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Global atmospheric distributions and source strengths of light hydrocarbons and tetrachloroethene

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Abstract. The atmospheric distributions of CH₄, C₂H₆, C₃H₈, C₂H₂, and C₂Cl₄ and their annual chemical removal rates in steady state are determined versus latitude using a modified version of the Oslo two-dimensional global tropospheric photochemical model. A photochemically calculated hydroxyl radical distribution, which has been validated with methylchloroform data, and seasonally varying surface measurements of the title species are used to compute their respective global annual surface source strengths and steady state lifetimes. Computed annual surface source strengths of CH₄, C₂H₆, C₃H₈, C₂H₂, and C₂Cl₄ are 490, 10.4, 8.4, 3.1 Tg (1 Tg = 10¹² g), and 432 kT (1 kT = 10⁹ g), respectively. The calculated annual chemical removal rates of these compounds show distinct latitudinal distributions. Because their steady state global lifetimes are less than the model interhemispheric exchange time (about 1 year), the calculated north to south ratios of the deduced surface emission strengths of C₂H₆, C₃H₈, C₂H₂, and C₂Cl₄ probably reflect the locations of their sources. Within the limits of previously estimated industrial emissions of C₂Cl₄ (3–4 kT) for the southern hemisphere, our calculations indicate that about 47 kT of additional southern hemispheric source of C₂Cl₄ is required for 1989–1990 to attain steady state mass balance in this region. There are two possibilities for this needed source: either other industrial sources are missing, or there are unidentified natural sources of C₂Cl₄. So far, oceans have been suggested as a natural source. Normalization of monthly varying ratios of hemispherically averaged calculated surface mixing ratios of C₂H₆, C₃H₈, and C₂Cl₄ and their respective observed mixing ratios with respect to those for C₂Cl₄ indicates that the sources of these hydrocarbons are seasonal in nature. It is also shown that convective transport effectively redistributes these short-lived species but their calculated surface source strengths are relatively independent of this transport process.

1. Introduction

The chemical composition of the Earth’s atmosphere and its spatial and temporal variabilities are controlled by coupled photochemical and dynamical processes. This coupling becomes even more complicated by changing biological phenomena [Prinn, 1994] and by active exchanges between the Earth’s surface and atmosphere. The Earth’s atmospheric composition has been continually modified by natural and anthropogenic forces, particularly during the industrial era. Observations of trace gases in the atmosphere have revealed the extent to which the Earth’s atmosphere and its oxidative capacity have changed [Isaksen, 1988; Thompson, 1992; World Meteorological Organization (WMO), 1994]. Although spatial and temporal variations in methane (CH₄), the most abundant hydrocarbon present in the atmosphere, have been studied extensively, non-methane hydrocarbons (NMHCs) have received less attention in studies of global atmospheric chemistry. Important roles played by NMHCs in urban photochemical smog, acid deposition, regional and global budgets of CO, OH, O₃, NOₓ (defined as NO + NO₂), heterogeneous and nighttime tropospheric photochemistry, and as indicators of air mass age, tracer transport, and halogen radical concentrations have been well documented (see a review by Singh and Zimmerman [1992, and references therein]). The Intergovernmental Panel on Climate Change (IPCC) [1995] report reviewed the indirect climatic importance of NMHCs and NOₓ on the radiative balance of the Earth’s atmosphere which modify tropospheric O₃ and CH₄ distributions through their nonlinear photochemistry [Ramanathan et al., 1985; Dickinson and Cicerone, 1986; Lin et al., 1988; Silman et al., 1990], but failed to quantify the magnitude of this indirect forcing because of uncertainties in the source strengths and global distributions of NMHCs and NOₓ. The uncertainties in the identity of natural and anthropogenic NMHC sources and spatial and temporal variability in their corresponding strengths are mainly due to their relatively reactive nature, and hence their short lifetimes and low abundances [Singh and Zimmerman, 1992]. Because of these uncer-
tainties in the source strengths of NMHCs, assessing the behavior of their oxidation byproducts such as organic nitrates, etc., which play important roles in tropospheric photochemistry, is also very difficult. Among all the NMHCs, only ethane, the longest-lived and the most abundant saturated NMHC, displays a significant increasing tropospheric burden [Ehhalt et al., 1991].

In this paper, we calculate the annual global surface source strengths of relatively long-lived \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_2 \), and \( \text{C}_3\text{H}_8 \) and their corresponding latitudinal distributions. In addition to these light parent NMHCs, \( \text{CH}_4 \) and tetrachloroethene (\( \text{C}_2\text{Cl}_4 \)), a mainly industrially produced chemical, have also been included in the present study to assess their tropospheric budgets. In steady state, in the absence of in situ atmospheric losses, for all these species the global surface source strengths can be equated to their corresponding total atmospheric photochemical losses. The fact that \( \text{OH} \) radicals are the main sink of surface-emitted light NMHCs and \( \text{C}_2\text{Cl}_4 \) (with more than 80% of their sources originating from the northern hemisphere (NH), as concluded in this paper) and because industrial emissions balanced by corresponding atmospheric chemical losses primarily by \( \text{OH} \) radicals. For some species, reactions with \( \text{O}_3 \), \( \text{NO}_3 \), and \( \text{Cl} \) radicals are other minor sinks. The characteristic that in steady state, global atmospheric chemical removals of hydrocarbons and \( \text{C}_2\text{Cl}_4 \) are equal to their total surface sources has made it possible to interactively calculate their surface emissions using a photochemical model and their corresponding surface measurements.

To accomplish this, we used surface observation data for the listed hydrocarbons and \( \text{C}_2\text{Cl}_4 \) collected during University of California, Irvine's (UCI's) trace gas program [Smith, 1993; Wang et al., 1995]. Under this program, air samples were collected each season along the Pacific rim over a wide latitude range from \( 71^\circ \text{N} \) to \( 47^\circ \text{S} \). To avoid the possible calibration differences among various working groups around the world [Apel et al., 1994], no effort is made to combine their data with UCI's observations. The use of data from a single investigator is required to allow the self-consistent deduction of latitude gradients of surface sources. For \( \text{CH}_4 \), seasonally varying data averaged over four successive years (1988–1991) and for NMHCs and \( \text{C}_2\text{Cl}_4 \) data for (1989–1991) and (1989–1990), respectively, were used. Before treating the raw data over these periods, data corresponding to contamination and pollution events were removed. All observation data collected at the same latitude for different days of the same season were averaged. For each model grid location, these averaged data were spatially interpolated using the running average technique. For the model latitudes that lie outside the domain \( 71^\circ \text{N} \) to \( 47^\circ \text{S} \), all these points were linearly interpolated on 1 day time resolution. Figure 1 shows the resultant seasonally and latitudinally varying treated surface mixing ratios of \( \text{CH}_4 \), approach these objectives, we have used the seasonally varying surface concentration measurements of these hydrocarbons and \( \text{C}_2\text{Cl}_4 \) (described in section 2) as their lower boundary conditions in a two-dimensional global photochemical model.

