



Detailed Chemistry of Current Diesel Engine Emissions

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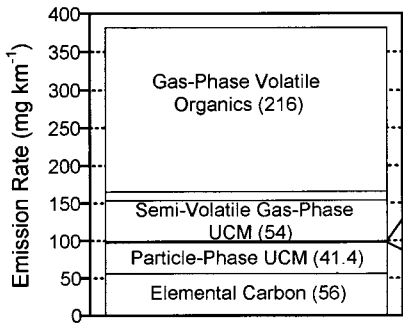
Questions

- What are the general classes of compounds present in today's emissions?
- Does the vehicle operating cycle change the chemical profile in the exhaust emissions?
- What quantities are being emitted?
- What are the limits of detection for future analytical techniques?

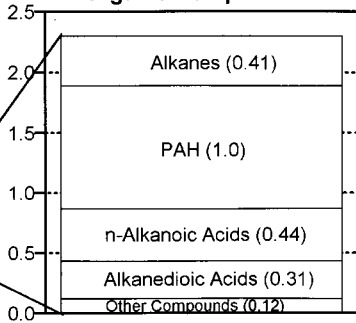


What make up diesel PM

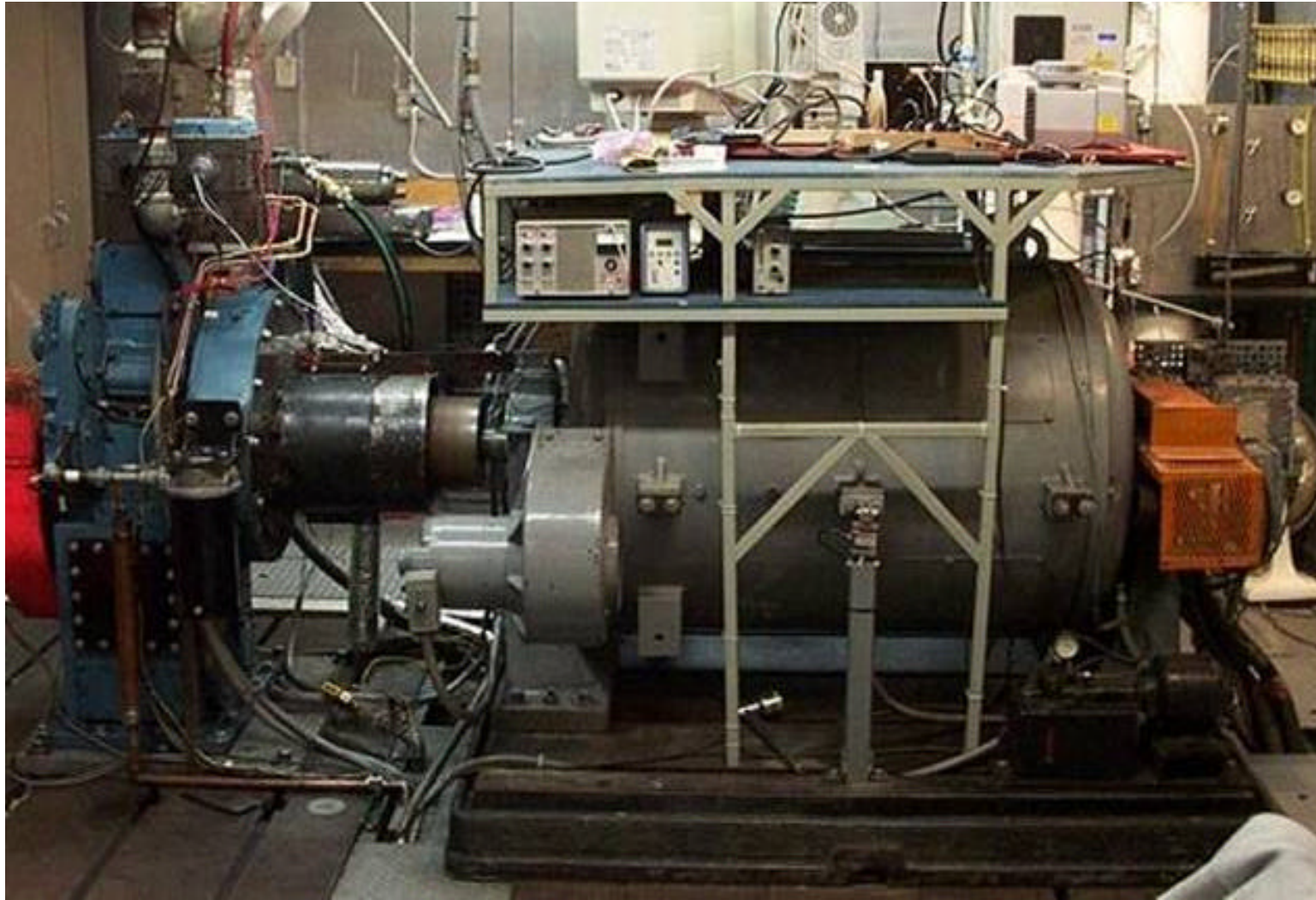
- **Unburned Fuel**
 - Predominately Unresolved Complex Mixture (UCM)
 - Fuel Additives
- **Unburned Lube oil**
 - Predominately Unresolved Complex Mixture (UCM)
 - Lube additives
- **Pyrolyzed Fuel (and Lube Oil)**
 - Source of Elemental Carbon (EC)
- **Residual of Combusted Fuel (and Lube Oil)**
 - Metals and other inorganic species
- **Engine Wear**
 - Trace metals



