Site Characterization and Monitoring in the New Millennium

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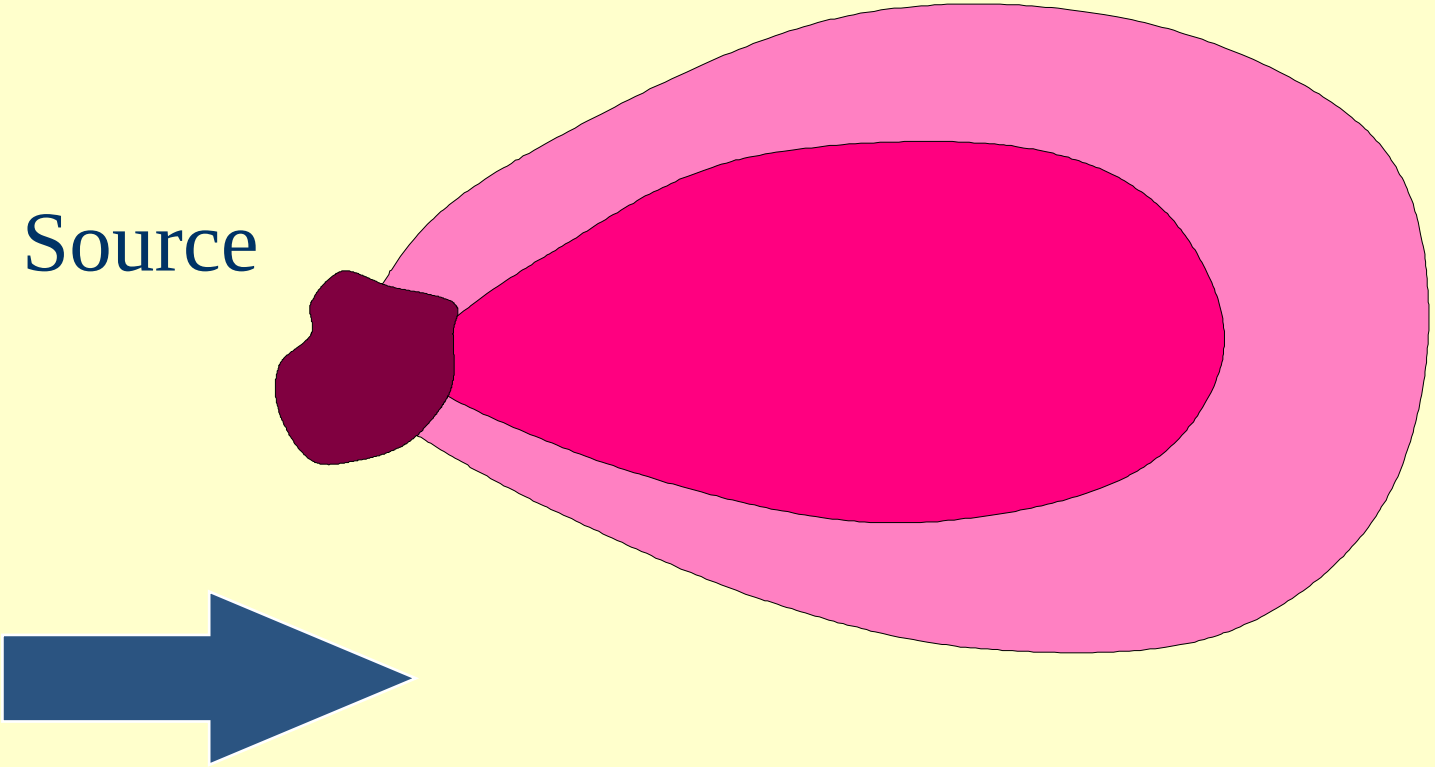
Subsurface Cleanup in the Last Millennium

- Good intentions
- Lots of $$
- Naïveté
- Goal: clean groundwater to MCLs
- Virgin sites
- Focus on physical remediation methods
  - Excavation
  - Pump & Treat (forced gradients)
- Limited success

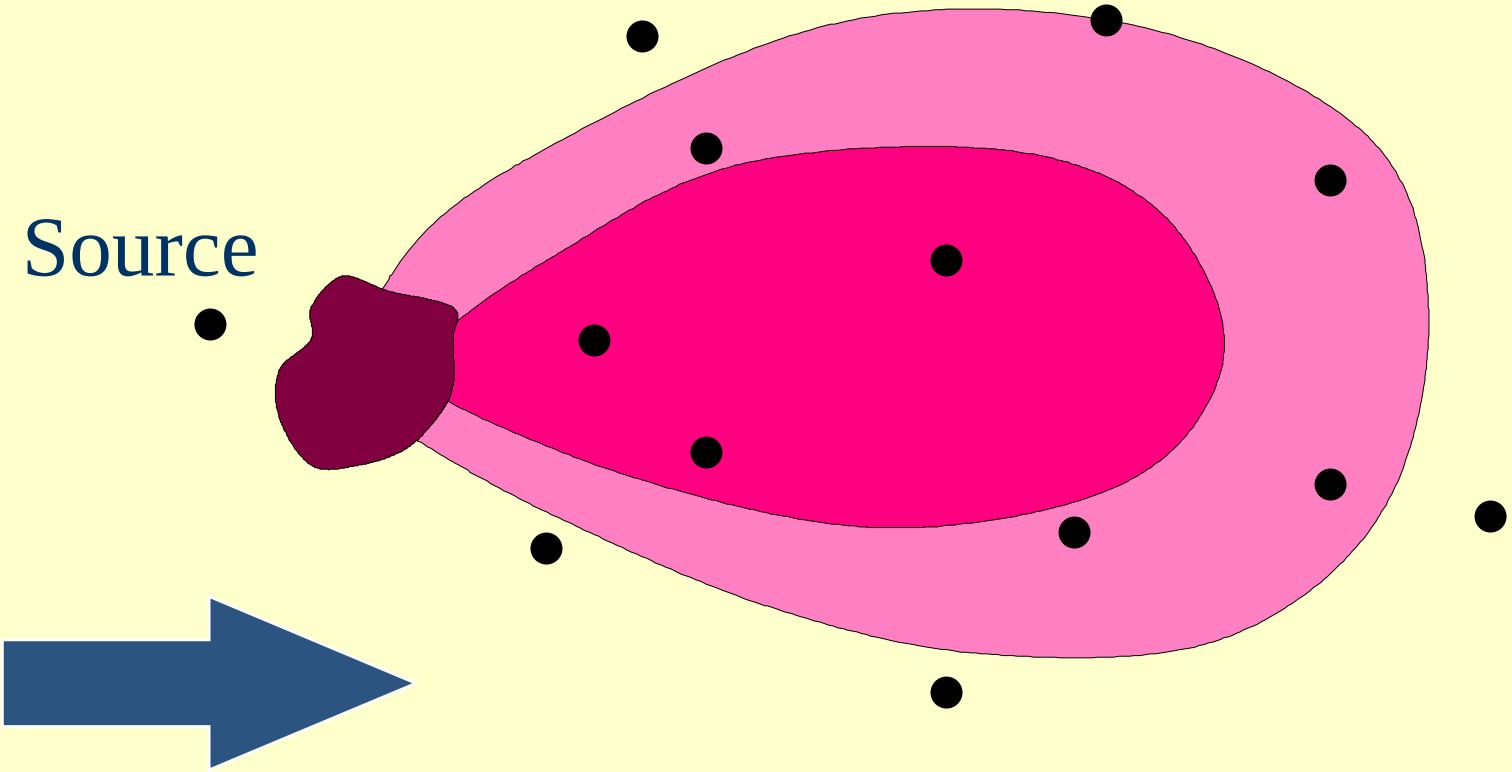
Site Characterization and Monitoring in the Last Millennium

- Founded on overly simplistic conceptual models of subsurface conditions

1980's Idea of a contaminant plume in groundwater

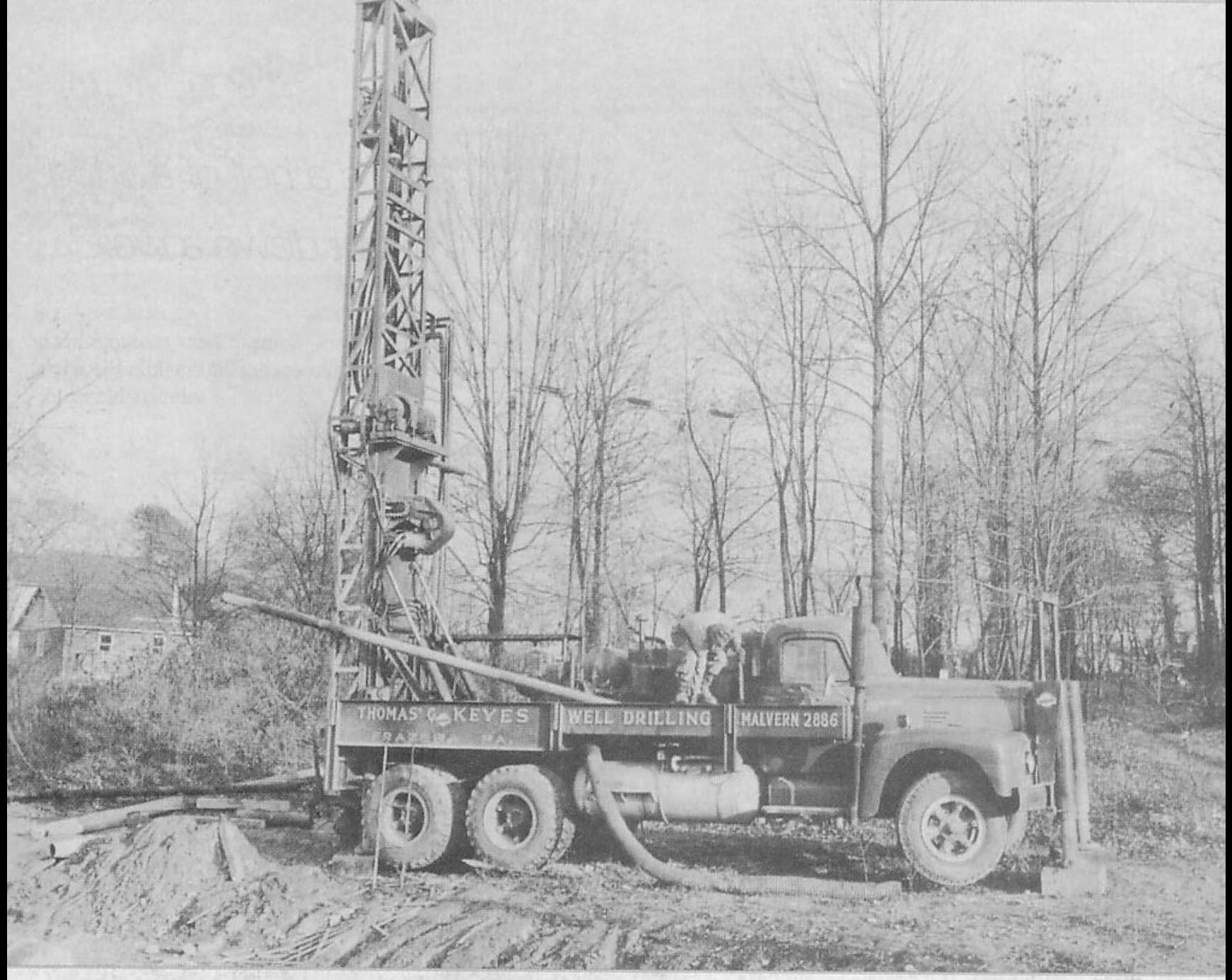


1980's Groundwater Monitoring Network



Site Characterization and Monitoring in the Last Millennium

- Founded on overly simplistic conceptual models of subsurface conditions
- Low-resolution site characterization and monitoring technologies



This rotary Schramm rig was built for water well driller Tom Keyes in 1952.

Conventional monitoring well = miniature water supply well

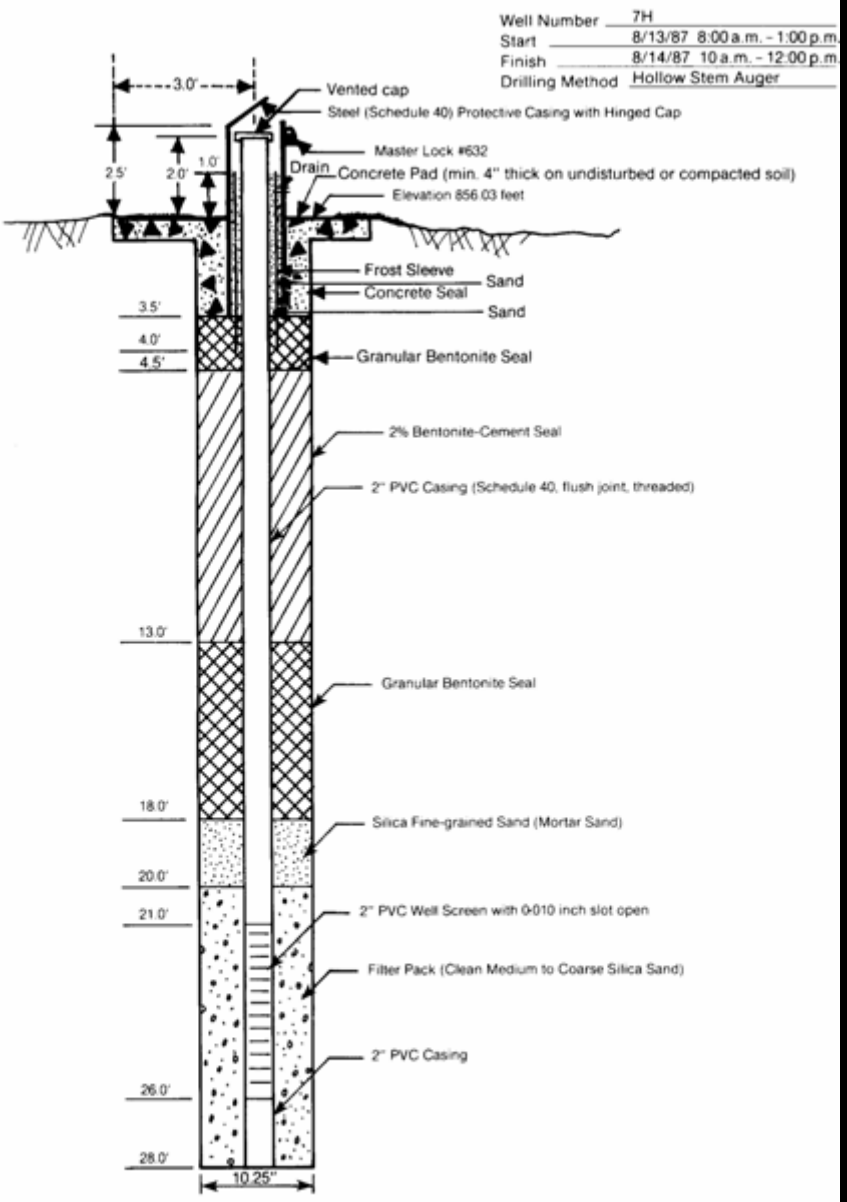
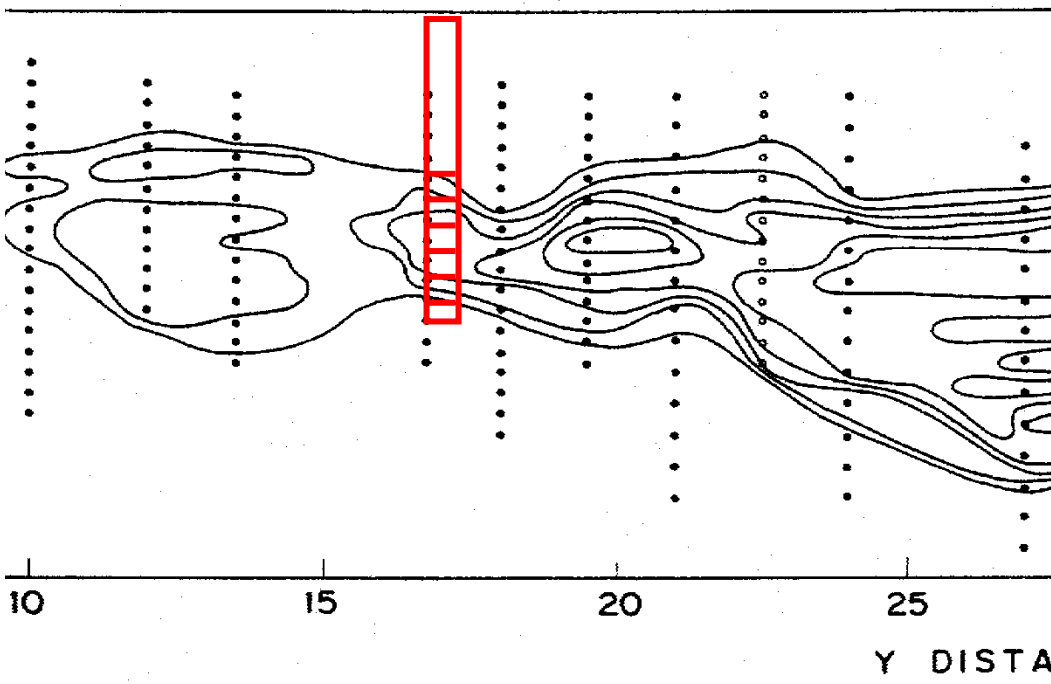


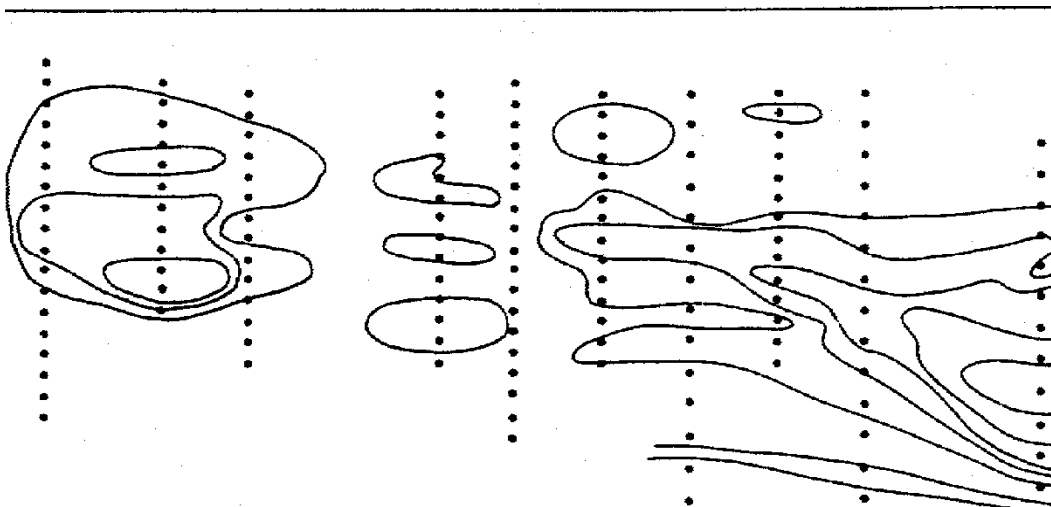
Figure 21. Format for an "as-built" monitoring well diagram.

