The Triple-Dare Challenge Facing the Automotive Industry:

Fuel Economy Standards, Emissions Regulations, and Renewable Fuel Use

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Energy and Transportation Science Division
Oak Ridge National Laboratory

The Center for BioEnergy Sustainability (CBES) FORUM

Oak Ridge National Laboratory

February 25, 2015

ORNL is managed by UT-Battelle
for the US Department of Energy

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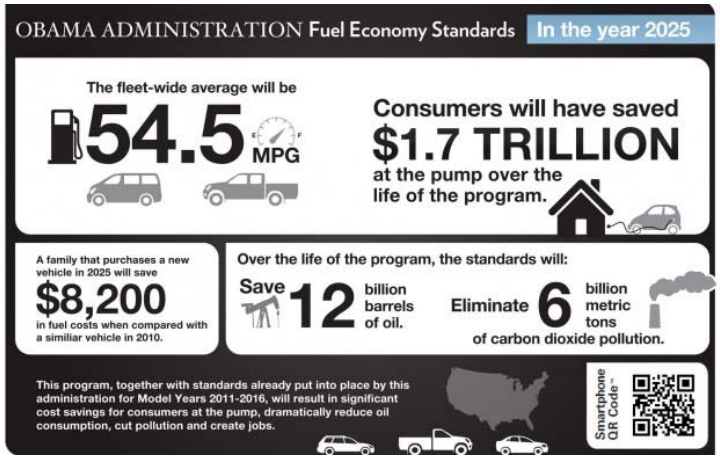
Convergence of three automotive challenges underlines the importance of advanced research

54.5 mpg CAFE by 2025

- per U.S. EPA and U.S. DOT standards
- Currently at 30.1 mpg for "cars"
- Gasoline dominating US light duty fleet



Fuel Economy Standards

EPA

Automotive Industry

>70% less NOx | **>85% less NMOG** | **70% less PM**

EPA Tier 3 Emission Regulations

<70% less NOx, >85% less NMOG, and 70% less PM emissions by 2017-2025 (phased in)

-per new U.S. EPA Tier 3 regulations

Renewable Fuel Standard

36 billion gallons of renewable fuel by 2022

-per Energy Independence and Security Act of 2007

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Presentation Outline

- **Mobile Source (Vehicle) Emissions and Air Quality**
- **Emission Regulations and Industry Challenges**
- **Catalyst Basics**
- **ORNL Impact on Heavy-Duty Trucks**
- **Current Science Research at ORNL Addressing Near-Term Challenges for Light-Duty Vehicles**

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Air Quality Critical to Human Health and Economic Security

Photos: California Air Resources Board

"…ground-level ozone air pollution reduces plant growth and yield, from negligible impacts in some species to over 30% losses in others."*

*from study in Fresno County (part of San Joaquin Valley Air Pollution Control District)
[reference: D. A. Grantz and A. Shrestha, *California Agriculture* **59**(2): 137-143 (2005)]

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Regulated Mobile Sources (Vehicle Emissions) Focus on Criteria Pollutants

- **Carbon Monoxide (CO):**
  - A colorless, odorless, and poisonous gas that restricts the flow of oxygen.
  - At high levels, CO poisoning can be fatal.
- **Hydrocarbons (HC):**
  - A mix of incomplete combustion products regulated as NMOG (non-methane organic gases).
  - HCs react with NOx to form ground level ozone (O_3), the primary component of smog, and some HCs are toxic.
- **Oxides of Nitrogen (NOx, NO and NO_2):**
  - NO and NO_2 are formed inside the engine cylinder during combustion at high pressures and temperatures.
  - NOx reacts with HCs to form ground level ozone (O_3), and NOx also causes acid rain and various health problems.
- **Particulate Matter (PM) or "soot":**
  - Small particles and liquid droplets formed during combustion.
  - PM has adverse effects on human health and the environment; of particular concern are small (<10 micron) particles that enter the lungs causing health problems.

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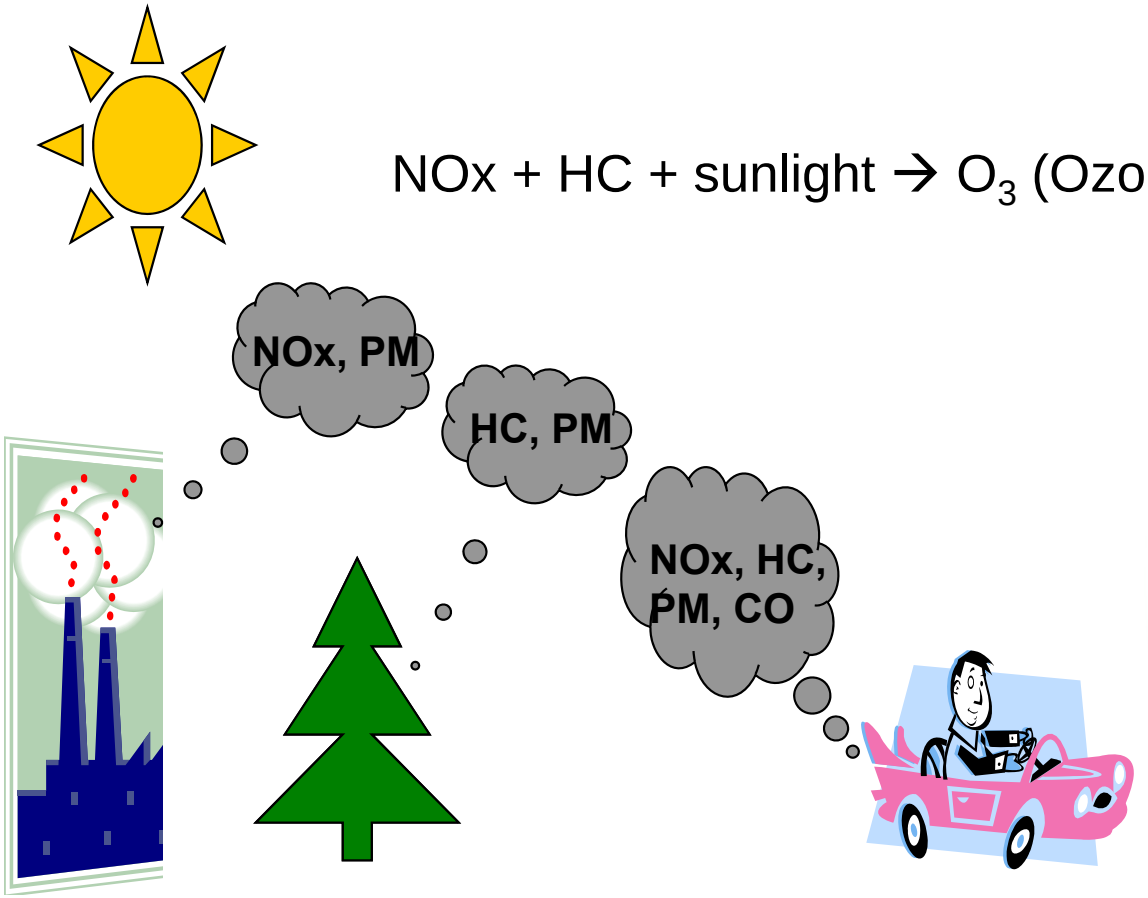
On-Highway Vehicle Pollutant Emissions are a Major Source for Ozone Formation

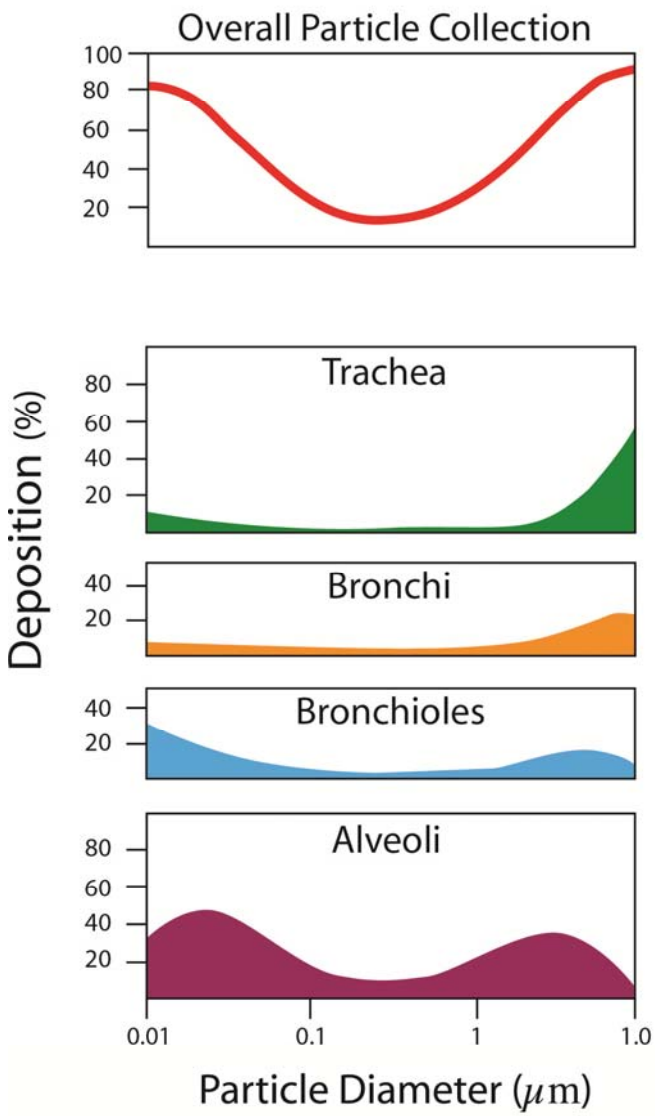
- Ozone (O_3) is formed when NOx and HCs react in sunlight.
- Ozone irritates eyes, causes shortness of breath, wheezing, fatigue, headaches and nausea, and aggravates respiratory problems.

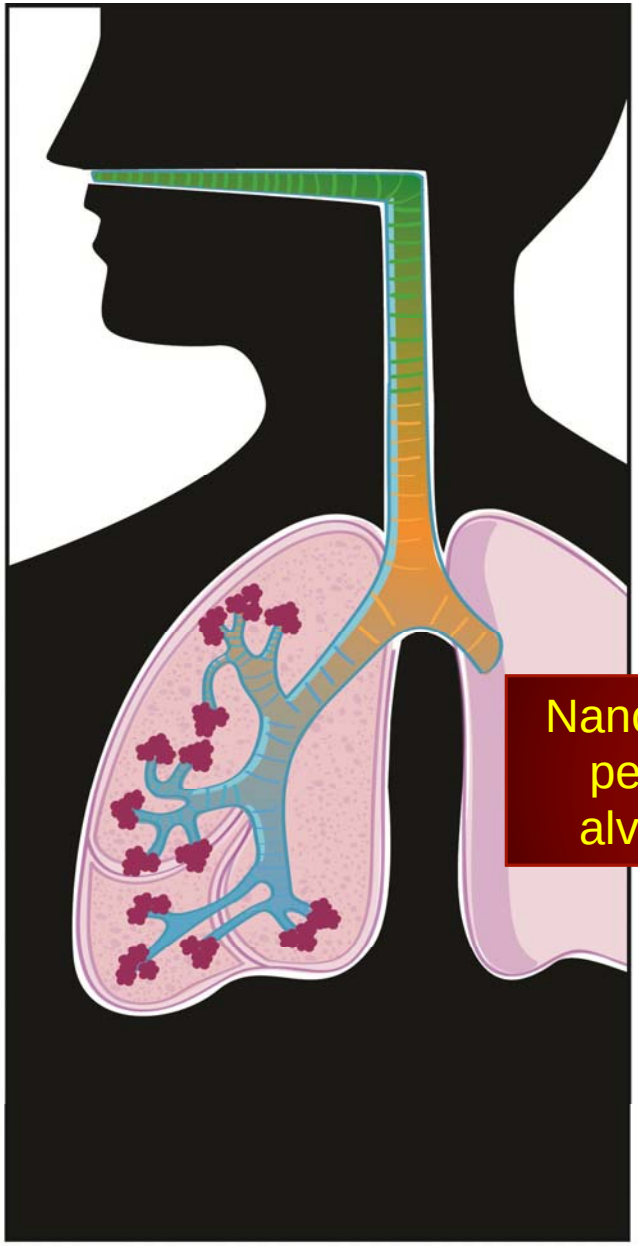


Percentage of Criteria Pollutant Emissions from On-Highway Vehicles (US, 2013)	
CO	33.8%
NOx	38.2%
VOC (HC)	12.2%
PM-2.5	3.0%

Transportation Energy Data Book (Ed. 33), S. C. Davis, S. W. Diegel, R. G. Boundy

Particle Size Influences Location of Deposition in Respiratory System





Nanoparticles can penetrate into alveolar region

***adapted* from Heyder (2004)**

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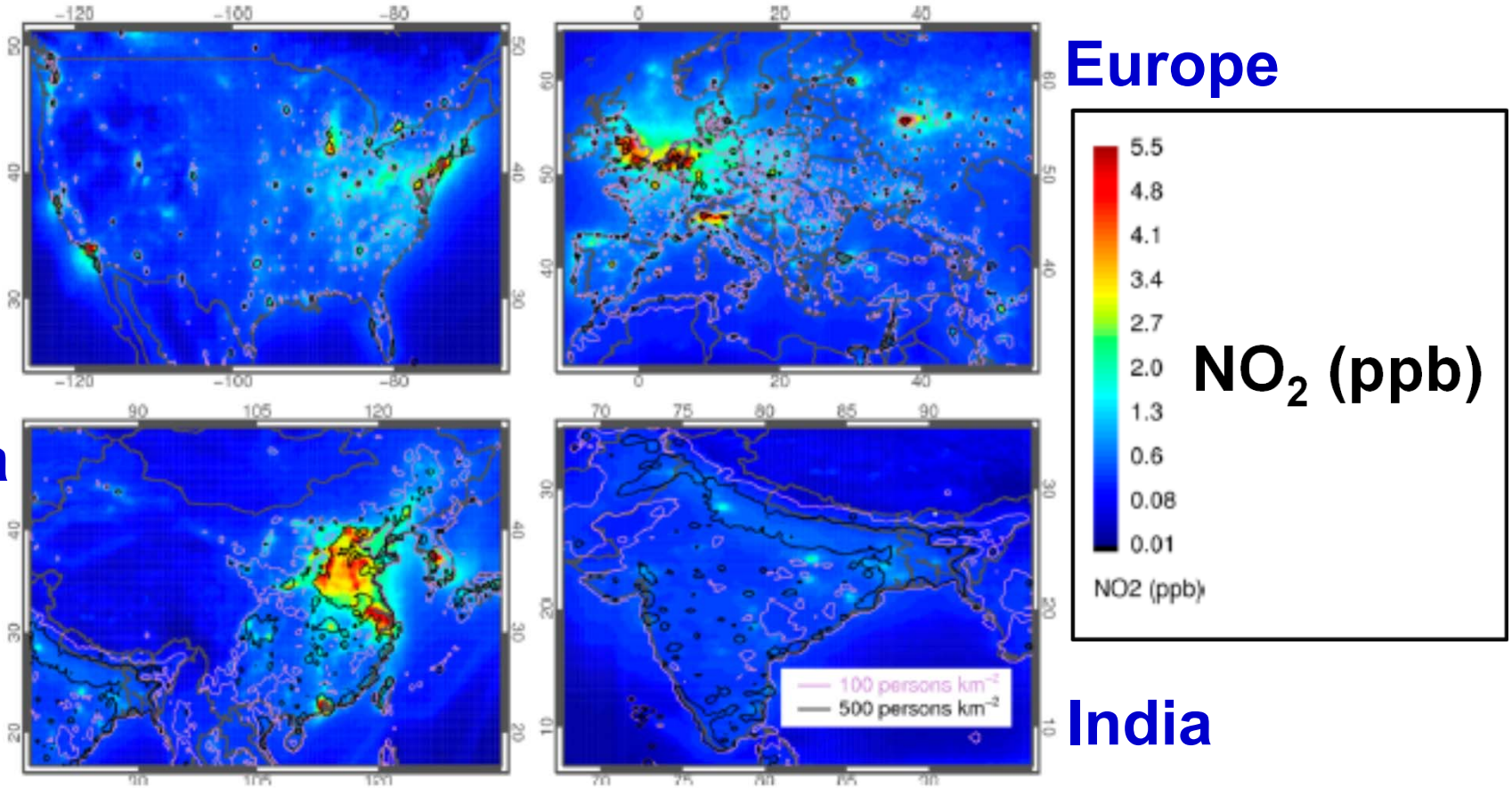
A Satellite View (NO_2) … Shows Global Problems

US

250M Light-Duty Vehicles

China

120M Light-Duty Vehicles and Growing Rapidly!



