Appendix 2B

Conceptual Model for PM2.5 in Connecticut

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Conceptual model for Particulate Matter (PM) in Connecticut

Executive Summary

PM2.5 events in CT can be categorized as winter or summer time events.

Winter events can be characterized as having:

1. 98th percentile value > 32 μg/m^3;
2. Low mixing heights (250m) and E/F Pasquill stability class (shallow, little mixing) for an extended period of time;
3. Warm fronts or overrunning warm air forcing low mixing heights with non-stagnant wind conditions;
4. Low level winds from the southwest (following the urban northeast corridor);
5. Extended periods of high values not just short duration diurnal rush hour peaks;
6. The primary PM source is motor vehicle (MV) (fresh and aged) and secondary aerosol (volatile species). Lesser contributions come from oil combustion aerosol and wood smoke;
7. Constituent aerosol is primarily carbon (oc/ec) and;
8. Wintertime sulfate aerosol is less than summertime sulfate aerosol. This can be attributed to cold temperature affinity of ammonium to nitrate over sulfate, the shallow mixing prohibiting deep mixing of Midwest aerosol downward, and reduced EGU emissions during the cold months (no air conditioning).

Summertime events can be characterized as having:

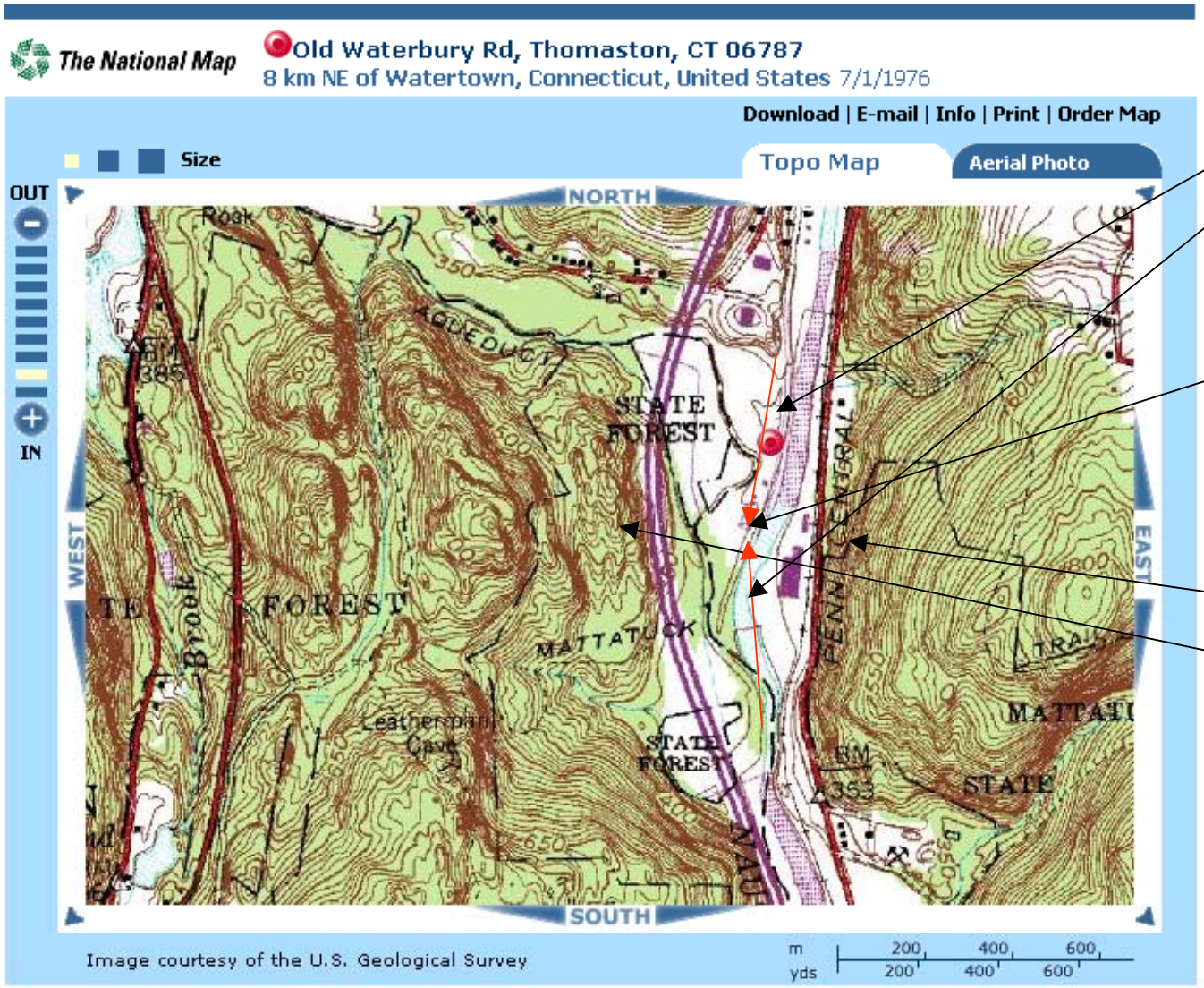
1. 98th percentile value > 40 μg/m^3;
2. High mixing heights 600-1200m coast, >1500m inland;
3. Bermuda high weather conditions lasting over several days;
4. Low level winds from the SSW-SW (NYC CMSA), midlevel winds from the SW and WSW enhanced by the nocturnal low level jet (LLJ) (following urban NE corridor;)
5. Extended periods of high values not just short duration diurnal rush hour peaks;
6. The primary PM25 source is coal burning EGUs, followed by carbon from mobile sources;
7. Constituent aerosol is primarily ammonium sulfate, followed by organic carbon and;
8. Summertime sulfate aerosol is greater than wintertime sulfate aerosol. This can be attributed to warm temperature affinity of ammonium to sulfate over nitrate, the deep mixing of western aerosol downward, and increased EGU emissions during the warm months (air conditioning).

Section 1.0 Wintertime PM2.5 Event Examples

With the recent availability of highly time resolved PM2.5 and pollutant gas measurements in CT, source type and region determinations can be made. One such site is in Thomaston, CT. It is a rural site that is adjacent to a four-lane highway, used primarily for commuting to Waterbury and points south, and truck transport to and from

Northwestern, CT. It is also within a few kilometers of some light industry and residential heating sources. In addition, it is in a valley with steep 300-500m sides, channeling airflow north and south (See Figures 1.1 and 1.2). The increased time resolution helps to differentiate between local and regional sources. Differentiation between rush hour, aging species and regional aerosol becomes apparent when time series of pollutants and wind speed are examined For example, a short duration peak of NO, CO, and black carbon between 7 and 10 am in the morning point can indicate a motor vehicle source for a monitor located close to a highway. This will be discussed further in Section 1.3 and also in Figure 1.3.6.

Figure 1.1 Topographic Features of Thomaston, CT Monitoring Site

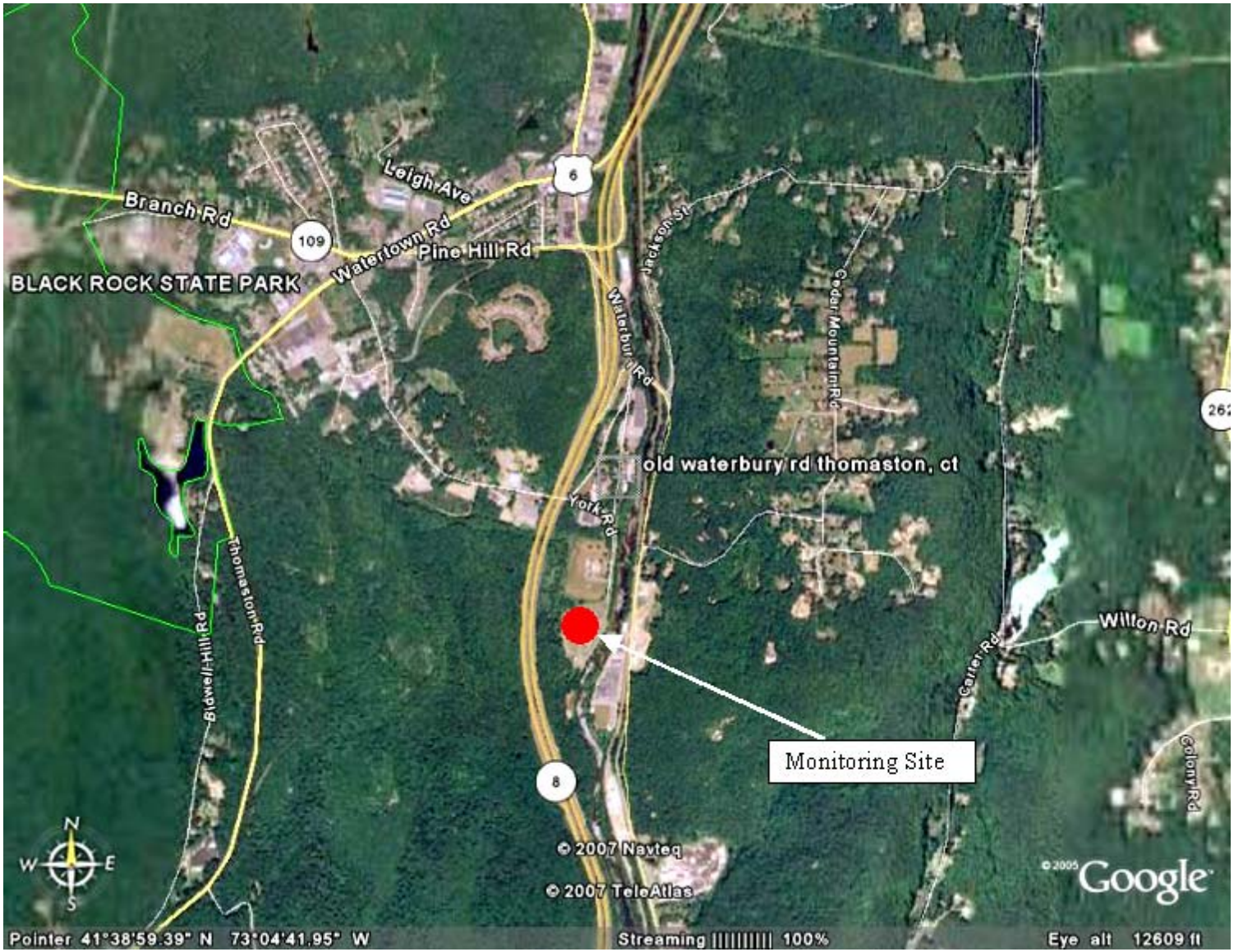


Channeled flow

Sewage treatment plant

Steep valley sides

Figure 1.2 Satellite Photo of the Thomaston, CT monitoring site



1.1 January 7-8, 2008 event

An approaching warm front, warm surface temperatures (Figure 1.1.1), SSW winds (Figure 1.1.2) and a stream of unseasonably warm overriding air aloft (+7-8ºC at 850 mb) (Figure 1.1.3) provided the stable conditions necessary for trapping and transporting pollutants in a shallow boundary layer of 250m (Figure 1.1.4). Daily average values above 50 ug/m^3 and hourly values above 60 ug/m^3 were measured at Danbury and Bridgeport in SW CT (Figure 1.1.2). Hourly SO_4 values of 4-5 µg/m^3 and regionally predicted values between 2 and 4 ug/m^3 hinted at a low sulfate eastern source to the PM2.5 measured (See Figure 1.1.5). Given the sources are usually: crustal (clean conditions), sulfate (Midwest EGUs) or carbonaceous material (urban MV), the latter is most likely.

