Bioremediation Coupled with Chemical Oxidation for Treatment of Oil-Based Drill Cuttings

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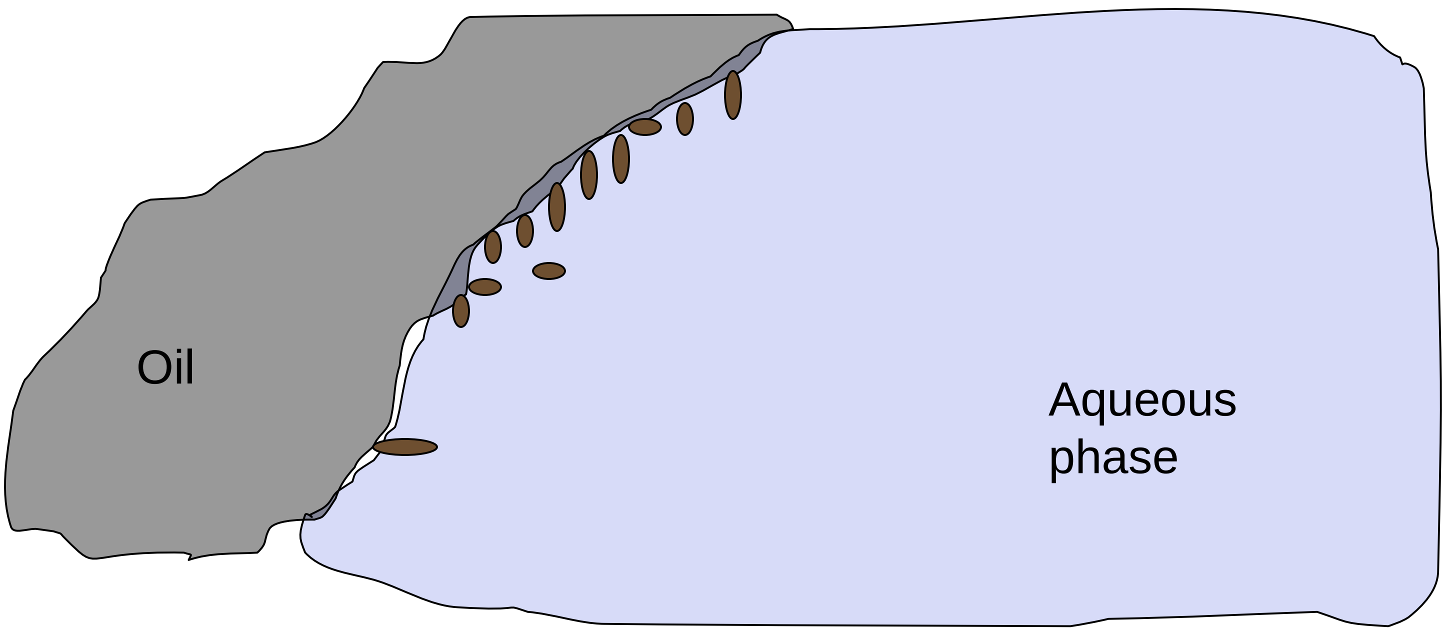
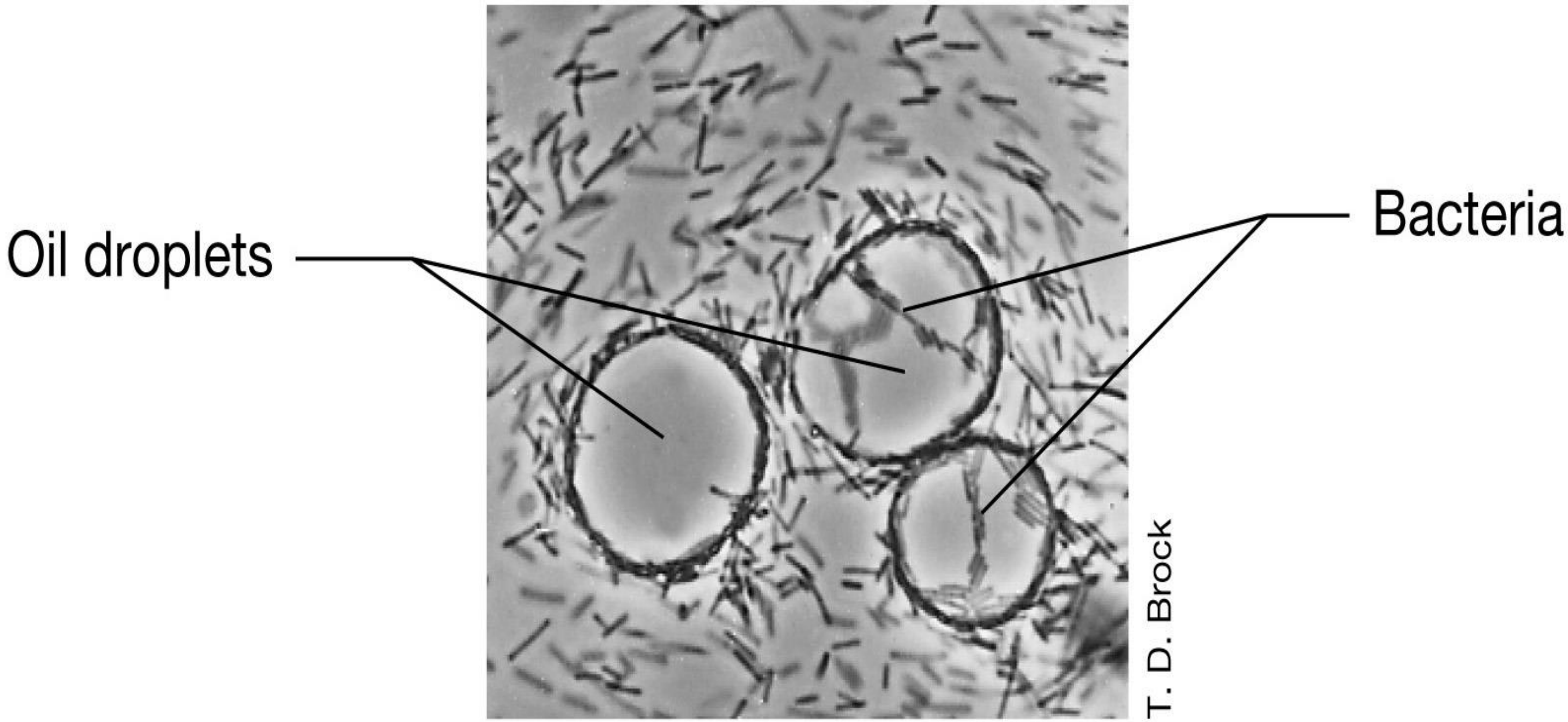
Remediation of Hydrocarbon in Soils

