Fuel and Aftertreatment Effects on Particulate and Toxic Emissions from GDI and PFI Vehicles: A Summary of CE-CERT's Research

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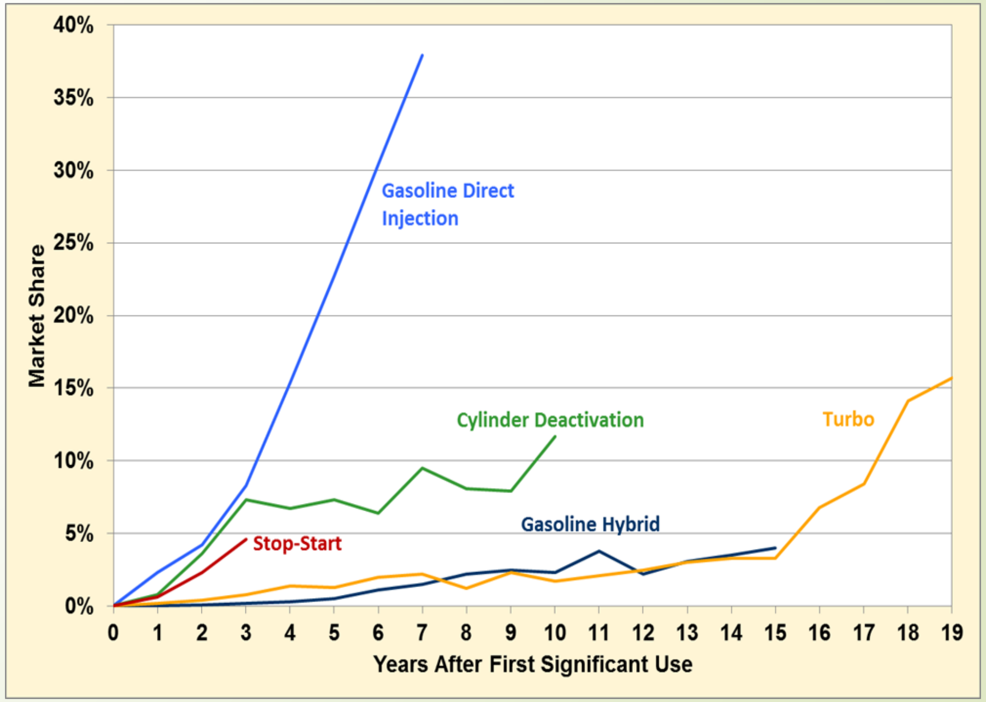
Background

- CE-CERT's research focuses in fuels (fossil and alternative) and their interactions with emerging engine technologies, with emphasis on emissions formation, measurement, and characterization.
- Our main body of research involves studies on gasoline direct injection (GDI) engines operated with alternative fuel formulations (i.e., ethanol and iso-butanol blends).

Why GDIs?

- GDI vehicles on the rise! More than 40% share of the gasoline engine sales in 2012 and a prognosticated market share of up to 97% by 2025
- By injecting gasoline at high pressure directly into the combustion chamber, DI delivers fuel more precisely and efficiently than PFI. The result is more complete combustion and cooler cylinder temperatures, enabling higher CRs for greater efficiency and power
- OEMs are looking for trouble!
  - GDI can lead to increased PM from:
  - Fuel impingement onto piston surface and cylinder walls
  - Fuel leakage from injectors
  - Overfueling during accelerations



Background

- Do we know enough about GDI exhaust?
  - Many studies have investigated gaseous and particulate emissions from GDI vehicles/engines
  - Less studies have looked at the fuel effect from GDIs
  - Few studies looked at the chemical characteristics of PM from GDIs
- Is GDI exhaust toxic?
  - Recent studies [Advanced Collaborative Engine Study (ACES)] have shown that there is no evidence of gene damaging effects in the animals studied for diesel exhaust with DPFs
  - A new worry: Studies have shown that polycyclic aromatic hydrocarbons (PAHs) are much higher in GDI exhaust than current technology diesel vehicles

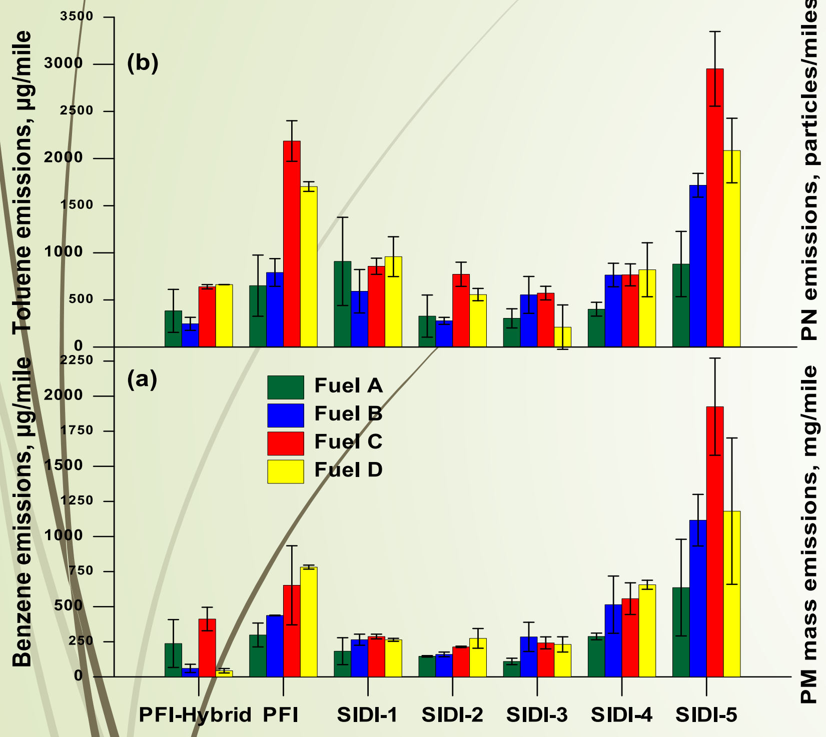
The Effect of Gasoline Aromatics on Tailpipe Emissions: A Straightforward Story

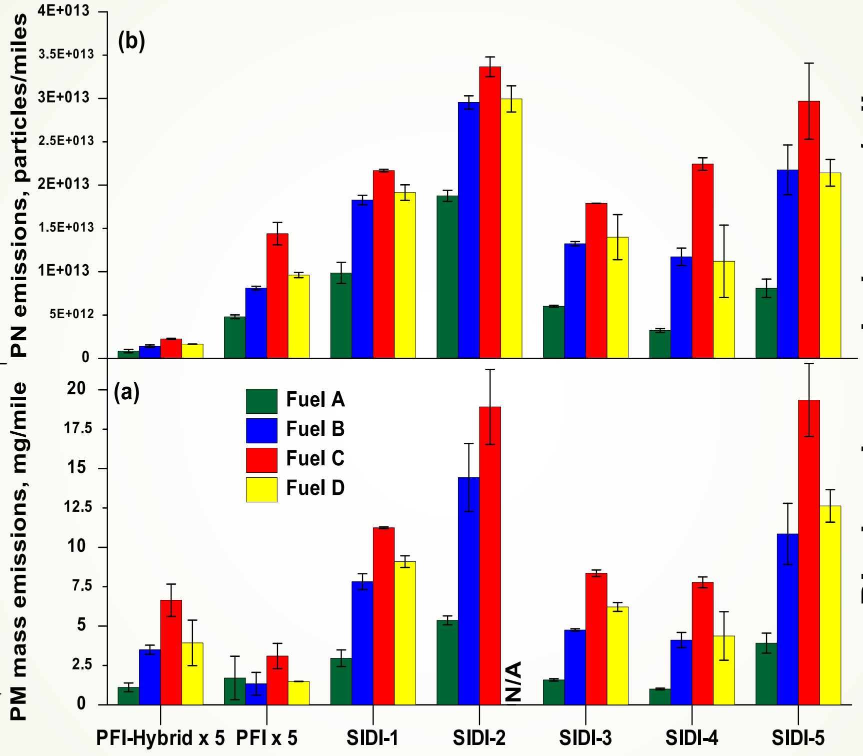
- **<u>Fuels:</u>** The fuel matrix included 3 gasolines blended to meet nominal total aromatics targets of 15% (denoted fuel A), 25% (denoted fuel B), and 35% (denoted fuel C) by volume. A fourth fuel (denoted fuel D) had the same aromatics as fuel C, but was blended to meet a target AKI value that was at least 3 octane numbers higher
- **<u>Vehicles:</u>** Seven 2012 MY LDVs were used, including one hybrid vehicle with PFI fueling (PFI-Hybrid), one conventional PFI passenger car (PFI), and five LD SIDI vehicles with wall-guided injection systems
- Testing was conducted on triplicate LA92 cycles

