Constant Flux-Layer Approach for Correction of Historical Schönbein-Type Ozone Measurements of the Gozo Series from 1884 – 1900 — Comparison with Present Day Ozone Records on Gozo

A contribution to subproject TOR-2

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Summary

Historical ozone records made by Sicilian Jesuits at the Seminary in Victoria on the rural island of Gozo (Malta) for the years 1884 to 1900 have recently been discovered. The ozone measurements, together with comprehensive meteorological variables, were made twice a day using the Schönbein test.

The original daily records of ozone from 1884 - 1900 were corrected for humidity dependence and exposure time and converted into mixing-ratio according to *Cartalis and Varotsos* (*1994*). Further evaluation of these converted ozone data under the aspect of the 'Constant-flux-layer Theory' and comparison with modern ozone measurements made under similar conditions on Gozo has shown that these corrections can give satisfying results regarding the relative changes of ozone. However, absolute ozone concentrations are far too high.

The results of our investigation is that, at the end of the 19th century on Gozo, the monthly averages of ozone mixing-ratio showed little annual variation with a maximum in winter/spring and a minimum in late summer. This is quite different to today's annual ozone variation which shows a maximum in spring changing then to a broad shoulder during the summer months and a minimum in winter. Assuming that the seasonal characteristics of dry ozone deposition have remained the same within Gozo's internal boundary layer during the last 100 years leads to the conclusion that the absolute values of the monthly averages of ozone mixing-ratio may have increased by more than five times in the Central Mediterranean.

Introduction

Measuring ozone by using the so-called Schönbein test paper was a very common method at many sites around the world at the end of the nineteenth century (e.g. *Pavelin et al., 1999, Sandroni et al., 1992, Anfossi et al., 1991; Bojkov, 1986*). In the case of the Gozo series, the paper strips (Dr. Lender's scale: 0 –14) were exposed and changed between 0900 and 2100 hrs local time. Additional meteorological measurements (temperature, humidity, wind speed etc.) were taken at 1500 hrs.

Unfortunately, this method shows a strong non-linear response to relative humidity and also to ozone itself. *Linvill et al.* (*1980*), *Kley et al.* (*1988*) and *Mühlheims et al.* (*1988*) carried out various laboratory experiments with the intention of quantifying these historical measurements and converting the relative Schönbein or Lender units into absolute ozone concentrations. *Cartalis and Varotsos* (*1994*) also included corrections considering 'over exposure effects' for the long exposure time of the paper strips over a period of 12 hours.

We were unfortunately not able to discover the manufacturer's name or recipe for the paper strips used on Gozo. Measurements made in Vienna published by *Lauscher* (*1983, 1984*) suggest that the 15 point Lender scale (0 – 14) is only a refinement of the original and most common 11 point Schönbein scale (0 – 10). The abscissa of the 'Schönbein unit – ppbv' conversion chart created by *Cartalis and Varotsos* (*1994*) needed to be multiplied simply by the factor of 1.4.
However, the above-mentioned laboratory experiments were conducted under simplified conditions such as constant relative humidity and constant ozone concentration over the whole exposure time which is not quite realistic for the conditions outdoors. Another critical factor in these attempts for absolute calibration is the fact that the original paper strips are not available anymore. Descriptions of their production are not uniform and vary widely throughout the literature (e.g. *Mühlheims et al., 1988, Linvill et at., 1980*) and may have also varied between the historical manufacturers.

Objectives, Results and Discussion

We demonstrate here that the ancient Lender ozone data in combination with constant-flux layer considerations (*Stull, 1991; Garratt, 1994*) can be used as proxy data for climatological evaluation of the past.
Instead of using the old humidity measurements of Gozo, which are more a spot-check rather than being representative for the whole 12 hour exposure time, we analysed the typical diurnal behaviour of the modern relative humidity measurements made at the Xewkija station over the last three years (*Nolle et al., 2002; Nolle, 2001*). The site at Xewkija is only 2.5 km away from the historical one in Victoria and also the environment and surroundings with respect to the boundary-layer meteorology are fairly comparable. Ozone measurements were also carried out at Xewkija from May 1997 to the end of 2001. The ozone distribution of this station has sub-urban characteristics and the influence of locally emitted pollutants is mainly expected from traffic during limited rush-hour periods (*Nolle, 2001*). In the following we analysed these modern ozone measurements for the same time intervals as used in the case of the historical ozone measurements. Rush-hour periods from 0530 hrs to 0830 hrs and from 1800 hrs to 2100 hrs were

