Source Apportionment for $PM_{2.5}$ at Houston Clinton Drive

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$PM_{2.5}$ Issues

- Clinton Drive, west end of Ship Channel, only site in Texas at risk of nonattainment.
- 2004-2006 design value 15.4 $\mu g/m^3$ exceeds 15.0 NAAQS.
- Next highest DV in HGB:13 $\mu g/m^3$
- Various methods show “soil” to be significant factor in why this site is area max.

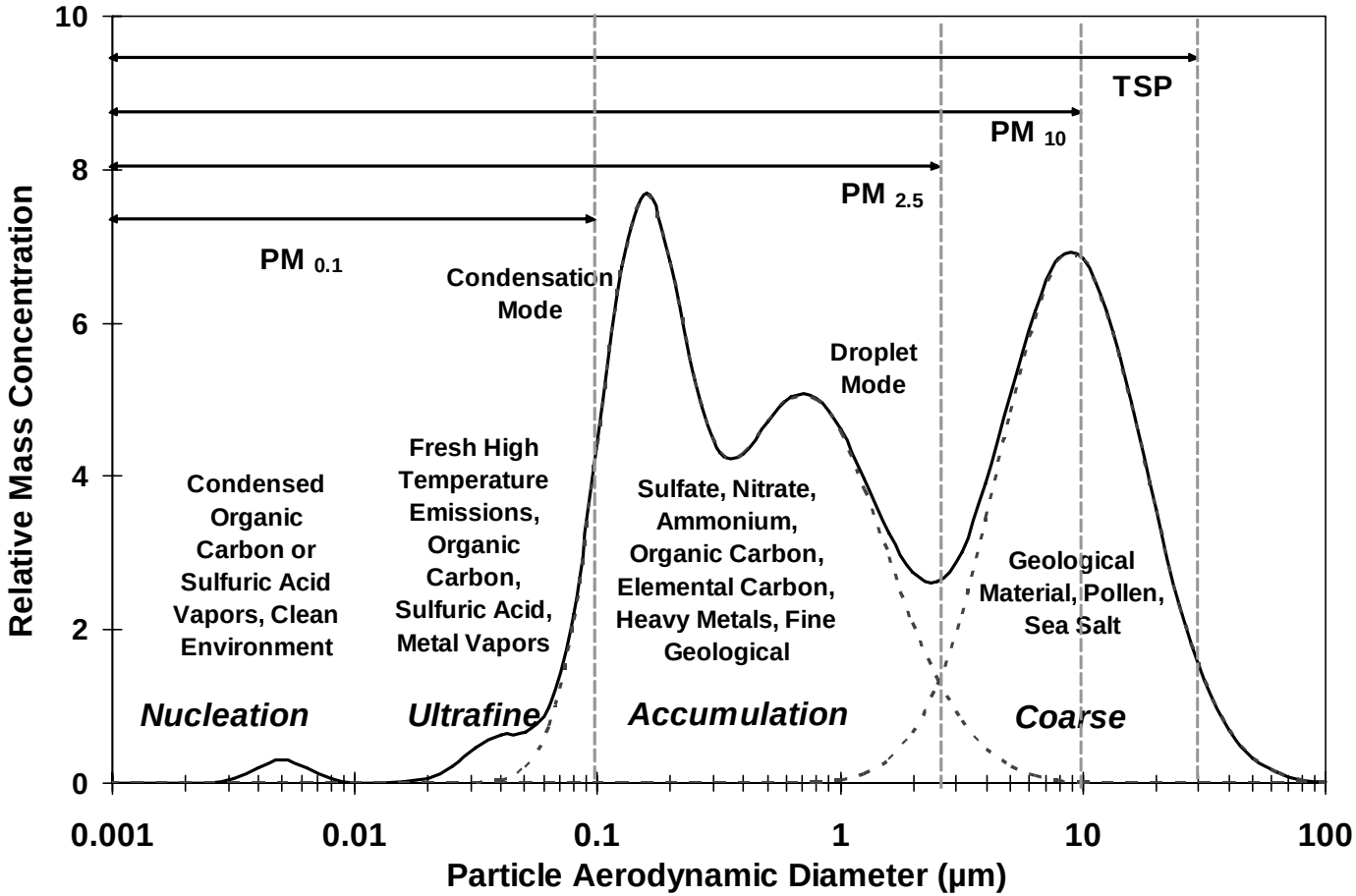
Methods of Data Analysis

- Analyze $PM_{2.5}$ = f(rain, wind speed, direction).
- Analyze $PM_{2.5}$ = f(time, weekday, season)
- Analyze PM_{10} & $PM_{10}/PM_{2.5}$ by wind direction.
- Use Hysplit[1] trajectories to assess transport.
- Use previous research results to describe factors.
- Apply Positive Matrix Factorization to speciation.

1. Draxler, R.R. and Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

Rolph, G.D., 2003. Real-time Environmental Applications and Display sYstem (READY) Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

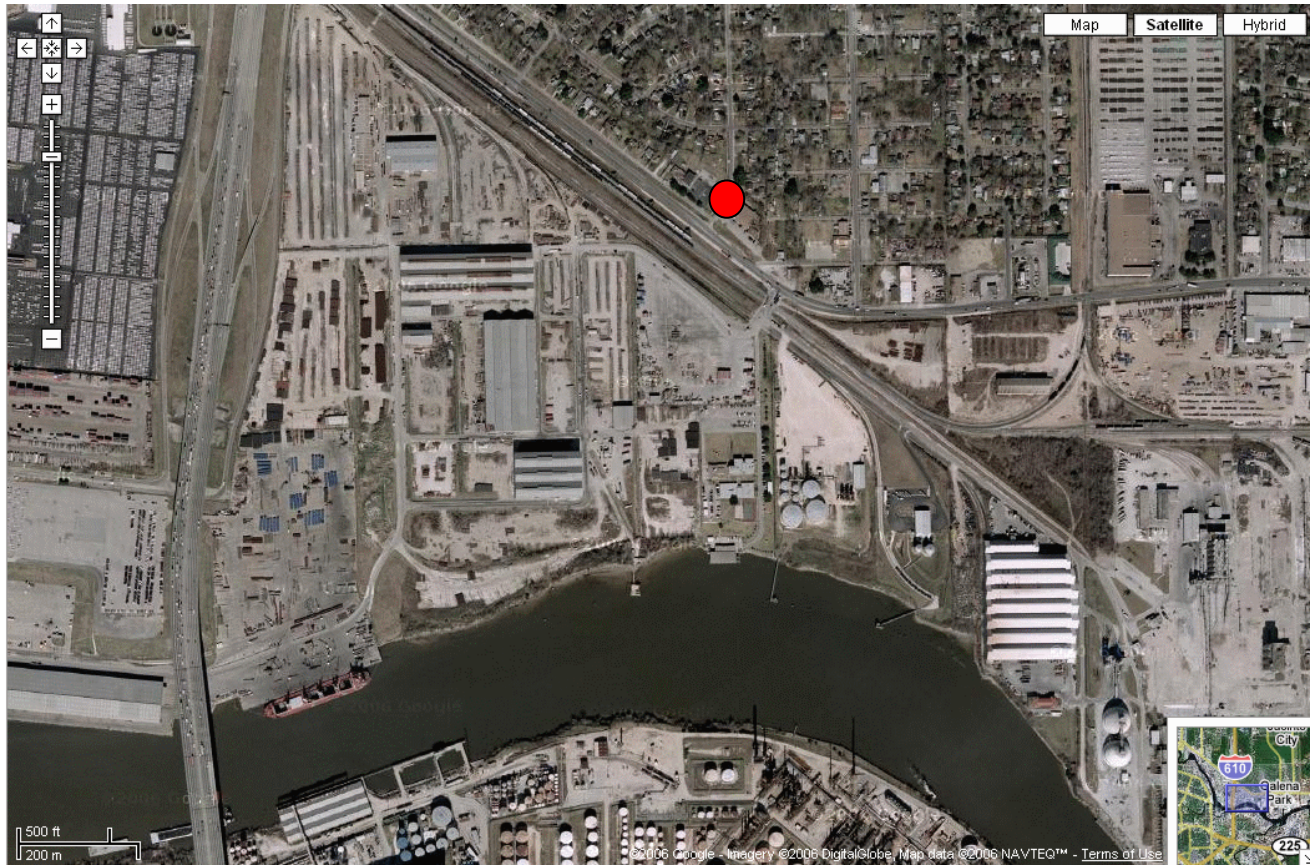
Major Features of Atmospheric Particle Mass Distribution



Data

- Clinton $PM_{2.5}$ FRM mass, hourly TEOM mass
- Clinton $PM_{2.5}$ special speciation for this study:
  - Quartz-filter: EC, OC,
  - Teflon-filter: ions, elements
- Clinton PM_{10} HiVol filter mass
- $PM_{2.5}$ FRM and Speciation Network mass and from other HGB sites
- $PM_{2.5}$ Speciation Network sample compositions
- Clinton wind speed resultant, wind direction resultant, and precipitation data.

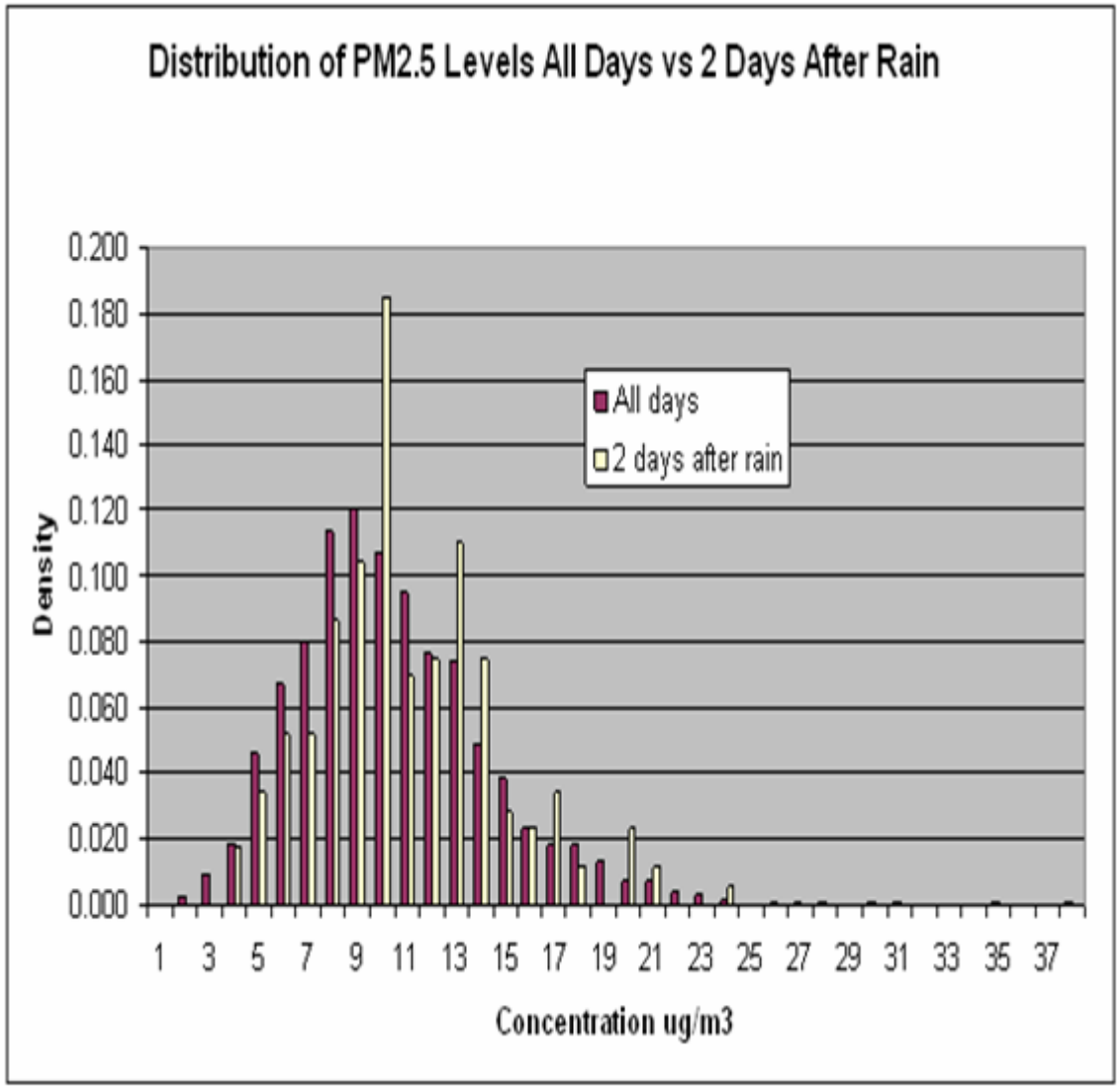
Clinton and environs



Clinton $PM_{2.5}$ and meteorology

- Look at effects of rain, wind direction, and wind speed.
- Compare $PM_{2.5}$ and PM_{10} directionality

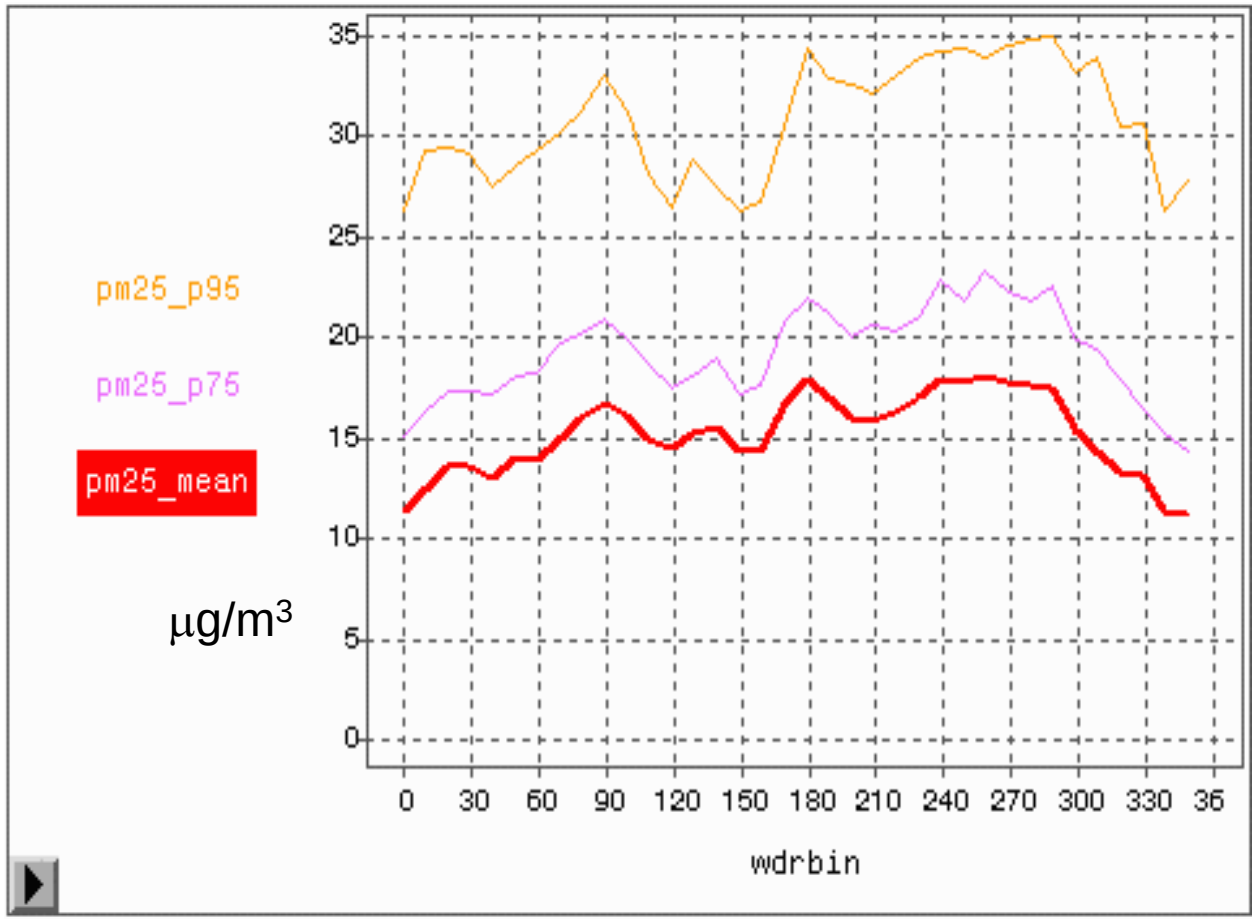
$PM_{2.5}$ and rain



- Using 24-hr avg'd TEOM data.
- Found average concentration 2 days after rain statistically significantly higher than all days.

