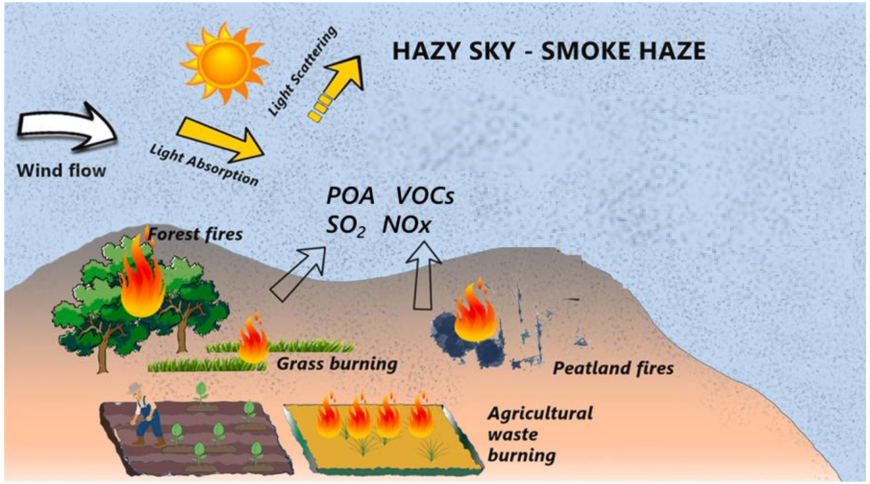

# Primary organic aerosol emissions and chemical composition from biomass and cow dung burning characterized using extractive electrospray ionization mass spectrometry

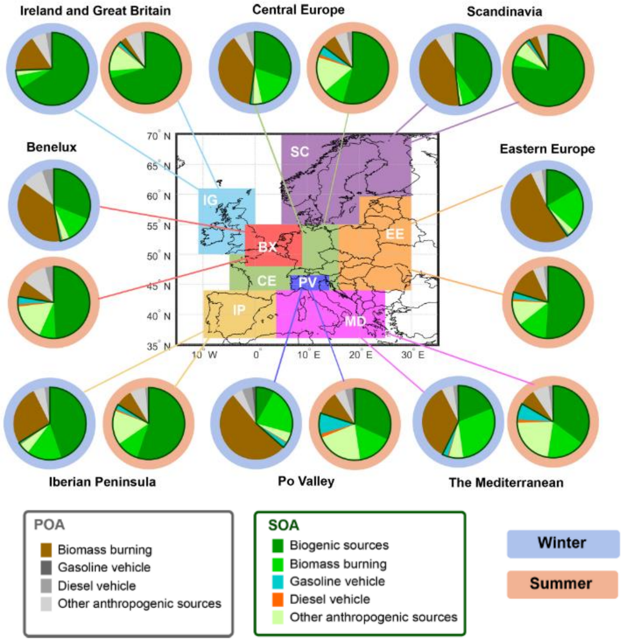
Jun Zhang– 2021 ETH Conference – 24.06.2021 - Zoom

# The importance of biomass and waste burning

Biomass burning makes a significant contribution to the primary organic aerosol (POA) and secondary organic aerosol (SOA), and strongly affect air quality and climate




modified from *Adam et al 2021*




Jiang et al 2019

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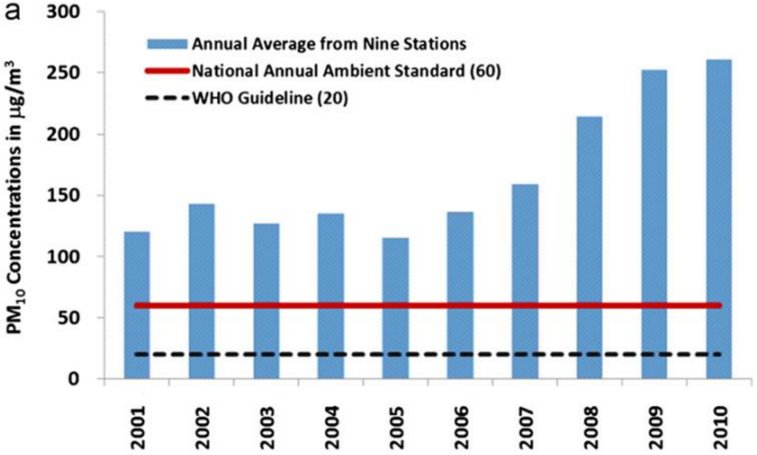
# Particulate matter pollution in India




The measured annual average of particulate matter (PM) exceeded the WHO guideline

