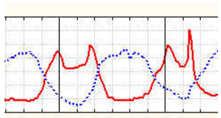
Seasonal and Diurnal CO_2 Patterns at Diekirch, LU, 2003 - 2005



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The original html version can be found at: http://meteo.lcd.lu/papers/co2_patterns/co2_patterns.html

Abstract:

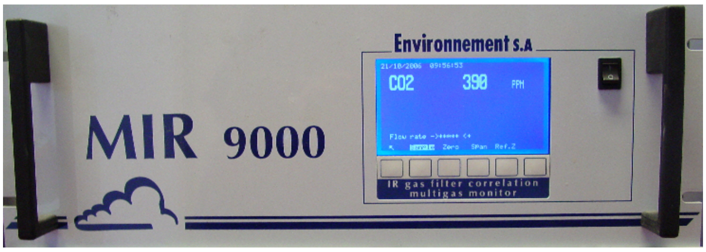
The seasonal and diurnal variations of the CO_2 mixing ratio measured at meteoLCD, Diekirch, LU from 2003 to 2005 are analysed for typical variation patterns and relationships with environmental parameters. For seasonal and long term mean CO_2 levels, it can be shown that sunshine (duration and energy) plays a variable and minor role, whereas the daily amplitude of air temperature and CO_2 variations correlate positively over the whole year as well for winter and summer months. Increased wind velocities always lower CO_2 levels, whatever the wind direction may be. Storm "Franz" passing over Diekirch the 11th Jan.07 allowed to quantify this relationship by a simple mathematical model, which might be used to compute an asymptotic CO_2 level close to the global mixing ratio. Diurnal variability (exceeding 100 ppm) shows up in 3 characteristic pattern due to different atmospheric mixing caused by wind speed disrupting ABL inversions.

Index:

1. How is CO_2 measured at meteoLCD?

Starting 28 Feb. 2002, the MIR 9000 from Environment SA, an EPA compliant professional NDIR instrument is used for CO_2 measurements. The specifications are:

range used:	0-500 ppmV
span and zero drift:	+/- 2% of full scale in 30 days
resolution	0.1 ppmV
sampling	1 minute, 30min. avg. stored



The instrument is recalibrated about every 3 weeks using span and zero gas (or CO_2-free dry air), a general overhaul done by Envitec SA four times a year. The span gas used is from Praxair: bottle concentration is 496 ppmV +/- 2%. The same bottle has been in use since 30 June 2003.

Zero drift has been found to be practically inexistant and is in fact not a problem as the sensor is built to make regular zero autocalibrations at night-time. The span-factor varies from check to check and is changed as needed.

Besides CO_2 many other meteorological parameters and gases are measured at meteoLCD; see http://meteo.lcd.lu/structure/readme.html for details.

In this paper, all major calculations are done using DADiSP and Statistica 7; missing data are not interpolated except for very few ones in a row. Impossible low CO_2 levels (<330 ppm) are treated as missing data. There remain 52245 valid CO_2 measurements for the 3 year period, which represents a fair data availability of 99.3%

2. Geographic location of meteoLCD

The small town of Diekirch (population ~5600) is located in a valley orientated South-West to North-East, at an altitude of about 200m asl. The dominant wind direction is that of the valley, South-West, and more rarely the opposite. It is a semi-rural town with few industries upwind: a brewery at a distance of 100-200m, a small industrial zone without much heavy machinery. A similar town (Ettelbruck) is situated upwind at a distance of 3 km. The only major industry is a Good-Year tire plant ensemble located upwind at about 8 km:

3. Seasonal variations of the CO_2 mixing ratio

3.1. Seasonal variation, mean and extreme levels.

CO_2 measurements made at locations undisturbed from industrial and traffic emissions show a clear seasonal pattern with winter-time levels usually several ppm higher than summertime ones: for instance the typical Mauna Loa seasonal amplitude is 8 ppm, the lower values corresponding to late summer or start of fall [1] (see fig. 1).

The situation is usually quite different in urban areas where patterns are heavily influenced by anthropogenic emissions which often cause strong short-time variations, but less visible seasonal patterns over the year. Nasralla et al [2] found an annual amplitude in Kuwait City less than 1.5 ppm from the mean monthly concentrations, whereas Idso et al [4] report almost constant daily minima but strong seasonal variations for the daily maxima over one year.

We will report the CO_2 measurements from 2003 to 2005 taken at the meteoLCD site. All measurements have been made by the same instrument, using the same calibration bottle with 496 pm span gas, at a frequency of one per minute. The 30 minutes means are stored in the data file that holds about 58600 data points for the 2003-2005 time span.

Many natural factors influence CO_2 mixing ratios: some parameters as wind direction, night or early morning inversions and daily changes in atmosperic boundary layer (ABL) mixing have a typical short time influence; others like mean air temperature, overall sunshine duration and vegetation activity show up as seasonal factors.

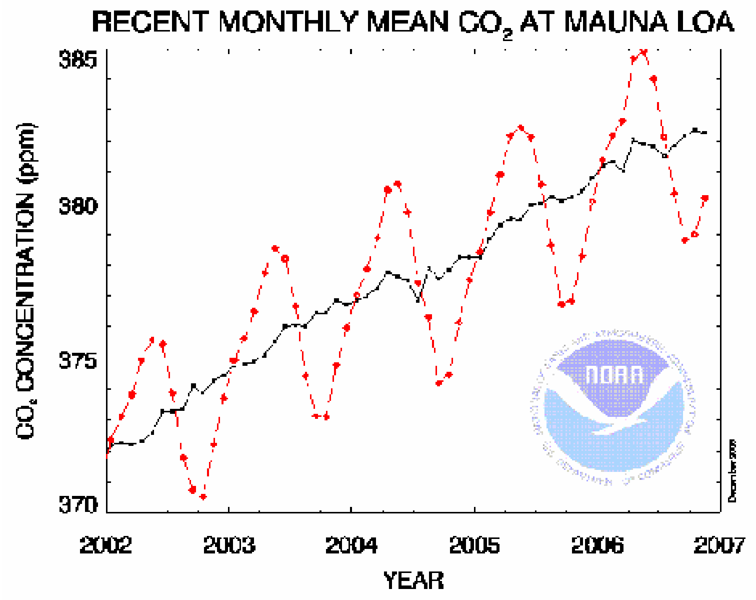


fig. 1 Mauna Loa mean monthly CO_2 mixing ratios.

Fig.2 and fig.3 show the 2003 to 2005 sequence of monthly CO_2 means, minima, maxima and the global monthly averages over the 3 years: the average for the 3 years is 405.6 ppm with a standard deviation of 8.9 ppm.

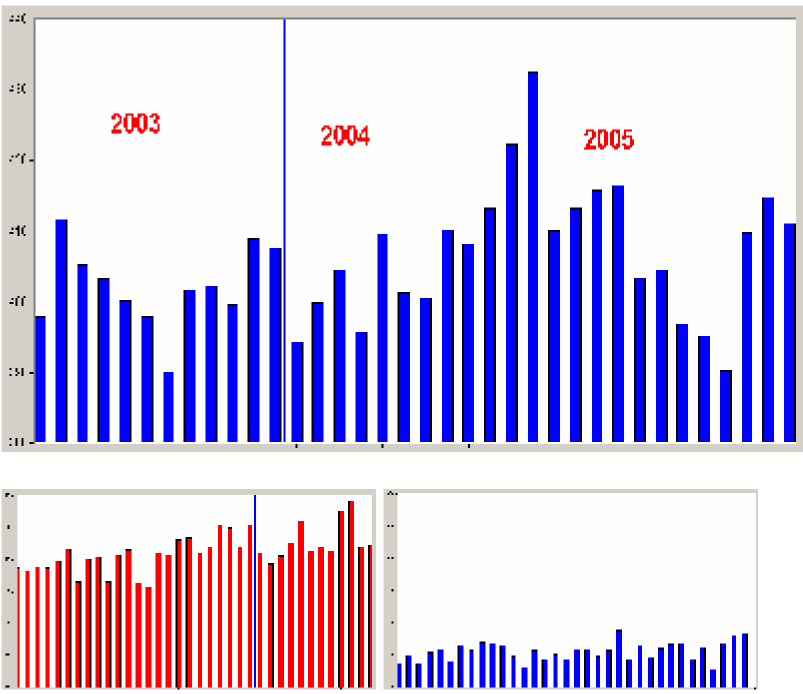


fig.2 Upper: monthly mean CO_2 levels; global mean is 405.6 +/- 8.9 ppm.
left axis scale: 360 to 440 ppm
Lower:
monthly max. = 511.7 +/- 30.6; monthly min. = 355.7 +/- 14.6

