

**Chemical & Bioassay Analyses of
Emissions from Biodiesel Fuel
Combustion**

**R. Kobayashi, X. Liu, C. Vogel, F. Matsumura, N. Kado
Dept. Environmental Toxicology
University of California, Davis
T. Cahill – Arizona State University**

**California Air Resources Board
Sacramento, CA.**

Research Objectives

- Study biodiesel and renewable diesel emissions:
 - Chemical characterization of toxics
 - Toxicity studies of emissions

Unregulated Toxic Emissions

- PAHs
- Alkyl PAHs
- Nitro-PAHs
- Selective reactive aldehydes

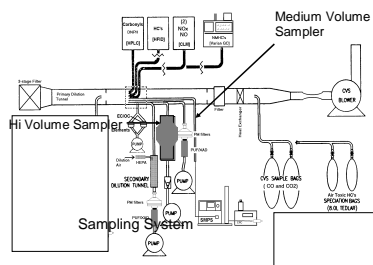
Toxicity Studies of Emissions

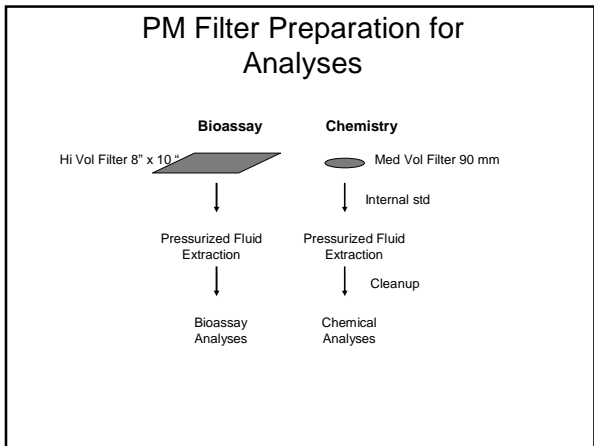
- Tests for markers of inflammation in human cells
- Tests for genotoxicity
 - Mutagenicity
 - Chromosomal Damage

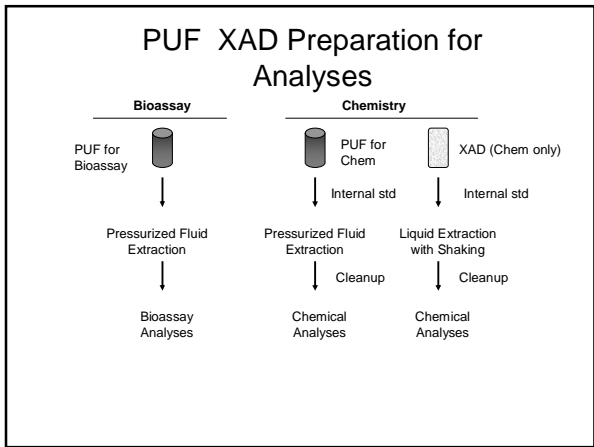
Test Vehicles

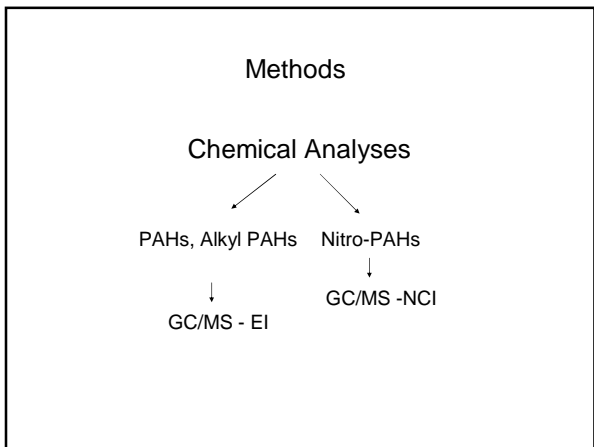
Vehicle/Engine	Engine Displacement (L)	Control Devices	Test Cycle	Fuels Tested
2000 Freightliner C15 Caterpillar	15	-	UDDS	CARB Diesel, Soy, Animal, and Renewable @ 20%, 50% and 100%
2008 Freightliner Mercedes Benz MBE 4000	12.8	DOC, DPF, EGR	UDDS	CARB Diesel, Soy, Animal, and Renewable @ 20%, 50% and 100%