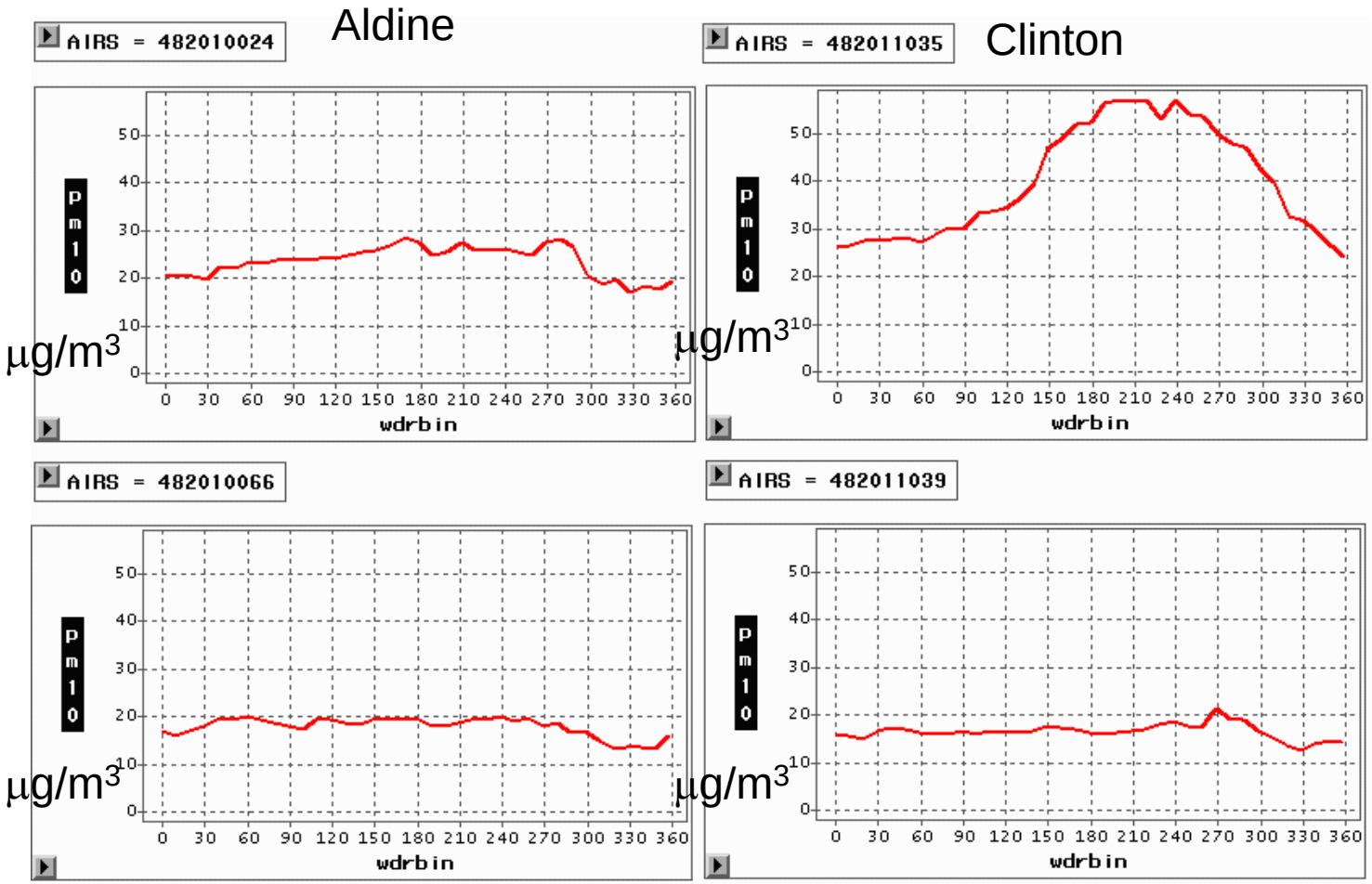
$PM_{2.5}$ and wind direction

- TEOM $PM_{2.5}$ concentration by 10 deg. wind direction bin 2002-2007
- Relatively weak directionality, lowest concentrations to the north



PM_{10} and wind direction

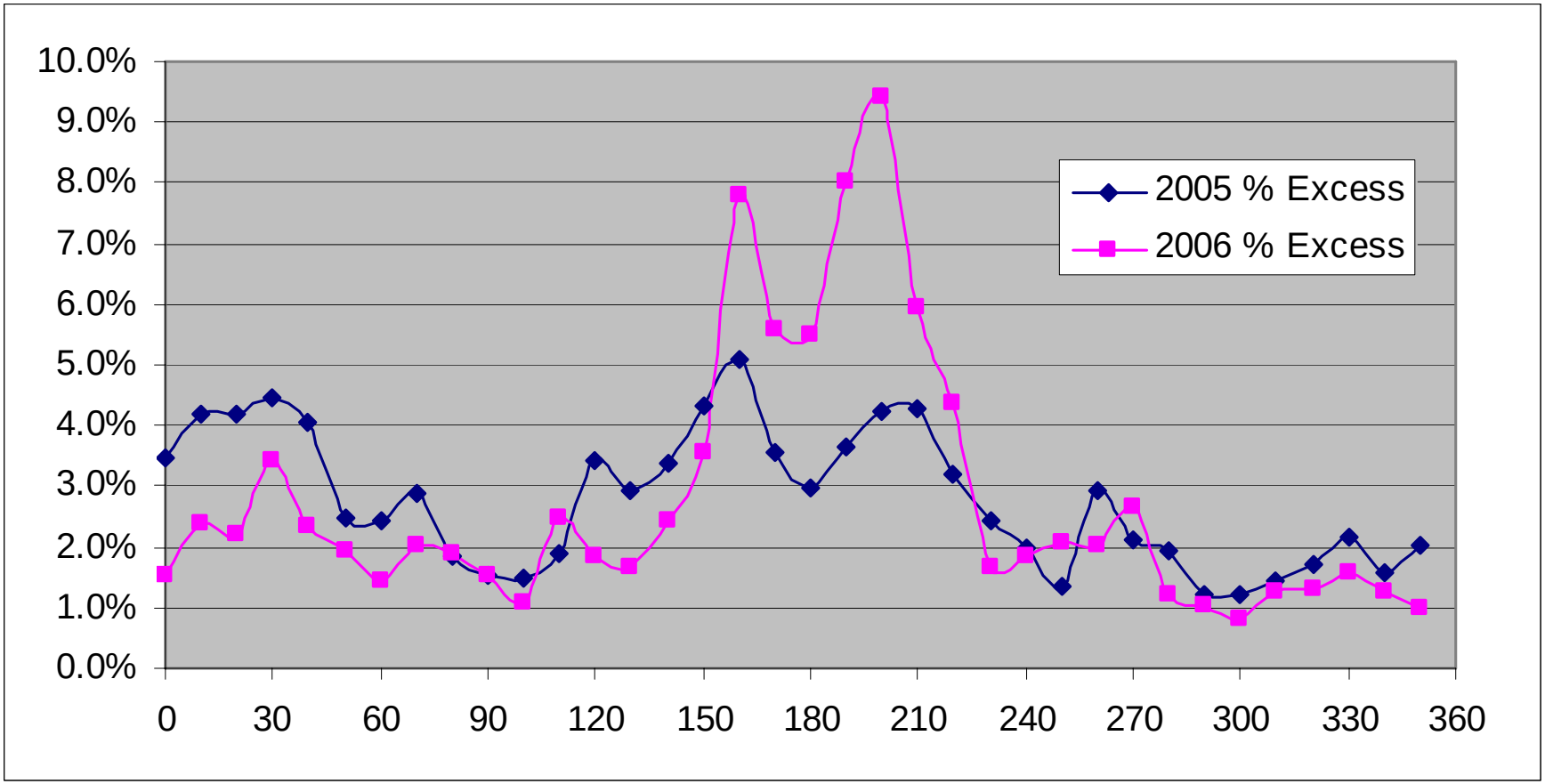
- 24-hour filter samples w hourly winds
- Clinton shows direction-ality to SW



Westhollow

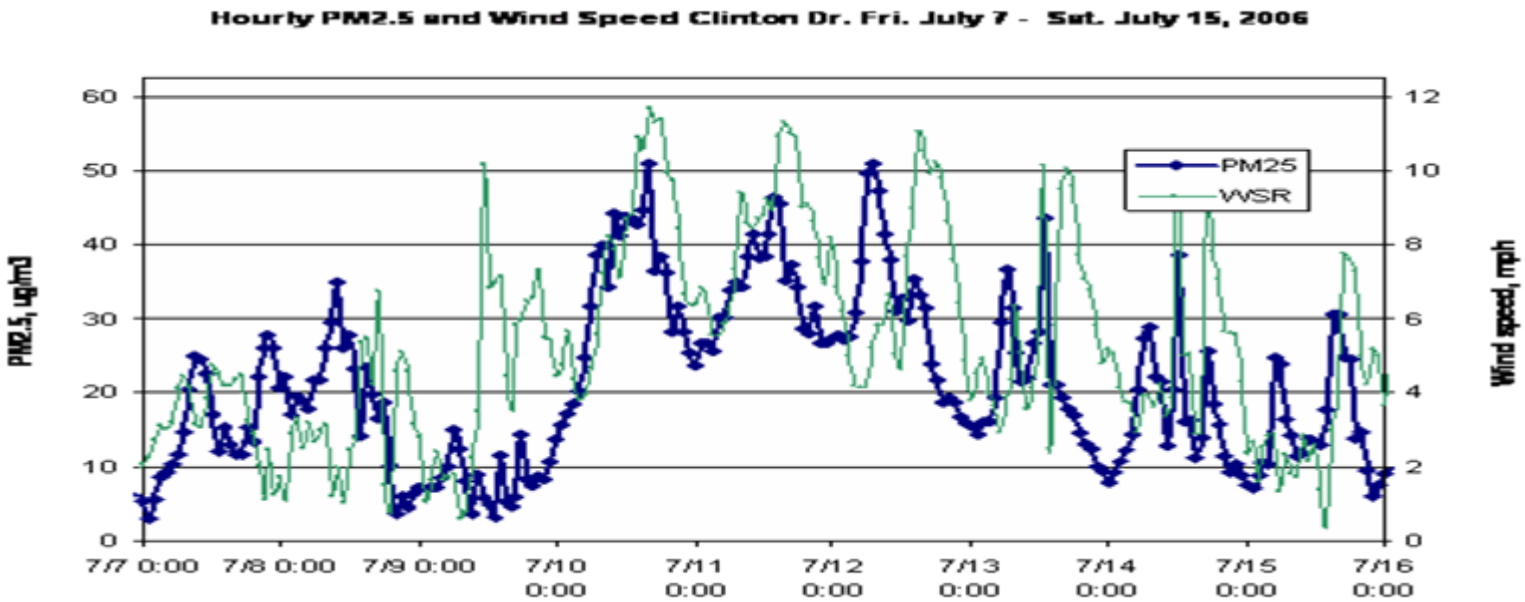
Deer Park

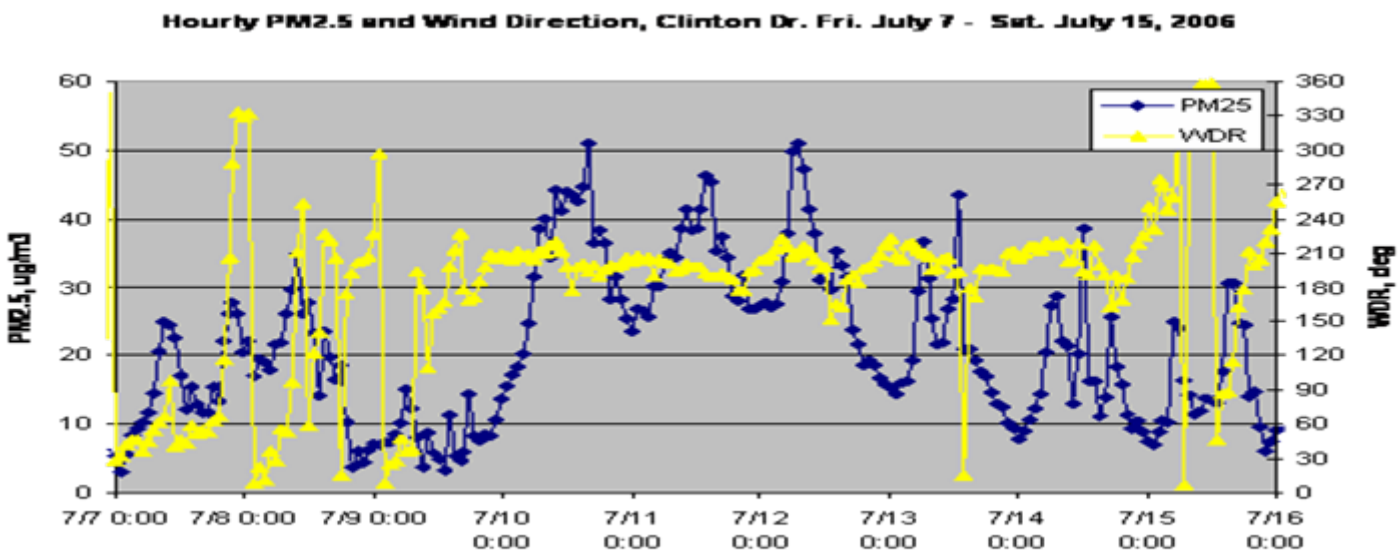
% of $PM_{2.5}$ > 15µg/m^3 from each wind direction in 2005, 2006 at Clinton



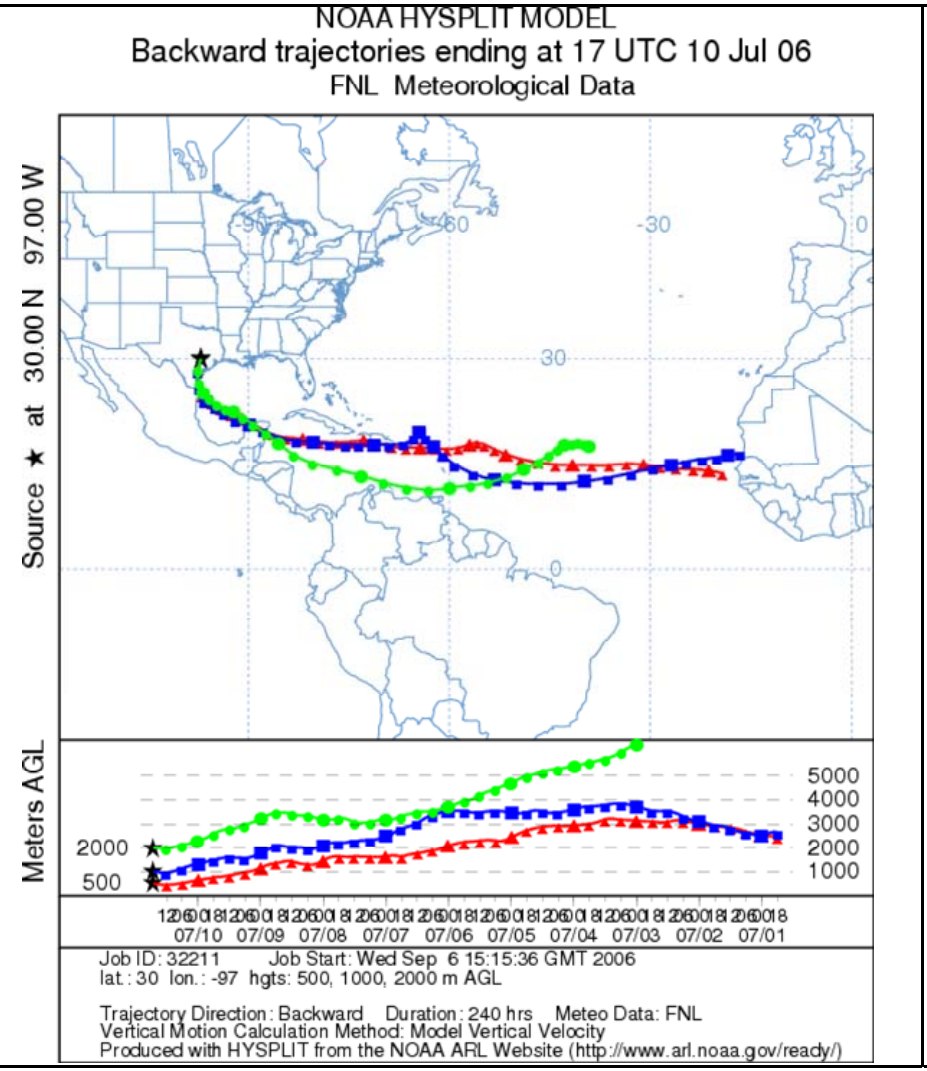
0°= north, 90°= east, 180°= south, 270°= west, 360° =north

