Presented at 2014 Remediation Technologies Symposium – Banff, Alberta, Canada

New Technologies for the Cleanup of Weathered Petroleum in Silt and Clay

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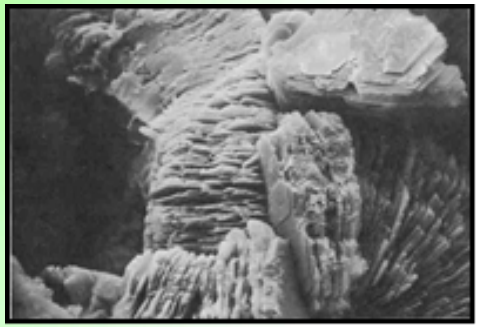
Alpha environmental

HARTCROWSER

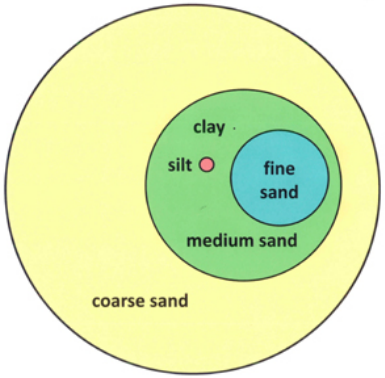
BIOREMEDIATION SPECIALISTS L.L.C.
A Billion Years in the Making™

The Problem

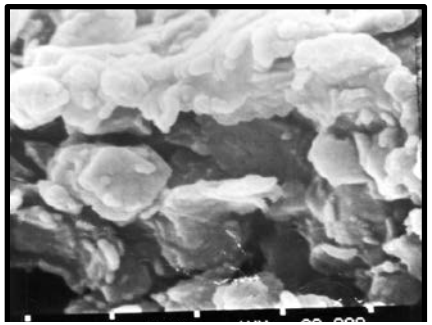
- Fine-grained materials
  - Retain contaminants in pores
  - Resist introduction of amendments
- Real world
  - Differing transmissivity impacts amendment distribution
- Petroleum doesn't like water or polar compounds



