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Sources and formation of carbonaceous aerosols in Xi'an, China: primary emissions and secondary formation constrained by radiocarbon

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Carbonaceous aerosol is a major contributor to severe particulate air pollution in China

Our goal:

- Understand sources of **carbonaceous aerosol** in China to develop effective reduction strategies.

Main open questions:

- Identification of the **main sources** of carbonaceous aerosols in polluted Chinese regions
- Separation of **primary emissions and secondary formation** of carbonaceous aerosols
- Source contribution changes with severity of pollution
- **Seasonality** of the source contributions

Method:

- **^{14}C measurements** on carbonaceous aerosols

Radiocarbon (^{14}C) source apportionment, *a powerful tool to apportion sources of carbon*

Living things: certain ^{14}C level
^{14}C in fossil fuel **decayed=0**

←

Half-life of ^{14}C: **5730 years**

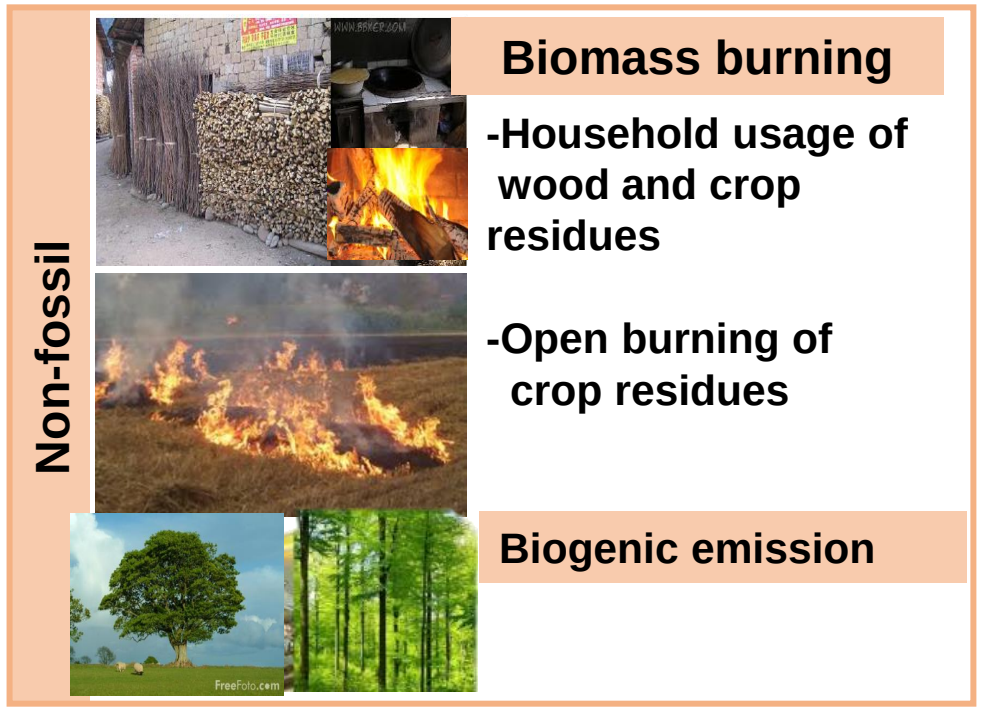
Time of fossil fuels buried: **million years**