63

Biases associated with monitoring wells

- Blended (composited) samples
- Results depend on position and length of screens
- Biased towards higher-K units
- Additional dilution due to effects of partial penetration
- May understimate maximum concentrations by an order of magnitude or more
- Ambient flow re-distributes contaminant mass in aquifer when vertical gradients are present





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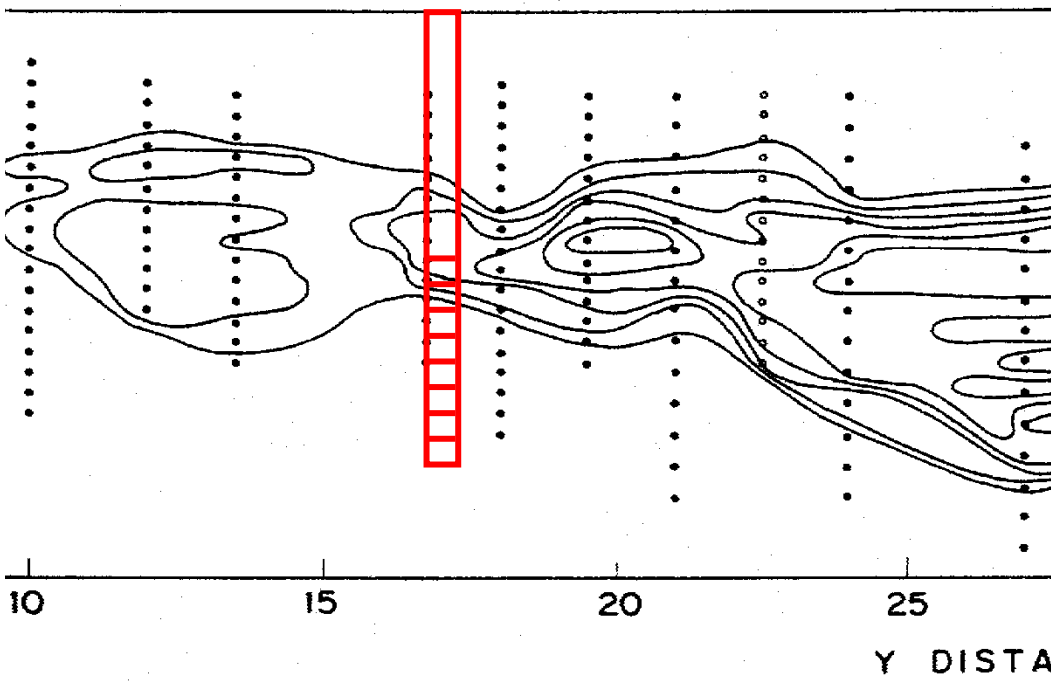

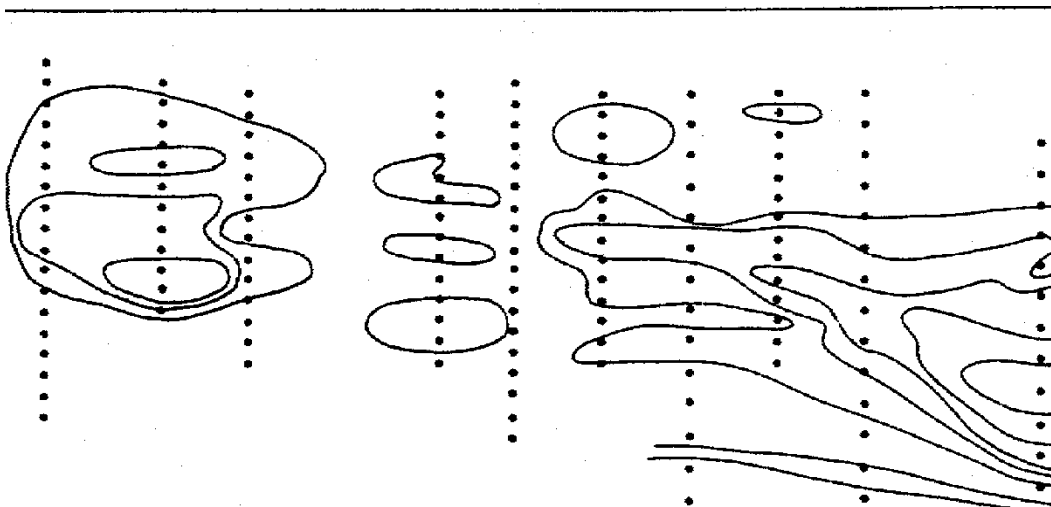

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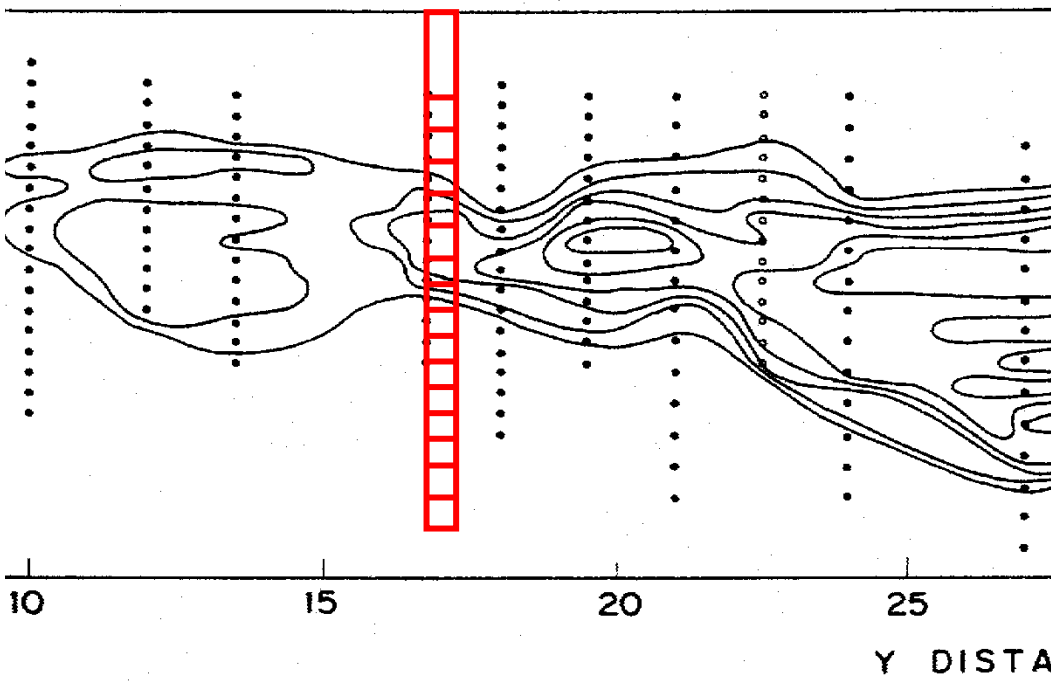

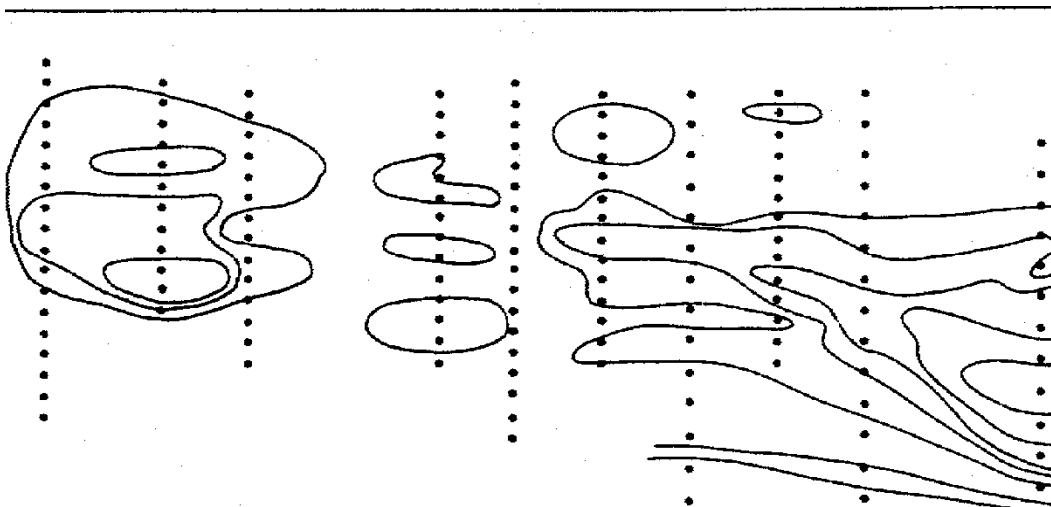

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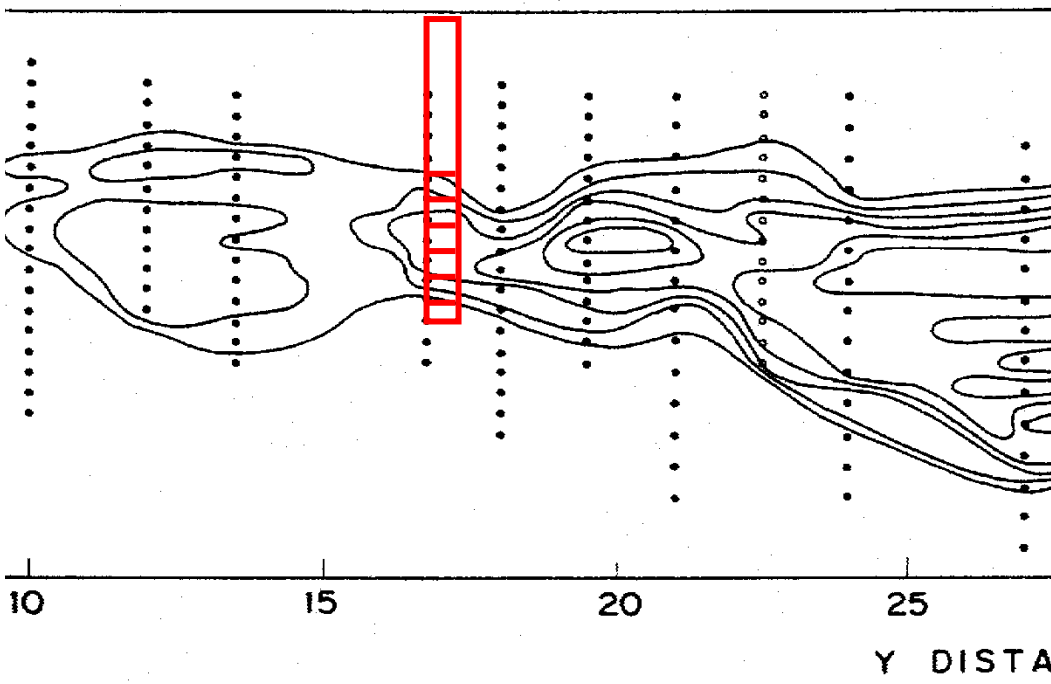
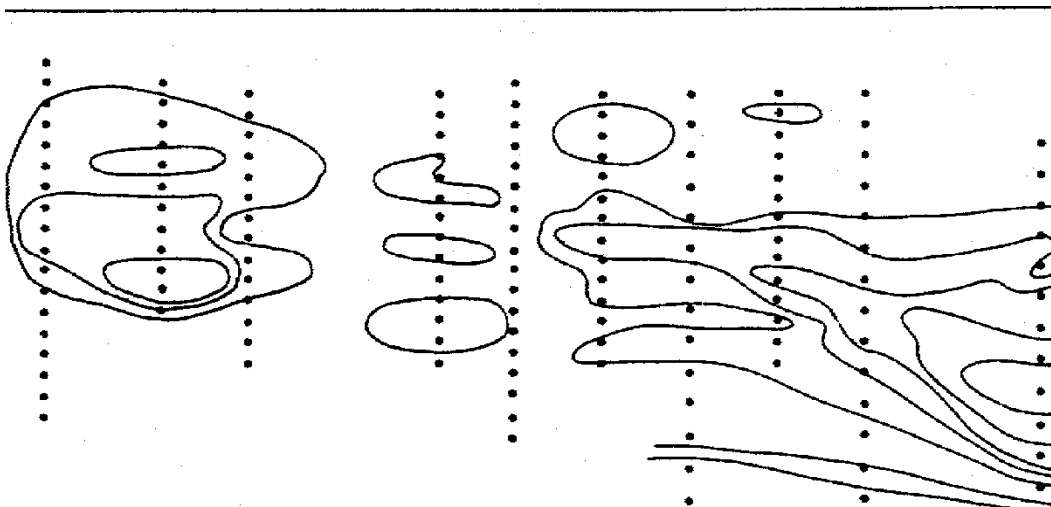
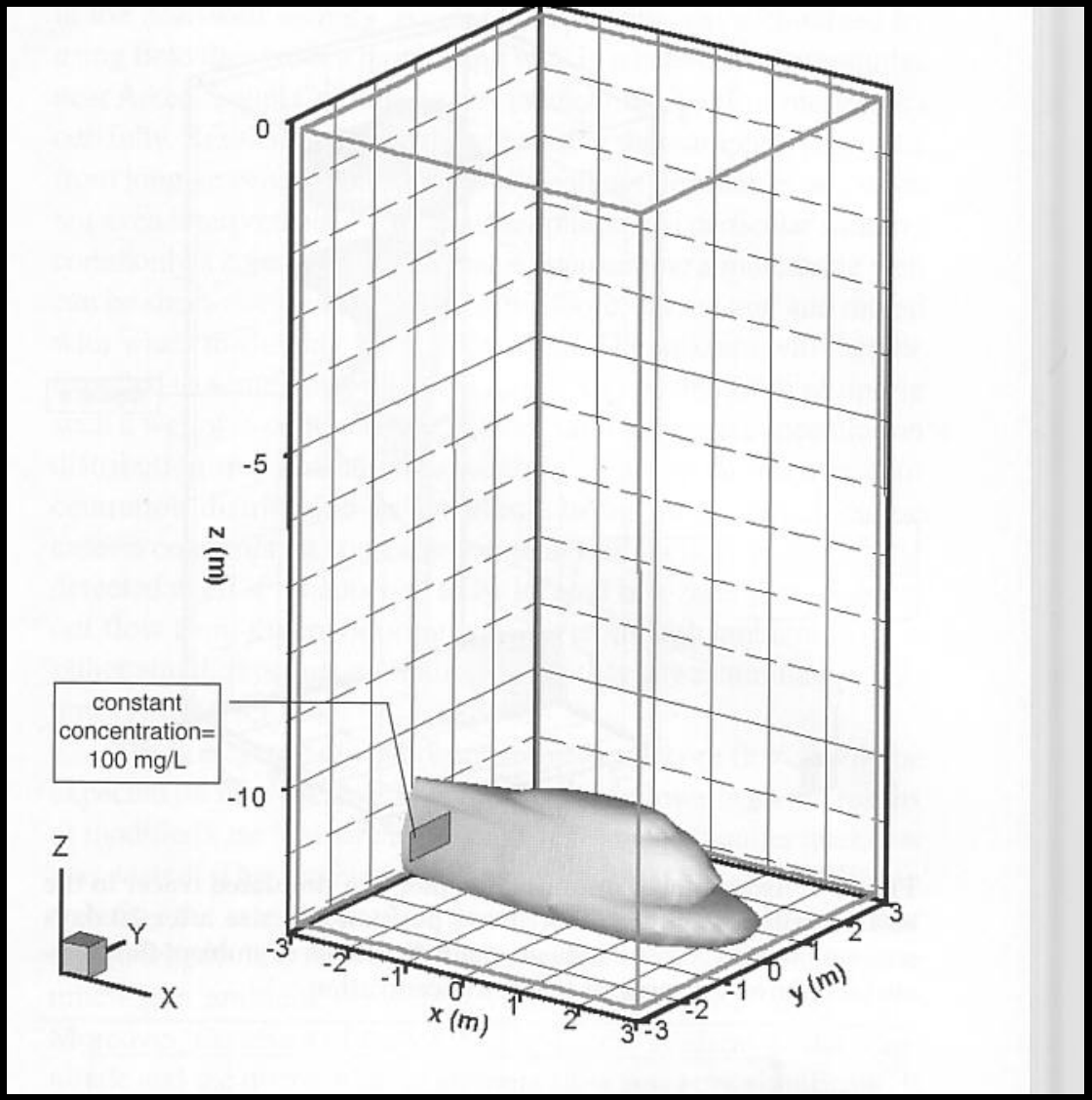
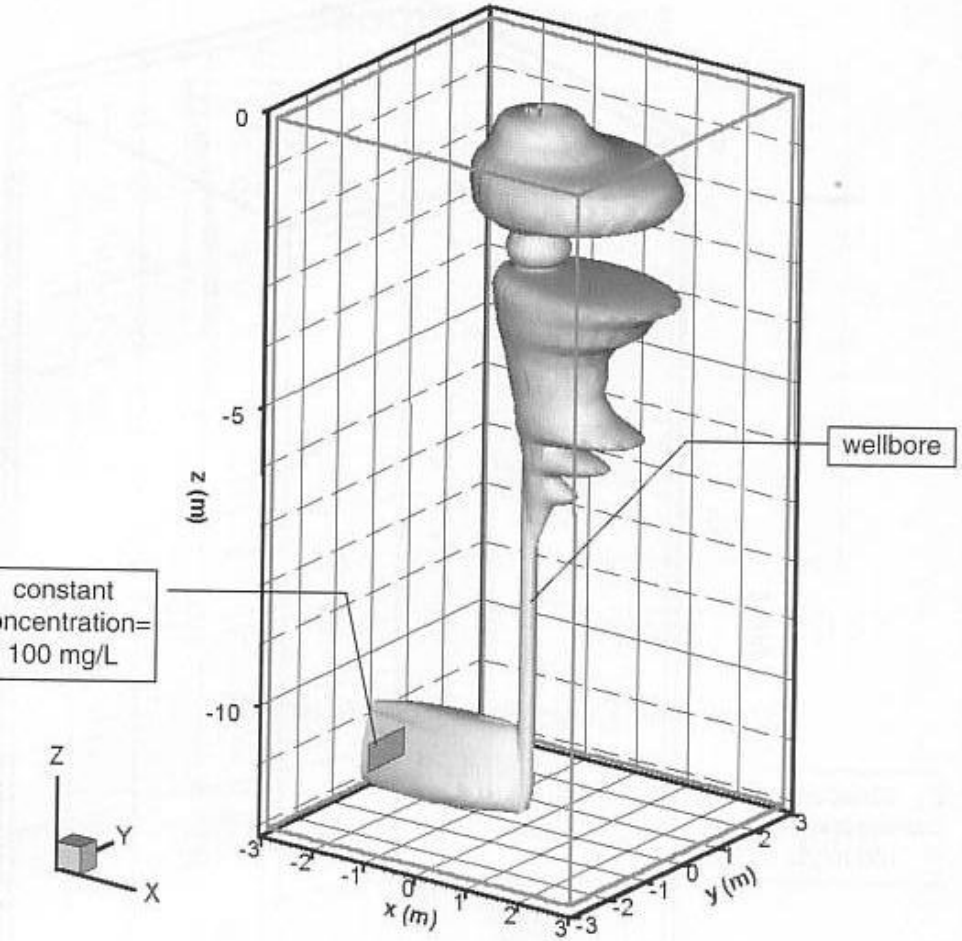
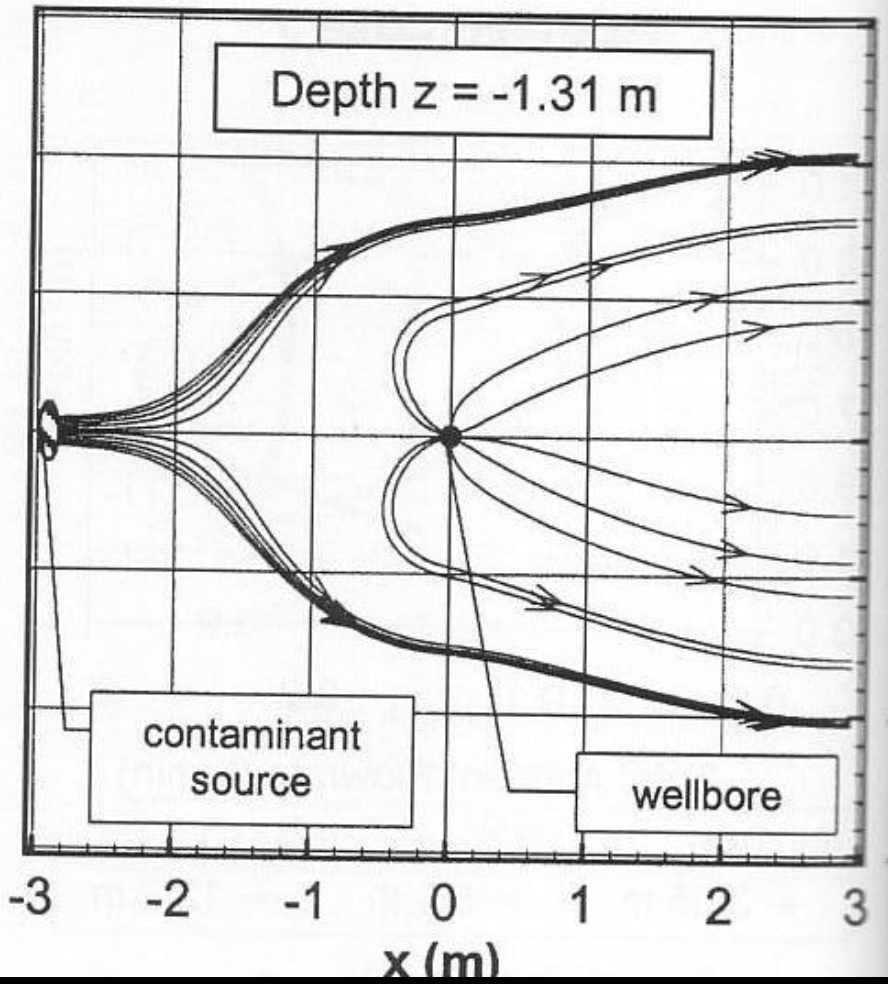


