Descriptive Model of PM Pollution in Baltimore

as derived from Analysis of Components of Discrete Episodes at the Ponca St. Supersite

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Baltimore Supersite Study Area

Typical MidAtlantic Seaport City
- **Populous, heavy industry, So. Baltimore**
- **Complex meteorology**

Major N.-S. transportation corridor

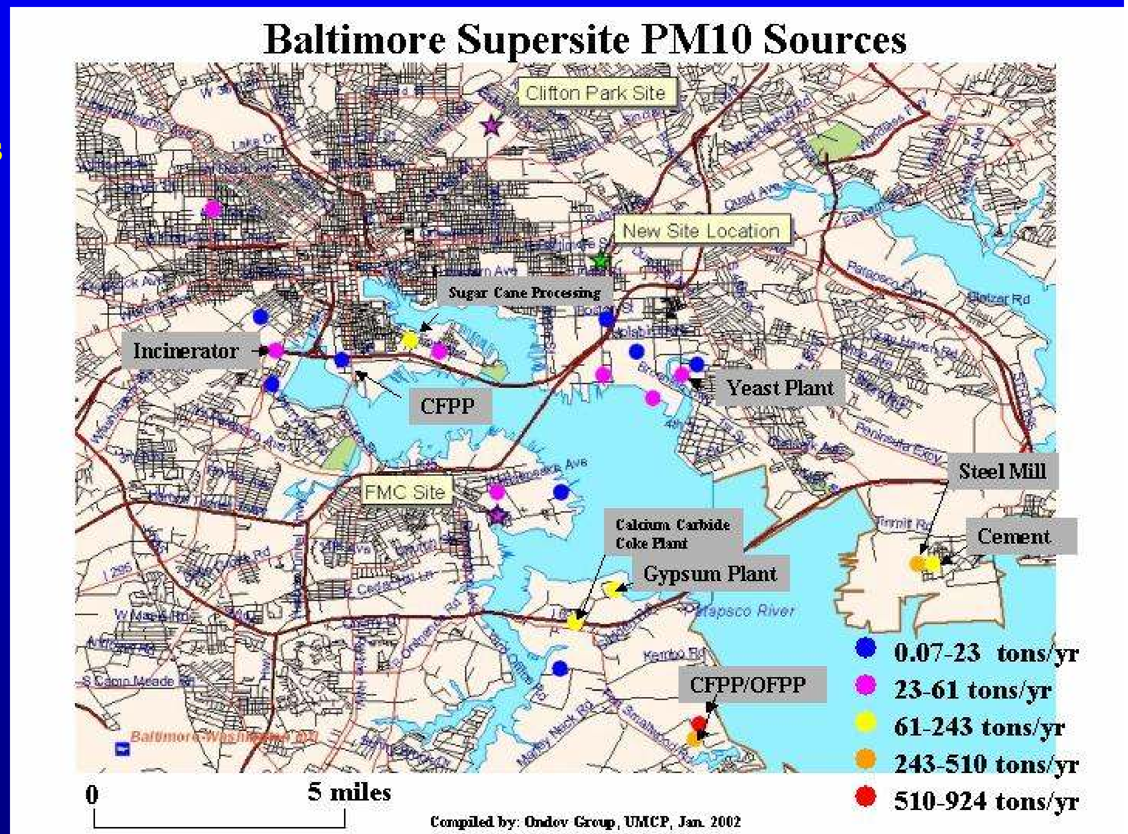
End member Washington - Boston Megalopolis

Variable Aerosol age
- **local, 50 km, 100's km source regions**
- **Appalachian Cloud-processed sulfate**

Environmental Justice
- **Downtown, weakly influenced**
- **So. Baltimore 10-X PAH, Metals**
  - **1.7-X deaths via pulmonary disease**

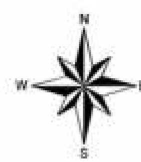
Interpretive Context
- **25 yrs receptor modeling in region**
- **EPA and AEOLOS studies in Baltimore**
- **IMPROVE site, Shennandoah Nat. Park**

Health Effects Studies
- **JHU & UMAB**



SAMPLING SITE

Baltimore PM Supersite Location



Measurements

– Primary Site: Ponca St., East Baltimore
  9.5 months: March – November, 2003
– Maximum temporal, size, compositional resolution
  - PM2.5, EC,OC, Nitrate, Sulfate,
  - Metals, Organic compounds
  - PAMS VOC, CO, NO_x, NO, NO_2, O_3
  - LIDAR, Single Particle MS
  - SMPS + APS size distributions 10 nm to 20 µm
– Measurement resolution 5 min, 10 min, 30 min, 1 hr, 3 hr, plus 24 Hr FRM mass and speciation

Interpretive Context

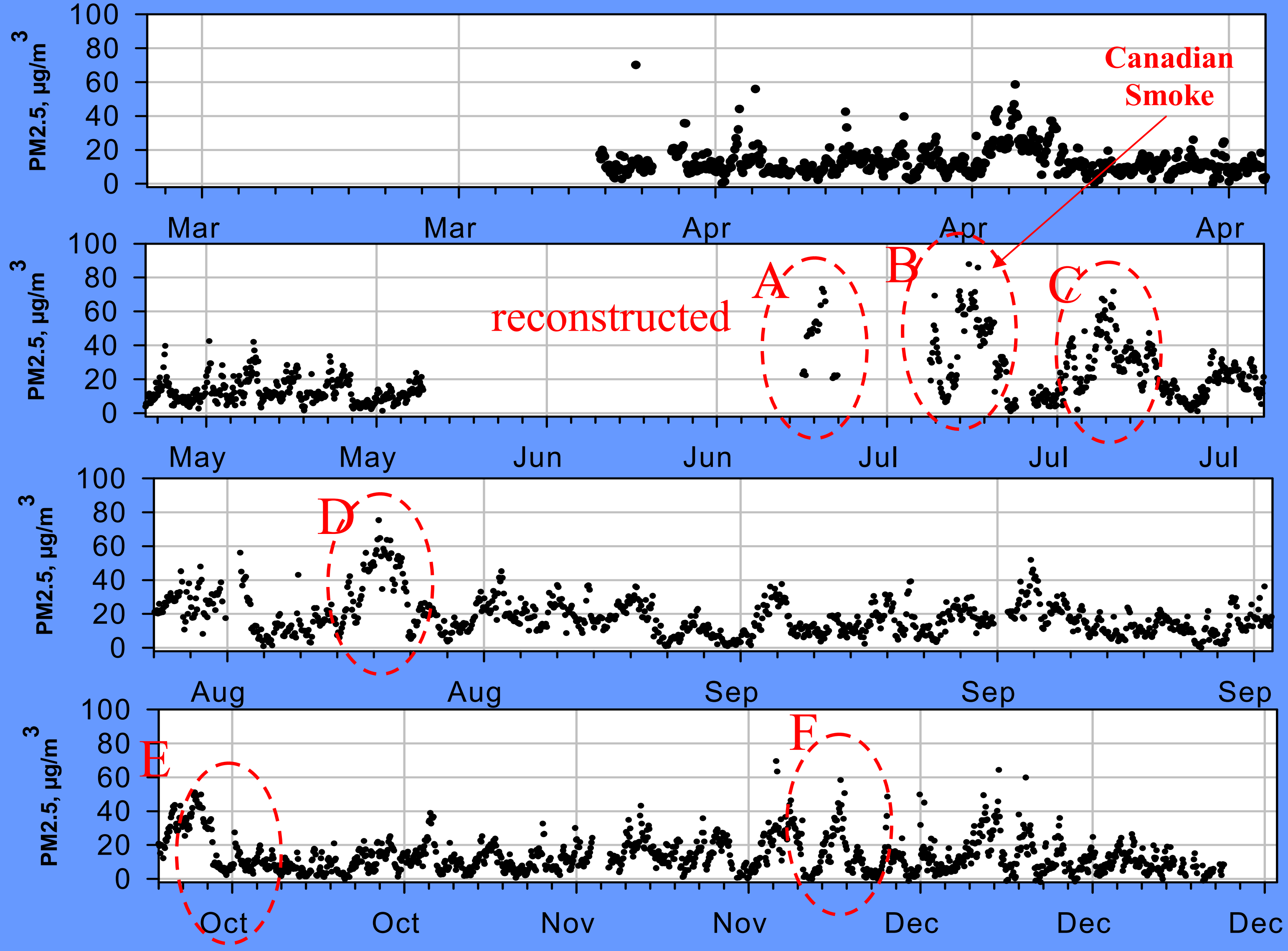
- PM air pollution may be viewed as occurring in a series of discrete meteorologically driven discrete episodes
- Transients often caused by one or two components
- Local vs. distant sources indicated by
  - Temporal behavior of constituents and marker species
  - Size distribution parameters
  - Detailed Analysis of episodes

Outline

- PM2.5 Episodes in 2002 (30 min data)
- Summary of major features of 6 worst
- Detailed description of highly time resolved data for worst summer and cool weather episodes
- Features of major components

30-min$PM_{2.5}$ Concentrations: 2002

show: series of discrete episodes of hours to 2 or 3 days duration



PM2.5 Statistics: 9.5 months, 2002

	w/Canadian Smoke	w/o Canadian Smoke*
Daily means:	3.5 to 85.6	3.5 to 64
Annual mean	16.9	15.8±13
No. daily exceedences	2	~1
No. daily means > 30 µg/m^3 (i.e., 16.9 + 13)		29

6 worst episodes described in Park et al., 2005
2 will be described in this talk

*Episode B; M\maximum 30 min concentration was 198 µg/m^3

Characteristics of Six Worst PM2.5 Episodes
Baltimore Supersite, Ponca St., 2002

			Ozone (ppb)[1]		Ambient temp (°C)		Relative humidity (%)		Maxima NOx and CO, ppb	
Episode	Date	Type	Avg.	Range	Avg.	Range	Avg.	Range	NOx	CO
A	June 24-25	Regional Haze	84	26-132	29.8	23.7-35.4	57.5	32-77	110	800
B	July 6-8	Canadian Smoke	-	-	25.6	19.7-33.8	45.4	28-70	155	1600
C	July 18-19	Regional Haze	70	14-91	29	23.2-34.0	57.9	38-81	130	800
D	Aug.12-14	Reg Haze + Local Traffic	76	22-122	29.2	21.6-35.6	53.8	35-79	300	1800
E	Oct. 2-5	Regional Haze	35	1-57	24.8	17.5-30.4	69.2	36-91	180	1300
F	Nov. 20-21	Local Traffic	2	0-6	8.4	3.1-14.5	83.2	48-98	780	2800

[1] Ozone mixing ratios represent measurements made between 10:00 and 20:00 hours.