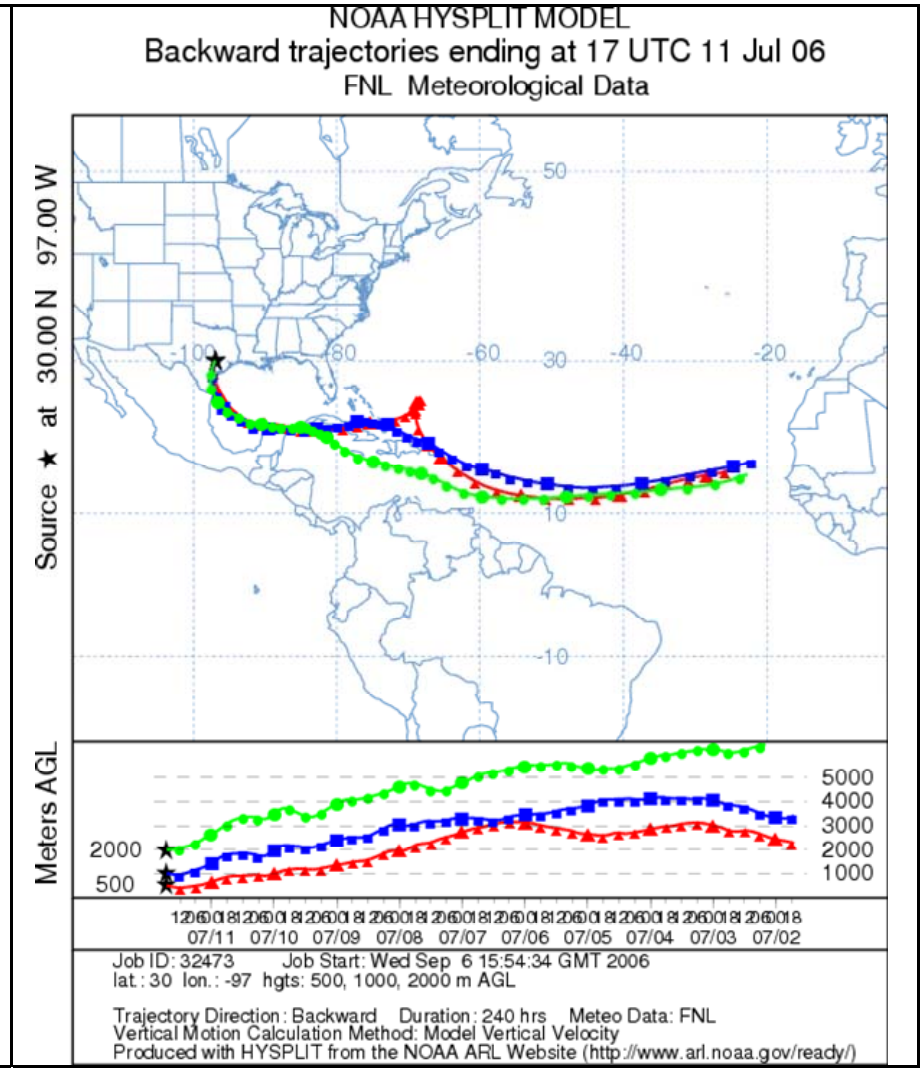
Case study


Hourly PM2.5 and Wind Speed Clinton Dr. Fri. July 7 - Sat. July 15, 2006
PM2.5, ug/m3
Wind speed, mph
PM25
WSR
0
10
20
30
40
50
60
0
2
4
6
8
10
12
7/7 0:00
7/8 0:00
7/9 0:00
7/10 0:00
7/11 0:00
7/12 0:00
7/13 0:00
7/14 0:00
7/15 0:00
7/16 0:00


Hourly PM2.5 and Wind Direction, Clinton Dr. Fri. July 7 - Sat. July 15, 2006
PM2.5, ug/m3
WDR, deg
PM25
WDR
0
10
20
30
40
50
60
0
30
60
90
120
150
180
210
240
270
300
330
360
7/7 0:00
7/8 0:00
7/9 0:00
7/10 0:00
7/11 0:00
7/12 0:00
7/13 0:00
7/14 0:00
7/15 0:00
7/16 0:00

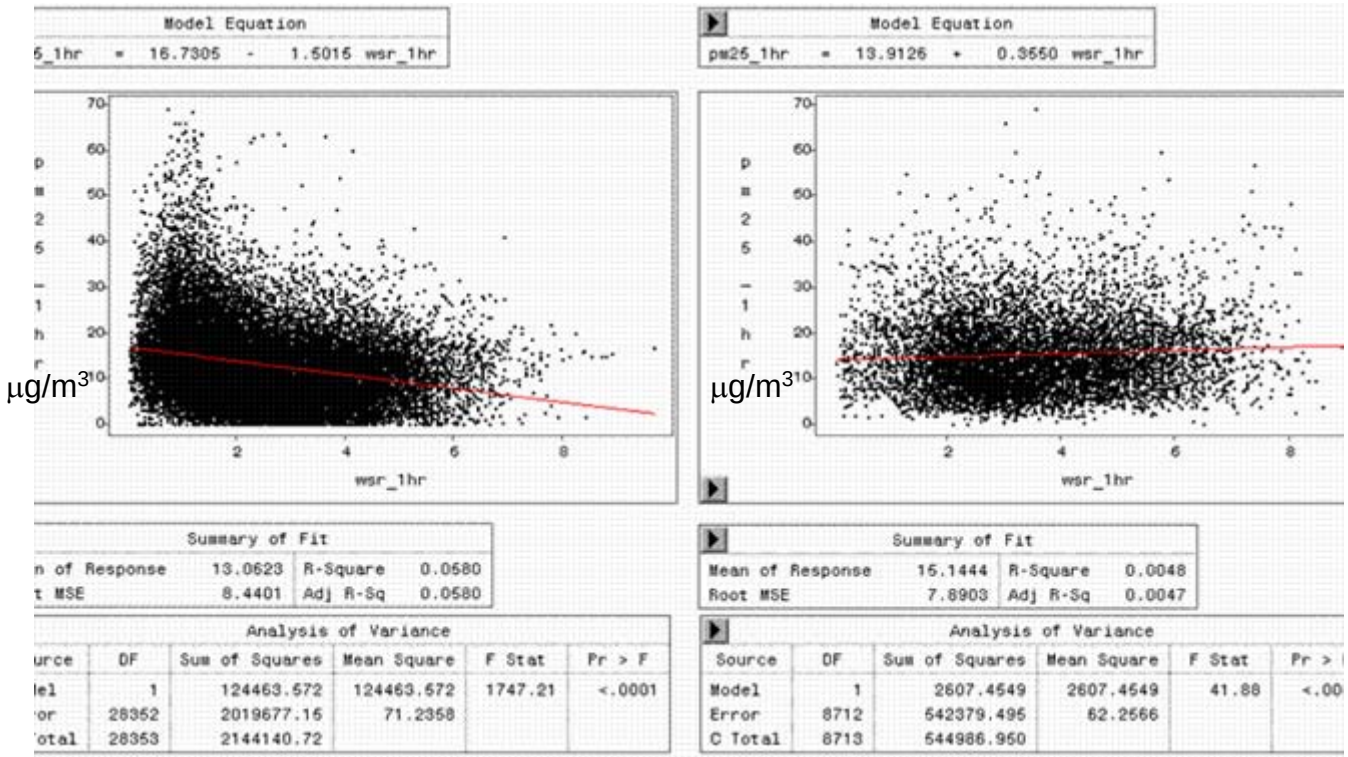
Case Study - transport





PM2.5 and wind speed

- Regress hourly PM2.5 on wind speed by 30-deg. wind direction bin
- Slope negative all but S & SW



Directions 0-164, 226-360 deg

Directions 165-225 deg

Meteorological evidence supports dust

- Higher $PM_{2.5}$ after rain from dried road dust
- Strong directionality for PM_{10} (crustal material in PM_{coarse})
- Positive association with wind speed that dislodges surface soil.

Use speciation from past studies

- As speciated data were collected:
  - Source profiles selected from EPS SPECIATE database for comparison
  - Reconstruction formulas from published work used to calculate factors:

Speciation data analysis

Speciation Analysis

- **Inventory of data validated to date**

Period	Sample types	Number of Ambient Samples
1/4/05 – 4/7/06	ions, elements (Teflon)	75
4/17/06 – 8/4/06	ions, elements (Teflon)	54
5/27/06 – 8/4/06	EC/OC (Quartz)	40
8/6/06 – 12/31/06	ions, elements (Teflon)	42
8/6/06 – 12/31/06	EC/OC (Quartz)	30
Combined 5/27/06 – 12/31/06	EC/OC, ions, elements	63

Teflon filters by XRF for elements and IC for ions

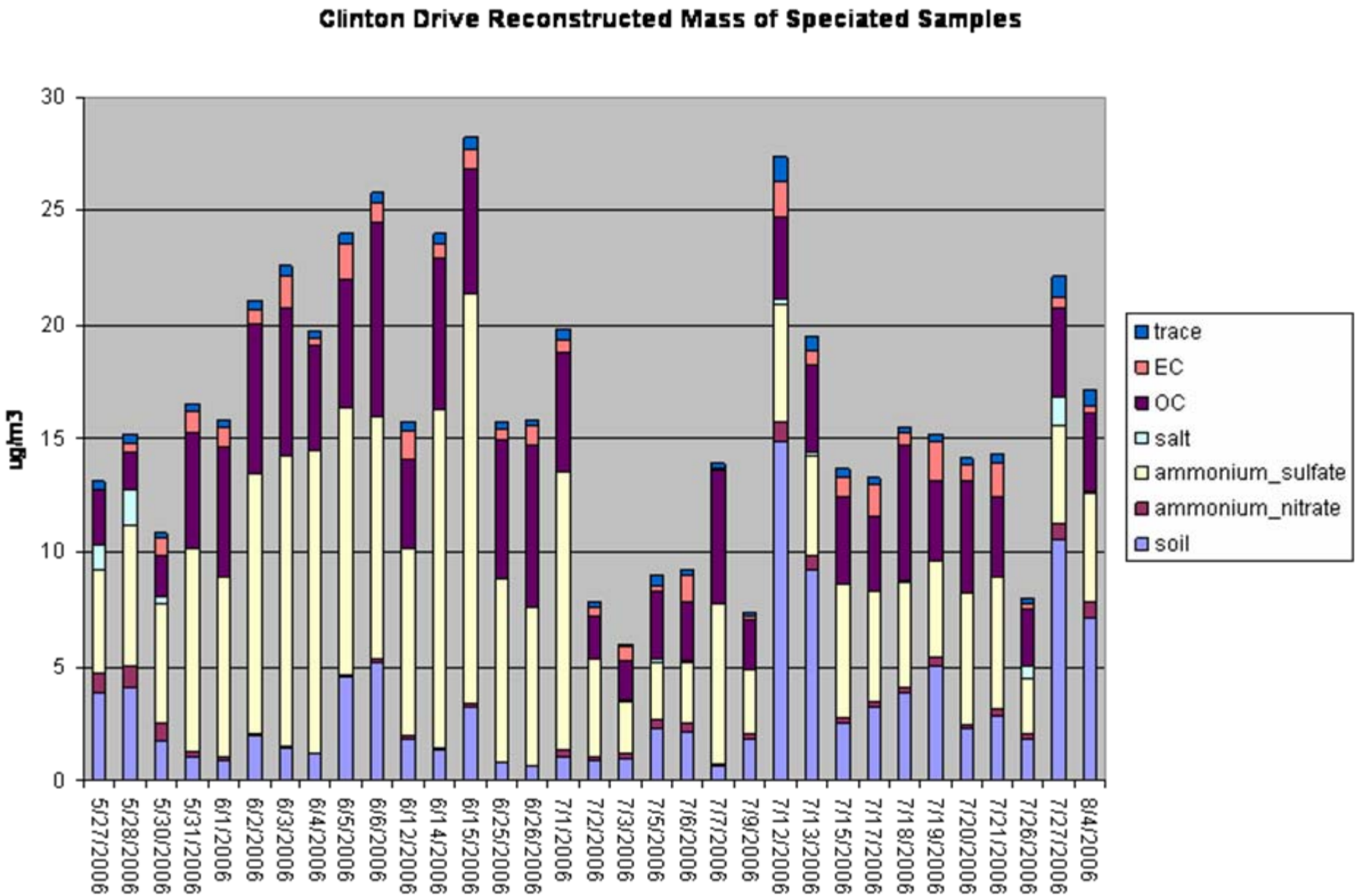
Quartz filters by thermal optical analysis for EC/OC

FRM R&P 2025 sequential samplers

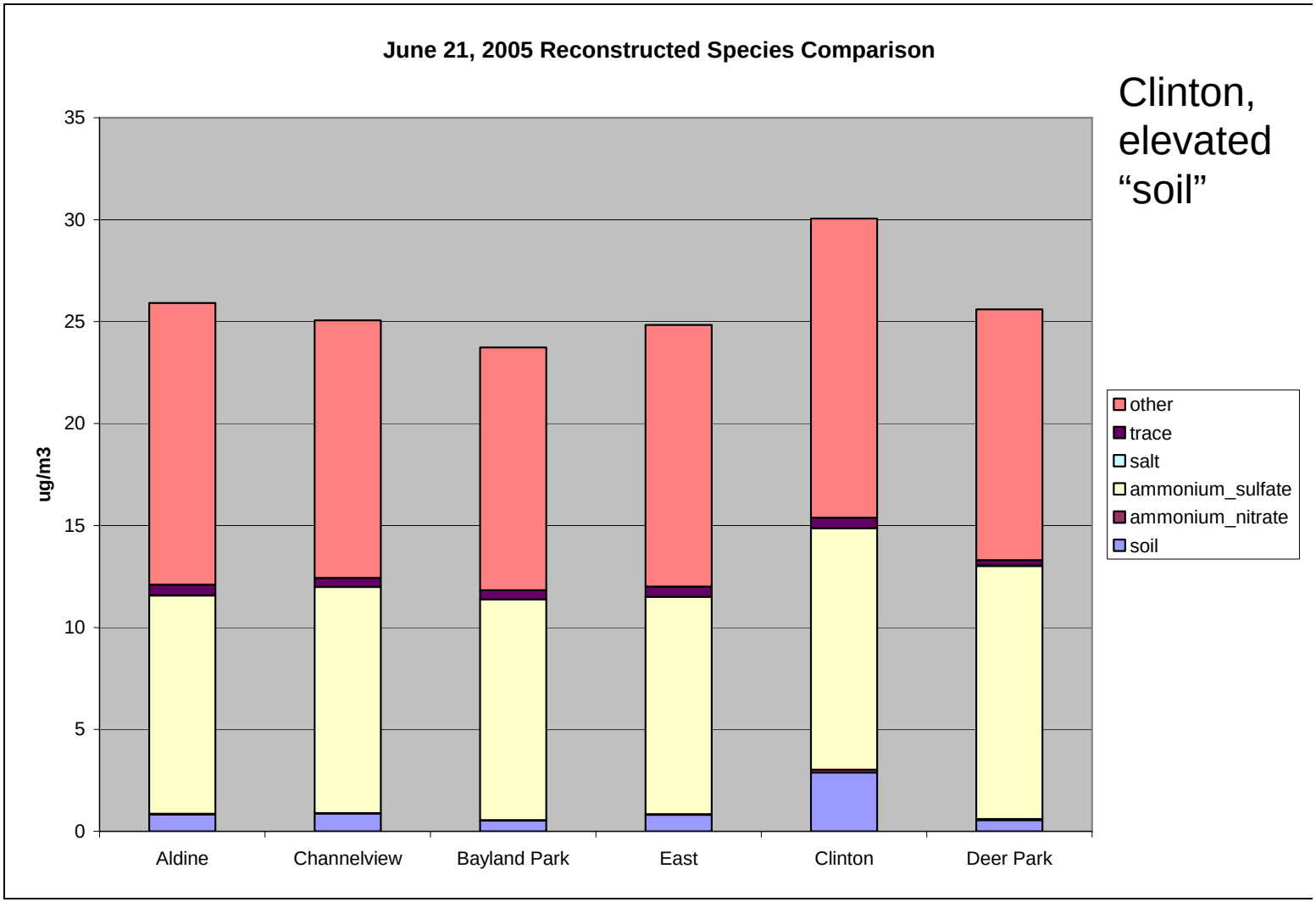
Tropp et al.'s (2006) Texas speciation

- *Soil* = 1.89 * Al + 2.14 * Si + 1.40 * Ca + 1.43 * Fe
- *Ammonium sulfate* = 1.38 * SO4=
- *Ammonium nitrate* = 1.29 * NO3-
- *Salt* = 1.65 * Cl
- *Trace elements* = sum of XRF species – (Al, Si, Ca, Fe, S, Cl, Na)
- *OC* = 1.4 * OCTTC
- *EC* = ECTTC
- *Other* = the $\mu g/m^3$ from Teflon filter minus seven constituents above.