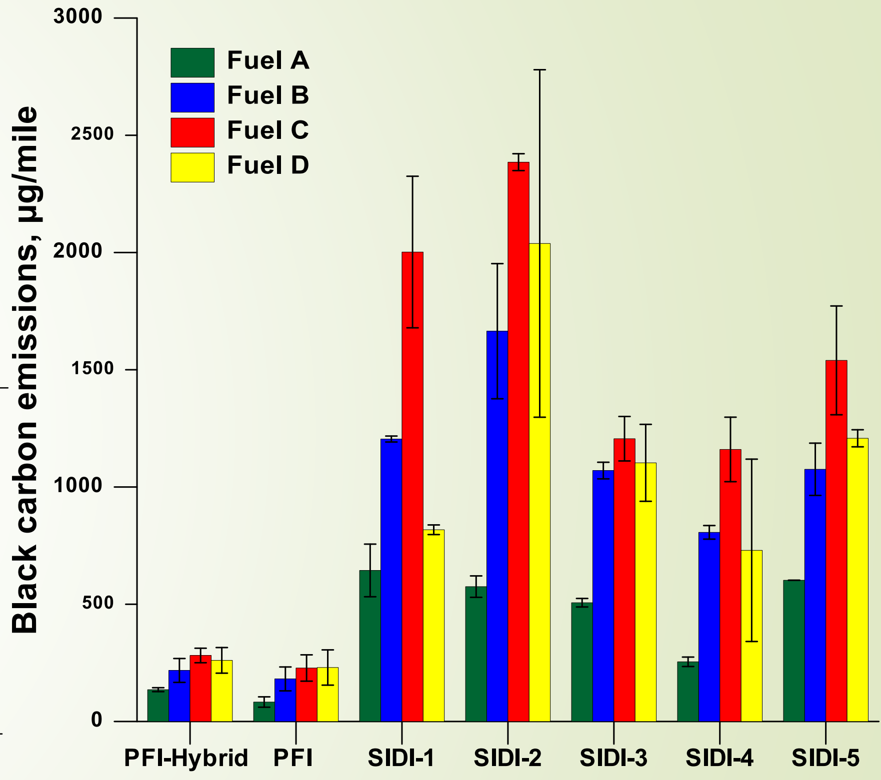
Property		Fuel A	Fuel B	Fuel C	Fuel D
Aromatics	Vol. %	14.7	25.4	34.7	34.7
Specific Gravity	g/cm^3	0.7309	0.749	0.7631	0.7597
RVP	kPa	54.33	54.33	51.71	54.12
Benzene	Vol. %	0.69	0.62	0.65	0.67
Ethanol	Vol. %	9.64	9.63	9.5	9.63
Gross Heating Value	kJ/kg	45117	44477	44040	43928

Karavalakis et al., Environ. Sci. Technol. 2015, 49, 7021-7031.
Short et al., Environ. Sci. Technol. 2015, 49, 10682-10691.

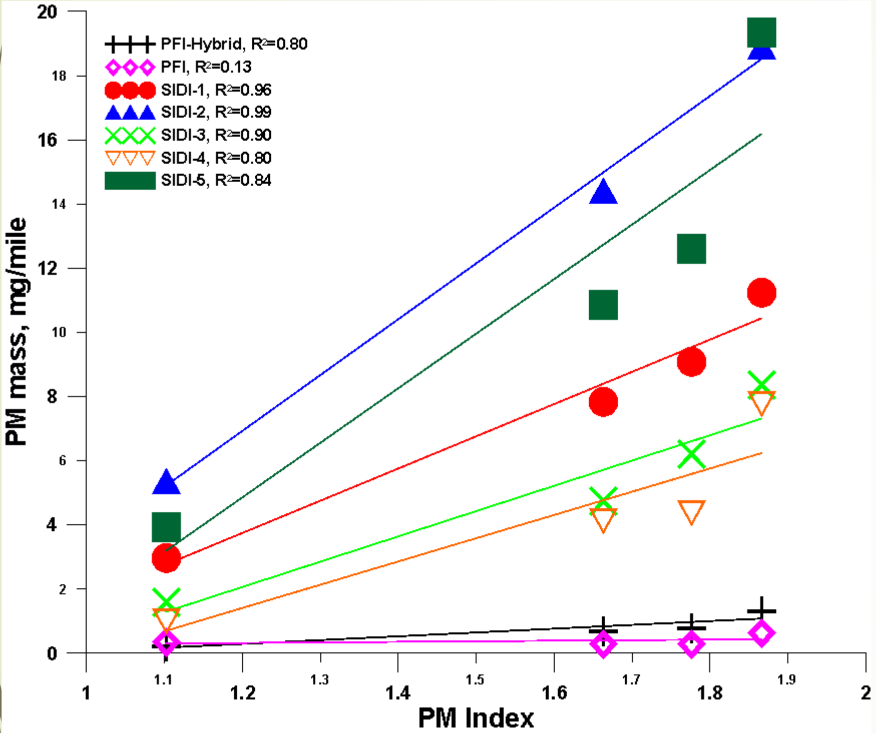
Mobile Source Air Toxics (MSATs), PM, PN, and BC Emissions







