PAUL SCHERRER INSTITUT

LABOR FÜR ATMOSPHÄREN-CHEMIE

PMF, CMB, ME-2

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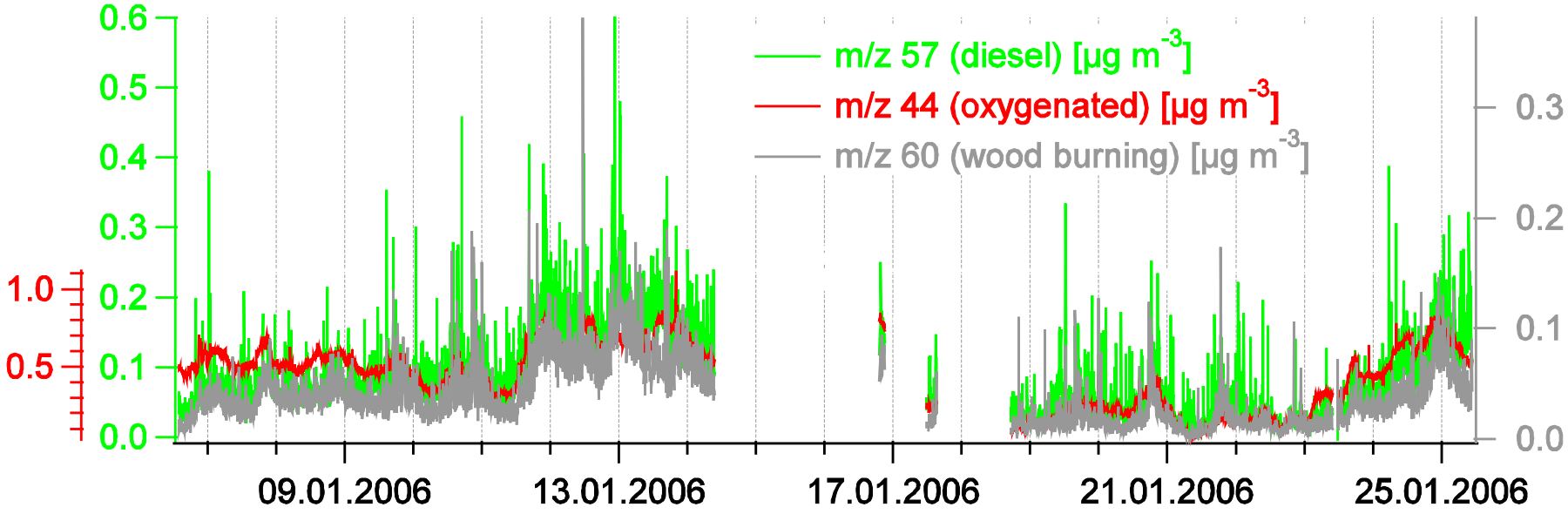
If contribution of various OA components do not vary much in time: Positive Matrix Factorization or similar unmixing methods do not work: Example Zürich winter



Lanz et al., ES&T, 2008

A solution could be to use chemical mass balance (CMB) methods or hybrid versions of CMB and PMF

$$x_{ij} = \sum_{p} g_{ip} f_{pj} + \sum_{p'} g_{ip'} f_{q} + e_{ij}$$

unknown sources/
free factors (PMF)

known sources/
fixed factors (CMB)

x x x

CMB ⟷ PMF

(**G** unknown)

(**G**, **F** unknown)

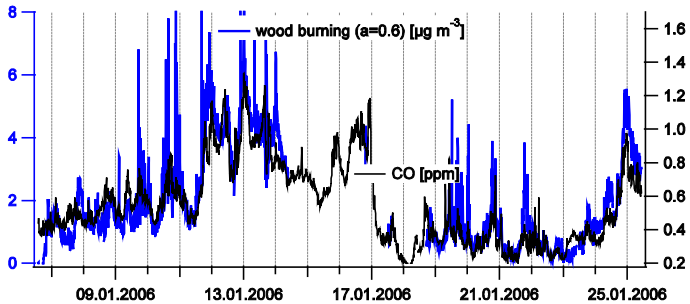
$$\mathbf{F}_{jm} = \mathbf{F}'_{jm} \pm a_j \mathbf{F}'_{jm} \qquad a = \{0 \ldots 1\}$$

