Atmos. Chem. Phys. Discuss., 4, S1968–S1970, 2004
www.atmos-chem-phys.org/acpd/4/S1968/

Atmospheric Chemistry and Physics Discussions

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

Received and published: 4 October 2004

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 $N_2O + O(^1D) \rightarrow 2\ NO$ is the only loss process for N_2O. It is the only chemical source of NO_y in the stratosphere but far from the only loss process for N_2O. It competes with $N_2O + O(^1D) \rightarrow N_2 + O_2$ (the two channels branch at 42% vs 58%, according to JPL (2002)) and with $N_2O + h\nu \rightarrow N_2 + O(^1D)$, 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_2O. 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_2O.

Also, the authors seem to suggest that, all else being equal, a fractional trend in N_2O 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_2O 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_2O. 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 longlived 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 CH_4.

Tables 1 and 2: The numbers are percentages of what? Columns? The fact that trends in NO_y are practically the same as those of N_2O rule out my stipulation above that shifts in N_2O oxidation to increasingly favour NO_y are responsible for the difference in the trend between NO_2 and N_2O.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 4545, 2004.