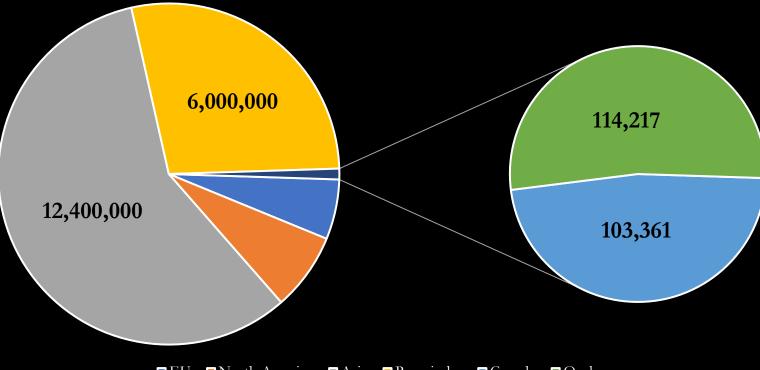
### Successful in situ biostimulation: An analysis of six case studies of impacted sites in Saskatchewan

Dr. Alix Conway, University of Saskatchewan Dr. Steven Siciliano, University of Saskatchewan Kris Bradshaw, Federated Co-operatives Limited Dr. Steven Mamet, formerly of UofS, now at EMS Inc.

### HOW MANY CONTAMINATED SITES ARE THERE?

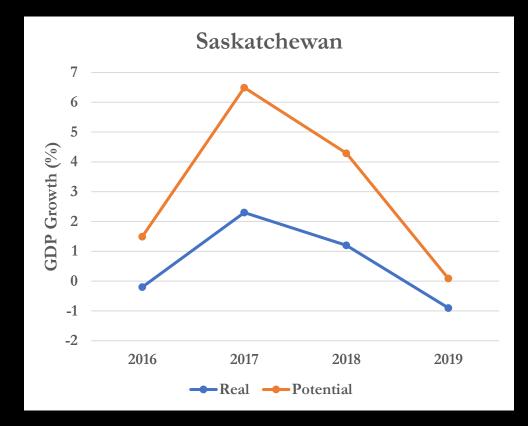
### ~ 21 Million Contaminated Sites Worldwide



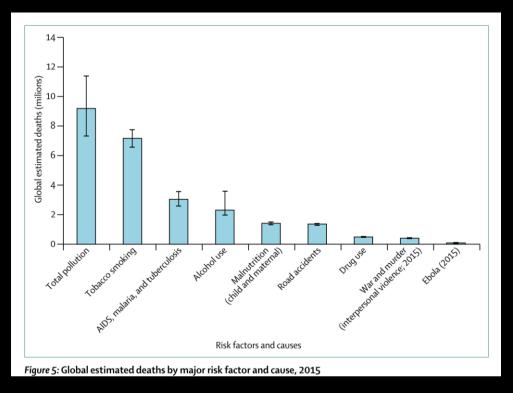
■EU ■North America ■Asia ■Remainder ■Canada ■Orphan

### Social Benefits of Bioremediation Economic Growth

- Contaminated sites reduce GDP due to stranded assets, capital flight, and reduced redevelopment.
- On going costs
  - Globally \$0.2 \$ 1.1 trillion USD /yr
  - EU specific \$6 billion € /yr
  - 0.0014 to 1.89% of GDP depending on jurisdiction.



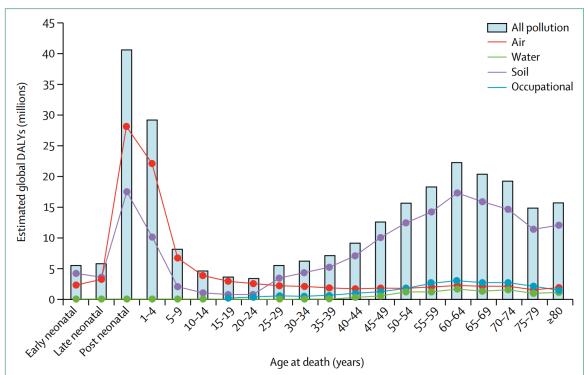
### Social Benefits of Bioremediation Reduced Mortality



Elkins and Zenghelis 2021. Sustainability Science.

