IN-SITU BIOREMEDIATION EVALUATION USING THE WATERLOO EMITTER™

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PRESENTATION OUTLINE

- Introduction
- Case Study
- Waterloo Emitter™ Evaluation
- Results
- Field Test Protocols
- Summary

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INTRODUCTION

- Since mid 1990s Natural Attenuation has progressed the understanding of "degradation" of hydrocarbons – Wiedemeier, ASTM, US EPA
- NA – "biodegradation, dispersion, dilution, sorption and volatization and/or chemical biochemical stabilization of contaminants…"
- Biodegradation – Primary mechanism of attenuating biodegradable contaminants
- Bioremediation – biochemical reactions of Natural Attenuation (five key oxidation/reduction reactions)

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REDOX REACTIONS

- **Oxidation by Aerobic Respiration**

  $7.5\ O_2 + C_6H_6$ --- $6\ CO_2 + 3\ H_2O$

  0.33 mg/L C_6H_6 degraded per mg/L O_2 consumed

- **Oxidation by Nitrate Reduction**

  $6NO_3^- + C_6H_6 + 6H^-$ --- $6CO_2 + 6H_2O + 3N_2$

  0.21 mg/L C_6H_6 degraded per mg/L NO_3^- consumed

- **Oxidation by Iron Reduction**

  $30\ Fe\ (OH)_3 + C_6H_6 + 60H^+$ --- $6CO_2 + 30\ Fe_2^+ + 78\ H_2O$

  0.047 mg/L C_6H_6 degraded per mg/L Fe_2^+ produced

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- **Oxidation by Sulphate Reduction**

  $7.5\ H^+ + 3.75\ SO_4^{2-} + C_6H_6$ --- $6CO_2 + 3.75\ H_2S + 3\ H_2O$

  0.22 mg/L C_6H_6 degraded per mg/L SO_4^{2-} consumed

- **Oxidation by Methanogenesis**

  $4.5\ H_2O + C_6H_6$ --- $2.25\ CO_2 + 3.75\ CH_4$

  1.3 mg/L C_6H_6 degraded per mg/L CH_4 produced

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BTEX UTILIZATION FACTORS

- Unit mass of hydrocarbon “degraded” per unit mass of electron acceptor consumed or redox product produced

Aerobic Respiration	0.32
Denitrification	0.21
Iron Reduction	0.05
Sulfate Reduction	0.21
Methanogenesis	1.28

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EXPRESSED ASSIMILATIVE CAPACITY

$$EAC = UF \,|\, C_b - C_p \,|$$

EAC – amount of hydrocarbon "degraded" based on amount of electron acceptor consumed or redox product produced

- UF – utilization factor
- C_b – background concentration of electron acceptor
- C_p – concentration of electron acceptor in plume

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CASE STUDY

- Former Service Station located in a small town in Northeast Alberta
- Operated for 30 years
- Assessed in 2002 & 2004

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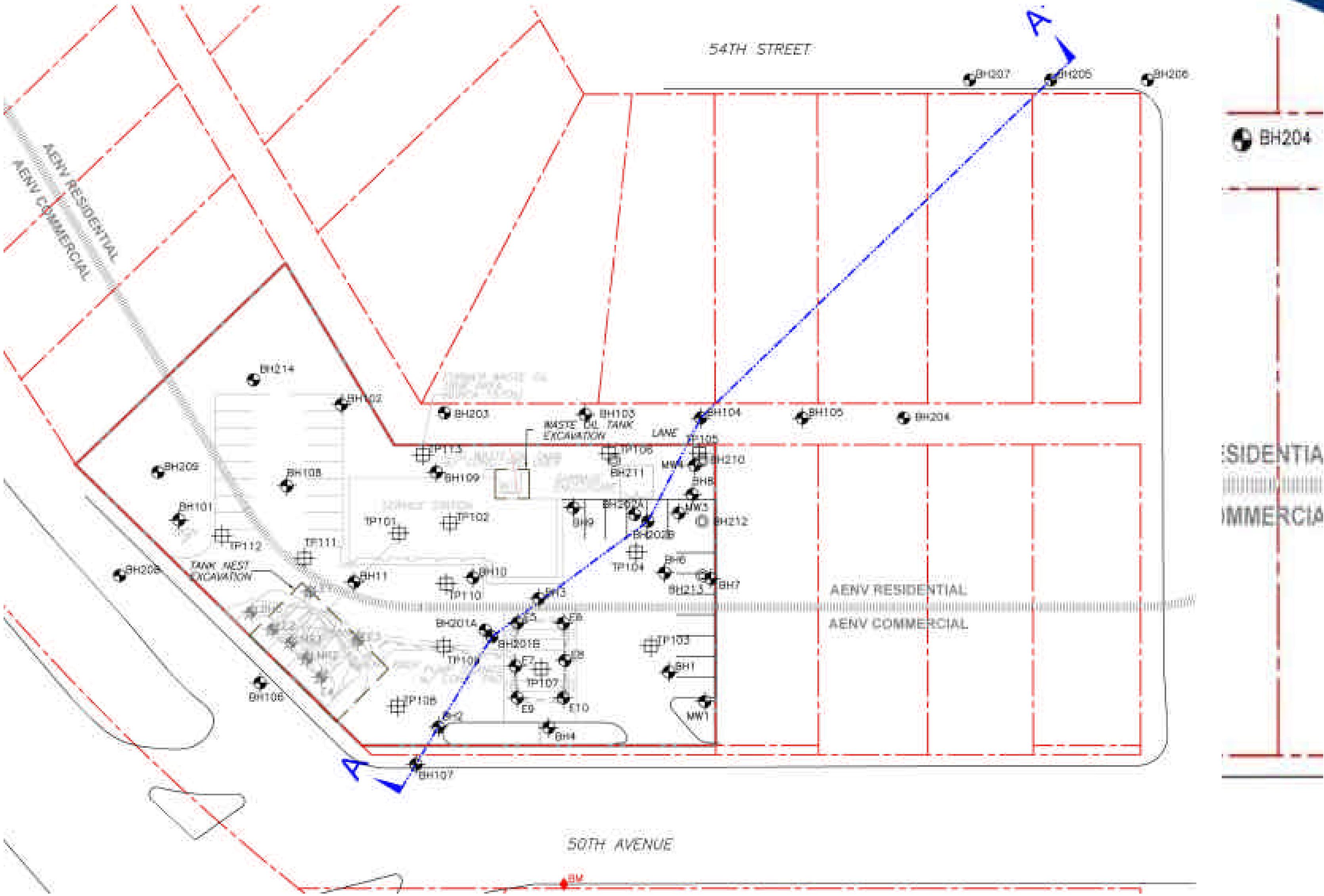
SITE PLAN


54TH STREET
50TH AVENUE
AENV RESIDENTIAL
AENV COMMERCIAL
A
BH204
BH207
BH205
BH206
BH214
BH102
BH203
BH103
BH104
BH105
WASTE OIL TANK EXCAVATION
LANE
BH209
BH108
BH109
BH101
TP101
TP102
TP111
TP112
TP113
BH211
BH210
BH8
MW3
BH212
BH202B
BH6
BH7
BH213
TP104
TP105
TP103
BH1
MW1
BH208
TANK NEST EXCAVATION
BH11
BH10
TP110
BH3
BH201A
BH201B
TP107
TP108
TP109
E9
E10
BH2
BH4
BH106
BH107
BM

CASE STUDY

- Stratigraphy
  - 2 m to 3 m of Clay Till
  - Clean – fine to medium grained sand
- Hydrogeology
  - Primarily confined aquifer
  - Groundwater levels approximately 2.2 m to 3.5 m below surface
  - Seasonal fluctuations of 0.5 m
  - Hydraulic Conductivity of 1 x 10^{-4} m/s to 5 x 10^{-5} m/s
  - Gradient .002 m/m to .003 m\m
  - Groundwater velocity 11 m/year to 32 m/year