Garbage

Crop residue

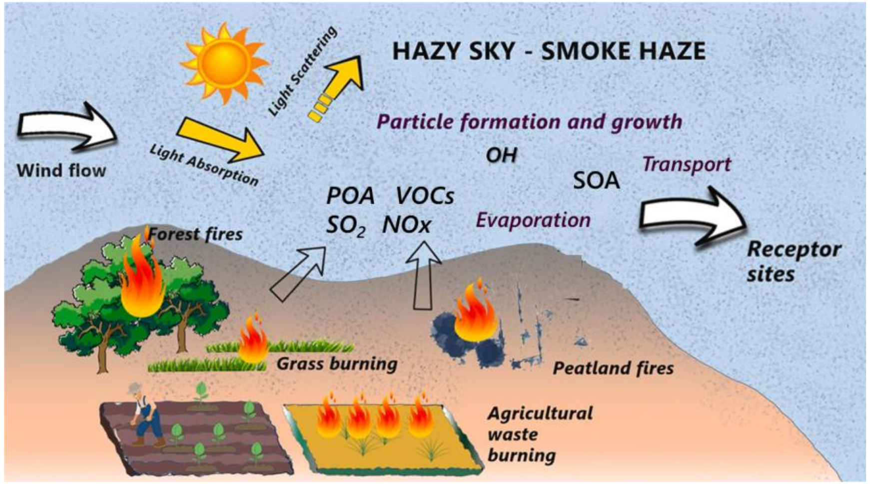
Cow dung

Cooking

Guttikunda et al 2013

# The importance of biomass and waste burning

After emitting to the atmosphere, some POA will evaporate and some of the VOCs are oxidized and result in secondary organic aerosol due to the change of volatility.




modified from *Adam et al 2021*

Garbage

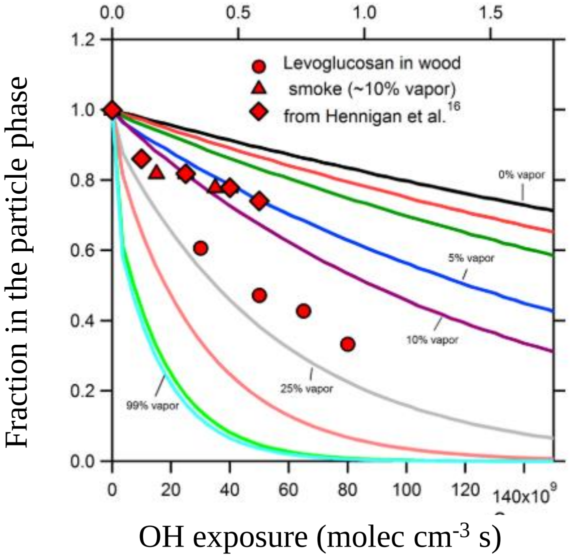
Crop residue

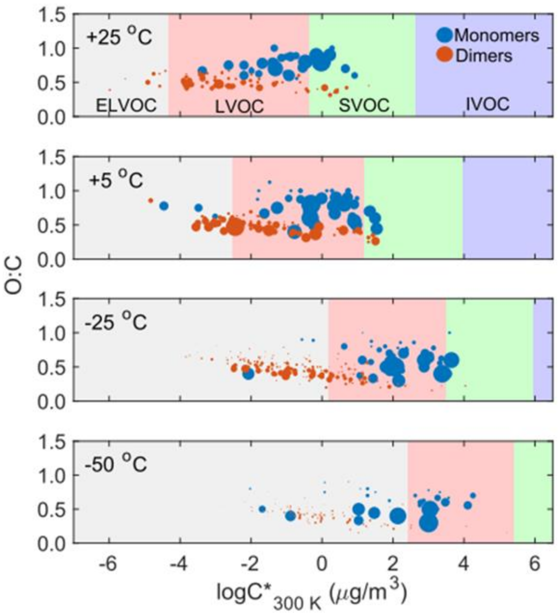
Cow dung

Cooking

# Volatility of organic species

Atmospheric age of levoglucosan




**Factors that influence the stability of makers:**

- Reactions

  Gas-phase reaction influence the gas-particle partitioning and further cause rapid depletion of marker concentrations

