The chemical sensitivity of stratospheric ozone to nitrous oxide and methane

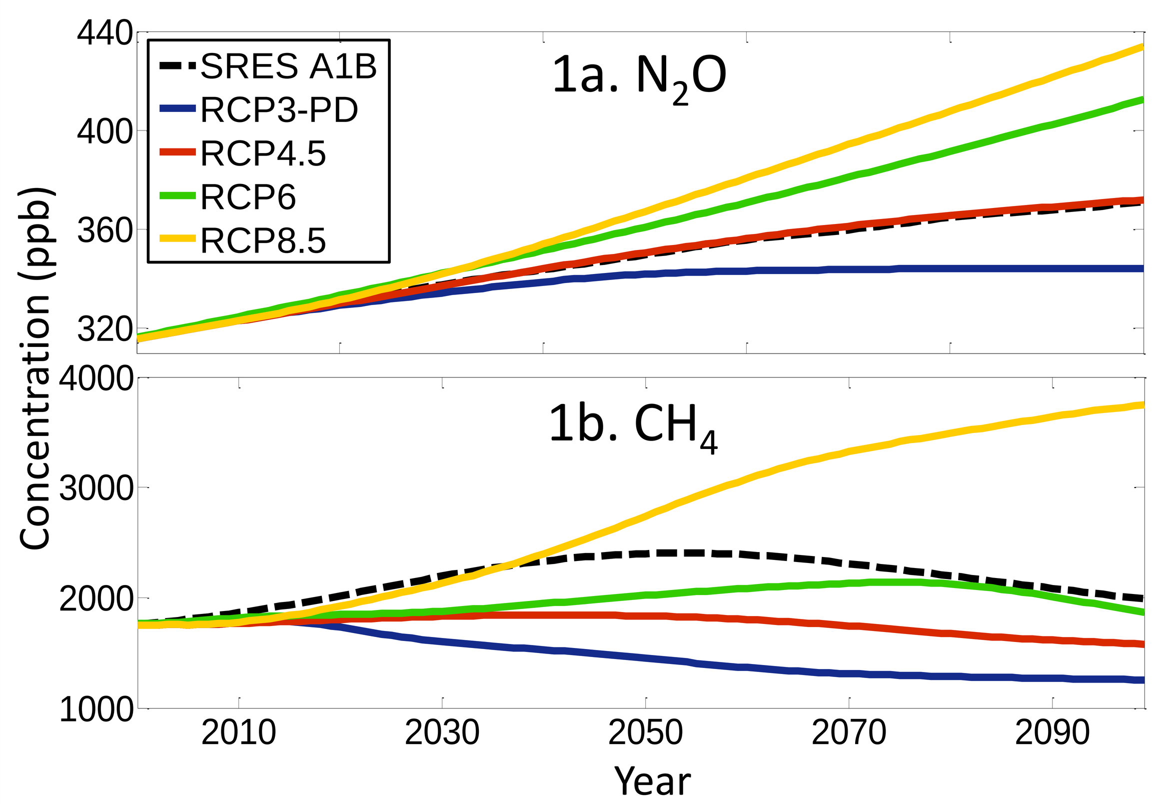
Laura Revell[1,2], Greg Bodeker[3], Petra Huck[3], Dan Smale[1] and Bryce Williamson[2]

1. National Institute of Water and Atmospheric Research, New Zealand. Contact: **l.revell@niwa.co.nz**; 2. Department of Chemistry, The University of Canterbury, New Zealand; 3. Bodeker Scientific, New Zealand.