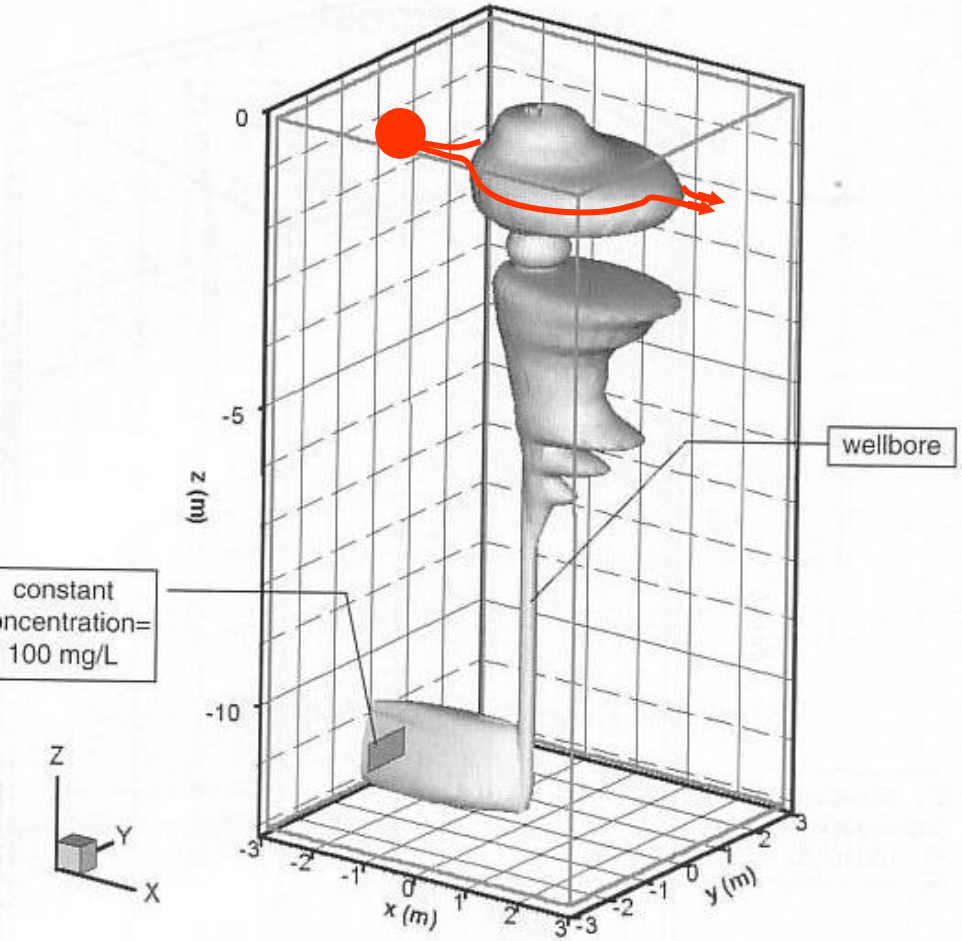


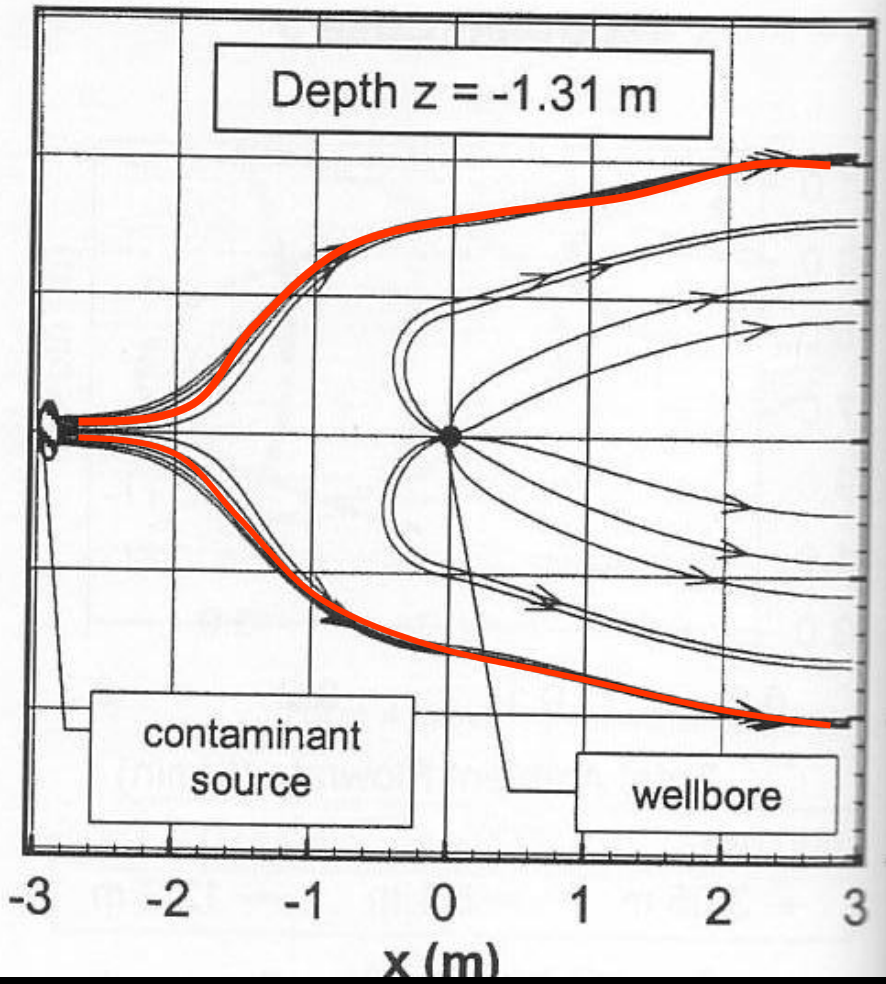
Implications of Observed and Simulated Ambient Flow in Monitoring Wells. Elci, Molz, and Waldrop, 2001.




wellbore
constant
ncentration=
100 mg/L
z (m)
x (m)
y (m)
Z
Y
X


Depth z = -1.31 m
contaminant
source
wellbore
x (m)

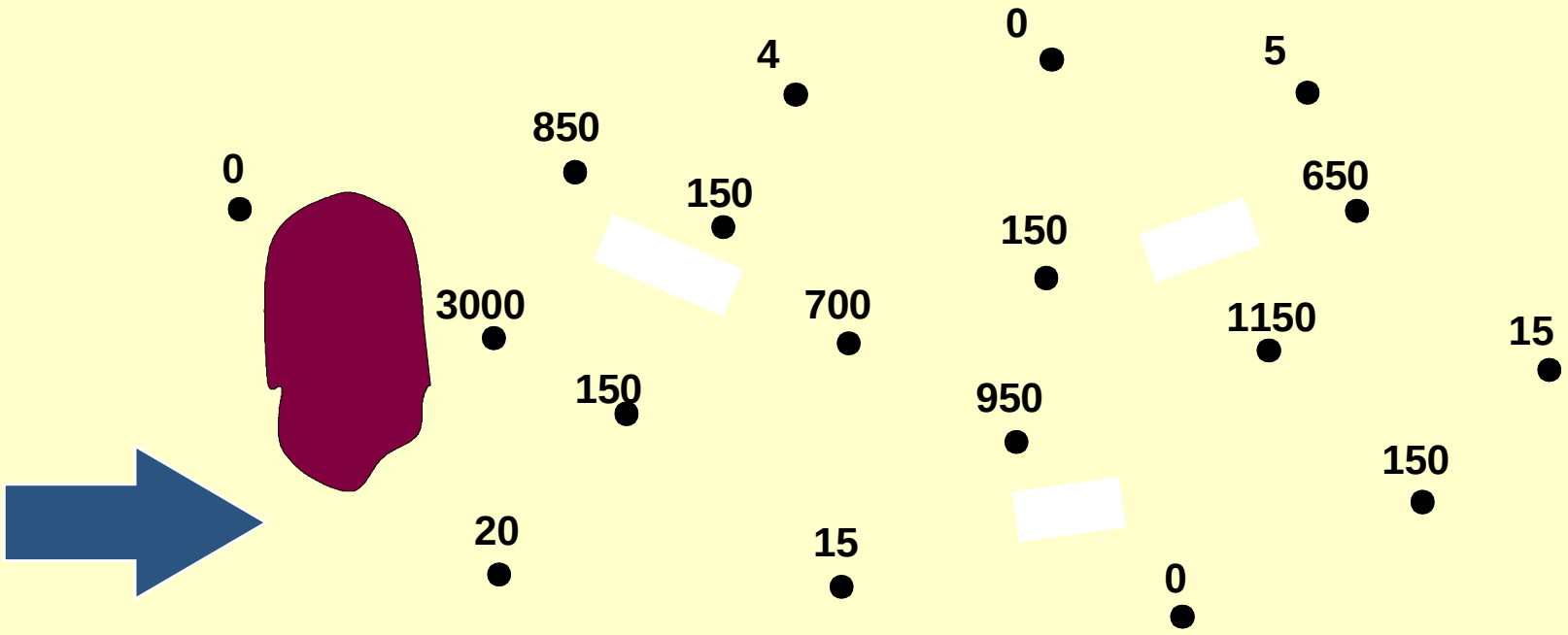

wellbore
constant
ncentration=
100 mg/L
z (m)
0
-5
-10
x (m)
y (m)
Z
Y
X


Depth z = -1.31 m
contaminant
source
wellbore
-3
-2
-1
0
1
2
3
x (m)

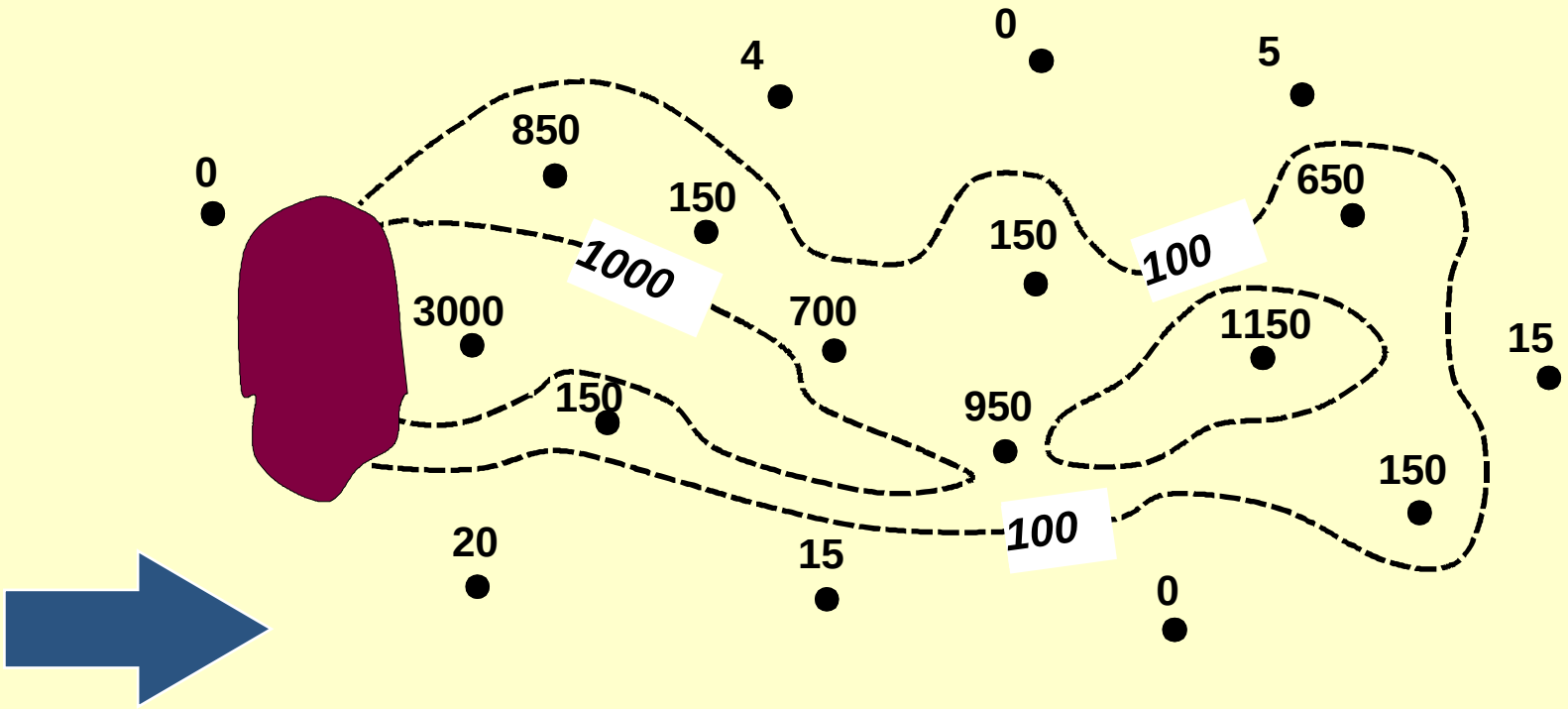
Site Characterization and Monitoring in the Last Millennium

- Founded on overly simplistic conceptual models of subsurface conditions
- Low-resolution site characterization and monitoring technologies
- Simplistic (& erroneous) 2-D depictions of contaminant plumes

Data we have historically collected



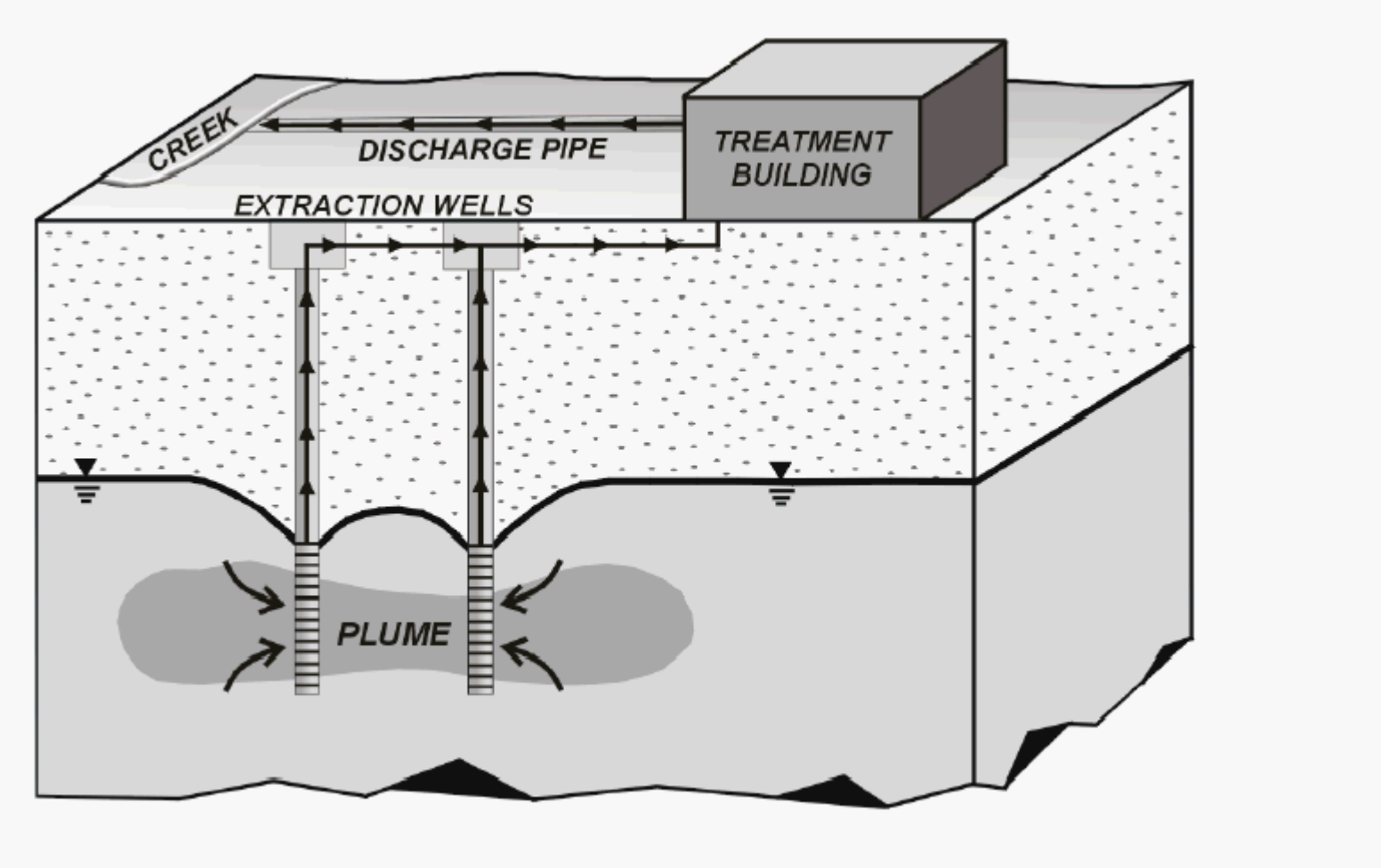
How we typically “analyze” the data



Site Characterization and Monitoring in Last Millennium

- Founded on overly simplistic conceptual models of subsurface conditions
- Low-resolution site characterization and monitoring technologies
- Simplistic, 2-D depictions of contaminant plumes
- One-size-fits-all assessments
- Checklist approach to site investigations
- Focus on hydraulic properties, not natural flow (gradients) & geochemistry

Pump & Treat Remediation



What we *now* know about subsurface contamination that we didn't know 30 years ago*

- The distribution of dissolved contaminants in the subsurface is spatially and temporally variable.
- NAPLs
- Hydrodynamic mixing is usually limited in directions transverse to flow
- Aquifers are contaminated, not just groundwater
- Biochemical reactions are important, but are spatially and temporally variable

* knowledge from high-resolution field research

CASE STUDY

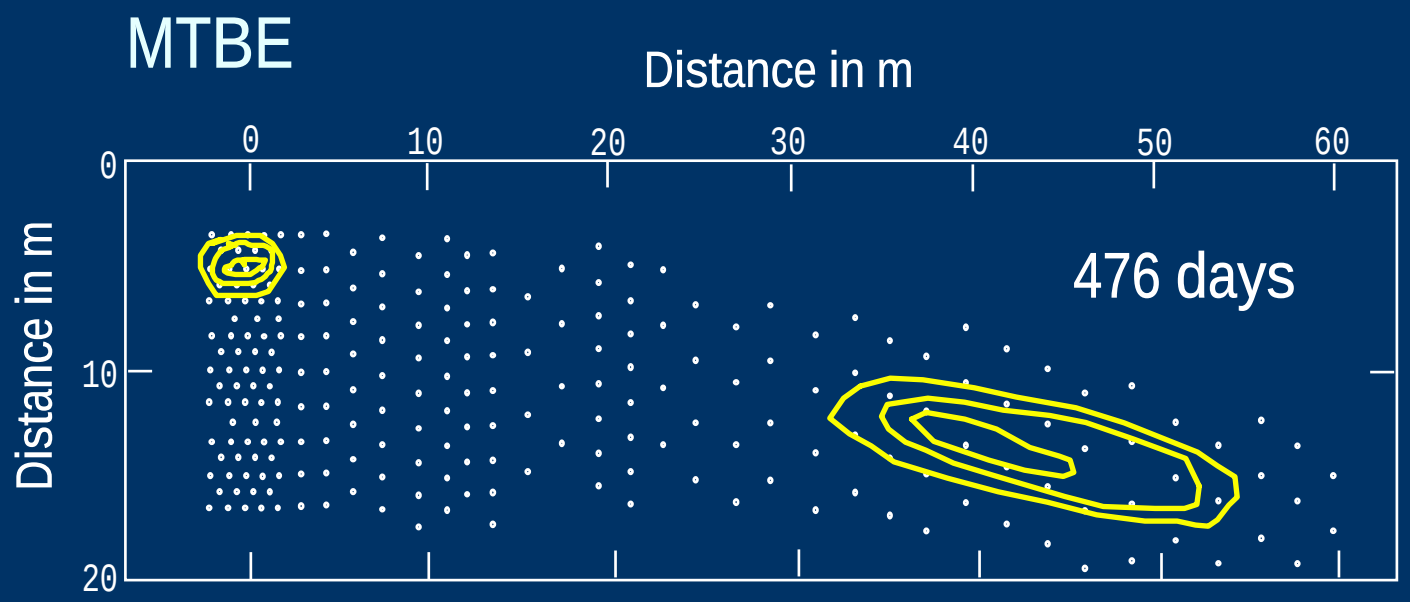
1988 Controlled Release of Dissolved MTBE & Methanol, CFB Borden, Ontario, Canada