Fraction modern

$$F^{14}C = \frac{\frac{^{14}C}{^{12}C}(sample)}{\frac{^{14}C}{^{12}C}(1950)}$$

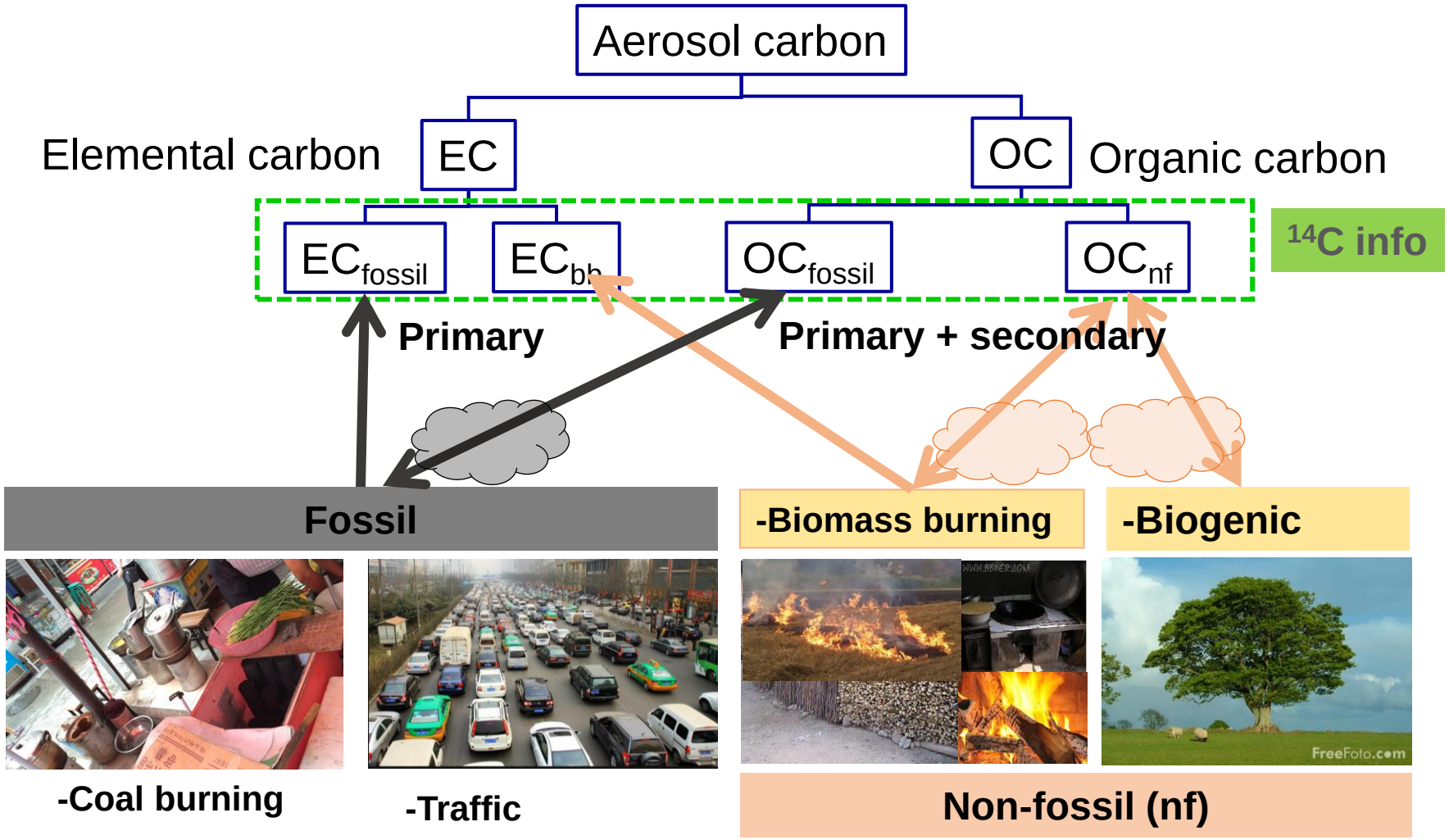
Fossil sources, $F^{14}C=0$

Non-fossil sources, $F^{14}C\sim1$

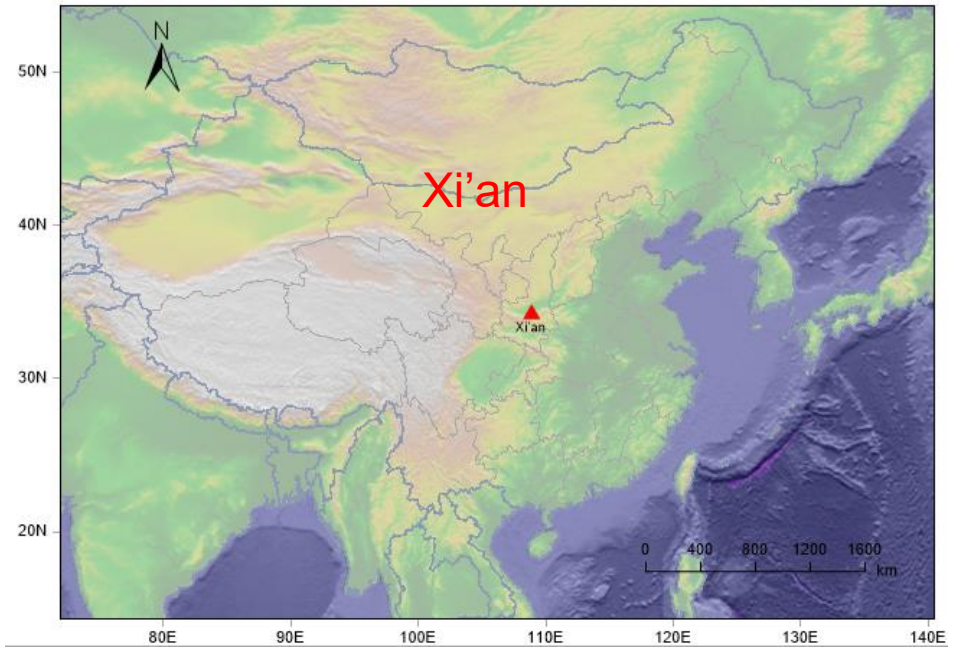


winter heating: City collective heating supply: coal ; rural heating source: biomass; coal

