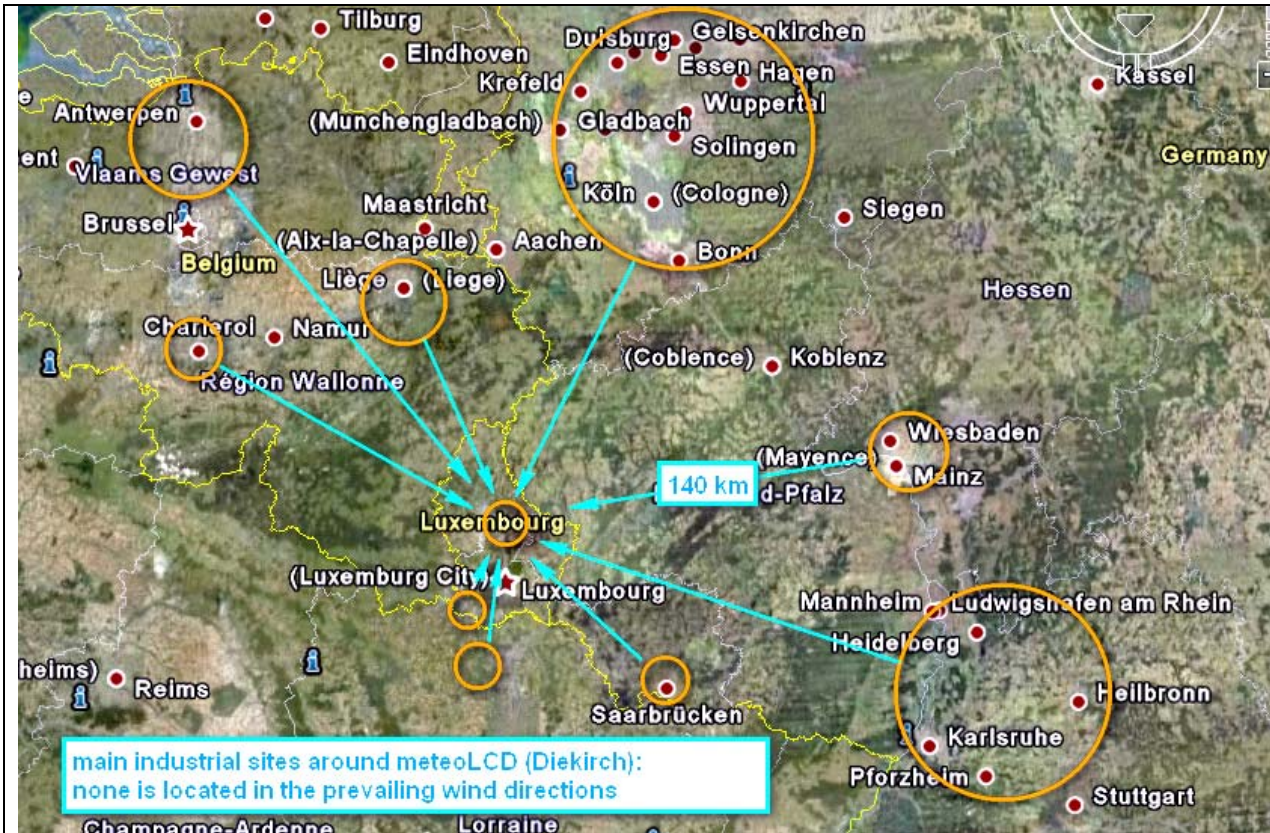


# 10 Years Ozone Measurements at meteoLCD (<http://meteo.lcd.lu>) delivering live O3 data since 1998



- meteoLCD - independant meteorological station of the Lycée Classique de Diekirch (alt. 218m asl, lat. 50° long. 6°E, semi-rural environment)
- station is specialized in measuring solar parameters (TSI, UVB, UVA), atmospheric gases (CO2, NO, NO2, O3) and total ozone column.
- agreed as **Station 412 of the WOUDC** (World Ozone and UV Radiation Data Center)
- delivering near-live data 24h/24h since 1998, unlimited free access to all data.
- managed by Francis Massen , Physics Lab and Computing Dept. of the LCD  
email: [francis.massen@education.lu](mailto:francis.massen@education.lu)



Location of the most important industrial neighbouring regions..