What we did

Eight simulations for the period 2015-2100 were performed using the chemistry-climate model Niwa-SOCOL (Schraner *et al.,* 2008; Morgenstern *et al.,* 2010). Boundary conditions generally followed the IPCC SRES A1B scenario for greenhouse gases (Nakicenovic *et al.*, 2001), but for four simulations, the prescribed nitrous oxide (N_2O) concentrations were replaced with concentrations consistent with N_2O emissions from each of the four representative concentration pathway (RCP) emissions scenarios (**1a**) (Meinshausen *et al.,* 2011). For the other four simulations, the methane (CH_4) concentrations were replaced with those consistent with CH_4 emissions from each of the four RCP emissions scenarios (**1b**). For each simulation, the contributions of 15 catalytic chemical cycles to ozone destruction (similar to Lee *et al.*, 2002), including three nitrogen cycles and five hydrogen cycles, were accumulated into daily means within each model grid cell.

1. Surface concentrations



N_2O and CH_4 surface concentrations used in the model simulations. Simulation RCP3-PD N_2O refers to the simulation in which the SRES A1B scenario for N_2O was replaced by the RCP3-PD scenario for N_2O, and so forth.

Why we did it

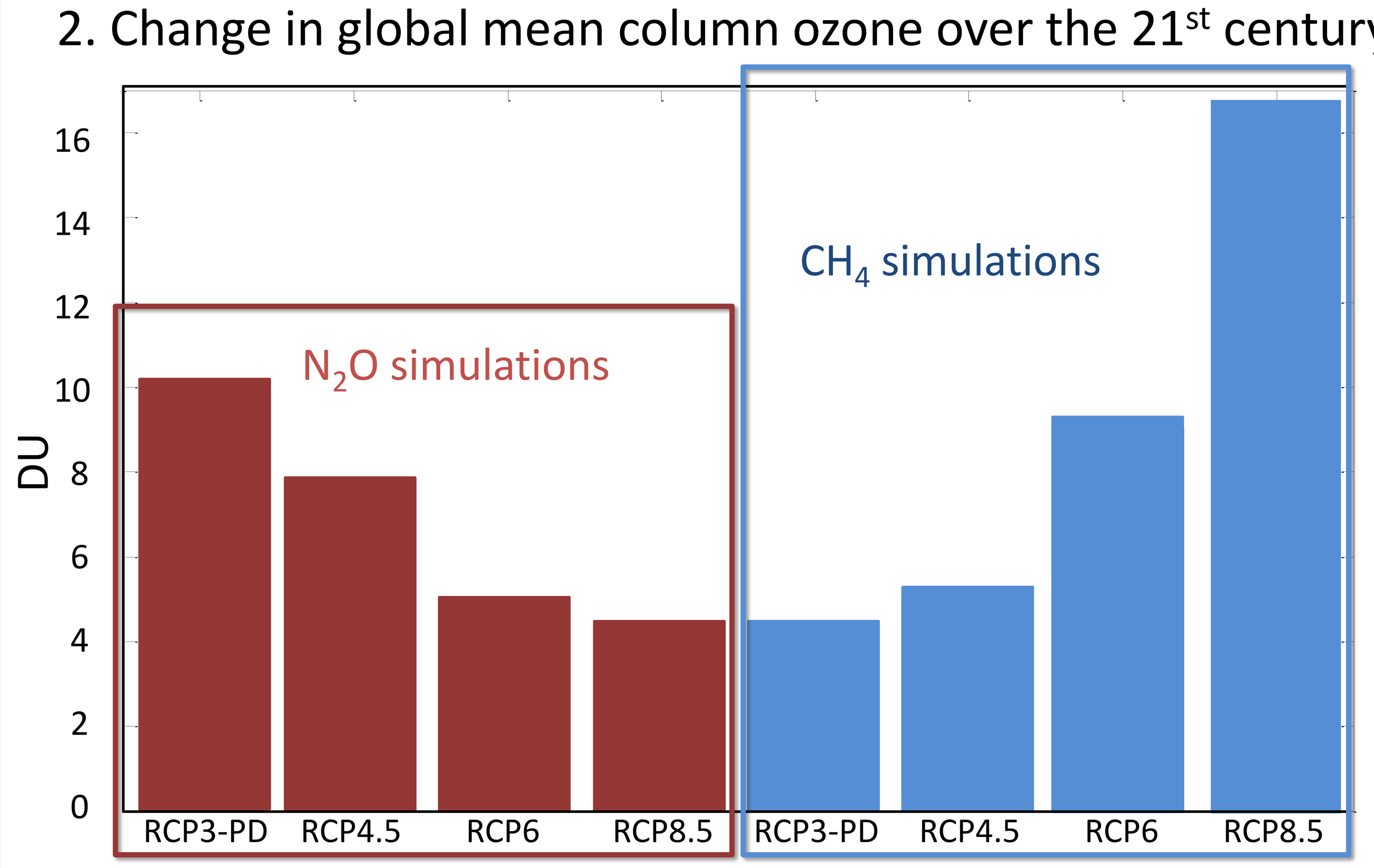
N_2O and CH_4 are the two primary anthropogenic greenhouse gases controlled under the Kyoto Protocol after CO_2, and cause ozone depletion when they are converted to active nitrogen oxides (NO_x) and active hydrogen oxides (HO_x), respectively. Because projected increases in N_2O and CH_4 emissions through the 21st century are expected to lead to changes in ozone, the results from this study provide insight into the effects of different greenhouse gas emission mitigation strategies on ozone.

