Urban EC and OC Trends
Using CSN, IMPROVE, SEARCH EC & OC, "BC" & OCMmb via FRM PM2.5
Findings and Issues

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For Presentation at IMPROVE Carbon Workshop
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Outline

Background

Part 1: Urban EC trends

- EPA's CSN, 2002-mid 2010
- CSN inter-comparisons
  - IMPROVE TOR 3000N EC v. NIOSH TOT MetOne EC
  - SEARCH vs CSN (Birmingham)
- Longer-term trends
  - Washington DC (1990-2009)
  - BC from Boston and S.F.

Part 2: Urban OC Trends

- CSN OC vs SANDWICHed OCMmb, 2002-mid 2010
- TC vs TC & OC:EC ratios

Background

CSN Carbon Measurements (~200 urban sites)

- **Until 2007 -- NIOSH-like TOT protocol,**
  - **mostly using MetOne sampler**
- **Starting May 2007, Switched to IMPROVE TOR protocol with URG 3000N**

Carbon Measurements Are Also Affected by Sampler & Filter Face Velocity

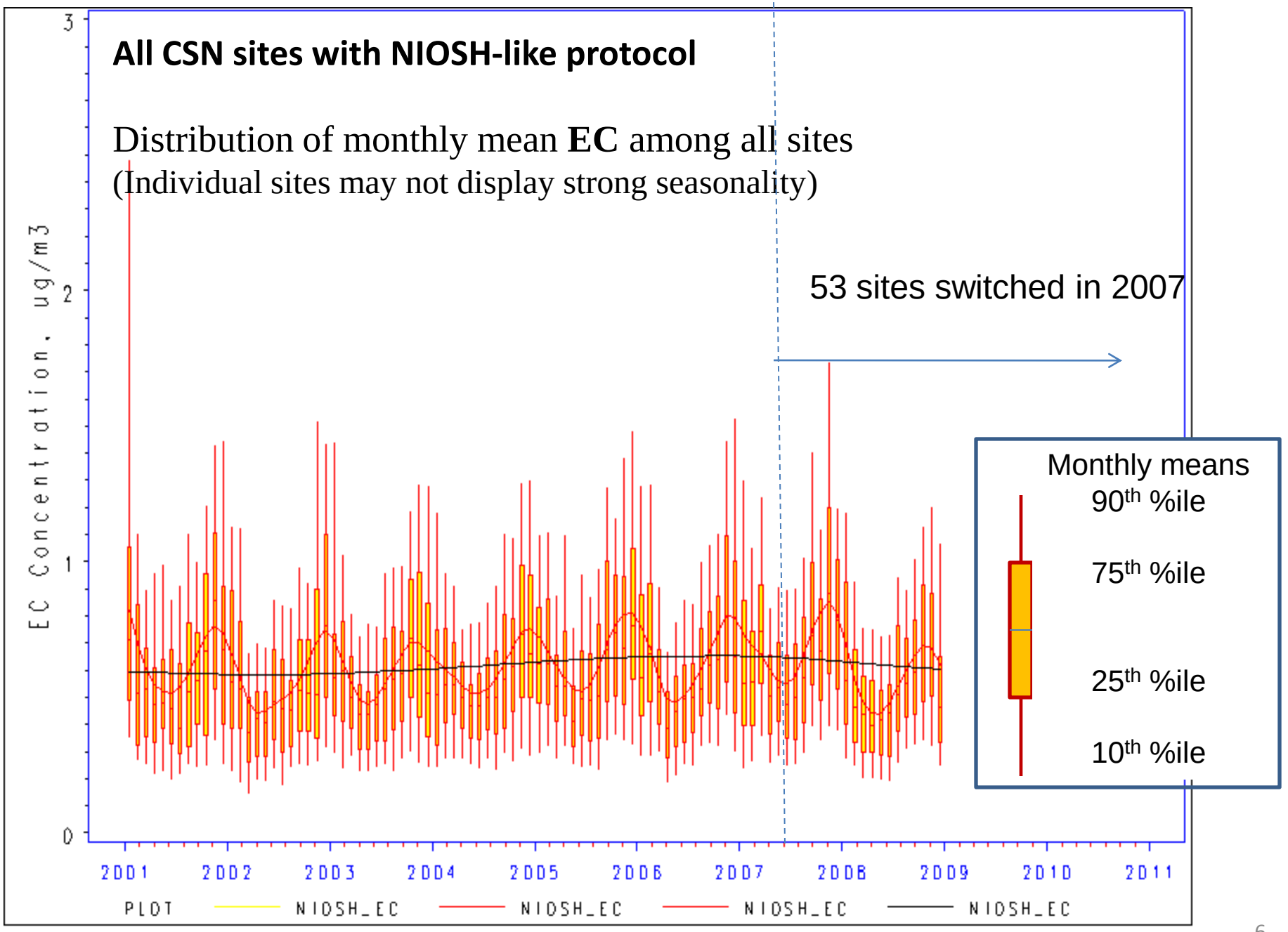
- **MetOne - 6.7 Lpm, 47 mm quartz**
- **FRM - 16.7 Lpm , 47mm Teflon**
- **URG 3000N - 22.8 Lpm, 25mm quartz (highest FV)**
  - **~12x MetOne,**
  - **~ 3x PCM3,**
  - **~1.3x FRM (w. McDade et al [2009] filter screen adjustment)**
- **SEARCH PCM3 (w IMPROVE TOA) - 16.7 L*pm* , 37mm quartz and denuder**

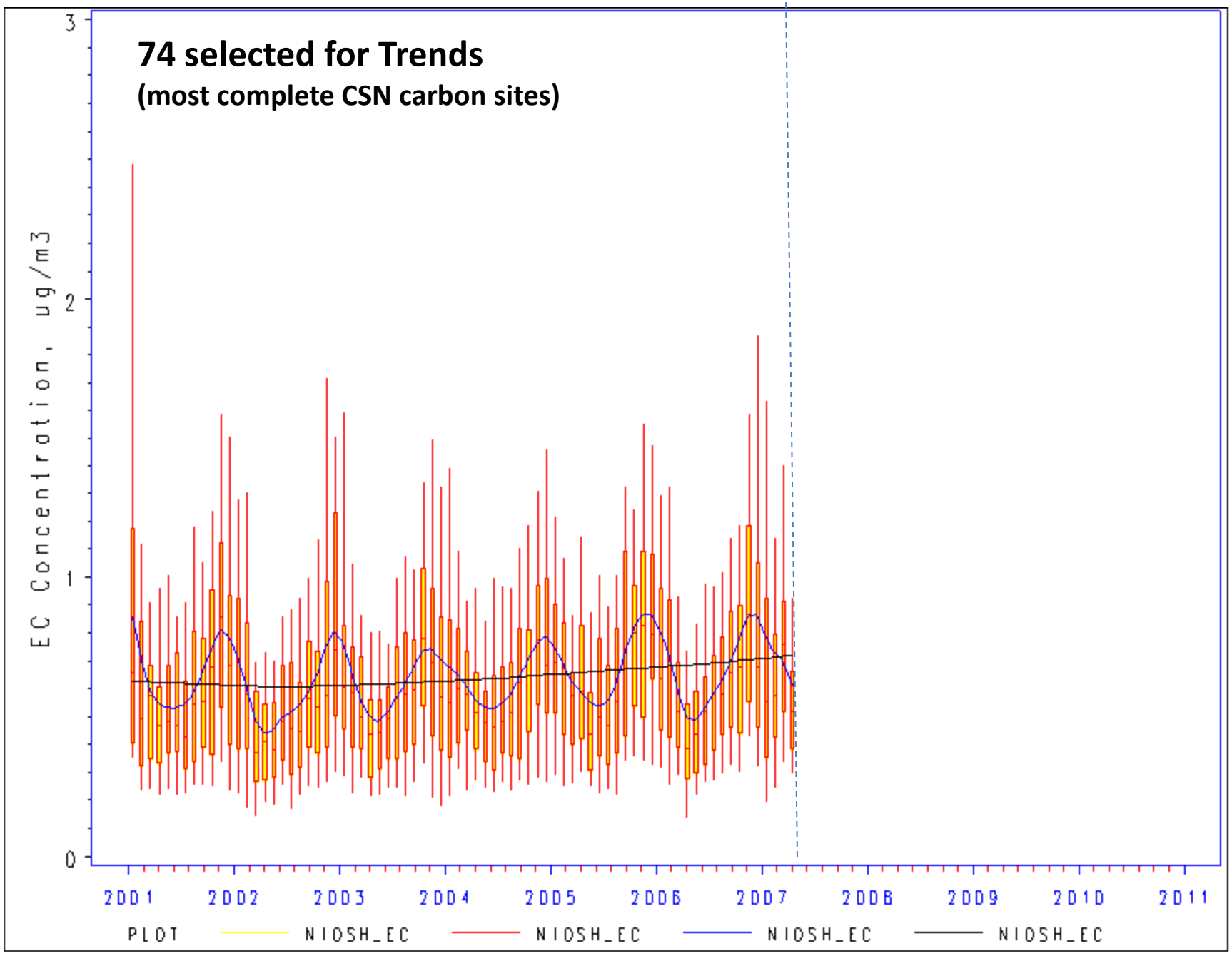
"Conventional" Thinking

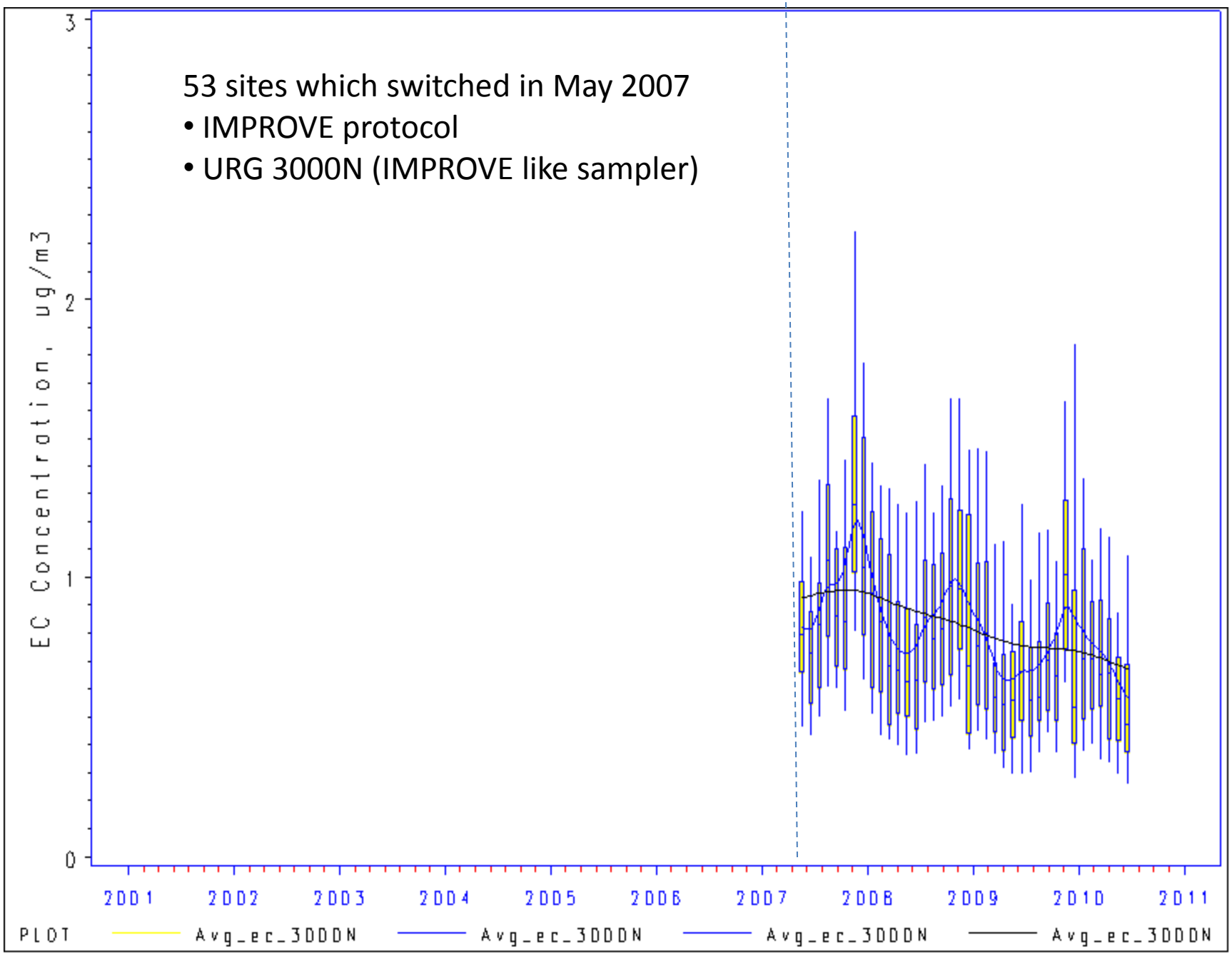
- **EC TOR > EC TOT**
- **IMPROVE TOR EC > NIOSH TOT EC**
- **OC is primarily affected by positive sampling artifact**
- **EC does not have sampling artifacts**

Some modifications may be needed for CSN !

CSN EC Trends, 2002-mid 2010


All CSN sites with NIOSH-like protocol
Distribution of monthly mean EC among all sites
(Individual sites may not display strong seasonality)
53 sites switched in 2007
Monthly means
90th %ile
75th %ile
25th %ile
10th %ile
EC Concentration, ug/m3
0
1
2
3
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
PLOT
NIOSH_EC
NIOSH_EC
NIOSH_EC
NIOSH_EC


74 selected for Trends
(most complete CSN carbon sites)
EC Concentration, ug/m3
3
2
1
0
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
PLOT
NIOSH_EC
NIOSH_EC
NIOSH_EC
NIOSH_EC

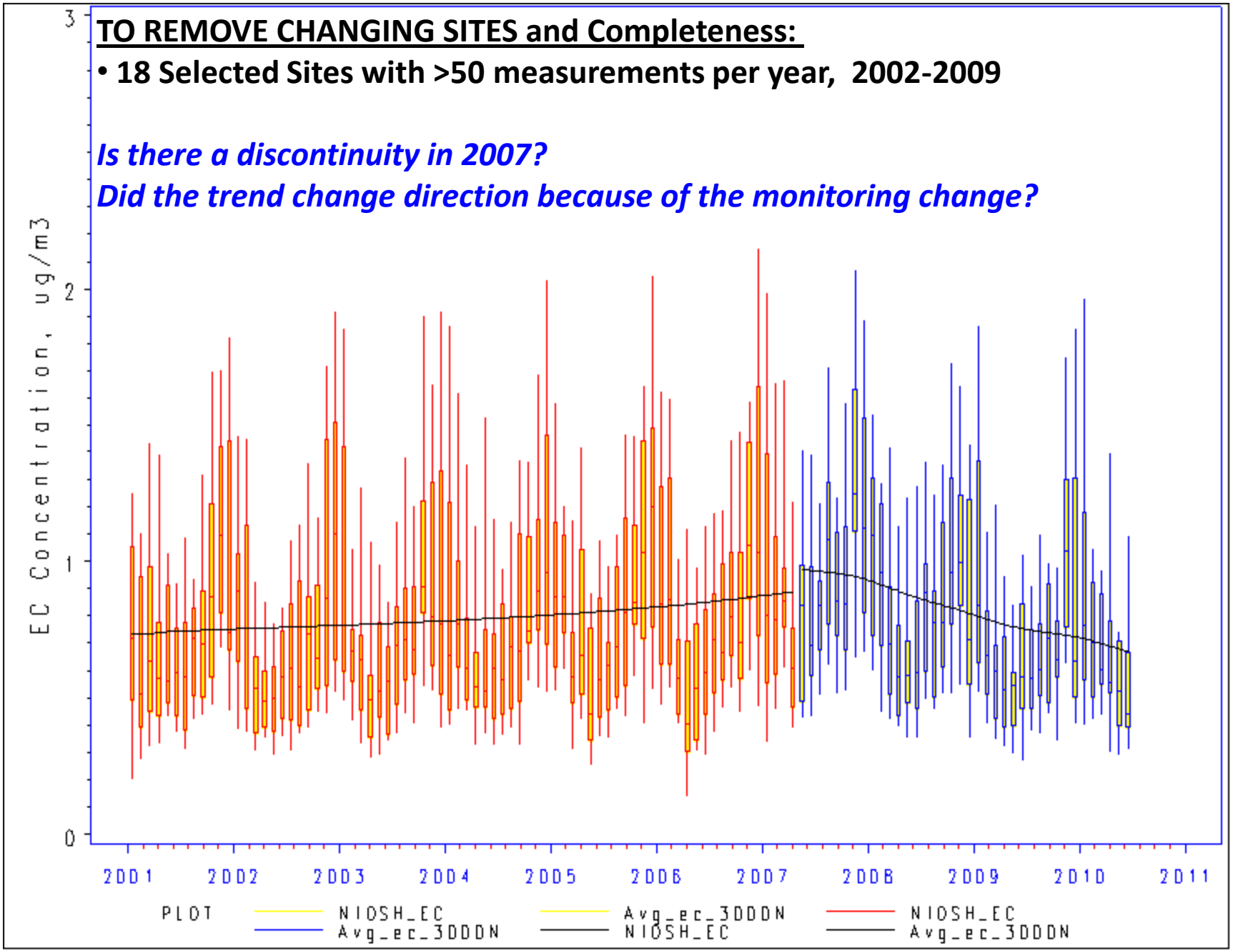

53 sites which switched in May 2007
• IMPROVE protocol
• URG 3000N (IMPROVE like sampler)
EC Concentration, ug/m3
3
2
1
0
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
PLOT
Avg_ec_3DDDN
Avg_ec_3DDDN
Avg_ec_3DDDN
Avg_ec_3DDDN

TO REMOVE CHANGING SITES and Completeness:

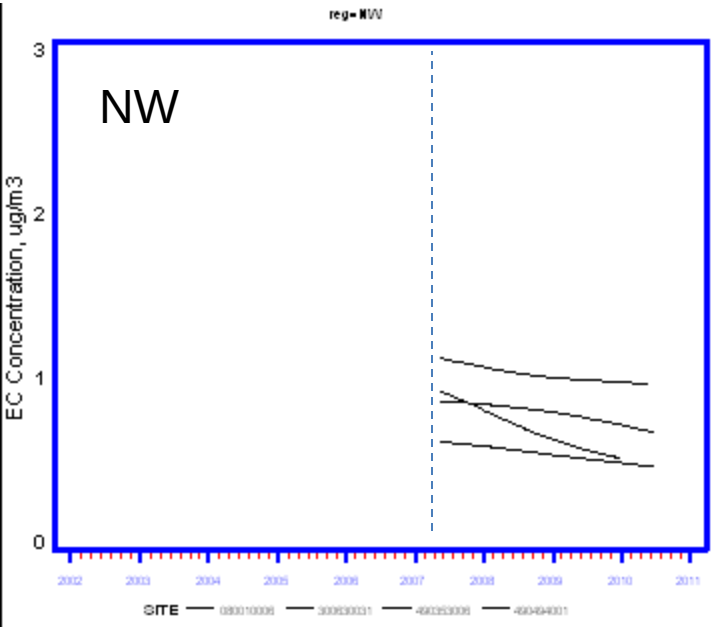
- **18 Selected Sites with >50 measurements per year, 2002-2009**

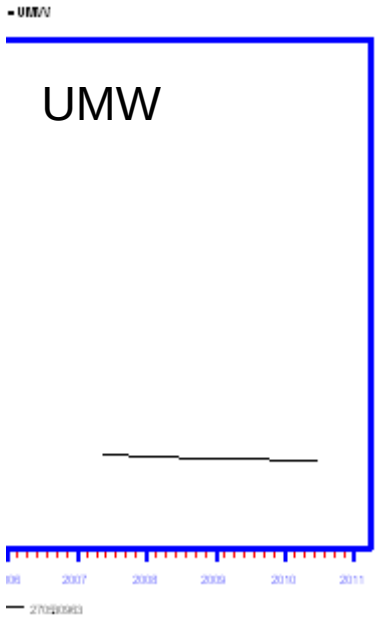
Is there a discontinuity in 2007?

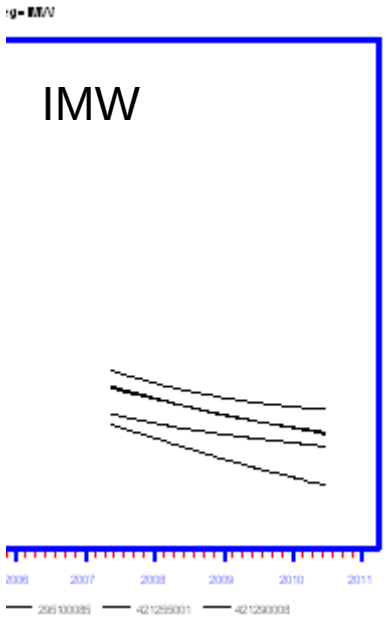
Did the trend change direction because of the monitoring change?

