Biocorrosion in the Diesel Fuel Infrastructure: Impact of Ultra Low Sulfur Diesel, Fatty Acid Methyl Esters and Select Alternative Fuels

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BIOCORROSION WORKSHOP
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Background

- Microbial biodegradation of fuels is associated with decreased product quality, compromised equipment performance, and the biocorrosion of metal surfaces

- Changing fuel formulations are routinely used in the existing carbon steel infrastructure.

- Many reports of increased corrosion problems.

Hypothesis

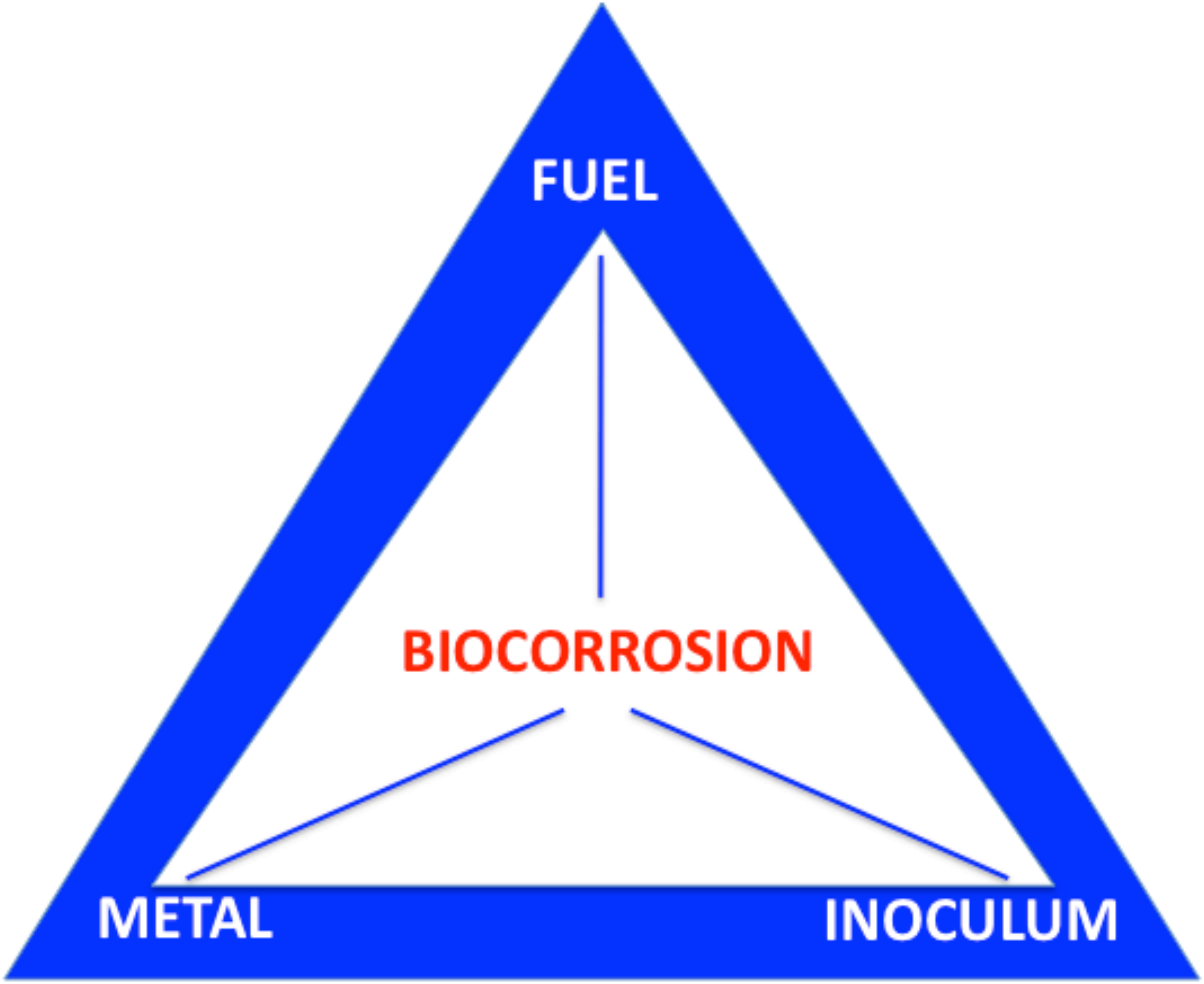
We hypothesize that fuel-induced metal corrosion is at least a function of:

i) the chemical composition of the fuel

ii) its inherent susceptibility to biodegradation

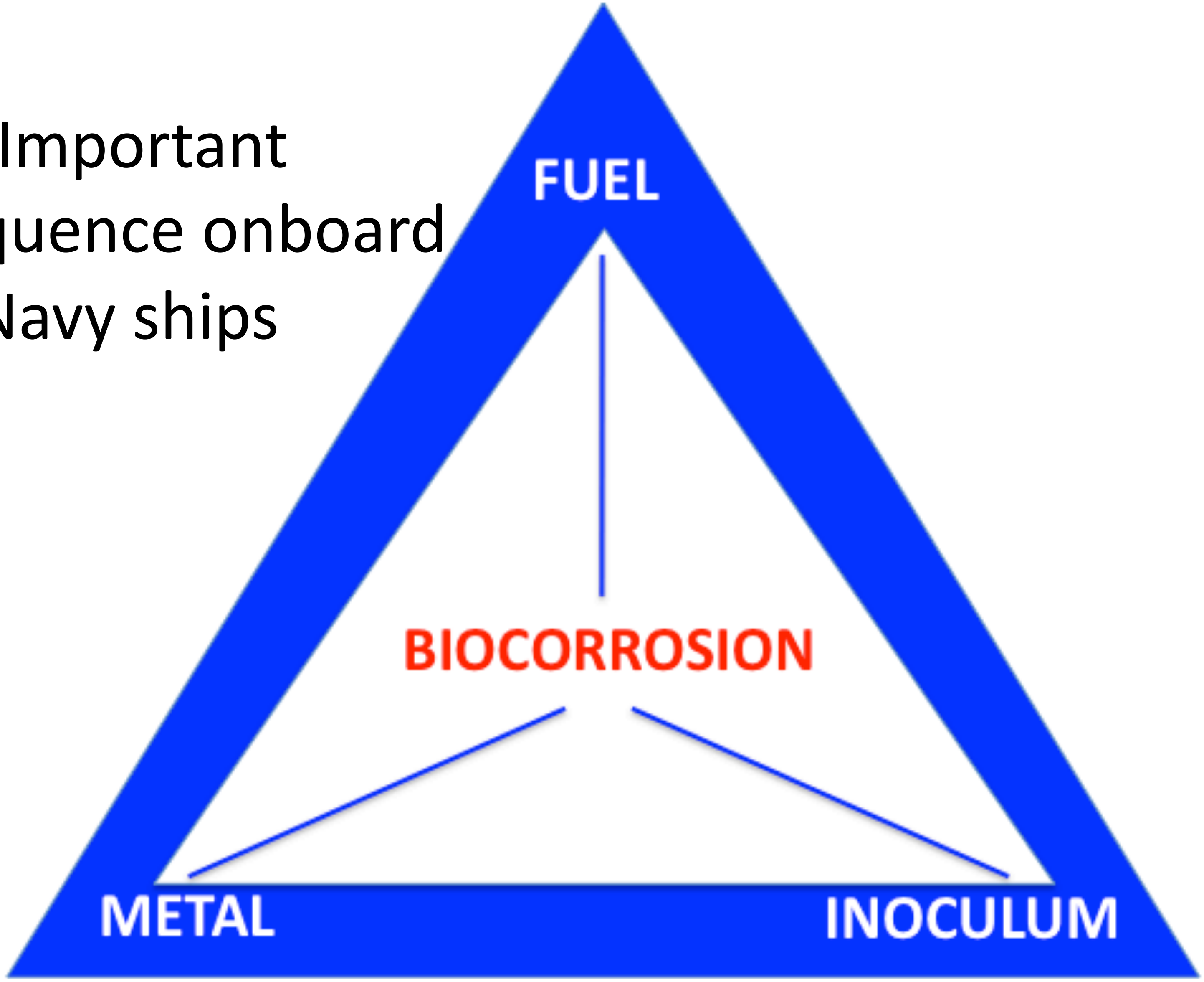
iii) the contact of the fuel with microorganisms that catalyze biodegradation/biocorrosion processes.

Perspective



Perspective

- Important consequence onboard Navy ships



Seawater Compensated Ballast Tanks

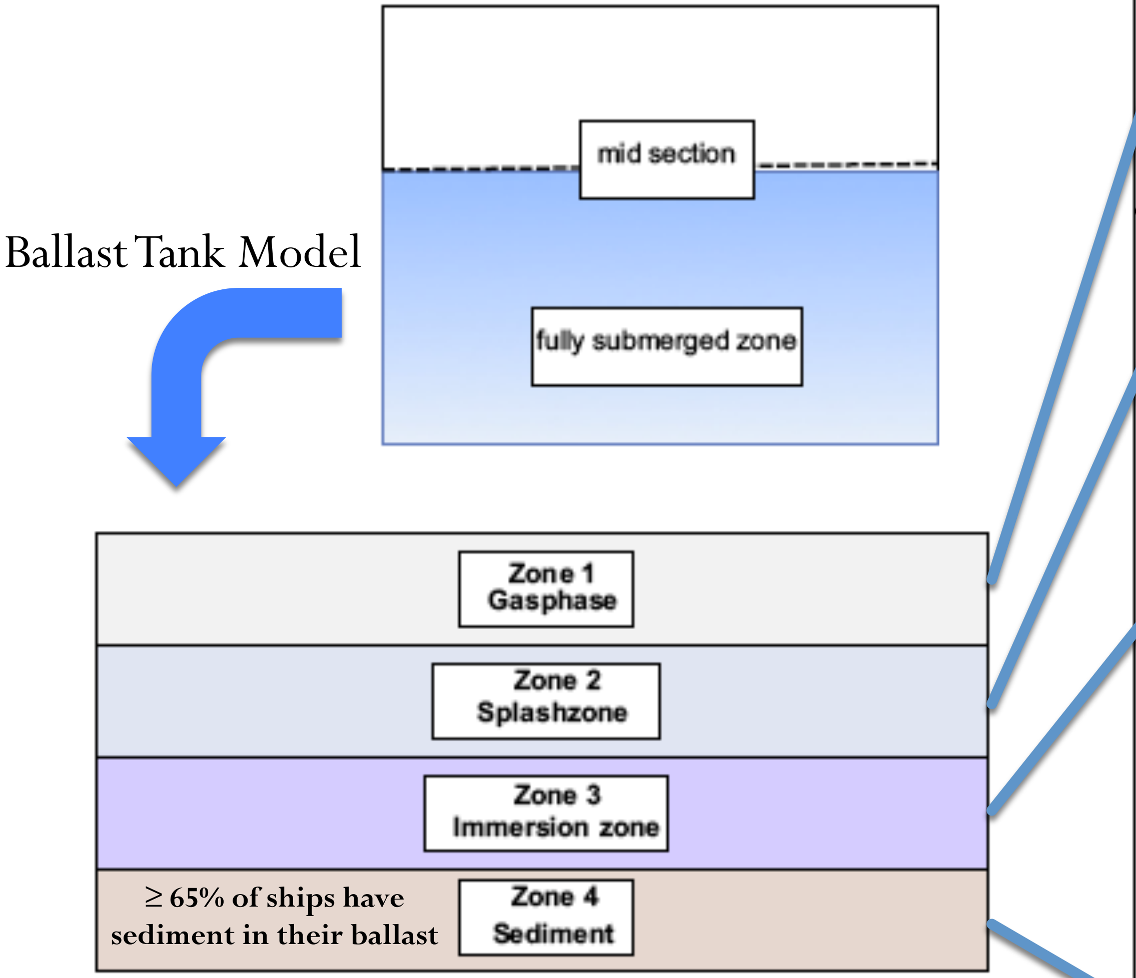
Cruiser (Ticonderoga Class), Destroyer (Arleigh Burke Class), Amphib (Wasp Class)

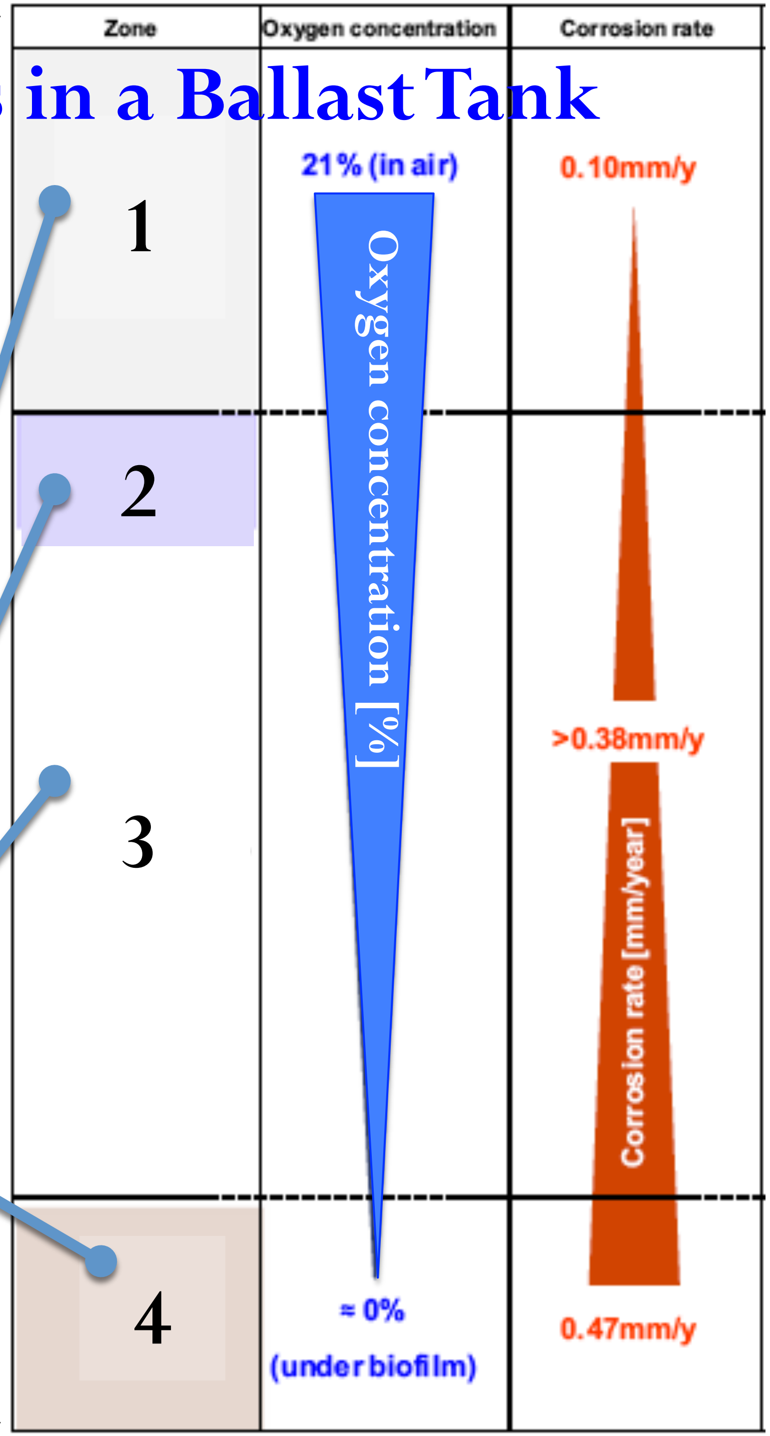
The use of different different diesel fuel blends can lead to a host of biologically-catalyzed problems:

•Biocorrosion	Cross contamination
•Biofouling of sensors	Clogging of fuel lines
•Deterioration fuel quality	Coalescer performance

Different Biocorrosion Zones in a Ballast Tank

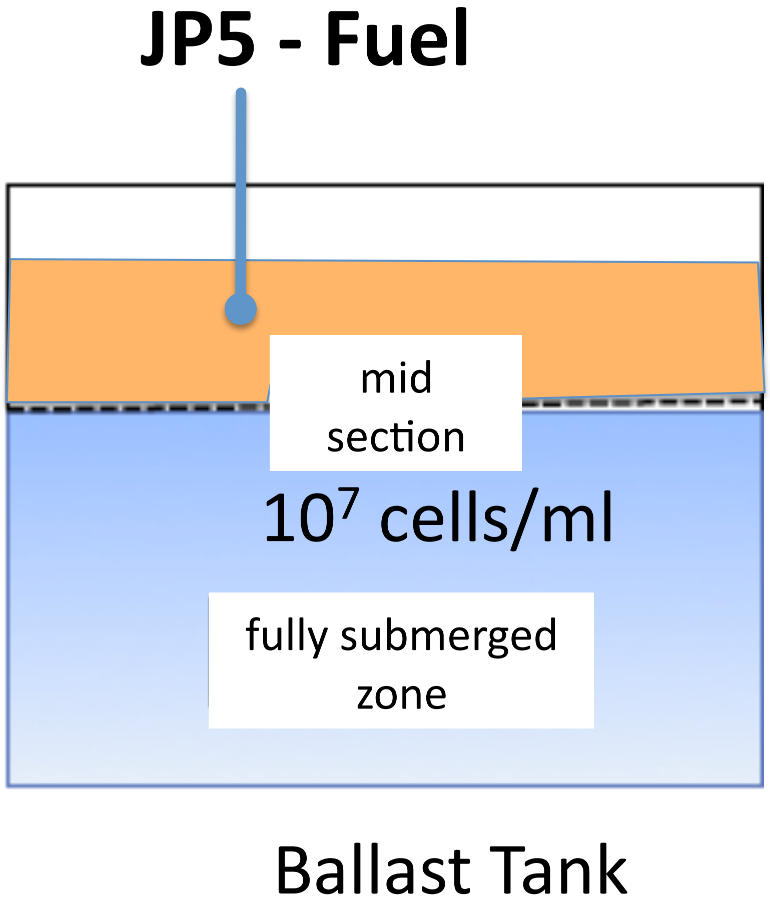
80% of the world's trade volume is transported by ships