- 9 million deaths from pollution.
- ~2 million from contaminated soil and water
  - $\sim 0.6$  million from soil alone.
- Majority of deaths due to artisanal mining, biocides and chemical manufacturing.

### Social Benefits of Bioremediation Reduced Disability



2, 5<sup>2</sup>, 5<sup>2</sup>, 6<sup>6</sup>, 5<sup>6</sup>, 6<sup>7</sup>, 7<sup>1</sup>, 5<sup>7</sup>, 7<sup>9</sup>, 2<sup>8</sup>

Above 25 years of age, soil is the

leading cause of life years lost to

disability

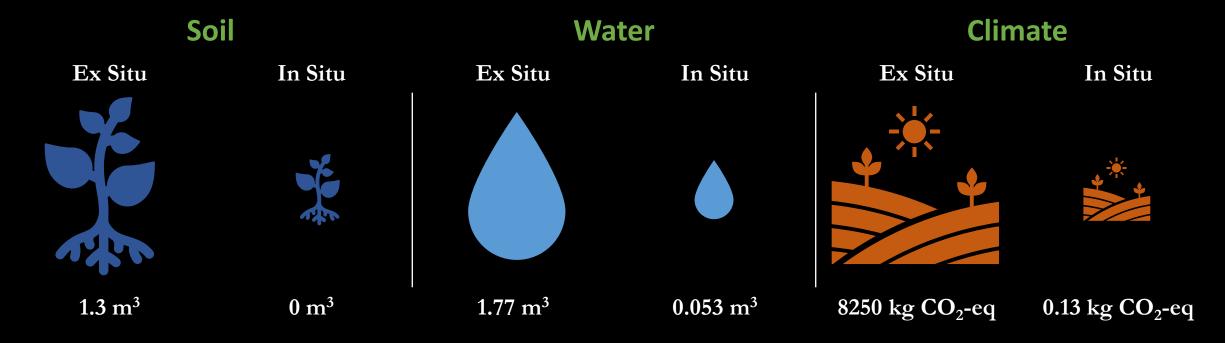
*Figure* **11:** Estimated global DALYs by pollution risk factor and age at death, **2015** GBD Study, 2016.<sup>42</sup> DALYs=disability-adjusted life-years.

### Bioremediation is a Cost-Effective Solution

					Western Canada
T	echnology	Average	Upper Range	Cost per m <sup>3</sup>	11,214 sites
Ex-Situ		\$816,900	\$1,429,575	\$204 to 357	\$10.4 Billion Ex-Situ
		In-Situ			
Physical	Multi-Phase Extraction	\$ 900,000	\$ 1,500,000	\$225 to 375	
Chemical	Chemical Oxidation	\$ 431,600	<b>\$</b> 755,300	\$108 to 189	
Biological	Stimulated Depletion	\$ 210,000	\$ 420,000	\$52 to 105	\$2.6 Billion In Situ

- Costs estimated assuming a 5-year closure time for an average site size of 4,567 m<sup>3</sup>.
- Ex-Situ will close a site in 1 year.
- Physical methods typically do not close sites but recover freely available product.
- 11,214 sites estimated in Western Canada exclude orphan wells.
- 34,143 sites Canada wide.

# Environmental Benefits of In Situ Bioremediation compared to Ex Situ Disposal



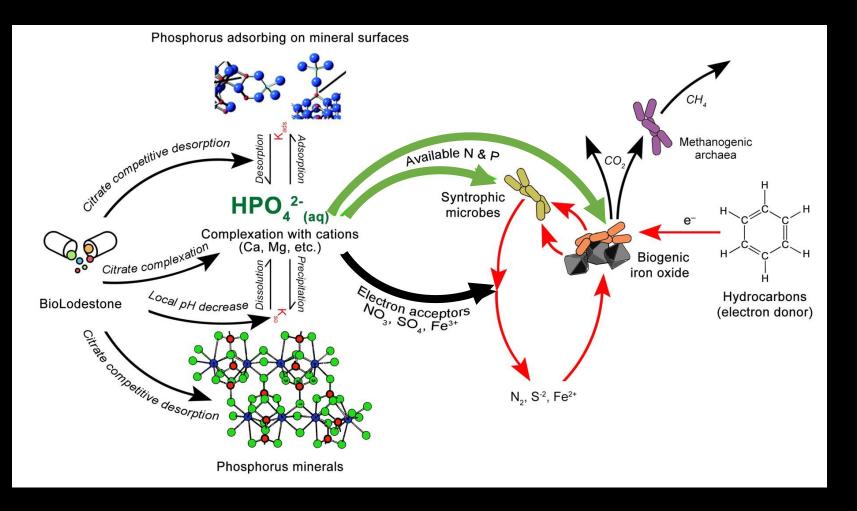
FACT: It takes 100 years to make 1 cm<sup>3</sup> & 100 million years to make a m<sup>3</sup>

