Wintertime Sources and Sinks of Volatile Organic Compounds in Fairbanks, Alaska

Damien Ketcherside[1] (damien.ketcherside@umontana.edu)

Vanessa Selimovic[1], Lu Hu[1], Robert J Yokelson[1], Ellis Robinson[2], Peter F DeCarlo[2], Andrew Holen[3], Judy Wu[3], Kerri Pratt[3], Karolina Cysneiros de Carvalho[4], Brent J Williams[4], Meeta Cesler-Maloney[5], Jingqiu Mao[5], William R Simpson[5], Brice Temime Roussel[6], Barbara D'Anna

[1]University of Montana, Missoula, MT, USA; [2]Johns Hopkins University, Baltimore, MD, USA; [3]University of Michigan - Ann Arbor, Ann Arbor, MI, USA; [4]Washington University - St. Louis, St. Louis, MO, USA; [5]University of Alaska Fairbanks, Fairbanks, AK, USA, [6]LCE, CNRS, Aix-Marseille Université, Marseille, France

A52P-1199

Background

- Fairbanks, Alaska is highly polluted during the wintertime and is currently a non-attainment area for $PM_{2.5}$. Strong thermal inversions trap primary pollutants resulting in accumulation of volatile organic compounds (VOCs), NO_x, particulate matter, and other trace gases.

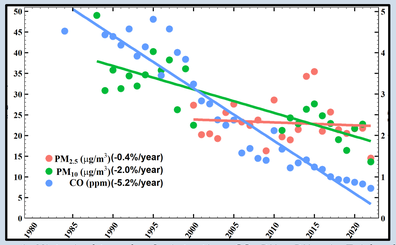

Figure 1. Historical trends of wintertime CO, PM_{10},$PM_{2.5}$ in Fairbanks, AK

- Due to the extreme cold, many individuals spend more of their time indoors. Residential wood combustion (RWC) is a popular choice for home heating, but fuel oil and natural gas are also prominent. The impact of these heat sources on the indoor environment is currently unknown.
- The impact of indoor VOCs from sources such as cooking, incense, and a combination of these sources is not fully understood.
- VOC oxidation mechanisms in extreme cold and dark environments remain unknown.
- The ALPACA field campaign provides the first comprehensive VOC measurements in Fairbanks, both indoor and outdoor to answer the following questions:

1. **How do outdoor VOC mixing ratios compare with indoor VOCs in cold and dark environments?**
2. **How do daily activities, such as the operation of a pellet stove insert and other events, influence indoor VOC mixing ratios?**
3. **Do regional and global emissions inventories accurately capture VOC emissions from these local sources?**

Methods

- Indoor and outdoor measurements of VOCs were collected by a proton-transfer-reaction time-of-flight mass-spectrometer (PTR-ToF-MS) as part of the ALPACA 2022 Field Intensive from January 19th to February 25th, 2022.
- Heated PTFE inlets were used to switch between indoor and outdoor sampling every 10 minutes.

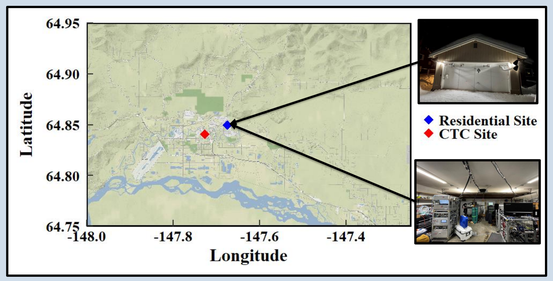

Figure 2. Map of Fairbanks, Alaska with residential and downtown sites labeled

- Indoor pellet stove experiments were conducted by operating the pellet stove insert for 3 hours, from ignition to 3 hours after extinguishing the flame.

Total VOC mixing ratios (tVOC) are ~5 times higher indoors than outdoors

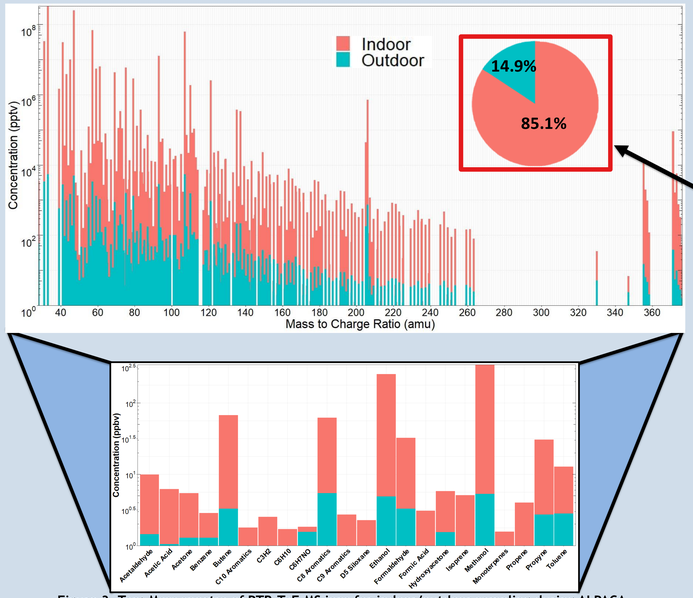

Figure 3. Top: Mass spectra of PTR-ToF-MS ions for indoor/outdoor sampling during ALPACA
Bottom: Most abundant VOCs measured indoor and corresponding outdoor concentrations

- Figure 2 represents the median VOC mixing ratios, both indoor and outdoor, during the ALPACA field intensive. This analysis excludes data during indoor experiments and a three-hour time buffer before and after each experiment.
- 192 unique masses were detected and quantified.
- 85.1% of the median tVOC mixing ratio was measured indoors.
- The median tVOC mixing ratio is 232 ppbv and 40.6 ppbv for indoor and outdoor, respectively.
- In a residential environment, exposure risk from hazardous air pollutants in the indoor environment is greater than outdoors. Indoor benzene mixing ratios are 75% higher than those measured outdoors, while HCHO is higher by a factor of 3 indoors.
- D5 siloxane and monoterpenes, both associated with personal care products, are significantly higher indoors due to researcher activity.

