Kinetics of Phytoremediation of Petroleum Hydrocarbon Contaminated Soil

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Earthmaster Environmental Strategies and the *University of Waterloo

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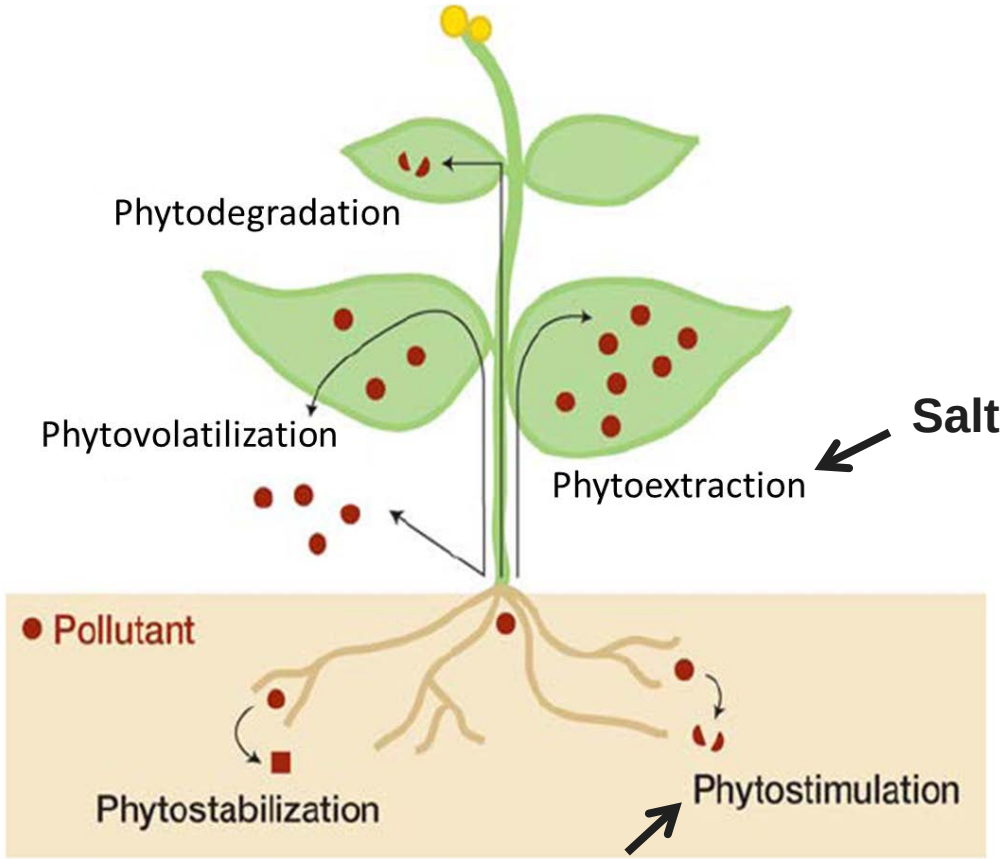
PEPSystems®

Earthmaster Environmental Strategies Inc.

A Canadian environmental technologies company:

- Based in Calgary, Alberta.
- Founded in 1998.
- Specializes in providing environmental services to the commercial/industrial and upstream oil and gas industry in Western Canada.
- Team of environmental consultants consisting of professional agrologists, biologists, chemists, ecologists, engineers, geoscientists, soil scientists, plant scientists, aquatic specialists, and foresters.
- Co-developed commercial phytoremediation systems (PEPSystems™) to treat contaminated soil in an eco-friendly and responsible manner.

Phytoremediation – How it Works



Rhizodegradation – Petroleum Hydrocarbons

- Improved rhizosphere
  - Soil
  - Organic matter
  - Bacteria
  - Water
  - Roots
  - Contaminants
- Phytostimulation
  - Petroleum Hydrocarbons
- Phytoextraction
  soil→root→foliage
  - Salts
  - Metals

Challenge – getting the plants to grow.

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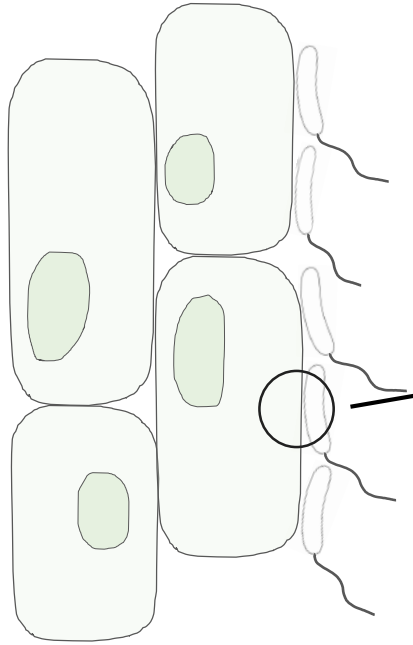
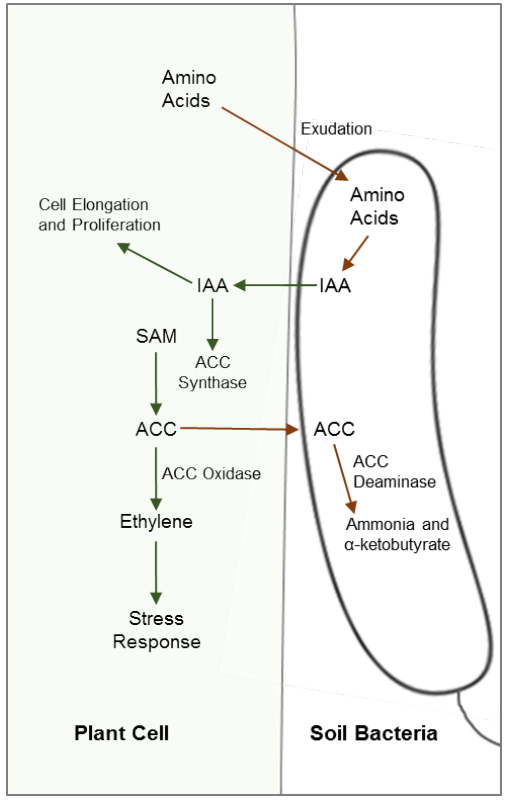
Plant Growth Promoting Rhizobacteria (PGPR) - Enhanced Phytoremediation Systems

PEPSystems®

- Developed through collaboration between Dr. Bruce Greenberg of the University of Waterloo and Earthmaster for contaminated site clean-up.
- Earthmaster has assumed control of the PEPSystems technology and now manages all PGPR testing, selection, seed treating and overall site specific remediation system design in Calgary. Dr. Greenberg continues to collaborate on PEPSystems.
- The use of specific soil or plant associated microorganisms to enhance plant growth for a variety of applications is gaining popularity due to its effectiveness (agriculture).
- Earthmaster continues to conduct research on how to improve PEPSystems for remediation of contaminated sites or other applications such as to enhance plant growth on marginal or poor quality soils.

PGPR – Facilitating Plant Growth in Challenging Conditions





Active rhizosphere:
PGPR co-localize with developing roots

- Stress ethylene
- Plant vigor
- Root development
- Rhizobacteria
- Leaves
- Salt and metals uptake
- Degradation of PHC

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Petroleum Hydrocarbon (PHC) in Soil

