Strong Dependence of Atmospheric Formaldehyde Concentration on Air Temperature

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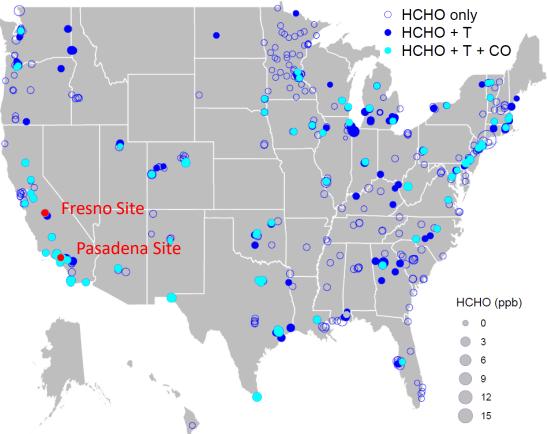
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Background

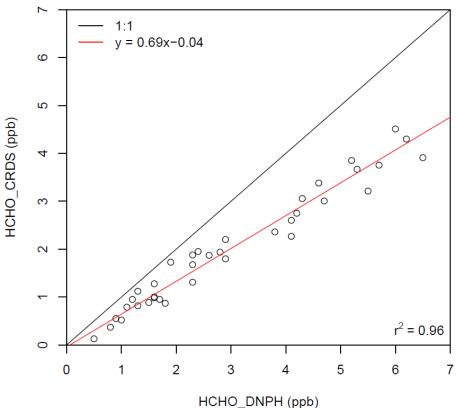
- Ubiquitous Presence: Found both indoors and outdoors.
- Diverse Sources: Biogenic emissions, biomass burning, fossil fuel combustion, industrial emissions, off-gassing from building materials, photochemical production.
- Health Implications: Irritates eyes, nose, throat, lungs, triggers asthma attack; prolonged exposure can cause cancer.
- Photochemical Significance:
 - Oxidation product of many VOCs.
 - Photolysis of HCHO is important source of HO_x radicals.
 - High ozone formation potential in the SJV and SoCAB of California (Liu et al. 2022 ACP).
- Monitoring Challenges: Not easy to measure, lack of high time resolution measurements.

Data Used in This Study



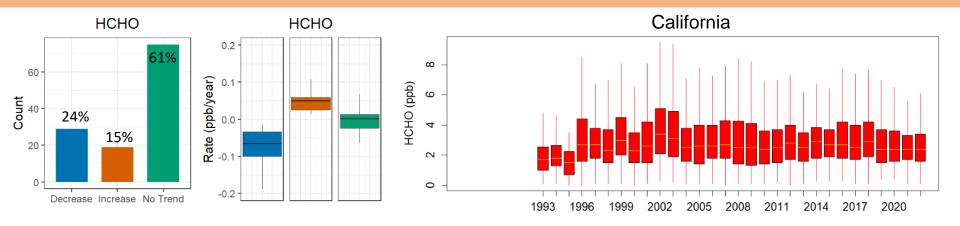
- AQ monitoring sites (535 total)
 - HCHO only: 357 sites
 - HCHO + T: 178 sites
 - HCHO + T + CO: 101 sites
 - Daily data every ~6-12 days 1987–2022 (35 years)
 - DNPH method
- Fresno Site
 - March 2019–July 2021 (2+ years)
 - 2-s data
 - CRDS (Picarro G2307)
- Pasadena (RECAP-CA Campaign)
 - August–September 2021 (1 month)
 - 2-s data
 - CRDS (Picarro G2307)

