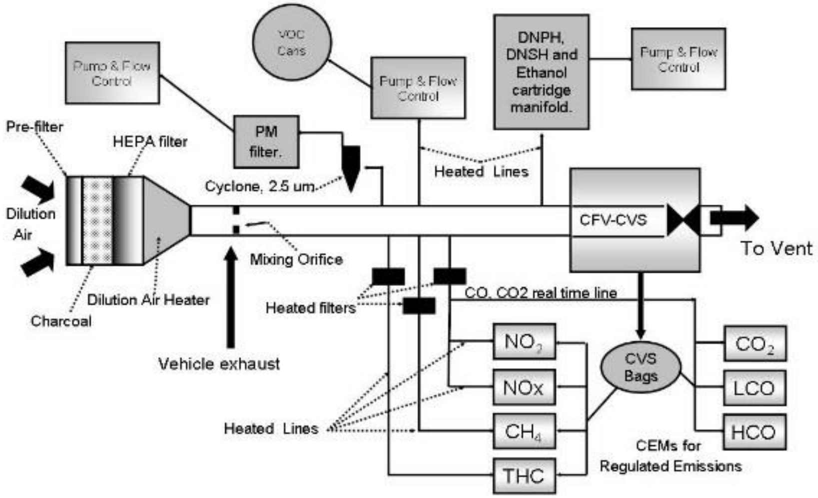
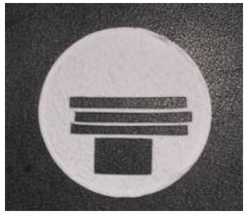
SVOC emissions from diesel trucks operating on biodiesel fuels





Michael D. Hays, William Preston, Ingrid J. George, Pamela Barfield, Bakul Patel, Richard Snow, James Faircloth, Thomas Long, Richard Baldauf, and Joseph McDonald

Office of Research and Development (ORD)—National Risk Management Research Laboratory (NRMRL)

Motivation

- The 2007 Energy Independence & Security Act (EISA) mandated renewable fuel use in the transportation sector
  - EPA sets Renewable Fuel Standards (RFS) annually (flexibility)
  - 36 billion gallons of renewable fuels by 2022

Volumes Used to Determine the Proposed 2014 Percentage Standards

Category	Volume[a]	Range
Cellulosic biofuel	17×10^6 gal	8-30×10^6 gallons
Biomass-based diesel (FAMEs)	1.3×10^9 gal	1.3×10^9 gal[b]
Advanced biofuel (non-corn EtOH)	2.2×10^9 gal	2.0-2.5×10^9 gal
∑Renewable fuel	15.2×10^9 gal	15.0-15.5×10^9 gal

[a]All volumes are ethanol-equivalent, except for biomass-based diesel which is actual
[b]EPA is requesting comment on alternative approaches and higher volumes

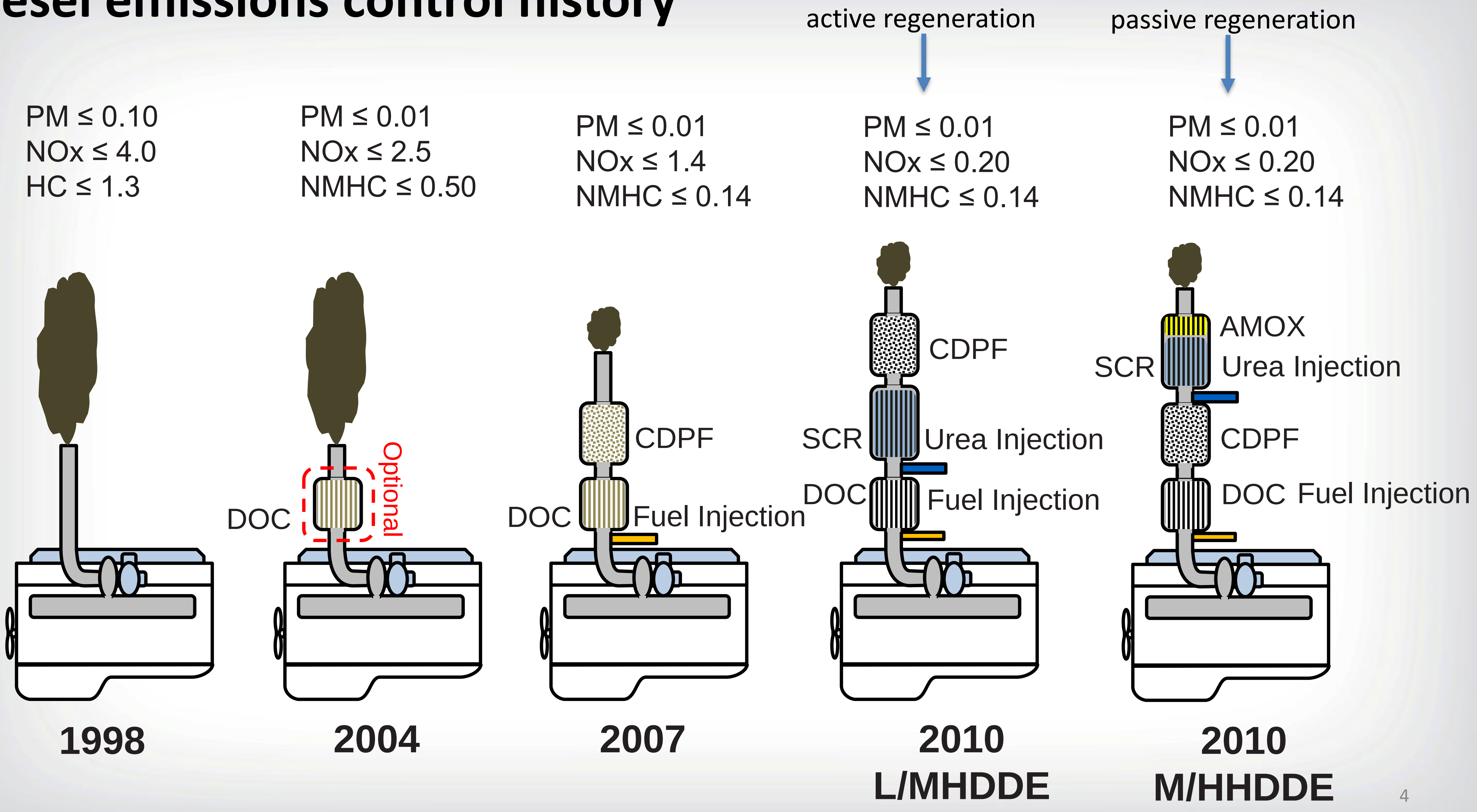
- As part of these requirements, EPA must:
  - Assess the impacts of changes in ethanol volume and other fuel properties on emissions and ambient concentrations of air toxics and criteria pollutants
  - Ensure "anti-backsliding" of air quality impacts and propose regulations to mitigate any adverse air quality impacts