A brief description of this model is given in section 3. For this purpose, we have developed two photochemical schemes PC1 and PC3 which contain \( \text{CH}_4 \) and \( \text{CH}_4 \), \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \), \( \text{C}_3\text{H}_8 \), and \( \text{C}_2\text{Cl}_4 \) as parent hydrocarbons, respectively. Details of these schemes are given in section 4. Features and dependence of \( \text{OH} \) radical distributions calculated using these schemes are described in section 5. Results and discussions of computed global source strengths for \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_3\text{H}_8 \), and \( \text{C}_2\text{Cl}_4 \) including \( \text{CH}_4 \), and seasonal variations in surface sources of light NMHCs are given in sections 6 and 7, respectively. Finally, section 8 summarizes the major findings of this paper.

2. Surface Measurements of Light Hydrocarbons and \( \text{C}_2\text{Cl}_4 \)

One of the goals of this paper is to estimate surface source strengths of light hydrocarbons and \( \text{C}_2\text{Cl}_4 \). Surface emission estimates of \( \text{CH}_4 \) from various sources are reasonably well constrained within a certain range [Cicerone and Oremland, 1988; Crutzen, 1991], but for NMHCs, as stated earlier, there still exist many uncertainties in the identities, and hence in the magnitudes of their source strengths. With the exception of \( \text{CH}_4 \) which also has soil sinks (about 6% of its total global sink [Cicerone and Oremland, 1988; WMO, 1994]), all the listed hydrocarbons and \( \text{C}_2\text{Cl}_4 \) included in this study have their surface emissions balanced by corresponding atmospheric chemical losses primarily by \( \text{OH} \) radicals. For some species, reactions with \( \text{O}_3 \), \( \text{NO}_3 \), and \( \text{Cl} \) radicals are other minor sinks. The characteristic that in steady state, global atmospheric chemical removals of hydrocarbons and \( \text{C}_2\text{Cl}_4 \) equal to their total surface sources has made it possible to interactively calculate their surface emissions using a photochemical model and their corresponding surface measurements.

Figure 1. Seasonal variations in interpolated latitudinal distribution of surface mixing ratios of \( \text{CH}_4 \) (averaged for 1988–1991), \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_3\text{H}_8 \) (averaged for 1989–1991), and \( \text{C}_2\text{Cl}_4 \) (1989–1990) measured by the D. R. Blake and F. S. Rowland group at UCI.
C$_2$H$_6$, C$_2$H$_2$, C$_3$H$_6$, and C$_2$Cl$_4$. Annually averaged observed mixing ratios at the surface for these species are 1.75 ppm (CH$_4$), 1150 ppt (C$_2$H$_6$), 330 ppt (C$_2$H$_2$), 230 ppt (C$_2$H$_4$), and 12 ppt (C$_2$Cl$_4$) for the NH and 1.67 ppm (CH$_4$), 310 ppt (C$_2$H$_2$), 50 ppt (C$_2$H$_4$), 40 ppt (C$_2$H$_4$), and 3 ppt (C$_2$Cl$_4$) for the southern hemisphere (SH). In general, all species show significant seasonal and latitudinal variations (see Figure 1) that are governed by their diverse spatially and temporally varying source distributions combined with their variable atmospheric lifetimes and interhemispheric exchange transport. For further discussion of these measurements and corresponding analysis and interpretation, refer to the references cited in this section.

3. Model Description

For the present study, we used a modified version of the Oslo two-dimensional (altitude-latitude) global tropospheric photochemical model [Gupta, 1996]. The original version of this model was developed by Isaksen and Rodhe [1978]. In the modified model the vertical domain has been increased by 8 km. In the vertical direction the model extends from the surface to 24.5 km with a total of 49 vertical layers and uniform resolution of 0.5 km. In latitude the model resolution is 10ø. The main purpose of extending the model domain is to isolate the dependence of atmospheric distributions of light NMHCs from their upper boundary condition and to better simulate their photochemistry in the upper troposphere. By making this change the rigidity of the upper boundary condition can be relaxed because of the combined fast removal of these NMHCs by O$_3$ and OH radicals in the upper troposphere and lower stratosphere [Chameides and Cicerone, 1978; Singh and Kasting, 1988].

The advective and diffusive transport coefficients for the modified model are those derived from the Geophysical Fluid Dynamics Laboratory general circulation model (GFDL GCM) [Plumb and Mahlman, 1987]. The transport features of this model have been tested with observed distributions and trends of CFC-11, CFC-12 [Cunnold et al., 1994], and $^{85}$Kr [Weiss et al., 1983] tracers yielding an interhemispheric exchange time of about 1 year [Gupta, 1996]. This model has been used to simulate the global distribution of $^{13}$CH$_4$ and its dependence on kinetic isotopic fractionations associated with various sinks of CH$_4$ [Gupta et al., 1996, 1997].

Another modification made to the Oslo model is the inclusion of parameterized treatment for convective or subgrid scale vertical transport. This transport process is very important for the short-lived species which have chemical lifetimes of the order of a few days to weeks. Through this process, a polluted air mass containing a mixture of nitrogen oxides and hydrocarbons and CO, in addition to other pollutants, can be transported upward from the planetary boundary layer (PBL) to the free troposphere where the chemistry of these pollutants very efficiently forms O$_3$ molecules and hence significantly affects its distribution [Liebeveld and Crutzen, 1994]. Changing the distribution of O$_3$ in the upper troposphere and lower stratosphere can be very important radiatively [Lacis et al., 1990]. In this model the treatment for fast vertical transport by convective clouds and frontal circulation due to cyclones at midlatitudes is based on the parameterization scheme developed by Langner et al. [1990]. For both of these fast vertical transports the model draws air out of the PBL (considered to be the first two model layers) at a specified rate depending upon the latitude and season. The boundary layer air is then detrained into the remaining part of the troposphere above the boundary layer according to a specified detrainment vertical profile which is also a function of latitude and season. For each latitude the mass continuity is maintained by compensating subsidence in the respective vertical column. For convective cloud transport this formulation is similar to the one developed by Chatfield and Crutzen [1984]. This approach is believed to capture the most important features of the convective transport mechanism for atmospheric species with a source in the boundary layer and has been applied to simulate the distributions for SO$_2$ and $^{35}$Kr [Langner et al., 1990]. For the modified model the seasonal and latitudinal distributions of mass fluxes due to cloud convection and midlatitude frontal cyclones and their respective vertical detrainment profiles are adopted from Langner et al. [1990].

4. Development of Photochemical Modules

In addition to the transport processes, sources and sinks of various chemical species and their mutual chemical interactions define the behavior of atmospheric pollutants. These pollutants may originate either from their surface emissions (natural and/or anthropogenic) or in situ production, or a combination of both. Various gas- and liquid-phase reactions and heterogeneous losses due to deposition at the Earth’s surface, on aerosols, and rain droplets account for the ultimate fate of atmospheric pollutants. The following subsections briefly describe these points including the details about the photochemical schemes PCI and PC3.