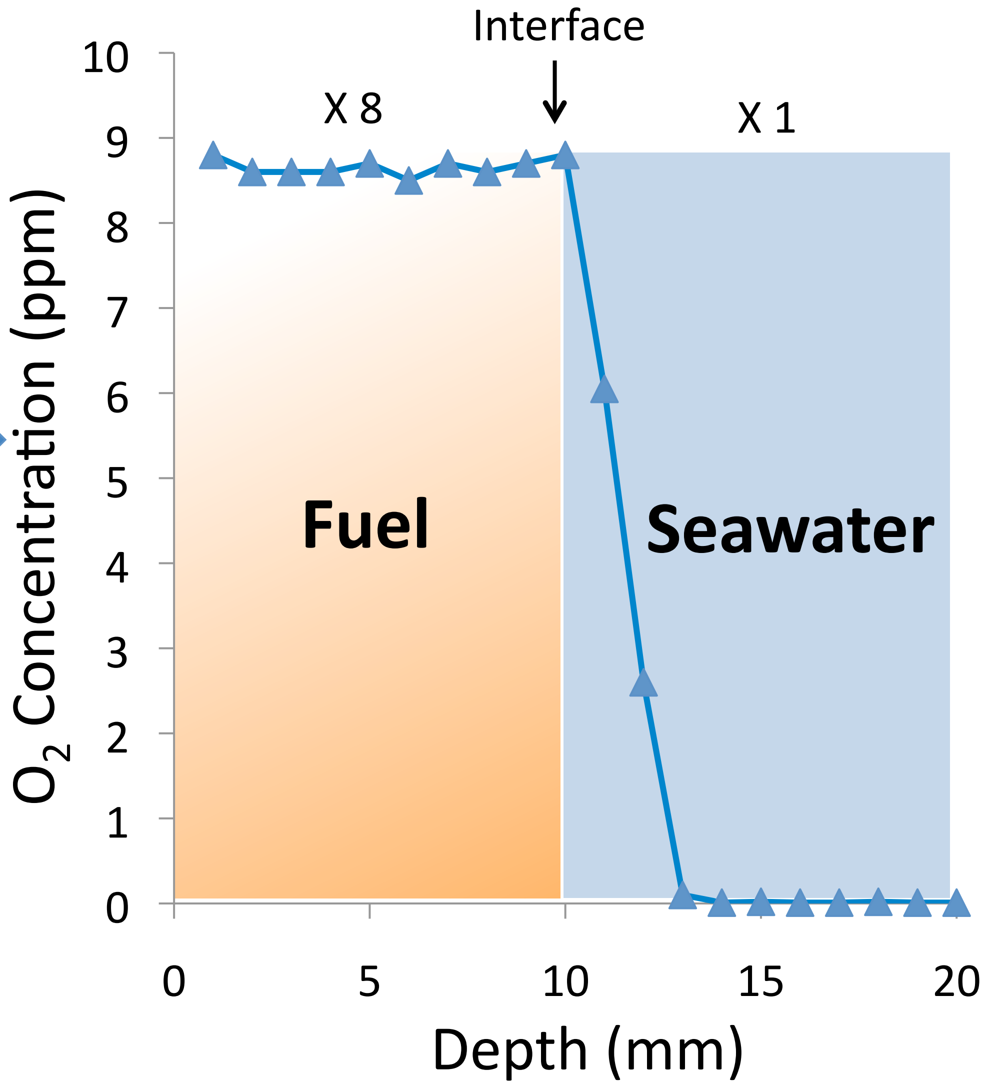




Adapted from: Heyer et al., 2013. Ship ballast tanks a review from microbial corrosion and electrochemical point of view *Ocean Engineering* 70:188–200.

Steep Gradients in Oxygen in Fuel/Filter Sterilized Seawater Incubations Inoculated with *Marinobacter*





- measurement by Wolfenden and Avci

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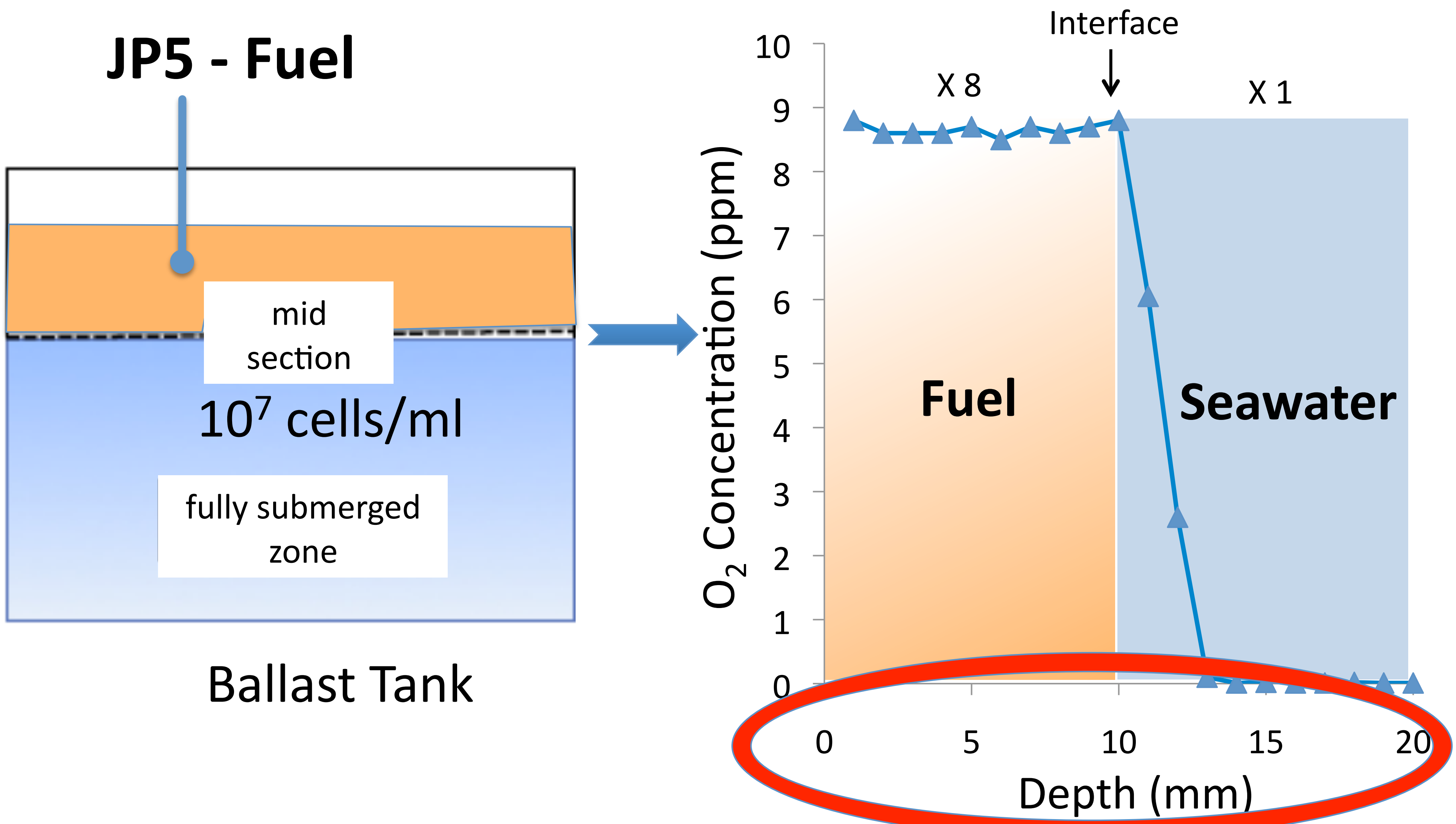

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Fuels of Interest

Traditional petroleum-based fuels:
HSD, LSD, ULSD, F76, JP5

First generation biofuel:
FAME-Biodiesel

Second generation biofuels:
Algal-based F76,
Camelina-based JP5

Questions and Approaches

1) Composition of the fuels?
Gas chromatography-mass spectrometry

2) Can fuel support microbial growth?
Anaerobic incubations; but oxygen exposure has important implications

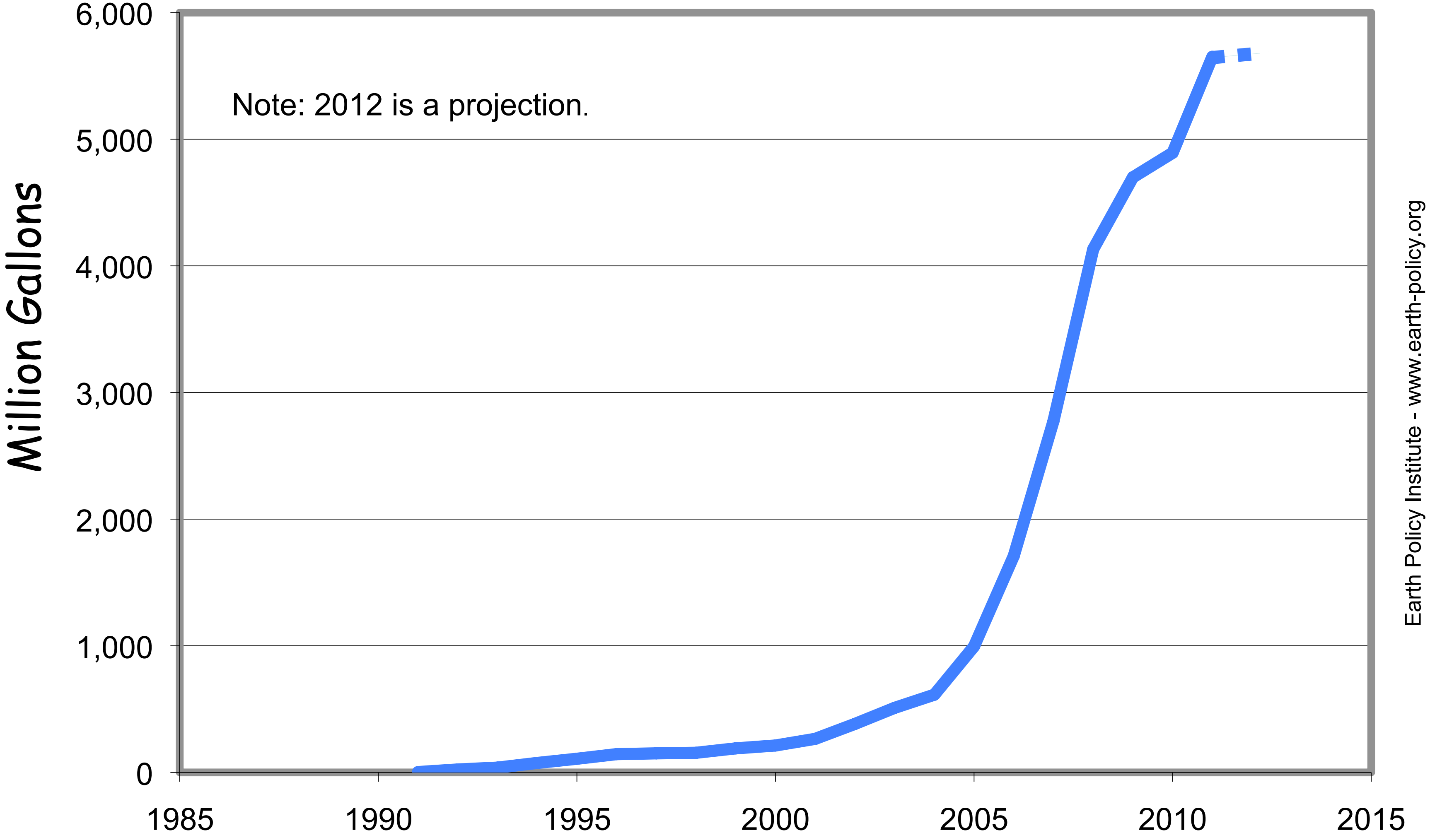
3) What can a targeted assay of the metabolome tell us? GC-MS

4) What microbes and activities should be monitored?
Host of procedures

5) Impact of fuel formulations on microbiologically induced metal corrosion?

First-Generation Biodiesel

World-wide annual biodiesel production, 1991-2012



Source: F.O. Licht; Worldwatch

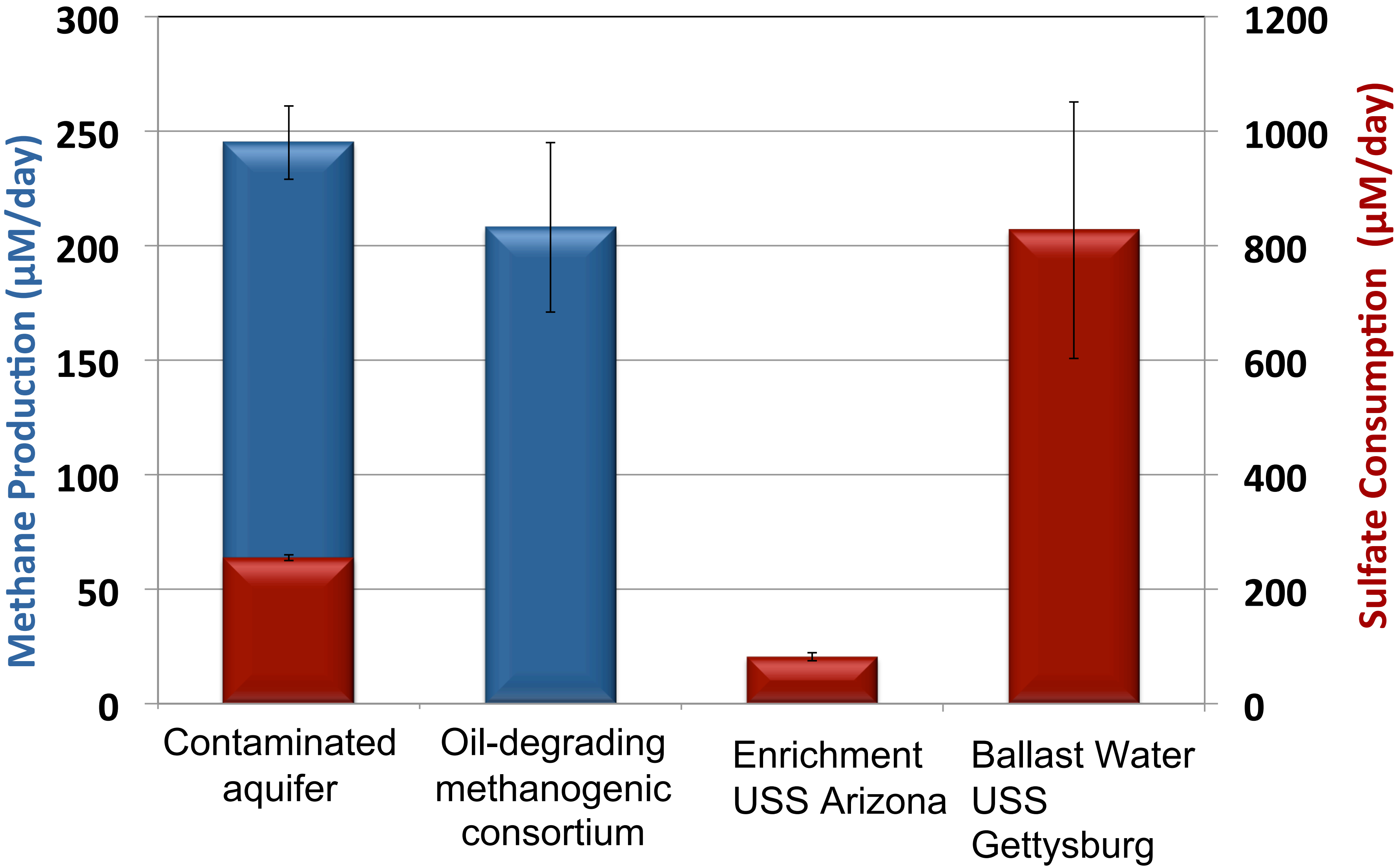
Freshwater and Marine Inocula Used to Examine the Fate of Fuels Under Anaerobic Conditions