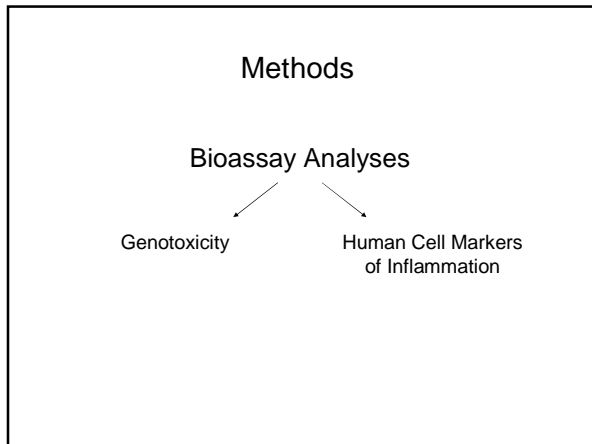
Methods

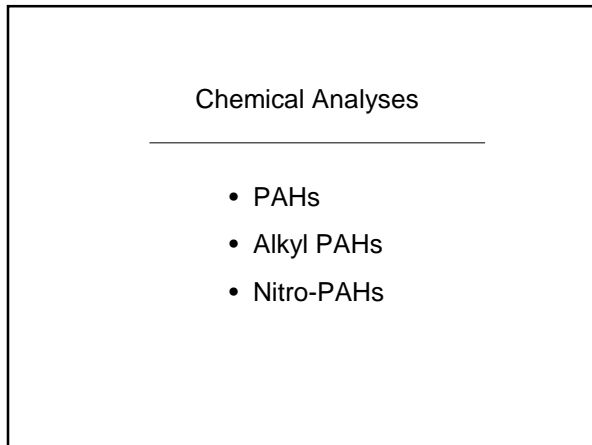








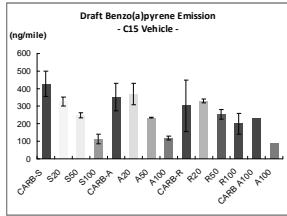




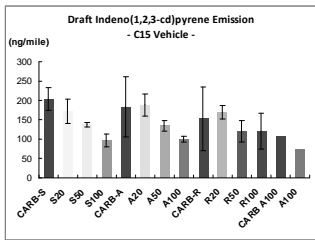
Compounds Analyzed

PAHs	Alkyl PAHs	Nitro-PAHs
Naphthalene	2-Methylnaphthalene	1N-naphthalene
Acenaphthylene	1-Methylnaphthalene	2N-naphthalene
Acenaphthene	2,6-Dimethylnaphthalene coelute	5N-acenaphthene
Fluorene	1,6-Dimethylnaphthalene	2N-fluorene
Phenanthrene	2,3,5-Trimethylnaphthalene coelute	9N-anthracene
Anthracene	3-Methylphenanthrene	3N-phenanthrene
Fluoranthene	2-Methylphenanthrene	2N-phenanthrene
Pyrene	9-Methylphenanthrene	3N-fluoranthene
Benzo(a)anthracene	1-Methylphenanthrene	1N-pyrene
Chrysene+triphenylene	2-Methylanthracene	7N-BaA
Benzo(b,h)fluoranthenes coelute	2-Methylfluoranthenes	6N-chrysene
Benzo(a)pyrene	1-Methyl & 3-Methylfluoranthenes	6N-BaP+1N-BaP
Benzo(b)pyrene	4-Methylpyrene	
Perylene	1-Methylpyrene	
Indeno(1,2,3-cd)pyrene	7,12-Dimethylbenzo(a)anthracene	
Dibenzo(a,h)anthracene		
Benzo(g,h,i)perylene		
Dibenzo(a,j)pyrene		

