VOC Instrument Intercomparisons Aboard the NASA DC-8

Morgan Selby[1,2], Victoria Treadaway[1,2], Colby Francoeur[1,2], Nell Schafer[1,2], Jeff Peischl[1,2], Chelsea Stockwell[2], Matthew Coggon[2], Lu Xu[1,2,3], Kelvin Bates[1,2], Georgios Gkatzelis[4], Carsten Warneke[2], and Jessica Gilman[2]

[1]*Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado,* [2]*NOAA Chemical Sciences Laboratory, Boulder, Colorado,* [3]University of Washington St. Louis, St. Louis, MO, [4]Forschungszentrum Jülich, Jülich Germany

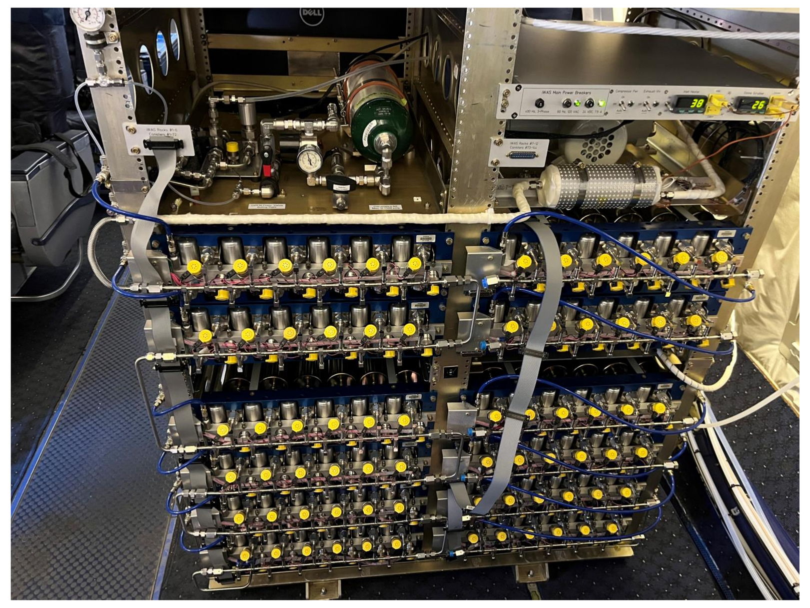
Atmospheric significance of VOCs

Volatile organic compounds (VOCs) are a class of gas-phase molecules in the atmosphere that have a wide range of volatilities, polarities, and reactivities. VOCs are ubiquitous in, and can be emitted directly into, the atmosphere from natural or anthropogenic activities. In polluted urban environments, VOCs can react to produce additional VOCs, ground-level ozone, and secondary organic aerosol (SOA; Glasius and Goldstein., 2016). These reaction products have direct negative health and climate impacts. To meet the observational demands of VOCs, multiple analytical techniques, sensitive to the differing properties of a wide range of VOCs, must be employed.

AEROMMA 2023: Aircraft measurements

During the summer of 2023, **A**tmospheric **E**mission and **R**eaction **O**bserved from **M**egacities to **M**arine **A**reas studied emissions in urban and marine environments. These emissions affect air quality and climate in the United States. The NASA DC-8 was outfitted with a large payload of gas phase and aerosol instruments. The integrated whole air sampling (iWAS) system, with post-flight analysis via GC-MS, was deployed to provide speciated VOC measurements.

Canisters filled during the campaign: 2710
Total duplicate samples: 444
Total cans per city:
New York City 536
Chicago 524
Los Angeles 510
Toronto 240
Salt Lake City 83
Indianapolis 46



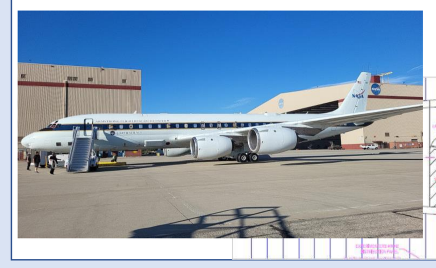


Figure 1: iWAS sampling rack on NASA-DC8 (above), NASA DC-8 (bottom left), and DC-8 floor plan with locations of PTR-MS and iWAS (bottom right)