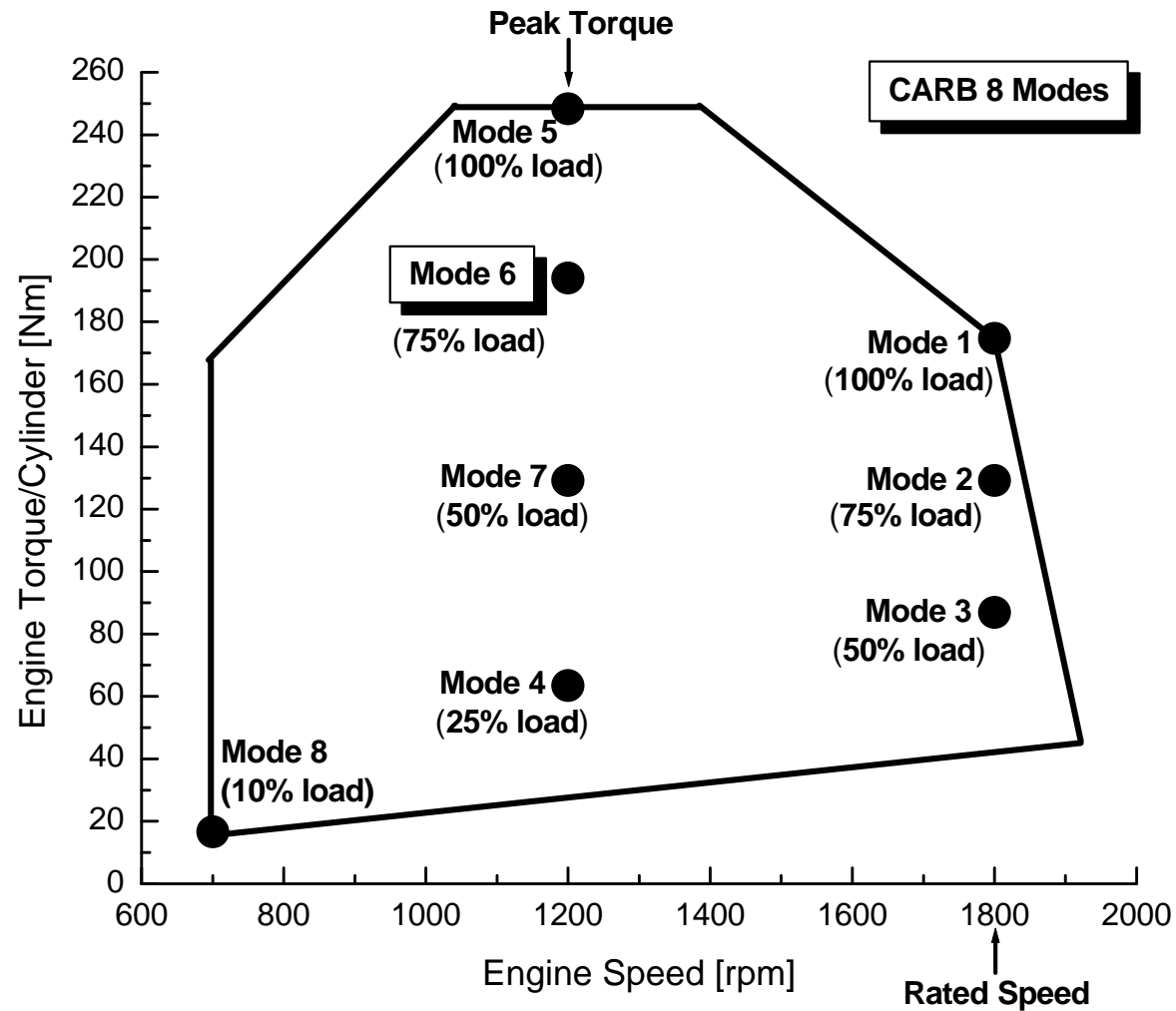
Resolved Particle-Phase Organic Compounds