Biodiesel study facts

- Roughly, 150 x 10^9 L of on-highway diesel produced annually in the U.S. of which 5 x 10^9 is biodiesel
- In many cases, biodiesel use actually reduces criteria pollutant emissions
- Water-soluble OC in PM can increase producing toxicological concerns
- To date, limited emphasis on the gas-phase SVOC emissions and the effect of increasing fuel oxidants
- MOVES model requires emissions information from this engine class
- As of 2016, greater than half of all vehicle miles travelled were for trucks with catalytic control for NOx and PM.

MOVES – Motor Vehicle Emissions Simulator

Diesel emissions control history



Experimental – HD Vehicles (6.7L)

George et al. (2014) *ES&T*, Vol. 48, Iss. 24, p. 14782

- 2011 Dodge Ram 2500
- GVWR = 9,600 lb
- DOC/NAC/CDPF
- 35,498 km
- HDV2B

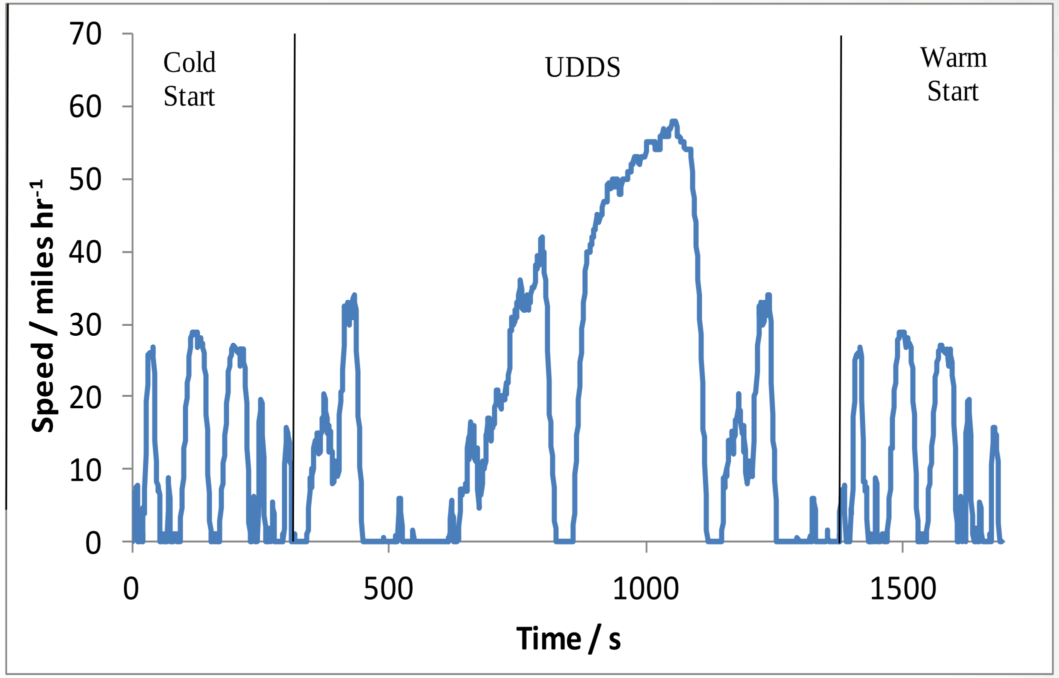
- 2011 Ford F550
- GVWR = 19,500 lb
- DOC/SCR/CDPF
- 4,333 km
- HDV5