OC, EC source apportionment based ^{14}C



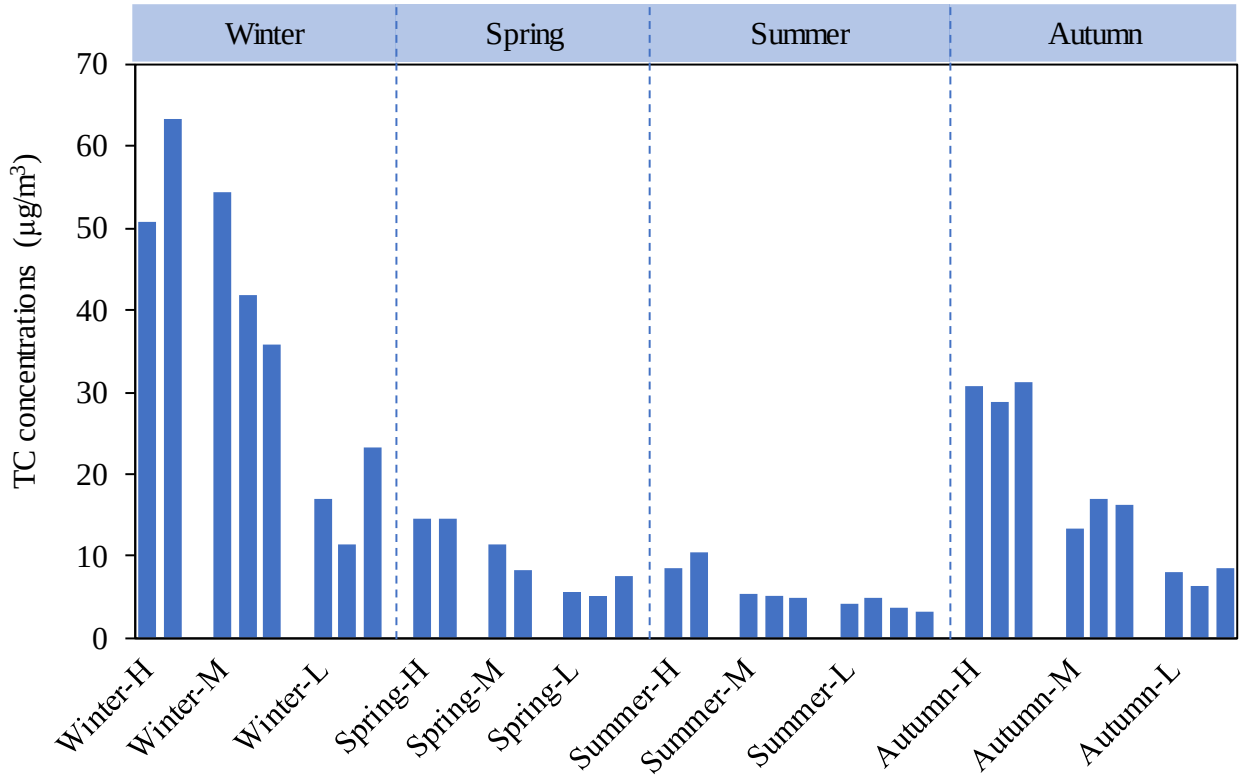
Sampling



Xi'an, China

- One of the most polluted cities in China

Selected samples for ^{14}C analysis

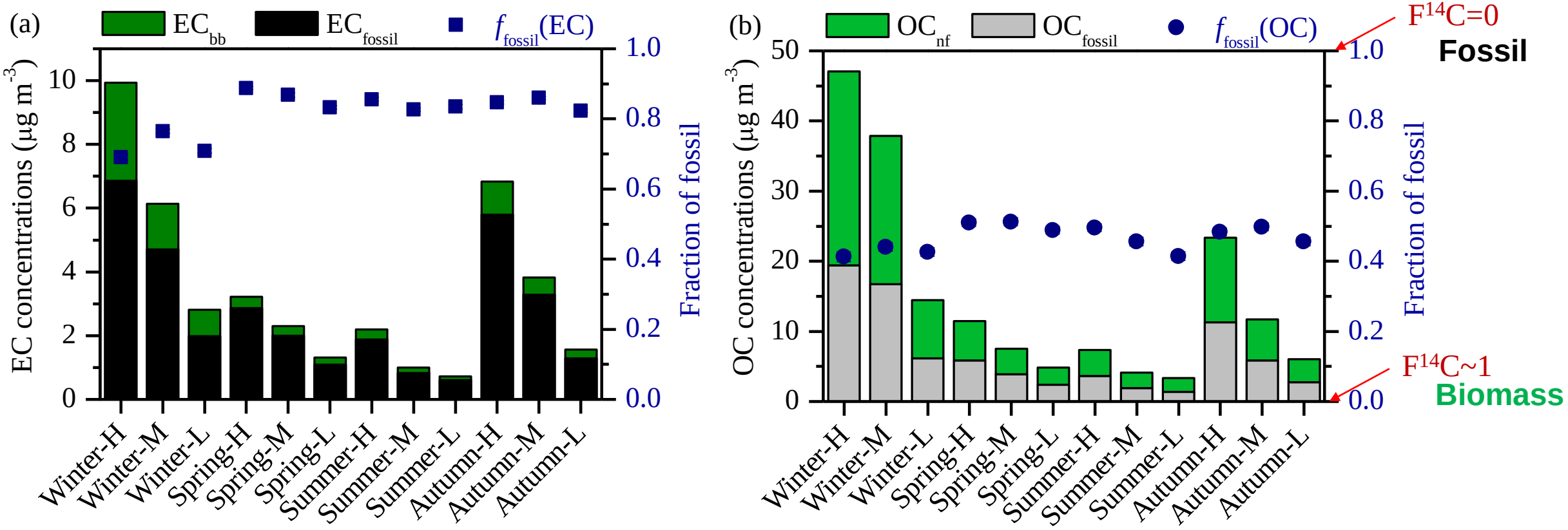


^{14}C: 3 composite samples/season

Sampling:

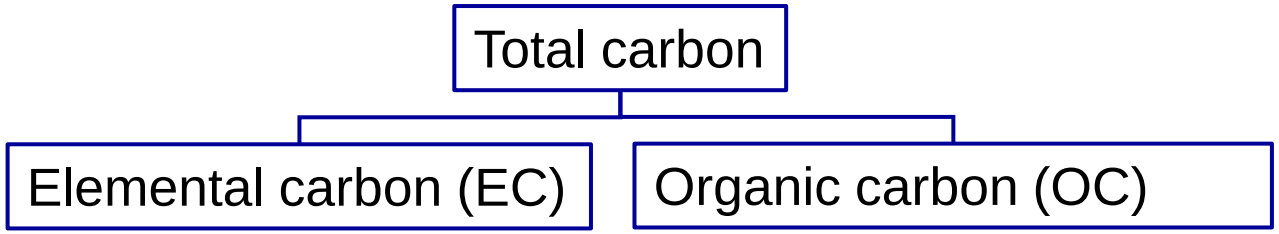
- Sampling site: a typical urban background site surrounded by residential and education areas