# Hydrocarbon remediation in Western Canadian sites

- Challenging due to:
  - Groundwater table fluctuations changes availability of electron acceptors
  - Low hydraulic conductivity and fractured flow
  - Inter-site variability of soil mineralogy, hydrology, biology, sources of hydrocarbons
- Our approach:
  - A biostimulation solution that is a mixture of nutrients and electron acceptors
  - Use fractured flow paths to our advantage

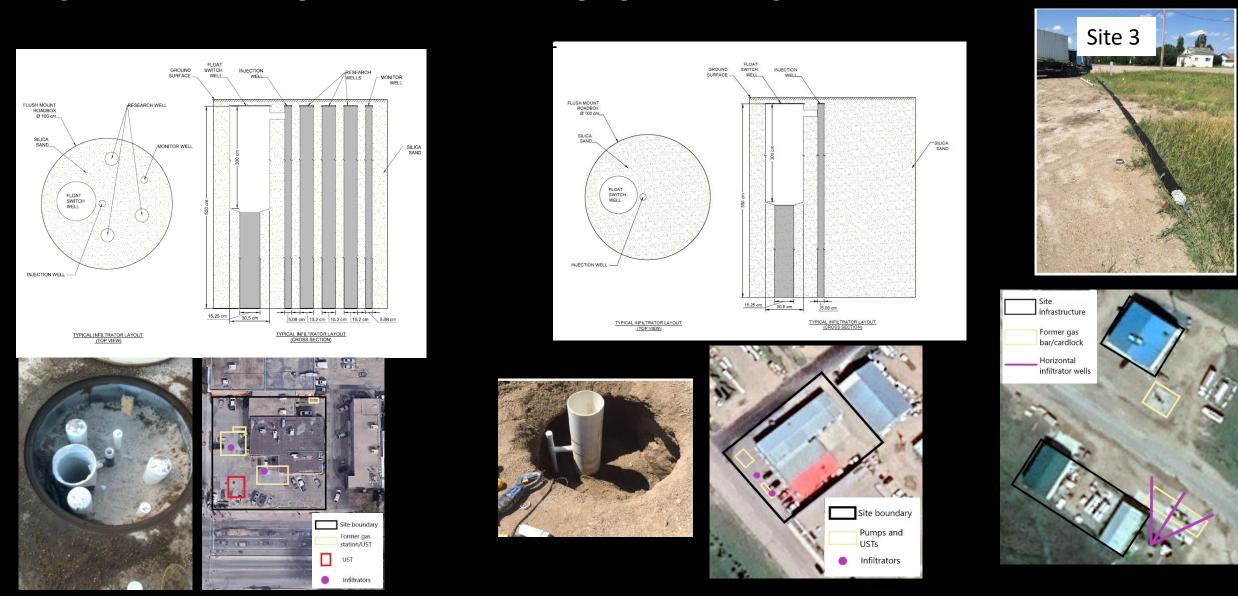
## In situ biostimulation

- The foundation of our remediation technology is to stimulate naturally occurring bacteria to degrade hydrocarbons.
- Naturally occurring microorganisms need nutrients and terminal electron acceptors such as O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2</sup>, Mn<sup>2+</sup>, and Fe<sup>2+</sup> to degrade hydrocarbons.
- Adding a diverse biostimulation solution with multiple electron acceptors reduces eutrophication and stimulates a diverse community of degraders.
- Our solution is ideally suited to Western Canadian sites with a fluctuating capillary zone.



