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# Recent changes in PM<sub>2.5</sub> Chemical Speciation Network (CSN) organic and elemental carbon measurements.

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EPA Region 10

NW-AIRQUEST

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## Background

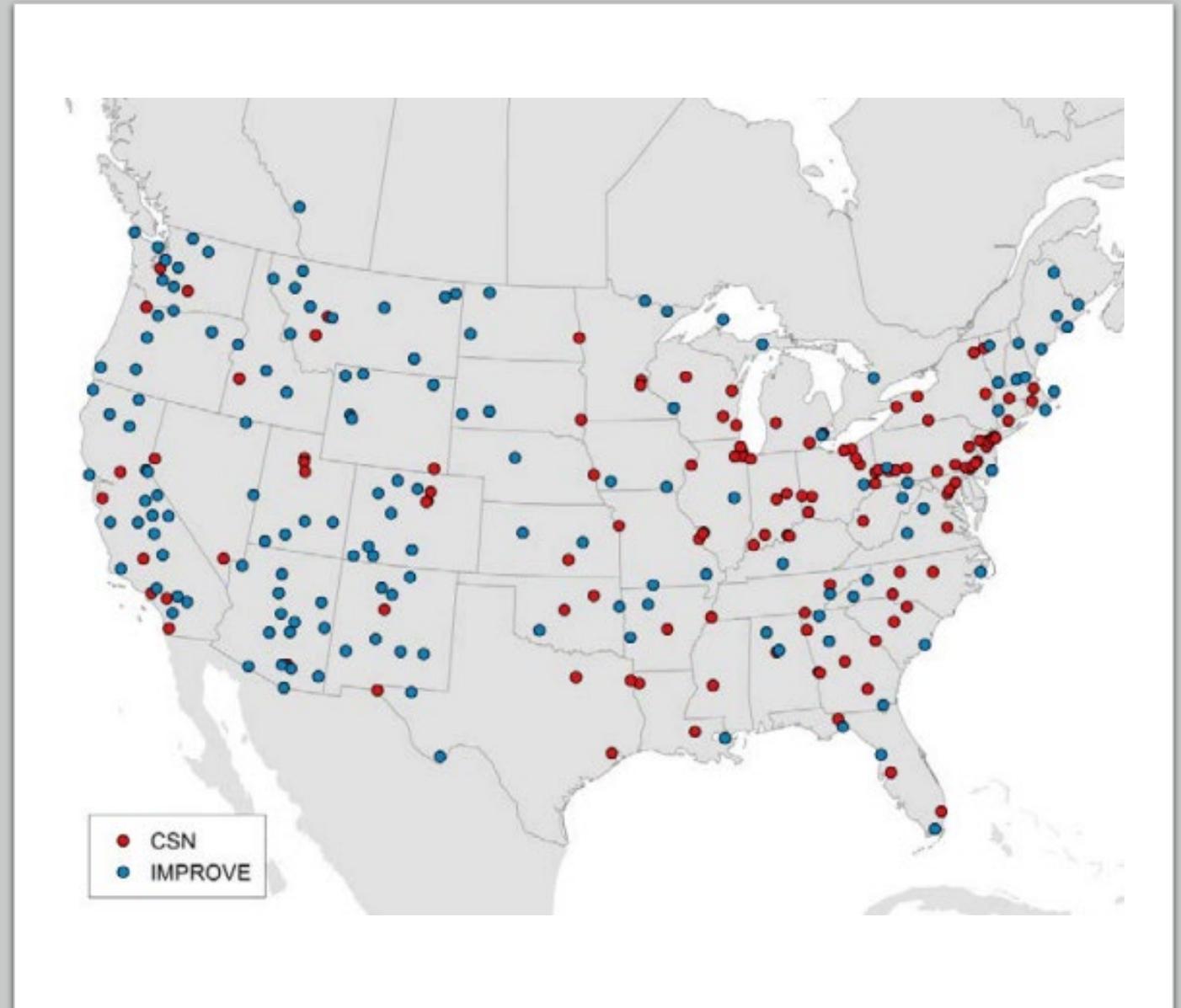
- Two widespread PM<sub>2.5</sub> chemical speciation networks in the US
- 24-hour integrated samples
- ~ 160 sites in each network

### **CSN (urban, suburban)**

- 1-in-1, 1-in-3, or 1-in-6 day sampling
- Created to support the 1997 PM<sub>2.5</sub> NAAQS

### **IMPROVE (rural – National Parks)**

- 1-in-3 day sampling
- Network greatly expanded to support implementation of the Regional Haze Rule in 1999.



