# IMPROVE TOR Analysis for Carbon – Assessment of Transition to a New Analyzer

Summary of DRI's assessment report
prepared by Marc Pitchford - 1/24/05

# Motivation for replacing the IMPROVE carbon analyzer

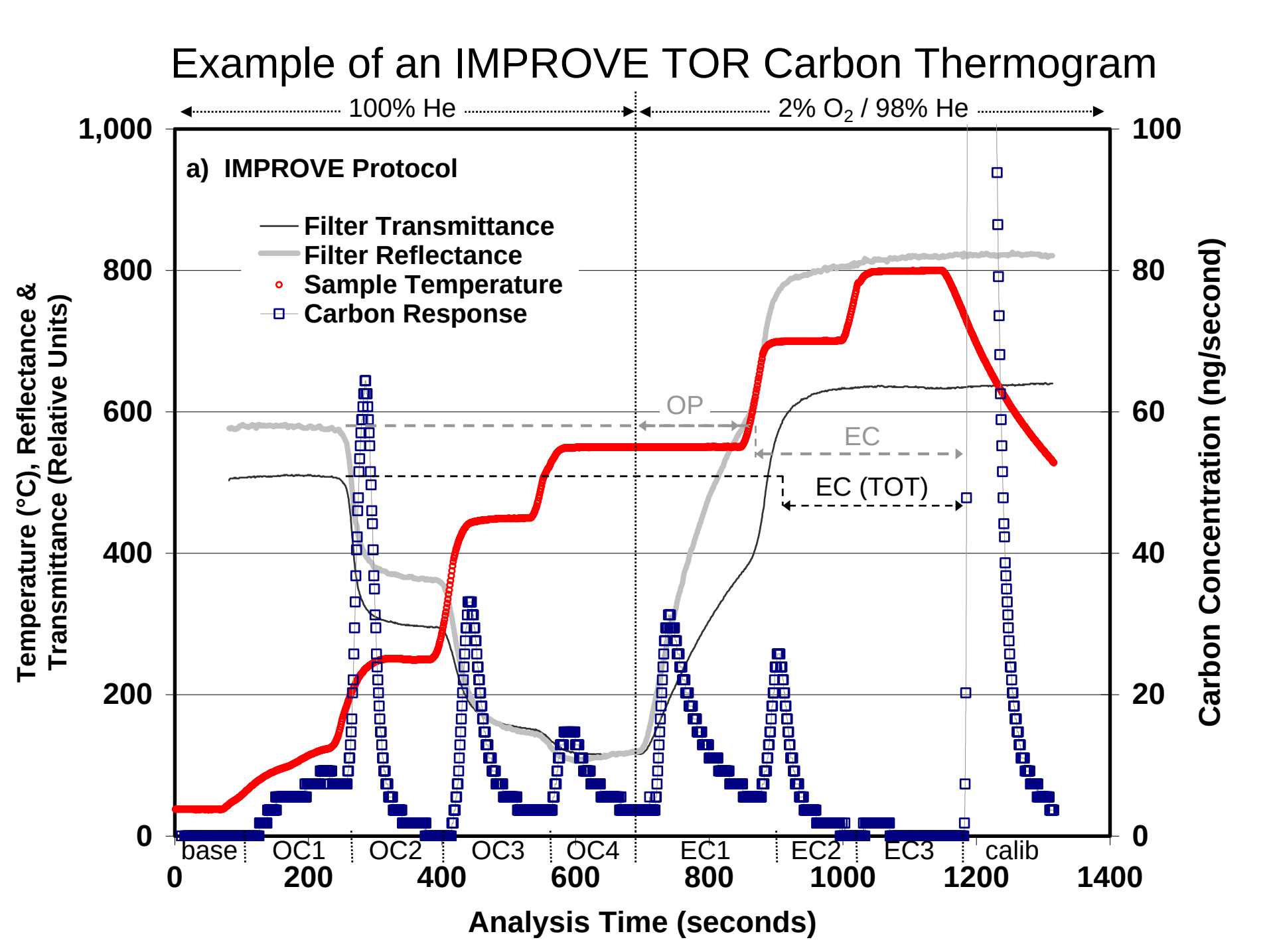
- Current systems (DRI/OGC analyzers) built in the mid-1980s are antiquated
  - frequently breaking
  - some parts are no longer available
  - only 4 of 5 systems are currently operational
  - already affecting analysis schedules
- Proposed replacement system (Model 2001 carbon analyzers) are more capable
  - Generates both reflectance and transmission data
  - Has better precision because of better controlled sample temperatures & lower $O_2$ contamination of the Helium atmosphere

# Desired characteristics of a replacement carbon analyzer

- Data comparable to the current IMPROVE system for total carbon (TC) and the organic carbon (OC) and elemental carbon (EC) splits
  - Critical because OC & EC are required to calculate light extinction for the regional haze rule
- As good or better analytical precision as the current system for OC, & EC
  - Important since OC & EC data have less precision than other components, though much of this is due to the uncertainty in field blank values used to adjust the OC data
- Data comparable to the current system for OC and EC subfraction data (OC1, OC2, OC3, OC4, OP, EC1, EC2, & EC3)
  - Desirable because subfraction data have been used in some receptor modeling source attribution

# How does Thermal Optical Reflectance Analysis Work?

- Carbon released from a sample that is raised to specific temperatures in a helium atmosphere is measured and labeled organic carbon
  - The 4 OC subfractions correspond to the carbon measured at each of the 4 temperatures used during the OC phase of the analysis
- Then oxygen is added and the temperature is raised so that additional sample carbon is oxidized, released and measured as elemental carbon
  - The 3 EC subfractions correspond to the carbon measured at each of the 3 temperatures used during the EC phase of the analysis
- Changes in optical reflectance of the filter (how dark it looks) during the analysis process are used to adjust biases due to
  - charring of OC that could be mistaken for EC, or
  - oxidation of EC in the helium atmosphere that could be mistaken for OC


Example of an IMPROVE TOR Carbon Thermogram
100% He
2% O2 / 98% He
a) IMPROVE Protocol
Filter Transmittance
Filter Reflectance
Sample Temperature
Carbon Response
OP
EC
EC (TOT)
base
OC1
OC2
OC3
OC4
EC1
EC2
EC3
calib
Temperature (°C), Reflectance & Transmittance (Relative Units)
Carbon Concentration (ng/second)
Analysis Time (seconds)
0
200
400
600
800
1000
1200
1400
1,000
800
600
400
200
0
100
80
60
40
20
0

# Initial Comparability of the Current and New TOR Analyzers

- Model 2001 system was programmed to operate the same as the current system (i.e. same temperatures, gas atmosphere, timing, etc.)
- TC, OC,& EC data were comparable for a wide range of IMPROVE and other samples (~240 samples),
- But the subfraction where not comparable though they were correlated
- DRI initiated extensive assessments (~10 months) to understand the differences between the systems and to make adjustments where possible

# DRI Assessments/Results

- Developed a method to calibrate analyzers' thermocouple temperature to actual sample temperature – using temperature indicator liquids on the filter punches
  - DRI/OGC – samples are 10$^{o}$C – 50$^{o}$C hotter than thermocouple
  - Model 2001 – samples are 5$^{o}$C – 20$^{o}$C hotter than thermocouple
  - Model 2001 has much better temperature precision (between separate analyzers) than the DRI/OGC
  - Model 2001 has much faster heating response time than the DRI/OGC

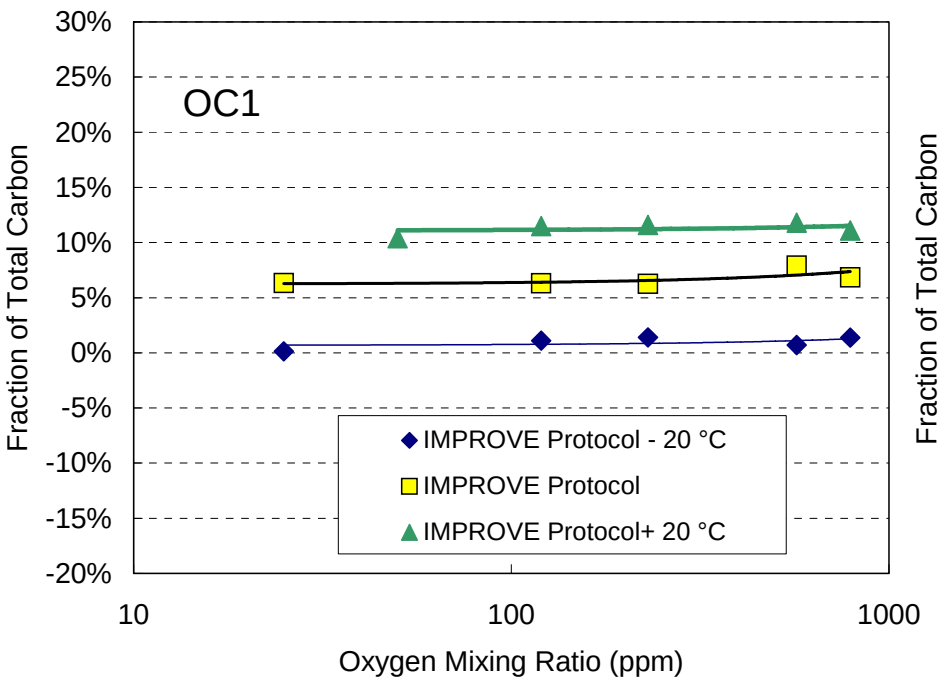
# DRI Assessments/Results (continued)

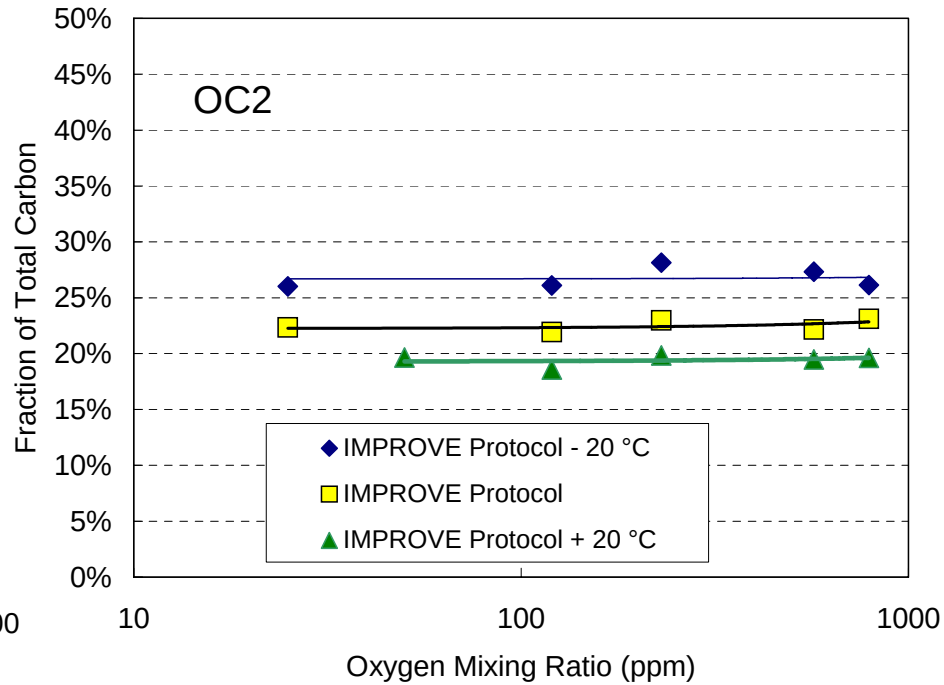
- Measured trace $O_2$ concentrations diffused into the helium atmosphere in the sample oven
  - $O_2$ concentration in ultra-pure helium gas used is <1ppmv
  - DRI/OGC $O_2$ – 150 to 320ppmv with an average among analyzers of ~250ppmv
  - Model 2001 $O_2$ – ~25ppmv