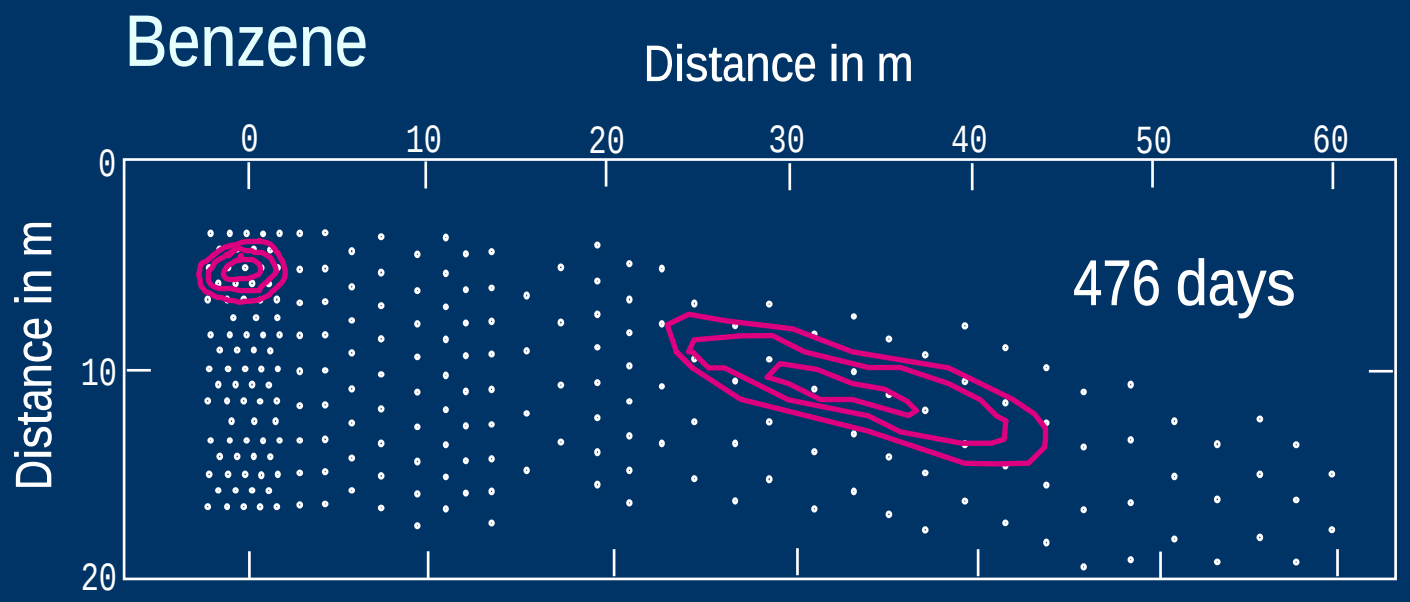
University of Waterloo

Jim Barker, Principal Investigator

Hubbard et al., 1994

Multi-level Piezometer Network

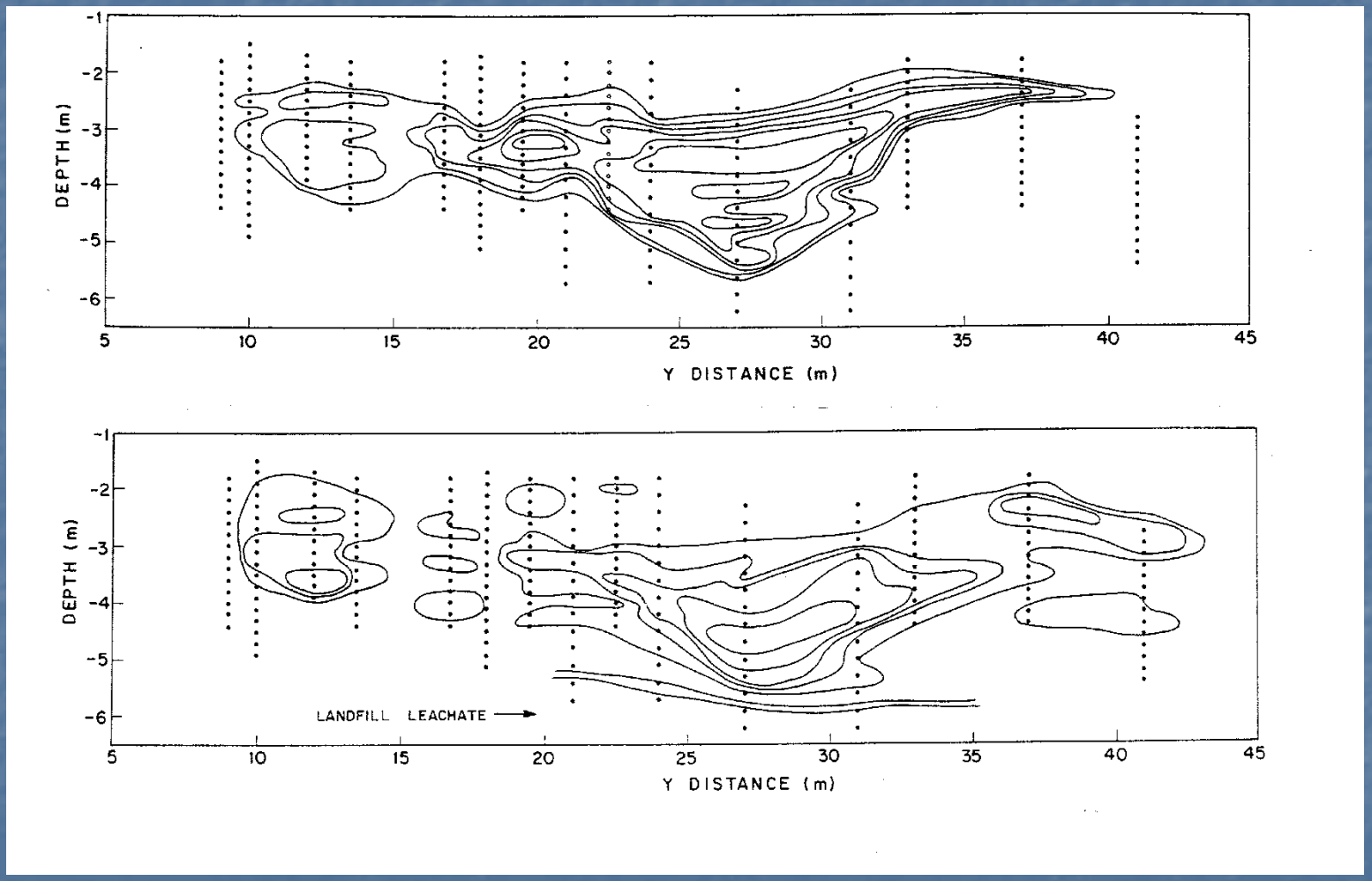

MTBE
Distance in m
0
10
20
30
40
50
60
Distance in m
0
10
20
476 days


Benzene
Distance in m
0
10
20
30
40
50
60
Distance in m
0
10
20
476 days

Cross Sections

Benzene

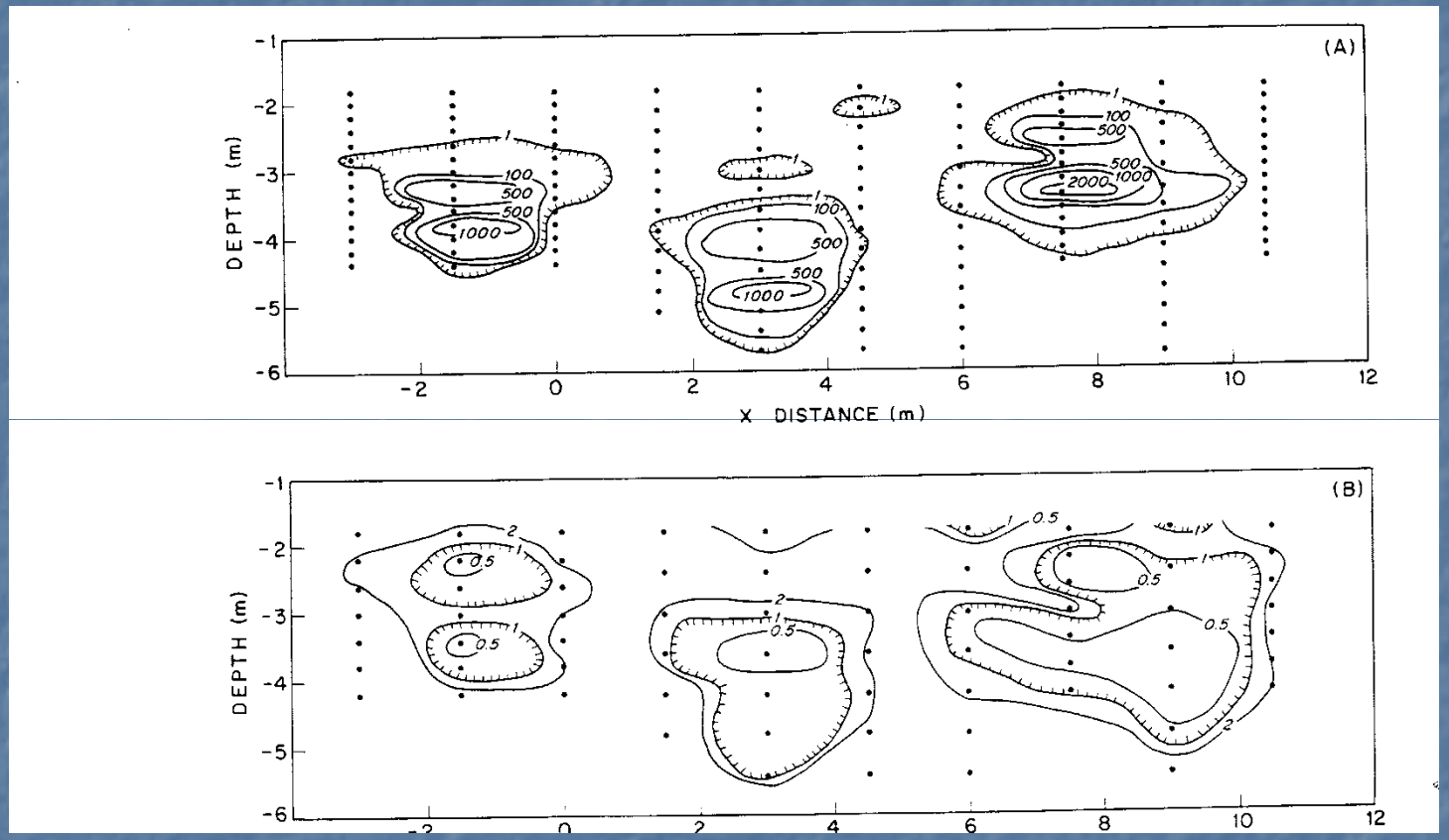
Chloride



Transects across plumes

Benzene

Dissolved Oxygen



ground water

CASE STUDY

Mass and Flux Distributions from DNAPL Zones in Sandy Aquifers

by Martin A. Guilbeault[1,2], Beth L. Parker[1,3], and John A. Cherry[1]

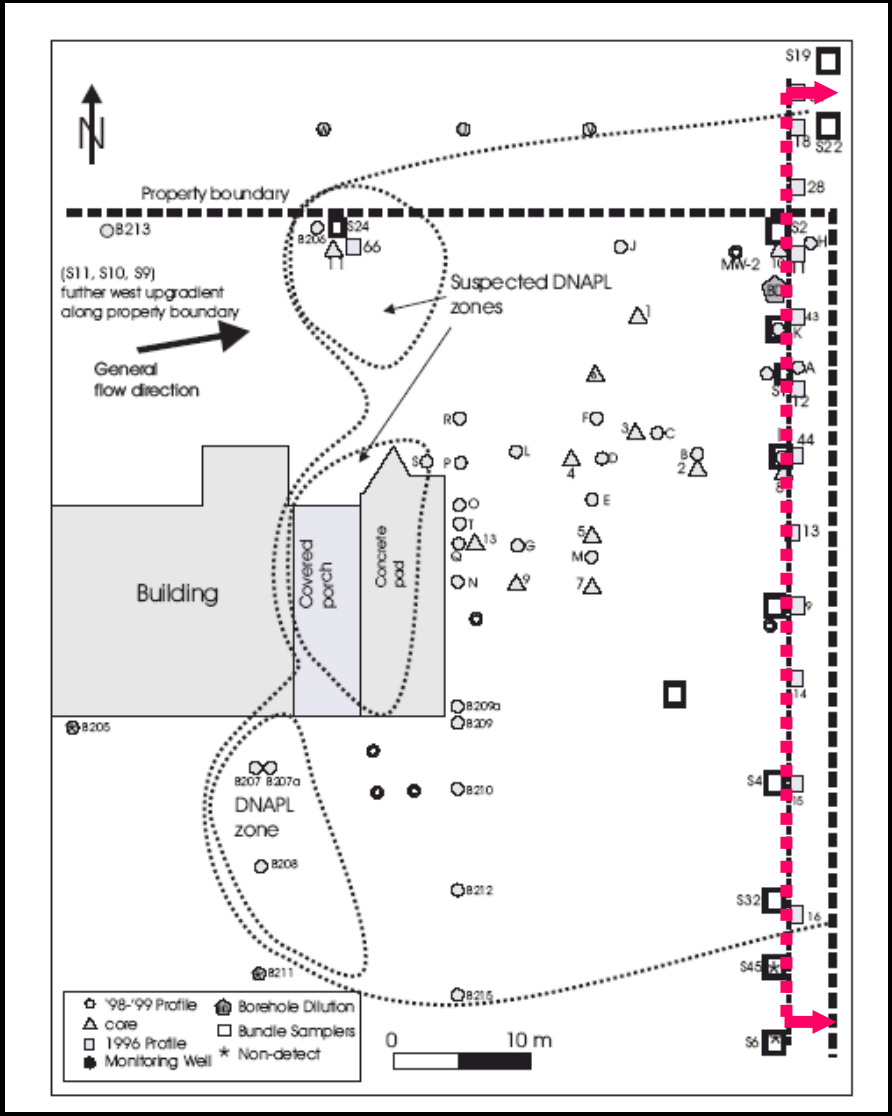
Abstract

At three industrial sites in Ontario, New Hampshire, and Florida, tetrachloroethylene (PCE) and trichloroethylene (TCE), released decades ago as dense nonaqueous phase liquids (DNAPLs), now form persistent source zones for dissolved contaminant plumes. These zones are suspended below the water table and above the bottoms of their respective, moderately homogeneous, unconfined sandy aquifers. Exceptionally detailed, depth-discrete, ground water sampling was performed using a direct-push sampler along cross sections of the dissolved-phase plumes, immediately downgradient of these DNAPL source zones. The total plume PCE or TCE mass-discharge through each cross section ranged between 15 and 31 kg/year. Vertical ground water sample spacing as small as 15 cm and lateral spacing typically between 1 and 3 m revealed small zones where maximum concentrations were between 1% and 61% of solubility. These local maxima are surrounded by much lower concentration zones. A spacing no larger than 15 to 30 cm was needed at some locations to identify high concentration zones, and aqueous VOC concentrations varied as much as four orders of magnitude across 30 cm vertical intervals. High-resolution sampling at these sites showed that three-quarters of the mass-discharge occurs within 5% to 10% of the plume cross sectional areas. The extreme spatial variability of the mass-discharge occurs even though the sand aquifers are nearly hydraulically homogeneous. Depth-discrete field techniques such as those used in this study are essential for finding the small zones producing most of the mass-discharge, which is important for assessing natural attenuation and designing remedial options.

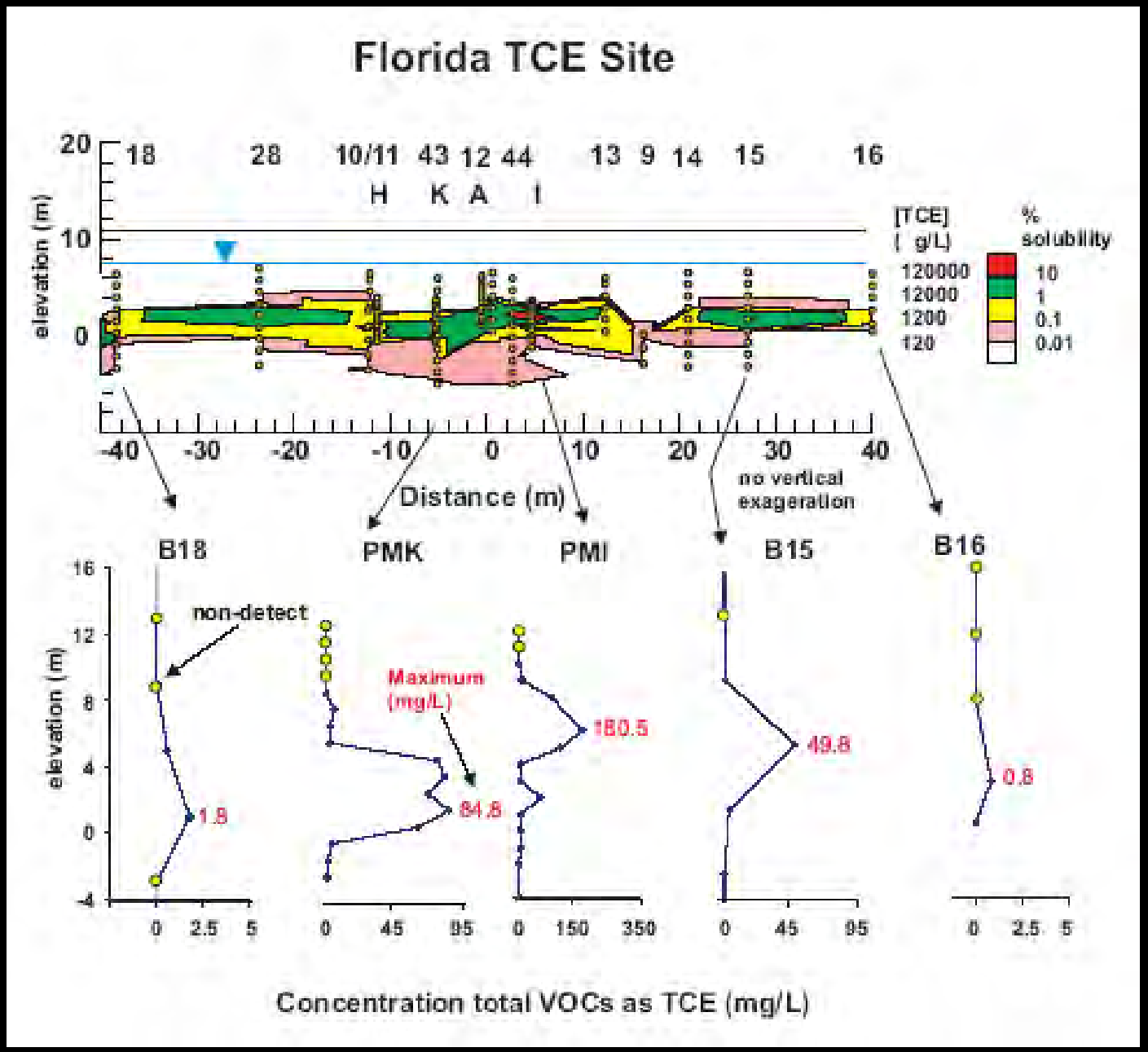
Introduction

Chlorinated solvents are the most prevalent organic contaminants found in ground water (Stroo et al. 2003), and in the dissolved phase they are typically mobile and recalcitrant, particularly trichloroethylene (TCE) and tetrachloroethylene (PCE). Schwille (1984, 1988) was the first to recognize that chlorinated solvent plumes (i.e., zones of plumes comprised of other types of organic contaminants (Mackay and Cherry 1989). Although the processes governing subsurface DNAPL and plume behavior are known (Cohen and Mercer 1993; Pankow and Cherry 1996) and numerous solvent contaminated sites have been investigated, DNAPL masses at field sites are not often quantified. (Feenstra 2003). Heterogeneity imposes severe limits for

Industrial Site, Florida



(Source: Guilbeault, Parker, & Cherry, 2005)



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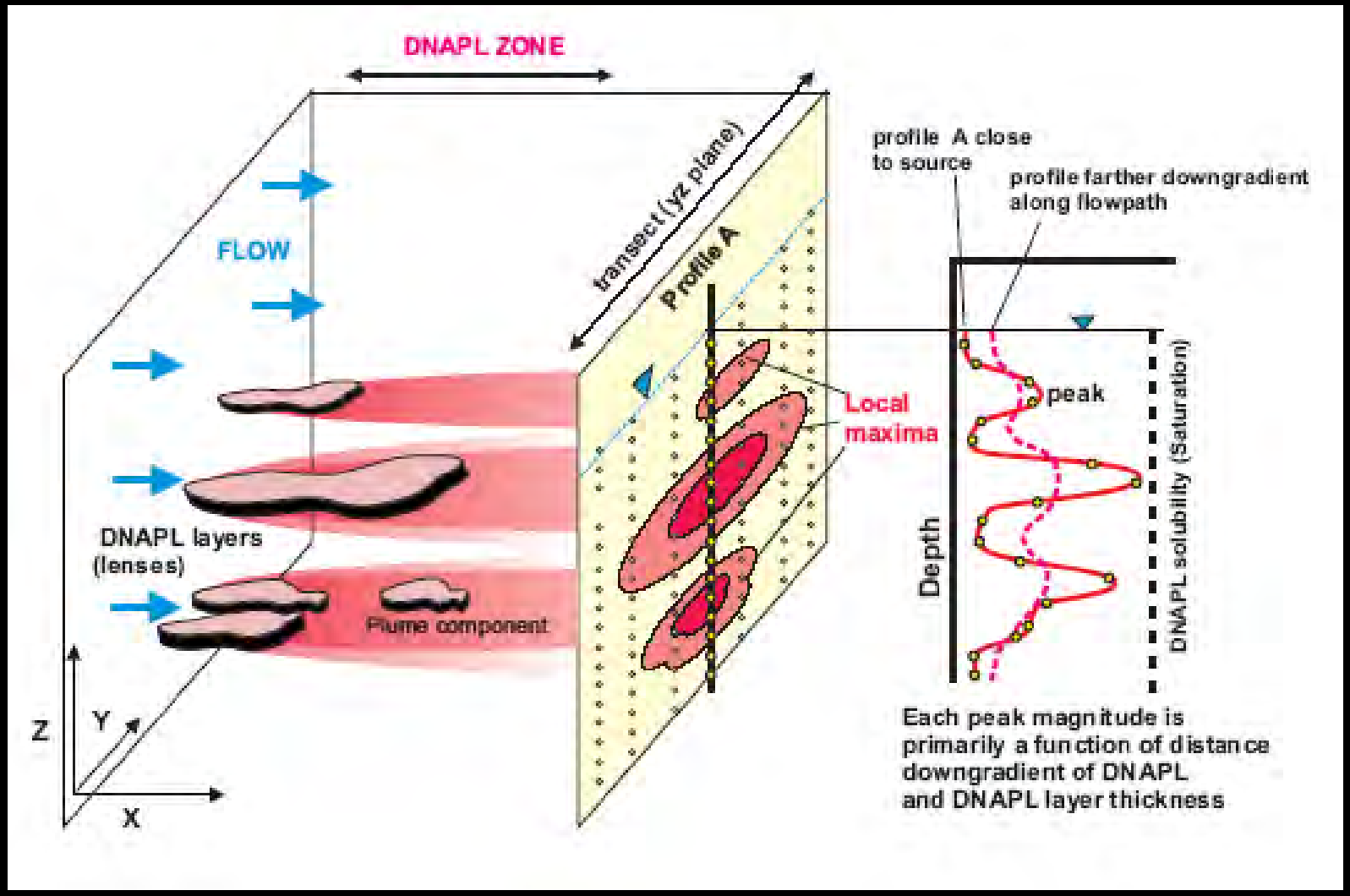
Conceptual Model for Dissolved Plumes Emanating from DNAPL Source Zones



(Source: Guilbeault, Parker, & Cherry, 2005)

Subsurface Cleanup in the New Millennium

- Good intentions
- Less $$
- Based on new knowledge of subsurface
- Goal: clean groundwater to MCLs; Risk-Based Cleanup
- Few virgin sites
- Have learned from our mistakes
- Focus on passive, in-situ methods
  - Monitored Natural Attenuation
  - Enhanced in situ treatment
- Mass flux/Mass discharge framework ⇨ partial source zone remediation
- Better success?