- 2011 Ford F750
- GVWR = 25,999 lb
- DOC/SCR/CDPF
- 5850 km
- HDV6

Active CDPF regeneration

Experimental – Testing

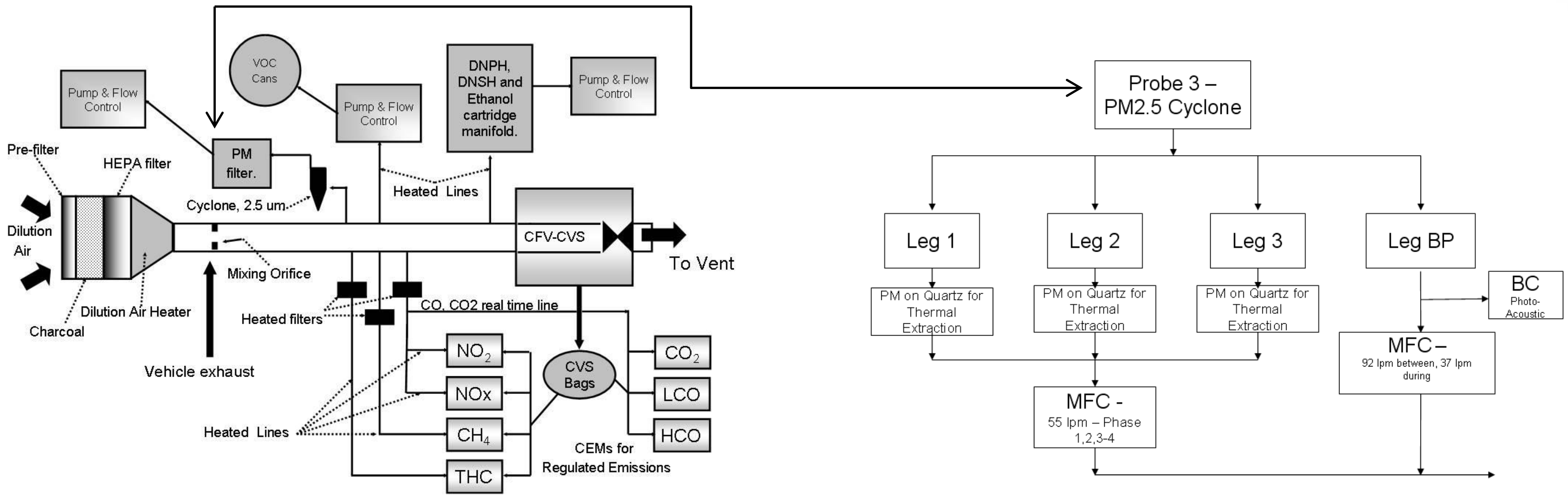
Clark et al. SAE Technical Paper, 2003-01-3284



- **Test variables**
  - Fuels: ULSD and B20 (soy)
  - Weight: laden/unladen (F550)
  - Temperature: -7 ºC and 22 ºC (F750)
  - Regeneration (WS-UDDS only)
  - Operating cycles (CS and WS-UDDS)

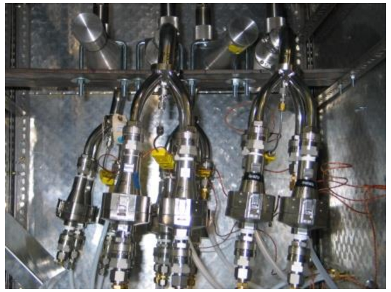
George et al. (2014) *ES&T*, Vol. 48, Iss. 24, p. 14782

Experimental – Sampling and Dilution



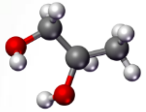
constant volume sampler
1:10 dilution

- 47 mm quartz fiber filter-PUFs
  - OC-EC (mod. NIOSH Method 5040)
  - **SVOC, particle-phase and gas-phase** speciation (TE- and SE-GC-MS)
  - Artifact using (Q_b)

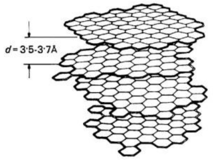


collected CS and UDDS-WS phases over N ≥3

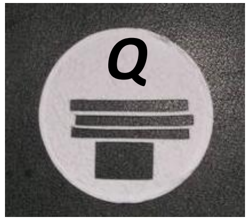
Experimental – Chemical Analysis



OC – EC



Thermal optical analysis (TOA; Sunset Labs)



Thermal optical transmission
(TOT; NIOSH 5040 modification)

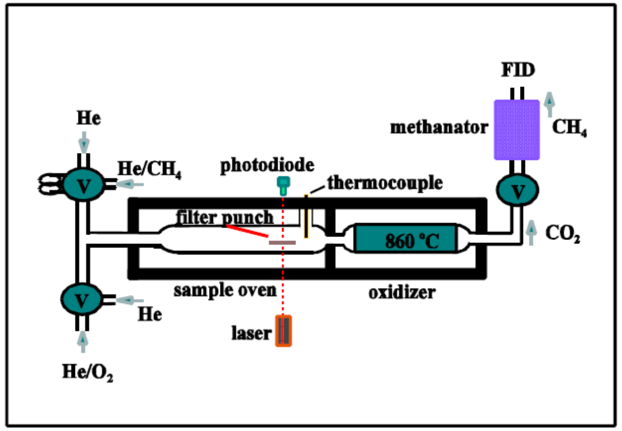


Figure 1. Schematic of Thermal-Optical Instrument (V=valve)

