

# Combined Effects of Anthropogenic Emissions and Resultant Climatic Changes on Atmospheric OH

Chien Wang and Ronald G. Prinn\*

The hydroxyl radical (OH), which has an average atmospheric concentration of  $10^6$  radicals/cm<sup>3</sup> and a very short lifetime,<sup>1</sup> is arguably the most important free radical in the troposphere. It is the primary removal mechanism for most gases entering the atmosphere, and therefore, determines the lifetimes of these species. Tropospheric OH is formed by H<sub>2</sub>O (water vapor) reacting with O (<sup>1</sup>D) produced by ozone photo-dissociation, and by NO (nitric oxide) reacting with the hydroperoxy radical (HO<sub>2</sub>). Major OH sinks include reactions with CO, CH<sub>4</sub>, and several other hydrocarbons.<sup>2</sup> Climatic changes affecting the water vapor concentration, anthropogenic emissions of CO, NO, and hydrocarbons, and changes in the fluxes of solar ultraviolet radiation entering the troposphere therefore can all affect OH radical concentrations. Anthropogenic emissions of CH<sub>4</sub>, NO, and CO have increased since the Industrial Revolution, and estimates indicate, these trends will continue in the future.<sup>3,4</sup> The possibility of changes in global OH concentrations due to increased emissions and variations in climate is therefore an important issue in atmospheric chemistry and global climate studies.

We have developed a coupled global atmospheric chemistry and climate model to better assess science and policy issues related to global change.<sup>5</sup> Using this model we have predicted the evolution of tropospheric concentrations of OH and other species along with climate parameters, based on a set of economic model predictions for anthropogenic emissions of chemically and radiatively important trace gases in the next 120 years.<sup>6</sup> These predictions for

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\* Corresponding author: Dr. Chien Wang, MIT E40-269, Cambridge, MA 02139, e-mail: wangc@mit.edu. Submitted to *Nature*, April 1998.

<sup>1</sup> Levy, H., 1971, *Science*, **173**, 141; Prinn, R.G. *et al.*, 1995, *Science*, **269**, 187-192.

<sup>2</sup> Sze, N.D., 1977, *Science*, **195**, 673-675; Crutzen, P.J., and P.H. Zimmermann, 1991, *Tellus*, **43AB**, 136-151; Derwent, R.G., 1996, *Phil. Trans. R. Soc. Lond. A*, **354**, 501-531.

<sup>3</sup> The Intergovernmental Panel on Climate Change (IPCC), 1994, *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, Cambridge Univ. Press, Cambridge, UK.

<sup>4</sup> Prinn, R.G. *et al.*, 1998, Integrated Global System Model for Climate Policy Assessment: Feedbacks and Sensitivity Studies, *Climatic Change* (in press).

<sup>5</sup> Wang, C., R.G. Prinn and A. Sokolov, 1998, *J. Geophys. Res.*, **103**, 3399-3417; Sokolov, A., and P.H. Stone, 1998, A Flexible Climate Model for use in Integrated Assessments, MIT Joint Program on the Science and Policy of Global Change *Report No. 17*, and *Climate Dynamics* (in press).

<sup>6</sup> Emissions of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CO, NO, and SO<sub>2</sub> are included in this model. Except for the chlorofluorocarbons, all emissions are divided into natural and anthropogenic components that are both functions of latitude and include many sub-categories. We treat total annual natural emissions as a constant with time in the present simulation. The annual natural emissions of CH<sub>4</sub>, N<sub>2</sub>O, CO, NO (without lightning), and sulfur are 130 Tg (CH<sub>4</sub>), 9.1 Tg (N), 158.6 Tg (C), 10 Tg (N), and 12.8 Tg (S), respectively. Production of NO by lightning is assumed to be 5 Tg (N). The annual amounts (*continued*)

tropospheric OH concentrations indicate the potential for substantial future changes affecting both atmospheric chemistry and climate.

## Design of Model and Numerical Experiments

In this study we use a global atmospheric chemistry model interactively coupled with a climate model.<sup>4</sup> It is two-dimensional with 24 latitude bands and nine pressure levels (two in the stratosphere, seven in the troposphere), with time steps of 20 minutes for climate dynamics and transport of chemicals and 3 hours for gaseous phase chemistry. The chemistry model contains 25 chemical species, including CO<sub>2</sub>, CH<sub>4</sub>, chlorofluorocarbons, N<sub>2</sub>O, CO, O<sub>3</sub>, NO<sub>x</sub>, HO<sub>x</sub>, SO<sub>2</sub>, and sulfuric acid, and 41 gas-phase and 12 heterogeneous reactions. These chemical processes, along with emissions, dry and wet deposition, transport by winds, mixing, and convection, serve as local sinks or sources of various chemical species in the atmosphere. The climate model provides wind speeds, air pressure, temperature, precipitation, convection parameters, and radiative fluxes at each model grid point and every time step for the chemistry model. Concentrations of CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, chlorofluorocarbons, and sulfate aerosols predicted by the chemistry model, in turn, are used in the climate model to calculate atmospheric radiative fluxes.

