

Yale



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Stable carbon isotope constraints on mixing and mass balance of CO₂ in an urban atmosphere: Dallas metropolitan area, Texas, USA

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Outline

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

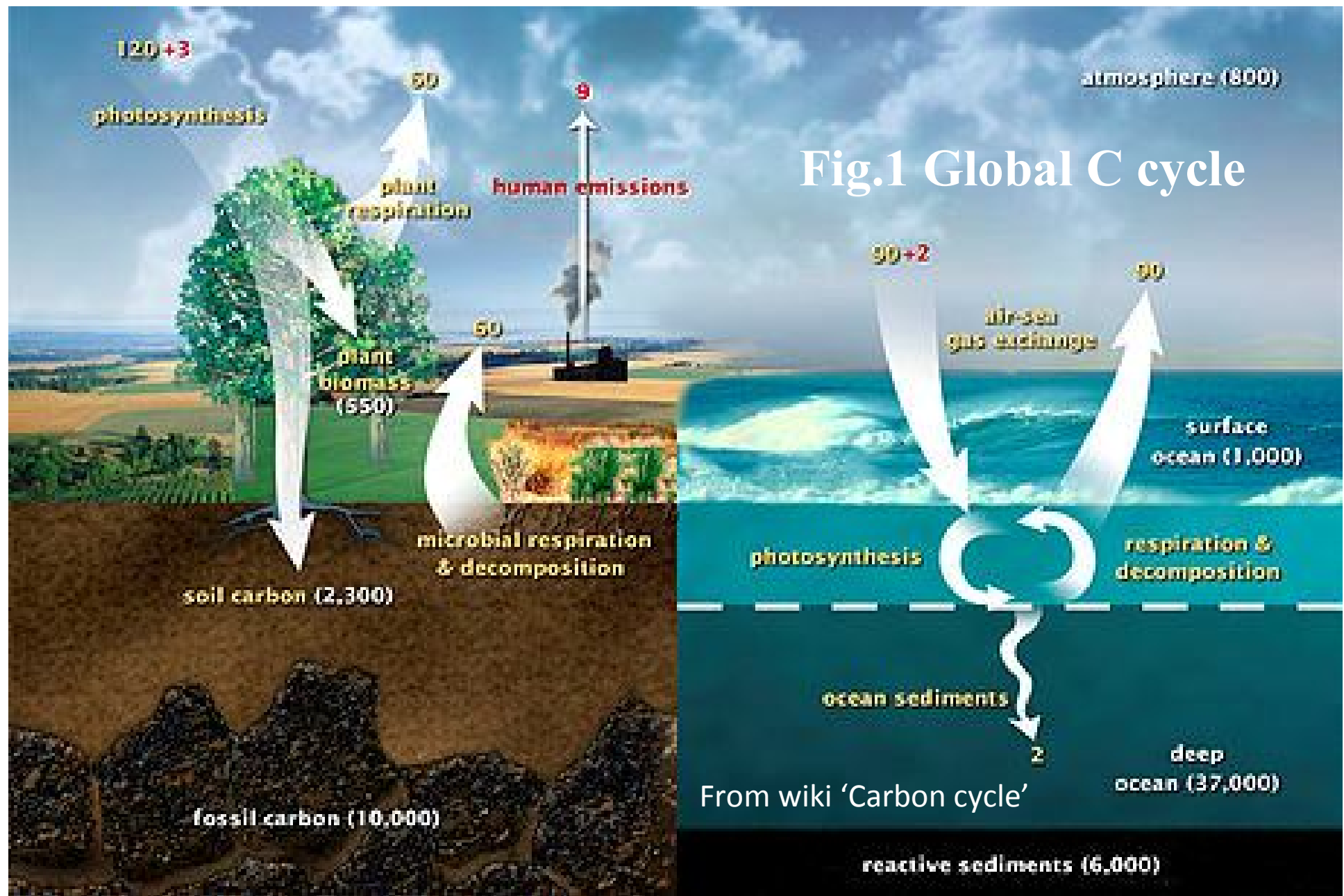


1. Background



- The atmospheric concentration of CO₂ has sharply added about 100 ppmv since pre-industrial with evident decrease of ¹³C [C D. Keeling, 1958; Forster et al., 2007] .
- Anthropogenic activities have strongly disturbed natural global C cycle, especially in short time scale [M.Battle et al. , 2000; Berner,1999]. And ‘Urban areas is key driver and recipient of global C cycle change.’ [Galina Churkina, 2012].





- Because the additional sources produced by human beings are ^{13}C -depleted, the isotope composition of CO_2 can be a effective tool to detect CO_2 in air and its contributors [Pataki, 2005].
- Rayleigh fractionation and Keeling Plot provided theoretical basis for relative studies. [C D. keeling, 1958, 1960; G D. Farquhar, 1993]



Simple Source-only binary mixing

$$C_M = C_a + C_F \quad (1)$$

Mass balance equation

$$C_M \delta^{13} C_M = C_a \delta^{13} C_a + C_F \delta^{13} C_F \quad (2)$$

$$\delta^{13} C_M = \left[(\delta^{13} C_a - \delta^{13} C_F) \frac{C_a}{10^4} \right] \frac{10^4}{C_M} + \delta^{13} C_F \quad (3) \quad \text{Eq. (1) in this study}$$

- M: Measured
- A: Background
- F: Fossil fuel
- \square : Constant

No respiration from
plants and soil!



$$f_R + f_G + f_N = 1 \quad (4)$$

Pataki, 2003

$$\delta^{13}C_R f_R + \delta^{13}C_G f_G + \delta^{13}C_N f_N = \delta^{13}C_S \quad (5)$$

- **R:** Biogenic respiration
- **N:** Natural gas.
- **G:** Gasoline combustion.



3 sorts linear regression models

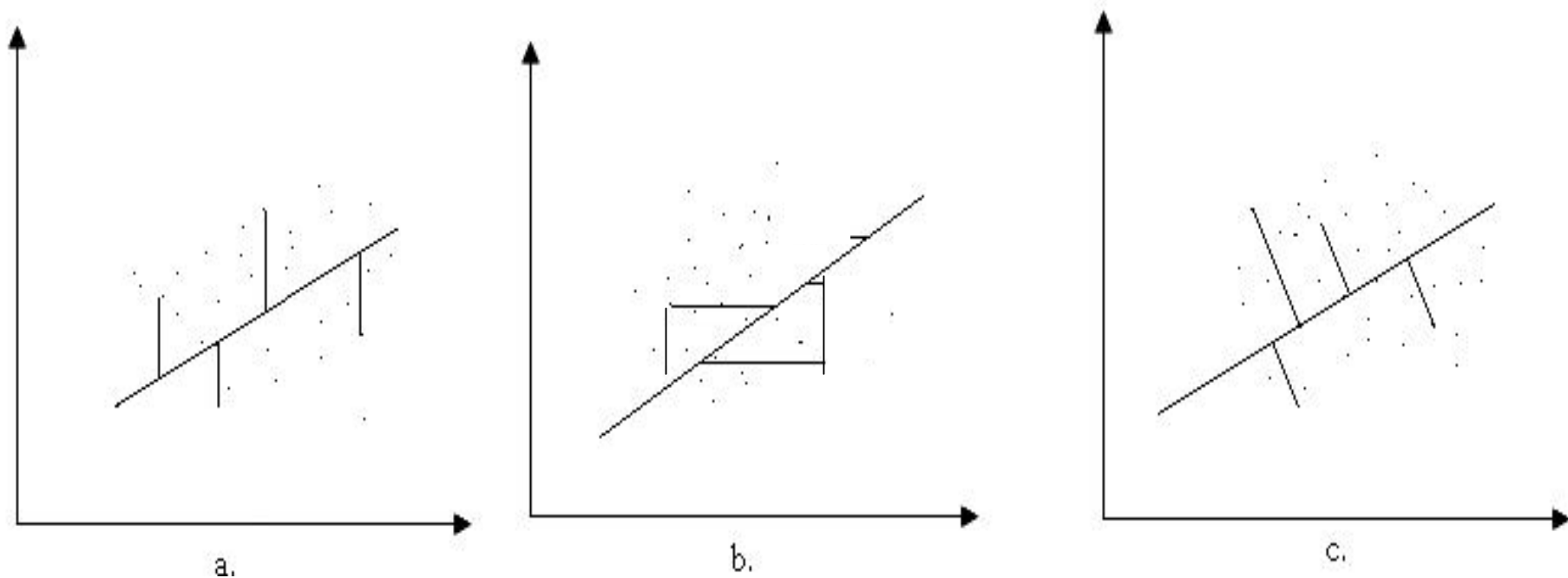


Fig.2 **a**, standard linear regression (Model I); **b**, geometric mean regression (Model II); **c**, orthogonal distance regression. [Ling Leng et al. 2007]

