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UNIVERSITY OF HELS
FOR THE ONLY PLANET WE HAVE

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Including inorganics AMS PMF

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University of Helsinki / INAR

AMS users meeting 2021, Jan 21st

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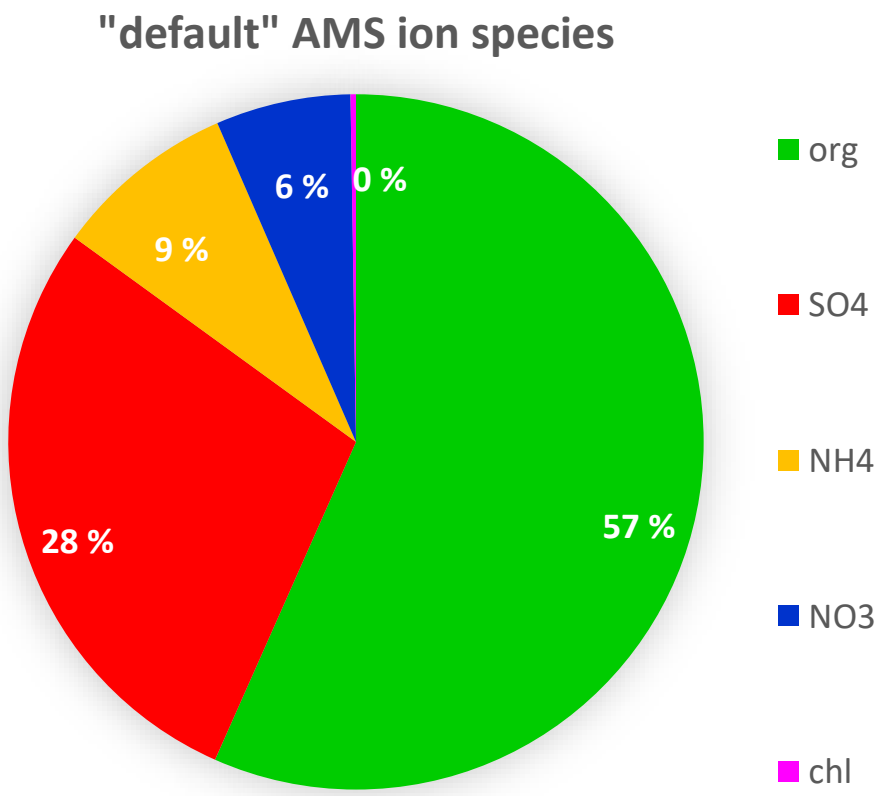
Background

- AMS ”default” chemical speciation (org, so4, no3, nh4, chl)
- Organics typically 30-80% of mass, chemically diverse class
- We think we know the inorganics (so4, no3, nh4, chl)



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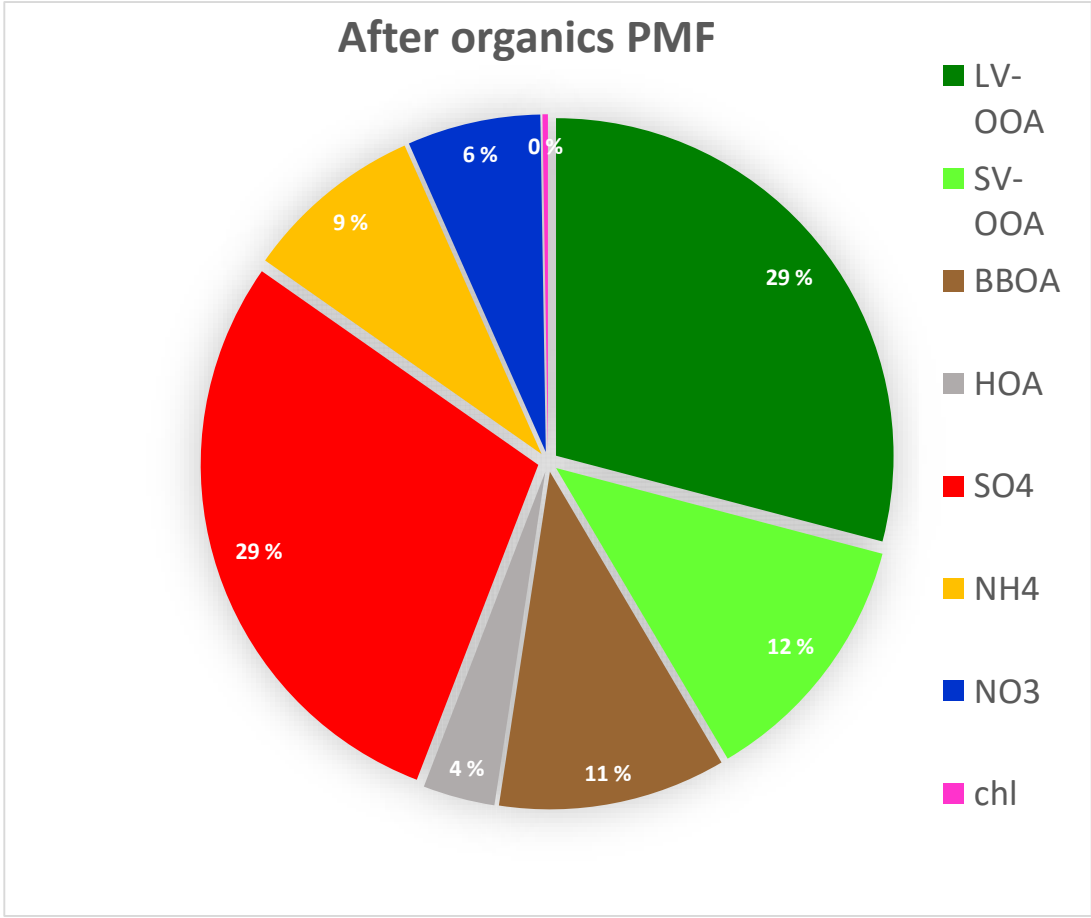
Background

- PMF developed in 1990's and early 2000's to additonally classify org into LV-OOA, SV-OOA, (BBOA, HOA, COA)
- Focus of studies on O:C, oxidation of organics, primary anthropogenic org classes