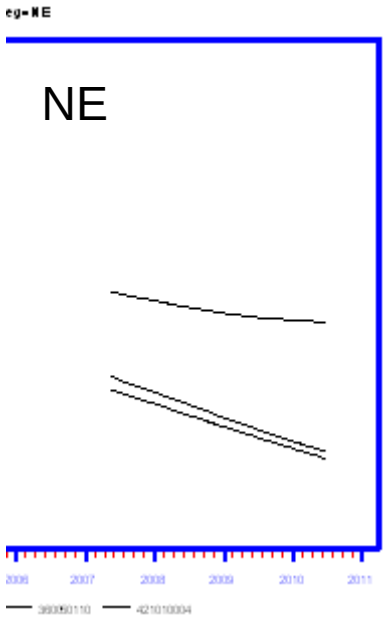


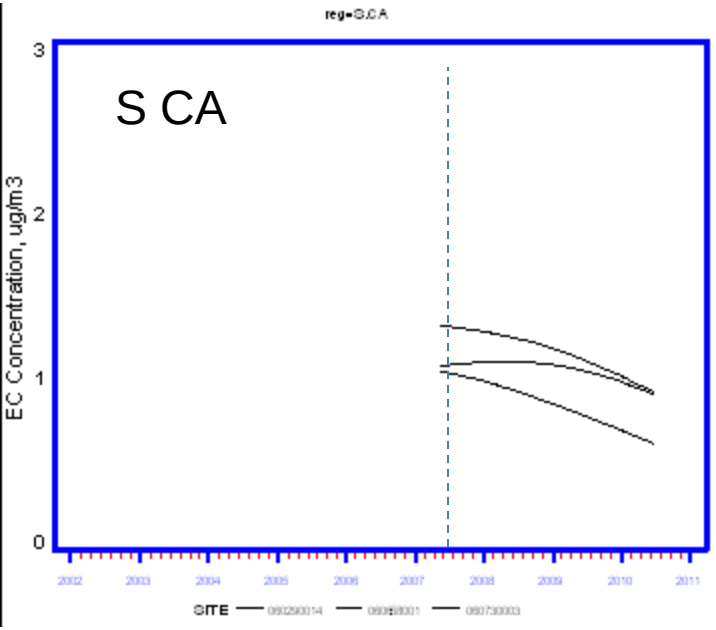
18 sites 3000N IMPROVE (site specific trends)



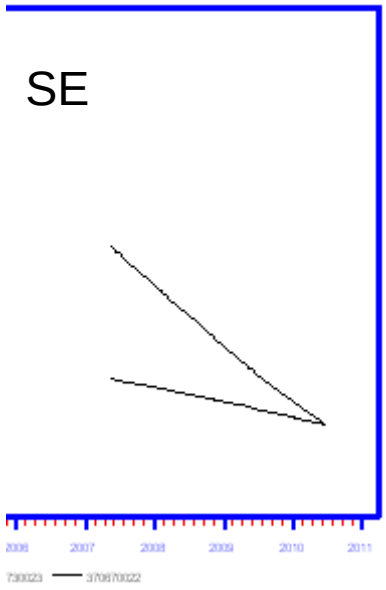




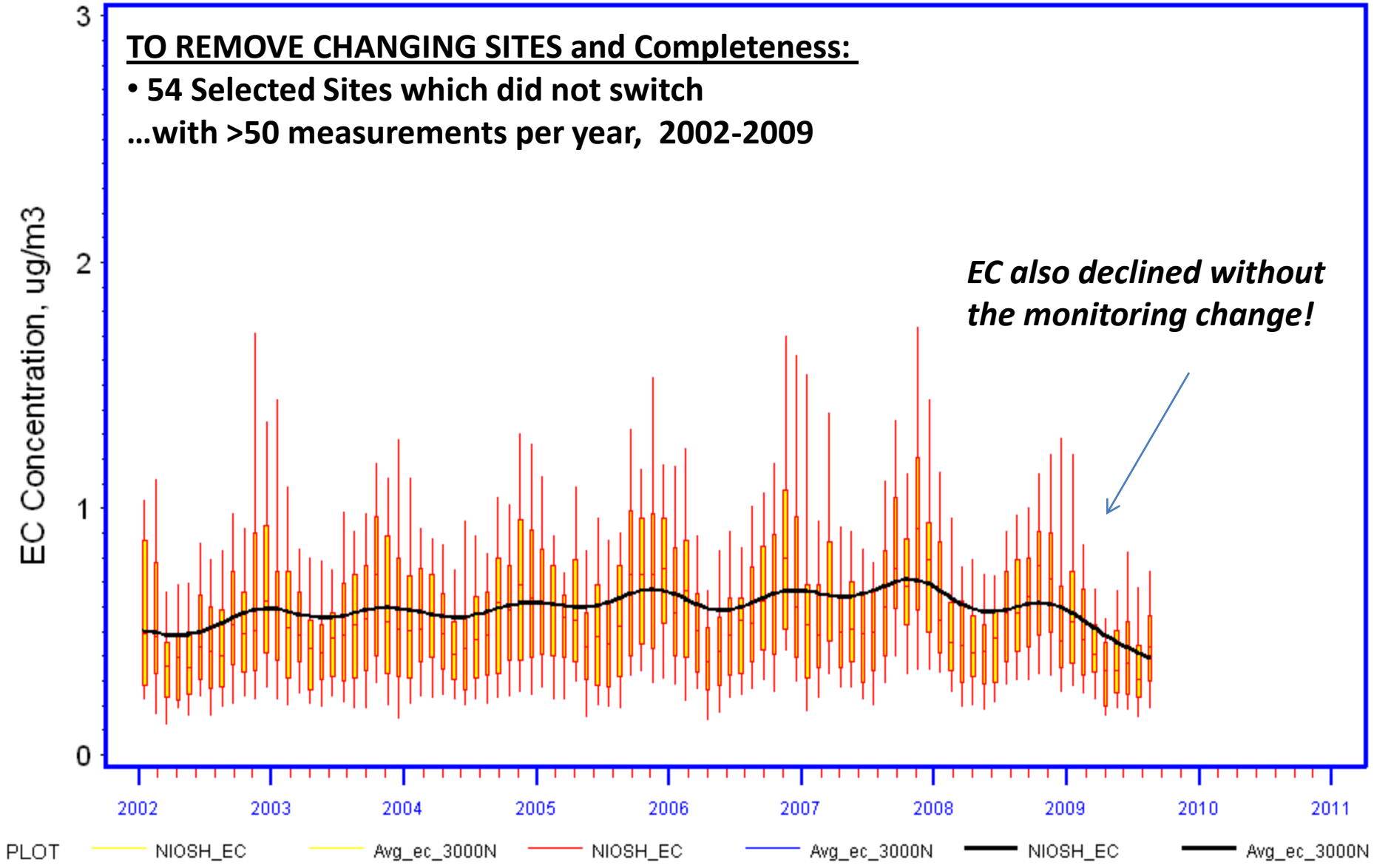




EC declined since 2007 at most sites

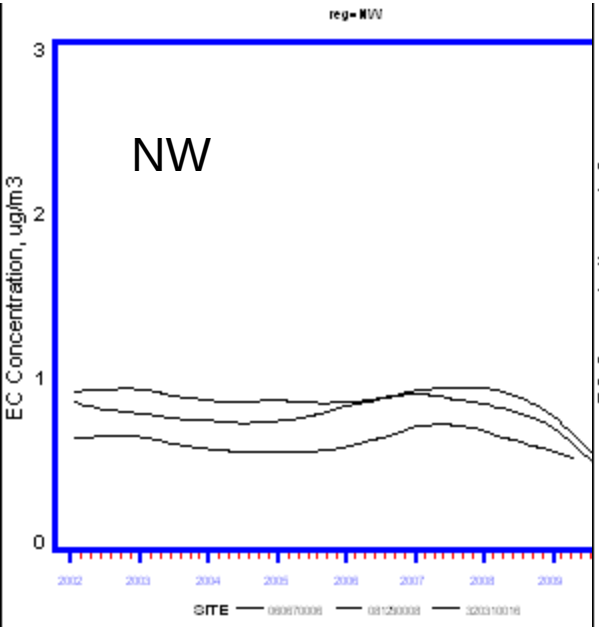


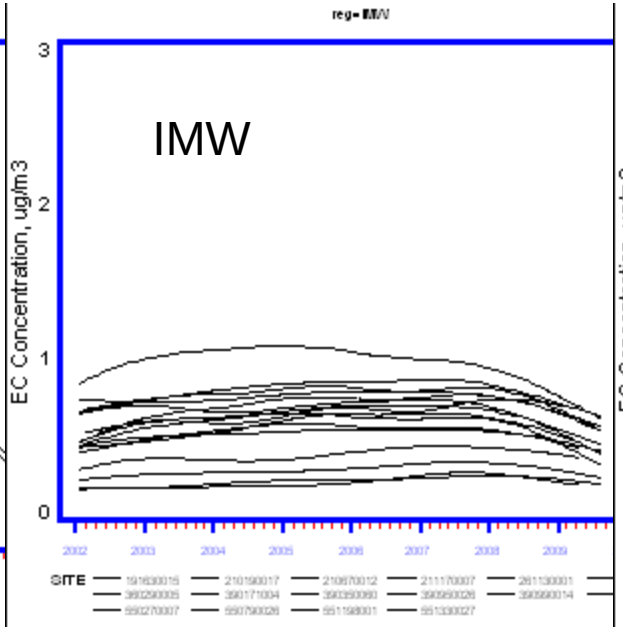
56 MetOne sites w. NIOSH

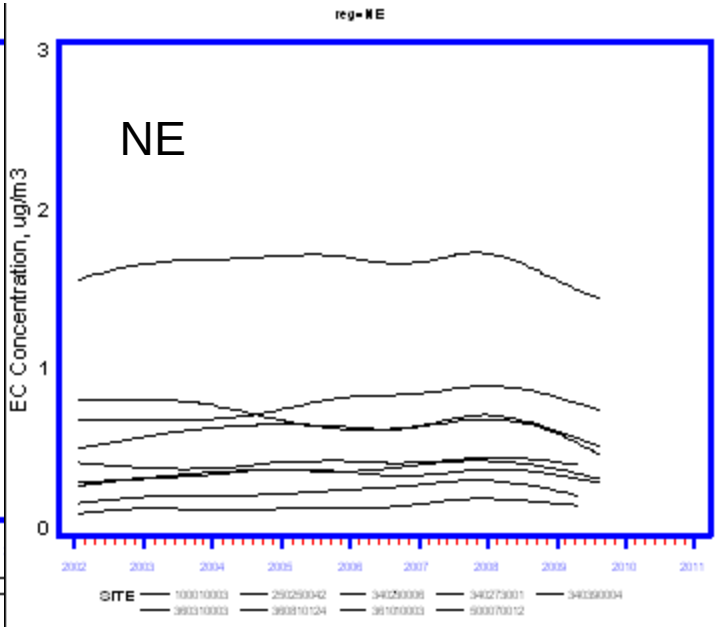


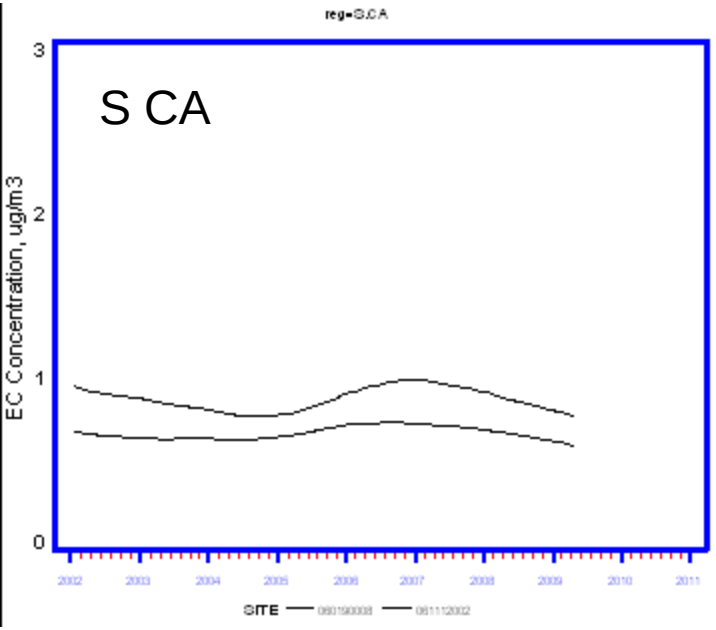
56 MetOne sites w. NIOSH

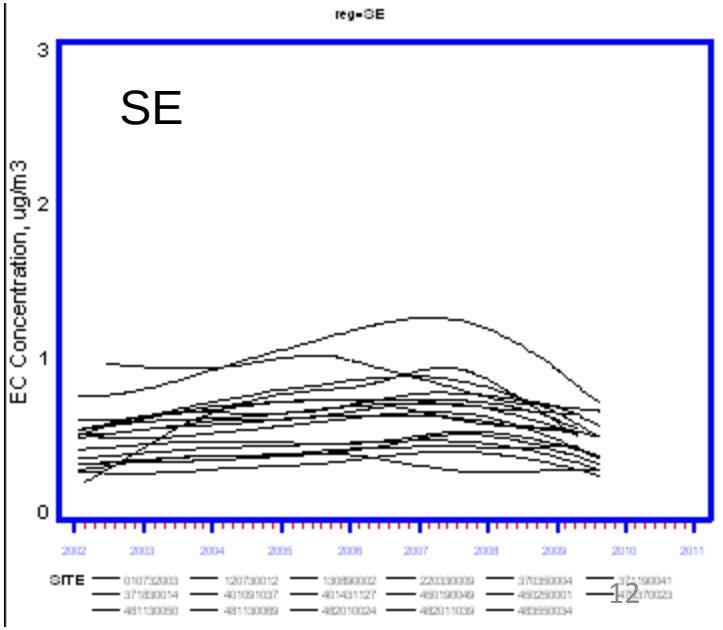
The decline after 2007 appears to be nationwide

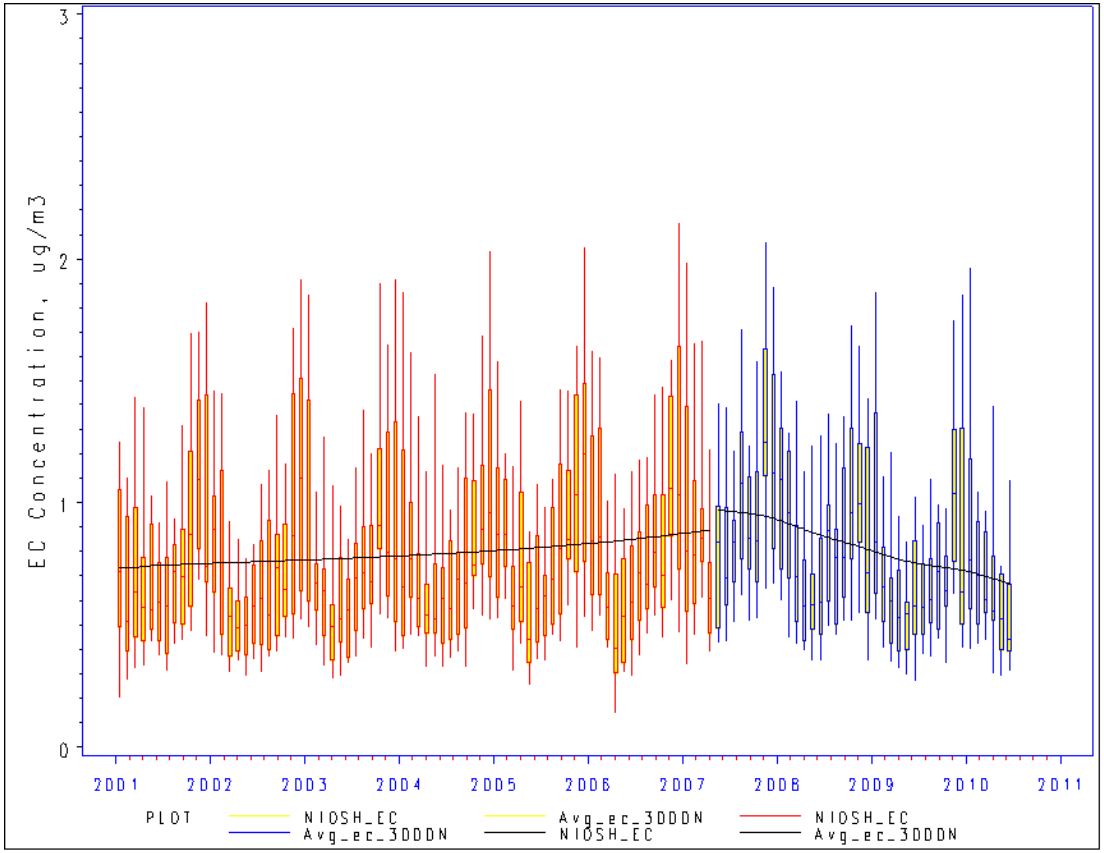










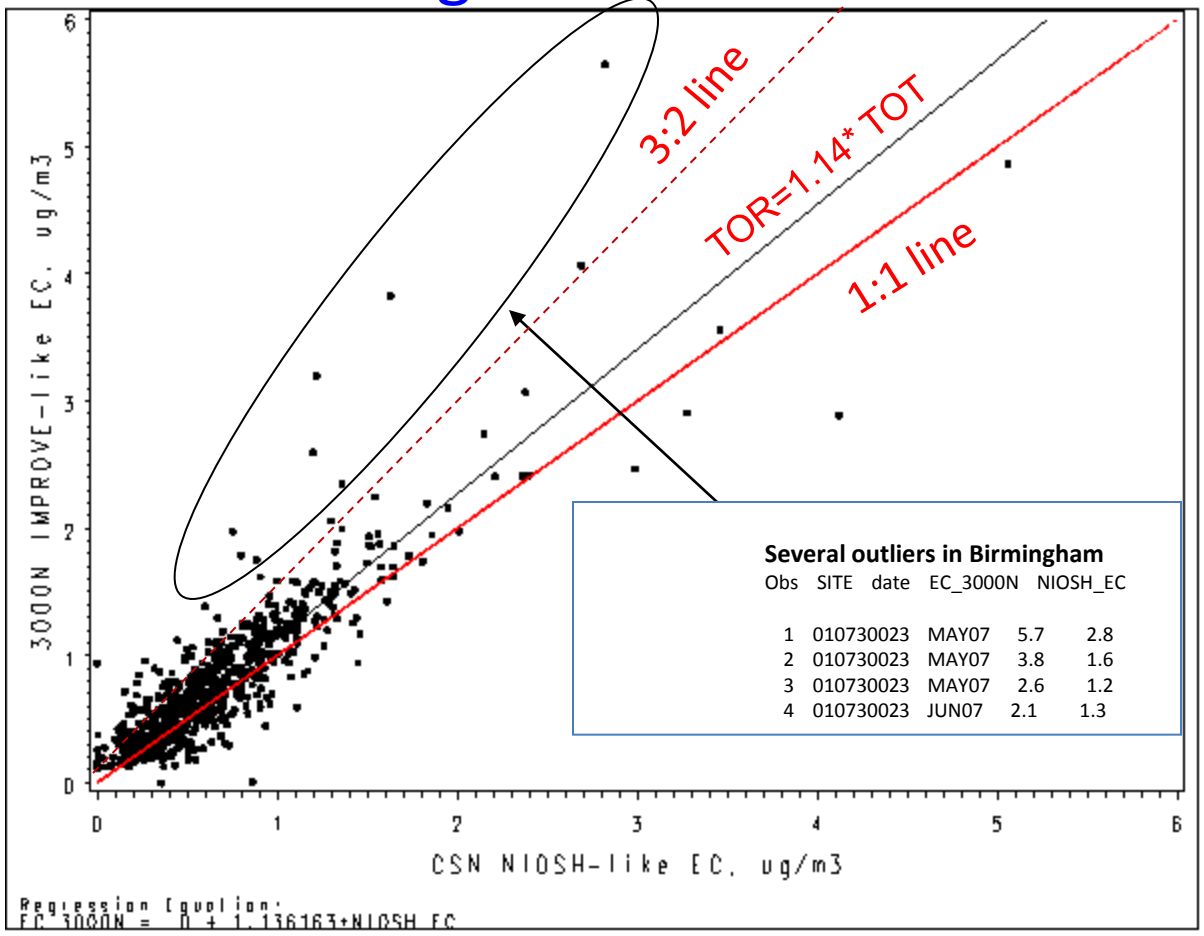


TO ESTIMATE THE APPARENT DISCONTINUITY IN 2007

Step 1

2 Month Collocation (May-June 2007)

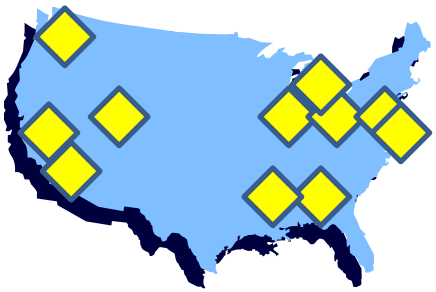
- 3000N = 14% higher than CSN MetOne NIOSH



