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Bad Zurzach, 11-14th April 2016

Wir schaffen Wissen – heute für morgen

Sources of organic aerosols during extreme haze events in China:

PMF optimization and validation

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New insights into $PM_{2.5}$ chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry

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Experimental

Period	Start	End
Xi'an	13.12.2013	06.01.2014
Beijing	10.01.2014	26.01.2014

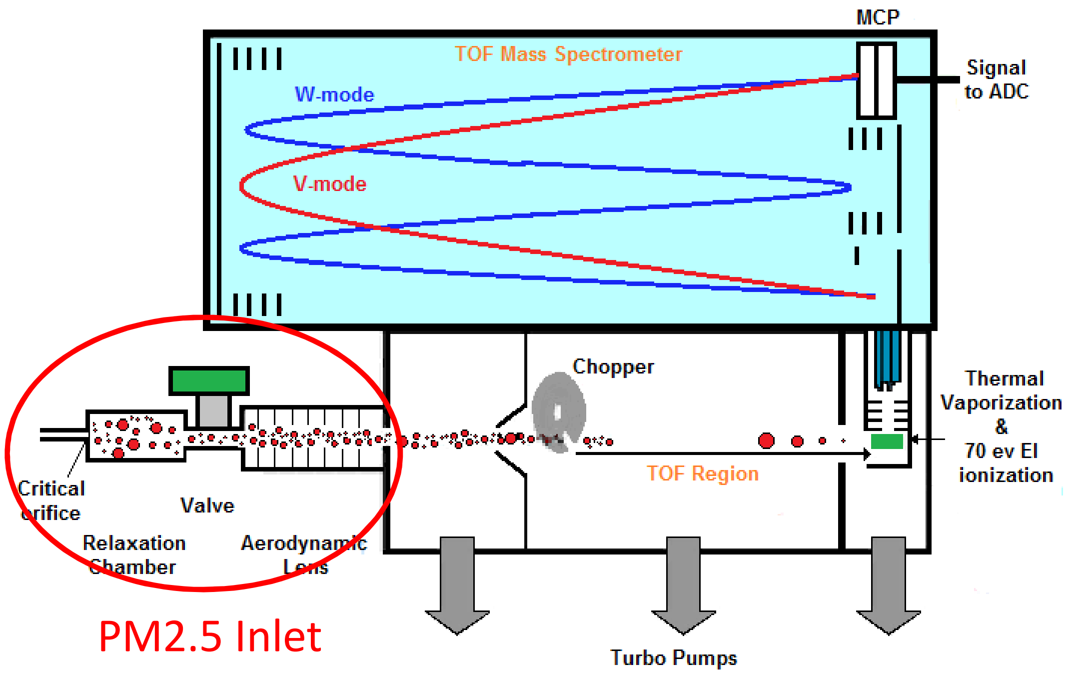
Instrumentation
HR-ToF-AMS
Aethalometer (7-λ)

Others:

RDI, ACSM, ATOF-MS, Nephelometer, Lidar, SMPS, SP2, HONO, NH_3, SO_2, NOx, O_3, CO_2, Meteo parameters…
8 High-Vol & 10 Mini-Vol samplers

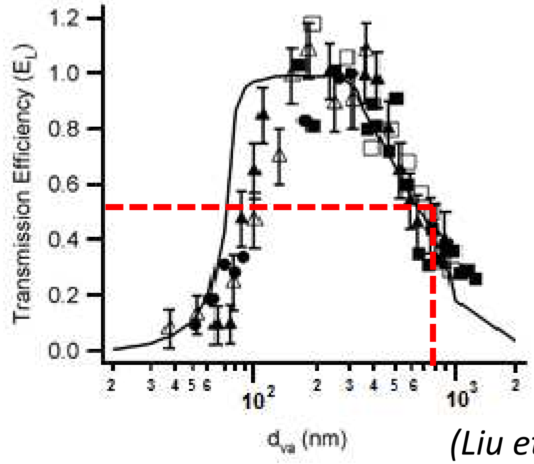
Experimental

HR-ToF AMS



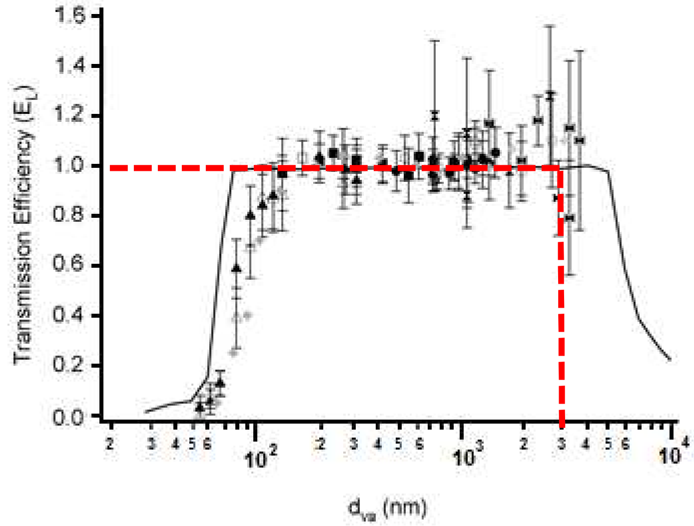
PM2.5 Inlet

PM1 inlet



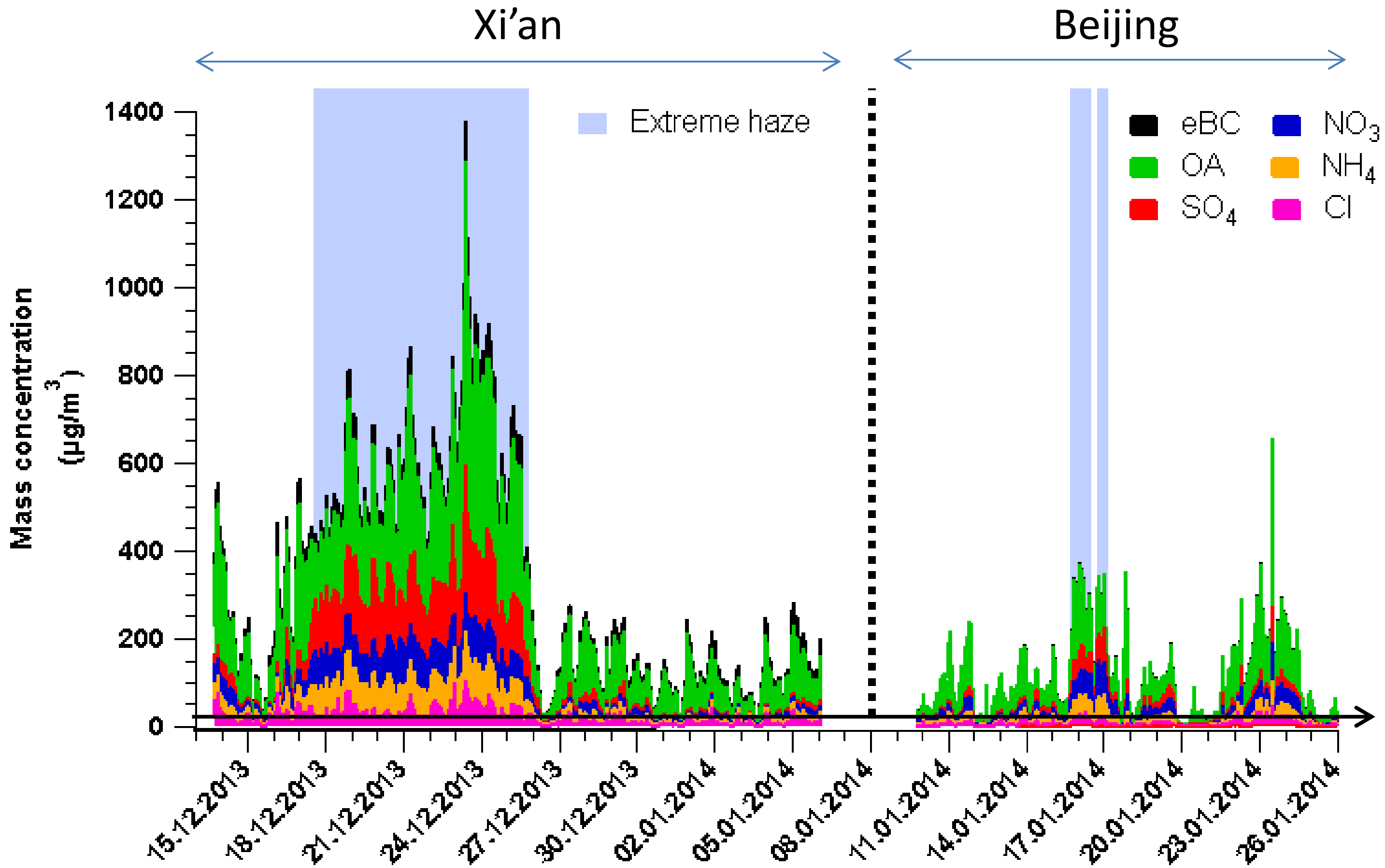
(Liu et al., 2007)

PM2.5 inlet



(Williams et al., 2013)

Bulk PM2.5 chemical composition



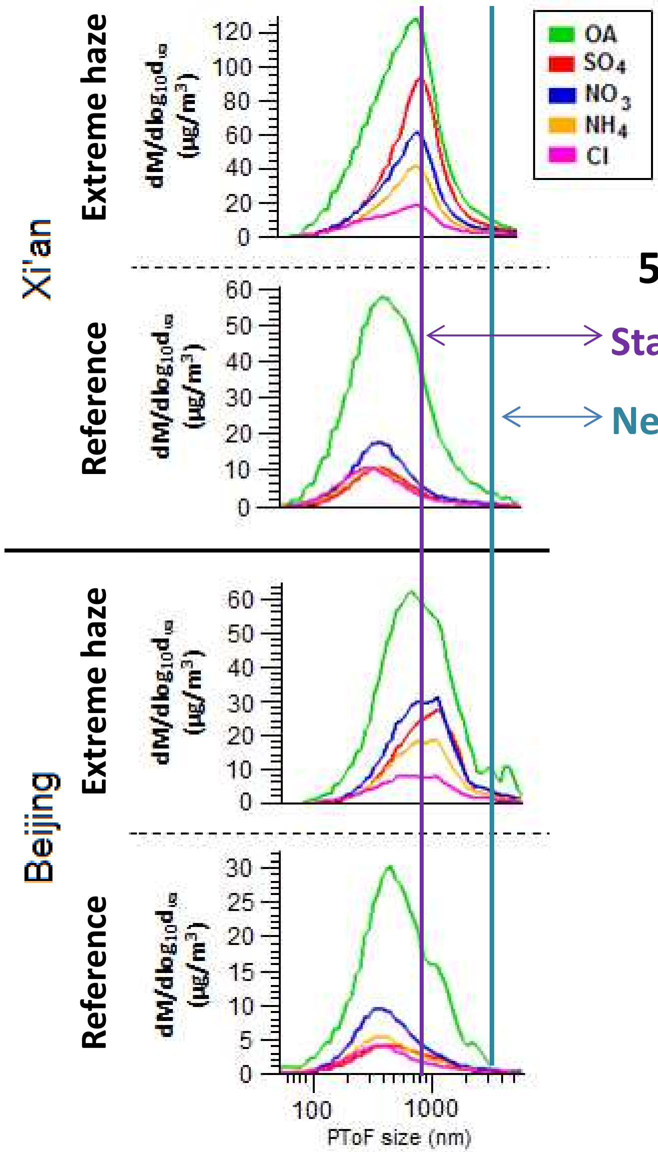
Extreme haze*
Visibility < 2km

WHO limit for PM2.5:
25 µg/m³ *(24-h mean)*

	Xi'an		Beijing	
	Extreme haze	**Reference**	**Extreme haze**	**Reference**
Mean PM2.5	**538.5 µg/m³**	**139.5 µg/m³**	**246.2 µg/m³**	**76.6 µg/m³**
	~22xWHO	**~6xWHO**	**~10xWHO**	**~3xWHO**

