Chemistry-climate model simulations of a mesospheric source of nitrous oxide

SEE-Chem talk

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Met Office

NERC SCIENCE OF THE ENVIRONMENT

Outline

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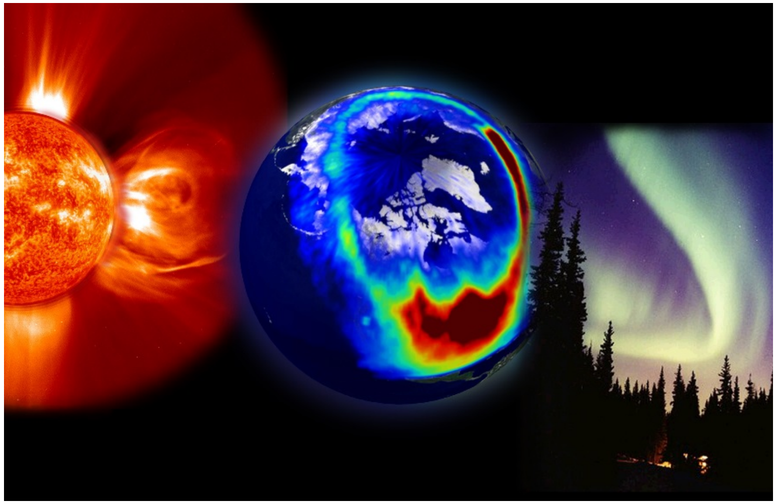
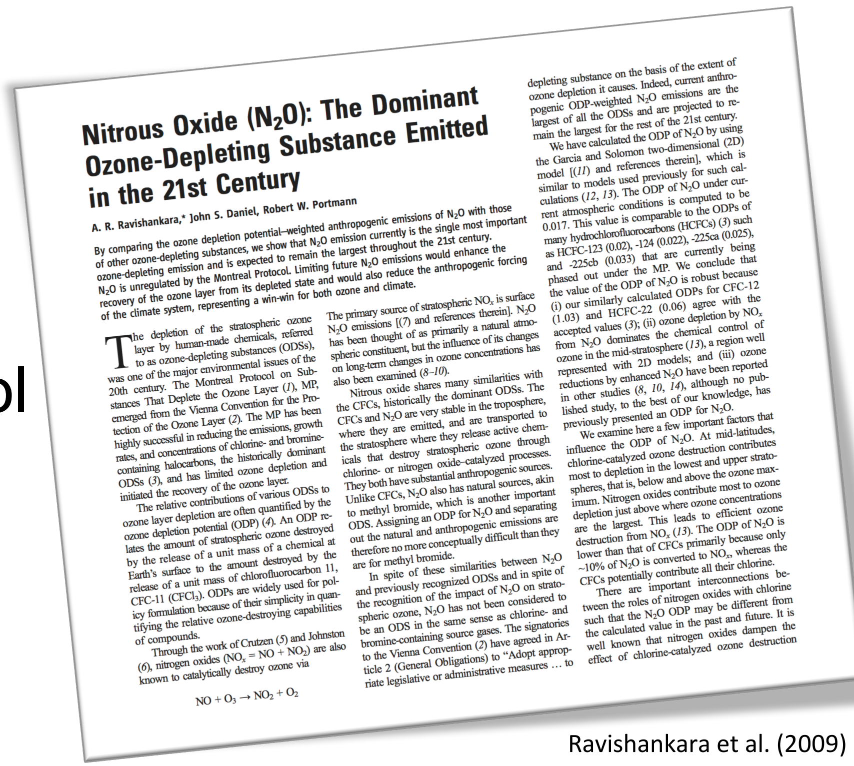
- N_2O as precursor to ozone destruction
- Upper-atmospheric N_2O production mechanisms
- Verifying feasibility of a mesospheric source
- WACCM model to ACE-FTS satellite comparisons
- Future work



Credit: NASA

Nitrous oxide (N_2O)

- Significant **ozone-depleting** substance
  - Not controlled by Montreal Protocol
- 3rd most important greenhouse gas
  - Mitigated by Kyoto Protocol
- Anthropogenic and natural sources



Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

By comparing the ozone depletion potential–weighted anthropogenic emissions of N_2O with those of other ozone-depleting substances, we show that N_2O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N_2O is unregulated by the Montreal Protocol. Limiting future N_2O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.

The depletion of the stratospheric ozone layer by human-made chemicals, referred to as ozone-depleting substances (ODSs), was one of the major environmental issues of the 20th century. The Montreal Protocol on Substances That Deplete the Ozone Layer (*1*), MP, emerged from the Vienna Convention for the Protection of the Ozone Layer (*2*). The MP has been highly successful in reducing the emissions, growth rates, and concentrations of chlorine- and bromine-containing halocarbons, the historically dominant ODSs (*3*), and has limited ozone depletion and initiated the recovery of the ozone layer.

The relative contributions of various ODSs to ozone layer depletion are often quantified by the ozone depletion potential (ODP) (*4*). An ODP relates the amount of stratospheric ozone destroyed by the release of a unit mass of a chemical at Earth's surface to the amount destroyed by the release of a unit mass of chlorofluorocarbon 11, CFC-11 ($CFCl_3$). ODPs are widely used for policy formulation because of their simplicity in quantifying the relative ozone-destroying capabilities of compounds.

Through the work of Crutzen (*5*) and Johnston (*6*), nitrogen oxides ($NO_x = NO + NO_2$) are also known to catalytically destroy ozone via

$$NO + O_3 \rightarrow NO_2 + O_2$$

The primary source of stratospheric NO_x is surface N_2O emissions [(*7*) and references therein]. N_2O has been thought of as primarily a natural atmospheric constituent, but the influence of its changes on long-term changes in ozone concentrations has also been examined (*8–10*).

Nitrous oxide shares many similarities with the CFCs, historically the dominant ODSs. The CFCs and N_2O are very stable in the troposphere, where they are emitted, and are transported to the stratosphere where they release active chemicals that destroy stratospheric ozone through chlorine- or nitrogen oxide–catalyzed processes. They both have substantial anthropogenic sources. Unlike CFCs, N_2O also has natural sources, akin to methyl bromide, which is another important ODS. Assigning an ODP for N_2O and separating out the natural and anthropogenic emissions are therefore no more conceptually difficult than they are for methyl bromide.