Step 2

12-month Carbon Inter-Comparison of 11 CSN sites

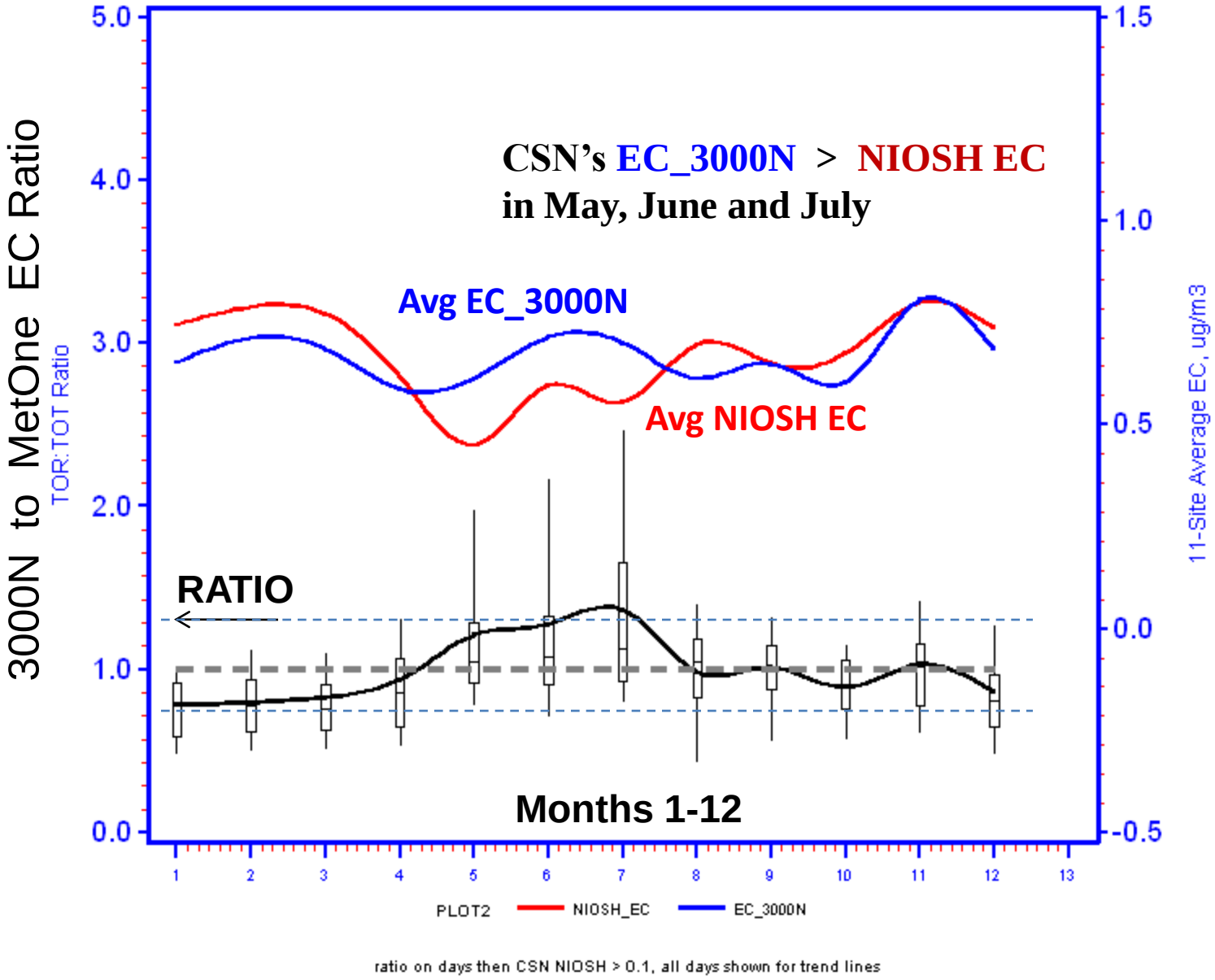
NIOSH OC/EC w. MetOne sampler
vs. **IMPROVE** OC/EC w. URG 3000N sampler



Bronx and Queens, NY;
Atlanta GA,
Birmingham AL,
Detroit MI;
Cleveland OH;
Chicago IL,
Denver CO,
LA (Rubidoux) CA;
Sacramento CA *
Seattle WA *

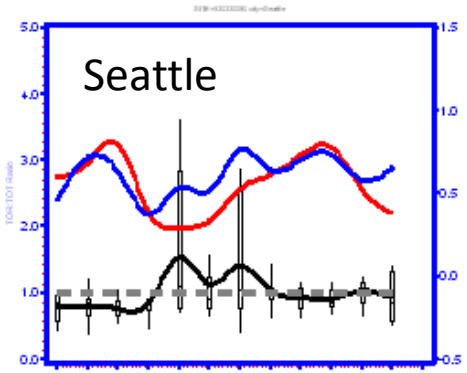
* woodsmoke sites

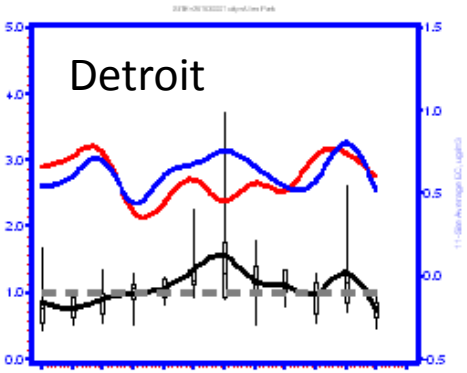
May 1009-April 2010, (not presented chronologically)

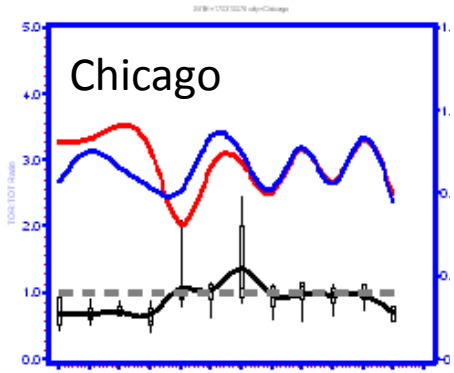


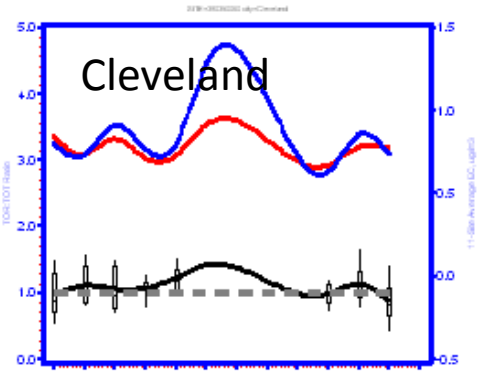
Monthly Distribution of EC:EC ratio between two EPA methods (IMPROVE TOR: NIOSH-like TOT), from 897 collocated measurements among 11 urban CSN locations. (Average Concentrations and Ratios)

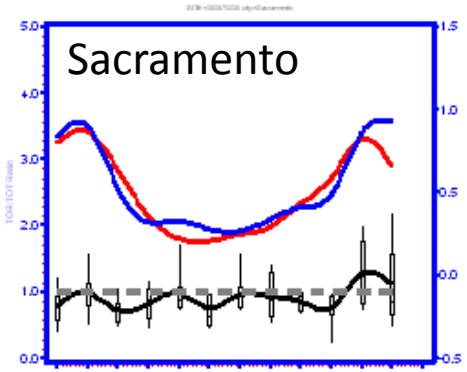
Many Sites show 3000N EC > MetOne EC Summer only Pattern

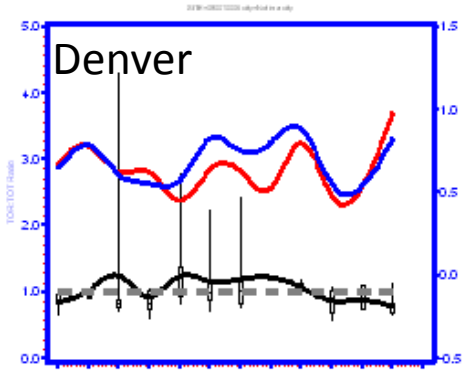


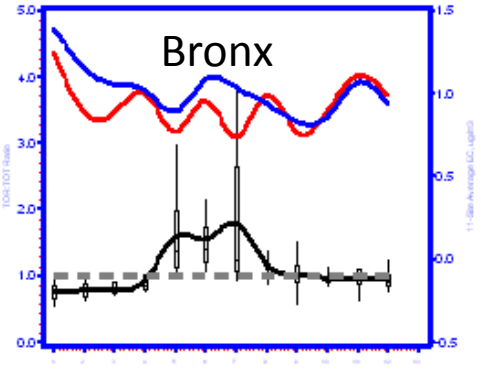


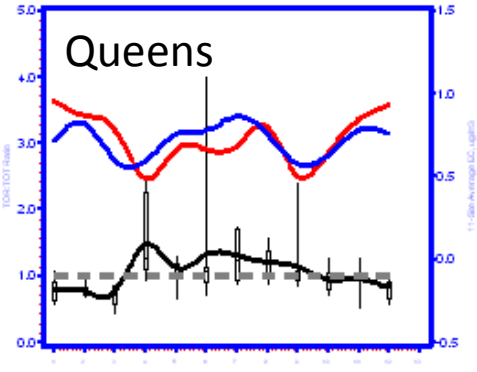


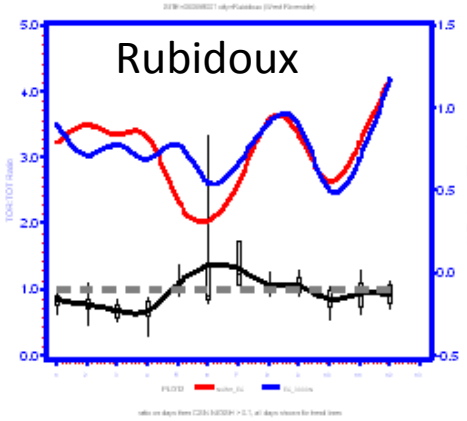


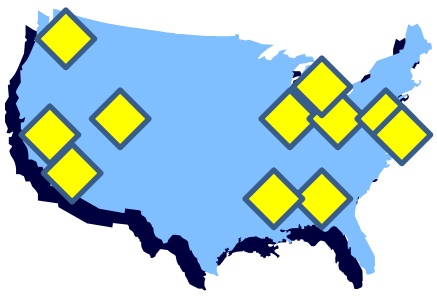


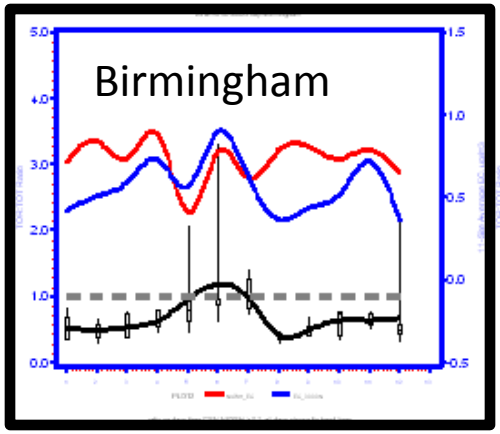


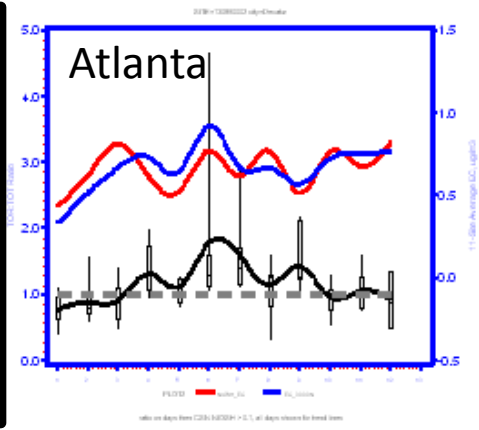






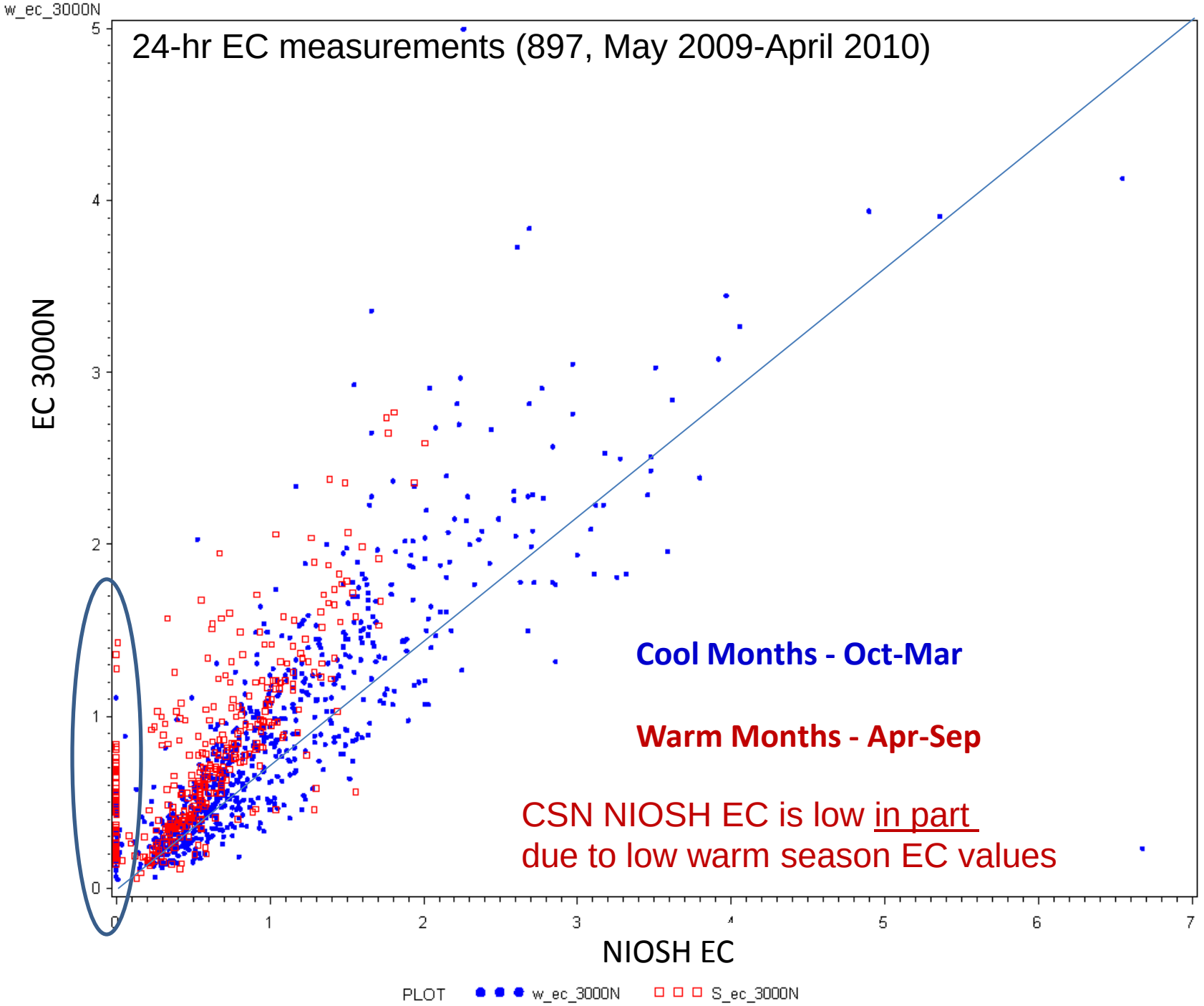


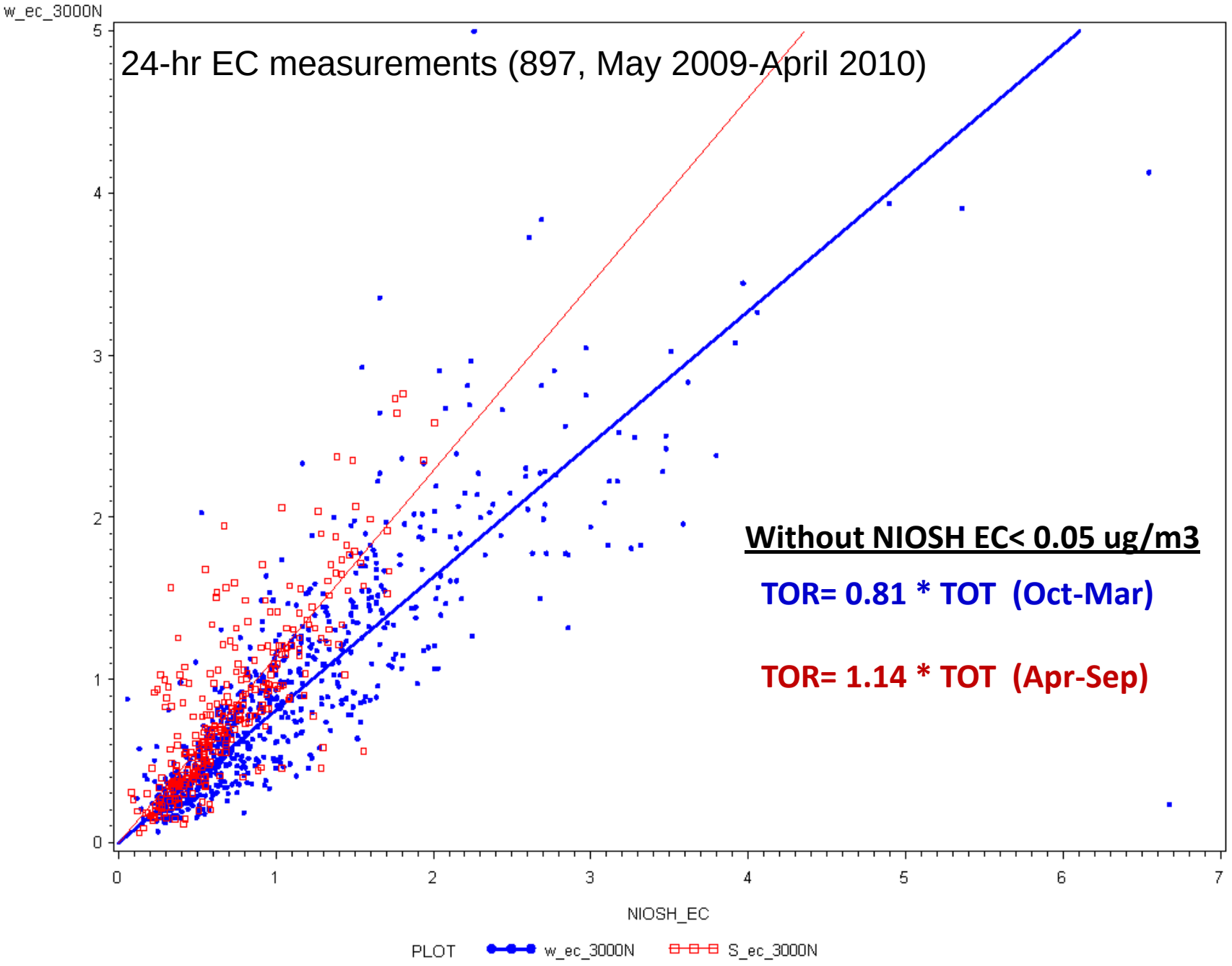




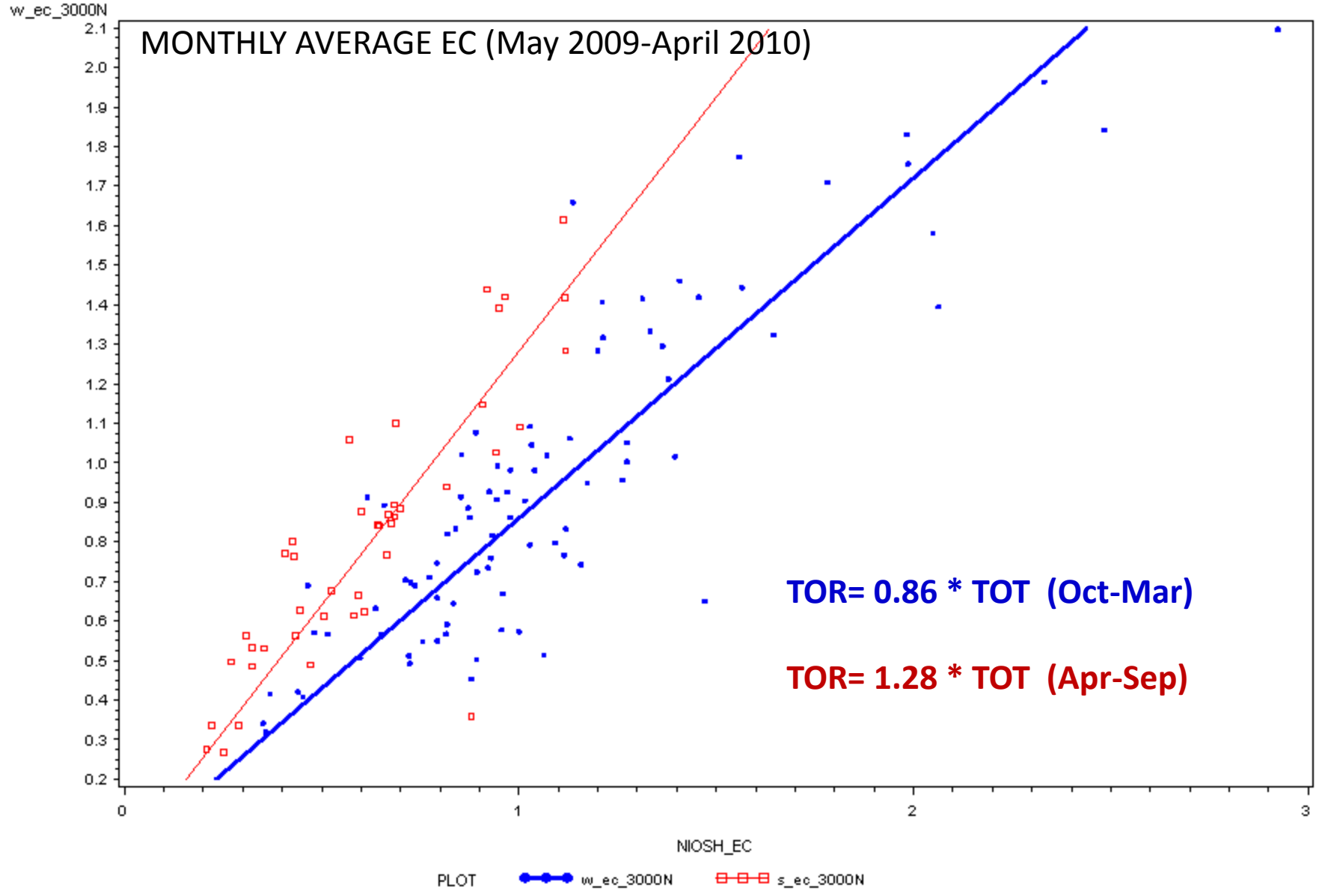
Monthly Averages: NIOSH (TOT), ug/m3 3000N(TOR), ug/m3