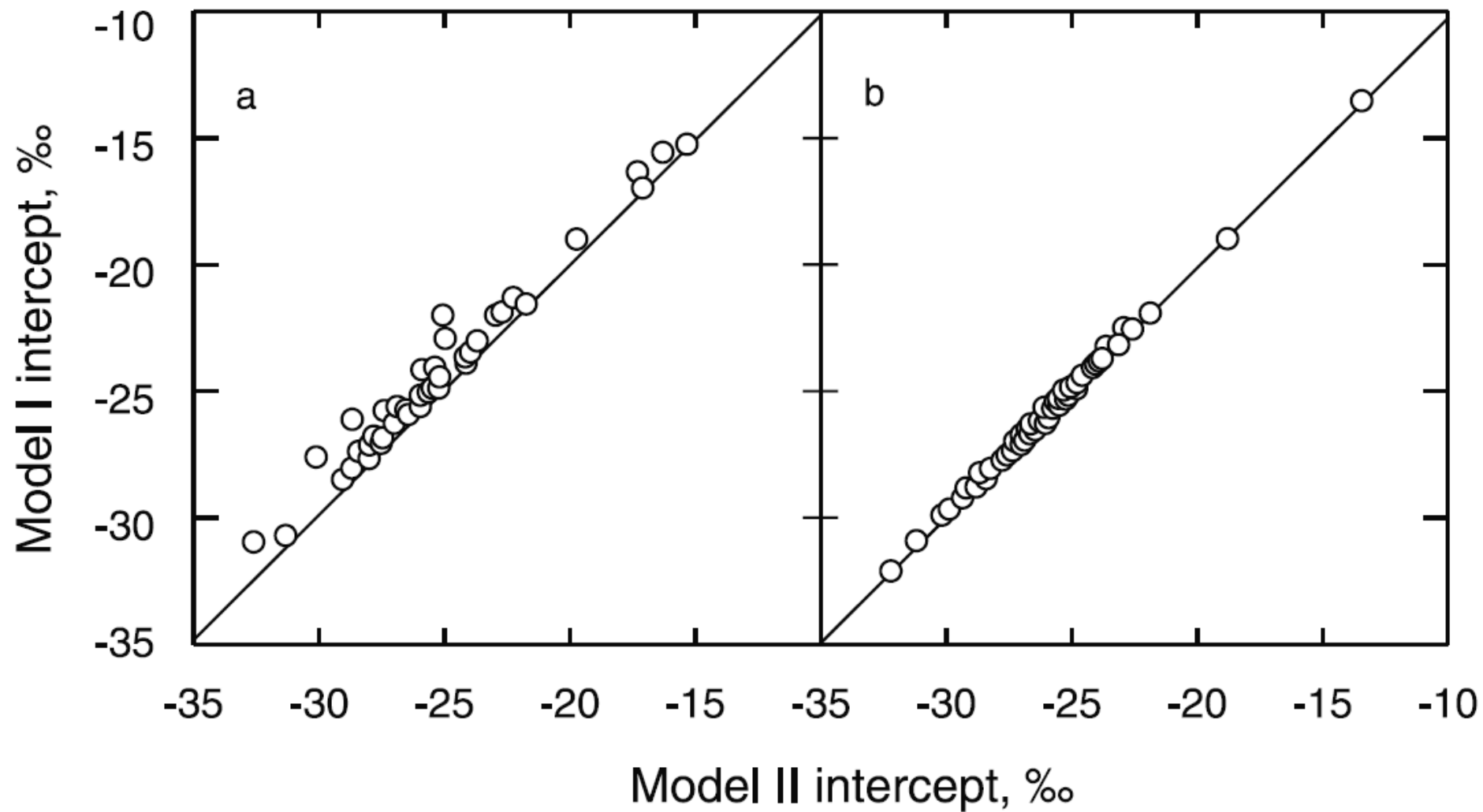


Fig.3 Comparison between Model I and Model II . [Pataki, 2003]



Rayleigh-type

$$\frac{[^{13}\text{C}] / [^{12}\text{C}]}{[^{13}\text{C}_0] / [^{12}\text{C}_0]} = \frac{R}{R_0} = f^{\alpha_K - 1} \quad (6) \quad \text{Rayleigh fractionation equation. [Sicheng Deng]}$$

$$\delta^{13}\text{C} = \left[\frac{(^{13}\text{C} / ^{12}\text{C})_{\text{cmp}}}{(^{13}\text{C} / ^{12}\text{C})_{\text{std}}} - 1 \right] \times 1000 \quad (7)$$

The isotope composition. [G D. Farquhar, 1993]

$$\delta = \frac{R_A}{R_s} - 1 \quad (8)$$

$$\delta^{13}\text{C} = (1000 + \delta^{13}\text{C}_0) f^{(\alpha_K - 1)} - 1000 \quad (9) \quad \text{Equation 2 in this study.}$$

- α_K : Net fractionation factor (0.981).
- f : C/C_0 .



2. Hypothesis





- Anthropogenic CO₂ emission is the key factor of the rise in CO₂ concentration.
- Photosynthesis is an important factor in urban areas.



3. Objectives



- Observation CO₂ in urban areas with intensive sites (9 sites).

- To testify photosynthesis is an important factor in urban areas.

- The establishment of keeling plot based on box model (conservation of mass) with the deviation between upwind and downwind (typical urban site and margin in city).



