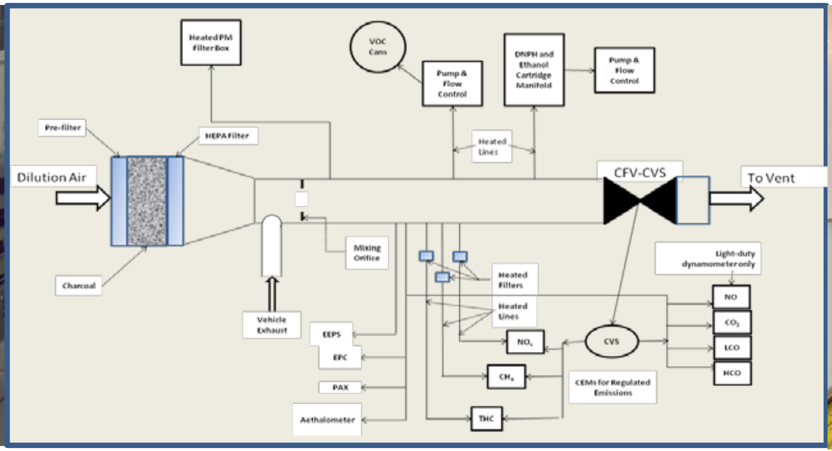
SVOC emissions from diesel trucks operating on biodiesel fuels



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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

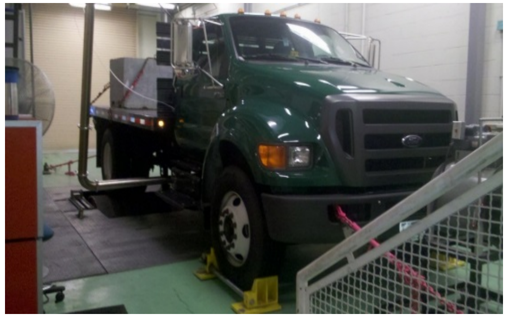
[a]All volumes are ethanol-equivalent, except for biomass-based diesel which is actual
[b]EPA is requesting comment on alternative approaches and higher volumes

- As part of these requirements, EPA must:
  - Assess the impacts of changes in ethanol 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

Experimental – Vehicles

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

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

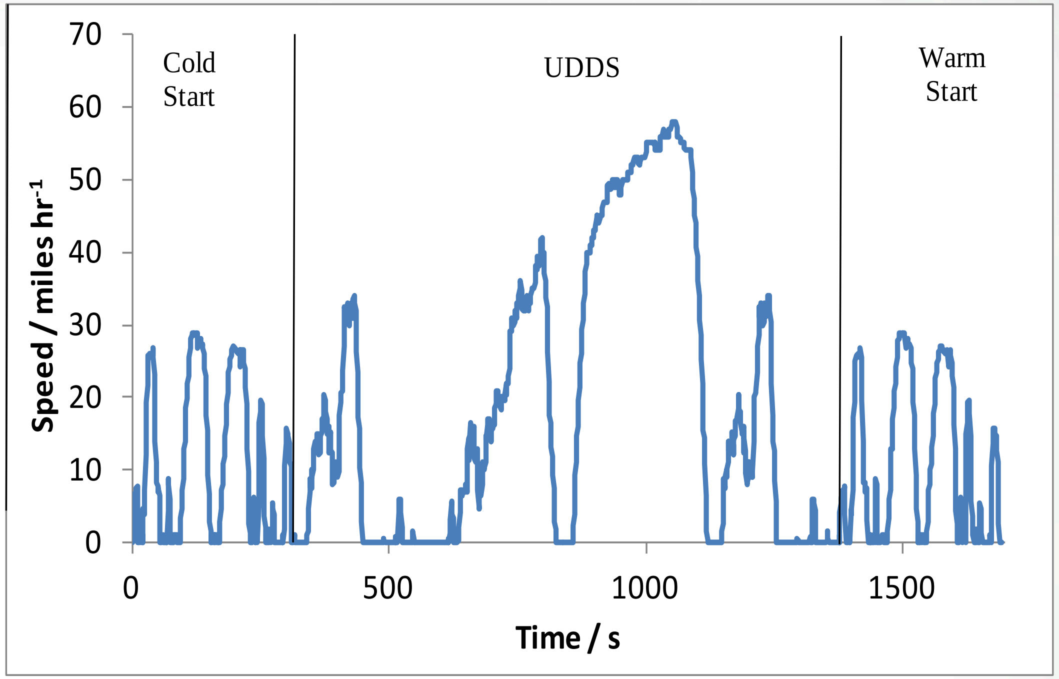


- 2011 Ford F750
- GVWR = 25,999 lb
- SCR/DOC/DPF
- 5850 km

George et al. *ES&T*,

Experimental – Testing

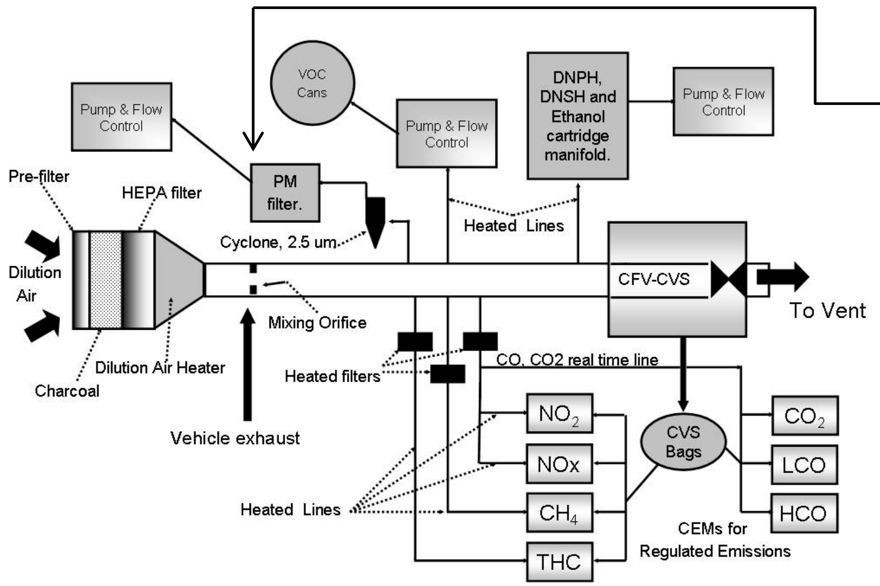
Clark et al. SAE Technical Paper, 2003-01-3284

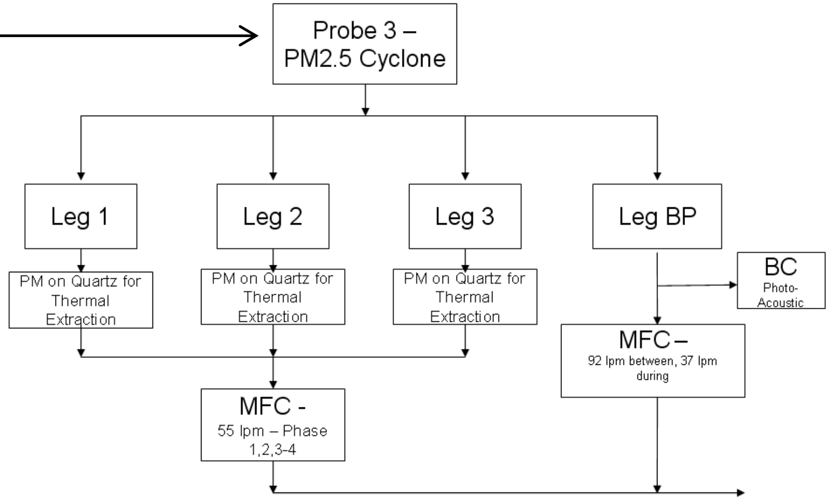


- **Test variables**
  - Fuels: ULSD and B20 (soy)
  - Weight: laden/unladen (F550)
  - Temperature: -7 ºC and 22 ºC (F750)
  - Regeneration
  - Operating cycles (CS and UDDS-WS)