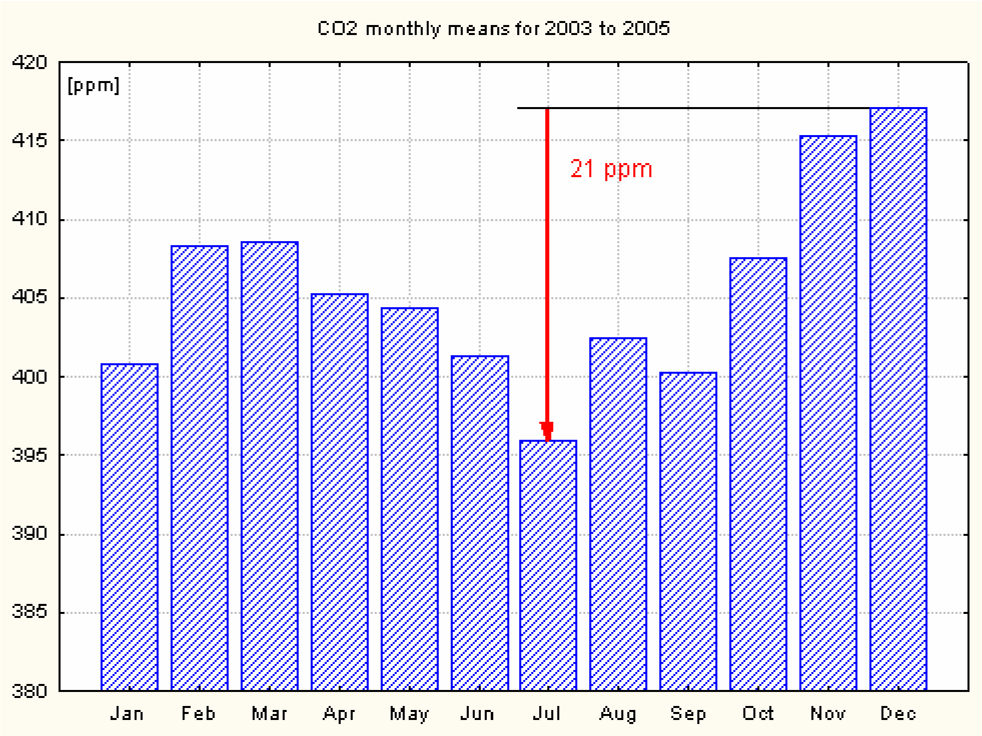


fig.3: Averages of the 2003 to 2005 monthly mean CO_2 levels

Fig. 2 shows that the yearly variations do not repeat in an identical manner even if the periods of low and high mixing rations usually extend over Jun-Sep and Nov-Feb; the mean of the 3 years shows a visible summer low and winter high. The exceptional high Nov. and Dec 2004 values are somewhat misleading: omitting 2004 the lowest means are in July, the highest in February (to be compared to Sept/Feb in Kuwait-City, and May/Sep at Mauna Loa). The difference of about 21 ppm between December and July mean levels is much higher than that found in Kuwait-City [2], pratically equal to Essen, Germany [8], but about only half of that given by Idso et al [4]; this same paper reports a surprisingly low standard deviation of 0.2 ppm for the **daily** minima over one year. The analogue **monthly** minima at Diekirch show a much greater variation with a standard deviation of about 15 ppm; the standard deviation of the monthly maxima is about 31 ppm; the daily minima. and maxima at Diekirch have standard deviations of 15.7 and 33.8, similar to the monthly values (all calculations over 3 years).

An autocorrelation computed on the **daily means** over the 3 years gives maxima peaks at 45, 91, 179 and 352 days, i.e. roughly 1.5, 3, 6 months and full year periods; whereas the full year cycle has to be expected, the other periods remain unexplained.

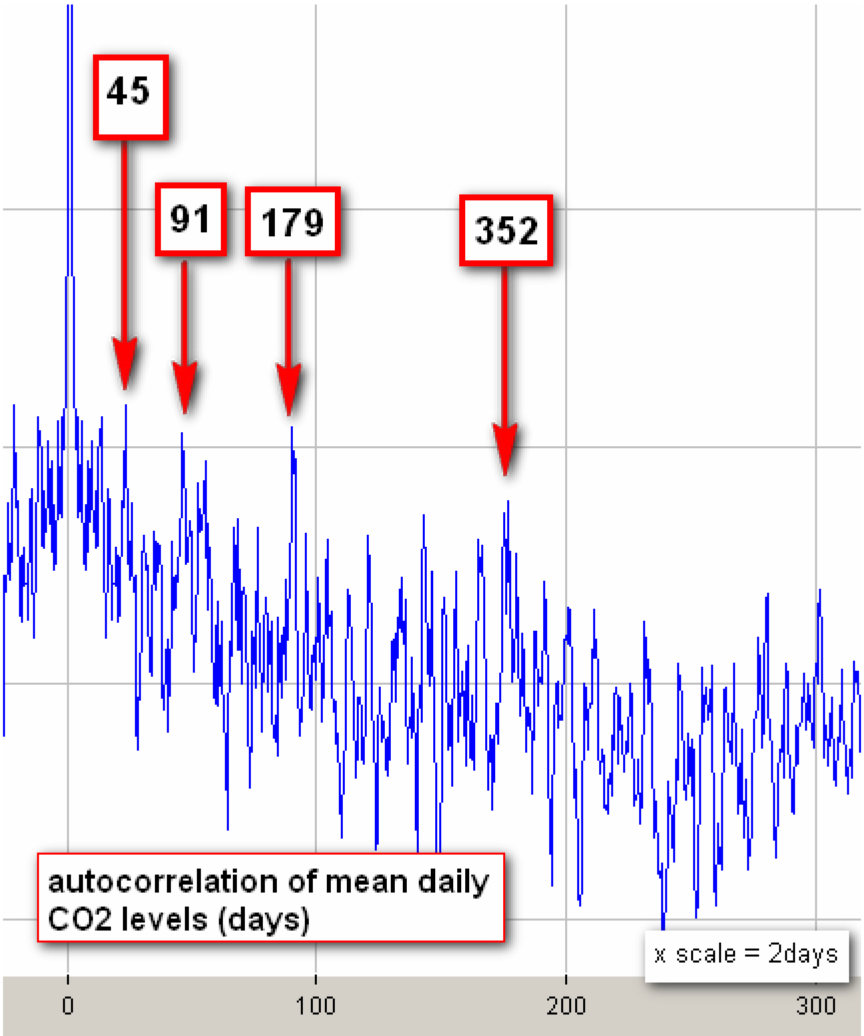


fig 4. Autocorrelation confirms long-time periodicities in daily mean CO_2 pattern

3.2. Relationship between CO_2 mixing ratios, temperature and sunshine duration according to season

We will now look for a relationship between the following parameters: daily mean CO_2, daily mean CO_2 amplitude, daily mean air temperature, daily mean temperature amplitude and daily sunshine hours. A total solar irradiance greater than 120 W/m^2 measured by the pyranometer will be taken as a sunshine condition. This convention differs from that of the WMO, where 120 W/m^2 corresponds to the irradiance of the direct sunbeam on a perpendicular surface; our convention (including direct and diffuse radiation) gives sunshine hours well in excess: for instance, applying the much more complex Olivieri method [3] amounts to 1768 hours for 2005, wheres the above criterion gives 2646 hours. So it should be remembered that in this paper a sunshine hour means a situation where the total (direct and diffuse) irradiance measured by the horizontal pyranometer is equal or greater than 120 W/m^2. Sunshine and air temperature are of course dependant parameters (for 2005 the correlations are 0.64 between sunshine and daily mean temperature resp. 0.69 between sunshine and daily mean temperature amplitude, both significant at $p < 0.05$). The following analysis searches the parameter having the best correlation with the mean daily CO_2 levels.To distinguish between the vegetation growing season and winter months we will take the months January and February (JF) as representive for winter and July-August (JA) as representative for summer. This differs from the ususal convention of DJF for winter and JJA for summer, but has the advantage to allow working on full year original data files. Outliers for CO_2 (usually caused by calibration work) have been interpolated when possible, else replaced by a missing data (NA = not available) placeholder.

Table 1 shows the relevant correlations for the full year, the JF and JA months, the **red** ones being significative at $p<0.05$

	year			**AirT_dailymean**			**AirT_dailyamp**			**Sunshine hours**		
CO_2 dailymean	2003	JF	JA	**-0.12**	-1.27	**0.57**	**0.35**	**0.72**	**0.61**	0.00	**0.55**	**0.31**
	2004			**-0.04**	**-0.33**	**0.53**	**0.22**	**0.30**	**0.61**	**-0.10**	0.13	**0.26**
	2005			**-0.32**	**-0.47**	**0.37**	**0.15**	**0.43**	**0.58**	**-0.12**	**0.30**	**0.34**
CO_2 dailyamp	2003	JF	JA	**0.46**	-0.16	**0.63**	**0.48**	**0.43**	**0.61**	**0.37**	**0.28**	0.23
	2004			**0.50**	0.12	**0.48**	**0.61**	**0.42**	**0.51**	**0.48**	0.21	**0.37**
	2005			**0.46**	-0.12	**0.35**	**0.59**	**0.36**	**0.64**	**0.43**	**0.36**	**0.27**

table 1

For the full year comparison the highest positive correlation exists between daily CO_2 amplitude (amplitude = maximum - minimum readings) and the corresponding daily temperature amplitude: regardless of season all coefficients are positive and significant at $p<0.05$; the correlations are better during the summer season.

