Dissolved Phase Stability Assessment of Benzene at a Downstream Petroleum Facility: A Case Study

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Agenda

1 What is a stability assessment, importance and information needed?

2 What we did (and why).

3 Results & take away lessons!

1 What is a stability assessment?

"Stability does not imply lack of change, but rather change and variability within predictable and manageable limits over time frames of regulatory interest" [1]"

<u>Objective:</u>
Demonstrate that dissolved phase of the contaminant plume is <u>stable</u> and <u>manageable</u> with conventional remediation techniques.

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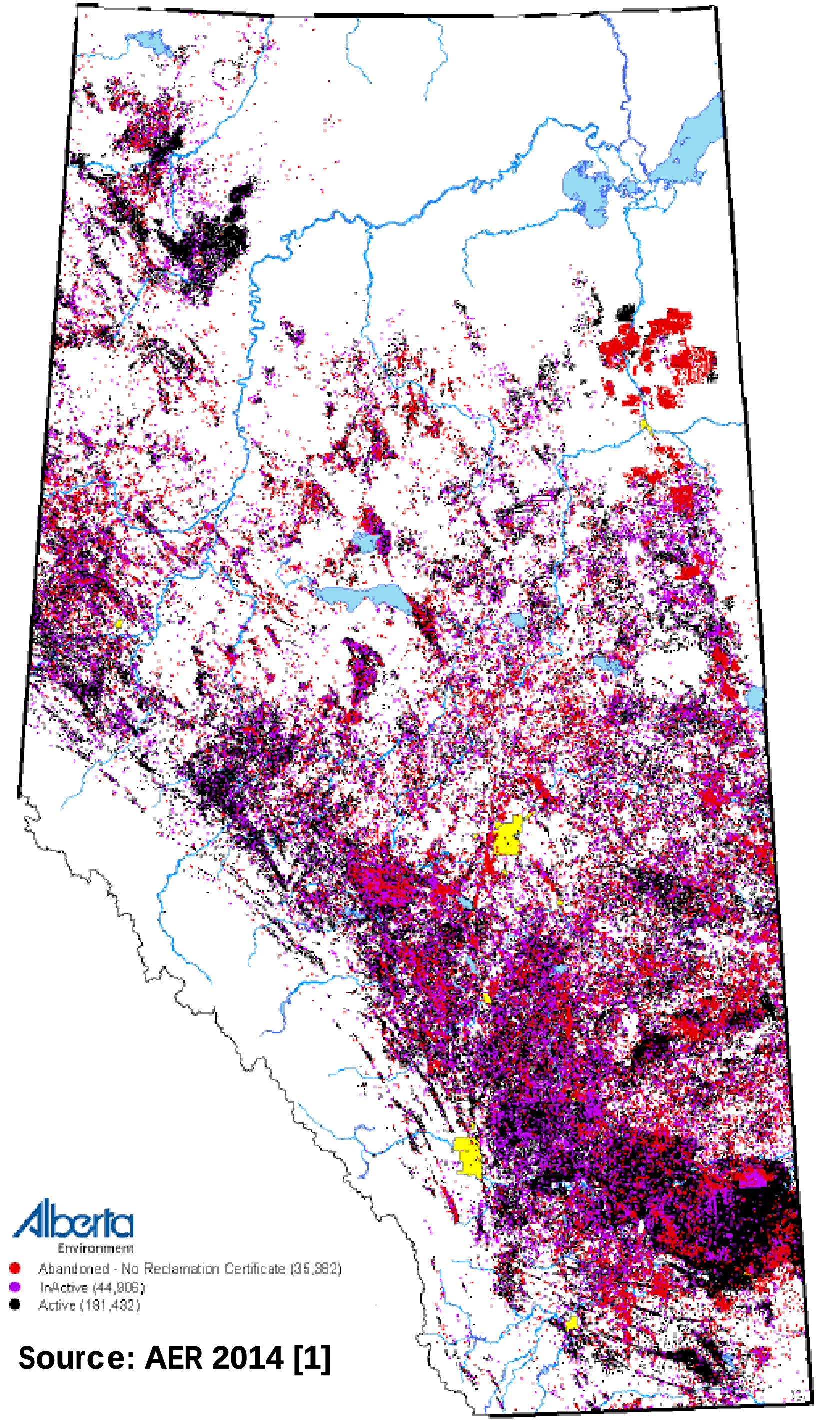
Why is Stability Assessment Important?

>50,000
abandoned wellsites[2]
+
>10,000
brownfield sites[3]
x
$100,000 / site
=
A $6 BILLION DOLLAR CHALLENGE FOR SOCIETY



Source: AER 2014 [1]

1

What you need to conduct a stability assessment?

<u>Contaminant Info:</u> What it is, Where it came from, Where it is, and Where it is likely going

<u>Hydrogeology:</u> Aquifer Properties, Hydraulic Gradients (lateral and vertical)

<u>Modeling Data*</u>
Soil information (stratification, organic carbon, bulk density, source concentration, plume dimensions, nutrient bioavailability, and natural attenuation by-products)

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2 What we did (and why).

“Begin at the beginning,“ the King said, very gravely, “and go on till you come to the end: then stop.”