- Temperature

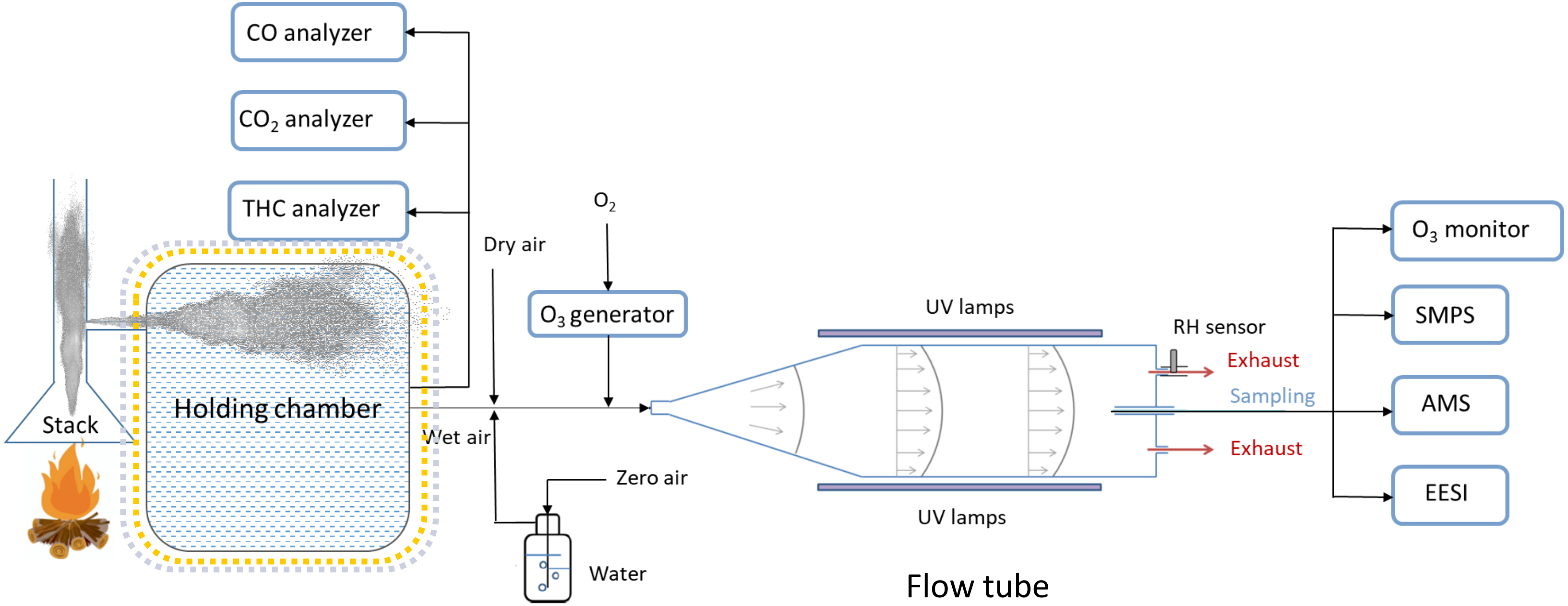
  More volatile with increasing temperature

May A. A et al 2012; Ye et al 2019

# Motivation

- What is the composition of POAs from different burning material?
- Can we find markers of each type of biomass burning?
- How will they change with evaporation / transport?

# Experimental setup

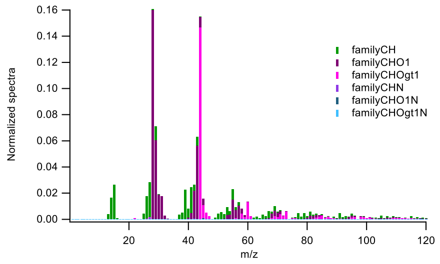


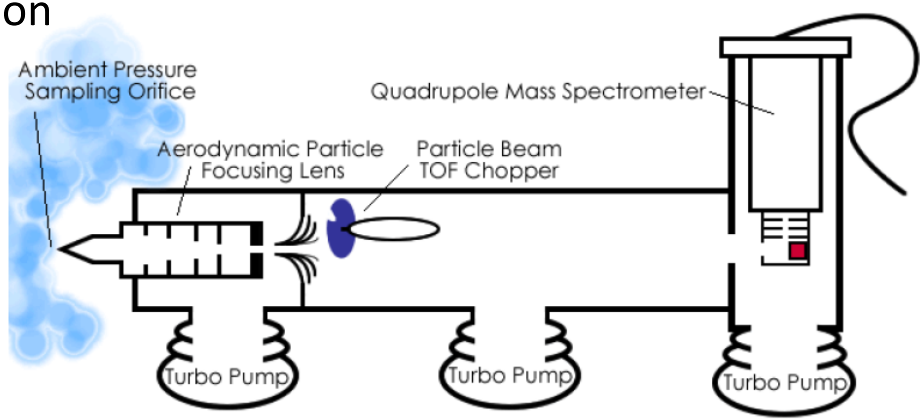

Temp: 0-100

Temp=20 C, RH=50%

# Electron Impact Ionization

- Real-time
- Can be quantitative
- Extensive fragmentation
- Difficult to retrieve molecular information



