Is There a Role for Chemical Oxidation in the Biodegradation of Hydrocarbons at High Concentrations?

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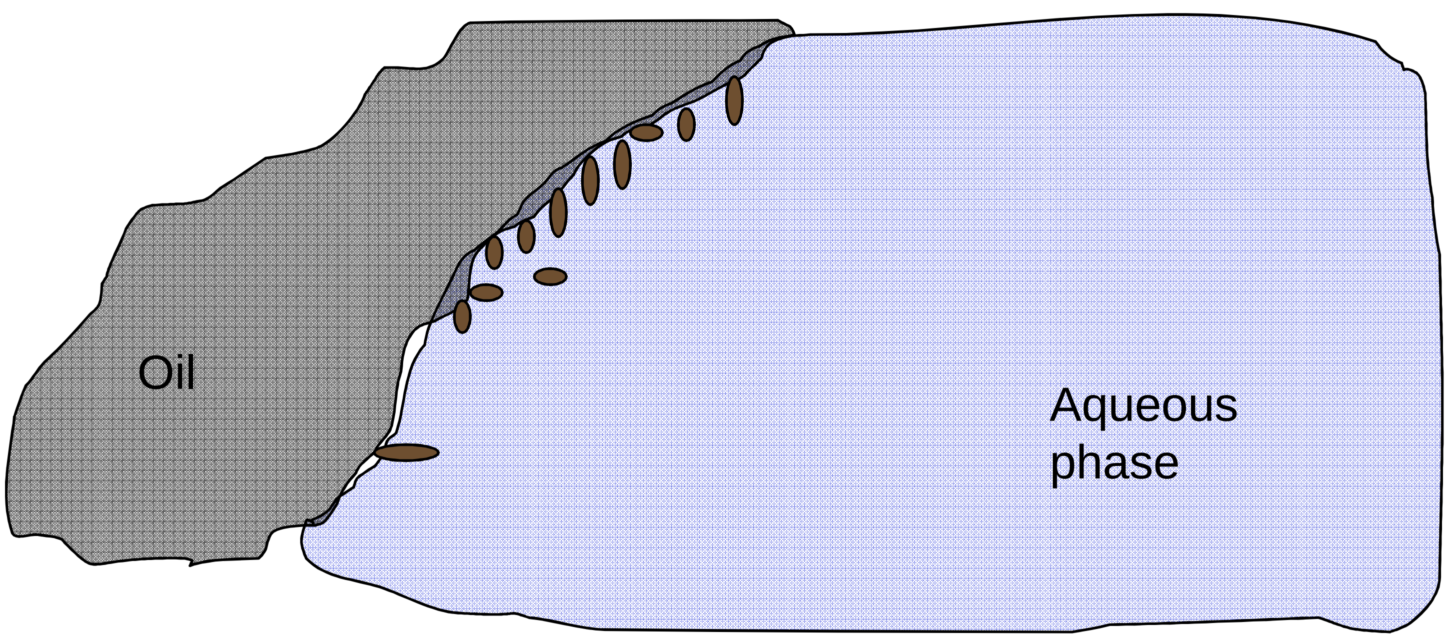
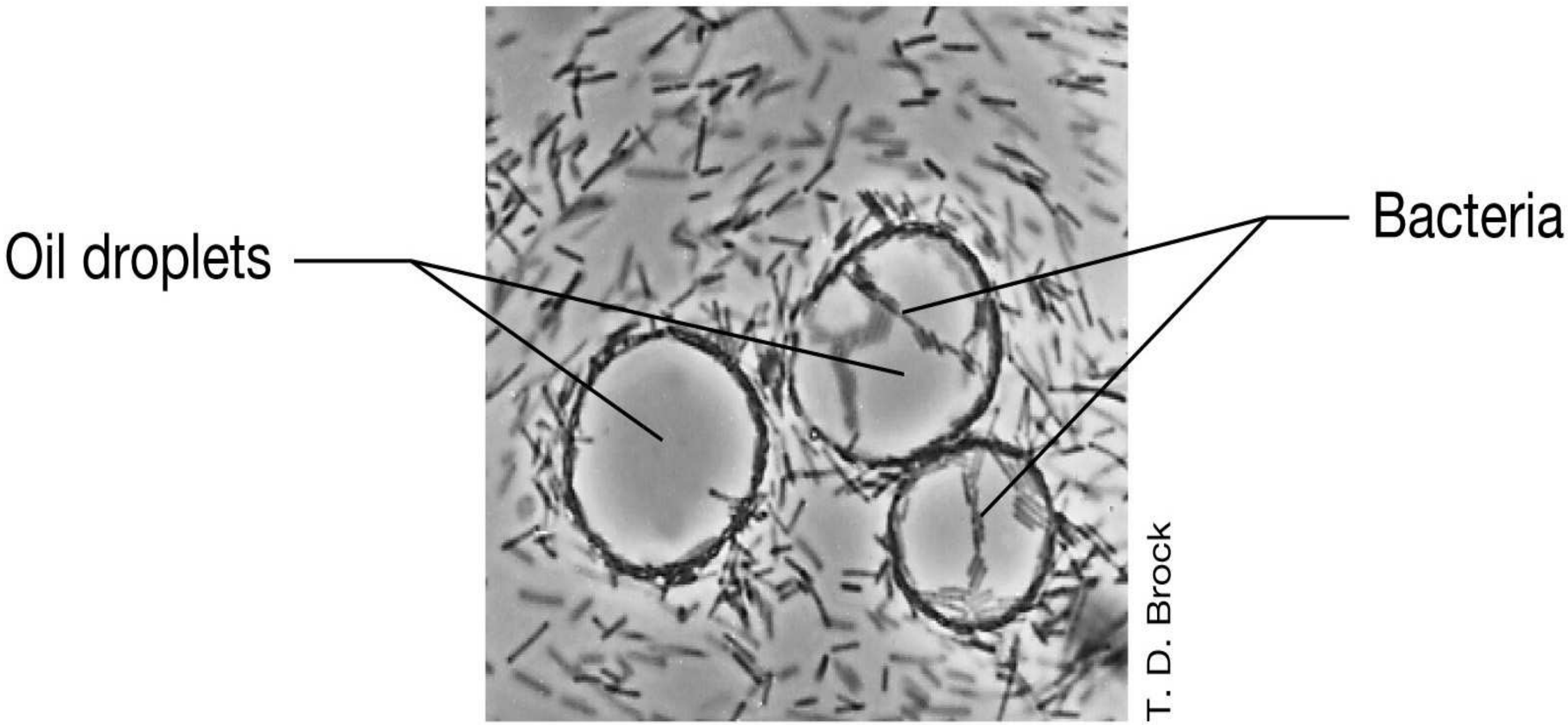
Remediation of Hydrocarbon in Soils