- Lewis Carroll, *Alice in Wonderland*

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2 Contaminant Info

What it is

Diesel & Weathered Gasoline

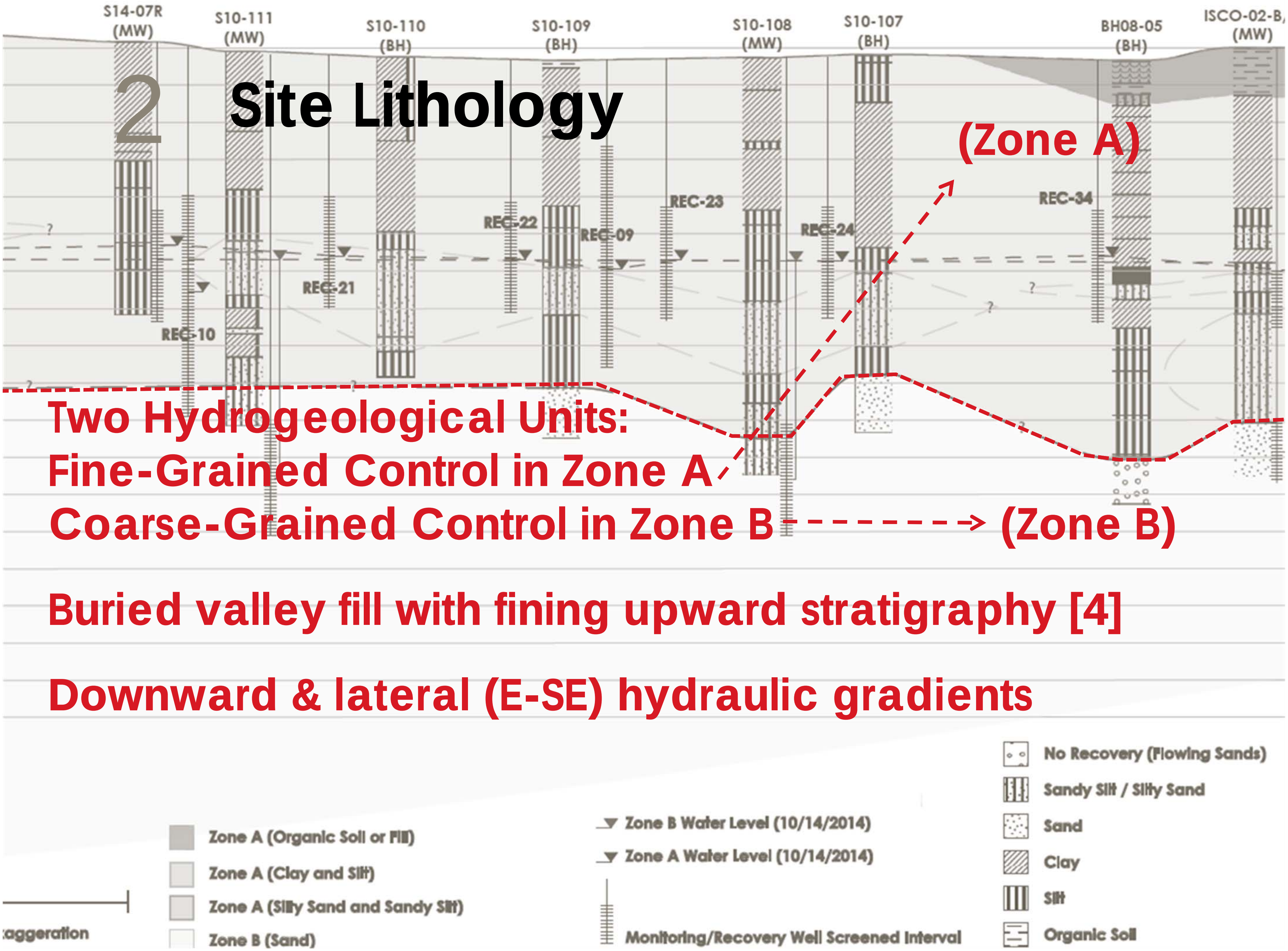
Where it came from

Top Down Impacts, Primarily Gasoline

Downward vertical migration through silty clays, followed by lateral migration through lower, higher permeability units

Possible exacerbation due to long screen wells & total fluid recovery (2000-2008)

2 Site Lithology



Two Hydrogeological Units:

Fine-Grained Control in Zone A

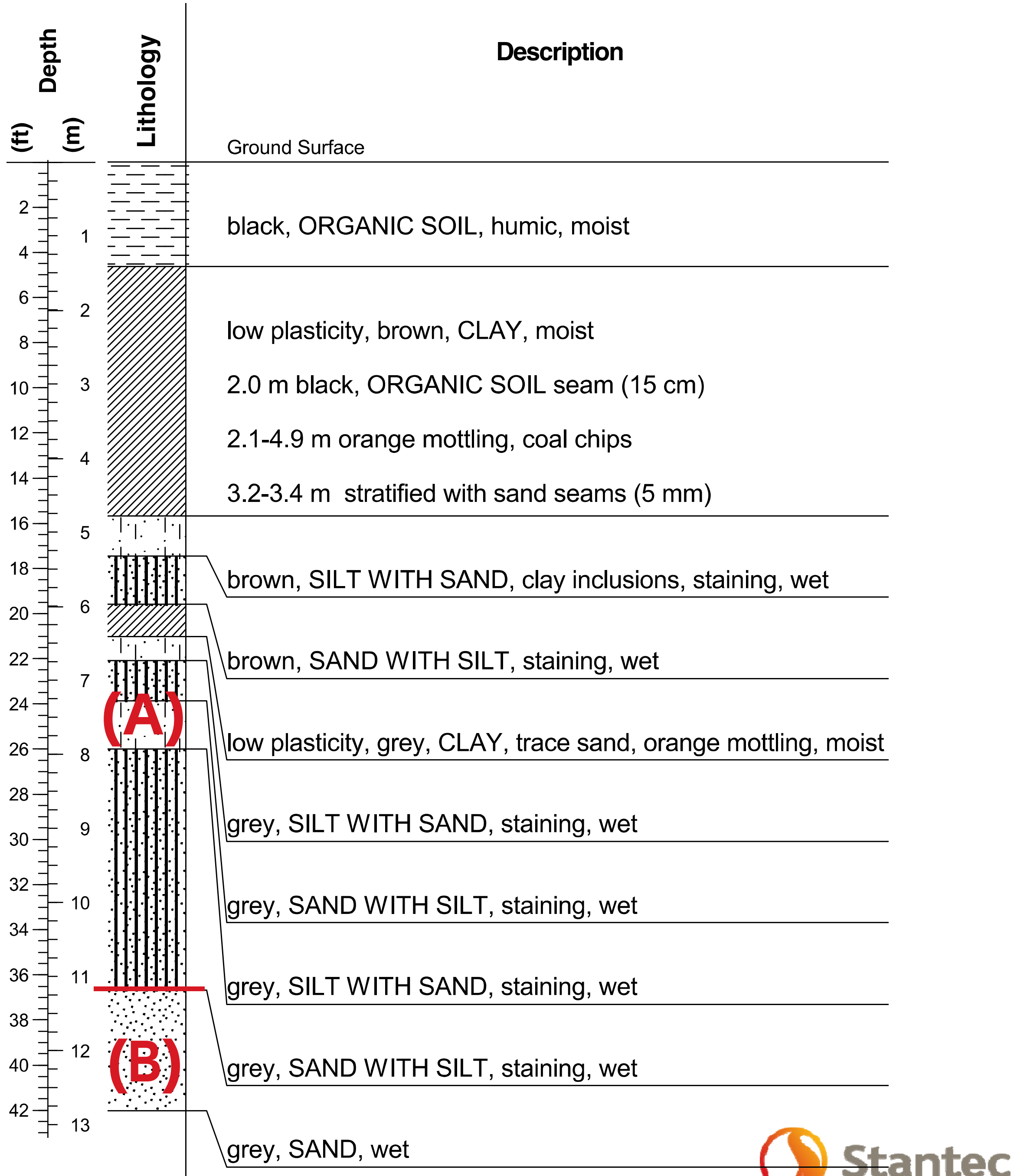
Coarse-Grained Control in Zone B

Buried valley fill with fining upward stratigraphy [4]

Downward & lateral (E-SE) hydraulic gradients


80
90
7 m


10
20


Depth
(ft)
(m)
Lithology
Description
Ground Surface
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
1
2
3
4
5
6
7
8
9
10
11
12
13
black, ORGANIC SOIL, humic, moist
low plasticity, brown, CLAY, moist
2.0 m black, ORGANIC SOIL seam (15 cm)
2.1-4.9 m orange mottling, coal chips
3.2-3.4 m stratified with sand seams (5 mm)
brown, SILT WITH SAND, clay inclusions, staining, wet
brown, SAND WITH SILT, staining, wet
low plasticity, grey, CLAY, trace sand, orange mottling, moist
grey, SILT WITH SAND, staining, wet
grey, SAND WITH SILT, staining, wet
grey, SILT WITH SAND, staining, wet
grey, SAND WITH SILT, staining, wet
grey, SAND, wet
(A)
(B)
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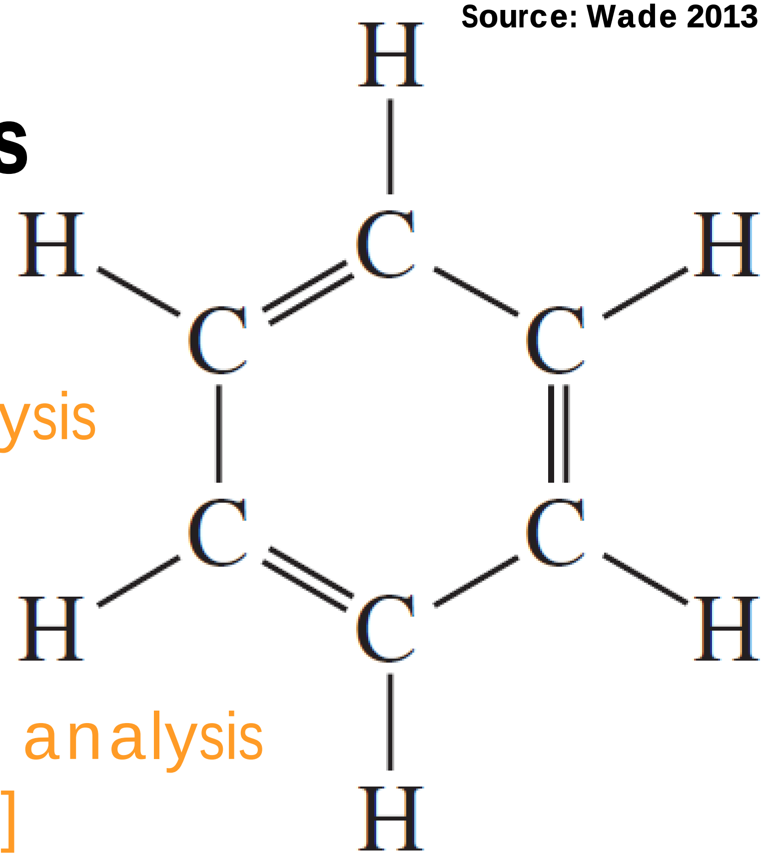
Source: Wade 2013 [5]



