Contributions of Non-tailpipe Emissions to $PM_{2.5}$ and PM_{10} near Highways

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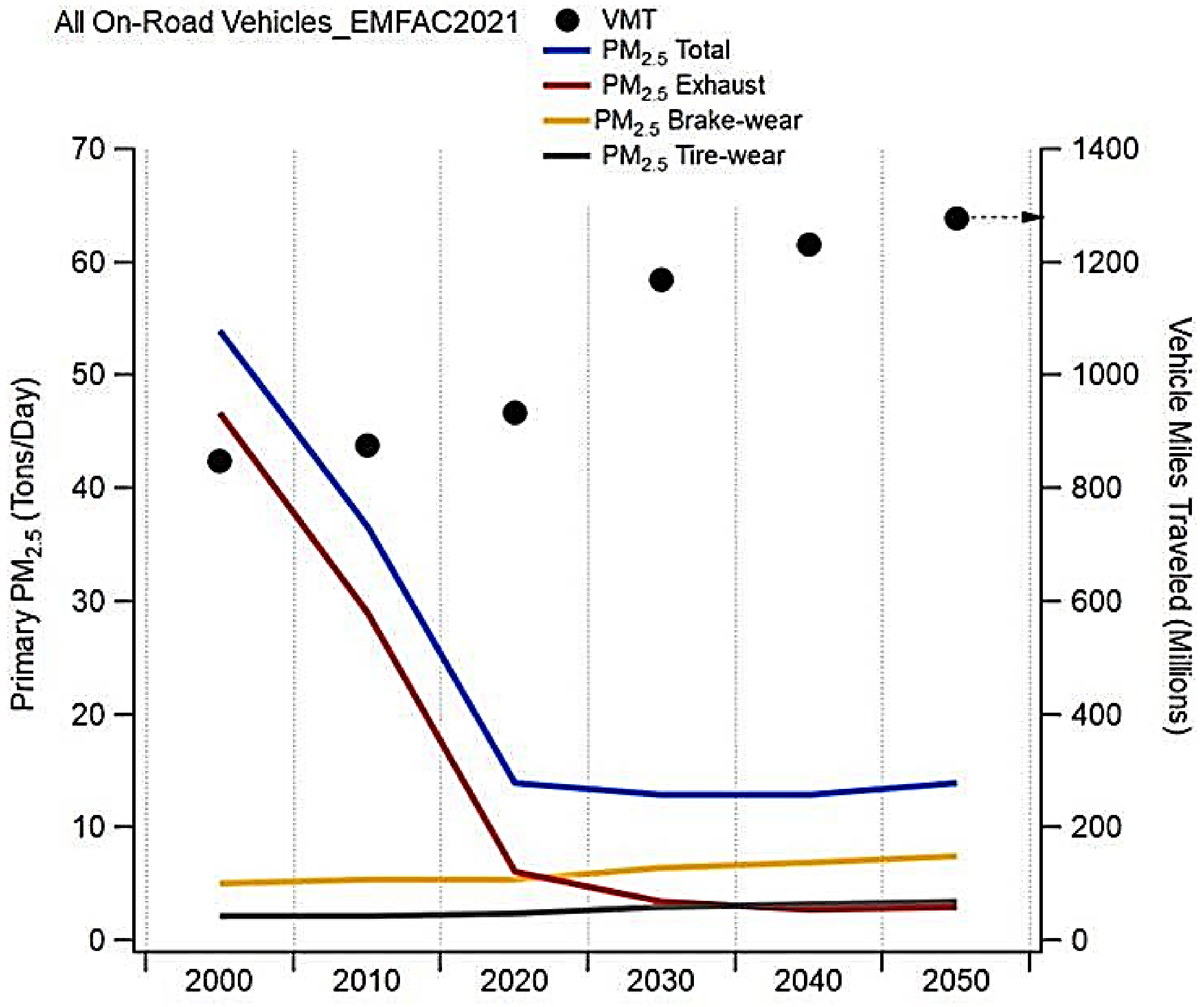
Outline

- Background and objectives
- Field measurement
  - Locations, instruments, and measurements.
- Results and discussion
  - Chemical composition
  - Source apportionment
- Takeaways

Non-tailpipe emissions are becoming a larger fraction of total vehicle emissions



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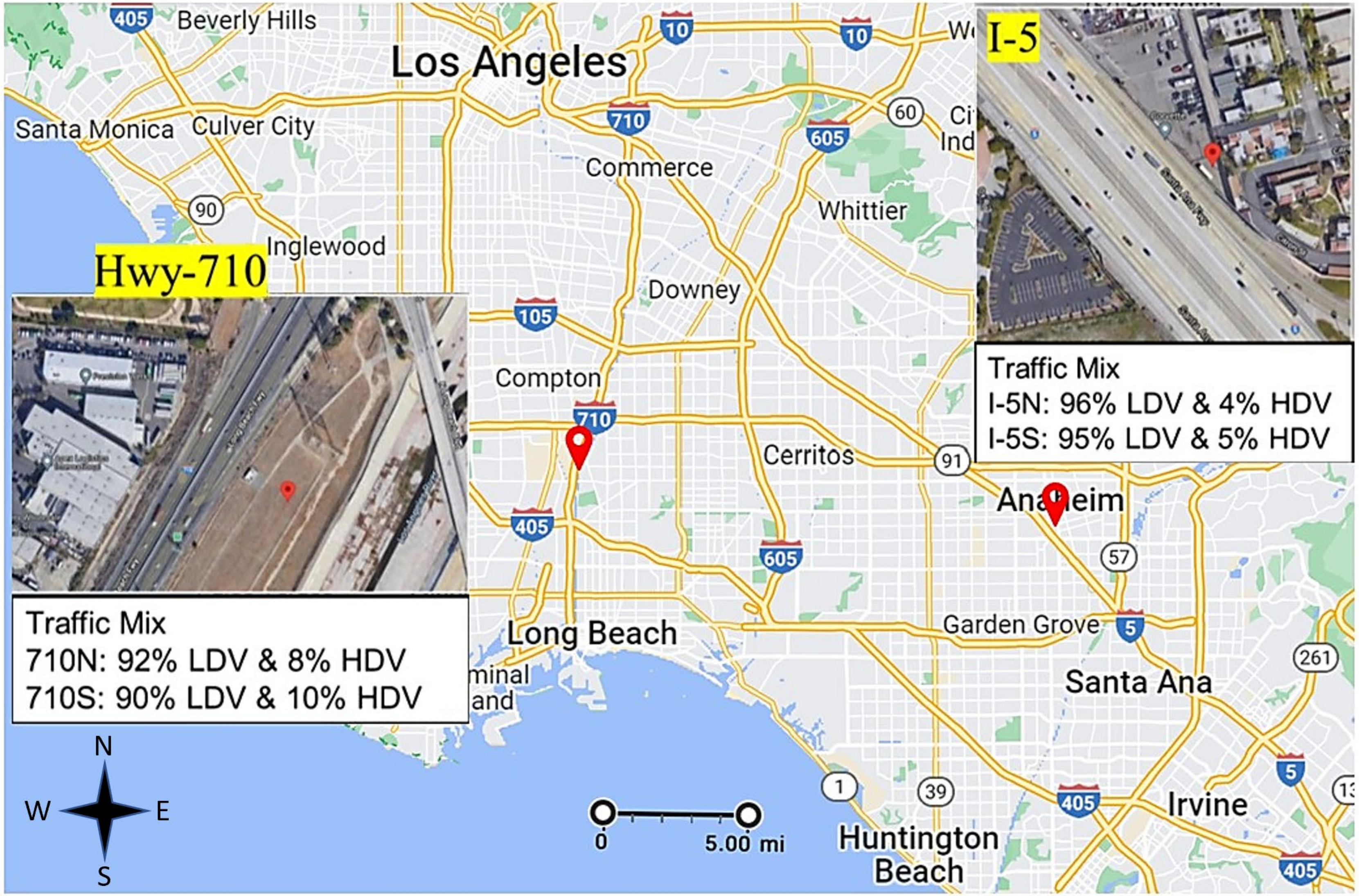
Study Objectives

- Characterize $PM_{2.5}$ and PM_{10} concentration and compositions near highways.
- Seek source markers for non-tailpipe emissions.
- Conduct source apportionment analysis to determine contributions of non-tailpipe particles to $PM_{2.5}$ and PM_{10}.