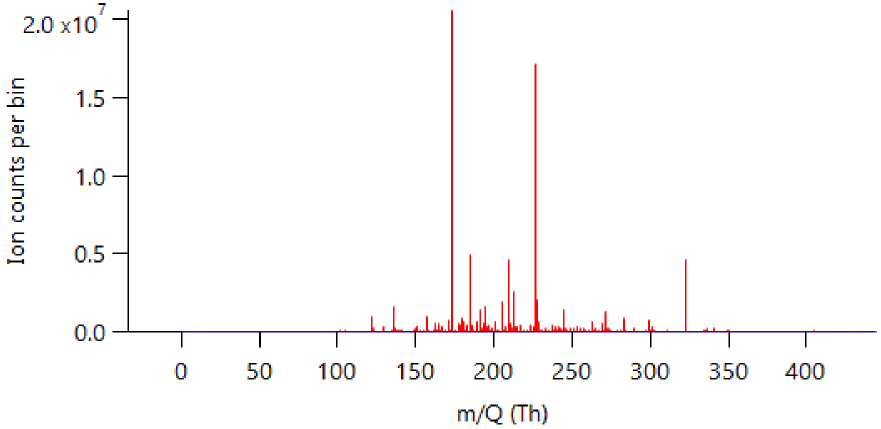



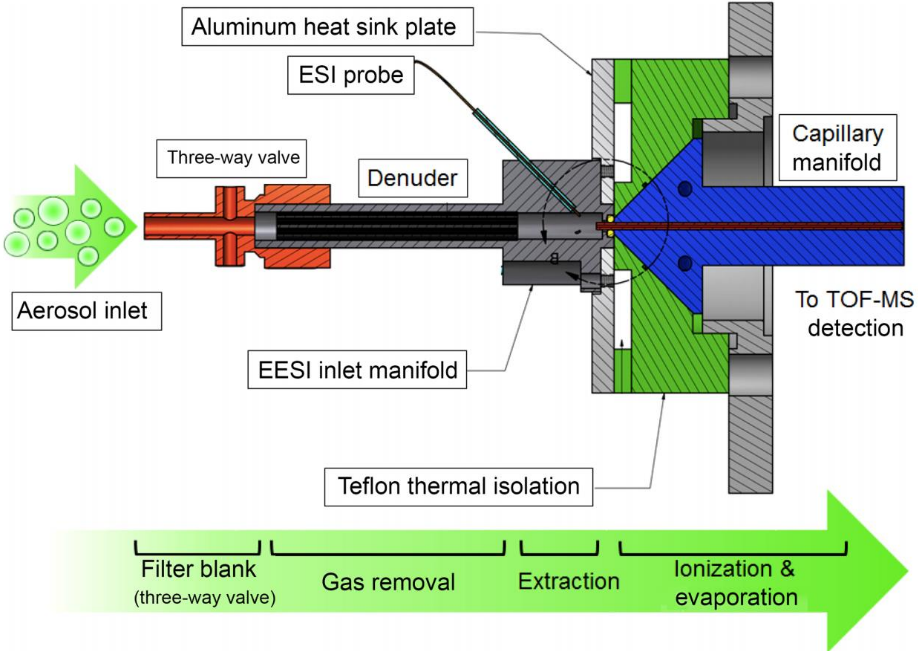

AMS

# Extractive Electrospray Ionization (EESI)

**Advantages:**

- 1 Hz time resolution
- No thermal decomposition and limited fragmentation
- Linear with mass, no matrix effects

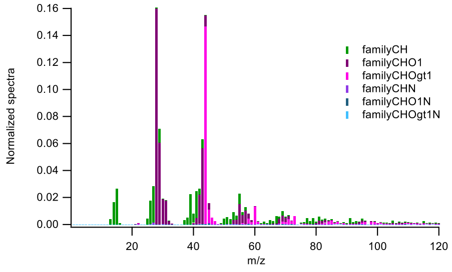


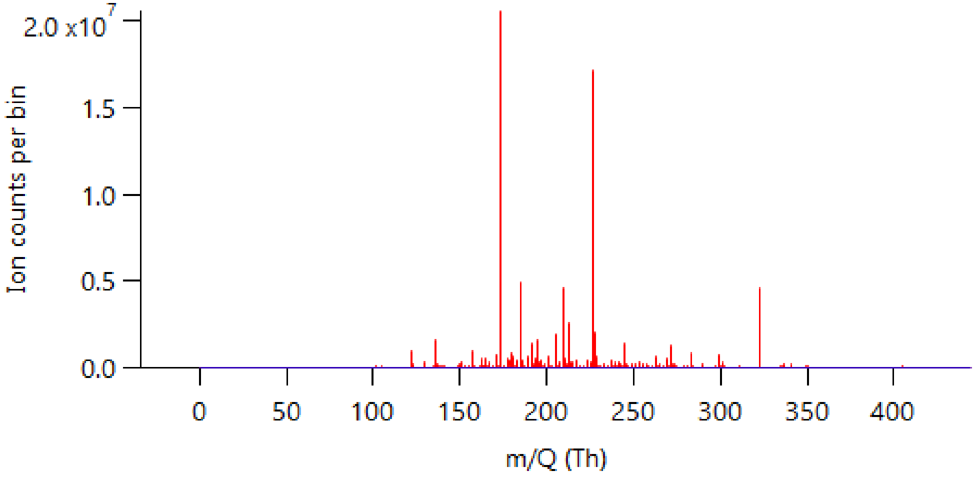




Lopez-Hilfiker et al 2019

# Mass spectrum: AMS vs. EESI

Possible to assign molecular formula




AMS: Hard ionization

EESI: Soft ionization

# Types of burning

Wood residential burning

Wood open burning

Straw burning

Cow dung burning

# Emission of gas and particulate matter

The emission factor of POA:

- Open burning > Residential burning
- Cow dung > Wood > Straw

$$EF_i = \frac{m_i \cdot xC}{\Delta CO + \Delta CO_2 + \Delta HC + \Delta OC + \Delta BC}$$

