

# **Biodiesel and Renewable Diesel Research Study**

**December 5, 2007**

California Environmental Protection Agency

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**Air Resources Board**

# Introductions

# Agenda

- Introduction
- Summary of previous workgroup discussions
  - Fuels
    - storage, blending, biodiesel and renewable diesel
  - Engine selection
- Engine test matrix-CECERT
  - On-road vehicle test matrix-MTA
    - Detailed description of unregulated emissions tests
- Test schedule
  - Others
- NOx mitigation
  - Selection of NOx mitigation strategies
- Presentation by others
- Open discussion

## Background

- Executive Order S-1-07 Low Carbon Fuel Standard (LCFS)
  - Reduce at least 10 percent of the carbon intensity of California's transportation fuels by 2020.
  - Early action item with a regulation to be adopted and implemented by 2010.
- Executive Order S-06-06, establishing targets for the use and production of biofuels and biopower
  - Includes biodiesel and ethanol.
  - California shall produce a minimum of 20 percent of its biofuels within California by 2010, 40 percent by 2020, and 75 percent by 2050.

- Low Carbon Fuels Standard
  - Biofuels Specifications adopted by the first quarter of 2009
  - Biodiesel and renewable diesel research study is needed

# Biodiesel and Renewable Diesel Research Study

- Biodiesel and renewable diesel emissions evaluation
- NOx formation and mitigation evaluation
- Multi-Media evaluation

# Funded Research Update

- Biodiesel and Renewable Diesel Research Study
  - Biodiesel and renewable diesel characterization and NOx mitigation study-\$1,689,000
  - Biodiesel and renewable diesel multimedia study-\$400,000
  - Total cost **\$2,189,000**
- Other contributors
  - South Coast Air Quality Management District-\$50,000
  - National Biodiesel Board-\$50,000
  - WSPA will provide CARB diesel
  - Innerstate Oil will provide transportation and short term storage of fuels
  - Tentative agreement on renewable diesel
  - Discussions on-going with other contributors

# Duration of Contracts and Grants

- Initial biodiesel characterization study: 6/06-6/08
- Biodiesel and renewable diesel characterization and NOx mitigation study: 6/07-6/09
- Biodiesel and renewable diesel multimedia: 6/07-6/09



# **Biodiesel and Renewable Diesel Emissions Characterization and NOx Mitigation Research**

“Assessment of the Emissions from the Use of Biodiesel as a Motor Vehicle Fuel in California- Biodiesel Characterization and NOx Formation and Mitigation Study”

Principal Investigators: Thomas D. Durbin (UCR) and J. Wayne Miller (UCR)

University California Riverside-CE-CERT

University California Davis

# Scope of Work

## Task 1: Biodiesel and Renewable Diesel Emissions Evaluation Study

- Evaluate emissions and health effects
- Evaluate NOx impact

## Task 2: NOx Formation and Mitigation Study

- Investigate the mechanism of NOx formation and evaluate possible NOx mitigation options
  - Changes in fuel specifications-match blending
  - Refinery process
  - Additives
  - **Engine recalibration**

# Summary of previous workgroup discussions

# Fuel Storage Update

- Long term storage
  - Difficulty in finding temperature controlled storage facility
  - Options:
    - Possibility of a non-temperature controlled cinder block storage facility
    - Also looking at non-temperature controlled storage facility on the coast where there is smaller temperature swings

# Fuel Blending

- No updates-still need to resolve how, when, and where to do fuel blending

# Biodiesel Feedstocks and Fuels Update

- Original proposal was to avoid additives
  - May need to consider anti-oxidants and anti-microbial
  - Which anti-oxidants and anti-microbial?

# Fuel Specification Analysis

- CARB diesel fuel-D975
- Renewable diesel fuel and blends-D975
- Biodiesel feedstocks-D6751
- Biodiesel blends
  - D975
  - D6751
- All analyses conducted in triplicate

## Storage Stability Criteria Update

- Conduct quarterly stability tests for biodiesel fuels and biannual stability tests for CARB and renewable diesel
  - EN14112 Rancimat 6 hrs
  - D664 Acid number 0.5
  - D2274 Gums ?
  - D3703 Peroxide ?



# CARB Diesel Update

- No update

## Renewable Diesel Update

- Original proposal was to test R20 and R50
- Add additional blend level: R100

# Test Engine Update

- Engine secured for testing
  - 2006 11 L Cummins ISM purchased
- Other engines under consideration
  - 2007 14 L Detroit Diesel series 60
  - 2007 International

# Additional Parameters Update

- Lube oil-API CJ4-OL
- Engine parameters-J1939

# Toxics Testing Update

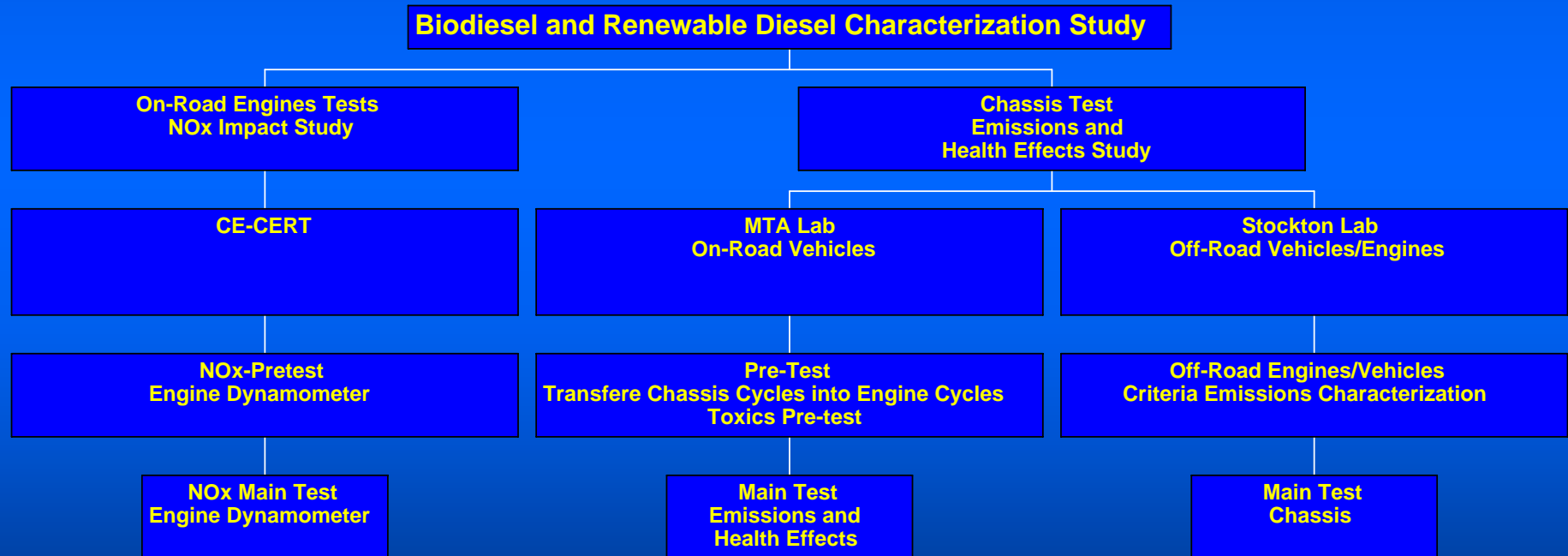
- Elements: Filter/XRF or ICP/MS
- No Chromium (VI) sampling and analysis will be conducted

