Remediation of Water Repellent Petroleum Contaminated Soil from Bemidji, Minnesota by Alkaline Desorption

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Water Repellency in Hydrocarbon Contaminated Soils

- Water repellency is the inability of soil to absorb water, especially when it is very dry
- It is a phenomenon that occurs especially after a long dry spell, or burning
- Problematic in sandy soils –Alberta, Tabasco, Minnesota

Water Repellency Models

Non-polar Hydrocarbons

Slightly polar Hydrocarbons

Natural organic material (charged/polar/non-polar)

Mineral Fraction (negative charge)

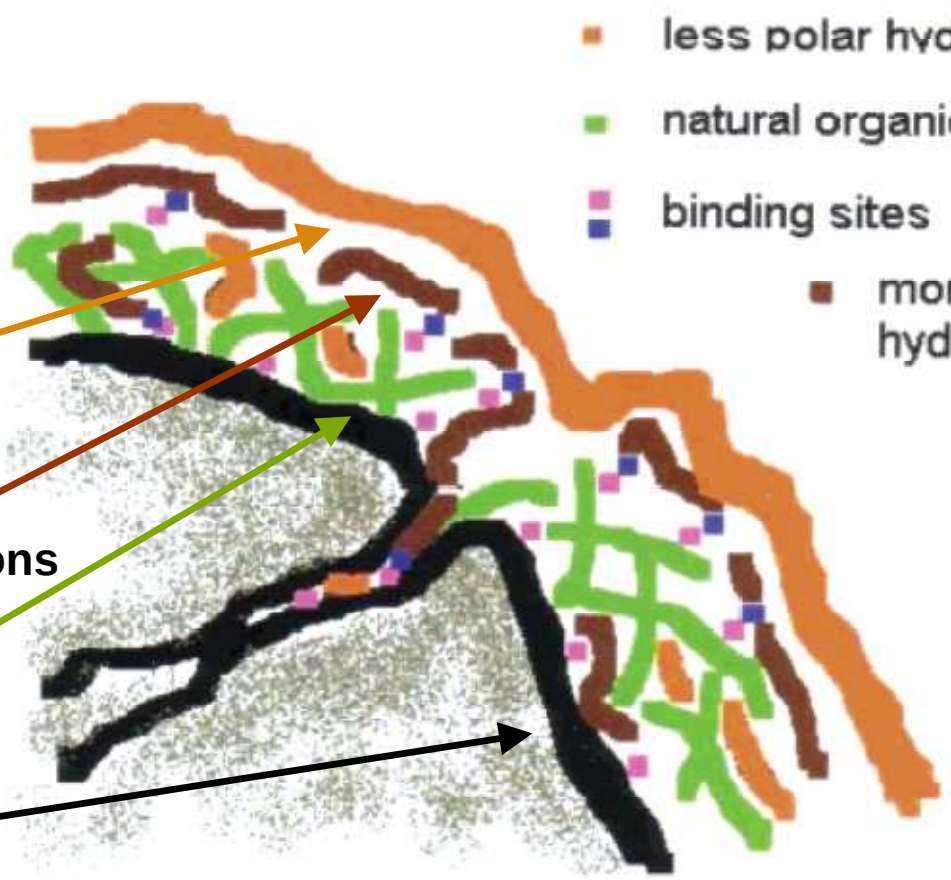


FIGURE 6. Model of the interaction between natural soil organic matter (NOM) and the diagenetic products of petroleum contamination that generates water repellency.

