Distributions and Correlations of Volatile Organic Compounds (VOCs) during AEROMMA 2023 over the Eastern United States and Los Angeles

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Motivation

Volatile organic compounds (VOCs) contribute to ground level ozone and particle formation and have both natural and anthropogenic sources. Long-term reductions in urban VOC sources, such as motor vehicles emissions, have resulted in volatile chemical products (VCPs) as the dominant VOC source sector in densely populated areas. VCPs include personal care products, paints, adhesives, cleaning agents, and more. VCP emissions and distributions are not well understood in part due to the diverse product usage[1,2]. The Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas (AEROMMA) targeted urban and marine emissions with a focus on how tropospheric composition, including VCPs, impacts air quality and climate over North America. The AEROMMA campaign was conducted during Summer 2023 with the NASA DC-8.

iWAS Sampled VOCs Across Several Major North American Megacities During AEROMMA

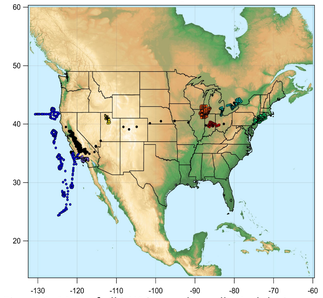


Figure 1: Map of all iWAS samples collected during AEROMMA colored by city

Total Number of iWAS Samples Collected	2710 samples
Average iWAS Canister Fill Time	5.4 seconds
Total Number of Calibrated Compounds	187 VOCs
Total Number of Duplicate Samples Analyzed	444 samples
Total Number of Samples Collected By City:	
•New York City	536 samples
•Chicago	524 samples
•Los Angeles	510 samples
•Toronto	240 samples
•Salt Lake City	83 samples
•Indianapolis	46 samples

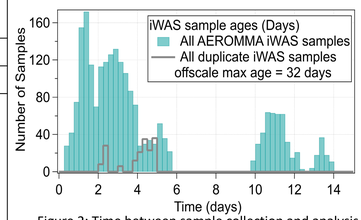


Figure 2: Time between sample collection and analysis for iWAS samples

The integrated Whole Air Sampler (iWAS) provided the most detailed chemical speciation of any instrument on the NASA DC-8. iWAS collected whole air samples that were analyzed on the NOAA GC-MS, a two-channel gas chromatograph coupled to a quadrupole mass spectrometer[3]. The NOAA GC-MS measures 200+ compounds including C2-C11 hydrocarbons, C1-C8 oxygenated VOCs, nitriles, and more.

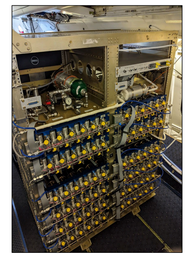


Figure 3: iWAS onboard the NASA DC-8 with 12 modules, 144 canisters

Similar On-Road Combustion Ratios For All Three Cities, Eastern U.S. Impacted By Biomass Burning, and NYC had the Highest Biogenic VOCs Mixing Ratios