# Discussion

# Test Design

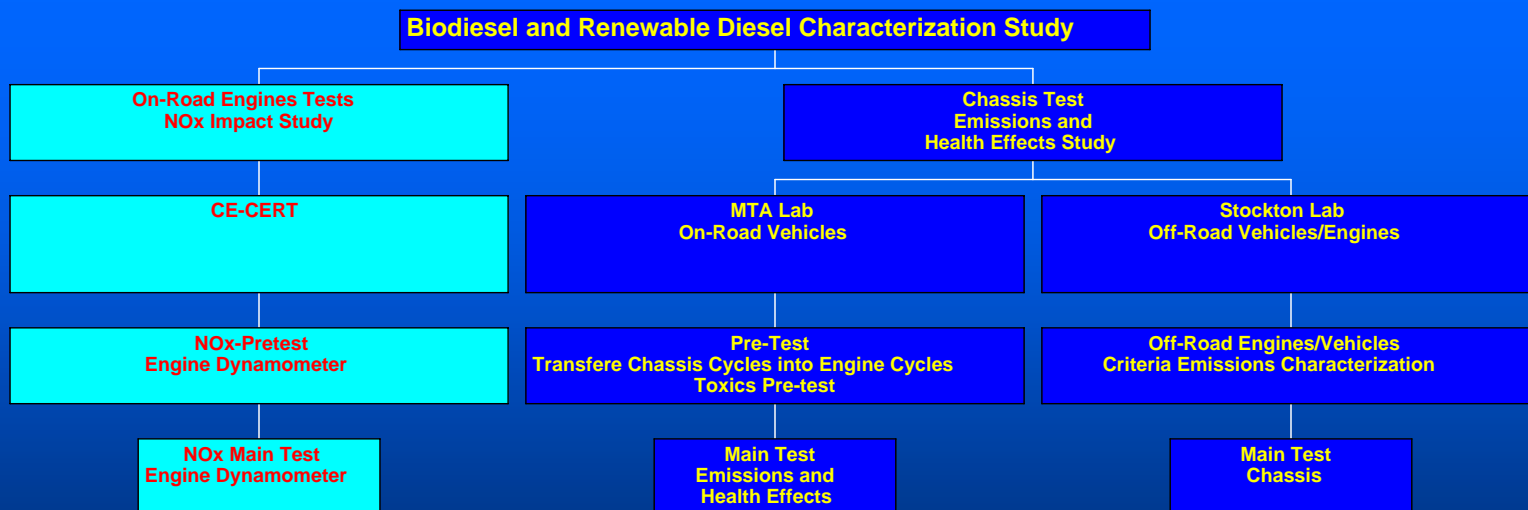
- Task 1: Biodiesel and Renewable Diesel Characterization Study
  - Unregulated emissions and health effects
  - NOx Impact
- Task 2: NOx Mitigation Study
  - Phase one
  - Phase two

# Test Design: Biodiesel and Renewable Diesel Characterization Study





# Biodiesel and Renewable Diesel NOx Impact Study

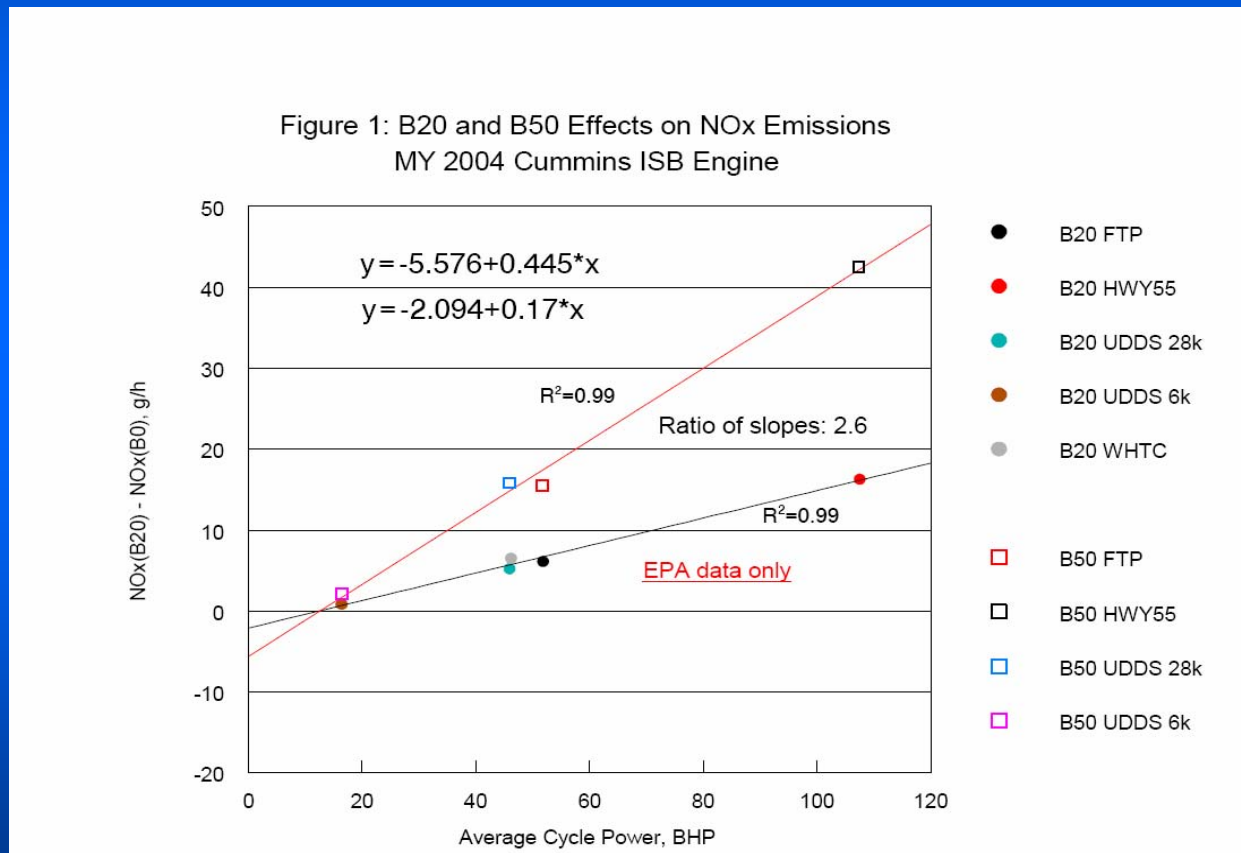


# Test Design Considerations

# Possible Biodiesel NOx Impacts

- Evaluate test cycle load effects on NOx
- Evaluate biodiesel level effects on NOx