- 24hr $PM_{2.5}$ samples were collected from Nov. 2015 to Nov. 2016.

^{14}C source apportionment of EC and OC



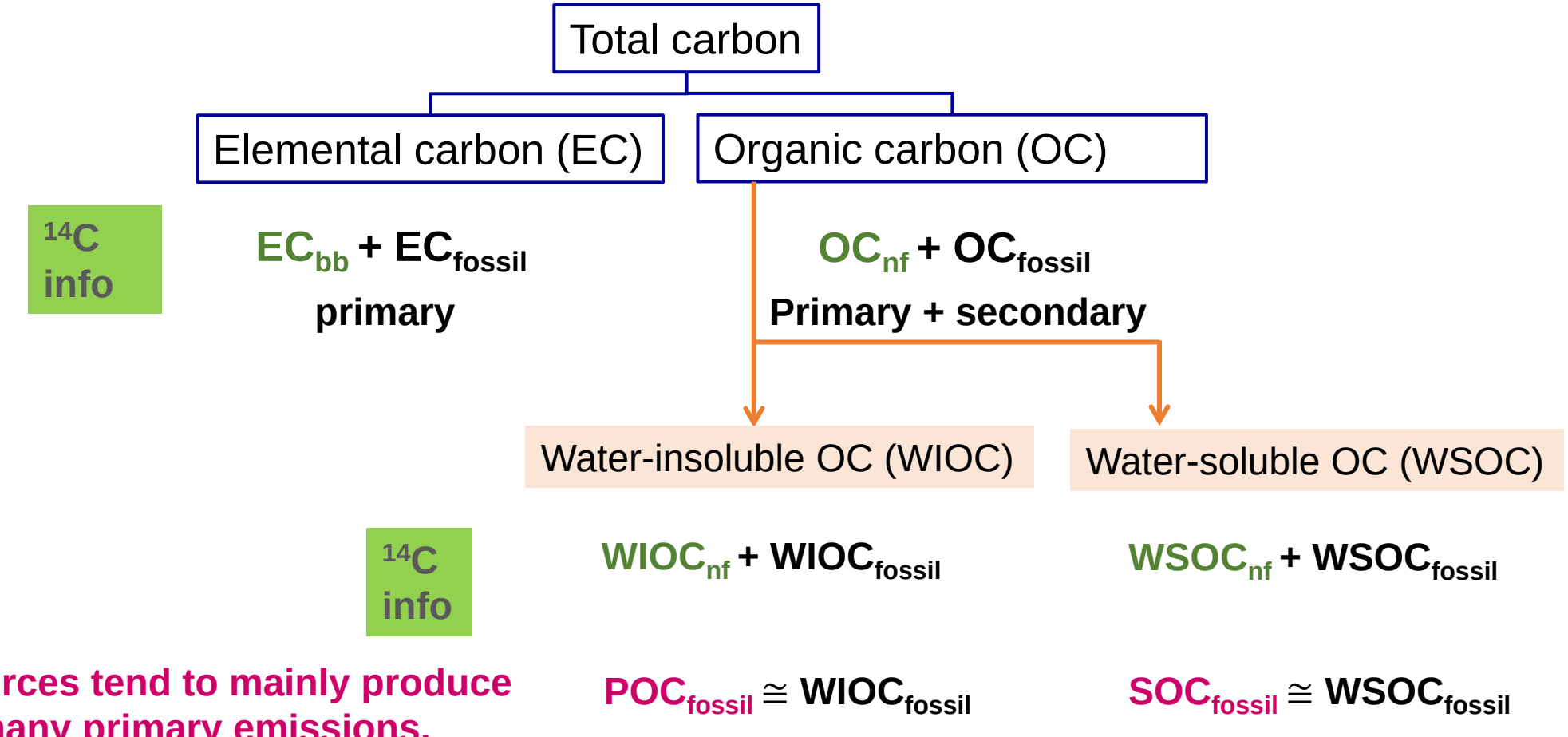
- **EC is dominated by fossil sources:** f_{fossil}(EC)= 82 ± 6% (69% to 89%)
- **f_{fossil}(OC) <f_{fossil}(EC)**
- Seasonal variation of f_{fossil}(OC) and f_{fossil}(EC): lowest winter→ enhanced biomass burning in winter

