

Seasonal cycle of carbon dioxide and its isotopic composition
in an urban atmosphere:
Anthropogenic and biogenic effects

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◆ Outline

- 1. Background
- 2. Hypothesis
- 3. Objectives
- 4. Method
- 5. Results and interpretation
- 6. Critique of their Interpretation

◆ 1. Background

● 1.1 Trends in Carbon dioxide

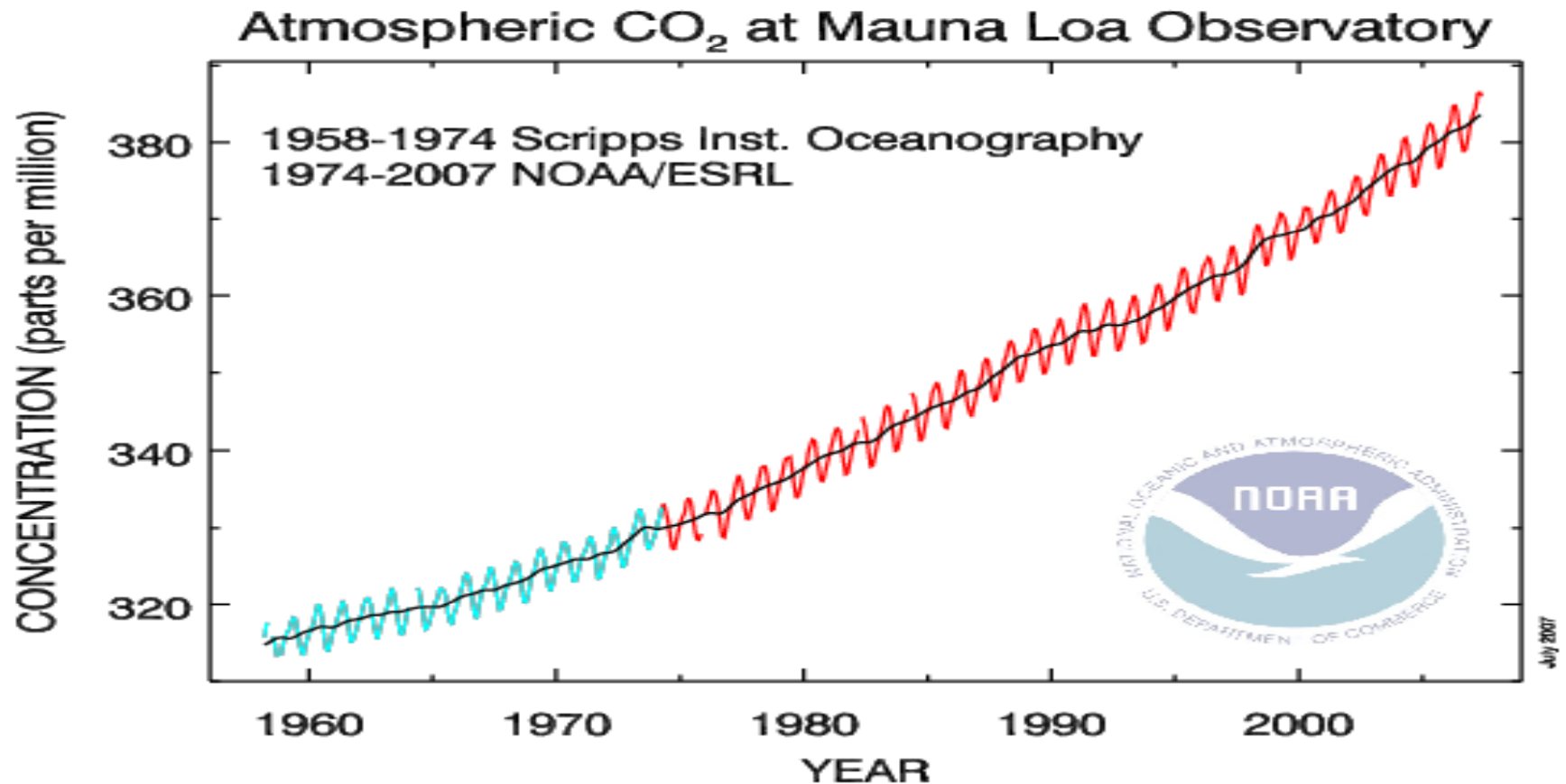


Fig 1. Here is the longest direct-measurement CO₂ time series.[NOAA,2007]

◆ 1. Background

● 1.1 Trends in Carbon dioxide

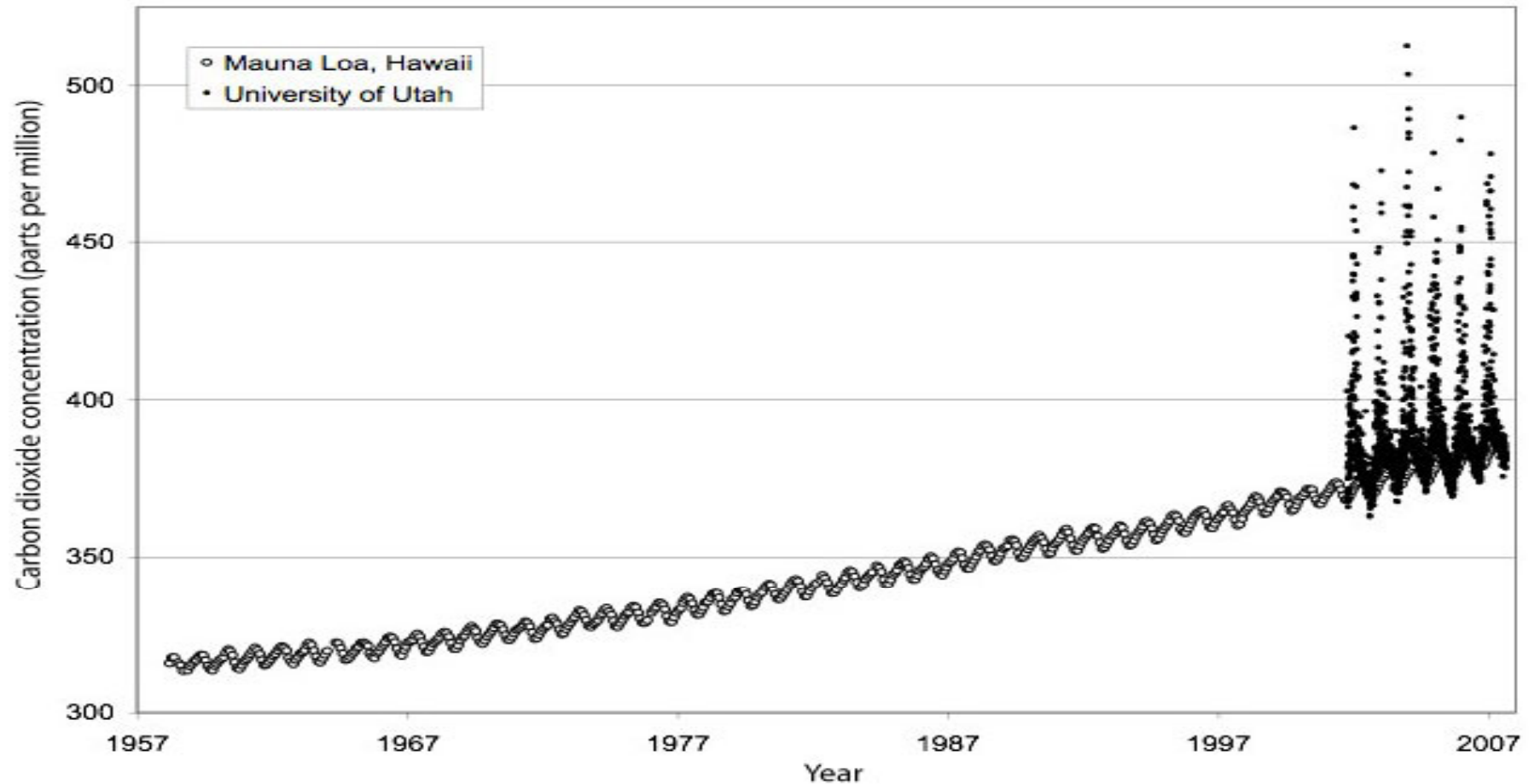


Fig 2. CO₂ concentration in UofU.[UofU,2007]

