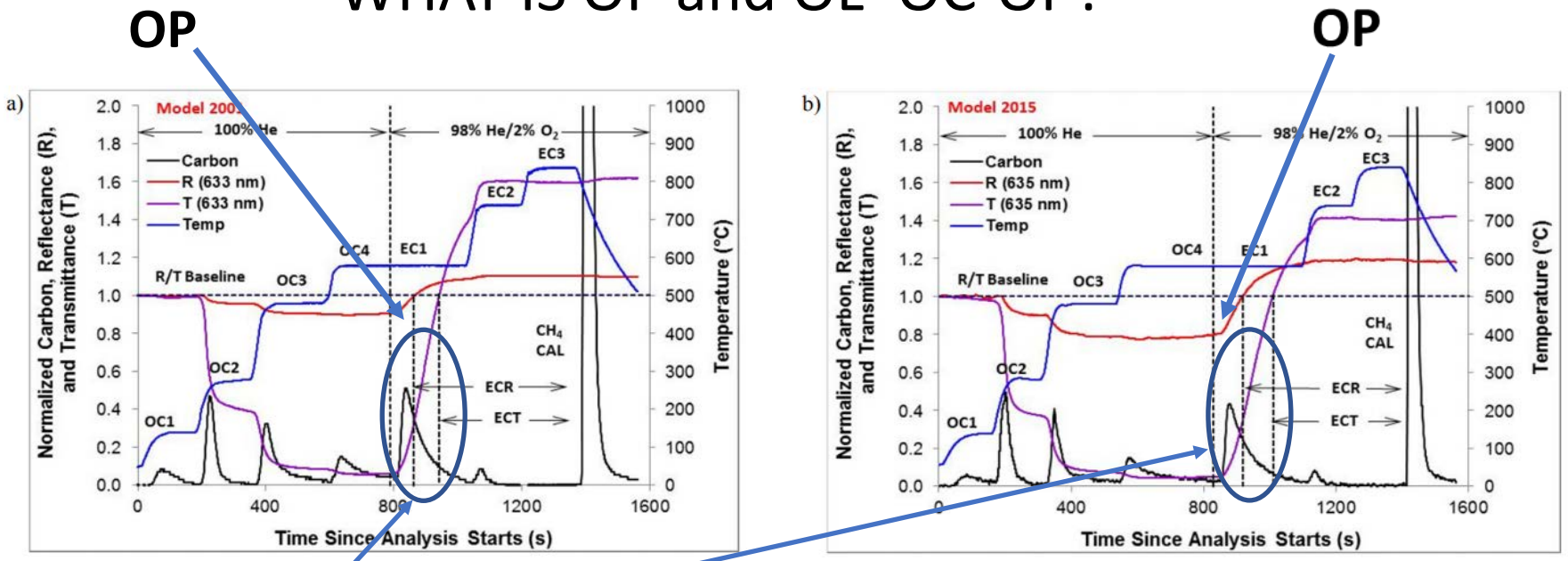
Reinterpreting Thermal Optical Reflectance Measurements

– the mystery of increasing R_{oc} values

What are TOR THERMOGRAMS
WHAT IS OP and OL=OC-OP?



- The EC1 peak contains pyrolyzed carbon (OP) which is considered to be OC and light absorbing carbon (LAC-EC).
- It is assumed that only OP oxidizes before filter reflectance returns to baseline and only LAC after.
- There is evidence that LAC is underestimated and that a significant fraction of LAC remains as part of OP and therefore counted as OC.

RECONSTRUCTED FINE MASS EQUATIONS

- RCFM=1.37*SO_4+1.29*NO_3 +R_{OC}*OC+ Soil+LAC+SS, or
- RCFM=1.37*SO_4+1.29*NO_3 +R_{TC}*TC+Soil+SS where TC= (OC+LAC)

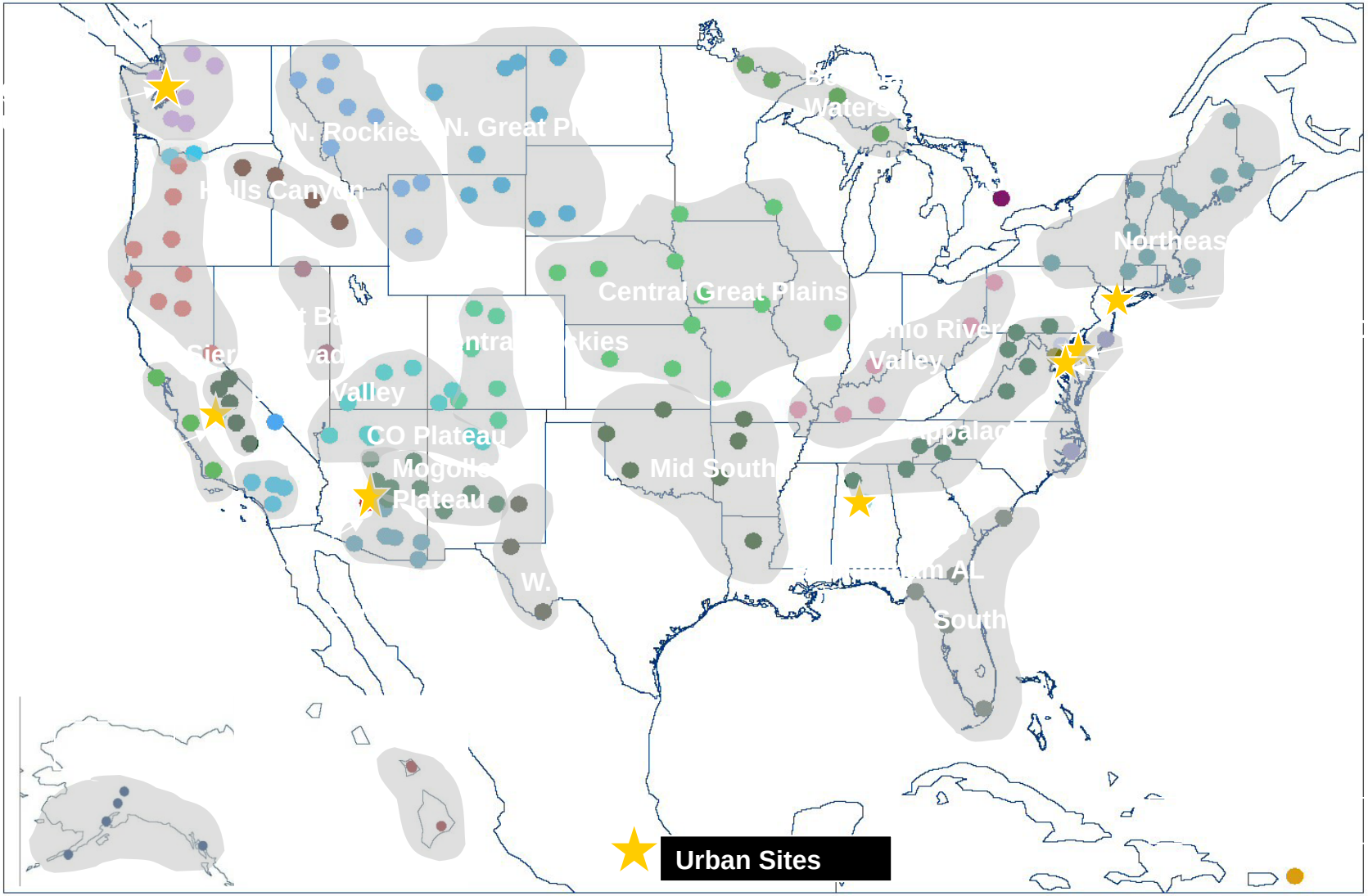
Currently R_{OC}= 1.8 all seasons but has a clear seasonal dependence.