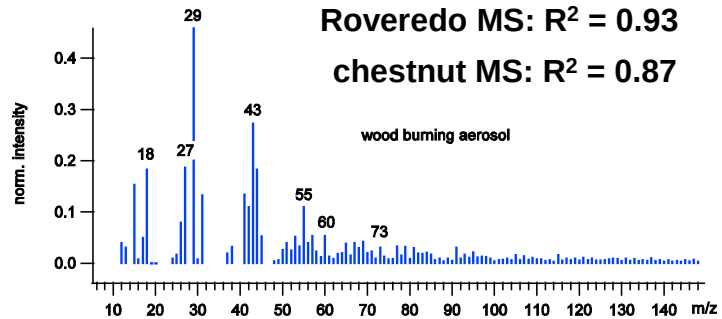
solved by the multilinear engine, ME (Paatero, 1999)

Lanz et al., ES&T, 2008

Plausibility of solution including 3 factors

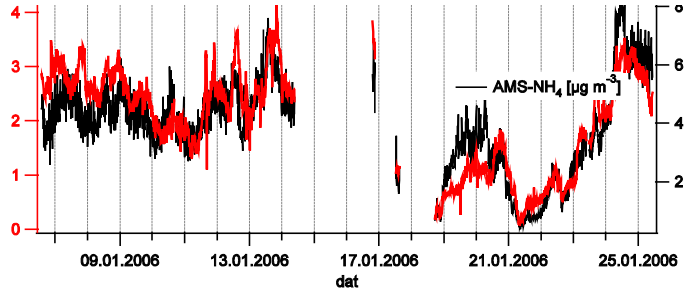
wood burning (modelled) vs CO (measured): $R^2 = 0.78$



