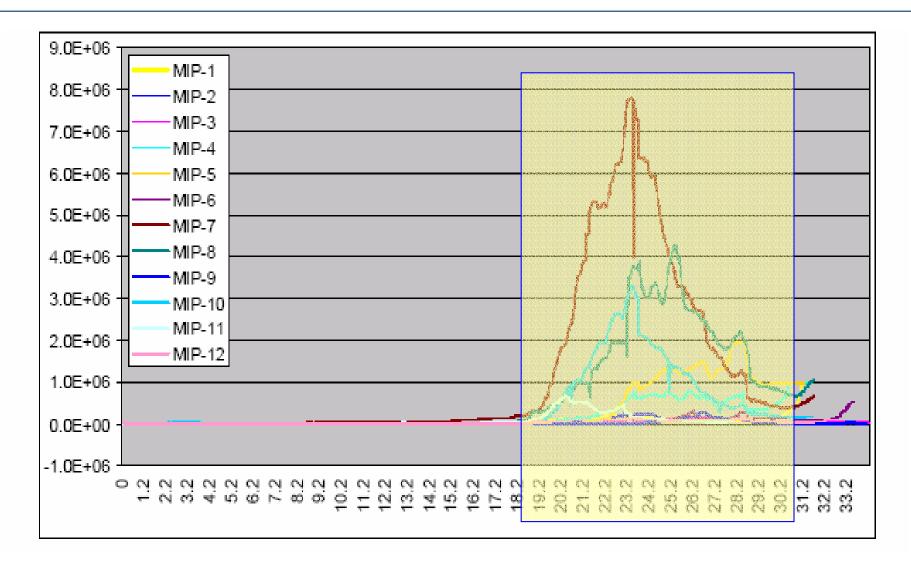
\* Chart is only for reference of soil type and should not be used to describe soil type without confirmation sampling to calibrate the soil conductivity readings.



#### MIP Results – Contaminant Mass



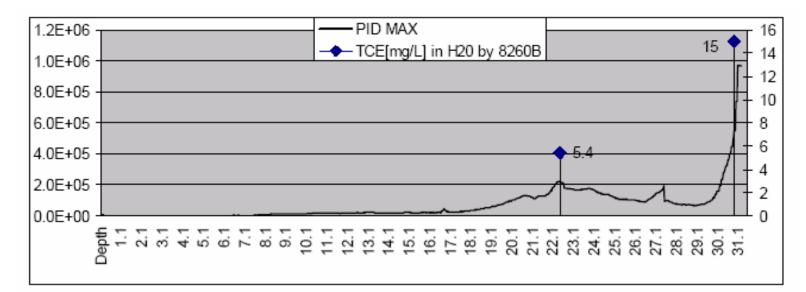
#### **MIP PID Results Summary**

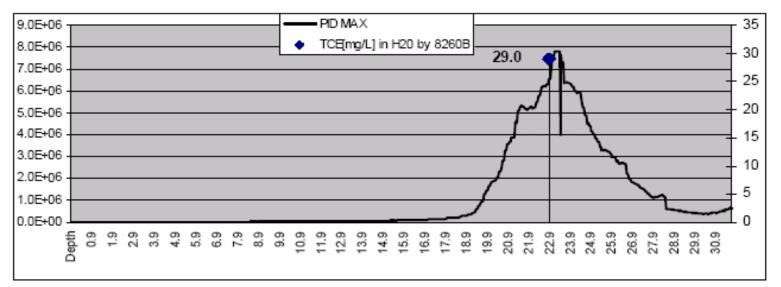




#### **Membrane Interface Probe**

# MIP 1 and 7 - GW Confirmation Sampling







#### MIP Cost Comparison

	Geoprobe	MIP Unit	EPA Method	Total
	66DT	Unit	8260	
MIP	\$3,150.00	\$1,500.00	\$125.00	
Units	2	2	3	
Total	\$6,300.00	\$3,000.00	\$375.00	\$9,675.00
Continuous Core	\$2,650.00	\$1,500.00	\$125.00	
Analyze Every 5 Feet				
Units	3	0	72	
Total	\$7,950.00	\$0.00	\$9,000.00	\$16,950.00
Continuous Core	\$2,650.00	\$1,500.00	\$125.00	
Analyze Every 1 Foot				
Units	3	0	360	
Total	\$7,950.00	\$0.00	\$45,000.00	\$52,950.00



#### Methodology Overview

To identify contaminant mass in relation to lithology through use of the MIP and confirmation sampling.