Dominant NO_x- and HO_x-catalyzed ozone-depleting cycles

$NO + O_3 \rightarrow NO_2 + O_2$	$OH + O_3 \rightarrow HO_2 + O_2$
$\mathbf{NO_2 + O \rightarrow NO + O_2}$	$\mathbf{HO_2 + O \rightarrow OH + O_2}$
$O_3 + O \rightarrow 2O_2$	$O_3 + O \rightarrow 2O_2$

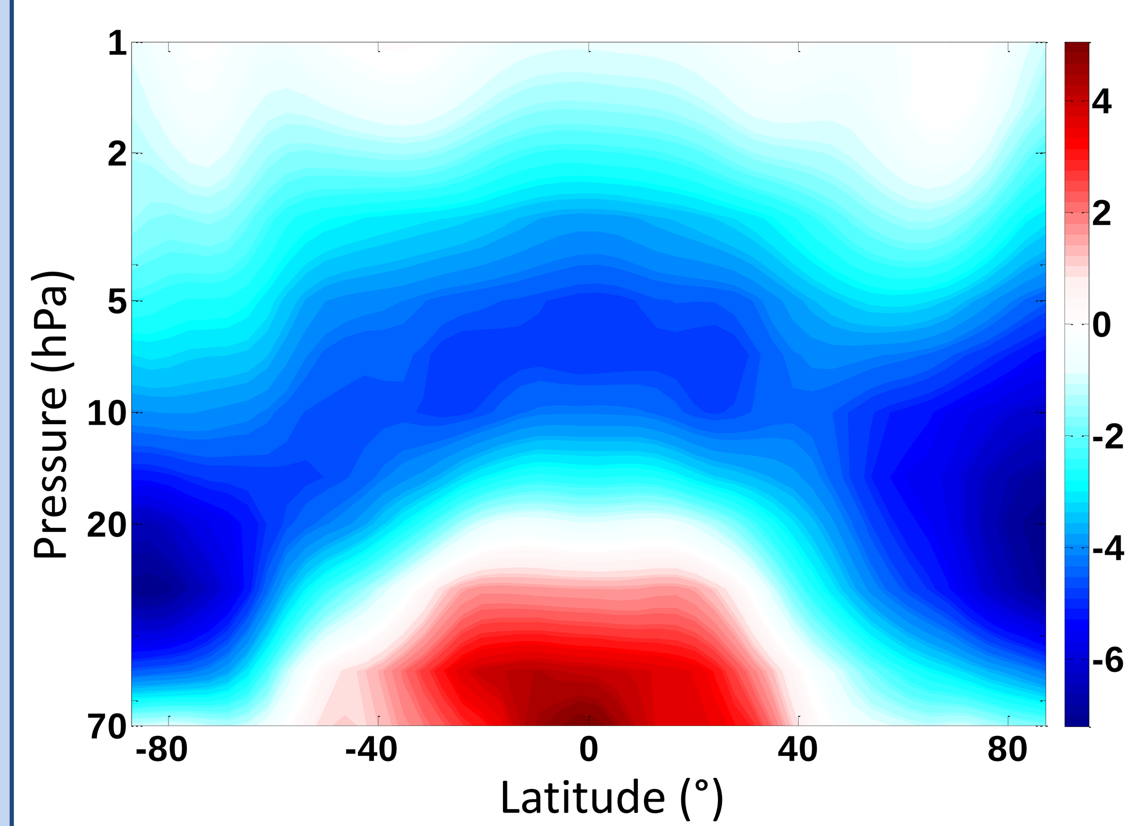
Rate-limiting reactions in bold

2. Change in global mean column ozone over the 21st century



The difference between decadal mean, global area-weighted mean column ozone for the first and last decades of the eight simulations. For all simulations, the general trend is that column ozone increases over the 21st century, due in part to stratospheric cooling slowing the gas-phase ozone loss cycles, and decreasing concentrations of active chlorine and bromine, which deplete ozone (WMO, 2011).

