

US EPA ARCHIVE DOCUMENT

# **Effect of Potassium Permanganate on the Biodegradation of Weathered Crude Oil from Indiana Harbor Canal**

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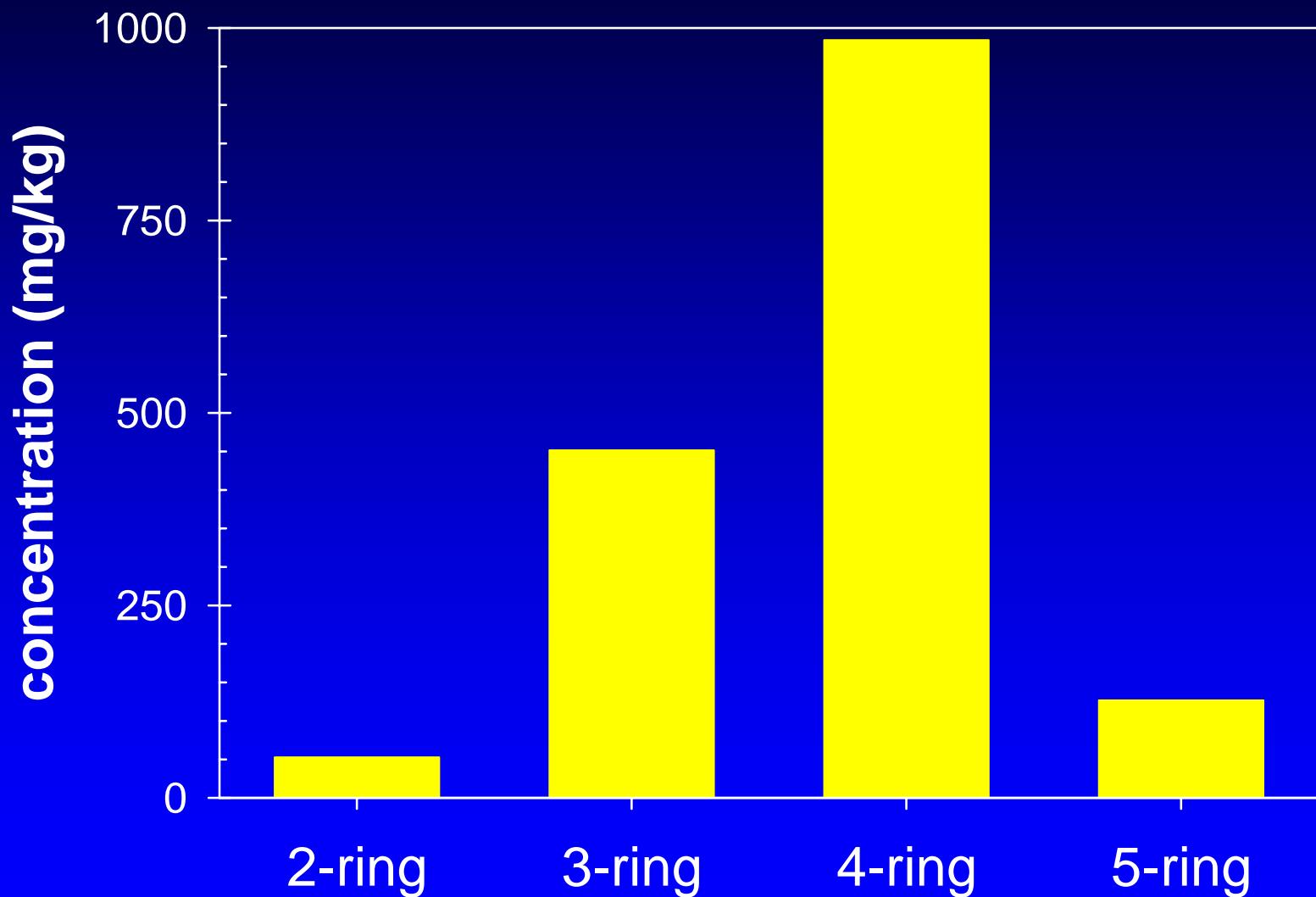
Xiaowei Ma, Thomas King, and Kenneth Lee  
Fisheries and Oceans Canada

Albert D. Venosa  
U.S. Environmental Protection Agency

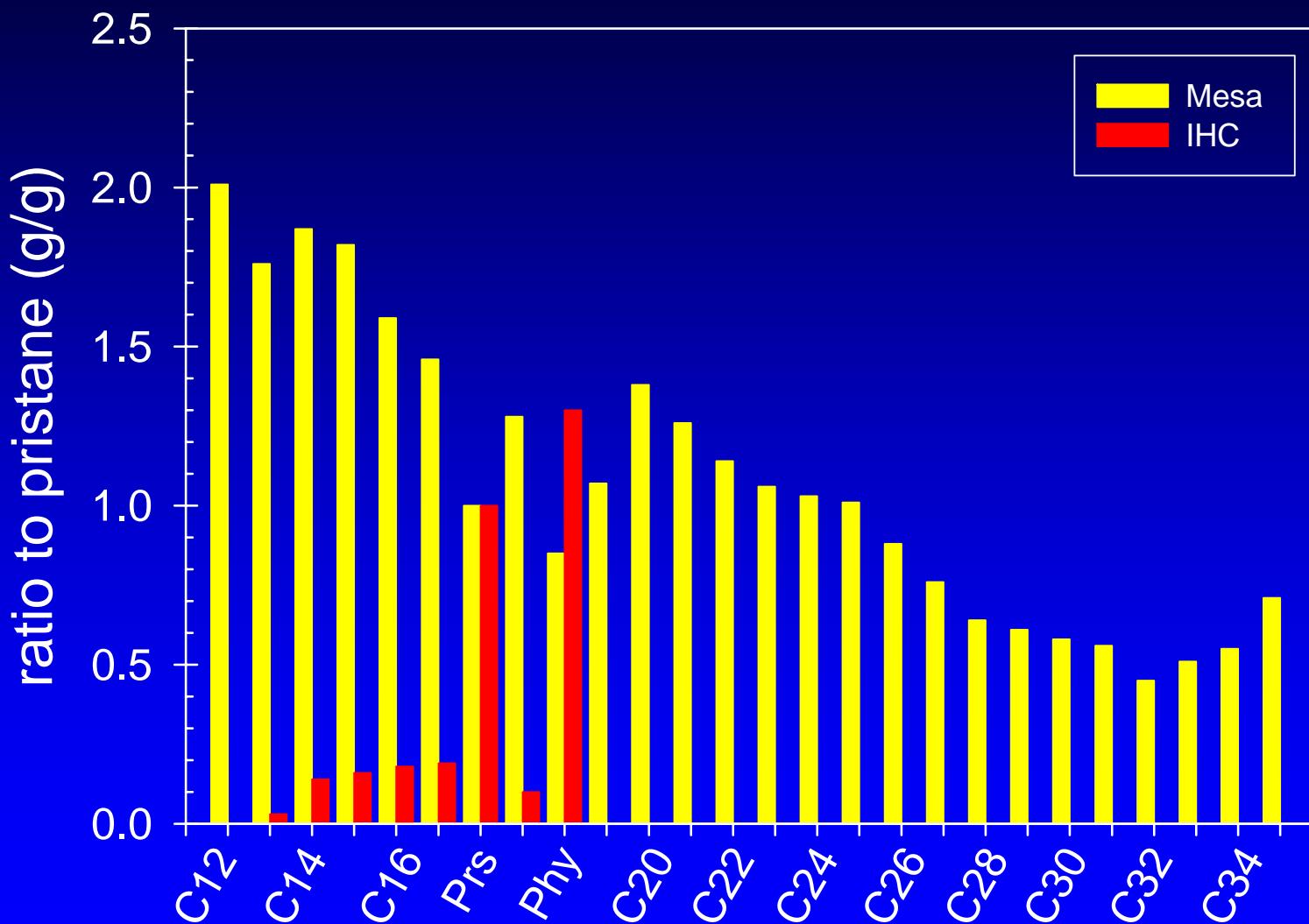
# Indiana Harbor



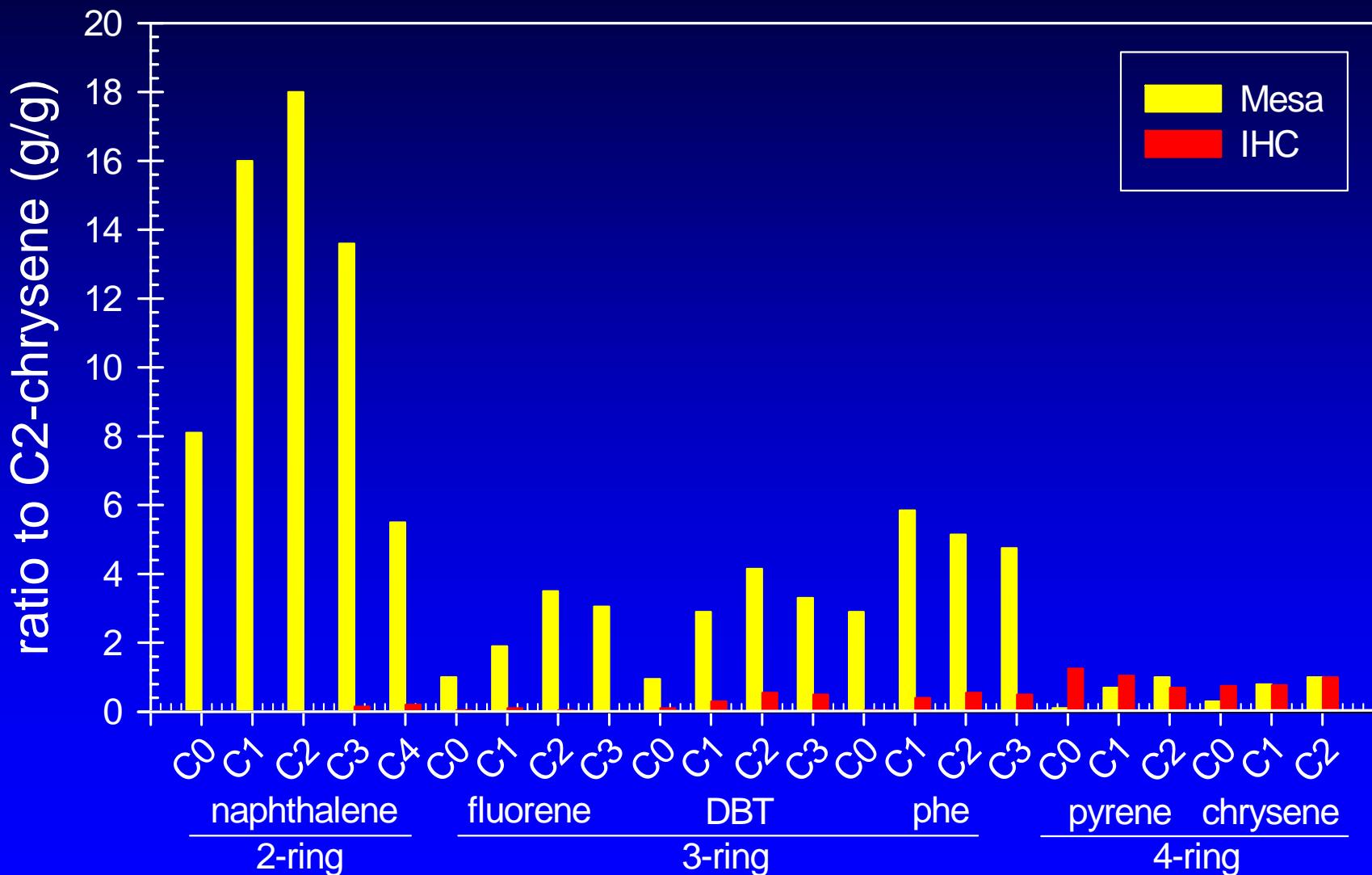
# PAH Concentrations in IHC Sediments



# Comparison of IHC Oil to Weathered Medium Crude Oil (Mesa): Alkanes



# Comparison of IHC Oil to Weathered Medium Crude Oil (Mesa): Aromatics



# Summary of Indiana Harbor Canal Shoreline Sediment Characteristics

- The IHC sediments are heavily contaminated
  - the sediments can be up to 40% oil by mass
- The IHC oil is highly weathered
  - the concentrations of easily degradable contaminants (e.g., normal alkanes and low MW PAHs) are very low relative to their more recalcitrant analogs (e.g., branched alkanes and alkyl-substituted high MW PAHs)
  - IHC oil contains high absolute concentrations of compounds of concern (e.g., 4- and 5-ring PAHs)