4. Method



4.1 Sites

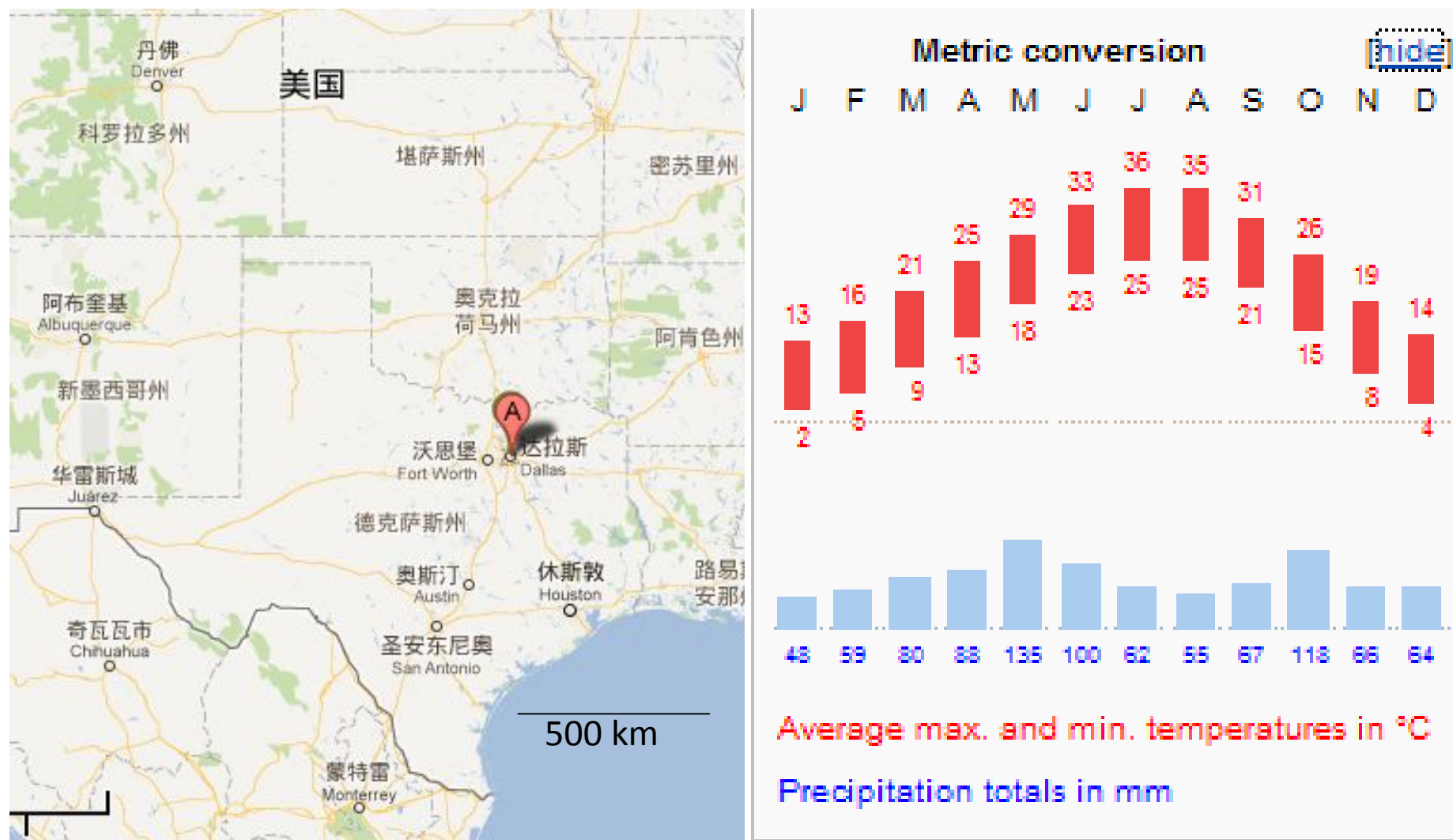


Fig.4 Dallas metropolitan area, Texas, USA and its climate.

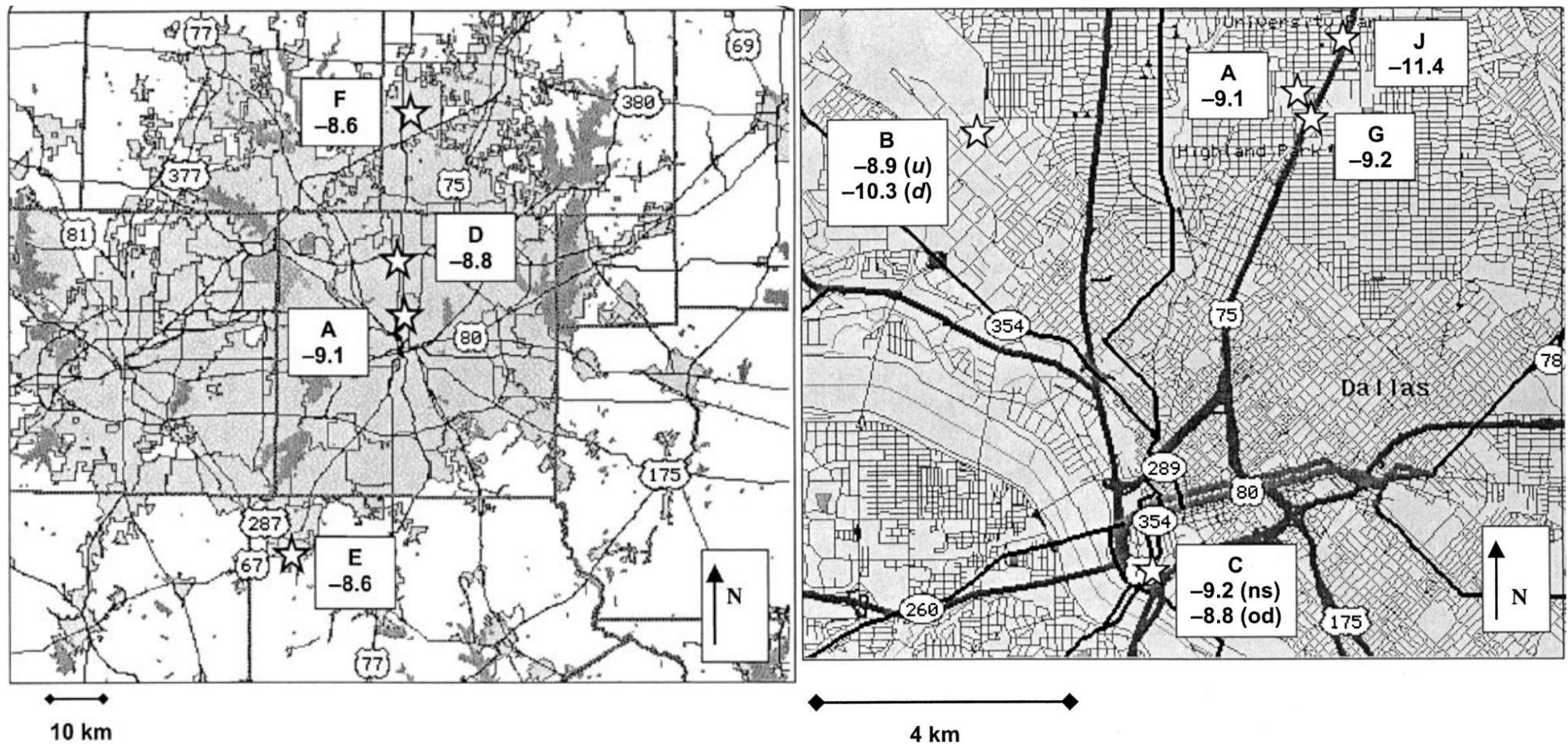


Fig.5 Sample sites and average $\delta^{13}\text{C}$ values of CO_2 .

Rural areas: site **E**, Midlothian, southern margin; and site **F**, Frisco, northern margin.

Urban areas: site **A**, SMU campus; site **B**, **G** and **J**, besides roads or highways; site **D**, North Dallas; .

Downtown: site **C**, 171m Tower.

- Possible sources were measured, including natural gas for heating, gasoline for transport and soil for organic matter.
- Weather data (5 elements) was obtained.



4.2 Measurement Method

- CO₂ concentration and its ratio of isotope:
adapted Keeling, 1958. (precision: ± 1 ppm and ± 0.1 ‰, respectively).
- C isotope of soil:
obeyed Coleman and Fry, 1991.