Regression model for estimating R_{oc} or R_{tc}

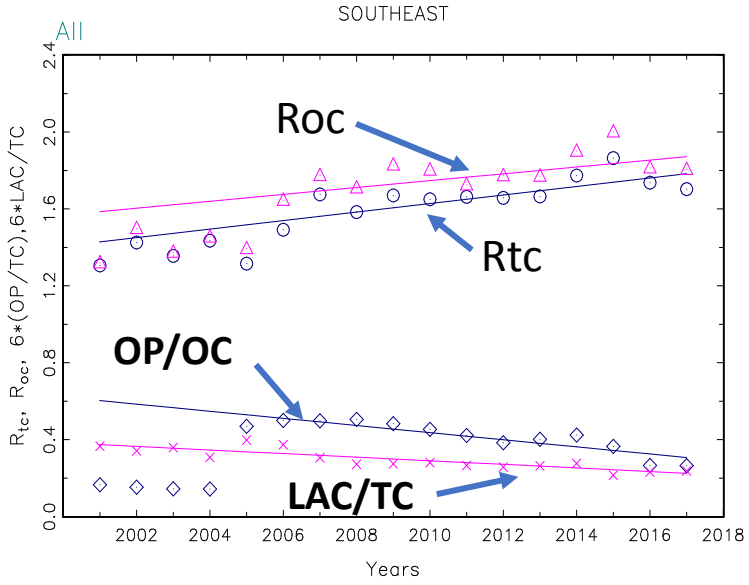
$FM=a_1Other+a_2OC$. a_2 is R_{oc}

$FM=a_1Other+a_2TC$. a_2 is R_{tc}
where $TC=OC+LAC$

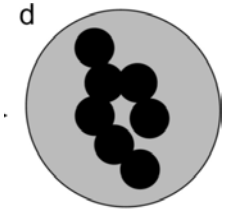
IMPROVE Network (Rural/Remote)



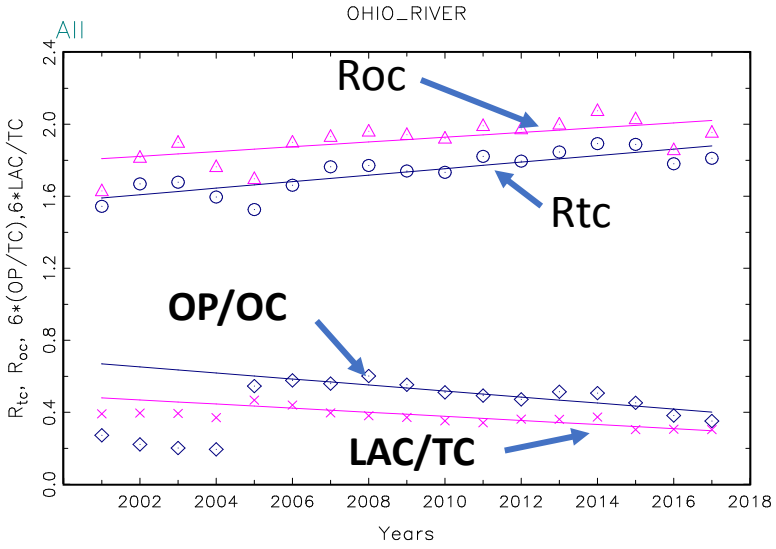
- Began operating in spring of 1988 with 20 monitoring sites
- Today has ~170 sites – 100+ sites with 10 or more years of data.

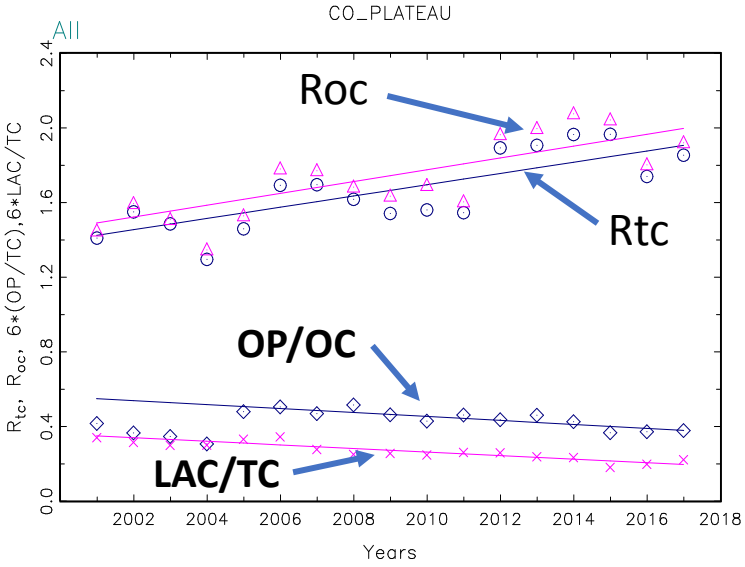


- A decrease in the LAC fraction of TC should result in a increase in R_{TC}.
- As LAC/TC decreases R_{TC} increases over time.

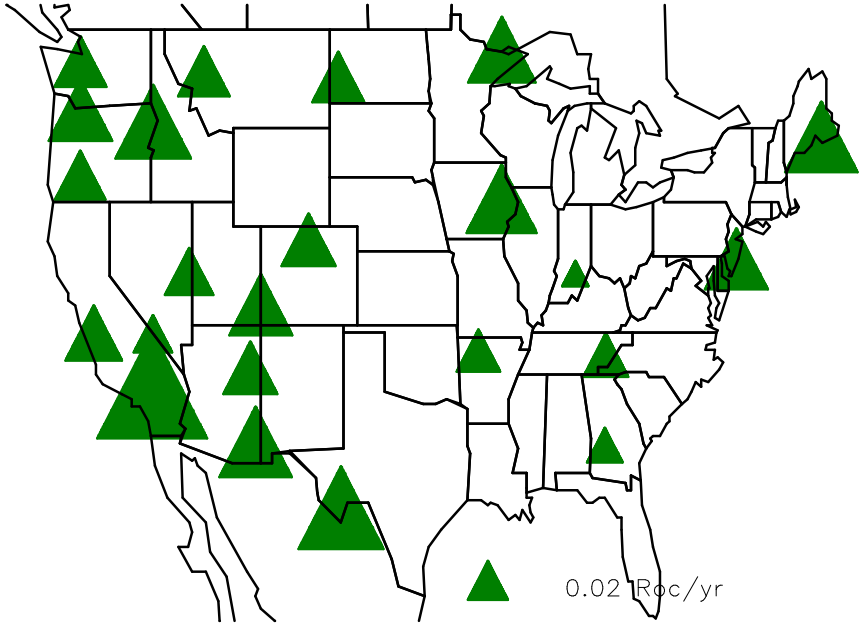


- But same trends are observed for OC and OP/OC suggesting an LAC component to OP.