Exposure to Biodiesel

Exposure to Hydrocarbons

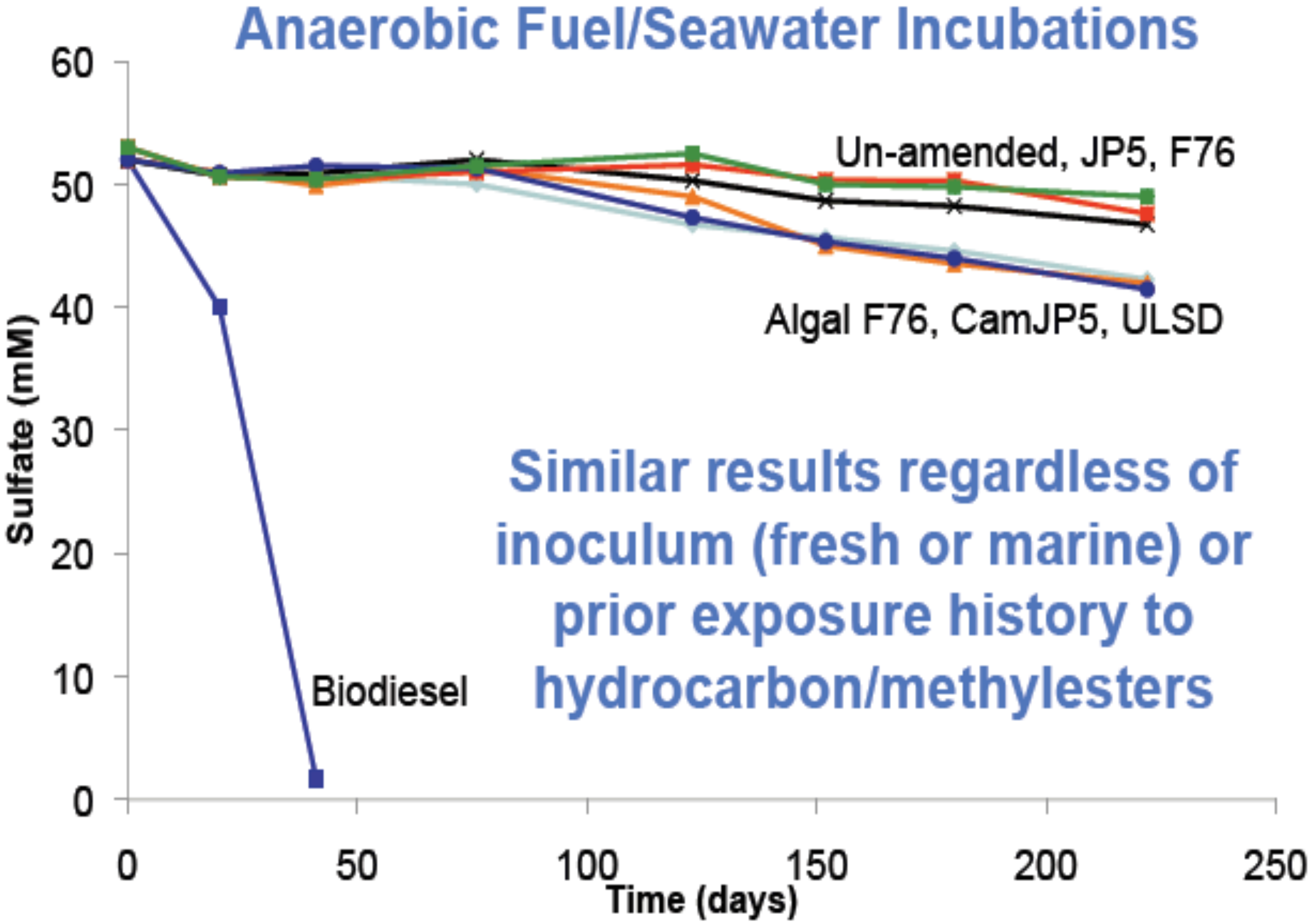
	Exposure to Biodiesel: YES	Exposure to Biodiesel: NO
Exposure to Hydrocarbons: YES	Ballast Water USS Gettysburg 	Enrichment USS Arizona HC - Contaminated aquifer Oil-degrading methanogenic consortium
Exposure to Hydrocarbons: NO		Florida Keys Coastal Seawater w/Lee & Little Persian Gulf Coastal Seawater

Biodiesel (BD) -Supported Anaerobic Microbial Metabolism with Various Inocula

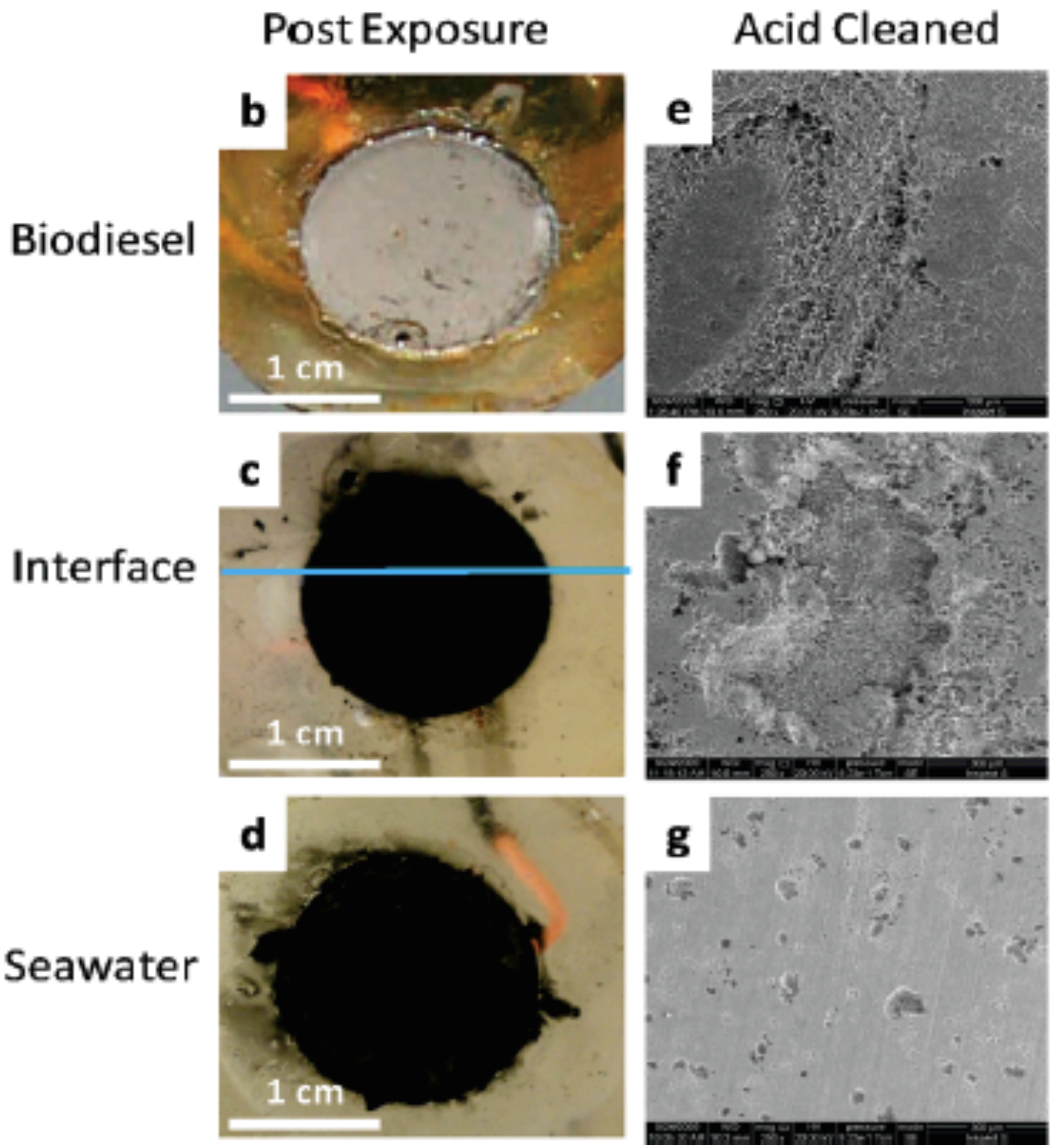


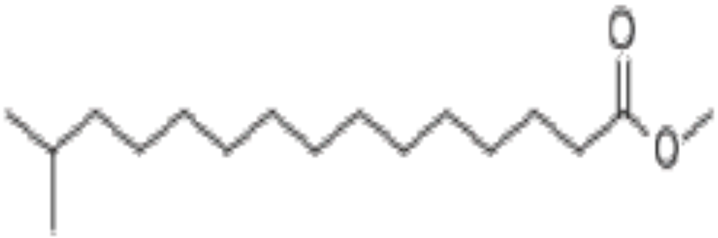
(The rates are corrected for biodiesel-unamended controls)

Fate of Biodiesel vs. Other Fuels

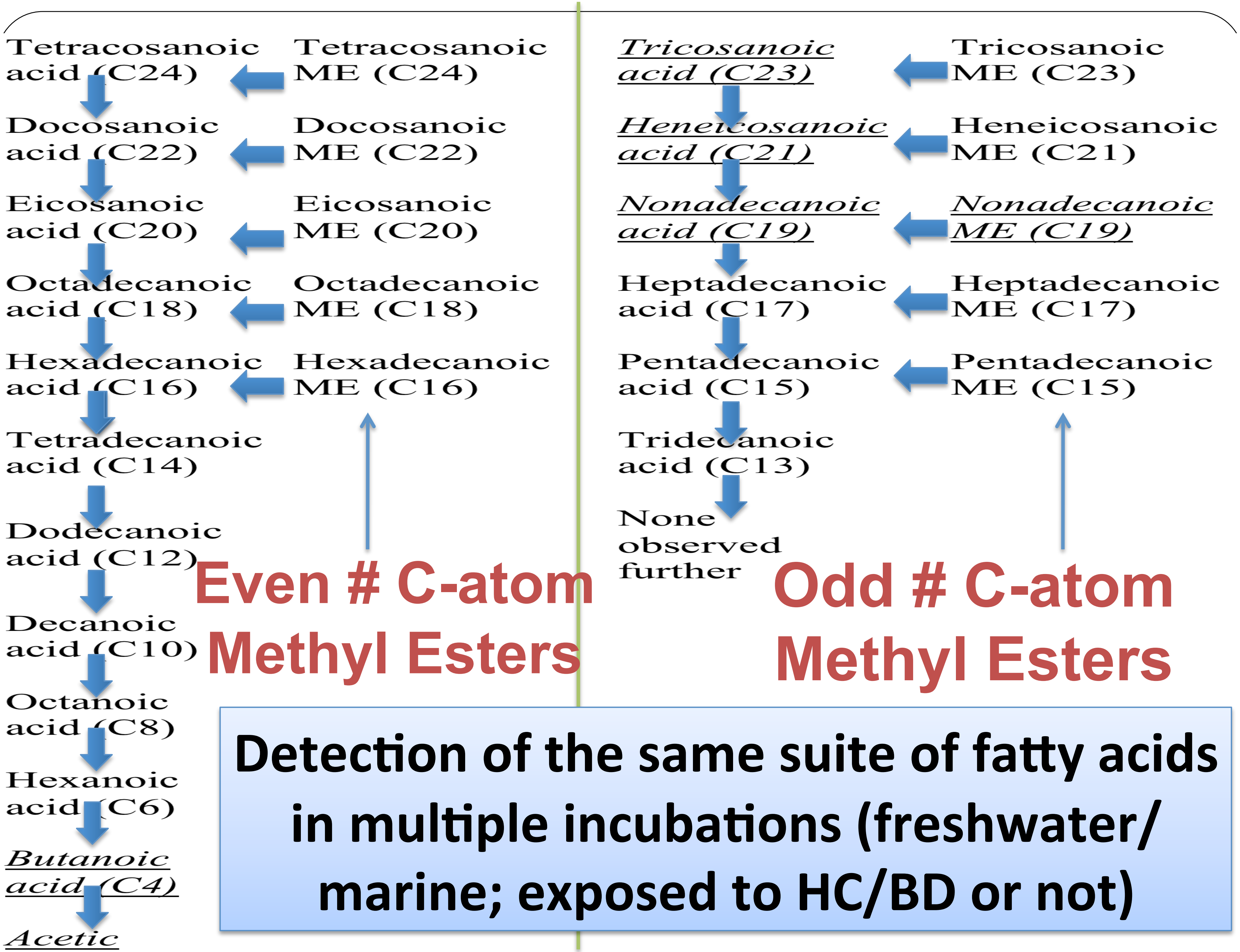


Biodiesel and Carbon Steel Corrosion





- Biodiesel is a mixture of fatty acid methyl esters
- Methyl esters are hydrolyzed to fatty acids within 60 days
- Fatty acids stimulate anaerobic bacterial communities leading to the rapid corrosion of carbon steel
- Aktas, D. F.; Lee, J. S.; Little, B. J.; Ray, R. I.; Davidova, I. A.; Lyles, C. N.; Suflita, J. M. Anaerobic Metabolism of Biodiesel and Its Impact on Metal Corrosion. *Energy & Fuels* (2010), 24(5), 2924-2928



Detection of the same suite of fatty acids in multiple incubations (freshwater/ marine; exposed to HC/BD or not)

First Generation Biodiesels are Very Labile

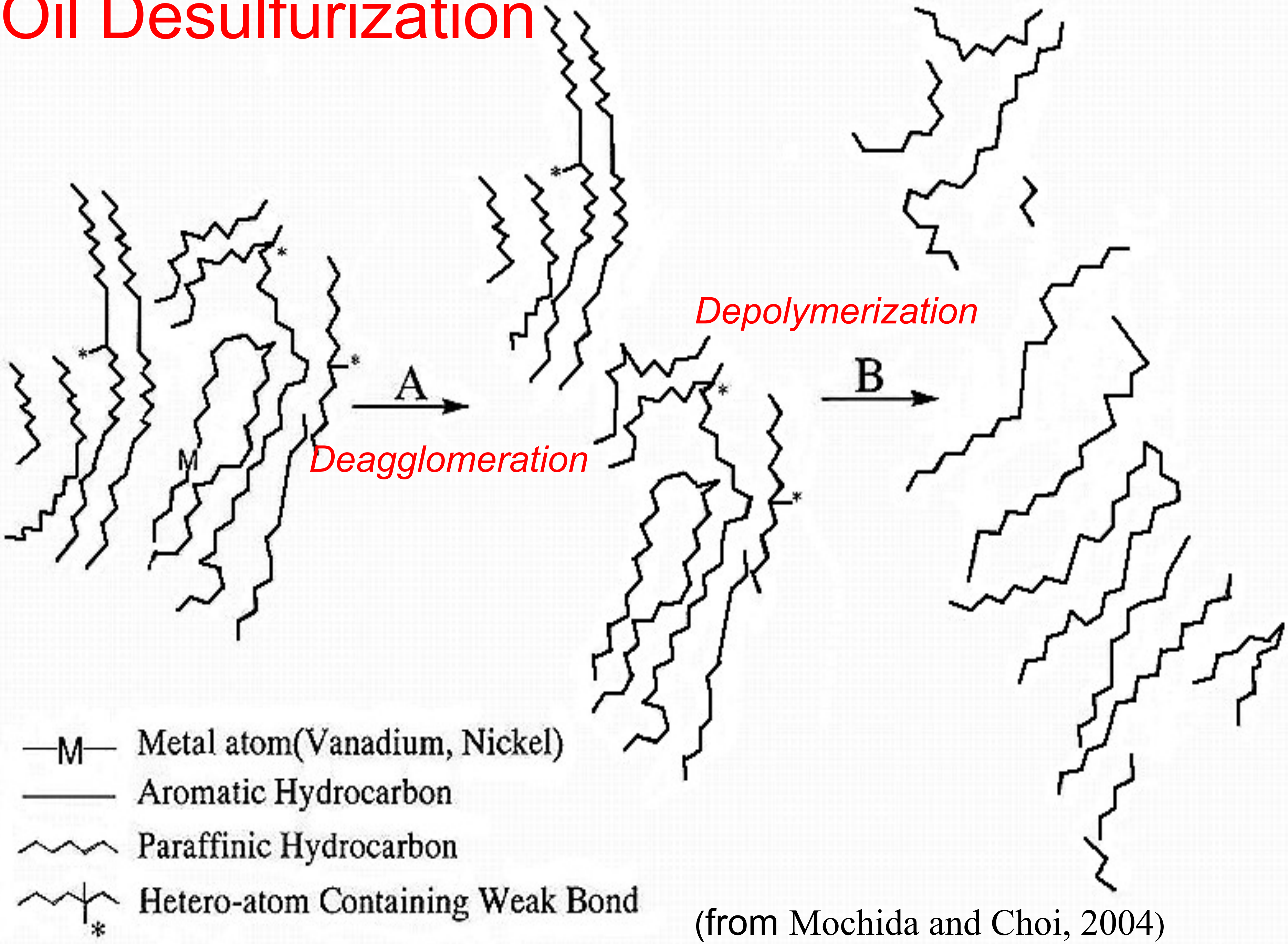
What About Other Fuels?

- Focus on ULSD
- Many reports of problems with ULSD
- Several hypotheses can be advanced

ULSD: Is It Really Different?