## **Proposed Method of Treatment:**

Use chemical oxidation by potassium permanganate ( $\text{KMnO}_4$ ) or hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to increase the biodegradability and bioavailability of IHC contaminants

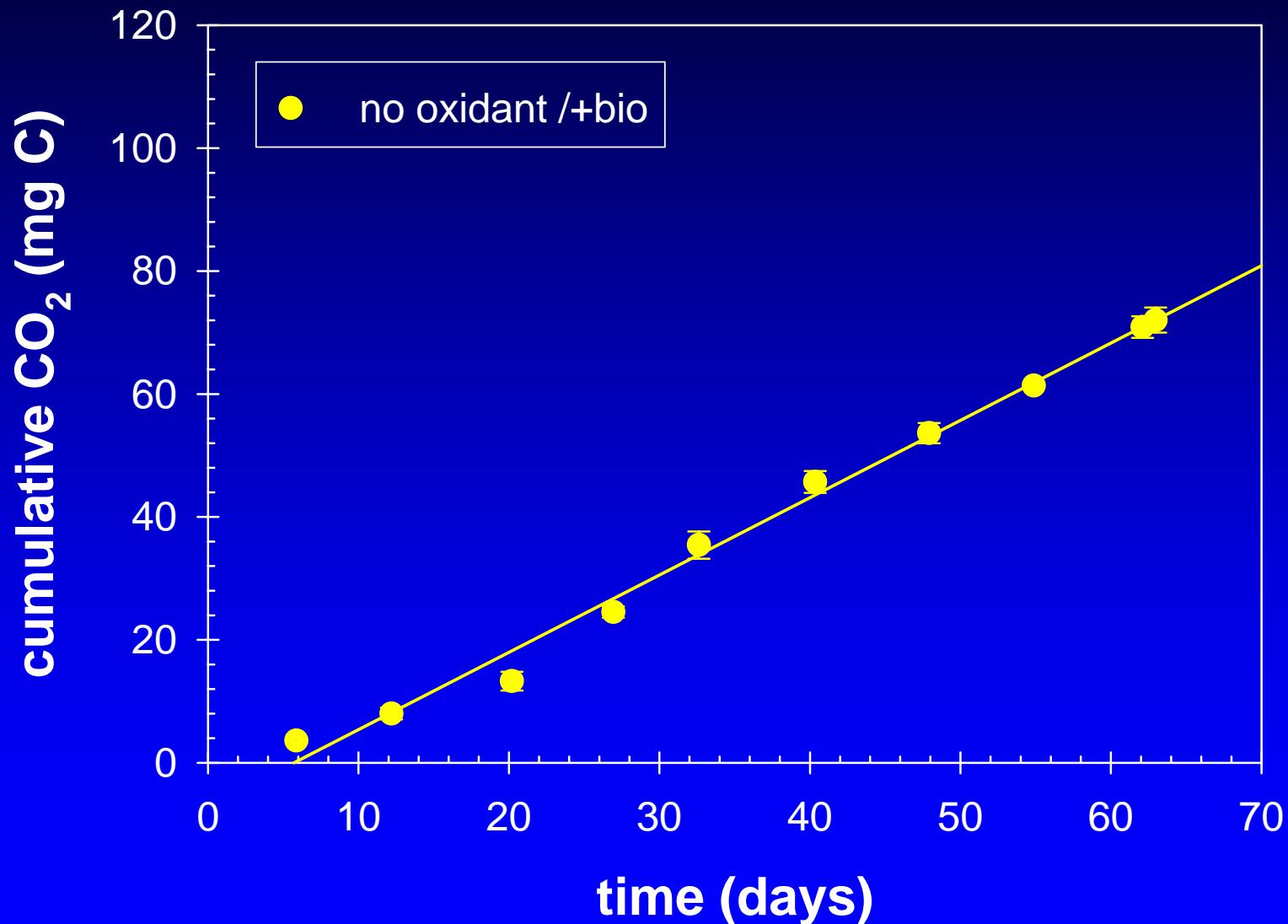
- 2.9 g  $\text{H}_2\text{O}_2/\text{L}$
- 9.0 g  $\text{KMnO}_4/\text{L}$

## **Proposed Mechanism:**

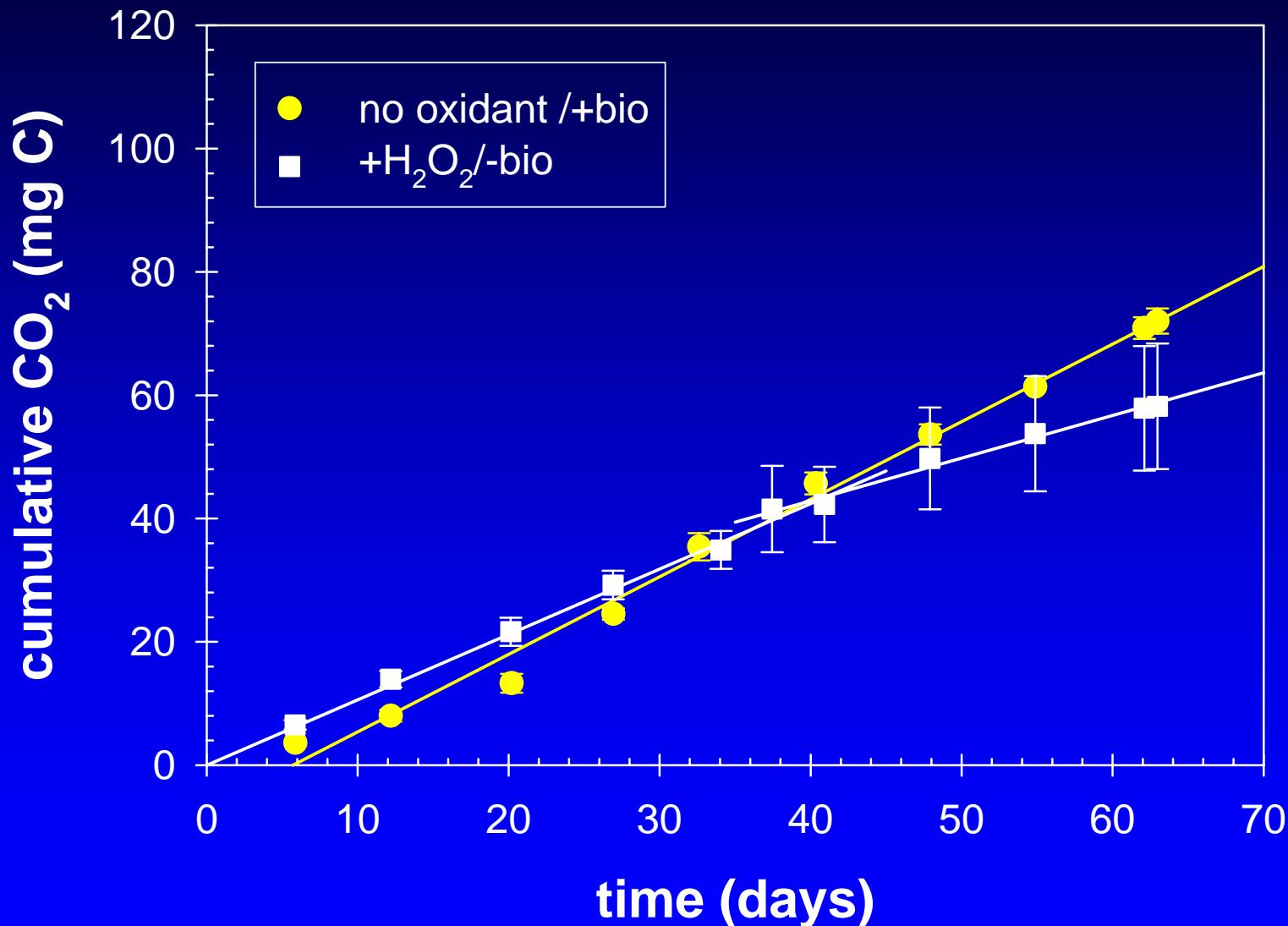
Oxidation will increase the bioavailability and biodegradability of contaminants by