Natural Kaolinite Clay Structure
1,600x Magnification

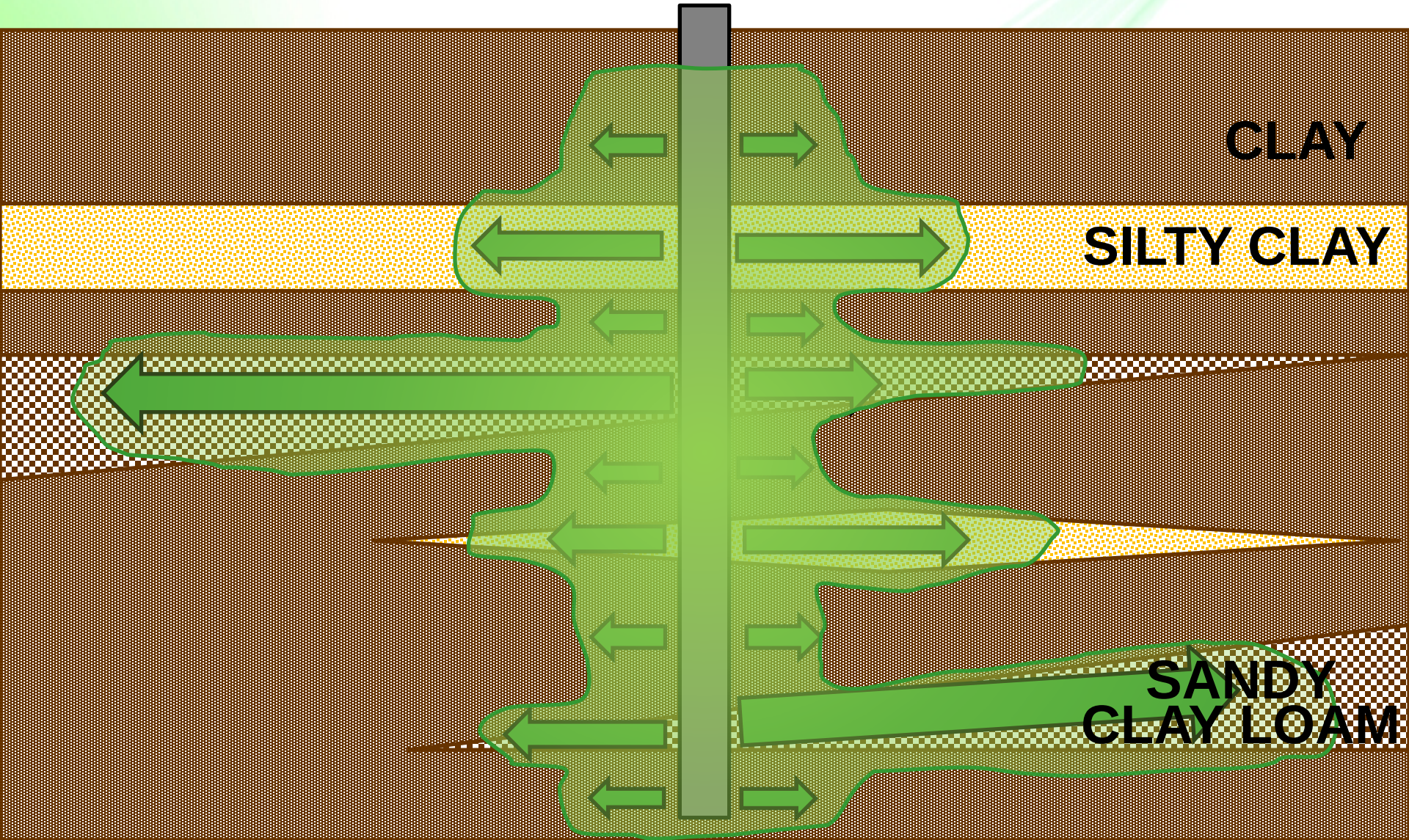


Soil Grain Size Distribution

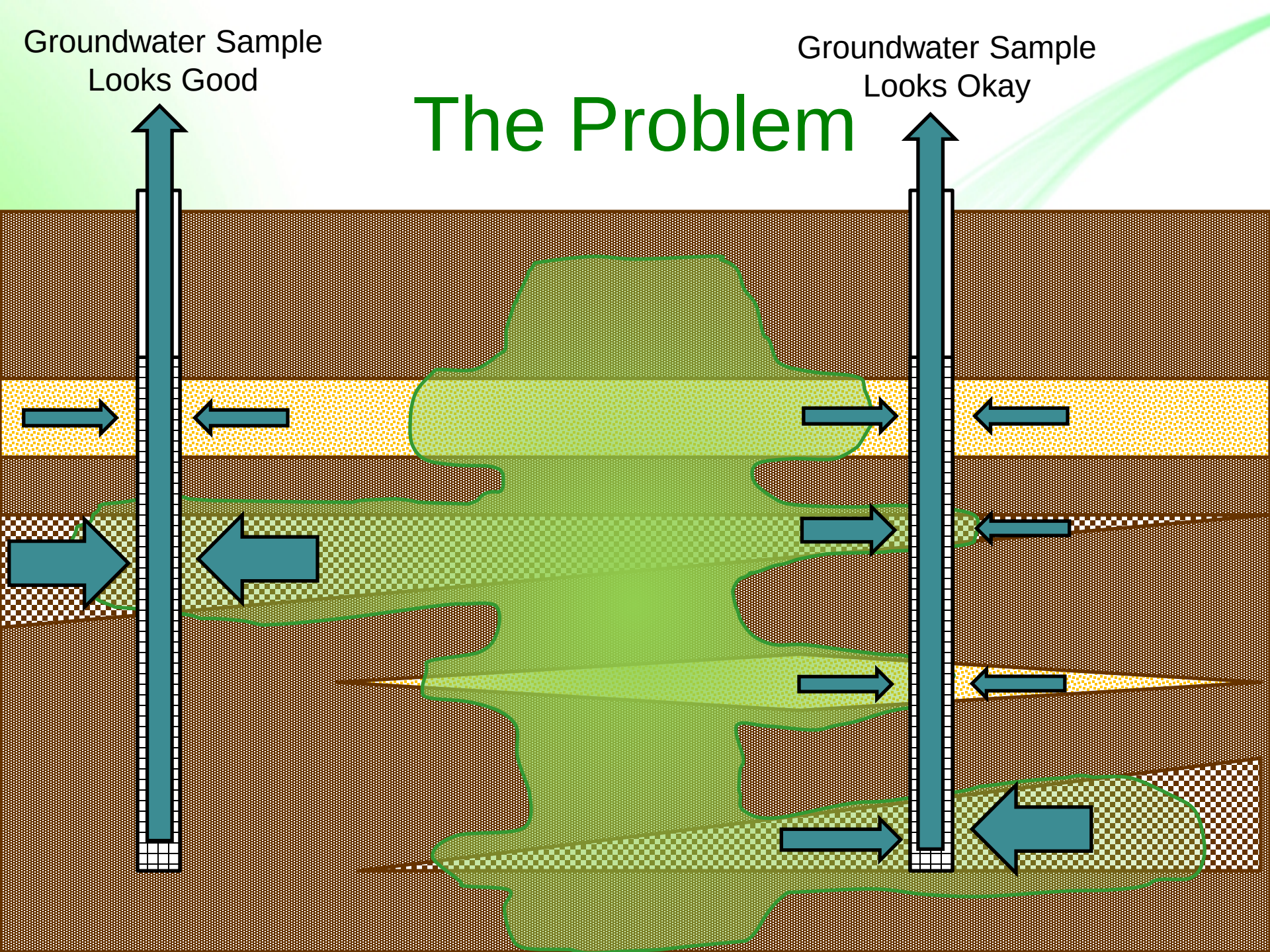


Natural Smectite Clay Structure
23,00x Magnification

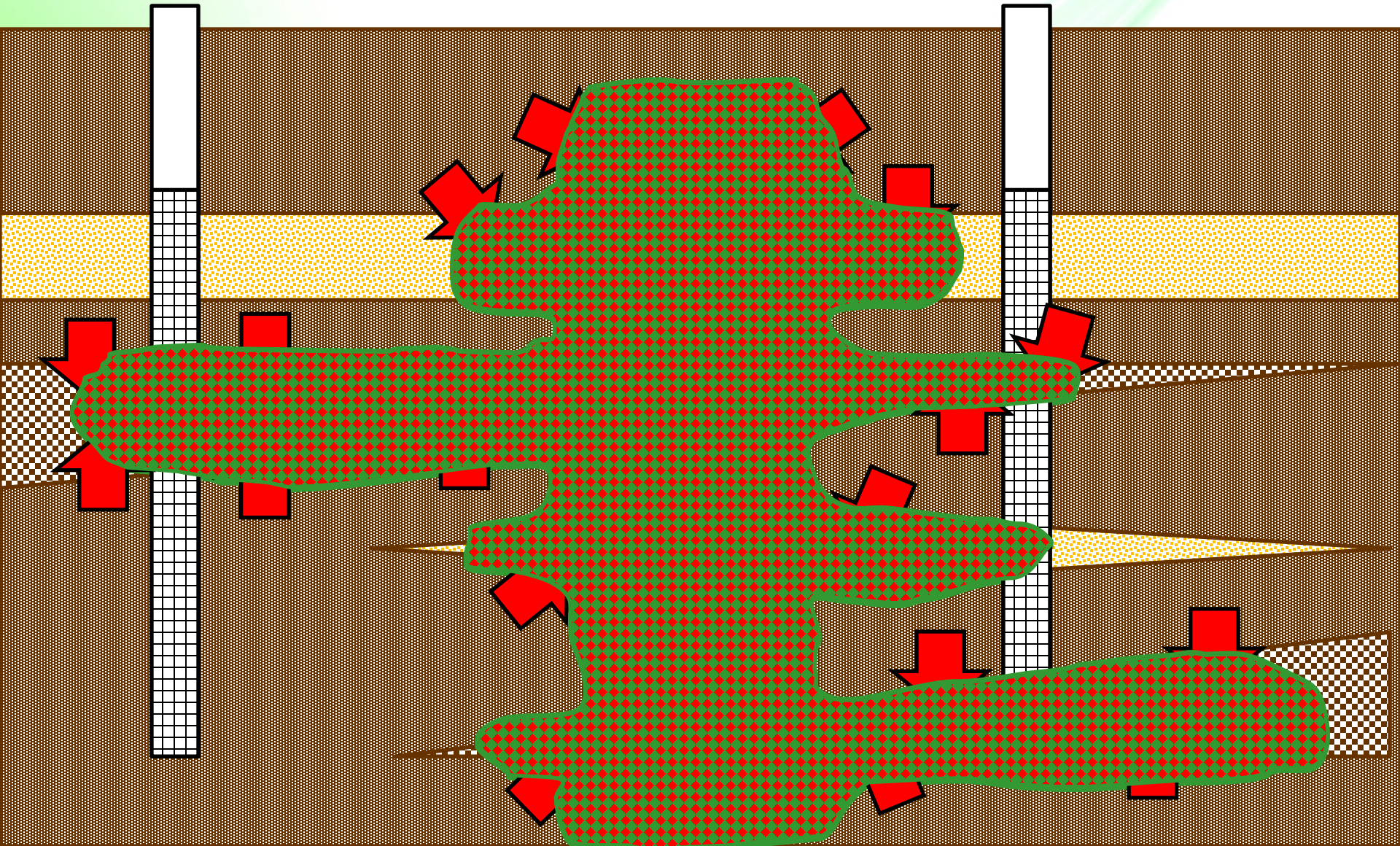
The Problem



The Problem


Groundwater Sample
Looks Good
Groundwater Sample
Looks Okay

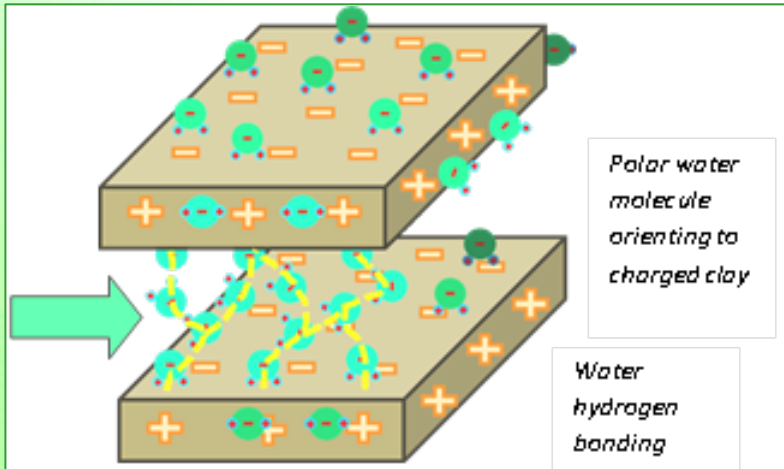
The Problem



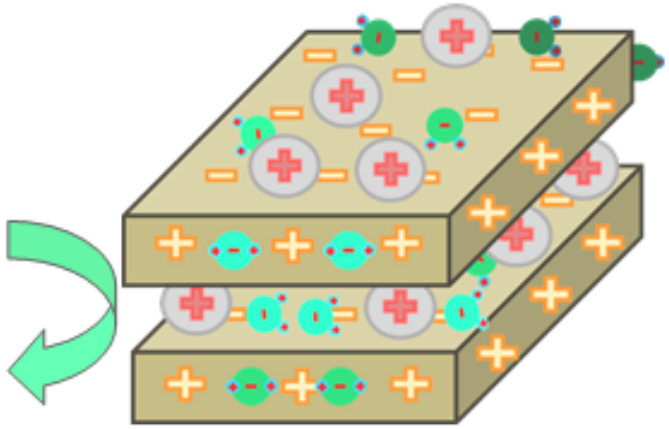
First Solution – NovIOX™

- Ion-exchange resin to treat soil
  - Breaks the forces that form clay sheets
  - Disrupts ionic bonding between soil and water
  - Increases transmissivity 1 to 3+ orders of magnitude
  - Clay behaves more like fine sand
- Chemical oxidation activity
  - Directly reacts with weathered petroleum
  - Heavier and more weathered, more reactions
- Surfactant activity
  - Lifts hydrophobic compounds from soil matrix
  - Improves bio-availability

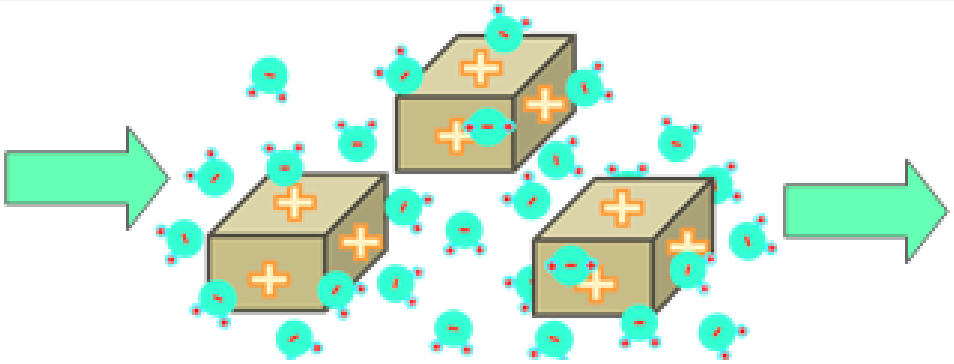
NovIOX™ Ion-Exchange Activity



Typical undisturbed clay

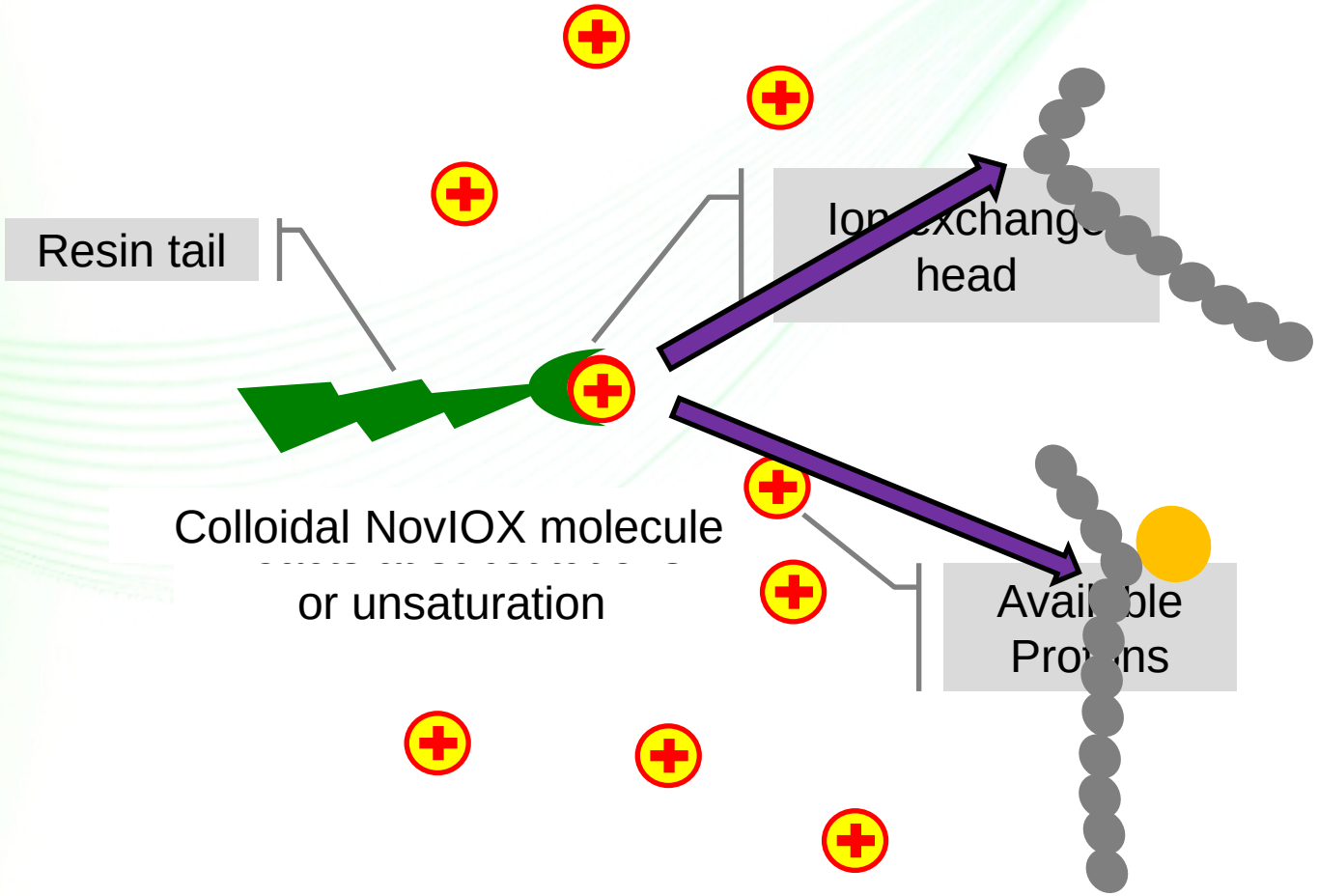


Cation-poisoned clay
(Produced water)

