Quantifying the Impact of Mobile-Source Reactive Organic Carbon Emissions on U.S. Air Quality

Benjamin N. Murphy[1], Darrell Sonntag[2], Karl Seltzer[3], Havala O. T. Pye[1], Claudia Toro[4], Evan Murray[4], Christine Allen[5], and George Pouliot[1]

[1]U.S. EPA Office of Research and Development, Research Triangle Park, NC | [2]Brigham Young University, Provo, UT | [3]U.S. EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC | [4]U.S. EPA Office of Transportation and Air Quality, Ann Arbor, MI | [5]General Dynamics Information Technology, Research Triangle Park, NC

Motivation

In standard regulatory test method procedures, primary organic particle emissions are captured with filter-based techniques which are susceptible to operational biases and sorptive artifacts.[1] Meanwhile, organic gas test methods may have missed intermediate volatility organic compounds (IVOCs), important for SOA production.[2,3] Nevertheless, the U.S. EPA Motor Vehicle Emission Simulator (MOVES) uses emission factors based on these datasets to predict mobile-source emissions across the U.S.[4]

Previous modeling studies have successfully introduced semivolatile organic compounds (SVOCs) and IVOCs using top-down assumptions for all anthropogenic emissions[5] or distinguishing mobile-sector fuel types (e.g. gasoline vs. diesel vehicles).[6] To fully address these complexities, emissions data must be carefully revised from the bottom up at the individual source level with the most recent scientific findings, while ensuring compatibility with existing emission factors data based on standard test method approaches.

Research Objectives

- Develop a post-processing method for translating existing emission rates predicted by MOVES to rates that include SVOCs and IVOCs.
- Include detailed chemical speciation when available from literature.
- Update all mobile-source relevant profiles including Onroad, Nonroad, Aircraft, Marine, and Rail.
- Quantify impacts of update with respect to national-level emissions contributions.

Integrating Measurements in Models

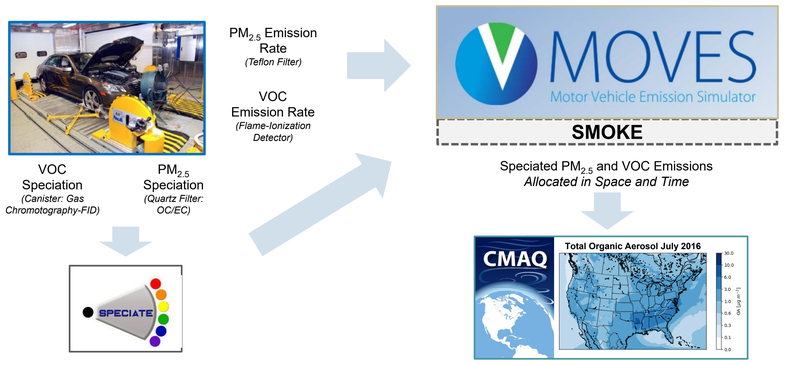


Figure 1. Dataflow of test method measurements to U.S. EPA emission model (MOVES) and chemical speciation database (SPECIATE), followed by processing in emission allocation model (SMOKE) for use in the CMAQ (Community Multiscale Air Quality) model.

ROC Framework

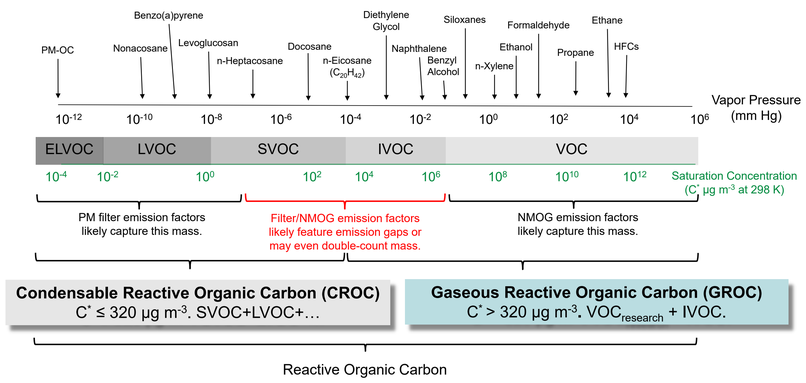


Figure 2. Schematic of Reactive Organic Carbon framework, which includes all organic particle and vapor mass excluding methane.

Particulate Filter Artifacts

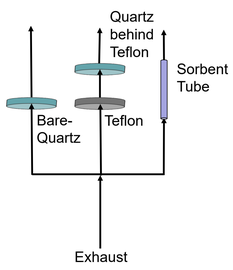


Figure 3. Emissions sampling techniques relevant for source characterization.