4.1. Emissions and Boundary Conditions

For the parent hydrocarbons, depending upon the purpose of the model simulation, two different types of lower boundary conditions were employed. For the deduction of surface emission strengths of light hydrocarbons and C$_2$Cl$_4$, their observed surface concentrations were used as the lower boundary condition. To investigate the seasonality in their sources, the calculated annual latitudinal surface emissions were uniformly applied on per time step basis at the lower boundary. For acetone, also a byproduct of C$_3$ or higher hydrocarbon oxidation, a surface emission strength of 25 Tg/yr due to biomass burning and biogenic emissions, as concluded by Singh et al. [1994], was equally distributed on per time step basis primarily at tropical latitudes. For C$_2$H$_4$ and C$_3$H$_6$, their seasonally varying observed surface mixing ratios averaged for (1989–1991), as described in section 2, were used as the lower boundary condition. At the upper boundary, CH$_4$ was allowed to diffuse through the top of the model according to the one-dimensional vertical steady state scale height approximation using its losses against OH and Cl radicals in the stratosphere. For NMHCs and C$_2$Cl$_4$, mixing ratios just above the model domain were fixed as 0.25 times that at the topmost layer; that is, $X_{50} = f \times X_{49}$, where $X$ is the mixing ratio and $f$ is equal to 0.25. This upper boundary condition for NMHCs is relatively rigid but is appropriate because by 25 km, their concentrations decrease very rapidly with altitude [Rudolph et al., 1981, 1984], thereby making their atmospheric distributions completely independent of upper boundary conditions. In fact, simulations performed with variable value of $f$ ranging between 0 and 1 showed no difference in the vertical profiles of these species [Gupta, 1996].

Annual source strengths of NO$_x$, HNO$_3$, O$_3$, and CO used in
present model simulations are summarized in Table 1. The
surface source estimates and NO₃ emissions from aircraft
lightning listed in this table with their corresponding latitudinal
distributions were adopted from Isaksen and Hov [1987] and
Fuglestvedt et al. [1993]. For NOₓ and CO, north to south
surface emission ratios are 4.2 and 2.6, respectively. For both
day of these species the surface emissions were applied equally on
per time step basis. Stratospheric subsidence rates of O₃, NO,
and HNO₃ and their corresponding latitudinal and seasonal
distributions were taken from the Oslo two-dimensional
tropospheric-stratospheric model [Stordal et al., 1985; Isaksen and
Stordal, 1986].

For all simulations, full interactive photochemical calculations
with transport were performed for the model region
between surface and 16.5 km. The extended region of the
model between 16.5 and 24.5 km was only used for the transport
of light hydrocarbons and C₅Cl₄ and for their chemical
losses due to prescribed distributions of OH and Cl radicals.
Monthly averaged distributions of Cl and OH radicals for the
extended region were taken from the Oslo two-dimensional
tropospheric-stratospheric model. Also, for the marine
boundary layer (MBL), monthly varying distributions of Cl radicals
were adopted from the Oslo model. In this model the only
source of chlorine radicals in the MBL is due to reaction of
HCl with OH radicals. The concentrations of Cl radicals in the
MBL and atmospheric region of (16.5-24.5) km are of the
order of (5×10²⁴-4×10⁵) and (7×10³-4×10⁴) molecules
m⁻³, respectively. Monthly varying two-dimensional water vapor
distributions were adopted from Barnett and Corney [1985].

Dry deposition loss frequencies for O₃, NO₂, H₂O₂, HNO₃,
and PAN were calculated for the lowest layer in terms of their
corresponding deposition velocity given at 1 m [Isaksen and
Rodhe, 1978]. These loss frequencies were weighted by the land
and oceanic areas per 10° latitude band. Also, the seasonal
dependence of land surface deposition velocity was also incorporated as mentioned by Isaksen et al. [1985]. Table 2 lists the
deposition velocities of various species used in the model
calculations. To examine the effects of the CO soil sink, the
deposition velocity corresponding to this loss is also given in
Table 2.

### 4.2. Photochemical Schemes

Two photochemical schemes, PC1 and PC3, were developed for the present study which focus on the fate of six light parent
hydrocarbons, namely CH₄, (C₂H₆, C₃H₆, C₂H₂) and (C₃H₅,
C₅H₆, and their oxidation byproducts. Photochemical scheme
PC1 contains only CH₄, while in addition to CH₄, scheme PC3
also includes C₂ and C₃ compounds. Tetrachloroethylene is
included in both of these schemes. Initially, we adopted the PC1
chemical scheme from Isaksen and Hov [1987] and modified it
to include some reactions of oxidation byproducts such as
methyl alcohol, formic acid, nitrous acid, etc. The rate
constants of this scheme were updated using the recommendations
of Atkinson et al. [1992] and DeMore et al. [1992]. Presently, the
chemical scheme PC1 has about 150 thermal and photolytic
reactions involving 45 species. Inclusion of complex and
extensively branched chemistry of C₂ and C₃ parent hydrocarbons
and their byproducts increased the total number of reactions to
about 750 involving more than 200 species [Gupta, 1996]. Some
reactions of parent hydrocarbons and their byproducts involving
Cl radicals in the MBL, upper troposphere, and lower
stratosphere were also included. For both schemes, rate
constants of primary reactions of parent hydrocarbons and C₂Cl₄
were updated from DeMore et al. [1997], Kaiser and Wellington
[1996], and Atkinson [1994].

Photodissociation rates for all species of both photochemical
schemes were calculated according to the two-stream approxima-
tion method developed by Isaksen et al. [1977] and modified
by Jonson and Isaksen [1991] to account for diffuse radiation
by Rayleigh and Mie scattering due to cloud droplets and
aerosol particles. The data for actinic solar flux and absorption
cross sections and quantum yields of all the species undergoing
photodissociation were taken from DeMore et al. [1985, 1992].
For the middle of each month, all photodissociation rates were
calculated off-line at 15 min time and 10° latitude intervals,
with and without cloud cover. Both sets of these photodissociation
rates (with and without cloud cover) were averaged
over 1 hour time intervals for their later use in diurnal pho-
tochemical calculations.

The chemical part of the two-dimensional model equation
was solved using the time-flux operator splitting method and
"quasi steady state approximation (QSSA)" [Hesstvedt et al.,
1978]. To maximize mass conservation and to use longer time
steps for integration, the chemical family technique was used in
addition to constraining the sum of concentrations of rapidly
cycling species such as OH/HO₂, HO₂/ HO₂NO₂, and NO/NO₂
[Bernsten and Isaksen, 1994]. For all the simulations, typically
the model was allowed to run for at least 4 decades to ensure
the attainment of steady state concentrations of CH₄ in the
entire model domain. More details about photochemical
schemes, calculation of photorates, and diurnal averaging and
their use for the solution of long-lived species are given by
Gupta [1996].