PHC contamination in soil from leaks and spills

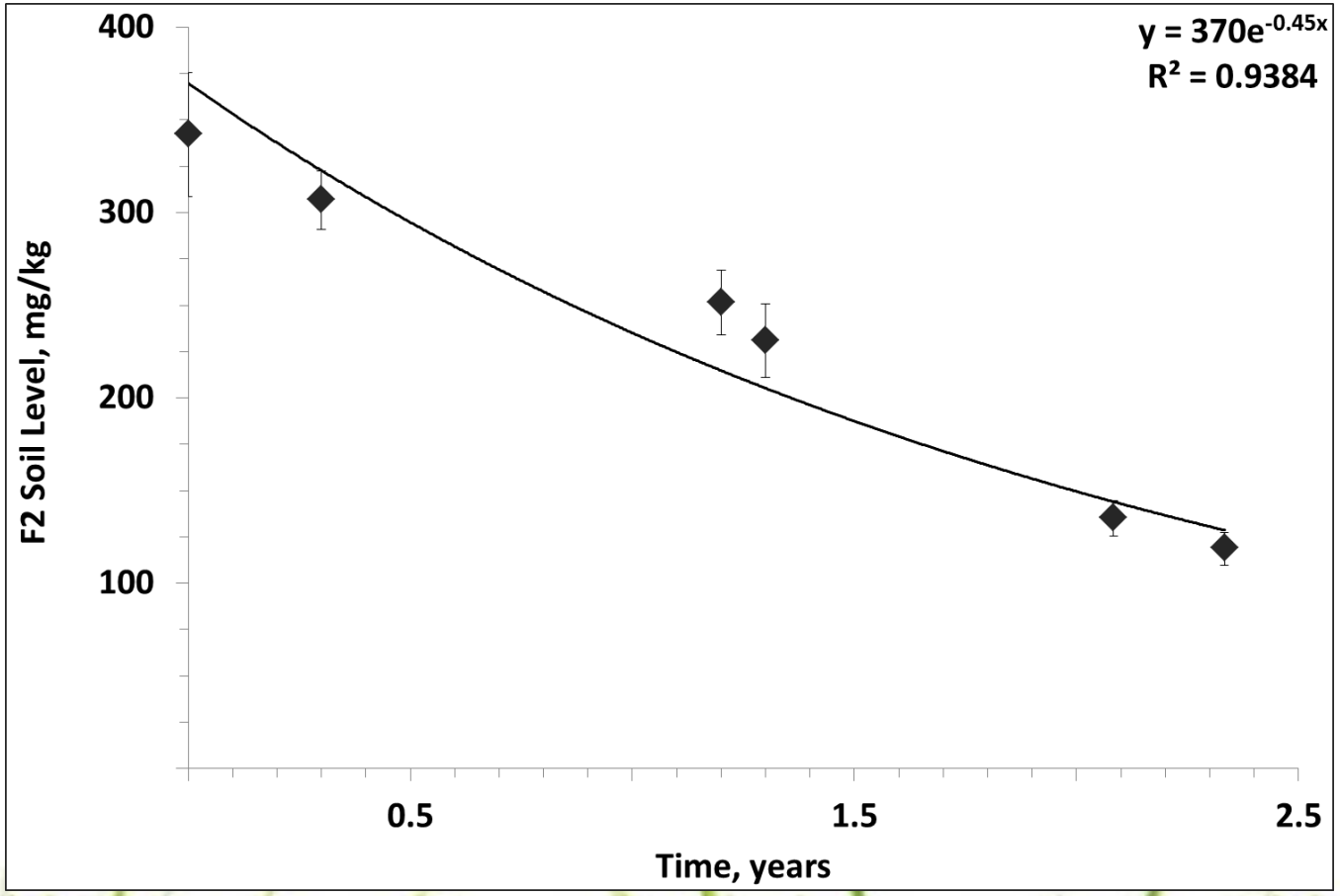
- Carcinogen, mutagen, and is an neurotoxic organic pollutant.
- Current treatment/disposal methods include:
  - Incineration/thermal – toxic by-products, soil damage
  - Disposal at a landfill – $$, liability, loss of soil
  - Mechanical methods – soil mixing/tillage
  - Chemical methods – not always effective, can be expensive
- PHC is prone to degradation by bacteria which makes it an excellent candidate for bioremediation.
  - Must have bacteria that have the appropriate metabolic capabilities (Pseudomonads are a good choice – produce rhamnolipids).
  - Must establish and maintain conditions that favor enhanced oil biodegradation rates in the contaminated environment – fertilizer use.

Predictive Kinetic Equations for PHC Remediation

Goal: to predict the amount of time it takes PEPSystems to degrade PHC in soil based on starting concentrations and desired end point.

- Kinetic equations developed in 2015 by Dr. Bruce Greenberg using data from six phytoremediation sites in Alberta.
- Based on PHC fractions F2(C_{10-16}) & F3(C_{16-34}) remediation kinetic data.
- Observed 25-35 % remediation per year for both PHC fractions.
- The remediation rates followed first order exponential decay kinetics.

F2 Remediation Trend



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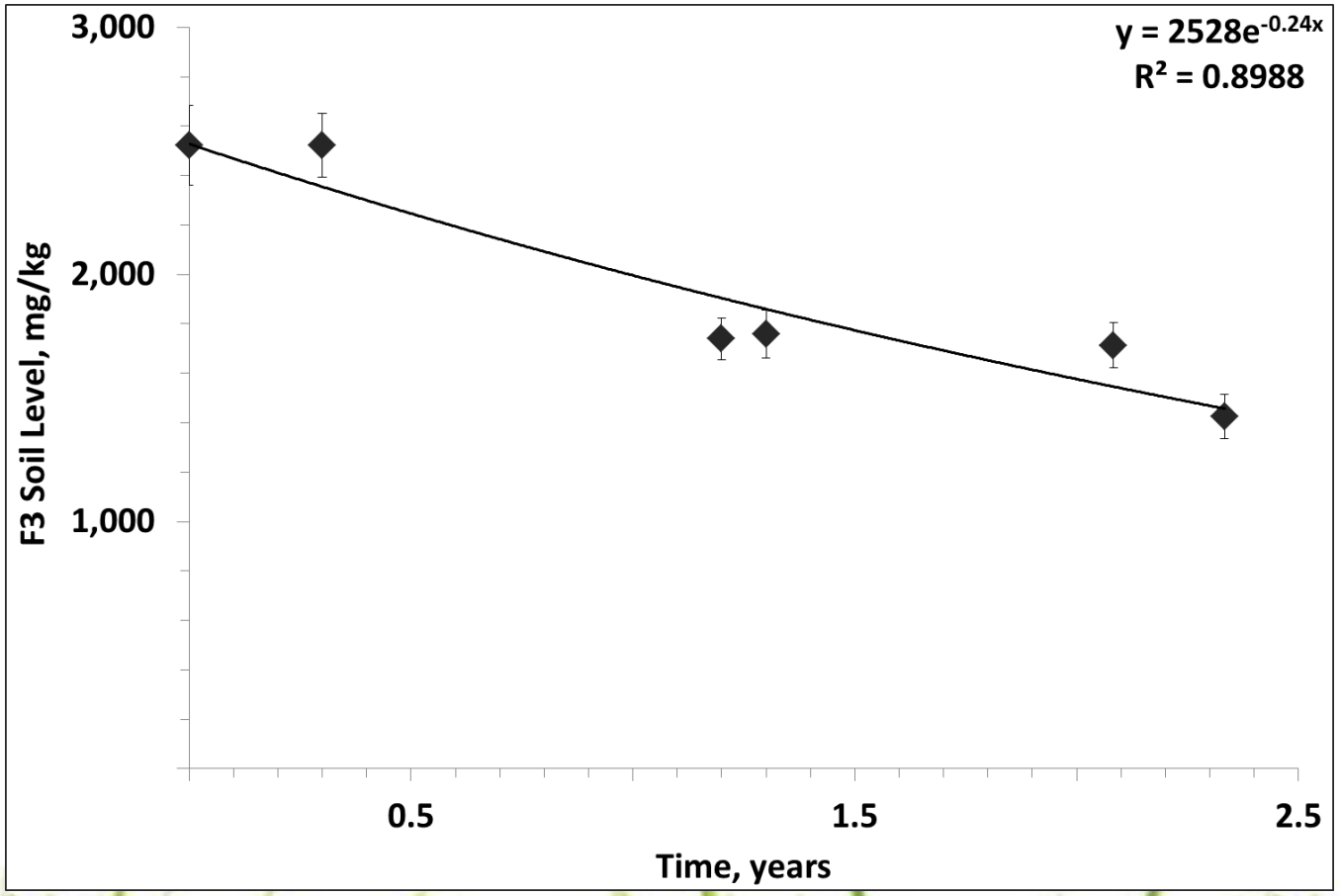
F3 Remediation Trend



