Organic Aerosol Components VAP for Aerosol Mass Spectrometers

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OA Components VAP

- **Goal**: To represent the enormously complex atmospheric OA system as lumped descriptions of a limited number of components that may be related to distinct sources, physicochemical properties, and atmospheric processes.
- **Methodology** : Multivariate statistical analysis of DOE ACRF and IOP aerosol mass spectrometer data.
- **Assumption:** An AMS organic aerosol data matrix is comprised of the linear combination of OA components with constant profiles that have varying contributions across the dataset.

Aerosol Mass Spectrometer (AMS) Systems

ACSM (mini-AMS)

Long term measurements (3 systems) –

Tropical Western Pacific in Darwin, Australia
The Southern Great Plains, Oklahoma
ACRF MAOS mobile facility

Q-AMS
c-ToF-AMS
HR-ToF-AMS

Intensive, focused studies (IOP)

- CARES: 3 HR-ToF-AMS (T0, T1, G1)
- BNL-IOP
- GVEX: at least 3
- ASP previous G1 studies: NEAQS (2002), MASE (2005), MAX-Mex (2006), MAX-Tex (2006), CHAPS (2007), and VOCALS (2008)

AMS Data

High time resolution

ACSM

(mini-AMS)

15 - 30 min.

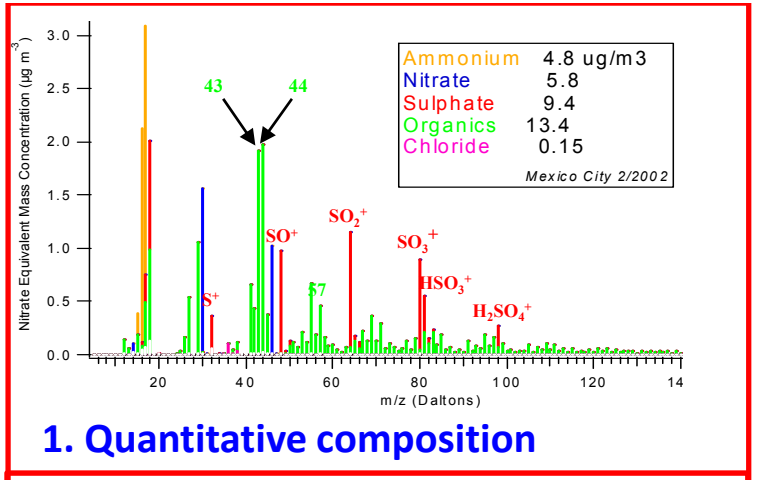
Q-AMS

c-ToF-AMS

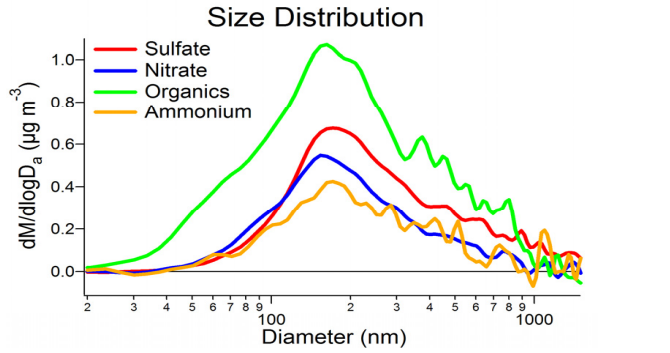
HR-ToF-AMS

2-5 min. (ground)

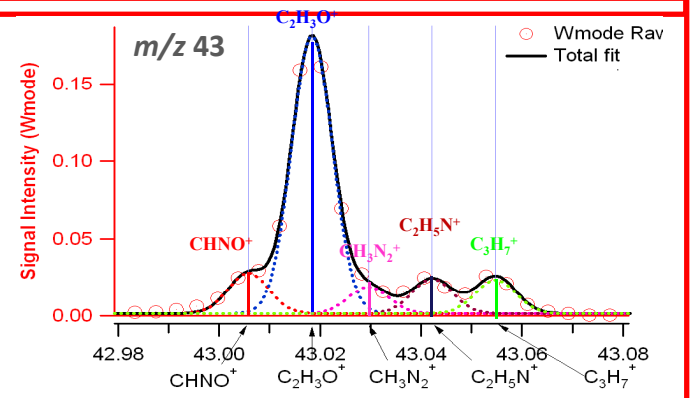
5-30 s (airborne)



