Assessing Source Zone Natural Attenuation and Source Zone Longevity

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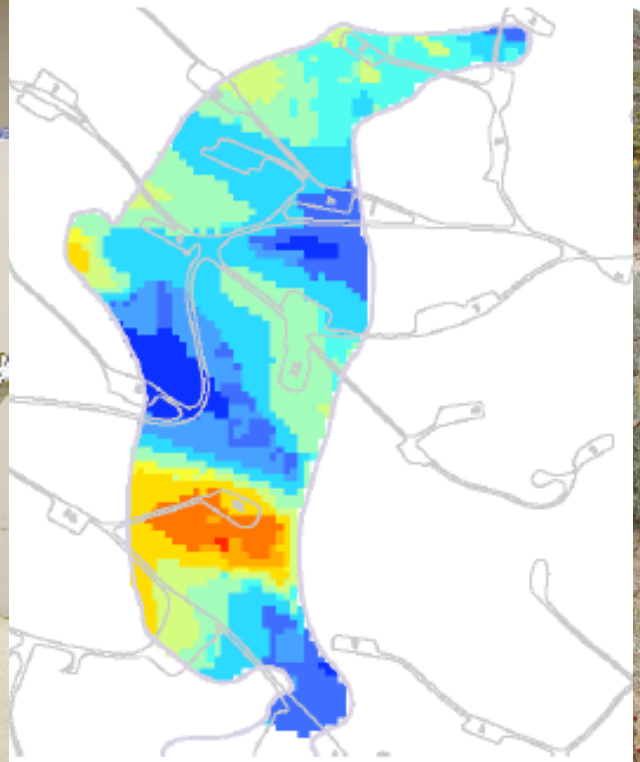
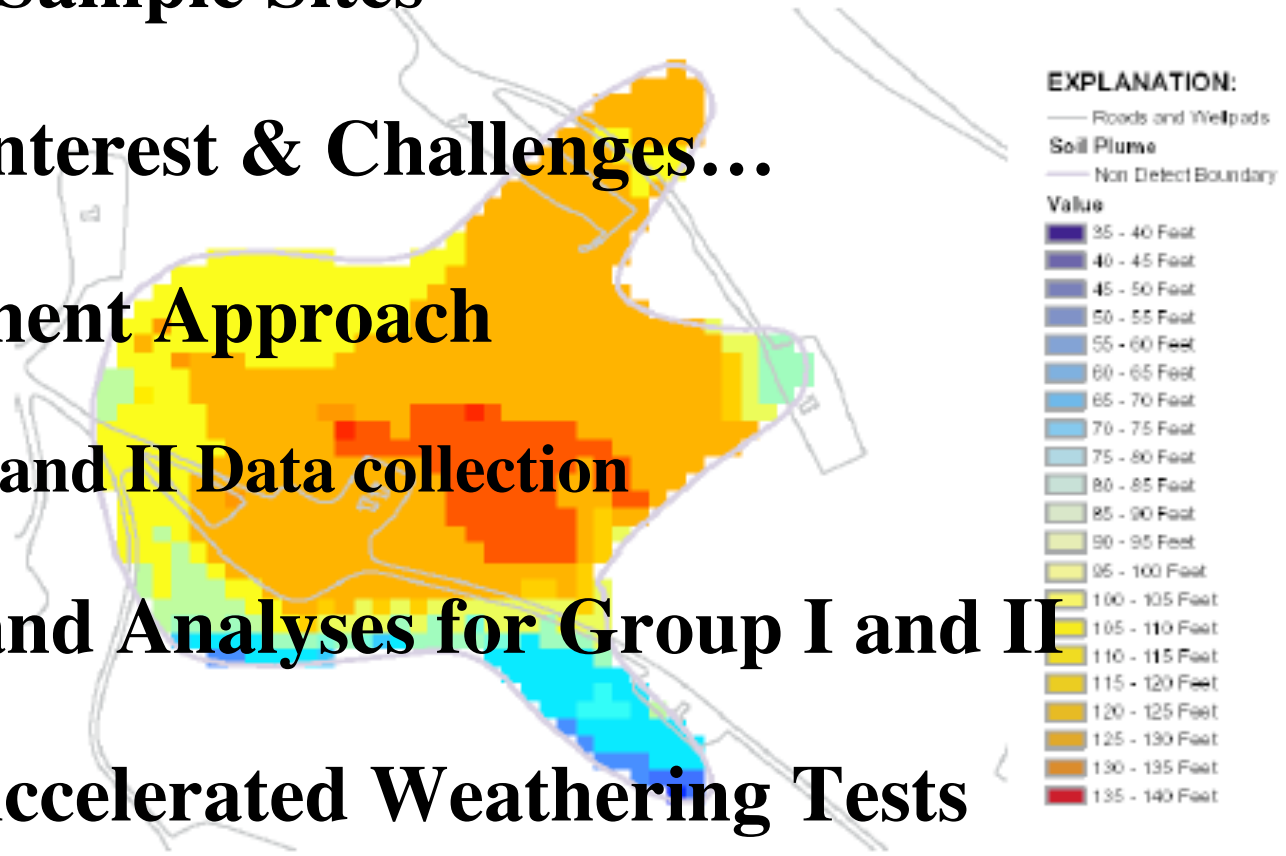


This work was sponsored by Rio Tinto (Thanks to Stuart Rhodes!) and the company formerly known as Unocal (now Chevron)

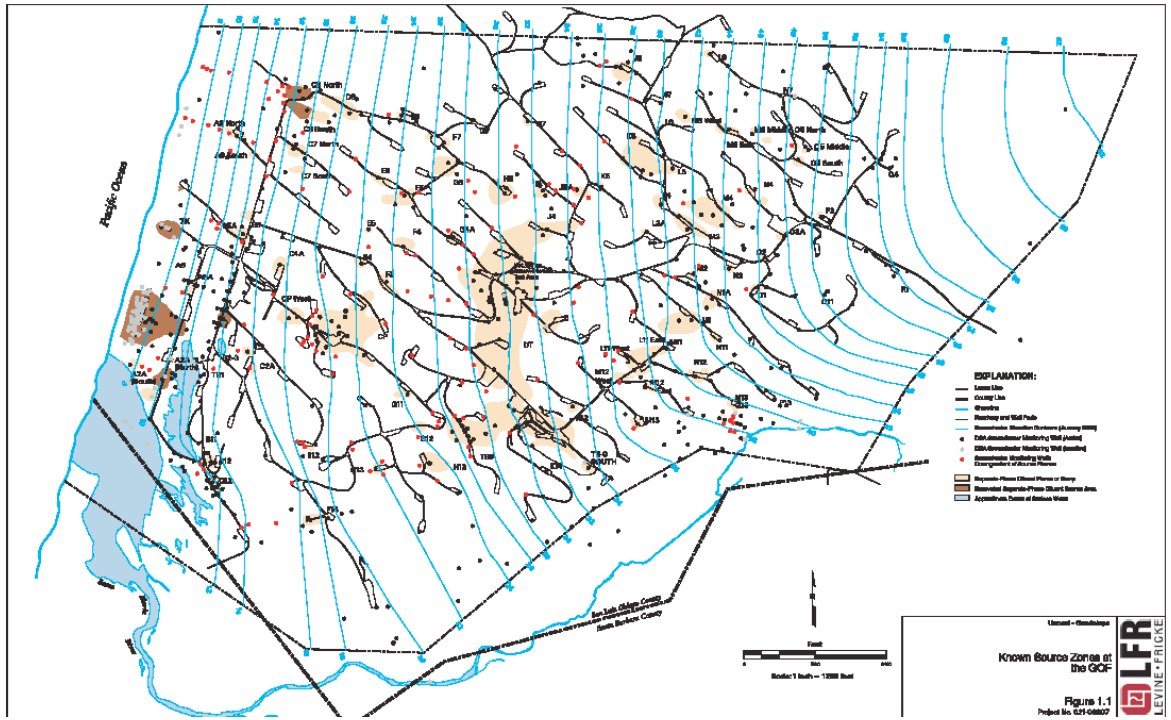
Outline

- Motivation & Sample Sites
- Questions of Interest & Challenges…
- SZNA Assessment Approach
  - ✓Group I, II, and II Data collection
- Sample Data and Analyses for Group I and II
- Bench-Scale Accelerated Weathering Tests
- In Progress…



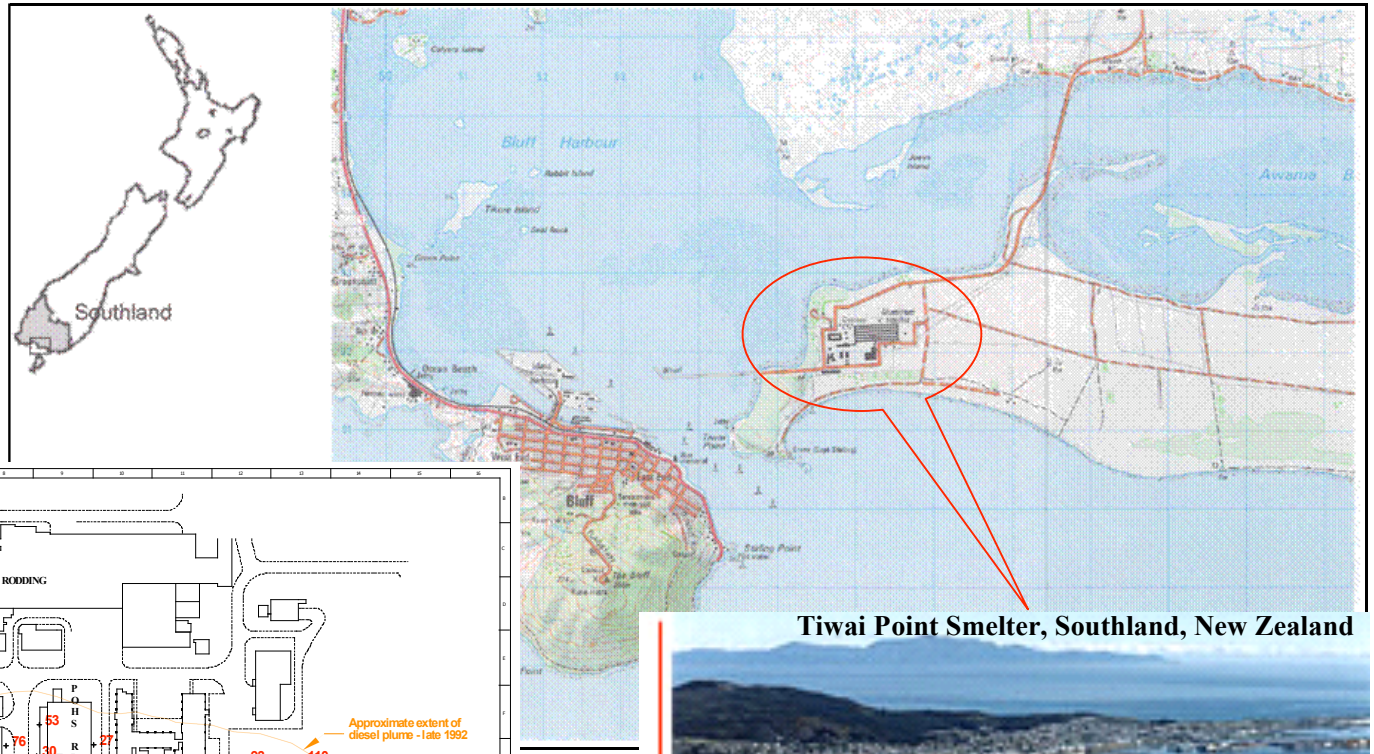
Guadalupe Restoration Project, CA

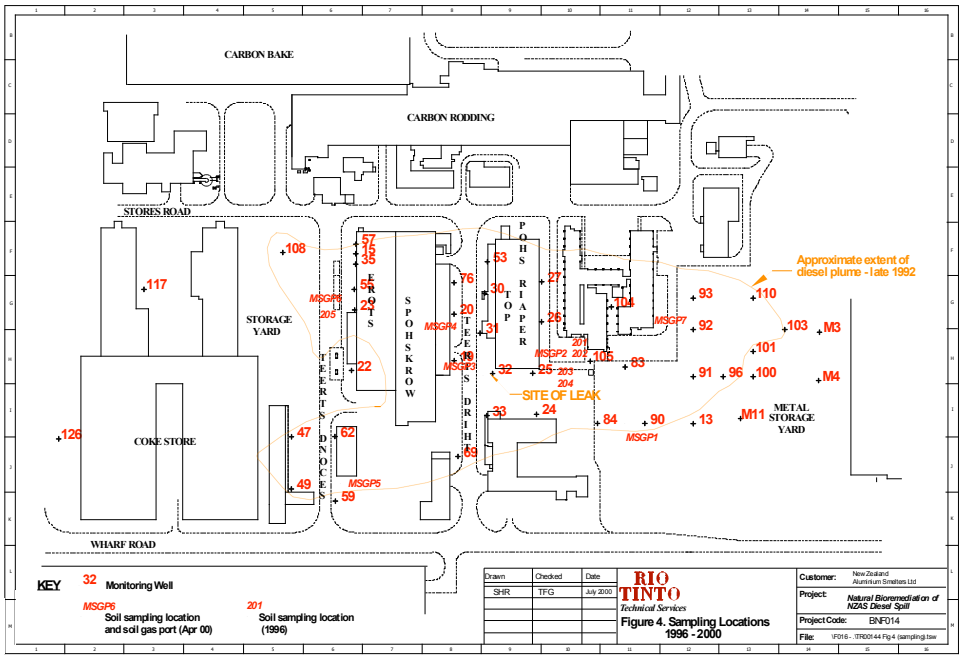
[about 25 square miles and 100 source zones]



