Tunable diode laser absorption spectroscopy for stable isotope studies of ecosystem－atmosphere CO2 exchange

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Outline

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1. Background

1.1 The development of isotope measurement instruments

- **1. IRMS (Isotope ratio mass spectrometry)**
- **2. TDL (Tunable diode laser) [Crosson at el., 2002]**
- **3. FTIR (Fourier transform infrared absorption spectrometry) [Esler at al., 2000]**
- **4. QCL (Quantum cascade lasers) [R. Wada et al. , 2011]**

Table 1. Detail of isotope measurement instruments. [David R. Bowling et al, 2003]

Instrument	Characteristic	Limit	Precision
IRMS	**High precision, discontinuous**	**Labor, not in filed**	**0.02-0.1‰ relied on method**
FTIR	**Continuous, high-frequency**	**Ultra-high precision optical**	**0.22‰ at 5％ CO_2-in-N_2 with CRDS**
TDL	**Continuous, high-frequency, $^{13}CO_2$ and $^{12}CO_2$ are measured independently**	**Pressure, temperature, humidity**	**0.1‰ at 350 μ mol mol^{-1} CO_2-in-air**
QCL	**Long-term ,real-time comparison**	**Pressure, temperature**	**0.1‰ per 30 min**

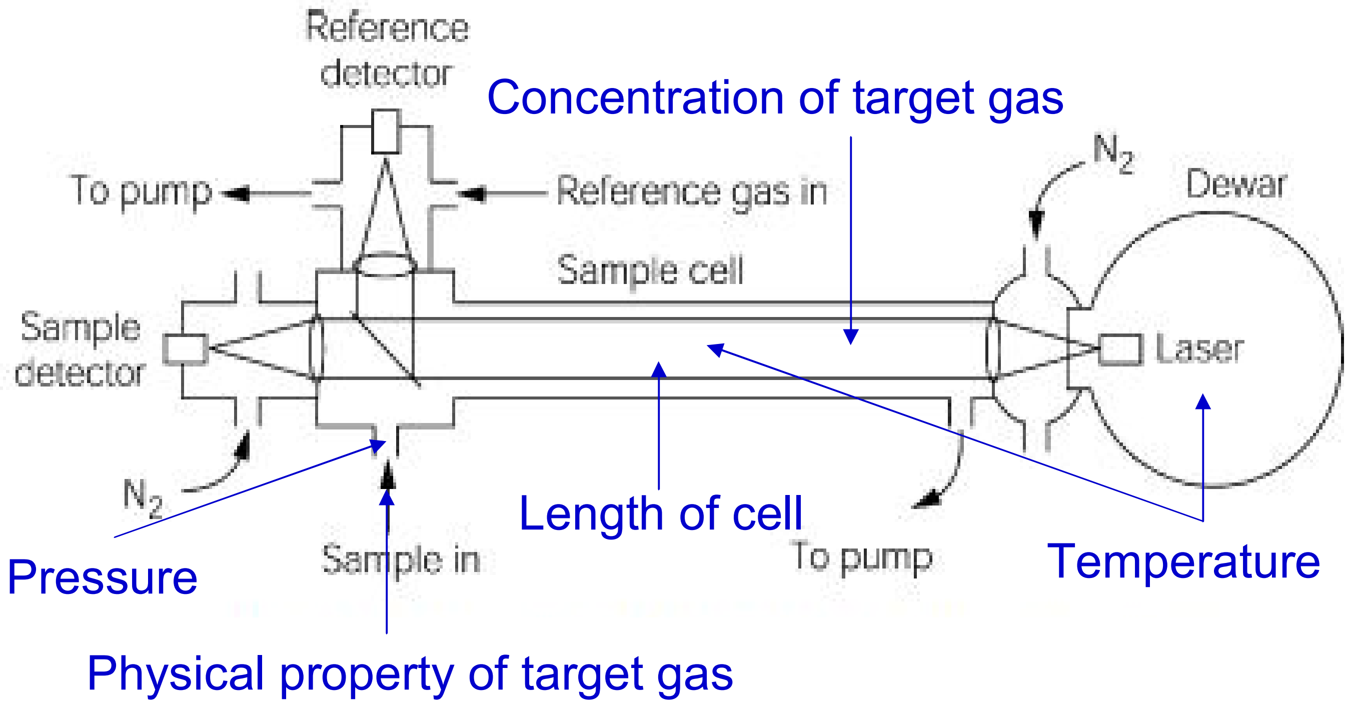
1.2 The development of isotope measurement technology

- **1. Flux gradient [Businger, 1986]**
- **2. HREA (hyperbolic relaxed eddy accumulation) [Bowling et al., 1999b]**
- **3. EC/flask [Bowling et al., 1999a]**

Table 2. Detail of isotope measurement technology. [R. Wada et al, 2011]

Method	**Advantage**	**Disadvantage**
Flux gradient	**Simplicity**	**Just adopted to surface layer**
HREA	**Applied on canopy, divided into updraft and downdraft**	**Low availability of data, uncertainty of samplings**
EC/flask	**Simplicity, complex surface**	**Difference with Keeling plot in regression, low frequency of flask samplings**

1.3 TDL system description



Concentration of target gas

Length of cell

Pressure

Temperature

Physical property of target gas

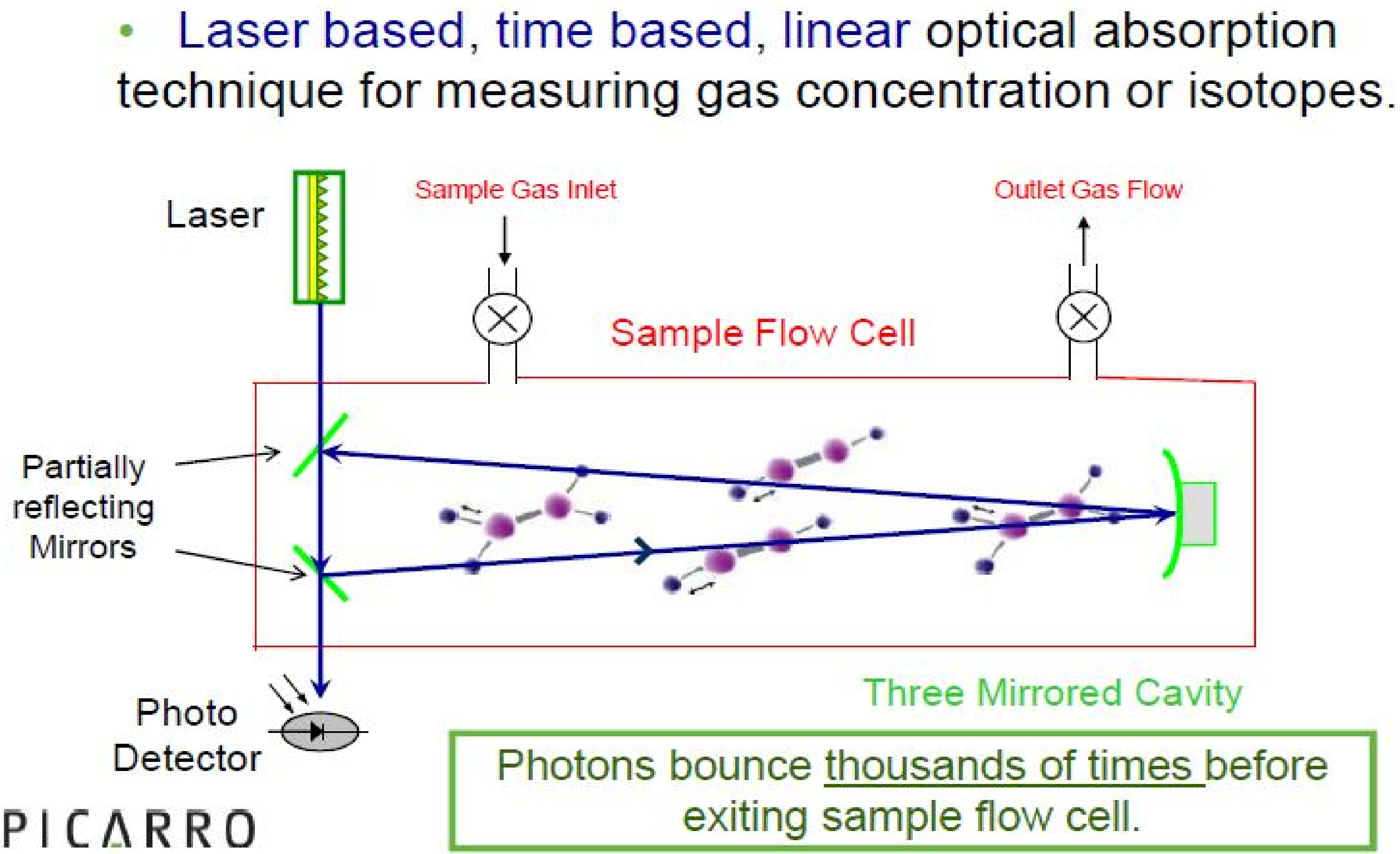
Fig.1 Diagram of the TGA100 tunable diode laser absorption system.

