Improving Residential Wood Combustion Emission Factors and Chemical Speciation with the Reactive Organic Carbon (ROC) Framework

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Motivation

Residential wood burning is one of the largest anthropogenic sources of organic carbon particulate matter (PM) and vapors to the atmosphere in the United States. The impact of these emissions on air quality is profound, especially in the wintertime when wood is used for heating, and it is expected to grow in relative importance in the future. Existing inventories and photochemical air quality models often use an outdated conceptual model of the phase partitioning of organic particulate and vapor mass.

Regulatory test methods are used to quantify PM emission factors from wood stoves with an operational definition of particulate matter (i.e., mass captured on a Teflon filter) that is susceptible to systematic temperature and dilution biases. Meanwhile, Volatile Organic Carbon (VOC) emission factors are informed by measurements of total hydrocarbon vapors. These vapors are characterized using flame-ionization detection (FID), which provides an uncertain measure of gas mixtures containing significant contribution from oxygenated molecules. Finally, the speciation of residential wood burning emissions needs to be revised with state-of-science understanding of key secondary organic aerosol precursors consistent with emerging chemical mechanisms (Pye et al., 2023).

Research Objectives

- Enumerate the sources of systematic reactive organic carbon (OC) measurement biases in wood burning emissions tests.
- Use a detailed wood-smoke speciation profile to develop a methodology for translating existing PM and VOC emission factors to ones that include semivolatile organic compounds (SVOCs) and intermediate volatility organic compounds (IVOCs). Characterize the uncertainty in this approach.
- Quantify potential impacts of update on ambient organic aerosol (OA) predictions.

PM Filter Measurement Artifacts

- Teflon filter – total $PM_{2.5}$ gravimetric weight
- Quartz filter – organic carbon concentration measured with thermal-optical method. Includes absorptive and adsorptive artifacts.
- Quartz-behind-Teflon – isolates organic carbon adsorptive artifacts.
- IVOCs and SVOCs may condense to the filter or break through depending on conditions.

$$EF_{OC,\,Artifact-Corrected} = EF_{OC,\,Bare-Quartz} - EF_{OC,\,Quartz-Behind-Teflon}$$

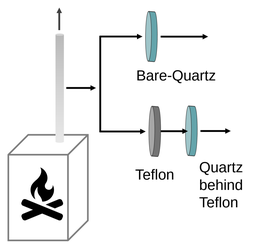

Figure 1. PM Emissions sampling techniques relevant for source characterization.

Bulk VOC Measurement Artifacts

Inline Flame Ionization Detector (FID) Sampling
- Particles are removed by the glass fiber filter.
- Sample line is heated to greater than 110 C, so IVOCs and SVOCs could evaporate from the glass filter.

Offline FID Sampling
- Volatile organic compounds (VOCs) are collected via Summa Canister. IVOCs are likely not efficiently captured (Lu et al., 2018).

FID analysis underrepresents molecules with oxygen groups present.

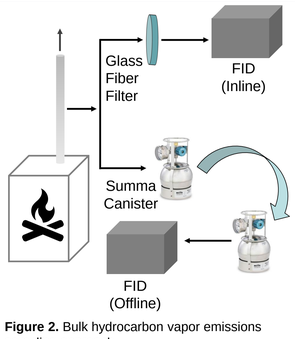

Figure 2. Bulk hydrocarbon vapor emissions sampling approach.

ROC Framework

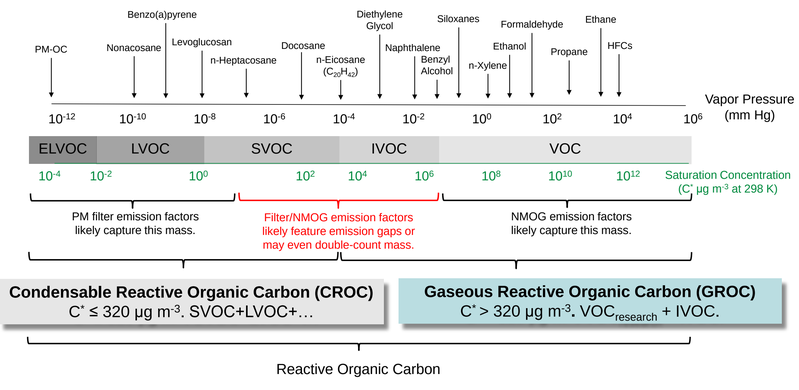

Figure 3. Schematic of Reactive Organic Carbon framework, which includes all organic particle and vapor mass excluding methane.