1. Quantitative composition



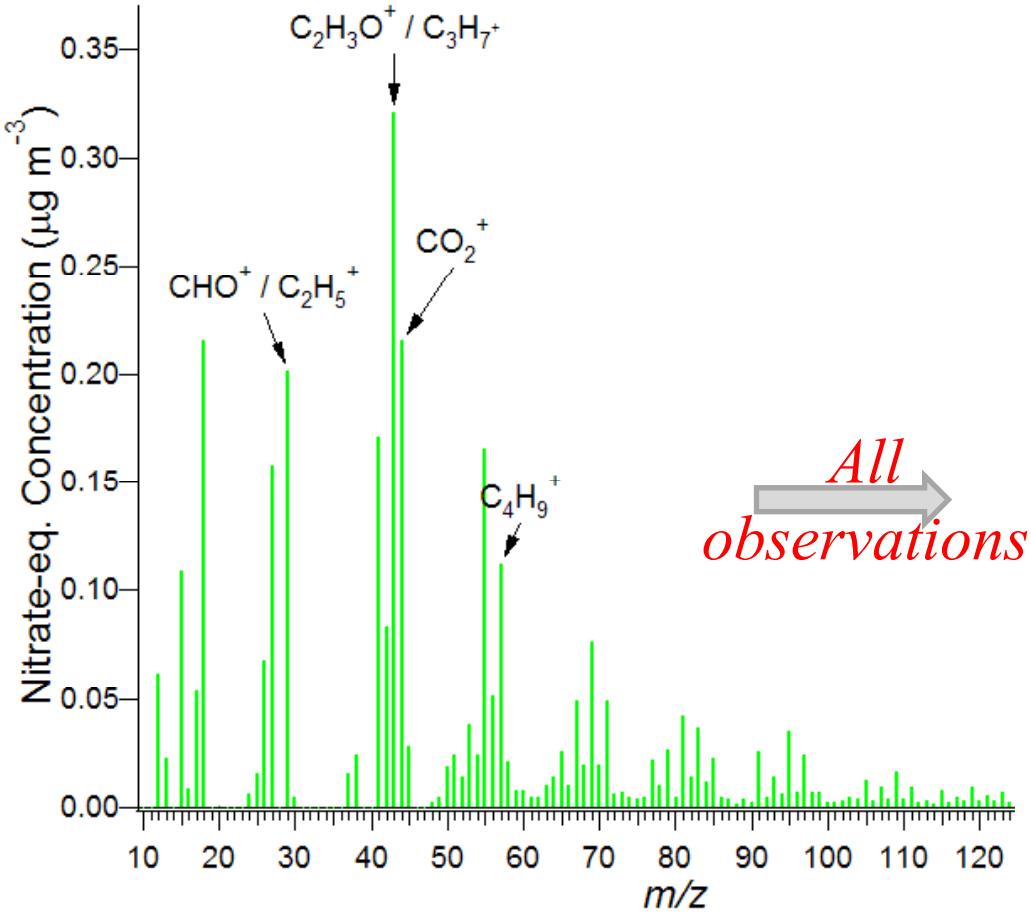
2. Size-resolved composition



3. Elemental comp. ($C_nH_mN_pO_zS_w$)

AMS Organic Mass Spectrum

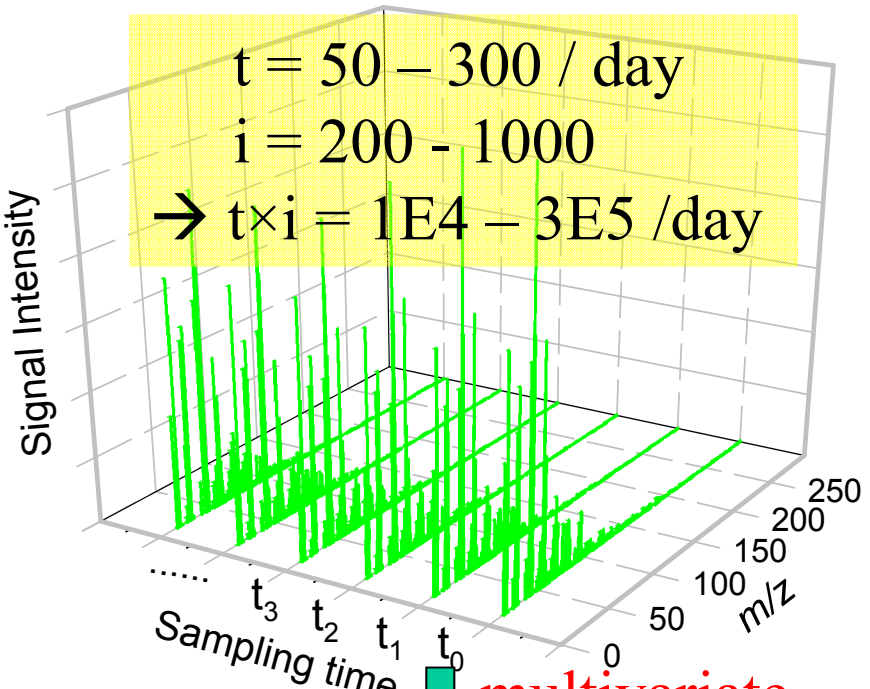
$$\overrightarrow{ms}_{measured} = c_a \cdot \overrightarrow{ms}_a + c_b \cdot \overrightarrow{ms}_b + c_c \cdot \overrightarrow{ms}_c + \ldots$$