- Typical bioremediation process for hydrocarbons:
  - Fertilizer
    - Provide N and P for hydrocarbon degraders
  - Bulking agent
    - Increase O_2 and water infiltration
  - Tilling
    - Mixing
    - Aeration
  - Moisture

Bioavailability of petroleum hydrocarbons

- Most important mechanism
  - Direct contact of microorganisms with a bulk liquid hydrocarbon phase (interfacial contact)





Droplets of mineral oil in a culture of hydrocarbon-degrading bacteria

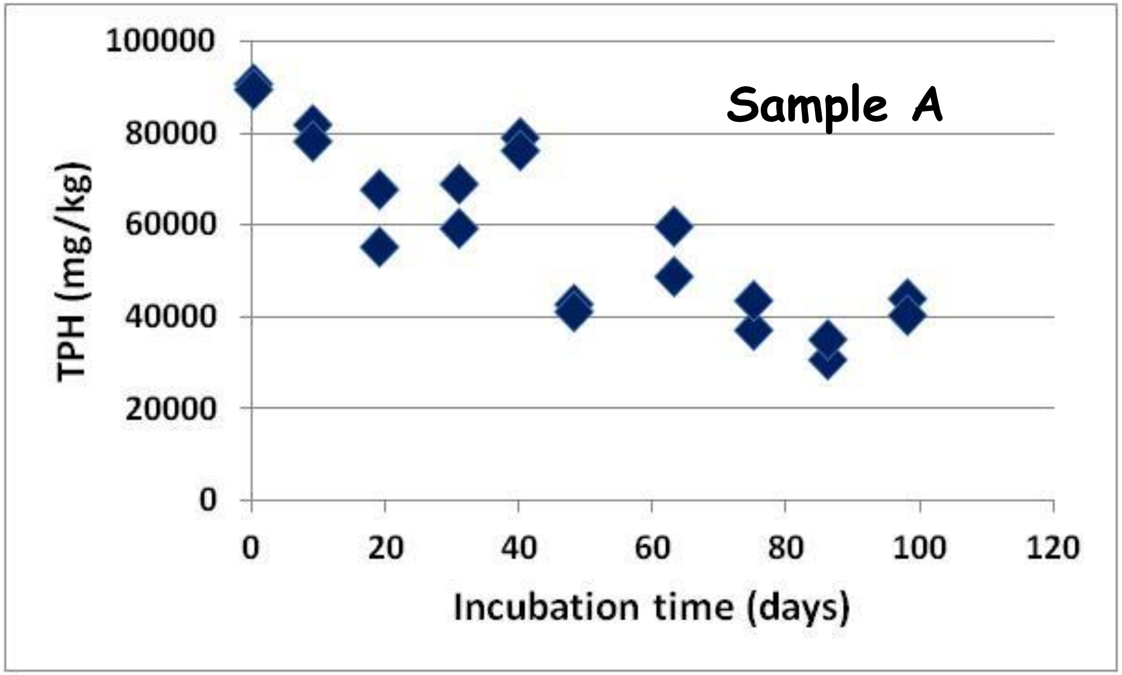
Recommended practice for landfarms

Getting the microbes together with the hydrocarbon

- Increasing surface area for contact between soil water and hydrocarbon is very important to increasing rates of biodegradation
- If the initial TPH concentration is too high for optimum treatment, you can dilute the contaminated soil with uncontaminated soil to increase rates of bioremediation:
  - Utilize full 6-8 inch depth
  - Utilize surrounding soil as a diluent
  - **Rule of thumb: dilute until the soil no longer glistens**

