TRENDS AND SOURCES OF PARTICULATE MATTER EMISSIONS FROM GASOLINE AND DIESEL ENGINES

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Dec 8, 2016

HEI – Effects of Fuel Composition on PM

Acknowledgments

UC Berkeley / Lawrence Berkeley National Laboratory

Tim Dallmann, Drew Gentner, Allen Goldstein, Gabriel Isaacman, Tom Kirchstetter, Brian McDonald, Chelsea Preble, Kevin Wilson, Dave Worton

Research Funding

- US Environmental Protection Agency (STAR Grant RD834553)
- California Air Resources Board
- Bay Area Air Quality Management District

Categories of Vehicle-Related PM

PM Constituent	Gasoline Engines	Diesel Engines
Black Carbon (BC), aka "soot"	Rich-running older engines & cold start. New GDI engines	Diesel fuel pyrolysis (spray combustion, fuel and air not premixed)
Primary Organic Aerosol (POA) – directly emitted in exhaust	Lubricating oil Heavy PAH (5-6 rings) in gasoline	Lubricating oil Heavy HC in diesel fuel
Secondary Organic Aerosol (SOA) – atmospheric oxidation of emitted gas-phase hydrocarbons	Aromatic HC	Aromatics, heavy HC

Long-Term Emission Trends

- Engine activity based on volume of fuel used
 On-road (taxable) gasoline & diesel from FHWA
 Off-road fuel sales from EIA surveys of fuel wholesalers, broken down by end user category
- Emission factors from on-road measurements
 Highway tunnels, roadside remote sensing
 Normalize pollutants to CO₂ to get emission factors in g/kg units (mass pollutant emitted per mass fuel)
 Use CO as basis for estimating other LDV emissions

Trends in Gasoline & Fuel Oil Sales

(FHWA and EIA data for California)



Heavy-Duty Diesel PM Emissions

(Highway Tunnel Measurements)



Black Carbon (BC) Emission Trends

(Los Angeles / South Coast Air Basin)



McDonald et al. (ES&T 2015)

Light-Duty Gasoline CO Emissions

(Highway Tunnel & Remote Sensing Measurements)



Organic Aerosol Trends

(Los Angeles / South Coast Air Basin)



McDonald et al. (ES&T 2015)

GC-MS Speciation Analysis

What is the Origin of Vehicular OA Emissions?

Use vacuum ultraviolet (VUV) photons for photo-ionization mass spectrometry of organic molecules in fuels, oil & OA

Advanced Light Source: A bright, laser-like, tunable source of ultraviolet radiation and X-rays





VUV-GC-MS Analysis

- Past work on speciating primary organic aerosol (POA) has resolved ~5% of total OA mass
 n-alkanes, PAH, hopanes, steranes
 The rest (95%) is unknown "unresolved complex mixture"
- This work provides much more complete speciation for diesel fuel, lube oil, and POA emissions
 Directly measure rather than infer composition
- Key advance is use of softer (VUV) ionization
 Minimize fragmentation of parent ions in the analysis

Electron Impact (EI) versus Vacuum Ultraviolet (VUV) Ionization







A Highway Tunnel Laboratory

Vehicle emissions measured at Caldecott tunnel in SF Bay area:
Light-Duty Gasoline: 1994-97, 1999, 2001, 2004, 2006, <u>2010</u>
Heavy-Duty Diesel Trucks: 1996-97, 2006, <u>2010</u>, 2014, 2015



Composition of Vehicle OA Emissions (Caldecott Tunnel 2010; 12-2 and 4-6 PM samples)

 $N_{\text{DBE}} = 0$ (straight chain) $N_{\text{DBE}} = 2$ $N_{\rm DBE} = 1$ $N_{\rm DBE} = 3$ Interpolated from EI $N_{\text{DBE}} = 4$ $N_{\text{DBE}} = 5$ $N_{\rm DBE} = 6$ $N_{\text{DBE}} = 7+$ high HD influenced low HD influenced POA average mass (ug C m⁻³ 1.4 - $LD = 6723 \pm 880$ $LD = 5268 \pm 1467$ $MD = 57 \pm 11$ $MD = 144 \pm 44$ 1.2 - $HD = 87 \pm 33$ $HD = 7 \pm 7$ 1.0-0.8 -0.6 -0.4 -0.2 -0.0 -20 25 30 35 20 25 30 35 N_C N_C Worton et al. (ES&T 2014)

Lubricating Oil Speciation



More Recent Diesel BC Emission Trends

(Port of Oakland Field Measurements)



California requires modernization of in-use heavy-duty trucks

Diesel Particle Filters: 100% DPF by 2018 Catalytic Converters: 100% SCR by 2023 Port drayage trucks: 100% DPF by 2013

Changes in Truck Age Distribution (Port of Oakland Drayage Truck Fleet)



Preble et al. (ES&T in prep)

Changes in Port Truck BC Emissions



Preble et al. (ES&T in prep)

Changes in Port Truck BC Emissions



Concluding Remarks

- Durable (long-lived) and robust (work well under all conditions) emission controls should be top priority
 Finding & fixing high-emitting vehicles is hard in practice
- Primary OA emissions dominated by lubricating oil
 Little POA benefit from changes to fuel composition
- Fuel changes can help to reduce BC and SOA
 - Trying to address atypical situations (e.g., high-emitting vehicles) using across the board fuel changes is **not** an efficient strategy

References

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