# Error Diagnostic Panel Demonstration

# ToF-AMS HR Analysis 1.10H

PIKA module for SQUIRREL 1.51 or higher

Version Websit | FAQs, Website | Upgrade Pika | Credits

Todo waves: smalldoto

Set Up HR Fits | HR Ion Groups | HR Fits One Spectra | HR Fits for Many Runs | HR Re

**Step 6i: Describe characteristics of HR results you want to generate.**

List of entities to generate

HR ions, families, and/or species (i.e. j15N,familyNH,HR ir): HROrg

* The RIE and CE for HR ions and HR families is 1 (

Integer m/z 69 | < Add HR ion to list of entities | family CH | < Add HR ions to list of entities

Set list to all HR species | Set list to aerosol HR species | Set list to all HR families | Clear list

Data Output Options

Data: Diff | Graph output: Plot single | Convert to μg/m3 * | Use MS AB correction | Calc, plot err. HRTotalOMinusClonCountErr

Ask for wave name suffix | Convert nan sticks to 0 | Convert neg. sticks to 0

**Step 6ii: Select the time series or average mass spectra type of result to generate.**

Sq vs Pk Species: Calc & display Sq vs Pk panel

Time Series: Calculate

Diurnal Time Series: whiskers Initialize | Calc diurnal trends

Elemental Time Series Ratios for HROrg: Calculate | Diurnal | H/C 0.910 | N/C 0.960 | O/C 0.750 | S/C** 1.000

**Not measured/published. Caution!

Avg Mass Spectrum: Sum to UMR | Stack sticks in graph | Normalize spectra (sum=1) | Calculate

Specialty Average Mass Spectrum: Single HR specie family-colored UMR graph | All aerosol HR species 5-axis family-colored UMR graph

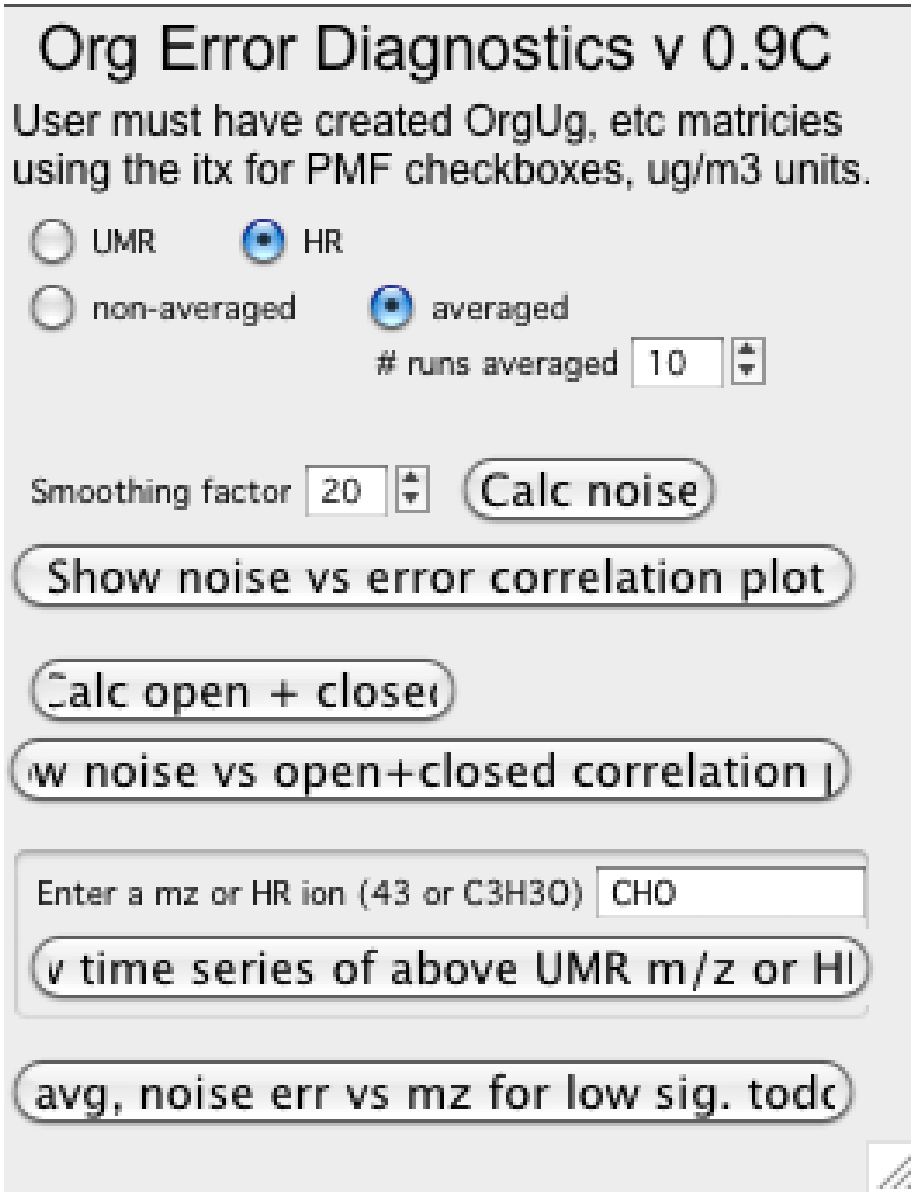
Elemental Mass Spectrum: Separate y axes for each elem. (only for 'plot single' option) | Elemental avg mass spectrum of HROrg

Export for AMS HR database | Main families 5-axis UMR graph (fitted HR ions only)

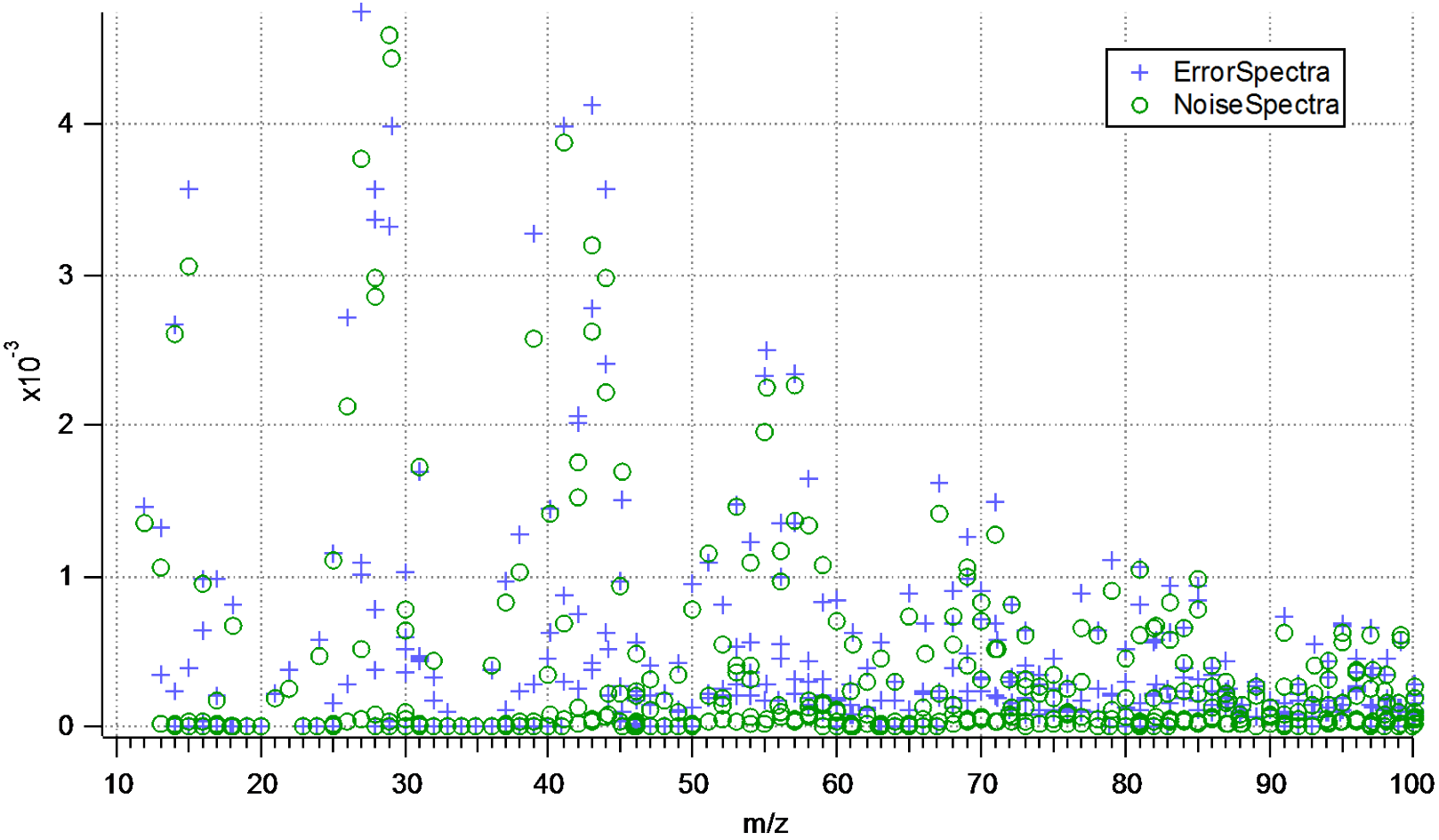
2-d Time Series Mass Spectra (HR input for PMF): Time series spectra (2d matrix, not plotted, leave list blank for all HR ions) | itx for PMF