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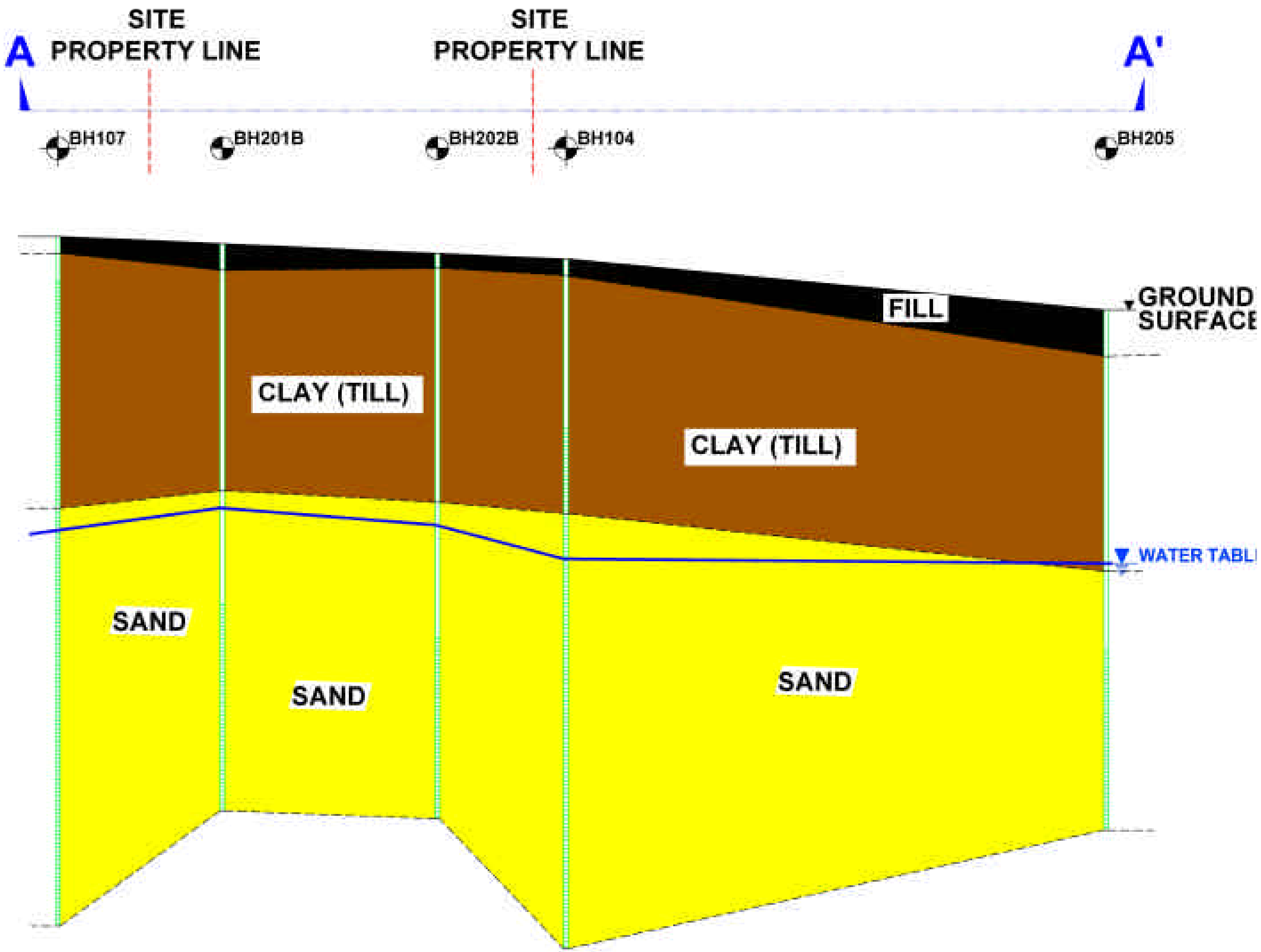
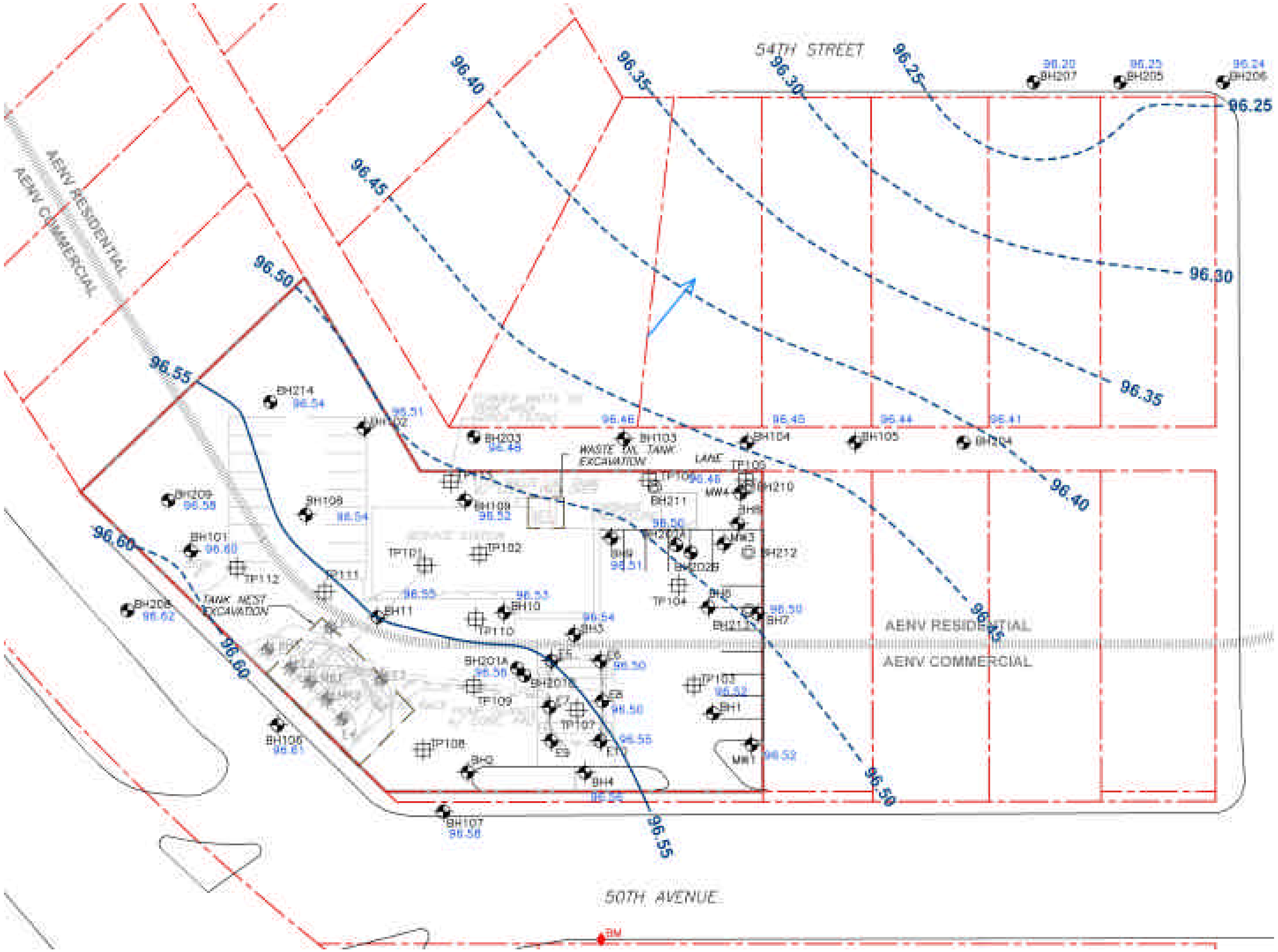
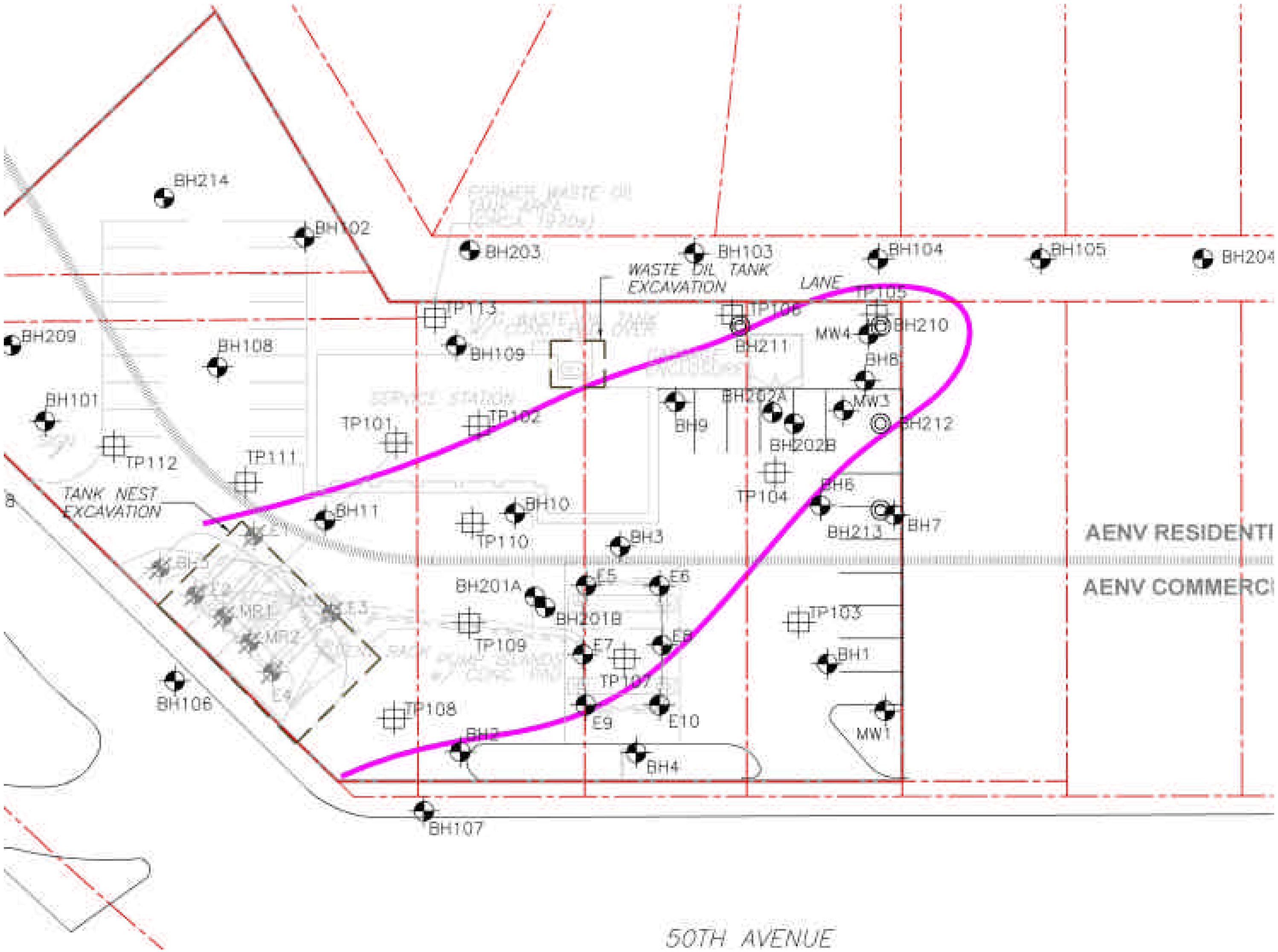
Cross Section