Figure 1.1.1 Surface Analysis for 1-7-08

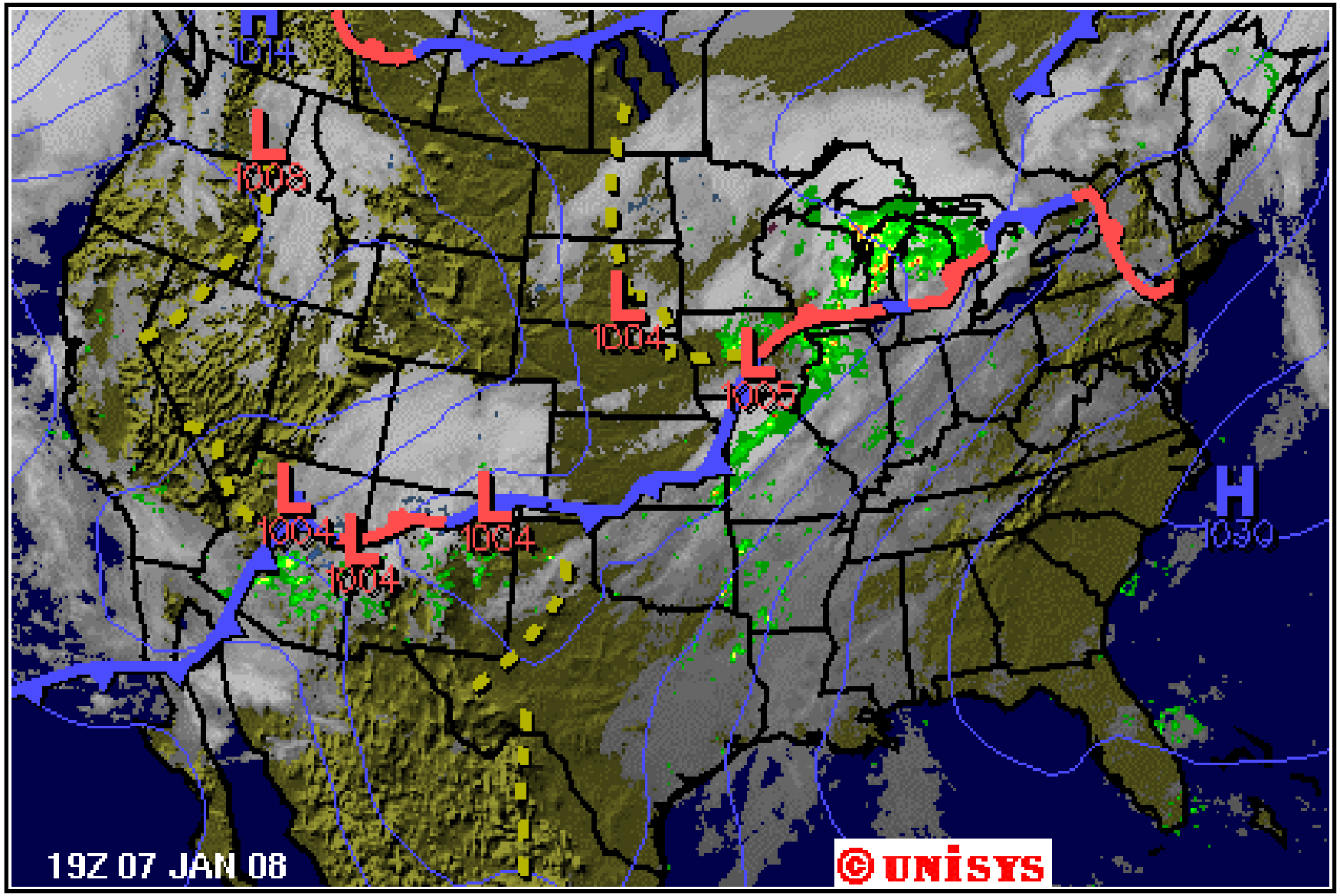


Figure 1.1.2 PM2.5 and 24 hr Back Trajectories for 1-7-08

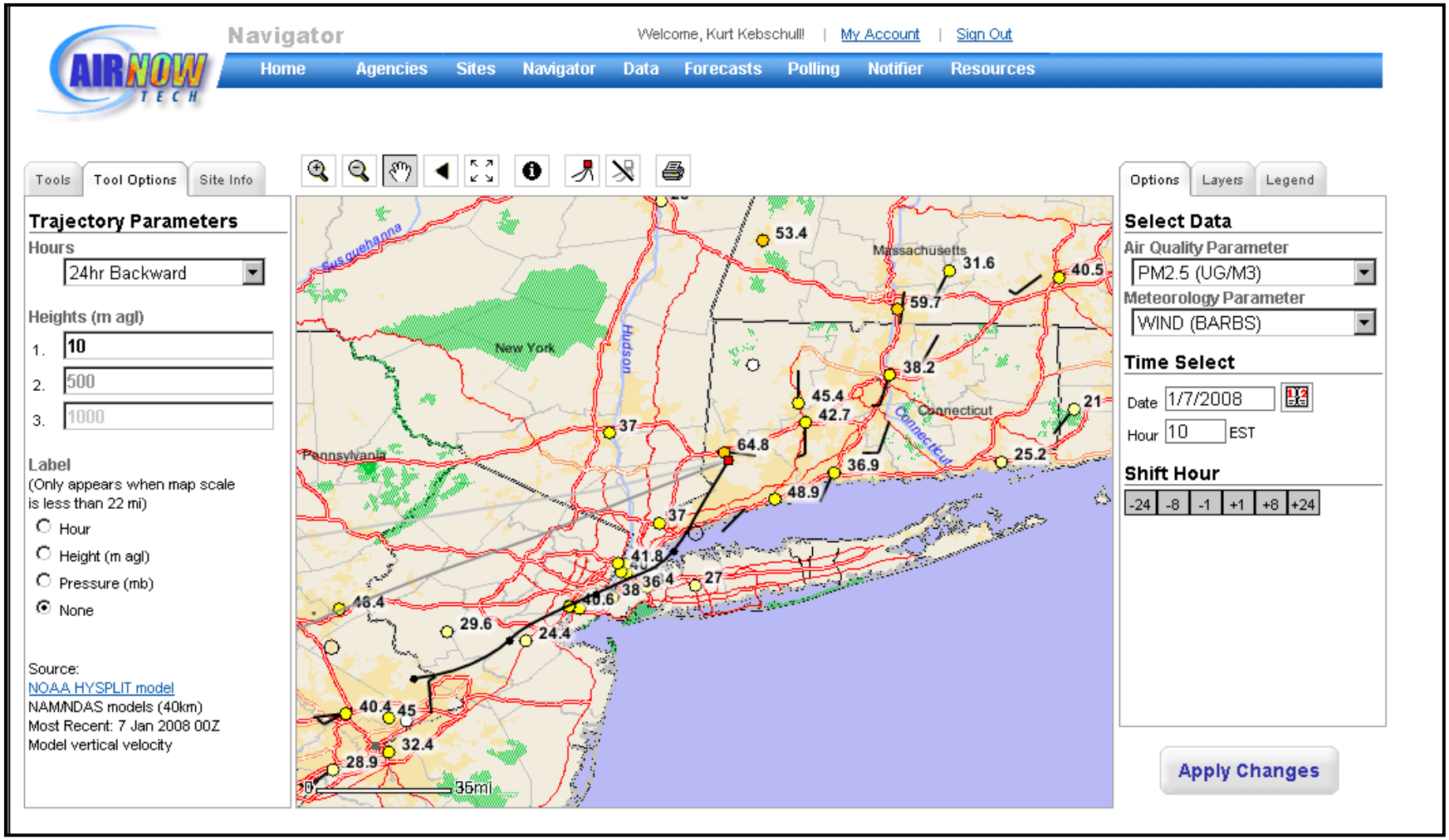


Figure 1.1.3 850 mb analysis for 1-7-08 12Z

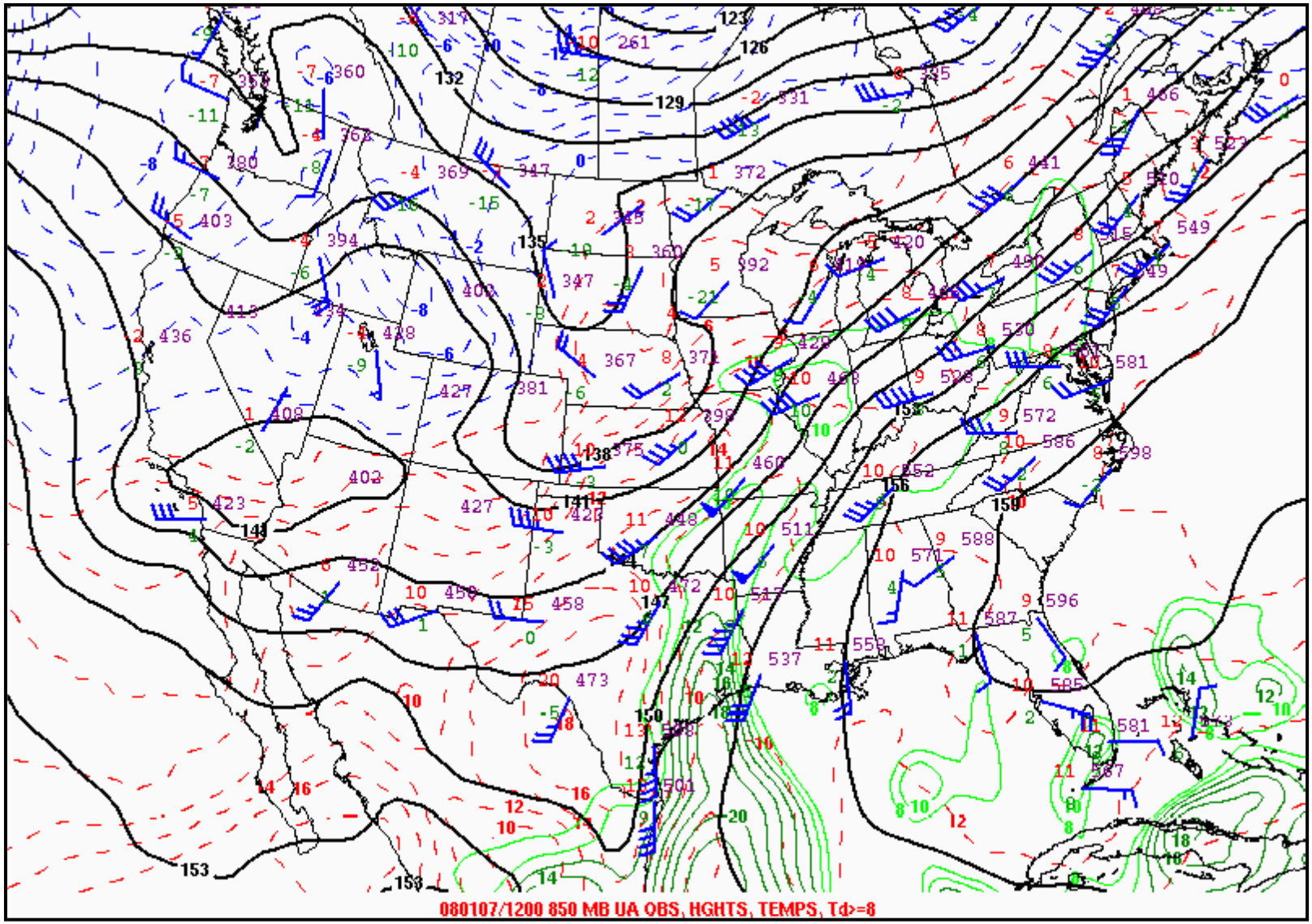


Figure1.1.4 NAM model Stability for 1/7-8/2008

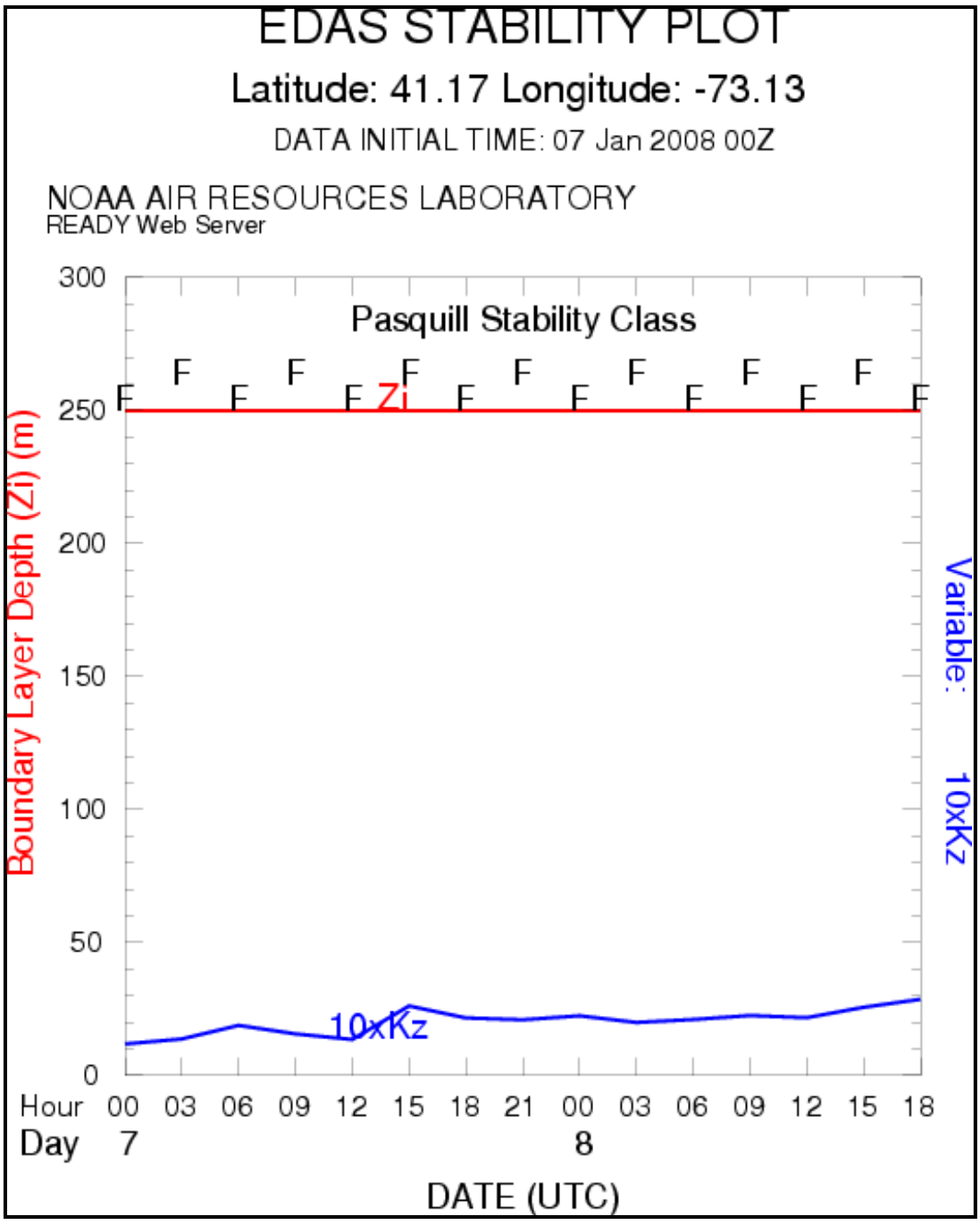
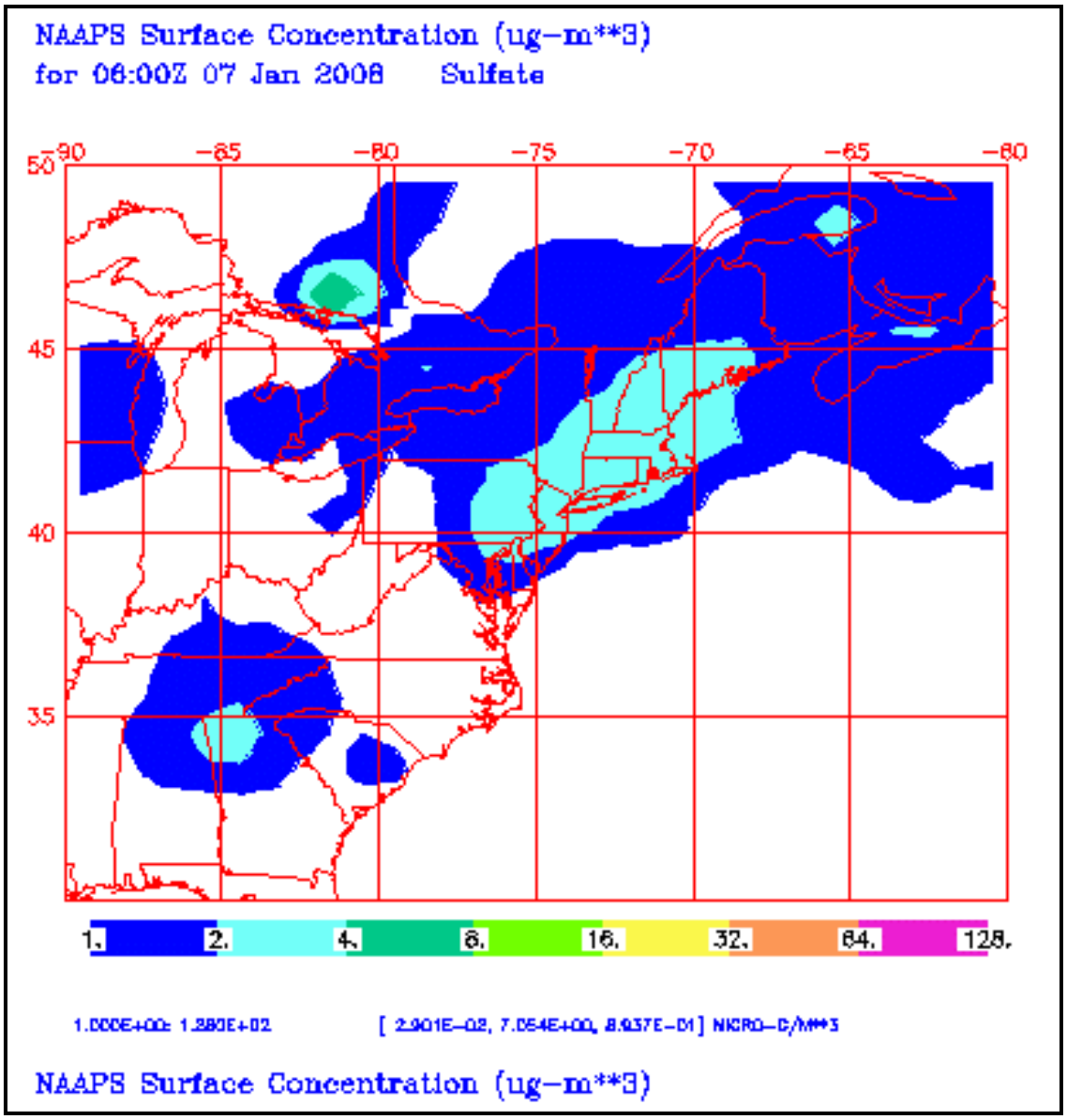


Figure 1.1.5 NRL Navy sulfate model for 1-7-2008



1.2 UNMIX receptor modeling

In their paper "Evaluation of a New Approach for Real Time Assessment of Wood Smoke PM" (Allen, Babich, and Poirot, 2006)[1] (Appendix 2C), UNMIX receptor modeling is used to differentiate a set of speciated samples between its various component sources. They used hourly measurements of particle black carbon, volatile and non volatile mass, and gaseous CO, NO, NO_2, SO_2 to detect five different source categories (aged and fresh MV, wood smoke, secondary aerosol (ammonium sulfate, ammonium nitrate, secondary organic aerosol), and residential oil combustion. A similar project was designed and is being implemented in Thomaston, CT. Data from Quarter 4, 2006 and Quarter 1, 2007 were available for analysis. The data was again analyzed using UNMIX and the component source composition results were similar to those of the previous study.

Figure 1.2.1 shows the source composition of each of the UNMIX "source" solutions in a bar chart format. Note the relatively high black carbon/deltac (difference between 2 channels of the nephelometer) contribution to wood smoke and the high volatile content of secondary aerosol (nitrate, sulfate, voc). Scatter plots (Figures 1.2.2-6) of each component vs. wind speed were made. Wood smoke and fresh MV have strong correlations with low wind speed. Aged MV, secondary aerosol, and residential oil combustion are invariant with wind speed, e.g. could be high with high wind speeds. Because of the N-S orientation of the Naugatuck river valley, winds are channeled N-S, making wind direction dependence of pollutant concentration not useful.

Time series plots are consistent with their emission and transport patterns. As will be discussed later (see Figure1.3.6) short duration peaks are analyzed for wood combustion to heat homes at night and morning rush hour fresh MV peaks. Not coincidentally, wind speeds were also low in these cases. Longer duration peaks are associated with air mass transport from the large urban areas. The presence of an air mass with higher concentrations of transport species such as aged MV, secondary aerosol, and oil combustion, are all sources that take time to form and travel from large urban areas. Stronger wind speeds are observed during these longer duration events.

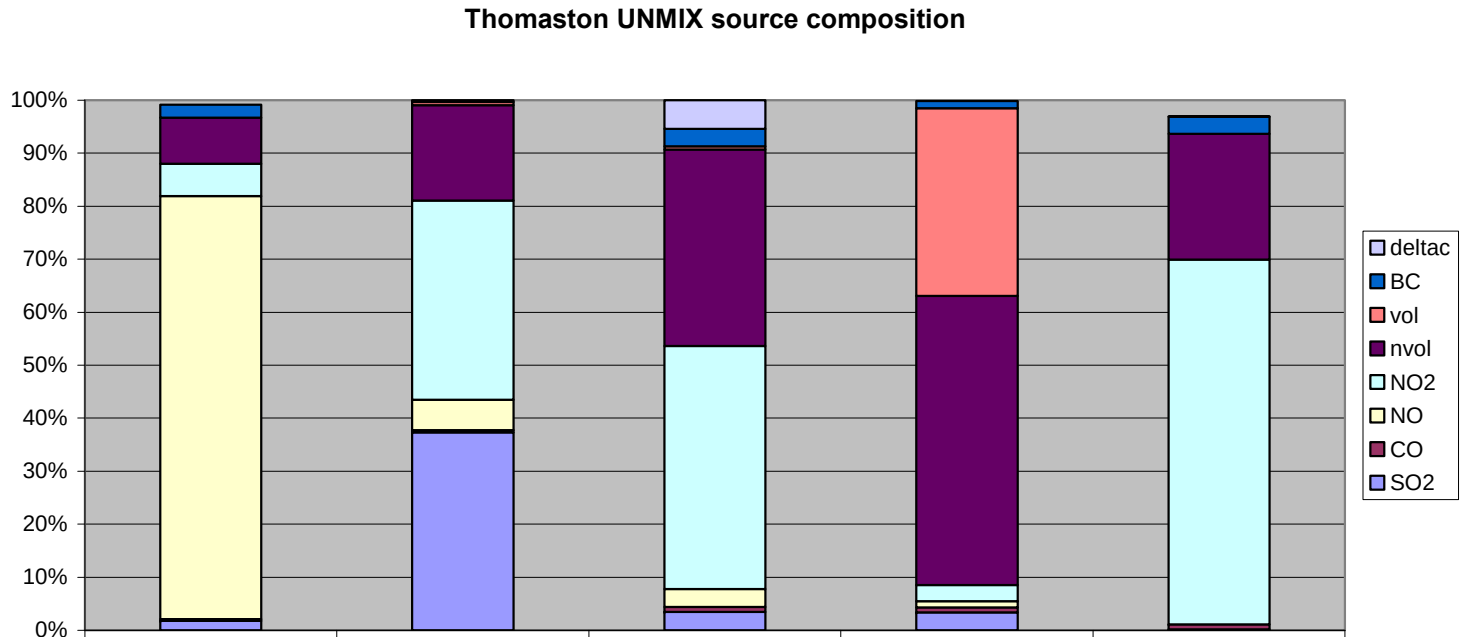
The table below (Table 1.2.1) tells the story of wintertime pollution events during the first quarter of 2007. On days above the 98th percentile value of PM (essentially exceedances of the new 35 $\mu g/m^3$ standard), wood smoke is only 12.4% of the aerosol measured on those days. Local contributions are ~40% of the total. The remaining 60% are from transport, with secondary aerosol making up 28% of the mix. The conclusions are: 1. Wood smoke is not as much of a contributor on very high days, but local and transport species combine to boost concentrations on high days; 2. On moderate days above 16.2 $\mu g/m^3$, (80th percentile) wood smoke can be significant (22% or 4 $\mu g/m^3$ of the total); and 3. Secondary aerosol (from EGUs and industrial facilities) is the most significant contributor on the high days, most likely transported regionally.