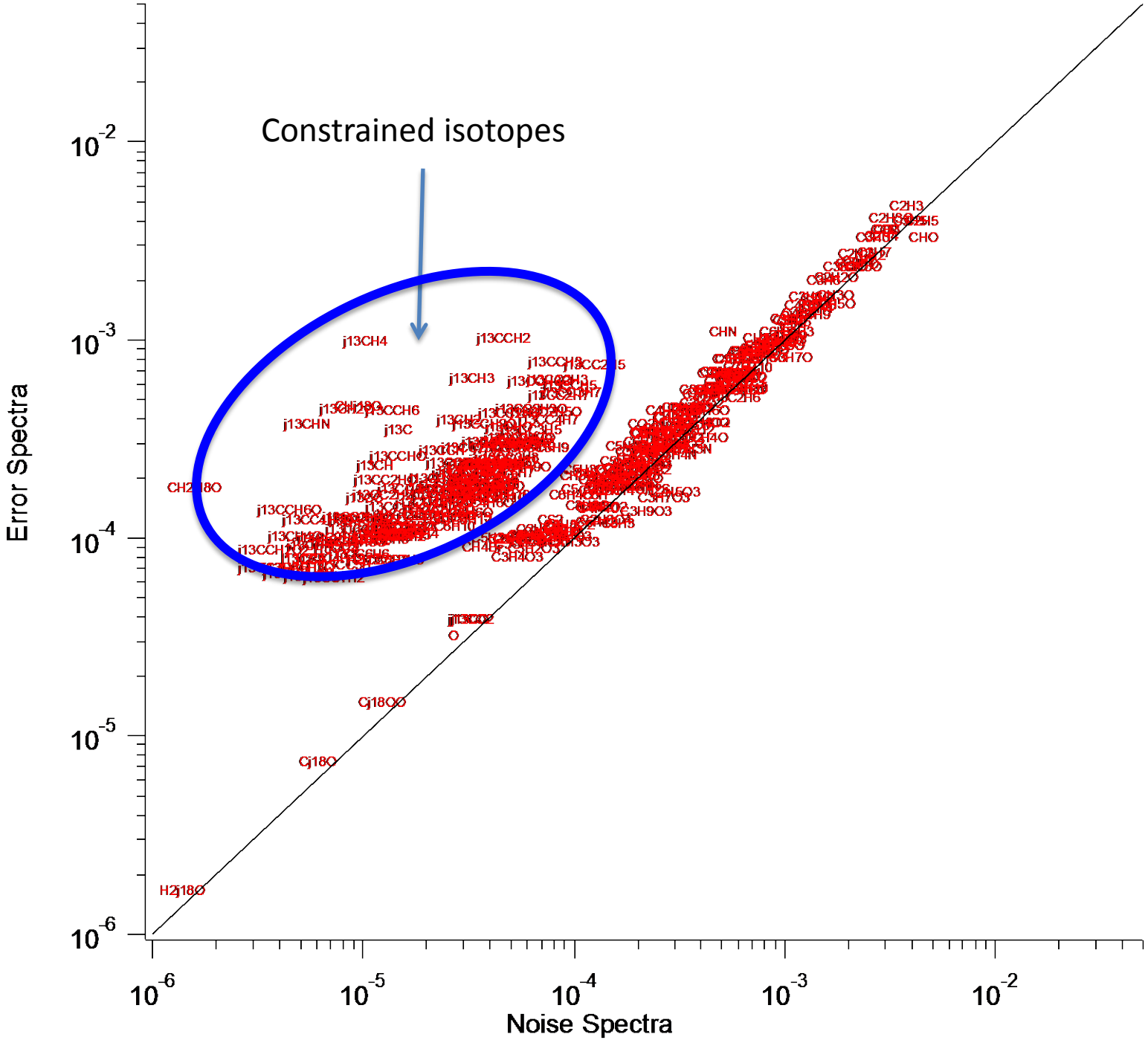
Useful Tables for Current Todo Wave: Fitted HR ions | ions for all HR species c | HROrg atomic mass fraction table

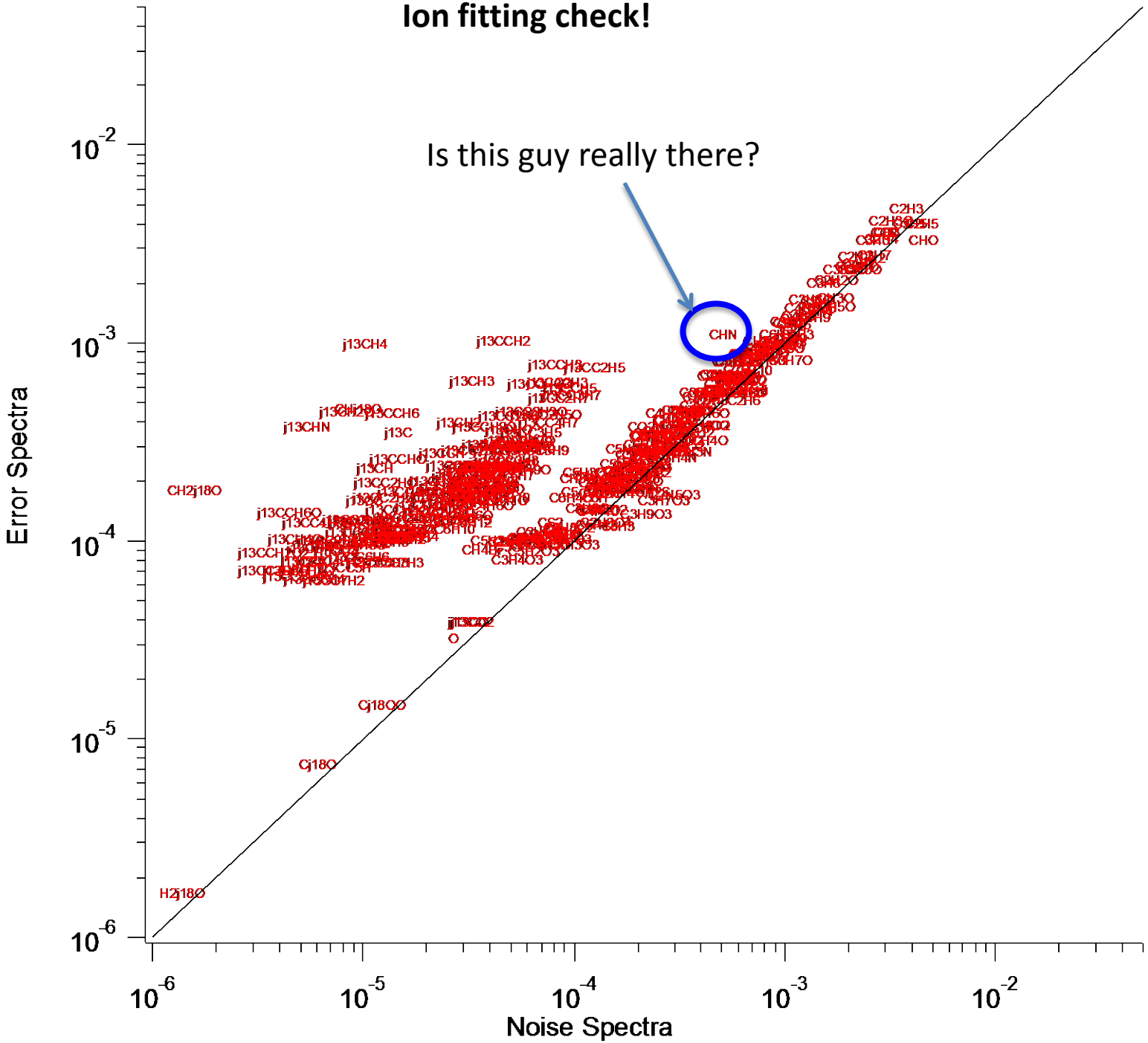
Load Error_Diagnostics_V0_9C.ipf into your PIKA to get this panel:

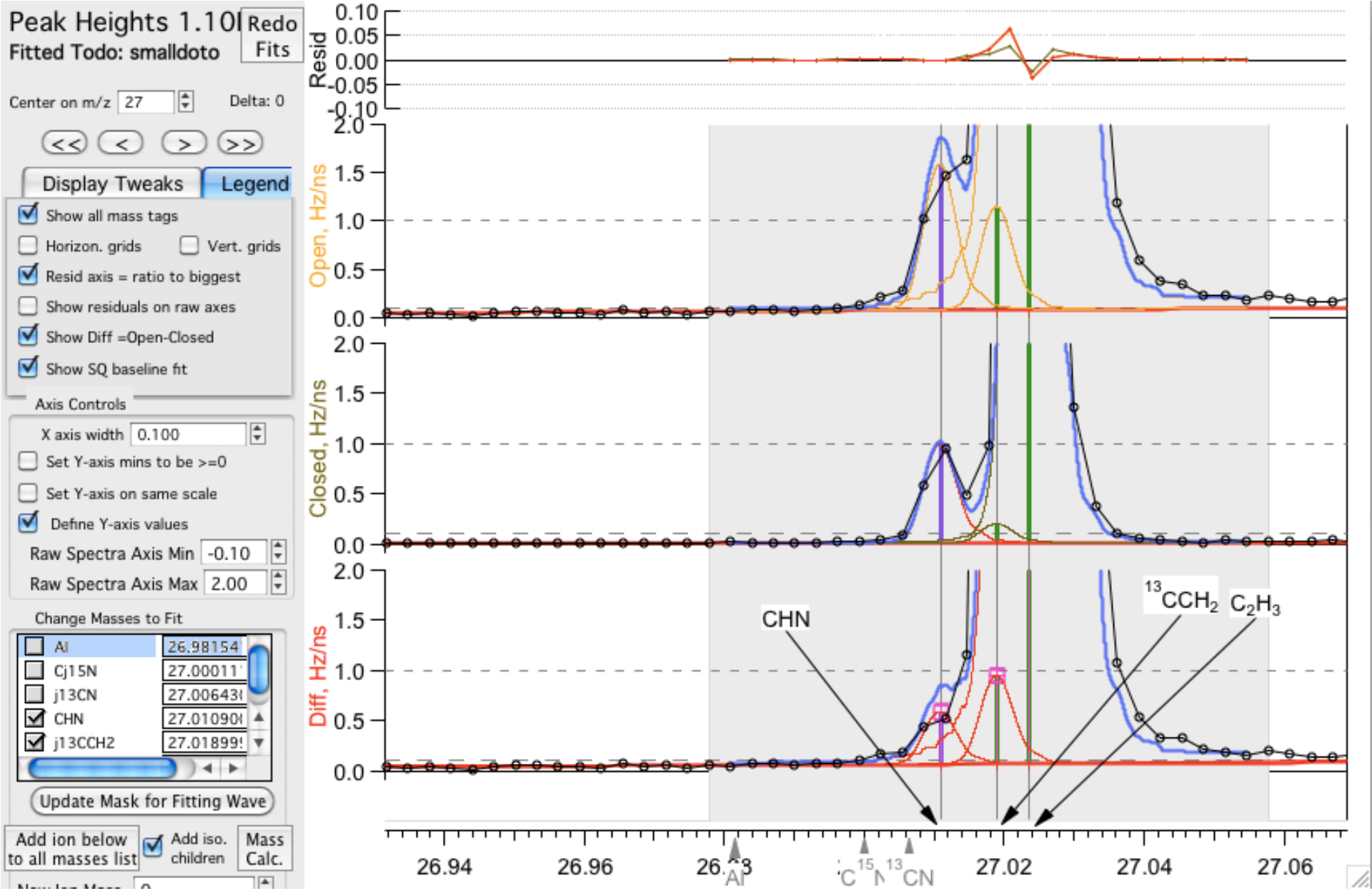



**Go to Demonstration**


ErrorSpectra
NoiseSpectra
x10^-3
0
1
2
3
4
10
20
30
40
50
60
70
80
90
100
m/z

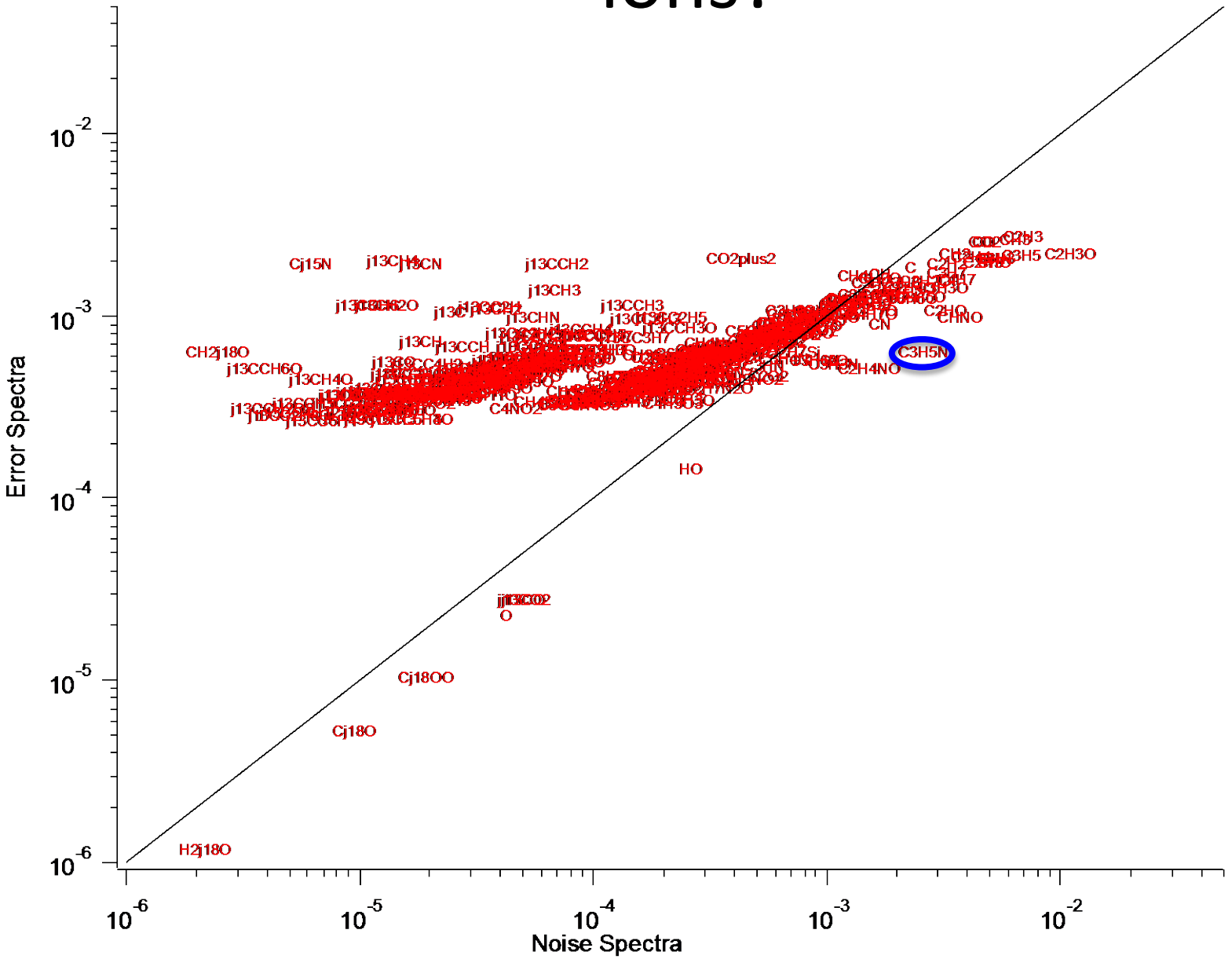

Constrained isotopes
Error Spectra
Noise Spectra
$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
$10^{-6}$
$10^{-6}$
$10^{-5}$
$10^{-4}$
$10^{-3}$
$10^{-2}$
j13CH4
j13CCH2
j13CH3
j13CHN
j13C
j13CH
CH2j18O
H2j18O
Cj18OO
Cj18O
CHN
CHO

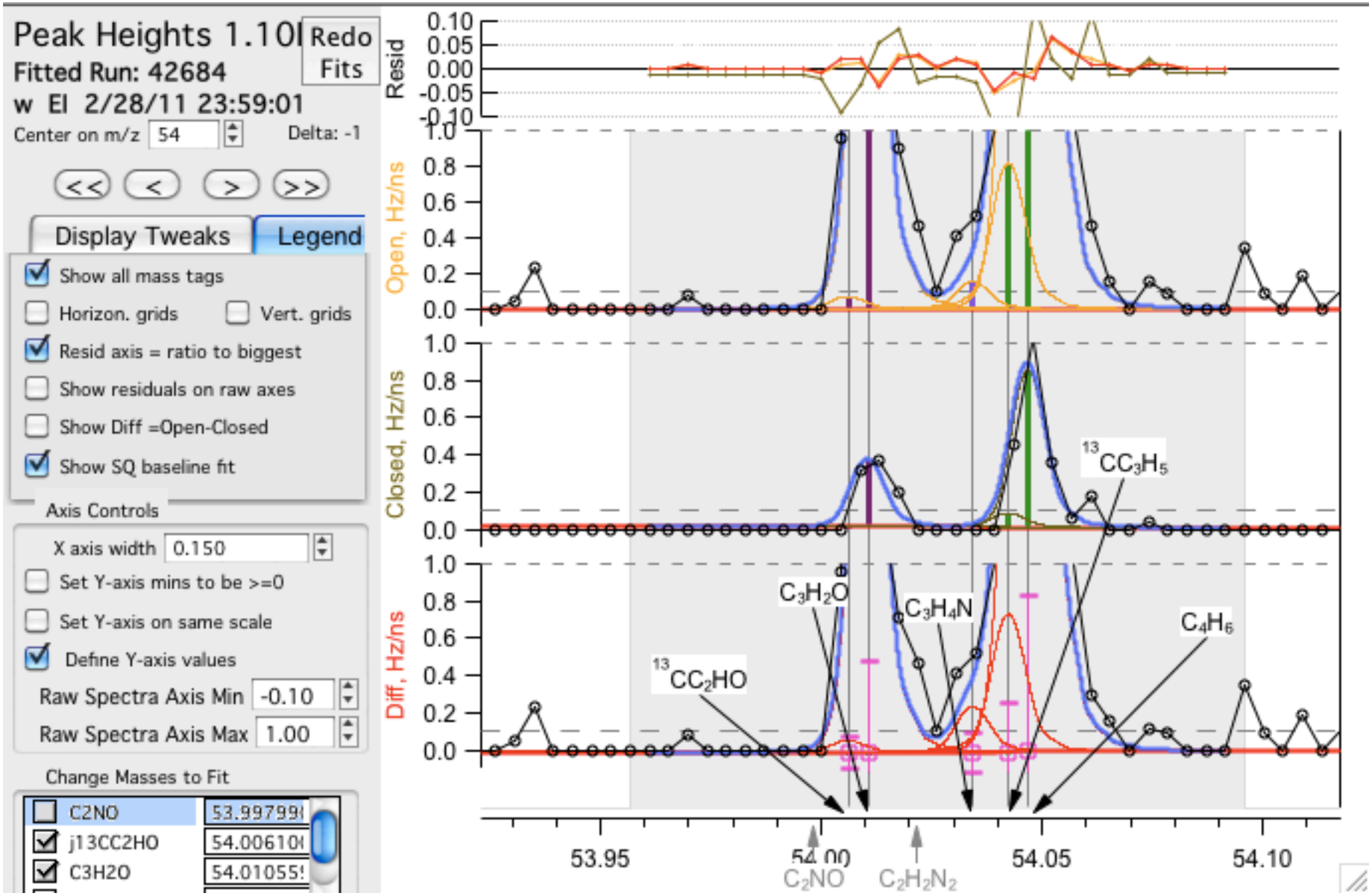

Ion fitting check!
Is this guy really there?
CHN
Error Spectra
Noise Spectra
$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
$10^{-6}$
j13CH4
j13CCH2
j13CH3
j13CHN
j13C
CH2j18O
Cj18OO
Cj18O
H2j18O
CHO