### Table 1. Annual Source Strengths of CO, O₃, NOₓ, HNO₃,
and Acetone Used in the Model Calculations

<table>
<thead>
<tr>
<th>Species</th>
<th>Source Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂, Tg N/yr</td>
<td>37</td>
</tr>
<tr>
<td>Lightning</td>
<td>8</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.67</td>
</tr>
<tr>
<td>Stratosphere</td>
<td>0.45</td>
</tr>
<tr>
<td>HNO₃ stratospheric source, Tg N/yr</td>
<td>0.66</td>
</tr>
<tr>
<td>O₃ stratospheric source, Tg O/yr</td>
<td>656</td>
</tr>
<tr>
<td>CO surface source, Tg CO/yr</td>
<td>1280</td>
</tr>
<tr>
<td>Acetone, Tg CH₃COCH₃/yr</td>
<td>25</td>
</tr>
</tbody>
</table>

With the exception for acetone, all other emission strengths listed in this table are adopted from Isaksen and Hov [1987] and Fuglestvedt et al. [1993]. For acetone the annual source strength estimate is taken from Singh et al. [1994].

### Table 2. One Meter Deposition Velocity of Various
Species for Land and Oceanic Surfaces Used in the Model Calculations

<table>
<thead>
<tr>
<th>Species</th>
<th>Land</th>
<th>Ocean</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>PAN</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>CO</td>
<td>0.03</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

All these deposition velocity values (cm s⁻¹) are adopted from Isaksen et al. [1985] and Bernsten and Isaksen [1994].
4.3. CH₄ Perturbation Study

Photochemical schemes PC1 and PC3 with seasonally and latitudinally varying observed mixing ratios of light hydrocarbons, fixed CH₄ mixing ratio of 1.75 ppm for all seasons, and latitudes and annual emissions of other species as listed in Table 1 were used to perform the experiment named “delta-CH₄.” This experiment was designed by IPCC working group I to evaluate the indirect effects of a 20% increase in CH₄ concentration on the tropospheric O₃ and NOₓ distributions and on OH concentrations. Following the protocol for this experiment (M. J. Prather, personal communication, 1996), we also determined the ratio of adjustment time to steady state lifetime [Gupta, 1996]. For both photochemical schemes PC1 and PC3 the calculated ratios were 1.43 and 1.39, respectively, which are in good agreement with estimate of 1.45 ± 0.25 reported by IPCC [1994]. The value of this ratio was also verified by direct adjustment time calculation for perturbation simulation. The adjustment time for a CH₄ pulse perturbation to scheme PC1 was found to be 14 years, which when divided by its steady state lifetime of 9.72 years yielded 1.44 as the ratio of adjustment time to steady state lifetime.

5. Computation of Hydroxyl Radical Distribution

The hydroxyl radical is central to tropospheric photochemistry. Despite its low concentration (of the order of 10⁵–10⁶ molecules cm⁻³), it is a principal sink for numerous atmospheric pollutants. Global spatial and temporal distributions of OH radical can be calculated using photochemical models [Chameides and Tan, 1981; Crutzen and Zimmermann, 1991; Spivakovsky et al., 1990]. The OH distributions calculated in this way can be validated by simulating the observed surface methyl chloroform distributions and their trends [Spivakovsky et al., 1990; Taylor et al., 1991; Tie et al., 1992].

In the present study, we have photochemically derived the OH distribution using the observed surface distributions of light hydrocarbons as their lower boundary condition. Emission strengths of all species other than hydrocarbons used in these calculations are shown in Table 1. For scheme PC1 the calculated diurnal variation of OH radical concentration is a strong function of altitude as shown in Figure 2 for July at 40°N and at 0.25, 6.25, and 15.25 km. At low altitudes, daytime OH concentrations are only 40–80 times higher than the corresponding nighttime values. We attribute this feature to the rapid recycling of HO₂ radicals due to HO₂NO₂ and O₃ molecules by the following sequence of reactions: During the nighttime the main source of HO₂ radicals is the unimolecular decomposition of HO₂NO₂:

$$\text{HO}_2\text{NO}_2 + \text{M} \rightarrow \text{HO}_2 + \text{NO}_2 + \text{M}$$

The NO₂ formed in this reaction recombines with HO₂ to form HO₂NO₂. Also, owing to the low concentrations of HO₂ and OH radicals during the night, the time constants of the decay of HO₂ species from (HO₂ + HO₂) and (HO₂ + OH) reactions, which account for the net loss of HO₂ species, are relatively higher (approximately by 2 orders of magnitude in the lower troposphere) compared to the corresponding values during the daytime. Very low nighttime OH concentrations at high altitudes is due to low HO₂ concentrations. For the lower troposphere this feature in diurnal variation has been reported by Lu and Khalil [1991] and Bey et al. [1997]. On the basis of nighttime measurement of HO₂ of about 10 ppt during night at 48°N, Mihelcic et al. [1993] estimated the nighttime OH concentration of 10⁶ molecules cm⁻³, which is in accordance with the analysis of Platt et al. [1990]. Recently, Tanner and Eisele [1995] reported nighttime OH concentration measurements in the range of 10⁶ molecules cm⁻³ using ion-assisted technique.

Figure 3 shows the diurnally averaged OH distributions for the months of July and January. During the summer of both hemispheres the maximum concentration is observed around 25° which is consistent with other model studies [Crutzen, 1987; Spivakovsky et al., 1990]. This seasonal variation in OH distribution is mainly due to seasonality in the solar UV flux reaching the troposphere which is responsible for the OH production through the photodissociation of O₃ molecules followed by the reaction O⁴⁺(D) + H₂O. Generally, OH radical number densities decrease with altitudes, but in the upper troposphere and lower stratosphere a slight increase in OH density is calculated. This pattern in vertical profile of OH radicals is consistent with that of Tie et al. [1992] but differs from that of Spivakovsky et al. [1990]. Despite the decrease in water vapor concentration in upper troposphere and lower stratosphere, the increase in O₃ concentration and its photolysis rate cause this increase in OH concentration. The monthly averaged OH concentration for each hemisphere (weighted by distributions of rate constant for reaction CH₄ + OH and CH₄ concentration [Prather and Spivakovsky, 1990]) shows the maximum value in summer (1.3 × 10⁸ cm⁻³ and 1.4 × 10⁹ cm⁻³ for NH and SH, respectively).
and SH, respectively) and the minimum (6.6 × 10^5 cm^{-3} and 7.4 × 10^5 cm^{-3} for NH and SH, respectively) in winter. Peak-to-peak ratio of hemispherically averaged OH concentration over a year is found to be higher in the SH (2.2) as compared to that in the NH (2.1). Globally averaged OH radical concentration derived from scheme PC1 is 1.03 × 10^6 molecules cm^{-3}. On the annual average basis the north to south hemispheric OH concentration ratio is 0.89 because of the higher OH concentration in the SH. This result is consistent with other modeling studies [Chameides and Tan, 1981; Crutzen and Gidel, 1983; Tie et al., 1992] and observations [Brenninkmeijer et al., 1992] but disagrees with the results of Spivakovsky et al. [1990].

