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

C. W. Kelly[1], M. P. Chipperfield[1,2], J. M. C. Plane[3], W. Feng[1,2,3], P. E. Sheese[4], K. A. Walker[4,5], and C. D. Boone[5]

[1]**School of Earth and Environment, University of Leeds, Leeds, UK**, [2]National Centre for Atmospheric Science (NCAS), UK, [3]School of Chemistry, University of Leeds, Leeds, UK, [4]University of Toronto, Toronto, Ontario, Canada, [5]University of Waterloo, Waterloo, Ontario, Canada

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Contact: eecwk@leeds.ac.uk

Outline

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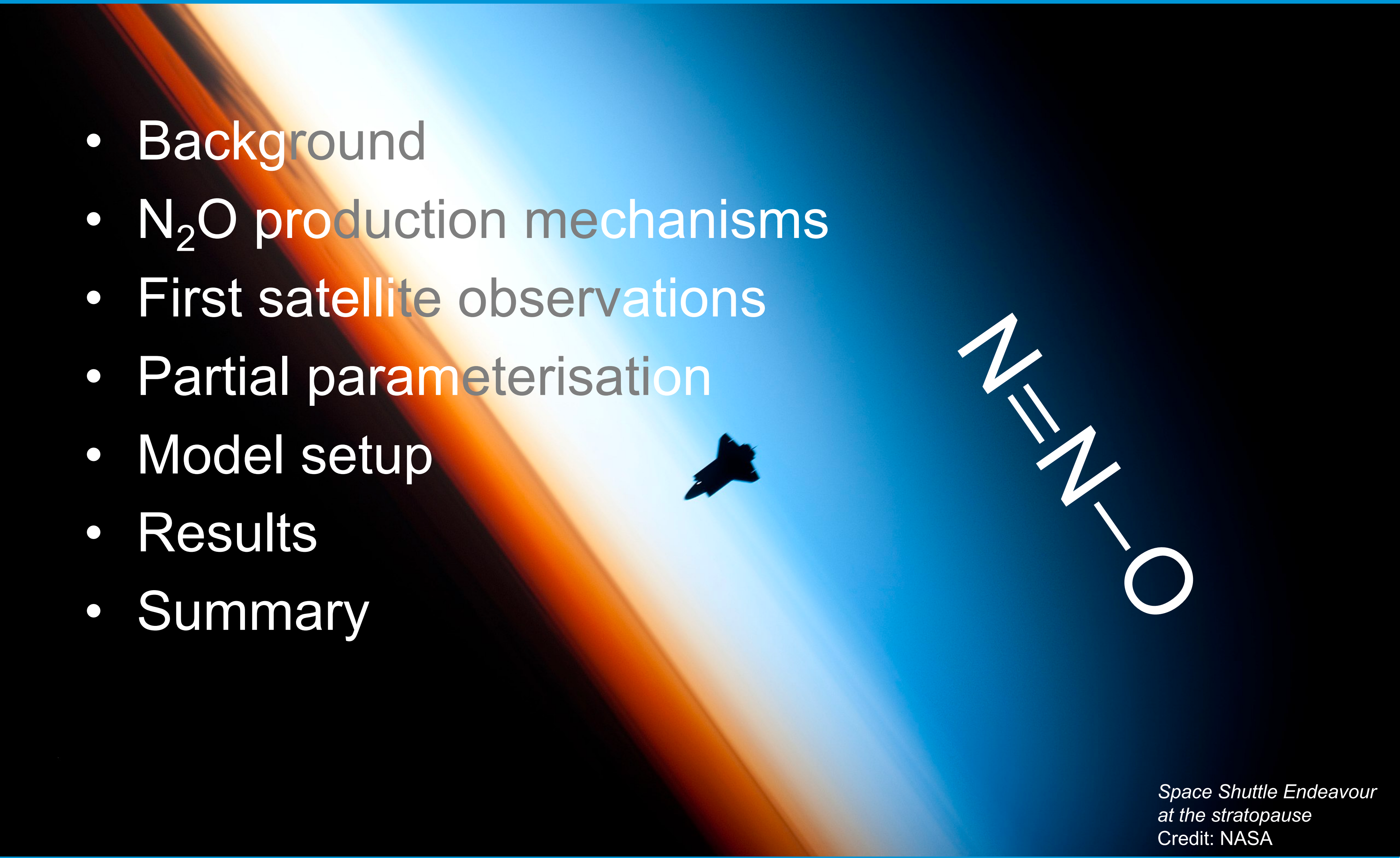