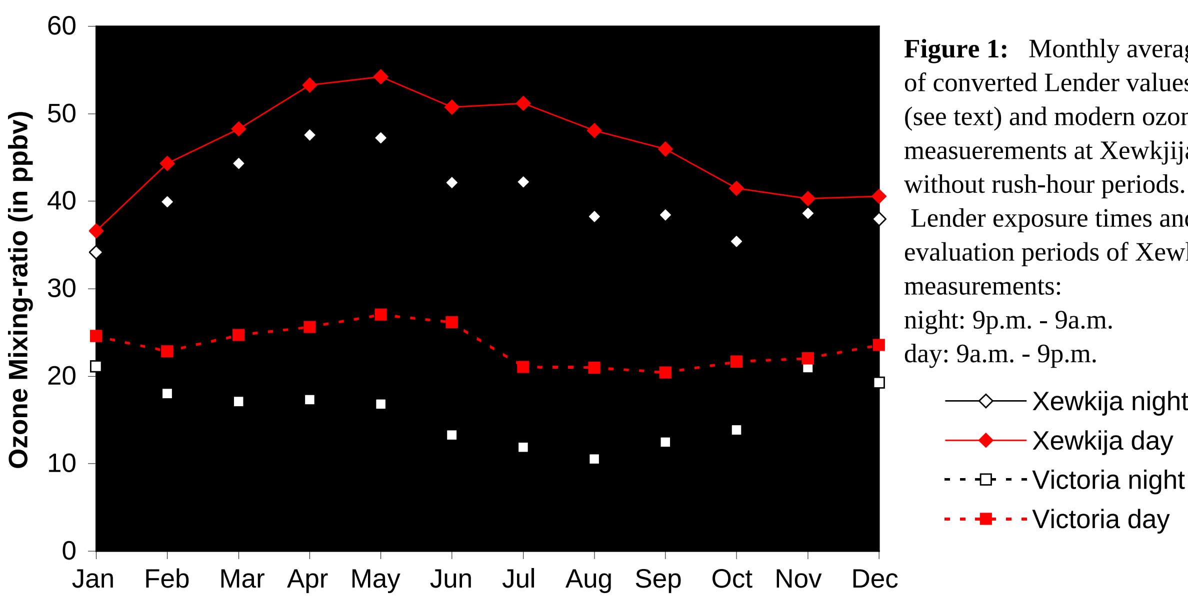

Figure 1: Monthly averages of converted Lender values (see text) and modern ozone measuerements at Xewkjija without rush-hour periods. Lender exposure times and evaluation periods of Xewkija measurements:
night: 9p.m. - 9a.m.
day: 9a.m. - 9p.m.

excluded from the computation of the averages to reduce the effect of ozone loss through titration with locally emitted NO.

Figure 1 shows the monthly averages of ozone mixing-ratio obtained from the converted Lender measurements according to *Cartalis and Varotsos* (*1994*). The curve of the converted day values (dashed line with filled squares) shows a primary ozone maximum in spring and a secondary one in mid-winter. The minimum in the late nineteenth century occurred in late summer. The curve for the night values (dashed, open squares) shows a more pronounced winter maximum. The minimum in summer appears to be deeper.

It is obvious that the difference of the ozone concentrations between the day and the night curves is caused by the loss of ozone within the stable nocturnal boundary layer. This difference is smaller during the winter months with prevailing strong winds (see Figure 2 for average wind speed at Giordan lighthouse, *Nolle et al.*, *2002*), creating a greater horizontal stress, that leads to stronger turbulence with greater vertical exchange of atmospheric parameters independent of the day or the night period. In summer, thermally driven convection is the most important transport regime during the day which is missing during the major part of the night period (*Nolle*, *2001*). From the climatological point of view we made the assumption that seasonal characteristics of dry ozone deposition (determined by the synoptically and turbulent advection and by the uptake of the surface) are the same for the historical and modern data series. The relative difference between the day and the night ozone values ($[O_3]_{day} - [O_3]_{night} / [O_3]_{day}$) can therefore be considered as a measure of the integrated ozone loss within the nocturnal boundary layer and should be a constant for each month of the year.