2 Analysis Methods

Non-Parametric Analysis:

Mann-Kendall Statistical Analysis using Pro-UCL

Visual Plume Analysis:

Surfer® gridding and volume analysis with Ricker (2008) methods [6]

Groundwater Model:

2-D BIOSCREEN-AT Model

Benzene used as indicator contaminant

2 Mann-Kendall Trend Analysis

Pro UCL® [7] and ERIMS® [8] database used to analyze relative variation (+/-) of data and trends

- Easily applied to "messy data" to provide statistical quantification

- Questionable results if near detection limit concentrations present and seasonality may need to be assessed

x_1	x_2	x_3	x_4	$\cdots$	x_{n-1}	x_n	No. of + Signs	No. of − Signs
	$x_2 - x_1$	$x_3 - x_1$	$x_4 - x_1$	$\cdots$	$x_{n-1} - x_1$	$x_n - x_1$		
		$x_3 - x_2$	$x_4 - x_2$	$\cdots$	$x_{n-1} - x_2$	$x_n - x_2$		
			$x_4 - x_3$	$\cdots$	$x_{n-1} - x_3$	$x_n - x_3$		
				$\ddots$	$\vdots$	$\vdots$		
					$x_{n-1} - x_{n-2}$	$x_n - x_{n-2}$		
						$x_n - x_{n-1}$		

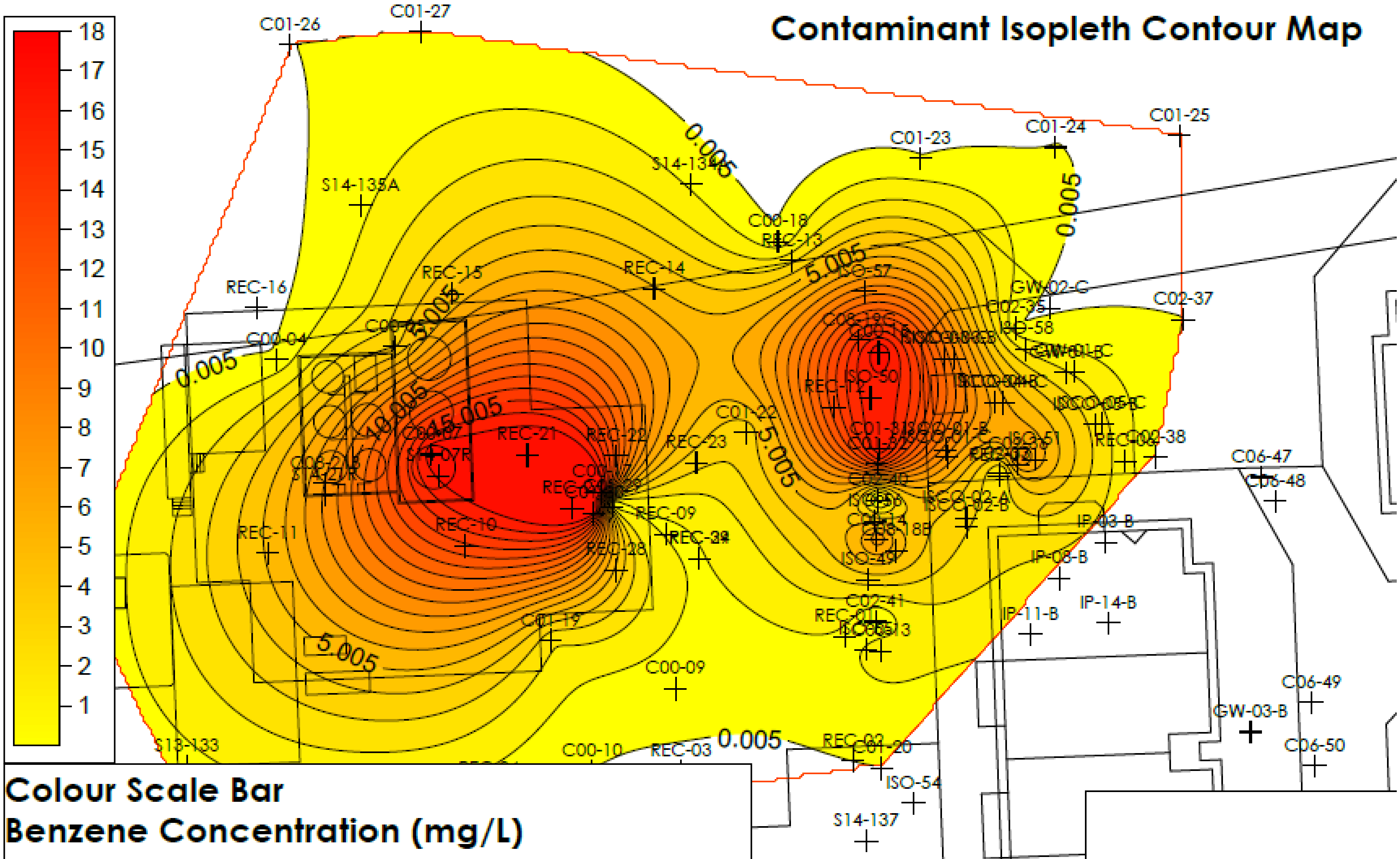
$$S = \begin{pmatrix} \text{sum of} \\ + \text{ signs} \end{pmatrix} + \begin{pmatrix} \text{sum of} \\ - \text{ signs} \end{pmatrix}$$

Source: Gilbert 1987 [9]


95%
Statistically Significant
Confidence Interval

2 Visual Plume Analysis Methods

Contaminant Isopleth Contour Map



Colour Scale Bar
Benzene Concentration (mg/L)

*LNAPL observations assigned a value of 17.8 mg/L (1% of the benzene solubility limit)