EC Ratio Distribution: (TOR/TOT)

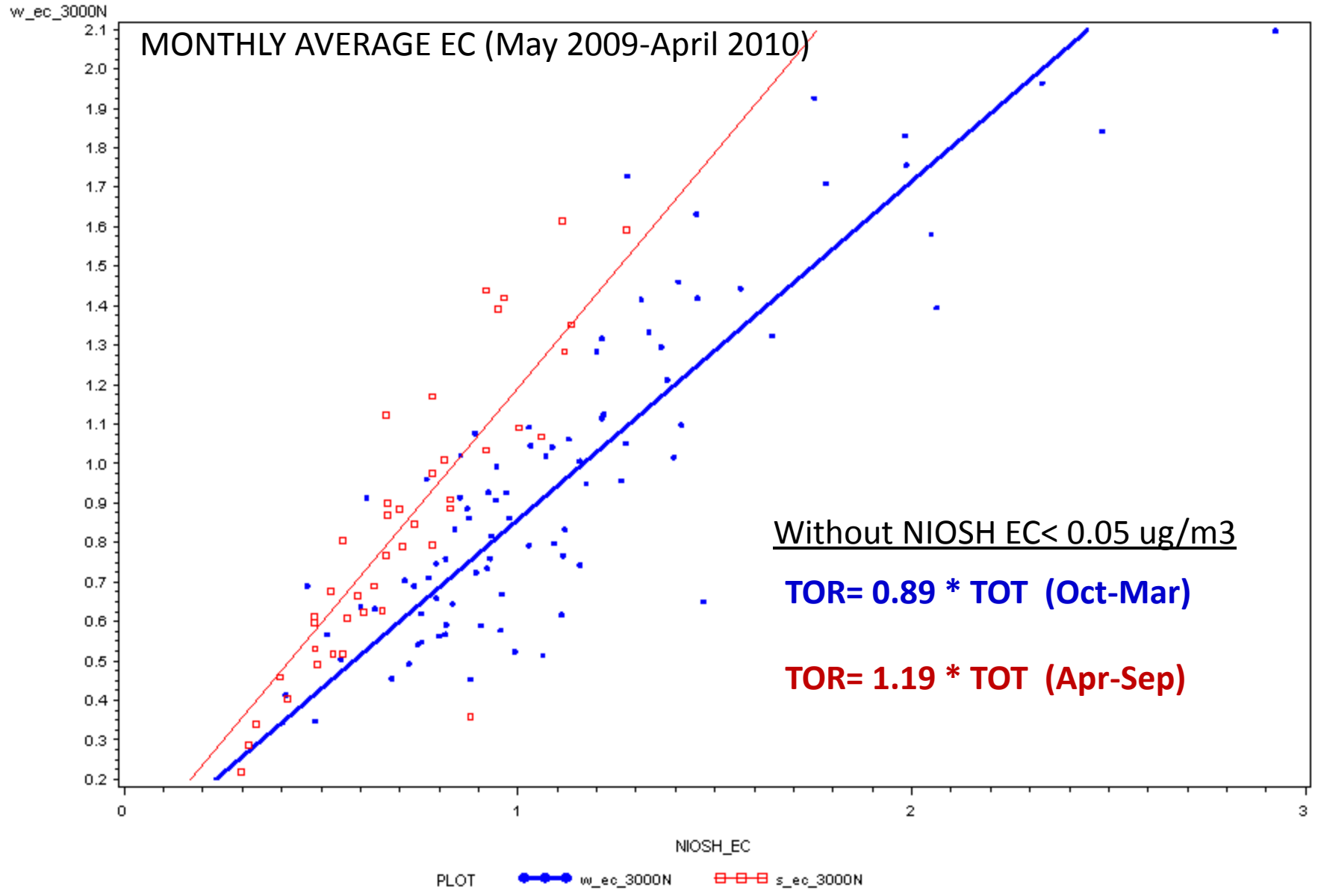

w_ec_3000N
24-hr EC measurements (897, May 2009-April 2010)
EC 3000N
NIOSH EC
Cool Months - Oct-Mar
Warm Months - Apr-Sep
CSN NIOSH EC is low in part
due to low warm season EC values
PLOT w_ec_3000N S_ec_3000N



Regression Equation:
w_ec_3000N = 0 + 0.818246*NIOSH_EC
S_ec_3000N = 0 + 1.146079*NIOSH_EC

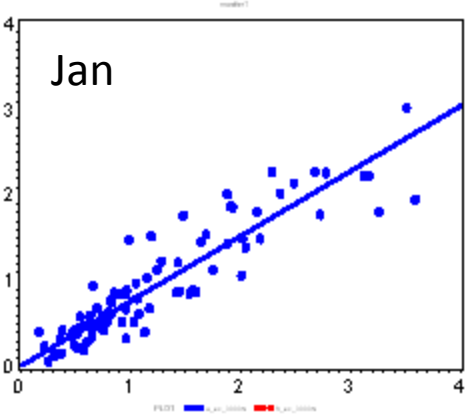


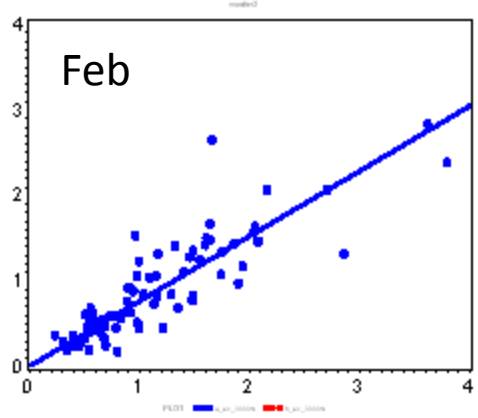
Regression Equation:
w_ec_3000N = 0 + 0.860958*niosh_ec
s_ec_3000N = 0 + 1.2828*niosh_ec

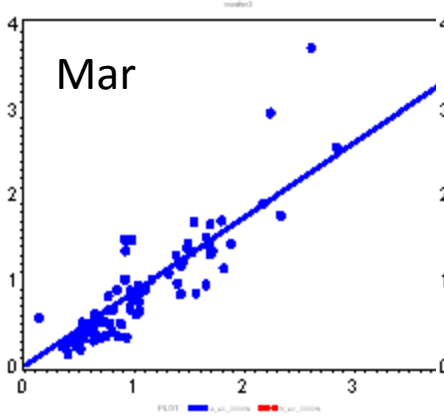


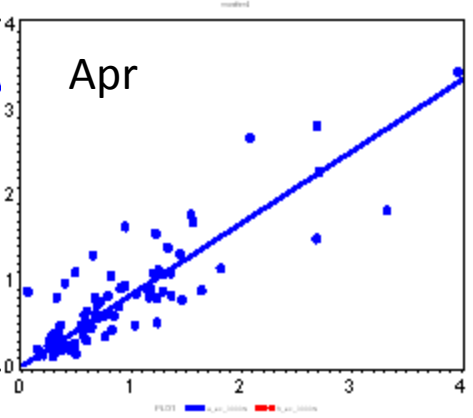
During 2009-2010,
there appears to be seasonal relationship

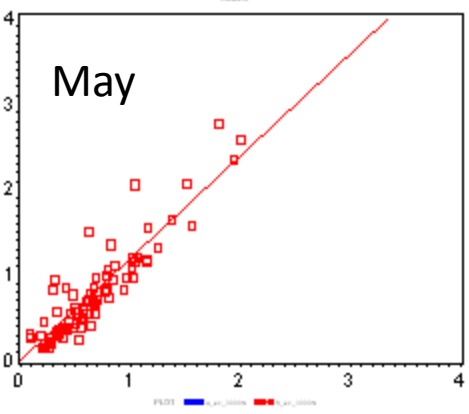
EC Inter-Comparison, by Month (11 CSN sites, May 2009-Apr 2010)

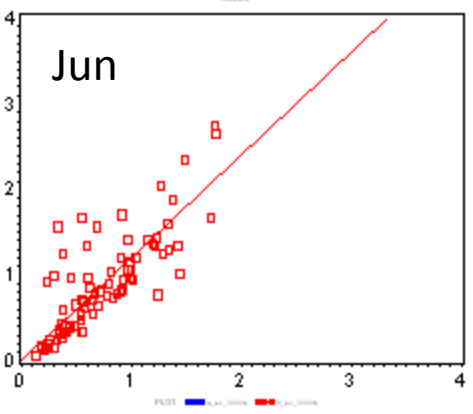


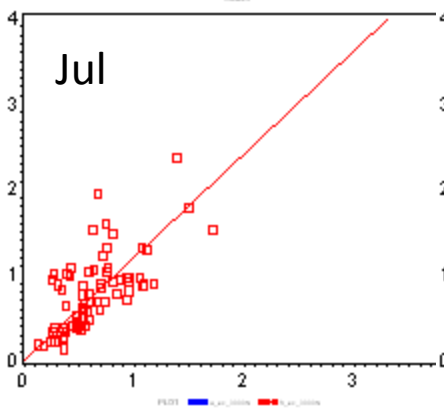


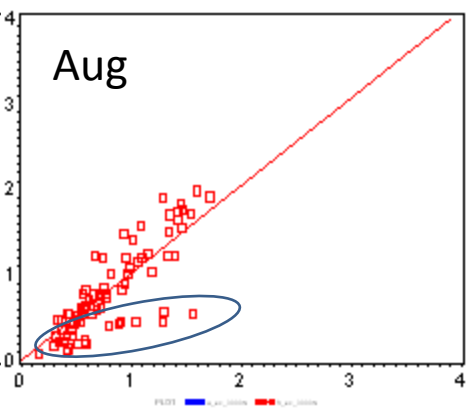


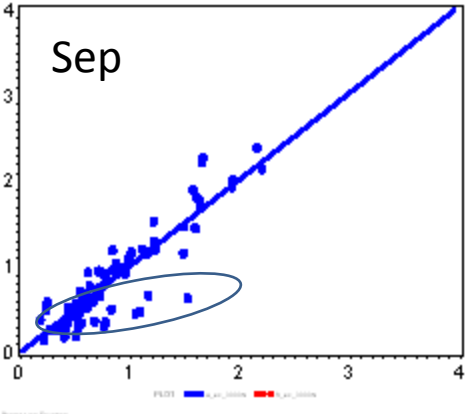


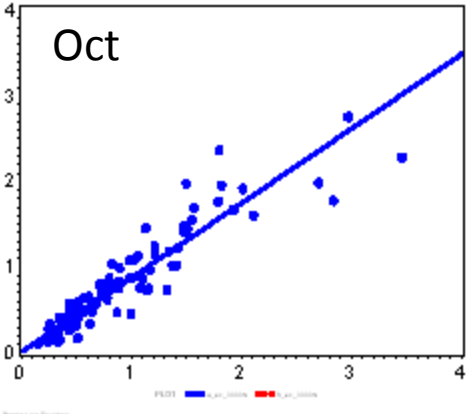


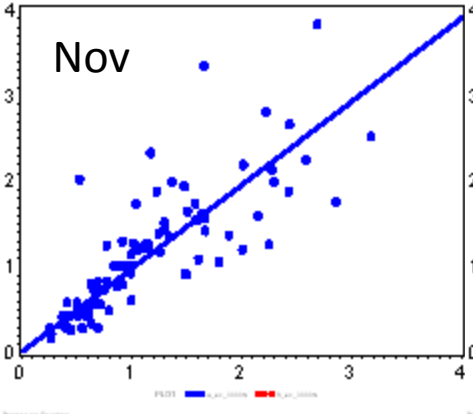


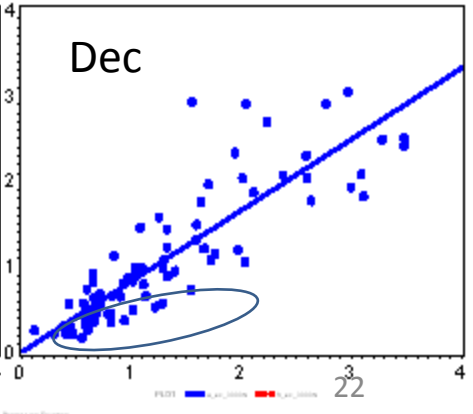


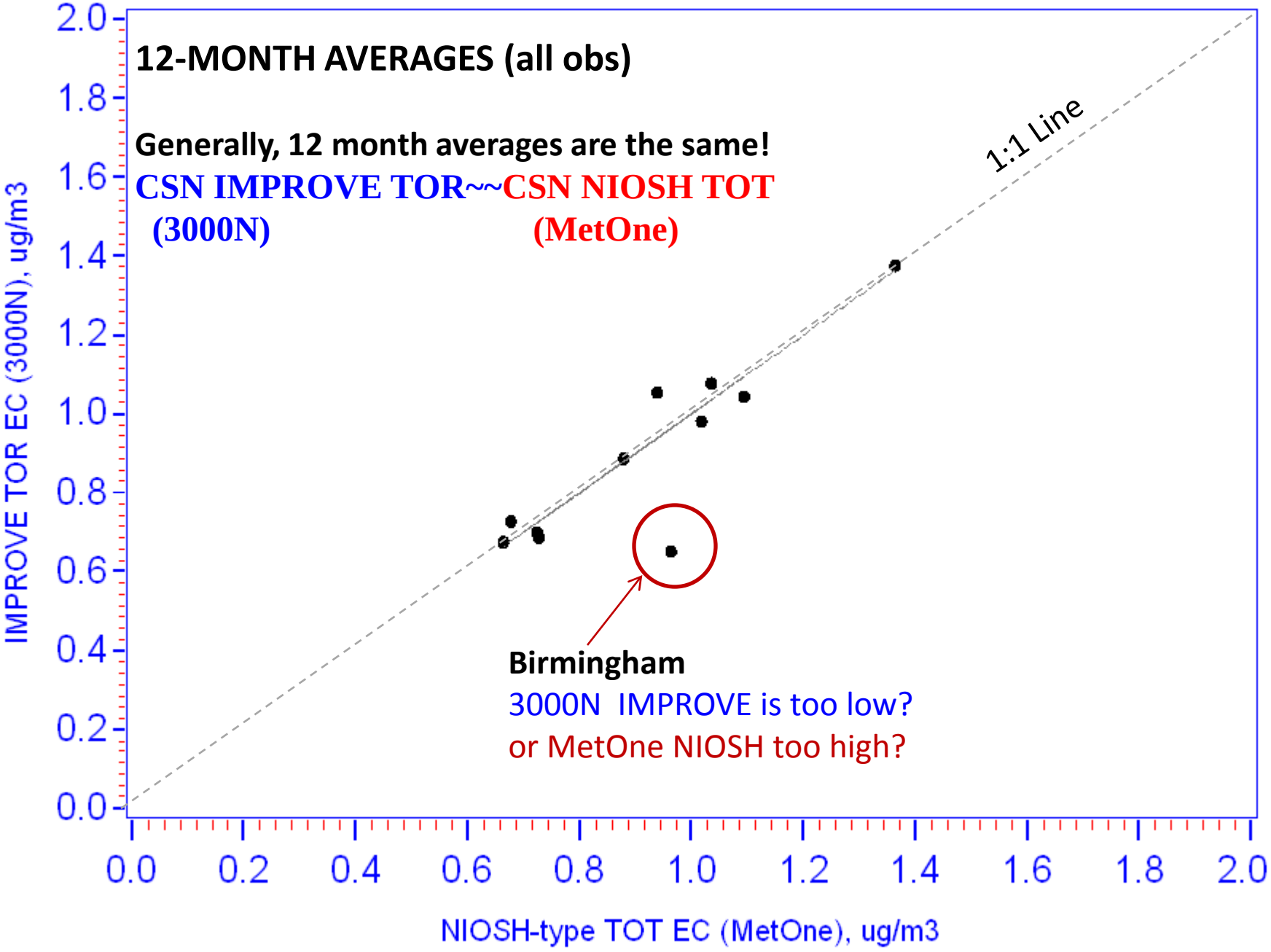











12-MONTH AVERAGES (all obs)
Generally, 12 month averages are the same!
CSN IMPROVE TOR~~CSN NIOSH TOT
(3000N)
(MetOne)
1:1 Line
Birmingham
3000N IMPROVE is too low?
or MetOne NIOSH too high?
IMPROVE TOR EC (3000N), ug/m3
NIOSH-type TOT EC (MetOne), ug/m3
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

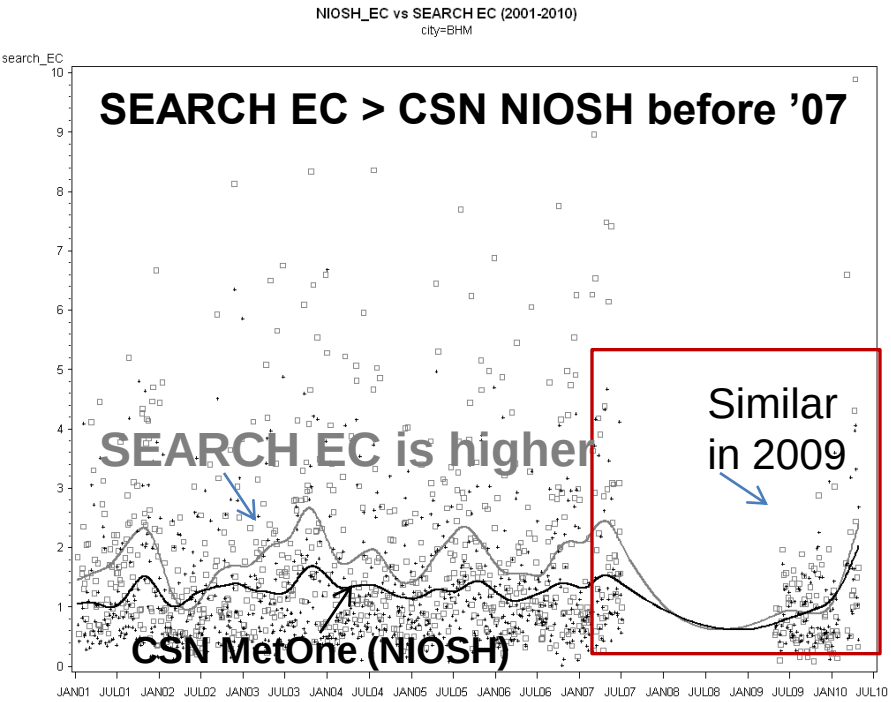
Birmingham EC (2000-2010)