- **Pressure: Molecular absorption lines at low pressure are narrower than at high pressure, and this effect can be called pressure broadening. The effect of samplings calibrated by CO_2 in air is better than 5％ CO_2 in N_2. [Griffith, 1982]**

- **Temperature: $^{12}CO_2$, $^{13}CO_2$ and δ^{13}C increase 1.5％, 0.1 ％and 14‰ per 1 ℃, respectively. (40 ℃, 2.1 Kpa) [Rothman at al., 1988]**

- **Length of cell: According to Lambert-Beer’s law, absorption strength of IR laser is linked with thickness and concentration of target gas. [Bouguer, 1729; Lambert, 1760; Beer, 1852]**

- **Physical property of target gas: humidity can influence the measurement of gas concentration, and increasing concentration can lead to decrease of δ^{13}C .[R.Wada,2012; Wen,2012]**



- Laser based, time based, linear optical absorption technique for measuring gas concentration or isotopes.

Photons bounce thousands of times before exiting sample flow cell.

Fig.2 Diagram of the CRDS.

- **Temperature control: 0.005℃, Pressure control: 0.00024 atm, Length of cell: about 12 km. [Picarro, Peking, 2012]**

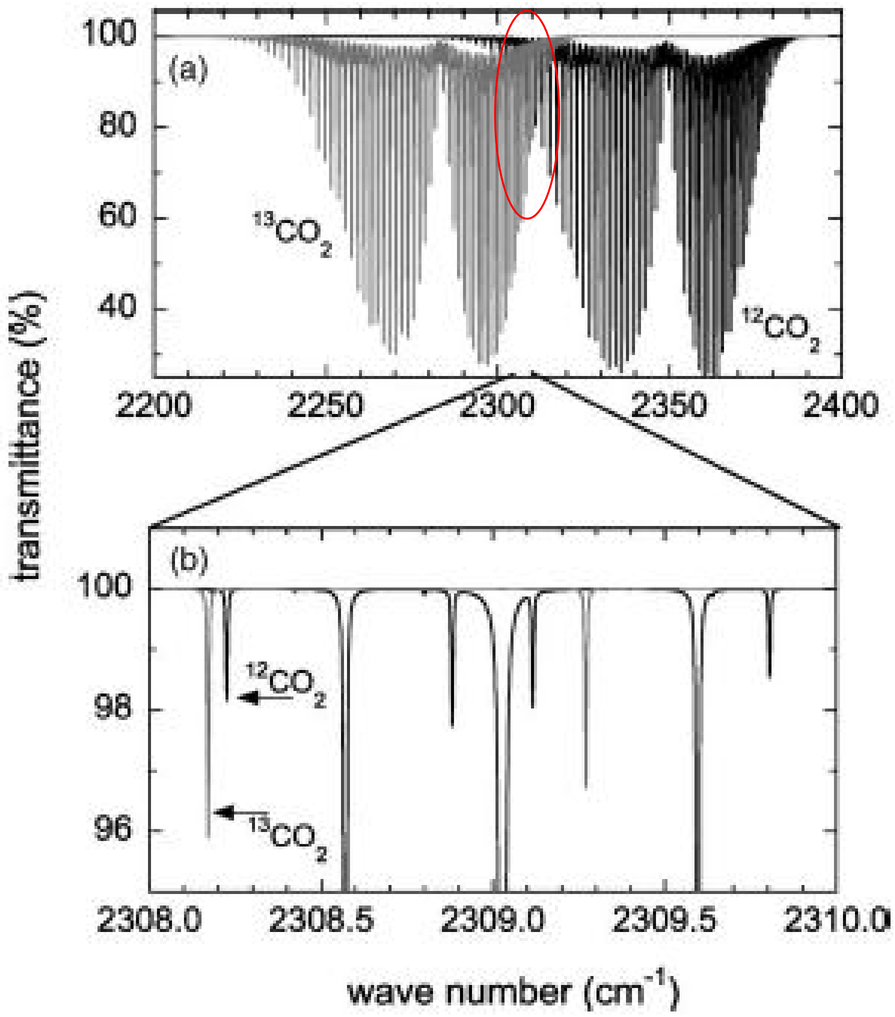


Fig.3 The principle of choosing absorption lines.

- **1. The similar/close wavelength range and high absorption strength.**
- **2. The suitable absorption lines are needed to eliminate disturbance at utmost from other gas.**

- **In addition, this study found 2308.416cm^{-1} for $^{12}C^{18}O^{16}O$ and 2308.570cm^{-1} for $^{12}C^{16}O_2$ presented a potential for measuring δ18O, although it's noise is 50 percent bigger than δ ^{13}C.**

2. Hypothesis

- **$\delta^{13}C_R$ (carbon isotope of respired CO_2) varies at night in vertical and temporal scale.**

3. Objectives

- **To compared the performance of TDL in field with MS in Lab.**

- **To observe the variation of $\delta^{13}C_R$ in different vertical and temporal scale, especially at night.**

4. Method

4.1 Site

Fig.4 The location of Cache Valley (1360m above sea level). [From google earth]

- **Filed : 800*400m. Glass: 15.2 ± 5.4 cm. Air temperature: -1.3 to 26.1 ℃ Weather: Sunny, clear. Vapor pressure: <3 Kpa (daytime)**

4.2 TDL system setup

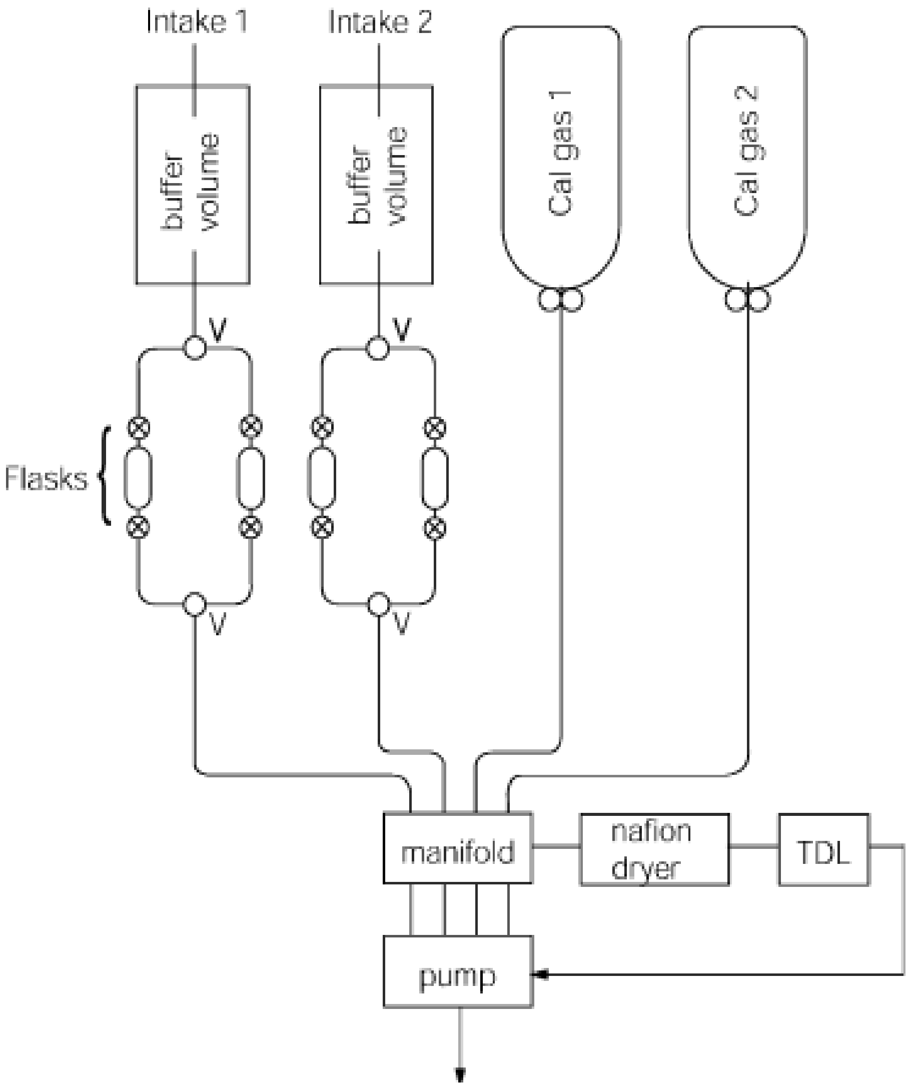


Fig.5 Diagram of TDL setup.

Intakes: at two heights. (1 and 60 cm above ground)

Buffers: To dampen rapid changes in CO_2 concentration.

Flasks: To control flow rate.

Valves: To switch among 4 intakes.

Dryer: To eliminate the influence of water vapor in air (humidity and pressure).

Calibrated gas: To calibrate TDL (two points).

4.3 Calibration gases

Table.3 Calibration gas were used in this study.