Measurements were made near Southern California I-5 and I-710



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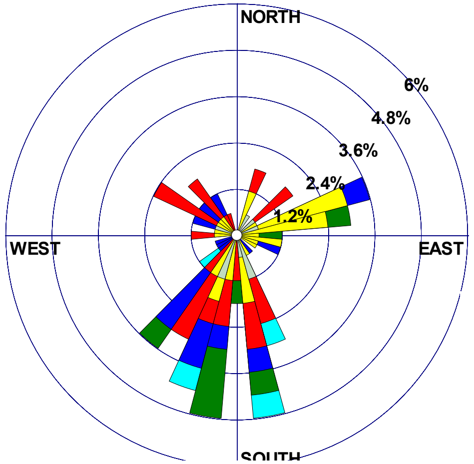
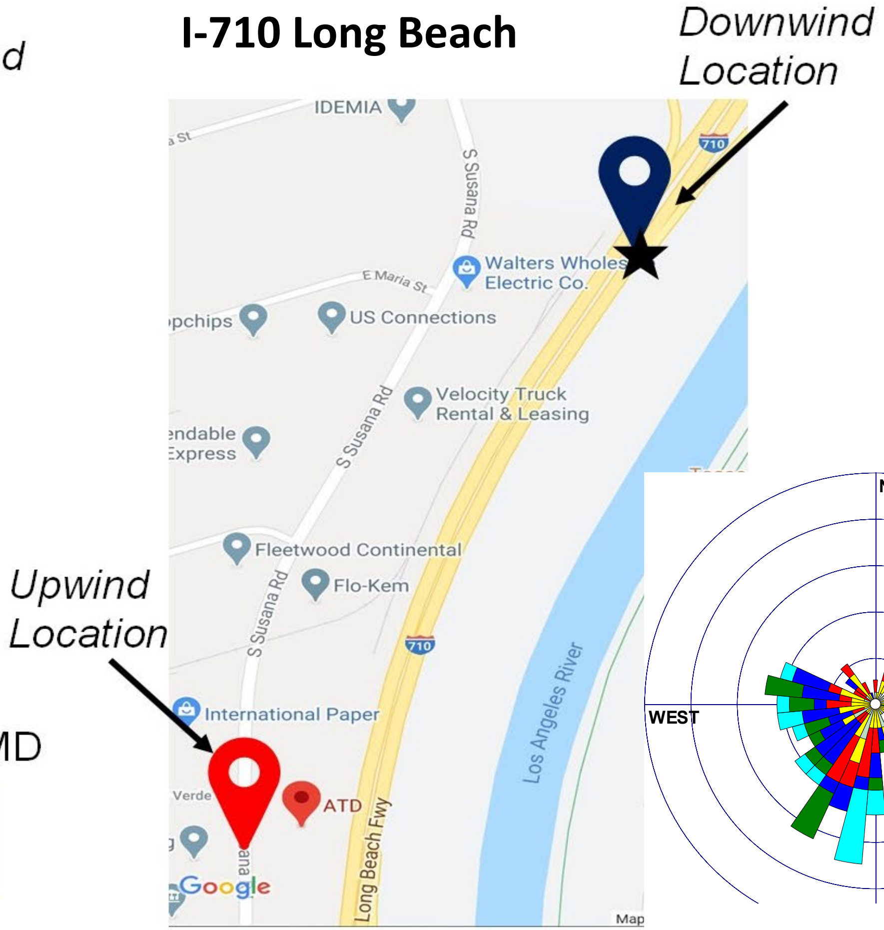
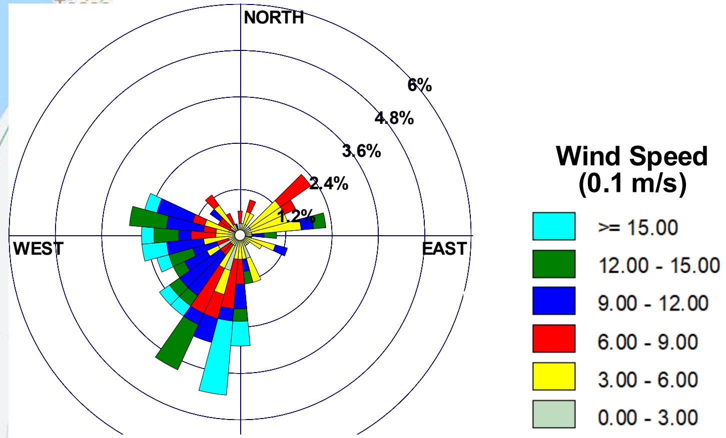
Samples were taken from both sides of highways



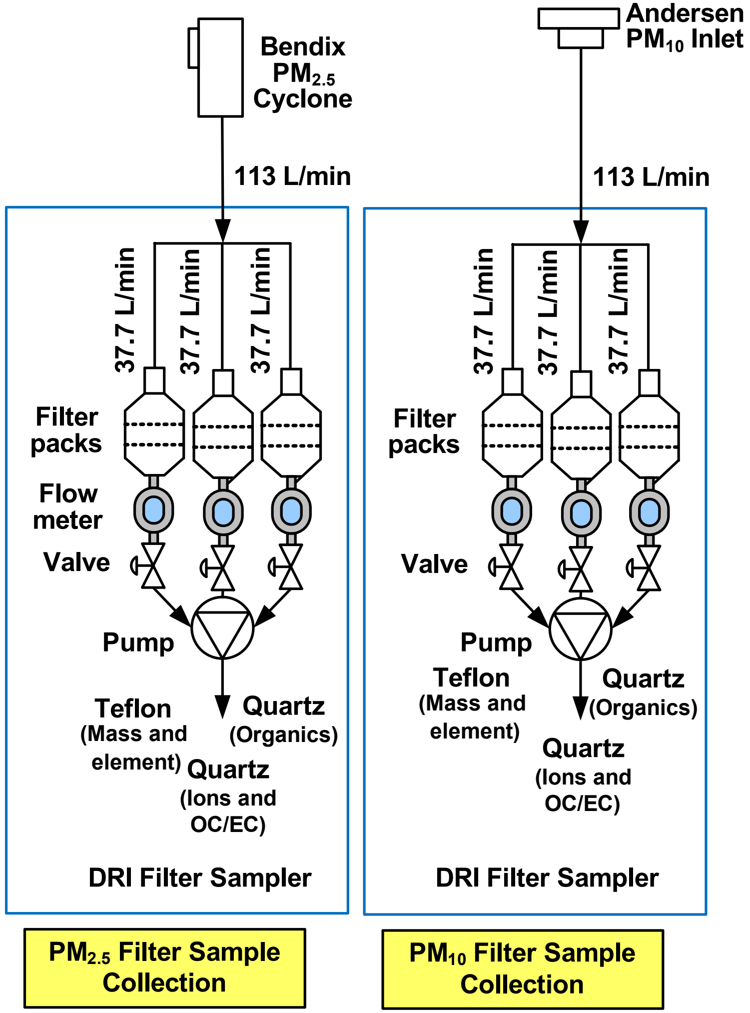
I-5 Anaheim

I-710 Long Beach





$PM_{2.5}$ and PM_{10} filter pairs were collected upwind and downwind of highways



Typical sampling periods:

- 0600-1000; 1000-1400; 1400-1800
- 1/28/2020–2/3/2020 (I-5); 18 sets
- 2/4/2020–2/10/2020 (I-710); 14 sets
- A total of 128 filters.

Filters were analyzed for source markers

Measurement Method	Species	Potential Markers
Gravimetry	PM mass	
X-ray Fluorescence (XRF)	Elements from sodium (Na) to uranium (U)	• Mineral dust: Al, Si, Ca, and K; • Brake wear: Cu, Sb, Ba, Fe, Zr, Mo, and Sn; • Tire wear: Zn; • Concrete road wear: Ca and S
Thermal/Optical Analysis	Organic, elemental carbon (OC and EC) and thermal fractions	• Tailpipe emissions
Ion Chromatography	Water soluble ions Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, Mg^{2+}, K^+, and Ca^{2+}	• Primary salt: Cl^- and Na^+ • Secondary salts: NO_3^-, SO_4^{2-}, and NH_4^+ • Biomass burning: K^+
Thermal desorption GC/MS	Nonpolar organics, including PAHs alkanes, cycloalkanes, hopanes, steranes, phthalates	• Tire wear: alkanes (C_{34}-C_{36}) • Tire wear: pyrene, benzo(ghi)perylene, fluoranthene, phenanthrene, and dibenzopyrenes • Motor oil emissions: hopanes and steranes
pyrolysis-GC/MS	Rubber markers, including styrene, isoprene, butadiene, dipentene, and vinylcyclohexene	• NR: isoprene, dipentene • BR: butadiene, vinylcyclohexene • SBR: styrene, butadiene, vinylcyclohexene
Ultra-performance liquid chromatography (UPLC)	Benzothiazole and derivatives	• Tire wear

