Can Ozone Assimilation Constrain Inorganic Chlorine in the Stratosphere?

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One of the potential of 4D-Var chemistry data assimilation is to use observed species to constrain directly coupled unobserved species.

- Past studies found that only few observed species convey to constrain unobserved modeled species using a simple stratospheric (Fisher and Lary, 1995) or tropospheric (Elbern et al., 1997) DA system.
- Using the CRISTA stratospheric data, Errera and Fonteyn (2001) showed that observations of ClONO$_2$ were able to constrain unobserved modeled HCl.
- Chai et al. (2006) showed that assimilating NO$_y$ aircraft data with a 4D-Var system improves the analyses of O$_3$, HNO$_3$, PAN and RNO3.

However, these experiments were based on short term datasets.
In order to support SPARC CCMVal, BIRA-IASB and DLR, within the PROMOTE project (www.gse-promote.org), are contributing to set a record of 3D fields of ozone and related trace gases using chemistry data assimilation of past observations.
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One of the issue of SPARC CCMVal is the lack of information on the total inorganic chlorines ($\text{Cl}_y$) at South Pole.

Using the Belgian Assimilation System for Chemical ObsErvations (BASCOE), BIRA-IASB already discussed the evaluation of ozone analyses from the assimilation of MIPAS (Errera et al., 2008) and UARS MLS (Viscardy et al., 2010).

In this talk, we will discuss:
1. How the ozone observations are able to constrain unobserved inorganic chlorine species in the stratosphere represented in the model.
2. How these inorganic chlorine analyses agree with independent observations.
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1. How the ozone observations are able to constrain unobserved inorganic chlorine species in the stratosphere represented in the model.
2. How these inorganic chlorine analyses agree with independent observations.
1. The link between $O_3$ and $Cl_y$
2. Influence of $O_3$ observations on $Cl_y$ species
3. Case study using UARS MLS $O_3$ and the BASCOE system
Interaction between $O_3$ and chlorines is carried out through $O_3$ destroying catalytic cycles, e.g.:

\begin{align*}
Cl + O_3 & \rightarrow ClO + O_2 \quad (1) \\
ClO + O & \rightarrow Cl + O_2 \quad (2)
\end{align*}

Net: \quad O_3 + O \rightarrow 2O_2
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Cl is produced by the photochemical destruction of the tropospheric organic chlorines (CFCs, CH$_3$Cl, ...)

Two regions/seasons where O$_3$ destruction by Cl is significant:
1. the upper stratosphere
2. the Winter/Spring polar lower stratosphere
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How O$_3$ Can Constrain Inorganic Chlorine Species

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Repartition of Cl\textsubscript{y} Within the Family

Figure: Zonal average of total inorganic chlorines (Cl\textsubscript{y}) and the most abundant members of the family, taken from BASCOE on 15-Jan-1994.
In the upper stratosphere, \([Cl_y] \approx [HCl]\)
Repartition of $Cl_y$ Within the Family

- In the upper stratosphere, $[Cl_y] \approx [HCl]$
- In the Winter/Spring polar lower stratosphere, $[Cl_y] \approx [ClO] + [Cl_2O_2]$

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Influence of O$_3$ on Chlorine Species

Influence functions are used to estimate the constraint of O$_3$ on Cl$_y$. The influence functions are defined as (Fisher and Lary, 1995):

\[ \gamma(Species \ j \rightarrow i, \ Time \ step \ n \rightarrow m) = \frac{(\nabla_{x_m}J_{m}^{obs})_i(x_m)_i}{(\nabla_{x_n}J_{n}^{obs})_j(x_n)_j} \]  

(3)

Where:

- $i, j$ denote the species index
- $m, n$ denote the time step, $n \geq m$
- $x$ denotes the volume mixing ratio (vmr)
- $(\nabla_{x_m}J_{m}^{obs})_i$ denotes the gradient of the cost function $J$ with respect to the vmr for species $i$ and time step $m$

By definition, $\gamma = 1$ for $i=j$ and $m=n$. 

Errera et al. (BIRA-IASB)
Influence of $O_3$ on Chlorine Species

- Influence calculated at every BASCOE grid point. Advection is OFF
- Influence of $O_3^{obs}$ at 12UT on VMR$_{model}$ at 0UT, on 15-Sep-1994

Errera et al. (BIRA-IASB)  Can $O_3$ Constrain Stratospheric Cl$_y$?  SPARC DAW 2010  8 / 16
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- However, the link between the influence function results and the strength of the constraint of O$_3$ data on modeled Cl$_\gamma$ is not clear.

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- Is the influence sufficiently significant to allow O$_3$ observations to constrain modeled Cl$_y$?

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- However, the link between the influence function results and the strength of the constraint of O$_3$ data on modeled Cl$_y$ is not clear.
- Is the influence sufficiently significant to allow O$_3$ observations to constrain modeled Cl$_y$?
- How long will be the spin-up?
UARS MLS O₃ has been assimilated from September 1991 to November 1994

In practice, no MLS data from mid September to mid October at South Pole for 1992-1994.

⇒ Influence of O₃ on ClO will be very limited.

