Using ambient CO_2 and CH_4 concentration to calculate the CH_4 emission rate of NanJing

Contents:

1 Theory、Data and Methods

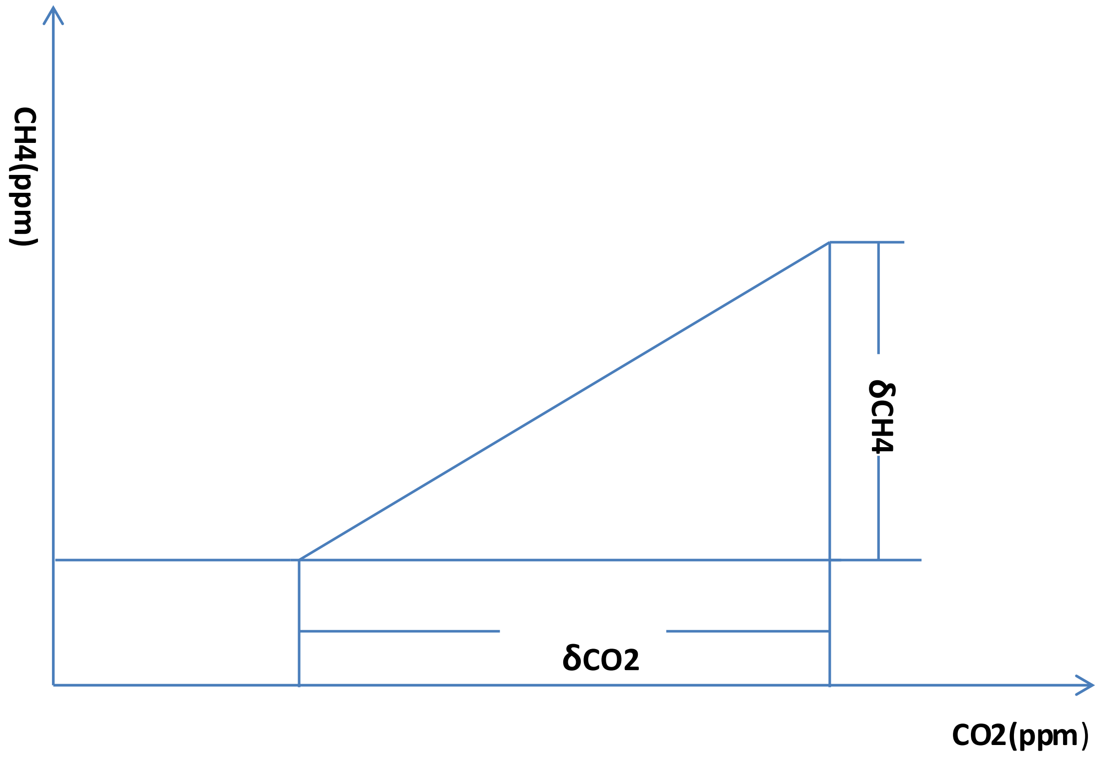
2 Temporal and spatial variation of CO_2 and CH_4

3 CO_2、CH_4 emission from anthropogenic active

4 CH_4 /CO_2(flux ratio)from anthropogenic emissions

Principle

A range (NanJing)of atmosphere was taken as a box， and the changes of CO_2、 CH_4 concentration was caused by adding a certain amount of CO_2, CH_4 to this box ,which was proportional to this adding amount.



Compared the flux ratio of CO_2 to CH_4 from anthropogenic emissions with the mixing ratios of CO_2 and CH_4 in the atmosphere, then, saw if them equal or close， If equal or close, CO_2、 CH_4 could be used to inverse calculation of CH_4 emissions in NanJing.

Data and Methods

Site introduction

The sampling site was set in a observation room that on the eighth floor of Atmosphere Building in NUIST, about 25m above ground surface. Besides a steel plant in about 3km away from the observation point, there were no noteworthy emission sources of carbon. But the observations were affected by emissions from the steel plant due to the weather and monsoon. The all-weather sampling of gas would have representative impact on Pukou.

Experimental apparatus

Picarro analyzer： Picarro G1301 CO_2/CH_4/H_2O analyzer

Temporal and spatial variation of CO2 and CH4

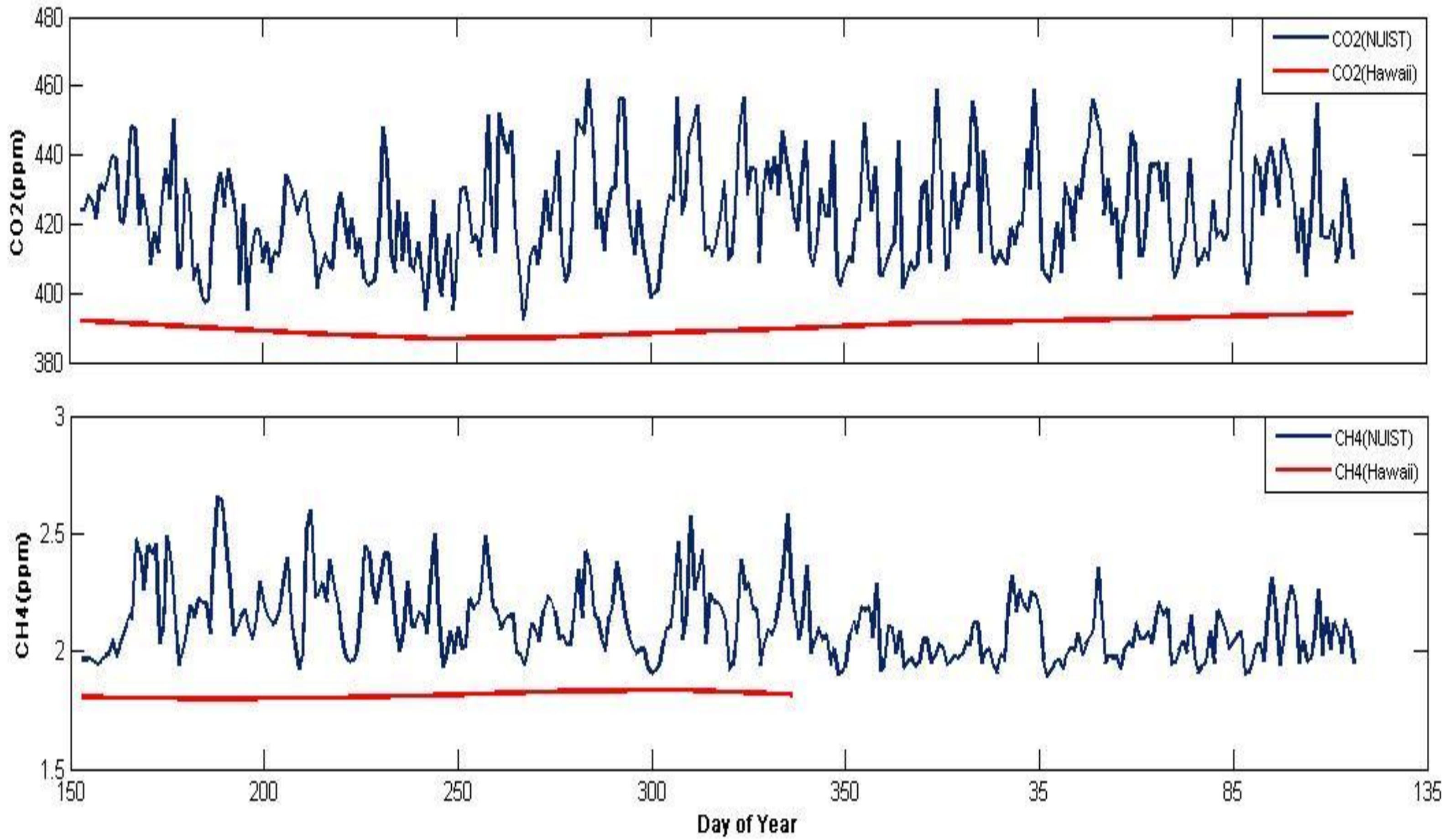


Figure 1. time series of 24 hr mean CO2, CH4 mixing ratios (CO2, CH4 versus DOY). black line---CO2、 CH4 mixing ratios of NUIST ; red line--- CO2、CH4 mixing ratios of Hawaii.

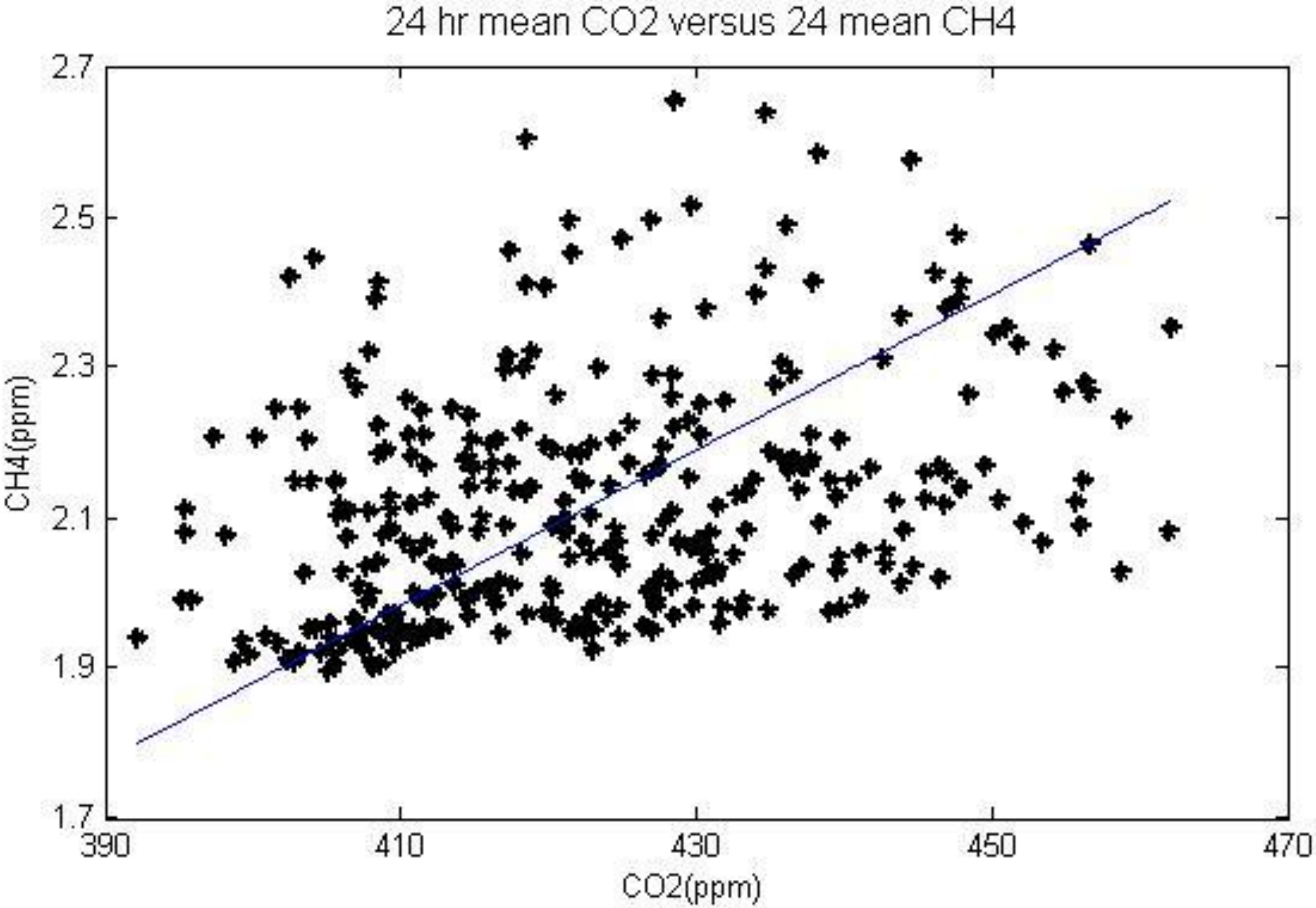


Figure 2. correlation (24 hr mean CO2 versus 24 h mean CH4)