* *Zhang et al., 2015*

Bulk PM2.5 chemical composition

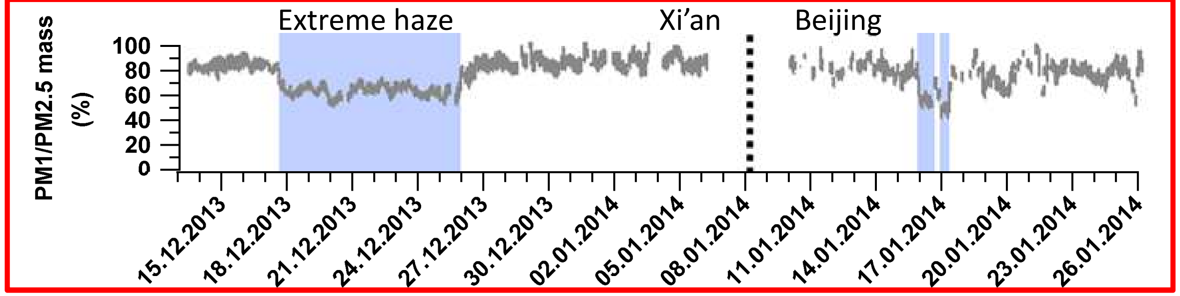


50% cut-off diameter (d_{va}):

Standard PM_1 inlet *(Liu et al., 2007)*

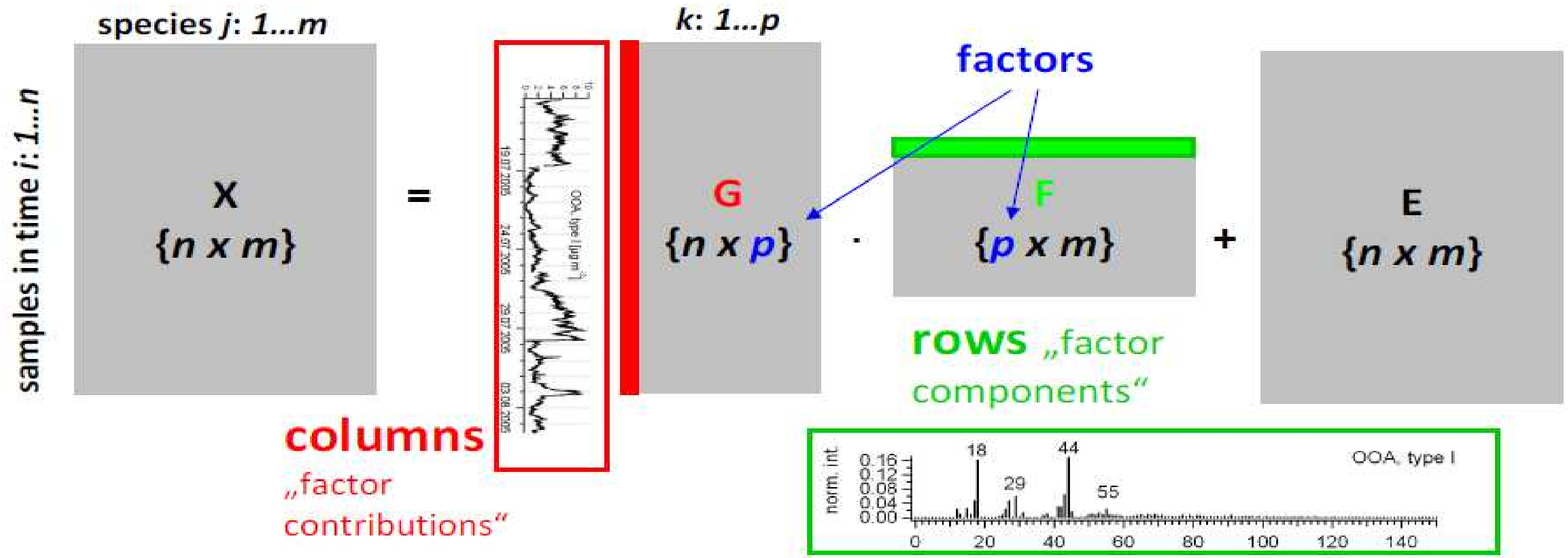
New $PM_{2.5}$ inlet *(Williams et al., 2013)*

Up to 50% of mass lost with PM1 lens during extreme haze events



OA source apportionment

Positive Matrix Factorization (PMF; *Paatero and Tapper, 1994*)



Iterative algorithm that aims to the minimization of:

$$Q = \sum_{i=1}^{m}\sum_{j=1}^{n}\left(\frac{e_{ij}}{\sigma_{ij}}\right)^2$$

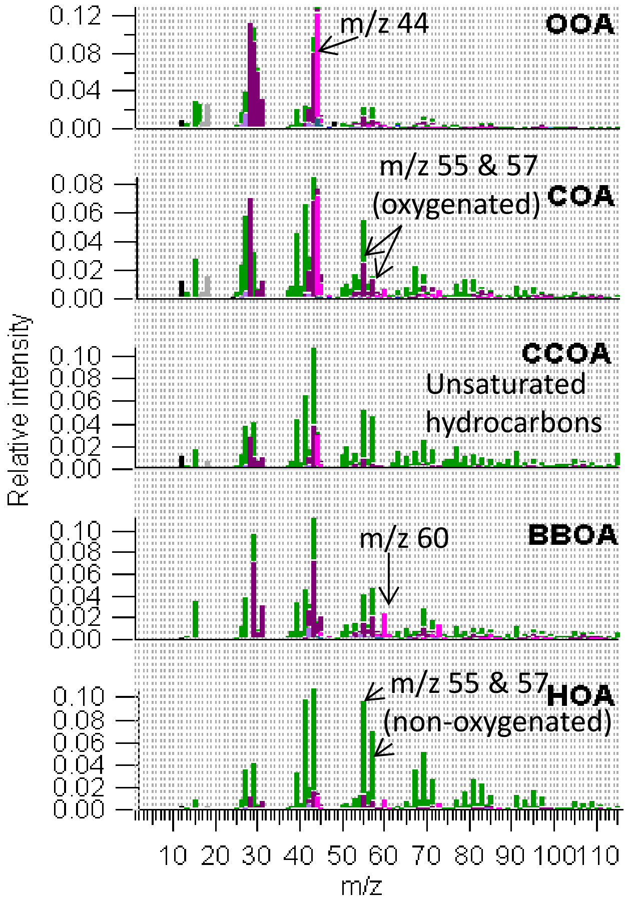
Multilinear Engine (ME-2; *Canonaco et al., 2013*)

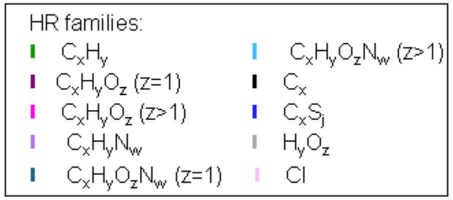
Constrain f_j (or g_j) with a-value approach:

$$f_{j,sol} = f_j \pm af_j$$

PMF results

5 FACTORS SOLUTION
(unconstrained run)





Mixing between sources?

- **HOA & BBOA:**
  High m/z 60 in HOA (also in 25 factors solution)
  → Constrain HOA Paris winter *(Crippa., 2013)*

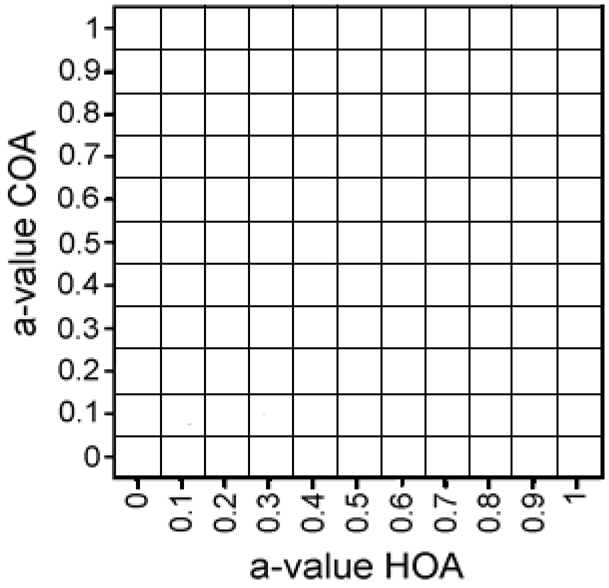
- **COA & OOA:**
  High m/z 44 in COA
  Diurnal COA disturbed if fixing HOA

TO GET A GOOD SEPARATION OF THE PRIMARY SOURCES WE NEED TO CONSTRAIN HOA & COA

Step 1- Run all possible a-value combinations:

This work: a-value: 0 to 1 with steps of 0.1

Step 1:



ME-2 results: Optimization of a-values

Step 1- Run all possible a-value combinations:

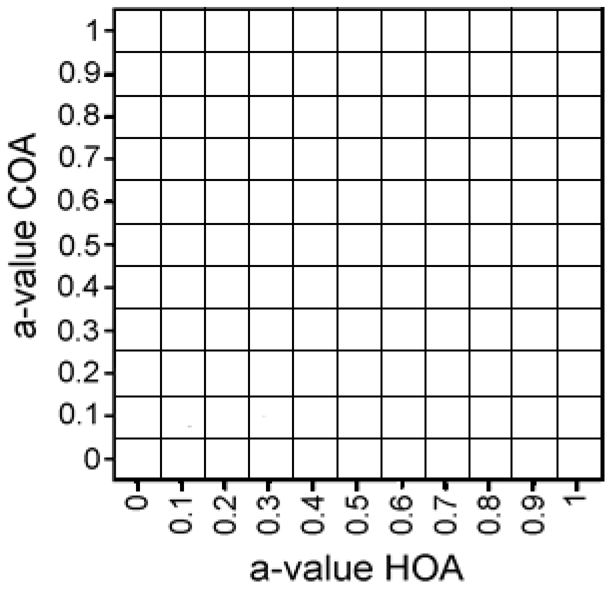
This work: a-value: 0 to 1 with steps of 0.1

Step 2- Establish criteria to chose best solutions:

This work:

1) Minimization of m/z 60 in HOA
2) Optimization of COA diurnals
3) Factor-tracer correlations (primary sources):
   - BC_{tr} *vs* HOA
   - BC_{wb} *vs* BBOA
   - PAH_{fitted} = a*BBOA + b*CCOA + c*HOA *vs* PAH[(1)]

Step 1:



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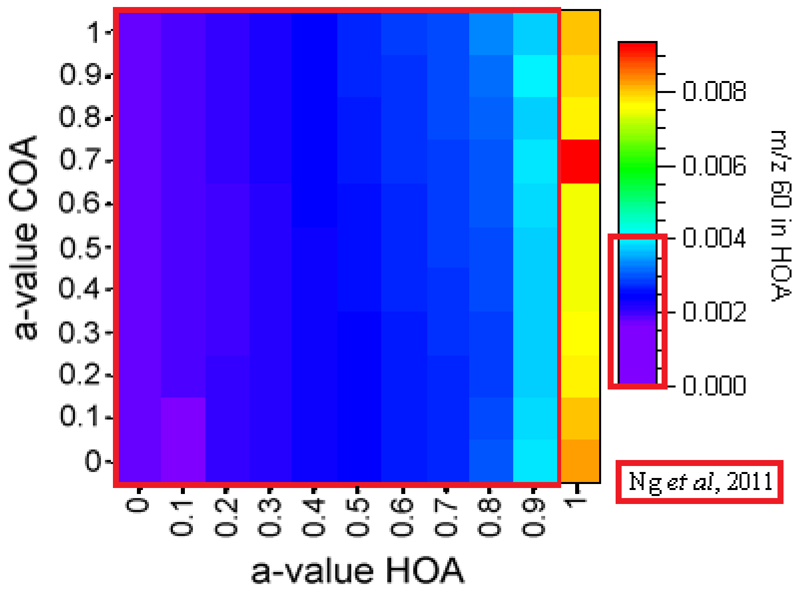
Step 2 (1):



(1) PAH from HR-AMS data, method by Bruns *et al.* (2015)

ME-2 results: Optimization of a-values

Step 1- Run all possible a-value combinations:

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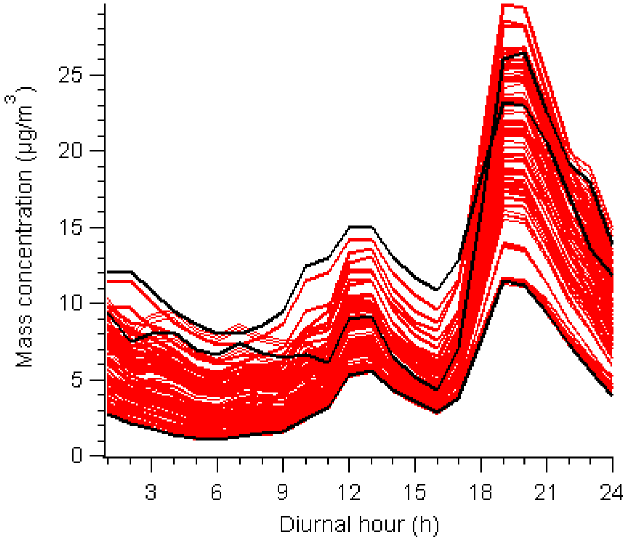
- PAH_{fitted} = a*BBOA + b*CCOA + c*HOA *vs* PAH(1)

Step 2 (2):



Accepted limits?

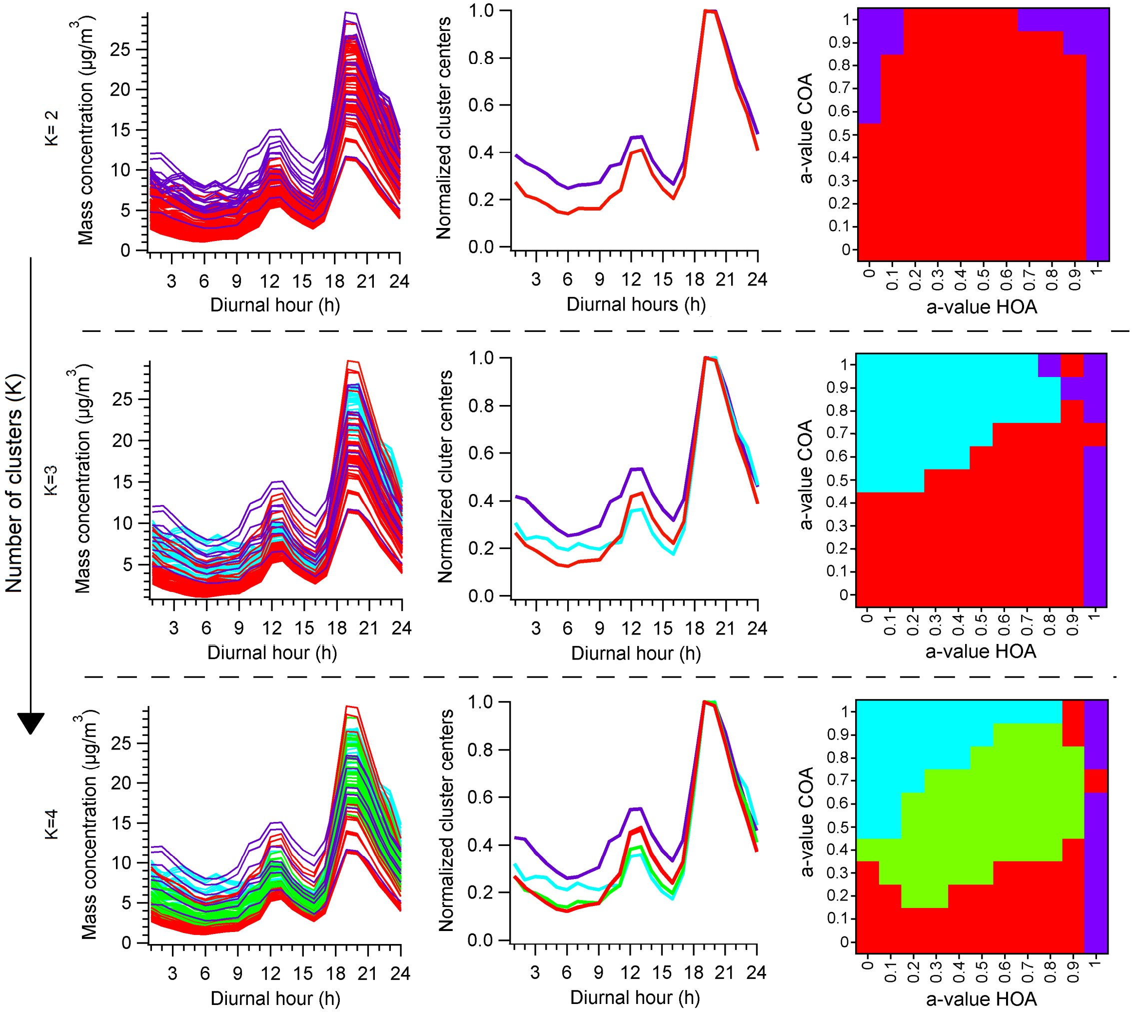
↓

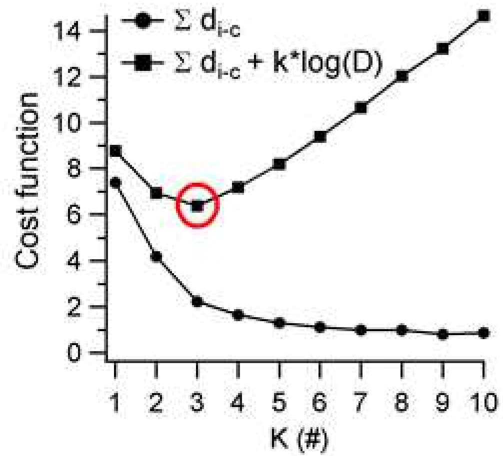
Cluster analysis

(1) PAH from HR-AMS data, method by Bruns *et al.* (2015)

ME-2 results: Optimization of a-values

2) Optimization of COA diurnals: cluster analysis (k-means algorithm)





m/z 44 in COA spectra:

literature[1]: 0.013 ± 0.004 %

red cluster: 0.013 ± 0.002 %

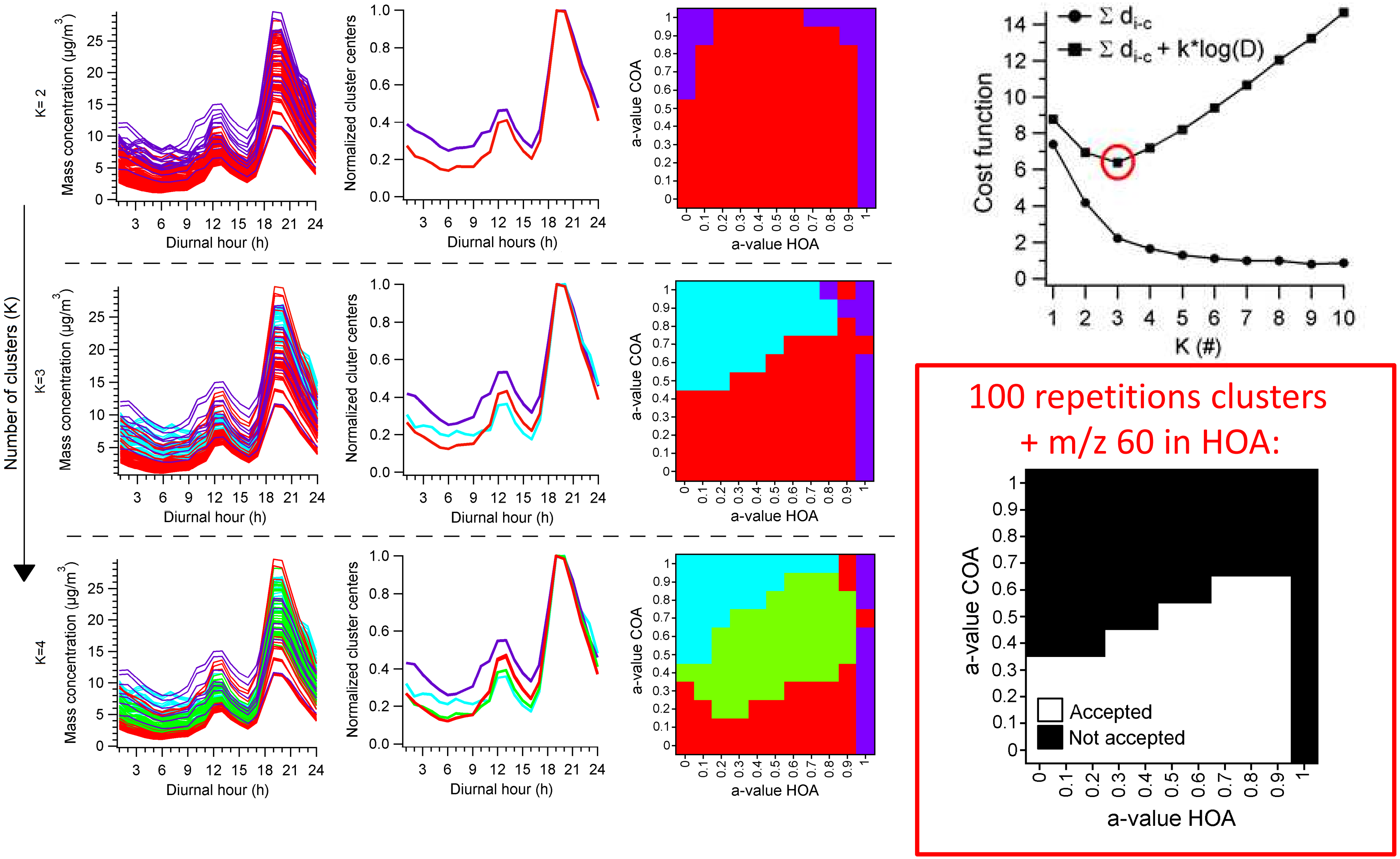
blue cluster: 0.026 ± 0.008 %

purple cluster: 0.025 ± 0.019 %

(1) He et al. (2010), Crippa et al. (2013) and Wolf (2014)

ME-2 results: Optimization of a-values

2) Optimization of COA diurnals: cluster analysis (k-means algorithm)



ME-2 results: Optimization of a-values

Step 1- Run all possible a-value combinations:

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This work:

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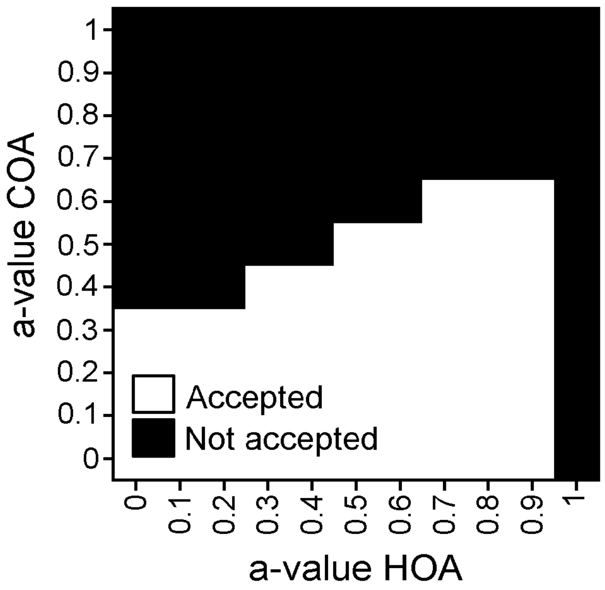


Step 3- Consider average of all good solutions to get an estimation of your errors.