Calibration gas	**Concentration (μ mol mol^{-1})**	**Isotope rate (‰)**	**Remark**
Tank A	**498.4**	**-30.68**	**Cal by IRGA et al.** **CO_2-in-air**
Tank B **(Cal 1 in field)**	**363.4**	**-29.55**	**Cal by Tank A** **5 ％CO_2-in-N_2**
Tank C **(Cal 2 in field)**	**1049.0**	**-40.58**	**Cal by Tank A** **5 ％CO_2-in-N_2**

Different Cal introduces an error. →

To compare 5 ％CO2-in-N2 and 5 ％CO2-in-air at about 300 or 700 μ mol mol-1.

$$G = \frac{X_C - X_B}{X_{Cm} - X_{Bm}}, \quad (1)$$

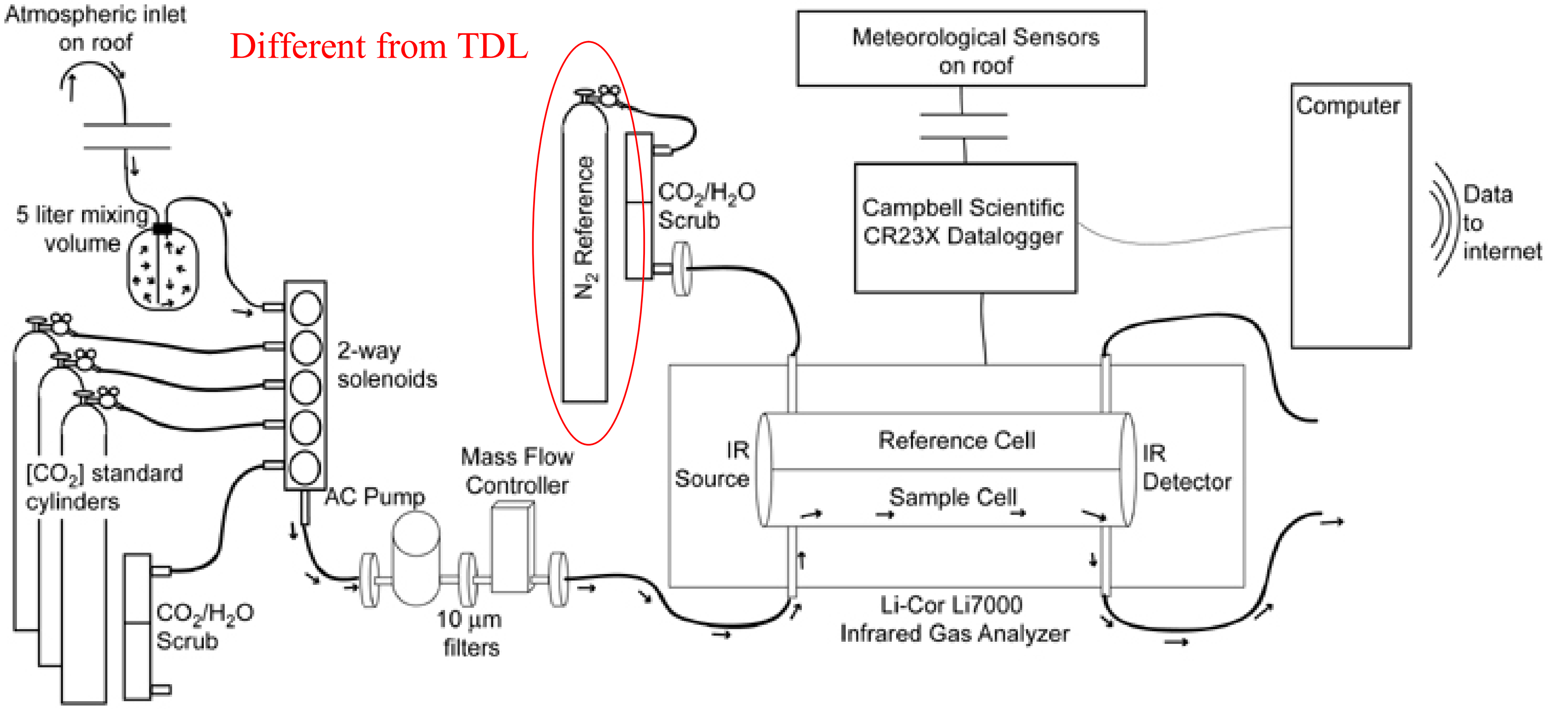
$$O = X_C - GX_{Cm}, \quad (2)$$

$$X_i = X_m G + O. \quad (3)$$

- **G: Gain factors (The slope of true values and observed values using two-points calibration).**
- **O: Offsets (The deviation amplitude between values of regression and observation).**
- **X_B, X_C : True mole fractions ($^{12}CO_2$ or $^{13}CO_2$) in tanks B and C.**
- **X_{Bm}, X_{Cm} : the measured mole fractions of each tank.**
- **X_m: Raw mole fractions of samplings.**
- **X_i: Concentration of unknown samples were calculated from X_m.**

4.5 Other equipment

- **IRMS: To analyze [CO_2] (mole fraction by volume in units of μ mol CO_2 mol^{-1} of dry air) and carbon isotope of CO_2 of all flasks from filed.**
- **IRGA: To measure [CO_2] (mole fraction by volume in units of μ mol CO_2 mol^{-1} of dry air) of all flasks.**
- **HMP45C: To observe air temperature and humidity at 1.1m.**



Different from TDL

UofU CO2 and Weather Station - 070525

Fig.6 Diagram of IRGA setup and calibration. [From UofU]

- **The method of calibrating IRGA: Firstly, using chemically scrubbed N_2 in reference cell of IRGA for zero correction. Secondly, using a WMO-traceable CO_2-in-air mixture near ambient [CO2] for one-point calibration. [Bowling, 2001]**

5. Results and interpretation

1. To define the frequency of calibration
    - Measurement without calibration
    - Allan variance
2. Potential for measurement of $\delta^{18}O$
3. Calibration TDL in field measurement
    - Calculation of Gain and Offset
    - To analyze the existence of this system error
4. Time-series data
    - Comparison TDL with MS
    - To analyze the existence of the offset between two instruments
    - To quantify the effect of broadening pressure
5. Spatial and temporal variation in $[CO_2]$, $[^{12}CO_2]$, $[^{13}CO_2]$ and $\delta^{13}C$

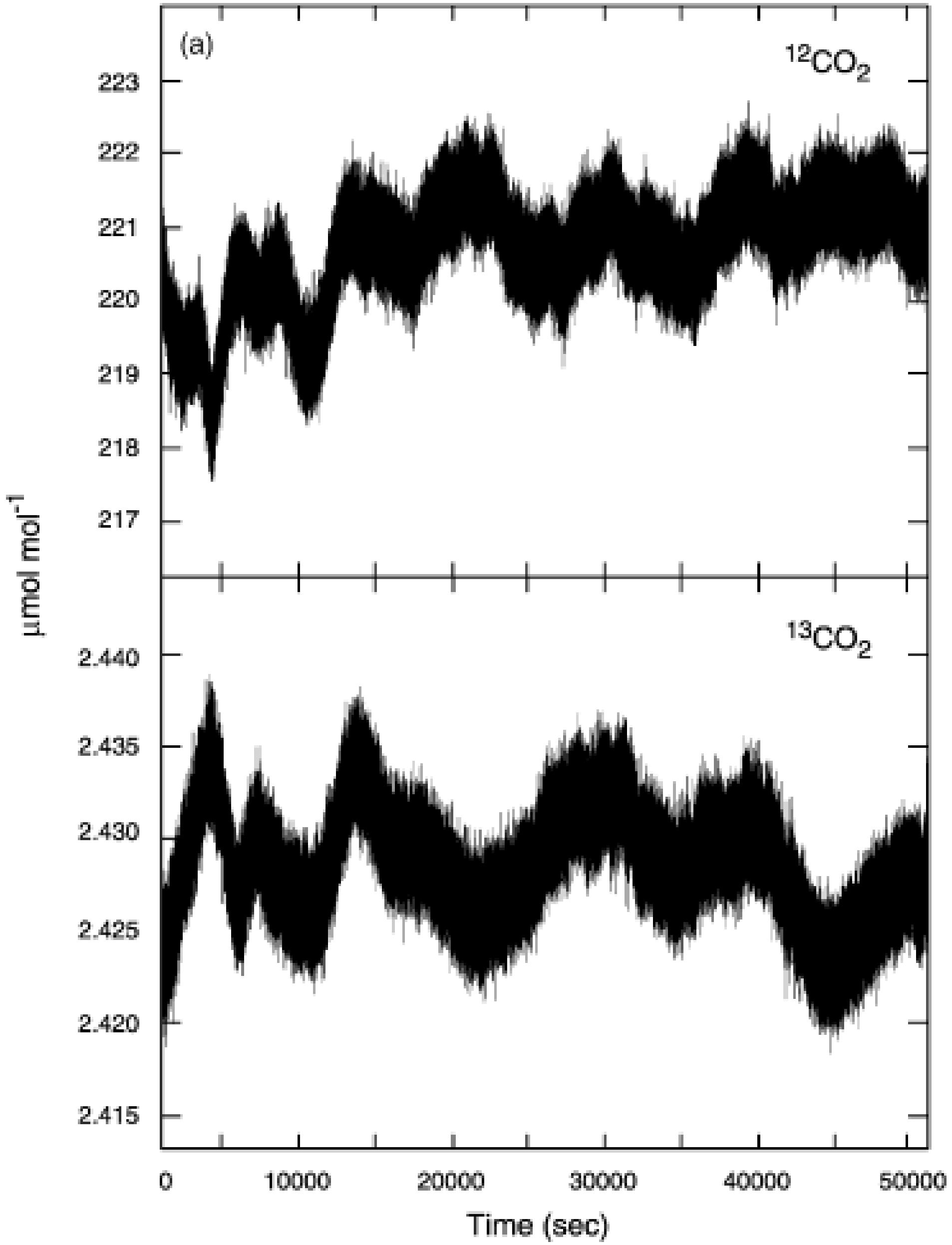


Fig.7 [$^{12}CO_2$] and [$^{13}CO_2$] measured every 100 ms for 13.9 hours.