Groundwater Flow



Residual Impact



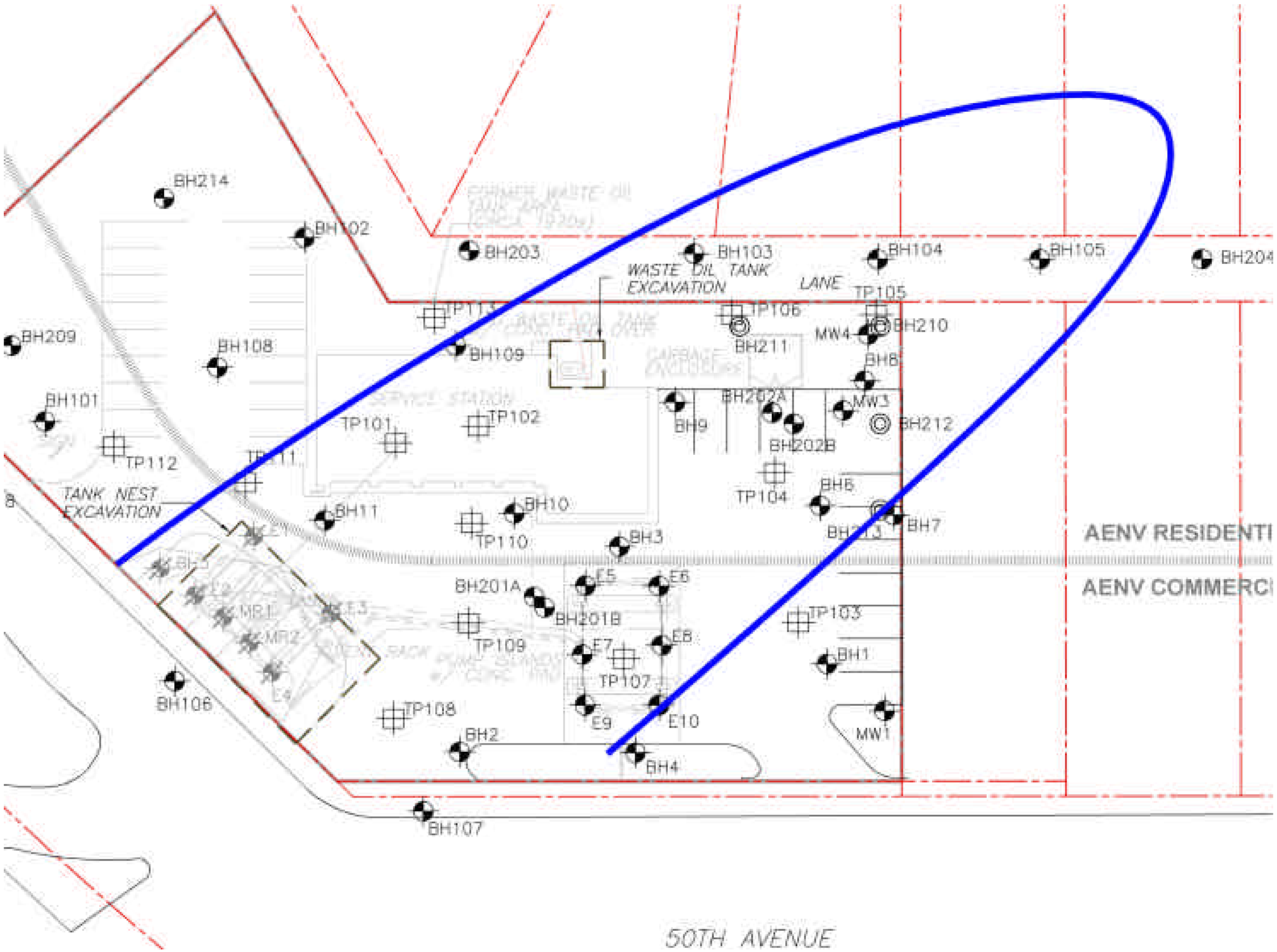
Total BTEX

- 200 µg/g to 20 µg/g

F1 and F2

- 2200 µg/g to 200 µg/g

Dissolved Impact

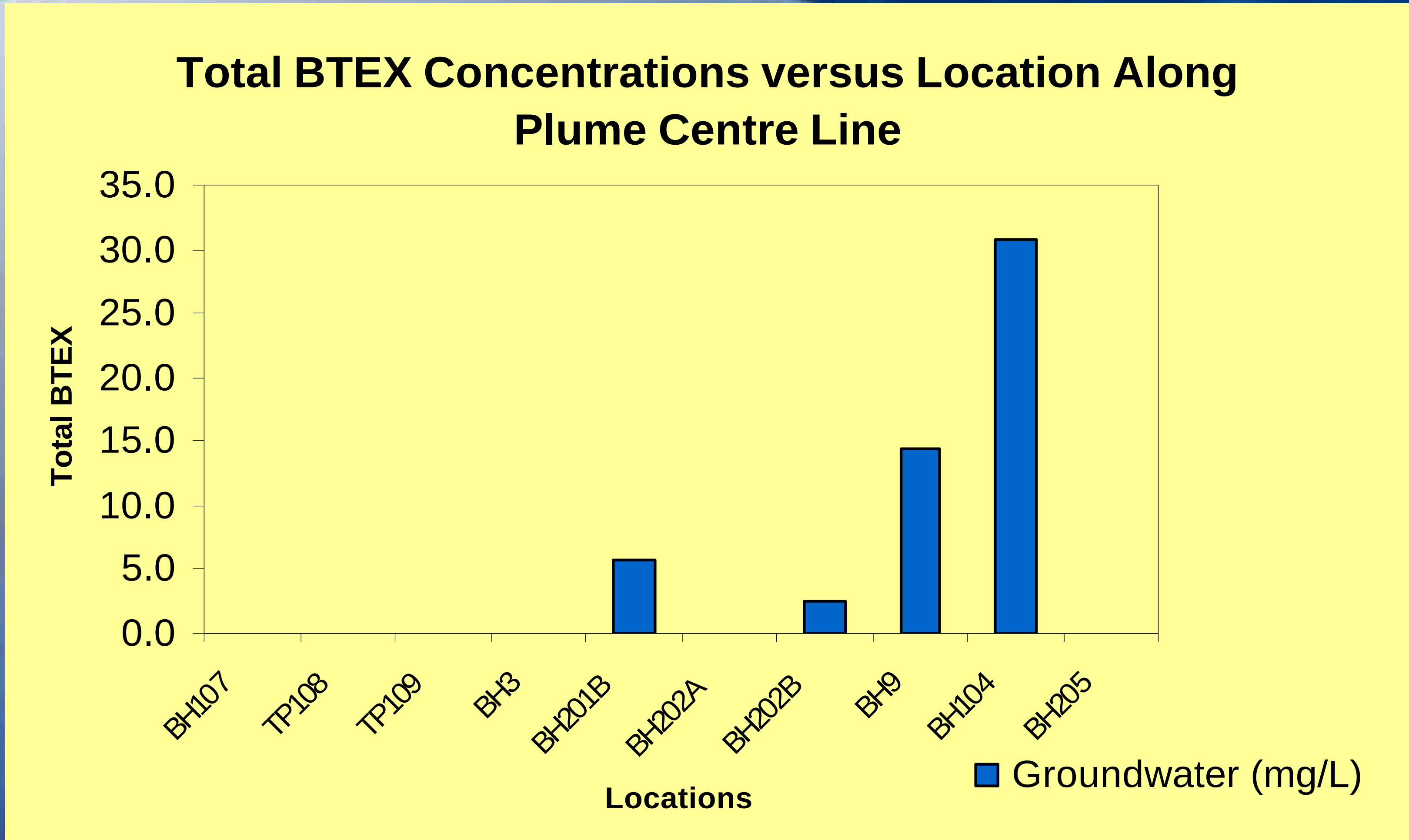


Total BTEX

- 5 mg/L to 30 mg/L

F1 and F2

- 2 mg/L to 12 mg/L



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REMEDIAL/RISK MANAGEMENT OPTIONS

- Excavation
  - Economics and Practical issues
- Dual Phase
  - Economic issues due to water treatment
- Air Sparging
  - Vapour Migration Control issues
- *In-Situ* Bioremediation
  - Further Evaluation