Europe

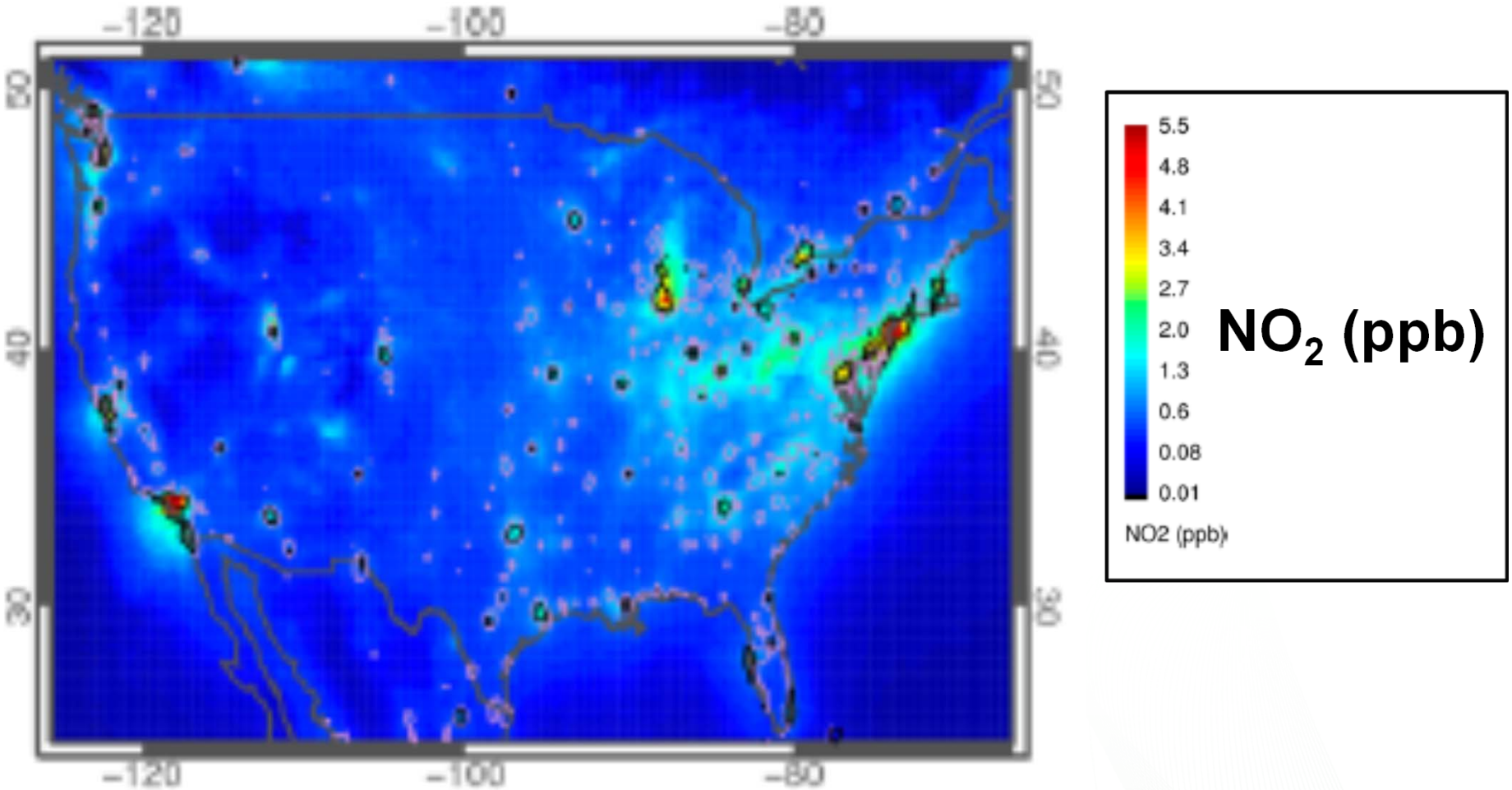
India

NO_2 (ppb)

Figure 1. Annual average afternoon surface NO_2 mixing ratios for the year 2005 binned at 0.25° × 0.25° from OMI over North America, Europe, China, and India. Contours represent population density data gridded at 0.25° × 0.25° resolution with 100 persons km^{-2} (pink) and 500 persons km^{-2} (black).

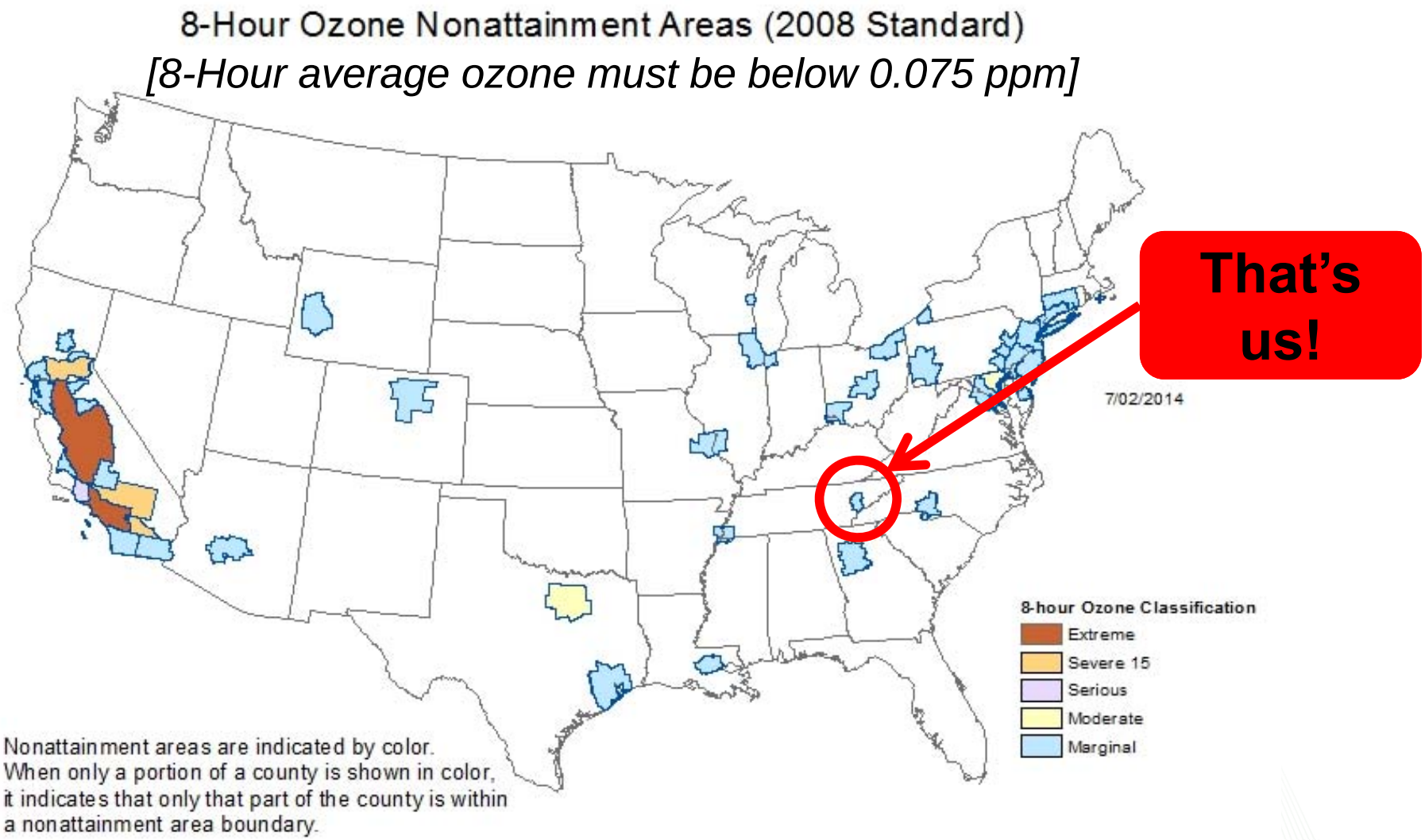
L. N. Lamsal, R. V. Martin, D. D. Parrish, and N. A. Krotkov, *Environ. Sci. Technol.* **47**, 7855-7861 (2013)

A Satellite View (NO_2) … US Hot Spots



L. N. Lamsal, R. V. Martin, D. D. Parrish, and N. A. Krotkov, *Environ. Sci. Technol.* **47**, 7855-7861 (2013)

U.S. Ozone Nonattainment Areas (July 2, 2014)



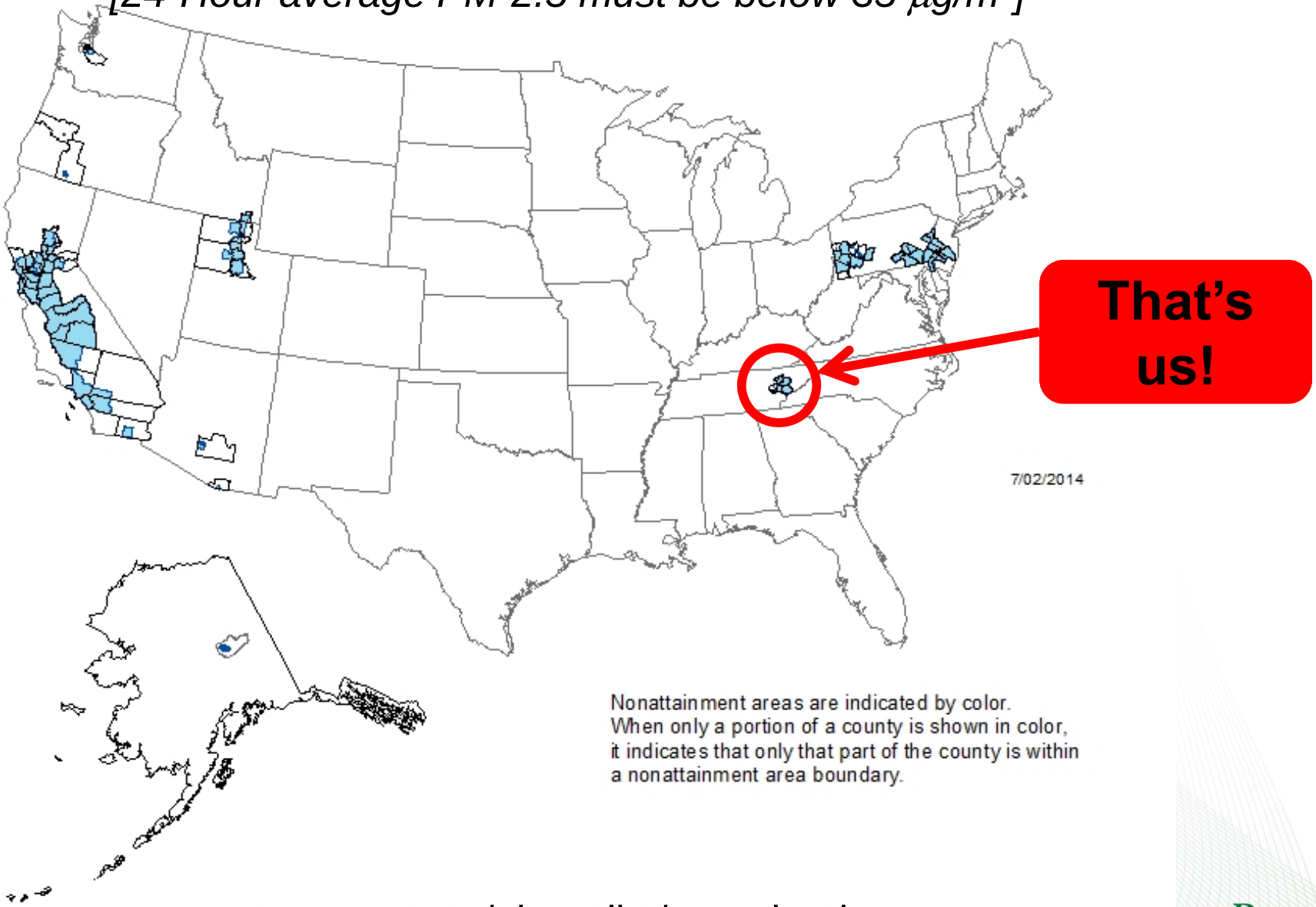
www.epa.gov/airquality/greenbook

U.S. PM-2.5 Nonattainment Areas (July 2, 2014)

PM-2.5 is Particulate Matter under 2.5 microns

PM-2.5 Nonattainment Areas (2006 Standard)

[24-Hour average PM-2.5 must be below 35 $\mu g/m^3$]



www.epa.gov/airquality/greenbook

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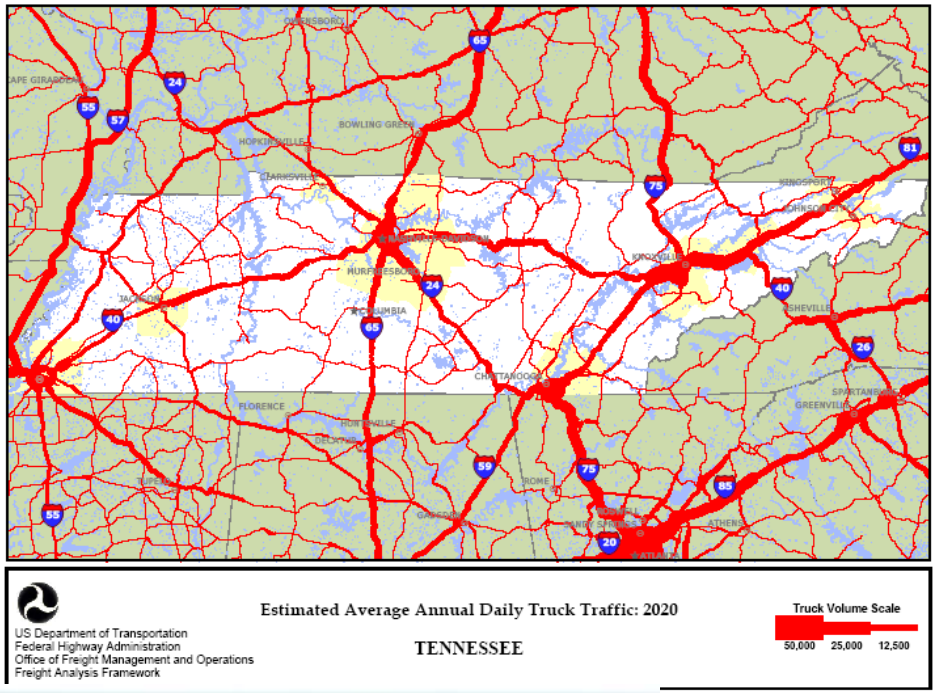
Our local air quality issues affect local tourism as well as health impacts

Our air quality is complicated by:

- >20,000 heavy-duty trucks per day travelling on I-40/I-75 corridor
- Our trees (HC emissions)
- Our geography (valleys can trap pollutants)



Good Visibility Day
Visual Range: 124 miles

Bad Visibility Day
Visual Range: 26 miles

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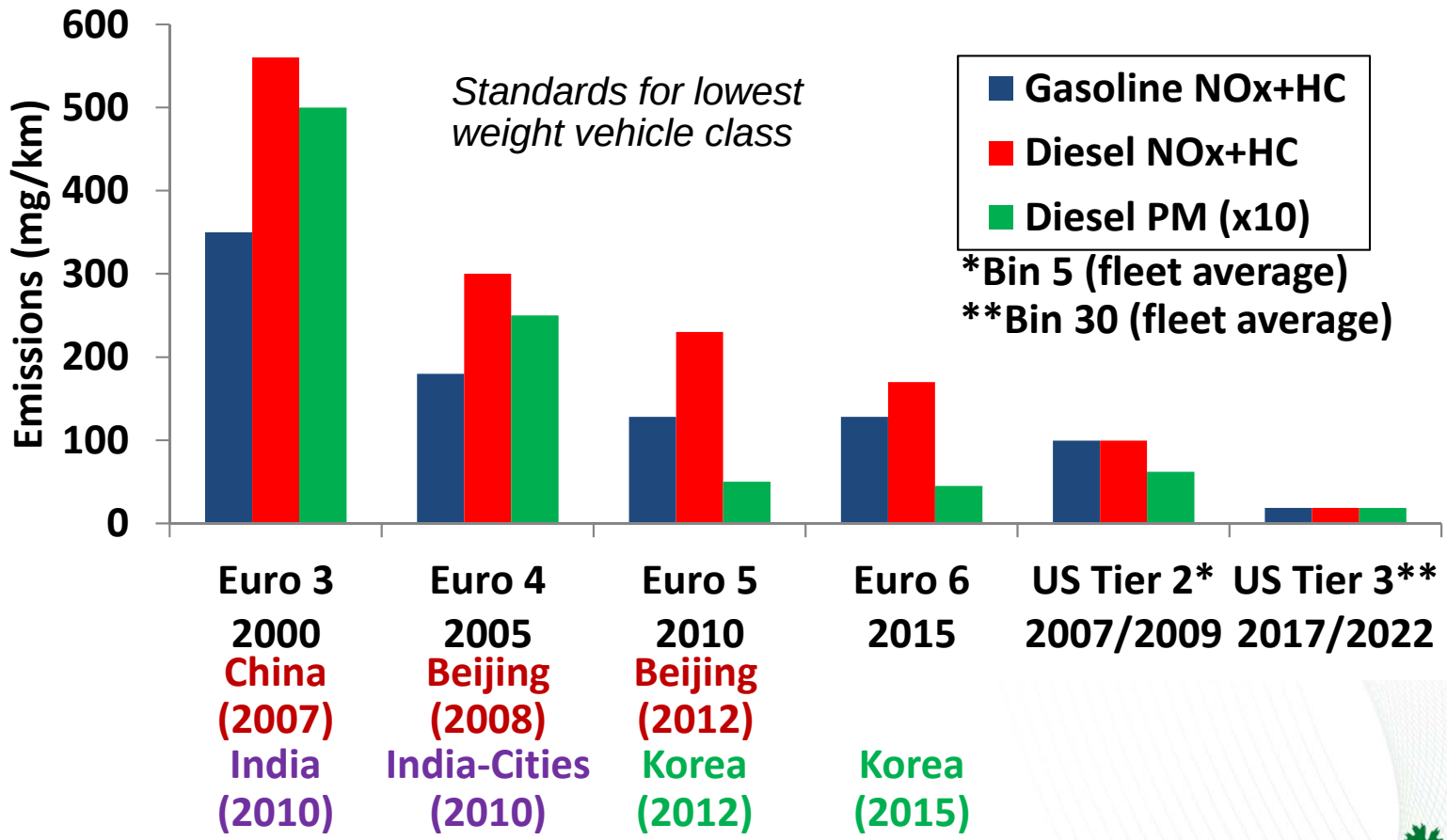
U.S. EPA Regulations Control Vehicle Emissions and are the World's Best

