Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "Tropospheric ozone budget: regional and global calculations" *by* F. M. O'Connor et al.

R. von Kuhlmann

KUHLMANN@MPCH-MAINZ.MPG.DE

Received and published: 6 April 2004

This short comment is not meant to generally critize O'Connor et al.'s valuable work investigating more closely the regional budget of ozone. But the ACP discussion forum seemed well suited for a critical elaboration on one of their statements, hopefully triggering an interesting discussion.

O'Connor et al. state that part of the uncertainty in the global net production or destruction of ozone "is due to the net photochemical term being the sum of two large but oppositely signed terms". Reviewer 1 has mentioned that "this is a common but misleading statement" and that "the net term may be more reliable than the gross production and loss" in part for numerical reasons. I also endorse that O'Connor et al. have included only net ozone production terms in their comparison and evaluation of

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

the global and regional budgets, not stating or discussing the commonly used gross production or loss terms of ozone. But given the commonness of this misconception I think that a more detailed discussion of this issue is warranted.

The case I want to make here is that net photochemical tendencies of ozone are not only more accurate or well defined, but also far more relevant. This is because the two large terms are not independent of each other, as already discussed by von Kuhlmann et al. (J. Geophys. Res., 108(D9), 4294, 2003). This close coupling can for example be seen in Figure 3 and 4 in Yienger et al. (J. Geophys. Res., 104(D3), 3655-3667, 1999) where the seasonal cycle of the gross production and loss for several regions is plotted. Both quantities have a very similar seasonal cylce and their difference is small compared to the gross terms. Using one year of output from the global model MATCH-MPIC at a resolution of $5.6° \times 5.6°$ I calculate that the monthly mean production and loss terms of ozone (based on the O_x family concept, see below) are correllated with $r = 0.78$ ($r^2 = 0.61$). This is calculated using all grid cells below the tropopause. Based on numerous sensitivity simulations (e.g. von Kuhlmann et al. (ACP, 4, 1-17, 2004) or by comparing different global model results (e.g. IPCC, Prather et al., 2001) it seems that the coupling for integrated values (e.g. regional averages as in Yienger et al. 1999 or tropospheric or hemispheric averages) of $L(O_3)$ and $P(O_3)$ is even higher, roughly 70-80%.

There are several reasons for this strong coupling of gross ozone loss and production. Upon deriving the commonly used definition of them one can already get an idea of the origin of problems with these terms. Strictly calculating ozone loss would include the full turnover of ozone photolysis, but would include a fast null cycle via recombination of $O(^3P)$ with molecular oxygen. Thus, the budget of the odd oxygen family $O_x = O_3 + O(^3P) + O(^1D)$ is calculated instead and since O_3 is the main component of this group, the O_x budget is commonly used synonymously for the O_3 budget. Next, the fast null cycle through photolysis of NO_2 to form NO and $O(^3P)$, with the latter rapidly returning O_3, is removed by also including NO_2 into the odd oxygen family. This, however, adds

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

© EGU 2004

a problem for polluted urban regions where NO_2 mixing ratios can be up to tens of nmol/mol and thus O_3 will not anymore be the dominating species in the O_x family. Then, how about the fast thermal decomposition and association reactions of unstable nitrates like peroxyacetyl nitrate (PAN)? Consequently, they also have to be included in the odd oxygen family. I am not disputing the usefullness of the family concept to filter out important reaction cycles in atmospheric chemistry, but it seems that its limitations need to be recognized more clearly. From a mathematical point of view the chemical reactions form a set of coupled differential equations, which cannot easily, and if at all only approximately, be decoupled.

In the case of ozone the complications arise from the intimate coupling of NO_x and HO_x reaction cycles with those of ozone, in addition to the dependence of the loss terms on the abundance of ozone itself. E.g. an increase of NO_x under most atmospheric conditions enhances HO_x levels, which enhance both ozone loss and production. It needs to be noted that there are two exceptions for such close coupling. The main one is the reaction of $O(^1D)$ with water vapour. Though the concentration of $O(^1D)$ is also dependent on that of ozone, water vapour varies independently in the atmosphere. Thus, when attempting to evaluate and compare 3D model results, it is probably better to evaluate the water vapour distribution and the photolysis rate $J(O_3 \rightarrow O(^1D))$ directly as done by O'Connor et al. The other exception are ozonolysis reactions of species including double bonds. However, due to their short lifetimes this effect will be mostly local.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 991, 2004.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

© EGU 2004