Detailed Wood-Burning ROC Speciation

- Fireplace pine smoke gas and particle emissions were measured and speciated with unprecedented detail by Schauer et al. (2001) and Nolte et al. (2001).
- Vapor speciation and OM/PM wt% were adopted by EPA for entire Residential Wood Burning sector.

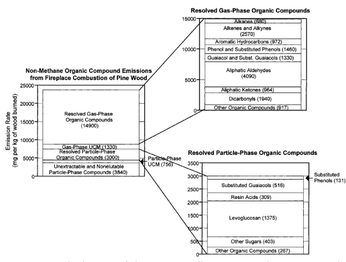

Figure 4. Mass balance of the non-methane organic compounds emitted from the fireplace combustion of pine wood. (Reprinted from Schauer et al. (2001).

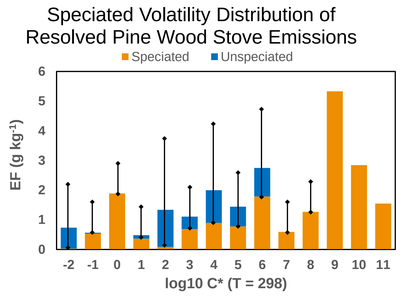

Figure 5. Default volatility of unspeciated mass informed by measurements and analysis of wood smoke by EPA and NC State (Sinha et al., 2022).

- Monte Carlo simulations varied unspeciated EF uniformly within error bars (10,000 runs).
- O:C of each unspeciated group was randomly assigned between 0.1 and 0.8.

PM and VOC emission factors are susceptible to artifacts in wood-burning emission tests. We quantify the uncertainties and suggest new standardized emission factors that account for all organic matter.

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Translating OM → CROC

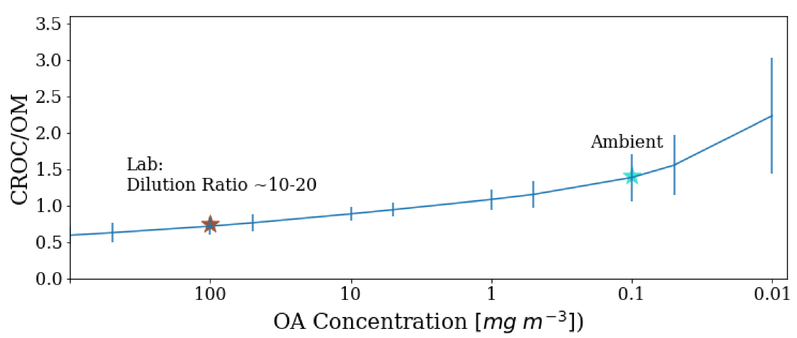


Figure 6. Ratio of total CROC emission factor to particle-phase OM emission factor at varying organic aerosol concentration and 25 C. Error bars reflect 2 standard deviations from the mean of the Monte Carlo simulations.

Translating VOC → GROC

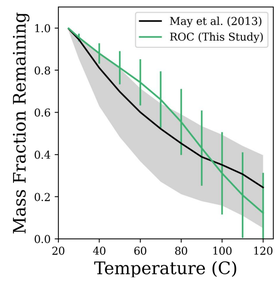


Figure 7. Temperature sensitivity of OM from wood smoke mixture depicted in Fig. 5. Error bars reflect two standard deviations from the mean of the Monte Carlo simulations.

- Detailed emissions behave similarly to temperature dependence documented by May et al. (2013) for emissions observed in the Missoula Montana FireLab.
- Hurley et al. (2020) parameterized relationship between O:C and FID response.

$$Equivalent\ Carbon\ Number\ Response = -0.61 * [O:C] + 0.99$$

- Calculate ratio of total GROC EF (speciated + unspeciated) to the EF inferred by the FID signal.

