Modeling stable isotopes of CO in the Yangtze River Delta region

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Background and Research Objective

- Carbon monoxide(CO) is a colorless, odorless and tasteless gas that poses significant health risk due to its high affinity for hemoglobin, leading to potentially fatal outcomes upon exposure.
- CO's major sink is hydroxyl radical(OH). Since OH is a crucial oxidant that reacts with greenhouse gases CH_4 and ozone(O_3), the abundance of CO in the atmosphere can affect the concentrations of these two greenhouse gases, thereby intermediately affecting the rate of global warming.
- CO's main sources are fossil fuels combustion, biomass burning, methane oxidation, and VOC oxidation. The stable isotopes of CO(^{13}CO and C^{18}O) can be used to distinguish the CO sources by comparing the isotopes composition in ambient air with those of potential sources. Different sources of CO exhibit distinct ratios of $^{13}C/^{12}C$ and $^{18}O/^{16}O$, allowing precise identifications of specific CO origins.

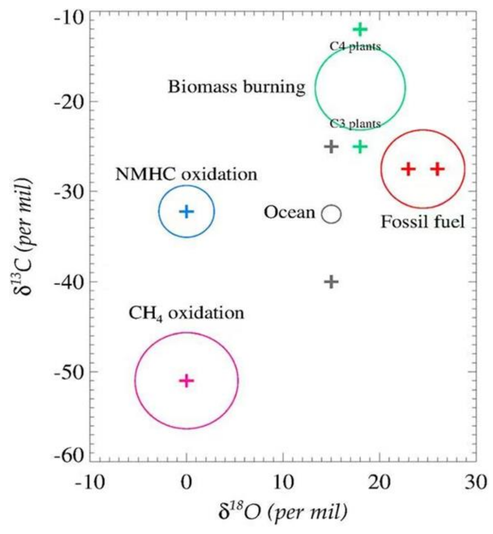


Fig1. Different sources have distinct isotopic signature[1]

- Identifying sources of CO provides huge benefits for public health and environmental protection. However, the effectiveness of this method has not been validated comprehensively, and the sensitivity of isotopic analysis in detecting low concentrations of CO remains underexplored.
- Objective of this research : To find out if stable isotopes(^{13}CO and C^{18}O) of CO are suitable for source identification.

Method

- **Models**

WRF-Chem

A numerical model considering aerosols' radiative forcing and its suppression of the planetary boundary layer.

Settings

Domain: 25.5-43.5°N; 105.0-126.0°E
Time Period: 2020.1.1--2020.1.31
Grid Resolution: 0.1°*0.1°

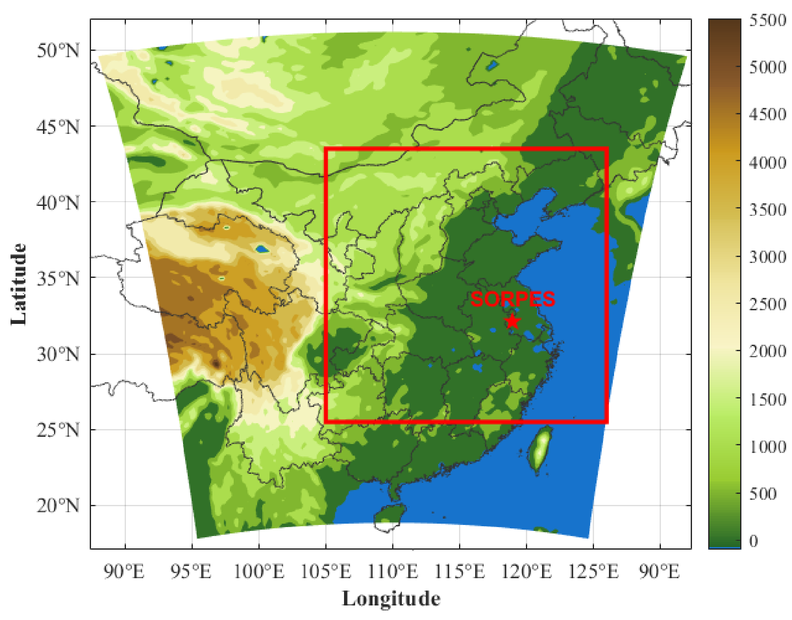


Fig2. Domain settings in WRF-Chem

Output

- Concentration of CH_4, VOCs, and OH
- Meteorological field(for WRF-FLEXPART model)

WRF-FLEXPART

A modeling system that combines weather forecasting with particle dispersion model to track atmospheric tracers and pollutants.

Table1. Settings of WRF-FLEXPART model

Items	Configurations/Parameters
Model	FLEXPART
Domain	25.5-43.5°N, 105.0-126.0°E
Meteorological drive	NCEP FNL global analysis
Grid Resolution	0.1°×0.1°
Number of Particles	5000 particles released at 40 m above ground level
Backward Period	72h
Footprint Level	100m above the ground
Emission Data	MEIC inventory

Output

- Footprint of CO

- **Formula**

$$R_{CO\_CH_4} = k_1[CH_4][OH]$$
$$R_{CO\_VOC} = k_2[CH_4][OH]$$
$$k = Ae^{-\frac{E_a}{RT}}$$
$$\Delta^{13}CO = \sum \text{footprint}(i,j) \cdot {}^{13}\text{CO}_{\text{emission}(i,j)}$$
$$\Delta^{12}CO = \sum \text{footprint}(i,j) \cdot {}^{12}\text{CO}_{\text{emission}(i,j)}$$
$$\Delta C^{18}O = \sum \text{footprint}(i,j) \cdot C^{18}O_{\text{emission}(i,j)}$$
$$\Delta C^{16}O = \sum \text{footprint}(i,j) \cdot C^{16}O_{\text{emission}(i,j)}$$
$${}^{13}R(CO) = \frac{[{}^{13}CO]}{[{}^{12}CO]} \quad {}^{18}R(CO) = \frac{[C^{18}O]}{[C^{16}O]}$$
$$\delta = (\frac{R_{sample}}{R_{reference}} - 1) \times 1000‰$$
$$CO_{total} = CO_{fossil\ fuels} + CO_{biomass\ burning} + CO_{VOC} + CO_{CH_4} - CO_{OH}$$