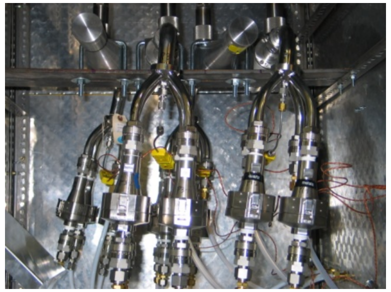
George et al. *ES&T*,(2015)

Experimental – Sampling and Dilution





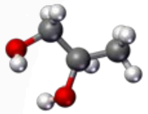
constant volume sampler
1:10 dilution



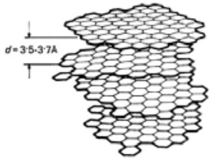
- 47 mm quartz fiber filter-PUFs
  - OC-EC (mod. NIOSH Method 5040)
  - SVOC, particle-phase speciation (TE- and SE-GC-MS)
  - Artifact using (Q_b)

<u>collected CS and UDDS-WS phases over N ≥3</u>

Experimental – Chemical Analysis



OC – EC



Thermal optical analysis (TOA; Sunset Labs)

Thermal optical transmission
(TOT; NIOSH 5040 modification)

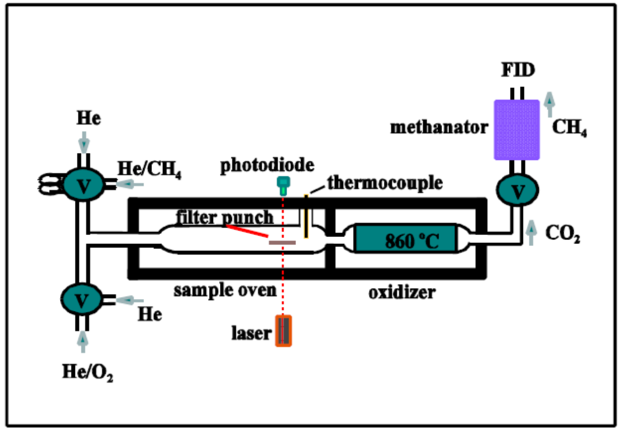


Figure 1. Schematic of Thermal-Optical Instrument (V=valve)

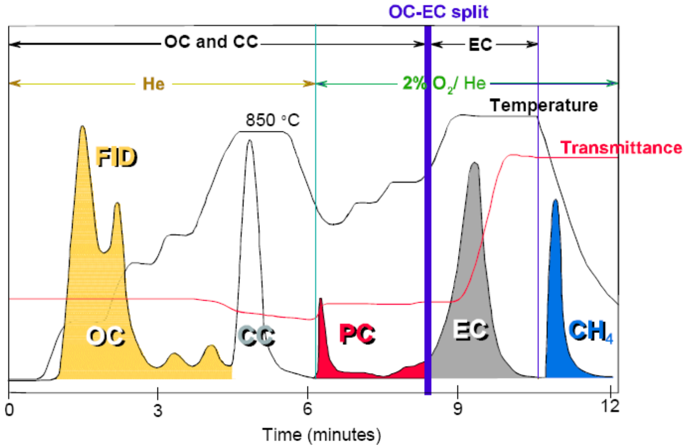
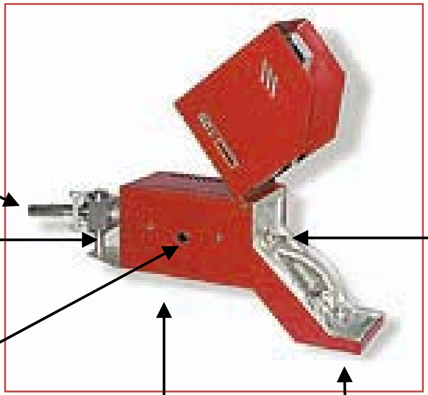
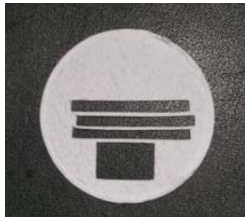


Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.

Experimental – Chemical Analysis (Q_f)

Thermal extraction system (TE; Gerstel Inc.)





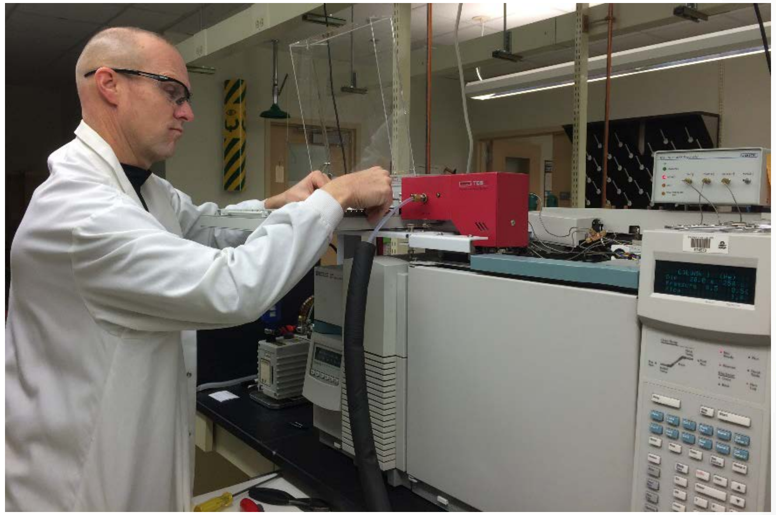
sample introduction (> 6 µg of OC)
(deactivated, pre-conditioned quartz tube)

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 (300 °C) transfer line (SilcoSteel)

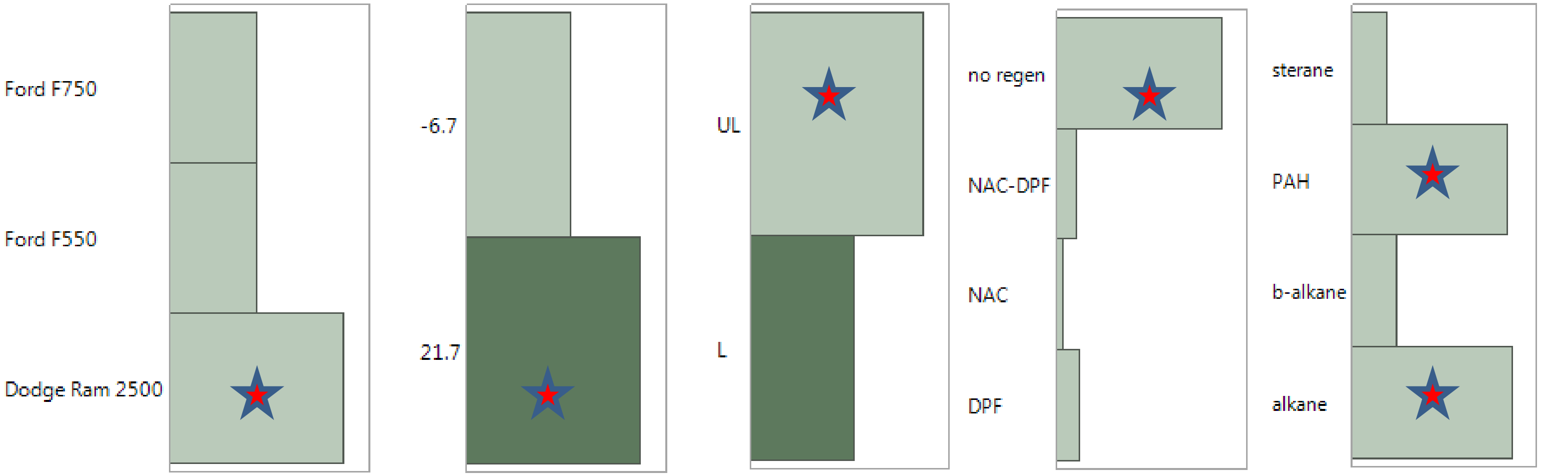
Hays, M. D. and R. J. Lavrich (**2007**). <u>TrAC Trends Anal. Chem.</u> **26**(2): 88-102.