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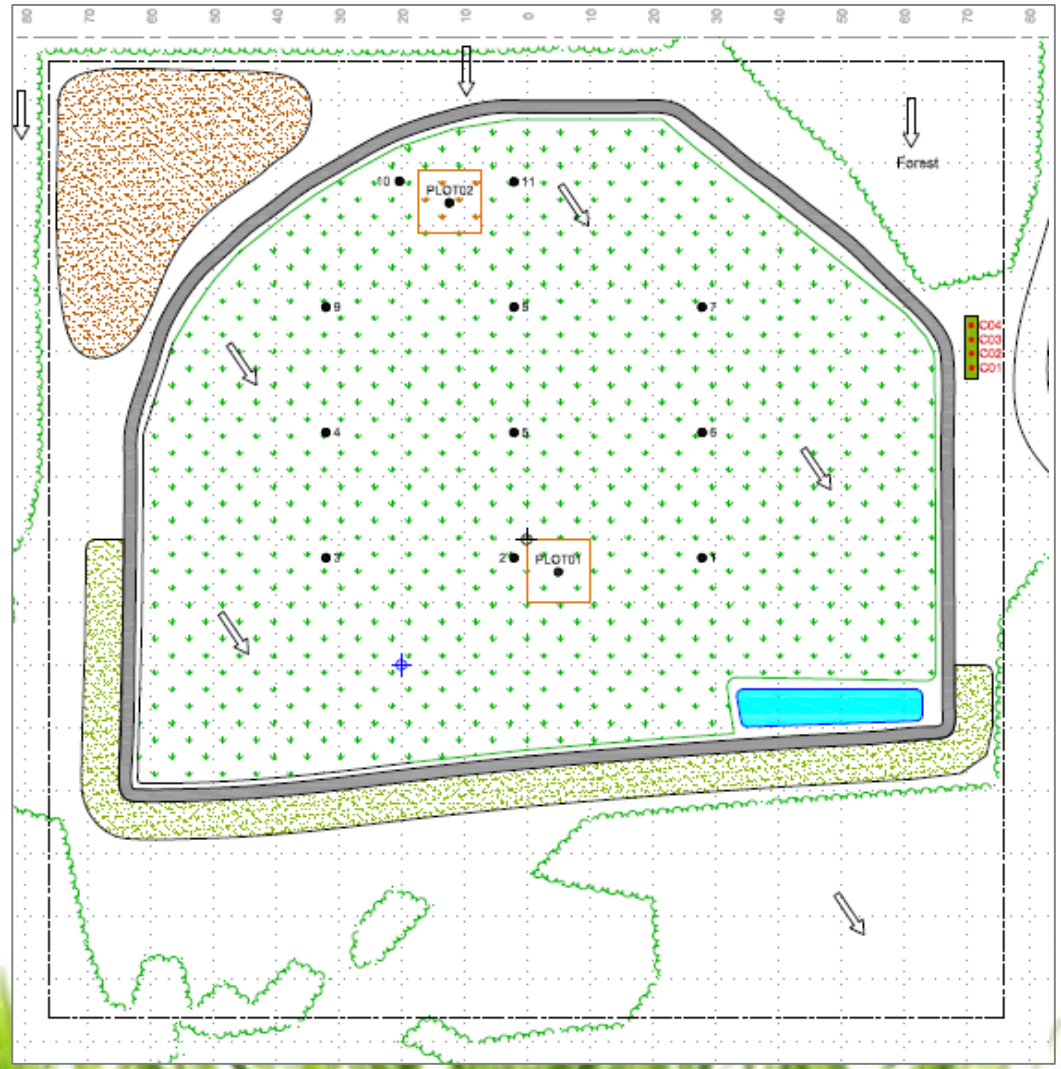
Limitations of the Kinetic Equations

Predictive kinetic equations are based on whole site averages. Limitations include:

- Heterogeneous soil containing ‘hot spots’ which may require additional treatment time
- Lack of precipitation or very low soil moisture
- Poor agronomic practices
- Treatment zone thickness of 0.30 m
- Rooting depth of 0.30 m corresponding to treatment depth
- Extremely high PHC levels (F3 of >10,000 mg/kg) not tested

Site 1 – West Central Alberta 14-19



12,000 m³ of material excavated from 2 former DWDAs, wellbore area, and disturbed area were spread to a depth of 1 m:

- Land use – natural
- Soil texture – fine
- AB remediation guideline values F2:
  - surface soil – 150 mg/kg
  - subsoil – 300 or 1000 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas sp.*
- Lift #1 T=0 October 2013
  - stripped 4000 m³ (to 0.25 or 0.50 m depth) in Mar 2016
- Lift #2 T=0 October 2016
  - includes hot spots from lift #1
  - treatment is ongoing

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Site 1 – West Central Alberta 14-19

Lift #1 Sample Chemistry T = 0				
Depth	PHC	# samples	Oct 2013	
			range	average*
0.00-0.25 m	F2	9 of 11	54-540	310 ± 46
0.25-0.50 m	F2	9 of 11	41-790	342 ± 76

samples exceeding surface soil guideline value

*average mg/kg ± standard error

Lift #1

Depth	T=0 C_0	x yrs	$C_{1.6\ yrs}$
0.00-0.25 m	310	1.6	66
0.25-0.50 m	342	1.8	126

Lift #2 Sample Chemistry T = 0				
Depth	PHC	# samples	Nov 2016	
			range	average*
0.00-0.25 m	F2	5 of 11	59-790	270±78
0.25-0.50 m	F2	10 of 11	110-1300	333±102

Lift #2

Depth	T=0 C_0	x yrs	$C_{0.25\ yrs}$
0.00-0.25 m	270	1.3	115
0.25-0.50 m	333	1.8	212

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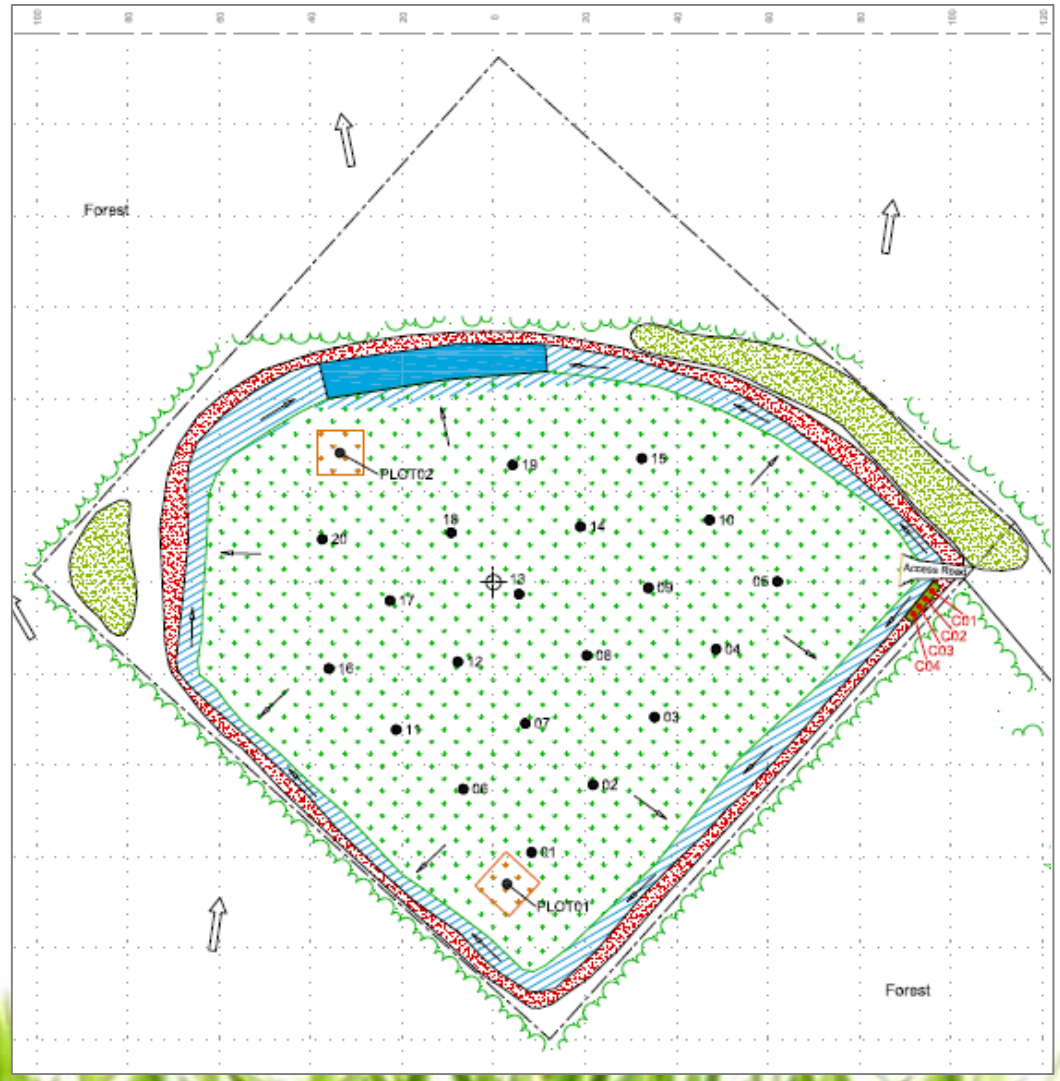
Site 2 – West Central Alberta 04-06



10,000 m³ of material excavated from a former drilling waste disposal area and earthen pit were spread to a depth of 1 m:

- Land use – natural
- Soil texture – fine
- AB remediation guideline values F2:
  - surface soil – 150 mg/kg
  - subsoil – 300 or 1000 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas sp.*
- Lift #1 T=0 October 2013
  - stripped 3500 m³ (to 0.25 or 0.50 m depth) in Mar 2016
- Lift #2 T=0 October 2016
  - includes hot spots from lift #1
  - treatment is ongoing

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Site 2 – West Central Alberta 04-06