In spite of these similarities between N_2O and previously recognized ODSs and in spite of the recognition of the impact of N_2O on stratospheric ozone, N_2O has not been considered to be an ODS in the same sense as chlorine- and bromine-containing source gases. The signatories to the Vienna Convention (*2*) have agreed in Article 2 (General Obligations) to "Adopt appropriate legislative or administrative measures … to

depleting substance on the basis of the extent of ozone depletion it causes. Indeed, current anthropogenic ODP-weighted N_2O emissions are the largest of all the ODSs and are projected to remain the largest for the rest of the 21st century.

We have calculated the ODP of N_2O by using the Garcia and Solomon two-dimensional (2D) model [(*11*) and references therein], which is similar to models used previously for such calculations (*12*, *13*). The ODP of N_2O under current atmospheric conditions is computed to be 0.017. This value is comparable to the ODPs of many hydrochlorofluorocarbons (HCFCs) (*3*) such as HCFC-123 (0.02), -124 (0.022), -225ca (0.025), and -225cb (0.033) that are currently being phased out under the MP. We conclude that the value of the ODP of N_2O is robust because (i) our similarly calculated ODPs for CFC-12 (1.03) and HCFC-22 (0.06) agree with the accepted values (*3*); (ii) ozone depletion by NO_x from N_2O dominates the chemical control of ozone in the mid-stratosphere (*13*), a region well represented with 2D models; and (iii) ozone reductions by enhanced N_2O have been reported in other studies (*8*, *10*, *14*), although no published study, to the best of our knowledge, has previously presented an ODP for N_2O.

We examine here a few important factors that influence the ODP of N_2O. At mid-latitudes, chlorine-catalyzed ozone destruction contributes most to depletion in the lowest and upper stratospheres, that is, below and above the ozone maximum. Nitrogen oxides contribute most to ozone depletion just above where ozone concentrations are the largest. This leads to efficient ozone destruction from NO_x (*13*). The ODP of N_2O is lower than that of CFCs primarily because only ~10% of N_2O is converted to NO_x, whereas the CFCs potentially contribute all their chlorine.

There are important interconnections between the roles of nitrogen oxides with chlorine such that the N_2O ODP may be different from the calculated value in the past and future. It is well known that nitrogen oxides dampen the effect of chlorine-catalyzed ozone destruction

Ravishankara et al. (2009)

Ozone destruction

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- N_2O is precursor of middle atmos. NO_y

$$N_2O + O(^1D) \rightarrow 2NO$$

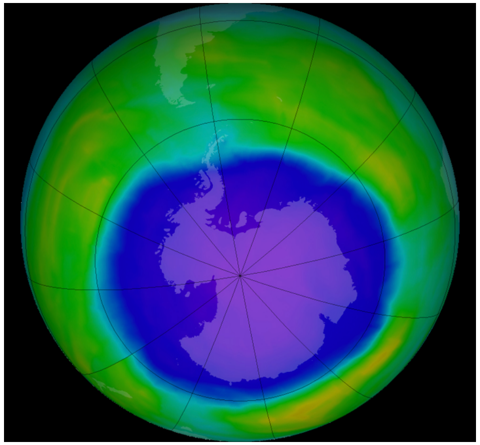
- NO_y destroys stratospheric O_3:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

- Previously assumed only surface sources of N_2O
- **Mesospheric sources** now identified

Ozone hole



Credit: NASA

Upper-atmospheric N_2O history

- Zipf and Prasad (1982) postulated:
  - **Excited N_2 from EEP**

$$e + N_2(X^1\Sigma_g^+) \rightarrow N_2(A^3\Sigma_g^+) + e$$

  - Reaction with O_2

$$N_2(A^3\Sigma_g^+) + O_2 \rightarrow N_2O + O$$

- Produces N_2O at around 95km

Upper-atmospheric N_2O history

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- ~25 years passed without high-altitude satellite obs.
- Semeniuk et al. (2008) reported stratospheric N_2O VMRs of **~5 ppbv** after 2004 SSW
  - Suggested mesospheric mechanism:

$$N(^4S) + NO_2 \rightarrow N_2O + O$$

  - Initially seen as upper atmospheric N_2O source

ACE-FTS

Credit: ACE – University of Waterloo

Upper-atmospheric N_2O history

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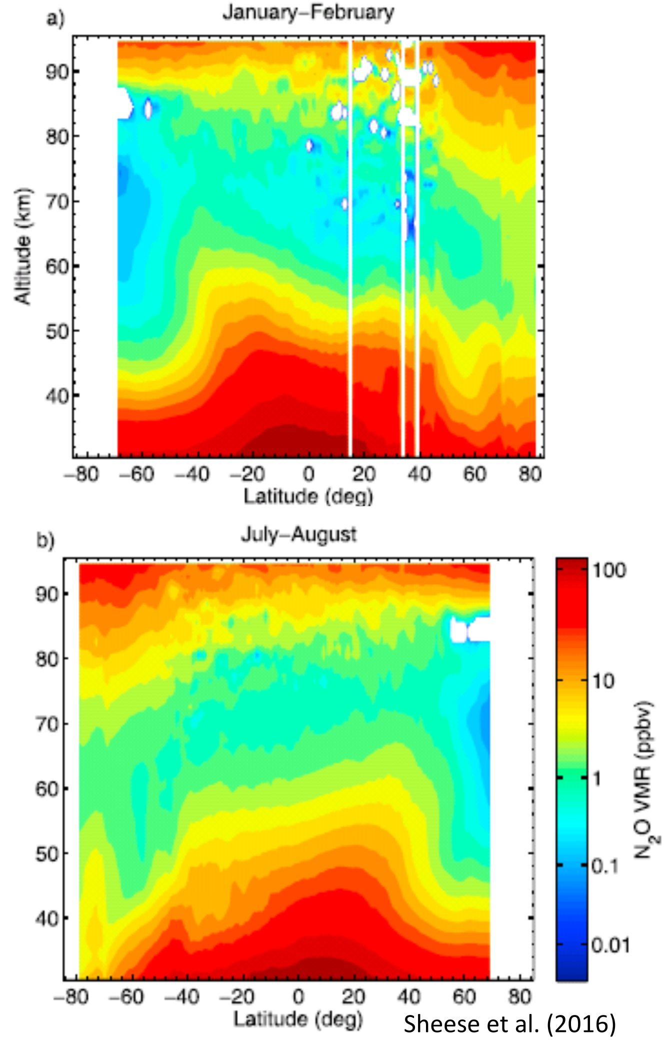
- Funke et al. (2008) verified '$N(^4S) + NO_2 \rightarrow$' mechanism
  - Via N_2O-CH_4 correlations
  - Also suggested potential for the '$N_2(A^3\Sigma_g^+) + O_2 \rightarrow$' source
- Sheese et al. (2016) provided first satellite obs. of 95km N_2O
  - Reported mean N_2O VMRs above 20 ppbv