- The Clean Air Act of 1970 established means to regulate vehicle emissions (to protect human health)
- Current vehicles sold meet U.S. EPA Tier 2 standards
- Recent new Tier 3 standards require even lower vehicle emissions

The U.S. has the most stringent vehicle emission standards in the world

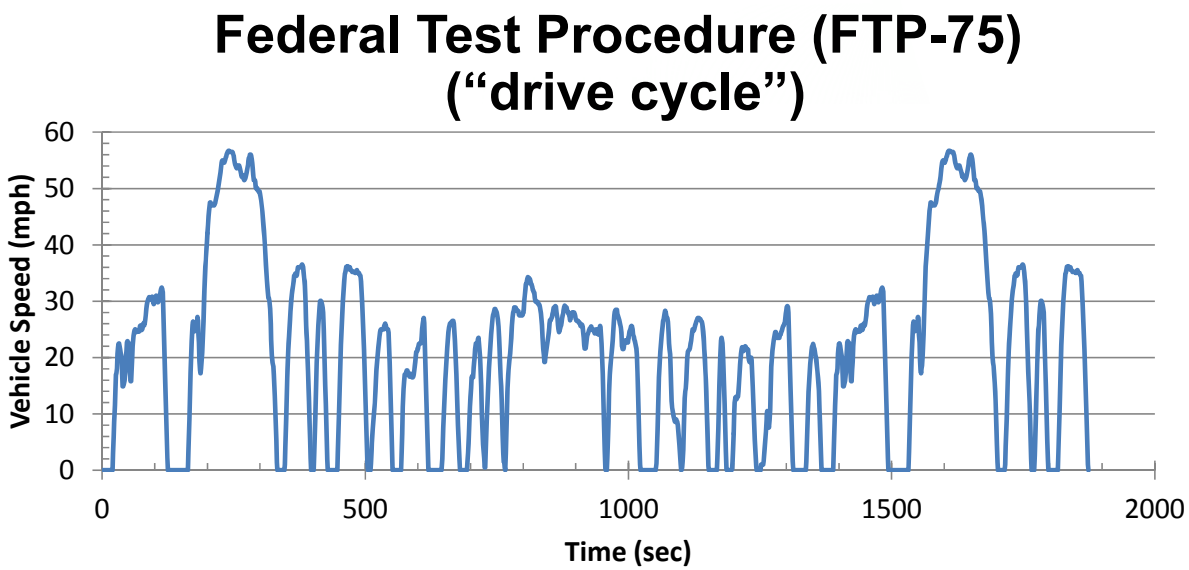


Thanks to Joe Kubsh of the Manufacturers of Emissions Controls Association for information

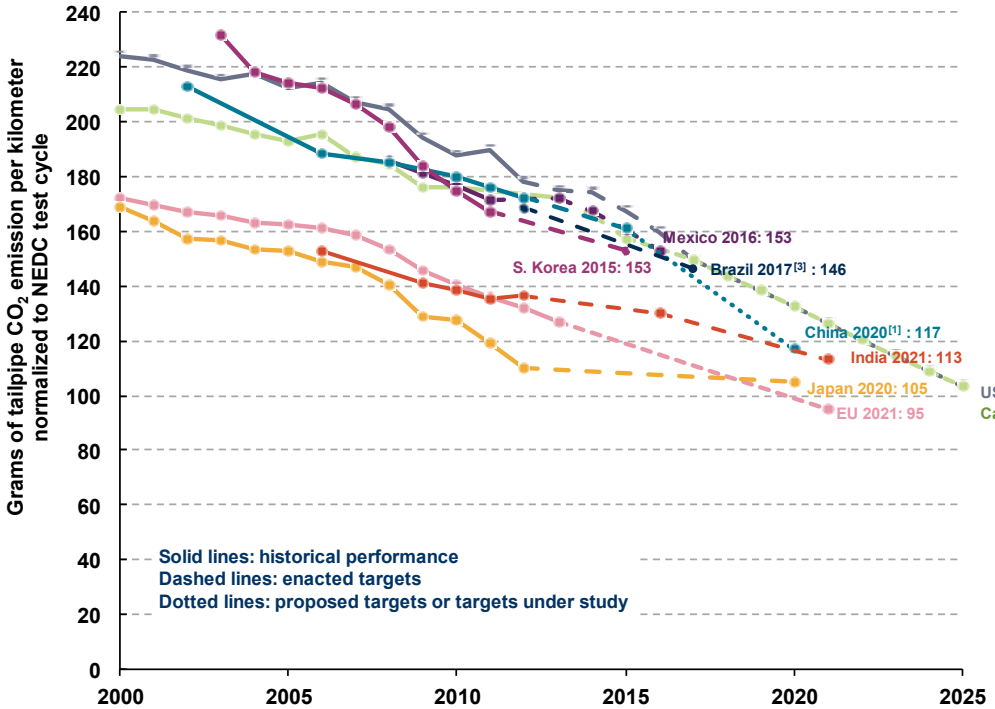
Certification to EPA regulations occurs by vehicle drive cycle on a chassis dynamometer

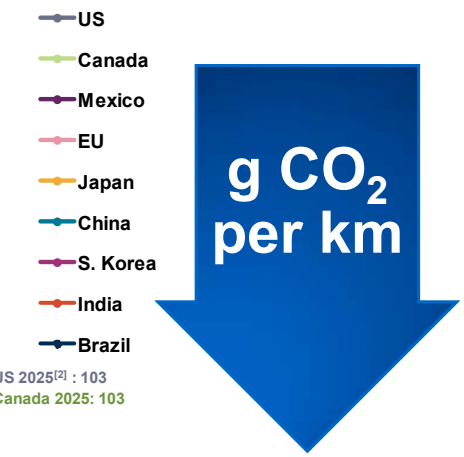
- Vehicle emissions over a drive cycle are studied on a chassis dynamometer, essentially a treadmill for cars
- A driver follows the speed trace defining a particular drive cycle
- The EPA Federal Test Procedure (FTP-75) includes a cold start
- Vehicle miles per gallon (MPG) is also obtained via the drive cycle

Vehicle on ORNL's chassis dynamometer



Greenhouse Gas Emissions from Passenger Cars also Being Regulated Worldwide

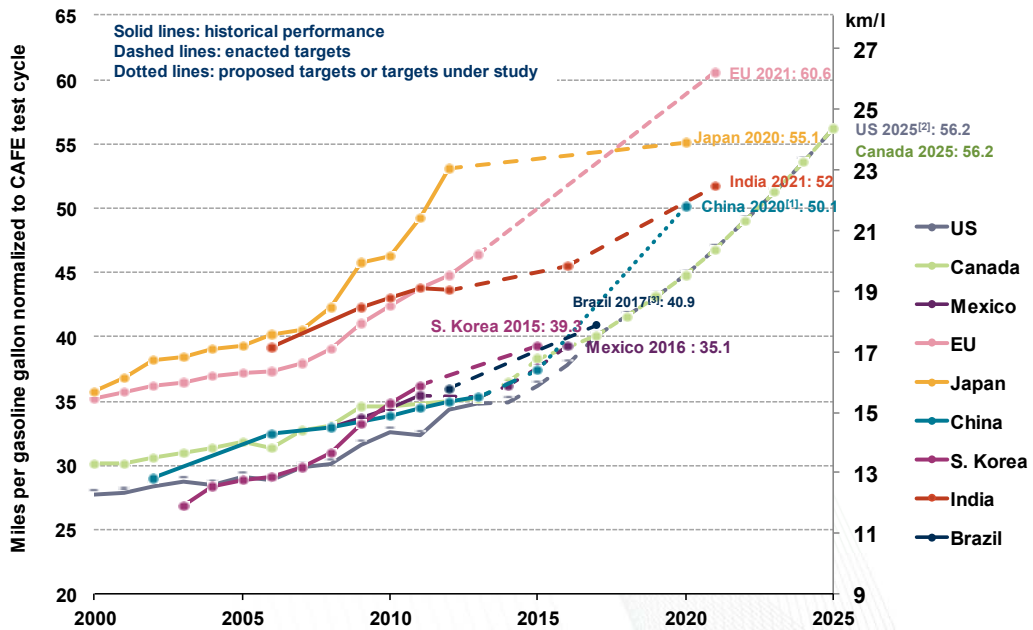




In 2012, transportation accounted for 34.7% of CO_2 emissions from fossil fuel in the U.S.

Tailpipe Greenhouse Gas Emissions also include CH_4 and N_2O

[1] China's target reflects gasoline vehicles only. The target may be higher after new energy vehicles are considered.
[2] US fuel economy stadards set by NHTSA reflecting tailpipe GHG emission (i.e. exclude low-GWP refrigerant credits).
[3] Gasoline in Brazil contains 22% of ethanol (E22), all data in the chart have been converted to gasoline (E00) equivalent
[4] Supporting data can be found at: http://www.theicct.org/info-tools/global-passenger-vehicle-standards.



[1] China's target reflects gasoline vehicles only. The target may be higher after new energy vehicles are considered.
[2] The U.S. standards are fuel economy standards set by NHTSA, which is slightly different from GHG stadards due to A/C credits.
[3] Gasoline in Brazil contains 22% of ethanol (E22), all data in the chart have been converted to gasoline (E00) equivalent
[4] Supporting data can be found at: http://www.theicct.org/info-tools/global-passenger-vehicle-standards.

Fuel economy and Greenhouse Gas Emissions directly linked: improving one, improves the other

Source: www.theicct.org (The International Council on Clean Transportation)

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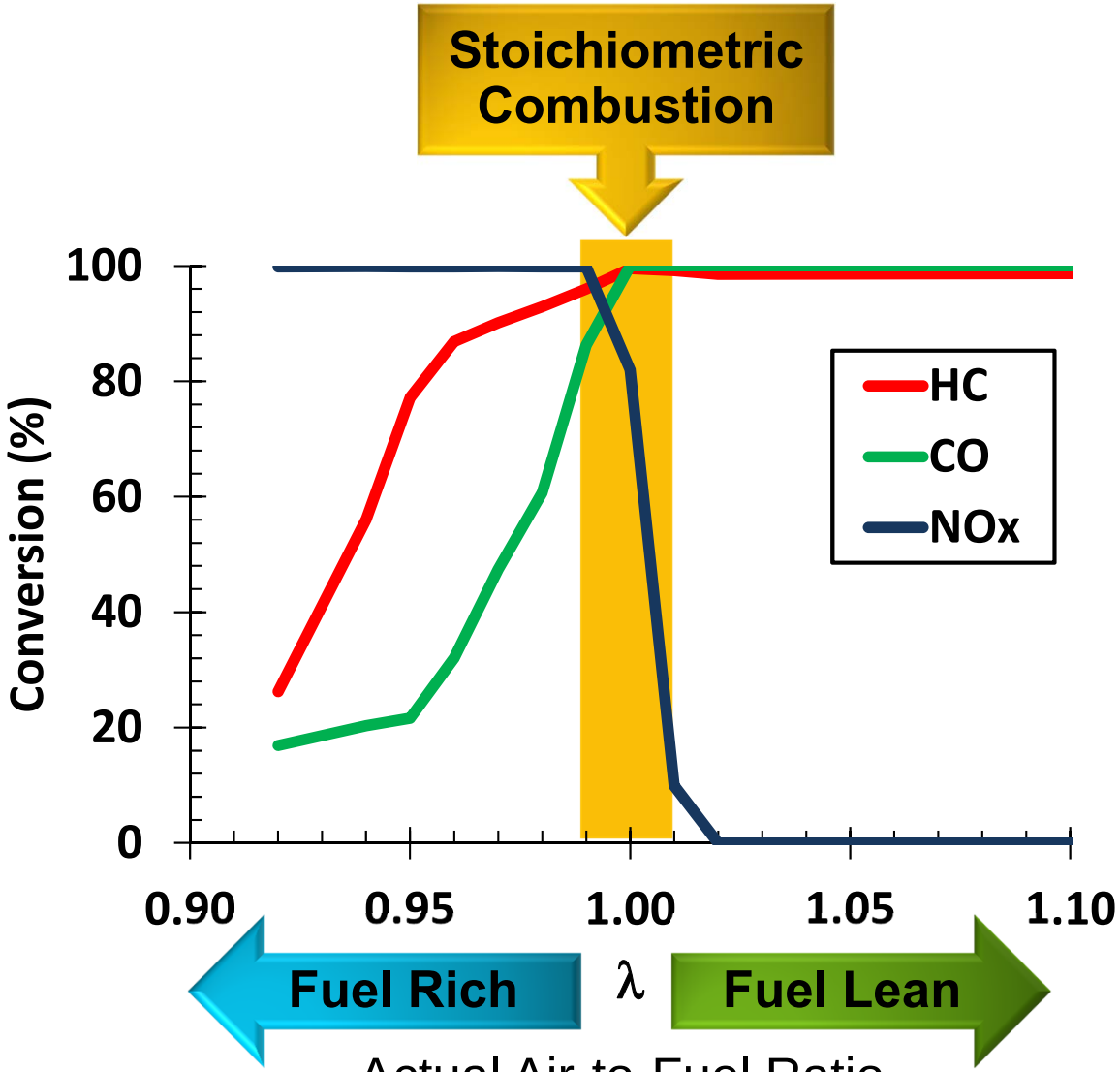
Since the 1970s, the Three-Way Catalyst (TWC) has dramatically reduced vehicle emissions

Spark-Ignited Gasoline Engine + **Three-Way Catalyst (TWC)**



$$\lambda = \frac{\text{Actual Air-to-Fuel Ratio}}{\text{Stoichiometric Air-to-Fuel Ratio}}$$

Stoichiometric Combustion:
Air-to-Fuel Ratio such that all fuel and oxygen are consumed in reaction (enabled by oxygen sensor feedback)

$$2HC + 2.5O_2 \rightarrow H_2O + 2CO_2$$

Three-Way Catalyst in Exhaust "Can"

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Vehicle Drivetrain Systems and Emission Controls

Less Petroleum*

Spark-Ignited Gasoline Engine + **TWC**

Stoichiometric engines dominate U.S. fleet; clean, but room for fuel efficiency improvement

Lean Gasoline SI Direct Injection Engine + **TWC** + **LNT** + **GPF** ?

or + **TWC** + **SCR** + **GPF** ?

Diesel Engine + **DOC** + **LNT** + **DPF**

or + **DOC** + **SCR** + **DPF**

Lean-burn engines are more efficient, but NOx is difficult to reduce in O_2-rich exhaust

Next Generation Internal Combustion Engine (R&D Stage) + ???

Hybrid Electric Vehicle + **TWC** + ???