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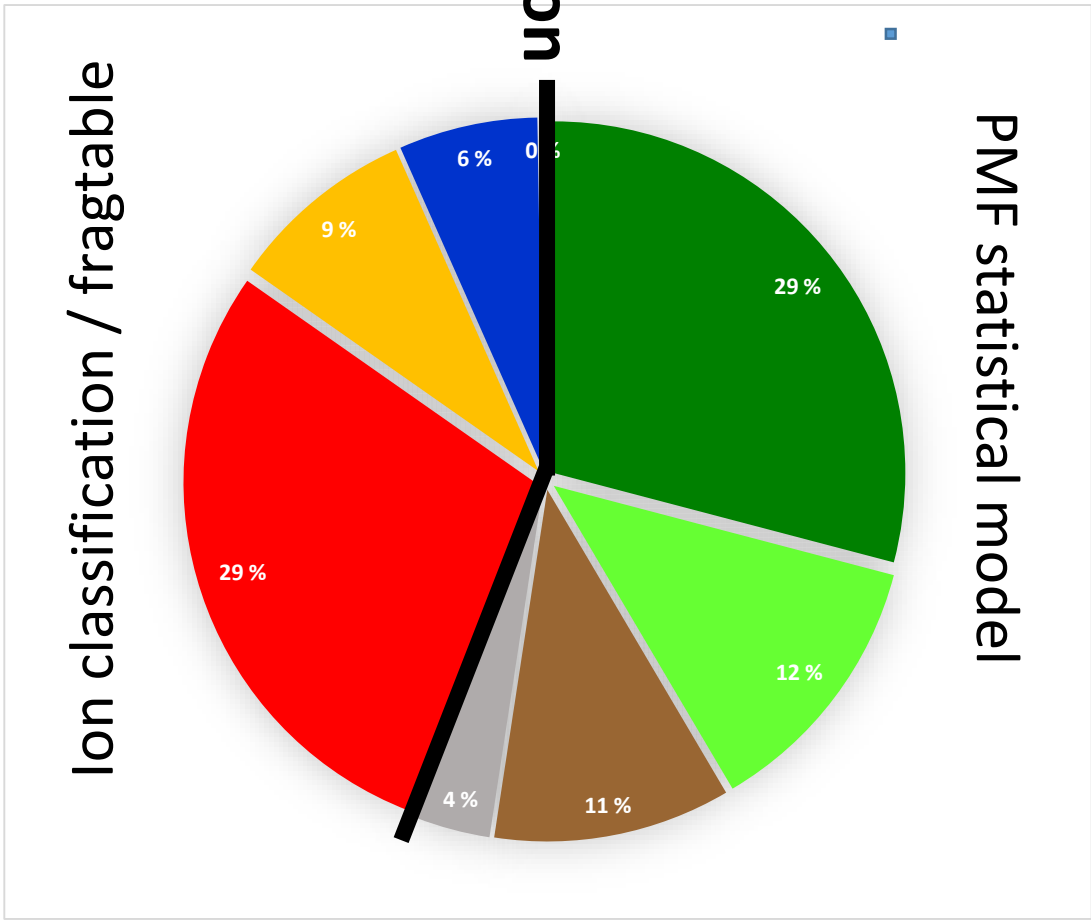
Background

- The past 15 years, org PMF has revolutionised our understanding of AMS organics
- Advances in inorganics classifications are minimal
- We don’t always know what is org and what is inorg (especially in UMR).



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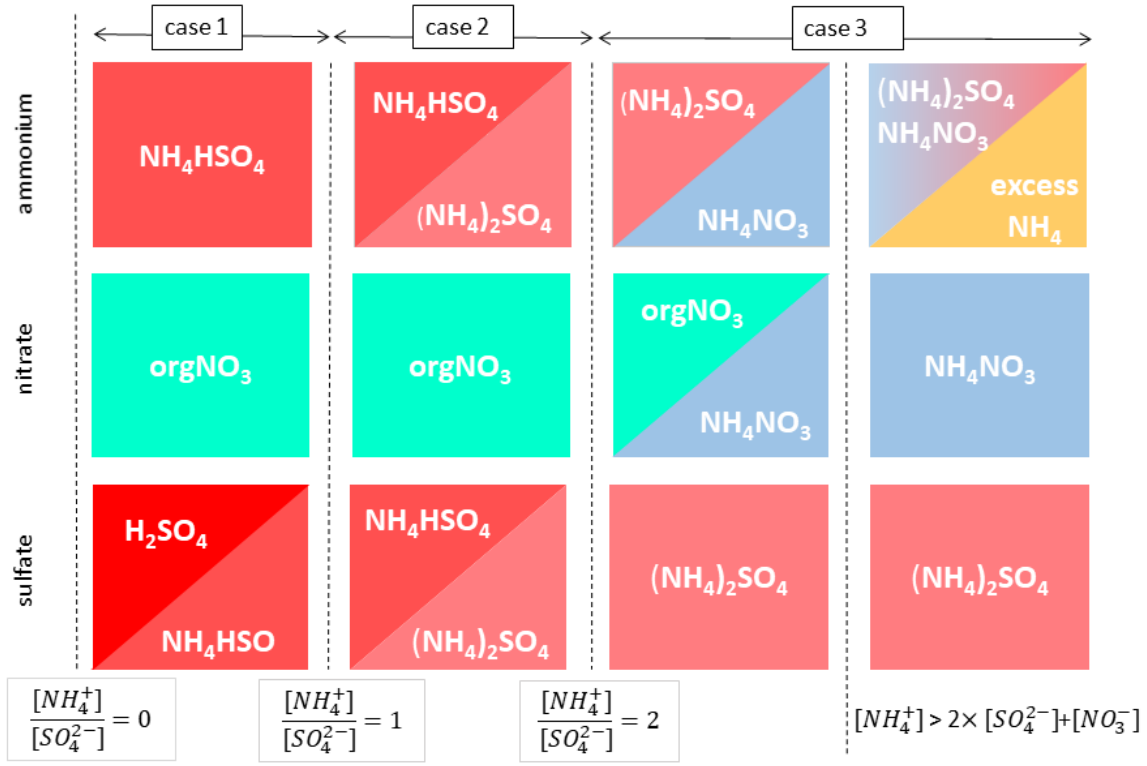
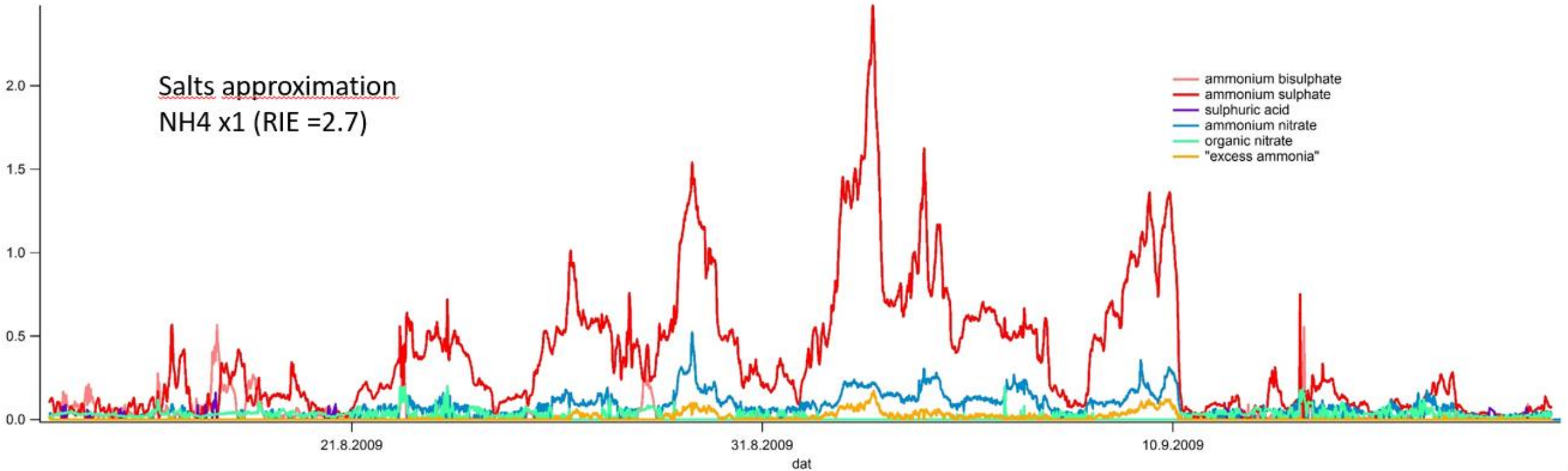
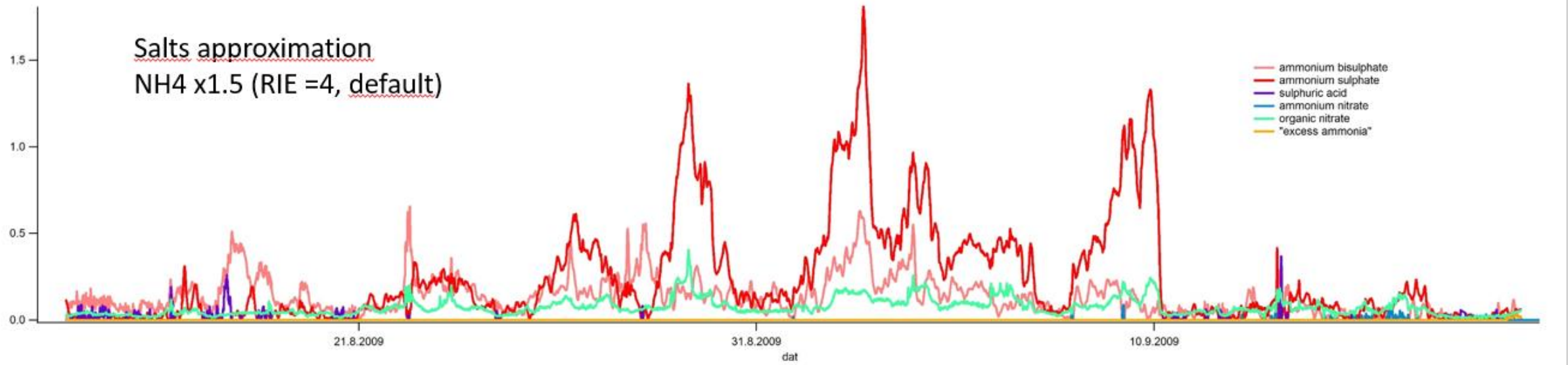
Ion balance models