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WATERLOO EMITTER ™

- Rational – effective method of oxygen delivery and relatively simple technology with potentially low maintenance issues
- Developed and patented by University of Waterloo – 1997, Wilson and MacKay
- Diffusion device based on Fick’s First Law - oxygen delivery is established by concentration gradient
- Coil of silicon tubing pressurized, providing a controlled and uniform delivery of dissolved oxygen

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WATERLOO EMITTER ™

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Waterloo Emitter™ EVALUATION

- Field and Laboratory Program
  - **Field Parameters and Geochemical testing (DO, Fe_2^+, NO_3^-, SO_4^{2-}, CH_4)**
  - **Current EAC**
  - **Potential EAC with delivery of Oxygen**
- Microbiological Program
  - **HAB BART Tests - Heterotrophic Bacteria**
  - **Potential for Biological plugging**
- Modelling
  - **Predict Long Term Performance**

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RESULTS

FIELD & LABORATORY PROGRAM

- Depressed DO levels within plume
- Depressed NO_3^- levels within plume
- Elevated Fe_2^+ levels within plume
- Depressed SO_4^{2-} at leading toe of plume
- Slightly elevated CH_4 levels within plume
- Clear "lines of evidence" of in-situ bioremediation occurring - NA

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SUMMARY OF EXPRESSED ASSIMILATIVE CAPACITY (EAC)

Sample ID	BH9	BH105		BTEX	
Location	Plume	Background	Delta	EAC	
Date	EA Concentration				
Aerobic respiration	0.4	25 to 30 mg/L	3.3	1.06	10
Dentrification	< 0.2	2.1	1.9	0.4	
Iron Reduction	3.17	0.01.01	3.16	0.16	
Sulfate Reduction	37	20	-	0	
Methanogenesis	0.0018	.0002	0.0016	0.002	
EAC Total				1.62	
Total BTEX (BH9)				14.4	

Insufficient "Capacity"

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RESULTS

Microbiological Program

- Significant correlation between HAB population and Hydrocarbon concentrations and evidence of oxidative aerobic activity within plume
- Increased Biodegradation rates possible if aerobic environment (oxidative bubble) maintained or increased for HAB to dominate
- Biomass build up could create potential for biological plugging – must be monitored, protocols developed

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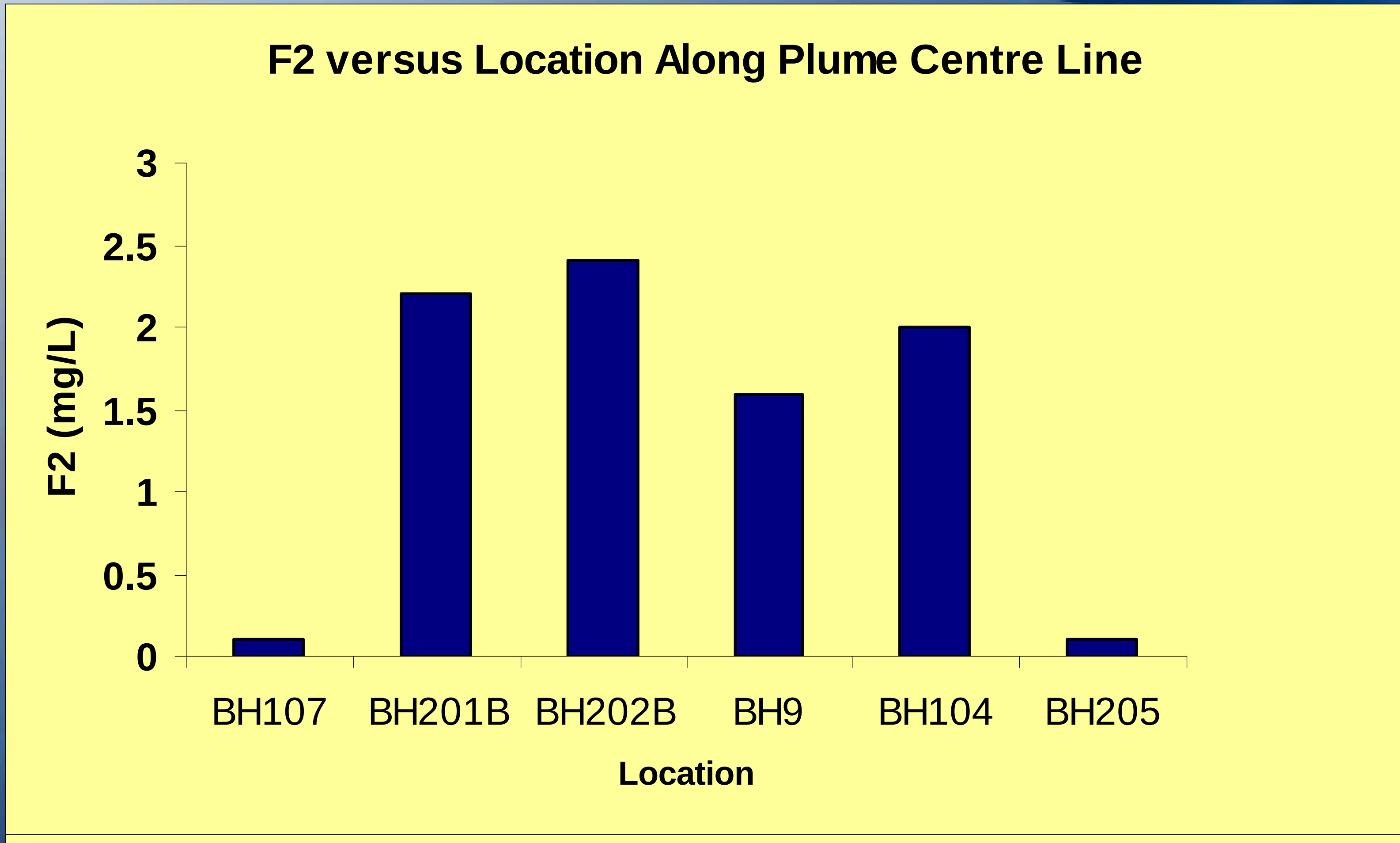

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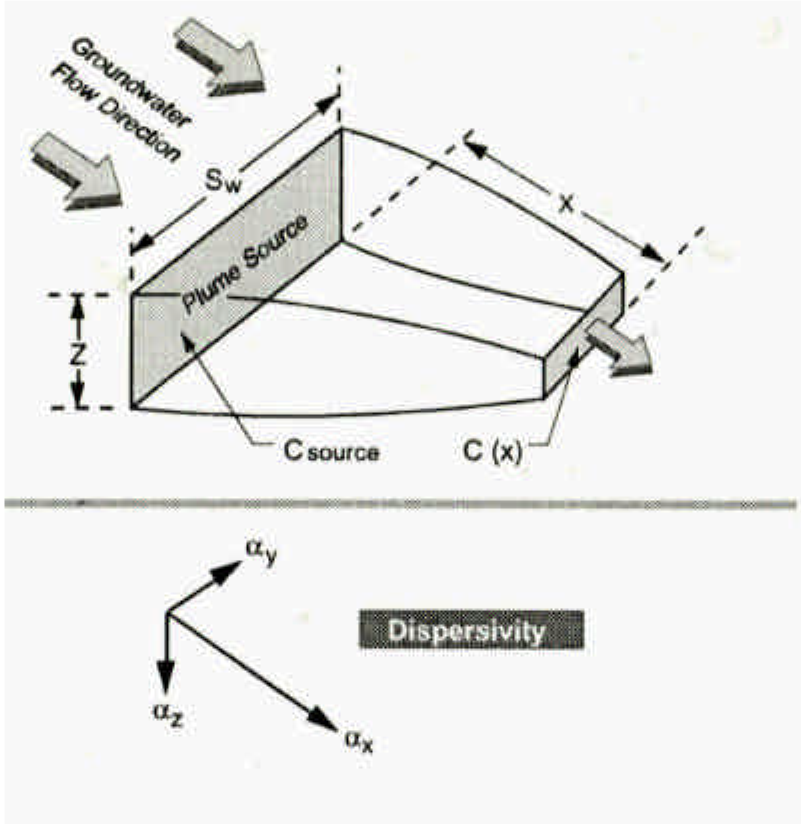
BIOSCREEN – Model Overview

- BIOSCREEN is a simple, spreadsheet-based model developed by the US EPA as a natural attenuation decision support system
- BIOSCREEN is based on the widely used Domenico analytical solute transport model

Domenico Model with Instantaneous Reaction Superposition Algorithm



$$\frac{C(x,y,o,t)}{(Co+BC)} = \frac{1}{8}\exp\left[\frac{x}{\alpha_x 2}\left(1-\left(1+4\lambda\alpha_x/v\right)^{1/2}\right)\right]$$

$$erfc\left[\frac{\left(x - vt\left(1+4\lambda\alpha_x/v\right)^{1/2}\right)}{2\left(\alpha_x vt\right)^{1/2}}\right]$$

$$\left\{erf\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right] - erf\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\}$$

$$\left\{erf\left[\frac{(Z)}{2(\alpha_z x)^{1/2}}\right] - erf\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right]\right\} - BC$$

where: $v = \dfrac{K \cdot i}{\theta_e R}$ $\qquad BC = \Sigma \dfrac{C(ea)_n}{UF_n}$

BIOSCREEN – Model Overview

- BIOSCREEN can be used to assess three different solute transport scenarios:
  - Transport without biodegradation
  - Transport with biodegradation modelled as a first order decay process
  - Transport with biodegradation modelled as an instantaneous reaction