## Background - CSN

### Why do we chemically speciate PM<sub>2.5</sub> in the CSN network?

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#### ➤ **NAAQS Attainment Demonstrations**

- In PM<sub>2.5</sub> NAAQS SIPs, chemical speciation of PM<sub>2.5</sub> is a necessary component in an attainment demonstration.
- We use bulk statistics on measured species (e.g., % OC, EC, NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub> ...)

#### ➤ **Source Apportionment Analyses**

- Chemical speciation of PM<sub>2.5</sub> is used to better understand the causes and sources of PM<sub>2.5</sub> through source apportionment analysis.
- Statistical models like PMF and CMB (e.g., estimates % wood smoke, % ammonium nitrate, % motor vehicles).

#### ➤ **Regional/National Trends Analysis**

## Background

Why is organic carbon (OC) and elemental carbon (EC) the focus in this presentation.

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- There was a recent change in the CSN network (October 2018) effecting the measured OC and EC.
- OC and EC are the biggest component of PM<sub>2.5</sub> for most areas with PM<sub>2.5</sub> problems in the Northwest (e.g., wood smoke)

A general note of caution, network changes have occurred that effect other chemical species. See data advisories:

CSN Network: <https://www.epa.gov/amtic/chemical-speciation-network-csn-data-reporting-and-validation-files>

IMPROVE network: <http://vista.cira.colostate.edu/Improve/data-advisories/>

## Background

### How are OC and EC measured in the CSN & IMPROVE networks?

➤ **PM<sub>2.5</sub> collected on quartz filters**

➤ **OC and EC are measured via thermal-optical analysis (TOA)**

- **TOA involves thermal evolution of carbon at increasing temperatures**
- **first under an inert atmosphere for OC1, OC2, OC3, OC4 (sum + OP = OC)**
  - **and then an oxidizing atmosphere for EC1, EC2, EC3 (sum = EC)**
  - **Laser optical reflectance or transmittance is used to correct the OC/EC split to account for OC charring (pyrolysis, 'OP', added to OC mass)**

➤ **The carbon mass evolved at different temperatures provides some information about the chemical composition of PM<sub>2.5</sub> carbon compounds.**



Figure 2, Gallagher et al, 2018 (<https://doi.org/10.2495/EI-V1-N2-127-138>)

## Background - CSN

### 3 main factors effecting measurements of OC and EC.

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- Sample collector design (PM2.5 inlet, filter size, flow rate ...).

Pre-2007: Several

Post-2009: URG-3000N

- Thermal protocol used by analytical lab (temperature thresholds, temp. hold times, method to evaluate OC pyrolysis [optical reflectance or transmittance] ...)

Pre-2007: NIOSH (optical transmittance)

Post-2009: IMPROVE\_A (optical reflectance)

[Note: Since 2009, sampler design and thermal protocol consistent in CSN.

However, three different analytical instruments used]

- Analytical instrument (oven design, sample placement, ...)

