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ESTIMATES OF THE CHANGES IN TROPOSPHERIC CHEMISTRY WHICH RESULT FROM
HUMAN ACTIVITY AND THEIR DEPENDANCE ON NO_x EMISSIONS AND MODEL
RESOLUTION

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ABSTRACT

As a consequence of the non-linear behavior of the chemistry of the atmosphere and because of the short lifetime of nitrogen oxides (NO_x), two-dimensional models do not give an adequate description of the production and destruction rates of NO_x and their effects on the distributions of the concentration of ozone and hydroxyl radical.

In this study, we use a three-dimensional model to evaluate the contribution of increasing NO_x emissions from industrial activity and biomass burning to changes in the chemical composition of the troposphere. By comparing results obtained from longitudinally-uniform and longitudinally-varying emissions of NO_x, we demonstrate that the geographical representation of the NO_x emissions is crucial in simulating tropospheric chemistry.

1. INTRODUCTION

The impact of anthropogenic trace gas emissions on ozone (O₃) and hydroxyl radical (OH) concentrations and generally on the oxidizing efficiency of the troposphere is a matter of great concern. There have been many modeling efforts devoted to simulating tropospheric chemistry and examining trends in the atmospheric concentrations of important trace gases (e.g. Isaksen and Hov, 1987; Crutzen and Zimmermann, 1991). However, the ability of models to adequately account for non-linear chemical interactions affecting the distributions of nitrogen oxides (NO_x), O₃ and OH needs to be examined carefully.

In this study, we use a three-dimensional model to evaluate the contribution of increasing NO_x emissions from industrial activity and biomass burning to changes in the

chemical composition of the troposphere. By comparing results obtained from longitudinally-uniform and longitudinally-varying emissions of NO_x, we demonstrate that the geographical representation of the NO_x emissions is crucial in simulating tropospheric chemistry.

2. MODEL DESCRIPTION

The model used is a climatological three-dimensional global model of the troposphere with a 10° latitude x 10° longitude spatial resolution. It contains 10 vertical layers from the surface to 100 hPa. The model design is described in detail by Zimmermann et al. [1989] and Crutzen and Zimmermann [1991]. The parametrization of deep cumulus convection, which is of particular importance for short-lived tracers, is described by Feichter and Crutzen [1990]. In its current form, the model is coupled with a chemical scheme containing about 100 photochemical reactions describing the O₃ - OH - NO_x - CO - CH₄ - C₂H₆ - C₃H₈ chemistry. The transport of 20 species in the troposphere is considered, whereas transport processes are neglected for another 31 species which are assumed to be in photochemical steady-state [Kanakidou et al., 1991]. A time step of 2 hours is used.

In the present study downward fluxes of O₃ at 100 hPa that vary monthly and latitudinally are adopted totalling approximately 300 Tg-O₃/yr. Global NO_x emissions amount to 34 Tg-N/yr. Their adopted distribution is discussed later. We also adopted CO surface emissions that vary monthly (including indirect CO emissions by oxidation of the NMHC other than C₂H₆ and C₃H₈) totalling about 1700 Tg CO/yr. C₂H₆ and C₃H₈ emissions amount to 15 Tg-C₂H₆/yr and 17 Tg-C₃H₈/yr, respectively, and vary by longitude, latitude, and month. CH₄ volume mixing ratios at the lower boundary are assigned, according to observations (Steele et al., 1987). Other

features of upper and lower boundary conditions used in the model are described in Crutzen and Zimmermann [1991] and Kanakidou et al. [1992].

Case Studies.

We will concentrate on the impact of NO_x emissions from industry and biomass burning on the oxidizing efficiency of the atmosphere. We will then evaluate uncertainties in the computed concentrations of OH radicals and in the net chemical production of O_3 related to the distribution of NO_x emissions.

For this purpose, 5 different scenarios of longitudinally and latitudinally varying NO_x emissions have been considered: In the base case, NO_x industrial emissions of 20 Tg N/yr are distributed proportional to the industrial CO_2 emissions [Marland and Rotty, 1984] and when possible readjusted to fit the NO_x emission data published by World Resources Institute [1990]. Tropical NO_x emissions of 6 Tg N/yr from biomass burning are spatially distributed according to the analysis of Hao et al. [1990]. These emissions occur mainly during the dry season in the tropics and subtropics. NO_x emissions from lightning totalling 5 Tg N/yr were varied spatially and temporally and are based on flash frequency observations [Turman and Edgar, 1982]. Another 4 Tg N/yr released by soils are distributed as a function of soil productivity [Crutzen and Zimmermann, 1991]. In the other 4 cases, we adopted the emissions of NO_x from industry and biomass burning shown in Table 1. The NO_x emissions by lightning and by soils are the same as in the base case.

3. RESULTS AND DISCUSSION

Changes in the chemical composition of the atmosphere due to increasing NO_x emissions from industry and biomass burning.