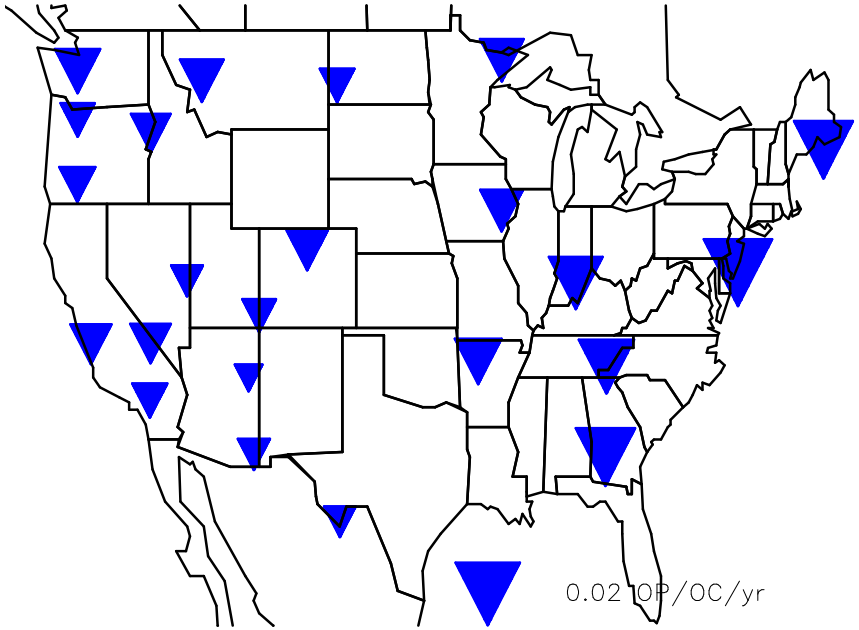




Rate of Increase in R_{oc}/yr 2005-2015



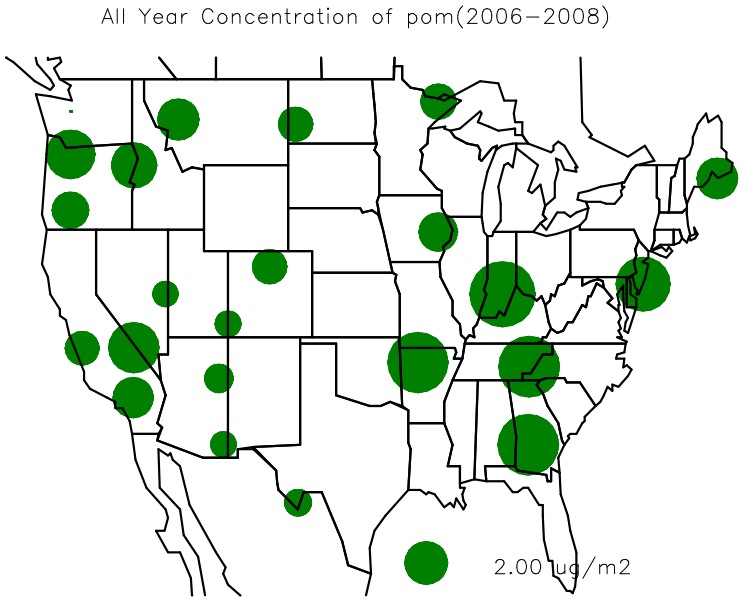
Trend in OP/OC Ratio 2005-2015

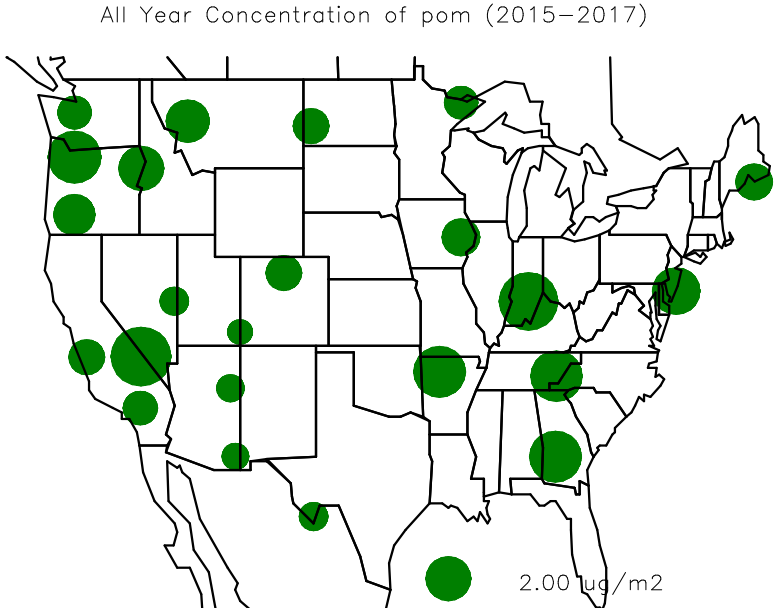


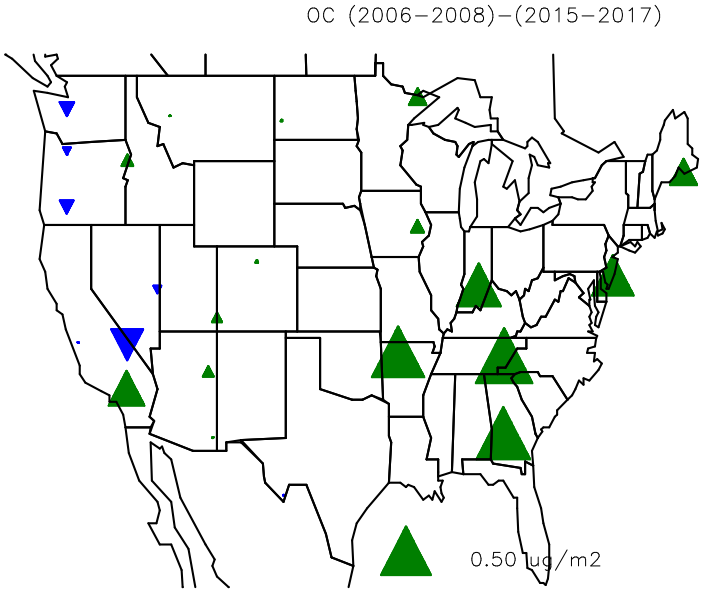
GREEN is positive or increase and BLUE is negative or decrease

- R_{oc} is increasing across entire United States.
- And OP/TC is decreasing across entire U.S with the highest rate of decrease in the Eastern U.S.
- If OP contains low molecular weight carbon and LAC is underestimated a decrease in OP/OC is consistent with R_{oc} increasing.

Average OC concentrations for years 2006-2008 and 2015-2017



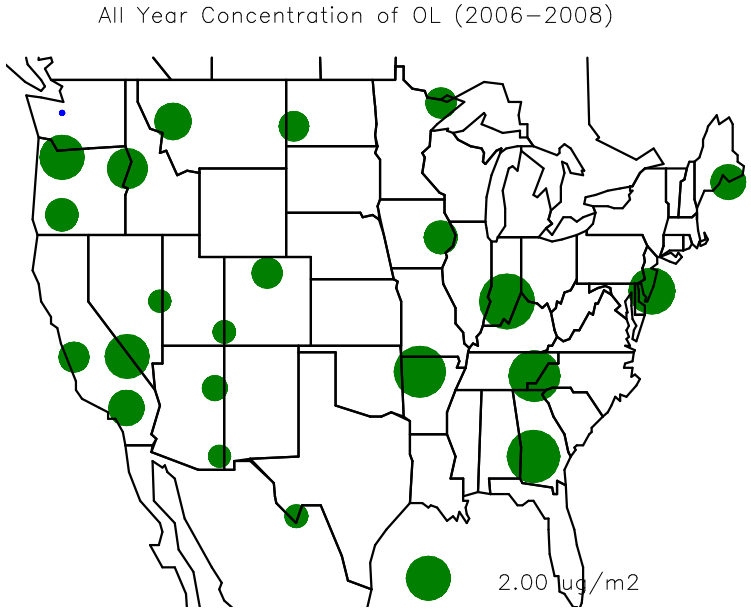


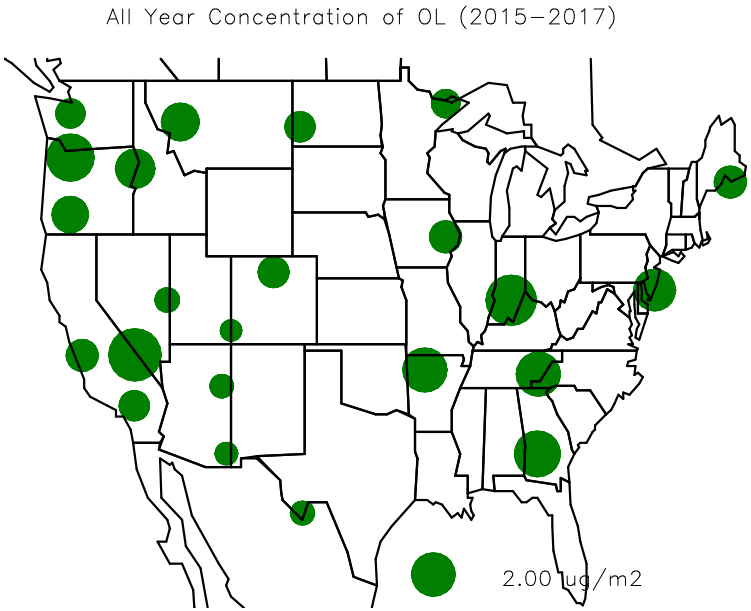


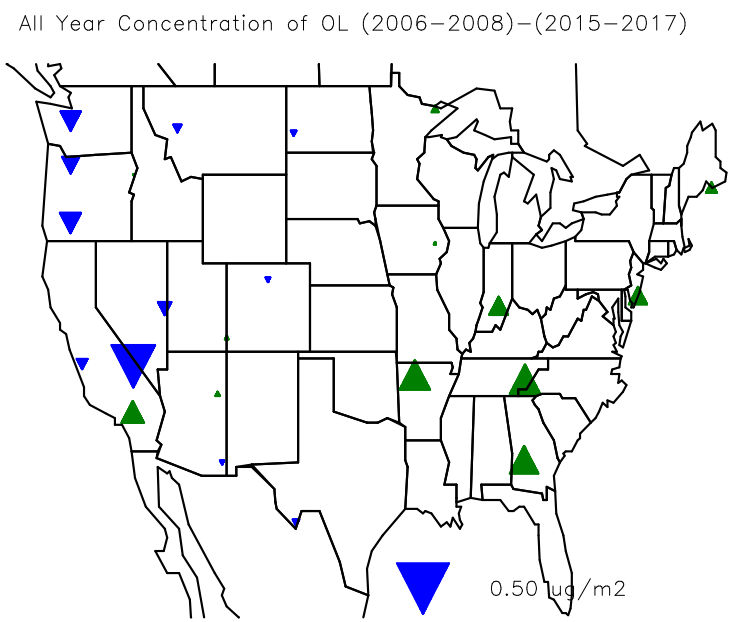
- In the East OC has decreased by about 0.5 ug/m^3 or about 25%
- Decrease in the West is significantly less.
- In parts of the West OC has increased over the same time period.