ACE data (2004-13)



Sheese et al. (2016)

Verifying feasibility

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- To sustain N_2O VMRs from Sheese et al. (2016):
  - Efficiency factor

$$\alpha = \frac{\mathrm{N_2O\ prod.\,rate}}{\mathrm{ion\ pair\ prod.\,rate}} \approx 0.1\%$$

  - Where

$$\mathrm{N_2O\ prod.\,rate} = [\mathrm{N_2O}]_{\mathrm{obs}} \cdot (\mathrm{N_2O\ loss\ rate})$$

  - Other constants from standard WACCM output

Verifying feasibility

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- N_2O loss mechanisms:
  - Photolysis in the stratosphere

$$N_2O + hv \rightarrow N_2 + O(^1D) \qquad (\sim 90\%)$$

  - Reaction with $O(^1D)$

$$N_2O + O(^1D) \rightarrow N_2 + O_2$$

$$N_2O + O(^1D) \rightarrow 2NO$$

Portmann et al. (2012)

- Upper mesospheric lifetime ~10 days
- Lower thermospheric lifetime ~100 days

Verifying feasibility

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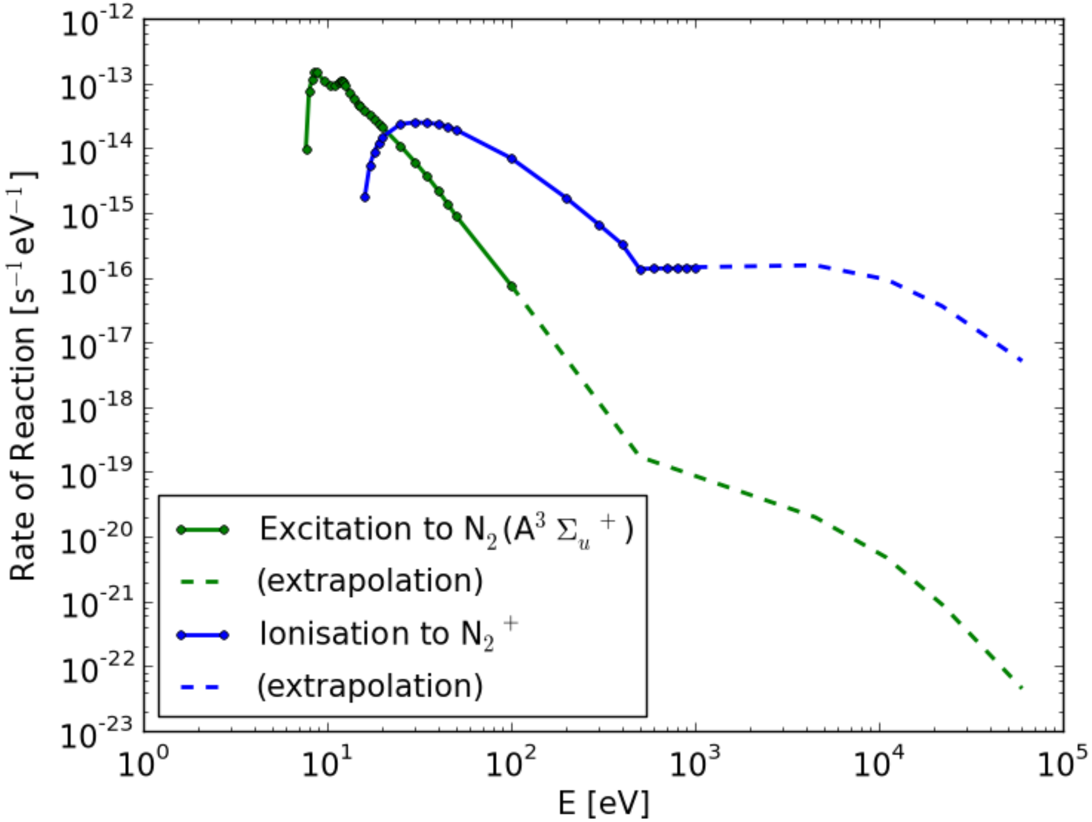
- Is efficiency factor (α = 0.1%) reasonable?
  - Recalculate α from first principles



  - Cross-section × electron flux at 100km
  - Linear extrapolation
  - Integrate up to auroral energies (~30keV)
- Yields $\alpha \geq 0.1\%$

Experimental set-up

Simulation	Configuration	
1. Standard WACCM run	$N(^4S) + NO_2 \rightarrow$	ON
	$N_2(A^3\Sigma_g^+) + O_2 \rightarrow$	OFF
2. Moderator run	$N(^4S) + NO_2 \rightarrow$	OFF
	$N_2(A^3\Sigma_g^+) + O_2 \rightarrow$	ON
3. Full run	$N(^4S) + NO_2 \rightarrow$	ON
	$N_2(A^3\Sigma_g^+) + O_2 \rightarrow$	ON