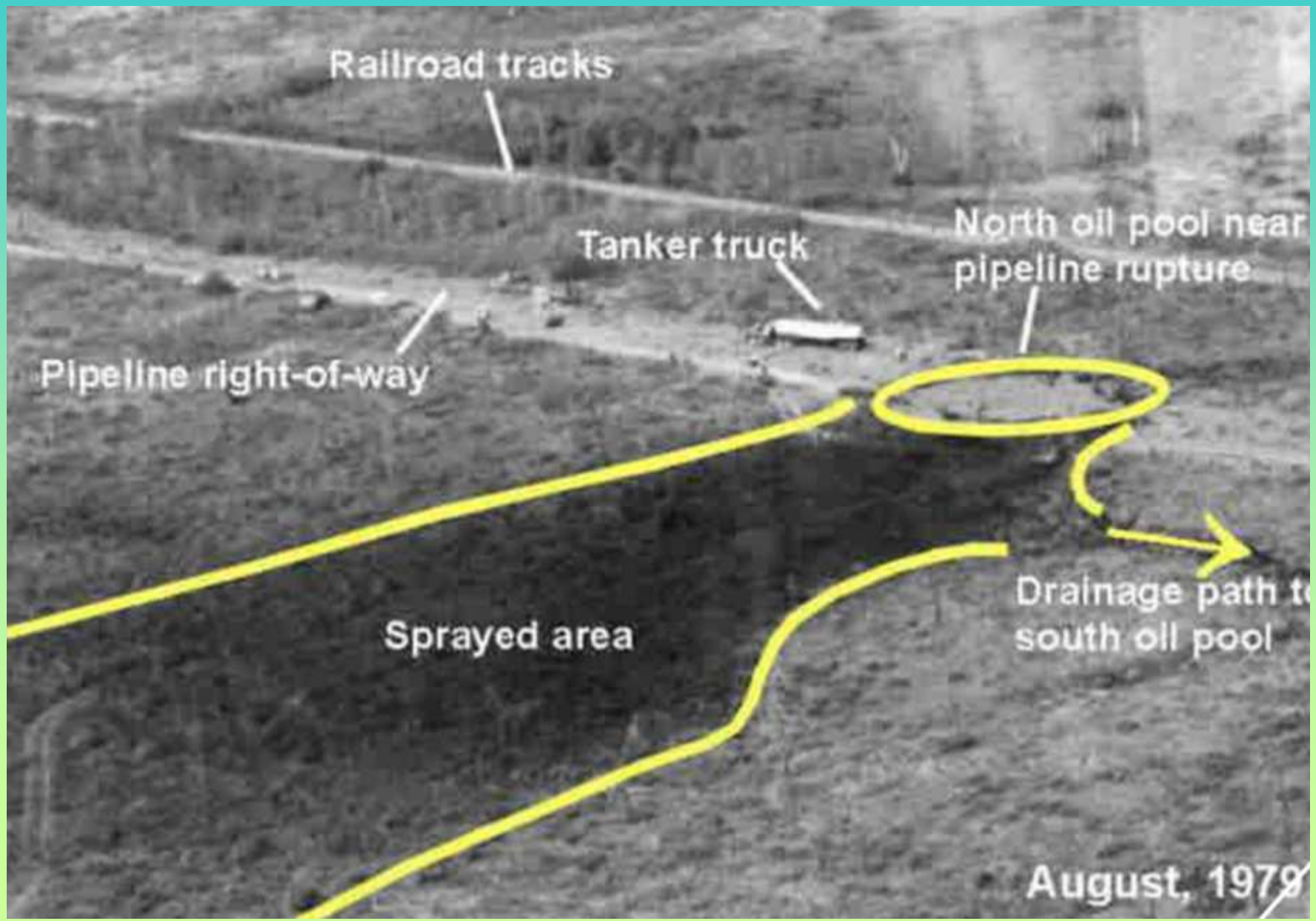
Bemidji Spill - Background

- **1979 Pipeline break**
  - **~2,500 BBLs light crude oil**
  - **surface spraying of roughly 1 Ha. (~2.5 Acre)**

- **Sprayed area was subsequently burned (to reduce oil content) and cleared**