Al = Aluminum	S = Sulfur
Si = Silicon	Na = Sodium
Ca = Calcium	SO4= = Sulfate ion
Fe = iron	NO3- = Nitrate ion
Cl = Chlorine	OCTTC = Organic Carbon by thermal-transmittance
	ECTTC = Elemental Carbon by thermal-transmittance

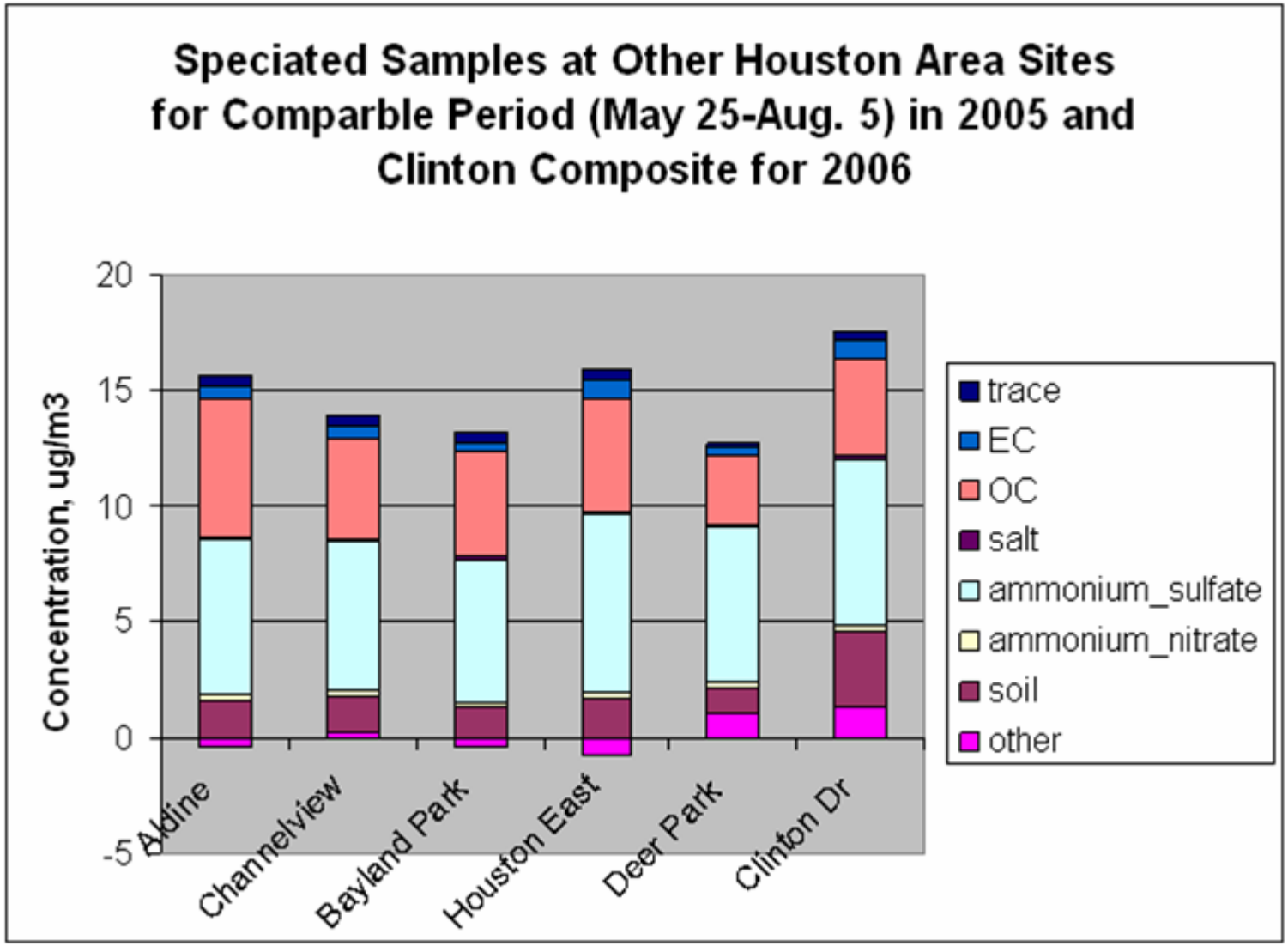

Clinton Drive Reconstructed Mass of Speciated Samples
ug/m3
30
25
20
15
10
5
0
5/27/2006
5/28/2006
5/30/2006
5/31/2006
6/1/2006
6/2/2006
6/3/2006
6/4/2006
6/5/2006
6/6/2006
6/12/2006
6/14/2006
6/15/2006
6/25/2006
6/26/2006
7/1/2006
7/2/2006
7/3/2006
7/5/2006
7/6/2006
7/7/2006
7/9/2006
7/12/2006
7/13/2006
7/15/2006
7/17/2006
7/18/2006
7/19/2006
7/20/2006
7/21/2006
7/26/2006
7/27/2006
8/4/2006
trace
EC
OC
salt
ammonium_sulfate
ammonium_nitrate
soil

Example of $PM_{2.5}$ concentration factors by sites

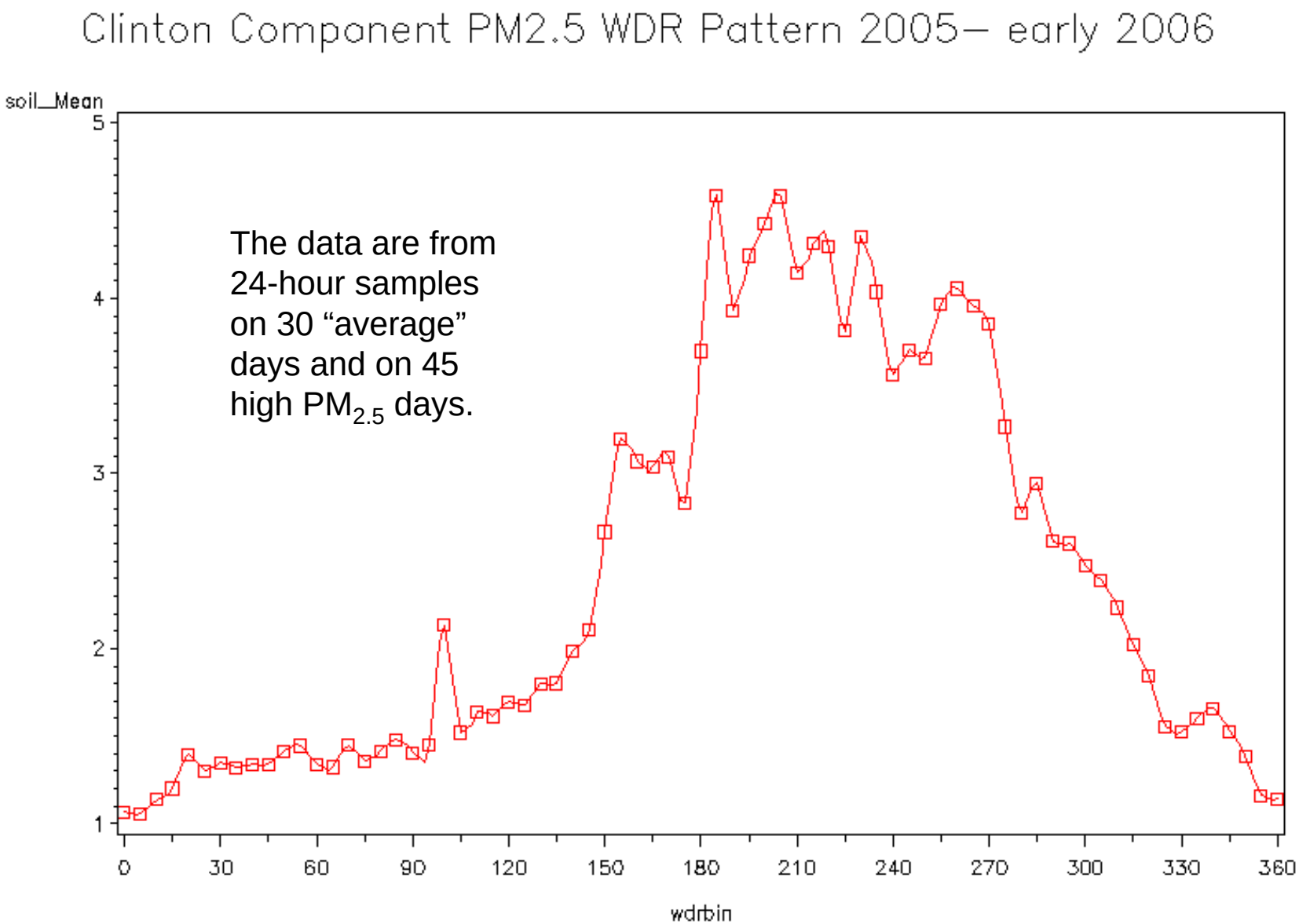


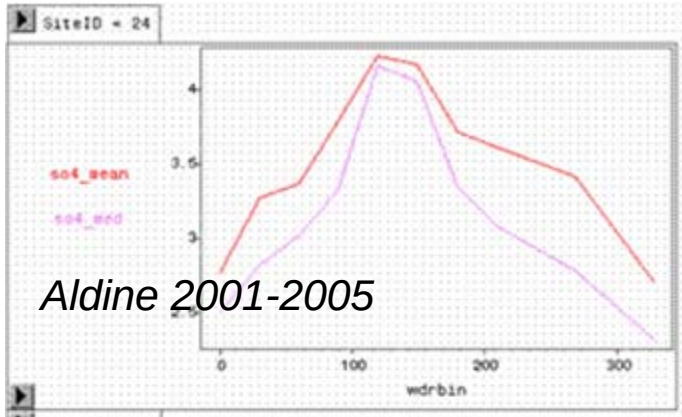
Clinton, elevated "soil"

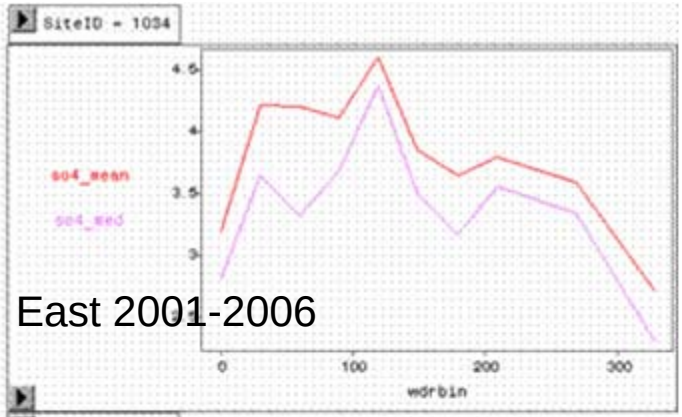
Composite PM2.5 factors by site

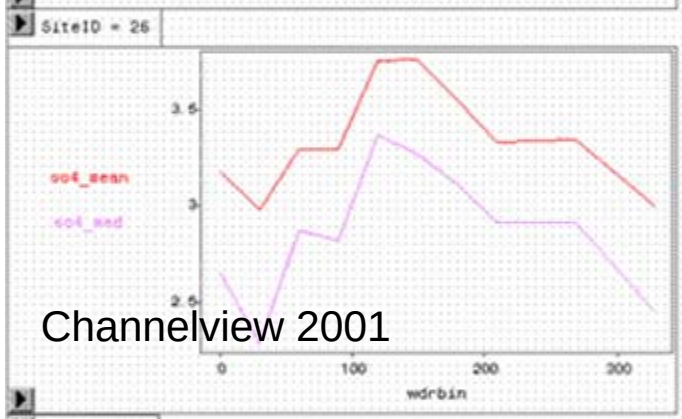


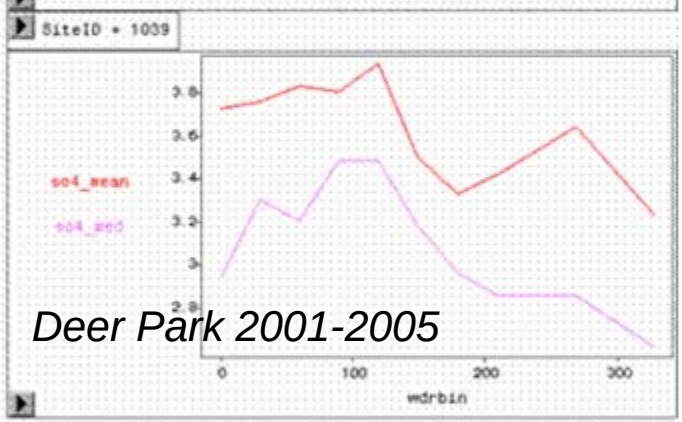
Soil $PM_{2.5}$ agrees w directions for "excess $PM_{2.5}$" and PM_{10} – SE-West