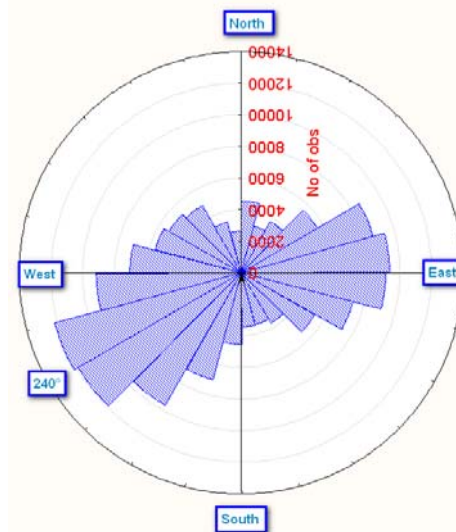
With the exception of the Wiesbaden-Mainz region, Diekirch is not downwind to any of the big industrial centres.

Please note the dense forest cover of German Rheinland-Pfalz and the Belgian Ardennes around Diekirch (deciduous and resinous trees).

Easterly winds travel over large forested regions before reaching Diekirch.



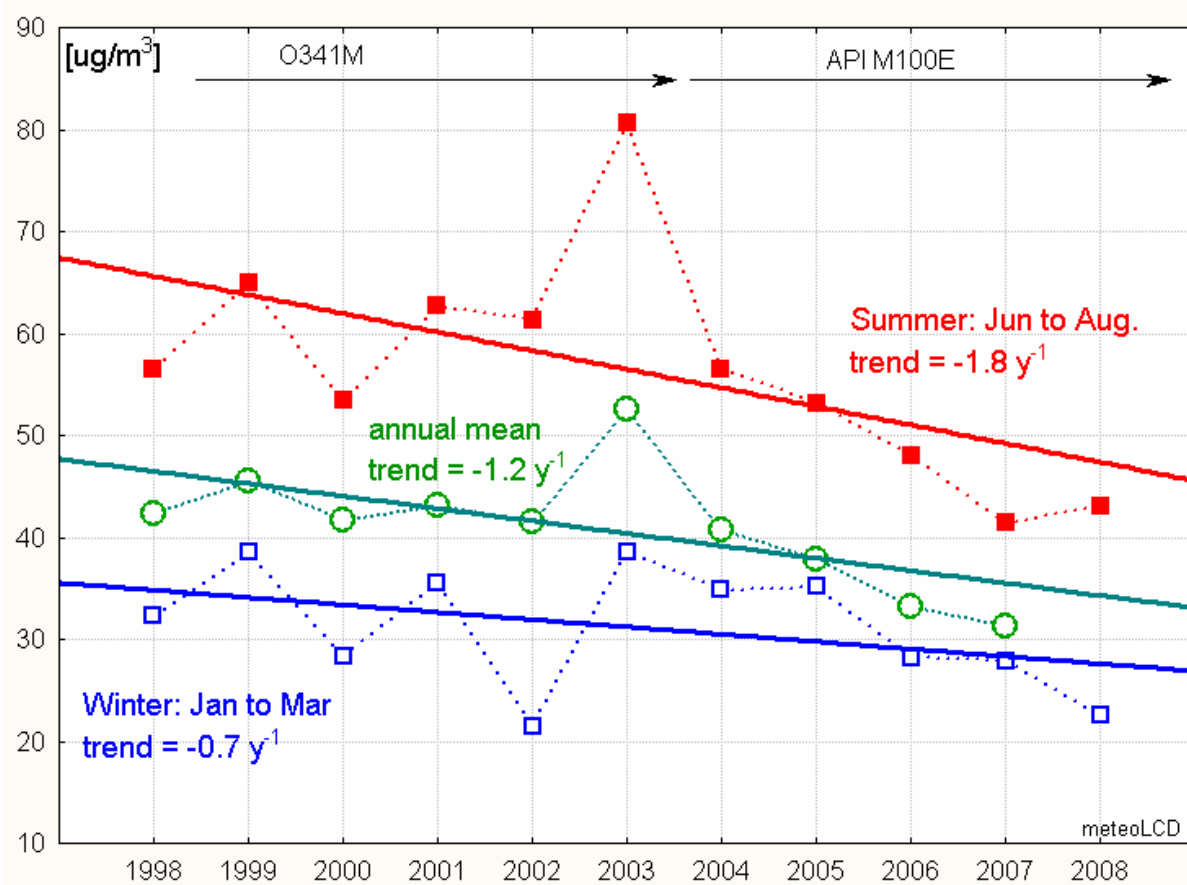
Prevailing wind directions correspond more or less to the orientation of the valleys leading to Diekirch