$y=0.0103x-2.24 \quad r=0.337$

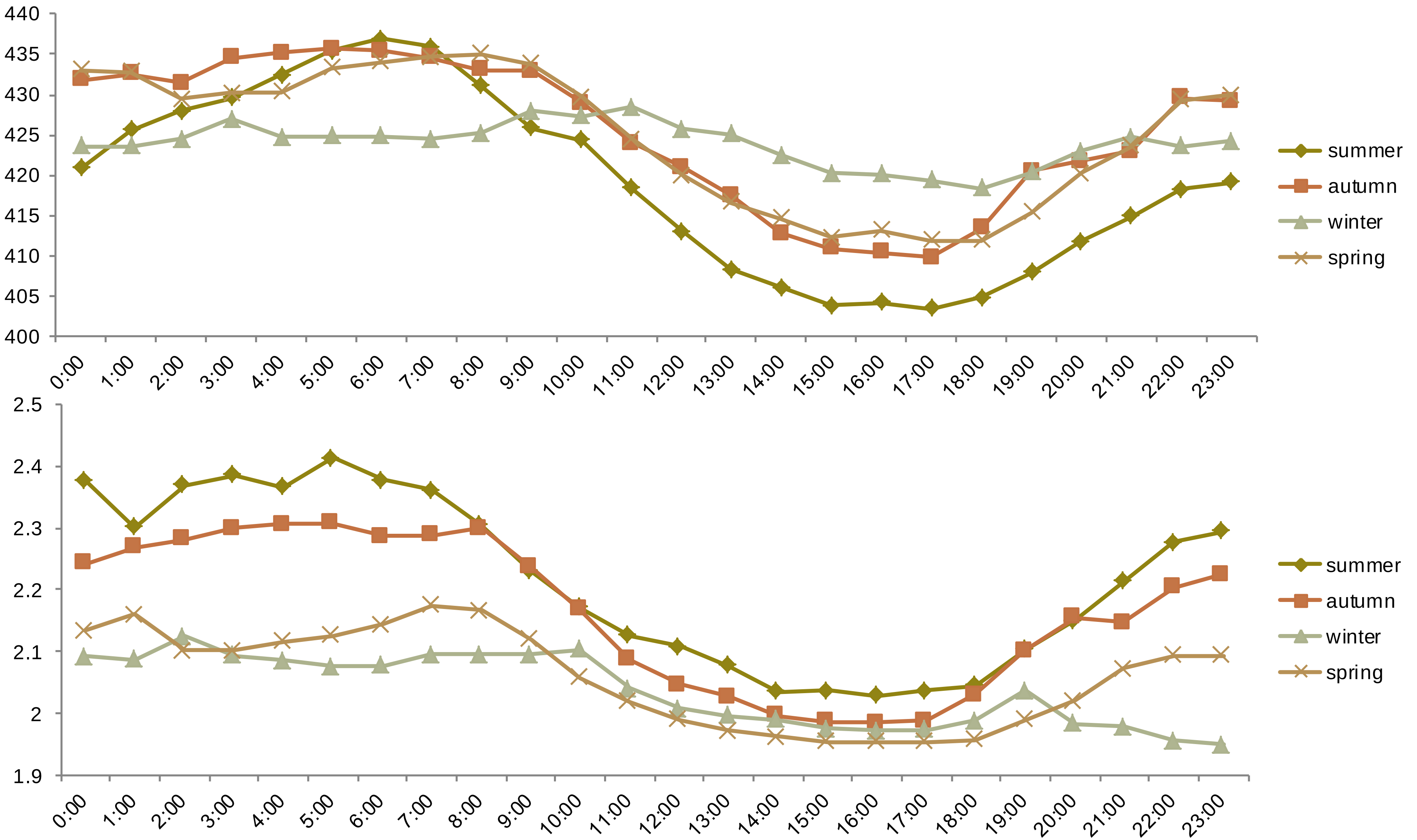


Figure 3. Seasonal average diurnal variations

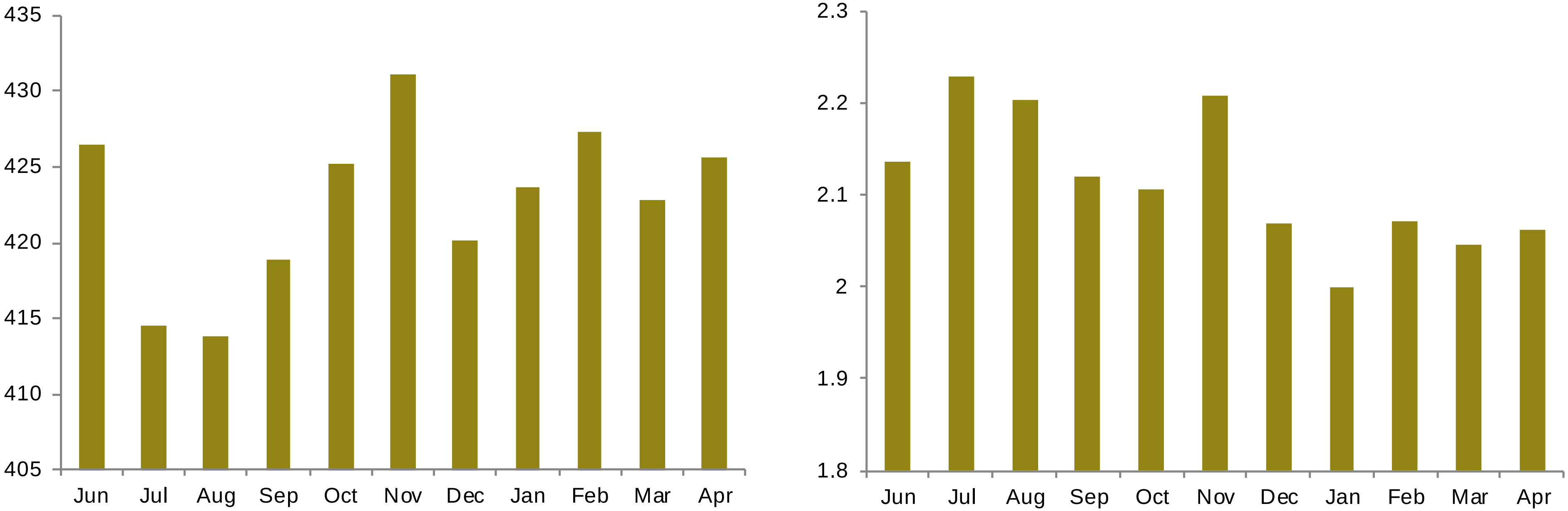


Figure 4. month mean CO_2、 CH_4 mixing ratios .From Nov to Feb, the trend was similar .The data (24hr mean CO_2 CH_4 of Dec Jan Feb) was used to build correlation like the table below. We choose Jan's(with the highest r) midday data to build correlation .

Table 1 correlation (month mean CO_2 versus month mean CH_4)

		slope	r	y
24hr mean	Dec	0.0083	0.679	y=0.0083x-1.41
	Jan	0.0033	0.808	y=0.0033x+0.57
	Feb	0.0086	0.505	y=0.0086x-1.60
midday	Jan	0.0027	0.750	y=0.0027x-1.60

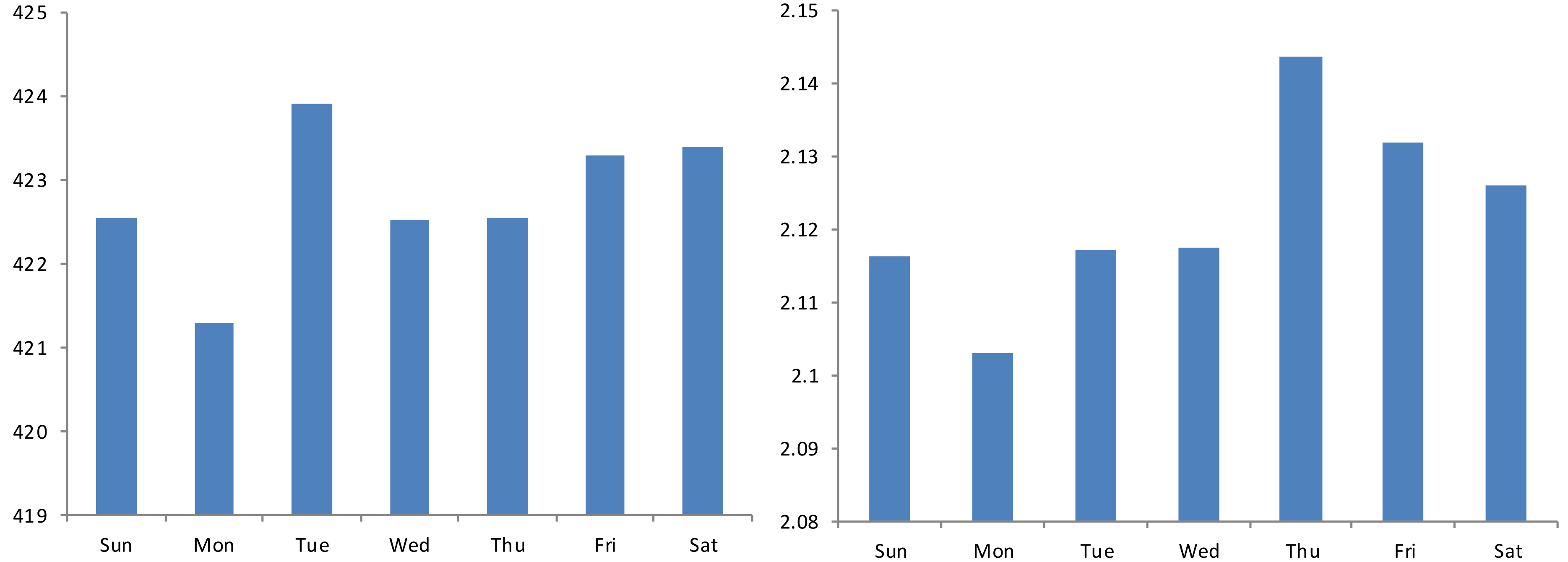


Figure 5. 24 hr mean CO2、CH4 mixing ratios weekly variation

Table 2 correlation (week mean CO2 versus week mean CH4)

	slope	r	y
Sun	0.0084	0.364	Y=0.0084x-1.42
Mon	0.0095	0.362	Y=0.0095x-1.89
Tue	0.0123	0.463	Y=0.012x-3.09
Wed	0.0117	0.315	Y=0.012x-2.84
Thu	0.0101	0.479	Y=0.010x-2.12
Fri	0.0104	0.195	Y=0.010x-2.26
Sat	0.0096	0.239	Y=0.0096x-1.95