New Zealand Aluminium Smelters Site

300,000 L
Diesel Release



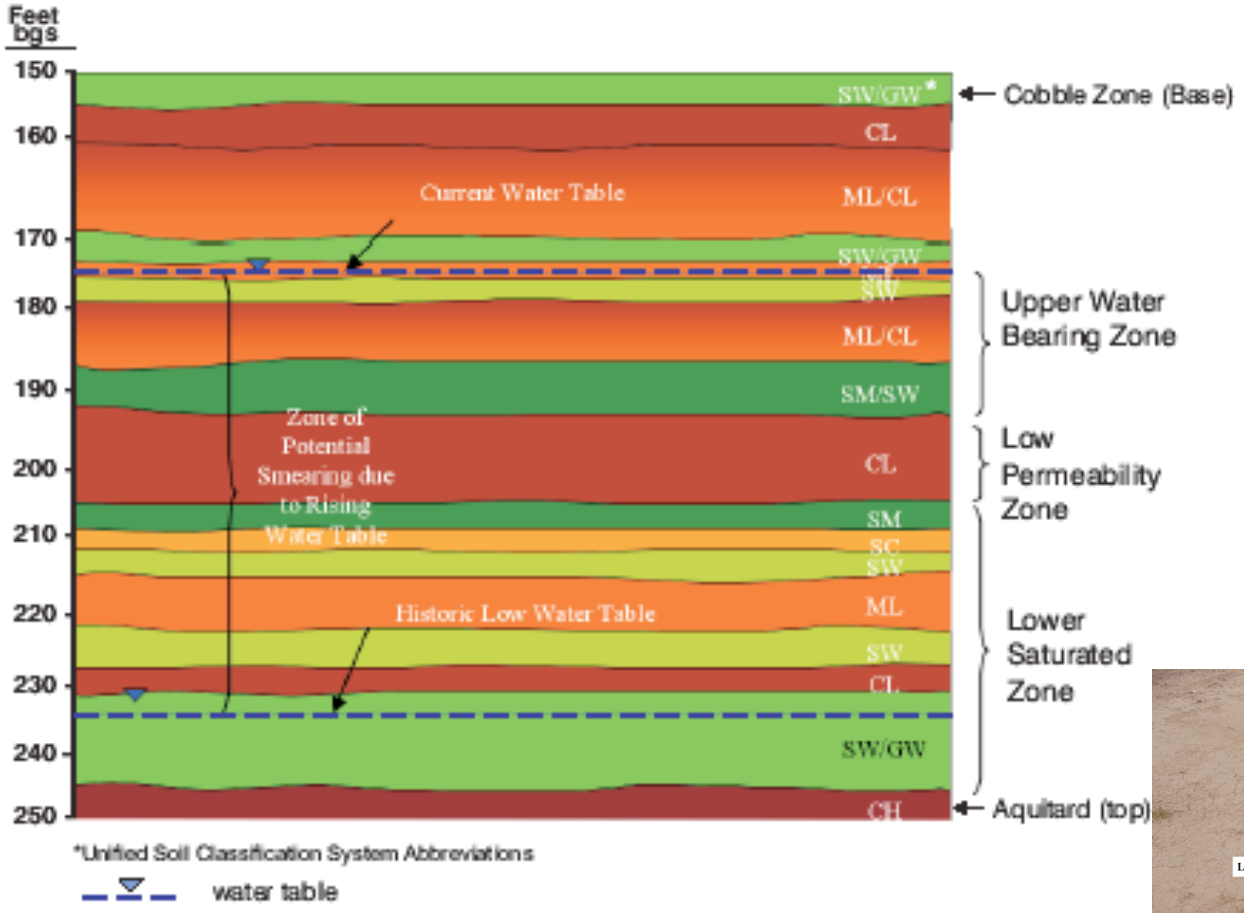


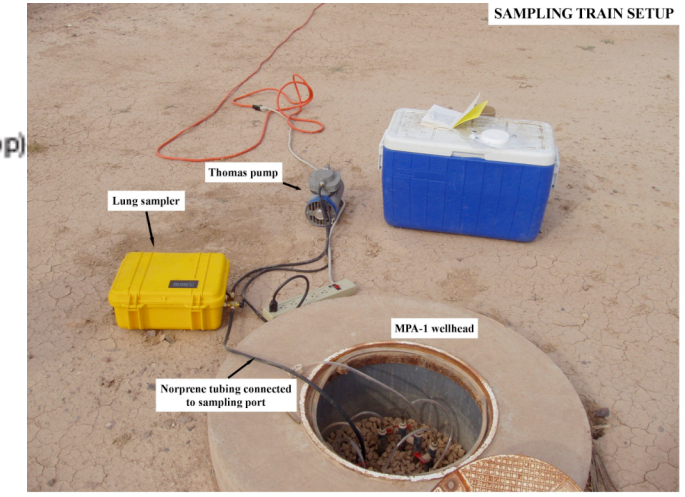
Tiwai Point Smelter, Southland, New Zealand

Photo source: Rio Tinto website, http://www.riotinto.com/default.aspx;
Turlough F. Guerin and Stuart Rhodes, 2000. Natural bioremediation of NZAS diesel spill – Draft. Rio Tinto Technical Report

Former Williams AFB ST-12 Site

[650,000 - 1,400,000 gal of aviation fuels (JP-4 and AVGAS)]



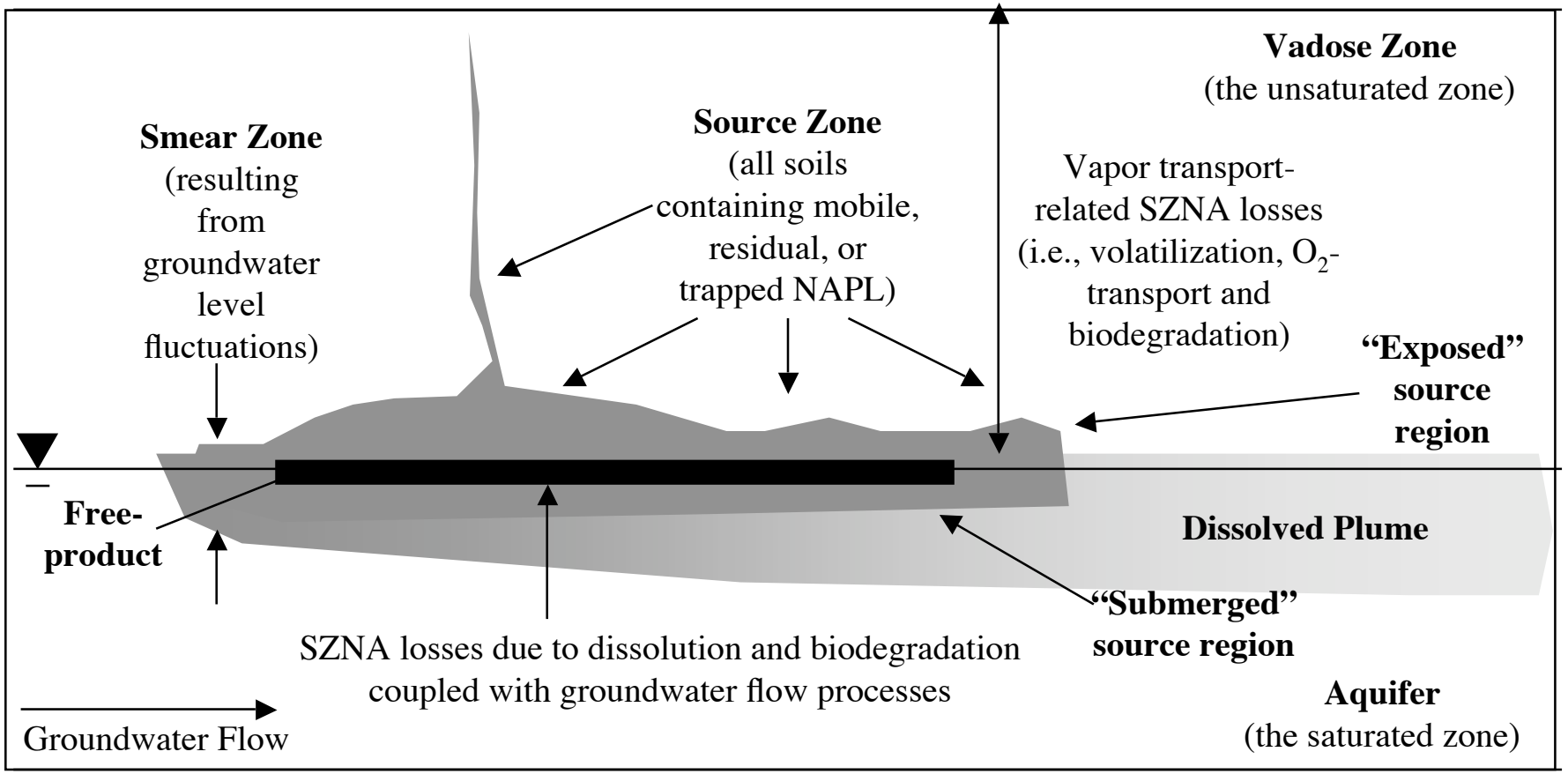


Relevant Questions…

- Is SZNA occurring?
- What are the rates of SZNA of key chemicals and cumulative mass?
- What are the implications for long-term groundwater quality?
- Are the SZNA processes sustainable?
- At what point in the future will groundwater quality goals be met?

Generalized Conceptual Model

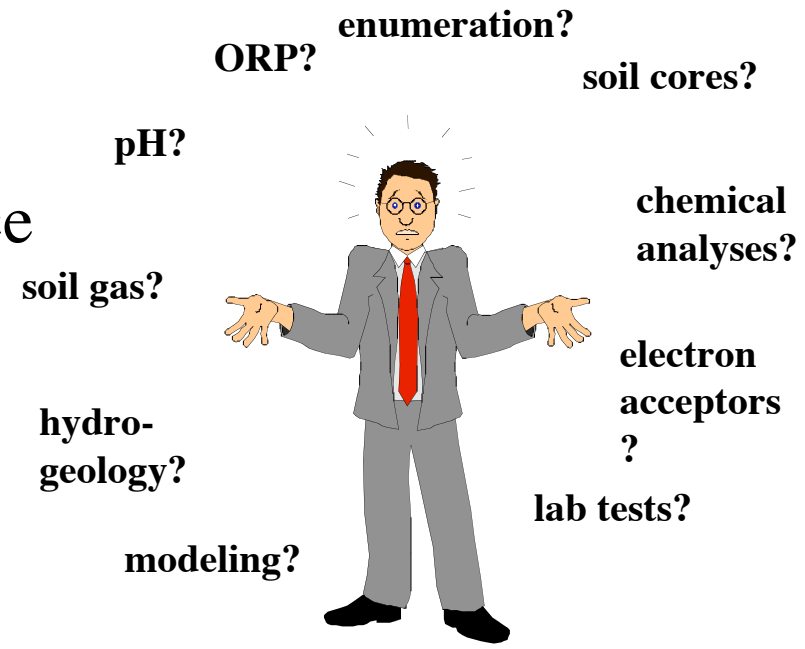
A Simplified View of SZNA Processes…



SZNA Framework…

A data-driven/multiple lines of evidence approach is used. Any projections are anchored in data.

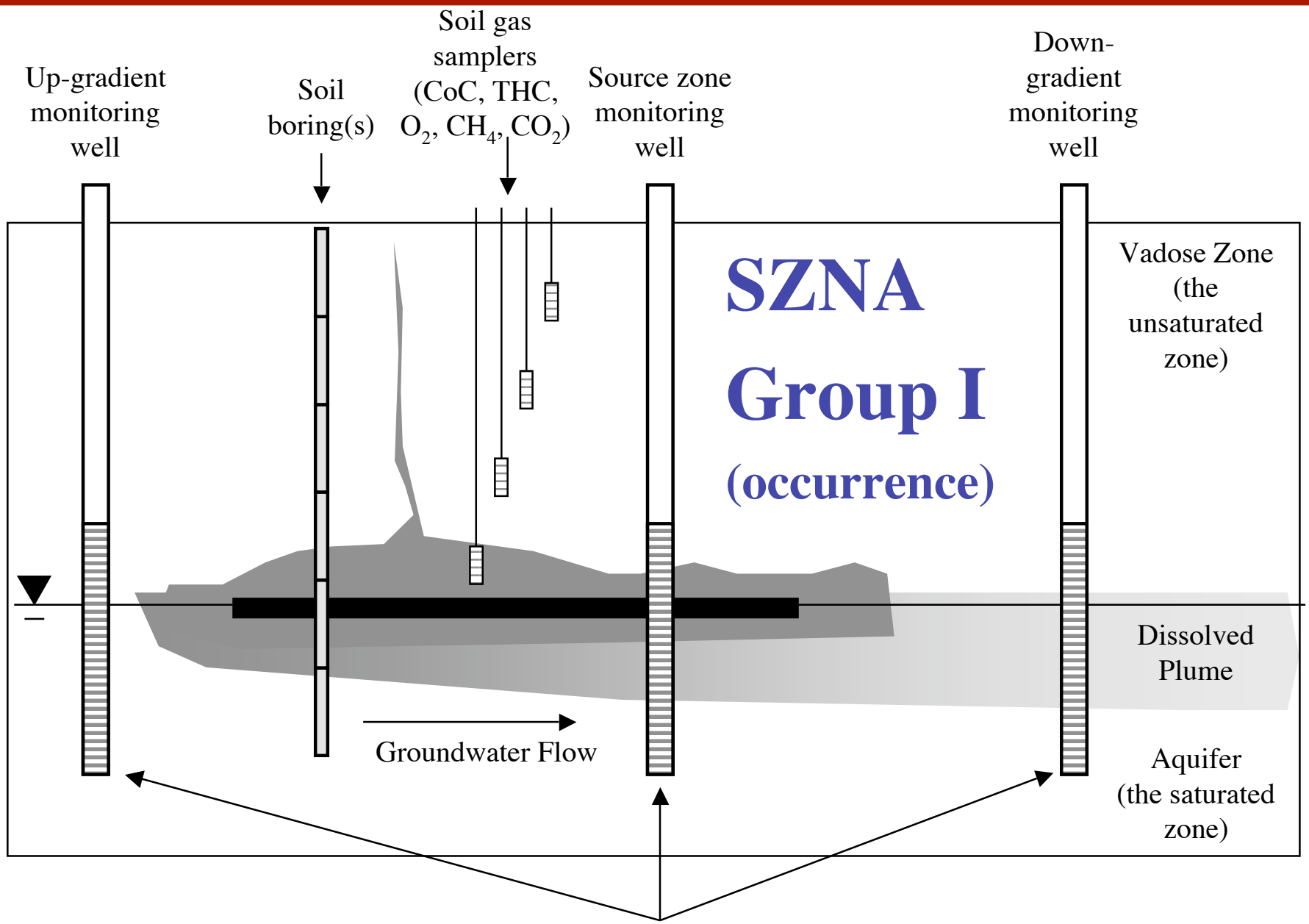
Data gathering and data reduction activities are grouped by their usage.



