FOR THE ONLY PLANET WE HAVE
Including inorganics
AMS PMF

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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)

"default" AMS ion species

- org: 57%
- SO4: 28%
- NH4: 6%
- NO3: 9%
- chl: 0%
Background

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

- Developments: Hong et al. (2017), Gysel et al. (2007), Reilly and Wood (1969)
- Salt formation schemes for AS, AN, orgNO₃
- Simplistic mathematical models
- Results difficult to verify
- Extremely sensitive to RIE calibrations

(Äijälä et al., ACP 2019)
Salts approximation
NH4 x1 (RIE = 2.7)

Salts approximation
NH4 x1.5 (RIE = 4, default)
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…

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(Fig: O. Garmash, 2020)

(Fig: L. Heikkinen, 2020)
Motivation

**Pro**
- Currently incomplete understanding 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, Ulbricht et al., xxx)
- Inorg used in correlation analyses
- Commensurability (calibration / stability issues)
Factor analysis of combined organic and inorganic aerosol mass spectra from high resolution aerosol mass spectrometer measurements

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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

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PMF: Org + inorg partly mixed

(Sun et al., 2012, NYC 2009) (Äijälä et al., 2019, Hyytiäälä 3 yr)
Improved chem. speciation

"default" AMS ion species [µg/m³]

PMF components [µg/m³]

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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

Air-29 artefact?

cluster # 12, (n=2), silh 0.49

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)
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!

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```
function DW_frags()
    make /o /N=0 variables_to_dw, dw_factor
    print "downweighted following m/z variables"
    // list of variables to downweight
    // 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
```
• Remember: Mass specs calculated in nitrate equivalent mass, not ug/m³
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

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