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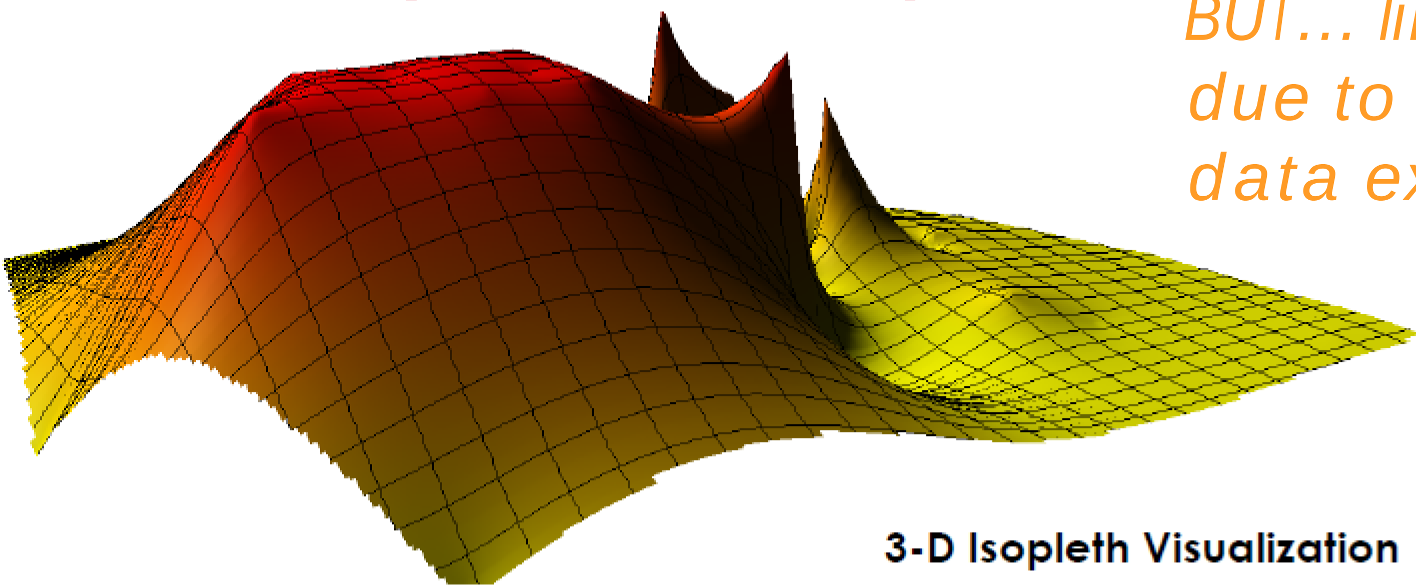
2 Visual Plume Analysis Methods

$$Plume\ mass(kg) = A[L^2] \times C_o \left[\frac{M}{V}\right] \times t\ [L] \times n_e \left[\frac{V}{V}\right]$$

where:
- A = positive planar area (m^2)
- C_o = mean benzene concentration (zeroth moment) (mg/L)
- t = mean aquifer thickness of Zone A (m)
- n_e = effective porosity of Zone A (unitless)

Calculated positive plume area, positive volume, centre of mass (first moment), and representative plume mass (zeroth moment)

BUT… limitations due to real world data exist.



3-D Isopleth Visualization

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2 BIOSCREEN-AT Methods

BIOSCREEN was used to answer three questions:

1. How far will the plume migrate if we stop work?
2. How long will the plume persist?
3. Is natural attenuation stabilizing the plume?

One model for each zone, using default (non-calibrated) inputs and a calibrate scenario to replicate field observations.

No-Decay, First-Order Decay,
& Instantaneous Reaction Models

2 Models (Zone A/Zone B)

3 Results & take away lessons!

“If there’s a way to do it better... Find it"

- Thomas Edison

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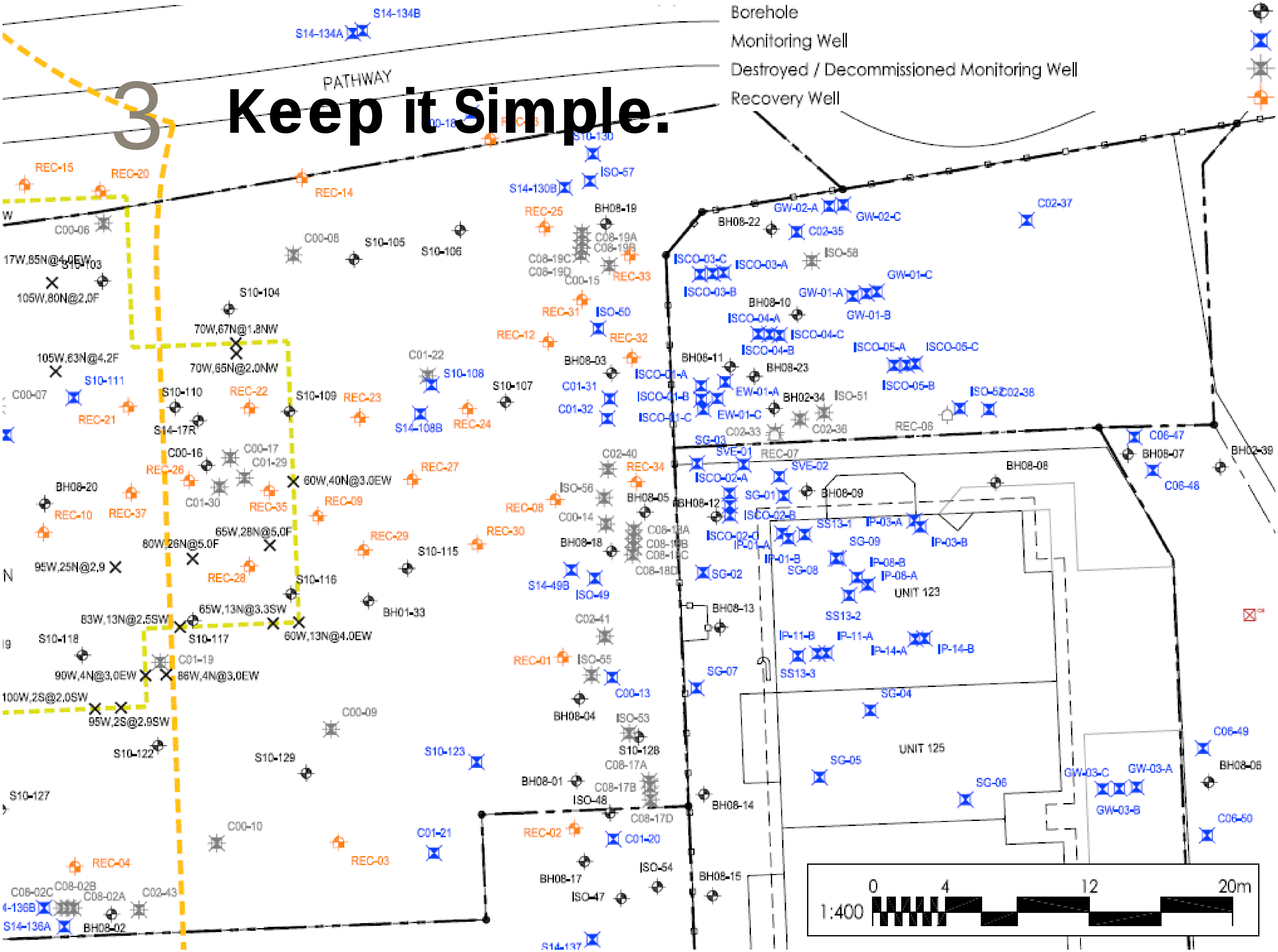
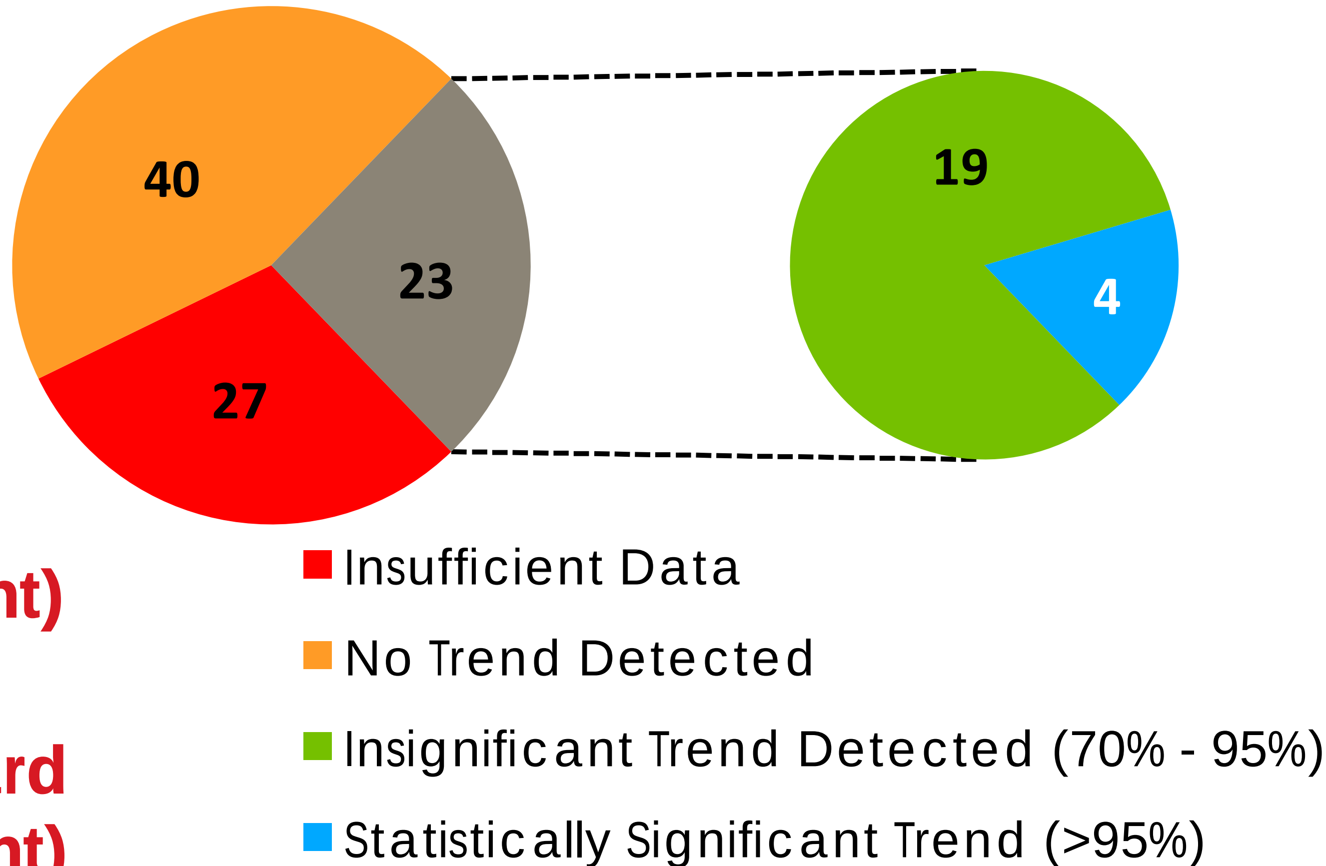
3 Keep it Simple.



