APBF-DEC Lubricants Project

Status Report and Preliminary Findings

Presented by:

Lisa Lanning, *ATL*

John Orban, *Battelle*

Hsing-Chuan Tsai, *Battelle*

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APBF-DEC, JCAP, CAFE Joint Meeting
Washington, DC

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Participating Companies/ Organizations

Government

- DOE
- NREL
- ORNL
- EPA
- CARB/SCAQMD

Automobile

- Ford
- GM
- DaimlerChrysler
- Toyota

Technology

- Battelle

Engines

- EMA
- Caterpillar
- Detroit Diesel
- Cummins
- John Deere
- Mack Trucks
- International Truck & Engine

Emission Control

• MECA • Johnson Matthey
• Delphi • 3M • Engelhard
• Siemens • Benteler • ArvinMeritor
• Clean Diesel Tech. • Corning
• Donaldson Co. • OMG
• NGK • Rhodia
• Tenneco Automotive

Energy/Additives

• API • American Chemistry Council
• BP • Castrol • Chevron Oronite
• ChevronTexaco • Ciba • Ergon
• Ethyl • ExxonMobil • Infineum
• Lubrizol • Marathon Ashland
• Motiva • NPRA
• Pennzoil-Quaker State
• Shell Global Solutions • Valvoline

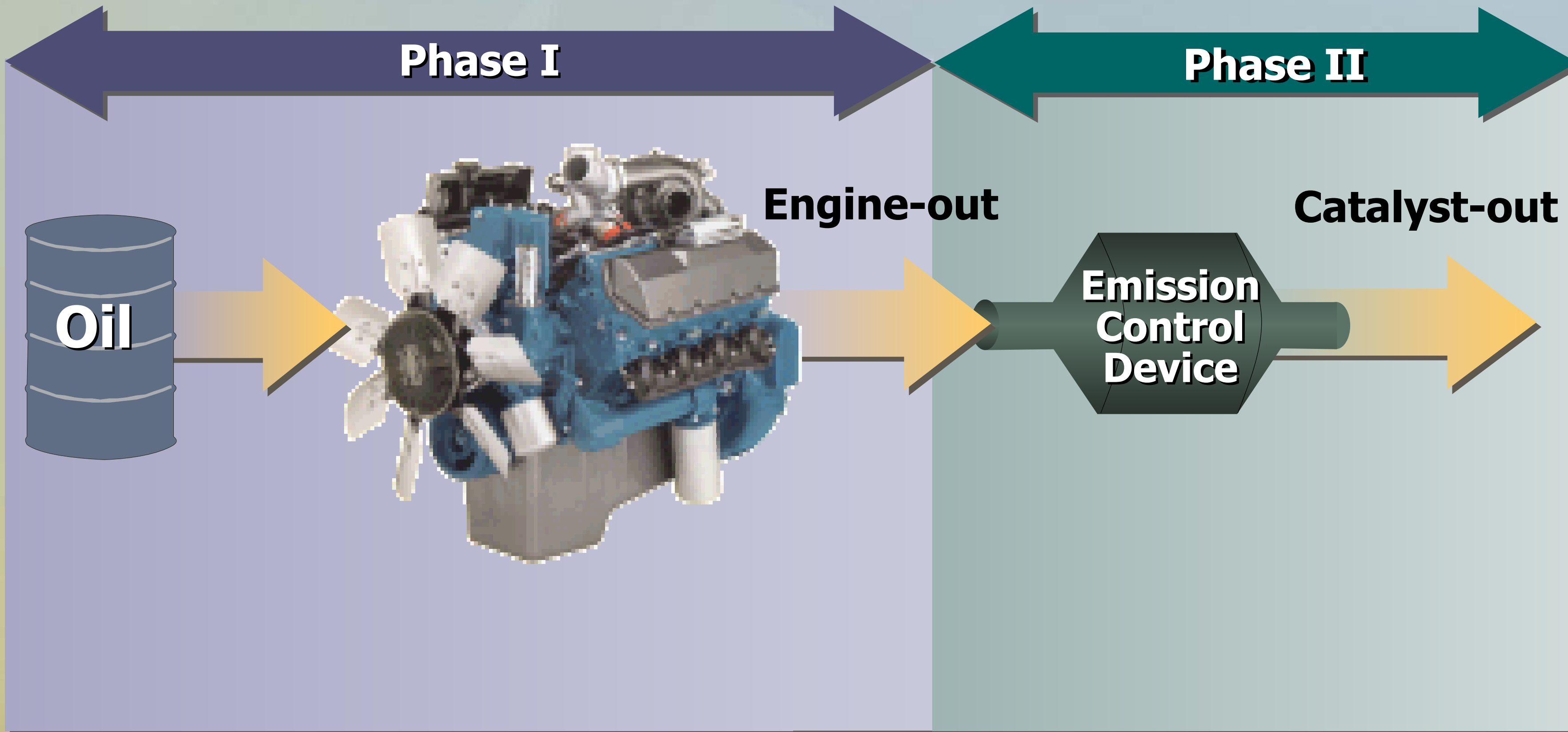
Presentation Outline

- Background and Project Objectives (Lanning)
- Experimental Design (Orban)
- Test Procedures (Lanning)
- Phase I (Part 1) Preliminary Findings (Tsai)
- Phase I (Part 2) Status Update (Orban)

Background

- 2007 HD standards and Tier 2 LD standards are "aftertreatment forcing"
- Growing concern: lube oil sulfur and ash
  - Potential to interfere with catalyst performance
    - NO_x adsorber catalyst poisoning
    - Diesel particle filter plugging
- A multi-year project was needed to quantify
  - Lubricant effects on engine-out emissions, and
  - Effects of lubricant-derived emissions on catalyst performance

Two-Phase Approach



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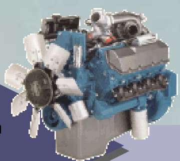
Objectives



Phase I

Determine the impact of lubricant properties and composition on engine-out/catalyst-in emissions

- Part 1: Characterize effects of lubricant properties on engine out emissions
- Part 2: Develop methods to accelerate exposures of emission control systems (ECS) to lubricant-derived emissions

Phase II

Determine if lubricant formulation impacts the performance and durability of diesel engine ECS

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Desired Outcome

- Determine which (if any) lube derived emission components are detrimental to ECS performance and durability

The results will provide:

Guidelines for lubricant formulation	Design guidelines
• Basestock selection • Additive chemistry	• Engine manufacturers • ECS suppliers

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Workgroup Participants

Project Leader: Shawn Whitacre (NREL)

- BP
- CARB
- Caterpillar
- ChevronTexaco
- Chevron Oronite
- Ciba Specialty Chemicals
- Cummins
- Shell Mobile Solutions
- Ethyl Corporation
- ExxonMobil
- Infineum
- International Truck and Engine
- John Deere
- Lubrizol
- Mack
- Marathon-Ashland Petroleum
- Motiva
- Pennzoil-Quaker State
- RohMax
- Shell Global Solutions
- Toyota
- Valvoline

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Experimental Design

John Orban, Battelle

Co-Chair, APBF-DEC Data Committee

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Phase I - Part 1
Study Questions

1. Are there significant differences in engine-out emissions that can be attributed to oil properties?
2. If so, how much of an impact is due to properties of the additive package? … base oil?
3. Which emissions species can be directly predicted from the properties of the oil and fuel? (e.g., mass balance for metals)
4. Can we identify indirect (empirical) relationships between engine-out emissions and oil properties (e.g., PM emissions versus oil ash level or sulfur content)?

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Experimental Design Criteria/Approach

Lubricant Selection

- Four base oil groups
- Additive packages represent current and future products
- Properties span practical ranges of elemental composition and ash levels

Test Matrix

- Randomize test sequence within oil groups
- Duplicate testing to evaluate repeatability
- Periodic tests with reference oil to account for testing trends
- Monitor oil consumption for mass balance analysis

Emissions Measurements

- Gases (HC, CO, CO_2, NO_x, SO_2)
- PM (TPM, SOF, SO_4, Metals, PAHs)

Lubricant Selection Base Oils

- Group I: Valero (Paulsboro)
  - 4800-5600-ppm S, 75% saturates
- Group II: Excel (Lake Charles)
  - <20-ppm S, >99% saturates
- Group III: Motiva (Port Arthur, TX)
  - <5-ppm S, >99% saturates
- Group IV: BP
  - PAO (poly-alpha olefin, synthetic)
  - 0 sulfur
  - 5% ester for additive solubility (from Uniqema)

Lubricant Selection — Additive Packages

- Five suppliers (Ciba, Chevron, Ethyl, Infineum, and Lubrizol) provided specifications on 26 candidate additive packages
- Range of constituents (in Group II base oil)

Ash	0 – 1.85%
Sulfur	0 – 6590-ppm
Calcium	0 – 4770-ppm
Zinc	0 – 1900-ppm
Phosphorus	0 – 1700-ppm
Magnesium	0 – 1700-ppm
Boron	0 – 1235-ppm

- Supplier and source of constituents not specified

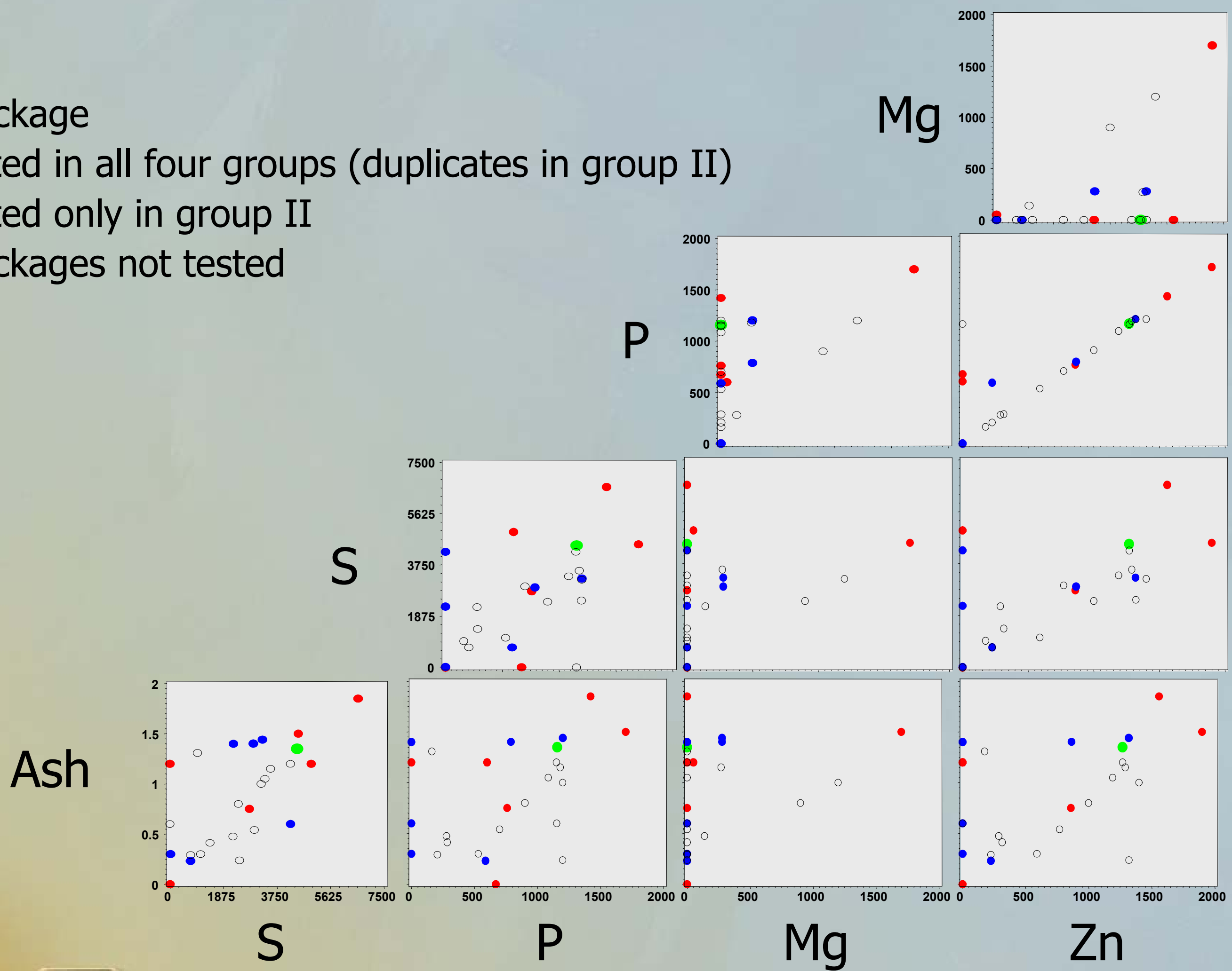
Lubricant Selection

Additive Packages
continued

- 12 additive packages selected to be statistically representative of the 26 candidates
  - Span the range of constituents and "principal components"
  - Representation from each supplier
  - All 12 tested in Group II base oil
- 6 of 12 packages selected for duplicate testing with Group II base oil and testing with Groups I, III, and IV
- One reference oil
  - Periodic testing throughout project
  - Sulfur level adequate for monitoring oil consumption using measured SO_2