OL=OC-OP (Low temperature OC)

Average OL concentrations for years 2006-2008 and 2015-2017

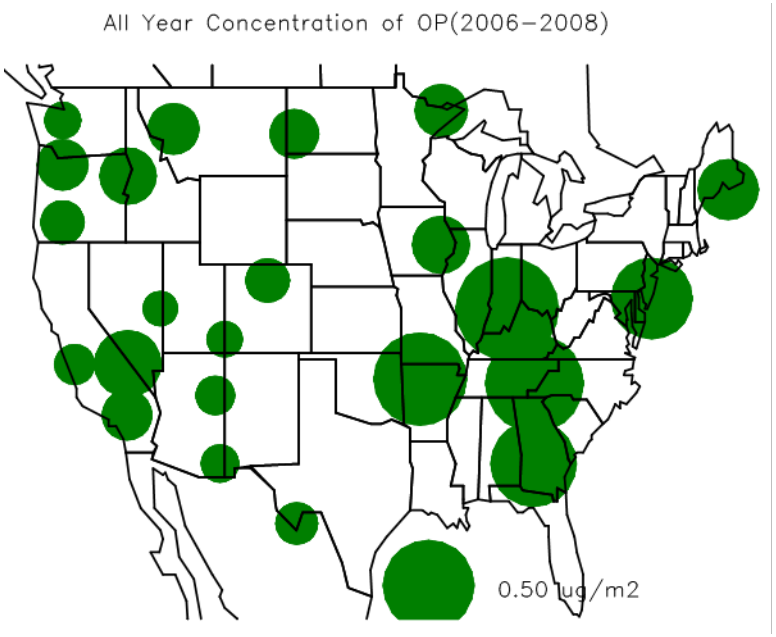


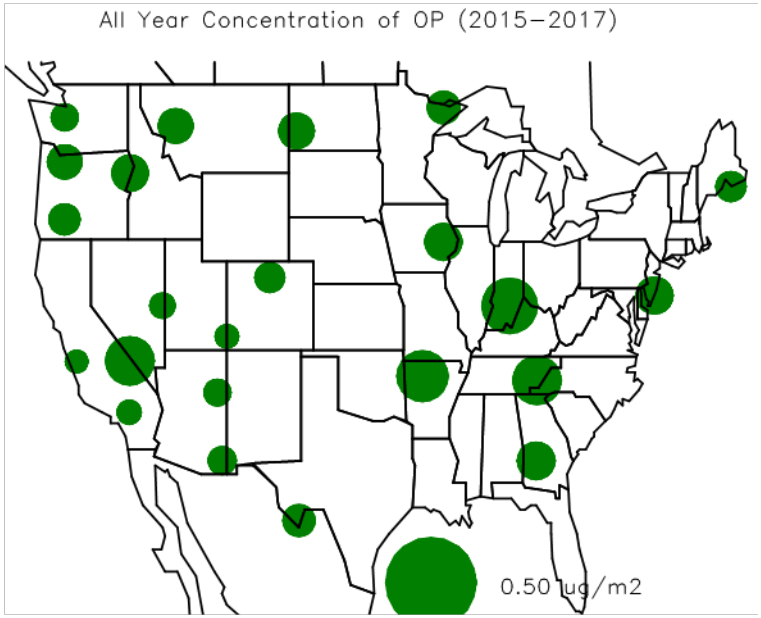




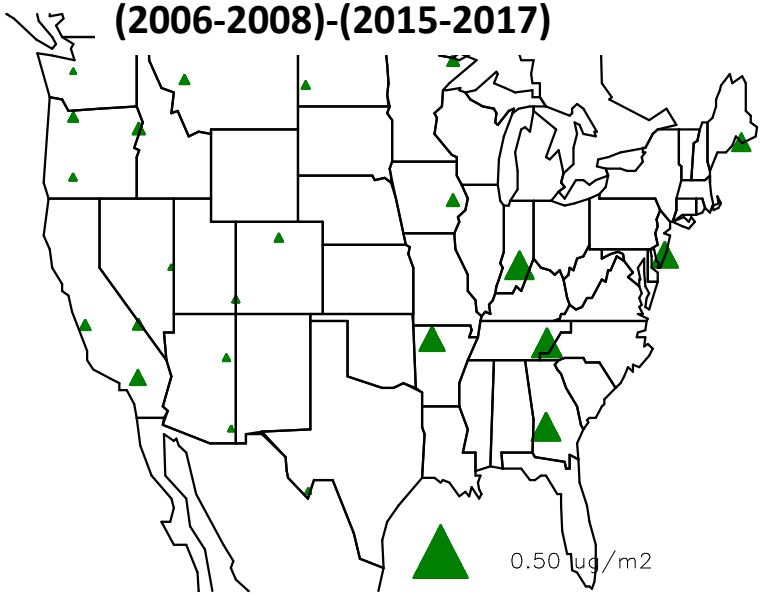
- In the East OL has decrease by about 0.25 ug/m^3 or about 12%.
- OL has stayed the same or increased slightly in most of the Western US.
- It has increased by about 0.5 ug/m^3 in the Sierra Nevada Mt Range.

Average OP concentrations for years 2006-2008 and 2015-2017





(2006-2008)-(2015-2017)

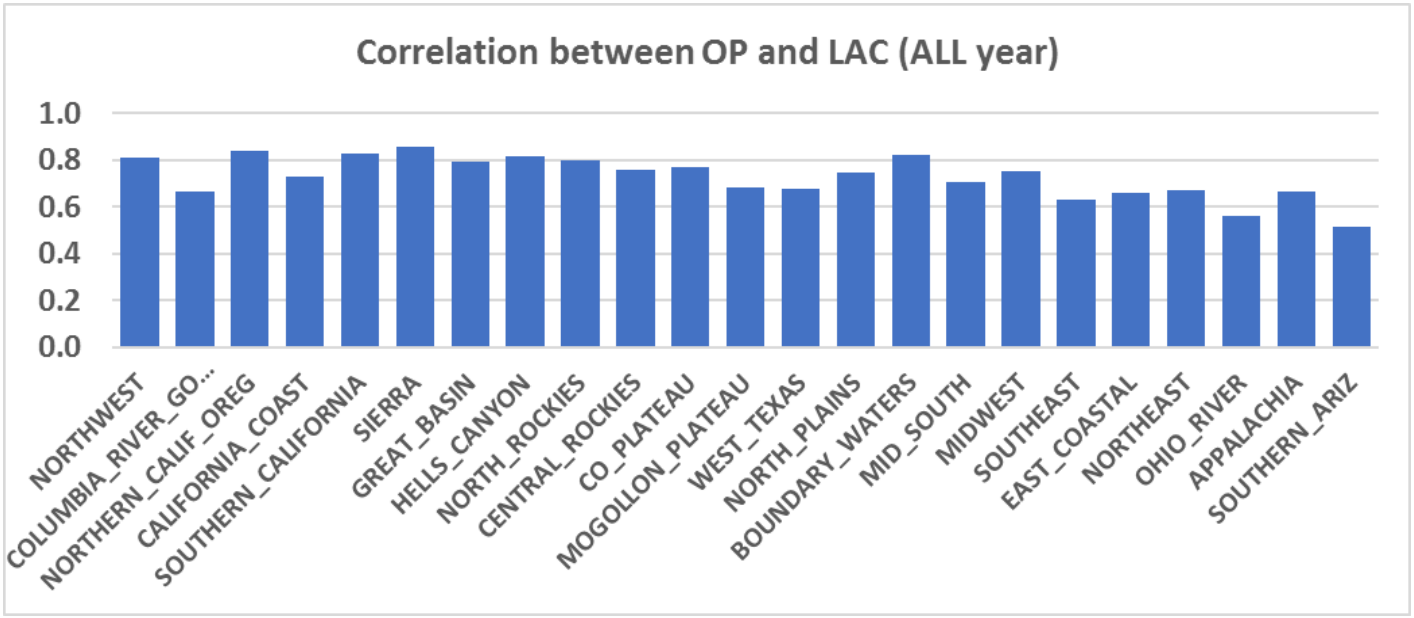


- OP has also decreased by about 0.25 ug/m3 but this corresponds to about a 50% decrease.

Can a accelerated decrease in OP affect the Roc adjustment?