(1) PAH from HR-AMS data, method by Bruns *et al.* (2015)

ME-2 results: Optimization of a-values

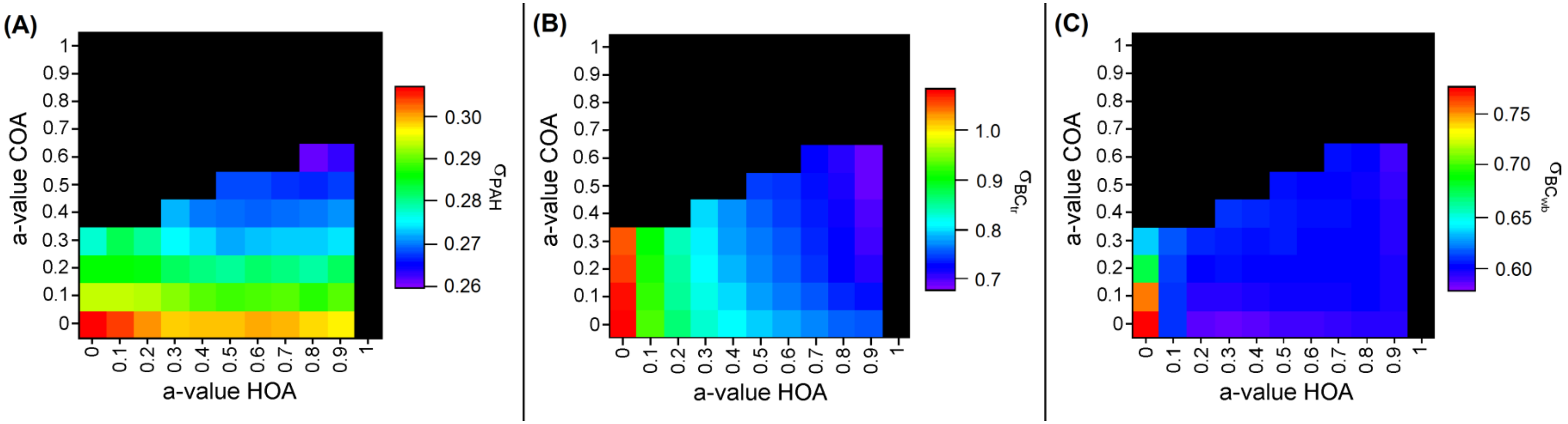
3) Factor-tracer correlations (primary sources):

(A) $PAH_{fitted}(t) = a*BBOA(t)+b*CCOA(t)+c*HOA(t)$

(B) $BC_{tr\ fitted}(t) = (BC_{tr}/HOA)_{av}*HOA(t)$

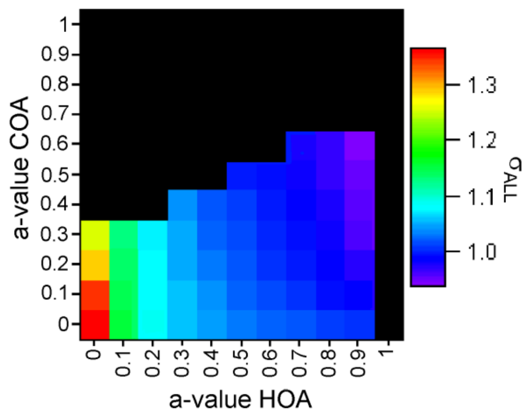
(C) $BC_{wb\ fitted}(t) = (BC_{wb}/BBOA)_{av}*BBOA(t)$

$\rightarrow S_{ext} = \frac{\text{Measured-Fitted}}{\text{Measured}} \rightarrow$ Minimize the error (σ_{fext})



Combine all errors:

$$\sigma_{ALL} = \sqrt{(\sigma_{PAH})^2 + (\sigma_{BC_{tr}})^2 + (\sigma_{BC_{wb}})^2}$$



ME-2 results: Optimization of a-values

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This work: a-value: 0 to 1 with steps of 0.1

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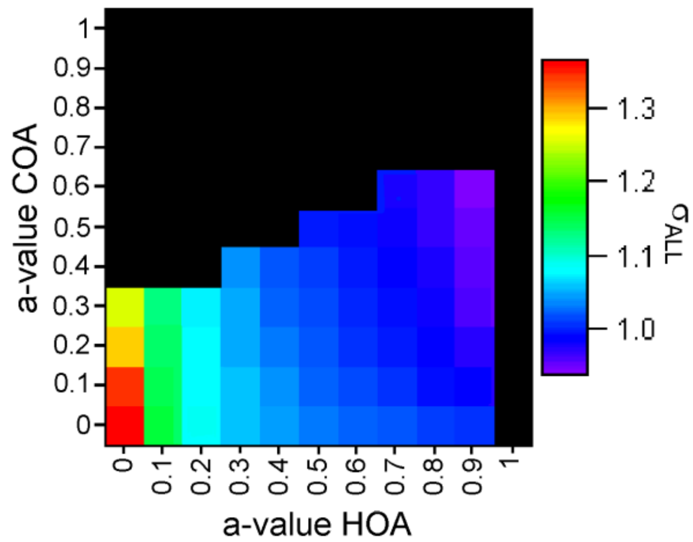
- PAH_{fitted} = a*BBOA + b*CCOA + c*HOA *vs* PAH[1]

Step 2 (3):



Step 3- Consider average of all good solutions

(1) PAH from HR-AMS data, method by Bruns *et al.* (2015)

ME-2 results: Optimization of a-values

Step 3- Consider average of all good solutions

- Best solution: σ_{ALL} min → a-value HOA = 0.9 & a-value COA = 0.6

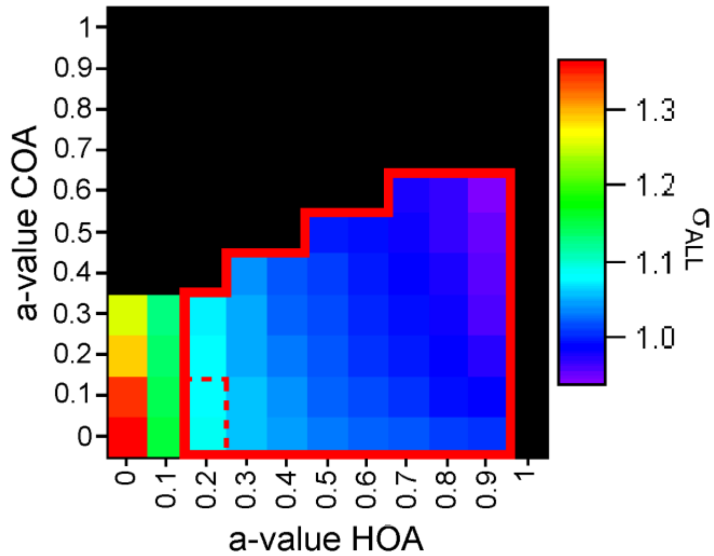
- Modify OA input matrix within it's errors and see variability of solution:

50 ME-2 runs [1] with:

$$\mathbf{OA_{mod}(i,j) = OA_0(i,j) \pm 2OA_{error}(i,j)}$$

⇩

Final accepted a-value combinations

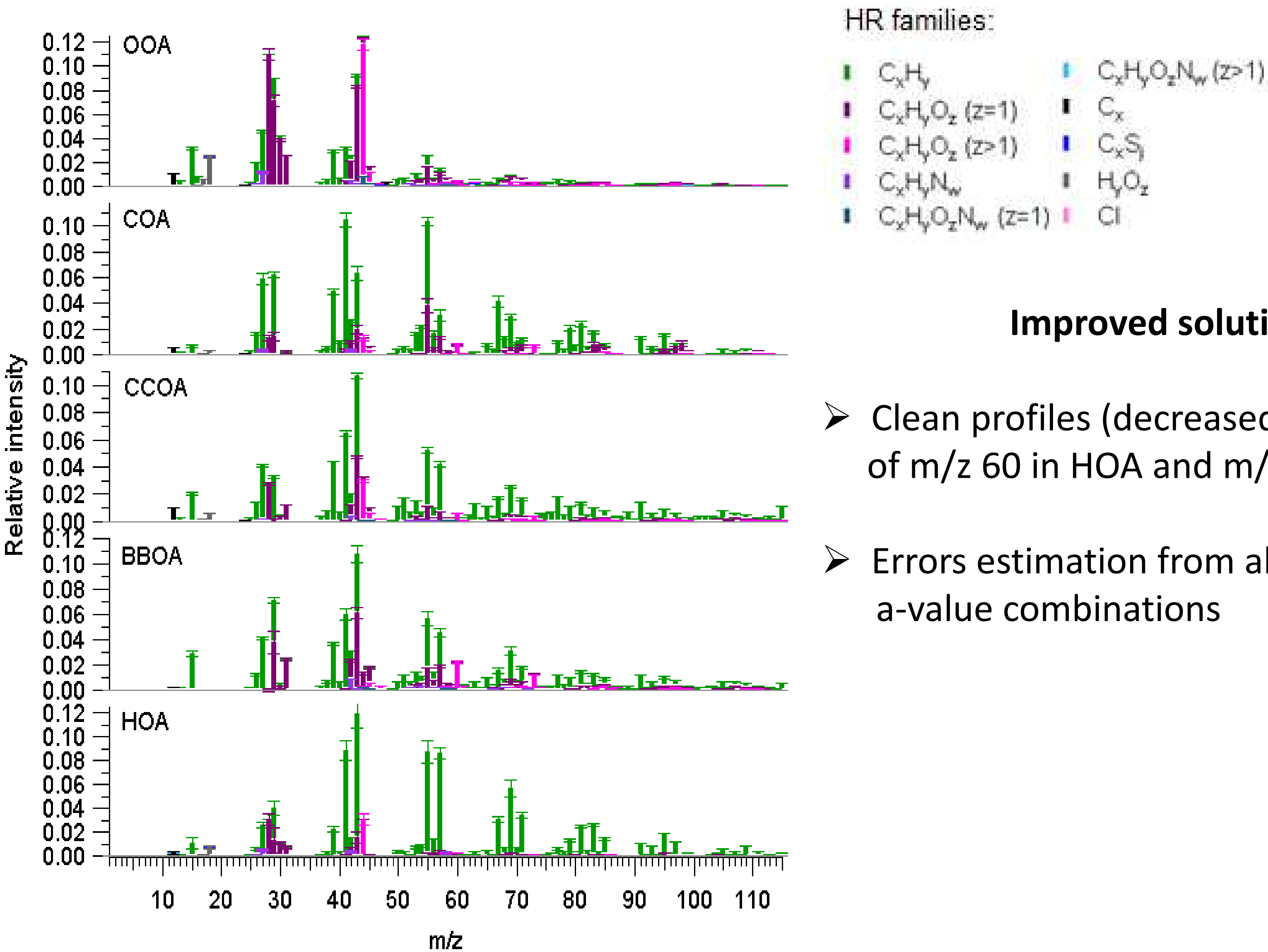


- As sensitivity check:

10 ME-2 runs [1] with $\mathbf{OA_{mod}(i,j) = OA_0(i,j) \pm 1OA_{error}(i,j)}$

[1] Using a-value of 0.9 for HOA and 0.6 for COA

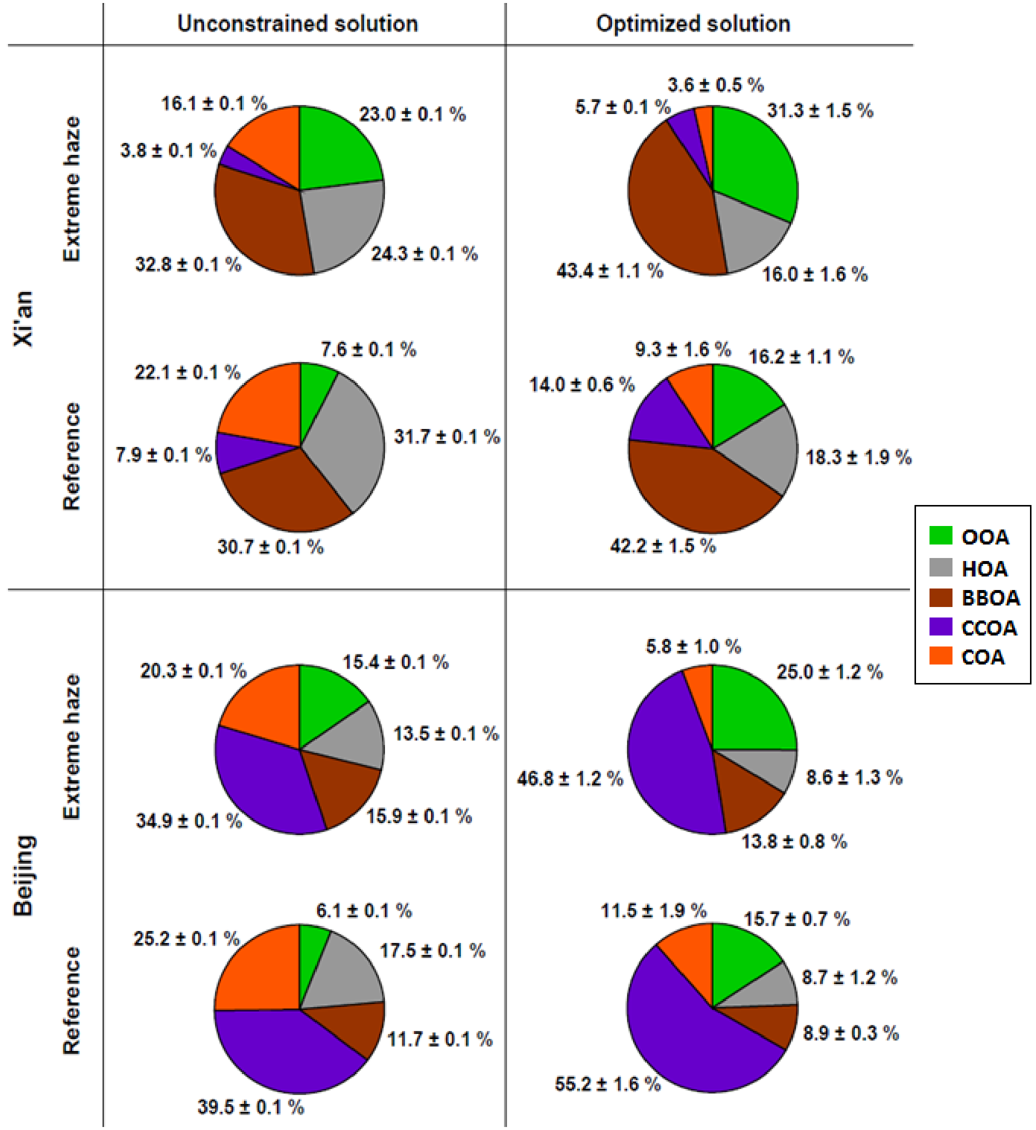
OA source apportionment results



Improved solution:

- Clean profiles (decreased contributions of m/z 60 in HOA and m/z 44 in COA)
- Errors estimation from all accepted a-value combinations

Unconstrained .vs. optimized solution



Conclusions

1) Importance of optimization of source apportionment

2) Importance of measuring PM2.5 fraction (specially during haze)

3) Characteristics of the haze events

- Increase of SOA (OOA) and inorganic ions (mostly SO_4& NO_3)
- Growth of particles towards higher sizes (~ 400 nm → 800 nm)
- Heterogeneous oxidation of SO_2 favored at high RH (e.g. during haze)

4) PM2.5 sources in Xi'an and Beijing

- PM2.5 dominated by emissions from:
  - BBOA in Xi'an
  - CCOA in Beijing

- High PAH from major combustion sources

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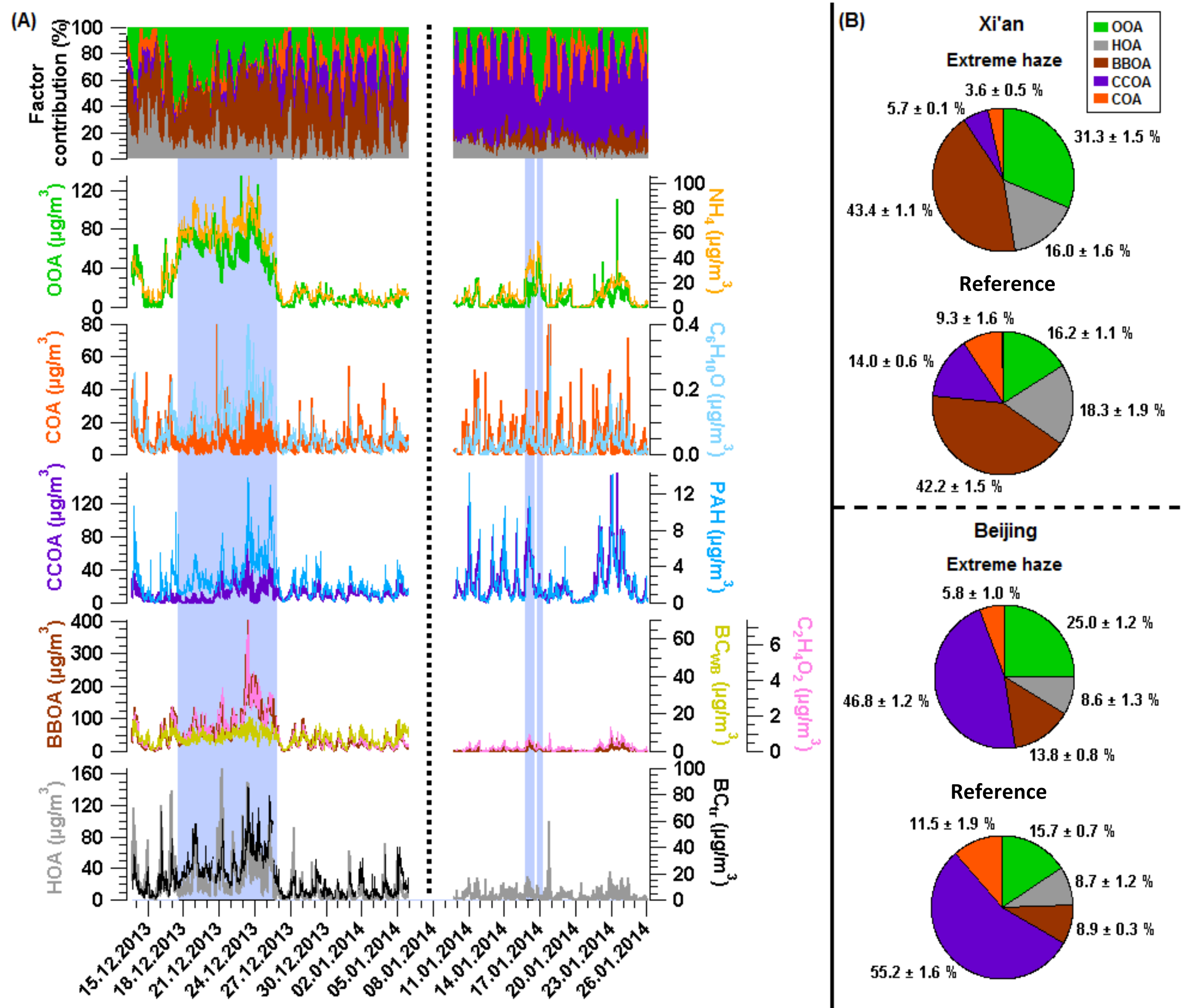
OA source apportionment results

