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Atmospheric
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Discussions

Interactive comment on "Measurements and modelling of I_2, IO, OIO, BrO and NO_3 in the mid-latitude marine boundary layer" *by* A. Saiz-Lopez et al.

A. Saiz-Lopez et al.

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We would like to thank the referees for their comments and suggestions, which have now been addressed and included in the final version of this paper.

Referee #1 (Roland von Glasow)

Specific comments:

p 9732, l. 13-15: It has now been pointed out in the abstract that a bromine chemistry model has been used to simulate the diurnal behaviour of the BrO radical showing that initially prescribed mixing ratios of photolabile precursors of atomic Br can be kept in

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the gas phase via halogen recycling in sea-salt aerosol.

p 9733, l. 11-12: The review paper by Sander et al., 2003 cited.

p 9733, l. 25: The paper by Vogt et al., 2003 has been added.

p 9733, l. 26-27: Reference to the importance of the reaction of IO with DMS has been removed from the introduction and the work of Toumi (1994) on the impact of the reaction of BrO + DMS added

p 9738, l. 16-18: It has now been mentioned in the text that during the NAMBLEX campaign DMS mixing ratios reached values up to 240 ppt with vertical profiles above Mace Head showing a marine influence up to an altitude of 3 km due to local convective processes (Purvis et al., 2005).

p 9738, l. 26-27: Figure 5 has been re-done and separated into 3 different figures for better image resolution of the dataset points. In the figure, the points without symbols imply lack of measurements during that time either because the instrument was off or because it was monitoring other absorbing species in a different spectral region. Given the volume of data points, an average detection limit, instead on individual point detection limits, is kept in the figure for clarity. The figures also show the 2-sigma error bars, including those points whose statistical lower error limit is below zero.

p 9739, l. 9-10: See above for improvement of figure 5. It has been included that since the time resolution of the instrument is 30 min for the I2 measurements, it must therefore be considered that larger values and shorter concentrations peaks can possibly occur

p 9739, l. 25-27: From our set of measurements it cannot be concluded that there is an open ocean source of I2. Therefore, this is treated only as a possibility based on previously published work (Garland and Curtis, 1981). However, in the text, other possibilities have been included such as re-circulating air-masses originated at the coast at low tide and that the tide can be higher and still result in moderate iodine emissions (i.e. the kelp beds extend further up the shore).

p 9740, last paragraph: The work of Ingham et al., (2000) has been cited alongside that of Joseph et al., (2005).

p 9742, l. 13: It has been added that this figure shows that the delay in the OIO peak appearance is ~10 min in the spatially limited box model, whereas in the measurements the subsequent OIO peak occurrence is not a consistent feature and, when happening, its delay is found to be variable (e.g. from minutes up to an hour). Note however the time resolution of the DOAS instrument, which, for I2 and OIO, provides averaged values every 30 minutes. In the boundary layer, apart from the consideration of vertical mixing, this variability could follow the dependence on the presence of NO3, whose values fluctuate with air-masses origin. Notwithstanding the above proposed reaction, the possibility of a different mechanism cannot be ruled out. We prescribe I2 mixing ratios so that a Gaussian distribution peak corresponds to the average night-time I2 peak of about 40 ppt that was observed during nocturnal low tide.

p 9747 and figure 9: Figure 9 has been replaced by one containing all three days when BrO was found to show a post sunrise increase during NAMBLEX. The detection limit for BrO at the hours around sunrise was ~1 ppt.

As the referee points out, it is not surprising that initializing the model with Br2 and BrCl mixing ratios leads to the formation of a post-sunrise pulse. However, the main reason of the study was to simulate whether these initial mixing ratios of photolabile precursors of Br atoms can be sustained for one day in the gas phase by halogen recycling on sea-salt aerosols under the parameterizations prescribed in the model. The slow decrease of BrNO3 at night responds to the accommodation coefficient used in the model. Sensitivity studies have been conducted for higher gamma of BrNO3. It must be recognized that this is a simple approach to the issue of halogen recycling on sea-salt aerosols and therefore a more thorough modeling treatment of the aqueous phase chemistry is believed to be beyond the scope of this time series paper.

p 9742, l. 13: The model is not initialized with 10.5 ppt of photolyzable bromine but with 4.5 and 1.5 ppt of Br2 and BrCl respectively. The model conserved the bromine mass throughout the simulations.

p 9748, l. 2-11: Thanks to the referee, it has been noted that Wachsmuth et al. (2002) measured the gamma of HOBr under conditions of pH ˜ 5.7

p 9748, l.14: This amounts a gas-phase bromine concentration of ˜ 4 x 108 atoms cm-3.

Figures:

Fig 1: It has been expanded into two different panels for clarity.