Group 1: Measurements that indicate that natural attenuation has been, or is currently occurring in the source zone

Group 2: Measurements that help assess the current rate(s) at which source zone natural attenuation is occurring and the sustainability of the processes

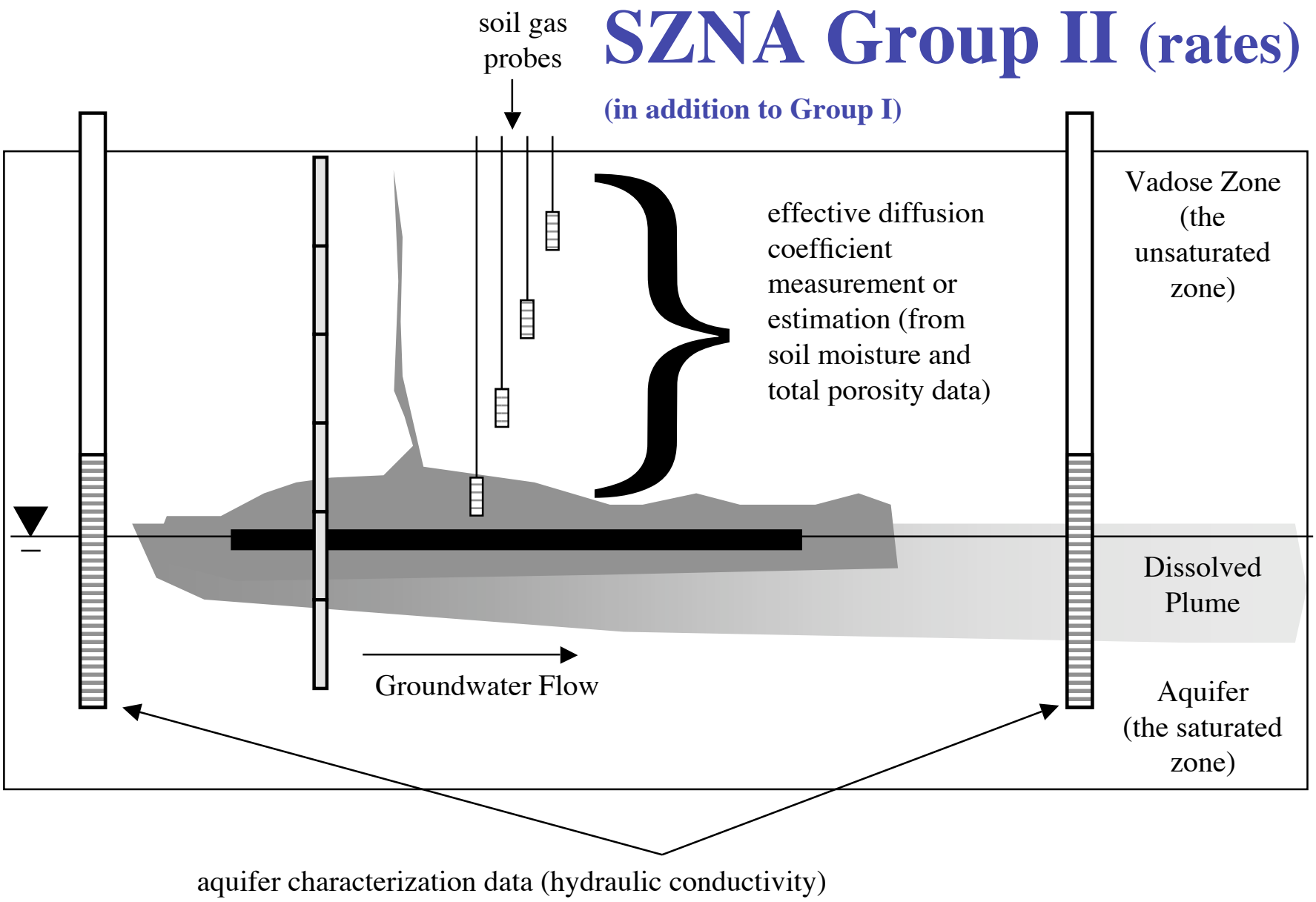
Group 3: Measurements that are indicative of long-term effects of source natural attenuation processes on the future extent, duration, and magnitude of impacts associated with the source



- dissolved hydrocarbon concentrations
- changes in electron acceptors & transformation products (O_2, Fe^{2+} , Mn^{2+}, SO_4^{2-}, NO_3^-,CH_4)
- groundwater table elevation

SZNA Group II (rates)

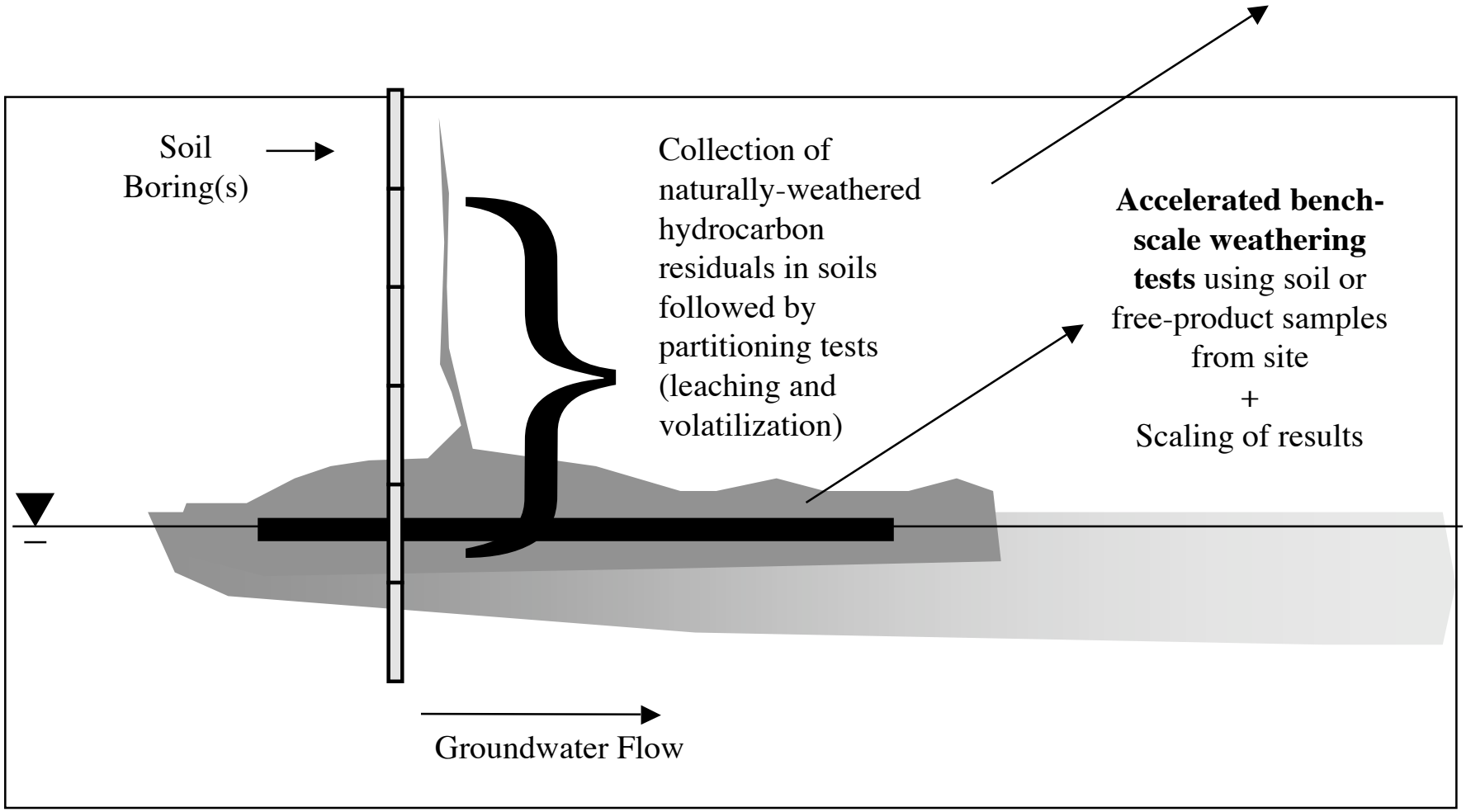
(in addition to Group I)



SZNA Group III (future projections)

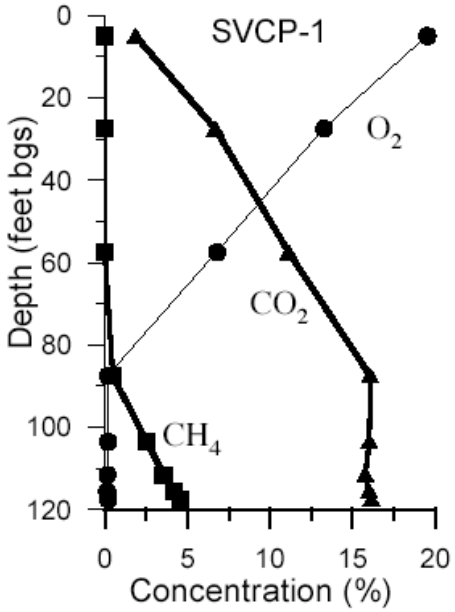
(in addition to Groups I and II)

Modeling…



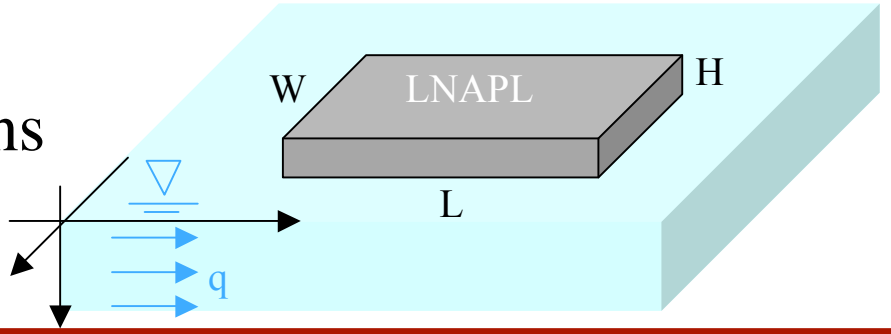
Data Reduction…

Group 1: Typically charts and tables showing that measurements (dissolved concentrations, soil gas concentrations, composition of residuals, spatial relationships) are consistent with what is expected if SZNA is occurring.