- Developments: Hong et al. (2017), Gysel et al. (2007), Reilly and Wood (1969)
- Salt formation schemes for AS, AN, $orgNO_3$
- Simplistic mathematical models
- Results difficult to verify
- Extremely sensitive to RIE calibrations



(Äijälä et al., ACP 2019)


Salts approximation
NH4 x1 (RIE =2.7)
ammonium bisulphate
ammonium sulphate
sulphuric acid
ammonium nitrate
organic nitrate
"excess ammonia"
2.0
1.5
1.0
0.5
0.0
21.8.2009
31.8.2009
10.9.2009
dat


Salts approximation
NH4 x1.5 (RIE =4, default)
ammonium bisulphate
ammonium sulphate
sulphuric acid
ammonium nitrate
organic nitrate
"excess ammonia"
1.5
1.0
0.5
0.0
21.8.2009
31.8.2009
10.9.2009
dat

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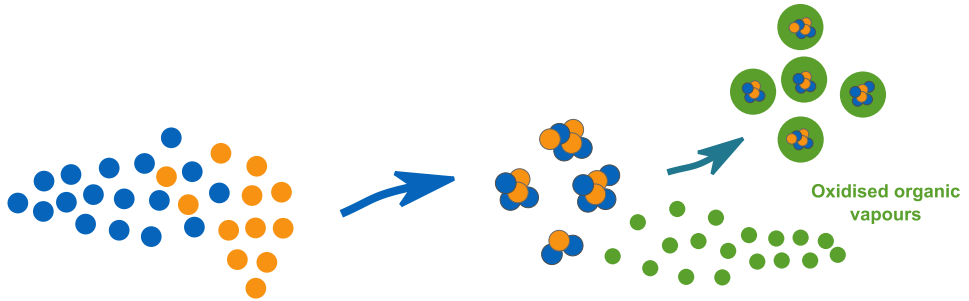
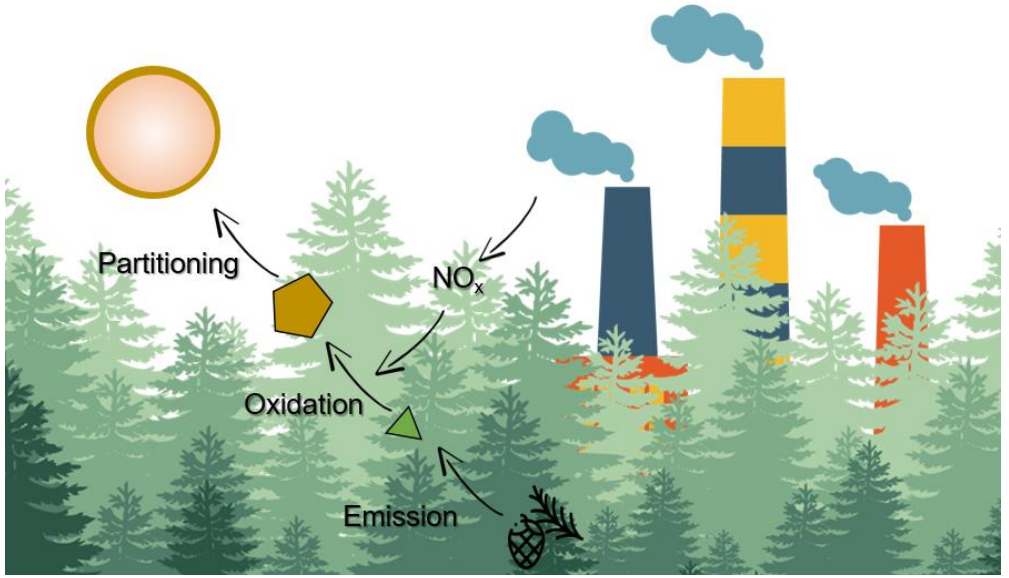
Motivation

