Discrete Measurements of $PM_{2.5}$ Mass and Composition in the Southeastern U.S.: Regional and Seasonal Trends between 1999 and Today

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Acknowledgement: J.L. Waynick, TN-DEC, K.J. Olszyna, TVA

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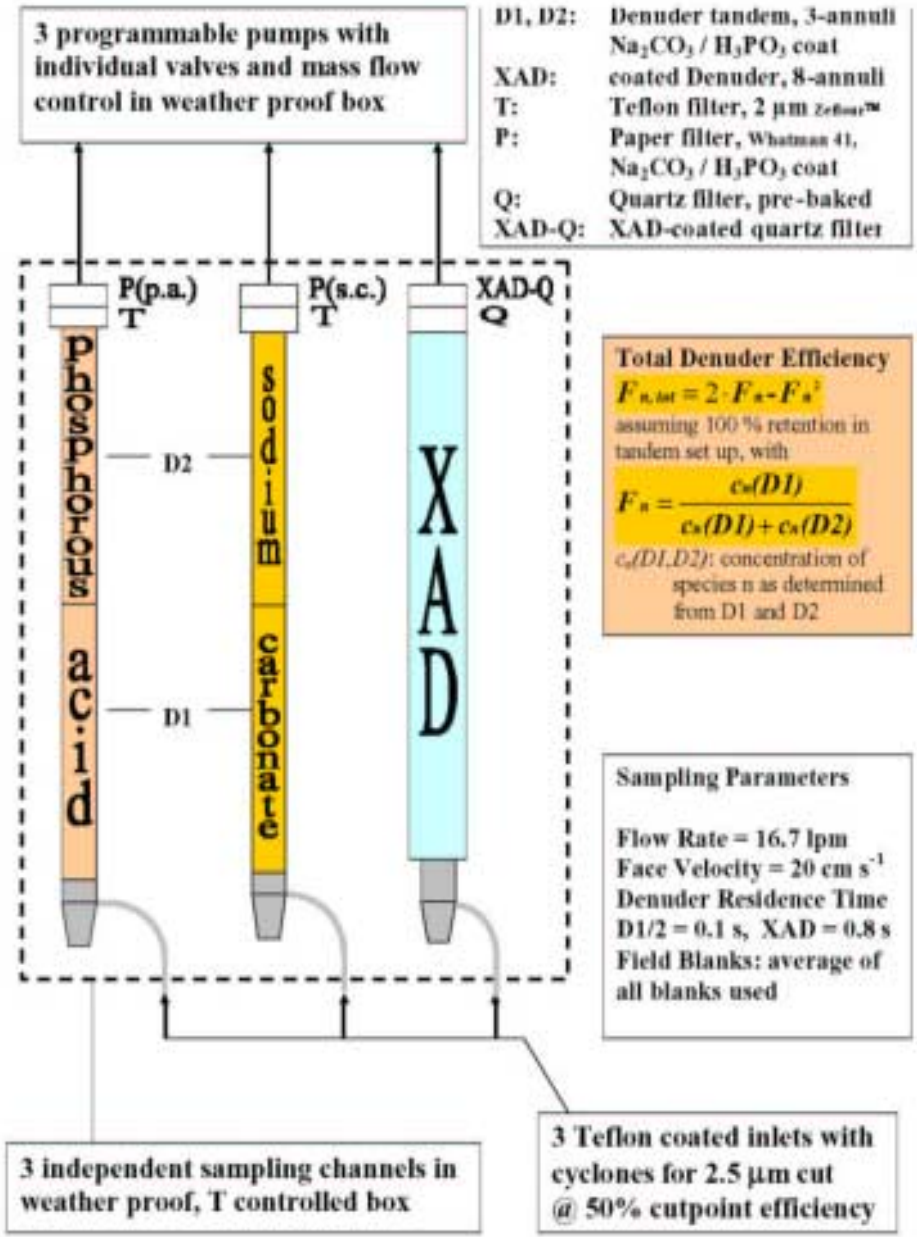
Funding provided by U.S.-EPA and GA-EPD

- **Instruments, Data Quality, Sites**
- **$PM_{2.5}$ - O_3 – Reactive Gases Relationships**
- **Estimating Organic Mass**

Particle Composition Monitor "PCM"



For each PCM sample 17 (!) components (incl. 5 field blanks) are being analyzed via IC & TOT.

The following species are being quantified and reported.

Channel 1:

NH_3

Na^+, K^+, NH_4^+, Ca^{+2}

Channel 2:

HF, HCl, HONO, HNO_3, SO_2,

HCOOH, CH_3COOH, $(COOH)_2$

F^-, Cl^-, NO_3^-, $SO_4^=$,

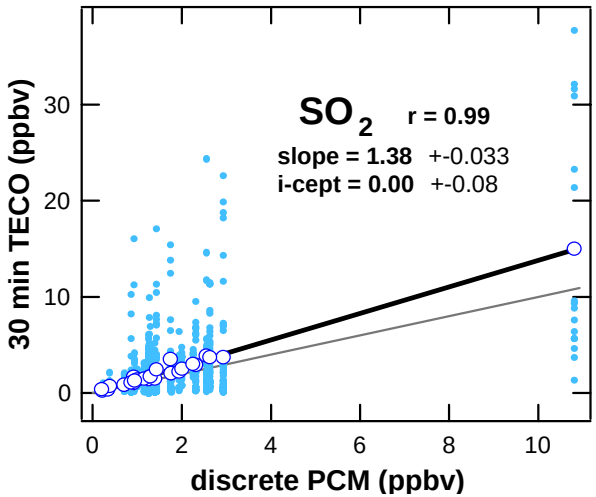
$HCOO^-$, CH_3COO^-, $C_2O_4^=$

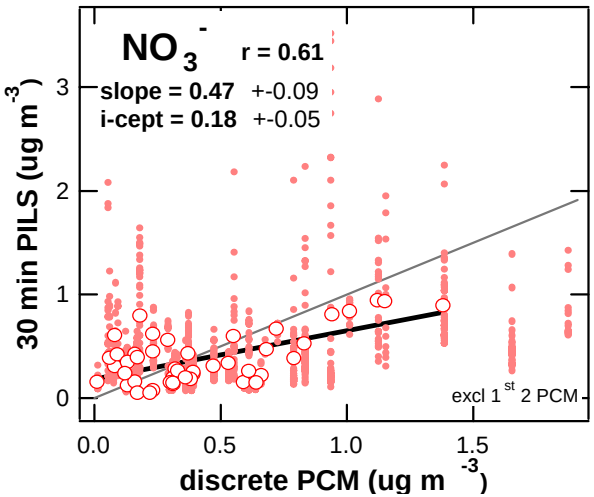
Channel 3:

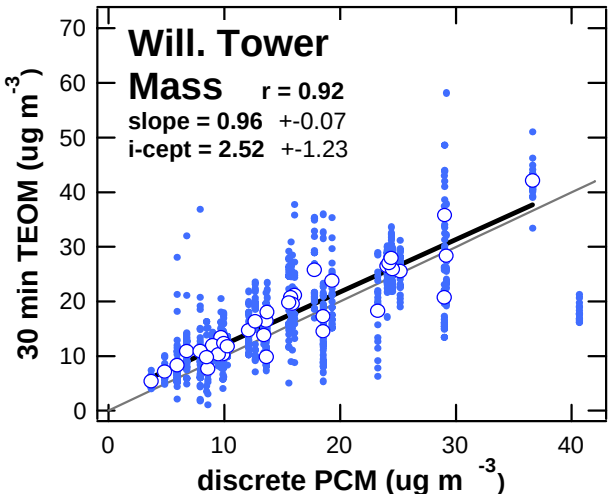
EC, OC, "SVOC"

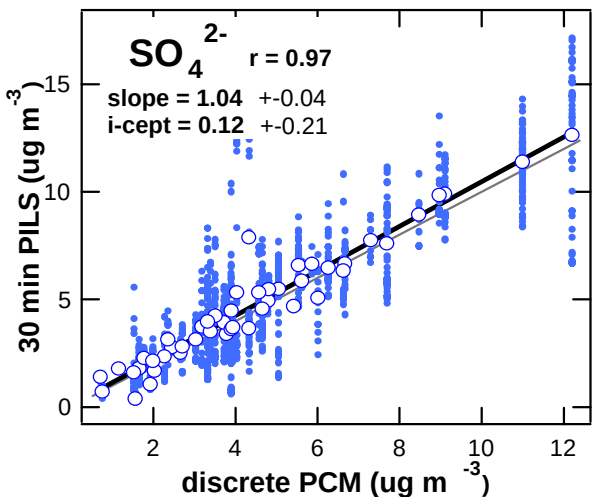
Special tests and procedures for eliminating positive water bias, OC artifacts and other details described in paper accepted to JGR "Atlanta Supersite" special section, coming out soon…