3 Mann-Kendall Results

90 Monitoring Wells Analyzed



4 Upward (1 Significant)

19 Downward (3 Significant)

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3 Mann-Kendall Results

Well #1	
09-11-15	**3.67**
09-12-09	**0.366**
10-05-26	**0.0264**
13-08-13	<0.0005
14-06-18	**0.305**
14-07-21	0.0011
14-10-17	0.0007

Mann-Kendall Test

Test Value (S)	-15
Tabulated p-value	0.015
Standard Deviation of S	6.658
Standardized Value of S	-2.103
Approximate p-value	0.0177

98.5%

Well #2	
09-12-09	0.0006
10-05-26	< 0.0005
12-09-26	0.0008
13-08-14	< 0.0005
14-06-18	**0.351**
14-07-17	< 0.0005
14-07-21	< 0.0005
14-10-16	< 0.0005

Mann-Kendall Test

Test Value (S)	10
Tabulated p-value	0.138
Standard Deviation of S	6.976
Standardized Value of S	1.29
Approximate p-value	0.0985

86.2%

Well #1 statistically significant decreasing trend
Well #2 is *nearly* statistically significant increasing trend due to one impulse

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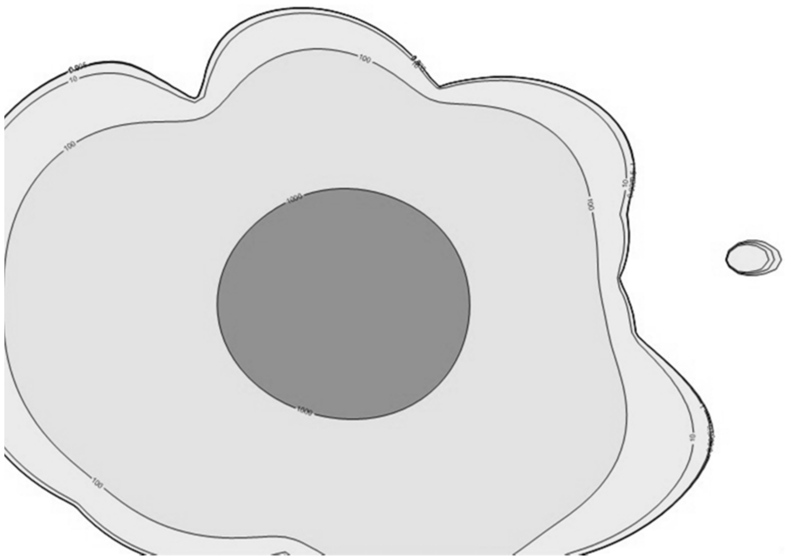
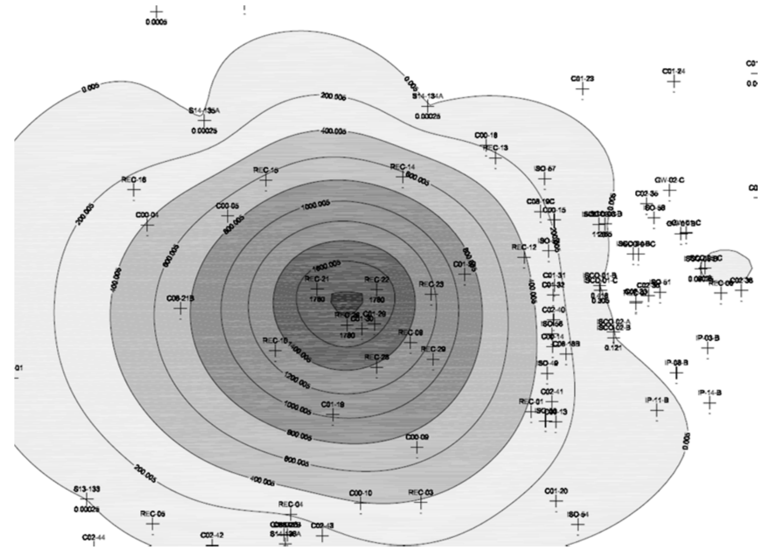
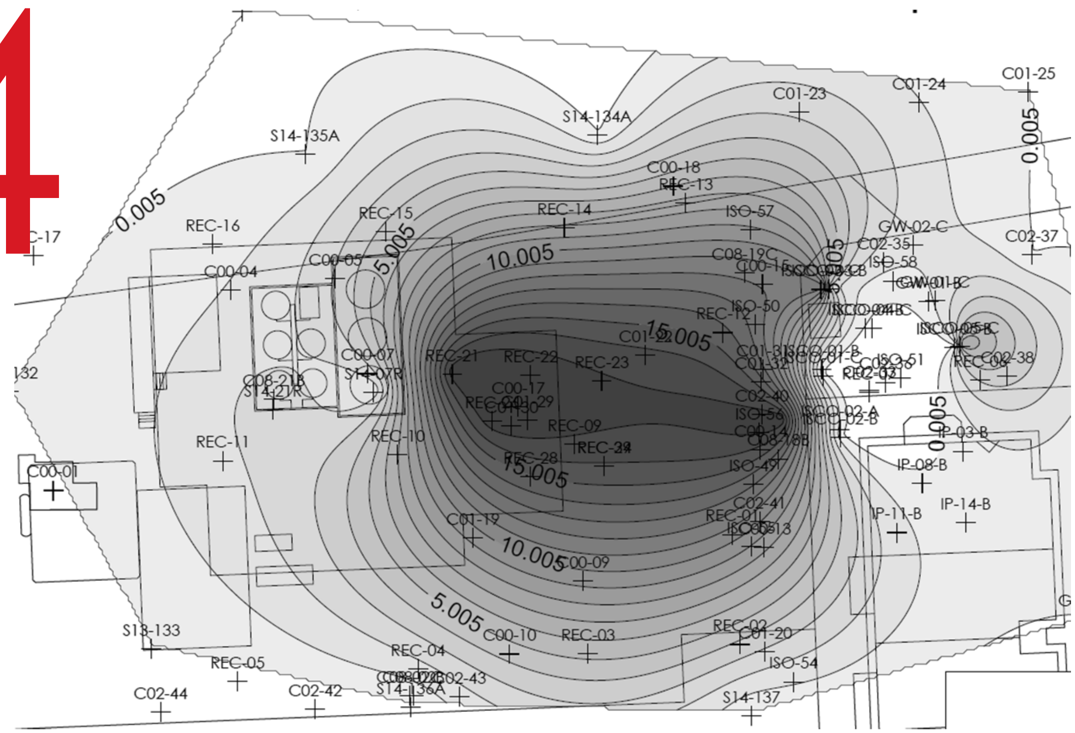