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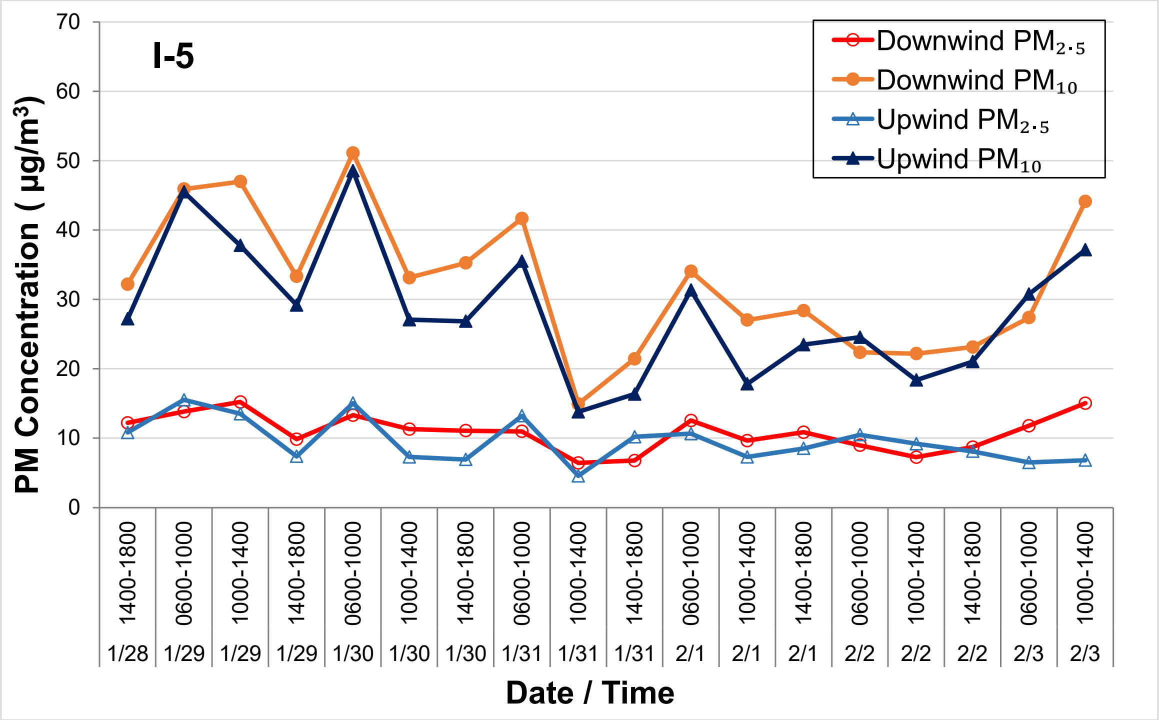
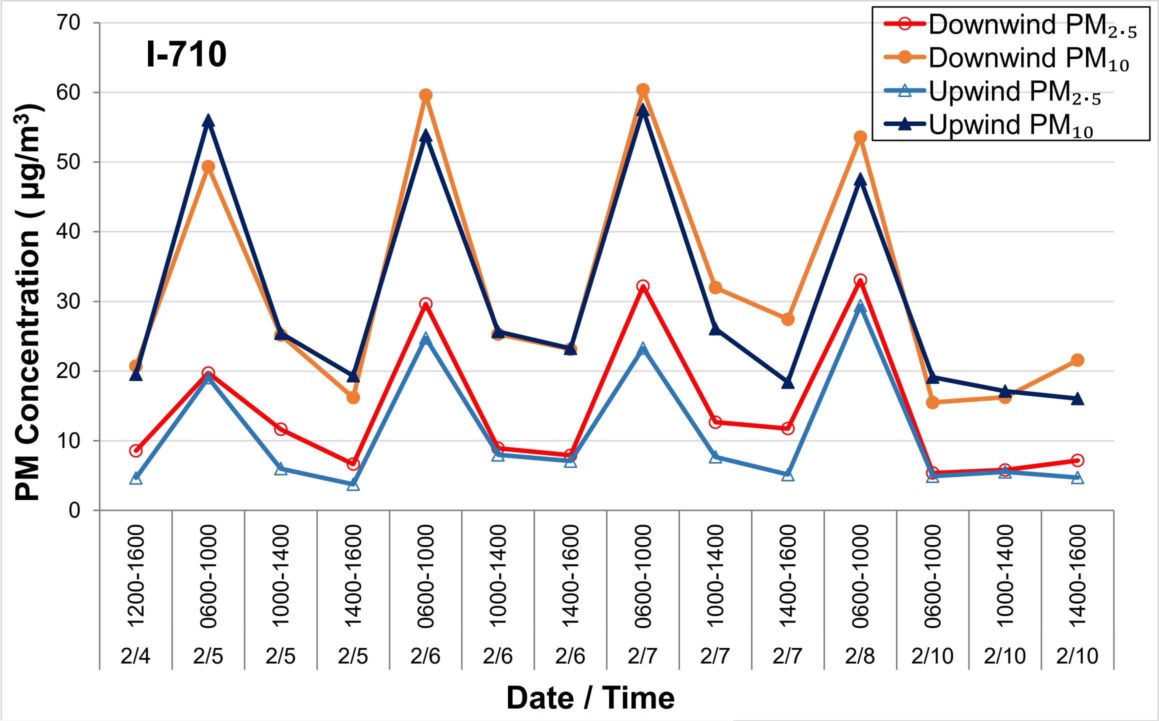
(Pant and Harrison, 2013)

PM_{10} concentrations were 2-3 times those of of $PM_{2.5}$; Up/downwind differences were small





Average PM Concentrations (µg/m³)				
Site	Upwind $PM_{2.5}$	Upwind PM_{10}	Downwind $PM_{2.5}$	Downwind PM_{10}
I-5	9.56	28.47	10.88	32.49
I-710	11.00	30.37	14.36	31.87

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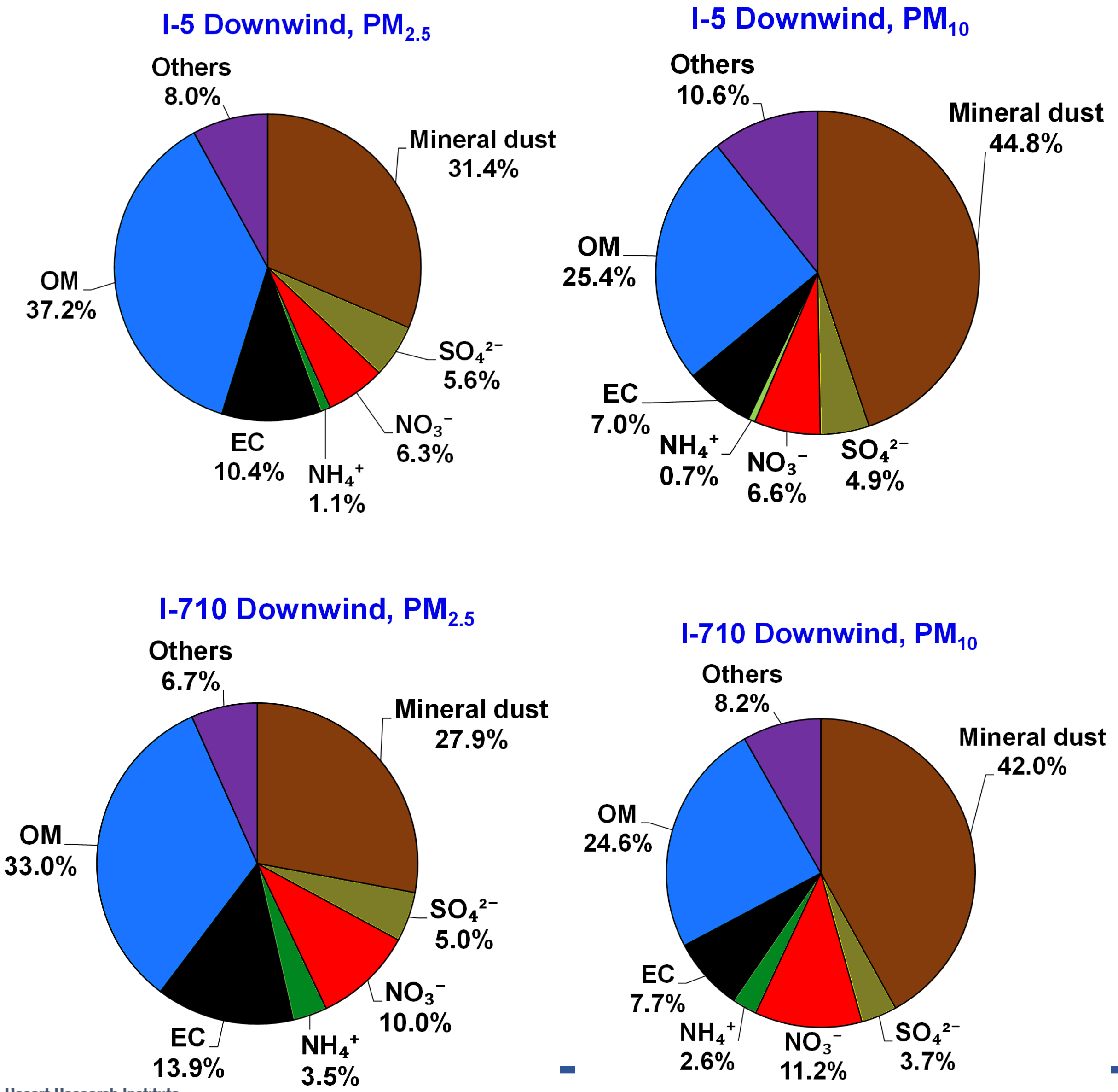
Mineral dust and carbon were major PM components



Main composition:

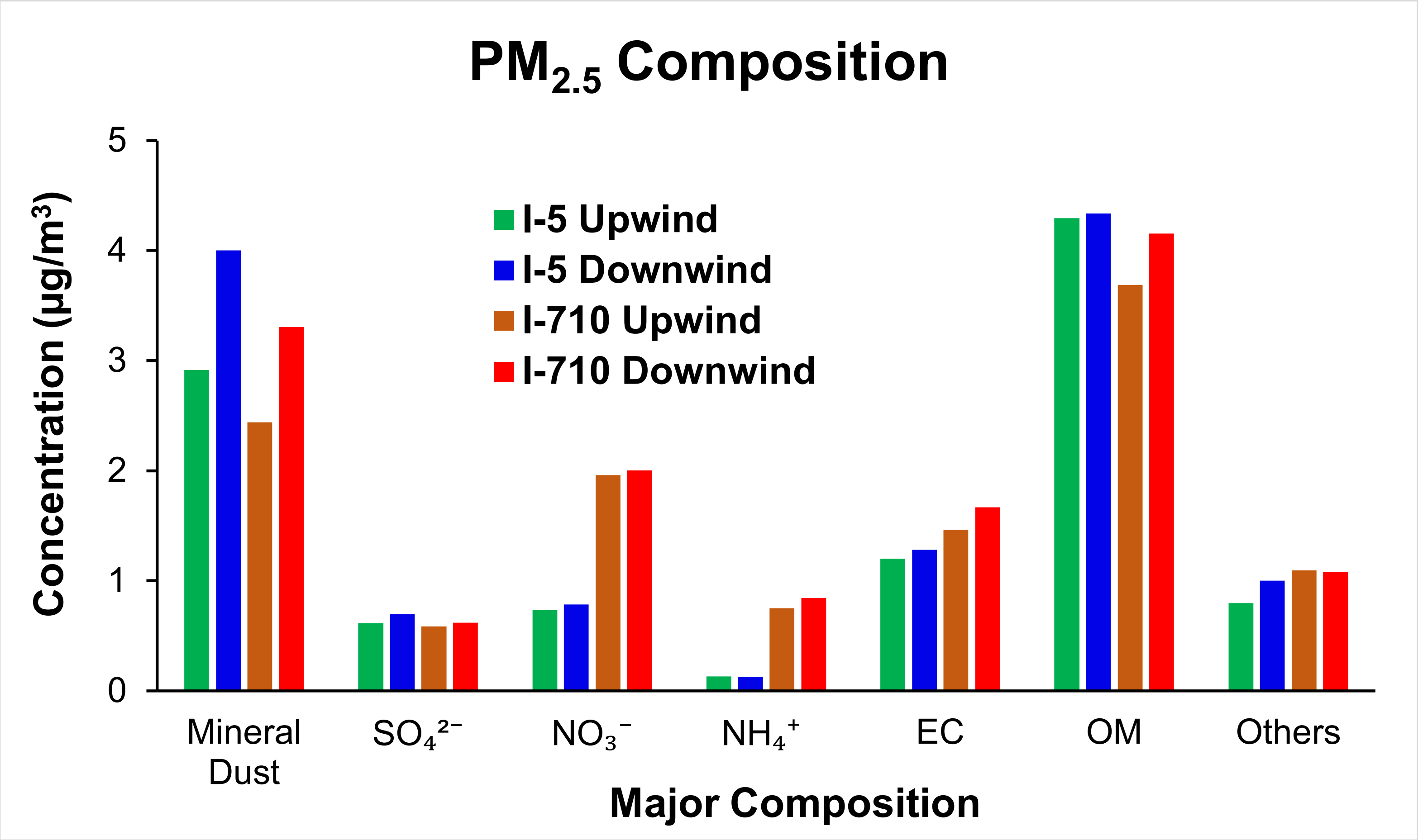
- $PM_{2.5}$: Organic matter (OM; ~30–40%), mineral dust (~30%), and elemental carbon (EC; ~10–15%)
- PM_{10}: mineral dust (>40%), OM (~25%); coarse NO_3^- due to Cl replacement
- More OM and EC% in $PM_{2.5}$ than PM_{10}; more dust and others (elements and ions) in PM_{10}

∗ OM=1.2 × OC

∗ Mineral dust = 2.2×Al + 2.49×Si + 1.63×Ca + 2.42×Fe + 1.94×Ti

(Chow et al., 2015)

Differences were found between upwind/downwind and I-5/I-710



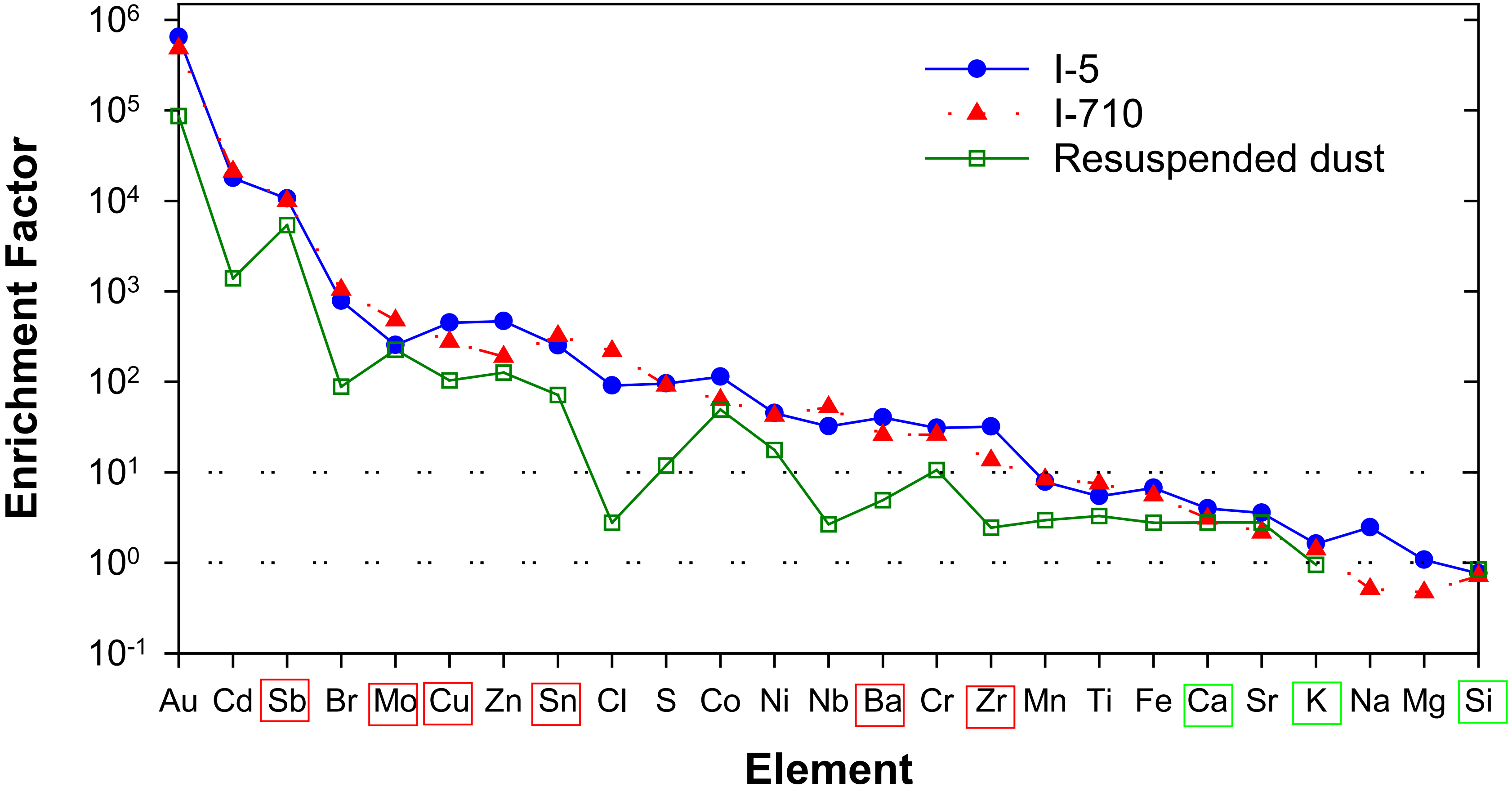
- Downwind > Upwind
- EC is ~20% higher at I-710 than I-5
- SO_4^{2-} is similar → regional distribution
- NO_3^- and NH_4^+ are much higher at I-710, due to two high NH_4NO_3 events

High correlations were found among elements from common sources

- Blue: 0.6<r≤0.8
- Red: 0.8<r≤1.0

Species	OC	EC	Mg	Al	Si	K	Ca	Ti	Mn	Fe	Co	Cu	Zn	Sr	Zr	Ba	W
EC	0.74																
Mg	0.36	0.19															
Al	0.56	0.51	0.58														
Si	0.57	0.49	0.57	0.99													
K	0.62	0.53	0.62	0.96	0.97												
Ca	0.60	0.52	0.62	0.96	0.98	0.95											
Ti	0.62	0.63	0.37	0.78	0.73	0.70	0.70										
Mn	0.64	0.65	0.47	0.91	0.91	0.90	0.90	0.78									
Fe	0.69	0.69	0.52	0.90	0.91	0.91	0.94	0.76	0.92								
Co	0.61	0.57	0.44	0.76	0.77	0.76	0.80	0.60	0.85	0.85							
Cu	0.68	0.63	0.45	0.68	0.70	0.73	0.76	0.61	0.75	0.89	0.78						
Zn	0.29	0.44	0.22	0.42	0.44	0.51	0.51	0.33	0.52	0.55	0.46	0.51					
Sr	0.52	0.43	0.62	0.86	0.86	0.86	0.84	0.67	0.81	0.82	0.73	0.71	0.44				
Zr	0.66	0.60	0.44	0.66	0.68	0.70	0.74	0.59	0.73	0.87	0.78	**0.98**	0.49	0.69			
Ba	0.66	0.63	0.43	0.72	0.74	0.76	0.79	0.63	0.78	0.90	0.77	**0.93**	0.53	0.71	**0.90**		
W	0.26	0.40	0.20	0.38	0.41	0.46	0.47	0.30	0.45	0.51	0.37	0.46	**0.92**	0.37	0.45	0.51	
Tire Tread	0.65	0.40	0.57	0.62	0.65	0.71	0.69	0.44	0.62	0.69	0.63	0.68	0.24	0.61	0.67	0.67	0.19

Vehicle-wear related elements were enriched



Enrichment Factor

$$= (X/\mathrm{Ref})_{sample} / (X/\mathrm{Ref})_{UCC}$$

- X = element of interest
- Ref = reference element (Al)
- UCC: the Earth's upper continental crust