Episode durations: 2 to 4 days

Summer haze: high O_3, hot, low NOx & CO

Fall local sources: low O_3, cool, high NOx & CO

Concentrations

Table 2. Concentrations of PM2.5 mass and major chemical species for 6 pollution episodes.

Episode	Interval	PM2.5, $\mu g/m^3$ TEOM	PM2.5, $\mu g/m^3$ Reconstructed	Constituent expressed as indicated, $\mu g/m^3$ [4] $(NH_4)_2SO_4$	OM	EC	NH_4NO_3
A	Episode Avg.[1]	N/A	55[1], 62[2]	**36**	16	1.2	1.7
Regional Haze	Episode Range[1]		43 - 77	28 - 60	11 - 22	0.6 - 2.8	0.6 - 5.2
	Bkgnd[3]	N/A	24	8.3	12	1.1	0.65
	Bkgnd Range		22 - 27	5.8 - 10	11 - 14	0.6 - 2.3	0.6 - 0.7
B	Episode Avg.	57[1], 86[2]	55[1], 82[2]	6.9	**54**	**1.9**	**2.1**
Canadian Smoke	Episode Range[1]	20 - 180	20 - 174	3.7 - 13	14 - 161	0.5 - 3.7	0.25 - 5.4
	Bkgnd[3]	19					
	Bkgnd Range	15 - 17					
C	Episode Avg.[1]	49[1], 52[2]					
Regional Haze	Episode Range[1]	24 - 72					
	Bkgnd[3]	23					
	Bkgnd Range	12 - 37					
D	Episode Avg.[1]	42[1], 57[2]					
Reg Haze + Local Traffic	Episode Range[1]	36 - 73					
	Bkgnd[3]	11					
	Bkgnd Range	9.8 - 12.					
E	Episode Avg.[1]	35[1], 35[2]					
Regional Haze	Episode Range[1]	8.9 - 52					
	Bkgnd[3]	12					
	Bkgnd Range	6.5 - 22	8.1 - 22	3.5 - 7.5	3.8 - 11	0.4 - 2.5	0.3 - 2.4
F	Episode Avg.[1]	32[1], 32[2]	34[1], 32[2]	7	**14**	3.3	**8.9**
Local Traffic	Episode Range[1]	9.1 - 87	14.5 - 83	4.4 - 11	5.2 - 55	1.2 - 12	3.6 - 15
	Bkgnd[3]	9.6	14	4.7	4.8	1	3.2
	Bkgnd Range	7,8 - 12	13 - 14	4.2 - 5.0	4.7 - 5.1	0.8 - 1.1	2.5 - 4.3

[1]Average concentration during period of elevation

[2]Highest midnight to midnight (24-hr) average during episode

[3]Average before and after episode

[4] Estimated, see text.

PM2.5, $\mu g/m^3$

	bkgnd	mean
* Summer	~20	~60
Fall	~ 14	~34

- Summer — more sulfate
- Fall — comparable OM, more EC, nitrate

Table 3. Relative Composition of PM2.5

Episode	Interval[1]	(NH4)2SO4[2]	OM[2]	EC	NH4NO3[2]
		Constituent, %			
A	Episode Avg.	65	29	2.3	3.3
	Episode Range	54 - 78	20 - 34	1.0 - 5.3	1.1 - 9.9
	Bkgnd	37	51	4.7	1.4
	Bkgnd Range	30 - 43	32 - 59	2.6 - 8.5	1.3 - 1.5
B	Episode Avg.	13	81	3	3.2
	Episode Range	3.8 - 30	65 - 92	1.4 - 6.2	1.2 - 9.0
	Bkgnd	25	70	2.8	1.5
	Bkgnd Range	15 - 36	60 - 81	2. 6- 3.0	1.2 - 1.7
C	Episode Avg.	71	25	2.1	2.3
	Episode Range	46 - 79	19 - 50	1.1 - 6.3	1.0 - 6.1
	Bkgnd	42	48	4.9	6.1
	Bkgnd Range	19 - 67	25 - 64	1.9 - 18	1.7 - 19

[1]Averages reflect periods when concentrations were elevated. Background values represents compostions before and after the episodoe.
[2]Estimated; see text.

Table 3, continued.

Episode	Interval[1]	$(NH_4)_2SO_4$[2]	OM[2]	EC	NH_4NO_3[2]
		Constituent, %			
D	Episode Avg.	49	42	3.8	4.5
	Episode Range	22 - 71	26 - 62	1.6 - 9.3	1.1 - 16
	Bkgnd	34	56	5.6	5
	Bkgnd Range	24 - 42	50 - 62	5.0 - 6.5	3.0 - 8.2
E	Episode Avg.	62	27	6	5.4
	Episode Range	47 - 77	19 - 34	2.9 - 11	1.4 - 13
	Bkgnd	44	44	6.4	5.2
	Bkgnd Range	30 - 55	38 - 51	3.7 - 11	2.2 - 12
F	Episode Avg.	22	41	9.6	27
	Episode Range	12 - 31	27 - 65	4.2 - 17	7.8 - 42
	Bkgnd	34	35	6.9	23
	Bkgnd Range	29 - 37	34 - 37	6.6 - 7.6	20 - 30

[1]Averages reflect periods when concentrations were elevated. Background values represents compostions before and after the episodoe.

[2]Estimated; see text.

PM Episode A
June 24-26, 2002

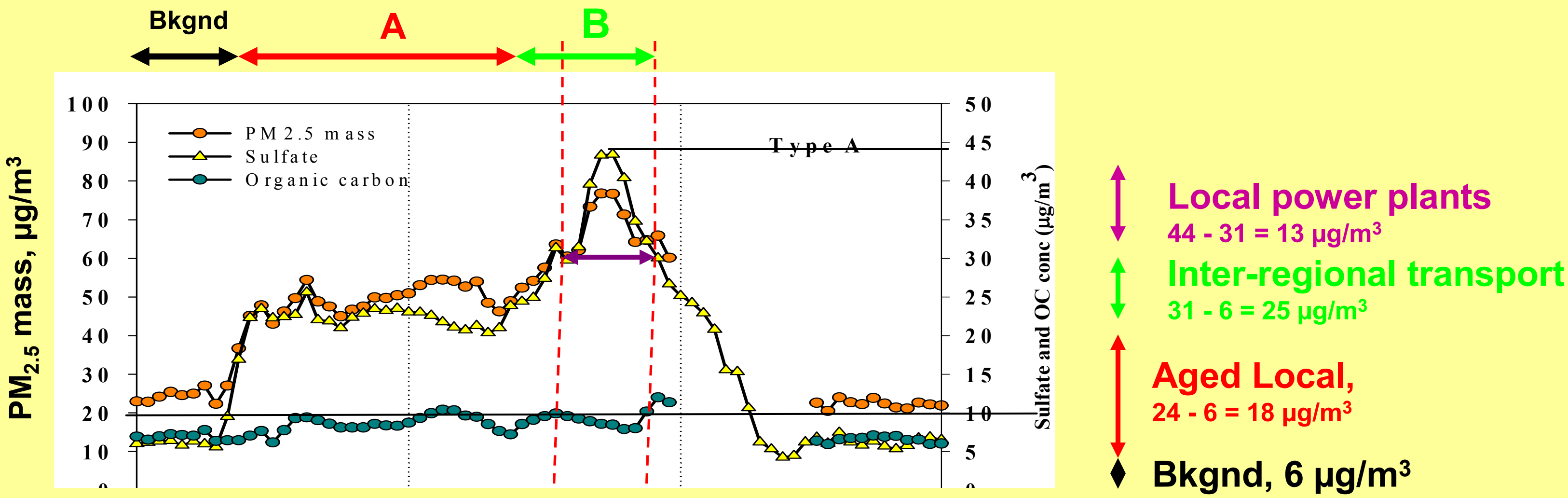
Summer Haze Episode, dominated by Sulfate,OM