- To make ULSD, refineries must treat it severely
- Molecules are broken apart to release the organosulfur moieties
- This changes several fuel properties: density, viscosity, lubricity, etc
- Additives used to maintain performance characteristics (e.g. often up to 2% biodiesel)

Oil Desulfurization



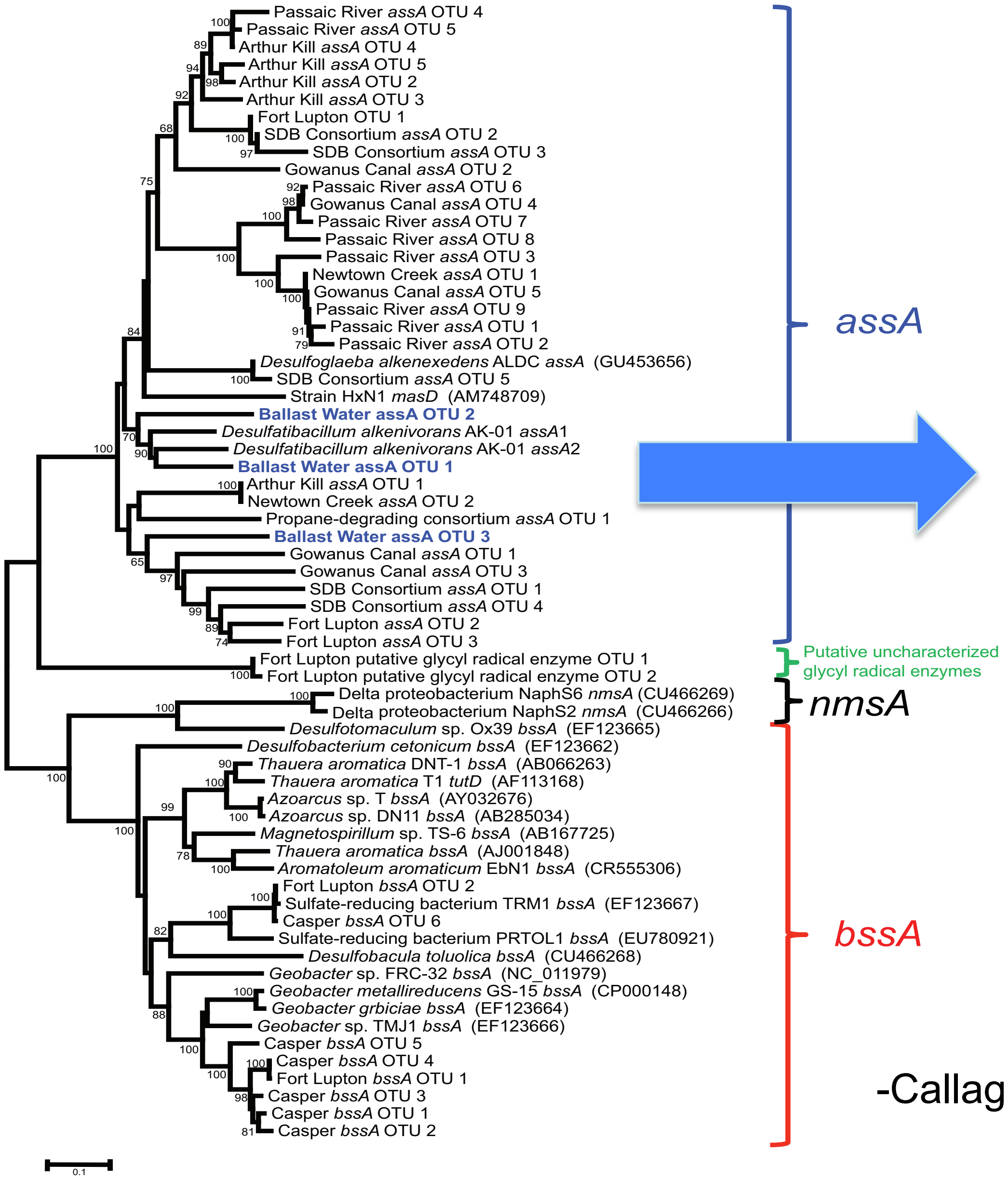
(from Mochida and Choi, 2004)

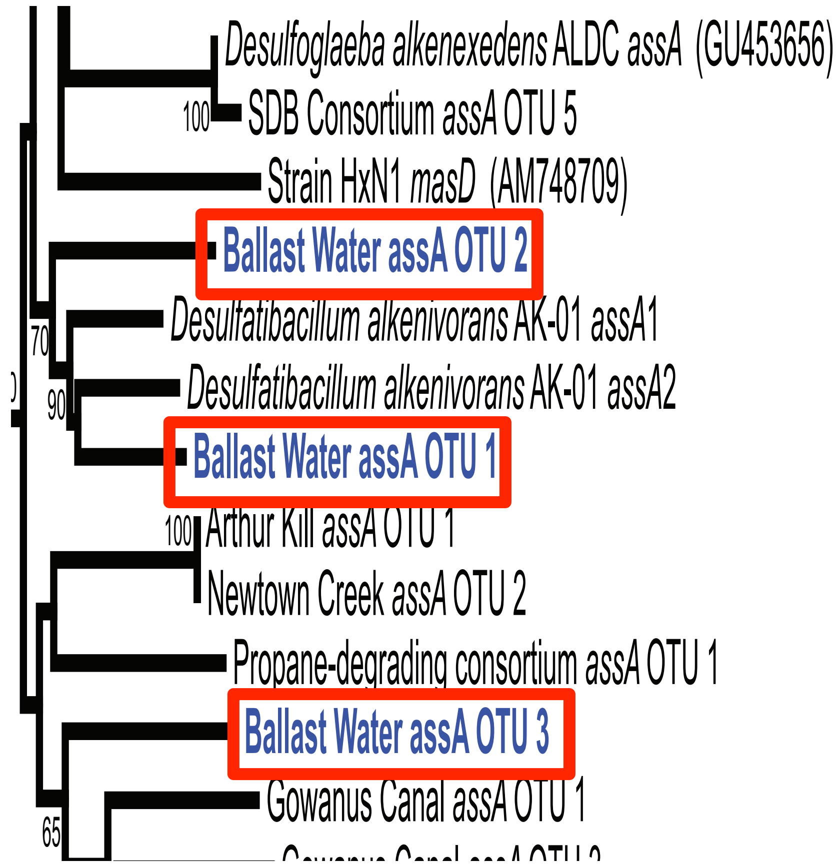
Need to Compare the Biological Stability of HSD, LSD & ULSD

Obtained Fuel Samples Directly From the Refinery - Before Any Additives

Incubated with Several Inocula – Marine and Freshwater

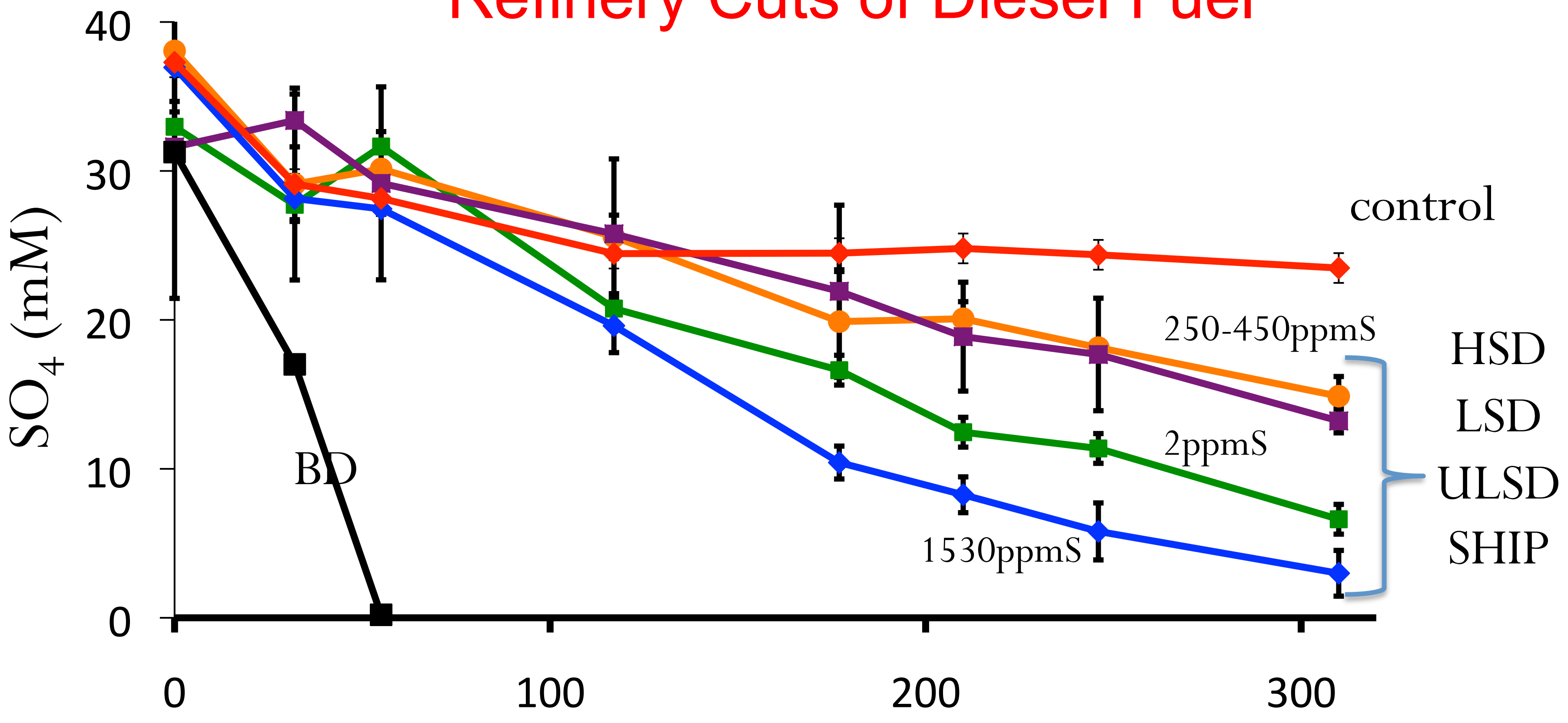
Anaerobic HC biodegradation gene probes described





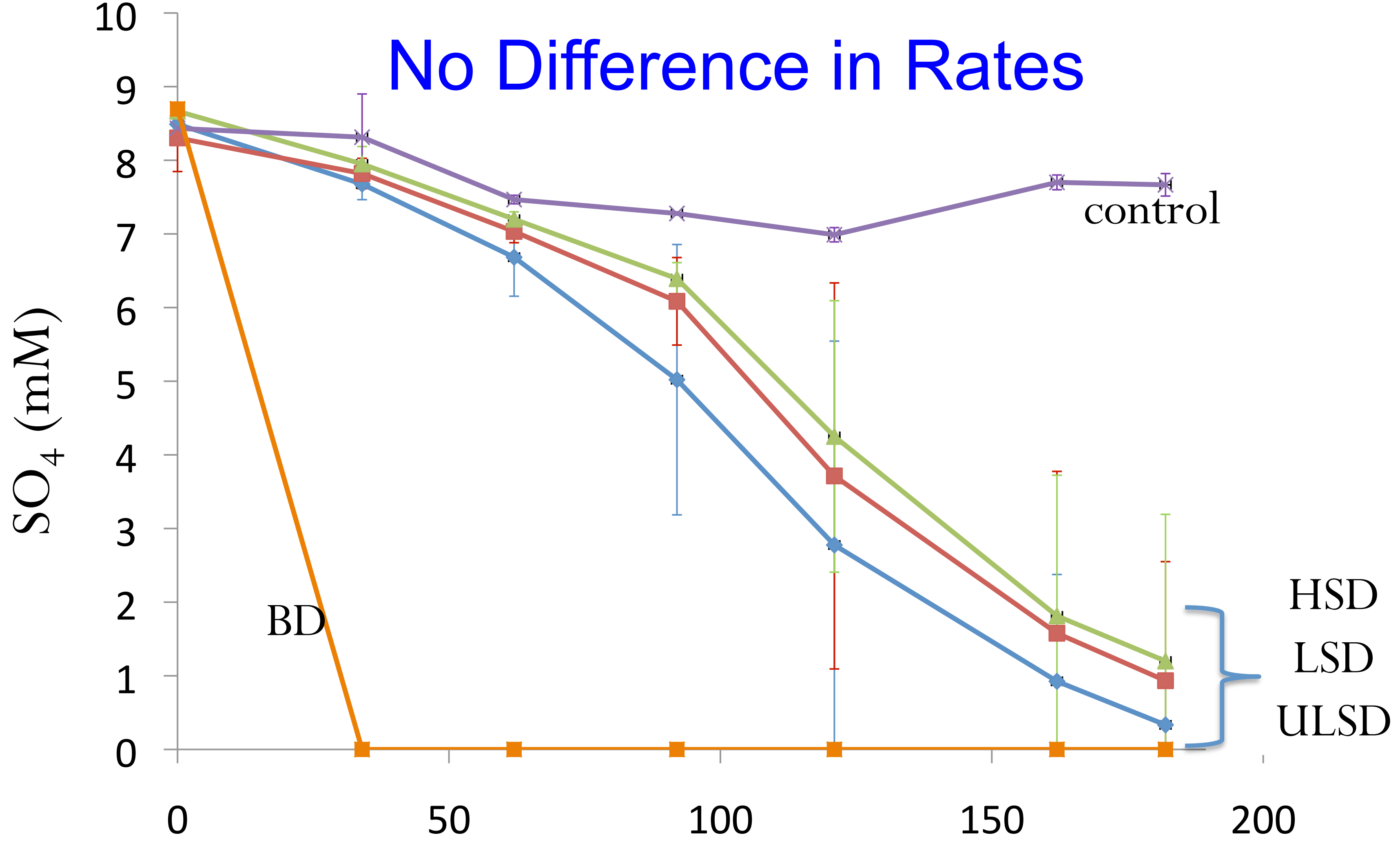
-Callaghan, et al., 2010. *ES&T.* 44(19), 7287-7294.

Sulfate Reduction by Incubations Containing Seawater from a Navy Ballast Tank and Refinery Cuts of Diesel Fuel