# Biodiesel NOx Effect-Average Cycle Power



# CE-CERT NOx Pre-test

- Test cycle and replicates:
  - Minimum of 9 FTP replicates of CARB diesel on day one and 9 replicates of biodiesel on day two
  - Additional test days may be required
- Test Pattern:
  - Minimum of 9 FTP replicates of CARB diesel on day one and 9 replicates of biodiesel on day two
  - **Additional tests maybe run on UDDS and HHDT cycles**

# CE-CERT NOx Impact Study: Main Test

- Build upon USEPA and NREL studies
- Test conducted on an engine dynamometer
  - Engine dynamometer is suited to conduct the NOx impact study
  - Provides precision necessary to distinguish small differences in NOx i.e. 2% change at B20
- Engines
  - 2006 Cummins ISM and 2007 engine
- Test cycles
  - FTP, UDDS light, HHDDT cruise

# CE-CERT Main Test

- Fuels:
  - Biodiesel: two feedstocks at four blend levels: B5, B20, B50, and B100
  - Renewable diesel at three levels: R20, R50, and R100
- Optional unregulated emissions testing:
  - VOCs, 1,3-butadiene, and carbonyls
  - Limited ultra-fines

## Revised CE-CERT Main Test

- Revised test matrix designed to better measure small differences between CARB and test fuels
  - Closer pairing of CARB fuel and test fuels
  - Account for differences in morning and afternoon testing
  - Testing all three test cycles in one day



## Revised CE-CERT Main Test

- Emission differences are expected to be lower for the 2007 engine and lower blend levels especially at the 5% blend level
- Low blends and the 2007 engine may require more test replicates
- Test matrix designed to take this into consideration
  - Split out B5 testing
  - Split tests of other fuels into main and supplemental testing
  - Evaluation of main test results will determine if the supplemental tests need to be conducted

## Emissions Characterization

Chemical species	Sampling method	Sampling schedule	Vehicle test cycle
Nitrogen Oxides	Direct Chemilumescence (CLM)	All tests	UDDS, FTP, ARB Hwy
NO:NO <sub>2</sub>	Direct Dual CLM	All tests	UDDS, FTP, ARB Hwy
Total hydrocarbons	Direct/Tedlar Bag FID	All tests	UDDS, FTP, ARB Hwy
Carbon monoxide	Direct/Tedlar Bags NDIR	All tests	UDDS, FTP, ARB Hwy
Carbon Dioxide	Direct NDIR	All tests	UDDS, FTP, ARB Hwy
Particulate matter	Filters	All tests	UDDS, FTP, ARB Hwy
Ultra-fines	Direct	TBD	UDDS, FTP, ARB Hwy

# CE-CERT Main Test (Revised)

- Test pattern for both biodiesel feedstocks and engines

Main program

Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8		Day 9		
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	
CARB	A	B20	A	B50	A	CARB	A	B100	A	B20	A	CARB	A	B50	A	B100	A	
	B		B		B		B		B		B		B		B		B	B
	C		C		C		C		C		C		C		C		C	C
B20	A	B50	A	CARB	A	B100	A	B20	A	CARB	A	B50	A	B100	A	CARB	A	
	B		B		B		B		B		B		B		B		B	B
	C		C		C		C		C		C		C		C		C	C

Supplemental

Day 1		Day 2		Day 3		Day 4		B5 Day 1		Day 2	
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	A	B20	A	B50	A	B100	A	CARB	C	B20	C
	B		B		B		B		C		C
	C		C		C		C		C		C
B20	A	B50	A	B100	A	CARB	A	B5	C	CARB	C
	B		B		B		B		C		C
	C		C		C		C		C		C

# CE-CERT Main Test (Revised)

Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8		Day 9		
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	
CARB	A	R20	A	R50	A	CARB	A	R100	A	R20	A	CARB	A	R50	A	R100	A	
	B		B		B		B		B		B		B		B		B	B
	C		C		C		C		C		C		C		C		C	C
R20	A	R50	A	CARB	A	R100	A	R20	A	CARB	A	R50	A	R100	A	CARB	A	
	B		B		B		B		B		B		B		B		B	B
	C		C		C		C		C		C		C		C		C	C

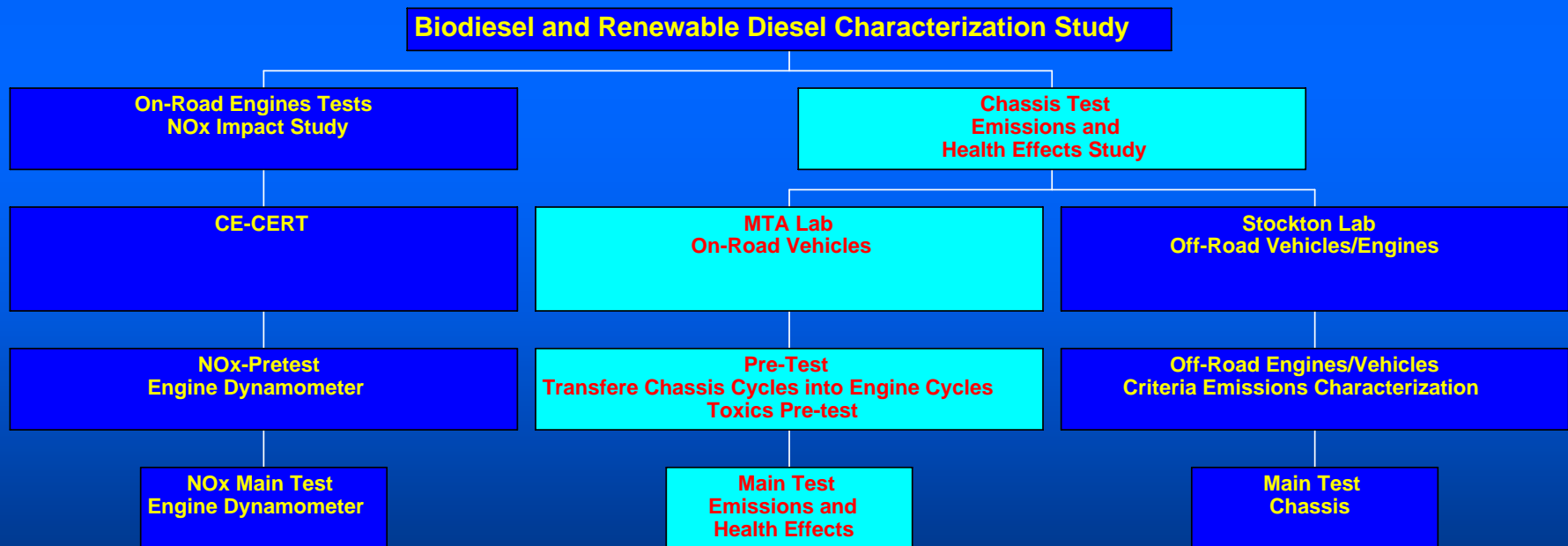
Day 1		Day 2		Day 3		Day 4	
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
CARB	A	R20	A	R50	A	R100	A
	B		B		B		B
	C		C		C		C
R20	A	R50	A	R100	A	CARB	A
	B		B		B		B
	C		C		C		C