# DRI Assessments/Results (continued)

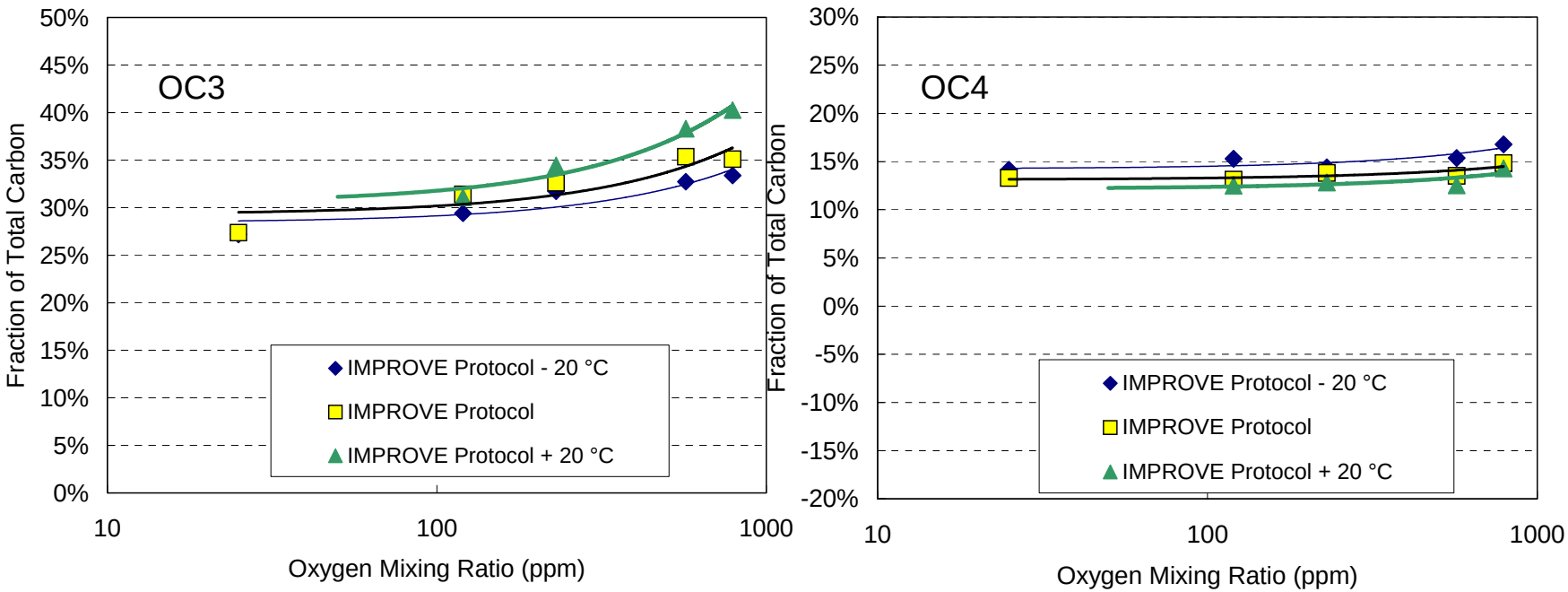
- Measured the sensitivity of OC and EC and subfractions to sample temperature and $O_2$ levels in the helium in the ranges seen in the DRI/OGC analyzers using Fresno samples
  - OC & EC are insensitive to temperature or $O_2$
  - OC1, OC2, OC3, OP, & EC2 are temperature dependent
  - OC3, OP, and EC1 are $O_2$ level dependent

# Impact of temperature and atmospheric environment (O2) on carbon fractions (OC1 and OC2)

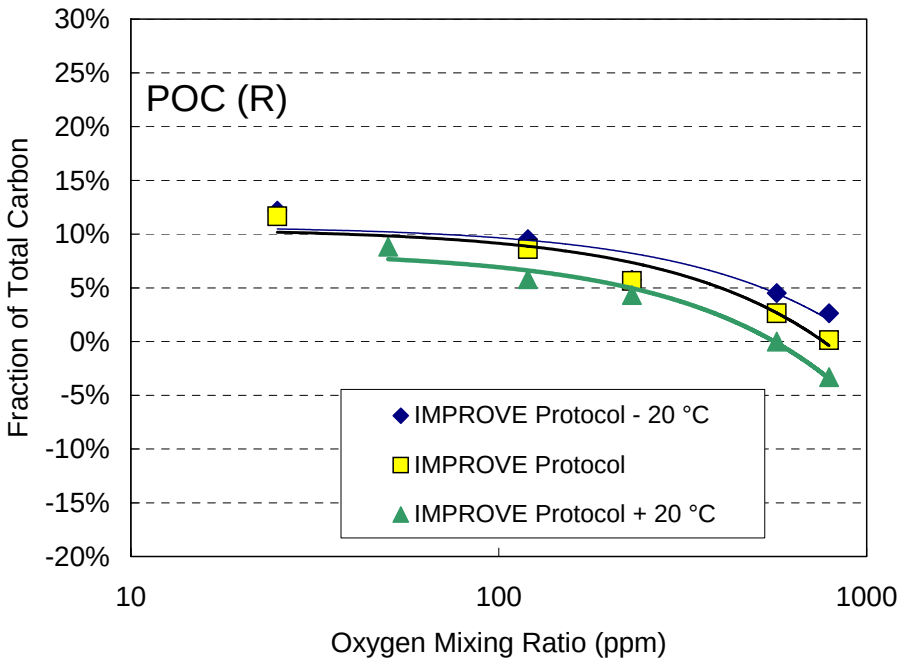


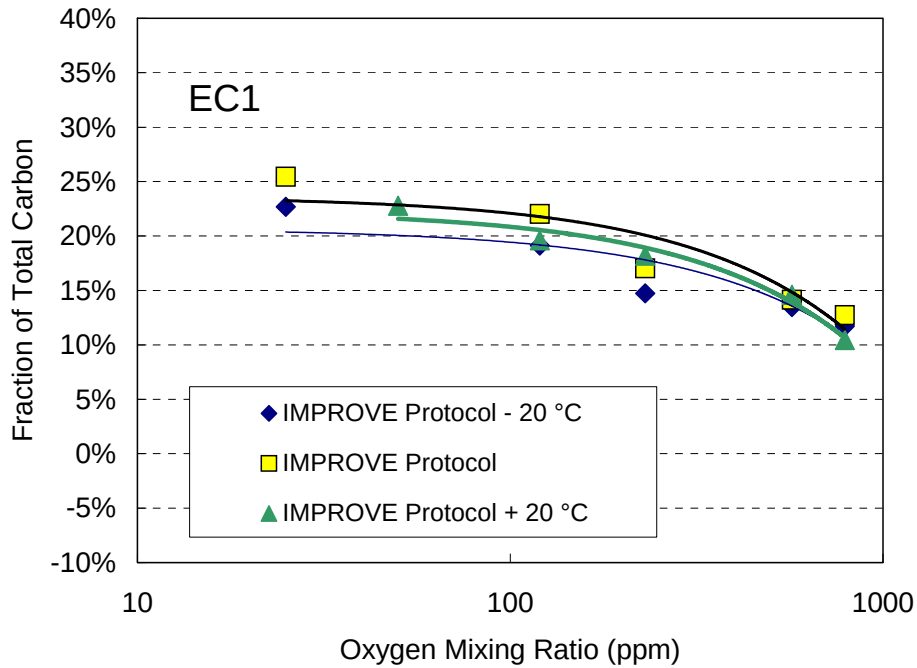



# Impact of temperature and atmospheric environment (O2) on carbon fractions (OC3 and OC4)

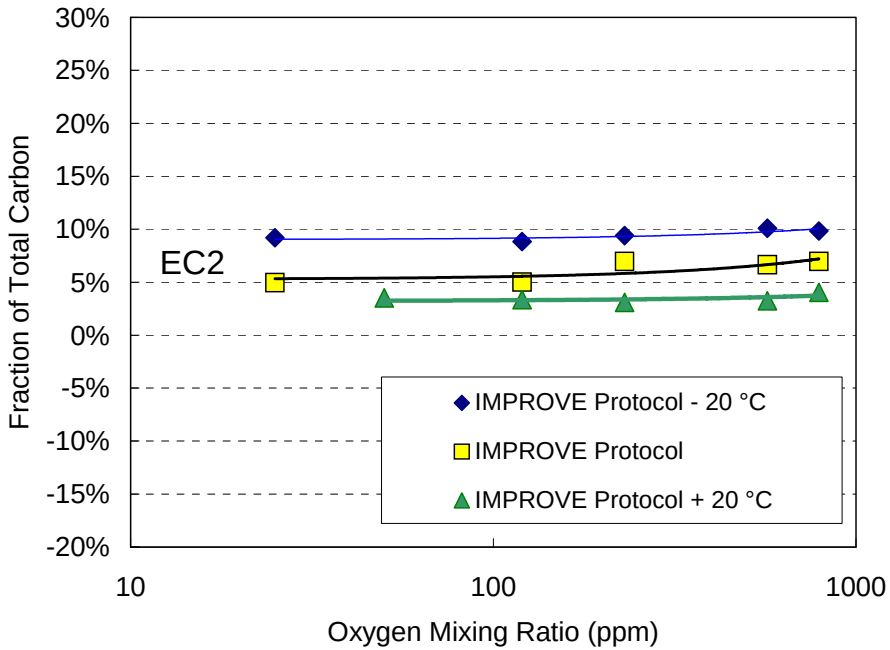


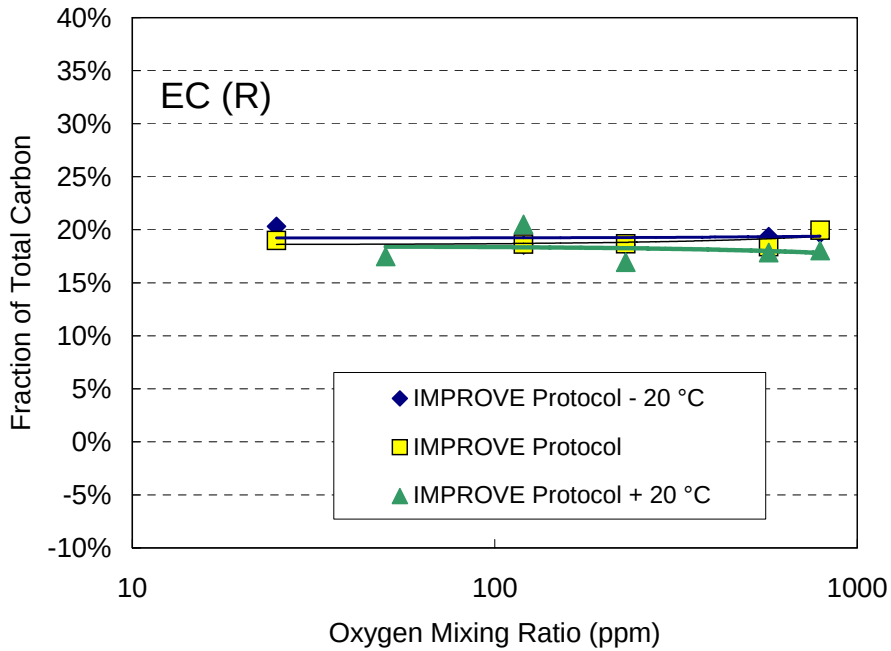
# Impact of temperature and atmospheric environment (O2) on carbon fractions (OP and EC1)