*☐ shows wear-related elements

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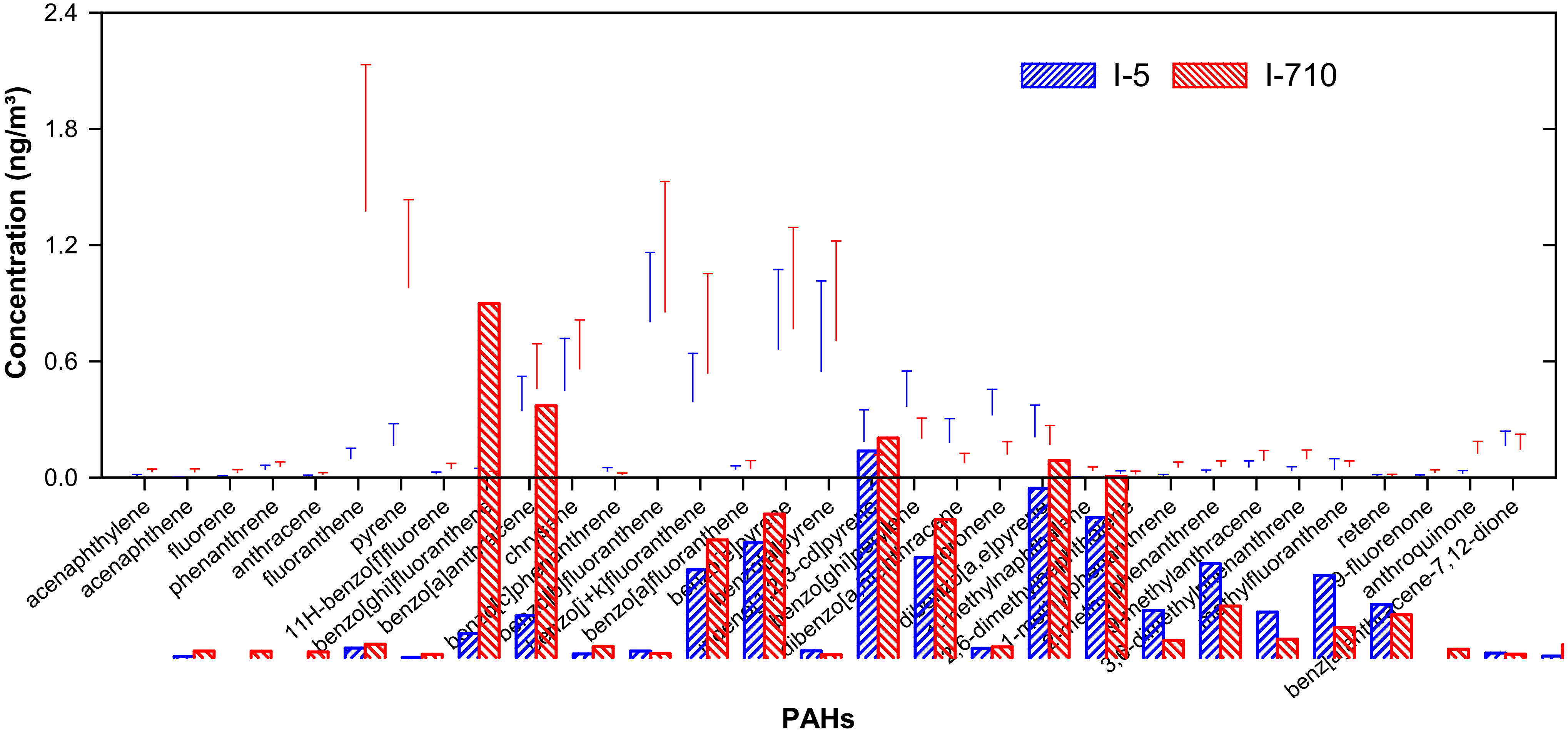
I-710 had higher PAHs from diesel emissions



- I-710 PAH concentrations are 47% higher than I-5
- Both highways have similar PAH distributions, but I-710 has higher fluoranthene and pyrene

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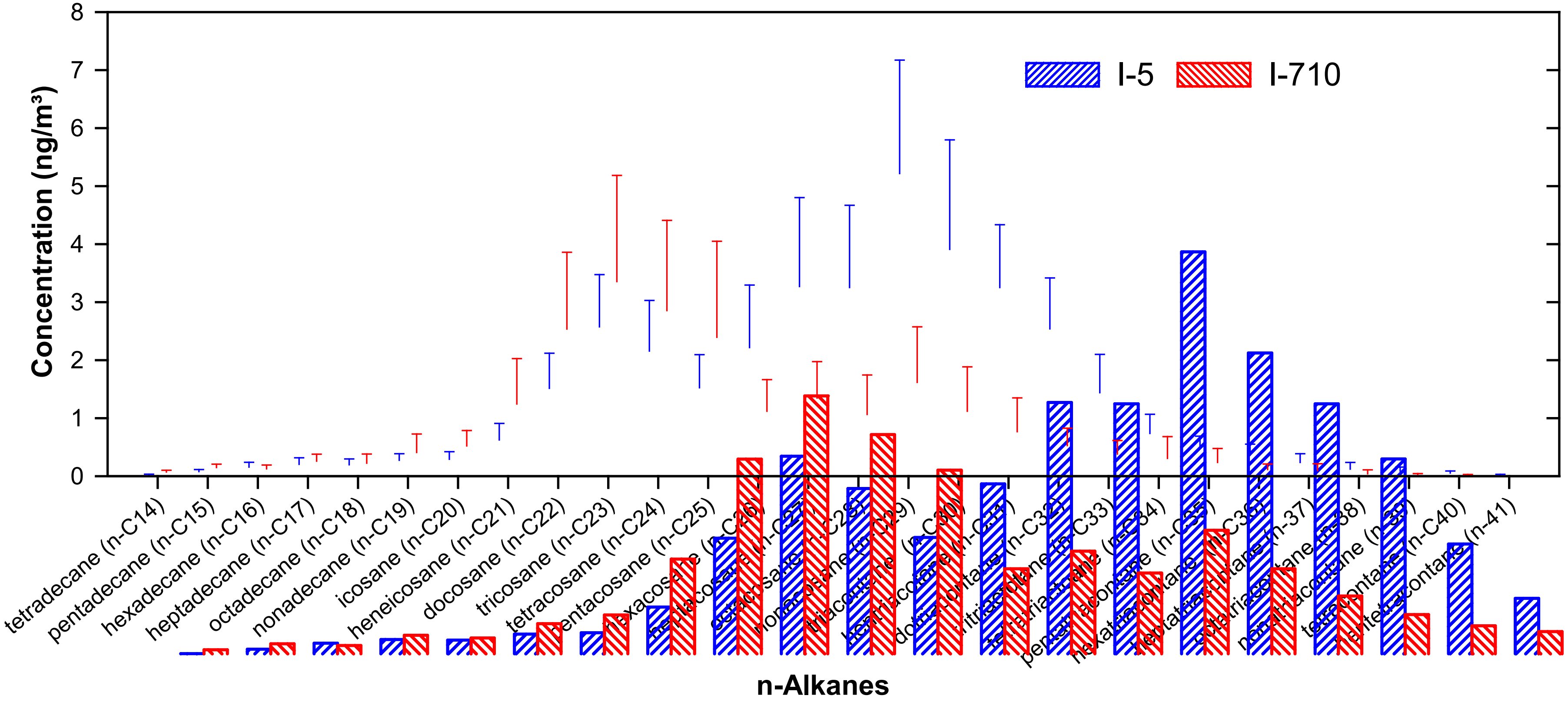
n-Alkanes indicate sources from lubricating oil and unburnt diesel fuel



- I-5 n-alkanes were dominated by lubricating oil (C_{max} = 29)
- I-710 shows increased contributions from unburnt diesel fuel (C_{max} = 23).

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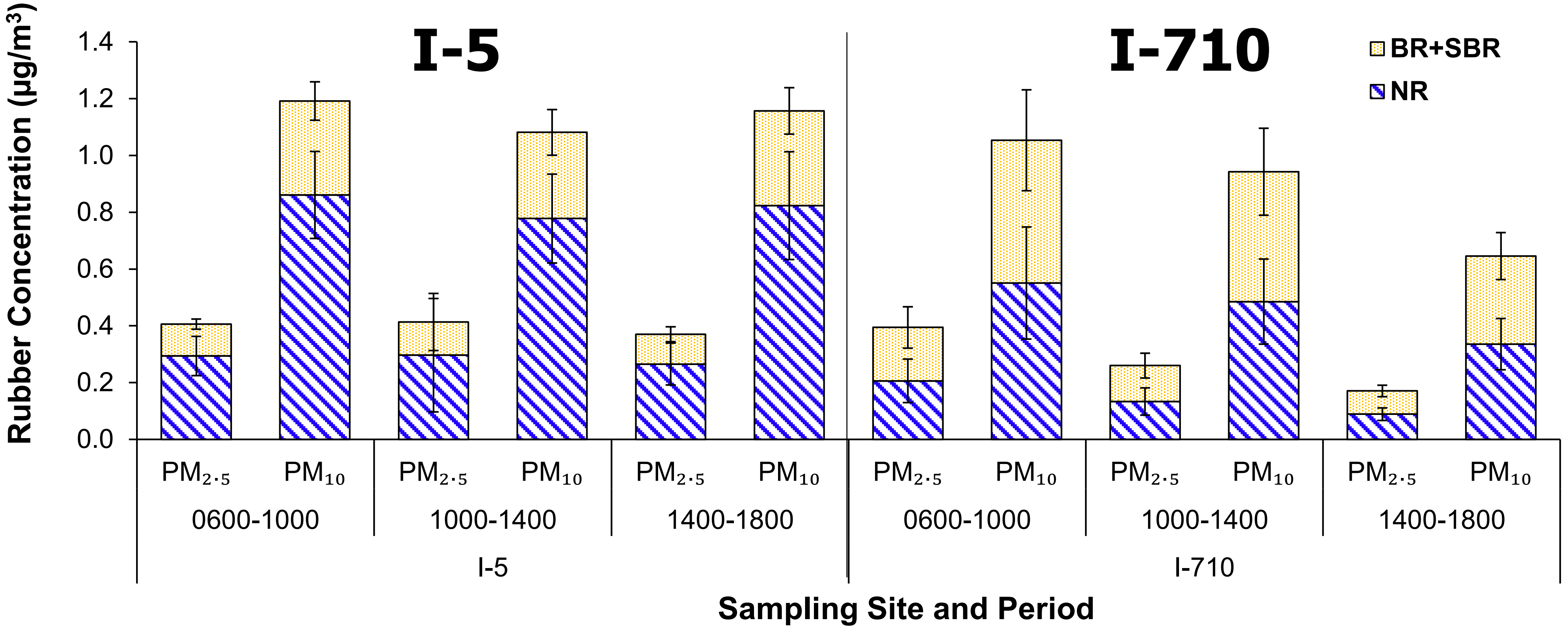
Tire tread was ~8.0% (I-5) and 5.5% (I-710) of $PM_{2.5}$ and PM_{10}