- It is becoming increasingly clear that the hard division to **org** vs **inorg** is a hindrance.
- Mixing of polluted and fresh air alters nucleation, SOA formation, volatility, oligomerization, mixing state etc.
- Many of the chemically interesting atmospheric compounds are org-inorg mixtures (ON, amines, OS…)
- Seems we really don't know the inorgs well enough…



(Fig: O. Garmash, 2020)



(Fig: L. Heikkinen, 2020)

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Motivation

Pro

- **Currently incomplete understading of inorganics, growing scientific interest**
- Procedures ~identical to org analysis, technically simple
- Does not exclude org only analysis, no reason not to
- Commensurability (calibration / stability issues)

Con

- **More factors required, harder to arrive at physicochemically correct solutions.**
- PMF ”detection limit” of 5% (rule of thumb, Ulbrict et al., xxx)
- Inorg used in correlation analyses
- Commensurability (calibration / stability issues)

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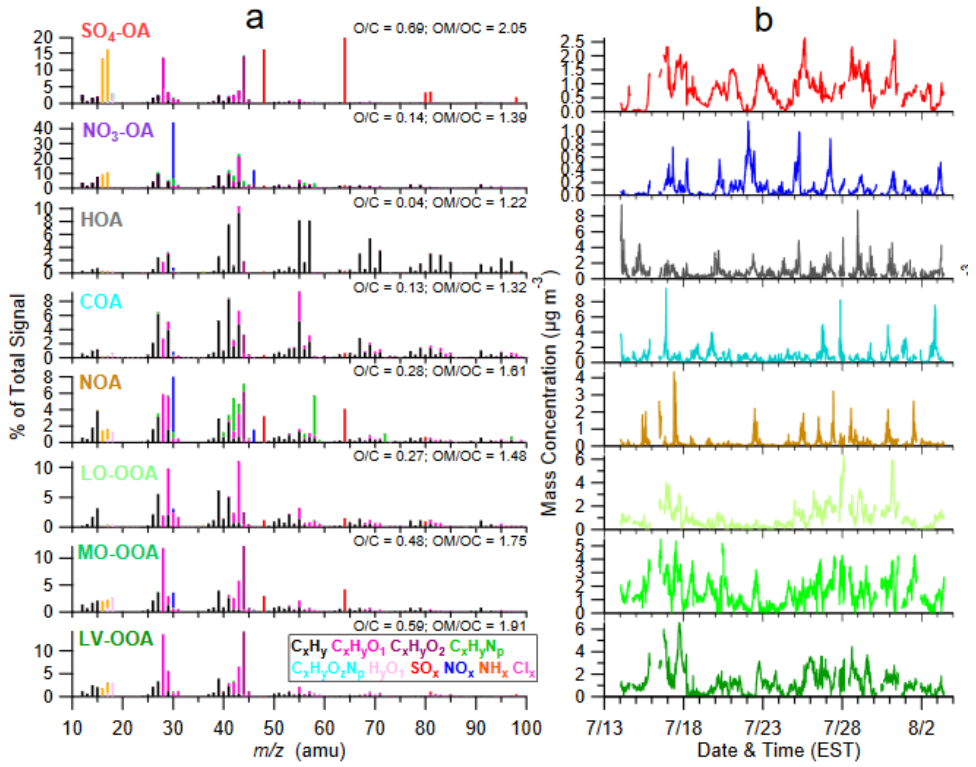
Sun et al., 2012 (ACP)



Atmos. Chem. Phys., 12, 8537–8551, 2012
www.atmos-chem-phys.net/12/8537/2012/
doi:10.5194/acp-12-8537-2012

Atmospheric Chemistry and Physics

Factor analysis of combined organic and inorganic aerosol mass spectra from high resolution aerosol mass spectrometer measurements

Y. L. Sun[1], Q. Zhang[2], J. J. Schwab[3], T. Yang[1], N. L. Ng[4], and K. L. Demerjian[3]

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[3]Atmospheric Sciences Research Center, State University of New York at Albany, Albany, New York, USA
[4]School of Chemical and Biomolecular Engineering and School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

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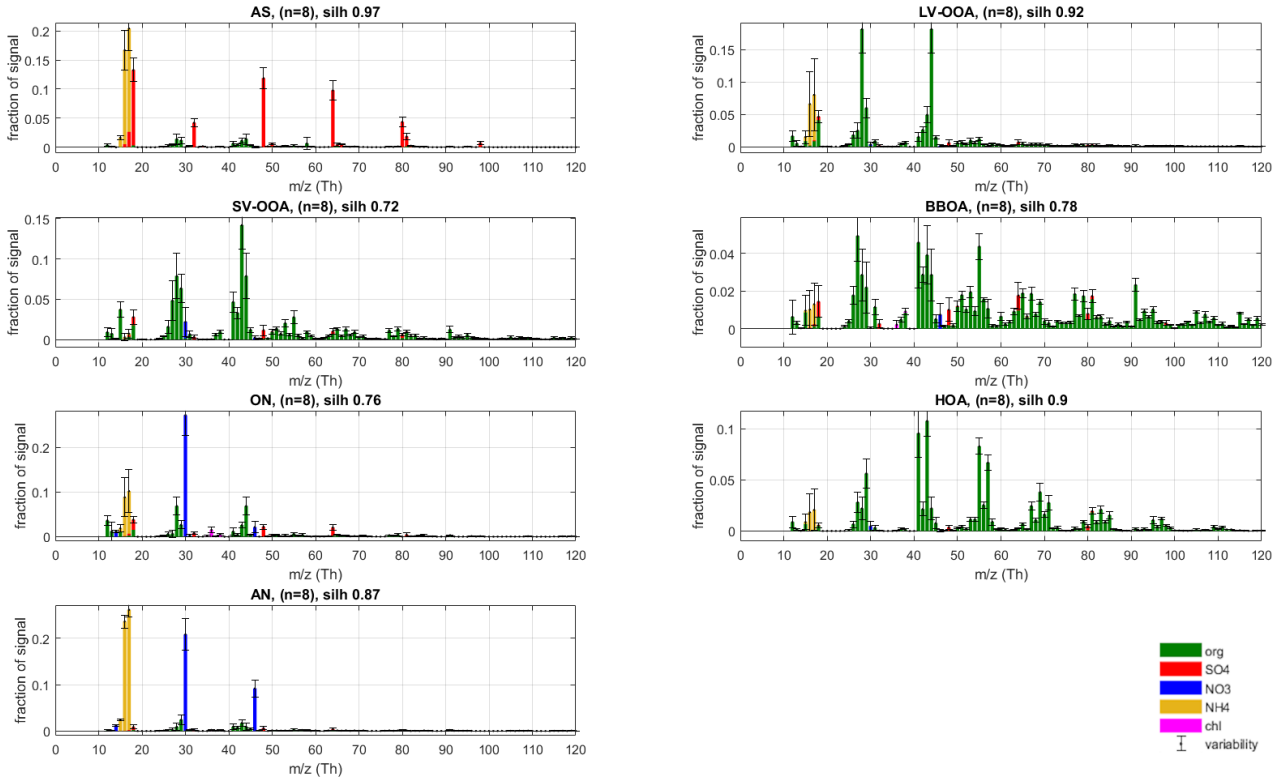
Äijälä et al., 2019 (ACP)