Histogram for 1998- 2007.wind diretions

- Equipment for gas measurements:
- O3M41 ozone sensor from Environnement SA (up to end 2003)
  - API M400E ozone sensor from API Teledyne
  - MIR9000 CO2 sensor from Environnement SA (up to 2007)
  - API E600 CO2 sensor from API Teledyne
  - AC31 NO/NO2 sensor from Environnement SA
  - Zero Air generator from Schmidlin



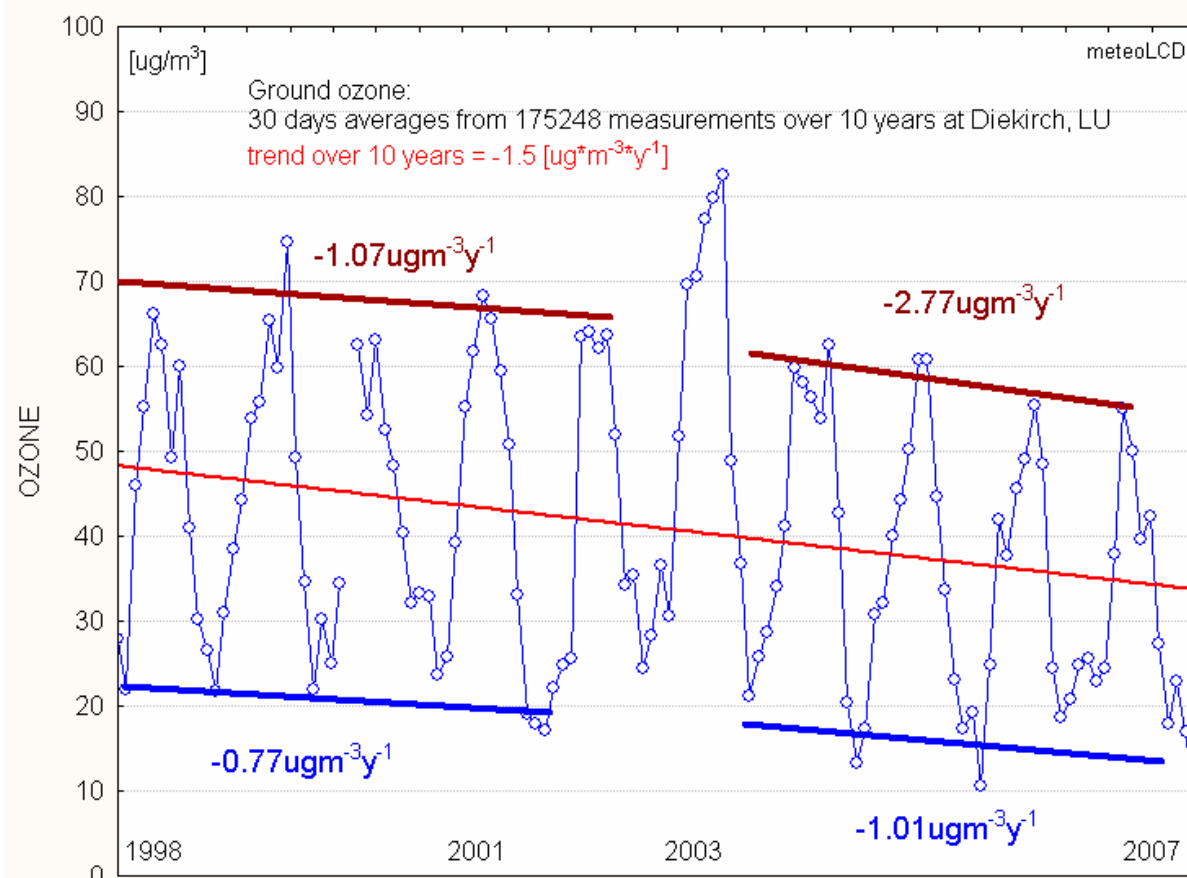


Ozone measurements are done every minute; the average of 30 minutes is kept in the data file.

Yearly average ozone levels are slightly decreasing up to 2002; the heat-wave year 2003 clearly shows up. After 2003 all trends become distinctly more negative. This is in accordance of observations made in Germany [Jonson, 2005], [EMEC], and baseline levels at Mace Head [EMEC].