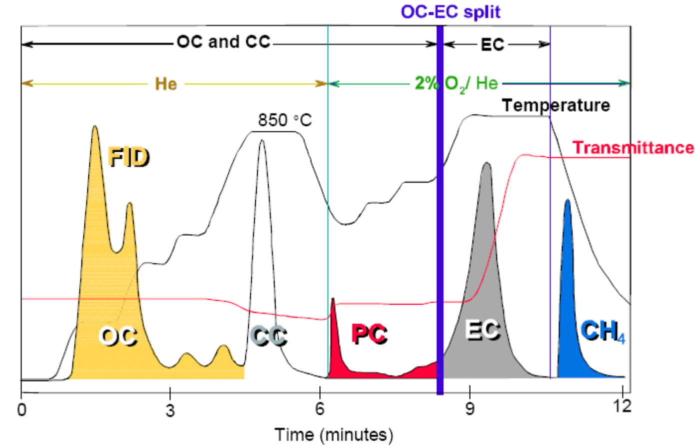
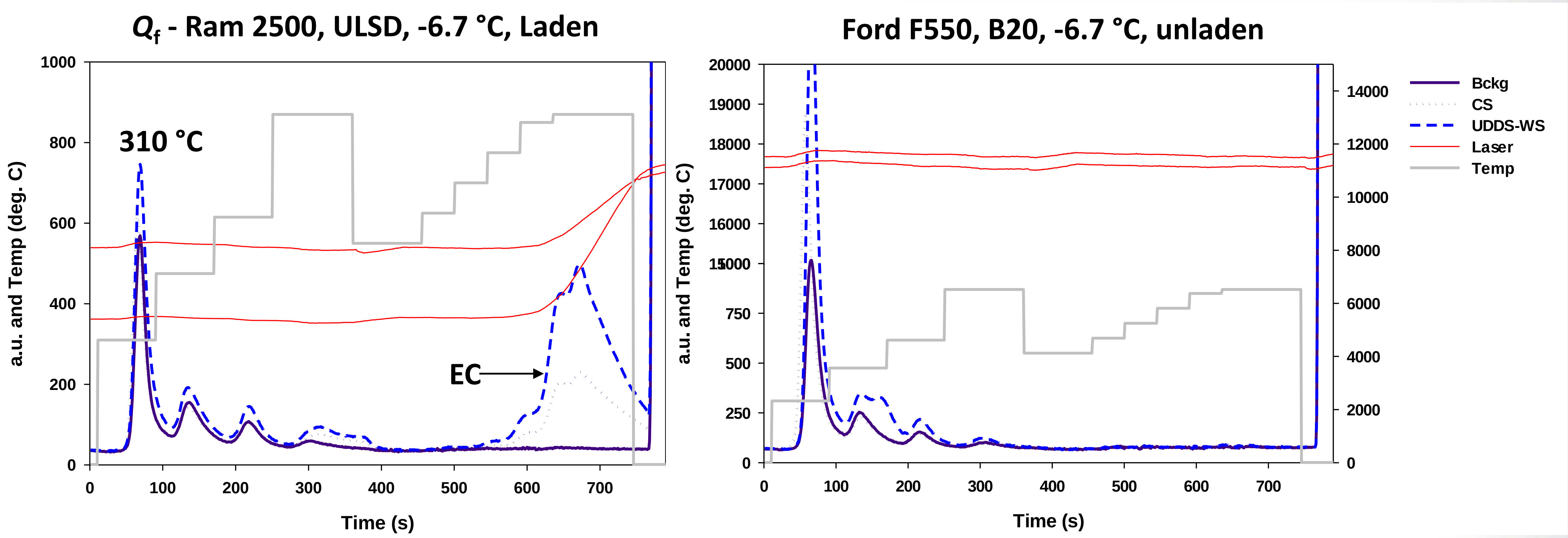


Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.

OC-EC Results

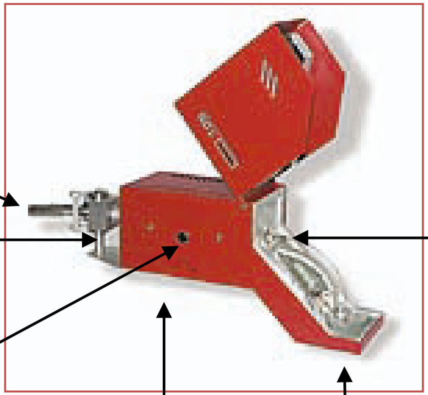


- **OC is likely gas-phase due to Q_b**
- **Some background contribution**
- EC slightly underestimated
- Limited if any pyrolysis

- more organic matter for this vehicle
- less EC in general
- **More OC associated with UDDS-WS**

Experimental – Chemical Analysis (Q_f)

Thermal extraction system (TE; Gerstel Inc.)



sample introduction (> 6 µg of OC)
(deactivated, pre-conditioned quartz tube)

He flow (50 cc/min)

Liquid N_2 coolant maintains tube at 25 °C
before and after extraction step

TE oven – programmable temperature control
ramped at 50 °C/min from 25 to 325 °C

GC-cooled, programmable temperature vaporization inlet system
(CIS-PTV); quartz wool packed; −80 °C during thermal extraction;
heated to 300 °C at 720 °C/min) splitless transfer modes (TE, CIS-PTV)
MS used in SIM mode

Short-path (152 mm) heated
(325 °C) transfer line (SilcoSteel)

Hays, M. D. and R. J. Lavrich (**2007**). TrAC Trends Anal. Chem. **26**(2): 88-102.

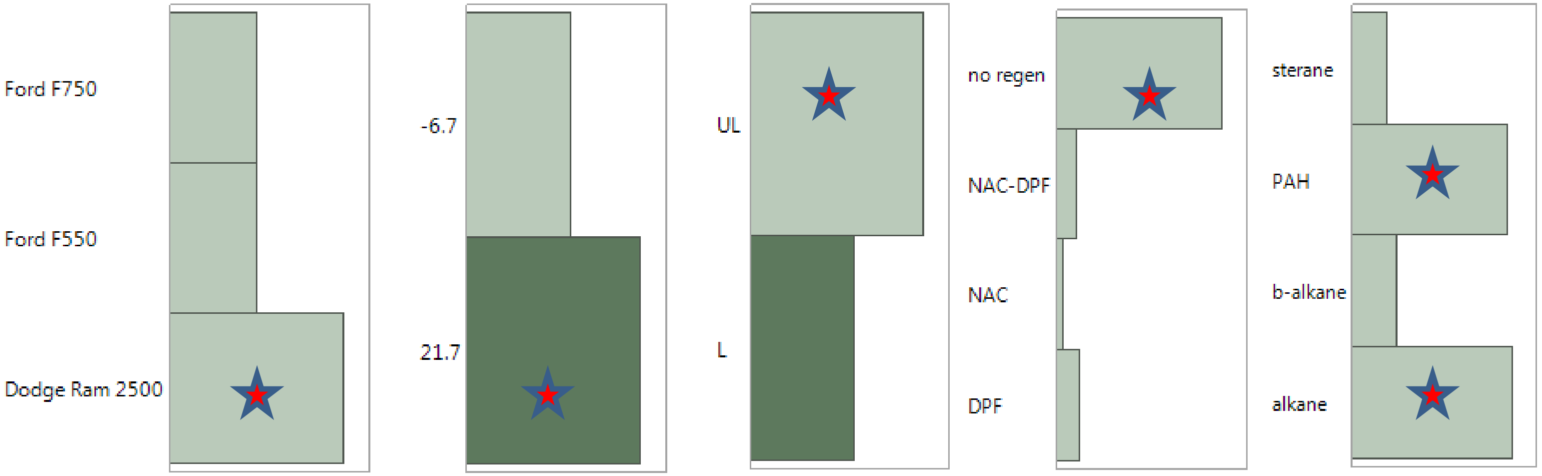
Experimental – Chemical Analysis (*PuF*)