- **Extensive research into groundwater transport and fate, but only recently surface impacts**

Bemidji Spill



Bemidji Spill

Bemidji Spill

Bemidji Spill

IPEC CONTACTS

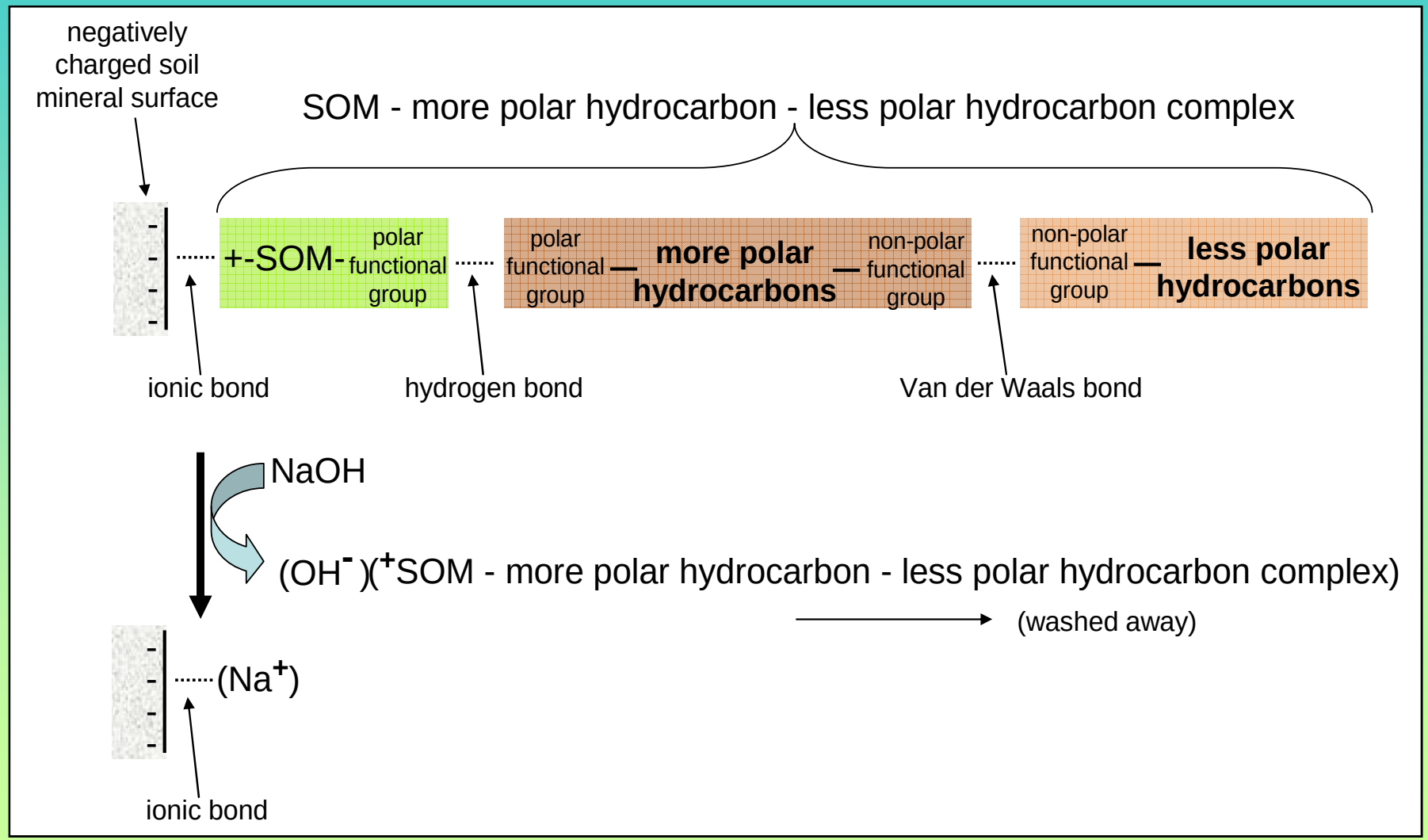
- **2011 Nieber et al. (U Minn) begin to investigate and map water repellency problems in surface soils**