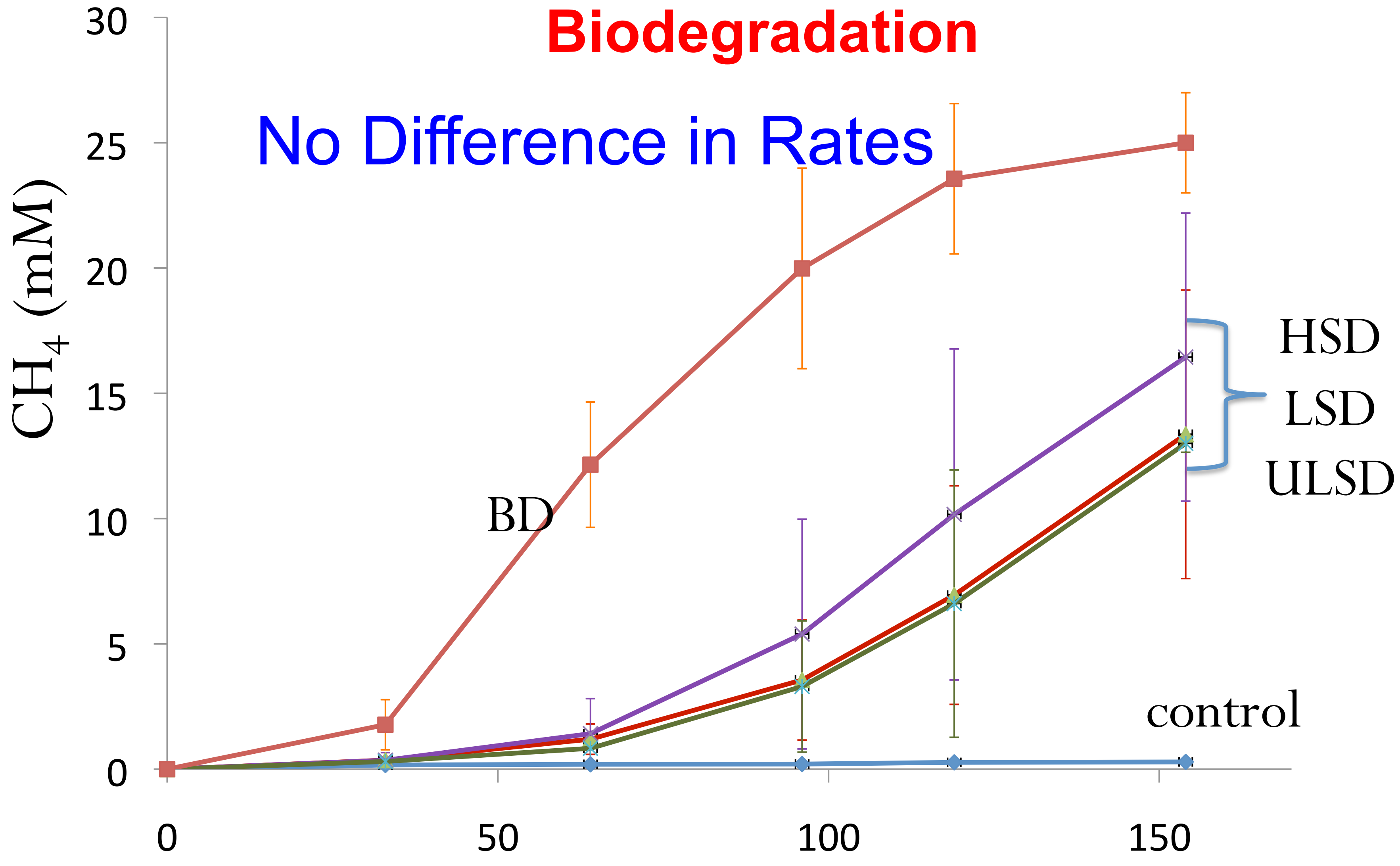


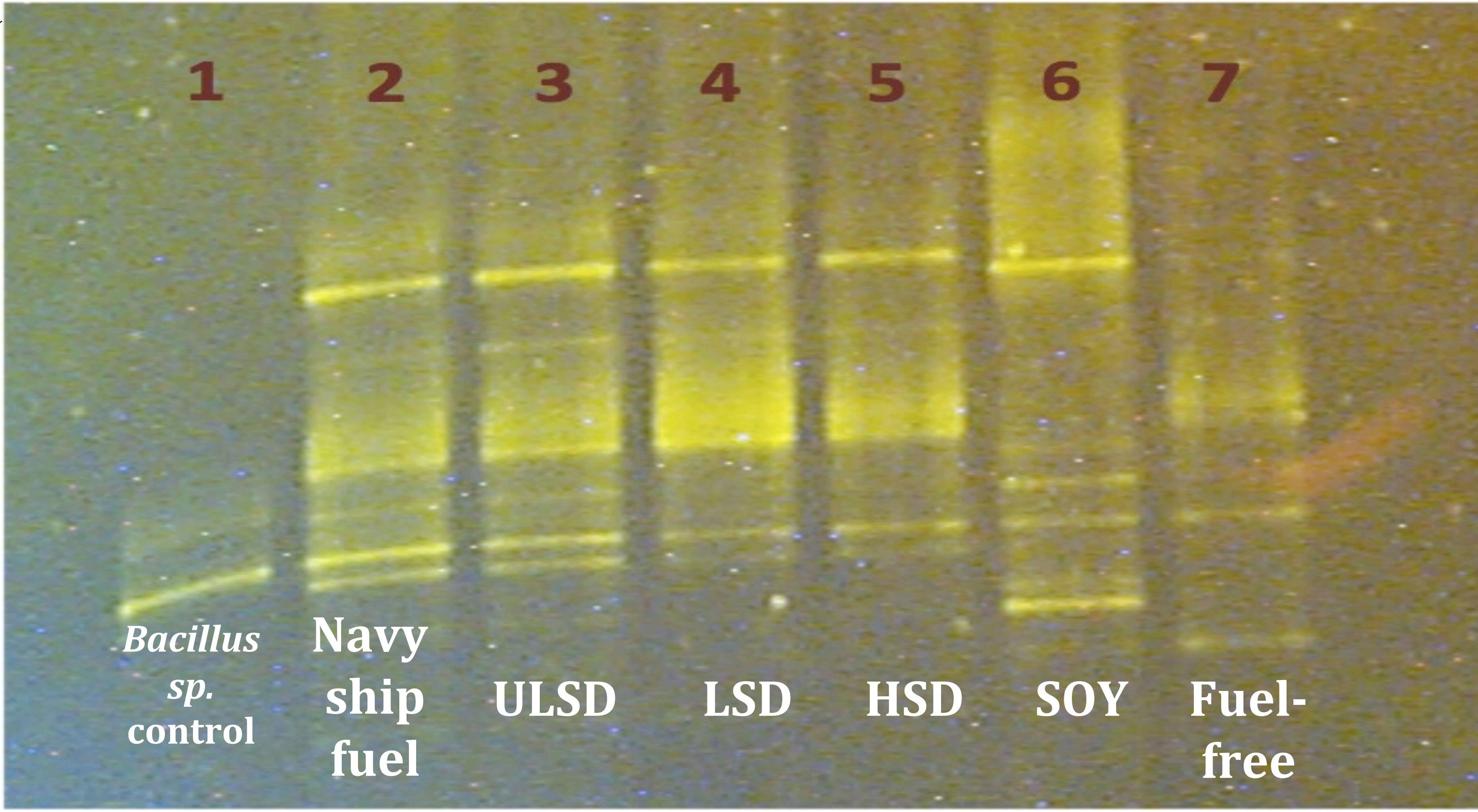
No Difference in Rates

Sulfate Reduction by Incubations Containing Contaminated Aquifer Sediments and Refinery Cuts of Diesel Fuel

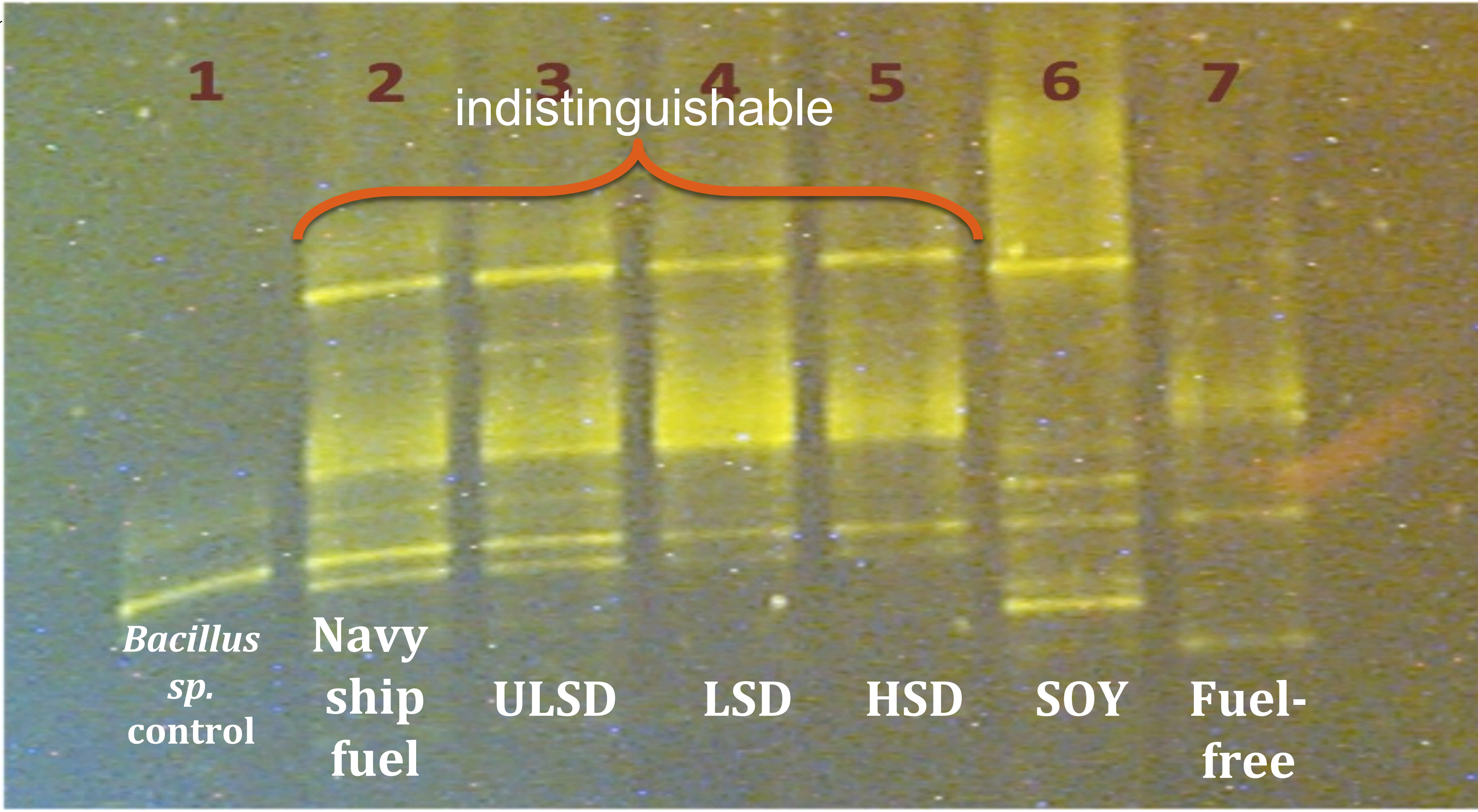


Methane Production from a Methanogenic Consortium Capable of Hydrocarbon Biodegradation





DGGE profile of NAVY ballast tank communities incubated with ship fuel, diesel fuels with different sulfur status, or biodiesel



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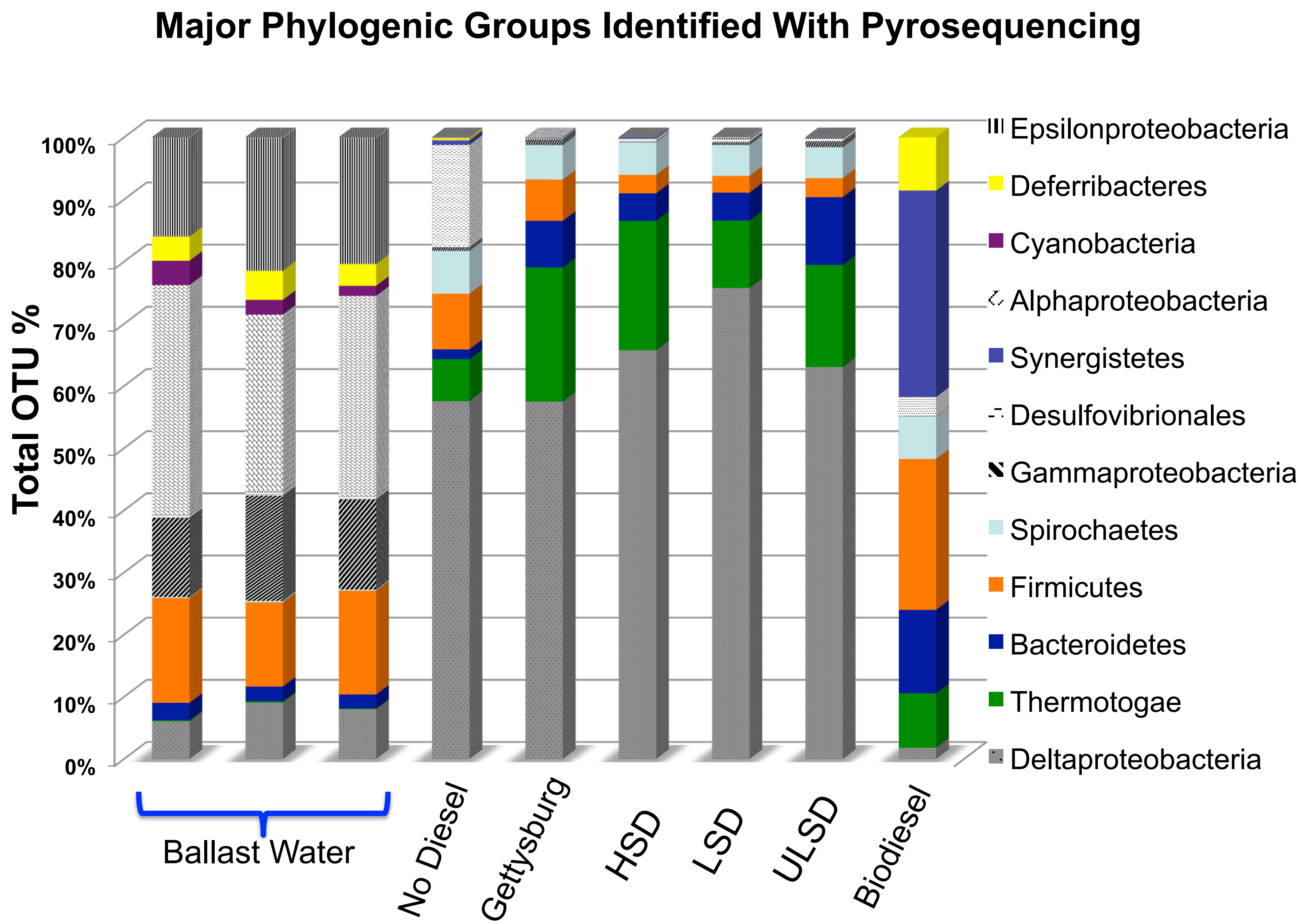
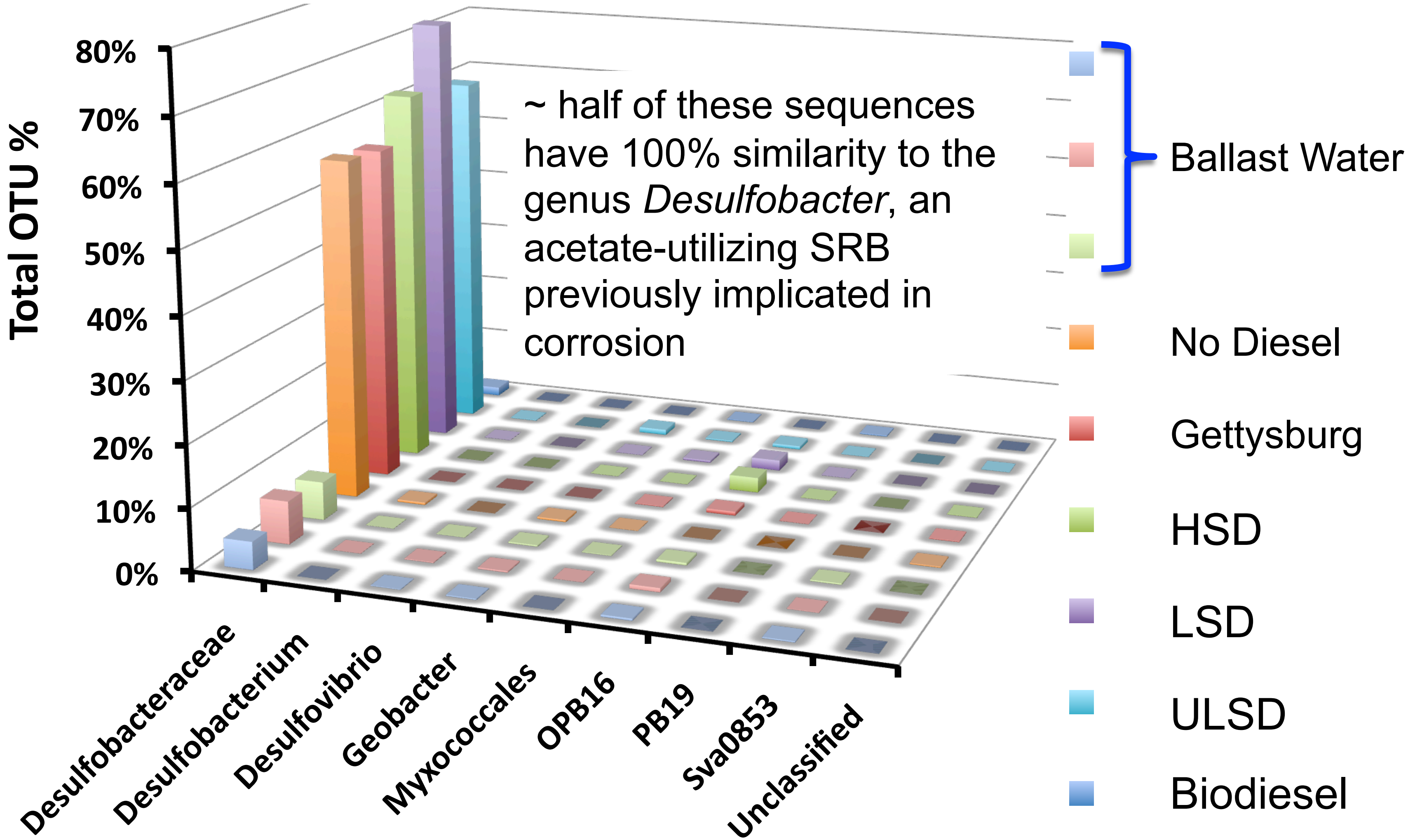