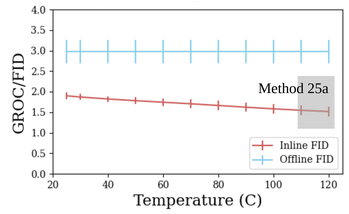


Figure 8. Correction factor to convert FID measurements to total GROC as a function of the sample line temperature. The extent of the swath captures 2 standard deviations from the mean response predicted from the detailed emission profiles.

Accounting for Total ROC

- CROC wood burning emissions are higher than filterable (FILT) OM but lower than condensable (Cond) OM due to high concentration in test (~1-10 mg m^{-3}).
- GROC emissions are larger than what would be typically inferred from FID measurements, assuming no information about oxygenated species is added to the VOC calculation.
- Total ROC is most likely much larger (> +25%) than current reported emission factors suggest.

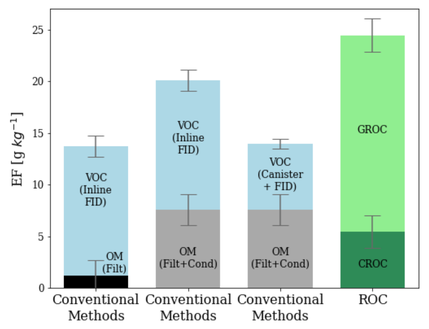


Figure 9. Emission factors simulated from detailed speciation profile. Error bars reflect variability in the Monte Carlo cases. Gray bars are equal to the filterable (Filt) and condensable (Cond) OM summed together.

OA Potential

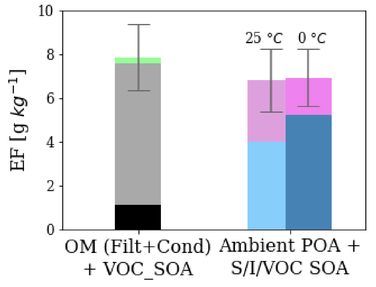
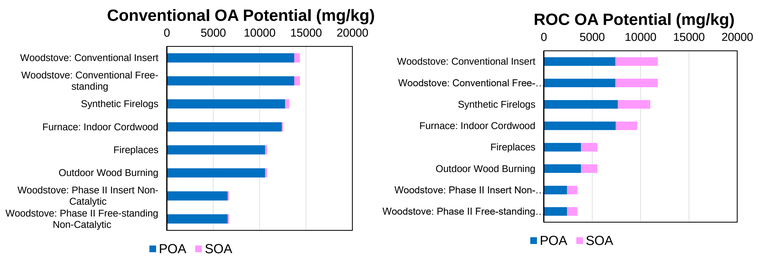


Figure 10. Conventional OA potential (left) including filterable (Filt) OM (black), condensable (Cond) OM (gray), and SOA (green). ROC OA potential (right) with ambient primary OA (blue) at 10 μg m^{-3} and secondary OA potential from SVOCs, IVOCs, and VOCs.

- SOA yields are associated with each species (or surrogate for unspeciated groups) using the carbon number and dominant functional group of the species (Seltzer et al., 2021).
- About 25-50% of wood burning filterable plus condensable OM evaporates under ambient conditions, depending on temperature.
- Much of this mass is replenished downwind by secondary OA (SOA) formed.

Impact on U.S. Emission Factors



U.S. Annual OA Potential from above sources when projected with 2020 activity:
289 kt yr^{-1} → 177 kt yr^{-1} = -39%

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Citations:
1. Pye et al., *Atmos. Chem. Phys.*, 23, 5043-5099, 2023 | **2.** Lu et al., *Atmos Chem. Phys*, 18, (23), 17637-17654, 2018 | **3.** Schauer et al., *ES&T*, 35, 1716-1728, 2001 | **4.** Nolte et al., *ES&T*, 35, 1912-1919, 2001 | **5.** May et al., *J. Geophys. Res.*, 118, 11327-11338, 2013 | **6.** Hurley et al., *Atmos. Meas. Tech.*, 13, 4911-4925, 2020 | **7.** Seltzer et al., *Atmos. Chem. Phys.*, 21, 5079-5100, 2021

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