PMI



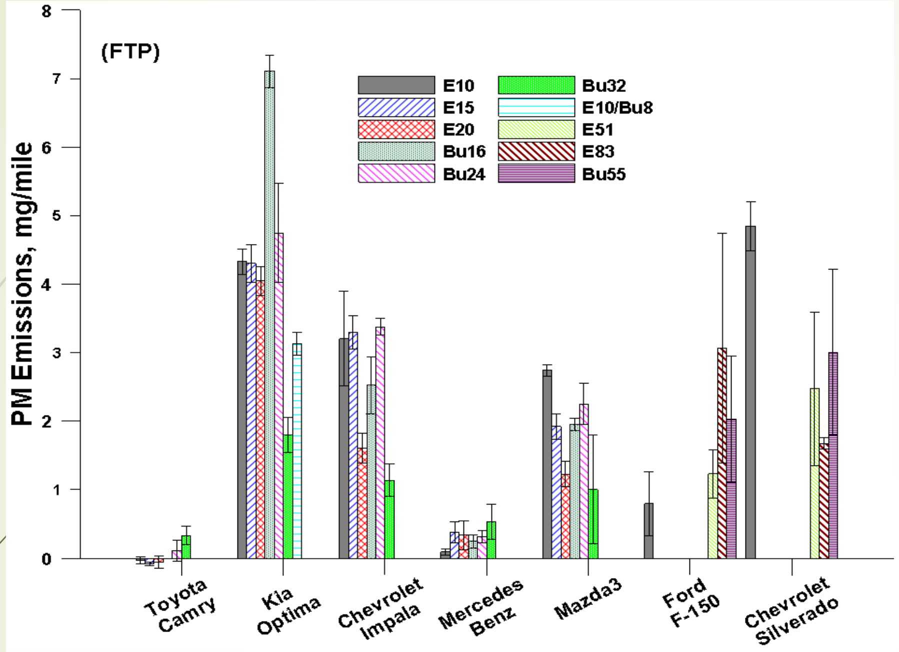
	Fuel A		Fuel B		Fuel C		Fuel D	
	Wt%	PMI%	Wt%	PMI%	Wt%	PMI%	Wt%	PMI%
Total PMI		1.102		1.663		1.866		1.777
Paraffin	11.084	2.311	14.638	1.462	15.568	1.611	12.765	0.678
Iso-Paraffins	44.317	8.381	28.497	3.682	18.535	2.040	23.343	2.181
Mono-Aromatics	18.436	68.783	31.428	75.013	41.375	81.790	41.376	82.754
Naphthalenes	0.225	7.603	0.295	6.865	0.225	4.512	0.230	4.967
Naphtheno/Olefino-Benzenes	0.319	3.912	0.503	4.301	0.396	3.068	0.402	3.246
Indenes	0.538	5.282	0.785	6.307	0.806	4.702	0.697	4.576
Mono-Naphthenes	5.231	1.814	5.087	1.158	5.325	1.204	3.310	0.532
n-Olefins	6.354	0.932	6.214	0.613	5.273	0.530	6.583	0.598
Iso-Olefins	0.793	0.344	0.761	0.155	0.747	0.140	0.521	0.076
Naphtheno-Olefins	0.099	0.038	0.134	0.045	0.131	0.052	0.089	0.021
Oxygenates	11.032	0.601	10.504	0.400	10.276	0.352	10.422	0.374

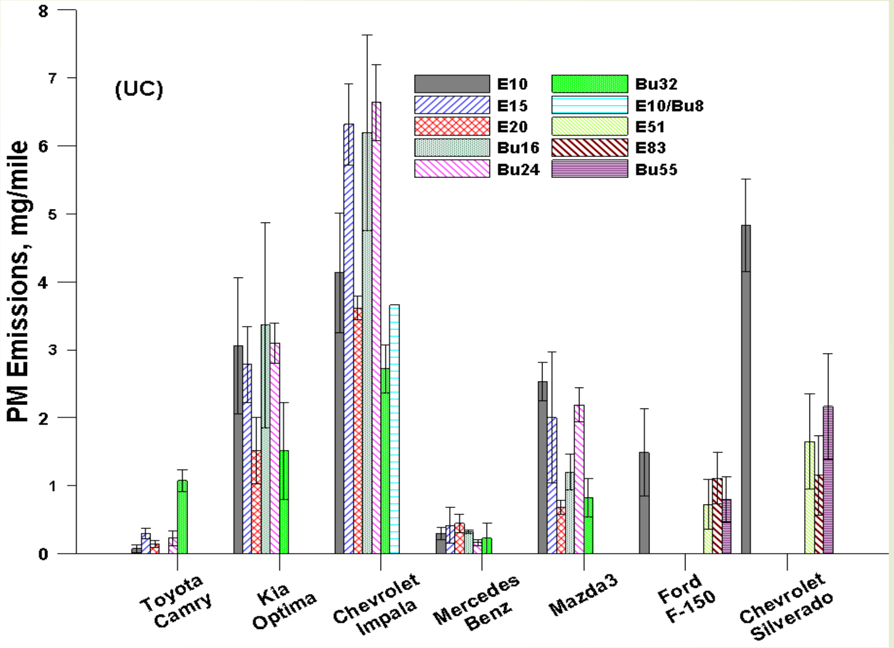
- Strong correlation between PM with higher double bond equivalent (DBE) values and higher boiling points (bp) for different chemical species in the fuel.
- PM mass and number increase as the bps of the hydrocarbons increased.
- The PM mass emissions showed increases with increasing the PMI and a good correlation with both PM mass and number emissions for all test vehicles, with the exception of the PFI vehicle.
- Paraffins and iso-paraffins showed little contribution to the total PMI compared to the total aromatics.
- Components with higher boiling points, such as heavier normal paraffins, indenes, mono-naphthenes, naphtheno/olefin-benzenes, and iso-olefins, produced a higher PMI.

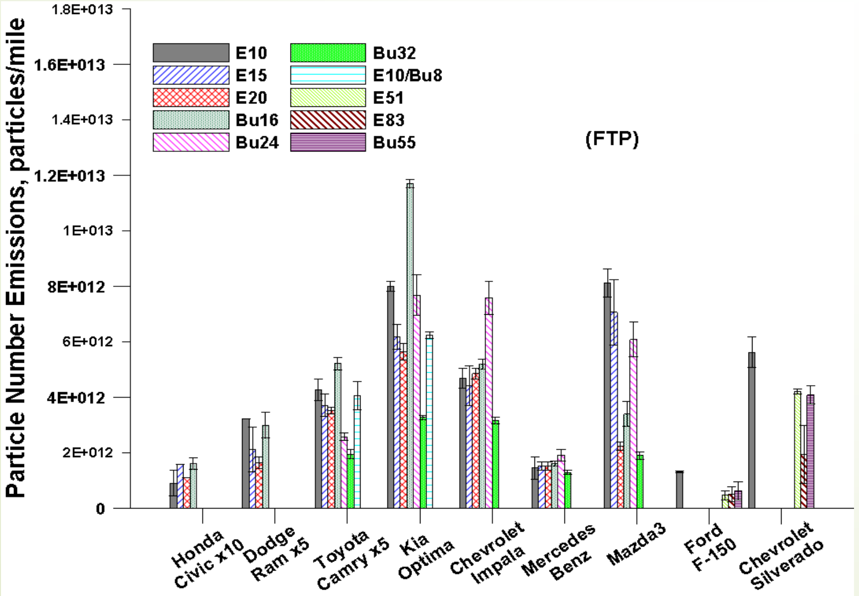
Assessment of Ethanol and Iso-butanol on Emissions from GDI and PFI Vehicles: A Less Straightforward Story

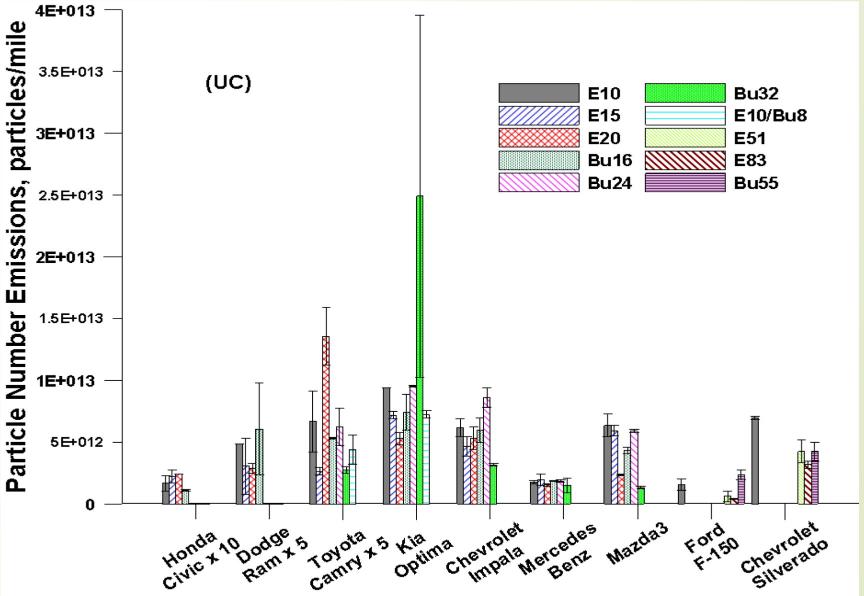
- **Vehicles:** 9 vehicles were used including 6 passenger cars and 2 LD trucks. 4 vehicles with PFI fueling (1 FFV) and 5 vehicles with DI fueling (1 FFV)
- **Fuels:** 10 fuels were employed in the study: E10, E15, E20, E55, E855, Bu16, Bu24, Bu32, Bu55, and E10/Bu8
  - The lower blends were custom blended to match the oxygen contents, maintain the RVP within certain limits, and match the fuel volatility properties.
  - The higher ethanol blends represent the upper and lower blend limits of the current E85 specification.
  - For Bu55, this was the highest volume of iso-butanol that could be blended while still meeting the California summer gasoline specifications.
- Testing was performed on triplicate FTP and LA92 cycles.