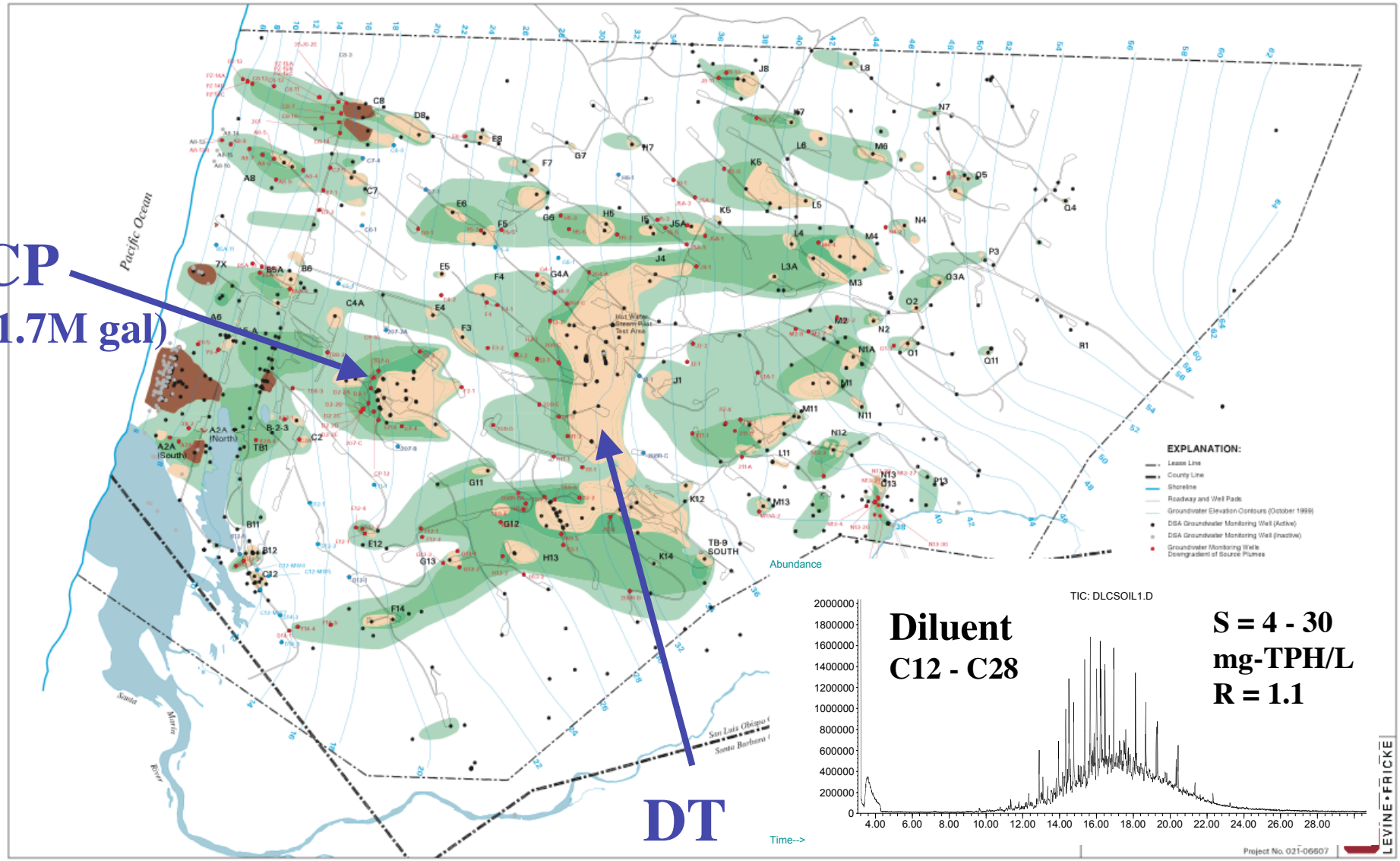


Group 2: Mass balance and simple order-of-magnitude mass transport calculations

Group 3: Time-scale conversions



Source Zones at GRP

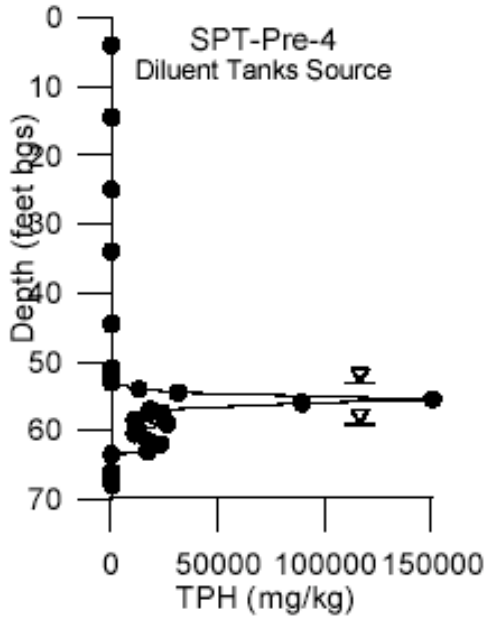


Sample Group I Data from GRP…

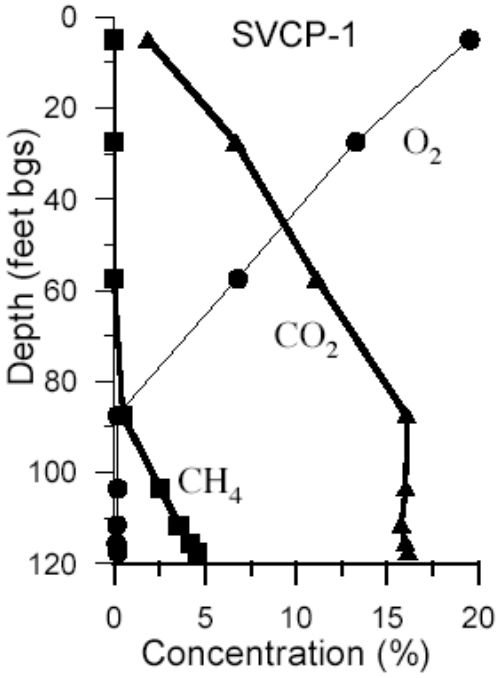
(SZNA occurrence)

	Oxygen (mg/L)	Alkalinity (mg/L CaCO3)	Iron (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Methane (mg/L)
Conventional Monitoring Wells Up-gradient of Source Areas						
Data Points	341	194	54	194	194	0
Median	3.7	180	0.04	18.2	30	---
Minimum	0.04	56	0.02	2.2	11	---
Maximum	11.0	400	0.83	93	220	---
Conventional Monitoring Wells Down-gradient of Source Areas						
Data Points	255	158	35	158	158	0
Median	0.3	325	16	2.2	9.2	---
Minimum	0.01	48	3.6	0.4	1	---
Maximum	5.8	690	45	14	160	---
Nested Wells Up-gradient of DT Source Area						
Data Points	5	5	5	5	5	5
Median	2.4	197	0.19	6.1	44	0.003
Minimum	0.8	172	0.06	1.9	23	0.001
Maximum	6.7	245	3.32	40	76	0.014
Nested Wells Within and Down-gradient of DT Source Area						
Data Points	23	26	26		26	26
Median	1.2	476	14.7	1.9	9	6.7
Minimum	0.5	280	0.13	1.5	0.7	0.130
Maximum	5.2	608	78	6.5	106	13.3

Not shown - dissolved TPH data, groundwater elevations, chromatographic comparisons of residual TPH, etc.



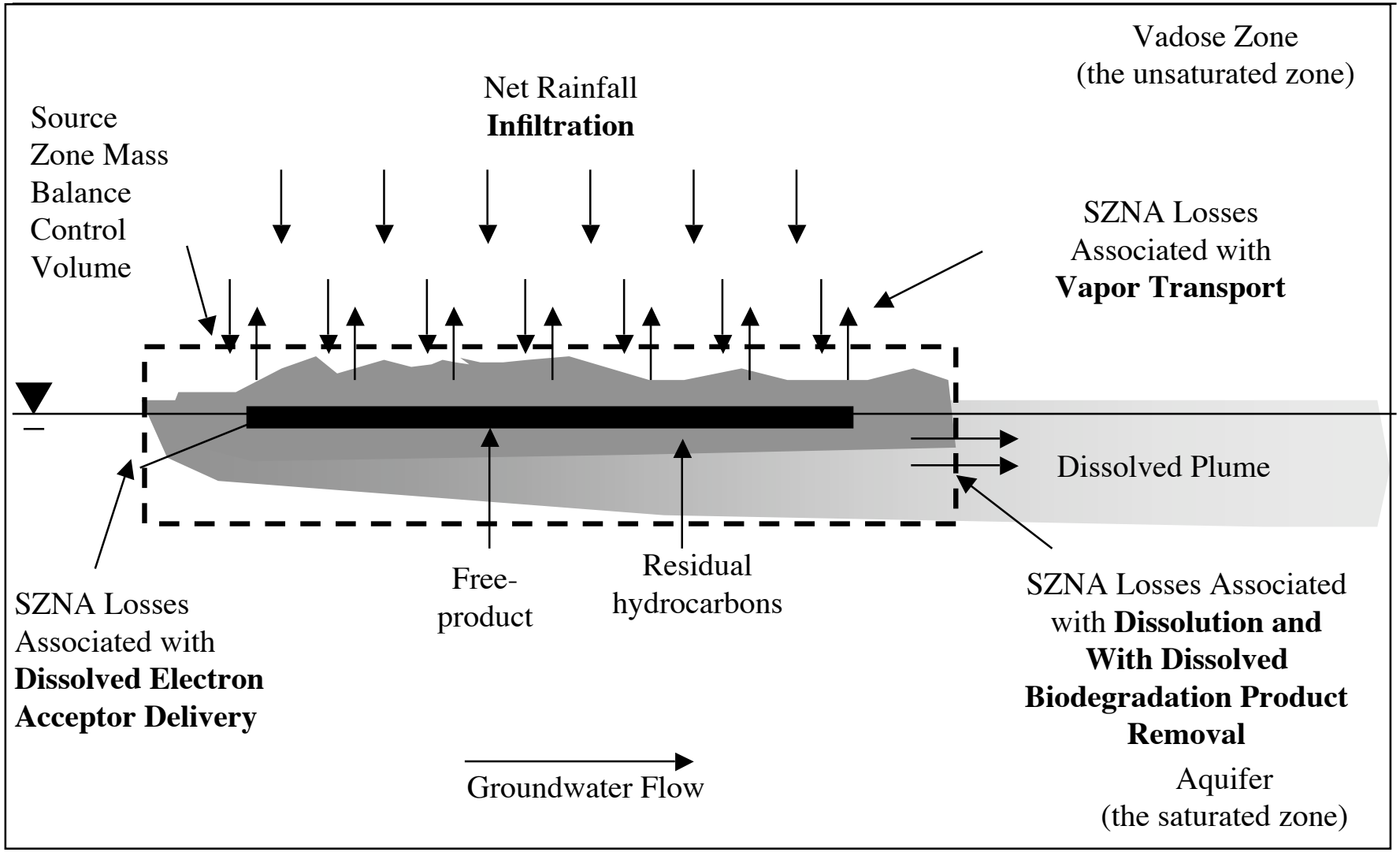
TPH Profiles in Soil



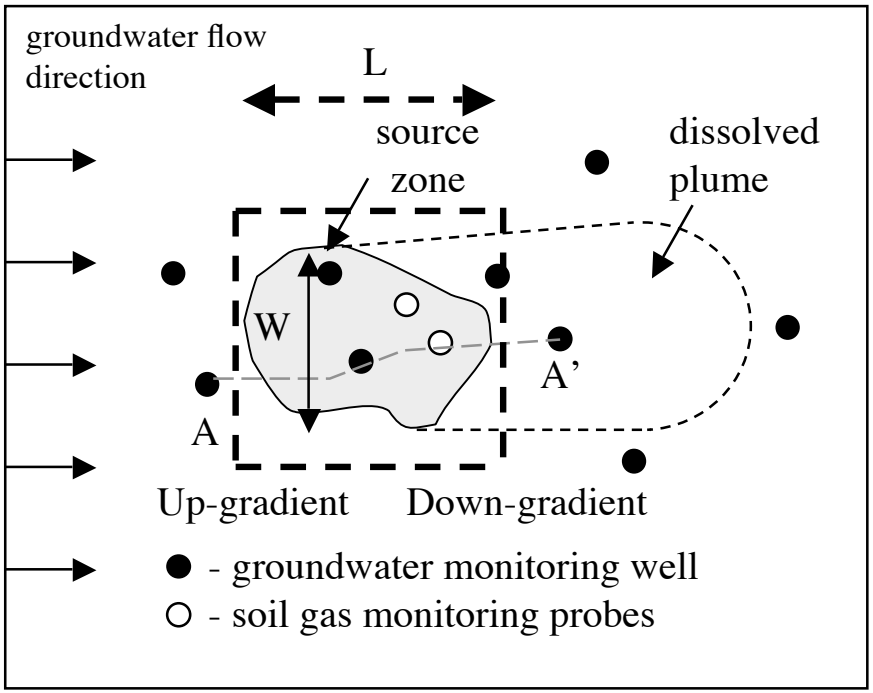
Soil Gas Profiles

Group II Data Reduction…

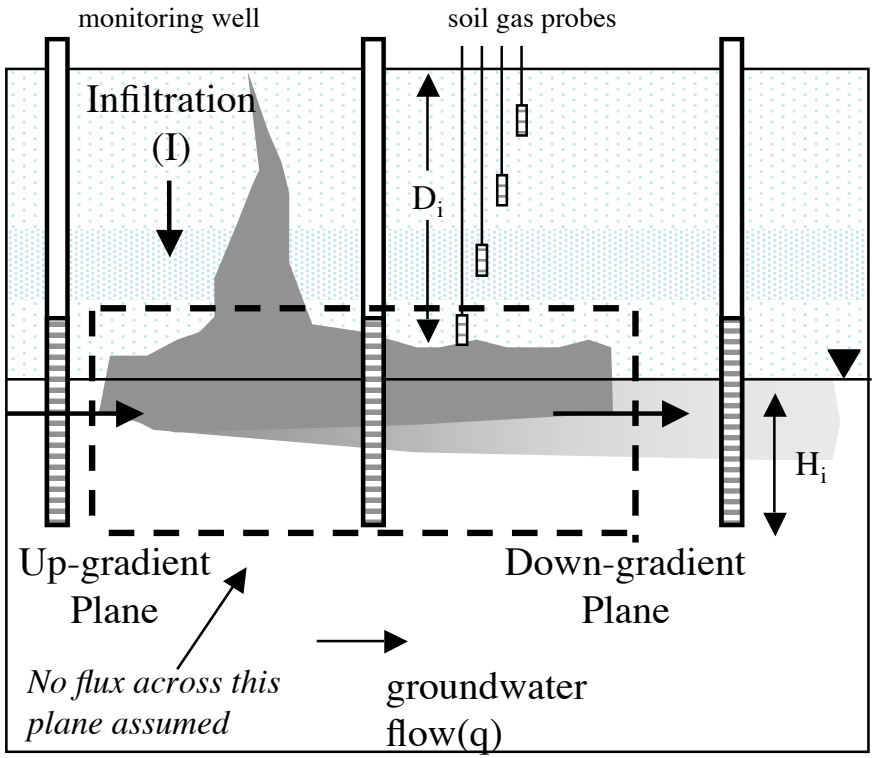
(use of macroscopic mass balances with field data)



Sample Group II Data Reduction - Dissolved-Transport-Related Processes..