5. Results and interpretation



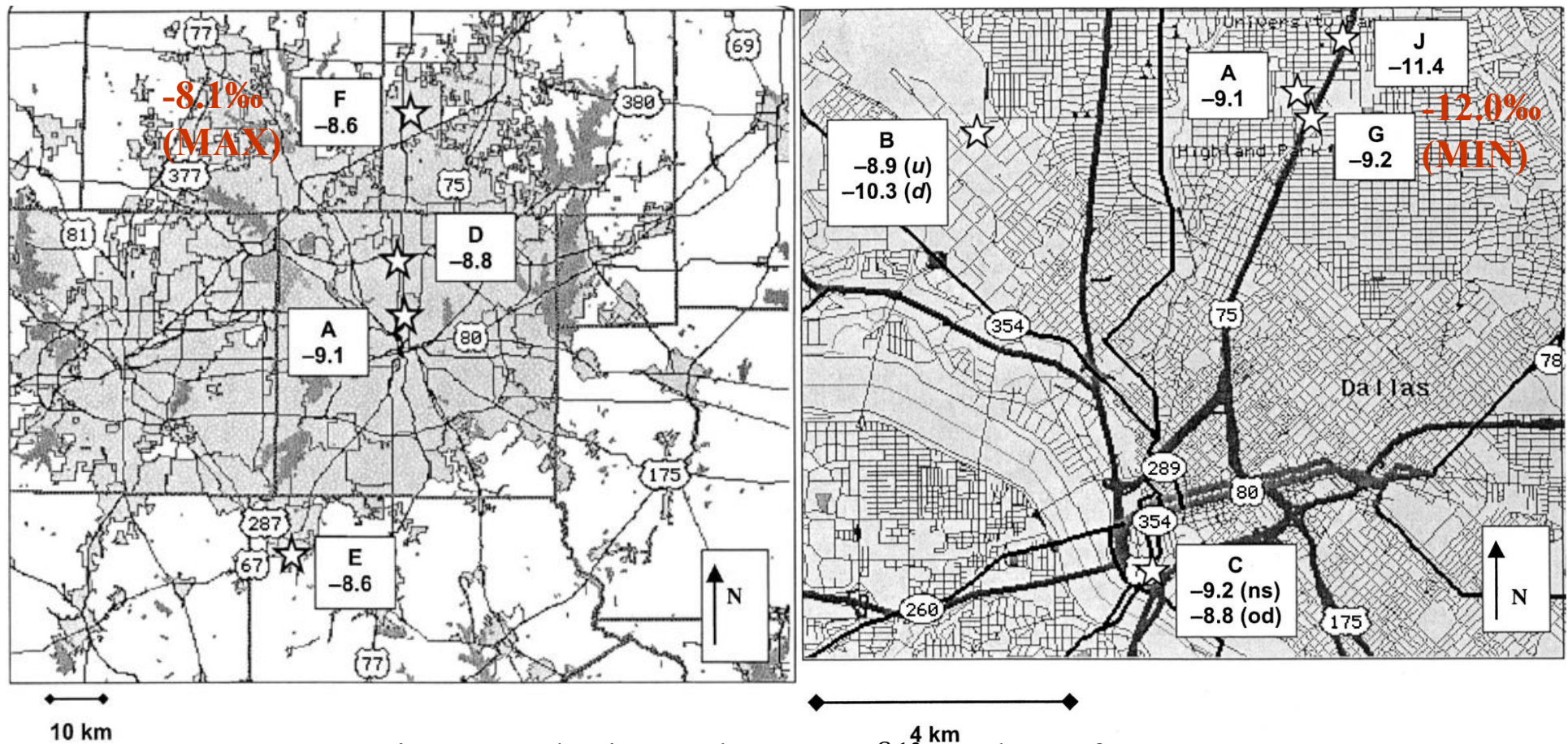


Fig.6 Sample sites and average $\delta^{13}\text{C}$ values of CO_2 .

(The light gray shading stands for urban areas.)

- $\delta^{13}\text{C}$ values of urban areas, highway, high level air and downwind are more lower than their opposite respectively.

Table 1
Fossil fuel and soil $\delta^{13}\text{C}$ values

Sample		Wt.% C	$\delta^{13}\text{C}$
	Fossil fuels		
OSC-16	CO ₂ from exhaust of a 1997 Toyota Corolla		−26.9
OSC-18	CO ₂ from exhaust of a 1998 Ford Ranger truck	Average about −27.2‰	−27.3
MPX-56	CO ₂ from exhaust of a 1994 Acura Vigor		−27.3
OSC-15	Natural gas from Rm 338, Heroy, SMU		−42.0
	Soils		
PLL-1	Soil from Curtis Park (near site A)	n.d. ^a	−18.0
SHD-1	Soil from 3030 Daniel Blvd. (near site A)	1.99	−23.5
MID-1	Soil from site E	Average about −19.2‰	−20.9
NDA-1	Soil from site D		−17.1
FRI-1	Soil from site F	3.60.	−16.3

^a n.d. = Not determined.



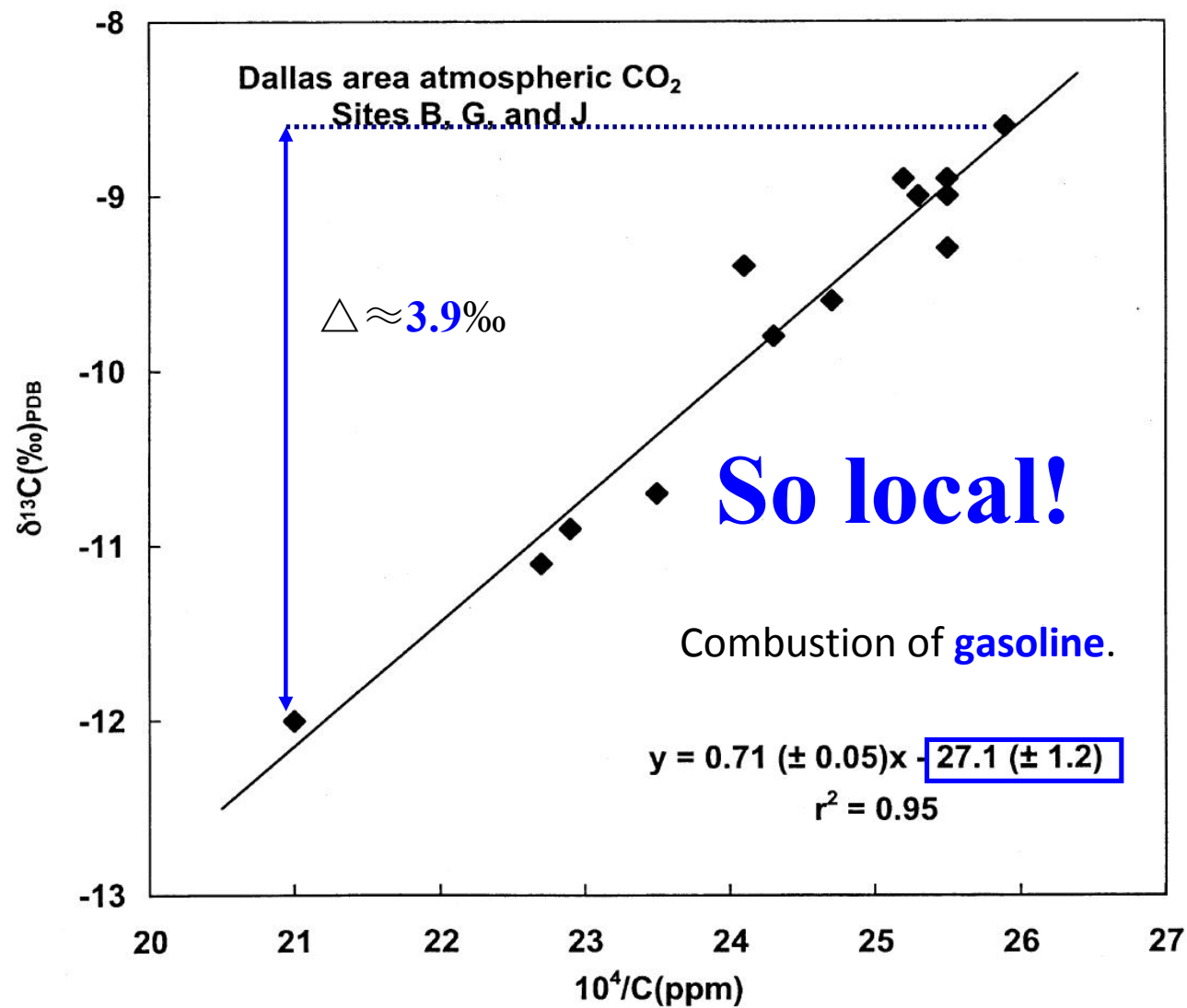


Fig.7 Plot for sites besides highways (or roadsides) .