Experimental – Chemical Analysis (*PuF*)

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

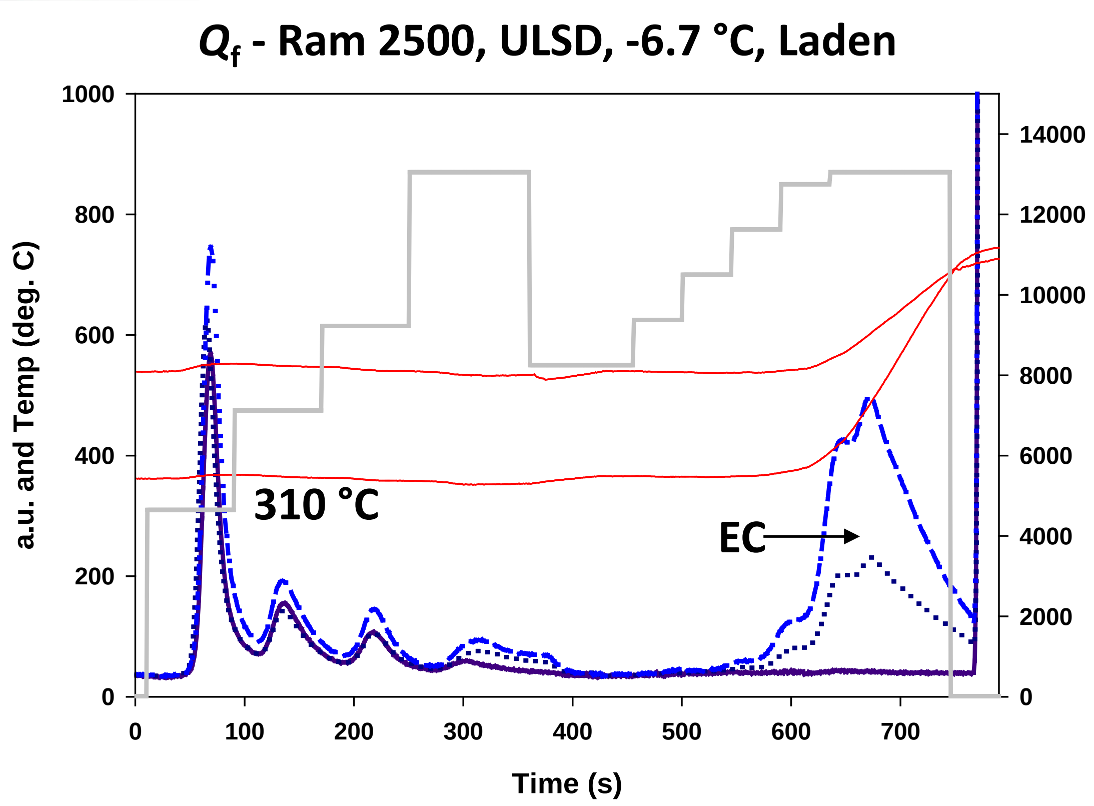
- GC-MS (qqq) in MRM mode
- ~200 target analytes (*n*-, *c*-, and *b*-alkanes, PAH, oxy-PAH, Steranes/hopanes, aromatic acids, *etc*.)
- Focus on non-polar compounds
- Everything is background subtracted