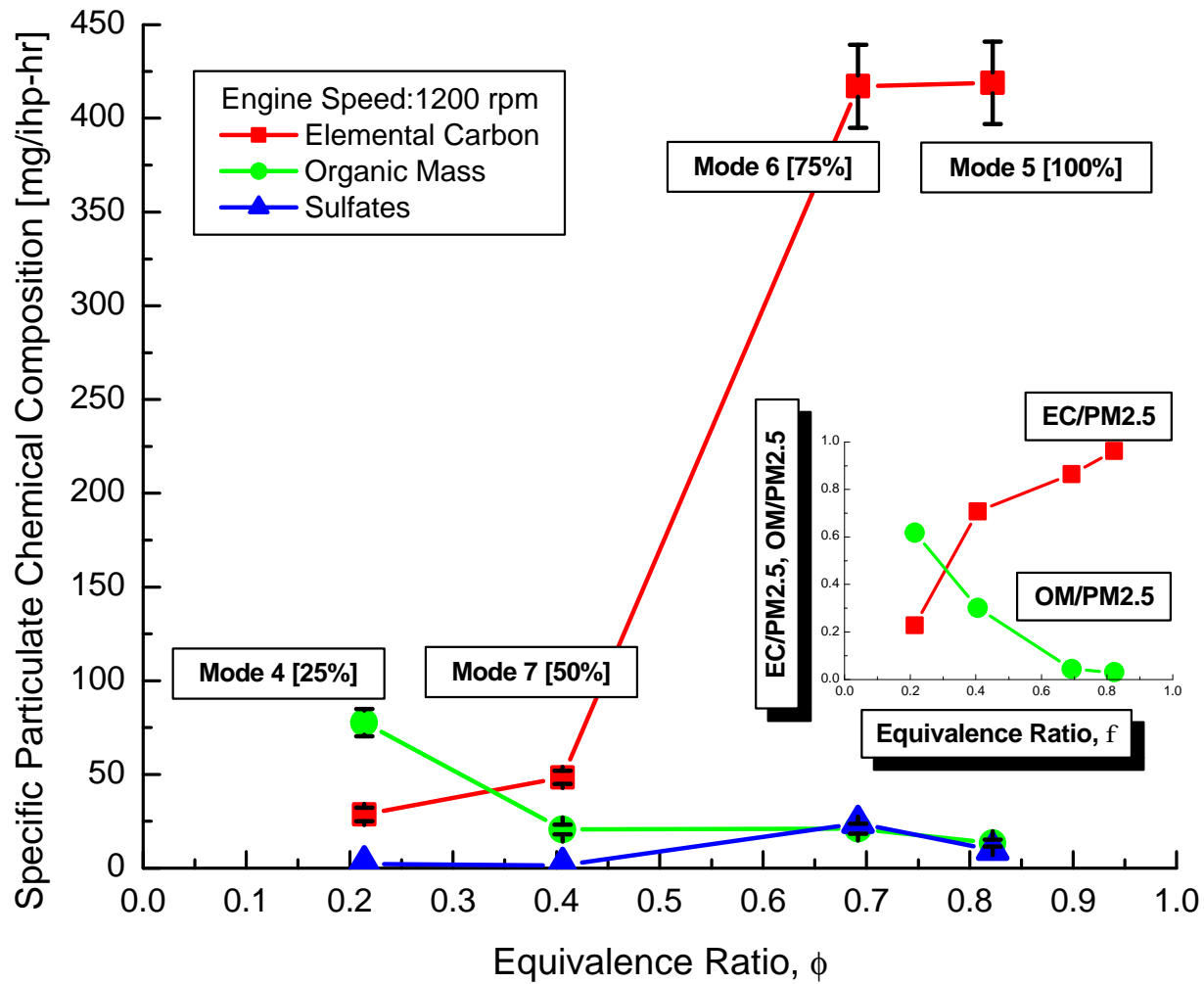
Diesel Engine Research Lab



CARB 8 Mode Cycle



Effect of Engine Load



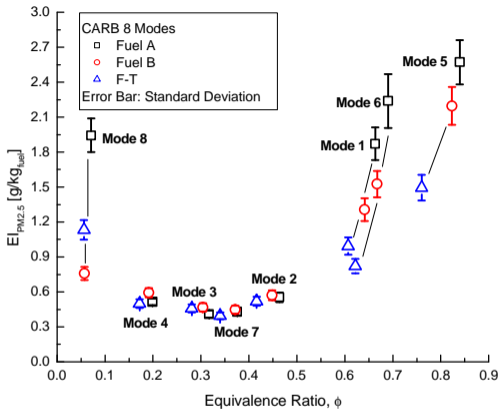
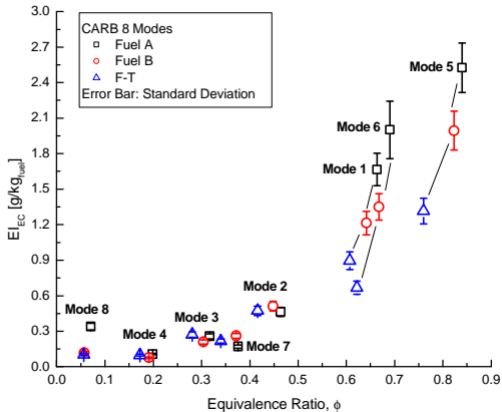


Figure 17. Emission index (EI) of PM_{2.5} vs. equivalence ratio for Fuel A, Fuel B, and F-T fuel for CARB 8-mode test cycle.



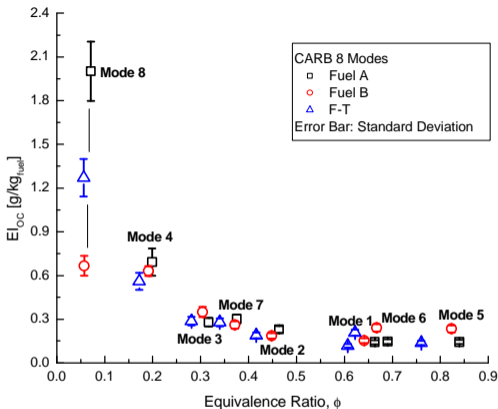


Figure 19. Emission index (EI) of OC vs. equivalence ratio for Fuel A, Fuel B, and F-T fuel for CARB 8-mode test cycle.



Changes in PM Composition

■ Factors Effective PM Composition

- Engine Design
- Engine Maintenance
- Fuel and Lube
- Engine Operating Condition

■ General Trends

- EC percent of mass increases with load
- OC percent of mass decreases with load
- Removal of contaminants from lube and oil can lead to reduction in emissions of these contaminants
- Metals emissions effective by lube oil consumption



Analytical Methods

- Significant advances in PM measurements that can benefit engine testing and certification
 - Chemical analysis
 - Instrumentation
- Core methods
 - Mass – Microbalance
 - Organic and Elemental Carbon
 - Thermal evolution and combustion
 - Sulfate – IC
 - Trace elements – ICP and ICPMS
 - Organic Speciation – GCMS



Detection Limit Assumptions

■ Example

- 400 BHP Engine
- 20 minute test
- Dilution ratio: 10-50
- Diluted exhaust sampling
 - 10 lpm – 47 mm filter
 - 16 lpm – 47 mm filter
 - 90 lpm – 90 mm filter

■ Detection limits dominated by field blanks

- Assume 10 times higher than “engine test” field blanks



Lower limit of “good measurement”