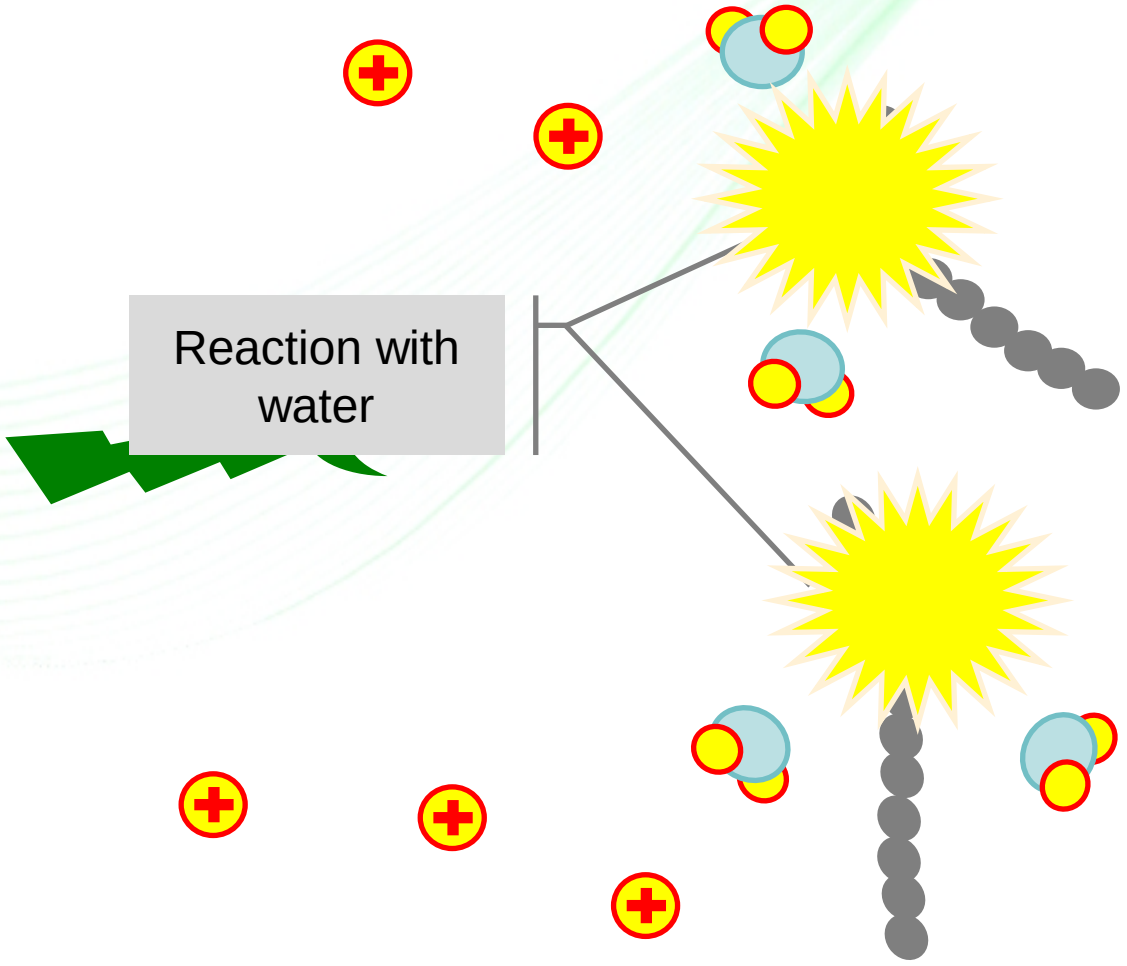


NovIOX-treated silt and clay
loses platelet configuration

NovIOX™ Oxidation Activity



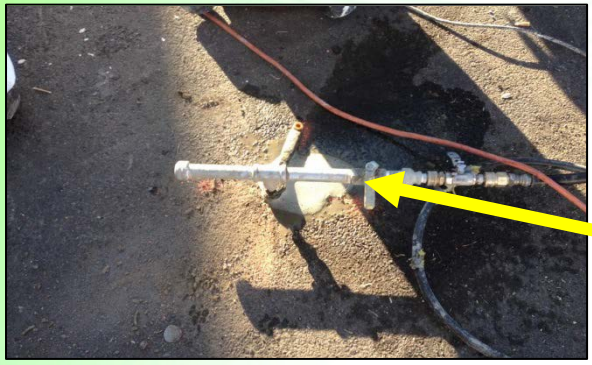
NovIOX™ Oxidation Activity



NovIOX™ Oxidation Activity

Petroleum is converted quickly degradable organics

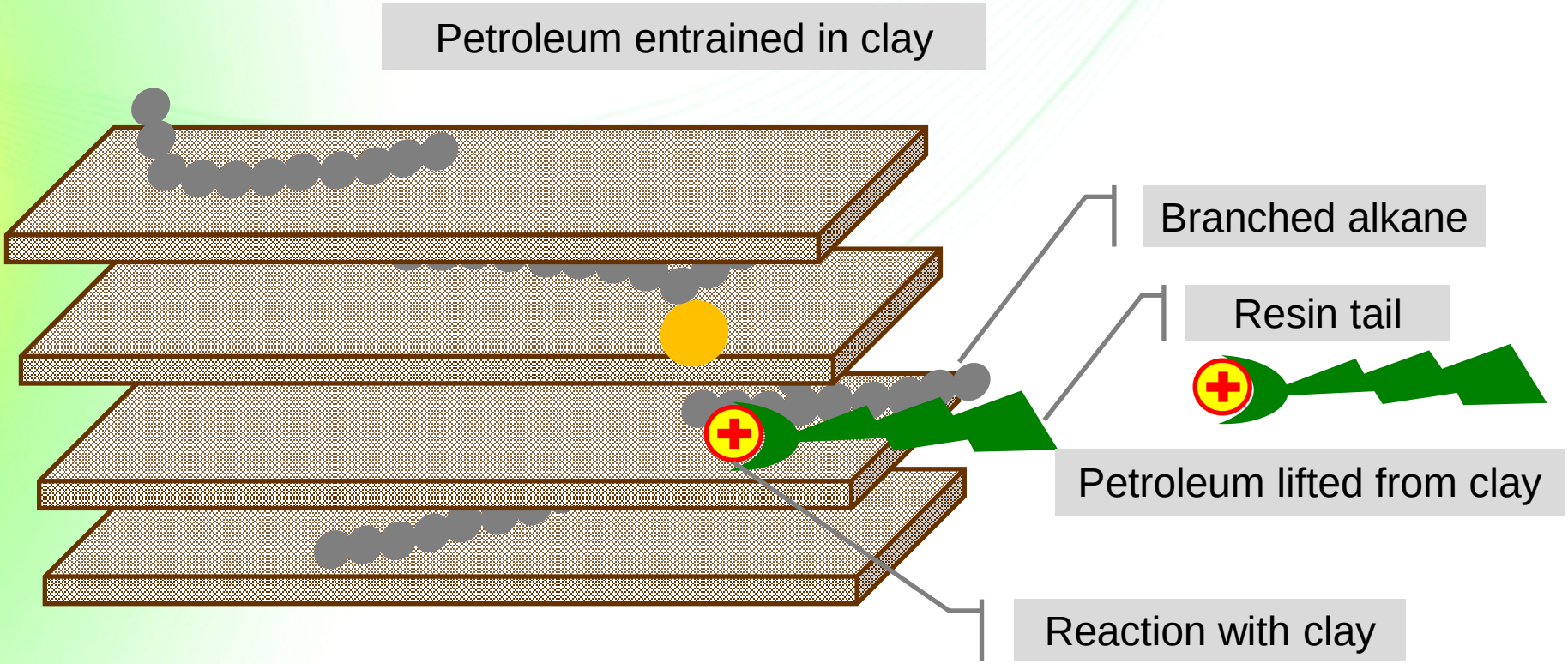
After reaction, various fatty acids, aldehydes, carbon dioxide, etc. are formed