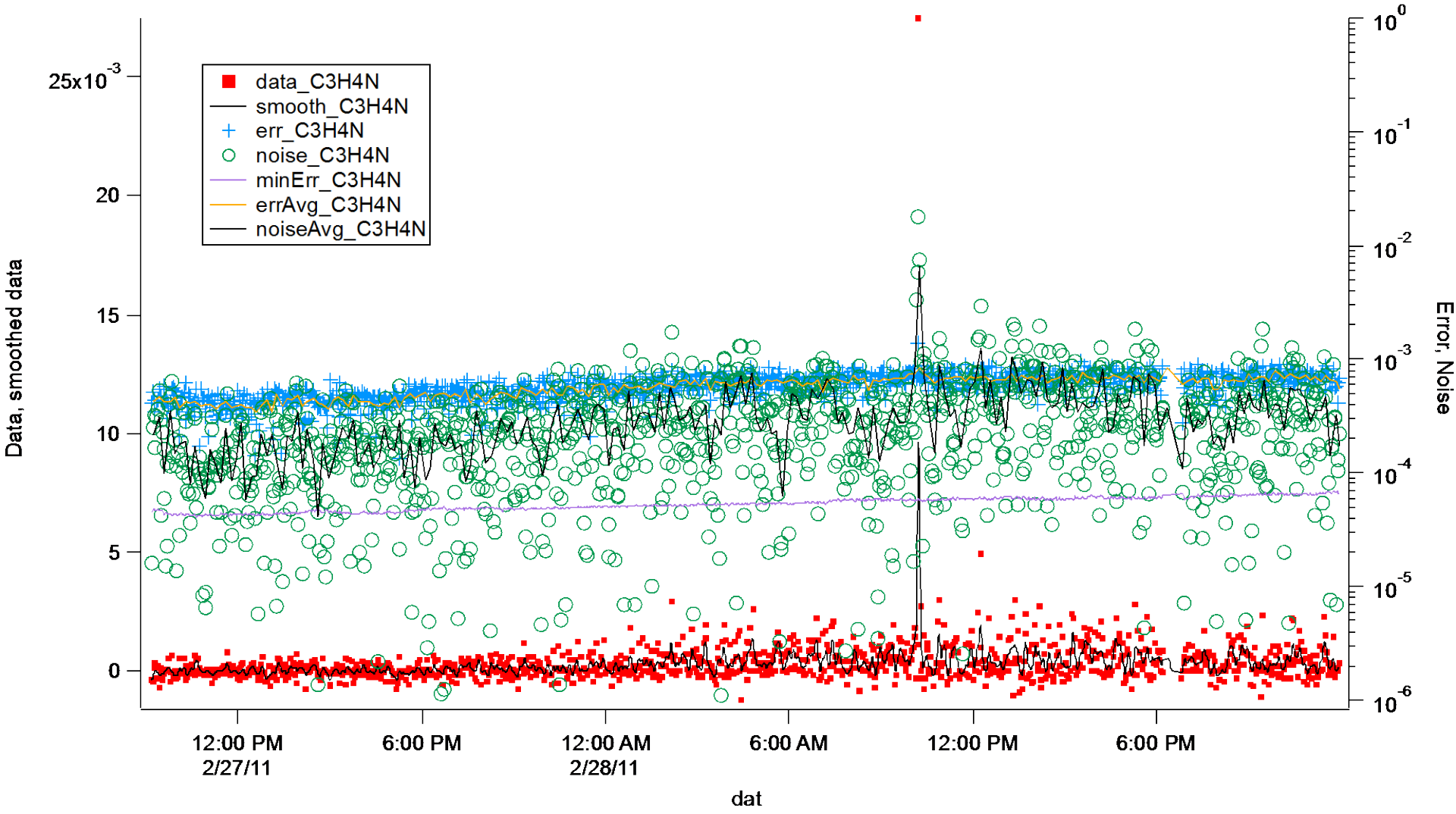

Yea, he's maybe there but need to **refine peak width and peakshape**

# What happens when you fit too many ions?

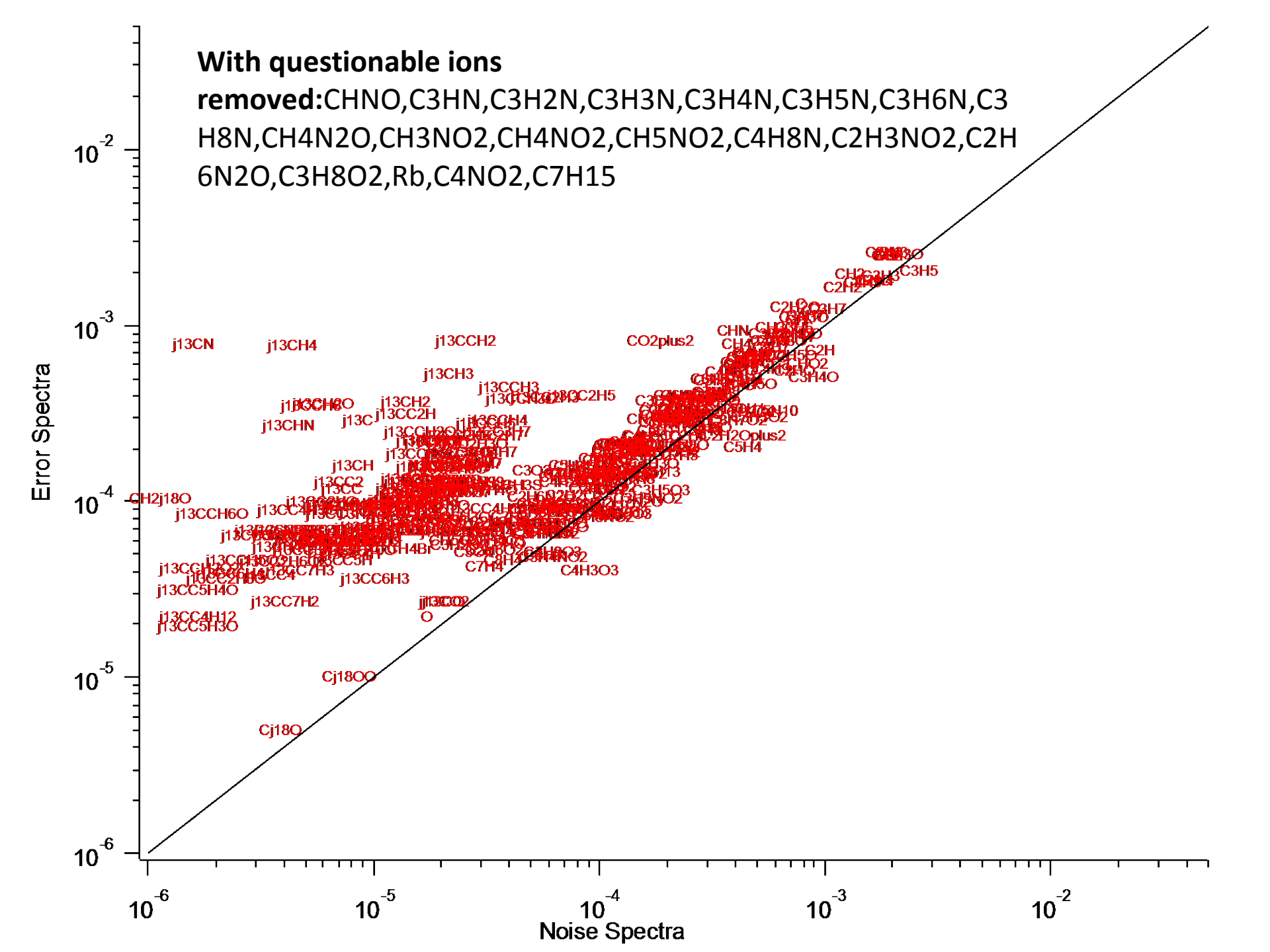





**Maybe it is there? But it is hard to quantify in this case.**




Either way its very small, and error is above noise, probably don't include in PMF


With questionable ions removed:CHNO,C3HN,C3H2N,C3H3N,C3H4N,C3H5N,C3H6N,C3H8N,CH4N2O,CH3NO2,CH4NO2,CH5NO2,C4H8N,C2H3NO2,C2H6N2O,C3H8O2,Rb,C4NO2,C7H15
Error Spectra
Noise Spectra
$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
$10^{-6}$
j13CN
j13CH4
j13CCH2
CO2plus2
j13CH3
j13CCH3
j13CH2
j13CC2H
j13CHN
j13CH
j13CC2
j13CC
CH2j18O
j13CCH6O
j13CC6H3
j13CC5H4O
j13CC7H2
j13CC4H12
j13CC5H3O
Cj18OO
Cj18O
C5H4
C3H4O
C3H5
C4H3O3
C7H4