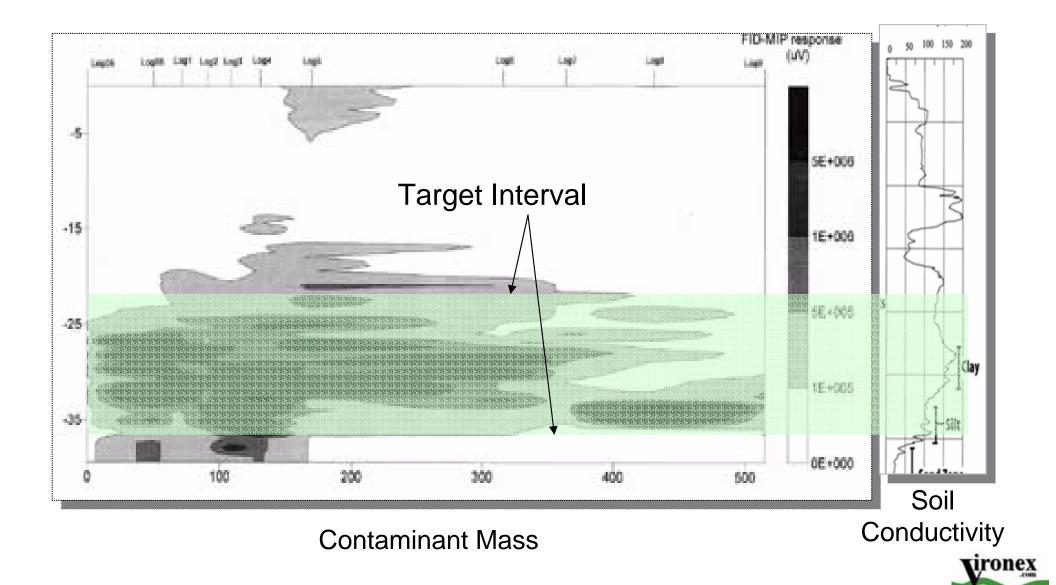
# □ To identify target injection intervals and delivery conduit.

To determine reagent volumes required to meet treatment objectives.

To select a pumping system to deliver reagent volumes at the design ROI and injection rate.