Selected Additive Packages

- ● = Reference package
- ● = Packages tested in all four groups (duplicates in group II)
- ● = Packages tested only in group II
- ○ = Candidate packages not tested



Test Matrix

Initial tests to demonstrate viability

Back-to-back 4-mode tests – randomized order

Reference oil every fourth test

Periodic 40-hour aging between reference tests to evaluate…

- oil consumption
- oil aging effects

Duplicate tests

Testing Order	Demo Runs	Base Oil			
		Group 2	Group 1	Group 3	Group 4
1	bbb	rr-age-rr	rr-age-rr	rr-age-rr	rr-age-rr
2	eee	aa	aa	aa	aa
3	bbb	bb	bb	bb	bb
4	eee	cc	cc	cc	cc
5		rr	rr	rr	rr
6		dd	dd	dd	dd
7		ee	ee	ee	ee
8		ff	ff	ff	ff
9		rr-age-rr			rr-age-rr
10		gg			
11		hh			
12		ii			
13		rr			
14		jj			
15		kk			
16		ll			
17		rr-age-rr			
18		dd			
19		bb			
20		ee			
21		rr			
22		cc			
23		ff			
24		aa			
# of Tests	12	54	18	18	22

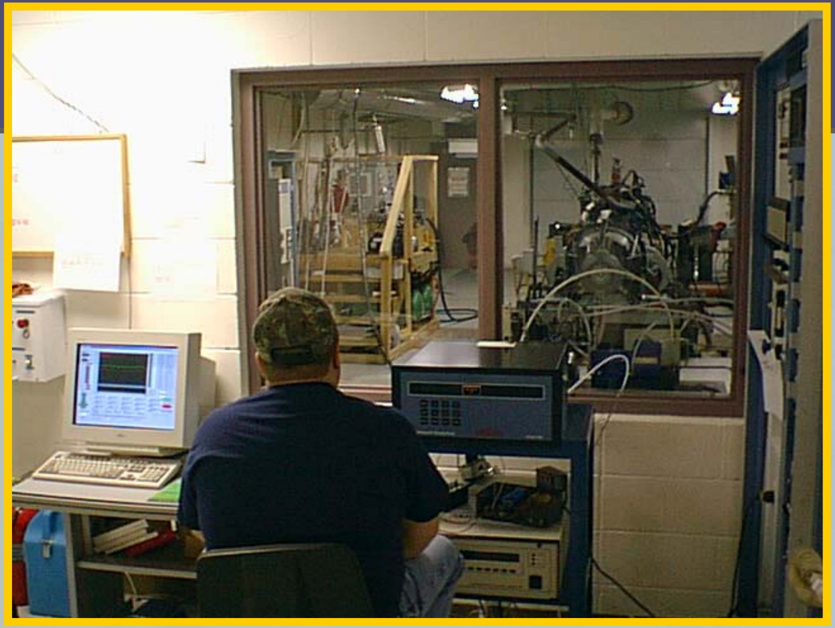
Test Procedures

Lisa Lanning, ATL

Principal Investigator

Test Laboratory – Phase I

- Subcontractor: Automotive Testing Laboratories, (East Liberty, OH)



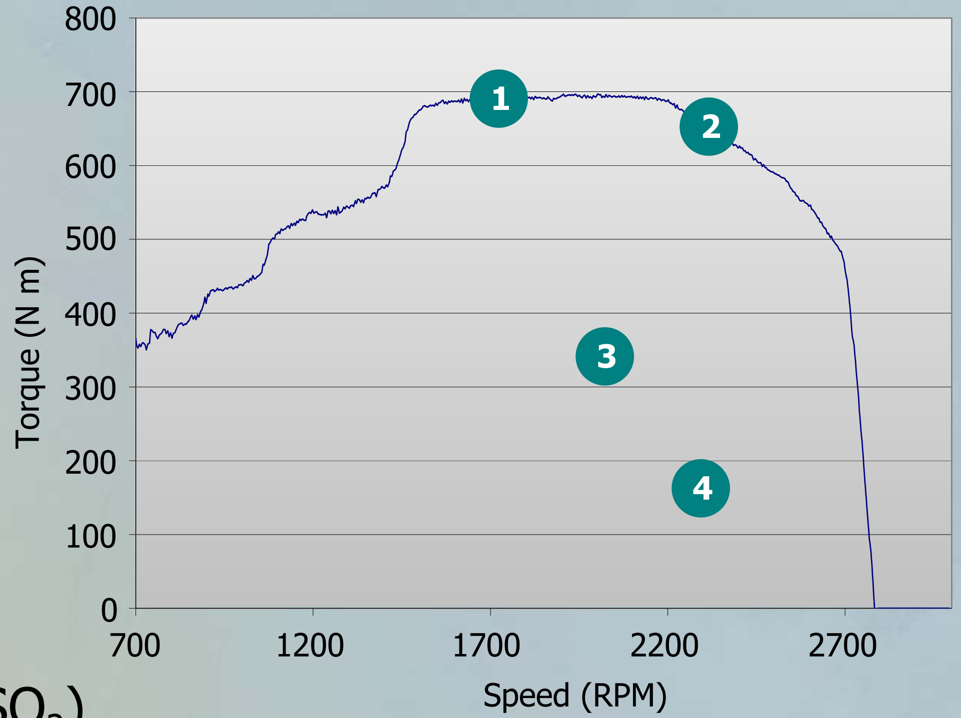
Test Engine

1999 International T444E

- 7.3L OHV V-8
- Direct injection, turbocharged w/ wastegate
- HEUI fuel system
- 215 hp at 2400 rpm
- 540 ft-lbs torque at 1500 rpm
- Exhaust gas recirculation (retrofit)
- Closed crankcase ventilation with filter
- Lube system capacity: 18 quarts

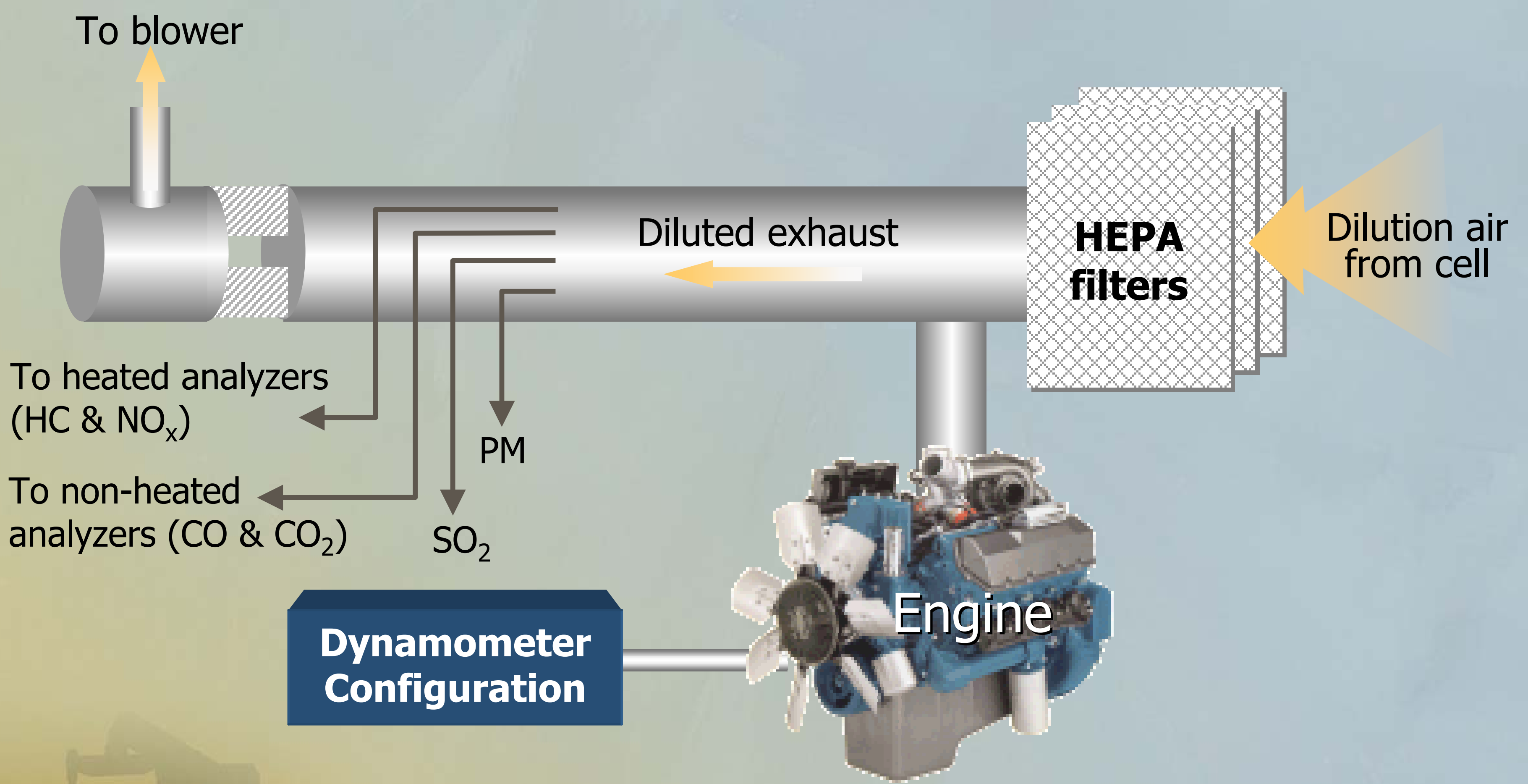
Test Modes and Emissions Measurements

- **Four Mode Steady-State (OICA)**
  - Mode 1: Rated Condition
  - Mode 2: High Torque
  - Mode 3: Road Load
  - Mode 4: Low Torque



- **Emissions Measurements**
  - Gases (HC, CO, CO_2, NO_x, SO_2)
  - PM – three sampling trains
    - TPM, SOF, SO_4
    - Metals
    - PAHs

Test Cell Layout



Particulate Matter Sample Collection

Train #1: PM mass (ATL/ORNL)

- 70 mm Pallflex 'Emfab' (glass fiber w/bonded PTFE)
- Analysis for sulfate and soluble organic fraction (ORNL)