Model to satellite comparisons

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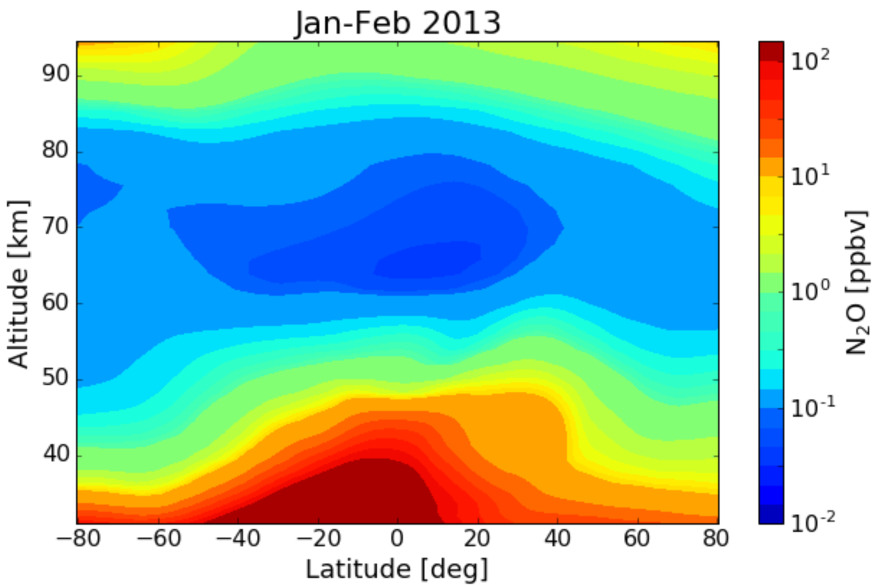
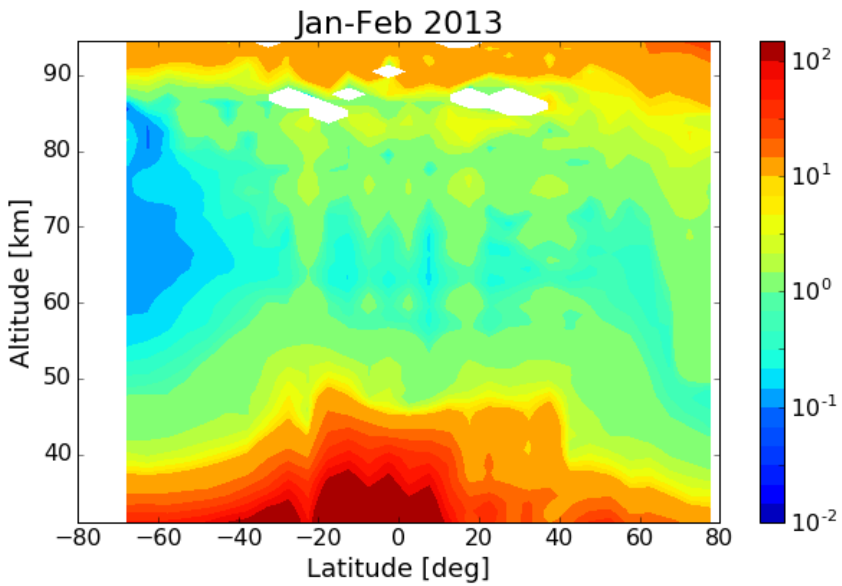
- Added 95km N_2O source into WACCM:

$$N_2(A^3\Sigma_g^+) + O_2 \rightarrow N_2O + O$$

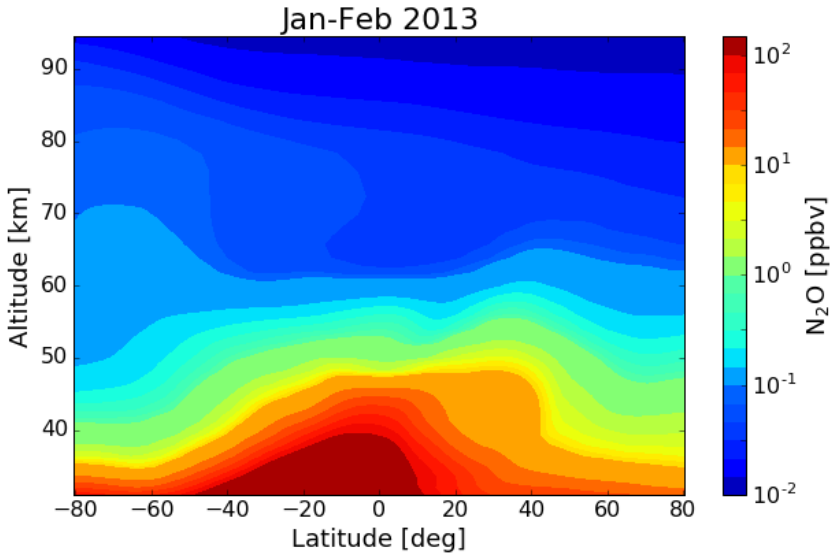
Full run (model)



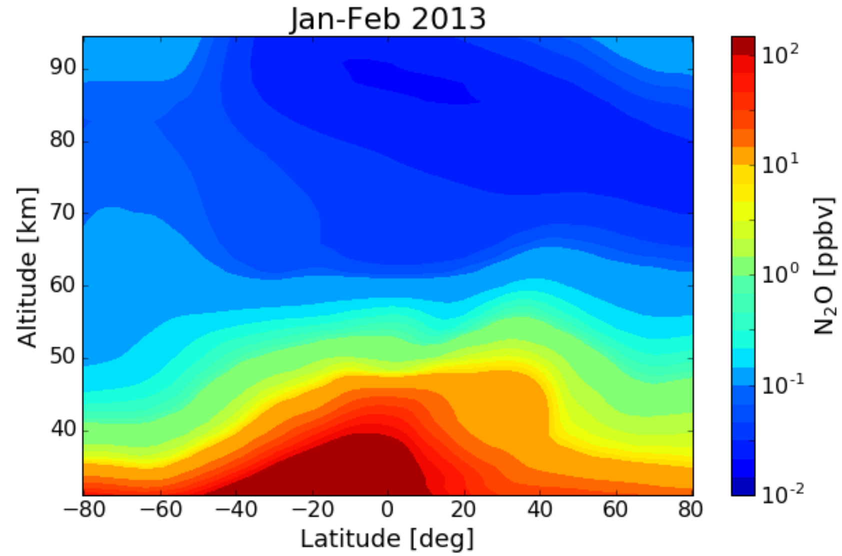
ACE-FTS (satellite)