[1] 1. Allen, G, P. Babich, and R. Poirot, "Evaluation of a New Approach for Real Time Assessment of Wood Smoke PM" , JAWMA, 2006 "

Table 1.2.1 First Quarter Fractional Component PM2.5 at the Thomaston site

	$\mu g/m^3$	Fresh MV	Oil Combustion	Wood smoke	Secondary Aerosol	Aged MV
80^{TH} PERCENTLE PM	16.2	0.22786	0.15	0.251	0.2	0.2
98^{TH} PERCENTILE PM	32.3	0.27	0.14	0.124	0.28	0.19

Figure 1.2.1 Thomaston UNMIX Source Strength Composition for January-March 2007



	s1-fresh mv	s2-residential oil combustion	s3-woodsmoke	s4-secondary aerosol	s5-aged mv
deltac	-0.0154	0.0203	0.3307	-0.0076	0.0094
BC	0.2414	0.0018	0.1977	0.0702	0.3082
vol	-0.0624	0.0355	0.0389	1.7706	-0.044
nvol	0.8466	1.1291	2.2565	2.7308	2.2967
NO2	0.5903	2.3583	2.7954	0.1558	6.6627
NO	7.7306	0.3574	0.2052	0.0574	-0.2485
CO	0.032	0.0285	0.0533	0.0482	0.0878
SO2	0.1753	2.3416	0.2129	0.1677	0.0188