To illustrate a range of plausible OH predictions and interactive features involving emissions, chemistry, and climate related to OH, we conducted nine experiments using three separate emission predictions from an economic model,<sup>6</sup> in combination with three selected sets of chemistry and climate model assumptions.<sup>7</sup> The emission predictions and model assumptions are labeled high (H), reference (R), or low (L), according to their predicted effects on Earth's surface temperature in the year 2100. In order to investigate the effects of including the chemistry-climate interaction, we also carried out three additional runs using high, reference, and low emissions but using the 1990 values of radiative forcing in all years beyond 1990 (designated "no-forcing" (NF) runs). Note the changing atmospheric

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(continued) ...of anthropogenic emissions changed with time. For CO, NO, and SO<sub>2</sub>, their latitudinal distributions of emissions are also functions of time in the model. Three anthropogenic emission sets, representing plausible high, reference and low predictions, used in this study are from runs of the MIT Emission Prediction and Policy Analysis (EPPA) Model (see Prinn, R.G. *et al.*, 1998, *ibid.*, and Yang, Z. *et al.*, 1996, MIT Joint Program on the Science and Policy of Global Change *Report No. 24*). The integrated emissions from 1977 to 2100 in the high, reference and low cases are 1912, 1654, and 1368 Pg (C) respectively for CO<sub>2</sub>, 110, 105, and 100 Pg for CH<sub>4</sub>, and 98, 97, and 96 Pg (C) for CO.

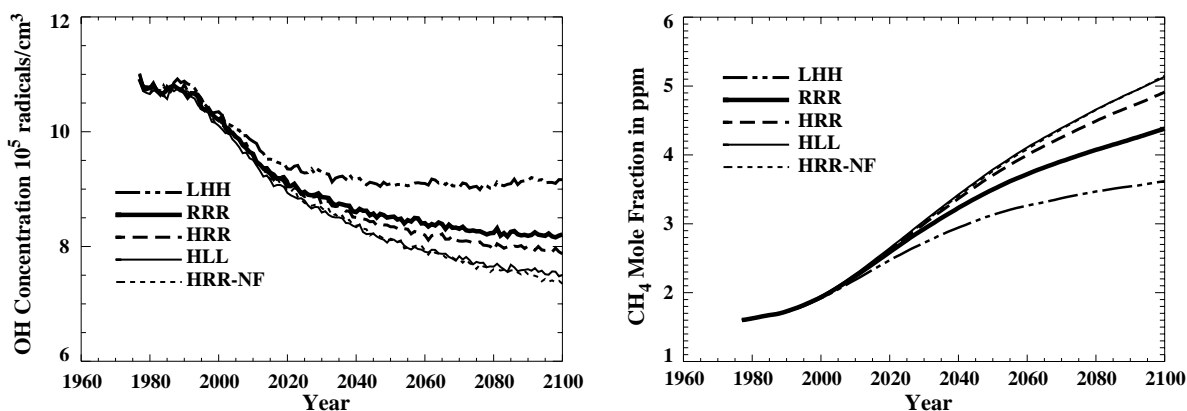
<sup>7</sup> See Prinn, R.G. *et al.*, 1998, *ibid.* Specifically, we made three plausible assumptions concerning: (A) the intensity of aerosol radiative forcing (including both direct and indirect effects) along with (B) the speed of oceanic uptake of CO<sub>2</sub> and heat; and (C) the sensitivity of the climate model to doubling of CO<sub>2</sub> in an equilibrium run. The aerosol radiative forcing per unit aerosol mass in the high and low cases is 200% and 50% respectively of its value in the reference case. Oceanic vertical diffusion coefficients for heat and CO<sub>2</sub> are five times larger or smaller than their reference value for fast or slow oceanic uptake, respectively. The climate model sensitivity is 3.5 °C for the high, 2.5 °C for the reference, and 2.0 °C for the low case.

concentrations of chemicals in these runs are predicted using the same methods as in the above nine runs.