Lift #1 Sample Chemistry T = 0				
Depth	PHC	# samples	Oct 2013	
			range	average*
0.00-0.25 m	F2	13 of 20	66-830	311 ± 58
0.25-0.50 m	F2	15 of 20	60-1500	403 ± 75

samples exceeding surface soil guideline value

*average mg/kg ± standard error

150 mg/kg
1300 mg/kg

$y/C_o = e^{-0.45x}$

Predicted # of years

-0.24 for F3

Lift #1

Depth	T=0 C_0	x yrs	$C_{1.6\ yrs}$
0.00-0.25 m	311	1.6	138
0.25-0.50 m	403	2.2	336

Lift #2 Sample Chemistry T = 0				
Depth	PHC	# samples	Nov 2016	
			range	average*
0.00-0.25 m	F2	7 of 20	21-520	161±30
0.25-0.50 m	F2	14 of 20	10-1100	417±78

Lift #2

Depth	T=0 C_0	x yrs	$C_{0.25\ yrs}$
0.00-0.25 m	161	0.2	253
0.25-0.50 m	417	2.3	247

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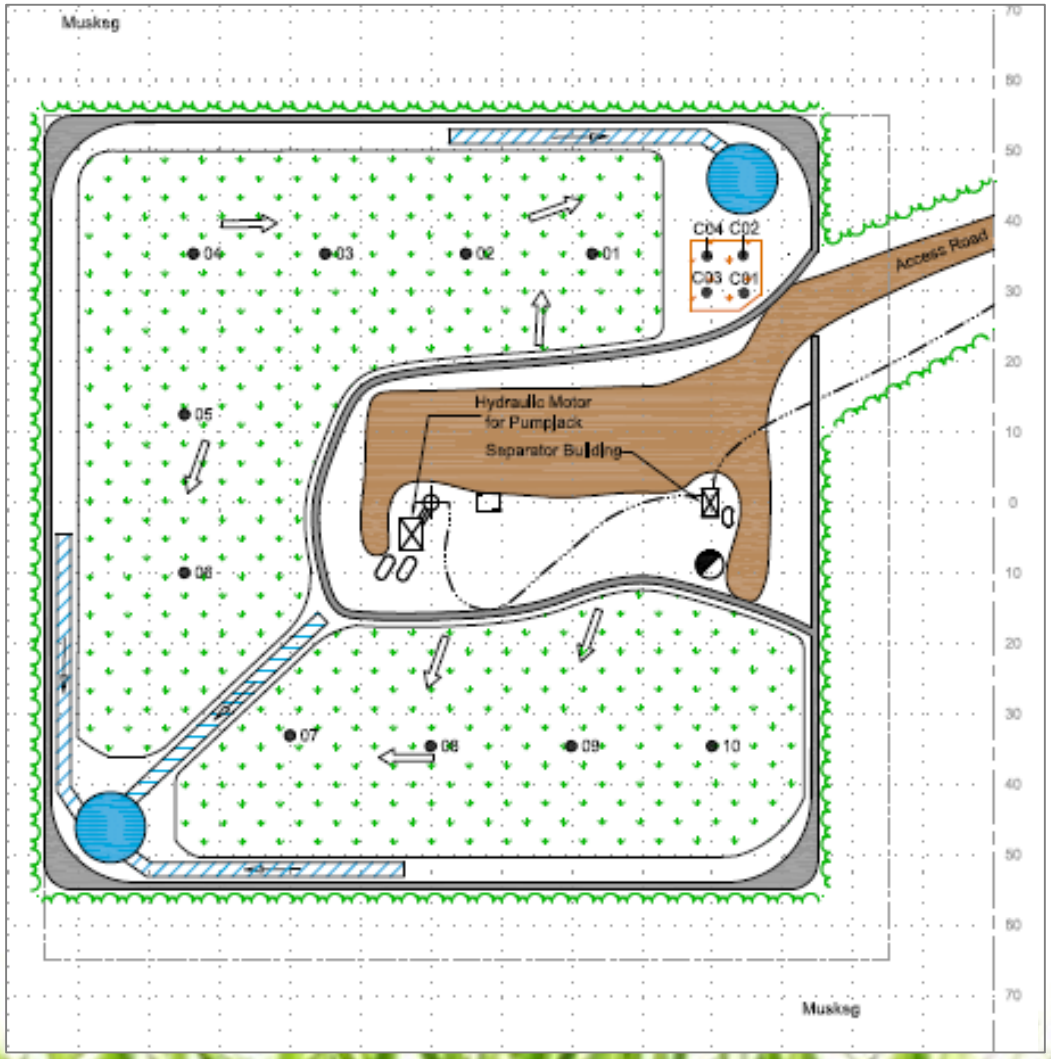
Site 3 – Red Earth 02-31



2,950 m³ of material from former emulsion spills were spread to a depth of 0.45 m:

- Land use – natural
- Soil texture – fine
- AB remediation guideline values F2:
  - surface soil – 150 mg/kg
  - subsoil – 300 or 1000 mg/kg
- AB remediation guideline values F3:
  - surface soil – 1300 mg/kg
  - subsoil – 2600 or 3500 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas sp.*
- Lift #1 T=0 Oct 2011, *used to generate equation*

Lift #1

Depth	PHC	T=0 C_0	$C_{2.5\ yrs}$
0.00-0.20 m	F2	752	165
0.20-0.40 m		906	110
0.00-0.20 m	F3	1740	884

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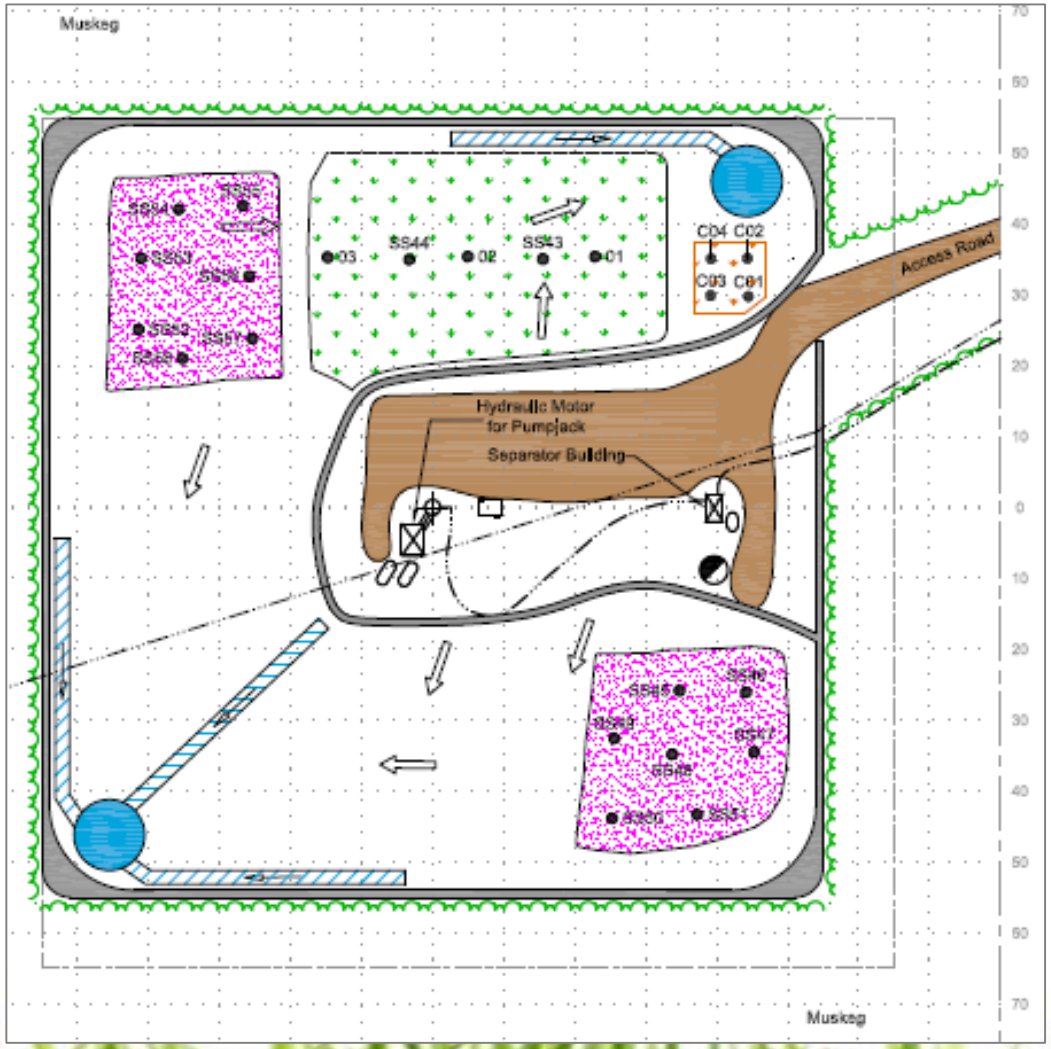
Site 3 – Red Earth 02-31



2,750 m³ of lift #1 was stripped and placed into stockpiles complying with either surface soil or subsoil criteria.