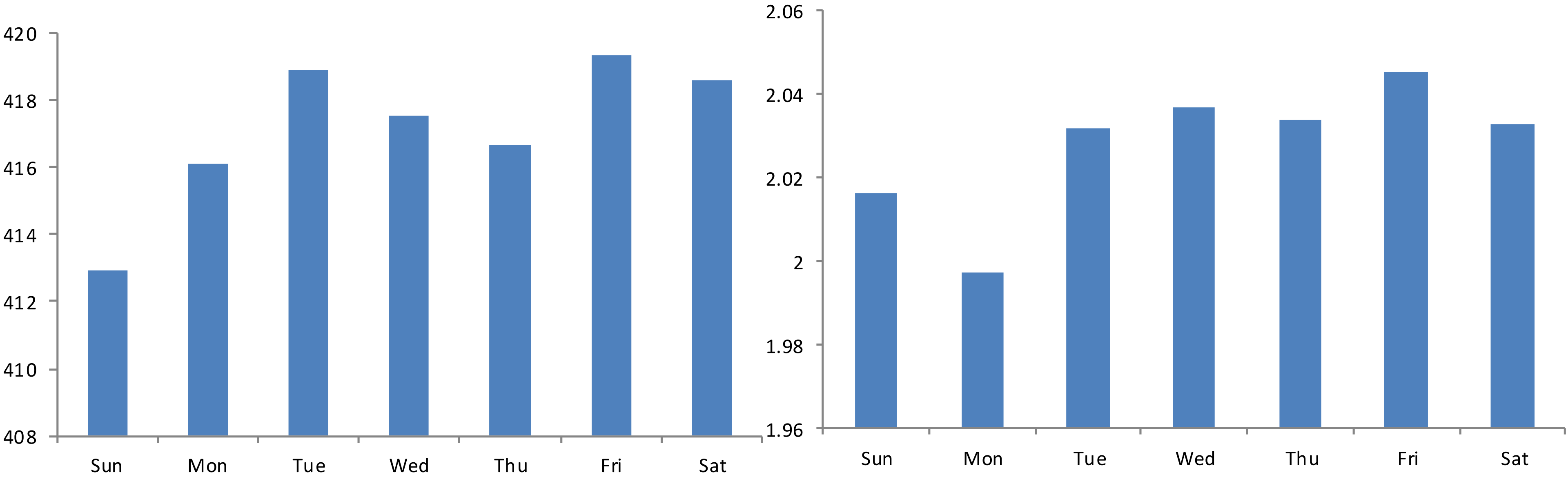


Figure 6. midday CO2、CH4 mixing ratios weekly variation

Table 3 correlation (midday weekly mean CO2 versus CH4)

	slope	r	y
Sun	0.0066	0.375	Y=0.0066x-0.690
Mon	0.0044	0.422	Y=0.0044x+0.174
Tue	0.0067	0.216	Y=0.0067x-0.766
Wed	0.0068	0.509	Y=0.0068x-0.783
Thu	0.0054	0.655	Y=0.0054x-0.232
Fri	0.0064	0.194	Y=0.0064x-0.632
Sat	0.0063	0.150	Y=0.0063x-0.594

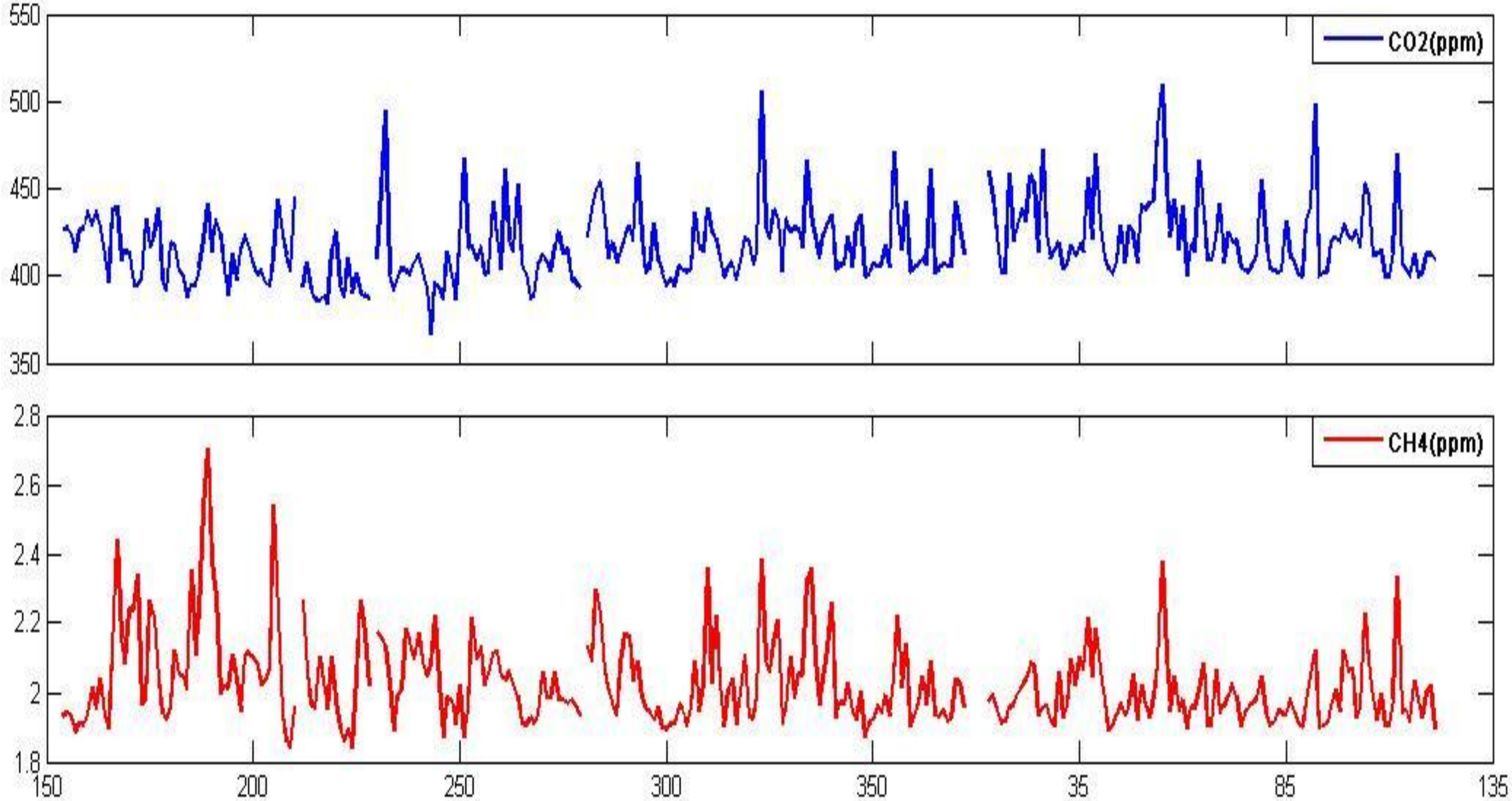


Figure 7. midday mean CO2, CH4 mixing ratios (CO2, CH4 versus DOY).
midday (10:00 to 17:00) – well mixed boundary layer, indicative of city-scale/regional influences

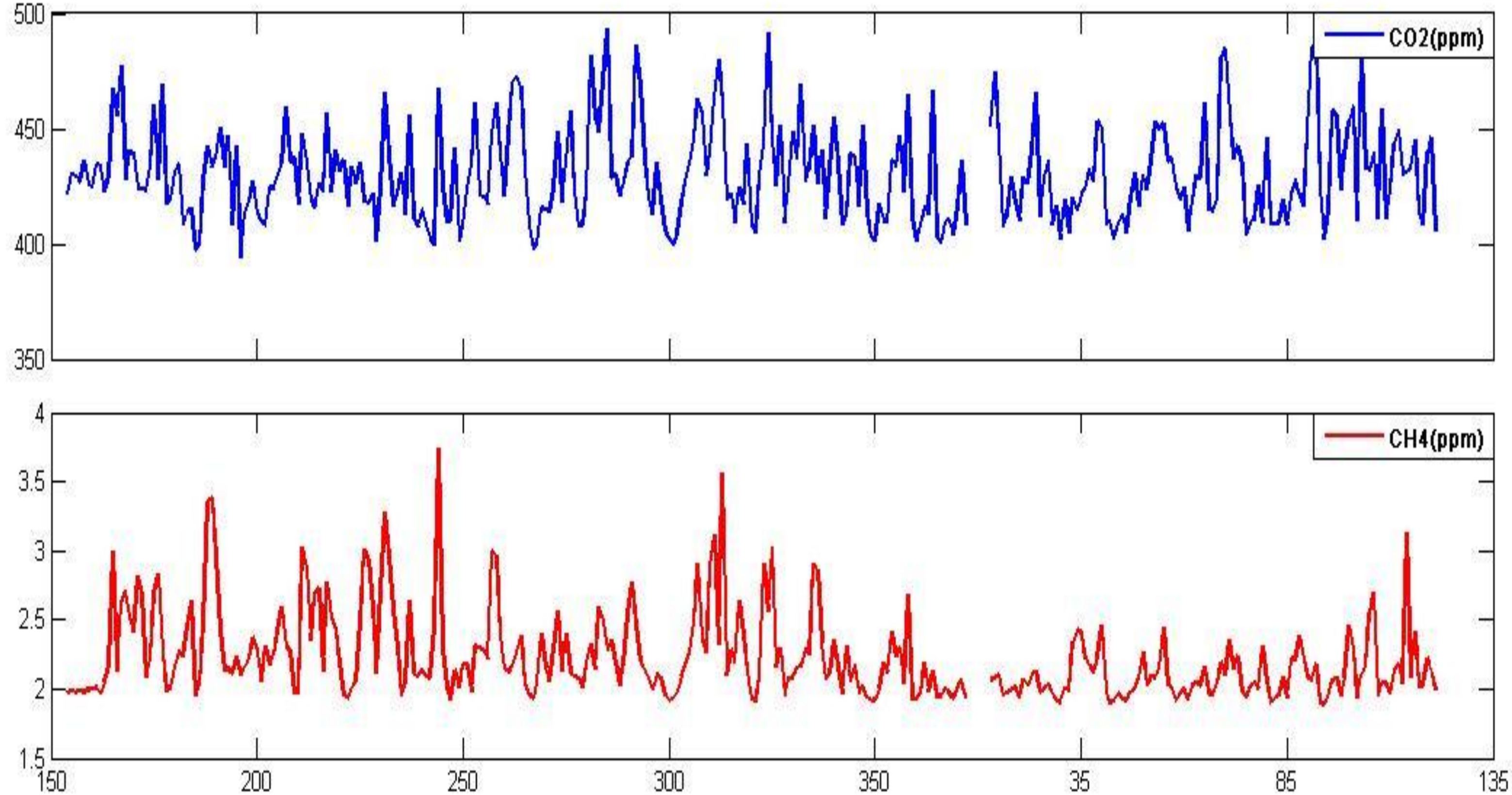


Figure 8. midday mean CO2, CH4 mixing ratios (CO2, CH4 versus DOY).
midnight (23:00 to 05:00) – stable boundary layer, should be more sensitive to local influence
(steel smelters)