Pre-2016: DRI Model 2001

2016 – 10/2018: DRI Model 2015

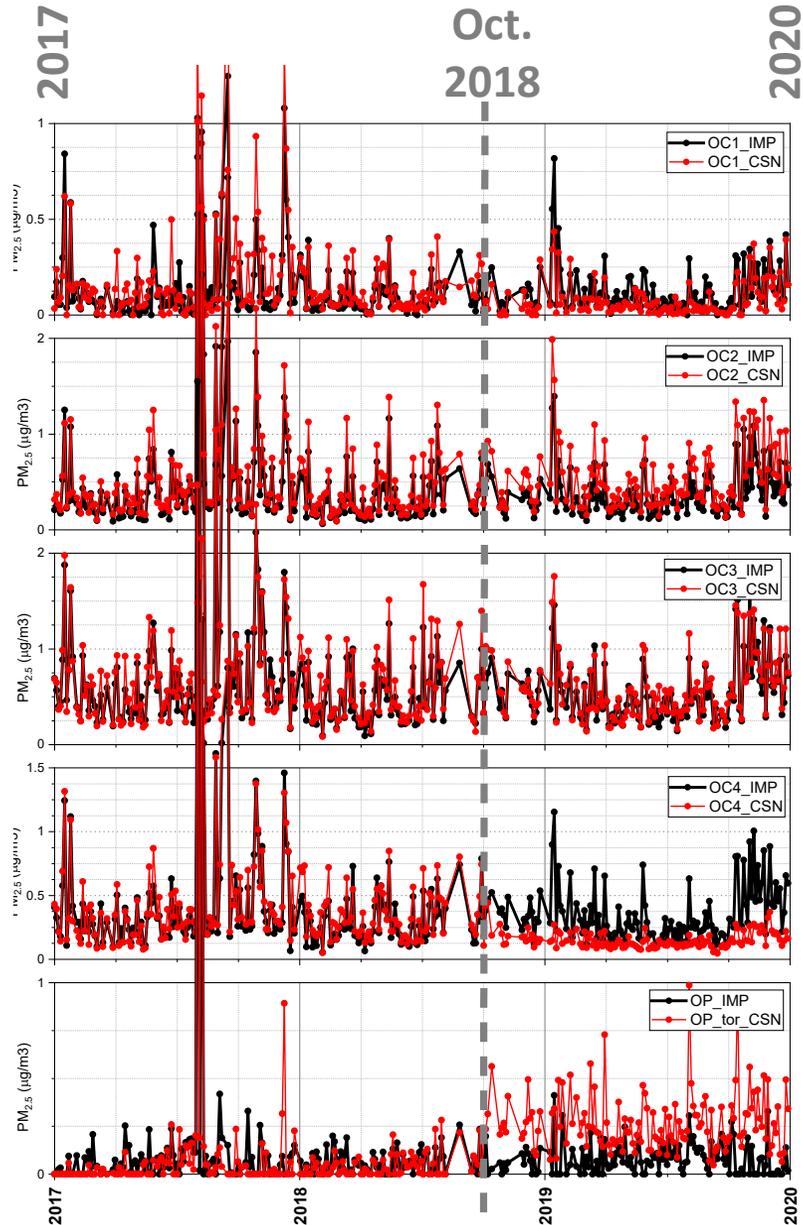
10/2018 -> present: Sunset-5L



**This ppt focuses on the effects of the transition in 10/2018.**

# How does the data look, pre and post 10/2018? [Note, no significant changes in IMPROVE network]

## Example: Co-located CSN and IMPROVE in Seattle



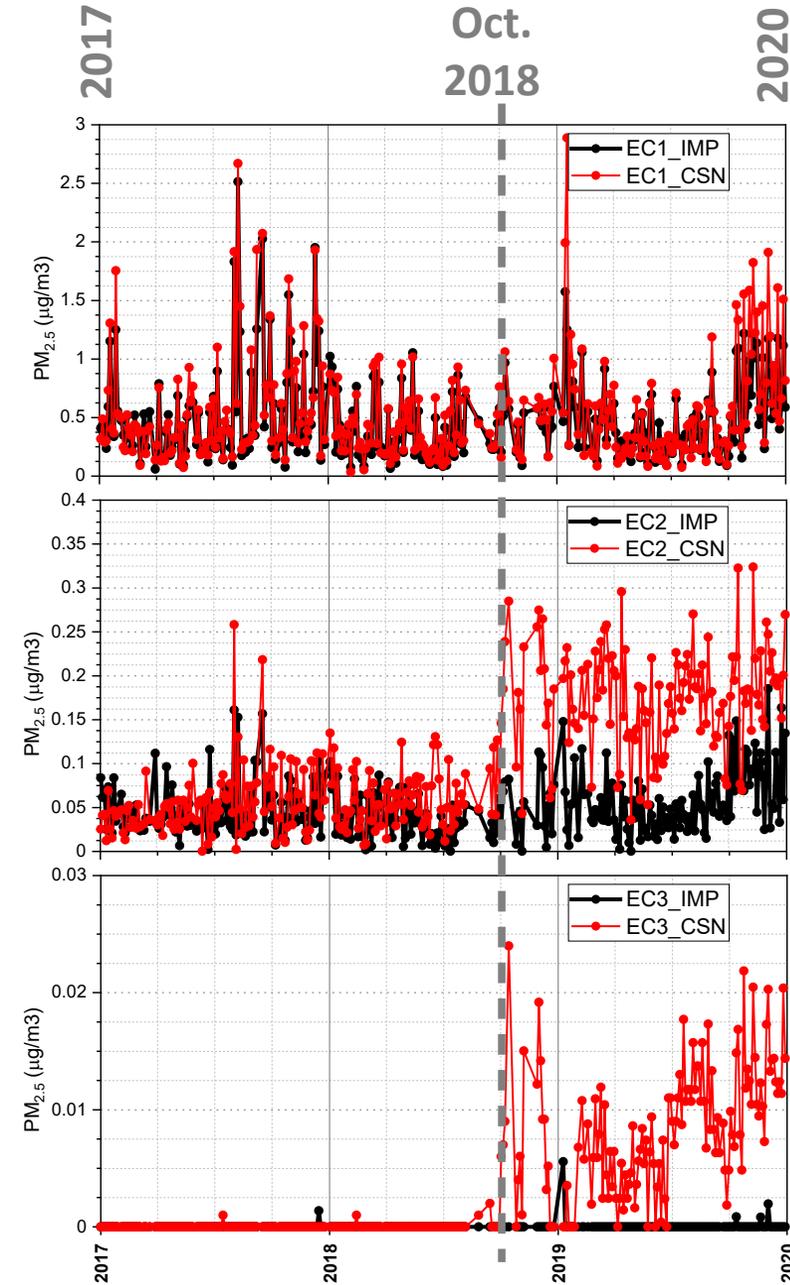
OC1 IMPROVE  
OC1 CSN

OC2 IMPROVE  
OC2 CSN

OC3 IMPROVE  
OC3 CSN

OC4 IMPROVE  
OC4 CSN

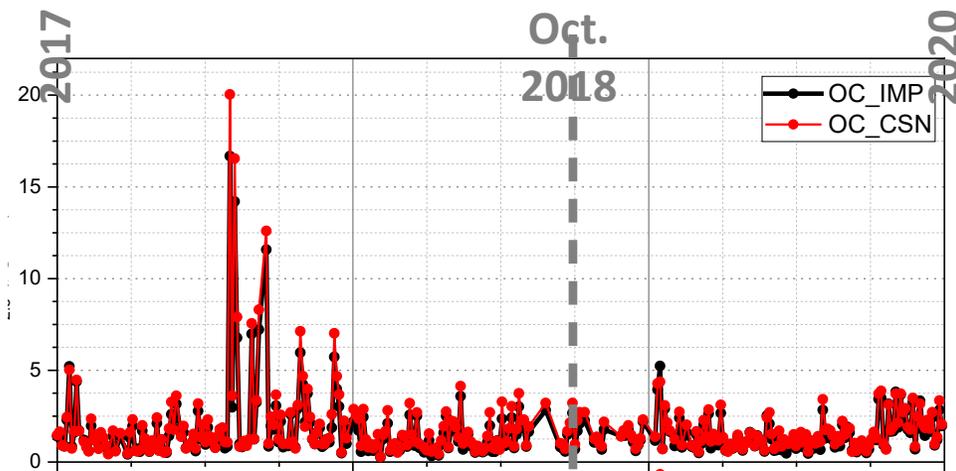
OP IMPROVE  
OP CSN



EC1 IMPROVE  
EC1 CSN

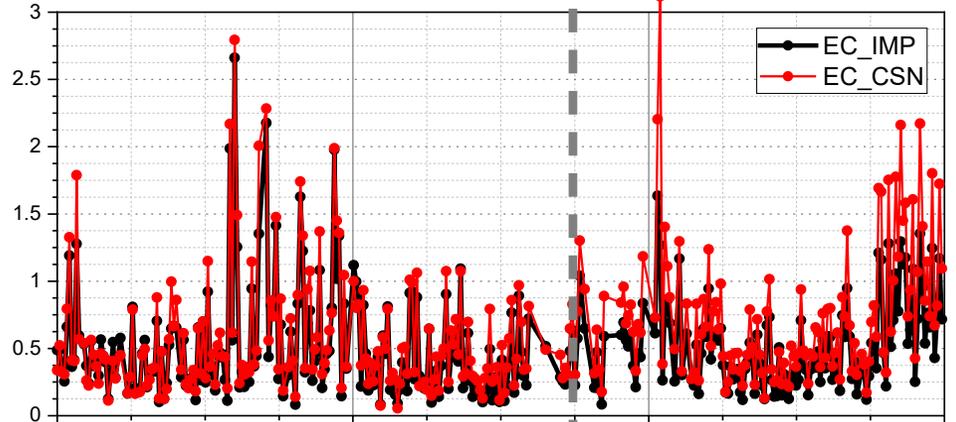
