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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Halogens and the chemistry of the free troposphere" *by* D. J. Lary

D. Lary

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Thank you for taking the time to read and comment on the paper. I appreciate your time and effort.

Reviewer comment:

> '*D. J Lary presents an interesting study of importance of halogens in the free troposphere, using data assimilation analysis of sulphate aerosol, ozone, HCl, HNO3 and water vapour. His results show that Cl can significantly contribute to methane oxidation, to NO to NO2 and OH to HO2 ratios and that heterogeneous hydrolysis of ClONO2 and BrONO2 can be important for HNO3 production in free troposphere. Halogens has been so far mostly considered in stratosphere and in the marine boundary layer as stated in the paper. The study of D.J. Lary presents new results on role of halo-*

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gen chemistry in free troposphere, however there exists studies that might be worth mentioning: a box model study of Hendricks et al. (1999) that estimates the effect of halogen chemistry in the tropopause region and a recent study von Glasow et al. (2004) that have studied effects of bromine chemistry in troposphere with global CTM, these are not mentioned in the paper.'

Reply: Thanks.

The Hendricks et al. (1999) and von Glasow et al. (2004) references have been added.

Reviewer comment:

'*The fact that the study is brief would not be of disadvantage by itself if the paper had presented enough information about how the results presented in figures 1-4 were obtained. This was, however, not done. What time period was simulated? '*

Reply: Thanks.

The time is given twice, in each figure caption and on page 5371 lines 8 to 10. The Figure 1 caption says it is October 1991. Figure 2 says it is for February 1993.

The assimilation system *is* described in detail in the quoted references, in particular: Lary, D. J., Khattatov, B., and Mussa, H. Y., Chemical data assimilation: A case study of solar occultation data from the ATLAS 1 mission of the atmospheric trace molecule spectroscopy experiment (ATMOS), J. Geophys. Res. (Atmos.), 108, 2003, and the references therein. In addition, the website referenced gives a detailed description, with flow diagrams, even all the annotated source code, detailed list of observations used, and all the figures shown in the paper and many more besides (`http://pdfcentral.shriver.umbc.edu/AutoChem/`). However, if it is felt by

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the editor that citing references in the usual way is not enough I will gladly give a detailed description. This will however add to the paper's length by about two pages.

Reviewer comment:

> '*Part of the shows the role of BrONO2 hydrolysis in HNO3 formation, but how was the bromine calculated in the model? How was the heterogeneous reactions treated: what reaction probabilities or sticking coefficients were used for ClONO2 and BrONO2 hydrolysis?*'

Reply: Thanks. The heterogeneous reactions were calculated in the standard way given in DeMore et al (cited in the paper). The surface areas come from SAGE II and HALOE observations as mentioned in the paper (the references are cited in the paper). You are right that I had forgotten to mention about the fields of total ClOy, BrOy, and NOy. So a new paragraph has been added that says:

> 'The fields of total ClOy, BrOy, and NOy were taken from a fifty year simulation of the Goddard Space Flight Center (GSFC) two-dimensional chemistry and transport model (Fleming et al., 1999). The 2D model transport captures much of the qualitative structure and seasonal variability observed in stratospheric long lived tracers, such as isolation of the tropics and the southern hemisphere winter polar vortex, the well-mixed surf-zone region of the winter subtropics and midlatitudes, and the latitudinal and seasonal variations of total ozone. The generally good model-measurement agreement of the 2D tracer simulations demonstrate that a successful formulation of zonal mean transport processes can be constructed from currently available atmospheric data sets (Fleming et al., 1999). '

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'Why was just the time point of mid October chosen? From Fig. 1 it can be understood that it is a snapshot at 11:15, how would part e and f of the figure look like if an average over a longer period would be chosen? I would like if those questions would be answered in the paper.'

Reply: Thanks. The first complete month of data after the large of UARS was October 1991. Because of the sparse observations made by HALOE (only 14 occultations a day) an entire month of data is considered together. This allows us to have a significant number of observations for most analysis grid cells. All of these observations are then considered as a probability distribution function (PDF) as described in detail in the cited reference Lary, D. J., Khattatov, B., and Mussa, H. Y., Chemical data assimilation: A case study of solar occultation data from the ATLAS 1 mission of the atmospheric trace molecule spectroscopy experiment (ATMOS), J. Geophys. Res. (Atmos.), 108, 2003. The median value of the PDF is taken as a representative observation for that grid cell and the 15 of each month is chosen as the nominal date. In reality the observations came from throughout the month, over which time the pressure, temperature, solar illumination and aerosol loading will obviously vary. To account for the uncertainty associated with this variability an ensemble of uncertainty calculations is performed. As assimilation not only time integrates the state vector but the full error covariance matrix we try to accurately estimate all the sources of error and how they evolve with time. At each time step the model uncertainty is accessed in detail by performing an ensemble of sensitivity experiments for that grid cell. The analyses is cast in equivalent PV latitude, potential temperature (ϕ_e-θ) coordinates that are derived from daily meteorological analyses (UKMO, ECMWF or GEOS). For each analysis grid cell in the flow tracking coordinates we have a probability distribution function (PDF) of temperatures, pressures, geographic latitudes (determining the solar illumination) and sulfate aerosol loadings (derived from daily SAGE and HALOE observations). The temperature, pressure, geographic latitude and sulfate aerosol loading used for the chemical analysis of each grid cell in the flow tracking coordinates is the median value of the PDF. In order