■ Mass

- 47 mm filter 50 µg per filter
- 90 mm filter 200 µg per filter

■ Carbon (EC or OC) – Thermal evolution

- 47 mm filter 20 µg per filter
- 90 mm filter 80 µg per filter

■ Sulfate - IC

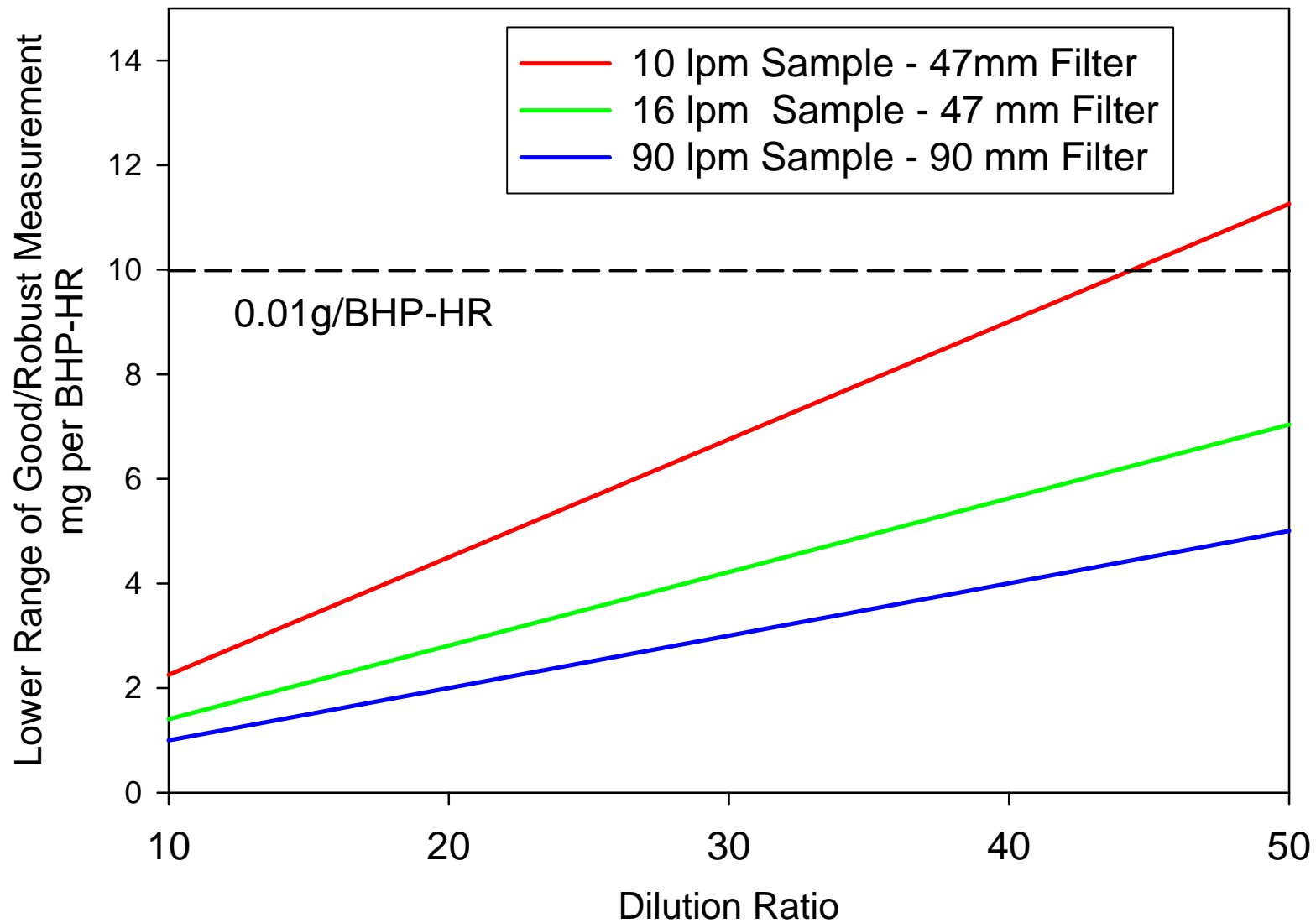
- 47 mm filter 15 µg per filter
- 90 mm filter 60 µg per filter

■ Metals – ICP (Ca, S, Si, Al, Fe, Mg, etc...)