### **Target Interval Identification**

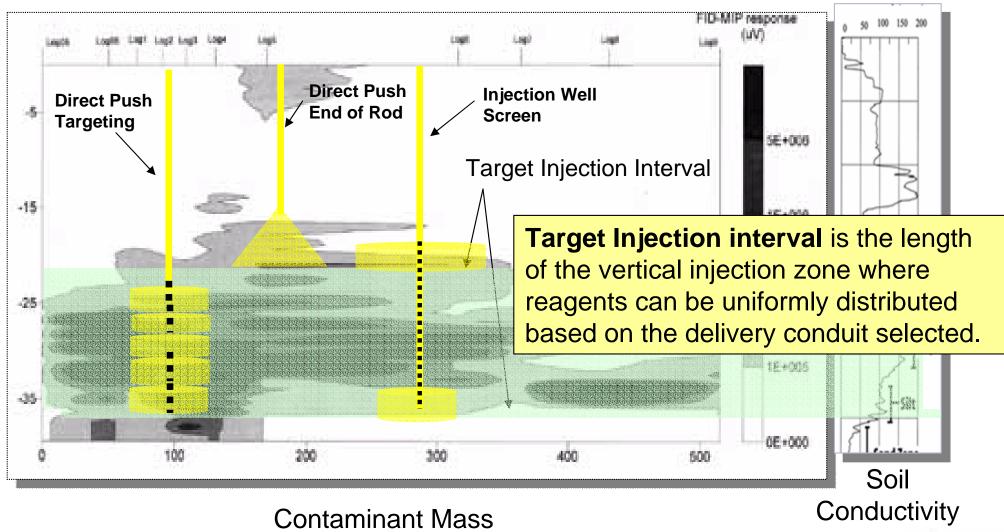


# **Delivery: Conduit**

Technology	Injection Zone Targeting	Specifications Reagent Considerations		Limitations	Injection Locations
DPT	1 foot Interval targeting	1.5" O.D. injection tooling	Bioremediation – None	Unconsolidated soils and bedrock	Moveable
		18,000 to 31,000 lbs of pushing force 40 to 110 feet	Oxidant - Peroxide surfacing Persulfate Acidity		
Injection Wells	Multiple screens Use of packers to isolate deep intervals	1" I.D. to 4" I.D PVC (Schedule 40 or 80), black iron, stainless steel DPT Installed Pre-packed	Bioremediation – Flush well Oxidants - Stainless steel for oxidant heat generation (e.g. DNAPL) Peroxide surfacing	Fixed injection locations Reagents preferential flow to higher permeable intervals within injection screen	Fixed

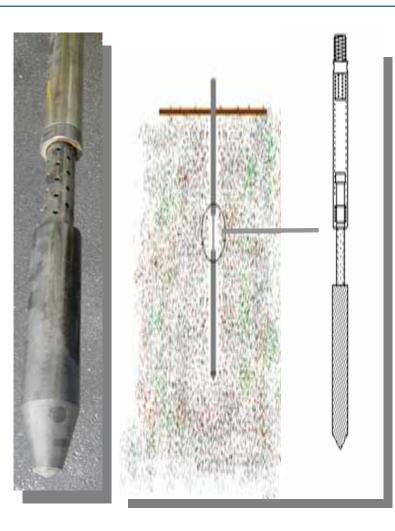


# **Target Interval Conduit Strategies**





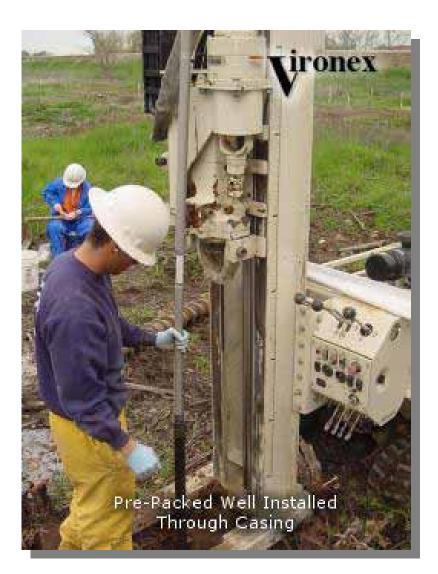
# **Target Interval: DPT Injection Tooling**



- Target injection zones
- Inject consistently through the formation
- Inject while advancing or retracting
- Check valve retains the compound in the subsurface



# Target Interval: Pre-Packed Stainless Steel Injection Wells







#### **Target Interval: Packer Isolation**



 2" PVC Injection wells to 175'



#### Methodology Overview

To identify contaminant mass in relation to lithology through use of the MIP and confirmation sampling.

□ To identify target injection intervals and delivery conduit.

□ To determine reagent volumes required to meet treatment objectives.

To select a pumping system to deliver reagent volumes at the design ROI and injection rate.