Figure 1.2.2 UNMIX Fresh Motor Vehicle Category vs Wind Speed

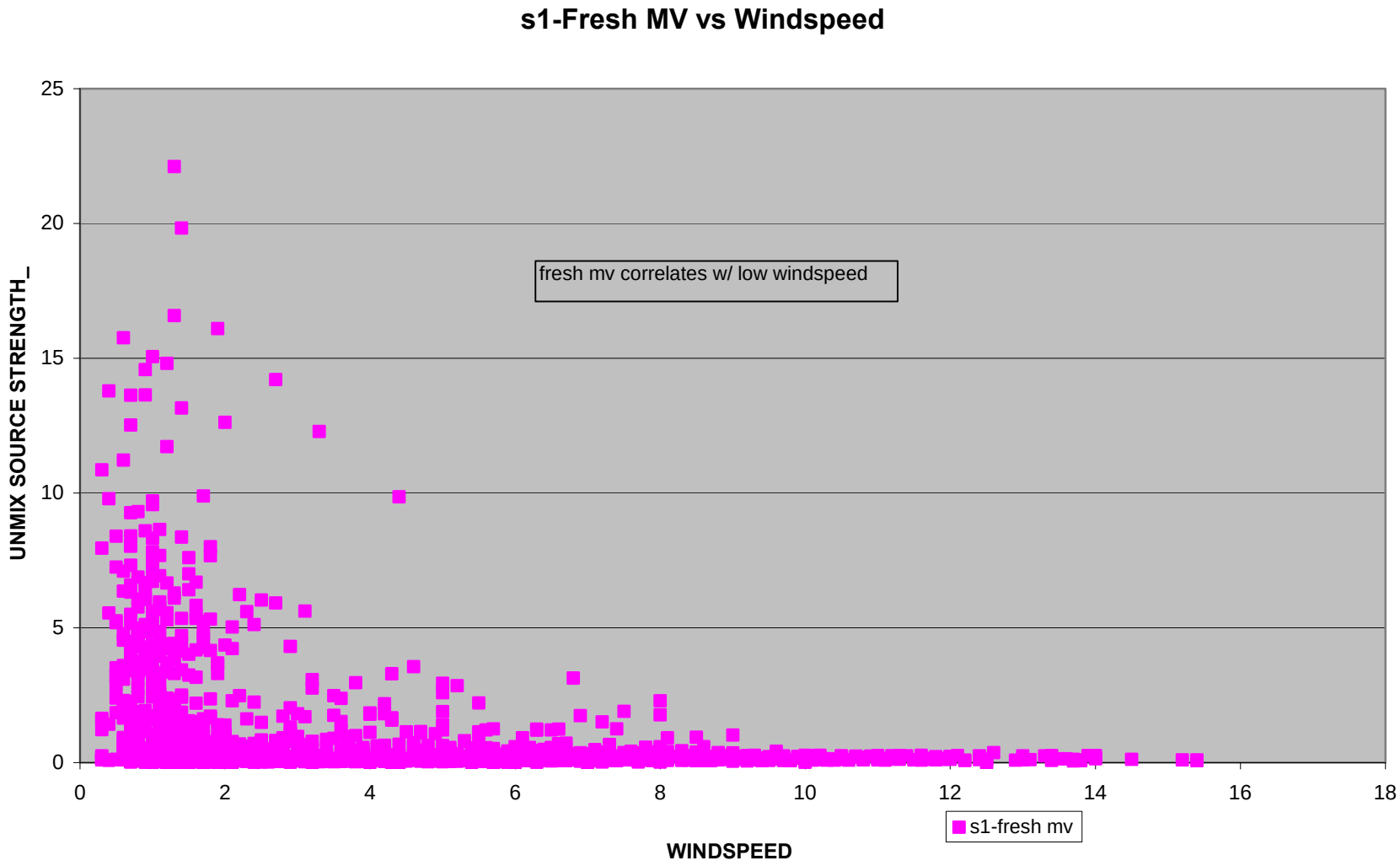


Figure 1.2.3 UNMIX Oil Combustion Category vs Wind Speed

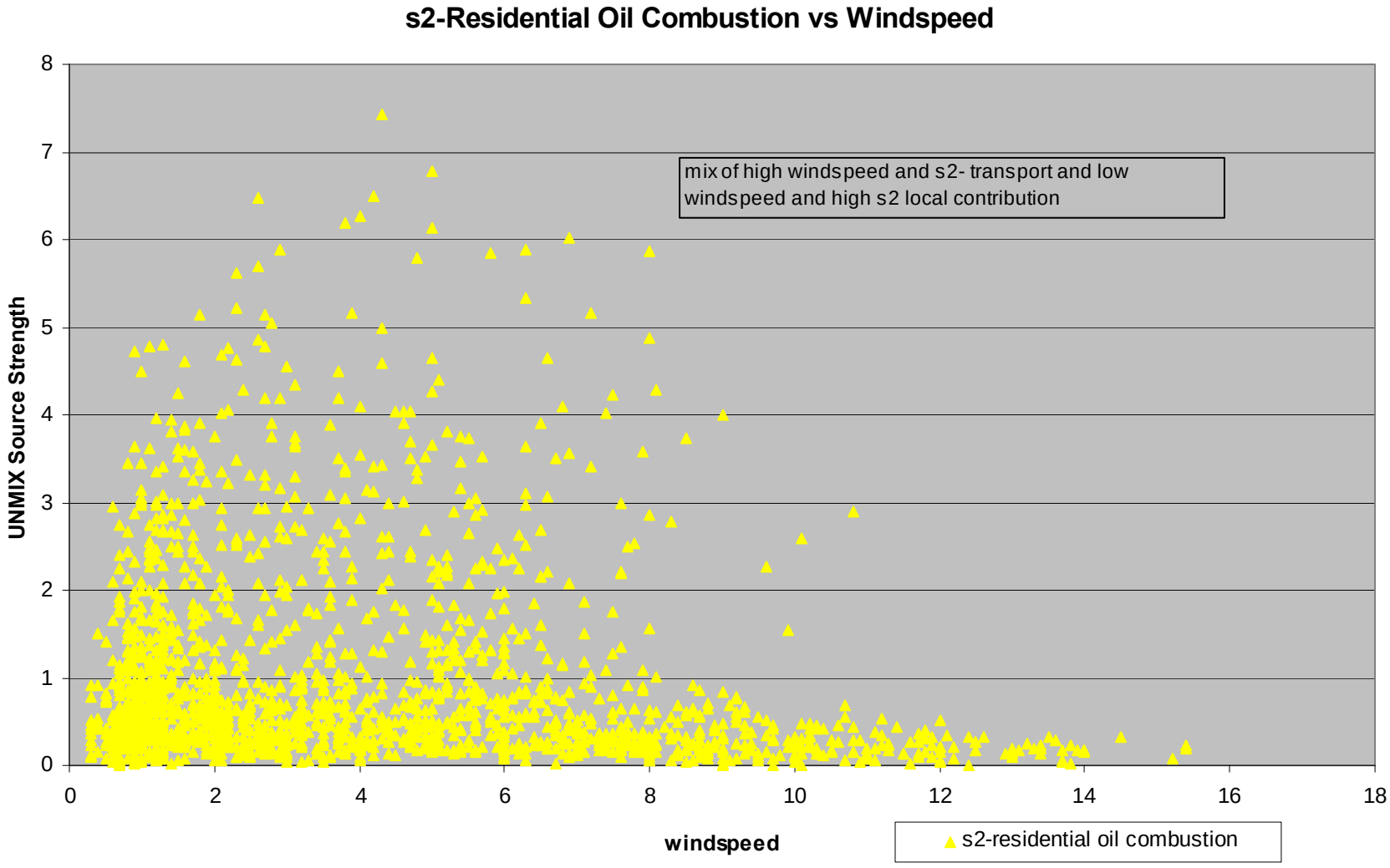


Figure 1.2.4 UNMIX Woodsmoke Category vs Wind Speed

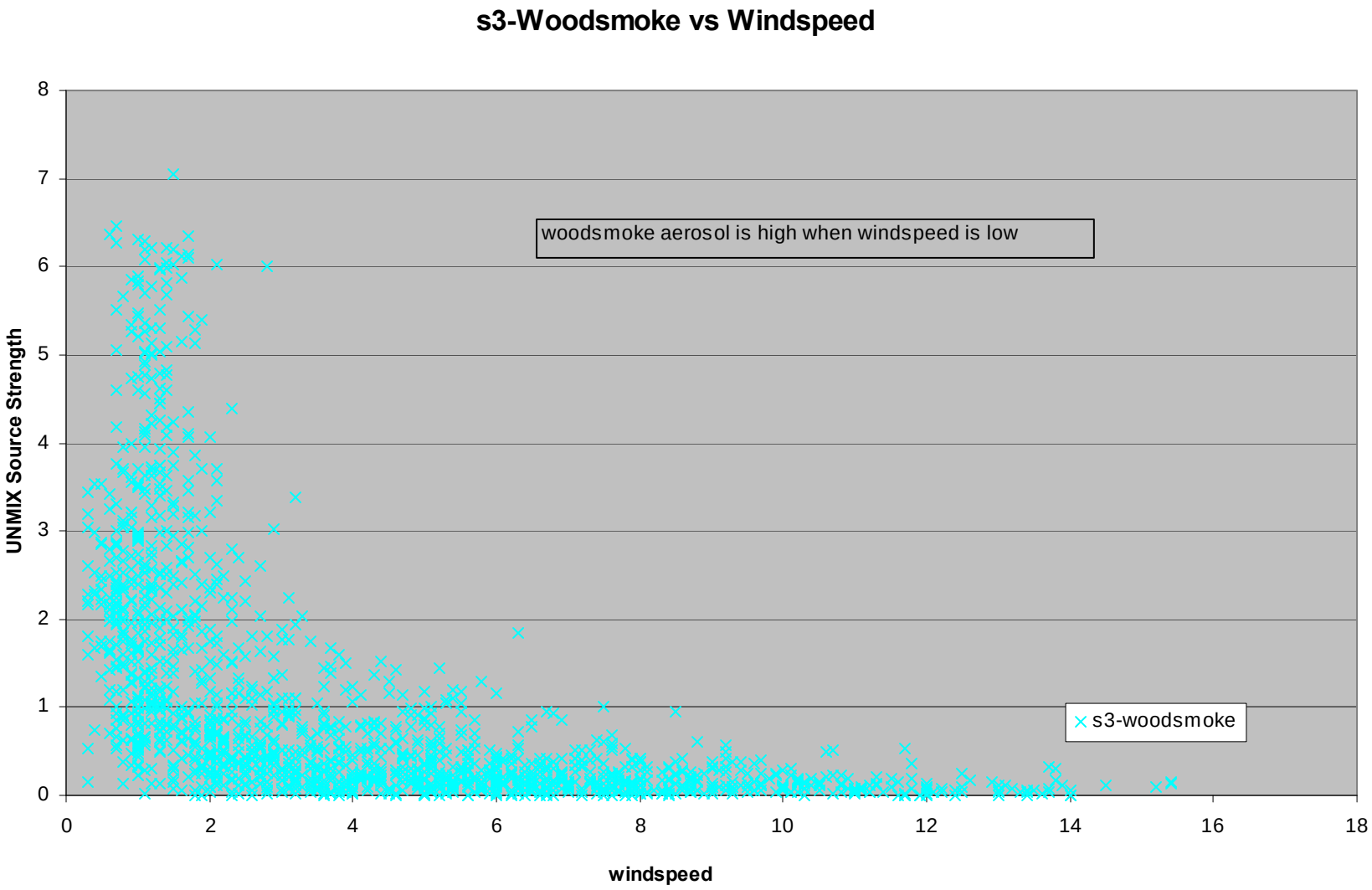


Figure 1.2.5 UNMIX Secondary Organic Category vs Wind Speed

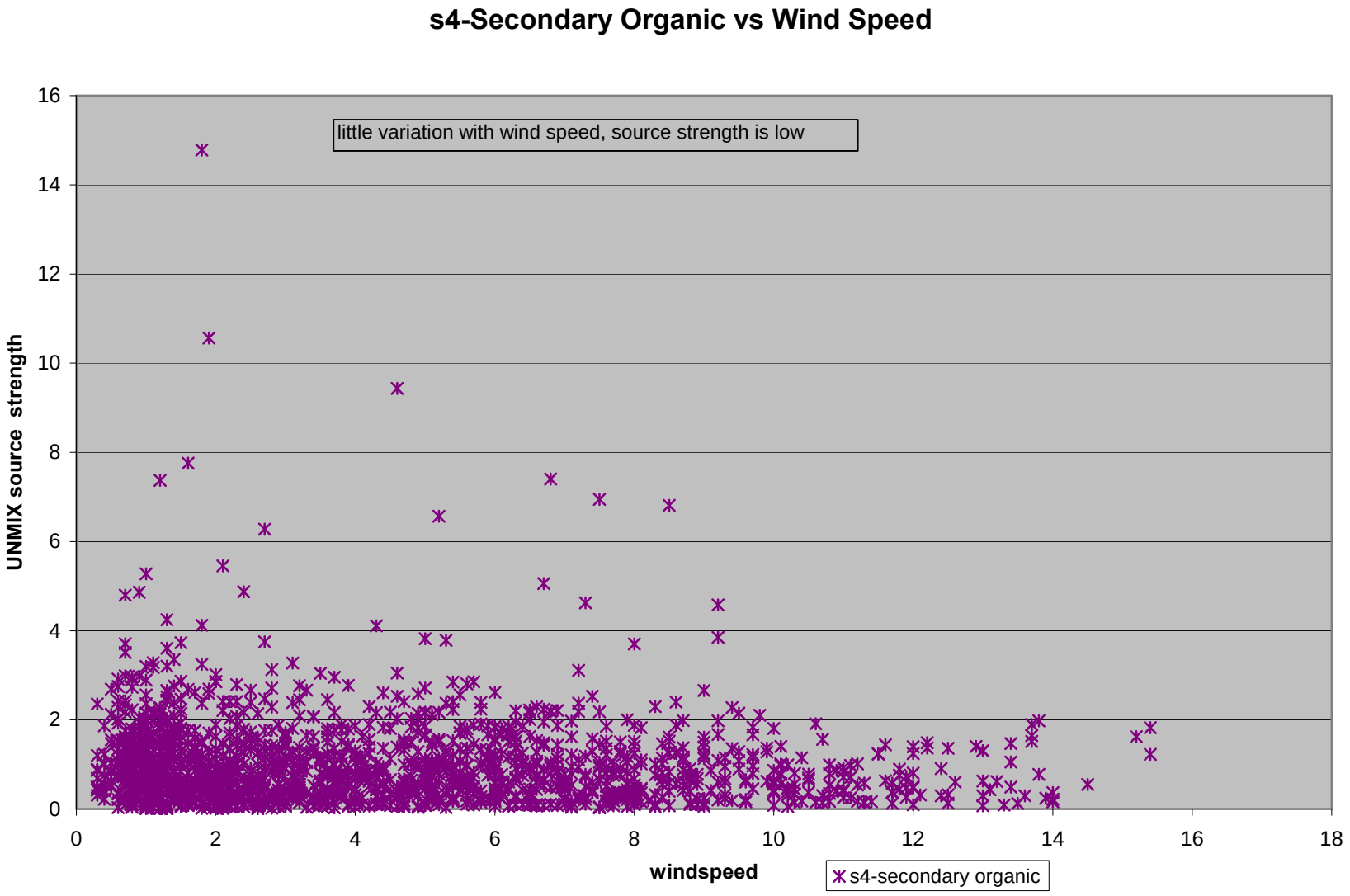
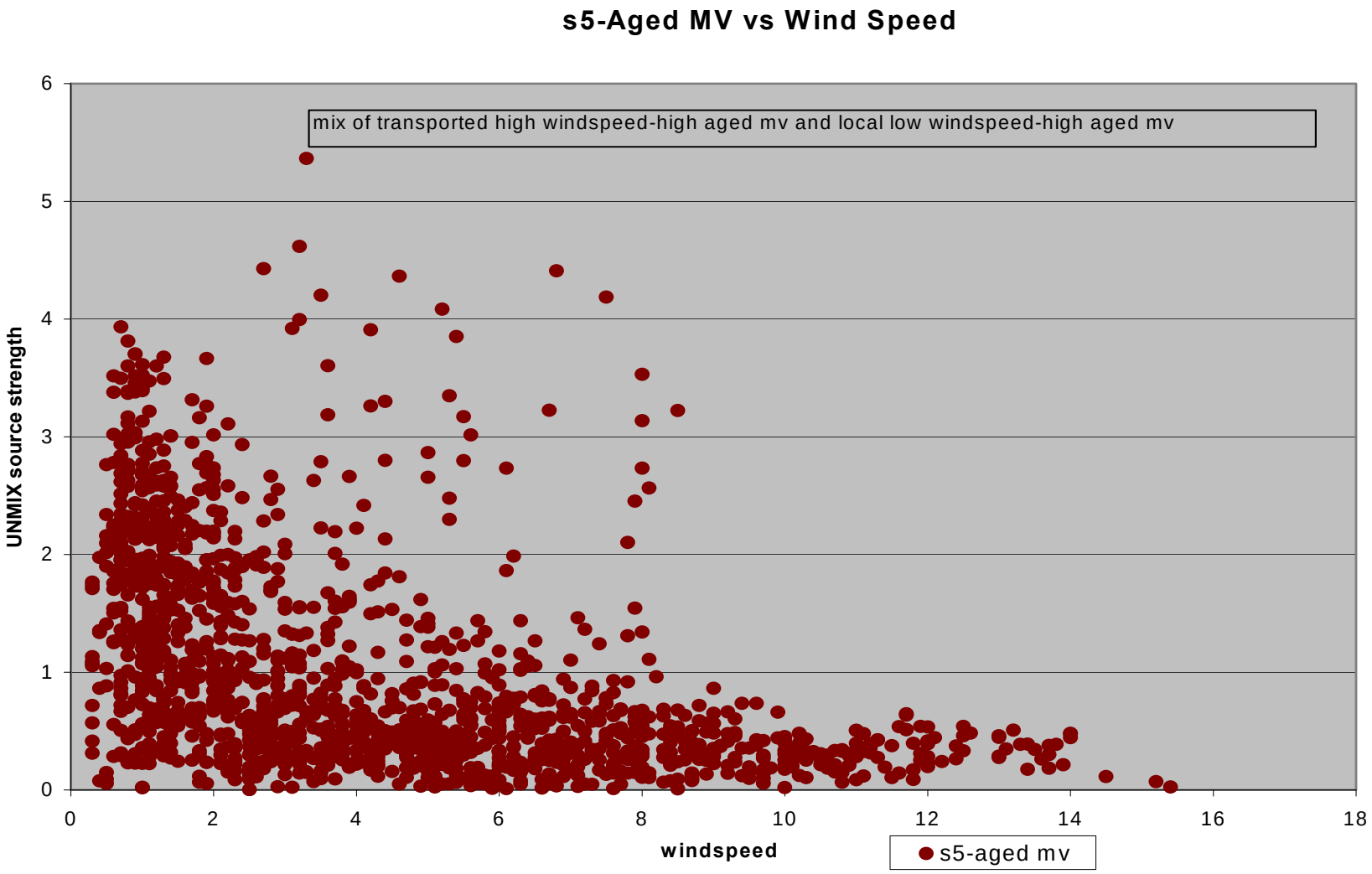


Figure 1.2.6 UNMIX Aged Motor Vehicle Category vs Wind Speed



1.3 March 14, 2007 event

An approaching warm front, cool surface temperatures, (Figure 1.3.1) SSW winds (Figure 1.3.2) and a stream of unseasonably warm overriding air (+7-8°C at 850 mb) (Figure 1.3.3) provided the stable conditions necessary for trapping pollutants in a shallow layer (250m) (Figure 1.3.4). Hourly values in excess of 80 $\mu g/m^3$ and a daily average above 44$\mu g/m^3$ were measured at the Thomaston site (Figure 1.3.5). At Thomaston, 2-wavelength nephelometer (black carbon) data, volatile and non-volatile mass, and gaseous measurements of CO, NO, NO_2, SO_2 help to resolve speciated data into categories of (aged and fresh MV, wood smoke, secondary aerosol, and residential oil combustion. The species associated most with transport to this rural site (residential oil combustion, aged mv, and secondary aerosol) are the highest combined with the highest wind speed and the broadest time series peak (Figure 1.3.6). When the wind speed was low during the early morning rush hour fresh MV and wood smoke peaked (local aerosol) for a short duration of time (short time peak). The combination of the local and transported components led to the highest wintertime PM event seen in the 2006-2008 time period of recorded data at Thomaston.