200 m³ of contaminated soil was re-spread to create lift #2:

- Lift #2 T=0 August 2015
  - includes any hot spots from lift #1
  - treatment is completed

Lift #2 Sample Chemistry T = 0					
Depth	PHC	samples		Aug2015	
		# surface	# subsoil	range	average*
0.00-0.20 m	F2	1 of 3	0 of 3	41-420	204±113

samples exceeding surface soil guideline value

*average mg/kg ± standard error

Lift #2

Depth	PHC	T=0 C_0	x yrs	$C_{1.1\ yrs}$
0.00-0.20 m	F2	204	0.7	23

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Site 3 – Red Earth 02-31

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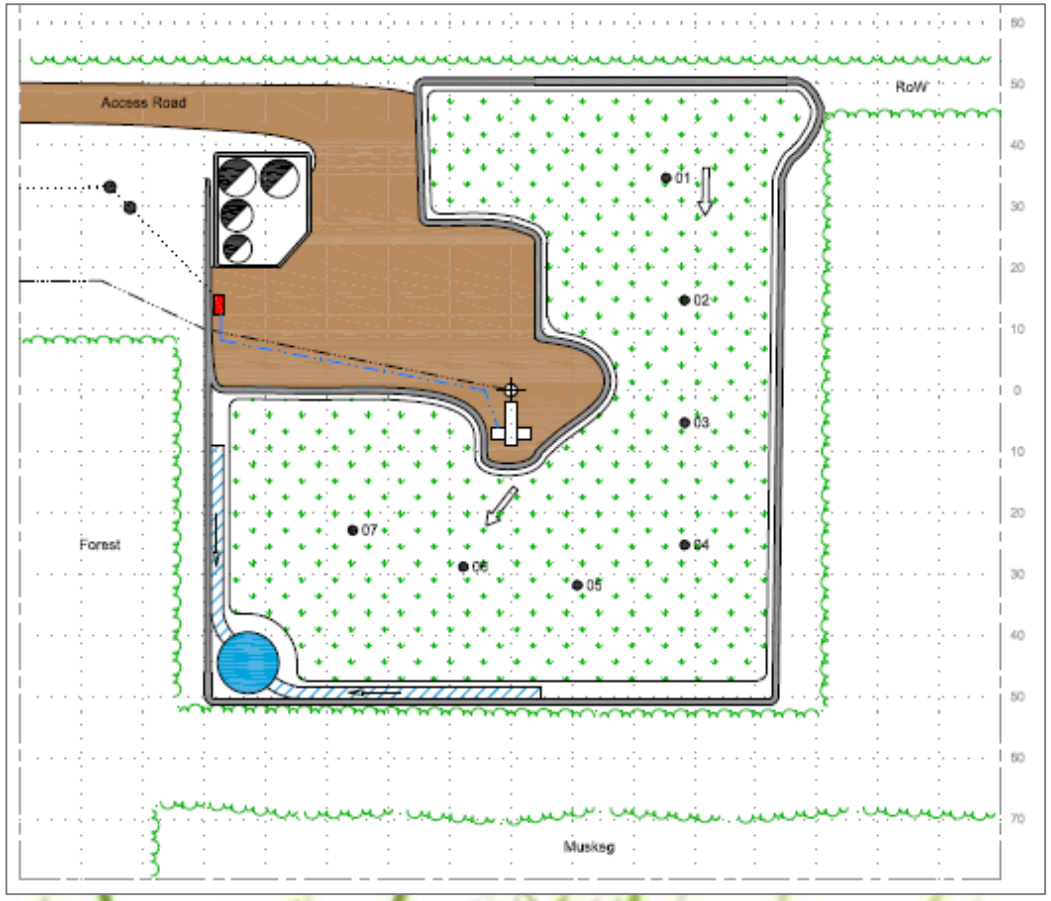
Site 4 – Red Earth 12-33



2,550 m³ of material from former emulsion spills were spread to a depth of 0.45 m:

- Land use – natural
- Soil texture – fine
- AB remediation guideline values F2:
  - surface soil – 150 mg/kg
  - subsoil – 300 or 1000 mg/kg
- AB remediation guideline values F3:
  - surface soil – 1300 mg/kg
  - subsoil – 2600 or 3500 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas sp.*
- Lift #1 T=0 Oct 2011, *used to generate equation*

Lift #1

Depth	PHC	T=0 C_0	$C_{2.5\ yrs}$
0.00-0.20 m	F2	620	167
0.20-0.40 m		702	230
0.00-0.20 m	F3	1537	1061
0.20-0.40 m		1423	833

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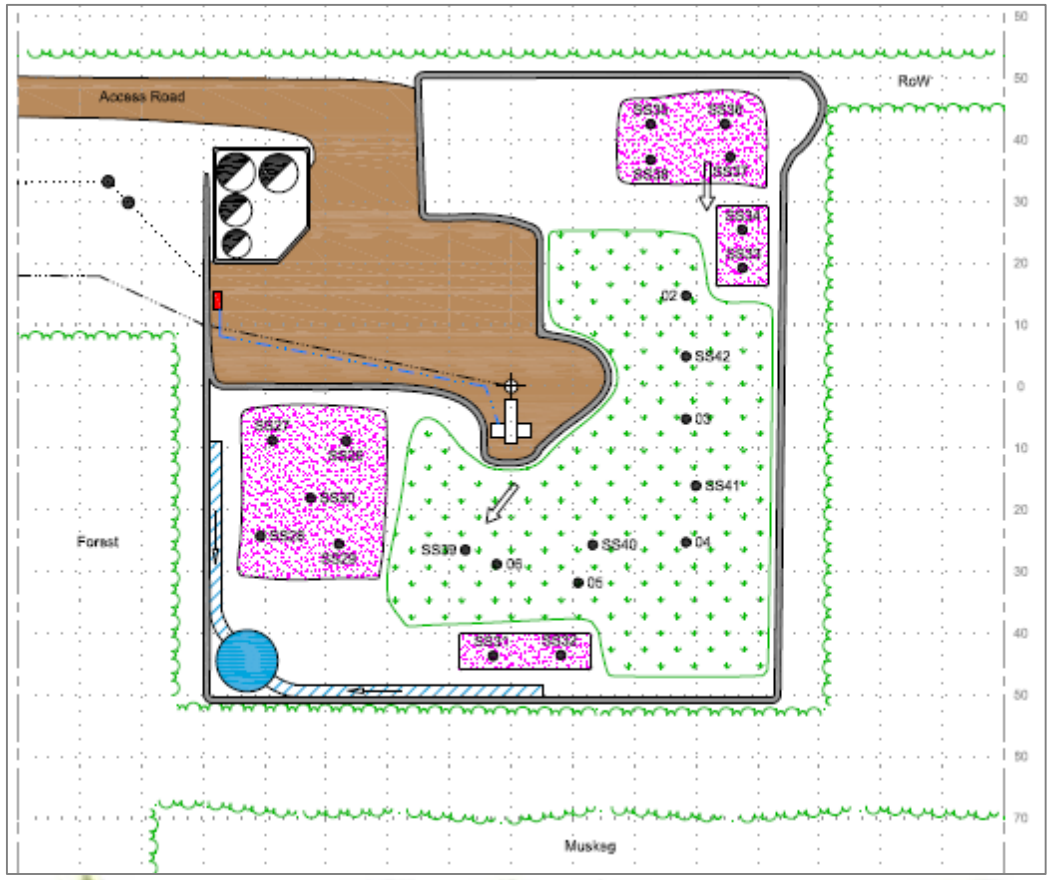
Site 4 – Red Earth 12-33



2,200 m³ of lift #1 was stripped and placed into stockpiles complying with either surface soil or subsoil criteria.