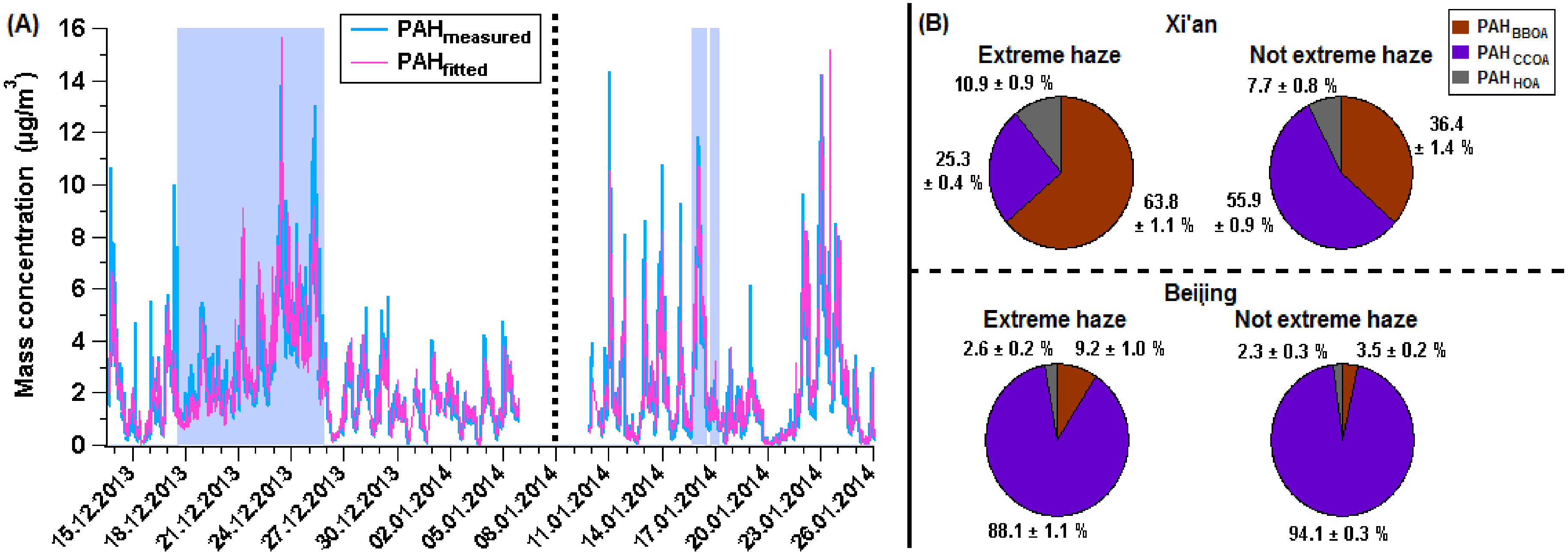
LABORATORY OF ATMOSPHERIC CHEMISTRY



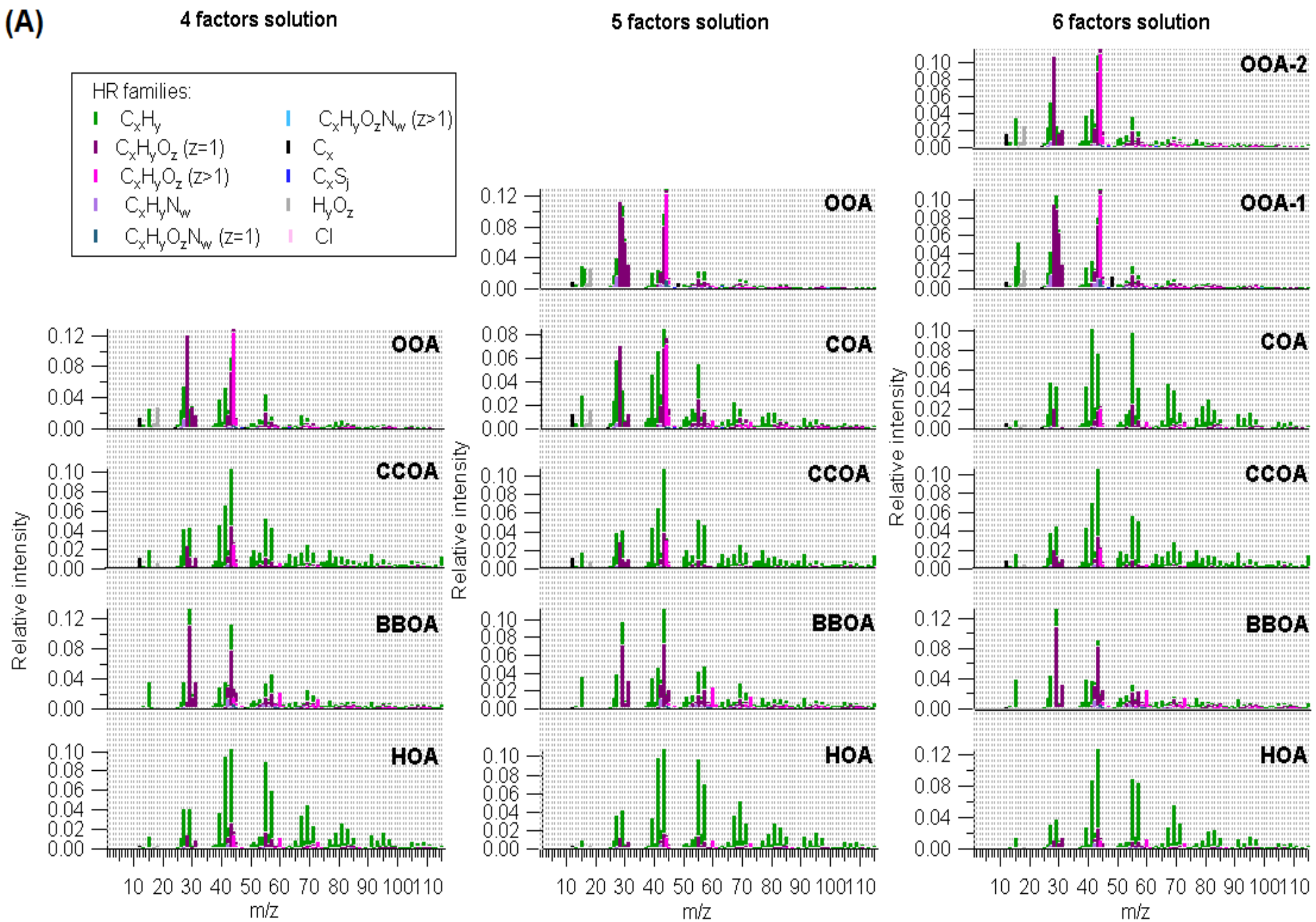
- **Enhanced OOA during extreme haze**
- Major sources are primary:
  - **BBOA in Xi'an**
  - **CCOA in Beijing**
- **COA** and **HOA** are minor sources

PAH sources

- PAH correlate very good with CCOA in Beijing but needs other sources in Xi'an
- PMF runs with Input = (OA|PAH) → PAH attributed to BBOA, CCOA and HOA
- PAH_{fitted}=a*BBOA + b*CCOA + c*HOA



PMF solutions with 4,5 and 6 factors



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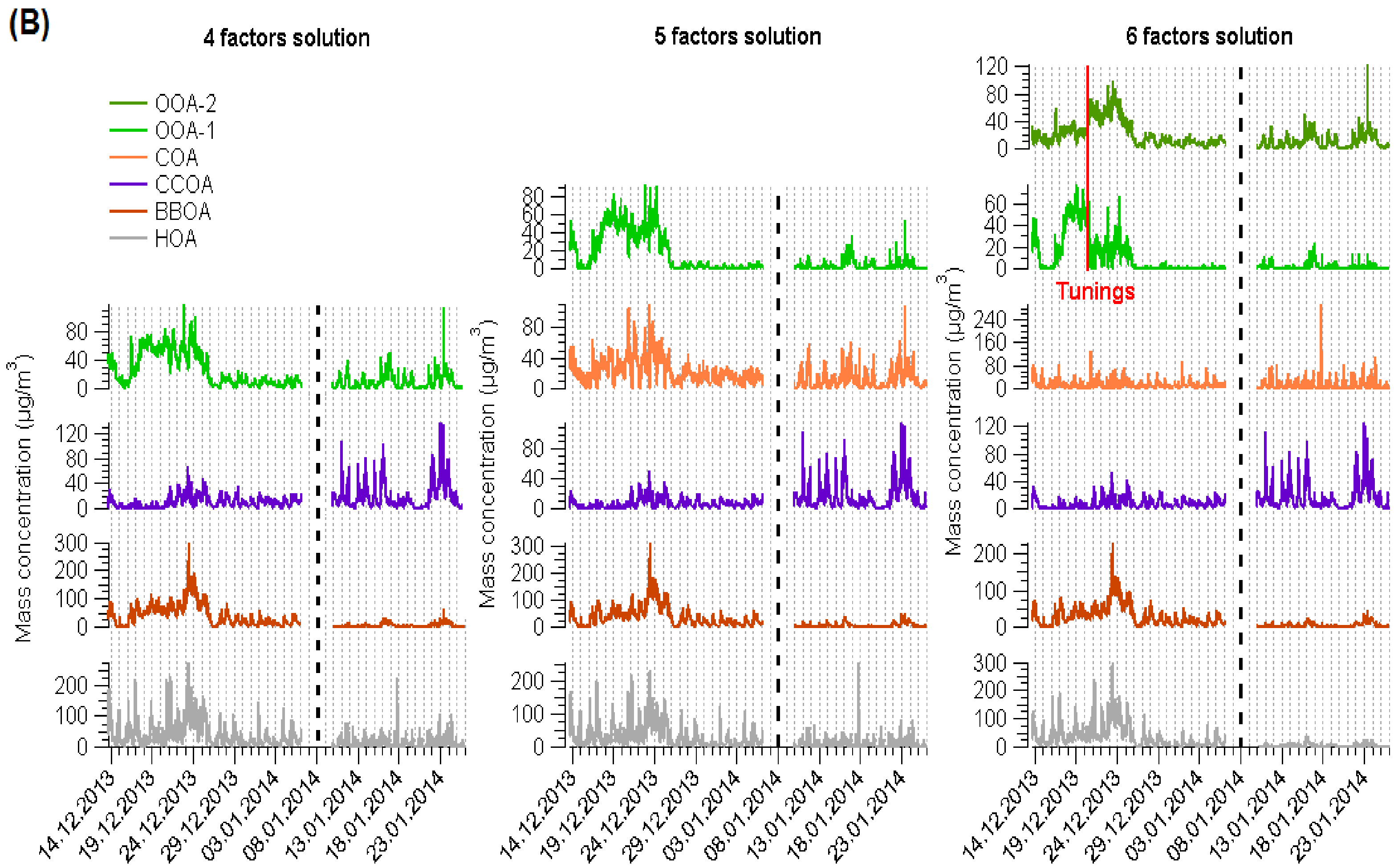
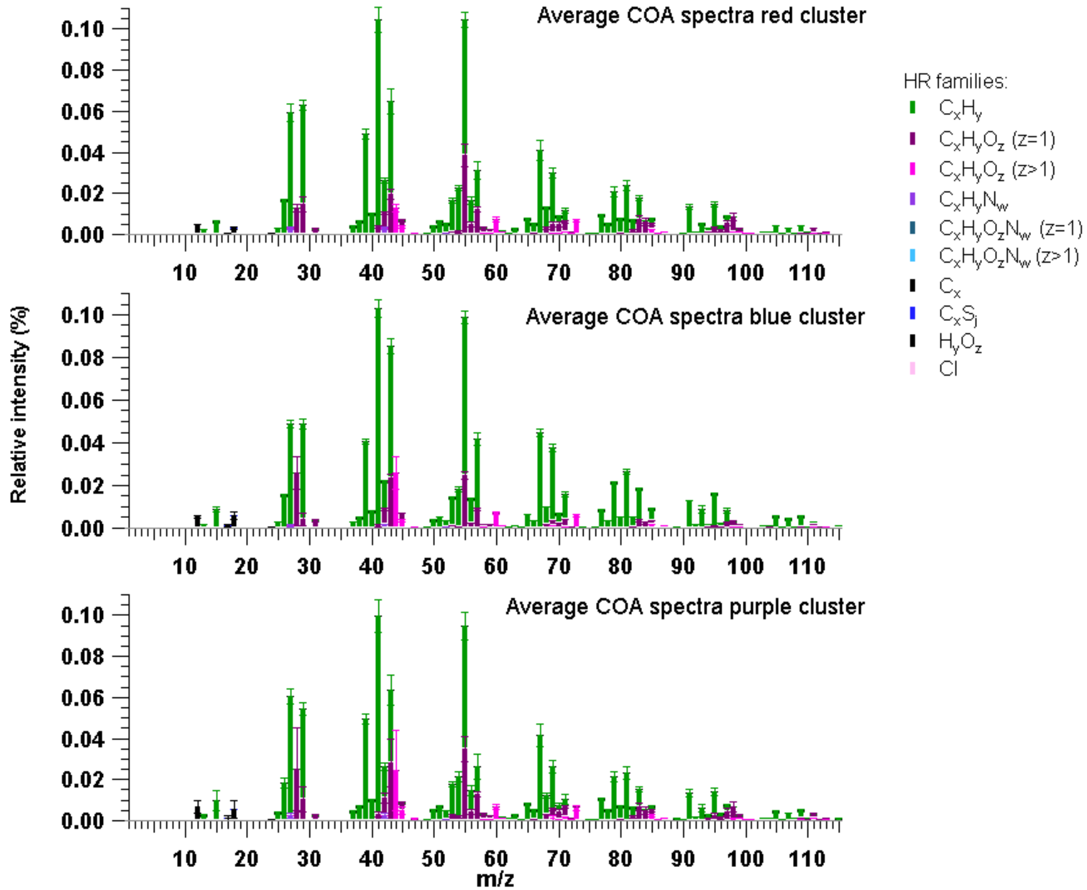