Defining Mass Discharge (M_d) in a contaminant plume can therefore help you predict the maximum concentrations in a downgradient supply well!

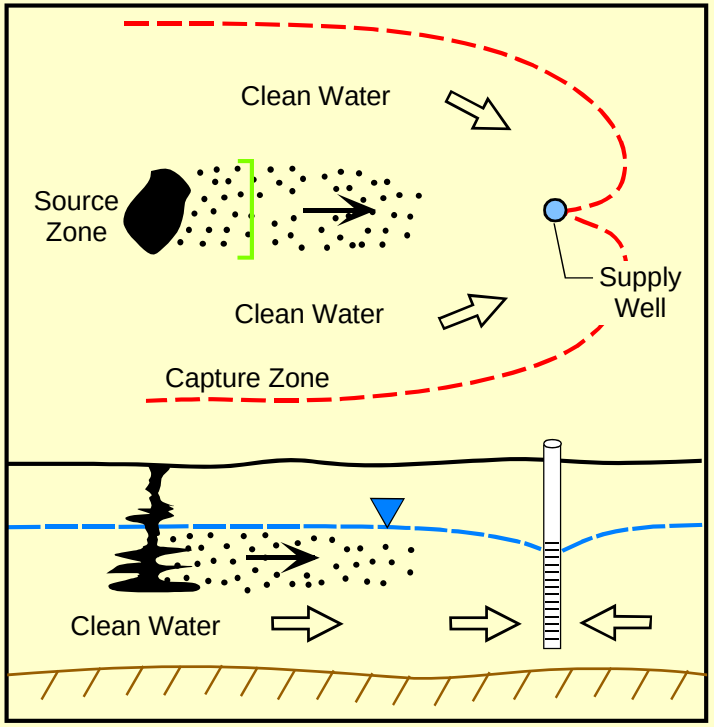
$$M_d \times \frac{1}{Q_w} = C_w$$

$$\frac{m}{t} \times \frac{t}{v} = C_w$$

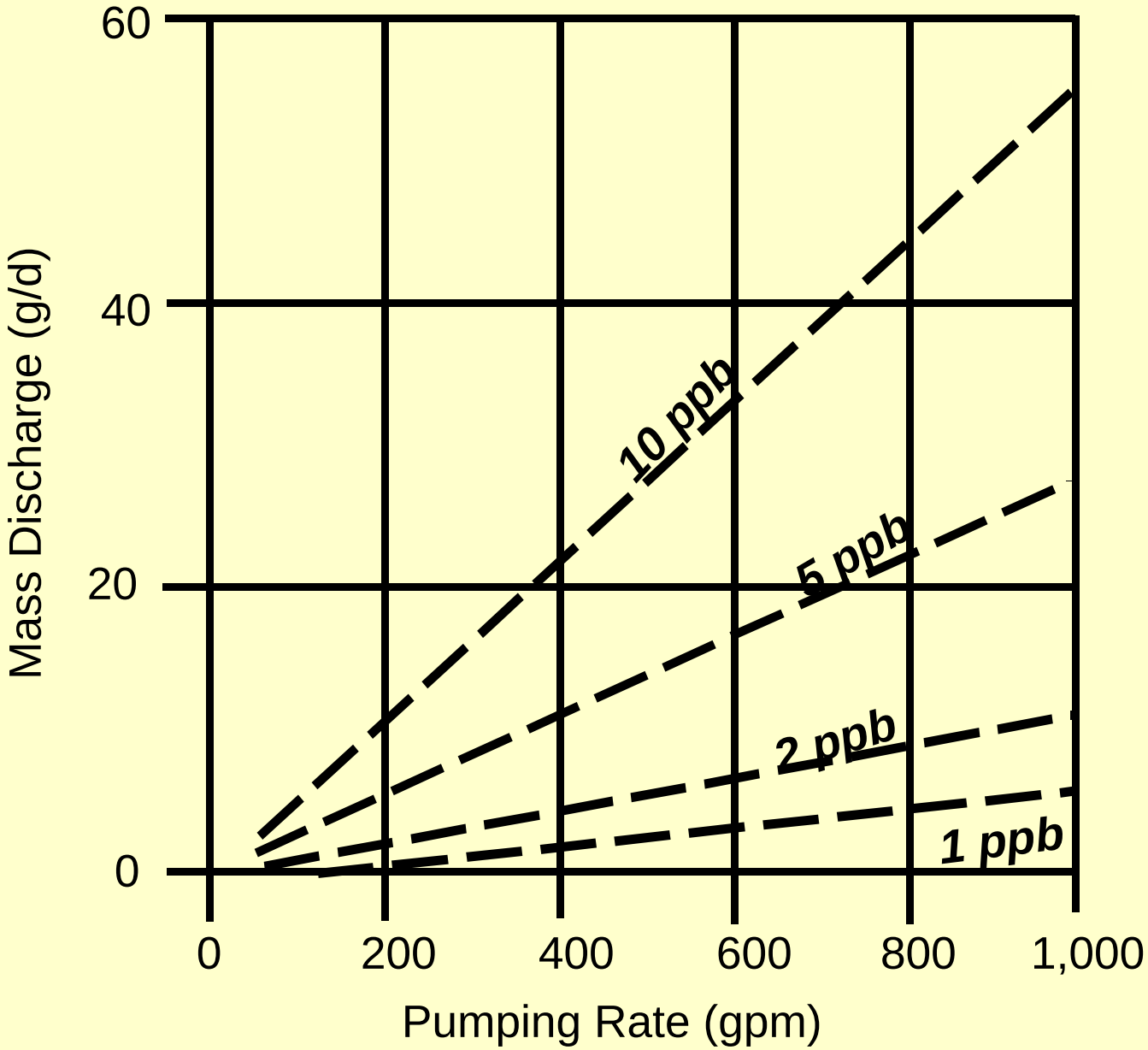
M_d = mass discharge

Q_w = Pumping rate

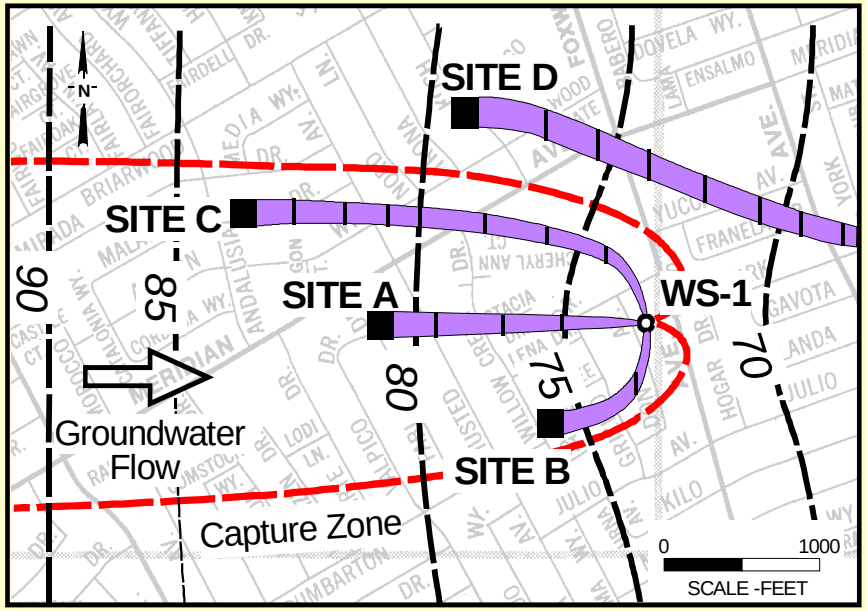
C_w = Concentration in well

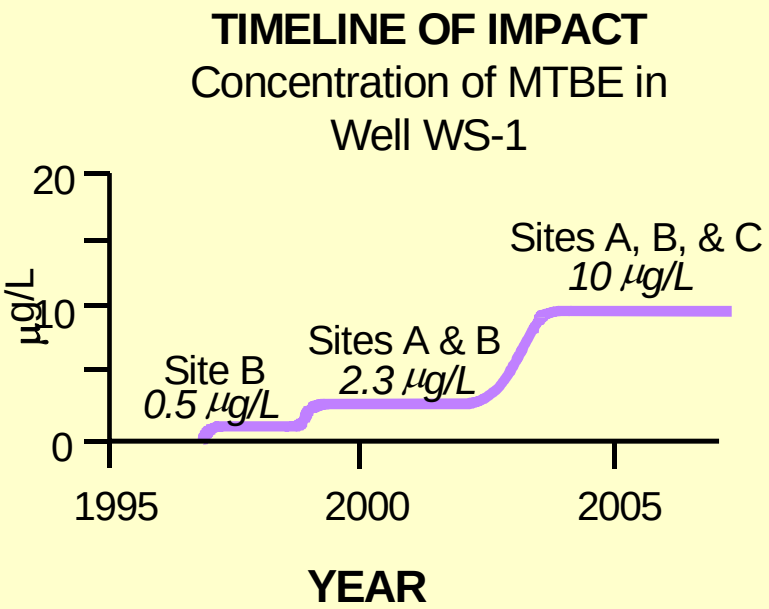


$$\frac{11.5\,g}{d} \times \frac{min}{300\,gal} \times \frac{1\,d}{1440\,min} \times \frac{10^6\,ug}{g} \times \frac{1\,gal}{3.79\,L} = \frac{7\,ug}{L}$$


60
40
20
0
Mass Discharge (g/d)
10 ppb
5 ppb
2 ppb
1 ppb
0
200
400
600
800
1,000
Pumping Rate (gpm)

Prioritization of remediation on releases with greatest mass discharge



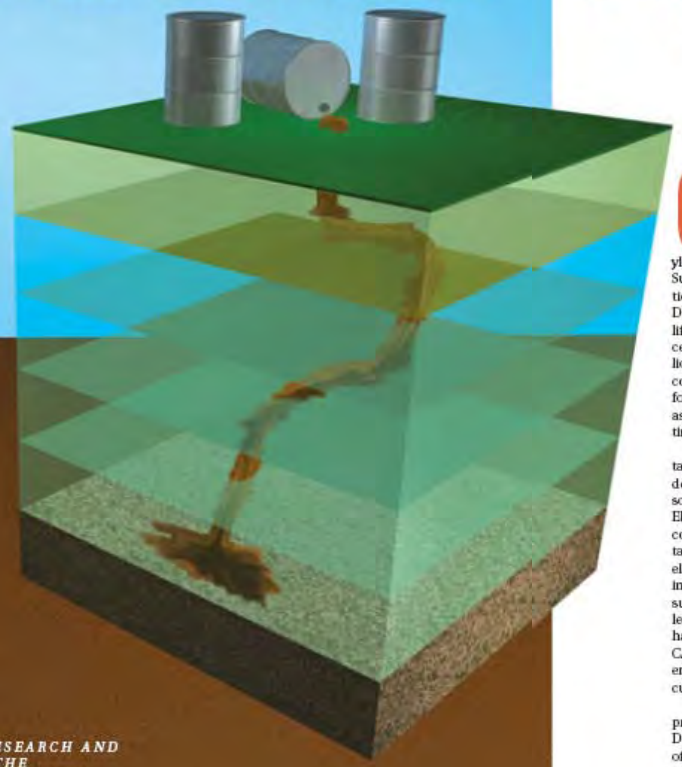


SITE	D_m (g/d)	Calc. Conc. (µg/L)
Site A =	2.0	1.8
Site B =	0.5	0.5
Site C =	8.5	7.8
	Σ 11.0	10.1

Q_{WS-1} = 200 gpm

REMEDIATING *Chlorinated Solvent* Source Zones

A workshop lists the challenges and research needs.



HANS F. STROO

MARVIN UNGER
THE RETEC GROUP, INC.

C. HERB WARD
RICE UNIVERSITY

MICHAEL C. KAVANAUGH
MALCOLM PIRNIE, INC.

CATHERINE VOGEL

ANDREA LEESON

JEFFREY A. MARQUSEE

BRADLEY P. SMITH
STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM AND THE ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM

Chlorinated solvents are by far the most prevalent organic contaminants in groundwater. For example, chlorinated aliphatic hydrocarbons (CAHs), such as trichloroethylene and perchloroethylene, are found at approximately 80% of all Superfund sites with groundwater contamination and more than 3000 Department of Defense (DoD) sites in the United States (*1*). The life-cycle costs to clean up these sites are uncertain, but they are likely to require several billions of dollars on a national level. DoD alone could spend more than $100 million annually for hydraulic containment at these sites, such as using pump-and-treat technologies, and estimates of life-cycle costs exceed $2 billion.

CAHs are also among the most difficult contaminants to clean up, particularly when their dense nonaqueous-phase liquid (DNAPL) sources remain in the subsurface. Both the U.S. EPA and the National Academy of Sciences have concluded that DNAPL sources may be contained, but remediation to typical cleanup levels for most DNAPL sites is often "technically impracticable" (*2–4*). Other DNAPL sources, such as coal tar and creosote, pose similar problems. Although these other DNAPLs tend to have significantly different properties than the CAH ones—notably lower solubilities and higher boiling points—much of the following discussion is relevant to them as well.

Over the past 10–15 years, pump-and-treat processes have not fully remediated sites with DNAPL occurrences (*5*). However, recent tests of innovative source remediation technologies, such as surfactant or alcohol flooding and in situ thermal treatment, suggest significant mass removal and reductions in mass discharge from sources is possible at some DNAPL sites (*6–8*). These results have led to increasing regulatory and public pressure to remediate sources. However, source remediation can be extremely expensive in the short term, and we can rarely predict with confidence whether it will be effective. Innovative technologies have not been thoroughly evaluated, and therefore, research and development (R&D) is clearly needed in several areas to better understand whether and how to attempt source remediation. Prioritizing the most urgent research is essential, given limited funds and the large number of potential projects. This article summarizes the results of a workshop conducted by the Strategic Environmental Research and Development Program and the Environmental Security Technology Certification Program during August 6–8, 2001, to identify the highest R&D priorities.

Nature of the problem

Interest in a more aggressive strategy for source removal has increased since the mid-1990s. Innovative technologies, such as in situ oxidation, various in situ thermal technologies, surfactant and cosolvent flushing, and bioremediation, were developed and marketed to overcome the perceived technical impracticability of source treatment. However, evaluating these technologies for specific site applications has proven difficult. The initial capital costs can be very high, and the long-term efficacy and economic return are difficult to predict (*9*). Moreover, DNAPL source zones are often very difficult to locate and characterize in the field, which complicates any assessment. In addition, aggressive treatments can cause pronounced changes in the distribution and the physical and chemical nature of the remaining DNAPL. For example, a DNAPL can be forced into less permeable zones or into previously uncontaminated areas. Table 1 demonstrates that controlled field tests performed on innovative source treatment technologies yield mixed results. Losses of greater than 90% of the source DNAPL have been measured at some sites, but 50–70% is more typical. As a result, there is considerable uncertainty regarding the efficacy of

TONY FERNANDEZ

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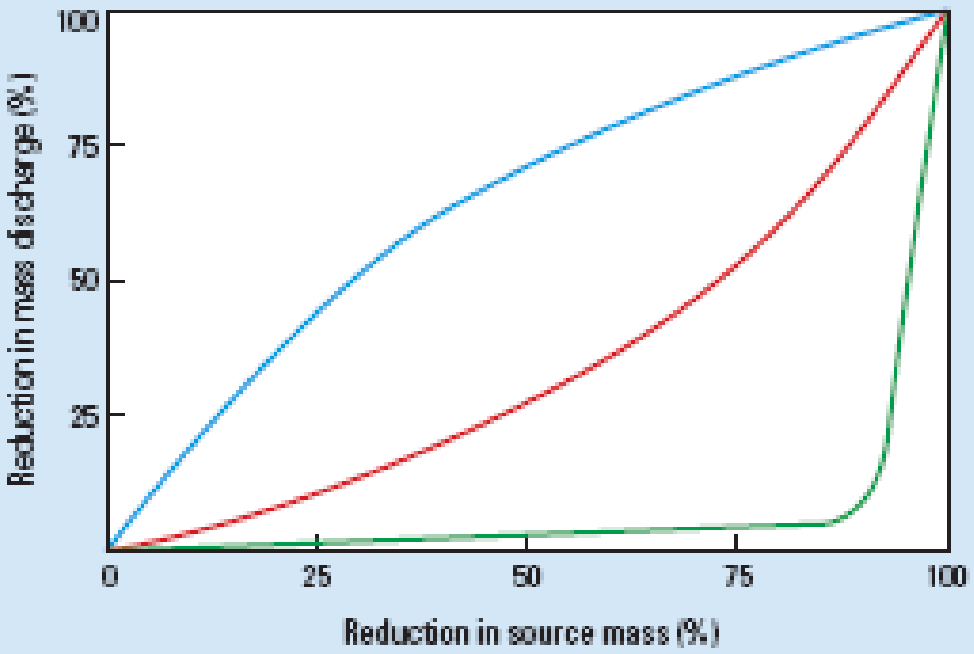
FIGURE 1

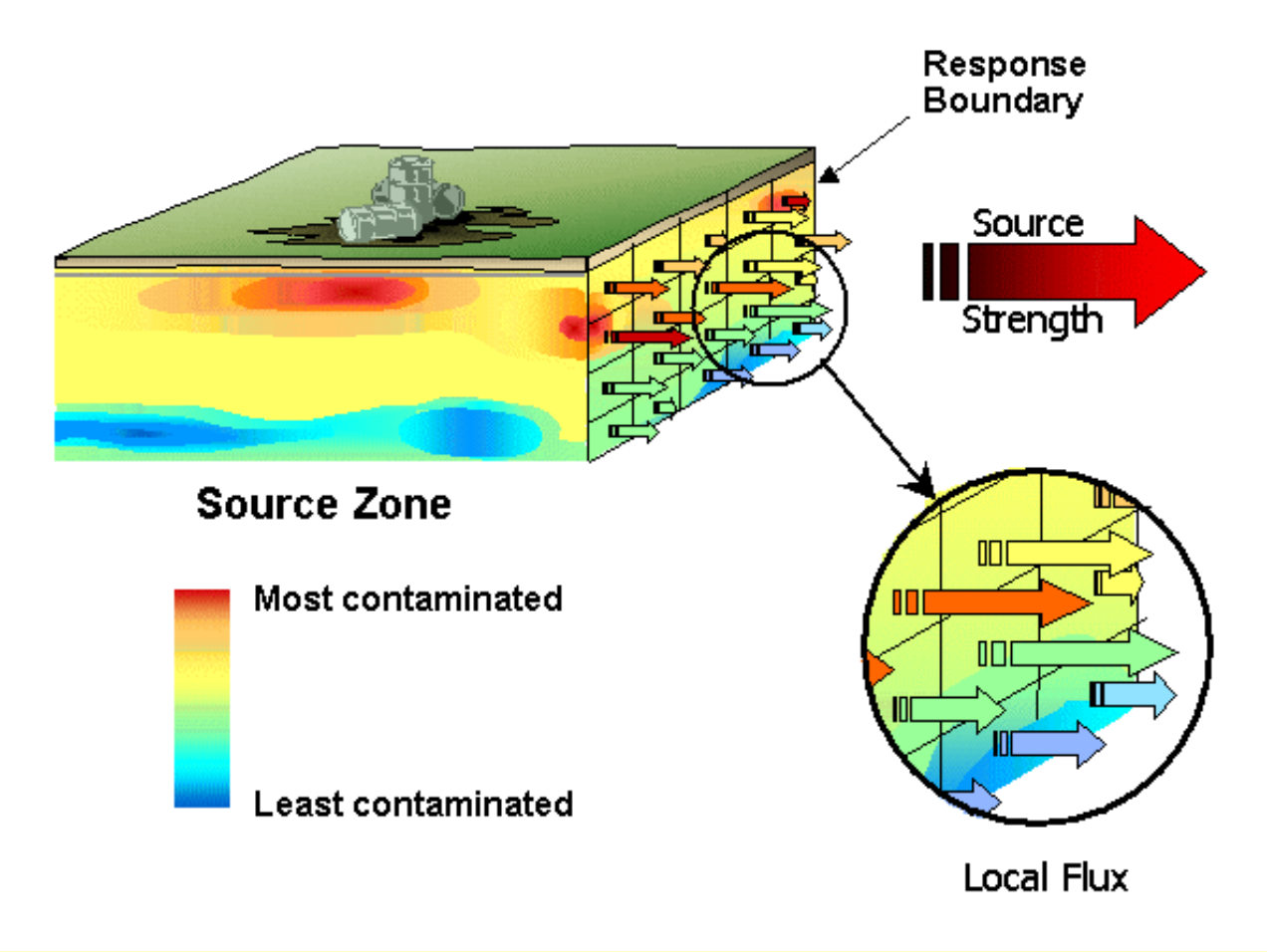
Relating DNAPL source to mass discharge

Modeling and limited data suggest that even removing more than 90% of the dense nonaqueous-phase liquid (DNAPL) source will not reduce concentrations in groundwater. However, this figure shows that if treatment removes the most accessible DNAPL, the mass discharge from sources in heterogeneous environments can be greatly reduced by even limited mass removal. The green line shows the theoretical relationship in a homogeneous aquifer with little reduction in source mass; the red line is extrapolated from data from a field demonstration at Dover Air Force Base in Dover, Del.; and the blue line shows the theoretical relationship in a highly heterogeneous aquifer with most of the DNAPL located in the higher permeability zones.