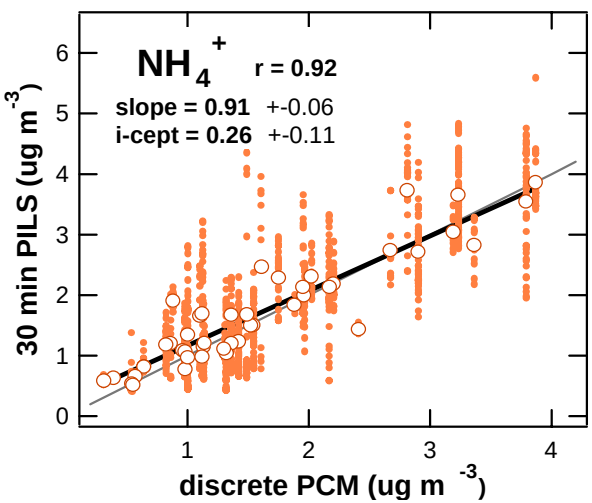
Assessing Accuracy of PCM Measurements

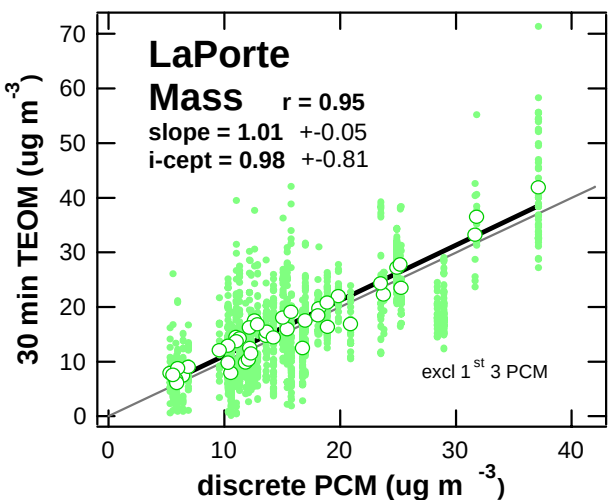






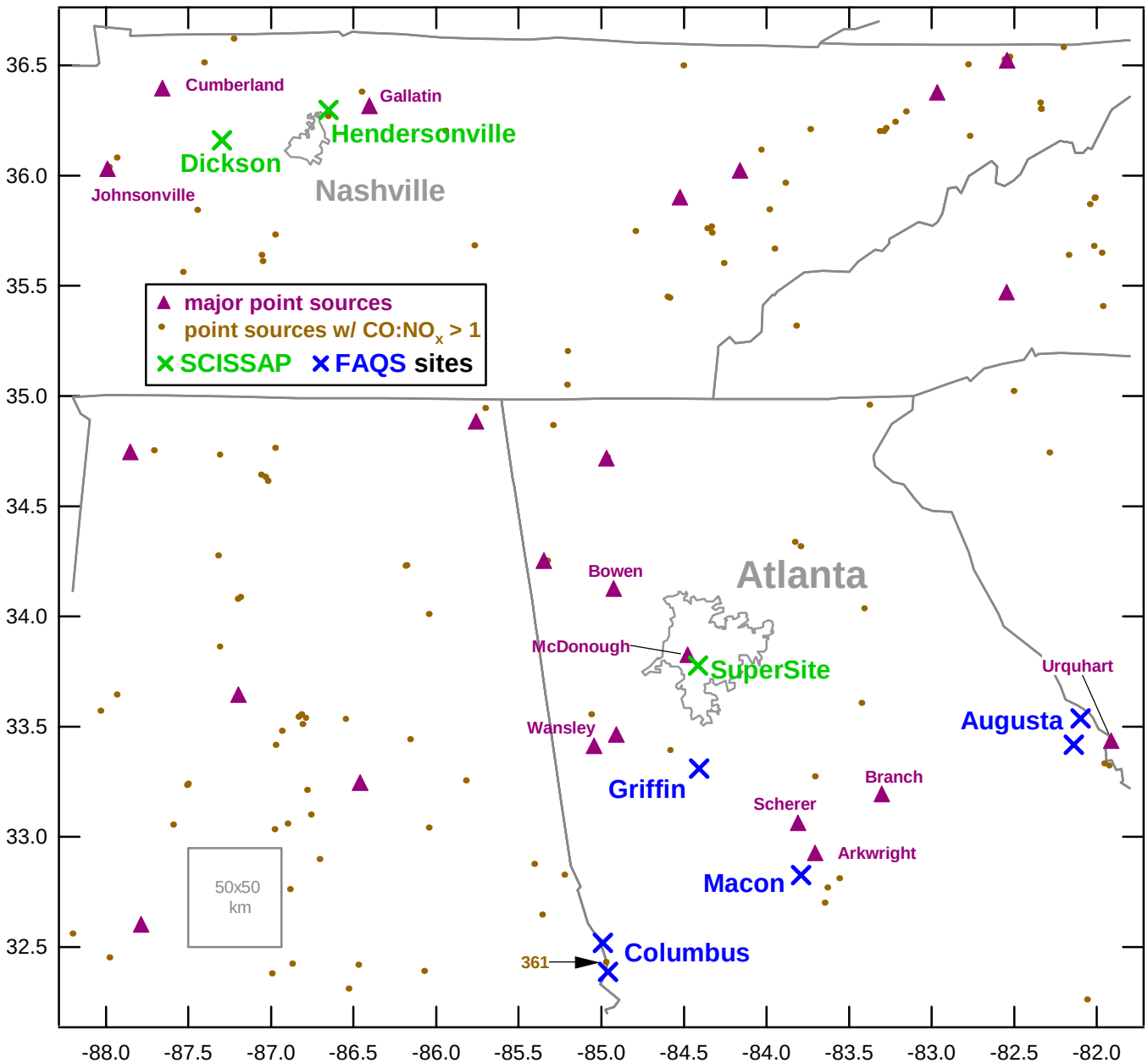






S-compounds and mass agree well, volatile species esp. NO_3^- more difficult to measure accurately

Measurement Sites



Southern Center for the Integrated Study of Secondary Air Pollutants (US EPA)

Fall-line Air Quality Study (GA-EPD)

Special Setup at Hendersonville

Set up to capture the Nashville urban plume.

Utilizing an instrumented 48 m tower during SOS'99, 16 June - 22 July 1999.

Measurements between 42 and 4 m agl :