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BIOSCREEN – Model Limitations

- The BIOSCREEN Model is a screening tool only. It approximates more complicated processes that occur in the field
- Simple groundwater flow conditions are assumed
- Uncertainties in a number of parameters are lumped together in the decay coefficient

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BIOSCREEN – Modelling Objectives

- To assess the extent of the benzene plume through time
- To assess benzene degradation rates presently occurring at the site
- To assess the feasibility of hydrocarbon remediation by enhancing aerobic biodegradation processes

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BIOSCREEN – Modelling Process

- Development of conceptual model and characterization of site-specific BIOSCREEN input parameters
- Calibration of model to current site conditions
- Sensitivity analysis to determine key parameters and ongoing data requirements

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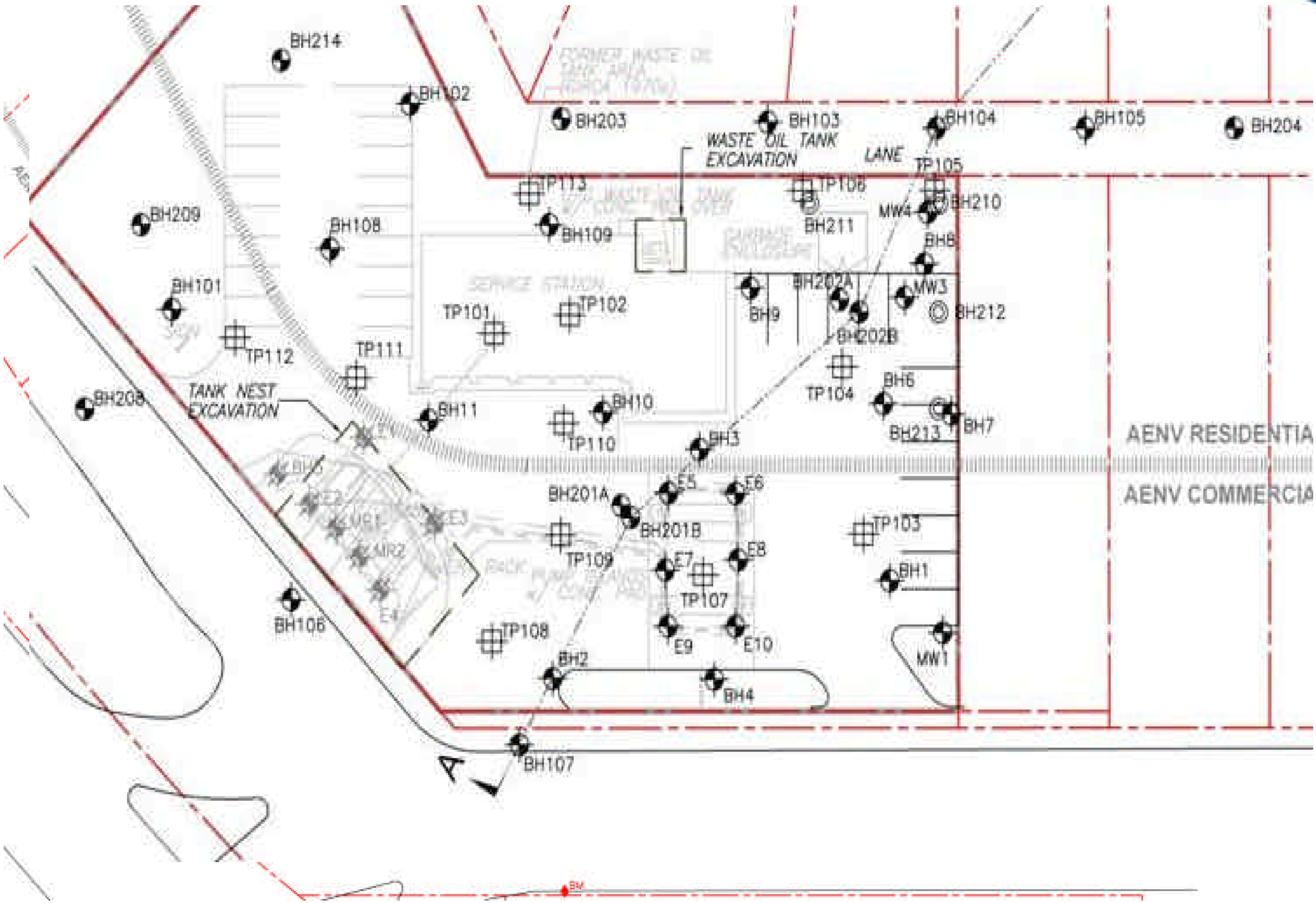
BIOSCREEN
Modelling Process



BIOSCREEN INPUT

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BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence

Version 1.4

Keesler AFB
SWMU 66
Run Name

Data Input Instructions:

115	1. Enter value directly....or
or	2. Calculate by filling in grey cells below. (To restore formulas, hit button below).
0.02	
Variable*	Data used directly in model.
20	Value calculated by model. (Don't enter any data).

1. HYDROGEOLOGY

Seepage Velocity*	*Vs*	63.5	(ft/yr)
or		or	
Hydraulic Conductivity	*K*	8.0E-03	(cm/sec)
Hydraulic Gradient	*i*	0.0023	(ft/ft)
Porosity	*n*	0.3	(-)

2. DISPERSION

Longitudinal Dispersivity*	*alpha x*	13.8	(ft)
Transverse Dispersivity*	*alpha y*	1.4	(ft)
Vertical Dispersivity*	*alpha z*	0.0	(ft)
or		or	
Estimated Plume Length	*Lp*	300	(ft)

3. ADSORPTION

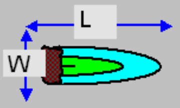
Retardation Factor*	*R*	1.1	(-)
or		or	
Soil Bulk Density	*rho*	1.7	(kg/l)
Partition Coefficient	*Koc*	83	(L/kg)
FractionOrganicCarbon	*foc*	2.0E-4	(-)

4. BIODEGRADATION

1st Order Decay Coeff*	*lambda*	6.9E-1	(per yr)
or		or	
Solute Half-Life	*t-half*	1.00	(year)
or Instantaneous Reaction Model			
Delta Oxygen*	*DO*	10	(mg/L)
Delta Nitrate*	*NO3*	2	(mg/L)
Observed Ferrous Iron*	*Fe2+*	16.6	(mg/L)
Delta Sulfate*	*SO4*	19.6	(mg/L)
Observed Methane*	*CH4*	0.01	(mg/L)

5. GENERAL

Modeled Area Length*	300	(ft)
Modeled Area Width*	85	(ft)
Simulation Time*	15	(yr)



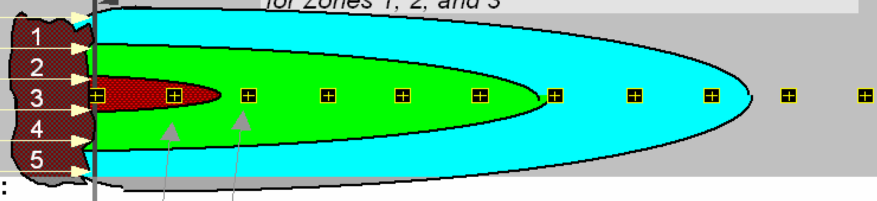
6. SOURCE DATA

Source Thickness in Sat.Zone* 8 (ft)

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3

Source Zones:

Width* (ft)	Conc. (mg/L)*
15	2
15	9
15	14
15	9
15	2



View of Plume Looking Down

Source Halflife (see Help):

40	90	(yr)
Inst. React.	1st Order	
Soluble Mass	300	(Kg)
In Source NAPL, Soil		

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)	11.0	8.6								.001	
Dist. from Source (ft)	0	30	60	90	120	150	180	210	240	270	300