- **In 2011 UJAT report on successful recovery of water repellent sandy soil in Mexico using novel alkaline-desorption method (IPEC)**

- **2012 visit UJAT→ U Minn and Bemidji site to begin collaborative research (Symposium - IPEC Contact)**

- **In present study Alkaline Desorption was applied to Bemidji site (IPEC 2014)**

Alkaline Desorption: Removal of Hydrocarbons by Ion Exchange



Molarity Ethanol Drop Test

- **Simple method developed in W. Australia/Alberta for hydrocarbon contaminated soils**
- **Drops with different molarities of ethanol are added in 0.2 *M* increments**
- **The molarity at which the drop absorbs in 10 seconds is considered the MED value (severity)**

Molarity Ethanol Drop - Modification

Water Drop Penetration Time
WDPT = Persistence

Dificulty for a drop of pure water (rain) to penetrate the soil

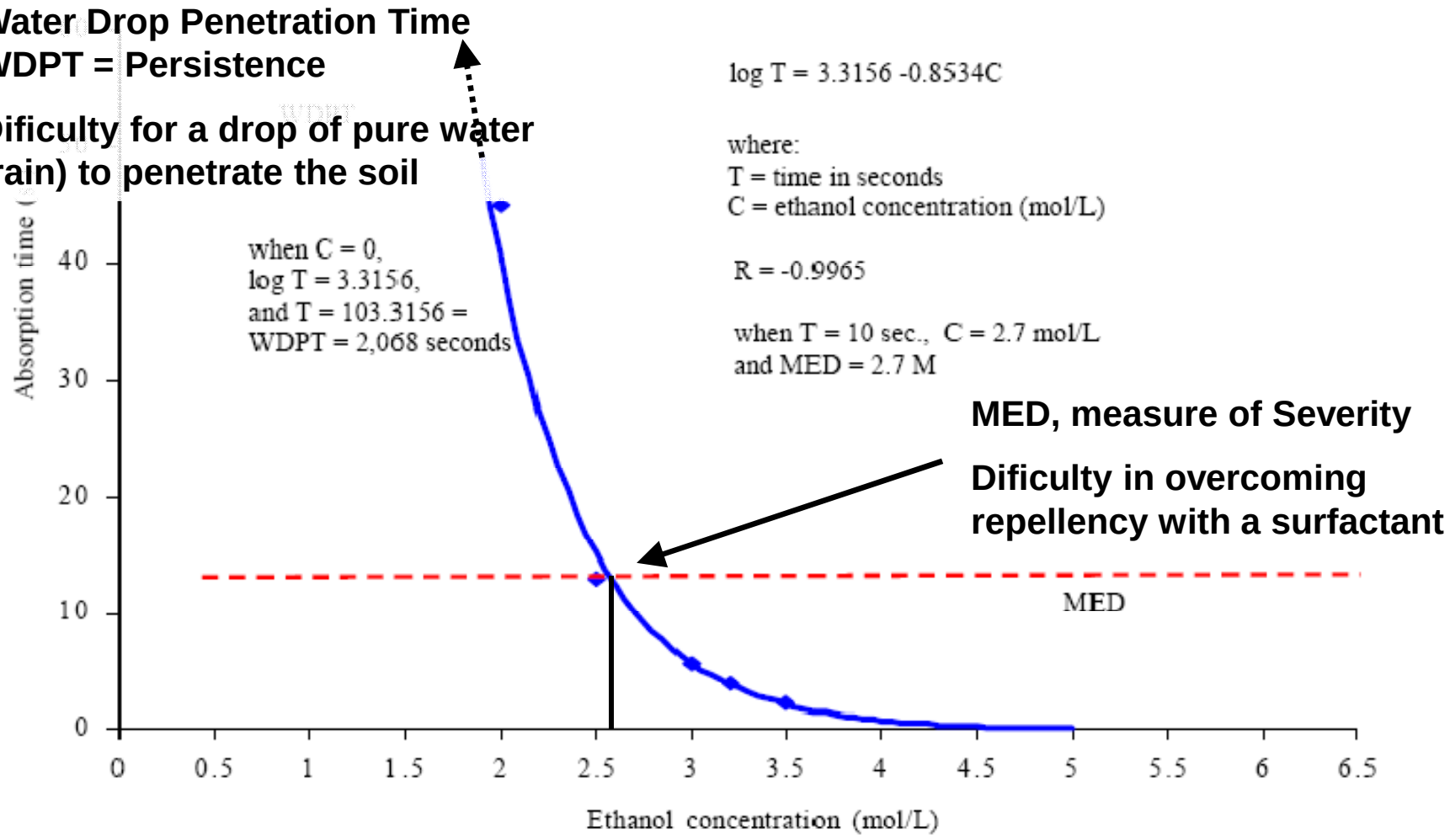


Fig. 2: Logarithmic relationship between ethanol concentration and absorption time used to calculate water repellency severity and persistence

