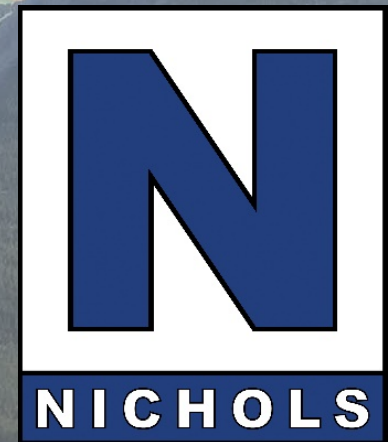


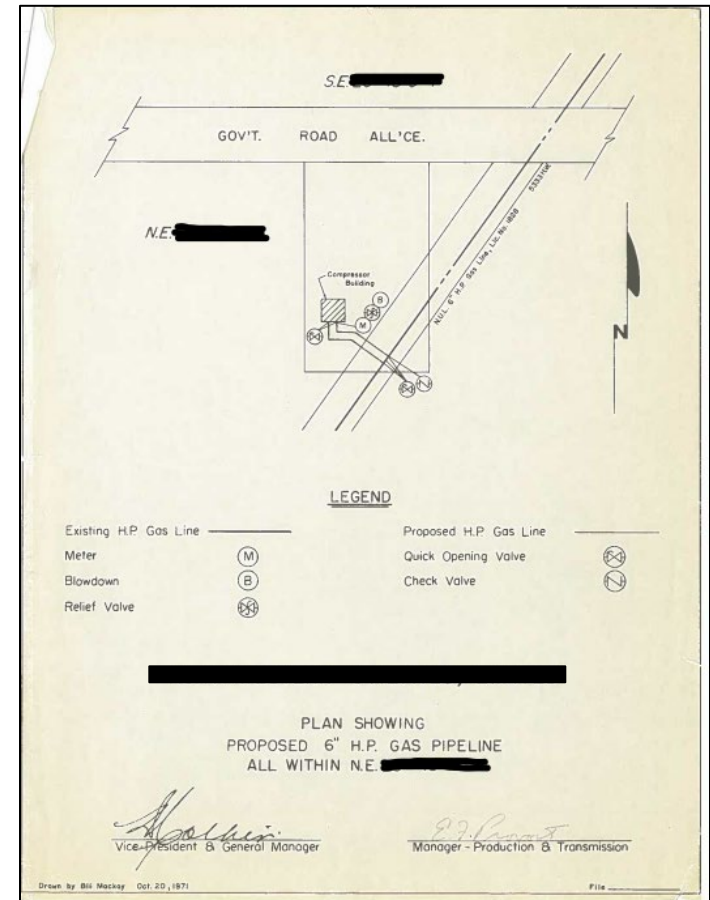
# Remediation of Bromacil and Dicamba-Impacted Groundwater

Barry Rakewich, P.Ag., EP  
Hans Bakker, P.Geo.  
Nichols Environmental (Canada) Ltd.



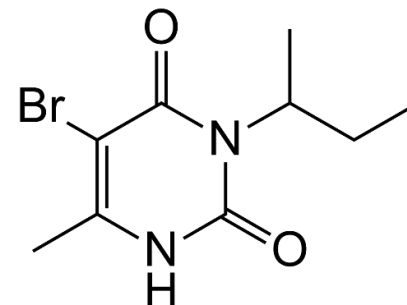
# Outline

- Background on Bromacil and Dicamba
- Site History
- Guideline Criteria Selection
- Assessment History
- Remediation Options
- In-Situ Chemical Oxidation
- Groundwater Recovery and Treatment
- Results
- Lessons Learned
- Sustainability Features



# Background on Bromacil

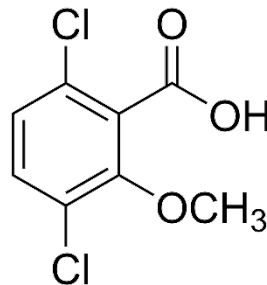
- Bromacil was first registered in 1963 and its typical trade name was Hyvar®. Non-selective long term residual herbicide.
- Persistence – High (soil half-life between 14 and 1494 days)
- Mobility – High (Due to high half-life, low soil adsorption coefficient and high water solubility value)
- Degradation – primarily microbial, which is dependant on availability of microbial population
- Occurrence – most likely to reside in pore or groundwater, unless organic content in soil is high