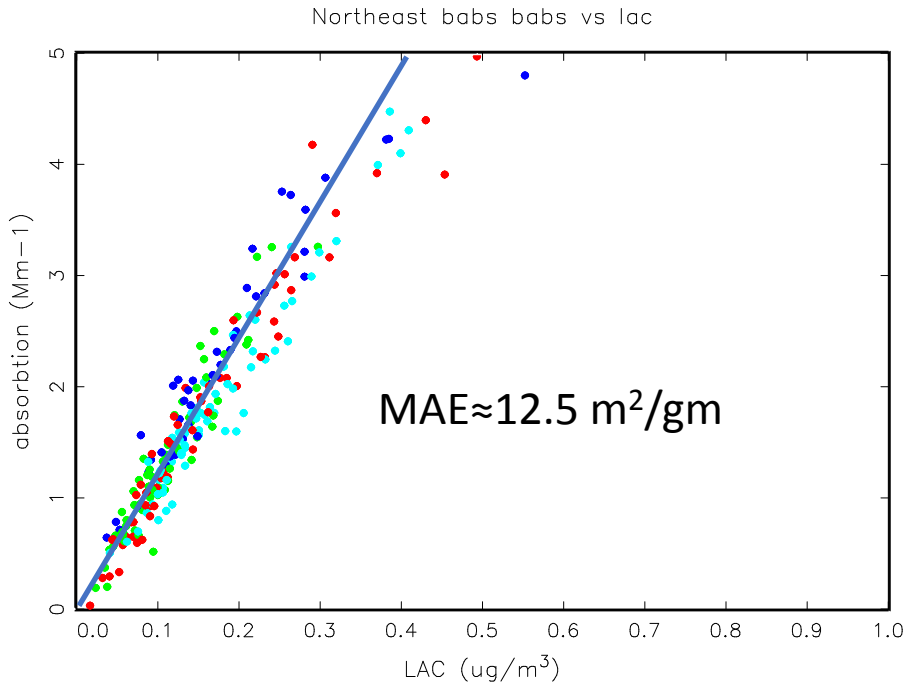
At least three processes point to LAC being part of OP

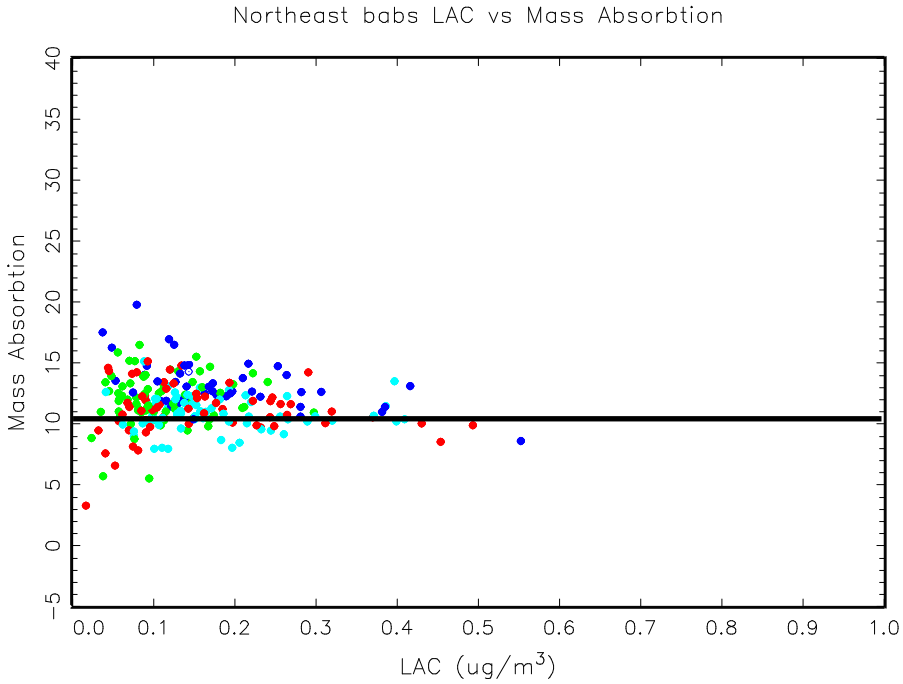
- High degree of correlation between OP and LAC
- Mass extinction efficiency of LAC is physically unreasonable at about 10 m^2/gm.
- As OP/OC has decreased R_{oc} has commensurately increased consistent with LAC in OC decreasing.

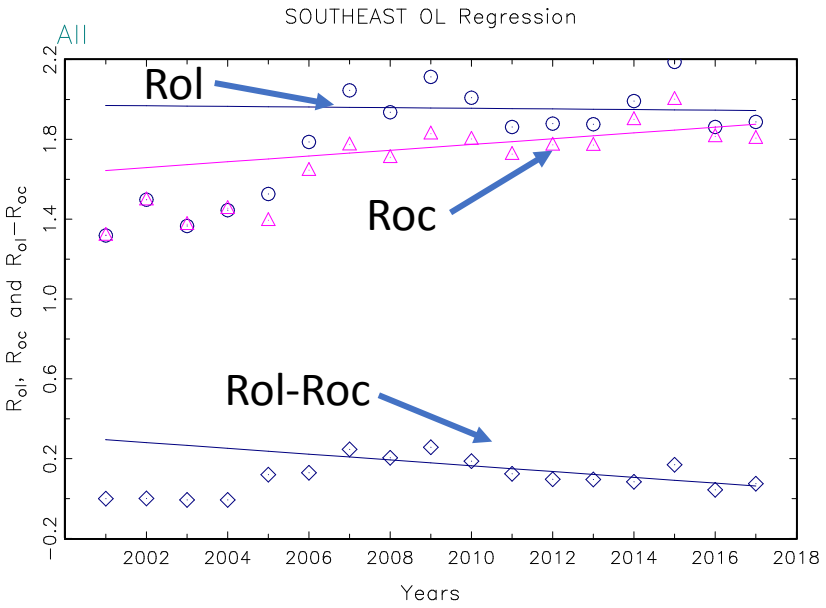


Implied mass absorption efficiency of LAC is greater than 5-7 m^2/gm. (Unrealistic!)

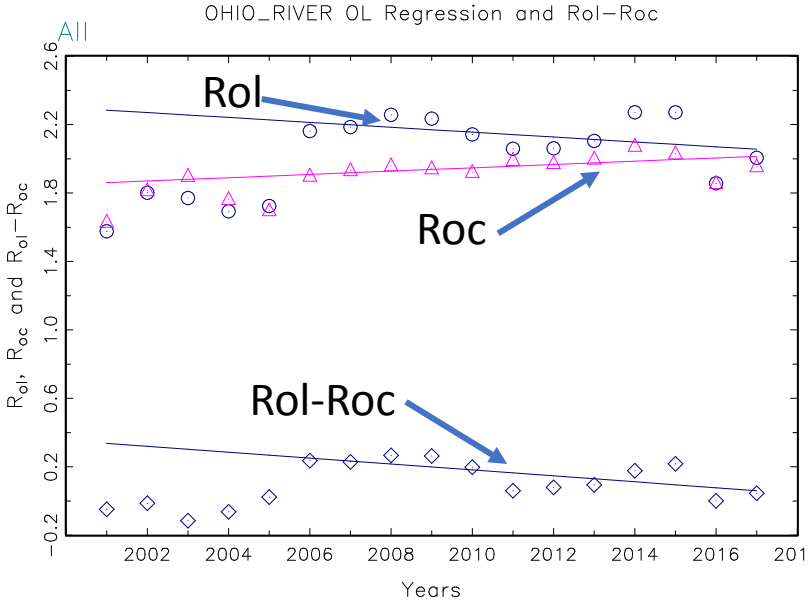
- Implies an underestimation of LAC.