- Manual solvent extraction
- DCM:hexanes:acetone [20:50:30]

- GC-MS (qqq) in MRM mode
- ~200 target analytes (*n*-, *c*-, and *b*-alkanes, PAH, oxy-PAH, Steranes/hopanes, aromatic acids, *etc*.)

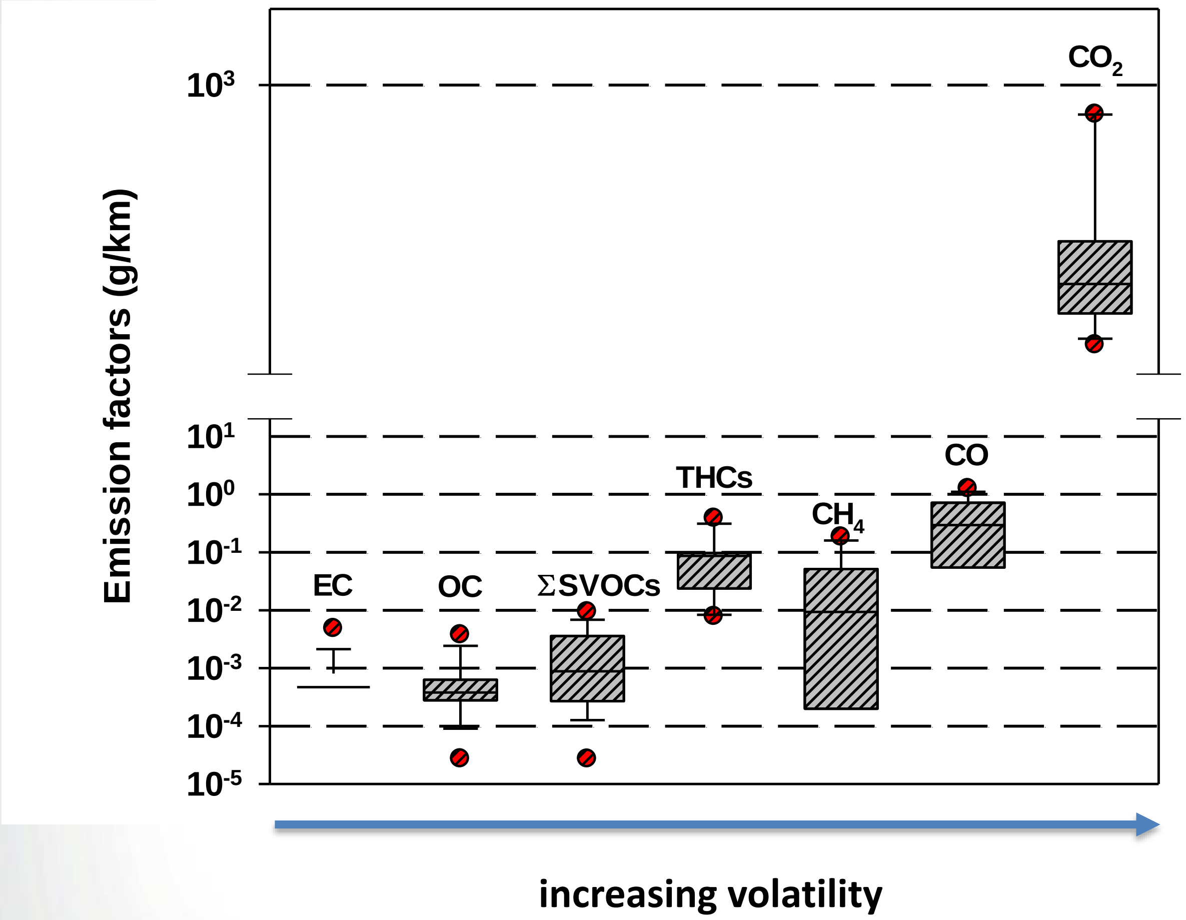
- **Focus on non-polar compounds**
- **All data are background subtracted**

Data distribution frequencies



- For OC-EC analysis:
  - *N* = 64
  - Cycle and fuel data evenly distributed
  - DPF data not represented
- For SVOCs:
  - *N* = 4574
  - Missing values = 3474
  - B20 slightly more data (300 data points)
  - PAH and alkanes drive analysis