Decreased m/z 44 in red cluster solution



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literature[1]: 0.013 ± 0.004 %

red cluster: 0.013 ± 0.002 %

blue cluster: 0.026 ± 0.008 %

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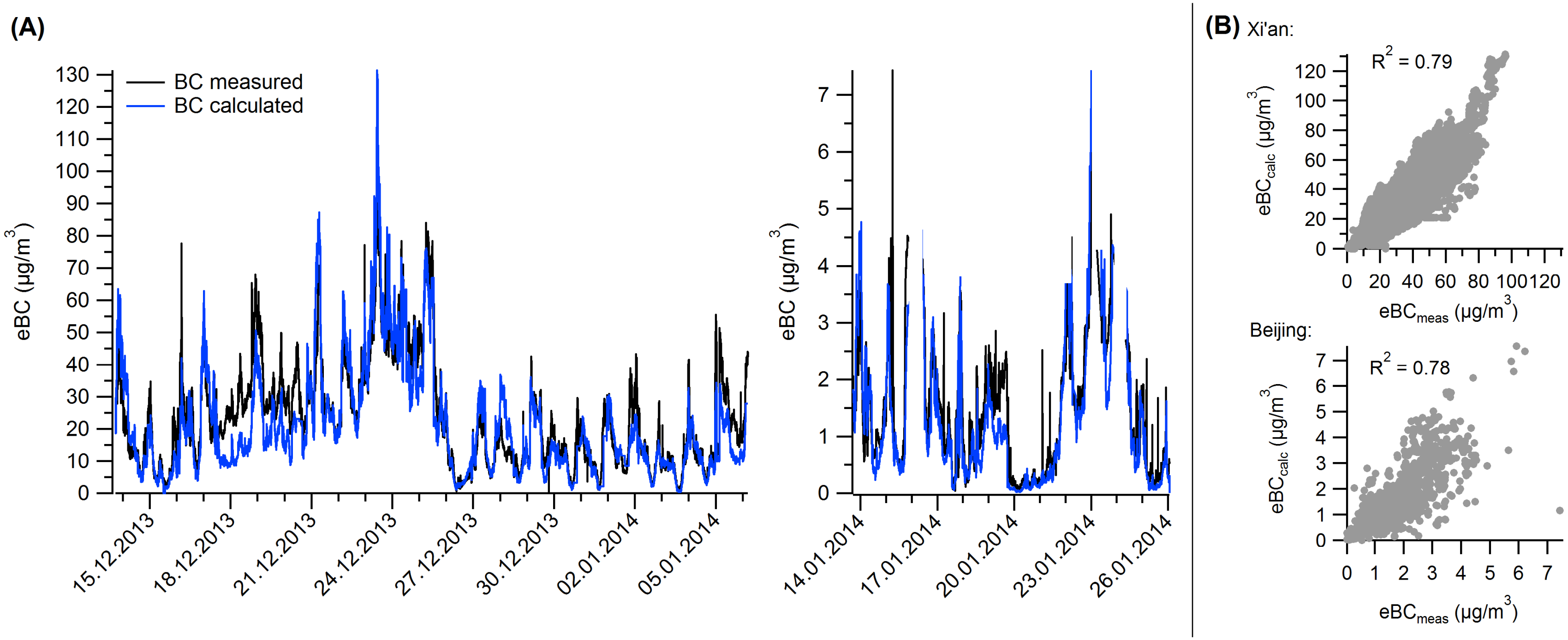
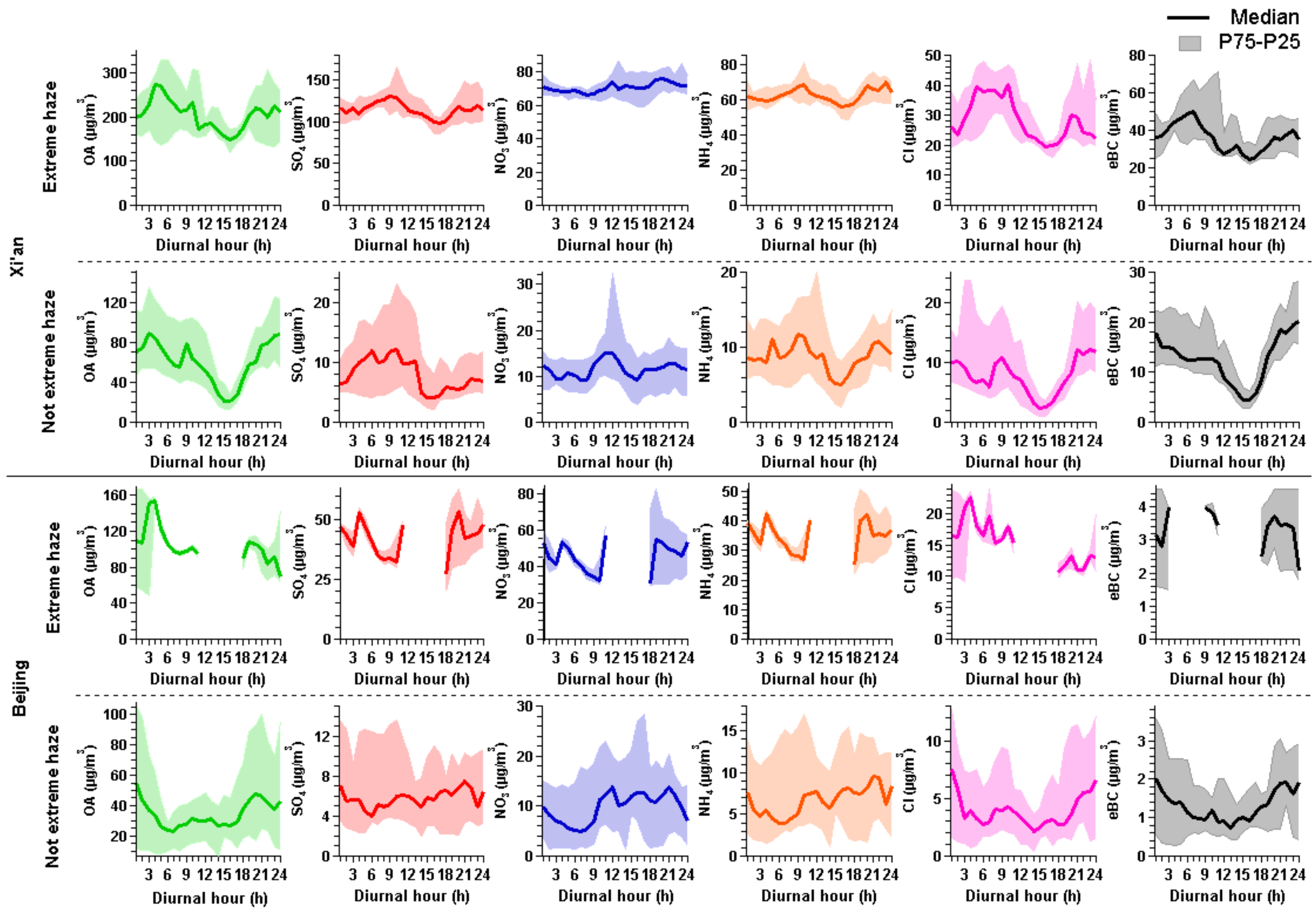
(1) He et al. (2010), Crippa et al. (2013) and Wolf (2014)

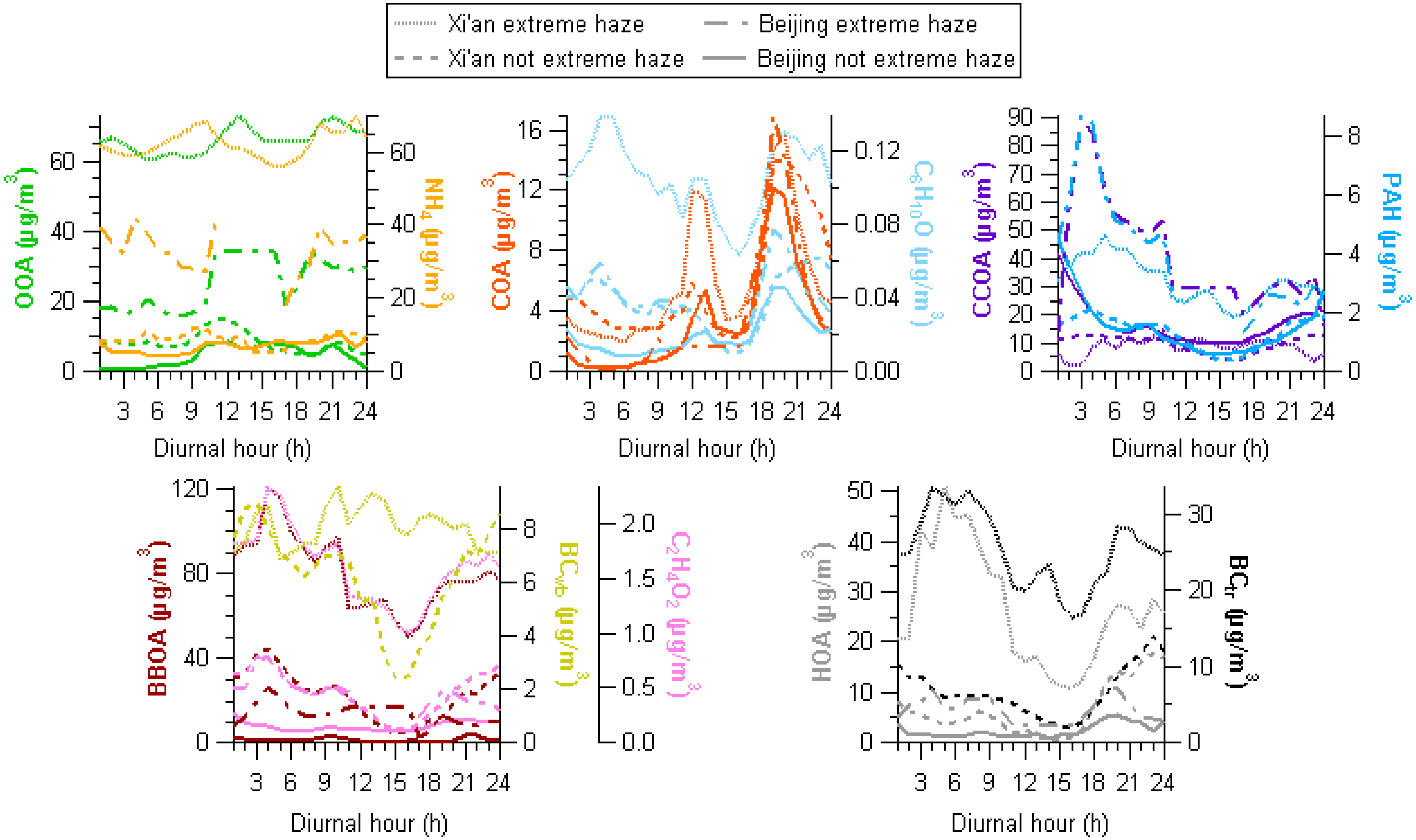
BC calculated as a linear combination of HOA, BBOA and CCOA