3. Ozone differences through the 21st century by N_2O emissions scenario

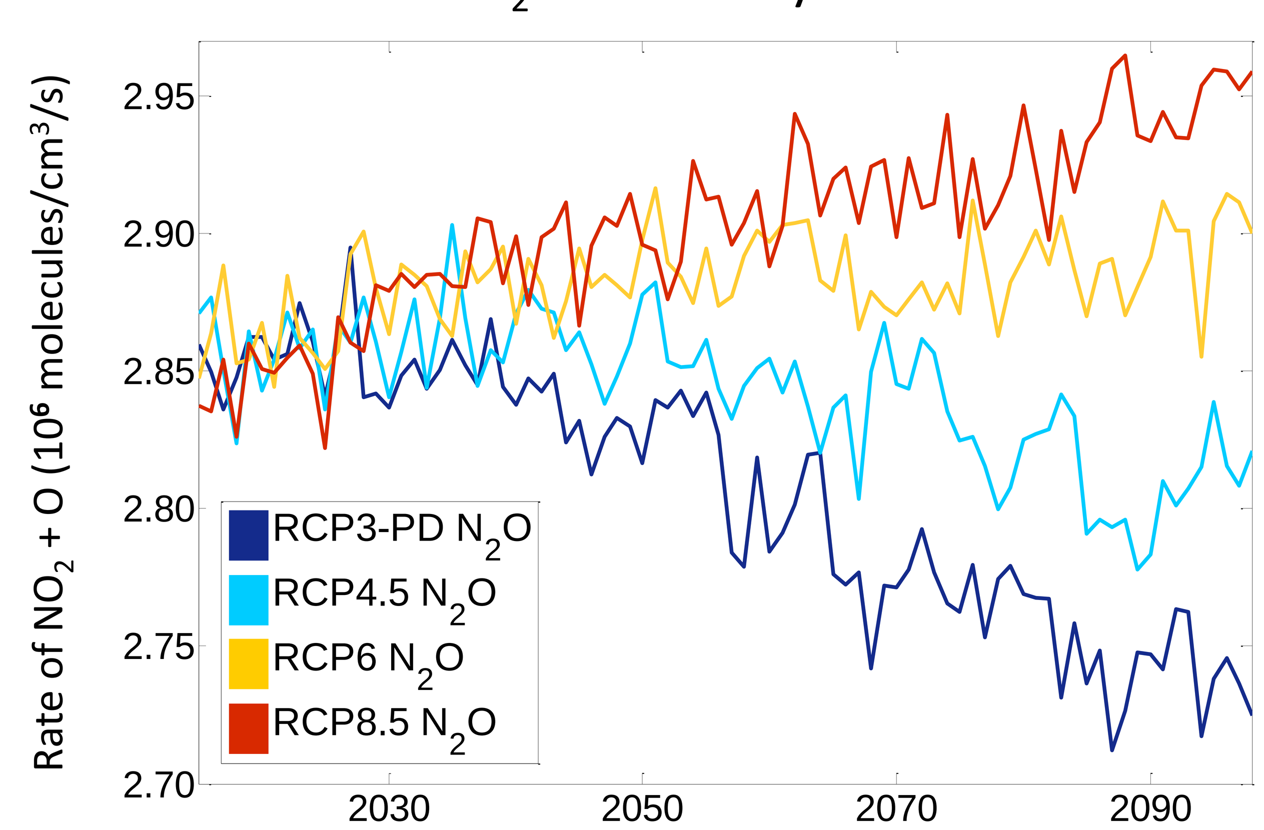


The percentage difference in ozone (averaged over the 2080 and 2090 decades) between simulation RCP8.5 N_2O (high N_2O emissions) and simulation RCP3-PD N_2O (low N_2O emissions), and displayed as a function of latitude and pressure.

What do we see? – N_2O simulations

- Column ozone increases over the 21st century, but increases less in simulations with higher N_2O concentrations (**2**), due to an increased rate of the ozone-depleting NO_x cycles (**4**).
- In all simulations, tropical lower stratospheric ozone decreases and upper stratospheric ozone increases over the 21st century. However, relative to simulation RCP3-PD N_2O (low N_2O emissions), stratospheric ozone in simulation RCP8.5 N_2O (high N_2O emissions) increases up to 7% less everywhere except for in the tropical lower stratosphere, where it decreases as much as 5% less, likely due to an increase in the rate of NO_x-induced ozone production (NO_2+hv→NO+O followed by O+O_2+M→O_3+M).

4. Rate of ozone loss attributed to the NO_2 + O catalytic cycle for the N_2O sensitivity simulations



Global area-weighted mean rate of NO_2+O, the dominant NO_x cycle in the stratosphere, for the four N_2O sensitivity simulations at 5 hPa. By the end of the 21st century, NO_2+O is almost 20% faster in simulation RCP8.5 N_2O compared with simulation RCP3-PD N_2O.