- 47 mm filter 0.5 µg per filter
- 90 mm filter 2.0 µg per filter

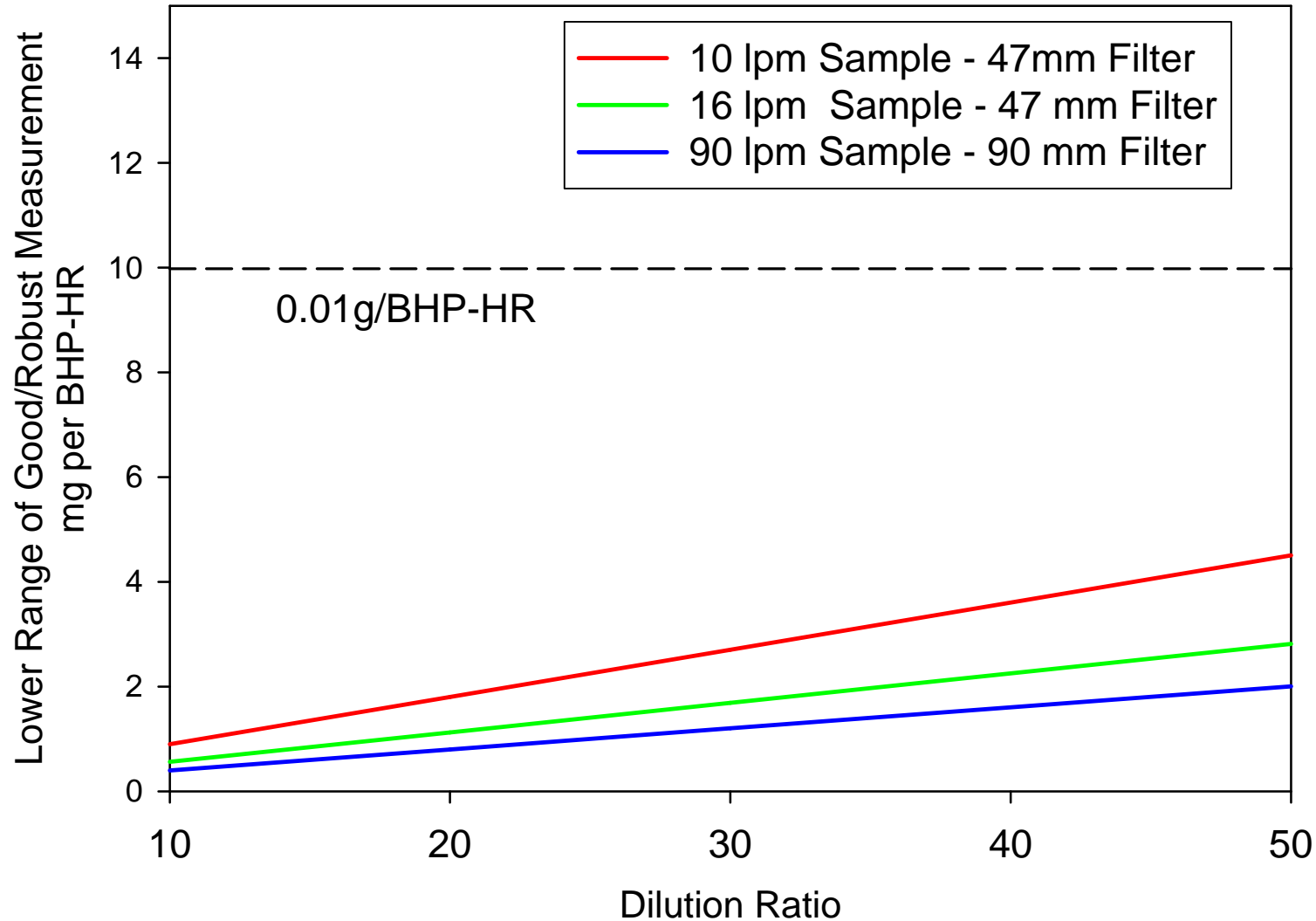
Measureability of Mass Emission Rate