For the termolecular reaction of OH and NO_2 leading to formation of HNO_3, we used the rate constant recommended by Atkinson et al. [1992]. New rate measurements for this reaction reported by Donahue et al. [1997] indicate that at 300 K and for pressure region 20–600 torr, the rate constant may be higher by 10–30%. It remains, however, to determine whether this correction applies to all tropospheric temperatures. If so, the revised rate constant will lead to an increase in OH concentration in comparison with that calculated here. There are two primary reasons for this speculation: lowering the OH radical loss rate due to the stated reaction and increase in O_3 formation due to more availability of NO_2 radicals to photolyze.

5.1. Effect of Convective Transport

As mentioned before, vertical convection draws polluted air from the boundary layer which has enhanced concentrations of CO, hydrocarbons, NO_x, and HNO_3 and returns the upper tropospheric air which is rich in O_3. Simulating this fast exchange of air makes tropospheric chemistry more complex and augments the oxidizing capacity of the troposphere by increasing overall OH concentration, as shown in Figure 4. This figure illustrates the percent change in OH concentration for the month of July from convection. In the lower troposphere this increase is as much as 5%, and for the upper tropical troposphere it ranges from 15% to more than 45%. On an annual basis, compared to the nonconvective PC1 case, the global average OH concentration increased by 3%. In the lower troposphere this increase is due to more O_3, whose photolysis forms O(^1D) and hence more OH radicals. Another important effect of convective transport on tropospheric chemistry is to increase the O_3 formation efficiency per NO molecule consumed. For given NO emissions the increase in O_3 formation efficiency per NO molecule in the PBL is due to decreased background NO concentrations caused by convective dilution [Liu et al., 1987]. Decreases in concentrations of CO and CH_4 resulting from dilution of the PBL layer also increased OH concentrations. In the upper troposphere the relatively enhanced oxidation of CO and CH_4 in the NO-rich environment increased the production of OH radicals.

5.2. Effect of Addition of C_2 and C_3 Parent NMHCs

Addition of C_2 and C_3 parent hydrocarbon oxidation has significant effects on regional OH concentrations, but little effect on global annually averaged OH concentration. In the lower troposphere at higher latitudes, diurnally averaged OH concentrations derived from scheme PC3 are decreased by as much as 10% relative to that from scheme PC1, as shown for July in Figure 5. However, in the northern hemispheric upper troposphere during summer, OH concentration is increased by more than 8% due to higher NO_x concentrations (from oxidation of organic nitrates) which caused increased oxidation of hydrocarbons and hence enhanced production of O_3 and OH radicals [Crutzen, 1987]. Also for this region, the OH removal
rate is small due to the negligible rainout probability of HNO
, a major sink of OH in the lower troposphere. Overall, the global averaged OH concentration is decreased by 2%. Also, for scheme PC3 the calculated interhemispheric north to south OH concentration ratio decreased slightly (to 0.888 as compared to 0.893) from scheme PC1 because of higher northern hemispheric concentrations of C2 and C3 parent hydrocarbons and their oxidation byproducts.

5.3. Effect of Soil Sinks of CO and CH4

Inclusion of soil sinks of CH4 and CO to photochemical scheme PC1 has a significant effect on global and hemispheric OH distributions. For the CO soil sink a surface deposition velocity of 0.03 cm/s was used [Crutzen and Zimmerman, 1991] which is higher than the 0.02 cm/s used by Crutzen and Zimmerman [1991]. In steady state the calculated magnitude of this soil sink for CO is 278 Tg/yr which is comparable to the lower limit (250 Tg/yr) recommended by WMO [1994]. Pinto et al. [1983] used 0.04 cm/s for the CO deposition velocity and calculated a corresponding sink of 480 Tg/yr. For CH4 we used a constant soil sink of 30 Tg/yr [WMO, 1994], which is distributed proportionally to the land surface area. For July, inclusion of both sinks increased diurnally averaged OH concentrations by as much as 8% at higher northern hemispheric altitudes. At lower altitudes this increase is relatively smaller as shown in Figure 6. On the global average basis the hydroxyl radical concentration increased by 2%, and the interhemispheric ratio increased to 0.91 as compared to the corresponding values of 0.89, respectively, derived without the soil sink and scheme PC1.

5.4. Test of Validation Using Methyl Chloroform

The hydroxyl radical distribution calculated interactively with photochemistry was validated by simulating the latest reported observed trend and surface distributions of methyl chloroform (MCF) [Prinn et al., 1995]. Like CFC-11 and CFC-12, MCF is also solely of anthropogenic origin. It is mainly destroyed by OH radicals in the troposphere, while oceans and stratospheric photolysis are two minor sinks. Thus MCF serves as an indicator for tropospheric OH concentrations. Using the industrial emission inventories of MCF for 1951–1991 and their latitudinal fractions as reported by Prinn et al. [1987, 1995] and Fischer et al. [1994], its atmospheric distributions and trends have been simulated [Gupta, 1996]. The model calculated an instantaneous global lifetime of MCF for 1991 of 5.2 years which is 7.5% higher than the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) estimates [Prinn et al., 1995]. The global averaged lower atmospheric (1000–200 mbar) lifetime of MCF for 1991 was 4.6 years which is exactly that reported by Prinn et al. [1995]. Similar to observed trends [Prinn et al., 1995], the model calculated a 2.5% MCF concentration decrease for northern hemispheric latitudes for the period December 1990 to December 1991.

6. Global Distributions and Source Strengths of Light Hydrocarbons and Tetrachloroethene

6.1. Light Hydrocarbons

Into the atmosphere a large number of NMHCs are emitted from natural and anthropogenic sources. The sum of total emissions of all NMHCs exceeds that of CH4 sources. Biomass burning, natural gas emissions, incomplete combustion, ocean, and vegetation are thought to be the main sources of NMHCs. Compared to CH4, at room temperature, chemical reactivities of C2H2 and C4H8 are about 40 and 170 times faster toward OH radicals, and about 550 and 1330 times faster toward Cl radicals. Therefore these species are relatively short-lived.

Study of the global distributions of parent NMHCs and their oxidation byproducts requires knowledge of their surface sources. Several regional sources and their strengths for individual and/or combined hydrocarbons have been reported [Brice and Derwent, 1978; Nelson et al., 1983; Tille et al., 1985; Lamb et al., 1987; Kanakidou et al., 1989; Field et al., 1992], but their global extrapolation is uncertain because of geographically varying industrial and natural activities. Also, global emissions of all NMHCs (classified into different categories such as paraffins, olefins, aromatics, and terpenes) in terms of total carbon content have been estimated [Duce et al., 1983; Piccot et al., 1992; Feihsenfeld et al., 1992; Muller, 1992; Guenther et al., 1995]. There are some estimates available for the global source strength of individual light hydrocarbons [Penkett, 1982; Isaksen et al., 1985; Elhalt et al., 1986; Blake and Rowland, 1986; Kanakidou et al., 1991a, b; Roemer and van den Hout, 1991; Hough, 1991; Singh and Zimmerman, 1992; Strand and Hov, 1994; Rudolph, 1995], but these individual estimates for particular species cover a large range. For example, annual global surface source strength of C2H2 from these estimates ranges from 5 to 52 Tg (1 Tg = 1012 g) (see Table 4). Because of the lack of understanding of types and strengths of various sources of individual hydrocarbons, we have calculated the total surface source strengths of C2H2, C3H4, and C4H8 using their seasonally and latitudinally varying observed surface mixing ratios, as described in section 2, and OH radical distribution derived from scheme PC3 and validated by methyl chloroform simulations. In addition, we have also calculated annual surface source strengths of CH4 and C2Cl4.