- decreasing molecule size
- inserting hydrophilic functional groups

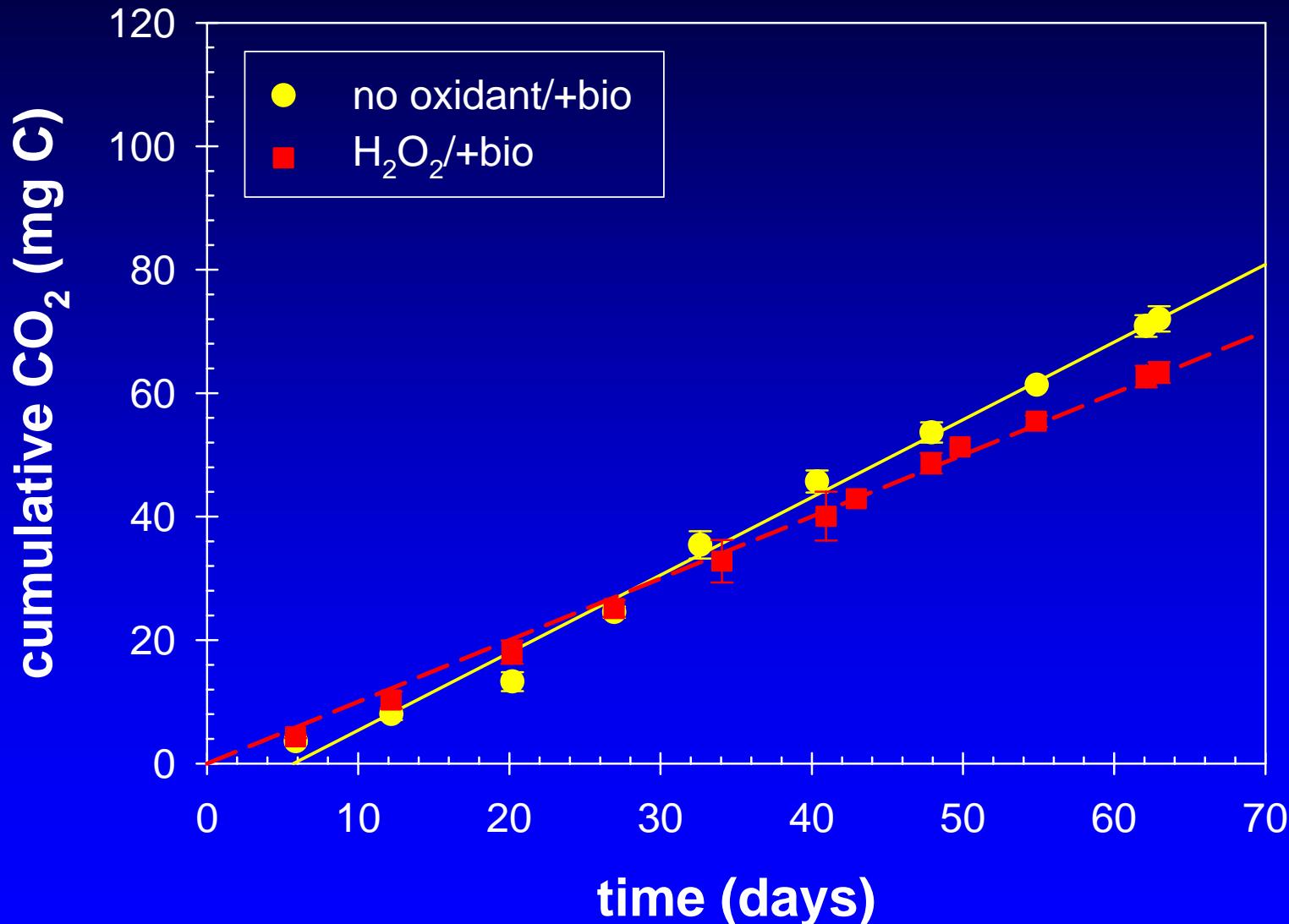
# Oil Mineralization: No Oxidant Control



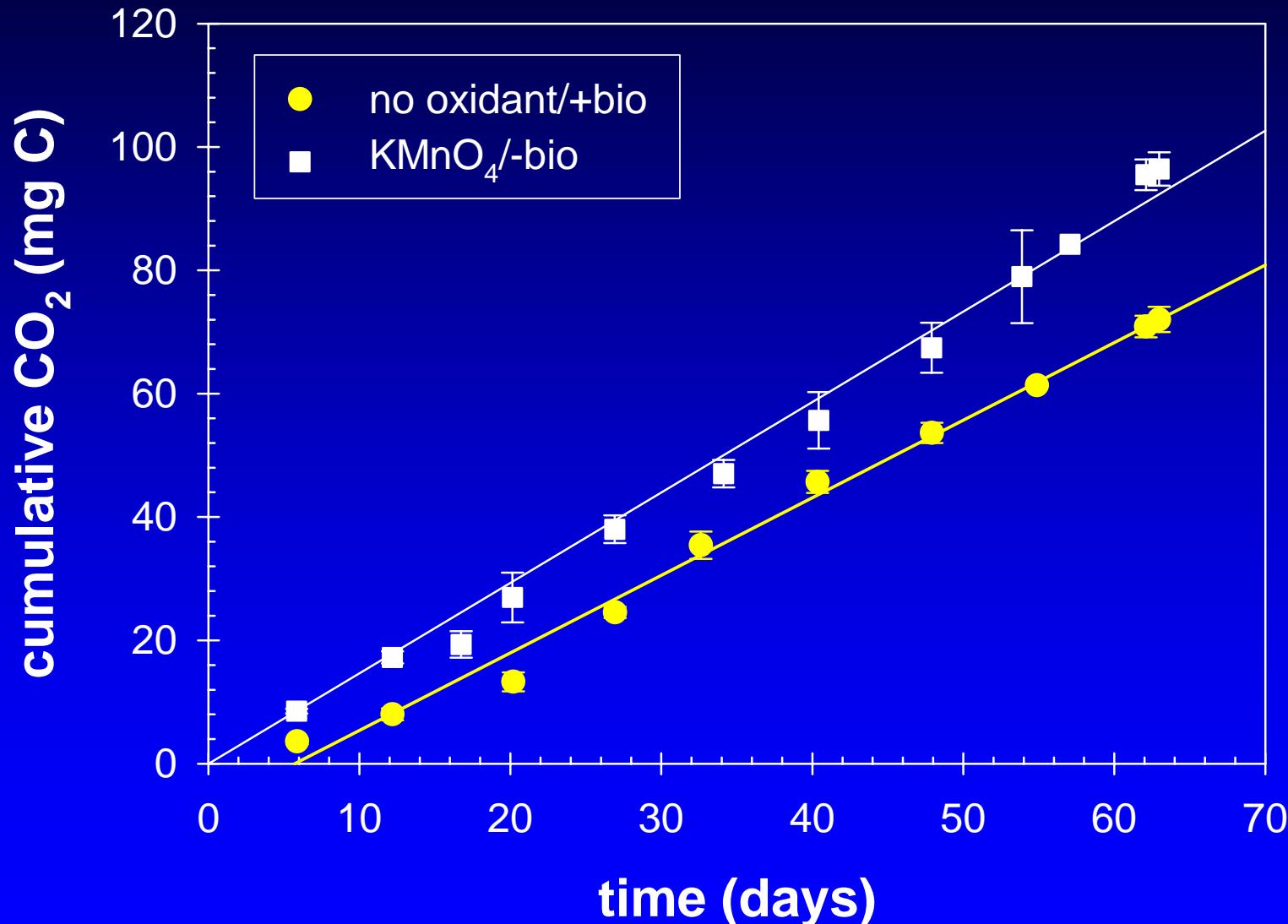
# Oil Mineralization: $+\text{H}_2\text{O}_2$



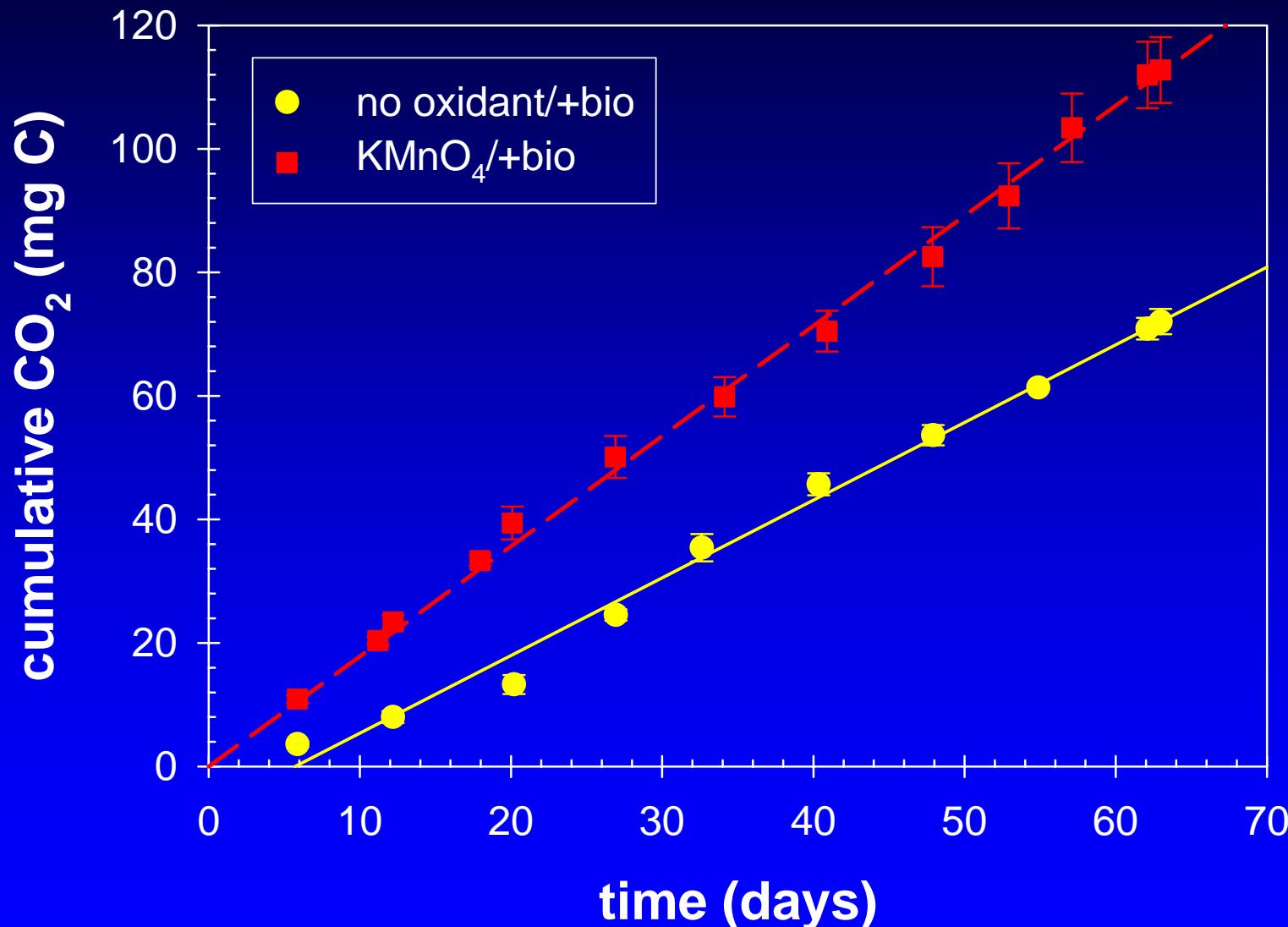
# Oil Mineralization: $+\text{H}_2\text{O}_2$



# Oil Mineralization: $+KMnO_4$



# Oil Mineralization: $+KMnO_4$



# Summary of IHC Oil Biodegradation Experiments

∴ Permanganate is a more effective oxidant for the IHC oil than hydrogen peroxide