Figure 2 shows the monthly averages of the relative ozone difference for the historical data in Victoria and the modern data set at Xewkija. Both curves are quite similar in their shape but differ quantitatively. Under the assumptions made and discussed above this can be interpreted that the converted Lender ozone values in Figure 1 are too high.

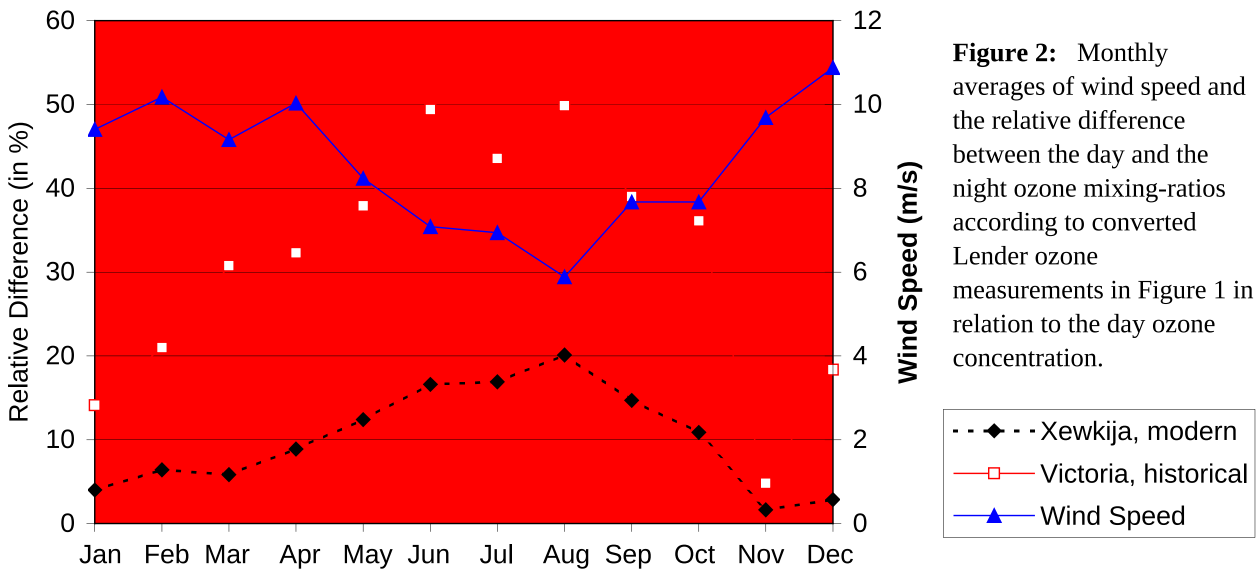

Figure 2: Monthly averages of wind speed and the relative difference between the day and the night ozone mixing-ratios according to converted Lender ozone measurements in Figure 1 in relation to the day ozone concentration.

The scatter plot (Figure 3) shows the correlation between the monthly paired data points of the relative differences between the day and the night ozone values. The fact that the correlation coefficient is high (if one considers the rather crude technique of the Schönbein – Lender measurements) and also that the best-fit regression line goes almost through the origin supports the correctness of the assumptions made.