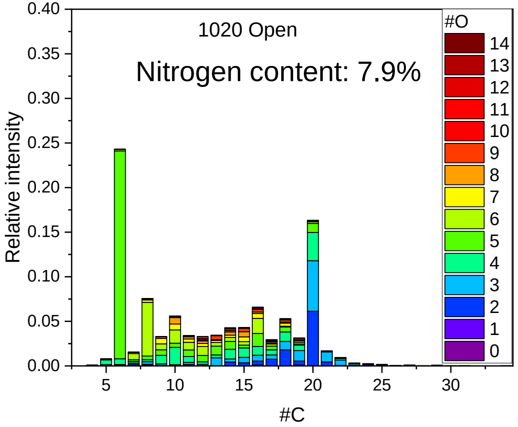
| Species | Wood | | Straw (n=1) | Cow dung (n=1) |
|---|---|---|---|---|
| | Open (n=4) | Residential (n=5) | | |
| MCE | 0.93±0.015 | 0.92±0.013 | 0.94 | 0.78 |
| CO | 63.5±6.8 | 73.2±15.4 | 45.1 | 78.9 |
| CO2 | 1668.9±26.7 | 1661.7±30.3 | 1726.4 | 1413.9 |
| NMHC | 10.4±2.7 | 11.7±2.9 | 6.3 | 22.3 |
| PM | 9.43±2.72 | 4.14±1.36 | 3.57 | 8.85 |
| POA | 3.79±1.09 | 1.80±0.49 | 0.99 | 7.85 |

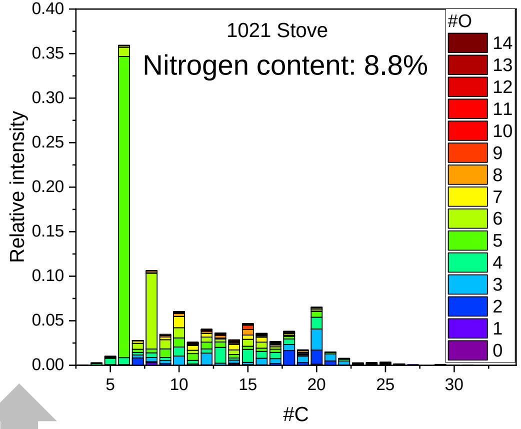
g/kg

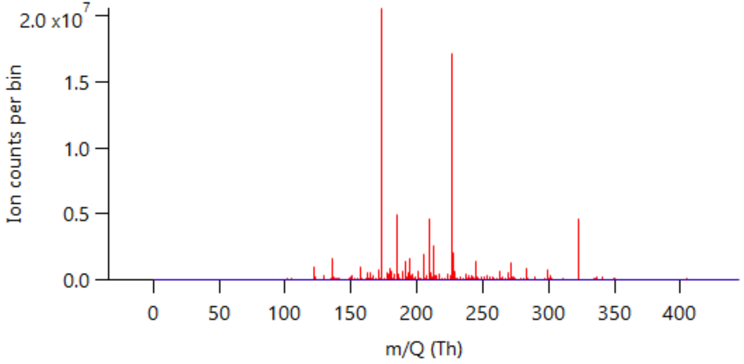
MCE: modified combustion efficiency

NMHC: non-methane hydrocarbon

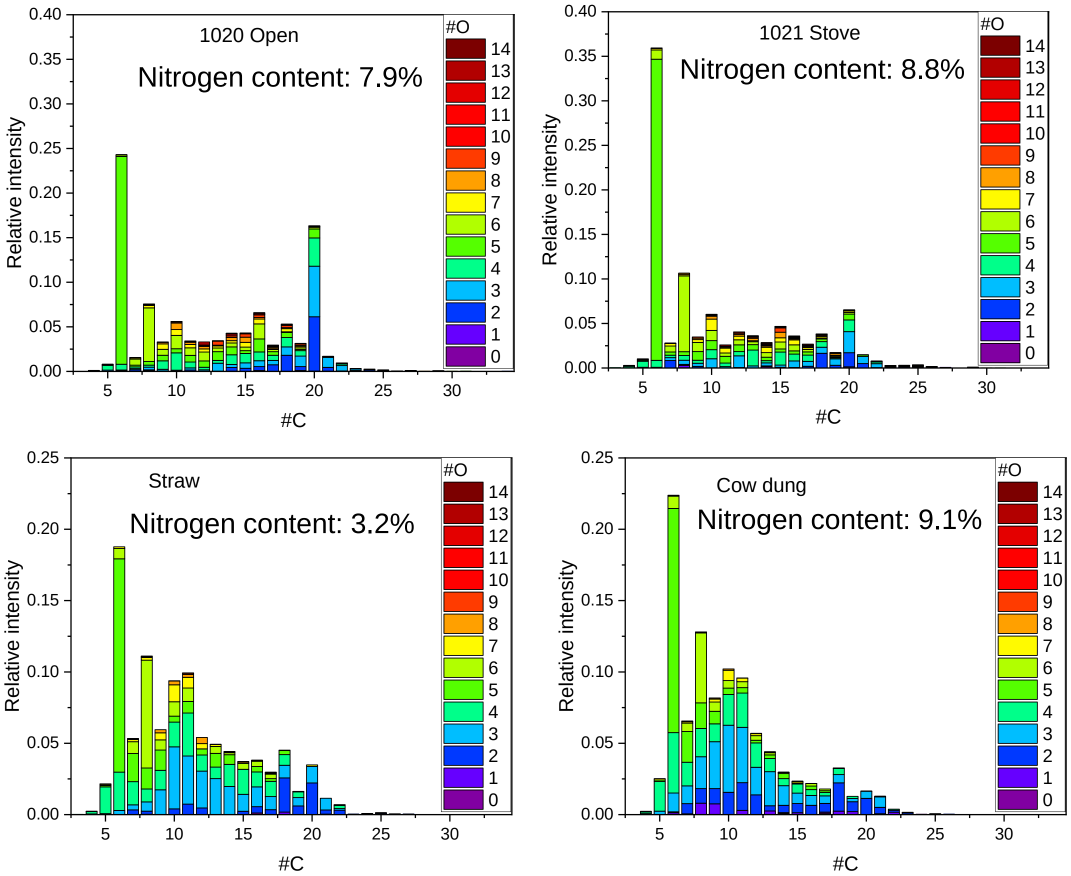
# Carbon and oxygen distribution and nitrogen content