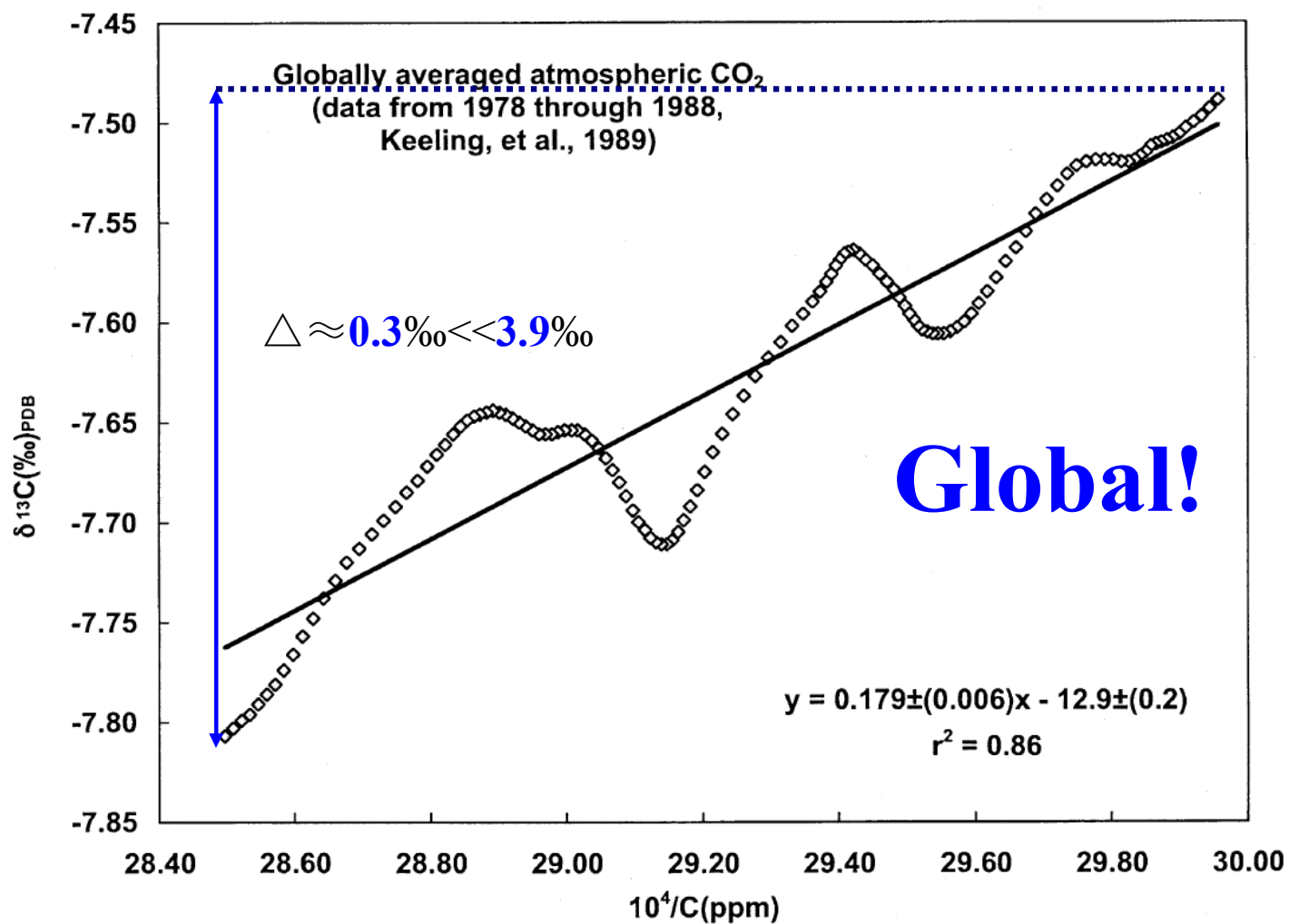


Fig.8 Keeling plot from 1987 to 1988.



$$\delta^{13}C_a = -8.0 \text{ ‰}$$

$$\delta^{13}C_G = -27.0 \text{ ‰}$$

$$\delta^{13}C_N = -42.0 \text{ ‰}$$

$$\delta^{13}C_S = -16.3 \text{ ‰}$$

$$C_a = 367 \text{ ppm}$$

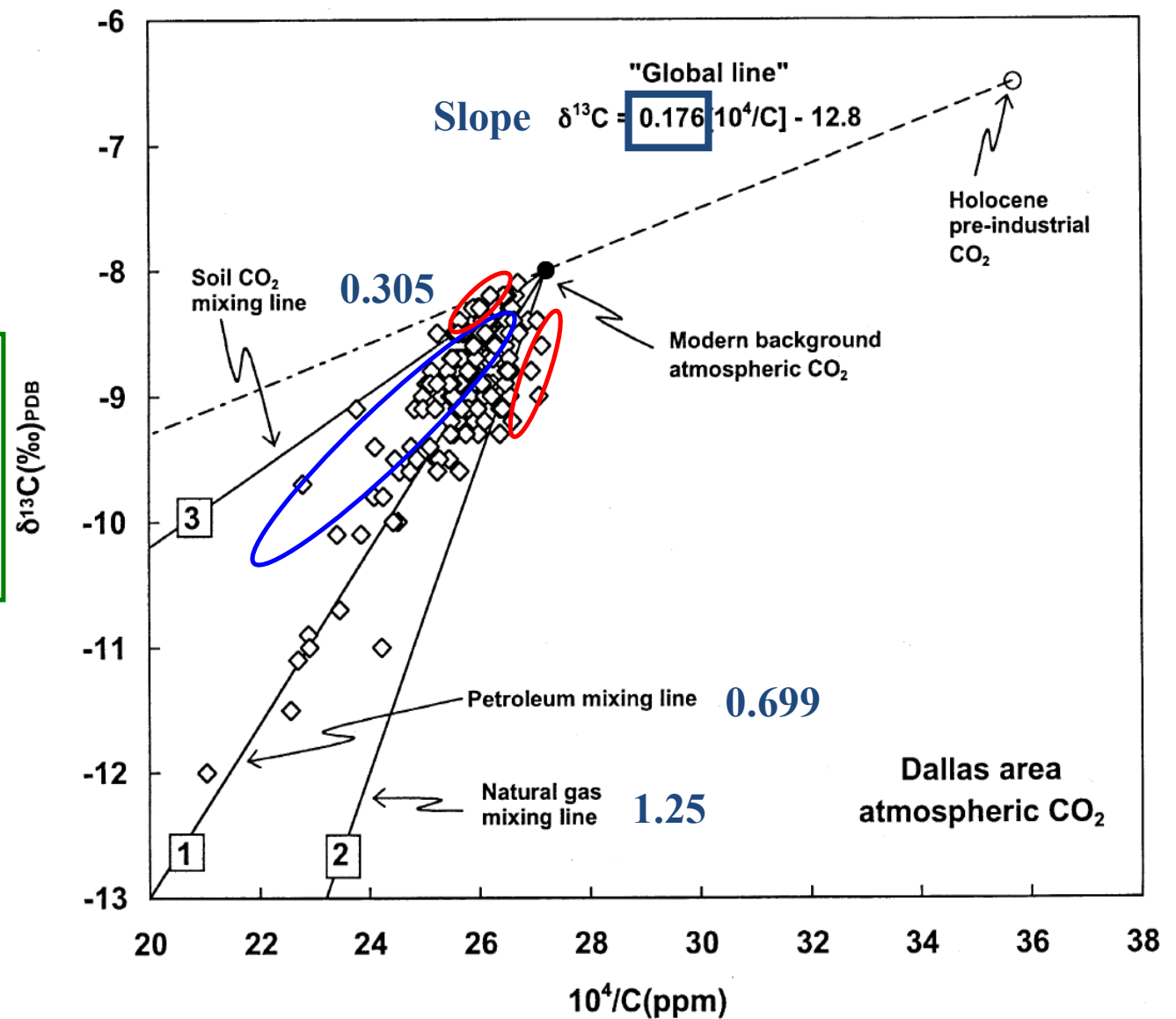


Fig.9 Keeling plot (all data from 8 sites).

Following Rayleigh-type, C3

$$\delta^{13}C = (1000 + \delta^{13}C_0) f^{(\alpha_K - 1)} - 1000$$

- $\alpha_K = 0.981$.

- $f = C/C_0$

- The initial values arbitrarily were chosen on square 1 and 2.

