Interactive comment on “Past and future simulations of NO$_2$ from a coupled chemistry-climate model in comparison with observations” by H. Struthers et al.

Anonymous Referee #1

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The authors examine NO$_2$ and other species’ trends derived from a chemistry-climate model simulation and compare to column measurements taken at Lauder and Arrival Heights. Measured trends in NO$_2$ are not fully understood and the authors aim to add to the discussion. I have some comments to make about their methodology and also about the model and recommend minor revision of the paper before publication in ACP.

Details: The authors appear to suggest that N$_2$O + O($^1$D) → 2 NO is the only loss process for N$_2$O. It is the only chemical source of NO$_y$ in the stratosphere but far from the only loss process for N$_2$O. It competes with N$_2$O + O($^1$D) → N$_2$ + O$_2$ (the two channels branch at 42% vs 58%, according to JPL (2002)) and with N$_2$O + h$\nu$ → N$_2$ + O($^1$D), which may well altogether be more important than the first two loss channels.
The latter two reactions may not be incorporated in the UMETRAC model because their products are unimportant or negligible and because of the way UMETRAC "transports" N$_2$O. When discussing observed trends, the authors should explain why these loss processes are not considered. Indeed, I think a hypothetical shift in the sinks to increasingly favour oxidation by O(1D) over photolysis is a candidate for explaining why NO$_2$ trends exceed those of N$_2$O.

Also, the authors seem to suggest that, all else being equal, a fractional trend in N$_2$O should lead to an equal fractional trend in NO$_y$. It took me a moderately complicated back-of-the-envelope calculation about sources and sinks of NO$_y$ and N$_2$O to convince myself that this does indeed follow. Perhaps the authors could spell out in a few sentences why they expected NO$_y$ and NO$_2$ to have the same fractional increase as N$_2$O. Failure to find such a correspondence in the observational record for NO$_2$ then triggers questions about shifts in the partitioning of NO$_y$, for example.

As far as the modelling is concerned, I think the main advantage of UMETRAC is that it is comparatively cheap. However, the treatment of long-lived tracers as all being derived from a single dynamical tracer concerns me. Plumb and Ko is only applicable in the case of slow chemistry, compared to transport timescales. In the presence of transport barriers this is not a good approximation. Also the method effectively prescribes the lifetimes of tracers, relative to that of the dynamical tracer. Hence it does not take into account possible changes in lifetimes due to changes in the environmental conditions. For example, one could expect a substantial variation of the lifetime of methane with Cl$_y$ due to the important sink of CH$_4$ + Cl. Finally the lumping of all Br, Cl and nitrogen species into single Br$_y$, Cl$_y$, and NO$_y$ tracers fails to account for the relatively long lifetimes of individual members of those groups (such as HCl, ClONO$_2$, HNO$_3$, NO$_x$) and might introduce serious errors in the partitioning of group members, compared to alternatives that transport more species individually. So I would like to encourage the authors to consider moving to a more modern formulation of chemistry that does away with the dynamical tracer. Modern advection schemes are probably cheap enough to
allow this. For the purposes of this paper however this is clearly not practical.

The paragraph on the importance of stratospheric water vapour possibly does not take into account the latest developments in this field. My understanding is that the claim that there is a substantial increase of stratospheric water vapour on top of what is explained by increases in methane, is largely based on the Boulder balloon record. HALOE satellite data however do not exhibit a significant unexplained trend, so there is a yet unresolved contradiction there. So I guess you need to give references for the quoted 1% per year trend and say whether that’s the same as the trend in CH₄.

Tables 1 and 2: The numbers are percentages of what? Columns? The fact that trends in NOₓ are practically the same as those of N₂O rule out my stipulation above that shifts in N₂O oxidation to increasingly favour NOₓ are responsible for the difference in the trend between NO₂ and N₂O.