Test-averaged, carbon-based pollutant emissions factors

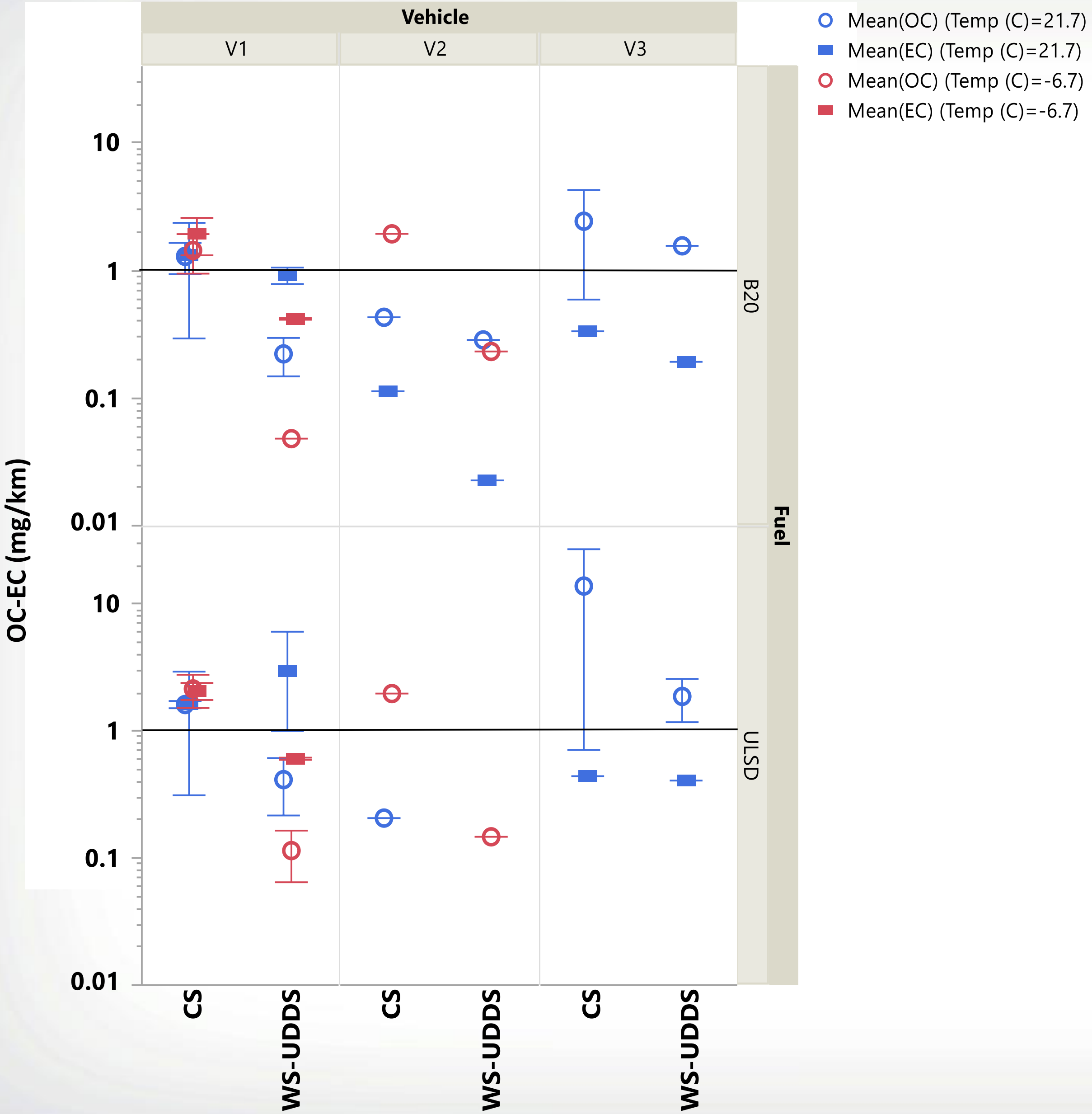


- Outlier – red circle
- Mean – bold line
- Median – thin line
- 25th and 75th percentiles – box end
- 10th and 90th percentiles - whiskers
- ∑SVOCs – identified Q-Puf array

- Classic emissions trend
- Reduced/oxidized species show anti-correlation

- THC includes CH_4 and likely some OC and SVOC

OC-EC emissions trends – by Temp, fuel, and vehicle



EC
- **EC decreases with B20 on average**
- lower chamber T -- higher mean EC emissions
- higher chamber T – wider EC range
- EC, CS > UDDS-WS
- **mostly Dodge RAM 2500 data**

