**Atmospheric
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Comment

Interactive comment on "Seasonal variability of measured Ozone production efficiencies in the lower free troposphere of Central Europe" *by* P. Zanis et al.

Anonymous Referee #2

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The authors have an impressive data set on O3 and NOz taken at a high altitude site in the Alps - which is used to calculate ozone production efficiencies and their variability with boundary layer influence and season. Interesting conclusions are reached regarding the influence of free troposphere photochemistry on the spring O3 maximum. The article is well constructed. I would like the authors to consider the comments below, especially the effects of using the magnitude of a correlation coefficient as a data acceptance criteria.

This article deserves to be published.

Interpretation of O3 vs. NOz regressions plots

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The measurements are done at a fixed site, so air mass changes could lead to changes in the O3 - NOz relation unrelated to photochemistry. Since JFJ, is not a preferred location (in the astronomical sense), these air mass changes will give scatter in the daily En values but should not introduce a bias.

The text should mention O3 loss processes. The observed O3 changes include chemical production and loss. Equation 2 is used to explain the observations but it does not include loss processes. An estimate of the relative importance of chemical production and loss of O3 during daytime hours would be useful.

I find it interesting that the data used for the regression is from the hours between 8AM and 8PM. In the summer these are photochemically active, but in the winter these hours include part of the night. Presumably one wants to concentrate on time periods where O3 is being formed and NOx being used up, with the ratio between these 2 processes given by En. Over a 24 hour cycle production and loss are on average in balance. So one should get the same value of En from nighttime measurements because, on average, there is no change in O3 and NOz from one 8AM to the next. The nighttime plot will have a positive En, differing from the daytime plot only in the time sequence that points are put on the graph. (lower left to upper right during the day; reversed during the night).

Three quarters of the days are removed from consideration by requiring that the correlation coefficient for the O3 versus NOz linear regressions exceed +0.5 (p9323, lines 10-11) . This criteria, no doubt, eliminates days where O3 and NOz don't follow each other because there is change in air mass. Without a large Delta O3 and/or Delta NOz, noise (atmospheric or instrumental) will lead to a poor correlation. The net effect is that using r as a screening criterion eliminates a class of day which may have low En (low Delta O3) or high En (low NOz). It should be noted in the paper that the values of En so deduced are biased towards those conditions that give better than average regression fits. This criteria will eliminate most low photochemistry days and will certainly eliminate days where there is net O3 loss. Worse, this criteria may distort the seasonal

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cycle. Figures 6 and 7, show that there is a seasonal variability in the frequency of days suitable for analysis (i.e. high r^2 days). Since low Delta O3 days are more likely to be rejected because of poor statistics, I conclude that there are more low Delta O3 days in the winter than in the spring. Including the low Delta O3 days would make the seasonal change from winter to spring more dramatic. Some of this is speculation on my part, but I urge the authors to investigate the possibility.

Seasonal cycle in O3 and NOz

Figure 8 has an interesting feature that I don't think was commented on. The seasonal cycle in O3 is due to 2 factors, the seasonal dependence of En and the seasonal dependence of NOz. Both are significant but the seasonal dependence of NOz is the more important.
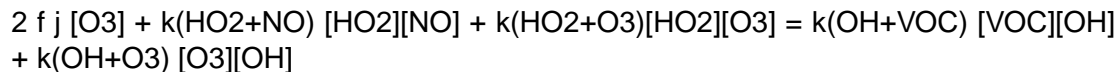
Other comments

p 9320, lines 2-4.

The order of magnitude increase of En attributed to Liu et al (1987) is probably taken from their Fig. 3. However, this graph does not show En. It shows Delta O3/NOx. The order of magnitude increase in the winter is due to the much longer lifetime of NOx and hence its higher concentration.

p9323, line 18 and Eq 1. reference that Equation is good for mid-NOx conditions.

I need some help on this one. My take is that Eq 1 is also valid for low NOx conditions.

The derivation in Zanis et al (2000) goes through a step (Equation B) that requires that NO be at least 50 pptv so that the cycling flux exceeds the primary rate of production. Given the simplified set of reactions that (1) depends on, I think that Equation 1 depends only on radicals being formed as OH and removed as HO2. NOx has to be below the point at which OH + NO2 is significant.

d[OH]/dt = 0, written out is:

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2 f j [O3] + k(HO2+NO) [HO2][NO] + k(HO2+O3)[HO2][O3] = k(OH+VOC) [VOC][OH] + k(OH+O3) [O3][OH]

(I'm ignoring RO2 for simplicity of notation)

d[OH + HO2]/dt = 0 yields

2 f j [O3] = 2 k' [HO2]^2.

[HO2] = (f j [O3] / k')^1/2

2 f j [O3] = 2 (k' f j [O3])^1/2 [HO2]

Substitute the last result into d[OH]/dt = 0. This gives Eq 1, without a lower limit on [NO].

p 9324 line 19. Sensitivity analysis of temperature dependence of En given by Eq (1).

The sensitivity analysis is done by varying single variables and thereby misses what might be an important factor. When temperature is varied the NO to NO2 ratio will change. Since the paper is considering seasonal cycles, this effect should be evaluated.

p9325, line 28. PAN is the dominant NOy species during spring and summer.

This raises an interesting question as to what the effect of PAN is since it is not in Eq 2.

p 9328, line 22. Discussion of exponential decrease of En as NOx levels increase.

Why isn't this plotted? Instead there is Fig. 5, which shows an exponential relation between En and NOy/CO. In order to make a connection with the cited literature one has to assume that changes in NOy/CO are mainly due to changes in NOy - and that changes in NOy are associated with changes in NOx. This is very indirect.

p 9328, lines 23 - 28. Discussion of dilution.

I don't follow the argument or understand what point is being made.

p 9331 lines 1 - 10 and Figure 7a in which data is split into 2 subsets

This could be eliminated. The results are shown and then discarded in favor of a split into 4 subsets. A split into 4 subsets does not have to be justified on the basis that 2 subsets don't adequately identify undisturbed free tropospheric air.

p 9333, line 2 "discernable selection rule"

Meaning?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9315, 2006.

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