Figure 1.3.1 Surface Analysis for 3-14-2007

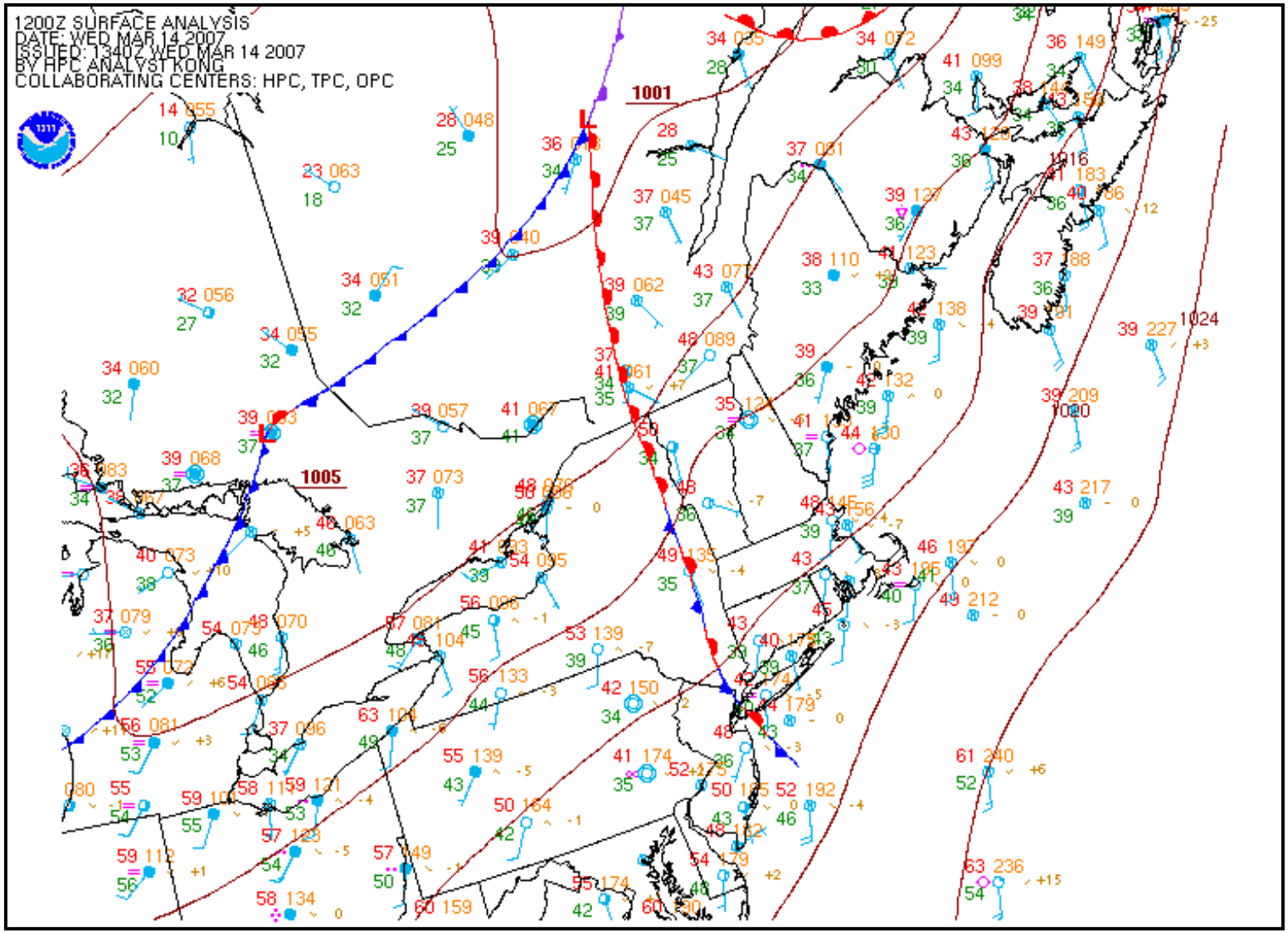


Figure 1.3.2 24-hr Back Trajectory Plot for 3-14-2007

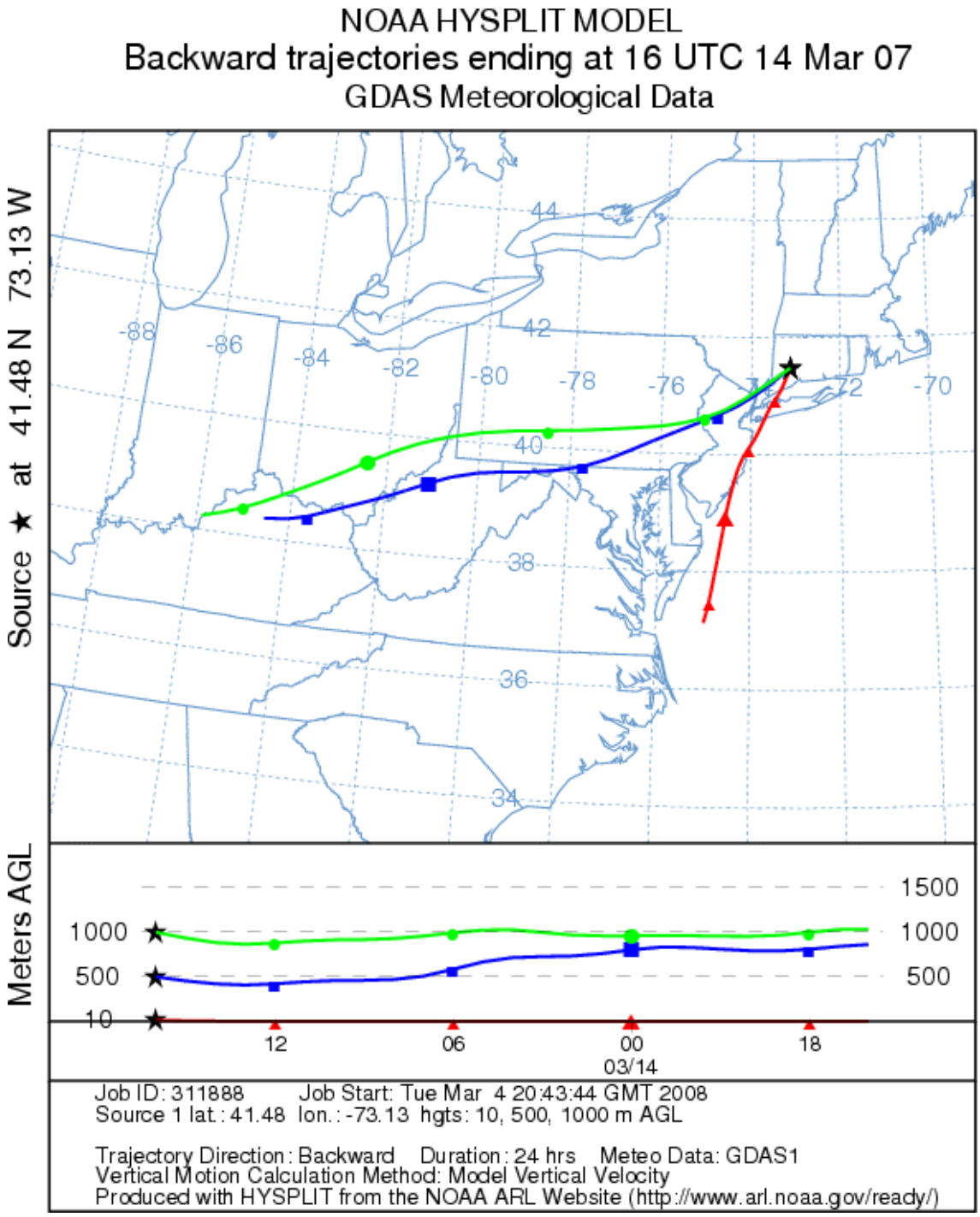


Figure 1.3.3 850 mb analysis for 03-14-2007 12Z

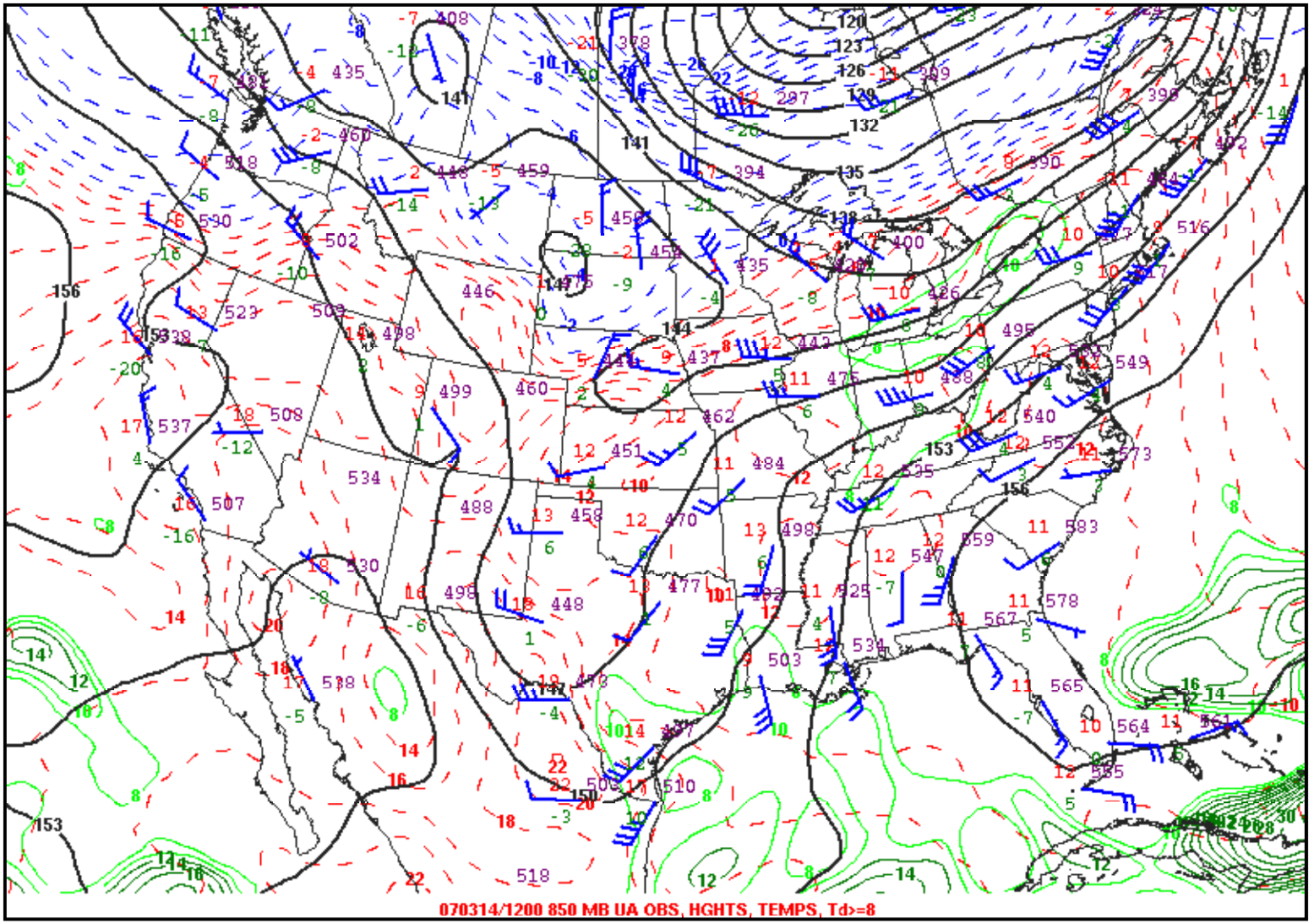


Figure 1.3.4 NAM model stability for 3-14-2007

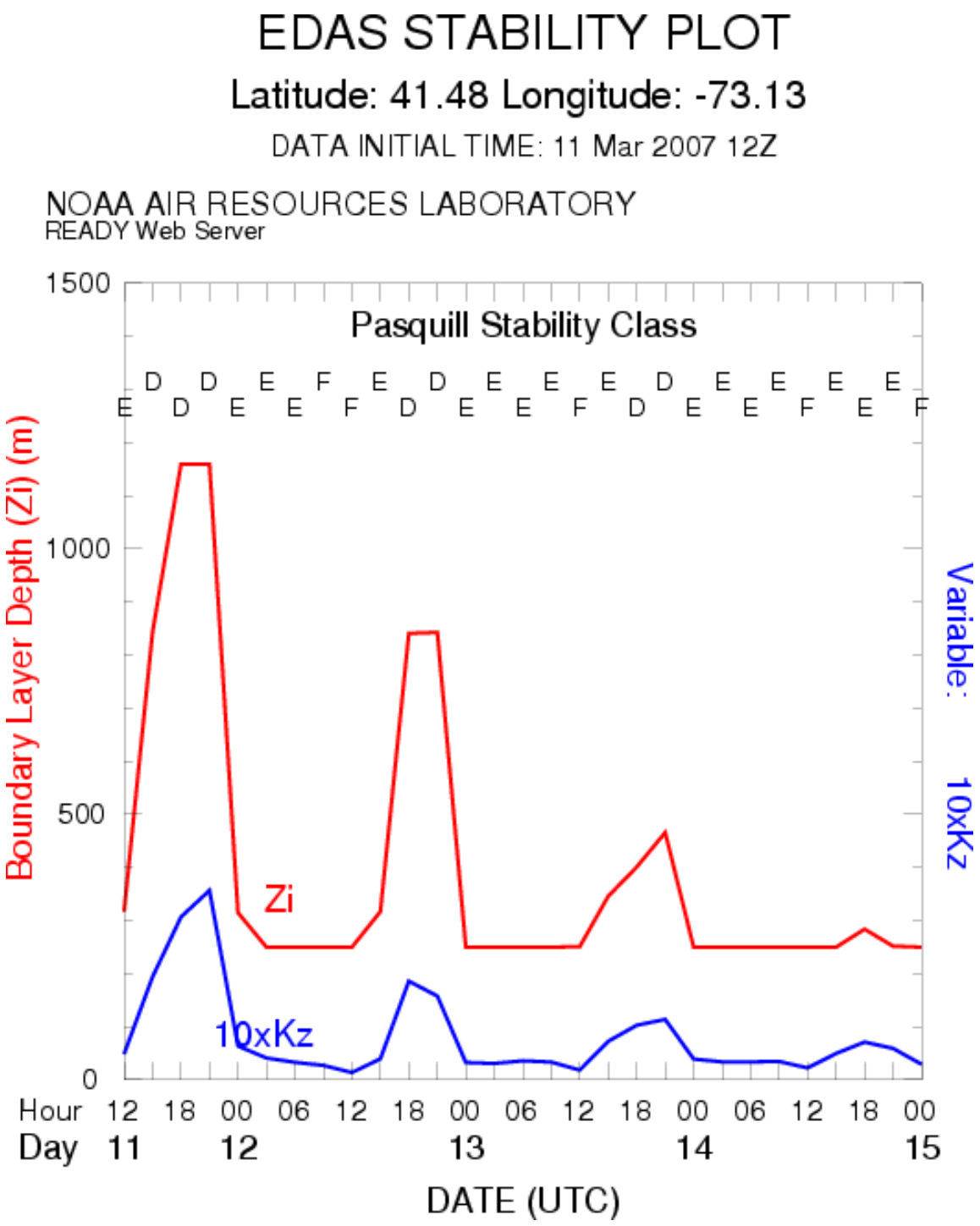


Figure 1.3.5 Thomaston Quarter 1, 2007 Hourly PM2.5 (annotated with Pasquill stability class for peak concentration times)

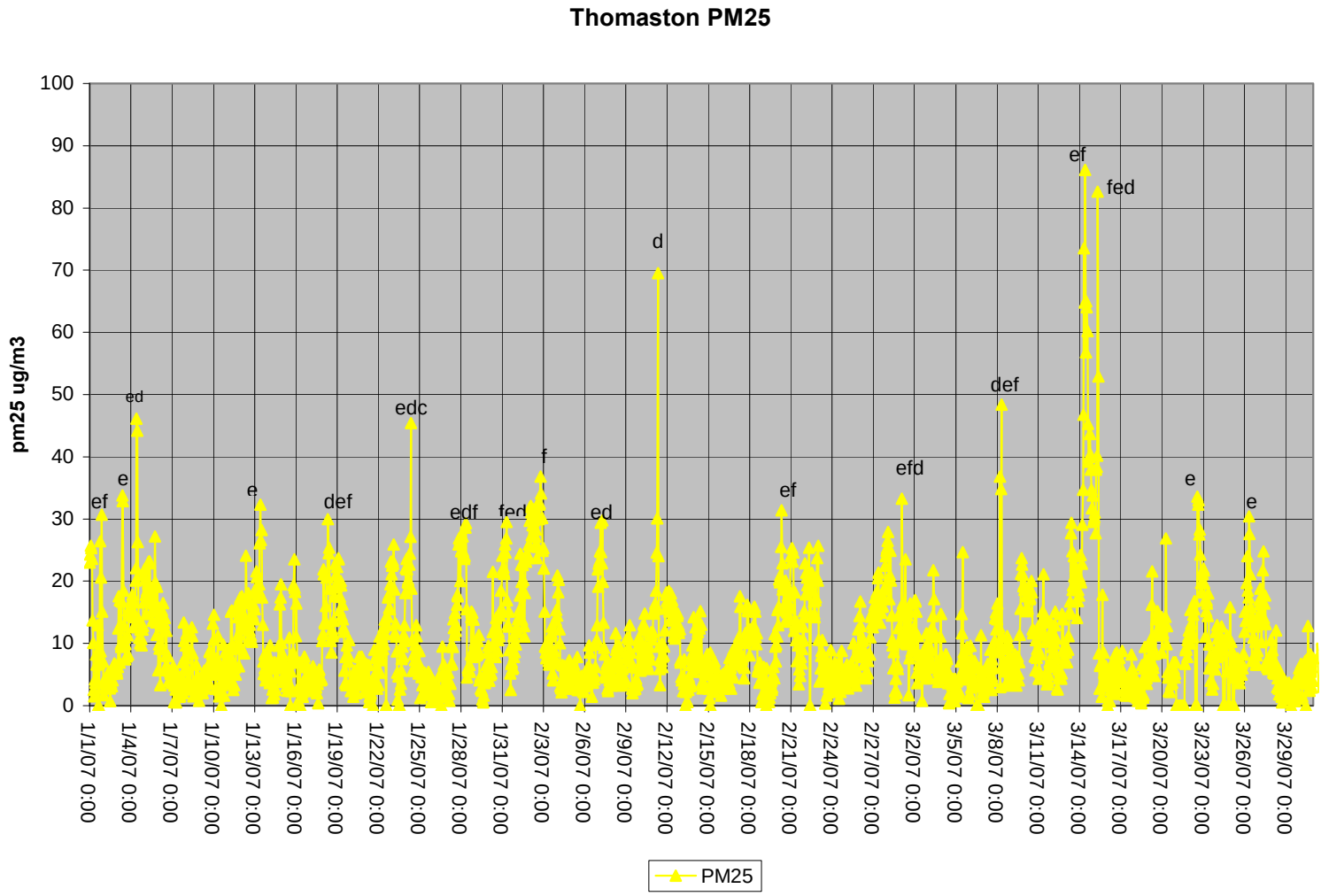
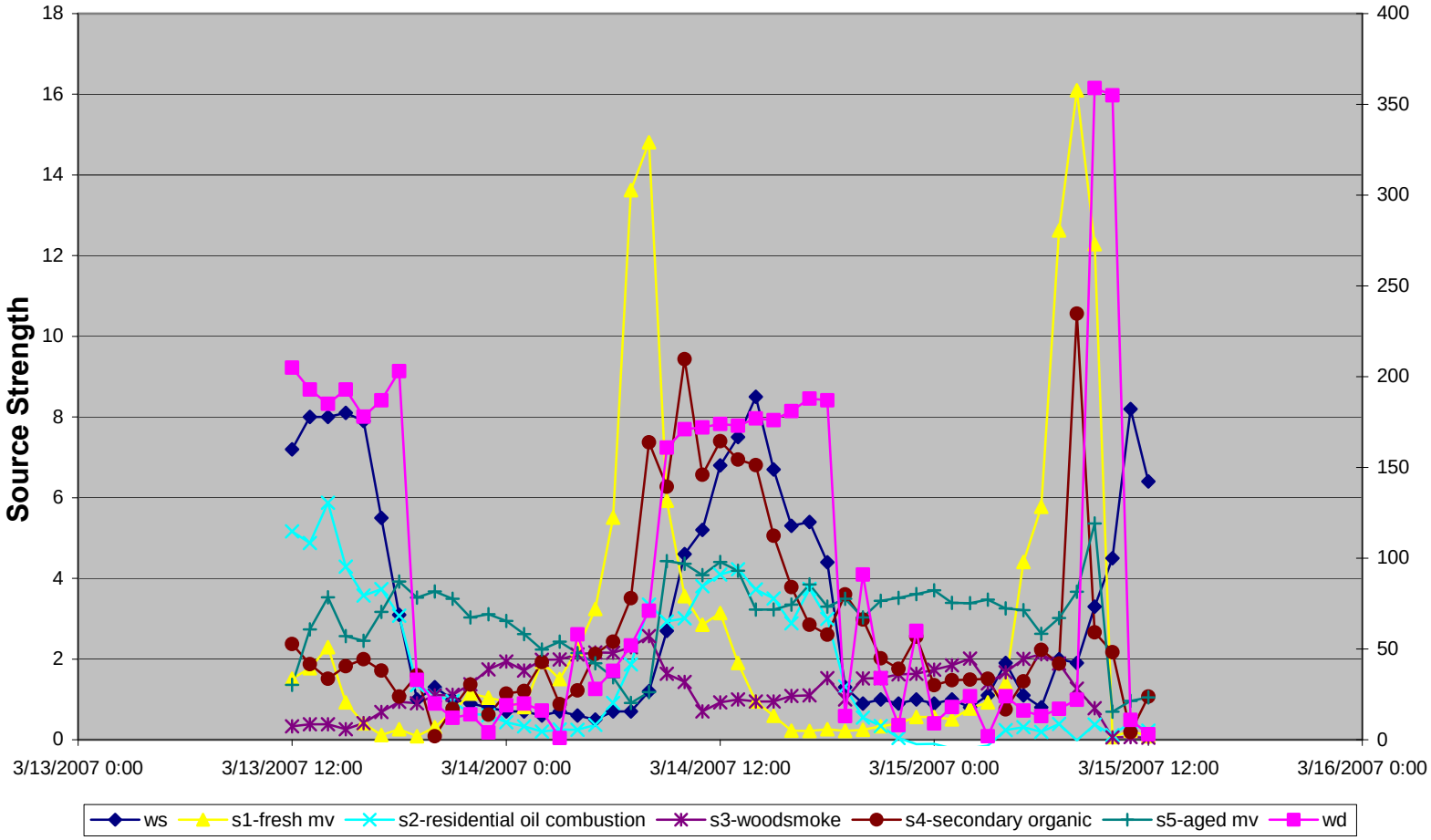


Figure 1.3.6 Thomaston Time Series of UNMIX Source Contribution for 3/13-15/2007



1.4 Summertime PM2.5 Event Examples

For the summer, highly time resolved data was not available. However speciated data was available for a rural site at Cornwall (IMPROVE network 10/01-12/04) and urban STN sites at Westport (4/02-5/03) and New Haven (6/03-present), with a 1 in 3 day time resolution. Thus some of the highest concentration days were missed by the sampling schedule.

1.4.1 UNMIX modeling of STN and IMPROVE samples

The STN and IMPROVE data records consist of 55 species taken every third day: NH_4, SO_4, NO_3, EC, OC, and many species of metals crustal materials such as Fe, Si, Ca, Al, Ti; heavy metals used in industry such as Zn, Pb, Cu, Sn, Cd and many more. In EPA's speciated modeling attainment test for PM2.5, crustal, ammonium sulfate, ammonium nitrate, elemental carbon, and organic carbon are tracked in the photochemical modeling. Species with large enough concentrations and identifiable sources would likely be targeted to design control strategies for. As before, UNMIX was used to differentiate and identify different source types from all species for all days. UNMIX modeling results for summer 2002 for both the urban STN and rural IMPROVE (Westport and Cornwall) are seen in Figures 1.4.1-2. In the first figure, UNMIX sources 1-4 are: Crustal, Coal combustion, Motor vehicle, and Oil combustion. Each has a unique combination of chemical markers and ratio of key components that make it identifiable as the sources indicated.

1.4.2 July 19, 2002

July 19, 2002 was chosen as it was the best combination of high PM and a record of speciated data from the STN urban network. As can be seen from Figure 1.4.1.1, source 2's highest peak for summer 2002 is on 7/19 (for the days sampled, two key days were missing). The total PM for that day was 34.2 $\mu g/m^3$. An approximate contribution of that source is seen in Table 1.4.2. 14.4 $\mu g/m^3$ of this source, identified as coal combustion, or 44% of the total. Source 4, oil combustion (local/regional EGU) accounted for ~9 $\mu g/m^3$, 26% of the total. With the sampler at a site along the coast with an onshore wind, it is likely transported aerosol from the northeast corridor. Sources 1 and 3 (a combination of motor vehicle exhaust, dispersed road dust from motor vehicles) account for 11 ug/m^3 or 32%. Weather maps and back trajectory plots for this day are included in Figures 1.4.2.1-4. They show that low level winds are out of the NYC area, and upper level winds from the western PA coal burning EGU's (Figure 1.4.2.2). Surface charts show a weak front draped across the area boundary with SW winds S of the front (Figures 1.4.2.1,3). The frontal boundary may have helped to trap air from moving north, setting up a convergence zone, concentrating the pollutants. Even coastal summertime mixing heights (600m) (Figure 1.4.2.4) can support the mixing down of transported aerosol from PA (500m trajectory coming from the west). Aerosol mixed down to the west (over the NY CMSA) also gets injected in the maritime boundary layer over Long Island Sound. A mixture of local, regional and long-range transport are involved in the mix of aerosol measured at Westport on the 19th of July.

The fractional breakdown of the species is shown in Figure 1.4.2.5. Sulfate captures almost all of the ammonium (very little nitrate in the sample) so 18.57 μg/m^3 of the 33.1 μg/m^3 of reconstructed fine mass is detected. Due to the humidity, 5 μg/m^3 of the sample was water. 7.695 μg/m^3 was made up of carbon (OC and EC, 6.95+ 0.74). Ammonium sulfate from EGUs appears to be the dominant species.

