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Atmospheric
Chemistry
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Discussions

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

D. J. 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:

> ‘*The paper is very brief and to-the-point which I like a lot, however, this comes with a description of the analysis/modeling procedure that is too short to understand. It is merely stated that a "chemical data assimilation analysis" (p. 5368) or a "careful constraint of a photochemical modeling system using chemical data assimilation" (conclusions) is being used.*’

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

Reviewer comment:

> '*It is still unclear to me how much photochemical modeling is involved in his study or what the chemical reaction set is.* '

Reply: A great deal of modeling is involved. In the assimilation of a given day's observations the following is involved:

1. The first guess calculation. A forward photochemical model simulation of the day's photochemistry from the 'first guess' (apriori) initial conditions.
2. A forward simulation of the whole day using the full Kalman filter which not only time integrates the state vector (the constituent concentrations), but also the full constituent-constiuent error covariance matrix (i.e. how the error in one specie's concentration is related to the error in another specie's concentration).
3. Ensemble of uncertainty calculations. 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. One of these errors is the theoretical error associated with the photochemical model. 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 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 ± 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.

4. The analysis simulation. A forward photochemical model simulation of the day's photochemistry from the Kalman filter updated state vector (the constituent concentrations) initial conditions.

So in the assimilation of one day ten one day simulations are performed.

Reviewer comment:

> '*Apparently the only observed species are sulfate aerosol (but which property: number, size, effective radius,.. ?), O3, HNO3, HCl, H2O, CH4 - therefore it is even more important to explain the approach used in this study because the main conclusions of this paper are about HOx, NOx, BrONO2, HOBr, BrO, Cl - all species that are not observed and only losely constrained by the observations..* '

Reply:

The aerosol product provided by both the SAGE II and HALOE measurements teams is aerosol surface area. This is the key variable for the rates of heterogeneous reactions and the variable used in the assimilation.

The key difference between conventional modelling and data assimilation is the use of observations and information on observational and other uncertainties. In this study for each analysis grid cell we consider a probability distribution function (PDF) of all the available observations. The 'observation' used by the assimilation system for a given grid cell is the median value of the PDF. The criteria used to determine at what location we use an observation are equivalent PV latitude (ϕ_e), and potential temperature (θ). An observation is used in ϕ_e-θ grid box where it lies. That means that no interaction between the boxes (meridional transport, mixing, diabatic ascent/descent) is considered.

Two criteria were used in choosing which observations to assimilate. First, we chose constituents for which we had observations over the entire period of 1991 to 1998. Second, where more than one instrument was observing a constituent we chose to us instruments that did not have significant relative biases. This was determined by looking at observation PDFs. This analysis is also available online at: `http://pdfcentral.shriver.umbc.edu/ PDFCentral/index.html`.

There appears to be good consistency between the sporadic observations of missions such as ATMOS and CRISTA with the long-term HALOE and MLS data-sets used. This was not the case for some possible combination of observations. For example, CLAES ozone and MLS ozone had some large differences. After conducting the PDF analyses it seems that the major problems are with CLAES. Another example is MLS, HALOE and SAGE water, SAGE water was not used after the results of the PDF analyses showed it has bias issues.

The resulting assimilated analyses are presented online, where observations were used these are overlaid on the assimilated analyses (`http://pdfcentral.shriver.umbc.edu/CDACentral/`) as color-filled circles using the same color scale as the color-filled contours used to depict the analyses. This allows appropriate comparison with observations to validate the assimilation. In addition, when observations of a constituent were used the web site also provides an assimilation statistics page (at the top of each page just below the java-script calendar bar). This page presents the observations, the various observation uncertainties, and the assimilation skill scores.

A paragraph in the paper already gives the datasets used, there are also online references to them from `http://pdfcentral.shriver.umbc.edu/AutoChem/`.