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE

RUN ARRAY

View Output

View Output

Help

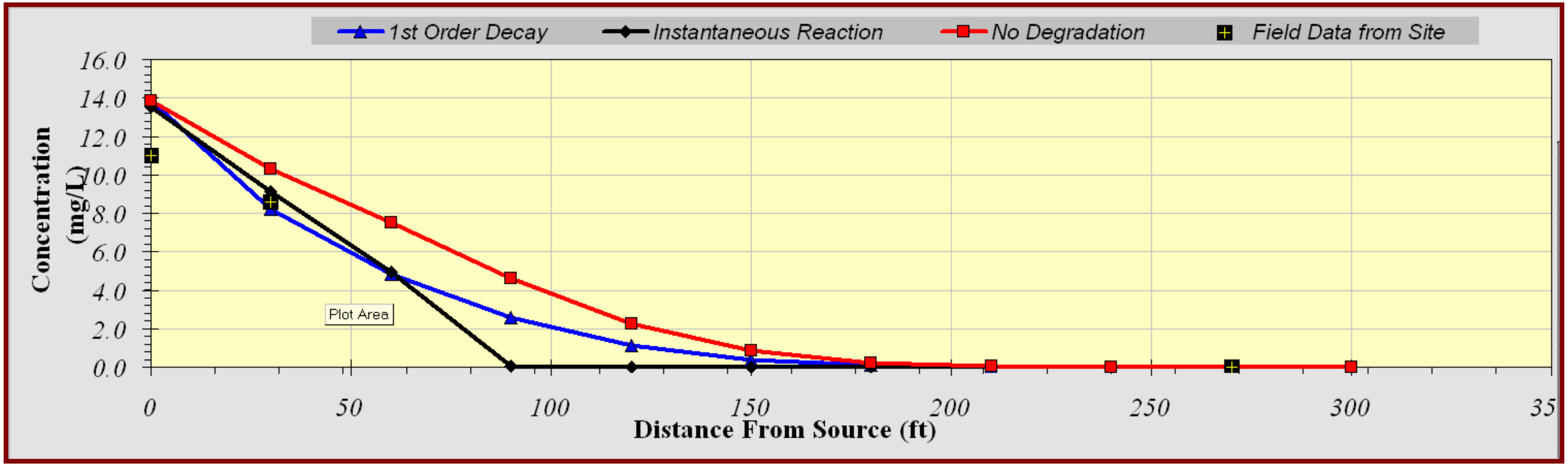
Recalculate This Sheet

Paste Example Dataset

Restore Formulas for Vs, Dispersivities, R, lambda, other

BIOSCREEN OUTPUT

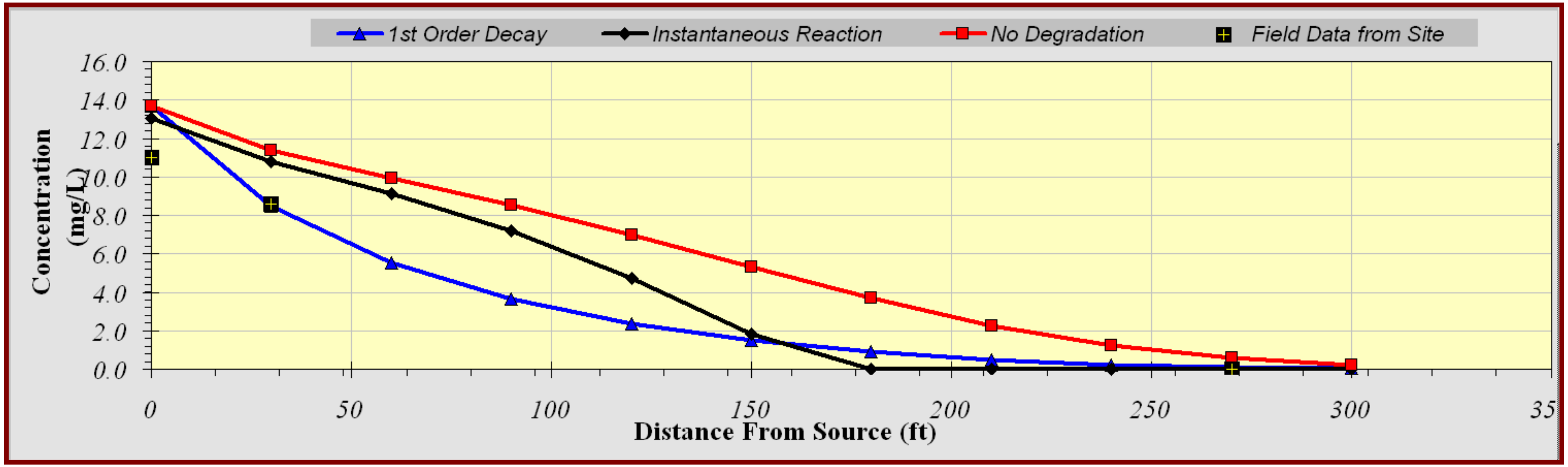
Benzene Concentration vs Distance



2 Years

BIOSCREEN OUTPUT

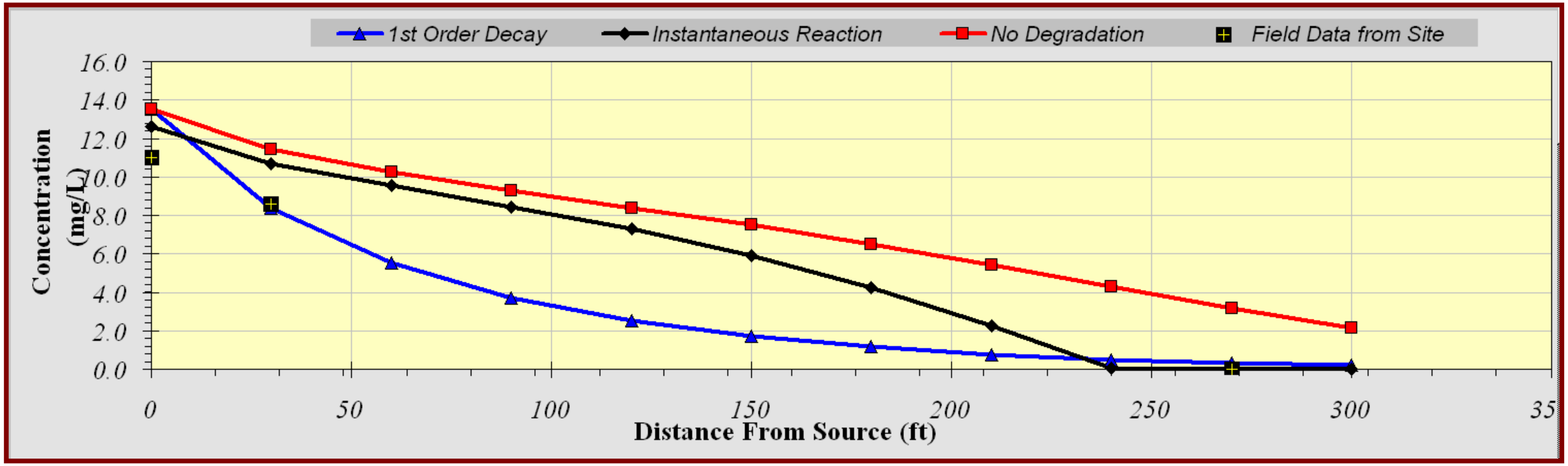
Benzene Concentration vs Distance



3 Years

BIOSCREEN OUTPUT

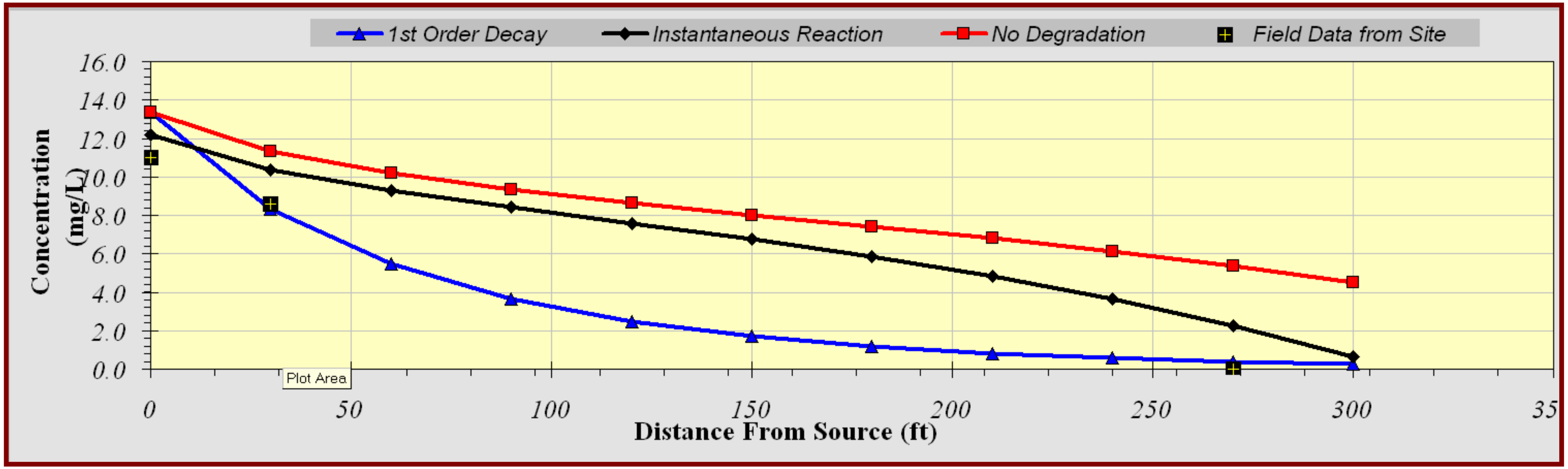
Benzene Concentration vs Distance



5 Years

BIOSCREEN OUTPUT

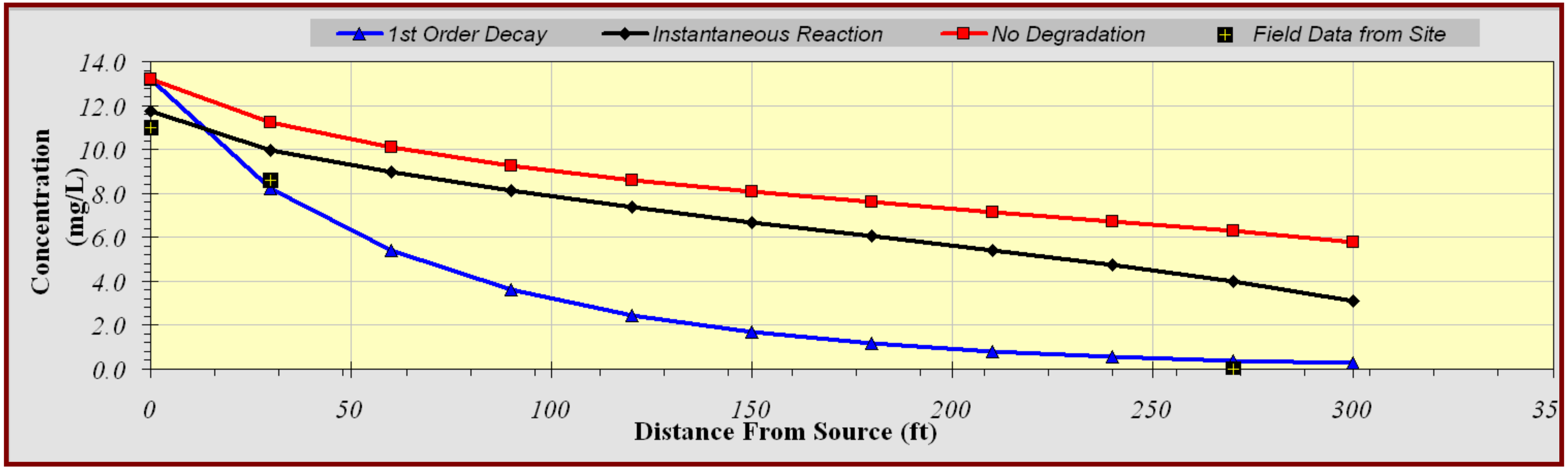
Benzene Concentration vs Distance



6 Years

BIOSCREEN OUTPUT

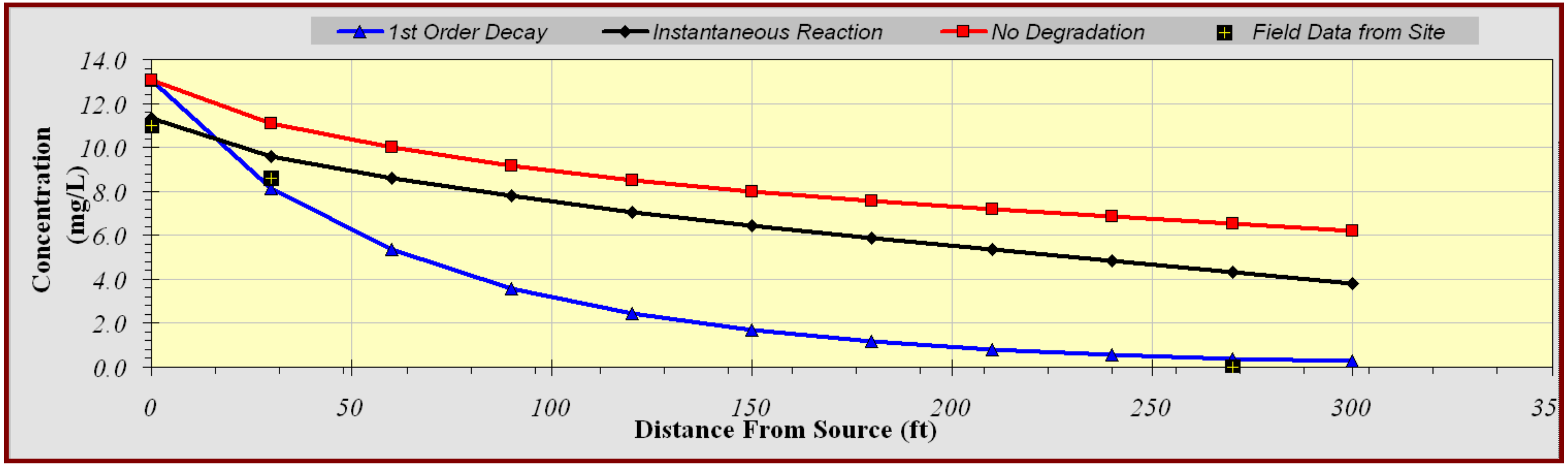
Benzene Concentration vs Distance



8 Years

BIOSCREEN OUTPUT

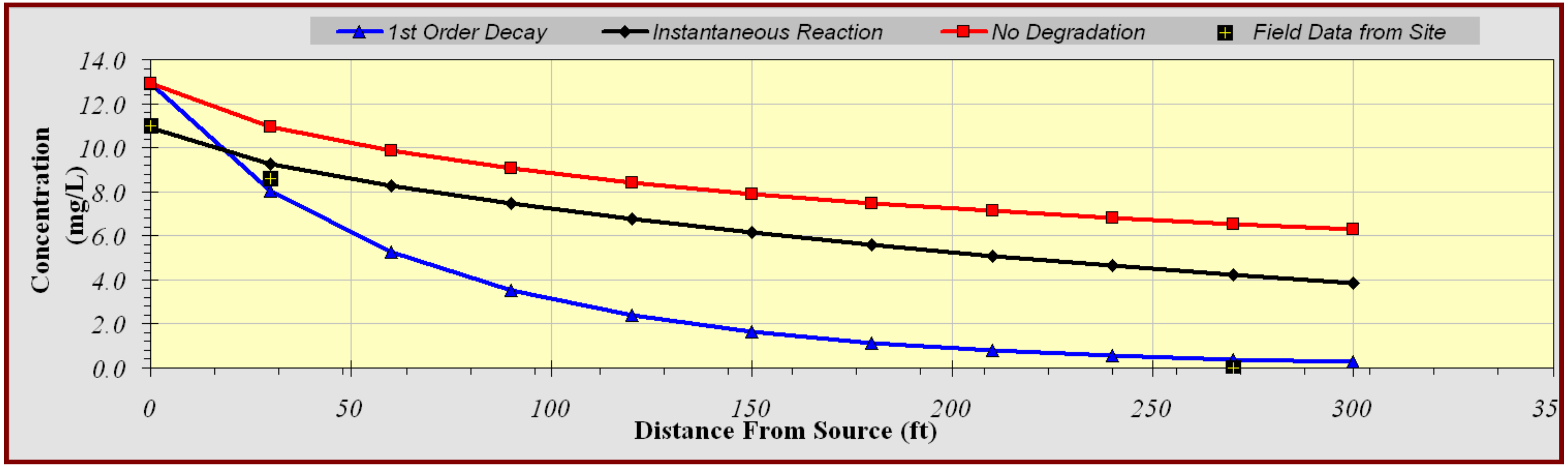