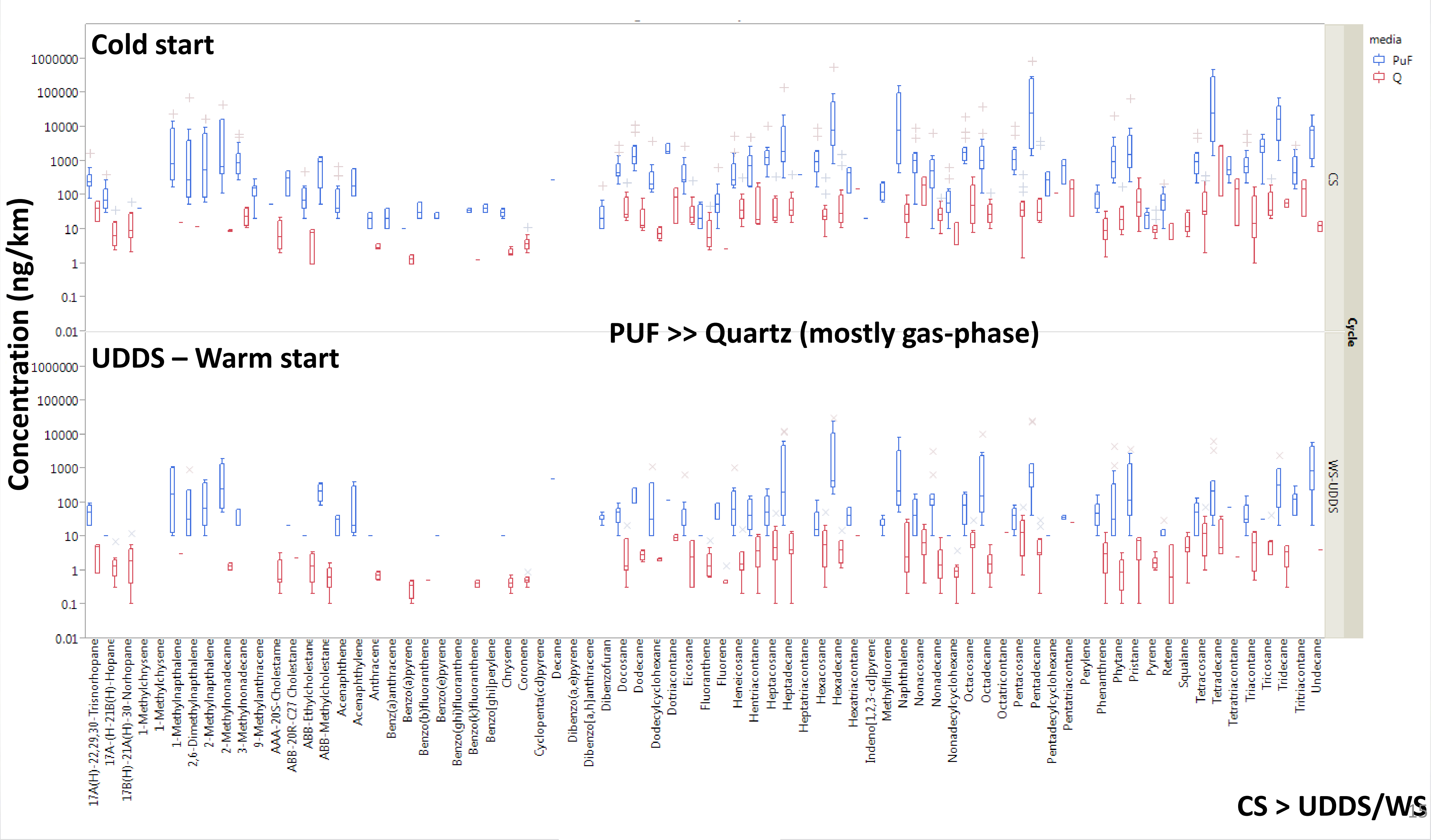
OC

OC increases slightly with ULSD

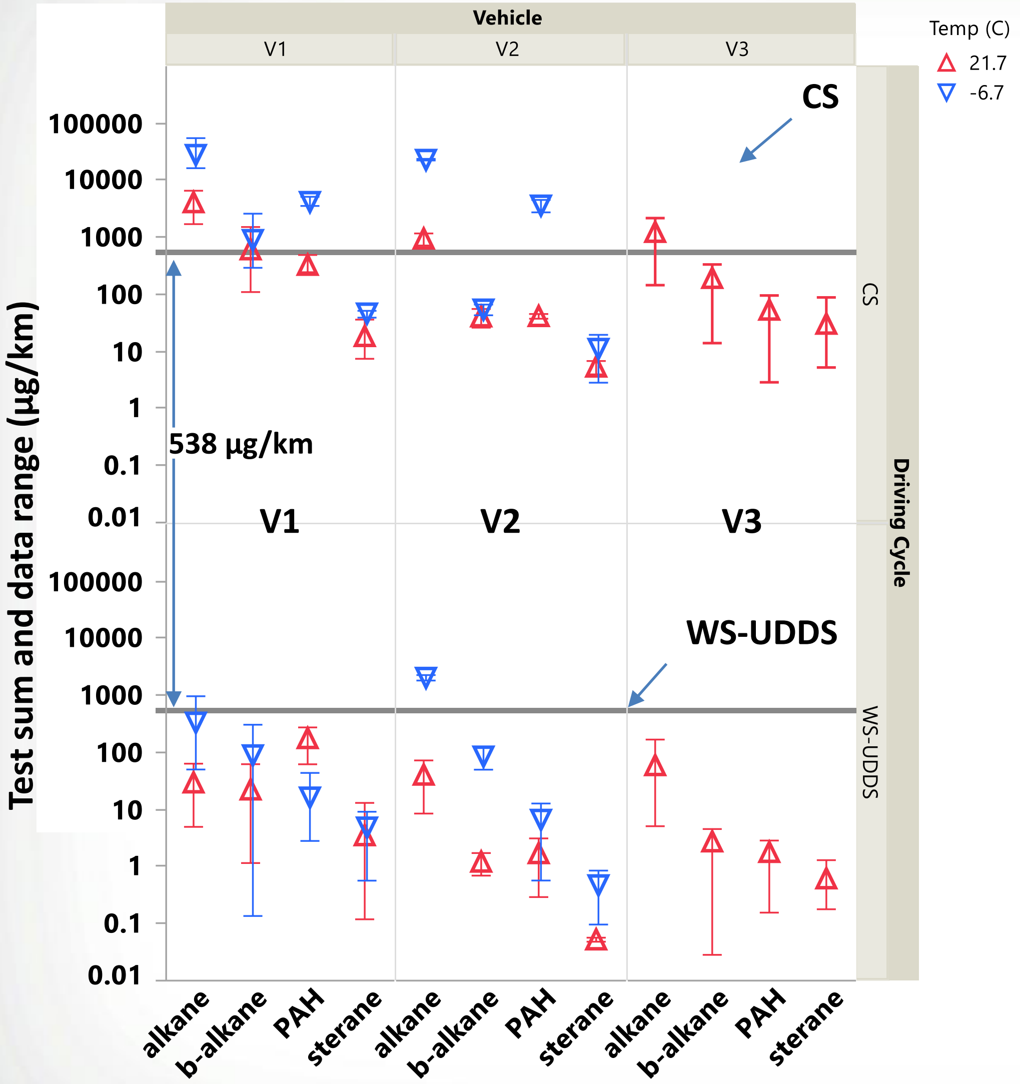
CS >> UDDS-WS

effect of chamber T is unclear

Chemical Analysis – Results (T, VTW, fuel, and vehicle combined)