# Impact of temperature and atmospheric environment (O2) on carbon fractions (EC2 and ECR)



# Alternate Model 2001 Operational Protocols

- IMPROVE Protocol – uses the nominal temperatures for the DRI/OGC analyzer
  - Use linear adjustment to relate new carbon subfraction measurements to historic data
- IMPROVE-A Protocol – uses the same sample temperatures (rounded to nearest 10$^{o}$C) as in the DRI/OGC analyzer
  - Attempt to better reproduce carbon subfraction of “typical” DRI/OGC without having to add $O_2$
- IMPROVE(250) – 250ppmv $O_2$ in the helium during the OC analysis phase and temperatures optimize for best agreement with DRI/OGC on Fresno samples
  - Attempt to better match the “typical” DRI/OGC carbon subfractions

# Temperature Protocols

| | IMPROVE ($^{o}$C) | IMPROVE-A ($^{o}$C) | IMPROVE (250) ($^{o}$C) |
|---|---|---|---|
| OC1 | 120 | 140 | 142 |
| OC2 | 250 | 280 | 238 |
| OC3 | 450 | 480 | 468 |
| OC4 | 550 | 580 | 579 |
| EC1 | 550 | 580 | 591 |
| EC2 | 700 | 740 | 738 |
| EC3 | 800 | 840 | 841 |

# Assessment of Alternate Model 2001 Protocols

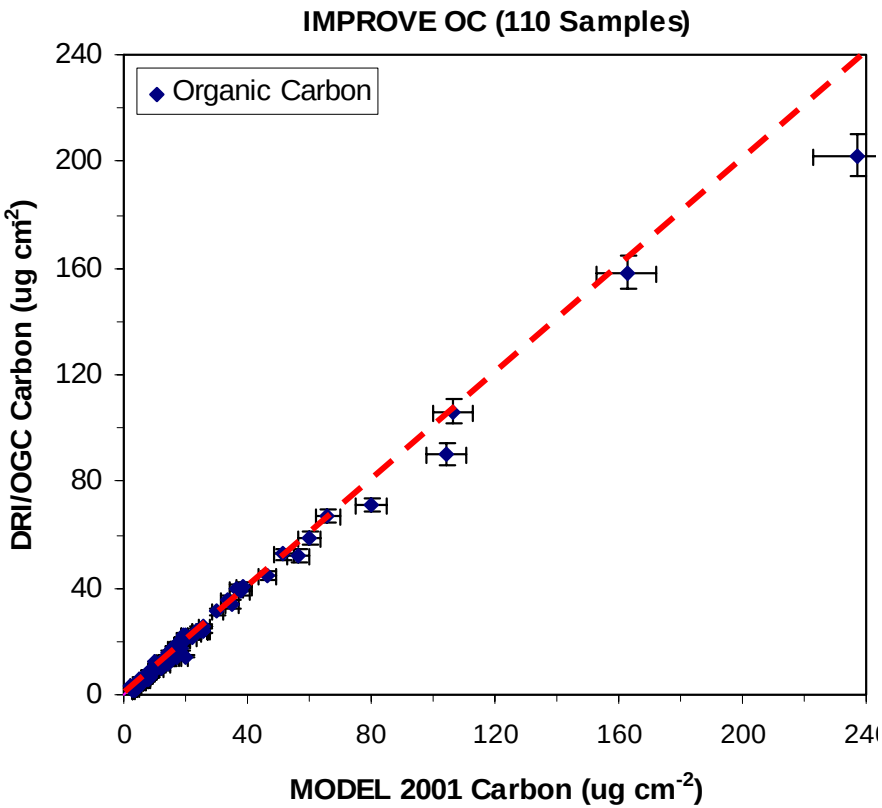
- DRI/OGC data for IMPROVE samples are compared to Model 2001 IMPROVE (n=243) and IMPROVE-A (n=160) protocols
- DRI/OGC data for IMPROVE samples (n=110) are compared to Model 2001 IMPROVE(250) protocol
- DRI/OGC data are the historic analyses, not recent re-analyses; the Model 2001 analyses are done on the archived portions of the quartz filters

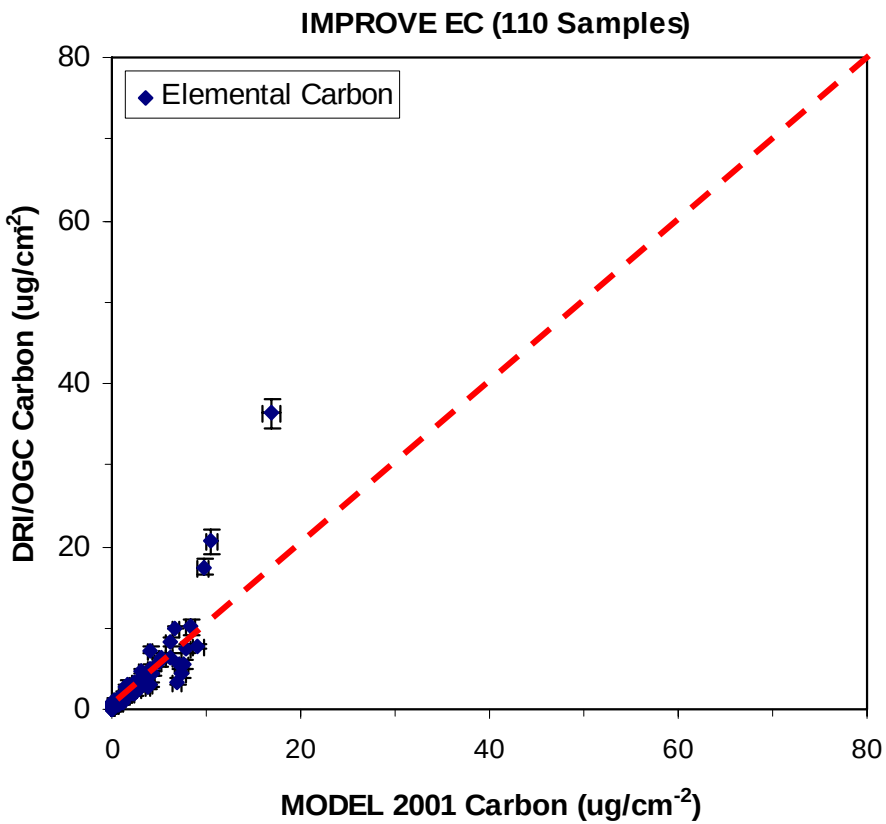
# Summary of DRI/OGC and DRI Model 2001

| Carbon Fraction | DRI/OGC (Y) to DRI Model 2001 with IMPROVE (Y), n=243 | | | DRI/OGC (Y) to DRI Model 2001 with IMPROVE_A (Y), n=160 | | | DRI/OGC (Y) to DRI Model 2001 with IMPROVE(250) (Y), n=110 | | |
|---|---|---|---|---|---|---|---|---|---|
| | slope | Y/X | R | slope | Y/X | R | slope | Y/X | R |
| Total Carbon | 1.05±0.005 | 1.03±0.10 | 0.99 | 1.02±0.007 | 1.00±0.13 | 0.99 | 0.98±0.00 | 0.96±0.12 | 1.00 |
| Organic Carbon | 1.08±0.006 | 1.05±0.10 | 0.98 | 1.01±0.008 | 1.00±0.13 | 0.99 | 0.92±0.01 | 0.93±0.13 | 1.00 |
| Elemental Carbon | 0.89±0.009 | 0.96±0.28 | 0.97 | 1.02±0.010 | 1.08±0.32 | 0.98 | 1.38±0.05 | 1.60±1.69 | 0.90 |
| OC1 | 1.83±0.09 | 4.85±16.60 | 0.45 | 1.12±0.05 | 1.89±2.81 | 0.80 | 0.85±0.03 | 1.22±0.89 | 0.95 |
| OC2 | 0.85±0.01 | 0.85±0.14 | 0.94 | 0.74±0.01 | 0.73±0.14 | 0.97 | 1.21±0.02 | 0.92±0.21 | 0.98 |
| OC3 | 1.55±0.02 | 1.48±0.30 | 0.94 | 1.12±0.02 | 1.19±0.29 | 0.93 | 0.74±0.02 | 0.87±0.19 | 0.97 |
| OC4 | 1.26±0.02 | 1.30±0.31 | 0.89 | 1.09±0.02 | 1.16±0.86 | 0.96 | 0.87±0.02 | 1.13±0.37 | 0.95 |
| OP | 0.37±0.01 | 0.44±0.21 | 0.49 | 0.78±0.03 | 0.86±0.35 | 0.76 | 1.03±0.18 | 3.07±9.35 | 0.29 |
| EC1 | 0.59±0.01 | 0.68±0.21 | 0.88 | 0.95±0.02 | 0.95±0.27 | 0.92 | 1.45±0.10 | 1.29±1.16 | 0.76 |
| EC2 | 0.57±0.01 | 0.63±0.23 | 0.72 | 0.84±0.02 | 0.96±0.35 | 0.80 | 1.24±0.04 | 1.28±0.47 | 0.79 |
| EC3 | 0.30±0.02 | 0.88±4.86 | 0.45 | 0.89±0.11 | 1.97±2.76 | 0.43 | 7.78±1.54 | 7.33±9.64 | 0.33 |

- IMPROVE-A is more comparable to DRI/OGC for all carbon components except for OC2 which is moderately less comparable
- IMPROVE(250) is not comparable to DRI/OGC for EC and has a poor correlation for OP & EC3

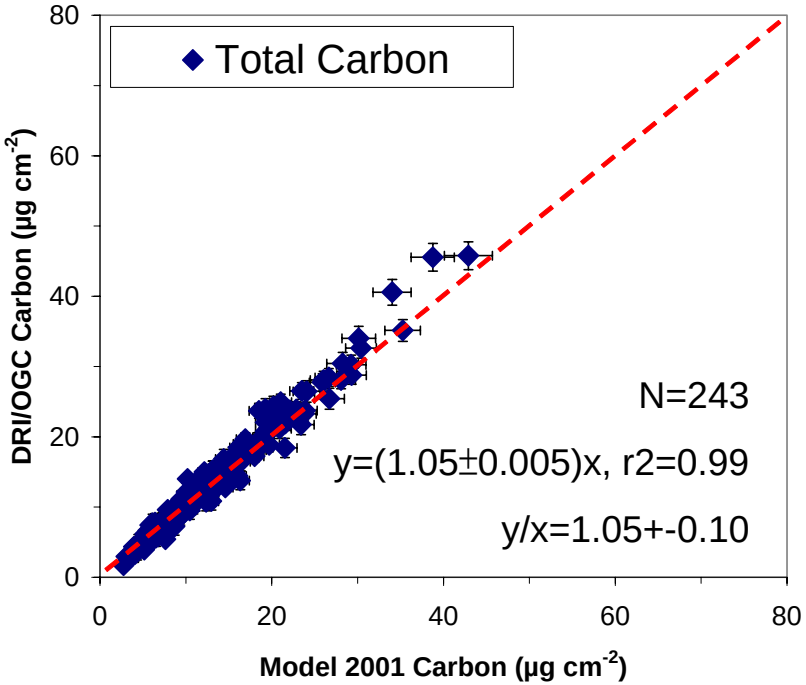
# Comparisons DRI/OGC to IMPROVE(250) for OC & EC