Benzene Concentration vs Distance



9 Years

BIOSCREEN OUTPUT

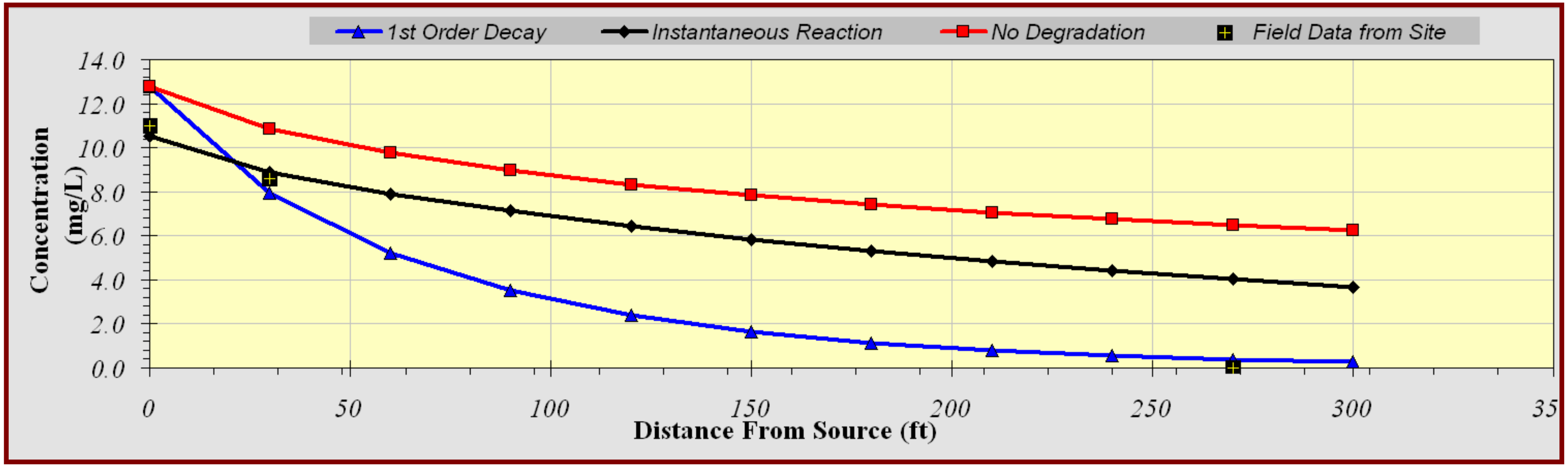
Benzene Concentration
vs
Distance



11 Years

BIOSCREEN OUTPUT

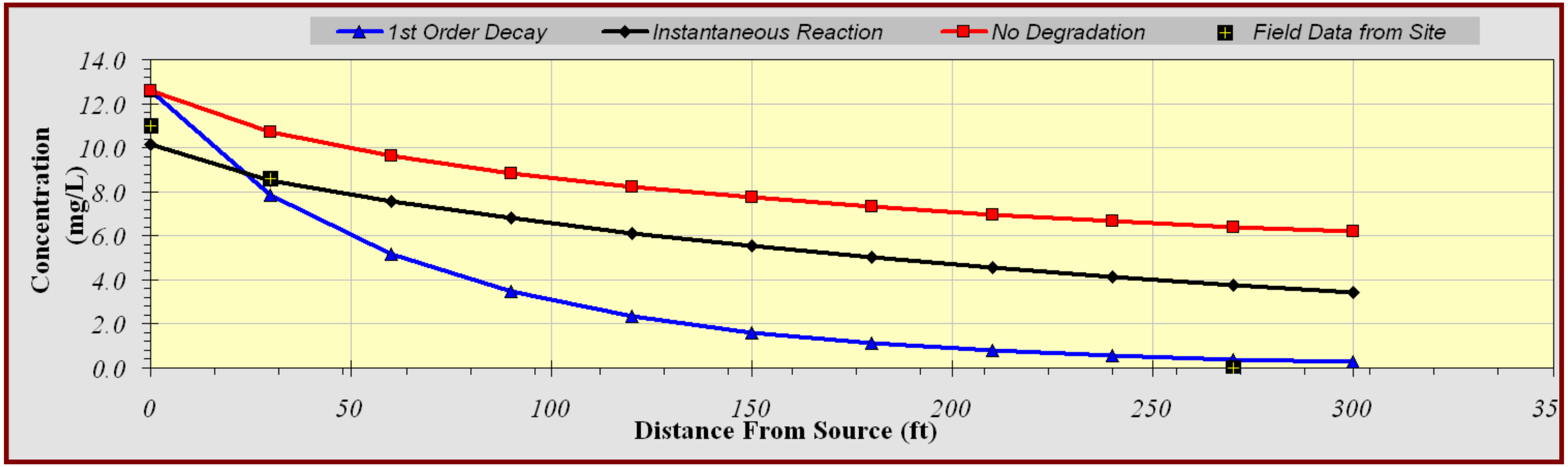
Benzene Concentration vs Distance



12 Years

BIOSCREEN OUTPUT

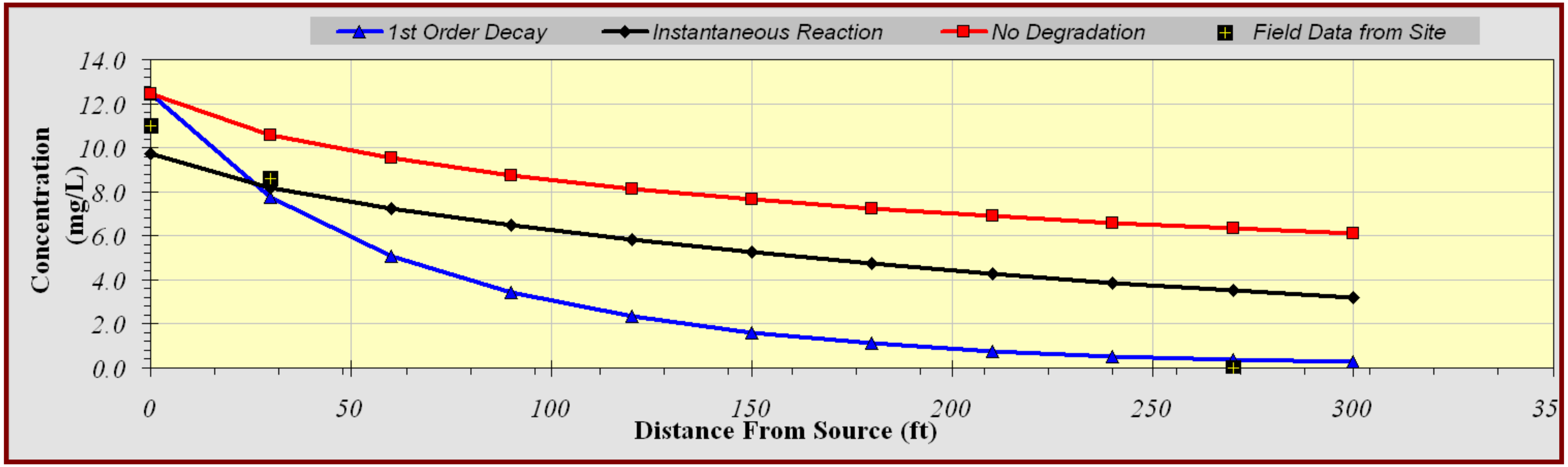
Benzene Concentration
vs
Distance



14 Years

BIOSCREEN OUTPUT

Benzene Concentration vs Distance



15 Years

BIOSCREEN - Conclusions

- Biodegradation of benzene is most closely approximated by a first order rate constant
- The dissolved plume is likely already at steady-state conditions
- If dissolved oxygen levels of 25 to 30 mg/L can be achieved, off-site regulatory compliance is expected to occur within 10 to 20 years

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PROPOSED FIELD TEST PROTOCOLS