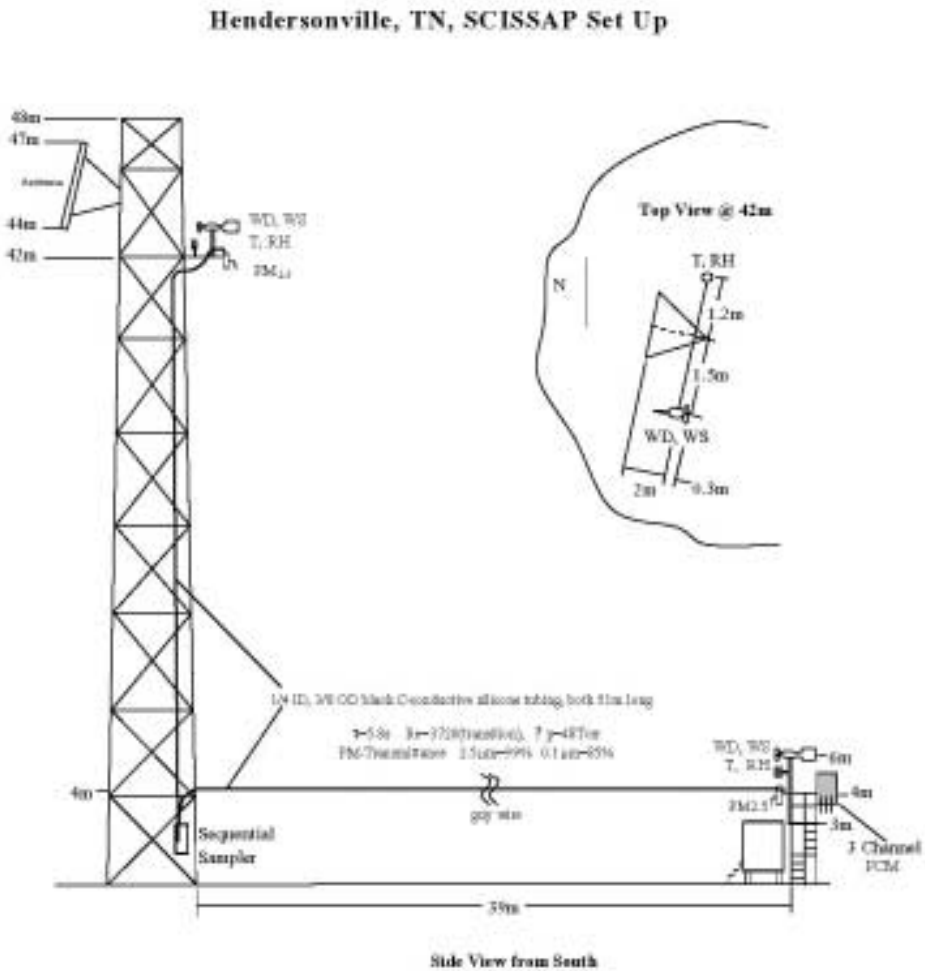
Positive vertical gradients for

60-70 % of all daytime, and

70-80 % of all nighttime samples of

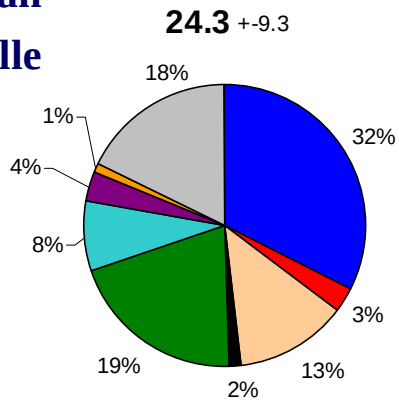
$PM_{2.5}$ mass, $SO_4^{=}$, NO_3^{-}, and NH_4^{+}!!

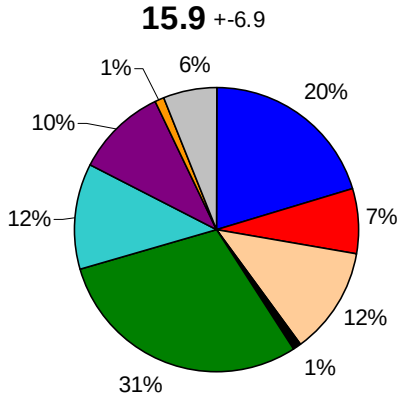
Direct emissions and/or secondary formation of fine PM aloft

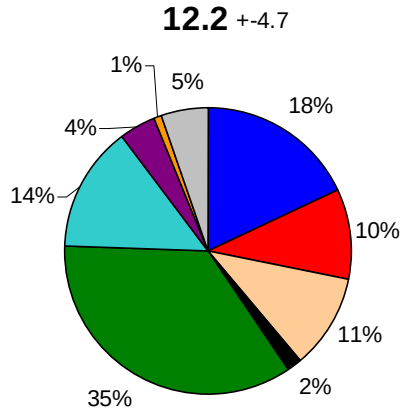


Seasonal Comparison of $PM_{2.5}$ Composition: Suburban vs Rural

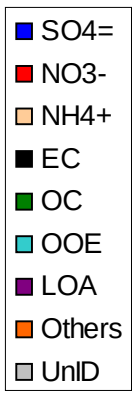
Suburban Hendersonville

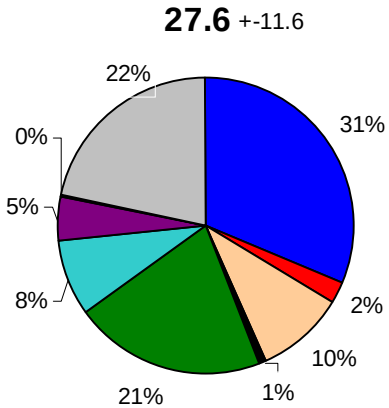


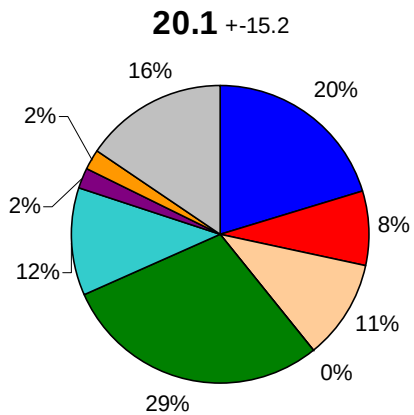


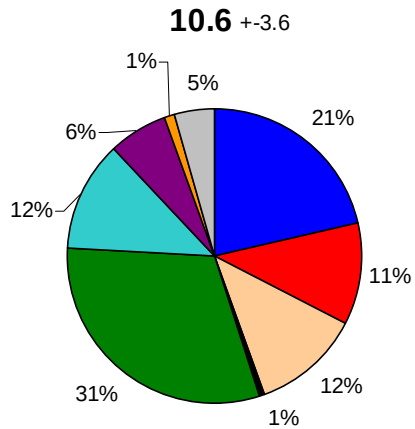


Rural Dixon





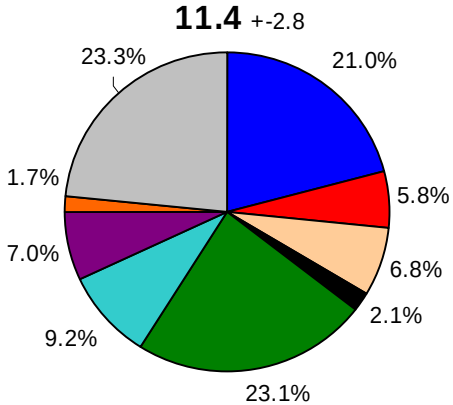




Summer-99 **Fall-99** **Winter-99/00**

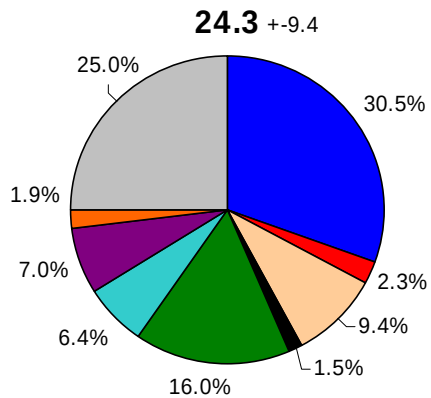
- **Differences in composition are insignificant regionally but not seasonally**
- **Differences in mass related to different BL dynamics**