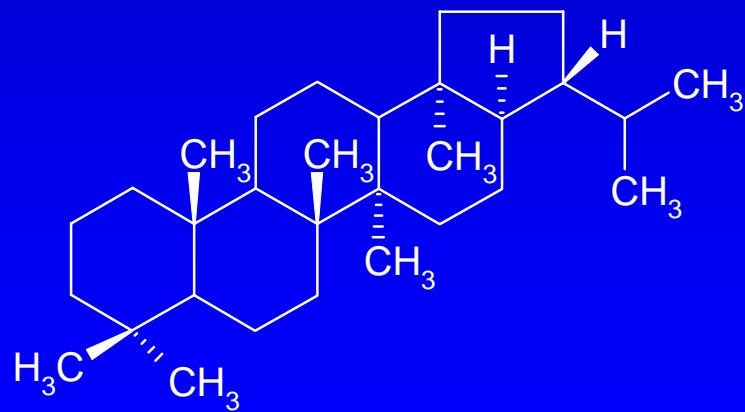
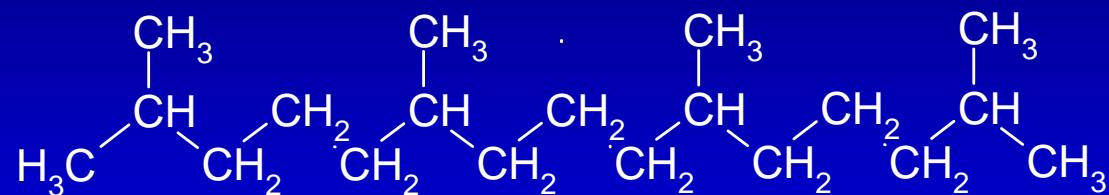
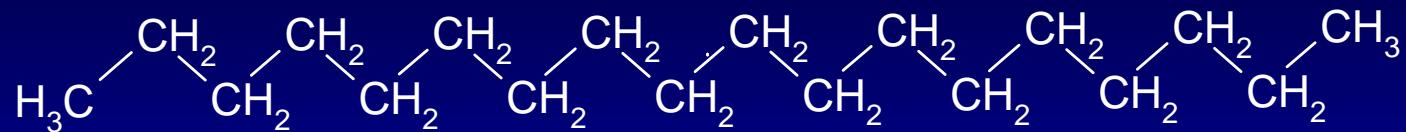
- effect of permanganate on components not measured by GC-MS is unknown

## Next Step:

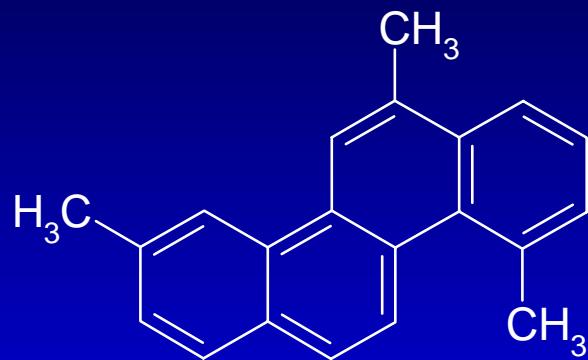
Determine effects of permanganate on the biodegradability of oil components with different chemical characteristics

- aliphatics, aromatics, resins, and asphaltenes

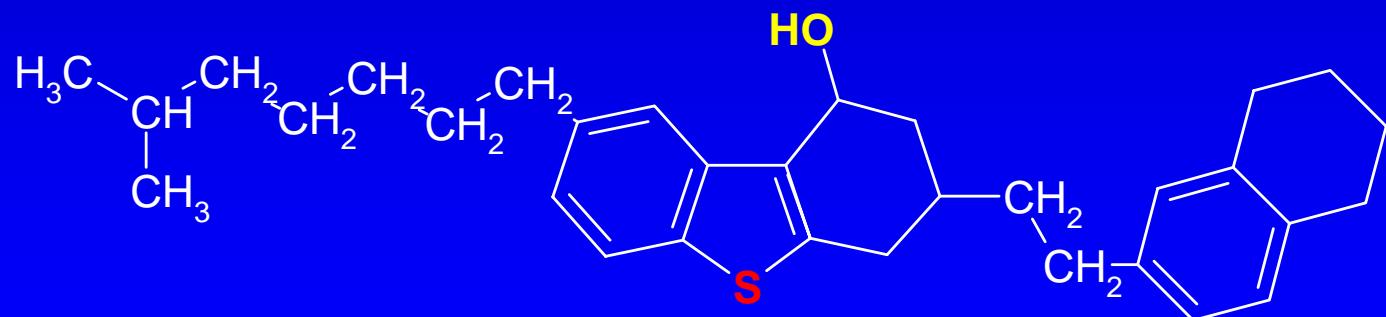
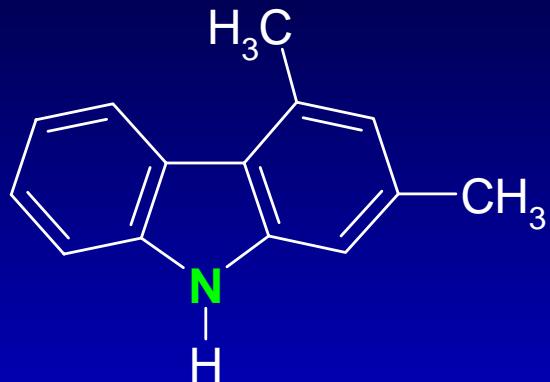
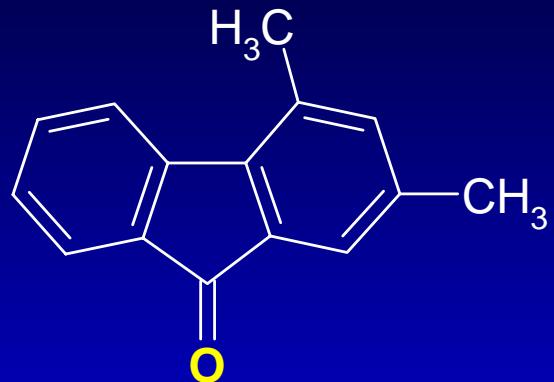
# Aliphatic Hydrocarbons