10 years average [O3] in  $\mu\text{g}\cdot\text{m}^{-3}$ :

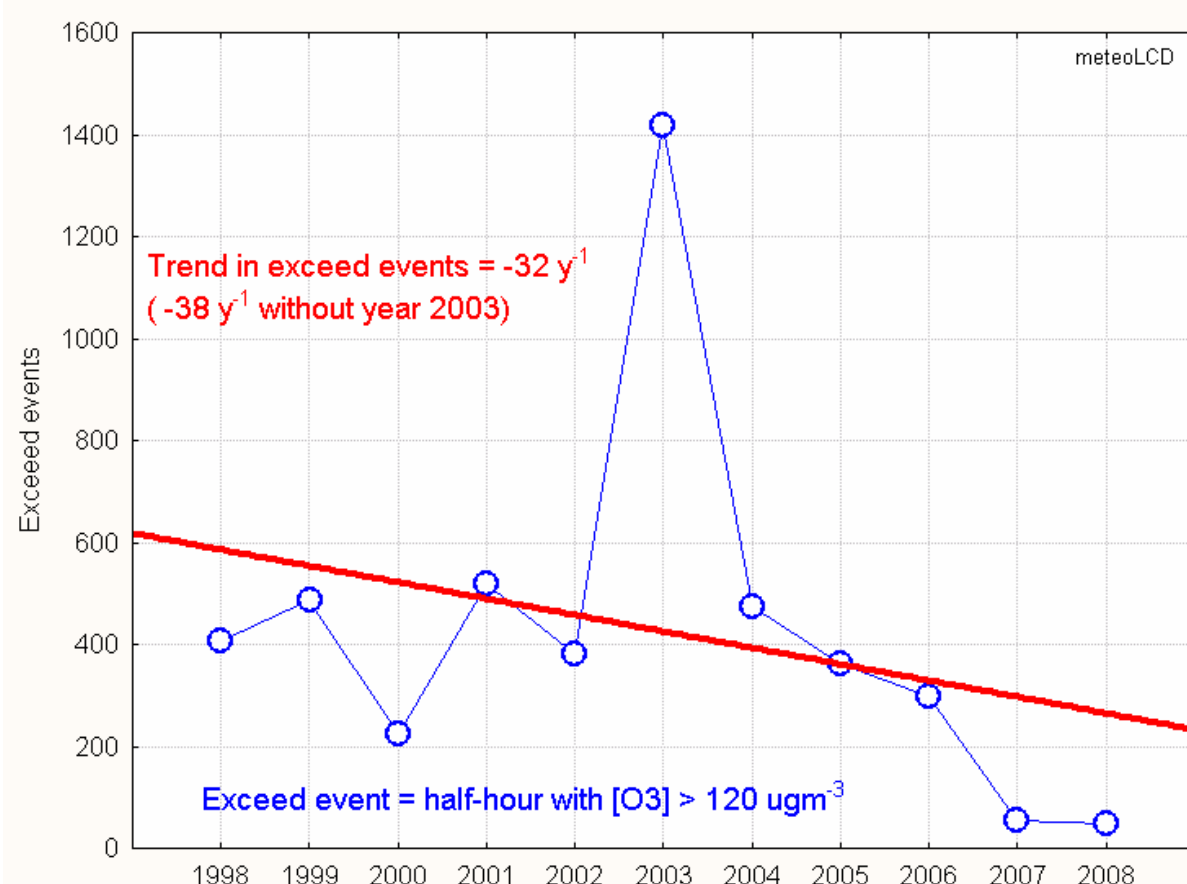
All	East wind	West wind
41.0	39.0	44.6



Monthly averages:

Despite increasing local air temperatures ( from 9.9°C to 10.8°C) most peak and minimum levels are falling since 1998. These negative trends become stronger after 2003.

The trend computed from all monthly averages suggests a decadal trend of  $-15 \mu\text{g}\cdot\text{m}^{-3}$  (about -7.5 ppb), same magnitude as the decadal trend computed from the yearly averages. 2007 ground ozone levels are the lowest in the decade, in accordance with [EEA, 5/2008]