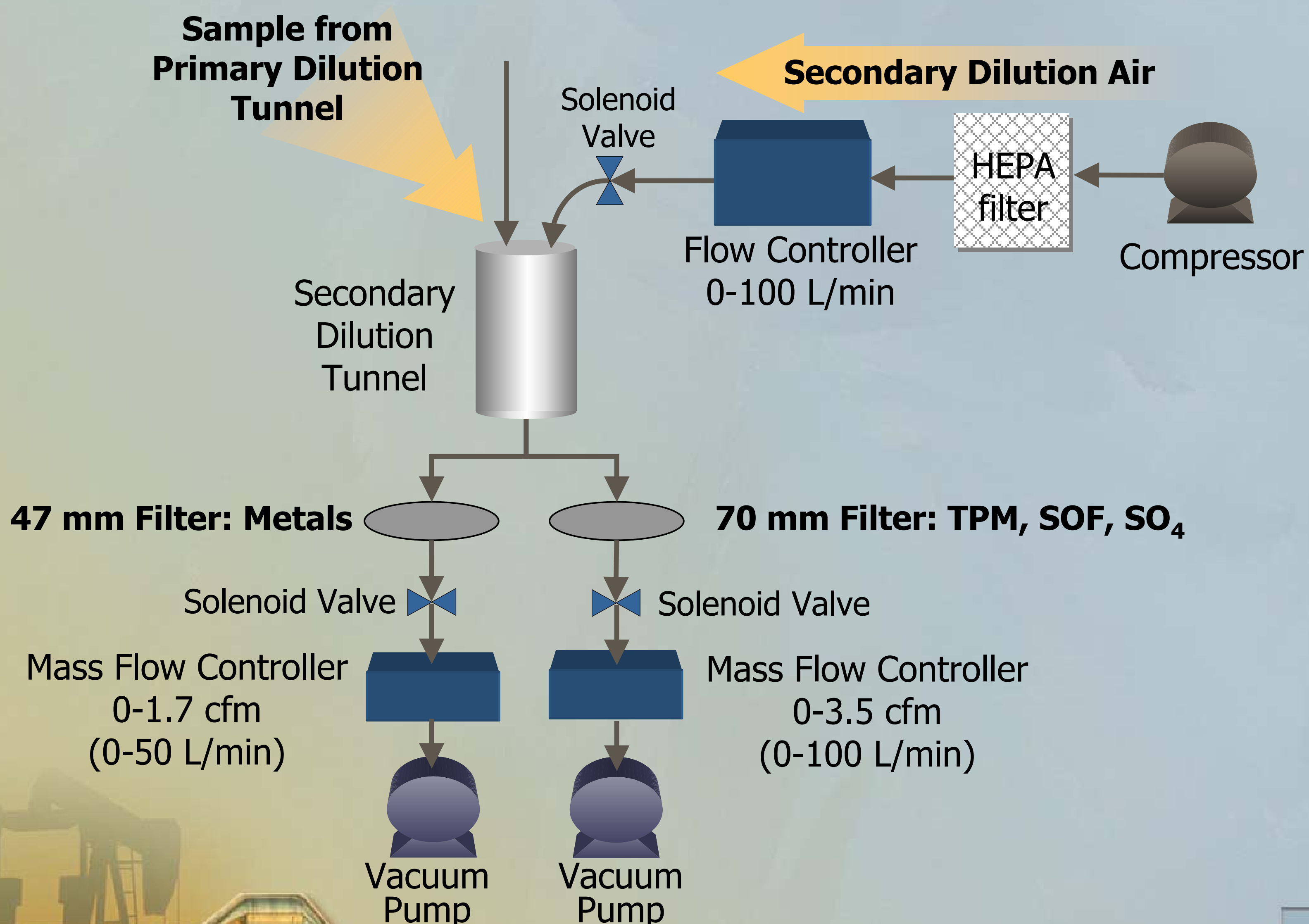
Train #2: PM metals

- 47 mm Gelman 'Teflo' (PTFE w/ PMP support)
- Determined by x-ray fluorescence (DRI)

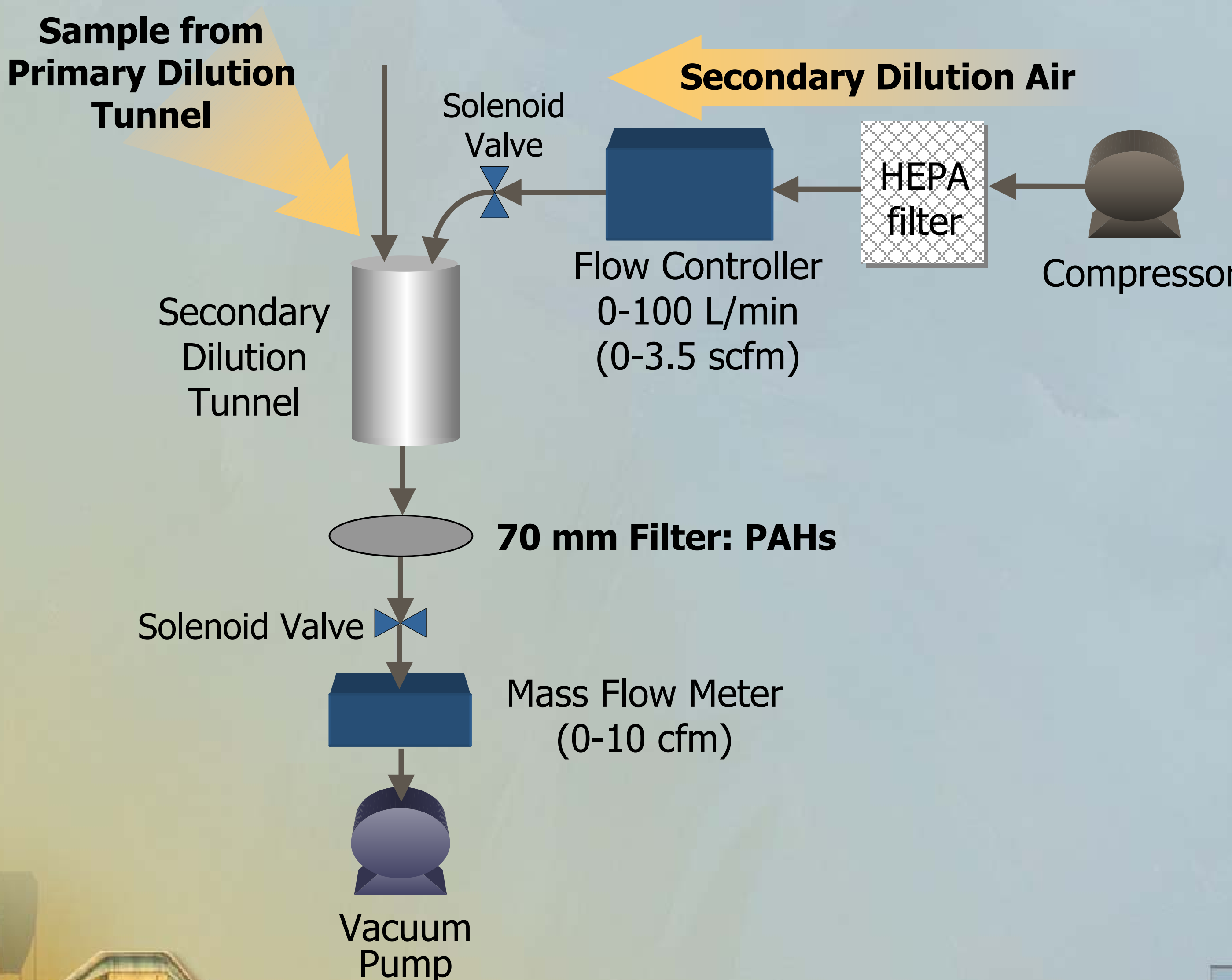
Train #3: Polycyclic Aromatic Hydrocarbons (PAH)

- 70 mm Pallflex 'Fiberfilm' (glass fiber w/bonded TFE)
- Determined by GC-MS (SwRI)

PM Train 1&2 Configuration



PM Train 3 Configuration



Filter Holders

SO_2 Analysis - Overview

- SO_2 measured via impingement in aqueous hydrogen peroxide (wet chemistry method)
  - SO_2 converted to SO_4
- Modeled after EPA methods 6, 8, 16
- Post-test quantification of SO_4 concentration using ion chromatograph yields SO_2 emission rate (exhaust flow measured)

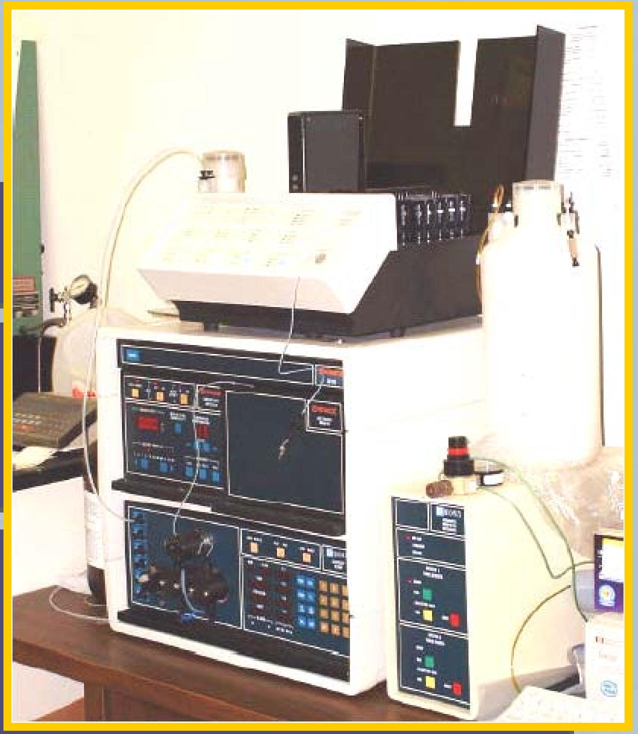
Impinging Apparatus

Sampling Parameters

- All plumbing from tunnel to impingers is heated (113°C / 235°F) – impingers in ice bath to cool vapor and facilitate reaction
- Cell-software controls impinging valves to direct exhaust to appropriate impinger set depending on Mode#
- Primary and secondary impingers used, each 25 ml: very little SO_2 reaches the secondary impinger
- Dilute exhaust is bubbled through impingers at 3.5 L/min and a 30-minute sampling period is used

IC Analysis

- Anion analysis: for SO_4^{-2}
- Large amount of sample injected to attain ppb detection
- 15-minute chromatogram, typically 2 evaluations run in overnight analysis
- 9 ppb to 950 ppb – typical impinger levels SO_4^{-2}
- Corrected for blank levels



Fluid Analysis

Oil samples collected at the time of actual emissions testing, between the two evaluations, each test day: full oil analysis performed by SwRI

Fuel samples taken from fuel supply line once every other week: analyzed for S at ATL

Other fuel analyses performed at SwRI (metals)