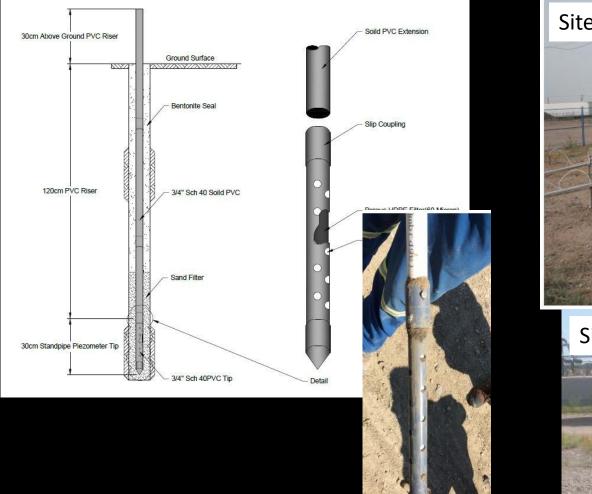
### Two injection designs: Injectors/Infiltrators and Drive-point networks

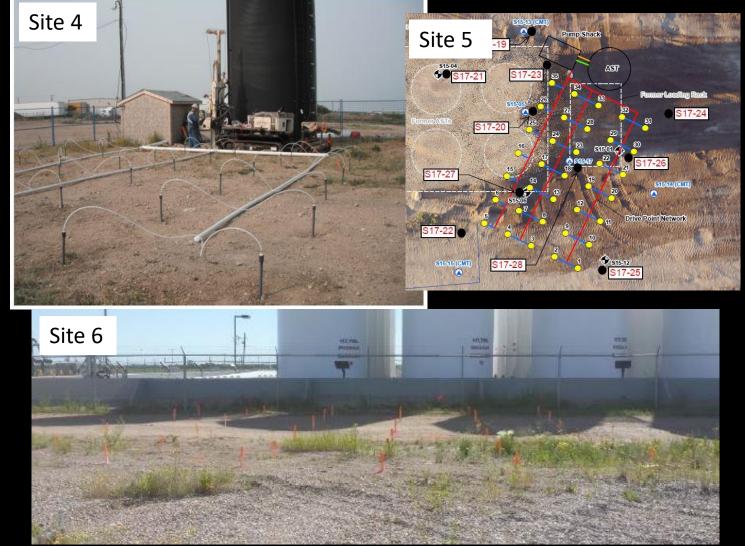
Design intended for source impacted areas such as a former pump island or storage tank area.



### Two injection designs: Injectors/Infiltrators and Drive-point networks

Design intended for locations where there was a higher potential for a surficial release over a wider area.





### Saskatchewan Case Studies

- Six impacted sites across Central and Southern Saskatchewan
- In situ biostimulation technology implemented for 1-5 years
- Sites had historical (>10 years) hydrocarbon impacts due to former pump islands, underground storage tanks, multi tank storage facilities on site
- Sites ranged between fine- and coarse-grained soils, depths of hydrocarbon impacts (1-7.5 meters), and depth of groundwater (1-4 meters)

### Four key indicators of robust technology and design

- Groundwater nutrient monitoring
  - Are we pumping in too many nutrients to change natural groundwater concentrations?
- Monitoring delineation wells
  - Are we moving the contaminant plume?
- Soil electrical conductivity
- Soil contaminant concentrations
  - Has the variance (i.e., spread of contaminant concentration values) changed?

### Four key indicators of robust technology and design: Groundwater nutrients

#### **Possible concern:**

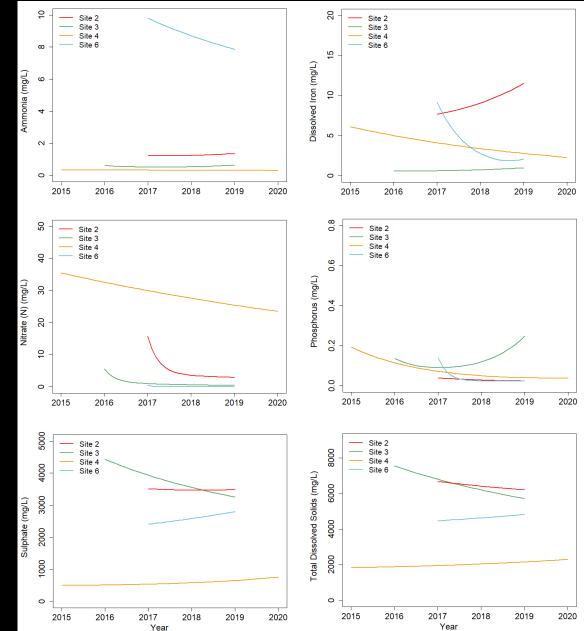
• Is our system pumping in high levels of nutrients that are increasing groundwater nutrient concentrations above guidelines?