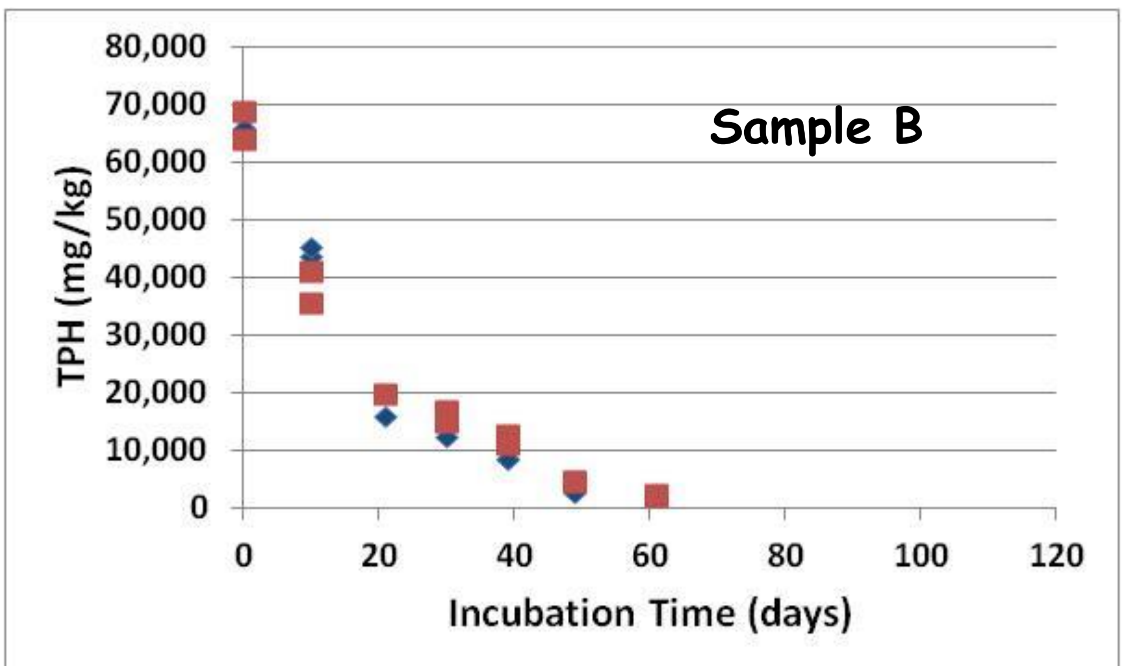
What about treatment of drill cuttings?

- Adding topsoil
  - Provides an inoculum
  - Improves moisture holding capacity
  - Improves nutrient retention
  - Improves permeability and aeration
  - Creates more surface area for contact between hydrocarbon and soil moisture
  - Decreases hydrophobicity and improves wettability
  - **Increases final volume of treated material which can generate disposal issues**



Two drill cuttings samples each blend with topsoil in same ratio and treated in the same way to encourage bioremediation of diesel hydrocarbons

- Nutrients
- Moisture
- Aeration



Clearly sample A is degrading very slowly compared to Sample B. It's not a salinity issue!

The Cool-Ox® process

(Producing hydrogen peroxide in situ)

$$CaO_2 + H_2O \rightarrow Ca(OH)_2 + H_2O_2$$

(Chelates activate intrinsic catalysts)

$$H_2O_2 + Fe^{+2} \rightarrow (OH)^- + [OH]^\bullet + Fe^{+3}$$

$$H_2O_2 + Fe^{+3} \rightarrow (OH)^- + [OOH]^\bullet + Fe^{+2}$$

(Radicals react with contaminants)