- 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

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




Oil droplets
Bacteria
T. D. Brock

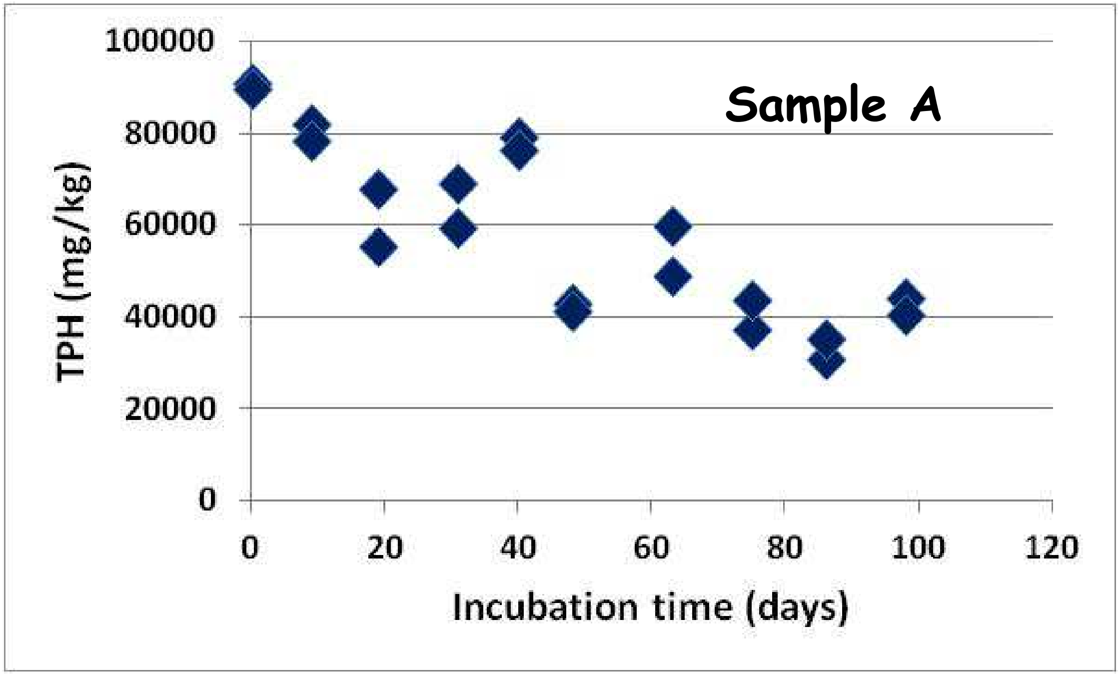
Recommended practice for landfarms

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**

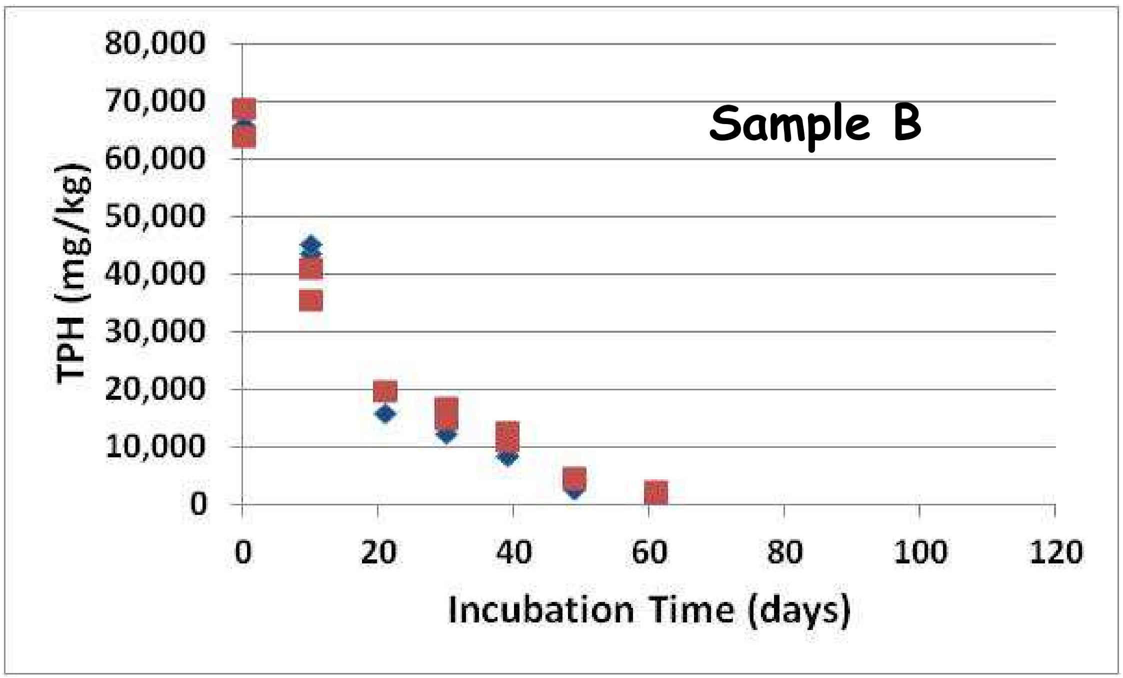
What about treatment of drill cuttings and tank bottoms?