#### Our approach:

- Amendment solution nutrients are injected at concentrations within the range of nutrients found on site.
- Dilution occurs once the solution enters the groundwater.

#### Have we been successful?

- Yes!
- We found no significant increases of amendment solution nutrients over the course of remediation at four core sites.



# Four key indicators of robust technology and design: **Delineation wells**

#### **Possible concern:**

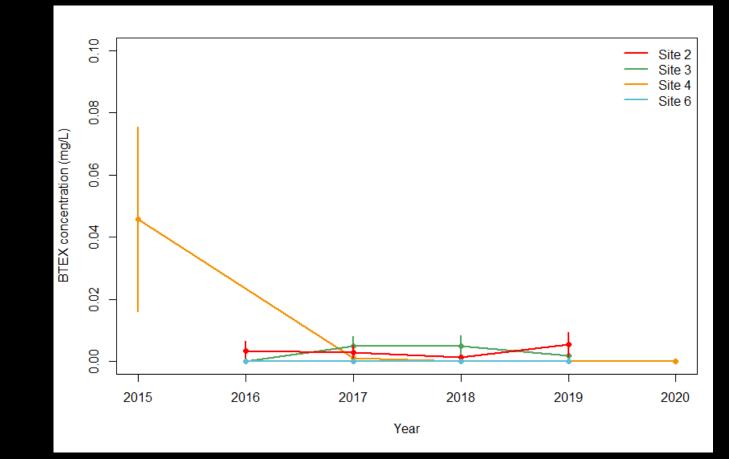
• Is our system increasing mobility of LNAPL?

#### Our approach:

- Technology is employed when the LNAPL plume is relatively stable or residual state.
- We inject the amendment solution at a slow rate (32 ml/min).

#### Have we been successful?

- Yes!
- No increase in LNAPL or dissolved BTEX concentrations observed over time in delineation wells.



### Four key indicators of robust technology and design: Soil electrical conductivity

#### Possible concern:

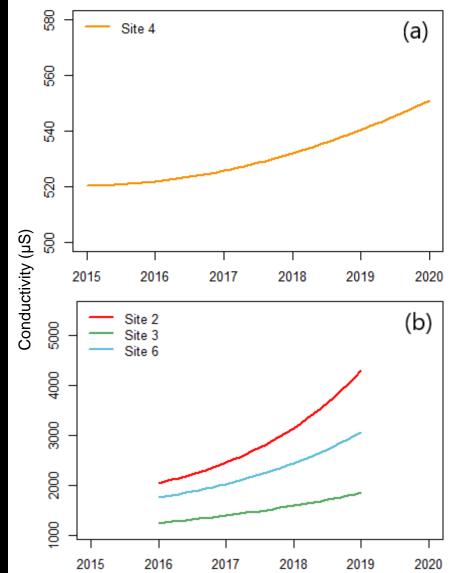
• Adsorbed in the soil?

#### Our approach:

• Slow injection rate of amendment solution should allow for nutrients to follow fractured flow and be made available to microbes throughout the impacted area.

#### Have we been successful?

- Yes!
- Electrical conductivity increased (from 6 109%,
  dependent on the site) after 4-5 years of remediation.



### Four key indicators of robust technology and design: Soil contaminant concentrations

#### **Possible concern:**

• High concentrations of soil contaminants?