Results and Discussion

Part1. Research on isotopic signatures(^{13}CO and C^{18}O) of sources of carbon monoxide

Table2. Data of isotopic signatures of CO(13CO and C18O) for each type of emissions used in the model[2][3][4][5][6][7][8][9][10][11][12]

	δ^{13}C(‰)	author	average	δ^{18}O(‰)	author	average
Fossil fuel combustion	-27.4	Stevens et al.,1972	-27.45	23.5	Stevens et al., 1972 and Brenninkmeijer, 1993	23.5
	-27.5	Gromov et al., 2017				
Biomass burning	-21.3	Conny et al., 1997	-23.425	18	Stevens and Wagner, 1989	17.167
	-24.5	Conny, 1998		16.3	Brenninkmeijer, 1993	
	-22.9	Brenninkmeijer et al., 1999				
	-25	Gromov et al., 2017		17.2	Brenninkmeijer et al., 1999	
Methane oxidation	-52.6[a]		-51.85	15	Stevens and Wagner, 1989	0[b]
	-51.1	Saueressig et al., 2001		0	Brenninkmeijer and Röckmann, 1997	
VOC oxidation	-32.2	Stevens and Wagner, 1989	-32.2	14.9	Stevens and Wagner, 1989	0[b]
				0	Brenninkmeijer and Röckmann, 1997	

[a]: Based on δ13C of CH4 is -47.2‰(Quay et al., 1991) and on the fractionation in CH4+OH of 5.4‰(Cantrell et al., 1990)
[b]: Choosing value "0" for further calculation.

Part2. Variability of ^{13}CO and C^{18}O from 2020.1.1 to 2020.1.31

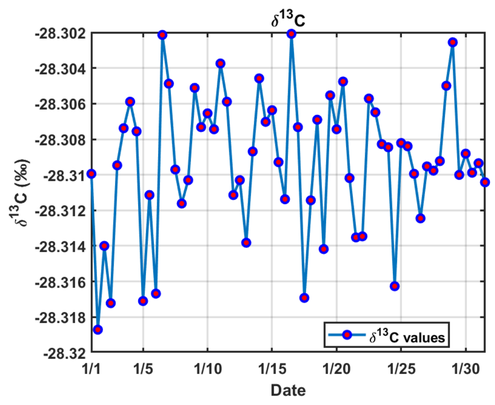


Fig3. Variation of δ^{13}C from 2020/1/1 to 2020/1/31

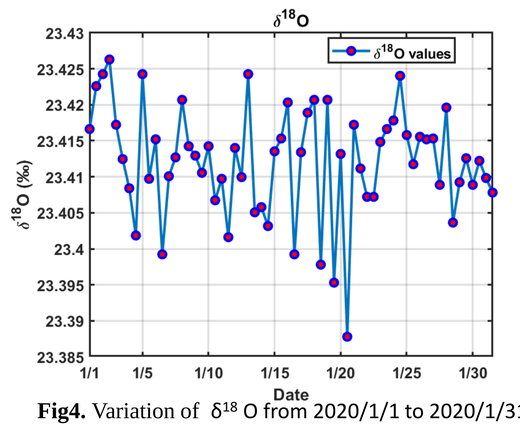


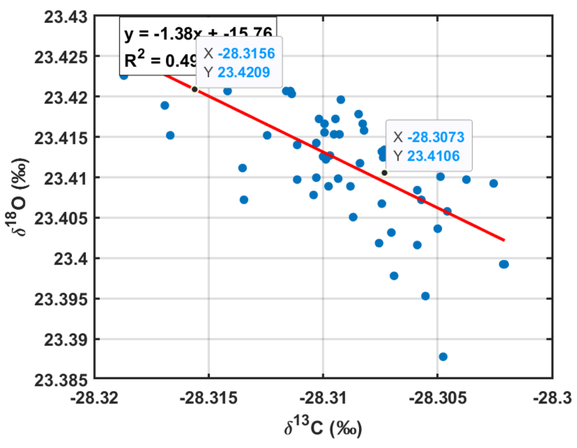
Fig4. Variation of δ^{18} O from 2020/1/1 to 2020/1/31

for δ^{13}C:

- Variation between -28.319 and -28.302(‰)
- Difference: 0.017(‰)
- Fluctuation rate: 0.06%

for δ^{18}O:

- Variation between 23.388 and 23.427(‰)
- Difference: 0.039(‰)
- Fluctuation rate: 0.17%



- Correlation between δ^{13}C and δ^{18}O (R^2=0.49)

Fig5. Linear correlation between δ^{13}C and δ^{18}O

Part3. Limitations

- Approximation of the concentration value of CH_4
- Uncertainty of the concentration value of OH
- Inaccuracy of concentration of some specific chemical substance in the model WRF-Chem

Conclusions

- δ^{18}O shows a larger fluctuation than δ^{13}C in the given period
- Correlation between δ^{13}C and δ^{18}O has been observed
- Further research based on real-life data is required to modify and upgrade the current model.

Key Reference

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