Perturbation to global tropospheric oxidizing capacity due to latitudinal redistribution of surface sources of NO\textsubscript{x}, CH\textsubscript{4} and CO

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Abstract. Economic and social projections indicate that during next several decades there will be major geographical redistribution of surface emissions of O\textsubscript{3} precursors, such as NO\textsubscript{x}, CH\textsubscript{4} and CO. A net decrease in their emissions from northern hemispheric mid-latitudes will be accompanied by substantial increases from the tropics. We have investigated a hypothetical scenario of currently underway transition of such emission patterns using a global two-dimensional photochemical model. With overall O\textsubscript{3} precursor releases held constant, a simultaneous transfer of their emissions by 25% from the latitude belt 75\textdegree{N}-35\textdegree{N} to 5\textdegree{S}-35\textdegree{N} increases tropospheric oxidizing capacity such that the methane global lifetime and concentrations fall by more than 3%. Seasonally dependent changes in surface O\textsubscript{3} concentrations are also calculated. In influencing OH concentration, redistribution of surface NO\textsubscript{x} emissions is 2-3 orders of magnitude more efficient per unit mass than CO emissions. Shifts in methane sources have insignificant effects on global photochemistry, but lead to a decrease in its interhemispheric gradient.

Introduction

Since the beginning of the industrial era, human activities have been influencing the global atmosphere, causing shifts from its natural state. Current projections of socio-economic indicators [Population Reference Bureau, 1997; World Resources 1996-97; Hargreaves et al., 1994] suggest that the developed countries (which we refer to as the North) are entering into an era of social and economic stability while the developing countries (here the South) are in the process of sustaining or even enhancing their industrial and urban growths. These disparities in demographic and economic change are imposing geographically variable human impacts on the global environment through the emissions of air pollutants.

In the future, major redistribution of human-related emissions of NO\textsubscript{x} (defined as NO\textsubscript{2}+NO), hydrocarbons and CO are all likely. A net decrease is predicted from the North accompanied by an increase in emissions from the South [World Energy Council, 1993; EPA, 1995; OECD, 1995; EMEP, 1997]. This redistribution may be accompanied by a net increase in the global source strength for each of these pollutants [Gaedel and Crutzen, 1991; Alcamo et al., 1994; Lee et al., 1997]. Some developed countries are already reducing their CO and NO\textsubscript{x} emissions by as much as 15% [World Resources 1996-97]. Qualitatively similar to trends in SO\textsubscript{2} emissions and concentrations in the Eastern United States [Husain et al., 1998], OECD [1995] has reported decreases in NO\textsubscript{x} concentration over several European countries and the United States. Note also that in Eastern Europe, changes in political system accompanied by shifts in industrial management from governments to the private sector are already resulting in a control on the emissions of air pollutants from the NH mid- and high latitudes [Benkovitz et al., 1996; Schoonover et al., 1997]. On the other hand, for 1980-1987, Kato and Akimoto [1992] estimated a 35-55% increase in NO\textsubscript{x} emissions from developing Asian countries. Dignon and Hameed [1989] calculated that between 1970-1980, more than 50% of the increase in global NO\textsubscript{x} emissions originated in Asia with only 9% and 18% coming from North America and Europe respectively. A case study referenced to 1990 by World Energy Council [1993] projects that by the year 2020 there will be a 13% increase in global surface NO\textsubscript{x} emissions accompanied by a net decline of 36% from the North and an increase of 80% from the South. For South Asian and Pacific regions, the estimated increases in NO\textsubscript{x} emissions are 118% and 60% respectively. With reference to 1990, EPA [1995] and EMEP [1997] expect significant decreases in surface emissions of NO\textsubscript{x} and CO from the North.

The global tropospheric photochemical tendency is quite inhomogeneous in space and time. Redistribution of surface sources of NO\textsubscript{x}, CH\textsubscript{4} and CO emissions will lead to variable trends in surface O\textsubscript{3} mixing ratios. For example, slowdown in its growth rate over NH high latitudes and Europe [Oltmans et al., 1998], and increase in its growth from Asian regions [Lee et al., 1998]. Similar variable trends are also expected in OH radical concentration. Much of the effort of photochemical modelers has been devoted to study the effects of uniformly increased or decreased global/regional emissions of air pollutants on the chemical balance of the troposphere. In this paper, we study the changes in tropospheric chemistry implied by the geographical redistribution in surface emissions of NO\textsubscript{x}, CH\textsubscript{4} and CO with their global source strengths fixed.