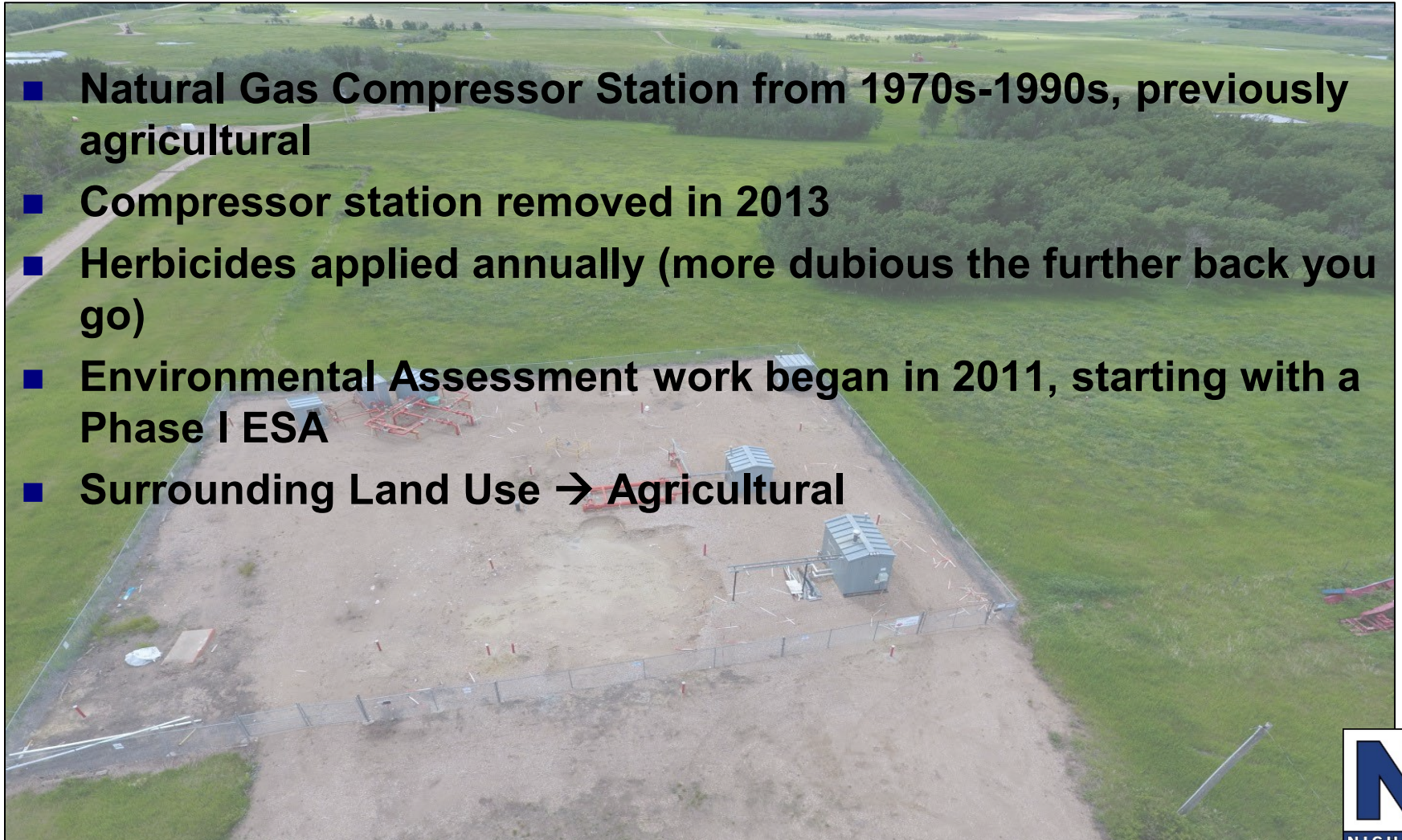
# Background on Dicamba

- Dicamba was first registered in 1964 and its typical trade name was Banvel®. Selective long term residual herbicide.
- Persistence – Low (half-life of Dicamba in soil ranges from 4 to 555 days, with the average half-life of 25 days. Water = <7 days)
- Mobility – High (high solubility in water and low soil adsorption coefficient)
- Degradation - primarily microbial, which is dependant on availability of microbial population
- Occurrence - most likely to reside in pore or groundwater, unless organic content in soil is high or pH is between 4 and 6.



# Site History

- Natural Gas Compressor Station from 1970s-1990s, previously agricultural
- Compressor station removed in 2013
- Herbicides applied annually (more dubious the further back you go)
- Environmental Assessment work began in 2011, starting with a Phase I ESA
- Surrounding Land Use → Agricultural



# Guideline Criteria Selection

- End land use is Agricultural
- Coarse-grained soils
- Most sensitive receptor is irrigation (cannot exclude)

		Potable Water	Ecological Contact	Irrigation	Livestock Watering	Aquatic Life
<b>Bromacil</b>	SK	0.95	0.3	0.0002	1.1	0.005
	AB	0.95	0.3	0.0002	1.1	0.005
<b>Dicamba</b>	SK	0.12	--	0.0000006	0.12	0.01
	AB	0.009	--	0.000008	0.12	0.0061

# Assessment History

- Phase I ESA – 2011
- Phase II ESA – 2011
- Delineation Drilling and GW – 2012
- Delineation Drilling and GW – 2013
- Chemical Oxidation Program and GW Monitoring – 2014/2015
- Carbon Treatment Pilot Study – 2015
- Recovery Well Installation and Pumping Test – 2016
- Groundwater Monitoring Program – 2017
- Groundwater Monitoring Program -2017
- Groundwater Recovery and Treatment Program – 2019/2020



# Phase I ESA (2011)

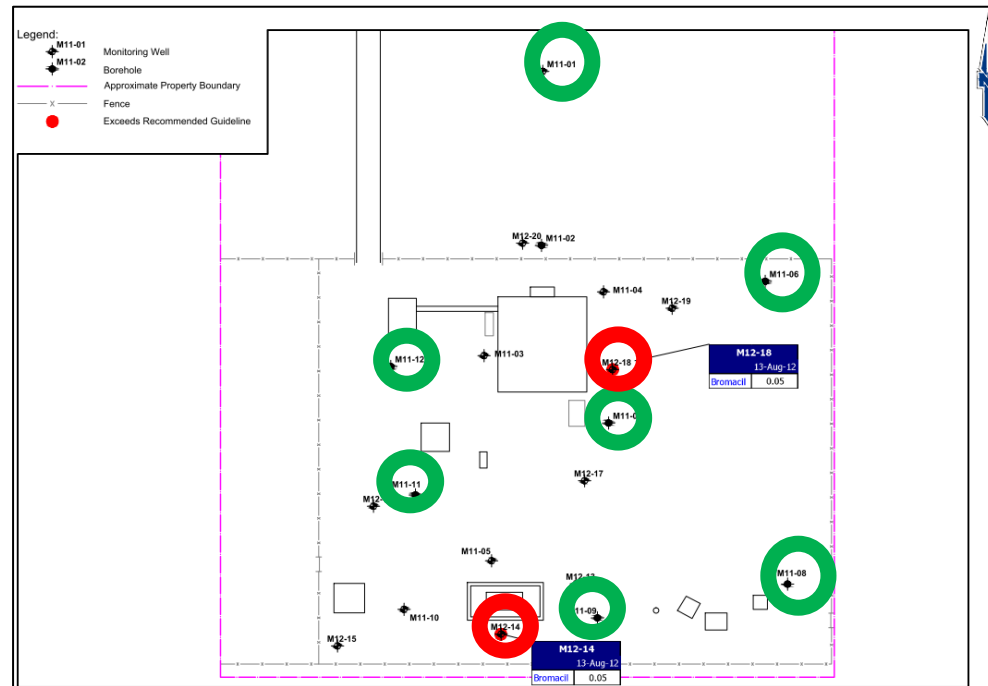
- APECs identified:
  - Condensate Tank
  - Compressor Building
  - Waste Storage (East side of Site)
  - Low areas across Site
  - Metering Building
- COPCs identified:
  - Petroleum hydrocarbons
  - Herbicides and sterilants
  - Metals (especially Mercury)