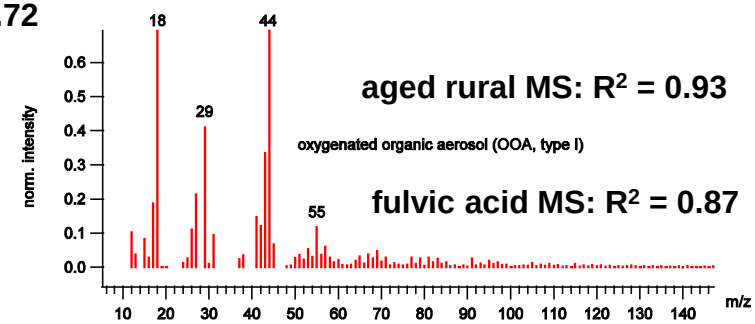


OOA (modelled) vs. AMS-ammonium (measured) $R^2 = 0.72$

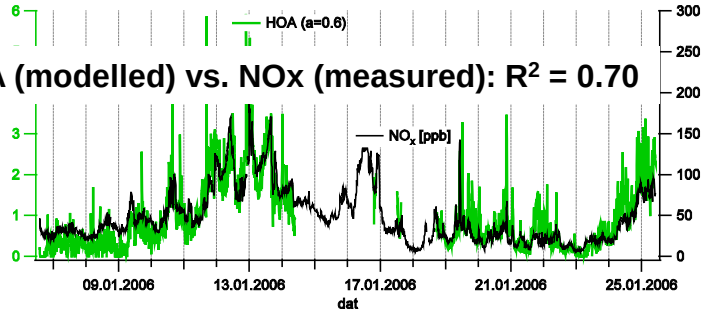
calculated **G**

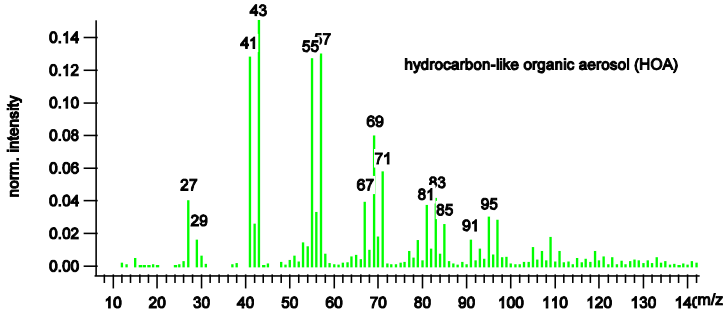


calculated **F**



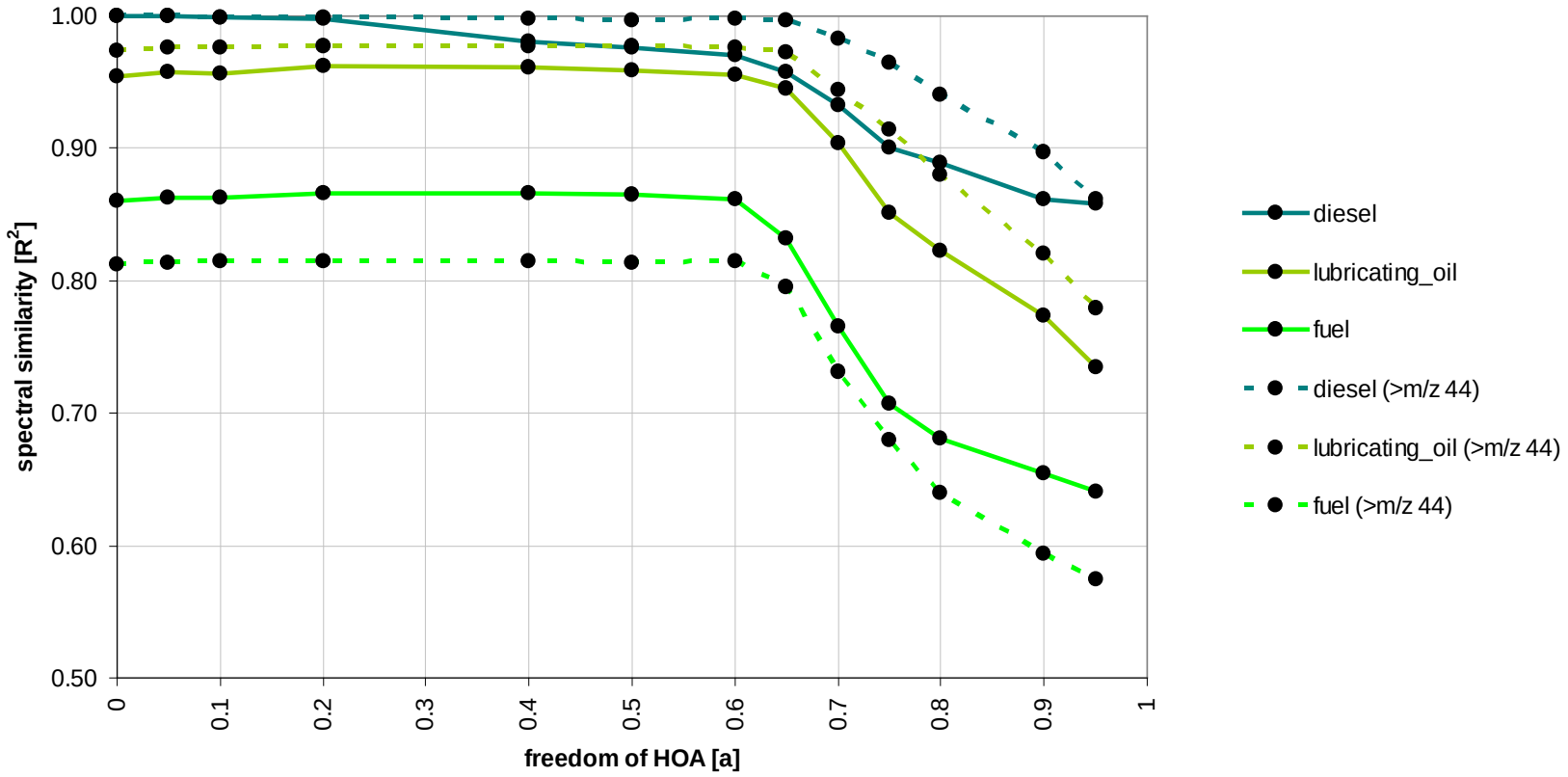
HOA (modelled) vs. NOx (measured): $R^2 = 0.70$





Lanz et al., ES&T, 2008

Correlation with reference diesel mass spectrum allowing more and more freedom (a=0 until a=1)



Interface in Igor for the Multilinear engine (Me-2)

- Algorithm solves the same equation as for PMF, namely:

$$X_{measured} = X_{model} + E_{model}$$

but…

- the factors can be given as constraints, if
  1. Profiles are already known for certain circumstances
  2. Bilinear models fail to produce a reasonable factor solution by describing the variability of the different m/z variables.