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

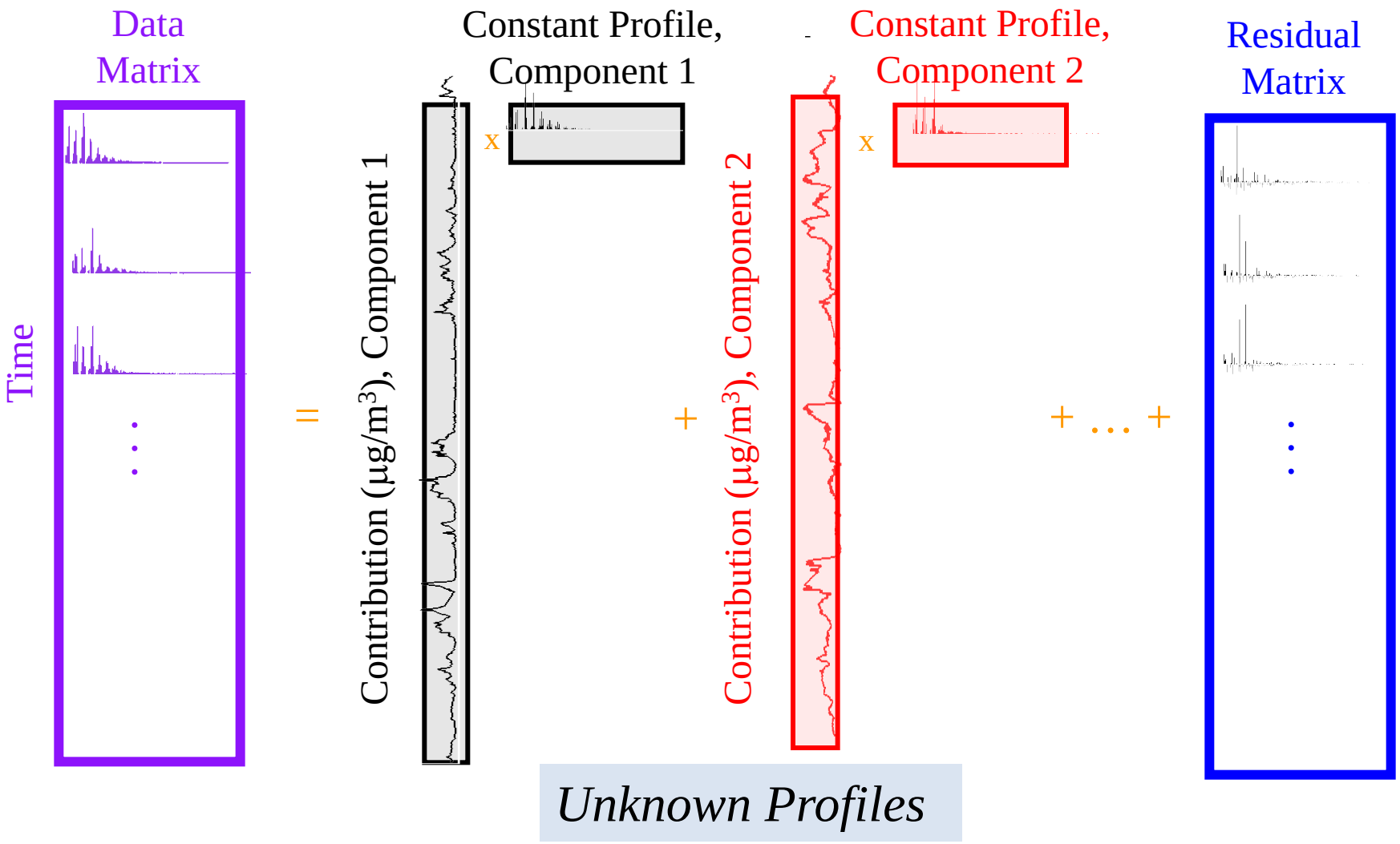



Figure courtesy of Ingrid M. Ulbrich of University of Colorado Boulder

# Quality of Fit

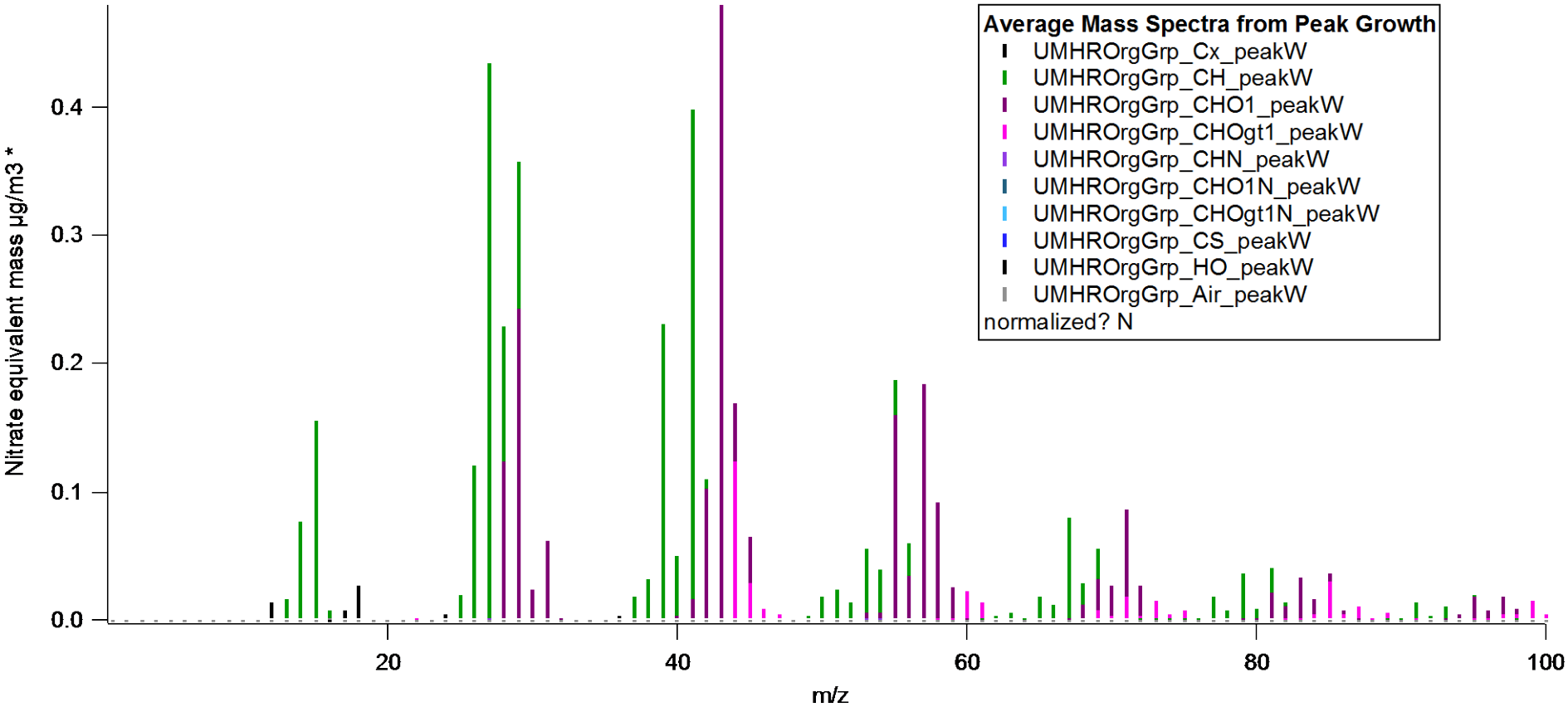
$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij} / \sigma_{ij})^2$$

- $e_{ij}$ is the element of the **residual matrix** for each data point
- $\sigma_{ij}$ is the element of the **estimated error** for each data point