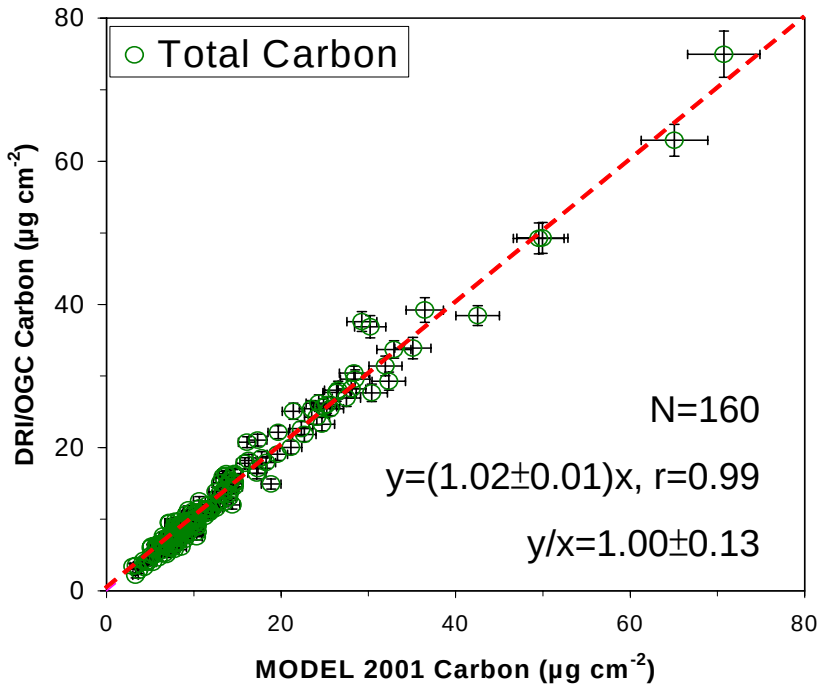




- Good correlation at low concentrations degrades at higher concentrations

# Comparisons of TC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

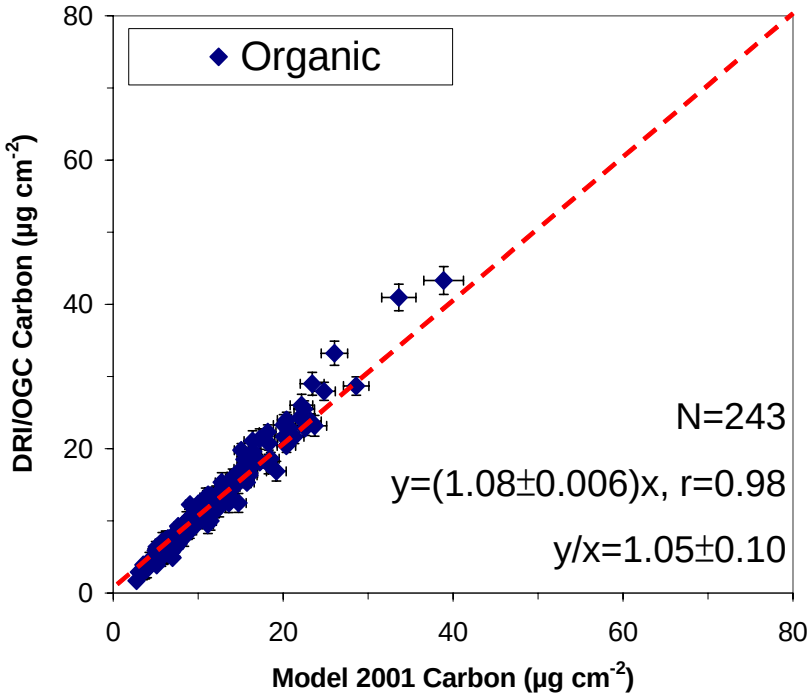



IMPROVE

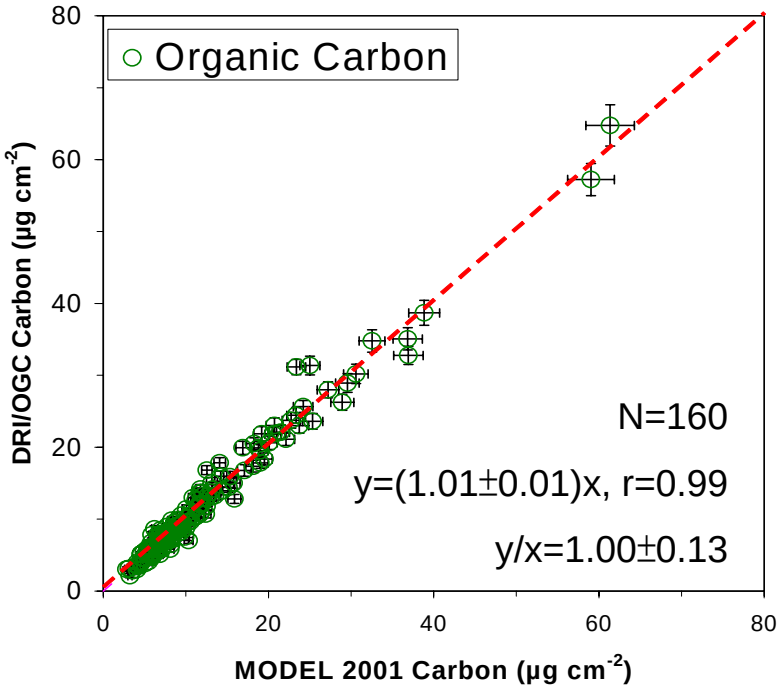



IMPROVE_A

# Comparisons of OC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

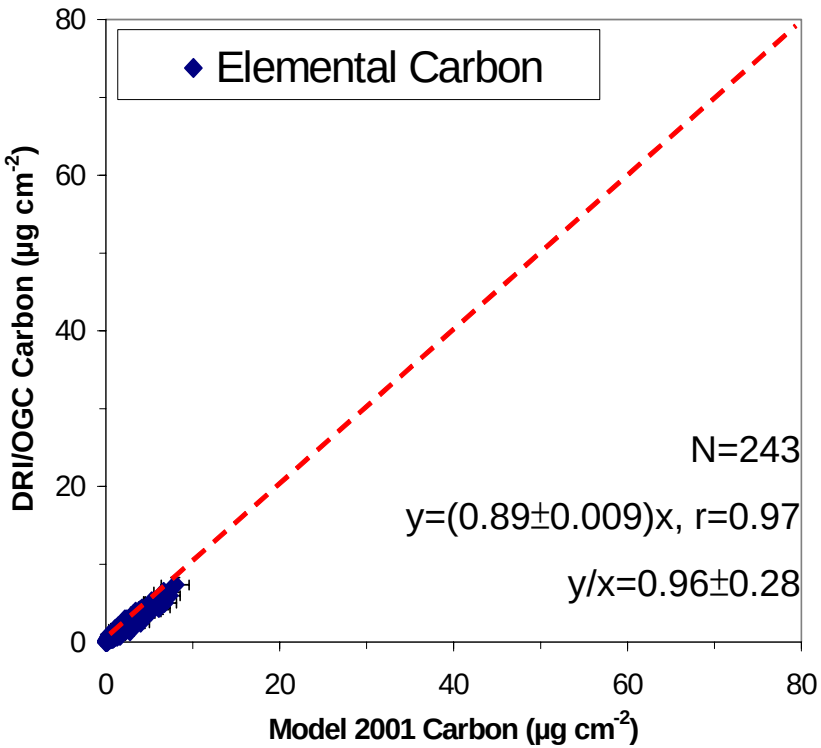



IMPROVE

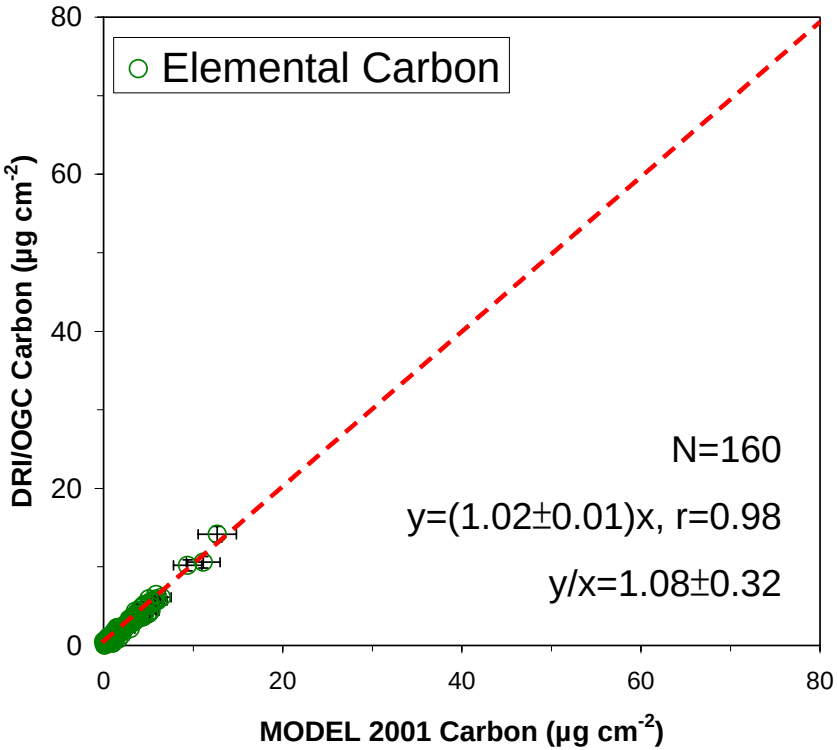



IMPROVE_A

# Comparisons of EC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

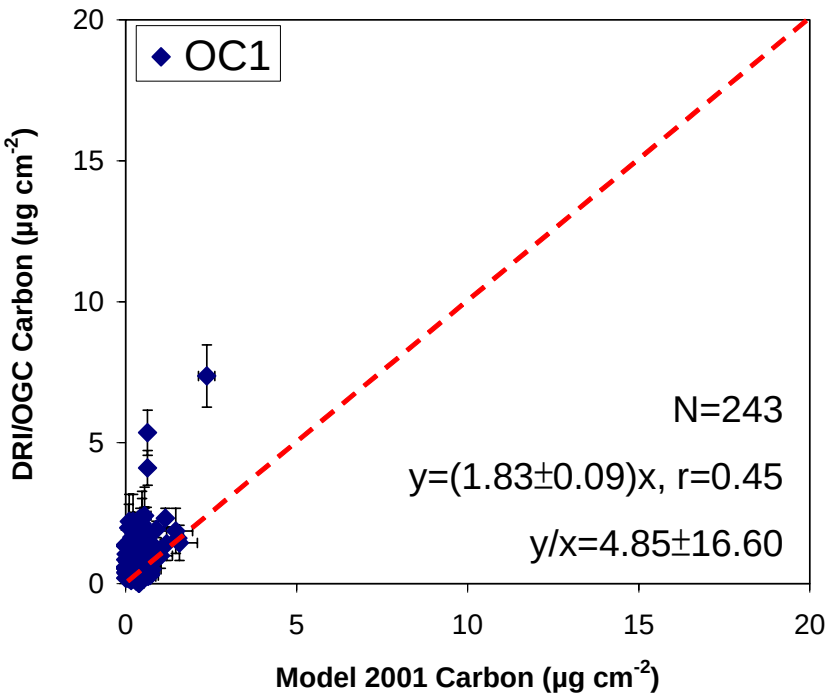



IMPROVE

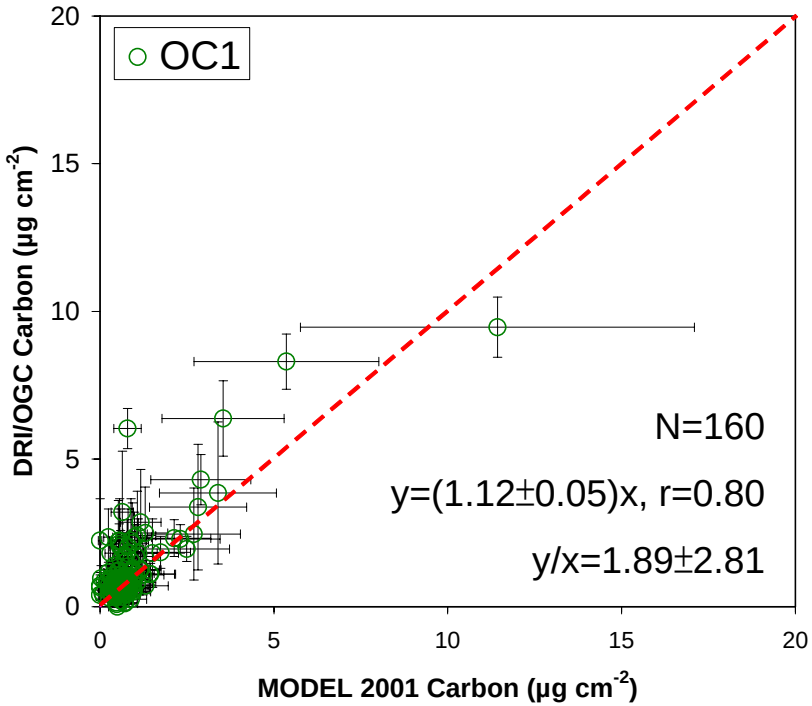



IMPROVE_A