Atmos. Chem. Phys., 19, 3645–3672, 2019
https://doi.org/10.5194/acp-19-3645-2019

Atmospheric Chemistry and Physics
Open Access
EGU

Constructing a data-driven receptor model for organic and inorganic aerosol – a synthesis analysis of eight mass spectrometric data sets from a boreal forest site

Mikko Äijälä[1], Kaspar R. Daellenbach[1], Francesco Canonaco[2], Liine Heikkinen[1], Heikki Junninen[1,3], Tuukka Petäjä[1], Markku Kulmala[1], André S. H. Prévôt[2], and Mikael Ehn[1]

[1]Institute for Atmospheric and Earth System Research/Physics, University of Helsinki, Helsinki, Finland
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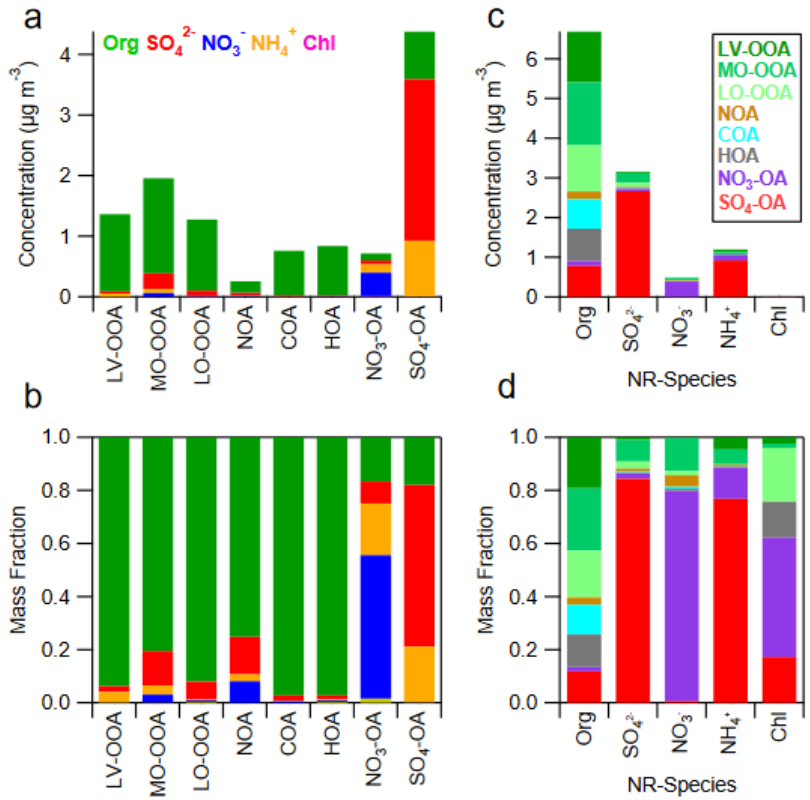
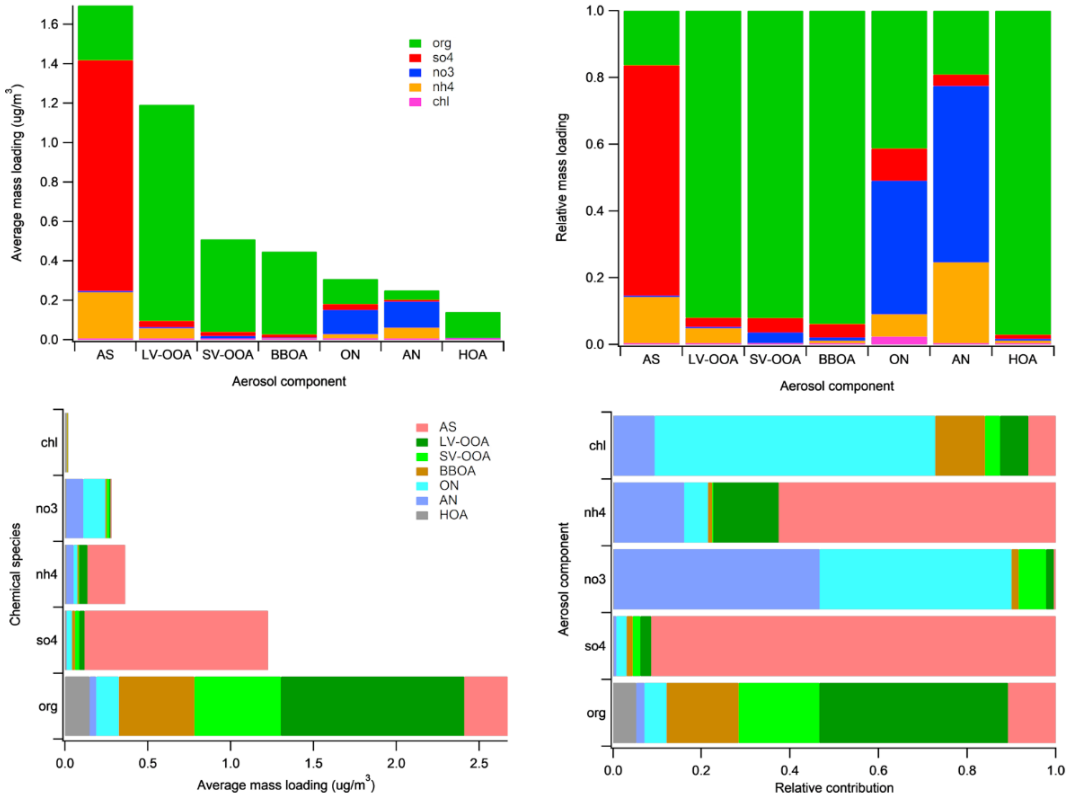
PMF: Org + inorg partly mixed

(Sun et al., 2012, NYC 2009)



(Äijälä et al., 2019, Hyytiälä 3 yr)