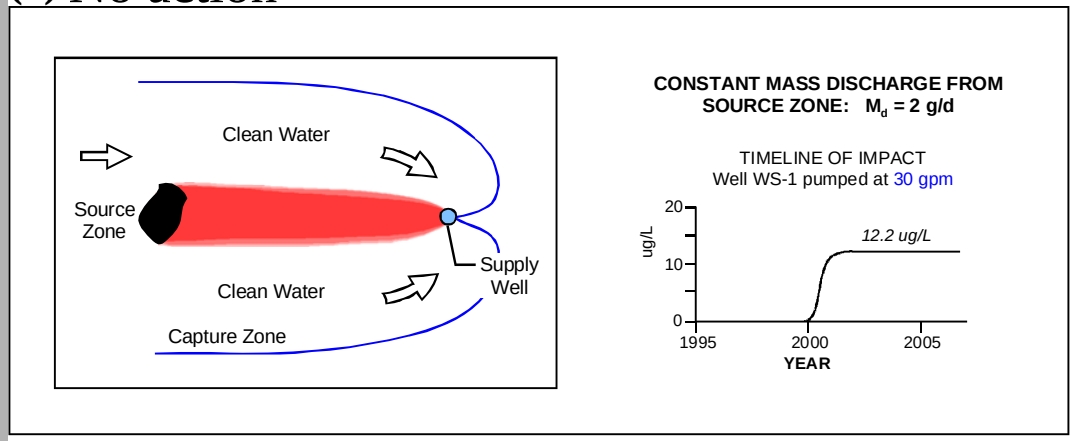
Source: Data for green line are from Ref. *18*, red line from Ref. *38*, and blue line from Ref. *20*.

Focus remediation on parts of source zone producing the greatest mass discharge

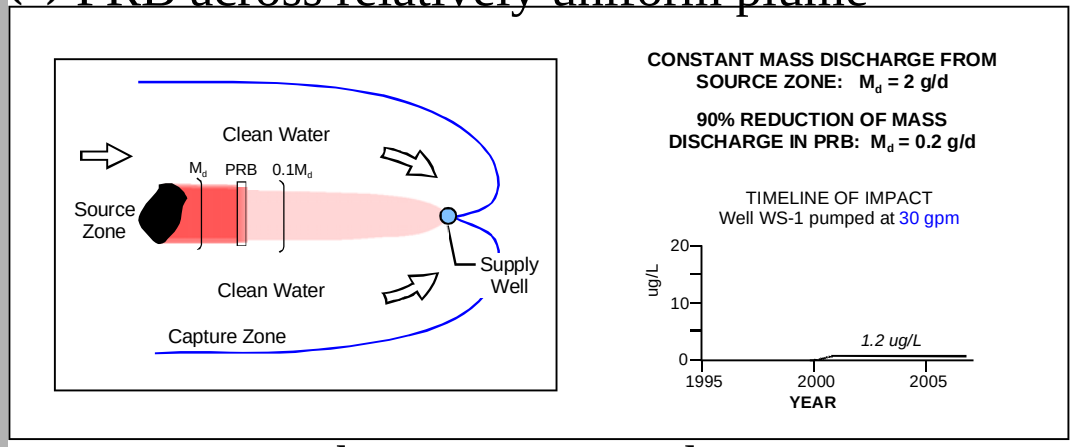


Partial treatment may still protect receptor

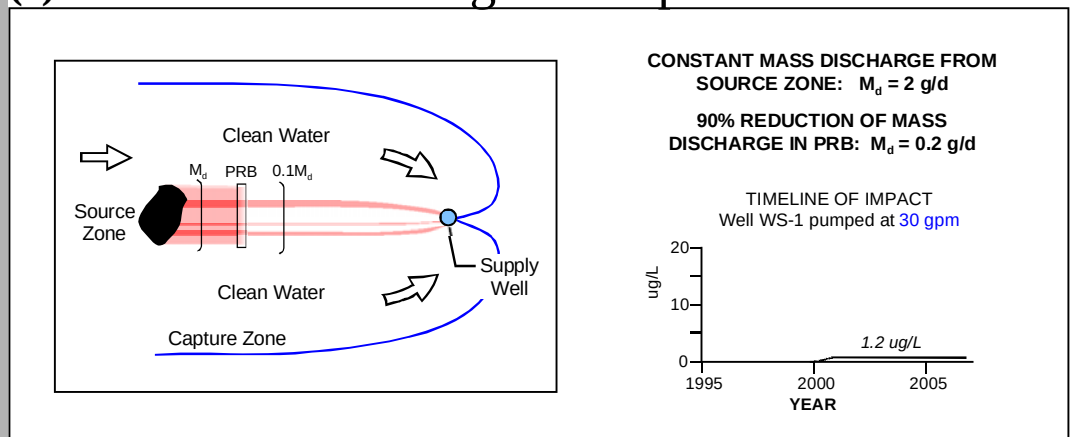
(a) No action



(b) PRB across relatively uniform plume



(c) PRB across heterogeneous plume

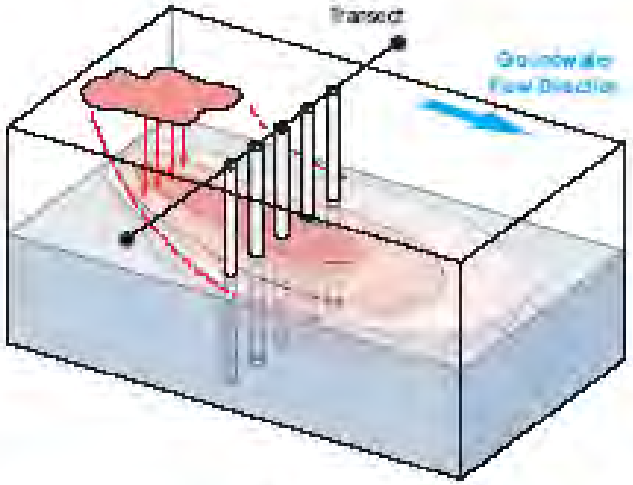


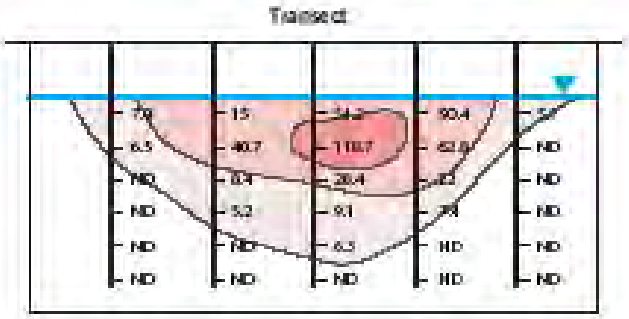
Site Characterization and Monitoring in the New Millennium

- Founded on more realistic conceptual models of subsurface conditions (sedimentology, contaminants)
- Scope varies depending on the anticipated remedy
- Utilization of the Scientific Method (ASC, ESC, TRIAD)
- Voluminous but biased historic data sets
- Horizontal contours for horizontal surfaces; <u>transects</u> of high-resolution data points to characterize linear features (e.g., buried channels, dissolved plumes)

A transect of closely-spaced DP samples or multilevel wells

- Ensures no part of the plume escapes detection
- Accurately identifies high-strength plume cores
- Monitors groundwater of the same age. Sampling the transect over time yields information about seasonal and longer-term variations in the “strength” of the plume
- Shows where concentrations are truly low or ND (not low or ND because of sample dilution)
- Allows the calculation of contaminant mass flux





7.0	15	34.2	90.4	5.7
6.5	40.7	118.7	62.6	0
0	8.4	28.4	22	0
0	5.2	9.1	7.4	0
0	0	6.3	0	0
0	0	0	0	0

$$M_t = \sum_{i=1}^{n} C_i \times A_z \times q_i$$

See Nielsen, 2006

(Source: LFR/API)

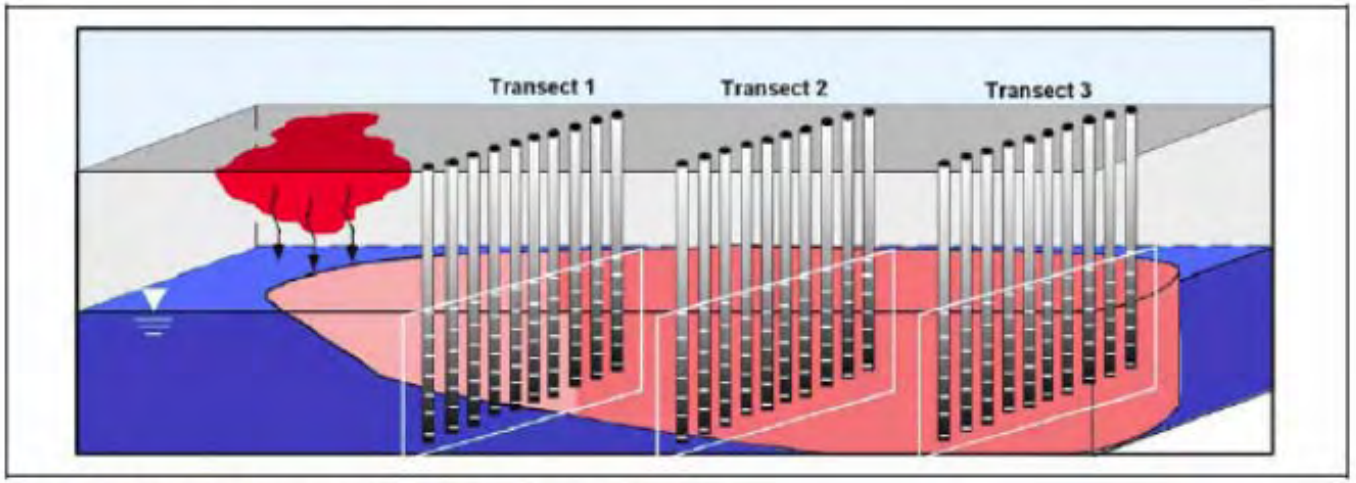


Figure 4. Example Transects through 3-D Plume Delineation

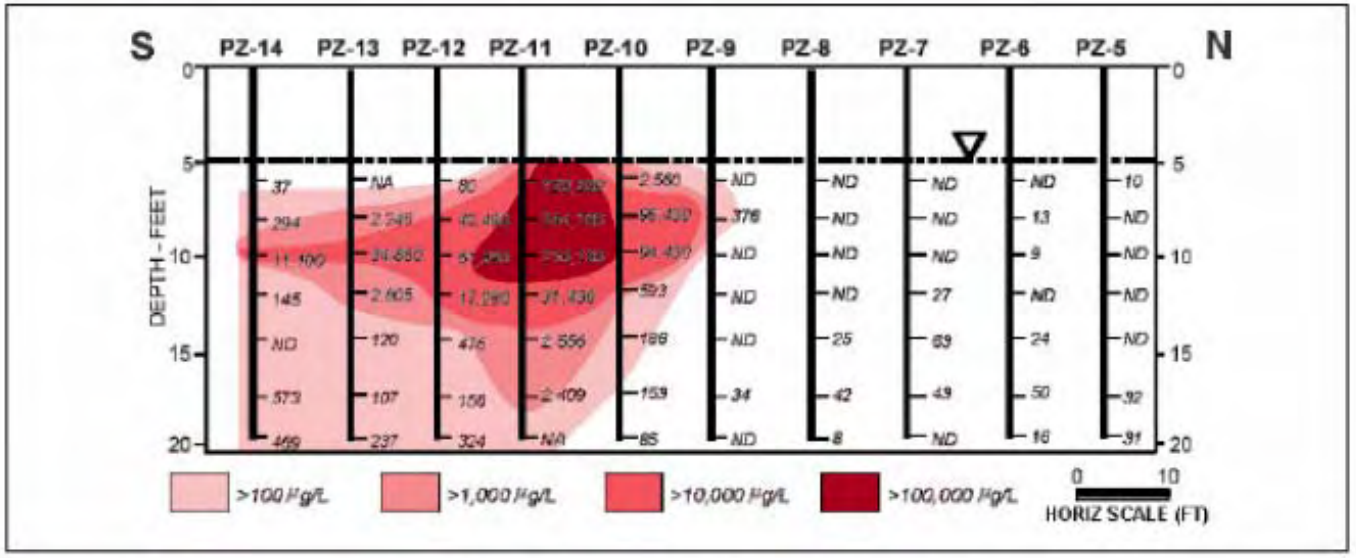
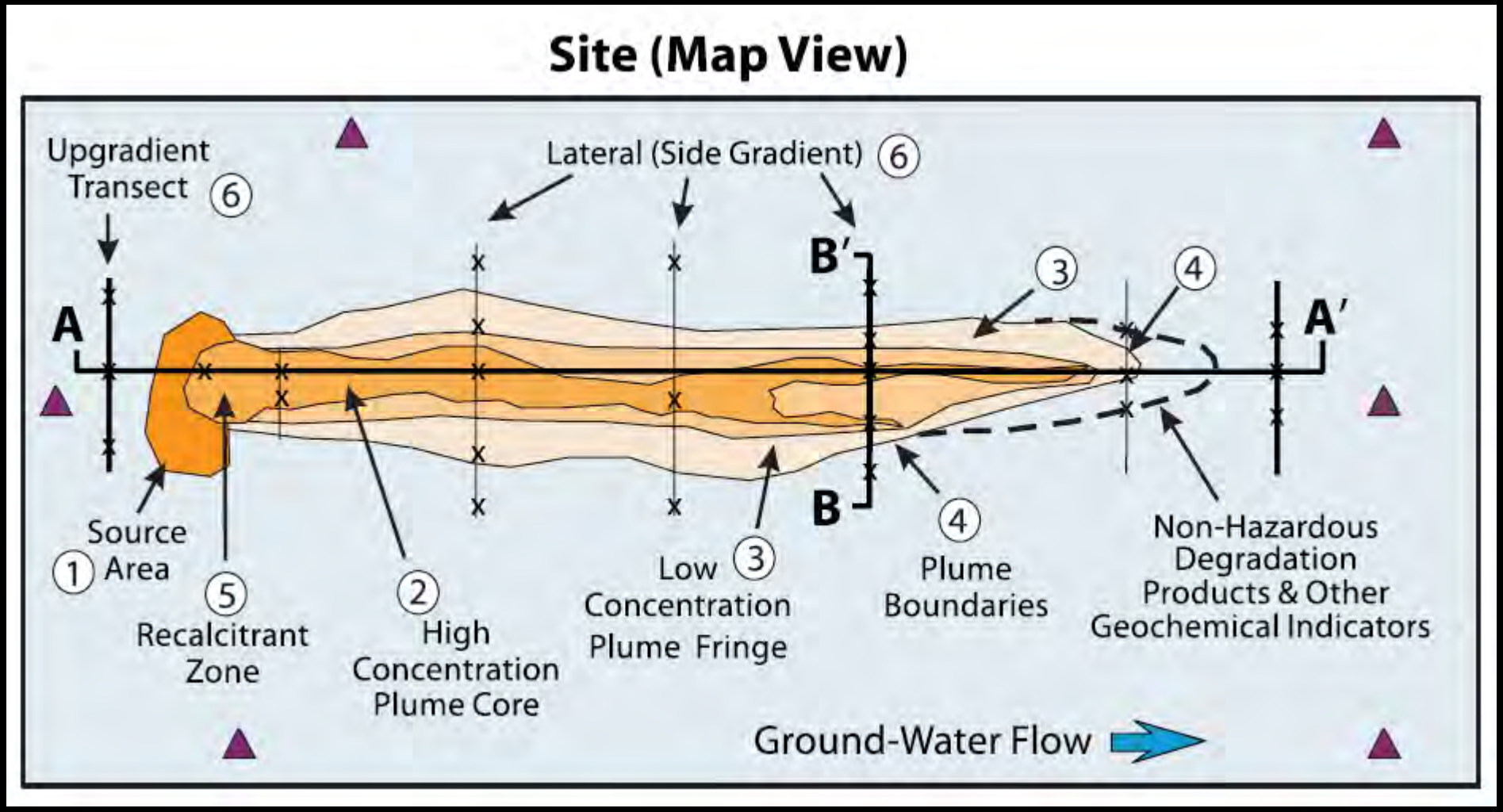
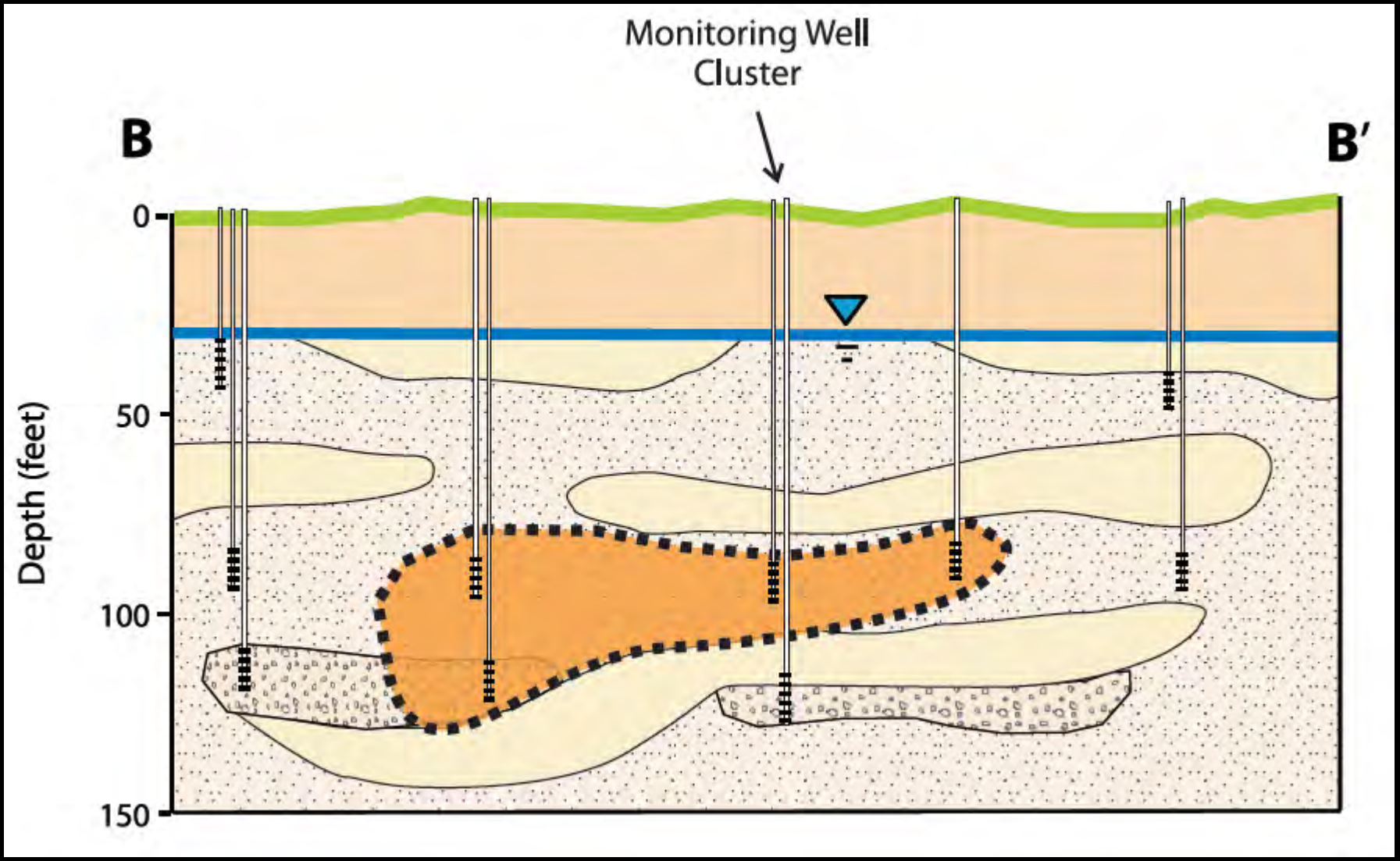


Figure 5. MTBE Concentration Profile for 3-D Transect No. 1 Shown in Figure 4
(Adapted from: Einarson, 2001)



Source: USEPA, 2004. Performance Monitoring of MNA Remedies for VOCs in Groundwater



Source: USEPA, 2004. Performance Monitoring of MNA Remedies for VOCs in Groundwater