All observations

$ORG_{t \times i}$

t = 50 – 300 / day
i = 200 - 1000
→ t×i = 1E4 – 3E5 /day



multivariate analysis

OA_1, OA_2, OA_3, …

Multivariate analysis methods:

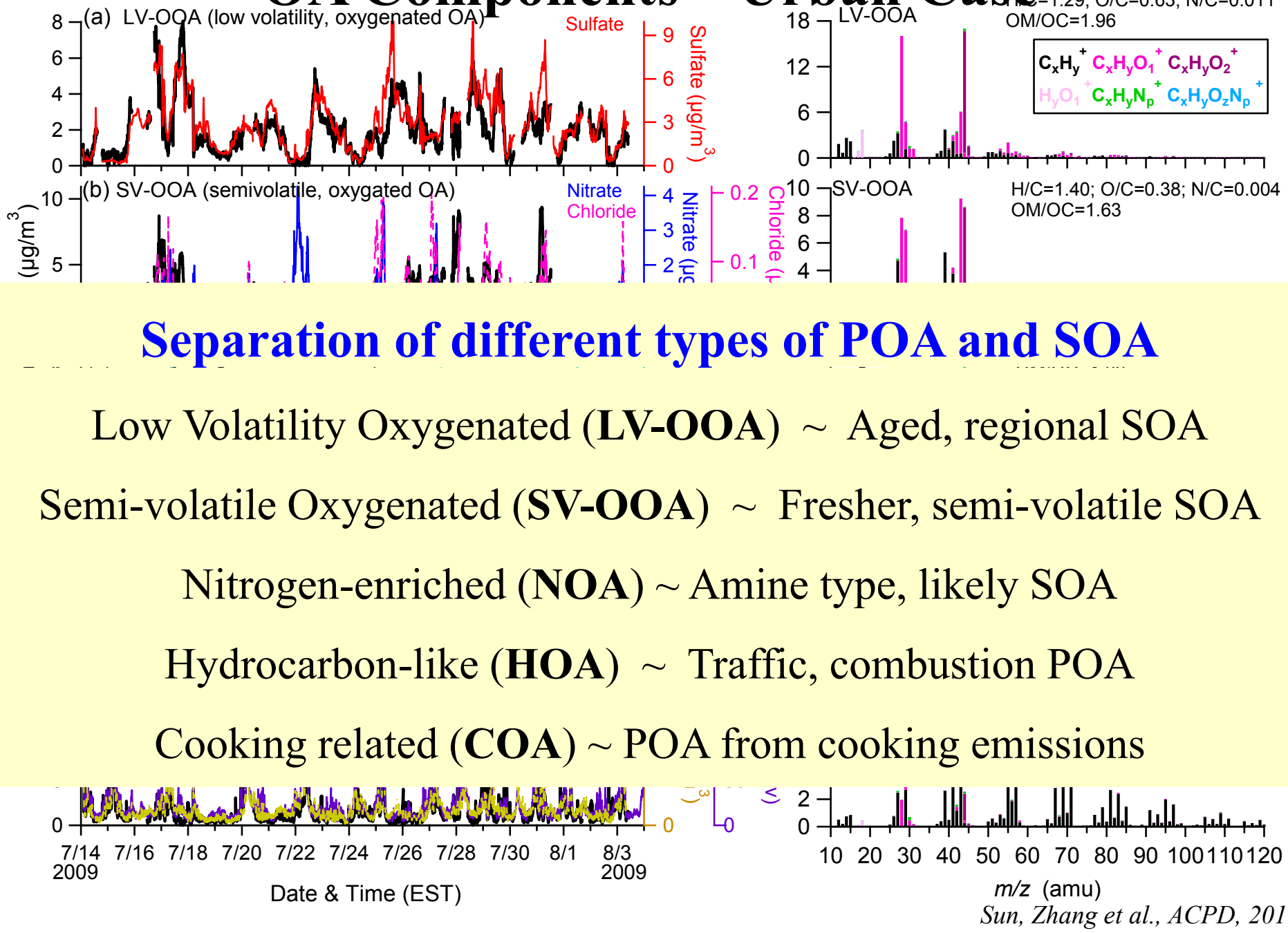
- Positive Matrix Factorization (PMF)
- Tracer-based linear decomposition
- Spectra-based linear decomposition (chemical mass balance-style)

