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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.

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General comments:

The paper presents measurements of peroxy radicals made at the Weybourne Atmospheric Observatory, a coast site of England using a Peroxy Radical Chemical Amplifier during the summer and winter of 2002. Very different levels of peroxy radicals and their diurnal cycles were observed in the two different seasons. The average level of peroxy radicals during the winter campaign was about twice as high as during the summer

campaign. The level of peroxy radicals peaked in the nights during the winter, while it peaked in the daytime during the summer. To interpret the measurements, the authors of the paper made detailed comparison studies and theoretical calculations. The higher peroxy radical levels during the winter night are attributed to the nighttime NO3 chemistry, which is believed to be much more intensive during the winter than during the summer campaign.

Peroxy radicals are key intermediates of photochemical reactions and very difficult to measure. New observational data of peroxy radicals presented in this paper are definitely of interest. Most of the data are presented, analyzed, and interpreted appropriately. The paper could be strengthened by more ancillary measurements, such as those of NO3, alkenes (key species for nighttime radical formation), etc. Even without these measurements the paper is acceptable for publication in ACP after some revisions.

The authors could consider (1) to change the title to “Seasonal dependence of peroxy radical concentrations at a Northern hemisphere marine boundary layer site during summer and winter: Evidence for NO3 chemistry in winter” (photochemical activity is not important in the winter nights) and (2) to make the paper more concisely by reducing some text in section 2.2 (descriptions can be found in Fleming et al., 2006), in section 3.8 (not absolutely needed in the paper), and in 4 Conclusions. In addition, addressing issues in the following specific comments and making necessary technical corrections should improve the paper.

Specific comments:

1. Abstract, line 11-15: “For a daylight average, net ozone production in summer than winter (1.51 +/- 0.5 ppbv hˆ-1 and 1.11 +/- 0.47 ppbv hˆ-1 respectively) but summer shows more variability of (meteoro-logical) conditions than winter.” First, the words “was higher” should be added between “net ozone production” and “in summer” and a “,” before “respectively”. Second, the but-clause seems to be unnecessary because

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there is virtually no logical relation between the both parts of the sentence.

2. P. 7237, line 6-7: I suggest adding the reactions “CO + OH -> CO2 + H” and “H + O2 + M -> HO2 + M” between line 6 and 7 because CO + OH reaction is mentioned in line 1-2 as one of the formation routes for peroxy radicals. It is true that both reactions are given as R12 and R13, but the purposes are different.

3. P. 7243, line 18-25: What is the difference between the “calculated accuracy” (line 18-25) and the “overall radical measurement uncertainty” (line 25)? If they are the same, please choose one expression and use it consistently. Here “42%” is given as “calculated accuracy” or “overall uncertainty”, however, in Fleming et al. (2006), to which the authors reference, it is stated that “the overall uncertainty for any given peroxy radical measurement is 38% (at 1s)”. Which figure is more reliable?

4. P. 7247, line 9: “NOx ($<$1 ppbv)” is not accurate because according to Table 1 NOx concentration for summer N is 1.03 ppbv, which is slightly $>$ 1 ppbv.

5. P. 7247, line 12-13: “The winter average NOx of 1.72 ppbv is more polluted than both the summer clean sectors (with 0.35 and 0.82 ppbv average)”. I believe either the figures given in the brackets or those in Table 1 are not correct. In Table 1 the authors give 1.03 and 0.39 for summer N and E sectors, respectively.

6. P. 7248, line 12: I suggest adding the estimated detection limit of the earlier instrument after “instrument”.

7. P. 7251, line 21-22: “The gradient of the increase in night-time peroxy radical levels from low to high NOx is greater in winter than in summer.” I believe this statement is based on Figures 8(a) and 8(b). If so, it would be better to present it more specifically, for example, by providing the increase gradients for winter and summer.

8. P. 7252, line 18-20: “Without supporting data it is difficult to confirm which other peroxy radical forming mechanisms (like ozone-alkene reactions) are important (see Salisbury et al., 2001).” No measurements of VOCs during the campaign?

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9. P. 7253, line 18: The expression “in the summer (when peroxy radical concentrations are higher)” is not supported by Figures 5 and 6 and Tables 1 and 2, which show peroxy radical concentrations are higher in winter than in summer.

10. P. 7253, line 19, Table 4, and Figure 10: Although the statement “the apparent N(O3) campaign averages are higher in summer compared to winter," are consistent with N(O3) data given in Table 4, it seems contradictory to the data in Figure 10. Looking at Figure 10 and trying to estimate N(O3) campaign averages for summer and winter, I cannot conclude that the N(O3) campaign average is higher in summer. I believe the values for both campaign are nearly the same or the winter average is higher than the summer average N(O3).

11. P. 7254, line 13-16 and Table 1: According to Table 1, the average [NO] in winter is 0.14 ppbv instead of 0.4 ppbv and the average [NO2] in winter is 1.58 ppbv instead of 1.3 ppbv. Either the data in Table 1 are wrong or the figures and the text in line 13-16 should be corrected.