PM and PN Emissions

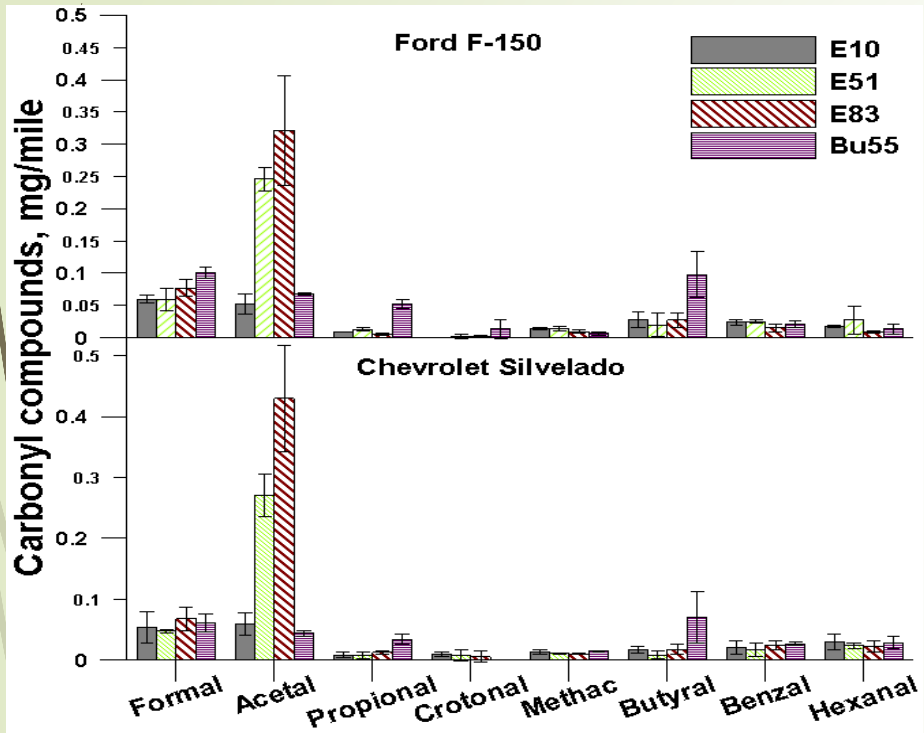


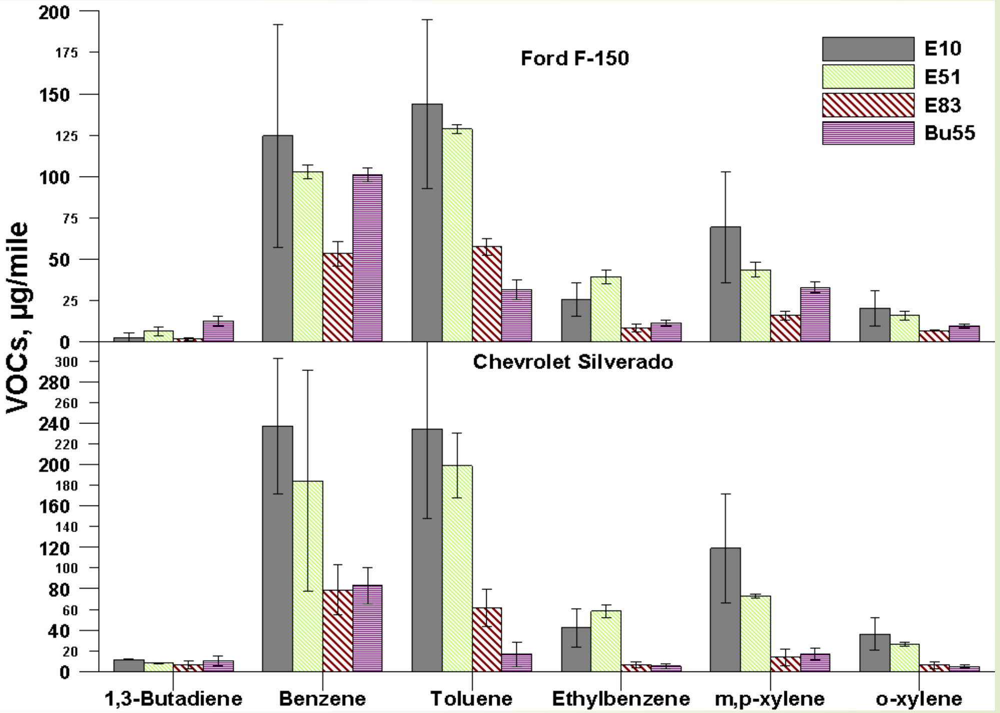






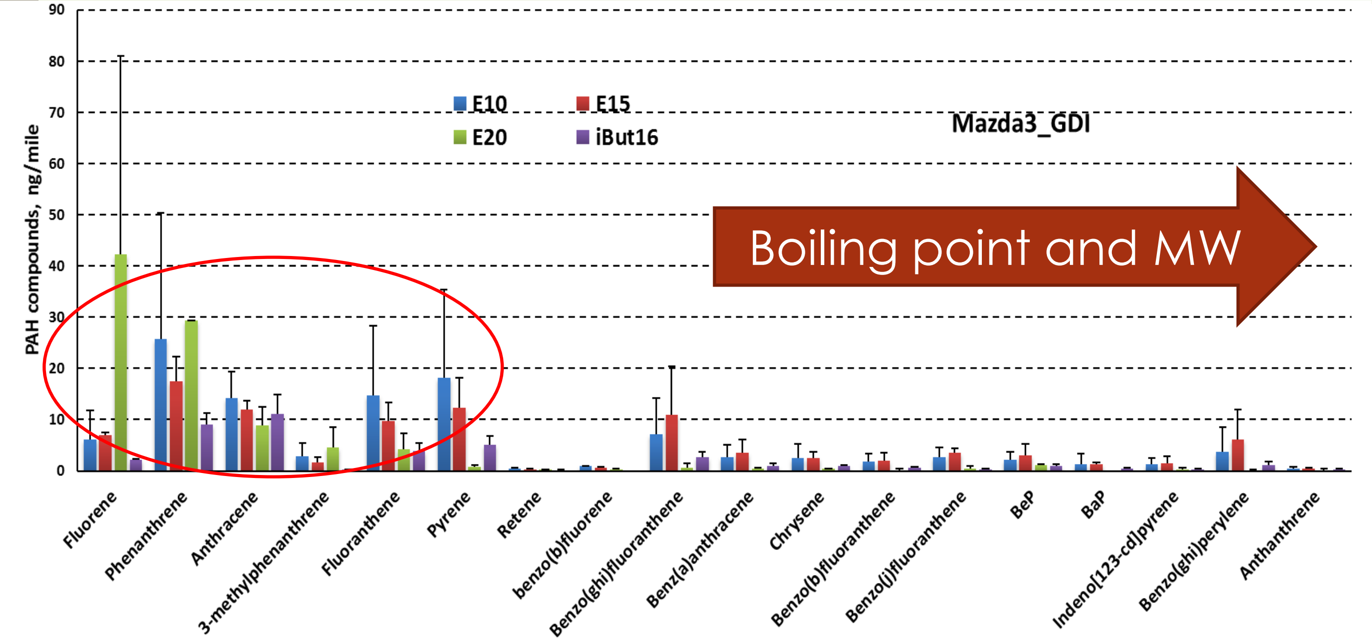
MSATs

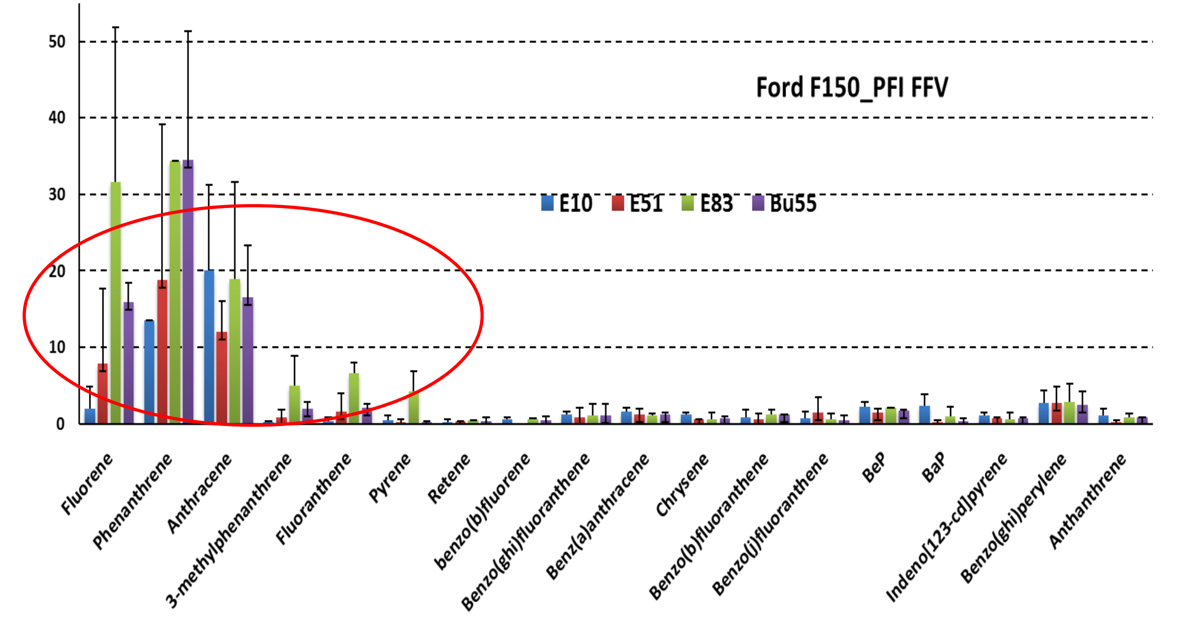


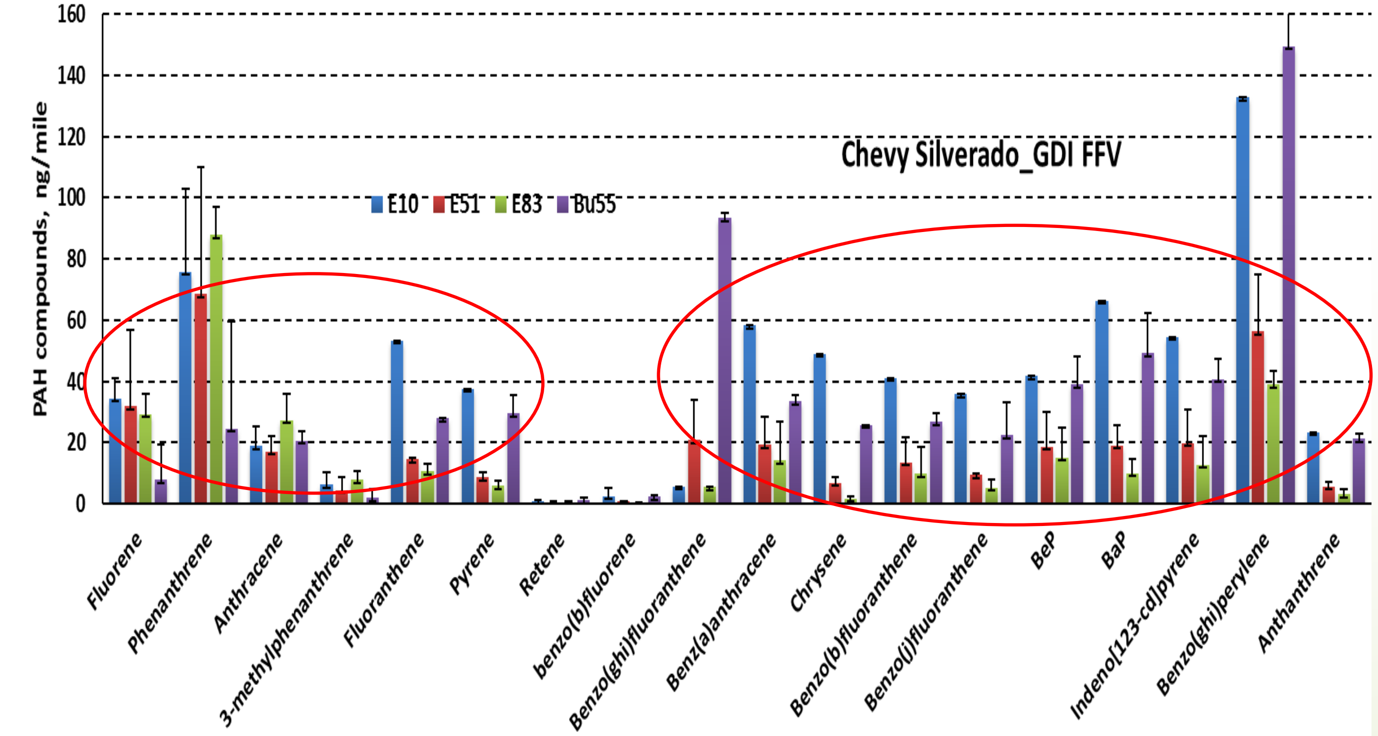


- No strong fuel effects on aldehyde emissions for the non-FFVs. For the FFVs, acetaldehyde showed statistically significant increases for E51 and E83 compared to E10, while Bu55 showed decreases compared to E51 and E83.
- Higher butyraldehyde emissions for the butanol blends, which could be due to sequential H-atoms abstractions from the iso-butanol hydroxyl moiety to form a C4H9O radical, which then undergoes β-scission to yield butyraldehyde.

- No strong fuel effects on BTEX and 1,3-butadiene emissions for the non-FFVs.
- For the FFVs, most BTEX species showed statistically significant decreases with the higher alcohol fuels compared to E10.