- **Standard deviation of [$^{12}CO_2$] and [$^{13}CO_2$] are 0.33 and 0.12％, respectively.**
- **Standard deviation of [CO_2] was 0.36％, which was bigger than the threshold 0.35％ that stands for the agreement [$^{12}CO_2$] and [$^{13}CO_2$] (calculated by $(0.0033^2+0.0012^2)^{1/2}$).**
- **So it is necessary to calibrate TDL with a proper frequency.**

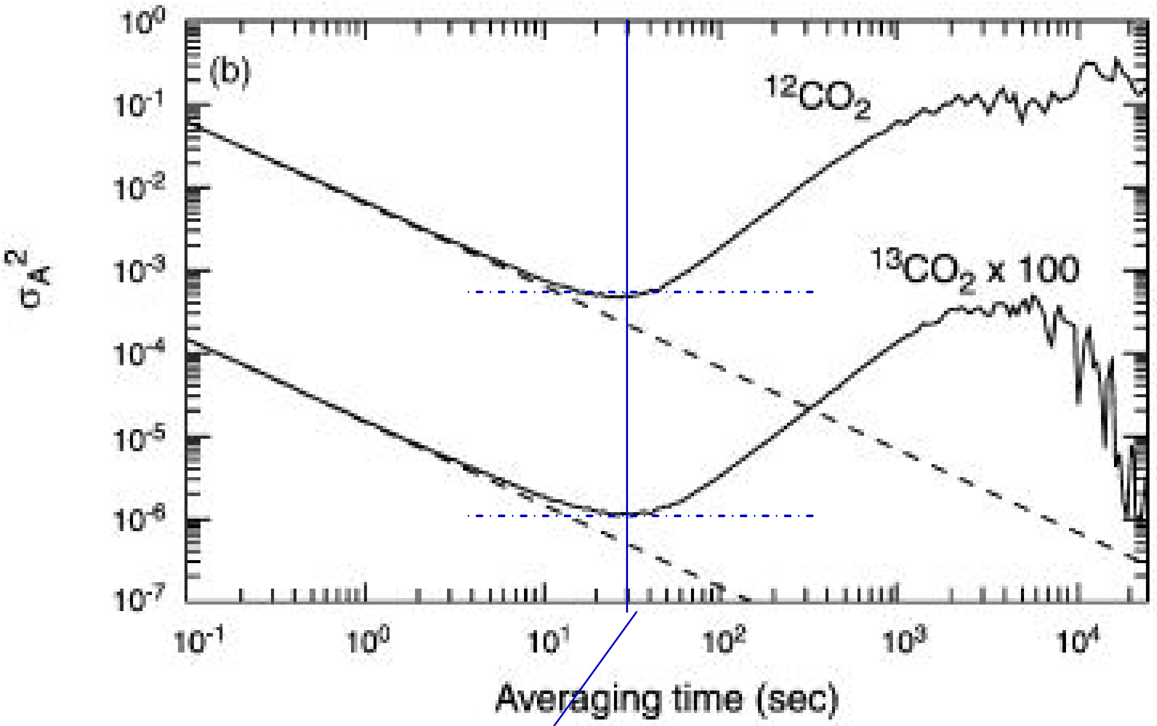
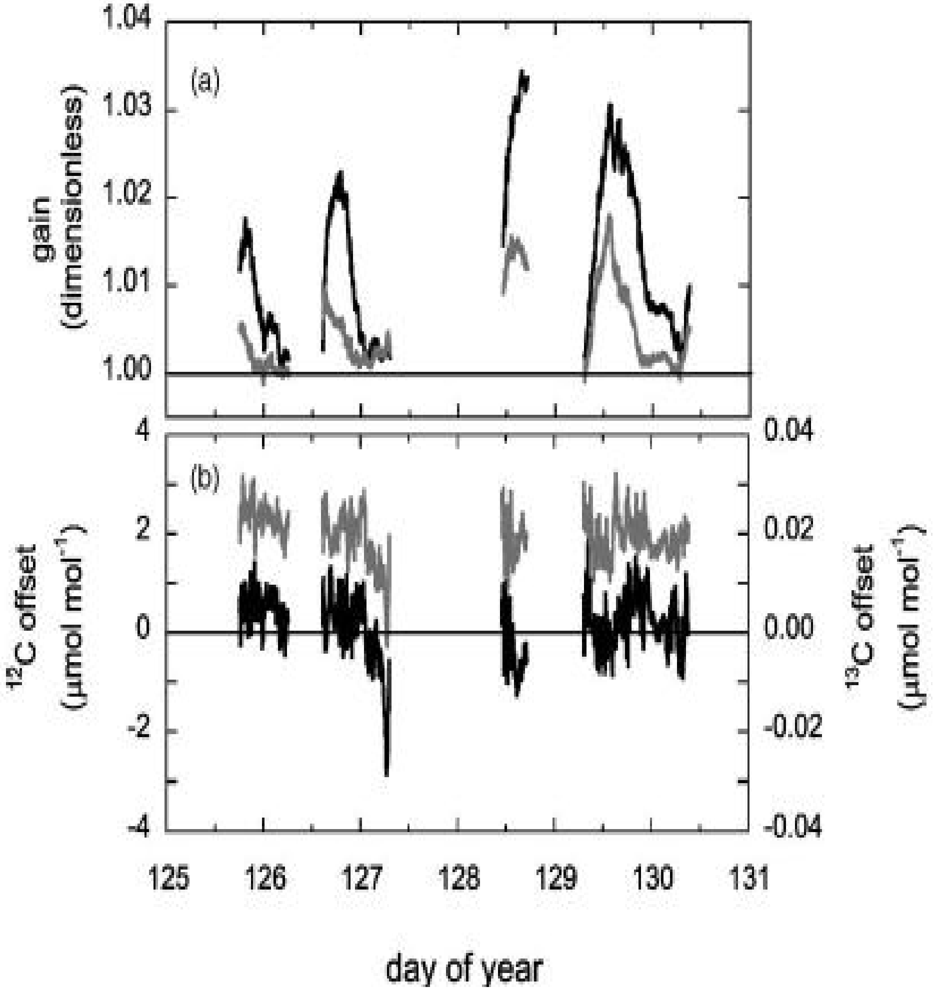


Fig.8 Examination of temporal changes in instrument response by Vllan variance.

$\approx$30S* 4 intakes =2 min

Definition: Vllan variance $\sigma_y^2(\tau)$. is intended to estimate stability due to noise processes and not that of systematic errors or imperfections such as frequency drift or temperature effects.



black line: [$^{12}CO_2$]

grey line: [$^{13}CO_2$]

Fig.9 Examination of temporal changes in instrument response by Vllan variance.

- **53% data for 4.6 days were collected.**
- **The value is lower than true mole fraction, especially in [$^{12}CO_2$] because of the error from temperature and parts of instrument depended on temperature, such as optical window, laser frequency and so on.**