Obviously we would like to use observations of HOx, NOx, BrONO2, HOBr, BrO, and Cl. However, with the exception of NOx these are not continuously available for the period 1991 to 1998. If accurate observations had been available we would have of course used them. When can observe from the chemical assimilation study of ATMOS data using the same system (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) that there is good consistency between the model and the observations of 14 constituents made by ATMOS. In addition, the web site `http://pdfcentral.shriver.umbc.edu/CDACentral/` presents uncertainty estimates for each concentration field, something that conventional modeling seldom provides. This uncertainty field (presented in %) contains contributions both from model and observational uncertainties.

Reviewer comment:

> ‘*Some of the more important questions regarding this point are: what are the sources and sinks for Cl and Br in his model, how are they determined, what is the uncertainty of them? How strong are the constraints of the*

satellite data assimilation for the presented results?'

Reply: Again all this information is given in the website referenced in the paper.

- Cl sources and sinks are all given on the site, for example `http://pdfcentral.shriver.umbc.edu/CDACentral/1991/10/Cl/Cl_1991_10.html` the reaction of Cl with methane produces the long-lived HCl reservoir (with a small contribution from Cl + HCHO) and the reaction of Cl with ozone produces ClO so is involved in the Cl/ClO partitioning.

- Br sources and sinks are all given on the site, for example `http://pdfcentral.shriver.umbc.edu/CDACentral/1991/10/Br/Br_1991_10.html` the reaction of Br with HCHO produces HBr reservoir and the reaction of Br with ozone produces BrO so is involved in the Br/BrO partitioning.

The constraints of the observations depends on the observation uncertainty, that is how assimilation works. The higher the uncertainty the less the constraint, the lower the uncertainty the greater the constraint. That is why the website referred to gives a detailed breakdown of all the uncertainty sources. Let us take ozone as an example:

- Observation uncertainty is given. This has components due to the observation uncertainty quoted by the instrument teams and the representativeness uncertainty (variability within a grid cell calculated using the average deviation of the ozone PDF)
  (e.g. `http://pdfcentral.shriver.umbc.edu/CDACentral/1991/10/O3/O3_1991_10_assim.html`)

- Modeling uncertainty due to temperature, pressure, latitude (illumination) an aerosol variability within an analysis grid cell is given
  (e.g. `http://pdfcentral.shriver.umbc.edu/CDACentral/1991/10/O3/O3_1991_10_model.html`).

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- The total uceratinty due to combining all these contributions is also given `http://pdfcentral.shriver.umbc.edu/CDACentral/1991/10/O3/O3_1991_10.html`.

The same is done for all observed species. For non-observed species an uncertainty is also given. This is calculated as the Kalman filter can propagate uncertainties from observed to non-observed species and we also still explicitly calculate the theoretical uncertainty with the ensemble of 8 photochemical simulations mentioned above.

So I hope you will agree that the questions raised were fully answered in the references already given in the paper as explained above. If you feel clarification is still needed I would be glad to do so and would appreciate some more specific clarification requests.

Thanks

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Reviewer comment:

> ‘*p. 5368, l. 24/25: One such study appeared around the time of submission of Lary’s manuscript in ACPD: von Glasow et al., 4, 4877 - 4913, 2004*’

Reply: Thanks!

Reviewer comment:

> ‘*On p. 5369, l. 2 it is stated that the analysis "start[ed] in October 1991" but only 2 months are presented (October 1991 and February 1993). Is there any information about seasonal cycles or year-to-year variability or are these 2 months the only ones completely analyzed? Do the presented results refer to these 2 months only or to a longer time span?*’

Reply: Again, many years of data are presented on line in the web site referenced, for example, if you go to the page `http://pdfcentral.shriver.umbc.edu/CDACentral/1991/10/CH3/CH3_1991_10.html` you can use the javascript navigation bars at the top of the page to view the role of all the methane oxidation initiation channels from October 1991 on, so far the record goes till at least November 1995 and we hope to soon have reached December 1998.