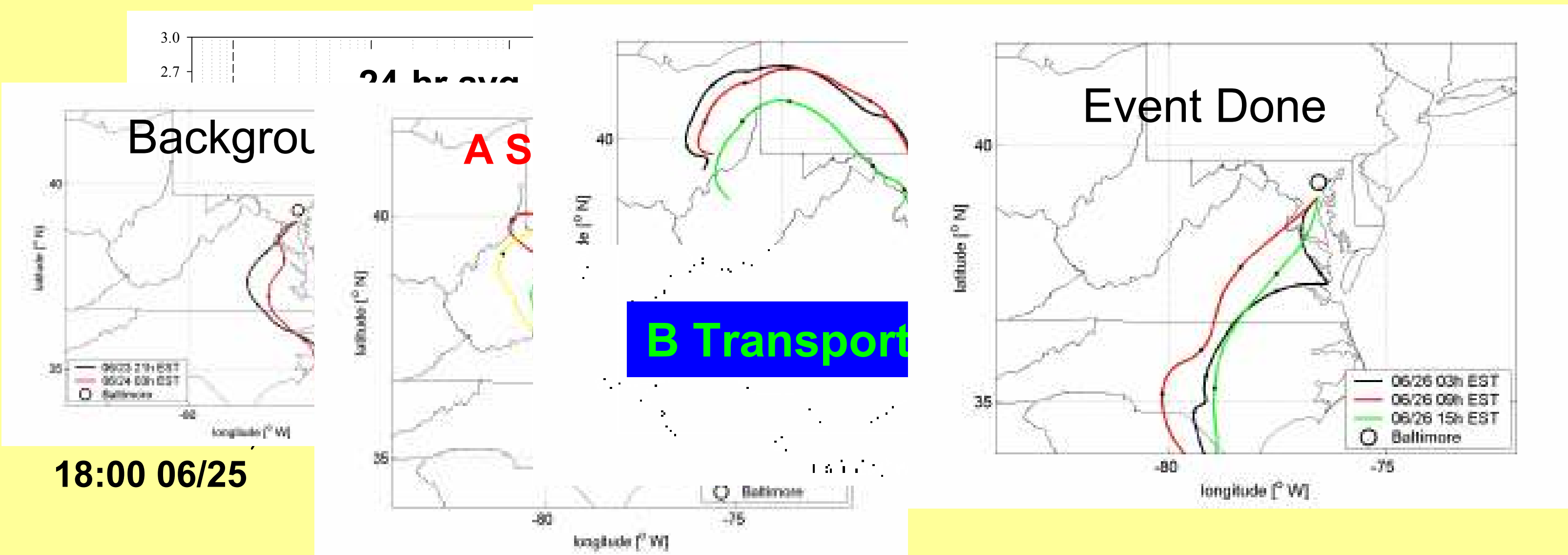
Influence of Local sources evident

Episode A: June 24-25: Sulfate Haze Event

Worst Episode in 9.5 month study (except Canadian Smoke)

Aged Local, regional, fresh local components





18:00 06/25

er local
to 170°
5.2 km

er plant 15
raise sulfate
µg/m³

Some important points

- Arguably, sources in the local region contributed substantial amounts of sulfate on day1
- Arrival of polluted air mass increases sulfate 7x relative to background on day 2
- OC increase only 1.5x over background, to 10 $\mu g/m^3$.

  Whereas for Episode F, local (traffic) induces 3x increase in OC!

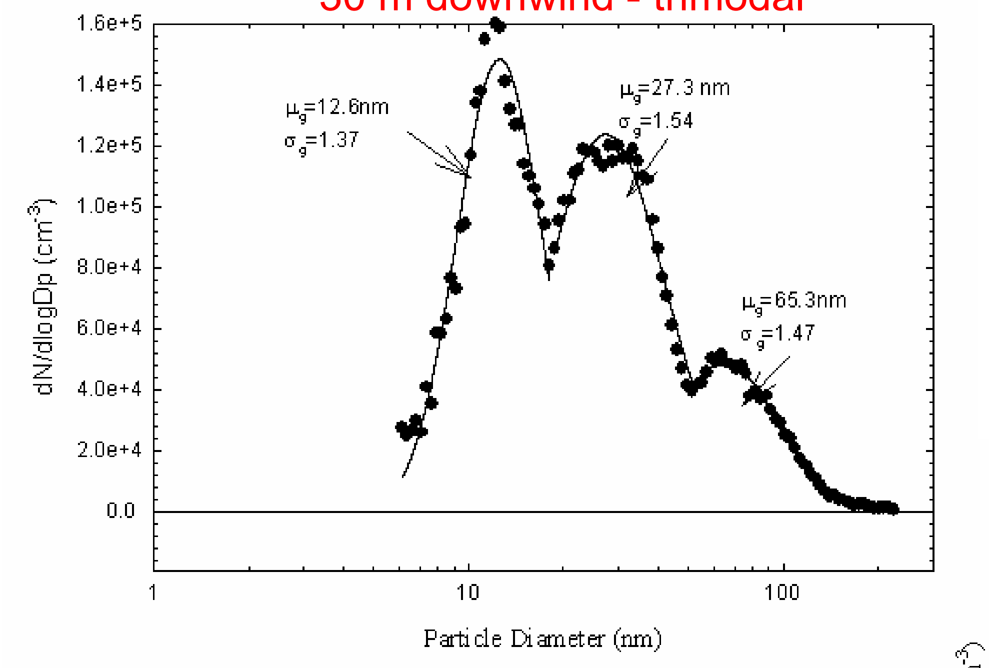
Influence of Traffic

revealed by
characteristic size spectra, diurnal profiles
show
EC, OC, Nitrate from traffic emissions heavily influence
PM2.5 in cool, moist, low-mixing height periods
i.e., Fall, Winter, Night time

LA: Size Distributions for motor vehicle traffic

3 narrow modes in ultrafine size range

30 m downwind - trimodal

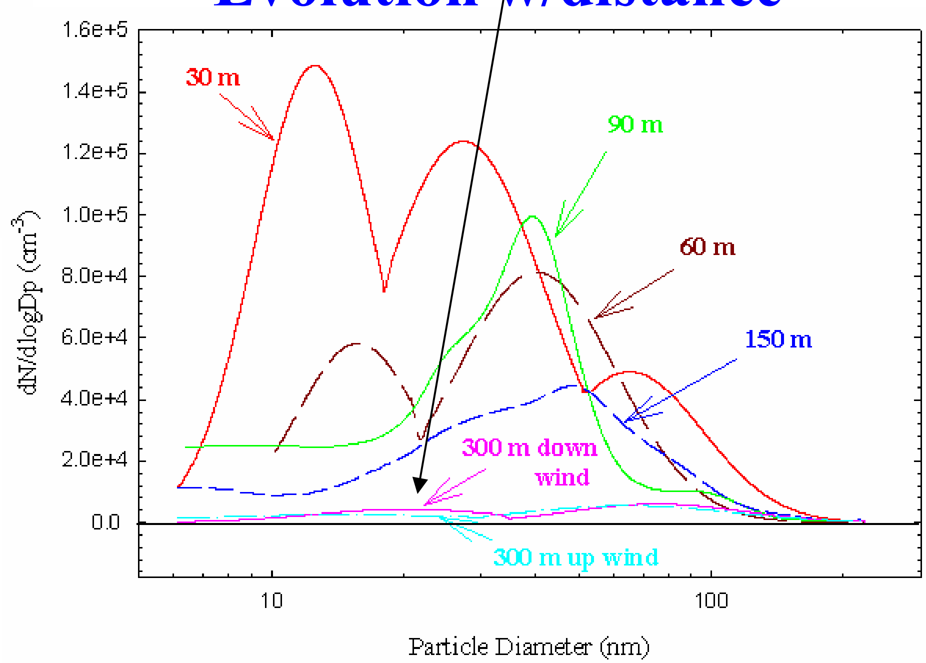


Size distribution indistinguishable from upwind at 300 m downwind

Fresh automobile aerosol Peaks

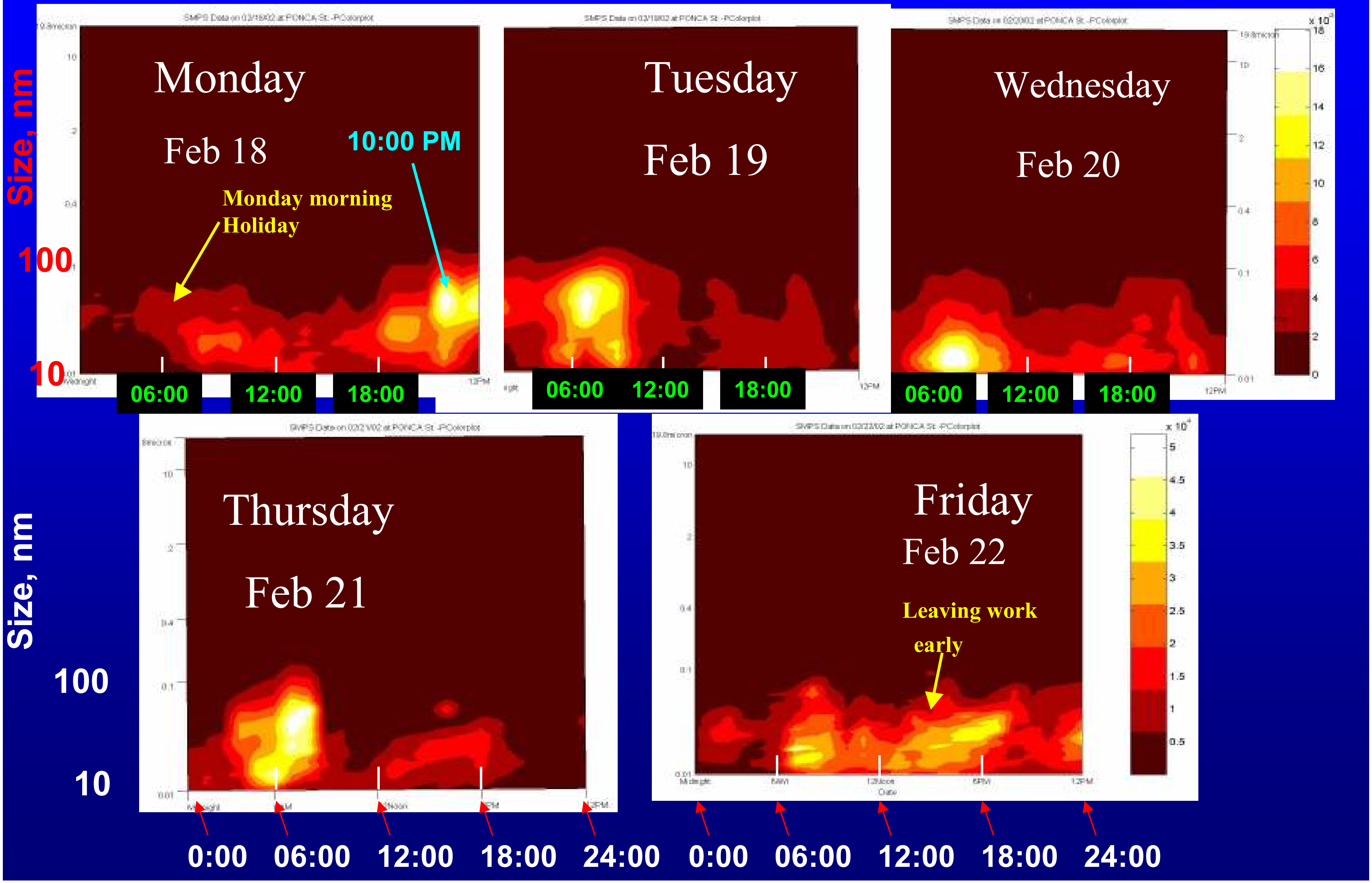
Modal diameter changes with distance due to evaporation/condensation of volatiles