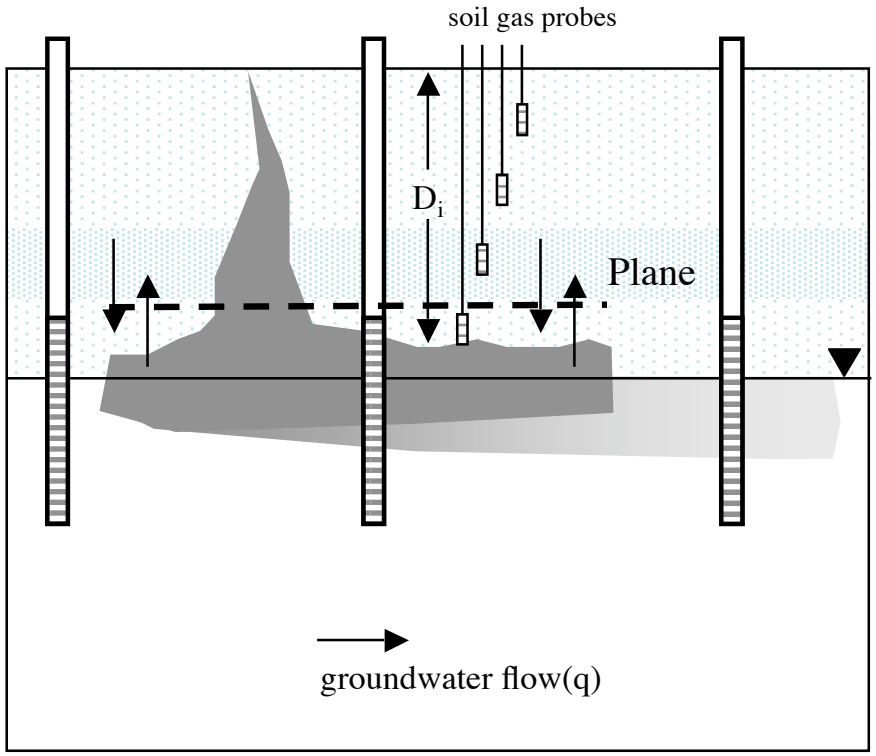
Plan View

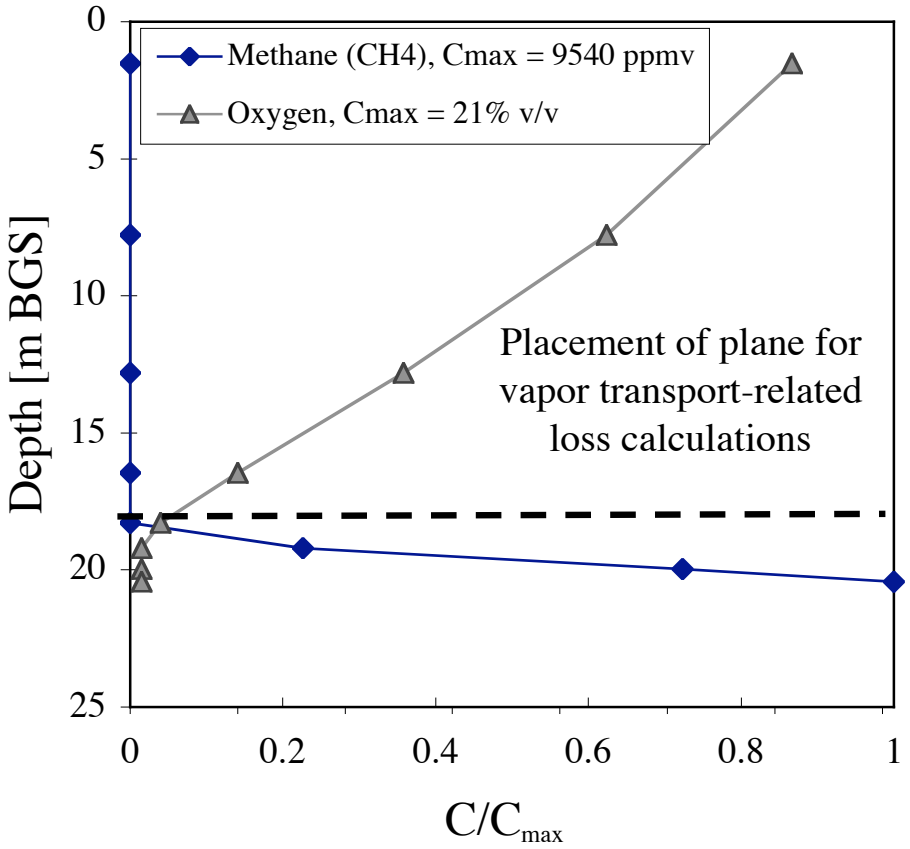


Cross-section A-A' (w/exaggerated vertical scale)

$$R_{bio-sat} = \int_{WH}\int q_u\{[S_O\,C_{O,u}]+[S_N\,C_{N,u}]+[S_S\,C_{S,u}]-[S_I\,C_{I,u}]-[S_{Mn}\,C_{Mn,u}]-[S_M\,C_{M,u}]\}dzdy$$
$$+\int_{WL}\int q_R\{[S_O\,C_{O,R}]+[S_N\,C_{N,R}]+[S_S\,C_{S,R}]-[S_I\,C_{I,R}]-[S_{Mn}\,C_{Mn,R}]-[S_M\,C_{M,R}]\}dxdy$$
$$-\int_{WH}\int q_d\{[S_O\,C_{O,d}]+[S_N\,C_{N,d}]+[S_S\,C_{S,d}]-[S_I\,C_{I,d}]-[S_{Mn}\,C_{Mn,d}]-[S_M\,C_{M,d}]\}dzdy$$

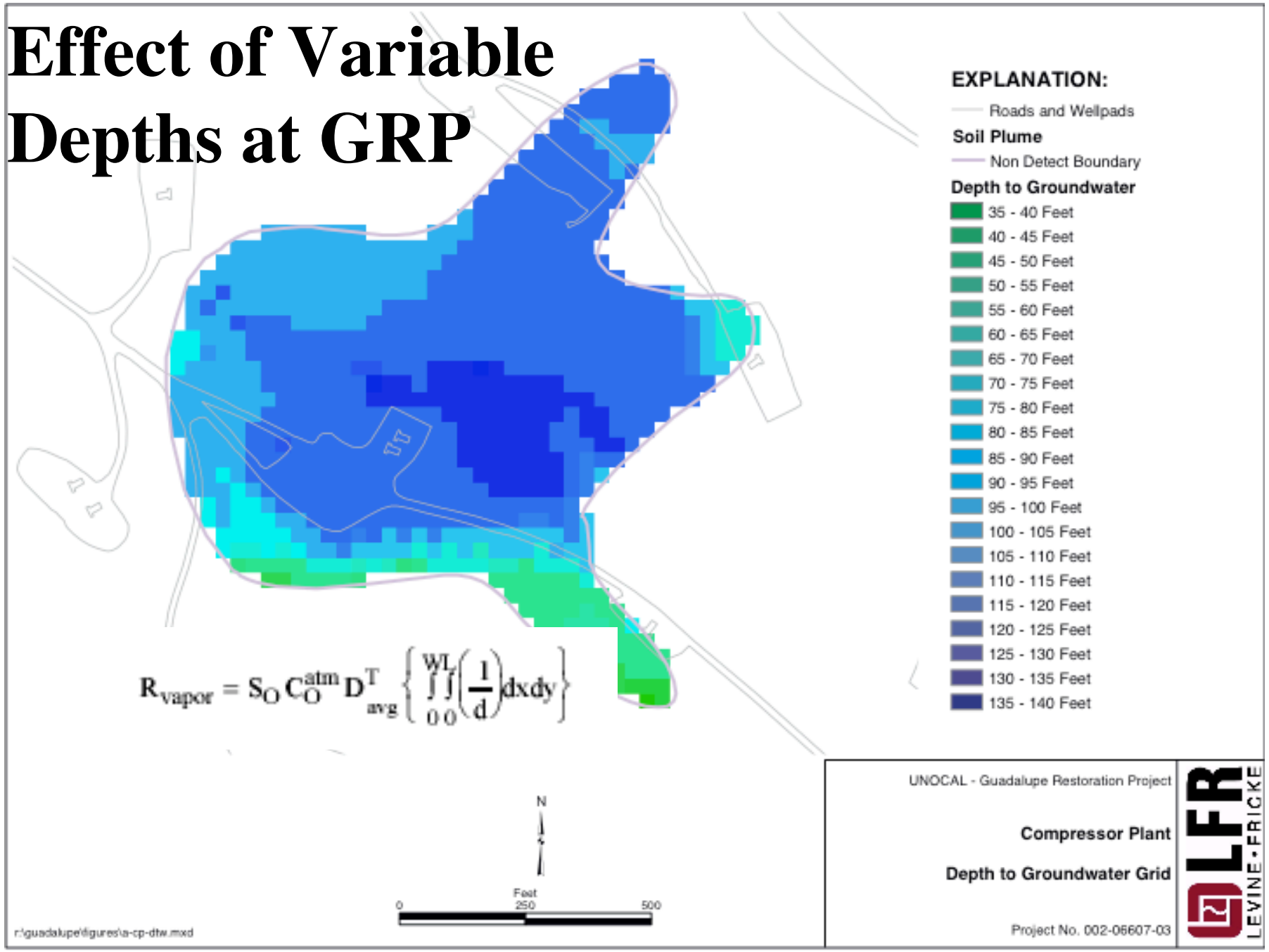
Sample Group II Data Reduction - Vapor-Transport-Related Processes..





$$R_{vapor} = \int_W \int_L \left\{ - D_{HC} \left(\frac{\partial C_{HC}}{\partial z} \right) - S_M D_{CH_4} \left(\frac{\partial C_{CH_4}}{\partial z} \right) + S_O D_O \left(\frac{\partial C_O}{\partial z} \right) \right\} dxdy$$

Effect of Variable Depths at GRP

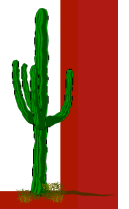


GRP Group II Data Reduction…

Source Area	Area (m^2)	Average Depth (m)	Average Deff,O_2 (cm^2/sec)	Aerobic Degradation Rate (kg/year)
Diluent Tanks	231212	18.9	0.038	1.36×10^5
Compressor Plant	71502	32.0	0.025	1.64×10^4
G6	9755	24.8	0.065	7.5×10^3

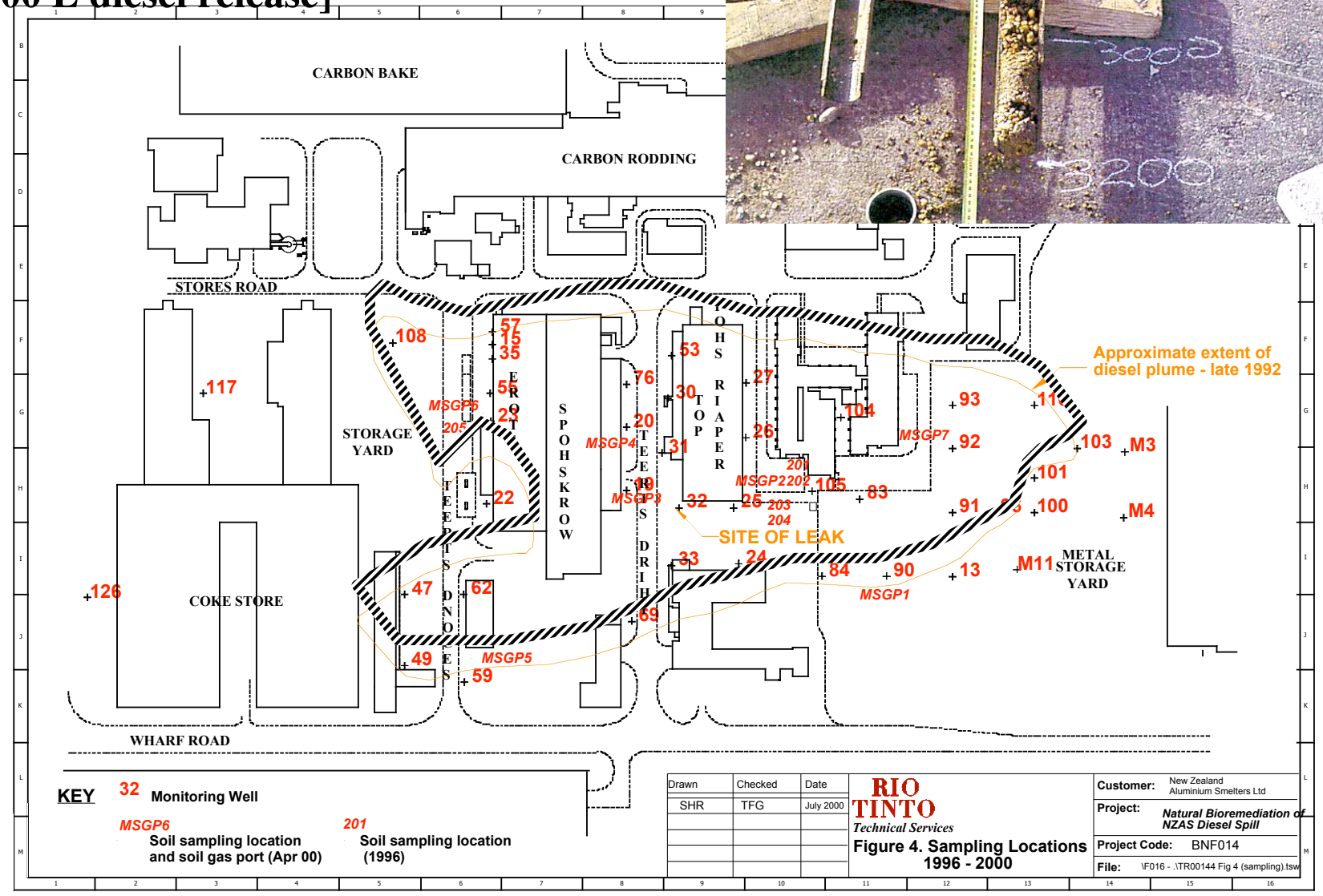
Source Area	Loss Rate Estimate Due to Dissolution [kg/y]	Loss Rate Estimate Due to Dissolved-Phase Transport-Related Biodegradation [kg/y]	Loss Rate Estimate Due to Oxygen Gas Transport [kg/y]
Diluent Tanks	500 - 1600	600 - 1600	140,000
Compressor Plant	300 - 500	0	16,000

- Gas transport-related losses are more significant than dissolved-phase transport related processes, but…
- SZNA rates are quite different in submerged vs. exposed source zone regions…