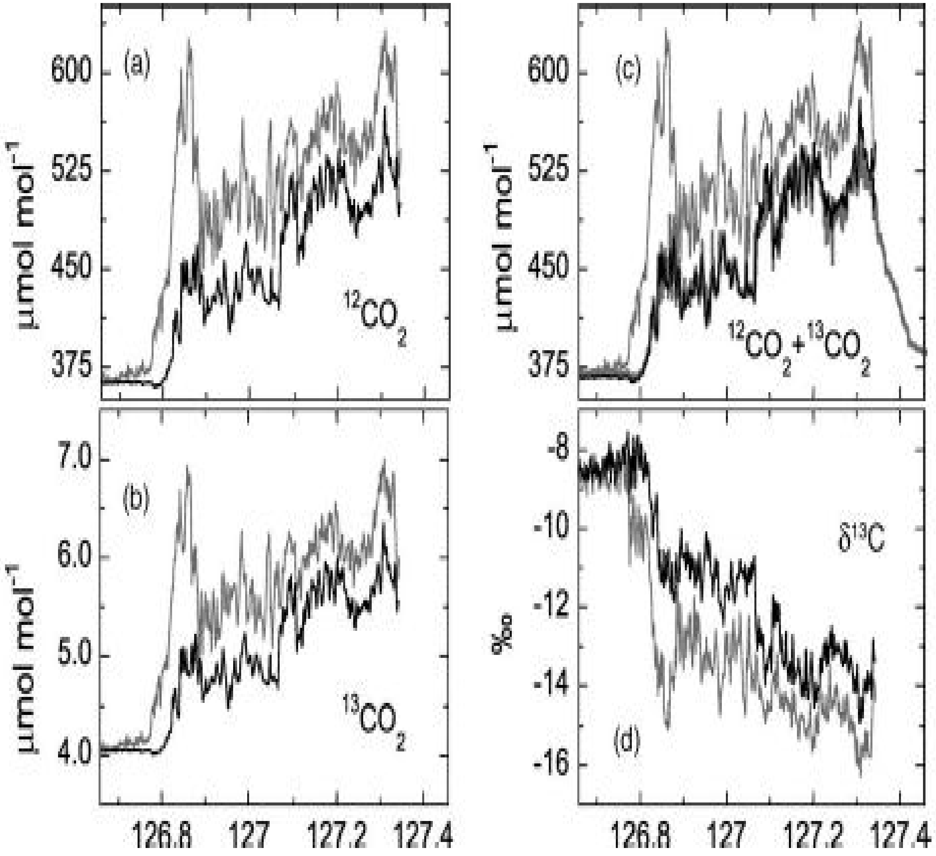
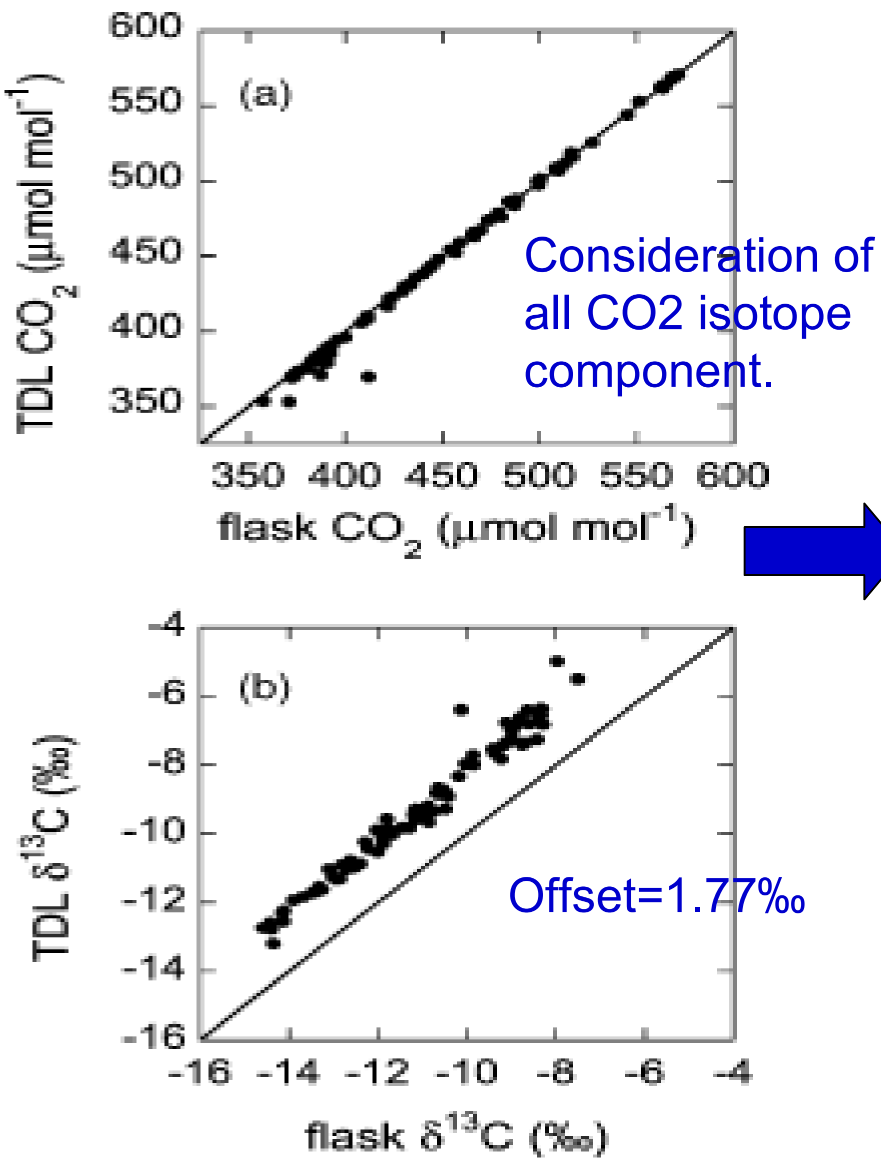


Fig.10 Time series of TDL measurement of $[^{12}CO_2]$, $[^{12}CO_2]$, $[^{12}CO_2 +[^{13}CO_2]$, and $\delta^{13}C$.

(1cm: grey line, 60cm: black line, IRGA at 60 cm: thick grey line)

- **The daily variation was agreed between $[^{12}CO_2]$ and $[^{13}CO_2]$. The ratio of $[^{12}CO_2]$ and $[^{13}CO_2]$ was always about 1.1%.**
- **The inverse trend of $\delta^{13}C$ appeared when $[^{12}CO_2]$ and $[^{13}CO_2]$ increased at night due to isotope discrimination of respiratory. [Fung, 1997]**



Consideration of all CO2 isotope component.

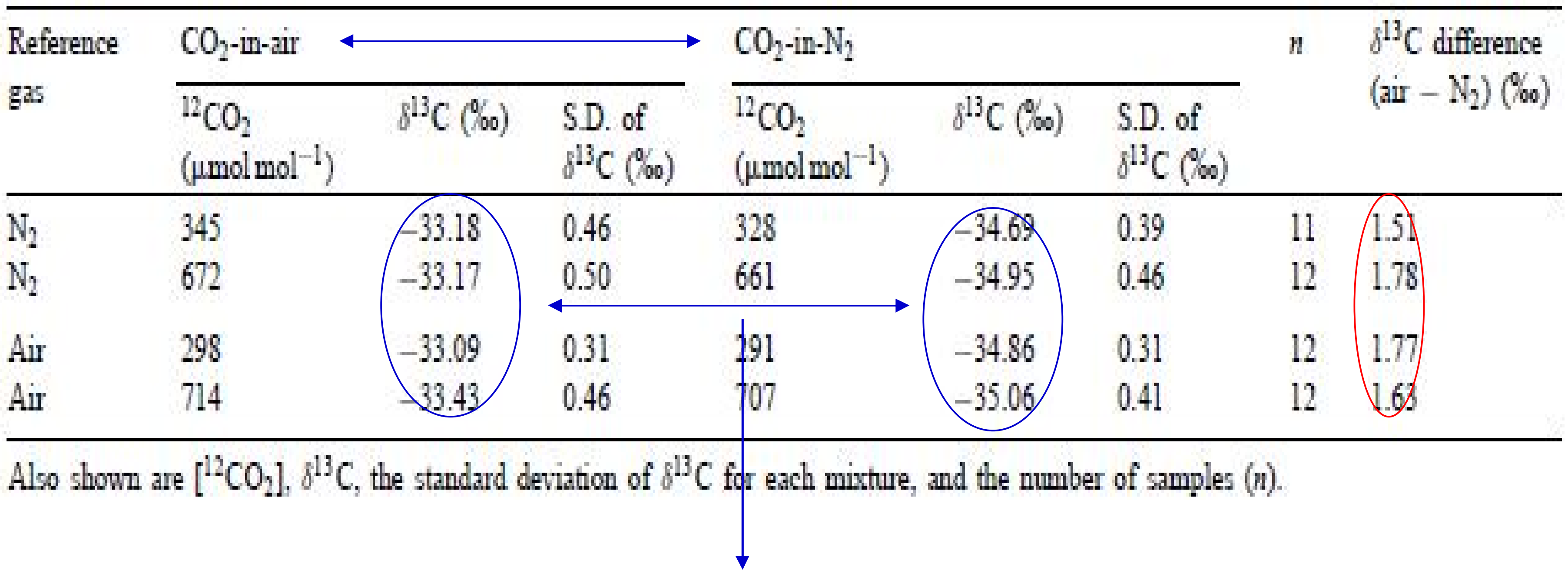
Offset=1.77‰

Fig.11(a) Comparison of [CO2] measured by IRGA and TDL, (b) Comparison of $\delta^{13}C$ measured by MS and TDL.

Table.4 The result of Fig.11.

Items	**Average error**	**S.D.**	**Remark**
$[CO_2]$ (n=81)	**2.3 µ mol mol^{-1}**	**5.6 µ mol mol^{-1}**	**IRGA-TDL (All CO_2 component considered).**
$[CO_2]$ (n=79)	**1.6 µ mol mol^{-1}**	**2.8 µ mol mol^{-1}**	
$\delta^{13}C$ (n=82)		**0.35‰**	**MS-TDL δ: -7.5~-16.3 ‰**
$\delta^{13}C$ (n=80)		**0.25 ‰**	

Table.5 Comparison 5 ％CO2-in-N2 and 5 ％CO2-in-air at about 300 or 700 μ mol mol-1.



Reference gas	CO$_2$-in-air			CO$_2$-in-N$_2$			n	δ^{13}C difference (air – N$_2$) (‰)
	^{12}CO$_2$ (μmol mol^{-1})	δ^{13}C (‰)	S.D. of δ^{13}C (‰)	^{12}CO$_2$ (μmol mol^{-1})	δ^{13}C (‰)	S.D. of δ^{13}C (‰)		
N$_2$	345	−33.18	0.46	328	−34.69	0.39	11	1.51
N$_2$	672	−33.17	0.50	661	−34.95	0.46	12	1.78
Air	298	−33.09	0.31	291	−34.86	0.31	12	1.77
Air	714	−33.43	0.46	707	−35.06	0.41	12	1.63

Also shown are [^{12}CO$_2$], δ^{13}C, the standard deviation of δ^{13}C for each mixture, and the number of samples (n).

