Atmos. Chem. Phys. Discuss., 7, S2781–S2790, 2007
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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Influence of altitude on ozone levels and variability in the lower troposphere:a ground-based study for western Europe over the period 2001–2004" *by* A. Chevalier et al.

A. Chevalier et al.

Received and published: 29 June 2007

First of all we thank the anonymous referees for their constructive comments, that have helped us to raise the scientific level of our study, especially on methodological ascpects but also because their comments have lead to complementary results. We are now able to provide rapidly a revised manuscript reaching – we hope – the standard of ACP.

We note that the referees in their comments go mostly in common directions, that we try to synthesize as follows:

1. Trend calculation and analysis

   Both referees:

   - request confidence intervals for the estimated ozone trends,
   - ask to what extent the interannual variability, and in particular the extreme values (e.g. August 2003), affect the calculated trends.

2. Representativity of surface stations vs. MOZAIC profiles over Frankfurt and balloon soundings over Payerne

   - Both referees question the relevance of the MOZAIC ozone profile over Franfurt as free-tropospheric reference for the rural and/or altitude stations, due to (i) the distance from the stations and (ii) the urban environment near Frankfurt.
   - Both referees ask for a clarification on the comparison of MOZAIC profiles over Frankfurt and Paris.
   - A common suggestion is made to additionnaly consider balloon-sounding data from Payerne (on the Swiss plateau).
   - It is requested to asses more quantitatively the ability of surface stations to represent the low-tropospheric background ozone stratification.

Replies to major points 1 and 2 are given in respective sections.

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1 Trend calculations and analysis

1.1 Trend calculation - confidence limits

In the ACPD paper (Table 2) trends were estimated from differences of average values between past periods of few years centred in the early 1990's on the one side, and the 2001-2004 period on the other side. The early set of average values were directly extracted from the literature (note that a number of the cited published references do not provide confidence intervals). We acknowledge that this methodology hardly allows estimates of confidence intervals and statistical significance. Consequently we have changed our strategy with a view to a revised manuscript.

First the former strategy (i.e. comparing average values from different periods) is now applied only to Pic du Midi, where no continuous series of data exists for the past decade. Nevertheless data from this site are available for a number of shorter periods in the past (Marenco et al., 1994), plus the recent 2001-2004 series. Thus we propose for the revised manuscript to keep the qualitative conclusion derived from Fig.2 – namely, stabilized ozone level at Pic du Midi since the early 1990's contrasting with the rapid increase in the 1980's. (As a support the comparable statement for Monte Cimone (see Table 2 in the ACPD paper) could also be kept.)

Then this result at PDM can be put in a wider perspective considering trends at other high altitude sites in the Alps, namely Jungfraujoch, Zugspitze and Sonnblick (JUN, ZSP, SON), where continuous and homogeneous data series exist from 1991 to 2004. On the base of yearly mean values obtained from those data, we calculated trends with associated 95% confidence intervals over different time periods: (i) 1991-2004 (the complete data series); (ii) 5 running decades starting in 1991, 1992, 1993, 1994 and 1995.

Over the longest period (1991-2004), trends are significant and positive, especially for

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the highest station JUN (0.62±0.23 ppb/yr). However, a closer look at the decadal trends and their evolution in time shows an overall decrease in both rate and statistical significance - even if the rates remain positive. Thus there is evidence that the increase of low tropospheric ozone in the Alpine area has slowed down since the early 1990s, in agreement with the evolution observed at Pic du Midi (and Monte Cimone).

1.2 Interannual variability - Impact of high ozone levels in 2003 (summer heat-wave)

To assess the impact of year 2003 while considering the running decadal trends, we paid attention to whether the decades involve year 2003 or not. The only noticeable impact is obtained for ZSP for the decade 1994-2003. The found rate (+0.30±0.38 ppb/yr) is higher than that for the 1993-2002 decade (+0.22±0.32 ppb/yr) and this result contrasts with the overall decrease of rates (mentionned in paragraph 1.1 above). This is explainable considering that 2003 being the last year of the decade, the high ozone value draws up the regression line at its endpoint. However this effect is not noticeable for JUN and SON (where decadal rates regularly decrease). Morevover the rate at ZSP almost vanishes for the decade 1995-2004 (+0.03±0.39 ppb/yr). So the impact of 2003 on trend calculations is minor at least in the condidered calculations from data series exceeding 10 years.

We also verified whether the interannual variability may affect the calculated trends. We estimated that variability to be the (square-rooted quadratic) mean departure of the yearly mean ozone levels from the linear regression curve. Considering the 1991-2004 period, we obtained 1.48, 1.47 and 1.39 ppb for JUN, SON and ZSP, respectively. (Note that at the rates calculated above, 3 to 5 years are needed for ozone trends to emerge from the interannual “noise”). For each station, years with ozone mean level departing (positively or negatively) from the trend curve by more than the calculated variability have been excluded for a new trend calculation (in particular year 2003 is

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filtered out in this way). The obtained results turn out to be very comparable to those found without filtering.