At the end of each 1 day time step our calculated surface mixing ratios of the stated species at all latitudes were replaced by the corresponding interpolated observed values of the next day. In steady state the cumulative annual difference between the calculated and updated observed surface mixing ratios at all latitudes for each species was translated into a global source strength. For these initial calculations the convective transport process was not included. Computed steady state annual surface emissions of these hydrocarbons, corresponding north to south ratios of their annual source strengths, and global lifetimes are given in Table 3. Among these NMHCs, C2H4 is the longest-lived with a global lifetime of 83 days.

Figures 7–9 show the latitude-time cross section of monthly surface removal rates (which are monthly integrated combined
Table 3. Global Source Strengths and Lifetimes of Light Hydrocarbons and C2C14 Calculated Using Nonconvective Photochemical Scheme PC3

<table>
<thead>
<tr>
<th>Species</th>
<th>Source Strength, Tg/yr</th>
<th>North/South Source Ratio</th>
<th>Global Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>490 (500)</td>
<td>2.11</td>
<td>9.9 years</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>10.35 (10.76)</td>
<td>4.02</td>
<td>83 days</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>8.37 (8.70)</td>
<td>4.70</td>
<td>25 days</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>3.14 (3.27)</td>
<td>3.97</td>
<td>32 days</td>
</tr>
<tr>
<td>C₂C₁₄</td>
<td>0.432 (0.448)</td>
<td>7.47</td>
<td>116 days</td>
</tr>
</tbody>
</table>

Numbers in parentheses correspond to simulation with convective transport.

losses due to chemistry and transport in the lowest model layer) of these NMHCs in steady state. For all three species the autumn season accounts for the maximum surface removal rate (more than 30% of the global annual removal rates). The calculated removal rates of these NMHCs at high latitudes represent their losses due to transport from other regions. The exact pattern of calculated removal rates depends on the model structure, for example, model resolution. Given the sparse spatial resolutions of surface measurements and geographical source distribution, our present use of model grid dimension is justifiable.

The latitude belt (30øN–60øN) accounts for more than 54% of the total annual global emissions of these NMHCs, and the latitude belt (20øN–20øS) accounts for more than 27% of their total annual global emissions. With lifetimes short compared to the model interhemispheric exchange time of about 1 year, the north to south source ratios of 4.0, 4.7, and 4.0 for C₂H₆, C₃H₈, and C₂H₂, respectively, indicate that 80% or more of their emissions occur in the NH. In steady state the total northern hemispheric annual sources are 8.3, 6.9, and 2.5 Tg for C₂H₆, C₃H₈, and C₂H₂, respectively, of which 1.1, 0.2, and 0.1 Tg, respectively, are transported to the SH where they are chemically destroyed. The maximum north to south interhemispheric flux for January of 0.2, 0.06, and 0.03 Tg for C₂H₆, C₃H₈, and C₂H₂, respectively, was calculated. Above 16.5 km, removal of C₂H₆ by chlorine dominates the total losses and causes a rapid decrease in its vertical mixing ratio; however, this loss of C₂H₆ by chlorine radicals is only 2% of its total global loss.

The calculated surface source strengths of these NMHCs and their comparison with other estimates are given in Table 4. For the given surface measurements the zonally averaged nature of our model and uncertainties in rate constants might cause some variations in our emission estimates. As mentioned before, inclusion of convective transport caused an increase in overall tropospheric oxidizing capacity which resulted in a net increase in annual source strength. For nonconvective and convective PCI simulations the calculated global source strengths for C₂H₆ are 10.6 and 11.0 Tg/yr. For scheme PC3 these calculated values are 10.4 and 10.8 Tg/yr for the cases without and with the inclusion of convective transport. These estimates are in good agreement with the 10 Tg/yr estimate of Isaksen et al. [1985] and are within the 10–15 Tg/yr range reported by Singh and Zimmerman [1992]. Using surface observations, Blake and Rowland [1986] estimated 13 Tg/yr as the global source strength of C₂H₆. For C₂H₆, Kanakidou et al. [1991a] calculated the total emission of 16 Tg/yr and later modified it to 14 Tg/yr using a three-dimensional model [Kanakidou et al., 1991b]. Recently, Rudolph [1995] estimated 15.5 Tg/yr emission strength for C₂H₆. The importance of chlorine-initiated oxidation of hydrocarbons has already been outlined by several studies [Singh and Kasting, 1988; Finlayson-Pitts, 1993; Wingenter et al., 1996; Keene et al., 1996]. Inclusion of chlorine removal of C₂H₆ throughout the troposphere increased the global emission to 13.3 Tg/yr calculated using the PCI scheme without convection. In the lower troposphere, chlorine atom concentrations are in the range of 10⁷ cm⁻³. About 4–6 Tg/yr of the C₂H₆ global source strength has been

Figure 7. Latitude-time cross section of integrated monthly surface removal rates of C₂H₆ per 10° bin in steady state calculated using scheme PC3 and its surface observations.
assigned to biomass burning [Ehhalt et al., 1986; Singh and Zimmerman, 1992; Hegg et al., 1990; Rudolph, 1995; N. J. Blake et al., 1996]. Ethane production from natural gas emission and oil combustion contributes about 2–6 Tg/yr to the total source [Singh and Zimmerman, 1992; Rudolph, 1995]. Plass-Dulmer et al. [1995] estimated oceanic C2H6 emission of 0.16 Tg/yr.

The steady state annual surface sources of C2H6 calculated using scheme PC3 without and with convective transport are 8.4 and 8.7 Tg, respectively, which are close to the estimates of Isaksen et al. [1985] but are lower than other reported estimates (see Table 4). Inclusion of chlorine removal of C2H6 in the troposphere increased its calculated emission from scheme PC1 (without convection) from 8.6 to 9.5 Tg/yr. Biomass burning (0.6–2.4 Tg/yr) [Ehhalt et al., 1986; Hegg et al., 1990; N. J. Blake et al., 1996], natural gas emission (1–2 Tg/yr) [Ehhalt et al., 1986; Singh and Zimmerman, 1992], and oceans (0.1–1.0
Table 4. Comparison of Calculated Global Surface Source Strengths of Light NMHCs and C₂Cl₄ With Other Estimates  