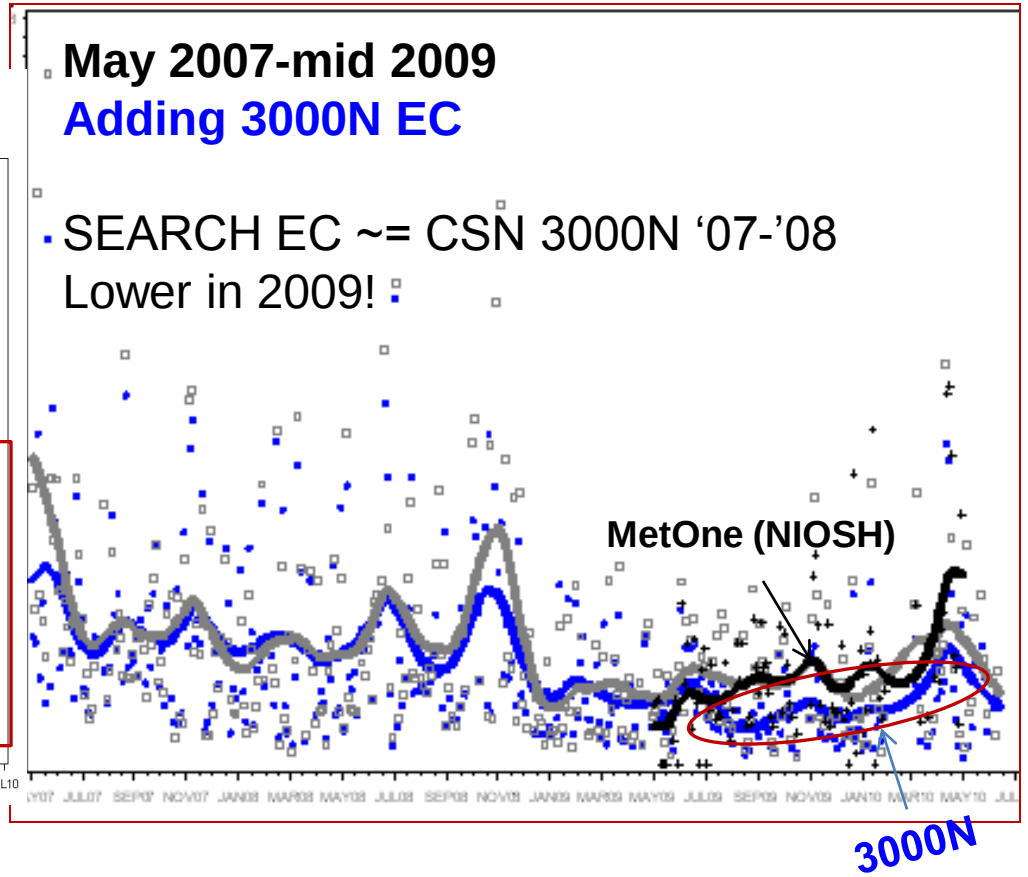
3 collocated METHODS

What can we learn from comparison to SEARCH's EC

SEARCH EC in Birmingham confirm EC decrease

but relative CSN to SEARCH concentrations have changed



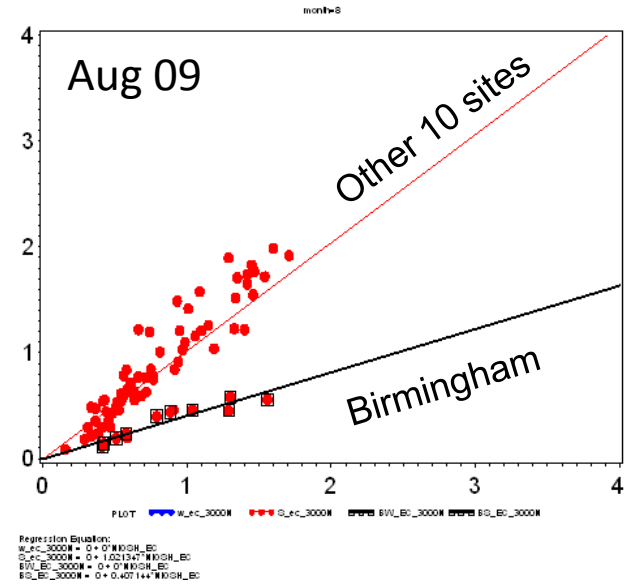


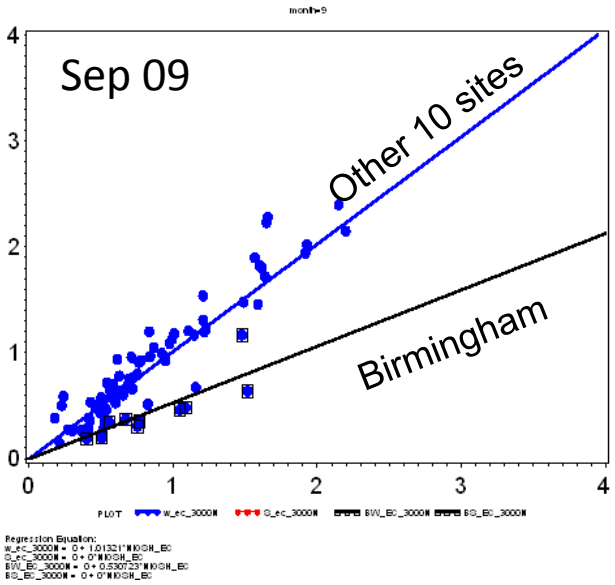
New 2009 agreement suggests NIOSH EC is too high

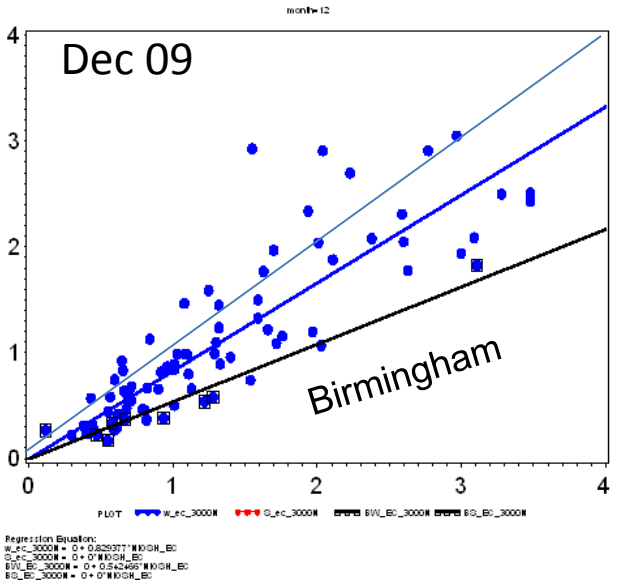
New disagreement suggests 3000N is too low

2009 EC in Birmingham

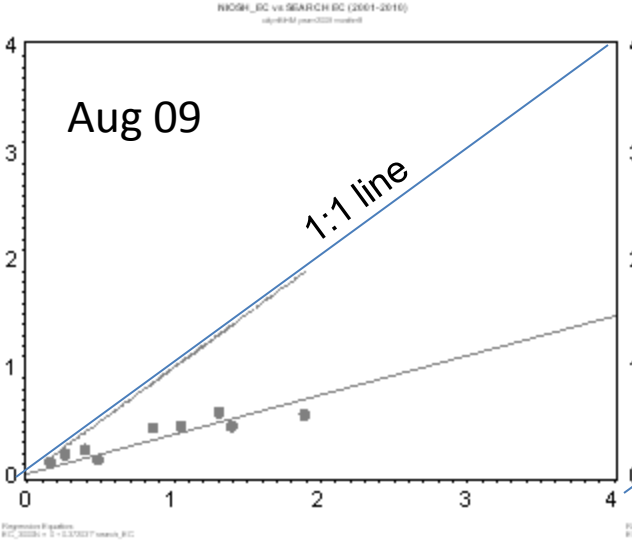
- 3000N TOR is consistently lower than CSN NIOSH TOT

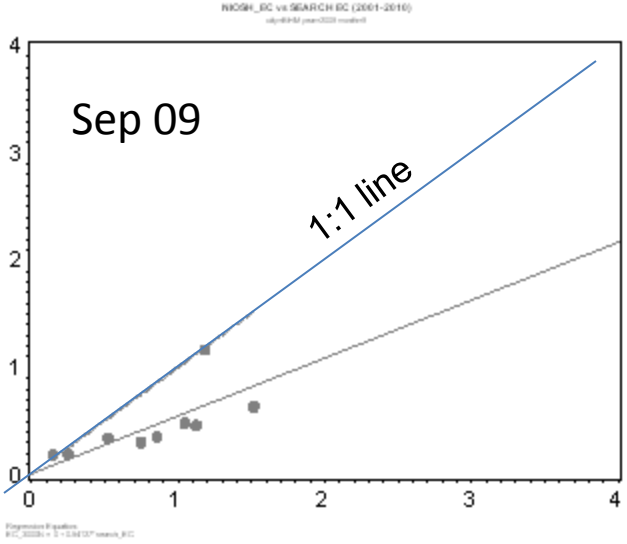


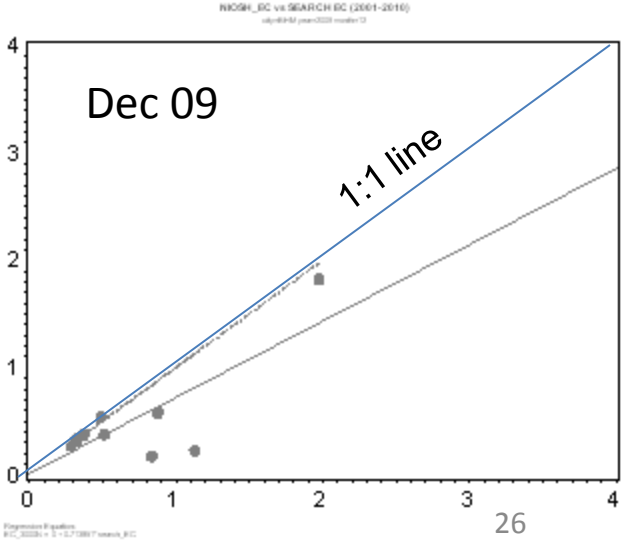


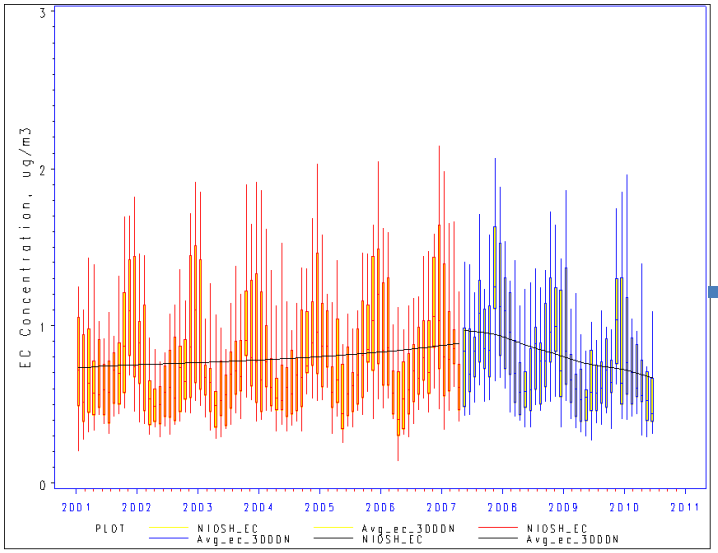


Also, 3000N TOR is lower than SEARCH EC TOR









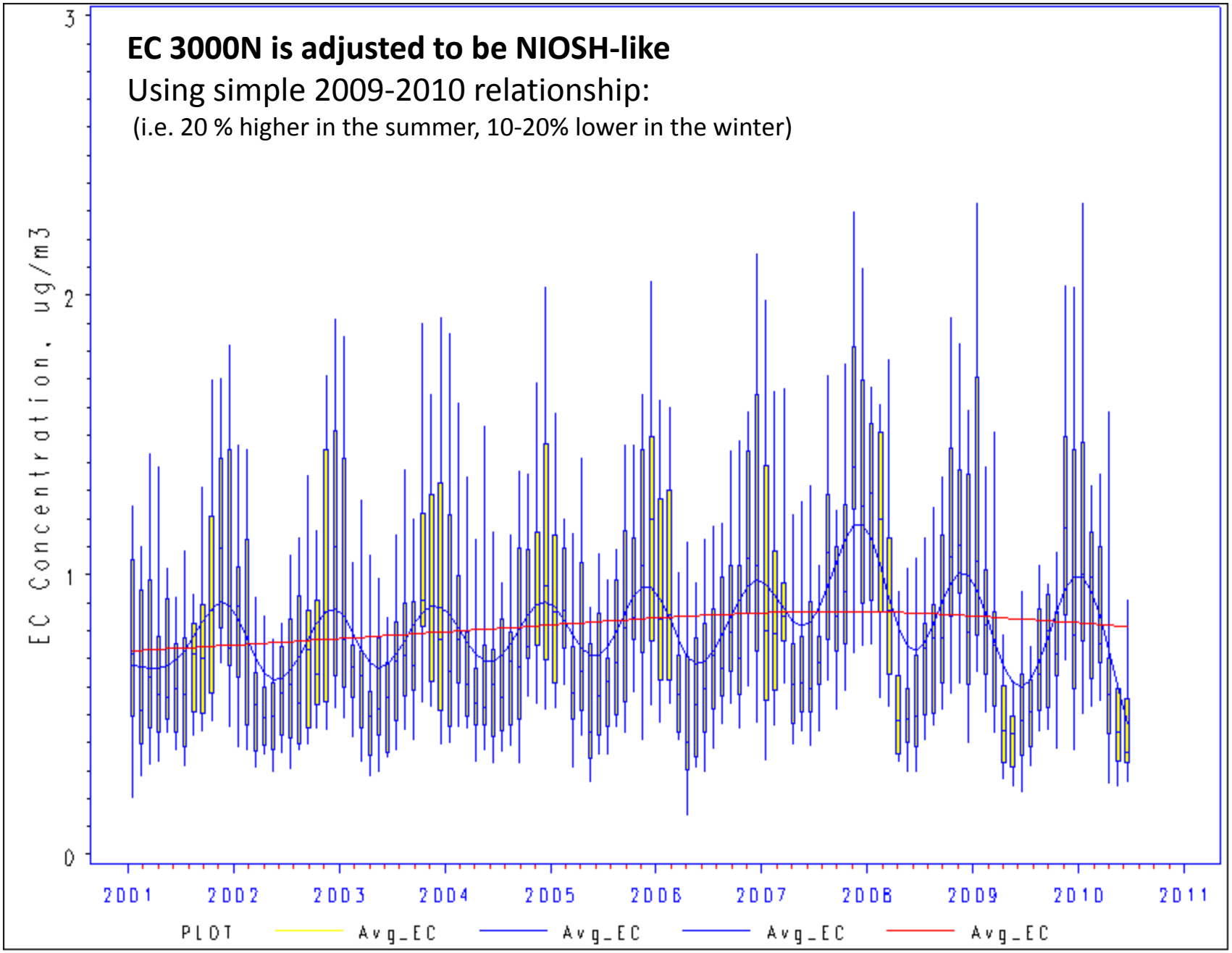
National CSN EC trend

Tentatively “HARMONIZED” to account for network change

EC 3000N is adjusted to be NIOSH-like

Using simple 2009-2010 relationship:

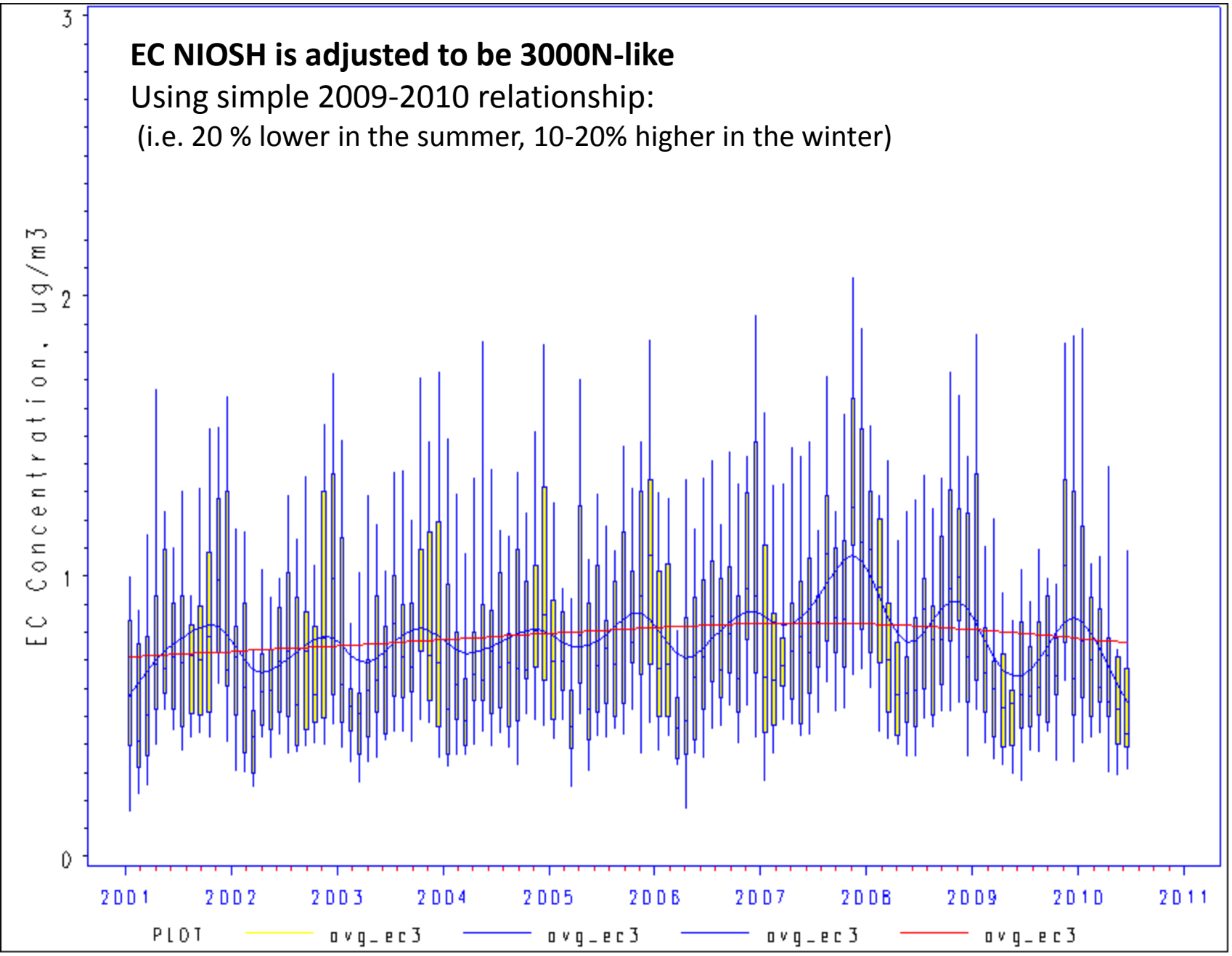
(i.e. 20 % higher in the summer, 10-20% lower in the winter)



EC NIOSH is adjusted to be 3000N-like

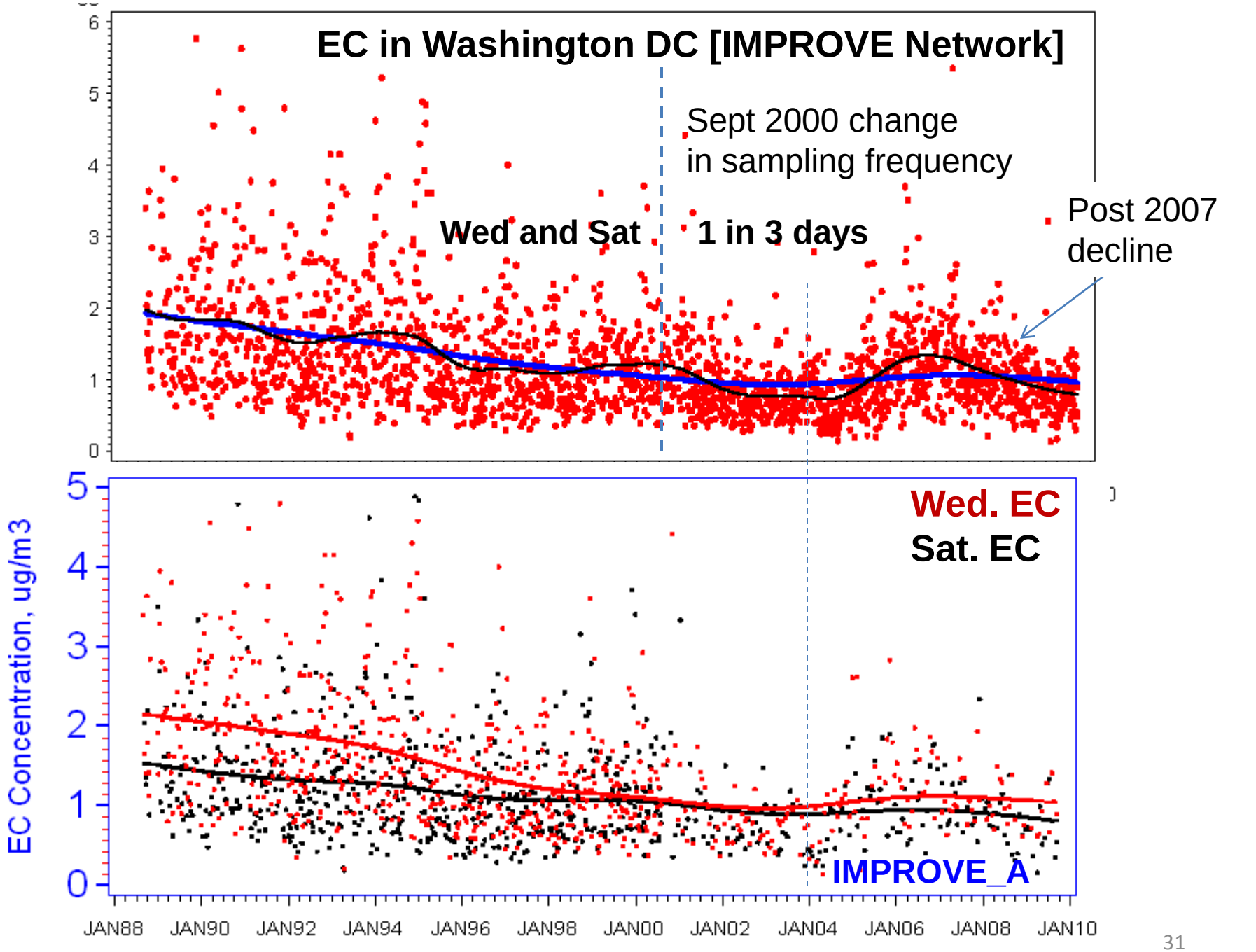
Using simple 2009-2010 relationship:

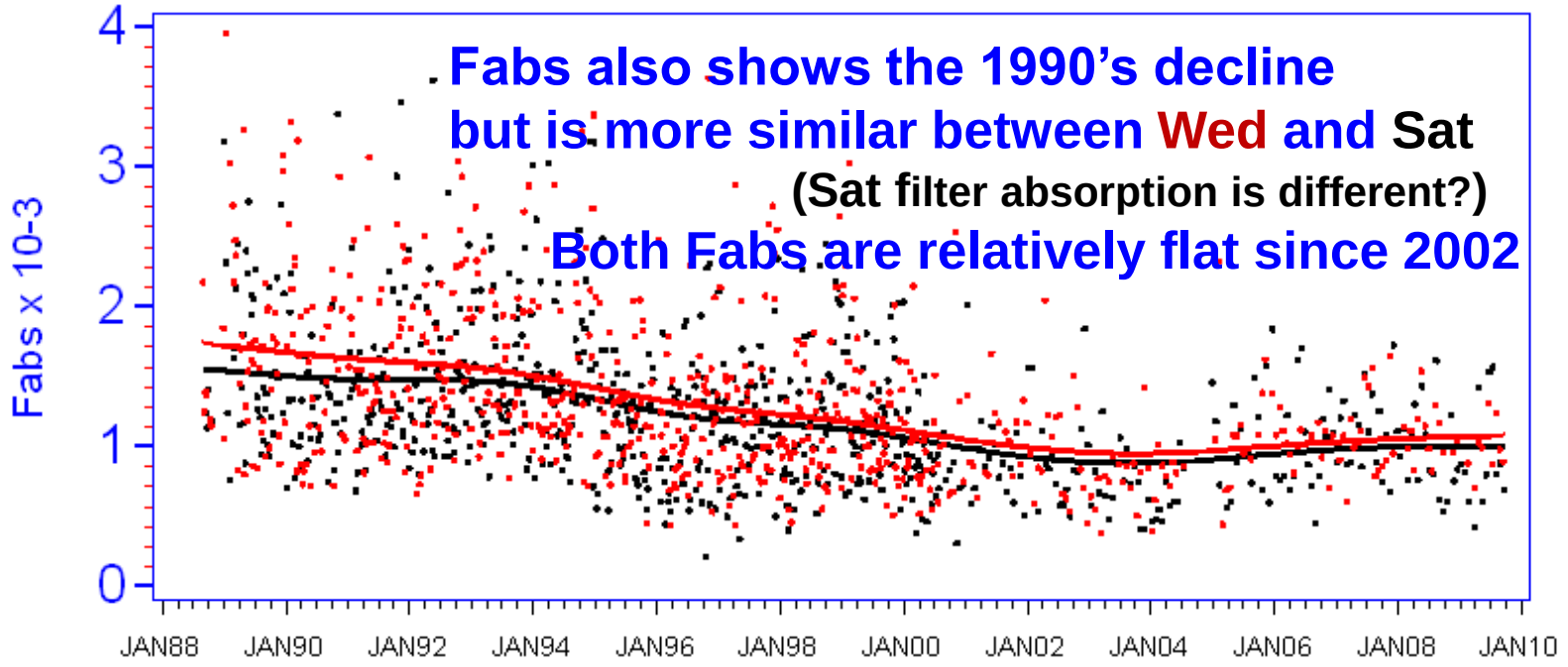
(i.e. 20 % lower in the summer, 10-20% higher in the winter)

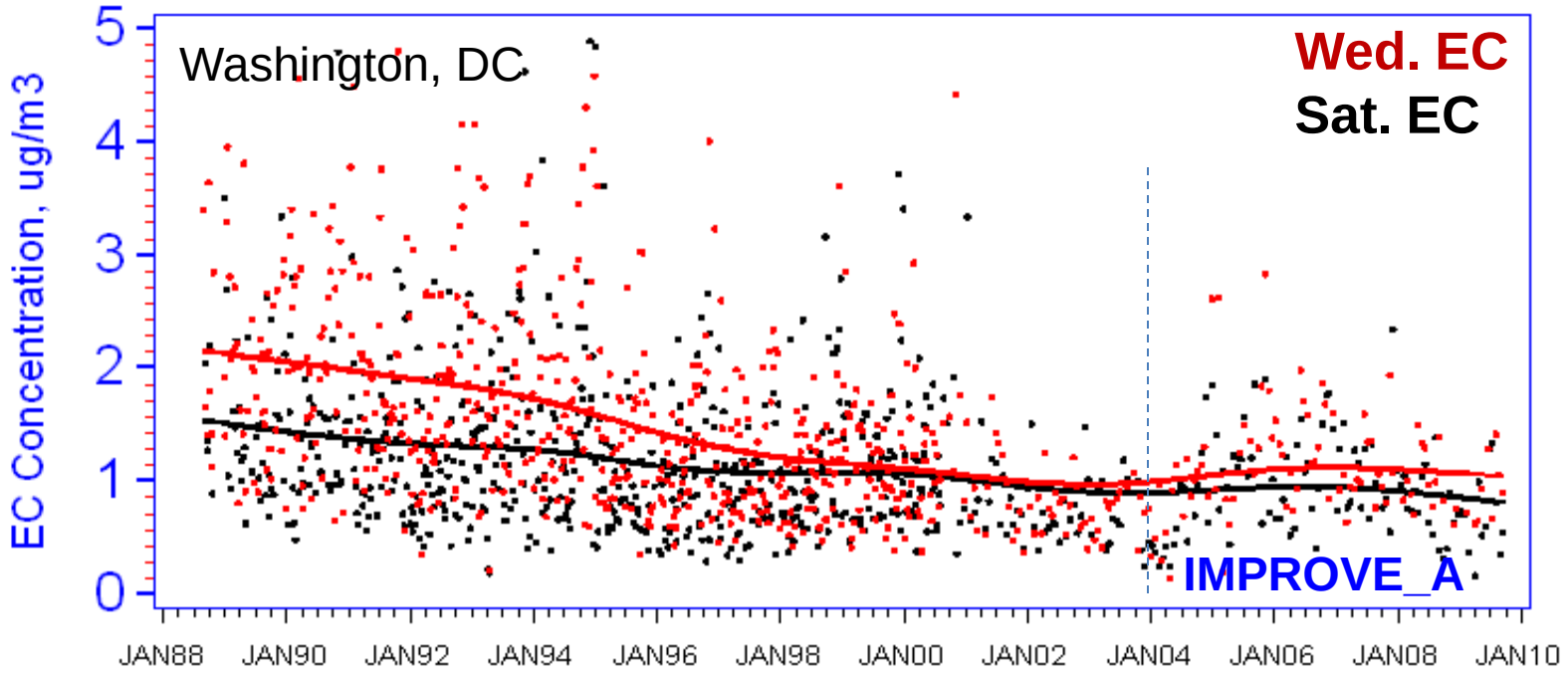


Urban EC & BC before 2002

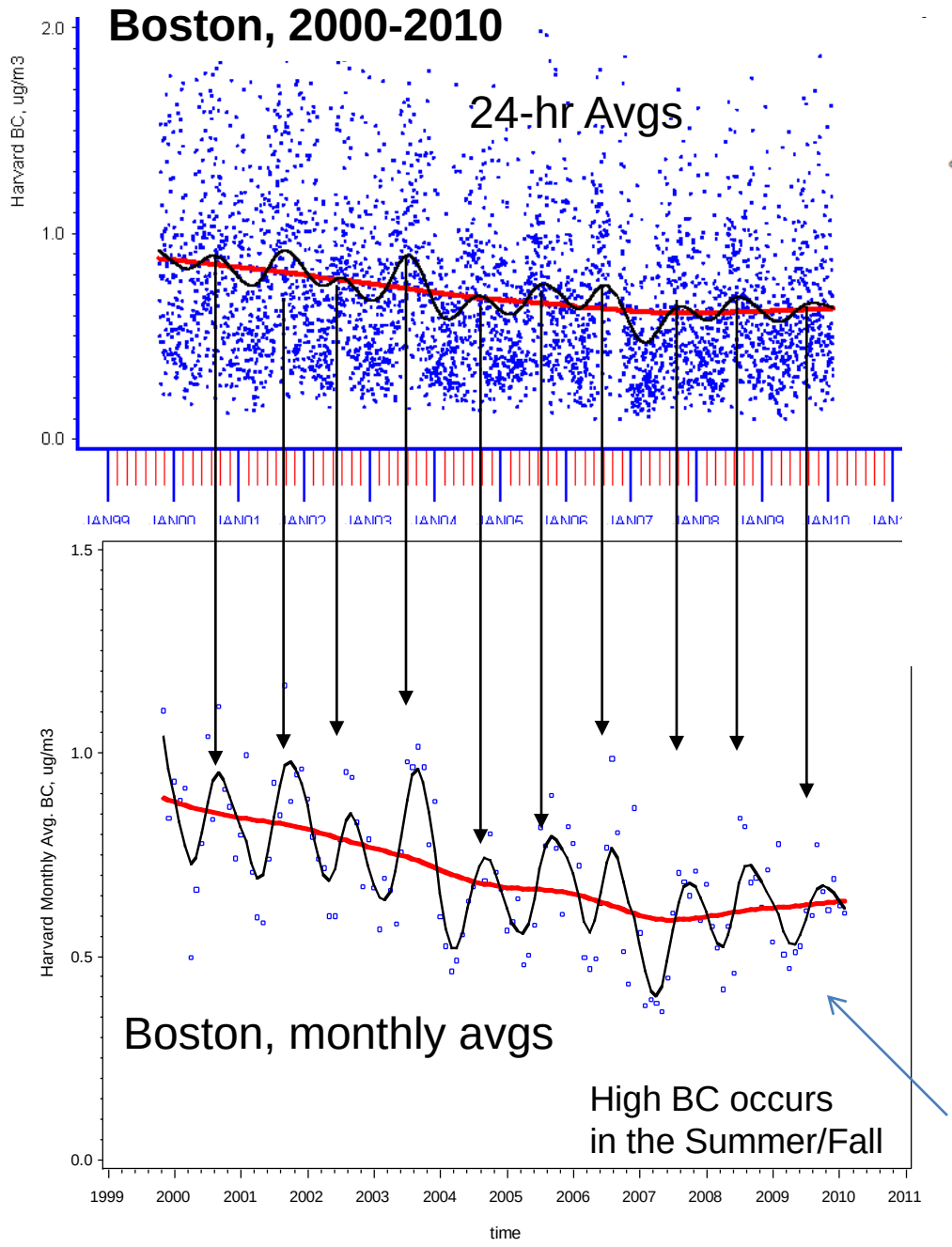
What can we say about longer-term urban EC trends


EC in Washington DC [IMPROVE Network]
Sept 2000 change
in sampling frequency
Wed and Sat
1 in 3 days
Post 2007
decline
Wed. EC
Sat. EC
IMPROVE_A
EC Concentration, ug/m3
0
1
2
3
4
5
6
JAN88
JAN90
JAN92
JAN94
JAN96
JAN98
JAN00
JAN02
JAN04
JAN06
JAN08
JAN10

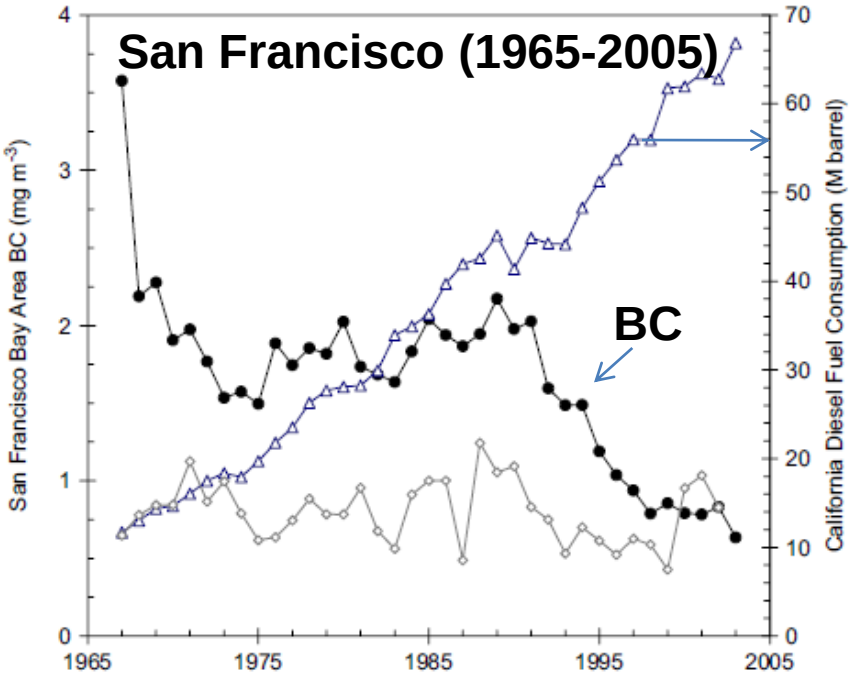

Fabs also shows the 1990's decline
but is more similar between Wed and Sat
(Sat filter absorption is different?)
Both Fabs are relatively flat since 2002
Fabs x 10-3
0
1
2
3
4
JAN88
JAN90
JAN92
JAN94
JAN96
JAN98
JAN00
JAN02
JAN04
JAN06
JAN08
JAN10


Washington, DC
Wed. EC
Sat. EC
IMPROVE_A
EC Concentration, ug/m3
0
1
2
3
4
5
JAN88
JAN90
JAN92
JAN94
JAN96
JAN98
JAN00
JAN02
JAN04
JAN06
JAN08
JAN10

Aethalometer BC



BC via COHs



BC was estimated using Coefficient of Haze measurements which are shown to be highly correlated with optical BC
Source: Kirchstetter et al., 2008.

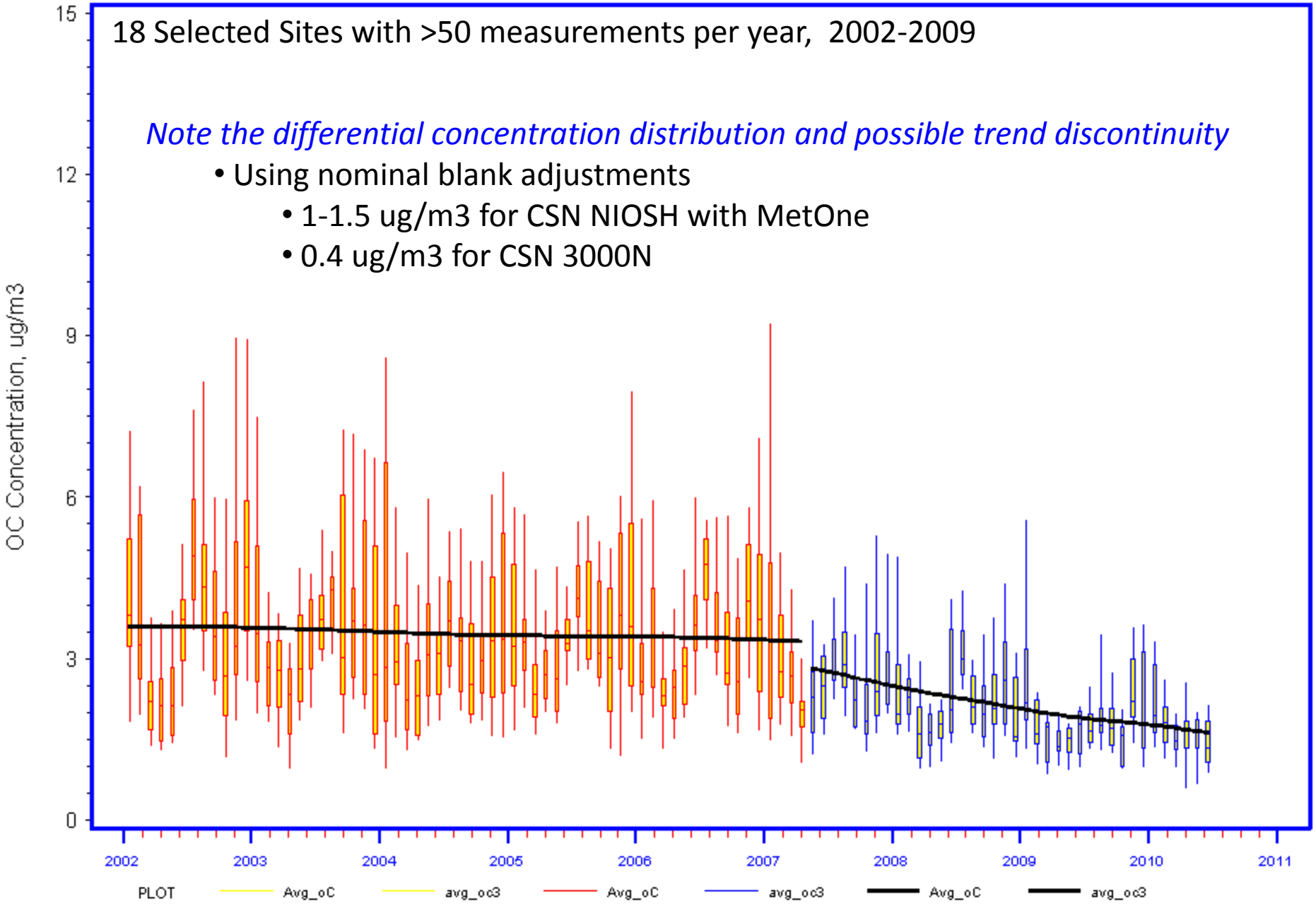
Relatively flat since 2004

Part 2: OC trends

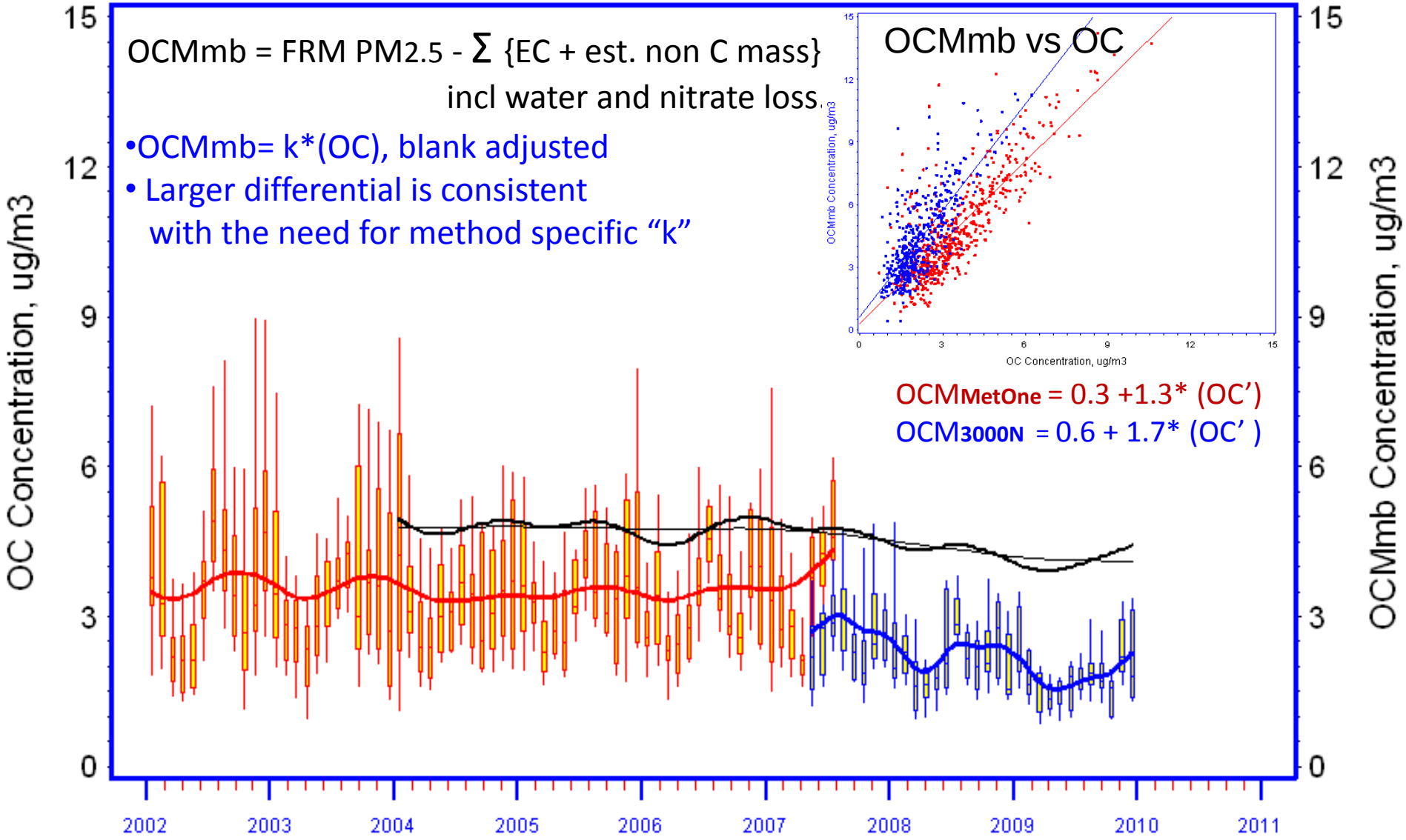
18 Selected Sites with >50 measurements per year, 2002-2009

Note the differential concentration distribution and possible trend discontinuity

- Using nominal blank adjustments
  - 1-1.5 ug/m3 for CSN NIOSH with MetOne
  - 0.4 ug/m3 for CSN 3000N