Simulations and Model Description

For the present study, we consider 25% decreases in surface emissions of NO\textsubscript{x}, CH\textsubscript{4} and CO from the developed countries (considered to be located between 35\textdegree{N}-75\textdegree{N}) and...
simultaneous increases in their emissions from the NH developing countries (considered to be located between 35°N-5°S) by the same absolute amounts for which they were reduced from the developed countries. This scenario allows geographical redistribution in surface emissions of NOx, CH4 and CO but leaves their global source strengths unchanged. To study the non-linearity in the chemical system induced by this scenario, multiple variations were introduced in the surface emissions of NOx, CH4 and CO. To examine the relative partial effects of adjustment in individual sources of NOx, CH4 and CO on the tropospheric oxidizing capacity, individual model simulations altered emissions for each of these species separately. In the future, global surface emissions of NOx, CH4 and CO may in fact increase. In the present study, this possibility is set aside. Moreover, we realize that the future changes in geographical emission patterns may or may not be the same for all three air pollutants.

All calculations were made using a modified version of the Oslo two-dimensional (altitude/latitude) global tropospheric photochemical model. This model has a horizontal resolution of 10° and extends from surface to 24.5 km with a vertical spacing of 0.5 km. Both advective and diffusive coefficients are derived from the GFDL GCM [Plumb and Mahlman, 1987]. The treatment for convective transport is based on the scheme of Langner et al. [1990]. The transport features have been tested with observed distributions and trends of CFC-11, CFC-12 and 85Kr. The photochemical scheme accounts for complete oxidation of most of the hydrocarbons containing up to 3 carbon atoms. In the model, the annual surface source strengths for NOx, CH4 and CO are 37 Tg of NOx as N, 500 Tg of CH4 and 1280 Tg of CO respectively. North to south ratios of their corresponding surface emissions are 4.2, 2.1 and 2.6 respectively. More details of their distinct latitudinal emission distributions are given in Gupta [1996] and Gupta et al. [1998]. For the reference case, the model latitude belts (75°N-35°N) and (35°N-5°S) account for 149 Tg of CH4, 484 Tg of CO, 20 Tg of NOx as N and 207 Tg of CH4, 491 Tg of CO, 12 Tg of NOx as N respectively. For 25% adjustment, about 5, 37 and 121 Tg of surface emissions of NOx, CH4 and CO respectively were assumed to have shifted from (75°N-35°N) to (35°N-5°S). The model was typically allowed to simulate for at least four decades so as to attain steady state concentrations of CH4 throughout the domain. In this paper, our analysis will concentrate on relative chemical changes brought by the redistribution of surface emissions of NOx, CH4 and CO. For steady state distributions of reactive species corresponding to the reference simulation, see Gupta [1996]. Simulations corresponding to the 25% shift of emissions of all three species combined and NOx, CH4 and CO individually are termed as ALL, NOX, CH4 and CO respectively.

Results and Discussion

Emissions of the air pollutants such as NOx, hydrocarbons and CO from the developing countries, which are mostly confined to tropical latitudes, very effectively perturb the global atmospheric chemical balance for two primary reasons. First, tropical regions experience year-round intensive photochemical activity. Also, at low latitudes, sub-scale convective events draw polluted air out of the planetary boundary layer and redistribute it in the photochemically efficient free troposphere. Along with non-linearities in the production of tropospheric ozone [Liu et al., 1987] and increasing tropical emissions, these two factors significantly affect the distributions of chemically reactive trace gases and oxidizing capacity of the global troposphere. Gupta [1996] has described some photochemical effects of increased tropical emissions of NOx, hydrocarbons and CO on the tropospheric chemical balance.