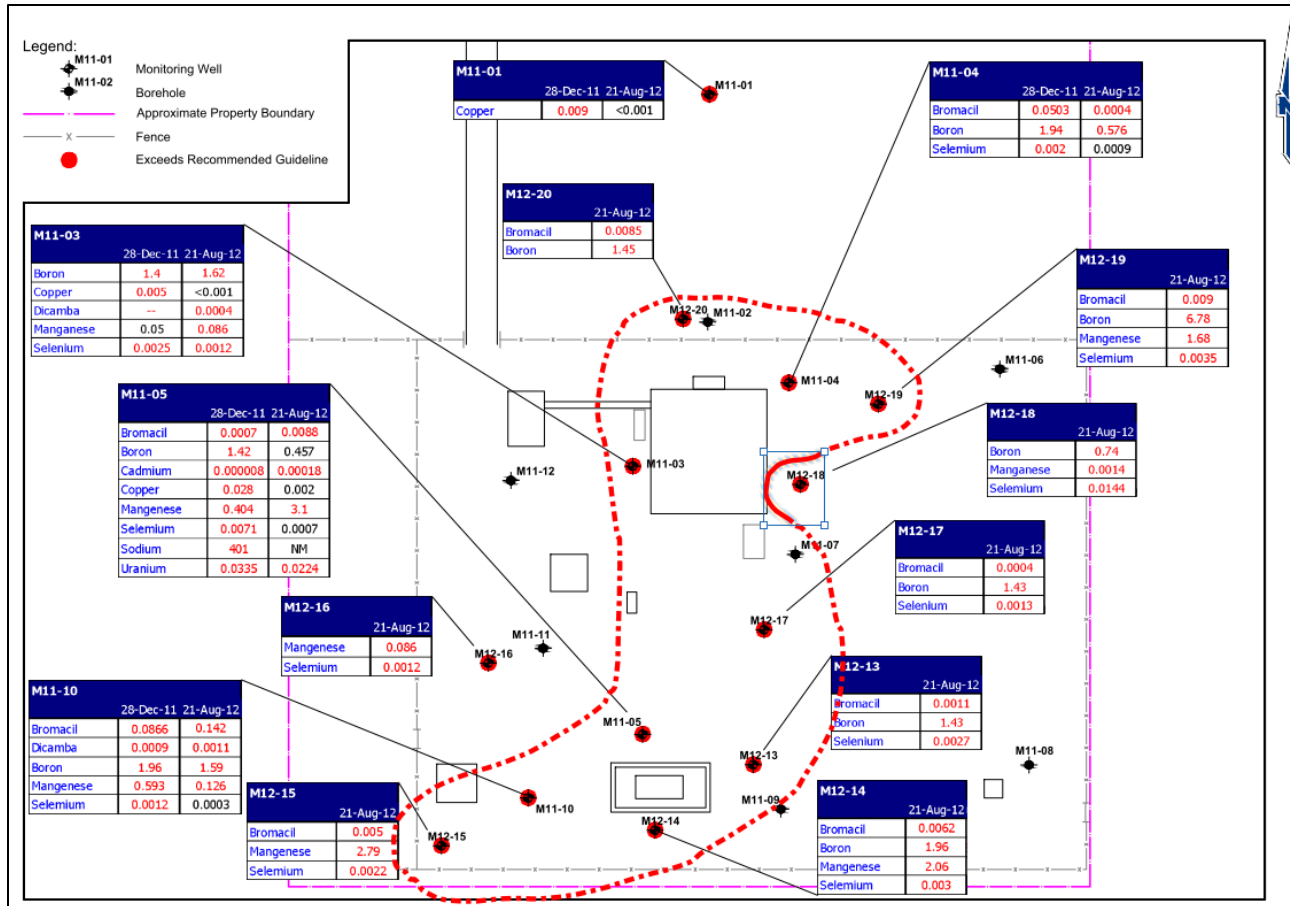


# Phase II ESA/Delineation Soil Results (2011/2012)

- Phase II ESA (2011): submitted samples between surface and 1.5 mbg for herbicides and sterilants.
- All results < laboratory MDL
- MDL > guideline.
- Delineation (2012) results reported two bromacil exceedances at 0.30-0.45 mbg and at 3.1 mbg.
- Challenges with variable depths/locations of impacts on site, laboratory detection limits in 2011, cost of analysis and field detection capabilities.