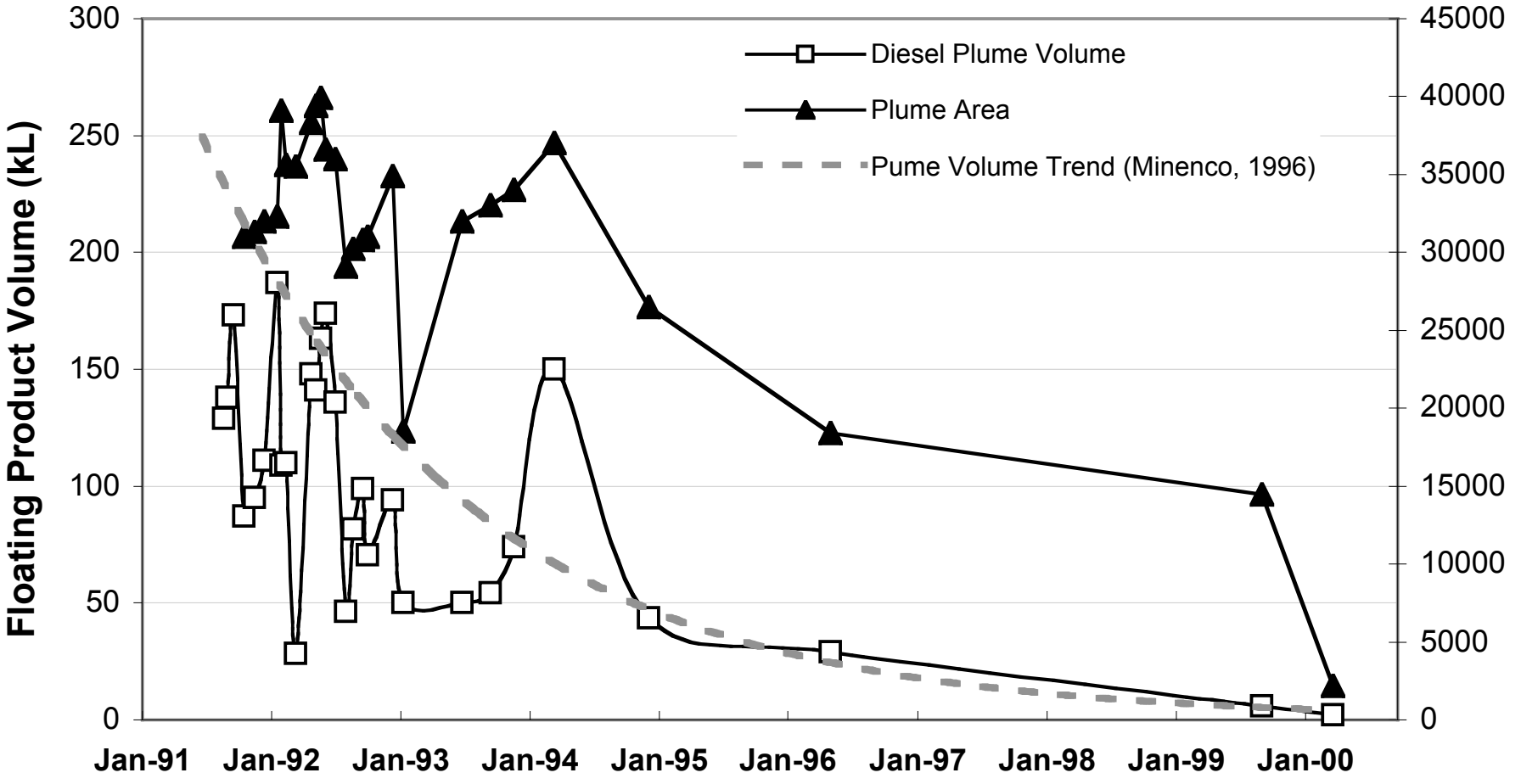
New Zealand Aluminium Smelters Site

[300,000 L diesel release]



NZAS Group II Data Reduction…

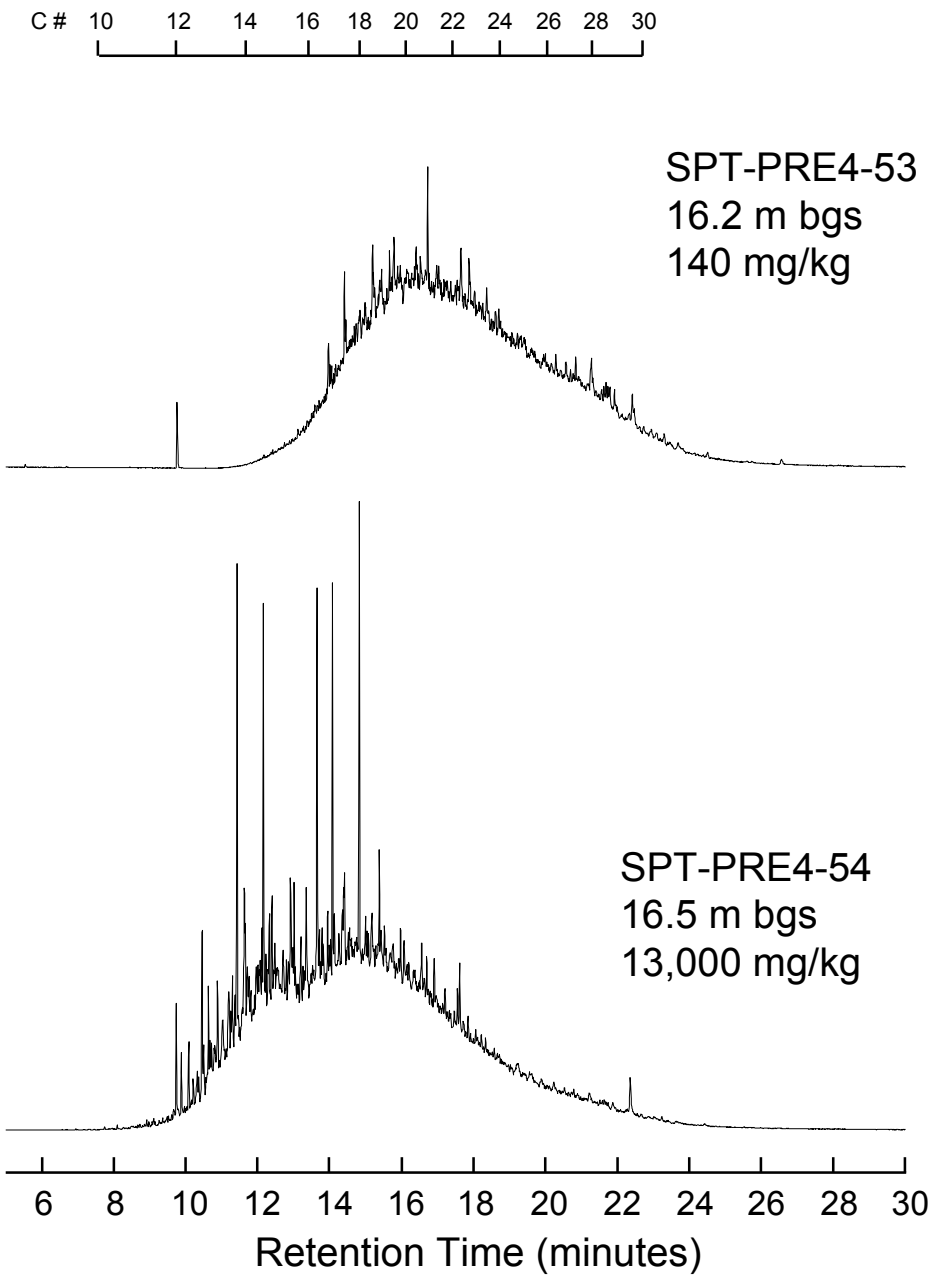
Estimated to be about 30,000 L/y from Group II data in 1991 and 12000 L/y in 2000 - vapor transport related processes are dominant at this site



Sample Group III Data:

TPH composition analysis with depth at GRP

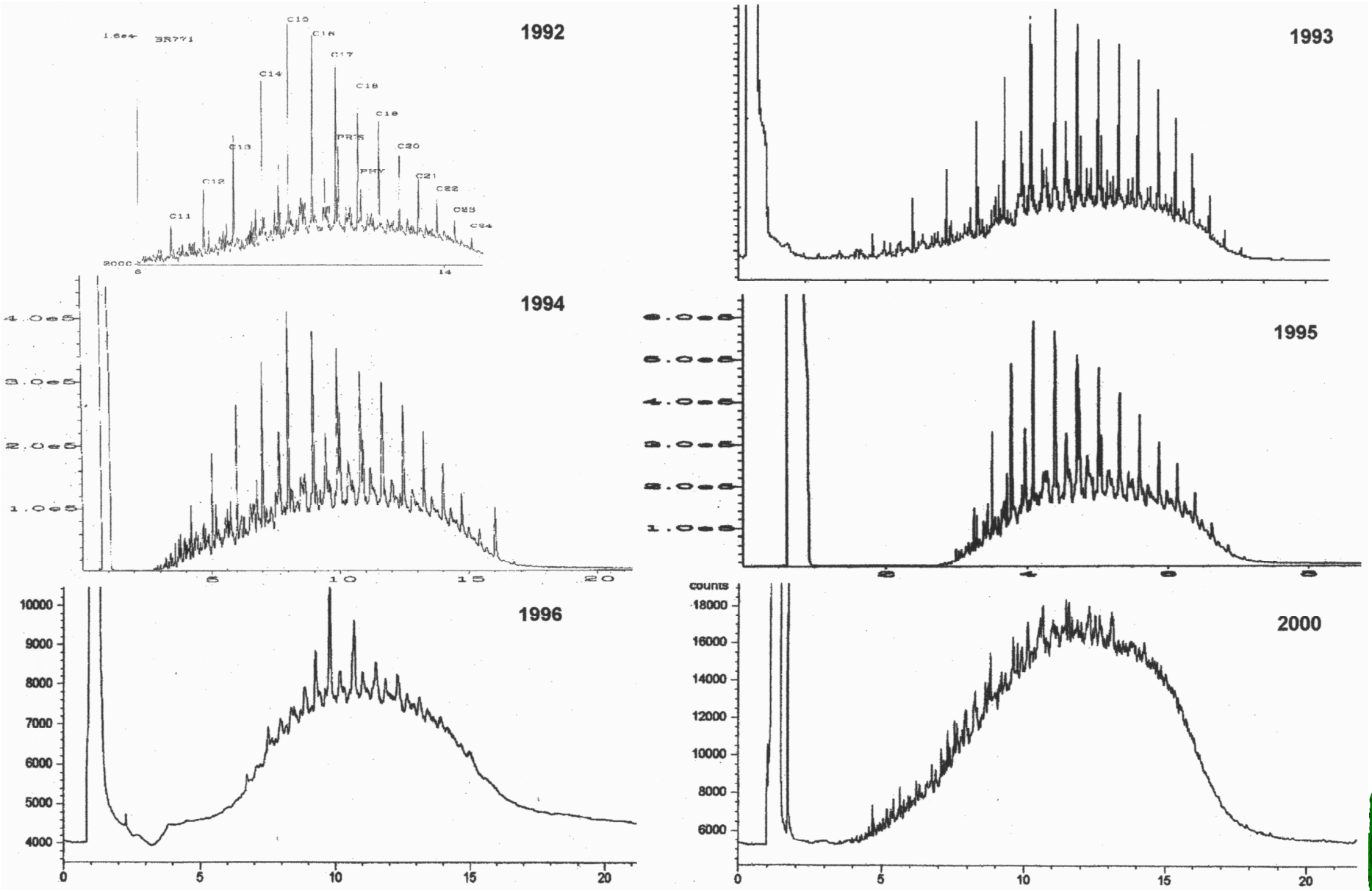
Vadose zone samples (1 ft vertical separation)



Future?

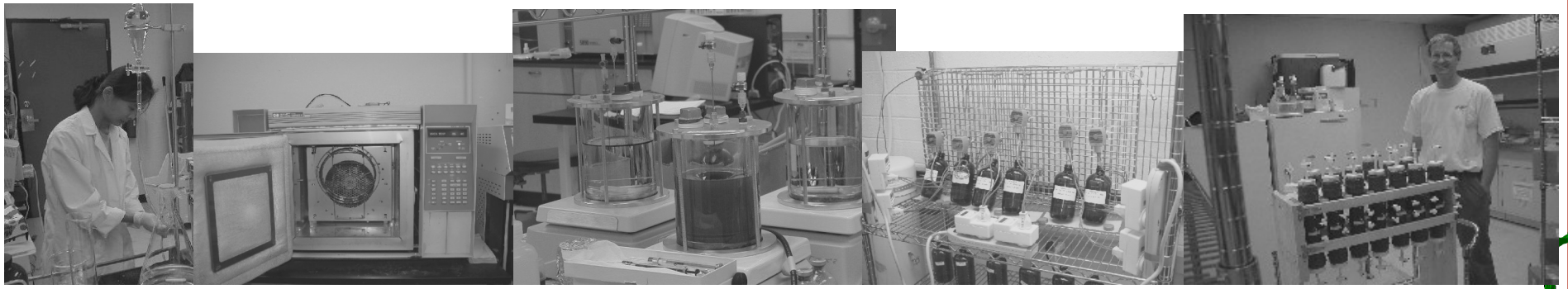
Current Condition

Sample Group III Data - NZAS…

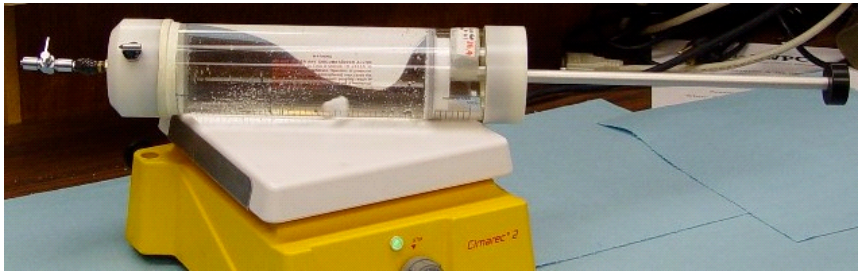


Group III: Accelerated Bench-Scale Weathering Experiments…

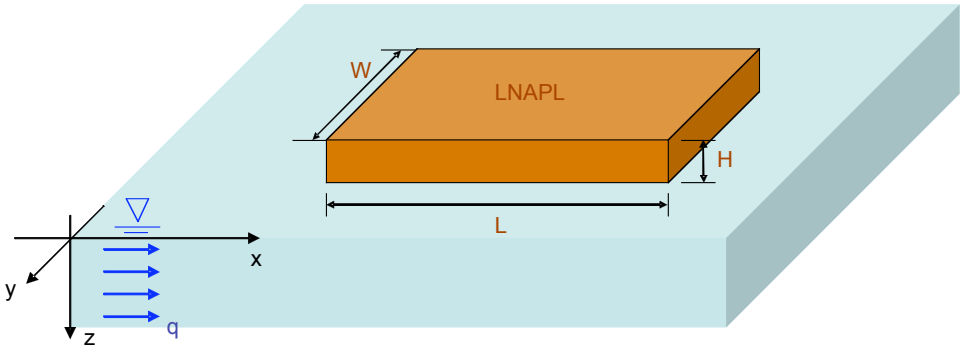
- Assess the effects of long-term (years/decades/longer) SZNA from the results of carefully designed and scaled "bench-scale accelerated weathering tests" that are conducted over the period of days to months…
  - Accelerated bench-scale dissolution tests
  - Accelerated bench-scale biodegradation tests
  - Accelerated bench-scale volatilization tests