$$[OH]^\bullet \;\&\; [OOH]^\bullet + C_x \rightarrow C_x(OH)_y$$

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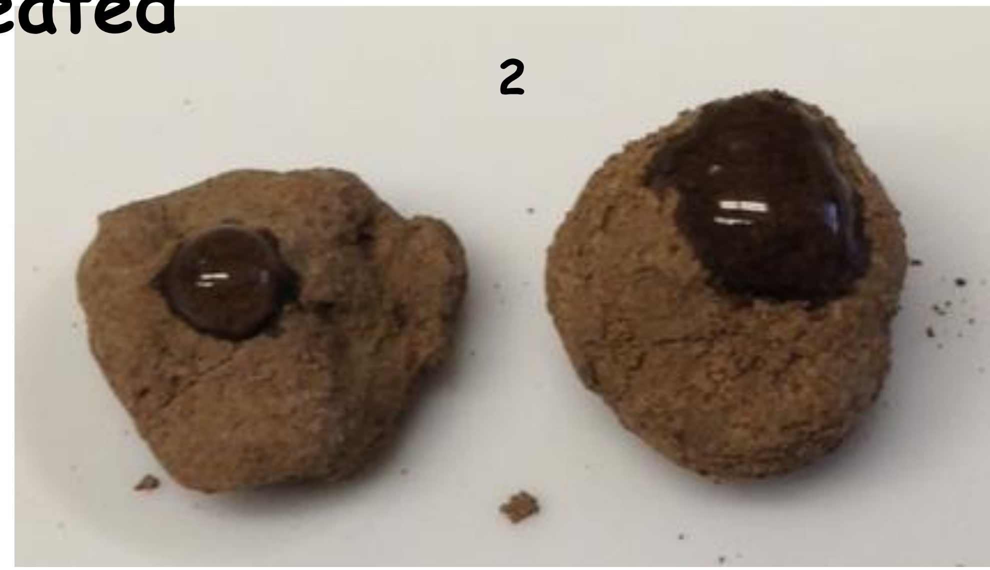
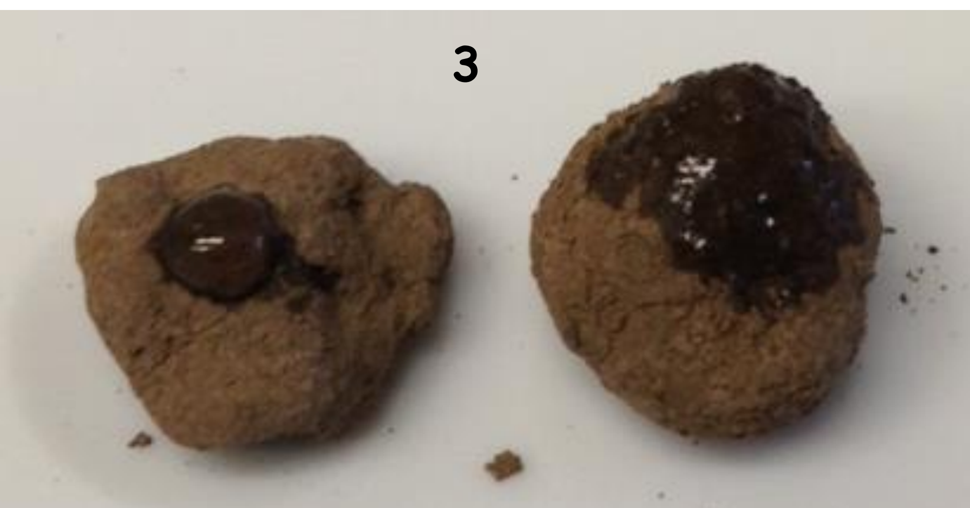
Highly biodegradable
and hydrophilic

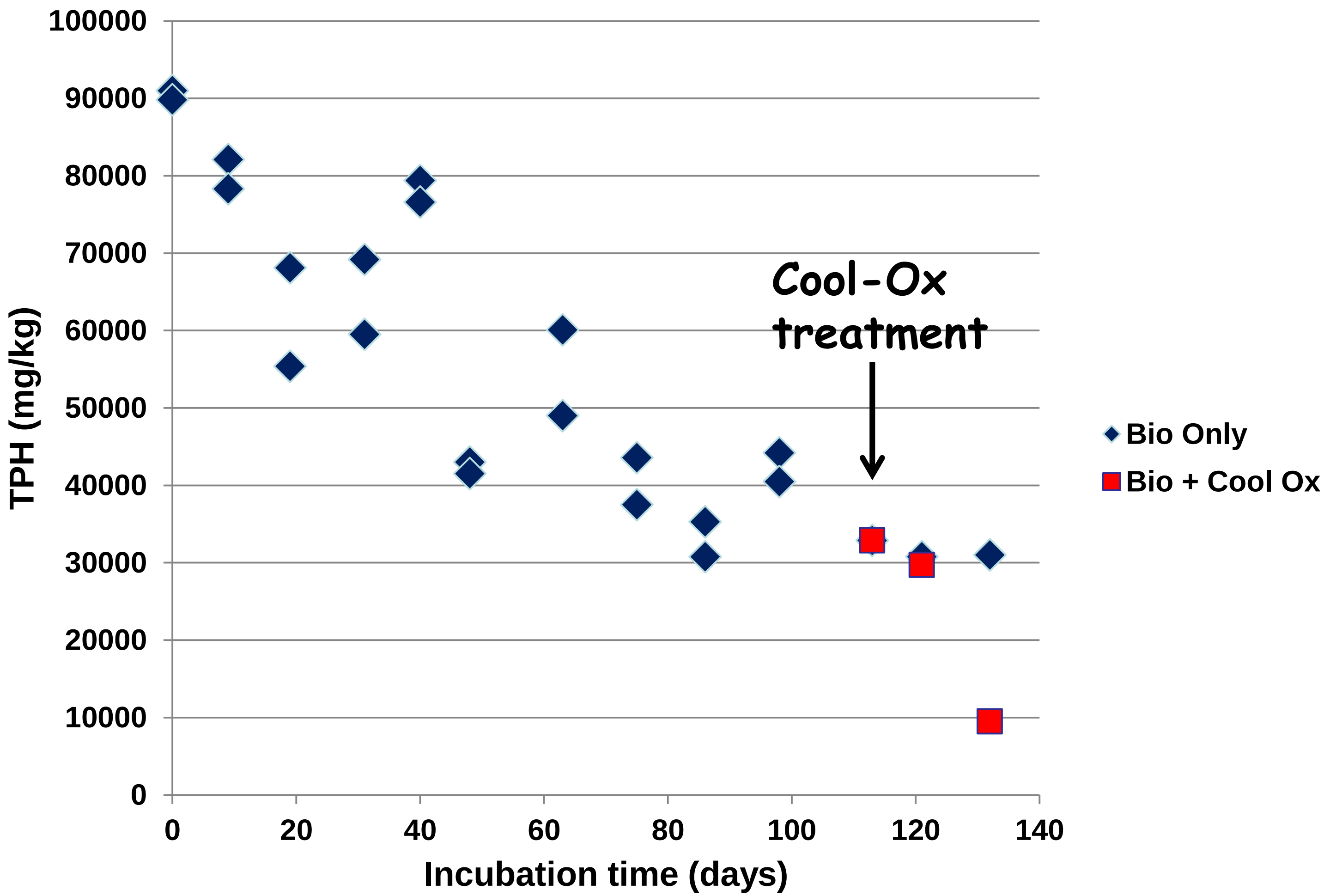
Wettability of Cool-Ox treated hydrophobic cuttings/soil blend: left, control; right, Cool-Ox treated