CRDS vs DNPH



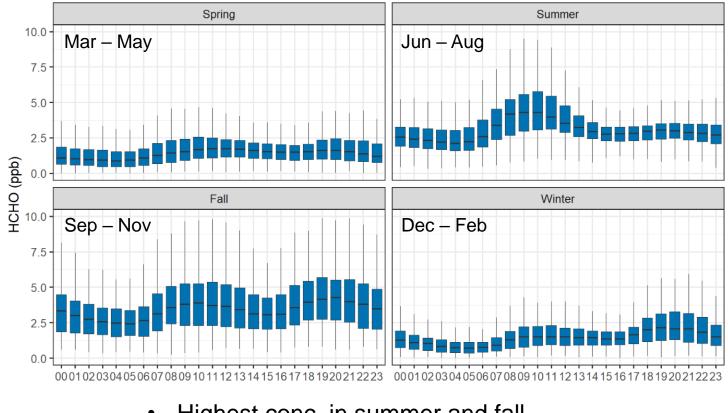
- HCHO from DNPH method is 30% higher. Similar findings from New York measurement.
- Possible explanation:
 - NO₂ reacts with DNPH and form a product that exhibits similar retention time compared to the HCHO derivatives (Vogel et al. 2000, Szulejko et al. 2015).
 - Matrix interference: compounds that have similar retention time to HCHO derivative.
 - Sample contamination during storage or shipment by diffusion of VOCs through the sample bottle seal.
 - Drifts in CRDS measurements

HCHO Trends from AQ Monitoring Sites



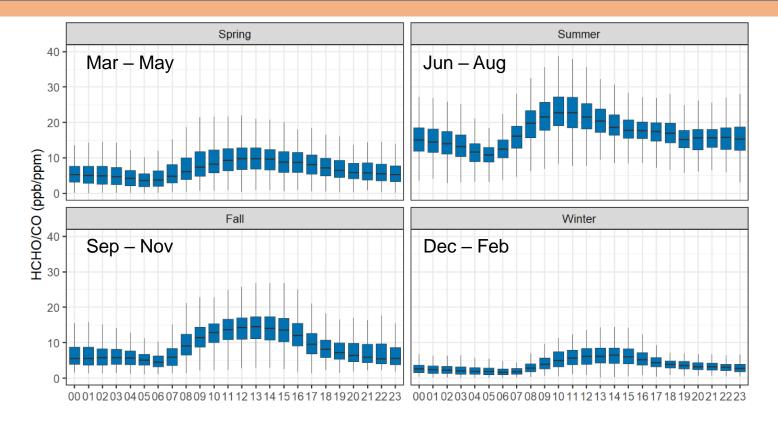
Lack of trend suggests HCHO is mostly secondary from natural precursors.

Seasonal and Diurnal Variation of HCHO in Fresno



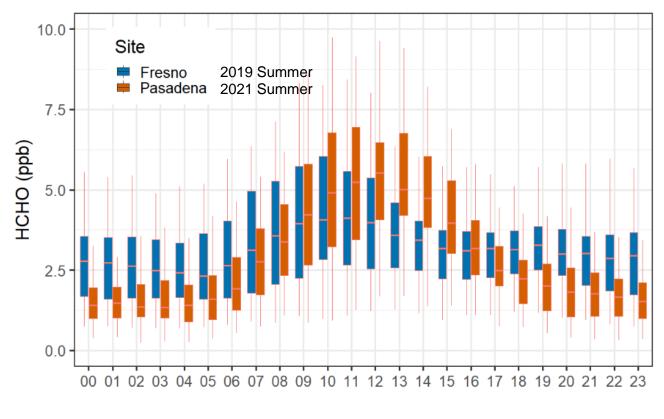
- Highest conc. in summer and fall.
- Two peaks in fall and winter.