^{14}C aerosol source apportionment



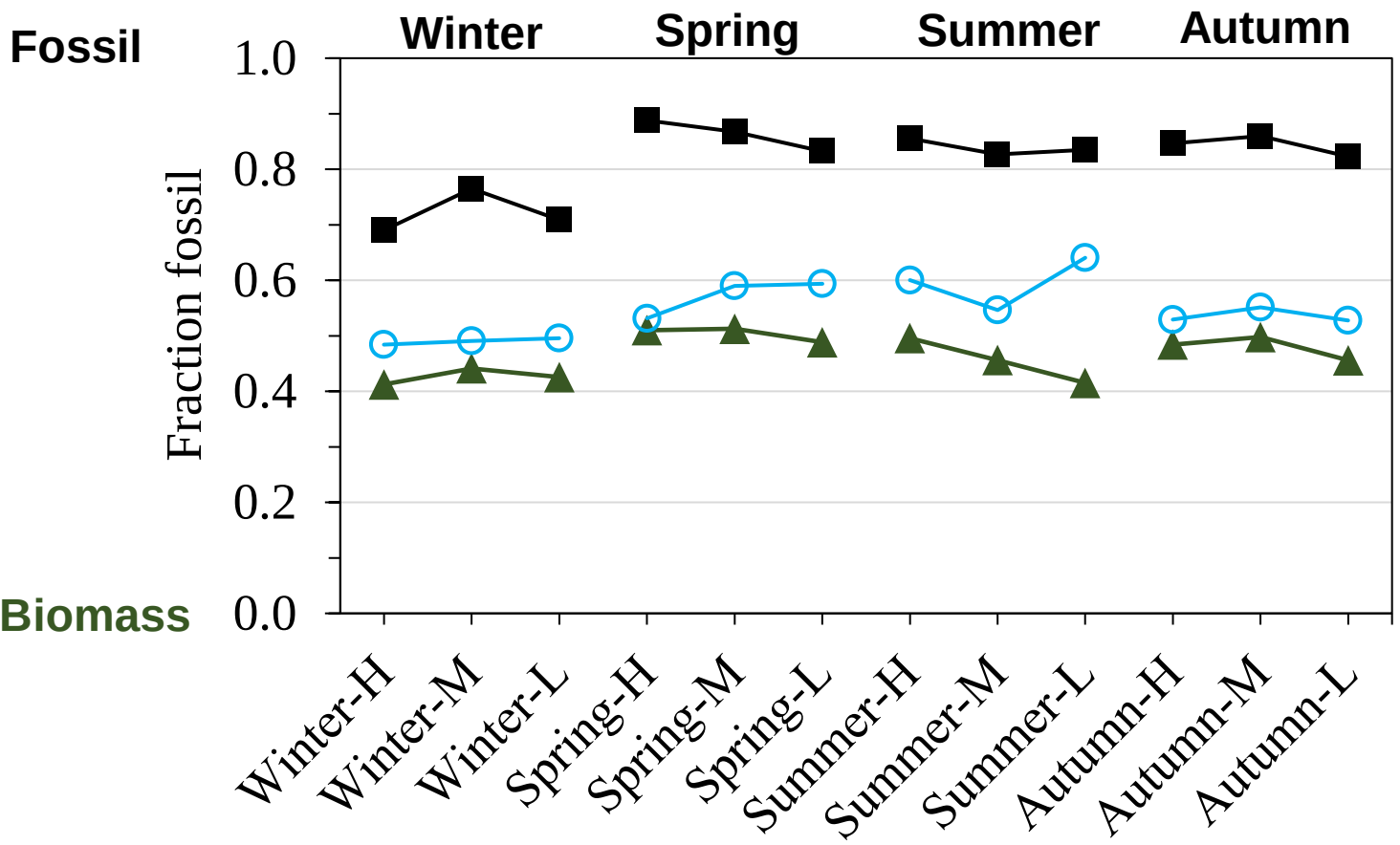
^{14}C info	$EC_{bb} + EC_{fossil}$	$OC_{nf} + OC_{fossil}$
	primary	**Primary + secondary**