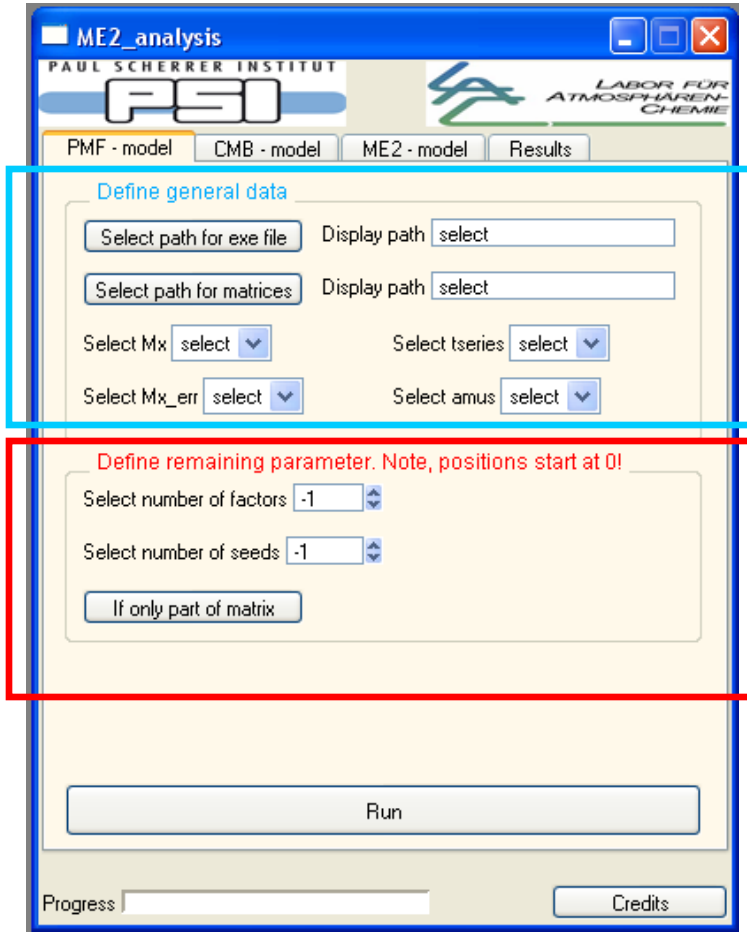
Interface in Igor for the Multilinear engine (Me-2)

- ME-2 has an exploiting potential, since
  1. One or more factors can be constrained
  2. A-value still accounts for variability of the profiles
  3. Different a-values can be chosen for the factors and/or for the m/z variables separately

  4. In addition the ME-2 engine is constructed in a way to solve
     - **PMF**, if factor profiles are not constrained
     - **ME-2**, some factors or m/z are constrained
     - **CMB**, if all factors are constrained
     - ⇨ Capability to run one of these models from one interface.

Interface in Igor for the Multilinear engine (Me-2)