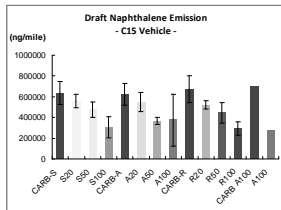
PAH Emissions
PM Associated PAHs
C15 Vehicle



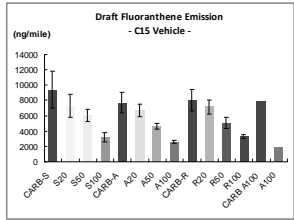
PAH Emissions
PM Associated PAHs



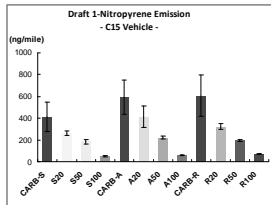
PAH Emissions
Vapor-Phase PAHs



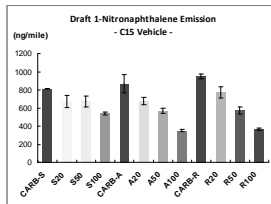
PAH Emissions Vapor-Phase PAHs



PAH Emissions Nitro-PAHs PM Associated

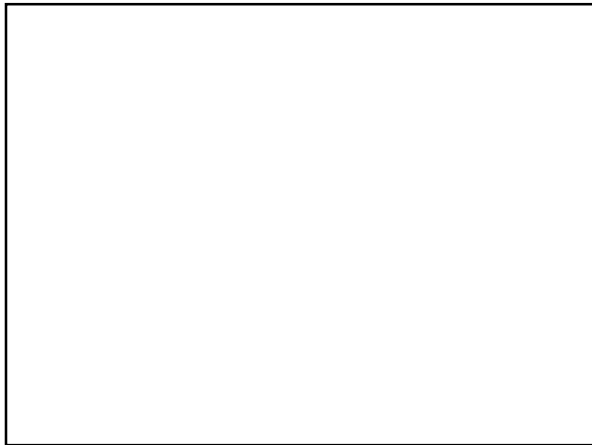


PAH Emissions Nitro-PAHs Vapor-Phase

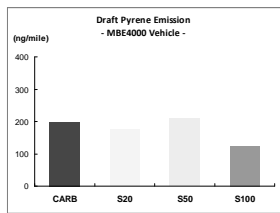


Summary PAHs
C15 Vehicle

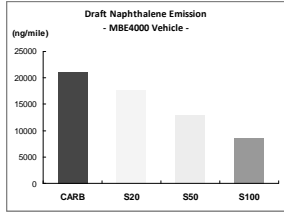
- PM and Semi-Volatile PAHs and Nitro-PAHs decreased with increasing blend level of biodiesels.



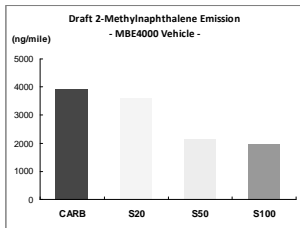
PAH Emissions
PM Associated PAHs
MBE 4000



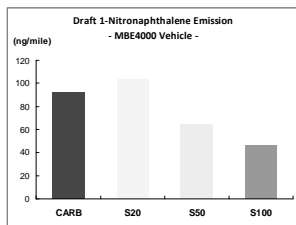
PAH Emissions
Vapor-Phase PAHs
MBE 4000



PAH Emissions
Vapor-Phase PAHs
MBE 4000



Draft PAH Emissions
Nitro-PAHs
MBE 4000



Summary PAHs
MBE 4000 Vehicle

- Low Levels of PM associated PAHs and Nitro-PAHs in CARB and Biodiesel Fuel Emissions
- Lower levels of Vapor-phase PAHs and Nitro-PAHs emissions

