

## Comment on "Methane photooxidation in the atmosphere: Contrast between two methods of analysis" by Harold Johnston and Douglas Kinnison

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In a recent study, *Johnston and Kinnison* [1998] (hereafter abbreviated JK98) analyzed the effect of methane photooxidation on ozone production in the atmosphere. Extending the analysis of reaction sequences leading from CH<sub>4</sub> to CO<sub>2</sub> by *Crutzen* [1973], they formulated a general method to quantify the contribution of methane photochemistry to ozone production (called the sequence or SEQ method).

JK98 contrasted the SEQ method against the differential rate equation (DE) method which they defined based on the odd oxygen family concept ( $O_x = O_3 + O(^3P) + O(^1D) + NO_2$ ), referring to authors who had previously used this concept. They claimed that in the past the DE method has been used as a "scientifically incorrect method" to determine the contribution of methane chemistry to ozone production in the atmosphere. We fully agree that the DE method indeed is not suited for calculating the contribution of methane chemistry to chemical ozone production. However, we found that none of the relevant studies quoted by JK98 used the DE method to separate the contribution of methane oxidation from other chemical processes affecting ozone.

Thus the criticism by JK98 seems to arise from a misunderstanding: The odd oxygen family concept has indeed been used by various groups (including our own) to approximate the net chemical production of ozone, both for the sake of chemical integration as well as for budget analyses. However, at least from our side it was always well understood that the difference between gross production and loss of odd oxygen represents the overall net chemical production of ozone, rather than specifically the contribution from methane oxidation. Clearly, the differential rate equations describing gross production and loss are influenced by all photochemical processes affecting odd oxygen and not just by oxidation of CH<sub>4</sub>. In fact, as JK98 already indicated, even if CH<sub>4</sub> (as well as CO, H<sub>2</sub>, and nonmethane volatile organic compounds) were completely absent from the atmosphere, there would still be gross photochemical production and loss of ozone in the troposphere due to HO<sub>x</sub> and NO<sub>x</sub> chemistry initiated by ozone transported downward from the stratosphere.

We are most concerned that the nonspecialized reader may get the impression from the JK98 paper that in most models the chemical production of ozone, and therefore the whole ozone budget and concentration fields in the troposphere, have thus far been calculated incorrectly, although this was not the message intended by JK98 (personal communication with H. Johnston).

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We want to emphasize that there is no conceptual problem with determining net chemical ozone production as the difference between gross production and loss of odd oxygen, as long as the odd oxygen family concept is applied consistently. The model calculations presented below reconfirm that the net photochemical production of ozone in a CH<sub>4</sub>-O<sub>3</sub>-HO<sub>x</sub>-NO<sub>x</sub> system can be accurately determined by means of differential rate equations for gross production and loss of odd oxygen. The degree of accuracy depends on the relative magnitude of neglected minor terms in the differential rate equations.

The analysis of reaction sequences presented by JK98 is instructive in depicting how CH<sub>4</sub> oxidation influences ozone. However, it appears questionable whether the effect of CH<sub>4</sub> oxidation on atmospheric chemistry (i.e., the influence of one variable on the solution of a large set of coupled differential equations) can be quantified by closed algebraic expressions as given in the SEQ method. In fact, there are more direct ways to determine the contribution of methane to atmospheric chemistry and the ozone budget. The most obvious one is to take the difference between model results with and without CH<sub>4</sub>; alternatively, one can determine the effect of incremental CH<sub>4</sub> changes. We will present an example for each analysis method in this study and compare the results with the SEQ method.