350 m³ of contaminated soil was re-spread to create lift #2:

- Lift #2 T=0 August 2015
  - includes any hot spots from lift #1
  - treatment is completed

Lift #2 Sample Chemistry T = 0					
Depth	PHC	samples		Aug2015	
		# surface	# subsoil	range	average*
0.00-0.20 m	F2	4 of 5	1 of 5	78-1600	612±261
0.00-0.20 m	F3	3 of 5	0 of 5	530-3400	1686±482

#samples exceeding surface soil guideline value

*average mg/kg ± standard error

Lift #2

Depth	PHC	T=0 C_0	x yrs	$C_{1.1\ yrs}$
0.00-0.20 m	F2	612	3.1	82
0.00-0.20 m	F3	1686	0.6	556

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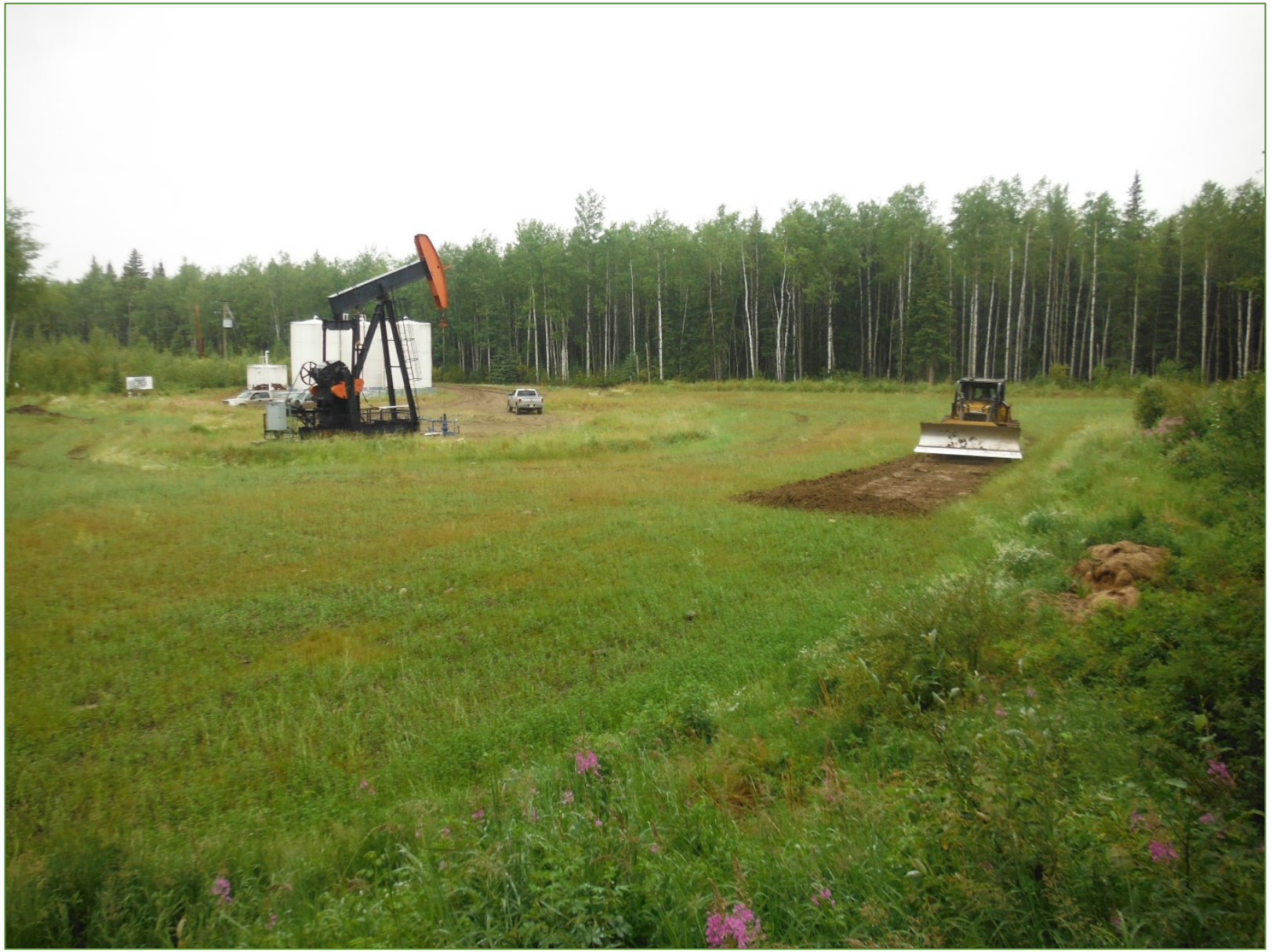
Site 4 – Red Earth 12-33



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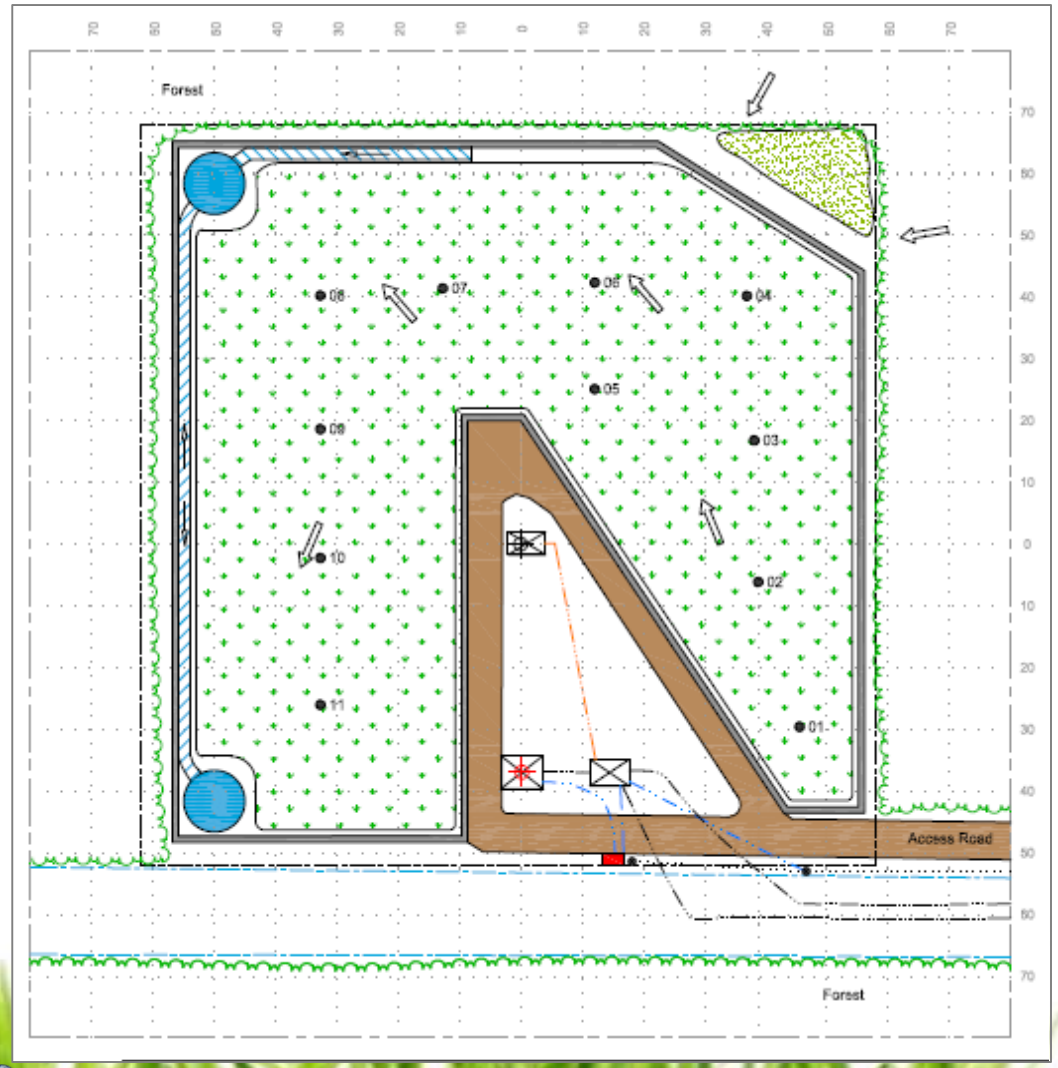
Site 5 – Red Earth 16-29



3,750 m³ of material from former emulsion spills were spread to a depth of 0.45 m:

- Land use – natural
- Soil texture – fine
- AB remediation guideline values F2:
  - surface soil – 150 mg/kg
  - subsoil – 300 or 1000 mg/kg
- AB remediation guideline values F3:
  - surface soil – 1300 mg/kg
  - subsoil – 2600 or 3500 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas sp.*
- Lift #1 T=0 Oct 2011, *used to generate equation*

Lift #1

Depth	PHC	T=0 C_0	$C_{2.5\ yrs}$
0.00-0.20 m	F2	916	106
0.20-0.40 m		826	221
0.00-0.20 m	F3	2394	925