We will insert the above results and discussion in the revised manuscript.

2 Representativity of surface stations vs. MOZAIC profiles over Frankfurt and balloon soundings over Payerne

2.1 Treatment of MOZAIC data - Paris/Frankfurt comparison

The available MOZAIC ozone profiles over Frankfurt (sampled during the ascent or descent phases of the aircraft) amount to 3083 for the period 2001-2004.

For both airports MOZAIC take-offs and landings are rare in the evening. They are distributed in time mostly from the early morning to the early afternoon. This coincides more or less with the period between the daily minimum and maximum ozone content in the lowest levels. Therefore averaging all the MOZAIC profiles will provide a result that is rather representative of a daily mean. That's why no kind of diurnal adjustement was performed on the MOZAIC data.

The MOZAIC flights are not uniformly distributed over the 12 months of a year. There are indeed about 25% more MOZAIC flights in summer than in winter. In addition the frequency of MOZAIC flights is increasing from 2001 to 2004. With a view to obtain a profile representive of the annual mean ozone profile over Frankfurt for the period 2001-2004, we adopted the following strategy to avoid overweighting the summer period, or a year with respect to another.

We first reduced all the available MOZAIC profiles for a given month and airport to a monthly mean profile with corresponding standard deviation. The data were gridded on

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the vertical with a regular 50m mesh, in asl coordinate. Thus we obtained 45 monthly mean profiles over Frankfurt airport over the 2001-2004 period (May 2002, December 2002, November 2004 are missing), with on average 64 profiles contributing to each monthly mean. (Over Paris, only 20 monthly mean profiles were obtained for 2001-2004, with on average 34 profiles (at least 12) contributing to each monthly mean).

Then we averaged together the available 45 monthly-mean profiles to produce the 2001-2004 mean profile shown in Fig.4 (for the bars we also averaged the monthly standard deviations). In this way the profile in Fig.4 can hence be considered with some confidence to be representive of the annual mean (daytime) ozone profile over Frankfurt for 2001-2004.

For Paris (as mentionned above) the data coverage is by far not as good, therefore Paris' data are not used in the paper except in Fig.3. The profile in this figure does not aim at any kind of climatological representativity but at justifiying that it makes sense comparing ozone background levels from sites distant of several hundred kilometres from each other (and subsequently to compare surface data in France or Switzerland to MOZAIC data in Frankfurt). Fig.3 is an average of all monthly profiles providing they are simultaneously available in both Paris and Frankfurt. (Note that we will provide a revised Fig.3 for the manuscript, where we have eliminated 4 spurious monthly profiles over Paris. Despite fewer monthly profiles contributing to the mean, the newly obtained profile is smoother.)

We will insert the above clarifications into the revised manuscript (in sections 2 and 4).

2.2 Background ozone levels

Both Referees argued that MOZAIC profiles above Frankfurt are perhaps not representative of background ozone levels due to the urban environment and thus should not be taken as a reference for surface rural and mountain stations. In particular the

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ozone gradient in the lowest levels is expected to be sharpest in urban environment due to enhanced fast titration (by NO) close to the surface.

This cannot be excluded within the first hundred meters above the ground. Actually the lowest three surface stations in Fig.4 of the ACPD paper provide higher concentrations than MOZAIC. However MOZAIC profiles are not strictly vertical because the aircrafts fly rapidly away from/to the airport during their ascent/descent. Morever the specific urban influence on the ozone profile above a city is expected to vanish with elevation above the ground but the question remains how rapidly.

For these reasons we followed the Referees' suggestion to additionnally consider mean ozone profiles from the balloon soundings at Payerne (WOUDC data) and compare the profiles. For the revised manuscript we have prepared modified Figures 4 and 6 where the Payerne profile is overlaid (with accompanying $\pm 1\sigma$ intervals). (Again no diurnal adjustement was performed on Payerne profiles because the soundings are launched at 11 UTC. This time is approximately the middle between the morning minimum and afternoon maximum ozone concentration in the boundary layer. So an average of the soundings is expected to be representative of the daily mean).

We also have produced a series of figures showing how much the three data sets (MOZAIC profiles, Payerne soundings and surface stations) depart from each other, in order to assess more quantitatively the representativity of the surface stations – also a request from both Referees.