The chemical production and destruction of O_3 in the troposphere and the global tropospheric annual mean diurnal-average OH concentration computed for each of the 5 case studies are presented in Table 1.

Focusing on the chemical production and destruction of O_3 in the troposphere computed when NO_x emissions by industry are neglected and those computed for the present day, we can derive that 26% of the present day net chemical production of O_3 (664 Tg- O_3 /yr) in the troposphere could be due to NO_x emissions by industrial activity. This is the net result of increasing both chemical production (+17%) and chemical destruction of O_3 (+14%) when NO_x emissions are increasing (from 0 to 20 Tg-N/yr).

Table 1. Adopted global NO_x emissions by industry (E_I) and biomass burning (E_B) (in Tg N/yr). Chemical production (PO_3), chemical destruction (DO_3) and net chemical production ($\text{PO}_3 - \text{DO}_3$) of O_3 in the troposphere (in Tg O_3 /yr) and global tropospheric annual mean diurnal average OH concentration (in 10^6 cm^{-3}).

E_I	E_B	PO_3	DO_3	$\text{PO}_3 - \text{DO}_3$	OH
20	6	3013	2349	664	0.83
0	6	2511	2020	491	0.72
20	0	2837	2222	615	0.76
40	6	3275	2518	757	0.89
20	12	3113	2405	708	0.85

The difference in the net chemical production of O_3 calculated without consideration of NO_x emissions by biomass burning (615 Tg- O_3 /yr) from that calculated for the base case (644 Tg- O_3 /yr) shows that only about 5% could be due to emissions by biomass burning. Similarly, NO_x industrial emissions may explain up to 13% of the changes in the global tropospheric mean OH concentration whereas the impact of biomass burning NO_x emissions on this OH concentration reaches 8%. Note however that in this study we do not take into account changes in the emissions of NMHC and CO or the concentrations of CH_4 .

Doubled industrial emissions of NO_x will perturb the OH global mean value by only 7% ($0.89 \cdot 10^6 \text{ cm}^{-3}$ instead of $0.83 \cdot 10^6 \text{ cm}^{-3}$ in the base case) and the O_3 net chemical production by about 14% (757 Tg- O_3 /yr compared to 664 Tg- O_3 /yr). This percent change is about half the present day effect of NO_x emissions by industry on the net chemical production of O_3 , which as above mentioned, is 26%. This clearly demonstrates that the effect of NO_x emissions on tropospheric chemistry is not directly proportional to the amount of NO_x emitted into the atmosphere.

Doubled NO_x emissions from industry or biomass burning do not imply a double impact of NO_x on tropospheric chemistry. These calculations suggest that the changes in the chemical composition of the atmosphere are not linearly related to the changes in NO_x emissions.

Differences between results obtained with longitudinally-uniform and varying emissions of NO_x .

Kanakidou and Crutzen [1992] demonstrated by running a three-dimensional model both with longitudinally-uniform (2-D) and varying (3-D) NO_x and NMHC input rates that the use of varying input rates leads to significantly lower O_3 and OH concentrations.

Here we examine the differences between results computed with "2-D" distribution of NO_x emissions and those computed with "3-D" distribution of NO_x emissions and in addition to the earlier study we discuss the dependence of these differences on the amount of NO_x emitted by industry and by biomass burning. We produced a second series of 5 simulations using a longitudinally-uniform distribution of NO_x emissions summing up at each latitude to those used in the previous cases, respectively. This second series of simulations should reproduce the main features of the results which are obtained with two-dimensional models. A direct comparison between two-dimensional and three-dimensional models is not strictly possible because of non-equivalent transport formulation.

We compare the results obtained with longitudinally-uniform NO_x emissions to those obtained with longitudinally-varying NO_x emissions. In Table 2 we report the percent differences for the 5 studied scenarios of NO_x emissions from industry and biomass burning.

Table 2. Differences (in percent) between values computed with longitudinally-uniform (2-D) and those computed with longitudinally-varying (3-D) NO_x emissions ($[2\text{-D} - 3\text{-D}] / 3\text{-D} \times 100$) for the 5 scenarios of NO_x emissions by industry (E_I) and by biomass burning (E_B).

E_I	E_B	% in the O_3 net chem. production	% in the OH global annual mean
a. Industrial emission scenarios *			
0	6	16	16
20	6	16	14
40	6	16	14
b. Biomass burning emission scenarios **			
20	0	13	12
20	6	16	14
20	12	18	17

* in increasing order of industrial emissions of NO_x .

** in increasing order of biomass burning emissions of NO_x .

The results of this comparison agree well with the earlier study by Kanakidou and Crutzen, [1992] and the reader is referred to this paper for further information regarding the spatial and temporal variation of the computed differences in O_3 , NO_x and OH concentrations.