We used a photochemical box model with a comprehensive representation of tropospheric CH<sub>4</sub>-O<sub>3</sub>-HO<sub>x</sub>-NO<sub>x</sub> gas phase chemistry (including 23 species and 48 chemical reactions with rate coefficients and photolysis frequencies based on *DeMore et al.* [1997], *Atkinson et al.* [1997] and *Brühl and Crutzen* [1989]). The differential equations describing the chemical kinetics of the system were solved with the accurate numerical solver FACSIMILE [*Malleson et al.*, 1990]. Heterogeneous reactions and the reactions of CH<sub>4</sub> with Cl and O(<sup>1</sup>D) atoms are neglected in our model calculations, which are focused on the troposphere. Since JK98 applied the SEQ method to analyze steady state model results, we also use steady state results in the following analyses to assure comparability.

The diurnally averaged steady state concentrations, as well as ozone/odd oxygen production and loss rates for a set of boundary layer scenarios, are shown in Table 1.  $T_n(O_3)$  represents the net change of ozone by nonchemical processes, which is the difference between the source term we included to represent advection of ozone,  $T_A(O_3)$ , and the loss term representing ozone deposition,  $T_D(O_3)$ . The net chemical production of odd oxygen,  $D(O_x)$ , was calculated as the difference between gross chemical production,  $P(O_x)$ , and gross chemical loss,  $L(O_x)$ , with the odd oxygen definition  $O_x = O_3 + O(^3P) + O(^1D) + NO_2$ . All 17 reactions affecting  $O_x$  in our model were considered in the calculation of the exact odd oxygen production and loss terms  $P(O_x)$ ,  $L(O_x)$ , and  $D(O_x)$ . In contrast, only the five major reaction rates were used to calculate the simplified terms  $P_{DE}(O_x)$ ,  $L_{DE}(O_x)$ , and  $D_{DE}(O_x)$ , by which JK98 defined the DE method:  $P_{DE}(O_x) = k_1[CH_3O_2][NO] +$

**Table 1.** Steady State Concentrations and Ozone/Odd Oxygen Budget Terms for Four Model Scenarios; the Base Case, Scenario 1, Approximates Midlatitude Summer Conditions in Unpolluted Boundary Layer Air Masses.

Scenario	1	2	3	4	$\Delta_{1-2}$	$\Delta_{1-3}$	$\Delta_{4-1}$
[CH <sub>4</sub> ]	1800	0	0	1890	1800	1800	90
[CO]	39	0	39	41	39	0	2
[H <sub>2</sub> ]	512	0	512	544	512	0	32
[O <sub>3</sub> ]	33	8	21	34	25	12	1
$T_A(O_3)$	6.00E+05	6.00E+05	6.00E+05	6.00E+05	0.00E+00	0.00E+00	0.00E+00
$T_D(O_3)$	1.68E+06	3.91E+05	1.07E+06	1.71E+06	1.29E+06	6.14E+05	2.92E+04
$T_M(O_3)$	-1.08E+06	2.09E+05	-4.71E+05	-1.11E+06	-1.29E+06	-6.14E+05	-2.92E+04
$P(O_x)$	3.16E+06	1.80E+05	1.60E+06	3.25E+06	2.98E+06	1.56E+06	9.06E+04
$L(O_x)$	2.08E+06	3.89E+05	1.13E+06	2.14E+06	1.69E+06	9.48E+05	6.14E+04
$D(O_x)$	1.08E+06	-2.09E+05	4.71E+05	1.11E+06	1.29E+06	6.14E+05	2.92E+04
$P_{DE}(O_x)$	2.00E+06	1.18E+05	1.04E+06	2.05E+06	1.89E+06	9.59E+05	4.65E+04
$L_{DE}(O_x)$	8.53E+05	2.74E+05	5.13E+05	8.70E+05	5.79E+05	3.40E+05	1.70E+04
$D_{DE}(O_x)$	1.15E+06	-1.56E+05	5.32E+05	1.18E+06	1.31E+06	6.20E+05	2.96E+04
$P_{SEQ}(O_3)$	2.02E+06	0.00E+00	9.68E+05	2.07E+06	2.02E+06	1.05E+06	5.20E+04
$L_{SEQ}(O_3)$	2.93E+05	0.00E+00	1.42E+05	3.07E+05	2.93E+05	1.51E+05	1.35E+04
$D_{SEQ}(O_3)$	1.72E+06	0.00E+00	8.27E+05	1.76E+06	1.72E+06	8.96E+05	3.85E+04

The concentrations are in units of nmol/mol, and the source/loss terms are in units of molecule cm<sup>-3</sup> s<sup>-1</sup>.