Evolution w/distance



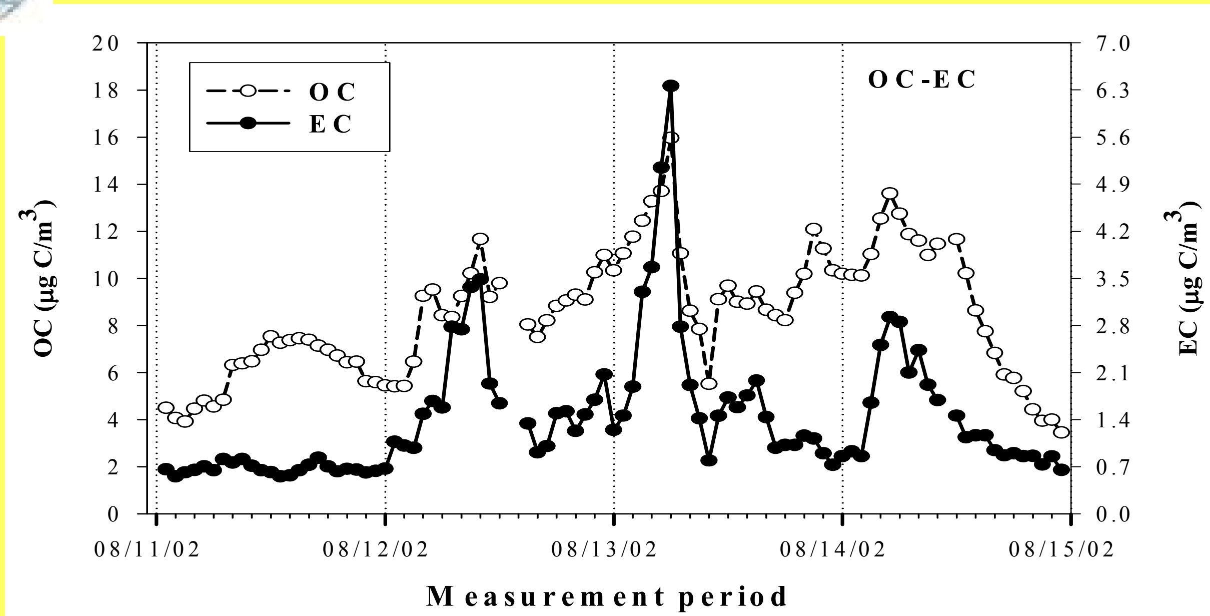
Source: LA Supersite/PM center, Sioutas

Baltimore: Ultrafine particles indicate traffic in AM
Any day, most any wind direction!
Less pronounced in afternoon, longer rush hour, greater mixing height and wind speeds

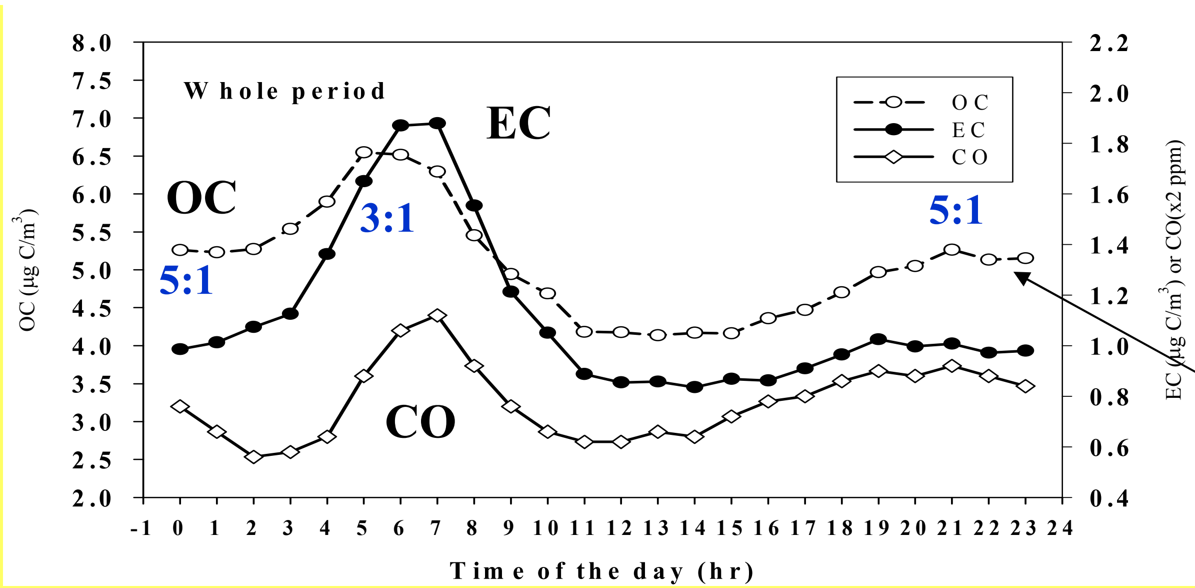


Baltimore Ponca St: EC – Strong Diurnal Cycles

Peaks correspond to morning Traffic



Even in August



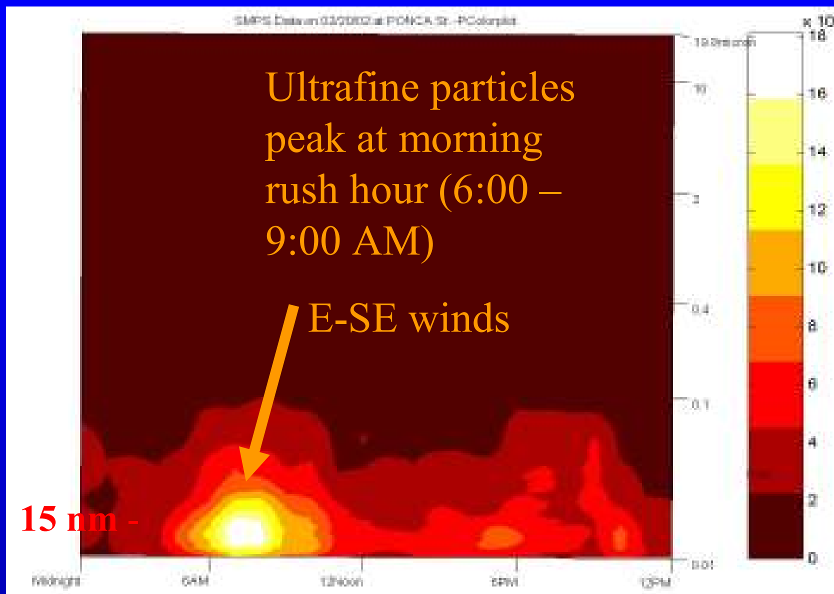
Average daily profile
(9.5 months)

OC:EC ratio increases evenings & early AM

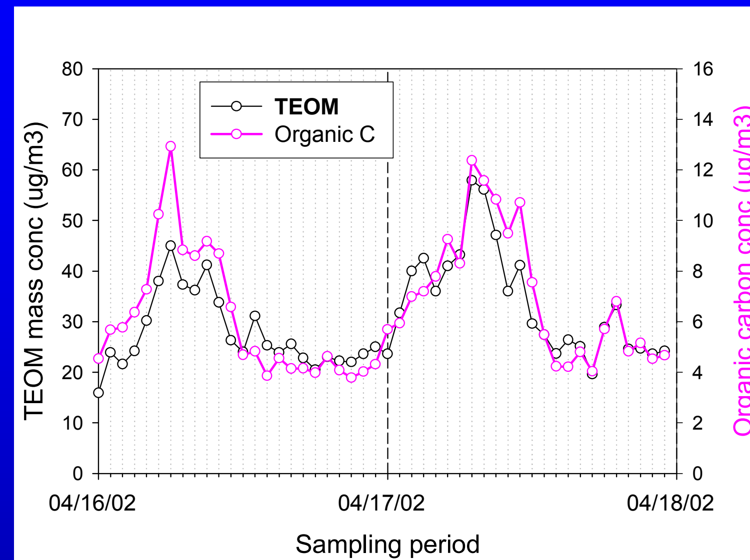
Night-time chemistry?