- Over half of the rubber is in coarse PM (2.5-10 µm)
- Natural rubber concentrations at I-5 were higher than I-710

NR: natural rubber
BR: butadiene rubber
SBR: styrene–butadiene rubber

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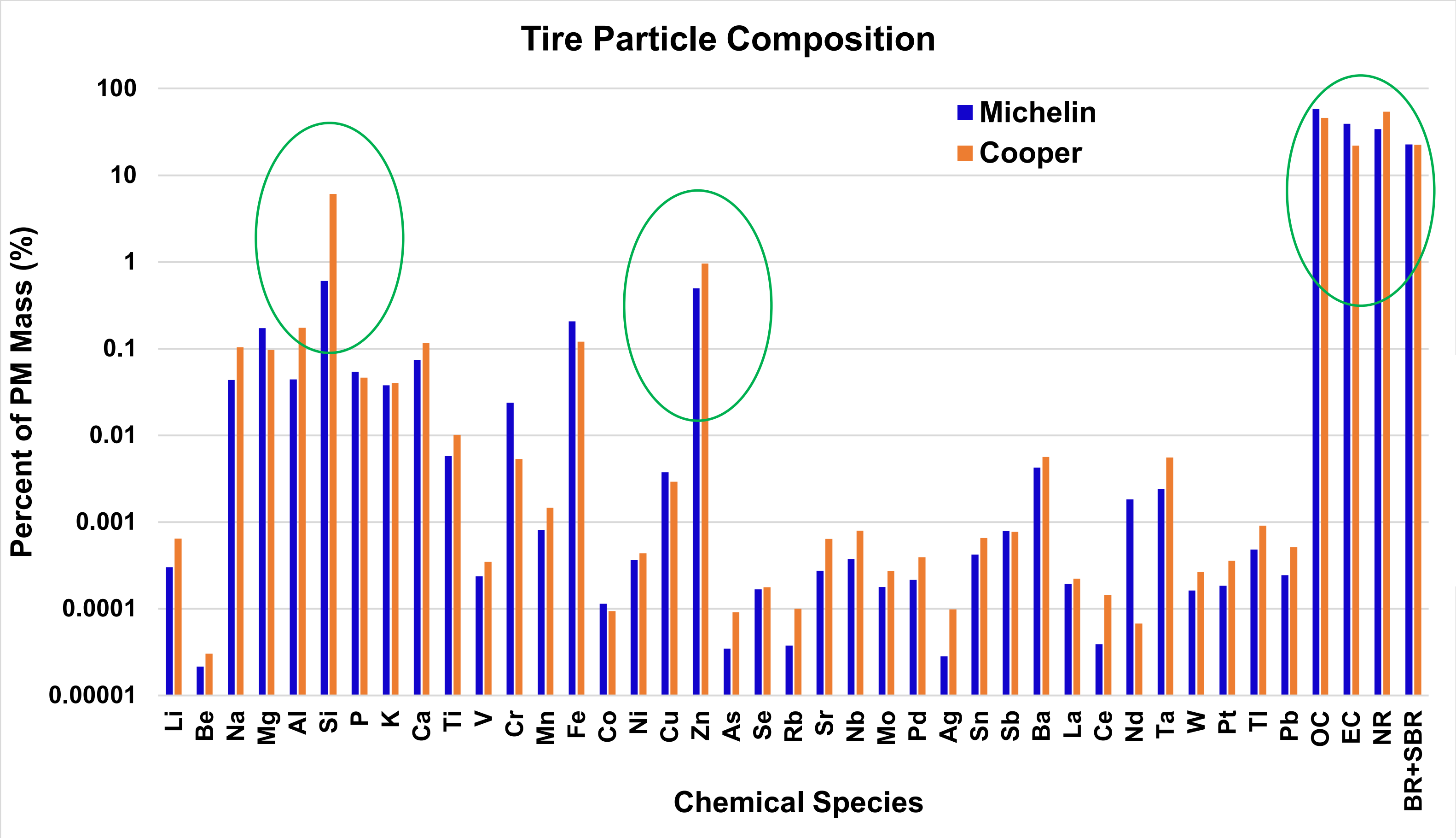
Different tire manufacturers show different elemental and organic abundances



Mass Percent (%)						
Composition	Si	Zn	OC	EC	NR	BR+SBR
Michelin	0.6	0.5	59	39	34	23
Cooper	6.1	1.0	46	22	54	23

NR: natural rubber
BR: butadiene rubber
SBR: styrene–butadiene rubber

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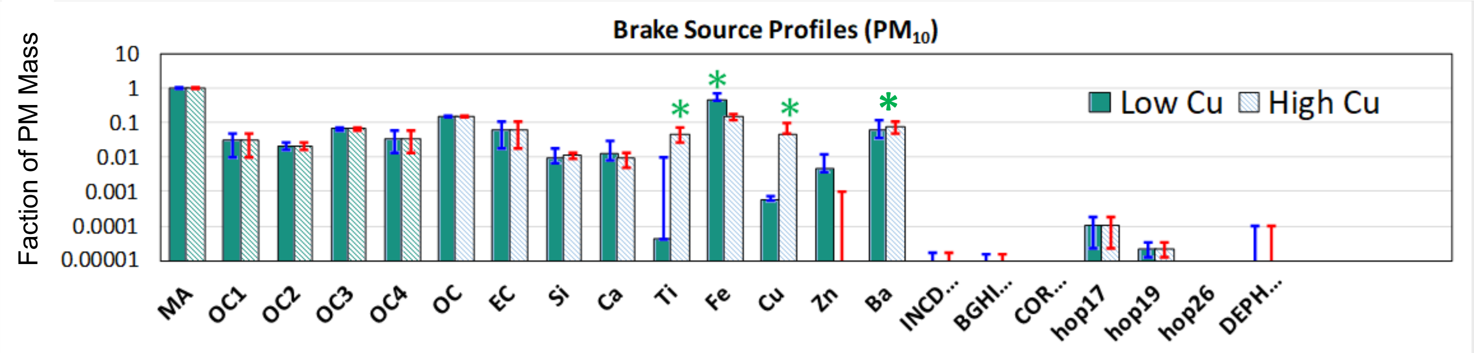
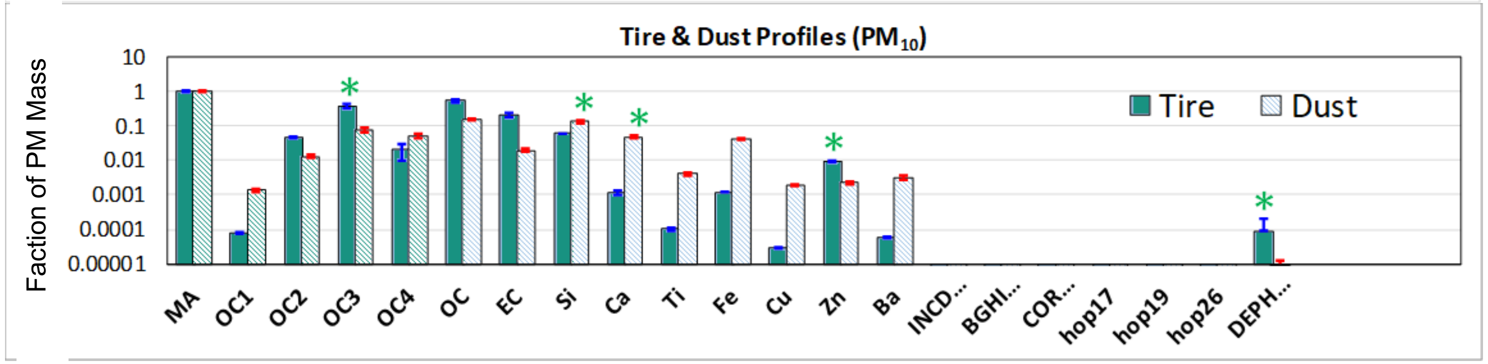
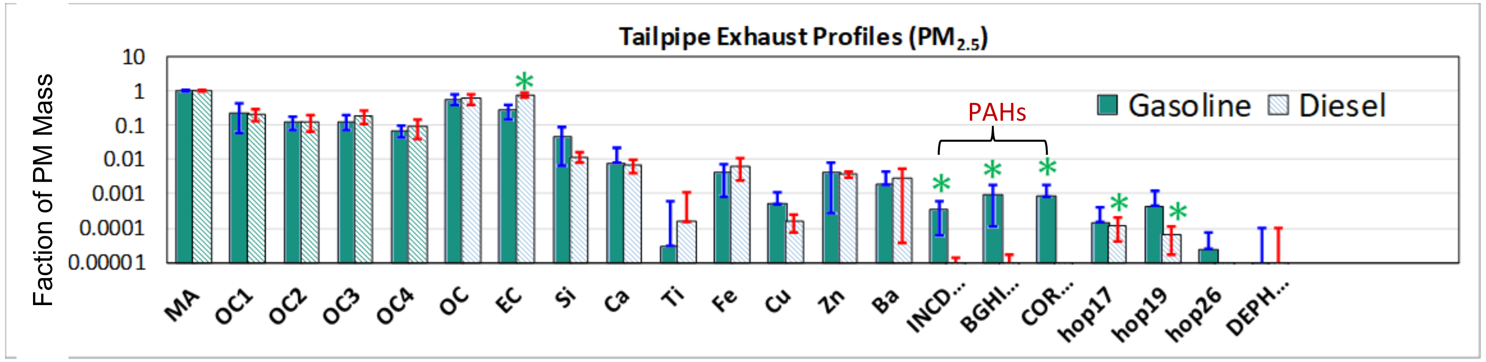
Examples of Source Profiles Explored