◆ 1. Background

● 1.2 Carbon and oxygen isotope

- Isotopes are variants of a particular chemical element. While all isotopes of a given element share the same number of protons, each isotope differs from the others in its number of neutrons.[Li,2009]
- Photosynthesis ,biogenic respiration, anthropogenic burning give different carbon and oxygen isotope signals which can trace gas exchange in biogeochemical cycles of terrestrial ecosystems. [Francey et al., 1985]

◆ 1. Background

● 1.2 Carbon and oxygen isotope

Table 1. Stable isotopes of C and O and their mass number and abundance.[Hoefs,2004; Fry,2006]

Elements	Isotope	Abundance/%
Carbon	^{12}C	98.89
	^{13}C	1.11
Oxygen	^{16}O	99.759
	^{17}O	0.037
	^{18}O	0.204

◆ 1. Background

● 1.2 Carbon and oxygen isotope

Table 2. International reference.[Liu,2009]

Medium	configuration	$d^{13}C(‰)$
Atmosphere	CO ₂	-7
Lake		-8—16
River		-10
Sea		0 ± 2
Terrestrial biology	C	-22
aquatic in lake	CO ₂	-25
	C	-5
aquatic in river	CO ₂	-25
	C	-12
aquatic in sea	CO ₂	-24
	C	0
Coal		-24
Natural gas		-40
Fossil fuel		-20

◆ 1. Background

● 1.2 Carbon and oxygen isotope

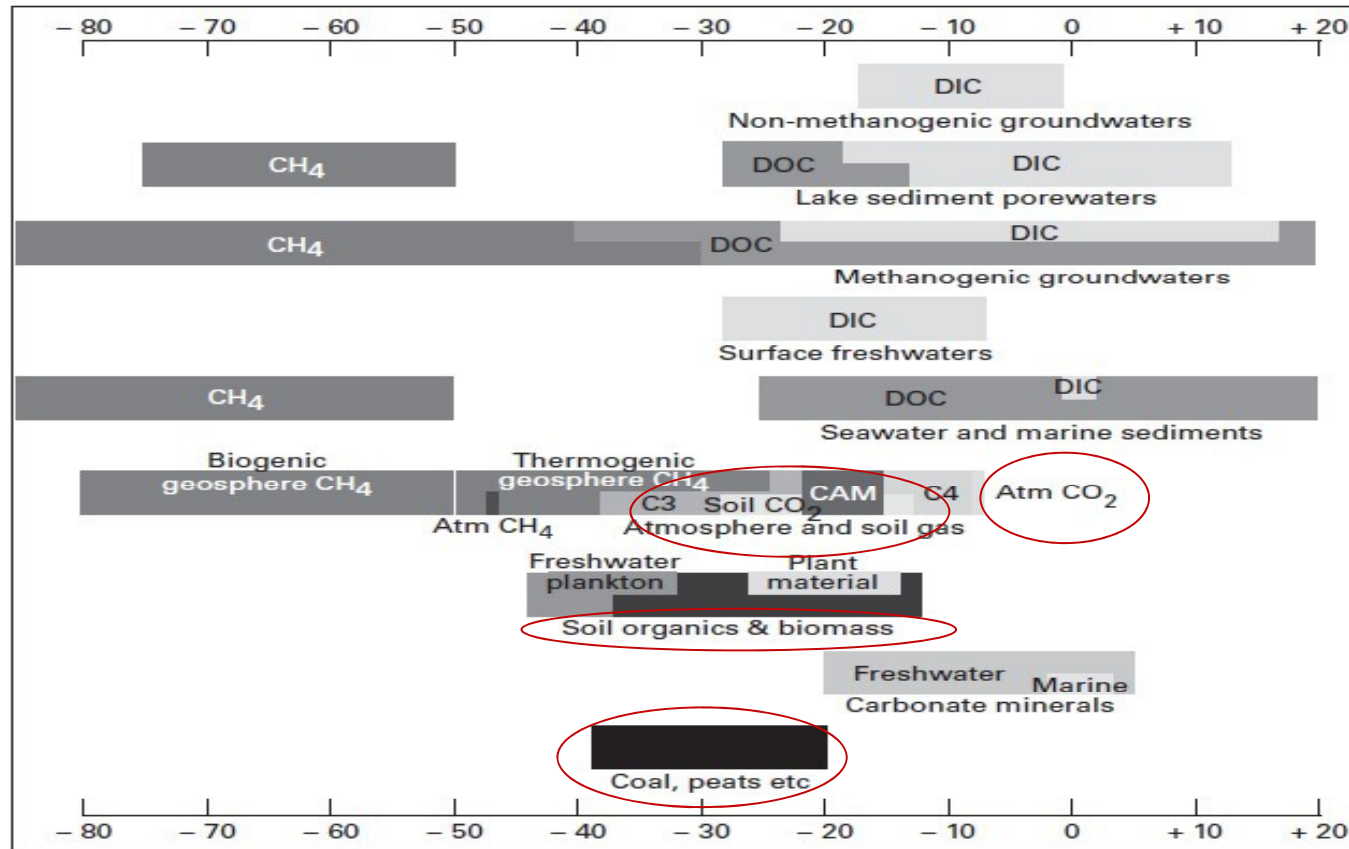


Fig 3. The ranges for dissolved carbon and its sources.[Darling,2005]

◆ 1. Background

● 1.2 Carbon and oxygen isotop

$$R = \frac{{}^m X}{{}^n X} \quad (1)$$

$$d = \left(\frac{R_A}{R_S} - 1 \right) \times 1000 \quad (2)$$

- R is the carbon isotope ratio of heavy(m) molecules and light(n) molecules.
- d is the ratio of R being examined(A) and R of the standard(S), which is dimensionless and is normally adopted as “parts per mil”(‰).