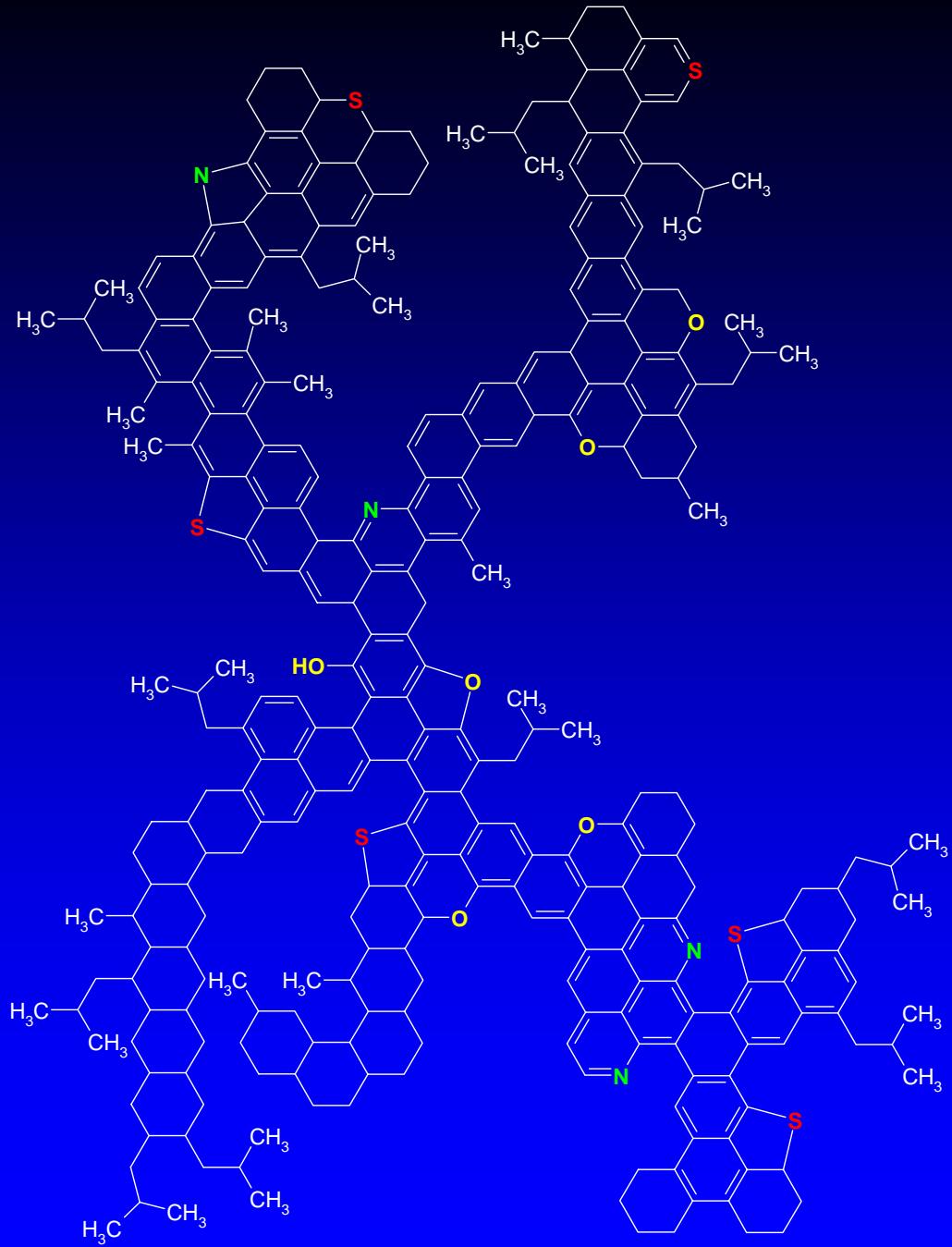
# Aromatic Hydrocarbons



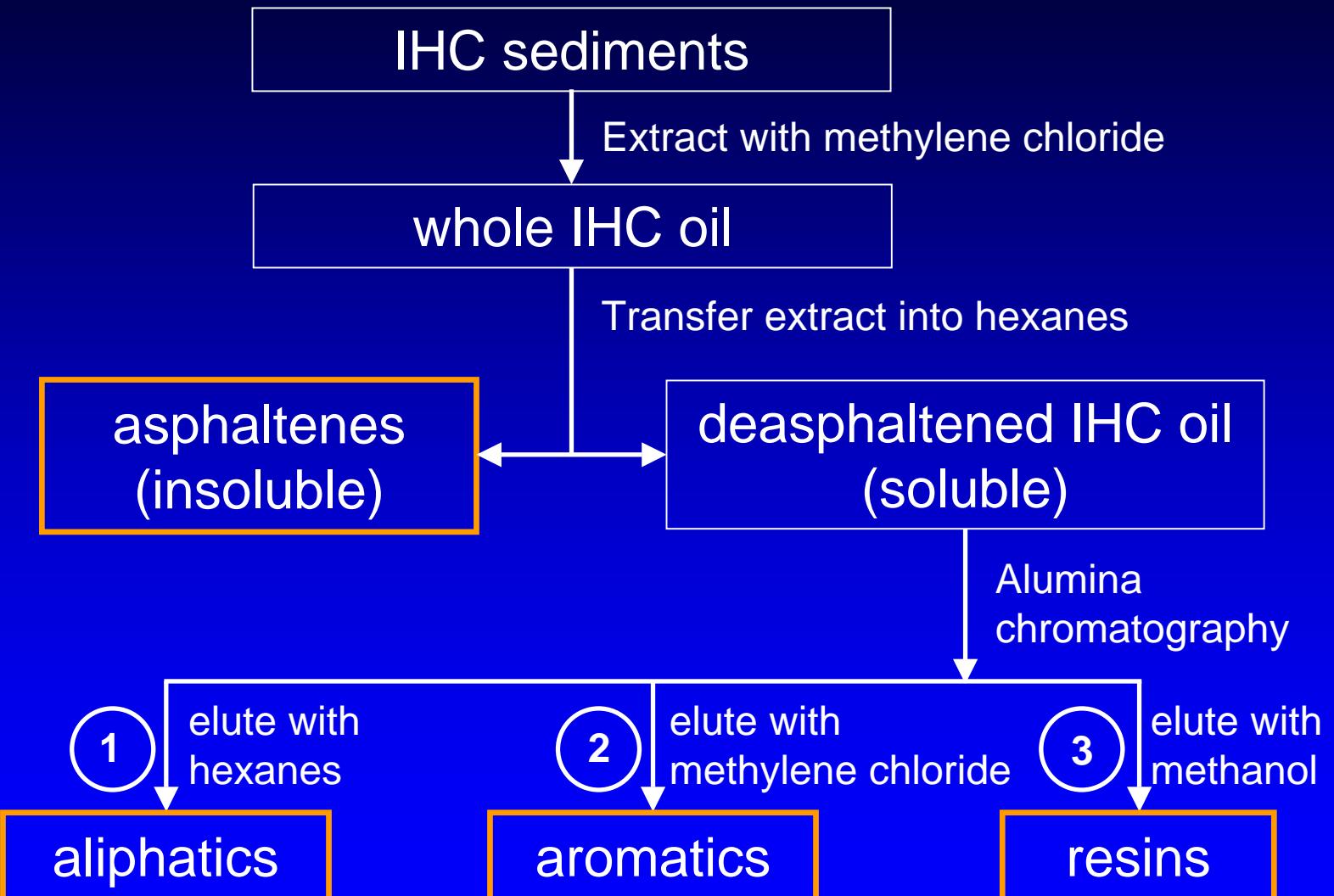
# Resins



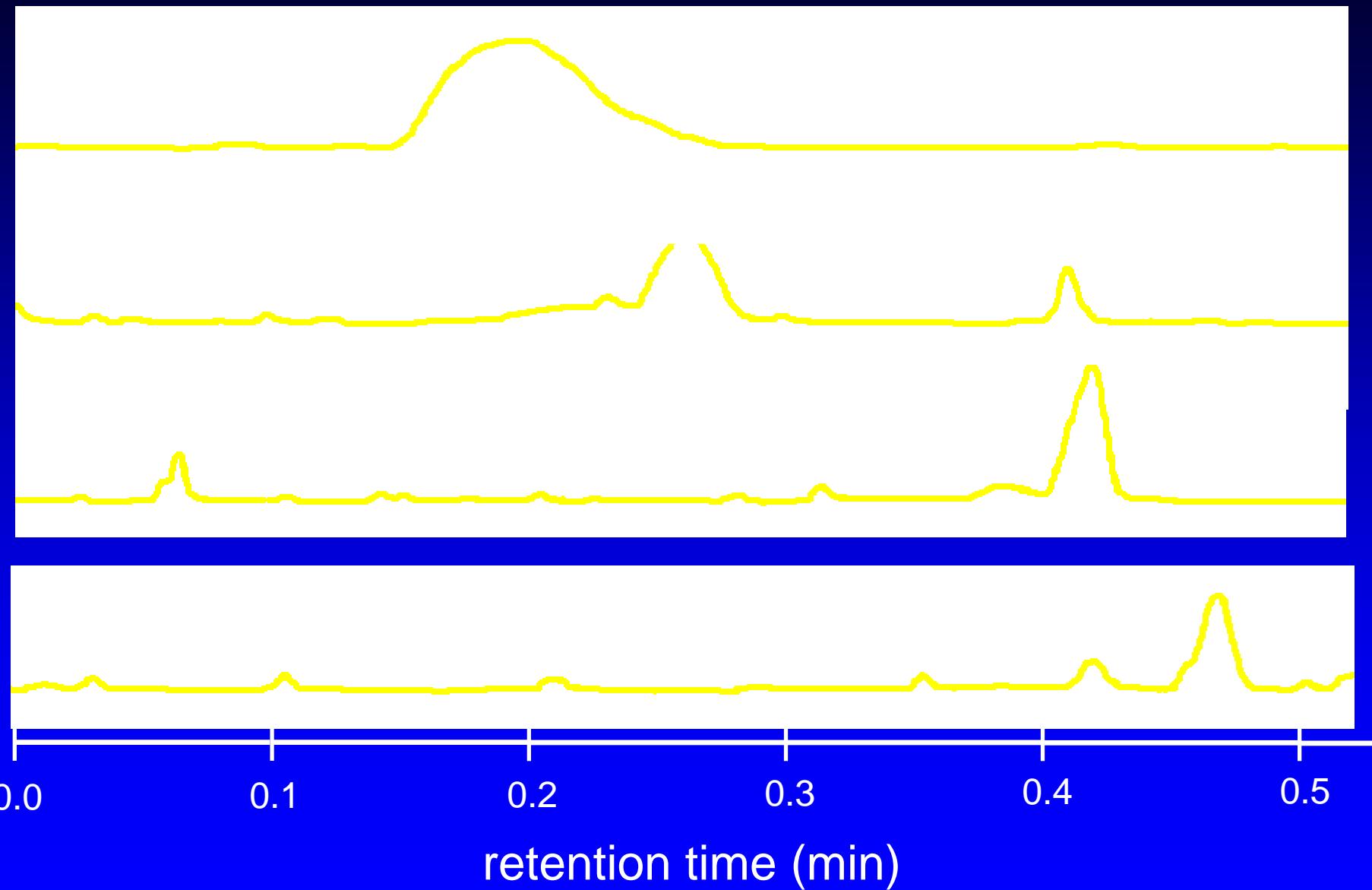
# Asphaltenes



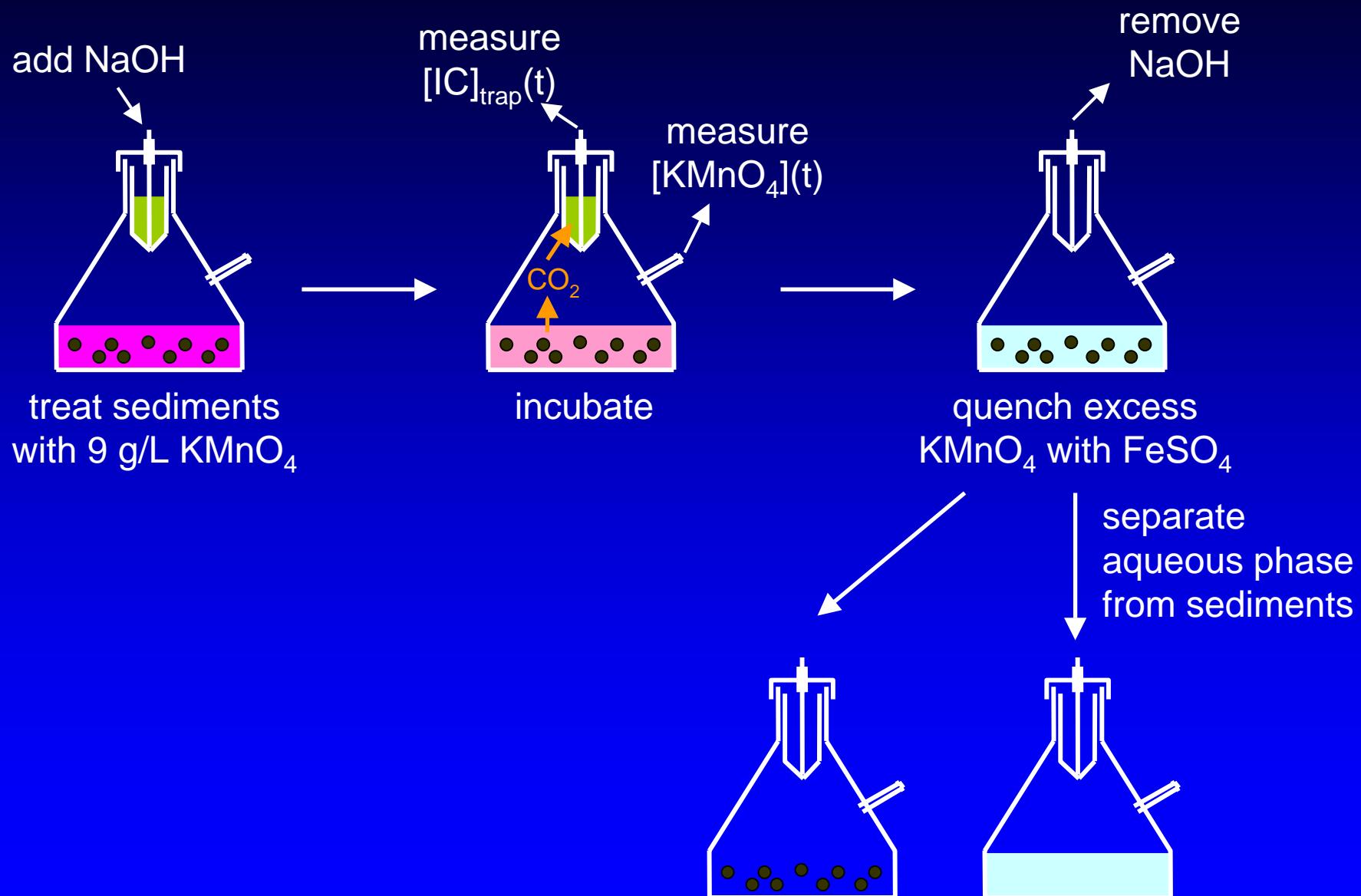
# Separation of IHC Oil into Discrete Fractions



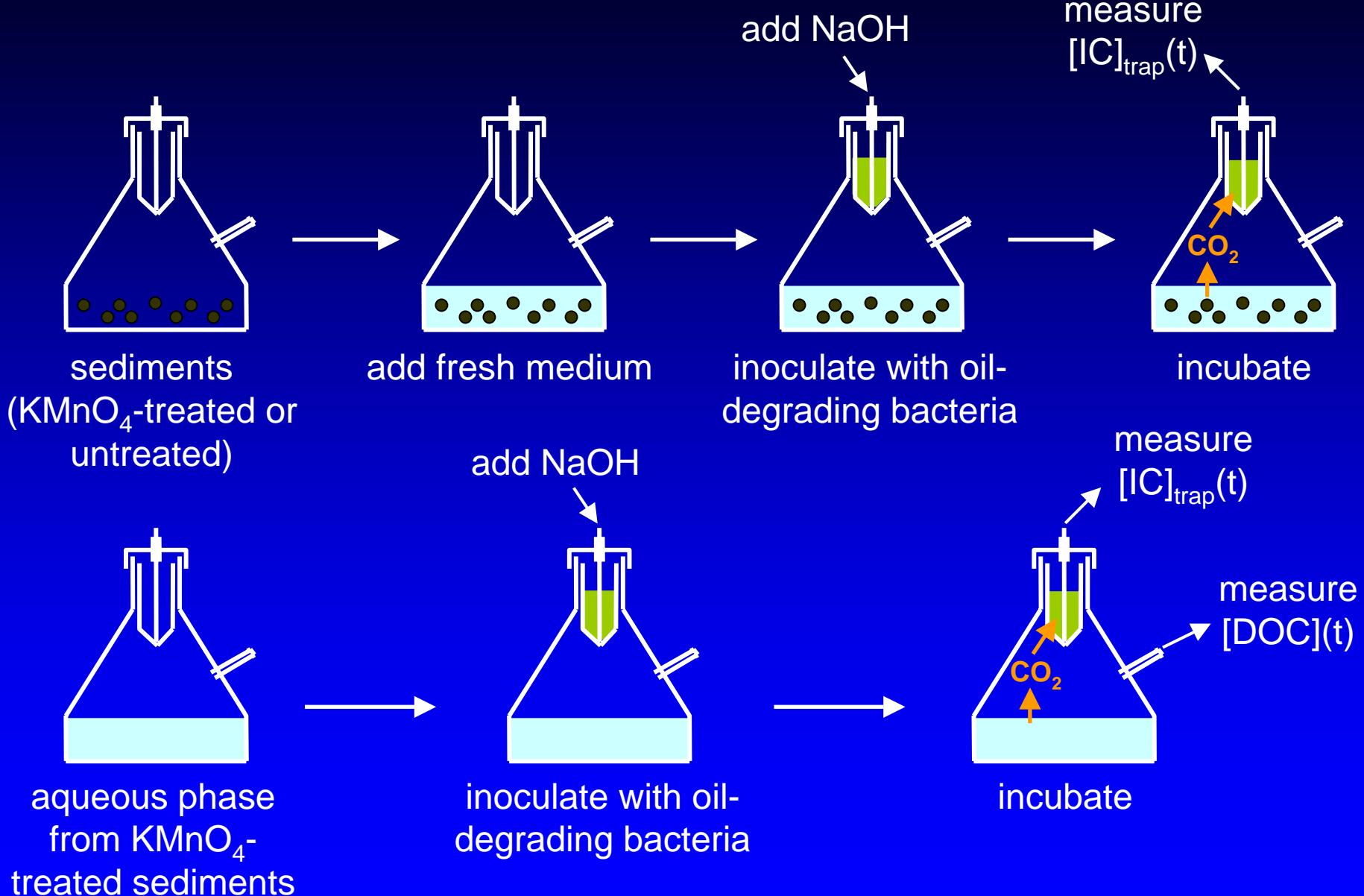
# latroscan Analysis of IHC Oil Fractions