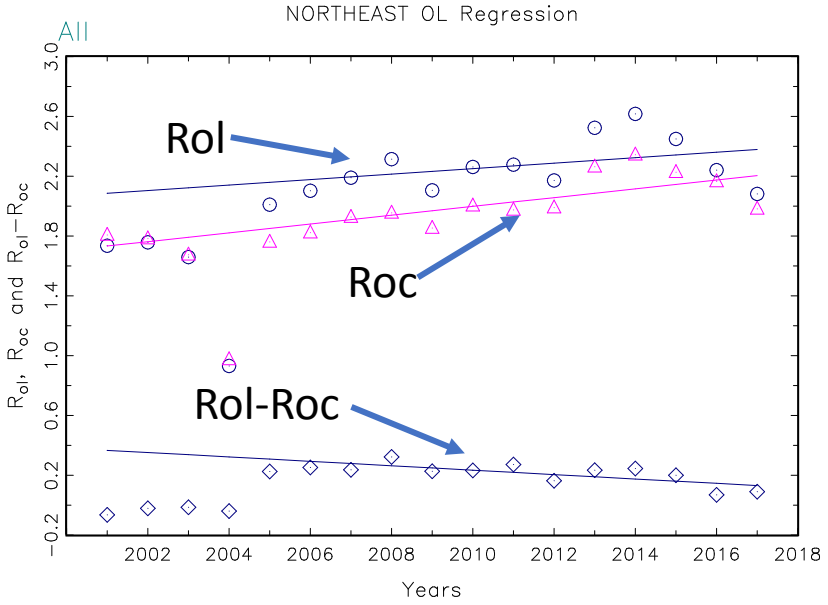




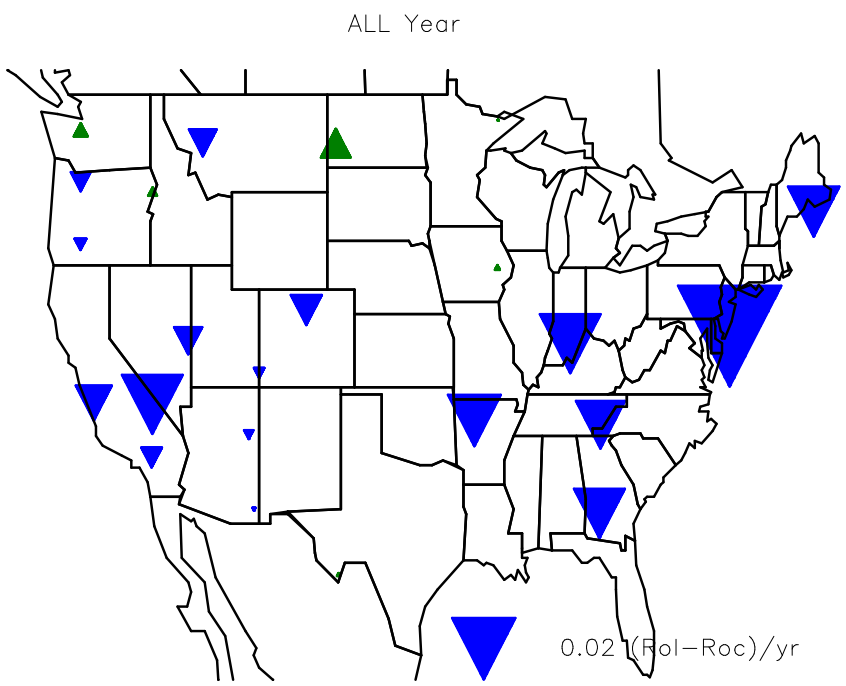


- OP is a mix of low molecular weight carbon (LAC) and typical organic carbon (OC).
- OL=OC-OP is referred to as “low temperature carbon”.
- FM=$a_1SO_4+a_2NO_3+a_3OL+a_4$Other, where Other=SS+LAC+OP+dust
- $a_3=R_{ol}$ is approximately constant over 2006-2017 time frame.
- Difference between R_{ol} and R_{oc} decreases over time consistent with a decrease in LAC fraction of OP.
- Roc is approaching value of R_{ol} implying organic fraction of OP has similar molecular mass as OL.

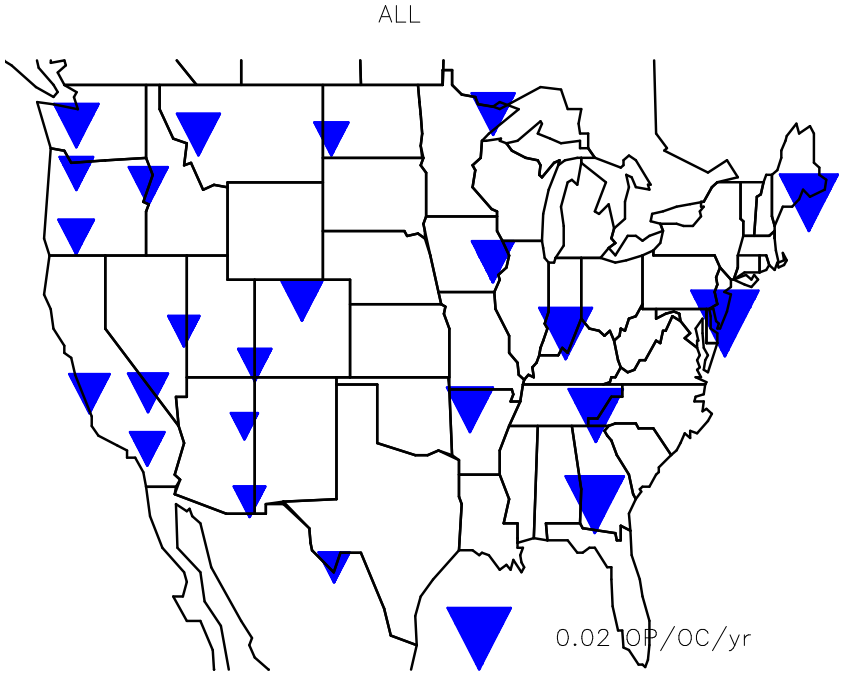




Rate of change in difference between R_{ol} and R_{oc} and OP/OC in CONUS.



$(R_{ol}-R_{oc})/yr$



(OP/OC)/yr

Estimating the fraction of OP that is OC

$OMC=R_{oc}*OC=R_{oc}(OL+OP)$

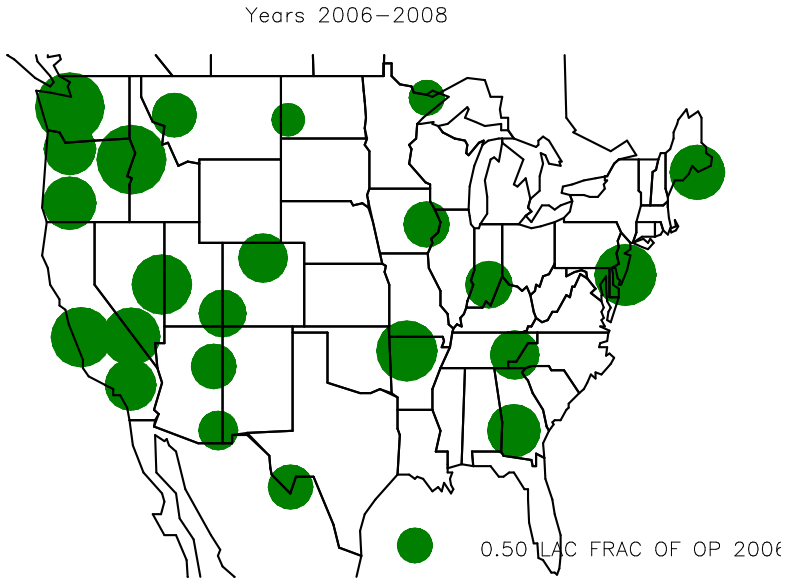
$OMC=R_{ol}(OL+f*OP)+(1-f)OP$

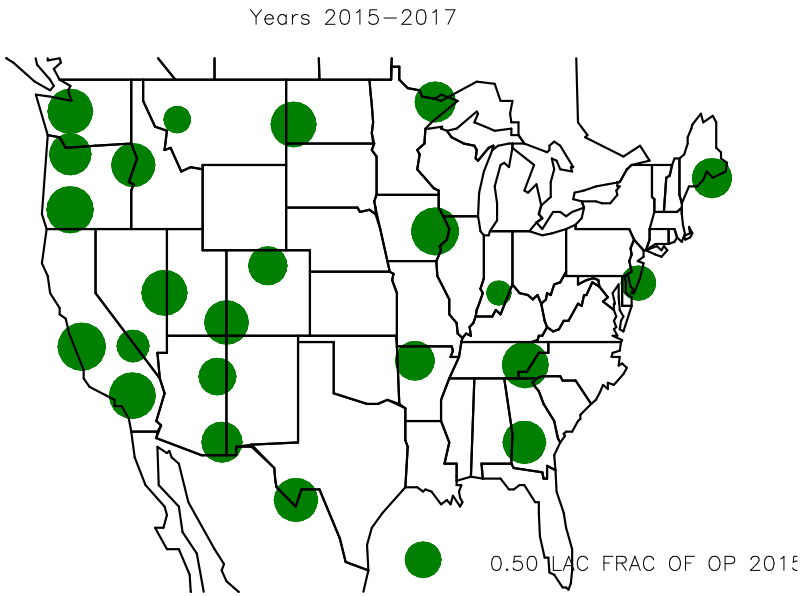
Where f is the fraction of OP that is OC and (1-f)OP is fraction of OP that is low molecular weight carbon (LAC).