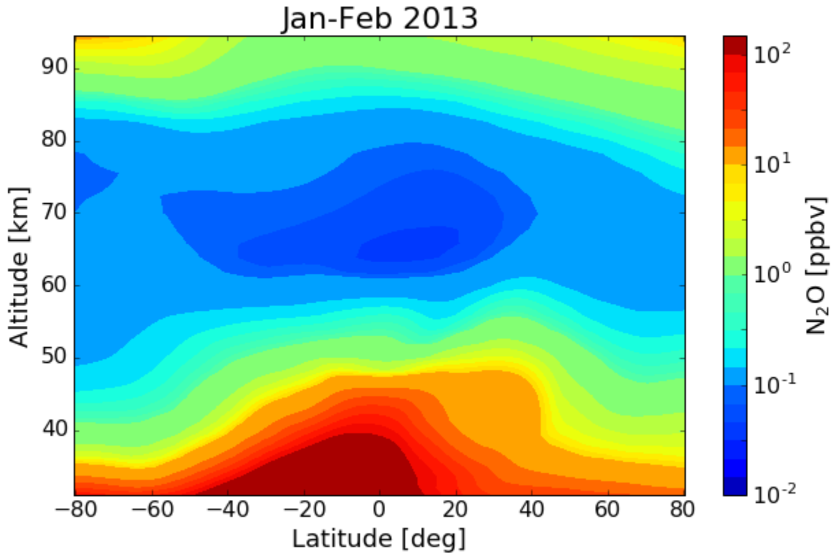
1. Standard WACCM run



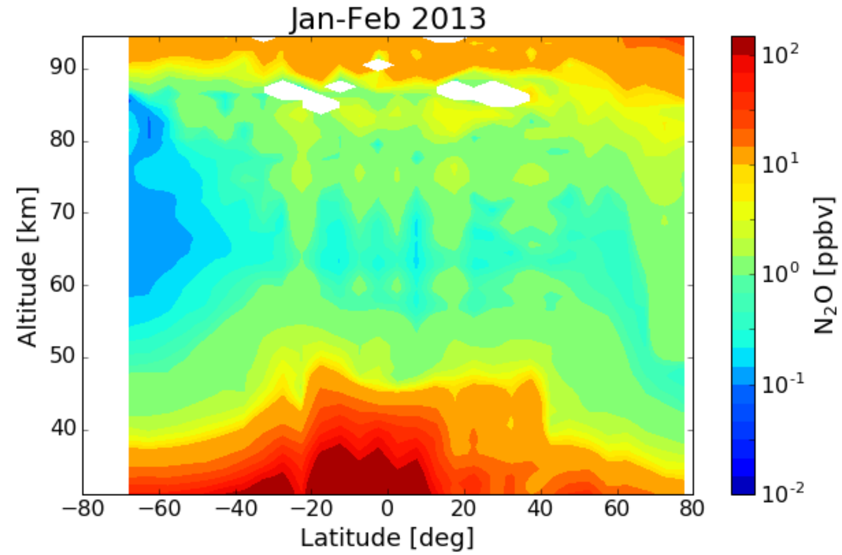
2. Moderator run



3. Full run



ACE-FTS (satellite)



Interpretation

Zipf: $N_2(A^3\Sigma_g^+) + O_2 \rightarrow N_2O + O$

Semeniuk: $N(^4S) + NO_2 \rightarrow N_2O + O$

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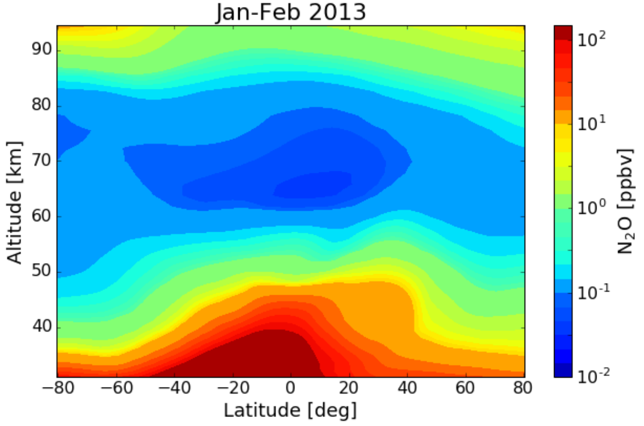
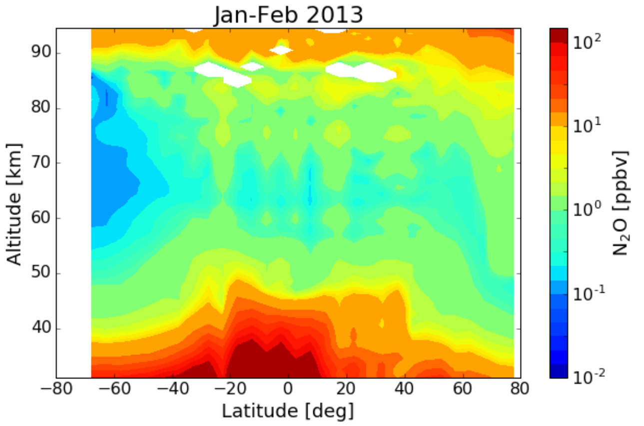
- ‘Steady-state’ reached quickly
  - Expected for short N_2O lifetime
- Abundances do not descend as low as in obs.
- N_2O minimum seen in WACCM at ~60km
  - Not observed, other sources?
- Seasonal polar trend not well replicated by model
- ‘$N(^4S) + NO_2 \rightarrow$’ is by far the dominant source

Full run (model)



ACE-FTS (satellite)



Future work

Zipf: $N_2(A^3\Sigma_g^+) + O_2 \rightarrow N_2O + O$

Semeniuk: $N(^4S) + NO_2 \rightarrow N_2O + O$

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- Investigate other production mechanisms
  - Photochemical N_2(A) source?
- Perform WACCM simulations for 2014:
  - Know to have less EEP than 2013
  - Significance of EEP on N_2O will be better quantified
- Impact of 95km source on stratospheric ozone