Sample Collection

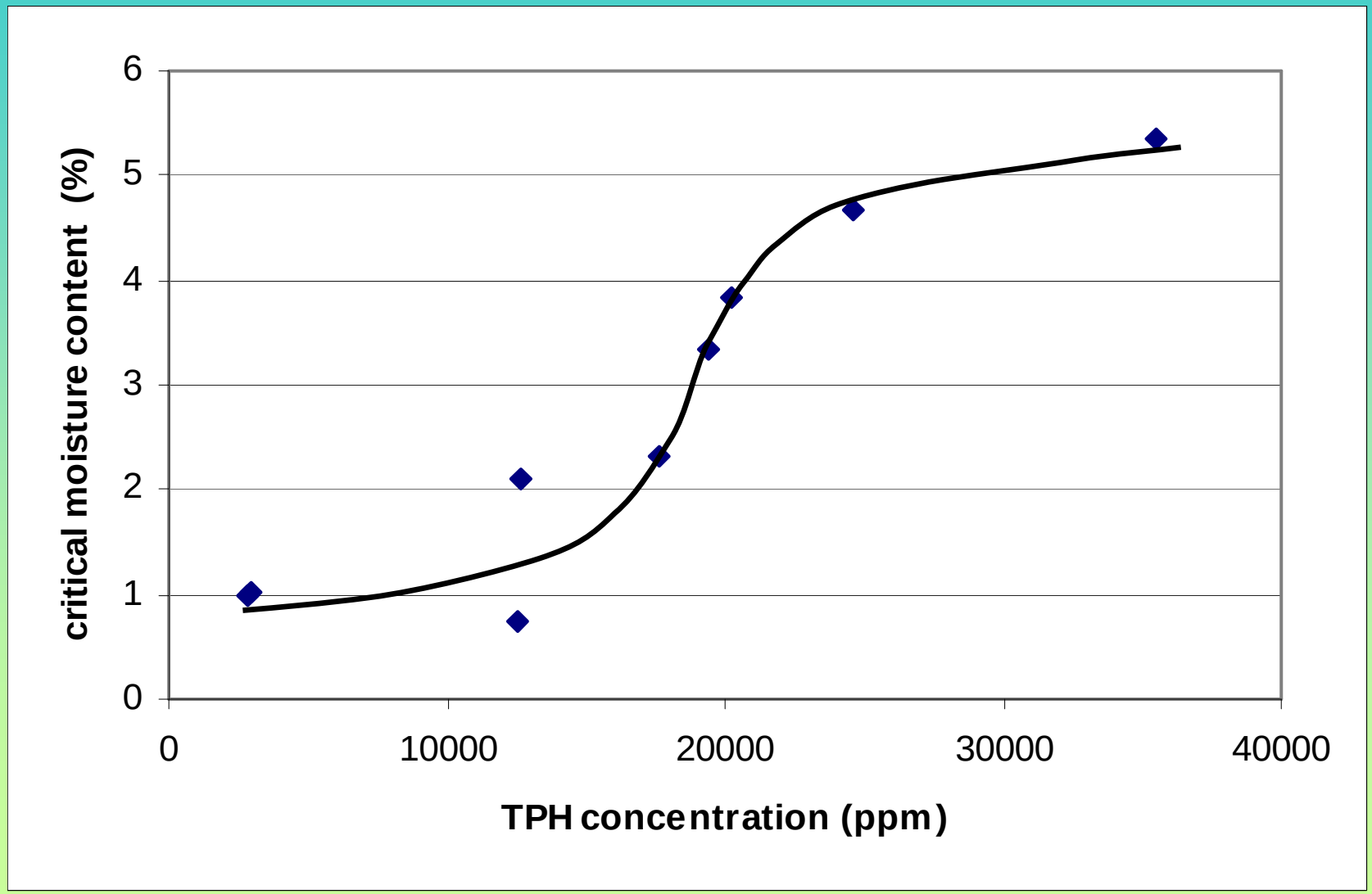
Initial Characterization

Sample	*in situ* moisture content %	MED	WDPT* (s)	Critical moisture content (%)* (60 secs)	Ratio ISMC/CMC	TPH conc. (ppm)	IRAP
Gs-1	0.5	5.08	21,652,098	0.99	0.51	2,809	ND
Gs-2	0.73	12.89	2.1 E+10	3.82	0.19	20,223	350
Gs-3	1.26	10.27	7.5 E+22	5.36	0.22	35,522	184
Gs-4	0.72	11.71	2.2 E+47	4.66	0.15	24,634	341
Gs-5	0.93	6.32	841,782,7077	0.73	1.28*	12,518	ND
Gs-6	0.84	6.67	32,553,673	2.33	0.36	17,652	ND
Gs-7	0.58	5.03	425,598	1.01	0.57	2,986	ND
Gs-8	0.47	11.44	1.7 E+105	2.09	0.22	12,715	ND
Gs-9	0.72	11.74	4.9 E+33	3.34	0.22	19,423	256

NOTE: all samples non-toxic by Microtox bioassay

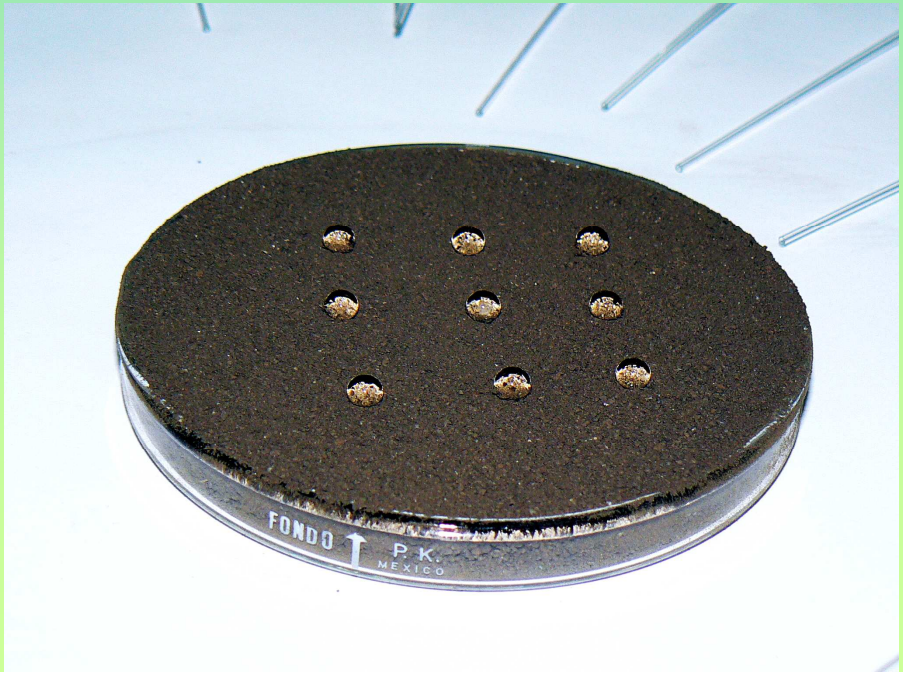
Critical Moisture Content measured on drying cycle (hysteresis)