Mazda3:

- 3-4 rings most abundant PAHs
- Reductions with higher boiling point and higher MW species
- PAH reductions with ethanol and iso-butanol blends

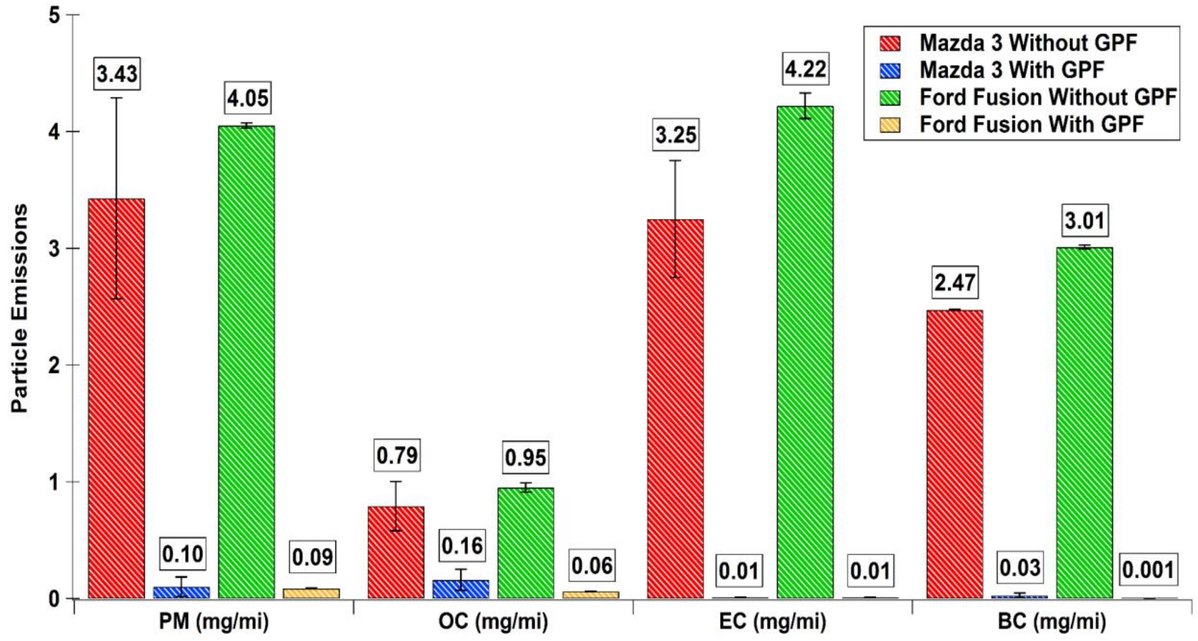
Chevy:

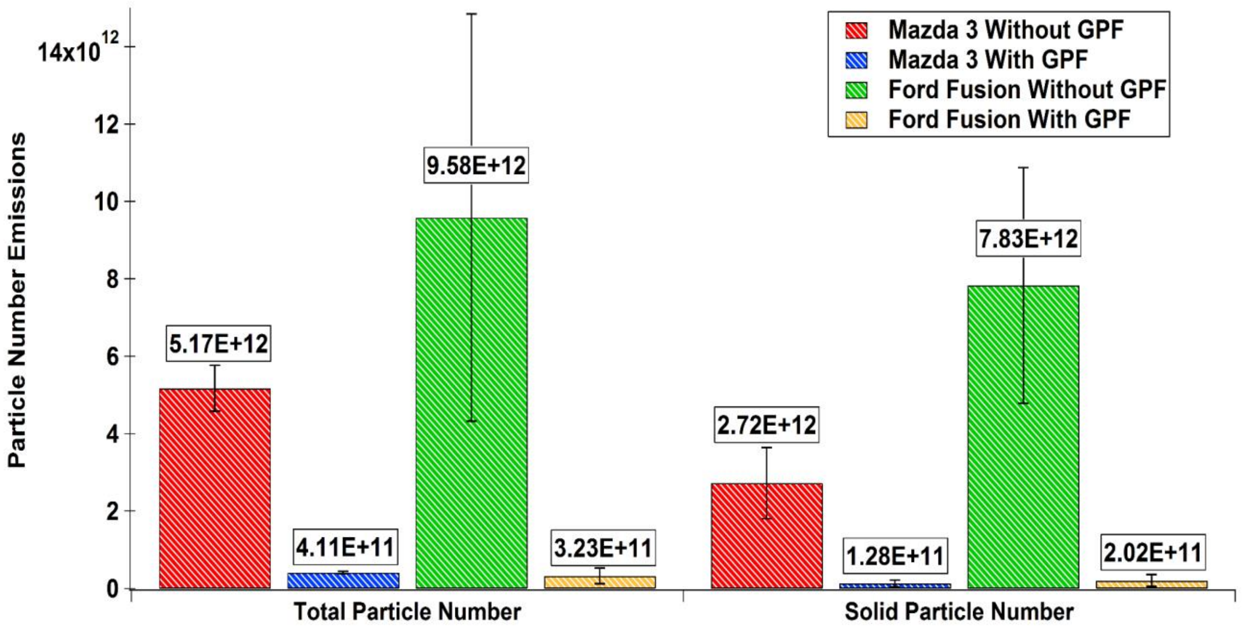
- Higher PAH concentrations than the GDI passenger car; 2-3 rings and 5-6 rings the dominant PAHs in the exhaust
- Overall, higher ethanol blends resulted in PAH decreases, whereas Bu55 blend in PAH increases.
- Bu55 led to increases in some carcinogenic & mutagenic PAHs.

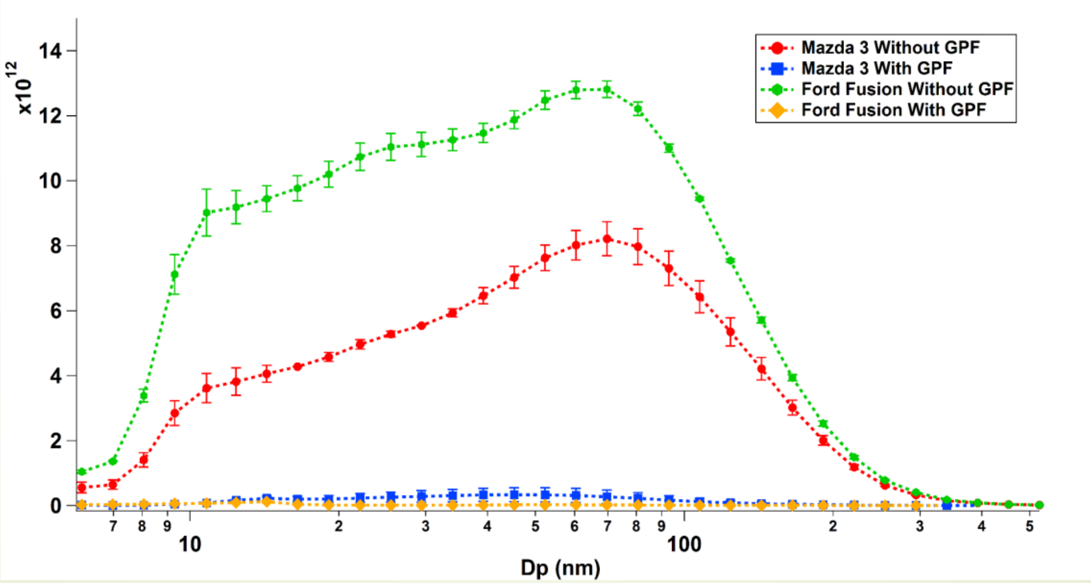
Ford:

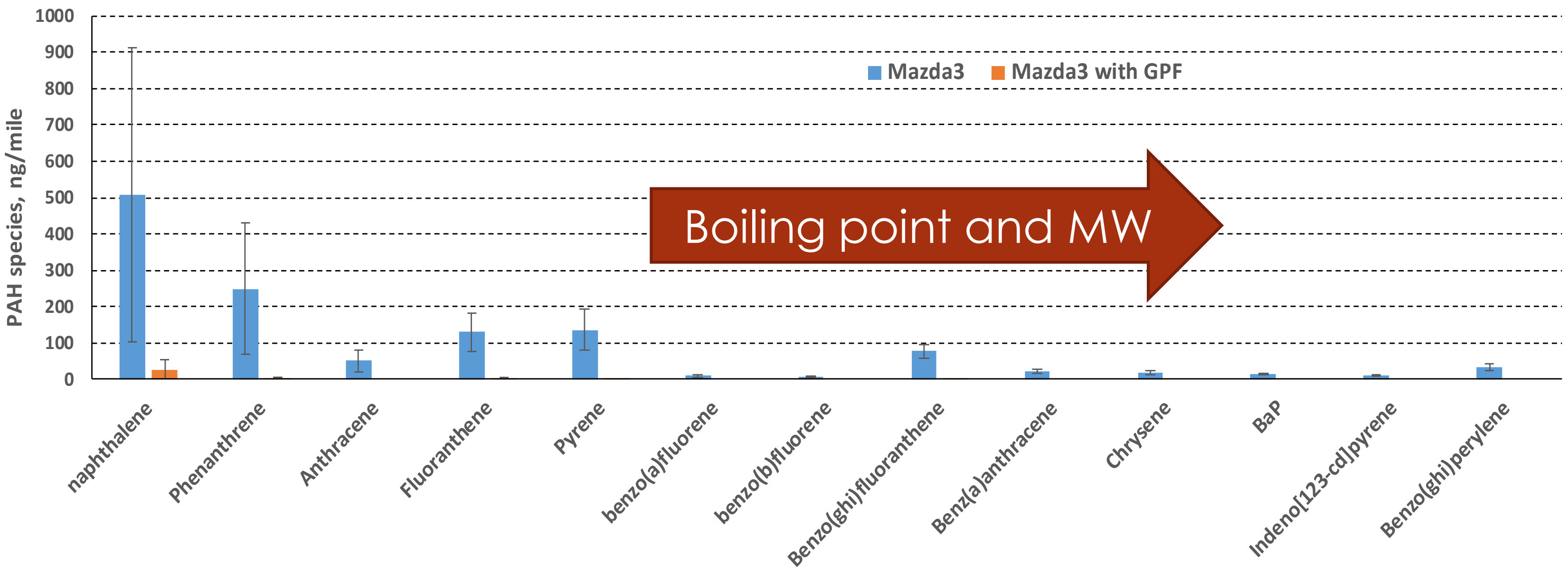
- 2-3 ring PAHs dominate the exhaust for the PFI vehicle.
- Some increases in light PAHs with higher ethanol and the iso-butanol blend.
- Lower concentrations for the heavier PAHs compared to the GDI vehicles.

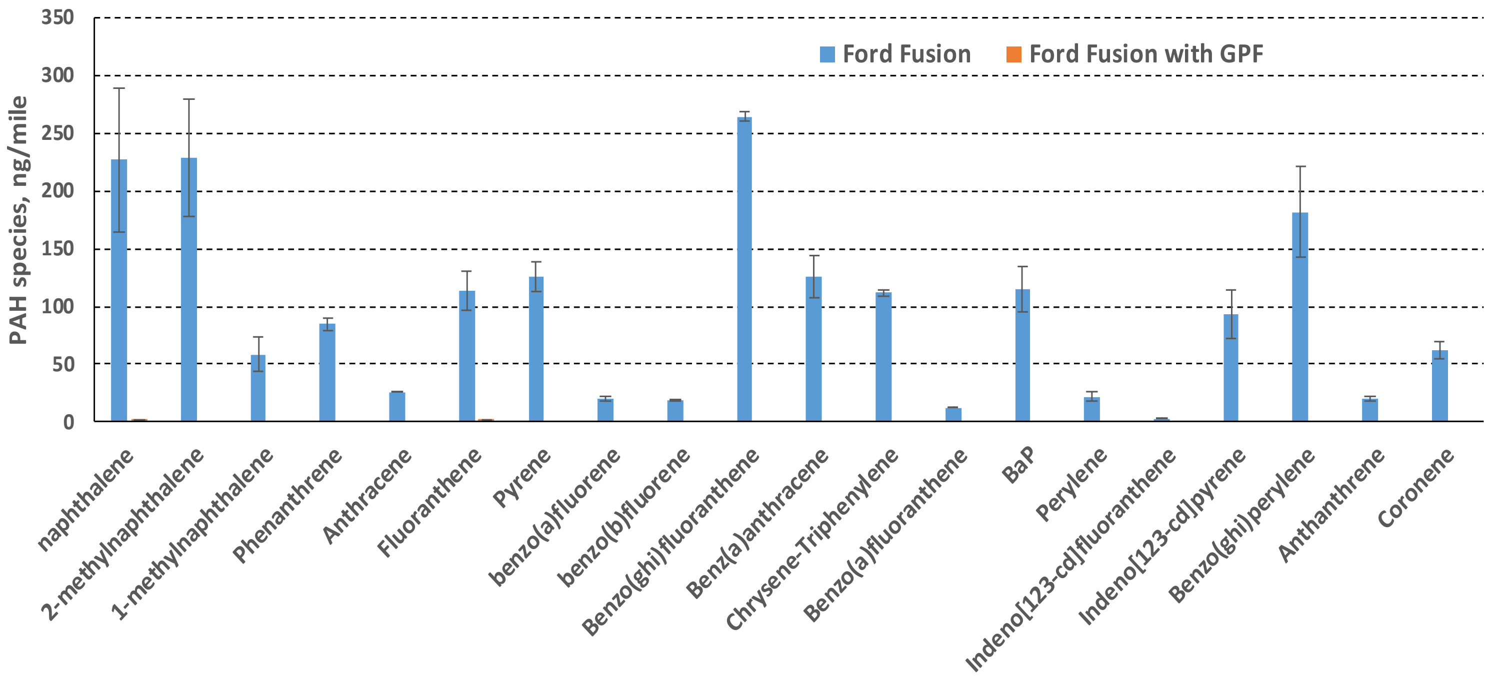
The GPF Influence: A Straightforward Story