Therefore $\mathbf{R_{oc}*(OL+OP)= R_{ol}*(OL+f*OP)+(1-f)*OP}$ and solving for f yields

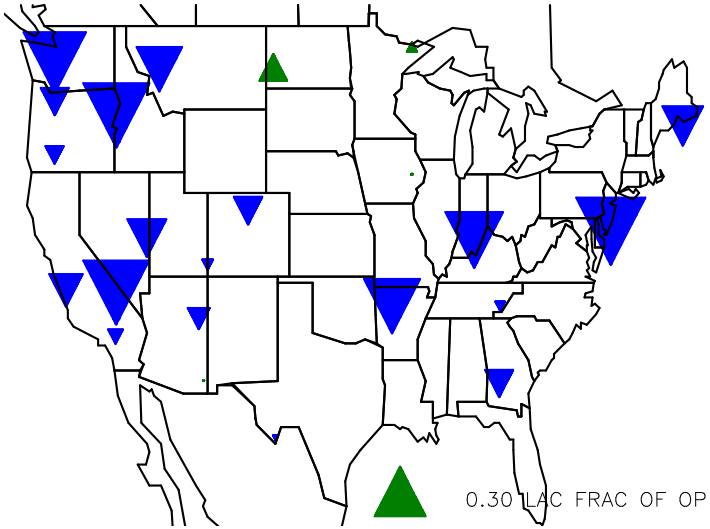
$$f = \frac{OL(R_{oc} - R_{ol}) + OP(R_{oc} - 1)}{OP(R_{ol} - 1)}$$

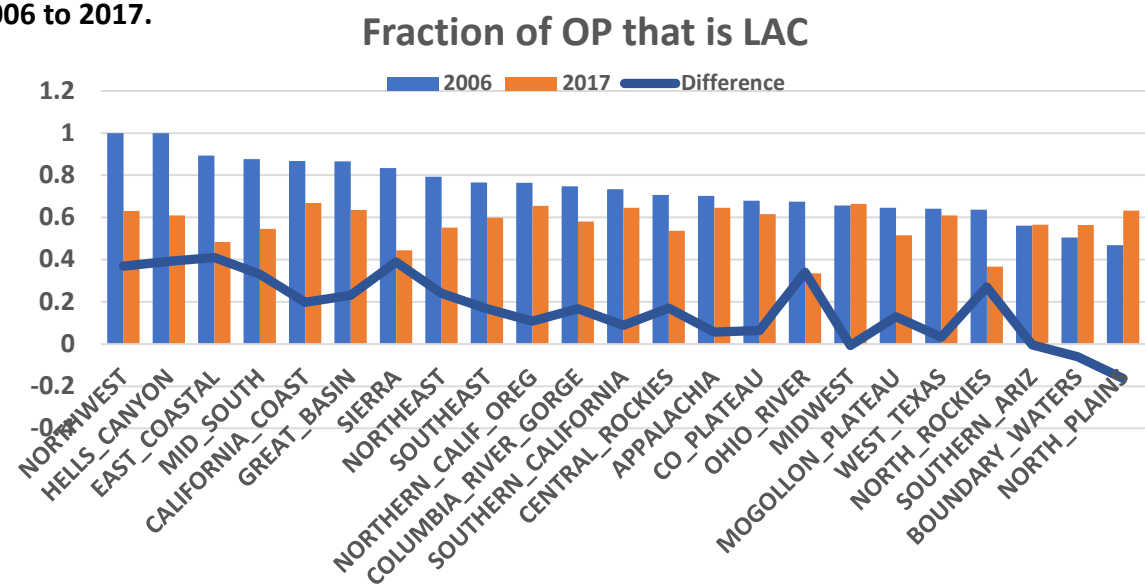
Fraction of OP that is LAC





The fraction of OP that is LAC has gone down from 2006 to 2017.





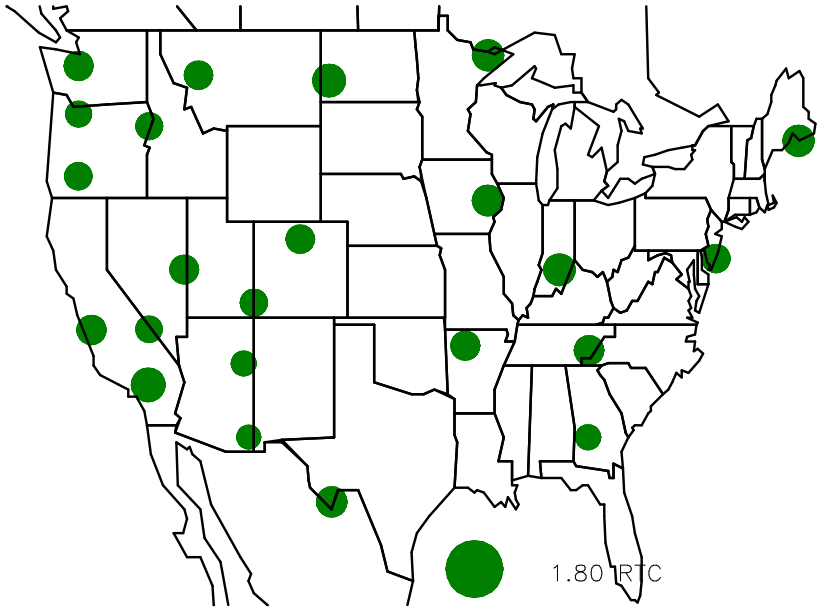
Questions/Issues

- Evidence strongly suggests that a significant fraction of LAC is being attributed to OP and counted as organic carbon resulting in an increase in R_{oc} as OP/OC decreases.
- With the introduction of O_2 during the TOR carbon analysis LAC and pyrolyzed organic carbon (PC) appear to be oxidized and detected during the entire E1 temperature step.
- If pyrolyzed and LAC carbon had the same optical characteristics and the optical characteristics of LAC did not change during heating a return of filter reflectance to its original value should correspond to a quantity of carbon left on the filter that is representative of collected LAC.

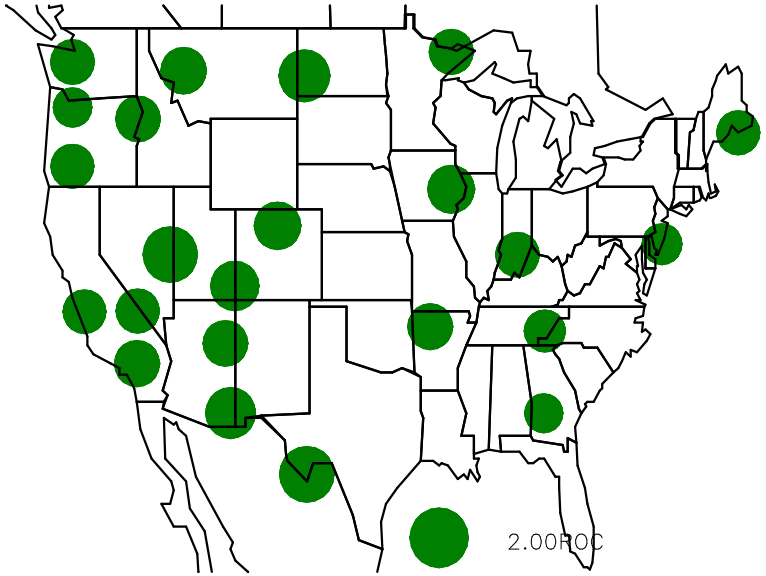
Possible cause for underestimation of LAC

- The PC may be darker (higher MAE) than EC resulting in reflectance that is less than the original EC which in turn results in an underestimation of LAC.
- Heating process results in a PC-EC mix that is darker than the original EC on the filter.
- Chemical structure of the PC-EC mix may change the wavelength dependency of reflectance.
- Thermal process (heating of the filter) in the presence of OC may change the filter reflectance characteristics
- Other processes?