Description of Instrumentation

- Sampling capability of up to 144 canister per flights
- 1.4 L electropolished stainless steel canisters pressurized to 50 psi during flights
- Programmable sampling interface allows for manual (grab) or automated sampling
- Custom dual column GC-MS analysis
  - Stirling cooler for analyte preconcentration
- Analyze up to 72 canisters in 25 hours
- Sufficient pressure for duplicate samples
- Average replicates agree within 10%
- Characterize over 200 C2 – C10 compounds
  - Hydrocarbons
  - Select halocarbons
  - Oxygenated VOCs
  - Nitriles
- Avg cleaning time of 4.5 hours for 36 canisters
- Average detection limit ≤ 5ppt, higher for oxygenates (Lerner et al. 2017)

Figure 2: GC-MS (left) and analysis rack in field.

Analysis Technique

1Hz data were averaged over the duration of the canister fill (average 5.4 seconds) to perform correlational analysis. 27 compound measured by GC-MS were compared with corresponding measurements from an Aerodyne tunable diode laser (TDL), proton transfer reaction-mass spectrometer (PTR-MS), and ammonium chemical ionization-mass spectrometer (NH_4^+ CIMS). Compounds were analyzed per flight, and for all of AEROMMA. Two sided linear regression (ODR 2) was used for slope and y-intercept values. Single sided linear regression (ODR 1) was used for correlation coefficient (r) values. GC-MS detected isomers are summed to compare with PTR-MS and NH_4^+ CIMS when necessary.

Compounds Analyzed: * PTR-MS ǂ NH_4^+ CIMS ° TDL
Alkanes: Ethane°
Isoprenoids: Isoprene*, Monoterpenes (MTs)*ǂ
Nitrogen and Sulfur: Dimethyl Sulfide (DMS)*
Aromatic: Toluene*, Benzene*, Styrene*, C8 Aromatics*, C9 Aromatics*, PCBTF*
Saturated OVOC: Methanol*, Ethanol*, Acetone*ǂ, Methyl Ethyl Ketone (MEK)ǂ
Unsaturated VOC: Acrolein*ǂ, Methyl Vinyl Ketone (MVK)*ǂ, Methacrolein (MACR)*ǂ

Summed GC-MS isomers for comparison:
MTs = α-pinene, β-pinene, camphene
C8 Aromatics = ethylbenzene, m,p-xylenes, o-xylene
C9 Aromatics = n-propylbenzene, i-propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1-ethyl-2methylbenzene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene
MVK+MACR = MVK, MACR

iWAS/GC-MS compares well for VOCs with different functionalities

iWAS effectively measures VOCs with a wide range of chemical functionalities. The compounds displayed are selectively targeted by other instrumentation, but iWAS/GC-MS analysis is effective for all of these measurements.