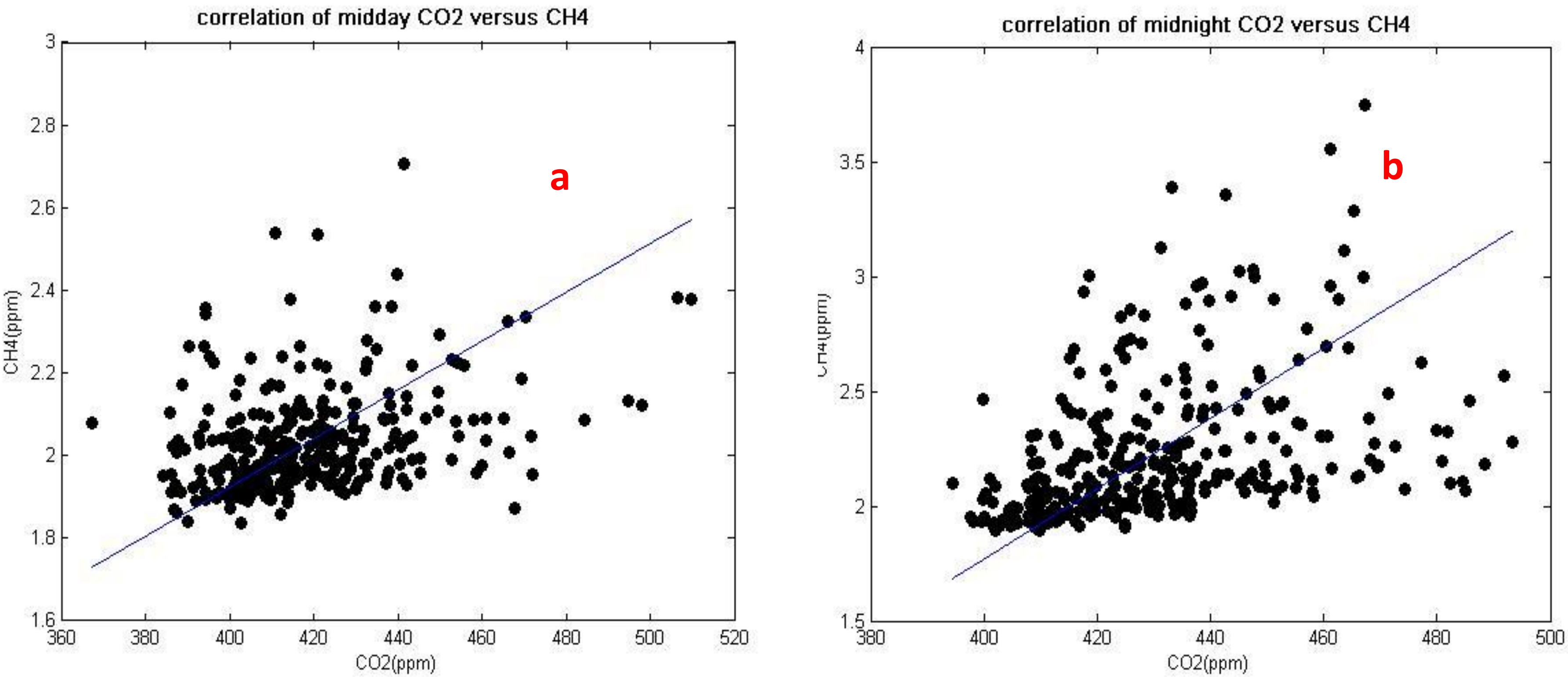


Figure 9. a :correlation of midday CO2 versus CH4
y=0.0059x-0.439 r=0.359
b:correlation of midnight CO2 versus CH4
y=0.015x-4.358 r=0.410