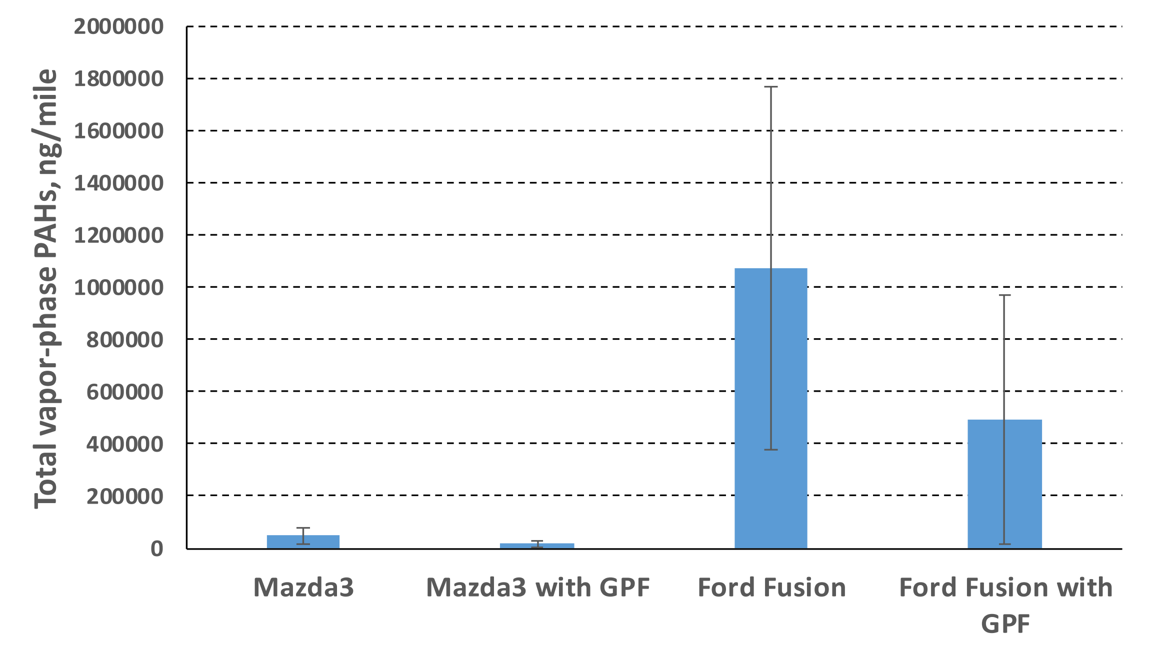


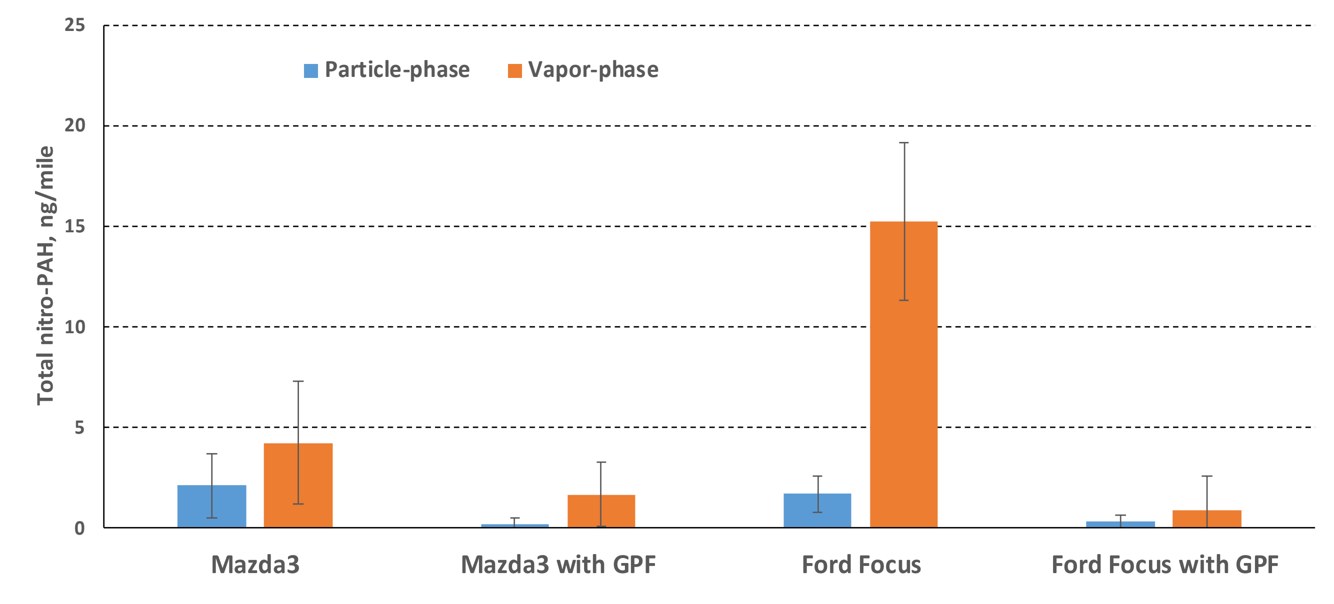


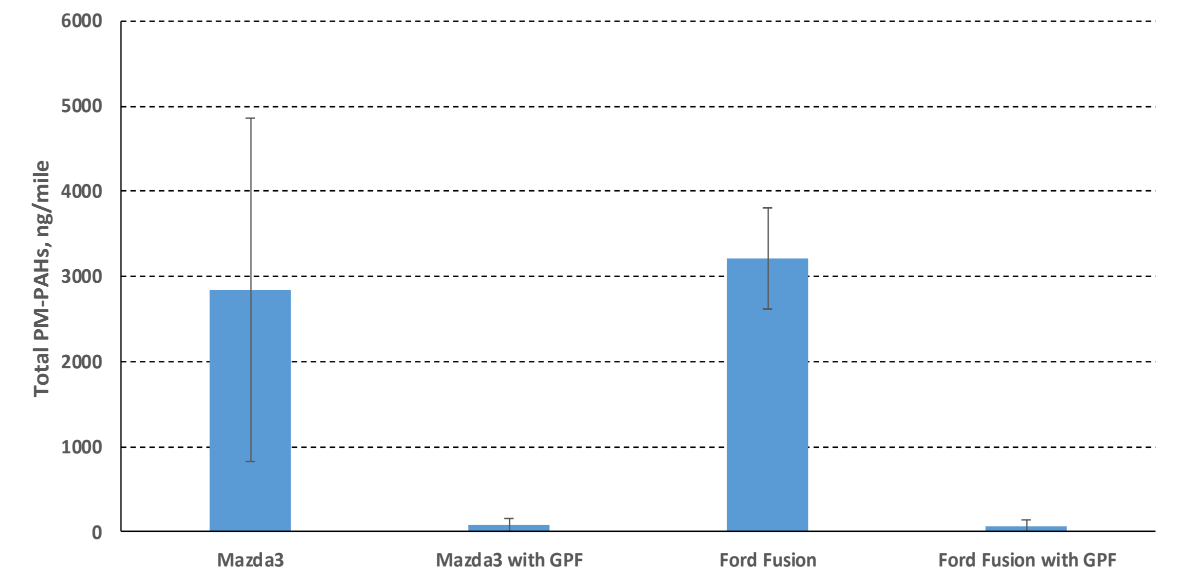




- The use of GPF practically eliminates most PAH species
- Both vehicles dominated by 2-3 ring PAHs, such as naphthalene, methyl- and ethyl-naphthalenes.
- Ford Fusion also emitted heavier PAHs, which are known as mutagenic and carcinogenic compounds.
- Oxygenated PAHs (PAH-ketones, PAH-aldehydes, etc.) were seen in high levels for the Ford Fusion.
- This specific Mazda3 showed higher PM mass and PAH emissions compared to the 2012MY Mazda3.







- Vapor-phase PAHs were found in significantly higher levels than those in the PM-phase
- The vapor-phase profile dominated by naphthalene and methyl- and ethyl-naphthalenes
- PM-phase nitro-PAHs were dominated by 1-nitropyrene, followed by nitro-naphthalenes, whereas vapor-phase profile dominated by nitro-naphthalenes and nitro-biphenyls

Lessons Learned

- Increasing gasoline aromatics will increase PM mass, number, and BC emissions, as well as MSATS
- PM mass and number were generally lower with ethanol and iso-butanol blends
- Mid-level and higher ethanol blends would lead to increases in acetaldehyde emissions from both PFI and DI fueling systems.
- Butyraldehyde, an aldehyde that posses similar reactivity and mutagenicity to acetaldehyde, would also increase with the use of butanol fuels.
- Overall, lower PAH emissions with higher alcohol fuels than E10.
- Some GDIs resulted in high concentrations of heavier PAHs
- The use of GPFs can significantly reduce particulate, PAH, and nitro-PAH emissions

Research Needs

- Targeted studies on PAH and nitro-PAH emissions from older technology and newer technology GDI vehicles, equipped with wall-guided and spray-guided systems
- Investigate particulate and MSAT emissions from GDI vehicles operated on gasoline fuels with varying oxygen and aromatics contents
- Evaluate the impacts of alcohol fuels and varying aromatics on SOA formation from GDI vehicles under different driving conditions (high speed driving, idling, cold vs. hot starts, etc.)
- Targeted health effect studies using older technology and newer technology GDI vehicles

Acknowledgements

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