[...]

- No testing on R5
- Renewable diesel tested only on 2006 Cummins ISM engine

# Discussion

# On-Road Biodiesel and Renewable Diesel Characterization Study Conducted at ARB's Heavy Duty Dynamometer Facility's (MTA) Chassis Dynamometer Test Laboratory in Los Angeles



# On-Road Biodiesel and Renewable Diesel Characterization Study

- Objective:
  - Test on-road vehicles
  - Emissions and health effects characterization
    - In-depth toxics characterization
    - Greenhouse gas emissions
    - Ultrafines and other species
- Conducted at MTA

## Linking Engine and Chassis Dynamometer Emission Tests Results

- Test an engine on a chassis dynamometer and then test the same engine on a engine dynamometer using the same test cycle
- Two of the test cycles will be used on both engine and chassis tests



## **Update: Un-regulated On-Road Characterization Study - Emissions Characterization**

- Eliminate 5% blend level fuels from test matrix
  - Variability much greater in chassis testing making it difficult to discern differences at the 5% blend level

## Emissions Characterization

Chemical species	Sampling method	Sampling schedule	Vehicle test cycle
Nitrogen Oxides	Direct Chemilumescence (CLM)	All tests	UDDS, ARB Hwy
NO:NO <sub>2</sub>	Direct Dual CLM	All tests	UDDS, ARB Hwy
Total hydrocarbons	Direct/Tedlar Bag FID	All tests	UDDS, ARB Hwy
Carbon monoxide	Direct/Tedlar Bags NDIR	All tests	UDDS, ARB Hwy
Carbon Dioxide	Direct NDIR	All tests	UDDS, ARB Hwy
Particulate matter	Filters	All tests	UDDS, ARB Hwy
Ultra-fines	Direct	All tests	UDDS, ARB Hwy

## Emissions Characterization

Chemical species	Sampling method/Analytical method	Sampling schedule	Vehicle test cycle
Carbonyls	DNPH coated cartridges HPLC/LCMS	General	UDDS, ARB Hwy
VOCs	Tedlar Bags GC/FID	General	UDDS, ARB Hwy
1,3-butadiene	Tedlar Bags GC/FID	in-depth	UDDS
Nitrous Oxide	Tedlar Bags/FTIR	in-depth	UDDS
EC/OC	Quartz filters Thermo-optical analyzer	in-depth	UDDS
Ions	Teflon filters Ion chromatography	in-depth	UDDS
Elements	Filters TBD	in-depth	UDDS
PAHs	Filters/PUF/XAD GC/MS	in-depth	UDDS
nitro-PAHs	Filters/PUF/XAD GC/NCIMS	in-depth	UDDS
Unsaturated Carbonyls	Bisulfite mist chamber GC/NCIMS	in-depth	UDDS

## Emissions Characterization

Biological Test	Sampling method	Bioassay/biological endpoints	Sampling schedule	Vehicle test cycle
Mutagenicity	Filters/PUF	TA98 +/-S9 TA100 +/-S9 TA102 (selected samples) TA104 (selected samples)	in-depth	UDDS
DNA damage	Filters	Comet assay	in-depth	UDDS
Oxidative stress and inflammation	Filters	Human lung and macrophage assays:  Inflammatory cytokines: IL-8 & TNF Prostaglandin synthase COX-2 Heme oxygenase-1 HO-1 C reactive protein	in-depth	UDDS

## In-Depth Emissions Characterization

In -depth	A	B
Vehicle 1		
TB	1	
CARB	3	0
SoyB20	3	0
SoyB50	3	0
SoyB100	3	0
TB	1	
CARB	3	0
AnB20	3	0
AnB50	3	0
AnB100	3	0
TB	1	
CARB	3	0
R20	3	0
R50	3	0
R100	3	0
TB		
Totals	39	0
Vehicle 2		
TB	1	
CARB	3	0
SoyB20	3	0
SoyB50	3	0
SoyB100	3	0
TB		
Totals	13	0

- Test only UDDS (A)
- Applies to all chemical species and biological assays except carbonyls, VOCs, and ultrafines
- Vehicle one equipped with 2006 ISM
  - Test all blend levels-CARB, 20, 50, and 100 percent
  - Test all feedstocks
- Vehicle two equipped with 2007
  - Test all blend levels
  - Test only soy feedstock

# Emissions Characterization of Carbonyls and VOCs

General	A		B	
Vehicle 1				
TB	1	1		
CARB	3	3		
SoyB20	3	3		
SoyB50	3	3		
SoyB100	3	3		
TB	1	1		
CARB	3	3		
AnB20	3	3		
AnB50	3	3		
AnB100	3	3		
TB	1	1		
CARB	3	3		
R20	3	3		
R50	3	3		
R100	3	3		
TB				
Totals	39	39		

Vehicle 2	A		B	
TB	1	1		
CARB	3	3		
SoyB20	3	3		
SoyB50	3	3		
SoyB100	3	3		
TB	1	1		
CARB	3	3		
AnB20	3	3		
AnB50	0	0		
AnB100	3	3		
TB	1	1		
Totals	24	24		

Vehicle 3	A		B	
TB	1	1		
CARB	3	3		
SoyB20	3	3		
SoyB50	0	0		
SoyB100	3	3		
TB	1	1		
CARB	3	3		
AnB20	3	3		
AnB50	0	0		
AnB100	3	3		
TB	1	1		
Totals	21	21		

Vehicle 3r	A		B	
TB	1	1		
CARB	3	3		
SoyB20	3	3		
SoyB50	0	0		
SoyB100	3	3		
TB	1	1		
CARB	3	3		
AnB20	3	3		
AnB50	0	0		
AnB100	3	3		
TB	1	1		
Totals	21	21		