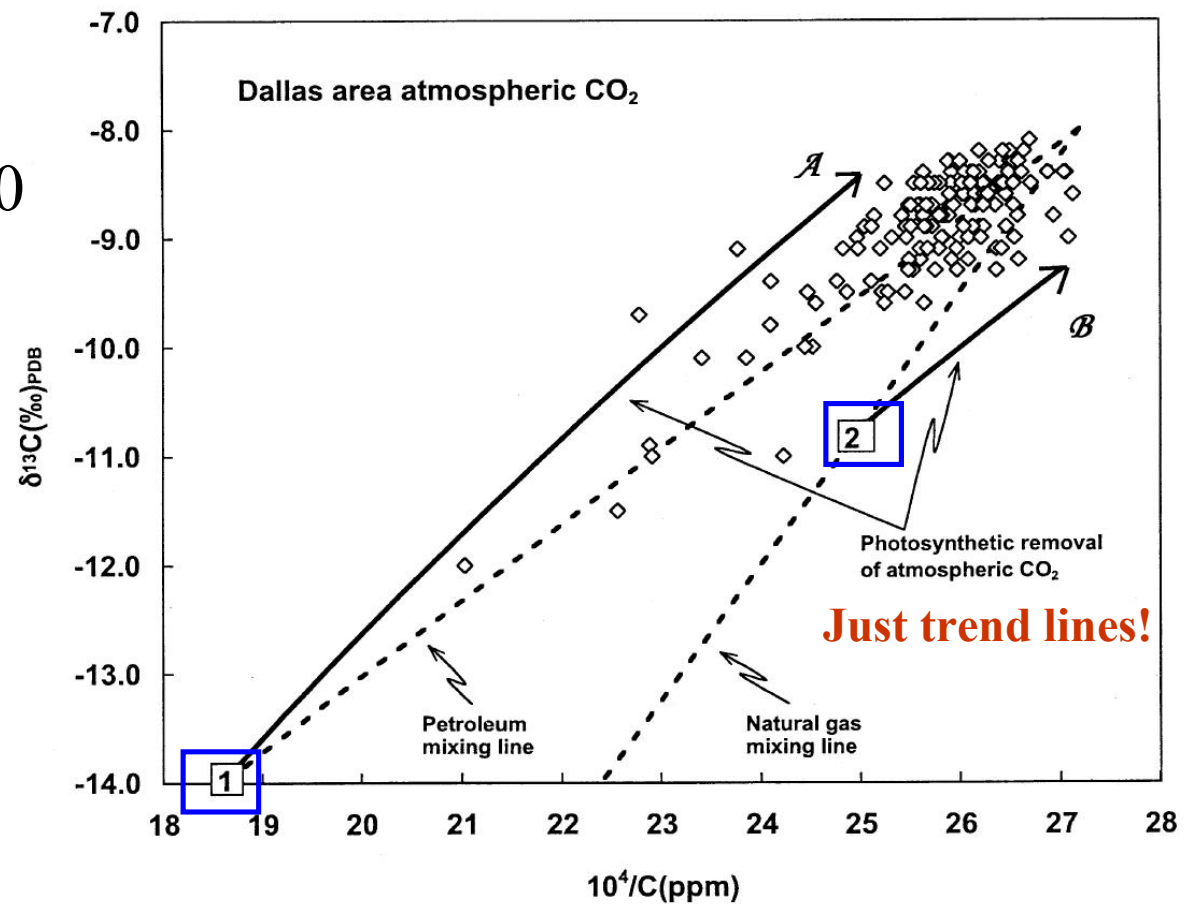


Fig.10 Keeling plot (all data from 8 sites) considered about photosynthetic effect.

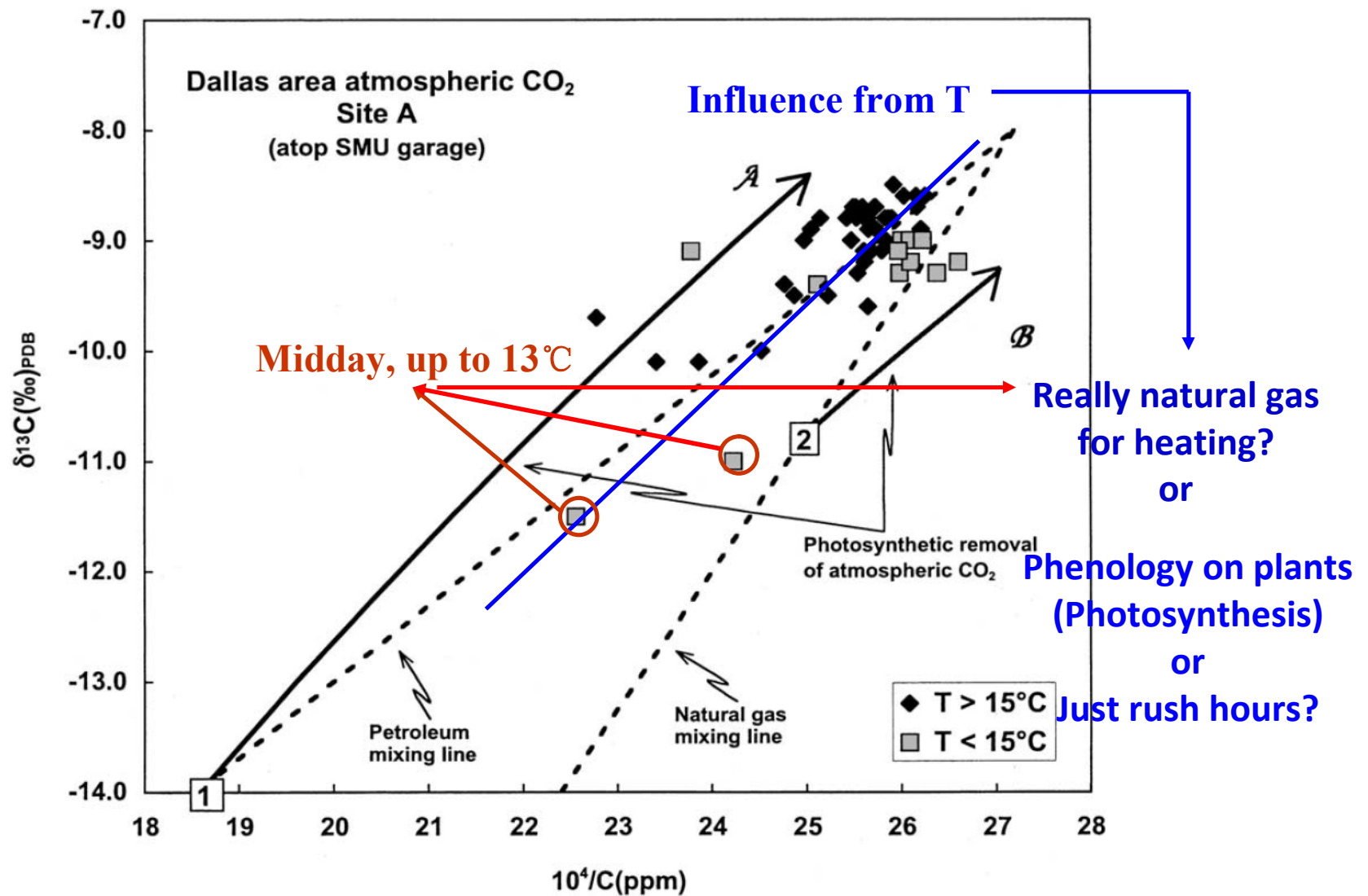


Fig.11 Keeling plot (A site) considered about photosynthetic effect.