Our calculations show that redistribution of emissions of NOx, CH4 and CO has significant effects on the tropospheric oxidizing capacity and distributions of chemically active trace species. For simulations ALL and NOX, Figure 1 shows the calculated percent changes in OH concentration for July. For case ALL, a combined decrease in sinks and sources of OH radicals from mid-latitude regions to the tropics led to an overall increase (ranging from 1.4-4.2% at various latitudes and altitudes) in OH concentrations throughout the mid-latitude NH troposphere. This net increase in OH concentration at mid-latitudes is caused mainly by the decrease in emissions of CH4 and CO and is counteracted somewhat by the decrease in NOx surface emissions. For case NOX, reduction in NOx emissions alone led to a decrease in OH concentration by 2.6% and 1.6% in the lower and middle NH troposphere respectively. This is due primarily to decrease in O3 concentration (see Figure 2). For tropical regions of the NH, an increase in OH concentration in the range of 3-8% is calculated. For ALL, despite an increase in emissions of CO and CH4, an increase in OH is obtained because of enhanced NOx emissions which are relatively more efficient in producing O3, and hence OH radicals. A comparison of the increase in OH concentration at NH tropics shows that increased emissions of NOx contributed the most to the calculated increase in OH concentration, with a small opposing effect from increased emissions of CO and CH4.

On the annual average, changes in global OH concentration weighted by CH4 mixing ratio and rate of reaction for CH4+OH [Prather and Spivakovskiy, 1990], calculated for ALL, NOX and CO cases are +3.6%, +3.9% and -0.2% respectively. For a scenario with only an increase in surface NOx emissions by 5 Tg as N (which is 25% of surface NOx emissions between 35°N-75°N) between 35°N and 5°S, the calculated increase in global annually averaged OH concentration is 5.2%, indicating that the largest factor for increase in global OH concentration for case NOX is increase in tropical NOx surface emissions. For NOX and CO, the calculated percent changes in global annual averaged OH concentration

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**Figure 1.** Calculated percent changes in regional OH concentration for July simulated for scenarios ALL and NOX.
per Tg adjustment in surface source are +0.78% and -1.6×10⁻³% respectively. Due to nonlinear photochemical interactions, the calculated changes in annually averaged global OH concentration per Tg shift in NOx emission are +0.86% and +0.68% respectively for 10% and 50% shifts in surface emissions of NOx. For scenario CH4, no net change in global annually averaged OH concentration is calculated.

Figure 2 shows the calculated percent changes in O3 mixing ratio for cases ALL and NOX in July. Because of decreased emissions of O3 precursors, a decrease in O3 mixing ratios ranging from 0.2% to 4.4% is calculated for all mid- and high latitude regions of the NH troposphere. The largest contribution is from the decreased NOx surface emissions. On the other hand, an increase in O3 is calculated in the tropics of both the hemispheres. This is caused by enhanced oxidation of CH4 and CO in the presence of increased NOx concentrations. For the NH tropics, the increase ranges from 1.3% to 3.8% and is localized in the lower troposphere. Over the entire tropical domain, most of the calculated increase in O3 can be attributed to increased tropical NOx surface emissions. For cases ALL and NOX, the annual average increase in surface O3 mixing ratios for the NH tropics lies between 5-6% (Figure 3).

A variable change in surface O3 mixing ratio is obtained for mid- and high- latitude NH regions. For case NOX, the surface O3 mixing ratio decreases by 0.4-3.4% for the months of June-November. At other times of the year, an increase of 0.5% to 2.1% is calculated for surface O3 mixing ratios despite decreased surface NOx emissions. These seasonally dependent changes in surface O3 mixing ratio are partially governed by the extent of O3 losses by NO forming NO2.

The changes in OH and O3 distributions are expected to alter the steady state lifetime, mixing ratio and interhemispheric gradient of CH4. For cases ALL and NOX, the decreases in CH4 time constants are 3.3% and 3.7% respectively. Annually averaged surface mixing ratios of CH4 for the region (75°N-35°N) changed by -4.7%, -3.4%, +0.05% and -1.1% for ALL, NOX, CO and CH4 respectively (Table I). For the region (35°N-5°S), the values are -3.0%, -3.7%, +0.1% and +0.6%. Table I also displays these changes on semihemispheric basis. The stated changes show that the scenario CO will lead overall to a minor increase in CH4 surface mixing ratios in the NH. For scenario NOX the effect is more pronounced and have opposite sign. For scenario CH4, the calculated changes in methane surface mixing ratios are variable. About 1% decrease is computed for model region (30°N-90°N) and is partially caused by the decreased emissions there. In other parts of the model, suppression of