Regional Comparison of Average $PM_{2.5}$ Composition in 2000



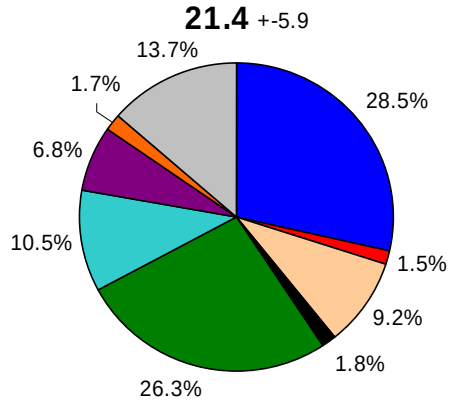
Macon, GA

Late June



Augusta, GA

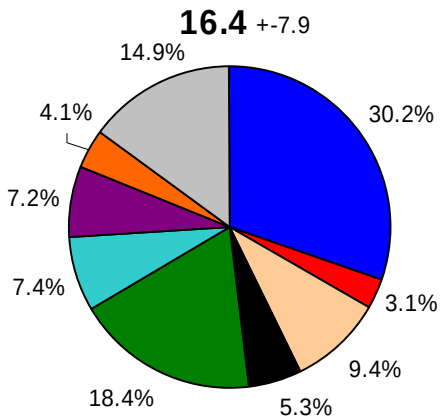
Early July



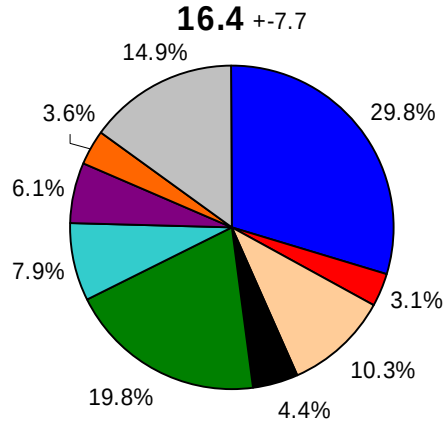
Columbus, GA

Late July

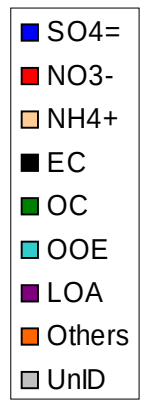
Sequential measurements at GA sites captured different episodes, e.g. July 4th weekend at Augusta!