Accelerated Bench-Scale Dissolution Weathering Test



Experiment (batch dissolution w/out introducing headspace)



Field-Scale (simplification)

Time Scaling:

Lab Conditions

Field Conditions

$$t_{field} = (\Delta V_{lab} / M_{o,lab}) \times \frac{WHLnS\rho}{WHq} = (\Delta V_{lab} / V_{o,lab}) \times (\frac{LnS}{q})$$

Water/NAPL ratio in lab

Source length, NAPL saturation, specific discharge

Accelerated Dissolution Experiment: Sample Results for Fuel from WAFB (TPH Results)

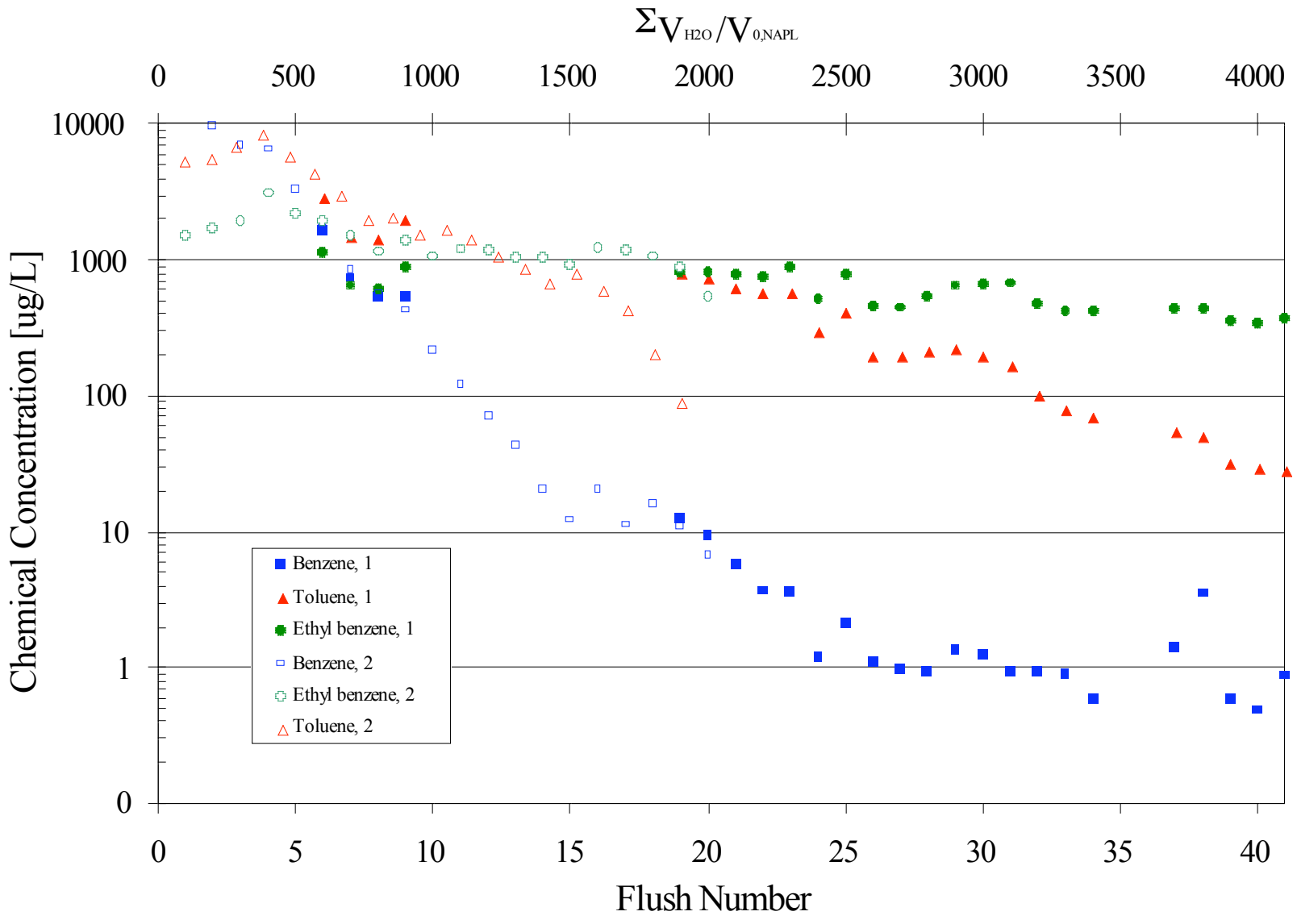
Flush #	Volume of water [mL]	TPH concentration[a] [mg/L]	Field scale estimate[b] [years] low	high
1	380	9.8	6.1	35
2	380	9.0	12.1	69
3	380	--	18.2	100
4	380	--	24.2	140
5	380	--	30.3	170
6	380	--	36	210
7	380	--	42	240
8	380	--	48	280
9	380	--	55	310
10	380	7.1	61	350
11	380	--	67	380
12	380	--	73	420
13	380	--	79	450
14	380	--	85	480
15	380	--	91	520
16	380	--	97	550
17	380	--	100	590
18	380	--	110	620
19	380	--	120	660
20	380	8.7	120	690

Flush #	Volume of water [mL]	TPH concentration[a] [mg/L]	Field scale estimate[b] [years] low	high
21	380	--	130	730
22	380	--	130	760
23	380	--	140	800
24	380	--	150	830
25	380	--	150	870
26	380	--	160	900
27	380	--	160	930
28	380	--	170	1000
29	380	--	180	1000
30	380	5.5	180	1000
31	380	--	190	1100
32	380	--	190	1100
33	380	--	200	1100
34	380	--	210	1200
35	380	--	210	1200
36	380	--	220	1200
37	380	--	220	1300
38	380	--	230	1300
39	380	--	240	1300
40	380	3.6	240	1400
41	380	--	250	1400

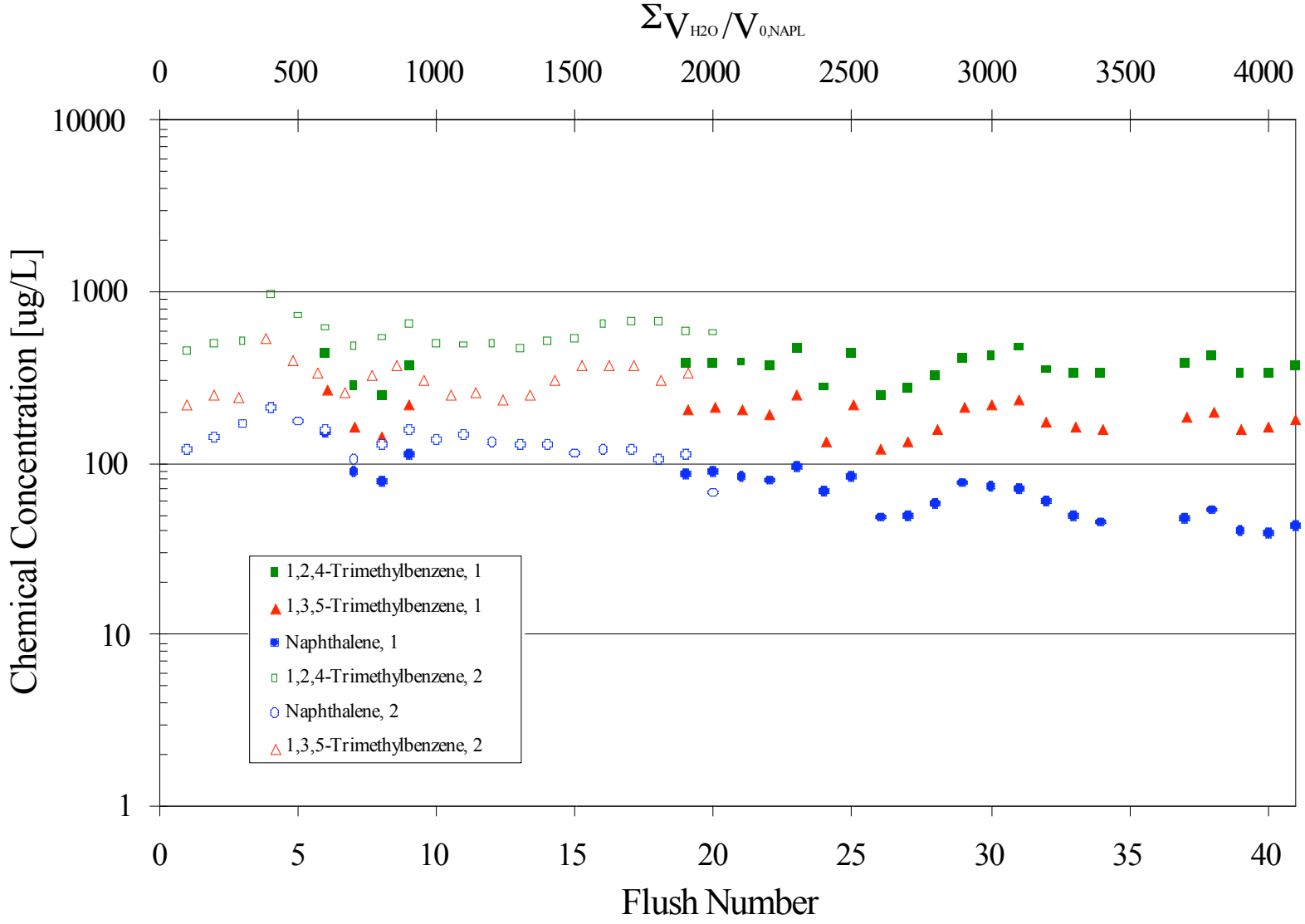
[a] TPH analysis performed by GC/FID

[b] Low estimate calculated using q = 0.023 m/d, source volume = 1,400,000 gal
High estimate calculated using q = 0.061 m/d, source volume = 650,000 gal

Accelerated Dissolution Experiment: Sample Results for Fuel from WAFB

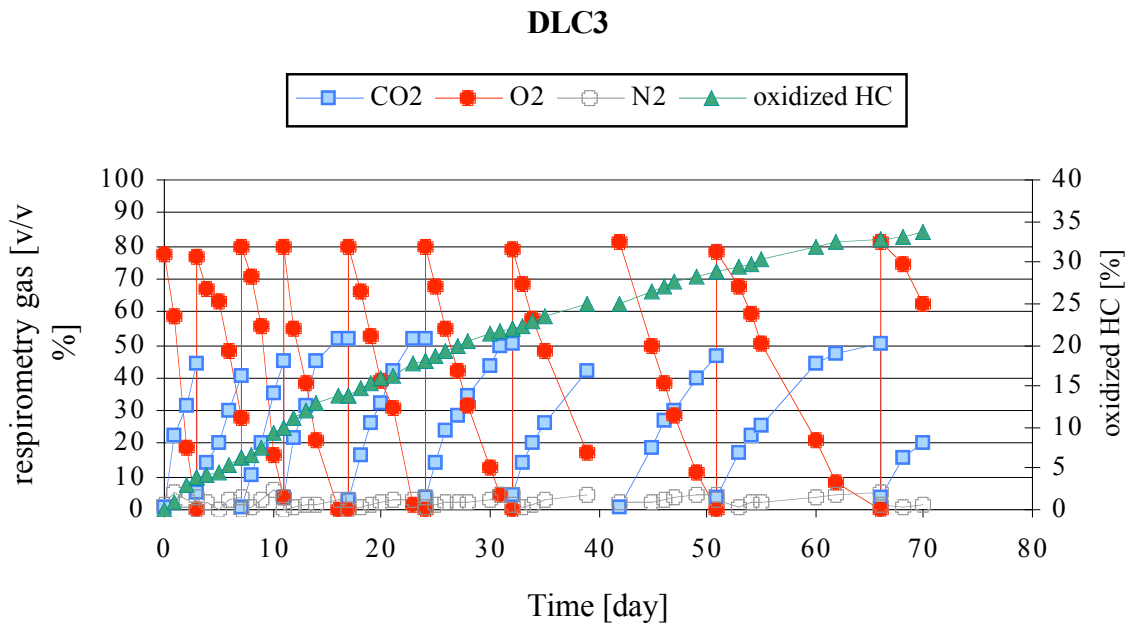


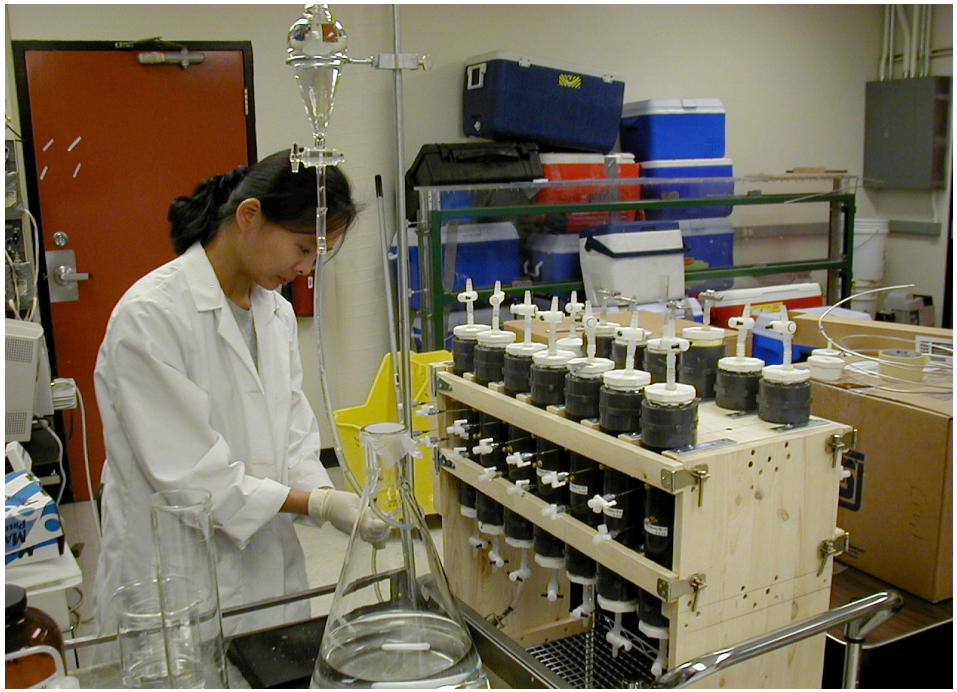
Accelerated Dissolution Experiment: Sample Results for Fuel from WAFB