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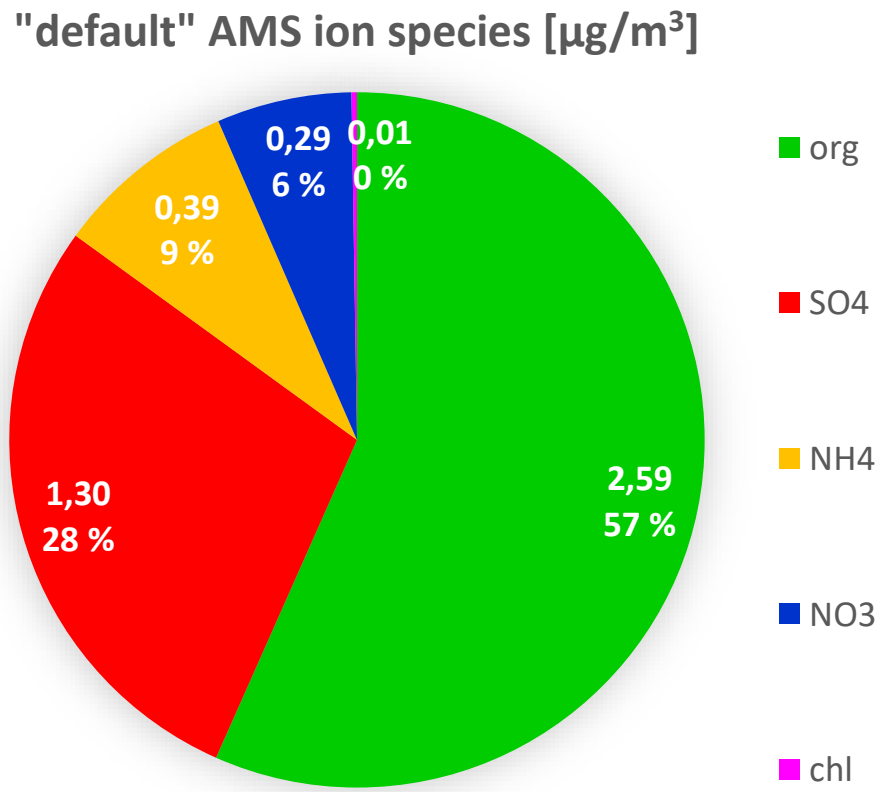
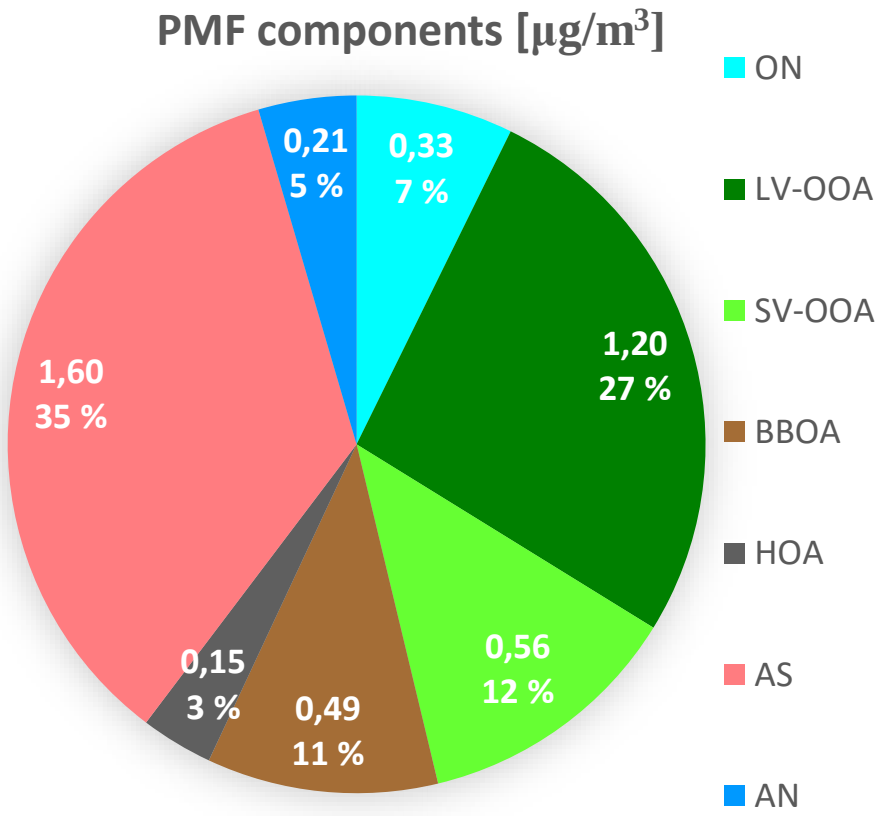
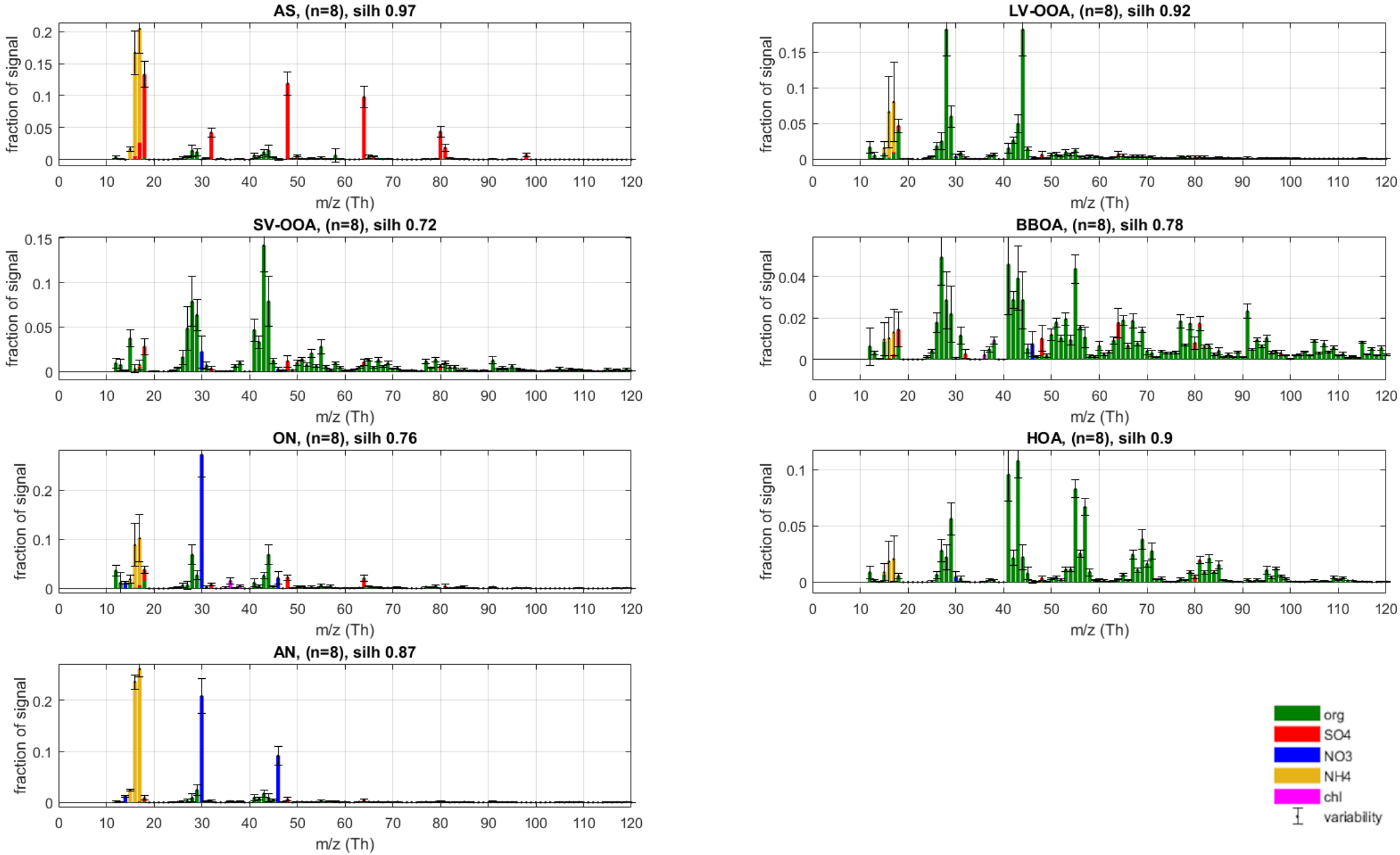
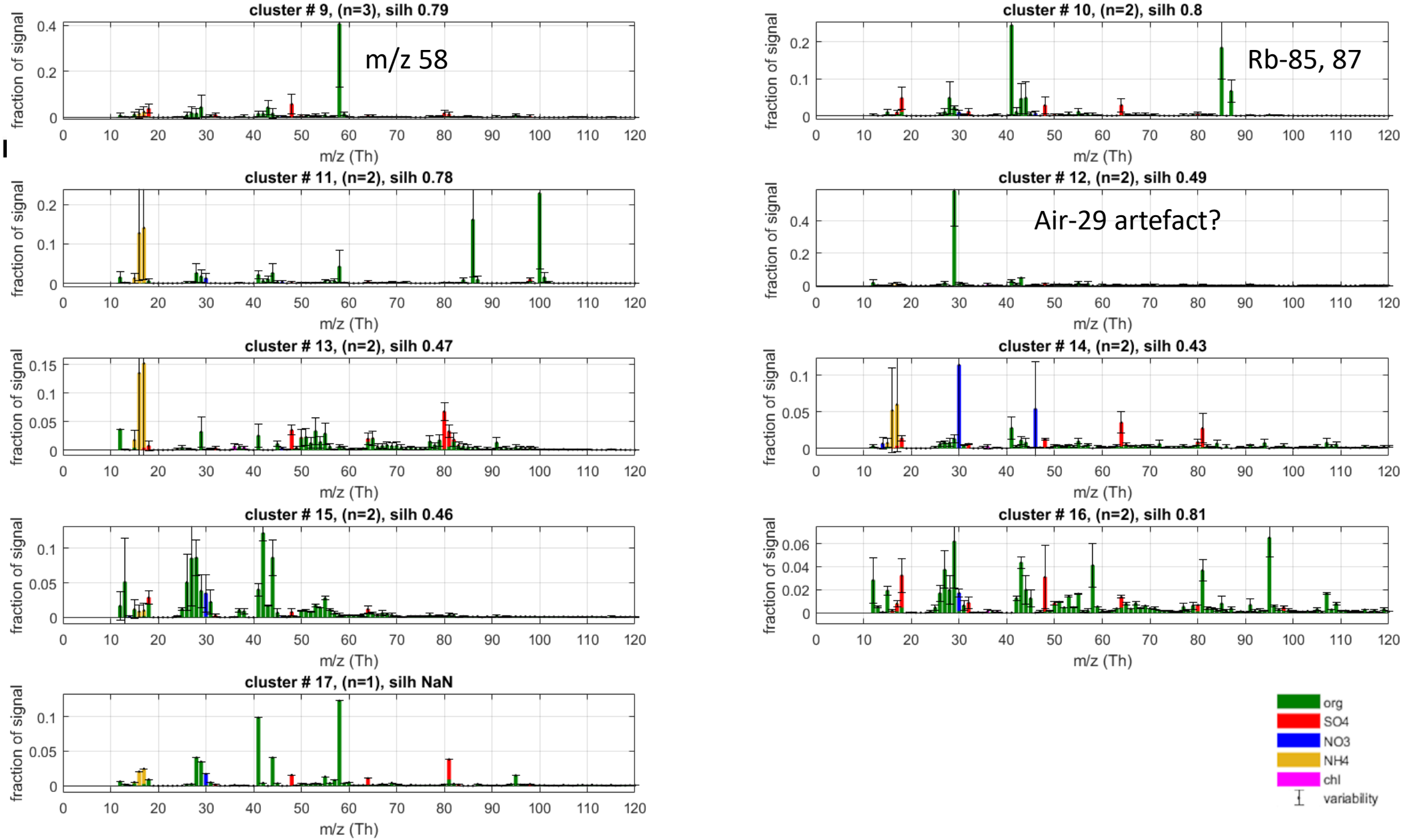
Improved chem. speciation