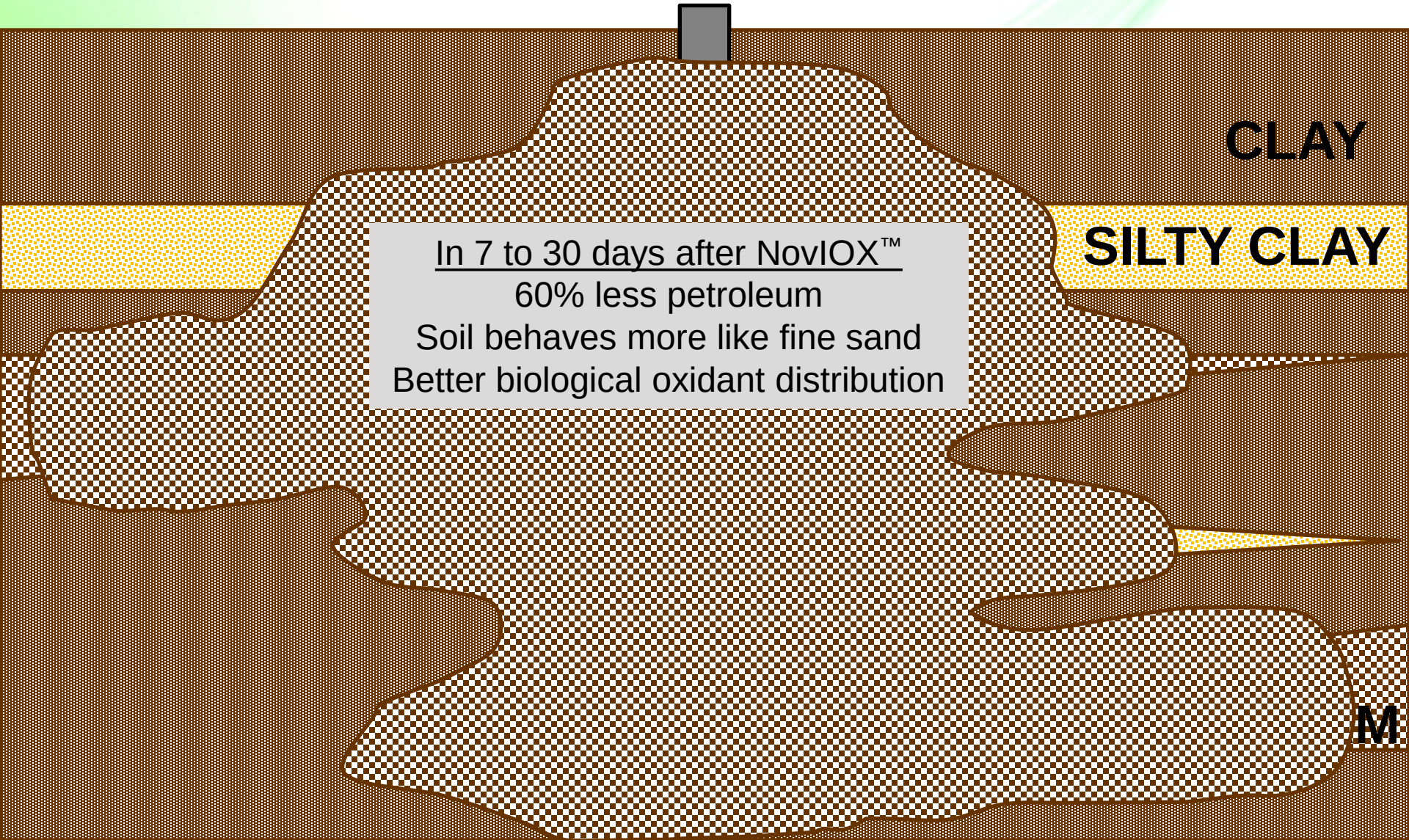
Note: Chemists, please calm down. This illustration is for the non-chemists.

Foam production provides a real-time, qualitative understanding of petroleum distribution

NovIOX™ Surfactant Activity

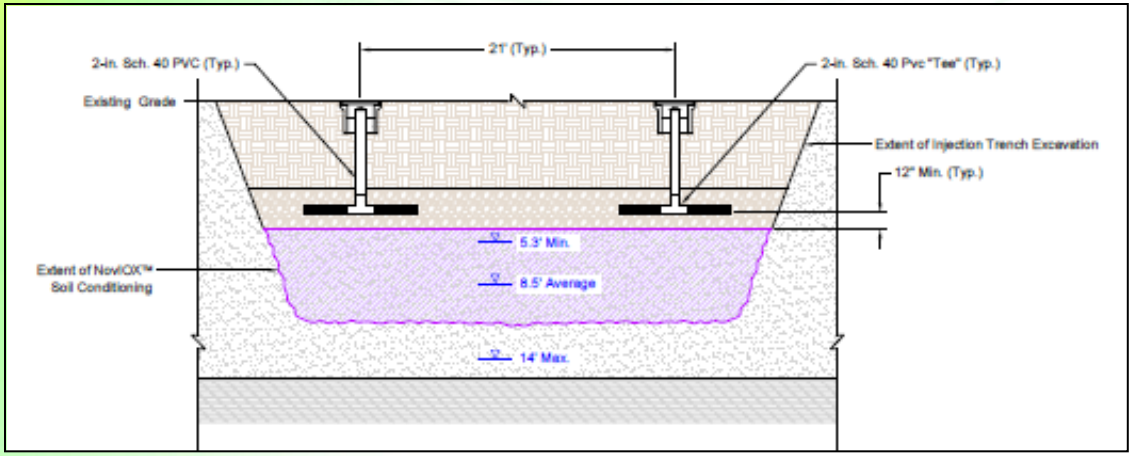


The Solution



Other NovIOX™ Applications

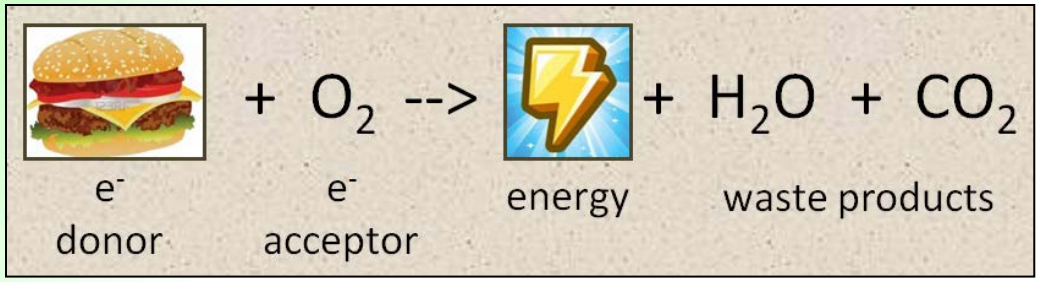
- Improve slug injection performance/distribution
- Well redevelopment
- Reduce injection well fouling
- TSS reduction



Second Solution – AnoxEA® AQ

– AnoxEA® AQ biological oxidant

- Allows microbes to “breathe” petroleum and fatty acids
- Patent-pending blend of multiple electron acceptors
- Nutrients to support microbial development
- 37% available oxygen by weight
- Fully water soluble
- Reduces metals mobility (lead, arsenic)



AnoxEA® Stand-Alone Performance

Treatment Week	Concentration (µg/L)	
	Gasoline	Diesel
Source Area Well MW-2		
+ 8	26,000	3,521
+ 16	7,300	712
+ 25	3,100	620
+ 45	850	63

Treatment Month	Diesel Concentration (mg/kg)
+ 0 (July)	2,616
+ 3 (October)	1,156
+ 10 (May)	372
+ 13 (August)	244

Treatment Week	Concentration (mg/kg)	
	Gasoline	Diesel
AnoxEA™ Treated Soil		
+ 0	2,330	4,040
+ 4	712	2,755
+ 16	336	617
Untreated Land-Farm Soil		
+0	2,285	2,535
+16	1,233	1,956

Summary

- NovIOX™ chemical oxidant
  - Improves soil permeability
  - Destroys/converts 60% of petroleum in soil in 14 days
  - Surfactant activity to release petroleum
- AnoxEA® AQ biological oxidant
  - Rapidly develops petroleum-degrading bacteria
  - Provides source of oxygen
  - Petroleum reduction dependent on soil type

Together…

Advanced Multi-Oxidative Remediation, or AMOR™

(Patent pending)

Case Studies

- Heavy oil in dense clayey silt
  - Pilot test showing mobilization and destruction
- Weathered heating oil in silty clay
  - Real estate transaction, 45 day closure
- Weathered heating oil in silty clay
  - Very high concentrations reduced in 38 days to closure
- Weathered gasoline in high organic silt/sediments
  - Lake front cleanup completed in 9 months

In Situ Application Study #1

– Source area pilot test at active gas station
  - Very dense clayey silt with sand
  - Oil and fuel odor in tank pit monitoring well
  - Site investigation conducted
  - AMOR™ source area pilot test

Mobilize and destroy

In Situ Application Study #1

Substantial source mobilization and destruction

Fatty acids and biomass

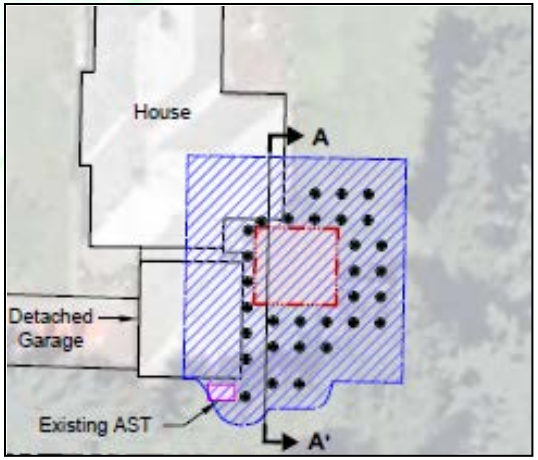
Well Name	Date	TPH - Gasoline Range	TPH - Diesel Range	TPH - Oil Range	Total Lead	Volatile Organic Compounds: Benzene	Toluene	Ethylbenzene	Total Xylenes	Total Oragnic Carbon
		Concentration in µg/L (ppb)								(mg/L)
Treatment Area Shallow Monitoring Wells										
MW-1	15-Dec-11	**9,100**	**930**	**330 Y**	**4.9**	**120**	**780**	**200**	**1,420**	NS
	24-Jul-12	**6,500**	**520**	< 250	< 2.0	**330**	**780**	**100**	**660**	**9.9**
	20-Sep-12	**6,500**	**540**	< 240	NS	**230 B**	**710**	**120 B**	**810**	**8.9**
	11-Dec-12	**6,000**	**790**	< 240	< 2.0	**430**	**550**	**70**	**1,250**	**9.8**
	Injections performed Feburary 12 - 13, 2013									
	4-Mar-13	**7,800**	**71,000**	**77,000**	**18**	**300**	**980**	**130**	**1,240**	**1,800**
	22-May-13	**20,000**	**3,700**	**44 J**	**2.5**	**720**	**2,600**	**360**	**2,850**	**710**
	9-Sep-13	**12,000**	**2,000**	**56 J**	**0.15**	**380**	**1,400**	**230**	**1,760**	**48**
MW-2	15-Dec-11	**19,000**	**4,500**	**540**	**4.7**	**5,700**	**1,700**	**660**	**2,930**	NS
	24-Jul-12	**18,000**	**2,700**	< 240	**2.0**	**6,500**	**1,700**	**680**	**3,250**	**6.2**
	20-Sep-12	**18,000**	**3,200**	< 250	NS	**5,800**	**940**	**580**	**2,440**	**26**
	11-Dec-12	**29,000**	**2,700**	< 240	**0.90**	**6,500**	**6,400**	**1,700**	**8,300**	**15**
	Injections performed Feburary 12 - 13, 2013									
	4-Mar-13	**25,000**	**16,000**	**15,000**	**7.6**	**6,900**	**3,000**	**760**	**3,790**	**1,100**
	22-May-13	**57,000**	**3,900**	< 480	**0.41**	**7,700**	**7,600**	**1,200**	**6,300**	**89**
	9-Sep-13	**59,000**	**2,800**	< 240	**0.25**	**7,000**	**6,500**	**500**	**8,300**	**48**