$k_2[HO_2][NO]$ ,  $L_{DE}(O_x) = k_3[O(^1D)][H_2O] + k_4[O_3][HO_2] + k_5[O_3][OH]$  and  $D_{DE}(O_x) = P_{DE}(O_x) - L_{DE}(O_x)$ . Here  $k_1$  to  $k_5$  stand for the respective reaction rate coefficients in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and the square brackets indicate concentrations in units of molecule cm<sup>-3</sup>. Gross production and loss as well as net production of ozone by the "methane smog process" as defined in the SEQ method,  $P_{SEQ}(O_3)$ ,  $L_{SEQ}(O_3)$ , and  $D_{SEQ}(O_3)$ , were calculated with the equations given by JK98.

Scenario 1 was chosen to simulate midlatitude summer conditions in unpolluted boundary layer air masses ( $P = 1$  atm,  $T = 288$  K, 1% H<sub>2</sub>O volume mixing ratio). CH<sub>4</sub> was kept constant at 1800 nmol/mol; advection of O<sub>3</sub> and advection/emission of NO were represented by source terms with the rates  $T_A(O_3) = 6 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup> and  $T_A(NO) = 6 \times 10^4$  molecule cm<sup>-3</sup> s<sup>-1</sup>, respectively. O<sub>3</sub> and HNO<sub>3</sub> deposition were represented by first-order loss terms with the rates  $T_D(O_3) = 2 \times 10^{-6} [O_3]$  and  $T_D(HNO_3) = 2 \times 10^{-5} [HNO_3]$ ; the deposition rate coefficients in units of s<sup>-1</sup> are based on *Ganzeveld and Lelieveld* [1995]. For simplicity, no CO sources other than CH<sub>4</sub> oxidation were included, which is the reason for the relatively low CO level (39 nmol/mol).

Since the data shown in Table 1 represent steady state conditions, the magnitude of net ozone change by nonchemical processes,  $T_M(O_3)$ , equals the actual net chemical production of ozone. The fact that  $D(O_x)$  equals  $-T_M(O_3)$  to within less than 1% shows that the difference between gross production and loss of odd oxygen is indeed a very good approximation for the net chemical production of ozone. Additional model runs under nonsteady state conditions gave similarly good agreement between the actual net chemical production of ozone and its approximation by the odd oxygen concept. On the other hand, for scenario 1 the simplified odd oxygen production term  $D_{DE}(O_x)$ , which considers only the five major reaction rates, deviates by ~6% from  $D(O_x)$ , which takes into account all reactions affecting O<sub>x</sub>. The deviation is due to the loss of NO<sub>2</sub> via HNO<sub>3</sub> formation and deposition, which is not considered in the DE budget terms. It illustrates that the neglect of minor terms in the odd oxygen family concept can lead to nonnegligible errors.

In scenario 2, CH<sub>4</sub> is set to zero, while all other conditions are the same as in scenario 1. The difference between scenarios 1 and

2 (column  $\Delta_{1-2}$  in Table 1) represents the effect of methane chemistry in scenario 1, in particular its contribution to ozone production. In this case the entire turnover of CO and H<sub>2</sub> oxidation is attributed to the "methane smog process" as proposed by JK98, since both species have no sources other than CH<sub>4</sub> oxidation in scenarios 1 and 2. The difference in net chemical ozone production,  $\Delta_{1-2}D(O_x) = -\Delta_{1-2}T_M(O_3) = 1.29 \times 10^6$  molecule cm<sup>-3</sup> s<sup>-1</sup>, represents the actual methane-related net chemical ozone production in scenario 1. The net ozone production term which the SEQ method attributes to methane,  $D_{SEQ,1}(O_3) = 1.72 \times 10^6$  molecule cm<sup>-3</sup> s<sup>-1</sup>, is clearly larger than  $\Delta_{1-2}D(O_x)$ .