Reactive Carbonyls

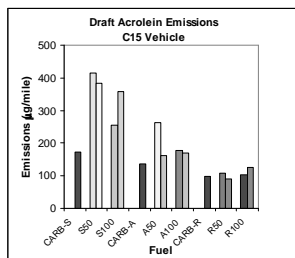
Reactive Carbonyl
Sampling

- Sampling from Dilution Tunnel to Mist Chamber
- Samples in parallel to Filtered/Charcoal dilution air
- Samples for single UDDS test cycle

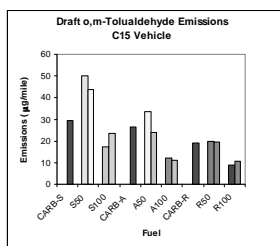
Reactive Carbonyl Analyses

- Stable carbonyls formed through reaction with bisulfite
- Carbonyls liberated from bisulfite
- Free carbonyls derivatized by o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA*)
- Derivatives detected & quantitated by GC/MS - NCI

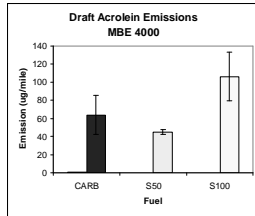
Carbonyl Emissions C15 Vehicle



Carbonyl Emissions C15 Vehicle



Carbonyl Emissions MBE 4000 Vehicle



Summary Reactive Carbonyls

- C15 Vehicle S50, S100 and A50, A100 were higher in certain carbonyls such as acrolein
- C15 Vehicle Renewable diesel no change over Carb
- MBE4000 Vehicle – carbonyls lower

Genotoxicity Tests

- Microbial
eg. Ames Salmonella test
- Mammalian cell
eg. Chinese hamster ovary (CHO)
- *In vivo*
eg. Big Blue transgenic rodent

Genotoxicity Tests Two Questions

- How consistent is it to hypothesized mechanisms of action for carcinogens?
- How does it compare to animal or human carcinogenicity tests?

Salmonella Tester Strains

- TA 98
- Frameshift mutation in the HisD gene coding for histidinol dehydrogenase
- Target site: series of 8 GCGCGGC's

Salmonella Tester Strains

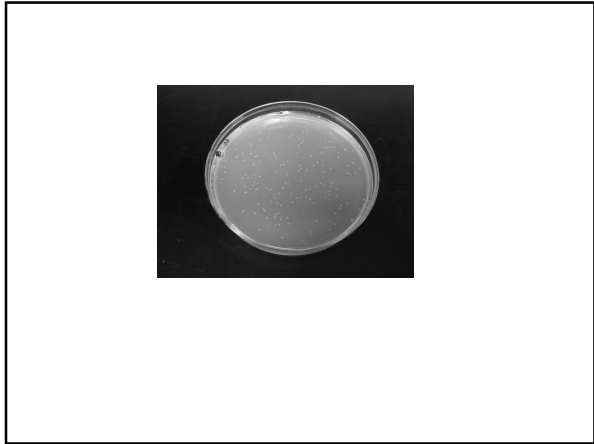
- TA 100
- Base-pair mutation in the His G gene coding for His biosynthesis
- Target site: GGG (proline) His dependent