# **Delivery: Reagents**

Reagent	Injection Concentrations	Catalyzed	Injection Considerations
Hydrogen Release, e.g.	100%	Bio- Augmentation,	Viscous material requires heating
HRC, HRC-X		e.g. INOCULUM	
Oxygen Release, e.g. ORC	30 to 40%	None	None
Hydrogen	5 to 17%	Iron	Gas generation, heat and surfacing
Peroxide		Chelated Iron	Catalyst and peroxide injected separately
			Gas generation can impede injection rates in fractured bedrock
Potassium Permanganate	3 to 4%	None	None
Sodium Permanganate	10% to 20%	None	None
Sodium Persulfate	10% to 20%	Iron, Chelated Iron, Heat,	Catalyst and persulfate can be mixed and injected together.
		Peroxide	Acidic

# **Injection Design: Reagent Mass**

Treatment Zone Stoichiometric					age bs.	•	ements		Injected F Require (Lb	ments		
Injection Intervals (Ft to Ft bgs)	Treatment Area (Ft <sup>2)</sup>	Treatment Interval (YD <sup>3)</sup>		enging IOD	Dissolved Phase	Sorbe Phas		Residual NAPL	Free Phase NAPL	Total	In-Situ Efficiency %	Total Reagent Injected
			-		atabilit					/		
					atabilit udies	у				Situ		
		endor culato	rs						Efficie	ency	<mark>%</mark>	

**Target Injection Interval** is the length of the vertical injection zone where reagents can be uniformly distributed based on the delivery conduit selected.



#### Methodology Overview

To identify contaminant mass in relation to lithology through use of the MIP and confirmation sampling.

□ To identify target injection intervals and delivery conduit.

To determine reagent volumes required to meet treatment objectives.

To select a pumping system to deliver reagent volumes at the design ROI and flow rate.



### Delivery: Pumps - Viscous, Low Volume

	Viscous, Low Volume Reagents, e.g. HRC or HRC-X									
Hydraulic Conductivity	Pumps	Max Injection Pressure	Max Injection Rate	Max ROI	Other Distribution					
Low < 3 ft/day	Piston Pump	1500 PSI	9 GPM	2 feet	Advection, Diffusion, Dispersion					
High > 3 ft/day	Piston Pump	1500 PSI	9 GPM	2 feet	Advection, Diffusion, Dispersion					



### Delivery: Pumps - Non-Viscous, Low Volume

	Non - Viscous, Low Volume Reagents, e.g. ORC									
Hydraulic Conductivity	Pumps	Max Injection Pressure	Max Injection Rate	Max ROI	Other Distribution					
Low < 3 ft/day	Piston Pump	1500 PSI	9 GPM	2 feet	Advection, Diffusion, Dispersion					
High > 3 ft/day	Piston Pump	1500 PSI	9 GPM	2 feet	Advection, Diffusion, Dispersion					



# Delivery: Pumps – Non-Viscous, High Volume

	Hydrogen Peroxide / Fenton's Reagent - Short Lived				Sodium Persulfate, Permanganate, Hydrogen Donor Compounds - Persistent				
Hydraulic Conductivity	Pumps	Max Injection Pressure	Max Injection Rate	Max ROI	Pumps	Max Injection Pressure	Max Injection Rate	Max ROI	
Low < 3 ft/day	Bladder	120 PSI	1 gpm	5 feet	Positive Displace ment	2500 PSI	10 gpm	10 feet + Dispersion	
High > 3 ft/day	Bladder	120 PSI	15 gpm	15 feet	Bladder Moyno Positive Displace ment	50 -1600 PSI	30 GPM	20 feet + Dispersion	



# Injection Design: ROI and Reagent Volume

Treatment Intervals (Ft-Ft bgs)	Hydraulic Conductivity (Ft/Day)	Reagent (Lbs)	Reagent ROI (Gals) (FT)		Injection Volume as a % Pore Volume	DPT or Fixed Well		# Injection Locations	or Inject	Screen Length or Injection target interval (Ft)	
			Re	Regulatory				PT Allo More			
				Issues			Conservative Spacing –				

**ROI** is a function of interval screen length or DPT targeting, injection pressure, reagent/flush volume, reagent persistence, and dispersion. Confirmation through pilot testing.