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to continuously access the representativeness uncertainty for each grid cell associated with the full PDF of temperatures, pressures, geographic latitudes and sulfate aerosol loadings in each grid cell an ensemble of sensitivity experiments is performed at each time step. The average deviation from the median is used as a robust estimator of the width of the PDF and the time step is repeated for the median $\pm$ average deviation of the temperature, pressure, geographic latitude and sulfate aerosol loading. This gives a total of eight simulations for each time step that allow a continuous real assessment of the model representativeness uncertainty associated with the analyses coordinate grid.

A key feature of this study is the quantification of a suite of uncertainties associated with the observations all on the analyses grid. The uncertainties provided are: The observational uncertainty as supplied by the instrument teams. The representativeness uncertainty, i.e. the concentration variability over the analyses grid cell. The total uncertainty due to all of the above. The representativeness uncertainty is calculated by taking the average deviation of the PDF of concentrations for the given grid cell.

In response to your request on this matter and the request of reviewer #1 I have added a section entitled observations where this is explained. Thanks!

I have now updated the plots to be for local noon, these and many more plots are also available from the website `http://pdfcentral.shriver.umbc.edu/CDACentral/`.

Reviewer comment:

> '*I have few technical comments to the paper: p. 5370, l. 7-8: OH reacts with CH4 and CO within a second - at 293K, 1013hPa and 1.72 ppm CH4 (ground) the lifetime of OH in CH4+OH is 4s, at 252K, 360 hPa and at the same mixing ratio of CH4 (upper troposphere) the lifetime is 25s. For the CO+OH reaction the corresponding lifetimes are 2 and 18s. Statement within seconds would be more appropriate. p. 5370 l. 14: Rate of reaction*

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in Eq. 4 is extremely slow, methane oxidation in troposphere is not usually initiated by this reaction.'

Reply: Thanks. I have changed second to seconds, and yes the reaction of Br with methane is slow and I have added a note to this effect. It was just included for the sake of completeness. The added sentence reads: 'It should be noted that reaction (4) is very slow and just included for the sake of completeness.'

Reviewer comment:

'*p.5371, l. 2-3: Halogen catalyzed methane oxidation can play a significant role in ?explain how or add a reference p.5372, l.'*

Reply: Thanks. I have added a reference to: Lary, D. and Toumi, R., Halogen-catalyzed methane oxidation, J. Geophys. Res., 102, 23 421-23 428, 1997.

Reviewer comment:

'*2: DeMore et al. (2000) gives compilation of rate constants, is not showing that key channels in HNO3 production are reactions X and Y. p. 5372, l.'*

Reply: Thanks. JPL Evaluation No. 14, Section 2, Termolecular Reactions, available on line as PDF file at `http://jpldataeval.jpl.nasa.gov/pdf/JPL_02-25_3_termolec_rev02.pdf` page 2-4 shows OH+NO2 → HNO3 as a tri-molecular reaction. This is well known, for example, Brasseur and Solomon, page 254, reaction 5.133, Aeronomy of the Middle Atmosphere : Chemistry and Physics of the Stratosphere and Mesosphere, D Reidel Pub Co, 1987, Atmospheric Science Library, Second Edition, ISBN: 9027723435.

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'*2: DeMore et al. (2000) is not the best reference strenghtening that BrONO2 and ClONO2 hydrolysis are routinely considered in stratosphere (as a compilation it rather lists all reactions that were investigated).*'

Reply: Thanks. Actually i thought it was ideal as this is a key reference work on kinetics. I would be glad to have a different reference if you wished to suggest one.

Reviewer comment:

'*P. 5377, Fig. 1: The figure is too small. The text on axes is not possible to read and colours in the rings are impossible to distinguished even if maximum enlargement is used.*'

Reply: Thanks. I have made the figure bigger now.

Reviewer comment:

'*P. 5377, Fig. 1: The figure is too small. The text on axes is not possible to read and colours in the rings are impossible to distinguished even if maximum enlargement is used.*'

Reply: Thanks. I have made the figure bigger now.

Thank you for taking the time to read and comment on the paper. I appreciate your time and effort.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5367, 2004.