AS, (n=8), silh 0.97
LV-OOA, (n=8), silh 0.92
SV-OOA, (n=8), silh 0.72
BBOA, (n=8), silh 0.78
ON, (n=8), silh 0.76
HOA, (n=8), silh 0.9
AN, (n=8), silh 0.87
fraction of signal
m/z (Th)
org
SO4
NO3
NH4
chl
variability


cluster # 9, (n=3), silh 0.79
m/z 58
cluster # 10, (n=2), silh 0.8
Rb-85, 87
cluster # 11, (n=2), silh 0.78
cluster # 12, (n=2), silh 0.49
Air-29 artefact?
cluster # 13, (n=2), silh 0.47
cluster # 14, (n=2), silh 0.43
cluster # 15, (n=2), silh 0.46
cluster # 16, (n=2), silh 0.81
cluster # 17, (n=1), silh NaN
fraction of signal
m/z (Th)
org
SO4
NO3
NH4
chl
variability

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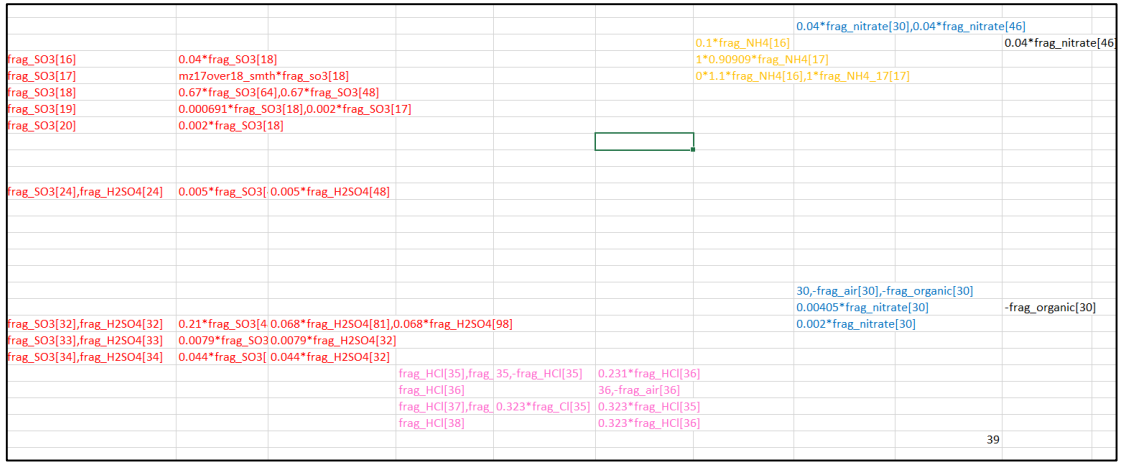
Steps (for UMR)