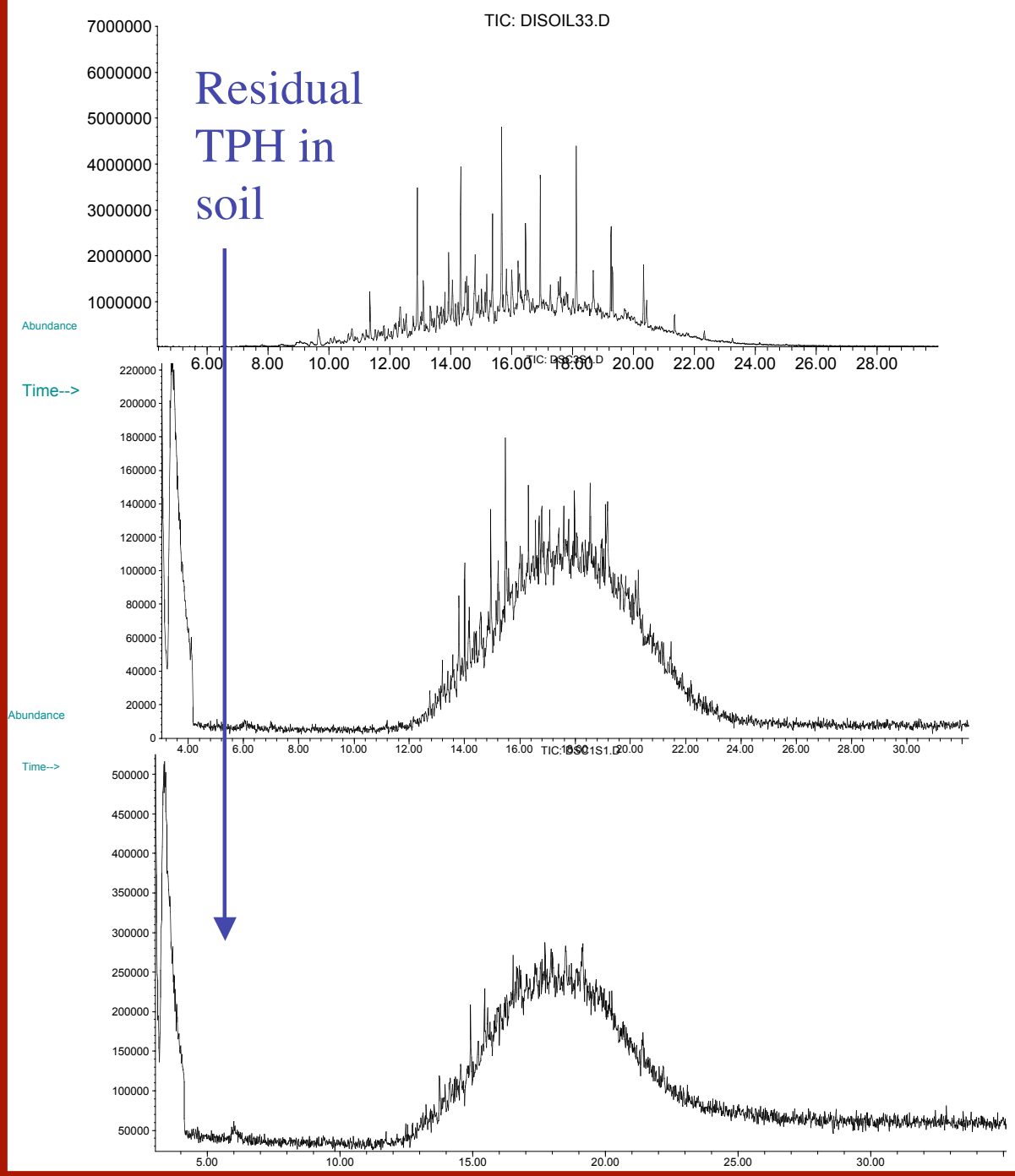


Accelerated Bench-Scale Biodegradation Weathering Test

monitor respiration -> estimate loss -> conduct periodic leach tests at different treatment levels -> sacrifice columns for soils analyses







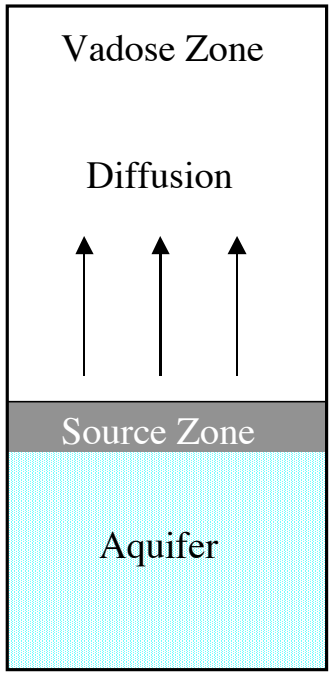
Diesel Results

3100 mg-TPH/kg-soil
2.2 mg-TPH/L-leachate
21 ug/L Benzene
76 ug/L Napthalene

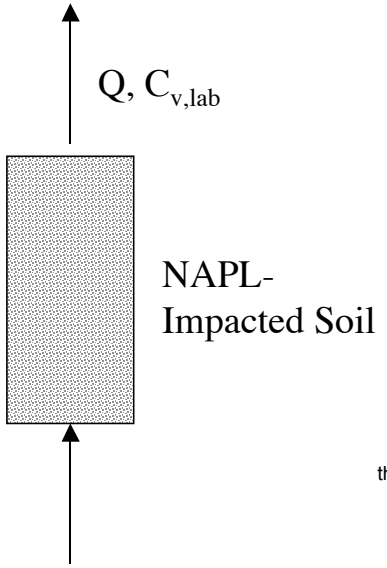
570 mg-TPH/kg-soil
2.8 mg-TPH/L-leachate

240 mg-TPH/kg-soil
2.3 mg-TPH/L-leachate
<0.1 ug/L Benzene
<0.1 ug/L Napthalene

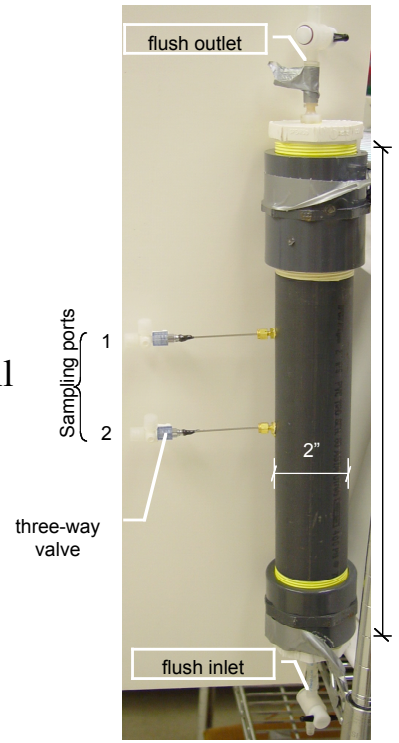
Accelerated Bench-Scale Volatilization Weathering Test



Field-Scale



Lab-Scale

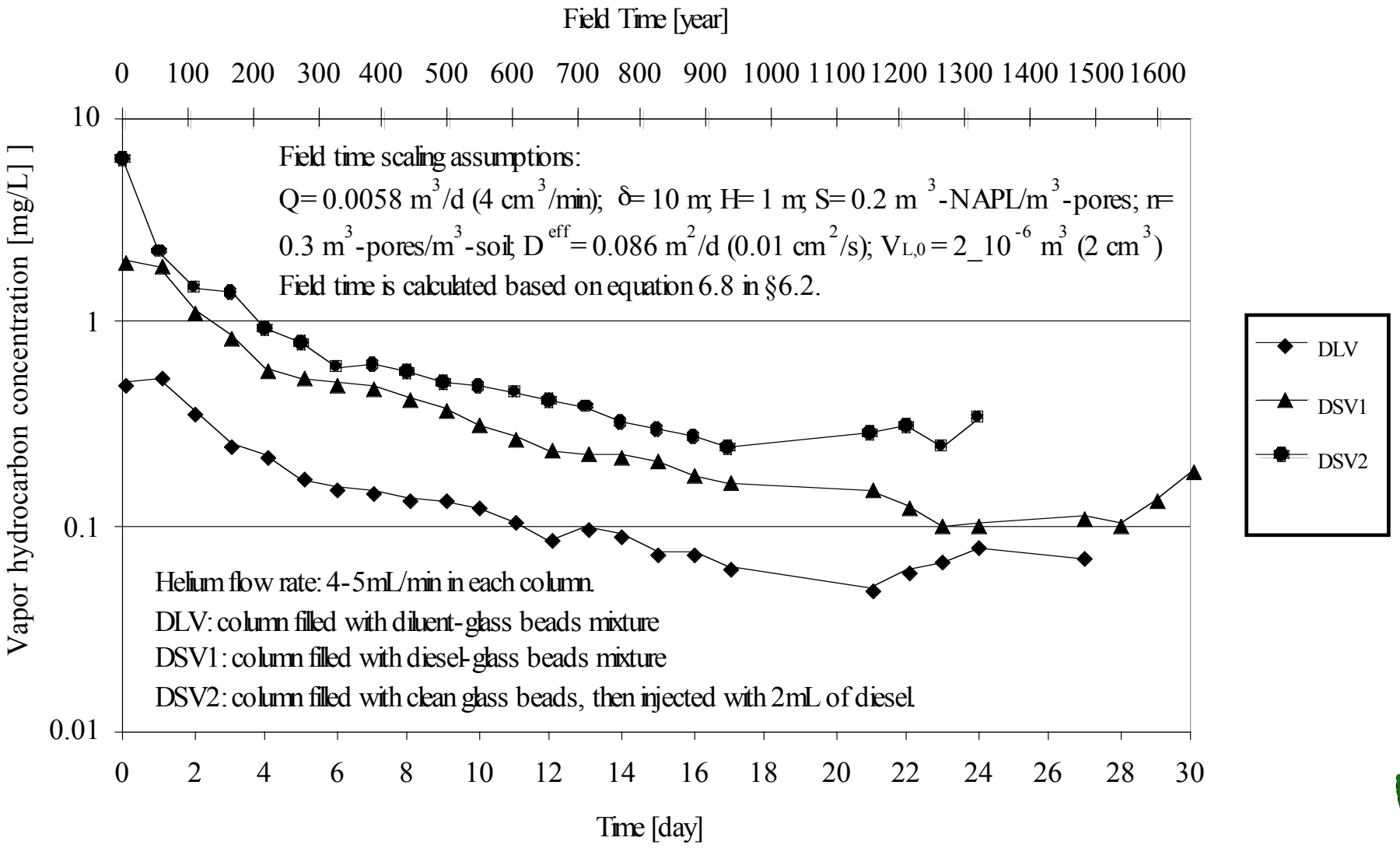


Q	=	0.0029 m^3/d (=2 cm^3/min)
δ	=	10 m
S	=	0.2 m^3-NAPL/m^3-pores
n	=	0.3 m^3-pores/m^3-soil
H	=	1 m
D^{eff}	=	0.09 m^2/d (=0.01 cm^2/s)
$V_{L.0}$	=	2 x 10^{-6} m^3 (= 2 cm^3)

$$T_F = 10^4 T_L$$

$$t_F = t_L\left(\frac{Q\delta SnH}{D^{eff} V_{L,o}}\right)$$

Accelerated Bench-Scale Volatilization Weathering Test (diluent and diesel)



Summary/In-Progress

- Data-driven framework for SZNA proposed and illustrated; data needs matched with key questions to be answered
- For exposed source regions - major contributor to loss is likely to be gas transport (working in combination with biodegradation for petroleum hydrocarbons)
- For submerged regions - dissolution and biodegradation may be comparable in many cases
- Accelerated bench-scale tests yield insight to future conditions and long-term behavior - especially for complex mixtures
- Fate/transport predictions using “representative compounds” as recommended in TPCWG documents would not match the data collected in this work.
- Sustainability of SZNA (in progress…)

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QUESTIONS?