- 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.
- Sorbent Tube – captures total organic particle plus vapor. Quantify CROC emissions and IVOCs.

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

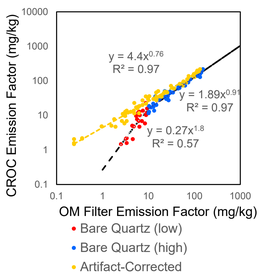


Figure 4. Relationship between CROC emission factors and filter-based OM emission factors.

Translating Emissions

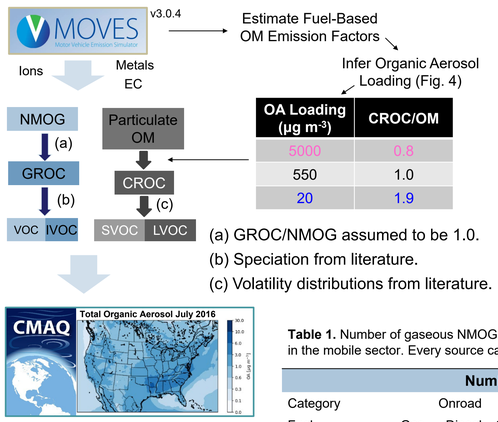


Figure 5. Dataflow for operational translation of conventional non-methane organic gas (NMOG) and primary organic matter (OM) emissions to speciated emissions including IVOCs and SVOCs.

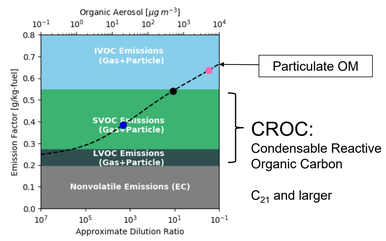


Figure 6. Hypothetical emissions from a combustion source. The dashed line illustrates the filter-based emission factor as a function of dilution ratio.

Table 1. Number of gaseous NMOG and particulate OM profiles that were revised for every source category in the mobile sector. Every source category has been addressed for this update.

Number of SPECIATE Profiles Updated											
Category	Onroad			Nonroad			Airports	Rail	Marine	Other	Total
Fuel	Gas	Diesel	Other	Gas	Diesel	Other					
Gas	6	5	4	4	7	2	4	5	2	13	52
Particle	6	5	4	4	7	2	4	5	2		39

An operational post-processing method is developed that translates Gas and Particle emissions to speciated organics including IVOCs and SVOCs in the U.S. mobile emission inventory

Author Contact: murphy.ben@epa.gov

Community Modeling and Analysis System (CMAS) Annual Meeting | Chapel Hill, North Carolina | 2022 October 17-19

Post-processed Emission Factors

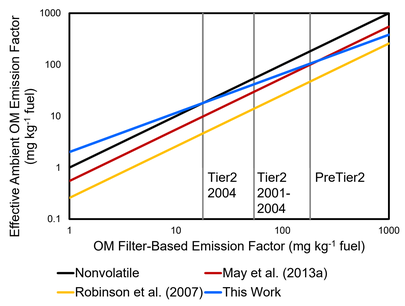


Figure 7. Effective Ambient POA Emission Factor calculated at 10 µg m^{-3} as a function of the OM filter emission factor estimated for cold starts from each class of onroad gasoline vehicles.

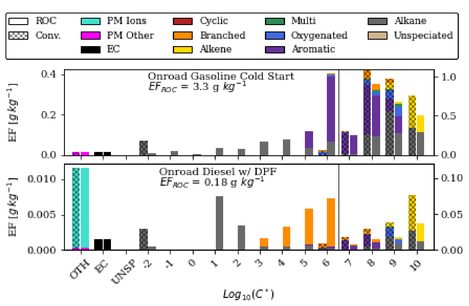


Figure 8. Conventional profile (hatched bars) and updated ROC profile (solid bars) for the full range of volatility in the ROC system. Inorganic components are also included for context.

ROC Emissions

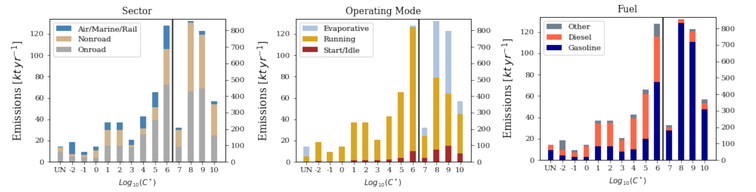


Figure 9. Volatility-resolved mobile source ROC emissions for the contiguous United States during 2016 stratified along several dimensions including sector (left), operating mode (middle), and fuel (right). Bins to the left of the solid black line are quantified by the left y axis and those to the right by the right y axis.