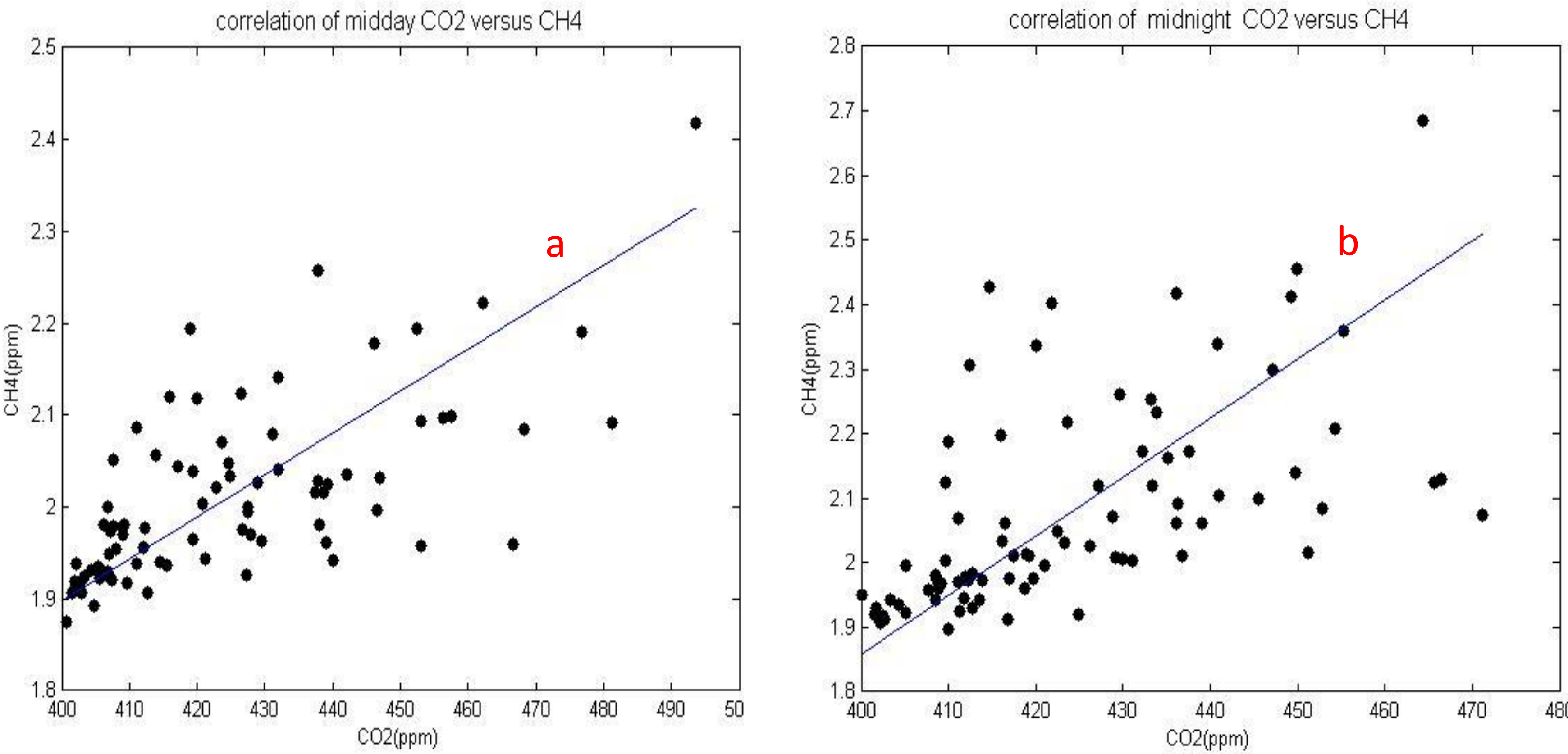


Figure 10. a: correlation of winter midday CO2 versus CH4

y=0.0046x+0.0706 r=0.671

b: correlation of winter midnight CO2 versus CH4

y=0.0092x-1.802 r=0.575

Winter months (Dec/Jan/Feb) – biological signals are weak

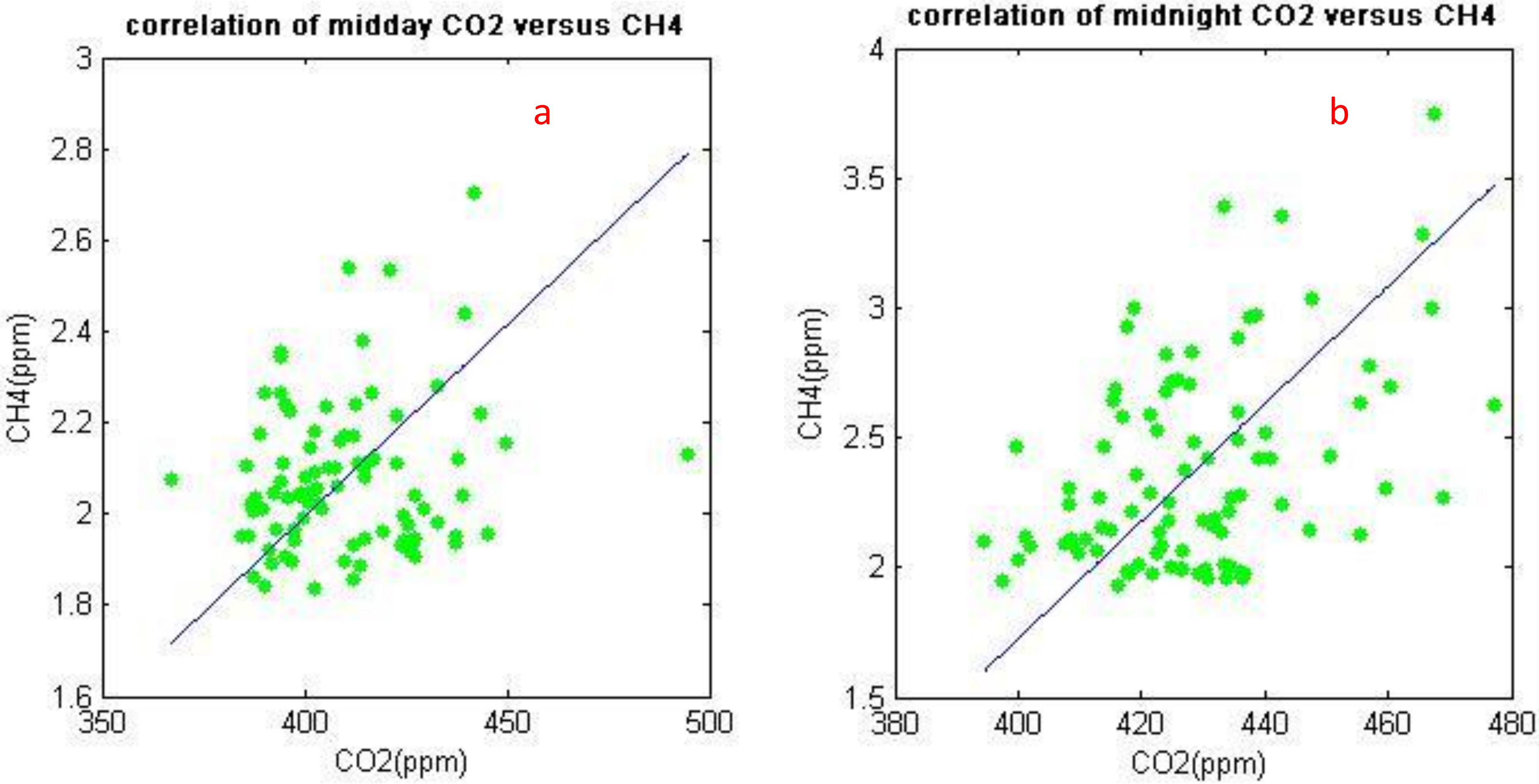


Figure 11. a:correlation of summer midday CO2 versus CH4

y=0.0084x-1.372 r=0.151

b: correlation of summer midnight CO2 versus CH4

y=0.023x-7.327 r=0.4245

Comparison of NUIST CO2 and lake Taihu CO2

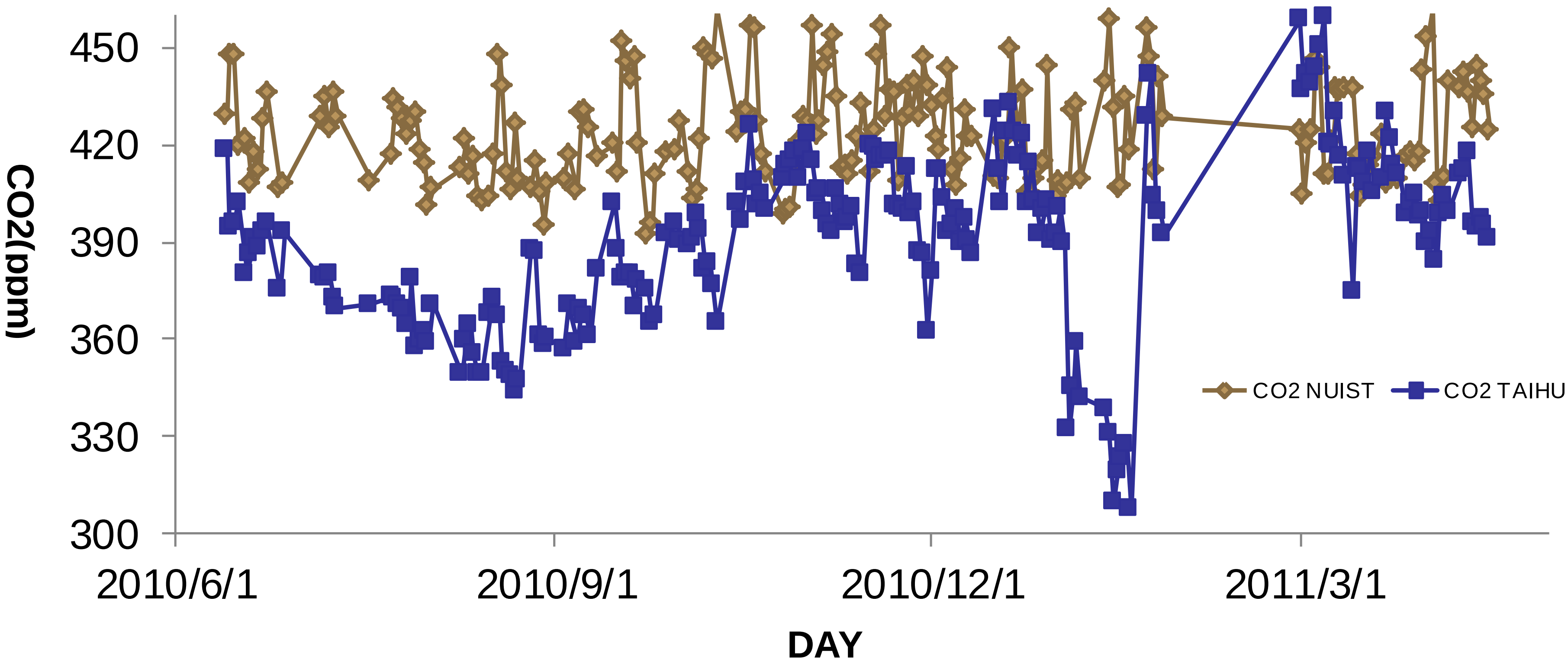


Figure 12. Comparison of NUIST CO2 and lake Taihu CO2: 24 hr mean
did not use rainy days' data as Taihu open-path CO2 analyzer was interfered by rain

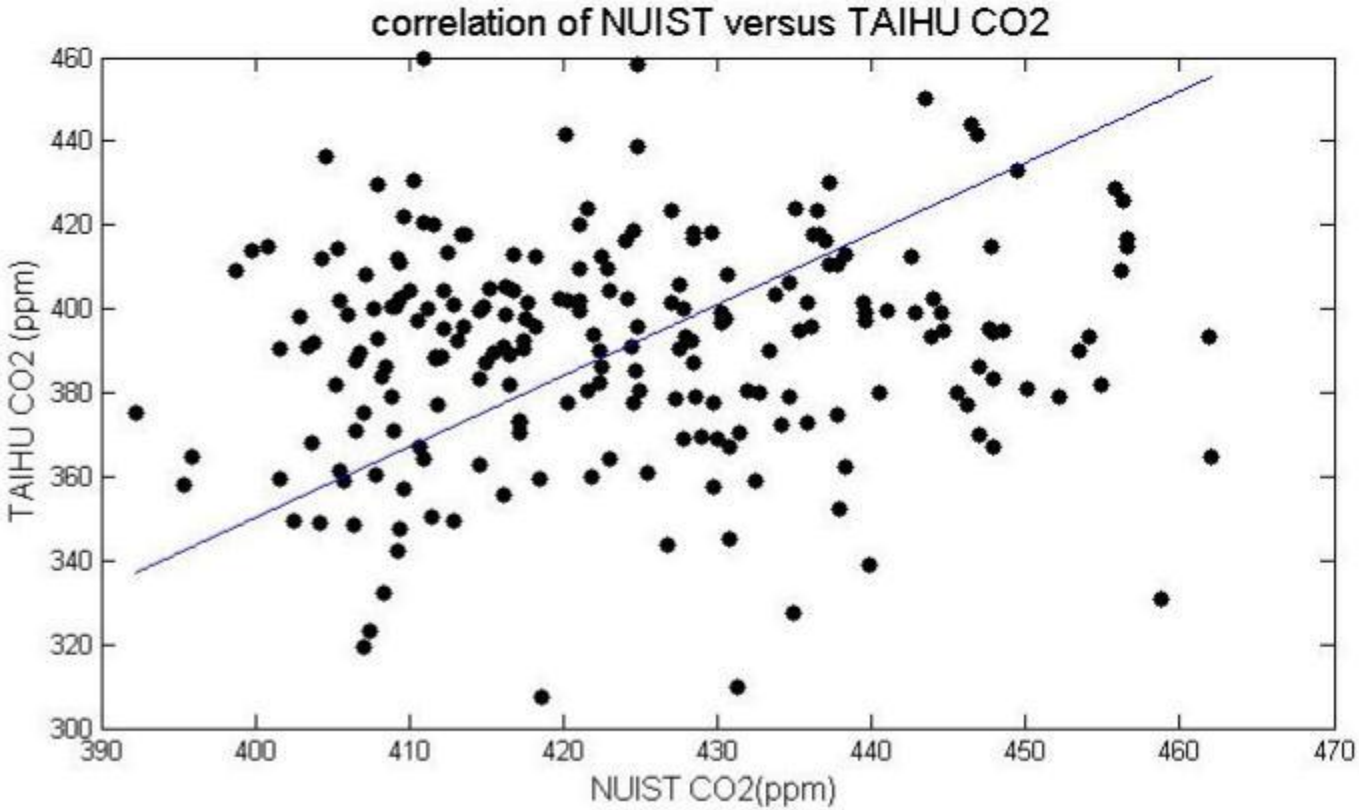


Figure 13. correlation of NUIST CO2 versus lake Taihu CO2(24 hr mean)
y=1.70X-327.8   r=0.125