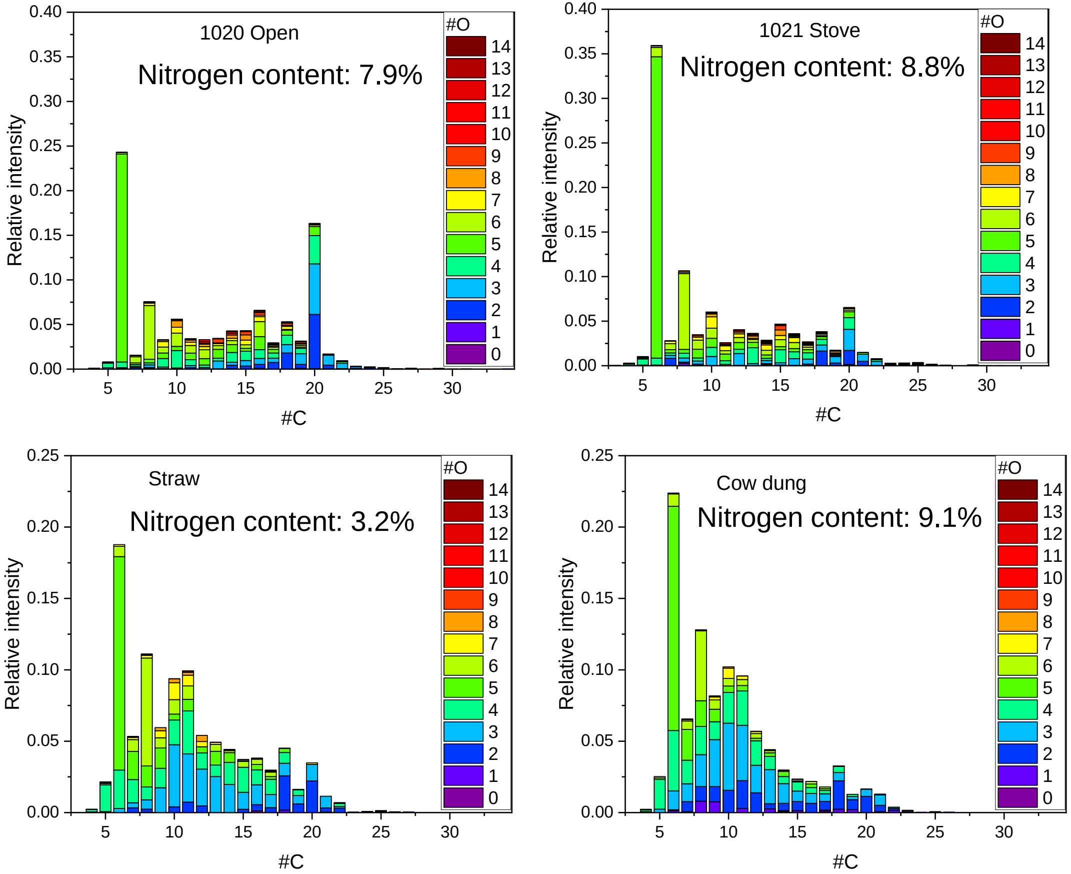



# Carbon and oxygen distribution and nitrogen content




- For wood burning, the composition is more dominated by **levoglucosan** ($C_6H_{10}O_5$) than straw and cow dung burning.
- Compounds with carbon number > 10 in the emission of straw and cow dung is higher than wood combustion.

# Carbon and oxygen distribution and nitrogen content




The proportion of nitrogen-containing compounds for **cow dung and wood burning** is around 8~9%, which is higher than the proportion for **straw combustion** with an average around 3%.