- Pure Oxygen versus Air – avoid nutrients in emitters
- Nutrient addition at edges of plume – “entice” biomass away from emitters
- 150 mm well diameter for 100 m emitter – avoid tight spacing
- Continuous operation - avoid biomass movement toward emitters
- BART testing to assess biomass accumulation and biological plugging

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SUMMARY

- Based on site characterization data and preliminary evaluation, the Waterloo Emitter™ may be an effective technology for delivery of oxygen to enhance In-Situ Bioremediation
- Protocols and a monitoring program have been established for a field trial

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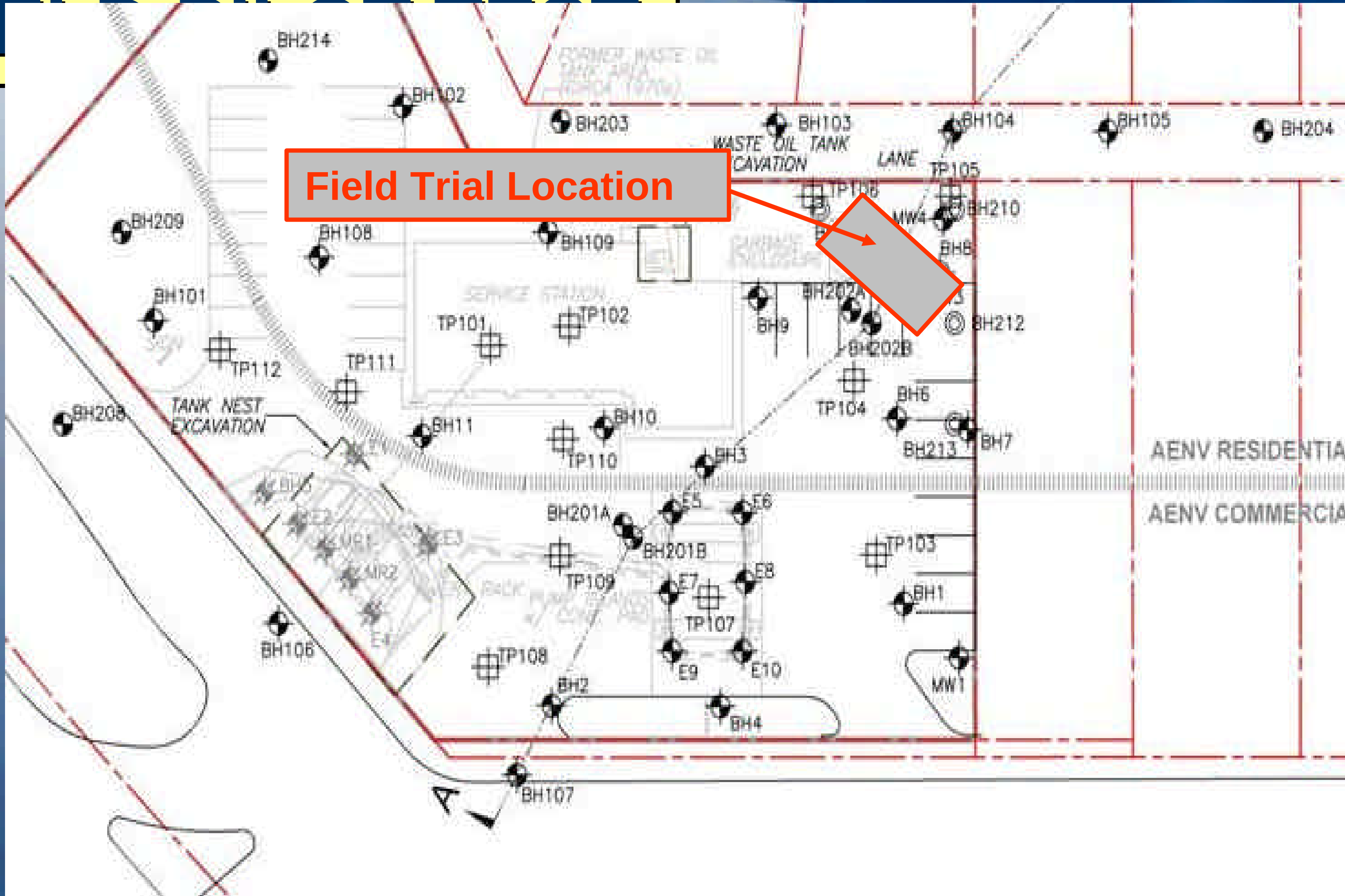

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