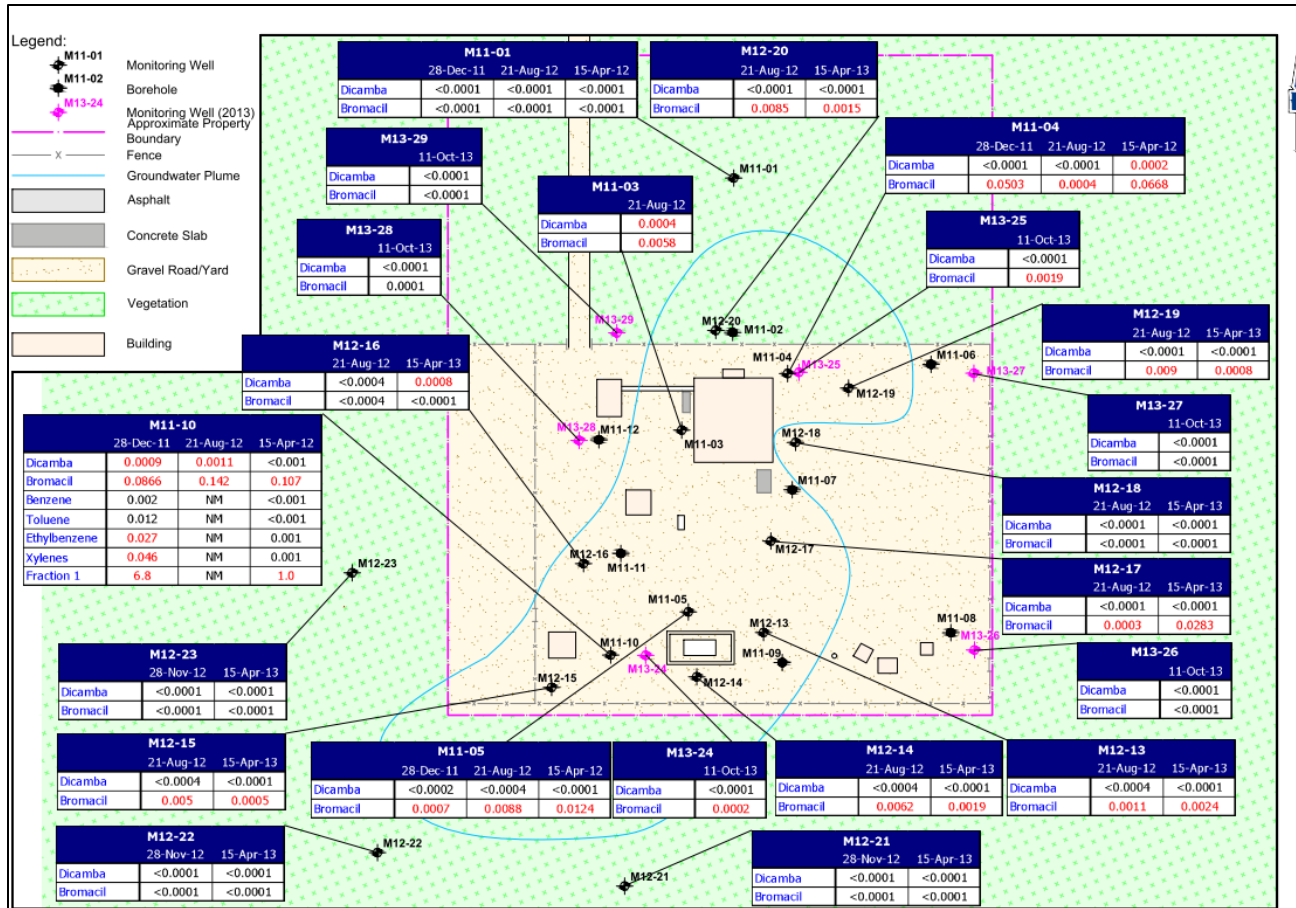
# Phase II ESA/Delineation and Groundwater Results (2011/2012)



Difficulty achieving delineation with two drilling events.

Bromacil impacts likely extended off-site to south and southwest.

# Delineation and Groundwater Results (2013)



Vertical and horizontal delineation achieved (plume defined).

Impacts do extend offsite to S/SW (flow direction).

Challenges with achieving low enough detection limit for Dicamba.