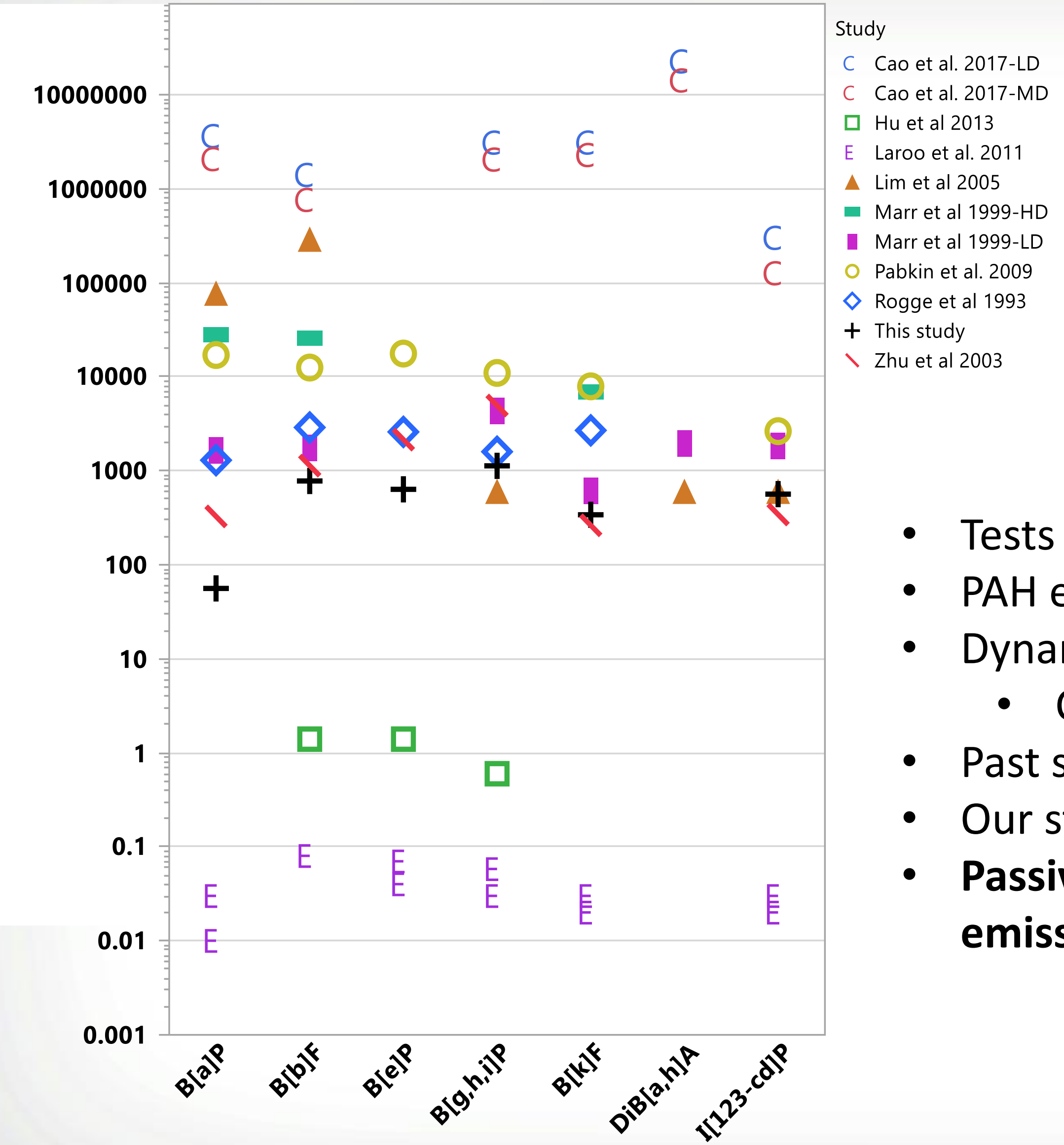


Chemical Analysis – SVOC class trends (combined by VTW and fuel)



- Gas-phase SVOC emissions dominate (90% w/w)
- **CS >>> WS-UDDS**
- **Lower test T produce higher SVOC emissions**
    - **PAH/alkanes were most sensitive**
- **Active regeneration had no effect on SVOCs**
- **Switch to B20 had no effect on SVOCs**
- **VTW had no effect**
- 538 µg/km mean sum

Multi-study heavy-PAH emissions comparison



- Tests conducted over several decades
- PAH emissions are highly variable
- Dynamometer emissions projections may be biased low
    - Cao et al. 2017
- Past studies indicated DPF sufficiently control PAH
- Our study shows PAH at the low-end of the uncontrolled emissions
- **Passive CDPF regeneration systems show potentially significant PAH emissions**

Conclusions for L/MHDDVs used presently

I. CO_2 dominates vehicle emissions and may have increased due to DOCs
II. Carbonaceous particle emissions are muted following CDPF after-treatment
III. For SVOCs: [gas-phase] >> [particle-phase]
IV. Driving cycle and T strongly affect SVOC emissions -- CS >> UDDS-WS
V. VTW, **fuel**, and regeneration had limited, if any, influence on SVOC emissions
VI. Passive CDP regeneration potentially increase PAH emissions
VII. Continue on-road testing to complement dynamometer studies