Summary

- N_2O source at around 95km via EEP
  - Until recently only surface sources considered
- $N_2(A^3\Sigma_g^+) + O_2 \rightarrow N_2O + O$
- At 90km α ~0.1%
- Production mechanism put in WACCM
  - N_2O observed, but not at mid-latitudes in lower mesosphere
- Next find impact on stratospheric ozone

1. Standard WACCM run (2013)

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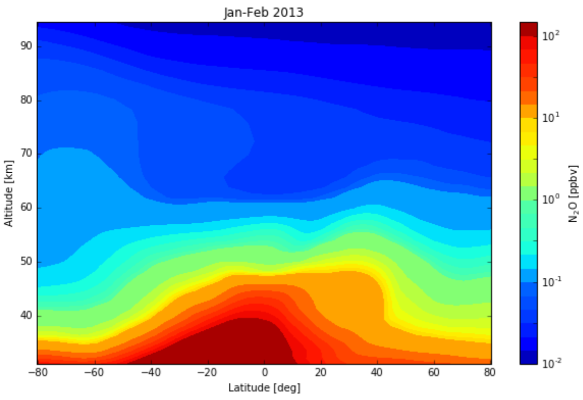
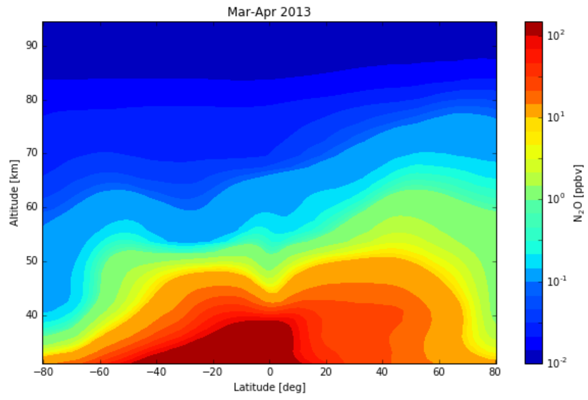
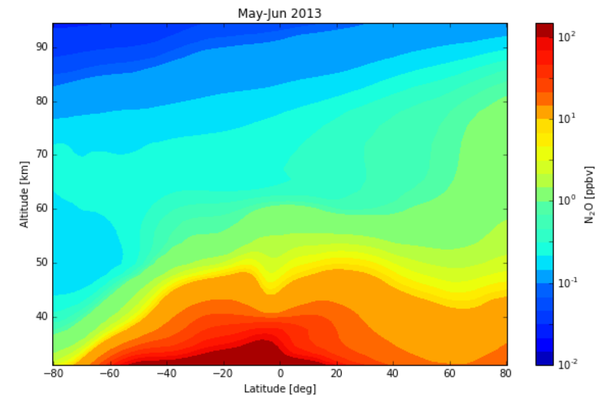
Jan-Feb