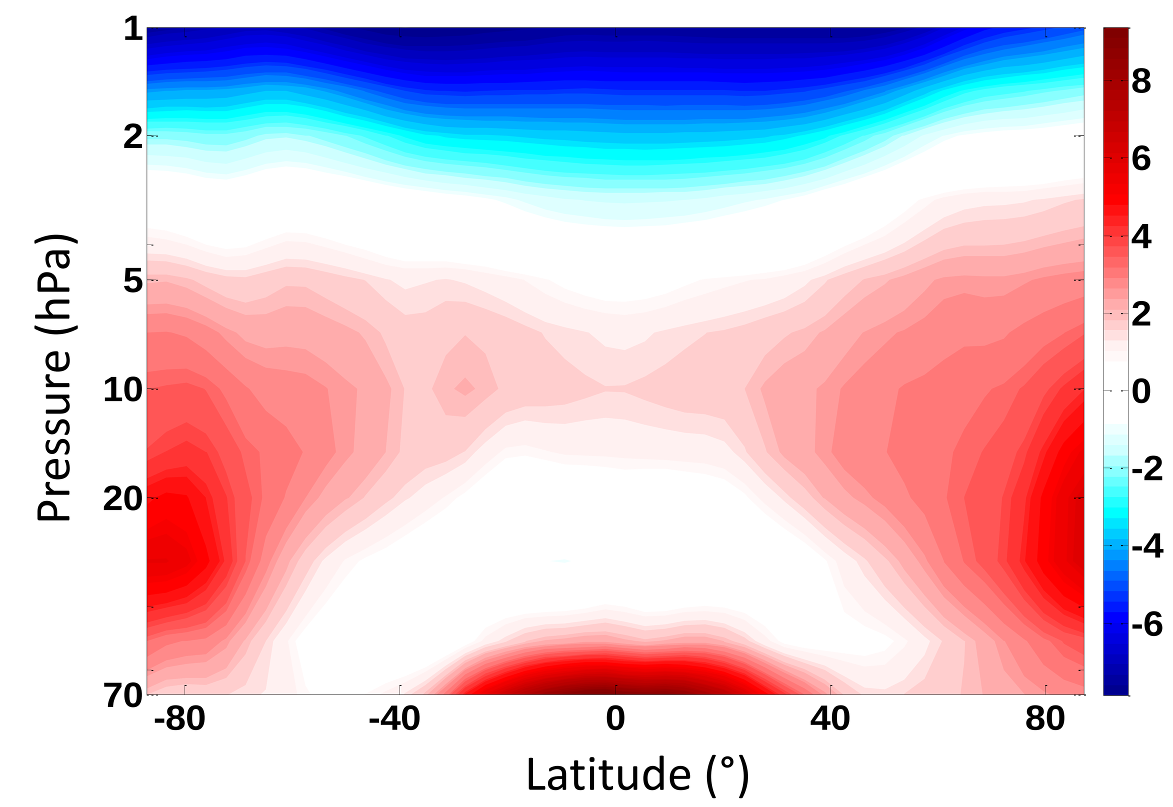
References

- Fleming *et al.* (2011), Atmos. Chem. Phys., 11.
- Lee *et al.* (2002), J. Geophys. Res., 107.
- Meinshausen *et al.* (2011), Climatic Change (Special Issue on RCPs).
- Morgenstern *et al. (*2010), J. Geophys. Res., 115.
- Nakicenovic *et al.* (2001), IPCC Special Report on Emissions Scenarios.
- Schraner *et al.* (2008), Atmos. Chem. Phys., 8.
- WMO (2011), Scientific Assessment of Ozone Depletion: 2010