<table>
<thead>
<tr>
<th>Reference</th>
<th>C₃H₈</th>
<th>C₂H₆</th>
<th>C₂H₂</th>
<th>C₂Cl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1A¹</td>
<td>10.57</td>
<td>8.63</td>
<td>3.22</td>
<td>0.441</td>
</tr>
<tr>
<td>PC1B²</td>
<td>10.97</td>
<td>8.96</td>
<td>3.36</td>
<td>0.457</td>
</tr>
<tr>
<td>PC3A¹</td>
<td>10.35</td>
<td>8.37</td>
<td>3.14</td>
<td>0.432</td>
</tr>
<tr>
<td>PC3B²</td>
<td>10.76</td>
<td>8.70</td>
<td>3.27</td>
<td>0.448</td>
</tr>
<tr>
<td>PC3C³</td>
<td>10.14</td>
<td>8.36</td>
<td>3.13</td>
<td>0.414</td>
</tr>
<tr>
<td>PC3D³</td>
<td></td>
<td></td>
<td></td>
<td>0.449</td>
</tr>
<tr>
<td>Ehhalt et al. [1986]</td>
<td>7.6</td>
<td>4.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Rudolph [1995]</td>
<td>15.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kanakidou et al. [1991b]</td>
<td>16</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kanakidou et al. [1991b]</td>
<td>14</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blake and Rowland [1986]</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isaksen et al. [1985]</td>
<td>10</td>
<td>10</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Roemer and Hour [1991]</td>
<td>15</td>
<td>25</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Fuglestvedt et al. [1995]</td>
<td>20</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penkett [1982]</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strand and Hov [1994]</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class and Bollschmiedner [1986]</td>
<td>0.580</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wiedmann et al. [1994]</td>
<td>0.479</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Koppmann et al. [1993]</td>
<td>0.580</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rudolph et al. [1996]</td>
<td>0.420</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>McCulloch and Midgley [1996]</td>
<td>0.423 ± 0.022</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All these source strengths are given in Tg/yr.

¹ Using scheme PC1 with chlorine removal between (16.5-24.5) km and without convection.
² Using scheme PC1 with chlorine removal between (16.5-24.5) km and with convection.
³ Using scheme PC3 with chlorine removal between (16.5-24.5) km and with convection.
₄ Using scheme PC3 with chlorine removal between (16.5-24.5) km and without convection.
₅ Using scheme PC3 with no chlorine removal in entire model domain and without convection.
₆ Using scheme PC3 with chlorine removal in the lowest model layer and without convection.

Tg/yr [Plass-Dulmer et al., 1995; Singh and Zimmerman, 1992] are the main contributors to the total annual source of C₂H₆. Recently, Blake and Rowland [1995] suggested leakage from liquefied petroleum gas (LPG) as an important source of C₂H₆. Our annual surface emission of C₂H₂ calculated using scheme PC3 is 3.1 Tg which increased to 3.3 Tg due to inclusion of convective transport. These estimates are close to those of Singh and Zimmerman [1992], Ehhalt et al. [1986], and Isaksen et al. [1985]. No significant effect on total computed source strength is observed when its removal by tropospheric chlorine is included. For example, for scheme PC1 the estimates of annual source strength for C₂H₂ with and without removal by Cl radicals in the troposphere are 3.23 and 3.22 Tg, respectively. Biomass burning [Hegg et al., 1990; N. J. Blake et al., 1996] and combustion are apparently the major sources of C₂H₂ [Whithy and Atiwicker, 1978]. Oceanic emissions have also been suggested as a minor source of C₂H₂ [Kanakidou et al., 1988; Plass-Dulmer et al., 1995]. For all these light NMHCs and for all simulation cases, no difference was noted in the estimates of annual source strengths when their outgoing flux varied between two extremes, defined by f in section 4.1 at the upper boundary.

Figure 10 shows the steady state distributions of C₃H₈, C₂H₆, and C₂H₂ for the month of January. Significant presence of all these species is calculated in the model region above 10 km. In the southern hemispheric tropics, vertical profiles of these species show some inversions, that is, increase in concentration with altitude at about 5-15 km altitude that we attribute to the interhemispheric transport mechanism in the model. The extent and frequency of occurrence of these inversions were found to be completely independent of upper boundary conditions. Computed vertical profiles of C₃H₈, C₂H₆, and C₂H₂ compare quite closely to those measured by Goldman et al. [1981], Rudolph et al. [1981], Rinsland et al. [1987], and Singh et al. [1988] (not shown here). Figure 11 shows the distribution of percent change in mixing ratios of C₃H₈, C₂H₆, and C₂H₂ for the month of January due to the inclusion of convective transport which is intense in the NH summer. For all three species a small decrease (more than 2%) was calculated in the lowest 2 km in the southern hemispheric tropics due to upward movement of air with high mixing ratios of these compounds and downward movement of air from the free troposphere, which is less concentrated in these species. Because of convective transport, throughout most of the free troposphere, C₃H₈ mixing ratios increased by 5-40%, whereas for C₂H₆ and C₂H₂ the calculated increase ranges between 25-125% and 25-75%, respectively. The difference in the extent of change in mixing ratio distributions of C₃H₈, C₂H₆, and C₂H₂ for the month of January calculated using photochemical scheme PC3 and their surface observations shown in Figure 1.
C$_2$H$_4$ due to convection is entirely governed by the differences in their lifetimes and their concentrations in the PBL. For C$_2$H$_4$, because of its longer chemical lifetime, diffusion tends to smooth out the excessive gradient distribution caused by convection. Because our convective transport scheme employs seasonally averaged mass fluxes to be drawn out of the PBL and detrainment profiles, the model does not predict the increase in the mixing ratio of these species with altitude in the NH observed by N. J. Blake et al. [1996] which was likely due to episodic convective phenomena.

We have also calculated the steady state global source strength of CH$_4$ using its surface measurements. For OH fields derived from scheme PC1, the computed emission is 498 Tg/yr with steady state global lifetime of 9.74 years. The ratio of northern hemisphere to southern hemisphere surface emissions for CH$_4$ is 2.1. Addition of C$_2$ and C$_3$ hydrocarbon photochemistry decreased the total surface emission to 490 Tg/yr. Inclusion of convection to scheme PC3 increased this source strength to 500 Tg/yr. Inclusion of soil sinks of CH$_4$ and CO to scheme PC1 increased the globally averaged OH concentration and resulted in total CH$_4$ surface emission of 538 Tg/yr, of which 10 Tg/yr is due to chemical feedback between OH and CH$_4$. These estimates of CH$_4$ emission are within the range reported by Cicerone and Oremland [1988], Crutzen [1991], WMO [1994], and IPCC [1994]. Because of its long lifetime and well-mixed distribution, only a very small increase (<1.0%) in the CH$_4$ mixing ratio was calculated in the free troposphere due to convection.