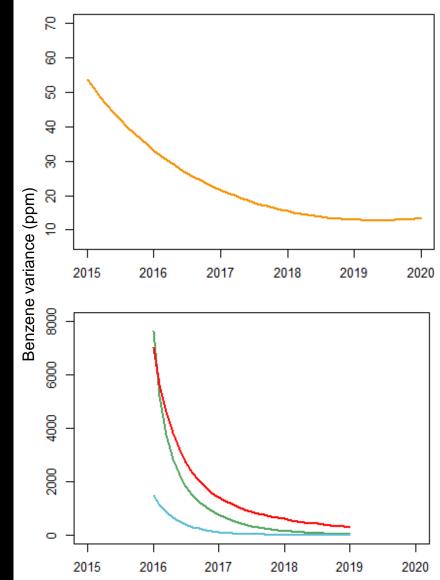
#### Our approach:

• Slow injection rate of amendment solution should allow for nutrients to follow fractured flow and be made available to microbes throughout the impacted area.

#### Have we been successful?

### • Yes!

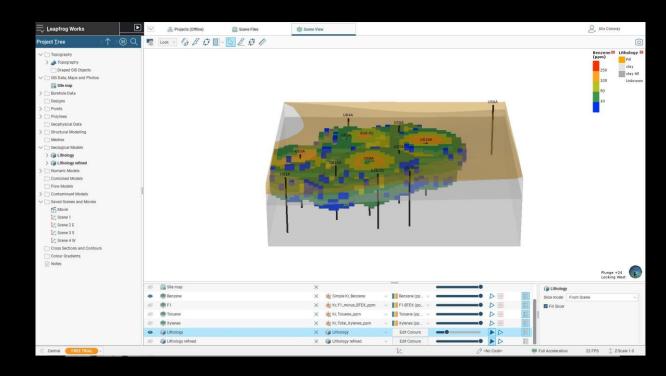
Sharp reductions in soil benzene concentrationvariance, which reflects the spread of the data, is astrong indicator that hotspots have been reduced.

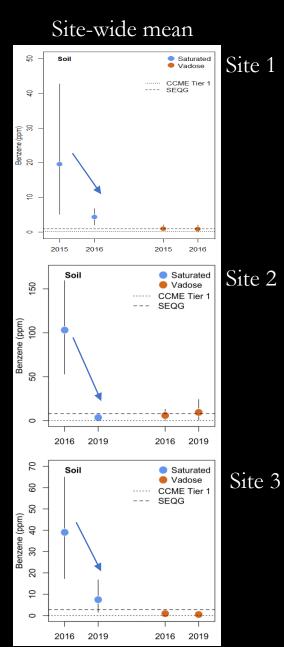


- Soil analyses comparing pre- and post-remediation:
- Site-wide mean PHC concentrations
- PHC volume (LeapFrog Works)

Groundwater analyses comparing preand post-remediation:

• Site-wide mean PHC concentrations





#### Areal extent and concentration Benzene (mg/kg A 200 100 50 10 1.2 Site Benzene (mg/kg В А 250 100 USAA 50 10 7.9 Site 2 Benzene (mg/kg 250 100 50 10 1.6 Site 3

#### Volume and concentration

g)	PHC volume (m <sup>3</sup> )			PHC maximum concentration (mg/kg)		
	Pre-	Post-	Annual	Pre-	Post-	
	treatment	treatment	reduction	treatment	treatment	
	74.5	44.3	40.4%	258.6	128.5	
g)						
			PHC maximum			
	PHO	C volume (I	m³)	concentration		
				(mg	/kg)	
	Pre-	Post-	Annual	Pre-	Post-	
	treatment	treatment	reduction	treatment	treatment	
	261.8		ears = 88		123.9	
g)						
				PHC ma	aximum	
	PHO	C volume (i	m <sup>3</sup> )	concen		
			,	(mg		
	Pre-	Post-	Annual	Pre-	Post-	
	treatment	treatment	reduction	treatment		
	988.1	14 4 ye	ears = 80	5% .9	106.2	

Site 2

Pre-remediation (2016)

Post-remediation (2019)