Seasonal and Diurnal Variation of HCHO/CO in Fresno



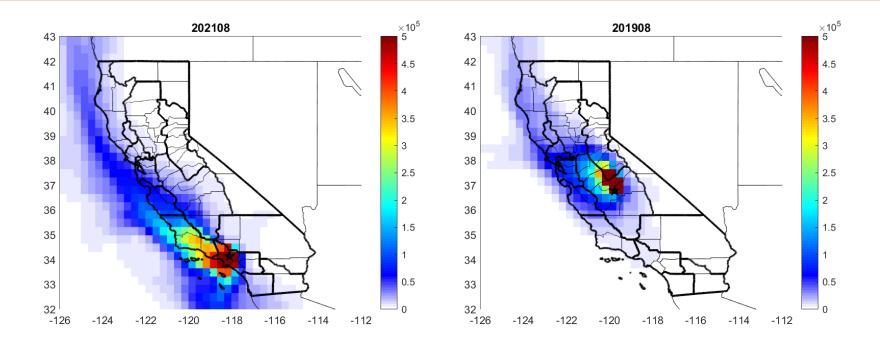
CO-normalized profiles show one peak.

Diurnal Cycle of HCHO: Pasadena vs Fresno



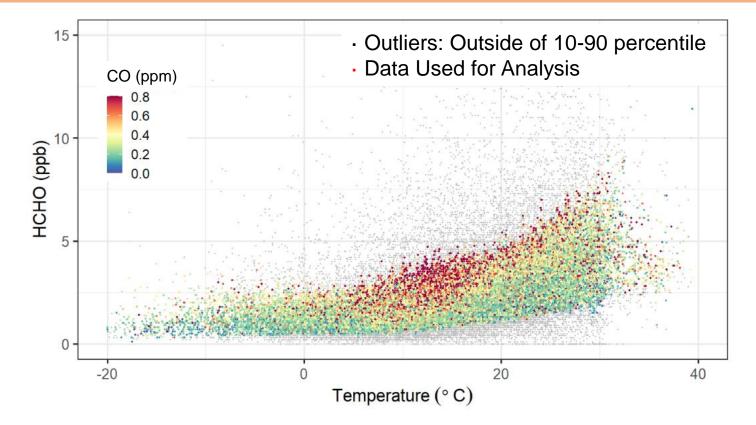
• The HCHO peak lags 2-3 hours in Pasadena.

Air Mass Back-Trajectories: Pasadena vs Fresno



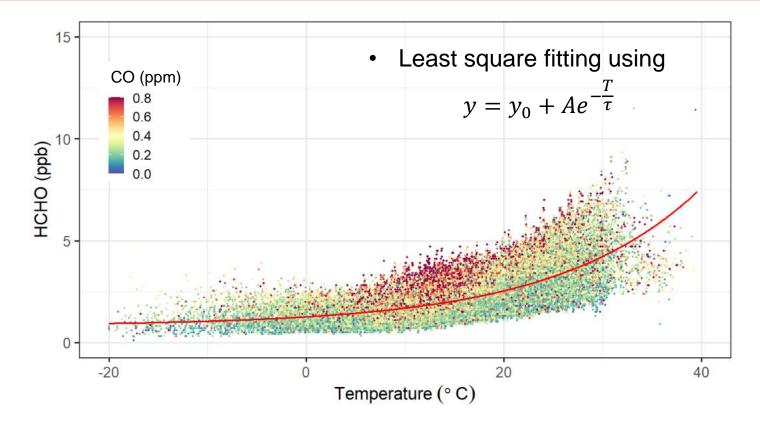
- Simulated using FLEXPART model with ERA5 hourly data (30 km).
- Pasadena is impacted by a larger region compared to Fresno.

HCHO Strongly Depends on Temperature



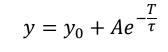
HCHO has strong correlation with temperature, scatters relate to CO.

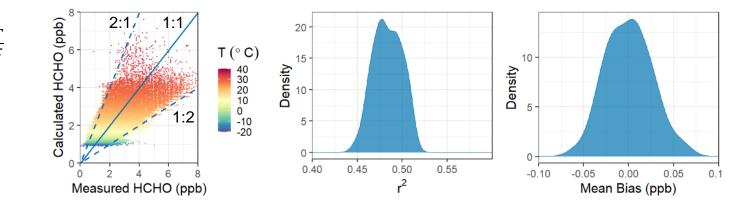
HCHO Parameterization Using of Temperature



HCHO has strong correlation with temperature, scatters relate to CO.