^{14}C aerosol source apportionment



Fossil sources tend to mainly produce WIOC in many primary emissions.

^{14}C results of WIOC



f_{fossil}(EC)

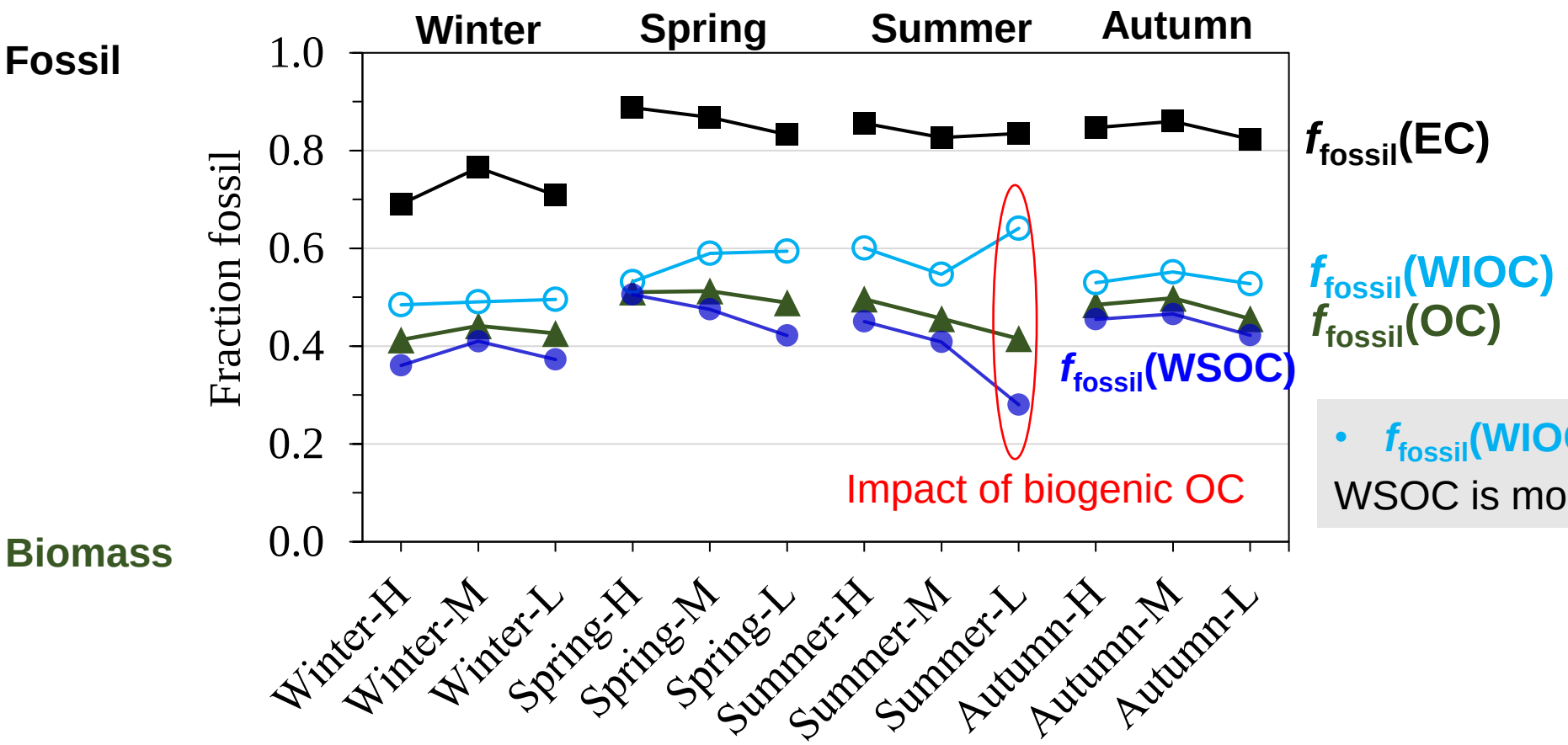
f_{fossil}(WIOC)

f_{fossil}(OC)