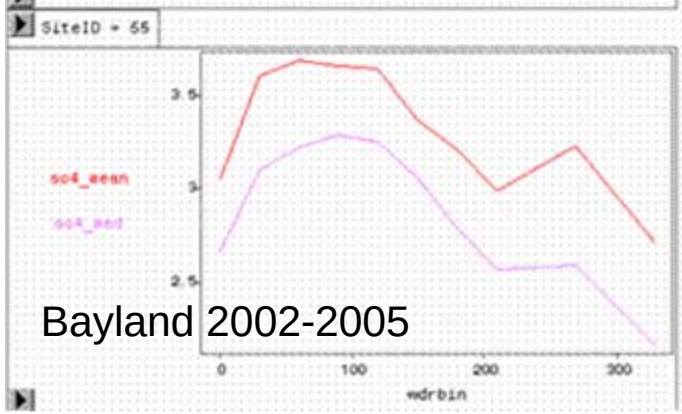


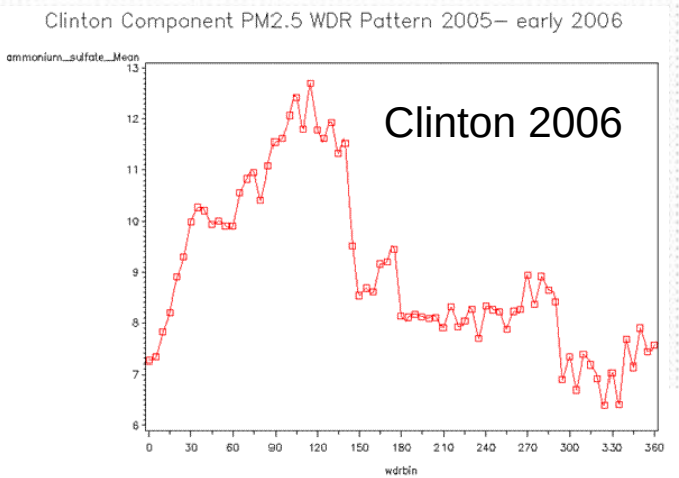












SO4 at 5 TCEQ spec. sites, and at Clinton

Positive matrix factorization

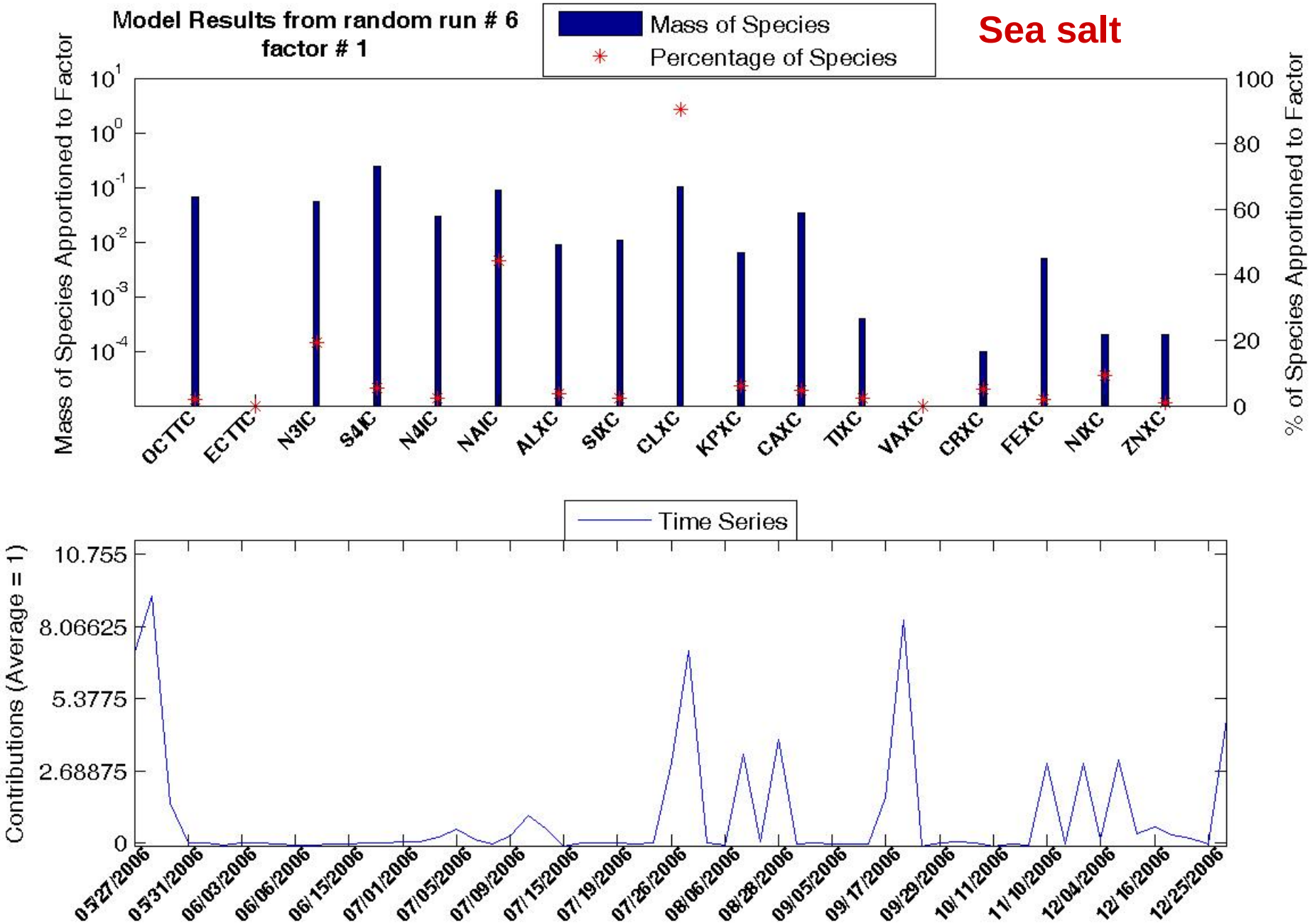
- Given multivariate data and <u>corresponding uncertainties</u>, EPA PMF 1.1 estimates factors.
- User selects desired number of factors, and must interpret output.
- Results at Clinton w ~~63~~ 62 samples in 2006 similar to results on longer time series at other Houston area speciation sites.

Positive matrix factorization

- Solve matrix eq. $X = G F + E$ where
  - X is $n \times m$ matrix of samples $\times$ species
  - G is $n \times p$ matrix of contribution of source to sample
  - F is $p \times m$ matrix of fixed source profiles
  - E is residual
- Min $Q = \mathrm{sum}_I(\mathrm{sum}_J(e_{IJ}^2 / s_{IJ}^2))$
- Generally, good soln has $Q^* = n * m$
- This model $n = 62$, $m = 17$, $Q_{target} = 1054$

Results

- Q* = 1091 (vs 1054)
- 7 factors
- However, reconstruction of total mass from the factor contributions has large residual.
- Hendler, 2006 has similar results
- Buzcu, et al. 2003 have different results


Sea salt
Model Results from random run # 6
factor # 1
Mass of Species
Percentage of Species
Mass of Species Apportioned to Factor
% of Species Apportioned to Factor
OCTTC
ECTTC
N3IC
S4IC
N4IC
NAIC
ALXC
SIXC
CLXC
KPXC
CAXC
TIXC
VAXC
CRXC
FEXC
NIXC
ZNXC
Time Series
Contributions (Average = 1)
10.755
8.06625
5.3775
2.68875
0
05/27/2006
05/31/2006
06/03/2006
06/06/2006
06/15/2006
07/01/2006
07/05/2006
07/09/2006
07/15/2006
07/19/2006
07/26/2006
08/06/2006
08/28/2006
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09/17/2006
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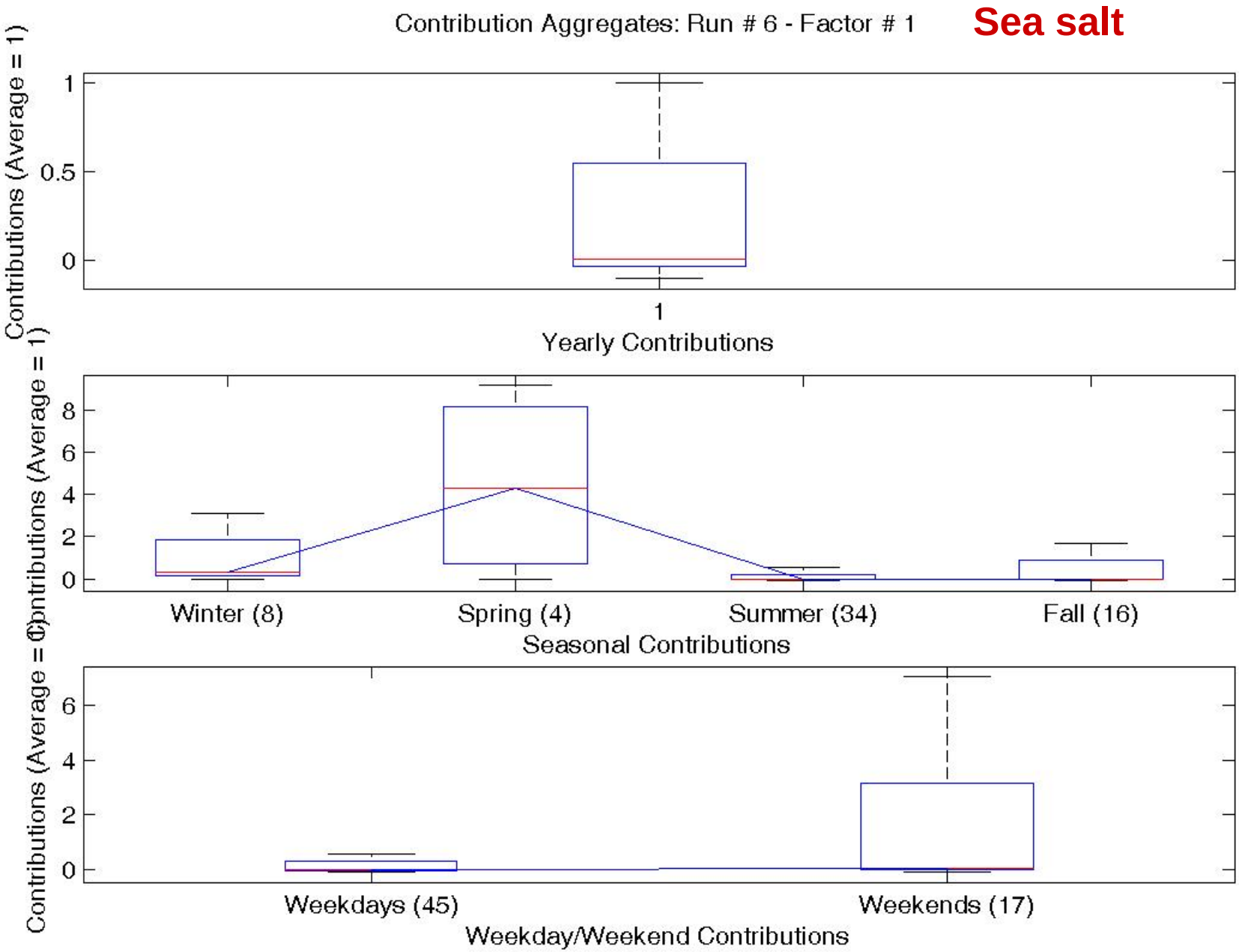
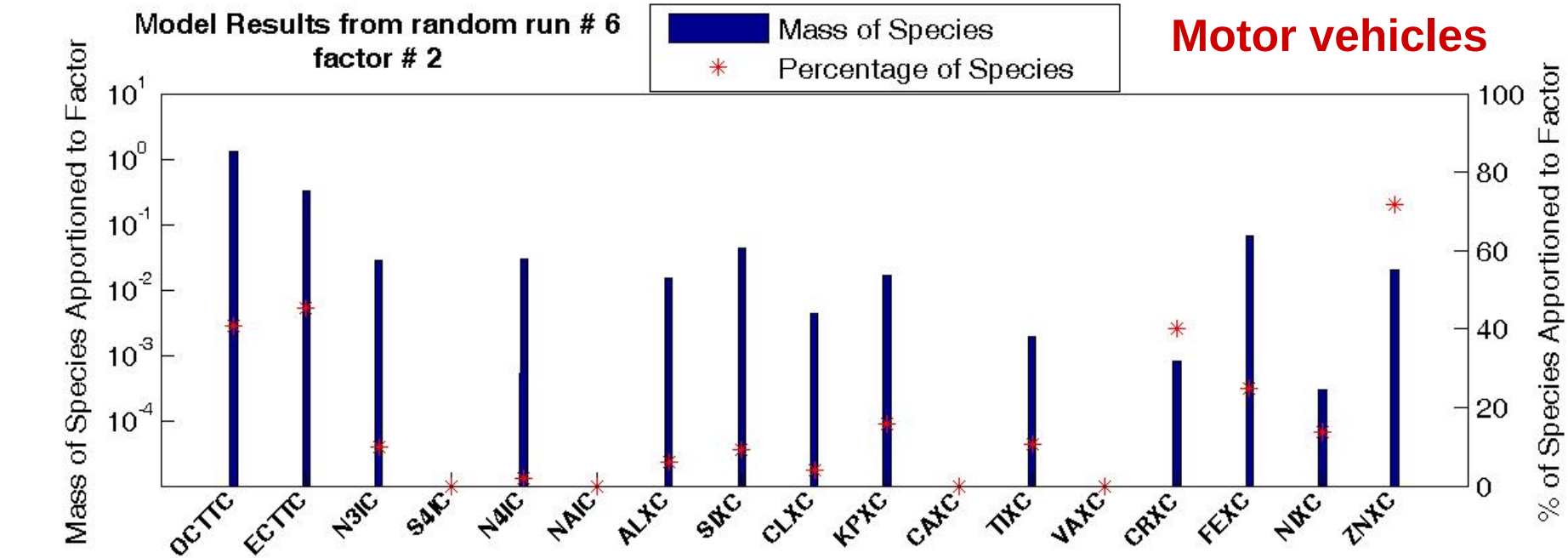
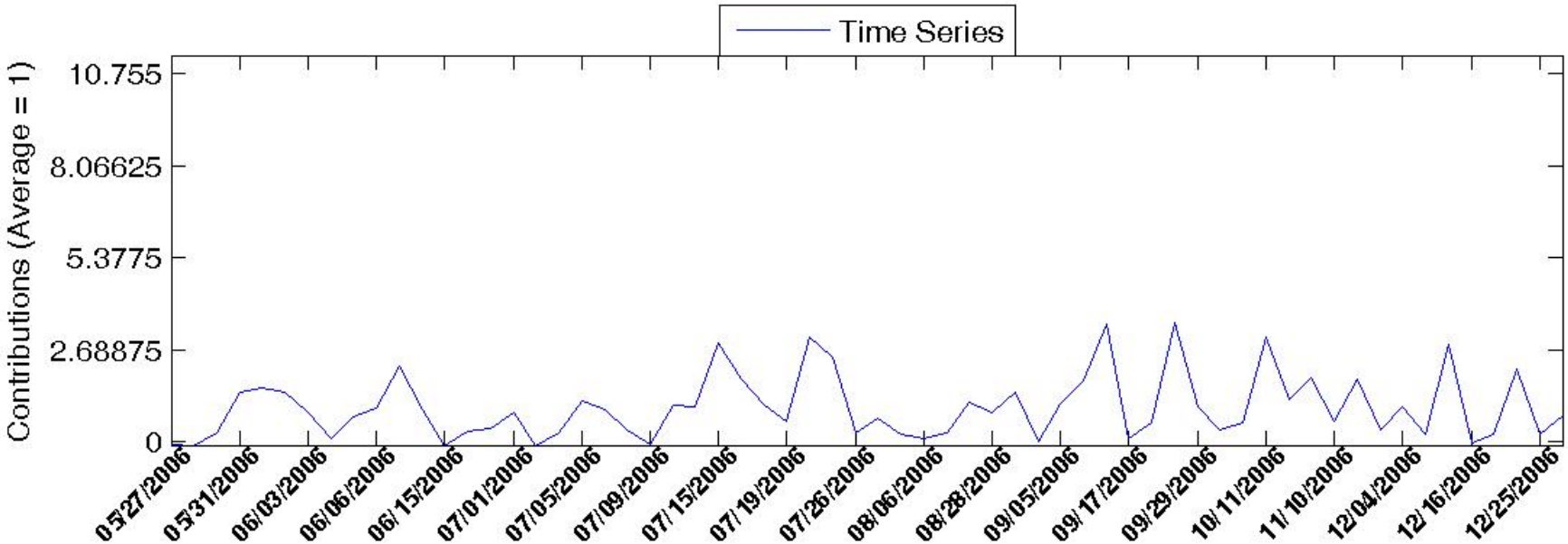
10/11/2006
11/10/2006
12/04/2006
12/16/2006
12/25/2006

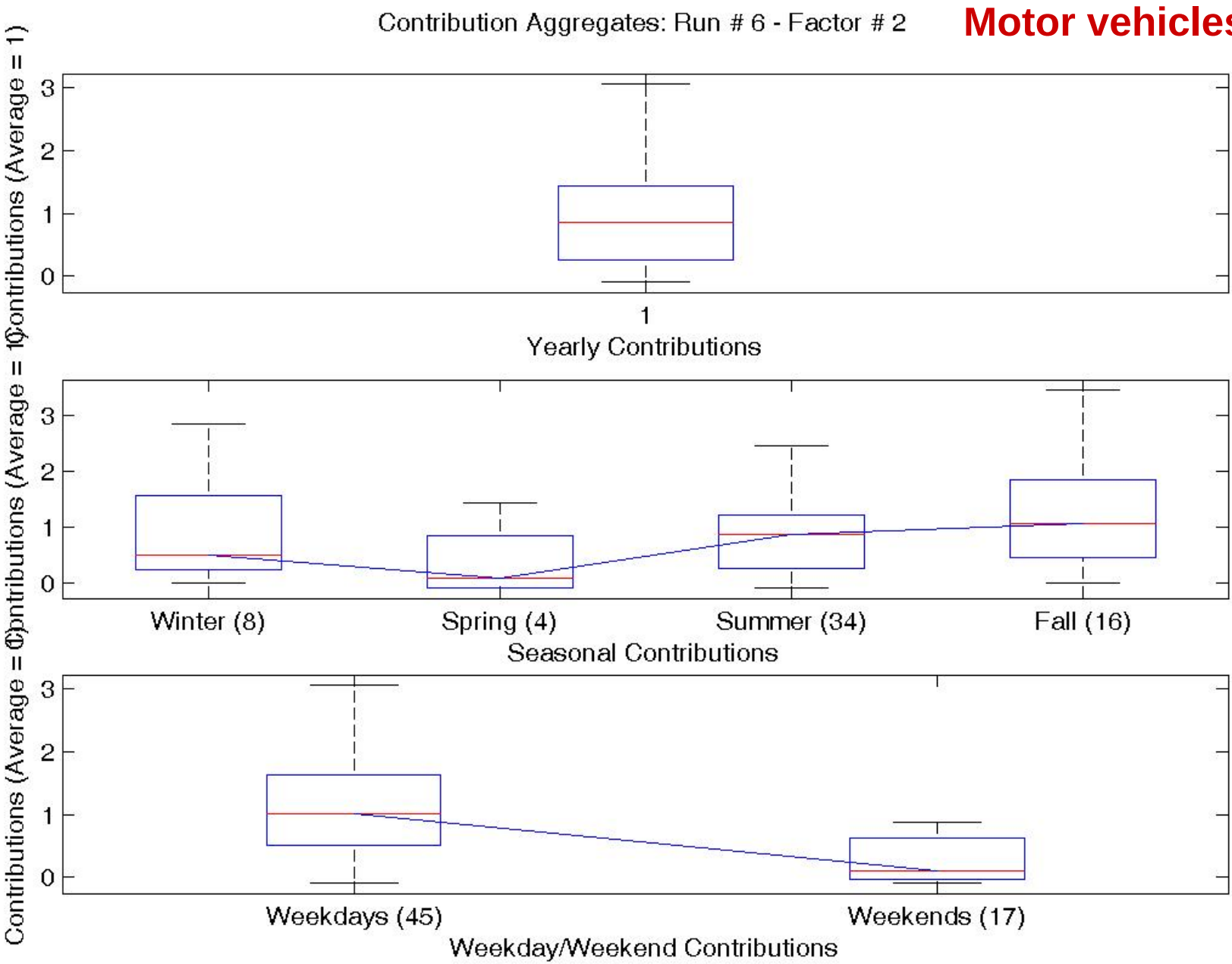

Contribution Aggregates: Run # 6 - Factor # 1
Sea salt
Contributions (Average = 1)
1
0.5
0
1
Yearly Contributions
Contributions (Average = 1)
8
6
4
2
0
Winter (8)
Spring (4)
Summer (34)
Fall (16)
Seasonal Contributions
Contributions (Average = 1)
6
4
2
0
Weekdays (45)
Weekends (17)
Weekday/Weekend Contributions