1. Extract raw matrices, join them together in one matrix
   - Preserve species info!
2. Downweight duplicate info similar to org PMF!
   - (i.e. similar to mz44 related dw)
3. Run PMF as usual, colour results by species info
4. Apply correct RIE to PMF results when calculating mass loading!




```
////////////////////////////////////////////////////////////////////////////////
// Downweight scheme for fragtable dependencies (duplicate information)
// this function downweights signals that are products of fragtable calcs
// Run _AFTER_ generating the combinex mx and applying PET preprocesing!
// 10.5.2017 /MÄ mod 29.5.2017 for better downweighting
////////////////////////////////////////////////////////////////////////////////
function DW_frags()

make /o /N=0 variables_to_dw, dw_factor                    // list of variables to downweight

print "downweighted following m/z variables"
// NO3
i+=1; variables_to_dw [i]={14.02};   dw_factor [i]={1.07} //no3, calculated from mz 30 & 46
i+=1; variables_to_dw [i]={30.02};   dw_factor [i]={1.08} //no3, calculated from mz 30
i+=1; variables_to_dw [i]={31.02};   dw_factor [i]={1.08} //no3, calculated from mz 30
i+=1; variables_to_dw [i]={32.02};   dw_factor [i]={1.08} //no3, calculated from mz 30
i+=1; variables_to_dw [i]={46.02};   dw_factor [i]={1.01} //no3, calculated from mz 46
i+=1; variables_to_dw [i]={47.02};   dw_factor [i]={1.01} //no3, calculated from mz 46
i+=1; variables_to_dw [i]={48.02};   dw_factor [i]={1.01} //no3, calculated from mz 46
i+=1; variables_to_dw [i]={63.02};   dw_factor [i]={1.07} //no3, calculated from mz 30 & 46
```

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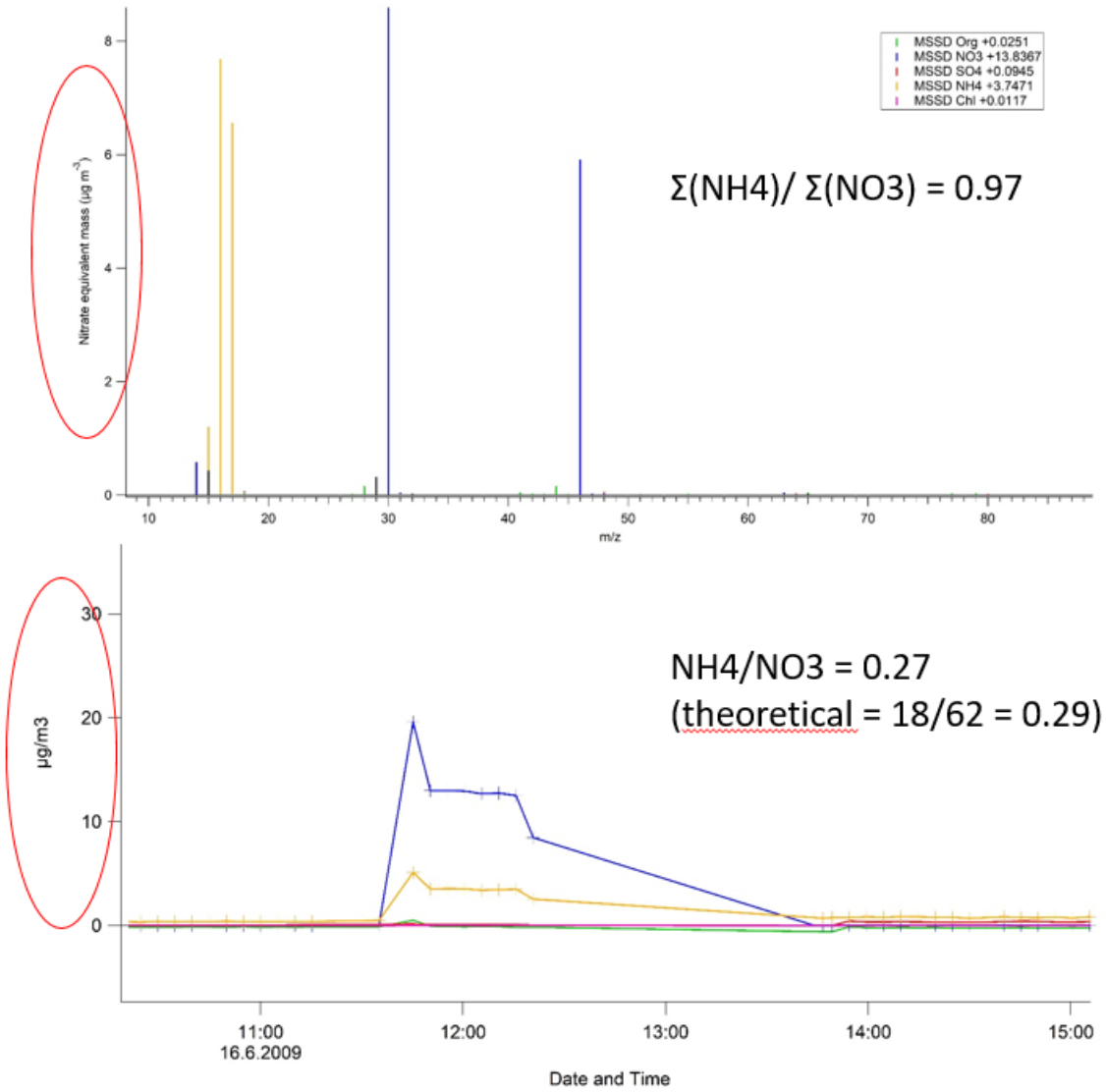
- Remember: Mass specs calculated in nitrate equivalent mass, not ug/m3



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Conclusion

- Many reasons to add inorganics when doing PMF (especially for UMR)
  - Org-inorg chemistry
  - Improved speciation
  - Understanding of data
- Requires some technical steps in pre/post-processing, still very similar to org PMF