Williams Tower

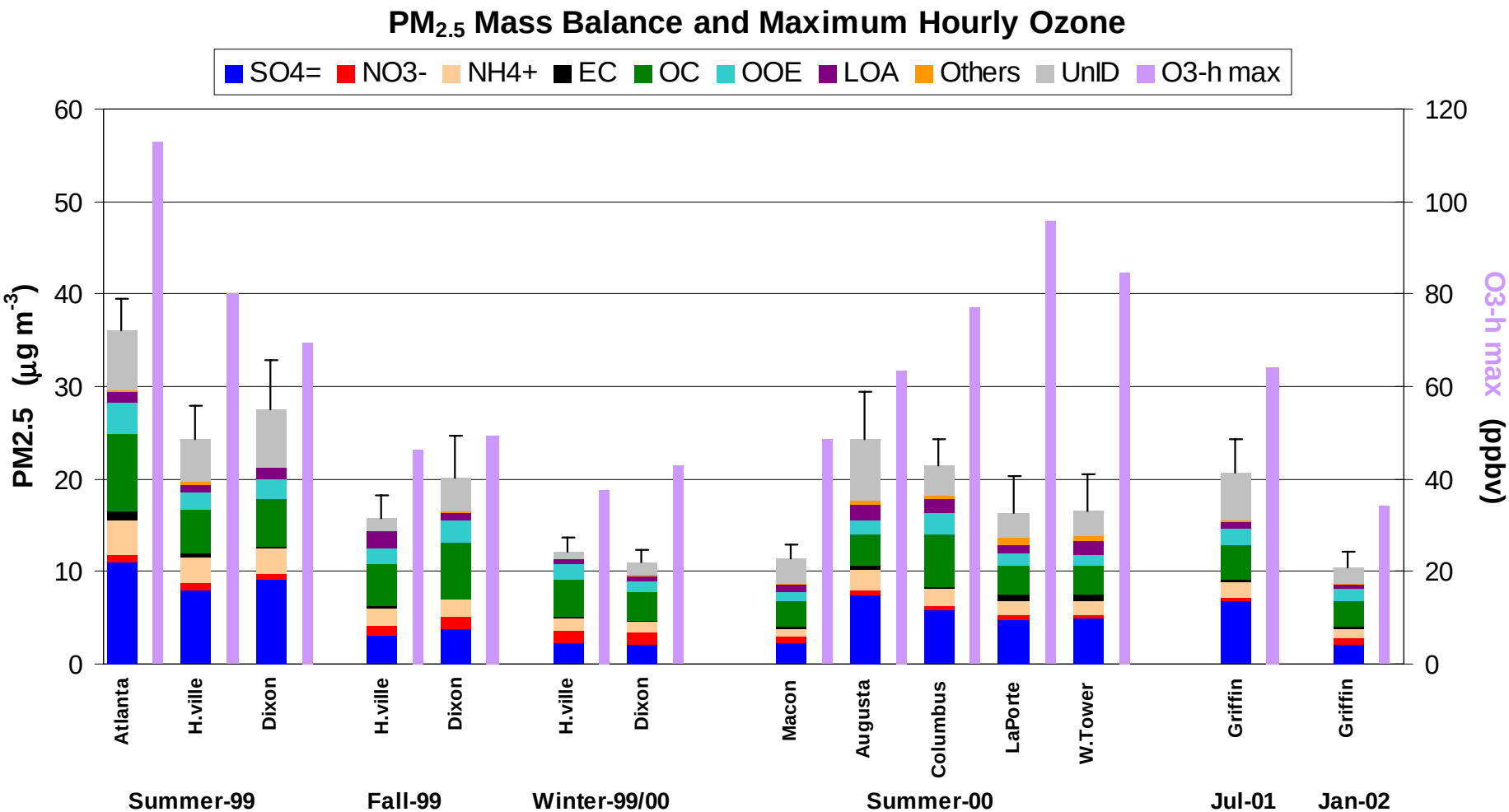


LaPorte



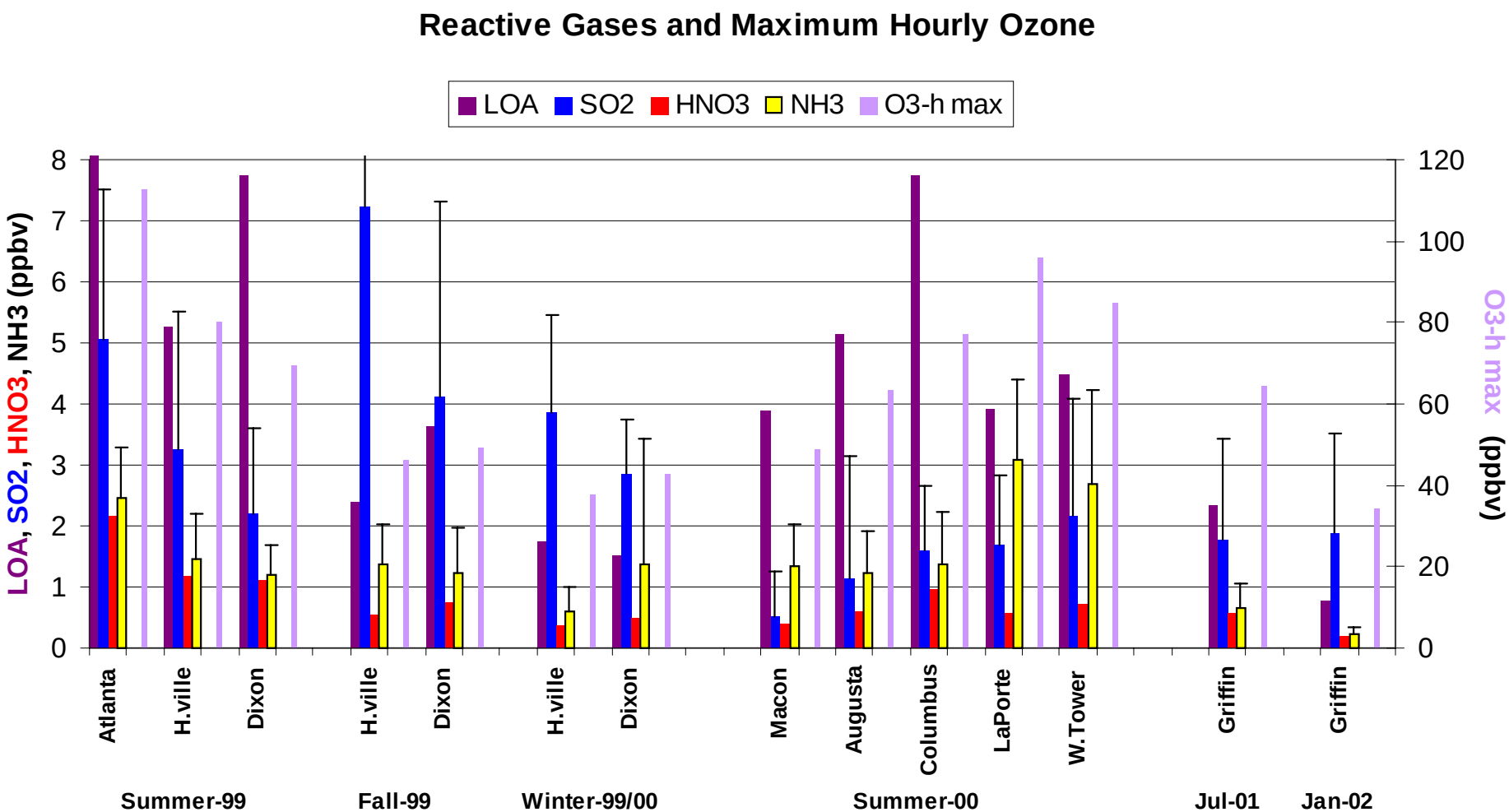
Both Houston, TexAQS sites from mid August to mid September