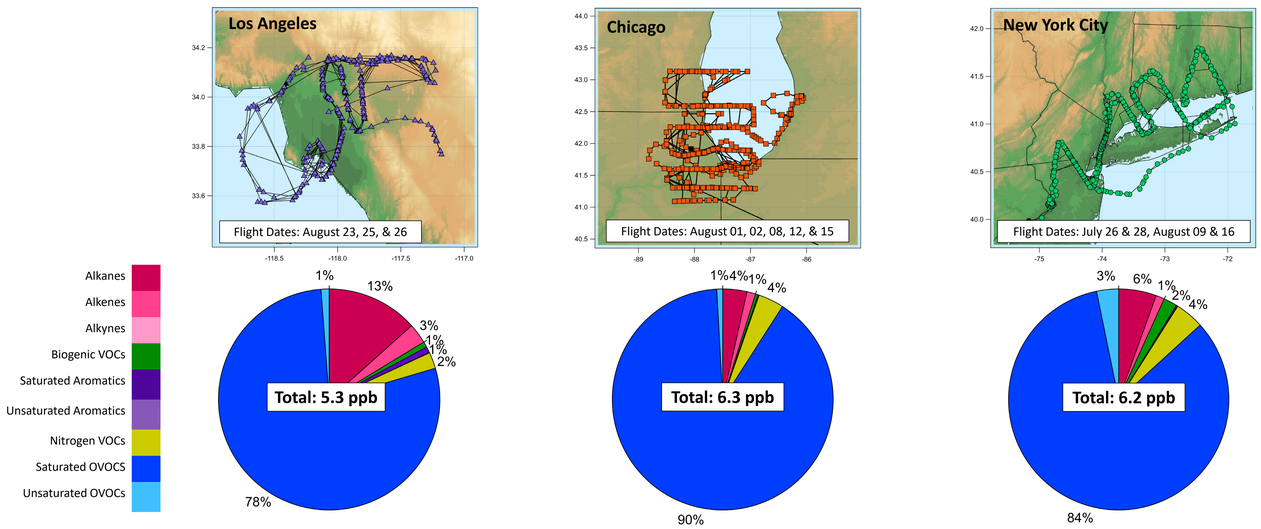


Figure 4: (Top Row) Map of iWAS samples (circles) collected during AEROMMA along the NASA DC-8 flight track (black line) in Los Angeles, Chicago, and New York City. All data presented were collected below 1.1 km. (Bottom row) Sum of all measured mixing ratios for Los Angeles, Chicago, and New York City for iWAS samples and high time resolution data averaged over canister open times. The total shown is the summed mixing ratio for all chemical species used for classifications for all flights. For all three cities, saturated oxygenated VOCs (OVOCs) represented the greatest fraction with methanol, ethanol, formaldehyde, and acetaldehyde as the dominant species in that fraction. Los Angeles had the highest fraction of alkanes. Chicago had the highest fraction of saturated OVOCs. New York City had the highest fraction of biogenic VOCs.

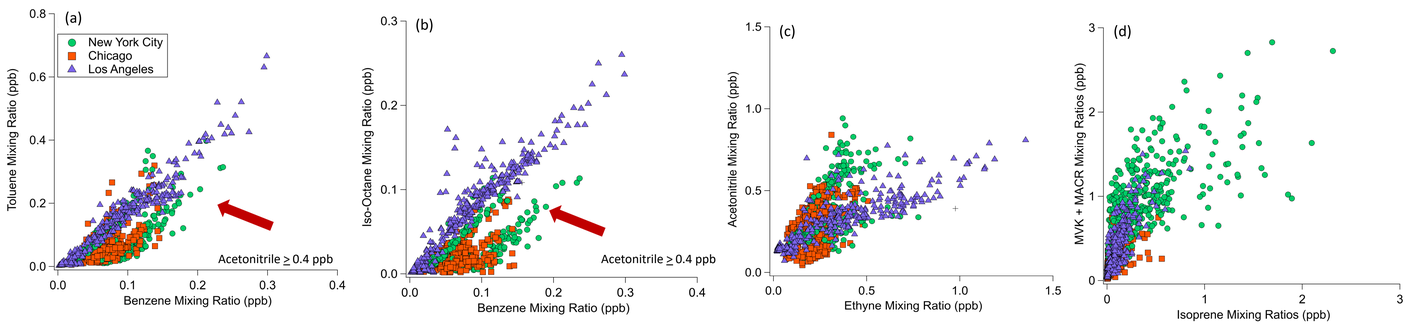


Figure 5: VOC correlation plots highlighting various emission source sectors: (a,b) combustion, (c) biomass burning, and (d) biogenic sources and photochemistry. The highest benzene, toluene, and iso-octane was measured in Los Angeles. The red arrow in (a) and (b) highlights the different slope corresponds with acetonitrile mixing ratios, a biomass burning tracer, greater than 0.4 ppb.