Phase I – Part 1
Preliminary Results

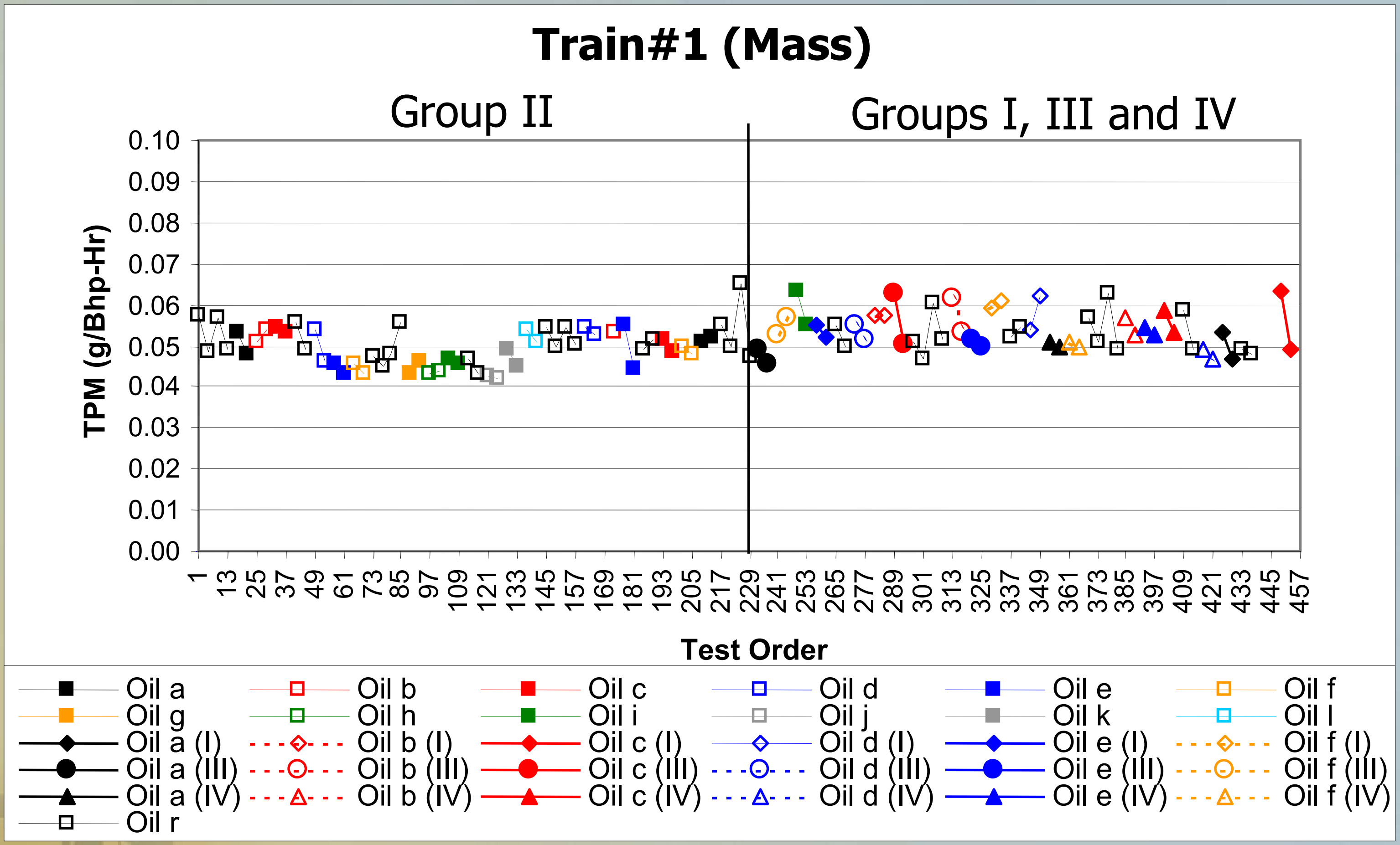
Hsing-Chuan Tsai, Battelle

Lubricants Project Statistician

Test Matrix

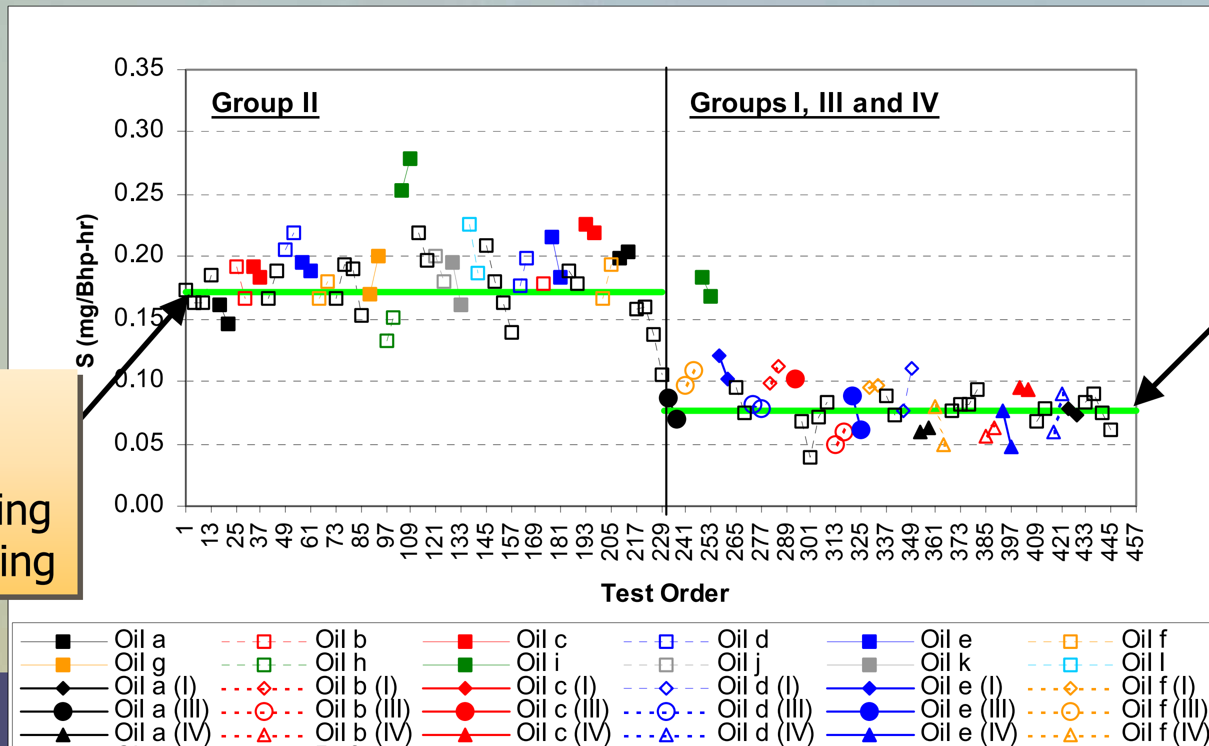
Testing Order	Demo Runs	Base Oil			
		Group 2	Group 1	Group 3	Group 4
1	bbb	rr-age-rr	rr-age-rr	rr-age-rr	rr-age-rr
2	eee	aa	aa	aa	aa
3	bbb	bb	bb	bb	bb
4	eee	cc	cc	cc	cc
5		rr	rr	rr	rr
6		dd	dd	dd	dd
7		ee	ee	ee	ee
8		ff	ff	ff	ff
9		rr-age-rr			rr-age-rr
10		gg			
11		hh			
12		ii			
13		rr			
14		jj			
15		kk			
16		ll			
17		rr-age-rr			
18		dd			
19		bb			
20		ee			
21		rr			
22		cc			
23		ff			
24		aa			
# of Tests	12	54	18	18	22

Test Data
(e.g., TPM emissions)



Adjusting for Trends

(e.g., Sulfur emissions)



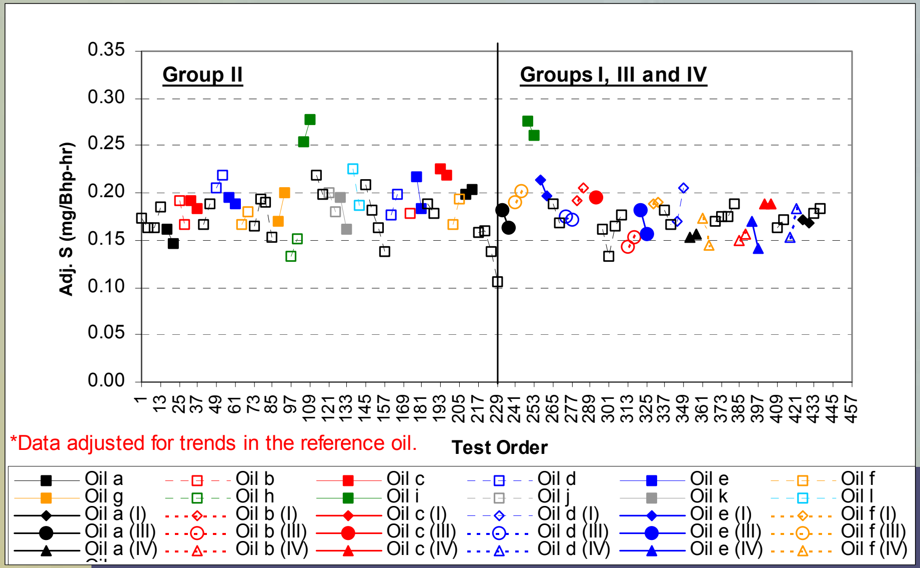
Average reference oil emission during Group II testing

Average reference oil emission after Group II testing

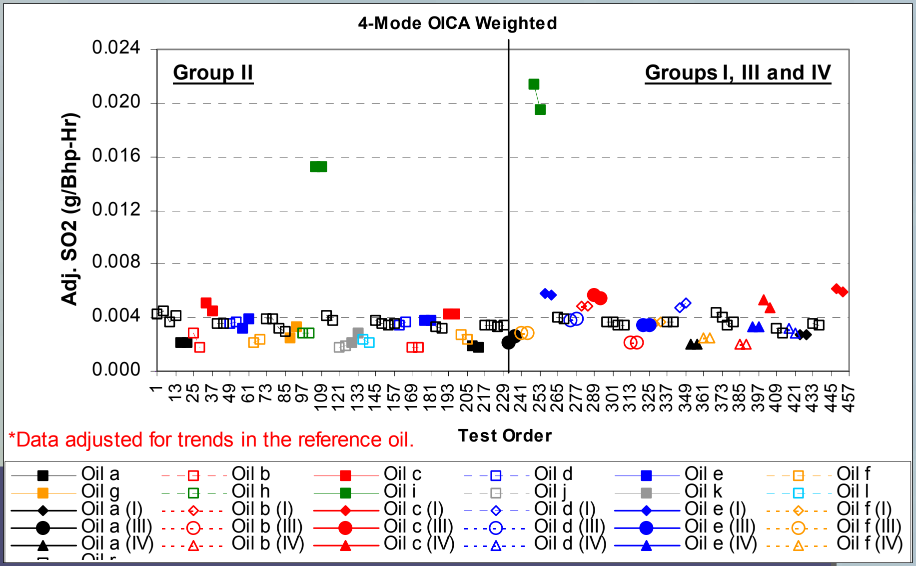
- Sulfur emissions dropped after Group II testing primarily due to fuel change (fuel sulfur 4.5-ppm => 1-ppm)

Examples of Adjusted Emissions

Adjusted Sulfur Emissions



Adjusted SO_2 Emissions



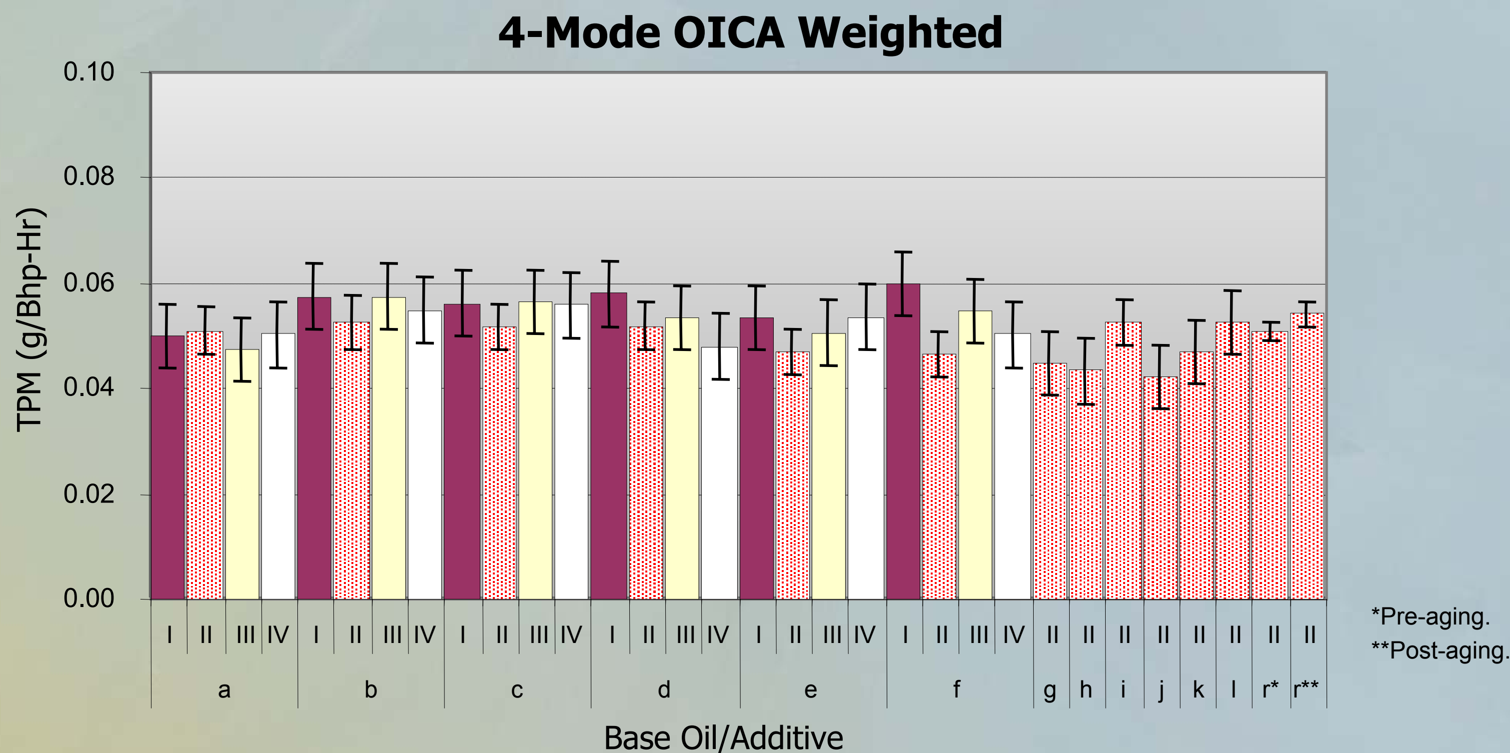
- Test data are adjusted for statistically significant trends observed in the reference oil emissions