А

\$15-0

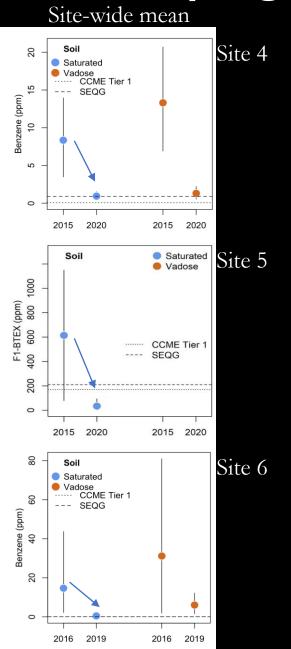
Site 4

Α

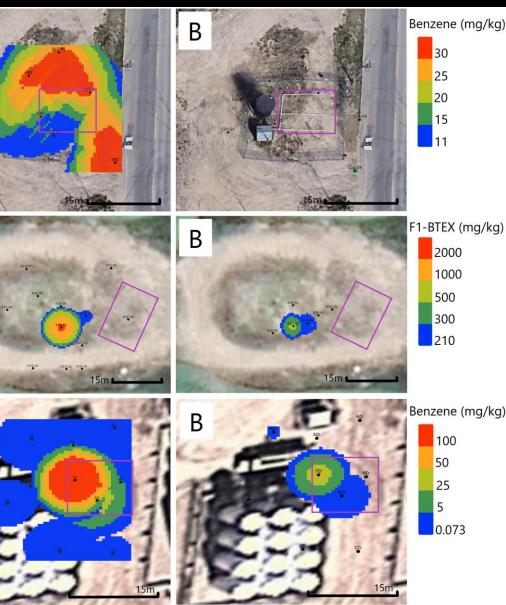
Site 5

Site 6

Α



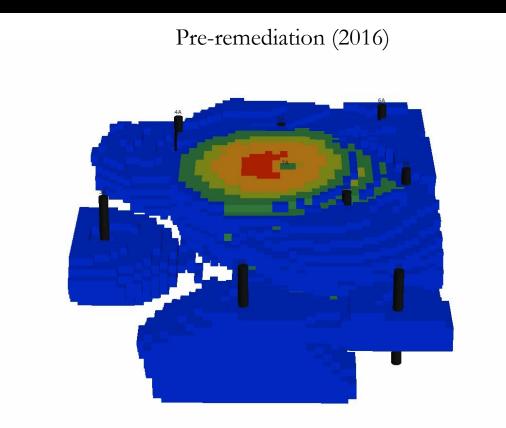
Areal extent and concentration

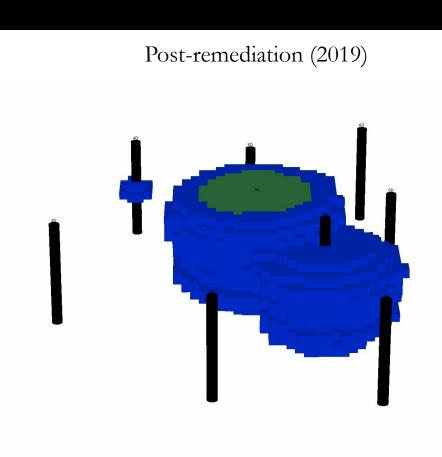


#### Volume and concentration

,	PHC volume (m³)			concen	PHC maximum concentration (mg/kg)	
	Pre-	Post-	Annual	Pre-	Post-	
	treatment	treatment	reduction	treatment	treatment	
	77.0	5 yea	rs = 99%	4.3	12.8	
)						
)				PHC ma	ximum	
	PHC volume (m <sup>3</sup> )				concentration	
					(mg/kg)	
	Pre-	Post-	Annual	Pre-	Post-	
	treatment	treatment	reduction	treatment	treatment	
	762.2	3 yea	rs = 90%	0 16.7	650.0	
)						
	PHC volume (m <sup>3</sup> )			concen	PHC maximum concentration (mg/kg)	
	Pre-	Post-	Annual	Pre-	Post-	
	treatment	treatment	reduction	treatment	treatment	
	432.2	4 years	= 97%	709.1	75.9	