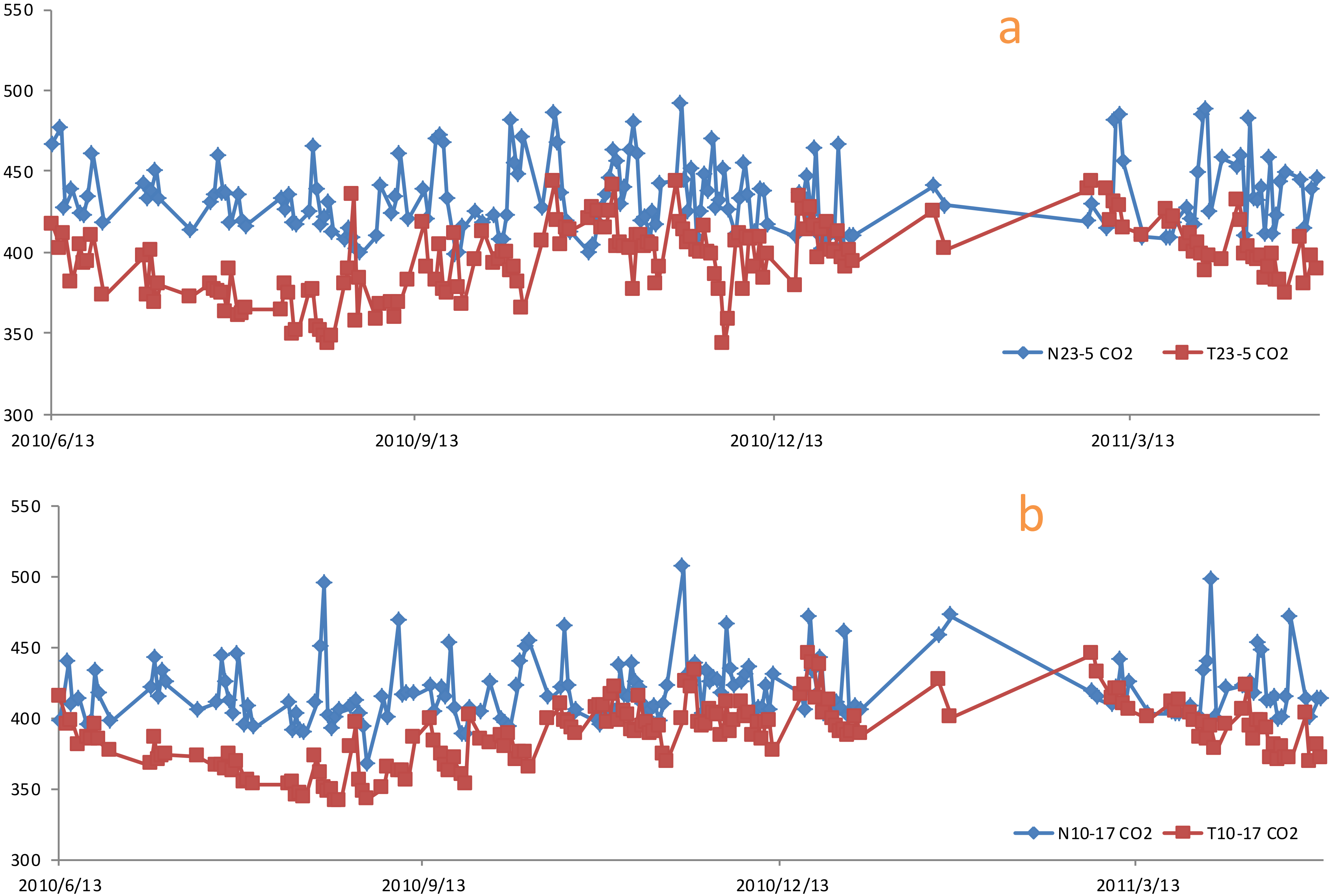


Figure 14. a: time series of NUIST and TAIHU midnight CO2
b:time series of NUIST and TAIHU midday CO2

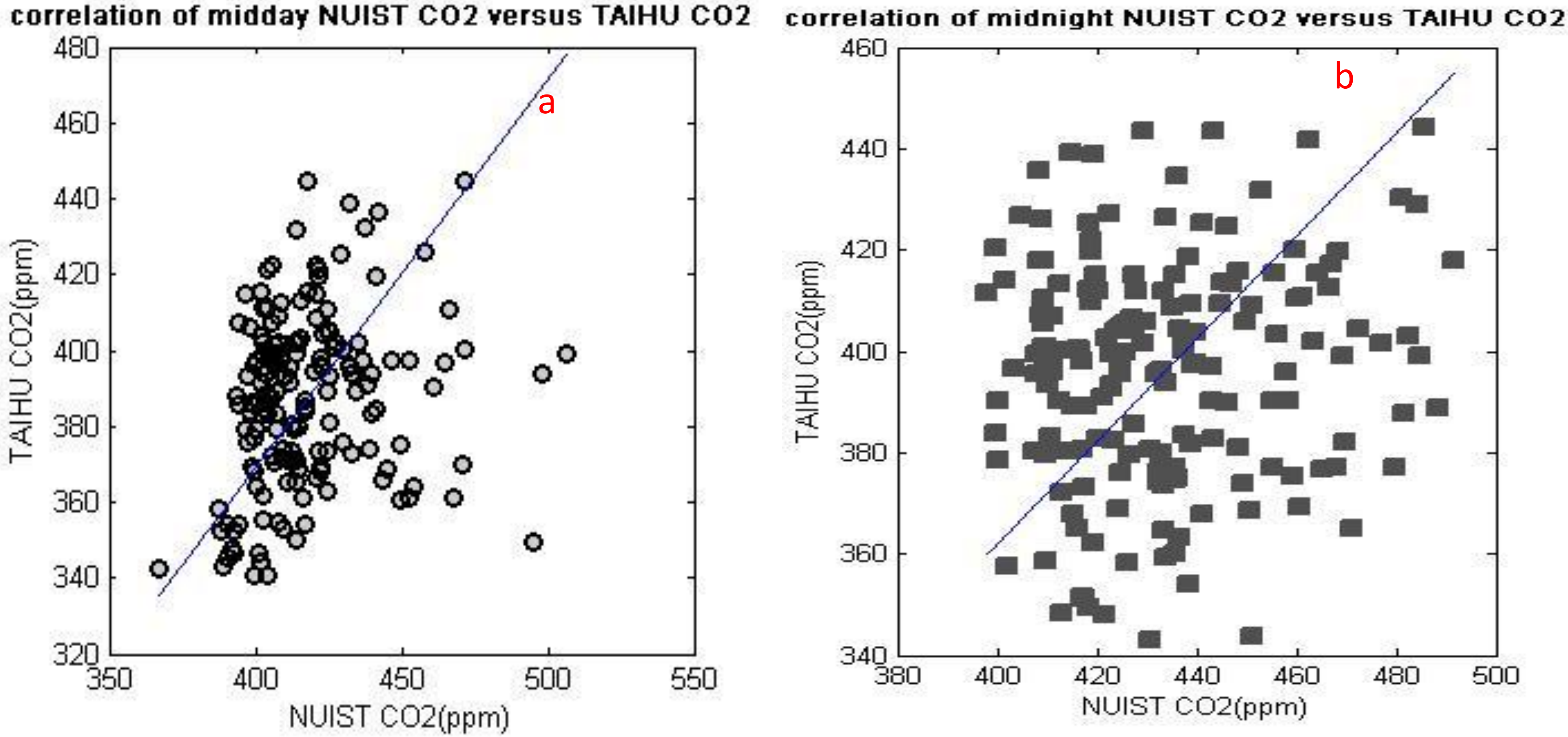


Figure 15. a: correlation of NUIST CO2 versus lake Taihu CO2(midday mean)

$y=1.02x-40.3 \quad r=0.215$

b: correlation of NUIST CO2 versus lake Taihu CO2(midnight mean)

$y=1.01x-44.1 \quad r=0.106$

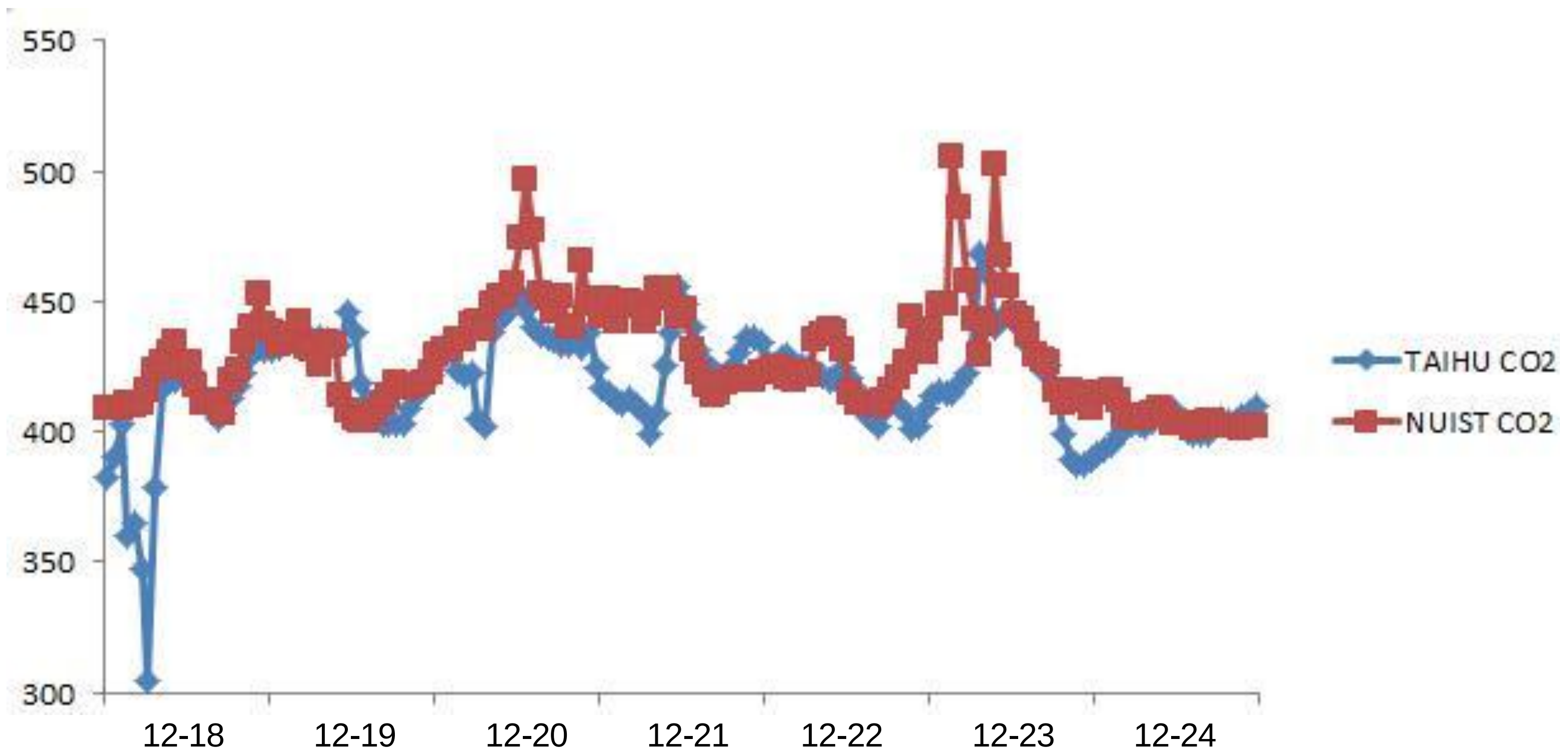


Figure 16. Taihu ‘s winter data missing was serious ,we choose the hour mean data from 12.18to12.24)

