<u>Aerosol PTR-MS</u> measurements during CalNex, Pasadena ground site

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<u>Outline</u>

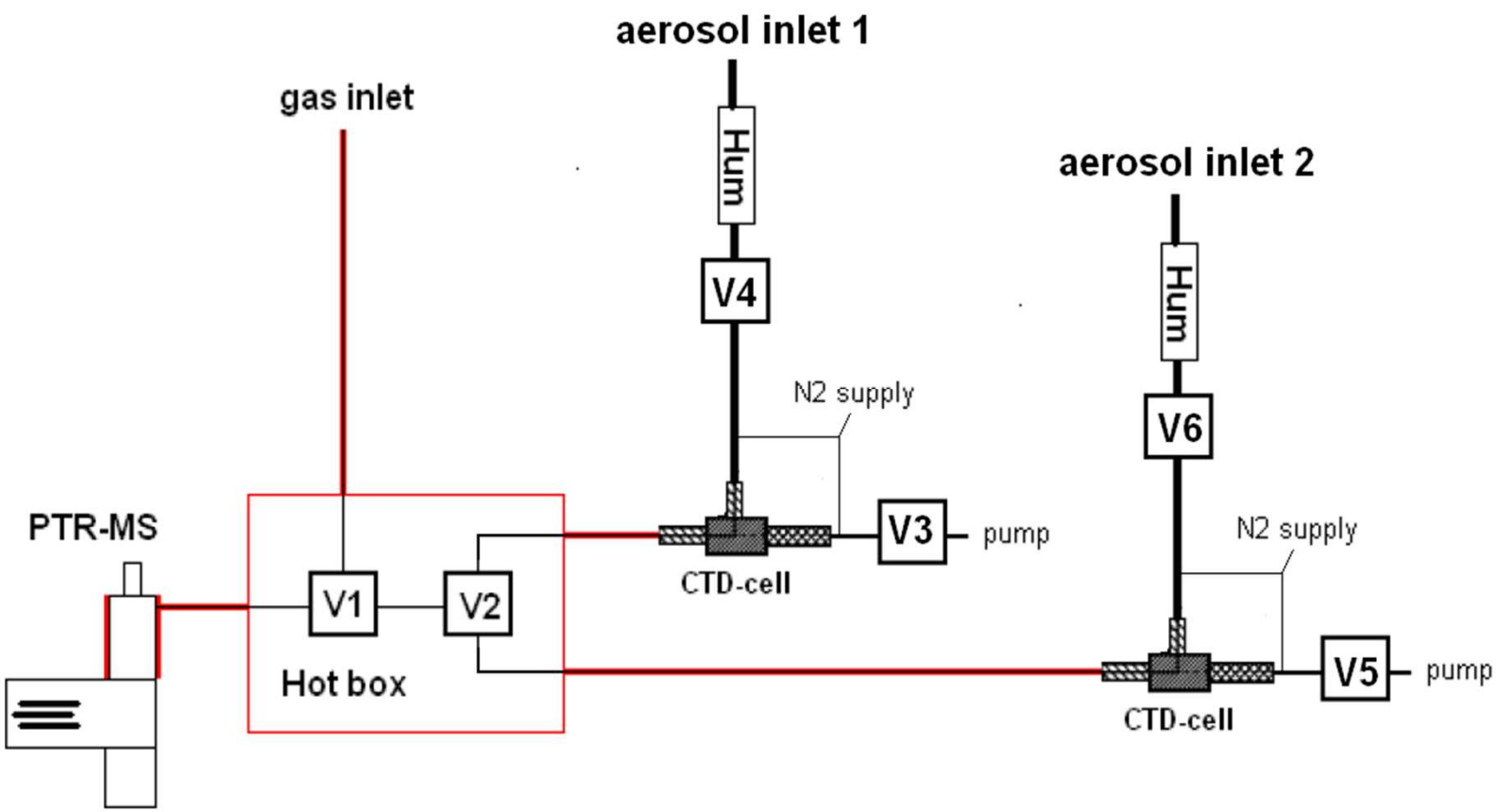
→Instrument

→Field operation & data processing

→Results

The instrument:

High-mass-resolution Thermal-desorption Proton-transfer-reaction Mass-spectrometer (hr-TD-PTR-MS)

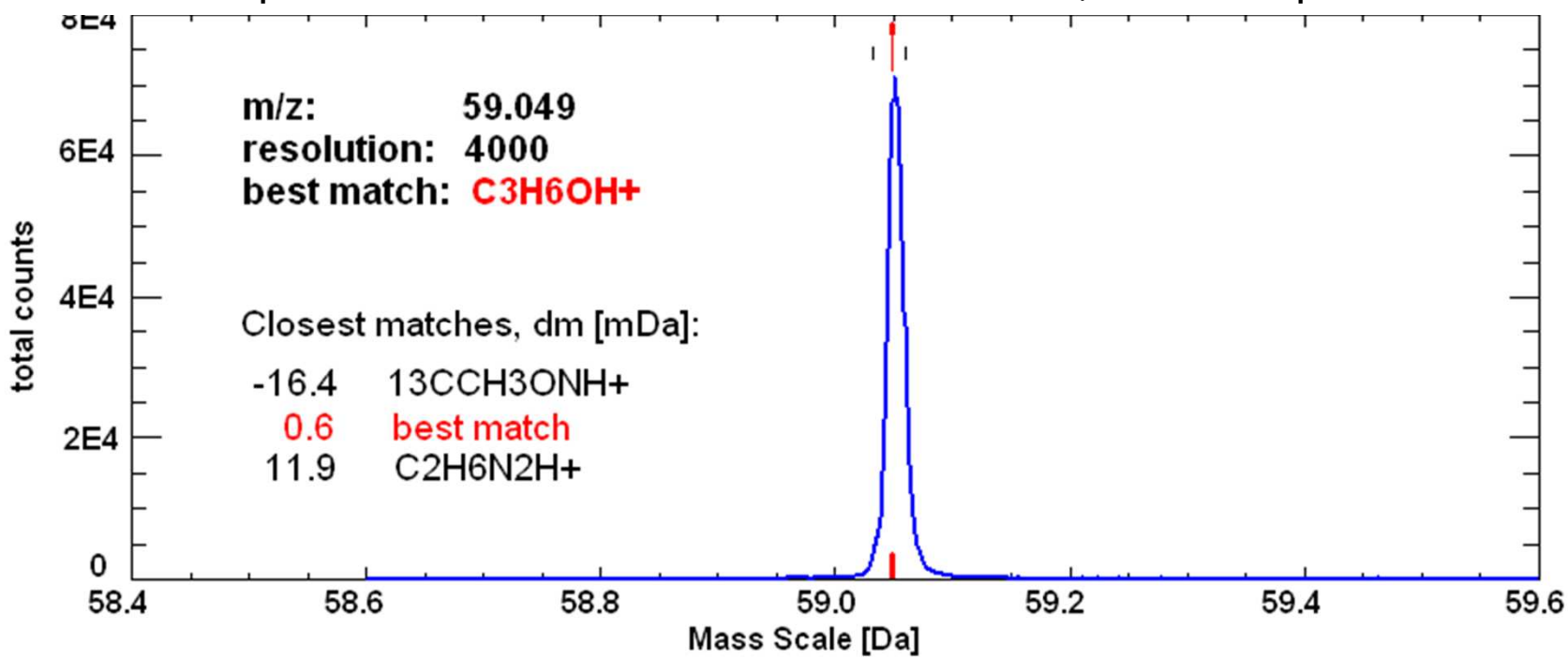


Field Operation and Data Evaluation:

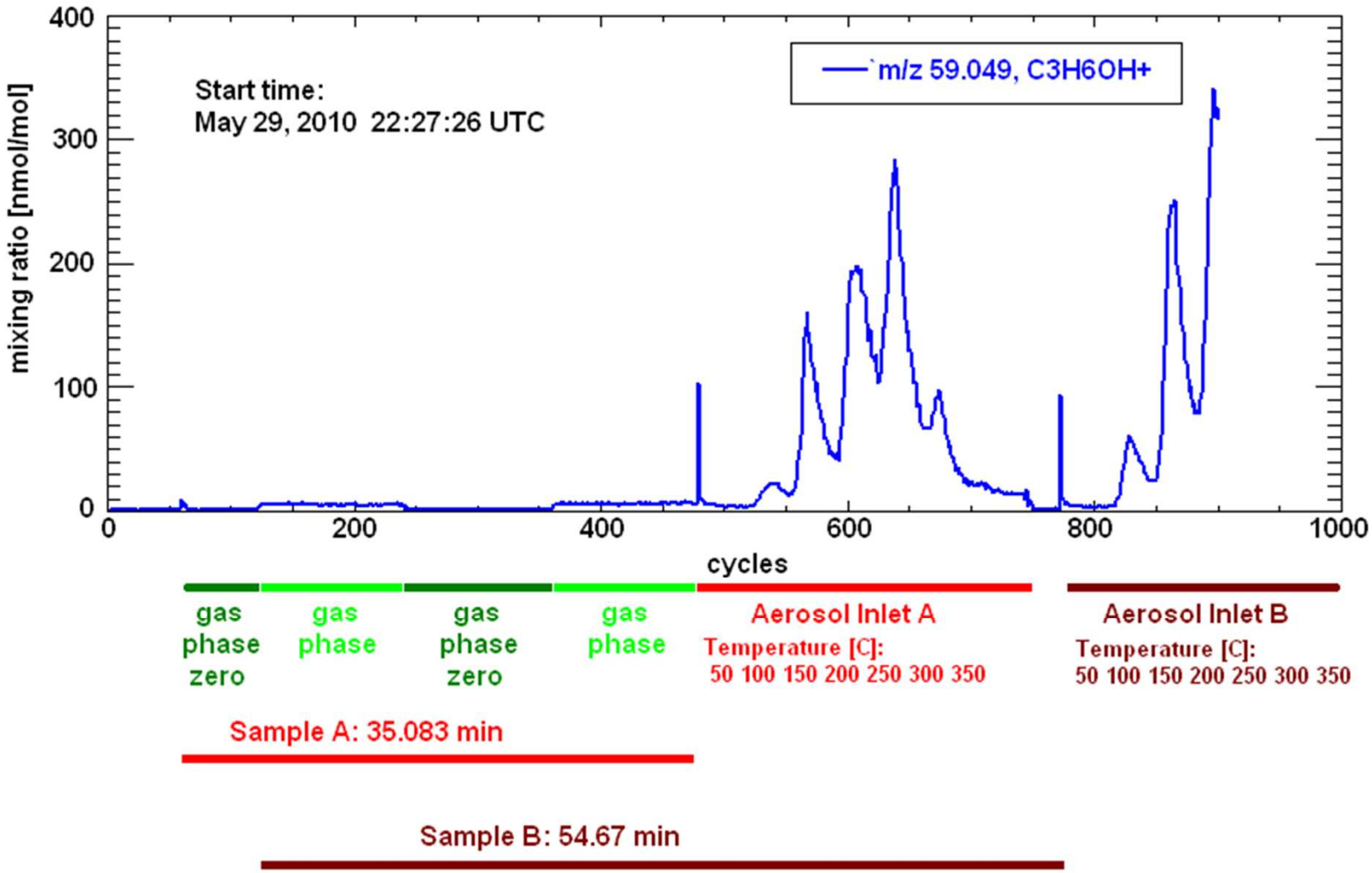
Data structure:
→Full mass scan (10-1200 Da) every 5 seconds
→Data files saved every 900 cycles, i.e. 1h 15 min.
→**496 data files collected**

FIRST STEP, initial file evaluation:
→mass scale calibration,
→peak detection

SumSpectrum, FILE: 2010.05.29-22h27m26s; Detected peaks : 738



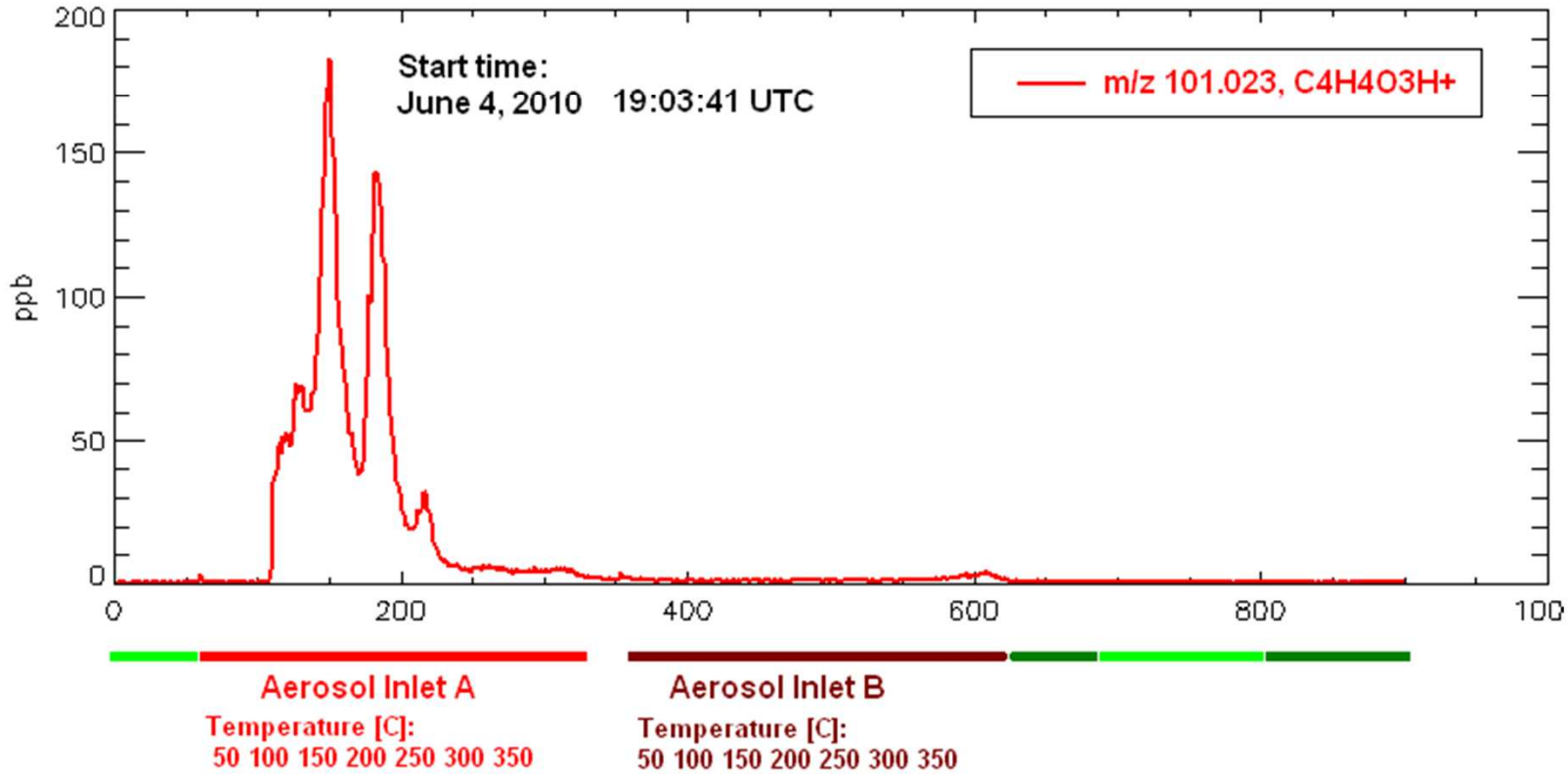
2nd STEP → integrate peak signal → mixing ratio:



→Cycling repeated every 90 min
→Aerosols background every other run

Example, aerosol background:

→Inlet A sampled ambient air
→Inlet B sampled ambient air through Teflon filter



Results:

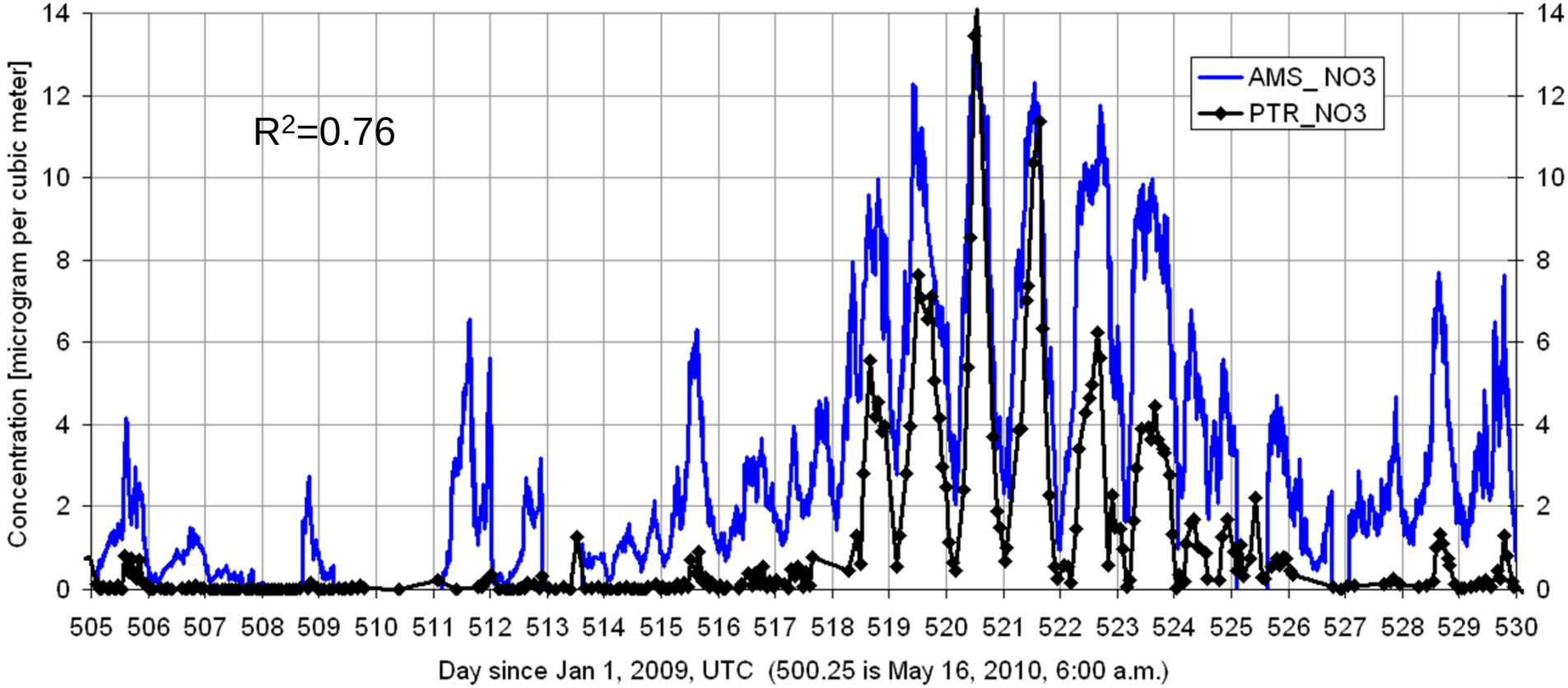
→**Directly comparable to AMS: nitrate and ammonia**

→**Organic constituents**

→**Fraction organic N-compounds**

Nitrate: detected at m/z 47.996 ($^{18}OON^{+}$)

→ Preliminary calibration with ammonium nitrate



We observe:

→Periods with good quantitative and qualitative agreement.

→Periods with good quantitative agreement.

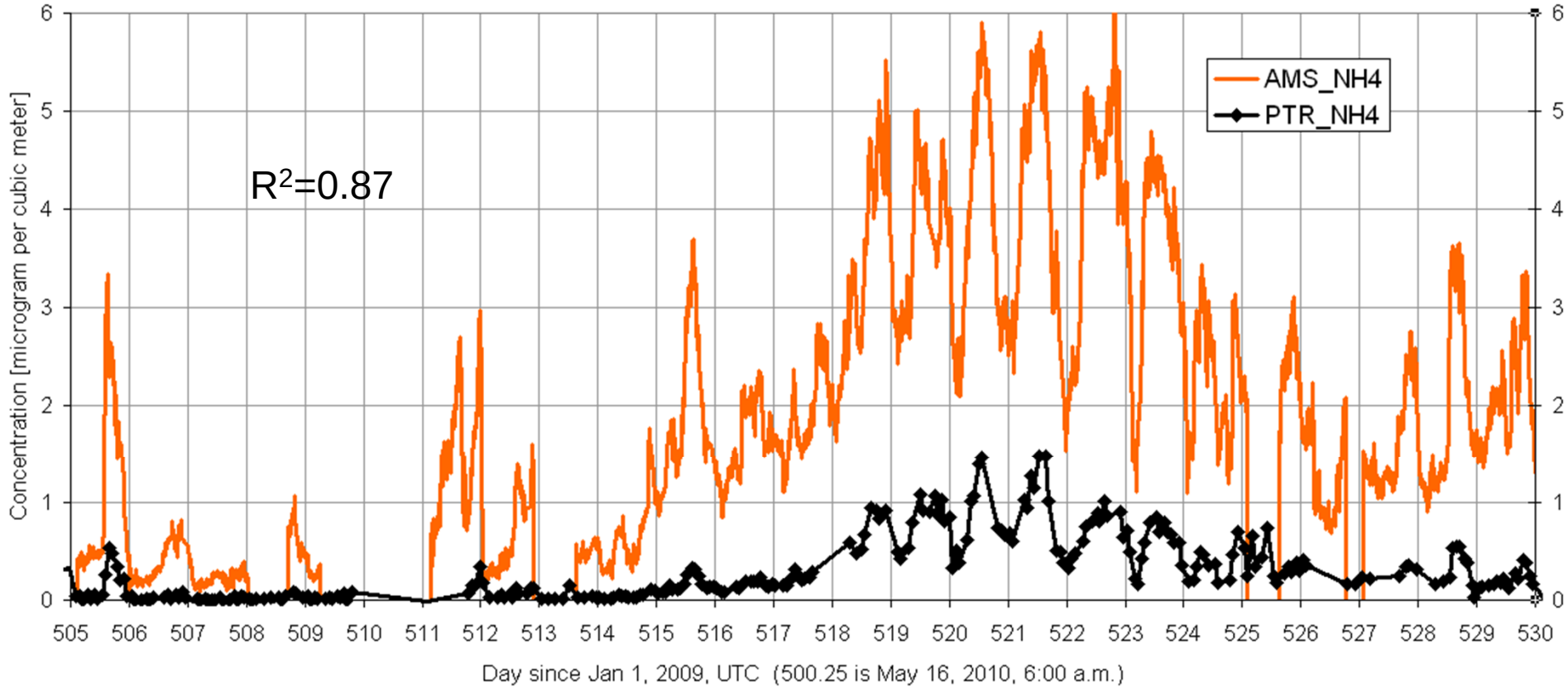
→Periods with no agreement.

Conclusion/Question:

→Is there a yet unknown effect on the CTD cell?

→(Is a major fraction of AMS_NO3 due to organic N species?)

Ammonia: detected at m/z 18.032 (NH_4^+)



Problem for highest concentrations:

→Detector saturated

→ Real signal likely 3-4 times higher

Results & conclusion:

→ Similar as for nitrate

Organics: detected at 724 m/z ratios

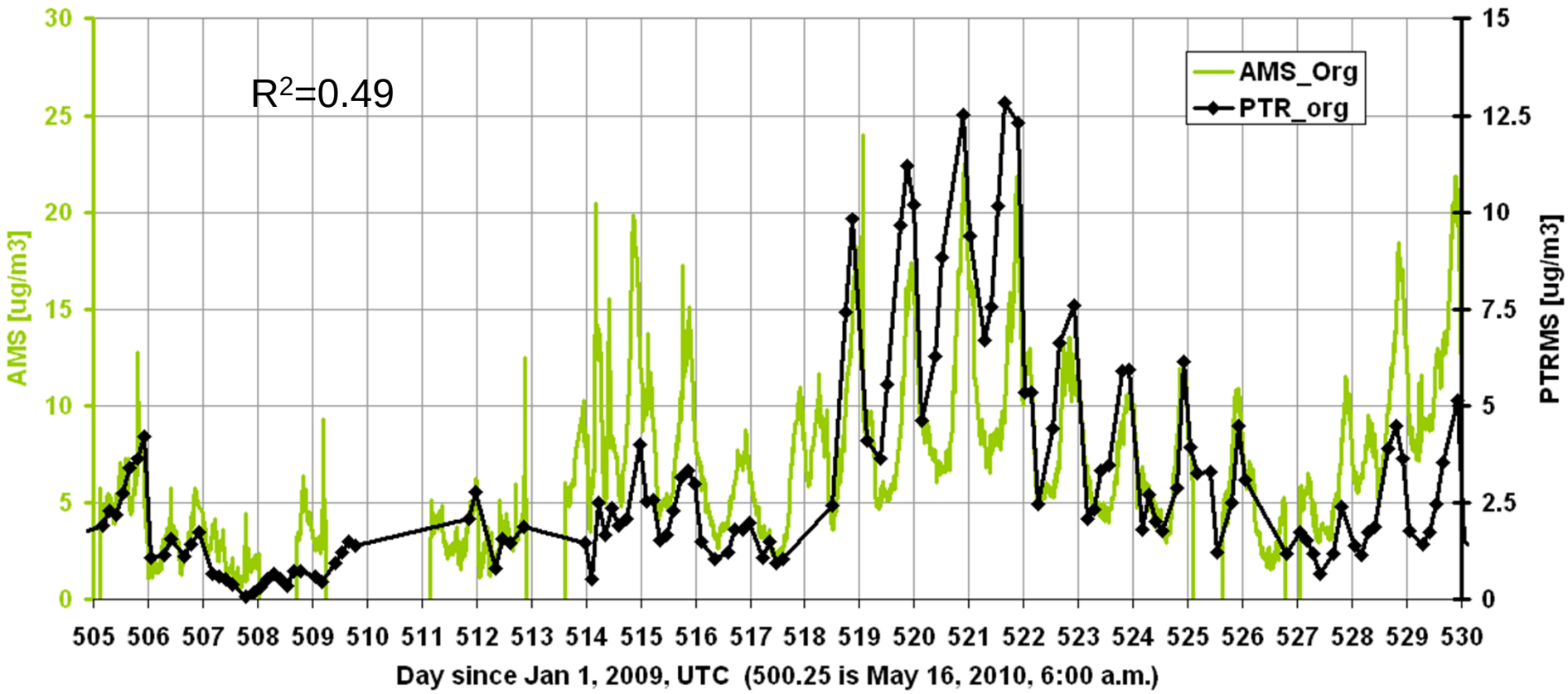
28.017	61.027	80.996	96.087	107.948	119.085	129.013	138.134	150.132	160.996	172.960	184.935	198.062	214.073	229.146	255.232	291.299	327.306	359.350	391.290	429.445
30.033	61.979	81.034	97.028	108.048	119.945	129.054	139.039	151.040	161.061	173.059	185.081	198.098	214.084	229.215	255.259	293.218	328.312	359.367	395.369	439.424
32.050	62.028	81.070	97.064	108.084	120.046	129.068	139.074	151.075	161.093	173.149	185.139	199.043	215.035	230.217	256.259	293.231	329.319	360.370	395.389	441.430
33.032	63.000	82.031	98.025	109.029	120.086	130.033	139.109	151.109	162.057	173.969	186.063	199.094	215.101	231.129	257.247	295.242	330.323	361.358	397.383	441.445
34.036	63.024	82.070	98.063	109.066	120.900	130.052	139.148	151.148	163.040	174.056	186.079	199.167	215.151	231.207	258.250	297.083	331.335	361.379	398.376	442.435
42.033	63.985	83.014	98.103	109.101	121.033	130.064	140.036	152.025	163.071	174.151	187.068	200.047	215.192	232.023	259.235	297.260	332.325	363.327	398.388	443.453
43.017	64.001	83.049	99.007	110.033	121.064	130.128	140.072	152.037	163.147	174.968	187.156	200.170	215.962	233.151	261.184	298.084	332.337	364.353	399.384	453.439
44.012	64.413	83.086	99.043	110.063	121.100	130.992	140.111	152.073	164.041	175.043	188.039	200.933	216.037	233.223	261.253	299.078	333.347	365.331	399.398	455.446
44.056	64.970	84.048	99.079	110.104	121.943	131.049	140.147	152.111	164.071	175.071	188.069	201.085	216.901	234.148	263.266	299.279	335.301	365.342	400.389	457.458
45.033	65.019	84.087	100.012	111.044	122.025	131.086	141.018	152.150	164.149	175.145	189.056	201.181	217.038	235.170	265.252	300.078	337.292	366.366	400.402	457.474
46.028	65.039	85.029	100.041	111.080	122.061	131.101	141.055	152.931	164.962	175.969	189.087	202.084	217.117	236.166	266.279	301.060	337.308	367.339	401.399	458.468
46.064	66.037	85.065	100.075	112.042	122.099	131.989	141.088	153.021	165.021	176.040	189.126	202.183	217.161	237.177	267.176	301.223	338.338	367.350	402.402	467.464
46.989	67.055	86.030	100.111	112.080	122.944	132.047	141.165	153.057	165.053	176.069	189.160	202.931	218.013	237.216	267.266	301.287	339.316	368.365	402.415	469.456
47.012	68.052	86.062	100.936	113.023	123.044	132.081	142.016	153.088	165.090	176.968	190.054	203.087	218.111	238.250	269.227	302.289	341.023	369.351	403.409	469.469
47.047	68.997	87.044	101.023	113.058	123.079	132.985	142.055	153.124	165.164	177.055	190.083	203.175	219.050	239.145	269.278	303.303	341.323	370.356	403.427	471.473
47.996	69.034	87.079	101.059	113.094	123.116	133.031	142.087	153.163	166.053	177.163	190.967	204.097	219.175	239.237	271.259	304.305	342.022	371.352	409.384	471.487
48.015	70.031	87.995	101.940	114.024	124.044	133.065	142.167	153.914	166.088	178.060	191.071	205.091	219.205	241.085	272.260	305.247	342.327	371.366	409.404	481.468
48.984	70.073	88.045	102.026	114.057	124.078	133.100	142.992	154.012	166.166	178.082	191.178	205.193	220.057	241.208	273.186	305.315	343.020	372.365	411.384	483.471
49.027	71.014	88.076	102.060	114.090	124.117	134.063	143.036	154.058	167.075	178.164	191.973	205.935	220.175	241.214	273.254	307.261	343.321	373.382	411.399	483.493
50.735	72.049	88.980	102.091	114.136	124.992	134.100	143.074	154.083	167.102	179.086	192.035	206.089	221.089	241.245	274.257	309.260	343.335	374.386	412.390	485.508
50.981	73.028	89.993	102.127	115.013	125.023	134.965	143.100	155.073	167.179	179.178	192.070	206.196	221.152	242.049	275.269	309.270	344.339	375.079	413.399	
51.023	74.030	90.018	103.041	115.039	125.059	135.045	144.048	155.180	168.033	180.088	192.180	207.118	222.068	243.131	277.217	311.280	345.335	375.380	413.413	
51.042	74.064	90.995	103.053	115.074	125.095	135.079	145.007	156.071	168.072	180.181	192.965	207.207	222.155	243.227	277.284	313.292	345.350	375.395	414.402	
52.018	74.096	91.947	103.074	115.111	126.023	135.115	145.053	156.088	168.100	180.939	193.013	207.931	223.161	244.230	279.162	314.298	346.354	381.350	414.416	
53.002	75.042	92.058	103.953	116.016	126.058	136.040	145.063	156.184	169.086	181.099	193.103	209.059	225.055	245.145	279.226	315.303	347.361	381.387	415.414	
53.038	75.995	93.011	104.049	116.038	126.095	136.077	145.119	157.007	169.196	181.193	193.194	209.144	225.141	245.223	280.163	316.306	349.317	383.353	417.424	
54.033	76.039	93.037	105.038	116.073	126.133	136.115	146.059	157.052	170.063	182.003	194.100	209.185	226.057	247.166	281.243	317.306	351.319	384.357	417.443	
55.036	76.981	93.070	105.070	116.111	127.039	136.960	146.120	157.107	170.081	182.102	194.195	210.063	227.041	247.238	283.264	317.319	353.327	385.381	419.329	
56.021	77.993	93.955	105.933	116.906	127.075	137.027	146.976	158.059	170.200	182.936	194.960	211.010	227.069	248.165	284.277	318.322	353.345	386.372	423.420	
57.033	78.037	94.031	106.036	117.017	127.111	137.059	147.045	158.103	170.931	182.987	195.087	211.078	227.078	248.243	285.277	319.333	354.341	386.382	425.414	
58.036	78.996	94.068	106.071	117.088	127.993	137.094	147.077	159.045	171.066	183.083	195.100	212.079	227.197	249.181	286.280	321.284	355.341	387.383	426.405	
58.072	79.030	94.990	106.991	118.067	128.040	137.132	147.115	159.088	171.126	183.097	195.116	212.931	227.229	249.253	287.270	323.280	357.337	387.397	426.420	
60.051	79.055	95.049	107.049	118.903	128.072	138.013	148.040	160.046	171.972	183.211	196.085	213.069	228.040	251.194	288.273	325.292	357.351	388.387	427.428	
60.080	80.014	95.086	107.085	118.991	128.113	138.057	149.131	160.075	172.045	183.998	197.094	213.177	228.084	252.163	289.284	325.309	358.354	389.388	428.434	
60.984	80.053	96.046	107.927	119.052	128.895	138.092	150.028	160.137	172.066	184.084	197.225	214.060	228.231	253.196	290.289	326.303	359.049	389.411	429.429	