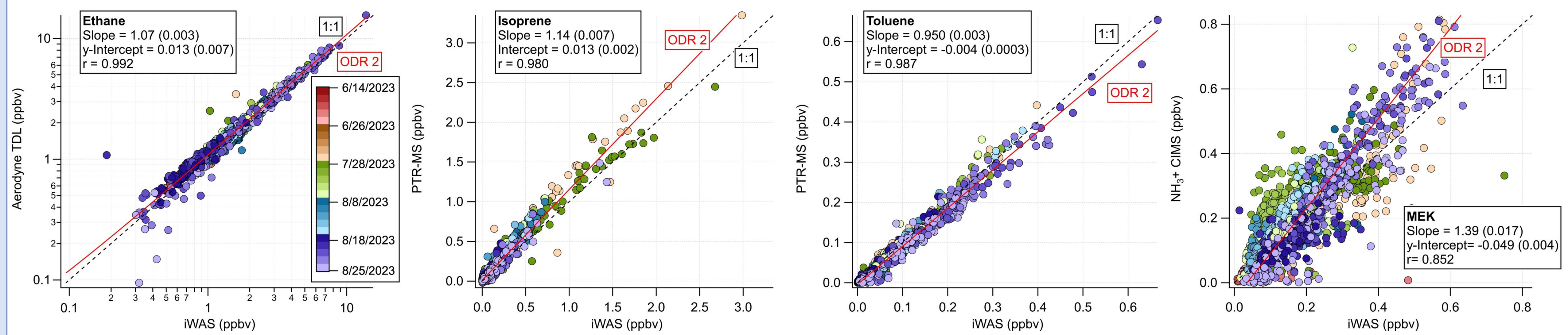


Figure 3: Ethane, Toluene, Isoprene, and MEK comparisons from TDL, PTR-MS, PTR-MS, and NH_3^+ CIMS versus iWAS respectively. NH_3^+ CIMS measures both MEK and butanal but is only compared to MEK measured by iWAS.

iWAS/GC-MS provides isomer resolution

Isomer speciation is important for calculating reactivity budget and spatial and temporal understanding of ion masses detected by CIMSs.

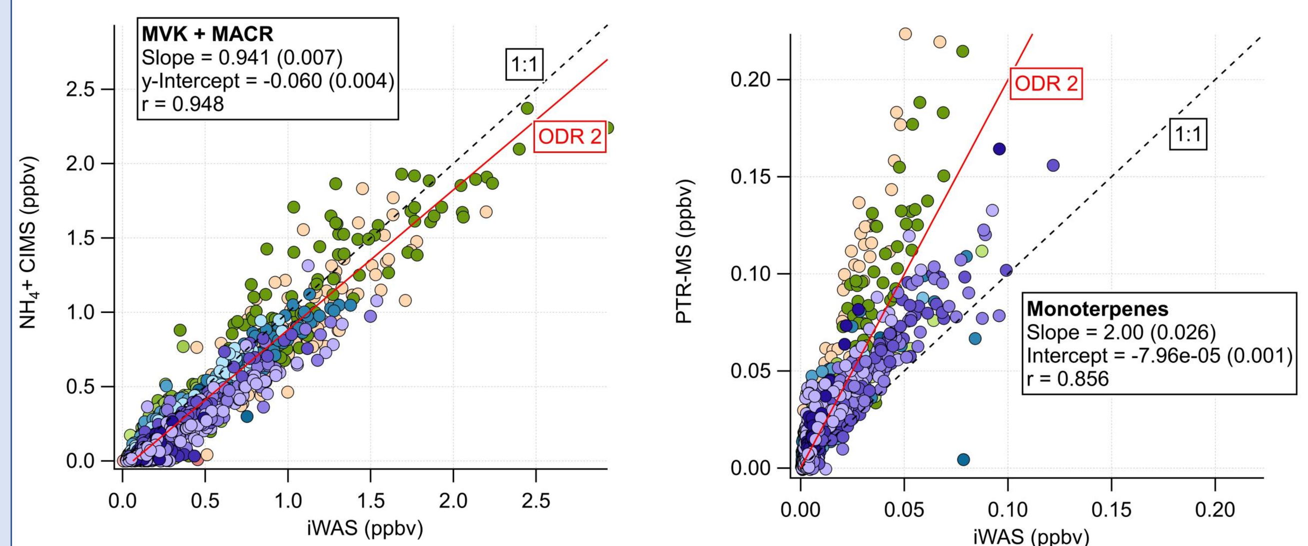


Figure 4: MVK+MACR and monoterpene comparisons for NH_3^+ CIMS and PTR-MS respectively.

iWAS/GC-MS is less consistent with oxygenates that are highly water soluble

CIMS measure light OVOCs better than iWAS. OVOCs that perform poorly on iWAS are not reported in final data.