Motor vehicles

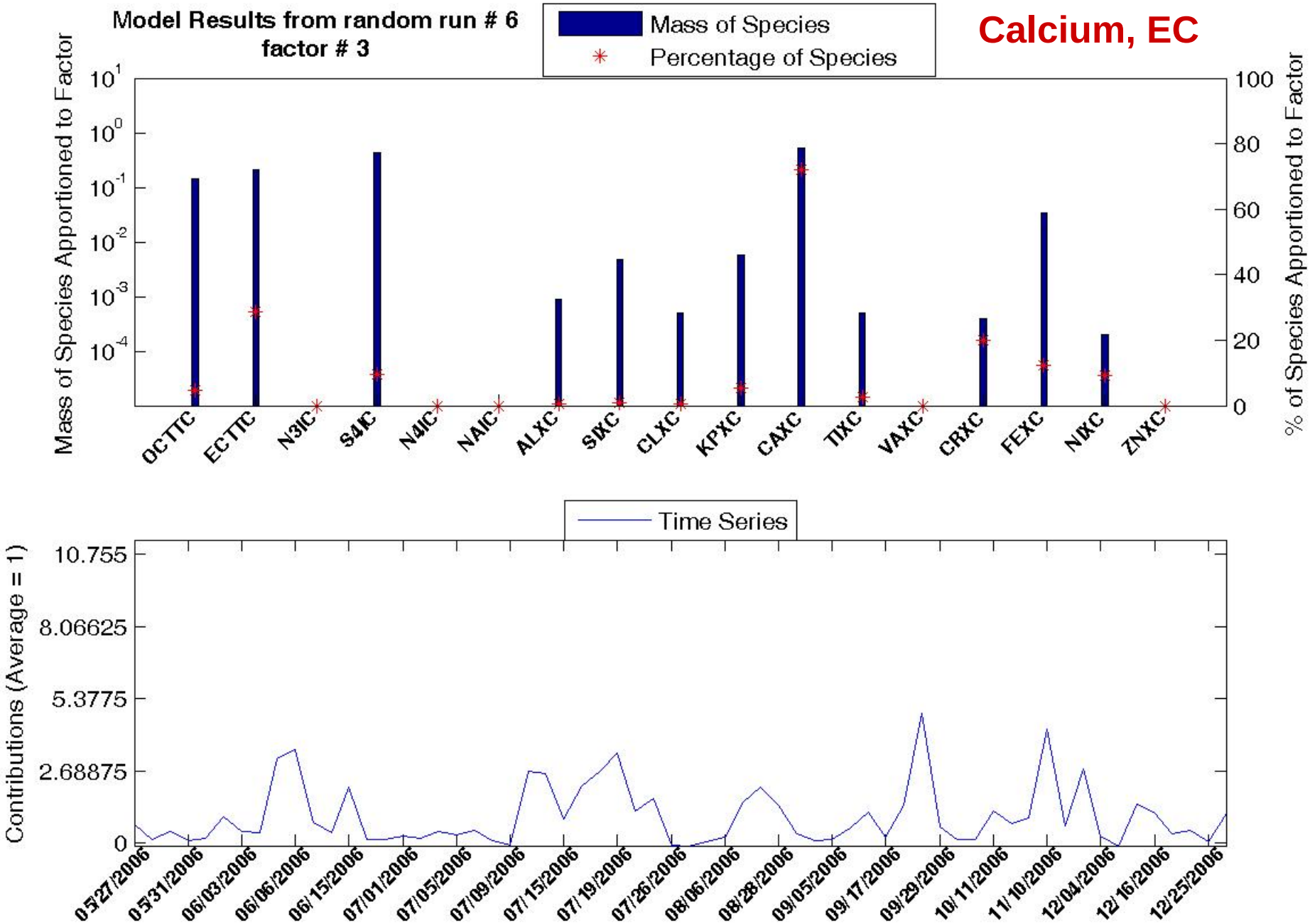




Motor vehicles



Calcium, EC


Model Results from random run # 6
factor # 3
Mass of Species
Percentage of Species
Mass of Species Apportioned to Factor
% of Species Apportioned to Factor
OCTTC
ECTTC
N3IC
S4IC
N4IC
NAIC
ALXC
SIXC
CLXC
KPXC
CAXC
TIXC
VAXC
CRXC
FEXC
NIXC
ZNXC
Time Series
Contributions (Average = 1)
10.755
8.06625
5.3775
2.68875
0
05/27/2006
05/31/2006
06/03/2006
06/06/2006
06/15/2006
07/01/2006
07/05/2006
07/09/2006
07/15/2006
07/19/2006
07/26/2006
08/06/2006
08/28/2006
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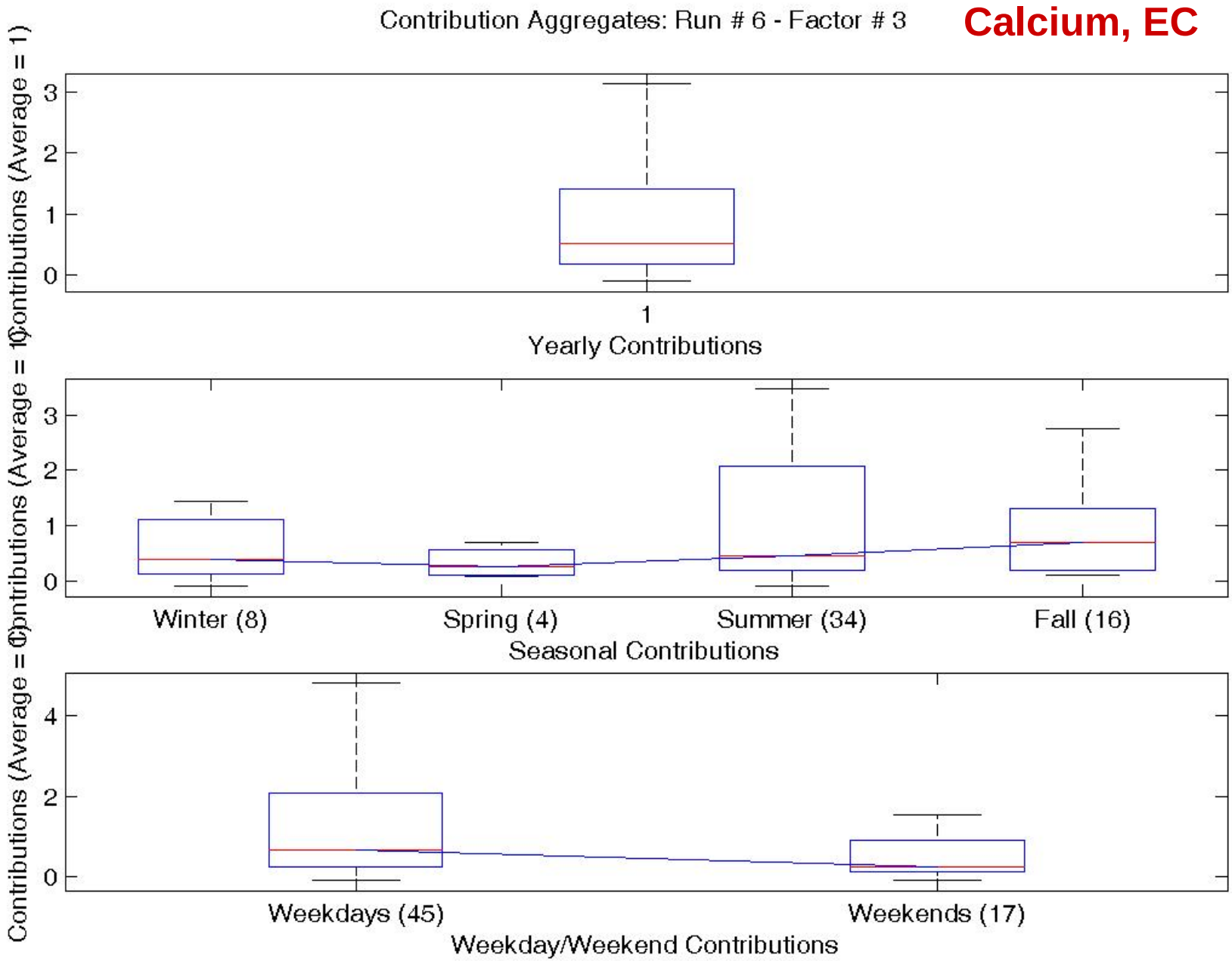
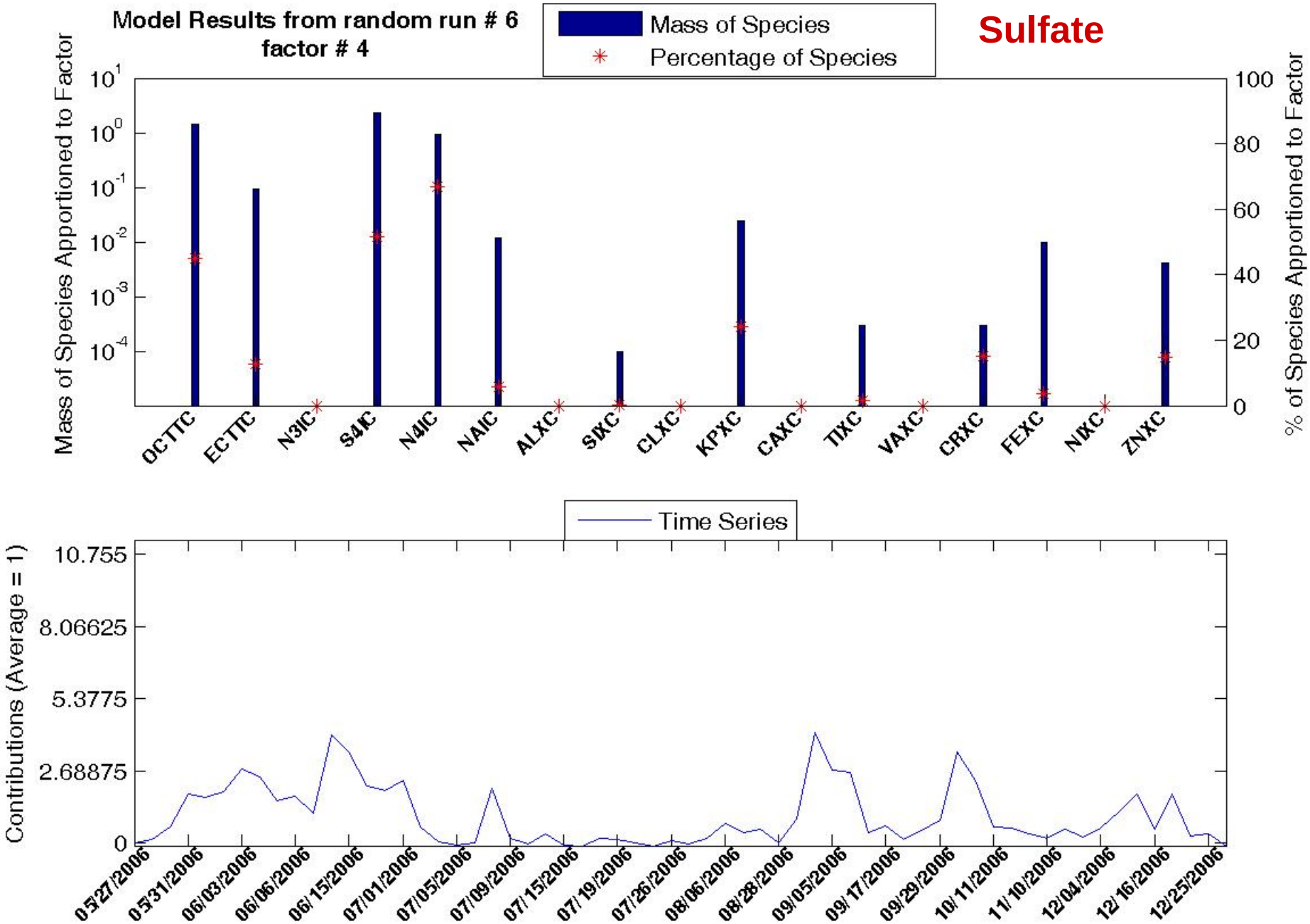
12/04/2006
12/16/2006
12/25/2006


Contribution Aggregates: Run # 6 - Factor # 3
Calcium, EC
Contributions (Average = 1)
3
2
1
0
1
Yearly Contributions
Contributions (Average = 1)
3
2
1
0
Winter (8)
Spring (4)
Summer (34)
Fall (16)
Seasonal Contributions
Contributions (Average = 1)
4
2
0
Weekdays (45)
Weekends (17)
Weekday/Weekend Contributions