- f_{fossil}(WIOC)>f_{fossil}(OC):
higher contribution of fossil sources to WIOC

- **Lowest f_{fossil}(WIOC) in winter:**
enhanced biomass burning is a source of non-fossil WIOC

^{14}C results： WIOC vs. WSOC

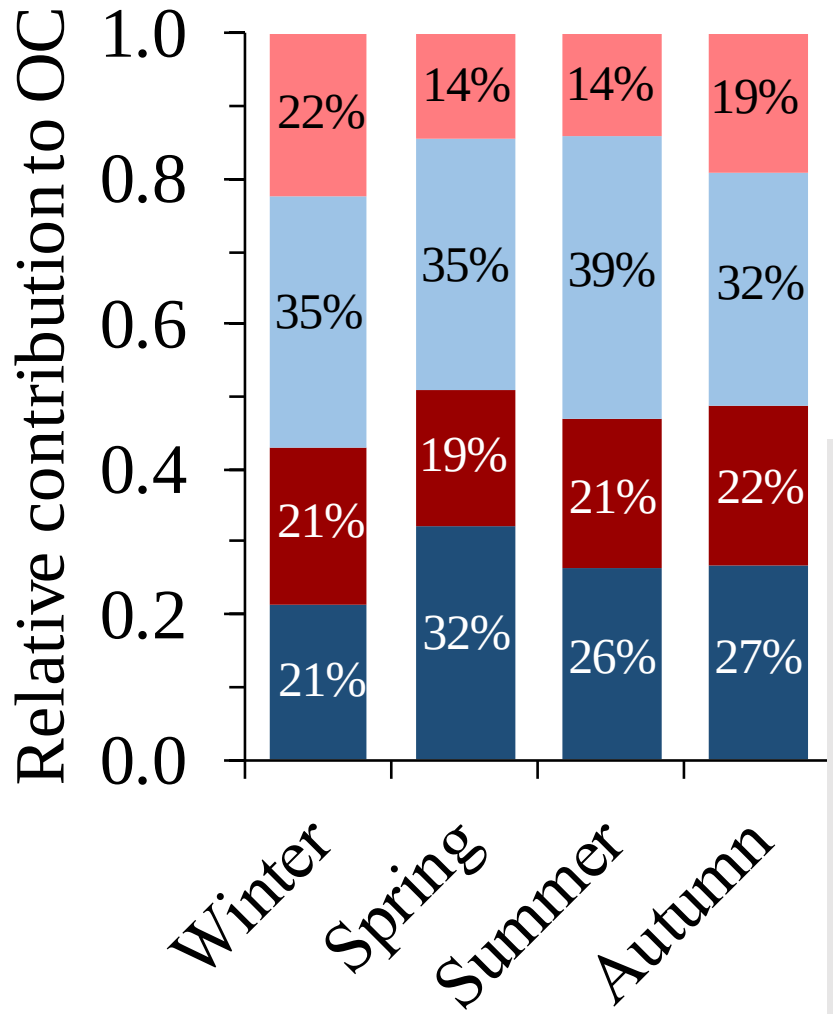


- f_{fossil}(WIOC)>f_{fossil}(WSOC) : WSOC is more modern than WIOC

- The biggest difference between f_{fossil}(WIOC) **and** f_{fossil}(WSOC) **is found for Summer-L**
- Summer-L has the lowest f_{fossil}(WSOC)← increased contribution from biomass burning and biogenic emissions

Fossil and non-fossil WIOC/WSOC

$WSOC_{fossil}/OC_{fossil}$	50%	**62%**	55%	55%



- $WIOC_{nf}$ ⟷ **Biomass burning POC**
- $WSOC_{nf}$
- $WIOC_{fossil}$ ⟷ **Fossil POC**
- $WSOC_{fossil}$ ⟷ **Fossil SOC**