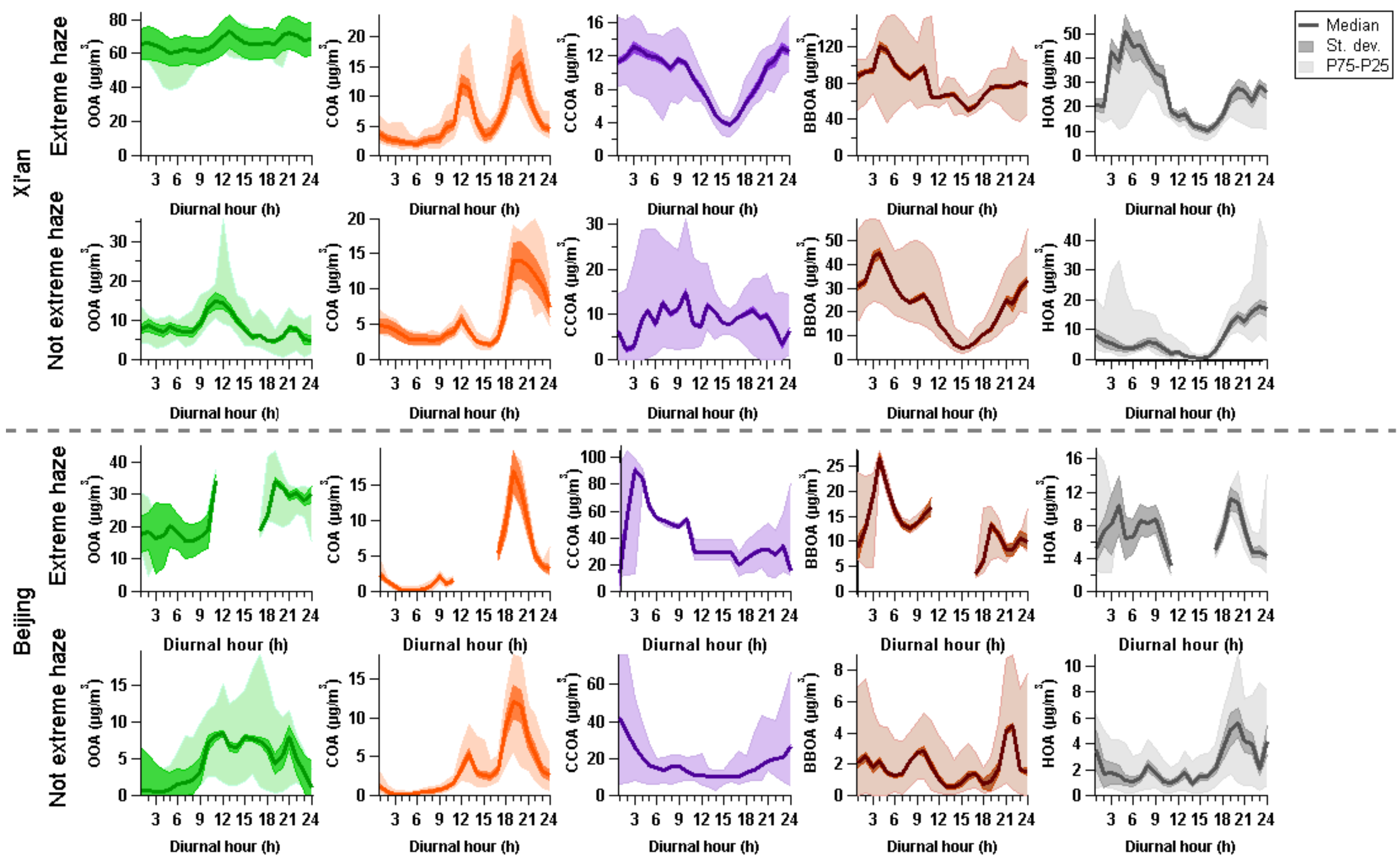
Diurnals AMS species and eBC with variability (P25-P75)



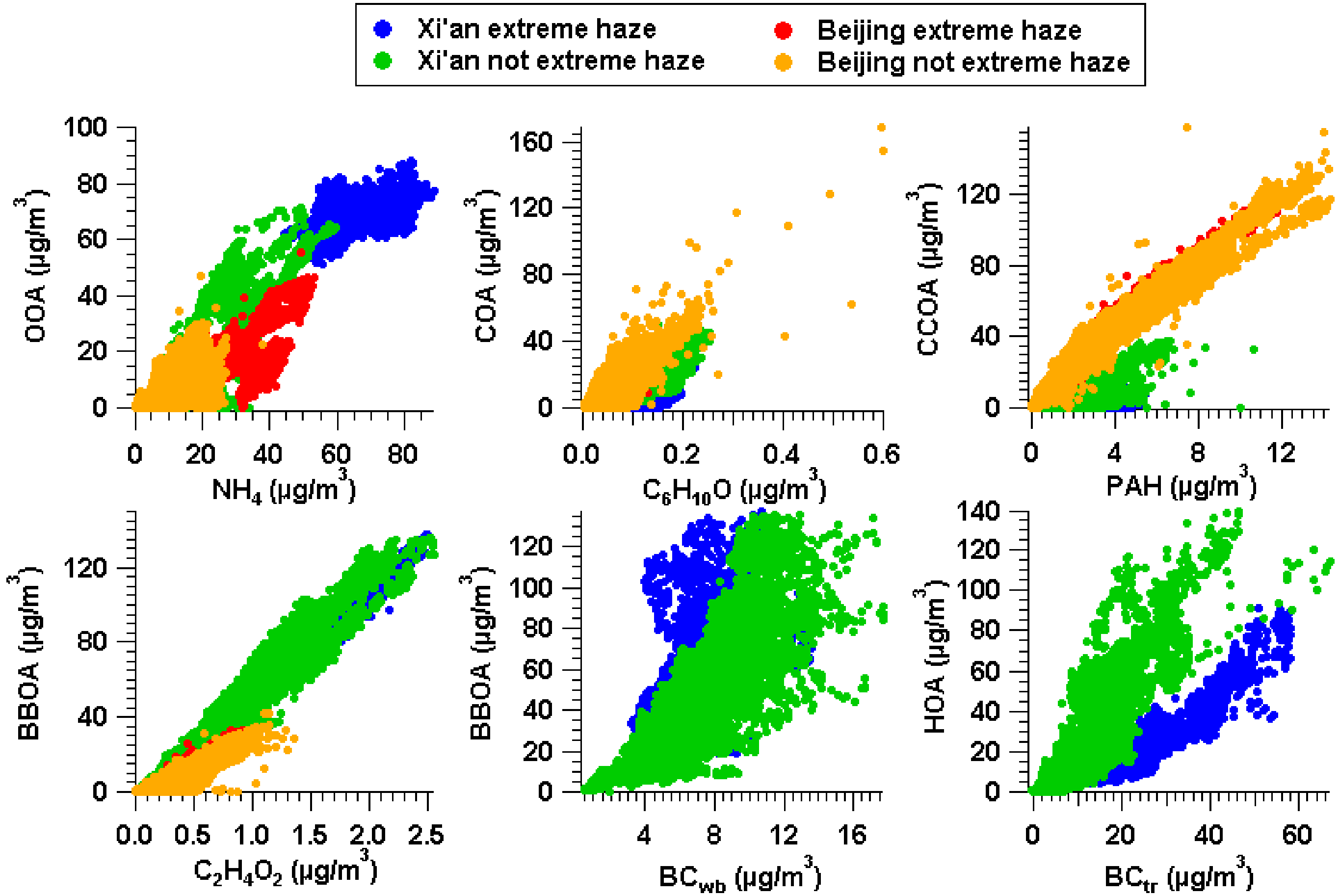
Diurnal trends of the OA sources and external tracers



Diurnal trends of OA sources with errors (st. dev. from all good a-values + daily variability (P25-P75))



Correlations OA sources vs external tracers

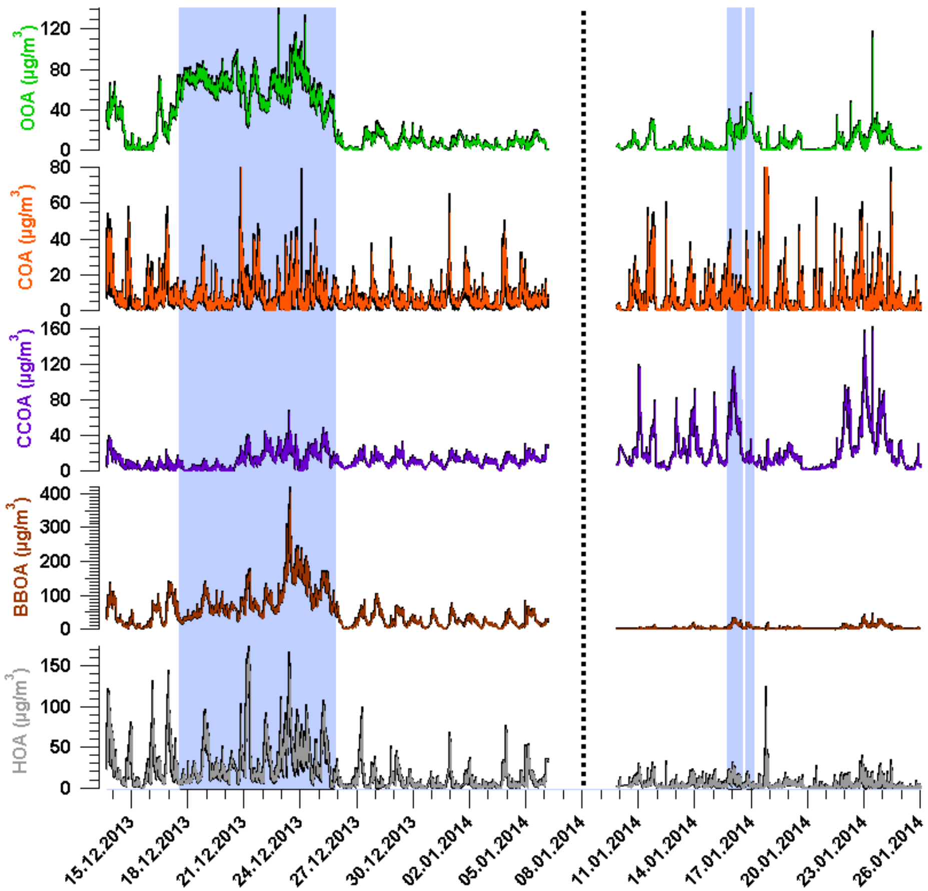


Correlations OA sources vs external tracers

R^2	Xi'an		Beijing		Overall
	Extreme haze	Not extreme Haze	Extreme haze	Not extreme Haze	
OOA-NH_4	0.22	0.71	0.38	0.60	0.88
COA-$C_6H_{10}O$	0.21	0.58	0.44	0.71	0.31
CCOA-PAH	0.57	0.59	0.96	0.96	0.62
BBOA-$C_2H_4O_2$	0.98	0.96	0.79	0.81	0.97
BBOA-BC_{wb}	0.33	0.53	N.A.	N.A.	0.38
HOA-BC_{tr}	0.61	0.61	N.A.	N.A.	0.61

Ratio (source/marker)	Xi'an		Beijing		Overall
	Extreme haze	Not extreme Haze	Extreme haze	Not extreme Haze	
OOA-NH_4	0.99	1.08	0.67	0.76	0.97
COA-$C_6H_{10}O$	60.21	144.01	125.54	197.79	96.35
CCOA-PAH	3.42	5.51	10.84	10.43	7.16
BBOA-$C_2H_4O_2$	51.02	53.98	28.75	21.68	50.60
BBOA-BC_{wb}	10.82	4.91	N.A.	N.A.	7.31
HOA-BC_{tr}	1.18	1.62	N.A.	N.A.	1.27

Time series of OA sources with standard deviation among all good a-value combinations (black shadow)



PSCF analysis