Site 6



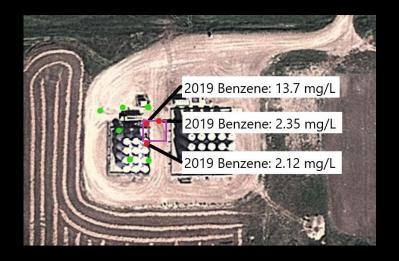


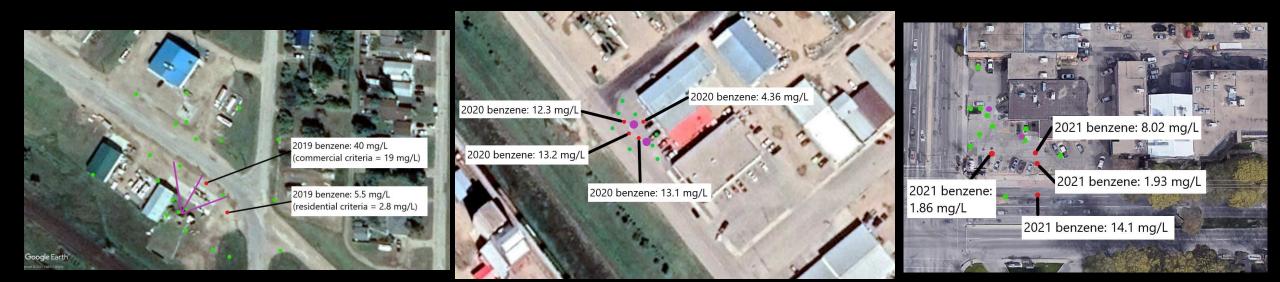
## Quantifying groundwater remediation success

		Mean (mg/L)	
Site	Hydrocarbon	Pre-	Post-
0100		treatment	treatment
1	Benzene	12.22	7.50
2	Benzene	3.40	5.91
3	Benzene	3.75	5.21
4	Benzene	6.47	2.03
5	F1-BTEX	0.10	< 0.10
6	Benzene	7.61	3.88

 $M_{oan}$  (mg/I)

	Maximum (mg/L)		
<b>P-value</b>	Pre-	Post-	
	treatment	treatment	
0.51	22.50	14.10	
0.56	7.98	13.20	
0.59	38.90	40.00	
0.23	27.00	6.40	
NA	0.34	< 0.10	
0.22	24.76	15.00	





# Summary

- Successfully reduced hydrocarbon concentrations by > 90% at six sites across Saskatchewan.
- All six case study sites are ready for risk-based site closure supported by a site-specific risk assessment.
- With refinements and optimizations over the past 5 years, our technology has proven robust and is a sustainable and economically feasible remedial solution to manage impacted hydrocarbon sites.

### Acknowledgements

- FCL's Environmental Advisor Team
- Consulting partners: Stantec, Nichols, Wood.
- Funding provided by NSERC's Industrial Research Chair program sponsored by Federated Cooperatives.

### Key References

- Chen TT, Philips C, Hamilton J, Chartbrand B, Grosskleg J, Bradshaw K, et al. Citrate Addition Increased Phosphorus Bioavailability and Enhanced Gasoline Bioremediation. Journal of Environmental Quality. 2017; 46(5):975-83.
- Huang L, Bradshaw K, Grosskleg J, Siciliano SD. Assessing Space, Time, and Remediation Contribution to Soil Pollutant Variation near the Detection Limit Using Hurdle Models to Account for a Large Proportion of Nondetectable Results. Environmental Science + Technology. 2019; 10.1021/acs.est.8b07110.
- Hyde K, Ma W, Obal T, Bradshaw K, Carlson T, Mamet S, et al. Incremental sampling methodology for petroleum hydrocarbon contaminated soils: volume estimates and remediation strategies. Soil & Sediment Contamination. 2019; 28(1):51-64.
- Mamet SD, Jimmo A, Conway A, Teymurazyan A, Talebitaher A, Papandreou Z, et al. Soil Buffering Capacity Can Be Used To Optimize Biostimulation of Psychrotrophic Hydrocarbon Remediation. Environmental Science & Technology. 2021; 55(14):9864-75.
- Mamet SD, Ma B, Ulrich A, Schryer A, Siciliano SD. Who Is the Rock Miner and Who Is the Hunter? The Use of Heavy-Oxygen Labeled Phosphate (P<sup>18</sup>O<sub>4</sub>) to Differentiate between C and P Fluxes in a Benzene-Degrading Consortium. Environmental Science & Technology. 2018; 52(4):1773-86.
- Siciliano SD, Chen TT, Phillips C, Hamilton J, Hilger D, Chartrand B, et al. Total Phosphate Influences the Rate of Hydrocarbon Degradation but Phosphate Mineralogy Shapes Microbial Community Composition in Cold-Region Calcareous Soils. Environmental Science & Technology. 2016; 50(10):5197-206.