Timeframe: 1 min



After > 100 days of bio treatment Sample A was split and half treated with Cool-Ox



Preliminary conclusions

- Cool-Ox treatment greatly accelerated degradation of diesel hydrocarbons in a cuttings/soil blend that was hydrophobic and biodegrading very slowly
- Was the effect purely oxidation, improved wettability, or both?

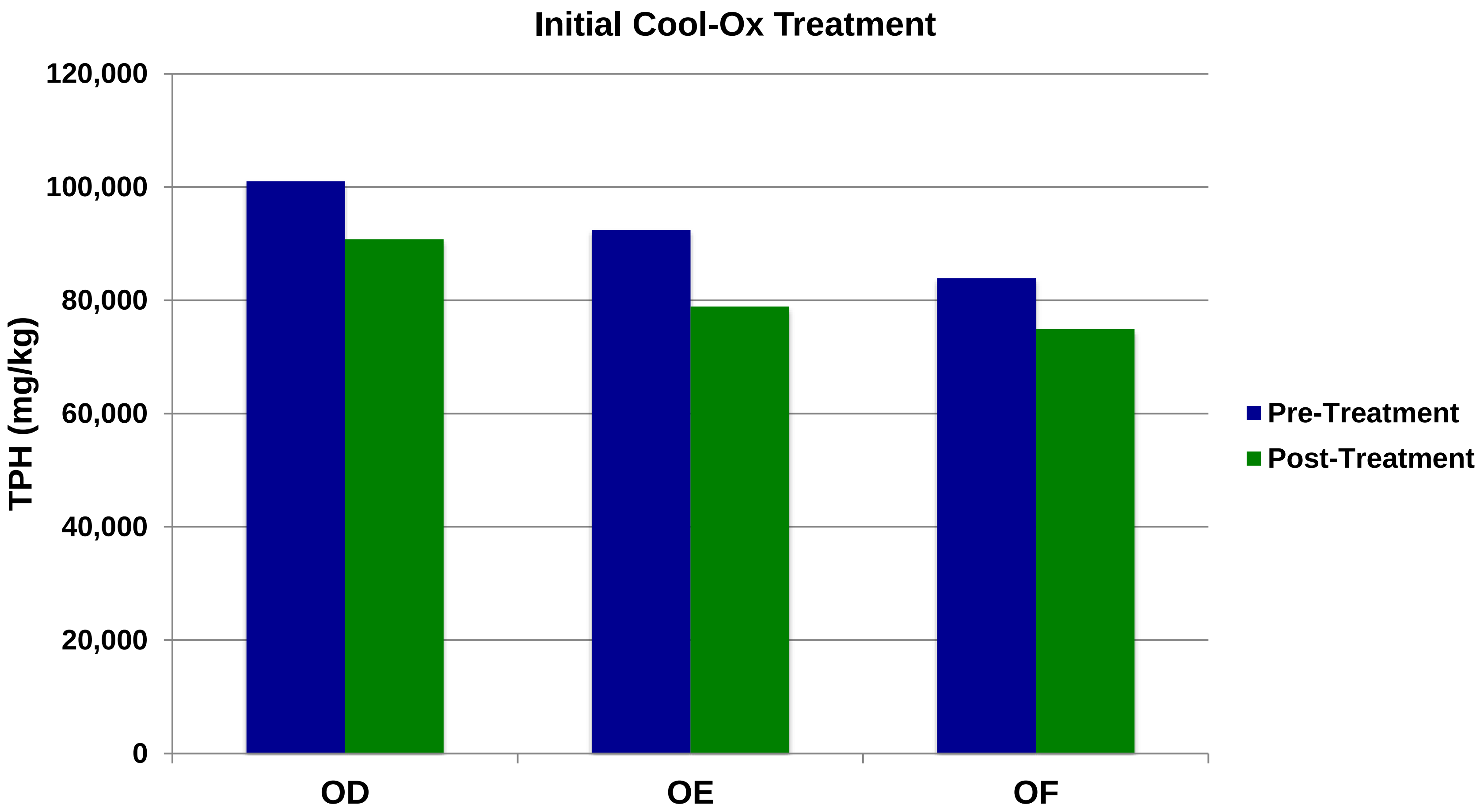
ISCO/Bio/ISCO Treatment of Oil-Based Drill Cuttings