- Brake profiles: Dynamometer studies (CRPAQS, 2004; CARB, 2020)
- Tire profiles: Tire dust collected in the lab and analyzed by DRI
- Dust profiles: Dust samples collected at monitoring sites, and analyzed after resuspension by DRI
- Exhaust Profiles: Dynamometer studies (Gas-Diesel Split Study 2001, CARB database)

***Potential markers for each profile marked**

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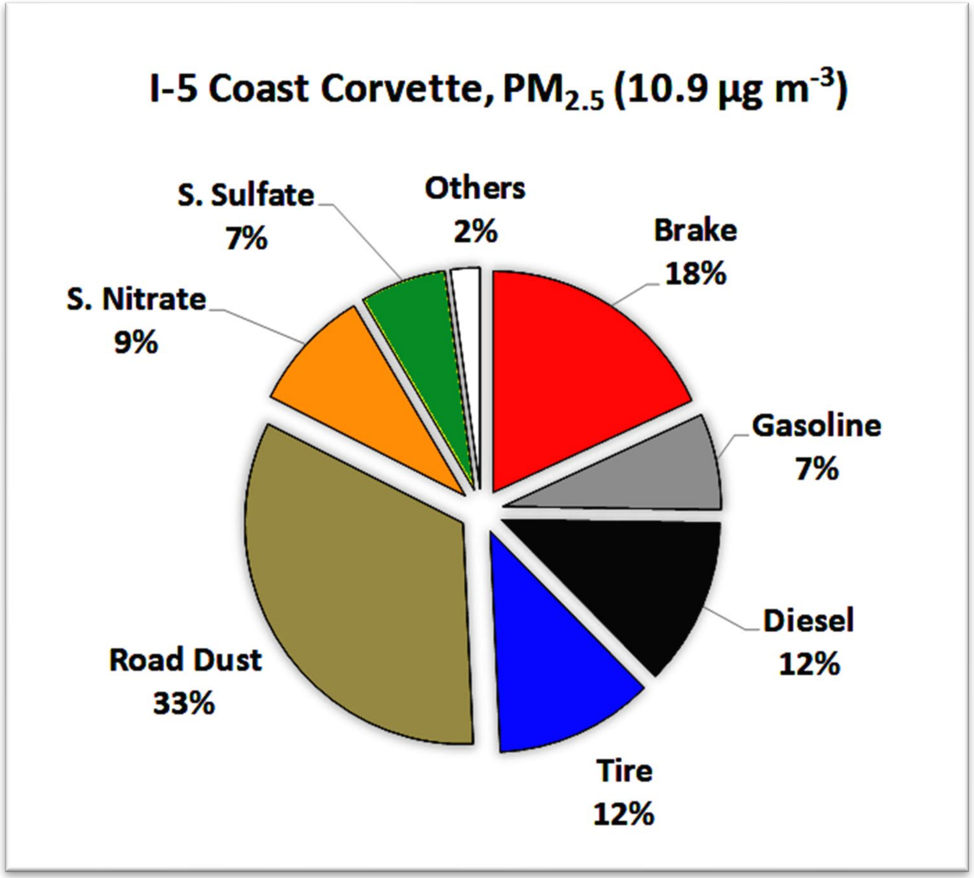
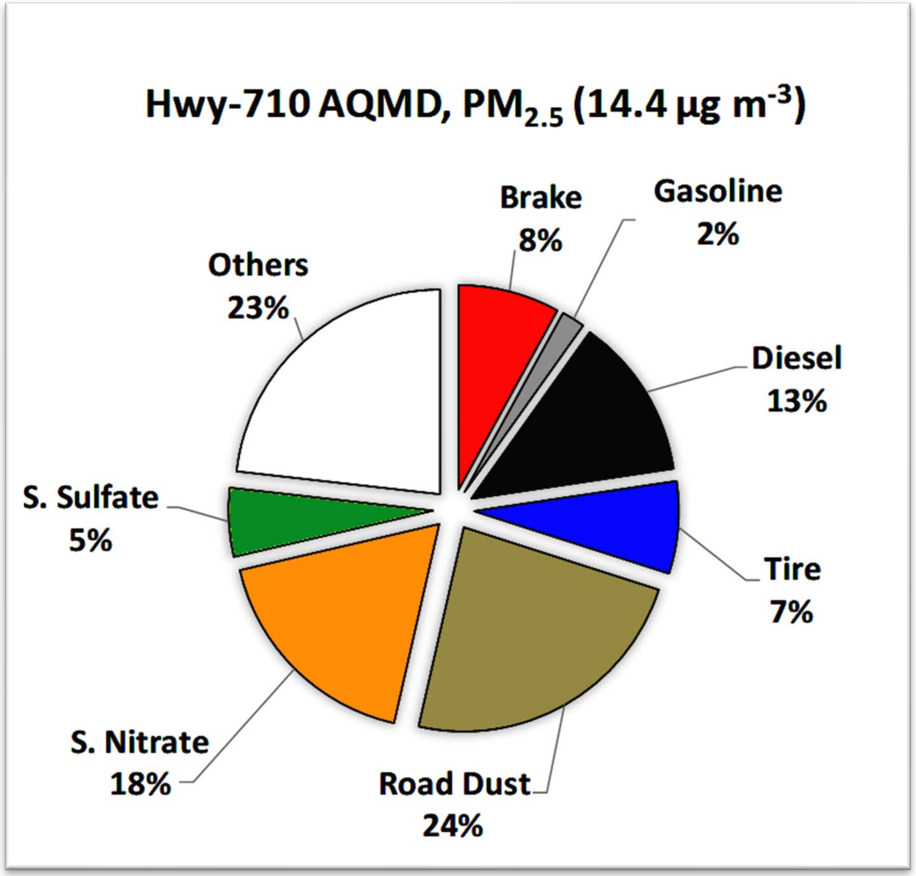
(Brake + Tire wear) ≥ (Gasoline + Diesel) in $PM_{2.5}$