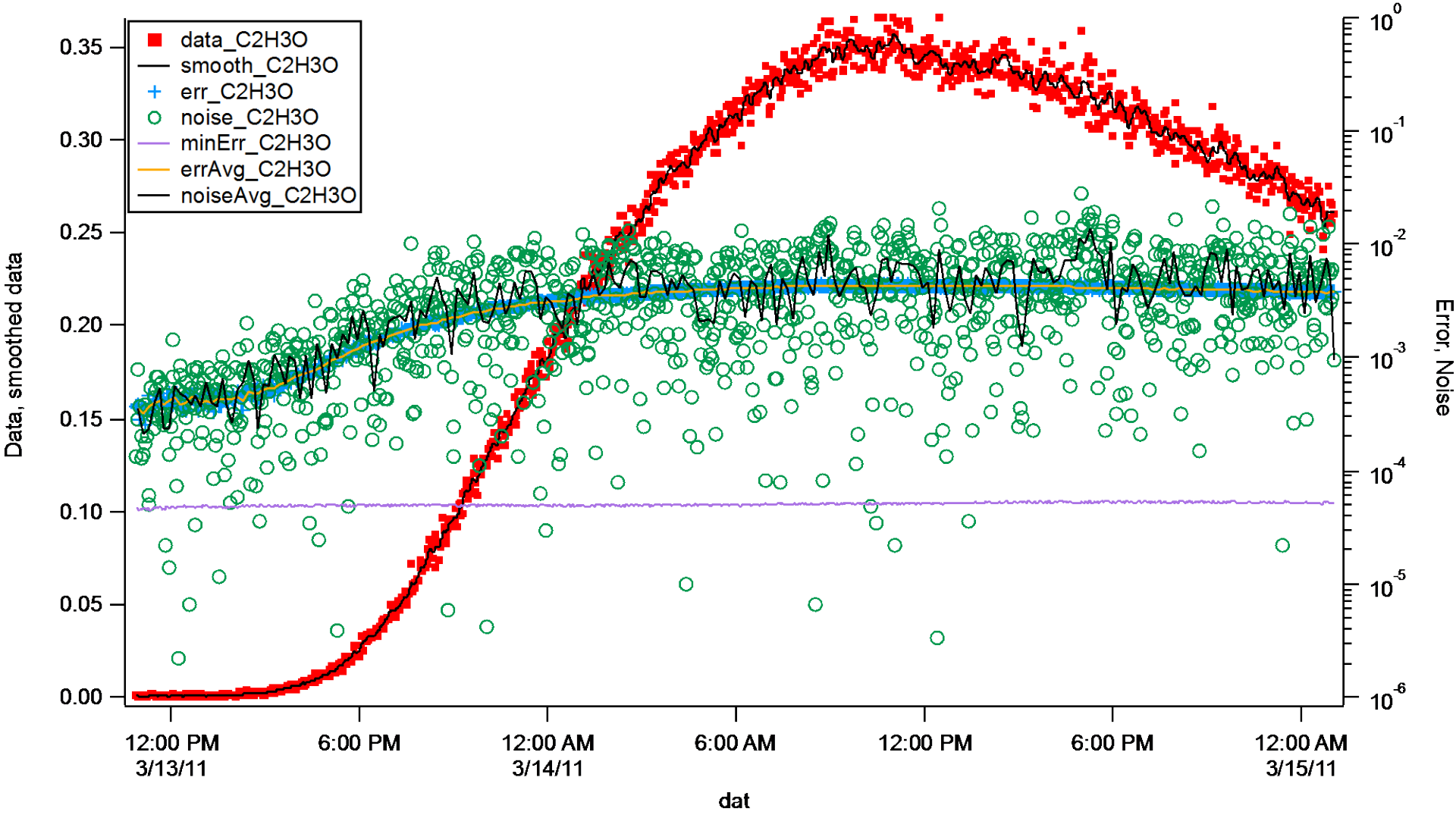
Goal is to minimize Q,

but it's not the only diagnostic!

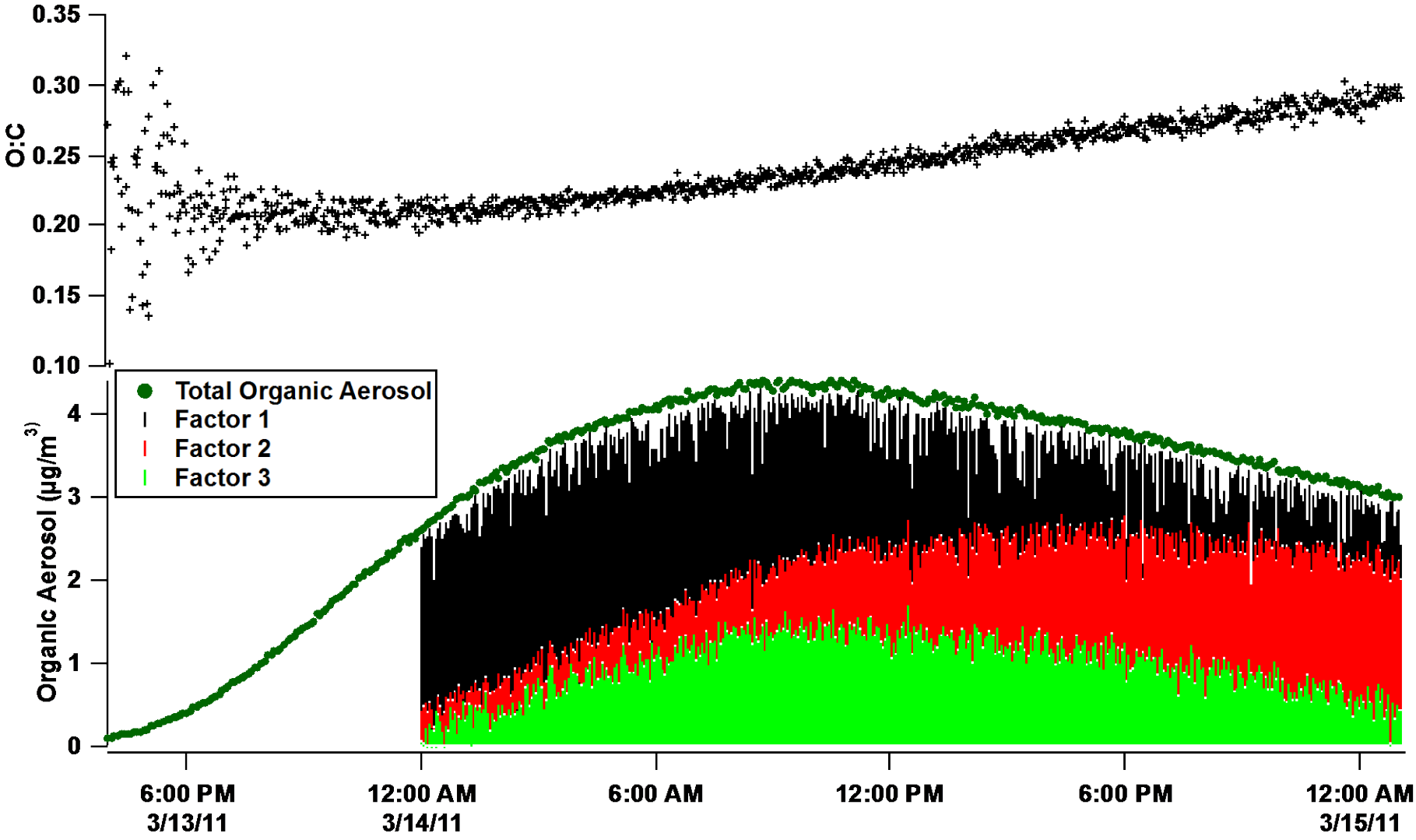
# Start out analyzing errors from most abundant ions



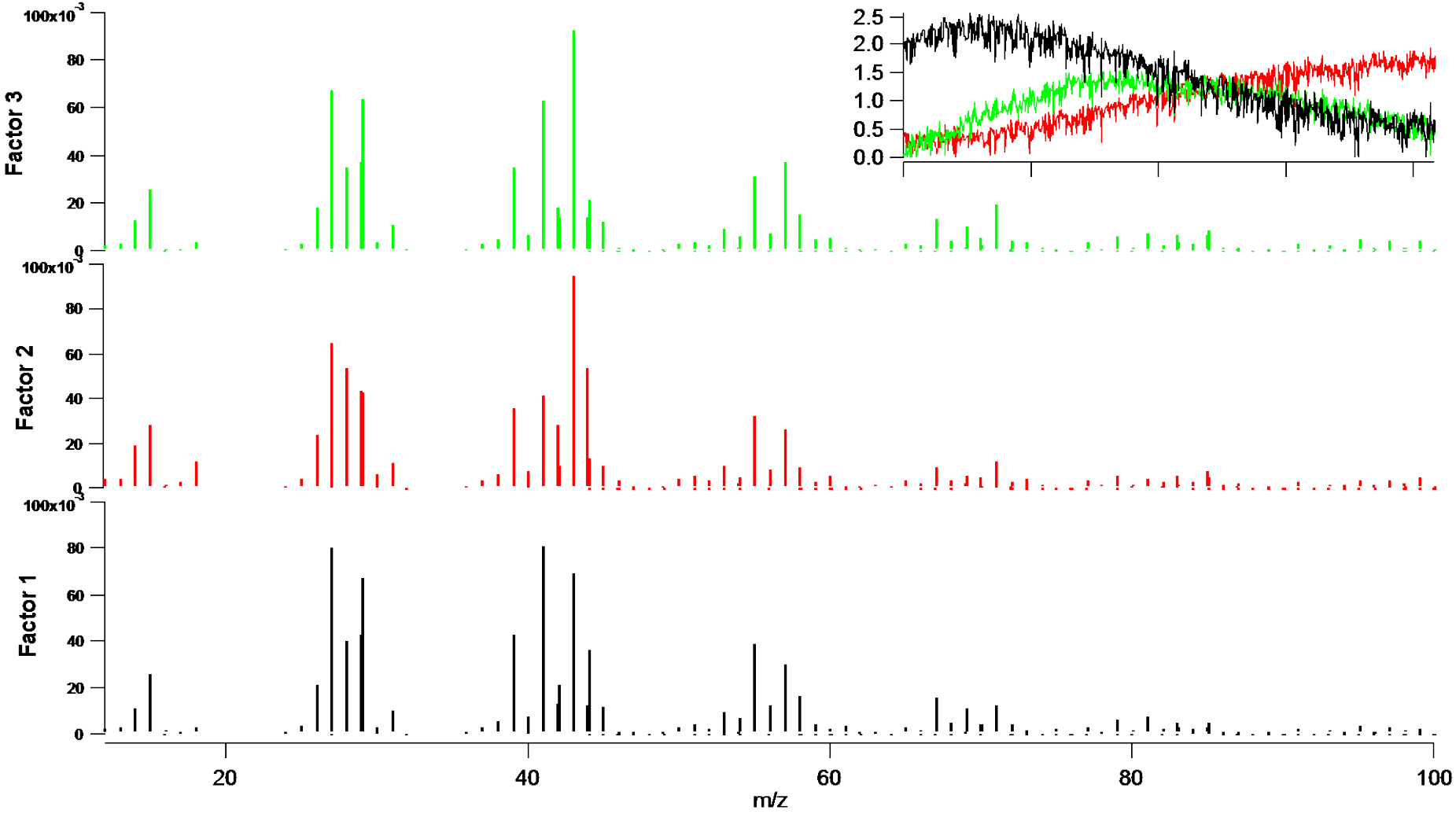
Use this graph to help you determine which ions you may consider removing from PMF (ie small signal ions that are not quantified well).