The next figure 5 gives the corresponding graphs.

One would expect that mean CO_2 concentrations and mean daily temperature vary in opposite sense as higher (summer) temperatures usually happen during days with maximum photosynthesis which lowers the CO_2 mixing ratios: actually the data show a clear negative correlation for the winter months and surprisingly a clear high positive correlation for the summer season. A computation of 18 linear regression slopes for every couple of months gives essentially negative slopes for the months of November to February and positive slopes for the remaining months (with only 2 exceptions): fig 6 gives the graphs for Jan-Feb and July-Aug 2003:

Idso et al. [4] report a negative slope for the regression between maximum daily CO_2 and minimum daily air temperature; the Diekirch data do not confirm this: CO_2 and temperature antiregress during the winter months of Nov-Feb, but the regression line slope is positive for all other months over 2003 to 2005.

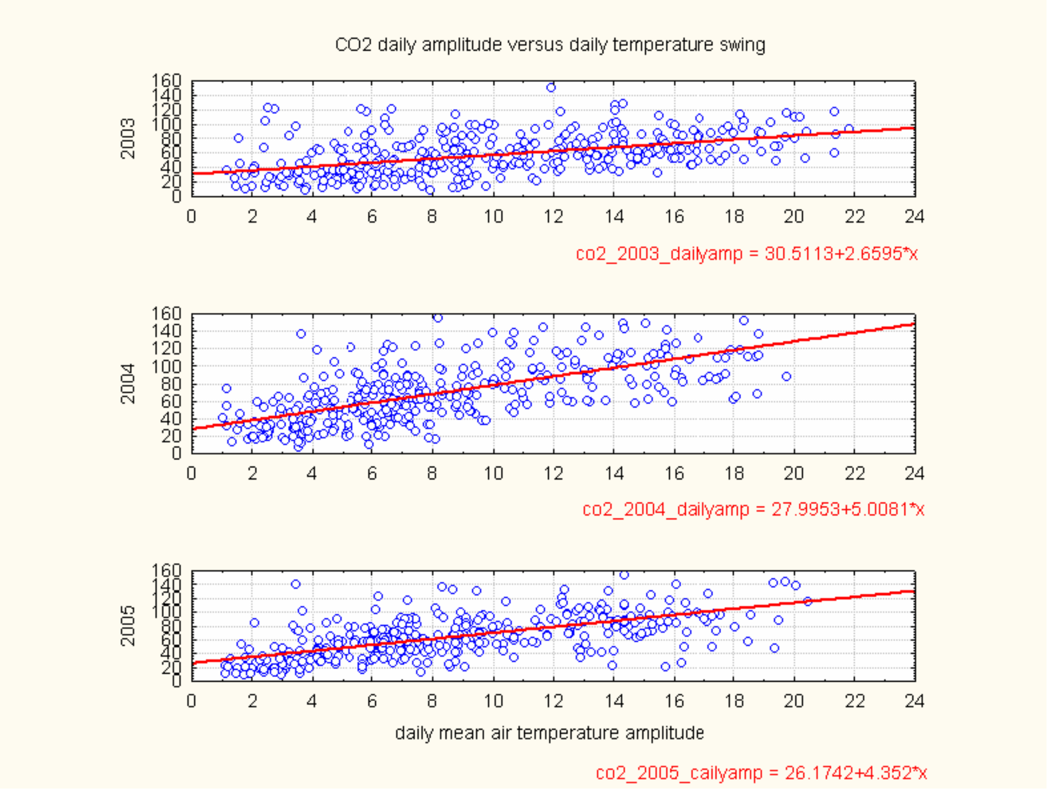


fig.5: Daily CO_2 amplitude versus daily temperature amplitude: slope of linear fit is always positive.

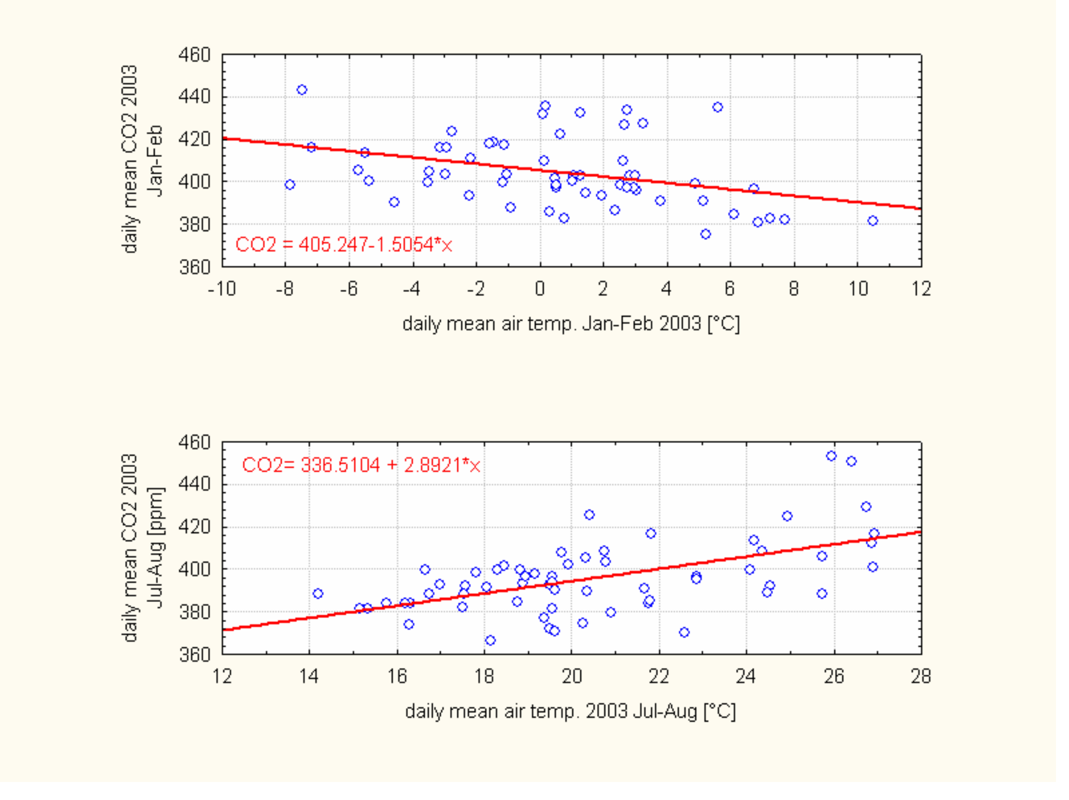


fig.6: Daily mean CO_2 versus daily mean temperature: slope of linear fit negative in winter, positive in summer.

Table 2 gives a mixed picture for the correlations between CO_2 and sunshine: the full year correlations are slightly negative, the winter JF and summer JA months all have a positive correlation. A similar result is obtained when computing the linear regressions between the daily CO_2 patterns and daily solar energy (in kW/m2 on a horizontal surface) for the full 3 year measurement series:

slope and offset of linear regression of daily mean CO_2 versus daily solar energy	**whole 3 year 2003-2005 period**	**mean of Jan-Feb**	**mean of Jul-Aug**
dailymean CO_2	-0.256 405.6	+5.485 395.9	+2.987 384.1
dailymin CO_2	**-2.791** 389.1	+4.176 381.7	+0.976 364.8
dailymax CO_2	+3.913 430.4	+4.296 420.8	+5.897 416.4
dailyamp CO_2	+6.704 41.3	+0.120 39.2	+4.922 51.6

table 2

Even if the daily mean CO_2 and daily solar energy antiregress for the full 3 year period they do not, contrary to what one would expect, antiregress for the summer months having the greatest solar energy. Over the 3 years high daily solar energy slightly lowers daily mean and noticably lowers daily minima CO_2 levels and increases daily maxima. As a consequence the slope for the daily CO_2 amplitude versus solar energy greatly increases for the months with higher solar input. The maximum solar energy per day is about 8 kWh/m2 on a horizontal surface in summer and 1 kWh/m2 in winter, which would increase the daily CO_2 amplitude by about 7*6.7 = 47 ppm from winter to summer (the measured mean winter and summer daily CO_2 amplitudes are 39.3 ppm and 76.1 ppm)

3.3. Relationship between mean CO2 parameters and mean wind velocity and direction

Windspeed and wind direction are measured at meteoLCD by an ultrasonic anonemeter (accuracy = 0.1 m/s) mounted on a mast 3 m above the terrasse holding the other instru-ments, and about 21m above groundlevel; the . The main wind directions over the whole period are SSW and NEE as shown by figure 7:

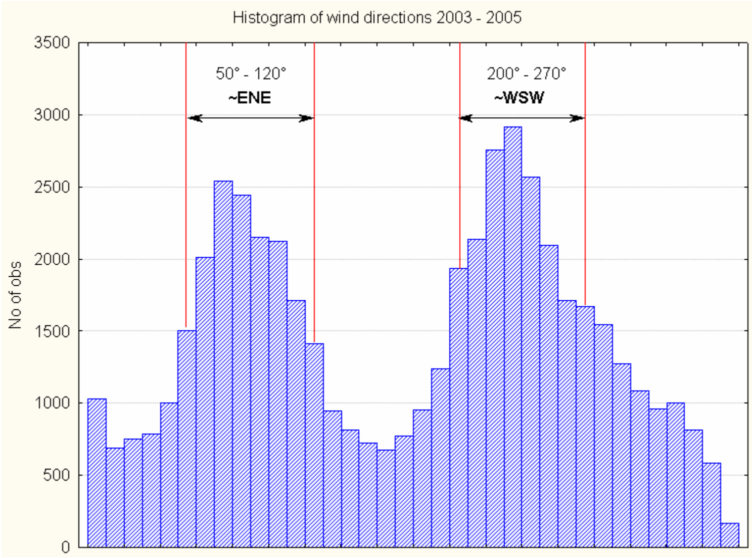


fig. 7: Histogram of wind direction; total sample size is 51516 (windspeed > 0).