Literature (*applications to AMS data*):

- Zhang, Q. et al. (2005), Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, *ES&T, 39(13), 4938-4952*
- Ulbrich, I., M. et al. (2009), Interpretation of Organic Components from Positive Matrix Factorization of Aerosol Mass Spectrometric Data, *Atmos. Chem. Phys.*, *9*, 2891-2918**.**
- Ng, N. L. et al. (2010), Development of Real-Time Methods for the Estimation of Organic Components for Aerosol Mass Spectrometer Data, *ES&T (submitted).*

Modelers are using the OA component data derived from AMS field data.

OA Components – Urban Case



Separation of different types of POA and SOA

Low Volatility Oxygenated (**LV-OOA**) ~ Aged, regional SOA

Semi-volatile Oxygenated (**SV-OOA**) ~ Fresher, semi-volatile SOA

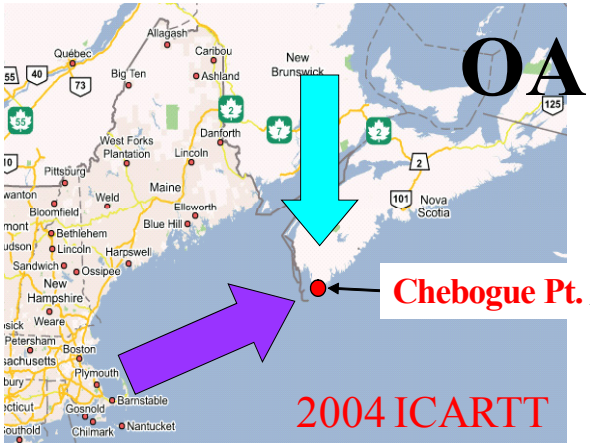
Nitrogen-enriched (**NOA**) ~ Amine type, likely SOA