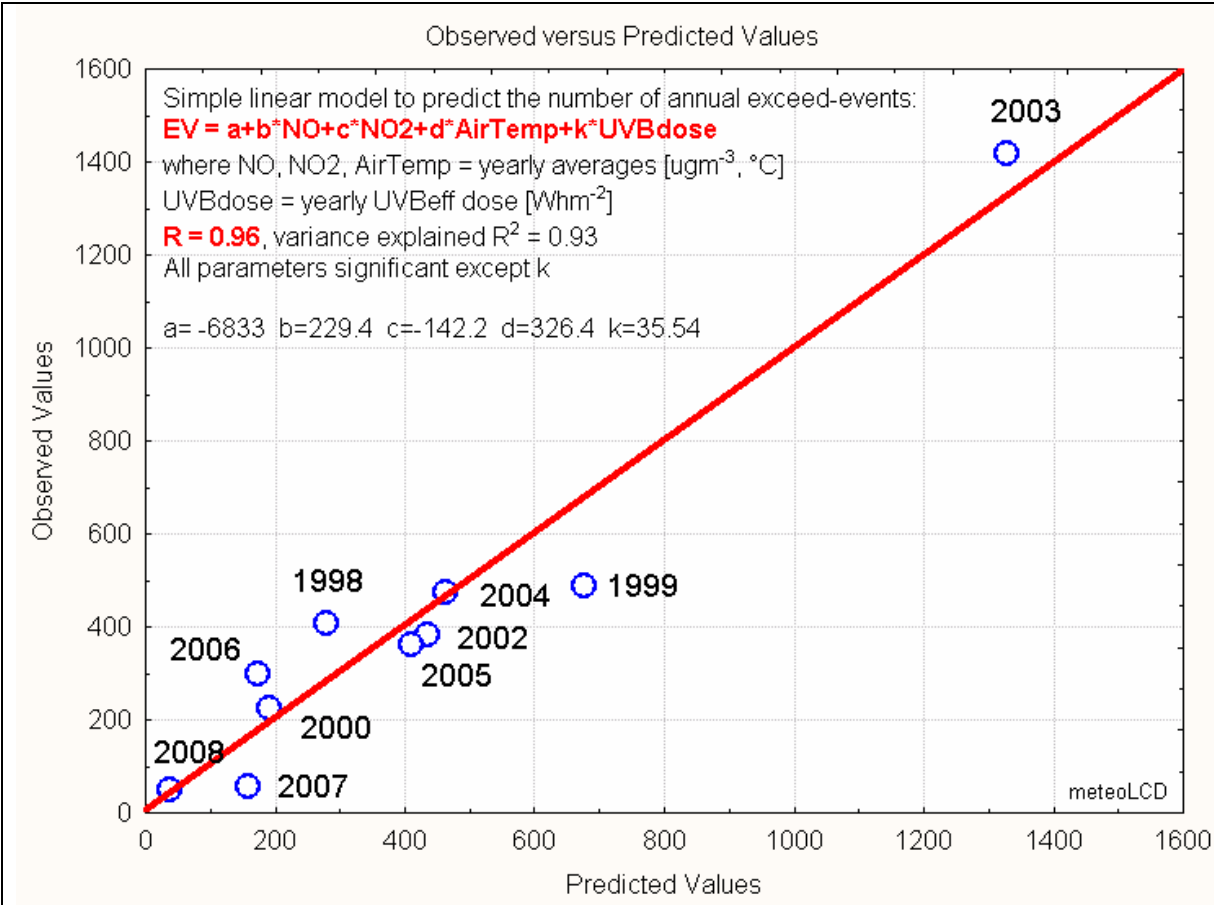


There is a remarkable reduction in the number of "exceed-events": the number of half-hours where the ozone concentration is **higher than  $120 \mu\text{g}\cdot\text{m}^{-3}$**  is diminishing since 1998 by **320** events per decade.

With one exception (2005) the number of exceed-events is slightly higher for easterly than westerly winds:

All	East wind	West wind
4551	2513	2038

This is opposite to the average O3 concentrations!