EC2 IMPROVE  
EC2 CSN

EC3 IMPROVE  
EC3 CSN



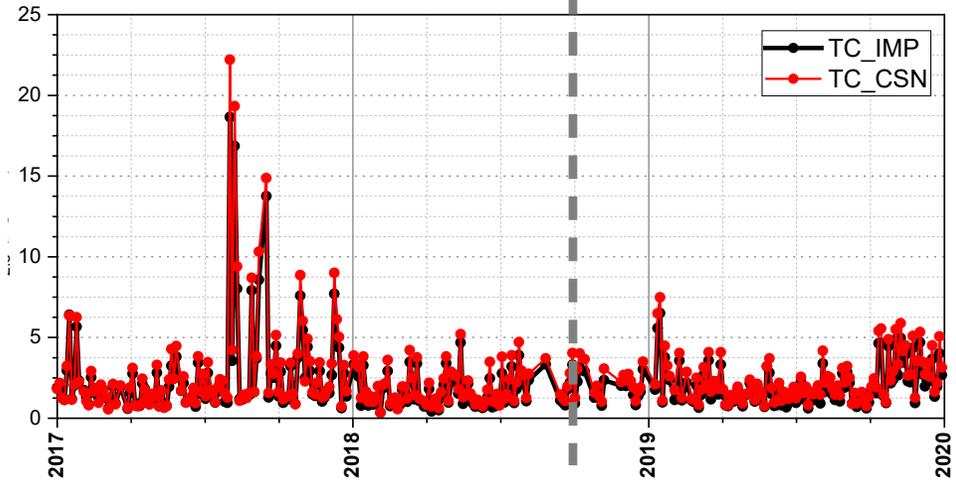
**OC IMPROVE**  
**OC CSN**

**[CSN Decrease in  
OC after 10/2018]**



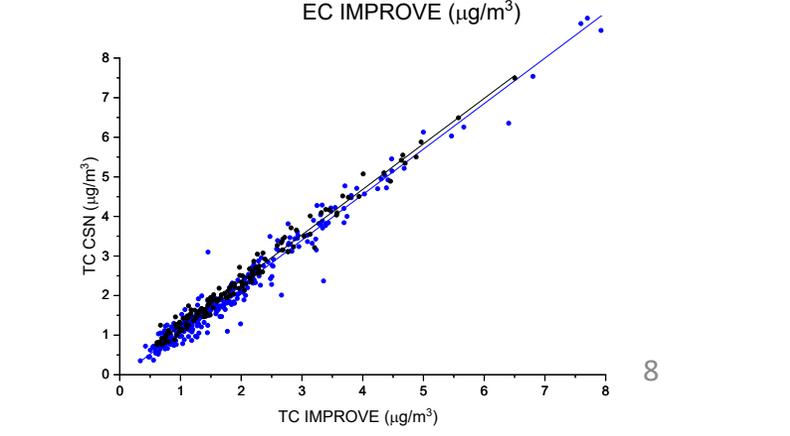
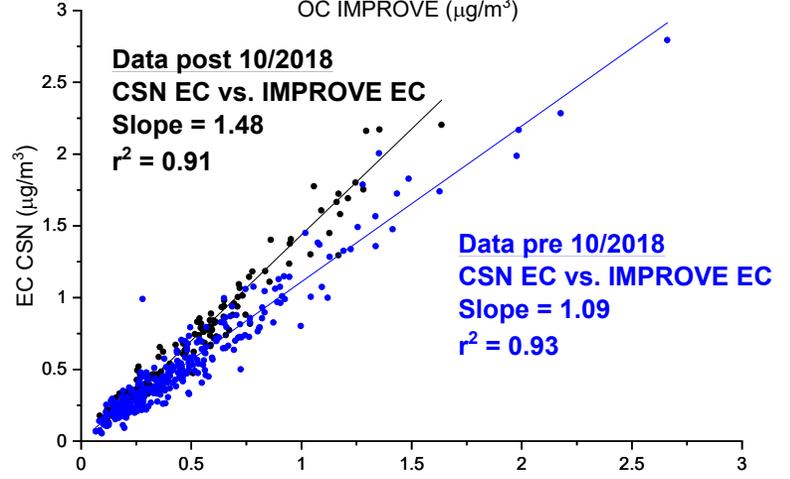
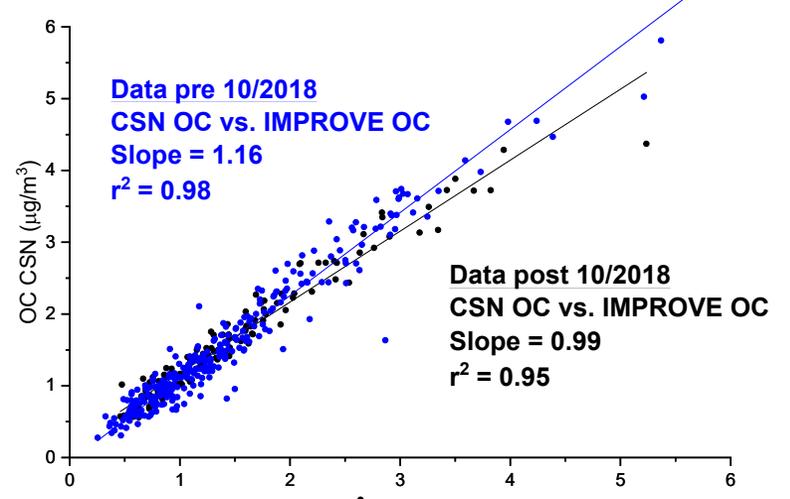
**EC IMPROVE**  
**EC CSN**

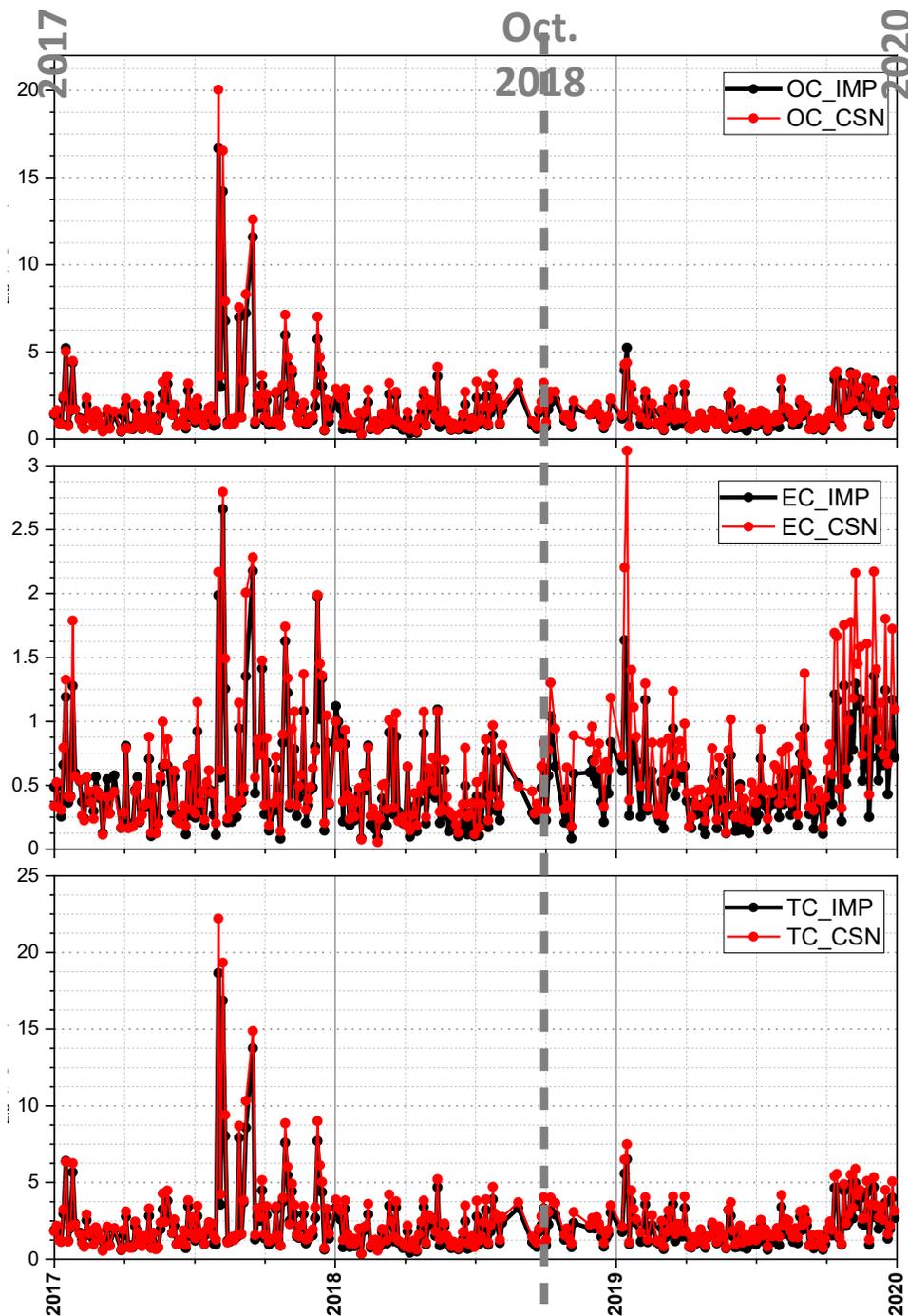
**[CSN Increase in EC  
after 10/2018]**



**TC = OC + EC**  
**TC IMPROVE**  
**TC CSN**

**[CSN TC no apparent  
change]**





**OC IMPROVE**  
**OC CSN**

[CSN Decrease in  
OC after 10/2018]

**-4.1**

**EC IMPROVE**  
**EC CSN**

[CSN Increase in EC  
after 10/2018]

**11.2**

**TC = OC + EC**  
**TC IMPROVE**  
**TC CSN**

[CSN TC no  
apparent  
change]

**-0.9**

**SRD between  
instruments pre (DRI)  
and post (Sunset) Oct.  
2018 (4073 samples)**

In 2021 Zhang et al.  
published results of an  
intercomparison  
between:

**DRI Model 2015 (x)**  
and **Sunset-5L (y)**

(<https://doi.org/10.5194/amt-14-3217-2021>)

They reported the  
**Scaled Residual  
Difference (SRD)**  
between the 2  
instruments

$$SRD = \frac{(y-x)/SQRT(2)}{(y+x)/2} \times 100$$

**Zhang et al. results jibe  
with IMPROVE vs. CSN  
co-located analysis**

## Effects of CSN Change on PMF Source Apportionment

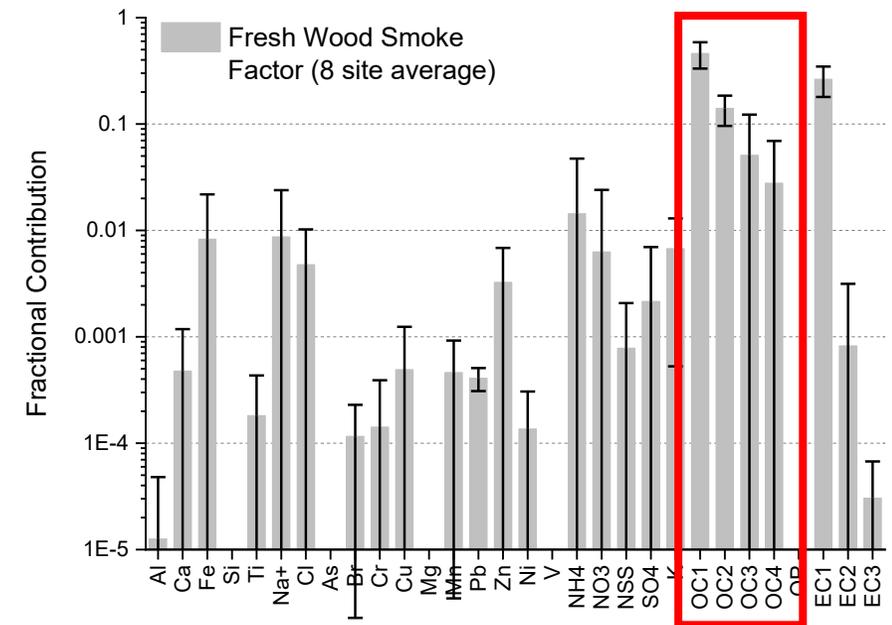
**Example - Shift in pattern of OC and EC that represents fresh wood smoke**