Hydrocarbon-like (**HOA**) ~ Traffic, combustion POA

Cooking related (**COA**) ~ POA from cooking emissions

Sun, Zhang et al., ACPD, 2010

OA Components – Rural / Remote Case



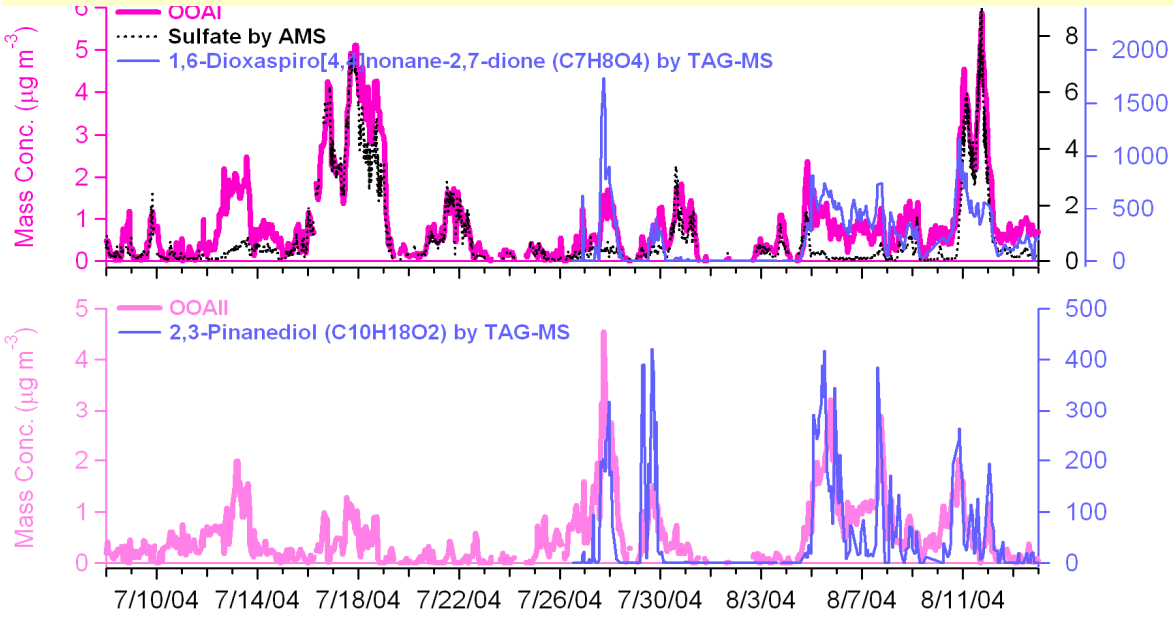
biogenically influenced

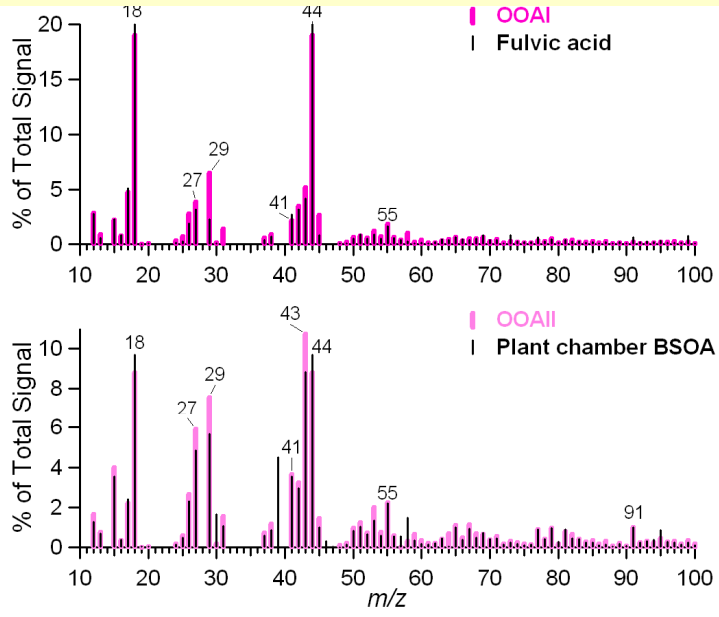
anthropogenically influenced.

Zhang et al., in prep.

Separation of biogenic and anthropogenic SOA

CARES may be a good study case





What Do We Get?

Products:

- Time series of OA comp. conc. (OA_i; $\Sigma OA_i \approx$ *OA mass)*
  ACSM: 15 - 30 min.
  ToF-AMS: 2-5 min (surface), 15-30 s (airborne)
- Mass spectra of OA comp. → distinct chemical properties, e.g., O/C, N/C, H/C, OM/OC
- Typical OA comp.: HOA, OOA (SV-, LV-), BBOA, COA, NOA...