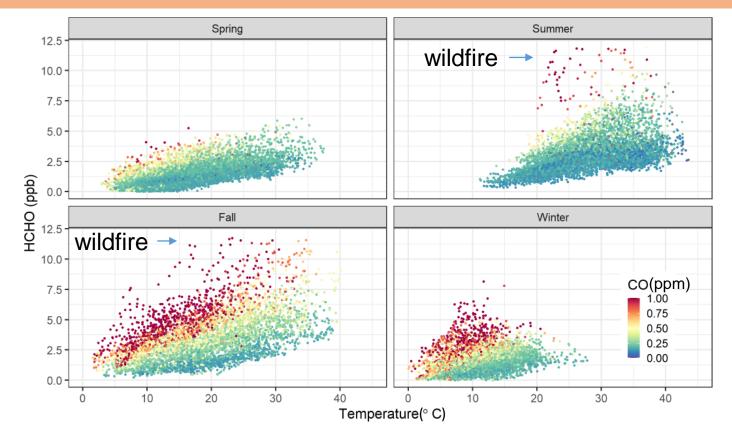
Parameterization Evaluation Using Cross-Validation





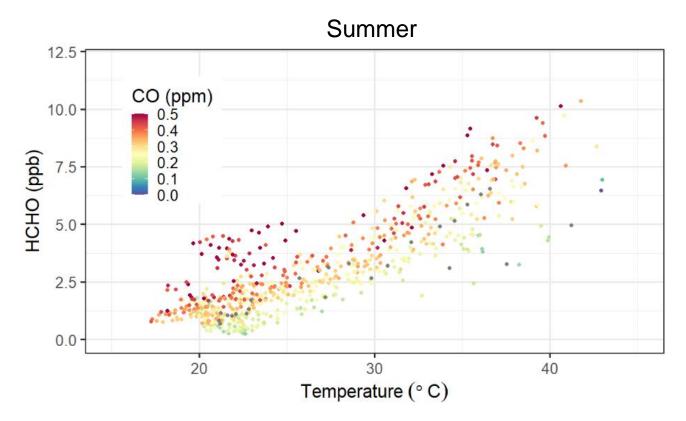
Temperature alone explains ~50% of the HCHO variability.

HCHO vs Temperature in Fresno



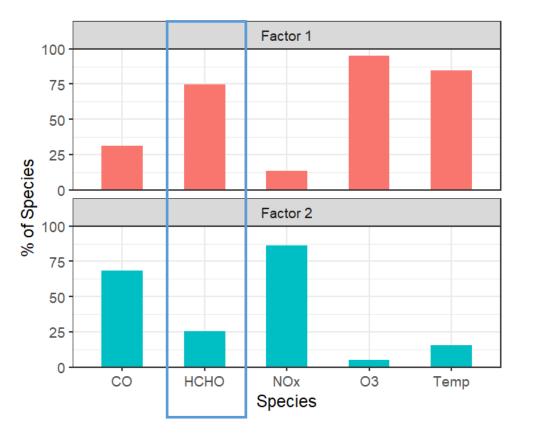
HCHO has strong correlation with temperature, scatters relate to CO.

HCHO vs Temperature in Pasadena



HCHO has strong correlation with temperature, scatters relate to CO. 14

Sources Apportionment of HCHO in Fresno



PMF Factors:

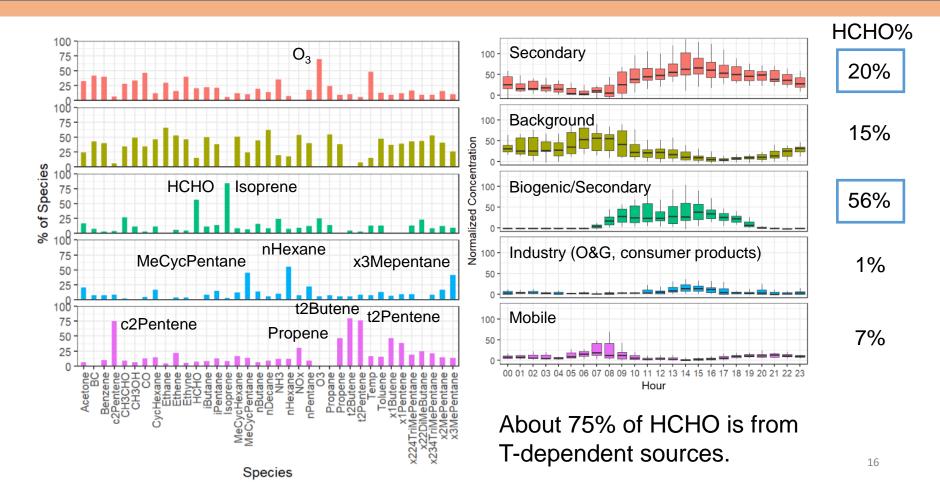
- Factor 1: T-dependent source
- Factor 2: Primary combustion

Notes:

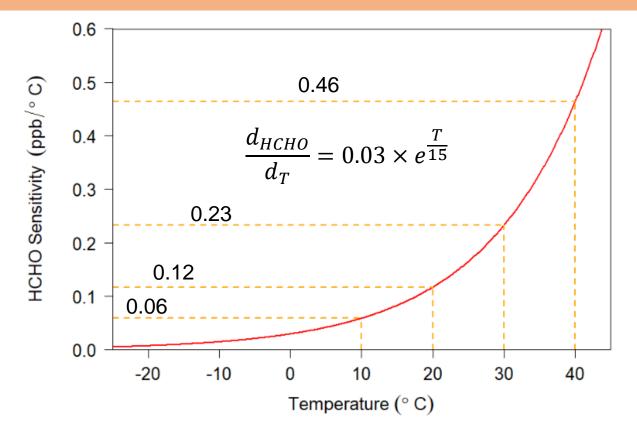
- Daily data
- 5 species
- 2-factor solution

About 75% of HCHO is from Tdependent source.

Sources Apportionment of HCHO in Pasadena



Sensitivity of HCHO to Temperature



HCHO becomes sensitive to temperature as temperature increases.

Conclusions and Future Work

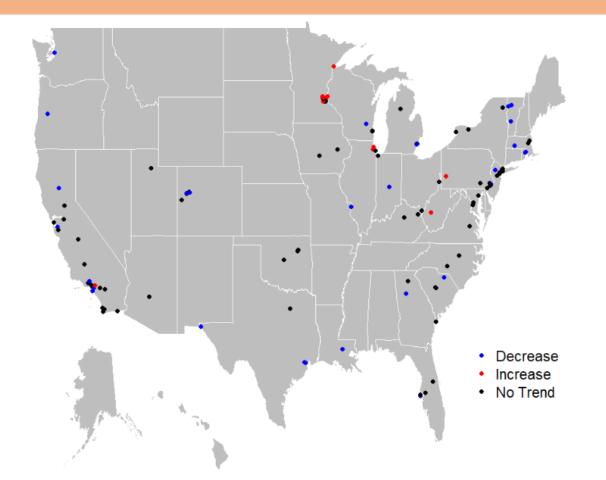
Conclusions

- HCHO measurements in the SJV, SoCAB, and the US consistently show exponential increase with temperature.
- Temperature alone can explain 50% of the HCHO variability.
- HCHO concentration is also affected by combustion sources, especially in fall and winter.
- Source apportionment suggest that 75% of HCHO is from temperaturedependence sources and 25% is from anthropogenic sources in CA.