- Vehicle one (2006 ISM): Test UDDS (A) and ARB Hwy (B) cycles
  - Test all blend levels and feedstocks
- Vehicle two (2007)
  - Test all blend levels
  - Test only biodiesel feedstocks
- Vehicle three with and without aftertreatment
  - Test A and B cycles
  - Test only biodiesel feedstocks
  - Test only CARB, B20, and B100

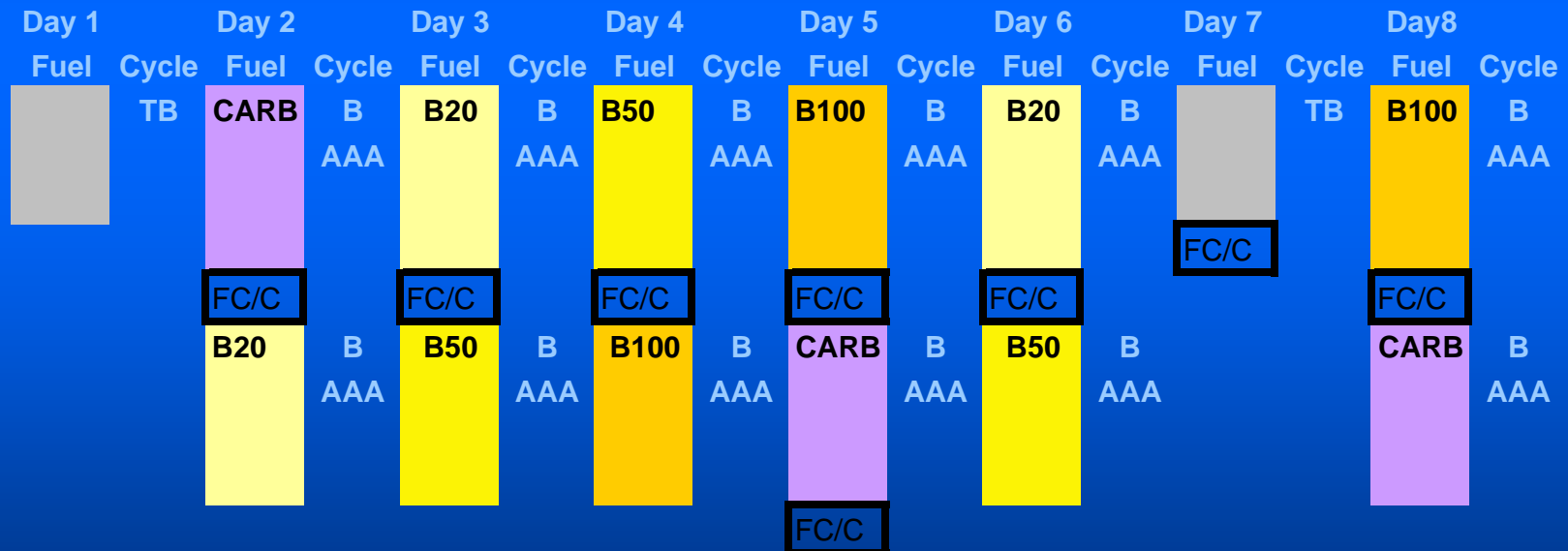
# Un-regulated On-Road Characterization Study - Emissions Characterization

- Vehicle one: 2006 Cummins ISM engine
- Test matrix soy feedstock
- Applies to second biodiesel feedstock and renewable diesel

Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8	
Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle	Fuel	Cycle
	TB	CARB	B	B20	B	B50	B	B100	B	B20	B			B100	B
			AA		AA		AA		AA		AA				AA
		FC/C		FC/C		FC/C		FC/C		FC/C		FC/C		FC/C	
		B20	B	B50	B	B100	B	CARB	B	B50	B			CARB	B
			AA		AA		AA		AA		AA				AA
								FC/C							