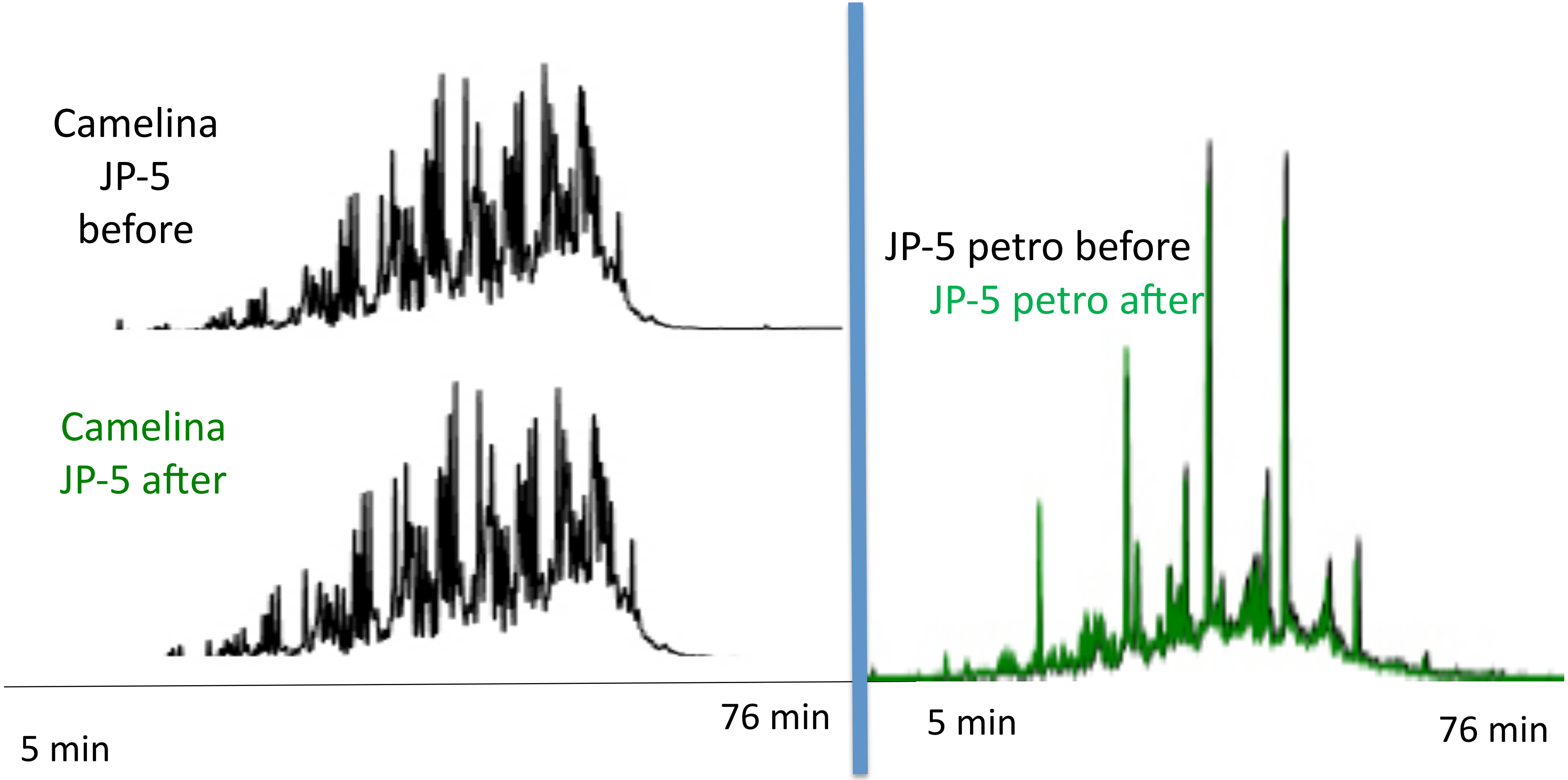
Major Phylogenic Groups Identified With Pyrosequencing
Total OTU %
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Ballast Water
No Diesel
Gettysburg
HSD
LSD
ULSD
Biodiesel
Epsilonproteobacteria
Deferribacteres
Cyanobacteria
Alphaproteobacteria
Synergistetes
Desulfovibrionales
Gammaproteobacteria
Spirochaetes
Firmicutes
Bacteroidetes
Thermotogae
Deltaproteobacteria

Dominant Deltaproteobacteria

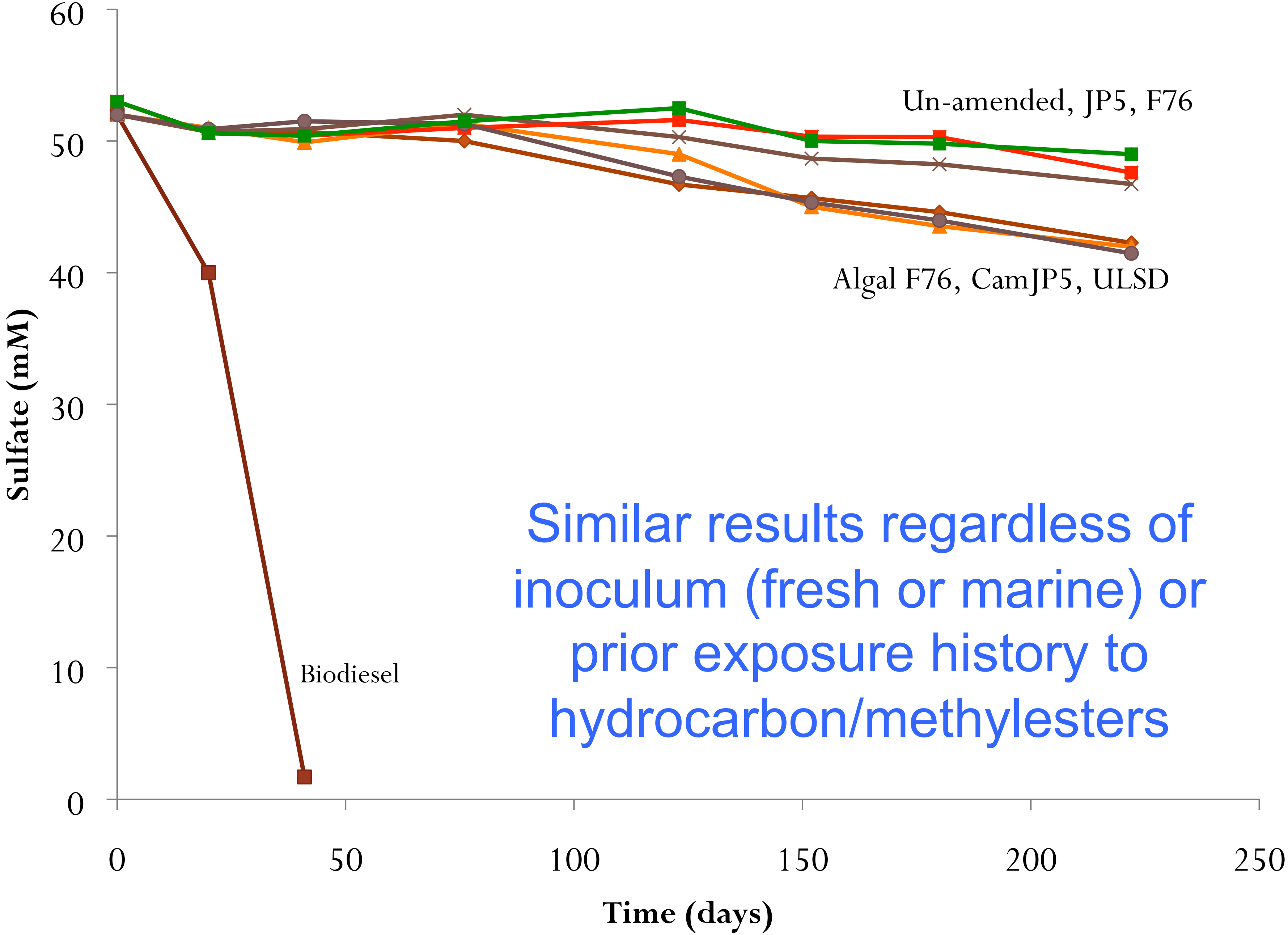


GC-MS Comparison of Traditional and Alternate Military Fuels

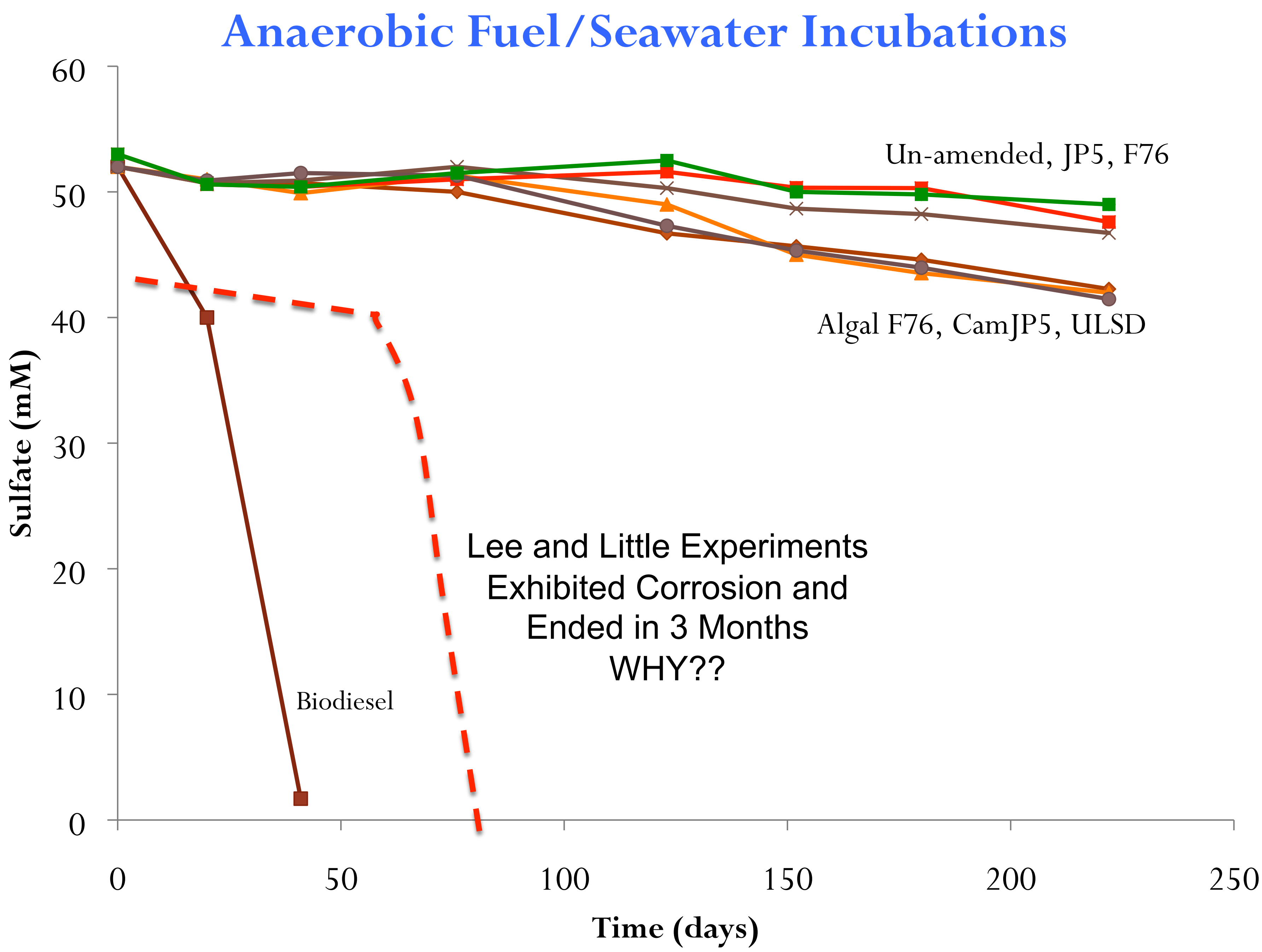
- before and after incubation in anaerobic seawater

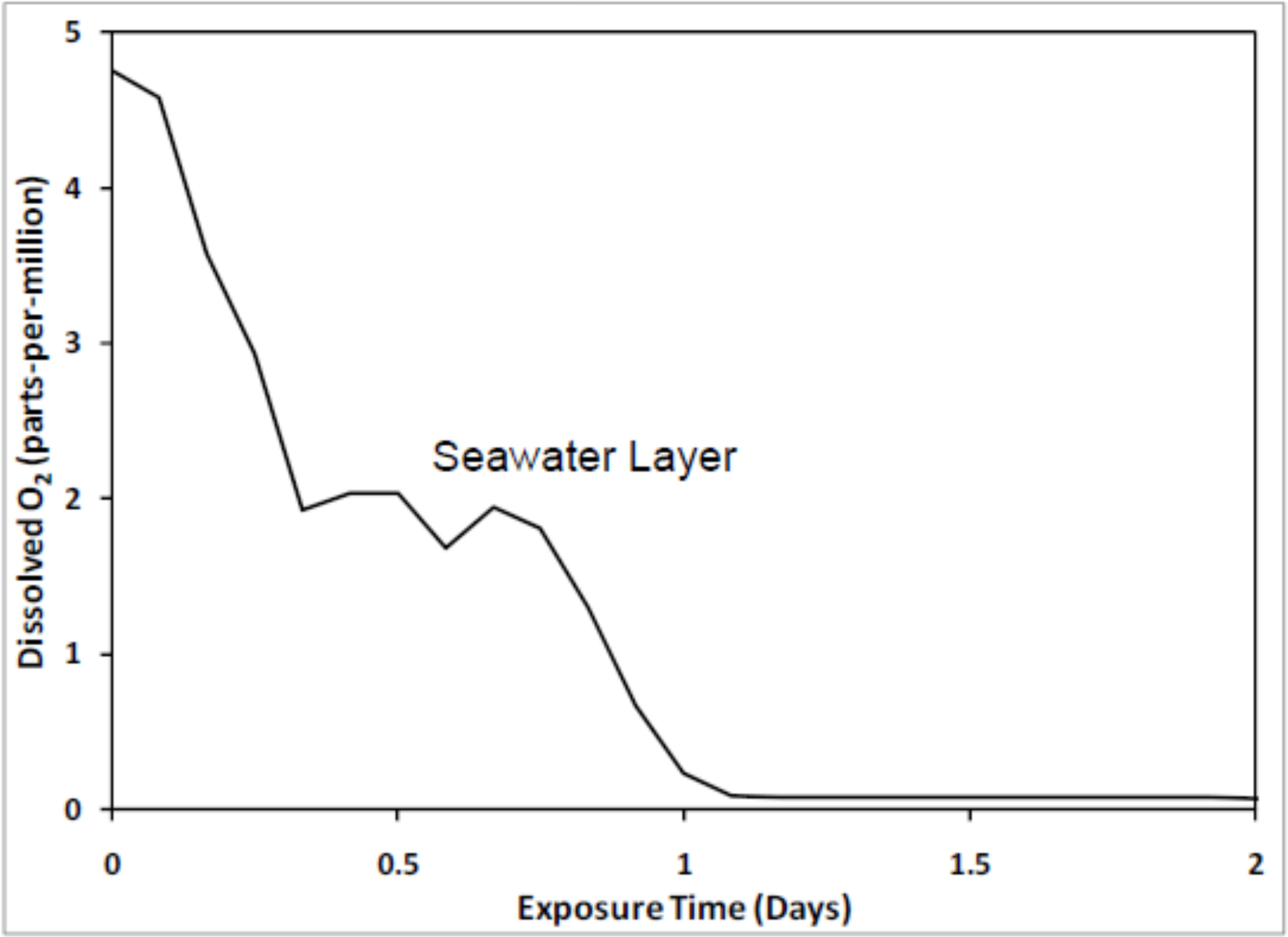


Anaerobic Fuel/Seawater Incubations



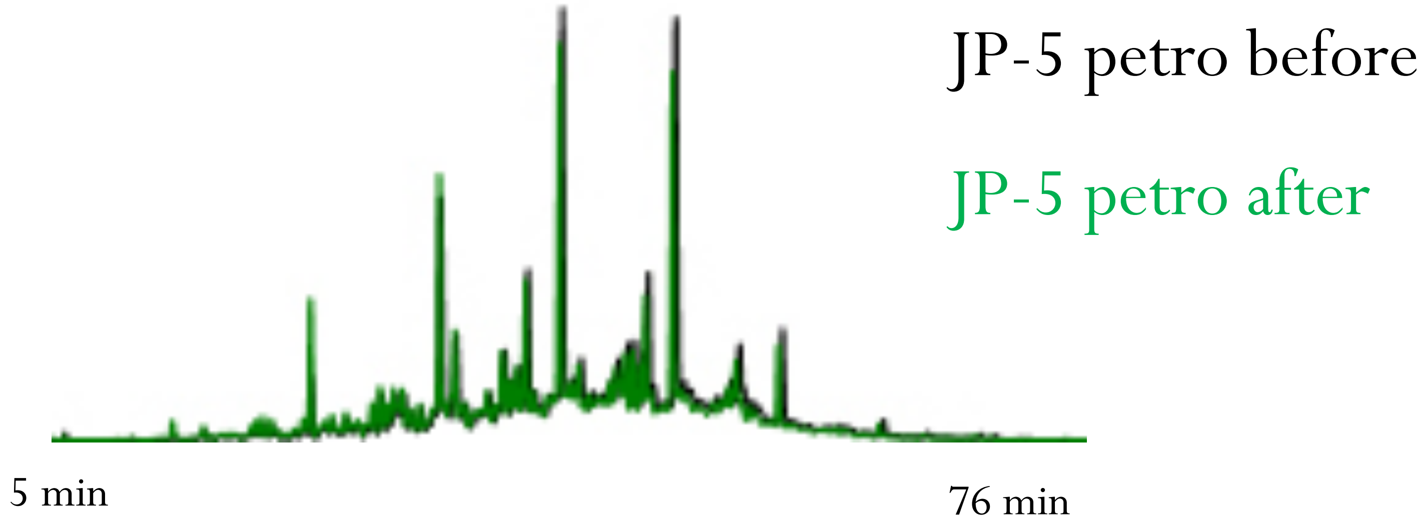
Similar results regardless of inoculum (fresh or marine) or prior exposure history to hydrocarbon/methylesters


Anaerobic Fuel/Seawater Incubations
60
50
40
30
20
10
0
Sulfate (mM)
0
50
100
150
200
250
Time (days)
Un-amended, JP5, F76
Algal F76, CamJP5, ULSD
Biodiesel
Lee and Little Experiments
Exhibited Corrosion and
Ended in 3 Months
WHY??