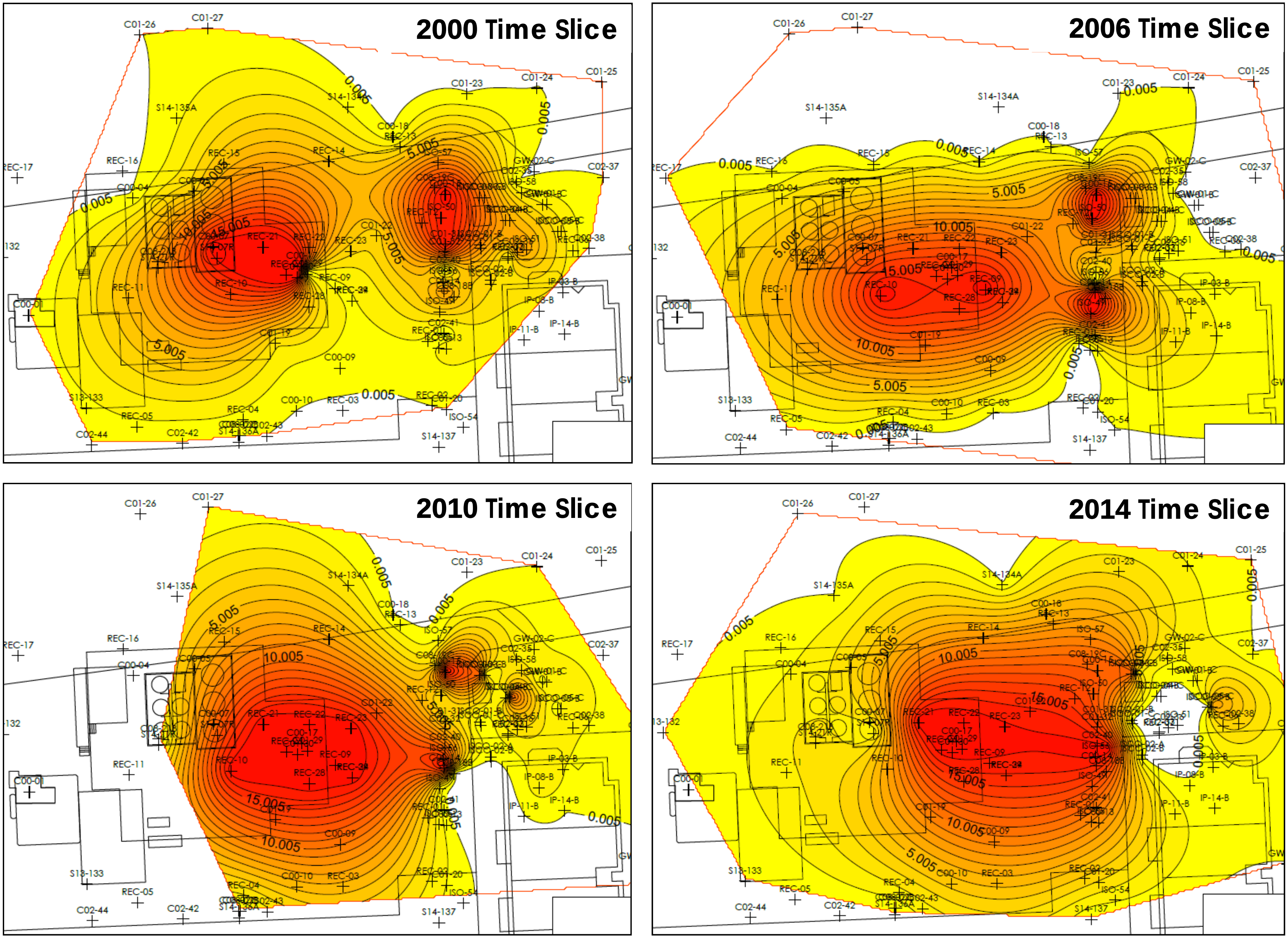


2014

Same Data...