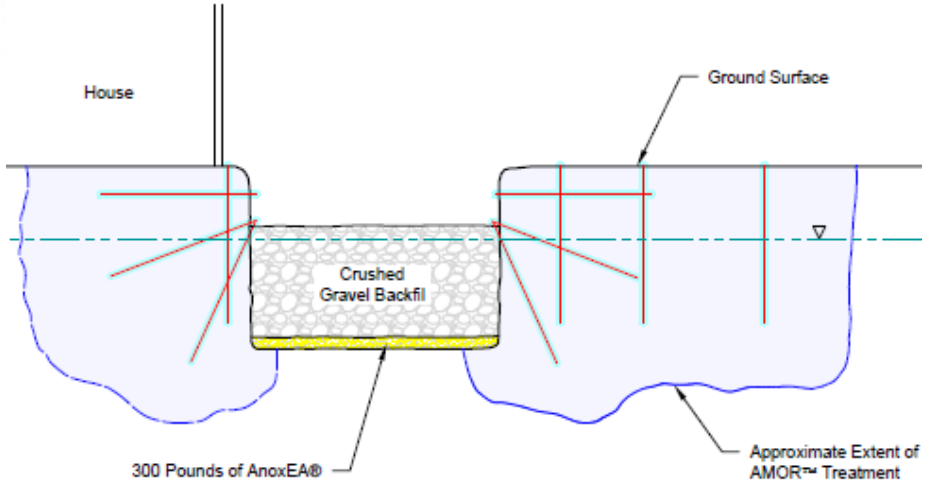
In Situ Application Study #2

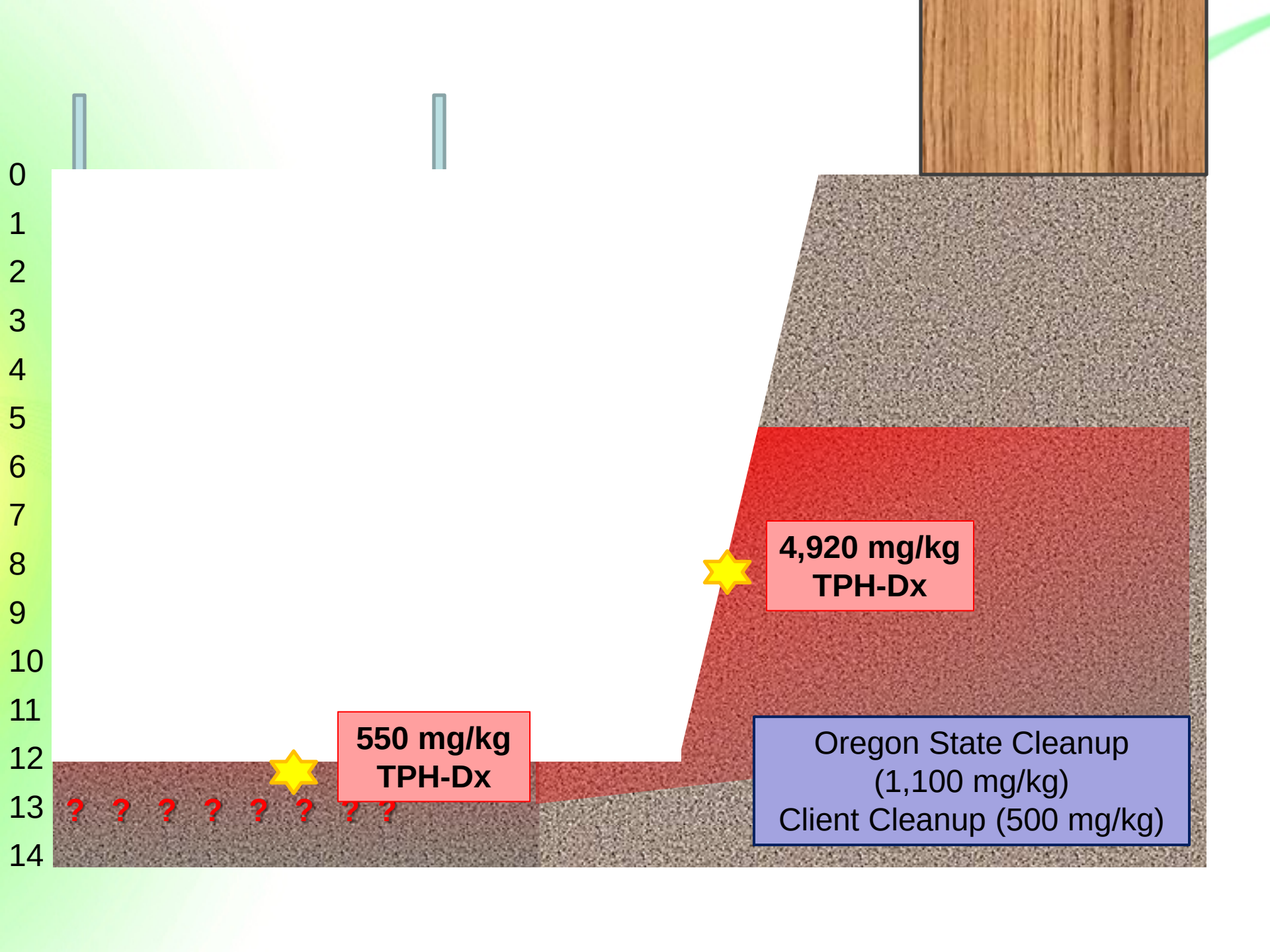
- Case example of weathered heating oil
  - Silty clay
  - Legacy heating oil UST (>10 years)
  - Real estate transaction
  - Standard excavation/removal initially conducted
  - Excavation 16’ W x 16’ L x 12’ D
  - 114 cu.yds. of soil removed before AMOR™
  - Further excavation not practical

In Situ Application Study #1

- Excavation up to structural limits
- Treatment goals
  - Reduce soil TPH
  - Reduce shallow groundwater TPH
  - Eliminate vapor intrusion risk to home