◆ 1. Background

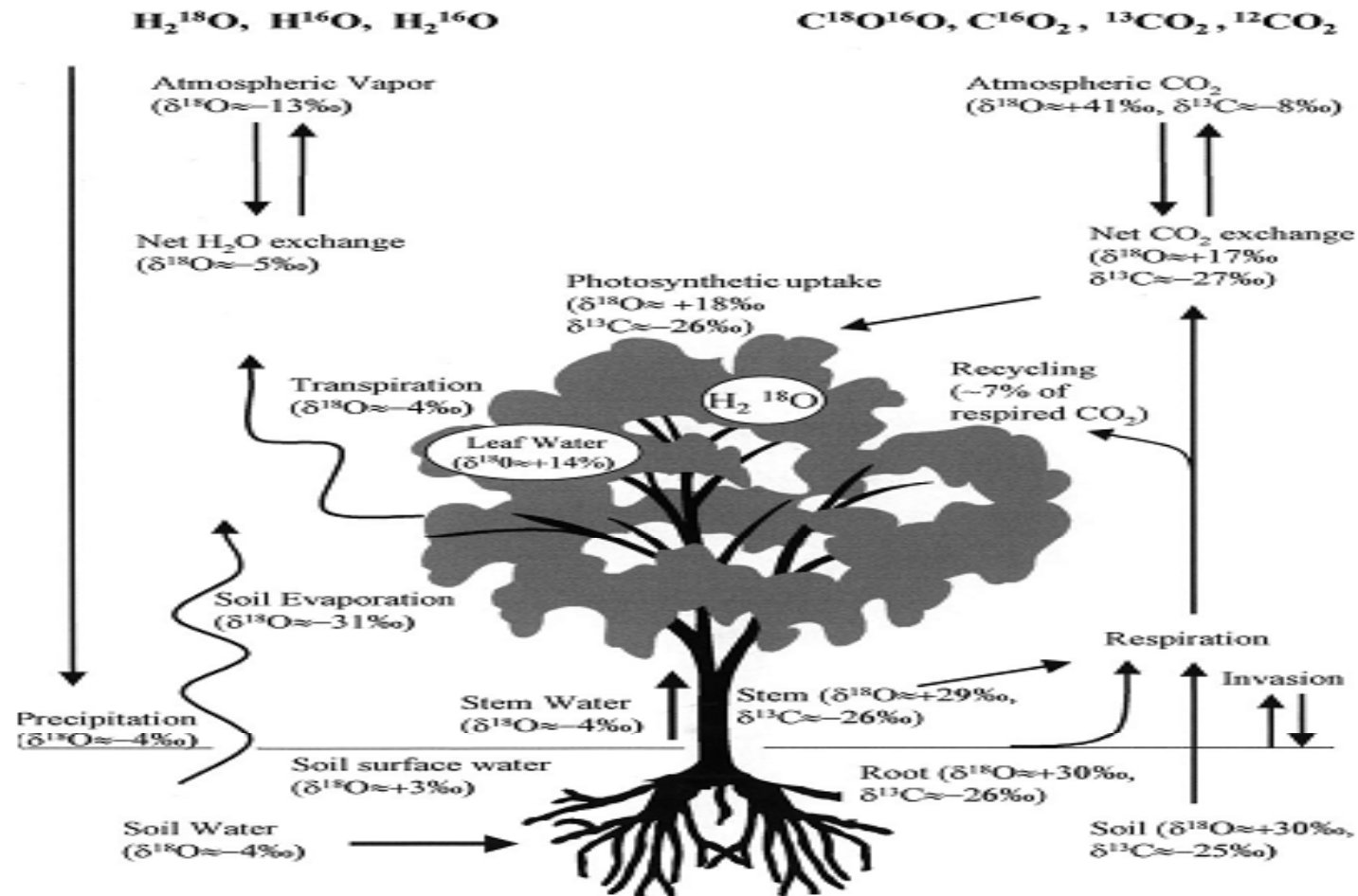


Fig 4. Isotopic compositions of the major components.[Yakir,2000]

◆ 1. Background

● 1.2 Carbon and oxygen isotope

- Compared with micrometeorological measurement technology, stable isotope techniques are much more possible to quantify various ecological processes. [Yakir & Sternberg, 2000]
- Isotopic measurements can reflect seasonal variability of uptake and release of CO₂ as the observed objection. [Ciais et al. 1995, 1997]

◆ 1. Background

● 1.3 Keeling plots

$$C_a = C_b + C_s \quad (3)[\text{Keeling, 1958}]$$

$$C_a d_a = C_b d_b + C_s d_s \quad (4)$$

$$d^{13}C_a = C_b \left(d^{13}C_b - d^{13}C_s \right) \left(1 / C_a \right) + d^{13}C_s \quad (5)$$

- C: CO₂ concentration.
- a: Atmospheric CO₂ concentration measured in the ecosystem.
- b: The background CO₂ concentration.
- s: The additional CO₂ concentration component produced by the source.

◆ 1. Background

● 1.3 Keeling plots

$$d_a = d_s + \frac{M}{C_a} \quad (6)$$

$$M = C_b (d^{13}C_b - d^{13}C_s) \quad (7)$$

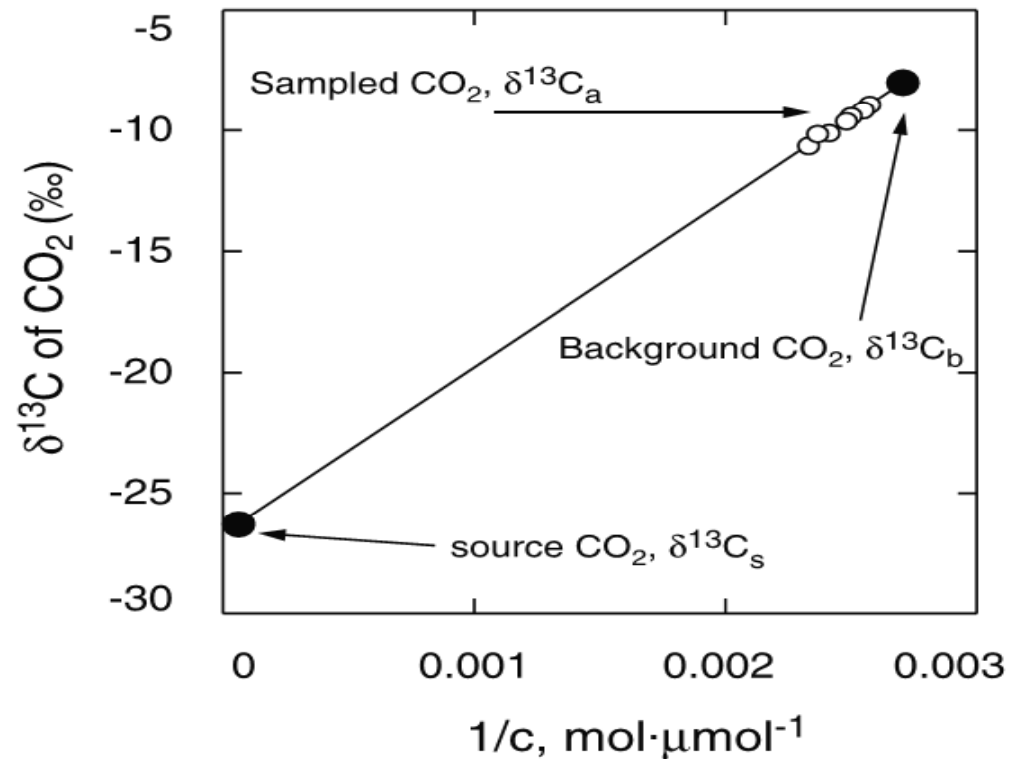


Fig 5. Keeling Plots.[Pataki,2003]

◆ 1. Background

● 1.3 Keeling Plot

- The plot of d_a versus $1/C_a$ appears a straight line relationship with a slope M and an intercept d_p .
- The basis of the Keeling plot method is conservation of mass, which can tell released from urban sources from background .
[D. E. Pataki et al. 2003]
- By 1960, Keeling et al found that CO_2 concentration was not just the diurnal and seasonal variations, but also a year-on-year increase that roughly matched the amount of fossil fuels burned per year.