Sulfate
Model Results from random run # 6
factor # 4
Mass of Species
Percentage of Species
Mass of Species Apportioned to Factor
% of Species Apportioned to Factor
OCTTC
ECTTC
N3IC
S4IC
N4IC
NAIC
ALXC
SIXC
CLXC
KPXC
CAXC
TIXC
VAXC
CRXC
FEXC
NIXC
ZNXC
Time Series
Contributions (Average = 1)
10.755
8.06625
5.3775
2.68875
0
05/27/2006
05/31/2006
06/03/2006
06/06/2006
06/15/2006
07/01/2006
07/05/2006
07/09/2006
07/15/2006
07/19/2006
07/26/2006
08/06/2006
08/28/2006
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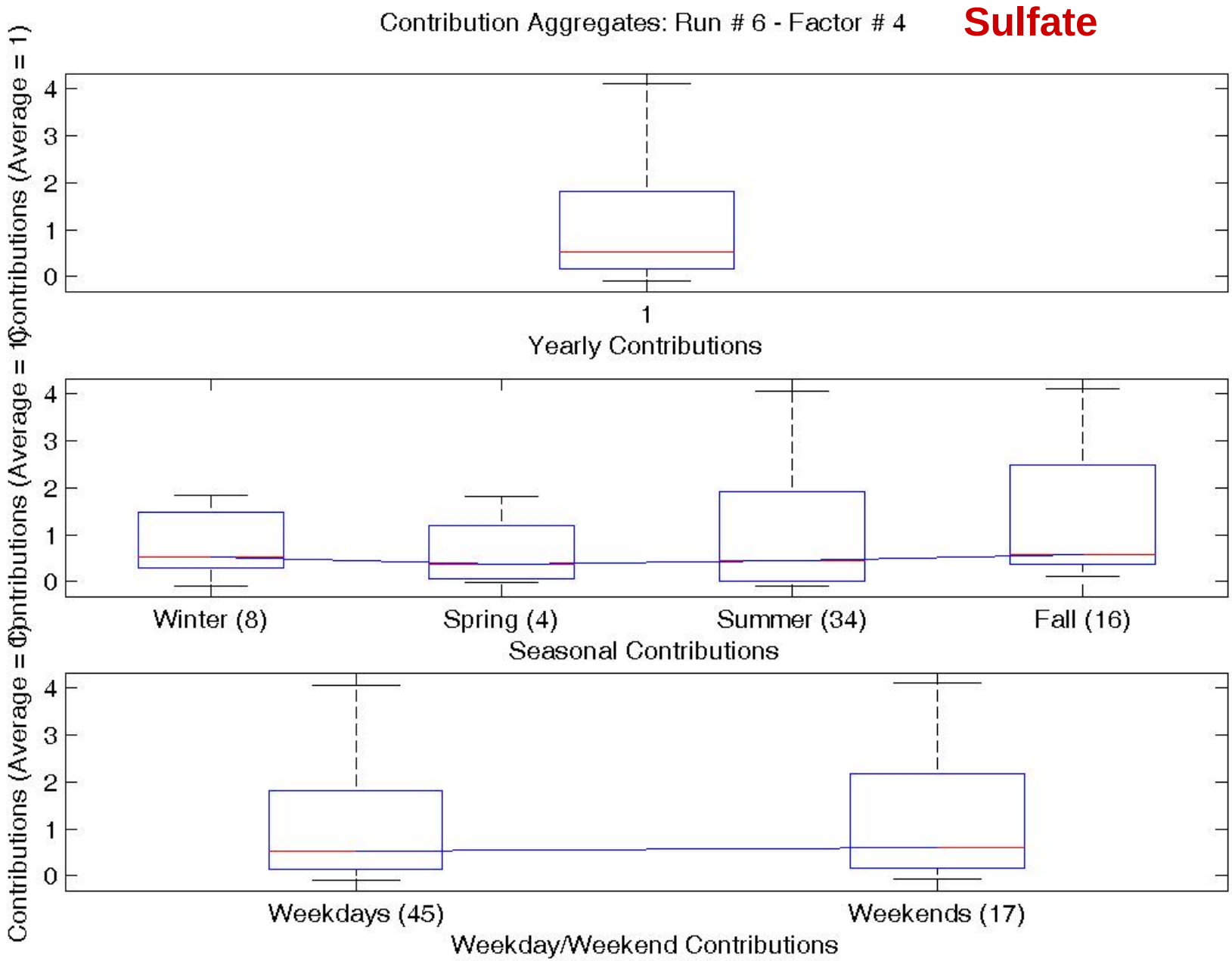
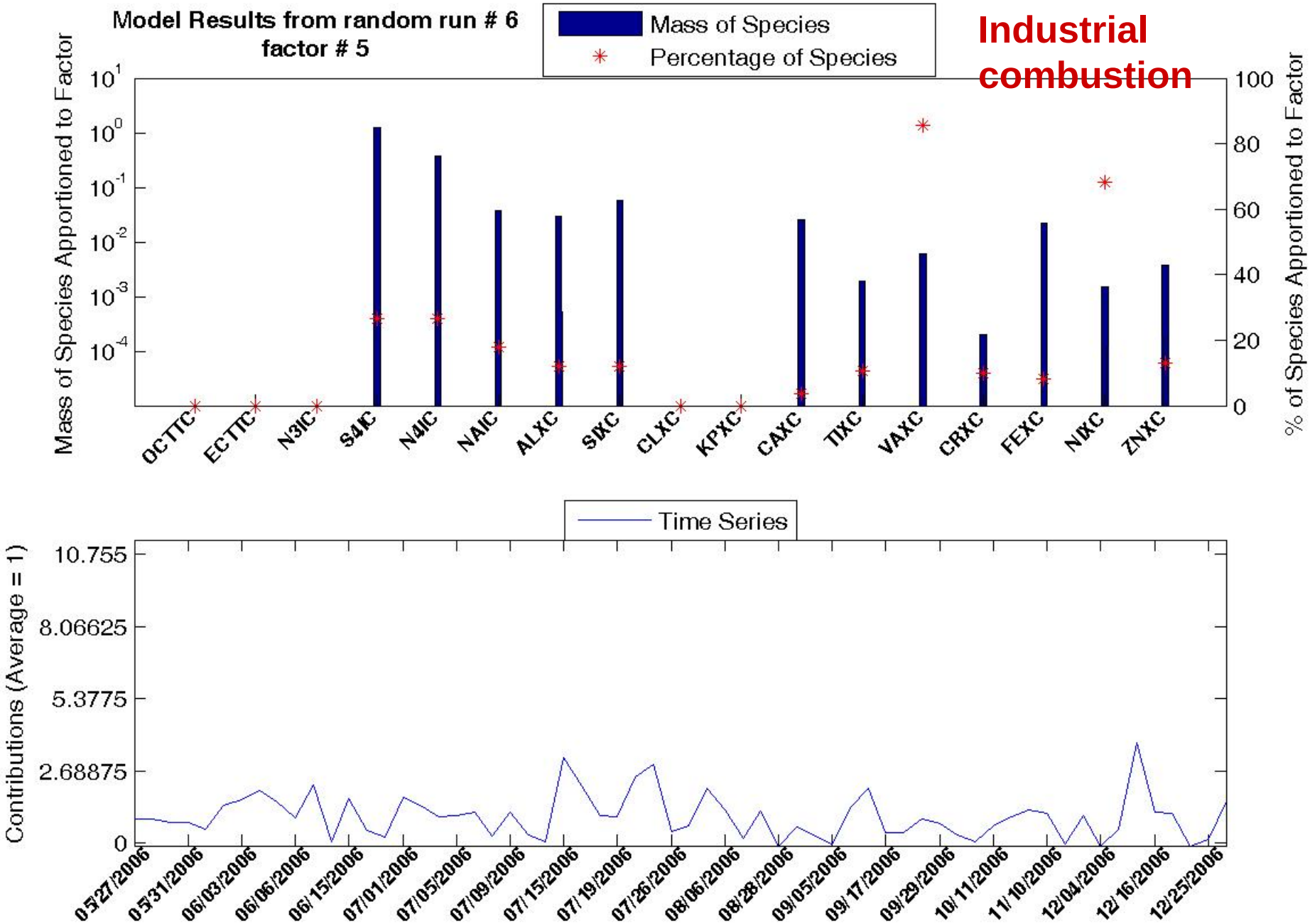
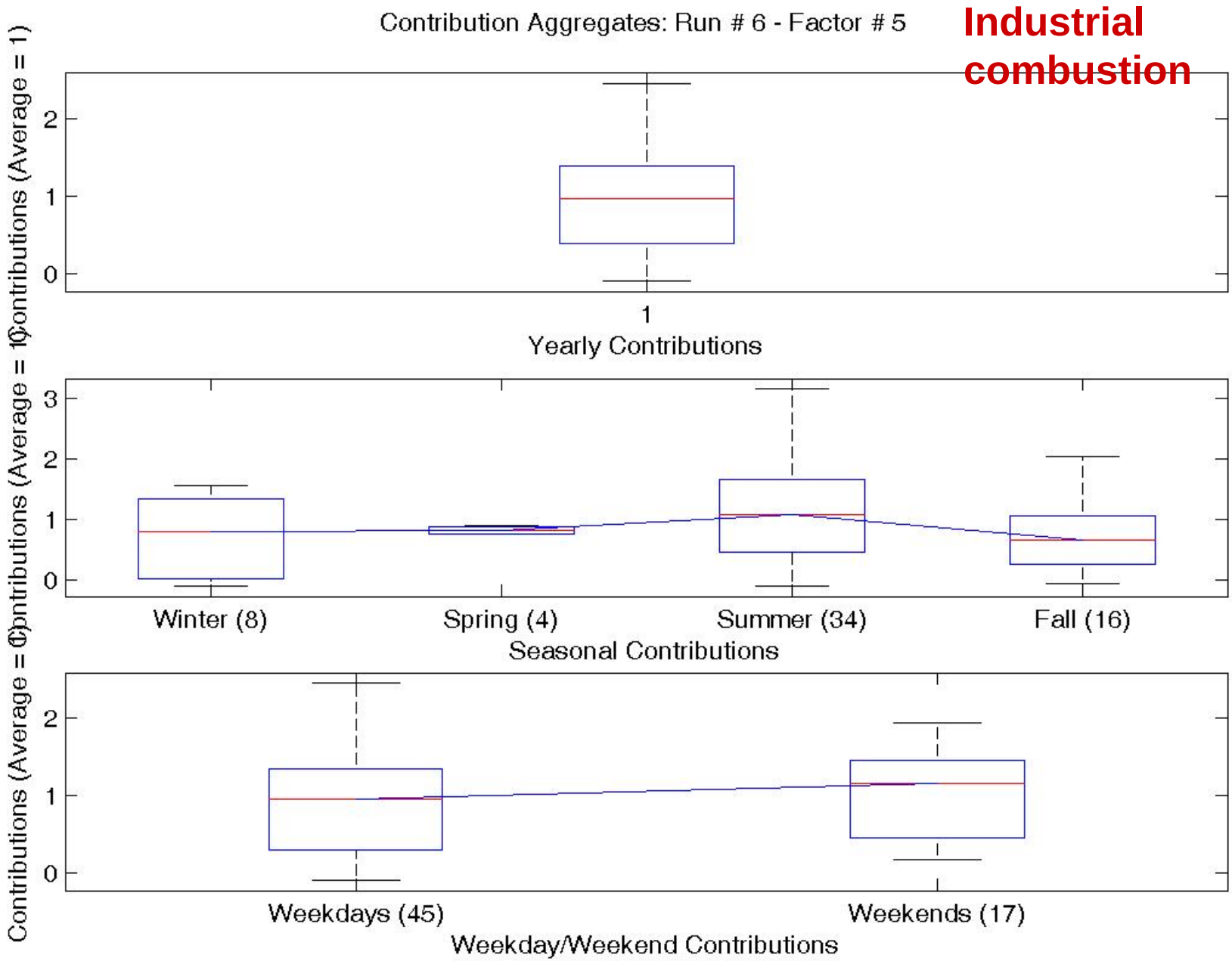
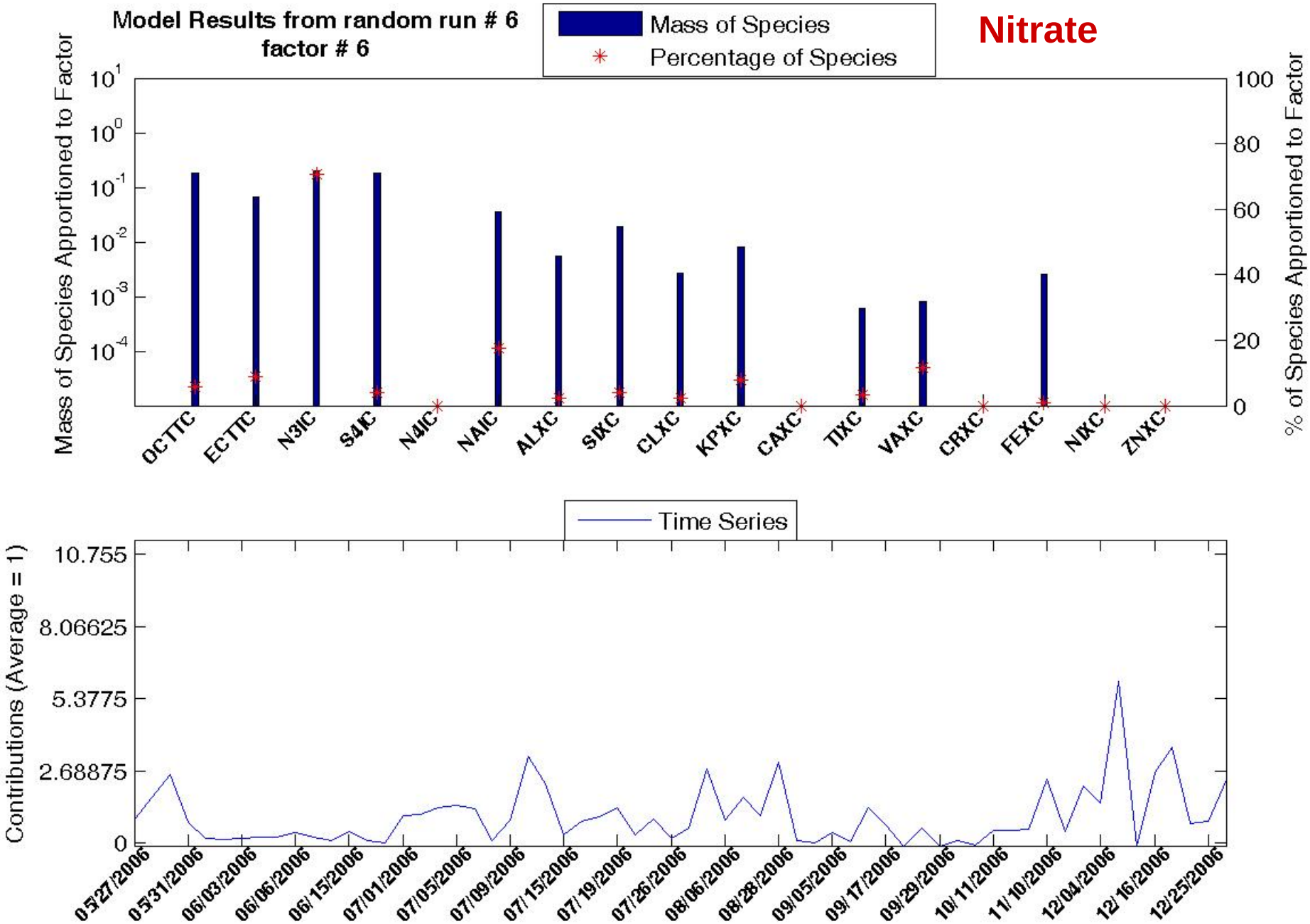
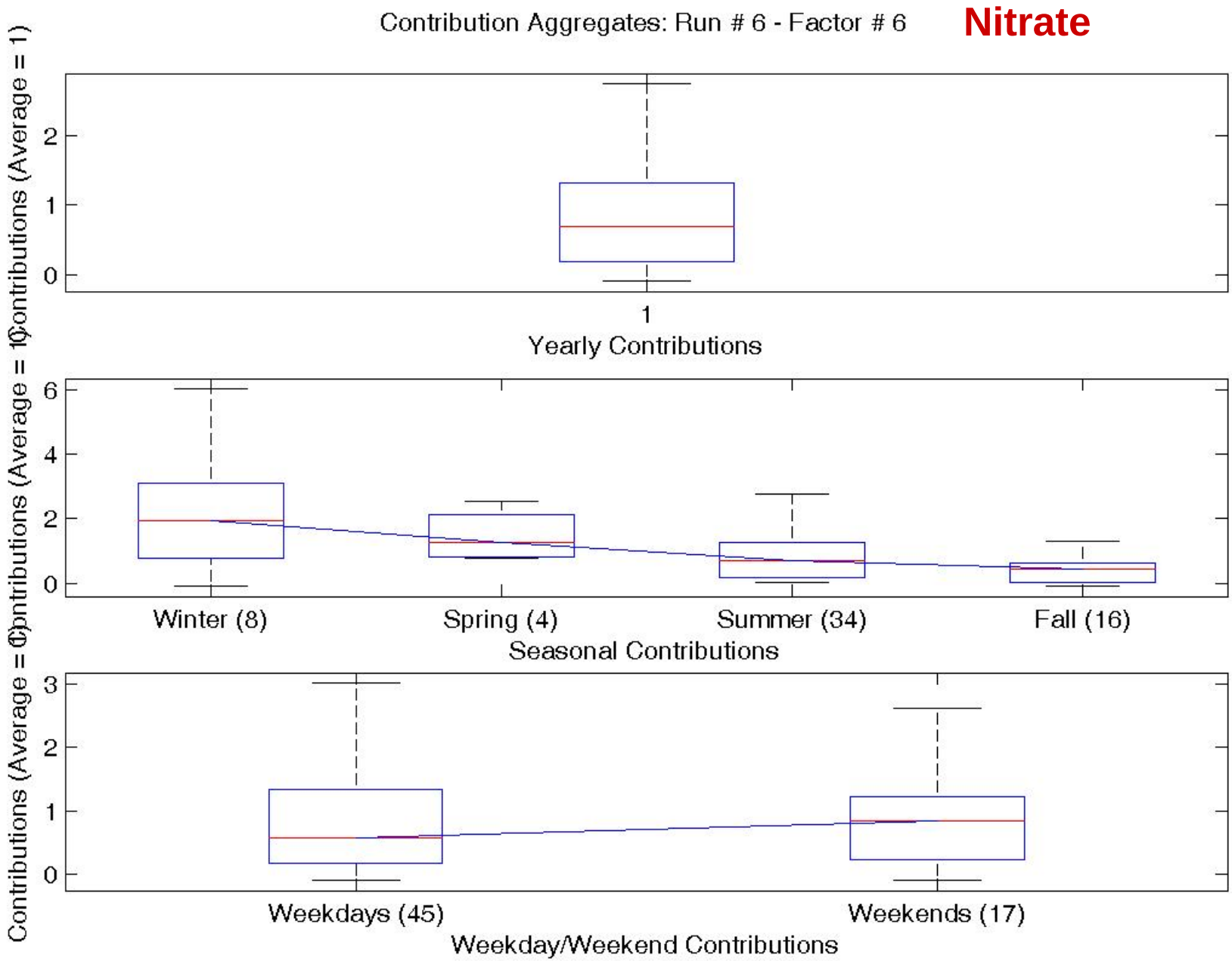
12/16/2006
12/25/2006