Let us limit the main directions to the ranges [50°-120°] and [200°-270°] for the easterly and westerly winds; the statistics are the following:

	Easterly Wind	**Westerly Wind**
data points with wind speed >0	17428	16111
mean wind speed of these points [m/s]	1.30	2.64
mean CO_2 level [ppm]	403.1	395.0

table 3

The table shows that the higher the wind speed, the lower the CO_2 level. Actually, the highest wind speeds correpond to a maximum mixing of the atmospheric boundary layer, and should be close to the global baseline CO_2 mixing ratio. Fig. 8 gives the plot of CO_2 versus wind speed, and points to a background of approx. 380 ppm.

Storm "Franz" passing over Luxembourg on Jan.11th 07 gave an opportunity to test the relationship on a much smaller data set. This storm had wind speeds reaching 30 m/s over open country and up to 11 m/s at the meteoLCD site. There was no sunshine, air temperatures changed between 5°C and 9.5°C and the wind blew constantly from a [200° - 270°] direction . Fig. 9 shows CO_2 concentrations and wind

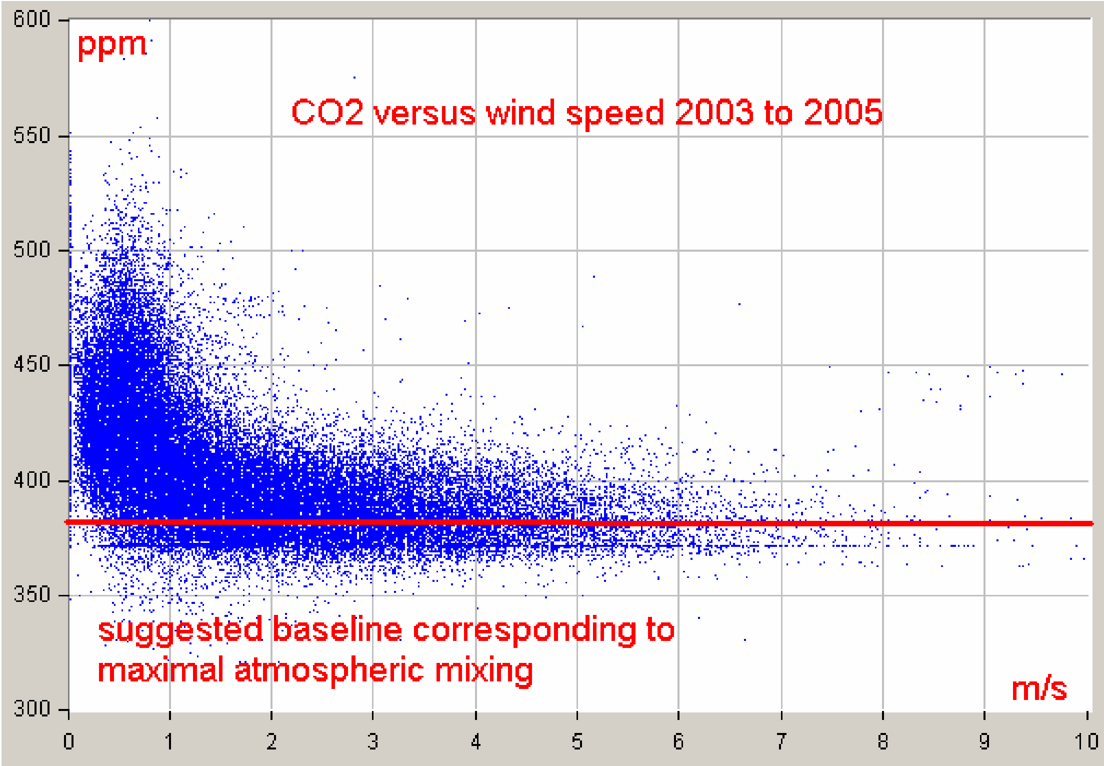


fig.8 : Baseline CO_2 mixing ratio corresponding to maximum windspeed

speeds varied during 48 hours; a simple model

$CO_2 = a + b*windspeed/(c+windspeed)$ [eq. 1]

gives a correlation R = 0.76. This suggests an asymptotic baseline CO_2 level of ~385 ppm for infinite wind speeds, i.e. for a maximum mixed-up atmospheric boundary layer. It should be noted that this asymptotic level is close to the Mauna Loa level of 382 ppm measured in December 2006.

The same model applied to the complete 2003-2005 data points gives a bad fit (R=0.22). The modified model

$CO_2 = a + b*(windspeed + c)/(d + windspeed)$ [eq. 2] (see also chapter 4.3)

gives 362 ppm as baseline CO_2 (R = 0.59). This is much too low; the line drawn by visual inspection in fig. 8 seems more adequate.

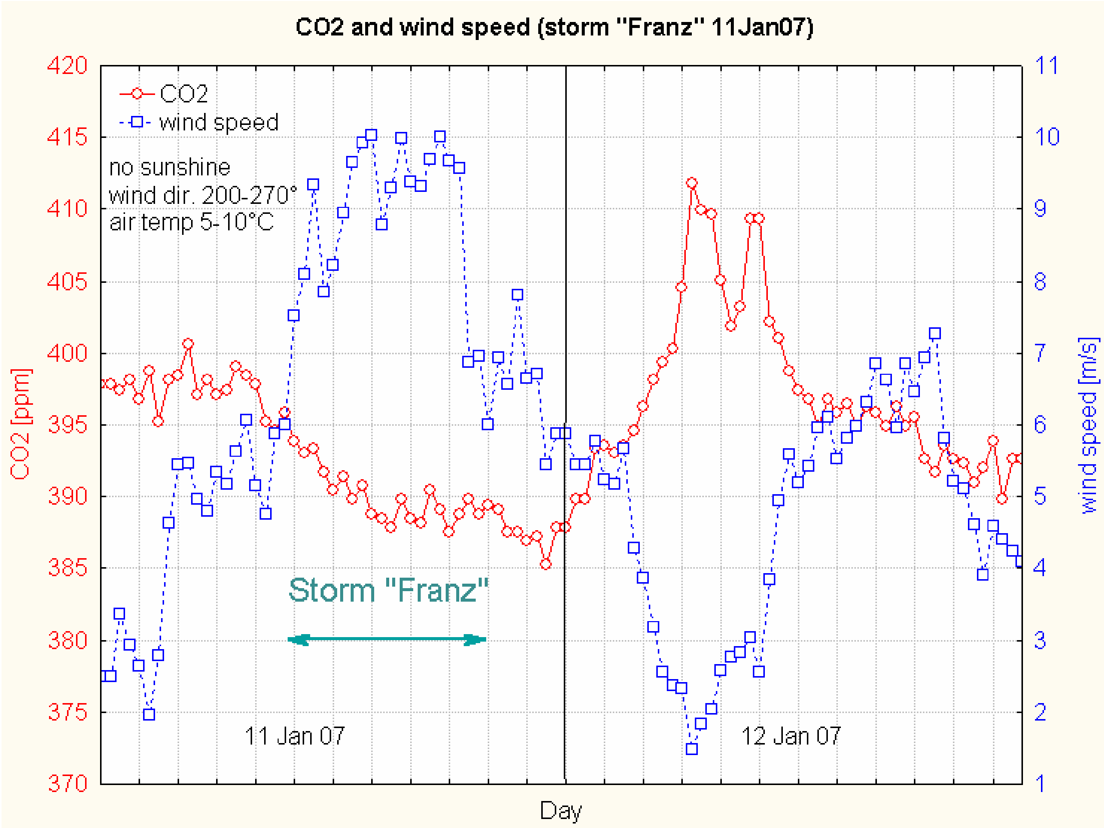


fig. 9: CO_2 and wind speed during storm "Franz"

