

Interactive comment on “Measurements and modelling of I₂, IO, OIO, BrO and NO₃ in the mid-latitude marine boundary layer” by A. Saiz-Lopez et al.

Anonymous Referee #2

Received and published: 25 October 2005

General comments This paper describes a series of measurements of NO₃, IO, I₂, OIO, and BrO made by the DOAS technique during the NABLEX campaign during the summer at Mace Head at the Republic of Ireland.

There is little coherence in the paper as the authors move relatively rapidly between discussing NO₃, iodine and bromine chemistry. There is little depth in each section and often the conclusions appear inconsequential. There is a tendency to refer the reader to the similarity of these observations to those made previously by this group or other groups. In many cases it appears that these observations have already been

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discussed in previous papers making it difficult to work out what is novel in this paper and what is a reiteration of previous work. The authors should attempt to strengthen the science in each section. What are the wider implications of their work? What do their results mean?

Overall it appears that the paper is a collection of thoughts that could not be drawn further into individual papers. It does not read very coherently.

Specific comments

Abstract

Why are there term symbols in the abstract? They do not appear elsewhere in the text and the method of detection has been described elsewhere by this group.

Introduction

Lots of the information in the 'results' section really belongs in the introduction. Previous work is extensively discussed in the results section making it difficult to assess what is new and what is describing previous efforts. There is often an effort to self cite where other older references would be more appropriate.

The authors describe the reaction between I₂ and NO₃ in the introduction and then go on to describe it in the results sections. Is this a new result or is this already known? It is confusing to the reader.

Section 3.1 The authors do not tell us how they have defined 'clean marine' and 'semi-polluted' airmasses.

Figures 2 and 3 are confusing. I would suggest the diurnal cycle and the trajectories are put on separate plots.

I don't find the argument about 22 pptv hr⁻¹ very convincing. This only works then the timescale of the change is much less than the NO₃ lifetime. What is the NO₃ lifetime assumed? How does this compare to the 2 hour timescale used for the gradient. Why

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is this result important or novel? I need to be persuaded more that this calculation is useful.

The inter-comparison between the long-path and cavity ring-down systems is mentioned briefly. This should go into the introduction and some comments be made about what the results are rather than just leaving a sentence to hang rather uncomfortably.

Where does the surface area used for the modeling of the N₂O₅ come from?

Section 3.2 I don't find the argument that the maximum in the NO₃ profile being at 5km being due to DMS oxidation particularly convincing. Are all the vertical points independent bits of information from the retrieval or is there overlap? How can they be convinced that this doesn't represent higher NO_x or O₃ concentrations at this layer transported from else where? Why is the graph plotted in # cm⁻³ whereas NO₃ is described in mixing ratios else where in the paper? What does the vertical profile look as mixing ratio? Does this degree of NO₃ depletion make sense given what we know about the vertical distribution of DMS and NO₃?

Section 3.3 Much of this section appears to have been discussed extensively in previous papers produced by the authors. Perhaps this information should be described in the introduction so that any novel work can be described in this results section. It is not clear what has already been described in previous papers and what is novel.

The authors should specify their oceanic I₂ source strength.

Section 3.5 Why are the reactions Br+CH₂O, Br+CH₃CHO and Br+ Hydrocarbons not included in the model? It would appear that the main BrO_x recycling chain termination steps are missing from the chemistry scheme. This presumably has quite large influence on the concentrations calculated. This is not discussed at all in the paper and seems like a major weakness.

There is uncertainty over the gamma BrNO₃ with the authors choosing a relatively low value. However, they should consider the implications of a gamma BrNO₃ which is

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higher which would make it more consistent with previous studies. Does this have any impact on their conclusions?

BrNO₃ concentrations become a relatively large proportion of the total active nitrogen in the model. The total NO+NO₂ is kept at 35 pptv during the day, 30 pptv at night. The BrNO₃ reaches up to 15 pptv. This implies a source of NO_x into the system. A simpler approach would be to let the NO and NO₂ concentrations float from their initial conditions and to then interpret the model. The same should be said for the OH and HO₂ concentrations. If the BrO is having a significant impact on these species this should be reflected in the equations that are being solved. These simplifications are not necessarily useful.

Fig 1 The figure should have a better description of time. It looks like the date but this is not explicit.

Fig 2 This should be split into 2 figures, one for the concentration time series and one for the trajectories. What are the arrival pressure levels? Doesn't only the bottom most one really matter?

Fig 5 Date | GMT suggests a time rather than the date given

Fig 8 Can we see a similar plot from the data, to compare the model with the observations. Something like figure 9.

Fig 9 There should be averaging error bars on the plot

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? See text 3) Are substantial conclusions reached? See text 4) Are the scientific methods and assumptions valid and clearly outlined? See text 5) Are the results sufficient to support the interpretations and conclusions? See text 6) Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Probably 7) Do the authors give proper credit to related work and

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clearly indicate their own new/original contribution? See text 8) Does the title clearly reflect the contents of the paper? Yes 9) Does the abstract provide a concise and complete summary? Yes 10) Is the overall presentation well structured and clear? See text 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? See text 14) Are the number and quality of references appropriate? See text 15) Is the amount and quality of supplementary material appropriate? Yes

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9731, 2005.

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