Electric Vehicle (Nothing onboard – control at power plant)

TWC=Three-Way Catalyst
LNT=Lean Nox Trap
SCR=Selective Catalytic Reduction
DOC=Diesel Oxidation Catalyst
GPF=Gasoline Particulate Filter
DPF=Diesel Particulate Filter

** Less petroleum but …cost, performance, CO_2, etc. may vary*

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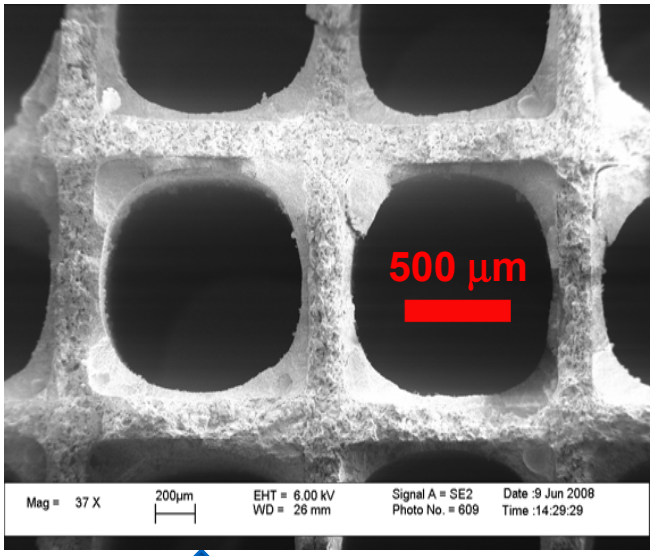
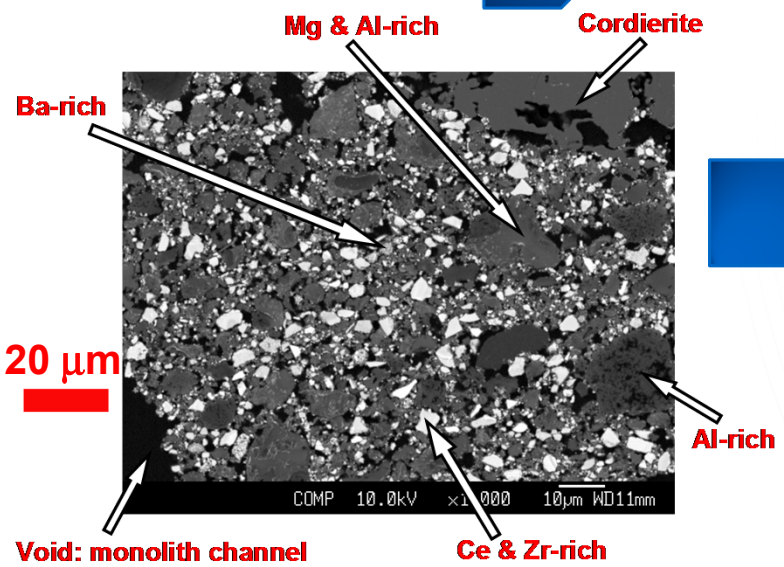
A closer look at catalysts...

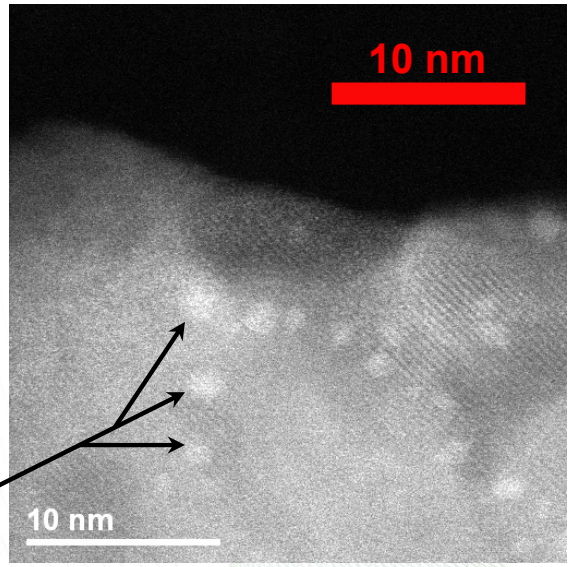
~10 acres of surface area!!!

Zoom



Goal is finely dispersed active sites





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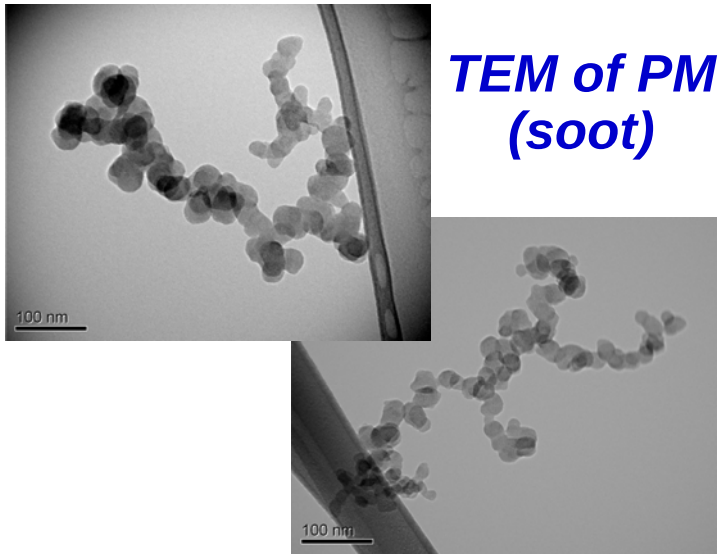
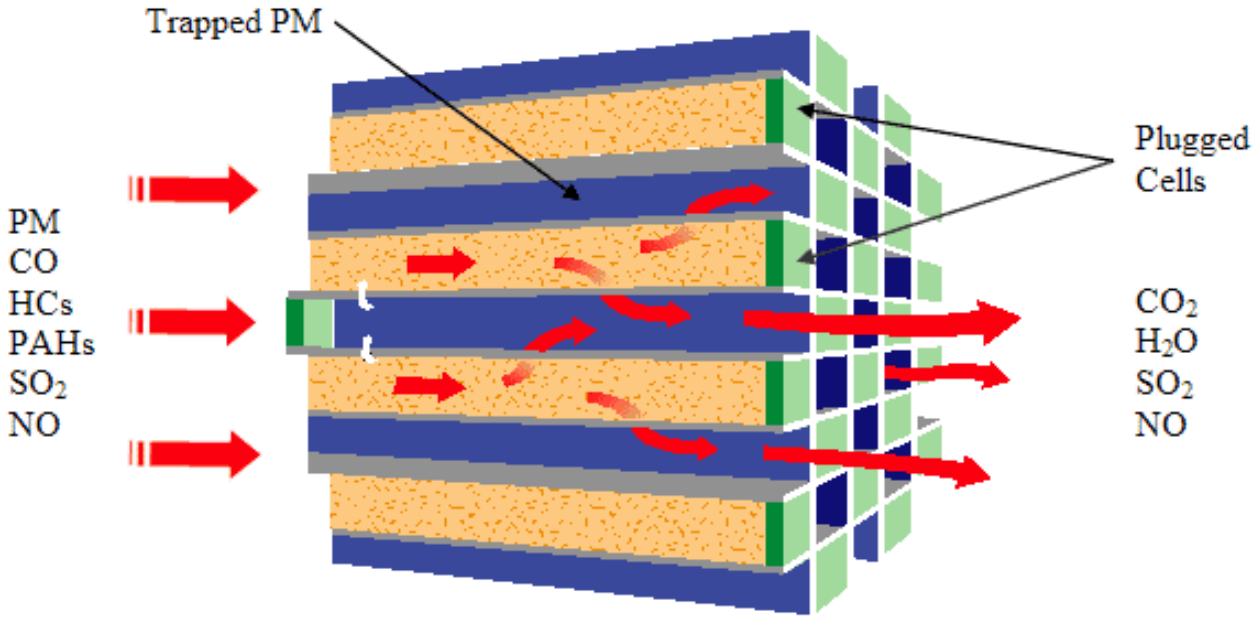
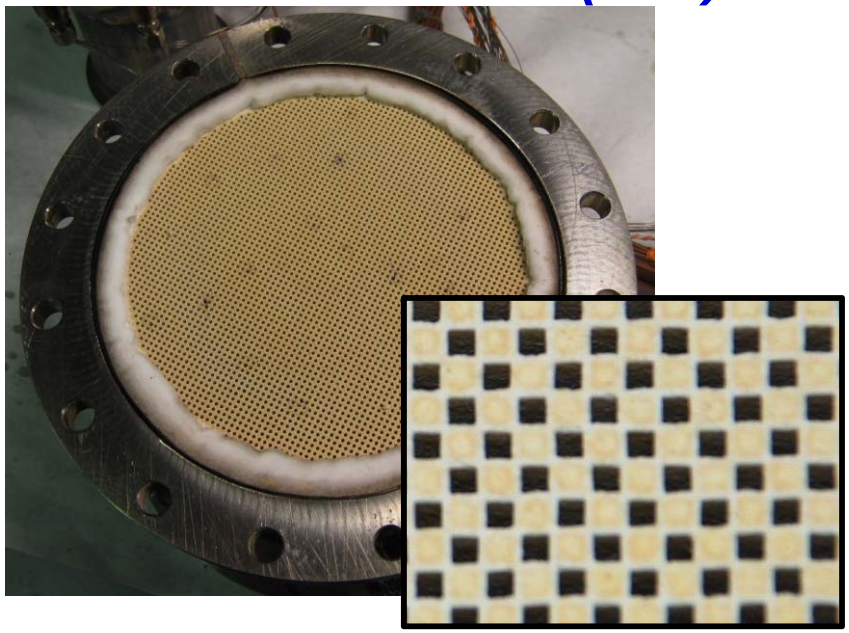
Particulate Filters Trap and Oxidize Soot

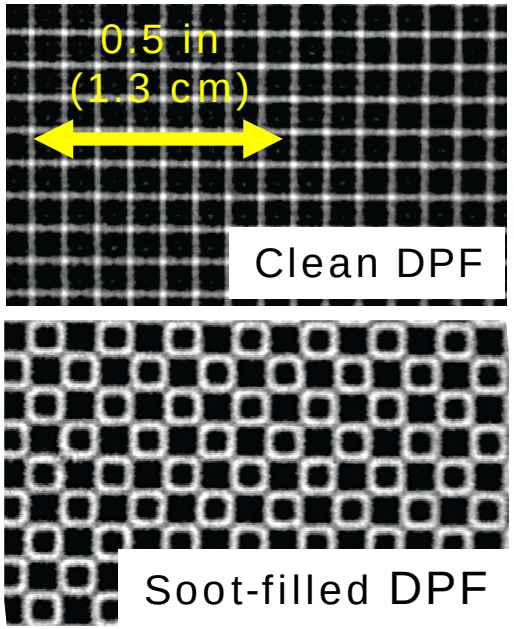


TEM of PM (soot)



Diesel Particulate Filter (DPF)





Neutron Images of DPF without (top) and with (bottom) soot

[ORNL's HFIR CG-1D Imaging Beamline]

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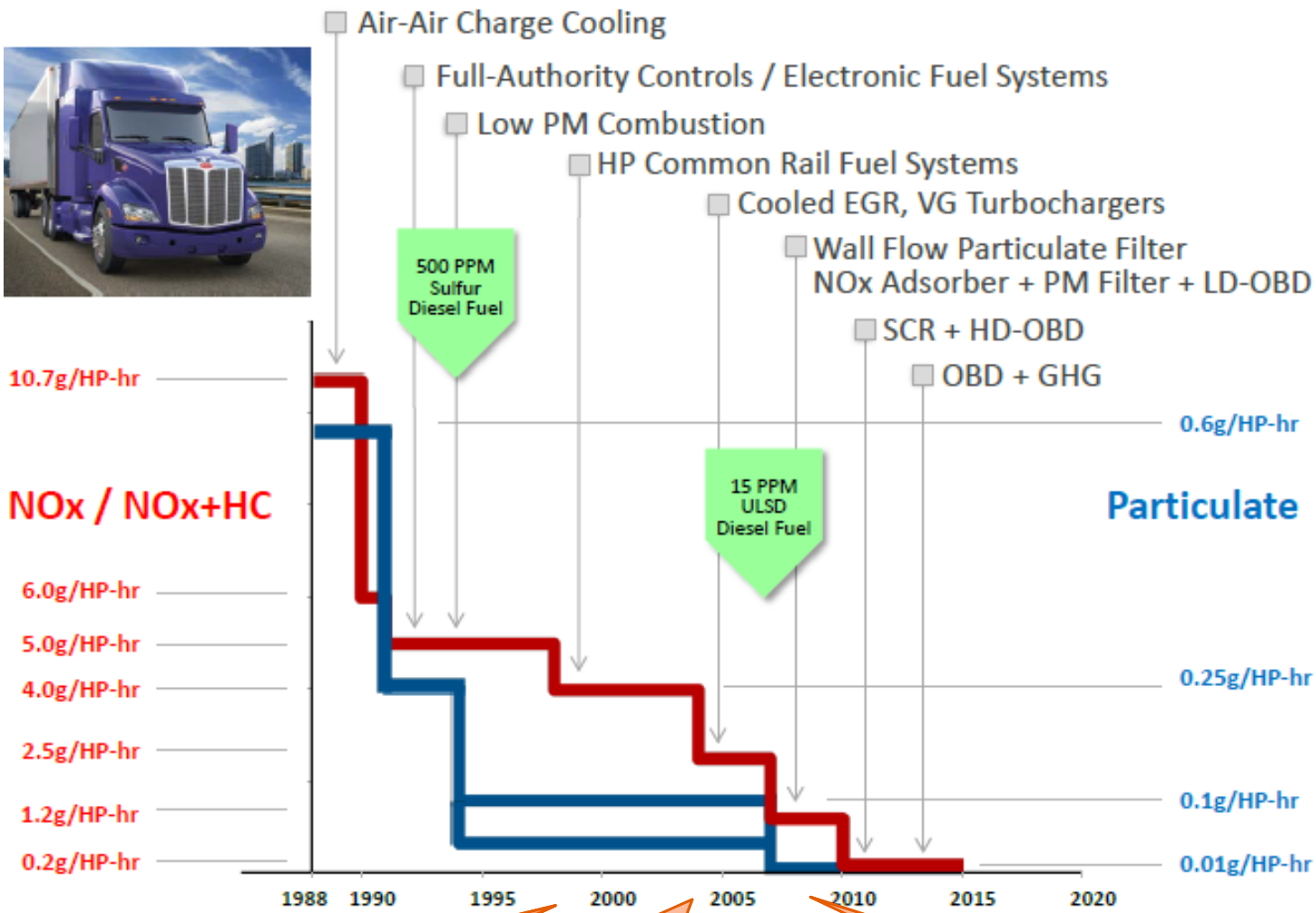
ORNL Contributions have Dramatically Cleaned Up Heavy-Duty Trucks (1998-)

ORNL research on sulfur effects cited by EPA in rulemaking to remove S from diesel fuel



2007: DPFs installed for all new models (>99% soot removal!)