Data Analysis Questions #1 and #2

1. Are there significant differences in engine-out emissions that can be attributed to oil properties?

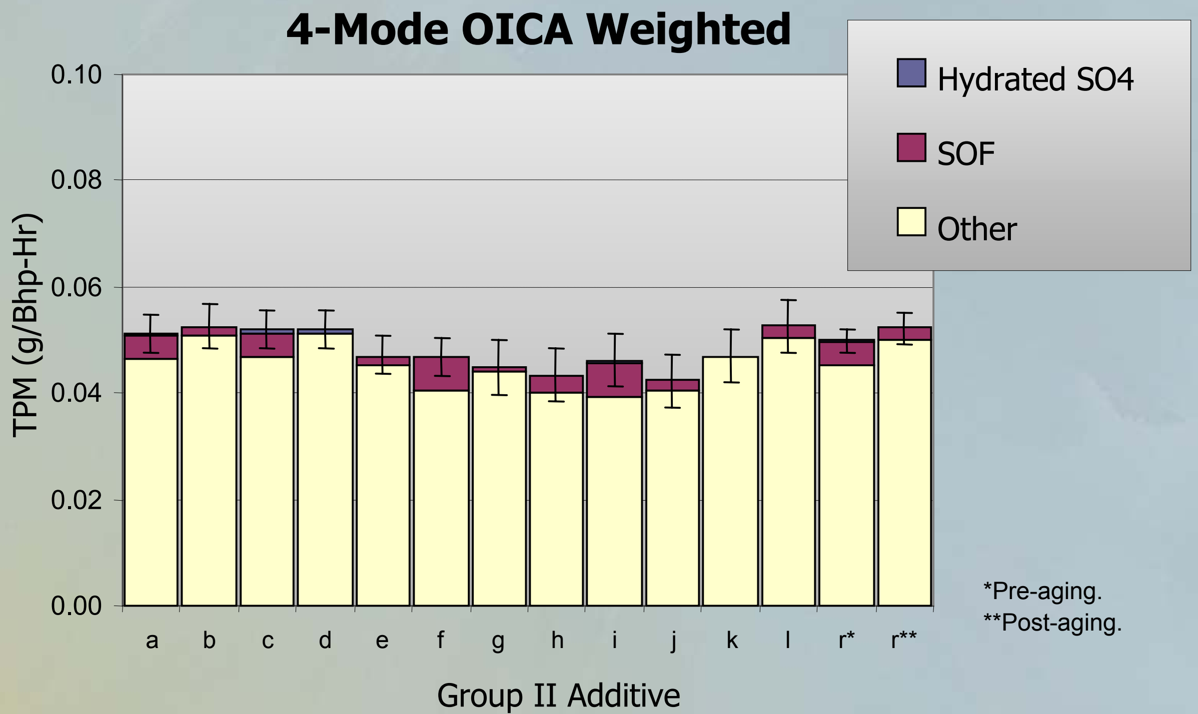
2. If so, how much of an impact is due to properties of the additive package? … base oil?

Total PM – Some Differences Among Oils



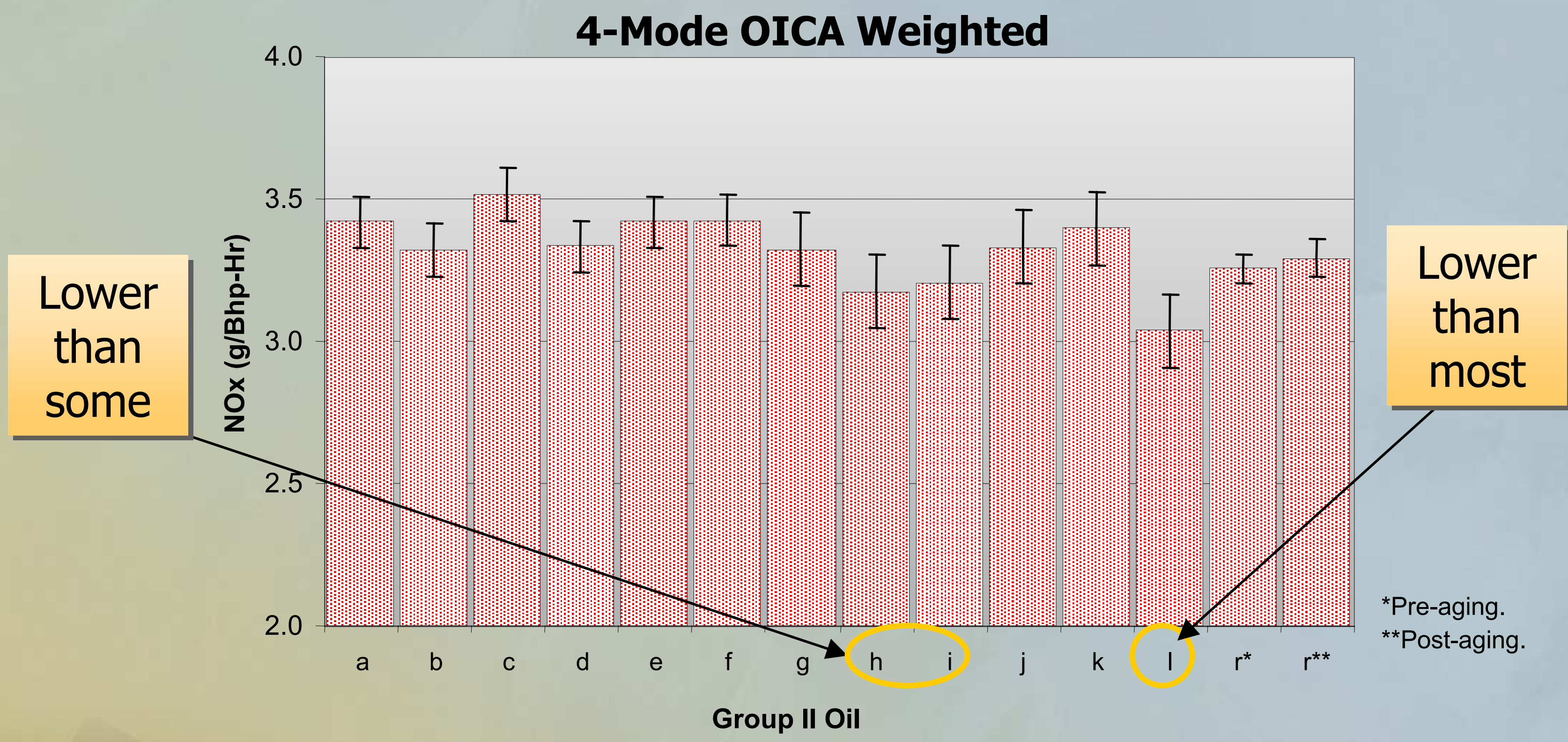
- Some statistically significant differences between Groups (across additive packages)
- Some statistically significant differences between additive packages (across Groups)

Contributions of Total PM Components



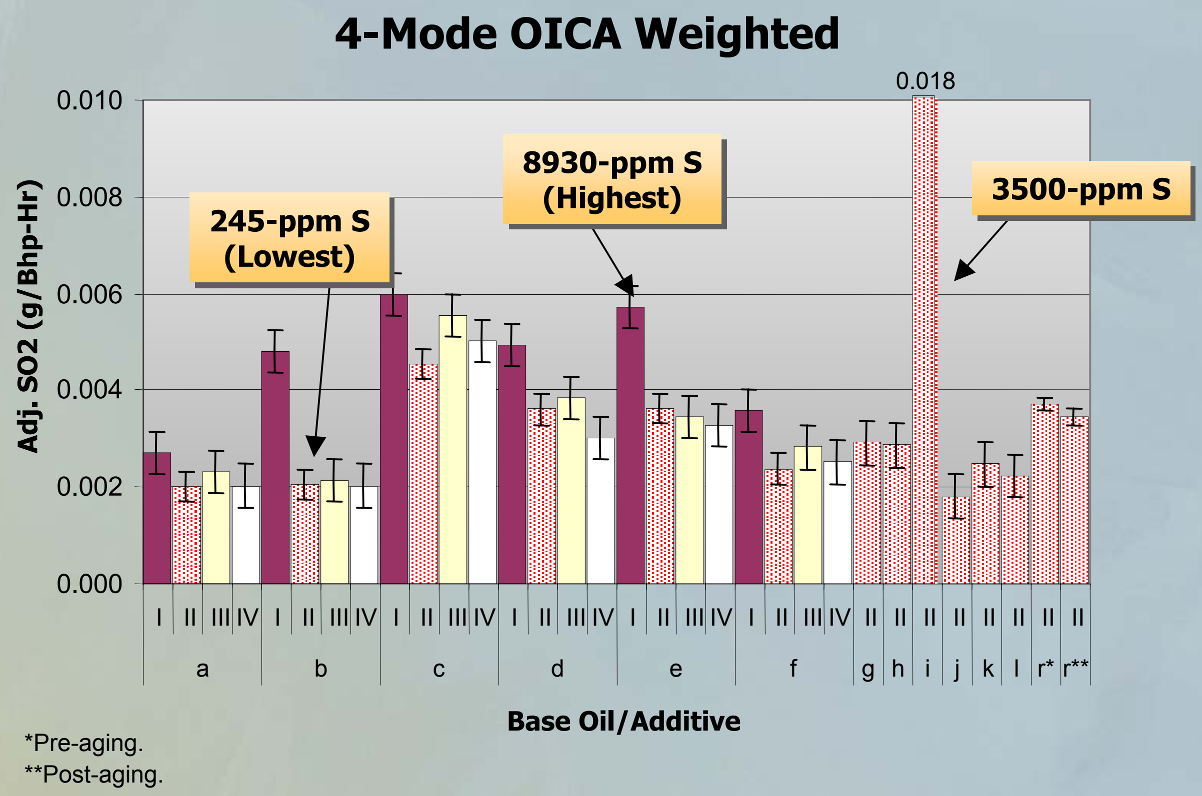
- No significant differences in total PM emissions among Group II oils
- Negligible contributions of SO_4 and SOF