Table 1.4.2 UNMIX 7/19/2002 source contribution

7/19/2002	Avg UNMIX source strength	Source fraction of total	Source contribution in μg/m^3
UNMIX source 1 crustal	2.9	0.261261	8.961261
UNMIX source 2 coal combustion	4.6	0.414414	14.21441
UNMIX source 3 MV	1.6	0.144144	4.944144
UNMIX source 4 Oil combustion/ industrial	2	0.18018	6.18018

Figure 1.4.1.1 Westport UNMIX Source Composition Timeseries

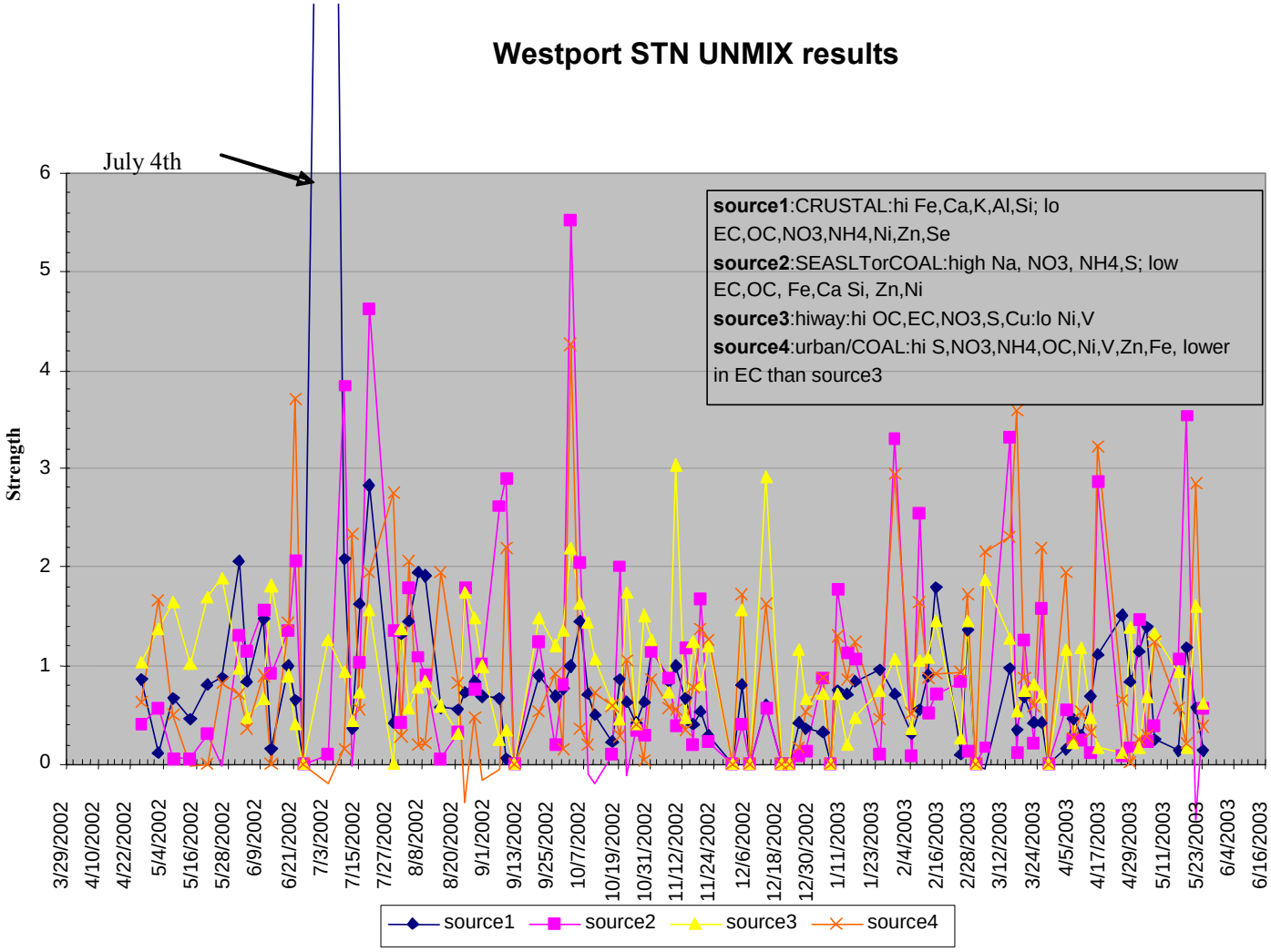
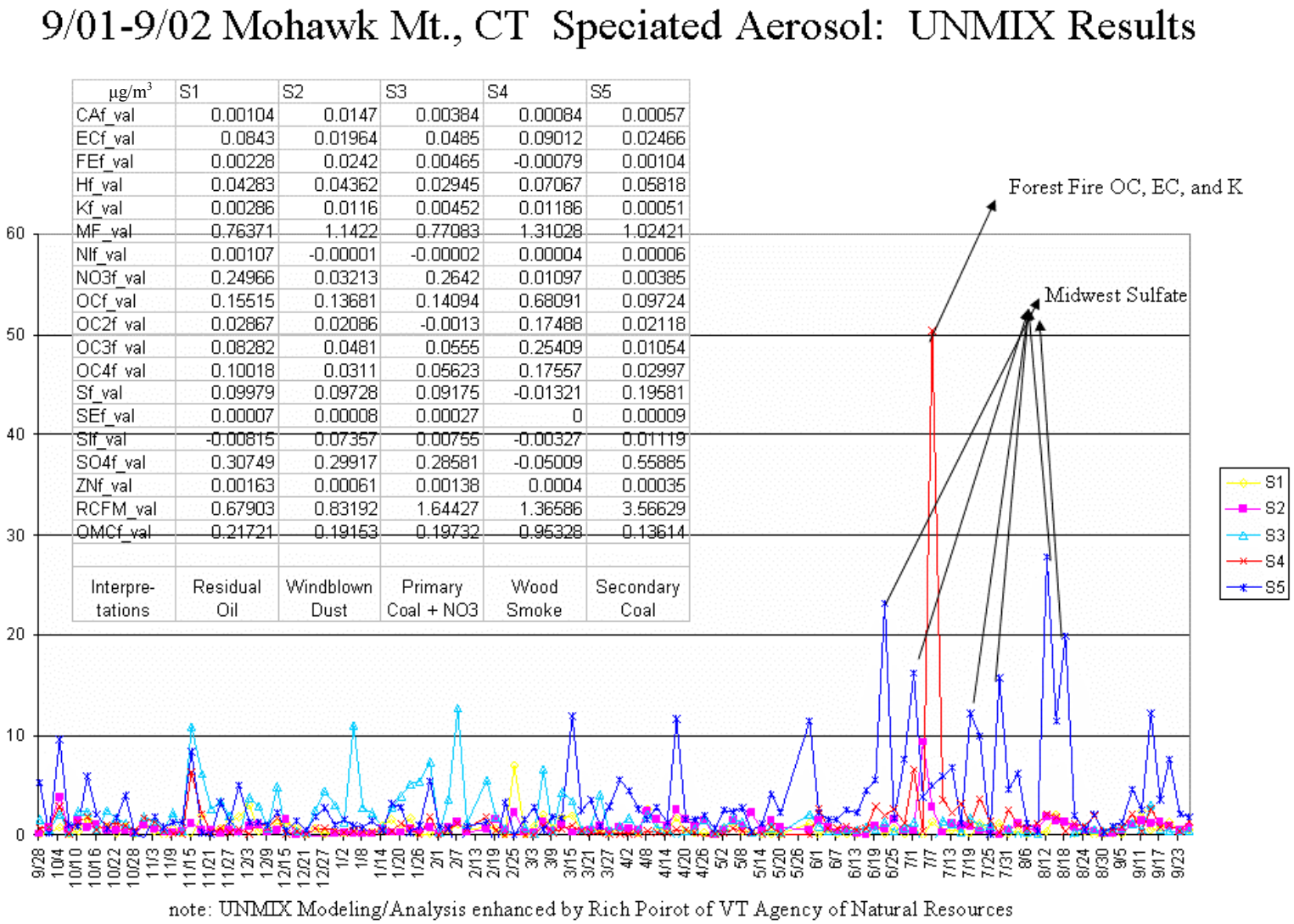


Figure 1.4.1.2 UNMIX IMPROVE Timeseries for Cornwall, CT (09/2001-09/2002)



µg/m³	S1	S2	S3	S4	S5
CAf_val	0.00104	0.0147	0.00384	0.00084	0.00057
ECf_val	0.0843	0.01964	0.0485	0.09012	0.02466
FEf_val	0.00228	0.0242	0.00465	-0.00079	0.00104
Hf_val	0.04283	0.04362	0.02945	0.07067	0.05818
Kf_val	0.00286	0.0116	0.00452	0.01186	0.00051
MF_val	0.76371	1.1422	0.77083	1.31028	1.02421
NIf_val	0.00107	-0.00001	-0.00002	0.00004	0.00006
NO3f_val	0.24966	0.03213	0.2642	0.01097	0.00385
OCf_val	0.15515	0.13681	0.14094	0.68091	0.09724
OC2f_val	0.02867	0.02086	-0.0013	0.17488	0.02118
OC3f_val	0.08282	0.0481	0.0555	0.25409	0.01054
OC4f_val	0.10018	0.0311	0.05623	0.17557	0.02997
Sf_val	0.09979	0.09728	0.09175	-0.01321	0.19581
SEf_val	0.00007	0.00008	0.00027	0	0.00009
SIf_val	-0.00815	0.07357	0.00755	-0.00327	0.01119
SO4f_val	0.30749	0.29917	0.28581	-0.05009	0.55885
ZNf_val	0.00163	0.00061	0.00138	0.0004	0.00035
RCFM_val	0.67903	0.83192	1.64427	1.36586	3.56629
OMCf_val	0.21721	0.19153	0.19732	0.95328	0.13614
Interpre-tations	Residual Oil	Windblown Dust	Primary Coal + NO3	Wood Smoke	Secondary Coal

Figure 1.4.2.1 Surface Analysis for 7-19-2002 12Z

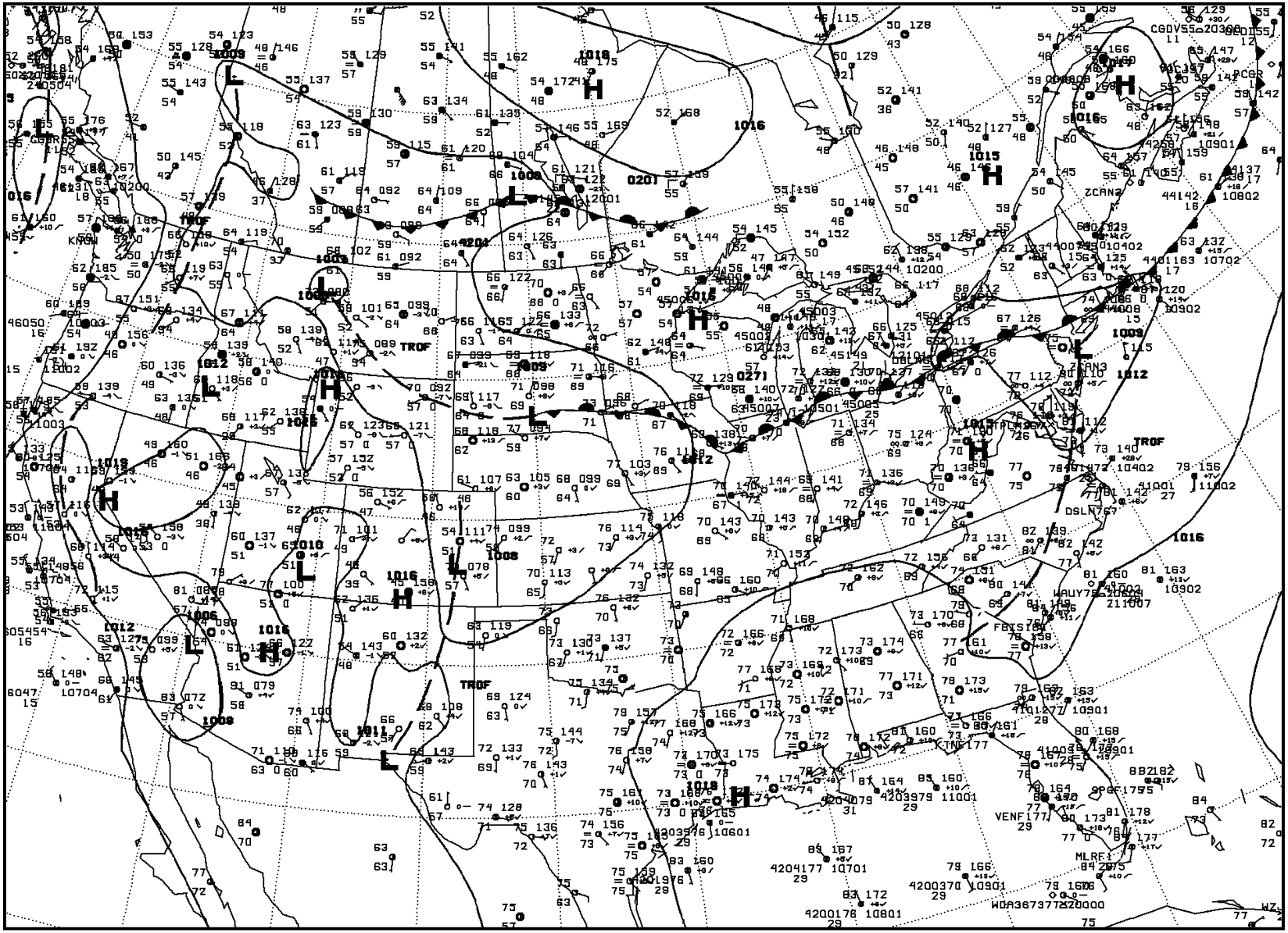


Figure 1.4.2.2 Back trajectories for Westport, CT on 7-19-2002

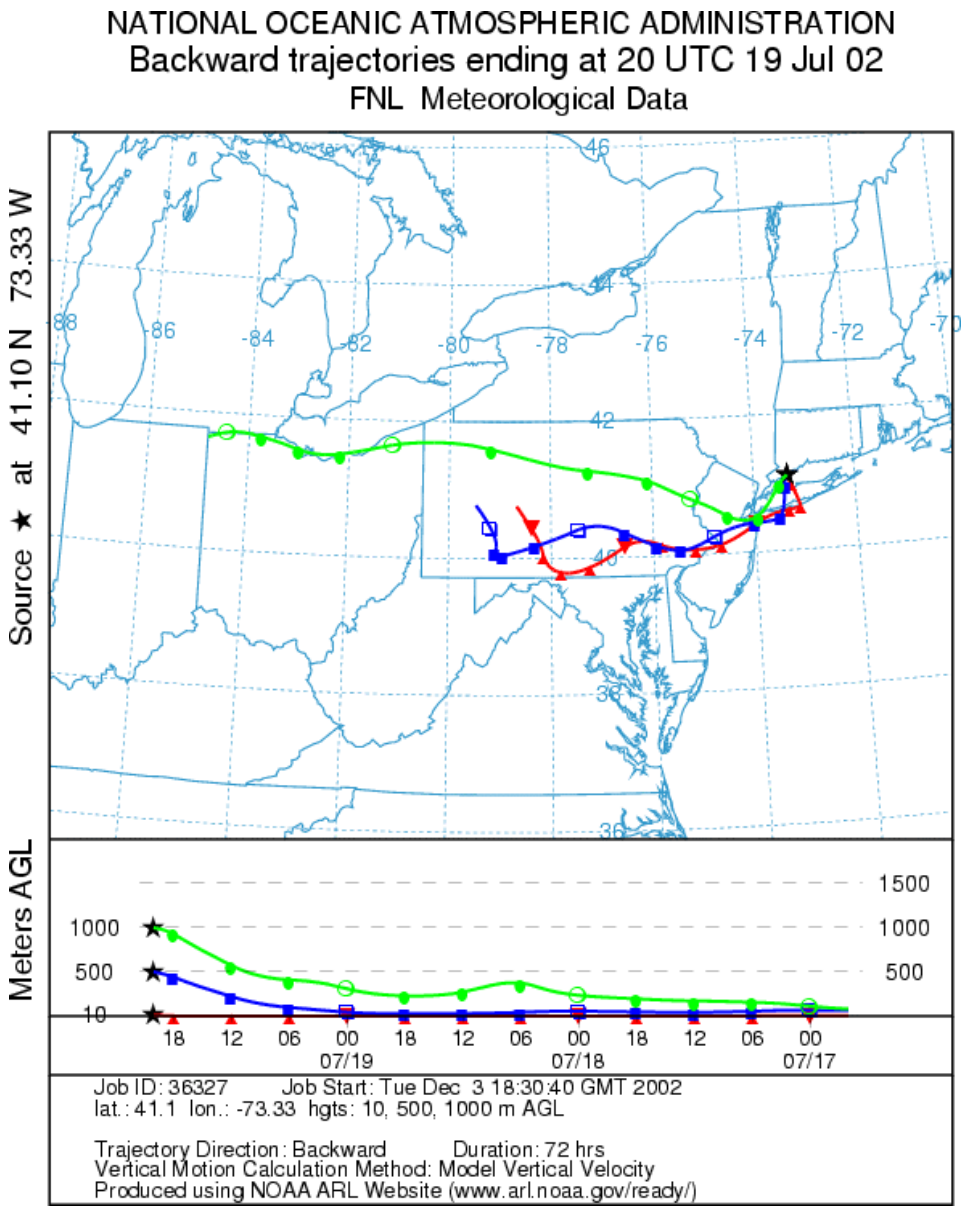
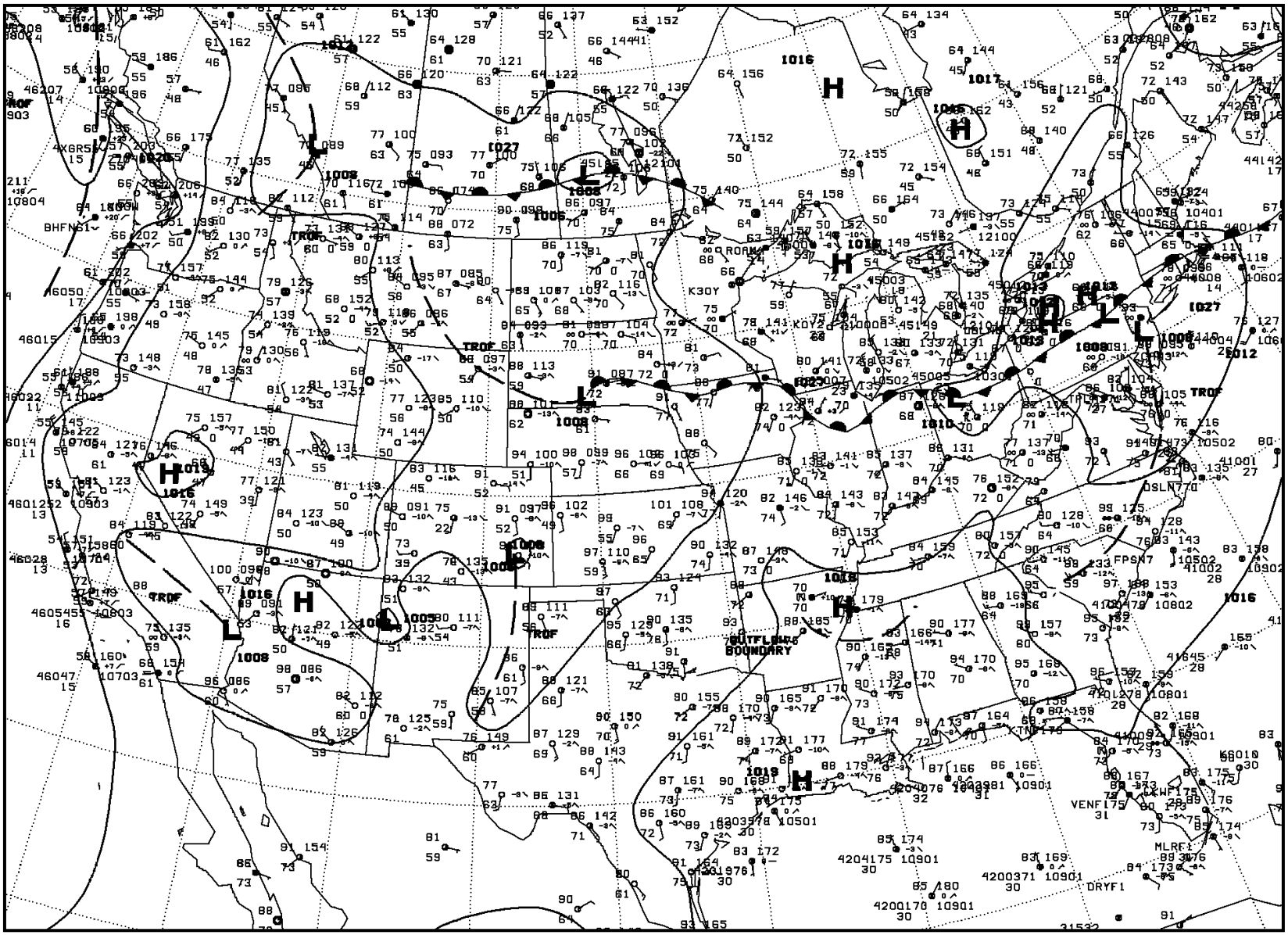