◆ 2. Hypothesis

- Isotope composition of carbon dioxide can be used to distinct different CO₂ contribution in an urban.

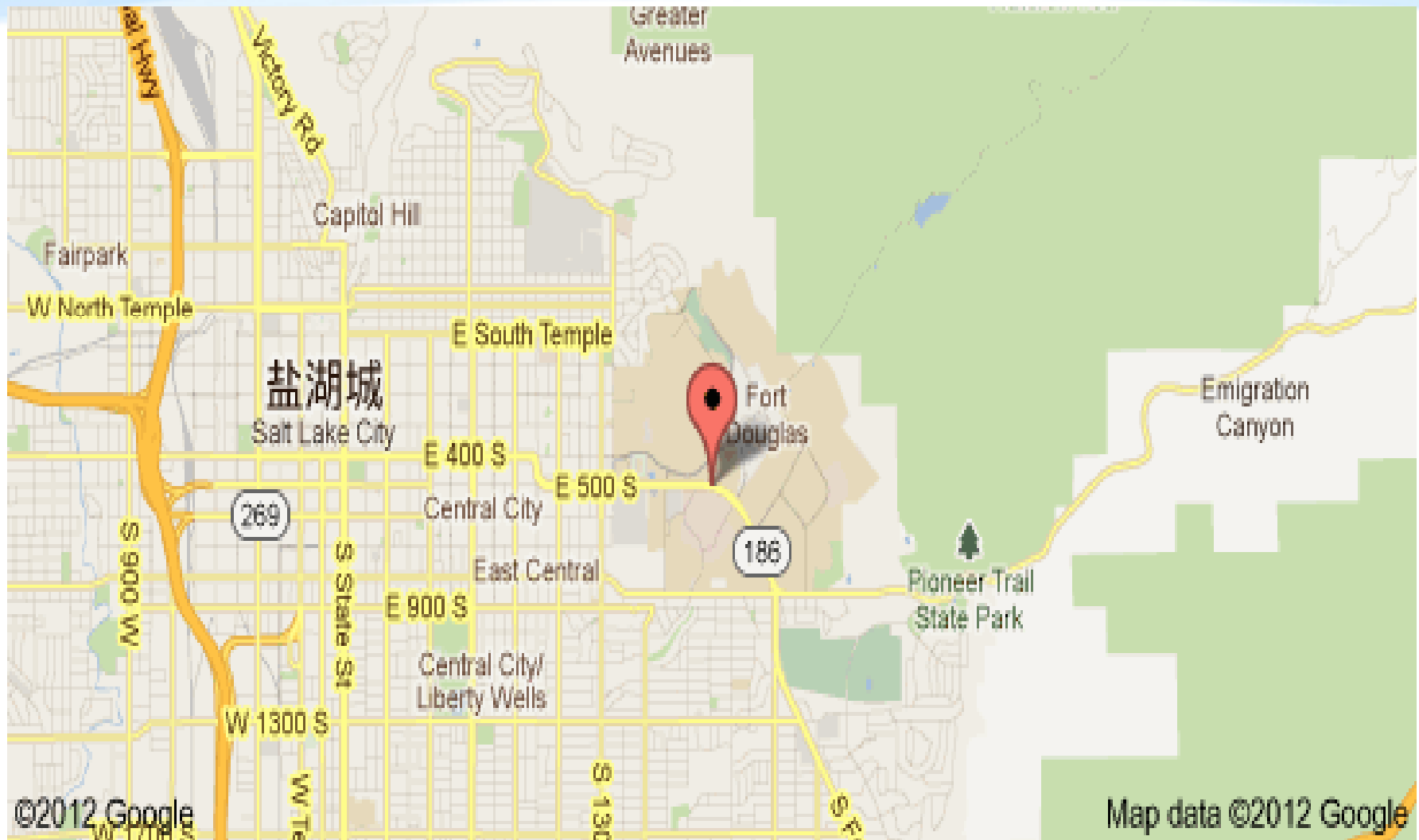
◆ 3. Objectives

- Using one kind of mass balance model and the Keeling plot method, to partition seasonal cycle of urban CO₂ emission and its isotopic composition without isotope composition of background air.

◆ 4. Method

- 4.1 Site Information
- 4.2 Experimental Design
- 4.3 Data Analysis

◆ 4.1 Site Information



◆ 4.1 Site Information



Fig 7. A photograph of the UofU Sites and its environments.[from UofU]

◆ 4.1 Site Information



Fig 8. A photograph of the Wendover Sites.[From Google]

◆ 4.1 Site Information



Fig 9. A photograph of the UofU Site and its environments.[From UofU]

◆ 4.2 Experimental Design

● 4.2.1 Atmospheric measurements:

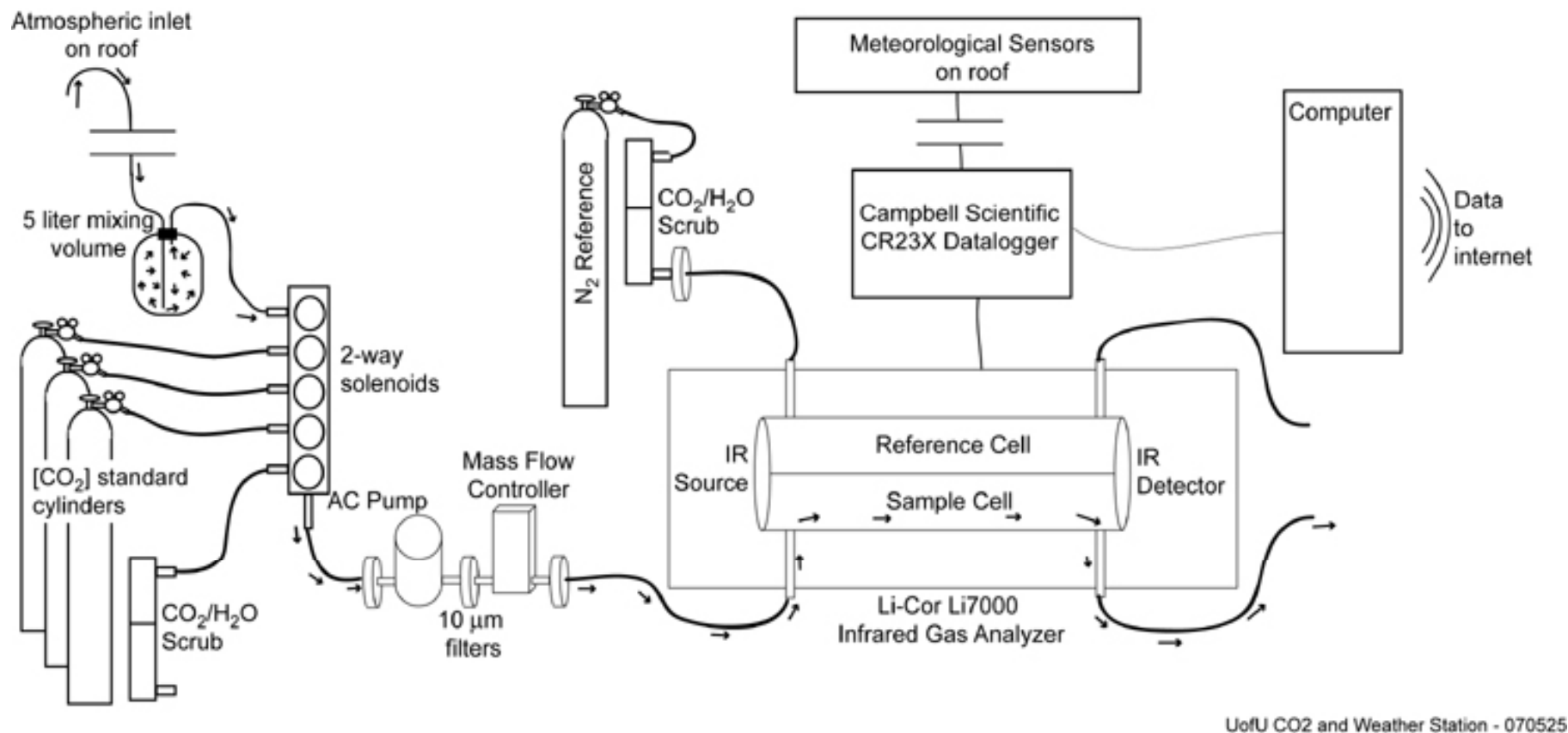


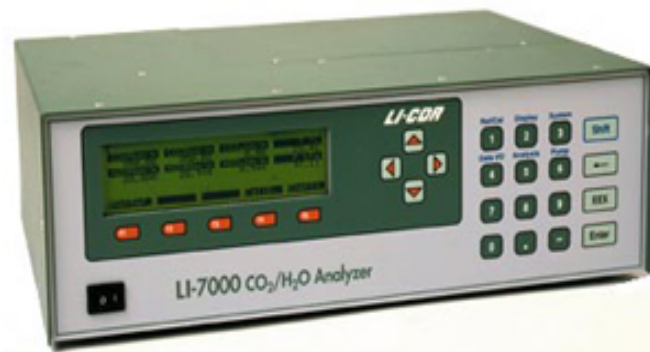
Fig 10. Illustration of atmospheric measurements.[From UofU]

◆ 4.2 Experimental Design

● 4.2.1 Atmospheric measurements:

The Instrument.

The instrument used for carbon dioxide measurement is typically an infrared gas analyzer. These come in many shapes and sizes.



The premise to most infrared gas analyzers is the same. A beam of infrared radiation is shown along a path through which the air sample of interest is passed, while an infrared radiation detector (opposing the beam) measures the quantity of infrared radiation. The greater the quantity of carbon dioxide within the path, the less infrared radiation is detected. Below is a schematic of a simple infrared gas analyzer.

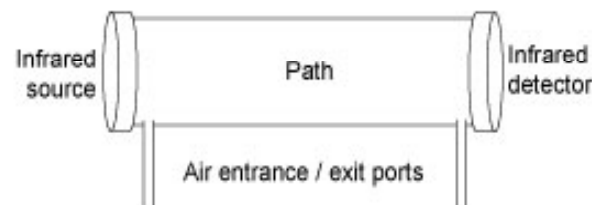


Fig 11. Analysis of atmospheric measurements.[From UofU]

◆ 4.2 Experimental Design

● 4.2.2 Mass balance approach

$$C_T = C_A + C_S \quad (8)$$

$$d_T = c_A (d_A - d_S) (1 / c_T) + d_S \quad (9)$$

$$d = \left(R_{\text{sample}} / R_{\text{standard}} - 1 \right) * 1000 \text{‰} \quad (10)$$

- **T**: The total CO₂ mixing ratio.
- **A**: The background CO₂ mixing ratio.
- **S**: The Urban sources CO₂ mixing ratio.

◆ 4.2 Experimental Design

● 4.2.2 Mass balance approach

$$f_R + f_G + f_N = 1 \quad (11)$$

$$d^{13}C_R f_R + d^{13}C_G f_G + d^{13}C_N f_N = d^{13}C_S \quad (12)$$

$$d^{18}O_R f_R + d^{18}O_G f_G + d^{18}O_N f_N = d^{18}O_S \quad (13)$$

● R: Biogenic respiration.

● N: Natural gas.

● G: Gasoline combustion.

◆ 4.3 Data Analysis

- Keeling plot intercept was calculated using geometric mean regression according to Pataki et al. [2003].
- Outliers were removed if the absolute value of the residual for an individual data point was more than 3 standard deviations from the mean residual.
- Intercepts were discarded when the regression model was not significant at $\alpha = 0.01$ according to Flanagan et al. [1997] and Bowling et al. [2003b].
- The standard error of the intercept was calculated by the ordinary least squares, ‘Model I’ regression method [Sokal and Rohlf, 1995].

◆ 5. Results and interpretation

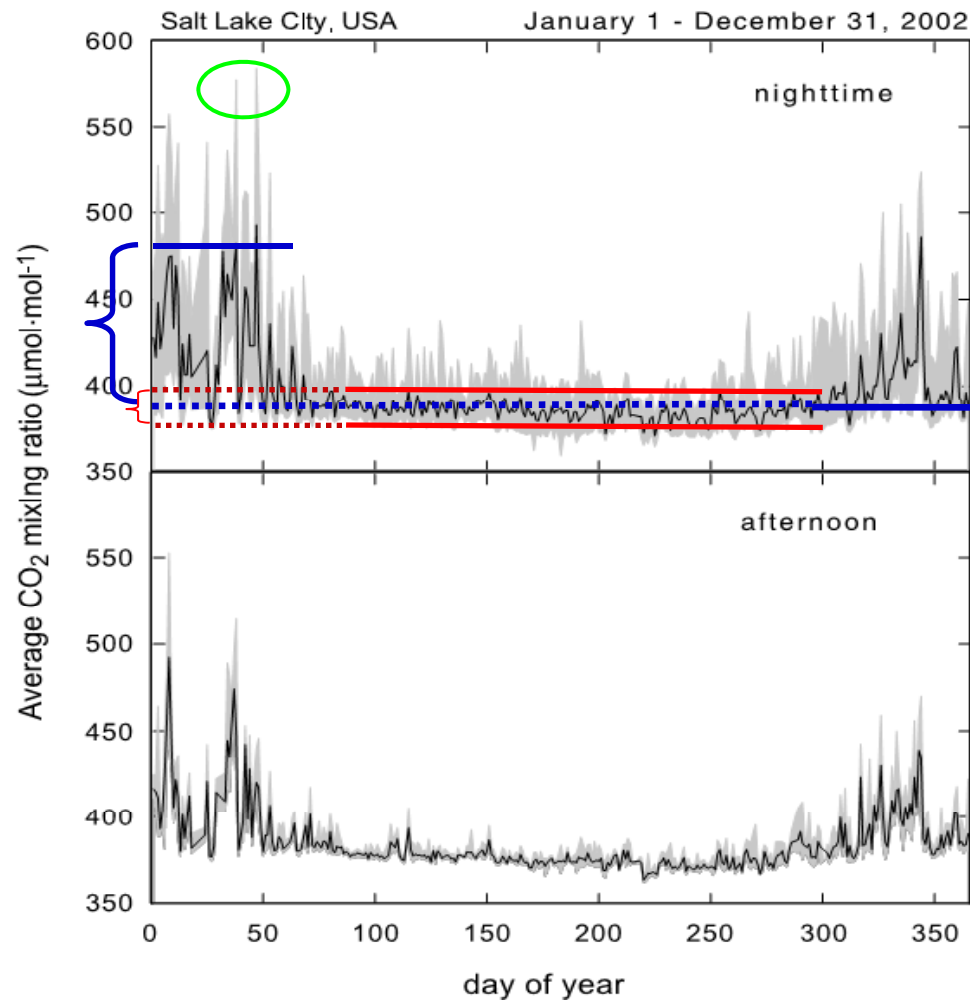


Figure 12. The average CO₂ mixing ratio measured at 18m.