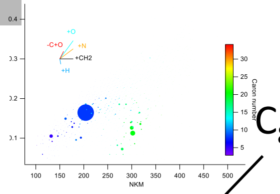
# Mass defect of POA

Mass defect = round(exact mass) – Kendrick exact mass

Base unit: $CH_2$

without $C_6H_{10}O_5$

KMD[CH2]

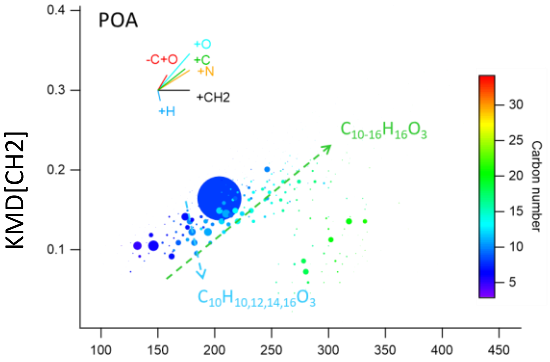



$C_8H_{12}O_6$

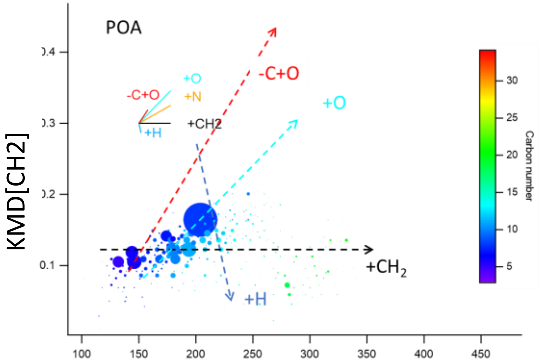
Carbon number

NKM

Wood-stove



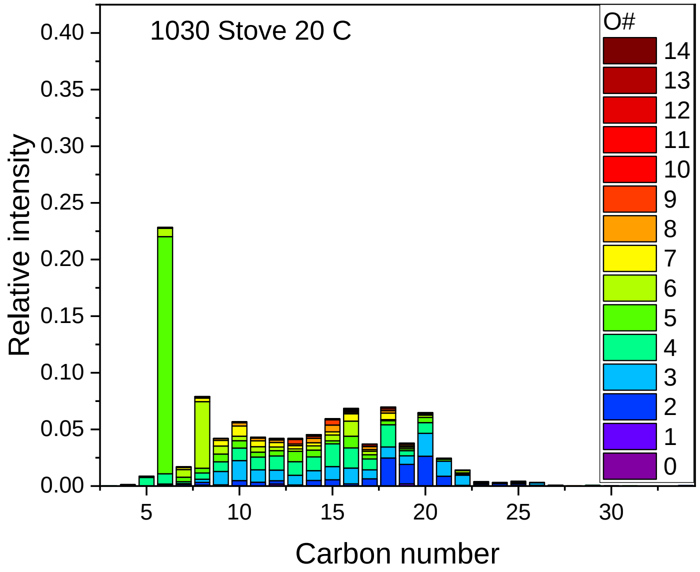

straw

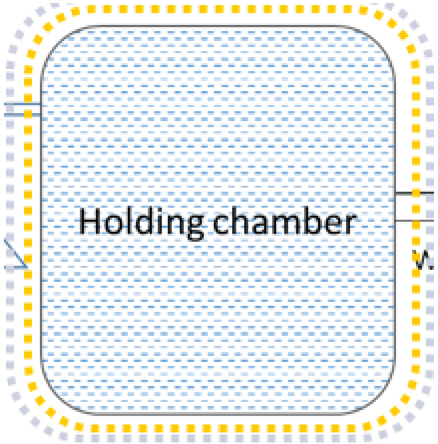



Cow dung

- Except for levoglucosan, $C_8H_{12}O_6$ is the main contributor in the emission of wood, straw, and cow dung.
- Emissions from cow dung and straw are more chemically complex than that from wood.

# Volatility distribution at different temperature



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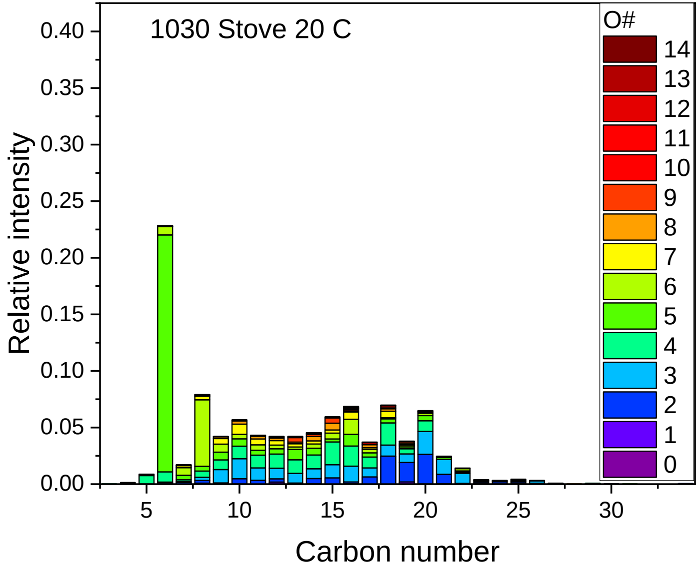