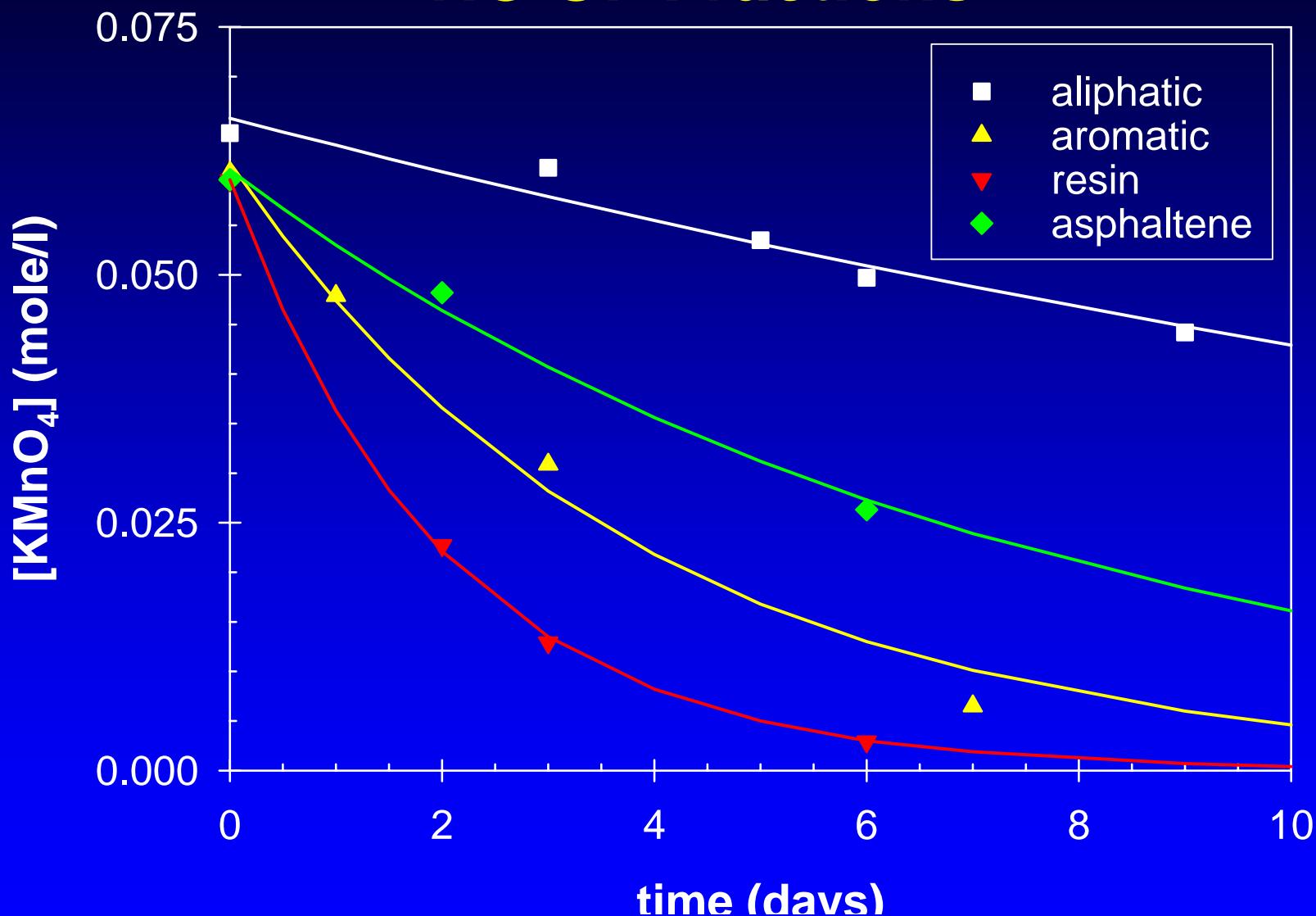
# Experimental Approach: Chemical Oxidation