# Site Decommissioned (2013-2017)

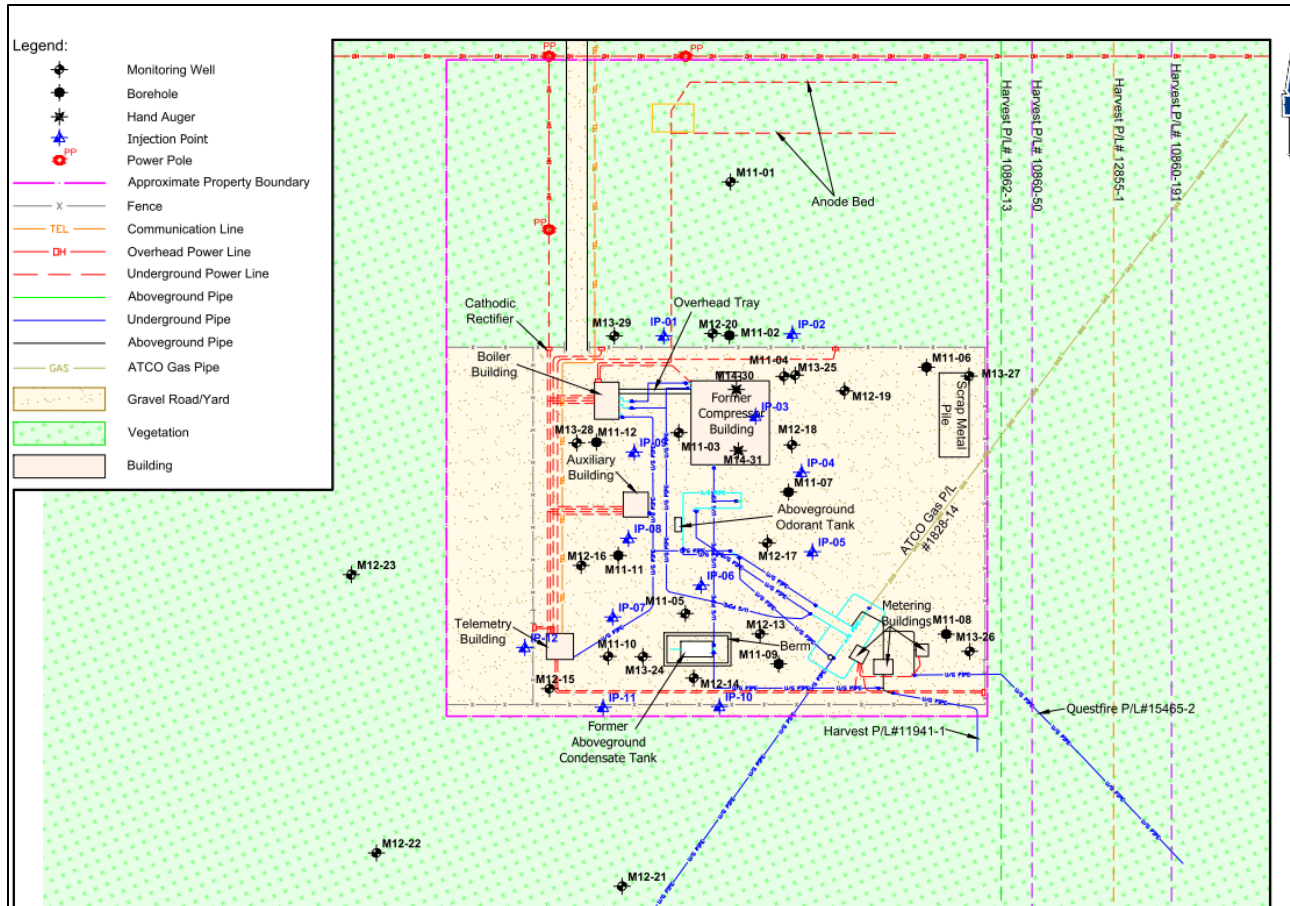




# Remediation Options

Remediation Option	Outcome
Mechanical Excavation	Too deep and primarily in groundwater
Bioremediation	Effective for impacted surface soils primarily
Phytoremediation	Effective for impacted surface soils primarily
Low-Temperature Thermal Desorption and Incineration	Effective for impacted soils and groundwater, need to worry about capturing combustion emissions. Costly
In-Situ Chemical Oxidation	In-Situ treatment of organic-based sterilants in groundwater with an oxidizer
Groundwater Recovery	Recover water in-situ, treat through granular activated carbon, and reinject back into formaton

# Chemical Oxidation and Groundwater Sampling Results (2014/2015)



Chemical injection was recommended given historical success with other organic sterilants and favorable bench study.

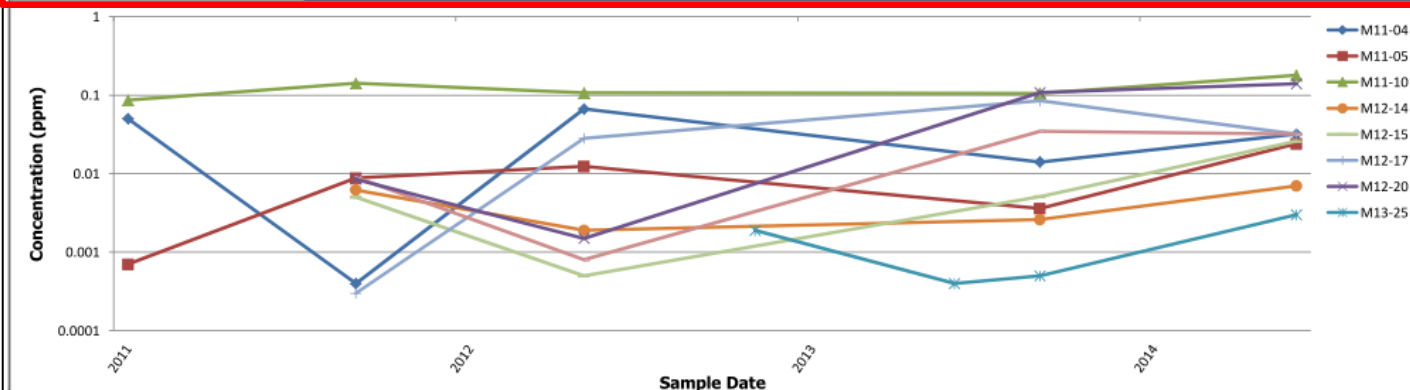
Sodium Persulphate injected at 12 pts over three events.

Above- and underground infrastructure limited amount and position of injection points.

# Chemical Oxidation and Groundwater Sampling Results (2014/2015)

- First injection event occurred in May 2014
- Groundwater sampled August 2014 and May 2015
- (No trend change)

Monitoring Well:		M11-04	M11-05	M11-10	M12-14	M12-15	M12-17	M12-19	M12-20	M13-25
Sampling Event	Sampling Date	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil
1	28-Dec-2011	0.0503	0.0007	0.0866						
2	21-Aug-2012	0.0004	0.0088	0.142	0.0062	0.005	0.0003	0.009	0.0085	
3	15-Apr-2013	0.0668	0.0124	0.107	0.0019	0.0005	0.0283	0.0008	0.0015	
4	11-Oct-2013									0.0019
5	21-May-2014									0.0004
6	12-Aug-2014	0.0141	0.0036	0.106	0.0026	0.0051	0.0852	0.0348	0.108	0.0005
7	11-May-2015	0.032	0.024	0.18	0.007	0.026	0.032	0.032	0.14	0.003
Mann-Kendall Statistic (S):		0	6	4	2	4	4	2	4	2
Confidence Factor		40.8%	88.3%	75.8%	62.5%	83.3%	83.3%	62.5%	83.3%	62.5%
Concentration Trend:		No Trend	No Trend	No Trend	No Trend	No Trend	No Trend	No Trend	No Trend	No Trend



Linear trend analyses were performed based on the Mann-Kendall statistical method (Gilbert (1987), EPA (2009), and Connor et al. (2014)). Values below the MDL were substituted with a value one-half of the historical low MDL. Datasets with a high proportion of samples below MDL were defaulted to "No Trend." (All concentrations in **mg/L = ppm**)

# Carbon Treatment Bench Study (2015)

- Extracted approximately 500-L of impacted water from the site and pushed through two drums containing granular activated carbon (GAC)

## Bromacil

Pre-Treatment Concentration	Post-Treatment Concentration
0.025 ppm	<0.0001 ppm

- Move forward with a Groundwater Recovery and Treatment Design.
- Initial installation of a recovery well and completed a pump test.

