Understanding Trends of Volatile Organic Compounds in the Los Angeles Basin across Gradients of Human Activity

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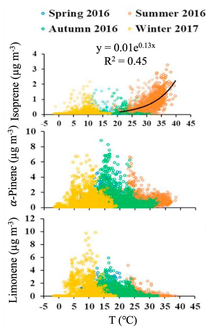
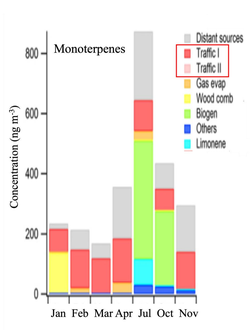
Motivation & Objectives

Part 1: Year-long measurements in Athens, Greece found that while isoprene concentrations were higher in summer months due to higher temperatures and solar radiance, monoterpenes showed more complex seasonal patterns, with maxima during the coldest months.

A study in Finland found that up to 60% of measured monoterpenes were associated with traffic related sources in non-summer months. Thus the first objective of this work was to see if: **gas chromatography data from the urban LA Basin could be used to differentiate biogenic and anthropogenic monoterpenes.**



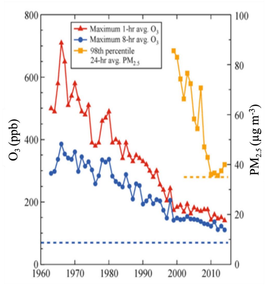
Panopoulou et al., 2020



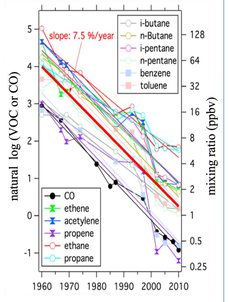
Hellen et al., 2012

Part 2: Volatile organic compounds (VOCs) emitted from various sources react to form tropospheric ozone (O_3) and secondary organic aerosol (SOA). Stringent regulation of vehicular emissions led to decreases in VOCs from on-road mobiles sources and decreases in O_3 levels between 1960 and 2000, however, since 2010 the decreasing trend in O_3 has slowed and in some regions has stopped.

Between 1960 and 2010, CO and VOCs associated with on-road mobile sources decreased ~7.5%/year indicating that in 2010 on-road gasoline emissions were still the dominant source of combustion-related VOCs in the LA Basin.
Our measurements in 2020 suggested a shift in this dominant source sector to off-road mobile sources. Thus the second objective of this work was to see if: **the observations made during the COVID-19 pandemic still hold, including the shift in combustion source sector.**



Parrish et al., 2016

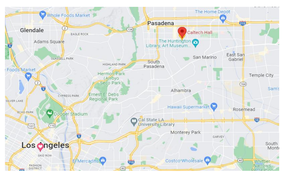


Warneke et al., 2012

LAAQC-2020 & LAAQC-2022 Sample Collection

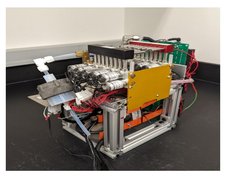
To document VOC profiles during and after the COVID-19 stay-at-home restrictions, samples were collected as a part of the Los Angeles Air Quality Campaign (LAAQC) in both 2020 & 2022. Both whole air samples (WAS) and dual-bed sorbent cartridge samples were collected in both years.

	LAAQC-2020	LAAQC-2022
Sampling Location	Caltech Campus Pasadena, CA	
Sampling Period	April-July 2020	March-August 2022
# UCI WAS Samples	314	448
# UCR Cartridge Samples	154	206
Analyzing Instrument	Gas chromatography (GC) with multiple detectors (flame ionization, electron capture and mass spectrometry) and two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-ToF-MS)	