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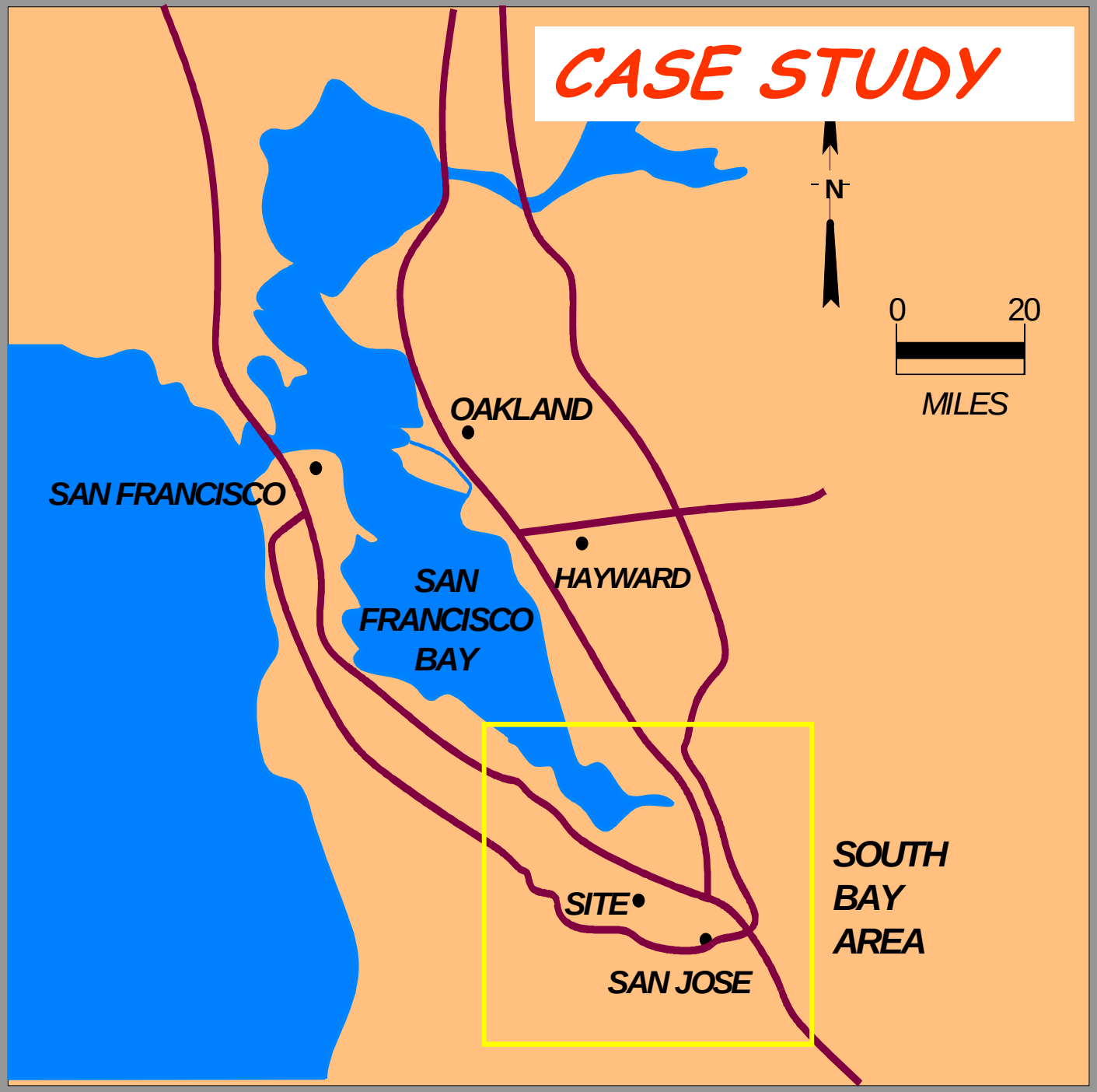
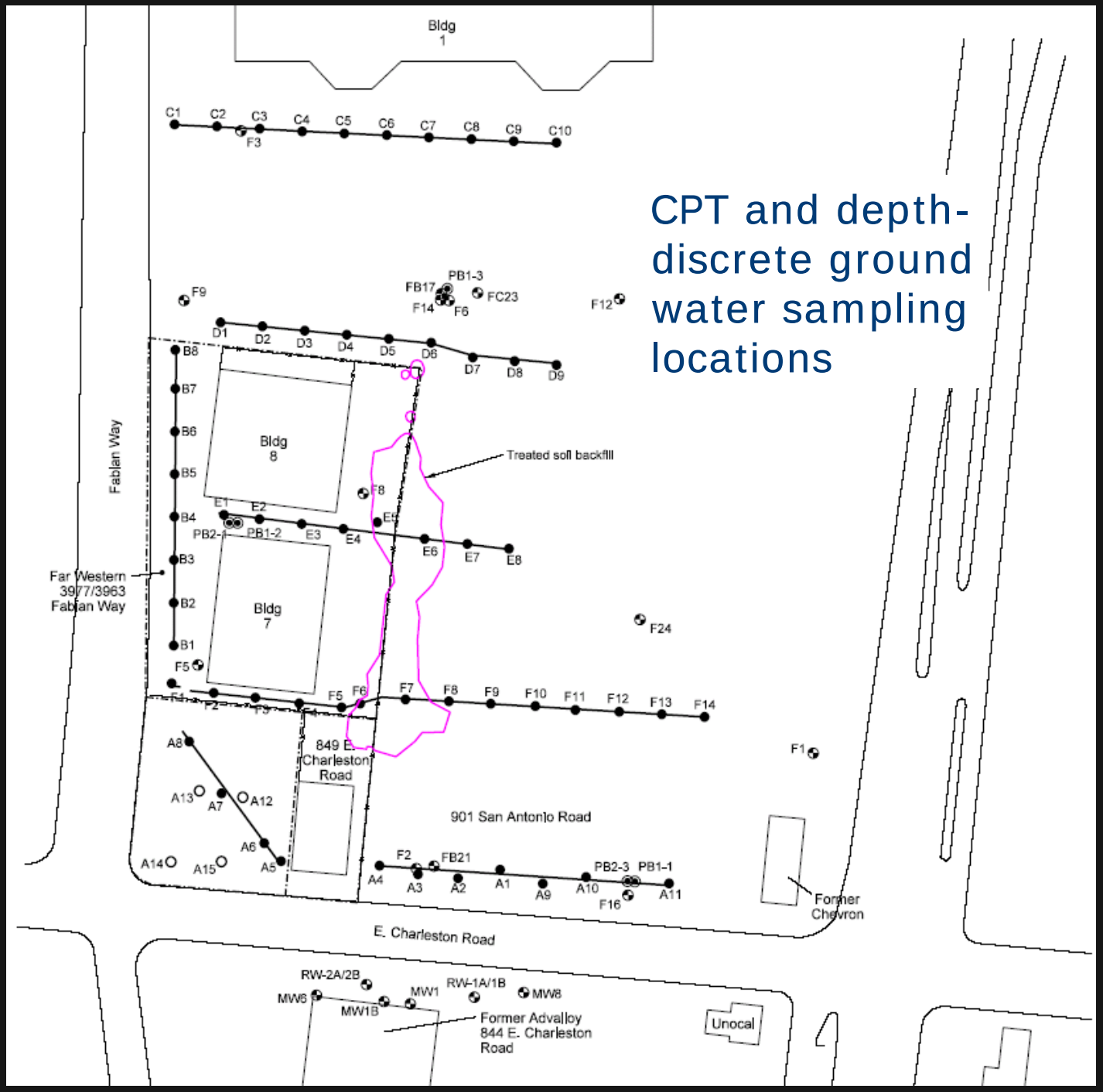
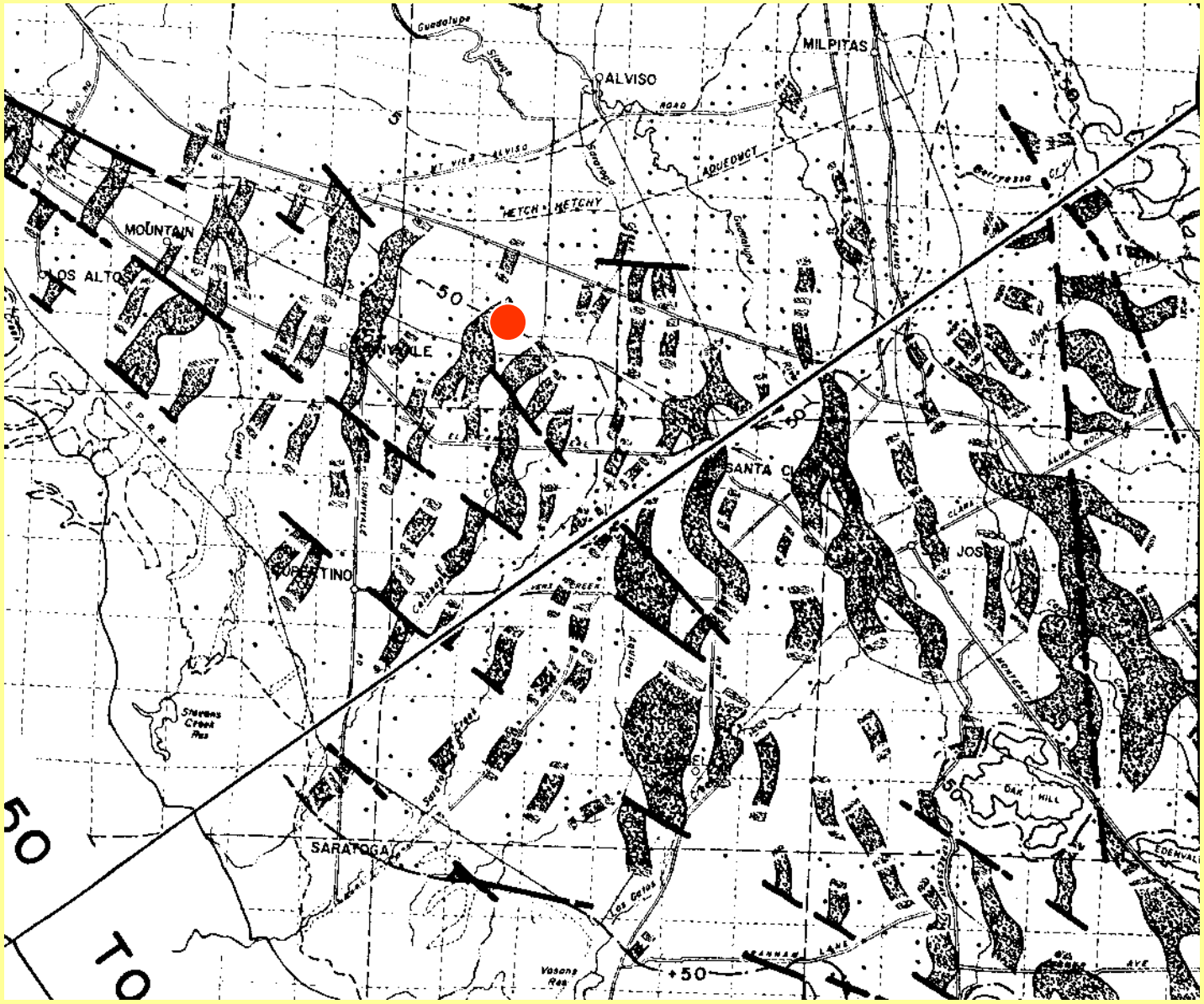
- Contour maps of surfaces that can be contoured; transects of high-resolution data points to characterize linear features (e.g., buried channels, dissolved plumes)
- New site assessment technologies

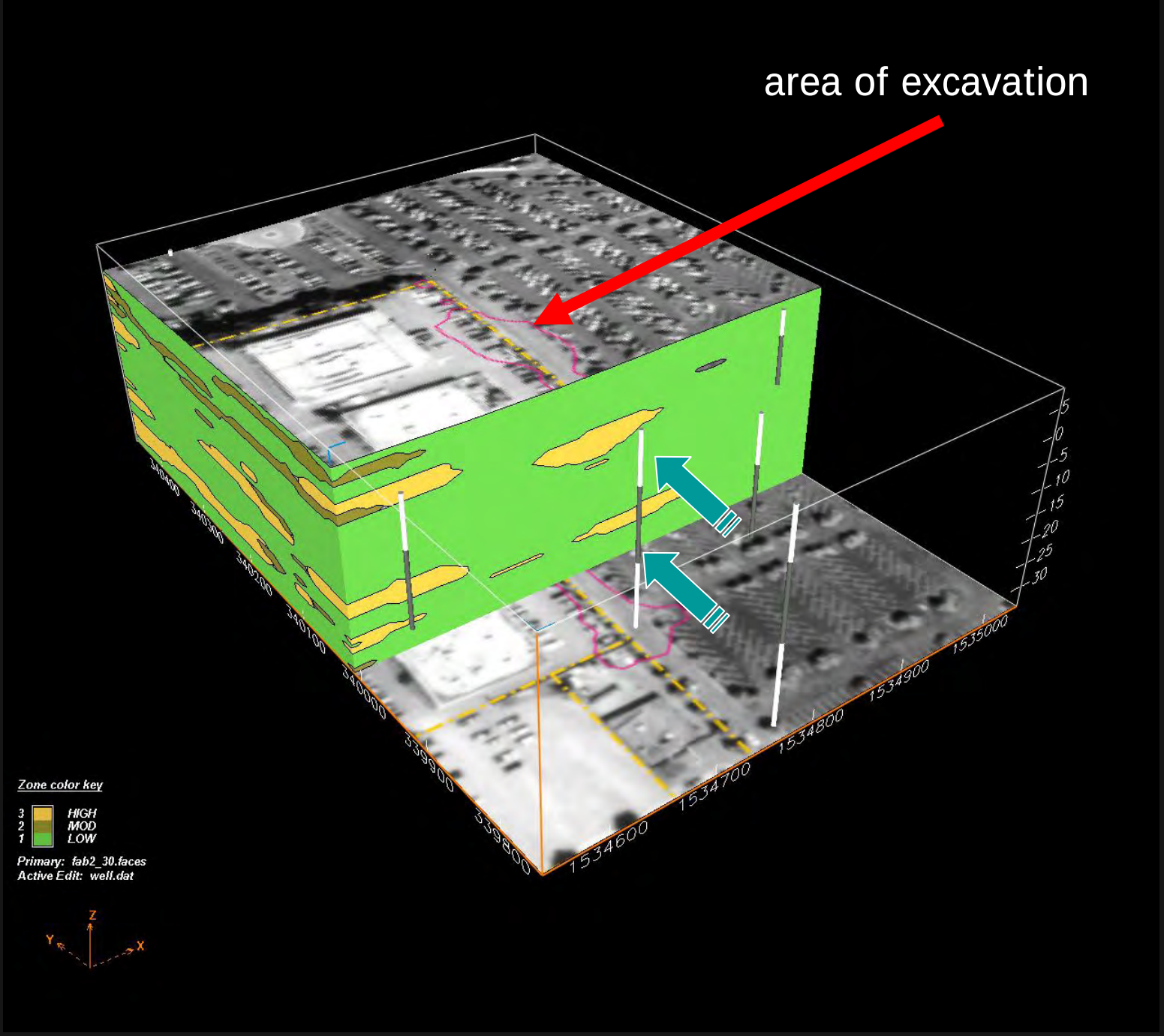

CASE STUDY
N
0
20
MILES
OAKLAND
SAN FRANCISCO
HAYWARD
SAN FRANCISCO BAY
SITE
SAN JOSE
SOUTH BAY AREA

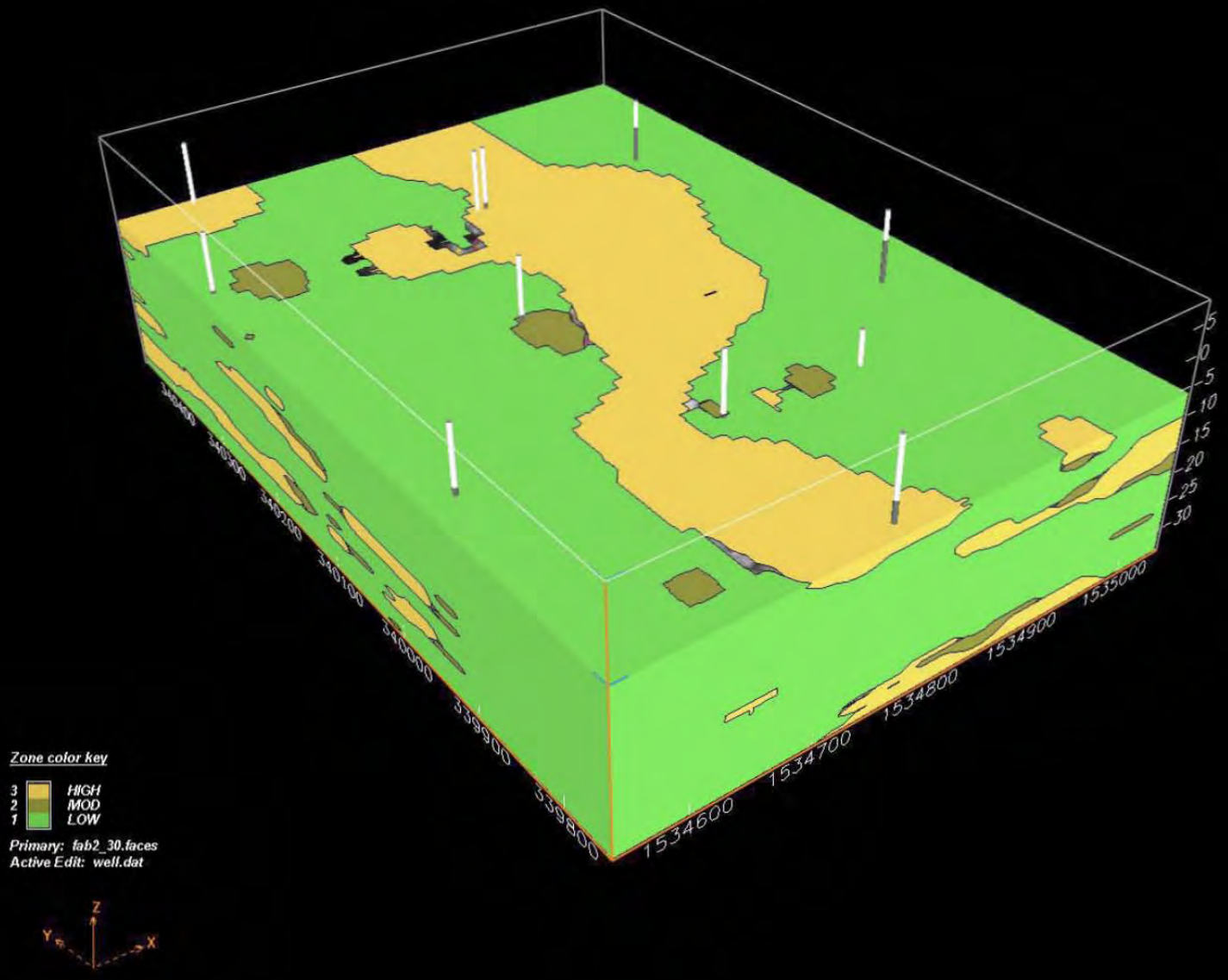
CPT and depth-discrete ground water sampling locations



+50 to 0 Feet MSL




area of excavation
Zone color key
3 HIGH
2 MOD
1 LOW
Primary: fab2_30.faces
Active Edit: well.dat
Z
Y
X
1534600
1534700
1534800
1534900
1535000
339800
339900
340000
340100
340200
340300
340400
5
0
-5
-10
-15
-20
-25
-30


Zone color key
3 HIGH
2 MOD
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Primary: fab2_30.faces
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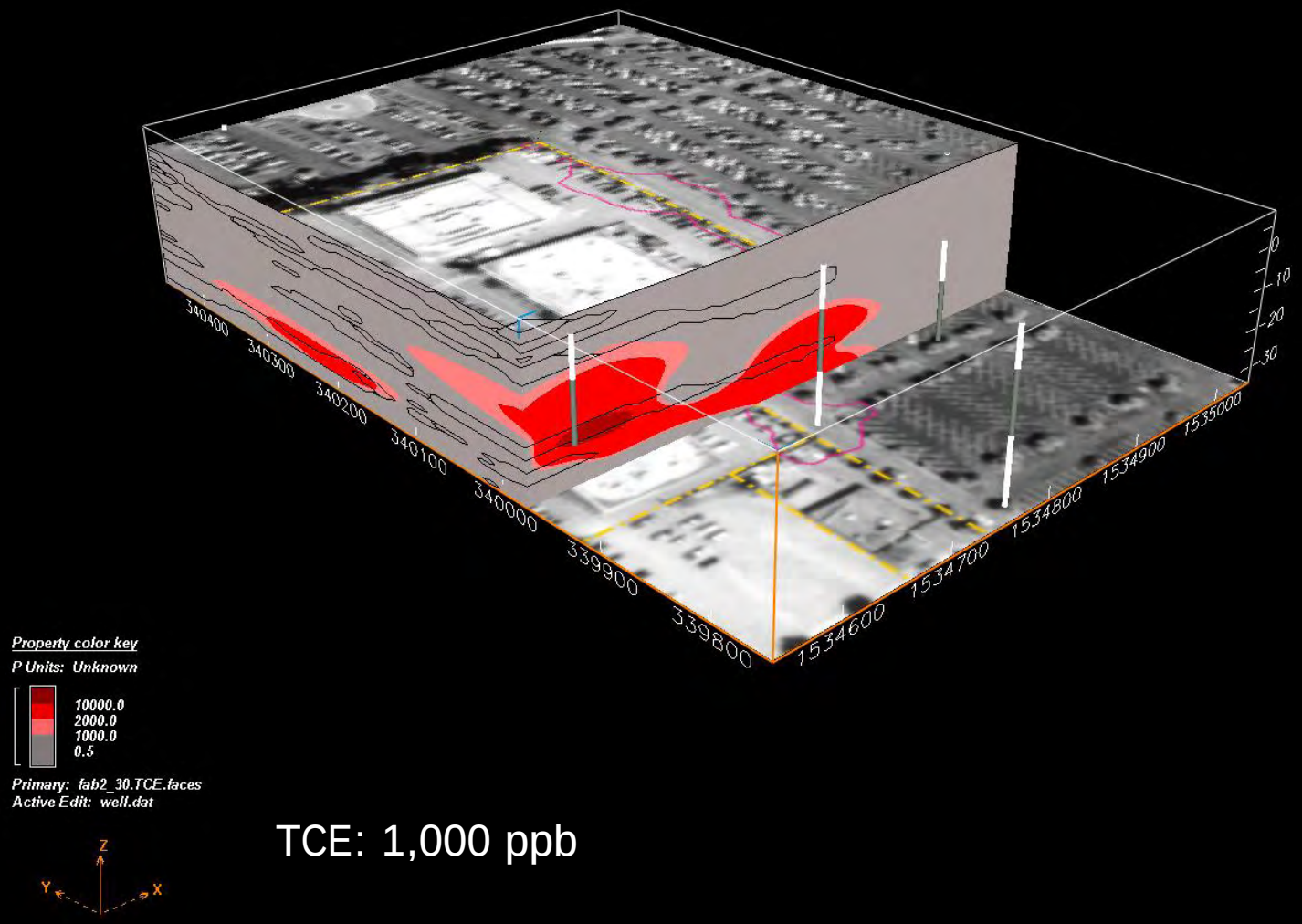
340400
340300
340200
340100
340000
339900
339800
1534600
1534700
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1535000
0
10
20
30
Property color key
P Units: Unknown
10000.0
2000.0
1000.0
0.5
Primary: fab2_30.TCE.faces
Active Edit: well.dat
Z
Y
X