# Dodecane Low NOx Chamber SOA Experiment PMF Results



# Positive Matrix Factorization: Dodecane Low NOx Factor Profiles

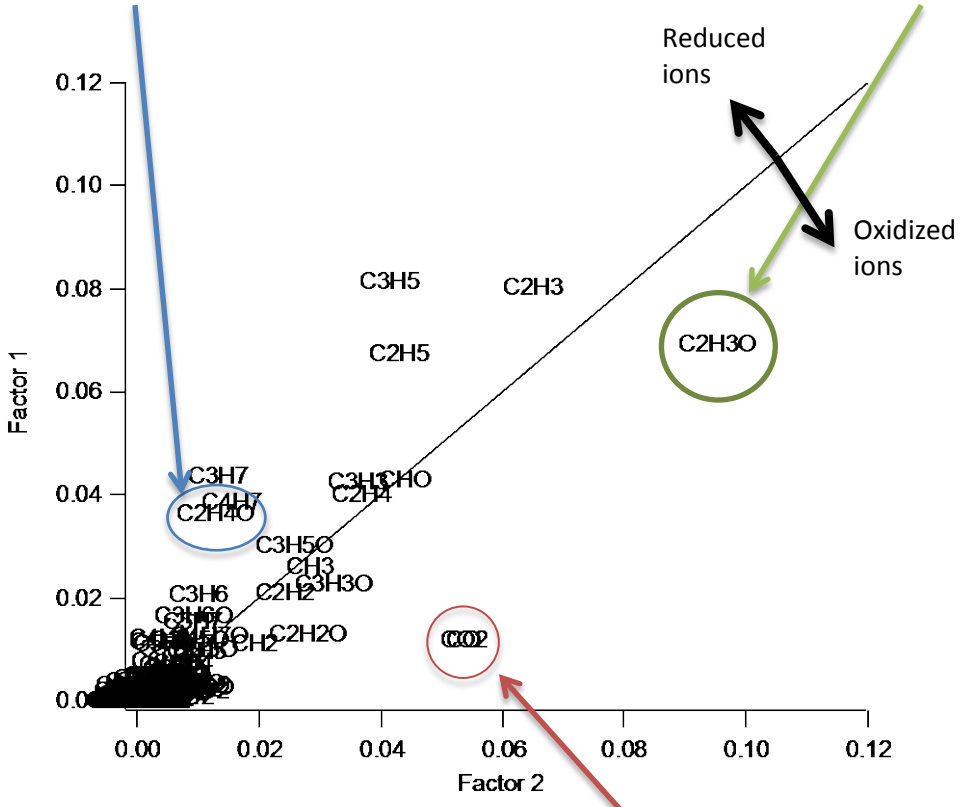


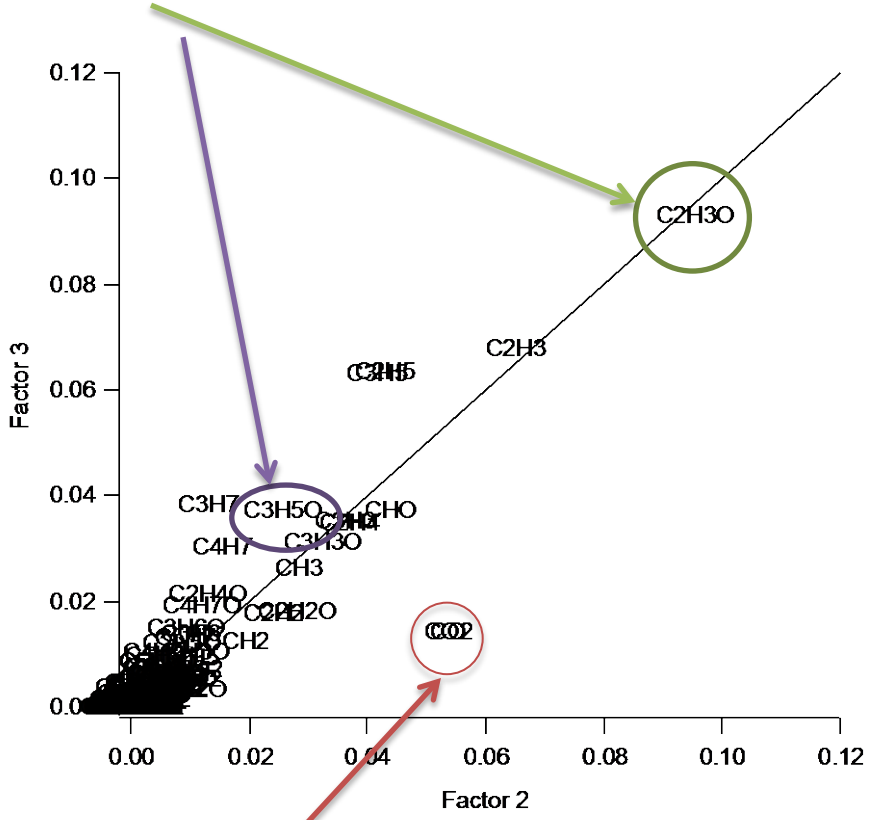

- Factors are expected to be very similar since they are born from the same parent hydrocarbon (as apposed to distinct sources in the atmosphere)