NO_x Emissions – Some Significant Differences Among Group II Oils

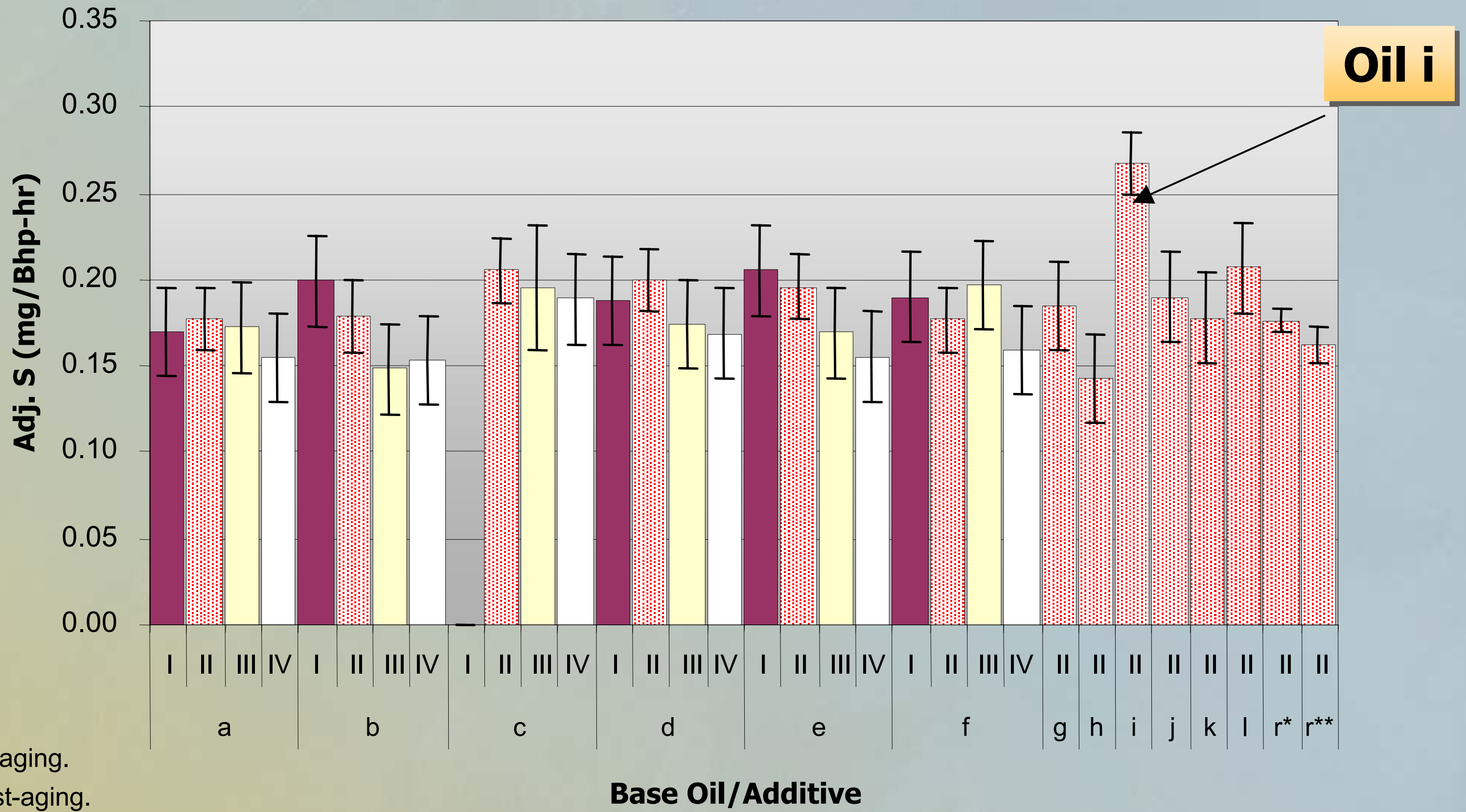


SO_2 Emissions – Significant Additive and Base Oil Effects

- Additive packages c and i produced highest SO_2 emissions
- Significant base oil effect – Group 1 highest
- Magnitude of the effects do not directly correlate with sulfur content of oil



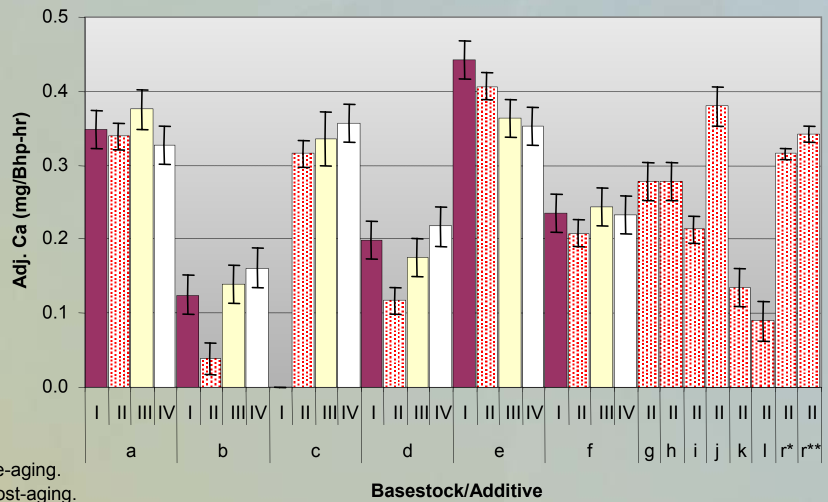
Elemental Sulfur Emissions



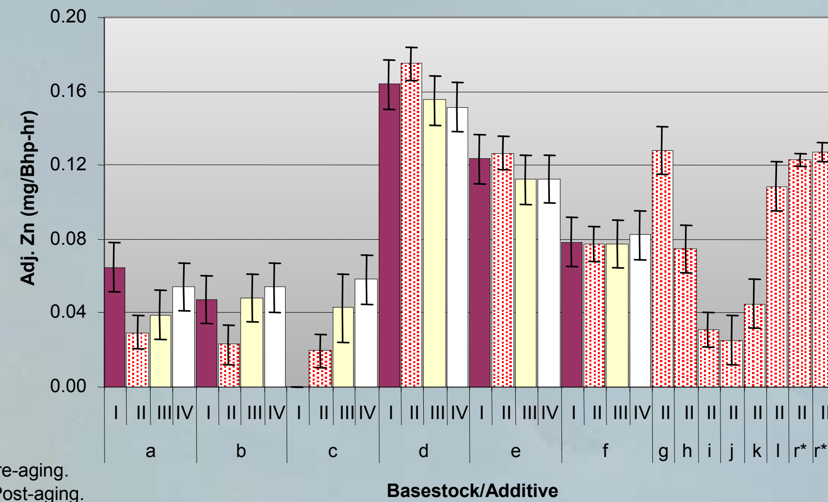
*Pre-aging.
**Post-aging.

Phase I - Part 1

Ca, Zn and P Emissions



*Pre-aging.
**Post-aging.



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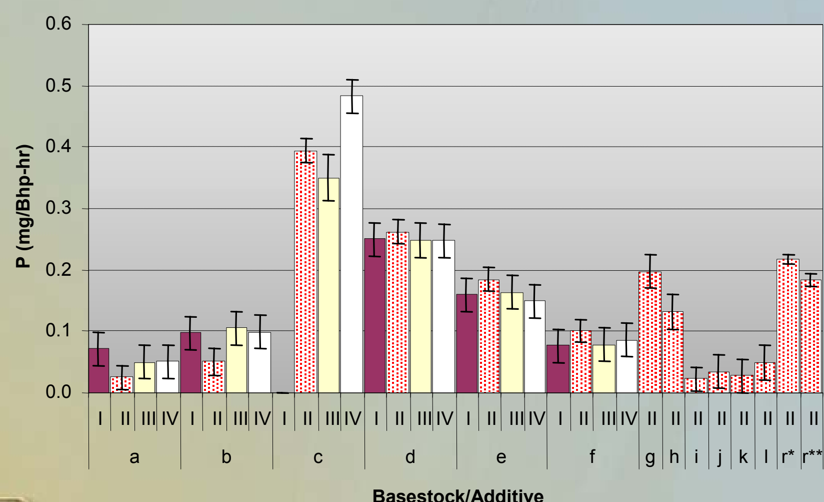
**Post-aging.



*Pre-aging.
**Post-aging.

Phase I - Part 1

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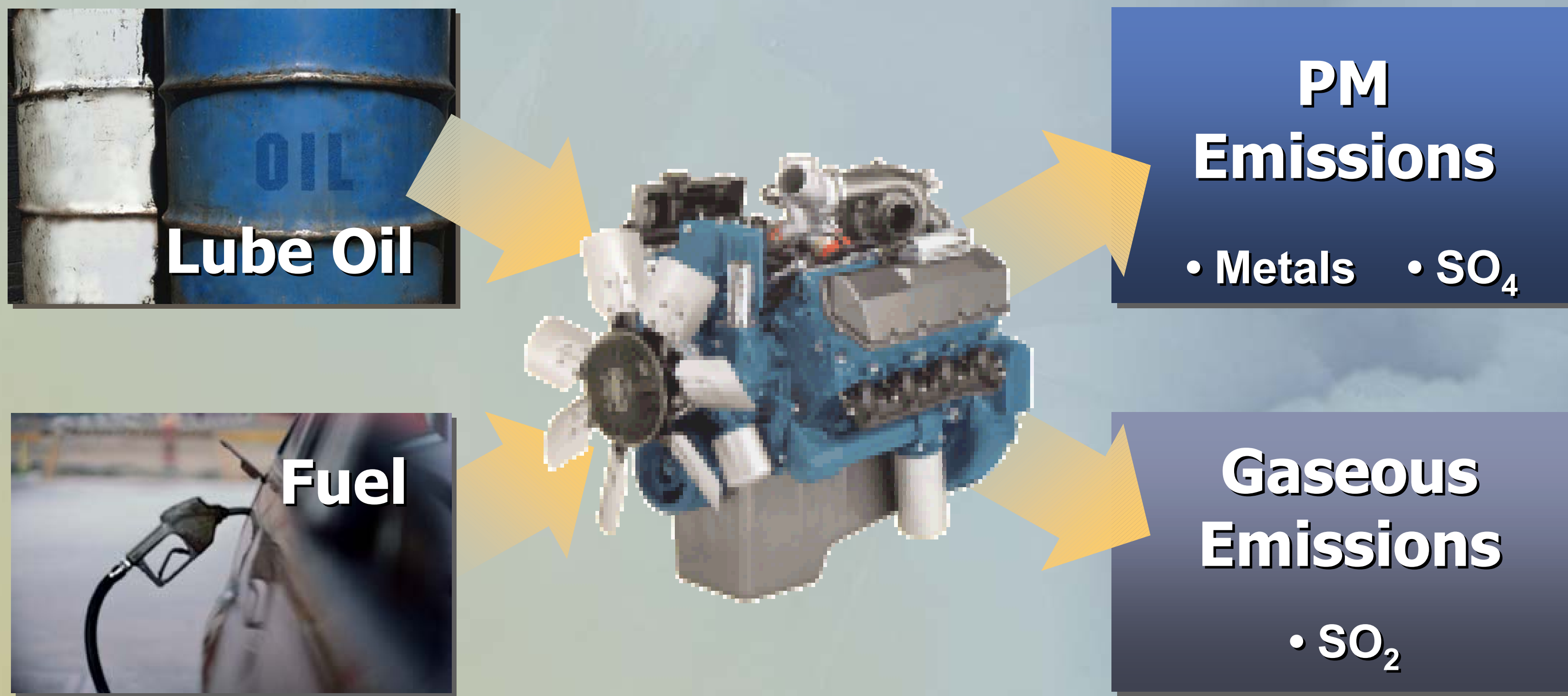
Data Analysis Question #3