# Un-regulated On-Road Characterization Study - Emissions Characterization

- Vehicle 2 equipped with 2007 engine
- Soybased biodiesel
- 





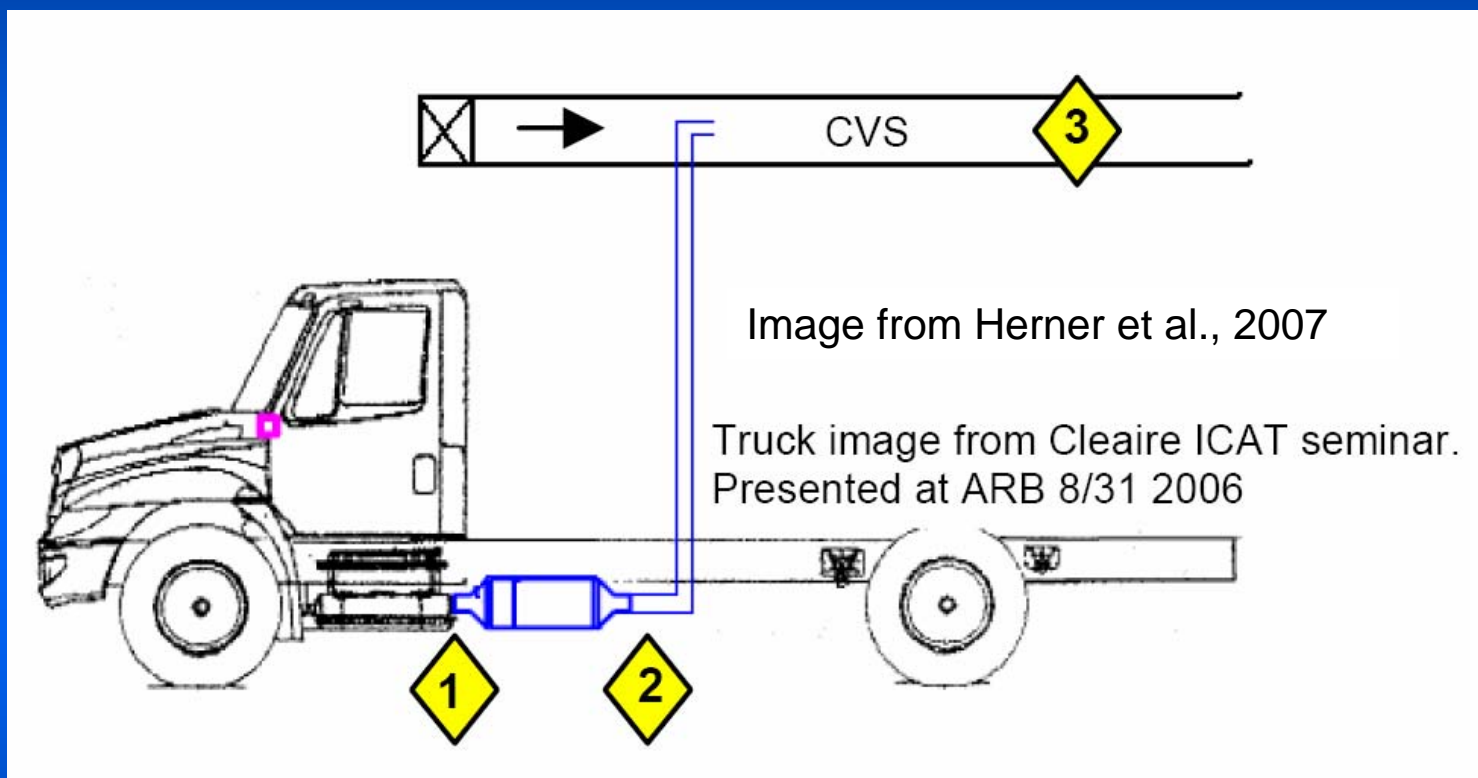
## Other Issues

- Discussed in detail at a later meeting
- QA/QC
  - QA samples
  - Dilution tunnel considerations
  - Sampling and analytical
  - Data review and tracking
- Data Reduction

## Ultrafine Particles Measurements

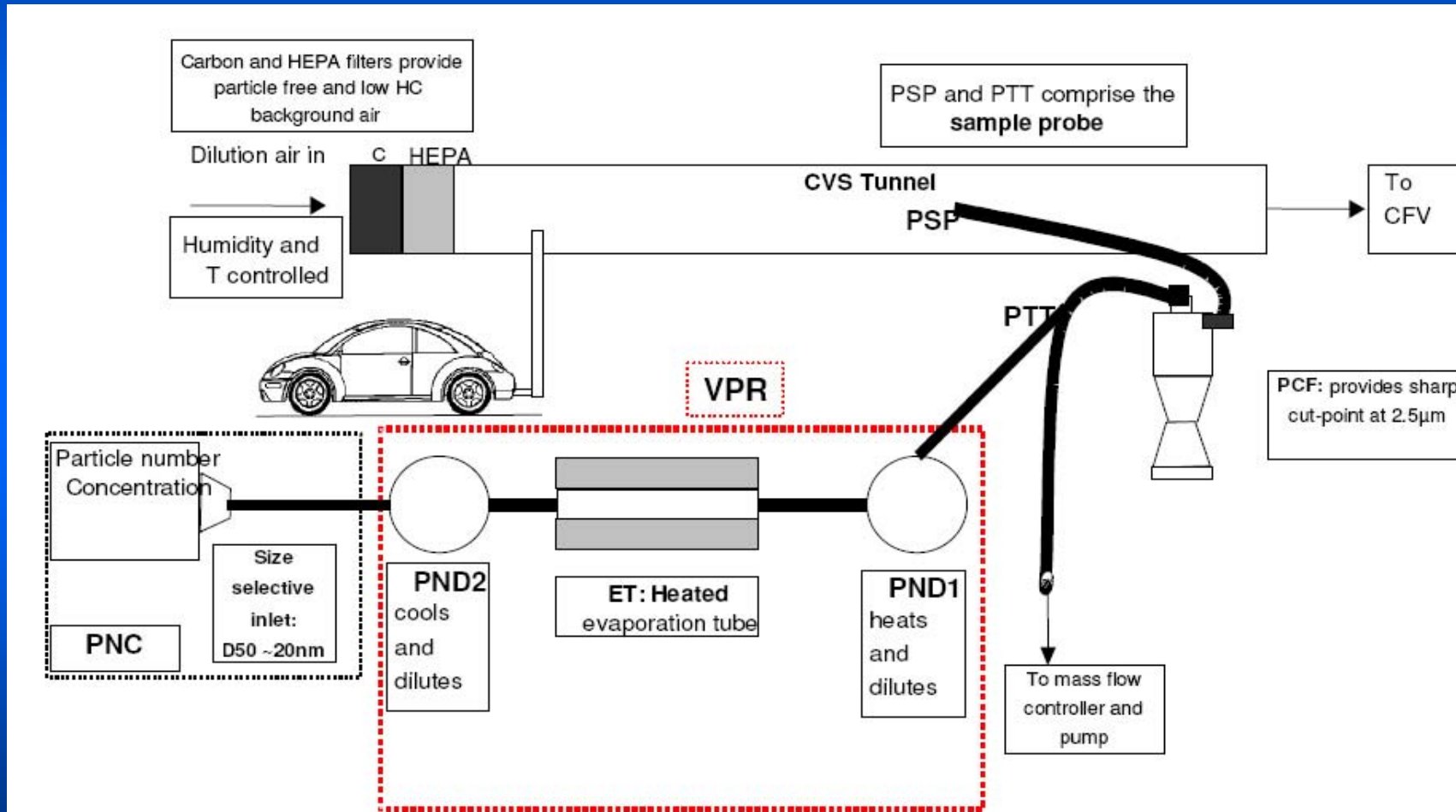
- Will be mainly conducted during vehicle testing
  - Particle Number
  - Particle Size Distribution
  - Real-time Mass
  - Surface Area
- European PMP protocol will be considered
- Sampling from CVS dilution tunnel for all three vehicles
- Pre-trap and post-trap partial flow sampling will also be conducted for vehicle 3 w/ aftertreatment configuration