In the real atmosphere, CO and H<sub>2</sub> have significant sources other than CH<sub>4</sub> oxidation, which implies that the actual atmospheric influence of methane on ozone is smaller than the difference between scenarios 1 and 2 suggests. This effect is illustrated by scenario 3 in which H<sub>2</sub> and CO are kept at the same level as in scenario 1 while [CH<sub>4</sub>] is set to zero. The difference between scenarios 1 and 3 (column  $\Delta_{1-3}$  in Table 1) reflects the influence of methane on ozone if the abundance of H<sub>2</sub> as well as of CO are determined by sources other than CH<sub>4</sub> oxidation. Again, the value obtained with the SEQ method,  $\Delta_{1-3}D_{SEQ}(O_3) = 8.98 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup>, is larger than the actual difference in net chemical ozone production,  $\Delta_{1-3}D(O_x) = -\Delta_{1-3}T_M(O_3) = 6.14 \times 10^5$  molecule cm<sup>-3</sup> s<sup>-1</sup>.

Scenario 4 equals scenario 1 except for a 5% increase of CH<sub>4</sub> from 1800 to 1890 nmol/mol. The difference between scenarios 4 and 1 (column  $\Delta_{4-1}$  in Table 1) divided by  $\Delta_{4-1}[CH_4] = 90$  nmol/mol reflects the incremental influence of methane: The actual increase of net chemical ozone production per nmol/mol of CH<sub>4</sub> added,  $\Delta_{4-1}D(O_x)/\Delta_{4-1}[CH_4] = -\Delta_{4-1}T_M(O_3)/\Delta_{4-1}[CH_4] = 324$  molecule cm<sup>-3</sup> s<sup>-1</sup> (nmol/mol)<sup>-1</sup>, is again exceeded by the value obtained with the SEQ method  $\Delta_{4-1}D_{SEQ}(O_3)/\Delta_{4-1}[CH_4] = 430$  molecule cm<sup>-3</sup> s<sup>-1</sup> (nmol/mol)<sup>-1</sup>.

The numbers given in Table 1 illustrate the contribution of methane oxidation to the ozone production in a well-defined CH<sub>4</sub>-O<sub>3</sub>-HO<sub>x</sub>-NO<sub>x</sub> reaction system approximating unpolluted boundary layer conditions; they are not meant to be representative for the ozone budget of the global troposphere. Nevertheless, the results confirm that the correct application of the odd oxygen

family concept allows the determination of net photochemical ozone production.

As mentioned before, the above model calculations were performed with the accurate numerical solver FACSIMILE, and the odd oxygen family concept was used in the budget analysis only. For most applications in large-scale models this numerical solver is prohibitively time- and storage-consuming. As a consequence, more approximate integration schemes based on family concepts are often used. In the application of such integration schemes it is advantageous to use further extended odd oxygen families (e.g.,  $O_x = O_3 + O(^3P) + O(^1D) + NO_2 + 2NO_3 + 3N_2O_5 + HNO_3 + HNO_4$ ). Thereby additional chemical flux terms which largely balance each other are implicitly removed from the gross production and loss terms, which helps to reduce numerical inaccuracies and possibly allows for longer time steps of integration. Note, however, that the application of the odd oxygen family concept in an integration scheme requires that the terms representing  $O_x$  species other than  $O_3$  are subtracted from the  $O_x$  term after each time step. Although this is generally a rather small correction, it can be significant in the vicinity of large sources of NO, particularly in models with high spatial resolution.

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