Critical Moisture Content vs Conc



Alkaline Desorption

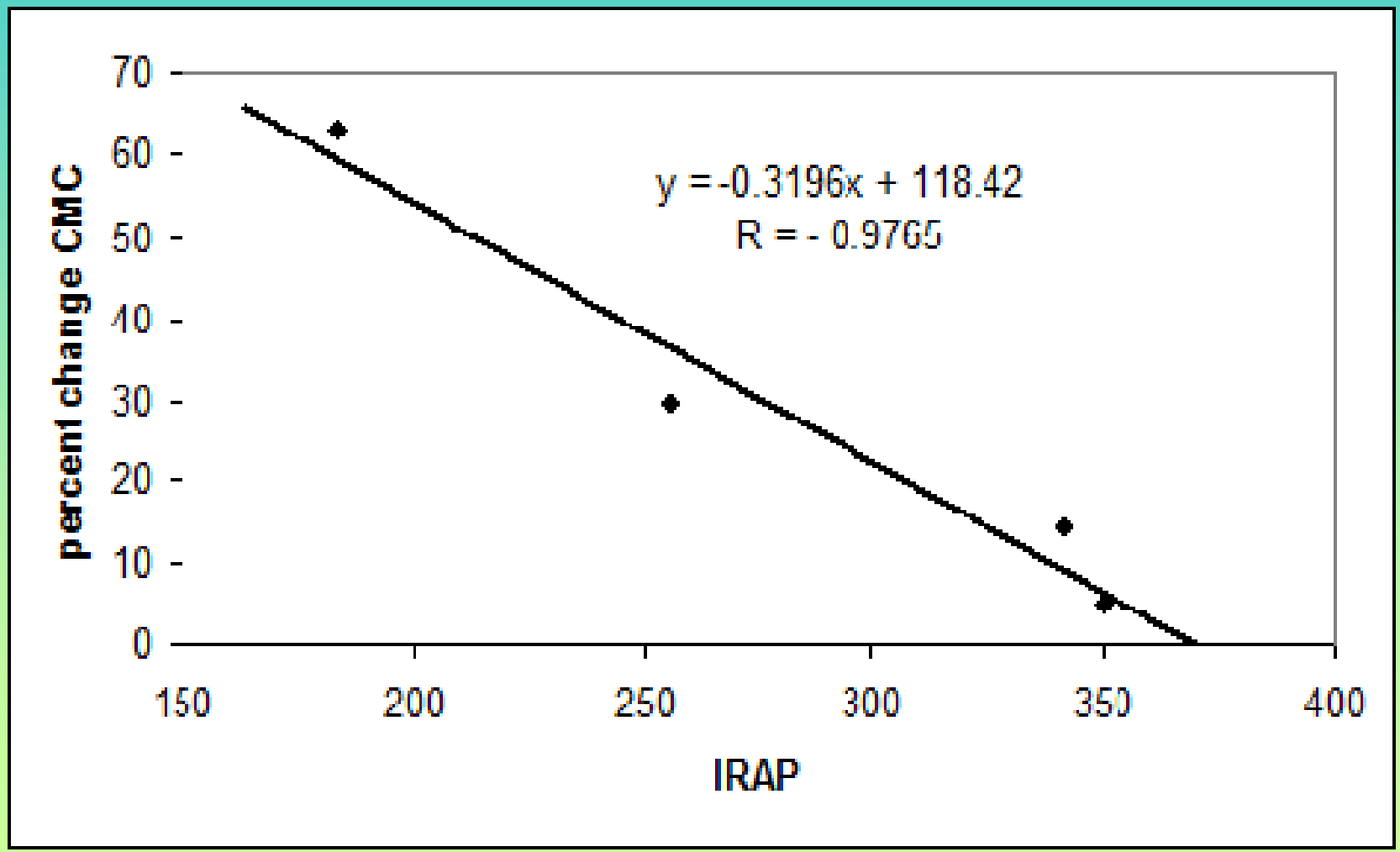
- **0.1 N NaOH at 1:3 solution to soil, divided into two doses**
- **let drain 48 hrs between additions**
- **Rinse with same volume de-ionized water**
- **Air dry completely for several days**
- **Retest for MED/WDPT, Critical Humidity**