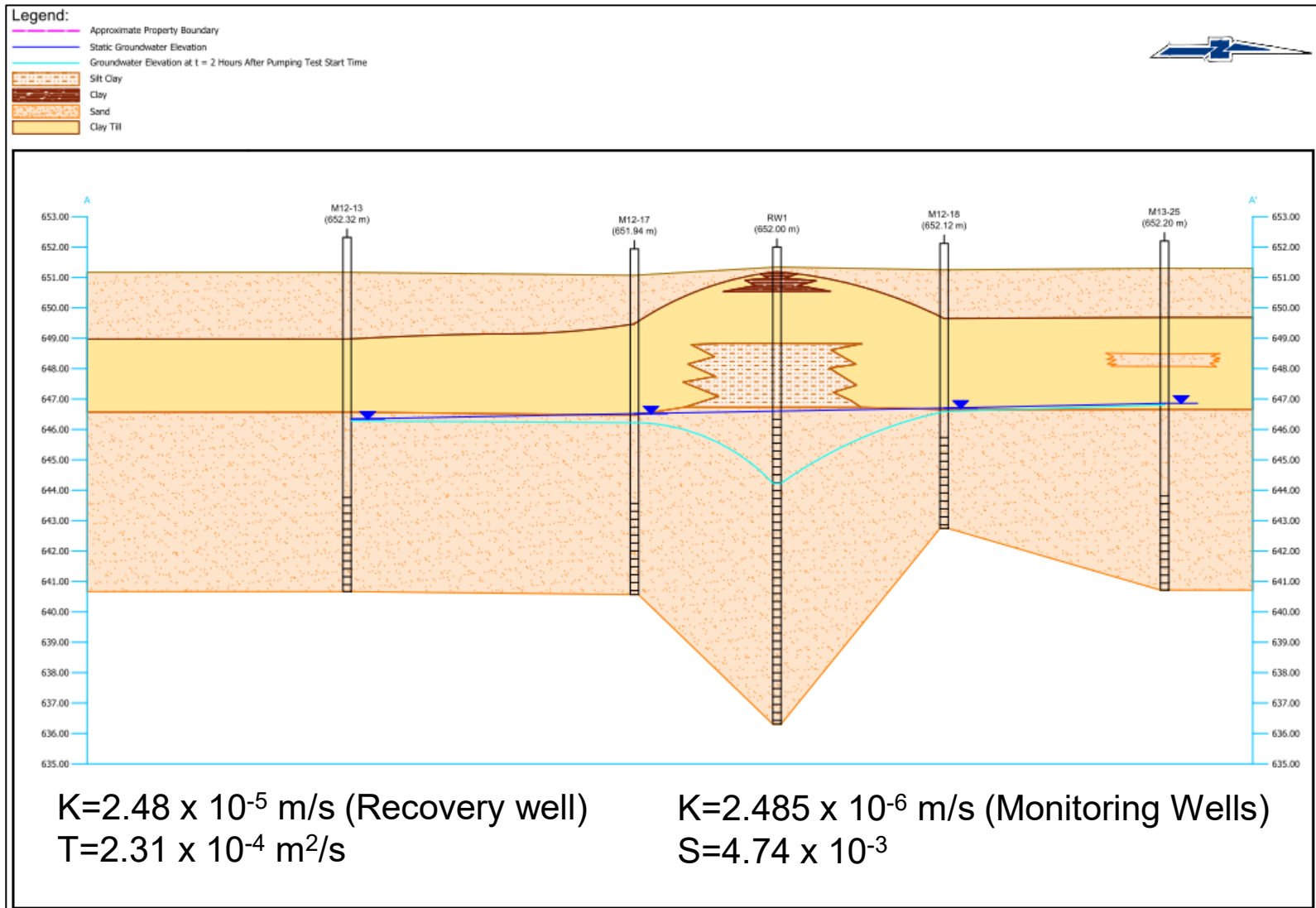


# Recovery Well Installation and Pump Test (2016)

- Installed 254 mm diameter recovery well to 15 mbg
- Completed pump test following well development