2010: SCR added to bring NOx to <0.2 g/bhp-hr

DECSE Program laid groundwork to justify S reduction in diesel fuel

Research in combustion and emission control technologies

Durability and controls (active regeneration) research

Graphic from Wayne Eckerle (Cummins), 2013 SAE Fuels, Lubricants, and Aftertreatment Symposium

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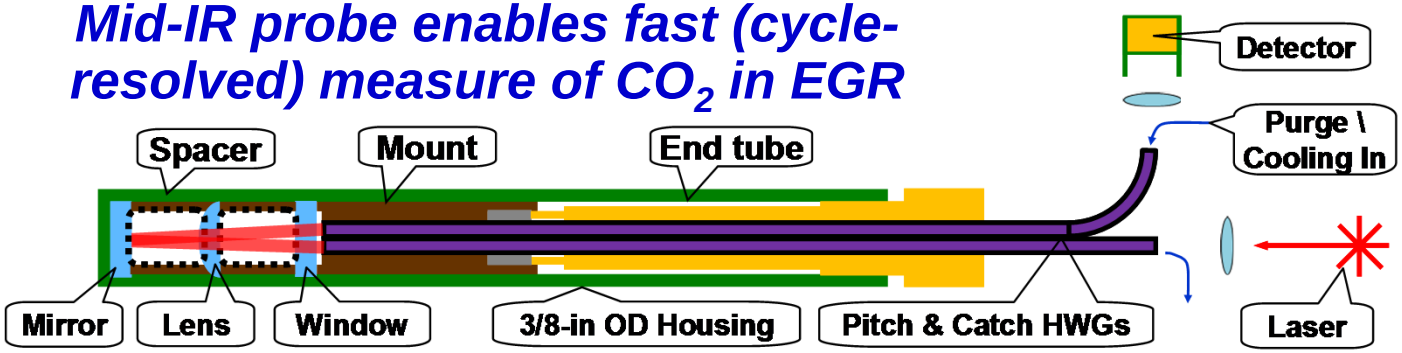
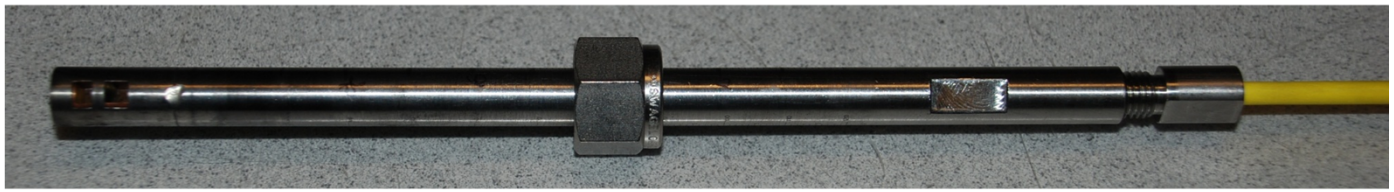
Heavy-Duty Truck Improvements Continue via ORNL's Unique Diagnostic for EGR

Mid-IR probe enables fast (cycle-resolved) measure of CO_2 in EGR

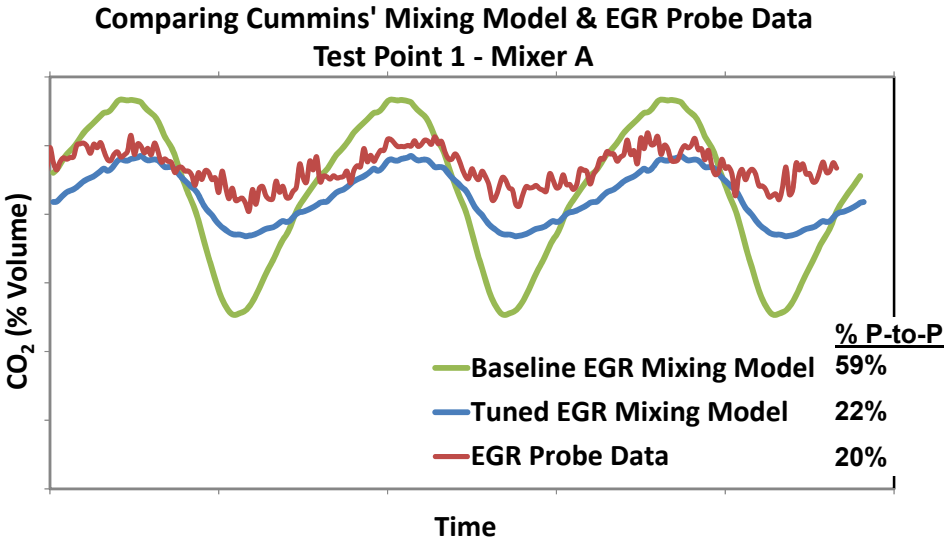




In partnership with Cummins

Mid-IR probe in engine intake

Unique ORNL mid-IR probe enables measurement of transient and spatially varying exhaust gas recirculation (EGR) process [EGR utilized to reduce emissions in-cylinder on engines]



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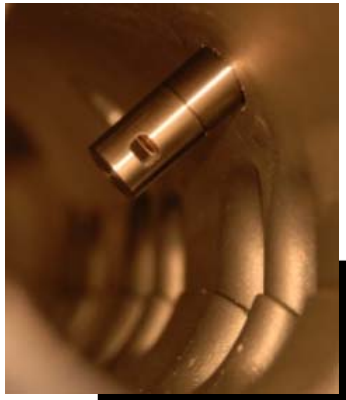
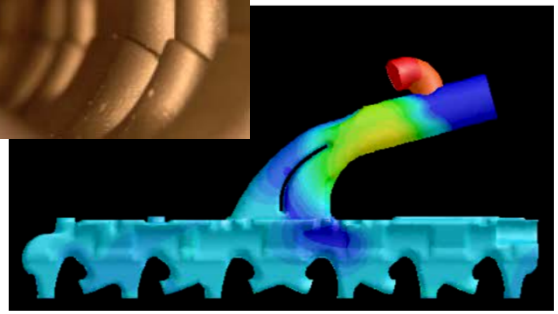
SuperTruck Achieves 75% Fuel Economy Gain

"Thanks to a partnership between industry and my administration, the truck behind me was able to achieve a 75 percent improvement in fuel economy,"
President Barack Obama
February 18, 2014

ORNL applied a novel infrared spectroscopy fiber optic probe to Cummins' engines to improve engine design and meet the critical fuel efficiency goals of the SuperTruck program



ORNL exhaust gas recirculation (EGR) probe in the intake manifold of an engine [left]



Cummins simulation of EGR mixing in the intake manifold (improved by ORNL experimental measurements) [left]

ORNL Post-Doc Jon Yoo deploying four multiplexed EGR probes in a Cummins engine at the Cummins Technical Center in Columbus, IN [right]

The SuperTruck team: Cummins, Peterbilt, ORNL, Modine, Purdue University, U.S. Xpress, Eaton, Bergstrom, and Goodyear [funded by DOE Vehicle Technologies Office and industry partners]

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Sustainable Transportation Program… "all of the above"

Electrification

- Wireless power transfer
- Modeling, manufacturing, and materials for improved batteries
- Advanced power electronics and traction motors.
- Fuel Cells

Efficiency

- Engine and aftertreatment technologies
- Hybrid powertrains
- Materials for lighter weight and more efficient propulsion

Alternative fuels

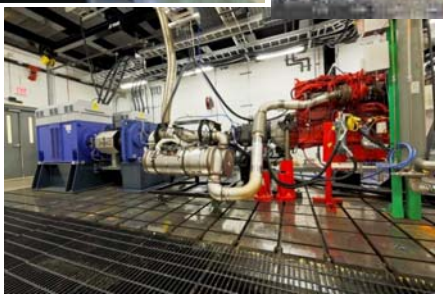
- Drop-in biofuels for legacy cars
- Renewable fuels for advanced engines
- Natural gas

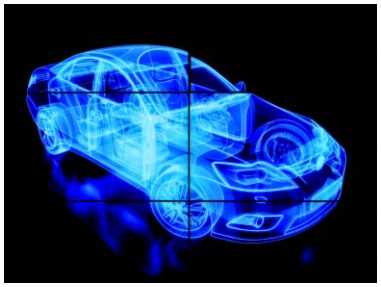
Intelligent systems

- Managing congestion
- Efficient operations in commercial vehicles
- Data for decision-making
- Communications

New technologies and processes for:

- Safe, secure, and affordable vehicles for passengers and freight
- Domestic production of transportation fuel
- Reducing environmental impacts of transportation
- Predictable, reliable transport schedules





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Sustainable Transportation Program… "all of the above"

Electrification

New technologies

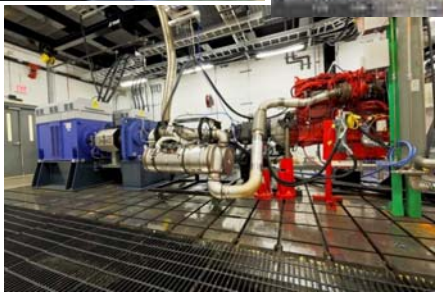
Although all of these technologies will be part of the transportation market, internal combustion engines (ICEs) will persist.

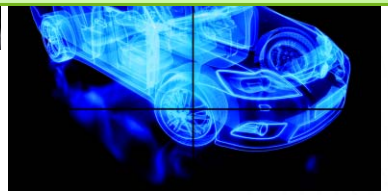
"…ICEs … are going to be the dominant automotive technology for decades, whether in conventional vehicles, hybrid vehicles, PHEVs, biofueled or natural gas vehicles."

Review of the Research Program of the U.S. DRIVE Partnership: 4th Report, NRC 2013

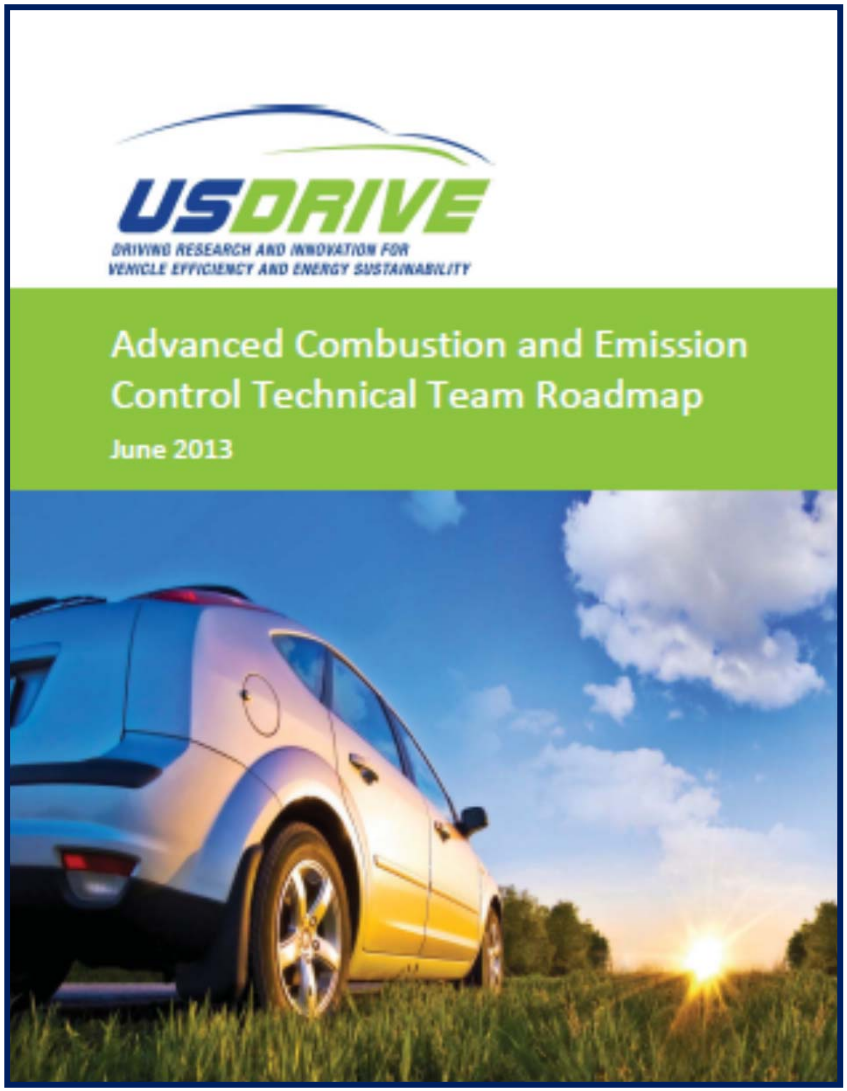
"…even by 2040, over 99% of vehicles sold will have internal combustion engines."

Annual Energy Outlook 2014, Early Release, December 2013





US DRIVE Industry Team Identifies Three Combustion Approaches to Meet Challenges



Combustion Approaches

- **Low Temp Combustion**
- **Dilute Gasoline Combustion**
- **Clean Diesel Combustion**

Each combustion approach has unique emission control challenges

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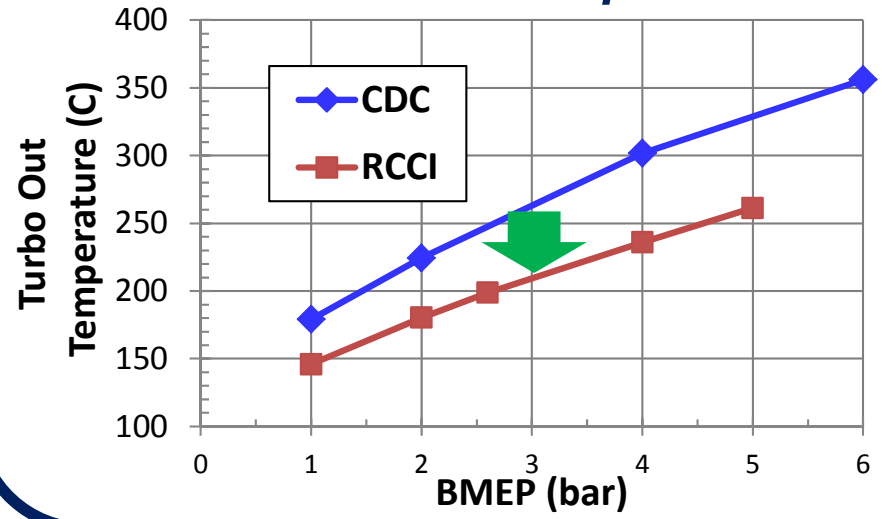
A common theme for combustion approaches is lower exhaust temperatures (need better catalysts)

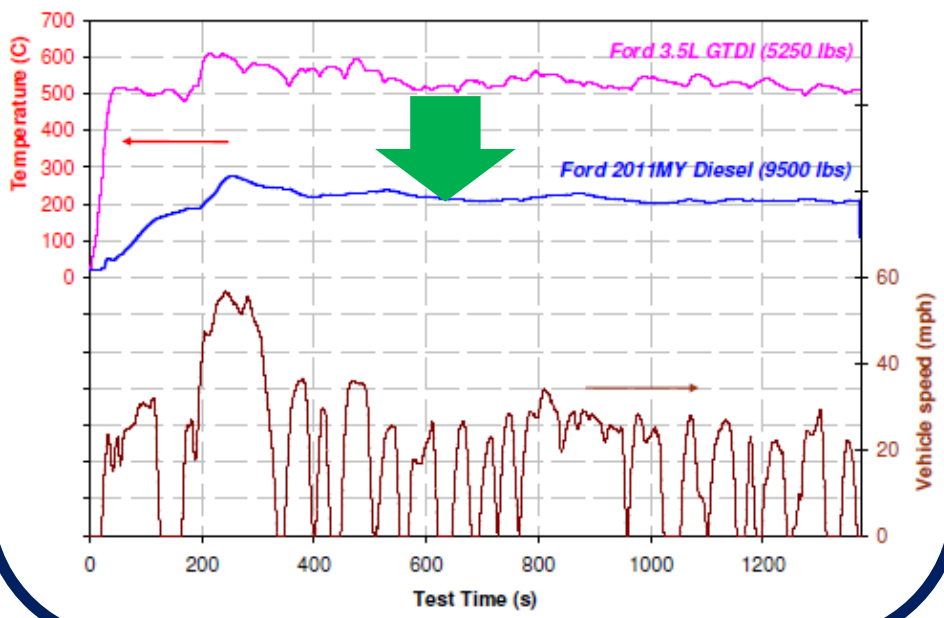
Lower exhaust temperatures require lower light-off catalysts to enable emission compliance and commercialization for:

- **Low Temperature Combustion (LTC)**
- **Dilute Gasoline Combustion**
- **Clean Diesel Combustion (CDC)**

Higher efficiency of LTC (RCCI) lowers exhaust temperatures



Diesel exhaust temperatures lower than gasoline over drive cycle



Turbochargers lower exhaust temperature

Diesel graph: C. Lambert, "Future Directions in SCR Systems", 2012 CLEERS workshop, 05/01/2012.
Turbo: http://www.autoblog.com/2012/10/03/turbo-sales-to-accelerate-by-80-could-make-up-40-of-global-of/

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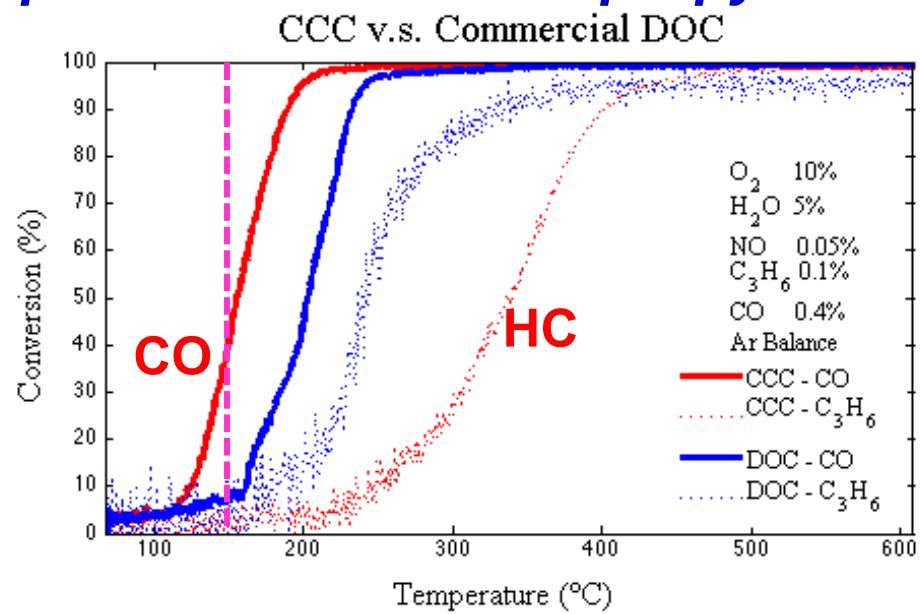
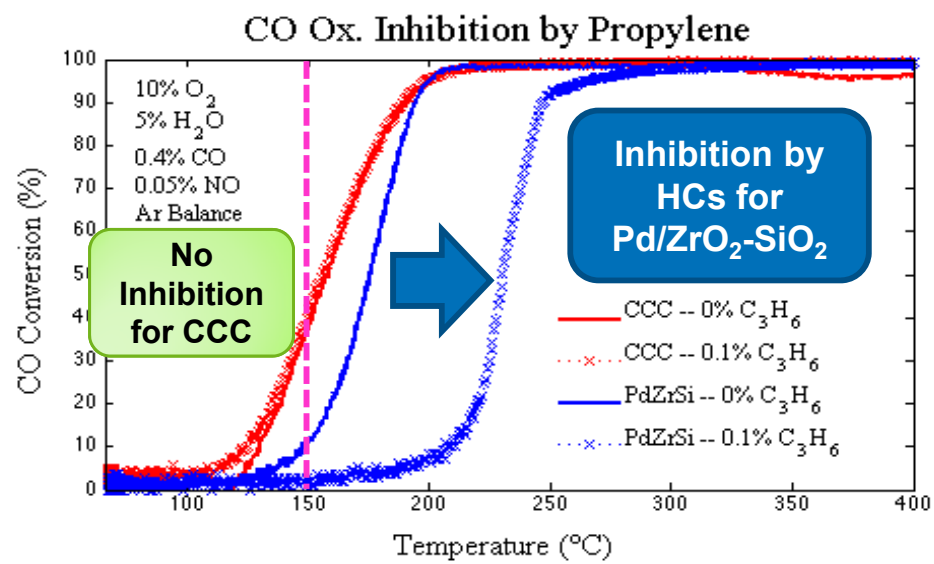
New CuO_x-CoO_y-CeO_2 catalyst oxidizes CO without HC inhibition (a major breakthrough)