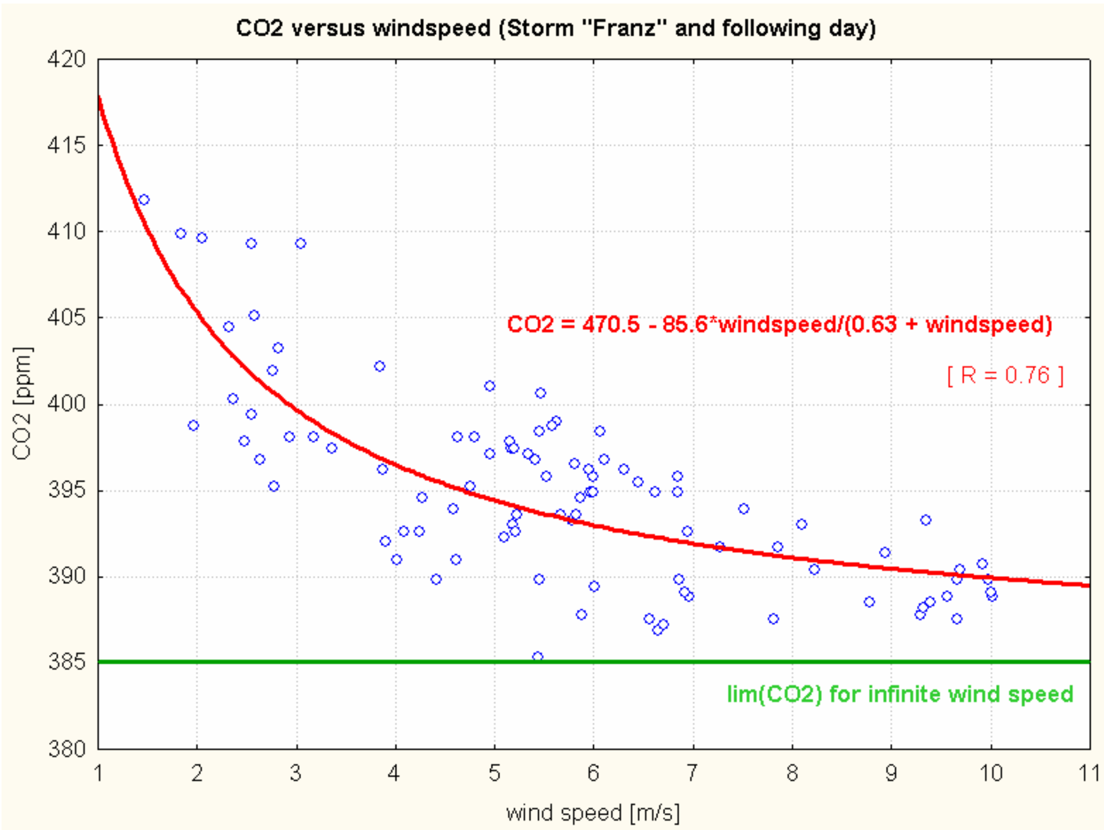


fig. 10: Simple model CO_2 versus wind speed

There are virtually no industries in the easterly direction, whereas the main potential emitters are located upwind to the west: nevertheless the corresponding mean CO_2 levels are lower. This suggests that the higher levels especially noticeable during calm wind conditions are not caused by CO_2 plumes from industrial emitters, but by slower wind speeds which do not mix up the boundary layer as well as the higher westerly winds do. When wind speeds are higher than 2 m/s the CO_2 levels are similar, regardless the wind direction (with and without upwind factories); this confirms the hypothesis:

	wind speed < 2 m/s			**wind speed > 2 m/s**		
	all directions	**~WSW**	**~ENE**	**all directions**	**~WSW**	**~ENE**
mean CO_2 mixing ratio	410.4	405.6	413.6	387.2	387.6	388.5

As a reminder: the overal mean CO_2 level computed from the 52445 measurements is 405.1 +/- 28.7 ppm for the period 2003-2005; Mauna Loa's average mixing ratio is 376 ppm for the same period.

4. Diurnal variations of CO_2 mixing ratio

Simple inspection shows that throughout the year, there is a periodic daily variation for most of the time; the autocorrelation computed on the 56000 data gives a clear indication of a 24h period.

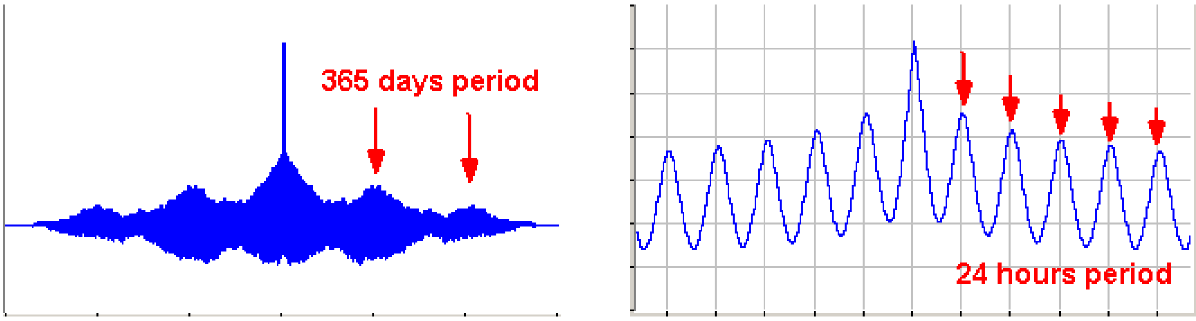


fig.11: Autocorrelation computed over all 56000 data points shows yearly and daily periods

Despite great variabilty in day to day CO_2 levels, a few typical diurnal patterns can be found. As shown in the preceeding chapter, wind speed is a dominant cause in lowering CO_2, and a stable atmosphere (often found at night and during morning hours) is an efficient trap of natural and anthropogenic CO_2 emissions, .

Three typical diurnal CO_2 patterns can be found: dual peak, single peak and no peak

Fair weather conditions with little cloud cover and low wind favor two stable atmospheric inversions per day [7]: one close to midnight (due to nighttime radiation cooling) and the other around 6 hour in the morning, due to the cooling of air layers in contact with the soil, the upper regions beginning to be heated by the rising sun (all times are UTC). This second inversion coincides with one of the 2 heavier traffic periods (7-9 and 17-18 local time) where many commuters pass through Diekirch (or pass through Ettelbruck 3km west, going southwards to Luxembourg-City). All roads around Diekirch are smaller roads, the nearest highway starts at Colmar-Berg, 8km from Diekirch. Wind is the enemy of inversions, so we should expect this dual peak situations only during hours of low wind.

Lets us first show in detail the situation from Saturday 8th toTuesday 11th July 2006.

These 4 days are dry, with only one small rain-fall of 1.8mm during 30 minutes at Tuesday; the night wind speeds are low (<0.5 m/s), but have daily maxima from 3 to 7 m/s; Monday is a blue sky day, all the others have intermittent moderate or heavy (Sunday) cloud cover, as shown by the variablitiy of the UVB and solar irradiance. All 3 nights display 2 peaks, the first at 00:00 and the second at 06:00 UTC; there is far less morning traffic during Sunday compared to Monday and Tuesday: NO peaks at 50 ug/m3 on Sunday and 60 ug/m3 on Monday.