**Injection volume** = (reagent mass / reagent solubility) x reagent inefficiency (e.g. gas generation)



# Hydraulic Conductivity

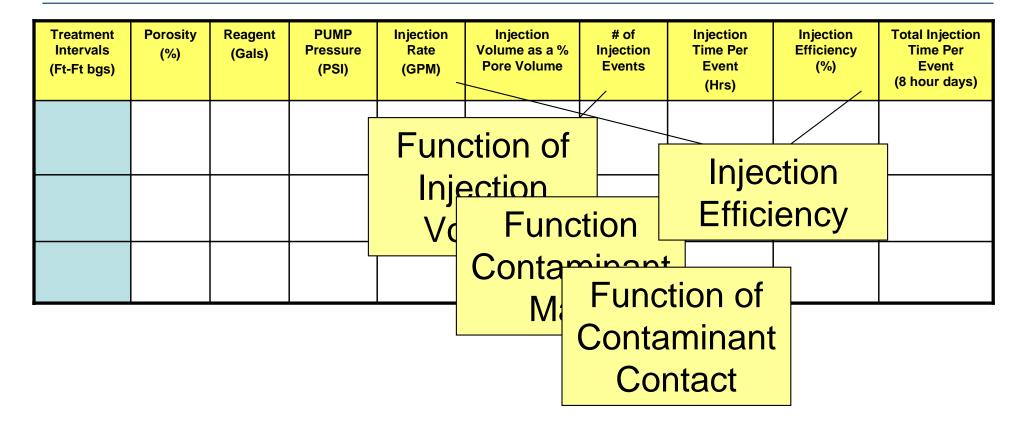
Pneumatic slug testsCone Permeameter







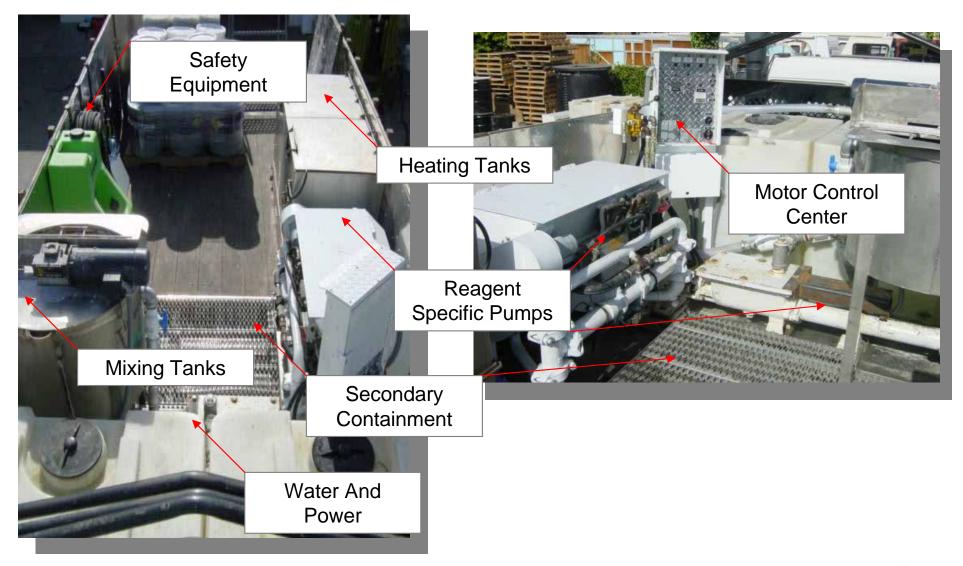
### Injection Design: Duration / # of Events



Injection efficiency = hours of injection at design rate / available injection hours



# Injection Efficiency: Dedicated Injection Rigs





Key Takeaways

□The MIP = definition of target intervals.

Remediation success = effective delivery of reagents into the target intervals.

Methodology = Accelerated site closure, improved performance, and reduced costs.