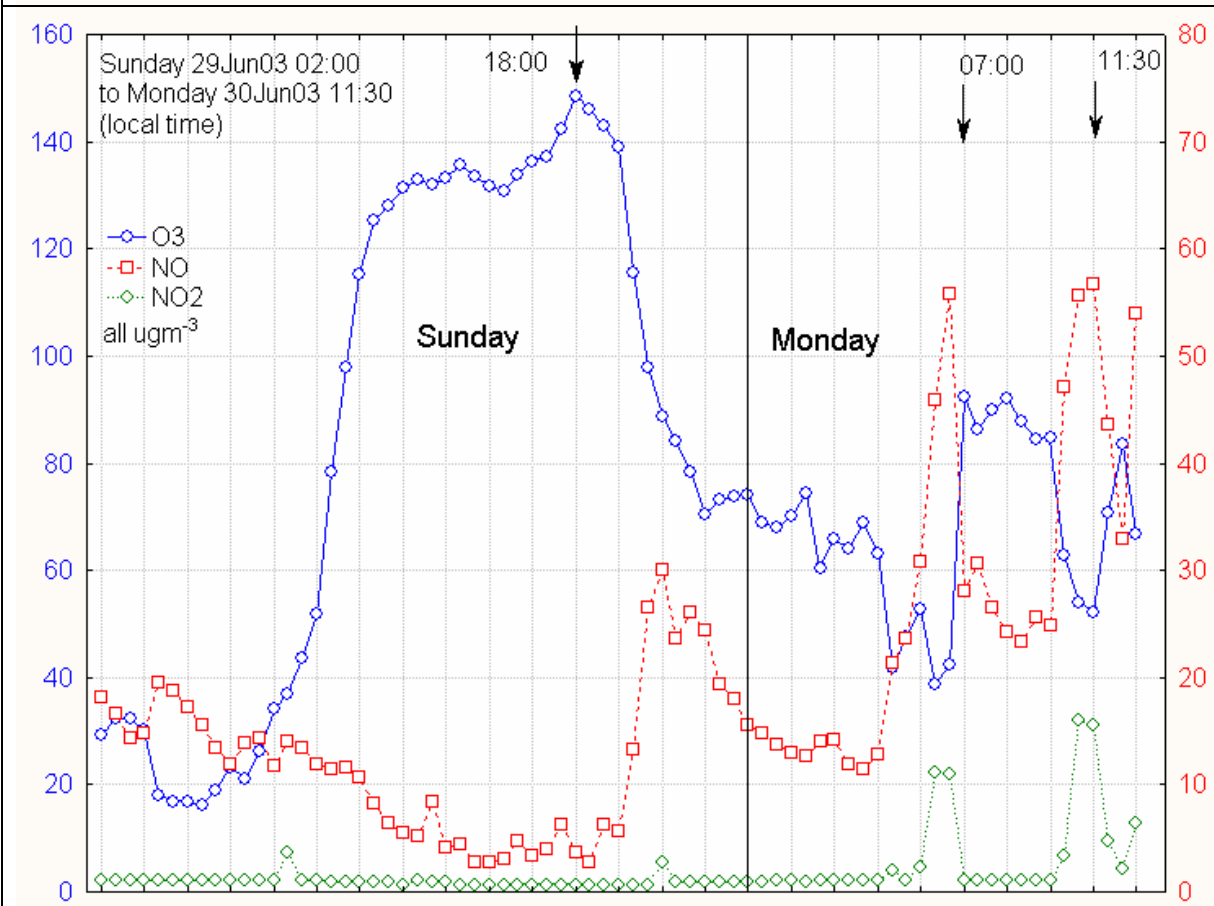


Linear model to predict the number of yearly exceed-events ( $\text{half-hour} > 120$ )

The best result (highest R) is given by a linear