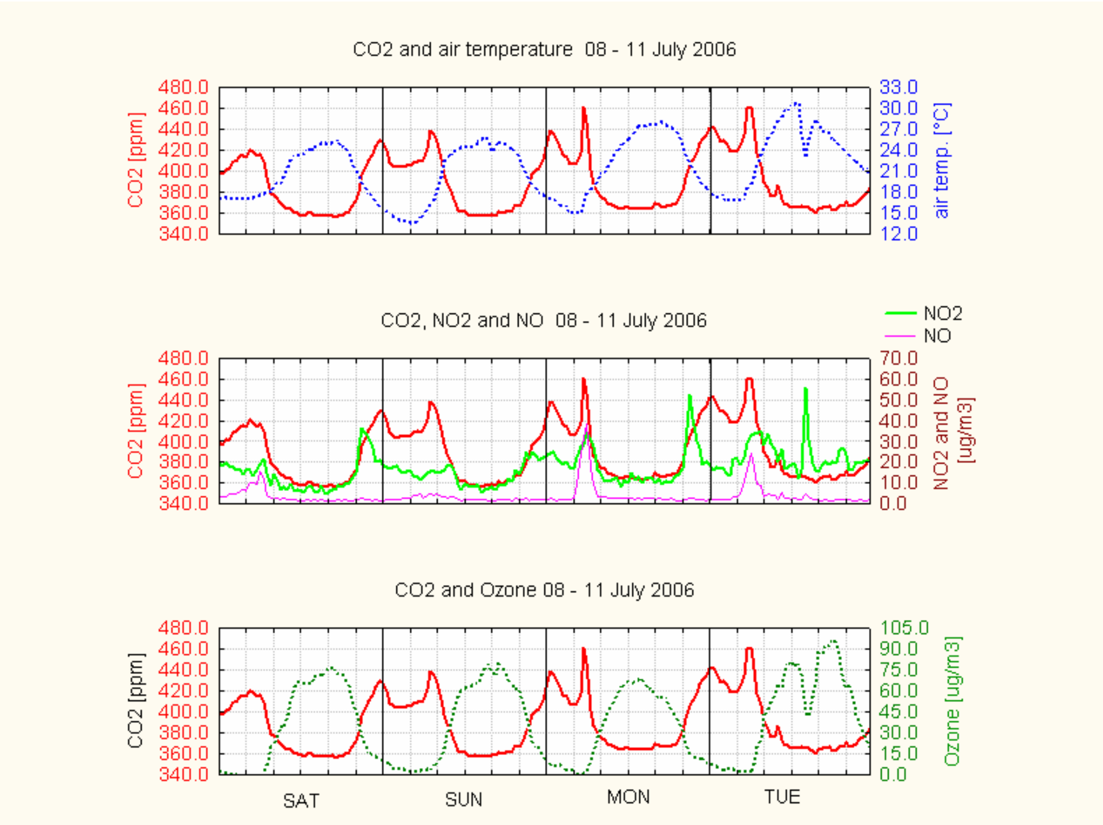


fig.12: CO_2, air temperature, NOx and ozone from 8 to 11 July 2006

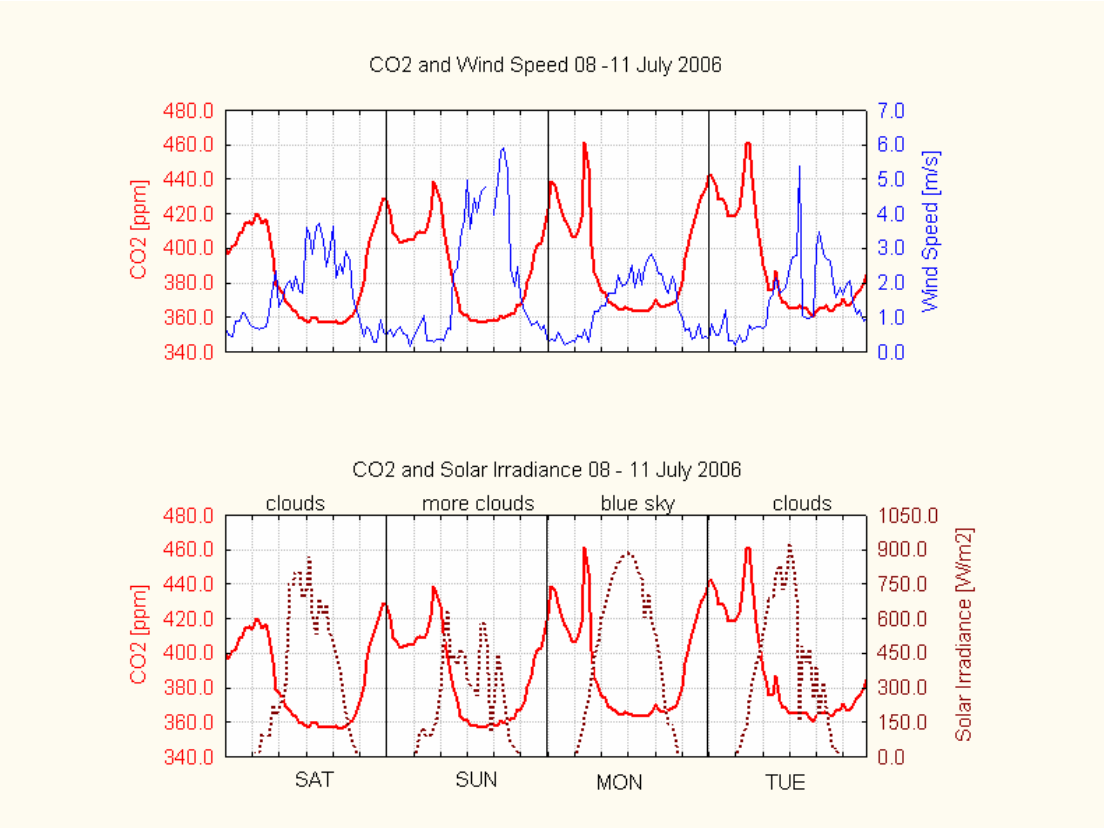


fig.13: CO_2, wind speed and solar irradiance from 8 to 11 July 2006

The same pattern can sometimes be found when temperatures are colder or freezing, as shown by fig. 14 for the 10th to 12th Dec. 2005 period; a double peak can be seen Saturday to Sunday night, and a much more preeminent one from Sunday to Monday. The last peak coincides with a NO maximum, sign of the Monday morning commuter traffic; the Monday CO_2 peak exceeds the Sunday peak by about 40 ppm. As soon as the air warms and wind speeds are higher than 0.5 to 1 m/s the boundary layer starts rapidly to be better mixed up and CO_2 levels fall to the daily minimum.

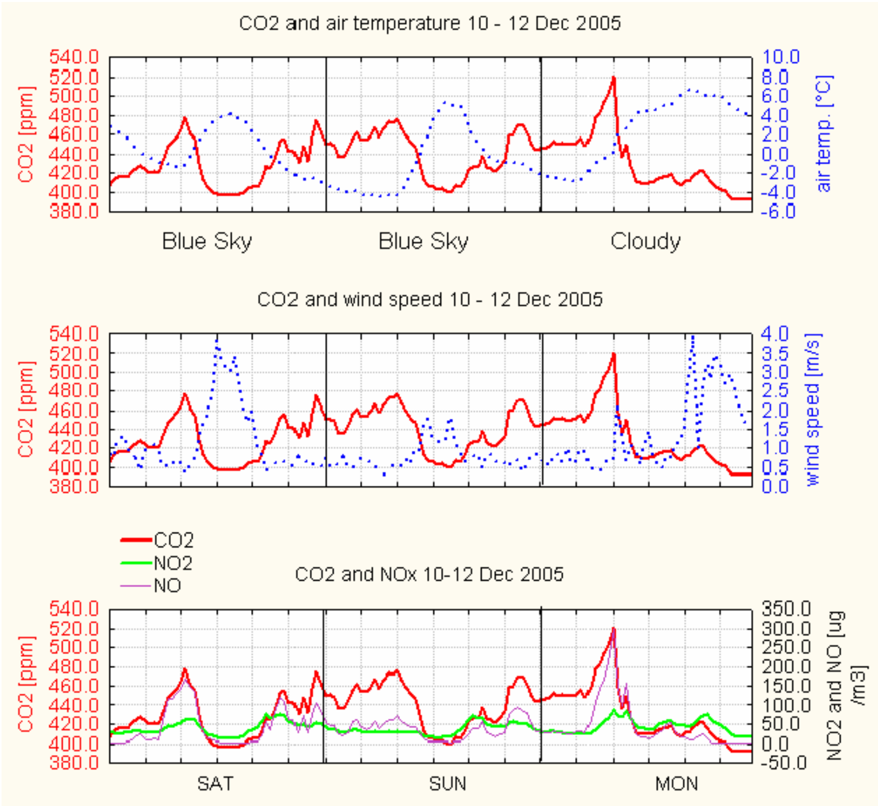


fig. 14: Double peak situation during cold winter days (SAT & SUN: blue sky, MON: cloudy)

4.2. The single peak diurnal CO_2 pattern

An interesting situation with single peak days alternating with dual peak ones happened from 8th to11th July 2005.

Inspection shows that the double peak coincides with a small nocturnal dip in air temperature; if we magnify the graph of CO_2 and wind velocity, it becomes clear that wind speed is the driver of the dual peak (and causes the small air temperature drop): a small rise of wind around midnight pushes down CO_2 levels by disrupting the inversioon layer; low wind nights do not show this.