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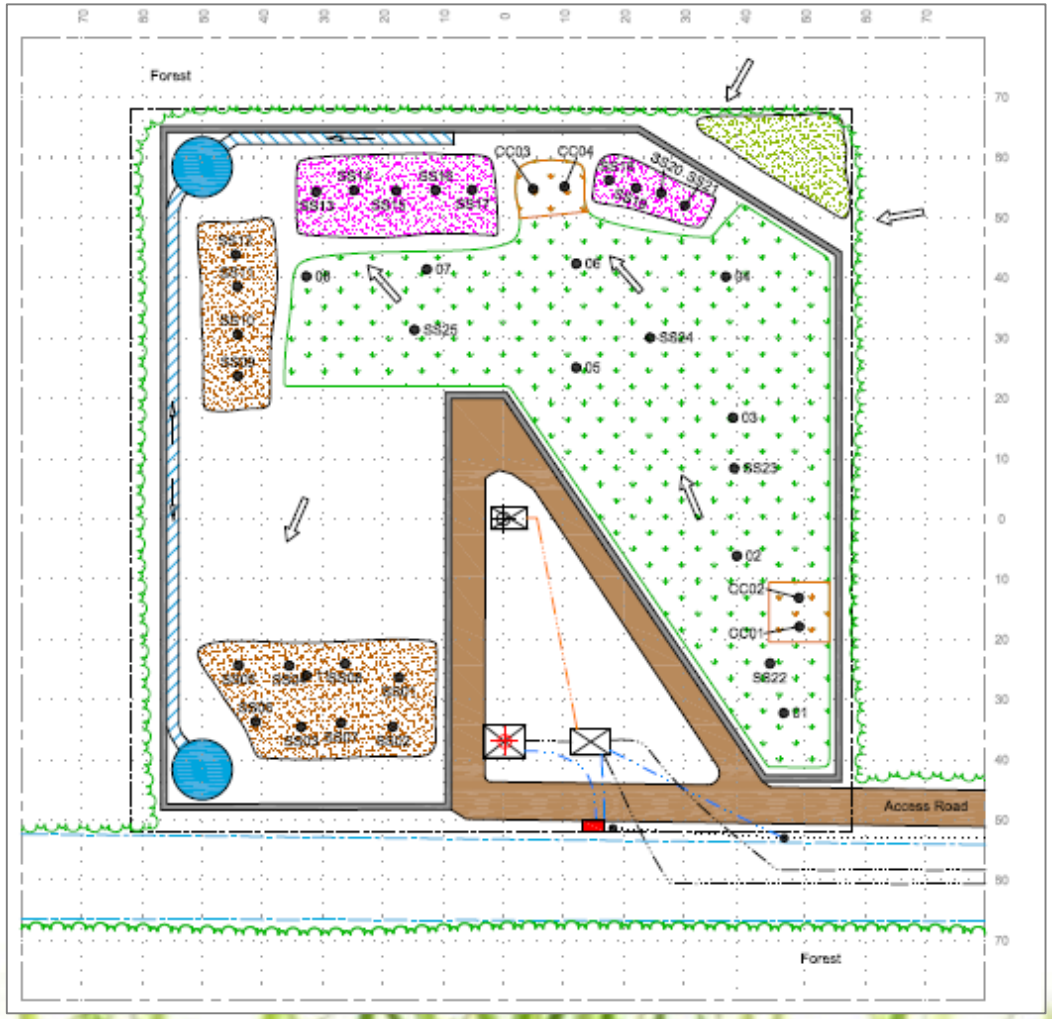
Site 5 – Red Earth 16-29



3,200 m³ of lift #1 was stripped and placed into stockpiles complying with either surface soil or subsoil criteria.

550 m³ of contaminated soil was re-spread to create lift #2:

- Lift #2 T=0 August 2015
  - includes any hot spots from lift #1
  - treatment is completed

Lift #2 Sample Chemistry T = 0					
Depth	PHC	samples		Aug2015	
		# surface	# subsoil	range	average*
0.00-0.20 m	F2	6 of 8	3 of 8	62-1400	669±196
	F3	5 of 8	3 of 8	230-4000	2093±570

samples exceeding surface soil guideline value

*average mg/kg ± standard error

Lift #2

Depth	PHC	T=0 C_0	x yrs	$C_{1.1\ yrs}$
0.00-0.20 m	F2	669	3.3	66
0.00-0.20 m	F3	2093	1.1	459

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Site 5 – Red Earth 16-29

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Site 6 – NWT C-17

Approximately 5,800 m³ of material excavated from former pits and sumps onsite to be treated for PHC contamination resulting from historical drilling activities:

- Land use – industrial
- Soil texture – course
- CCME remediation guideline values F2:
  - surface soil – 260 mg/kg
  - subsoil – 320 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas corrugata and P. marginalis.*
- Lift #1 T=0 June 2008
  - Surface soil treated for salt and PHC.
  - Completed in July 2011 and left in place.
  - Additional material excavated and placed on top of Lift #1 for treatment.

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Site 6 – NWT C-17

Lift #2

Depth	T=0 C_0	x yrs	$C_{2.0\ yrs}$
0.00-0.30 m	549	1.7	84

Lift #3: 900 m³ spread on lift #2. Treated for F2 contamination.

Lift #3

Depth	T=0 C_0	x yrs	$C_{2.1\ yrs}$
0.00-0.30 m	1417	3.8	275

Lift #4: 1,600 m³ spread on Lift #3. Treated for F2 contamination and 1250 m³ stripped in June 2017.

Lift #4

Depth	T=0 C_0	x yrs	$C_{0.3\ yrs}$
0.00-0.30 m	644	2.0	360

Lift #5: 350 m³ mixed with 750 m³ of additional soil. Treated for F2 contamination starting June 2017.

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Site 6 – NWT C-17 Challenges

Site 6 – NWT C-17 Challenges

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Site 6 – NWT C-17 Challenges

Lift #4 Sample Chemistry T = 0							
Depth	PHC	Jul 2016			Sep 2016		
		# samples	range	average*	# samples	range	average*
0.00-0.30 m	F2	23 of 25	57-1350	644±73	12 of 25	50-802	360±45

samples exceeding surface soil guideline value

*average mg/kg ± standard error

LEGEND

- Wellbore
- Sample Location (Remediated)
- Sample Location (Exceedance)
- Control Area
- Former Gel Chem. Impacted Material Area
- Topsoil Stockpile
- Historical Excavation
- Plant Growth Area
- CFIA Control Area
- Field Trailer
- Field Equipment
- Shrubs / Trees Edge
- Slope Direction

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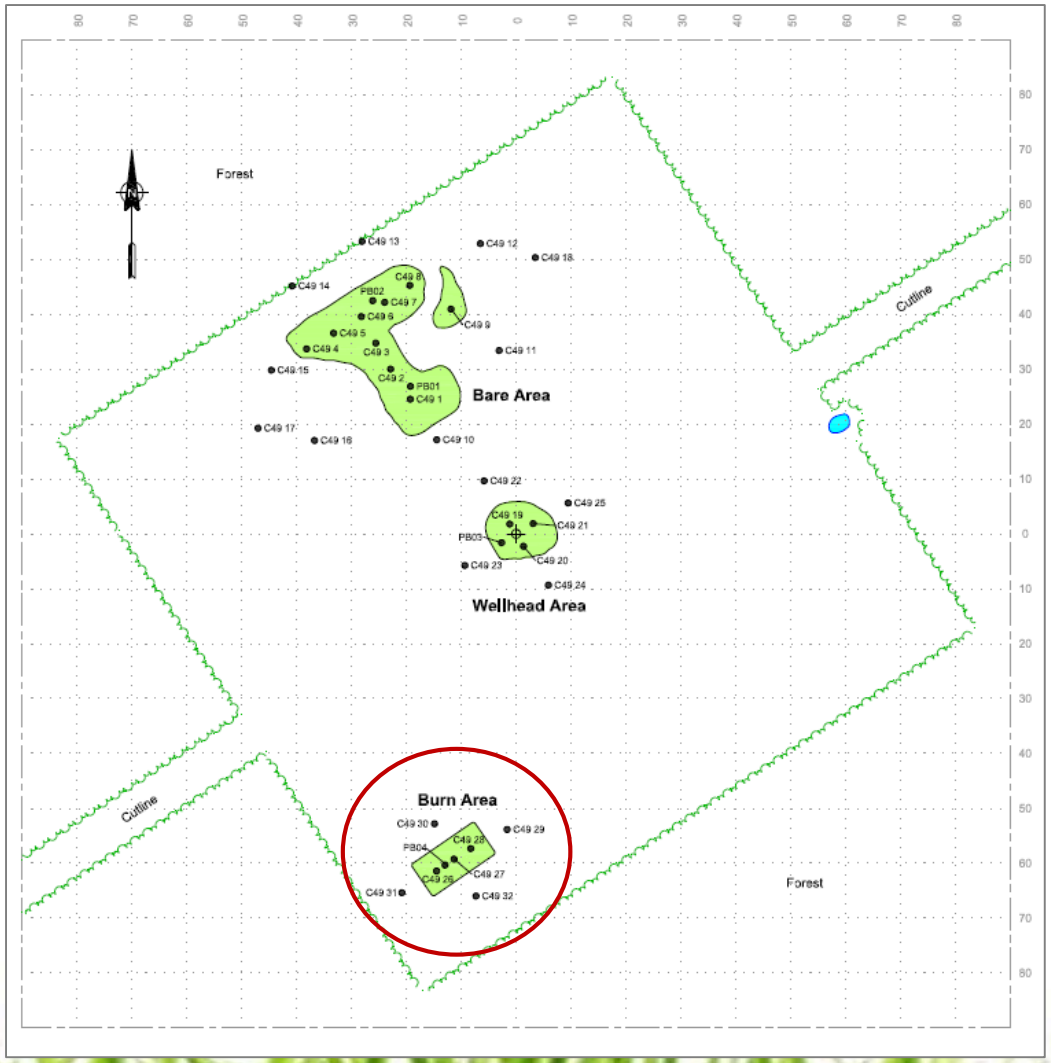
Site 6 – NWT C-17