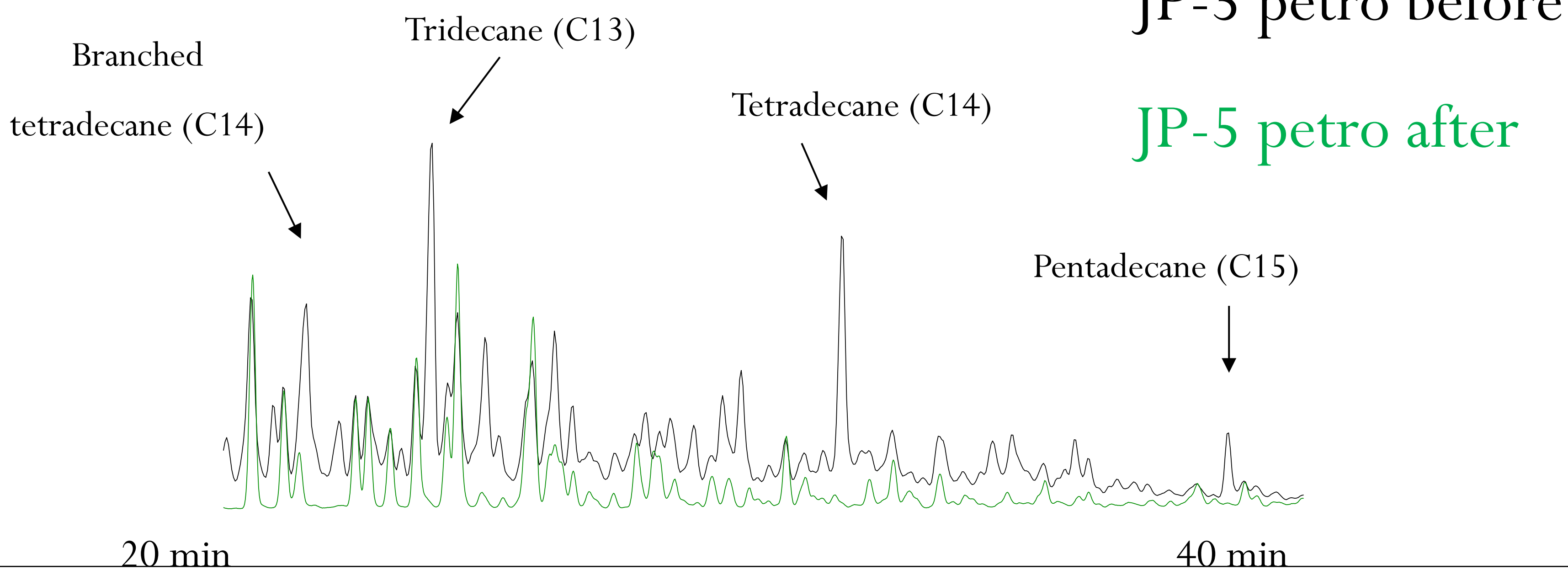


Seawater Layer
Dissolved O_2 (parts-per-million)
Exposure Time (Days)
0
1
2
3
4
5
0
0.5
1
1.5
2

Strict anaerobic incubations



Less stringent anaerobic incubations



Less Stringent Anaerobic Incubations

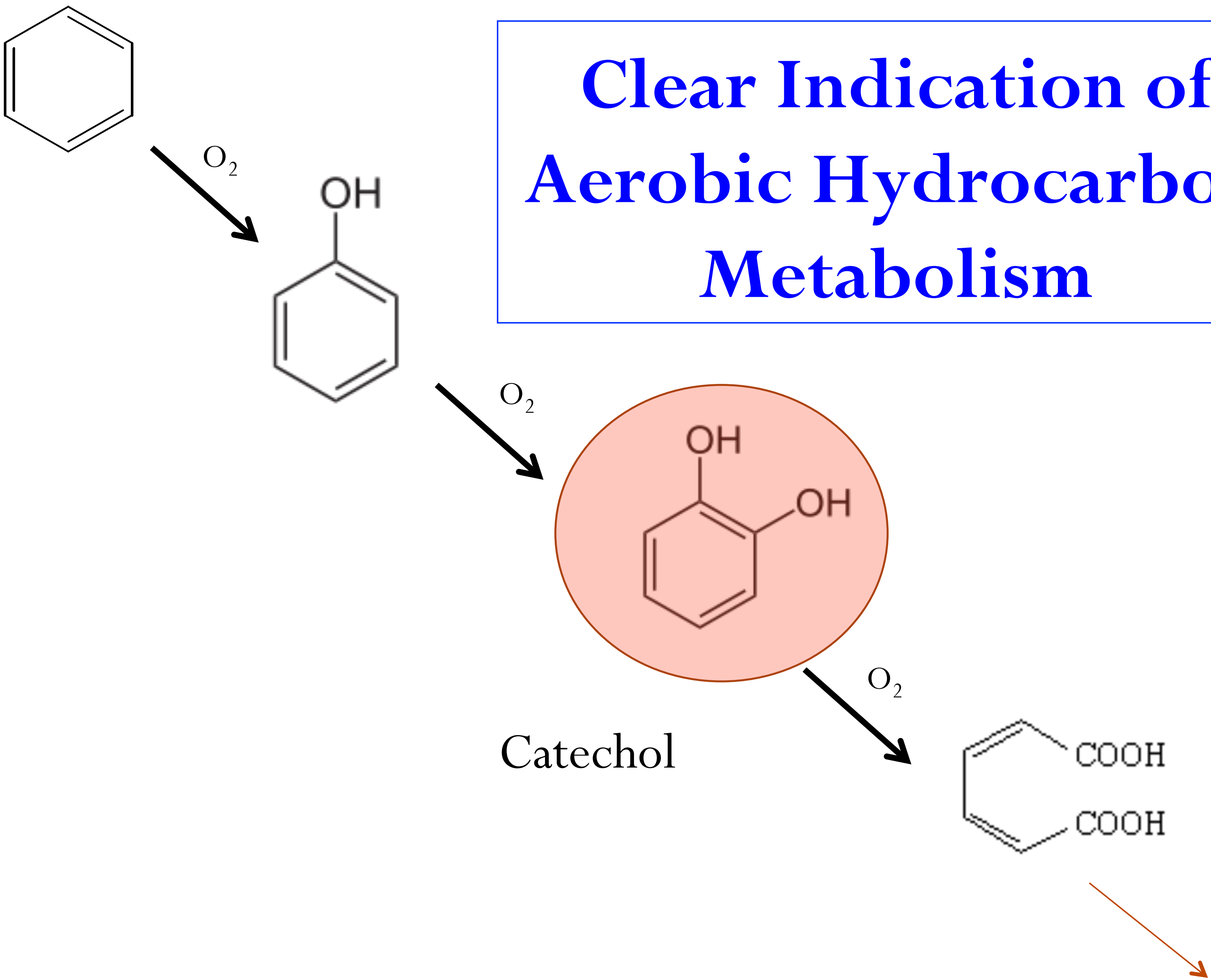
	Straight chain alkanes	Branched alkanes	Notable Fatty acids	Metabolites or other observations
JP5	C10-C15	A few		Alkylated catechols, benzoates, and phenols/a few low MW alcohols and acids
Camelina-based JP5	C10-C18	C9-C20		Alkylated catechols,and benzoic acid / a few low MW alcohols and acids
F76	C11-C15 and C22	-		Alkylated benzoates
Algal-based F76/petro F76	C10-C20 and C25	C11-C21		Catechol and alkylated benzoates / a few low MW alcohols and acids
Soy-based BD (20%)	C11-C14 and C22-C25	A few	C5-C18 and C20	C:16, C18:0/1/2 removed; Catechols
ULSD	C11-C22	-		Alkylated catechols, benzoate, alkylated phenol

Less Stringent Anaerobic Incubations

	Straight chain alkanes	Branched alkanes	Notable Fatty acids	Metabolites or other observations
JP5				Alkylated catechols, enols/a ols and
Camelin based J				ls,and low MW cids
F76				oates
Algal-ba F76/petro				ylated ow MW cids
Soy-based BD (20%)	C11-C14 and C22-C25	A few	C5-C18 and C20	C:16, C18:0/1/2 removed; Catechols
ULSD	C11-C22	-		Alkylated catechols, benzoate, alkylated phenol

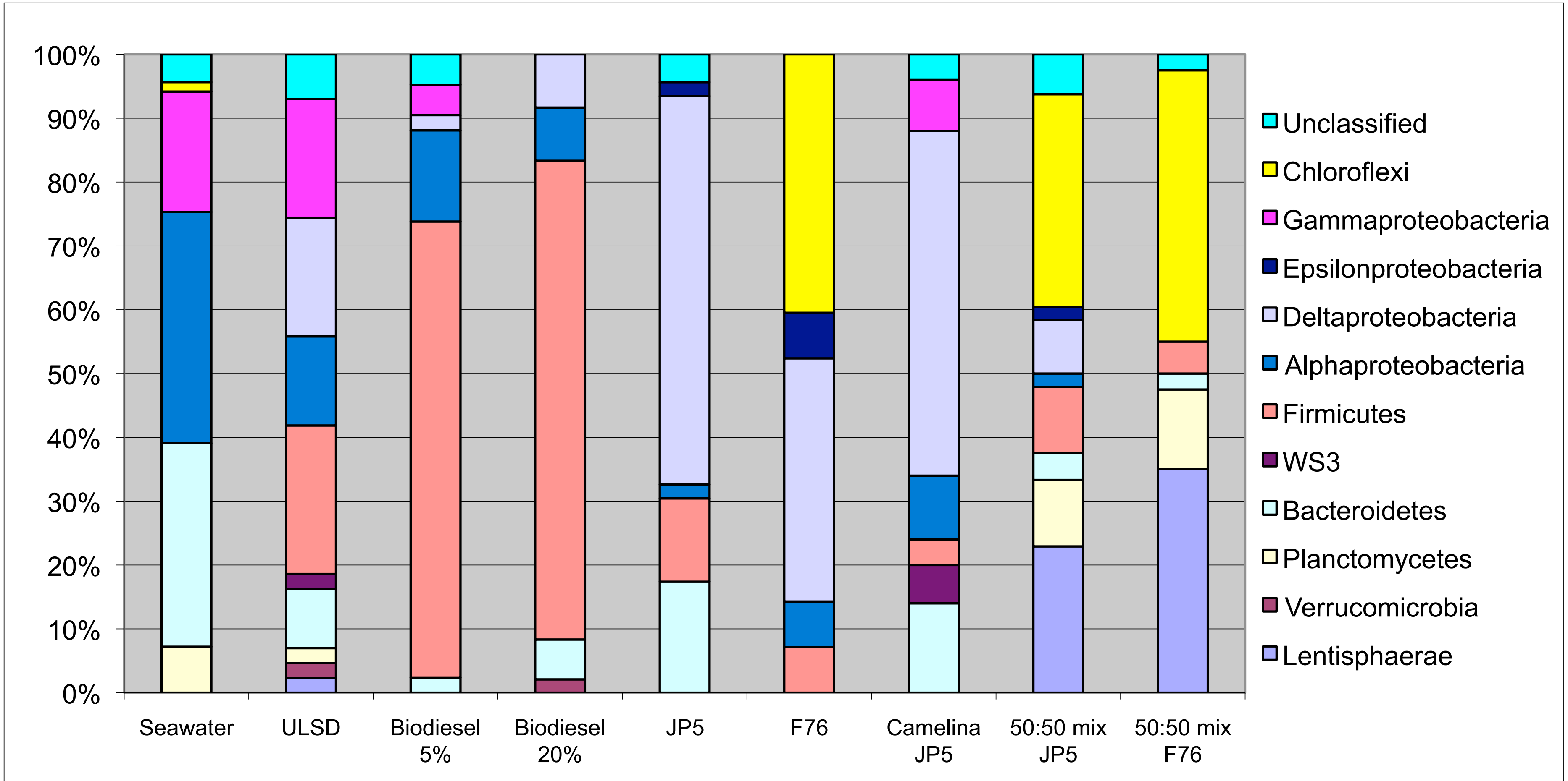
Phenols & Catechols and Low MW Fatty Acids

Clear Indication of Aerobic Hydrocarbon Metabolism



Catechol

Bacterial Communities in Less Stringent Anaerobic Incubations

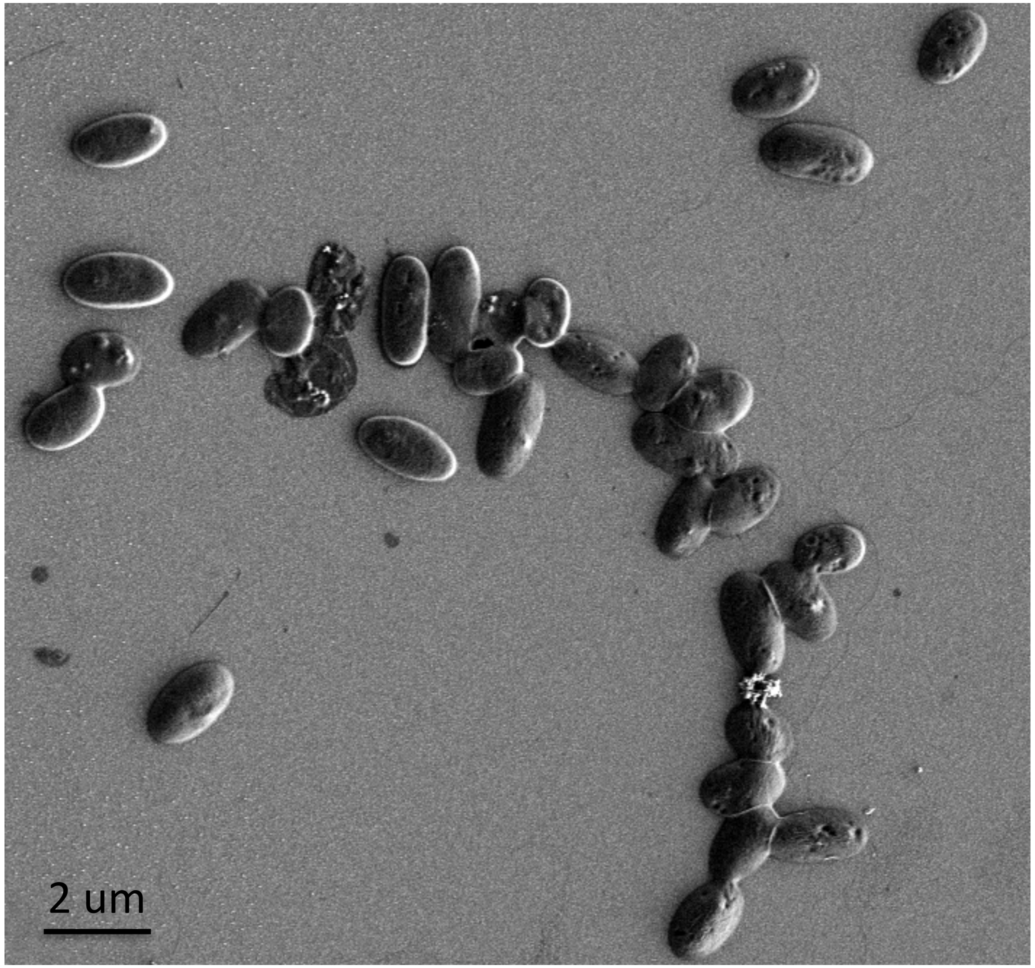


*Deltaproteobacteria: SRBs

Firmicutes: Clostridia

A Model Hydrocarbon-Degrading SRB

Desulfoglaeba alkanexedens strain ALDC



•Reduces sulfate

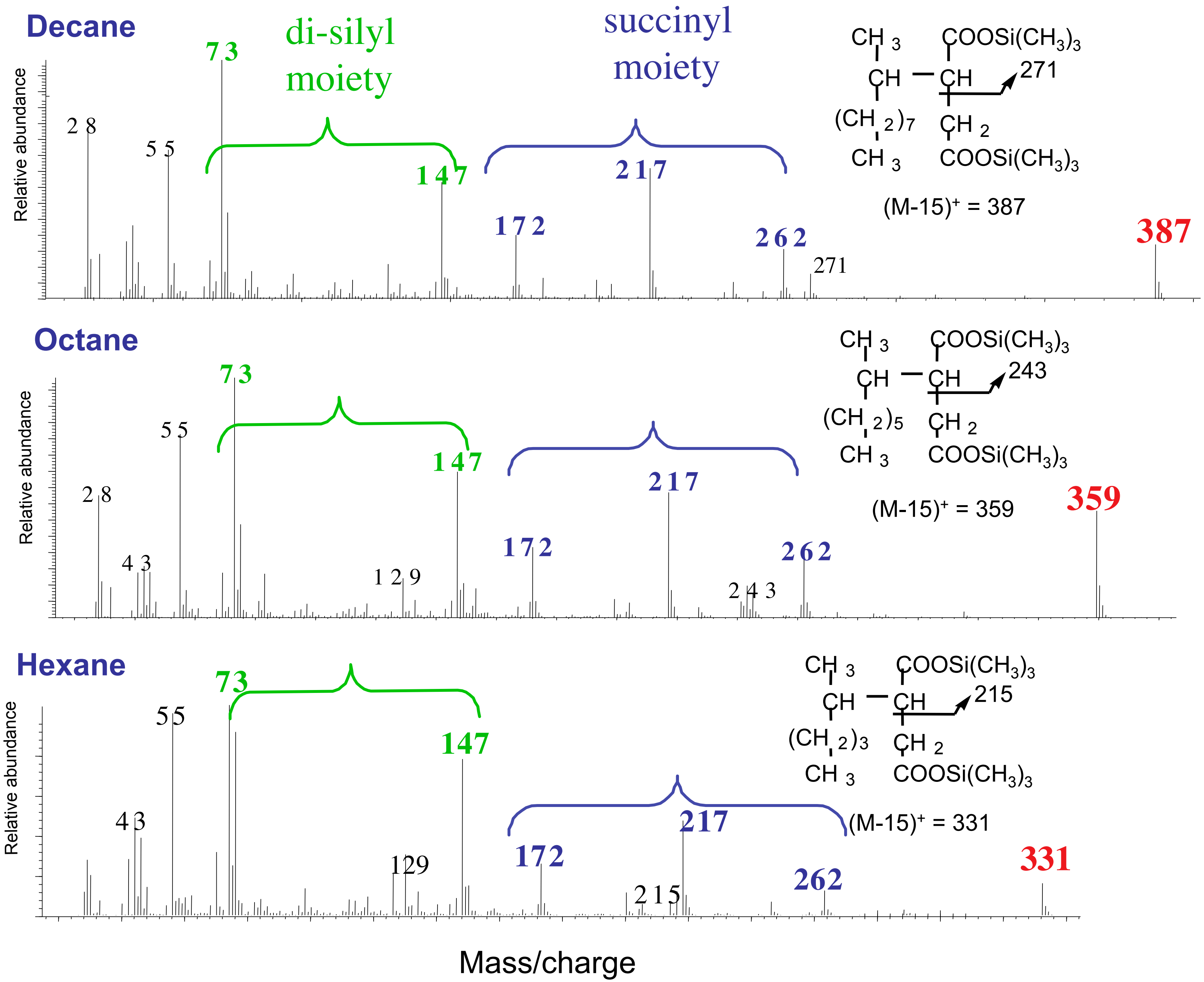
•Degrades hydrocarbons via fumarate addition