Figure 1.4.2.3 Surface Analysis for 7-19-2002 18Z



1.4.2.4 Height of Boundary Layer at Westport, CT on 7-19-2002 (FNL reanalysis)

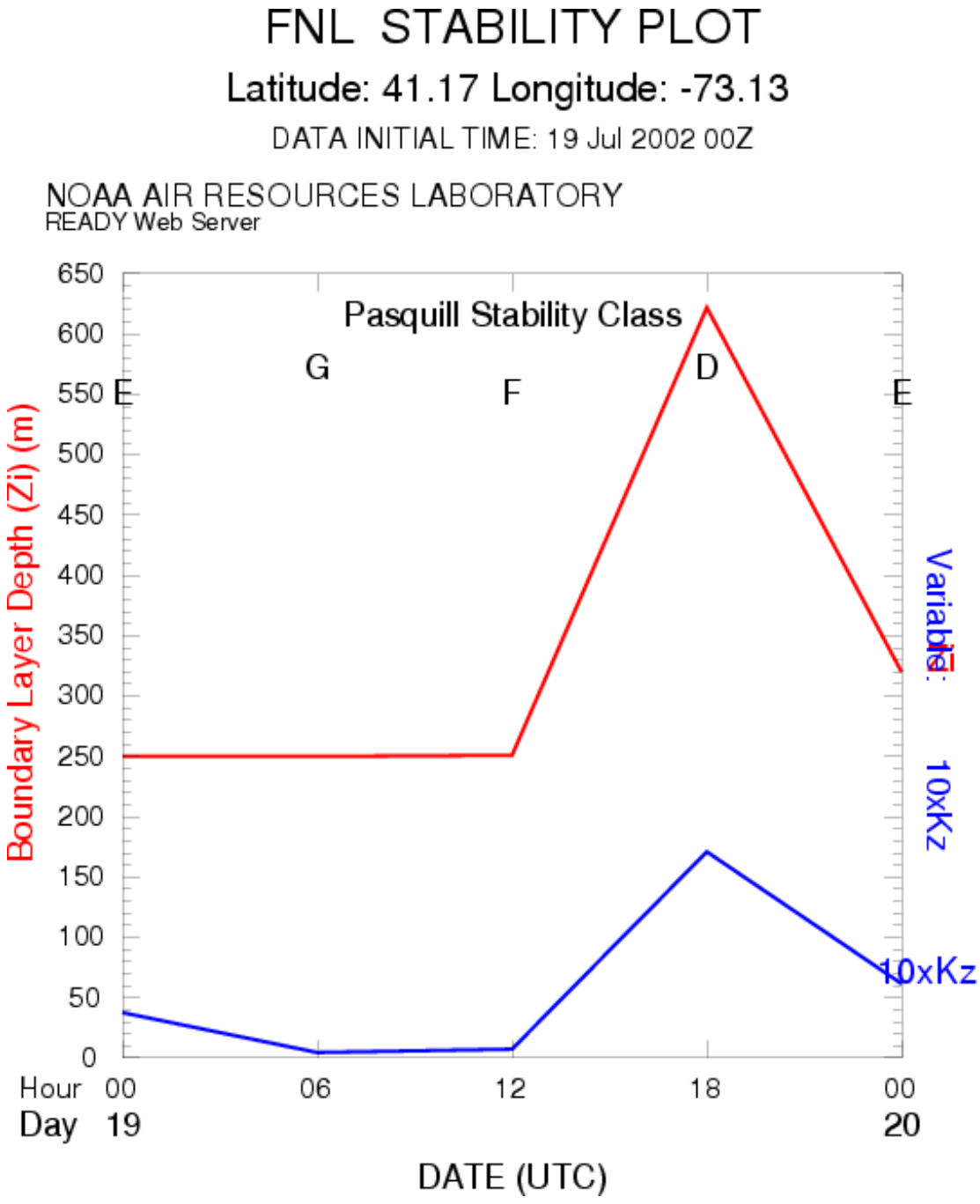
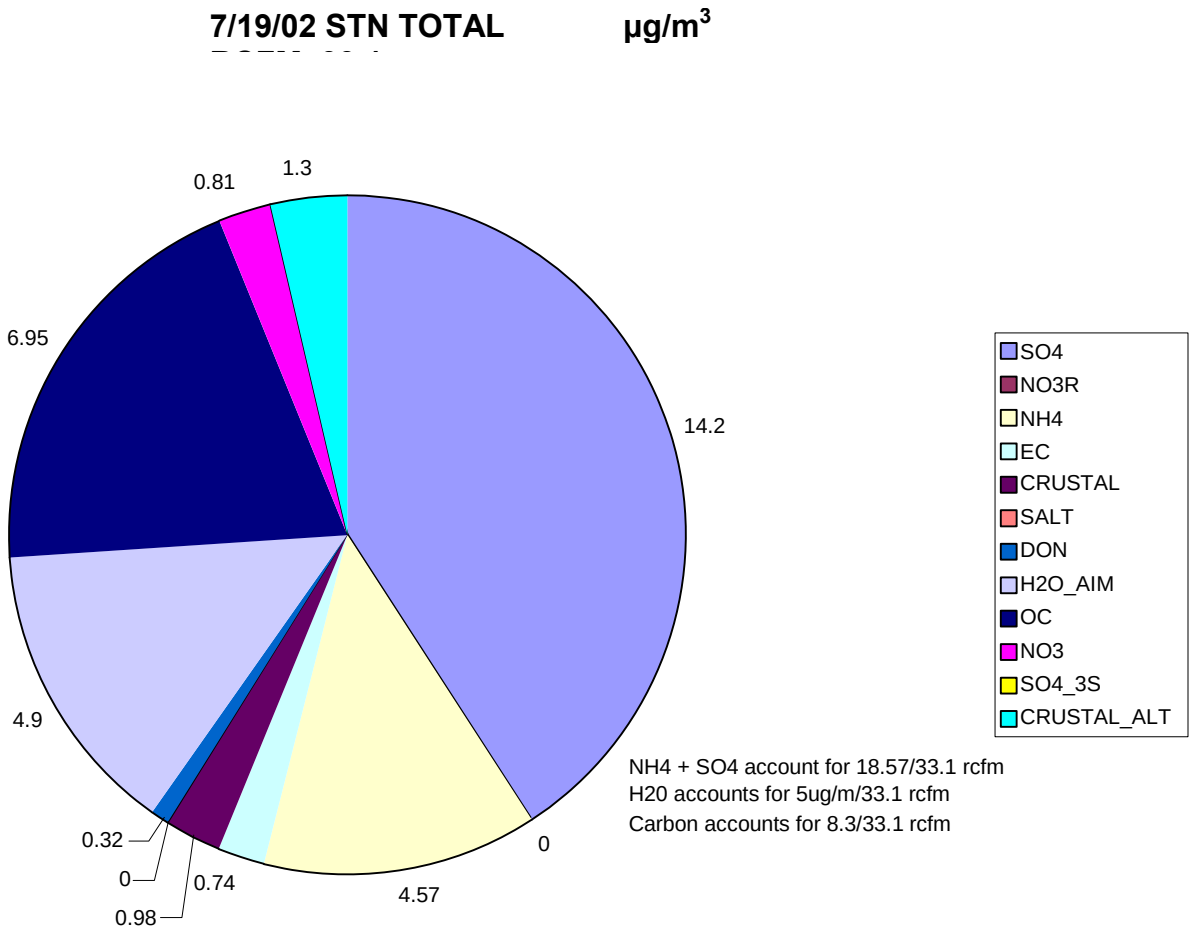


Figure 1.4.2.5 STN Speciated PM2.5 for Westport, CT on 7-19-2002



1.4.3 August 12, 2002 Event

August 12, 2002 was a classic example of an east coast regional air pollution event. A large, hot air mass laden with sulfate drifted east and was transported northeastward at all levels. The next two days, hourly values exceeded 60 $\mu g/m^3$ (Figure 1.4.3.1).

Weather conditions consisted of a hot surface Bermuda high, WSW winds (Figure 1.4.3.2), mid-level nocturnal low-level jet lee of the Appalachian mountains (Figure 1.4.3.3) and upper level westerly winds out of Pennsylvania and the Ohio River Valley (See Figures 1.4.3.4-5). Using the UNMIX IMPROVE results, 28 of the 32 $\mu g/m^3$ of fine mass was coal aerosol (Figure 1.4.3.6), and in the IMPROVE speciated data, 23/33 $\mu g/m^3$ was comprised of ammonium sulfate (Figure 1.4.3.7). This event provides further evidence that in order to reduce elevated PM levels during the summer in Connecticut, a regional pollutant reduction strategy will be needed.