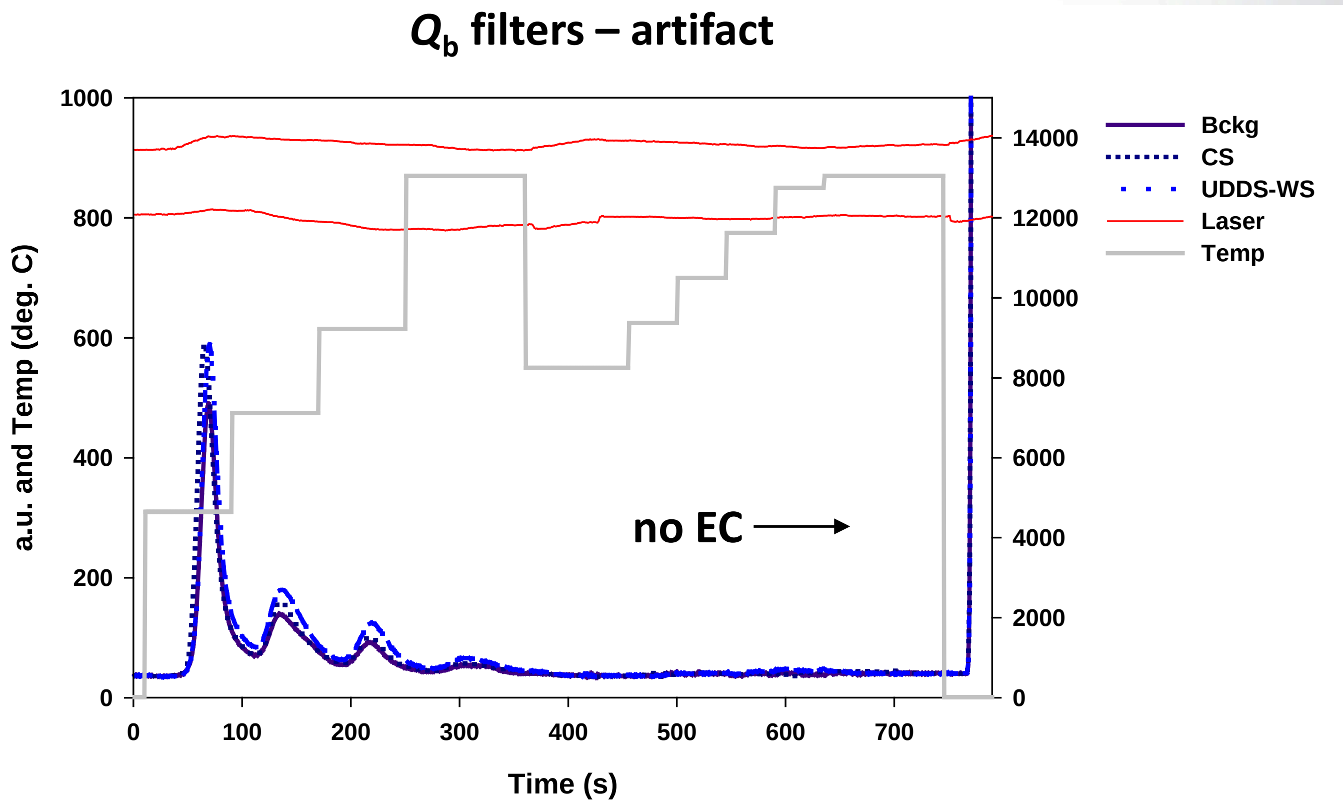
Data distribution frequencies



- 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

OC-EC Results



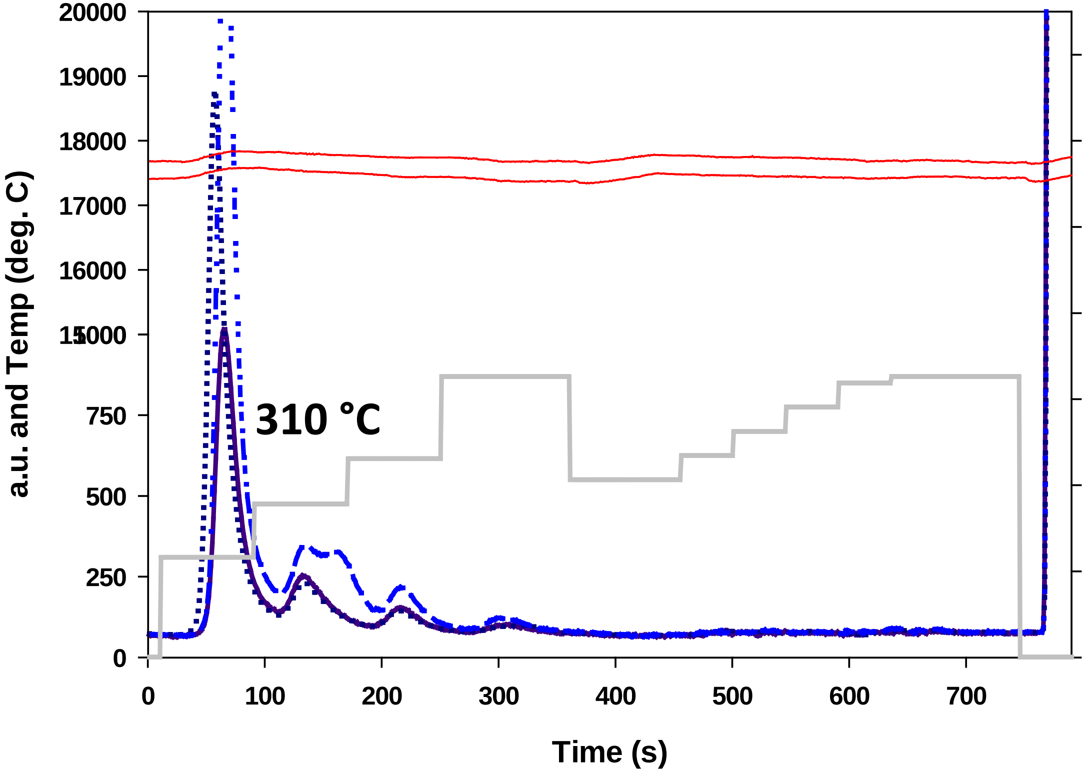


- limited PyC
- overall thermal profiles very similar
- EC slightly underestimated

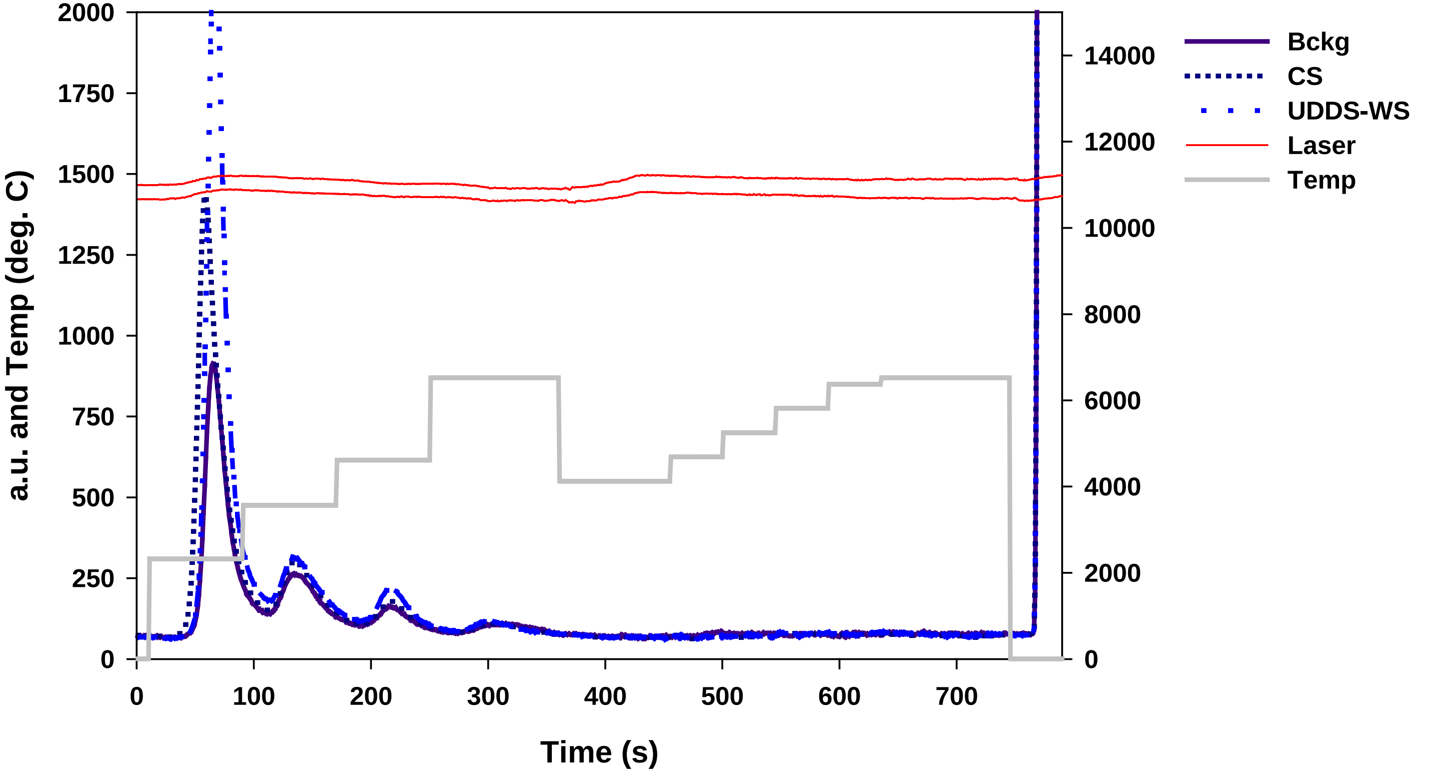
- volatile matter OC profiles are similar
  - Phase, bckg