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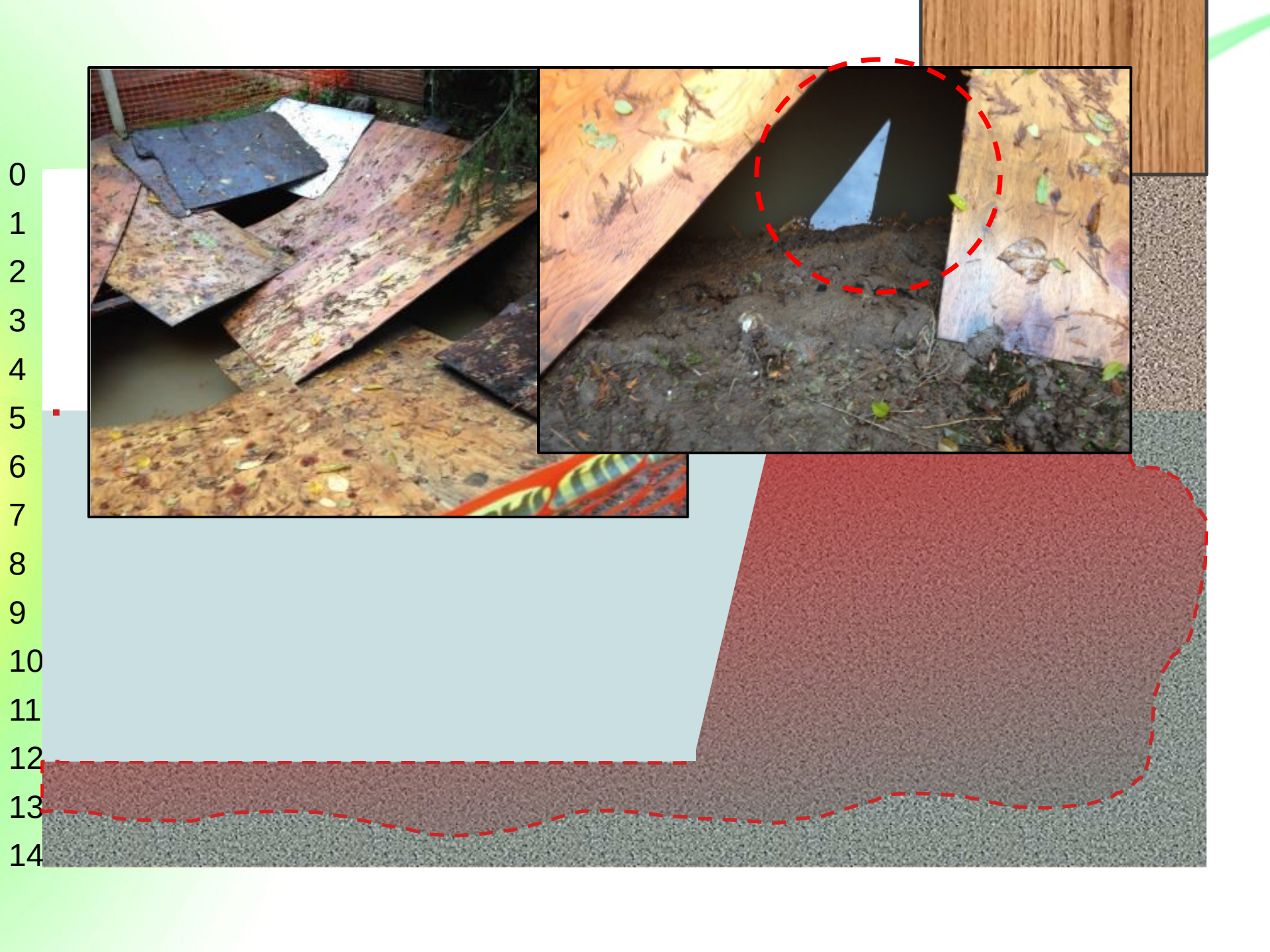
4,920 mg/kg
TPH-Dx
550 mg/kg
TPH-Dx
? ? ? ? ? ? ? ?
Oregon State Cleanup
(1,100 mg/kg)
Client Cleanup (500 mg/kg)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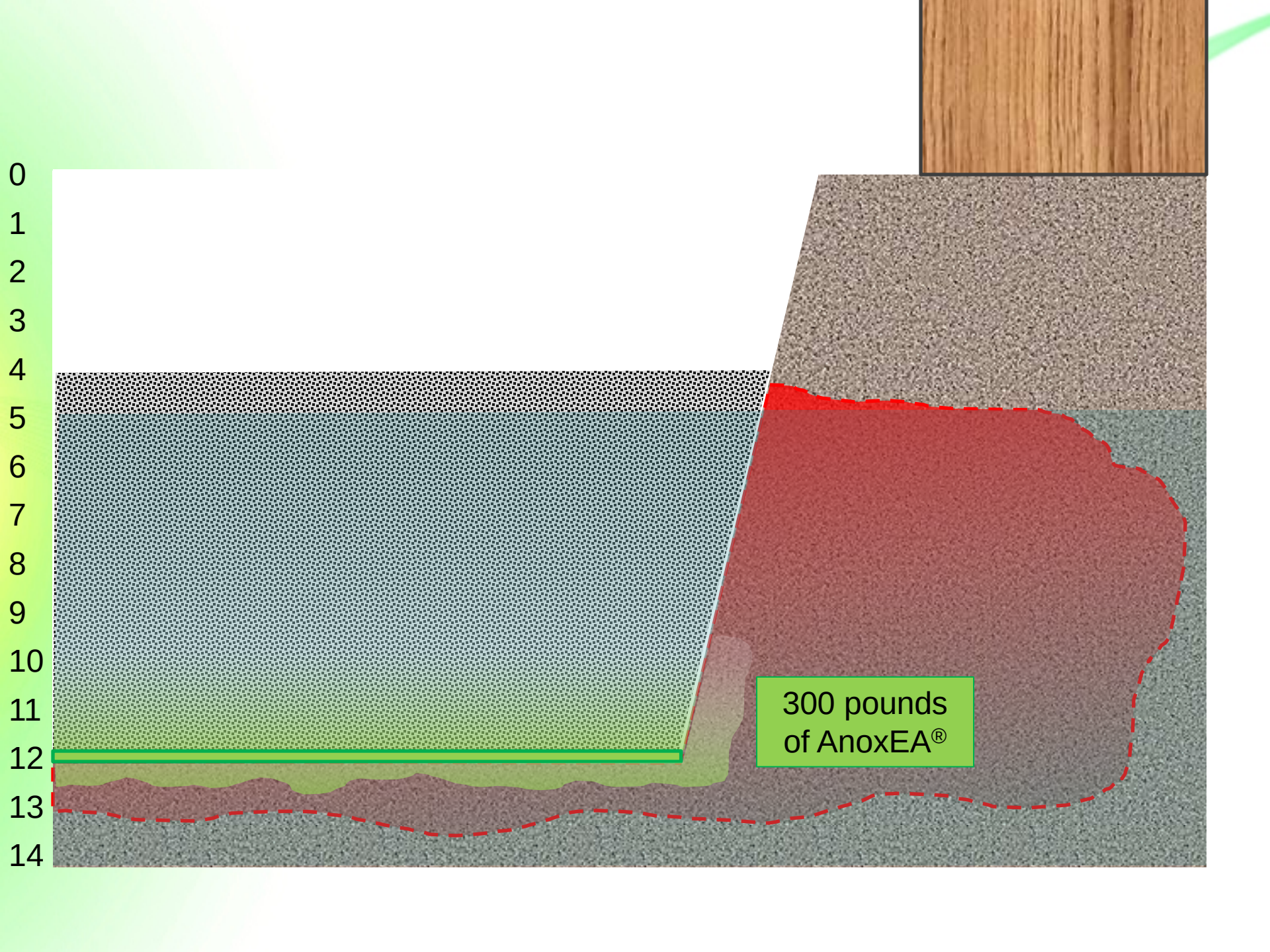
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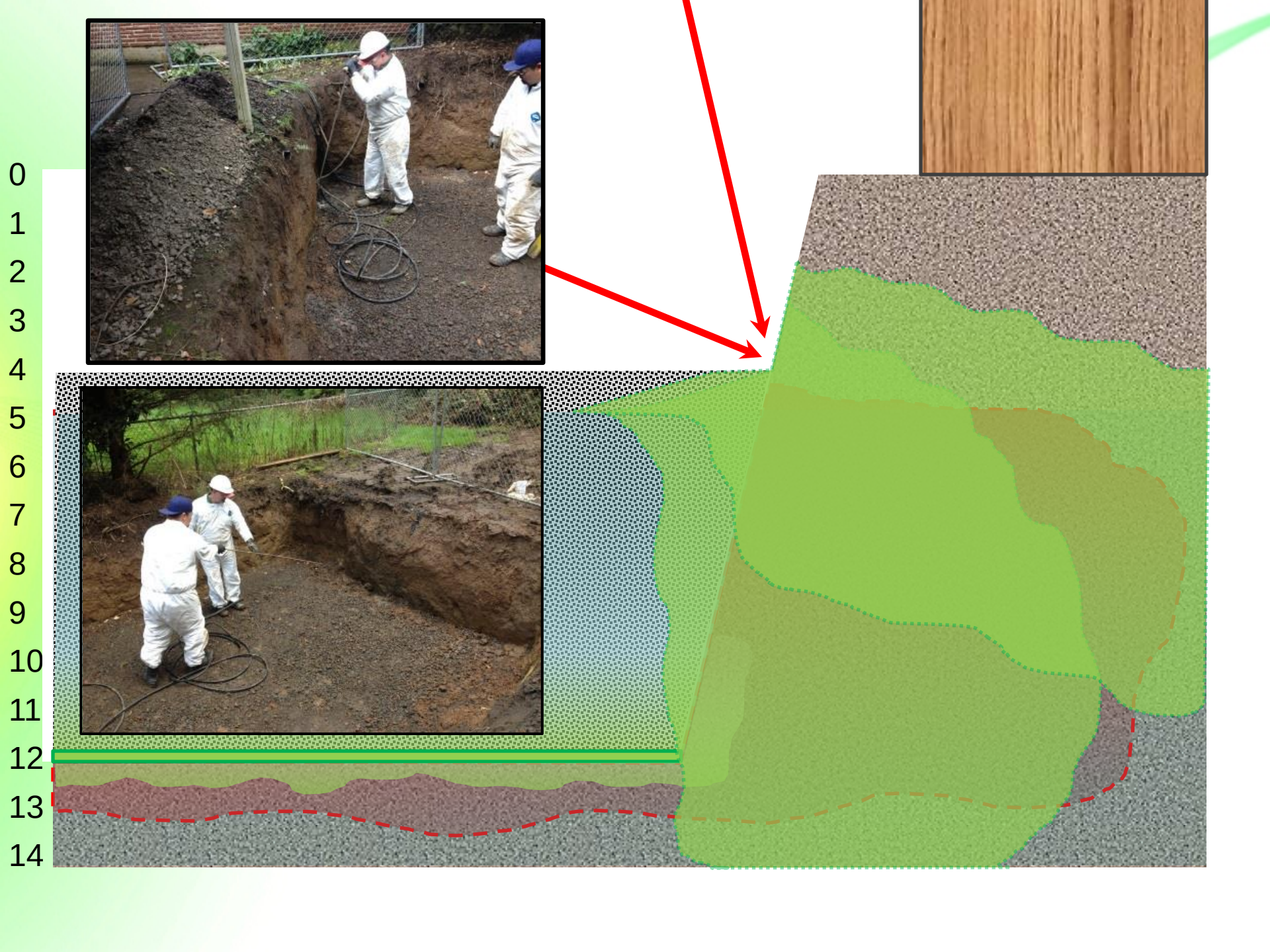
300 pounds
of AnoxEA®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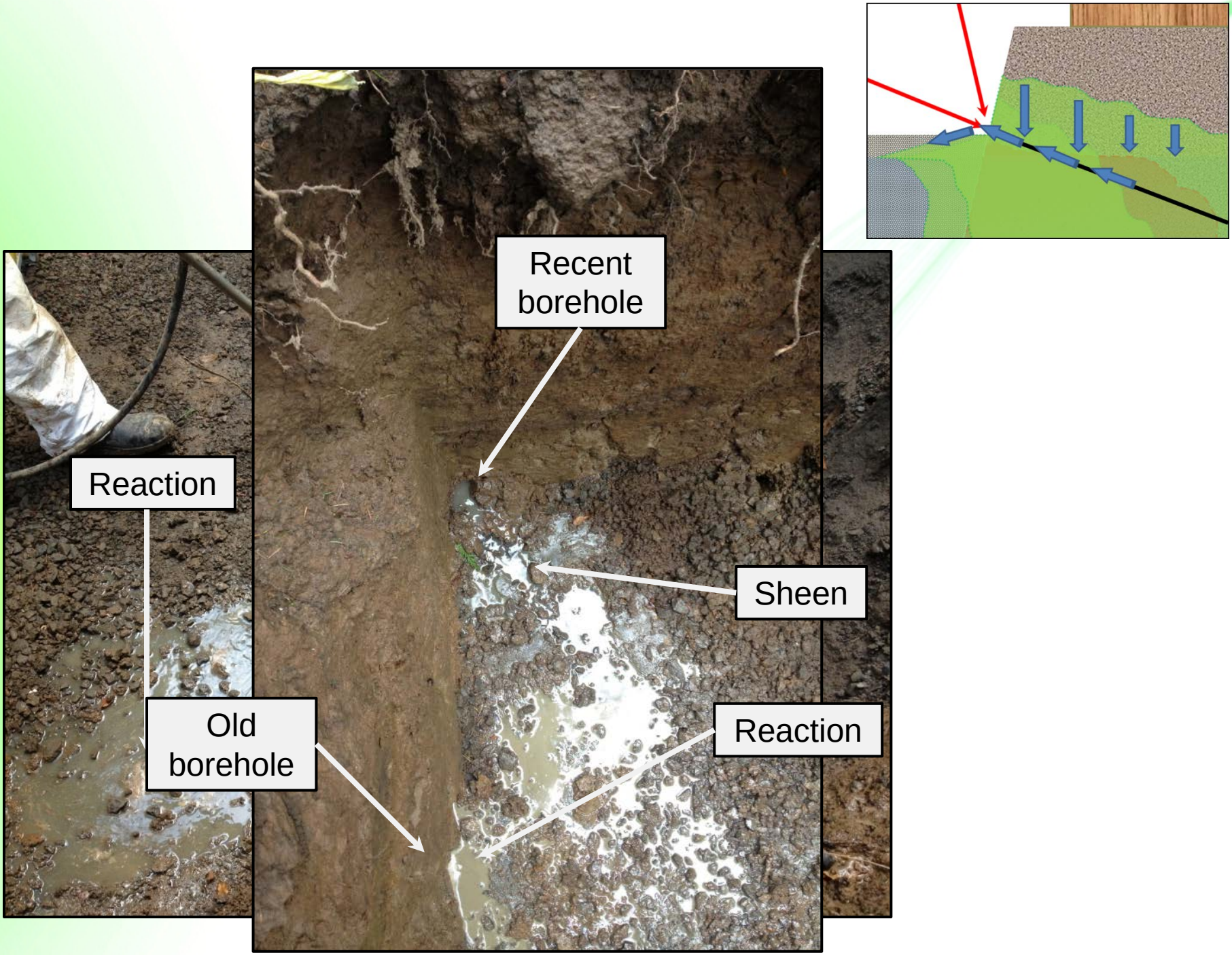
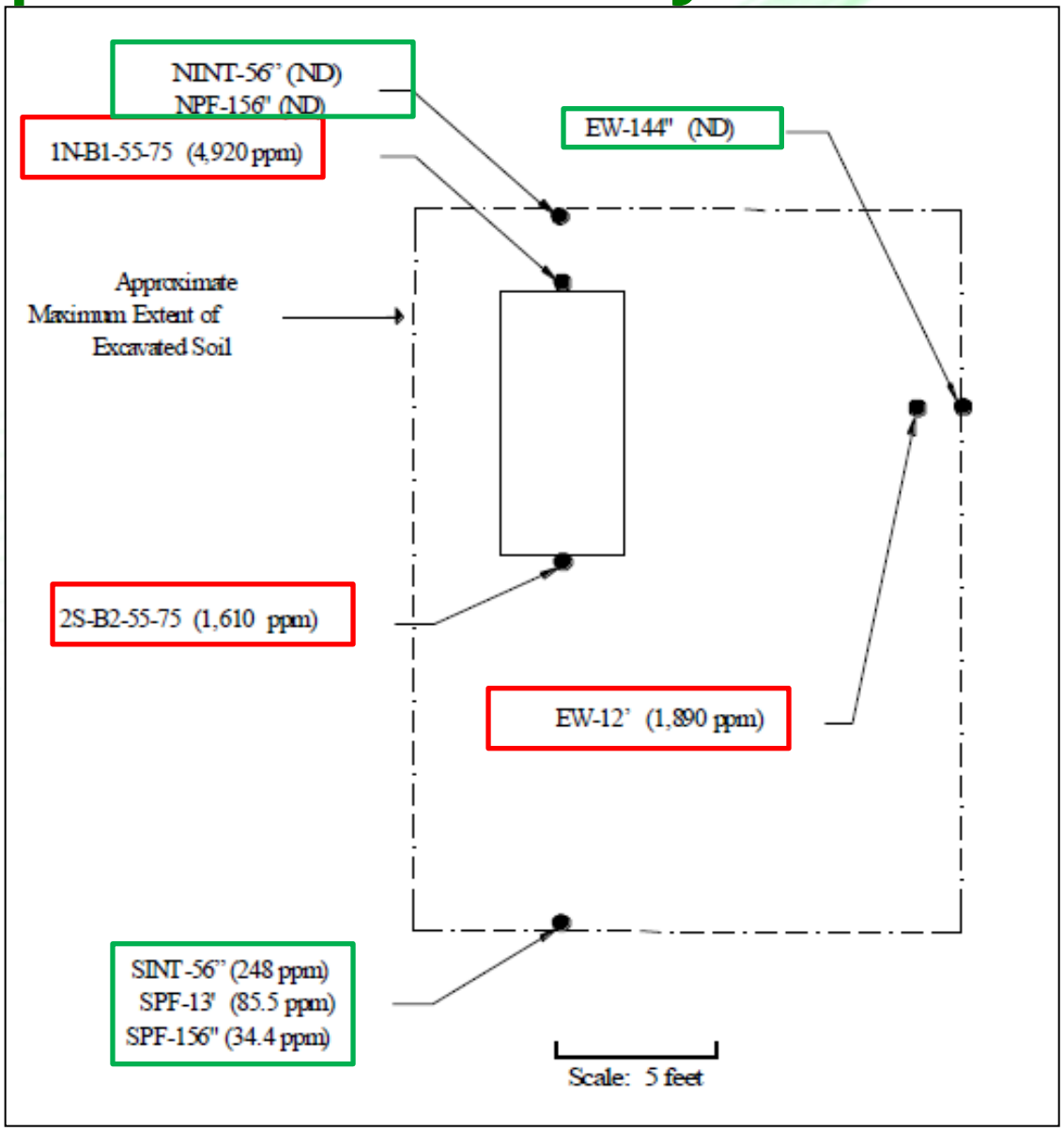