12. P. 7255, line 12-14: Why is the value for 27 January not given?

13. P. 7256, line 2-3: Data of net ozone production are not included in Table 2. Where are the production rates 1.11 and 1.55 ppbv hˆ-1 from?

14. P. 7256, line 17-20: “The lower P(O3) and N(O3) values are more different to each other as ozone loss affects N(O3) much more but due to the density of values, it is hard to see any differences between Figs. 13a and b.” If there are differences between quantities and the data are graphically displayed, it is better to make the differences visible on the graph. Please try to use logarithmic instead of linear axes.

15. P. 7256, line 25-28: Is the expression “at [NO]$<$0.1 pptv” correct? The detection limit of the NOx instrument is 1-2 pptv (P. 7244). How reliable is the [NO] value $<$ 0.1 pptv? In addition, the facts described in this paragraph are hardly visible in Figure 13.

16. P. 7257, line 8: “The Weybourne 2002 data showed no such decrease in ozone

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production". Why? Is there any explanation?

17. P.7257, line 9-13: "The average dlnP(O3)/dln[NOx] (with standard deviations in brackets) for summer and winter were 1.04 (6.70) and 2.00 (21.3). These values imply that NOx affects P(O3) in an essentially linear fashion in summer, and that the same NOx leads to twice as much ozone production in winter as it would in summer (see also Fleming et al., 2006)." Here the statement "the same NOx leads to twice as much ozone production in winter as it would in summer" is mathematically not correct. Since dlnP(O3)/dln[NOx] was about 1 in summer and 2 in winter, one may obtain the relationships P(O3)=A[NOx] and P(O3)=B[NOx]ˆ2 for summer and winter, respectively, with A and B being constants. The effect of NOx on P(O3) can be expressed as dP(O3)/d[NOx]. In summer dP(O3)/d[NOx]=A and in winter dP(O3)/d[NOx]=2B[NOx]. This means that dP(O3)/d[NOx] is dependent of [NOx] in winter but not in summer. Even if A equals B, the above mentioned statement is not always correct.

18. P. 7258, line 20-24: "However, during the night, large concentrations of peroxy radicals were formed in winter, making night-time levels much higher than daylight levels and even up to twice as high as the maximum summer daytime concentrations. Night-time peroxy radical formation leads to much higher average peroxy radical concentrations in winter than summer." As a reader I would like to see at this place the concrete reason for this extraordinary phenomenon (higher night-time levels of peroxy radicals in winter). However, this reason is given two paragraphs after. Perhaps it is better to modify the structure of the text in "Conclusions", making the conclusions clearer and more concisely.

19. Table 1: It is strange that for the sectors Summer N, NW, and SSW the levels of [NOx] are much greater than those of [NO] + [NO2]. Is this caused by measurement error, wrong calculations or typos? Please check these carefully and also compare the values in the table with those mentioned in the text.

20. Table 2: There is a problem regarding [NOx]>>[NO]+[NO2], as in Table 1. In

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addition O3 data (especially those for winter) in this table should be checked for correctness. For the winter O3 curve I estimate the winter average of O3 to be lower than 36 ppbv.

21. Table 3: O3 data should be checked for correctness. O3 level for “winter all” is 27 ppbv. However, the winter diurnal cycle of O3 shown in Figure 7 indicates that all hourly averages of O3 are higher than 28 ppbv.

Technical corrections:

1. P. 7241, line 28: I believe “(1995)” is not correct and should be changed to “(1996)”.

2. P. 7242, line 3: Please change “CO2 and NO2 respectively” to “NO2 and CO2, respectively”.

3. P. 7244, line 8: Change “was” to “were”.

4. P. 7247, line 15: Should not the “NW and S sectors” be NW and SSW sectors”?

5. P. 7248, line 13: Change “lower than in winter than summer” to “lower in winter than in summer”.

6. P. 7249, line 28: Change “where implicated” to “were implicated”.

7. P. 7255, line 16: Change “The 31 January” to “The 28 and 31 January” because the average φ value for 28 January is 1.35.

8. P. 7255, line 24: Change “the diurnal P(O3) diurnal cycle” to “the P(O3) diurnal cycle”.

9. P. 7256, line 12: “Fig. 13b” should be “Figure 13(a)”.

10. P. 7256, line 16: “Fig. 13a” should be “Figure 13(b)”.

11. P. 7256, line 20: “Figs. 13a and b” should be “Figures 13(a) and (b)”. To be consistent, the authors should use either “Figure x” or “Fig. x”, but not mixed.

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12. P. 7258, line 10: Change “in summer. (Stroud et al., 2004) leading to” to “in summer (Stroud et al., 2004), leading to”.

13. P. 7259, line 23: Change “The second is the by the substantially” to “The second is the substantially”.

14. Fig.3: According to the figure caption black and grey represent winds $<$ 3m/s and $>$3m/s, respectively. Therefore legend in the figure is wrong.

15. Fig. 4: The quality of this figure is low. Please use higher dpi and different color.

16. Fig. 5: Please use different colors for different quantities and choose larger font size for the axis labels.

17. Fig.13, figure caption line 2: “(Grey diamonds: summer; crosses: winter)” is not correct and can be removed.

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