The plots on the web site show that the region where Cl+methane is playing a significant role in the free-troposphere is a region with low OH/HO2, NO/NO2, HCl/ClOy, and HNO3/NOy ratios (see ratio web page for each month), and high ClONO2/ClOy and ClONO2/NOy ratios. Understanding this partitioning is straightforward when both the solar zenith angle and sulfate aerosol loading are examined (Physical conditions web page). At higher solar zenith angles more HOx is in HO2 than OH, and for higher sulfate aerosol loadings there is a lower HCl/ClOy ratio and higher ClONO2/ClOy

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and ClONO2/NOy ratios. At higher solar zenith angles the HOx reservoirs HOBr and HO2NO2 are also favored.

The region where Cl+methane is playing a major role is at high solar zenith angles when there is also a significant sulfate aerosol loading. Interestingly, for this same occasion there is no significant difference in the Cl/ClO ratio between regions where Cl+methane is playing a significant role and regions where it is not. So the enhanced significance of Cl+methane is primarily due to a reduced effectiveness of the OH+methane channel. The solar zenith angle and aerosol loading factors overlap to give a significant role to Cl+methane in the mid-latitude free-troposphere.

The question that is naturally asked is what happens during periods with lower aerosol loadings and at other times of year? The contribution of Cl+methane in the mid-latitude free-troposphere was almost the same for January 1993 as it was for January 1992, by January 1994 as the peak in the sulfate aerosol loading as descended so the contribution of Cl+methane plays a significant role at slightly lower altitudes. The role of Cl+methane in the mid-latitude free-troposphere remains almost unchanged during periods of background sulfate aerosol loadings. The lowest contribution of Cl+methane in the northern mid-latitude free-troposphere is during August and September when the contribution has fallen from around 55% to around 20%.

Thanks.

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Reviewer comment:

> ‘*p. 5369, l. 18: please explain what "equivalent PV latitude" is. The description in this whole paragraph was a bit too short for me.*’

Reply: Because a major component of the variability of trace gases is due to atmospheric transport it makes sense to use a coordinate system that ‘follows’ the large scale flow pattern to perform our analyses. In this study Lagrangian flow-tracking coordinates are used.

Under adiabatic conditions air parcels move along isentropic surfaces (surfaces of constant potential temperature, θ). So when considering tracer fields θ is a suitable vertical coordinate. Isentropic maps of Ertel’s potential vorticity (PV) are useful for visualising large scale dynamical processes. PV plays a central role in large scale dynamics where it behaves as an approximate material tracer.

As a result, PV can be used as the horizontal spatial coordinate instead of latitude and longitude. PV is sufficiently monotonic in latitude on an isentropic surface to act as a useful replacement coordinate for both latitude and longitude, reducing the tracer field from three dimensions to two. These ideas have already led to interesting studies correlating PV and chemical tracers such as $\mathrm{N_2O}$ and $\mathrm{O_3}$. A key result of these studies is that PV and ozone mixing ratios are correlated on isentropic surfaces in the lower stratosphere, as was first pointed out by Danielsen in 1968.

Since the absolute values of PV depend strongly upon height and the meteorological condition, it is useful to normalise PV and use PV equivalent latitude (ϕ_e) as the horizontal coordinate instead of PV itself. ϕ_e is calculated by considering the area enclosed within a given PV contour on a given θ surface. The ϕ_e assigned to every point on this PV contour is the latitude of a latitude circle which encloses the same area as that PV contour. Therefore, for every level in the atmosphere ϕ_e has the same range of values, -90° to 90°. This provides a vortex-tracking, and indeed a flow-tracking, stratospheric

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coordinate system.

All of the above is explained in the cited reference mentioned twice so far (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). If the editor feels that more is required in the paper I would be glad to add more. Thanks.

Reviewer comment:

> ‘*p. 5369, l. 19: "coordinates. With.." maybe change into: "coordinates, with .."?*’

Reply: Thanks! I changed it!

Thanks again for your time!

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