# Comparisons of OC1 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

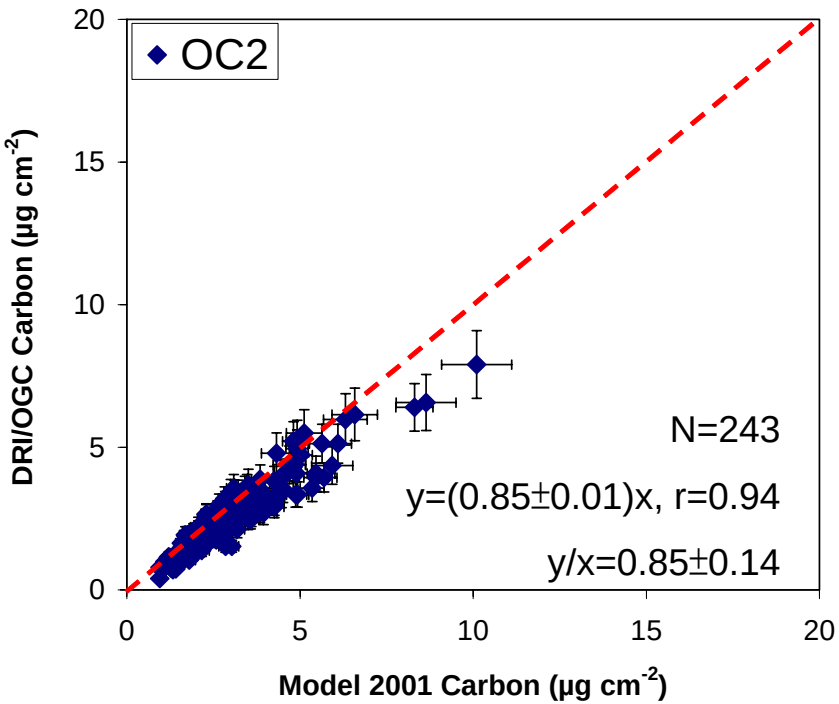



IMPROVE

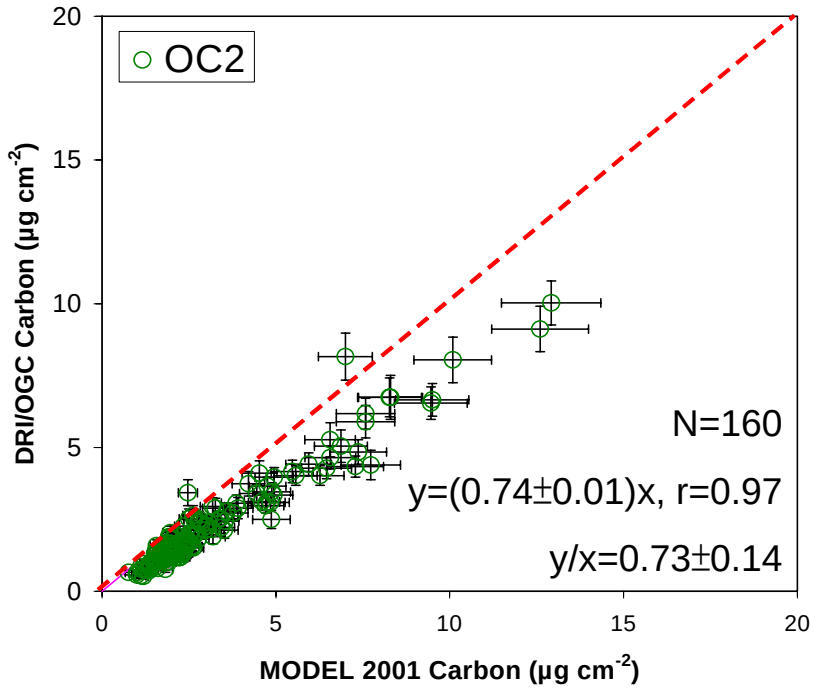



IMPROVE_A

# Comparisons of OC2 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

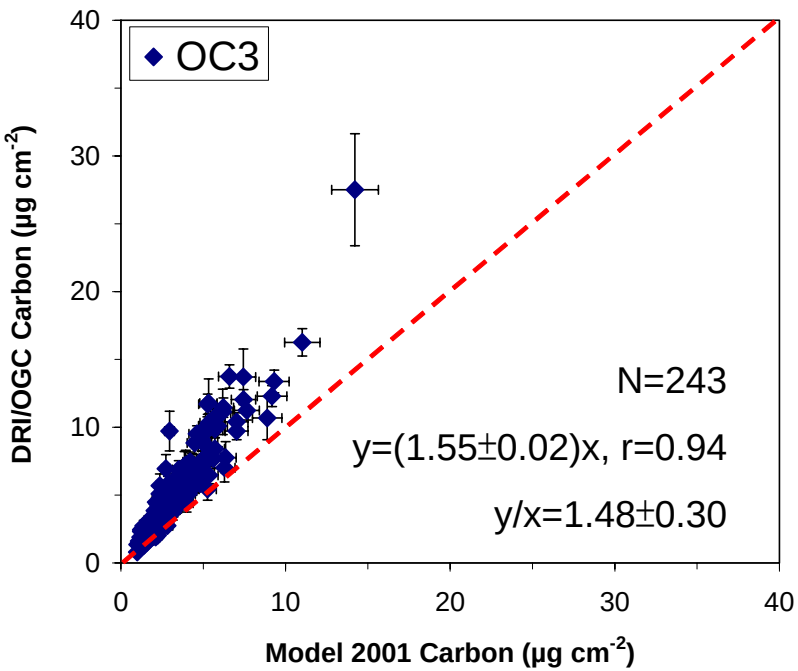



IMPROVE

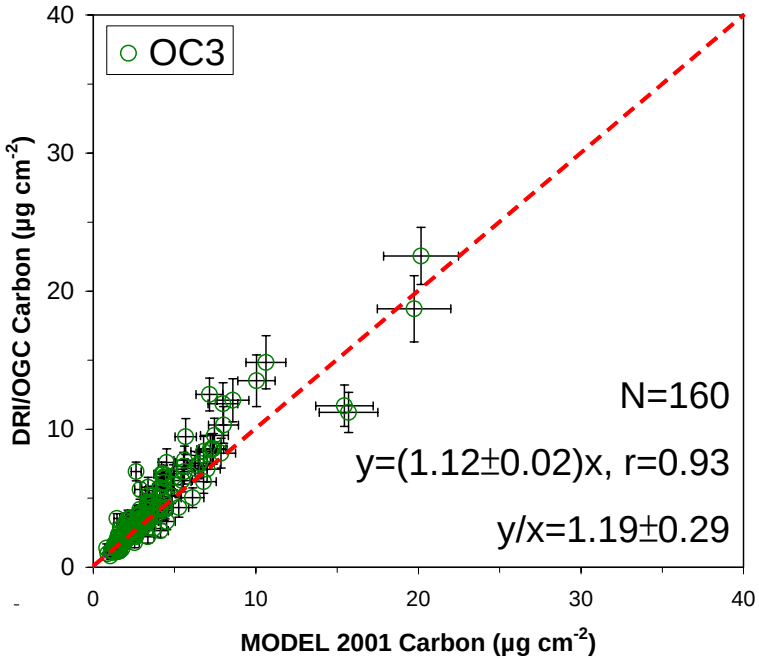



IMPROVE_A

# Comparisons of OC3 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

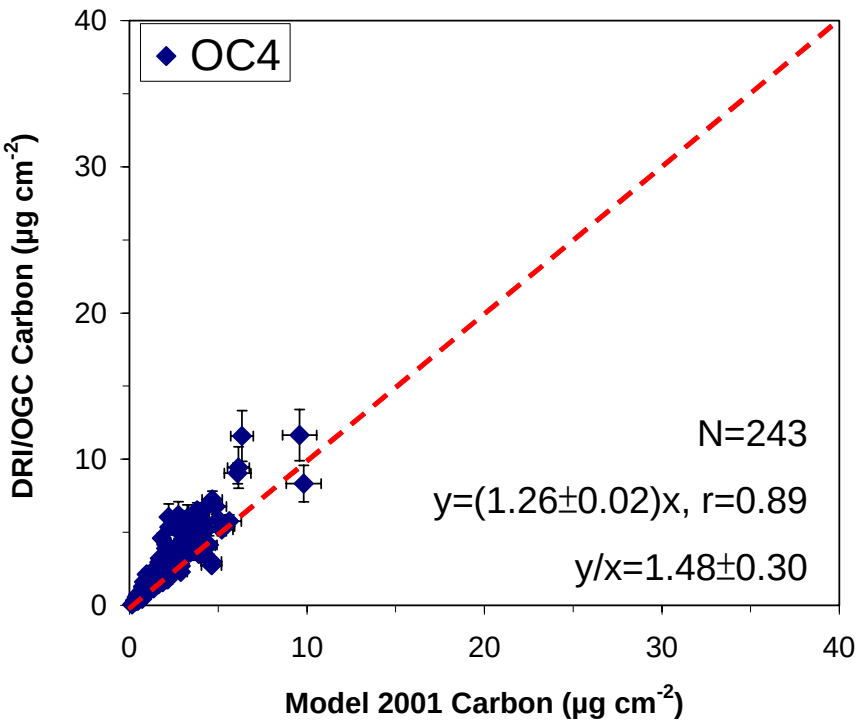



IMPROVE

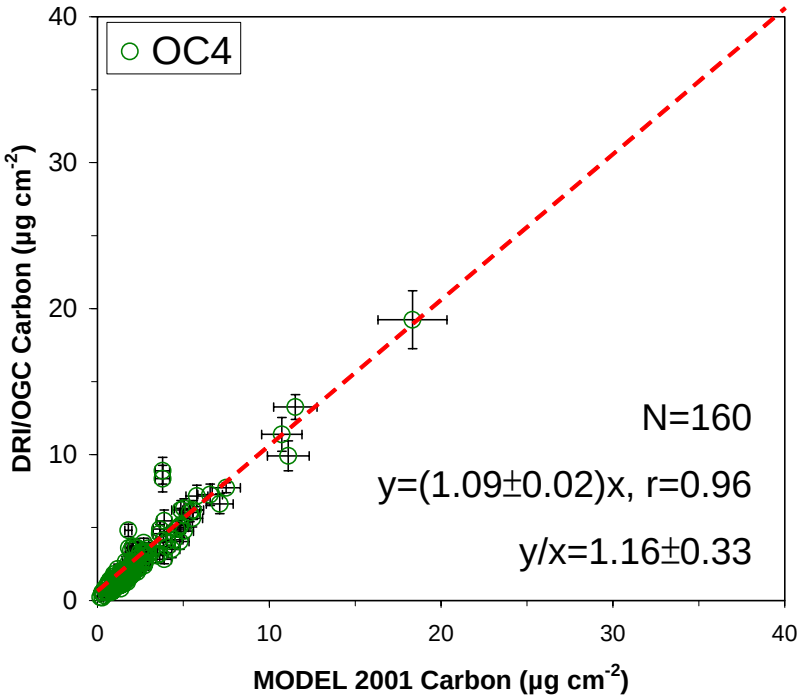



IMPROVE_A

# Comparisons of OC4 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

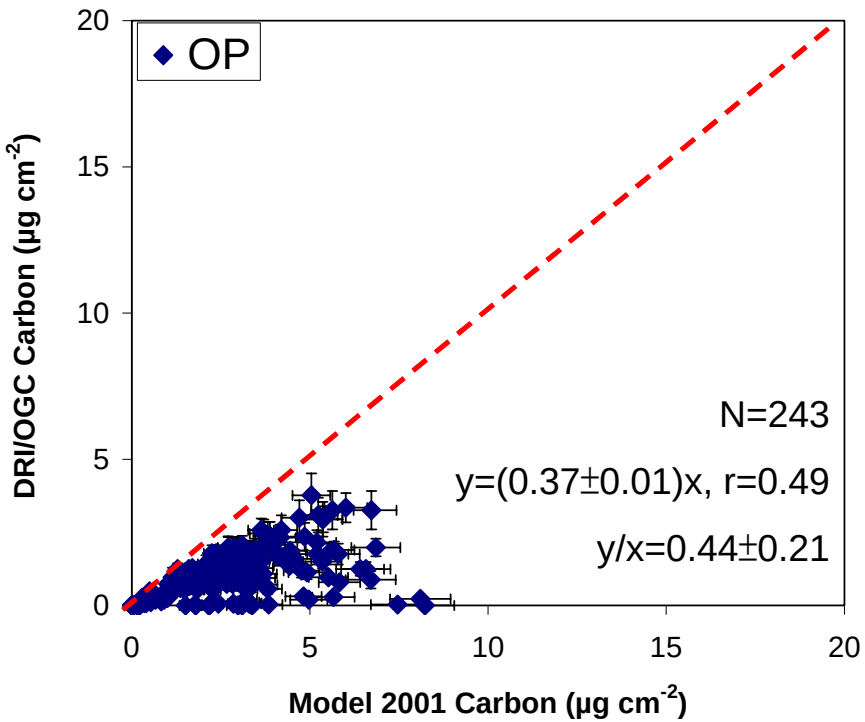



IMPROVE

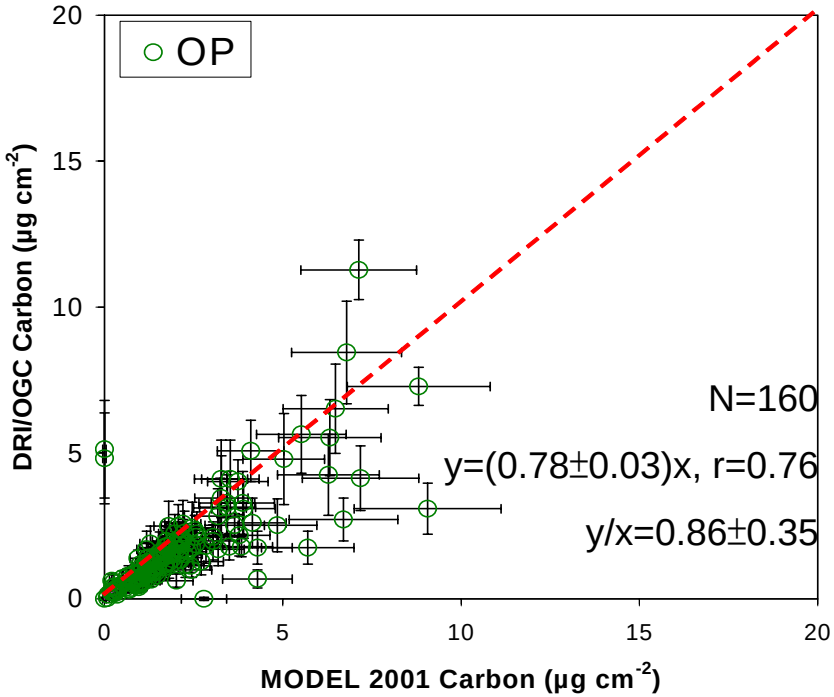



