Chemical Speciation of $PM_{2.5}$ in the Treasure Valley, Idaho, USA

Rong Li[1], Alice L. Li[2], Brian Himes[1], Wei Zhang[1]

1. Idaho Department of Environmental Quality
2. Boise High School

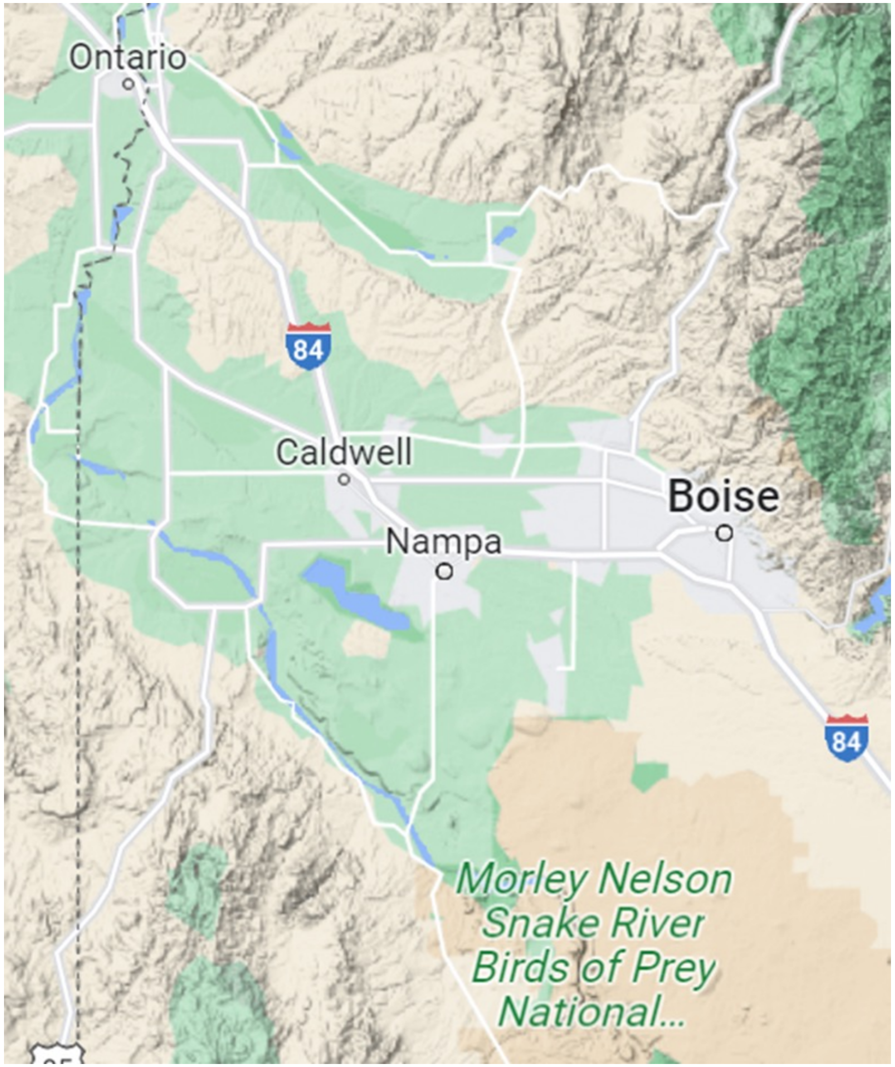
NW AIRQUEST Annual Meeting, June 28-29, 2022

Background

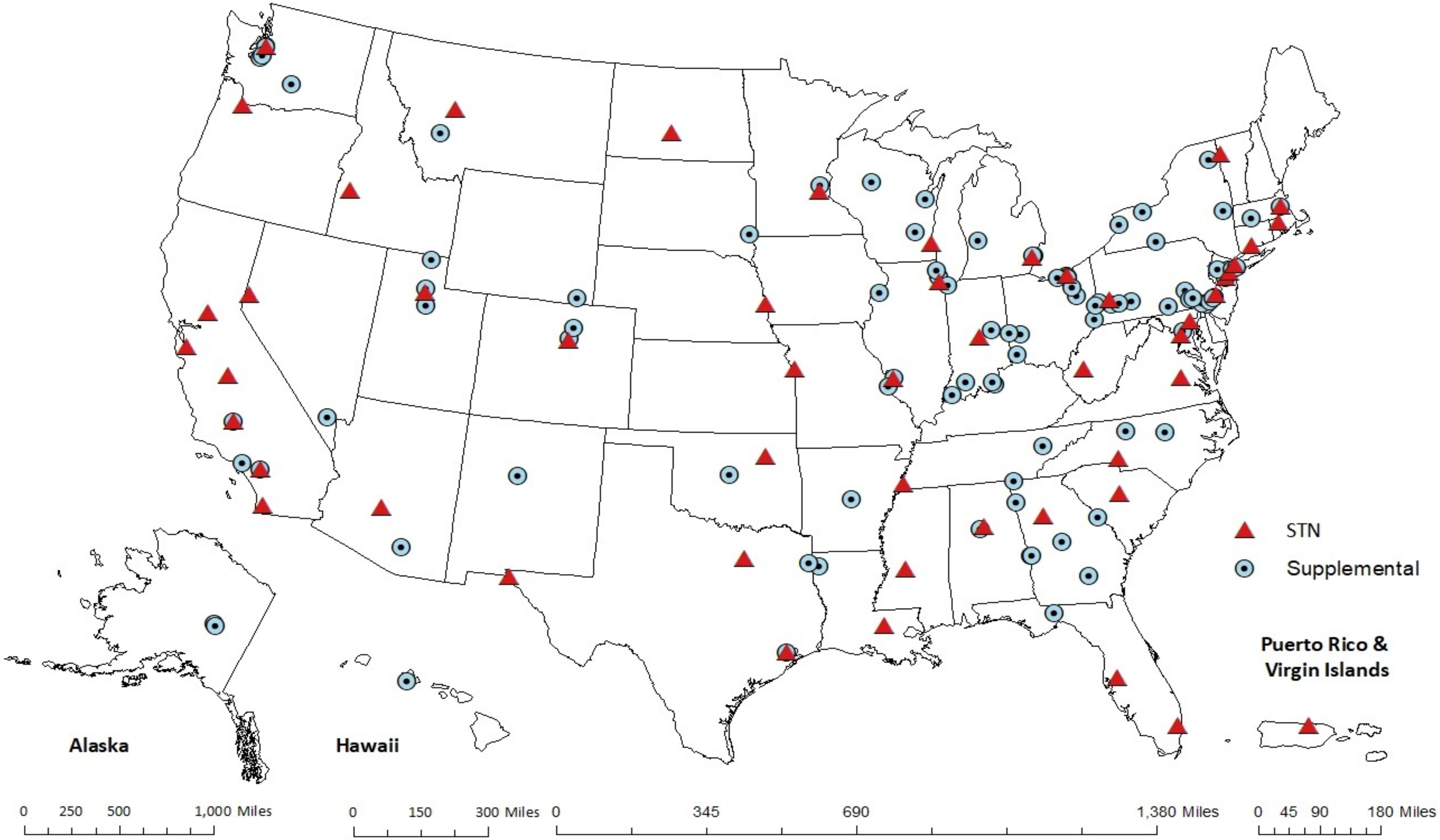
- $PM_{2.5}$ and Ozone: Adverse health effects
- EPA: National Ambient Air Quality Standards (NAAQS), The Clean Air Act
- EPA is considering to re-set tighter air quality standards (NAAQS)
- More nonattainment areas

Plans for the Treasure Valley

- The most populous metropolitan area in Idaho (a combined population of ~750k)
- SIP: Removal of Inspection and Maintenance program
- Sources of $PM_{2.5}$ and ozone
- Speciation of $PM_{2.5}$
- Receptor modeling of $PM_{2.5}$
- Regional Chemical Transport Modeling: ozone and $PM_{2.5}$
- Control measures



Chemical Speciation Network (CSN)



- ~50 STN sites: use the national contract for shipping, handling and analysis of samples for consistency
- ~100 supplemental sites: have the option of using other state, local or contract laboratories for analysis


Ontario
84
Caldwell
Boise
Nampa
St Luke's
84
Morley Nelson
Snake River
Birds of Prey
National...

Chemical Analyses and Calculations

- X-ray fluorescence; PTFE filter: elements (e.g. Al, Si, Ca, Fe, Ti, Ni, Cu, Zn, As, Mg, Sc, Na, Cl, V, Cr, Se, Br, Rb, Sr, Yt, Cs, Ba, La, Ce, Sm, Eu, Tb, Pb, K, ….)
- Ion chromatography; nylon filter: e.g. NO_3^-, SO_4^{2-}, NH4$^+$, and Na^+, Cl^-
- Thermal optical analysis (TOA); quartz filter: Carbon species (e.g. OC1, OC2, OC3, OC4, OP, EC1, EC2, EC3)

Chemical Analyses and Calculations

$$Soil = 2.2*Al + 2.49*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti$$

$$Salt = 1.8 * Cl$$

$$AS = 4.125* S$$

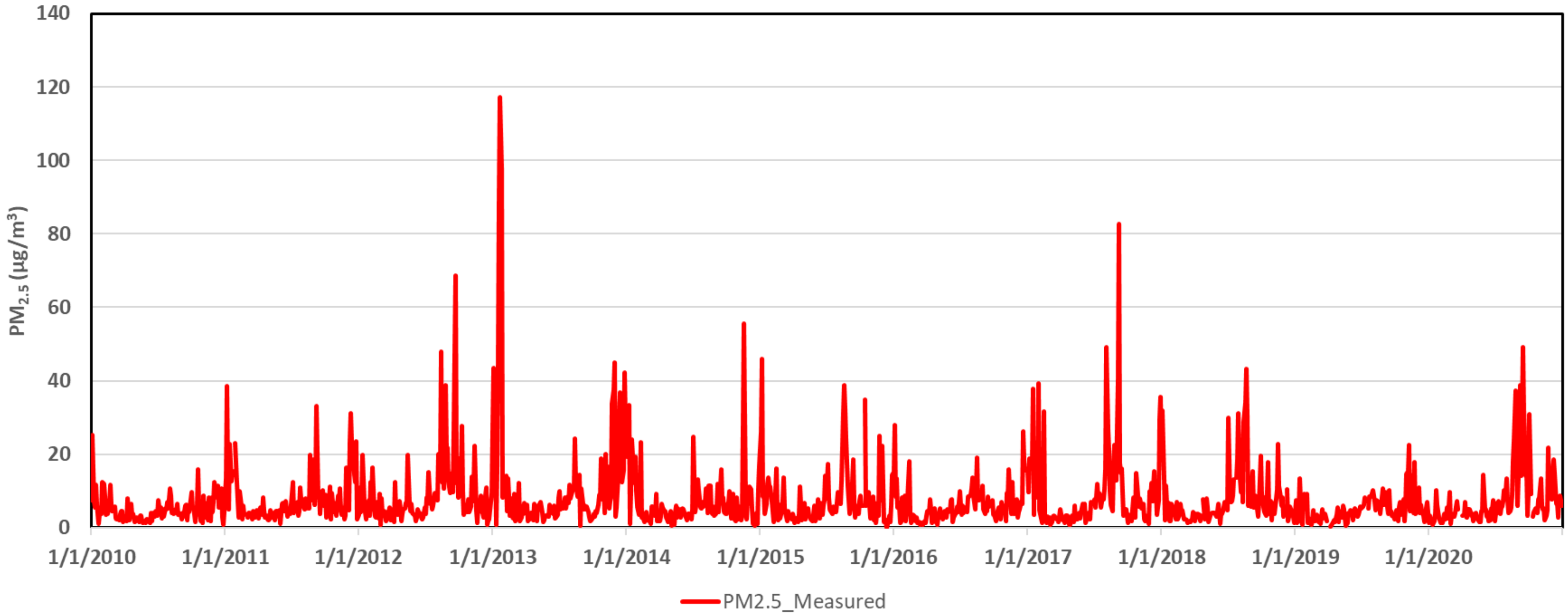
$$AN = 1.29*NO_3$$

$$OC = OC1+OC2+OC3+OC4+OP$$

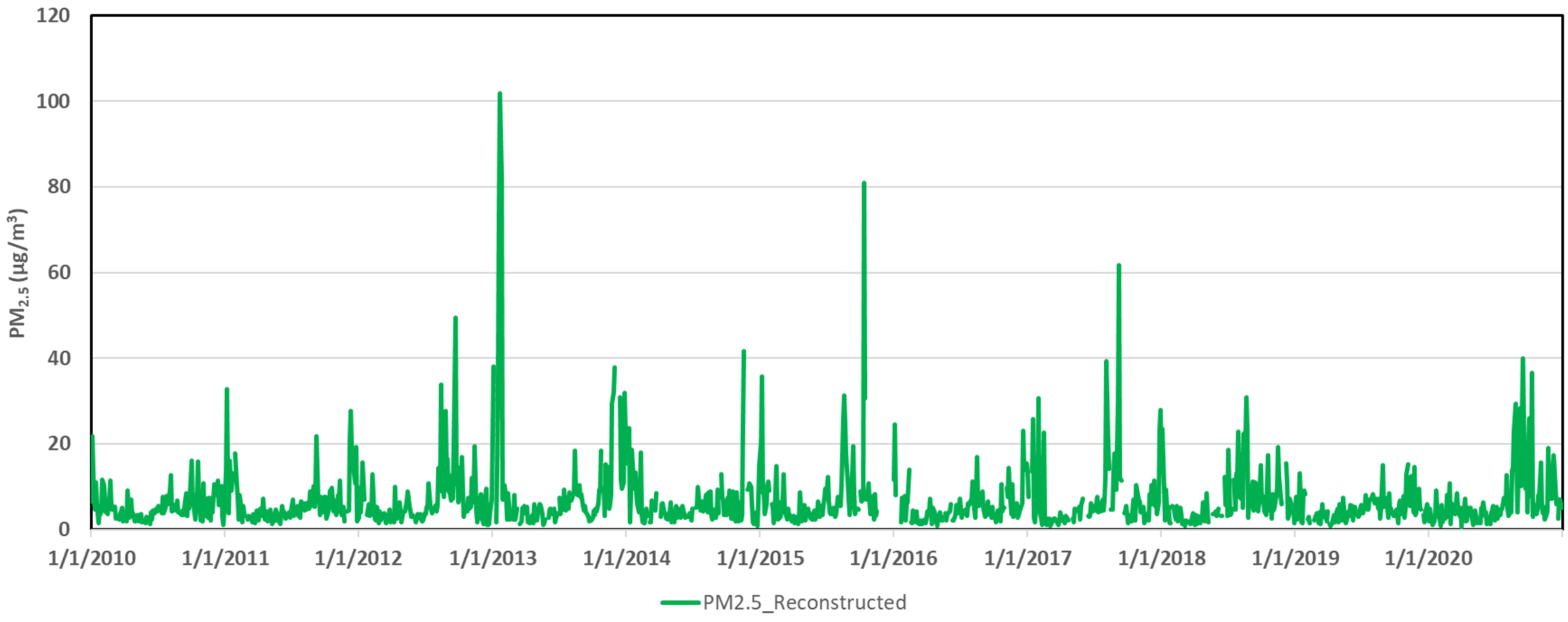
$$EC = EC1+EC2+EC3-OP$$

$$OM = 1.4* OC$$

$$\text{Reconstructed } PM_{2.5} = OM + EC + Soil + Salt + AS + AN$$

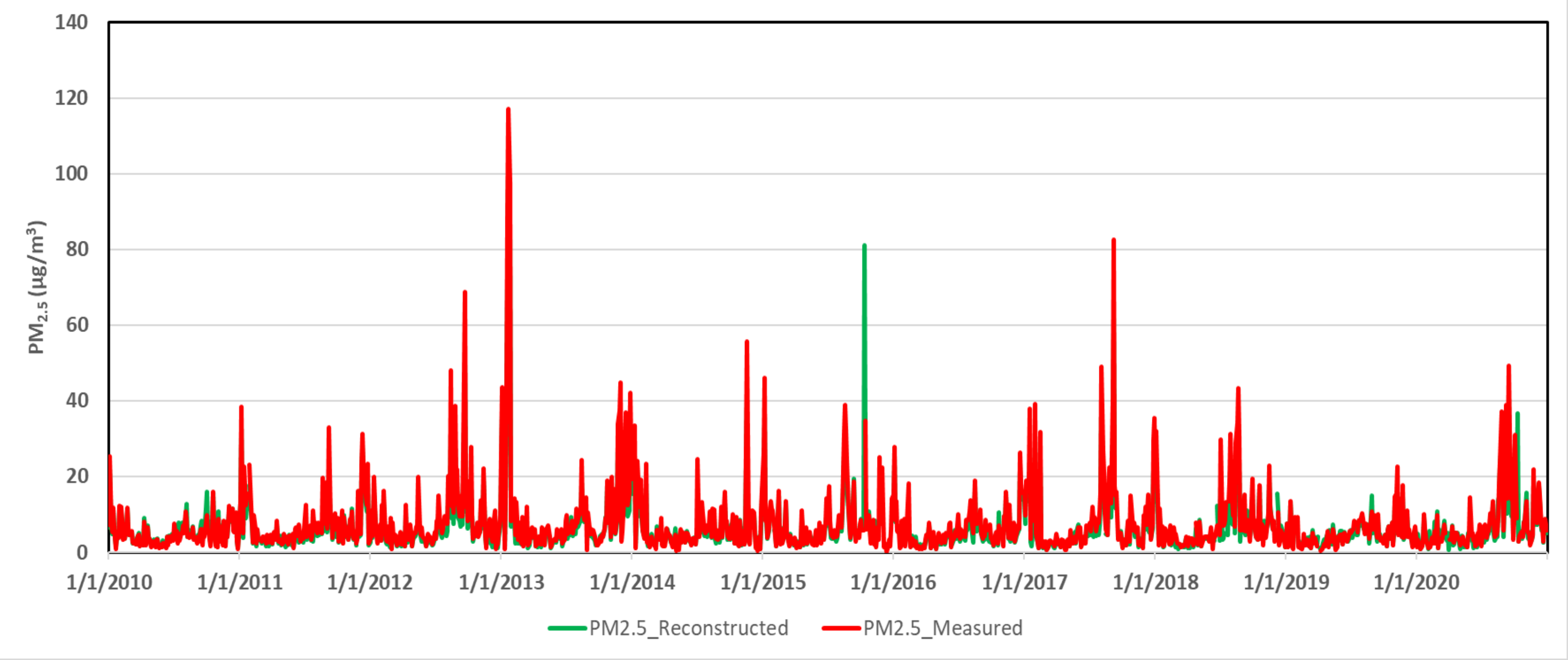


140
120
100
80
60
40
20
0
PM2.5 (μg/m3)
1/1/2010
1/1/2011
1/1/2012
1/1/2013
1/1/2014
1/1/2015
1/1/2016
1/1/2017
1/1/2018
1/1/2019
1/1/2020
PM2.5_Measured



120
100
80
60
40
20
0
PM2.5 (μg/m3)
1/1/2010
1/1/2011
1/1/2012
1/1/2013
1/1/2014
1/1/2015
1/1/2016
1/1/2017
1/1/2018
1/1/2019
1/1/2020
PM2.5_Reconstructed

-13.53%



140
120
100
80
60
40
20
0
PM2.5 (μg/m3)
1/1/2010
1/1/2011
1/1/2012
1/1/2013
1/1/2014
1/1/2015
1/1/2016
1/1/2017
1/1/2018
1/1/2019
1/1/2020
PM2.5_Reconstructed
PM2.5_Measured

Limitations & artifacts

- Ammonium sulfate is calculated with an assumption that all sulfur is present as ammonium sulfate
- 100% neutralization
- Particle-bound water is not measured
- Many species were not included in the calculations

Calculations

$DON = (NH_{4,SO4})/SO4,$

$NH_{4,SO4} = NH_4 - 0.29 * NO_3$

$AS = (DON+1) * SO4$

The ionic fractions:

$S = SO4 / (SO4 + NO3 + NH4);$

$N = NO3 / (SO4 + NO3 + NH4);$

$A = NH4 / (SO4 + NO3 + NH4);$

Particle-Bound Water (PBW)

(MATS, 2014); based on results of Aerosol Inorganic Model (AIM)

$DON \leq 0.225$

$$
\begin{aligned}
PBW = \{&595.556 - 1440.584*S - 1126.488*N + 283.907*(S**1.5) - 13.384*(N**1.5) \\
&- 1486.711*(A**1.5) + 764.229*(S**2) + 1501.999*(N*S) \\
&+ 451.873*(N**2) - 185.183*(S**2.5) - 375.984*(S**1.5)*N \\
&- 16.895*(S**3) - 65.814*(N**1.5)*S + 96.825*(N**2.5) \\
&+ 83.037*(N**1.5)*(S**1.5) - 4.419*(N**3) + 1720.818*(A**1.5)*S \\
&+ 1220.383*(A**1.5)*N - 311.496*(A**1.5)*(S**1.5) \\
&+ 148.771*(A**1.5)*(N**1.5) + 1151.648*(A**3)\} * (SO4+NO3r+NH4);
\end{aligned}
$$

$DON > 0.225$:

$$
\begin{aligned}
PBW = \{&202048.975 - 391494.647 *S - 390912.147 *N + 442.435 *(S**1.5) \\
&- 155.335 *(N**1.5) - 293406.827 *(A**1.5) + 189277.519 *(S**2) \\
&+ 377992.610 *N*S + 188636.790 *(N**2) - 447.123 *(S**2.5) \\
&- 507.157 *(S**1.5)*N - 12.794 *(S**3) + 146.221 *(N**1.5)*S \\
&+ 217.197 *(N**2.5) + 29.981 *(N**1.5)*(S**1.5) - 18.649 *(N**3) \\
&+ 216266.951 *(A**1.5)*S + 215419.876 *(A**1.5)*N \\
&- 621.843 *(A**1.5)*(S**1.5) + 239.132 *(A**1.5)*(N**1.5) \\
&+ 95413.122 *(A**3)\} * (SO4+NO3r+NH4)
\end{aligned}
$$

Reconstructed $PM_{2.5}$

$PM_{2.5}$ = OM + EC + Soil + Salt + AN + AS + PBW + NSS + OPP

Where

$PM_{2.5}$ = $PM_{2.5}$ mass

OM = organic mass

EC = elemental carbon

Soil = oxides of crustal elements

Salt = road salt

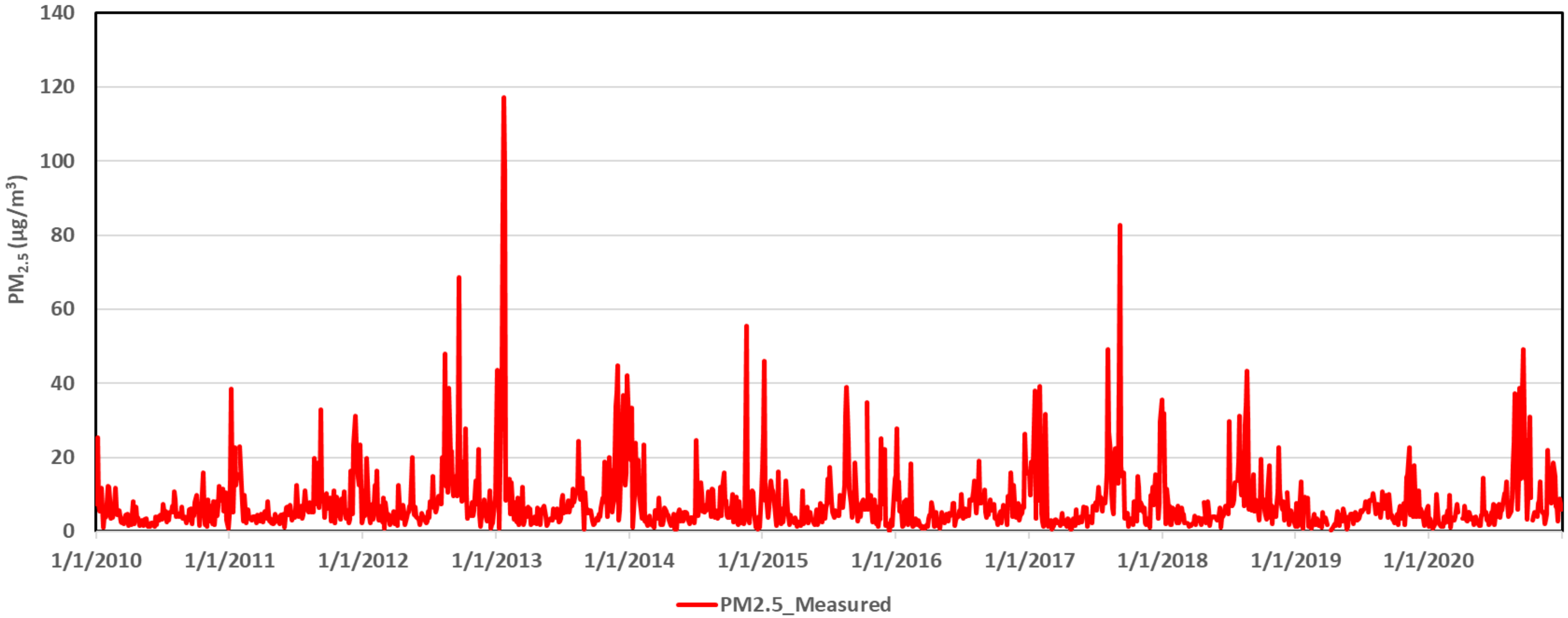
AN = ammonium nitrate

AS = ammonium sulfate

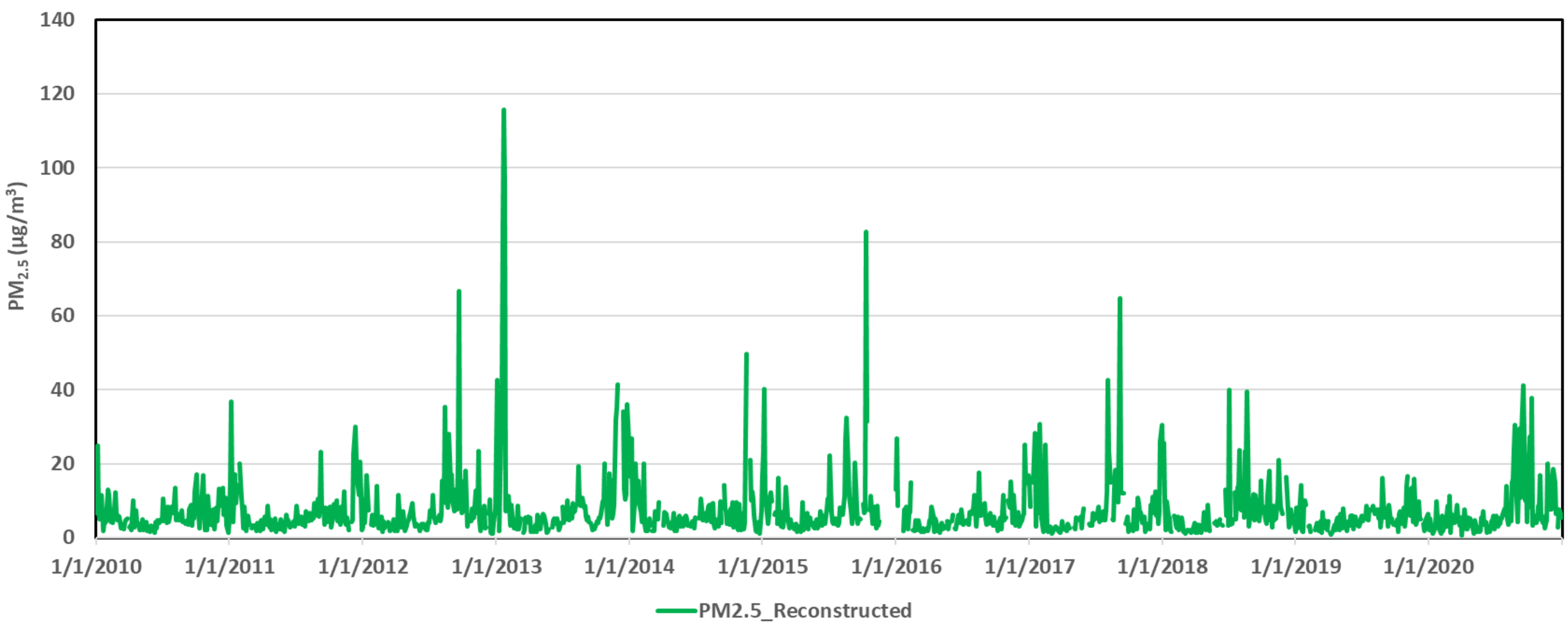
PBW = particle-bound water

NSS = non-sulfate sulfur NSS= S - 0.338 * SO4

OPP = other primary particulate {Mg, Ni, Cu, Zn, As, Pb ...}



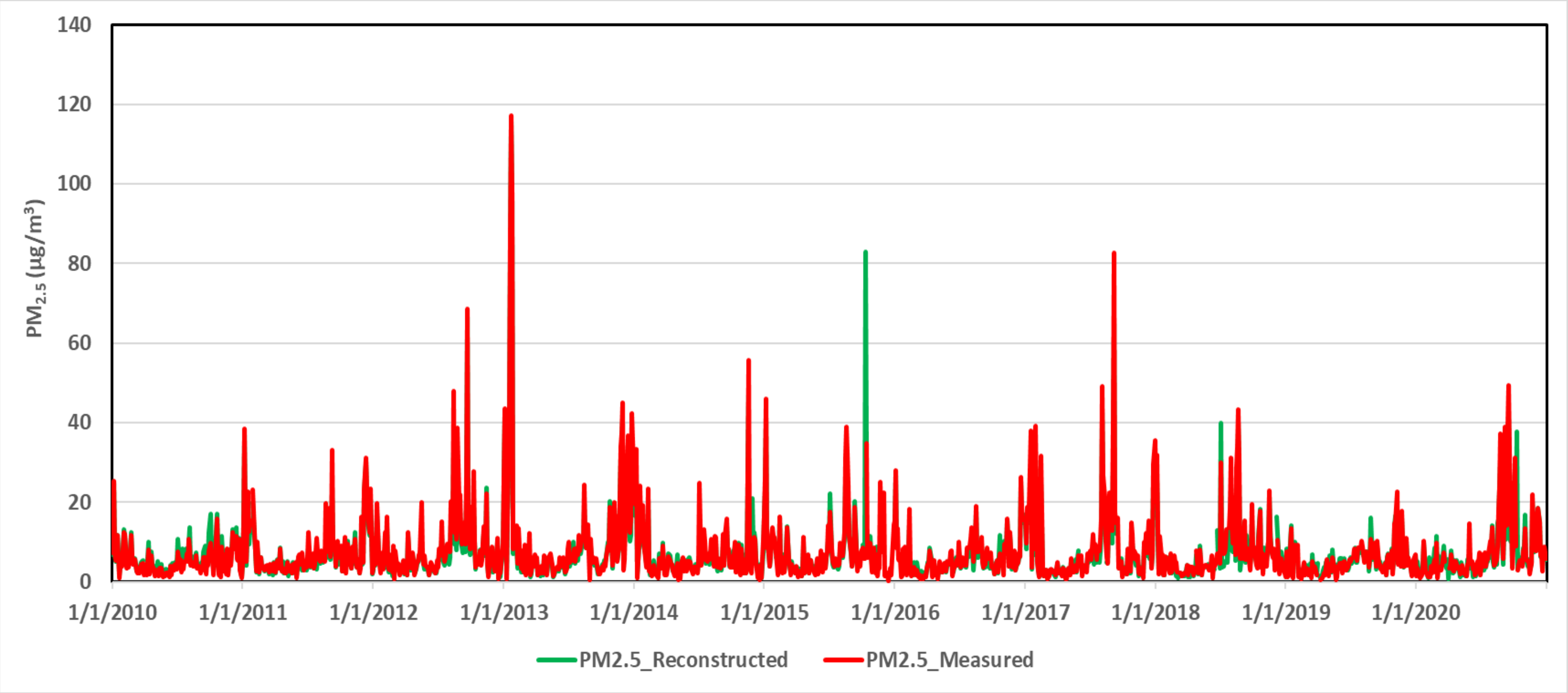
PM$_{2.5}$ (µg/m^3)
140
120
100
80
60
40
20
0
1/1/2010
1/1/2011
1/1/2012
1/1/2013
1/1/2014
1/1/2015
1/1/2016
1/1/2017
1/1/2018
1/1/2019
1/1/2020
PM2.5_Measured

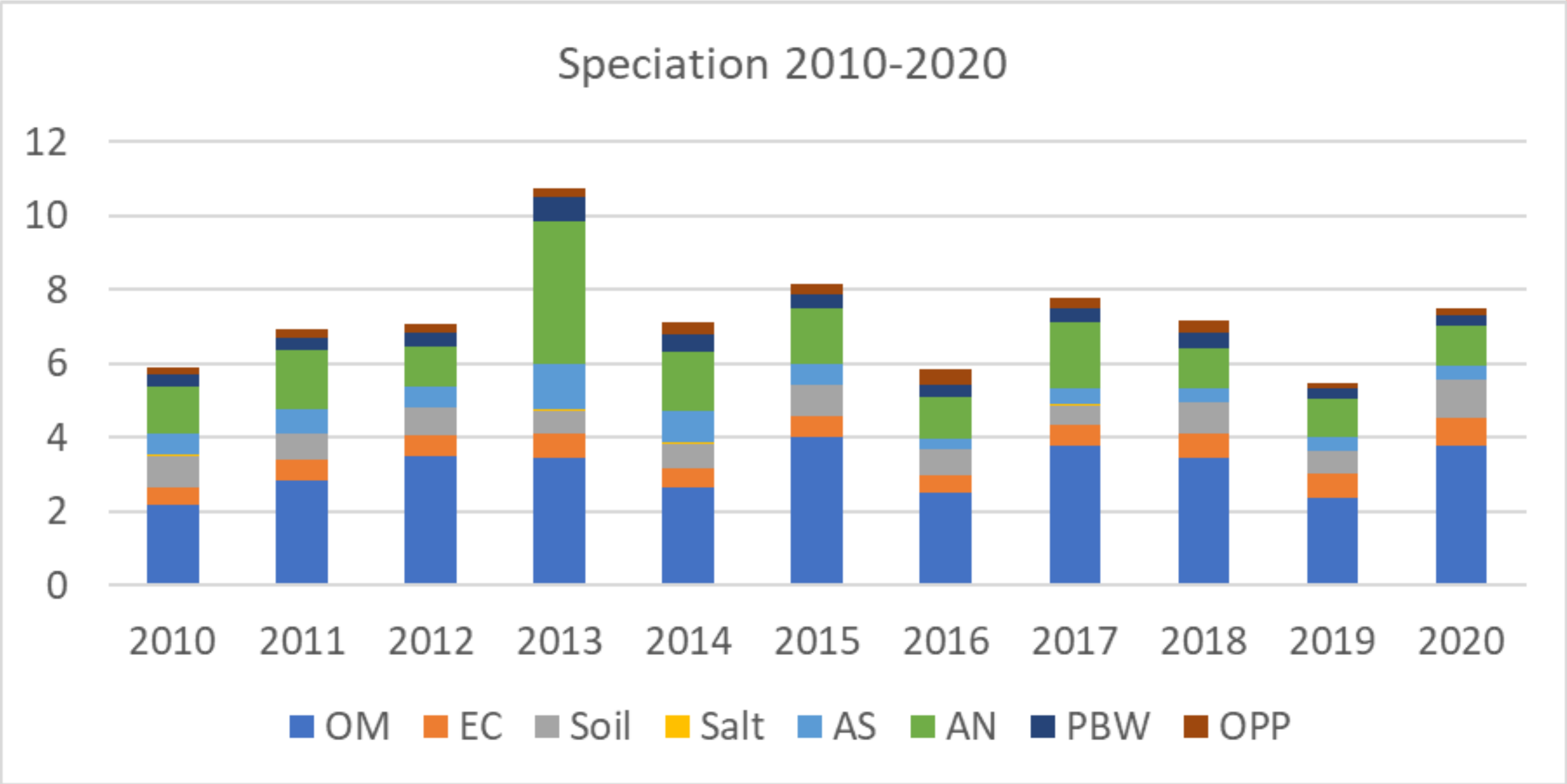


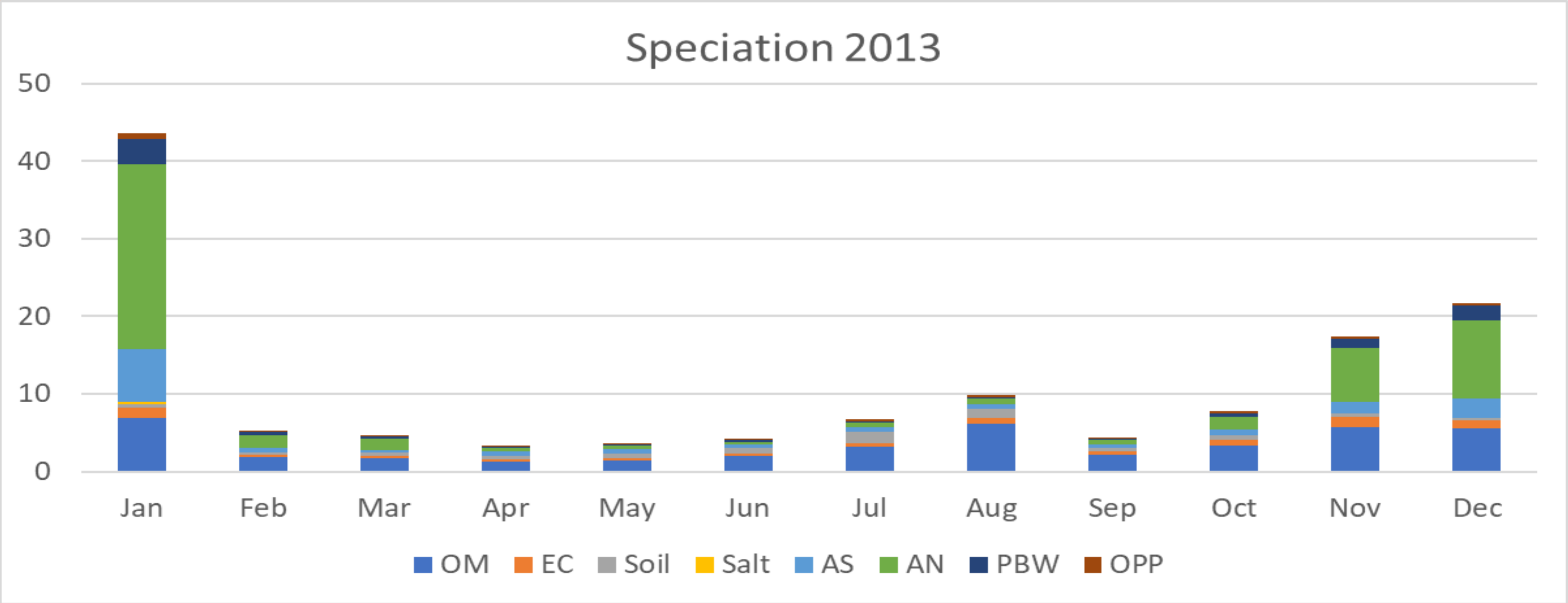
PM$_{2.5}$ (µg/m^3)
140
120
100
80
60
40
20
0
1/1/2010
1/1/2011
1/1/2012
1/1/2013
1/1/2014
1/1/2015
1/1/2016
1/1/2017
1/1/2018
1/1/2019
1/1/2020
PM2.5_Reconstructed