- Interface still in progress…

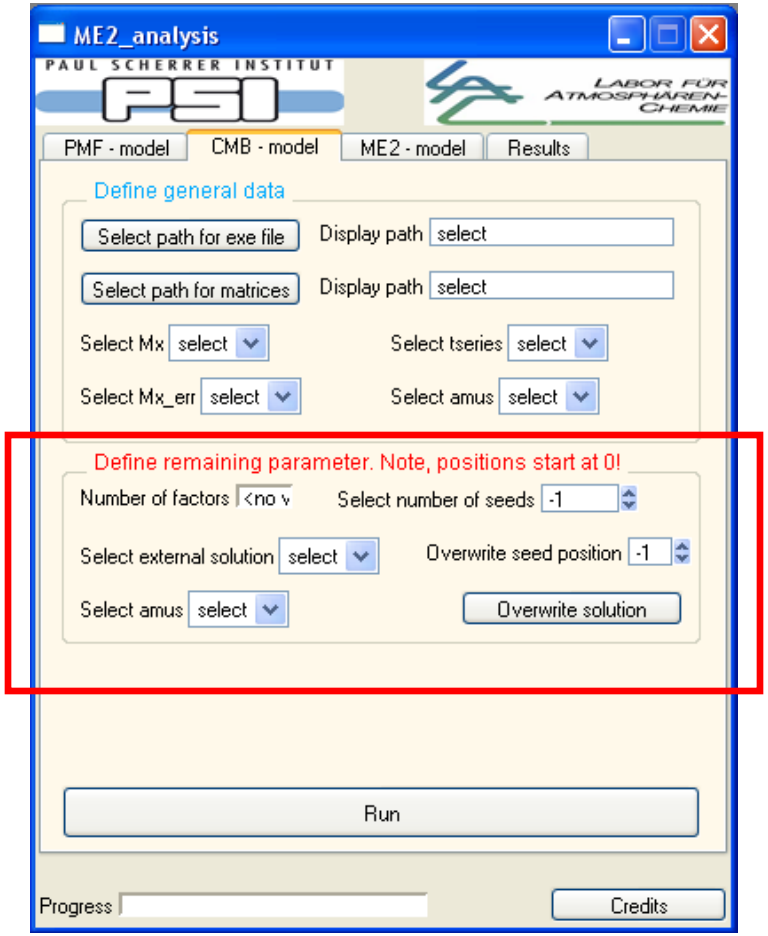


Define location of matrices and ini file in the windows hierarchy and in Igor.

Choose nb. of factors and of seeds

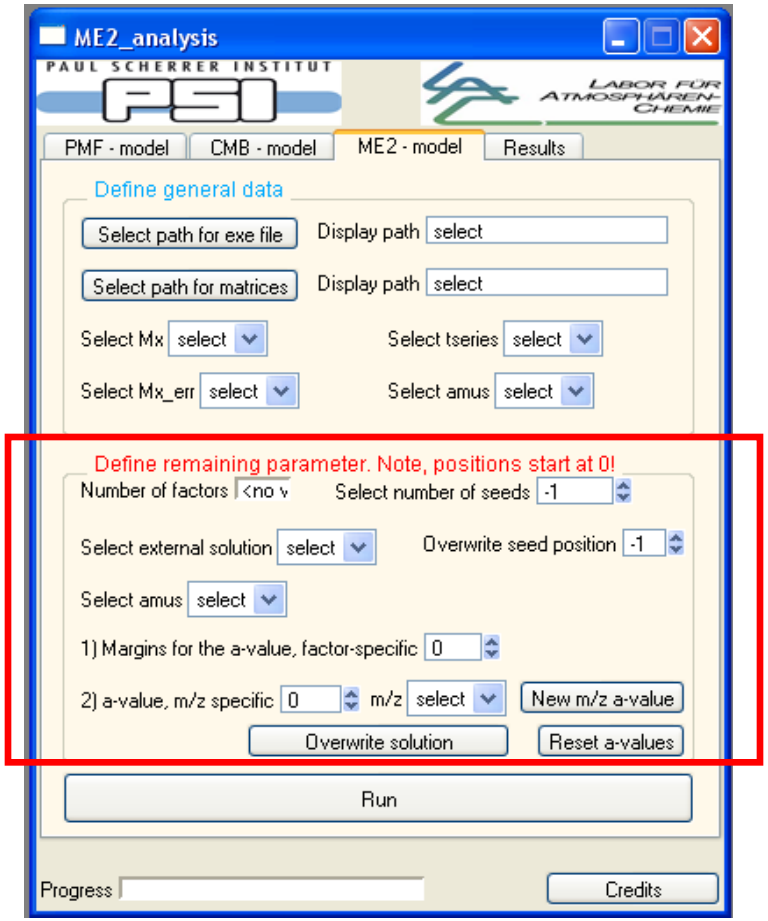
=> Should be implemented, so that the user can choose between e.g., exactly 4 or from 1 to 4 factor sol.

Interface in Igor for the Multilinear engine (Me-2)



Choose nb. of factors, seeds and since it is CMB, overwrite and/or fix factor profiles.