◆ 5. Results and interpretation

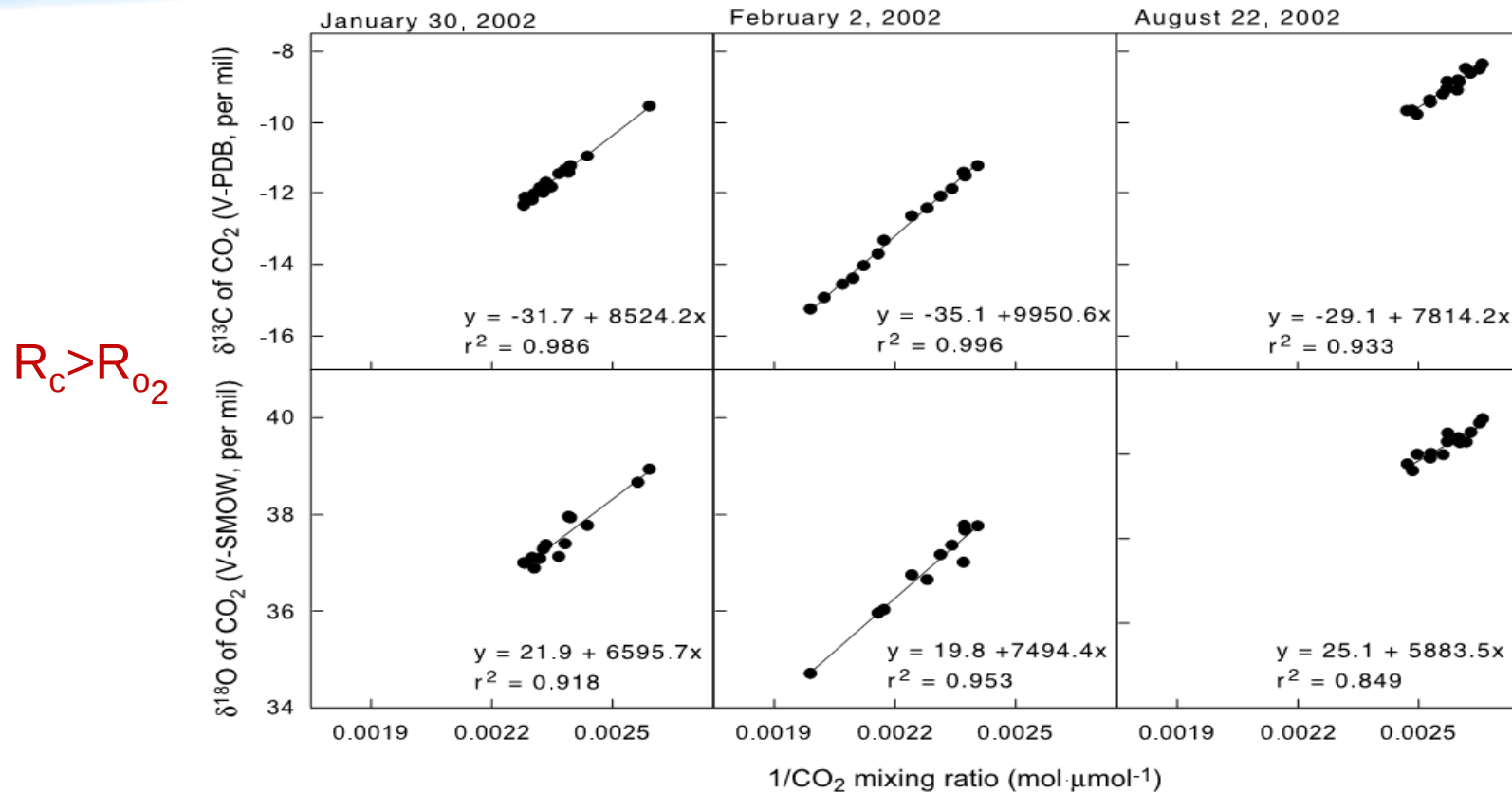


Figure 13. Representative Keeling plots of carbon and oxygen isotope ratio during three discrete sampling periods.

◆ 5. Results and interpretation

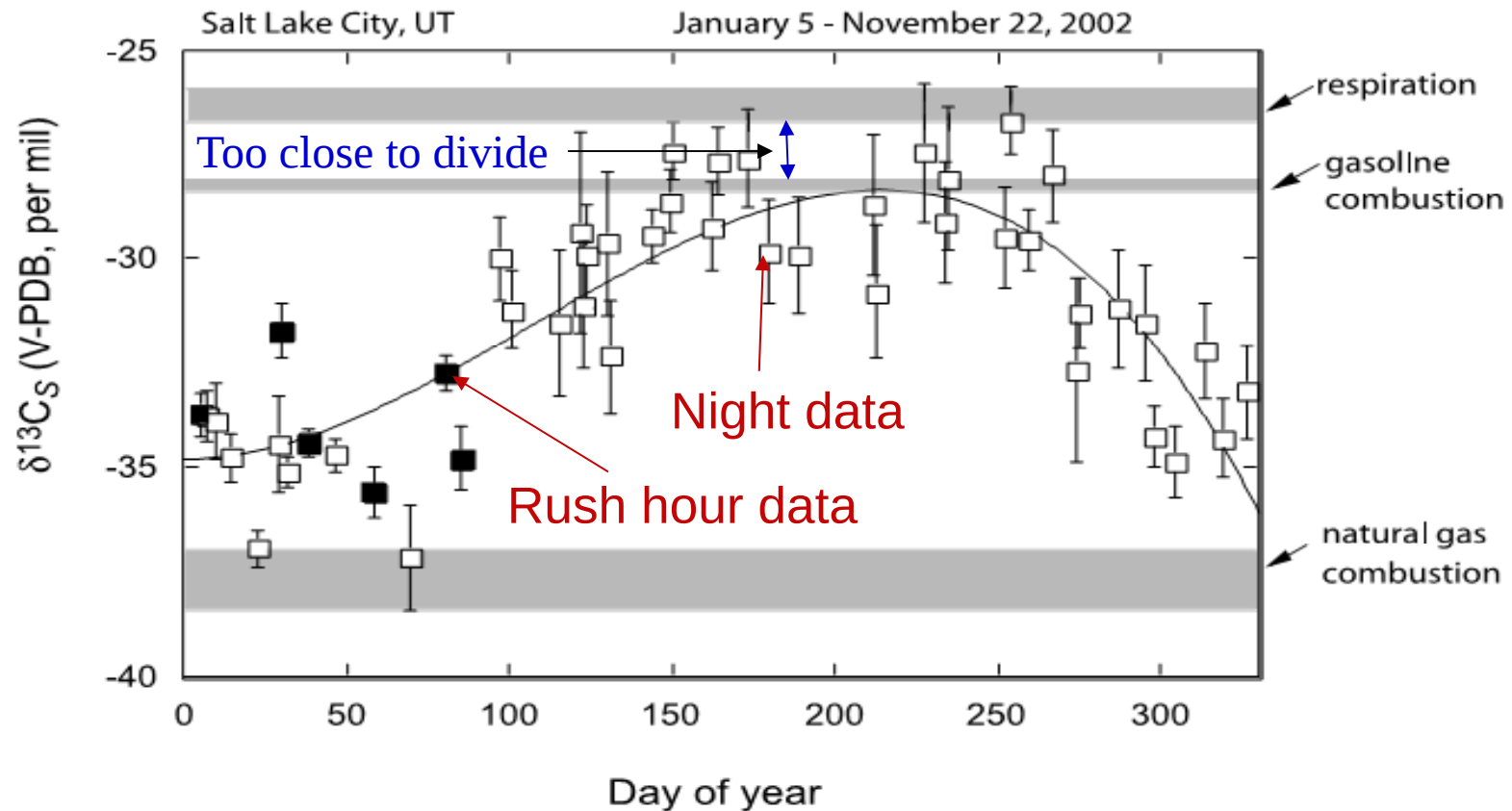


Figure 14. The carbon isotope ratio of the urban CO₂ source.