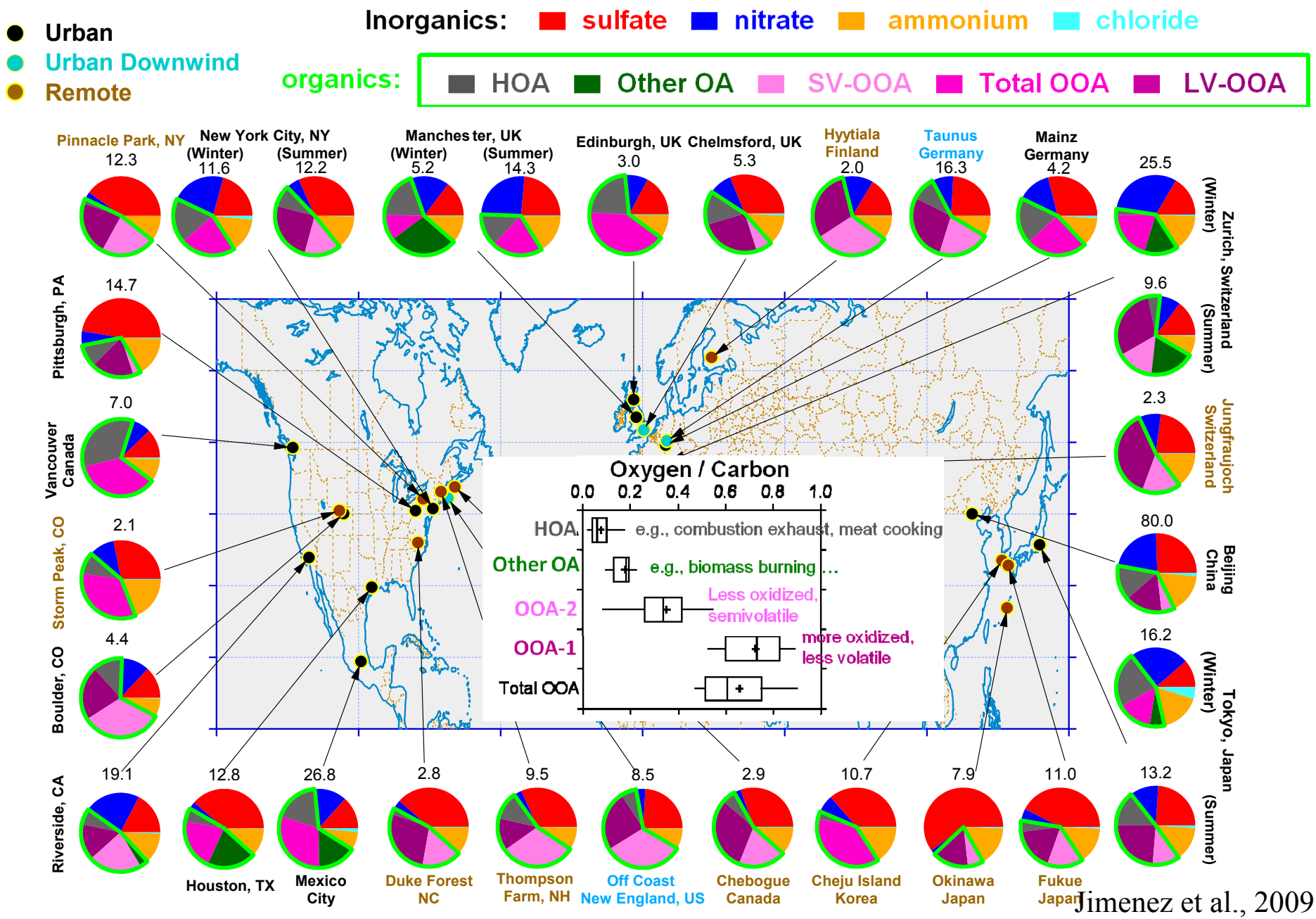
Accuracy:

- Propagated uncertainty for AMS data: < 30%, mainly due to the collection efficiency (CE) correction.
- Uncertainties in OA components:
  Can be evaluated: e.g., running the PMF algorithm from different random starting points; bootstrapping analysis (Ulbrich et al., 2009, ACP).