## Ultrafine Particles Sampling Locations



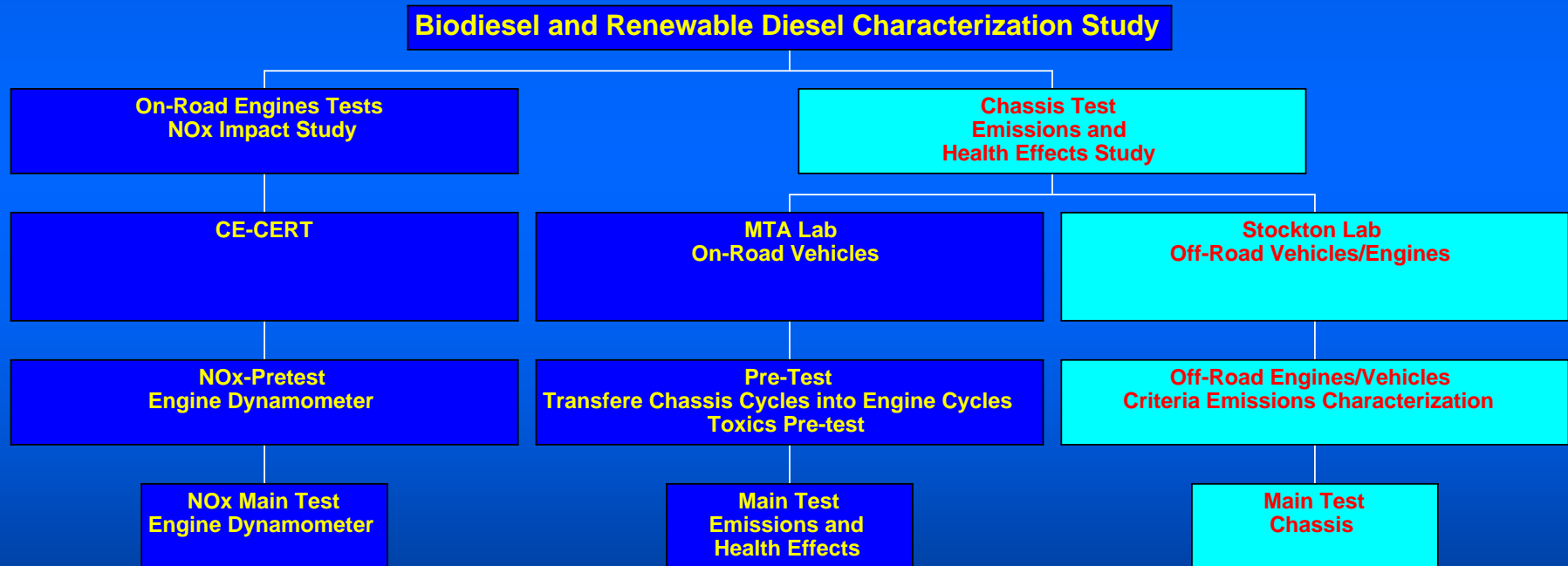
- 1: Pre-trap partial flow sampling: vehicle 3 w/ aftertreatment only
- 2: Post trap partial flow sampling: vehicle 3 w/ aftertreatment only
- 3: Full flow sampling (post trap): all vehicles

# Recommended PMP Sampling System



# Discussion

# Off-Road Characterization Study- Emissions Characterization



## Off-Road Characterization Study- Emissions Characterization

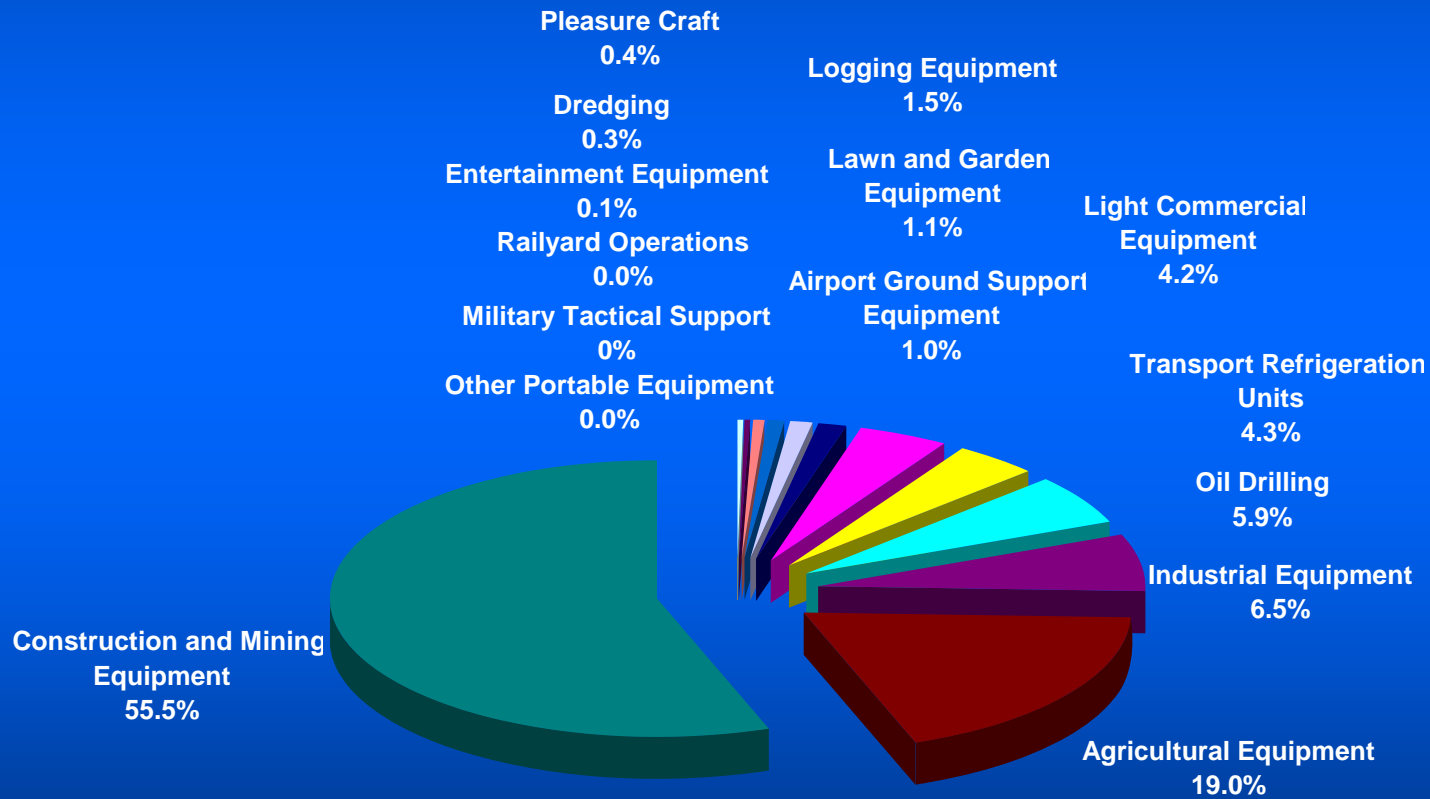
- ARB's emissions test facility in Stockton
- Propose test design
  - Two Vehicles/Engines-TBD
  - Criteria emissions only
  - Two biodiesel feedstocks and four blend levels B5, B20, B50, B100 compared to CARB diesel
  - Three renewable diesel blends R20, R50, and R100 compared to CARB diesel
  - Eight mode steady state
- Detailed test matrix presented at next meeting