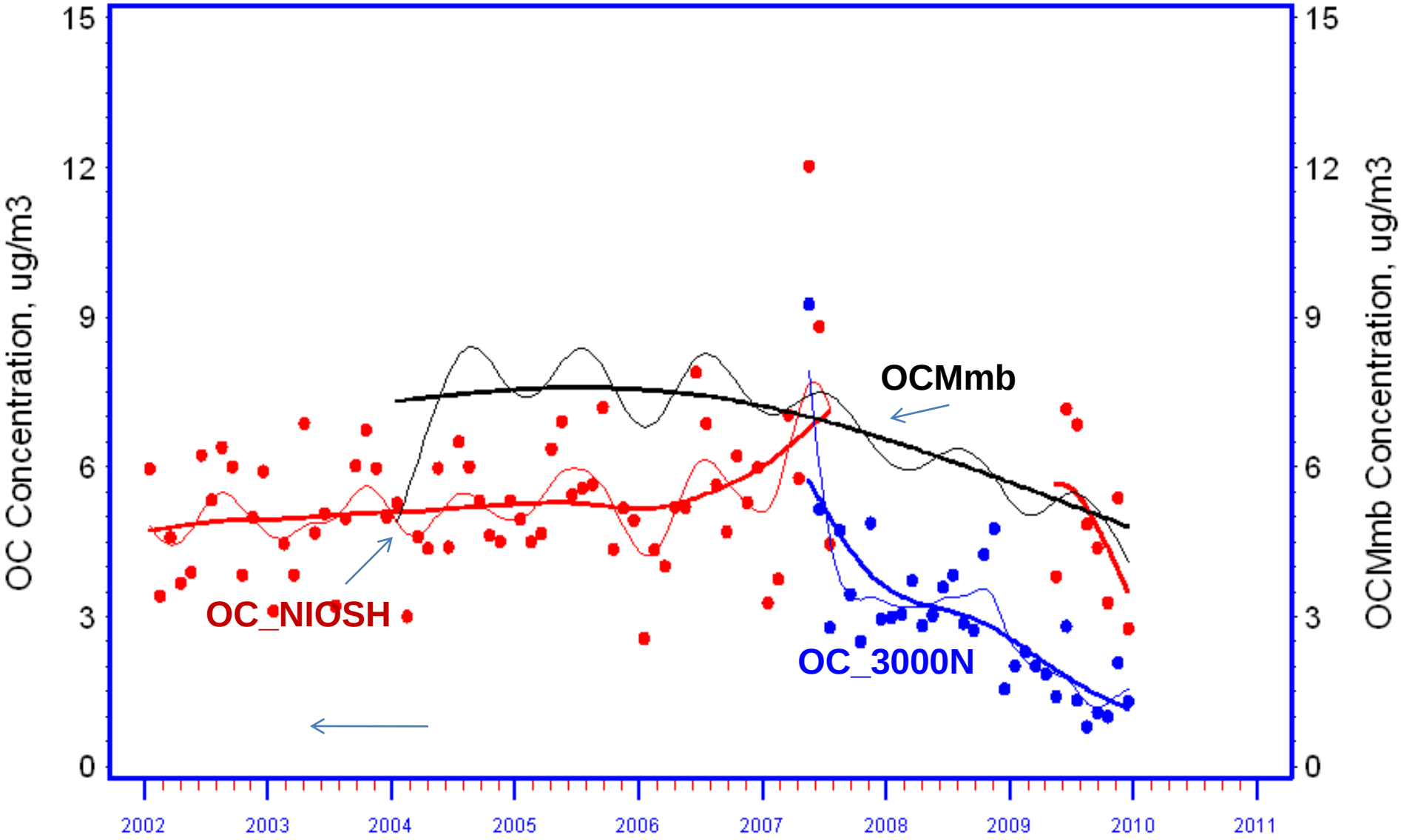


Overlay 18 sites with SANDWICHed OCMmb

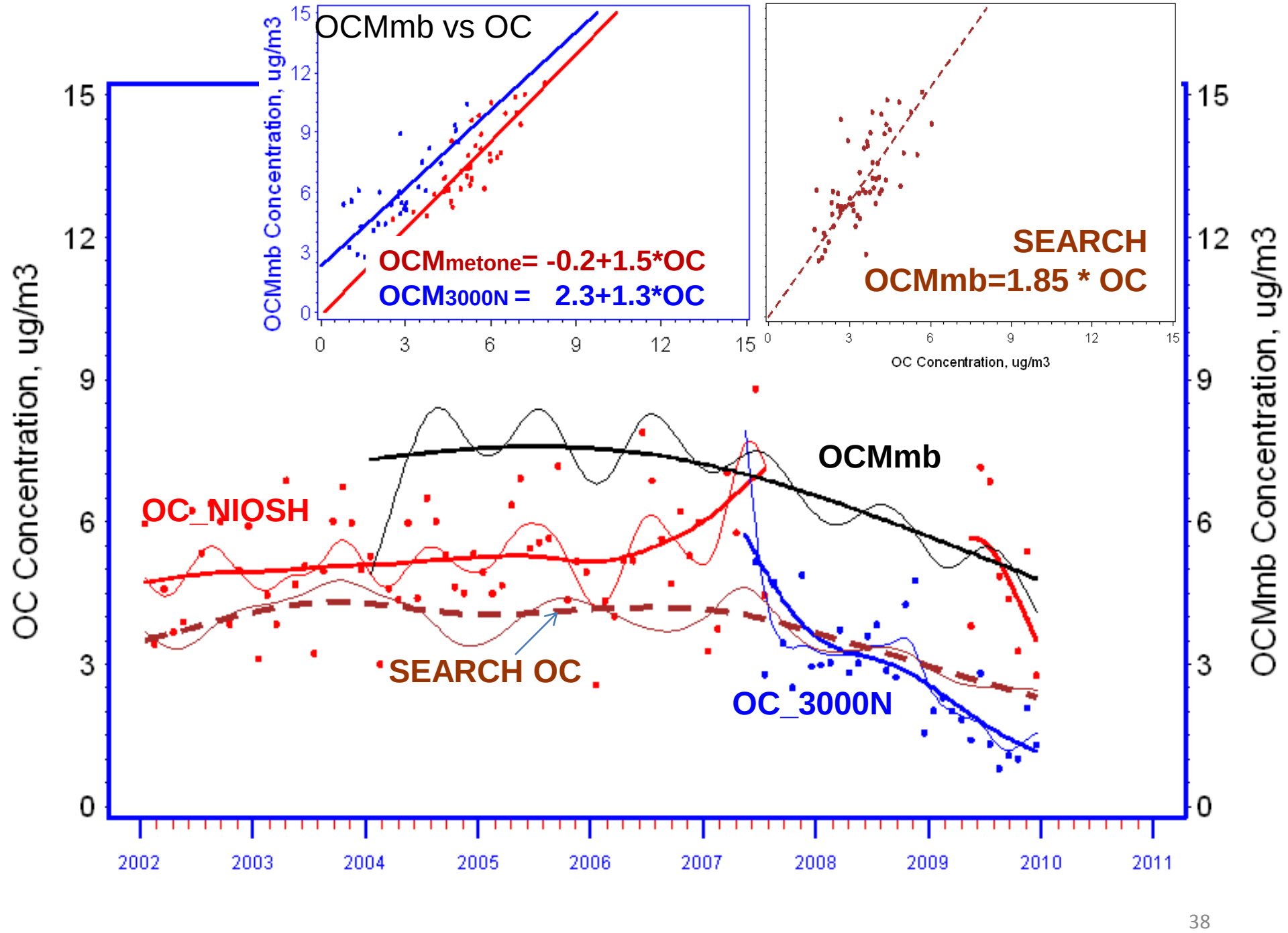


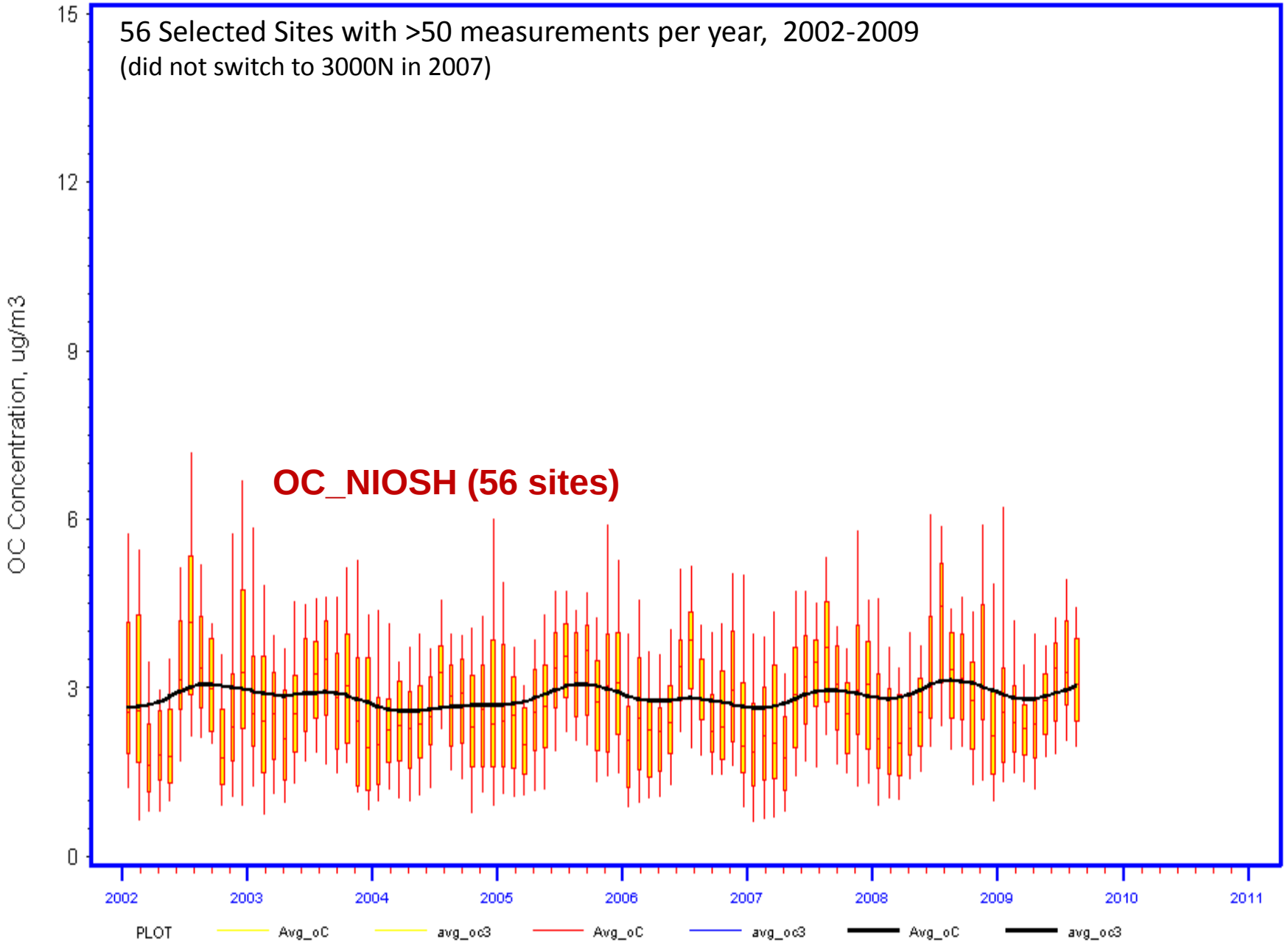
Birmingham

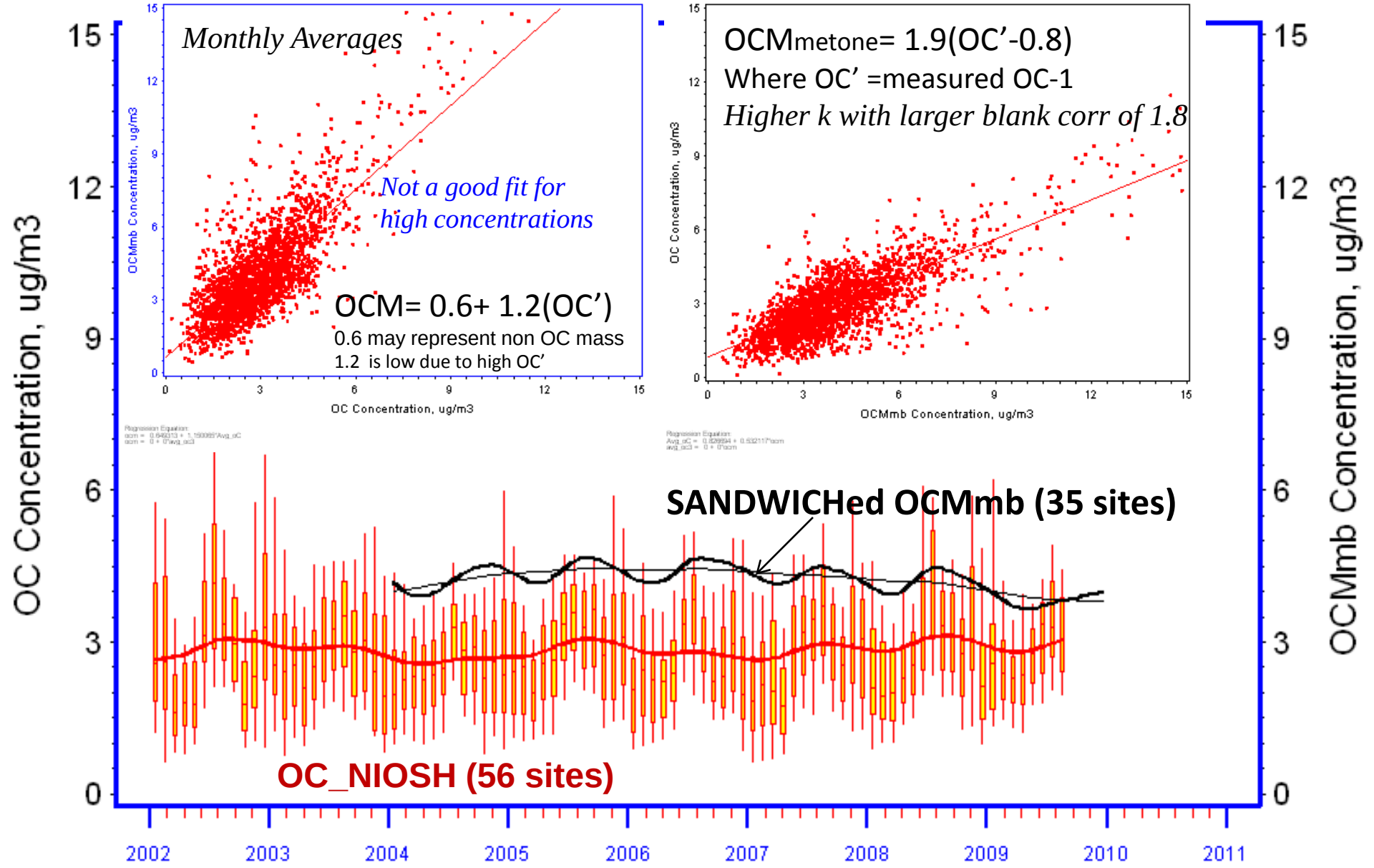
OC and OCMmb, monthly avgs.



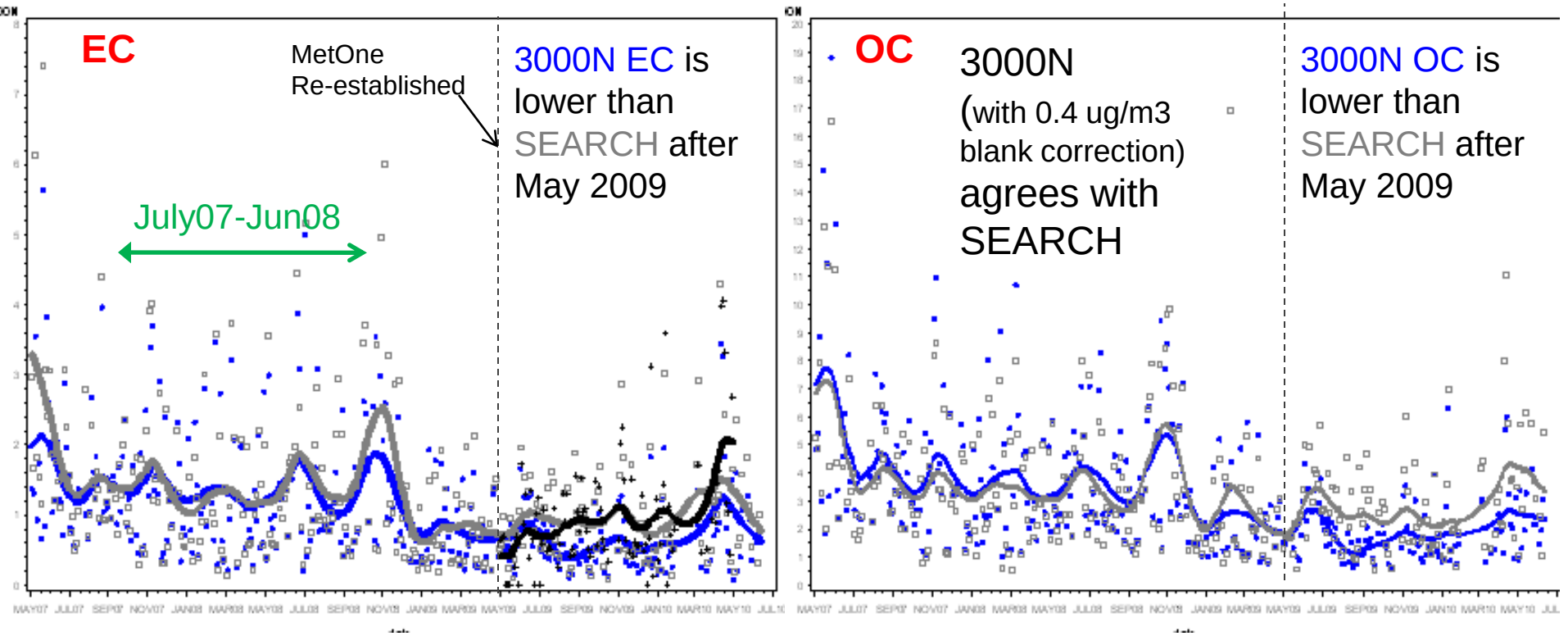
OCMmb= a+ k*(OC') OC' includes nominal blank corrections of 1 and 0.4 ug/m3


OCMmb vs OC
OCMmb Concentration, ug/m3
OCMmetone= -0.2+1.5*OC
OCM3000N = 2.3+1.3*OC
SEARCH
OCMmb=1.85 * OC
OC Concentration, ug/m3
OC Concentration, ug/m3
OCMmb Concentration, ug/m3
OCMmb
OC_NIOSH
SEARCH OC
OC_3000N
0
3
6
9
12
15
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011


56 Selected Sites with >50 measurements per year, 2002-2009
(did not switch to 3000N in 2007)
OC_NIOSH (56 sites)
OC Concentration, ug/m3
15
12
9
6
3
0
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
PLOT
Avg_oC
avg_oc3
Avg_oC
avg_oc3
Avg_oC
avg_oc3


Monthly Averages
Not a good fit for high concentrations
OCM= 0.6+ 1.2(OC')
0.6 may represent non OC mass
1.2 is low due to high OC'
OCMmetone= 1.9(OC'-0.8)
Where OC' =measured OC-1
Higher k with larger blank corr of 1.8
OC Concentration, ug/m3
OCMmb Concentration, ug/m3
SANDWICHed OCMmb (35 sites)
OC_NIOSH (56 sites)
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011

Birmingham,
Shows Declines in EC and OC (SEARCH and CSN 3000N)



Randy Dillard (Jeff Co. AL) is checking for possible changes to CSN instrumentation

SEARCH Carbon Protocol:

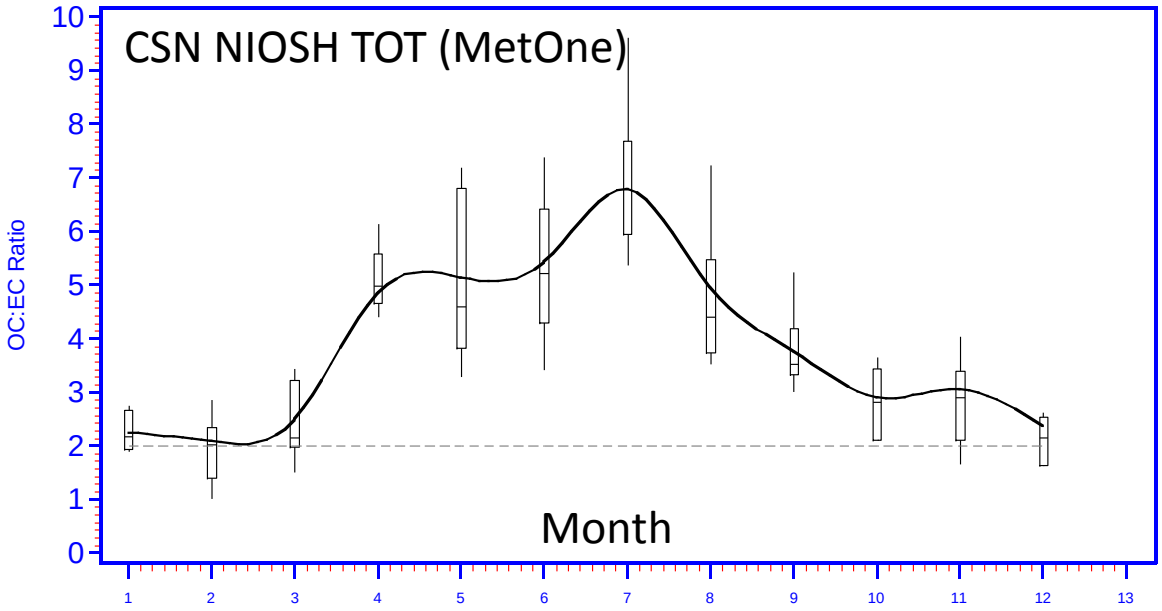
IMPROVE TOR by DRI

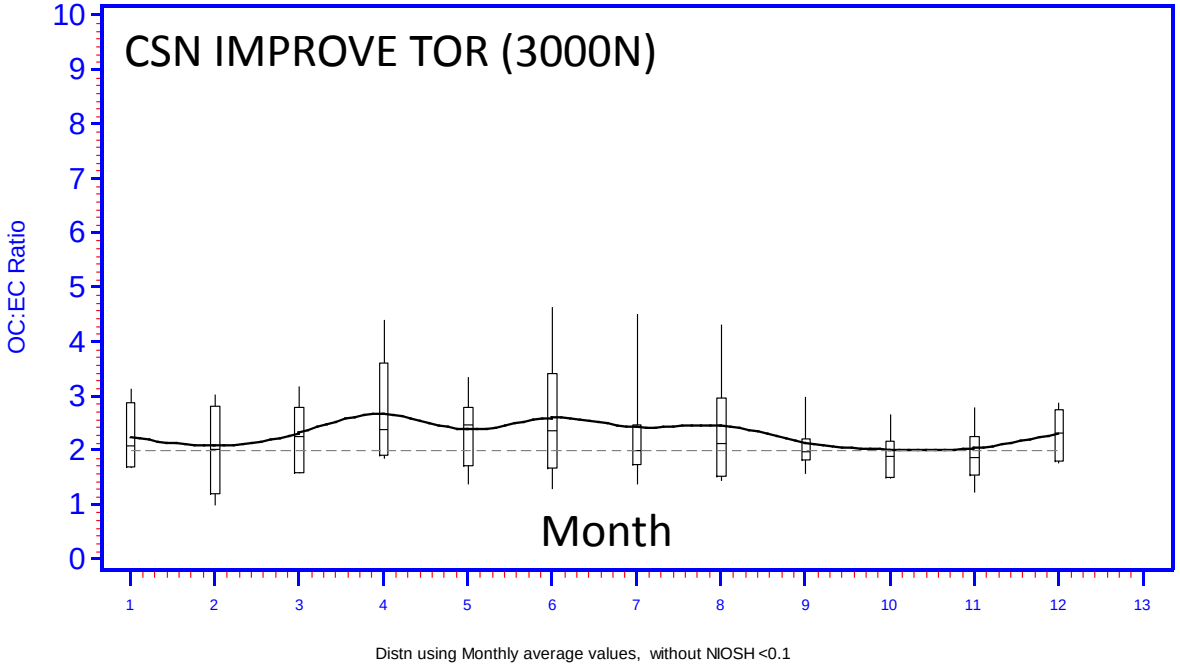
Sampler: 16.7 LPM, 37mm Pallflex® Tissuquartz, Denuder, backupfilter

OC (blank corrected, using quarterly average values) = OCQF + OCQBQ - 2OCbQF

backup field blank

OC:EC ratios and Sampling Artifacts





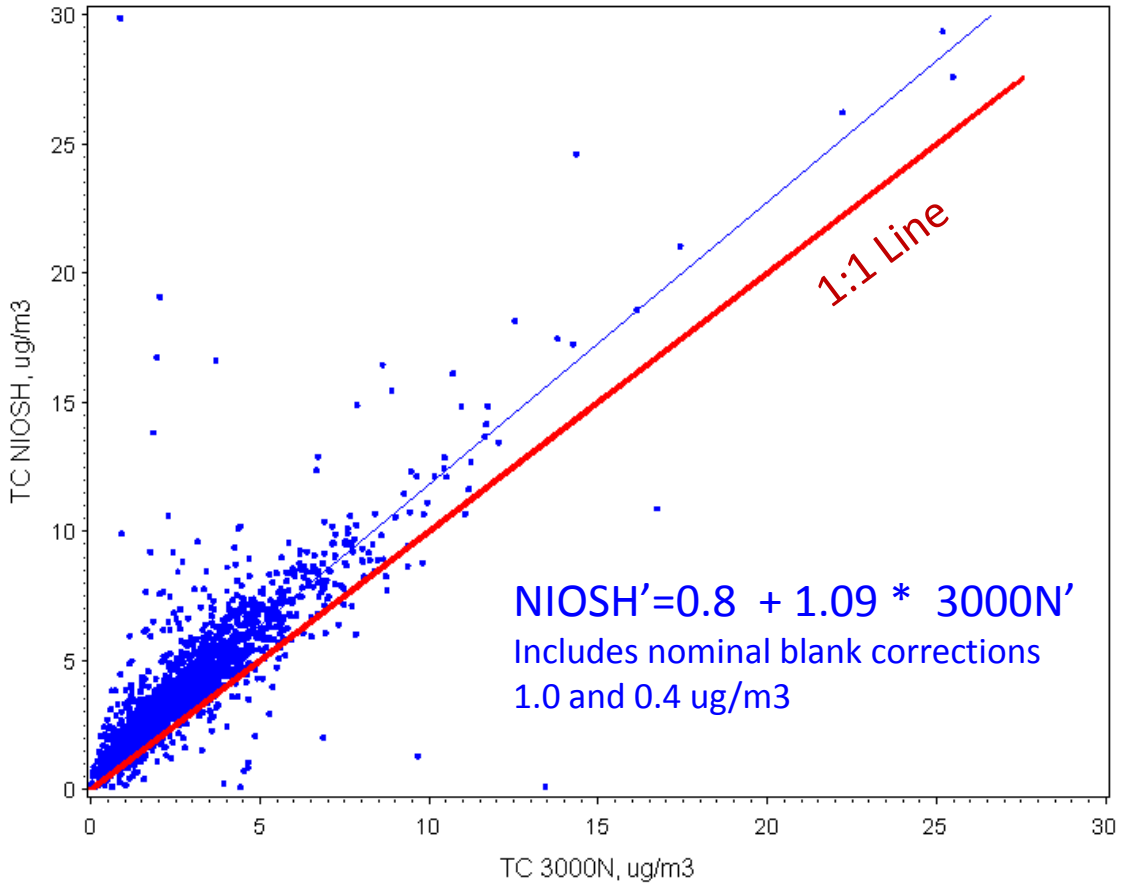
Urban OC:EC ratio

Is the true urban ambient ratio somewhere in between?

With nominal blank adjustments

Ratios are not the same because TC is <u>not</u> the same
different CSN samplers, face velocity and artifacts- positive (and negative?)

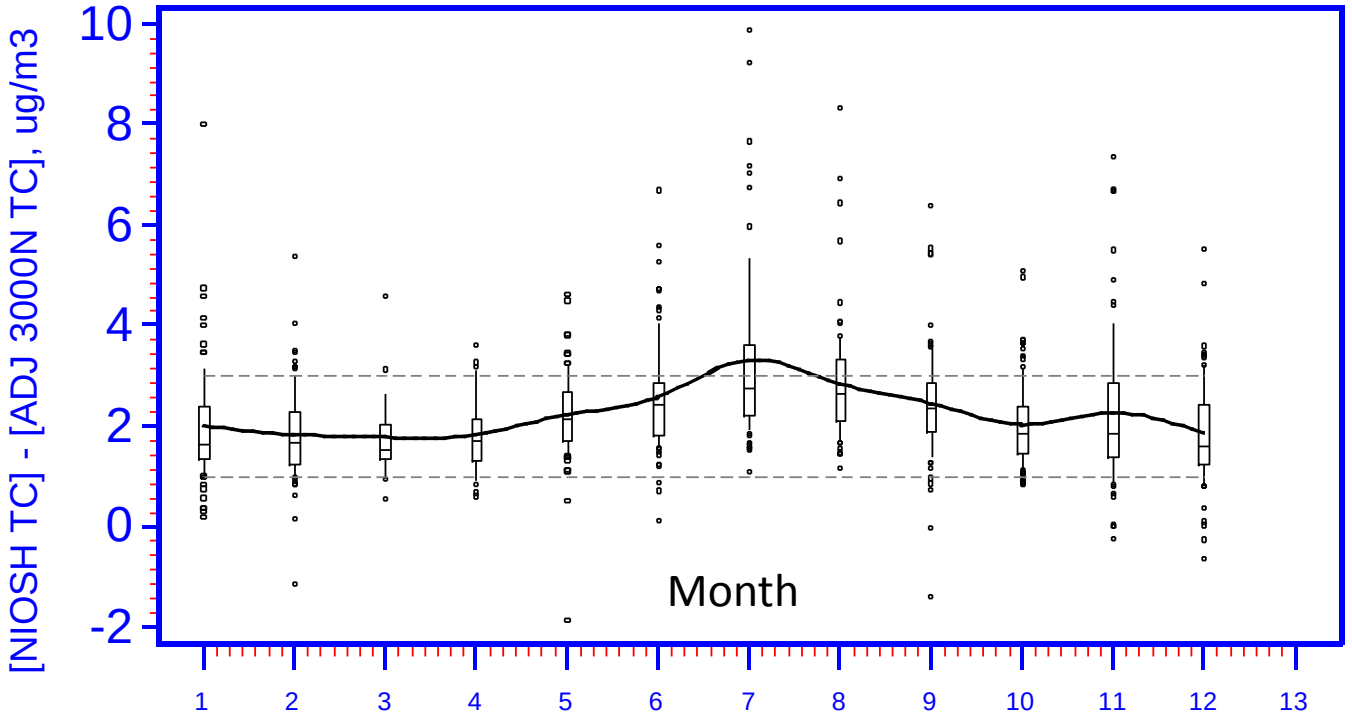
Low flow rate sampler collects relative more OC
(and high flow rate sampler collects relatively more)



Note: Chow et al. (2009)
CSN NIOSH = 1.65 + 1.08 IMPROVE (PHOE1)
(without blank corrections)

Relative Difference is Seasonal
(Additional 2-3 ug/m3 NIOSH TC)

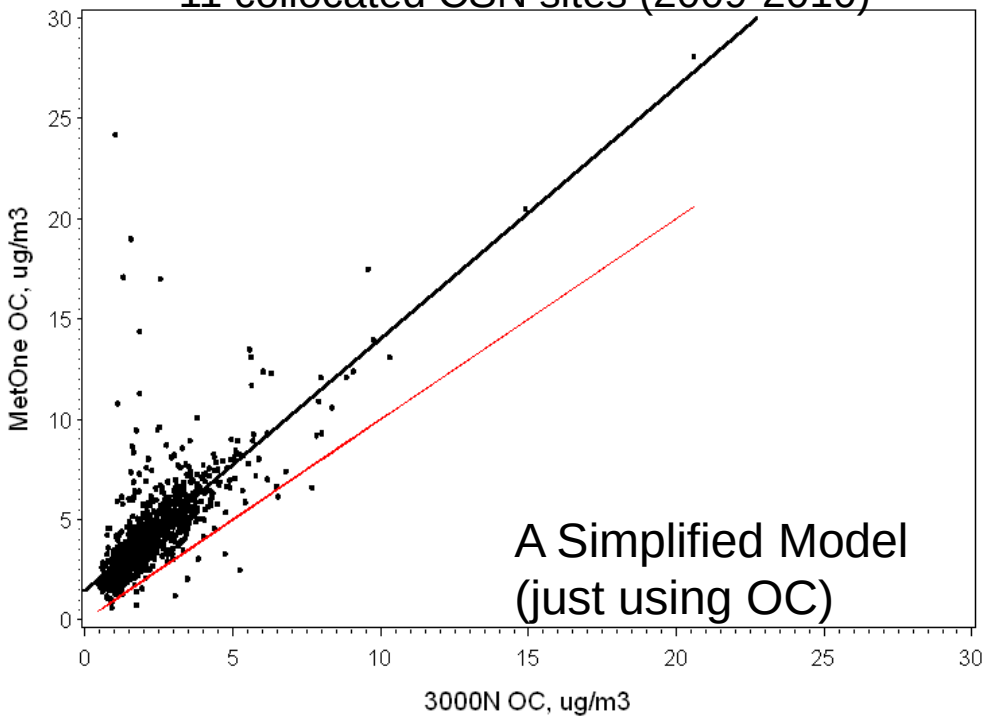
Represents estimated CSN NIOSH positive artifact and/or lost 3000N semi-volatile OC



As per Schichtel et.al.,

- Relating CSN to IMPROVE data:
  - $[EC]^{CSN\text{-}URG} = [EC]^{IMP}$
  - $[OC]^{CSN\text{-}URG} = [OC]^{IMP} + A^{CSN\text{-}URG}$
  - $[TC]^{CSN\text{-}Metone} = [EC]^{IMP} + (1+B^{IMP}*)[OC]^{IMP} + A^{CSN\text{-}MetOne}$
  - $[EC]^{CSN\text{-}Metone} = (1-g)*[EC]^{IMP}$; multiplicative bias between EC by TOT and TOR

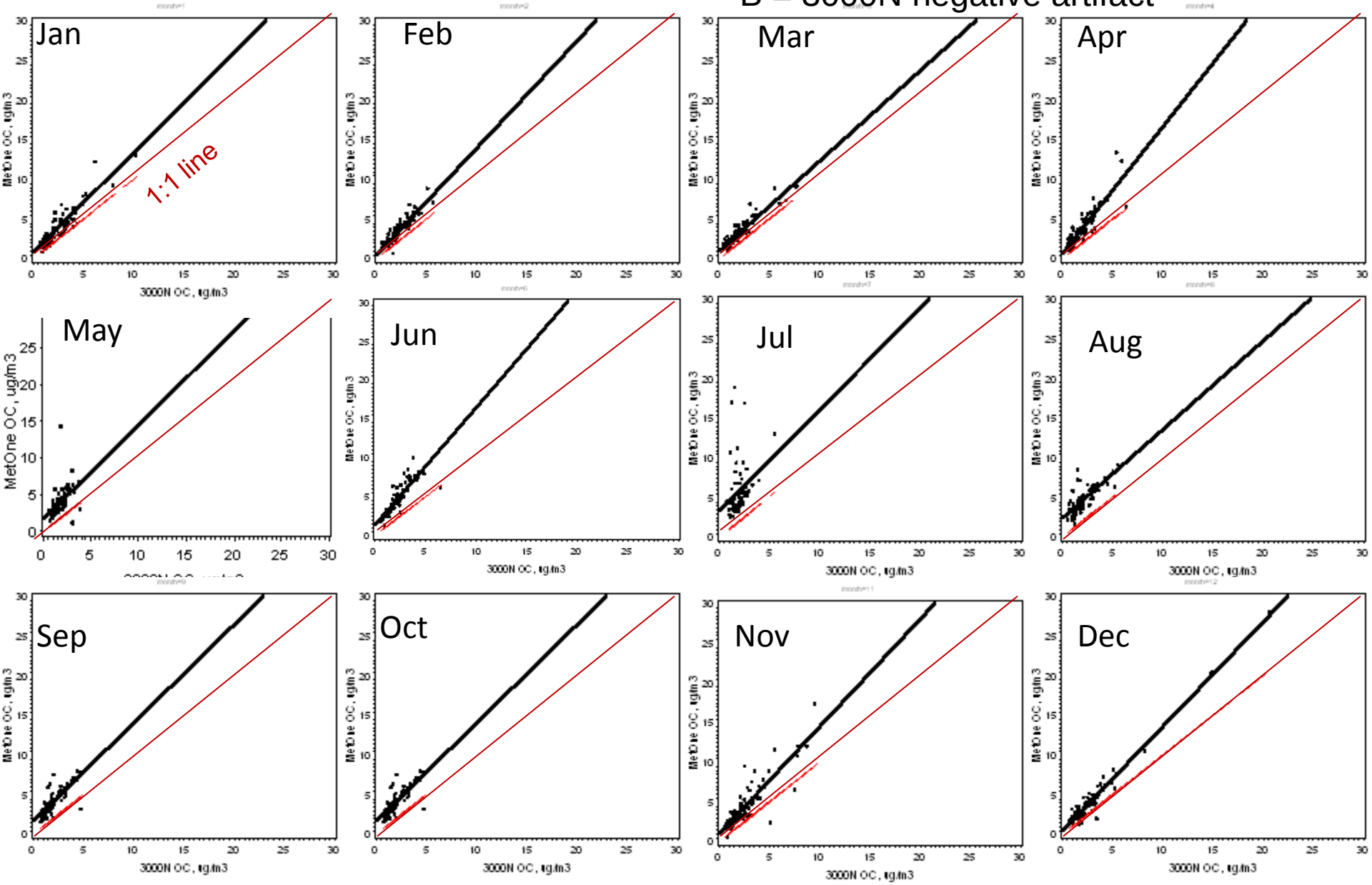
11 collocated CSN sites (2009-2010)



Without any OC adjustments

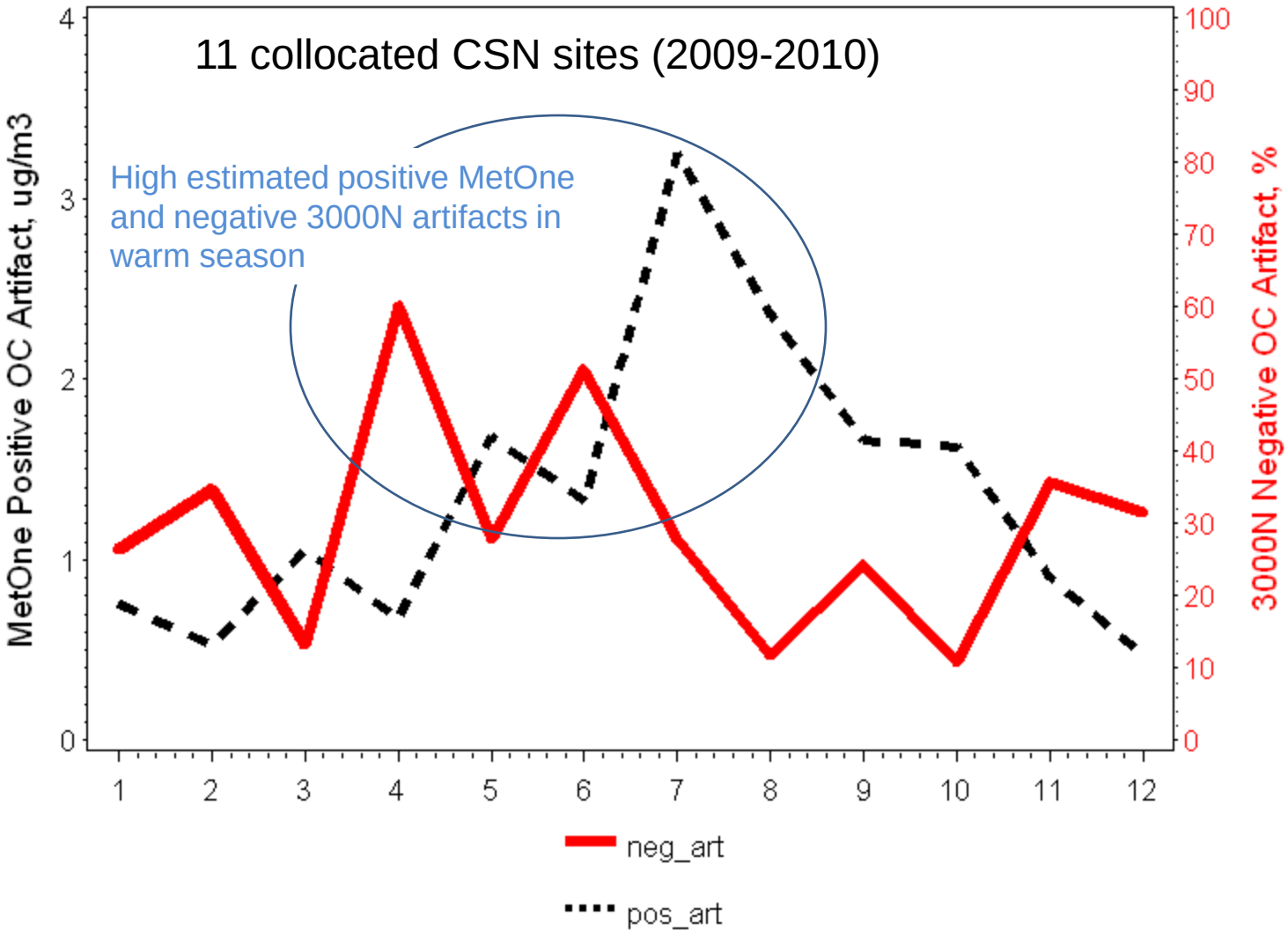
MetOne OC = A + (1+B) 3000N ➔ A = MetOne positive artifact

B = 3000N negative artifact



11 collocated CSN sites (2009-2010), by month - without any OC adjustments

MetOne OC = A + (1+B) 3000N ➔ A = MetOne positive artifact
B = 3000N negative artifact



Conclusions/Questions

Part 1 (EC Trends)

- Urban trends appear level 02-07, followed by 07-09 decline
- Evidence that urban declined during the 1990's thru early 2000's.
- Why do CSN EC agree?
  - Due to sampling artifacts? ….pyrolosis?… and/or different 2009 -10 conditions?
  - Would this relationship hold prior to 2009? Analyze archived filters?
  - e.g. Why does Birmingham behave differently (check samplers….)

Part 2 (OC Trends, OC:EC)

- What are the CSN sampling artifacts?
  - MetOne -- positive artifact (> >1 ug/m3), and party responsible for high EC (pyrolized carbon?)
  - URG3000N -- negative? , and partly responsible for low OC:EC ratio?
- Implications ?...Sampling study needed to estimate negative artifact?