**Conclusion – Data pre and post Oct. 2018 should be run in separate PMF analyses.**

Average PMF Wood Smoke Factors using data from 2007 – Sept. 2018

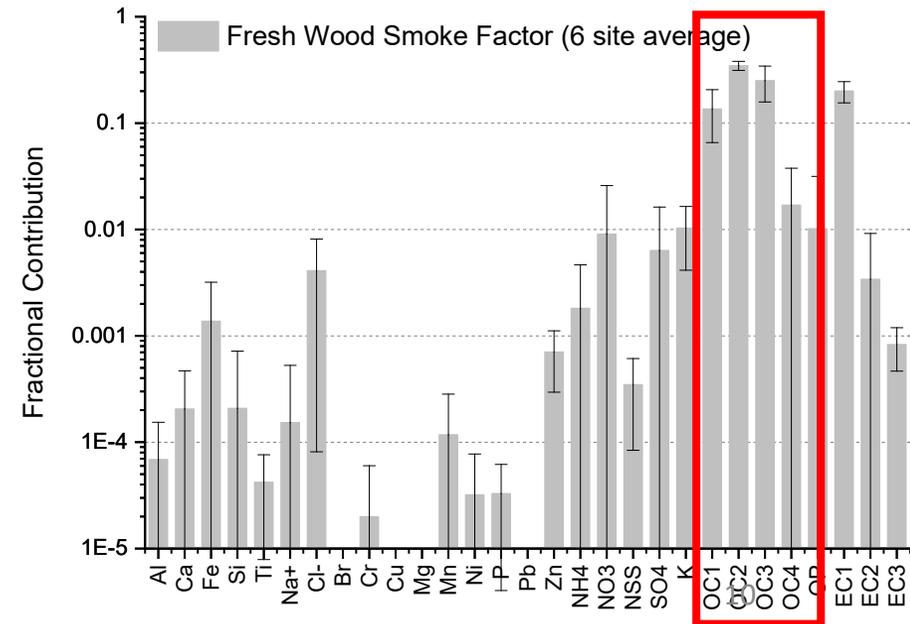
Mostly OC1 & EC1

*Kotchenruther, Atmospheric Environment 237 (2020) 117724*



Average PMF Wood Smoke Factors using data after 10/1/2018

Mostly OC2, OC3, & EC1

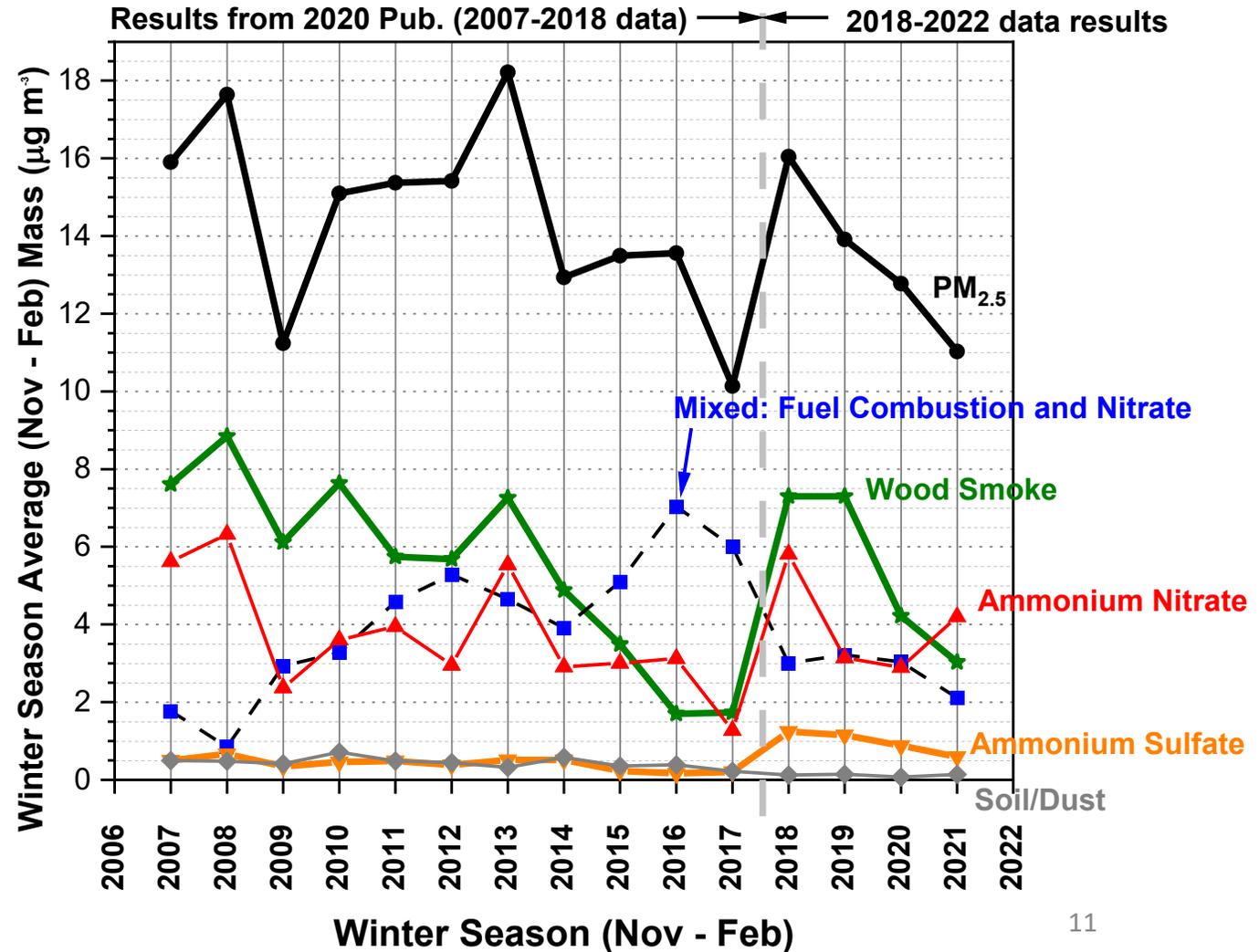


Example of combining source apportionment results - Yakima Source Apportionment – annual winter season analysis

Items to note:

- Plot is of yearly seasonal average mass for PM2.5 and PMF Factors.
- E.g., ‘2021 season’ average = average of Nov 2021 through Feb 2022
- Data for 2007 – 2017 seasons from 2020 publication\*
- Data for 2018 – 2021 seasons from new PMF modeling
- Modeling pre and post 10/2018 needs to be separate because of analytical lab changes
- Some changes in source apportionment can be artifacts of the separate analysis (e.g., ammonium sulfate)

Combined results of 2 source apportionment analyses, separating data pre and post Oct. 2018



\*R. A. Kotchenruther, Atmospheric Environment 237 (2020) 117724

## In summary

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- **CSN lab and analytical instrumentation change in Oct. 2018 causes:**
  - **Decrease in reported OC**
  - **Increase in reported EC**
  - **Little change in reported TC**
  - **Significant changes in reported carbon fraction masses, especially OC4, OP, EC2, & EC3**
  
  - **Recommend keeping this in mind when reviewing site statistics on OC and EC pre and post Oct. 2018**
  
- **Instrumentation change effects PMF analyses**
  - **Recommend running separate PMF analyses pre and post Oct. 2018 (if there is enough data)**