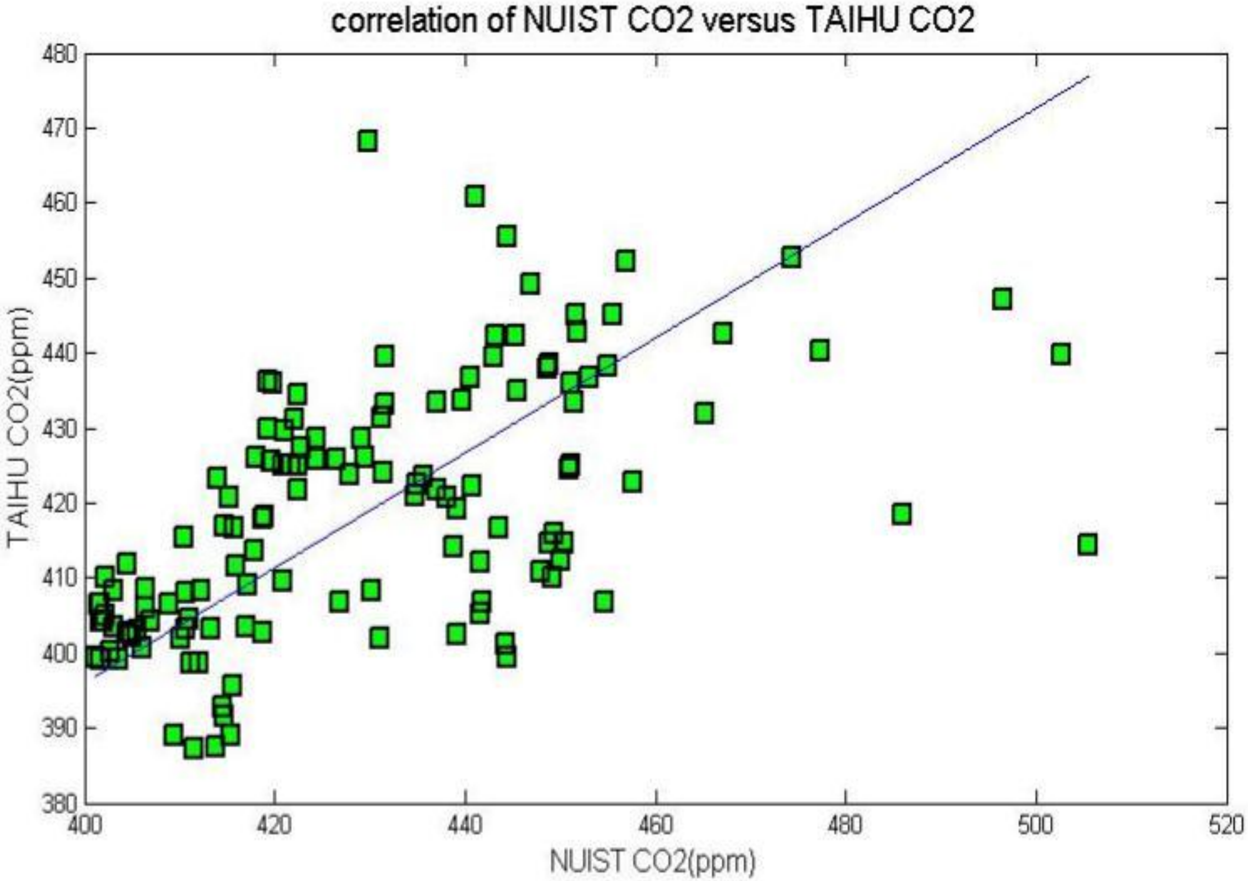


Figure 17. correlation of NUIST winter CO2 versus TAIHU winter CO2

y=0.77x+89.5 r=0.570

the data was choosen from 12-18 to 12-24(hour mean)

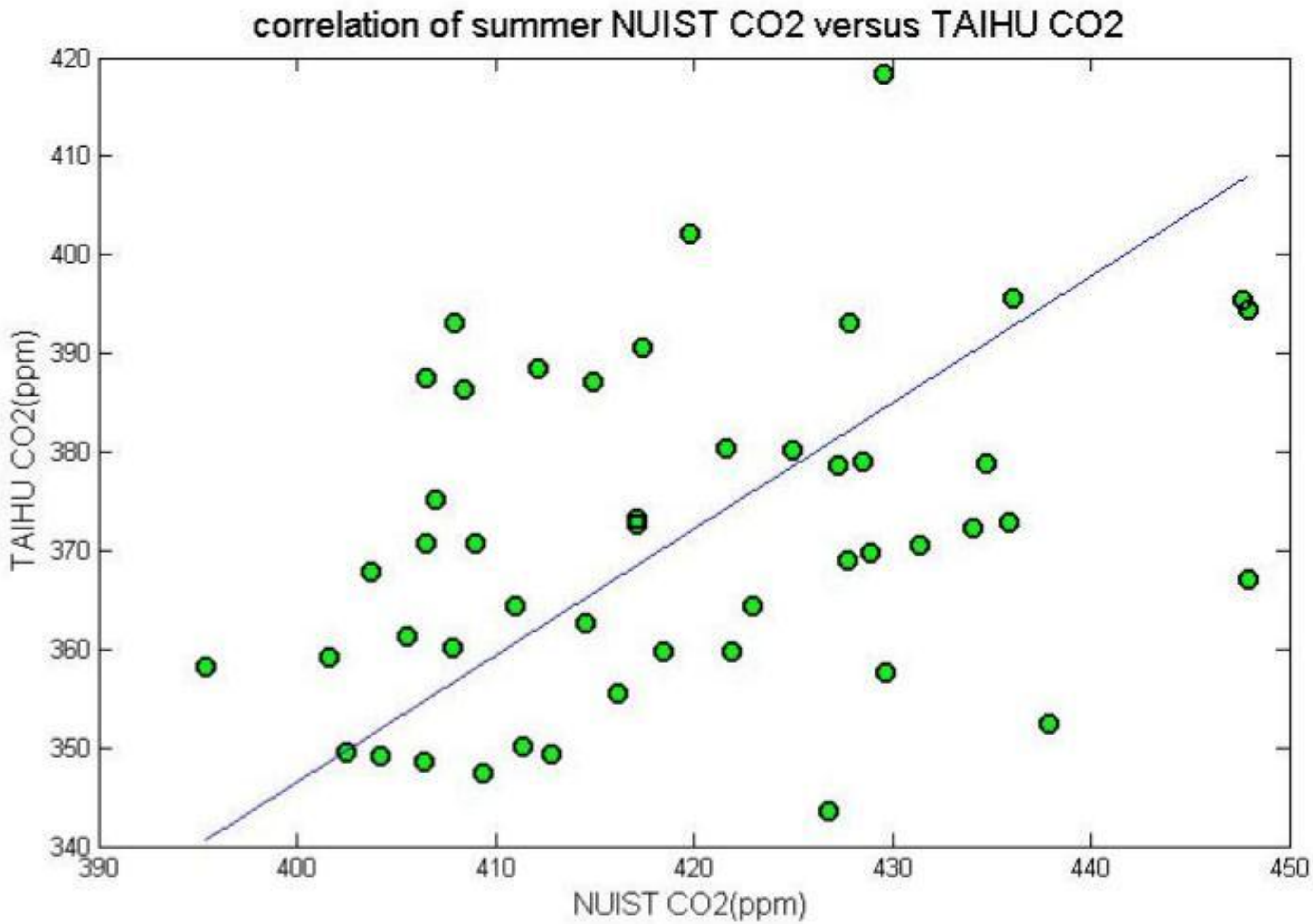


Figure 18. correlation of summer NUIST CO2 versus TAIHU CO2

$y=1.28x-166.6 \quad r=0.344$

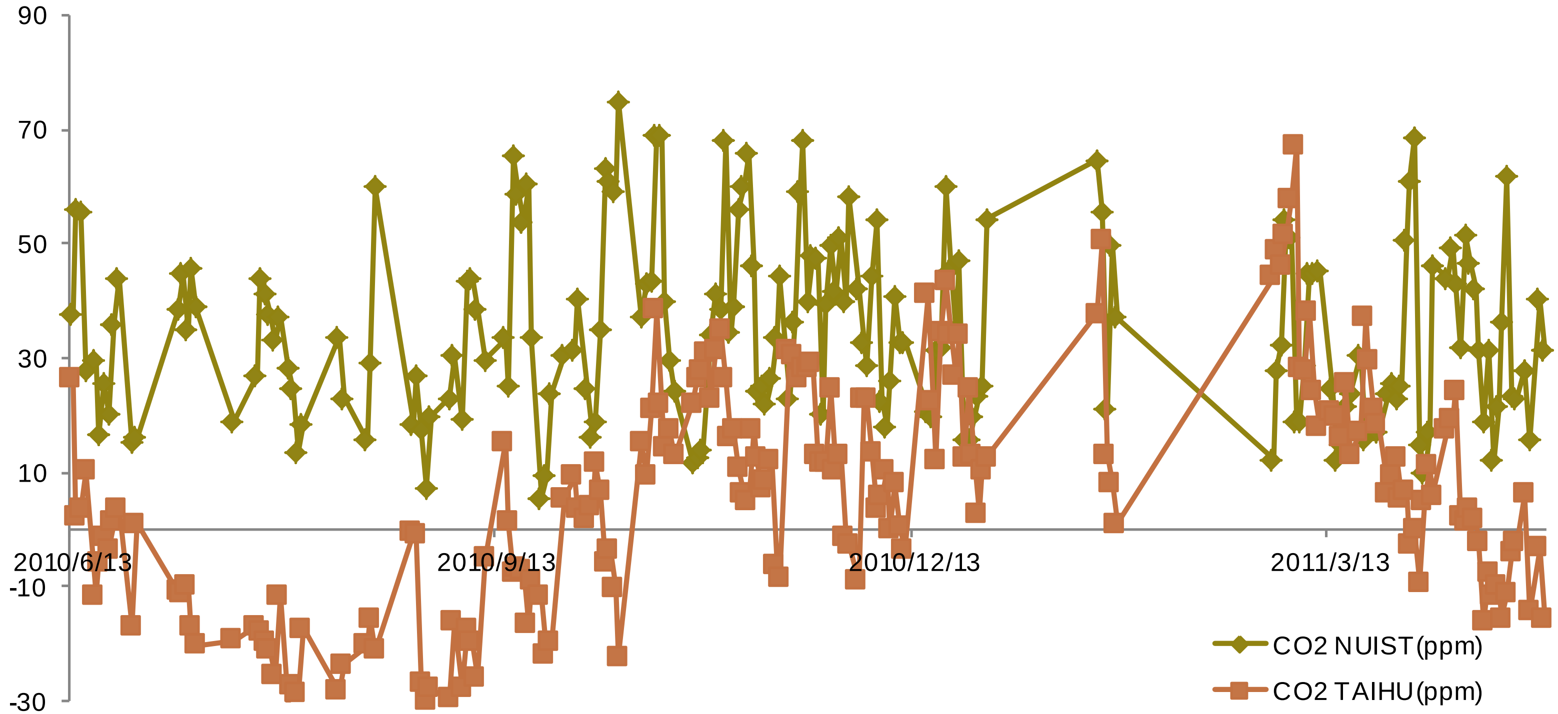


Figure 19. two sites CO2 concentration minus background concentration , the effect of human activity become much more intuitive