Pellet stove operation enhances indoor VOCs

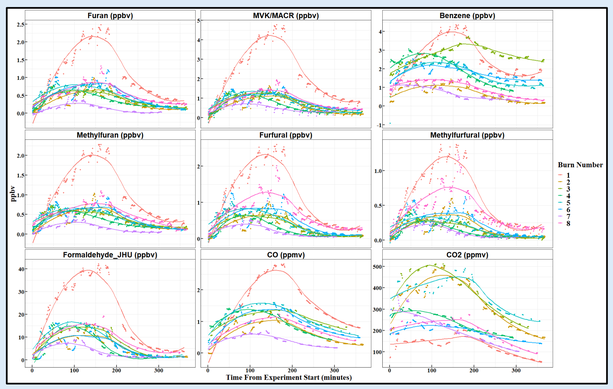

Figure 4. Indoor VOC enhancements during 8 pellet stove experiments

- Experiment 1 resulted in the largest enhancement for most species, potentially due to off-gassing from the new stove's paint.
- Furanic species were all elevated during each burn, while acetonitrile only showed appreciable enhancement during a single burn.
- Hazardous VOCs such as benzene and formaldehyde exhibit and maintain high concentrations during pellet stove use.
- Emission ratios derived from measurements of the stove exhaust will be compared to regional and global emissions inventories

Figure 5. Researchers conducting pellet stove experiment 1. Photo Credit: Peter F DeCarlo

RWC is a major source of VOCs in Fairbanks, AK

Fraction of VOC from RWC ← $[VOC]_{RWC} = ER_{VOC/F}[F]$ ← Furfural Mixing Ratio

Emission Ratio of VOC/Furfural

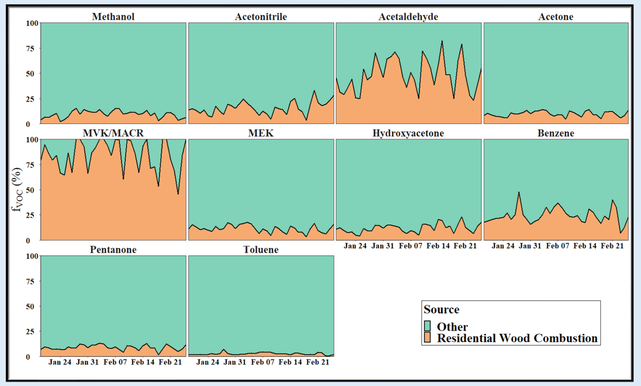

Figure 6. Contribution of RWC to outdoor VOC abundance in Fairbanks

- It is estimated that RWC contributes between 10% and 25% for most measured VOCs.
- RWC may be the main source of acetaldehyde (48.7%) and MVK/MACR (84.3%) during the wintertime.
- Using furan and methylfuran as tracers produced similar results; PMF will be used to compare with this method.

CEDS compares well with source measurements

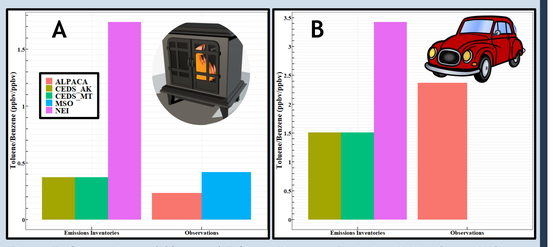

Figure 7. Comparison of Observed Toluene/Benzene Emission Ratios from RWC (*A*) and on road sources (*B*) with the Community Emissions Data System (CEDS) and the National Emissions Inventory (NEI)

- The RWC emission ratio from CEDS agrees well with conventional wood stove emissions (MSO) but is slightly higher those derived from the pellet stove insert.
- The on-road T/B emission ratio from CEDS is lower than observed cold start emission ratios.
- NEI T/B ratios are consistently higher than CEDS and observations.

NEI overestimates contributions of RWC VOCs, underestimates $PM_{2.5}$ fraction

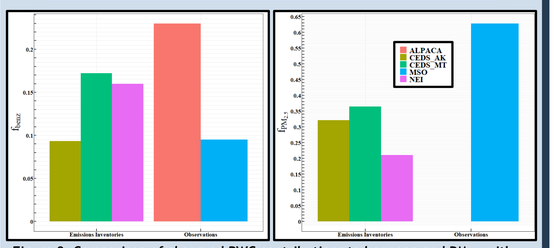

Figure 8. Comparison of observed RWC contributions to benzene and $PM_{2.5}$ with CEDS and NEI

- The fraction of benzene attributed to RWC is 2.5 times lower in CEDS than observed during ALPACA.
- Benzene from RWC in MSO is overestimated by a factor of 2 in CEDS and NEI.
- $PM_{2.5}$ contributions from RWC are underestimated in both CEDS (2x) and NEI (3x) compared to observations in MSO.

Future Directions

- Analysis of mixed, cooking, and incense experiments
- FOAM: FOAM box modeling to examine fates of outdoor VOCs in the cold/dark environment
- Source attribution of outdoor VOCs at the house site

Acknowledgements
This study was supported by NOAA Climate Program Office's Atmospheric Chemistry, Carbon Cycle, and Climate program, grant number NA20OAR4310296.