### Table I: Calculated Percent Changes in Annually Averaged CH4 Surface Mixing Ratios Brought by Latitudinal Redistribution of Surface Sources of NOx, CH4 and CO

| Case | MR1 | MR2 | R1 | R2 | R3 | R4 |
|------|-----|-----|----|----|----|----|
| ALL | -4.66 | -3.04 | -3.03 | -3.00 | -2.98 |
| NOX | -3.43 | -3.70 | -3.45 | -3.71 | -3.76 | -3.75 |
| CO | +0.05 | +0.13 | +0.05 | +0.13 | +0.17 | +0.17 |
| CH4 | -1.13 | +0.59 | -0.94 | +0.62 | +0.69 | +0.64 |

Note: MR1, MR2, R1, R2, R3 and R4 correspond to latitudes (75°N-35°N), (35°N-5°S), (90°N-30°N), (30°N-0°), (0°-30°S) and (30°S-90°S) respectively.

### Table II: Seasonal Variations of Calculated Changes in Interhemispheric Gradient of CH4 Surface Mixing Ratios Brought by Latitudinal Redistribution of Surface Sources of NOx, CH4 and CO

| Season | Percent Change in CH4 Interhemispheric Gradient |
|--------|-----------------------------------------------|
|        | ALL | NOX | CH4 |
| R1-R4  | R2-R3 | R1-R4 | R2-R3 | R1-R4 | R2-R3 |
| JJA | -26.3 | -6.1 | +0.6 | -2.9 | -25.4 | -2.1 |
| SON | -27.5 | -7.7 | +1.4 | -2.5 | -26.7 | -3.1 |
| DJF | -21.8 | -5.4 | -0.1 | -1.4 | -20.7 | -2.7 |
| MAM | -20.8 | -4.6 | -0.1 | -2.1 | -19.7 | -1.5 |

Note: Regions R1, R2, R3 and R4 are defined in Table I.
OH radical led to about 0.6% increase in CH₄ surface mixing ratios. Hydroxyl is lowered by the increase in CH₄ emissions in the NH tropics and by enhanced transport of CH₄ to the SH. For simulations ALL, NOX and CH₄, Table II displays percent changes in the CH₄ interhemispheric gradient. For simulations ALL and CH₄ at all seasons, decreases of more than 19% are calculated in north-south gradient (for 90°N-30°N and 30°S-90°S) of CH₄ surface ratios. The reduced gradient is found to be seasonally dependent with a maximum value for season SON and minimum for MAM. For case NOX, the change in this gradient is positive for seasons JJA and SON with magnitudes 0.6% and 1.4%. It is slightly negative for other seasons. The change in north-south gradient for tropical surface mixing ratios is negative for all three scenarios. For ALL, decrease in this gradient lies between 4.6-7.7%. These results show that the reduced CH₄ interhemispheric gradient observed by Dlugokencky et al., [1998] could be partly due to geographical redistribution of surface sources of CH₄ and NOₓ.

Most intense economic and industrial transitions are currently being experienced in the northern hemispheric Asian and Pacific developing countries. In future, this transition is expected to spread to the so far neglected African continent, resulting in larger tropical emissions to the atmosphere and a more pronounced increase in tropospheric oxidizing capacity. Our present calculations do not consider increases in tropical aircraft NOₓ emissions and also the effects of biogenic hydrocarbons which are mostly confined in tropical regions. These two factors could enhance the magnitude of chemical effects described here. Within given latitude band, the longitudinal surface emissions of O₃ precursors, especially NOₓ, are inhomogeneous, therefore, three-dimensional chemical models should also simulate the stated emissions scenarios to better quantify the results of this study.

Conclusion

Surface emissions of NOₓ, CH₄ and CO are decreasing from developed countries which lie mainly in the latitude belt (75°N-35°N). The opposite is true for the developing countries of the tropics. We have conducted two-dimensional photochemical modeling investigations of the shift in emissions. Assuming constant global source strengths, a shift of 25% of the surface emissions of NOₓ, CH₄ and CO from the developed countries led to a decrease in steady state methane lifetime by more than 3%, and also caused a net increase in tropical surface O₃ and variable changes in its concentrations at NH mid-latitudes. These changes are mostly attributable to variations in emissions of NOₓ, primarily from the tropics. Further, the interhemispheric gradient of CH₄ concentrations, a variable often used to deduce CH₄ sources, was decreased.

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