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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Diurnal variability, photochemical production and loss processes of hydrogen peroxide in the boundary layer over Europe" *by* Horst Fischer et al.

Anonymous Referee #1

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The manuscript describes the diurnal variability of hydrogen peroxide and its precursors presented as median values averaged for the whole campaign for five different locations in Europe spanning southerly (Spain and Cyprus) to northerly (Finland) field sites. The median diurnal variability is proposed to be a robust signature representative for a 'typical' pattern during the campaigns.

Based on these data hydrogen peroxide budgets are calculated from photochemical production, photochemical loss and dry deposition loss. Photochemical production is linked to the main H2O2 production pathway via recombination of HO2 radicals, chemical loss through reaction with OH radicals and photolysis while dry deposition is

deduced from periods with constant mixing rations but still measurable production. Dry deposition losses than should be equal to production. HO2 and OH radicals were measured as well during the campaigns. As the production of H2O2 is a fast reaction from atmospheric radicals it's production term should thus basically follow the HO2 mixing ratios. The procedure to derive dry deposition loss rates requires also a constant mixed boundary layer as well as low impact from horizontal transport with probably different composition.

General comments

The manuscript is rather difficult to read even for somebody who is familiar with atmospheric chemistry. While the chemistry introduction is state of the art, see also Tremmel et al (1993) (there also vertical profiles of H2O2 in the planetary boundary layer and free troposphere) the description of the meteorological parameters controlling the composition of air masses investigated is marginal. Only for the HUMPPA campaign in Finland a more detailed meteorological description is available. However, it's necessary to consult an additional paper. This paper includes also the vertical structure of the atmosphere which is important for both, the production term of H2O2 during the morning hours between sunrise and noon as well as for the afternoon hours deposition calculation.

Meteorological data given in the companion paper for CYPHEX are marginal. For the campaign HOPE, that's especially low in H2O2 mixing ratios no measurements of the MBL and no meteorological data are available at all.

The diurnal patterns presented are only contained in the supplement. Besides varying vertical axis units the time axis is plotted as UTC. This is basically a good way to plot a diurnal cycle, however, given the varying local time it makes a comparison of the different campaign data more difficult.

As three of the five stations (PARADE, HOPE and CYPHEX) are located either on mountain tops or in hilly terrain it is not clear, whether the assumptions made about

a single vertical column over the filed site without only marginal impact of additional horizontal transport and depth of the nocturnal boundary layer are valid. These field sites are during the day subject to significant upslope winds and even in low elevation above the site horizontal wind speeds may increase strongly. Also the nocturnal inversion layer is often far below the elevation of the field site. This is addressed in the manuscript, but it's significance is not discussed.

The data base is better for the HUMPPA campaign in Finland, however, the meteorological description of the campaign by Williams et al (2011) indicates that the summer 2010 was extraordinary hot in Finland and not representative for a 'typical' summer, making the results for HUMPPA less comparable to the other campaigns.

In summary I would recommend to consider publication after major revisions including a detailed meteorological chapter and a clear argumentation that even at the mountain stations the procedures to derive production and loss are valid. Looking at figure 2, it's obvious that hydrogen peroxide mixing ratios in Cyprus and at the Hohenpeißenberg are clearly out of phase to solar radiation and probably horizontal advection plays a major role although the chemistry is rather fast.

What is the time scale of the horizontal advection of the marine airmasses mentionded on page 13, compare to the time scale of advection of air masses at other mountain sites?

Missing mixing height data for the day and the nocturnal inversion can be obtained for example from HYSPLIT. They agree relatively well with the HUMPPA measurements. Contained also in HYSPLIT is the information of rain during the transport. This is important for example for Föhn conditions where H2O2 mixing ratios are reduced due to washout shortly before arrival at the HPB observatory.

Tremmel, H.G., Junkermann, W. Slemr, F., and Platt, U., The Distribution of Hydrogen Peroxide in the Lower Troposphere over the Northeastern U.S. during Late Summer 1988, Journal of Geophysical Research, Vol. 98, 1083-1099, 1993

Minor comments

A statement about the detection limit of the method would be helpful, AERO-LASER claims < 100 ppt, but without mentioning whether this is 1 or 3 sigma. DOMINO, PARADE and HOPE mixing rations are often very close to this level.

The argument, that the mixing layer depth cannot be used for the CYPHEX campaign on page 11, line 5-6 also holds for the HOPE campaign.

The figures in the supplement are hardly readable. The paper is not understandably without these supplementary figures.

A figure illustrating graphically the budget calculations would be helpful.

Typing errors

Page 5, lines 30 /31, Meteorologie Consult instead of Metorologie Consult

Page 11, line 27 and 29. With an uncertainty of +- 100 % it's unreasonable to estimate a deposition velocity within the percent accuracy.

Page 12. Line 32 morning instead of mourning

1. Does the paper address relevant scientific questions within the scope of ACP? YES

2. Does the paper present novel concepts, ideas, tools, or data? YES

3. Are substantial conclusions reached? NOT ALWAYS CLEAR, see detailed Review

4. Are the scientific methods and assumptions valid and clearly outlined? NOT ALWAYS, see detailed review

5. Are the results sufficient to support the interpretations and conclusions? NOT ALWAYS see detailed review

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? NO

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8. Does the title clearly reflect the contents of the paper? YES

9. Does the abstract provide a concise and complete summary? YES

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11. Is the language fluent and precise? YES

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? YES

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? YES, see detailed review

14. Are the number and quality of references appropriate? YES

15. Is the amount and quality of supplementary material appropriate? NO, see detailed review

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