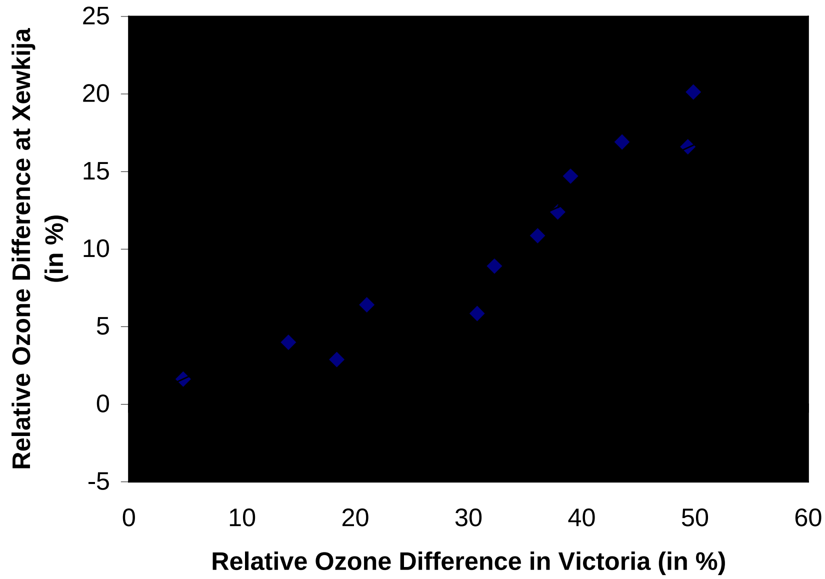

Figure 3: Scatter plot for the averages of monthly paired relative ozone differences between the historical ozone series in Victoria and the modern one at Xewkija.The dashed line is the best-fit regression line through the data points. The unbroken line is the trendline which was set to intercept the origin.

Figure 4 shows the monthly averages of corrected Lender ozone measurements (as in Figure 1) which were reduced by the multiplication factor of 0.335 obtained from the linear regression in Figure 3.

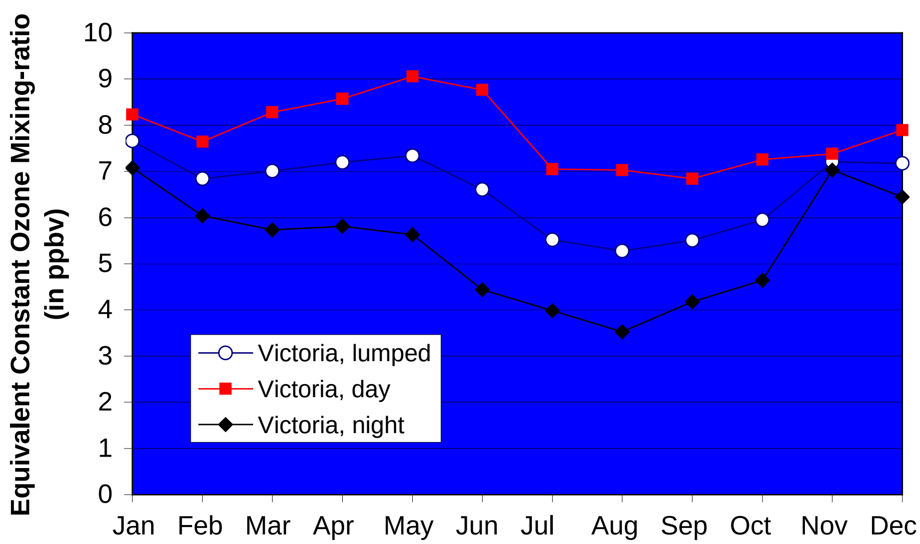

Figure 4: Corrected Lender ozone measurements (according to the one in Figure 1) multiplied by the factor 0.335 obtained from the regression line in Figure 3. The middle line (with circles) represents the lumped data sets (day and night).

The curve for the lumped ozone data shows a kind of winter/spring maximum of about 7 ppbv to 8 ppbv and a minimum in late summer of about 5 ppbv to 6 ppbv. This is very similar to what *Volz and Kley* (*1988*) reported regarding the calibrated Montsouris series of surface ozone during the second half of the nineteenth century near Paris. The low concentrations on Gozo during the end of the nineteenth century reveal that the ozone mixing-ratio in the Central Mediterranean increased by more than five over the past 100 years. There still remain some questions as to whether these low absolute ozone concentrations at the end of the 19th century are real. A detailed analysis, which also includes a sensitivity analysis for the corrections made, will be the subject of a forthcoming publication. However, the fact that the annual variation of ozone concentration showed a minimum in summer and a maximum in winter may be interpreted as the expected behaviour in the boundary layer of a 'clean' troposphere.

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