TCE: 1,000 ppb

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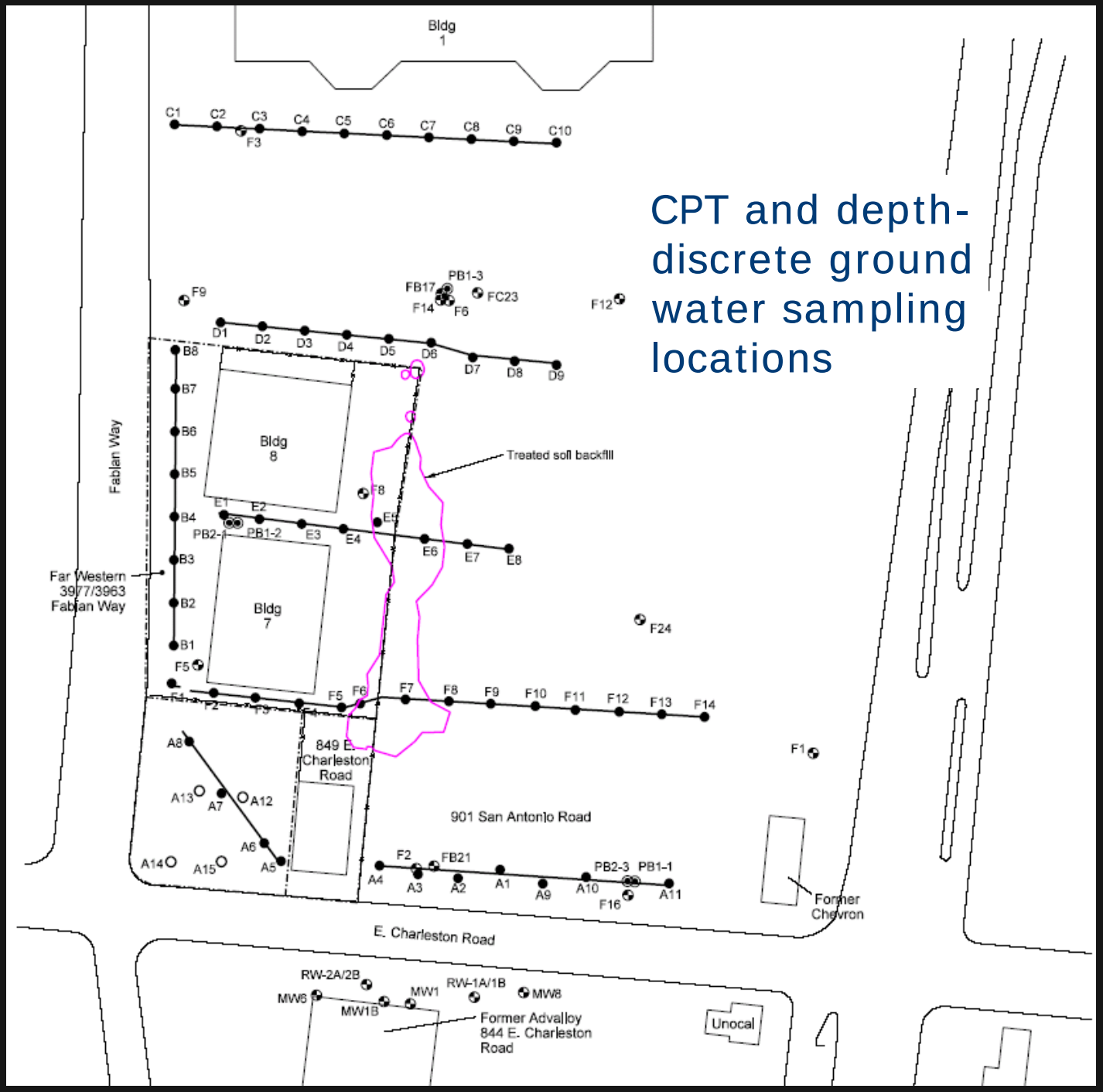
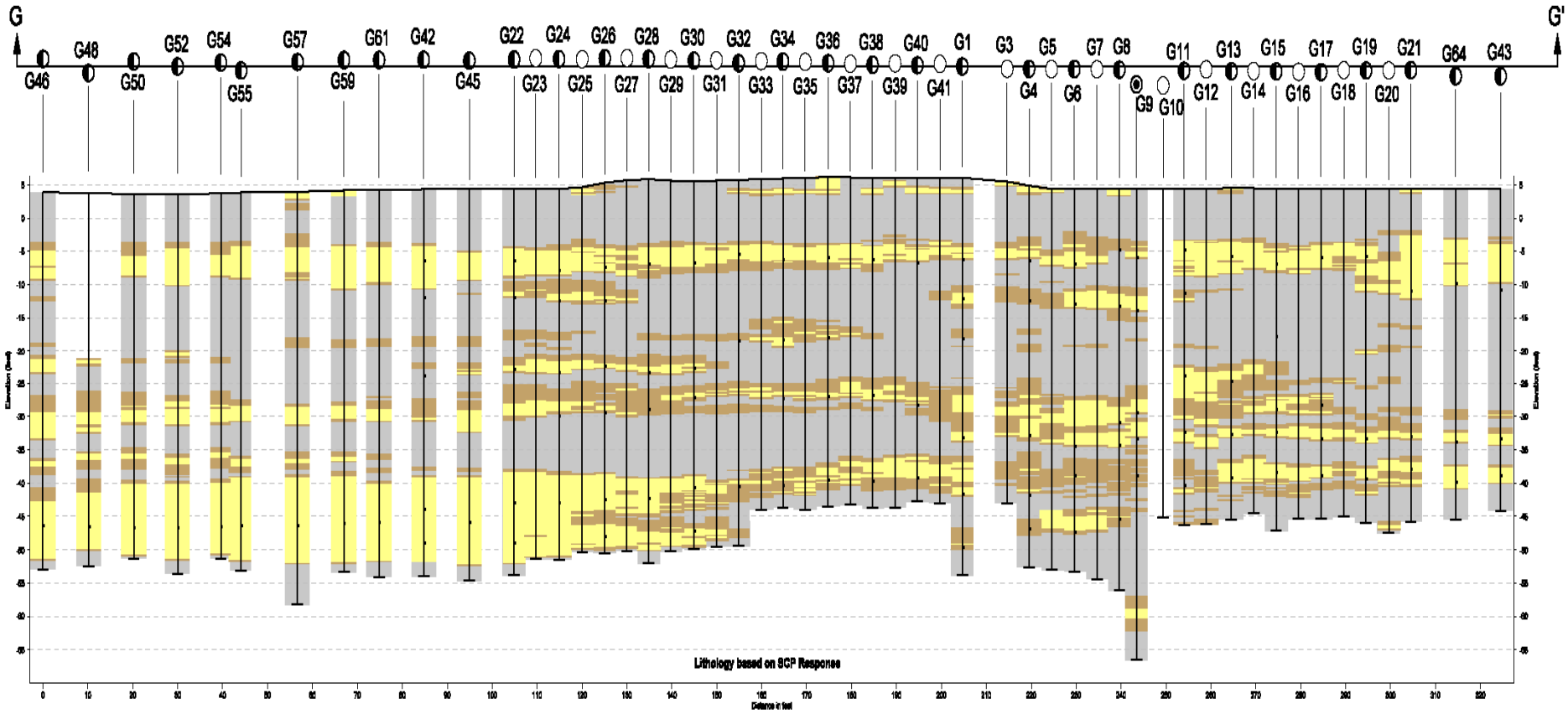
- Voluminous but biased data sets
- Contour maps of surfaces that can be contoured; transects of high-resolution data points to characterize linear features (e.g., buried channels, dissolved plumes)
- New site assessment technologies
- Focus on natural flow system, gradients, geochemistry, etc.

CPT and depth-discrete ground water sampling locations

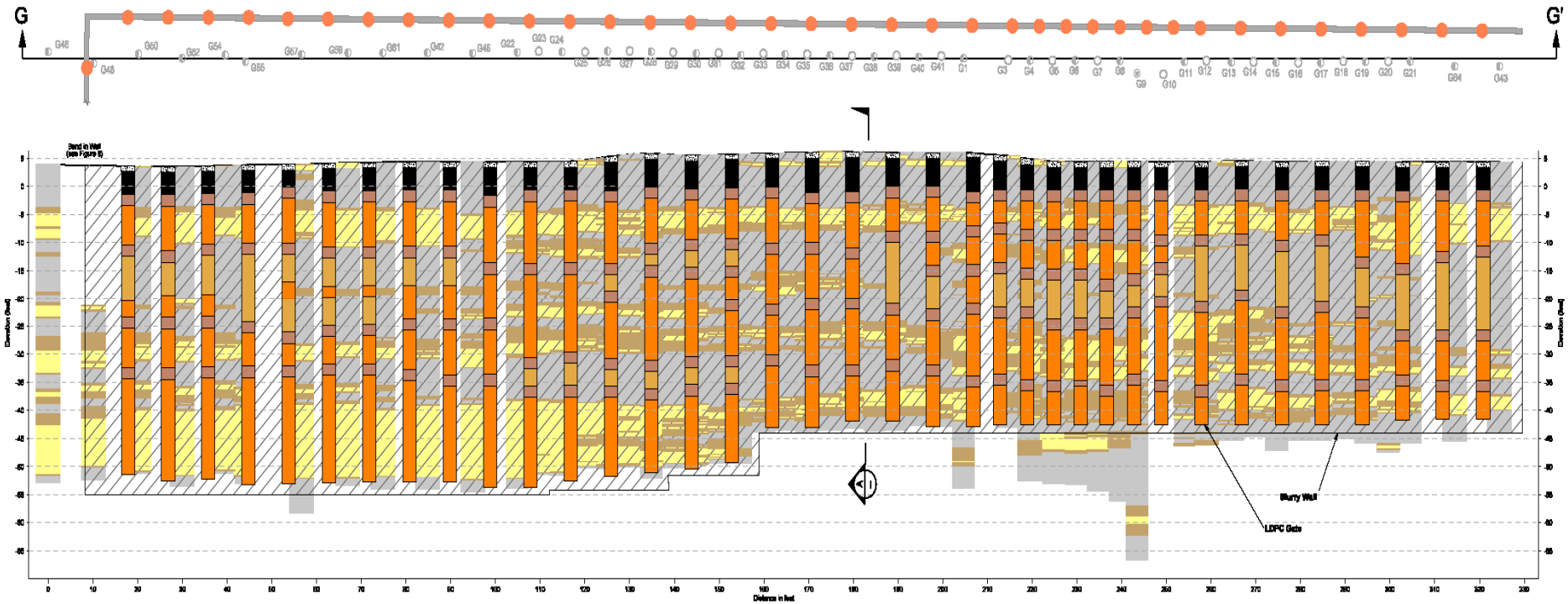


Cross-section Along PRB

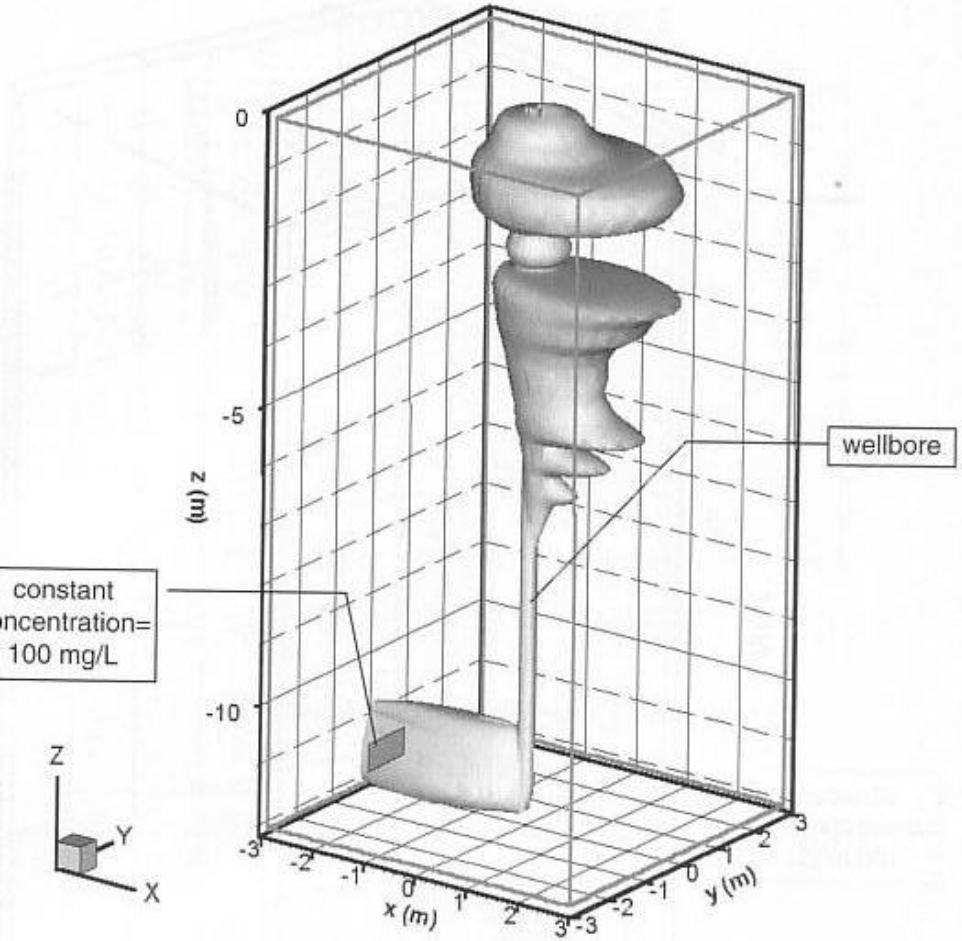


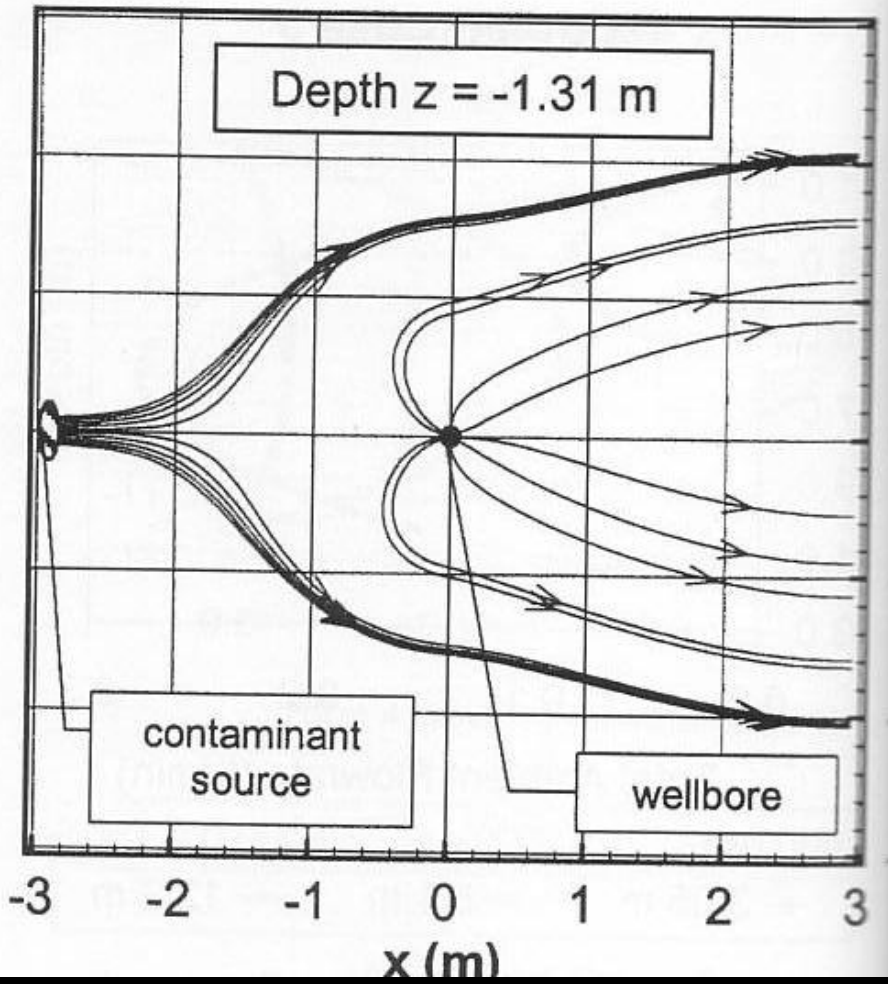
Geomatrix

PRB Design



Geomatrix


wellbore
constant
ncentration=
100 mg/L
z (m)
x (m)
y (m)
Z
Y
X


Depth z = -1.31 m
contaminant
source
wellbore
x (m)

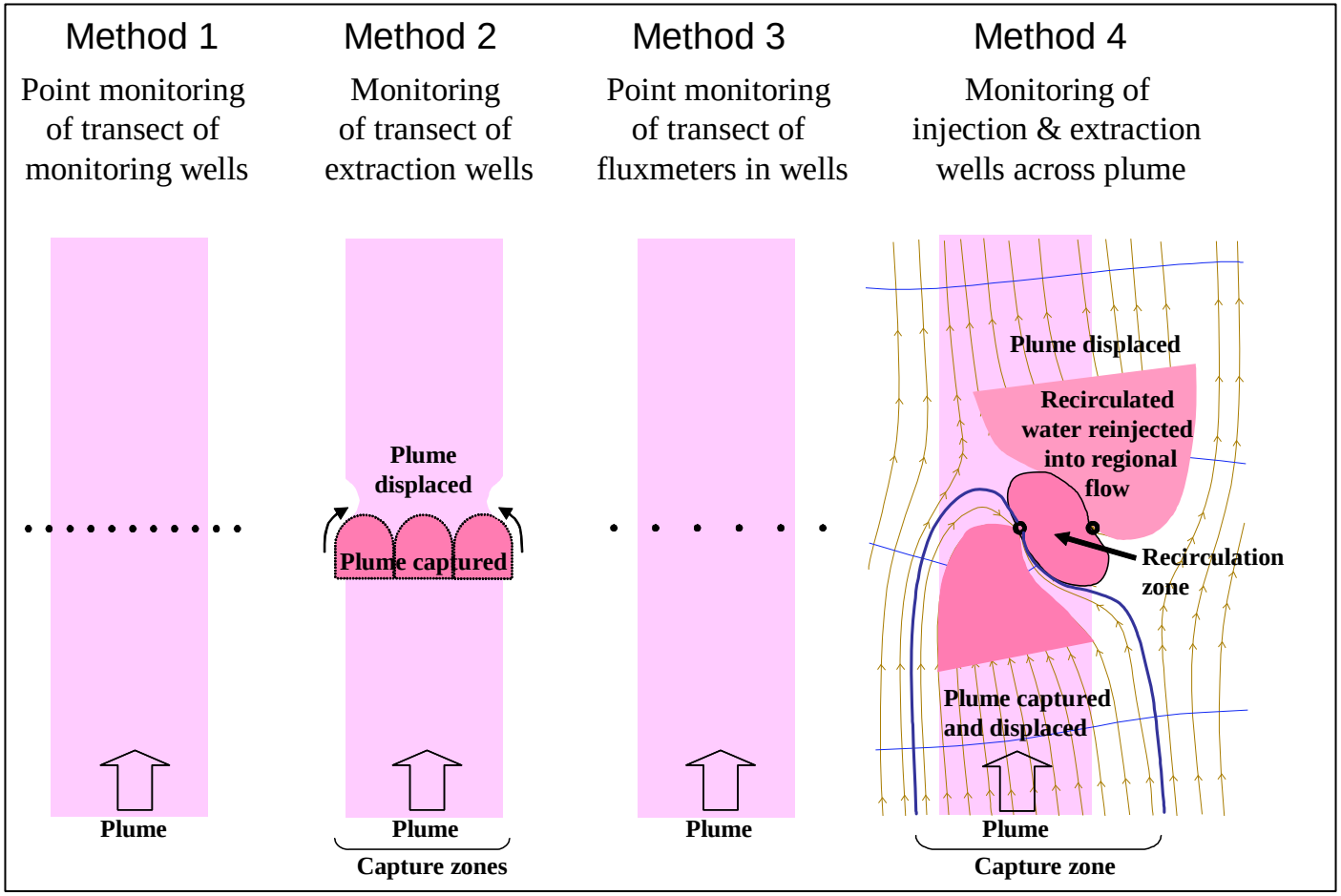
Site Characterization and *Monitoring* in the New Millennium (continued)

1. Process Monitoring
   - CSIA
   - Biotraps
   - Molecular tools
2. Performance Monitoring
   - Reduction in mass discharge

BioTrap™ Sampler (www.microbe.com)

Site Characterization and *Monitoring* in the New Millennium (continued)

1. Process Monitoring
   - CSIA
   - Biotraps
   - Molecular tools

2. Performance Monitoring
   - Reduction in mass discharge

Comparision of Approaches Underway at Vandenberg Air Force Base in California (Doug Mackay, UC Davis, Principal Investigator; Overall project Principal Investigator: Mike Kavanaugh, Malcolm Pirnie.)