0

More Positive due to the pressure broadening of O$_2$ in air.

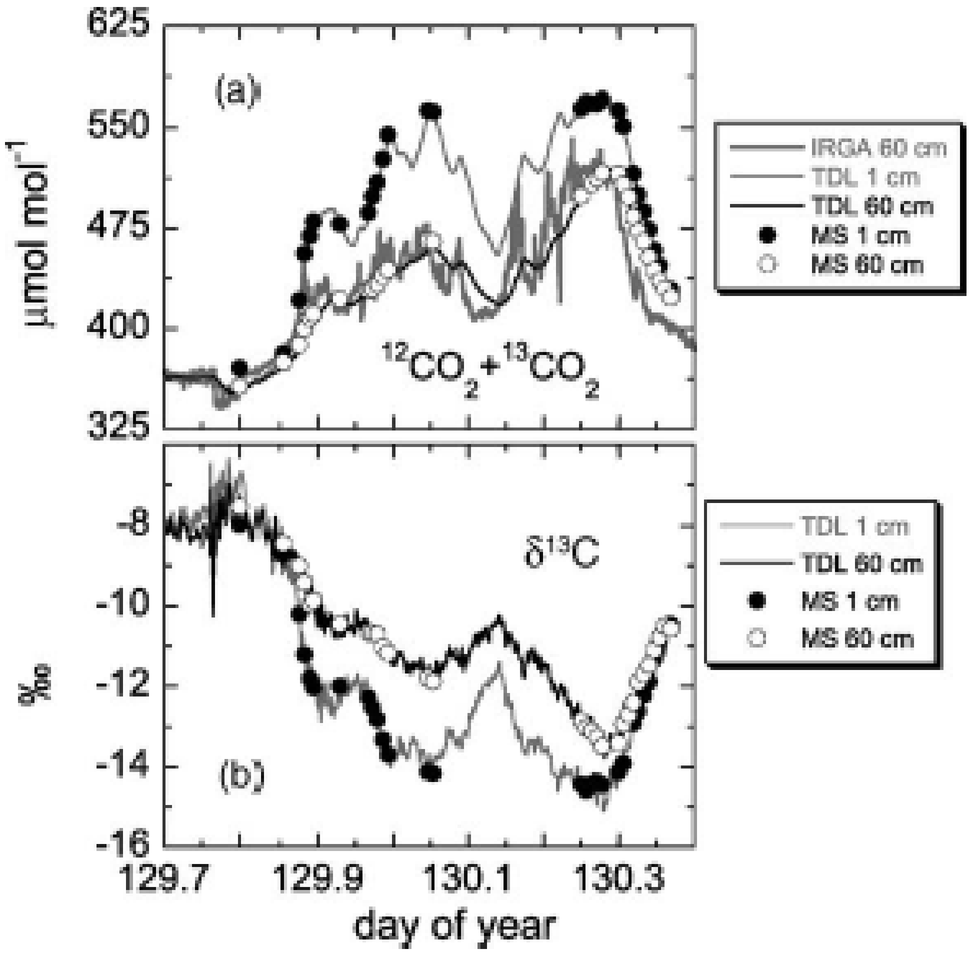
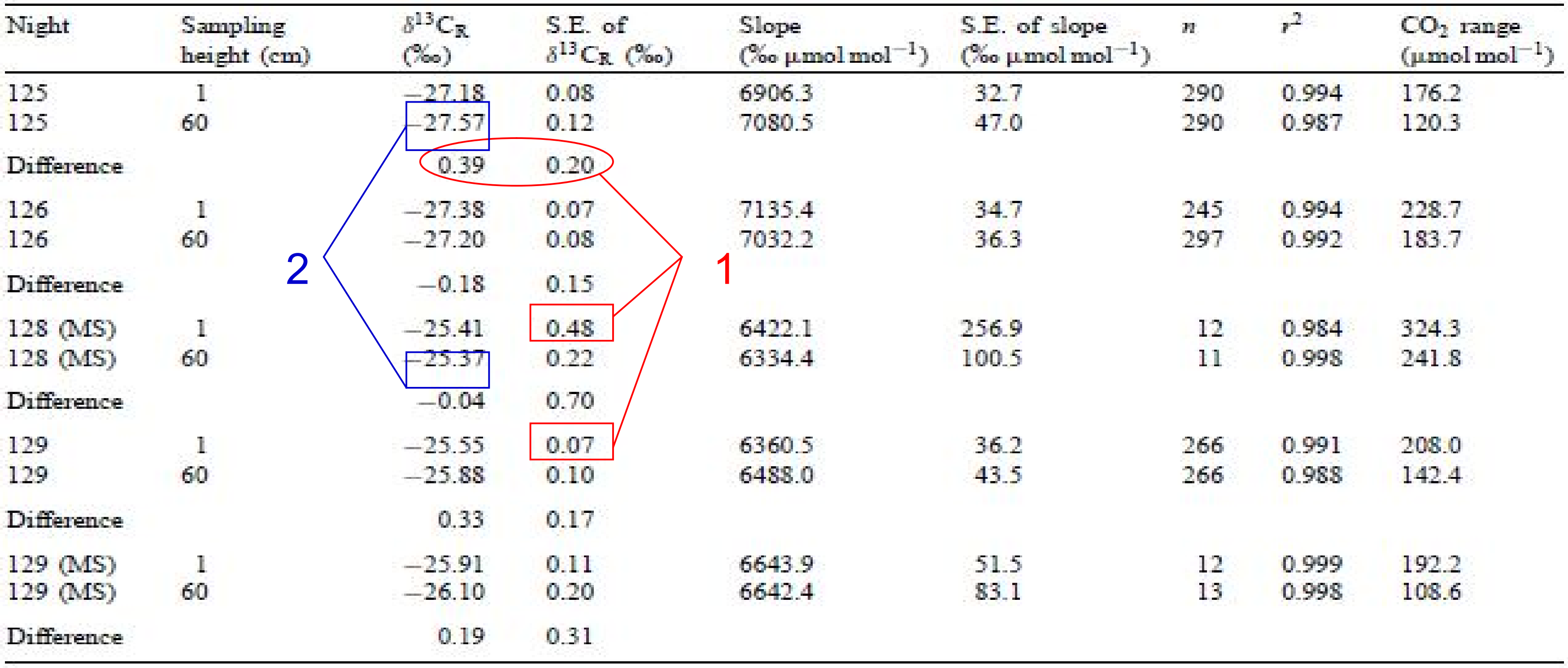


Fig.12 Comparison among TDL, MS and IRGA after considering offset.

- **At both height, the excellent agreement appeared.**
- **The rapid fluctuations of IRGA derived from no buffer.**

Table.6 Height dependence of Keeling plot intercepts ($\delta^{13}C_R$) and slopes and their standard error (S.E.)



Night	Sampling height (cm)	$\delta^{13}C_R$ (‰)	S.E. of $\delta^{13}C_R$ (‰)	Slope (‰ µmol mol^{-1})	S.E. of slope (‰ µmol mol^{-1})	n	r^2	CO_2 range (µmol mol^{-1})
125	1	−27.18	0.08	6906.3	32.7	290	0.994	176.2
125	60	−27.57	0.12	7080.5	47.0	290	0.987	120.3
Difference		0.39	0.20					
126	1	−27.38	0.07	7135.4	34.7	245	0.994	228.7
126	60	−27.20	0.08	7032.2	36.3	297	0.992	183.7
Difference		−0.18	0.15					
128 (MS)	1	−25.41	0.48	6422.1	256.9	12	0.984	324.3
128 (MS)	60	−25.37	0.22	6334.4	100.5	11	0.998	241.8
Difference		−0.04	0.70					
129	1	−25.55	0.07	6360.5	36.2	266	0.991	208.0
129	60	−25.88	0.10	6488.0	43.5	266	0.988	142.4
Difference		0.33	0.17					
129 (MS)	1	−25.91	0.11	6643.9	51.5	12	0.999	192.2
129 (MS)	60	−26.10	0.20	6642.4	83.1	13	0.998	108.6
Difference		0.19	0.31					

- **1. It is hard to define the difference between two layers due to the instrument precision.**
- **2. Low air temperature can lead to positive $\delta^{13}C$ because stomatic closure reacts to cold temperature.**

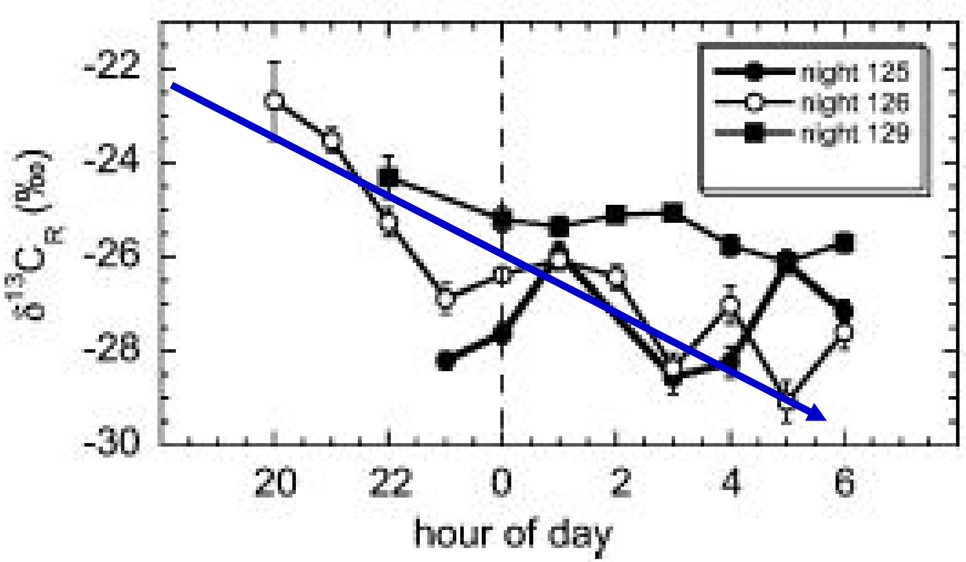


Fig.13 Temporal changes in $\delta^{13}C_R$ over the course of three night.