- Samples of neutralized drill cuttings (avg. 9 wt% TPH) were pretreated with Cool-Ox: objective was reduction in hydrophobicity

Pre-bio Cool-Ox treatment of Ohio stabilized cuttings, application rate 10 gal/yd^3 (10 day incubation)

Fraction	% H_2O_2	% Cool-Ox Solids
Ohio D	5	8
Ohio E	4	6
Ohio F	0	0

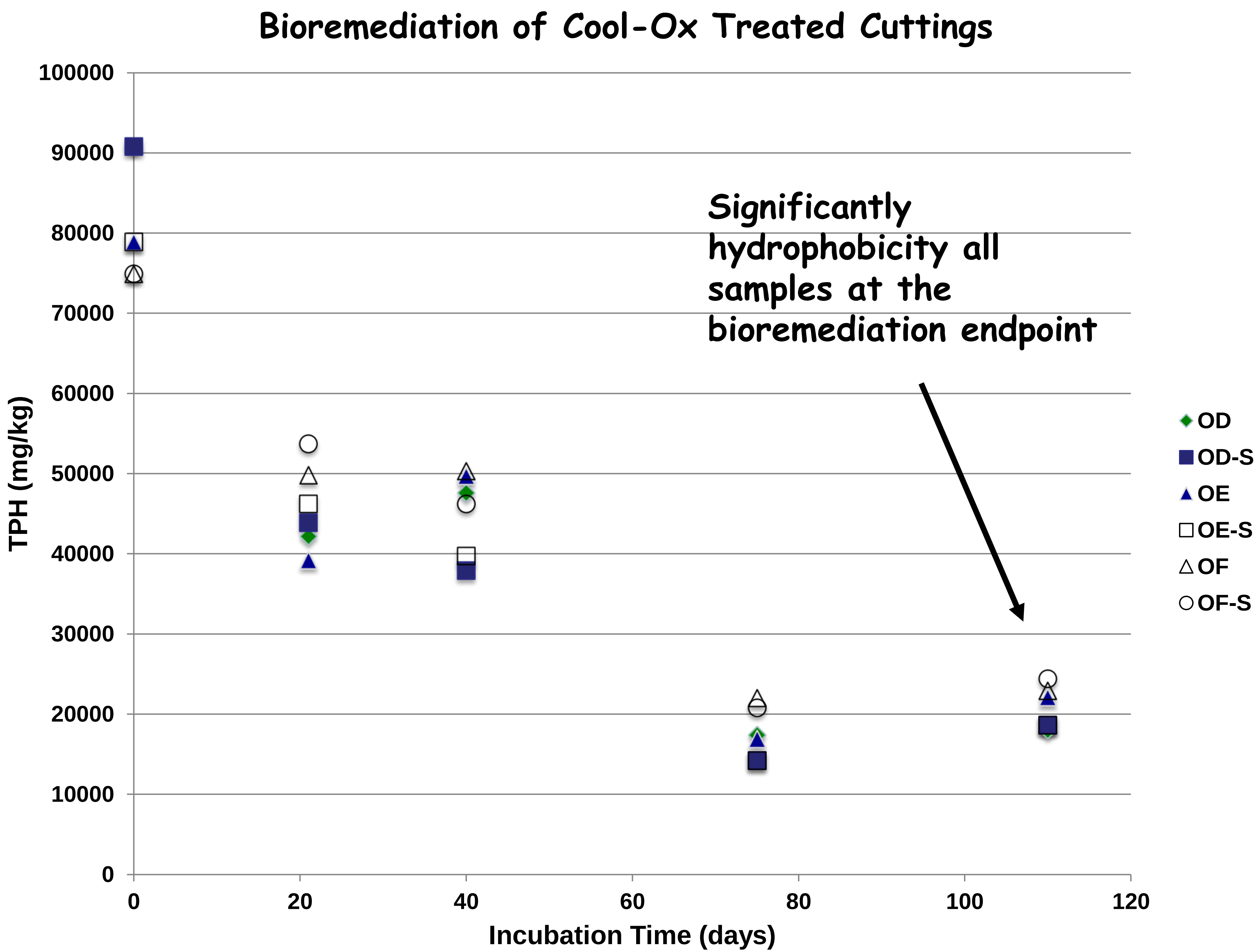
TPH concentrations in stabilized and neutralized cuttings pre- and post-initial treatment with Cool-Ox