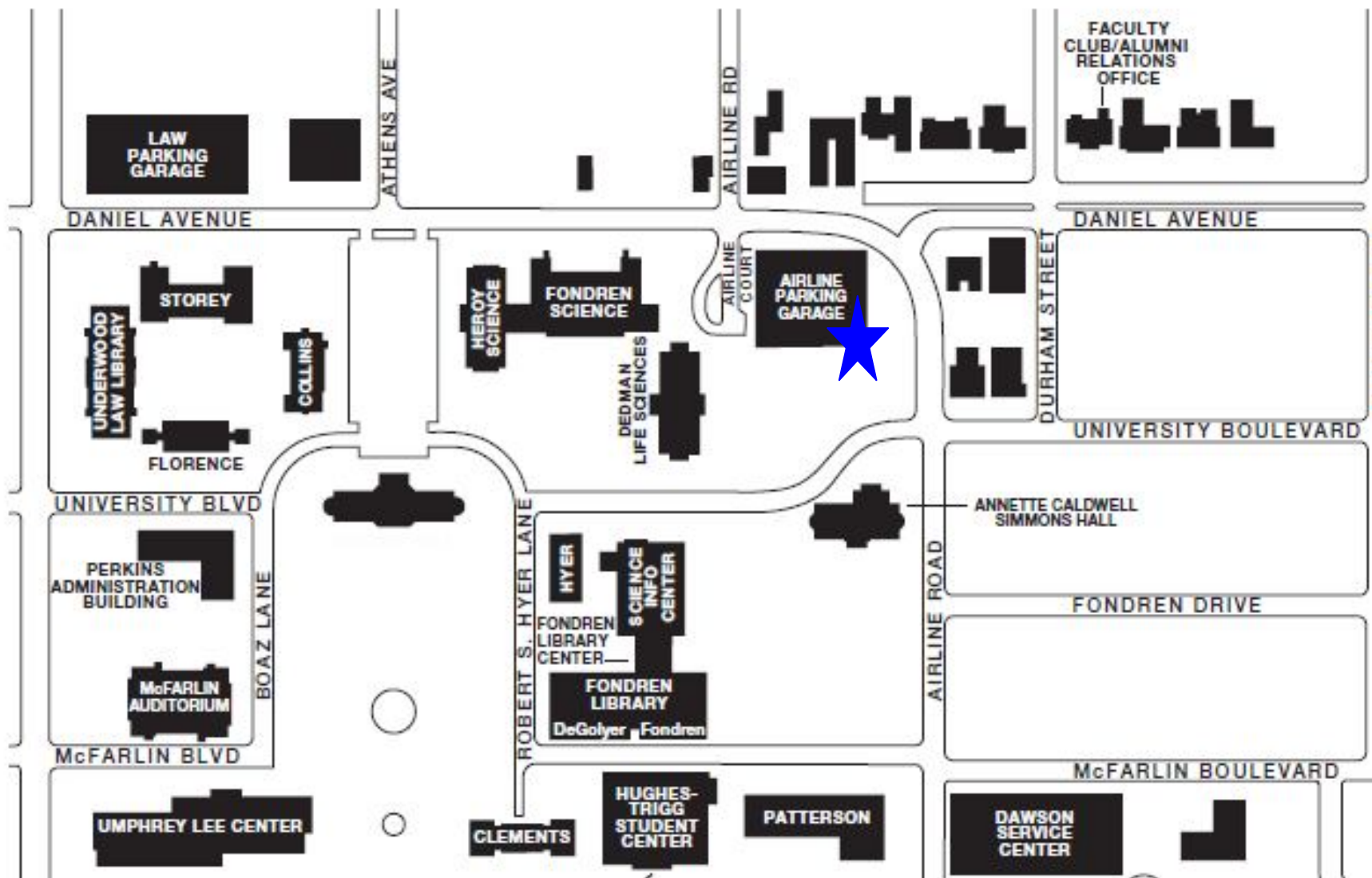


Fig.12 The location of site A in SMU campus.

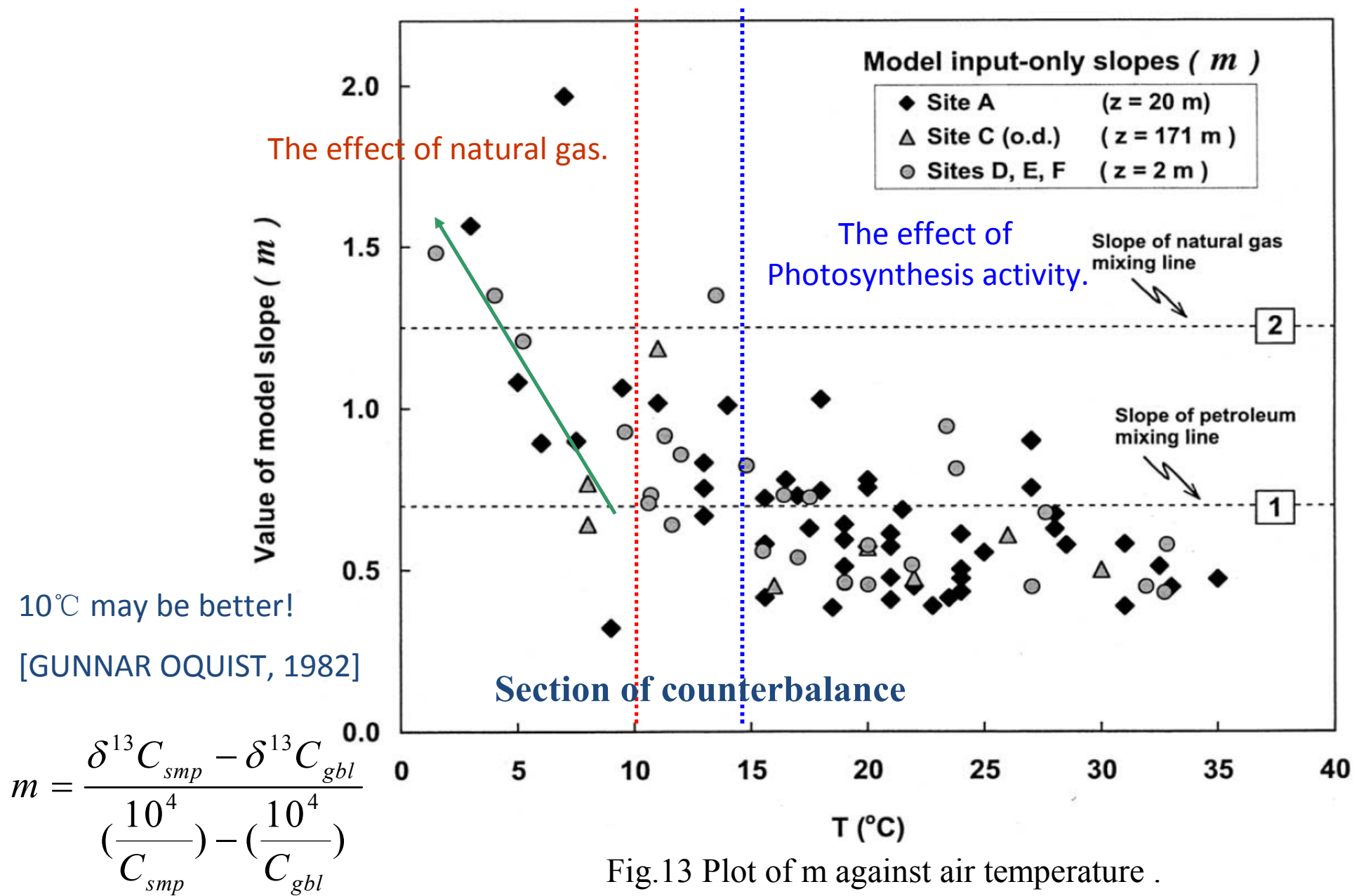


Fig.13 Plot of m against air temperature .