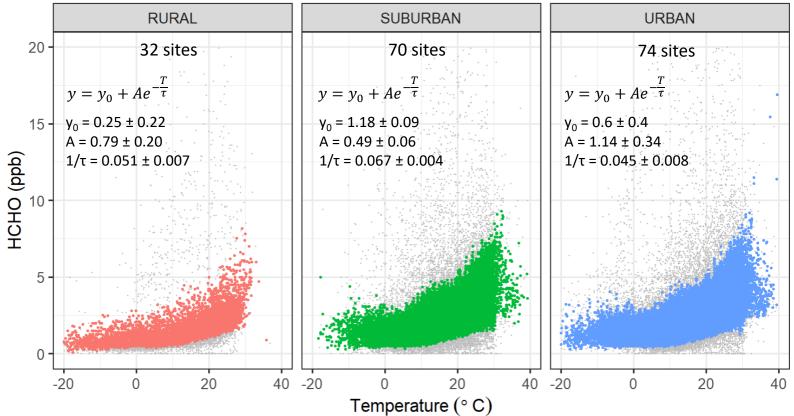
Future Work

- Contributions of emissions vs chemistry to the T-dependence.
- Refine source apportionment analysis.

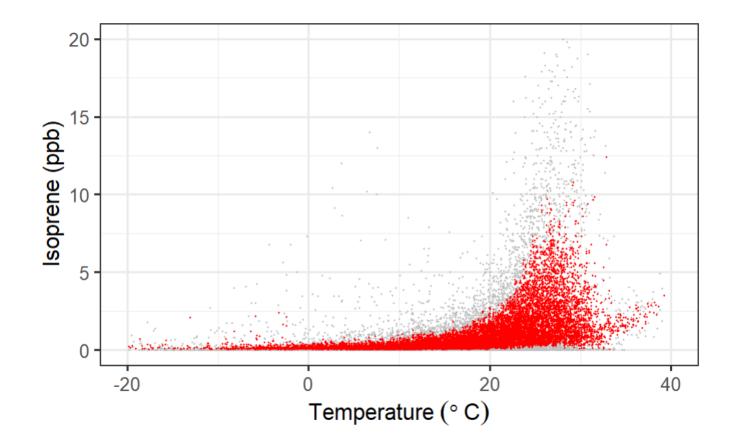
HCHO Trend Map



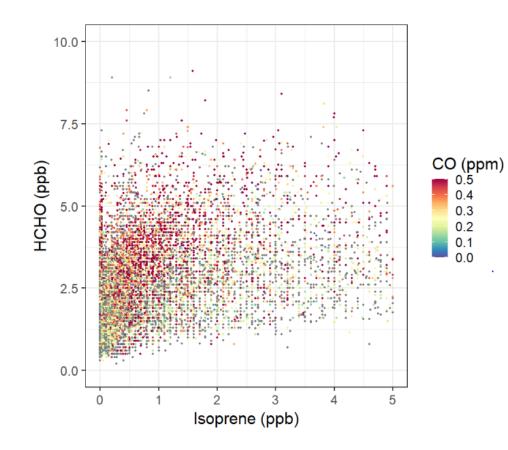
HCHO vs T by Location Setting



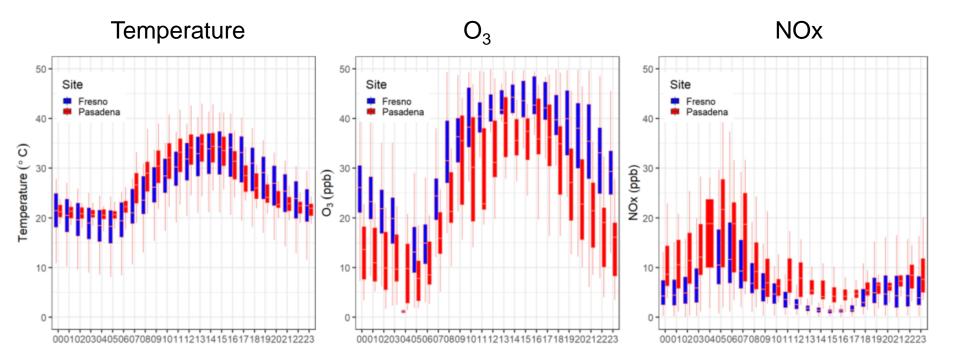
Isoprene vs Temperature



HCHO vs Isoprene

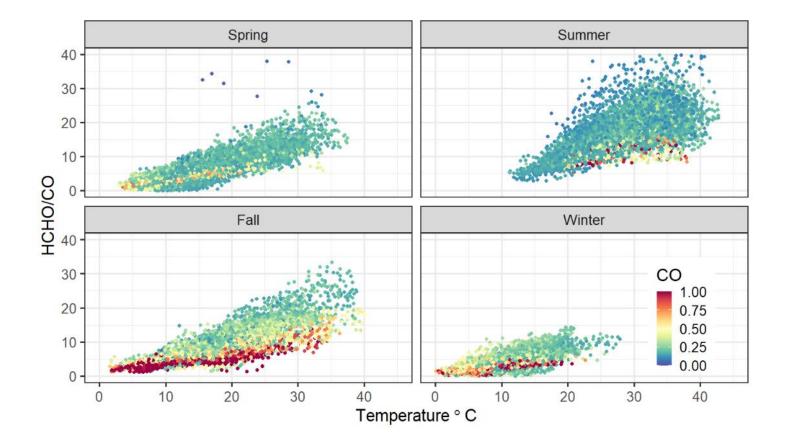