Applications of the OA Component VAP

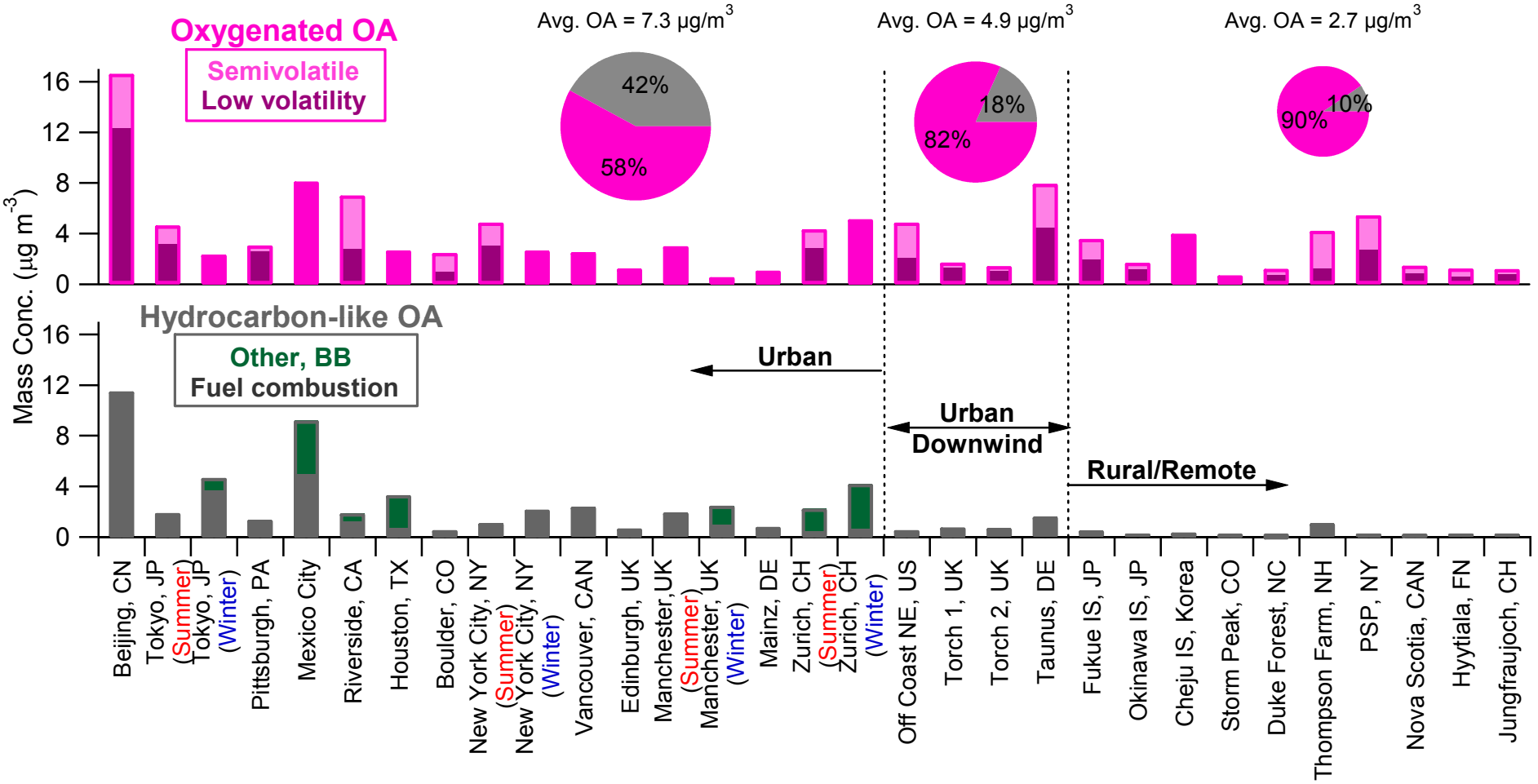
- Addressing the lifecycle processes of atmospheric OA.
  - Temporal variations
  - Correlations with tracer compounds
  - *size distributions…, integrated analysis*
- Addressing the radiative properties of OA.
  - Surrogates (e.g., O/C) for hygroscopicity and/or volatility.
  - Correlations and intercomparison with aerosol optical and radiative measurements.
- Validation and evaluations of models
- Model development

Global Distribution of SOA and POA



Jimenez et al., 2009

Global Distribution of SOA and POA



- **OOA** (largely SOA) dominance, **OOA** % increase with distance from urban
- **HOA** (largely urban POA) less significant at rural/remote, due to dilution

Zhang et al., 2009

Factor Analysis of AMS Organic Mass Spectra

$$\overrightarrow{ms}_{measured} = c_a \cdot \overrightarrow{ms}_a + c_b \cdot \overrightarrow{ms}_b + c_c \cdot \overrightarrow{ms}_c + \ldots$$

$ORG_{t \times i}$