Co-precipitated CuO_x, CoO_y, and CeO_2 (dubbed CCC catalyst) has shown to have both ***high CO oxidation activity*** *and* ***exceptional tolerance for propylene.***

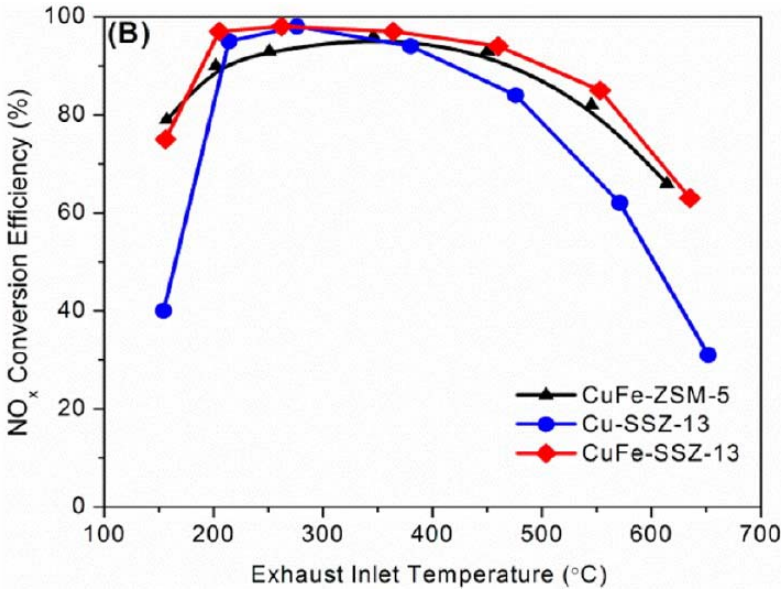
- PGM-Free CCC (red) **outperforms commercial catalysts** currently used in DOC (blue) washcoats for oxidation of CO
  - However, hydrocarbon oxidation temperature higher
- **Projected cost to be very low**.

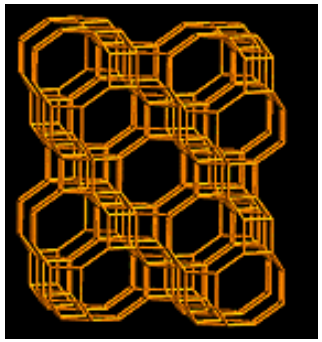


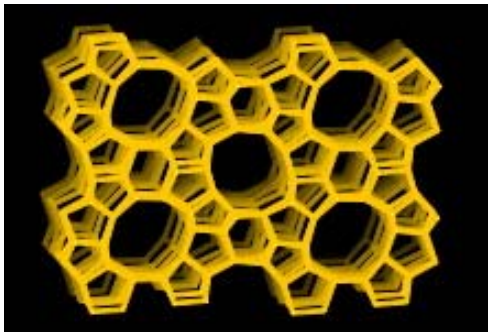
- CO oxidation inhibition by propylene is readily seen on platinum group metal (PGM) catalysts such as the Pd/ZrO_2-SiO_2 catalyst shown here (blue).
- **But…No inhibition found for CCC catalyst** (red).



New Advances in SCR Formulations Show Lower Temperature Performance







Theoretical studies suggest that iron exists as small oxide cluster with the pores of Cu-SSZ-13 (left) and Cu-ZSM-5 (right) and is bonded to Cu via oxygen bridge. [unpublished results] This arrangement enhances formation of NO+, required for NO_x reduction [JPC C 2012].

- A new Low Temperature NH_3 SCR catalyst (CuFe-SSZ-13) shows **remarkable low temperature reactivity** as compared with commercial (state-of-the-art) Cu-SSZ-13
- CuFe-SSZ-13 is hydrothermally stable when tested after subjecting to accelerated aging protocol

Reference (ORNL): X. Yang, Z. Wu, M. Moses-Debusk, D. R. Mullins, S. M. Mahurin, R. A. Geiger, M. Kidder, and C. K. Narula, *J. Phys. Chem. C* 2012, 116, 23322−23331

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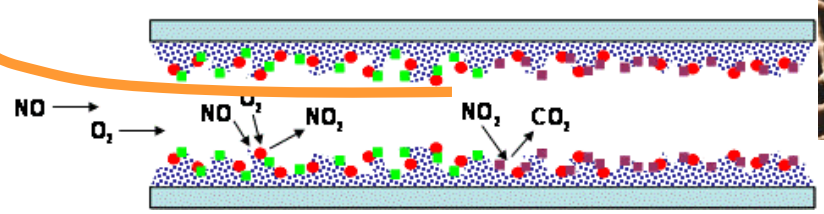
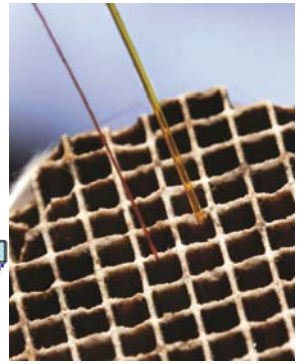
Unique diagnostic tools like SpaciMS developed at ORNL enable new insights

R&D 100

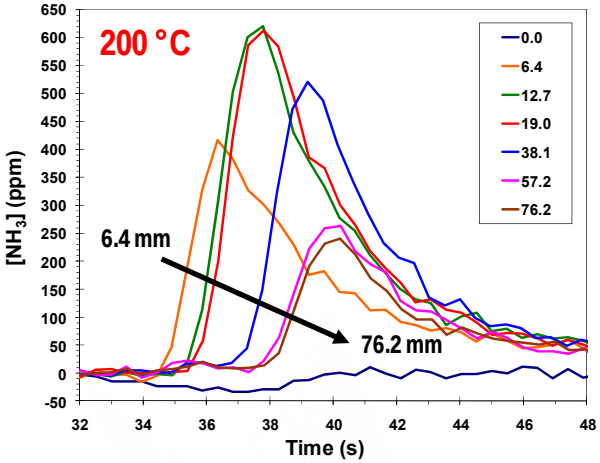
Extensive reactor study of LNTs with spatiotemporal resolution of reactions

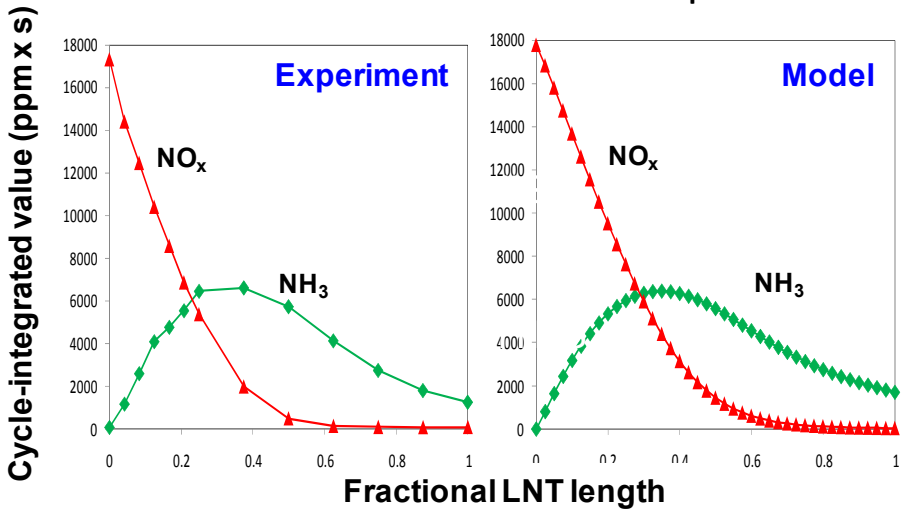




Insights from experiments strengthen LNT models through better understanding of

- Intermediate roles of NH_3
- Spatial distribution of NO_x





Findings and global model development enable efficient management of LNT ammonia leading to:

- Reduced NH_3 slip for stand-alone LNT
- Improved NO_x conversion via coupled LNT-SCR

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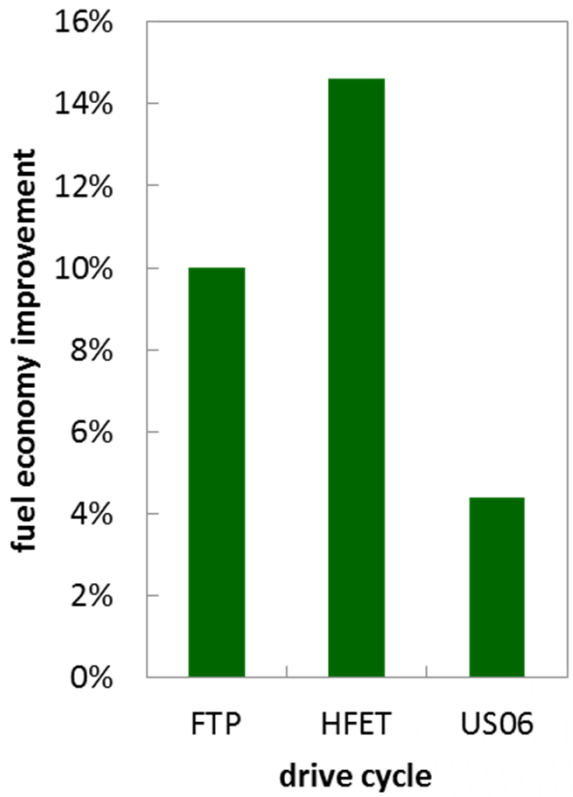
Lean gasoline direct injection (GDI) engine improves efficiency, but creates emissions challenges

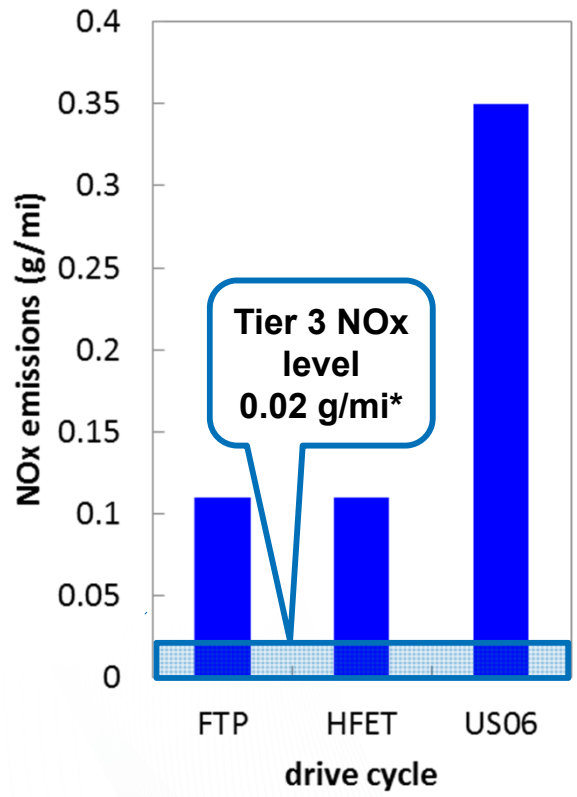
Case in Point:
The **European BMW 120i…**
a lean gasoline vehicle of marketable size that achieves **4-15% better fuel economy** than common "stoich" gasoline vehicles, but…

does *not* meet U.S. Tier 2 Bin 5 emission regulations (and Tier 3 even lower!)

Fuel economy improvement with lean operation (relative to stoichiometric)



NOx emissions problematic (from lean operation)



NOTE: fuel economy and emissions measurements included effects from operation of lean NO_X trap (stock on BMW 120i vehicle)

**assuming HC level of 0.01 g/mi (NOx+HC standard is 0.03 g/mi)*

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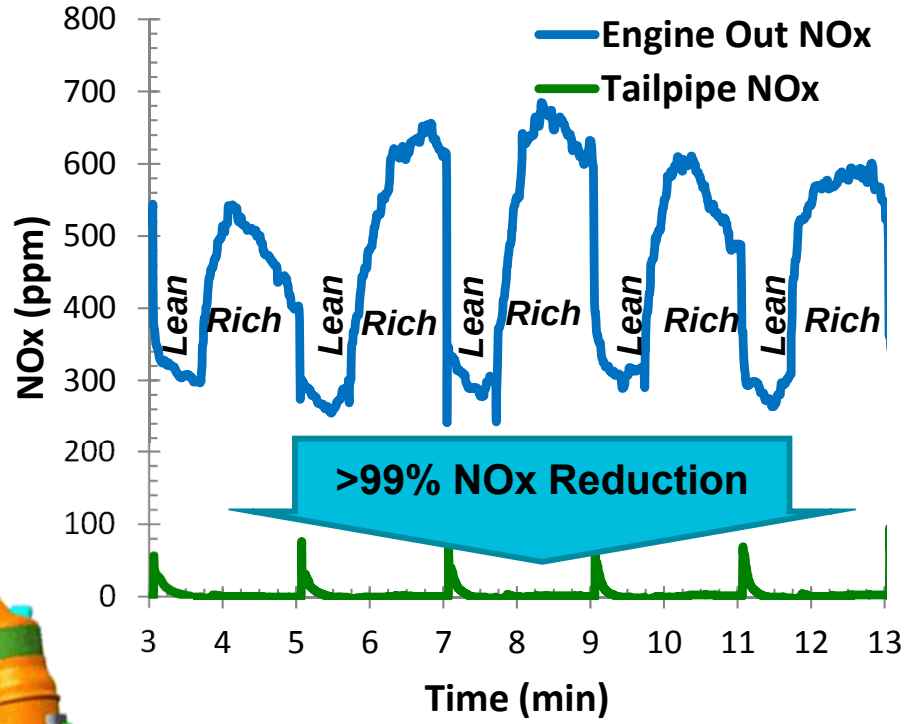
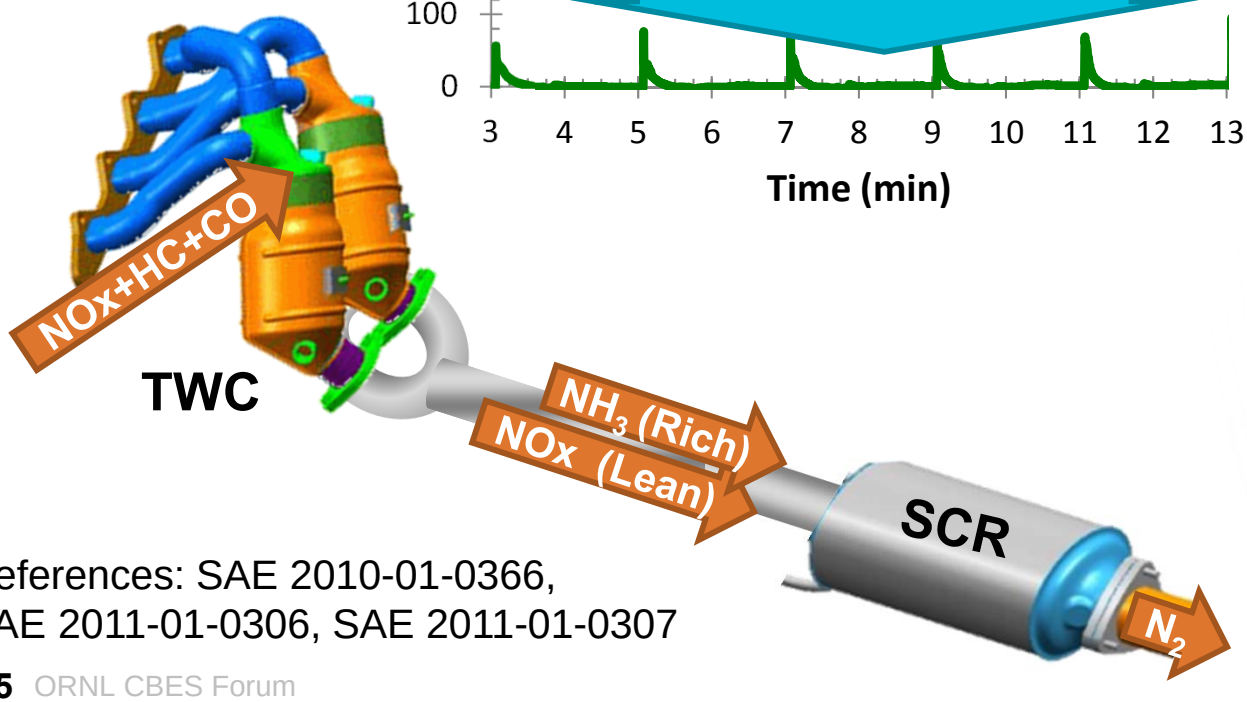
Passive SCR Approach Enables Fuel-Efficient Lean Gasoline Engine to Achieve Low Tailpipe NOx

