Emissions of Gas-Phase Low-Volatility Organic Compounds from Mobile Sources


EPA STAR-OTAQ Transportation Emissions Research Forum
4 March 2014
Emissions of organic species

VOC: volatile organic compounds (gas phase)
IVOC: “intermediate volatility” organic compounds (gas phase)
SVOC: semivolatile organic compounds (gas, particle phase)
Emissions of organic species

Partitioning

- Gas Phase
- Particulate

- Increasing volatility

- Mass loading

- Saturation vapor pressure (µg/m³)

- VOC: volatile organic compounds (gas phase)
- IVOC: “intermediate volatility” organic compounds (gas phase)
- SVOC: semivolatile organic compounds (gas, particle phase)
High-resolution electron impact mass spectrometer

- Syringe Injection
- PM Filter
- Sampling Inlet
- UHP He
- Capillary Transfer Line
- Pump
- Electron Impact Ionization
- 2-Stage Turbo Pump
- Ultra Zero Air
- Liquid N₂
- LICOR CO₂
High-resolution electron impact mass spectrometer
High-resolution electron impact mass spectrometer

Syringe Injection

PM Filter

LICOR CO₂

Ultra Zero Air

Sampling Inlet

UHP He

Capillary Transfer Line

2-Stage Turbo Pump

Electron Impact Ionization

Liquid N₂
HR-EI-MS data

a) mass spectrum (total organic mass)

b) individual ion abundances (elemental ratios)
High-resolution electron impact mass spectrometer

1) Temperature: Volatility
2) EI signal: Total mass
3) Mass spectrum: Composition
4) HR ions: Elemental ratios
Instrument response (n-alkanes)

Desorption Temperature (C)
Calibration (volatility, mass concentration)
Emissions characterization: aircraft

AAFEX II: Alternative Aviation Fuels Experiment II
Dryden Aircraft Operations Facility, Palmdale CA, March-April 2011

DC-8, two turbofan CFM56-2C1 engines (JP-8 and FT fuels)
Measurements: 150 m downwind
Engine power sweep

- Semicontinuous measurements (2 min collection, 10 min desorption/cooling cycle)
- Can detect rapid changes, transients

[Cross et al., Atmos. Chem. Phys., 2013]
Emission factors, I/SVOC contributions

Low powers: I/SVOCs account for 10-20% of organic emissions

High powers: I/SVOCs account for >50% of organic emissions

[Cross et al., Atmos. Chem. Phys., 2013]
Volatile distribution (7% power)

[Cross et al., Atmos. Chem. Phys., 2013]
PMF factors

[Cross et al., Atmos. Chem. Phys., 2013]
PMF factors

[Saturated HC Factor]
H:C = 2.07
O:C = 0.03

[Aromatic HC Factor]
H:C = 1.36
O:C = 0.04

[Oxygenated HC Factor]
H:C = 1.46
O:C = 0.26

[Cross et al., Atmos. Chem. Phys., 2013]
Unsaturated HC factor

[Cross et al., Atmos. Chem. Phys., 2013]
Unsaturated HC factor

[Cross et al., Atmos. Chem. Phys., 2013]
Aromatic HC factor

[Cross et al., Atmos. Chem. Phys., 2013]
Oxygenated HC factor

[Cross et al., *Atmos. Chem. Phys.*, 2013]
Summary: I/SVOCs from aircraft

[1]: Alkanes from unburnt fuel
[2]: Aromatics from unburnt fuel
[3]: Aromatics from pyrolysis
[4]: Oxidized fuel components
[5]: Partially oxidized lubricant(?)

[Cross et al., Atmos. Chem. Phys., 2013]
Trace elements in emitted particles

[Cross et al., *J. Eng. Gas Turbines and Power*, 2012]
Trace elements in emitted particles

Unambiguous identification of trace metals:
- Exact mass
- Isotopic abundances

[Cross et al., J. Eng. Gas Turbines and Power, 2012]
Trace elements in emitted particles

Lubricant components: B, Ca, Mg, P, Zn
Engine-wear markers: Fe, Pb
Others: K, Na, S, Cl

[Cross et al., J. Eng. Gas Turbines and Power, 2012]
Summary/conclusions

- New instrument for measuring amount, volatility, and (ensemble) composition of IVOCs and SVOCs in near-real time

- Aircraft emissions: Emissions, composition (alkane/aromatic/oxygenate), and volatility all strongly power-dependent (fuel → pyrolysis)

- Diesel engine emissions: Emissions of 0.2-20 mg/kg fuel, depending on engine power; analysis of volatility and composition still in progress

- Follow-on work: Comparison of multiple IVOC/SVOC techniques on the same engine (May-June 2014)
## Acknowledgements

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