3 Which emissions species can be directly predicted from the properties of the oil and fuel?

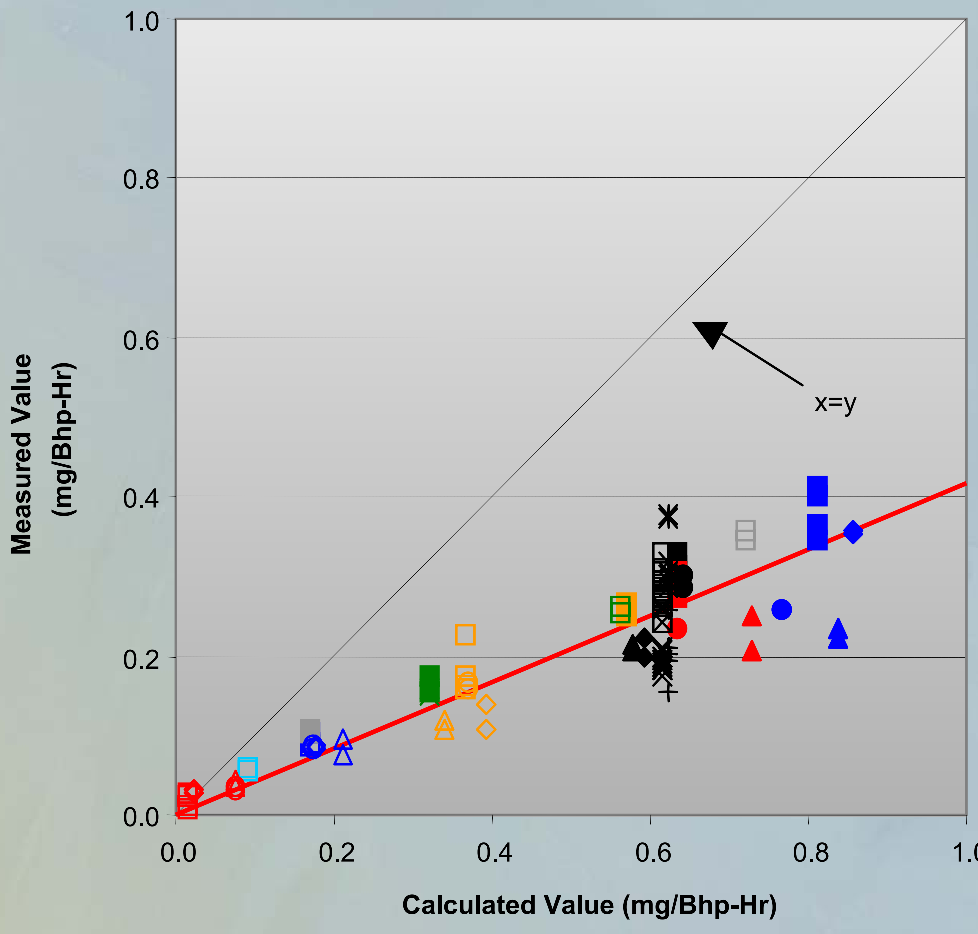
Mass Balance



- Emissions from fuel and oil consumptions and wear metals
- Recovery rates obtained by comparing measured emissions with calculated values based on fuel and oil properties

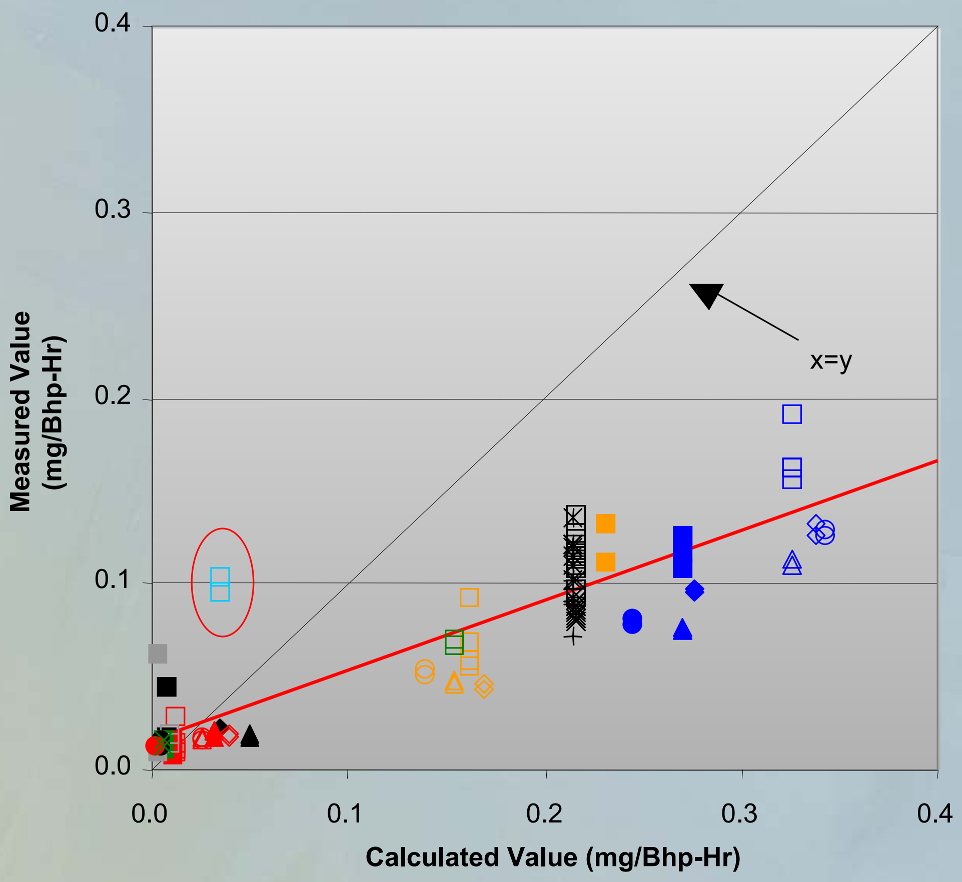
Ca Mass Balance

- Ca emissions directly correlated with concentration in oil
- No apparent composition effects
- 42% recovery rate



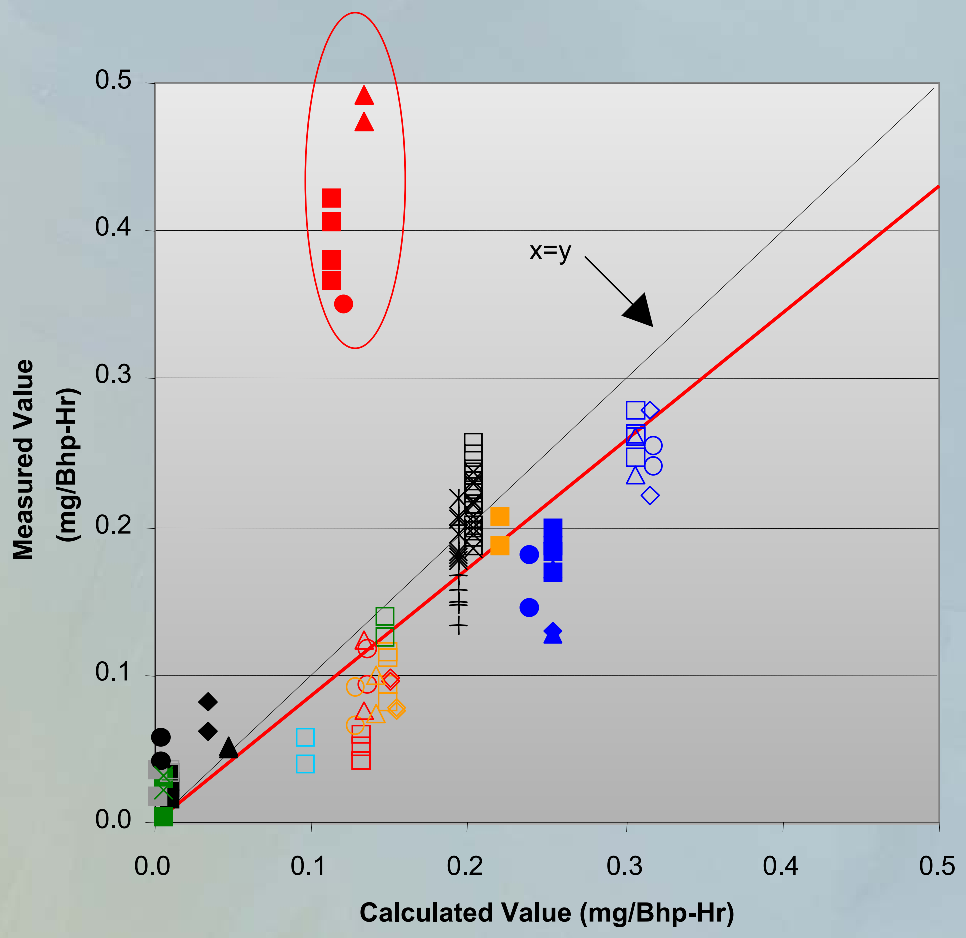
Zn Mass Balance

- Zn emissions directly correlated with concentration in oil
- Possible composition effects – zinc in oil I2 is preferentially consumed
- 38% recovery rate

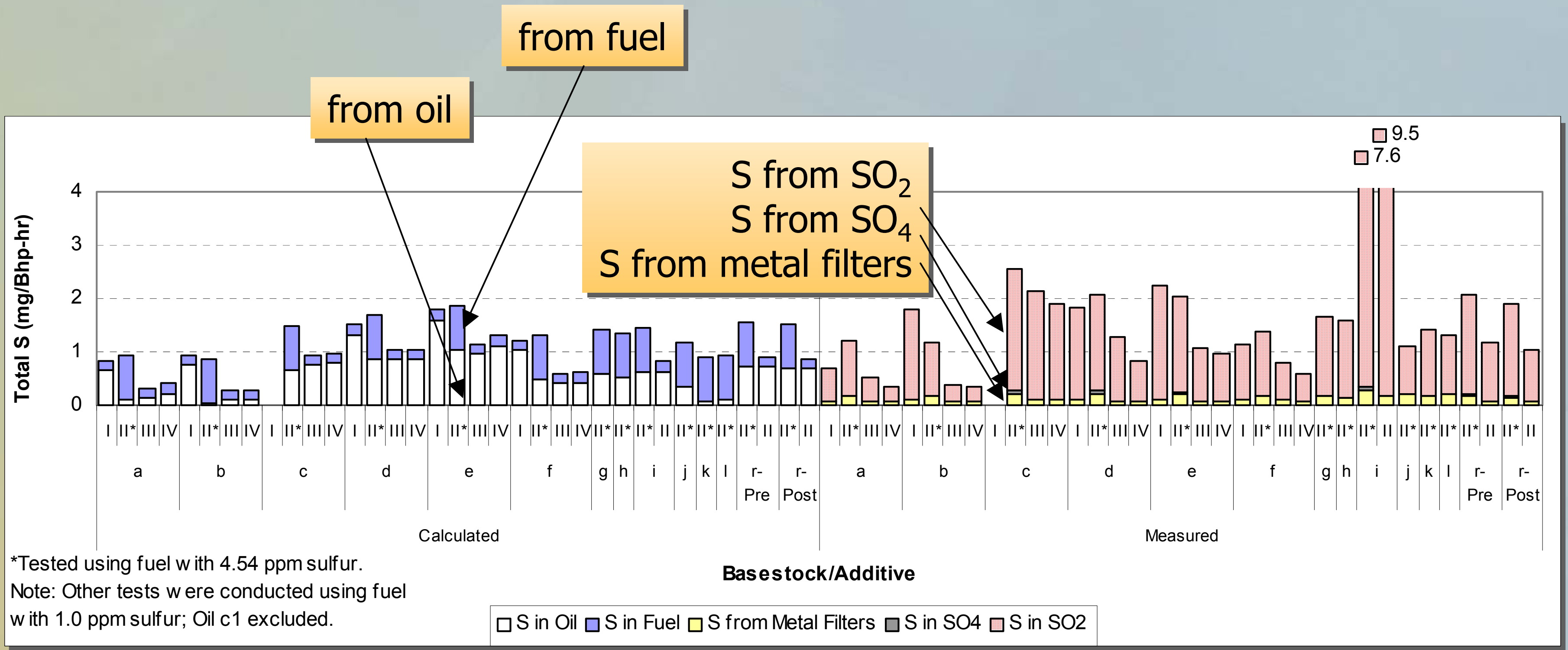


P Mass Balance

- P emissions directly correlated with concentration in oil
- Oil c2, c3 and c4 deviate significantly
- 86% recovery rate (excl. Oils c2, c3 and c4)

