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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal dependence of peroxy radical concentrations at a northern hemisphere marine boundary layer site during summer and winter: evidence for photochemical activity in winter" *by* Z. L. Fleming et al.

Anonymous Referee #1

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General comments:

The paper by Fleming et al. presents peroxy radical data for two different seasons obtained at the Weybourne Atmospheric Observatory. The data are of high quality and reveal some interesting and sometimes surprising results. In particular the observation of higher ROx mixing ratios during the night compared to daylight hours in winter comes somewhat surprising, at least for me. The authors discuss the data with respect to peroxy radical sources and sinks, as well as their influence on net ozone tendency and photostationary state of the NO/NO2/O3 system. The paper is well written and

deserves publication in ACP after some revision.

From my point of view the discussion on night-time peroxy radical sources is highly speculative. The authors state that in particular during winter NO3 chemistry or reaction of alkenes with O3 are the major source of ROx. Although this is suggestive, the author don't give any proof for their conclusion. Such an explanation based on NO3 and/or alkene measurements or model results would be much more convincing. Similarly, the author argue that the slowly decreasing ROx levels in the late afternoon are due to HCHO photolysis, without presenting evidence for their conclusion. Again HCHO observations or modelling studies would be helpful. The authors should also consider and test alternative explanations for the high ROx levels at night. E.g. the ROx levels in Figure 7a (summer) show a decrease after midday and a minimum around 5 pm. After 5 pm the concentrations increase again reaching a local maximum around 8 pm. I think it is very unlikely that HCHO photolysis is responsible for this behaviour, since I can't see how it should produce a minimum at 5 pm. But what is the influence of changing airmasses. At the coast a land sea breeze system often establishes during the summer. Could this influence the measurements by transport of air from the sea predominately during the day and advection from the land after sunset? Also, what is the influence of a changing boundary layer height from day to night?

My other major concern is related to the calculation of the net ozone tendency. As documented in formula 2 (page 7252) calculation of the ozone loss requires measurements or model results on OH, HO2 and f. Unfortunately the paper lacks any information about the assumptions made for these species. The authors should therefore give information, how these parameters have been determined.

Minor comments:

In tables 1, 2 and 3 NOx is larger than the sum of NO and NO2. How is this possible?

On page 7247, line 17 the authors state that there is slightly more O3 in summer for SW conditions that in winter, but Table 1 gives identical values (34 ppb).

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On the same page, line 20 the authors mention that Table 1 also includes ozone production and destruction terms, which are not listed in the referenced table.

In section 3.8 the assignment of N(O3) and P(O3) as functions of NO are not in agreement with Fig. 13. In the Figure PO3 vs NO is Fig. 13b, while the text cites Fig. 13a for this relation.

Page 7256, line 25: I guess it should read at NO less than 0.1 ppbv.

References: I could not find a reference for Cardenas et al., 2000 in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7235, 2006.