Site 7 – NWT C-49



A small burn area on a remote exploratory wellsite showed F2 and F3 concentrations that exceeded the CCME remediation guideline values:

- Land use – industrial or parkland
- Soil texture – fine
- CCME remediation guideline values F2:
  - industrial soil – 260 mg/kg
  - parkland soil – 150 mg/kg
- CCME remediation guideline values F3:
  - industrial soil – 1700 mg/kg
  - parkland soil – 1300 mg/kg
- Seed – Arg, Prg, TF
- PGPR – *Pseudomonas sp.*
- In situ T=0 July 2013

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Site 7 – NWT C-49

In situ Sample Chemistry T = 0				
Depth	PHC	# samples	Jul 2013	
			range	average*
0.00-0.25 m	F2	1 of 3	10-600	208±196
0.25-0.50 m	F2	2 of 3	25-2400	858±772

samples exceeding surface soil guideline value

*average mg/kg ± standard error

Lift #1

Depth	T=0 C_0	x yrs	$C_{1.0\ yrs}$
0.00-0.25 m	208	0.7	55
0.25-0.50 m	858	3.9	10

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Predictive Equation Summary F2

site	layer #	depth	C_0	goal	predicted yrs	C_{end}	actual yrs	notes
1	1	0.00-0.25 m	310	150 or ***300***	1.6	66	0.9	
		0.25-0.50 m	342		1.8	126	2.4	
	2	0.00-0.25 m	270		1.3	115	0.7	
		0.25-0.50 m	333		***0.2***	212	0.7	
2	1	0.00-0.25 m	311	150 or ***300***	1.6	138	1.6	
		0.25-0.50 m	403		2.2	336	1.6	removed before complete
	2	0.00-0.25 m	161		0.2	253	0.7	removed before complete
		0.25-0.50 m	417		***0.7***	247	0.7	
3	2	0.00-0.20 m	204	150	0.7	23	1.0	no spring assessment
4	2	0.00-0.20 m	612	150	3.1	82	1.0	
5	2	0.00-0.20 m	669	150	3.3	66	1.0	
6	2	0.00-0.30 m	549	260 or ***520***	1.7	84	2.0	
	3	0.00-0.30 m	1340		***2.1***	275	2.0	
	4	0.00-0.30 m	644		***2.1***	360	0.3	
	5	0.00-0.30 m	381		0.9	152	0.3	
7	1	0.00-0.25 m	208	260	0.7	55	1.0	no spring assessment
		0.25-0.50 m	858		2.7	10	0.3	
8	1	0.00-0.30 m	343	150	1.8	335	1.0	project terminated
9	1	0.25-0.50 m	512	150	2.7	309	1.3	project terminated
19 layers			**467**		**1.7**	**171**	**1.1**	**all layers**
15 layers			**497**		**1.6**	**147**	**1.1**	**all completed layers**

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Predictive Equation Summary F3

site	lift #	depth	C_0	goal	predicted yrs	C_{end}	actual yrs	notes
4	2	0.00-0.20 m	1686	1300	0.6	556	1.0	
5	2	0.00-0.20 m	2093	1300	1.1	459	1.0	
8	1	0.00-0.30 m	1950	1300	1.7	1300	1.7	
9	1	0.00-0.25 m	1714	1300	1.6	1399	1.0	project terminated
		0.25-0.50 m	3885		3.9	2657	1.3	project terminated
10	1	0.00-0.25 m	2267	1300	2.7	1786	1.3	project terminated
		0.25-0.50 m	1881		2.5	1096	1.0	project terminated
7 layers			**2211**		**2.0**	**1322**	**1.2**	**all layers**
4 layers			**1903**		**1.5**	**853**	**1.2**	**all completed layers**

Conclusions:

- The predictive equations are conservative and remediation is almost always achieved before the predicted amount of time.
- Number of growing seasons is a better timeline to work with.
  - Often seeding is done in the fall which will increase the # of following year growth season months.

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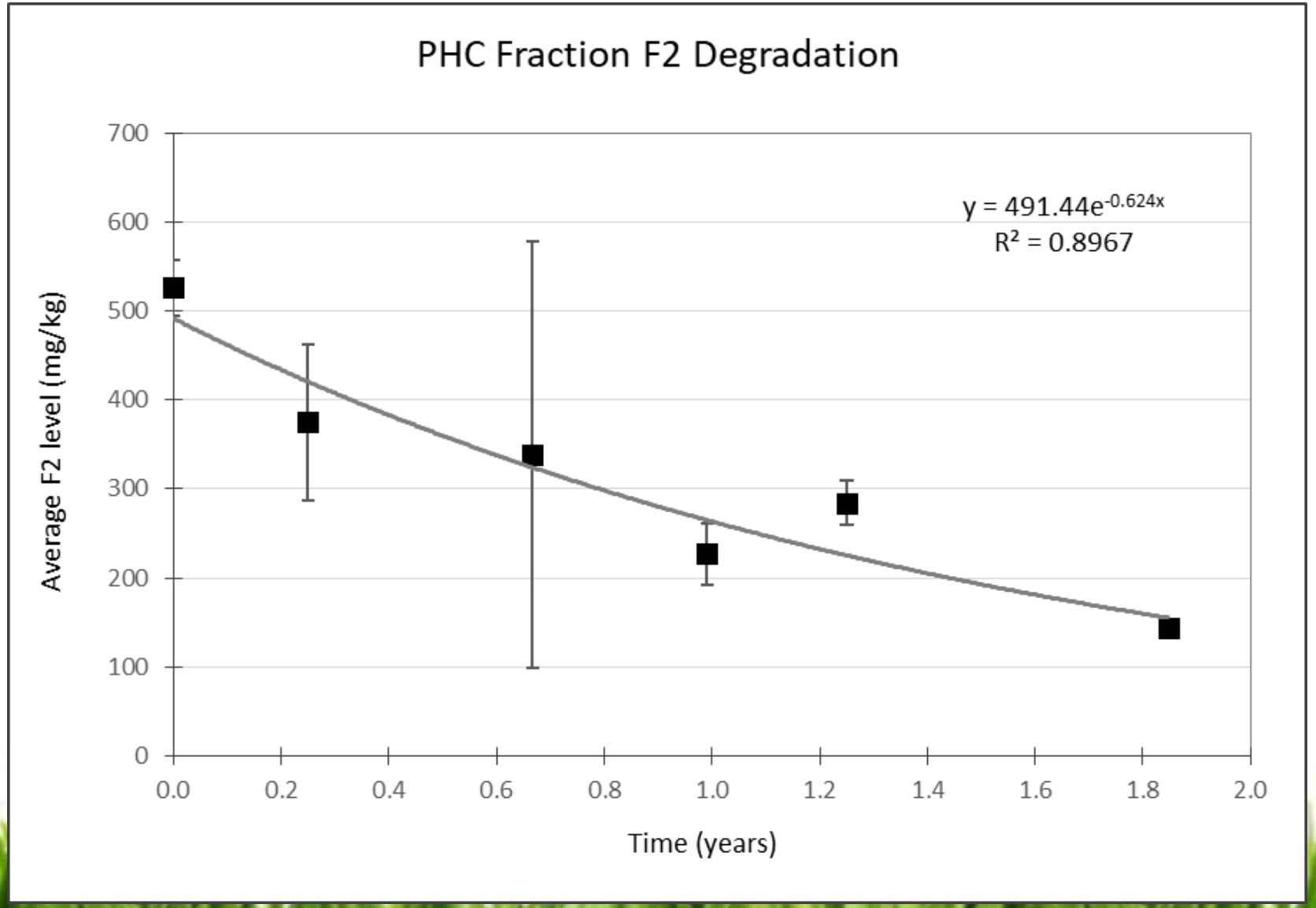
Revised PHC Fraction F2 Predictive Equation

- Used data collected from commercial phytoremediation programs over last 6 years.
- Starting F2 concentrations (C_0) for the updated kinetic equation data ranged from 400-600 mg/kg with an average of 526 mg/kg.
- The target remediation guideline value (y) was 150 mg/kg with the exception of one northern site which had a target remediation guideline value of 260 mg/kg.
- F2 revised: $y = C_0 e^{-0.624x}$
- Insufficient data was available to update the F3 kinetic equation.

Revised PHC Fraction F2 Equation



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Questions?

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