Space Shuttle Endeavour at the stratopause
Credit: NASA

Ozone destruction

- N_2O is precursor of middle atmos. NO_y

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

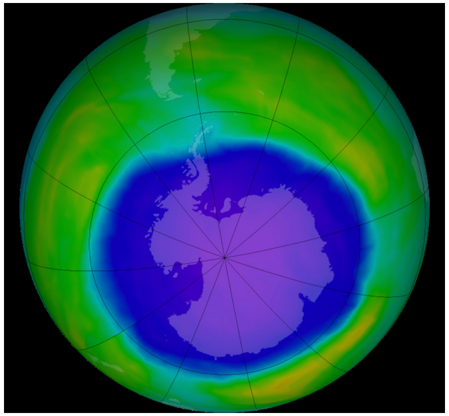
- NO_y destroys stratospheric O_3:

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

~30% total ozone destruction

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

Ozone hole



Credit: NASA

Production mechanisms (1/3)

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

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

$\Delta E = 7.63$ eV

  - Reaction with O_2

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

- Produces N_2O at around **95km**
- But ~25 years without high-altitude infrared satellite observations to verify, until ACE-FTS

ACE-FTS

Credit: ACE – University of Waterloo

Production mechanisms (2/3)

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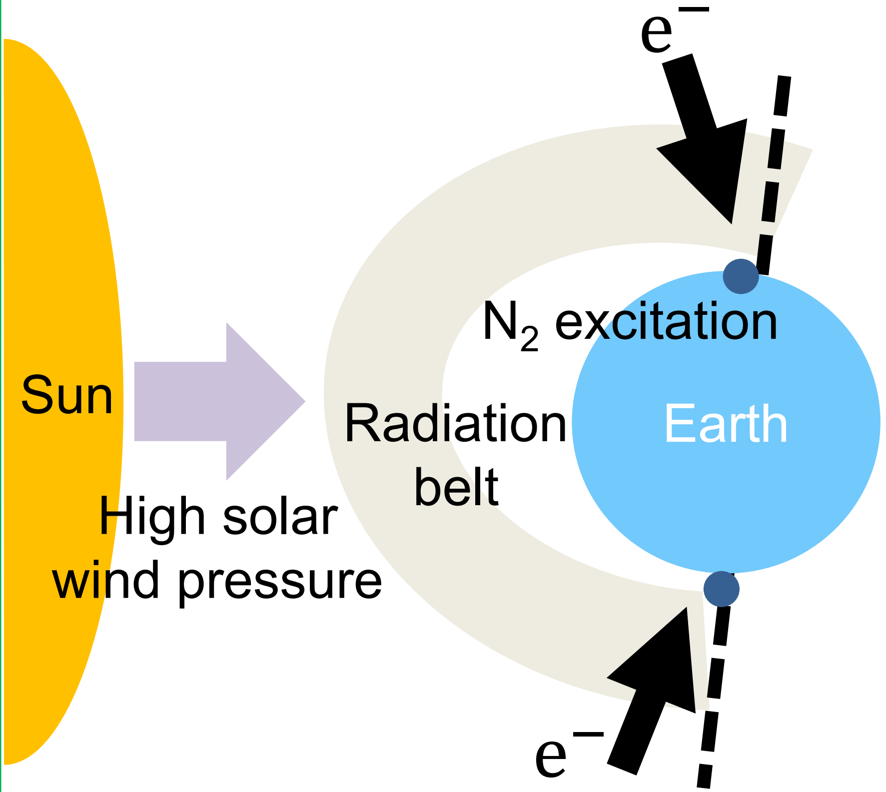
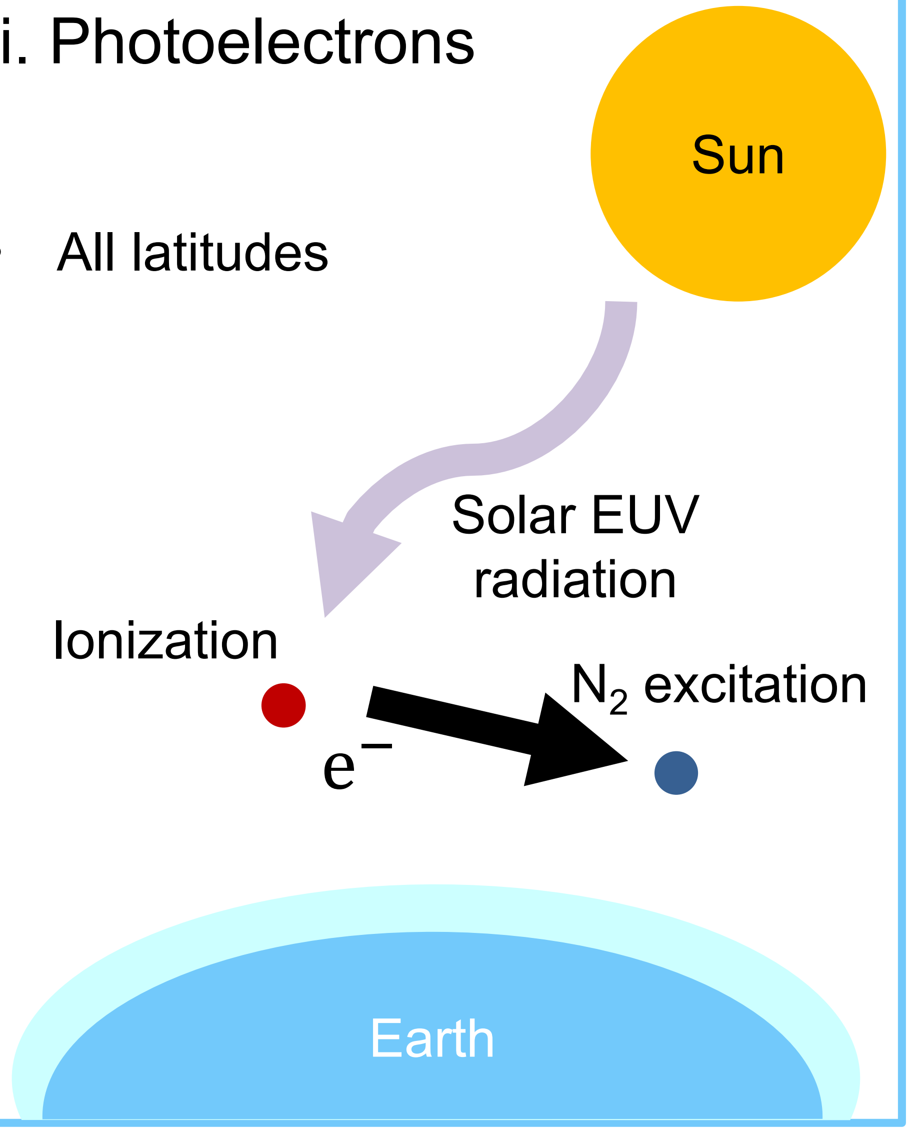
i. Energetic electron precipitation (EEP)

- High latitudes



ii. Photoelectrons

- All latitudes



Production mechanisms (3/3)

- Semeniuk et al. (2008) reported N_2O VMRs of ~5 ppbv at around 55 km using ACE-FTS data
  - Suggested production mechanism at around **75 km**:

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

  - Initially seen as upper atmospheric N_2O source

- *WACCM code already has…*

$$\textbf{M1:} \quad N(^4S) + NO_2 \rightarrow N_2O + O$$

Semeniuk et al. (2008)