# Pump Test Results (2016)

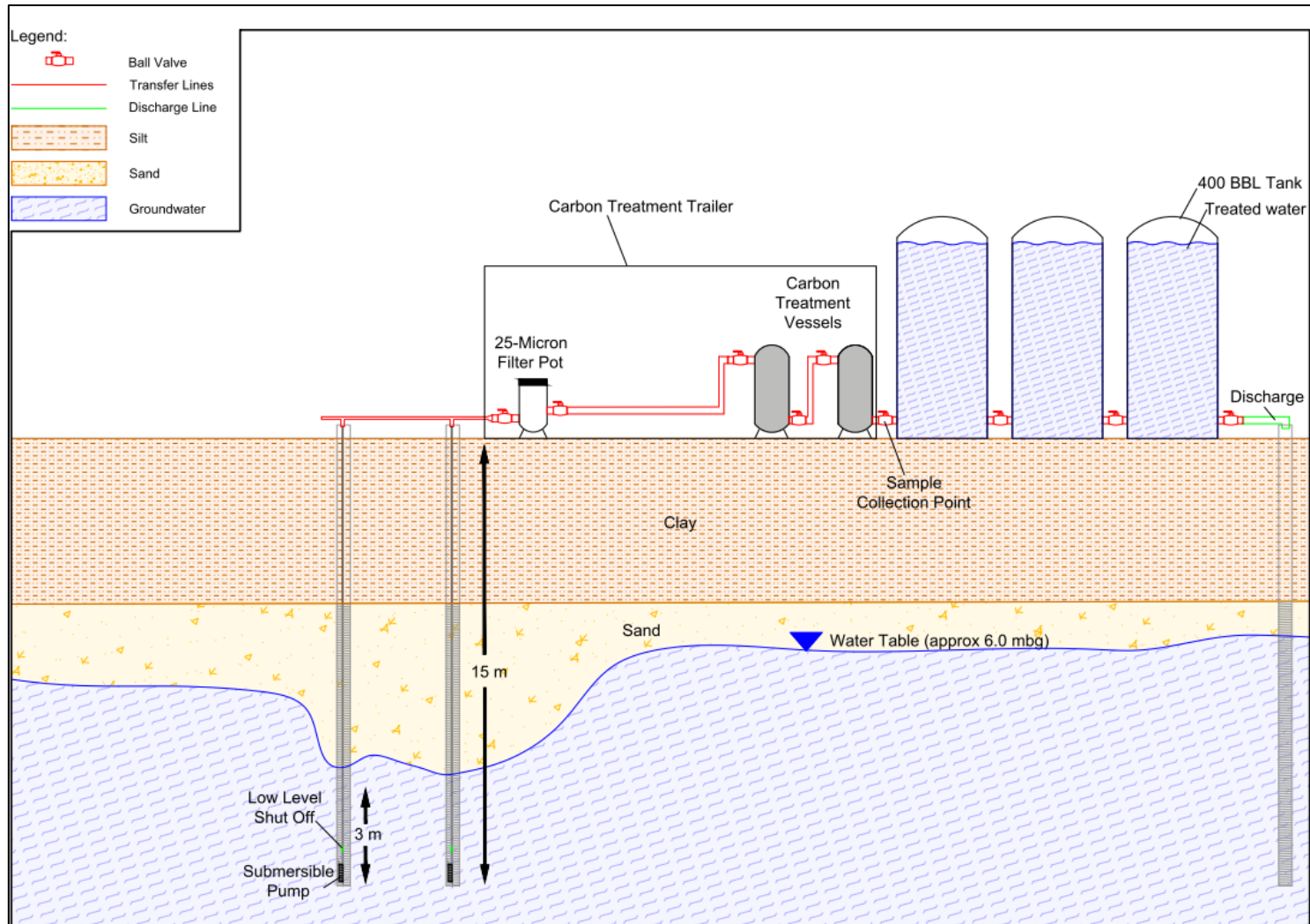


# Pump Test Results (2016)

- System design driver...especially for pump selection and pumping rate.
- Results indicate there is lots of water and it flows into the well quickly.
- Not worried about over pumping the well, given treatment capacity of GAC system.

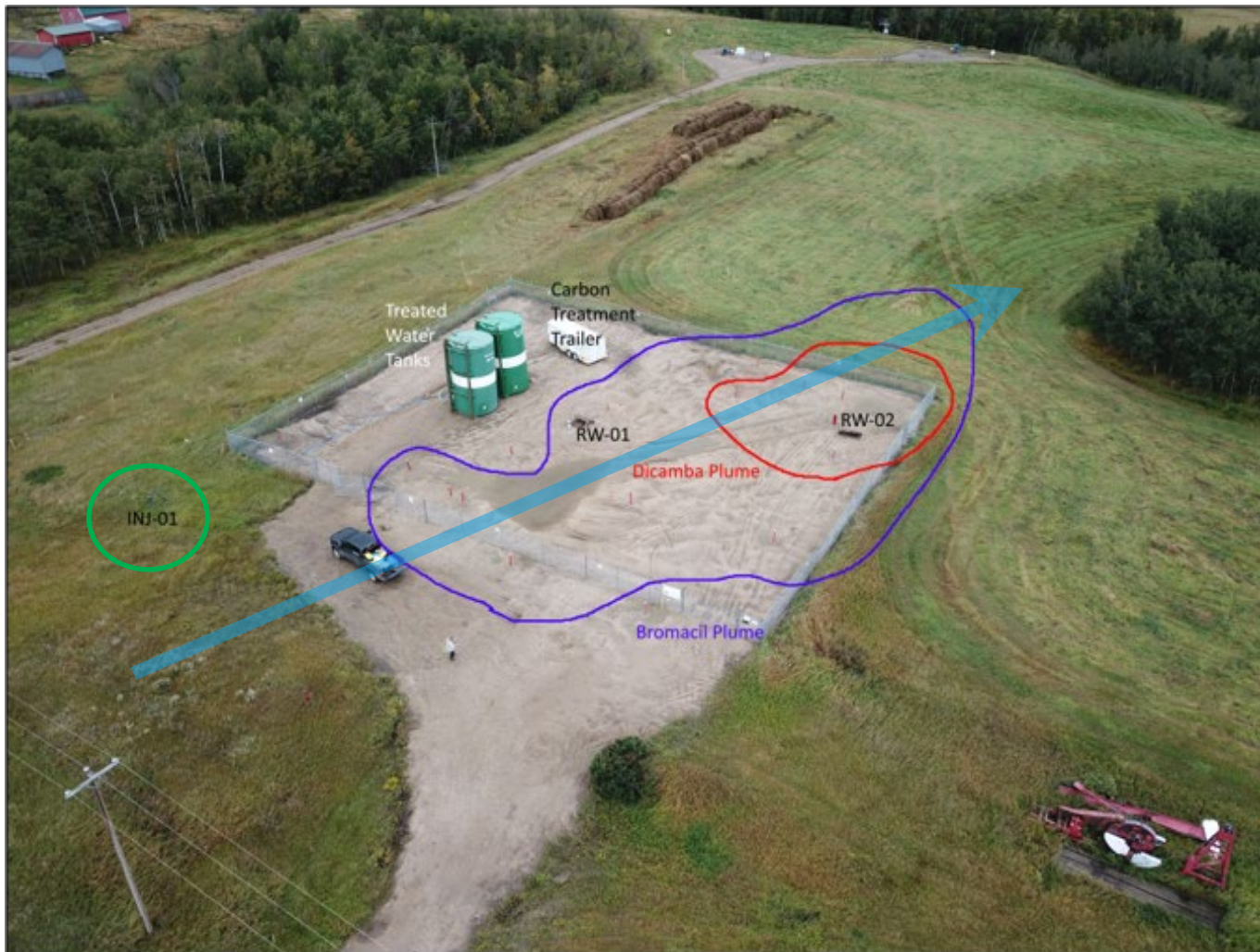


# Recovery and Treatment Design (2016)





# Recovery and Treatment Design (2016)



# Results (Bromacil - 2019)

- Recovered and treated ~230,000 L of impacted groundwater between May and September of 2019
- Groundwater sampling in November 2019
- Trend Analysis shows:

Monitoring Well:		M11-04	M11-05	M11-10	M12-13	M12-14	M12-15	M12-17	M12-19	M12-20	M13-25
Sampling Event	Sampling Date	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil
1	28-Dec-2011	0.0503	0.0007	0.0866							
2	21-Aug-2012	0.0004	0.0088	0.142	0.0011	0.0062	0.005	0.0003	0.009	0.0085	
3	15-Apr-2013	0.0668	0.0124	0.107	0.0024	0.0019	0.0005	0.0283	0.0008	0.0015	
4	11-Oct-2013										0.0019
5	21-May-2014										0.0004
6	12-Aug-2014	0.0141	0.0036	0.106		0.0026	0.0051	0.0852	0.0348	0.108	0.0005
7	11-May-2015	0.032	0.024	0.18	0.002	0.007	0.026	0.032	0.032	0.14	0.003
8	6-Oct-2016	0.028						0.091			
9	5-Jun-2017	0.028	0.02	0.16	0.057	0.027	0.0094	0.17	0.016	0.079	0.0059
10	7-Nov-2019	0.075	0.0143	0.0707	0.0118	0.0455	0.00176	0.116	0.0133	0.00046	0.0059
Mann-Kendall Statistic (S):		5	11	1	6	11	3	17	1	-1	10
Confidence Factor		76.5%	97.2%	50.0%	88.3%	97.2%	64.0%	>99.9%	50.0%	50.0%	95.2%
Concentration Trend:		No Trend	Increasing	No Trend	No Trend	Increasing	No Trend	Increasing	No Trend	No Trend	Increasing

- Even though increasing trends are appearing in some monitoring wells, this is good news as there was no trending in 2015.
- Indicative of plume movement/contaminant mobilization.
- Increase opportunity for recovery and treatment of contaminants.

# Results (Bromacil - 2020)

- Recovered and treated ~160,000 L of impacted groundwater between June and September of 2020
- Groundwater sampling in September 2020
- Trend Analysis shows:

Monitoring Well:	M11-03	M11-04	M11-05	M11-10	M12-13	M12-14	M12-15	M12-17	M12-19	M12-20	M13-25	M13-28
Sampling Event	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil	Bromacil
1	28-Dec-2011		0.0503	0.0007	0.0866							
2	21-Aug-2012	0.0058	0.0004	0.0088	0.142	0.0011	0.0062	0.005	0.0003	0.009	0.0085	
3	15-Apr-2013		0.0668	0.0124	0.107	0.0024	0.0019	0.0005	0.0283	0.0008	0.0015	
4	11-Oct-2013											
5	21-May-2014										0.0019	0.0001
6	12-Aug-2014	0.0723	0.0141	0.0036	0.106		0.0026	0.0051	0.0852	0.0348	0.108	0.0005
7	11-May-2015	0.13	0.032	0.024	0.18	0.002	0.007	0.026	0.032	0.032	0.14	0.003
8	6-Oct-2016		0.028						0.091			0.0004
9	5-Jun-2017	0.14	0.028	0.02	0.16	0.057	0.027	0.0094	0.17	0.016	0.079	0.0059
10	7-Nov-2019	0.0311	0.075	0.0143	0.0707	0.0118	0.0455	0.00176	0.116	0.0133	0.00046	0.0059
11	20-Sep-2020	0.0627	0.0229	0.0139	0.0736	0.0165	0.0194	0.006	0.126	0.0082	0.0498	0.0123
Mann-Kendall Statistic (S):		3	1	12	-4	9	13	5	22	-3	-1	16
Confidence Factor (CF):		67.5%	50.0%	98.2%	69.0%	97.5%	99.2%	76.5%	>99.9%	64.0%	50.0%	>99.9%
Concentration Trend:		No Trend	No Trend	Increasing	No Trend	Increasing	Increasing	No Trend	Increasing	No Trend	No Trend	Increasing

- Continued plume movement/contaminant mobilization.
- Some additional wells now have enough data sets for trending.
- Increase opportunity for recovery and treatment of contaminants.

# Results (Dicamba - 2020)

- Recovered and treated ~160,000 L of impacted groundwater between June and September of 2020
- Groundwater sampling in September 2020
- Trend Analysis shows:

	Monitoring Well:	M11-05	M11-10	M12-14	M12-15	M12-16
Sampling Event	Sampling Date	Dicamba	Dicamba	Dicamba	Dicamba	Dicamba
1	28-Dec-2011		0.0009			
2	21-Aug-2012		0.0011			
3	15-Apr-2013					0.0008
4	12-Aug-2014	0.000019	0.0011	0.000031	0.000013	0.00076
5	11-May-2015	0.000021	0.0003	0.000021	0.000021	0.000015
6	5-Jun-2017	0.000065	0.0015	0.00038		
7	7-Nov-2019	0.0000274	0.00188		0.000059	0.0000298
8	16-Sep-2020		0.00196	0.000163	0.000236	0.0000075
Mann-Kendall Statistic (S):		4	14	2	6	-8
Confidence Factor (CF):		83.3%	>99.9%	62.5%	95.8%	95.8%
Concentration Trend:		<b>No Trend</b>	<b>Increasing</b>	<b>No Trend</b>	<b>Increasing</b>	<b>Decreasing</b>

- Enough data sets in 2020 to complete trend analyses.



# Lessons Learned

- Extended turnaround time between groundwater recovery, sampling the treated water and discharging tanks/reinjecting treated water (turnaround time approximately 4 months)
- Some simple design changes could eliminate this extended turnaround time such as:
  - Double storage capacity on site (two being filled and two being discharged at the same time)
  - Additional solar panels to increase flow rate, decrease recovery time.
  - Potentially discharge treated water into highway ROW with regulatory approval.
  - Remote telemetry for real time monitoring and overall system optimization.

# Sustainability Features

Treated groundwater re-injected on-site providing savings on transportation and disposal transportation cost.

Keeps water within the same hydrological system and creates preferred hydraulic gradient, moving the plume to recovery wells.



Solar-powered pumping system provides low cost, renewable energy source.

# Questions??



Time traveler: What year is it?

Me: 2020

Time traveler:

