Organic functional group composition of particulate matter from fresh and aged wood burning and coal combustion

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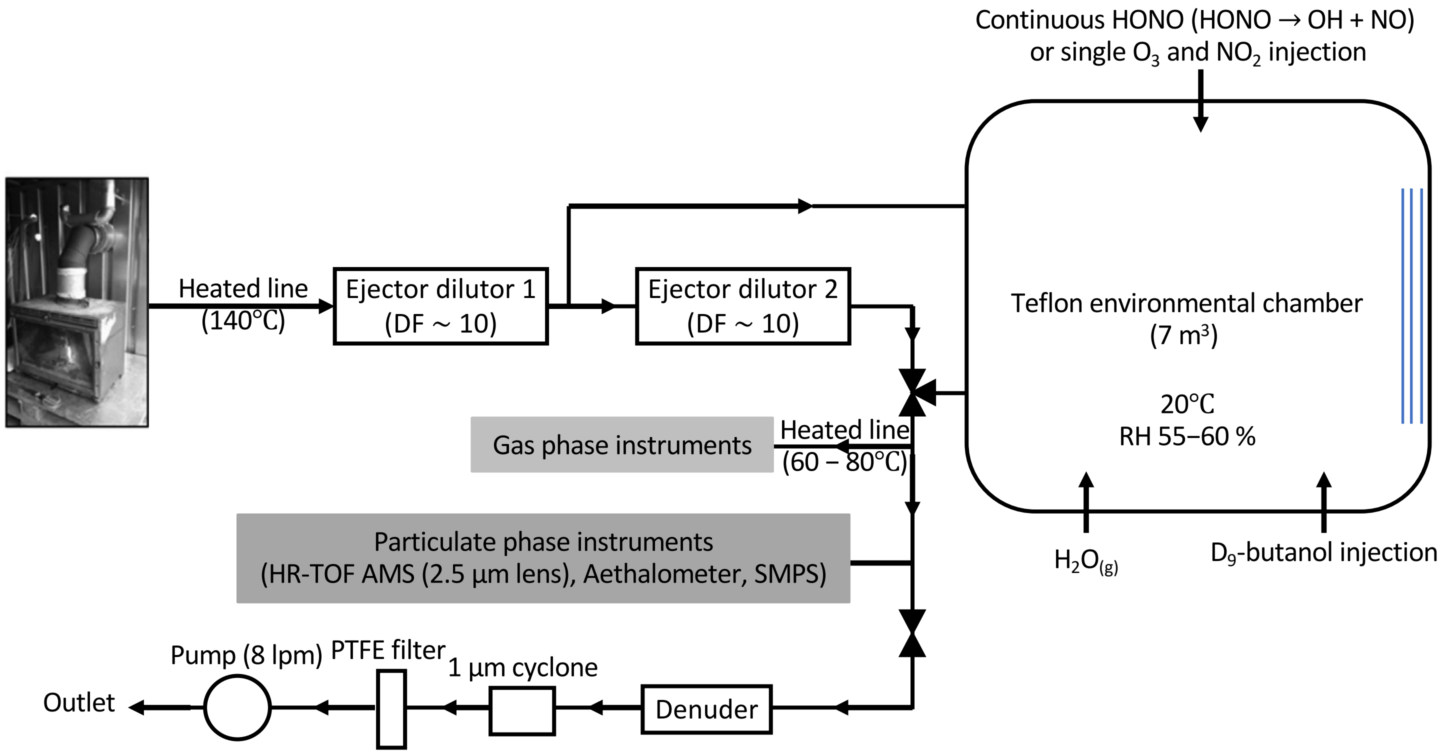
Experimental Set-up

Environmental chamber

- 2–3 logs of **beech wood** for WB (Wood burning), and **bituminous coal** for CC (Coal combustion) experiments.
- The OH radical was produced by photolysis of HONO (injected in the chamber).
- The NO_3 radical was produced by titration of O_3 (injected in the chamber) by NO_2.



FT-IR spectroscopy

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FT-IR spectroscopy for OM

- FT-IR analysis on PTFE filters is a fast and non-destructive offline method that takes around five minutes for scanning each filter.

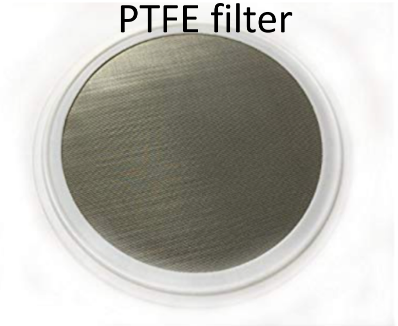
- Only bonds with dipole moment that changes with vibration are detected.

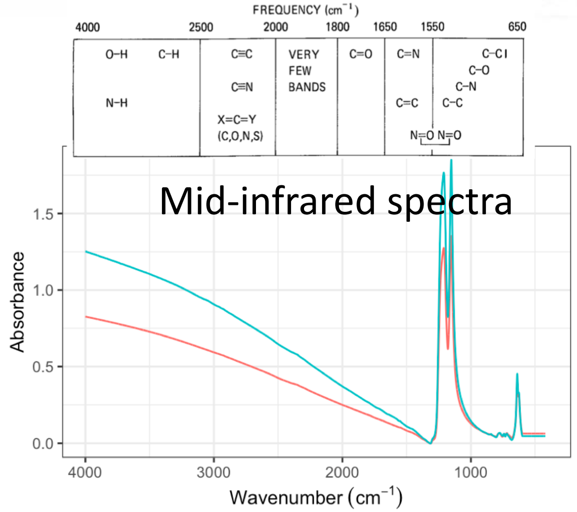
- Spectra should be corrected for filter and particle scattering.

- Peak fitting is applied on baseline-corrected spectra (Reggente et al., *Atmos. Meas. Tech.,* 2019).

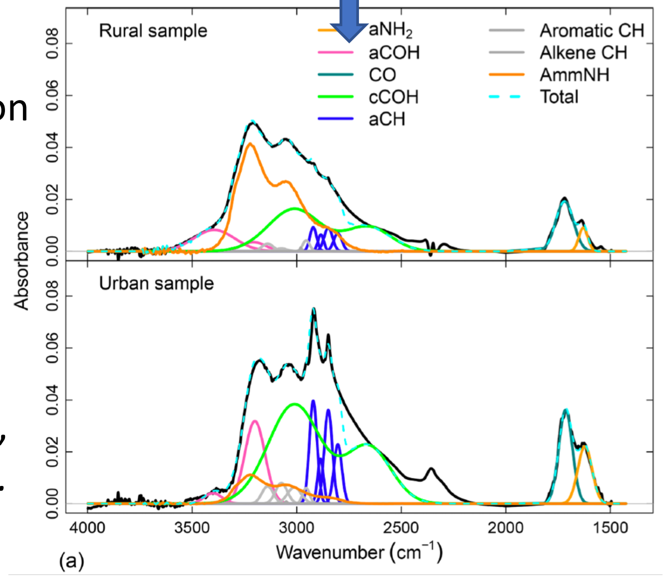
FT-IR machine

PTFE filter





Baseline correction and peak fitting



Reggente et al., *Atmos. Meas. Tech.* (2019)

Scientific questions

1

How well do AMS and FT-IR agree in their characterization of OM?

2

How does functional group composition evolve with aging?

3

How relevant are these experiments toward understanding ambient aerosol?

4

How can we use the WB OA characteristics to identify atmospheric burning-influenced samples

Functional group analysis with FT-IR

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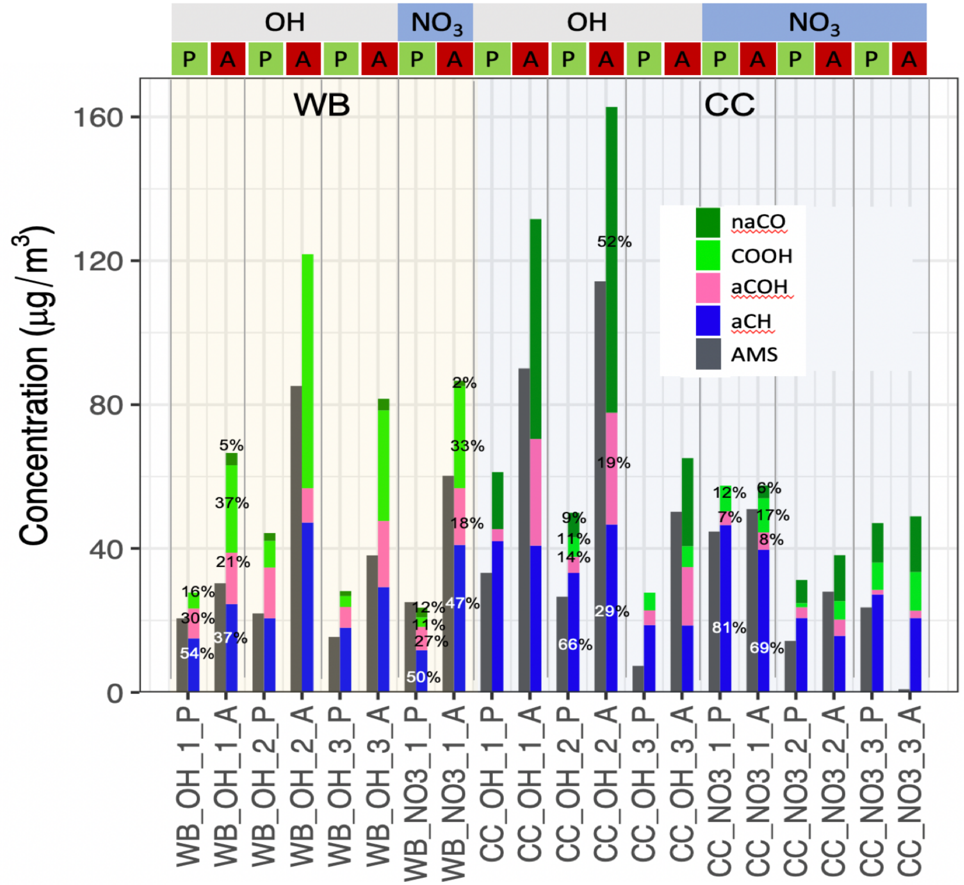
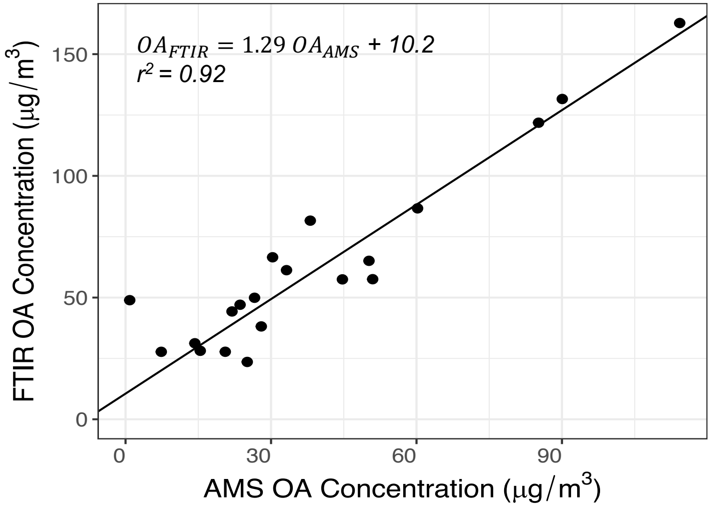
Mass concentration (OA)

- Flow rate was set to 8 *lpm* for the filter line.
- Sampling time was around 20 minutes.
- FT-IR OA concentration estimates are 1.3 that of AMS (consistent considering AMS collection efficiency* and filter volatilization artifacts).
- Concentrations from the 2 methods are highly correlated (r^2 = 0.92).





*Canagaratna et al., *Mass Spectrom. Rev.* (2007)

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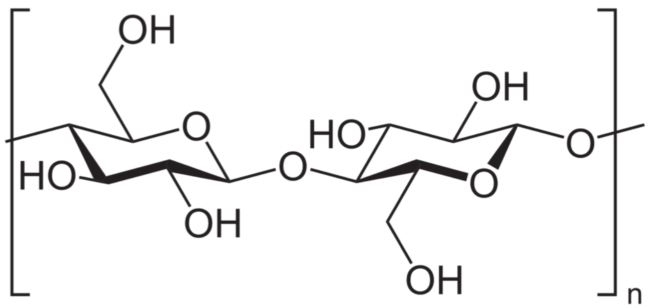
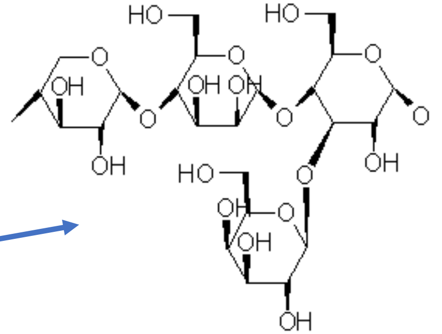
Wood burning (WB)



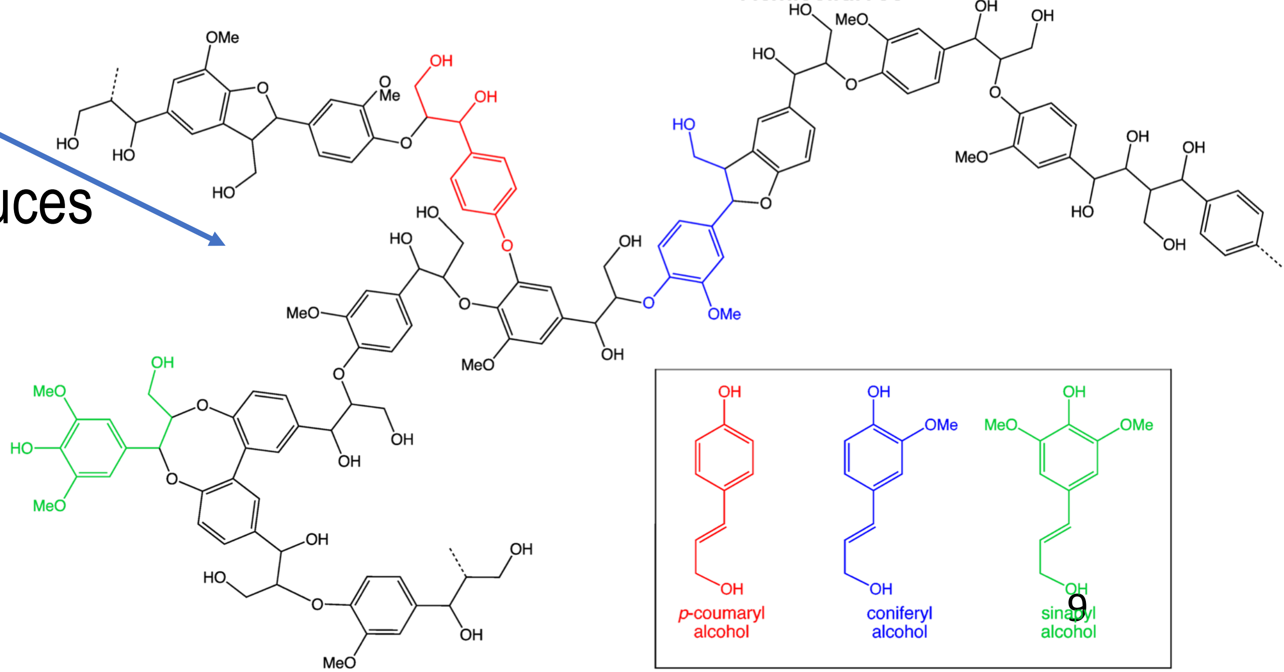
Wood contains 50% carbon and 42% oxygen by weight.

- Cellulose constitutes 41−43% of wood.
- Next in abundance is hemicellulose (20−30%).
- Lignin is the third component (23−27%).



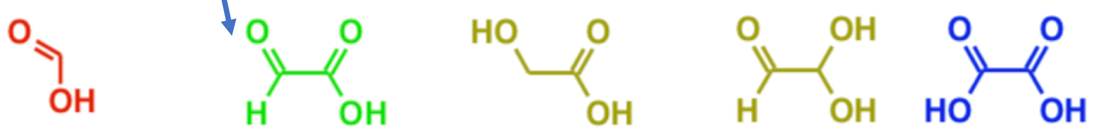
- Xylose - ß(1,4) - Mannose - ß(1,4) - Glucose -
- alpha(1,3) - Galactose

Hemicellulose



Thermal decomposition of cellulose produces levoglucosan, furan and pyran.

photooxidation



formic acid | glyoxylic acid | glycolic acid | glyoxal monohydrate | oxalic acid

Zhao et al., *Atmos. Chem. Phys.* (2014)

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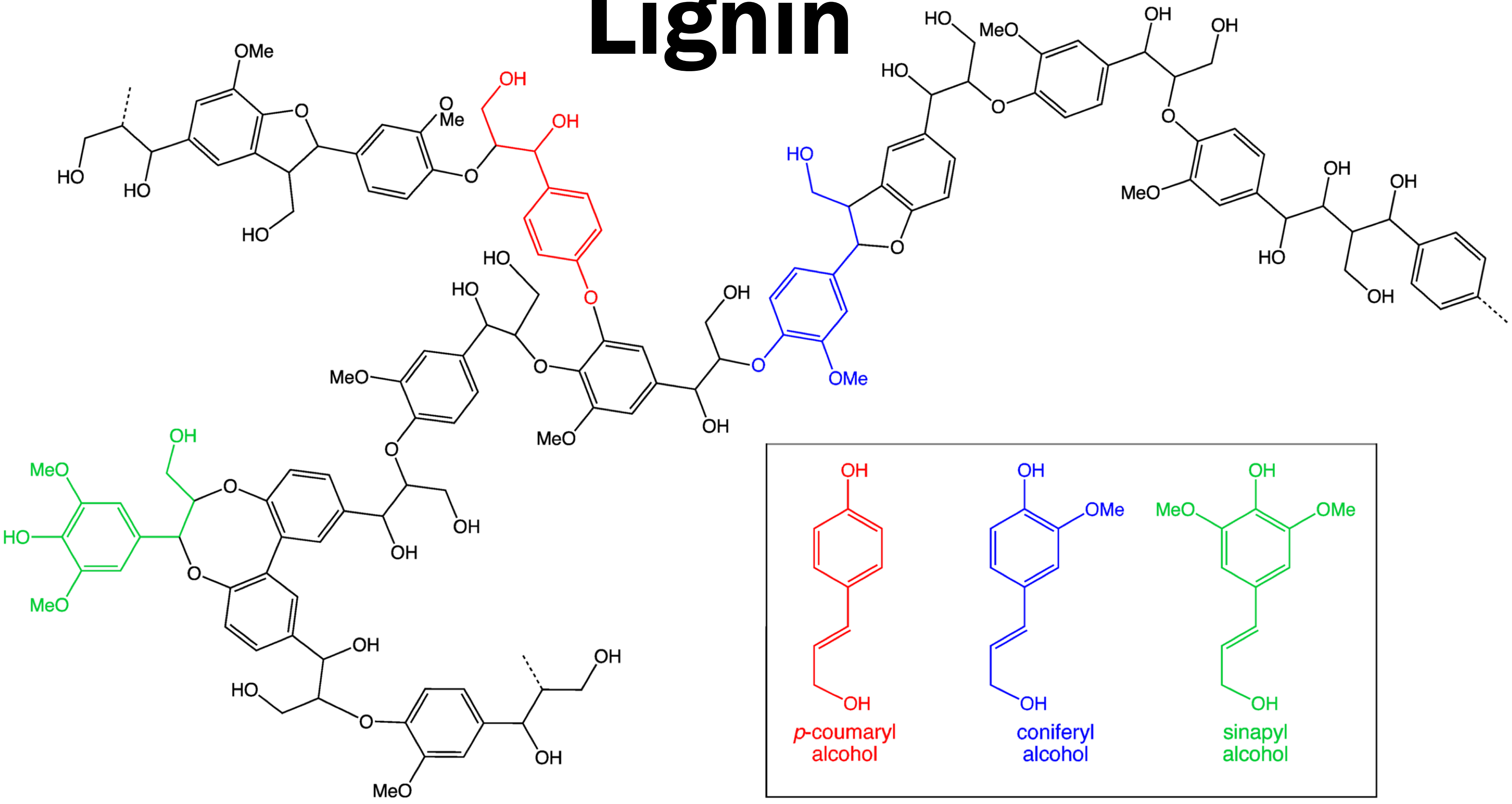
Lignin



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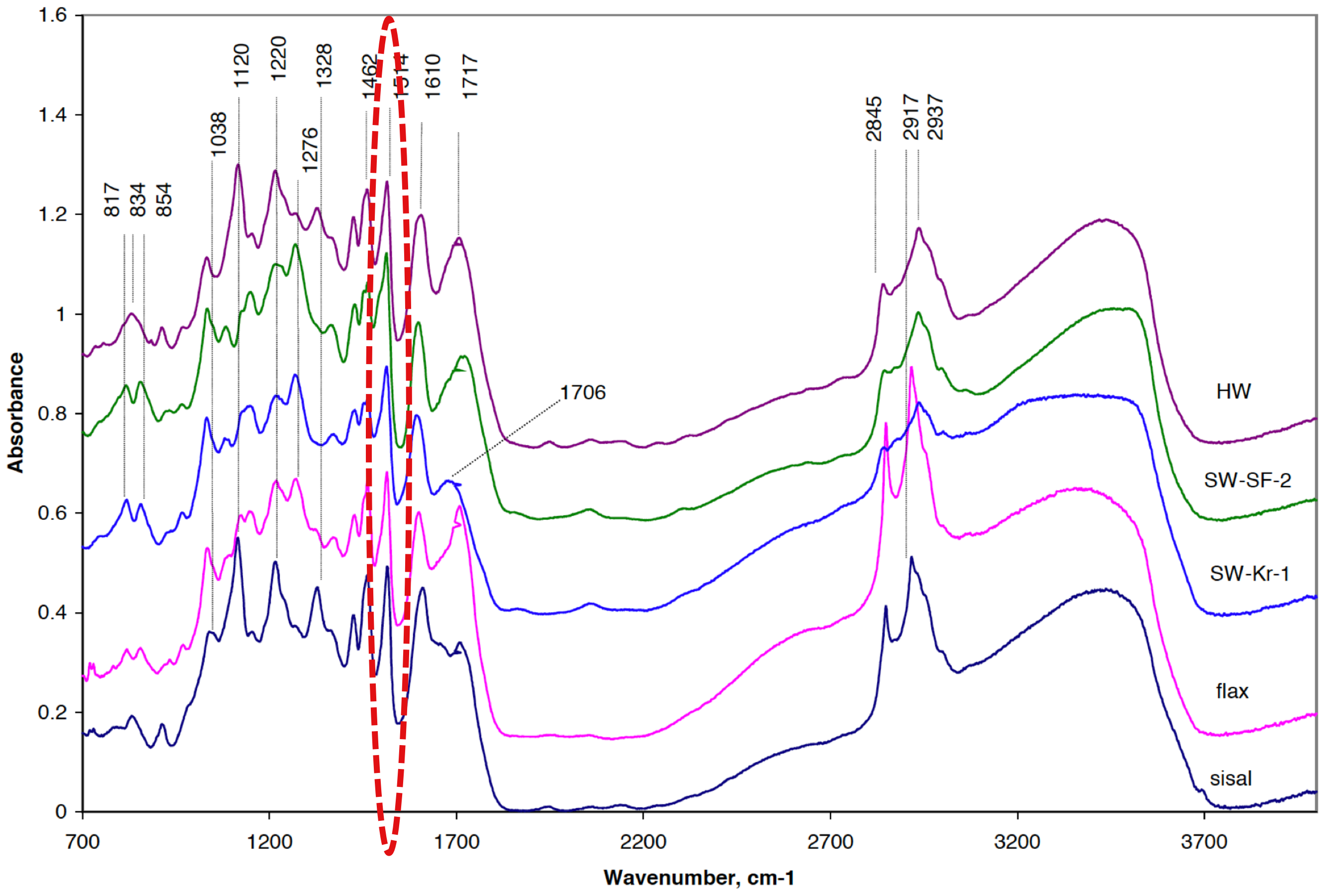
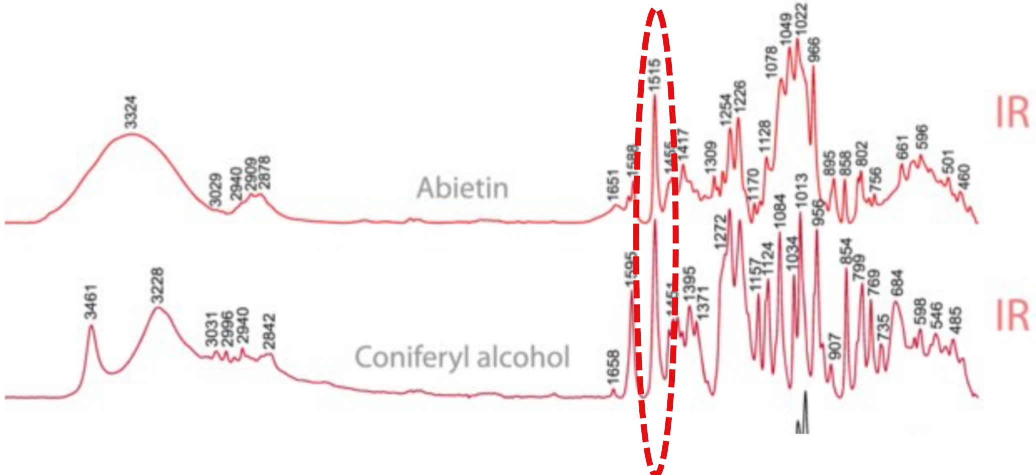
Lignin – FTIR spectra

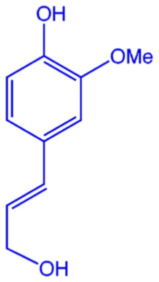
- Aromatic ring in lignin and primary lignin monomers absorbs at 1520 cm^{-1}.



Boeriu et al., *Ind. Crops Prod.* (2004)

Bock and Gielinger, *J. Raman Spectrosc.* (2019)





coniferyl alcohol

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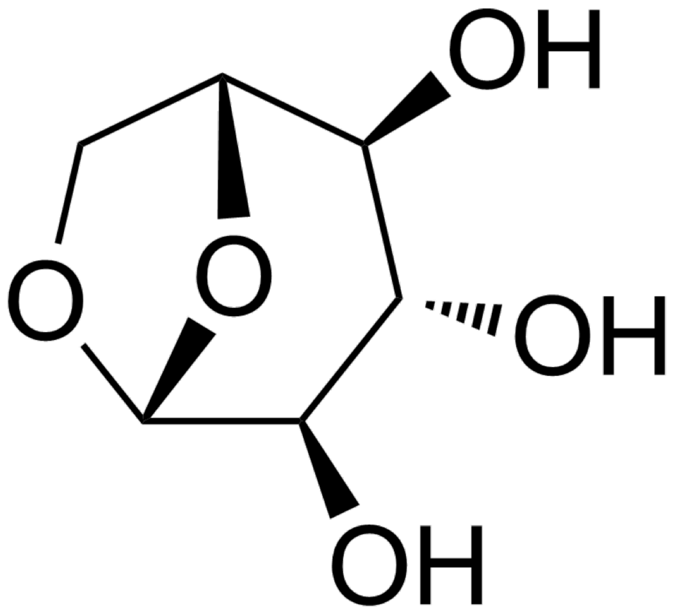
Levoglucosan



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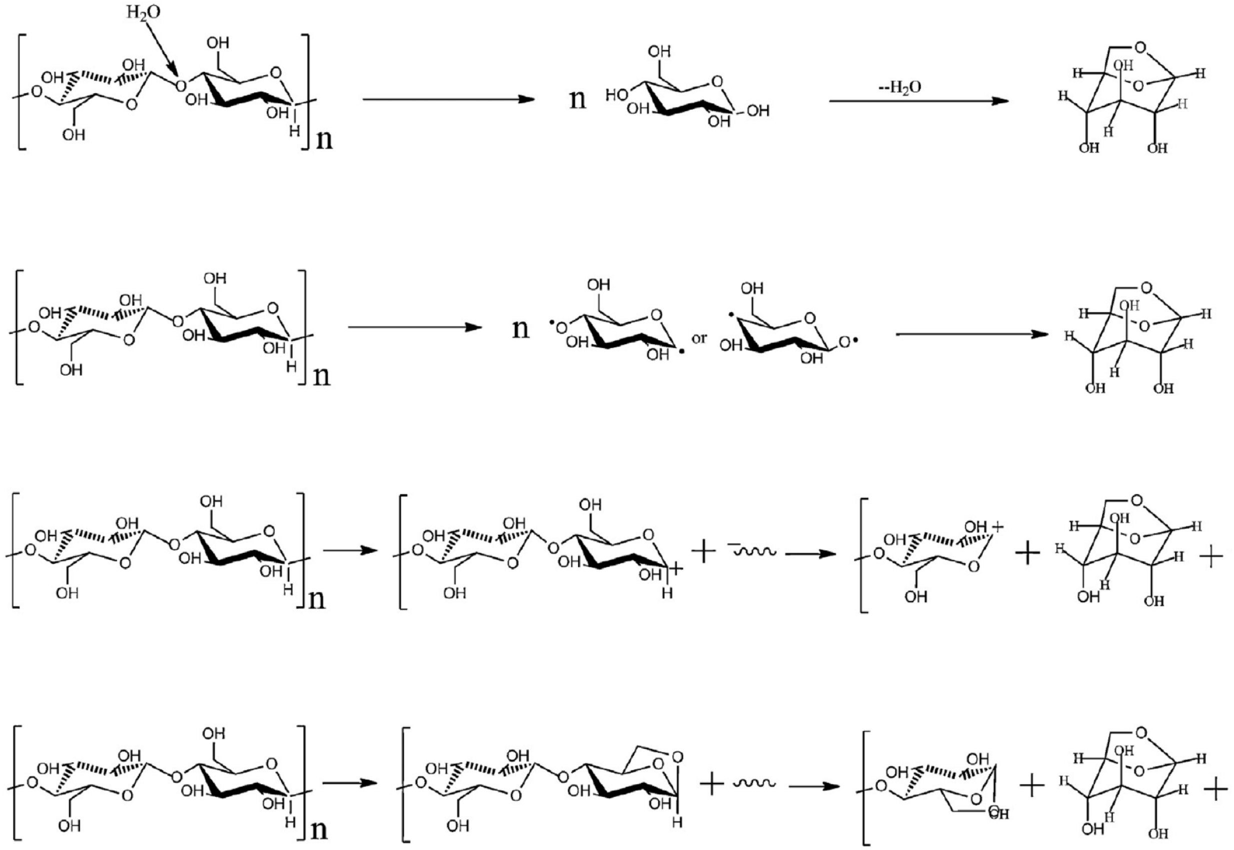
Biomass burning and levoglucosan

- Levoglucosan is an important primary product of cellulose pyrolysis either as an intermediate or as a product (Sullivan et al., *J. Geophys. Res. Atmospheres*, 2008).

- Levoglucosan reacts with ˙OH on a timescale similar to that of aerosol transport and deposition.

- Relative kinetics indicate that levoglucosan has an atmospheric lifetime of 0.7–2.2 days (Hennigan et al., *Geophys. Res. Lett.*, 2010).



Zhang et al., *J. Anal. Appl. Pyrol.*, 2019

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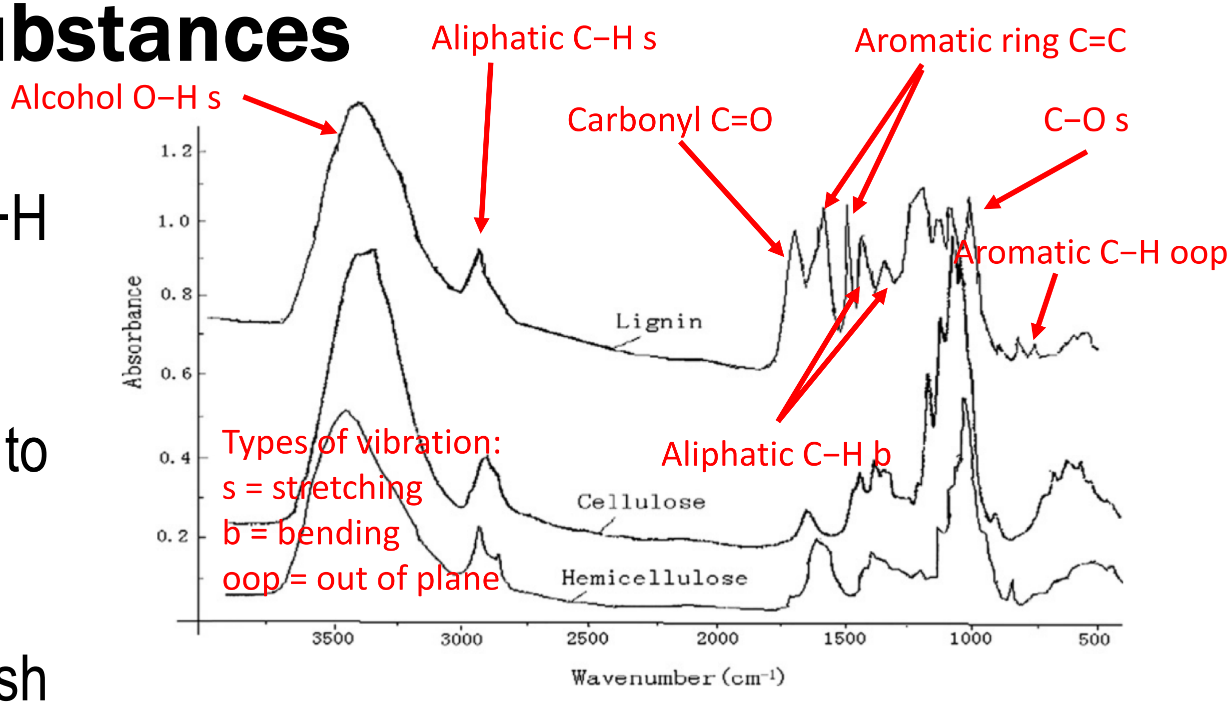
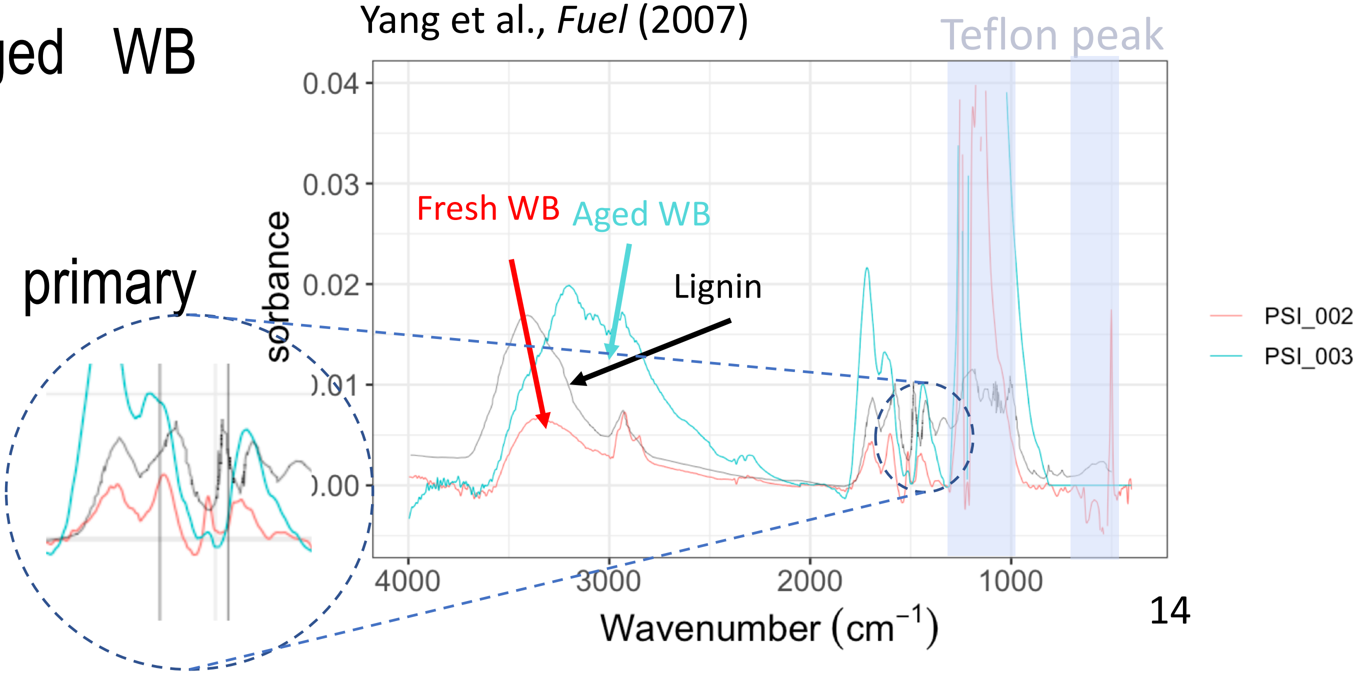
Mid-infrared spectra of parent substances

- All parent compounds have strong alcohol O−H absorbance.
- Spectra of fresh WB aerosols are similar to lignin.
- Aromatic structure of lignin is visible is fresh WB spectra and diminishes in aged WB spectra.
- Levoglucosan signature is observed in primary WB spectra and diminishes with aging.



Yang et al., *Fuel* (2007)



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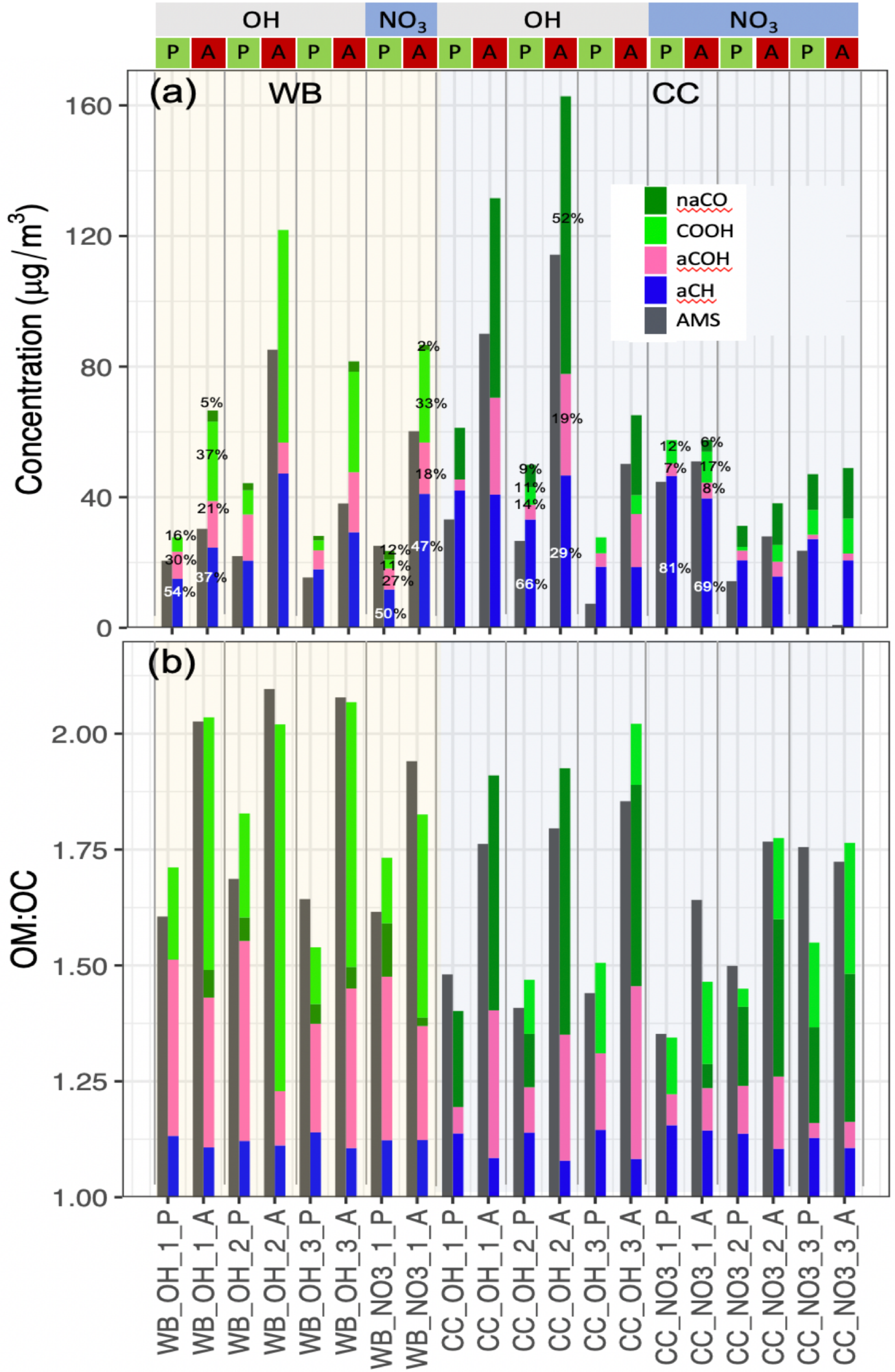
Fresh wood burning aerosol

- High abundance of aliphatic C−H.
- High abundance of alcohol O−H (20 % from levoglucosan).
- Low abundance of carboxylic acid COOH.
- Low abundance of inorganic salts.
- Moderate OM/OC ratio (1.6−1.9).
- AMS and FT-IR estimate close OM:OC ratios.



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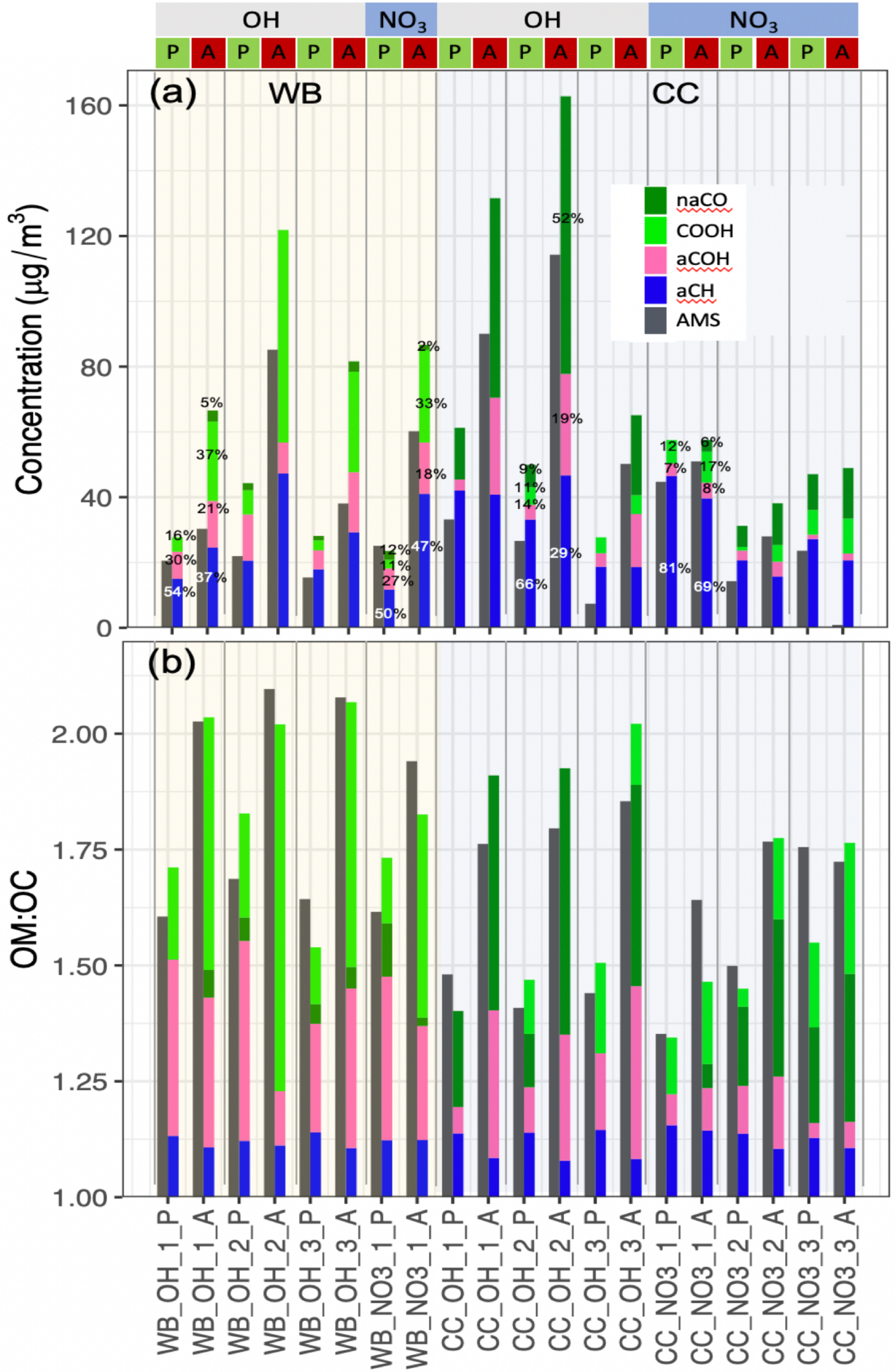
Aged wood burning aerosol

- Lower relative abundance of aliphatic C−H.
- Lower relative abundance of alcohol O−H (lower levoglucosan and weaker *m/z 60 signal*).
- Higher abundance of carboxylic acid COOH (a dominant SOA oxidation pathway).
- Lower abundance of lignin aromatic ring.
- Higher abundance of organonitrate (when aged with NO_3).
- Higher abundance of inorganic salts (ammonium sulfate and nitrate).
- Higher OM/OC (1.9−2.1) ratio and concentration.



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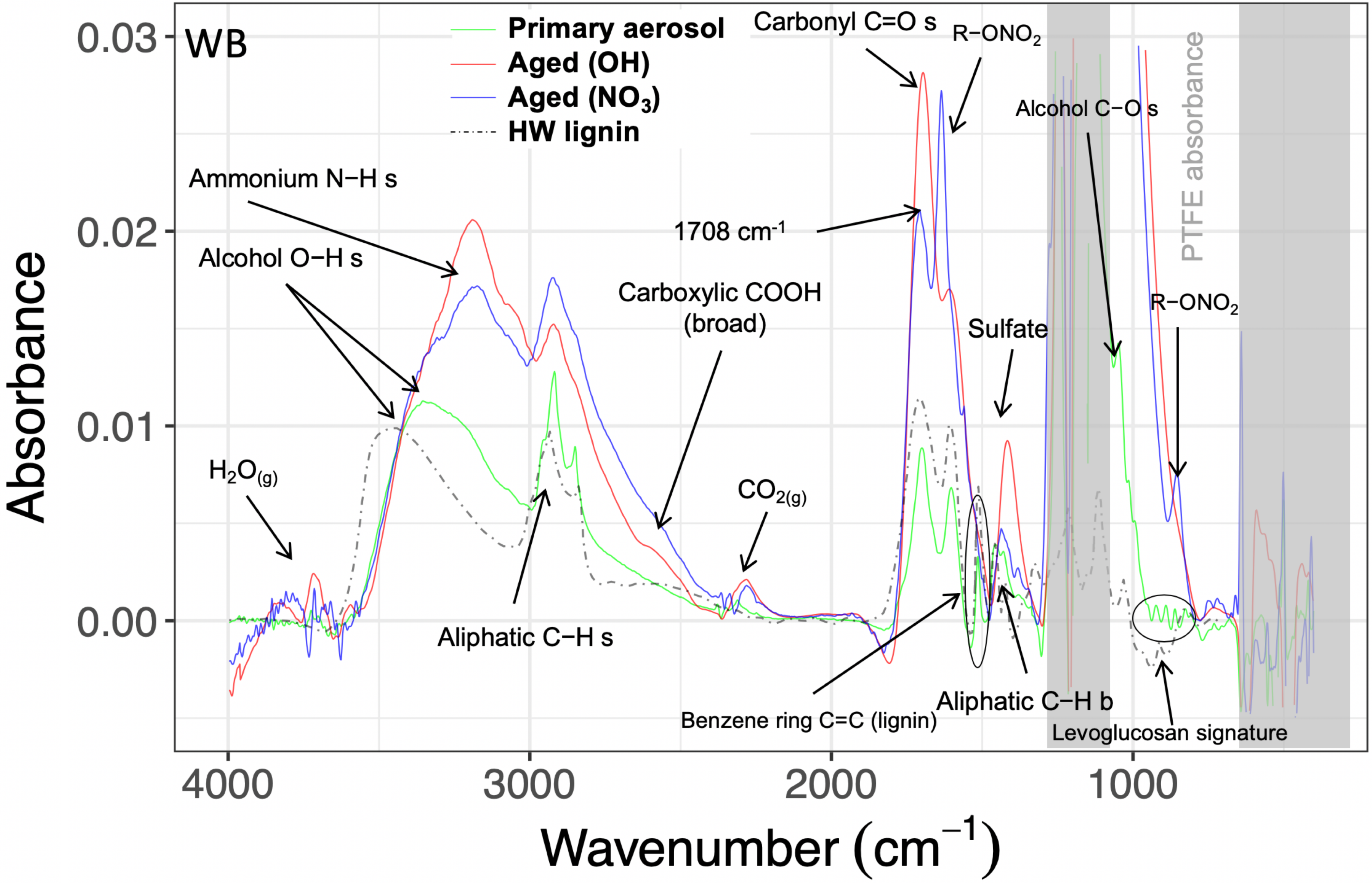
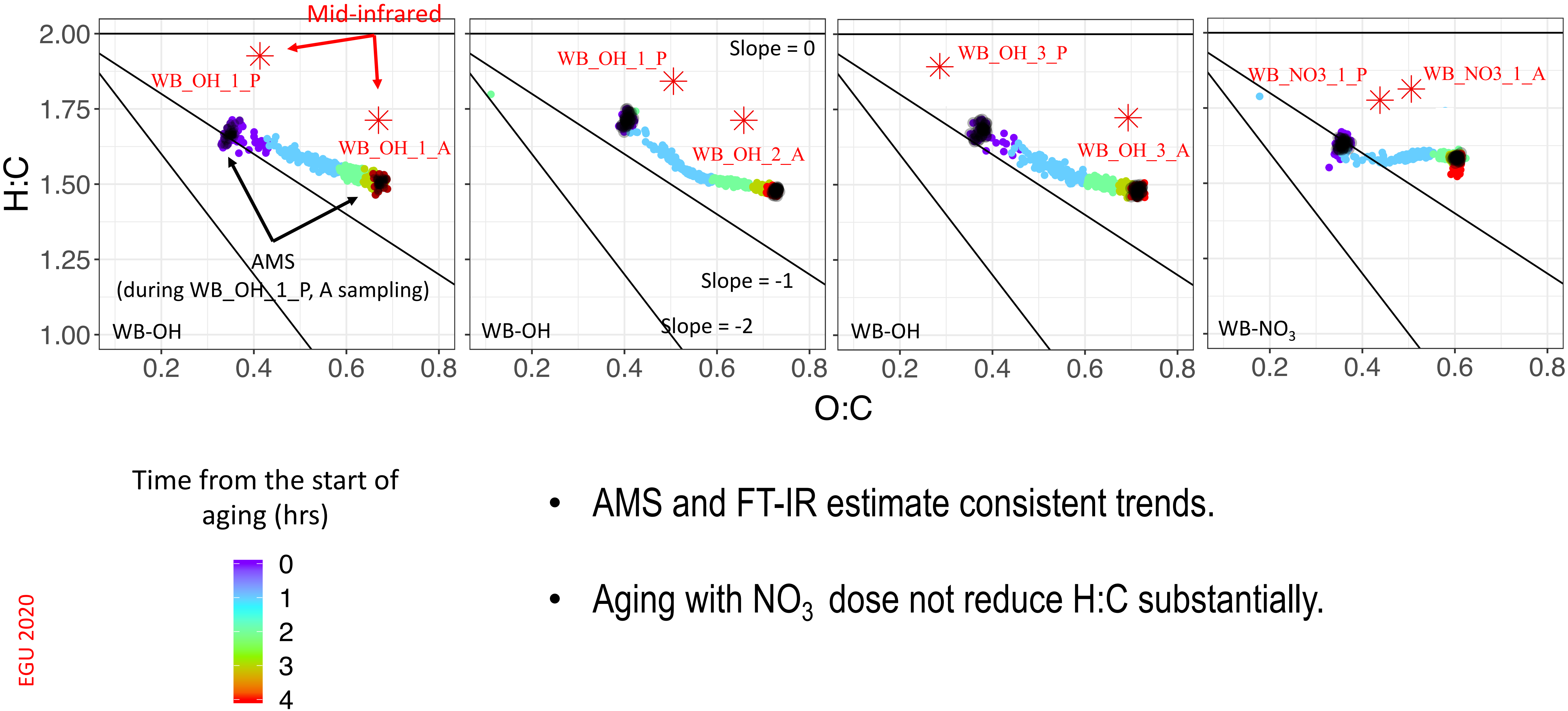


WB
Primary aerosol
Aged (OH)
Aged (NO_3)
HW lignin
Absorbance
0.03
0.02
0.01
0.00
Ammonium N−H s
Alcohol O−H s
$H_2O_{(g)}$
Aliphatic C−H s
Carboxylic COOH (broad)
$CO_{2(g)}$
Carbonyl C=O s
$R-ONO_2$
1708 cm^{-1}
Alcohol C−O s
PTFE absorbance
Sulfate
$R-ONO_2$
Benzene ring C=C (lignin)
Aliphatic C−H b
Levoglucosan signature
4000
3000
2000
1000
Wavenumber (cm^{-1})

Van Krevelen plot (Wood burning)



- AMS and FT-IR estimate consistent trends.
- Aging with NO_3 dose not reduce H:C substantially.

Coal combustion (CC)

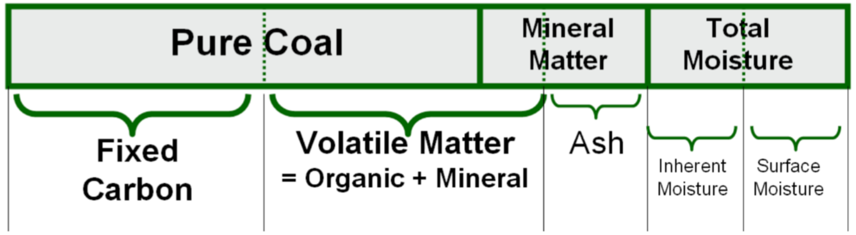
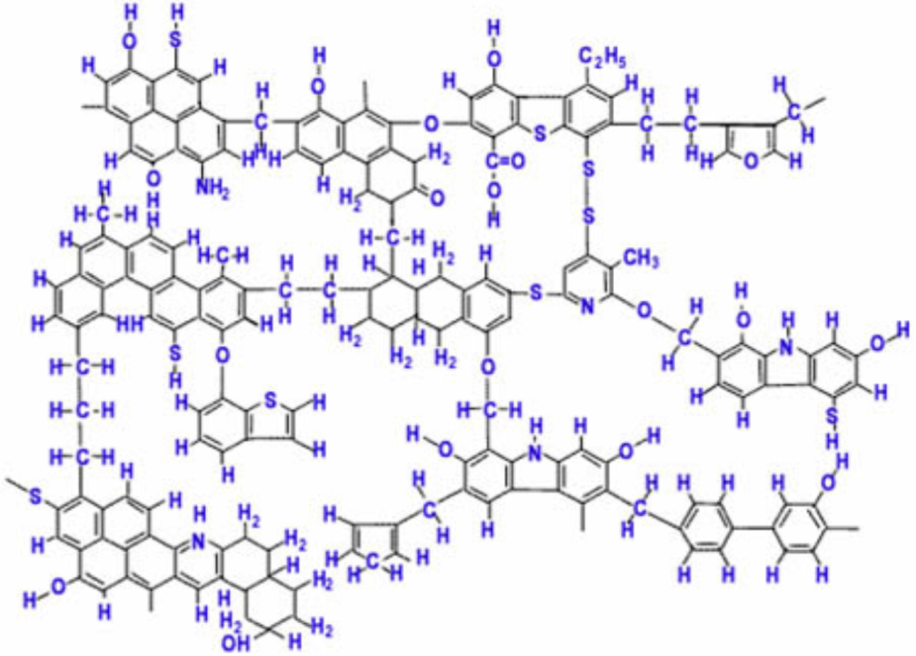


Photo Credit: *Indiana center of coal technology research*

Bituminous coal contains 69% to 86% carbon by weight and is composed of:

- Volatile matter consists of short- and long-chain hydrocarbons (linked in open chains).
- Aromatic hydrocarbons
- Mineral matter.



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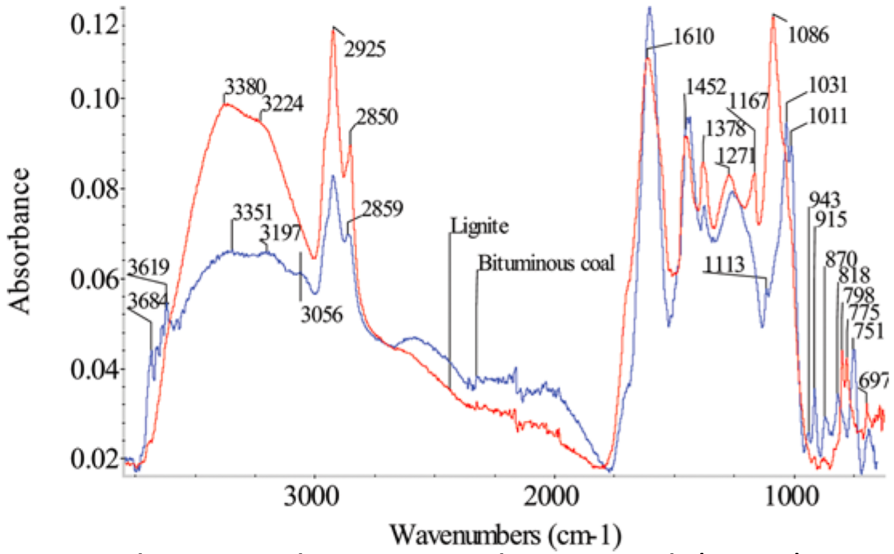
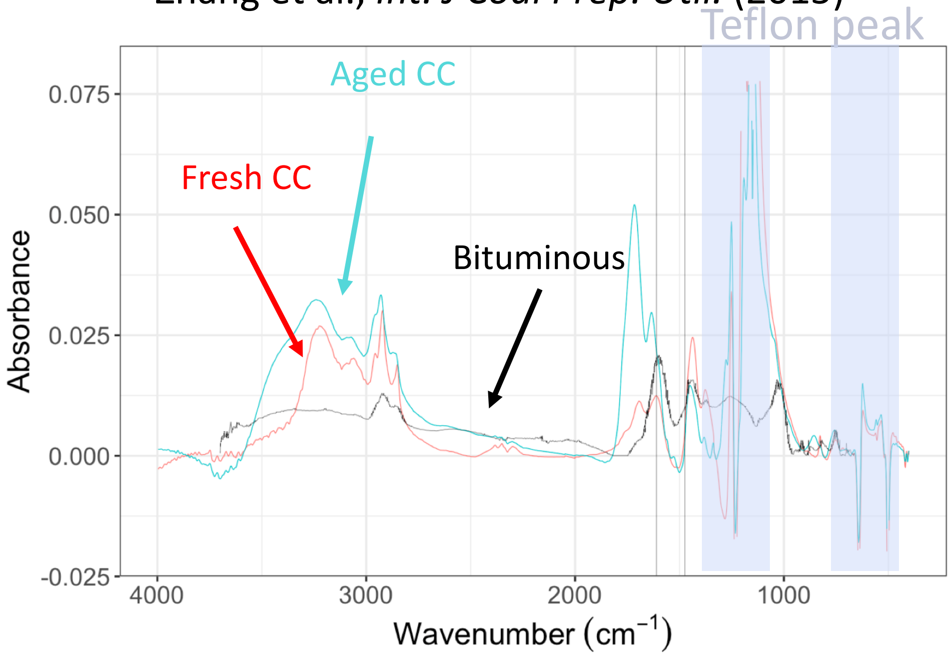
Mid-infrared spectrum of parent substance

- Bituminous coal absorbs weakly in alcohol O−H region.
- Aromatic C=C absorption is visible is bituminous coal and CC spectra.
- Aliphatic C−H is sharper in fresh CC spectra than in coal spectra.
- Carbonyl C=O absorbs very weakly in bituminous coal spectrum (a dominant oxidation pathway for CC SOA).
- Out-of-plane aromatic C−H vibration is visible in bituminous coal and CC spectra (750 cm^{-1}).

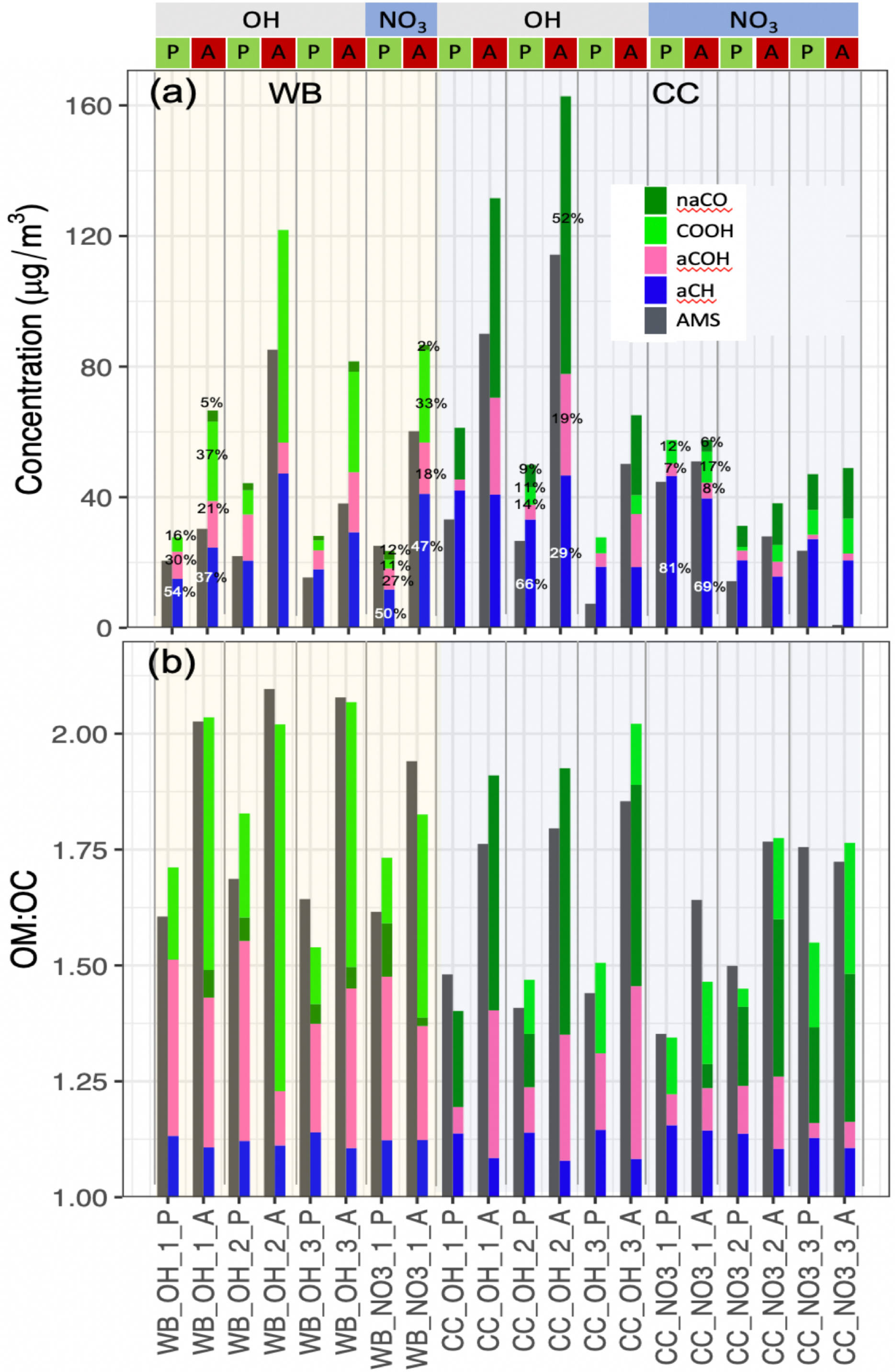


Zhang et al., *Int. J Coal Prep. Util.* (2015)



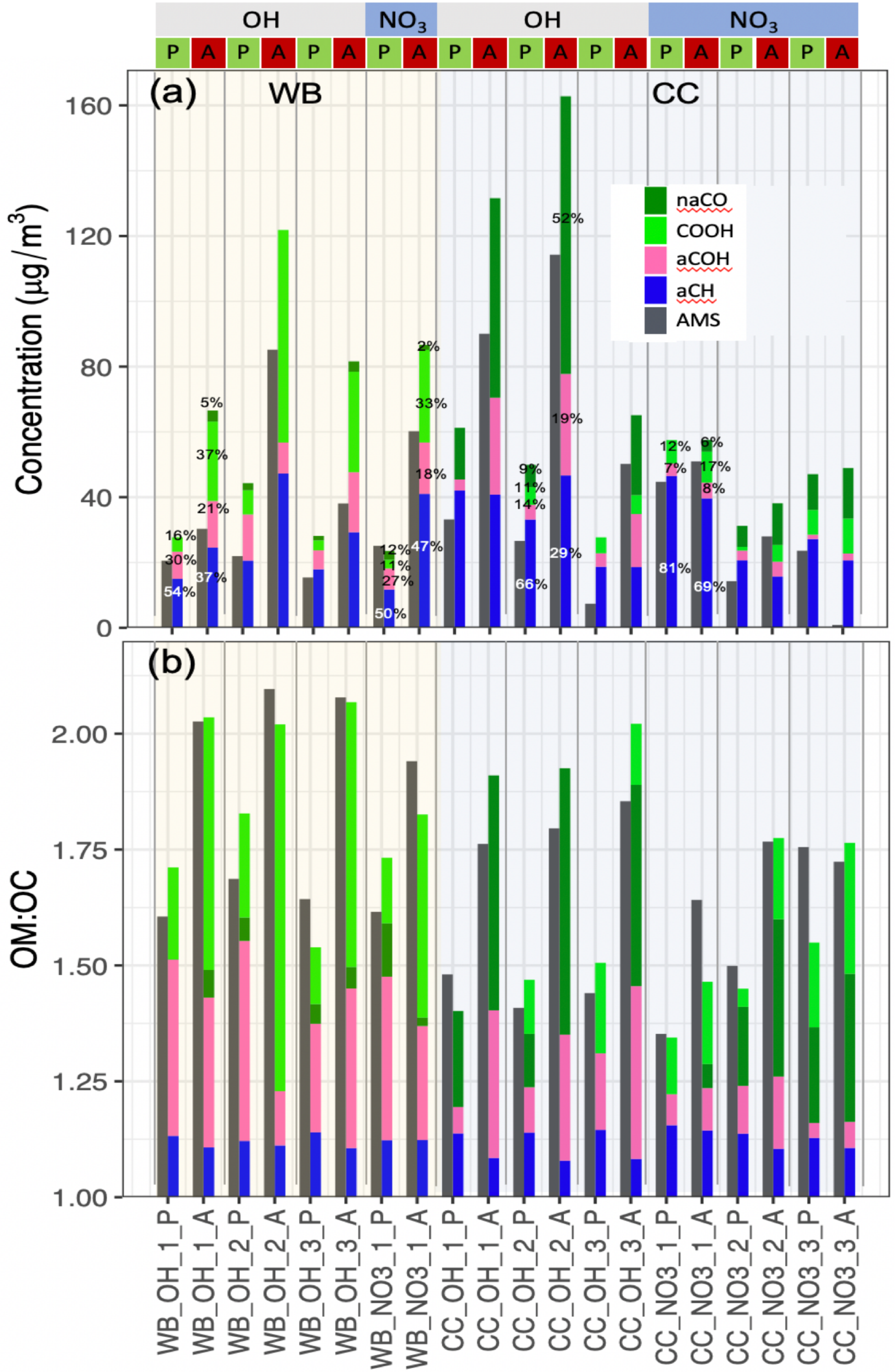
Fresh coal combustion aerosol

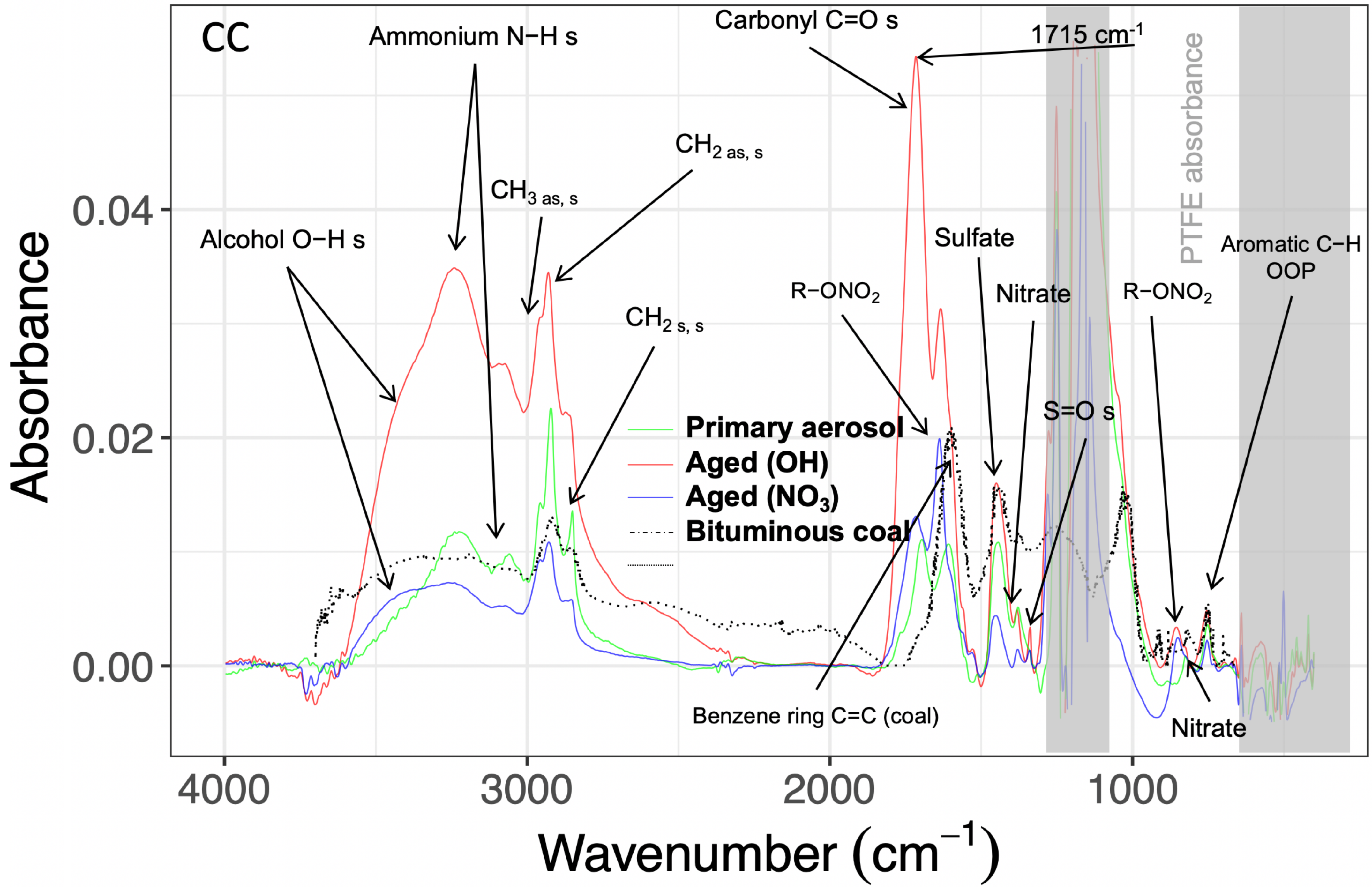
- Very high abundance of aliphatic C−H.
- Low abundance of alcohol O−H.
- Medium abundance of non-acid carbonyl.
- High abundance of inorganic salts (ammonium sulfate).
- Has the lowest OM/OC (~1.6) ratio due to high aliphatic C−H abundance.



Aged coal combustion aerosol

- Lower abundance of aliphatic C−H.
- Higher abundance of alcohol O−H.
- Higher abundance of non-acid carbonyl.
- Higher abundance of acid carbonyl (in some cases).
- Higher abundance of aromatic C−H.
- Emergence of sulfonate S=O band.
- Higher abundance of inorganic salts (ammonium sulfate due to sulfur in coal).




CC
Ammonium N−H s
Carbonyl C=O s
1715 cm-1
PTFE absorbance
CH2 as, s
CH3 as, s
Alcohol O−H s
CH2 s, s
R−ONO2
Sulfate
Nitrate
S=O s
R−ONO2
Aromatic C−H OOP
Primary aerosol
Aged (OH)
Aged (NO3)
Bituminous coal
Benzene ring C=C (coal)
Nitrate
Absorbance
0.04
0.02
0.00
4000
3000
2000
1000
Wavenumber (cm−1)

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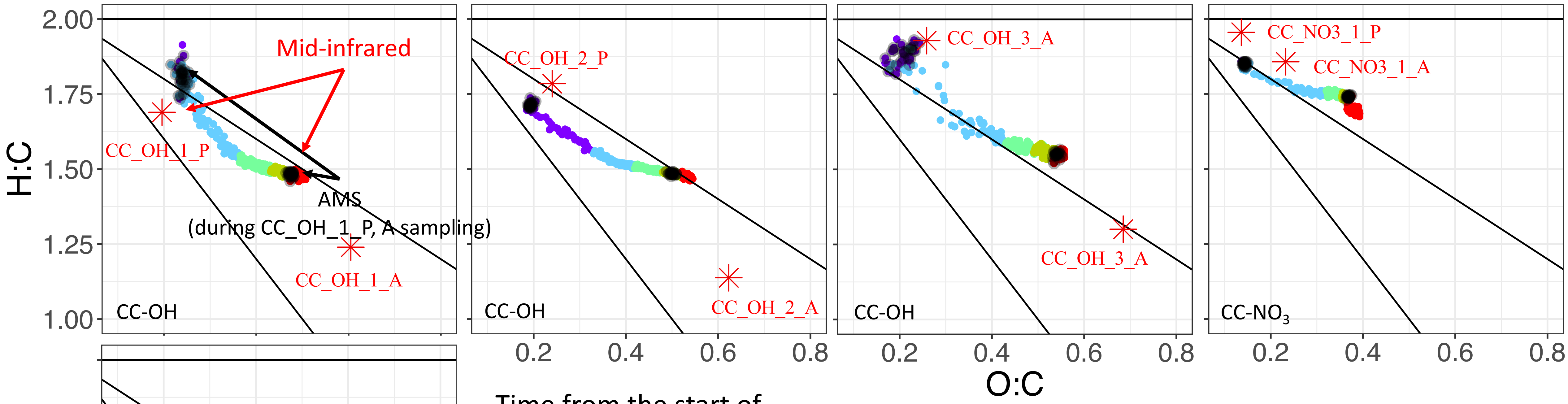
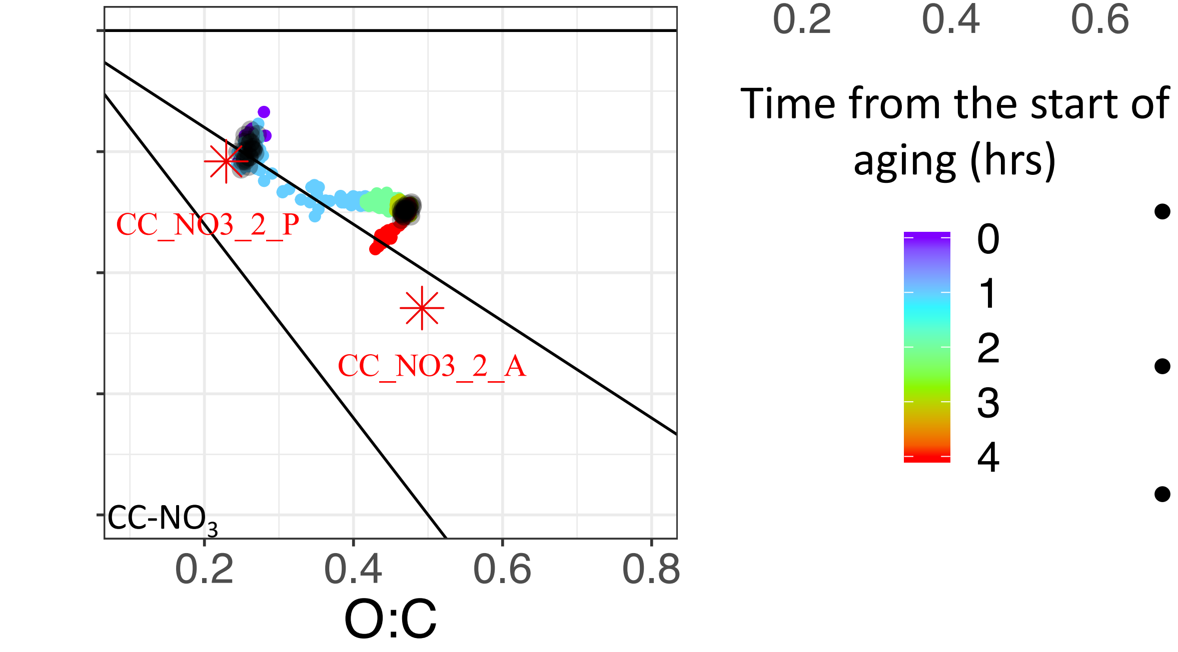
Van Krevelen plot (Coal burning)

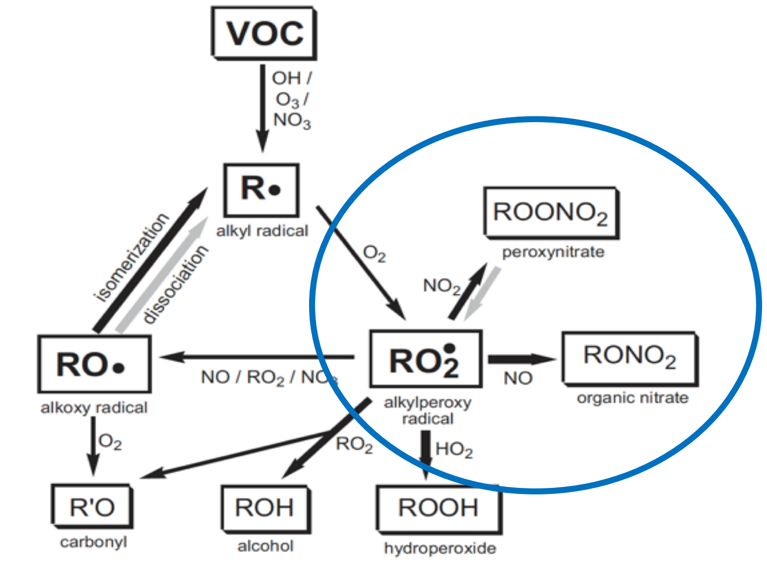




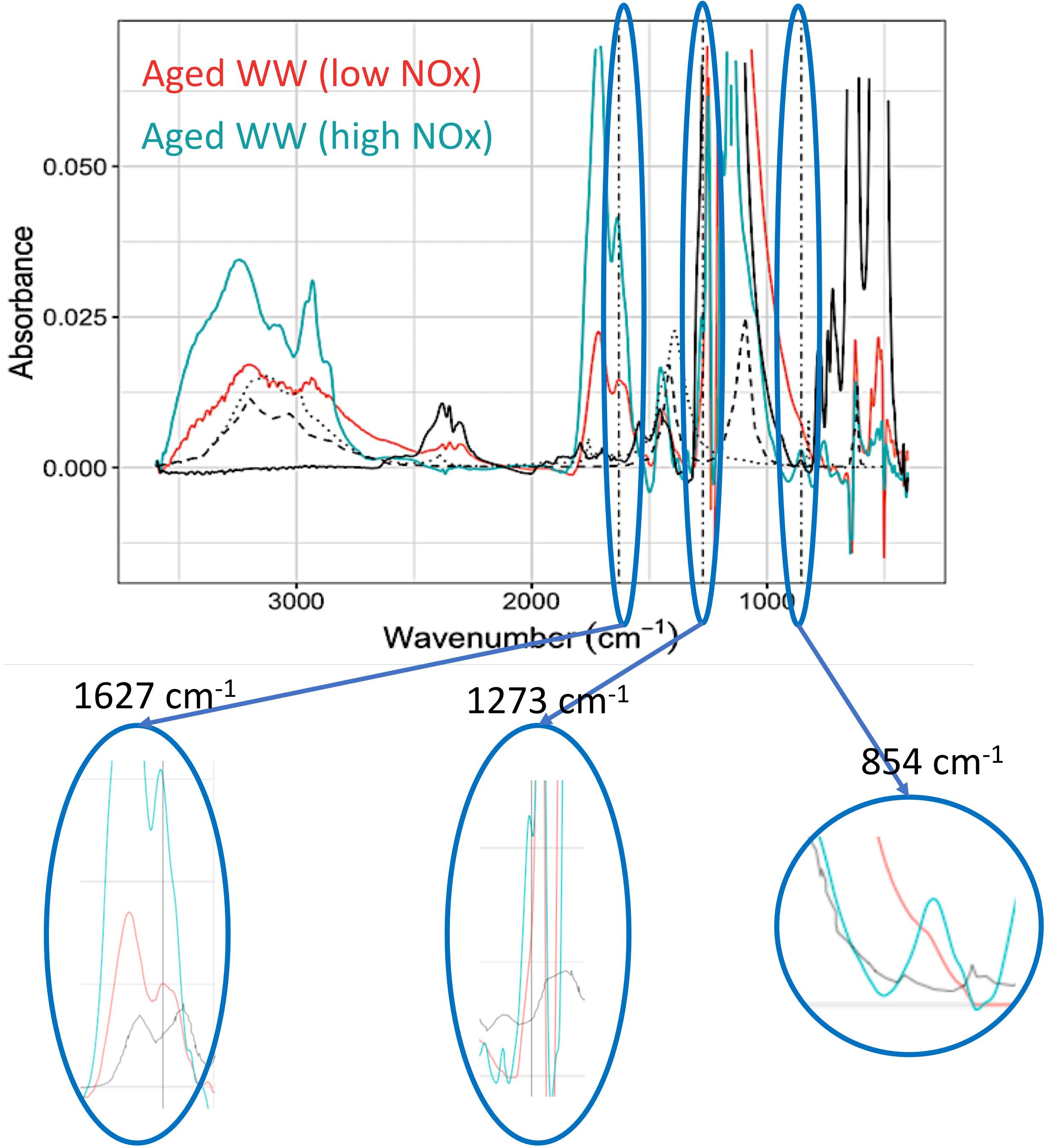
- AMS and FT-IR estimate consistent trends.
- Aging with NO_3 dose not reduce H:C substantially.
- Both instruments estimate higher average trajectory slopes in Van Krevelen diagram for CC compared to WB (more non-acid carbonyl production for CC).

Effect of different NO_x levels

- Aging in the presence high levels of NO_x (even with the hydroxyl radical) results in visible signatures of organonitrates in mid-infrared spectrum.



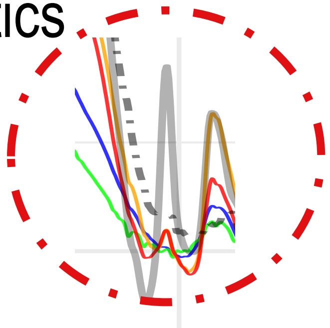
Kroll et al., *Atmos. Environ.* (2008)

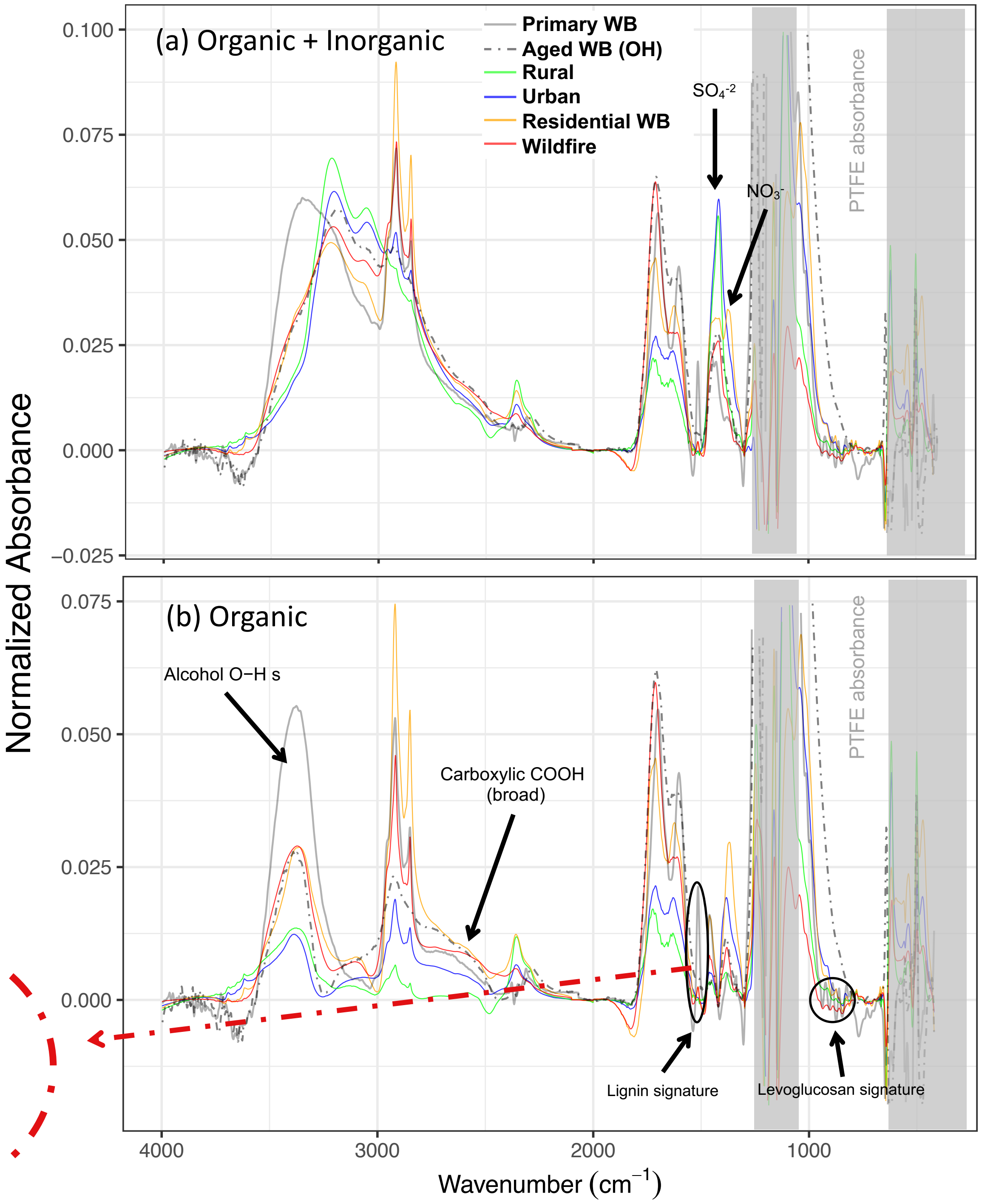


Comparison with Ambient Fire Periods

FTIR – IMPROVE network

- Burning-influenced samples were identified by Bürki et al. (2020) using cluster analysis.
- Mean spectra of four mutually exclusive sub-groups (with and without inorganics) are demonstrated.
- We still observe visible lignin and levoglucosan signatures in burning-influenced samples.
- High abundance of alcohols and sharp aliphatic C-H peak are other characteristics atmospheric of burning-influenced OA.





Identification of burning-influenced atmospheric samples on PTFE filters of the IMPROVE network (2011 and 2013)

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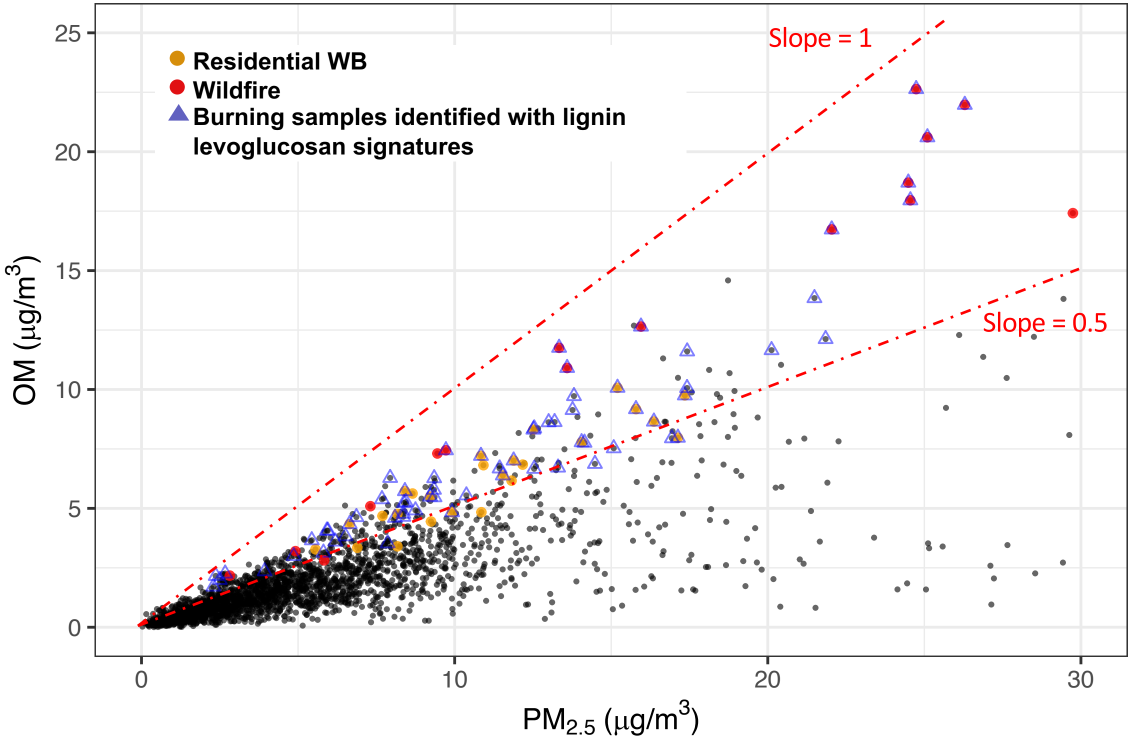
Identification

- We observe that the burning-influenced samples have high OM content (red envelope).
- Cluster analysis by Bürki et al. (2020) identified 45 burning influenced samples (RIM fire and residential wood burning in Phoenix) in IMPROVE samples of 2011 and 2013.
- By using **biomass burning tracer** method (working based on signatures of lignin and levoglucosan in mid-infrared spectra), we identify 99 samples in the same dataset (31 common with the cluster analysis).



Concluding remarks

- AMS and FT-IR generally agree rather well in terms of overall OM concentration and also OM:OC.
- Primary aerosols have mid-infrared signatures of the parent substance (especially levoglucosan and ligning).
- FT-IR on PTFE filters can be used to identify levoglucosan directly.

- Coal and wood burning SOA follow different oxidation pathways:
  - More non-acid carbonyl production in coal burning with aging.
  - More carboxylic acid in wood burning with aging.
  - With nitrate radical or high NO_x, organonitrate signature is visible in mid-infrared spectra.

- Mid-infrared spectra of aged wood burning OA share similarities with ambient wildfire spectra.

- Biomass burning tracer method, introduced in this work, is an effective method for identifying burning influenced atmospheric samples on PTFE filters and is complementary to cluster analysis.

Thank you for your attention!

Questions ?