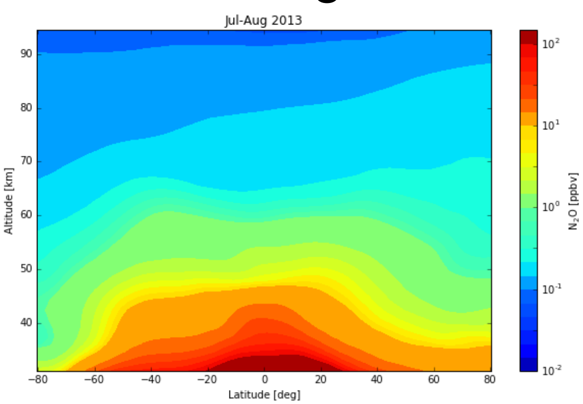
Mar-Apr



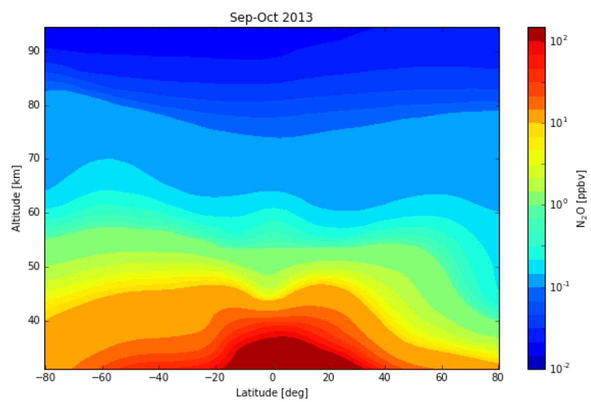
May-Jun



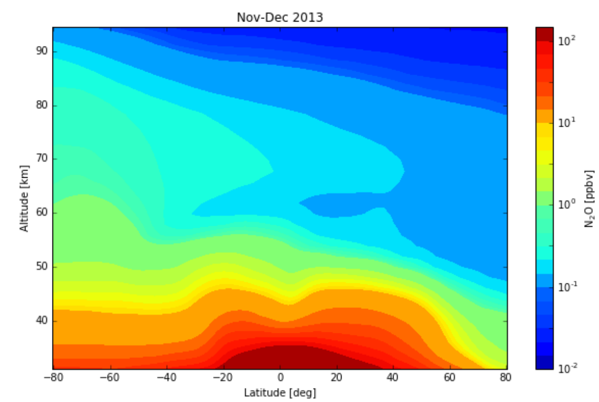
Jul-Aug



Sep-Oct



Nov-Dec



2. Moderator run (2013)

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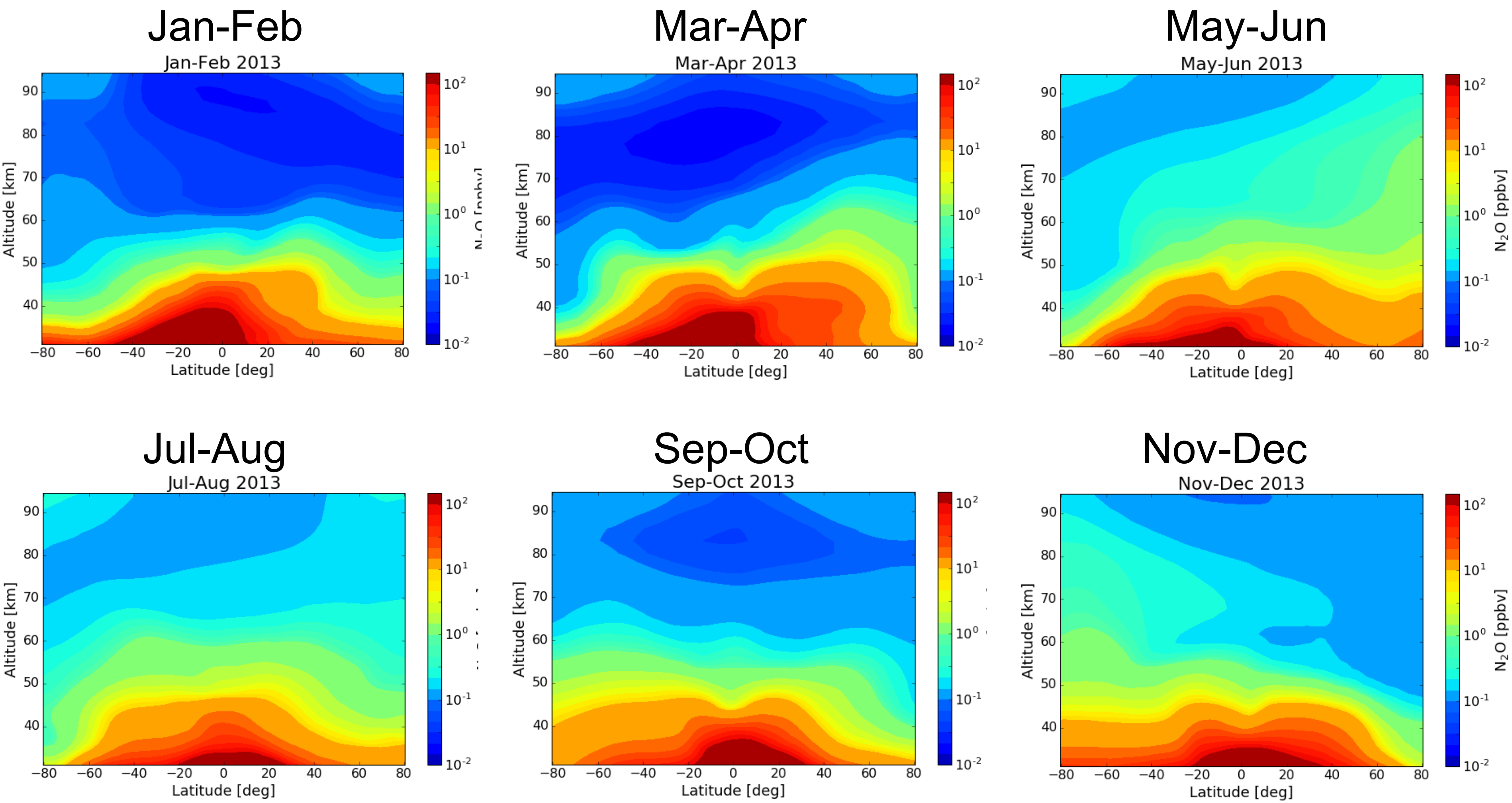

3. Full run (2013)

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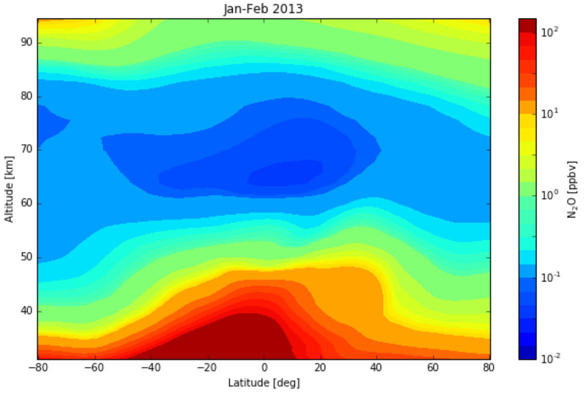
Jan-Feb



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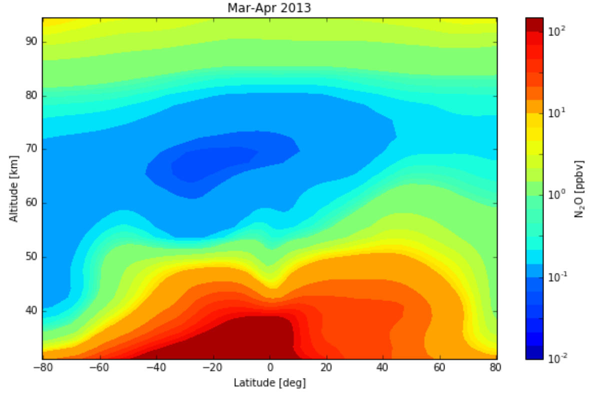

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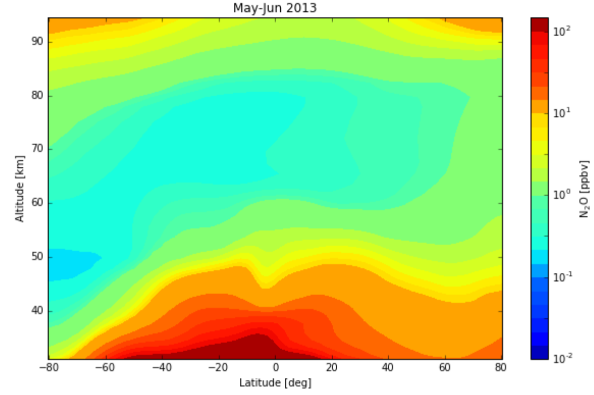