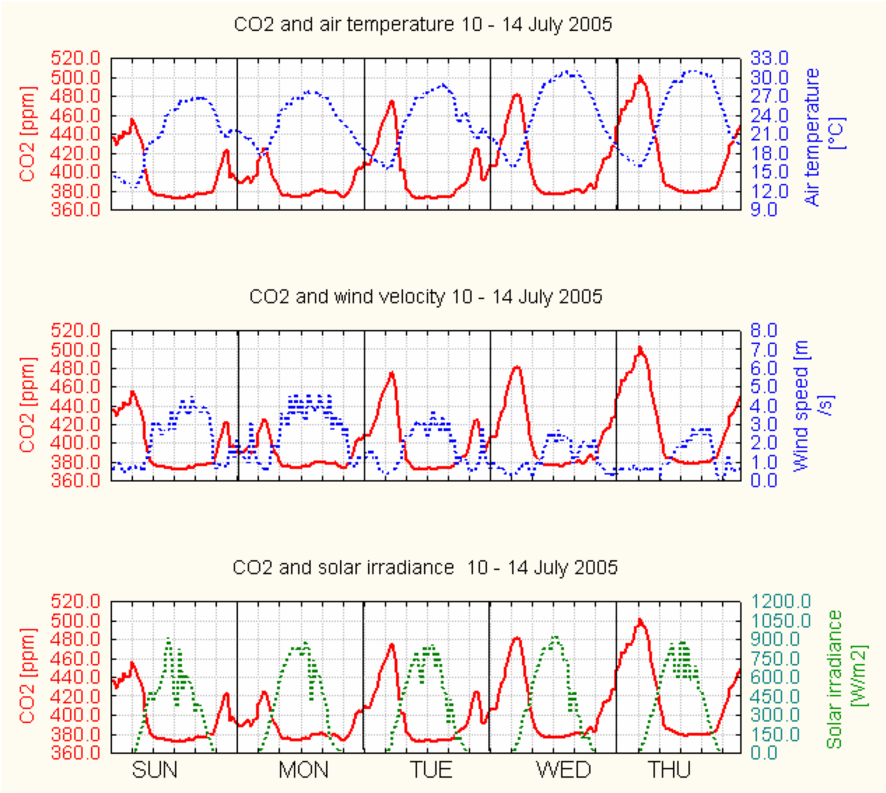


fig. 15: Alternating dual and single peak days 10 to 14 July 2005

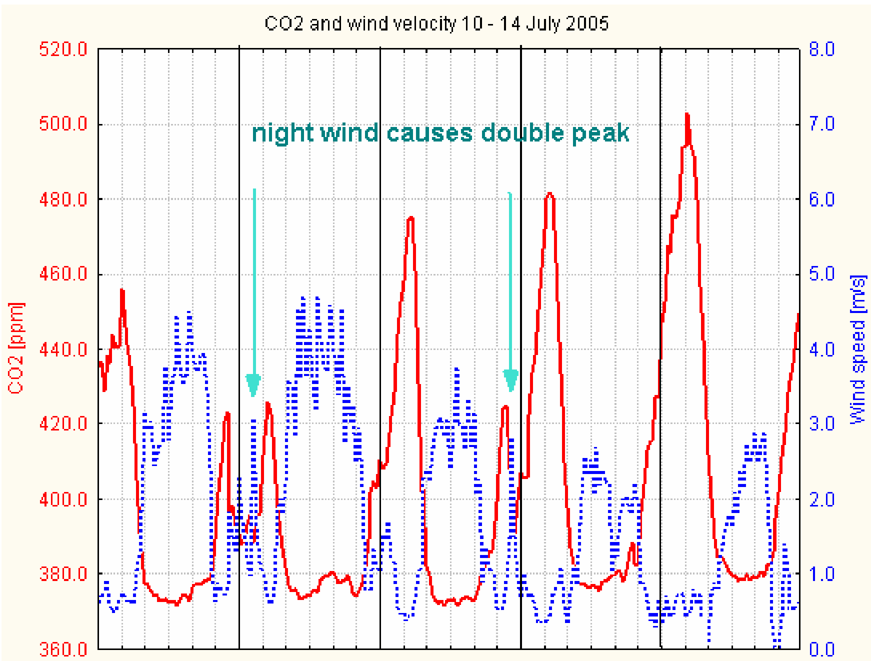


fig. 16: midnight wind causes double peak

From the preceeding chapters one should expect rather flat diurnal CO_2 levels when wind speed exceeds a certain threshold. This is indeed the case, as shown by fig.17 which represents a windy 4 days period from 3rd to 6th Feb. 2005. Wind speeds over approx. 1 m/s are probably strong enough to disable most night and morning inversions and the corresponding CO_2 peaks.

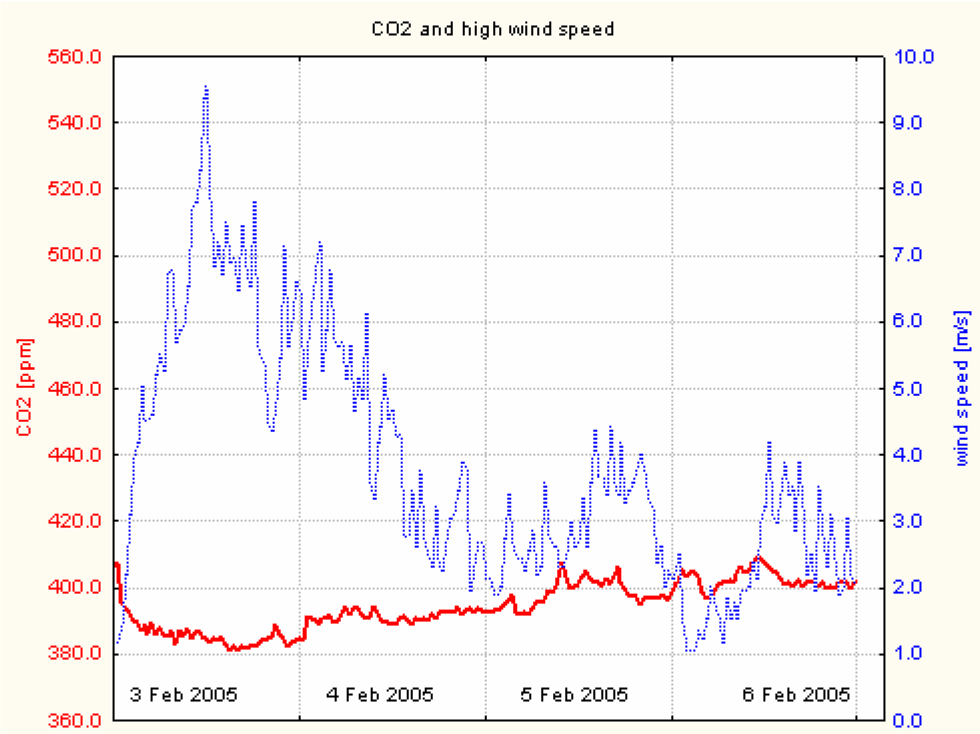


fig. 17: Four days flat CO_2 levels

Diurnal CO_2 variations are wind driven and as periods of low nighttime and higher daytime wind speeds are the norm, the mean overal diurnal pattern is more or less sinusoidal (R=0.97), whereas the mean diurnal wind speed can be modeled (R = 0.99) by a Gaussian bell curve (fig.18).

A plot of these mean hourly CO_2 levels versus wind speed suggests, similar to figure 8, a baseline CO_2 level of about 376 ppm: the applied model [eq. 2] gives an excellent correlation R=0.988:

$$CO_2 = a + b*(windspeed + c)/(d + windspeed)$$

The Mauna Loa measured mean CO_2 mixing ratio for 2003-2005 is 377.6 ppm, very close to this baseline (fig.19)

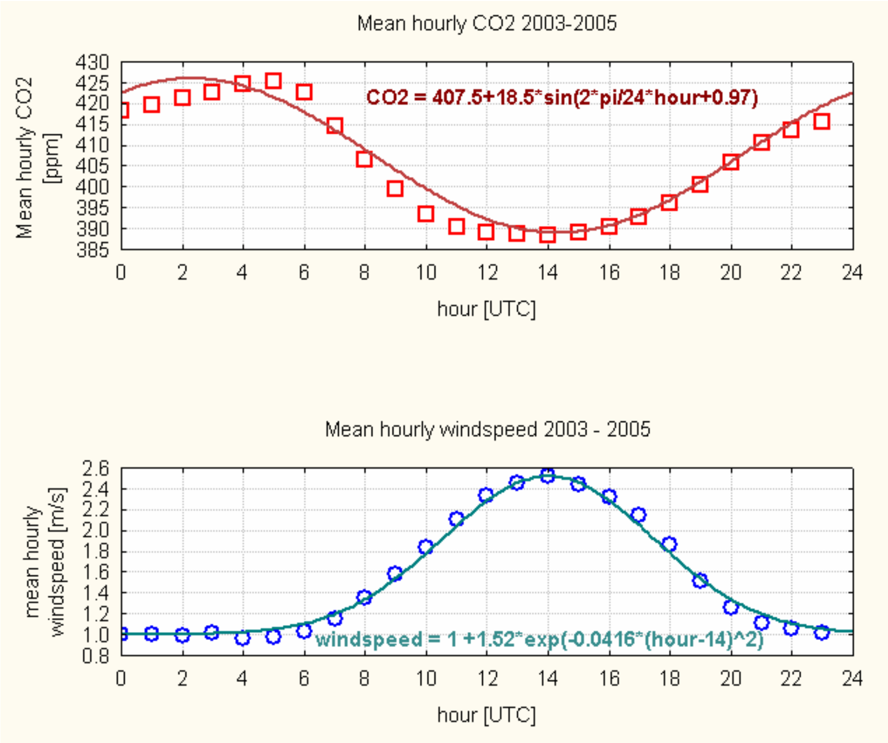


fig. 18: mean hourly CO_2 level and windspeed (2003-2005)