Good/Robust - 10 times higher than Field Blanks



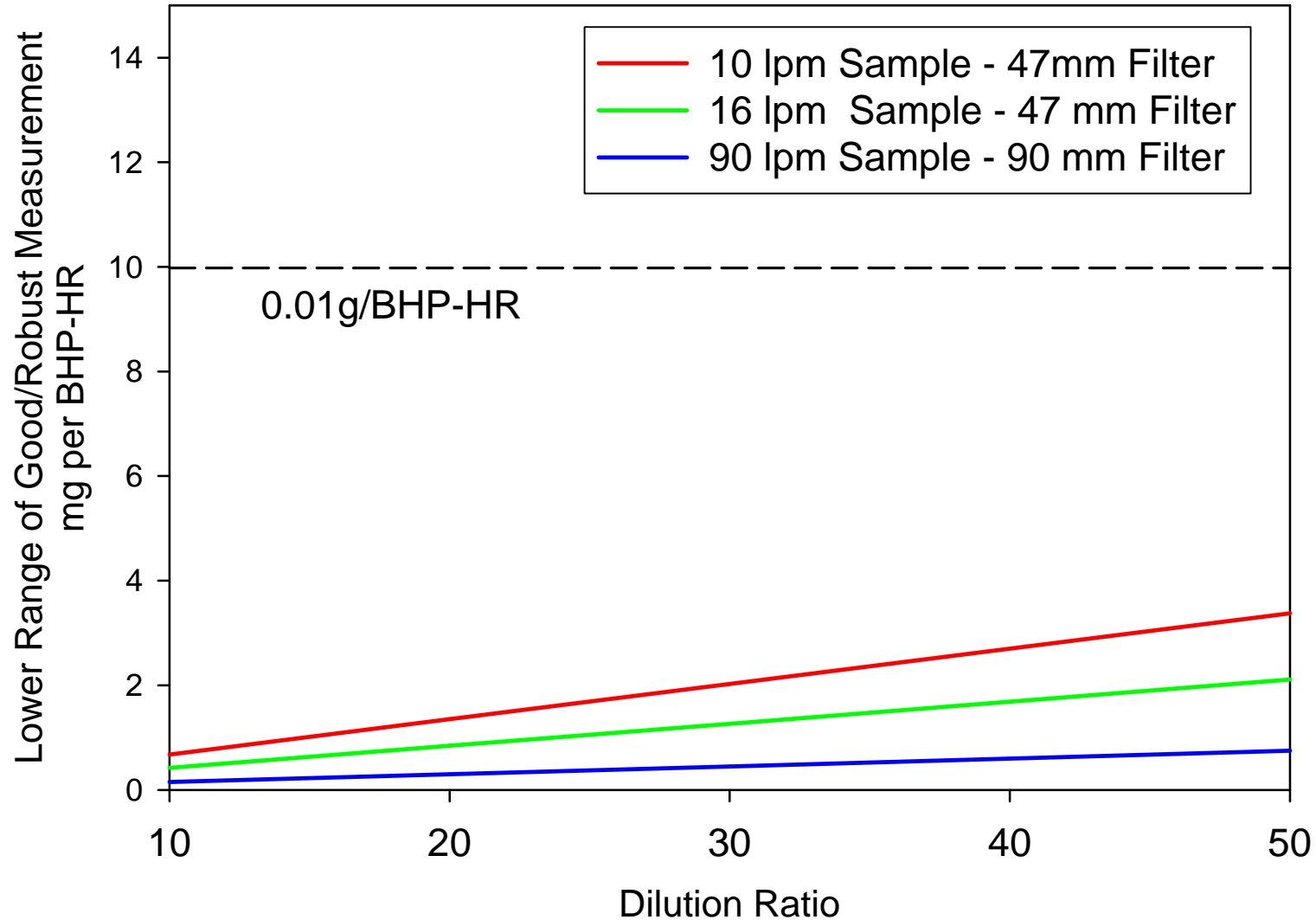
Measureability of Particulate Carbon Emission Rate