- *New mechanism…*

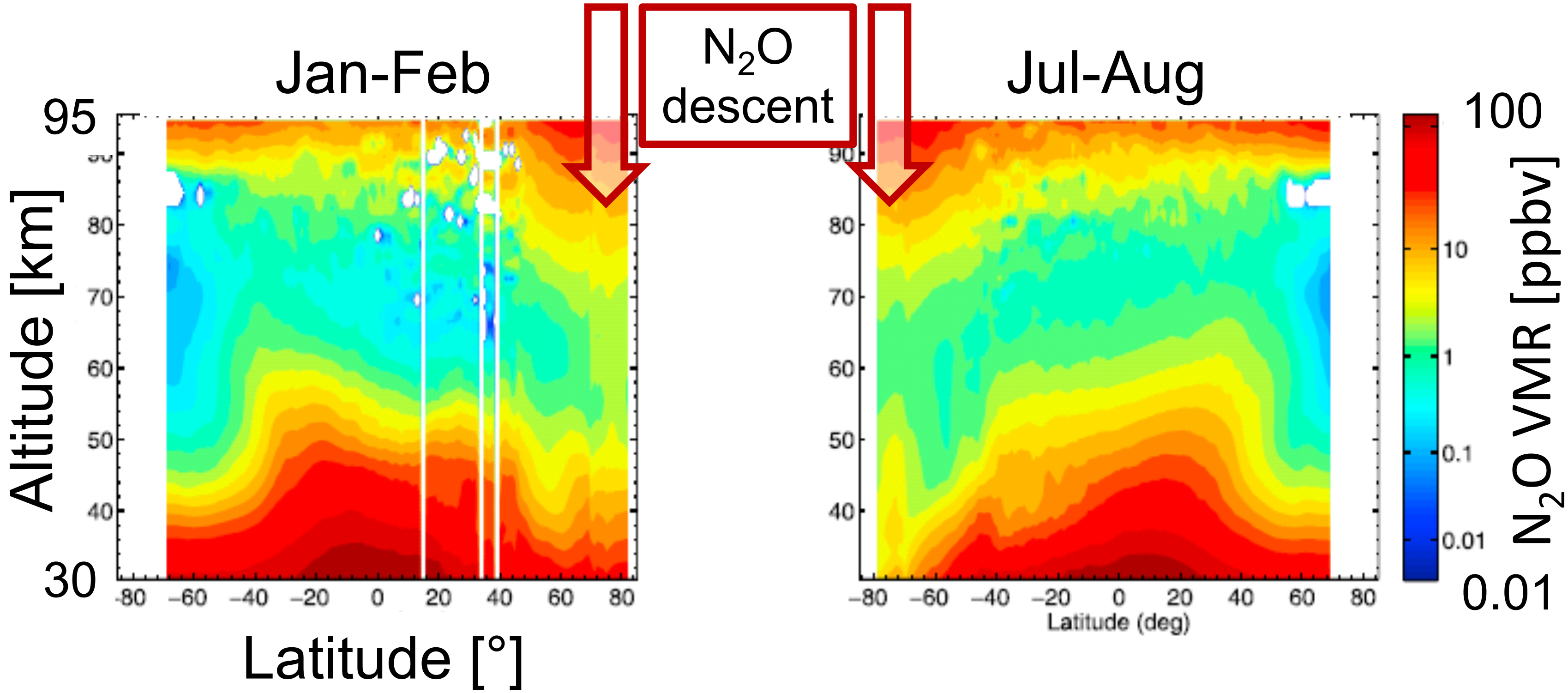
$$\textbf{M2:} \quad N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2O + O$$

Zipf and Prasad (1982)