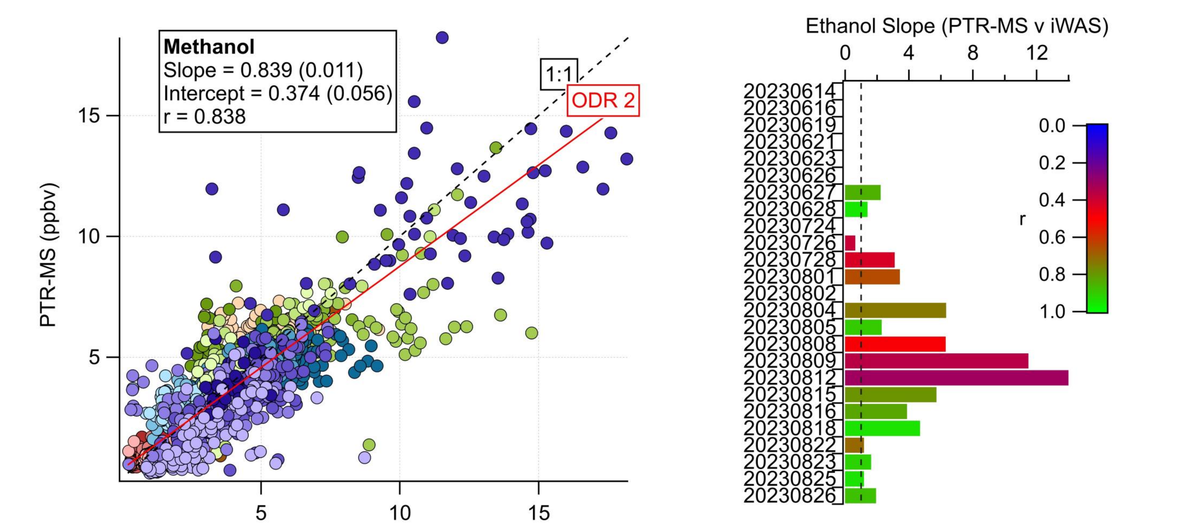


Figure 5: Methanol PTR-MS versus iWAS (left) and category plot of ethanol slope colored by r value per flight for ethanol.

Average slopes and r agree within 33% and 15% of 1

Table 1: Fit statistics for over the course of AEROMMA. ◊ = not reported in iWAS final data. Perfect agreement slope =1 and r = 1

Compound	Instrument	Slope	y-Int	r
Toluene	PTR-MS	0.950 (0.003)	-0.004 (0.0003)	0.987
MVK + MACR	NH4+-LTOF-MS	0.941 (0.007)	-0.059 (0.004)	0.948
Ethane	Aerodyne TDL	1.074 (0.003)	0.013 (0.007)	0.992
MVK + MACR	PTR-MS	0.904 (0.007)	-0.030 (0.004)	0.949
Isoprene	PTR-MS	1.14 (0.006)	0.013 (0.002)	0.980
Styrene	PTR-MS	0.807 (0.009)	-0.001 (0.0001)	0.947
Methanol◊	PTR-MS	0.769 (0.014)	1.08 (0.067)	0.688
Acetone + Propanal◊	NH4+-LTOF-MS	0.666 (0.009)	0.319 (0.036)	0.838
Acetone + Propanal◊	PTR-MS	0.662 (0.008)	0.180 (0.033)	0.845
Butanal + MEK	NH4+-LTOF-MS	1.39 (0.017)	-0.049 (0.004)	0.852
Benzene	PTR-MS	0.596 (0.007)	-0.011 (0.001)	0.860
Ethanol◊	PTR-MS	1.40 (0.015)	0.569 (0.029)	0.891
C8 Aromatics	PTR-MS	0.486 (0.002)	0.0004 (0.0002)	0.979
Acrolein◊	PTR-MS	0.482 (0.013)	0.023 (0.002)	0.523
Acrolein◊	NH4+-LTOF-MS	0.479 (0.012)	0.007 (0.002)	0.587
PCBTF	PTR-MS	1.63 (0.006)	-0.002 (0.0001)	0.987
C9 Aromatics	PTR-MS	0.359 (0.004)	0.002 (0.0002)	0.911
Monoterpenes	PTR-MS	1.99 (0.026)	-0.0001 (0.0005)	0.856
Monoterpenes	NH4+-LTOF-MS	2.32 (0.042)	-0.006 (0.001)	0.768
DMS	PTR-MS	7.50 (0.231)	-0.025 (0.002)	0.708

Issues: DMS (DL issue), OVOCs marked with ◊ (not reported), benzene (PTR-MS interference), heavy aromatics (sensitivity issue), and MTs (potential interference).

Acknowledgements

- AEROMMA team
- NASA DC-8 flight crew

References

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Contact Information:

Email: Morgan.Selby@noaa.gov