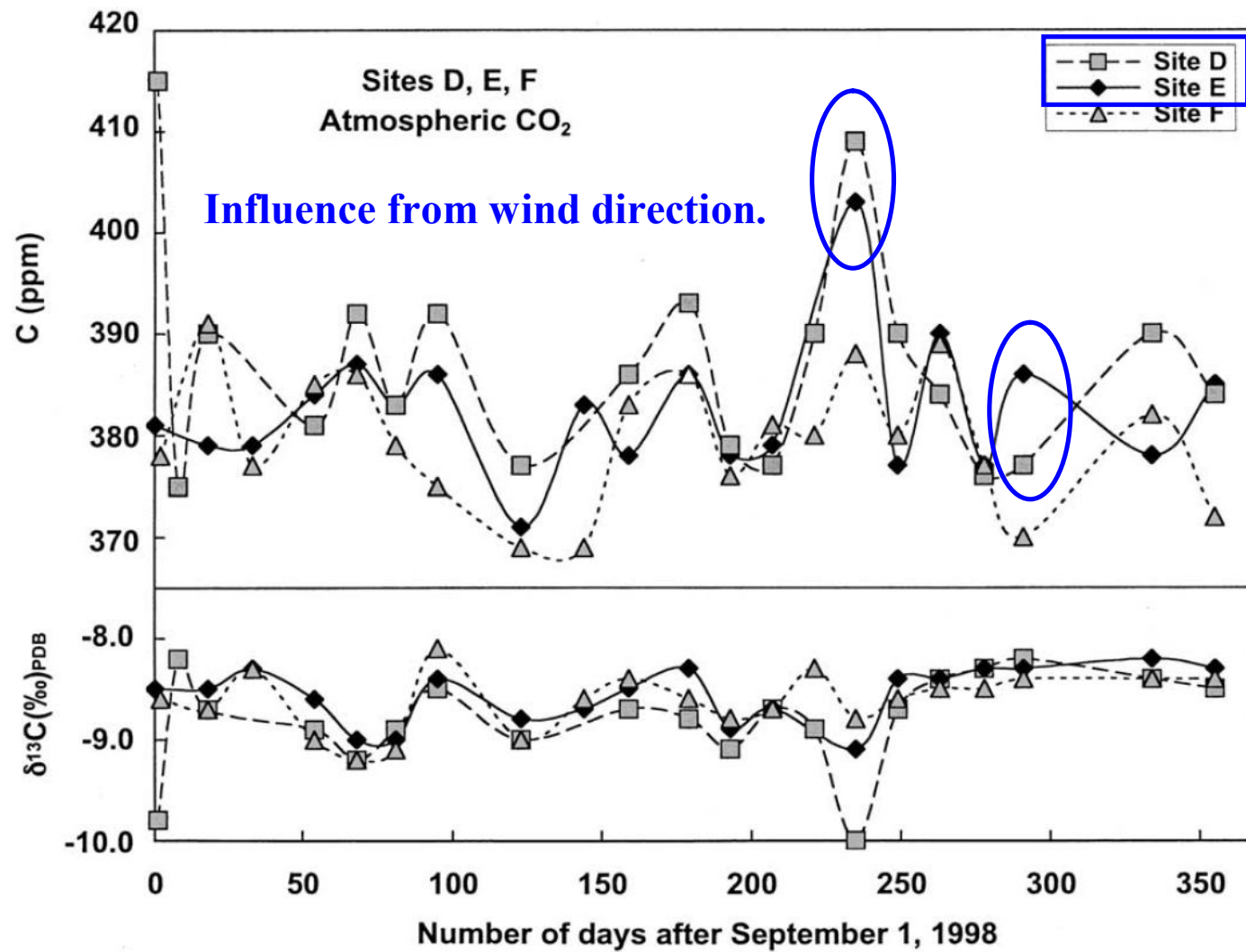


Fig.13 Temporal variation at sites D, E and F.

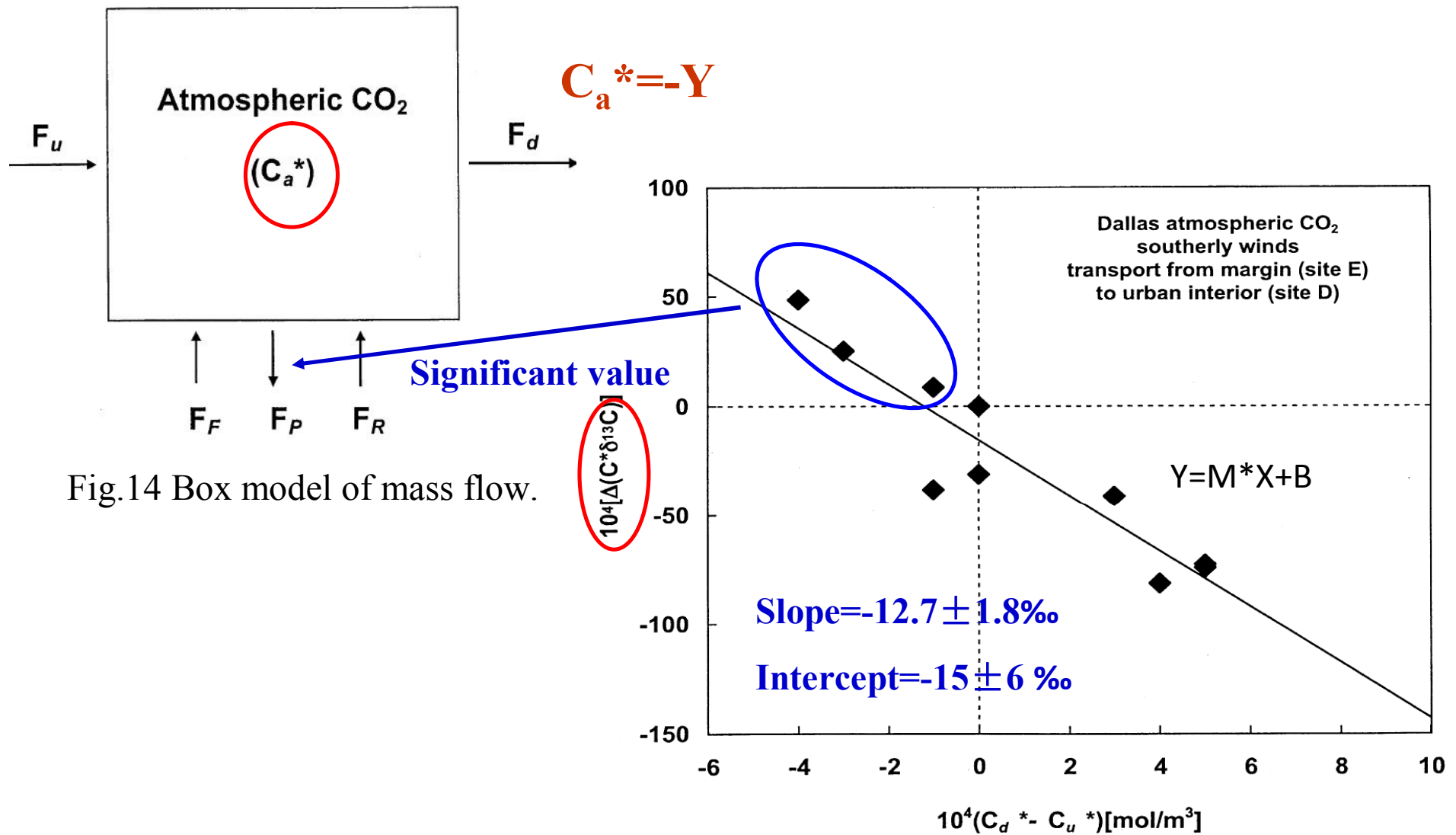


Fig.14 Box model of mass flow.

Fig.14 Concentration-weighted against concentration between Site E and D.

6. Conclusion



- The concentration of carbon dioxide and the ratio of carbon isotope are various for different function districts in metropolitan area (from urban areas to rural sites).
- CO₂ concentration and its isotope ratio can be influenced by temperature not only because of combustion of natural gas for heating but also photosynthesis activity.
- Wind direction (sources) is the mainly factor in a short time scale.



7. Critique of their Interpretation



- The author partly ignored the difference between soil respiration and plant respiration.
- $\delta^{13}C_s$ value were more positive than other studies(-26‰). [Pataki, 2007]
- Some too negative values were gotten because automobile observation was not professional.



Thank You