Three Results




2000 Time Slice
2006 Time Slice
2010 Time Slice
2014 Time Slice

3 Visual Plume Analysis Results

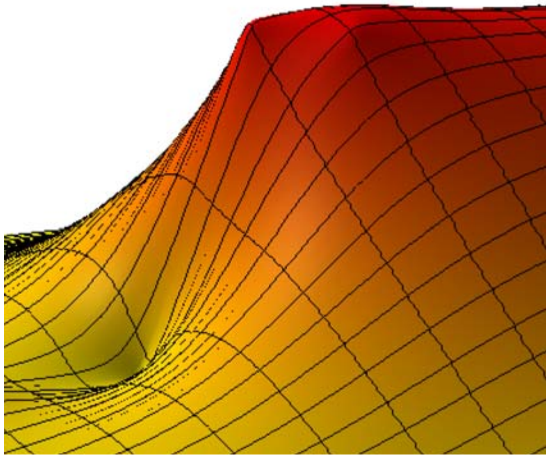
Main Results:

Plume area increased 50%

Benzene concentration variable, but stable

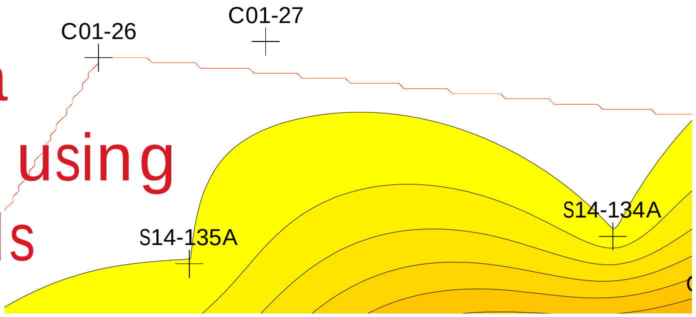
Average plume mass increased 25%

Centre of mass generally stable,
moving 5 m east and 1m south in 14 years



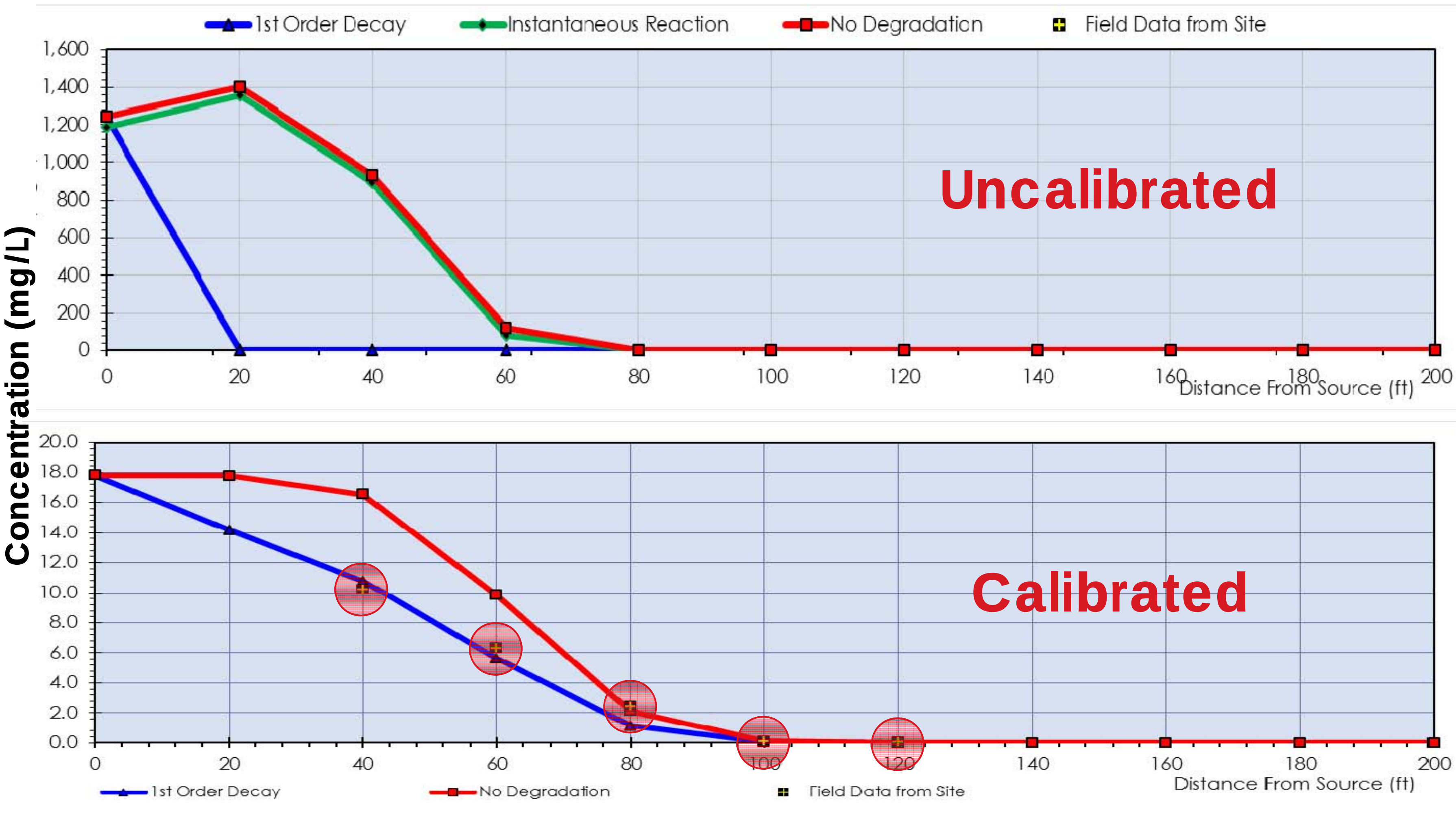
Mass calculated
using grid mesh

Plume area
calculated using
zero bounds



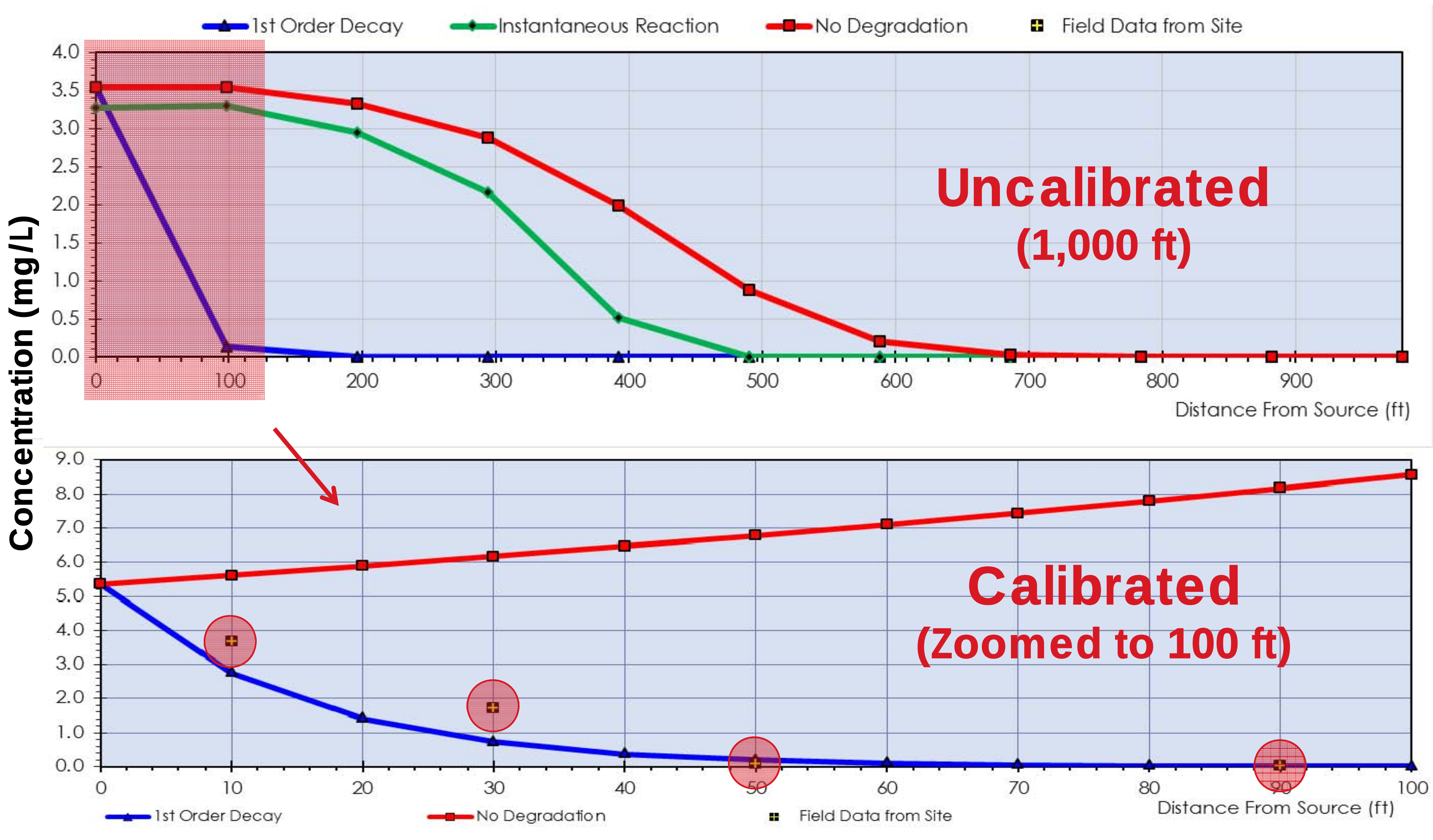
3 BIOSCREEN-AT Zone A Results

(Year 30)



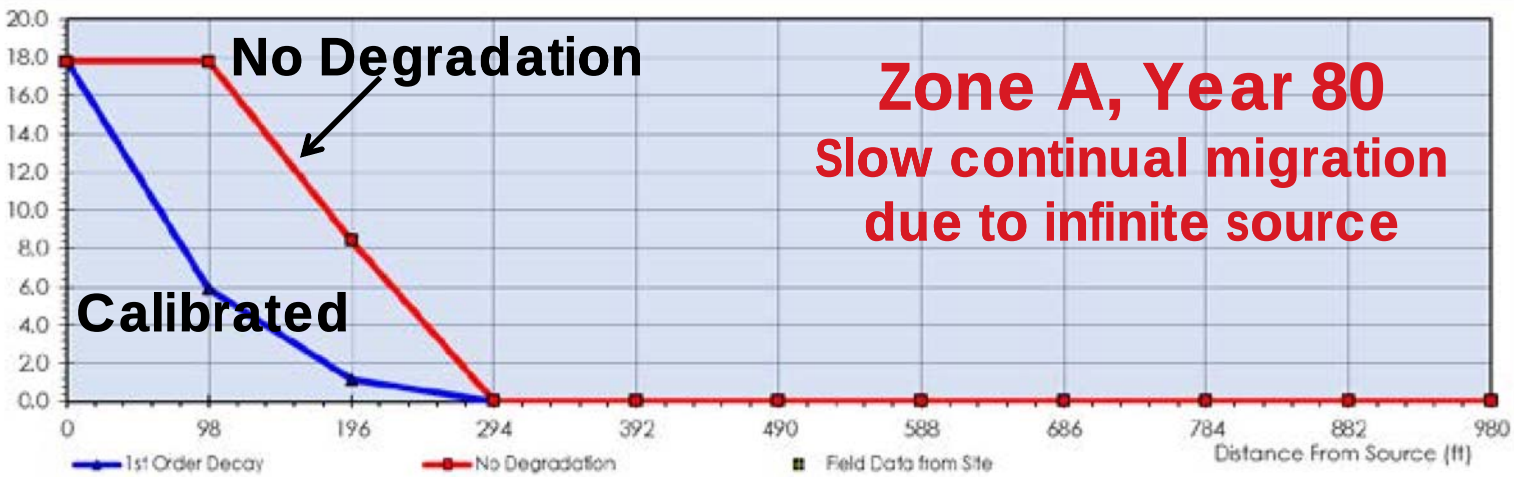
3 BIOSCREEN-AT Zone B Results

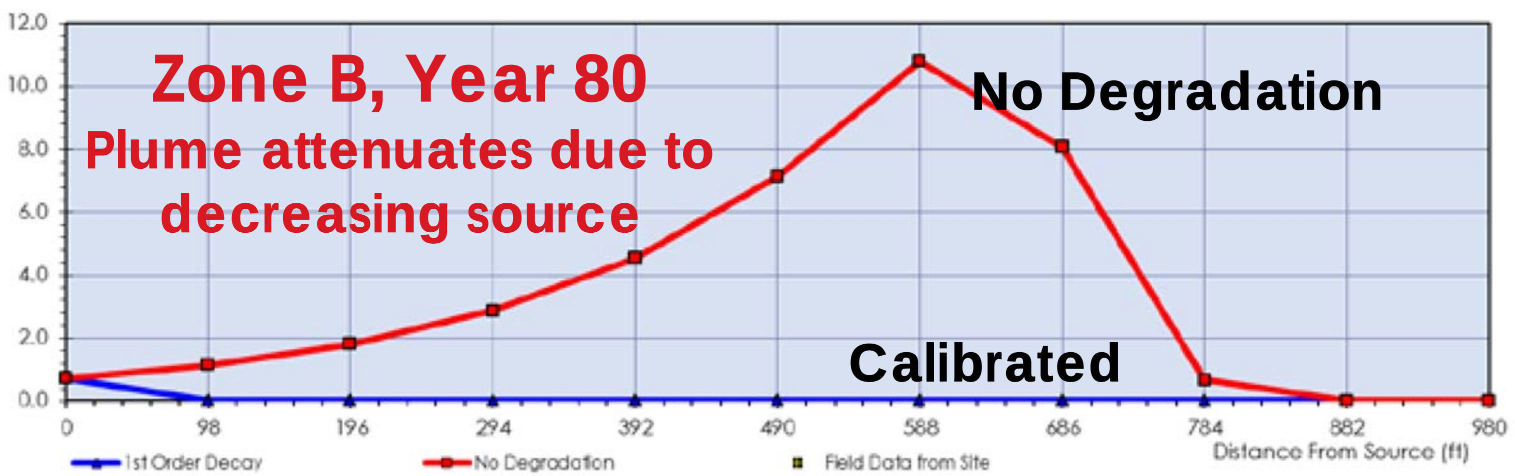
(Year 30)



3 BIOSCREEN-AT Zone B Results

(Forecasting)





3 Summary

- ☑ Mann-Kendal indicated a generally decreasing or flat concentration trend with time
- ☑ Visual assessment indicated a larger plume area, but with a centre of mass that is barely moving (0.5 m/year)
- ☑ BIOSCREEN indicated that if remediation ceased, Zone B would attenuate and Zone A would migrate very slowly (0.5 m/year)
- ☑ Regulators have provided acceptance of this approach during meetings

3 Conclusions

1 Statistics and physics have to play nice together.

2 Consistency with both data analysis and monitoring/sampling programs is key.

3 Calibrate your assumptions and conceptual understanding of your Site against reality!

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Norlito Cezar, M.Sc., P.Eng., Stantec Consulting Ltd.

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Questions?

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[2] AER. 2014. Alberta's Energy Regulator, Reclamation and Remediation, Kevin Ball, March 21, 2014

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[6] Ricker, J. 2008. A Practical Method to Evaluate Groundwater Water Contaminant Stability. Groundwater Monitoring and Remediation, Vol. 28, No. 4, Fall 2008 (pp. 85-94).

[7] USEPA. 2013a. ProUCL Software. Version 5.0.00. Published September 2013.

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[9] Gilbert, 1987. Statistical Methods for Environmental Pollution Monitoring

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