Biotreatment

Sample	Cool-Ox pretreatment	Soil inoculum (2 wt%)
OD	yes	no
OD-S	yes	yes
OE	yes	no
OE-S	yes	yes
OF	no	no
OF-S	no	yes

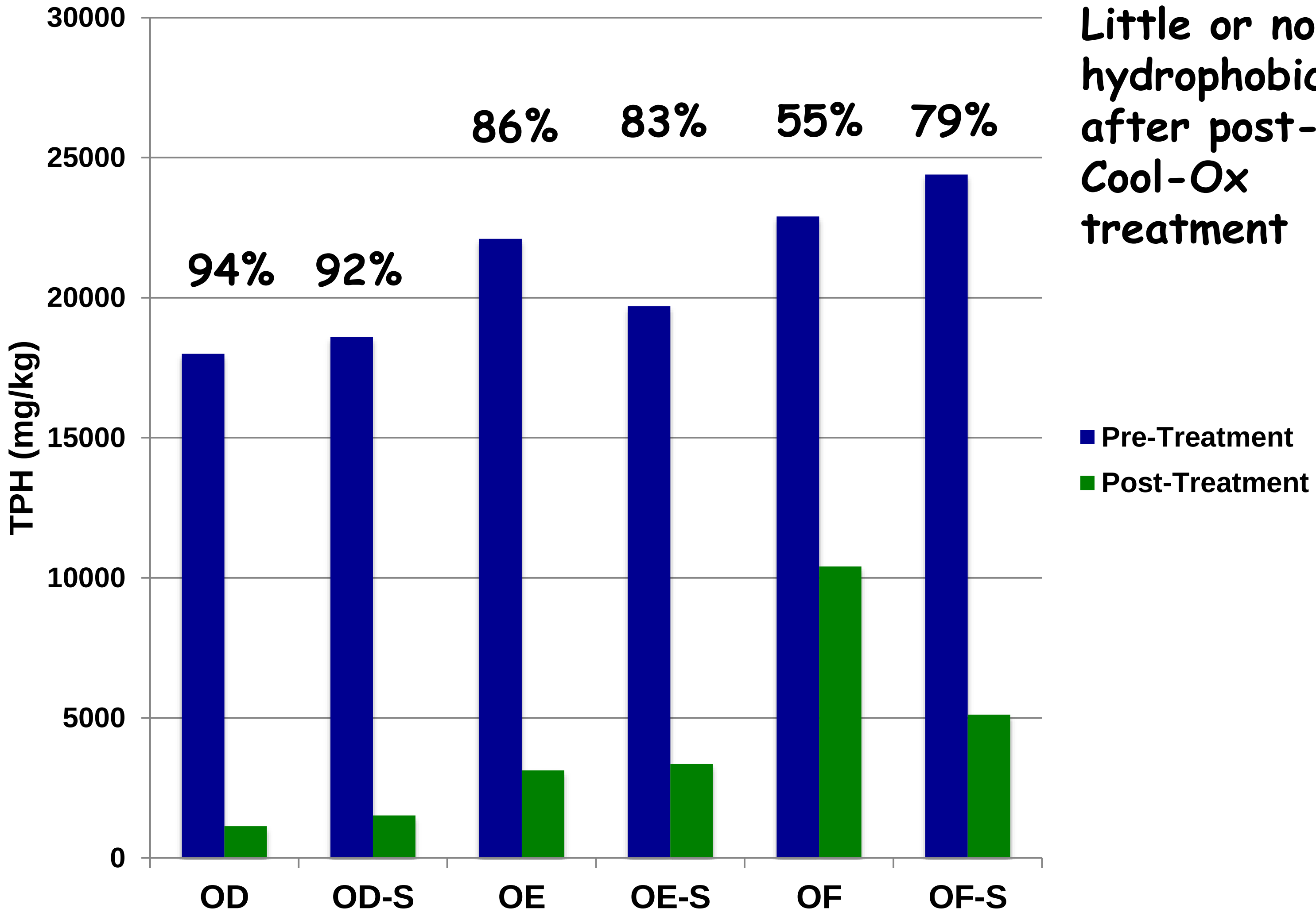
+ nutrients


Bioremediation of Cool-Ox Treated Cuttings
Significantly hydrophobicity all samples at the bioremediation endpoint
TPH (mg/kg)
Incubation Time (days)
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
20
40
60
80
100
120
OD
OD-S
OE
OE-S
OF
OF-S