Recent borehole
Reaction
Sheen
Old borehole
Reaction

In Situ Application Study #1

- Results
  - Cleanup met in under 45 days
  - >99% reduction
- Did not have to shore house
- NFA secured



In Situ Application Study #2

- Total Costs
  - Excavation and tank removal = $34,000 US
    - Remove and dispose of 111 cubic yards
    - Dispose of 13,000 gallons of petroleum contaminated water
    - Sampling
    - Backfill material
    - Closure paperwork
  - Bioremediation = $26,000 US
    - Price cap guarantee
    - Work plan, UIC registration/closure, and report
    - AnoxEA in floor of excavation
    - One round of AMOR treatment

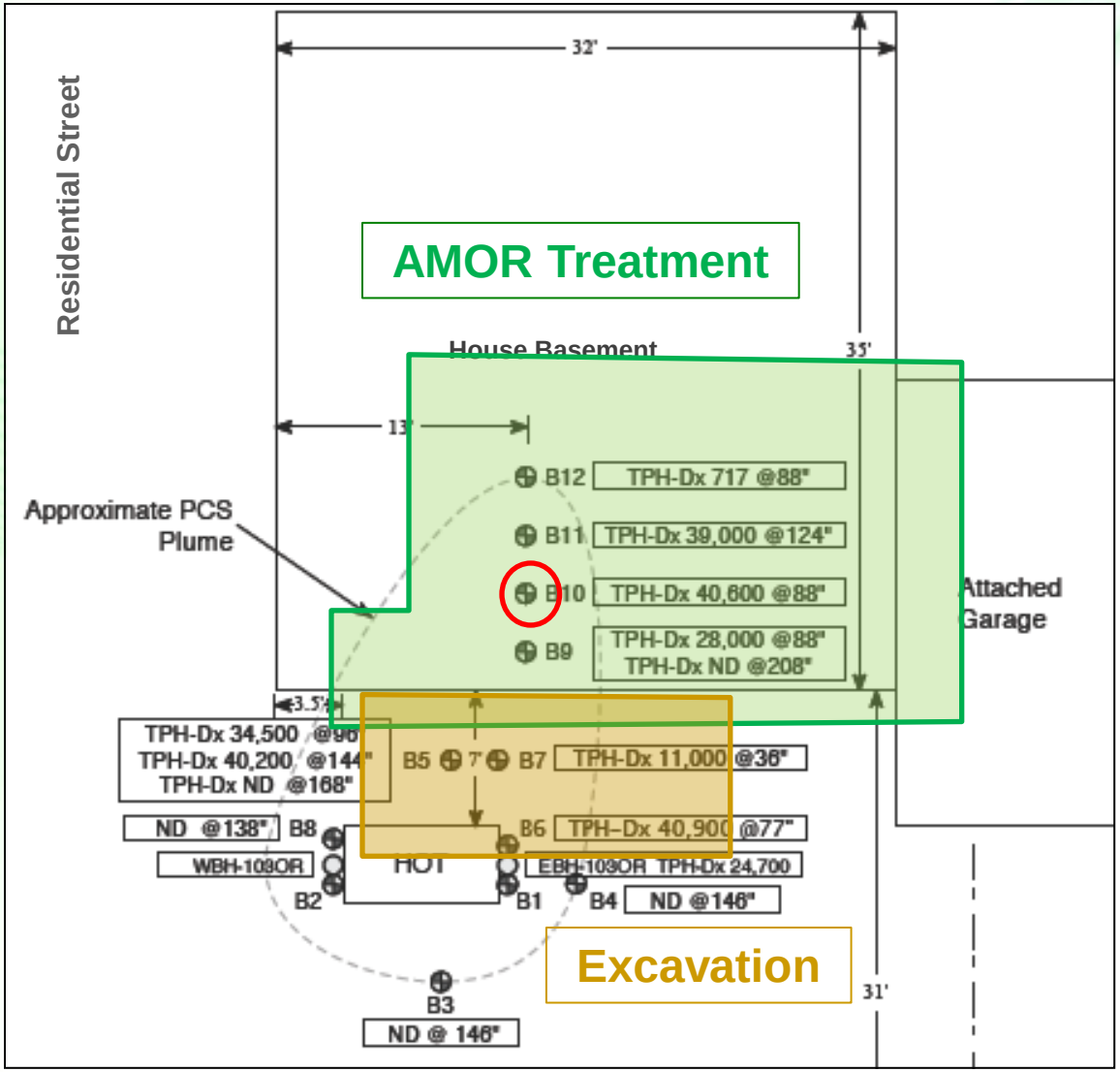
$306 US per cubic yard for excavation

$58 US per cubic yard for AMOR treatment

In Situ Application Study #3

- Weathered heating oil
  - Silty clay vadose zone soil (DTW >35’)
  - Long-term release migrated under basement
  - Standard excavation/removal initially conducted
  - Replaced basement wall due to oil saturation
  - High concentrations under basement
  - Further excavation not possible

In Situ Application Study #3



In Situ Application Study #3

- Injections 4-foot on center
- Confirmation sampling at +38 days following treatment

Soil Analysis (mg/kg)	11/21/12	10/5/13	% Reduction
TPH-Dx	40,600	13,300	**67%**
Ethylbenzene	3.54	0.386	**89%**
Total Xylenes	11.4	1.2	**90%**
Naphthalene	42.2	11.6	**73%**
Fluorene	19.1	7.6	**60%**
Phenanthrene	38.9	15.8	**59%**