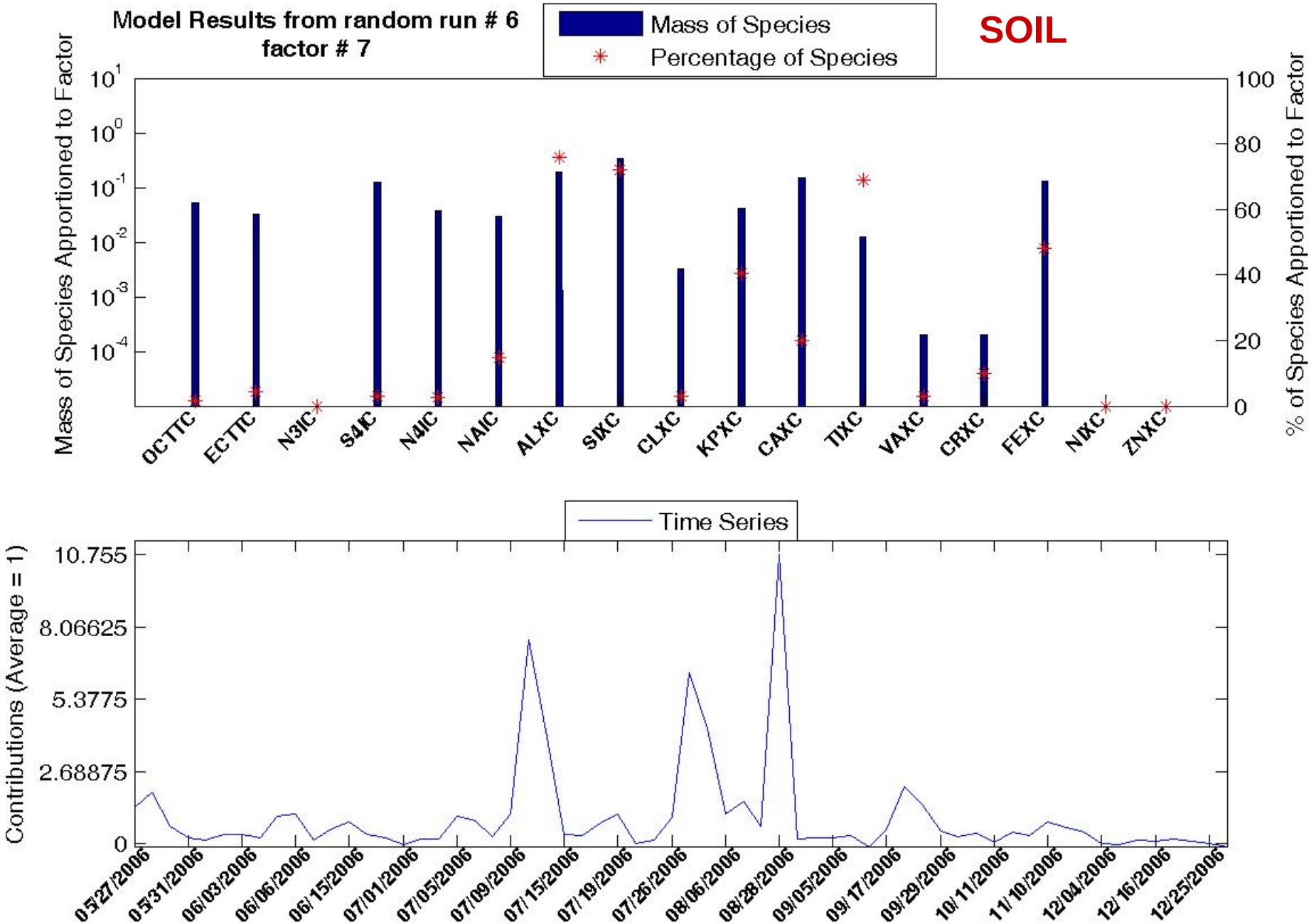

Contribution Aggregates: Run # 6 - Factor # 4
Sulfate
Contributions (Average = 1)
4
3
2
1
0
1
Yearly Contributions
Winter (8)
Spring (4)
Summer (34)
Fall (16)
Seasonal Contributions
Weekdays (45)
Weekends (17)
Weekday/Weekend Contributions


Industrial combustion
Model Results from random run # 6
factor # 5
Mass of Species
Percentage of Species
Mass of Species Apportioned to Factor
% of Species Apportioned to Factor
OCTTC
ECTTC
N3IC
S4IC
N4IC
NAIC
ALXC
SIXC
CLXC
KPXC
CAXC
TIXC
VAXC
CRXC
FEXC
NIXC
ZNXC
Time Series
Contributions (Average = 1)
10.755
8.06625
5.3775
2.68875
0
05/27/2006
05/31/2006
06/03/2006
06/06/2006
06/15/2006
07/01/2006
07/05/2006
07/09/2006
07/15/2006
07/19/2006
07/26/2006
08/06/2006
08/28/2006
09/05/2006
09/17/2006
09/29/2006
10/11/2006
11/10/2006
12/04/2006
12/16/2006
12/25/2006


Contribution Aggregates: Run # 6 - Factor # 5
Industrial combustion
Contributions (Average = 1)
2
1
0
1
Yearly Contributions
3
2
1
0
Winter (8)
Spring (4)
Summer (34)
Fall (16)
Seasonal Contributions
2
1
0
Weekdays (45)
Weekends (17)
Weekday/Weekend Contributions


Nitrate
Model Results from random run # 6
factor # 6
Mass of Species
Percentage of Species
Mass of Species Apportioned to Factor
% of Species Apportioned to Factor
OCTTC
ECTTC
N3IC
S4IC
N4IC
NAIC
ALXC
SIXC
CLXC
KPXC
CAXC
TIXC
VAXC
CRXC
FEXC
NIXC
ZNXC
Time Series
Contributions (Average = 1)
10.755
8.06625
5.3775
2.68875
0
05/27/2006
05/31/2006
06/03/2006
06/06/2006
06/15/2006
07/01/2006
07/05/2006
07/09/2006
07/15/2006
07/19/2006
07/26/2006
08/06/2006
08/28/2006
09/05/2006
09/17/2006
09/29/2006
10/11/2006
11/10/2006
12/04/2006
12/16/2006
12/25/2006


Contribution Aggregates: Run # 6 - Factor # 6
Nitrate
Contributions (Average = 1)
0
1
2
1
Yearly Contributions
Contributions (Average = 1)
0
2
4
6
Winter (8)
Spring (4)
Summer (34)
Fall (16)
Seasonal Contributions
Contributions (Average = 1)
0
1
2
3
Weekdays (45)
Weekends (17)
Weekday/Weekend Contributions


SOIL
Model Results from random run # 6
factor # 7
Mass of Species
Percentage of Species
Mass of Species Apportioned to Factor
% of Species Apportioned to Factor
OCTTC
ECTTC
N3IC
S4IC
N4IC
NAIC
ALXC
SIXC
CLXC
KPXC
CAXC
TIXC
VAXC
CRXC
FEXC
NIXC
ZNXC
Time Series
Contributions (Average = 1)
10.755
8.06625
5.3775
2.68875
0
05/27/2006
05/31/2006
06/03/2006
06/06/2006
06/15/2006
07/01/2006
07/05/2006
07/09/2006
07/15/2006
07/19/2006
07/26/2006
08/06/2006
08/28/2006
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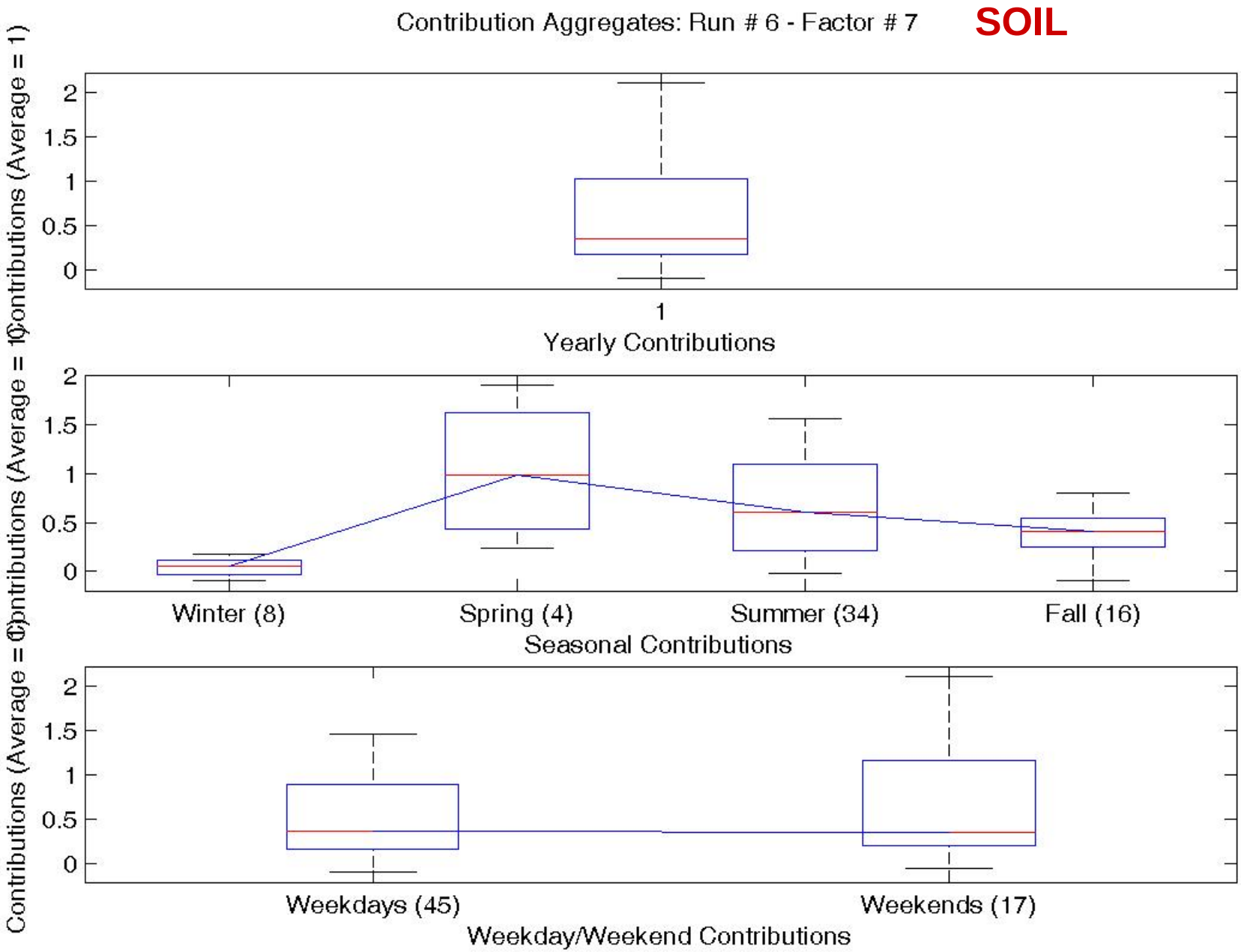
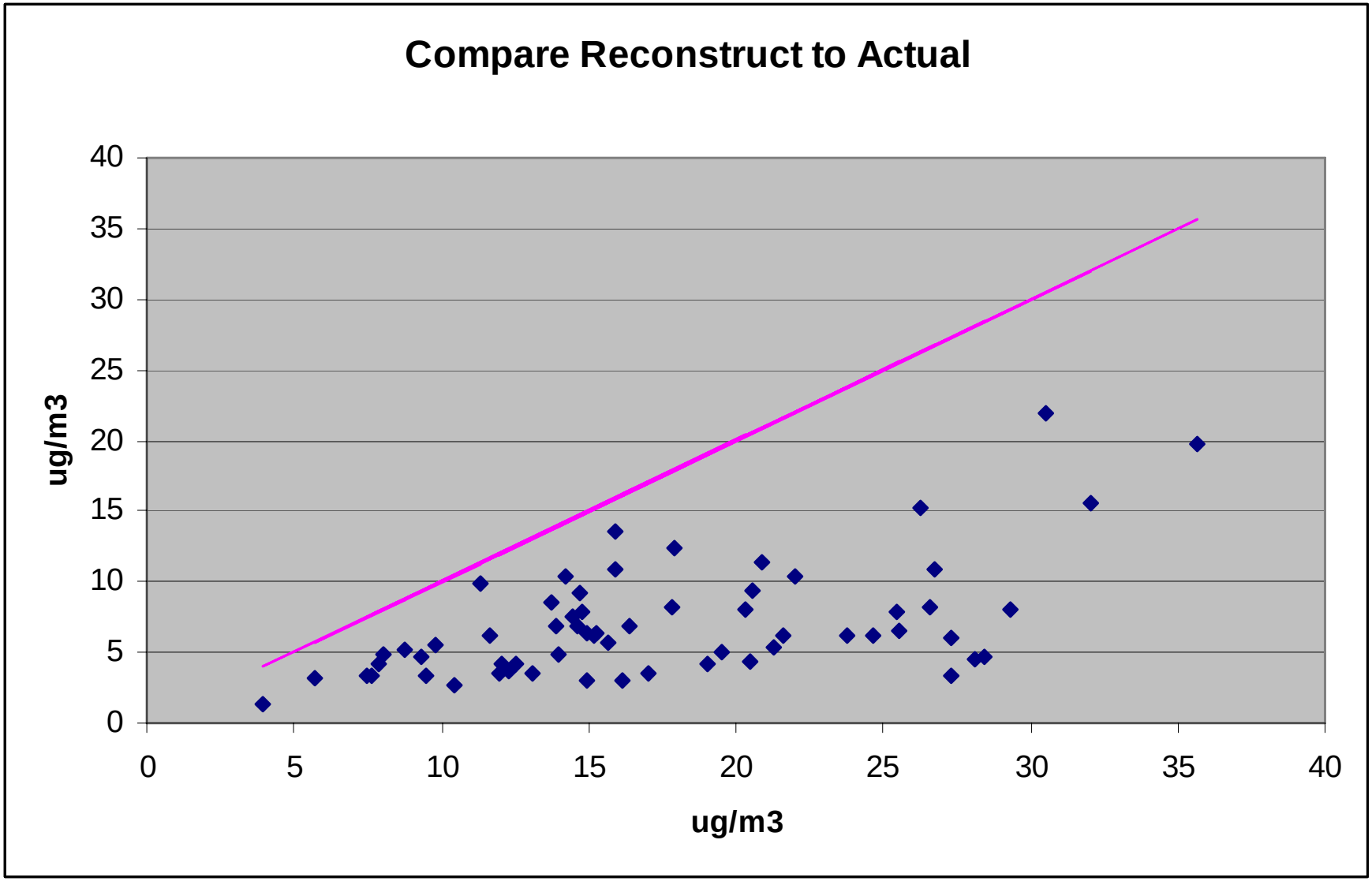
09/17/2006
09/29/2006
10/11/2006
11/10/2006
12/04/2006
12/16/2006
12/25/2006


Contribution Aggregates: Run # 6 - Factor # 7
SOIL
Contributions (Average = 1)
2
1.5
1
0.5
0
1
Yearly Contributions
Winter (8)
Spring (4)
Summer (34)
Fall (16)
Seasonal Contributions
Weekdays (45)
Weekends (17)
Weekday/Weekend Contributions

End comparison suggests need more data….



Compare Hous. East (Hendler)

Factor	Houston East	Clinton Dr
Sulfate-rich secondary aerosol	Sept. – Oct.	fall
Nitrate-rich aerosol	Nov. – Mar.	winter
Motor vehicles	Aug. – Jan.	fall
Sea salt	Mar., May-Jun.	spring
Soil/crustal matter	Jul. – Aug.	spring
Industrial combustion	Year-around	summer
Biomass burning	*May*	*Not observed*
“Calcium”	*Not found*	*Year-around*

Conclusion

- Soil-like material provides some 2 $\mu g/m^3$ add-on at Clinton.
- Soil and dry bulk material samples have been taken for analysis and source profile development.
- Additional projects to assess transport of Mex.-CenAm smoke and to assess regional trends apportionment ongoing.

Photos of dusty nearby areas

At Clinton Gate – Facing East

Valero Asphalt
Immediately to the East of the Gate

At Gate – Facing West towards PTRA / A&L Loading Yard

At Monitor – Across from UP, PTRA and A&L Loading Yard

A&L Trucking/Ranger Steel
Use of Emulsified Asphalt

Emulsified Asphalt…cont
(tracking from outside roads?)

Crushed Concrete Material