On annual average, the agreement between MOZAIC profiles and Payerne soundings is excellent (deviation $< 2\%$) above 1200m asl (this is not really a surprise since, as we have already shown in the ACPD paper (Fig.3), the agreement between the MOZAIC profiles at Frankfurt and Paris is also very good).

Below, the Payerne mean concentration profile shows a negative bias (of 5ppb) with respect to MOZAIC. As a result mean ozone contents depart from each other up to 15% in the lowermost levels. Surprisingly the found bias is opposite to that expected

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by Referee #2 (who suspected enhanced ozone titration in the airport area), especially in winter. To explain that the following arguments can be invoked[1]:

- The Payerne site is at 491m asl, i.e. about 400m higher than Frankfurt airport. If focusing on the influence of surface emissions on ozone in the lowest levels, the agl vertical coordinate is more appropriate to compare ozone profiles (contrasting with the free troposphere where the asl coordinate is relevant). Shifting downwards the Payerne profile of about 400m indeed provides a much better agreement for the lowest levels (this is shown with evidence by the related figure in the revised manuscript).

- Payerne is located just between the Alps and Jura mountain ridges. There a cold-air basin forms frequently in winter under anticyclonic conditions. The very stable air stratification in the levels below the Jura crest (1300-1500m asl) might lead to relatively important NOx concentrations even at this rural site. Low temperature and radiation (stratus layer) do not favour photochemical ozone production but rather destruction.

Interestingly the transition around 1200m between good (deviation < 2%) and poorer (deviation > 10%) agreement is very sharp.

In summary, either Frankfurt or Payerne data above 1200m can be taken as free tropospheric reference for the surface stations. Below surface effects specific to each site are expected.

Focusing on the surface stations, their annual mean ozone levels depart less than 15% from the free-tropospheric reference profiles above 1000m and less than 8% above 2000m (as one could expect, these altitude thresholds raise in summer and lower in winter, and the overall agreement is better in winter than in summer, due to a deeper

[1]We thank René Stübi (Meteoswiss) for his interesting hints to interpret the Payerne profiles.

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PBL in summer). Again, a sharp transition is found around the less-than-15% limit, with quite large disagreement below (up to 40%) – likely caused by specific surface effects at each site. Thus it is hard to say whether surface stations agree better with either Frankfurt or Payerne profiles.

As a conclusion, surface stations devoted to the monitoring of background low-tropospheric ozone should be placed in any case above 1000m, and if possible above 2000m.

We propose to include these new figures and conclusions in the revised manuscript.

2.3 Variability

In his major comment 2, Referee #2 suggests we could compare variabilities (estimated as the standard deviation) from MOZAIC data on the one hand, surface stations data on the other hand – and of course this could be also done from the balloon data.

This information was to some extent already provided in the ACPD paper, Fig. 4 and 6 ($\pm 1\sigma$ bars). For the comparison with MOZAIC, the standard deviations related to surface stations were calculated on the base of hourly data. This timestep was chosen (instead of a daily one) because MOZAIC take-offs and landings are not at fixed hours but distributed in the daytime (due to varying destinations or origins of the aircrafts) and this can add a diurnal component to the variability of MOZAIC ozone data.

Regarding the MOZAIC data, the intervals given in Fig. 4 and 6 result from an average of the standard deviations related to each considered monthly mean profiles (see section 2.1 of this reply). Therefore they do not rigorously represent standard deviations but the provided information is qualitatively equivalent.

Even if the amount of MOZAIC profiles (3083 for the 2001-2004 period) is enough to provide representative mean values, their distribution within the day is too sparse (few

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profiles per day and at varying hours) to allow a rigorous comparison of their standard deviation to that from hourly data.

For those reasons, in the ACPD paper we deliberately avoided a quantitative comparison of variabilities from MOZAIC and stations. We rather focused the discussion on the variability from the surface stations only (Fig. 5). However, even if those variabilities can hardly be compared, they both show much higher values in summer than winter. This qualitative statement was already present in the ACPD paper. It is further supported by the new data from Payerne.

For the revised manuscript some emphasis will be put on this result but however accompanied with a comment on the method to estimate those variabilities and the difficulty of a rigorous quantitative comparison.

2.4 Gradients

Since the Frankfurt and Payerne profiles agree very well with each other above 1200m, the gradient of 3 ppb/km estimated from Frankfurt profiles in the ACPD paper is also valid for Payerne.

Below this altitude the gradient given by MOZAIC over Frankfurt is of about 30 ppb/km. The Payerne profile shows a comparable gradient. Fig. 4 shows with some evidence that a gradient derived from the stations below 1200m would be gentler than the Frankfurt/Payerne gradient. However a very low statistical significance is clearly expected. This can be qualitatively stated in the revised manuscript but we feel that the only quantitative estimation that can be reasonably provided is from airborne measurements.

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