IMPROVE_A

# Comparisons of OPC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

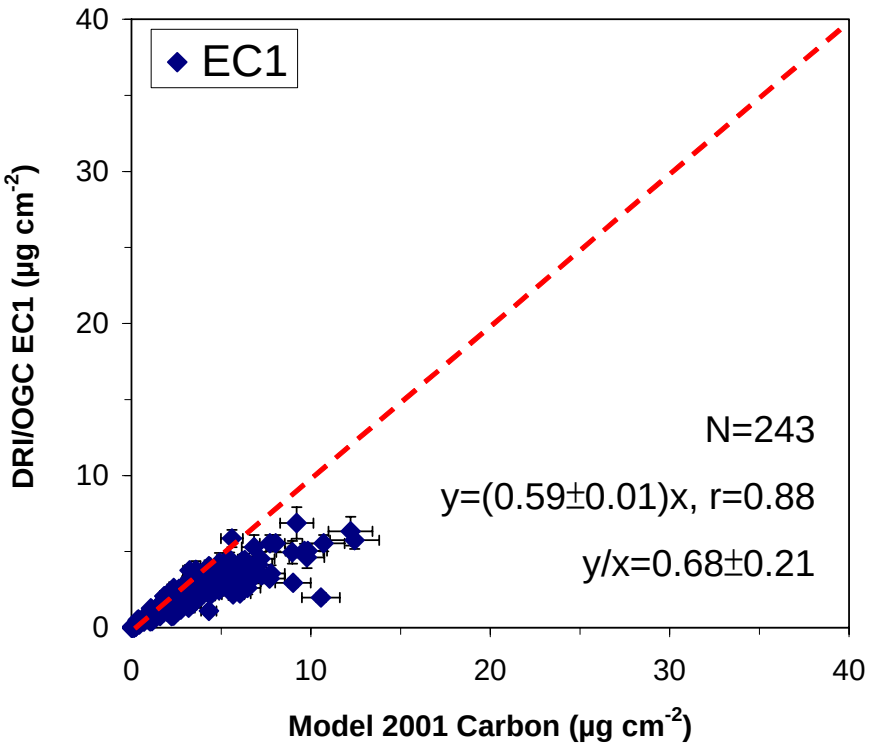



IMPROVE

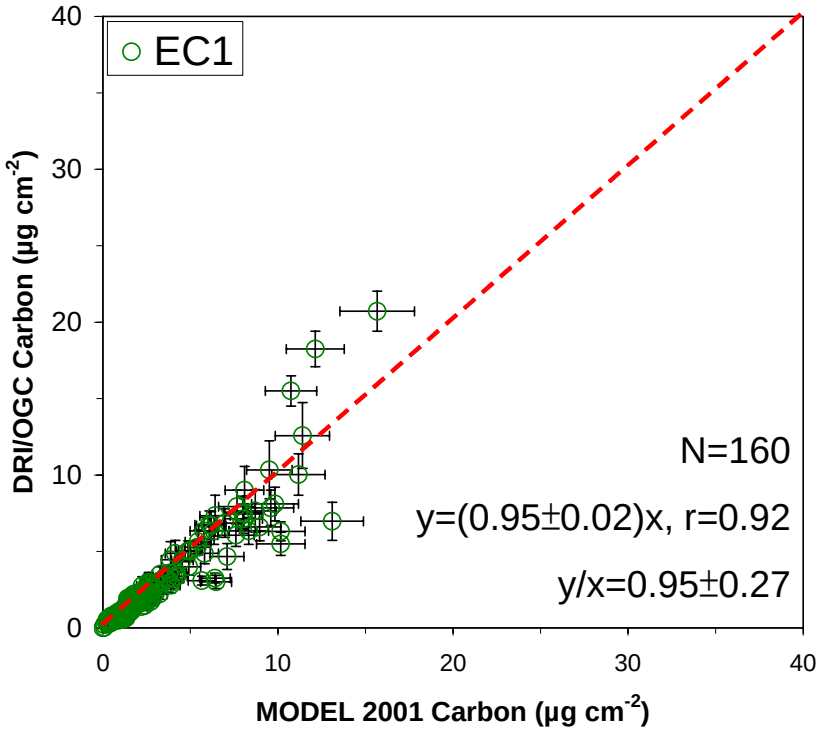



IMPROVE_A

# Comparisons of EC1 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

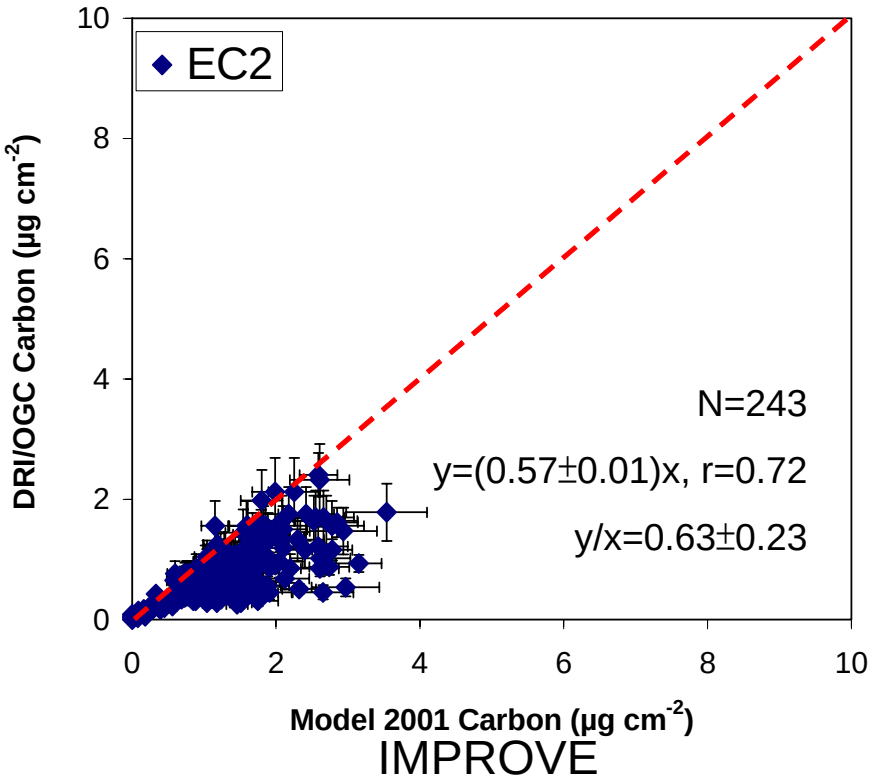


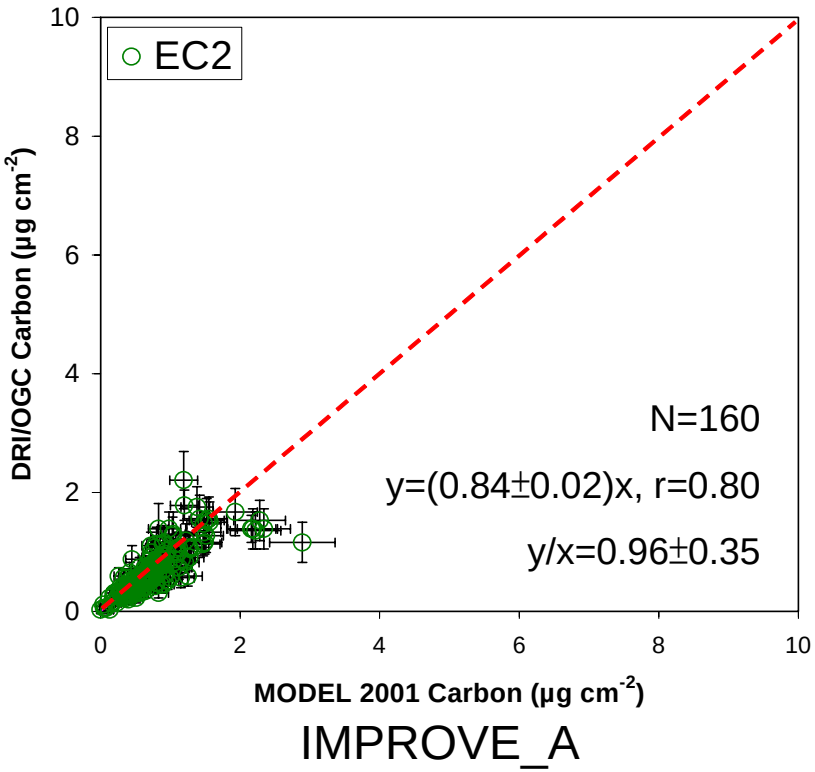

IMPROVE



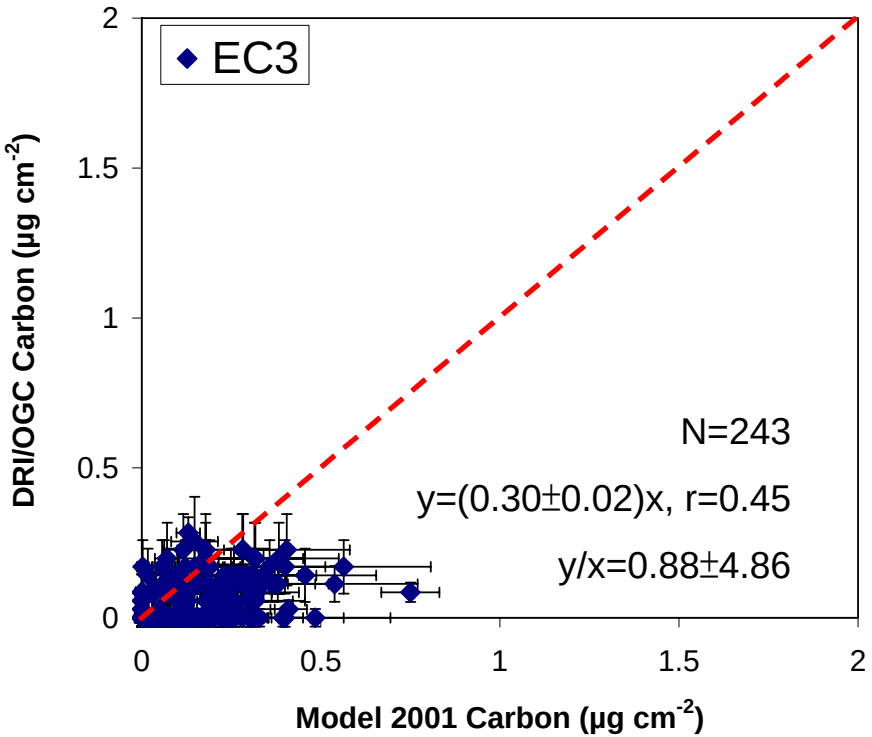

IMPROVE_A

# Comparisons of EC2 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

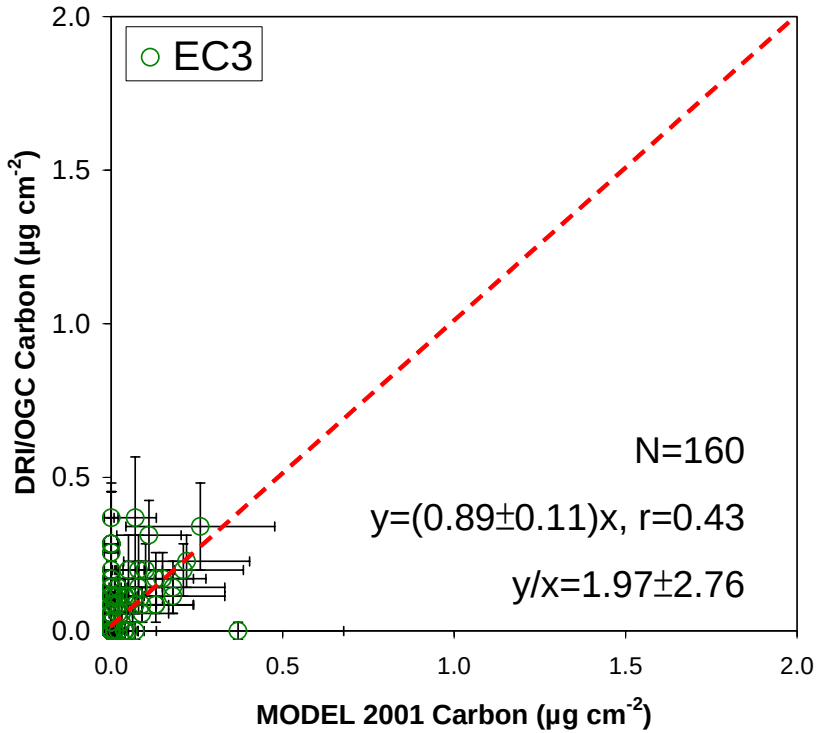


# Comparisons of EC3 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A




IMPROVE




IMPROVE_A

# Summary/Recommendations

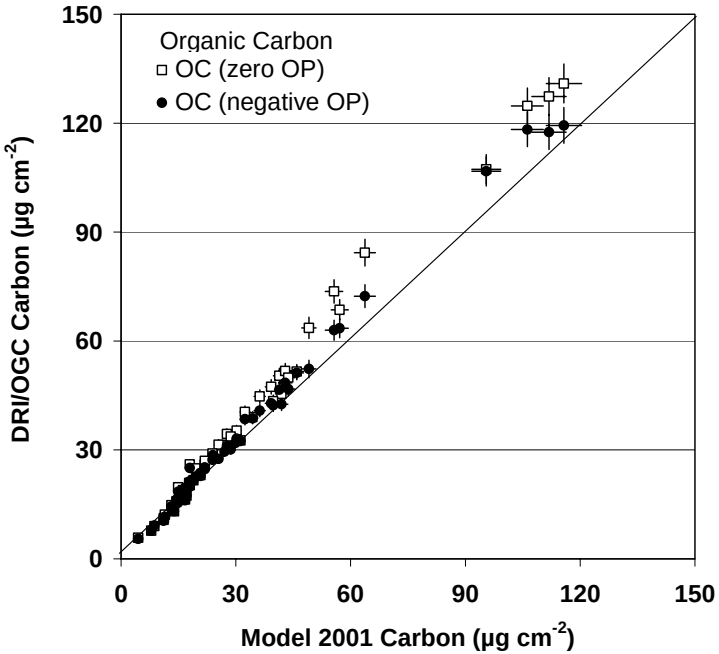
- Model 2001 analyzer using IMPROVE(250) protocol does not reproduce EC data from the currently used DRI/OGC very well for high carbon concentration IMPROVE samples
- IMPROVE & IMPROVE-A produces comparable OC & EC data to the DRI/OGC analyzer data
- IMPROVE-A protocol produces more comparable carbon subfraction data to the DRI/OGC analyzer data than the IMPROVE protocol
- Temperature profiles for all Thermal/Optical Carbon (TOC) analyzers should to be calibrated to actual sample temperatures to aid in understanding their operation
- $O_2$ levels in the helium of the organic phase of the TOC analyzers should be periodically monitored & kept low