→Mass range aerosol species: 28-485

→Selection rule:

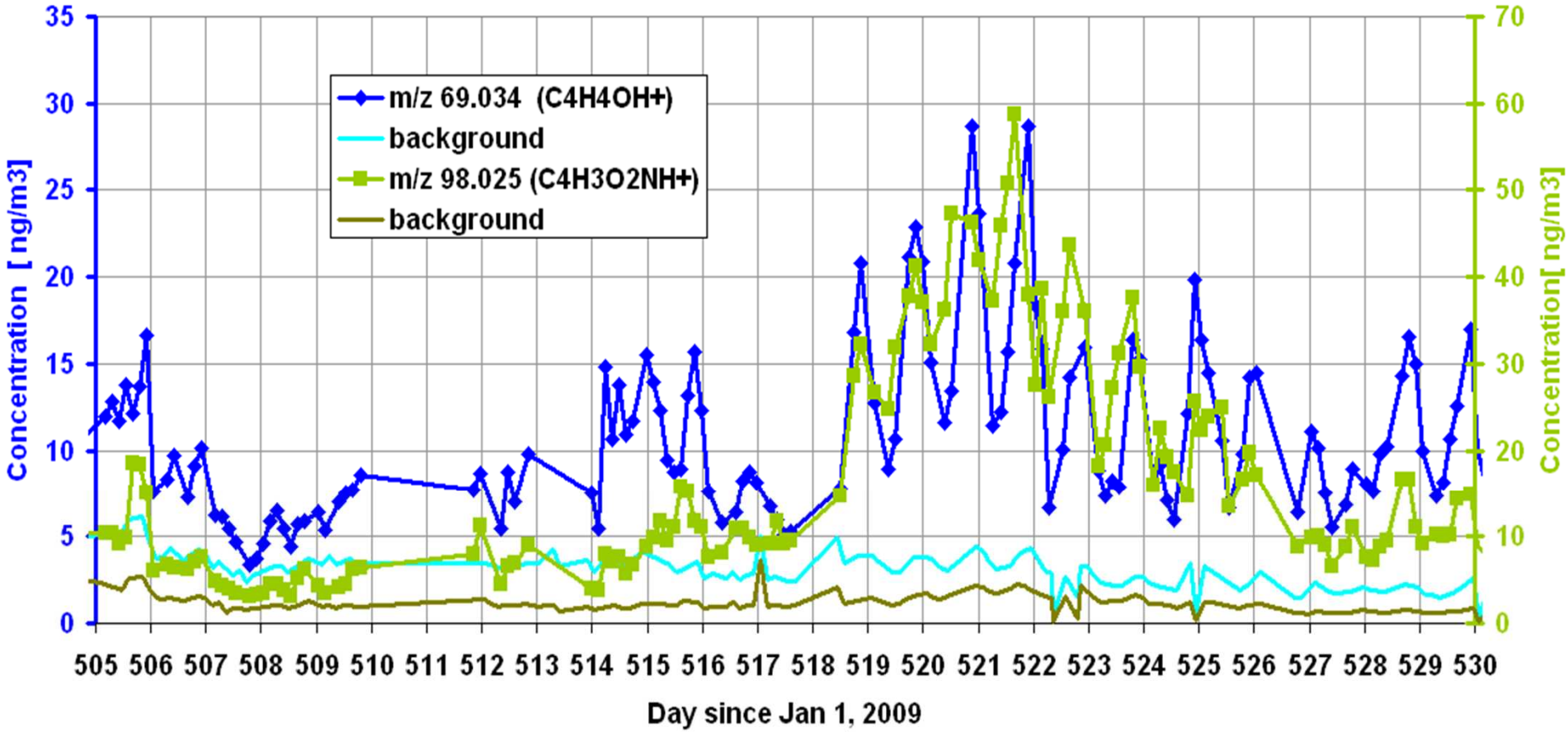
mean(aerosol) > median(background) + 3 * stdev(background)

Total Organics: TD-PTR-MS vs AMS



→PTR-org is 50% of AMS-org during most times.
→ Sometimes more, sometimes less…

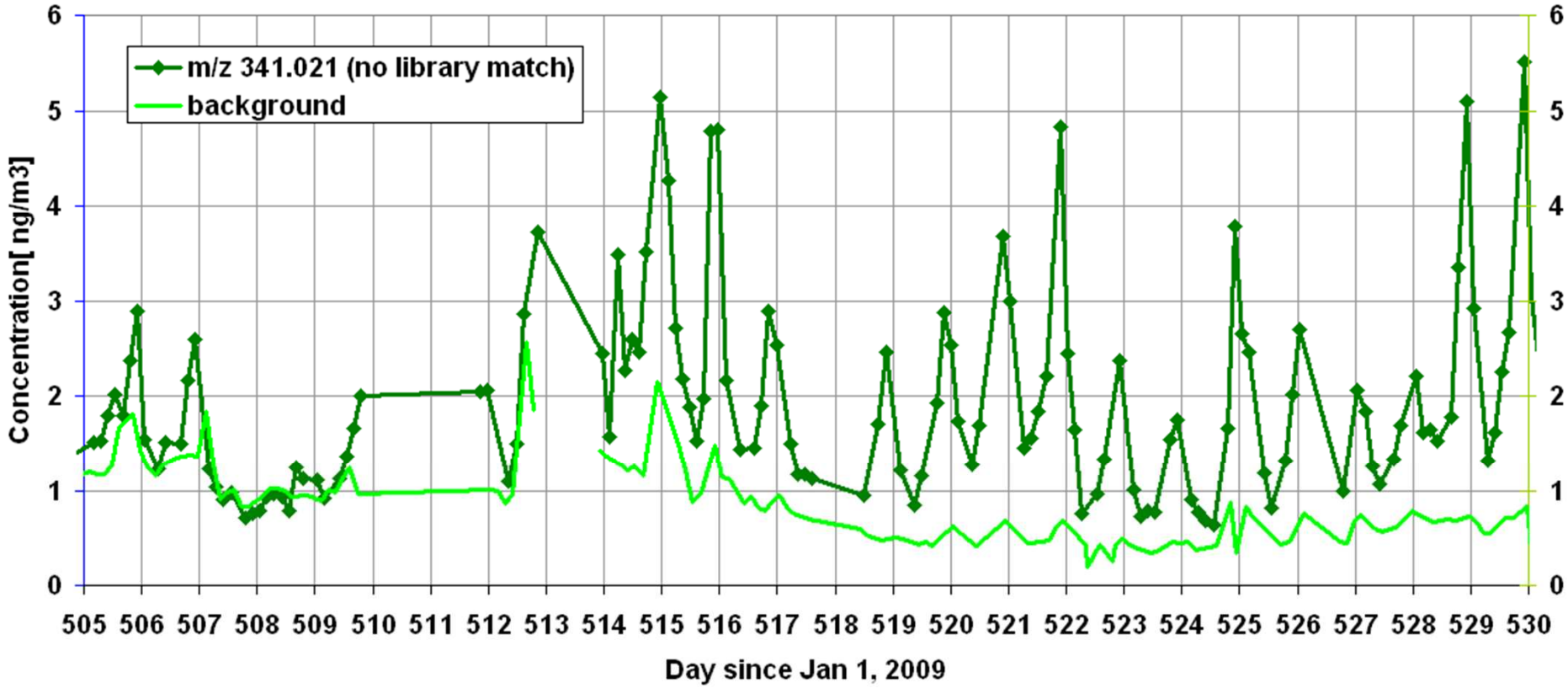
Two individual example species:



→ m/z 69.034 high variability, good correlation with AMS-org (r^2=0.71)

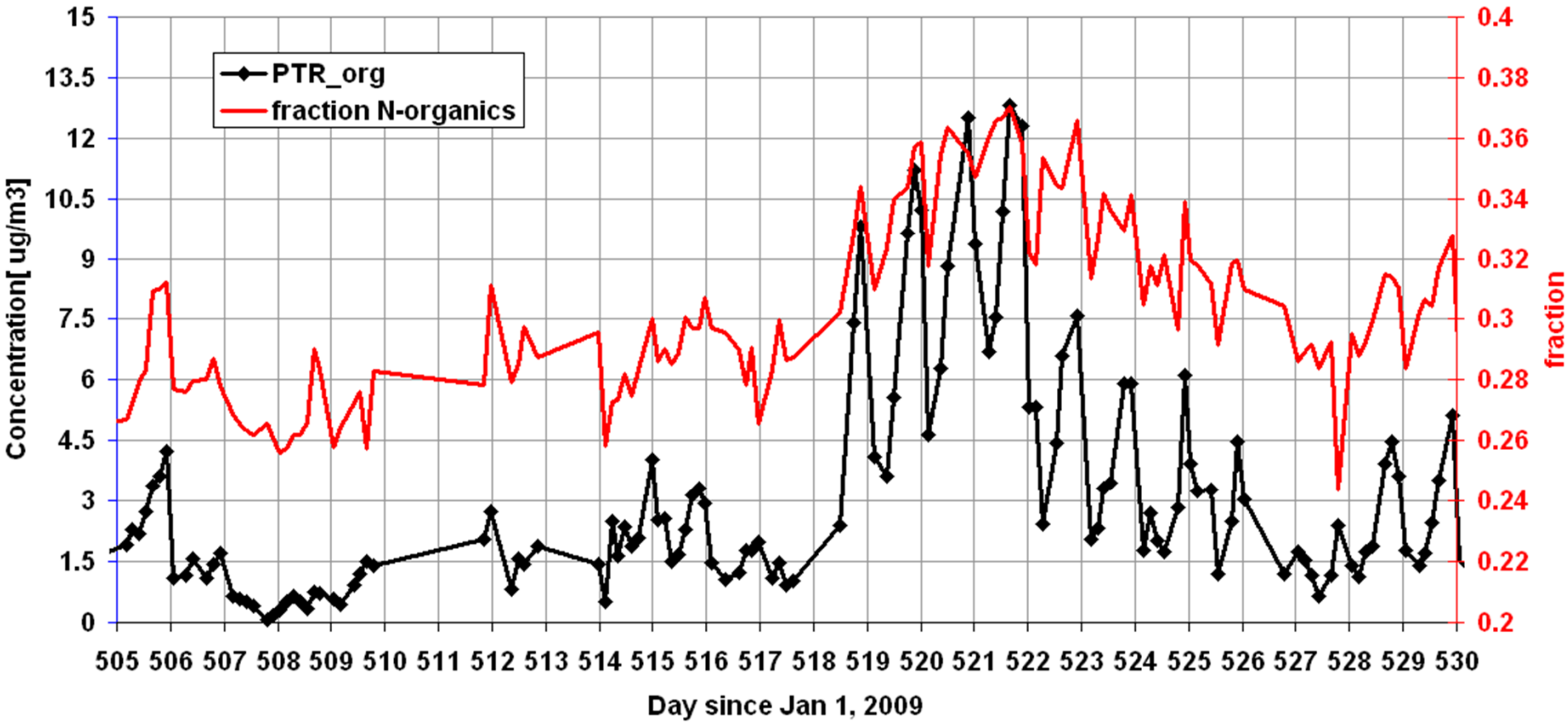
→ m/z 98.025 lower variability, best correlation with AMS-NH4 (r^2=0.75)

Different species:



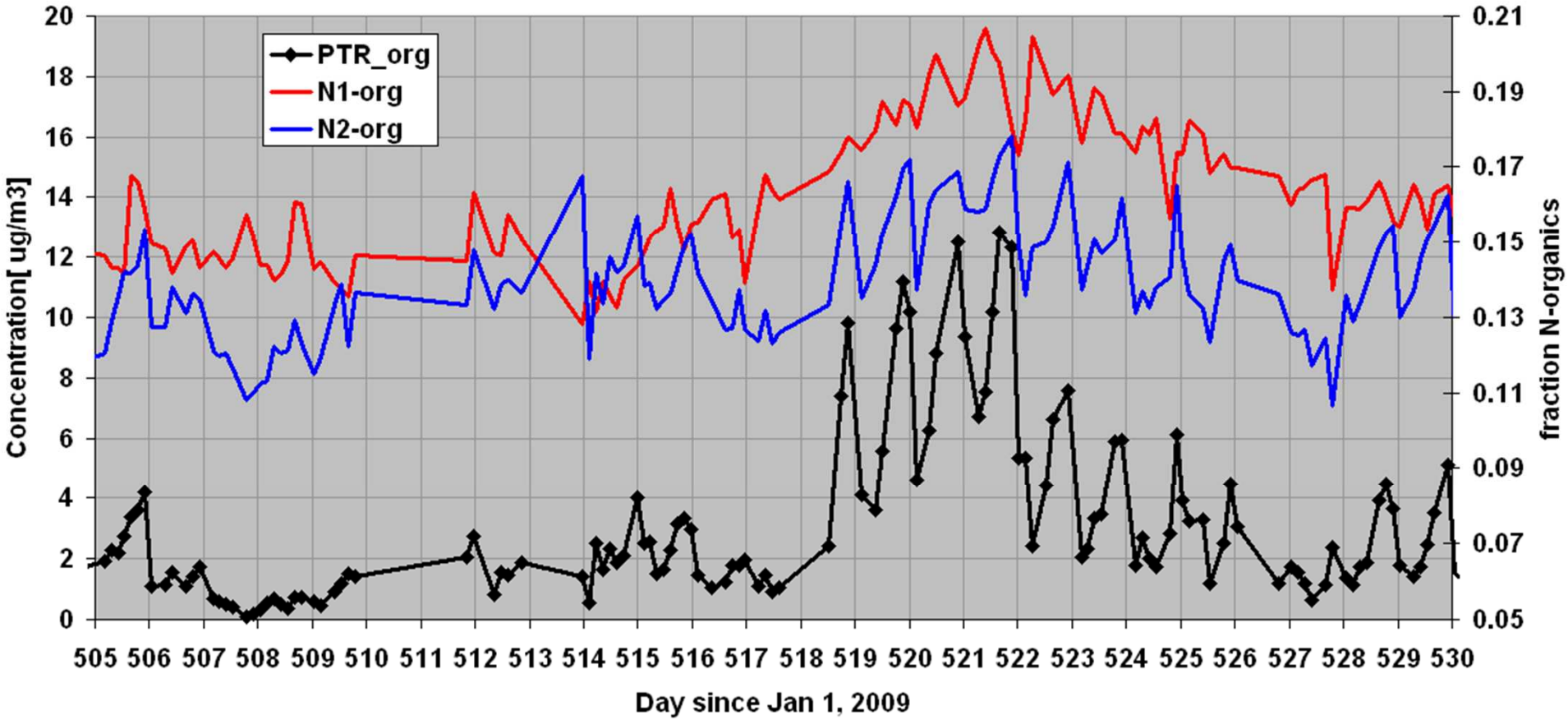
Consistent with $C_{18}H_9O_5ClH^+$

Fraction of organic nitrogen compounds:



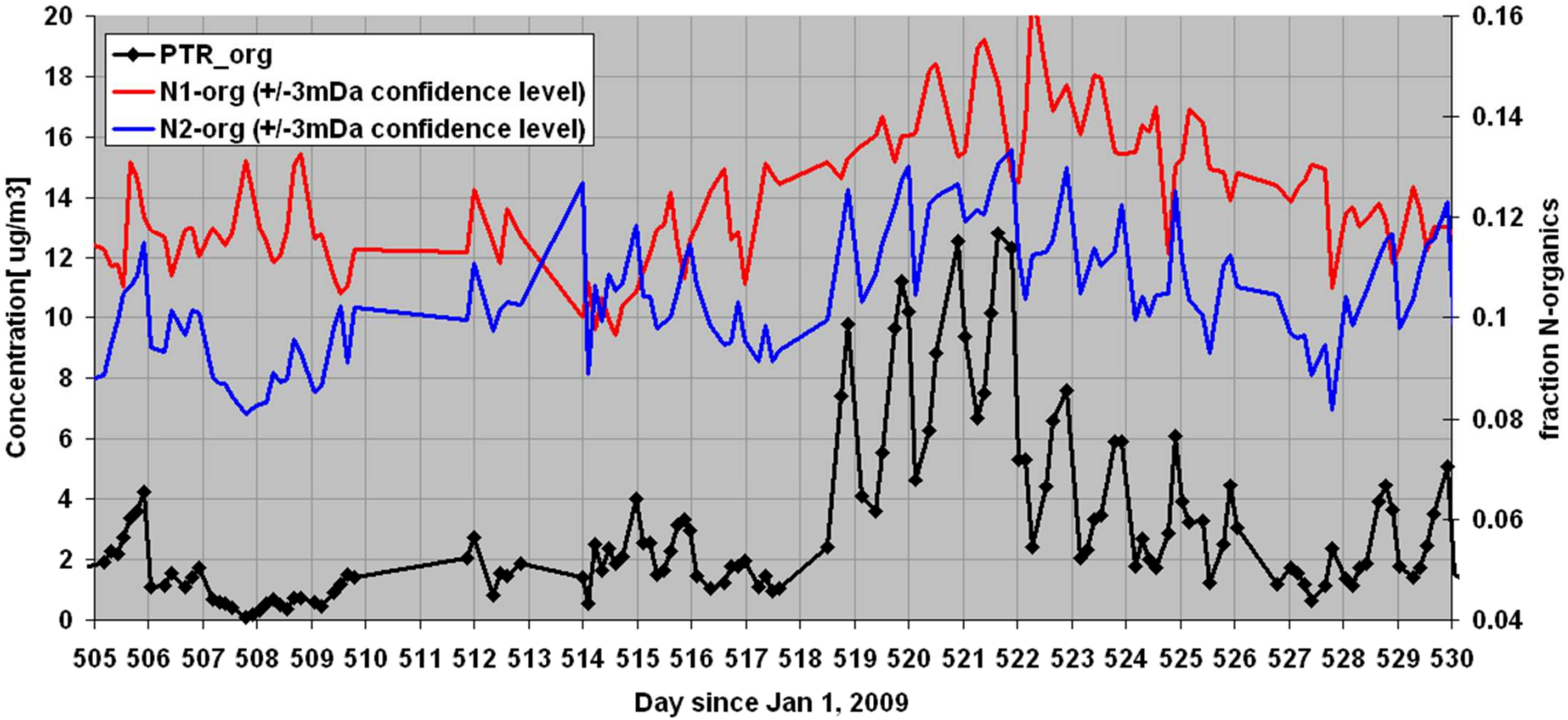
→Fraction of N-organics increases with higher aerosol loads!
→N_1 and N_2 species

Comparison N_1-organics and N_2-organics



→Both N_1 and N_2 organic fractions increase during pollution event.
→Different diurnal cycle.

Subset of N-organics with good confidence for correct identification



→Accuracy for Formula attribution is considered +/-2mDa for most species.
→Species with non-N option in the +/-3mDa range were removed from the set.
→**<u>Same message as for the complete set.</u>**
→ The fractions decrease but this is trivial.

Next steps:

→Manual inspection of all peaks/empirical formulas.
→Should some of the N-peaks be better attributed to organosulfates?
→Exploit stable isotope information.
→More clues from thermograms?

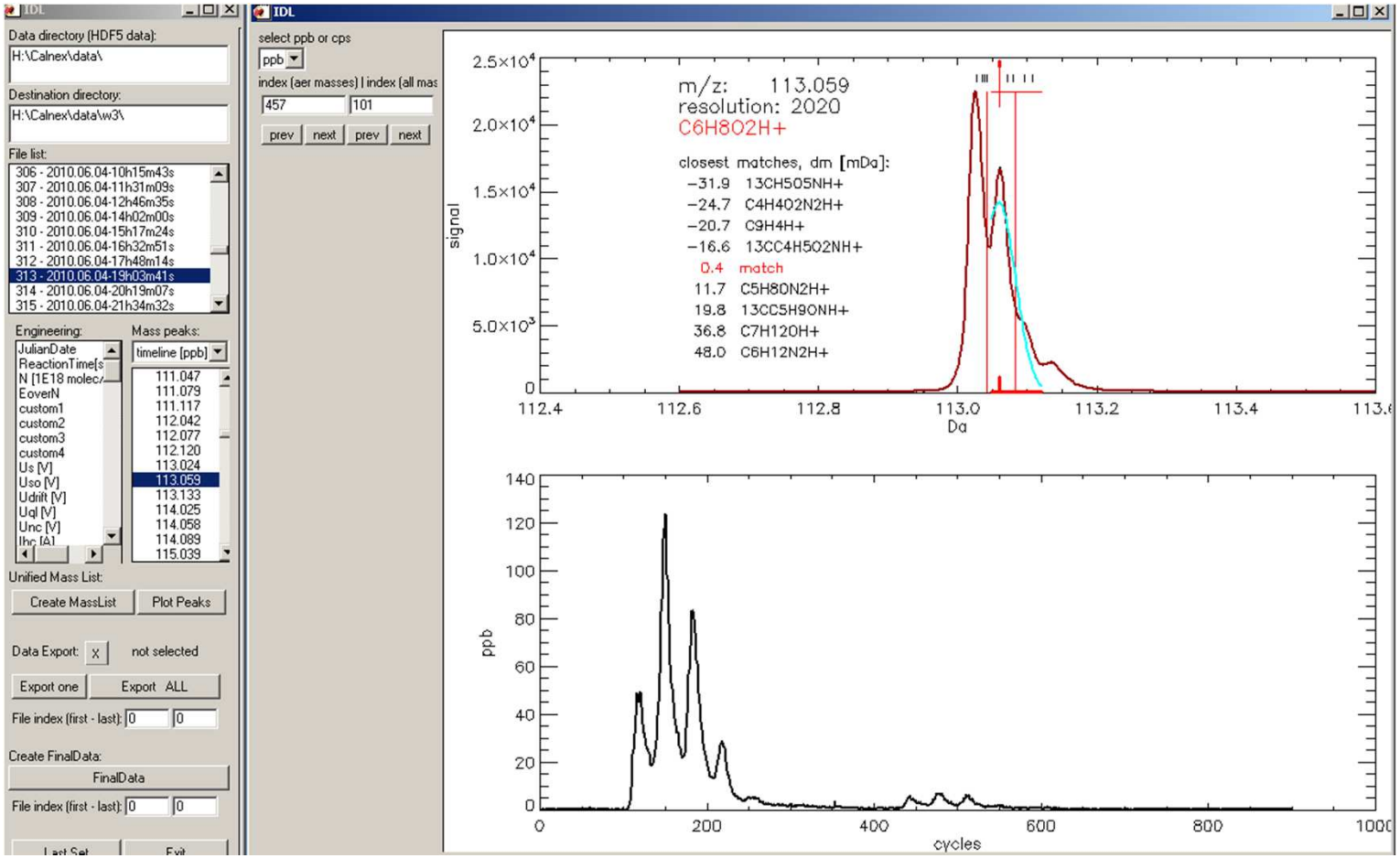
Take home message:

→N organics may constitute more than 35% of the measured organic burden.