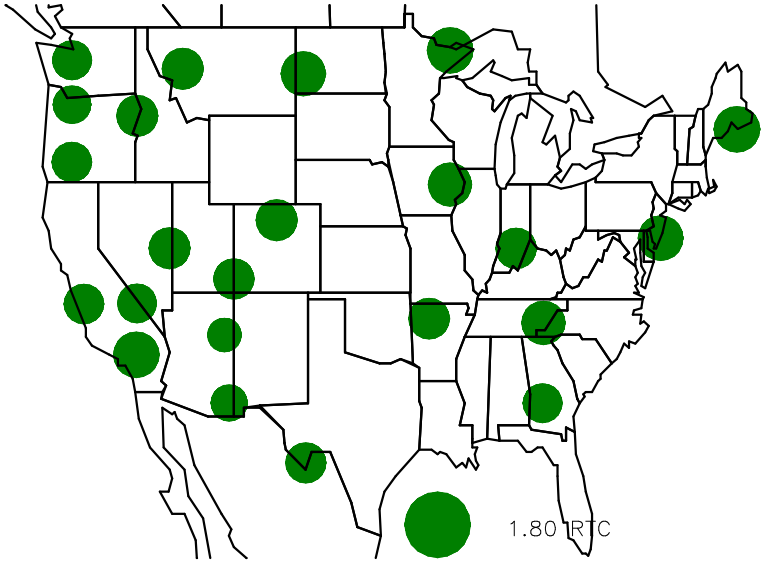
Regress TC 2000–2002 All



Regress POM 2000–2003 All



Regress TC 2014–2016 All



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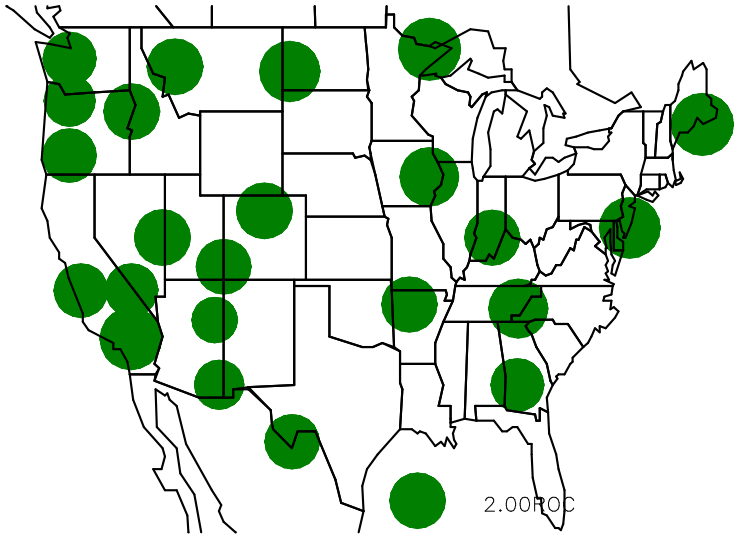
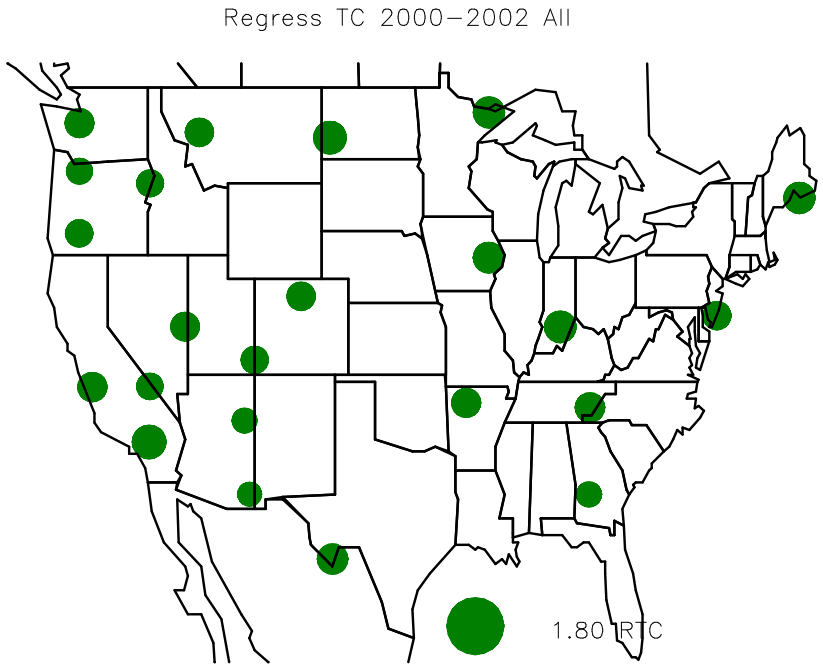
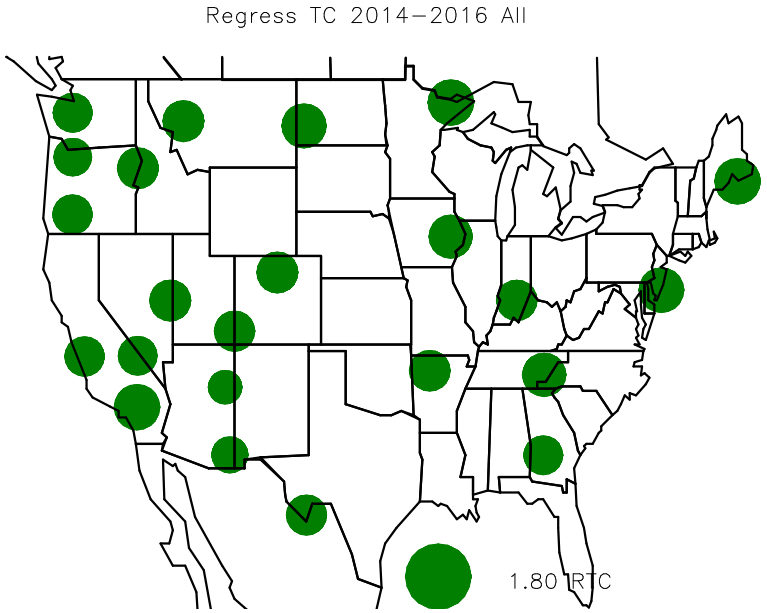
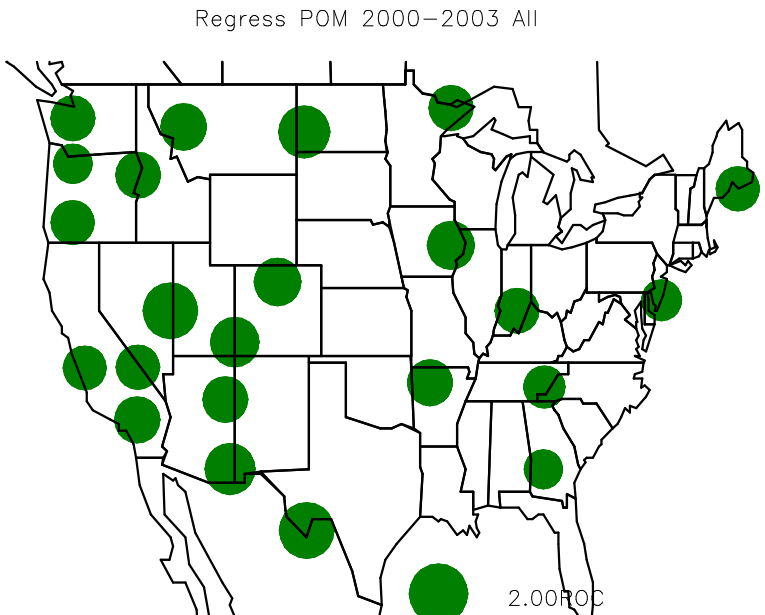
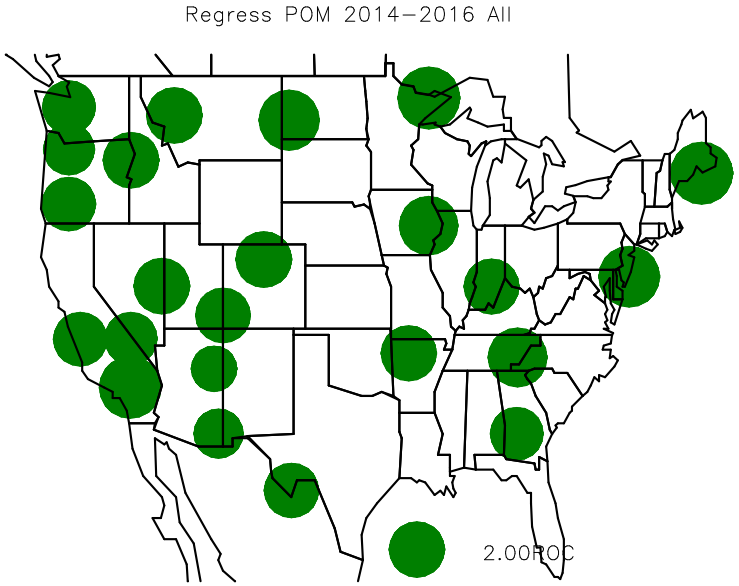


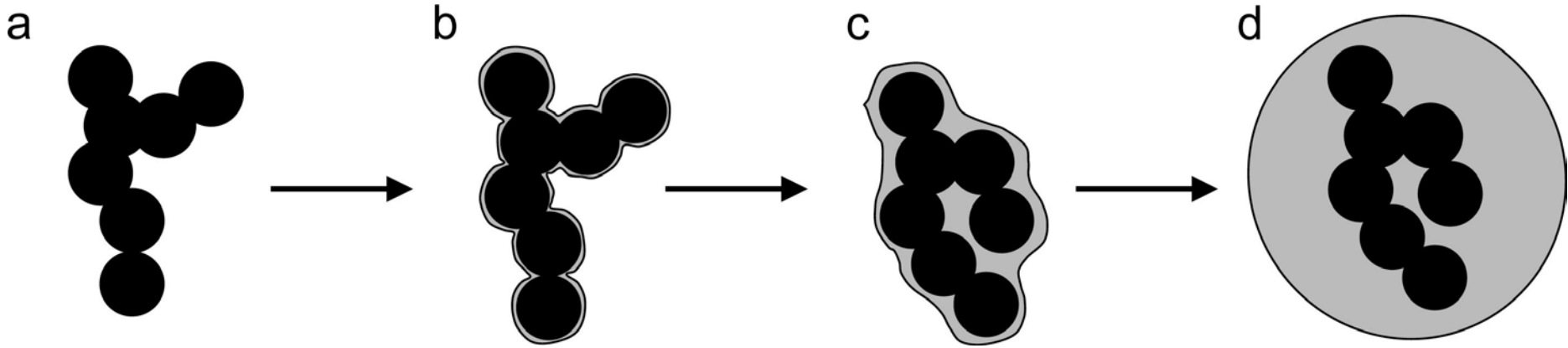
R_{tc} and R_{oc} for years 2000-2002 and 2014-2016







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