- 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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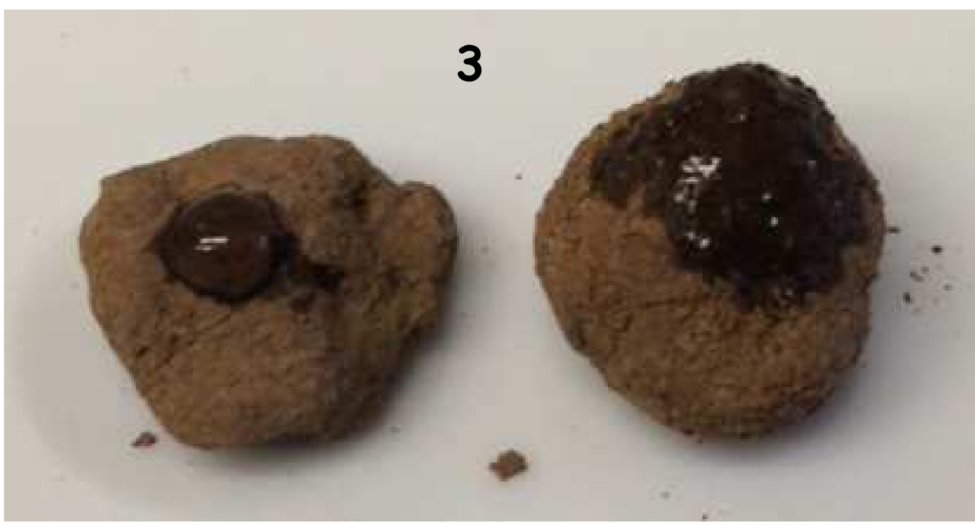
Highly biodegradable and hydrophilic

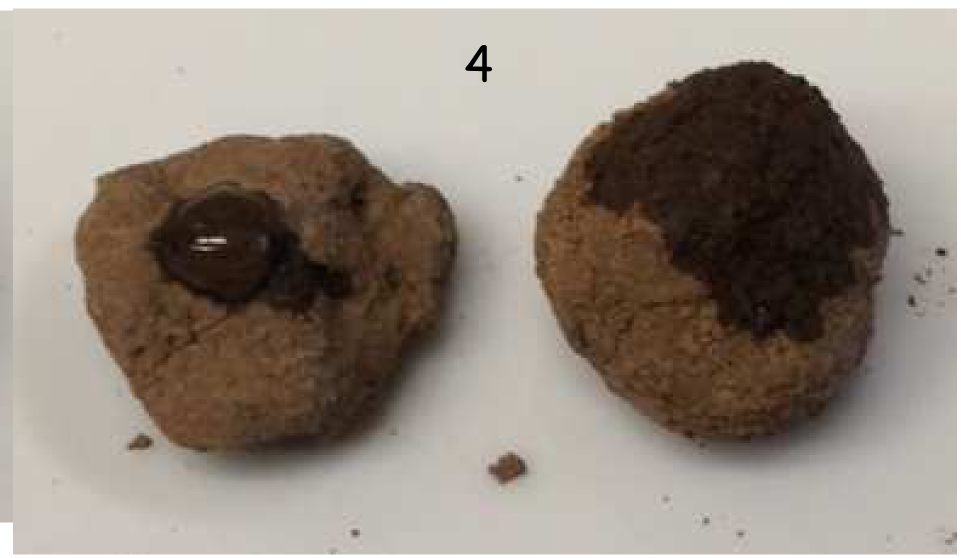
Advantages of Cool-Ox over other chemical oxidation processes relative to oil and gas applications

- Sustained oxidation
  - CaO_2 dissolves slowly
- pH 8
  - No corrosion
  - Compatible with biodegradation
- No heat
- No sodium (does not raise the SAR, in fact it **reduces SAR**)