OC-EC Results

Ford F550, B20, -6.7 °C, unladen

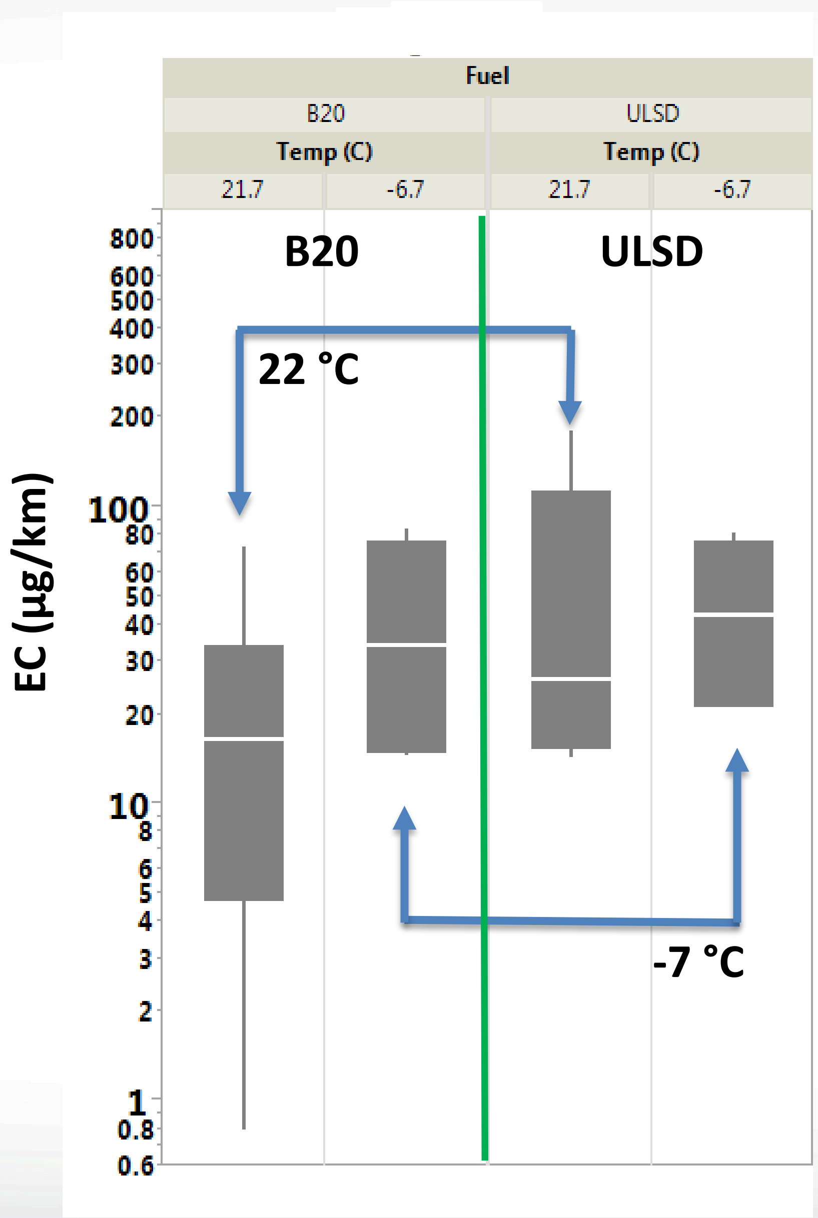


Q_b filters – artifact



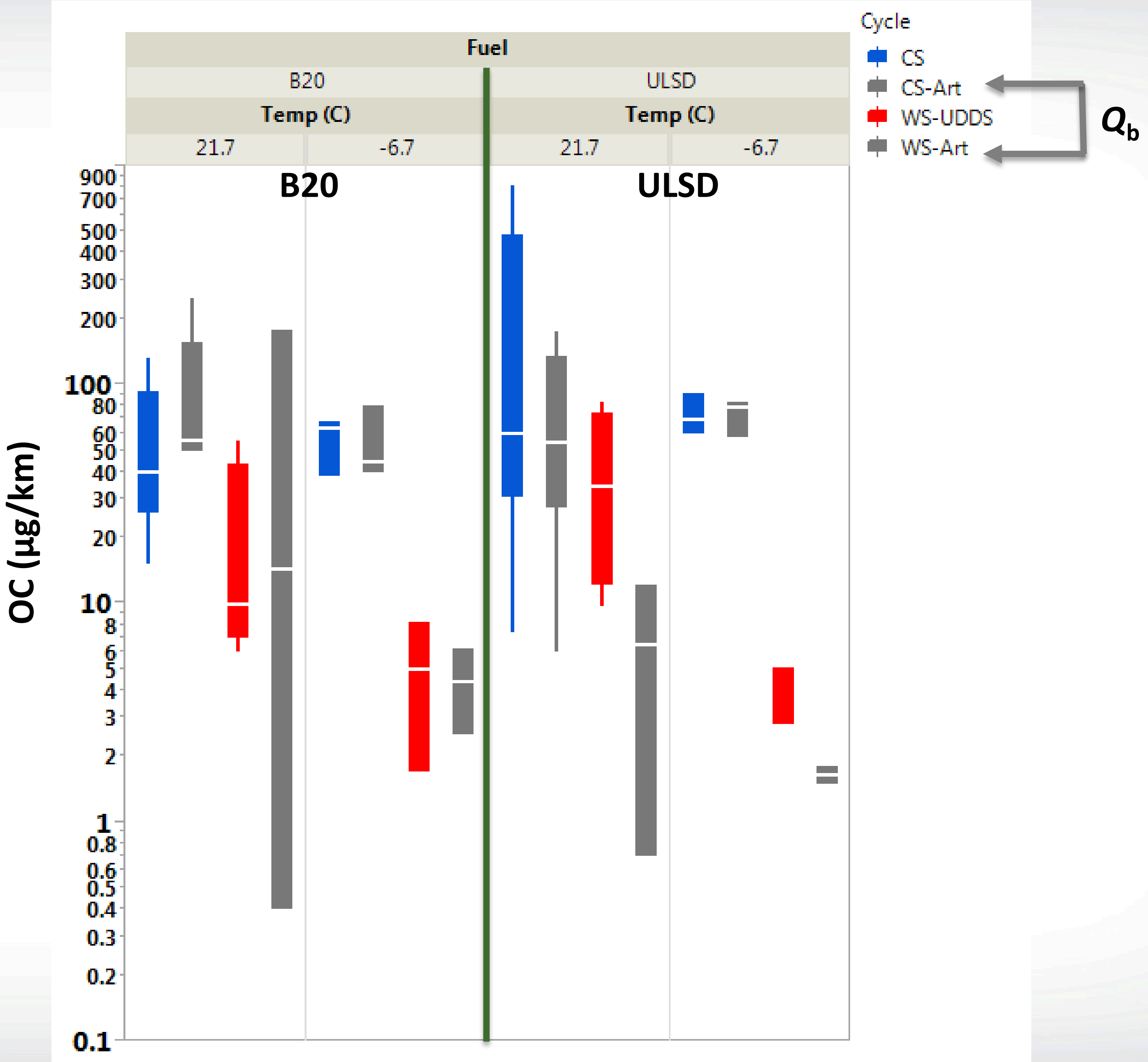
- more organic matter for this vehicle
- less EC in general
- More OC associated with UDDS-WS