- Passive SCR utilizes NH_3 formation over TWC and NOx reduction with stored NH_3 on downstream SCR catalyst to achieve >99% NOx reduction



Tailpipe	Avg (ppm)	Max (ppm)
NOx	5	126
NH_3	2	5
N_2O	1	10
CO	*1782*	*4658*
NMOG	*<1*	*16*

5.4% Fuel Economy gain at 2000 rpm/2 bar (steady-state)



References: SAE 2010-01-0366, SAE 2011-01-0306, SAE 2011-01-0307

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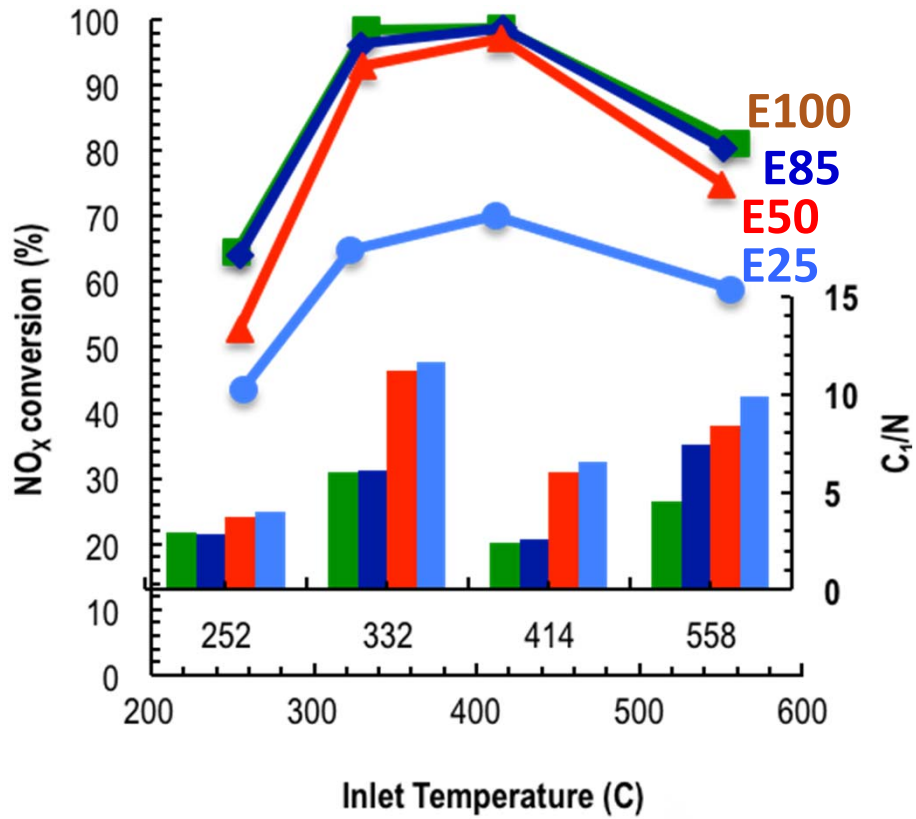
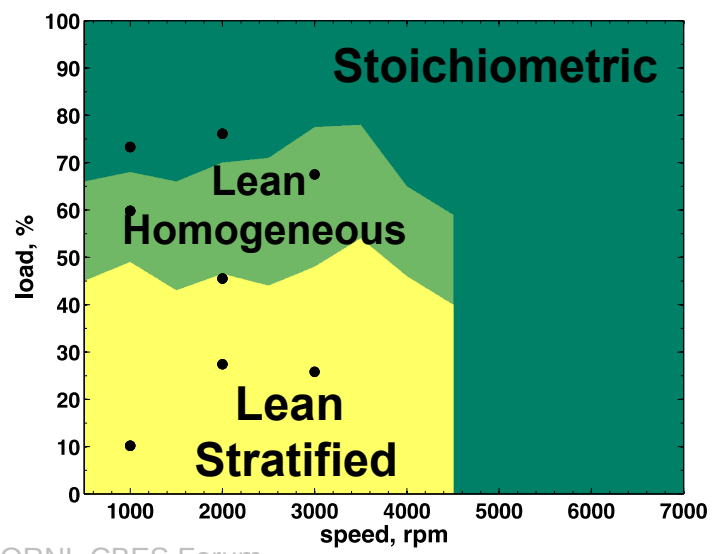
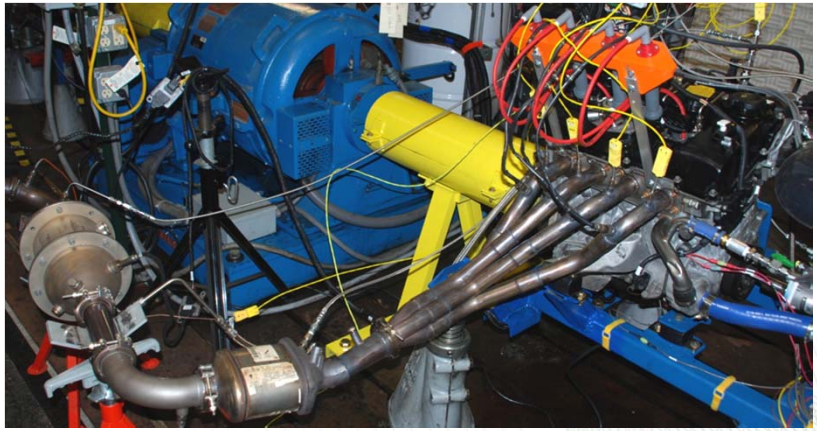
Lean NOx Emission Control with Ethanol-Gasoline Blends Shows Promise for Greater Fuel Economy with Ethanol Fuels

- Greater use of ethanol in gasoline blends can reduce petroleum use, but…tank mileage declines with higher ethanol due to lower energy density
- Lean gasoline combustion can regain lost tank mileage by improving fuel efficiency, but…lean NOx emissions are difficult to control
- ORNL team has demonstrated ability of Ag-based catalyst to reduce NOx with ethanol reductant
- >95% NOx reduction observed for E50-E100 blends in experiments on 2.0-liter engine





Lean gasoline engine (right) and operating map (left)



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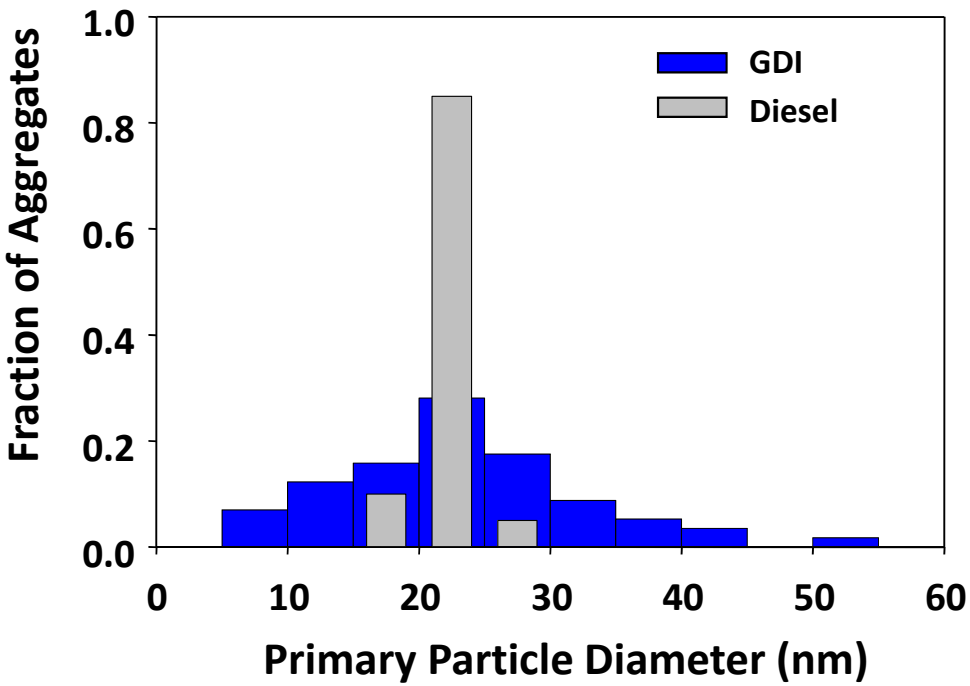
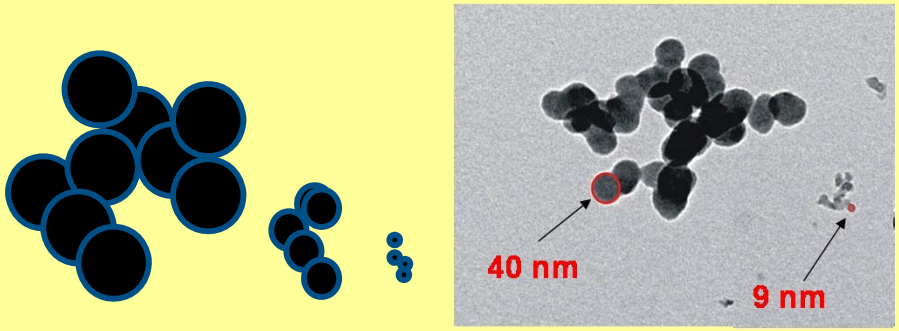
Particulate Matter (PM) Emissions from Gasoline Direct Injection (GDI) Engines Display Different Morphology Than Diesel PM

- GDI engines generally have higher PM emissions than port fuel injection gasoline engines
- PM morphology from GDI engines is notably different than diesel PM
- While in-cylinder control techniques are being studied, aftertreatment options must be optimized for unique GDI PM



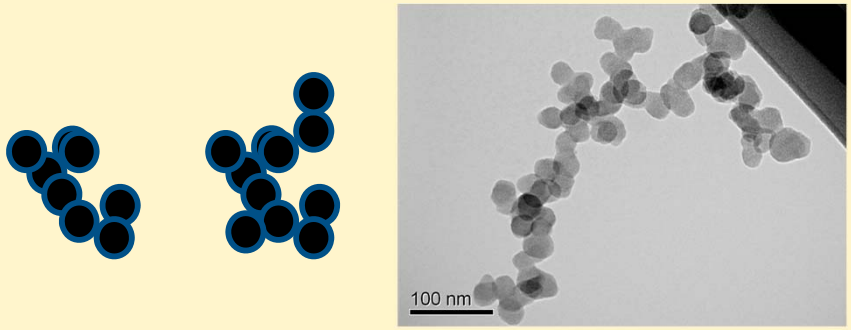
GDI PM emissions

- Aggregates of <u>different</u> size primary particles
- More single particles and less aggregates



Diesel PM emissions

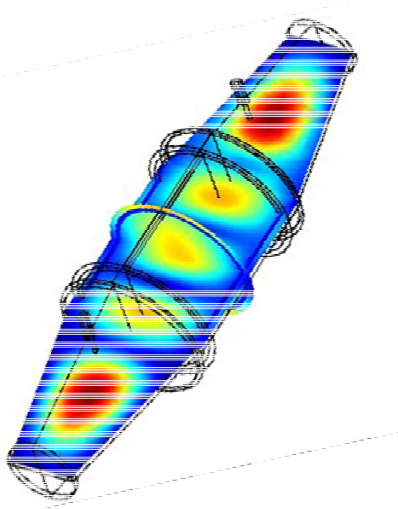
- Aggregates of <u>same</u> size primary particles
- Almost entirely aggregates