◆ 5. Results and interpretation

$$d^{13}C_G = -28.3 \pm 0.1\text{‰}$$

$$d^{13}C_N = -37.7 \pm 0.3\text{‰}$$

$$d^{13}C_R = -26.2 \pm 0.2\text{‰}$$

$$d^{18}O_R = 0.5 * d^{18}O_{Leaf} + 0.5 * d^{18}O_{Soil}$$

$$d^{18}O_G + d^{18}O_N \gg d^{18}O_S = 21.3\text{‰} \text{ (In winter)}$$

Source water value: -15‰

Water vapor value: -21‰

The optimal periods to response photo-

synthetic activity and soil decomposition (bottom)The oxygen isotope of the urban CO₂ source.

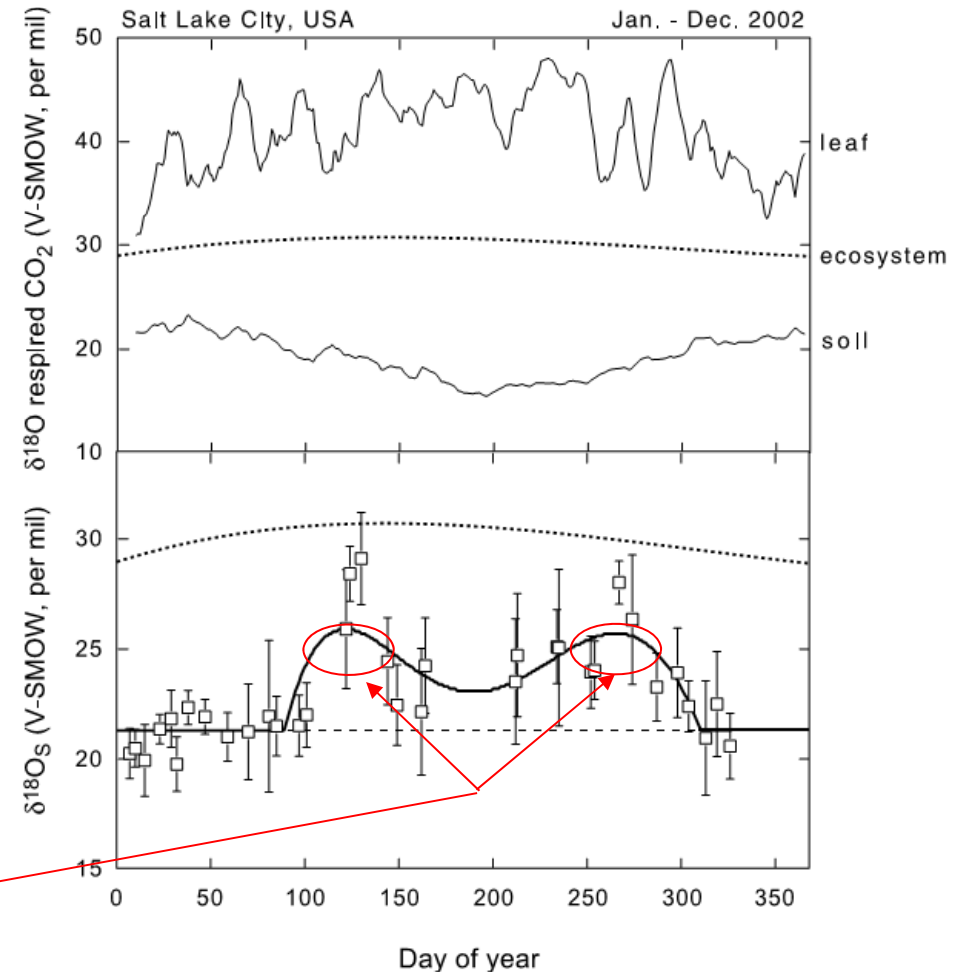


Figure 15.(top)A ten-day running average.