Good/Robust - 10 times higher than Field Blanks



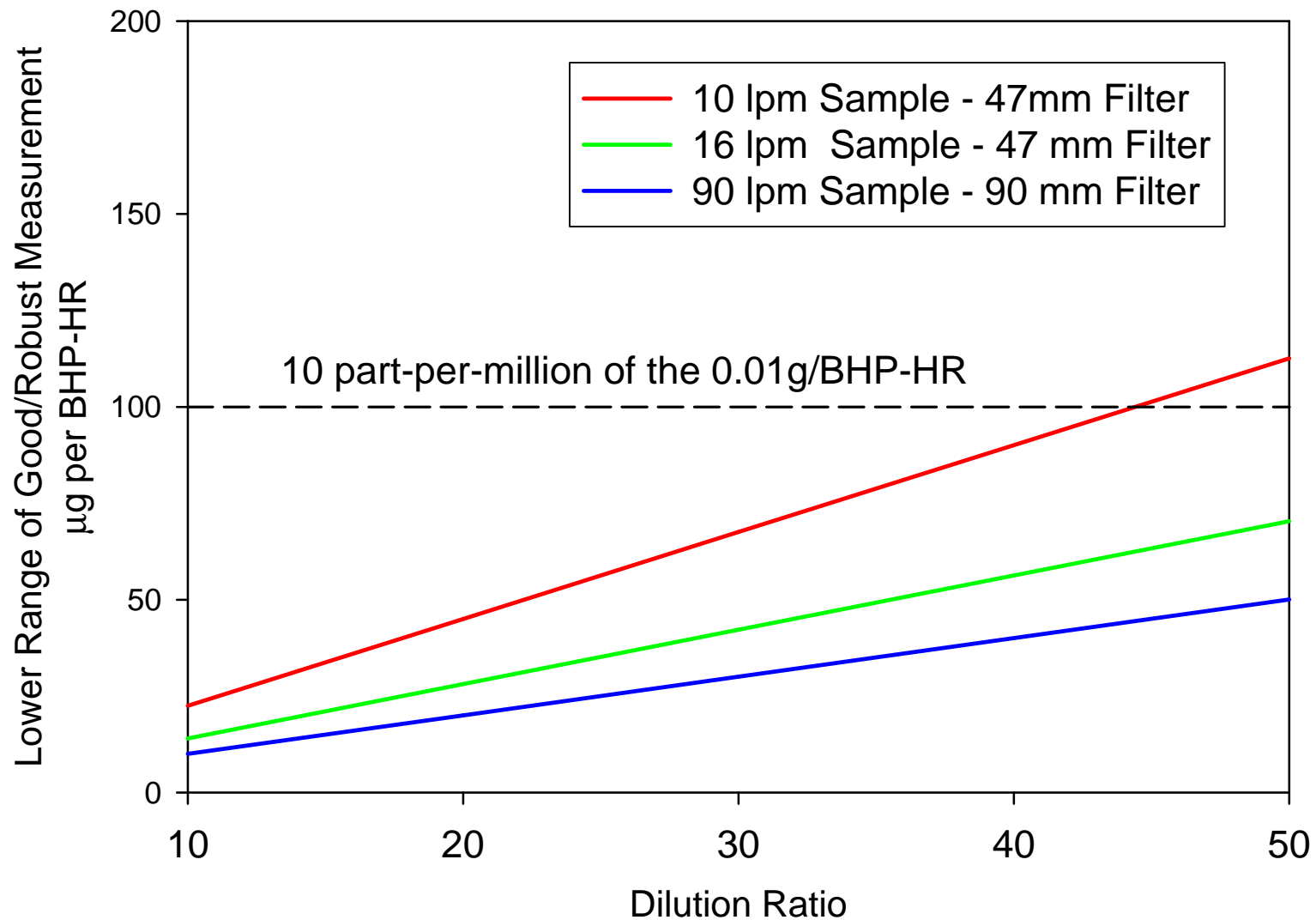
Measureability of Sulfate Emission Rate

Good/Robust - 10 times higher than Field Blanks



Measureability of Metals Emissions Rates

Good/Robust - 10 times higher than Field Blanks





Conclusions

- Composition of diesel PM can be directly related to fuel, lube, and engine wear
- Relative composition of diesel PM varies significantly as a function of engine, fuel, lube oil, and operations
 - Elemental carbon
 - Organics
 - Trace elements
- Analytical tools exist for detailed speciation of PM from future technology diesel engines
 - Attention needs to be focused on field contamination
 - Attention needs to be focused on sampling artifacts