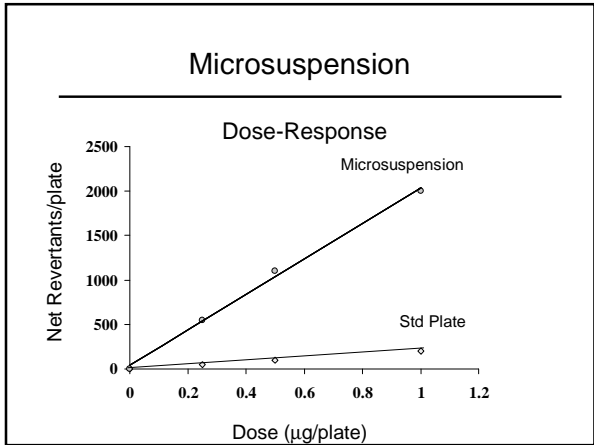
Salmonella/microsome Test

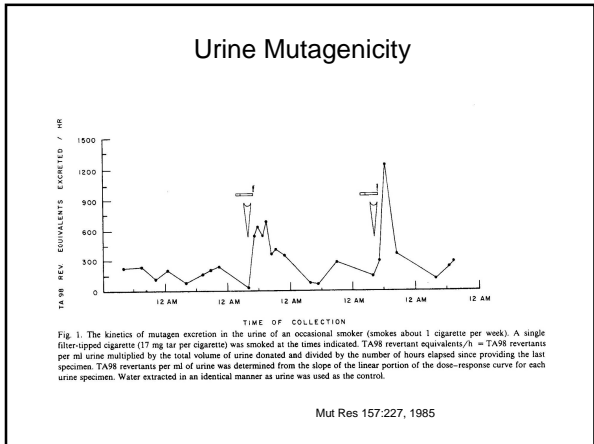
- A feature of the Test:
- Metabolic enzymes can be added to detect activation

Salmonella/microsome Test

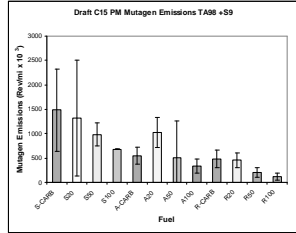
- Metabolic enzymes needed for activation of certain compounds – eg. PAHs
- Enzymes from various tissues can be used – e.g. Lung, liver



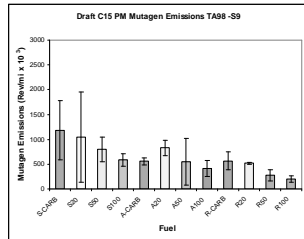




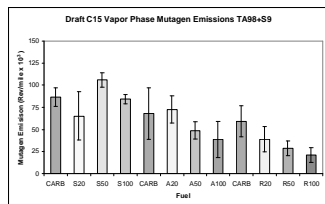
Mutagen Emissions TA98 (+S9)
C15 Vehicle PM



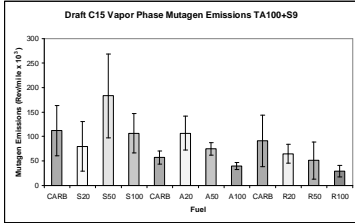
Mutagen Emissions TA98 (-S9)
C15 Vehicle PM



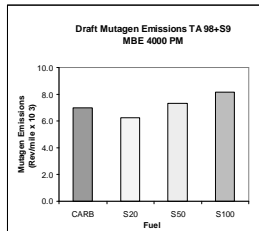
Mutagen Emissions TA98 (+S9)
C15 Vehicle VP



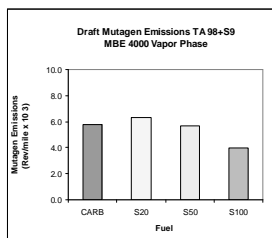
Mutagen Emissions TA100 (+S9)
C15 Vehicle VP



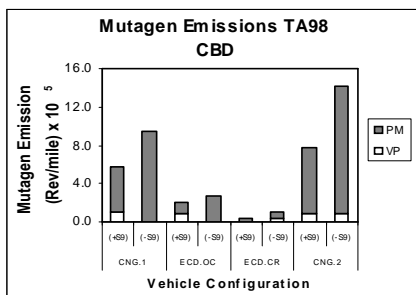
Mutagen Emissions
MBE 4000 Vehicle PM



Mutagen Emissions
MBE 4000 Vehicle VP



Bus Emissions Compressed Natural Gas



ES&T 39:7638, 2005

Summary

- For C15 Vehicle: Generally decrease in Mutagen emissions with blend level
- For C15 PM Samples TA98 (+ or – S9) more sensitive than TA100 for all fuels
- Vapor Phase samples lower mutagen emissions than PM TA100 slightly more sensitive
- MBE Mutagen Emissions considerably lower than C15

Summary

- Chemical and Biological tests were overall very consistent with each other regarding emission results for the fuels tested

Acknowledgments

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