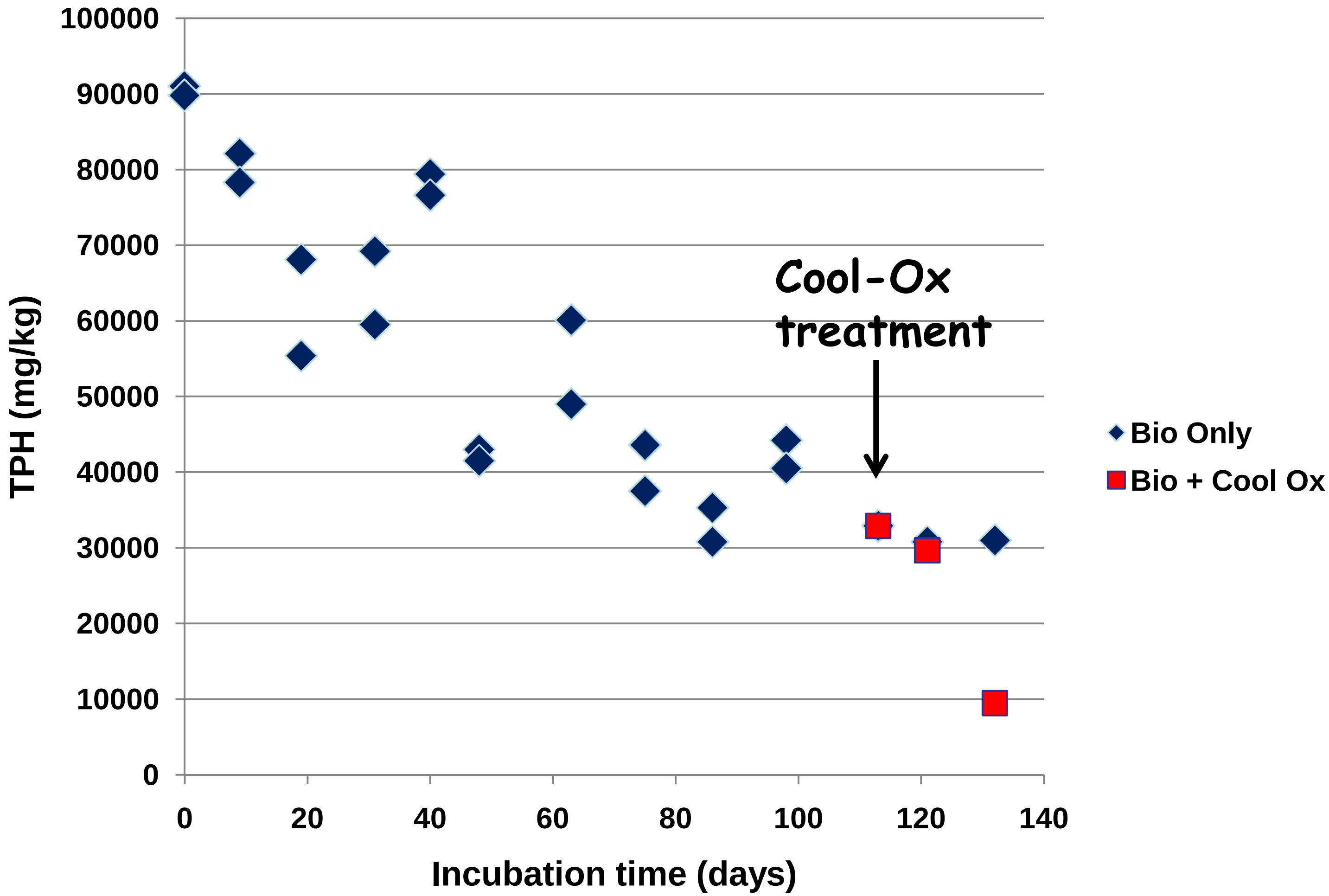
Wettability of Cool-Ox treated hydrophobic cuttings/soil blend: left, control; right, Cool-Ox treated

Timeframe: 1 min





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



Preliminary conclusions and future work

- 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?
- Future work will shed more light on the mechanism but the effect was dramatic


Any Questions?
SCENIC
TURNOUT
AHEAD