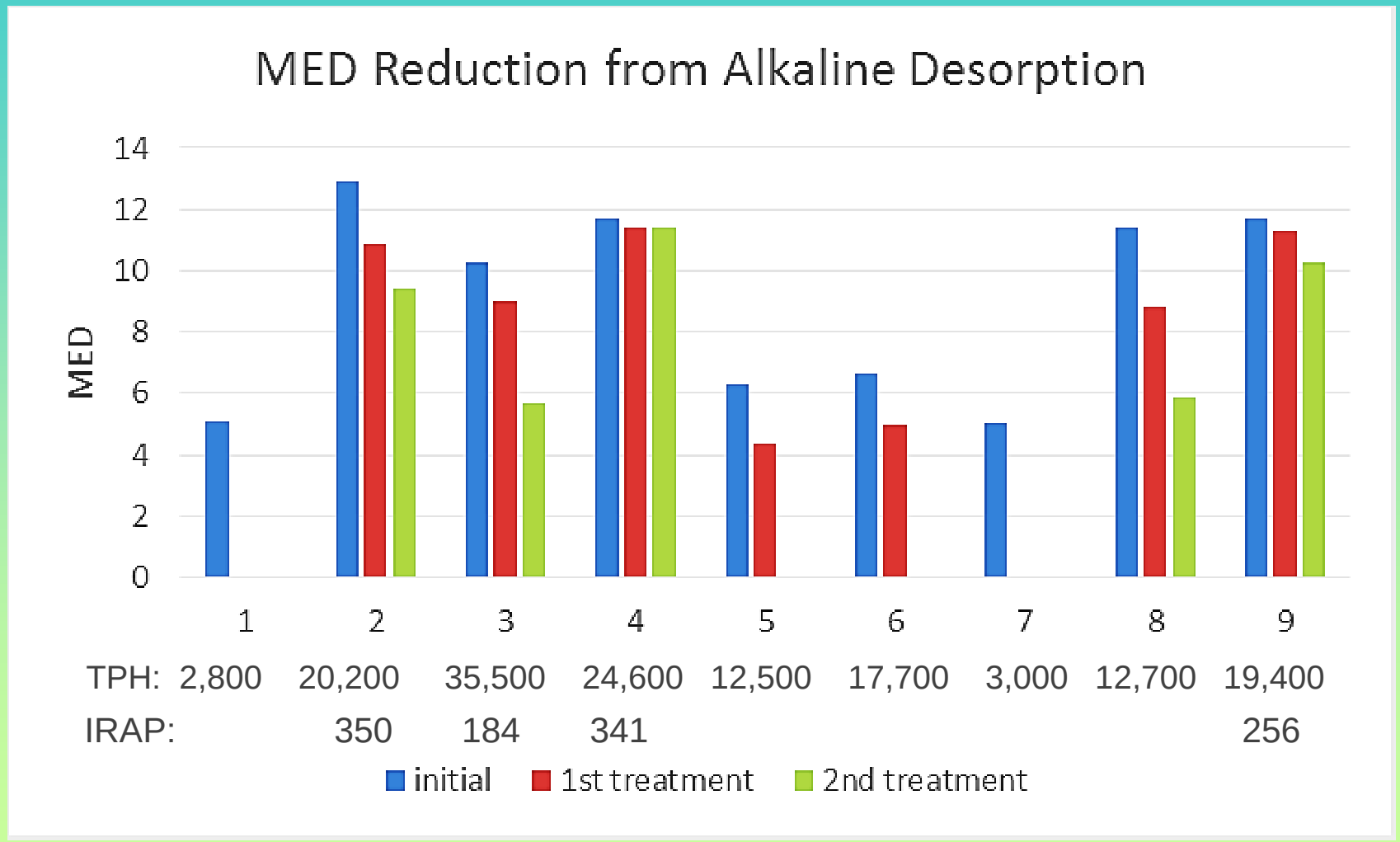
Water repellency after alkaline desorption treatment

Sample	*in situ* moisture content %	MED	WDPT (s)	Critical moisture content (%)	Ratio ISMC/CMC	Percent reduction CMC
Gs-1	0.5		25	NR	NR	100.0
Gs-2	0.73	10.89	1.6 E+19	3.64	0.20	4.8
Gs-3	1.26	9.02	8.2 E+27	1.97	0.64	63.3
Gs-4	0.72	11.41	2.9 E+31	3.98	0.18	14.5
Gs-5	0.93	4.36	6,002	-0.05*	NR	93.7
Gs-6	0.84	4.95	124,079	-0.10*	NR	95.9
Gs-7	0.58		50	NR	NR	100.0
Gs-8	0.47	8.85	1.5 E+14	1.90	0.25	9.0
Gs-9	0.72	11.3	4,293,386,635	2.35	0.31	29.6

HC Polarity vs Reduction in Critical Moisture Content



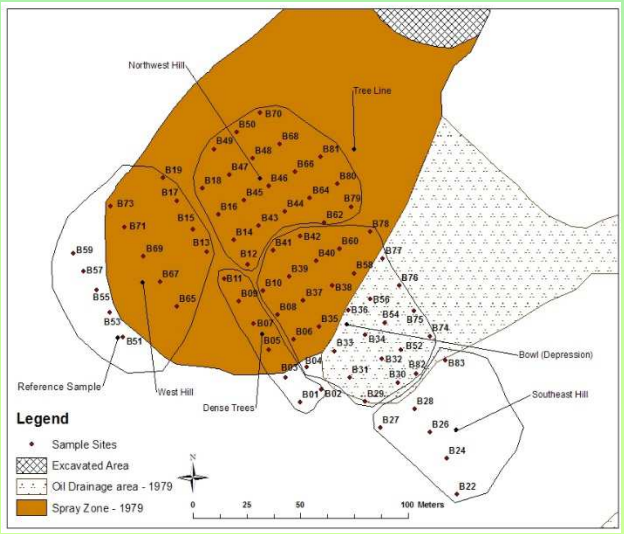
Effectiveness of Sequential Treatments



Restoration of Water Repellent Soil

- **Previous results from Tabasco included:**
  - **final addition of organic amendment (cachasse)**
  - **phytorestoration with fine, diffuse rooted grass**