Baltimore Air is Heavily influenced by Traffic

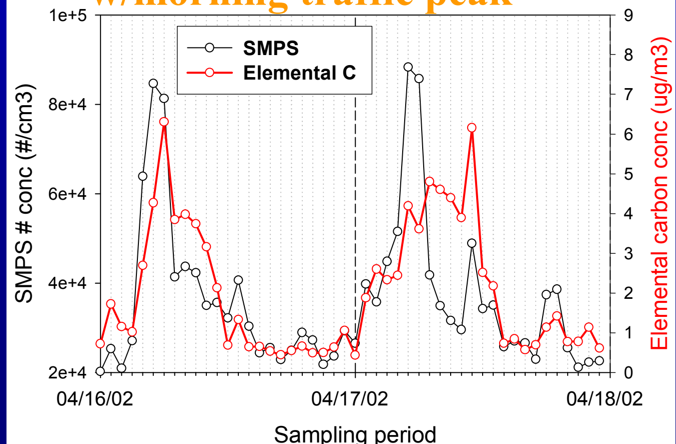
(Especially in Fall/Winter/Spring months)



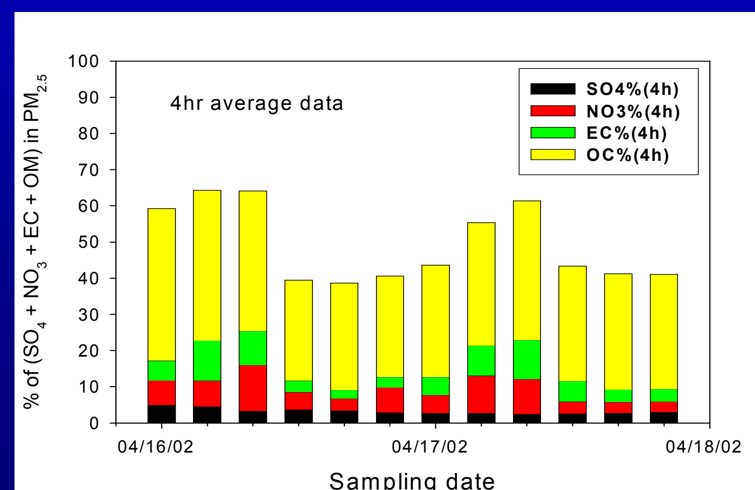
OC highly correlated w/TEOM



OC & EC highly correlated w/morning traffic peak



OC a substantial fraction of PM2.5



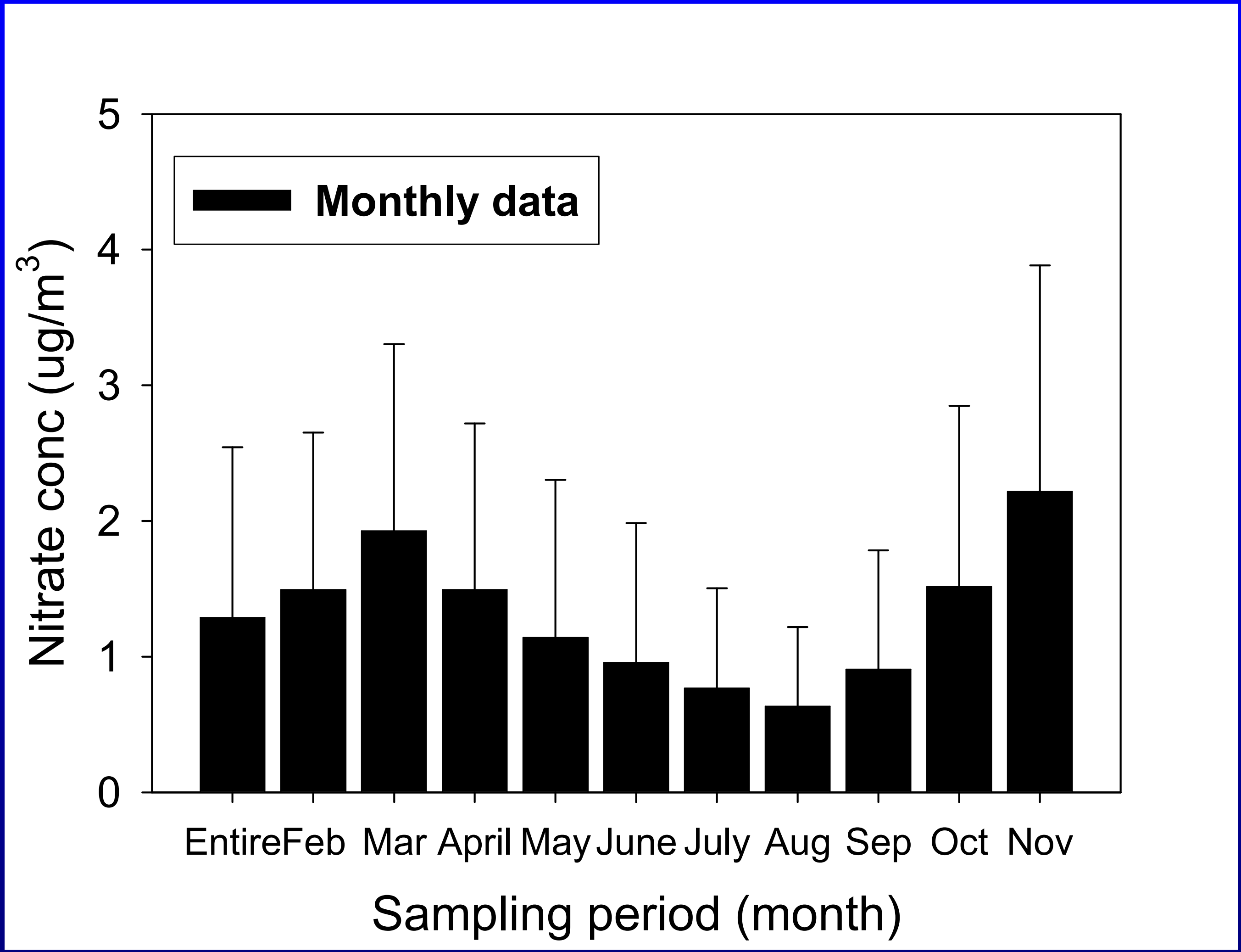
Nitrate is more complicated

NOx converted to nitrate 10x faster than SO_2 to sulfate, therefore local sources much more important for nitrate

NH_4NO_3 dissociation equilibrium favors nitrate at low T, high RH

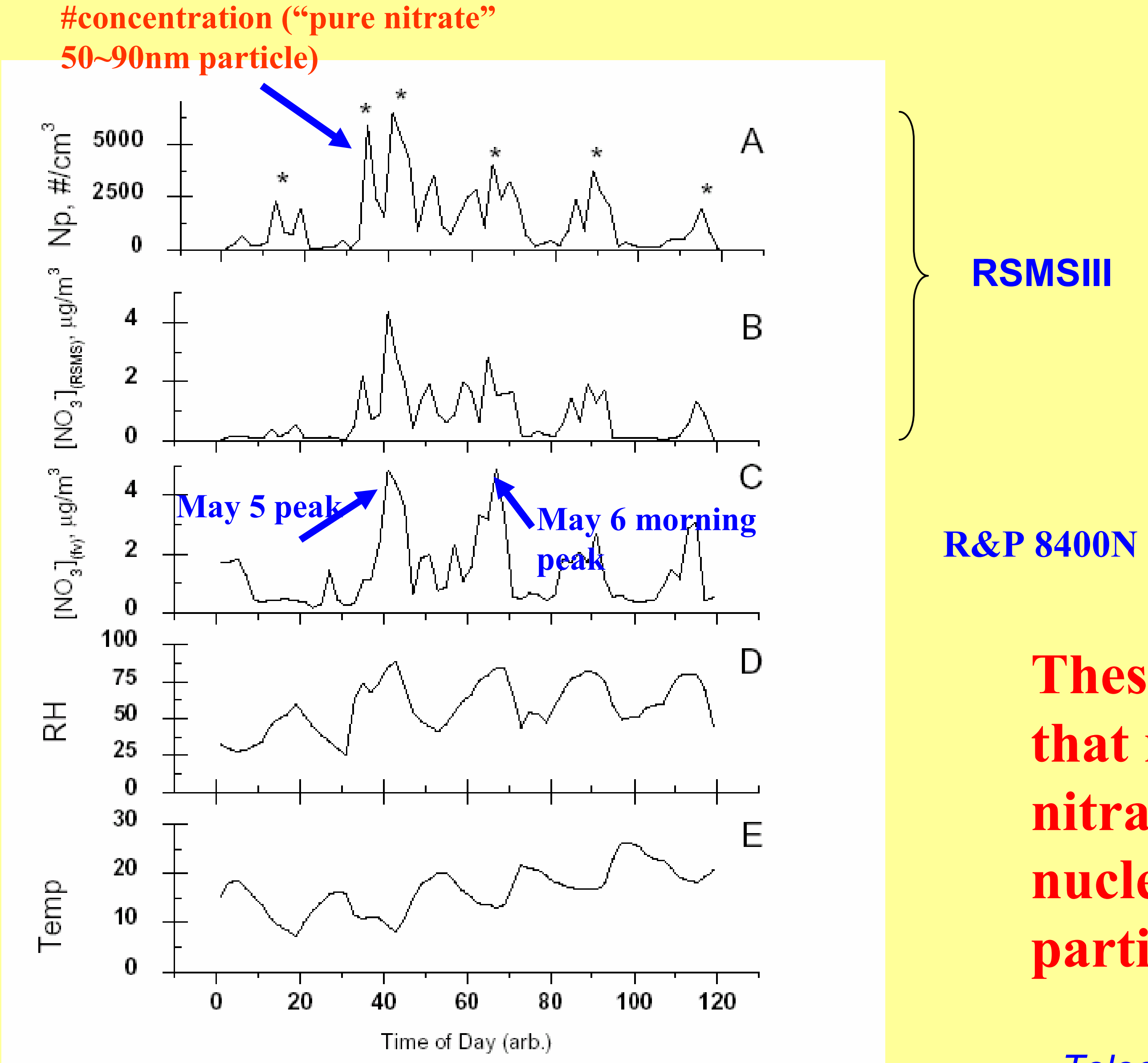
Night time radical chemistry forms nitric acid from NO_2 when temperatures are typically cooler and RH higher