Comparison of Seasonal and Regional Averages: $PM_{2.5}$ & O_3



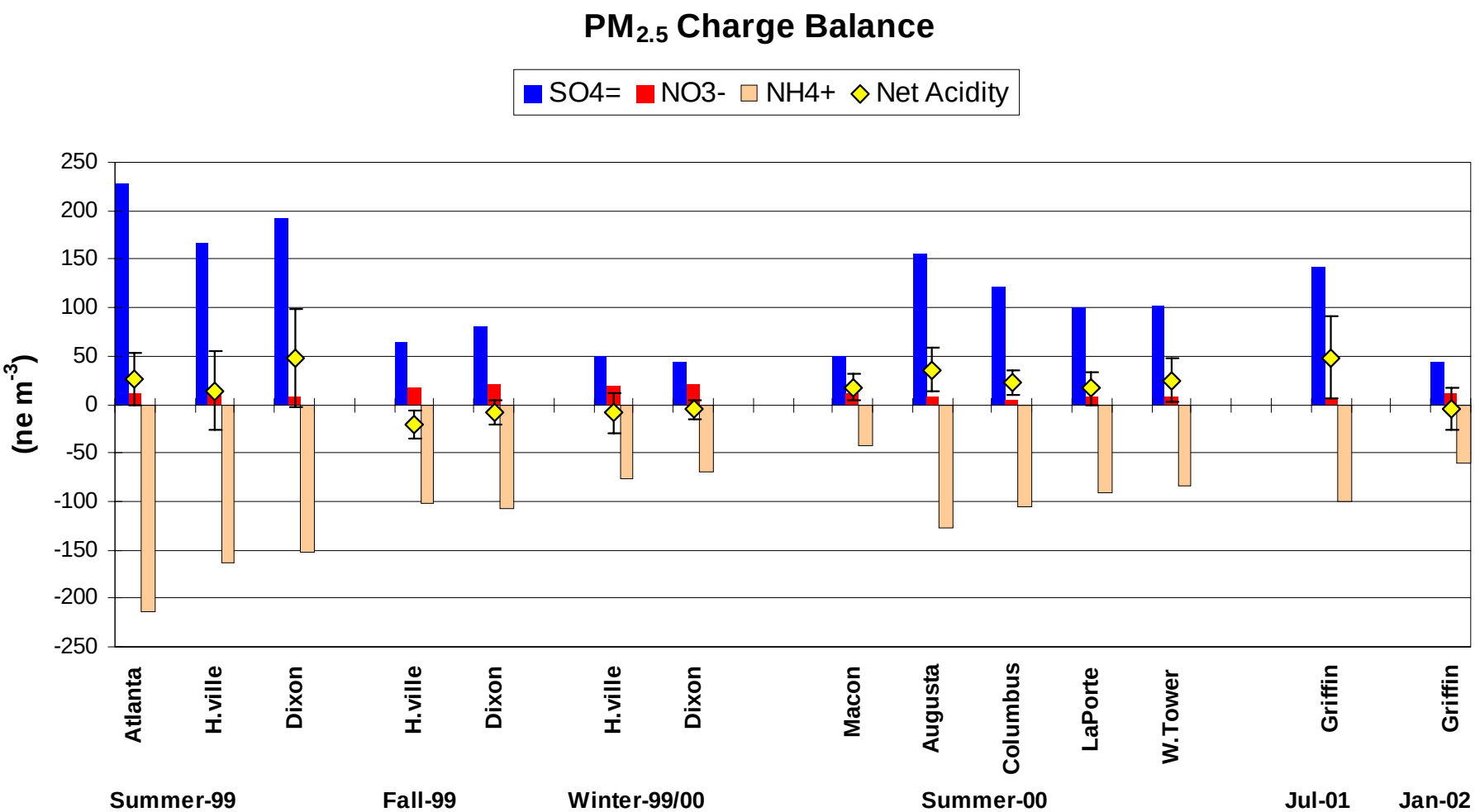
- Seasonal [$PM_{2.5}$]-mass /-$SO_4^=$ / [O_3] correlation: high in summer, low in fall & winter
- Houston TexAQS measurements governed by local emissions, episodes and meteorology
- BL dynamics possibly causing sub-regional differences between H.ville & Dixon
- Unidentified [$PM_{2.5}$] mass highest and most variable in summer (and fall)

Comparison of Seasonal and Regional Averages: Reactive Gases



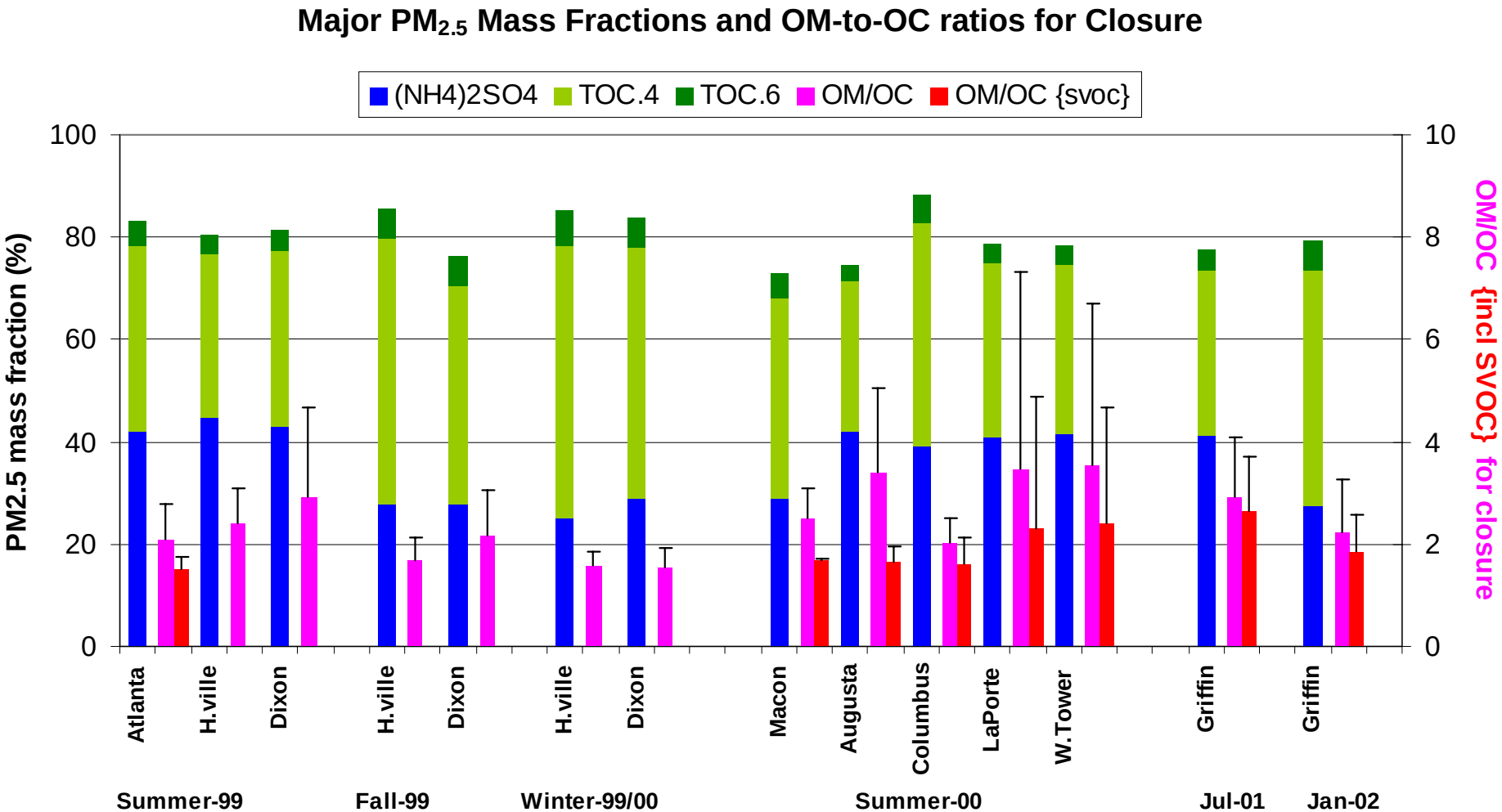
- Strong seasonal trend of acidic gases (LOA, HNO_3) pointing to photochemical sources
- Neutralizing NH_3 less variable seasonally but regionally: highest in metro areas
- High abundance of precursor gases combined correlates with high [$PM_{2.5}$]