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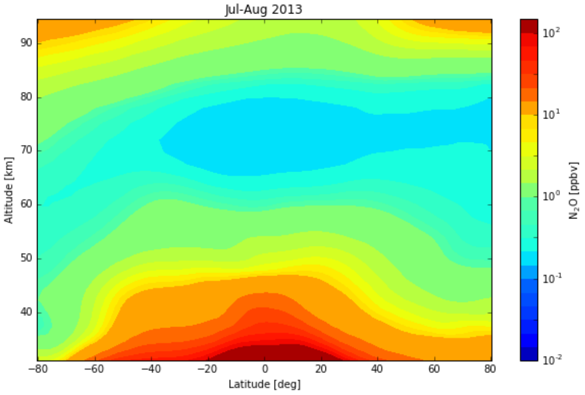

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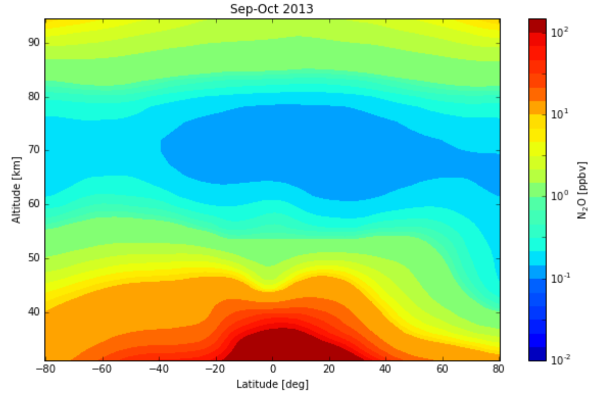

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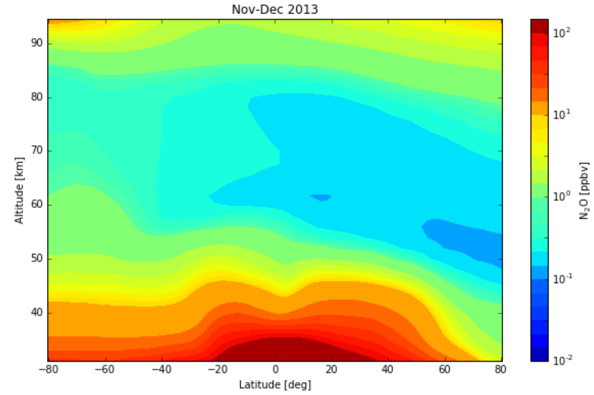

ACE-FTS 2013

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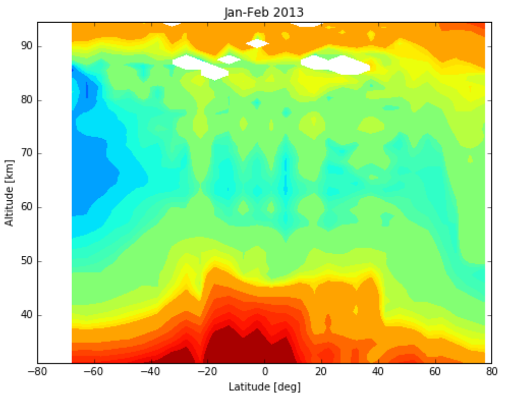
Jan-Feb



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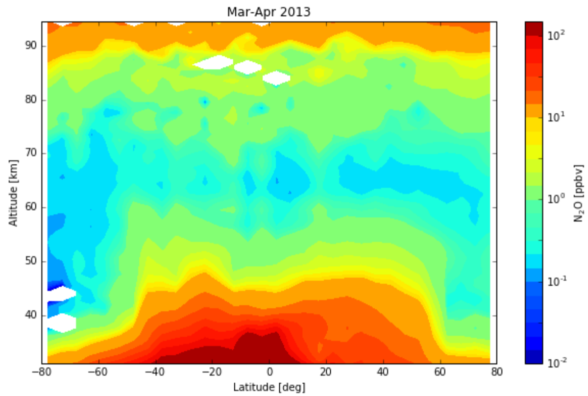

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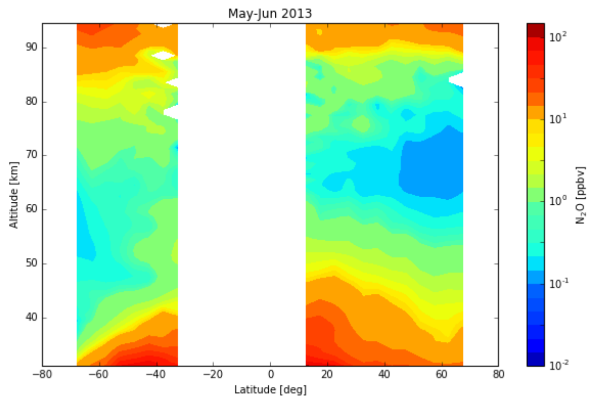

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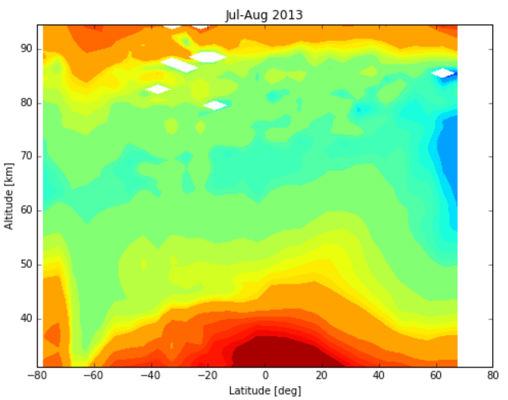

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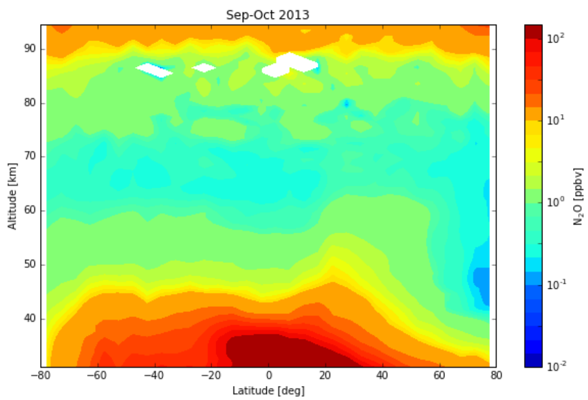

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