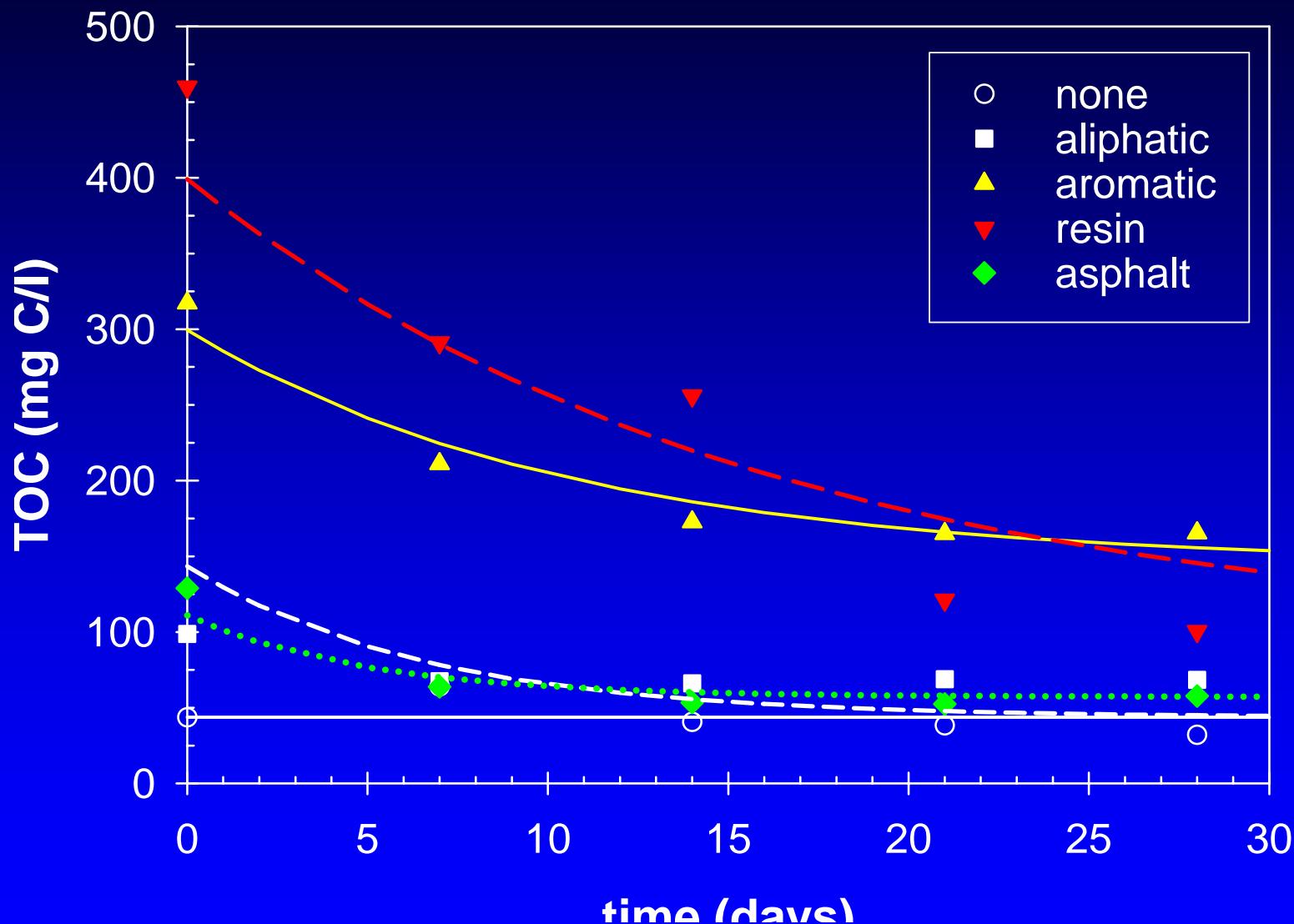
# Experimental Approach: Biodegradation



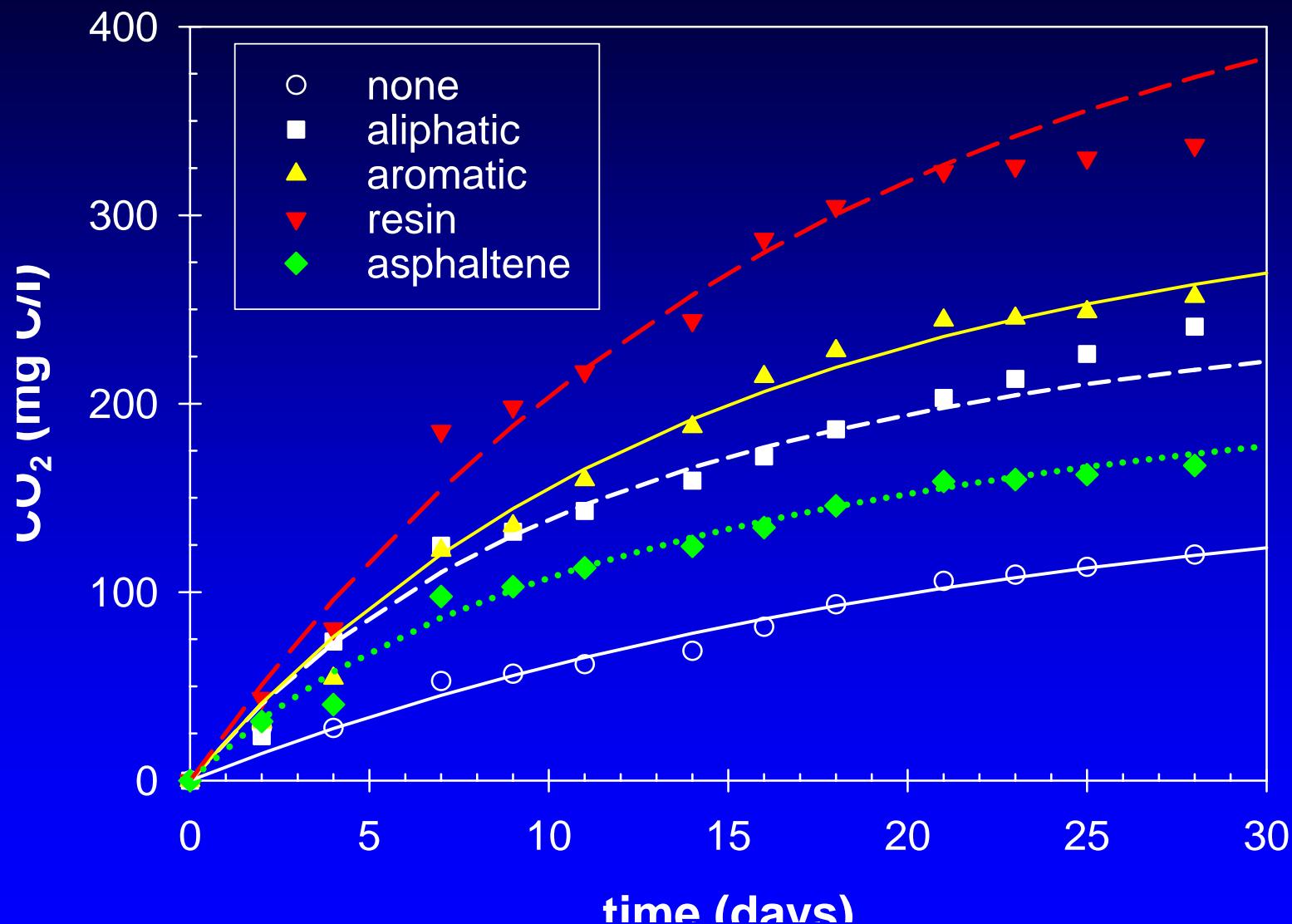
# Reaction of Permanganate with IHC Oil Fractions



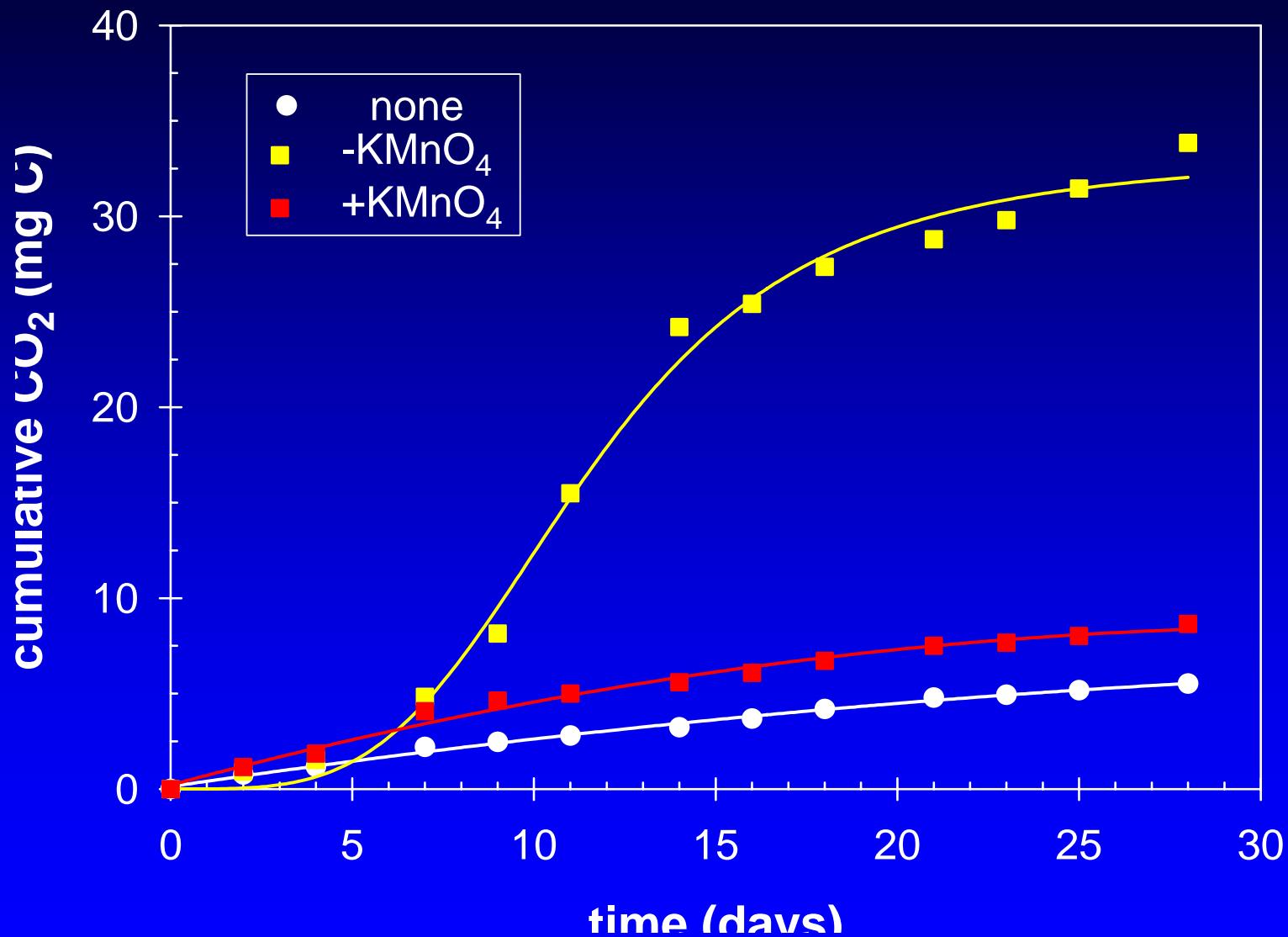
# Biodegradation of Aqueous-Phase Products



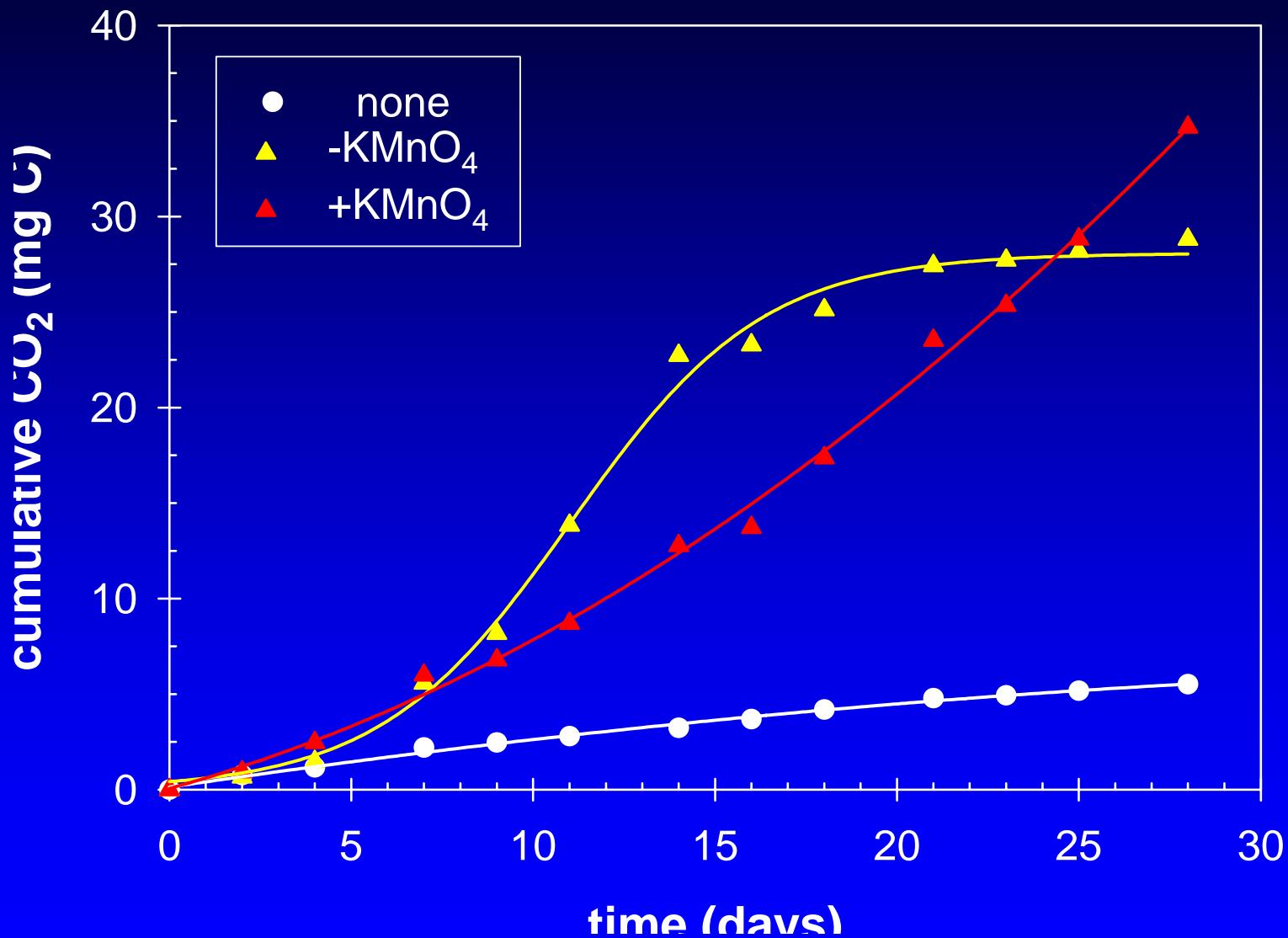
# Mineralization of Aqueous-Phase Products