CO2、CH4 emission from anthropogenic active

CO2、CH4 emission from fuel combustion

Table 4 CO2、CH4 emission from fuel combustion

燃料类别	消耗量	CO2建议排放系数之不确定性		CO2排放量	CH4建议排放系数之不确定性		CH4排放量
		95%信赖区间下限	95%信赖区间上限	吨	95%信赖区间下限	95%信赖区间上限	吨
原料煤(吨)	1.46E+07	-7.7%	+6.8%	3.93E+07	-70.0%	+200.0%	416.30
燃料煤（吨）	6.44E+06	-7.7%	+6.8%	1.63E+07	-70.0%	+200.0%	172.68
焦炭（吨）	4.26E+06	-10.6%	+11.2%	1.34E+07	-70.0%	+200.0%	124.72
原油（吨）	2.05E+07	-3.0%	+3.0%	6.97E+07	-66.7%	+233.3%	2853.30
汽油(吨)	3.38E+04	-2.6%	+5.3%	1.03E+05	-69.6%	+244.0%	37.28
煤油（吨）	1.40E+03	-1.5%	+2.5%	4.26E+03	-66.7%	+233.3%	0.18
柴油（吨）	1.23E+05	-2.0%	+0.9%	3.91E+05	-66.7%	+233.3%	20.63
燃料油（吨）	2.37E+05	-2.5%	+1.8%	7.05E+05	-66.7%	+233.3%	27.45
液化石油气(吨)	2.46E+05	-2.4%	+4.0%	7.97E+05	-70.0%	+200.0%	782.85
其他油品（吨）	1.04E+07	-1.5%	+1.5%	3.59E+07	-66.7%	+233.3%	1469.83
天然气（万立方米）	1.55E+05	-3.2%	+3.9%	3.24E+06	-70.0%	+200.0%	57.84
炼油气(吨)	6.73E+05	-16.3%	+19.8%	2.09E+06	-70.0%	+200.0%	36.26
炼焦炉气（万立方米）	6.18E+04	-16.0%	+21.8%	5.75E+05	-70.0%	+200.0%	12.92
高炉气（万立方米)	1.37E+06	-15.8%	+18.5%	1.07E+07	-70.0%	+200.0%	318.44
热力（百万千焦）	7.78E+07			8.34E+06			777.84
电力（万千瓦时）	2.03E+06			2.58E+07			240.34
总排放量（吨）				2.28E+08			7367.55

CH4 emission from landfill

Table 5 three models for landfill CH4 emission

模型	公式	参数含义
IPCC推荐模型	$Q=\sum_x \{[A\bullet k\bullet MSW_T(t)\bullet MSW_F(t)\bullet L_0(t)]\bullet e^{-k(t-x)}\}$	Lo---垃圾产甲烷潜能； Q---第t年产生的甲烷，m^3/a； A---加和修正系数，$A=(1-e^{-k})/k$； K---甲烷产生速率常数； MSWT(t)---第t年垃圾产生量，t/a； MSWF(t)---第t年垃圾填埋百分比，%。
Gardner-Probert 模型	$P=C_d X\sum_{i=1}^{n} F_i(1-e^{-Kit})$ $MP=MP_0\exp\left[-\frac{t}{d}\right],\ D(t)=-\frac{dMP}{dt}\Rightarrow D(t)=\frac{MP_0}{d}\exp\left[-\frac{t}{d}\right]$	P---单位质量垃圾在t年内产CH4量(kg•kg-1)； Cd---垃圾中可降解有机碳的比率(kg•kg-1)； X---填埋场产气中CH4的分额； n---可降解组分的总数； Fi---各降解组分中有机碳占总有机碳分数； Ki---各降解组分的降解系数(1/a)； t---填埋时间(a)。
Marticorena 模型	$F(t)=\sum_{i=1}^{t} T_i\bullet D(t-i)=\sum T_i\left(\frac{MP_0}{d}\exp\left[-\frac{t-i}{d}\right]\right)$	MP---t时间垃圾产CH4量($Nm^3\cdot t^{-1}$)； MP0---新鲜垃圾产CH4潜能($Nm^3\cdot t^{-1}$)； t---时间(a)； d---垃圾持续产CH4时间(a)； D(t)---垃圾产CH4速率($Nm^3\cdot t^{-1}a^{-1}$)； F(t)---填埋场CH4产率($Nm^3\cdot a^{-1}$)； Ti---第i年填埋垃圾量(t)。

Table 6 CH4 discharge value estimated by three models

降解时间 模型	4年	5年	6年	7年	8年	mean	标准差
IPCC模型	63262.28	63524.27	63587.15	66798.18	61090.98	61488.23	4329.67
Gardner-Probert 模型	58790.02	62215.38	64814.67	66784.54	68430.04		
Marticorena模型	58448.46	57409.53	56649.71	55699.29	54818.88		

CH4 emission from Domestic and Industrial Wastewater Treatment

Table 7 CH4 emission from Domestic wastewater (Septic Systems)

Factor	Value	Units	Source/Comments
Septic Systems			
% BOD Directed to Septic Systems	21	%	American Housing Survey - U.S. Census Bureau
per Capita BOD Production Rate	0.04	kg/cap/day	IPCC Guidelines, Table 6.4
NanJing Population for 2009	7.7131	millions	http://www.njtj.gov.cn/2004/2010/renkou/3-1.htm
Domestic Wastewater BOD Produced	112611	t	=7713100x 0.04kg BOD/capita/day x 365 days/1000
Default Max CH4 Producing Capacity	0.6	kg CH4/kg BOD	IPCC Guidelines, Table 6.2
MCF-septic	0.5	unitless	IPCC Guidelines, Table 6.3, 1/2 of BOD settles in septic tank
Septic Systems Emissions	7094.51	t CH4	=21% x 112611t BOD x 0.6 tCH4/t BOD x 0.5

Table 8 CH4 emission from Domestic wastewater(Centrally Treated "Anaerobic" Systems

Centrally Treated "Anaerobic" Systems			
% BOD Directed to Collection Systems	79	%	American Housing Survey - U.S. Census Bureau
per Capita BOD Production Rate	0.04	kg/cap./day	IPCC Guidelines, Table 6.4
NanJing Population for 2009	7.7131	millions	http://www.njtj.gov.cn/2004/2010/renkou/3-1.htm
Domestic Wastewater BOD Produced	112611	t	==7713100x 0.04kg BOD/capita/day x 365 days/1000
Default Max CH4 Producing Capacity	0.6	kg CH4/kg BOD	IPCC Guidelines, Table 6.2
Flow to Anaerobic / Total Collected Flow	0.05	unitless	Clean Watershed Needs Survey - EPA
MCF-Anaerobic Systems	0.8	unitless	IPCC Guidelines, Table 6.3
Centrally Treated "Anaerobic" Systems	2135.11	t CH4	=79% 112611t BOD x 0.6 kg CH4/kg BOD x 0.05 x 0.8

公式 6.4
源自工业废水的 CH_4 排放总量

$$CH_4\ 排放 = \sum_i \left[\left(TOW_i - S_i \right) EF_i - R_i \right]$$

其中：

CH_4 排放量 = 清单年份的 CH_4 排放量，单位为 kg CH_4/年

TOW_i = 清单年份源自工业 *i* 的废水中可降解有机材料总量，单位为 kg COD/年

i = 工业部门

S_i = 清单年份以污泥清除的有机成分，单位为 kg BOD/年

EF_i = 工业 *i* 的排放因子，单位为 kg CH_4/kg COD
清单年份所用的处理/排放途径或系统

如果一家工业采用了不止一个处理作法，则此因子需要一个加权平均值。

R_i = 清单年份回收的 CH_4 量，单位为 kg CH_4/年

Table 9 CH4 emission from Industrial wastewater

指　标	2000年	2005年	2006年	2007年	2008年	2009年	CH4排放量（t）
工业废水排放量（亿吨）	6.49	4.7	4.32	4.04	3.77	3.63	
废水中化学需氧量排放量（万吨）	3.61	3.03	2.84	2.69	2.56	2.25	5625

CH4 emission from livestock

源自某一牲畜类别的肠道发酵排放

$$\text{排放} = EF_{(T)} \bullet \left(\frac{N_{(T)}}{10^6} \right)$$

其中：

排放 = 肠道发酵中的甲烷排放，Gg CH_4 /年

$EF_{(T)}$ = 圈养的牲畜种群的排放因子，kg CH_4/头/年

$N_{(T)}$ = 国内牲畜种类/类别 T 的头数

T = 牲畜的种类/类别

源自粪便管理中的甲烷排放

$$CH_{4\text{粪便}} = \sum_{(T)} \frac{\left(EF_{(T)} \bullet N_{(T)} \right)}{10^6}$$

其中：

$CH_{4\text{粪便}}$ = 来自某种限定种群粪便管理中的 CH_4 排放，Gg CH_4/年

$EF_{(T)}$ = 来自某种限定牲畜种群的排放因子，kg CH_4/头/年

$N_{(T)}$ = 国内牲畜品种/类别 *T* 的数量

T = 牲畜的品种/类别

Table 10 CH4 Emission from livestock

指　标	当年出栏头数	年末存栏头数	动物肠道发酵CH4排放 (t)	动物粪便管理系统中的CH4排放 (t)
黄牛（万只）	0.05	0.06	60.5	1.1
良种及改良乳牛（万只）	0.07	1.76	1116.3	256.2
水牛（万只）	0.58	1.24	1001	18.2
猪（万头）	99.08	52.01	1510.9	4532.7
山羊（万只）	32.65	12.79	2272	77.25
家禽（万只）	3197.2	1052.5		849.94
兔（万只）	25.83	10.05		28.70
总量			5960.7	5764.1

选择排放因子的不确定性：±30%

CH_4/CO_2 (flux ratio)from anthropogenic emissions

Table 11 various anthropogenic CH_4 emission categories

	CH4(min)	CH4(mean)	CH4(max)	CO2
Fuel	3062	7349	21482	2.17E+08
Landfill	54819	61488	68430	
Wastewater	14855	14855	14855	
Livestock	8207	11725	15242	
Total	80943	95417	120009	

Table 12 CH_4/CO_2(flux ratio)

	Min	mean	max
CH_4/CO_2(flux ratio)	0.001	0.0012	0.0015

Compare the slope as listed above to the flux ratio , the most similar one was the slope of Jan's midday (table 1) 0.0027.

Use ambient CO_2 and CH_4 concentration to calculate the CH_4 emission rate of NanJing ?