# Positive Matrix Factorization: Dodecane Low NOx Factor Profiles

More reduced ion at m/z 44

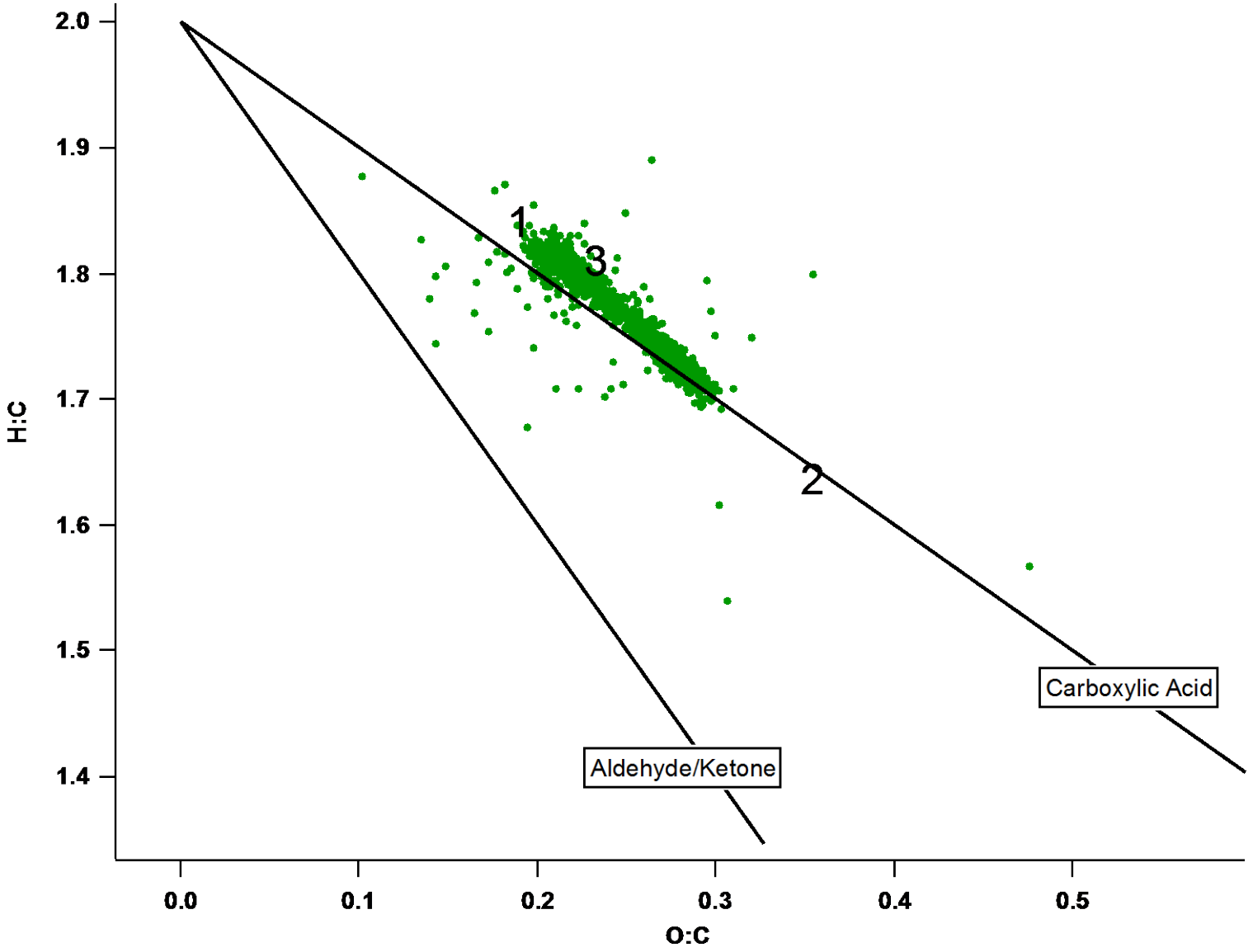
Nonacid oxygenate tracer



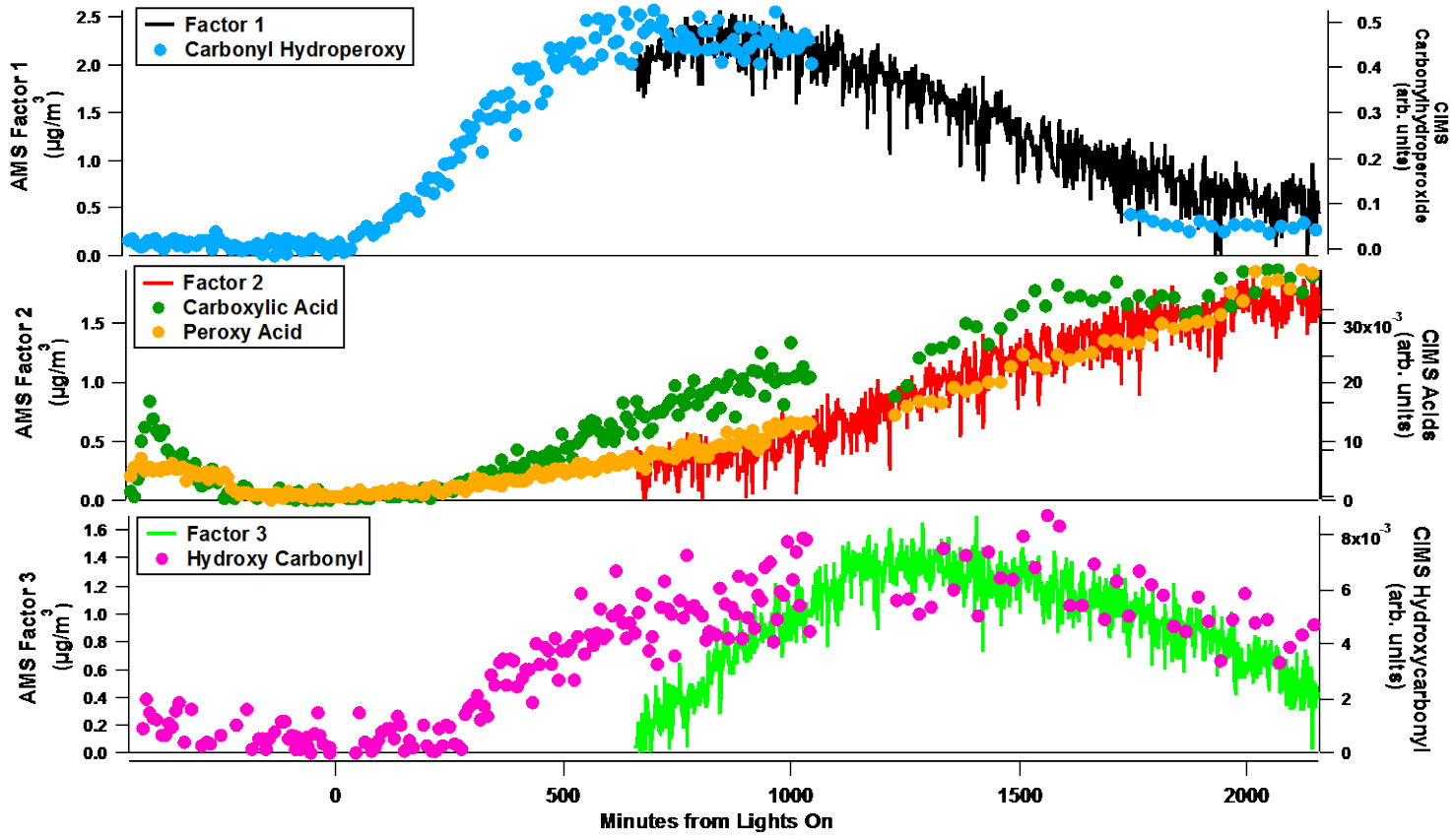

Carboxylic acid tracer

# Factors on Van Krevlen Diagram



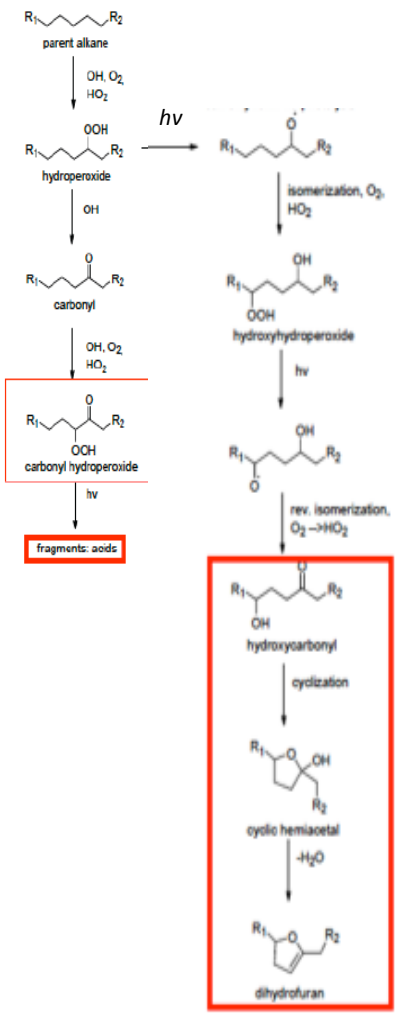

- Make sure your ions in PIKA and PMF are the same to compare on VK Diagram!
- Use EA light ipf to calculate O:C and H:C for PMF Factors

# Positive Matrix Factorization: Comparison with Q-CIMS gas phase data

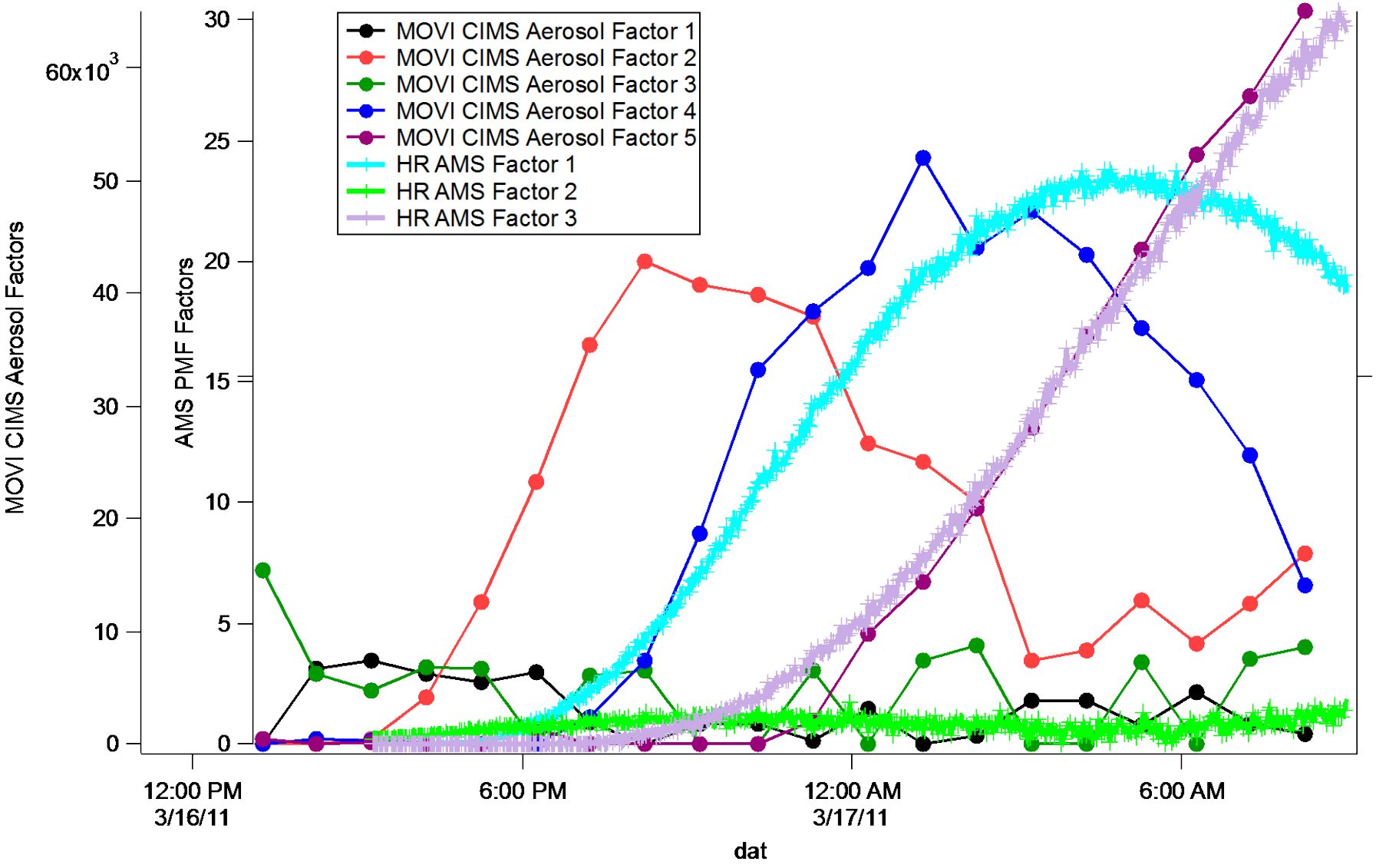



## Gas Phase Mechanism

Yee et al. in Prep



# AMS and MOVI-CIMS Aerosol Data PMF Comparison



# The End