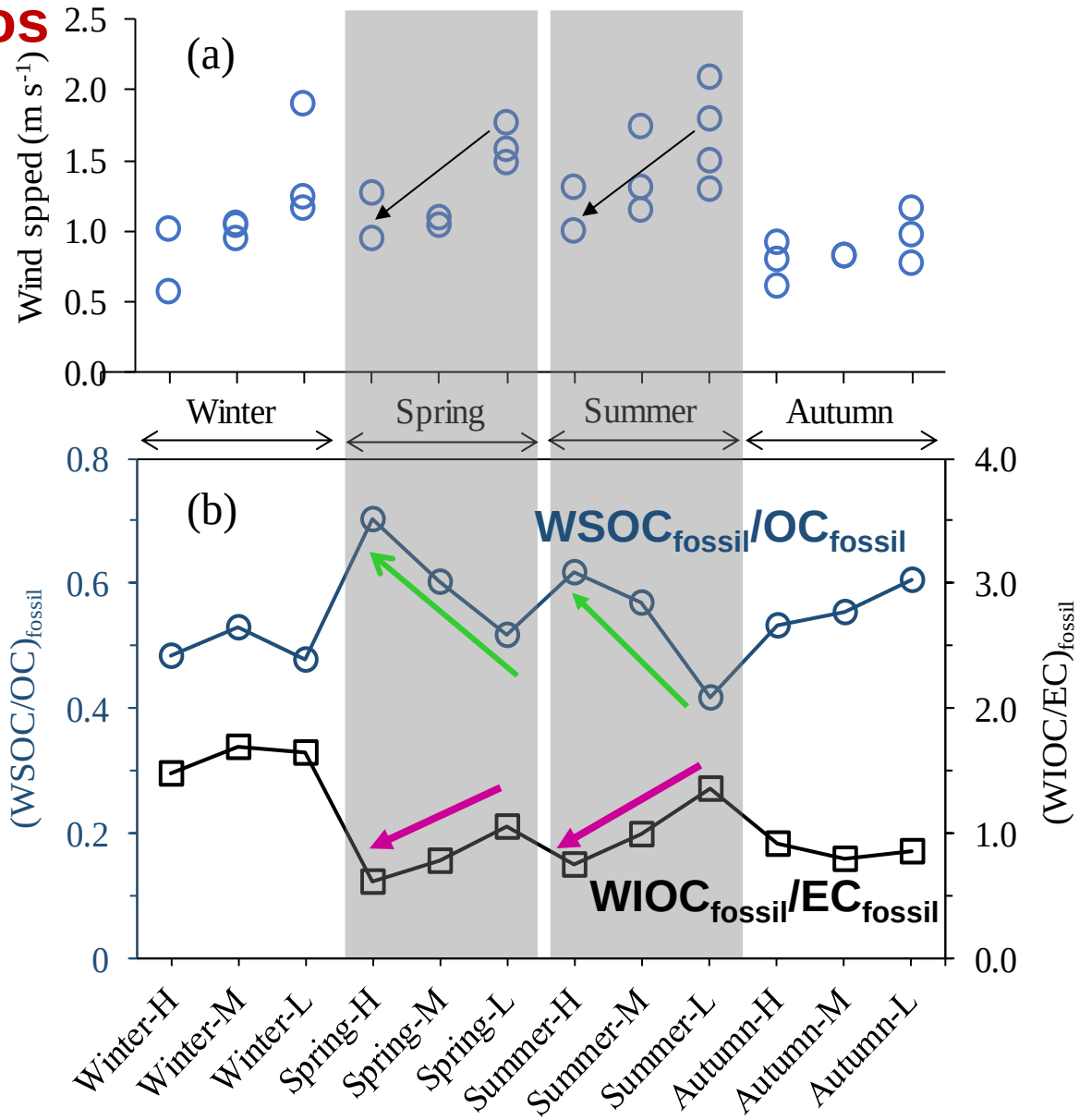
- **$WSOC_{nf}$** was the largest contributor to OC
  - Biomass-burning POC and SOC
  - Biogenic SOC
- Increased **$WSOC_{nf}$** in summer: impact of biogenic OC
- The higher **$(WSOC/OC)_{fossil}$ ratio** in the warm period(spring, summer and autumn) suggests an enhanced SOC formation from fossil VOCs

$WSOC_{fossil}/OC_{fossil}$, $WIOC_{fossil}/EC_{fossil}$ ratios

In spring and summer:
lower wind speed in more polluted periods

In spring and summer: a clear increasing tend of $(WSOC/OC)_{fossil}$ in more polluted periods

$(WIOC/EC)_{fossil}$ ratios decline when pollution gets worse, suggesting removal of WIOC, likely through photochemical reactions



Conclusions

- **EC is dominated by fossil sources**
- non-fossil sources are an important contributor to OC
- lower f_{fossil}(OC) and f_{fossil}(EC)in winter-→ **enhanced biomass burning in winter for heating**
- $WSOC_{fossil}/OC_{fossil}$: winter < warm seasons → **an enhanced SOC formation from fossil VOCs in the warm period.**

In spring and summer:

→**fossil WSOC formation as well as fossil WIOC removal increase under the stagnant conditions**

→stagnant conditions during polluted periods allow for accumulation of pollutants and also photochemical processing and secondary OC formation.

Ni, H., Huang, R.-J., Cao, J., Guo, J., Deng, H., and Dusek, U.: Sources and formation of carbonaceous aerosols in Xi'an, China: primary emissions and secondary formation constrained by radiocarbon, Atmos. Chem. Phys., 19, 15609–15628, https://doi.org/10.5194/acp-19-15609-2019, 2019.

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