### Predicted Trend of Tropospheric OH Concentration in the 21<sup>st</sup> Century

Our nine simulations show that the tropospheric-mean OH concentration may decrease 16.5-31.1% from its current level by the year 2100. In our reference run, the tropospheric-mean OH concentration started from  $10.9 \times 10^5$  radicals/cm<sup>3</sup> in 1977 and decreased to  $8.2 \times 10^5$  radicals/cm<sup>3</sup> in 2100. The sharpest decline is predicted between the years 2000 and 2040 (Figure 1, left panel).

The increase of atmospheric CH<sub>4</sub> predicted for the next century (Figure 1, right panel) is found to be mainly responsible for the predicted decline in tropospheric OH concentration. Our analyses show that the ratio of photochemical destruction of CO molecules in the troposphere to that of CH<sub>4</sub> molecules (both are mainly destroyed by reaction with OH) falls from its current value of 2.6 to 2.1 near the end of the next century. The global rate of CH<sub>4</sub> photochemical destruction is also found to be significantly higher in the year 2100 than currently. Observational data for various gases, including CO, CH<sub>4</sub>, and O<sub>3</sub>, from stations at different latitudes have been used to evaluate the model's performance.<sup>5</sup> These evaluations show that model-simulated surface concentrations and trends of these gases since the late 1970s and through to the early 1990s fairly closely approximate zonal-average observations, thus providing some confidence in the model predictions for the future.



**Figure 1.** Annually averaged and tropospheric-mean values of the concentrations of OH radicals (right panel,  $10^5$  radical/cm<sup>3</sup>) and mole fractions of CH<sub>4</sub> (left panel, ppm) predicted by the model. The results are from five selected runs from the full set of 12 (Table 1): the LHH and HLL runs that give the highest and lowest OH concentrations, respectively, at 2100 among the “forced” runs; the reference run RRR; and the run HRR-NF that predicts the largest OH depletion among the three “no-forcing” runs and its corresponding “forced” run HRR.

## **Tropospheric OH Concentrations and CH<sub>4</sub> and CO Emissions**

Results from numerical experiments using various emission predictions with the same chemistry-climate model parameters are used to identify the impact of emissions on future trends in tropospheric OH concentrations (Table 1, Groups A, B, and C). Higher emissions for the various gases (including CH<sub>4</sub> and CO) lead to lower tropospheric OH concentrations for the same climate model settings. For example, in runs at the reference climate model settings, the predicted 124-year-average (from 1977 to 2100) tropospheric OH concentrations for the high, reference, and low emission predictions are  $8.96$ ,  $9.06$ , and  $9.22 \times 10^5$  radicals/cm<sup>3</sup>, respectively. The tropospheric-mean OH concentrations at the end of the runs (*i.e.*, December 2100) for these three scenarios are  $7.87$ ,  $8.16$ , and  $8.27 \times 10^5$  radicals/cm<sup>3</sup>, when runs are started from the same level in 1977. Note that higher emissions lead to a warmer climate and higher water vapor concentrations which along with higher NO<sub>x</sub> concentrations that favor an increase of OH concentrations. This partially offsets the OH depletion due to the rising CH<sub>4</sub> and CO levels. The contribution of the climate change to this offset is quantified by comparing these “no-forcing” runs (Table 1, Group D) with the corresponding “forced” runs (Table 1, Group B). This comparison shows that the increased water-vapor concentrations associated with a climate warming offset about 14 to 17% of the emission-induced reductions in OH concentration. The Group B to D comparison also shows that whether we consider the two-way interaction of chemistry and climate or not, the model gives similar differences in the OH depletion among runs with different emissions. Specifically, the climate effects on the OH concentrations among the runs with different emissions but the same climate model settings do not differ enough to offset the differences generated by the CH<sub>4</sub> and CO emissions.

## **Tropospheric OH Concentrations and Climate Change**

Comparing results from sensitivity tests using the same emission scenario but different chemistry-climate model settings, we find that a warm climate leads to high OH concentrations due to increases in atmospheric water vapor (Table 1, Groups E, F, and G). For example, in tests using the reference emission scenario, the 124-year-averaged OH concentrations in the troposphere for high, reference, and low climate warming cases are  $9.42$ ,  $9.06$ , and  $8.86 \times 10^5$  radical/cm<sup>3</sup>, respectively. The difference between the high and low cases is about 6%—about twice the difference seen in the above emission sensitivity runs (3%). This result indicates that changes in various chemistry-climate model parameters modify the rate of decrease OH in the troposphere even more than changes in emission scenarios, over the investigated parameter ranges.