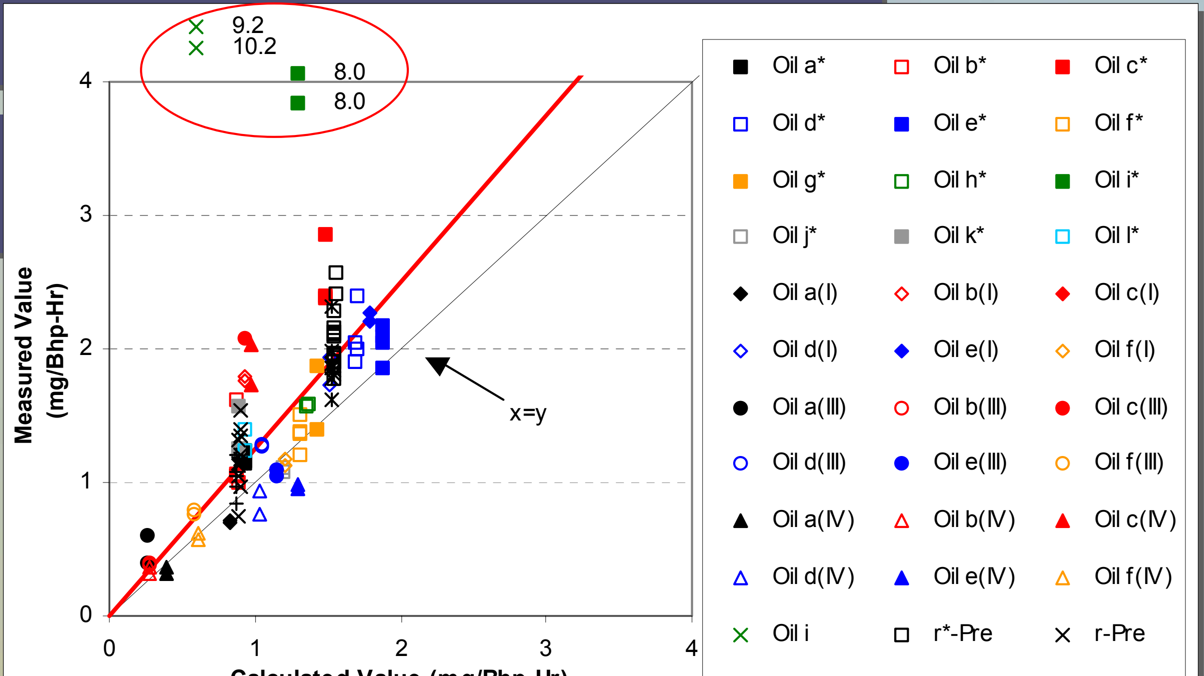


Sulfur Mass Balance



Sulfur Mass Balance (continued)

- S emissions directly correlated with concentration in oil
- Oil i significantly deviates
- 125% recovery rate (excl. Oils i)



*Tested using fuel with 4.54 ppm sulfur.
Note: Oil c1 excluded.

Data Analysis Question #4

4 Can we identify indirect (empirical) relationships between engine-out emissions and oil properties?

Under investigation

PM versus oil ash?	PM versus oil sulfur level?	NO_x versus principal components?

Phase I Preliminary Observations

- Lubricant formulation has modest effects on regulated emissions
  - $\pm$10% for CO and NO_x, $\pm$20% for PM, and $\pm$30% for HC
- Sulfur content in the oil has significant effects on sulfur emissions.
- However, oil formulation (beyond oil sulfur content) can have a significant impact on SO_2 emissions (e.g. oils c and i)
- Metals (S, P, Zn, Ca) emissions correlate with concentration in oil

Phase I – Part 2

Status and Early Results

John Orban, Battelle

APBF-DEC

Phase I – Part 2

Objective

Develop methods to accelerate exposures of emission control systems (ECS) to lubricant-derived emissions

Approach

Test three oil types using three different oil consumption acceleration methods (blending with fuel, direct injection and combination)

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Study Questions

1. How do emissions change as a function of oil consumption rate? (for each oil type and acceleration method)
2. How are these changes affected by oil type (reference oil, oil i, oil c)
3. How are these changes affected by oil consumption method (blending, injection, combination)?
4. Can the differences among methods be predicted from the combined estimated effects of each method? (i.e., interactions)

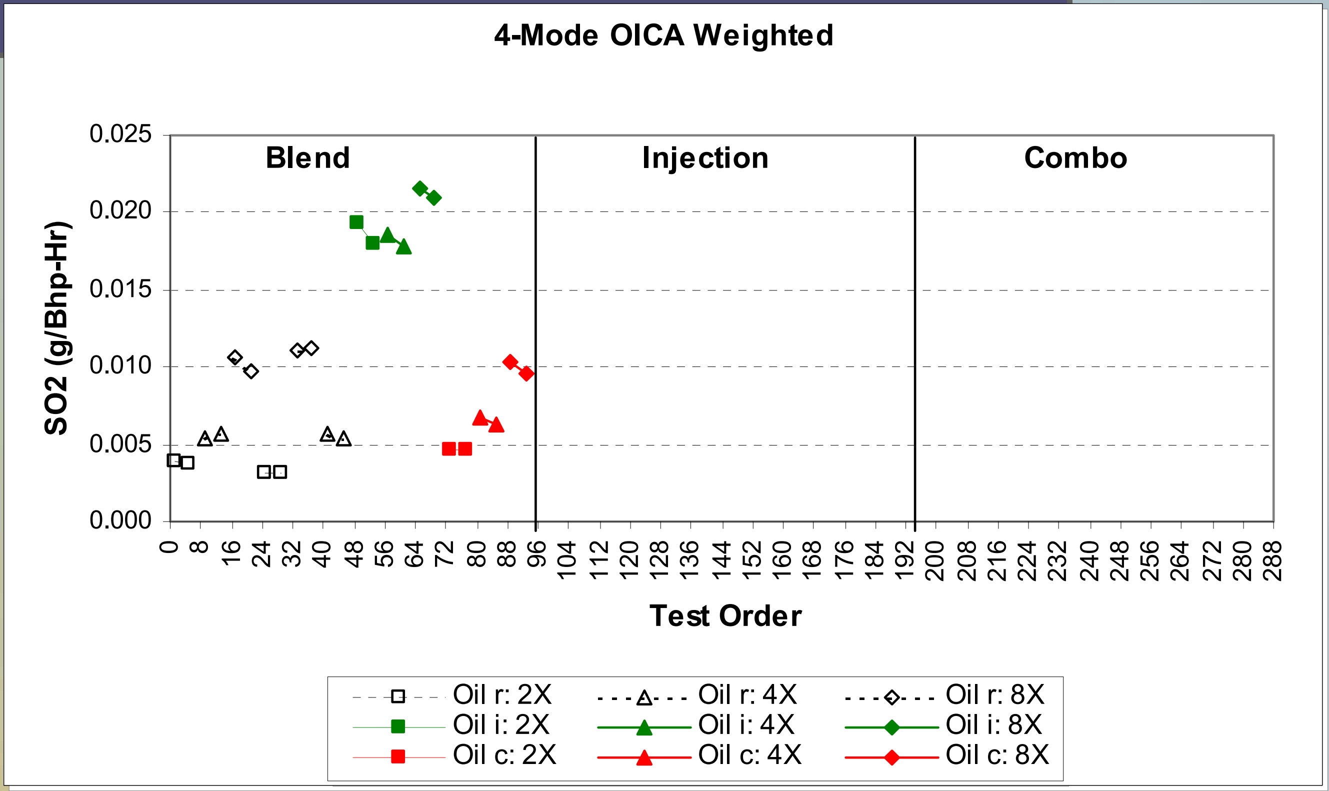
Test Matrix

Testing Order*	Oil Consumption Acceleration Technique								
	Blending			Injection			Combination		
	Oil r2	Oil i2	Oil c2	Oil r2	Oil i2	Oil c2	Oil r2	Oil i2	Oil c2
1	2X, 2X	2X, 2X	2X, 2X	2X, 2X	2X, 2X	2X, 2X	2X, 2X	2X, 2X	2X, 2X
2	4X, 4X	4X, 4X	4X, 4X	4X, 4X	4X, 4X	4X, 4X	4X, 4X	4X, 4X	4X, 4X
3	8X, 8X	8X, 8X	8X, 8X	8X, 8X	8X, 8X	8X, 8X	8X, 8X	8X, 8X	8X, 8X
4	2X, 2X			2X, 2X			2X, 2X		
5	8X, 8X			8X, 8X			8X, 8X		
6	4X, 4X			4X, 4X			4X, 4X		
# of Tests	**12**	**6**	**6**	**12**	**6**	**6**	**12**	**6**	**6**

(green)	Tests completed
2X	2 times base rate

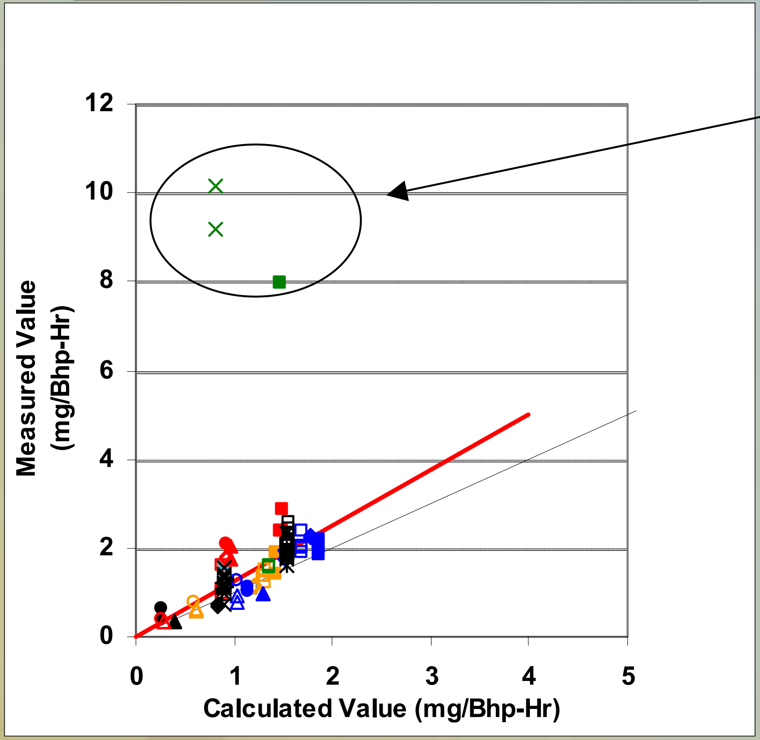
Early Results

- Confirms unusually high SO_2 emissions with oil i
- Emissions correlate with oil concentration in fuel

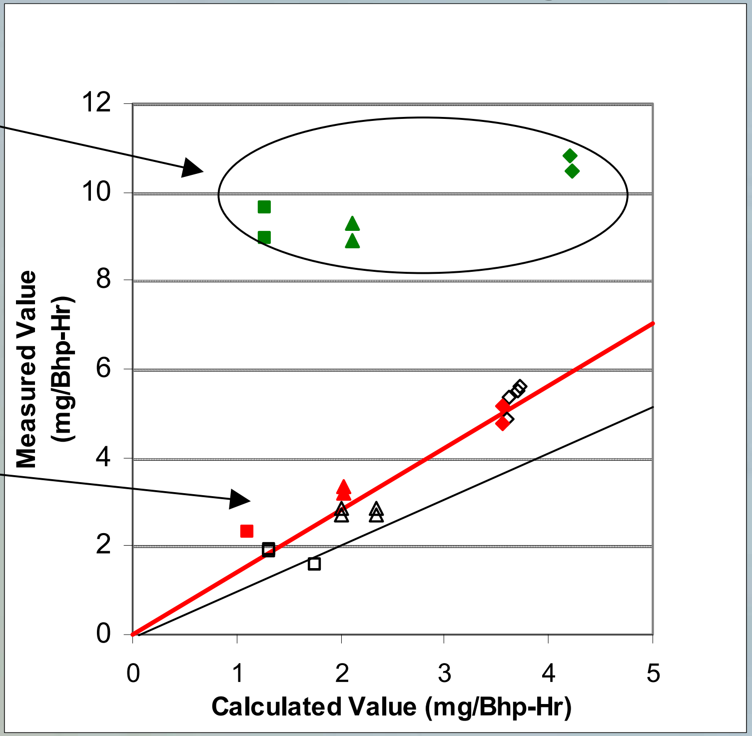


Mass Balance Results

Part 1 Results - Various Oils



Part 2 Results – Fuel Blending



Oil i

Oils c & r

Acknowledgements

Special thanks to:

- Shawn Whitacre (NREL), Project Leader
- Additive suppliers (Ciba, Ethyl, Chevron, Infineum, Lubrizol)
- Base oil suppliers (Valero, Excel, Motiva, BP)
- International Truck and Engine
- APBF-DEC Lubricants Project Workgroup
- U.S. Department of Energy (John Garbak and Steve Goguen)
- **APBF-DEC Funding Partners**: ACC, API, CARB, DOE, EMA, MECA, SCAQMD