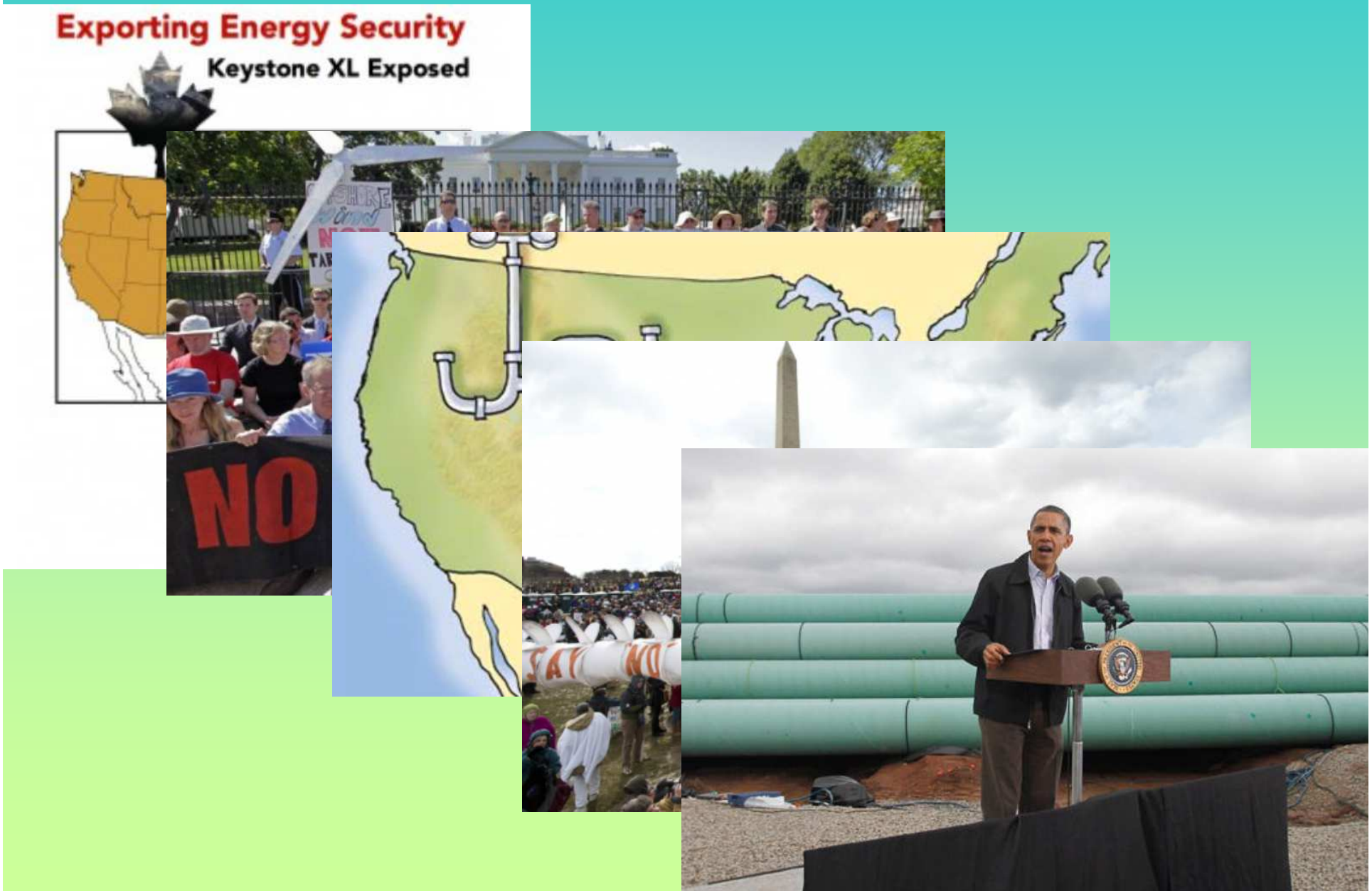
- **In Bemidji, need to add organic amendment and/or clay addition (unpublished work – U Minn)**



Relevance

- **Large Pipeline Projects Planned**
  - **Alberta Clipper Pipeline Expansion (double current capacity)**
  - **Keystone XL Pipeline**

Pipeline Projects



Pipeline Projects

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  - **Keystone XL Pipeline**

- **Important to have adequate spill contingency plans for possible future spills.**

Conclusions

- **Don’t burn! -especially in sandy soils**
  - **long term - loss of vegetation not due to toxicity, but water repellency (also, field capacity)**
- **effectiveness of Alkaline Desorption depends on polarity of HC, (and secondarily, concentration)**
- **sequential treatments**
- **combinations with:**
  - **clay additions**
  - **organic amendments**
  - **phytorestoration -grasses with diffuse root system**
- **Field test started in July 2014**

Field Studies


Thank you for you attention
Questions?