Fig. 3 and 3: The NO3 measurements and the back trajectories and pressure levels of the different air-masses have been plotted in different figures.

Fig. 5: Different figures have now been made for I2, OIO and IO to improve the resolution of the time series.

Fig 9: It has been replaced by a figure containing the three days of measurements when post-sunrise increase of BrO was observed.

Typos:

- Hönninger has been corrected

- Canosa-Mas has been amended

- von Glasow has also been amended

Referee # 2

General comments:

The referee is concerned that this paper is a collection of essentially unconnected measurements. In fact, what we have reported here is a comprehensive and close to unique set of DOAS measurements, made during 6 weeks of the NAMBLEX campaign, which we think are closely connected (hopefully the revised text has made the links clearer). The data set is rare because measurements of IO, OIO, BrO, I2 and NO3 were made. The observations of mid-latitude boundary layer BrO are a first, as are the measurements of I2 and the night-time observations of IO. We therefore consider that it is crucial to bring the entire data-set together in a single publication. As we show in the paper, NO3 is the likely source of iodine oxide radicals at night, and iodine oxides and N2O5 (NO3, indirectly) are important for activating bromine from sea-salt aerosol. Both of these aspects are modelled in detail in the paper.

Nevertheless, we agree that the paper could have been better organized to stress these connections. Following the referee's comments, we have now re-organized the text and moved some of the introductory material provided in Sections 3.1, 3.2 and 3.3 to the introduction section.

Specific comments:

Abstract

In a previous publication we reported the first detection of I2 by DOAS, in this paper the entire dataset of I2 measurements is shown and we therefore considered appropriate to provide the spectral interval and the electronic transition of the molecule used in the spectral analysis.

Introduction

Some of the information given in following sections has now been included in the introduction. In the case of the I2 and NO3 reaction, it has been deleted from the results section and only mentioned in the introduction.

Section 3.1

The 'clean marine' and semi-polluted' air masses have been defined according to their origin relative to Mace Head as westerly and easterly respectively.

Figures 2 and 3 have been re-plotted so that the NO3 measurements and the back trajectories and pressure levels of the different air-masses have been plotted in different figures.

Following the referee's suggestion the discussion on the rate of formation of the NO3 radical in Section 3.1 has been deleted (accordingly from the corresponding figure).

The intercomparison between the long-path and the in-situ instrument in the measurement of NO3 has been included in the introduction. Also, it has been pointed out that the in-situ BBCRDS values tended to be lower than those measured with the DOAS. This difference can possibly be explained by titration of NO3 by NO from soil emissions (see Bitter et al, 2005).

A reference has been given to the surface area for clean marine environments used in the different box models (e.g. Sander et al., 1999; von Glasow et al., 2002).

Section 3.2

Each of the altitude bins (e.g. 4 km spread for the lowermost) is an independent bit of information arising from the retrieved profile information. Fig. 4(b) shows that at lower altitudes the vertical resolution is finer than that possible above 25 km (Coe et al., 2002). During the NAMBLEX campaign DMS mixing ratios reached values up to 240 ppt with vertical profiles above Mace Head showing a marine influence up to an altitude of 3 km due to local convective processes (Purvis et al., 2005). In addition to DMS, O3, NO2 and sea -salt aerosol gradients may also have an impact on the vertical profile of NO3 over Mace Head. In the text, the reference to the vertical information retrieved from the OEM model is shown as gas phase concentration units to be consistent with figure 4b.

Section 3.3

This section has been re-organized and some paragraphs have been moved to the introduction section.

Regarding the oceanic I2 source strength, from our set of measurements it cannot be concluded that there is an open ocean source of I2. Therefore, this is treated only as a possibility based on previously published work (Garland and Curtis, 1981). However, in the text, other possibilities have been included such as re-circulating air-masses originated at the coast at low tide and that the tide can be higher and still result in moderate iodine emissions (i.e. the kelp beds extend further up the shore).

Section 3.5 The reactions of atomic Br with measured mixing ratios of HCHO and CH3CHO during NAMBLEX (Still et al., 2005; Lewis et al., 2005) have now been included.

To the best of our knowledge the uptake of BrNO3 on deliquesced sea salt aerosols does not appear to have been measured. However, a larger value than that used here has been measured for sulfuric acid aerosols (Hanson et al., 1996). Sensitivity studies with higher gamma of BrNO3 have been included.

Fig 1: It has been expanded into two different panels for clarity.

Fig. 3 and 3: The NO3 measurements and the back trajectories and pressure levels of the different air-masses have been plotted in different figures.

Fig. 5: Different figures have now been made for I2, OIO and IO to improve the resolution of the time series. GMT has been deleted from the x-axis.

Fig 9: It has been replaced by a figure containing the three days of measurements when post-sunrise increase of BrO was observed.

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