Interface in Igor for the Multilinear engine (Me-2)

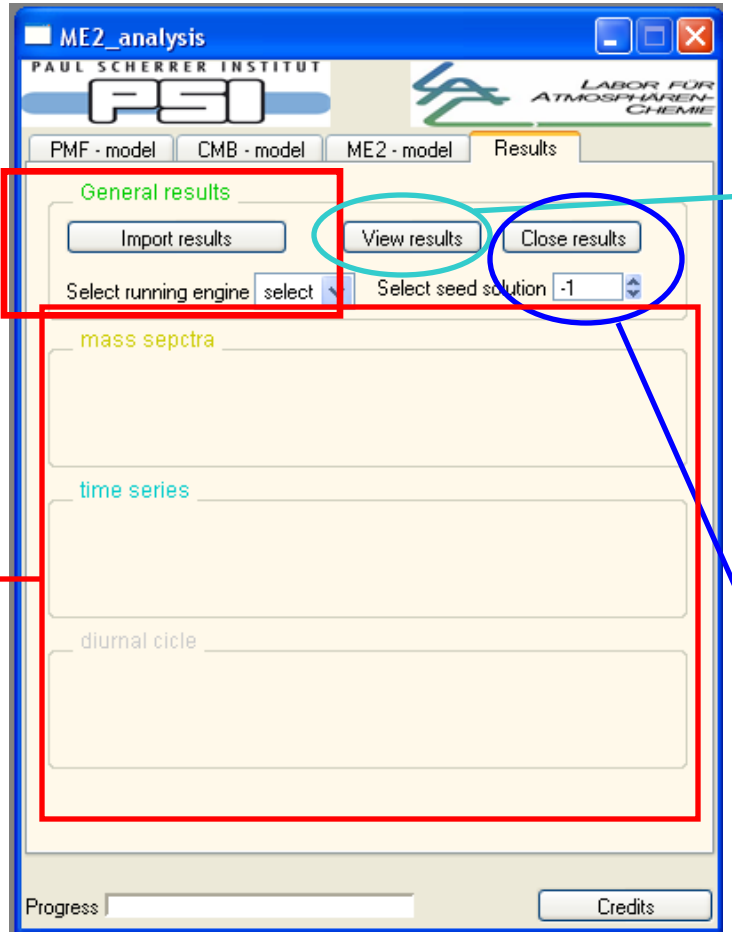


Choose nb. of factors, seeds and since it is ME2, overwrite and/or fix factor profiles and or m/z separately.

Interface in Igor for the Multilinear engine (Me-2)

Read results from the output file in the window hierarchy

Here it will be possible to plot and correlate the factor solution (time series, mass spectra, diurnal) together with ext. information.

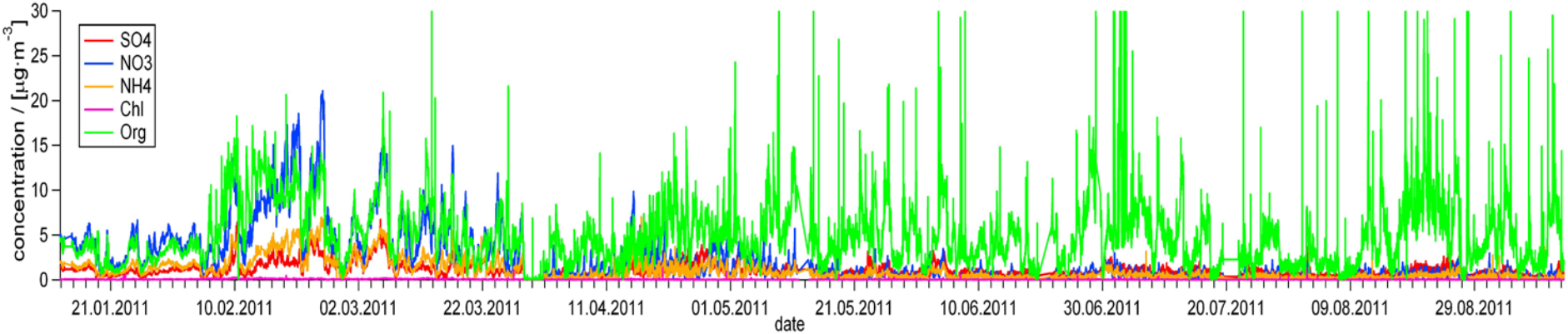


General plots, like time series, diurnal cycle, mass spectra, total Resid and residual based on m/z, time series and diurnal

Choose which seed solution should be visualized

ACSM in Zurich

- time series



Possible applications

- Locations where you know there should be a certain source but PMF fails. (This can be e.g. due to high correlation of components or low contribution)
- You have several stations during a campaign and a certain source you can only resolve at one station
- You do single particle measurements and find a certain type of particle with cluster analyses but it does not show up in the PMF solution
- Exploratory analyses (e.g. test if cooking could be present by prescribing it and look at diurnal cycle)