## Off-Road Equipment

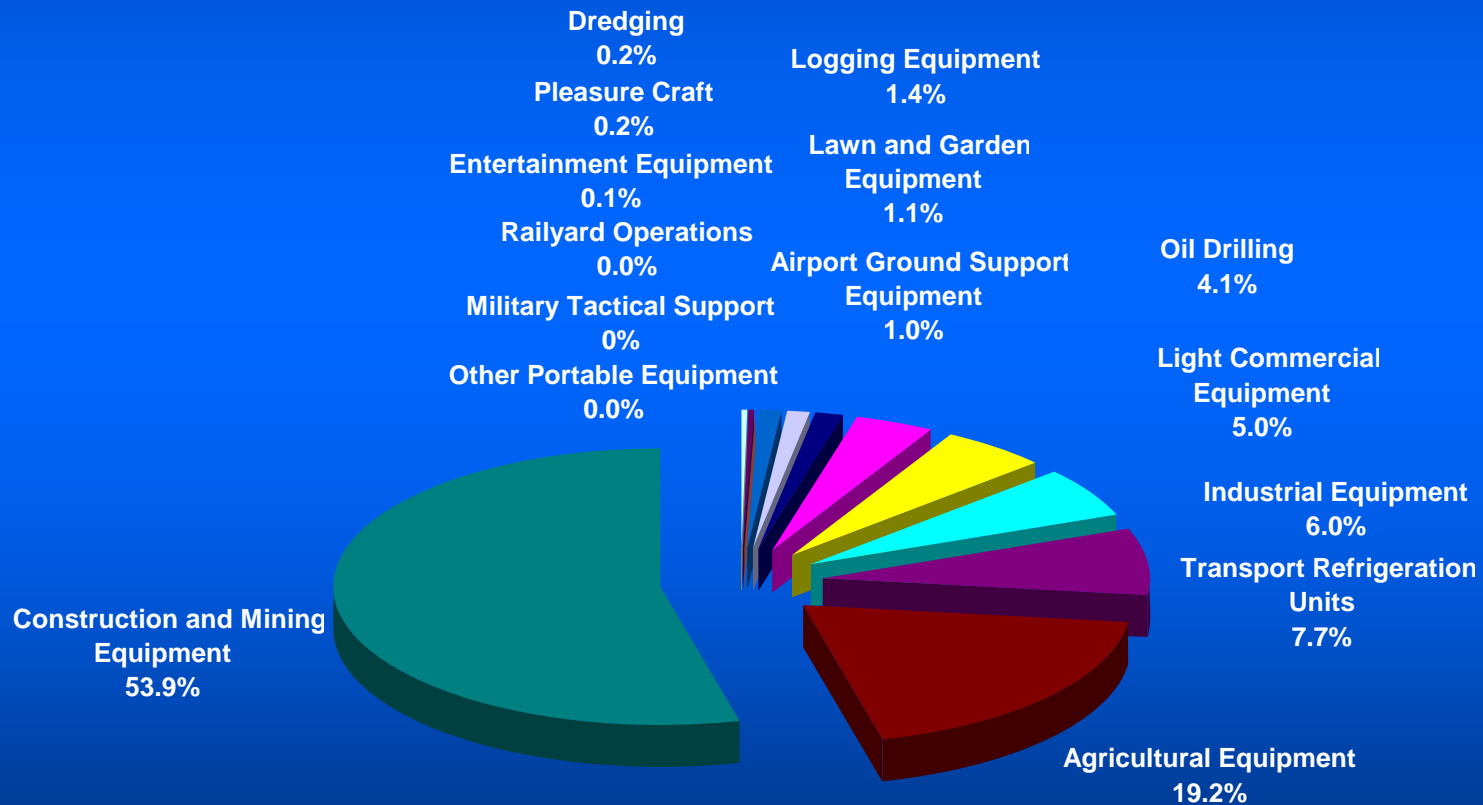
- Top Emission Contributors
  - Construction & mining equipment (~55%)
  - Agriculture equipment (~20%)
- Issues:
  - Speed limitation of Stockton Chassis Dyno: 25 mph
  - Most construction and agriculture equipment cannot run higher than 25 mph



# Off-Road Diesel NOx Emission Inventory (2007)



# Off-Road Diesel PM Emission Inventory (2007)



# Discussion

# Test Schedule-Test Plan

- Fall 2007
  - Test design
    - Biodiesel/renewable diesel advisory group, stakeholders
  - Collaborators: working with stakeholders in obtaining in-kind contribution and funding for the study
  - Test protocol

# Test Schedule-Logistics

## Fuels

- Estimated time line
  - Delivery of CARB and biodiesel fuels in December
  - Delivery of renewable diesel fuel in January-February
  - Blend fuels biodiesels in December-January
  - Blend renewable diesel fuels in January-February
  - Fuel specifications conducted by independent laboratory

# Test Schedule-Logistics

- Engines/vehicles
  - Purchased truck equipped with a 2006 Cummins ISM engine in November
  - Truck equipped with a 2007 C15 Caterpillar engine will be available in February for testing
  - Discussions on second engine is ongoing
  - Other vehicles are also being considered

# Test Schedule-Pretests

- MTA emissions characterization pretest, December 2007-January 2008
- CE-CERT pre-test-January 2008

# Test Schedule-Main Tests

- Biodiesel and renewable diesel characterization study
  - NOx impact study (CE-CERT)
    - Engine one-January-February
    - Engine two-March-April
    - Phase one NOx mitigation study Summer 2008
  - On-road vehicle characterization study (MTA)
    - Feb-May 2008
  - Stockton-off-road vehicle study
    - Start in 2008
  - NOx Mitigation Study
    - CE-CERT Phase one
    - MTA Phase two



# Discussion

# Test Design: Diesel NOx Mitigation Study

## Biodiesel and Renewable Diesel NOx Mitigation Study

Engine Dynamometer  
CE-CERT  
Phase One

Engine Dynamometer  
MTA  
Phase Two

# NOx Mitigation Study – Phase One

- Conducted at CE-CERT
- Collaborate with CRC
- Evaluate four strategies
- Selection Considerations
  - Data supporting the effectiveness of strategy
  - Feasibility to be commercially relevant
  - Compatibility with existing infrastructure

# NOx Mitigation Study – Phase One

- Additives
- Match blending properties
- Biodiesel/renewable diesel blends
- Renewable diesel
- Engine re-calibration

# Stakeholders Suggested NOx Mitigation Strategies

- Water/biodiesel/diesel emulsified fuels
- Viscon additive

# NOx Mitigation Study - Phase Two

- Conducted at MTA
- Select most successful NOx mitigation strategies
  - Confirmation engine
  - Conduct more in-depth study
    - Needs to be fleshed out
  - Limited toxics tests
- Evaluate other strategies if necessary

# Discussion

## Light-Duty Diesel Vehicle Testing

- To be collaborated with Research Division Light-Duty Test Program
- Two vehicles
  - One passenger car
  - One pick-up truck/SUV/minivan
- Plan to start test in August 2008



## Other Research

- Durability Study
- Will be discussed in detail in upcoming meetings

# In Kind Contributions

- Fuels
  - US EPA diesel fuel
  - Biodiesel and biodiesel blends
  - Storage (long term)
  - Fuel analysis
- Engines
- Vehicles
- Other

# Future Discussion Topics

- UL certification of biodiesel pumps
- Guidelines for converting a diesel engine to biodiesel

# **Biodiesel and Renewable Diesel Advisory Group**

- Next meeting in January/February