Monthly trend of Nitrate concentration at Ponca



Lower concentrations in summer when ammonium nitrate more volatile

“Pure” Nitrate particles correlate with PM2.5 Nitrate peaks: occur at high RH, low temperatures



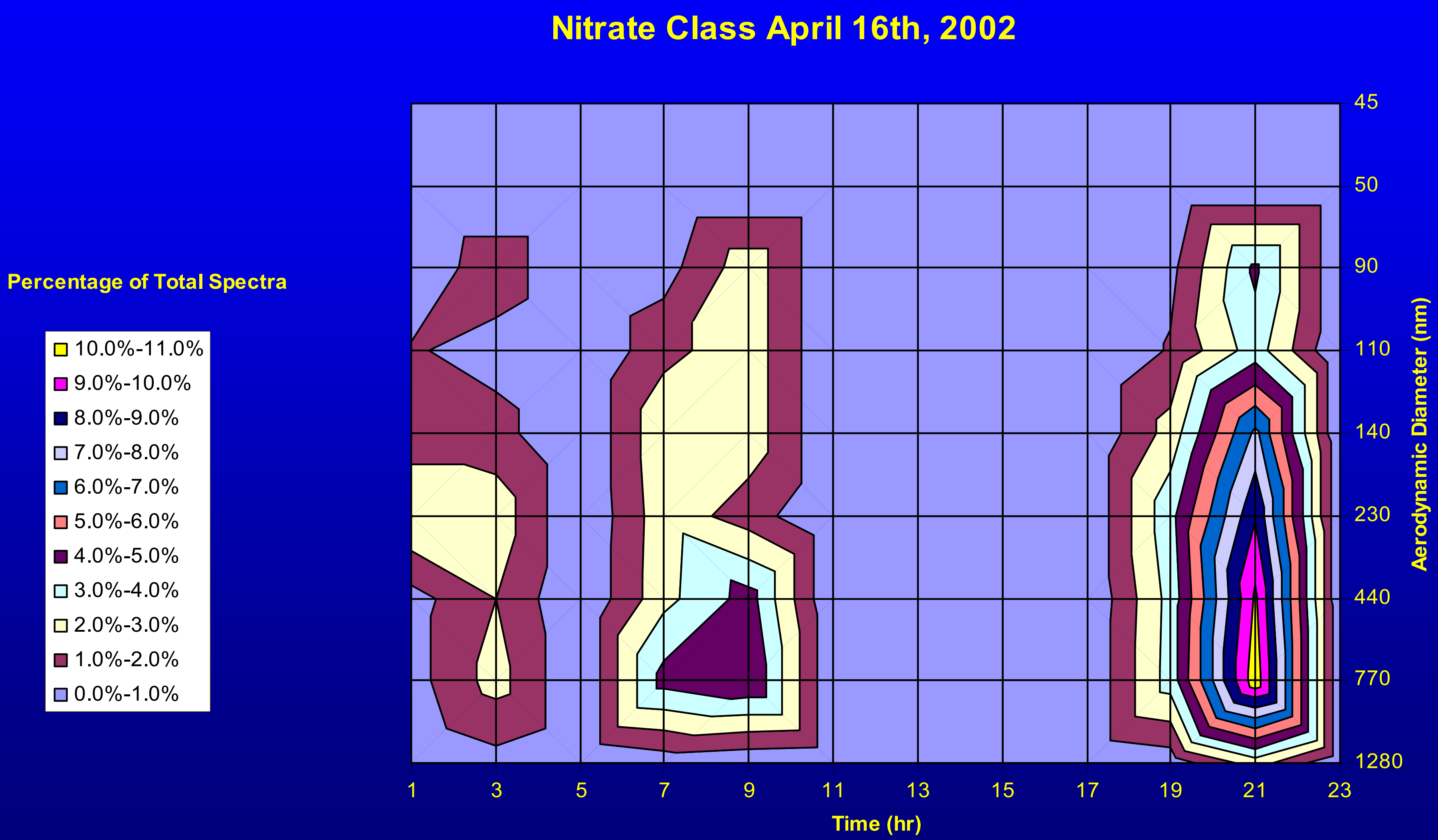
May 3-8, 2002

These data suggest that much of the nitrate is formed by nucleation of new particles!

Tolocka et al., Submitted

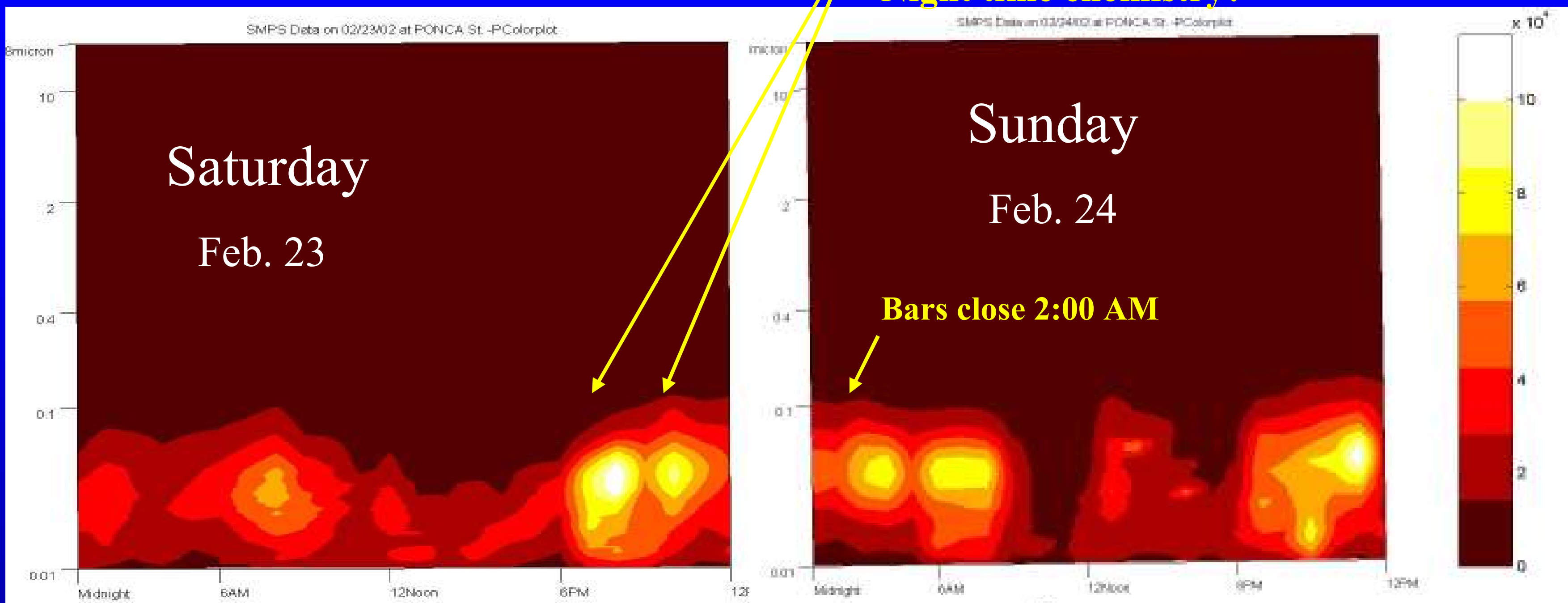
But other times – much forms on "droplet" mode