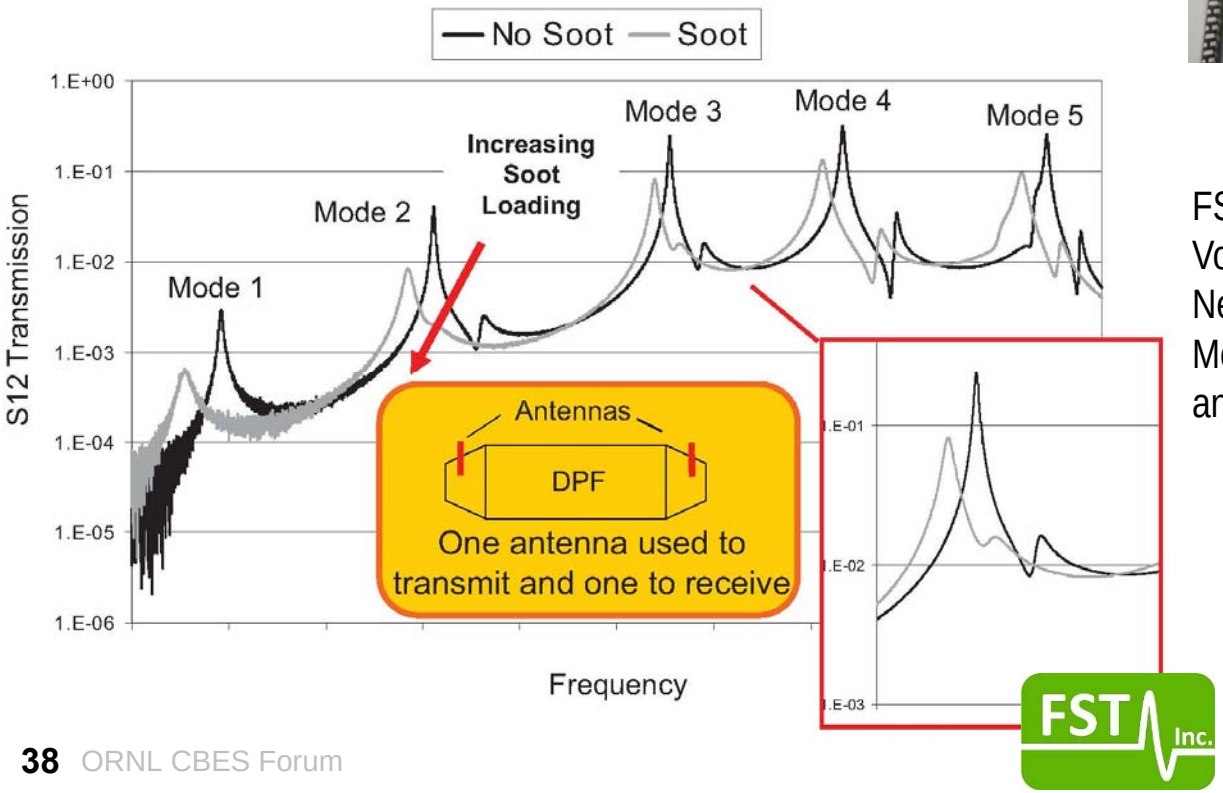


Reference (ORNL): SAE 2012-01-0437

ORNL partners on RF-DPF™ sensor for fuel efficient diesel filter control

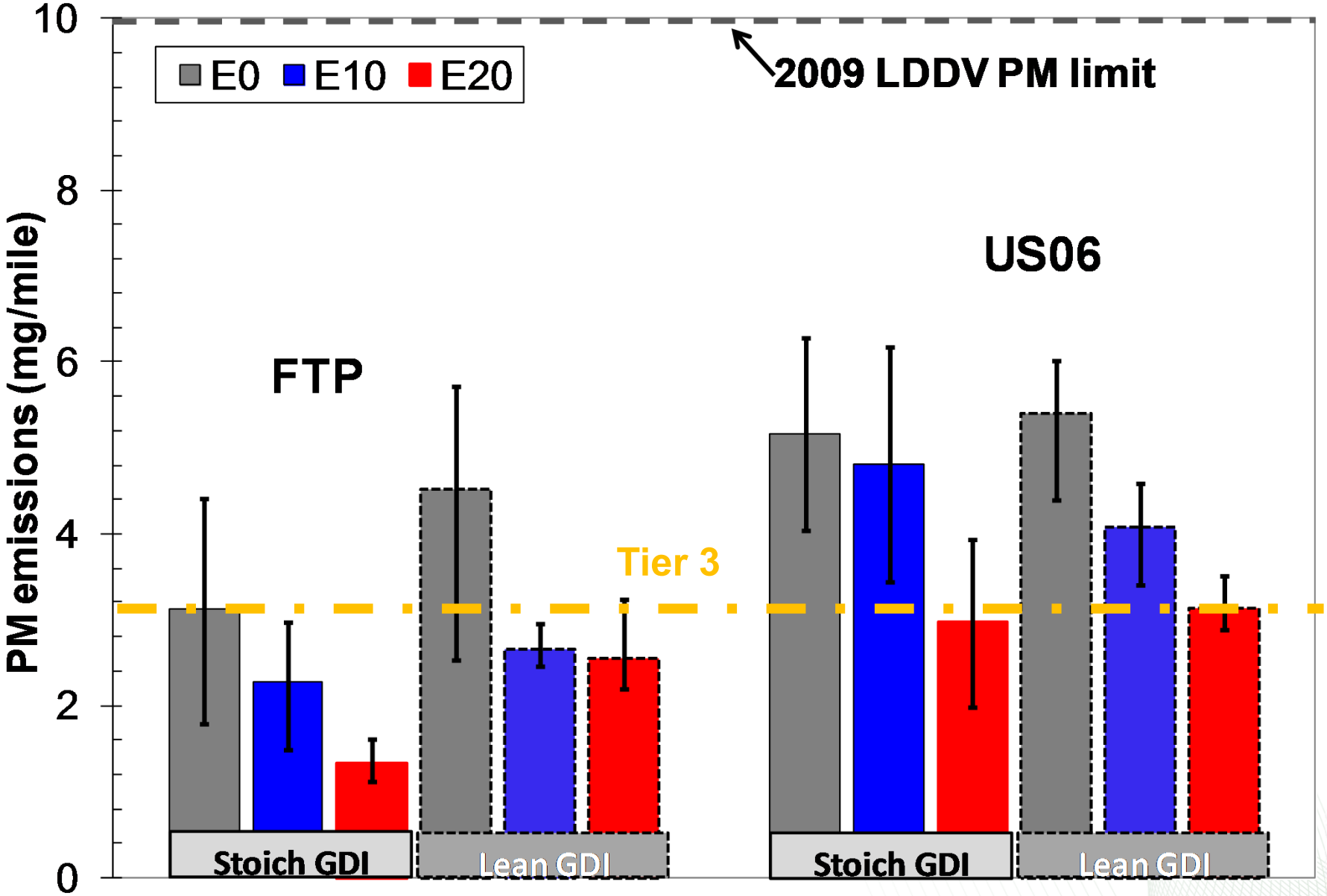
- Filter Sensing Technologies, Inc., in collaboration with ORNL and MIT, developed a radio frequency-based sensor and control system for diesel engine emission control.
- The sensor provides rapid real-time assessment of soot on diesel particulate filters, which allows greater precision in filter control.
- Greater filter control *enables reductions in fuel consumption and greenhouse gas emissions* while still enabling cost-effective control of soot emissions.





FST RF-DPF™ prototype installed next to DPF stack on Volvo/Mack truck operated by the Department of Sanitation New York as part of an extended on-road fleet test (left). Model of RF field strength in DPF (above right). RF antenna for FST RF-DPF™ (below right).

Ethanol content in gasoline helps reduce PM emissions from GDI engines



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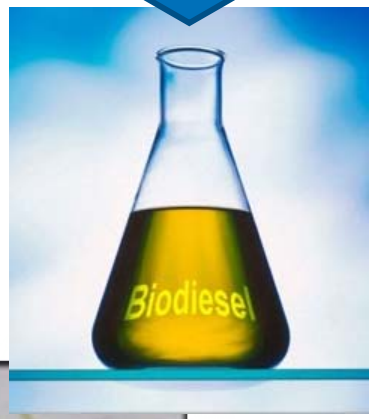
Understanding potential impact of emerging fuels is an important consideration for their acceptance

- As new fuel sources are introduced/discovered it is important to understand the potential ramifications
  - High durability requirements of emissions control
  - Trace impurities can build-up and have big impact
- Production of biodiesel historically relies on NaOH/KOH
- Study by collaborators NREL, ORNL, NBB, MECA, and Ford investigated potential harmful effects of Ca, Na, and K on catalysts on Ford MY2011 F250 Diesel Truck with DOC+SCR+DPF emission control system

Vegetable Oil + Methanol

NaOH or KOH



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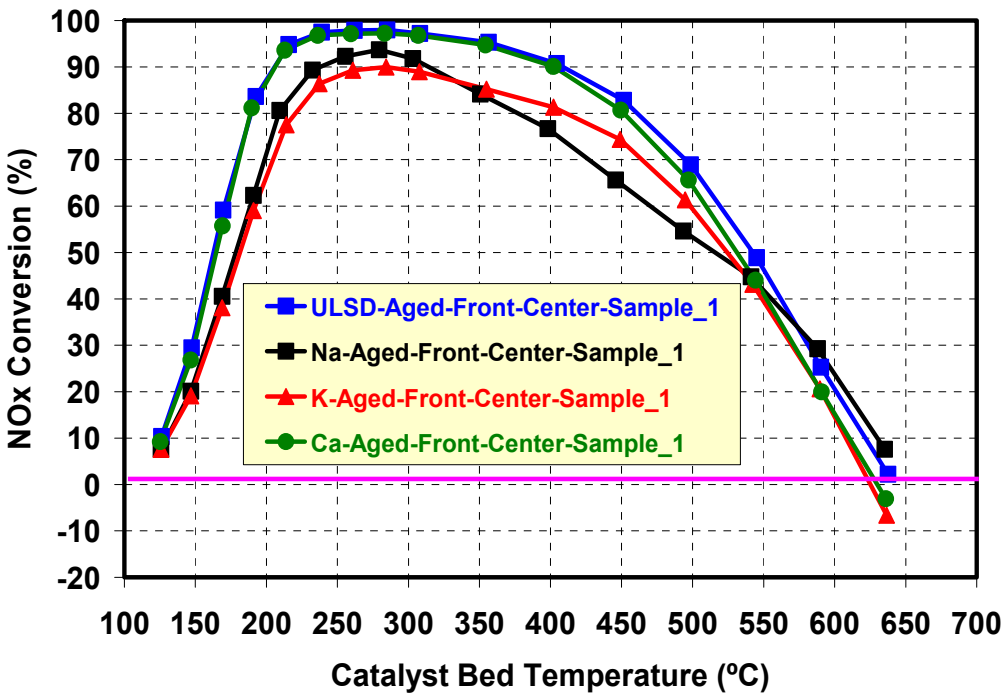
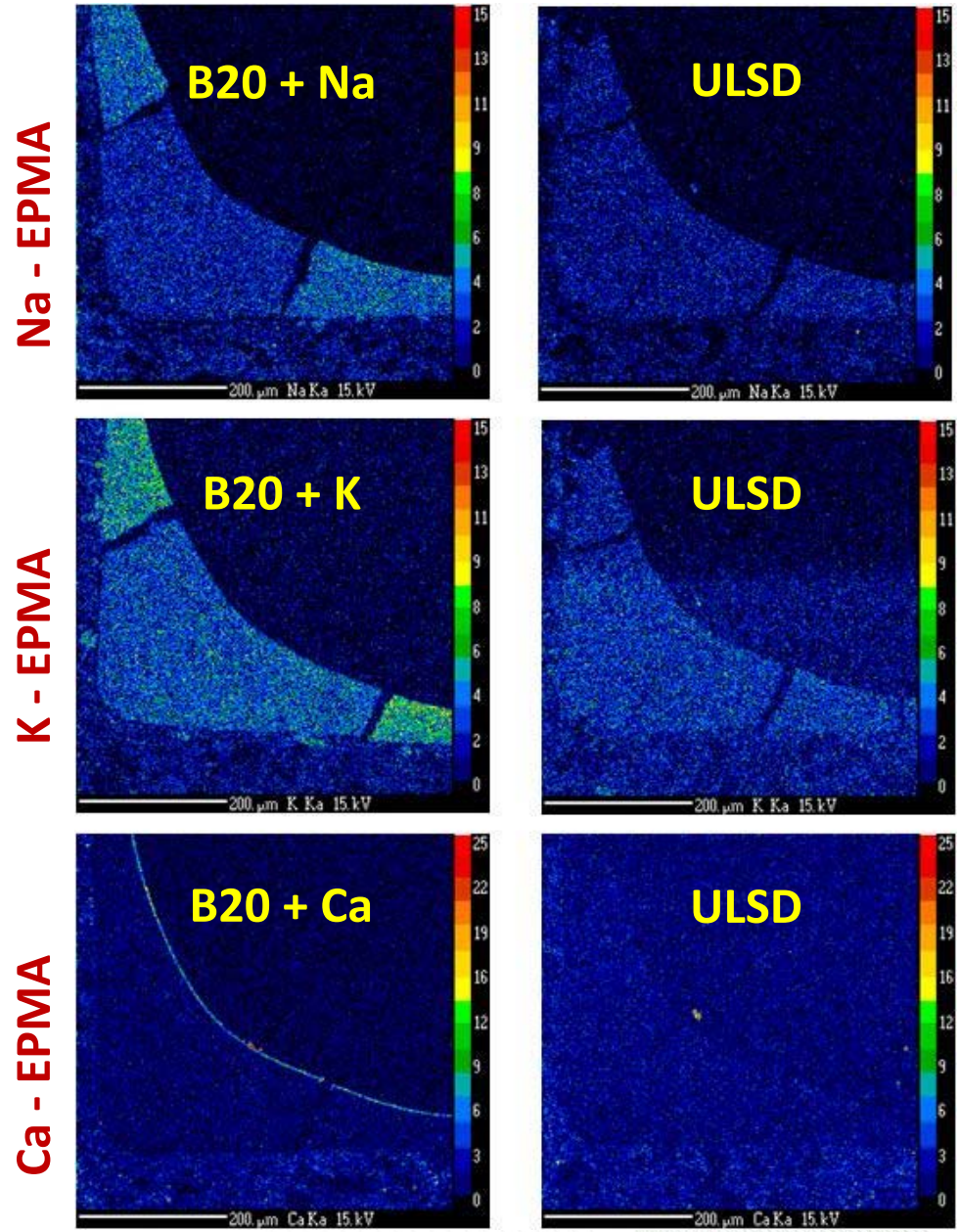
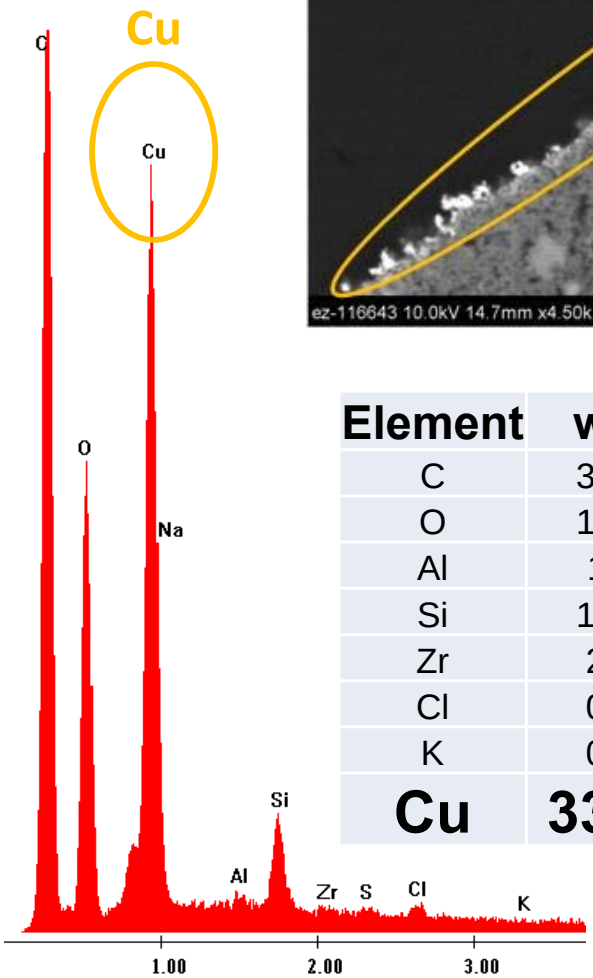
SCR catalysts after aging: Na+K observed throughout washcoat; Ca at surface

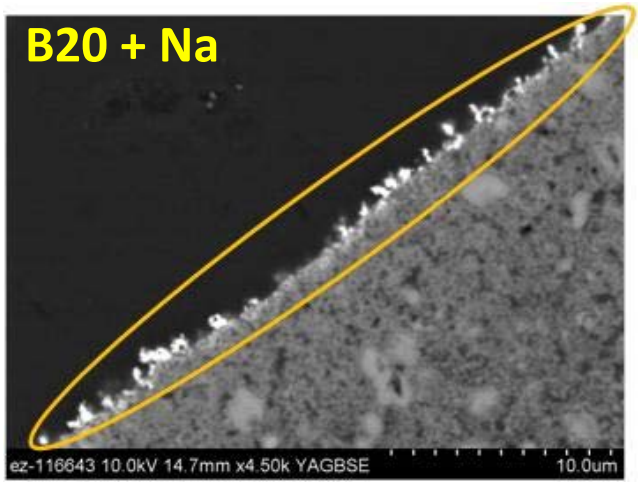
- Significant Na and K observed in B20-aged SCR samples
- Ca continues to only interact with surface of washcoat
- 10-20% NOx conversion loss observed in K- and Na-aged catalysts





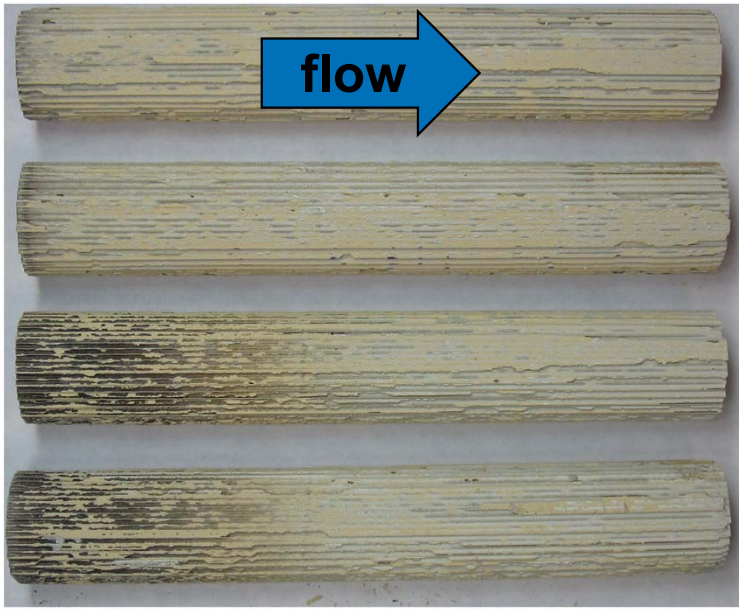
Na- and K-aged samples negatively interact with SCR causing Cu displacement and performance loss





Element	wt%
C	32.09
O	17.49
Al	1.11
Si	13.71
Zr	2.09
Cl	0.31
K	0.06
Cu	**33.14**

Front SCR Catalyst



- Highly concentrated Cu particles observed on washcoat surface for Na and K aged SCR catalysts (via SEM)
- Na and K exchanged/displaced Cu from zeolite active centers to form CuOx on surface and cause 10-20% performance loss (not observed in ULSD/Ca cases)
- **<u>Bottom Line: need standards for biodiesels to minimize harmful effects from impurities</u>**

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Conclusions

- ORNL science contributions have supported industry in commercializing fuel efficient heavy-duty and light-duty vehicles with low emissions
- Current research on emission control technologies is enabling further improvements to aid industry in meeting new challenging regulations for fuel economy, emissions, and renewable fuel use

Acknowledgements

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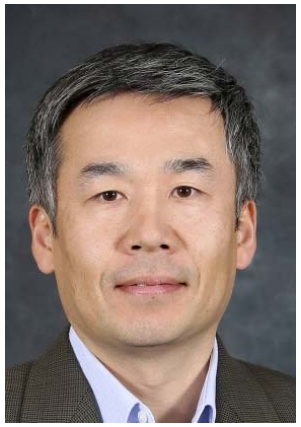
Many, many contributors spanning the ORNL Sustainable Transportation Program as well as neutron sciences, high performance computing, basic energy sciences (catalysis) and materials analysis

Thanks to the many ORNL researchers working to clean our air!



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Gavin Wiggins
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