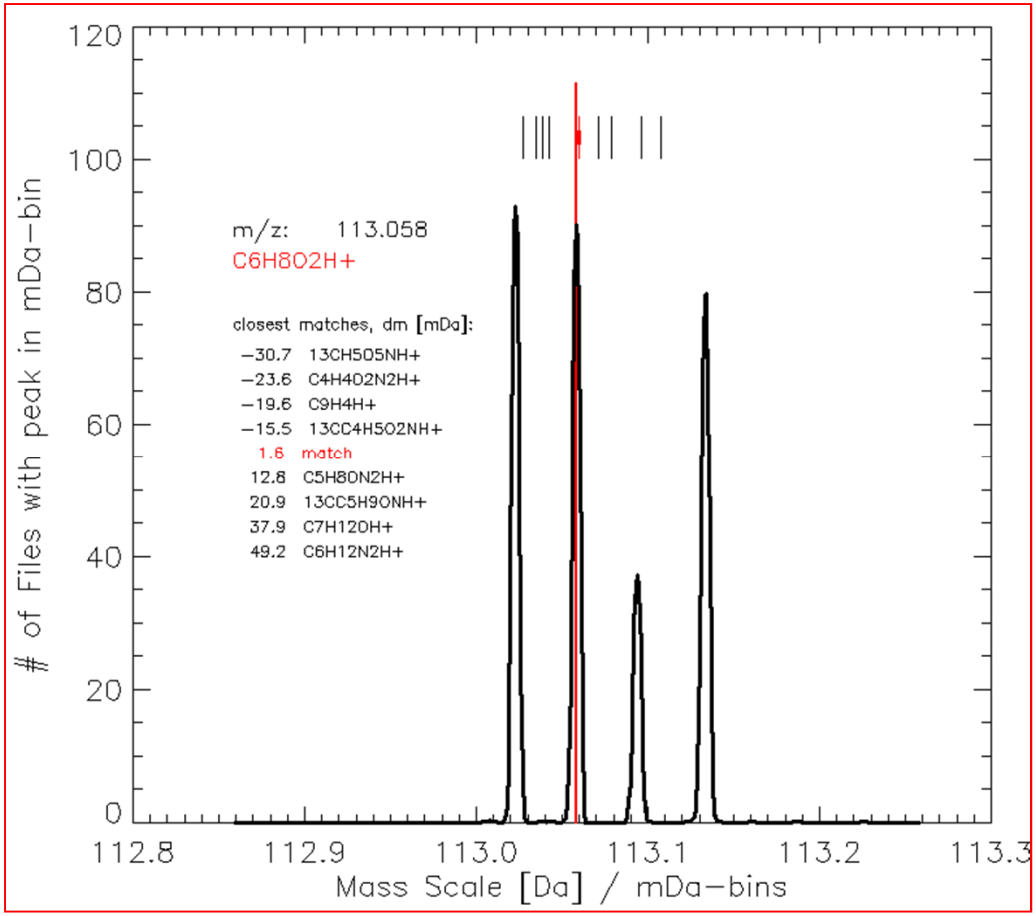
→TD-PTR-MS measurements may allow constraining the role of N-chemistry for SOA formation at the Pasadena site.

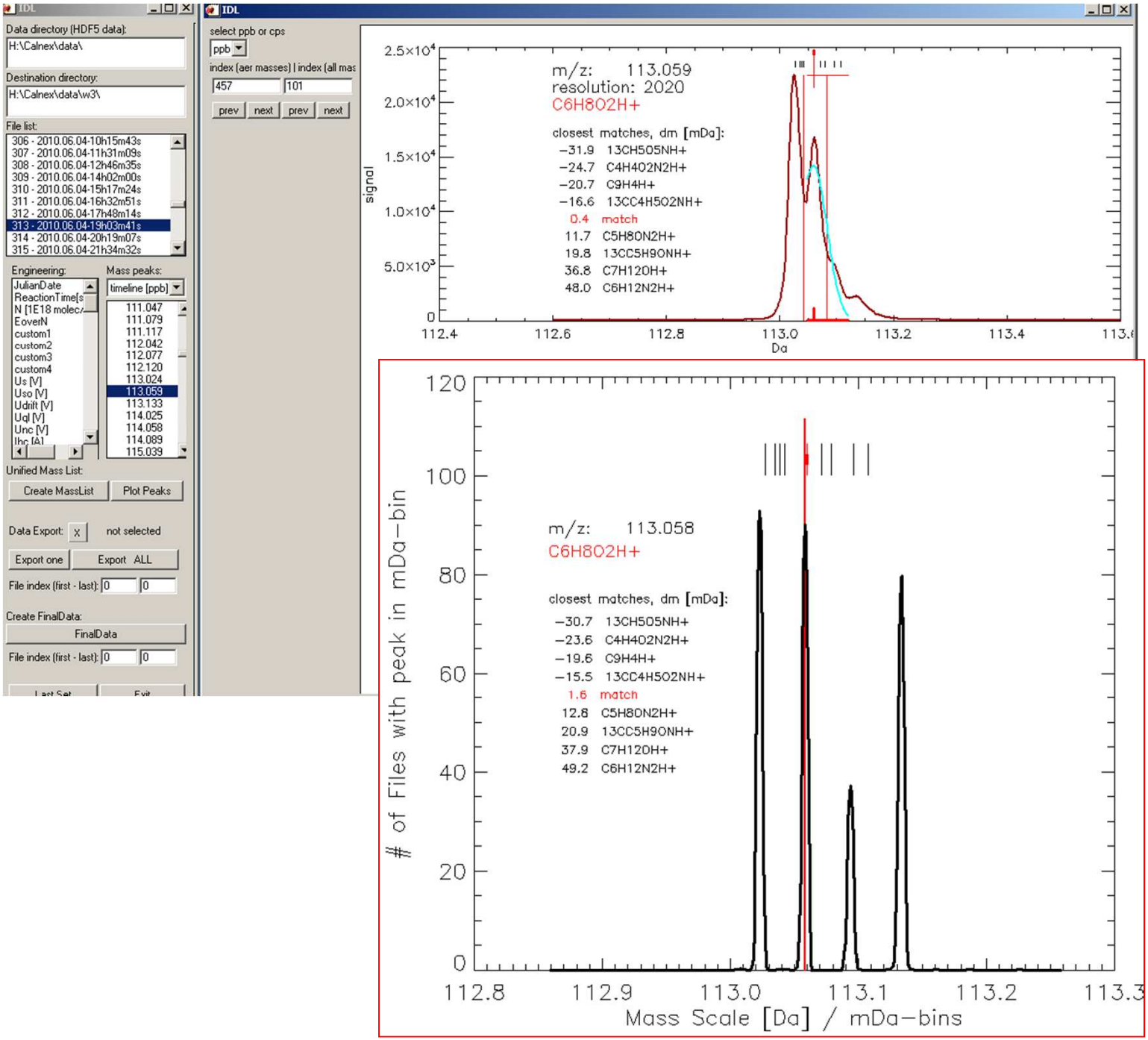
→ Can it be that AMS-NO3 and AMS-NH4 originate partly from organic species?

Example Mass 113, single file (June 4, 2010, 19:03:41)



Histogram of peak centers detected at Mass 113 (495 files)




IDL
Data directory (HDF5 data):
H:\Calnex\data\
Destination directory:
H:\Calnex\data\w3\
File list:
306 - 2010.06.04-10h15m43s
307 - 2010.06.04-11h31m09s
308 - 2010.06.04-12h46m35s
309 - 2010.06.04-14h02m00s
310 - 2010.06.04-15h17m24s
311 - 2010.06.04-16h32m51s
312 - 2010.06.04-17h48m14s
313 - 2010.06.04-19h03m41s
314 - 2010.06.04-20h19m07s
315 - 2010.06.04-21h34m32s
Engineering:
JulianDate
ReactionTime[s
N [1E18 molec/
EoverN
custom1
custom2
custom3
custom4
Us [V]
Uso [V]
Udrift [V]
Uql [V]
Unc [V]
Ihc [A]
Mass peaks:
timeline [ppb]
111.047
111.079
111.117
112.042
112.077
112.120
113.024
113.059
113.133
114.025
114.058
114.089
115.039
Unified Mass List:
Create MassList
Plot Peaks
Data Export:
x
not selected
Export one
Export ALL
File index (first - last):
0
0
Create FinalData:
FinalData
File index (first - last):
0
0
Last Set
Exit
IDL
select ppb or cps
ppb
index (aer masses) | index (all mas
457
101
prev
next
prev
next
m/z: 113.059
resolution: 2020
C6H8O2H+
closest matches, dm [mDa]:
−31.9 13CH5O5NH+
−24.7 C4H4O2N2H+
−20.7 C9H4H+
−16.6 13CC4H5O2NH+
0.4 match
11.7 C5H8ON2H+
19.8 13CC5H9ONH+
36.8 C7H12OH+
48.0 C6H12N2H+
signal
Da
m/z: 113.058
C6H8O2H+
closest matches, dm [mDa]:
−30.7 13CH5O5NH+
−23.6 C4H4O2N2H+
−19.6 C9H4H+
−15.5 13CC4H5O2NH+
1.6 match
12.8 C5H8ON2H+
20.9 13CC5H9ONH+
37.9 C7H12OH+
49.2 C6H12N2H+
# of Files with peak in mDa−bin
Mass Scale [Da] / mDa−bins