Figure 1.4.3.1 PM2.5 Time Series for Cornwall and Waterbury, CT Summer 2002

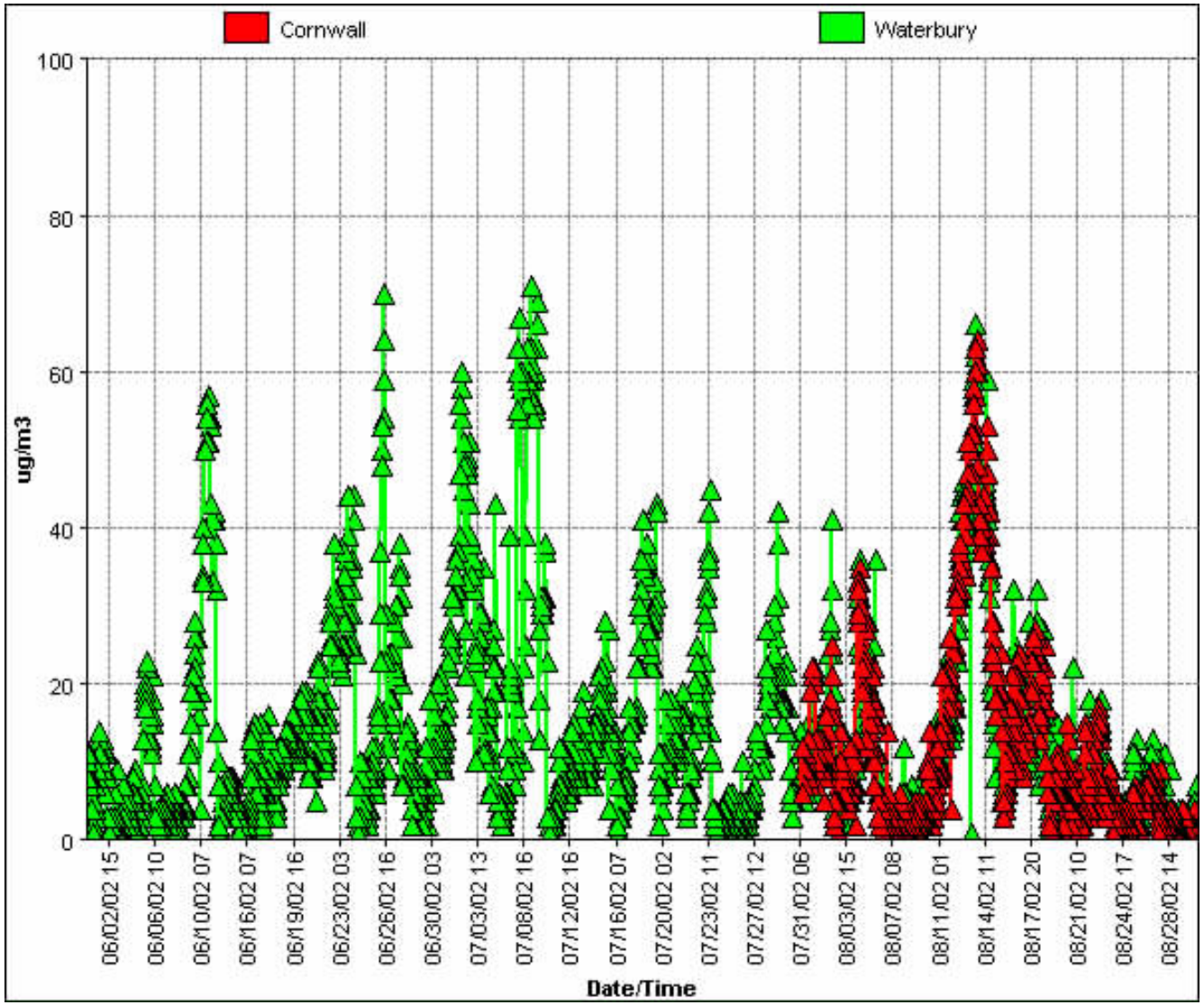


Figure 1.4.3.2 Surface Analysis for 18Z 8/12/02

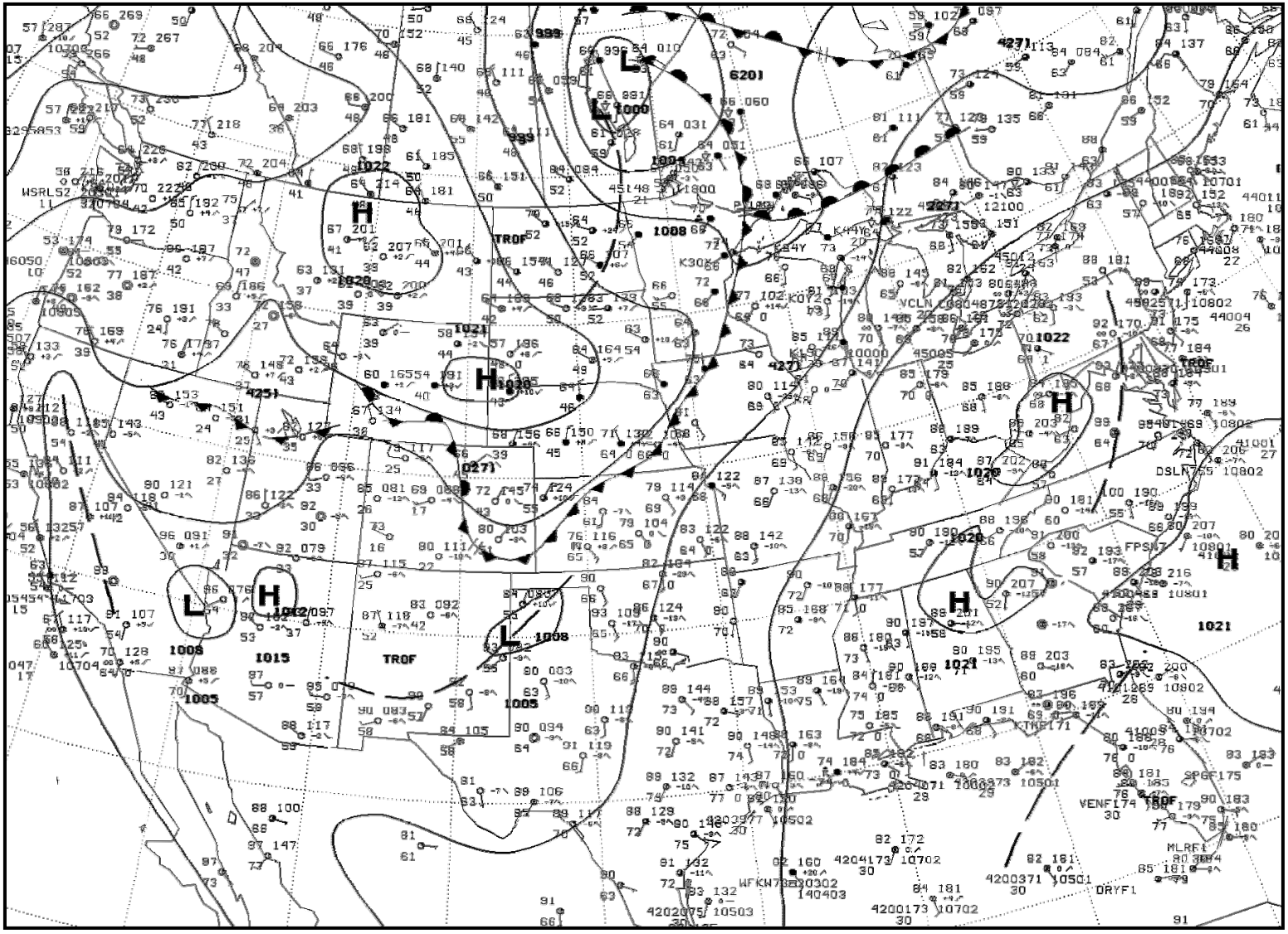


Figure 1.4.3.3 Profiler time series for New Brunswick, NJ 8-12-2002

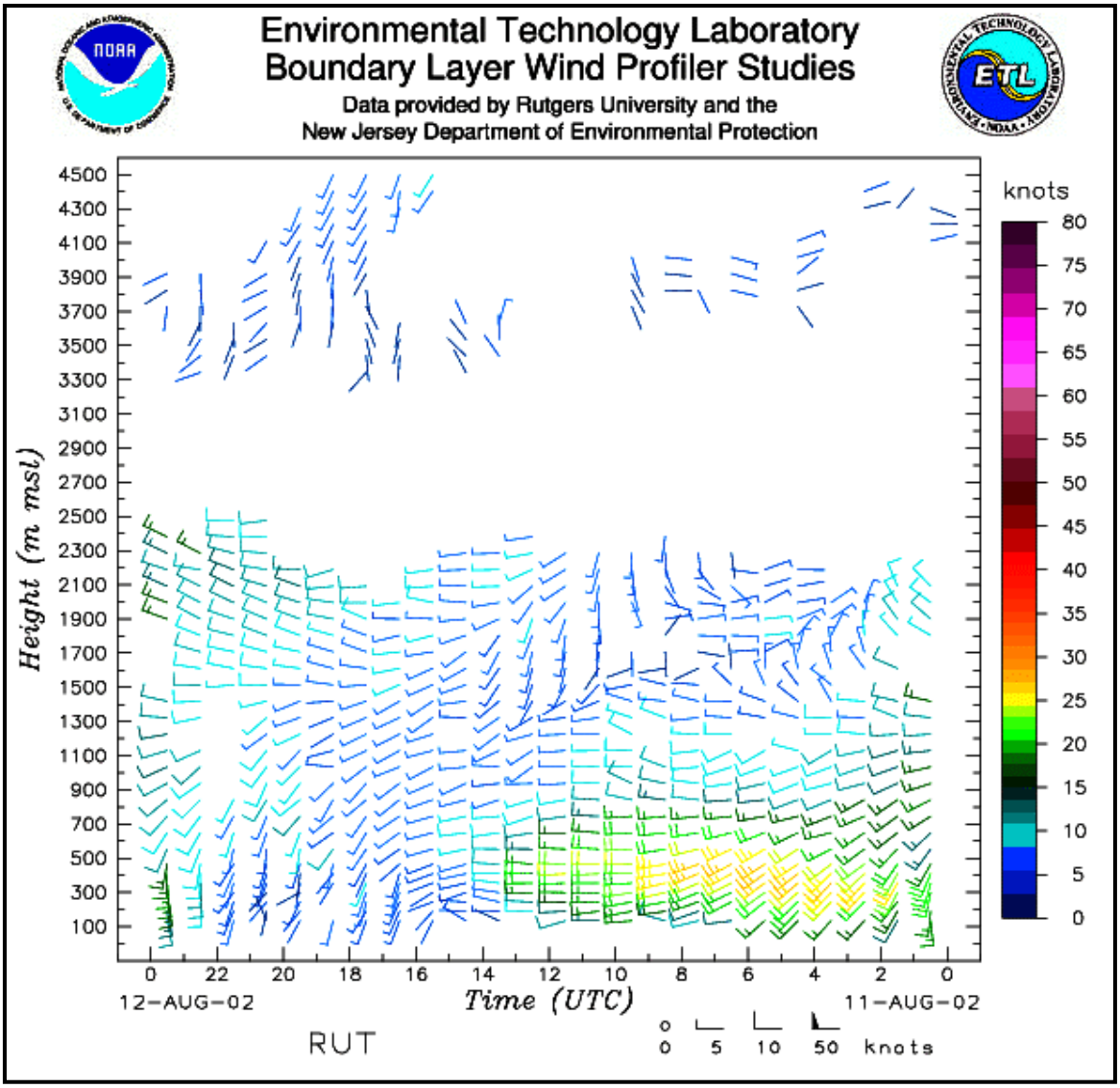


Figure 1.4.3.4 850mb Chart for 8-13-2002 0Z

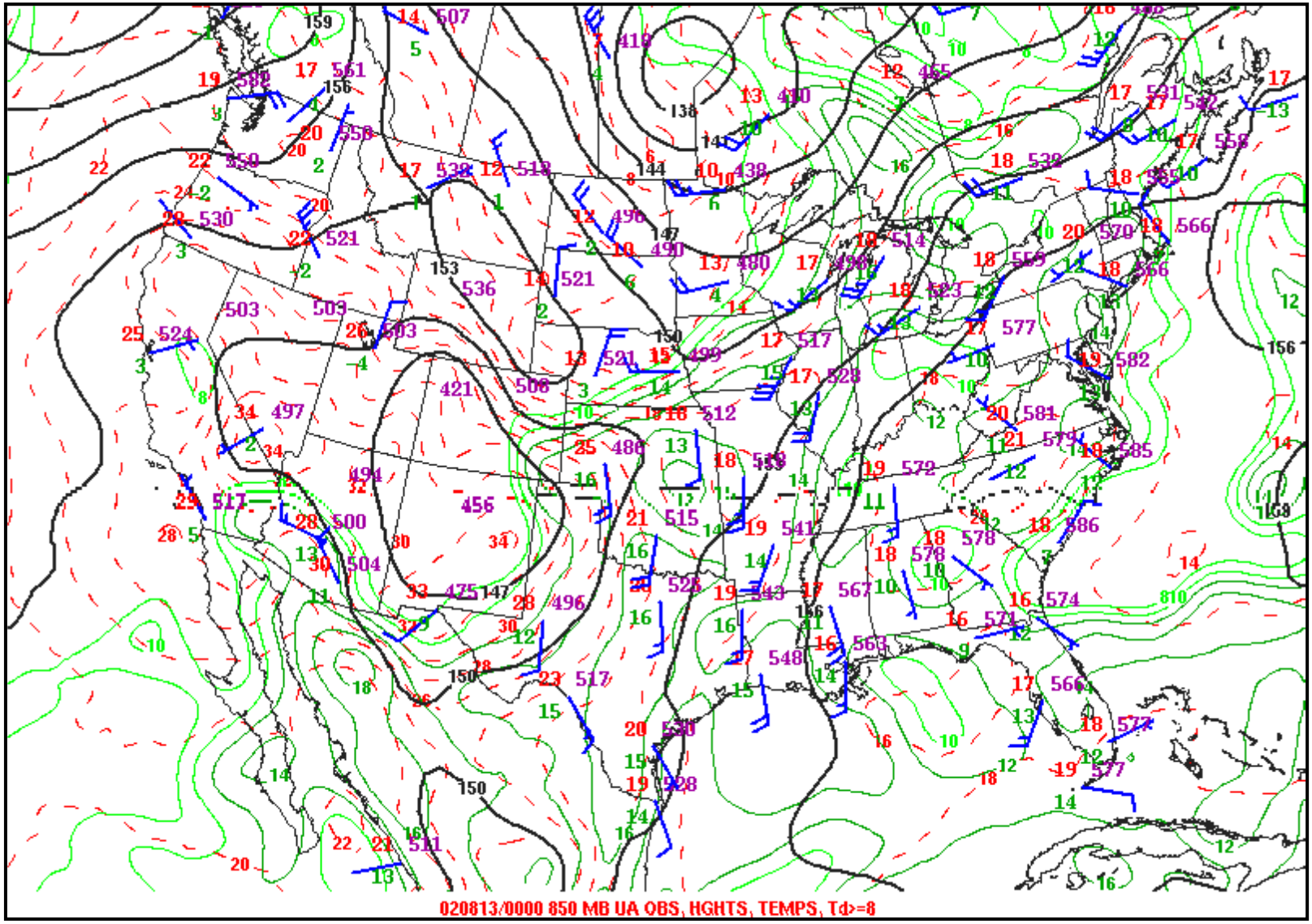


Figure 1.4.3.5 72-hr Back Trajectories for Cornwall 8-12-2002

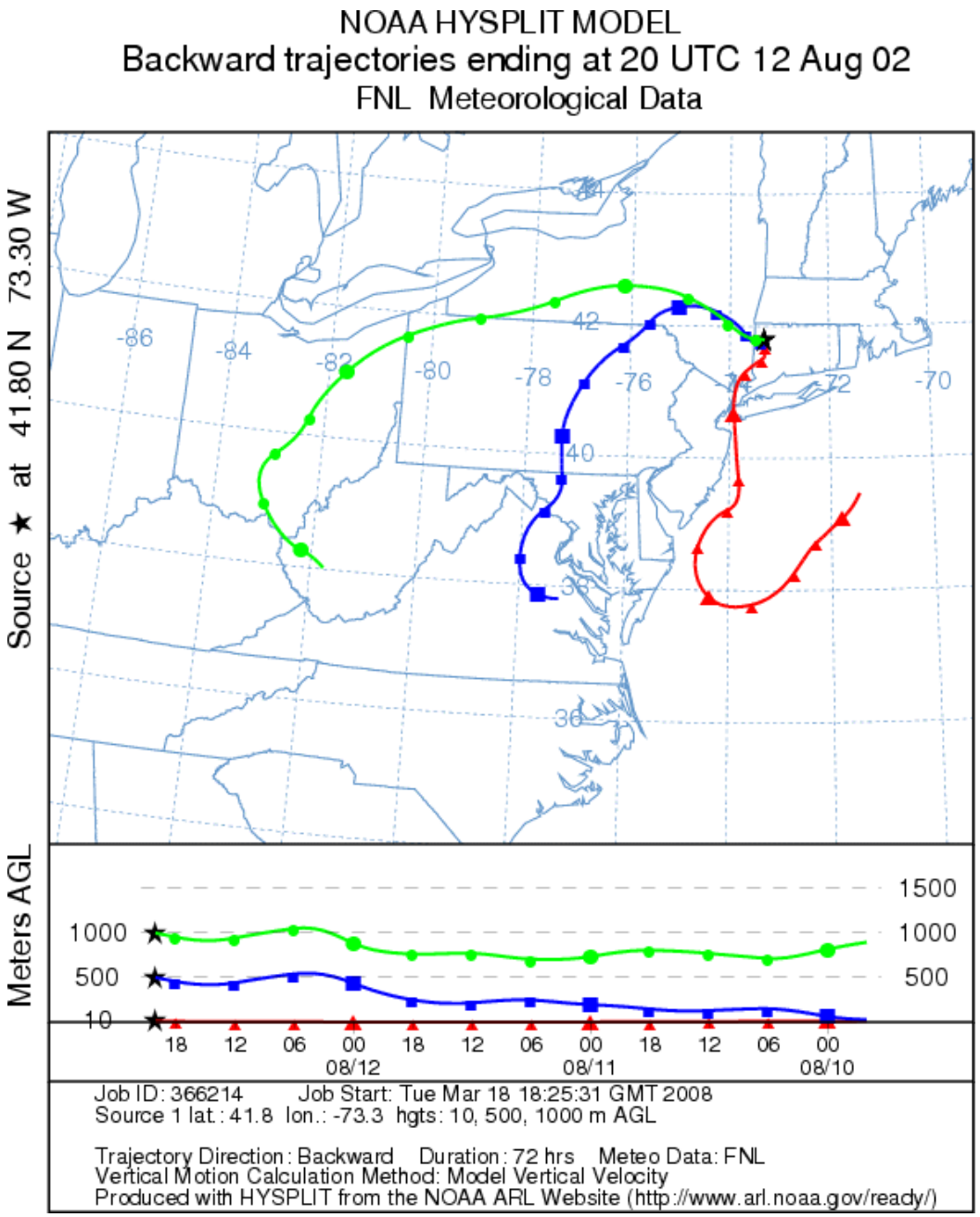
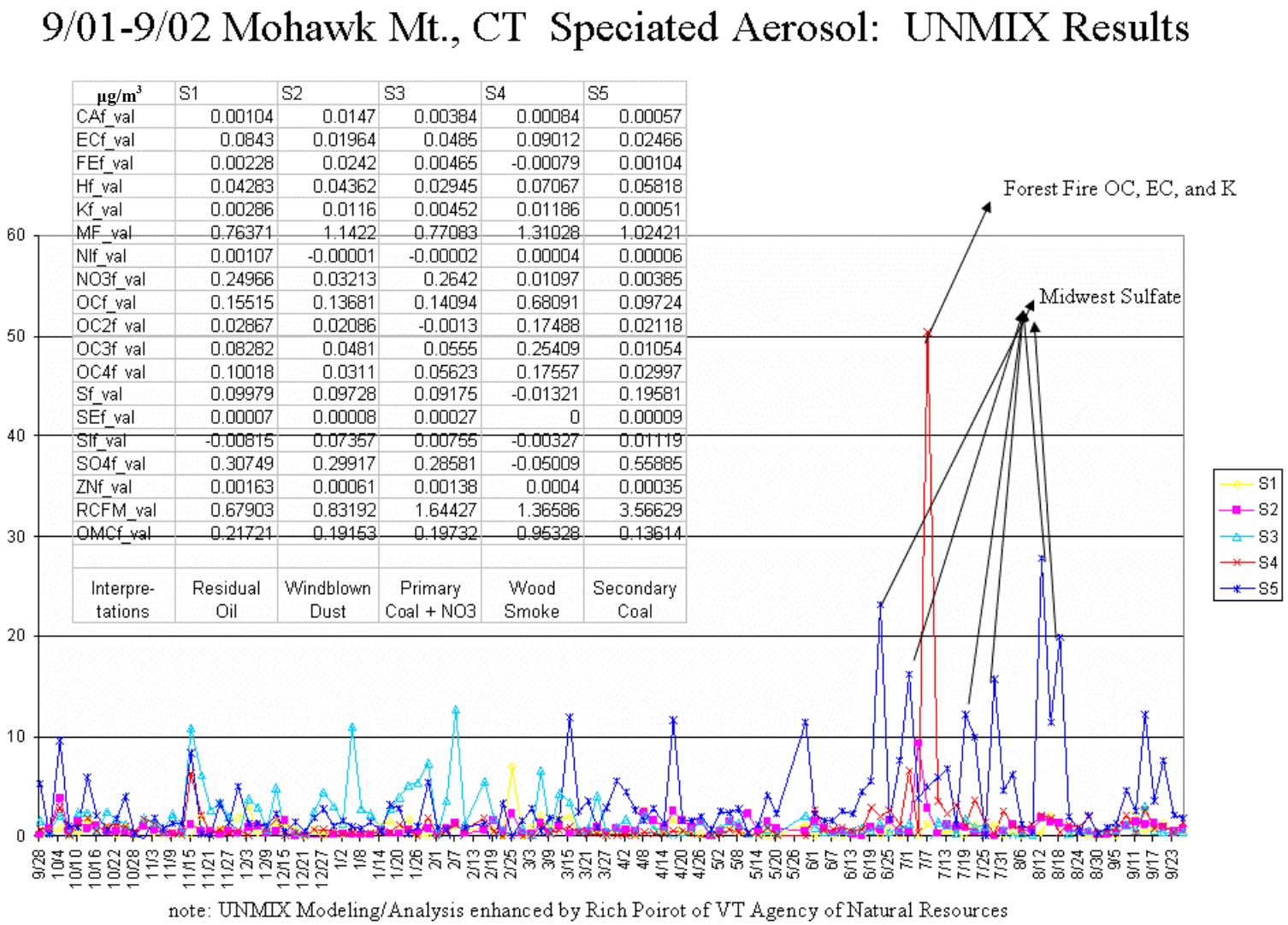


Figure 1.4.3.6 UNMIX IMPROVE Timeseries for Cornwall 9/2001-9/2002



µg/m³	S1	S2	S3	S4	S5
CAf_val	0.00104	0.0147	0.00384	0.00084	0.00057
ECf_val	0.0843	0.01964	0.0485	0.09012	0.02466
FEf_val	0.00228	0.0242	0.00465	-0.00079	0.00104
Hf_val	0.04283	0.04362	0.02945	0.07067	0.05818
Kf_val	0.00286	0.0116	0.00452	0.01186	0.00051
MF_val	0.76371	1.1422	0.77083	1.31028	1.02421
Nlf_val	0.00107	-0.00001	-0.00002	0.00004	0.00006
NO3f_val	0.24966	0.03213	0.2642	0.01097	0.00385
OCf_val	0.15515	0.13681	0.14094	0.68091	0.09724
OC2f_val	0.02867	0.02086	-0.0013	0.17488	0.02118
OC3f_val	0.08282	0.0481	0.0555	0.25409	0.01054
OC4f_val	0.10018	0.0311	0.05623	0.17557	0.02997
Sf_val	0.09979	0.09728	0.09175	-0.01321	0.19581
SEf_val	0.00007	0.00008	0.00027	0	0.00009
Slf_val	-0.00815	0.07357	0.00755	-0.00327	0.01119
SO4f_val	0.30749	0.29917	0.28581	-0.05009	0.55885
ZNf_val	0.00163	0.00061	0.00138	0.0004	0.00035
RCFM_val	0.67903	0.83192	1.64427	1.36586	3.56629
OMCf_val	0.21721	0.19153	0.19732	0.95328	0.13614
Interpre-tations	Residual Oil	Windblown Dust	Primary Coal + NO3	Wood Smoke	Secondary Coal

note: UNMIX Modeling/Analysis enhanced by Rich Poirot of VT Agency of Natural Resources

Figure 1.4.3.7 Speciated PM25 from 8/12/2002 IMPROVE sample