- **The trend of decease may be caused by 3 reasons as followed:**

1. The existence of autotrophic respiration which is more negative.

2. The effect of photosynthesis is contrary with respiration in daytime.

3. Respiration may use different sources of substrates at night with the lapse of time.

- **The variation during night (6.4‰) is almost as much as seasonal variation. [Pataki, 2003; Bowling, 2002].**

6. Conclusion

- **1. The Precision of TDL with a 2-min frequency of calibration (0.25‰ Compared with MS, 0.4‰ Compared with IRGA) can be accepted because of its high frequency measurement .**

- **2. The error of TDL itself stems from the variation of temperature, while the offset between TDL and MS originates from the broadening pressure due to O_2 in air. So drying sampling are recommended, and the broadening pressure effect from calibration gas should be considered.**

- 3. It exists enormous variation of $\delta^{13}C_R$ at a single night. It is hard to find out obvious difference in vertical gradient, and this result met with the condition of pine forest. [Ogee at al, 2003]

- 4. Low temperature can lead to positive $\delta^{13}C_R$ due to the stomatic closure influenced by temperature.

7. Critique of their Interpretation

- **There are roads, car parking lots, resident areas and even factories around the measuring site which can not be ignored at night, especially for the former three negative $\delta^{13}C$ sources, because wind (the primary factor of $\delta^{13}C$ in a short time) will carry negative carbon isotope messages to the site. [R. Wada et al. , 2011]**

- **Some scientists think that making samplings dry may lead to additional discrimination. And with the development of analyzer, the influence of humidity, broadening pressure and concentration can be eliminated at utmost. [Picarro, Peking, 2012]**

8. Implication

- **How to setup an isotope analyzer which includes the setup of calibration, the control of flow, the time of switch and so on.**

- **How to remove error data from instrument itself and ambient factors, to eliminate offset among instruments and to analyze calibrated data.**

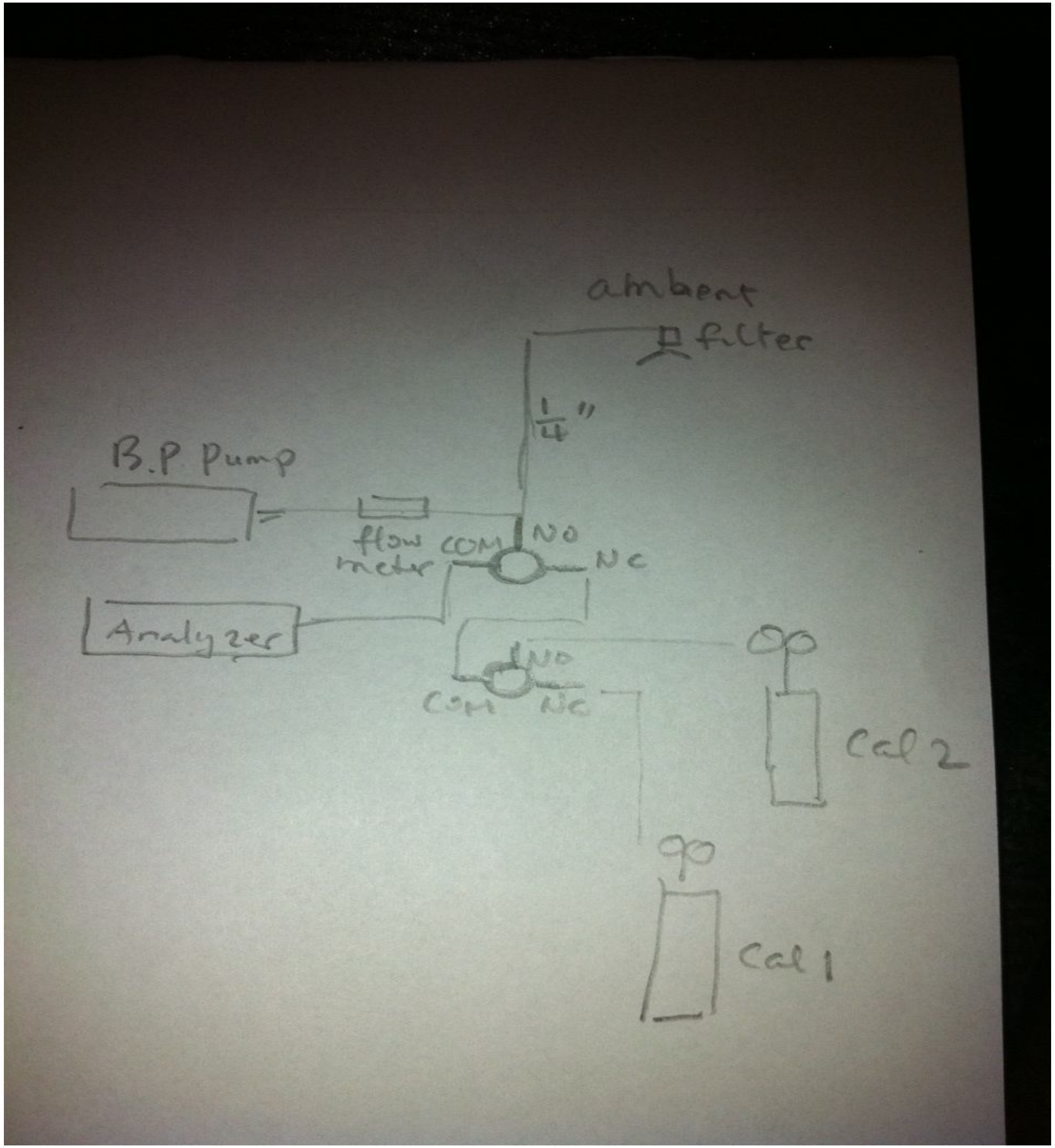


Fig.14 Design of Picarro sampling system. [Xuhui.lee, 2012]

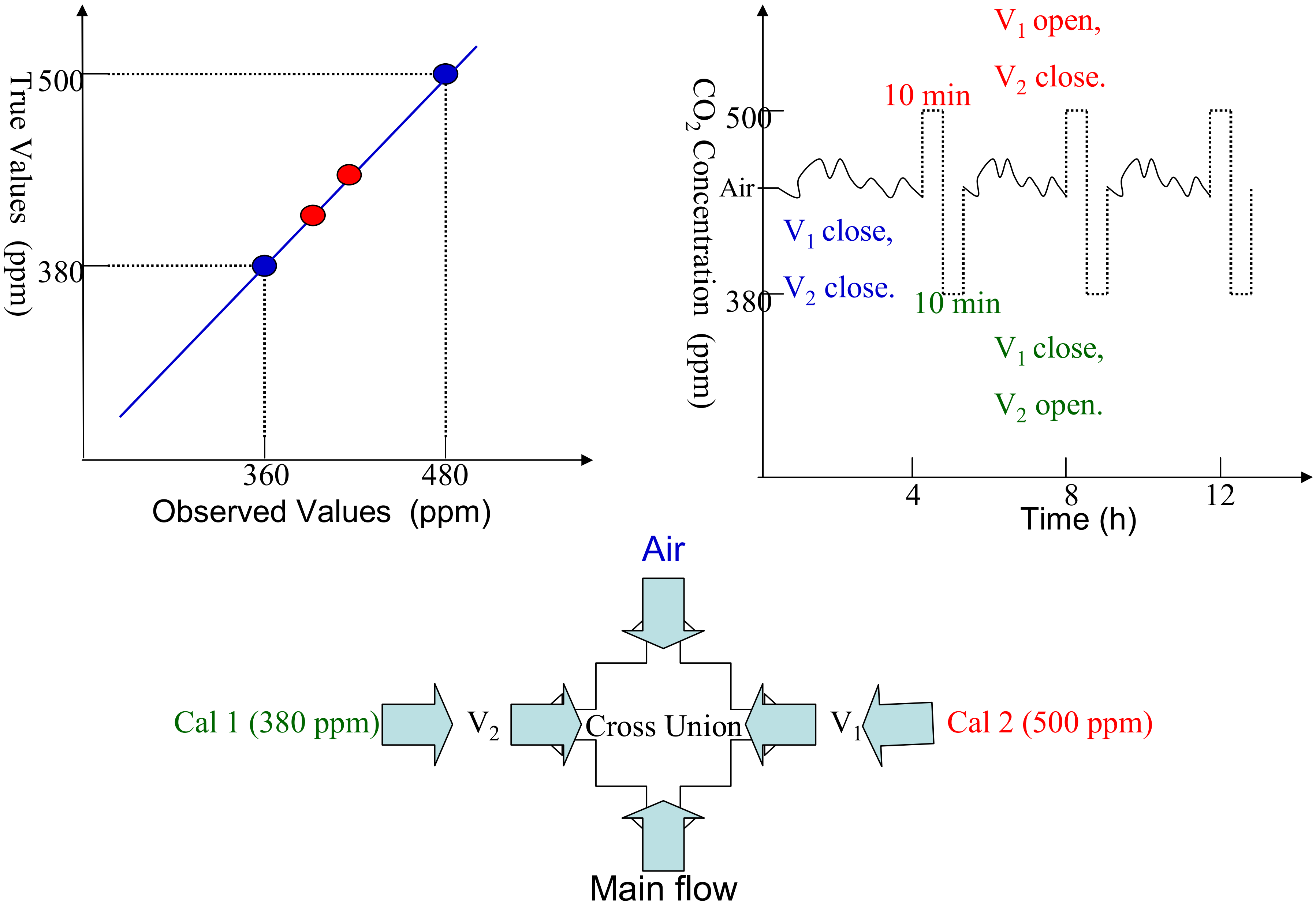


Fig.15 The calibration protocol of TDL with two- point calibration.