Errera et al. (BIRA-IASB)
Case study: UARS MLS O$_3$ data

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UARS MLS O$_3$ has been assimilated from September 1991 to November 1994

- No assimilation after Nov. 1994 because the number of operated days is too small
- This period occurs during the increase of stratospheric HCl, before the impact of the Montreal Protocol
- UARS performs a yaw maneuver every 36 days.
  - In practice, no MLS data from mid September to mid October at South Pole for 1992-1994 ⇒ Influence of O$_3$ on ClO$_x$ will be very limited
Case studies: The BASCOE System

The BASCOE (Belgian Assimilation System for Chemical ObsErvations, Errera et al., 2008) uses the 4D-Var method with a 3D-CTM

- The CTM advects 57 stratospheric species that interact through 200 chemical reactions
- The effect of PSC microphysics are calculated by a simple parameterization
- Surface emissions of organic chlorines is NOT modeled
- In this study, the CTM is run at 5° long × 3.75° lat × 37 vertical levels (surface to 0.1hPa) and driven by the ECMWF ERA-Interim reanalyses
- Only O$_3$ is assimilated where 10% of data are dropped for a posteriori verifications
- The $\mathbf{B}$ matrix is set diagonal with a variance set to 50% of the first guess in order to give a strong weight to the observations
- First guess on day 1 taken for SOCRATES 2D model
- A free model run (no assimilation) initialized by SOCRATES was done to assess the benefit of DA
Case study: Innovation of Chlorine Species

The innovation is maximum for HCl around 2hPa.

The innovation appears to be very small for ClO in the Antarctic polar vortex.

<table>
<thead>
<tr>
<th>Latitude [deg]</th>
<th>Pressure [hPa]</th>
<th>HCl innovation [%]</th>
<th>Min. Value</th>
<th>Max. Value</th>
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<td>-0.4</td>
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Figure: Zonal mean of the innovations of HCl, ClONO₂ and ClO on 10-Sep-1994, for UARS MLS O₃ assimilated by BASCOE.
The innovation is maximum for HCl around 2hPa

Figure: Zonal mean of the innovations of HCl, ClONO$_2$ and ClO on 10-Sep-1994, for UARS MLS O$_3$ assimilated by BASCOE
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Figure: Zonal mean of the innovations of HCl, ClONO$_2$, and ClO on 10-Sep-1994, for UARS MLS O$_3$ assimilated by BASCOE

Errera et al. (BIRA-IASB) Can O$_3$ Constrain Stratospheric Cl$_y$? SPARC DAW 2010
Case study: Evaluation of O₃ analyses

- A very good argument is found between MLS O₃ and BASCOE: BASCOE is able to reproduce MLS dropped data within the MLS error bars

![Figure: Bias and standard deviation of mean(MLS-BASCOE) for O₃ using all MLS data (red) and only the 10% of dropped MLS data (blue) between October 1991 and October 1994. Gray line represent the MLS accuracy (left figure) and precision (right figure).](image)

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Case study: BASCOE HCl in the upper stratosphere

Figure: Time series of tropical (between -30° S and 30° N) monthly averaged HCl from HALOE, the analyses, and the control run at 0.46 hPa (a), 1.47 hPa (b) and 4.61 hPa (c).
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The difference between the analyses and FMR clearly shows the influence of O$_3$ observations on modeled HCl.

Figure: Time series of tropical (between -30° S and 30° N) monthly averaged HCl from HALOE, the analyses, and the control run at 0.46 hPa (a), 1.47 hPa (b) and 4.61 hPa (c).
The effect of the spin-up at 0.46 and 4.6 hPa (4 and 3 months, respect.) reflects the relatively weak constraint of O$_3$ on HCl.

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The analysed and observed trends are in good agreement at 0.46 and 1.47 hPa.

**Figure:** Time series of tropical (between -30° S and 30° N) monthly averaged HCl from HALOE, the analyses, and the control run at 0.46 hPa (a), 1.47 hPa (b) and 4.61 hPa (c).
This is possible because HCl vary slowly regarding the constraint by O$_3$ data.
Differences with upper stratosphere conditions

1. Here, the production/loss cycle of Cl$_y$ is achieved in few months ($>\ll$ many years in the upper stratosphere)
2. As the influence functions are relatively small here, the spin-up period is expected to be much longer than the Cl$_y$ cycle.

UARS MLS O$_3$ assimilation shows no significant differences against the FMR (not shown)

Aura MLS O$_3$ assimilation - no yaw maneuver - between April-November 2005 shows that (not shown):

1. Analyses are closer to Aura MLS independent observations HCl and ClO than the FMR ...
2. ... but the analyses still too far to the observations

Modeling the constraint of O$_3$ on Cl$_y$ in the B matrix might improve this issue
Stratospheric chemical scheme (and their adjoint) allows $O_3$ observations to constrain $Cl_y$ in the upper stratosphere

HCl analyses from the assimilation of UARS MLS $O_3$ by BASCOE over three years allow to reproduce the HALOE HCl trend

The constraint of $O_3$ data on modeled HCl appears to be relatively weak:
- This might be increased by modeling this constraint in the $B$ matrix

An alternative of the influence function is necessary to derive \textit{a priori} the time of the spin-up

Two potential applications:
- Estimation of the upper stratosphere HCl trend using assimilation of SBUV from 1978 to 1991 (no HCl data)
- Estimation of the Winter/Spring polar stratospheric $Cl_y$ using assimilation of ozonesondes