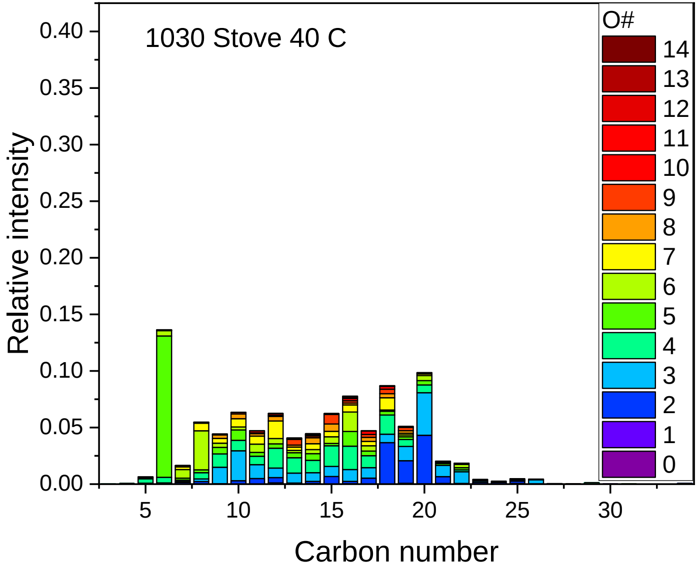

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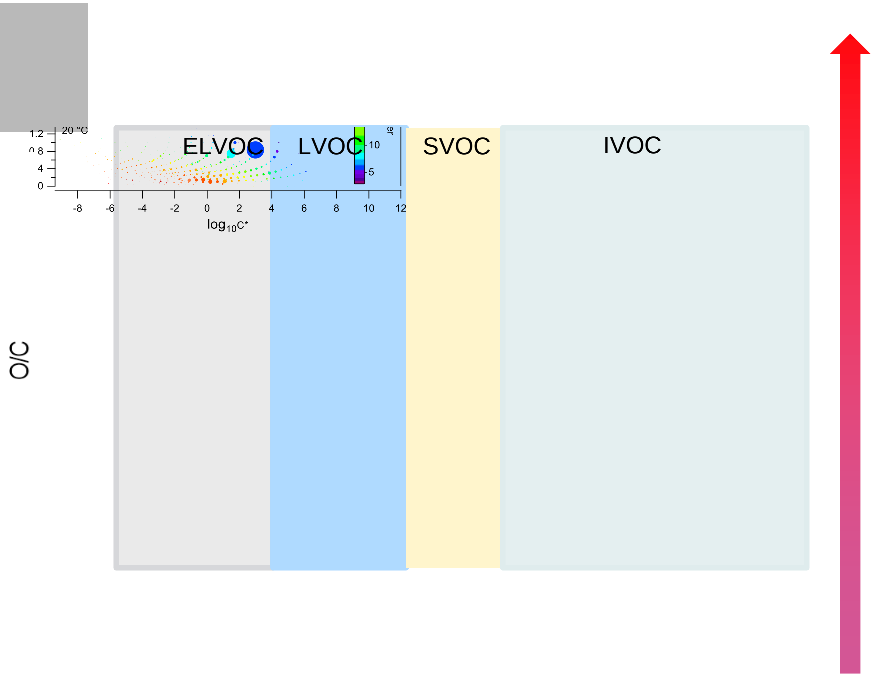


Compounds shift their volatility classes with temperature

The higher #C compounds also evaporate with increasing temperature

Compounds evaporate about 80% when temperature goes up to 40 C from 20 C

The relative intensity of higher #C compounds increased due to the evaporation of IVOC

$$\log_{10} C^*(T) = \log_{10} C^*(300K) + \frac{\Delta H_{vap}}{R\ln(10)}\left(\frac{1}{300} - \frac{1}{T}\right)$$

$$\log_{10} C^*(300K) = (n_C^0 - n_C)b_C - n_O b_O - 2\frac{n_C n_O}{n_C + n_O} b_{CO} - n_N b_N$$

Marker size corresponds to the square root of the ion intensity

Li, Y et al 2016

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# Summary

- POA from wood, straw, and cow dung
- Quantitative with AMS, molecular characterization with EESI
- Carbon and oxygen distributions of POA vary between different fuel types
- Levoglucosan main marker for wood combustion, contribution to straw and cow dung burning is lower
- proportion of nitrogen-containing compounds for straw is lower than wood and cow dung
- evaporation of main components of POA with temperature provides insights into the volatility of POA

❖Thanks the great support from the LAC group especially:

- Dr. Andre Prevot
- Dr. David Bell
- Dr. Kun Li
- Tiantian Wang
- Dr. Tianqu Cui
- Dr. Lu Qi
- Dr. Deepika Bhattu
- Dr. Dongyu Wang
- Mihnea Surdu
- Dr. Houssni Lamkaddam
- Dr. Jay Slowik
- Dr. Imad El Haddad


Thanks for your listening!

❖This work is supported by the SNF grant MOLORG (200020_188624).