(Cal: Calibration gas, V: Valve) [Lee, 2012]

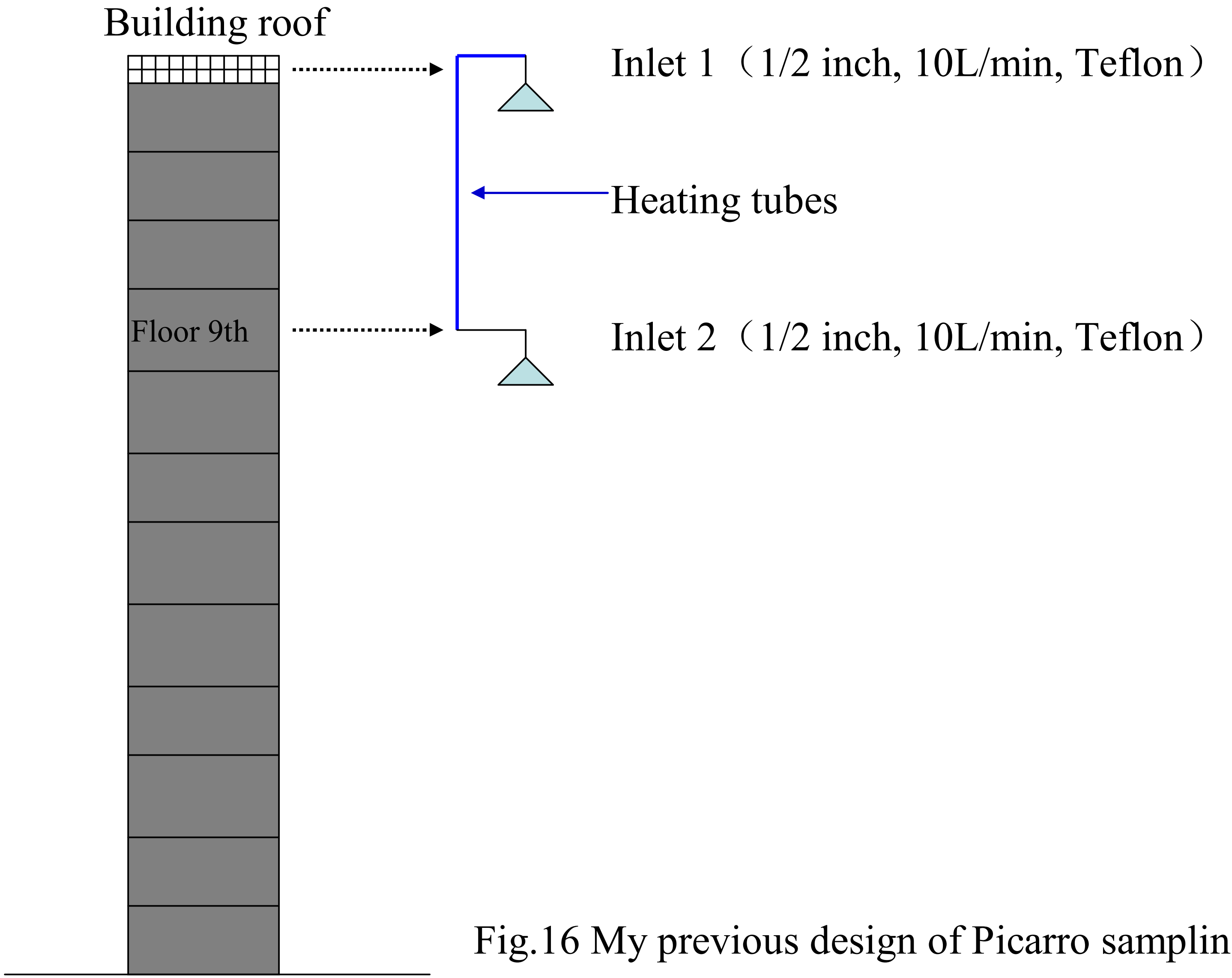
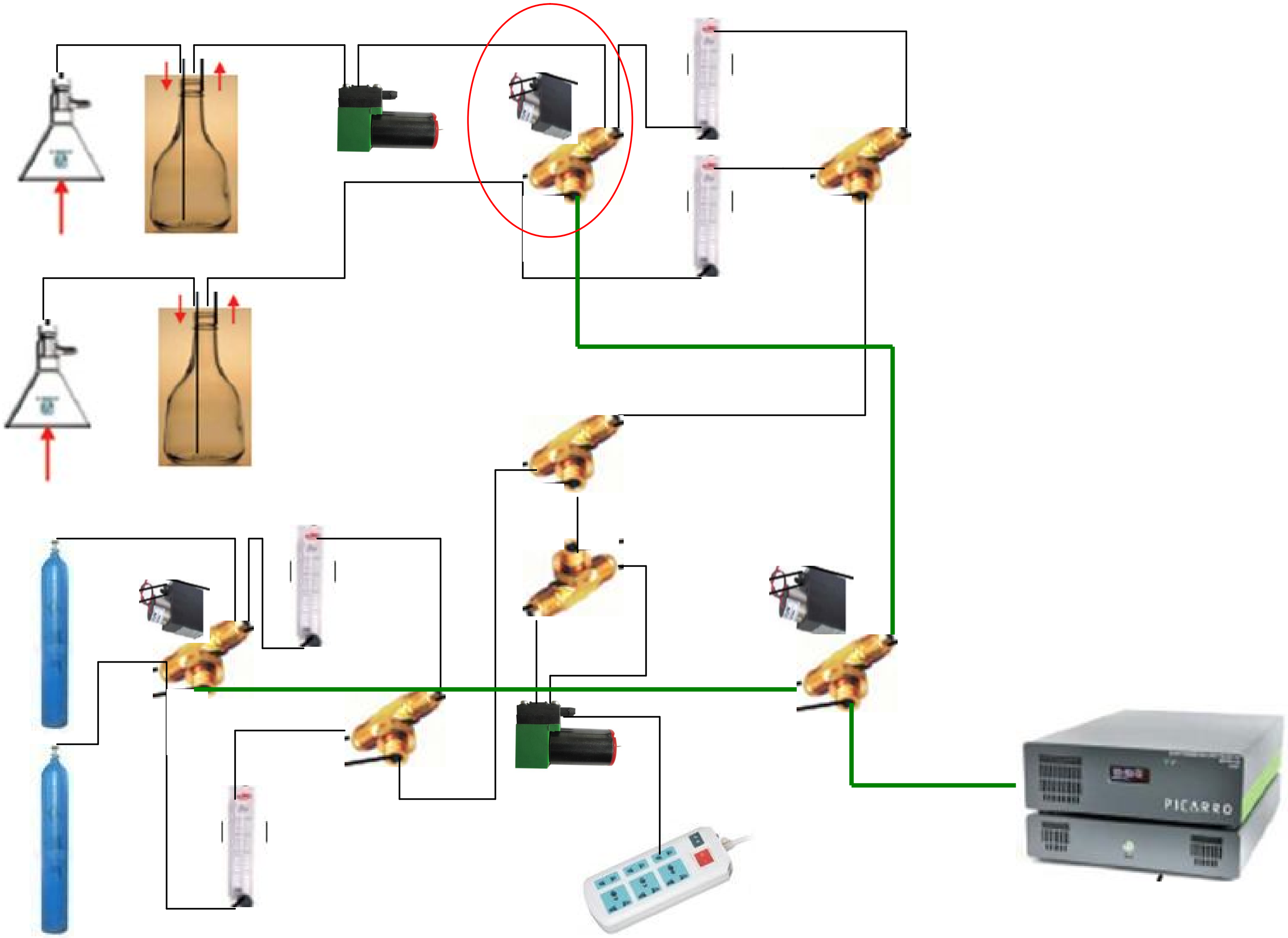


Fig.16 My previous design of Picarro sampling system.



Building roof

Floor 9th

Cal1 380ppm

Interval time 4h

Cal2 500ppm

Fig.17

My previous design of Picarro sampling system.

Thank You