combination of the annual averages of air temperature, [NO] and [NO2] and the annual UVBeff dose.

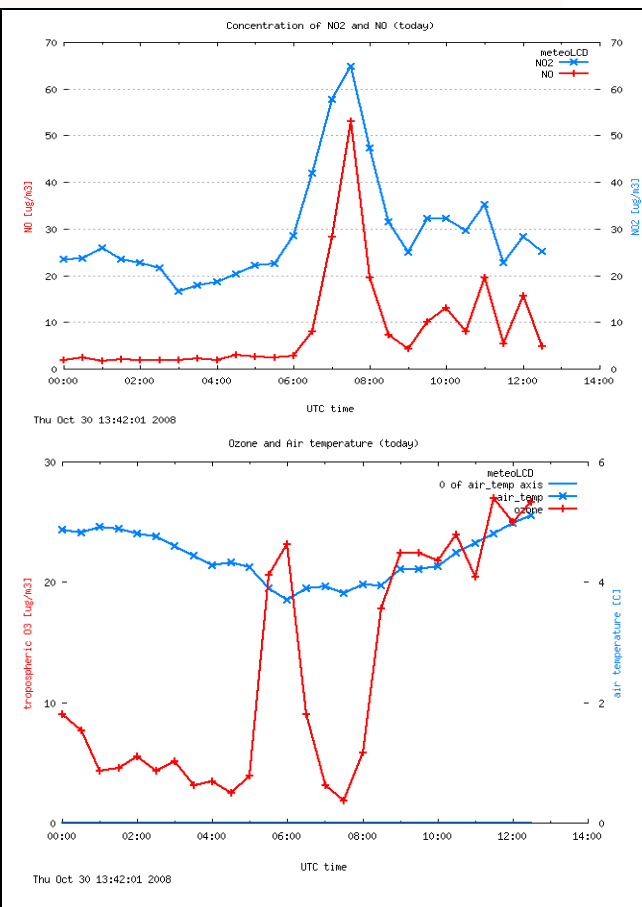
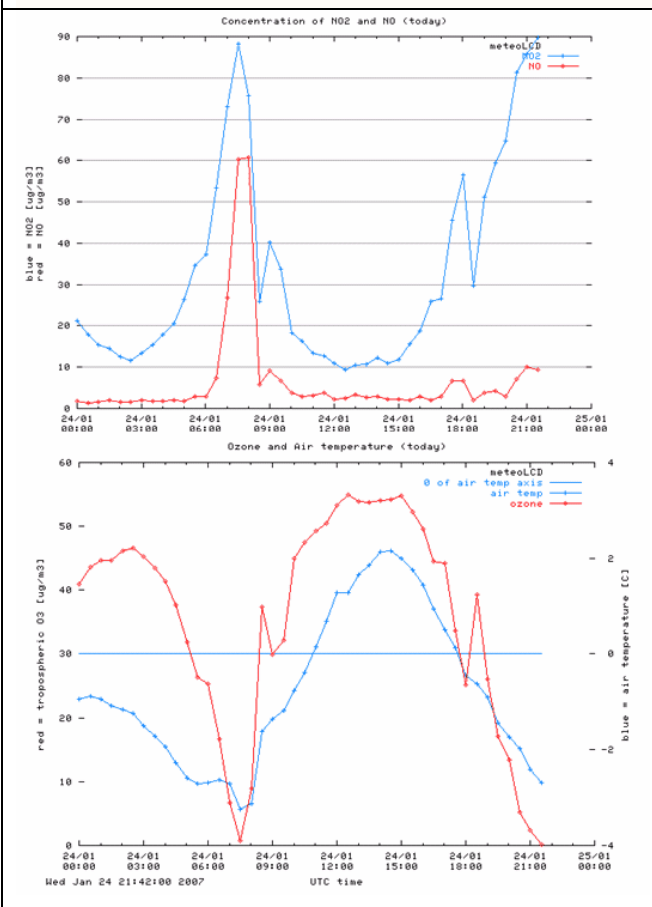
$R = 0.96$