Post-bio Cool-Ox treatment

Sample	% H_2O_2	% Cool-Ox Solids
OD	3	6
OD-S	3	6
OE	4	8
OE-S	4	8
OF	5	10
OF-S	5	10

Results of post-bio Cool-Ox treatment



Little or no hydrophobicity after post-bio Cool-Ox treatment

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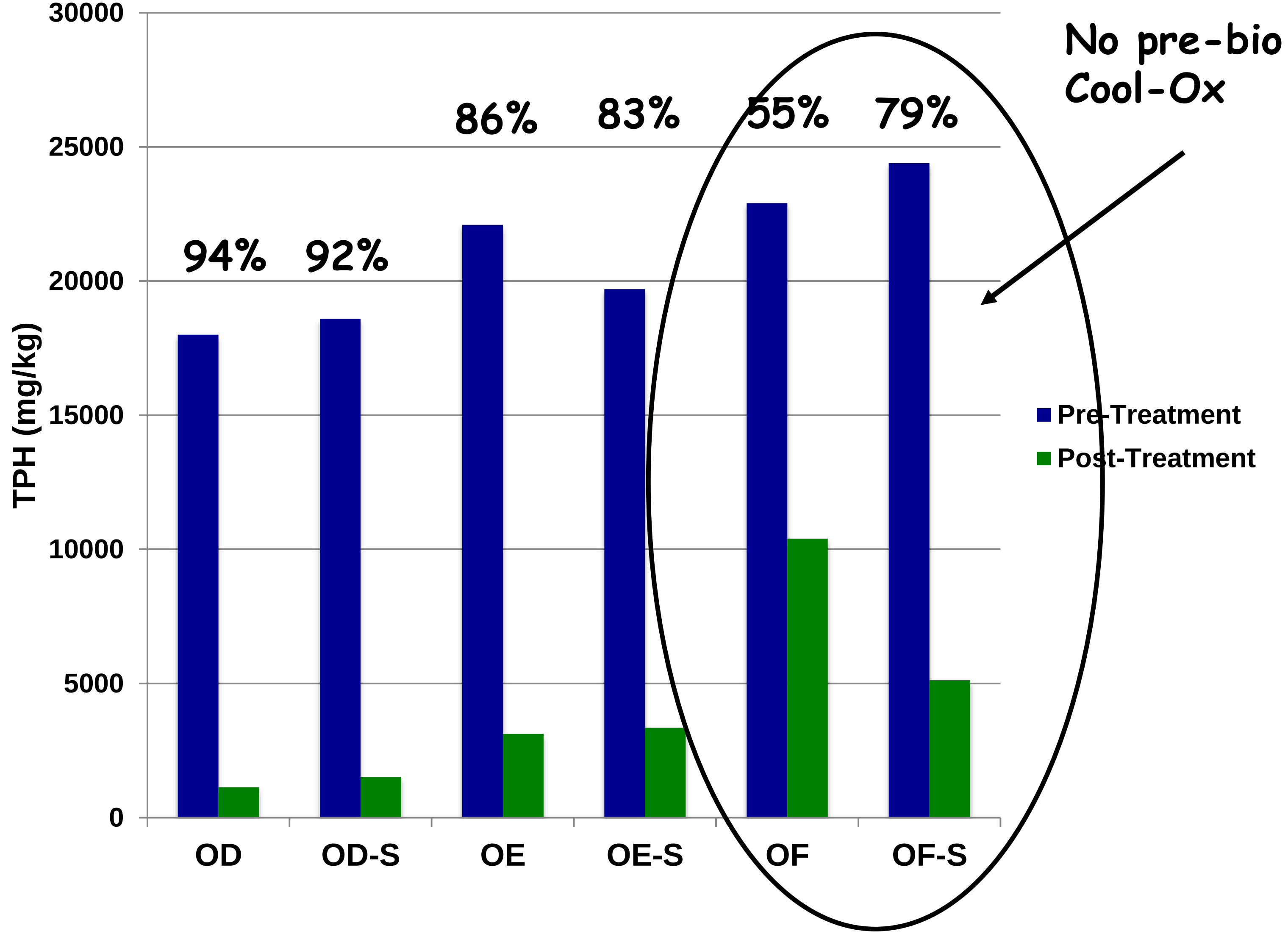

Conclusions

- Pre-bio Cool-Ox treatment of stabilized drill cuttings had no detectable effect on TPH concentration but may have positively affected final results of a ISCO/bio/ISCO treatment chain
- Biotreatment alone did not achieve treatment goals likely due to hydrophobicity
- Biotreatment followed by ISCO achieved treatment goals and rendered cuttings non-hydrophobic
  - Reductions in hydrophobicity makes soil washing to remove salts feasible


Any Questions?
SCENIC
TURNOUT
AHEAD