Fraction of Particles in Nitrate Class vs. Size / Time of Day



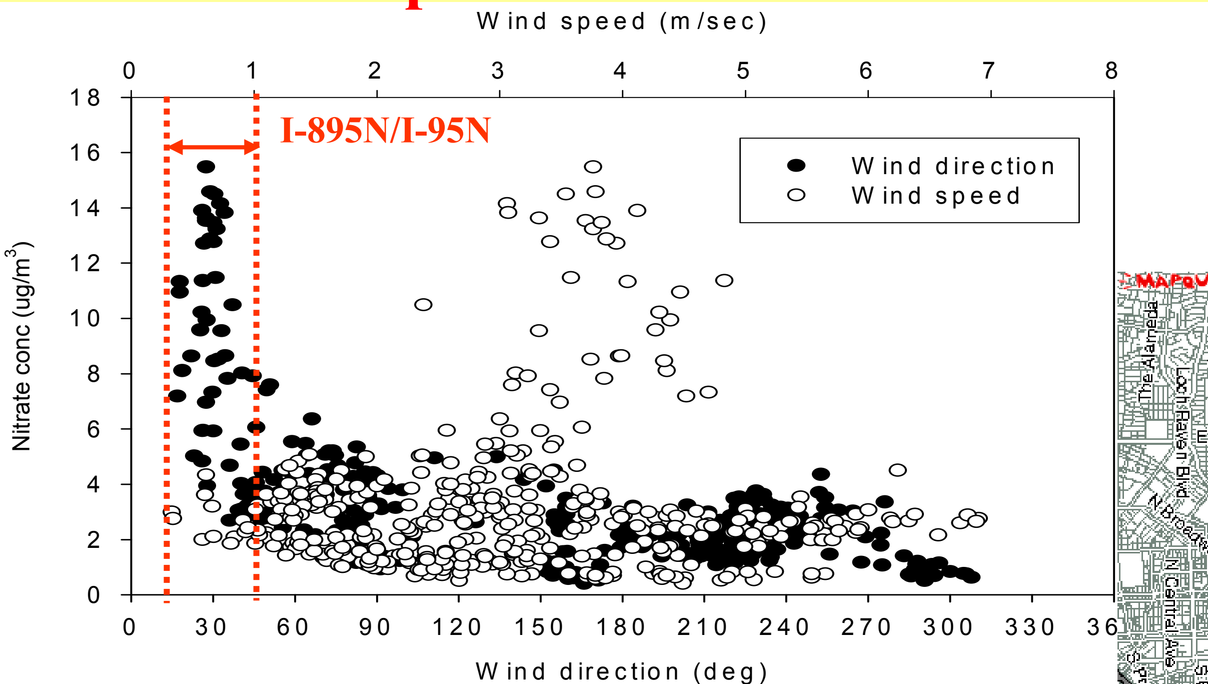
Weekend patterns

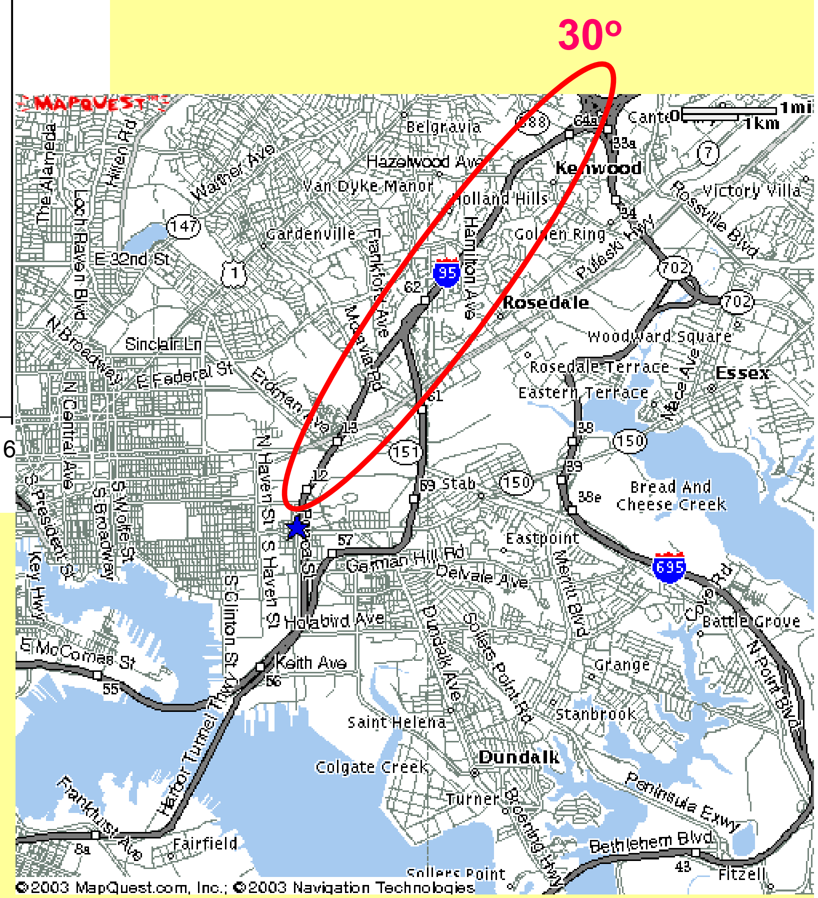
Saturday night entertainment traffic or Night time chemistry?



Locally Produced Nitrate concentrations frequently observed at 30° and at wind speeds 0 to 1 m/s

Example: March 23 – 25 data





Park et al., Atmos. Environ. 39:2011, 2005:

32% of Nitrate transients were > 1 μg/m³

64% w high/NOx between 5 – 8 AM

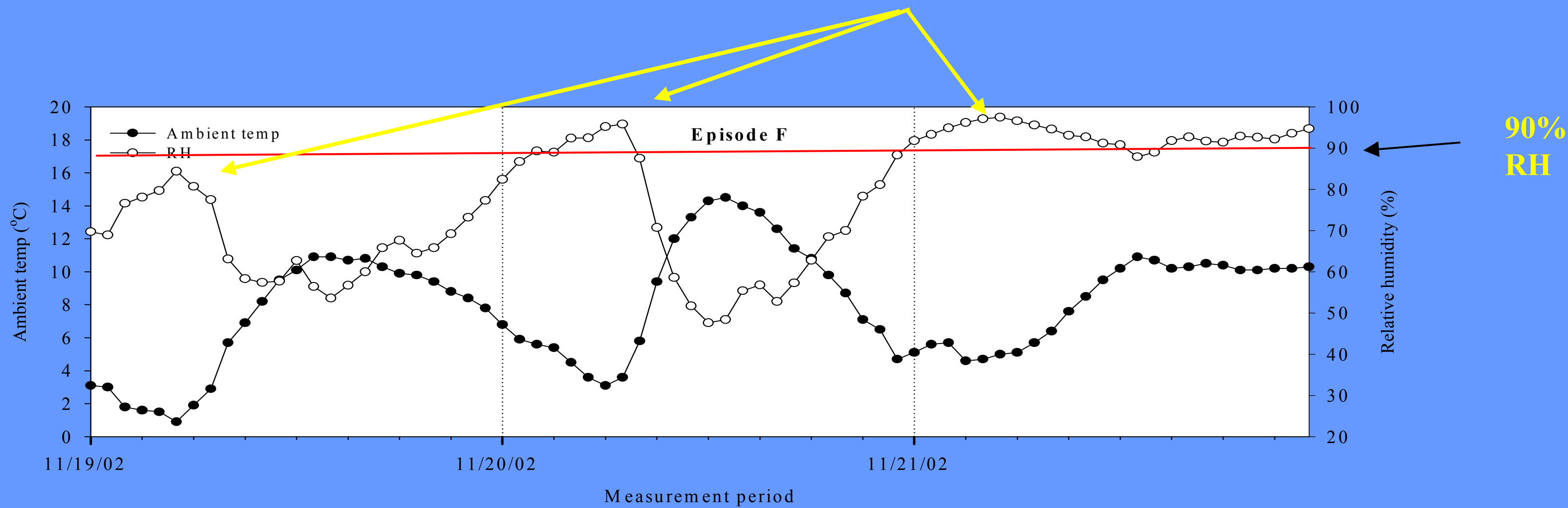
26% between 10 PM – 2 AM

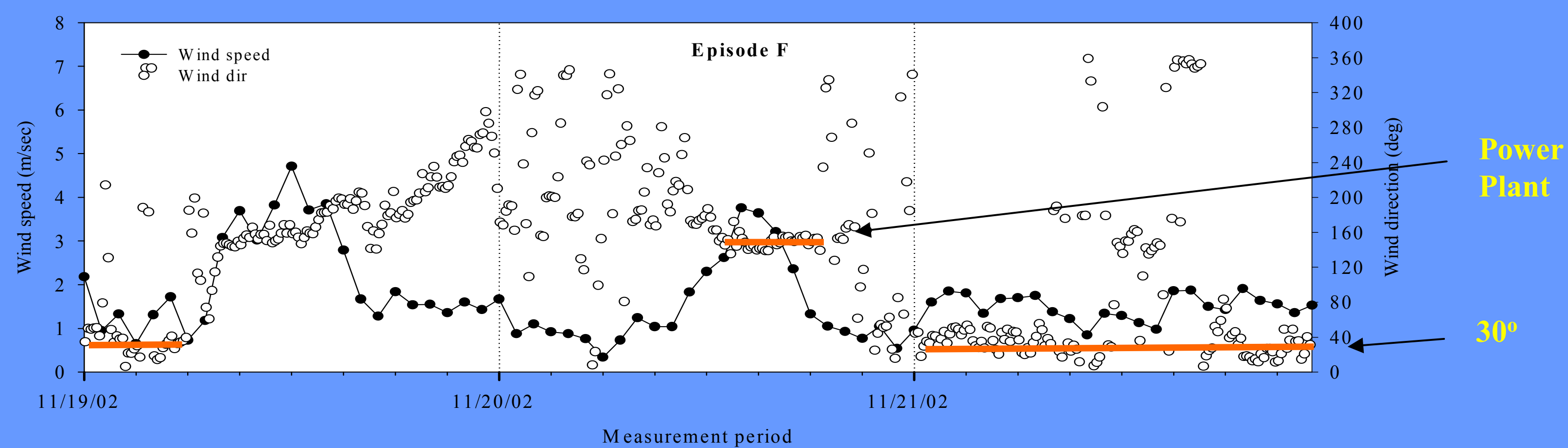
Episode F: November 20, 21

Cool Temperatures, Morning RH >90%

Winds light, variable on 20th,

Winds light, 30º, very high RH, on 21st





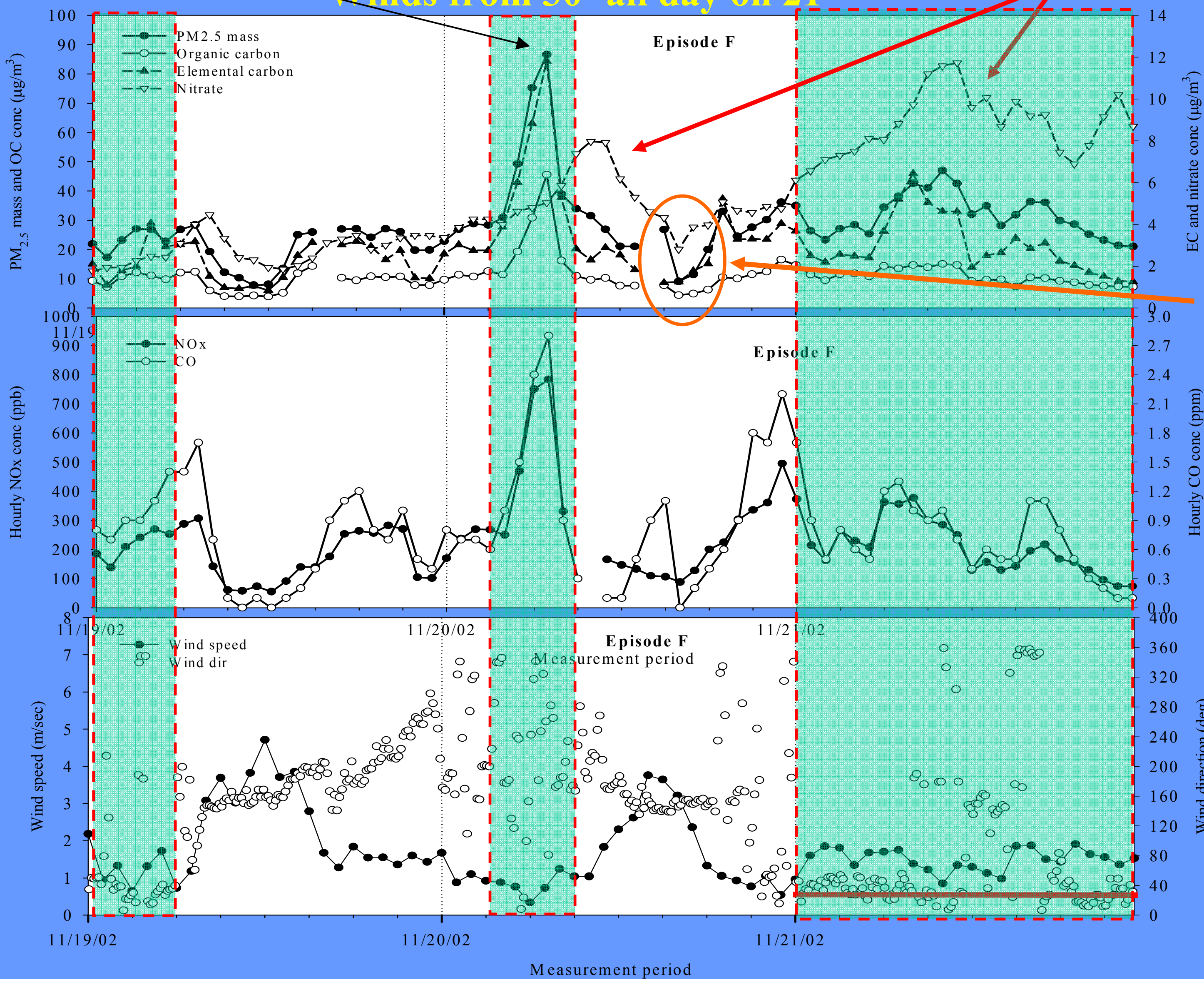
Episode F: November 20, 21

Cool Temperatures, Stagnation, High RH, morning traffic peak; Nitrate deposits on wet particles; Winds from 30° all day on 21st

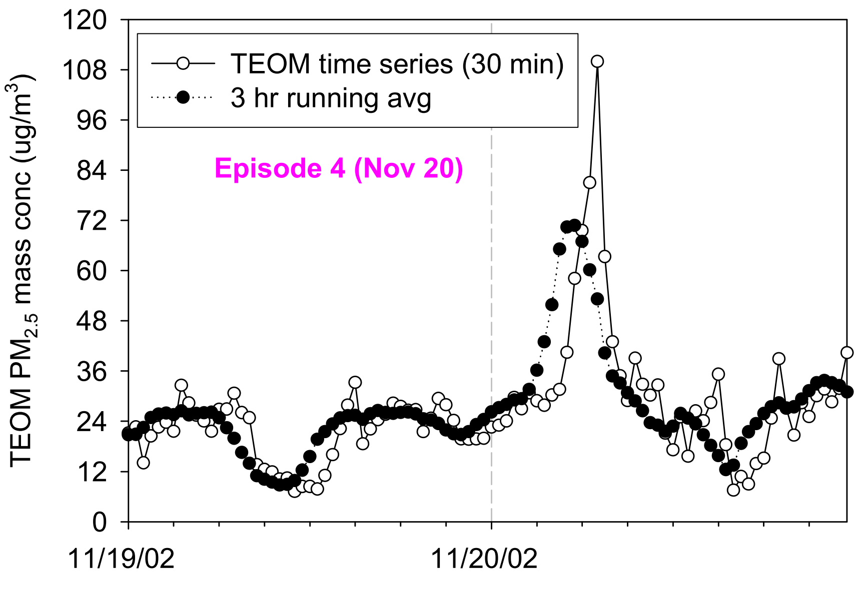
Highest PM2.5 max

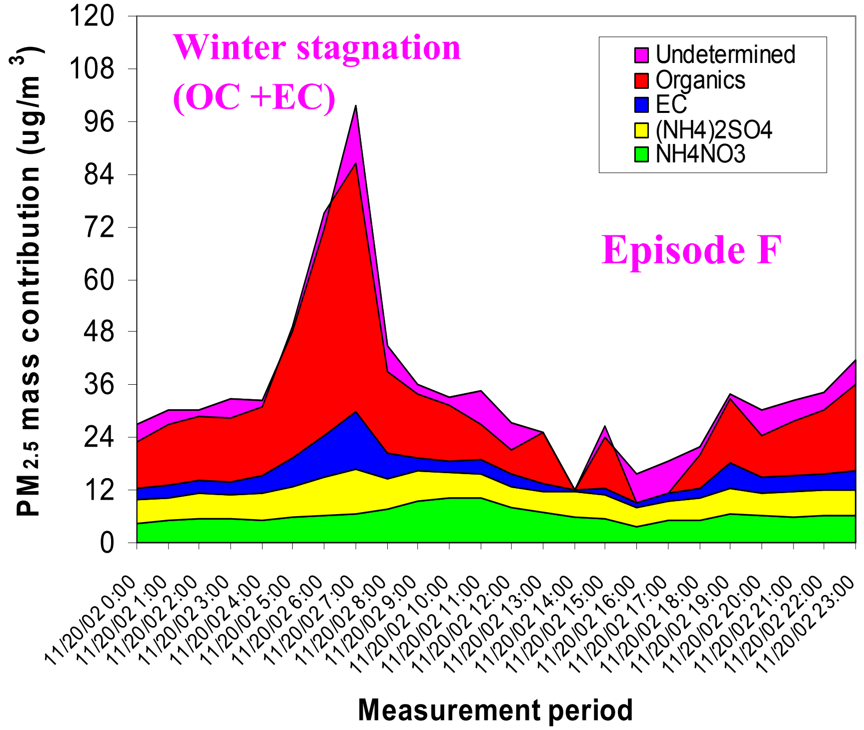
Nitrate (lags NOx)

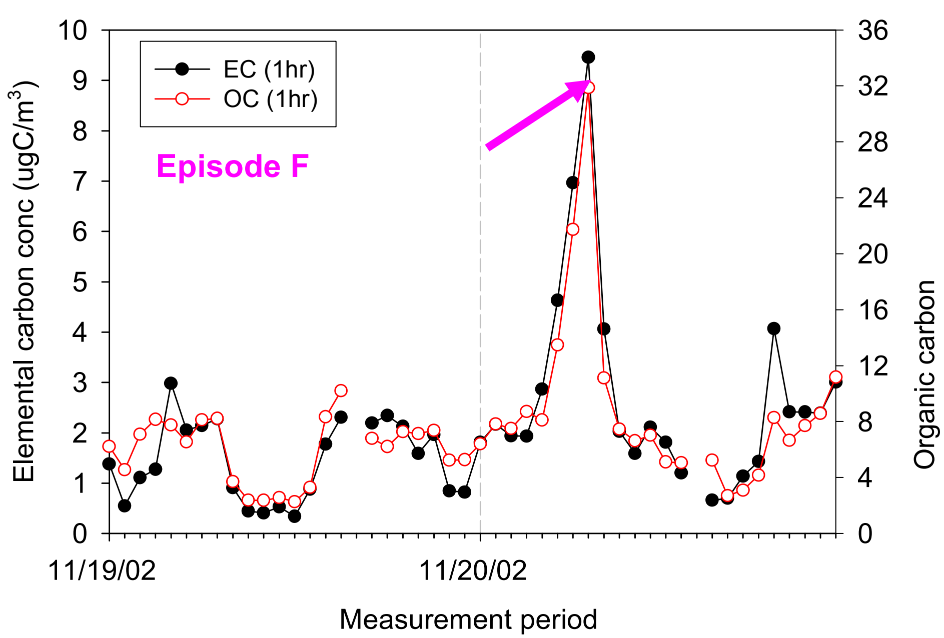
No obvious power plant influence; mixing hgt too low



Episode F : well correlated EC, OC, PM2.5 (Local traffic): Max conc







TEOM ($\mu g/m^3$) = 7.39 EC ($\mu g/m^3$) + 13.92 $R^2=0.85$

TEOM ($\mu g/m^3$) = 2.57 OC ($\mu g/m^3$) + 10.53 $R^2=0.88$

Summary

- 24-hr PM2.5 standard rarely exceeded during 2002 at Ponca st. – Episode A, max 24-hr PM2.5 was ~65 ug/m^3
- 9.5-month 30-min average barely exceeded annual PM2.5 standard.
- Episodes occur during periods of stability/stagnation
  Summer episodes caused by stationary fronts; end by break by passage of cold fronts
- Local sources – traffic; So. Baltimore industry; and local regional sources contribute substantially, to EC, OC, Nitrate, especially in fall, winter, spring
- Major summer haze events; dominated by sulfate & OC – worst event after air stagnant over Ohio Valley arrived in Baltimore w/local wind direction from So. Baltimore; but Local So. Baltimore sources contributed ≥5% of PM2.5 – enough to trip standard
- Urban traffic corridor creates PM “hot spots.”