EC emissions trends



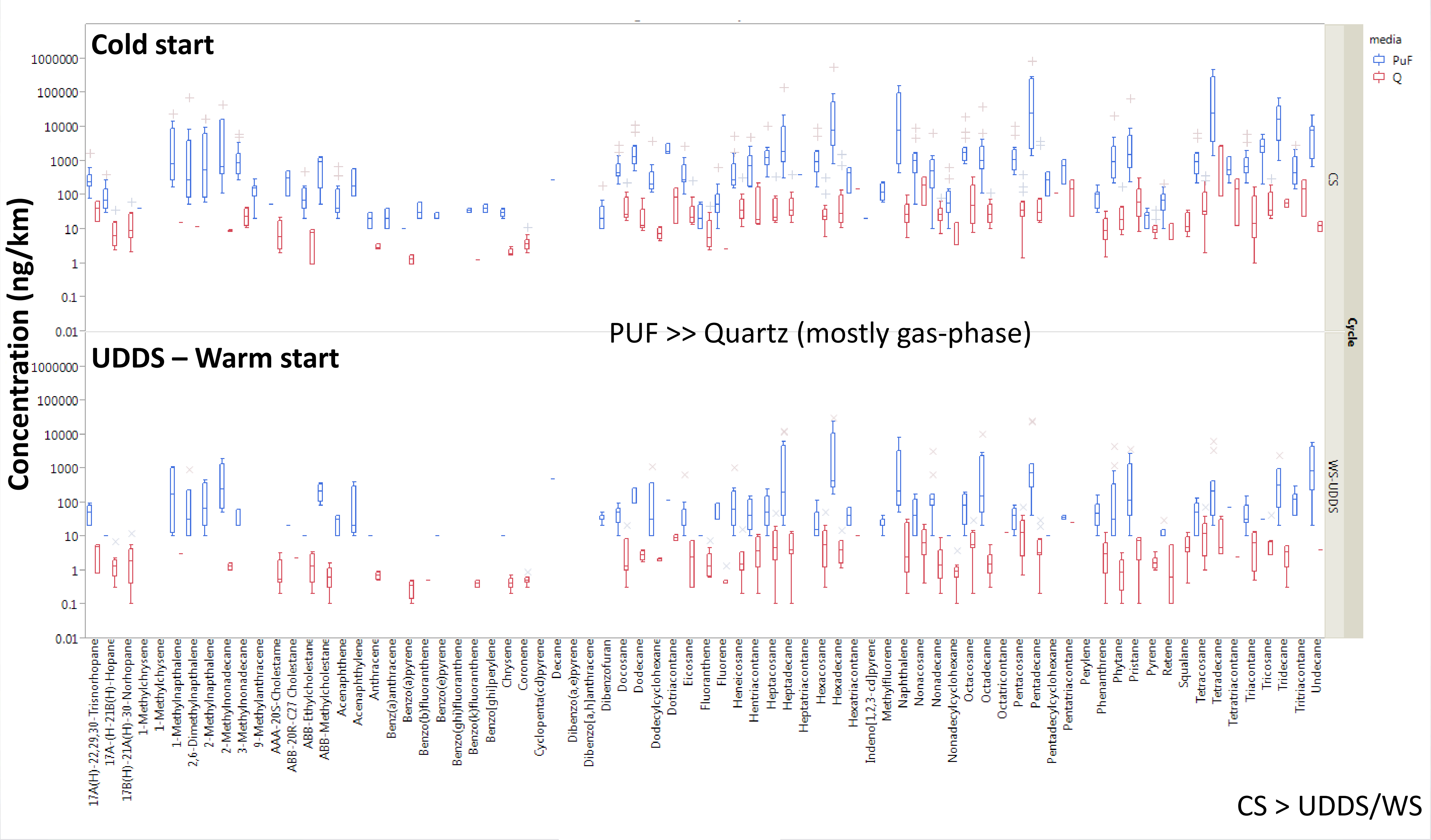
- EC decreases with B20 on average
- lower chamber T -- higher mean EC emissions
- higher chamber T – wider EC range
- EC, CS > UDDS-WS
- mostly Dodge RAM 2500 data

OC emissions trends

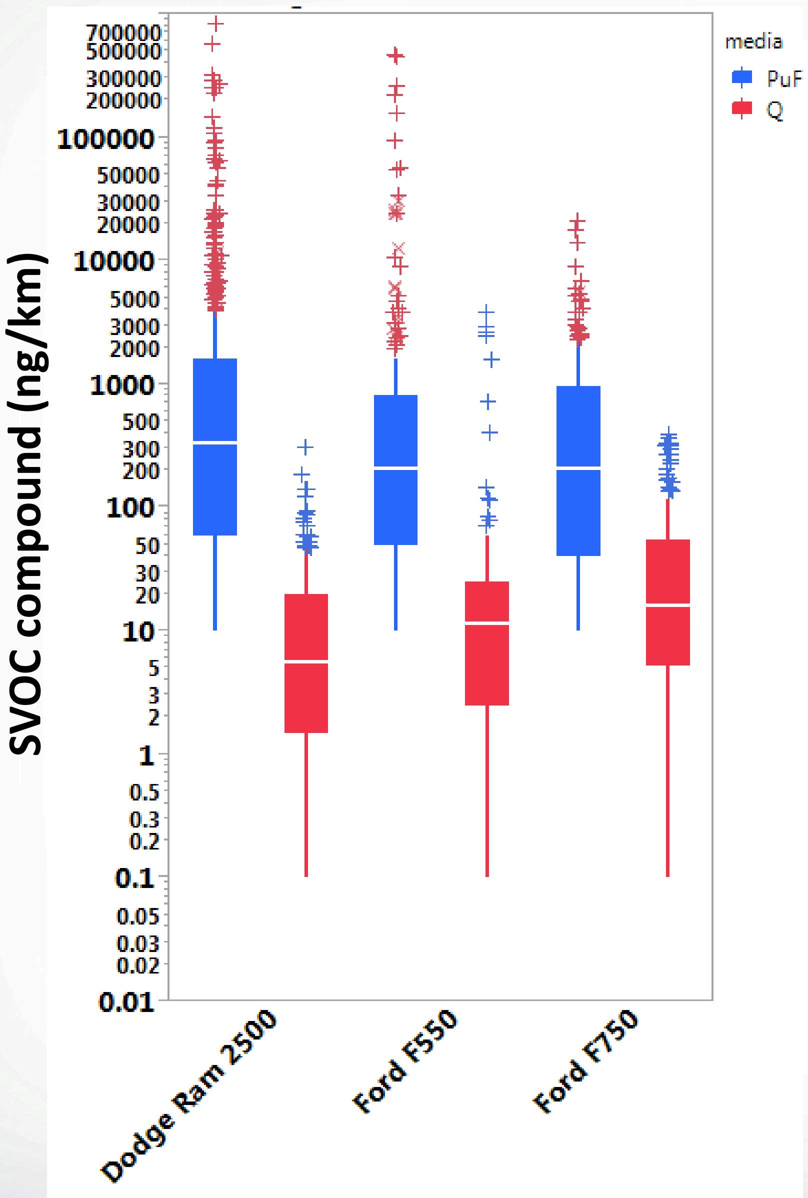


- OC increases slightly with ULSD
- **CS >> UDDS-WS**
- effect of chamber T is unclear
- Contribution to Q_b varied
- Q_b influence stronger for B20 tests

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

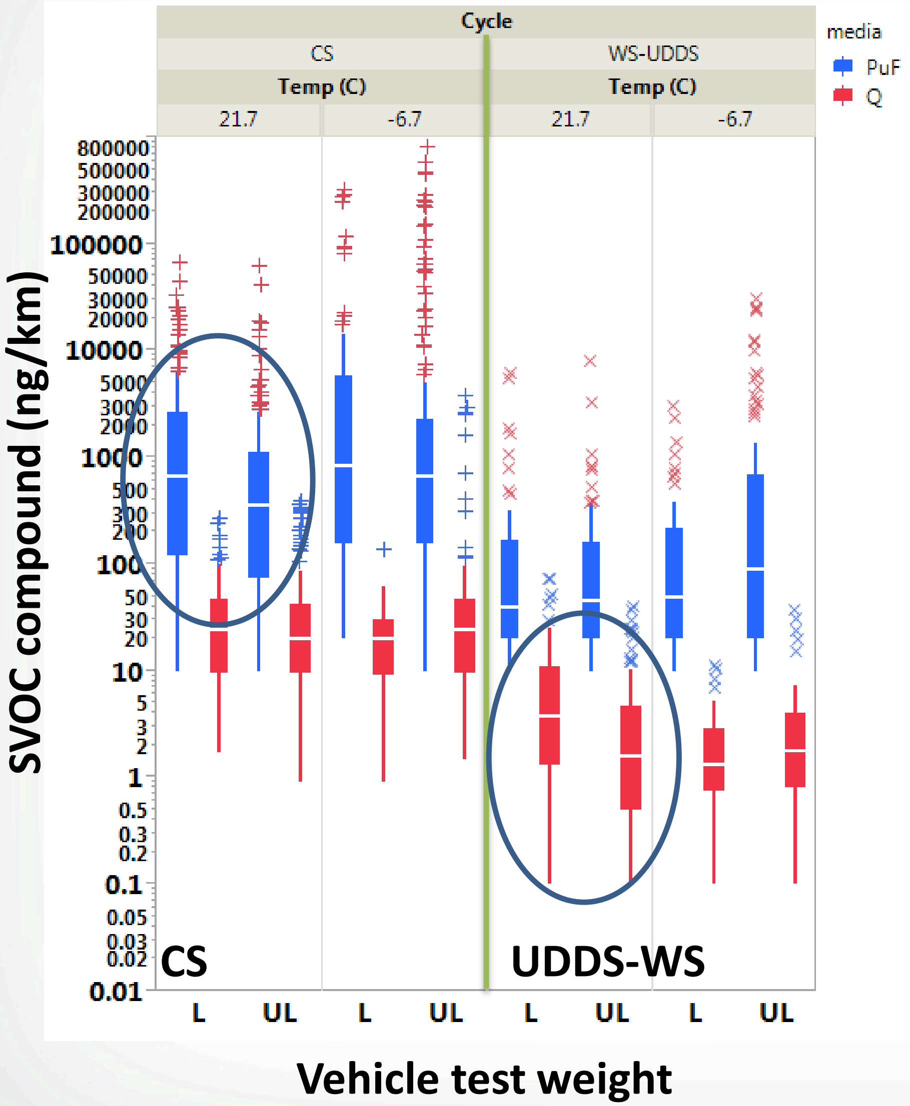


Chemical Analysis – SVOC trends (combined by T, VTW, and fuel)