We focus here on the dependence of the degree of non-linearity (i.e. of the computed differences between "2-D" and "3-D" global tropospheric amounts) on the amount of NO_x emitted in the atmosphere. As shown in Table 2, increasing emissions of NO_x by biomass burning lead to an increase in the differences between the computed "2-D" and "3-D" O_3 net chemical production and OH global tropospheric mean concentration. This is not the case for increasing NO_x emissions from industry mainly in the northern hemisphere where zonal mixing by the winds is more effective than at the equator. The strong dependence of the computed results on the strength of the NO_x source in the tropics is probably due to the relatively small zonal mixing by the winds, implying that the assumption of longitudinally-uniform emissions of NO_x leads to large inaccuracies in the computed O_3 and OH concentrations in this region.

Furthermore, the difference between the results computed with longitudinally uniform and those computed with longitudinally varying emissions depend also on the adopted CO levels. For instance, a preliminary test of sensitivity of these differences to CO emissions shows that a reduction on the surface CO emissions by a factor of 3 (to about 500 Tg/yr instead of about 1700 Tg/yr adopted in this study) leads to a higher degree of non-linear dependence of the net chemical production of O_3 on NO_x emissions (up to 23% compared to 18%) but simultaneously to smaller differences between the 2-D and 3-D computed OH concentrations (9% to 12%).

4. CONCLUDING REMARKS

These results clearly show that O_3 and OH concentrations computed with longitudinally-uniform emissions of NO_x are higher than those computed with longitudinally-varying emissions. However, the relationship between the overestimation of the computed O_3 and OH concentrations and the adopted distribution and strength of the NO_x atmospheric sources is not straightforward. Thus, the accuracy in NO_x emissions data is crucial to simulating changes in tropospheric chemistry resulting from human activity.

REFERENCES

- Crutzen P. J., 1988: Tropospheric Ozone: An overview, in Tropospheric Ozone, I. S. A. Isaksen (ed.), D. Reidel Publ., 3-32.
- Crutzen P. J., and P. H. Zimmermann, 1991: The changing photochemistry of the troposphere, Tellus, **43AB**, 136-151.
- Feichter J., and P. J. Crutzen, 1990: Parametrization of vertical tracer transport due to deep cumulus convection in a global transport model and its evaluation with ²²²Rn measurements, Tellus, **42B**, 100-117.
- Hao W.M., M. H. Liu, and P. J. Crutzen, 1990: Estimates of annual and regional releases of CO₂ and other trace gases to the atmosphere from fires in the tropics, based on the FAO statistics for the period 1979-1980, in Fire in the tropical Biota, edited by J. G. Goldammer, Springer-Verlag, New York, pp. 440-462.
- Houghton, J. T., G.F. Jenkins, and J. J. Ephraums (eds), 1990: Report of Working Group, Intergovernmental Panel on Climate Change (IPCC), WMO/UNEP, New York.
- Isaksen I. S. A. , and O. Hov, 1987: Calculations of trends in the tropospheric concentrations of O₃, OH, CO, CH₄, and NO_x, Tellus, **39 B**, 271-285.
- Kanakidou M., H. B. Singh, K. M. Valentin, and P. J. Crutzen, 1991: A two-dimensional study of ethane and propane oxidation in the troposphere, J. Geophys. Res., **96**, 15,395 - 15,413.
- Kanakidou M., P. J. Crutzen, P. H. Zimmermann, and B. Bonsang, 1992: A 3-dimensional global study of the photochemistry of ethane and propane in the troposphere: Production and transport of organic nitrogen compounds, Proceeding of the NATO/CCMS 19th ITM on Air Pollution Modelling and its Application, Ierapetra, Greece, 29 Sep. - 4 Oct., H. van Doop Editor, in press.
- Kanakidou M., and P. J. Crutzen, 1992: Scale problems in global tropospheric chemistry modeling: Comparison of results obtained with a three-dimensional model, adopting longitudinally uniform and varying emissions of NO_x and NMHC, Chemosphere, in press.
- Lin X., M. Trainer, and S. C. Liu, 1988: On the nonlinearity of the tropospheric ozone production, J. Geophys. Res., **93**, 15,789-15,888.
- Marland G., and Rotty R. M., 1984: Carbon dioxide emission from fossil fuels: A procedure for estimation and results for 1950-1982, Tellus, **36B**, 232-261.
- Steele L. P., P. J. Fraser, R. A. Rasmussen, M. A. K. Khalil, T. J. Conway, A. J. Crawford, R. H. Gammon, K. A. Masarie, and K. W. Thoning, 1987: The global distribution of methane in the troposphere, J. Atmos. Chem., **5**, 125-171.
- Turman B. N., and B. C. Edgar, 1982: Global lightning distribution at dawn and dusk, J. Geophys. Res., **87**, 1191-1206.
- Zimmermann P. H., J. Feichter, H. K. Rath, P. J. Crutzen, and W. Weiss, 1989: A global three-dimensional source receptor model investigation using ⁸⁵Kr, Atmos. Environ., **23**, 25-35.