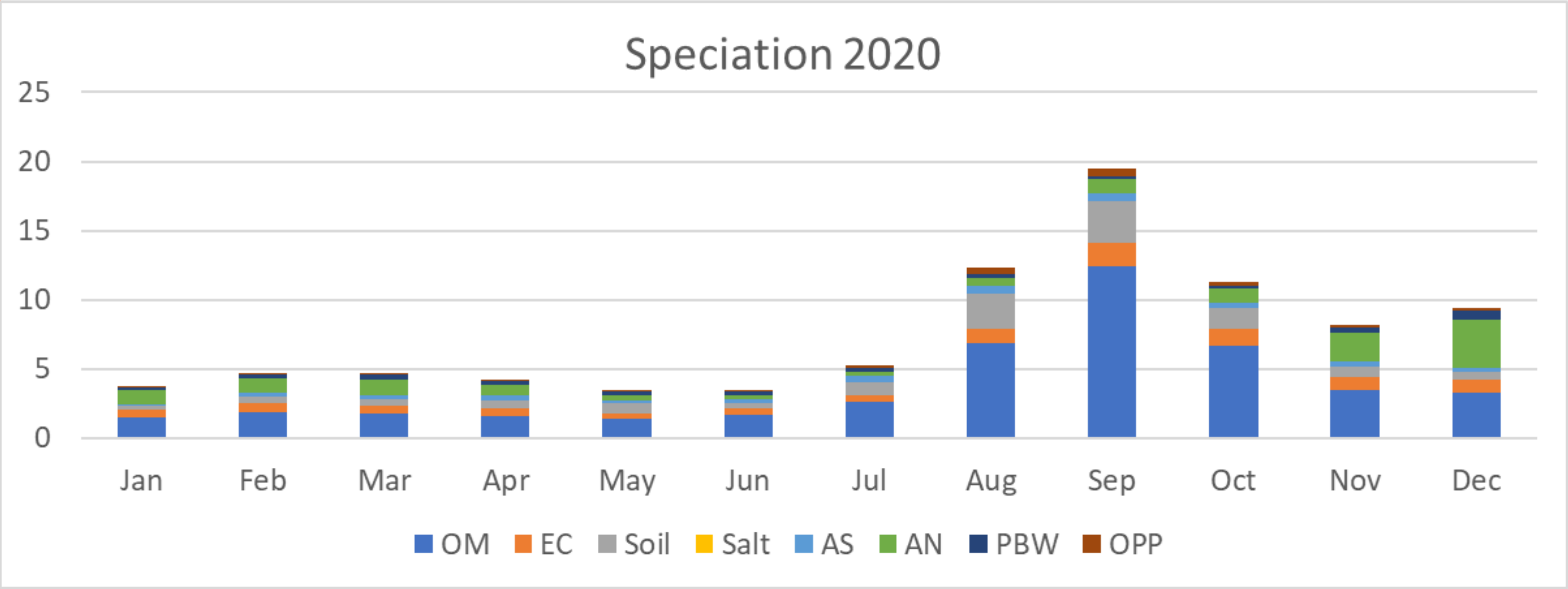
Comparison of reconstructed and measured $PM_{2.5}$

-4.60%




Speciation 2010-2020
12
10
8
6
4
2
0
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
OM
EC
Soil
Salt
AS
AN
PBW
OPP


Speciation 2013
50
40
30
20
10
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
OM
EC
Soil
Salt
AS
AN
PBW
OPP


Speciation 2020
25
20
15
10
5
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
OM
EC
Soil
Salt
AS
AN
PBW
OPP

Summary

- Performed long-term speciation to understand the sources of $PM_{2.5}$ in the Treasure Valley, Idaho, USA
- Evaluated CSN-recommended speciation method
- Reduced bias
- Different seasonal patterns and dominant species:
  - Inversion: Highest $PM_{2.5}$ was observed in winter; nitrate
  - Wildfire & other fires: Highest $PM_{2.5}$ was observed in Summer & Fall; Organic Carbon

- Future work: Receptor modeling & chemical transport modeling