- Gas phase >>> particle phase
- Vehicle emissions were generally similar
  - No significant difference
  - **Including compound class differentiation**

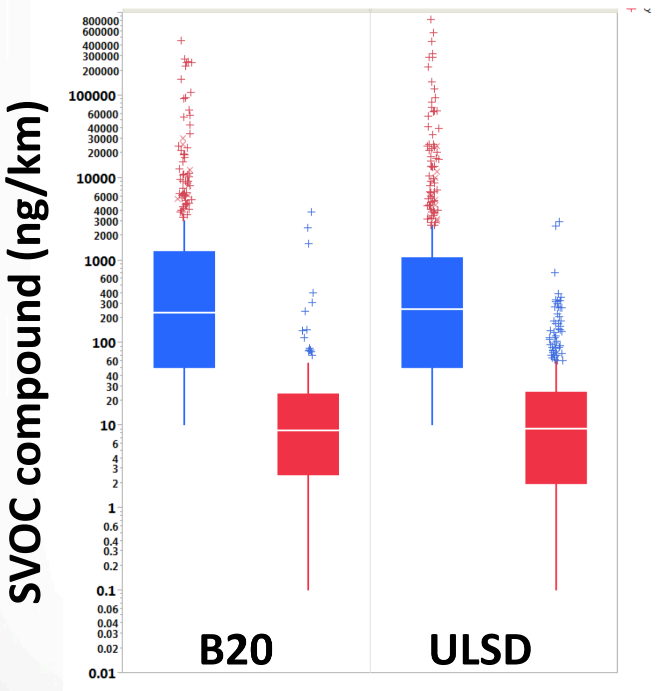
Effect of vehicle test weight on SVOC emissions