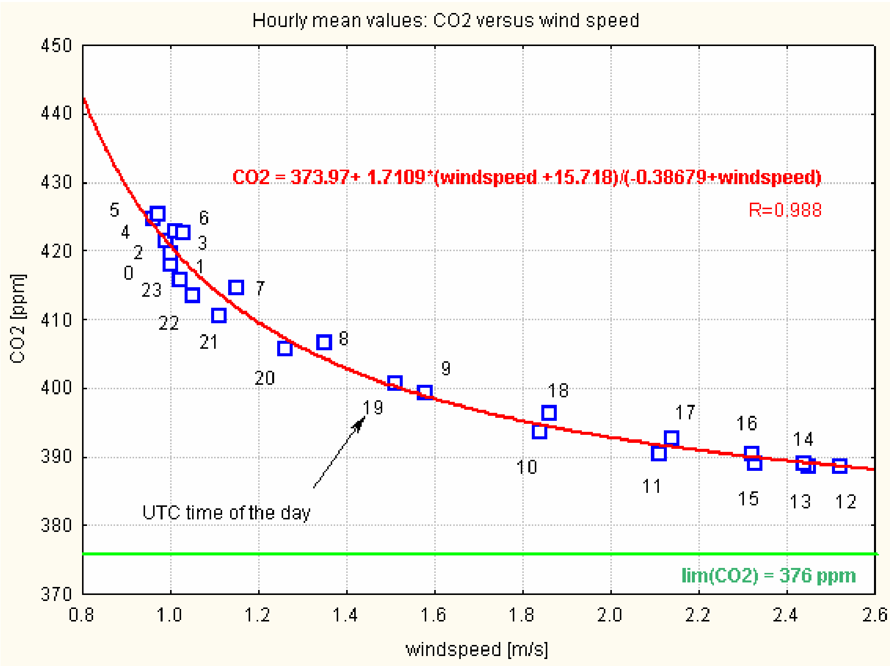


fig. 19: 2003-2005 mean hourly CO_2 versus wind speed, with asymptotic baseline level

The principal cause of the antiregression with air temperature seems to be temperature driven changes in night and day wind speeds; actually enhanced biological activity as daytime CO_2 fixation should give lower day levels during the greening period. This can be shown for instance using the 2003 daytime means for CO_2 levels and wind speed:

	Jan-Feb 2003	**Jul-Aug 2003**
mean of (mean daytime 06:00-18:00) CO_2 levels	406.2 +/- 19.1	400.9 +/- 18.2
mean of (mean daytime 06:00-18:00) windspeed	1.27 +/- 0.98	0.86 +/- 0.50

Even if the summer daytime wind speeds are lower, the corresponding CO_2 levels are not higher, but also lower: this could be seen as a fingerprint of photosynthetic CO_2 fixation. But the difference in winter/summer levels could also be caused by higher anthropogenic winter emissions from increased heating. As a consequence, it is difficult or impossible to detect a photosynthesis fingerprint unambiguously in the daytime CO_2 signal.

Table 5 resumes some of the influences of environmental factors on CO_2 pattern:

Environmental Parameter	**Influence on CO_2 maxima**	**Influence on CO2 minima**	**Influence on double peak**	**Influence on no peak**
Wind speed	lowest night windspeeds often coincide with CO_2 peak (inversion)	higher wind speeds during daytime give lower CO_2 minima; lower windspeeds at night give higher CO_2 minima	higher midnight wind speeds (> 1m/s) cause double peak	continous high wind (> 1 m/s) give flat daily CO_2 pattern
Solar irradiance		CO_2 daylight minima practically independent of solar irradiance		
Cloud cover		CO_2 daylight minima practically independent of cloud cover		
Traffic	visible influence of morning traffic on CO_2 peak during			

	inversions: Monday high traffic morning hour has peak 20-40 ppm higher then same Sunday hour (lower traffic confirmed by lower NO and NO_2 concentrations)			
Ozone		CO_2 daylight minima practically independent of ozone concentration		

table 5

5. Conclusion

Our report confirms some findings of other papers: CO_2 peaks during inversion hours, and we often find the same dual maximum situation as in [4]. On the contrary, we can not confirm an antiregression with air temperature as being the general rule. Biological periodic activity (which causes a mean drop of about 21 ppm) can only be seen in autocorrelations and overall monthly averages. It is not easily detectable from the hourly measurement series. Diurnal variability is important and depends essential on atmospheric stability [5][6]: when there exist night or morning inversions, CO_2 peaks may exceed the daily minimum by well over 100 ppm. The influence of morning traffic (detected by NO and NO_2 variations) shows up in an increase of 20-40 ppm of the peak level. Overall traffic and anthropogenic emissions are too low to cause an urban CO_2 dome. Ozone concentrations do not seem related to CO_2 levels. Periods of very high wind speeds allow to find by inspection an asymptotical level close to the global mixing ratio measured at isolated reference stations like Mauna Loa; this same level can be found by applying a simple mathematical model which expresses the mean hourly CO_2 levels as a function of wind speed. The mean hourly levels per day computed over the 3 years period can be modelled by a sinus function.

6. References

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[8] Henninger S. et al: Mobile Measurements of Carbon Dioxide within the Urban Canopy Layer of Essen, Germany.
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All data files are available in the data archive of meteoLCD at http:/meteo.lcd.lu/data/

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7. Addendum A

A revised relationship between CO2 and windspeed

The rational function used in chapters 3.3 and 4.3 for fitting CO2 mixing ratios to wind speed may give a good asymptotical base level, but it lacks a clear physical base and represents nothing more than a mathematical trick. Using a physical sensible exponential function of the type

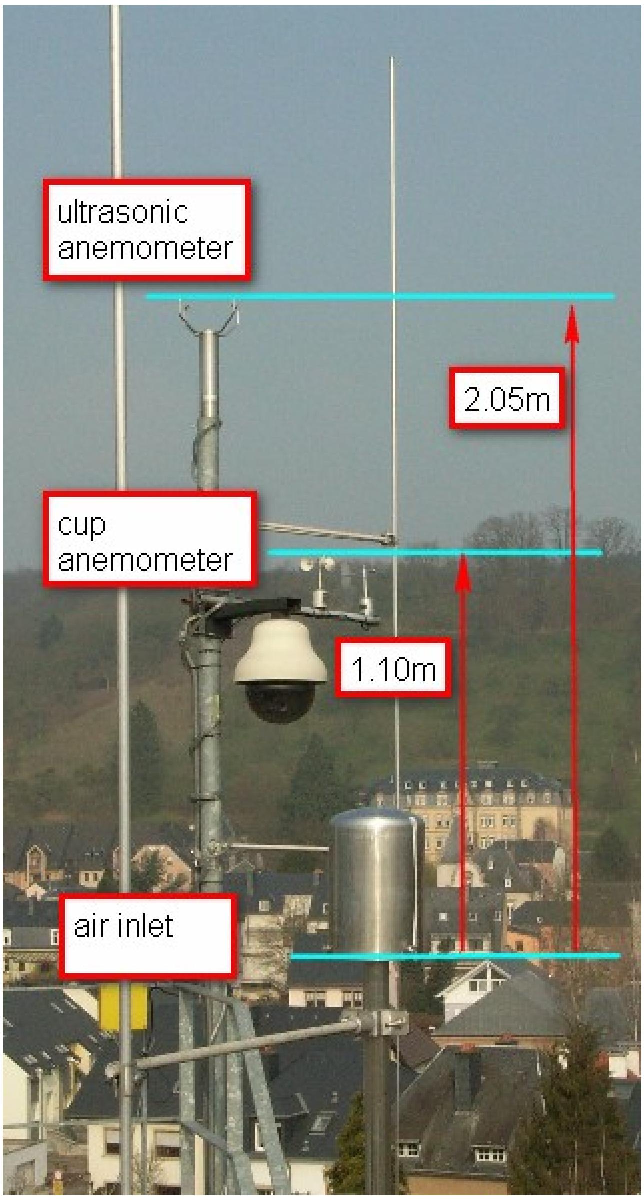
*CO2 = a +b*exp(-c*windspeed)   [eq. 4]*

resolves this problem. The horizontal asymptote for infinite windspeeds is the parameter a.

Here are the results of applying this model to different data sets; all parameters are significant at the 0.05 level

data set and time period	number of datapoints	anemometer	asymptotic base level Mauna Loa level	goodness of fit R
storm FRANZ 11/01/07 00:00 to 12/01/07 13:00	74	cup	**386.3** **382.0 (Dec. 2006)**	0.82
2003 to 2005	52608	ultrasonic	**381.3** **377.6**	0.39
2003 to 2005	52608	cup	**375.9** **377.6**	0.50

The cup anemometer has the best goodness of fit R: this might not be surprinsing if one considers the different mounting heights of the air inlet, cup- and ultrasonic anemometers: the cup anemometer is mounted 1.10m, the ultrasonic 2.05m above the air inlet (see fig.20). The higher mountings show up in different mean windspeeds over 2003-2005: 1.58 m/s (cup, lower) and 1.77 m/s (ultrasonic, higher).



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