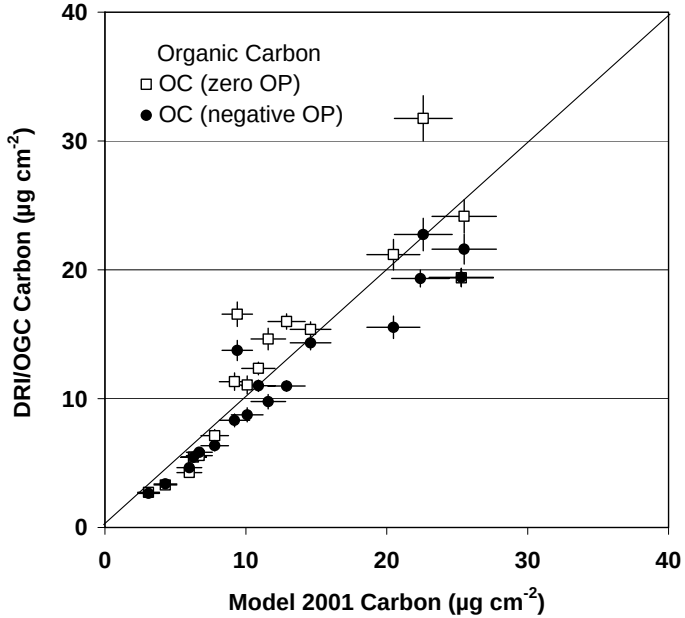
# IMPROVE Carbon Analysis Decision

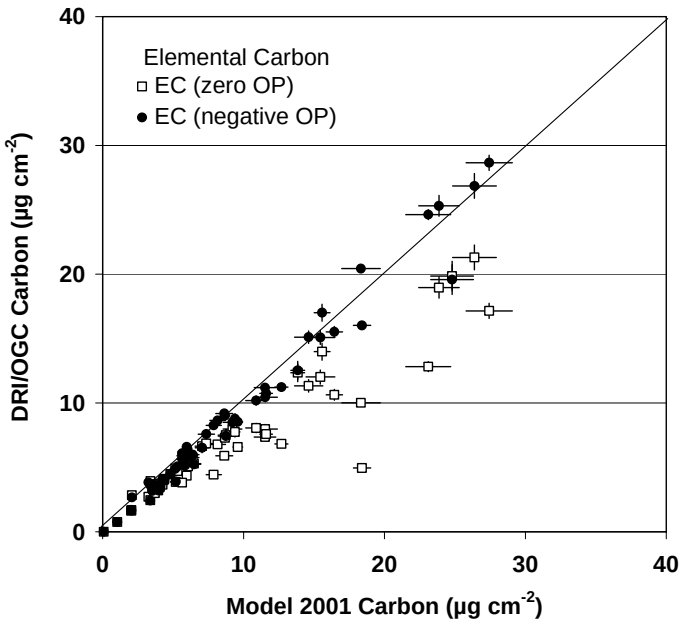
- IMPROVE Steering Committee will
  - review the information,
  - discuss it as needed via emails & conference calls and
  - make the decision concerning the use of IMPROVE or IMPROVE-A, or “back to the drawing board”
- If the decision to use IMPROVE or IMPROVE-A is made by the end of February, all samples collected during calendar year 2005 can be analyzed by the same new protocol
- A “back to the drawing board” decision could affect carbon analysis backlogs and slow data turn-around

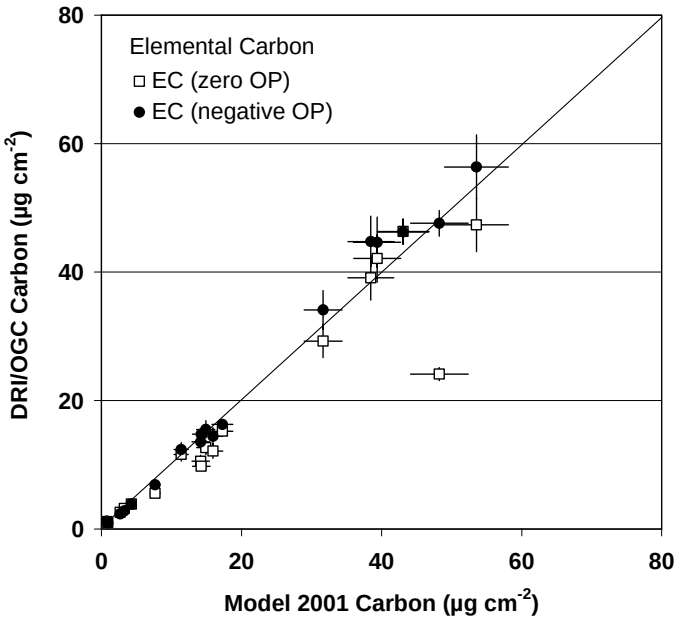
# Additional Assessment Results Included in the DRI Report

- The OP values that are sometimes negative (<5% of IMPROVE samples) should not be set to zero, but should be applied as a negative correction to the OC (increasing the EC value)
- TOR produces more comparable OC & EC results among the different temperature profiles than TOT (specifically useful for relating IMPROVE to STN OC & EC data)



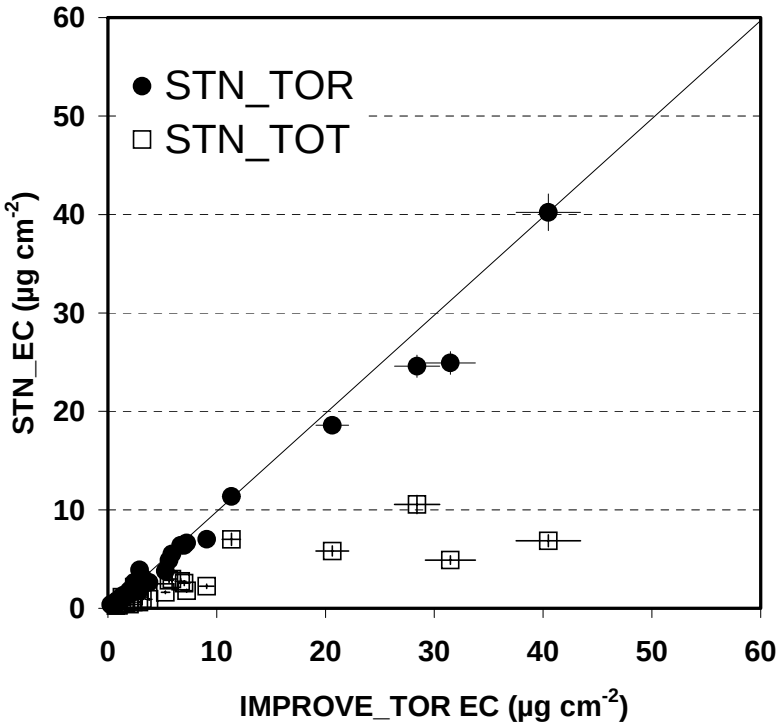



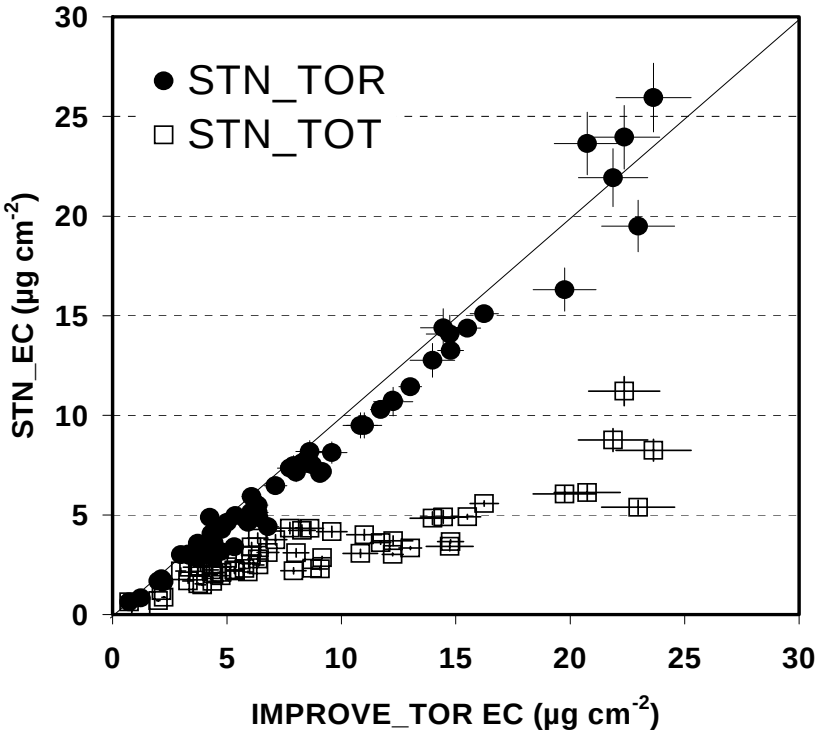

57 Fresno Samples

18 Hong Kong Samples

# Comparison of STN_TOT and STN_TOR with IMPROVE_TOR

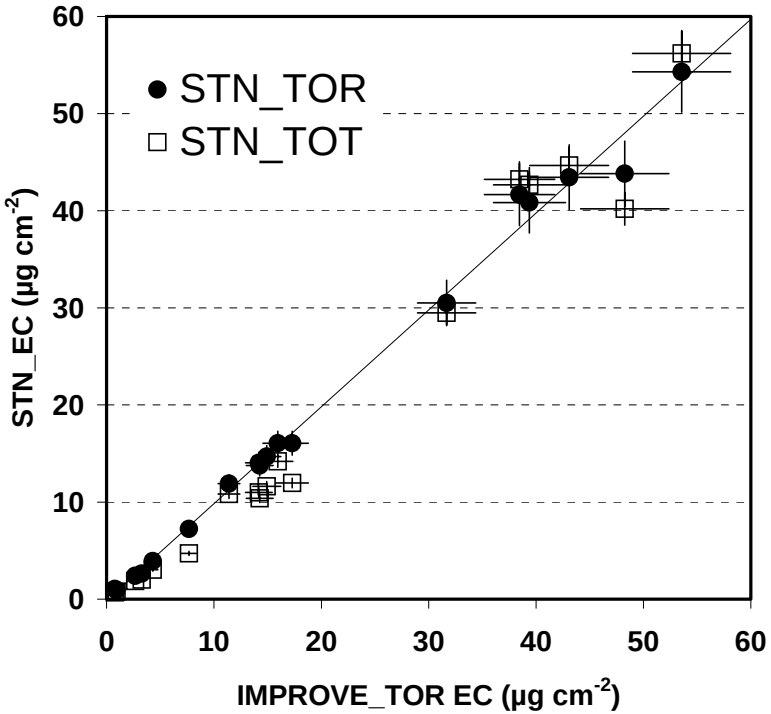



**IMPROVE III Samples**

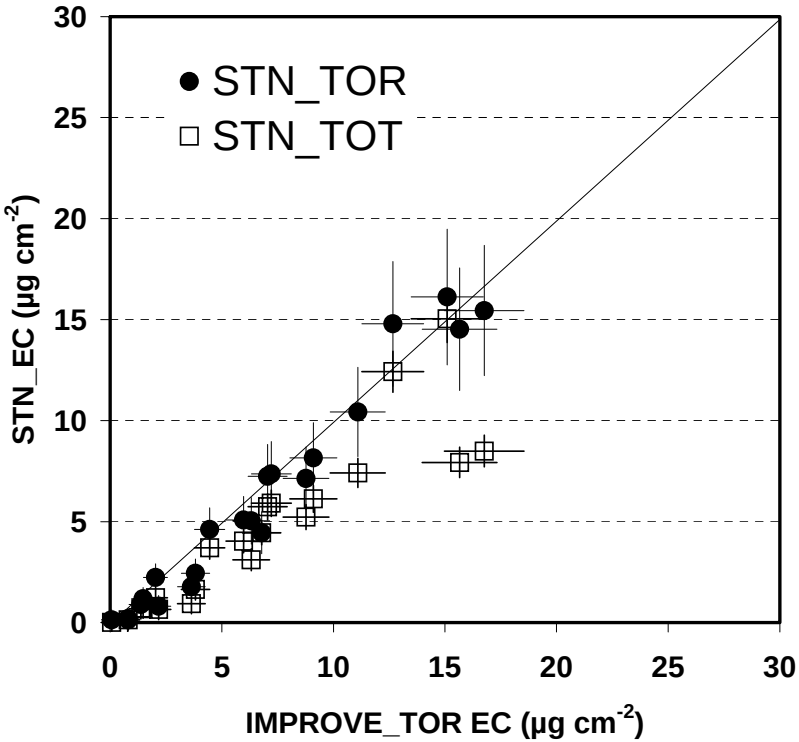



**Fresno Samples**

# Comparison of STN_TOT and STN_TOR with IMPROVE_TOR (cont'd)




**Hong Kong Samples (Road Side)**




**Montana Fire Samples**