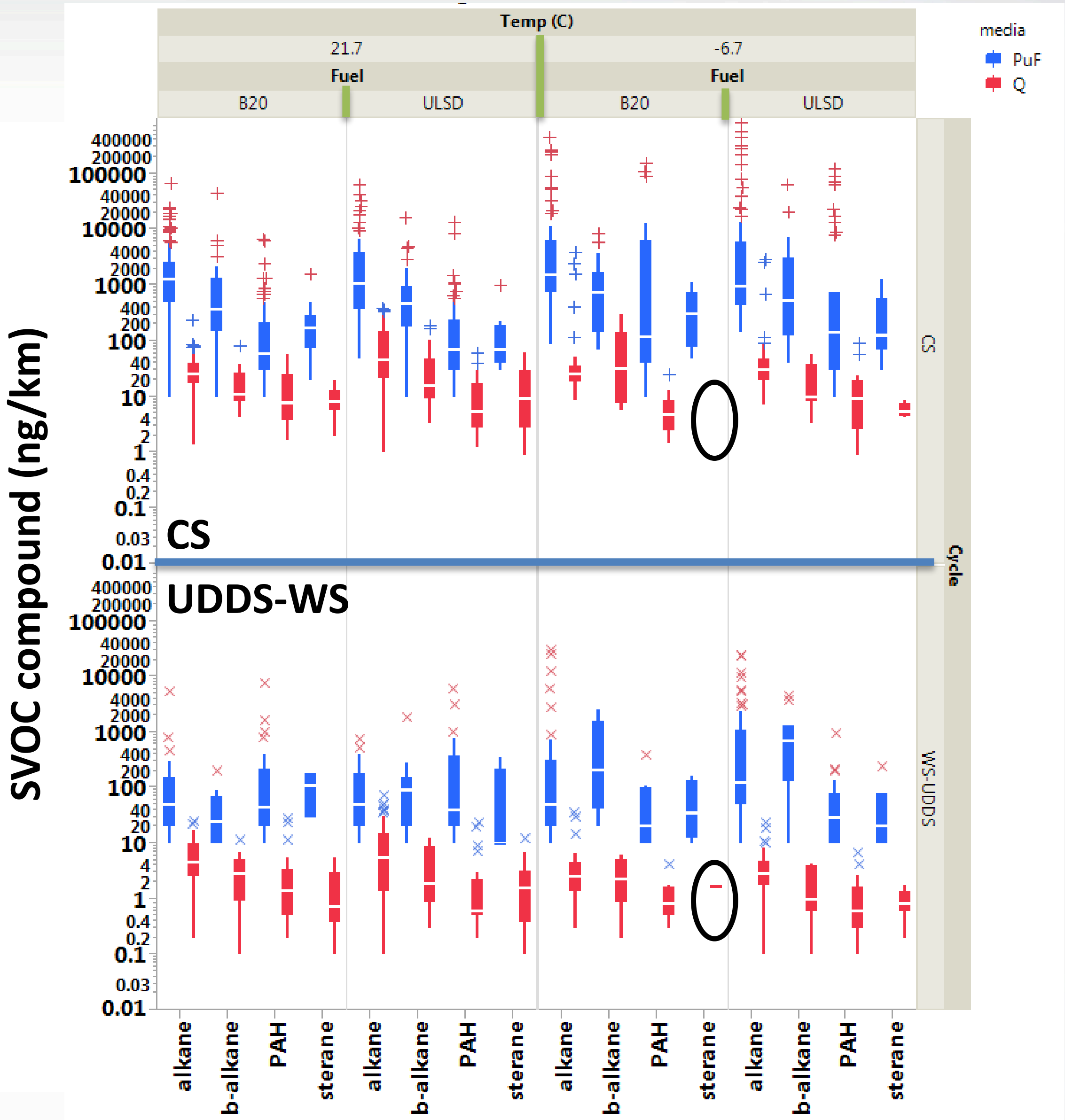


- VTW seemed to have limited effect
  - UL < L emissions in some cases

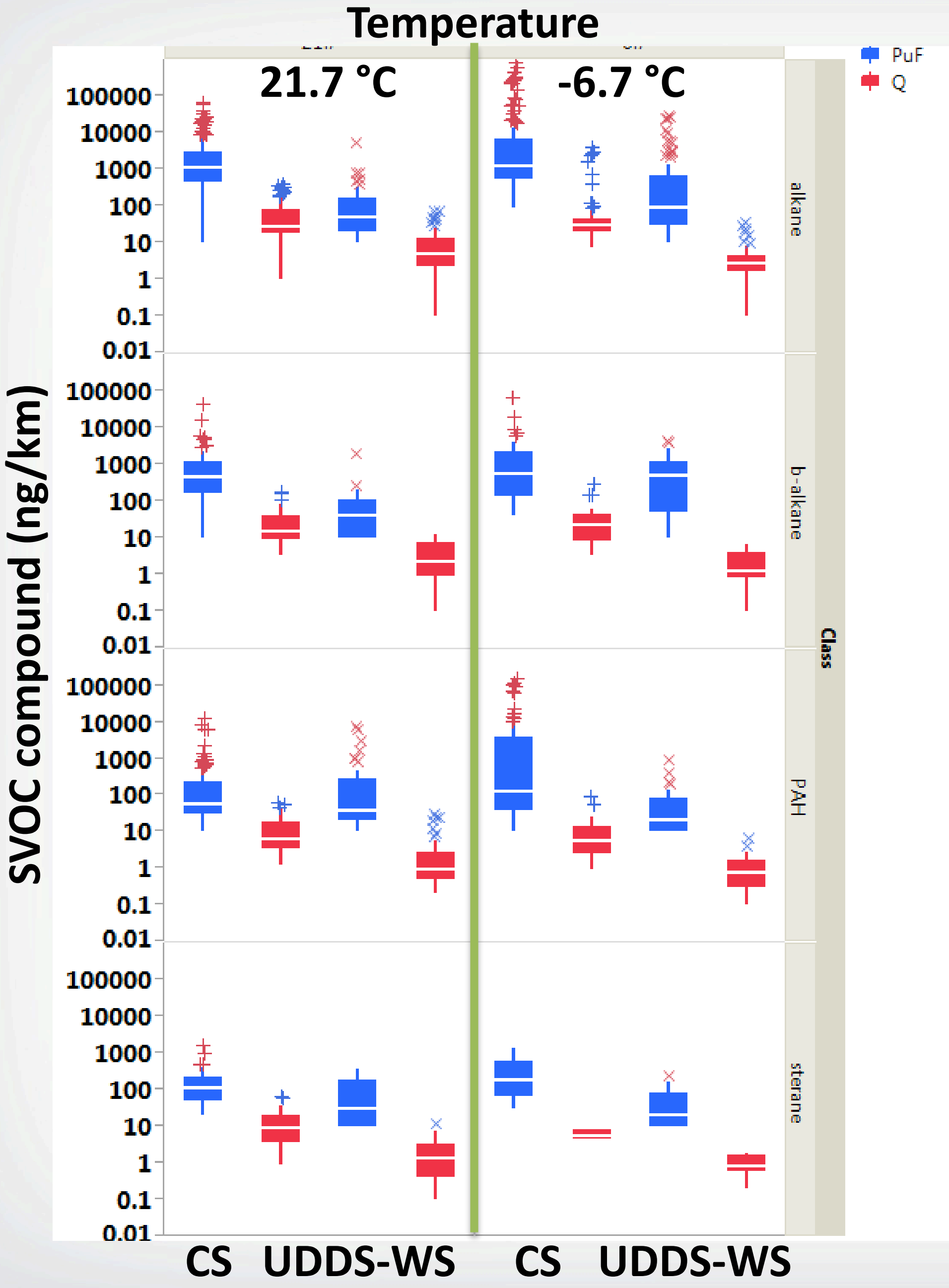
Fuel effects on SVOC emissions

- Fuel effects seem negligible
  - Steranes may decrease when using B20 at -6.7 °C
  - Examination of individual SVOCs needed



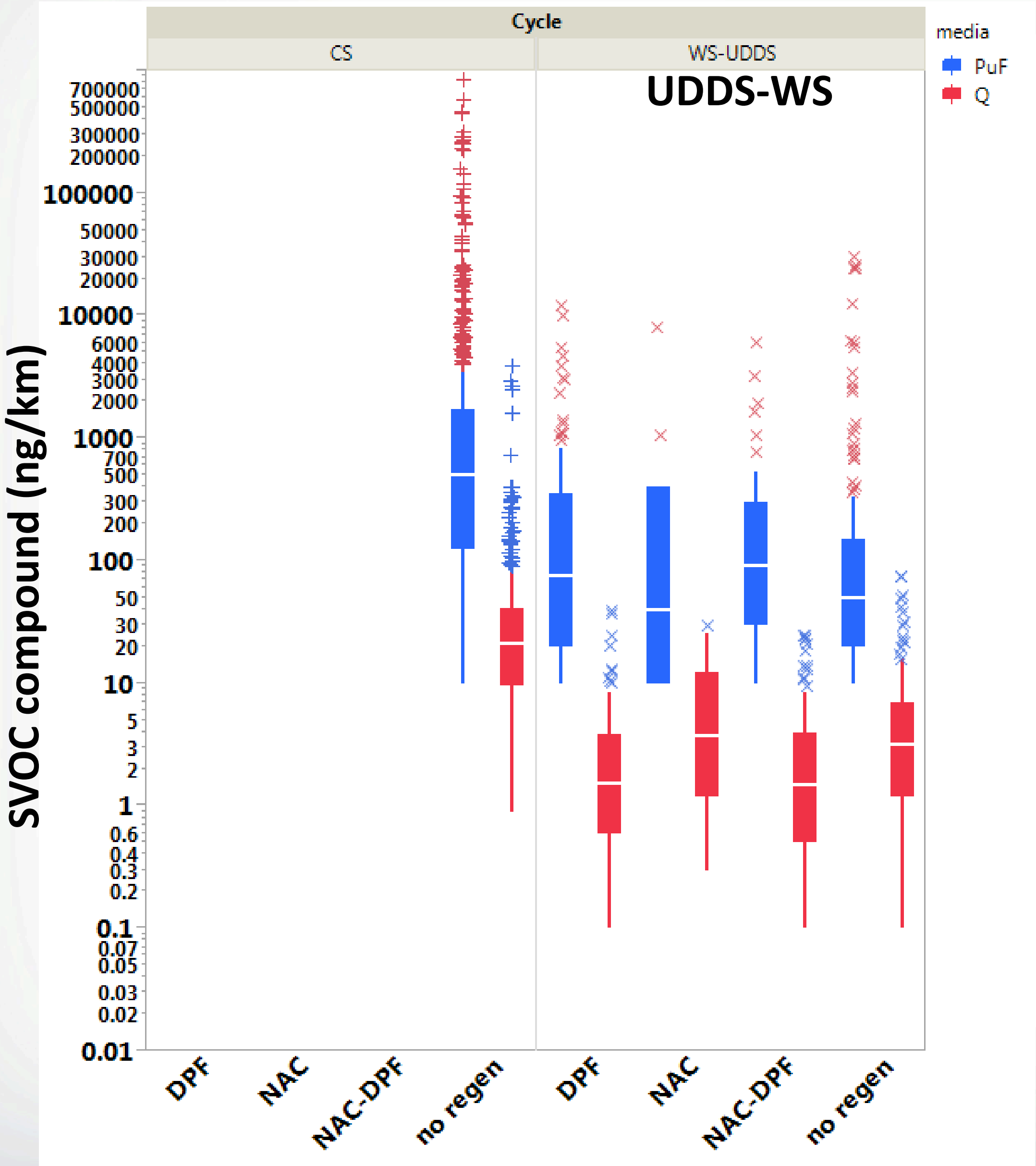


Effect of temperature and driving phase on SVOC emissions



- For gas phase and particle phase by class
  - CS >> UDDS-WS (largest effect)
  - -6.7 °C > 21.7 °

Effects due to regeneration



- Regeneration happens in the UDDS-WS only
- For DPF:
  - Generally lower Q_f collection
  - Higher PuF collection
- NAC influence on SVOCs slight if any
  - uncertain due to low *N*

General conclusions

I. B20 fuel potentially decreases EC emissions
II. Driving phase strongly affects OC and SVOC emissions -- CS >> UDDS-WS
III. OC results are strongly influenced by artifact
IV. For SVOCs: [gas-phase] >> [particle-phase]
V. VTW, fuel, and vehicle model had limited influence on SVOC emissions
VI. DPF regeneration decreases PM but may have increased SVOC gases