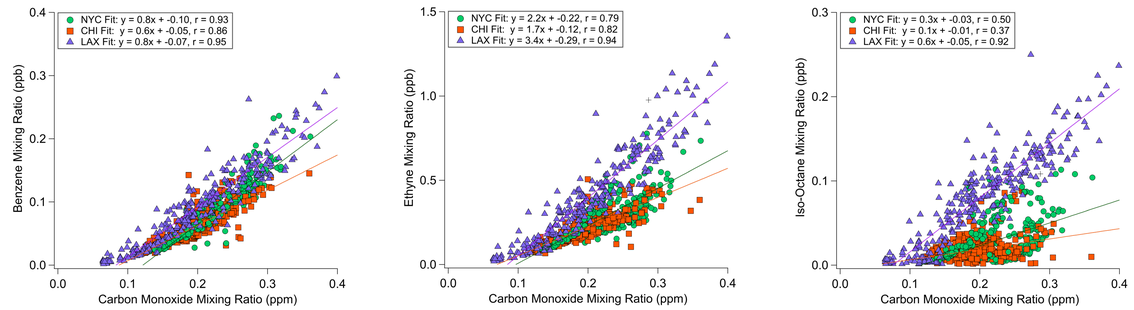
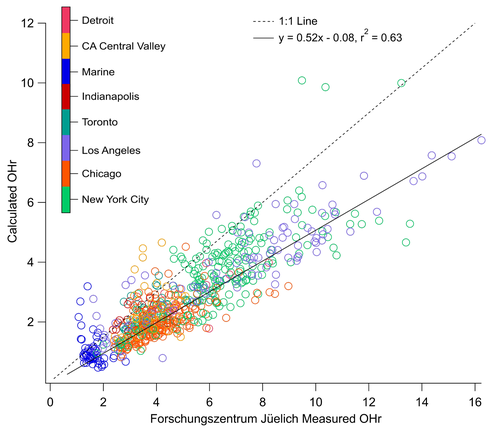


Figure 5 (left): CO enhancement ratio with fits for benzene, ethyne, and iso-octane for all three cities. There is good agreement, and similarity, for all three cities for benzene and ethyne. In general, the highest ethyne and iso-octane was measured over Los Angeles.

Measured OH Reactivity Greater Than Calculated



The table below displays the average and standard deviation calculated and measured OH reactivity. The measured reactivity was higher than calculated for all locations except for marine data.

City	Calculated OHr (s^{-1})	Measured OHr (s^{-1})
New York City	3.3 ± 1.4	6.1 ± 2.2
Chicago	2.0 ± 0.6	4.1 ± 1.1
Los Angeles	3.3 ± 1.8	6.3 ± 3.5
Toronto	2.2 ± 0.6	3.8 ± 1.1
Indianapolis	2.1 ± 0.5	3.0 ± 0.5
Marine	1.1 ± 0.5	1.6 ± 0.3
Central Valley	2.3 ± 1.2	3.8 ± 0.7
Detroit	2.8 ± 0.6	4.8 ± 1.2

Figure 6: Correlation plot of the calculated and measured OH reactivity along with a 1:1 line colored by city. OH reactivity is a simple metric for ozone formation potential. This includes iWAS VOCs and high time resolution instruments including the NOAA PTR-MS, LTOF, ACES, LGR, and I-CIMS (colored circles). The calculated values are colored by city. Forschungszentrum Jüelich measured OH reactivity were averaged over the iWAS can times (black crosses). The measured OHr used laser photofragmentation laser-induced fluorescence[4]. The measured reactivity was greater than the calculated reactivity suggesting that there may be "missing" VOCs not measured contributing to OH reactivity.

Take Home Messages

- OVOCs were the dominate VOC fraction for all three cities.
- The best CO correlation for all three cities was for benzene and ethyne indicating a strong common source from combustion.
- New York City had a higher contribution from biogenic VOCs compared to the other cities as evidenced by isoprene, methyl vinyl ketone (MVK), methacrolein (MACR), and α-pinene.
- Los Angeles had the highest relative amount of iso-octane (2,2,4 – trimethylpentane) relative to New York City and Chicago.
- Biomass burning impacted the eastern portion of AEROMMA with the greatest impact to New York City.
- The calculated OH reactivity using iWAS samples and high time resolution data was lower than measured.

Acknowledgments

AEROMMA Science Team
NASA DC-8 Crew
NASA ESPO

References

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