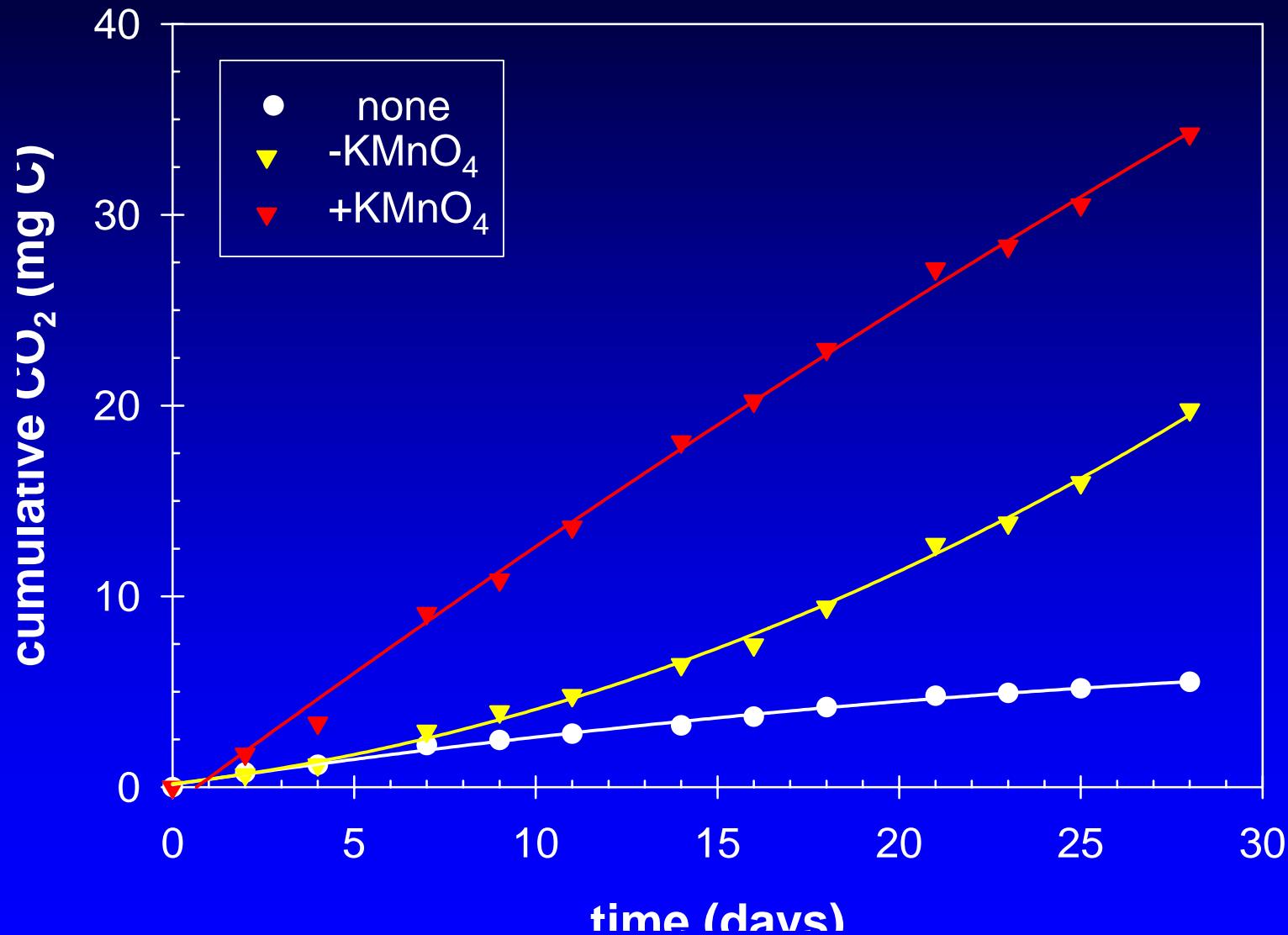
# Biodegradation of Aliphatic Fraction



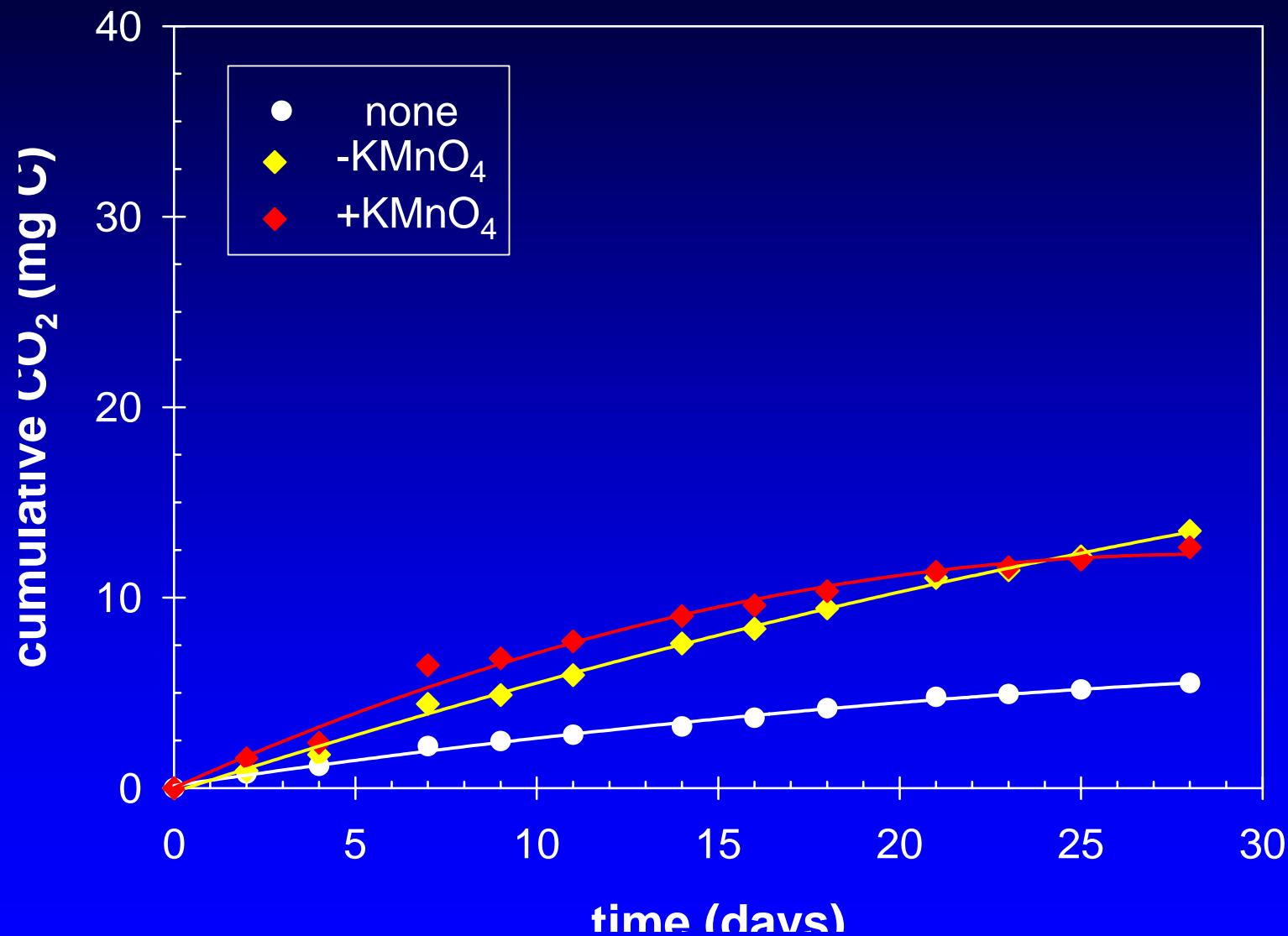
# Biodegradation of Aromatic Fraction



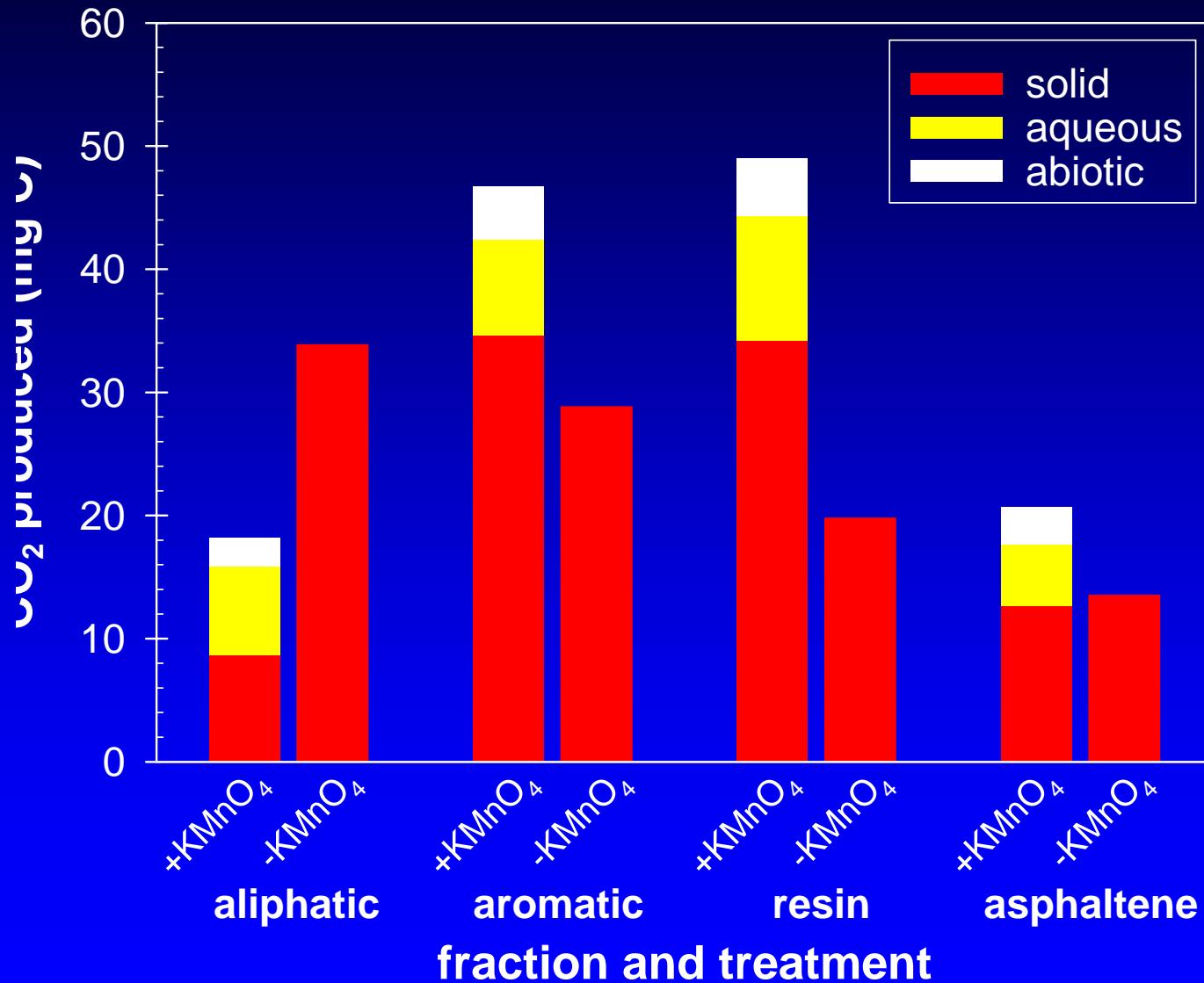
# Biodegradation of Resin Fraction



# Biodegradation of Asphaltene Fraction



# Effect of Chemical Oxidation on Biodegradation of IHC Oil Fractions



# Conclusions

- Permanganate reacted slowly with the aliphatic and asphaltene fractions
  - the solid-phase products were not more biodegradable than the parent compounds
    - treatment with permanganate reduced the biodegradability of the aliphatic fraction, probably by coating the oil-water interface with  $\text{MnO}_{2(s)}$
  - very low concentrations of water-soluble products were formed
- Permanganate reacted quickly with the aromatic and resin fractions
  - the solid-phase products were more biodegradable than the parent compounds
  - the water-soluble products that were formed were easily biodegradable

# Acknowledgements

- Funding provided by U.S. EPA and Department of Fisheries and Oceans Canada