Diurnal Cycle of T/O₃/NOx in Pasadena vs Fresno

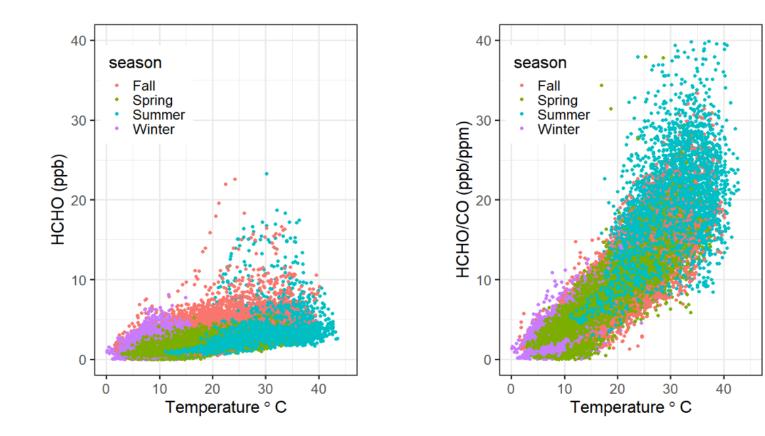


• Diurnal cycles of T, O₃, and NOx are similar between Pasadena and Fresno.

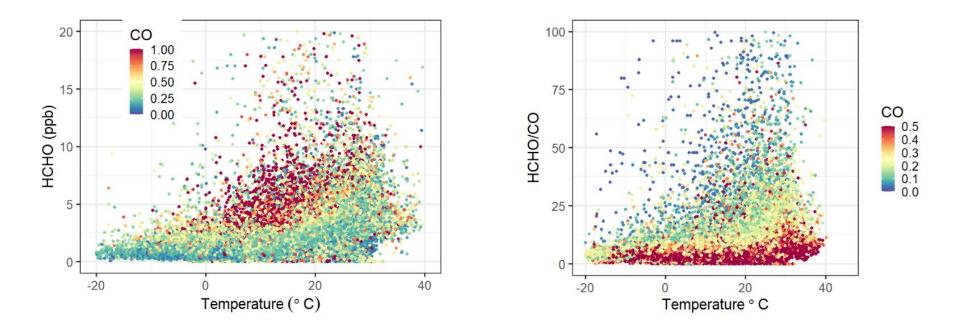
HCHO/CO vs Temperature in Fresno



HCHO vs T and HCHO/CO vs T in Fresno



HCHO and HCHO/CO vs Temperature in the US



HCHO has strong correlation with temperature, scatters relate to CO.