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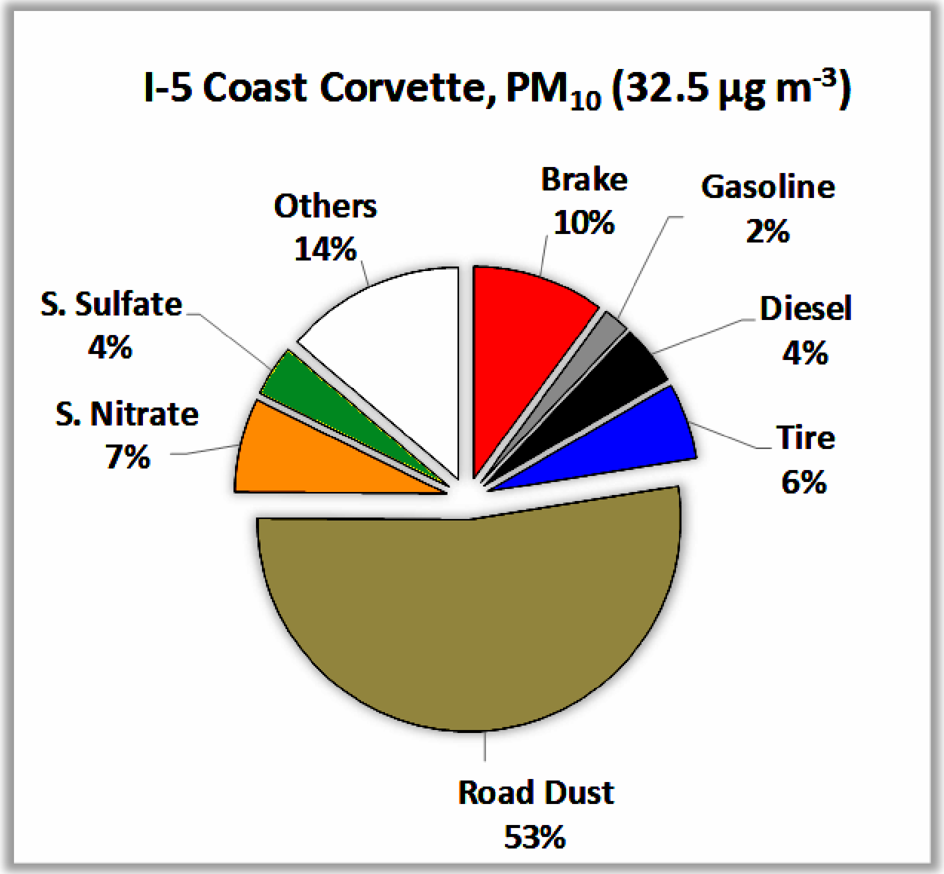
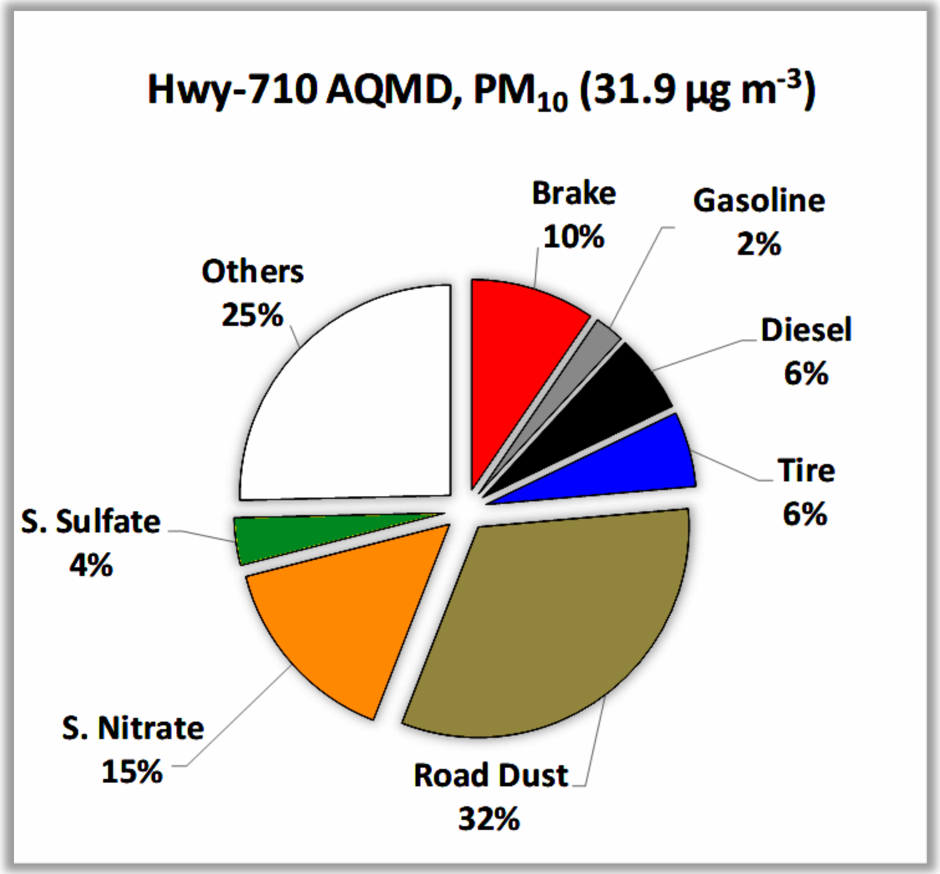
(Brake + Tire wear) ≥ 2× (Gasoline + Diesel) in PM_{10}





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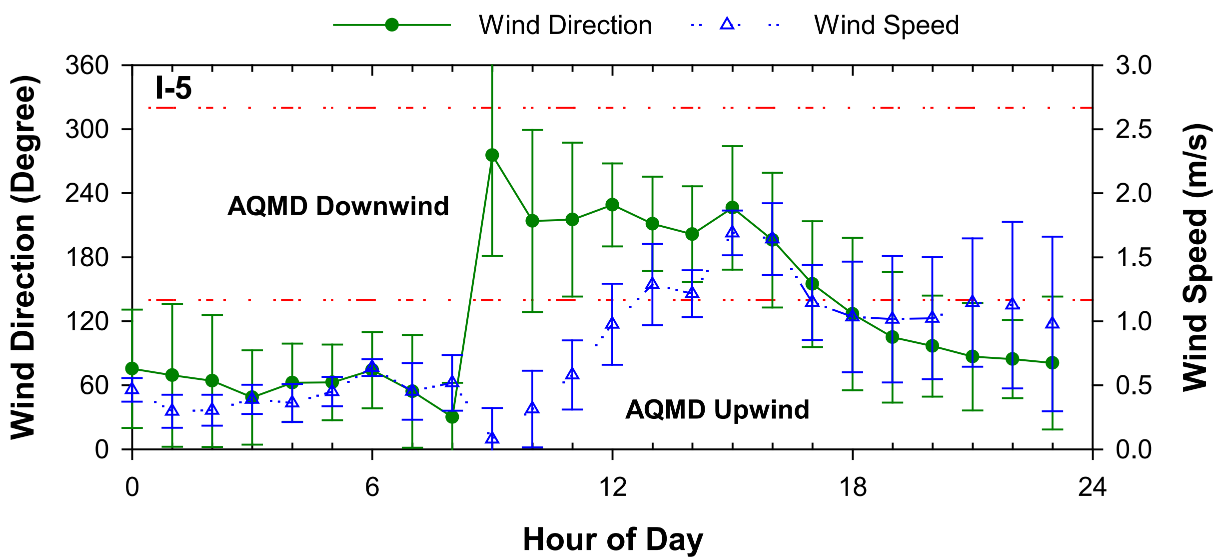
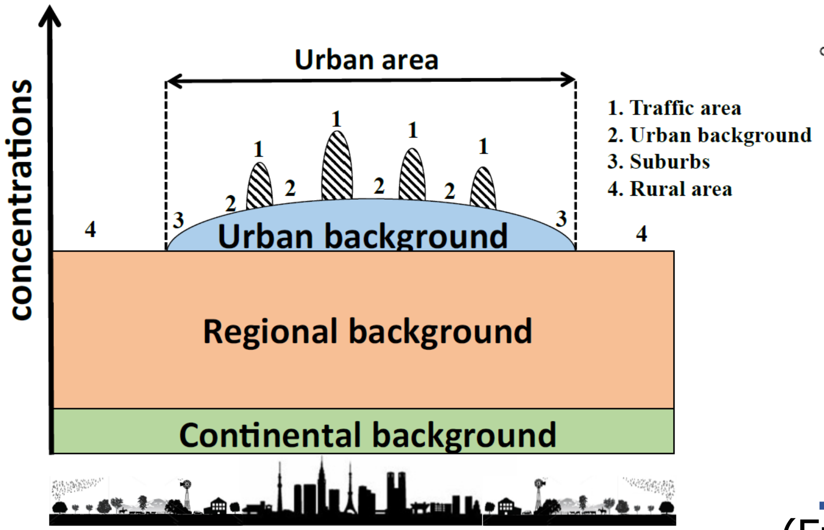
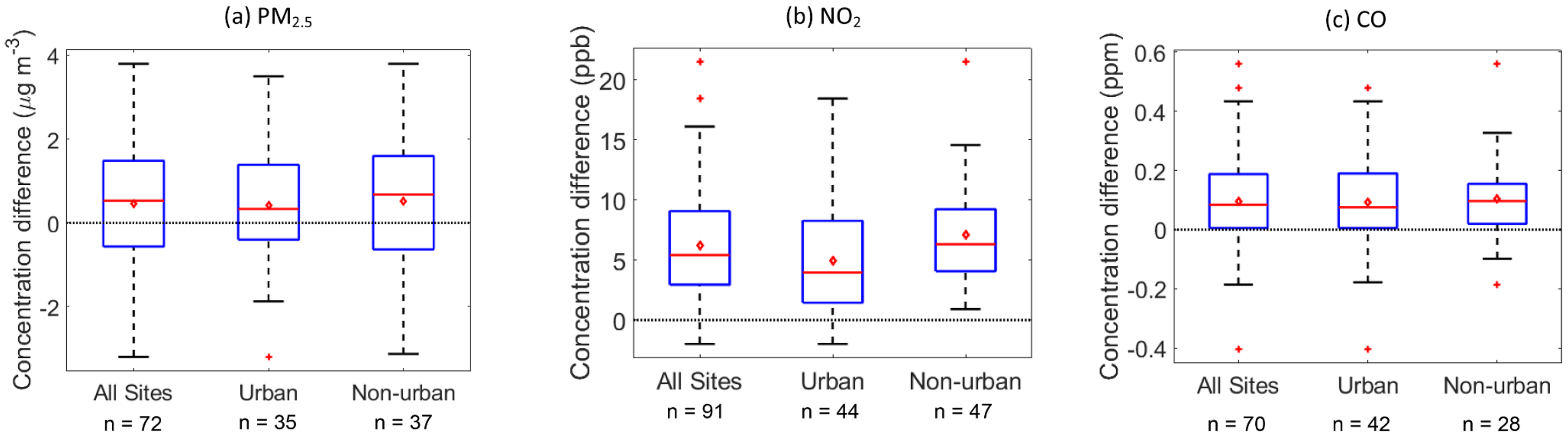
Challenges in upwind/downwind sampling

- Varying wind and vehicle induced turbulence
- Small differences between upwind and downwind $PM_{2.5}$ and PM_{10} concentrations
- Interferences from other sources





(Fuzzi et al., 2015)



(Lai et al., 2020)

Takeaways

- Average concentrations of near-road $PM_{2.5}$ and PM_{10} were 10-15 and ~30 µg/m^3, respectively.
- Higher concentrations of EC, PAHs, and lower molecular weight n-alkanes were found near I-710 than I-5, likely due to more diesel vehicles.
- High correlations were found for elements with common sources, such as markers for brake wear (e.g., Ba, Cu, and Zr) and road dust (e.g., Al, Si, K, and Ca).
- For $PM_{2.5}$, non-exhaust (brake + tire) contributions exceeded exhaust (diesel + gasoline) for I-5 (29–30% vs. 19–21%); they were comparable for I-710 (15–17% vs. 15–19%).
- For PM_{10}, the non-exhaust contributions were 2 – 3 times the exhaust contributions.

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