•Mineralizes C_6-C_{12} *n*-alkanes

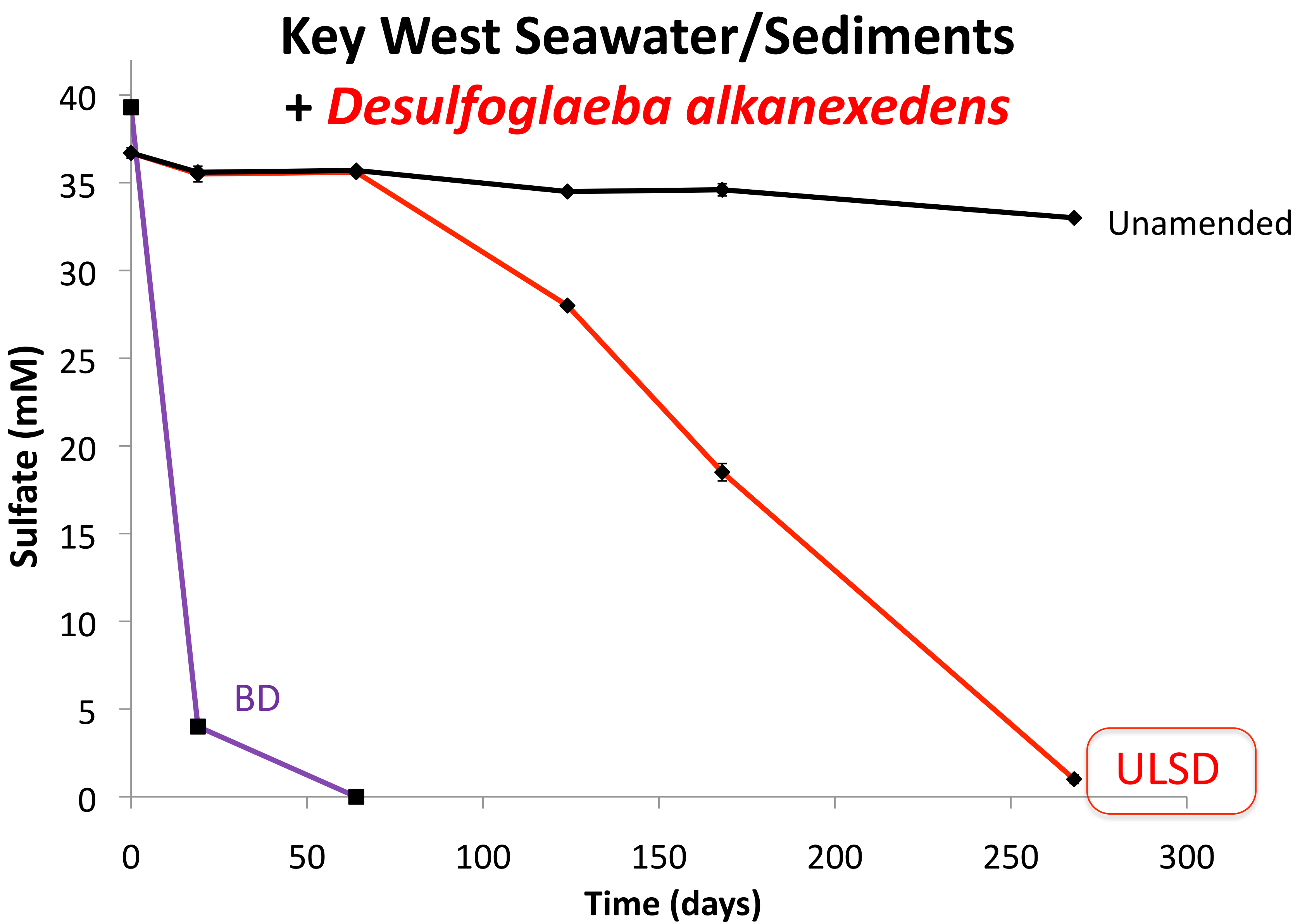
•Known to cause localized corrosion of carbon steel

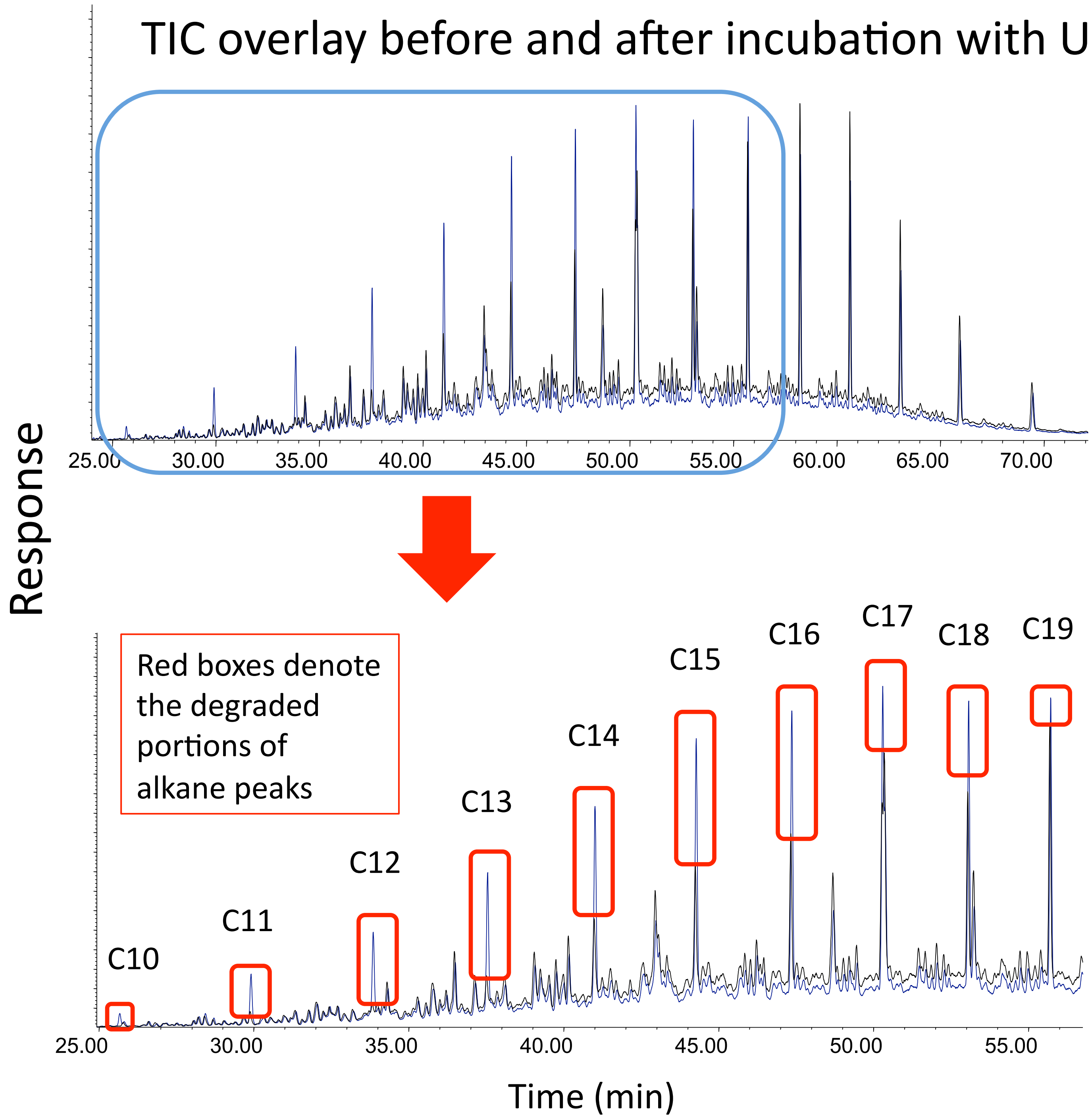
•Syntrophic growth

Mass Spectra of Alkylsuccinic Acid Metabolites



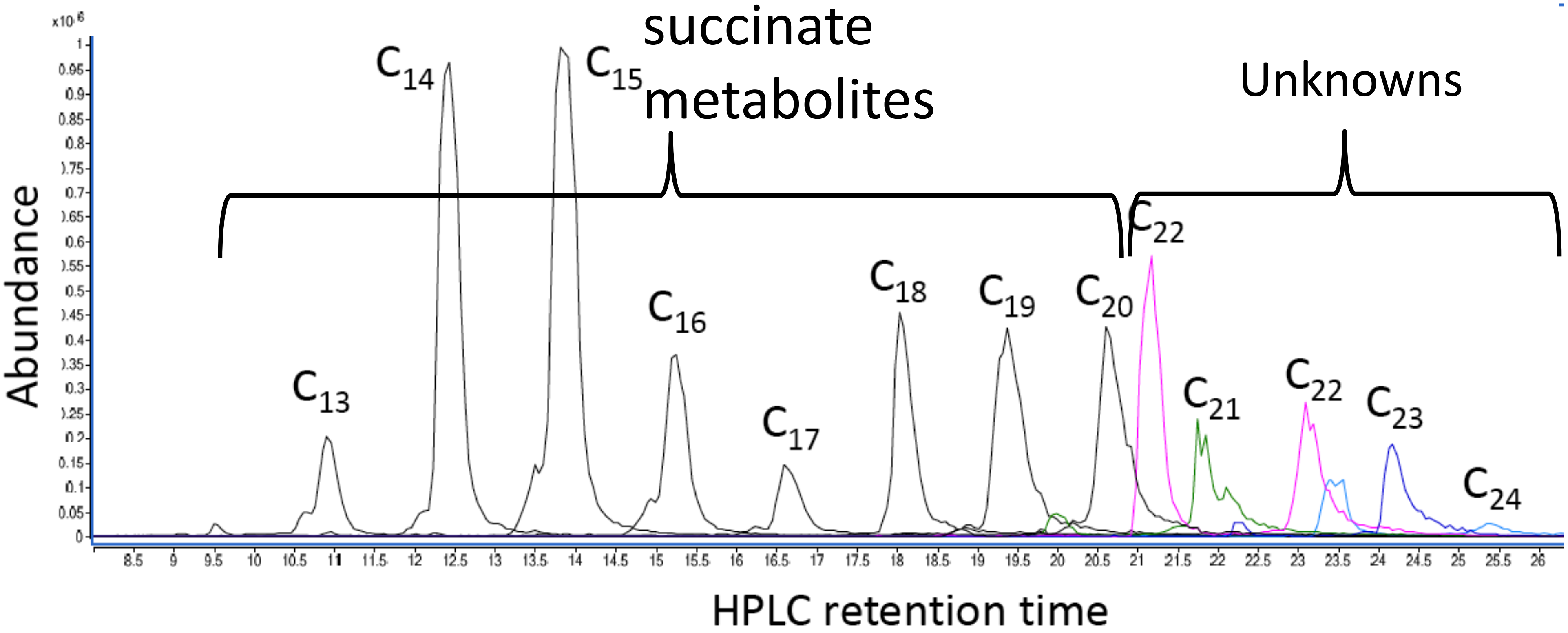
Anaerobic Biodegradation of ULSD





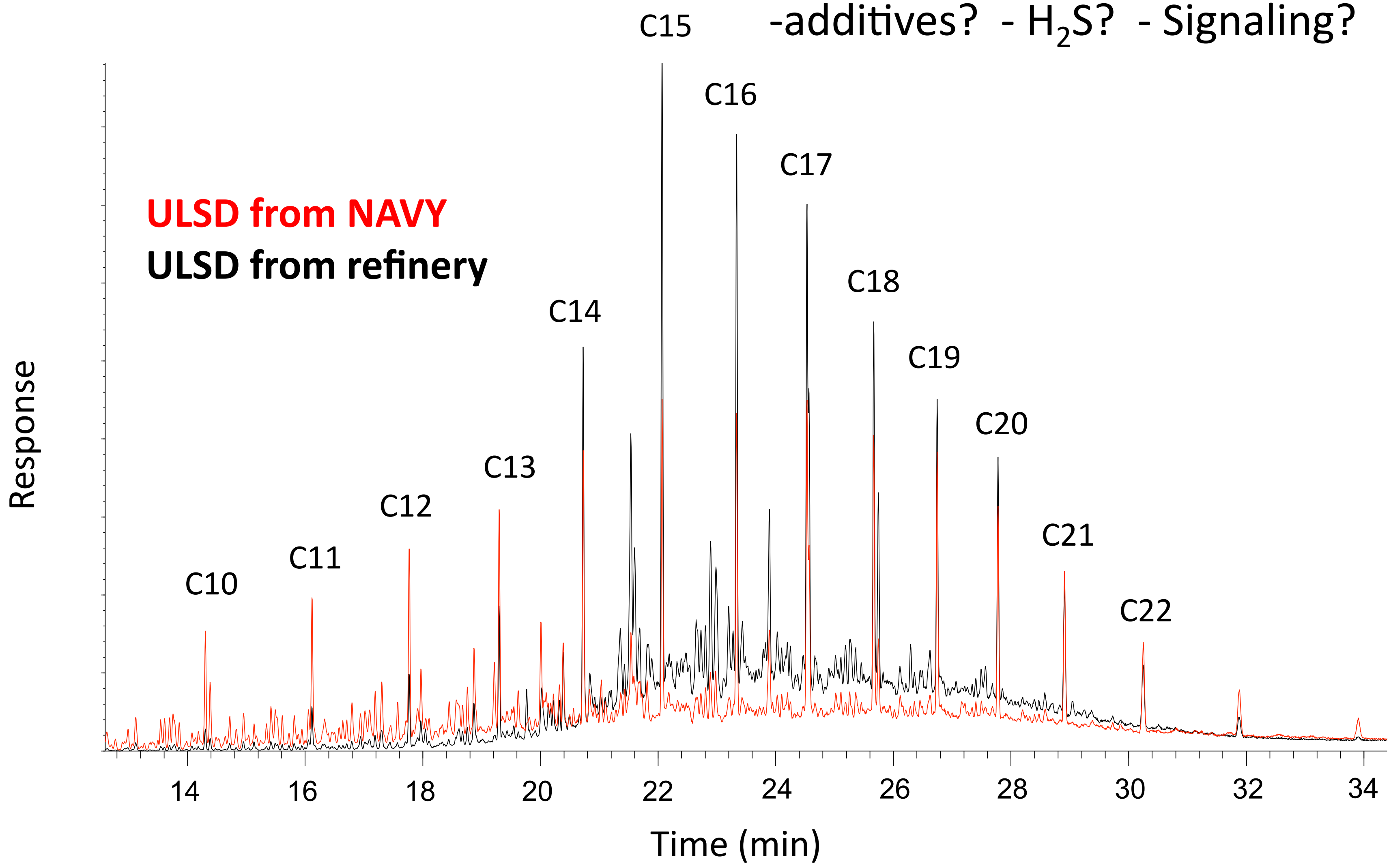
***_Desulfoglaeba_ is known to degrade C6-C12 n-alkanes

Extracted Ion Chromatograms Of $C_nH_{(2n-2)}O_4$ Signature Hydrocarbon Metabolites Detected by LC-QToF Analysis



But Why??

- Two 'different' ULSDs were used……..
  - One directly from a refinery the other from NAVY
  - Slightly different when analyzed by GC/MS
  - -additives? - H_2S? - Signaling?



Summary

1) FAME biodiesel is more labile than other fuel components and can exacerbate metal biocorrosion
2) No difference in the susceptibility of HSD, LSD or ULSD to anaerobic biodegradation in marine or freshwater environments; additives in fuel likely important
3) Whenever fuel biodegradation was coupled to sulfate reduction, the corrosion impact was high
4) Not all ULSDs are created equal; slight differences in chemical composition can be important
5) Small amounts of oxygen can have a large impact on both biodegradation and biocorrosion
6) The presence of the requisite microorganisms is important; inoculation with a hydrocarbon-degrading sulfate reducing bacterium

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Brenda Little
Jason Lee

ConocoPhillips

Paul Ryder

Crew of the USS Gettysburg

Revolutionary Research . . . Relevant Results