- Onroad and nonroad sources contribute similarly to total ROC emissions although onroad appears to play a larger role for lower-volatility compounds (IVOCs and below).
- Running conditions dominate most emissions despite the start emission factors being much larger.
- Adjusting OM emission factors for missing SVOCs or interfering IVOCs has a significant impact on CROC emissions (Fig. 10).

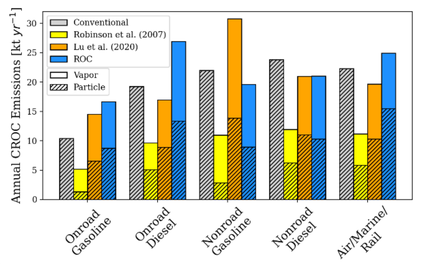


Figure 10. Bottom-up predictions of mobile ROC emissions classified by sector, model approach, and equilibrium phase distribution. The height of each bar corresponds to total CROC emissions. Gas-particle partitioning is calculated for conditions at 298 K and organic aerosol loading of 10 µg m^{-3}.

Impact of ROC Distribution

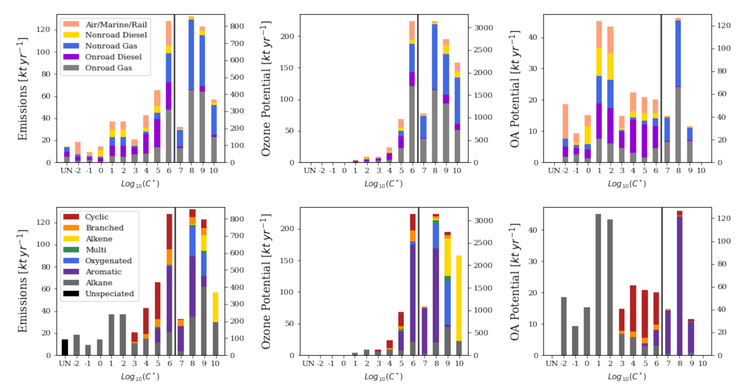
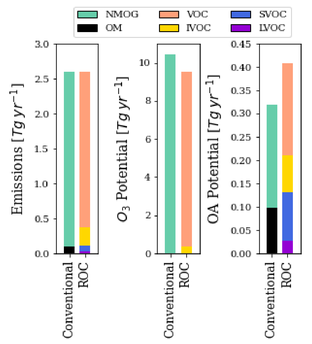


Figure 11. Volatility-resolved ROC emissions, O_3 potential and OA potential. Ozone potential is predicted by weighting emissions by the minimum incremental reactivity (MIR) of each species. Organic aerosol potential is calculated by weighting vapors by their SOA yields and lower volatility compounds by the aerosol mass fraction at 10 µg m^{-3}.



- O_3 and OA potential are developed as part of the CRACMM Project.[7]
- Gasoline sources dominate O_3 potential, and these are mainly aromatics and alkenes in the VOC range.
- Aromatics from gasoline sources contribute substantially to SOA, but branched alkanes from diesel sources have a large role to play in the IVOC range.
- Total OA potential has increased slightly in the new method, while O_3 potential has diminished slightly.

Figure 12. Total U. S. mobile-source emissions for 2016 with aggregate O_3 and OA potential calculated at the species level.

Conclusions

- We have developed a robust method for converting bulk NMOG and PM filter-based emission factors to GROC and CROC quantities, which are well-aligned with speciation profiles currently being published by the academic community.
  - Resolves biases from operational definition of filter OM by translating to CROC
  - Leads to high values of CROC/OM for clean vehicles like onroad diesel vehicles with particulate filters installed.
- Mobile-source LVOCs, SVOCs, IVOCs and VOCs contribute 6.8%, 25.4%, 19.1%, and 48.7% to the total OA potential nation-wide, but this distribution may not accurately reflect surface concentrations near sources.

Citations:

1. Robinson et al., JAWMA 2010, 60, 1204-1222 | 2. Zhao et al., *Environ. Sci. Technol*, 49, (19), 11516-26, 2016 | 3. Lu et al., *Atmos Chem. Phys*, 18, (23), 17637-17654, 2018 | 4. U.S. EPA, EPA-420-R-21-004, 2021. | 5. Murphy et al., *Atmos Chem Phys*, 17, (18), 11107-11133, 2017 | 6. Lu et al., *Atmos Chem Phys*, 20, (7), 4313-4332, 2020 | 7. Pye et al., The Community Regional Atmospheric Chemistry Multiphase Mechanism, Github Repository, https://github.com/USEPA/CRACMM, 2022.

U.S. Environmental Protection Agency
Office of Research and Development