This suggests no abrupt or fundamental changes during the last 10 years.



NOx titration:

O3 destruction by NO is shown here for Sunday and Monday (29 to 30 June 03). No morning traffic on Sunday. High Monday 07:00 NO peak by commuters lowers [O3]. A second [O3] lowering caused by 11:00 traffic. Often NO remains trapped in the morning inversion layer and reacts very quickly with O3, eventually bringing O3 concentrations to nearly zero (especially during colder days).

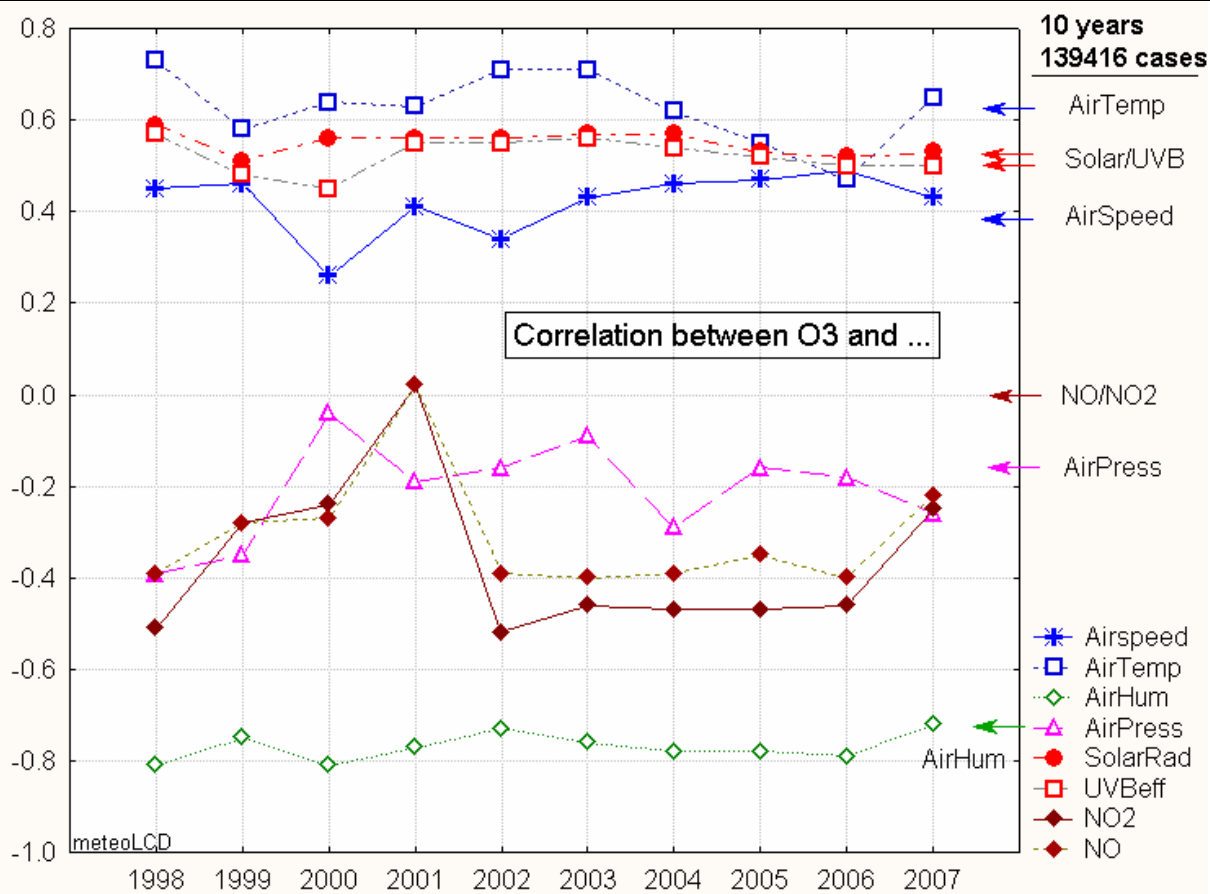


Example of a near total O3 destruction by NO peak during cold January morning (16Jan07) and fall (30Oct08).

Over the 10 years: [NO] trend is flat, [NO2] trend is  $+1 \mu\text{g m}^{-3} \text{y}^{-1}$

Mean [NO] and [NO2] are very low. Averages from 1998 to 2007:  
 [NO] =  $9.9 \mu\text{g m}^{-3}$   
 [NO2] =  $18.5 \mu\text{g m}^{-3}$

[NO2] (blue) and [NO] (red)  
 Air temperature (blue) and [O3] (red)



Correlations between [O3] and main atmospheric parameters.

Highest positives are for air temperature and solar radiation or UVBeff. Most negative correlation is for relative air humidity.

Note that correlations with [NO] or [NO2] are always negative: this suggests an overall VOC sensitive regime [Sillman, 1999].

All shown correlations are significant at the 5% level.

### Are peak O3 events always caused by pollution centres located upwind?

The common explication of summer O3 peaks is that they are caused by polluters located upwind.

There are some reasons to question this hypothesis for the Diekirch site.

Most industrial sites are located East of Diekirch; when wind blows from the East, the number of exceed-events ( $[O_3] > 120 \mu\text{g m}^{-3}$ ) is indeed higher than during westerly winds (55% versus 45% of total events). This small difference is not large enough to rule out natural factors.

Negative correlations of [O3] with [NO] and [NO2] suggest an overall VOC sensitive regime. Vast regions of deciduous (isoprene emitters) and coniferous (terpene emitters) forests are located East (Eifel) and West (Ardennes) from Diekirch: **the biogenic extremely reactive VOC's emitted during hot summer days may well be the dominant precursors.**

A polluted air mass is known to have VOC-sensitive chemistry, when it is located close to the emission sources, which would be here the neighbouring forest regions. Overall wind speeds are low (about 7 km/h) and polluting plumes would have a 20 hours transport time from the Wiesbaden region, switching the regime from an eventual VOC sensitive to NOx sensitive, contrary to the observations.

Transboundary measurements of O3, NOx and VOC's will be needed to clarify this situation, and to give a greater confidence in the validity of restrictions imposed to the public during summer ozone events.

One may even question the validity of these restrictions:

*"..dass für Nordwest- und Mitteleuropa das zusätzliche Potential besonderer lokaler..Kurzfristnahmen zur Vermeidung der Überschreitung von Ozonschwellenwerten mehr und mehr zu vernachlässigen ist und möglicherweise sogar obsolet geworden ist" [Prof.. P. Bruckmann, Die Ozonepisode im Juli und August 2003, Landesumweltamt Nordrhein-Westfalen]*

The role of biogenic VOC's (isoprenes, terpenes) is often neglected and/or unknown in its magnitude. [Sillman,1999].

It is assumed that natural VOC's globally outweigh anthropogenic sources:  
isoprene:  $675 \text{ Tgy}^{-1}$   
aVOC's:  $140 \text{ Tgy}^{-1}$   
[Royal Society, 2008].

This is in accordance with the observation that despite large anthropogenic nmVOC (-44%) and NOx (-32%) reductions, ozone base-levels have not changed in many parts of Europe during the last years [EEA, 5/2008].