Seasonal/Regional Aerosol Acidity Based on [$SO_4^{=}/NO_3^{-}/NH_4^{+}$]



- Aerosol is closely neutralized / slightly alkaline in fall & winter but more acidic in summer
- Acidity caused by $(NH_4)HSO_4$, or unaccounted for organic amines (with higher OM/OC)?

Estimating Organic Mass (OM) Using Mass Closure



- OM/OC highly variable within sites/periods; average 1.4 too low!
- Factors need to be higher in summer: more oxygenated species
- Factors seem to increase from urban, suburban, to rural sites (aging?)
- Incl. SVOC from XAD-backup filter leads to range: 1.5 (Atlanta) to 2.7 (Griffin)

Summary

- **Positive vertical gradients of $PM_{2.5}$ mass and sulfate point to atmospheric aerosol formation.**
- **Insignificant regional differences in $PM_{2.5}$ composition, but noticeable seasonal differences, esp. %-$SO_4^{=}$, likely due to higher SO_2 emissions and photochemical activity in summer.**
- **Based on $SO_4^{=}/NO_3^{-}/NH_3^{+}$ system, $PM_{2.5}$ in SE-US is slightly alkaline in winter but more acidic in summer ($(NH_4)HSO_4$ only or some species possibly not accounted for?).**
- **OM/OC= 1.4 seems mostly too low but is highly variable reflecting different air masses.**
- **Higher factors necessary in summer due to more oxygenated species from photochemistry.**
- **General trend for higher factors away from urban areas pointing to secondary processes.**
- **Different factors might have to be applied for OC from quartz front and XAD backup filters due to different volatilities (true for Atlanta Supersite 08/99, see JGR paper)**

Outlook

Developing lab techniques for WSOC and ISOC

Speciation of OC via GC-MS: collaboration with Dr. Mei Zheng !!

PCM

Data Quality

Gas Phase

	Site	NH_3	HNO_3	HONO	SO_2	HCl	HCOOH	CH_3COOH	$(COOH)_2$
Retrieved from		D (pa)	D (sc)	D (sc)			D (sc)	D (sc)	D (sc)
D-eff [%]	LP	91±18	90±22	91±8	87±19	97±6	83±10	81±18	78±17
	WT	92±22	85±23	88±9	91±18	96±17	83±11	89±19	73±21
DL [ppbv]	LP	0.49	0.33	0.03	0.07	0.18	0.08	0.21	0.01
	WT	1.40	0.36	0.04	0.20	0.15	0.11	0.28	0.02
Bias [%]	n/a	10	11		6	14	6	12	20
Accuracy [%]	LP				-27 *				

Solid Phase

	Site	NH_4^+	NO_3^-	SO_4^{-2}	EC	OC	SVOC	M_{tot}
Retrieved from		T+P	T+P	T	Q	Q	XAD-Q	T
DL [µg m^{-3}]	LP	0.23	0.09	0.06	0.42	0.80	0.51	1.1
	WT	0.22	0.10	0.05	0.59	0.93	0.51	1.1
BIAS [%]	LP	12	33	13	7	5	25	12
	WT	13	19	3	7	5	25	12
Accuracy [%]	n/a				-9 **	+10 **		+5/+11 ***

	Site	Na^+	K^+	Ca^{2+}	Cl^-	F^-	$HCOO^-$	CH_3COO^-	$C_2O_4H^-$
Retrieved from		T	T	T	T	T	T+P	Q	Q
DL [µg m^{-3}]	LP	0.15	0.10	0.18	0.07	0.02	0.88	1.71	0.18
	WT	0.10	0.07	0.14	0.07	0.02	0.84	0.84	0.16
BIAS [%]	LP	20	35	17			17	11	25
	WT	22	37	26			17	11	27

D (pa): phosphorous acid-coated denuder
D (sc): sodium carbonate-coated denuder
* from linear regression with cont. SO_2 UV absorption measurements
** from NIST standards
*** from linaer regression with TEOM measurements for LP and WT, respectively

OM/OC Estimates With & Without "SVOC"

		OM/OC for closure		OM/OC {svoc} for closure	
		AVG	STD	AVG	STD
Summer	**Atlanta**	**2.1**	0.7	**1.5**	0.3
-99	**H.ville**	**2.4**	0.7		
	Dixon	**2.9**	1.8		
Fall-99	**H.ville**	**1.7**	0.5		
	Dixon	**2.2**	0.9		
Winter	**H.ville**	**1.6**	0.3		
-99/00	**Dixon**	**1.6**	0.4		
Summer	**Macon**	**2.5**	0.6	**1.7**	0.1
-00	**Augusta**	**3.4**	1.7	**1.7**	0.3
	Columbus	**2.0**	0.5	**1.6**	0.5
	LaPorte	**3.5**	3.8	**2.3**	2.6
	W.Tower	**3.5**	3.2	**2.4**	2.3
Jul-01	**Griffin**	**2.9**	1.2	**2.7**	1.0
Jan-02	**Griffin**	**2.2**	1.0	**1.9**	0.7

Note, due to technical difficulties, only undenuded quartz filter samples were taken at H.ville & Dixon!