Date

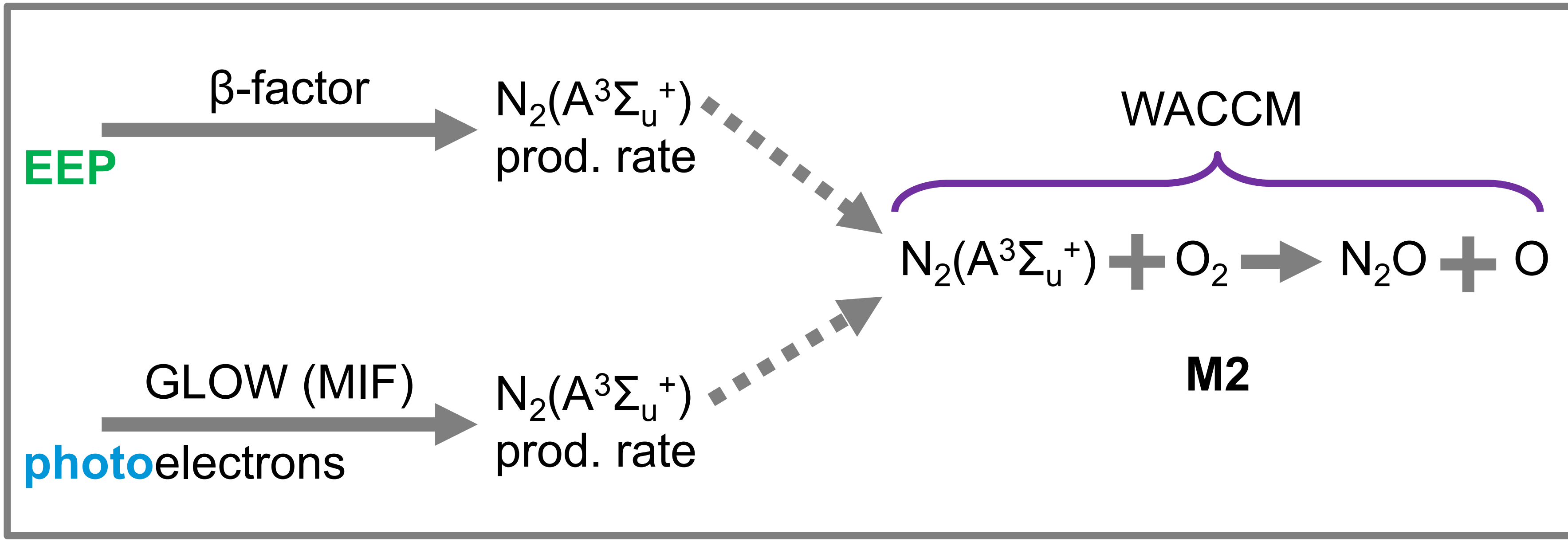
First satellite observations

- Sheese et al. (2016) provided first satellite obs. of 95 km N_2O with ACE-FTS
  - Reported maximum N_2O VMRs of 49 ppbv at 94.5 km



Partial parametrisation of M2 (1/2)

Inclusion of **M2** in WACCM:



EEP contribution

- Partially parameterise
- Efficiency (*β*) factor from steady-state assumption

Photoelectron contribution

- $N_2(A^3\Sigma_u^+)$ prod. rate from NCAR GLObal airgloW model (*Solomon, 2017*)

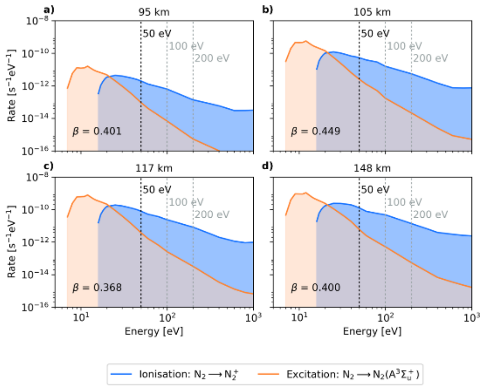
Steady state assumption:

$$\frac{d[N_2O]}{dt} = Prod. - Loss \cdot [N_2O]_{obs} = 0$$

Total prod. rate: $Prod. = \left(Prod._{\mathbf{photo}} \cdot \alpha\right) + \left(Prod._{\mathbf{EEP}} \cdot \alpha\right)$

Verified by second estimate based on first principles:

- *Lab. measurements of integrated cross section (ICS)*
- *Excitation of $N_2 \rightarrow N_2(A^3\Sigma_u^+)$ and the ionisation of N_2*
- *Convolved with auroral electron energy spectra*
- $\beta \approx \mathbf{0.4}$



$$\beta = \frac{Loss \cdot [N_2O]_{obs} - \left(Prod._{\mathbf{photo}} \cdot \alpha\right)}{\left(I_{\mathbf{MEE}} + I_{\mathbf{aur}}\right) \cdot \alpha} \approx \mathbf{0.5}$$

Model setup

Simulation/ configuration	$N_2(A^3\Sigma_u^+)$ production via EEP	$N_2(A^3\Sigma_u^+)$ production via photoelectrons	(M2) $N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2O + O$	(M1) $N(^4S) + NO_2 \rightarrow N_2O + O$	GLOW coupled
Standard	On	On	On	On	Yes
Control_0	Off	Off	Off	Off	No
Control_1	On	On	On	Off	Yes
Control_2	Off	Off	Off	On	No
Sensitivity_E	On	Off	On	On	No
Sensitivity_P	Off	On	On	On	Yes

WACCM changes:

- $N_2(A^3\Sigma_u^+)$ tracer added
- M2 and other depletion routes included

All simulations completed over 2013

Latitude cross-sections (1/2)

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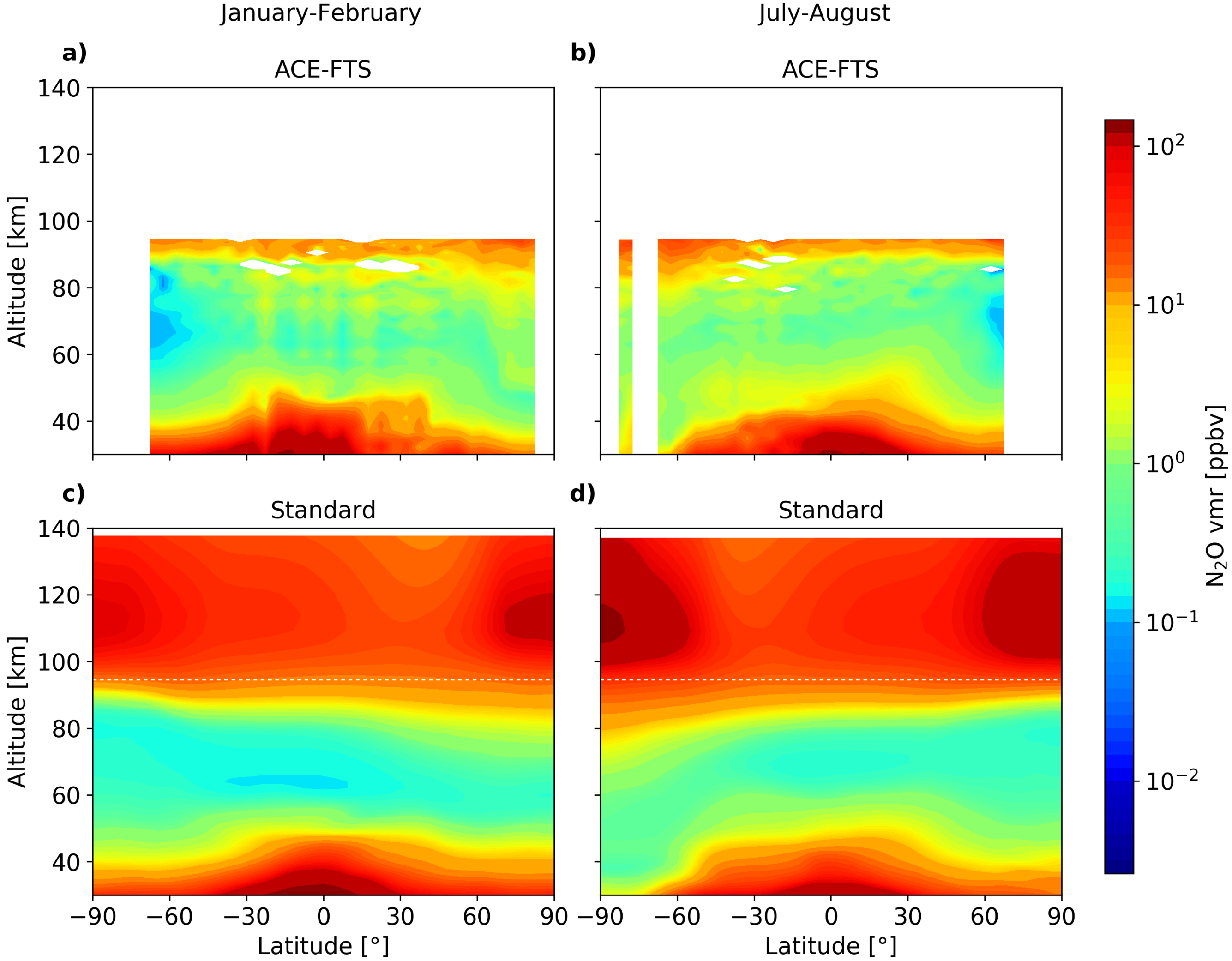

- 2D latitude cross-sections of N_2O ppbv
- Satellite (top), model (bottom)
- Note mixing ratios – not concentrations

Latitude cross-sections (2/2)

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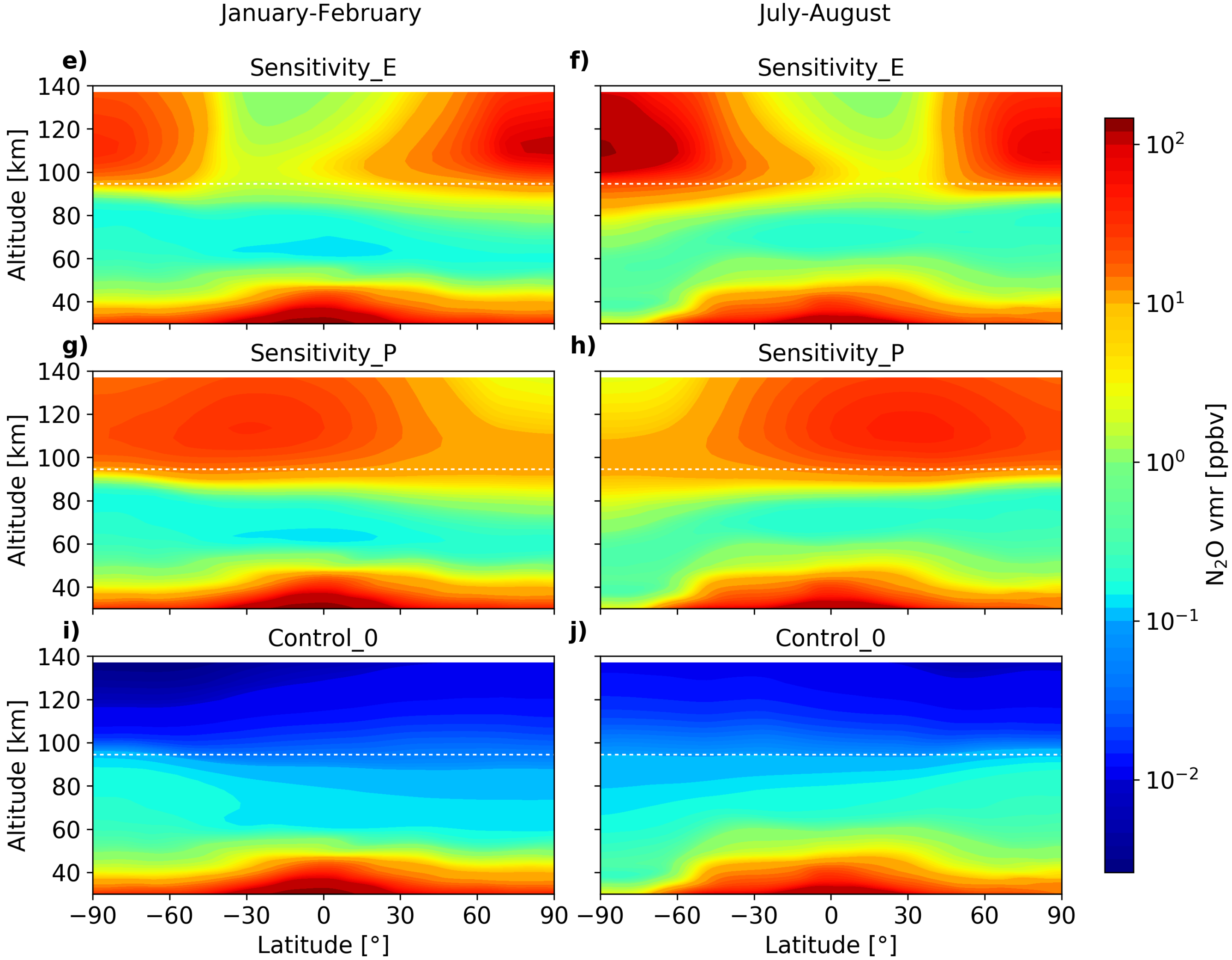
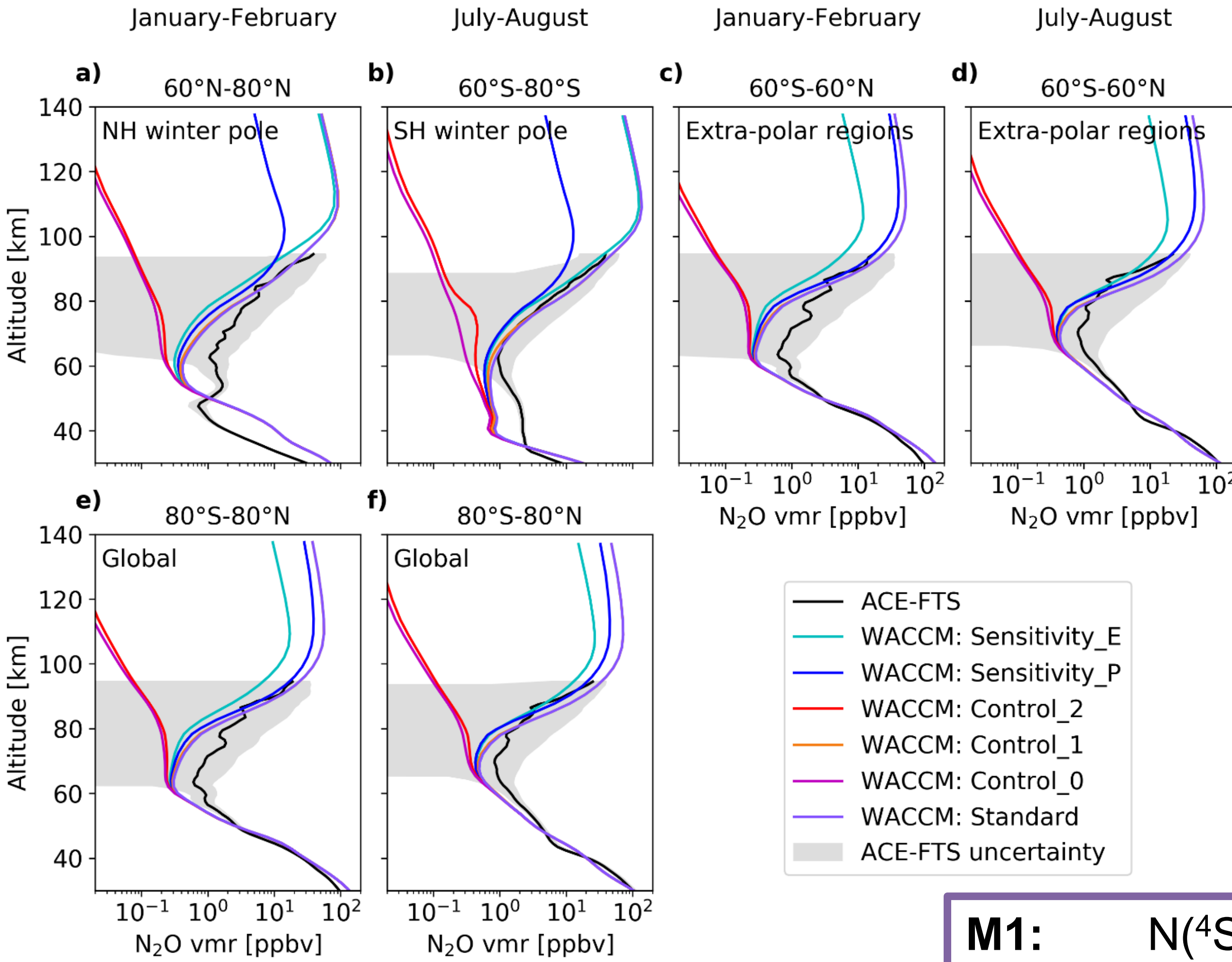


- **EEP** dominant at poles
- **Photo**electrons dominant at mid and low latitudes
- Without *in-situ* N_2O prod. mixing ratios decrease exponentially with altitude

Altitude profiles



- Model matches satellite in MLT
- >99% N_2O prod. from **M2** above 80 km
- Max **M1** impact over SH winter pole (~20%)

M1: $N(^4S) + NO_2 \rightarrow N_2O + O$

M2: $N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2O + O$

Summary

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- *In-situ* N_2O production in the mesosphere lower-thermosphere
- Excited N_2 from **EEP** or **photoelectrons** reacts with O_2 to form N_2O
- Added into WACCM via partial parametrisation
- Model replicates observed vertical, latitudinal and seasonal profile
- **EEP** dominant at poles, **photo**electrons dominant at mid and low latitudes

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