**Table 1. Relative changes of selected variables<sup>†</sup>**

Test Set	Test	R(OH)	R(T <sub>s</sub> )	R(CO)	R(CH <sub>4</sub> )	R(LCH <sub>4</sub> )	R(H <sub>2</sub> O)
A	HHH	-20.7	37.4	102.9	180.5	123.9	33.4
	RHH	-19.3	31.3	89.2	152.8	105.5	27.4
	LHH	-16.5	27.5	73.2	125.7	89.6	23.6
B	HRR	-28.5	20.0	124.7	206.5	119.7	14.9
	RRR	-24.9	19.2	103.6	173.2	105.6	15.3
	LRR	-23.0	16.2	87.1	142.7	88.6	12.0
C	HLL	-31.1	12.2	133.0	220.3	120.3	7.6
	RLL	-29.1	10.5	114.5	185.3	103.5	6.7
	LLL	-25.7	10.0	93.5	152.2	89.9	6.7
D	HRR-NF	-32.6	0.1	135.6	221.3	119.3	0.4
	RRR-NF	-30.0	-0.4	115.5	186.4	102.9	0.2
	LRR-NF	-26.8	0.2	96.0	152.5	87.4	0.7
E	HHH	-20.7	37.4	102.9	180.5	123.9	33.4
	HRR	-28.5	20.0	124.7	206.5	119.7	14.9
	HLL	-31.1	12.2	133.0	220.3	120.3	7.6
F	RHH	-19.3	31.3	89.2	152.8	105.5	27.4
	RRR	-24.9	19.2	103.6	173.2	105.6	15.3
	RLL	-29.1	10.5	114.5	185.3	103.5	6.7
G	LHH	-16.5	27.5	73.2	125.7	89.6	23.6
	LRR	-23.0	16.2	87.1	142.7	88.6	12.0
	LLL	-25.7	10.0	93.5	152.2	89.9	6.7

<sup>†</sup> Relative change of a given variable  $x$  is defined as  $R(x) = (x_{2100} - x_{1977})/x_{1977} \times 100\%$ . Here  $x_{1977}$  and  $x_{2100}$  represents the value of  $x$  at year 1977 and year 2100, respectively. Results from 12 tests are listed in this table. Groups A, B, and C are designed to show the impact of different emission scenarios. Results are then rearranged into groups E, F, and G to show the impact of climate variations on the relative changes of these variables. Group D lists results from three “no-forcing” runs (denoted by “NF”) where the radiative forcing beyond 1990 in the climate model is kept constant at 1990 levels. We use three characters (*e.g.*, HRR) to label a test as listed in the Test column: the first character represents the emission level, the second the combination of the rate of oceanic uptake of heat and CO<sub>2</sub> and the aerosol forcing intensity, and the third the sensitivity of the climate model. H denotes the high, R the reference, and L the low case. For the second and the third characters, H and L denote choices leading to higher or lower temperature changes from 1977 to 2100 compared to the reference (R) choice. Here OH represents the tropospheric average concentration of OH in 10<sup>5</sup> radicals/cm<sup>3</sup>, T<sub>s</sub> the global-mean surface temperature, CO and CH<sub>4</sub> the tropospheric mole fraction of CO (ppb) and CH<sub>4</sub> (ppm), respectively, LCH<sub>4</sub> the annual photochemical loss rate of CH<sub>4</sub> (Tg/year), and H<sub>2</sub>O the tropospheric average concentration of water vapor in g/kg.

## Summary and Conclusions

Our research indicates that if CH<sub>4</sub> and CO emissions continually increase as expected through the next century, the tropospheric concentration of OH could decrease by as much as 29% from its current value. As a result, the lifetime of CO in the year 2100 is predicted to lengthen by 0.6 months beyond its current value of 2 months, and the CH<sub>4</sub> lifetime in 2100 would exceed its current value (9 years) by 2.5 years in the reference (RRR) case.

Although the higher water-vapor concentrations associated with a warmer climate help offset a certain amount (about 14 to 17% according to this research) of emission-induced reductions in OH concentration, none of the predicted climate changes prevent the predicted reduction in tropospheric OH concentrations and related increases in CO and CH<sub>4</sub> lifetimes. Our research indicates that sustaining OH at current levels will require a cessation or reversal of the predicted trends of increasing emissions of CO and especially CH<sub>4</sub> in the future.

Quantitative differences between this work and earlier work<sup>2</sup> exist, due to the more comprehensive approach including economic and climatic predictions used in this research. Our results indicate that effects on OH of the increase of CH<sub>4</sub> emissions, based on the prediction of the economic development model,<sup>6</sup> are more substantial than those caused by the increase of CO emissions. Consequently, lowering the future emissions of CH<sub>4</sub> is more important for limiting future depletion of tropospheric OH than lowering the emissions of CO. Future emissions of CH<sub>4</sub> are thus very important to both climate change and tropospheric chemistry change (represented by the OH concentrations).