Cost-

$10,000

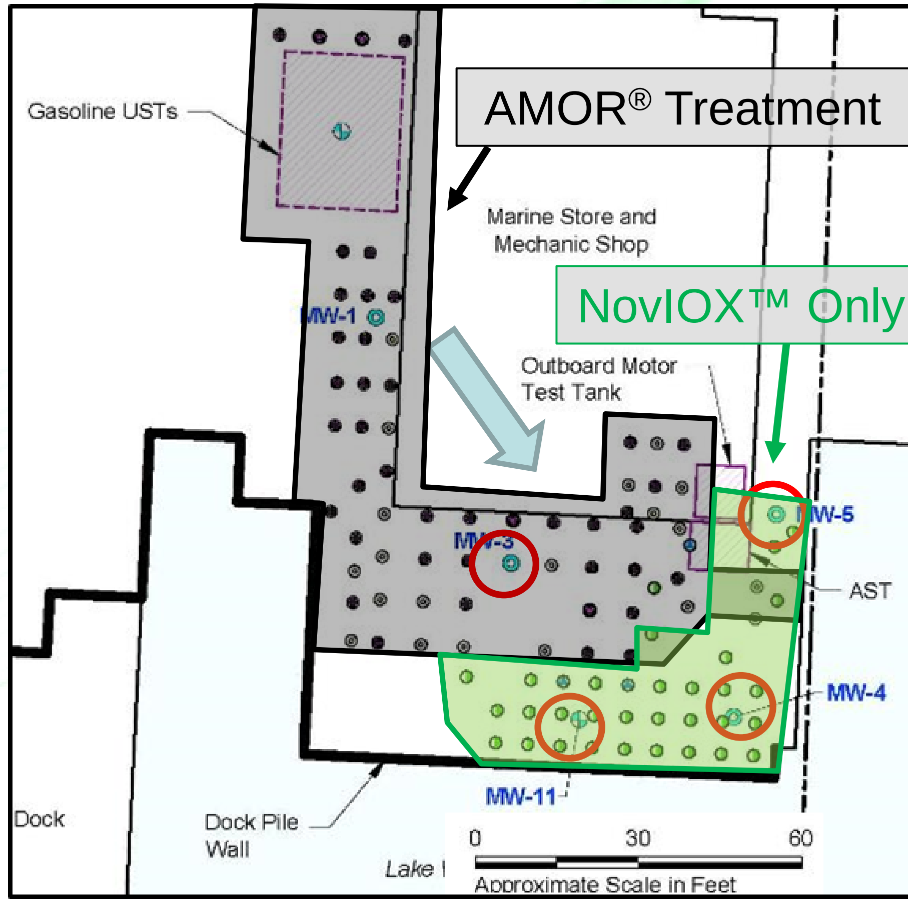
$64 US per cubic yard for AMOR treatment

In Situ Application Study #4

– Weathered gasoline at active lake marina
  - High organics silt and lake sediment fill
  - Depth to water 1.5 feet
  - Marina continued operations

In Situ Application Study #4

Well Name	Date	TPH - Gasoline Range	Total Lead	Benzene	Toluene	Ethylbenzene	Total Xylenes	Naphthalene
				Volatile Organic Compounds				
		Concentration in µg/L (ppb)						
Shallow Monitoring Wells								
B-7	*27-Apr-12*	***11,000***	***170***	***79***	***36***	***170***	***24***	*NS*
MW-3	16-Sep-13	**110**	<2	<1.0	<1.0	**1.6**	**1.2**	<1.0
	31-Oct-13	<100	<2	<1.0	<1.0	<1.0	<1.0	<1.0
	6-Feb-14	<100	<2	<1.0	<1.0	<1.0	<1.0	<1.0
	24-Apr-14	<100	<2	<1.0	<1.0	<1.0	<1.0	<1.0
	22-Jul-14	<100	<2	<1.0	<1.0	<1.0	<1.0	<1.0
B-6	*27-Apr-12*	***1,900***	***88***	***23***	***6.0***	***15***	***12***	*NS*
MW-4	16-Sep-13	**910**	<2	**6.7**	**3.3**	**1.0**	**17**	**2.2**
	31-Oct-13	**1,200**	<2	**19**	**2.3**	**3.3**	**11**	**6.8**
	6-Feb-14	**1,200**	<2	**25**	**7.0**	**26**	**14**	**2.4**
	24-Apr-14	**930**	<2	**12**	**4.8**	**30**	**13**	**2.0**
	22-Jul-14	**500**	<2	<1.0	**1.3**	**7.0**	**2.8**	**2.0**
MW-5	23-Sep-13	**1,600**	<2	**2.9**	**2.6**	**6.1**	**100**	**3.5**
	31-Oct-13	**2,900**	<2	<1.0	**2.4**	**9.6**	**93**	**16**
	6-Feb-14	**1,500**	<2	<1.0	<1.0	**6.0**	**43**	**18**
	24-Apr-14	**780**	<2	**1.7**	<1.0	**3.9**	**28**	**10**
	22-Jul-14	**380**	<2	<1.0	<1.0	**1.6**	**5.3**	**9.0**
B-9	*27-Apr-12*	***2,900***	*NS*	***12***	***10***	***4.7***	***15***	*NS*
MW-11	16-Sep-13	**950**	<2	**16**	**5.0**	**1.3**	**22**	**2.1**
	31-Oct-13	**1,200**	<2	**16**	**3.1**	**3.1**	**14**	**6.7**
	6-Feb-14	**1,200**	<2	**79**	**6.4**	**17**	**20**	**6.7**
	24-Apr-14	**1,100**	<2	**76**	**4.2**	**10**	**12**	**9.0**
	22-Jul-14	**850**	<2	**6.0**	**2.4**	<1.0	**3.7**	**9.5**
	5-Sep-14	**700**	NS	**3.1**	**2.9**	<1.0	**3.2**	**1.0**

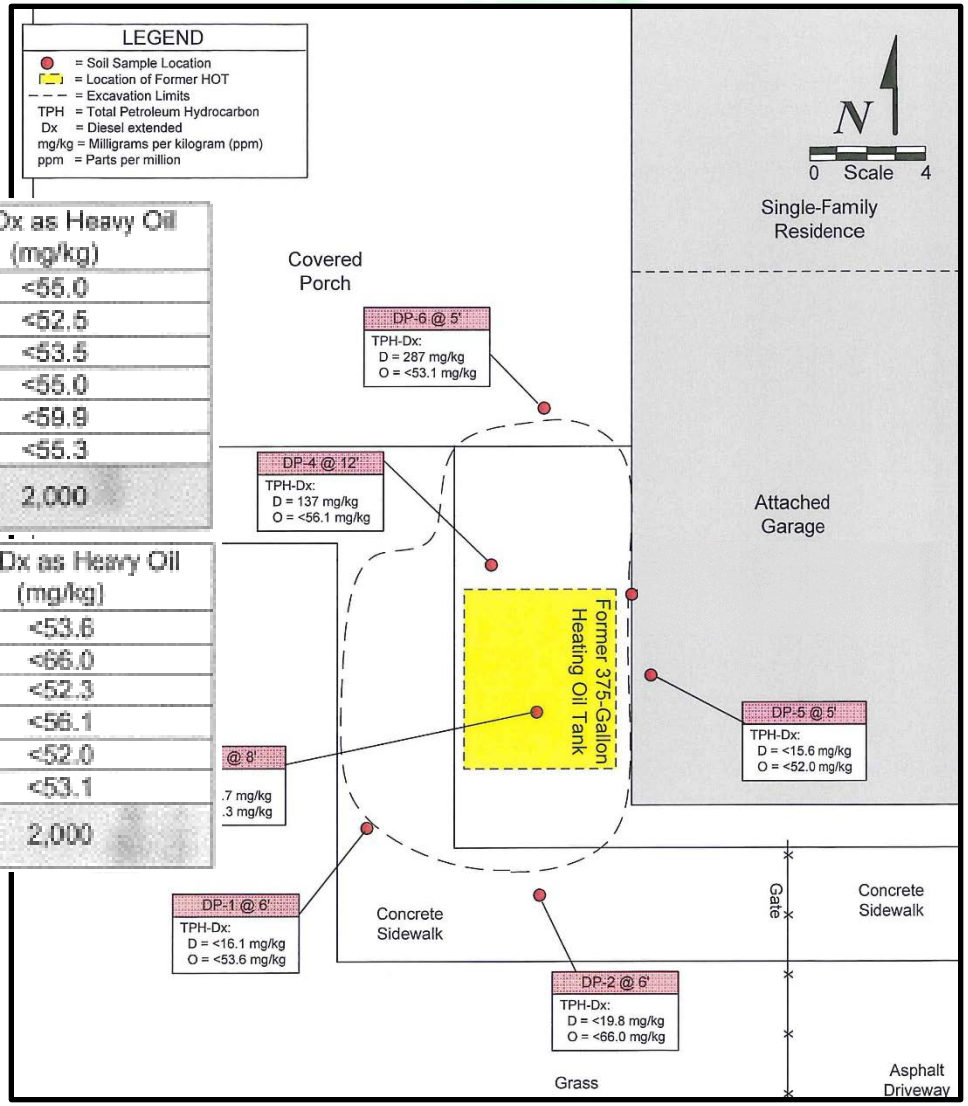


[illegible]
[illegible]
BTEX spikes to investigation levels
No observed mobilization

Bonus – Coarse Sand with Silt

Sample Identification	Date Sampled	TPH-Dx as Diesel (mg/kg)	TPH-Dx as Heavy Oil (mg/kg)
N-Wall @ 78"	5/23/2014	2,950	<55.0
E-Wall @ 84"		19,300	<52.5
E-Wall @ 120"	5/23/2014	3,050	<53.5
S-Wall @ 86"	5/23/2014	685	<55.0
W-Wall @ 86"	5/23/2014	<18.0	<59.9
Base @ 124"	5/23/2014	4,290	<55.3
Washington DOE MTCA Method A Cleanup Level		2,000	2,000

Sample Identification	Date Sampled	TPH-Dx as Diesel (mg/kg)	TPH-Dx as Heavy Oil (mg/kg)
DP-1 @ 6'	8/25/2014	<16.1	<53.6
DP-2 @ 6'	8/25/2014	<19.8	<66.0
DP-3 @ 8'	8/25/2014	<15.7	<52.3
DP-4 @ 12'	8/25/2014	137	<56.1
DP-5 @ 5'		<15.6	<52.0
DP-6 @ 5'	8/25/2014	287	<53.1
Washington DOE MTCA Method A Cleanup Level		2,000	2,000



Presented by:

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