◆ 5. Results and interpretation

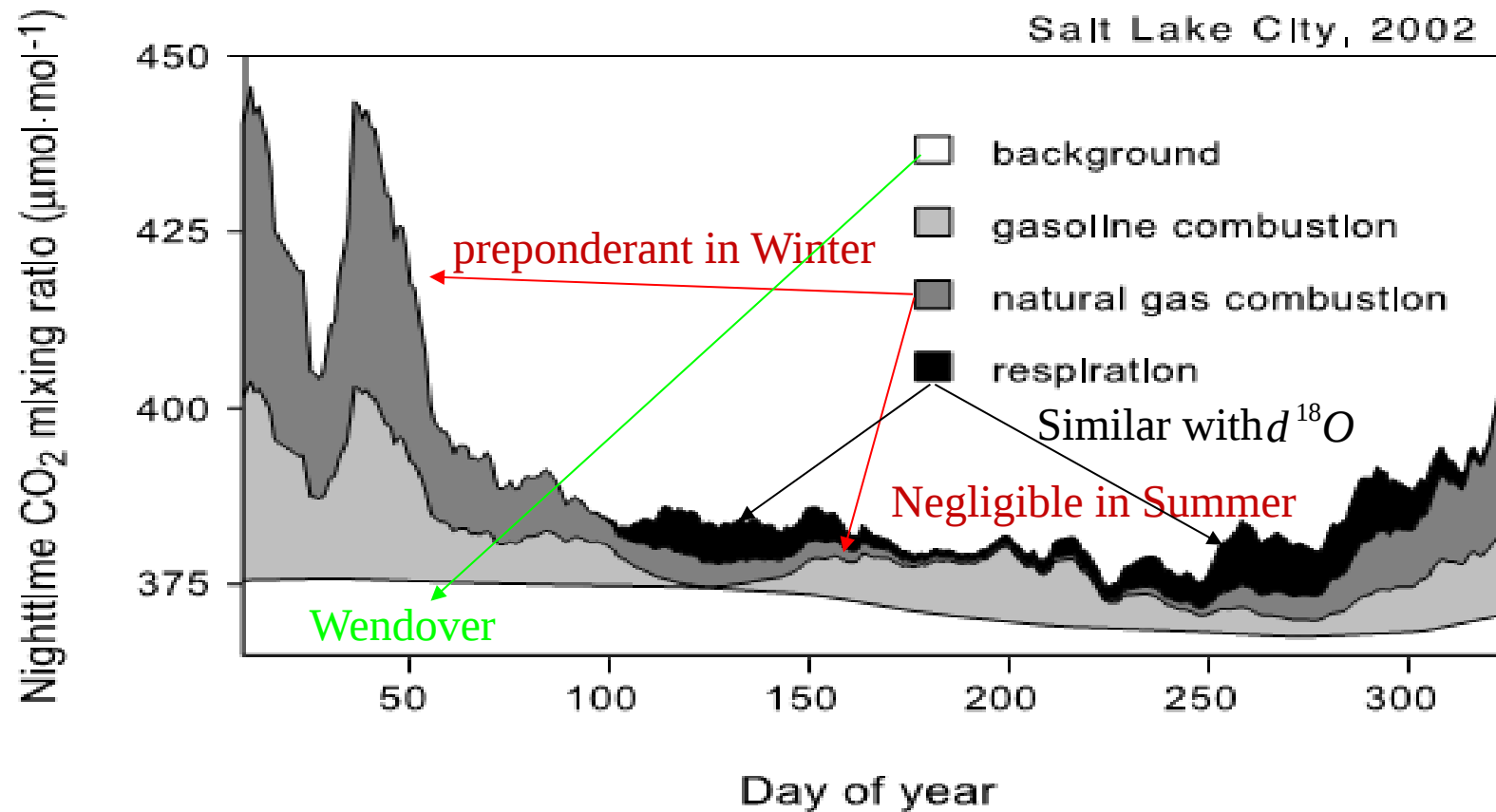


Figure 16. Components of the night time CO₂ mixing ratio.

◆ 5. Results and interpretation

Table 3. Sensitivity analysis of calculations of the mean fractional contribution of f_R , f_G and f_N to the total CO_2 source during winter and the growing season.

Too low for typical ecosystem

The proof that f_N is low if no heating

f_R can be ignored in winter

	January 1 to April 15			April 16 to November 15		
	f_R	f_G	f_N	f_R	f_G	f_N
Baseline	0.02	0.42	0.57	0.32	0.43	0.25
i) 1‰ depletion $\delta^{13}\text{C}_R$	0.02	0.42	0.56	0.32	0.47	0.21
ii) 1‰ depletion $\delta^{13}\text{C}_G$	0.02	0.47	0.52	0.32	0.48	0.19
iii) 1‰ depletion $\delta^{13}\text{C}_N$	0.02	0.47	0.51	0.32	0.46	0.22
iv) 30% soil respiration 70% plant respiration	0.01	0.42	0.56	0.26	0.51	0.23
v) 70% soil respiration 30% plant respiration	0.03	0.40	0.57	–	–	–
vi) 7.2‰ kinetic fractionation of soil diffusion	0.02	0.41	0.57	0.34 ^b	0.43 ^b	0.23 ^b
vii) 3‰ enrichment of soil water	0.02	0.42	0.57	0.35 ^b	0.40 ^b	0.25 ^b
viii) No enrichment of leaf water at night	0.00	0.42	0.58	–	–	–

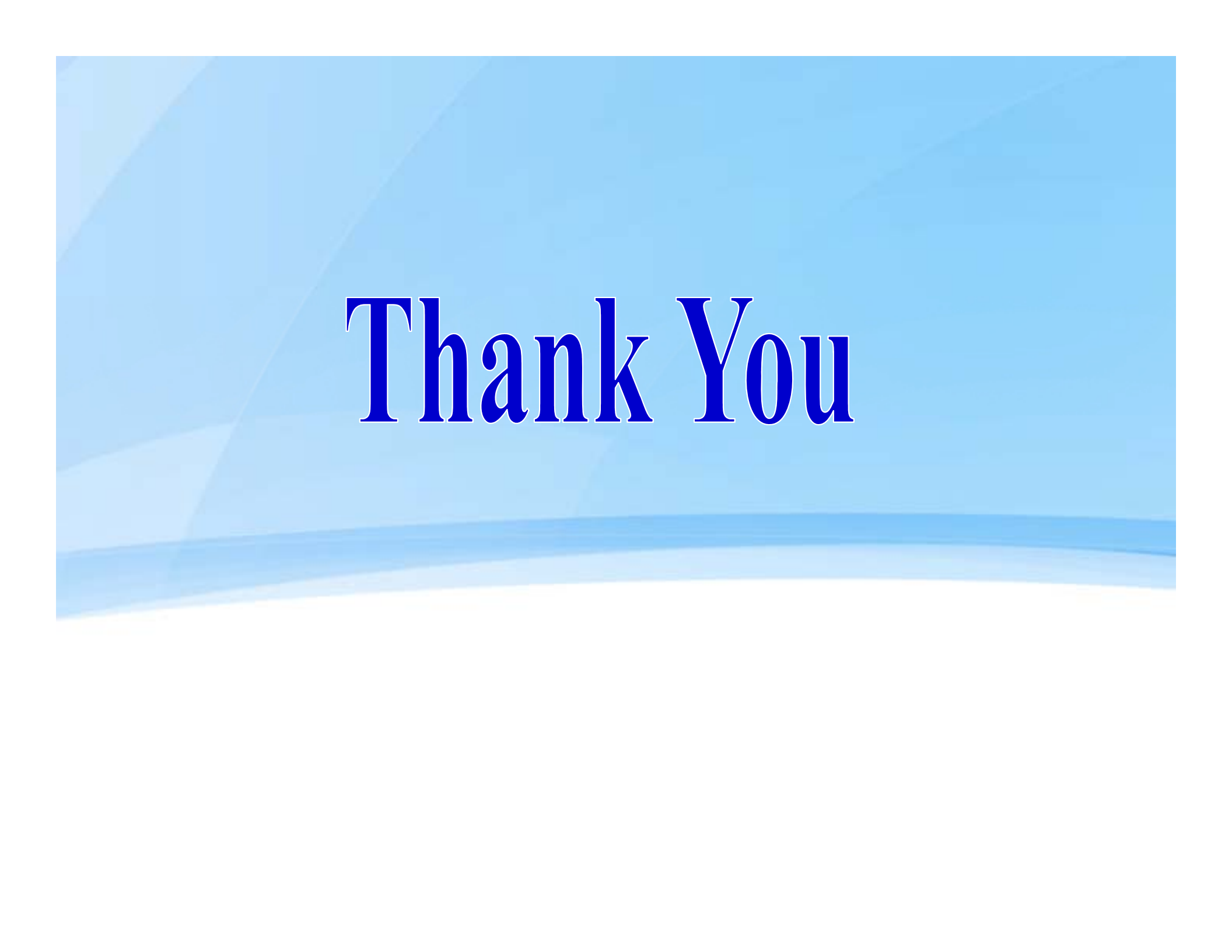
Violating mass balance

^aCalculations are from equations (4)–(6). Baseline refers to the calculations shown in Figure 5 and described in the text. In analyses *i–iii*, the carbon isotope ratios of ecosystem respiration ($\delta^{13}\text{C}_R$), gasoline combustion ($\delta^{13}\text{C}_G$), or natural gas combustion ($\delta^{13}\text{C}_N$) were decreased by 1‰ from the baseline simulation. The remaining analyses are changes to the assumptions in the model of the oxygen isotope ratio of ecosystem respiration ($\delta^{18}\text{O}_R$). A dash indicates that a solution was less than 0 for much of the season; i.e., the solution was invalid.

^bValues of f_G were negative in April.

◆ 6. Critique of their interpretation

- The sampling site can't really represent urban environment, because energy structure in campus and its surroundings differs with urban regions.
- The C-G model based on steady-state hypothesis, which is hard to reach and is controlled by relative humidity in short time scale. In addition to Peclet effect and various inner leaves in spatial, the evaluation will be higher than real value.
- Keeling plot only can detect two sources at a time. Due to this reason, it's hard to accurately partitioning urban sources into component parts.



Thank You