What do we see? – CH_4 simulations

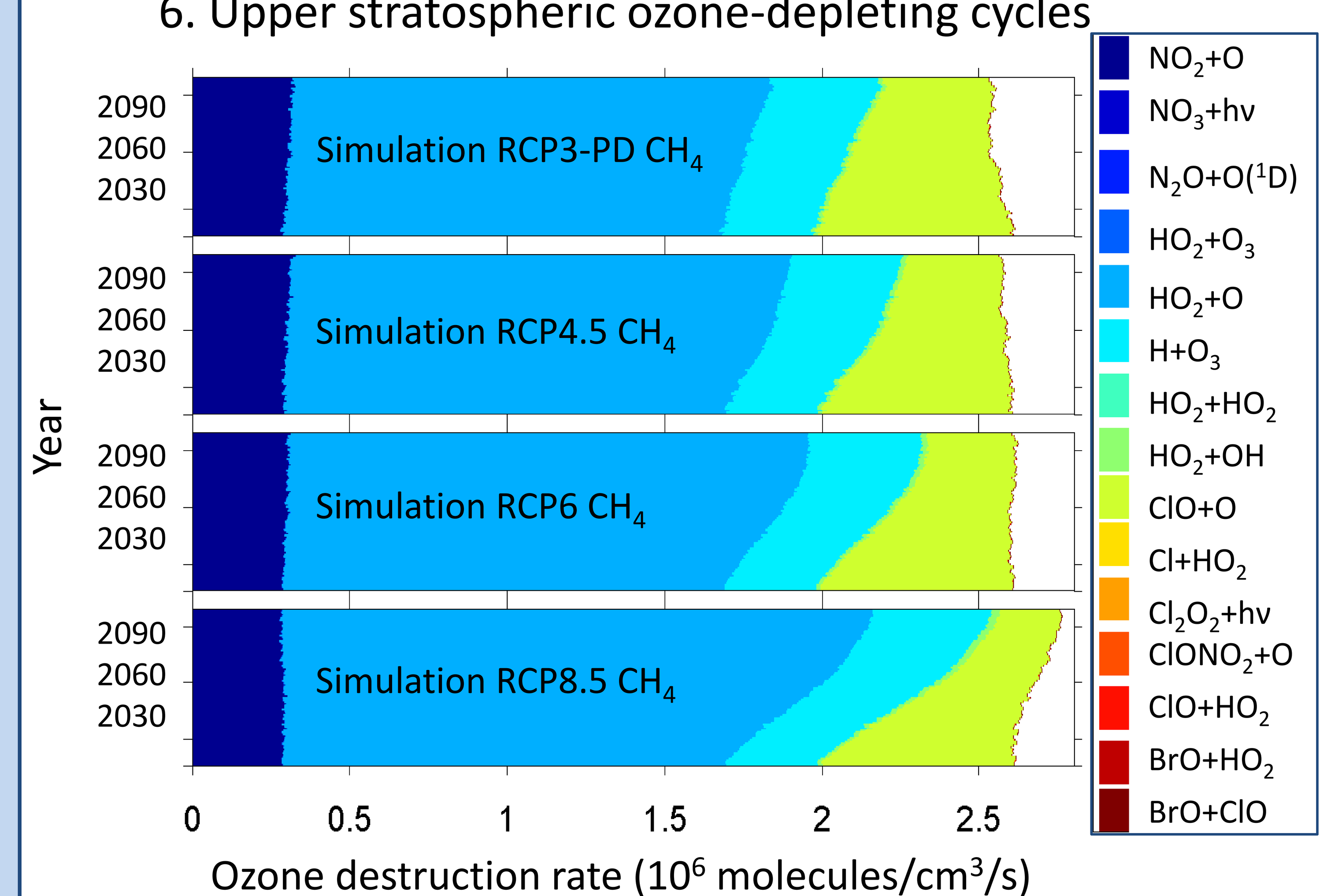
- Simulations with greater CH_4 emissions lead to a greater increase in column ozone (**2**); the increase in column ozone over the 21st century is four times greater for simulation RCP8.5 CH_4 (high CH_4 emissions) than for simulation RCP3-PD CH_4 (low CH_4 emissions).
- In simulation RCP8.5 CH_4 relative to simulation RCP3-PD CH_4, global upper stratospheric ozone decreases as much as 7% (**5**) due to an increased rate of the ozone-depleting HO_x cycles (**6**), but increases up to 9% elsewhere, particularly in the polar middle stratosphere and tropical lower stratosphere (**5**).
- CH_4-induced increases in ozone occur due to: a) NO_x-assisted ozone production (via HO_2+NO→NO_2+OH then NO_2+hv→NO+O and O+O_2+M→O_3+M) in the lower stratosphere and troposphere; b) Decreasing concentrations of active chlorine, and thus decreasing importance of chlorine-catalyzed ozone loss cycles, via the reaction CH_4+Cl→CH_3+HCl (**6**); c) Slower ozone loss rates, due to increased H_2O-induced cooling of the atmosphere (Fleming *et al.,* 2011).

5. Ozone differences through the 21st century by CH_4 emissions scenario



As for Figure (**3**), calculated for simulation RCP8.5 CH_4 (high CH_4 emissions) and simulation RCP3-PD CH_4 (low CH_4 emissions).

6. Upper stratospheric ozone-depleting cycles



Contributions of 15 chemical cycles to the global rate of ozone destruction for the CH_4 sensitivity simulations. Plots are for the upper stratosphere (1 hPa), where the HO_x cycles are fast.

Conclusions

Our results indicate that the sensitivity of stratospheric ozone is such that increasing N_2O emissions will negatively impact ozone recovery in the 21st century via active nitrogen chemistry, while increasing CH_4 emissions will increase the total ozone column overall, but lead to global ozone depletion in the upper stratosphere.