Sampling Location

WAS & Cartridge Samples

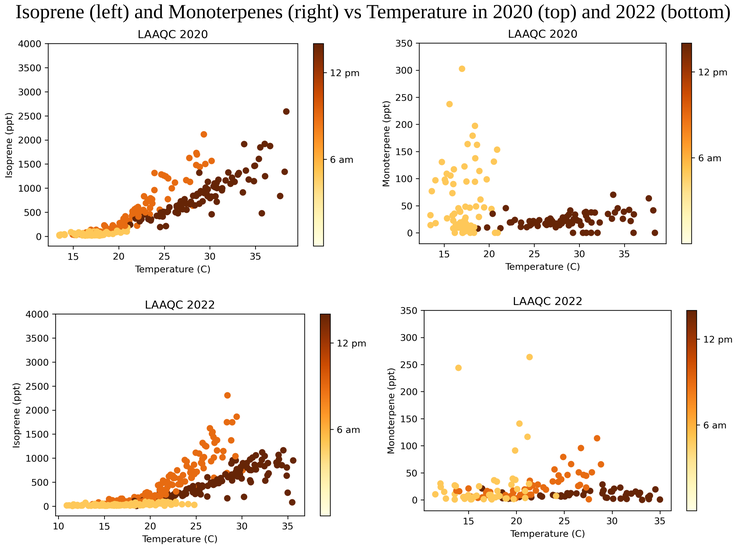


UCR VOC Sampler

Part 1 Results: Evidence for Anthropogenic Monoterpenes

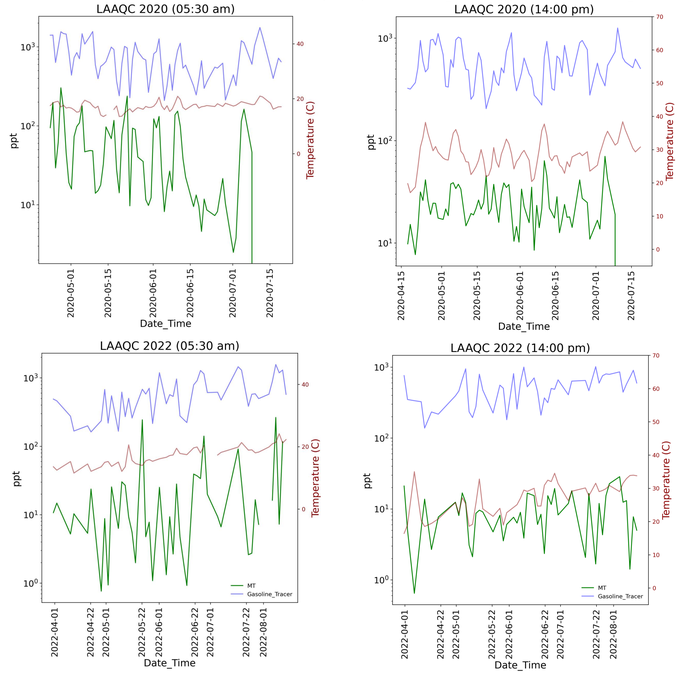
Isoprene and monoterpenes showed non-linear relationships with temperature in the 2020 and 2022 data. Isoprene mixing ratios generally increased exponentially with temperature, similarly to the Athens study. In contrast, monoterpenes (sum of a-pinene, b-pinene and limonene) showed little to no correlation with temperature. This suggests that these terpenes may have different sources, with isoprene being predominately biogenic.

Isoprene (left) and Monoterpenes (right) vs Temperature in 2020 (top) and 2022 (bottom)



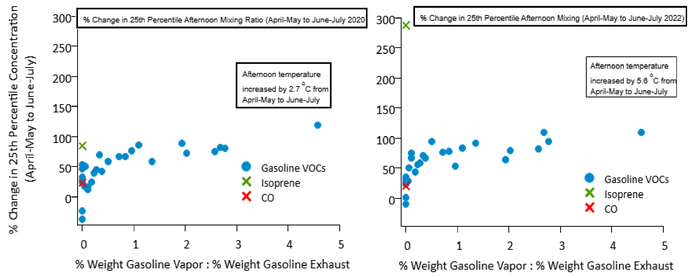
BTEX compounds are common tracers for on-road gasoline vehicles. In both our 2020 and 2022 data, peak monoterpene mixing ratios were temporally correlated with the peak mixing ratios of gasoline tracers, particularly in the nighttime samples (5:30 am). This suggests an anthropogenic source of monoterpenes correlated with on-road activity. However, in the afternoon samples, monoterpenes showed better temporal correlation with temperature suggesting that the afternoon monoterpenes might be predominately biogenic.

Time Series of On-Road Gasoline Tracers (blue), Monoterpenes (green) and Temperature (red)



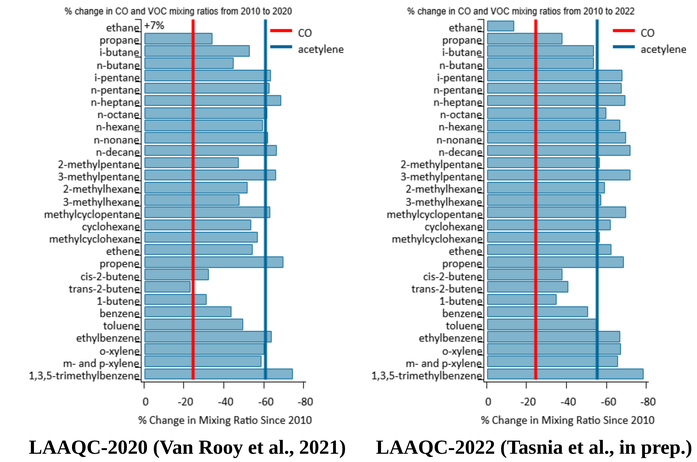
Part 2 Results: Pandemic Trends Hold

In 2020 (left) we observed that VOCs with increases in Q1 (25th percentile) afternoon mixing ratios between April-May and June-July were correlated with higher weight % in gasoline vapor relative to gasoline exhaust, indicating that higher temperatures in June-July resulted in increased gasoline evaporation, which was observable in the GC data. This trend was also observed in 2022 (right).



LAAQC-2020 (Van Rooy et al., 2021) **LAAQC-2022 (Tasnia et al., in prep.)**

Also in our 2020 data, we observed that relative to 2010, CO decreased by 24.5% whereas acetylene decreased by 61% (left figure). Most of the VOCs followed acetylene more closely than CO. We wanted to investigate whether the 2020 trends were robust, as changes in human activities during the shelter in-place-orders likely had some influence on chemistry and composition. Using the 2022 data, relative to 2010, CO decreased by 25% and acetylene by 55% (right figure), with most VOCs following acetylene. This divergence in the CO and combustion-related VOC mixing ratios is robust, and indicates a change in the combustion source sector, likely from on-road mobile sources to off-road sources.



LAAQC-2020 (Van Rooy et al., 2021) **LAAQC-2022 (Tasnia et al., in prep.)**

Conclusions

- Nighttime (5:30 am) monoterpene mixing ratios showed little to no correlation with temperature, but showed some temporal correlation with anthropogenic VOCs, specifically on-road gasoline tracers, suggesting the possibility of an anthropogenic source. Monoterpenes measured in the afternoon appear to be predominantly biogenic.
- Afternoon mixing ratios of VOCs with higher weight % in gasoline evaporation profiles than gasoline exhaust profiles increased with temperature in June-July relative to April-May in both the 2020 and 2022 datasets, indicating gasoline evaporation leads to measurable changes in ambient mixing ratios.
- Since 2010, the percent change in many combustion-related VOCs follows the trend of acetylene more closely than CO. This divergence between CO and these VOCs indicates a shift in the combustion sector and was robust using 2020 and 2022 data.

Funding Source and References:
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