### 6.2. Tetrachloroethene

Tetrachloroethene, C$_2$Cl$_4$, is a gas whose only known sources are anthropogenic, although it was suggested that it may have some natural sources from seawater algae [Abrahamsson et al., 1995]. Commercially, C$_2$Cl$_4$ is mainly used as a solvent and as a degreasing and dry cleaning agent. In the atmosphere it mainly reacts with OH radicals [DeMore et al., 1997]. Photodissociation in the stratosphere, chlorine-initiated oxidation [DeMore et al., 1997], and oceans [Pearson and McConnell, 1975] are other minor sinks of C$_2$Cl$_4$. Its global lifetime from reaction with OH radicals is about 4 to 5 months [Koppmann et al., 1993; Wang et al., 1995]. Because of its anthropogenic sources (spatially distributed similar to CFCs and MCF), and its relatively short lifetime, C$_2$Cl$_4$ has been suggested as a very useful chemical tracer for the identification of origin of sources and sinks of other trace species [Rudolph et al., 1996; Singh et al., 1996a, b] and for transport mechanisms. Because of its higher sensitivity toward OH radicals, relative to MCF, C$_2$Cl$_4$ can be a better indicator of seasonal changes in OH concentration, as suggested by Wang et al. [1995]. Using C$_2$Cl$_4$, Rudolph et al. [1996] and Singh et al. [1996c] estimated an upper limit for average tropospheric chlorine radical concentration of the order of $(10^2-10^3)$ molecules cm$^{-3}$. Oxidation of C$_2$Cl$_4$ contributes about 12% to the total production of atmospheric phosgene [Kindler et al., 1995] and 0.5% to the total tropospheric organochlorine [Wang et al., 1995]. Several groups have reported remote surface concentrations of C$_2$Cl$_4$ [Pearson and McConnell, 1975; Crutzen and Ballaschmittler, 1986; Koppmann et al., 1993; Wiedmann et al., 1994; Wang et al., 1995].

Here we used the seasonally varying surface mixing ratios of C$_2$Cl$_4$ for 1989-1990 of Wang et al. [1995]. Using the monthly varying OH radical distribution derived from scheme PC3 and the surface observations, latitudinally varying monthly surface removal rates of C$_2$Cl$_4$ are calculated as shown in Figure 12. For this simulation the only sinks of C$_2$Cl$_4$ considered are OH radicals for the entire model domain and Cl radicals for the model region between 16.5 and 24.5 km. The calculated annual steady state source strength of C$_2$Cl$_4$ is 432 kT with a north to south ratio of 7.5. Of this total chemical loss, about 5% occurs between 16.5 and 24.5 km from chlorine radicals. The steady state corresponding global lifetime of C$_2$Cl$_4$ is 3.9 months. This calculated annual source strength differs significantly from 580 kTyr estimated by Class and Ballaschmittler [1986] and Koppmann et al. [1993] (see Table 4) and 480 kT/yr estimated by Rudolph et al. [1996]. For 1990, Fisher et al. [1994] estimated 358 kT for global emissions of C$_2$Cl$_4$ and speculated that an additional 100 kT/yr of C$_2$Cl$_4$ emissions could come from residue processes in developing nations. For the present calculations, latitudinal belts of (30°-60°)N and (20°N-20°S) account for 62 and 24% of its global annual source strength. About 73 kT of the total annual NH source of 381 kT is transported to the SH where it is chemically destroyed, with a maximum amount (11 kT) during January. In steady state the annual SH C$_2$Cl$_4$ sink strength is 124 kT.

The calculated annual source strength of C$_2$Cl$_4$ is very close to the estimated anthropogenic emission strength averaged for 1989 and 1990. According to McCulloch and Midgley [1996], for 1989 and 1990, the global industrial source strengths of C$_2$Cl$_4$ are (423 ± 22) kT and (366 ± 19) kT, respectively. Of this total...
strength they estimated about 3–4 kT emissions of C$_2$Cl$_4$ from the SH. For this estimate to be correct, our model calculation indicates that about 47 kT additional sources of C$_2$Cl$_4$ from the SH are needed to satisfy the southern hemispheric mass balance in the steady state. To some extent, this conclusion may depend upon the model structure, chromatographic artifacts, data treatment for the observed surface mixing ratios of C$_2$Cl$_4$, and its rate of reaction with OH radicals. There are two possibilities for this required additional source of C$_2$Cl$_4$. Either other industrial sources are missing or there are unidentified sources of C$_2$Cl$_4$. So far, oceans have been suggested as a natural source [Abrahamsson et al., 1995; Singh et al., 1996c]. Singh et al. [1996c] estimated 35 kT/yr, with an upper limit of 70 kT/yr, as the global oceanic source strength of C$_2$Cl$_4$. Following the speculation of Fisher et al. [1994], some fraction of this missing emission of C$_2$Cl$_4$ might come from developing countries.

Inclusion of chlorine oxidation of C$_2$Cl$_4$, which at 288 K is 270 times faster than that due to its reaction with OH radicals, in the MBL (assumed to be the lowest model layer) increased the calculated source strength by 17 kT/yr. Adding convective transport to schemes PC1 and PC3 resulted in total calculated annual strengths of 457 and 448 kT, respectively. Owing to its primary emissions in the NH and relatively short lifetime, C$_2$Cl$_4$ is most concentrated there, as is evident from its surface measurements (Figure 1) and the simulated distribution using scheme PC3 shown in Figure 13 for the month of July. The calculated mixing ratios of C$_2$Cl$_4$ for most of the NH at 13 km range between 3 and 4 ppt, whereas, for the entire SH, C$_2$Cl$_4$ mixing ratios are always lower than 3 ppt. Similar to light NMHCs, inclusion of convective transport decreased the C$_2$Cl$_4$ mixing ratios by 1% in the lowest 2 km around 20°N and increased its mixing ratios by 10–20% in most of the free northern hemispheric troposphere, as shown in Figure 13.

7. Seasonal Nature of Surface Sources of Light NMHCs

Wang et al. [1995] suggested that C$_2$Cl$_4$ could be a sensitive chemical tracer to examine the seasonal amplitude in the hemi-
spherically averaged OH concentration because major sources of C₂Cl₄ are industrial, while it is primarily destroyed by OH radicals. Moreover, OH radicals are the main sink of surface-emitted light NMHCs which, as shown in section 6, are mostly (>80%) emitted in the NH. Using this information and the conclusion of McCulloch and Midgley [1996] that industrial sources of C₂Cl₄ are seasonally independent (and assuming that the calculated minor oceanic source of C₂Cl₄ is also seasonally independent), we have attempted to estimate seasonality in the source strengths of relatively short-lived species C₂H₆, C₃H₈, and C₂H₂. Of these species, C₂H₆ is the longest-lived, and its steady state global lifetime is about one fourth of the model interhemispheric exchange time.

To achieve this objective, we simulated the steady state atmospheric distributions of light NMHCs and C₂Cl₄ using photochemical scheme PC3 (without convection) and their deduced annual source strengths (applied equally per time step) and latitudinal distributions, as described in previous sections, as their lower boundary conditions. For all 12 months the observed and simulated surface mixing ratios of C₂H₆, C₃H₈, C₂H₂, and C₂Cl₄ were hemispherically averaged. For each species the ratios of hemispherically averaged simulated and observed mixing ratios, denoted as S/O, were calculated. For all four species this ratio was found to be different from 1.0, as shown in Table 5. For C₂Cl₄, for the NH during the months of June–October and for the SH during July–October, the ratio S/O exceeded 1.0. Over 1 year, for the northern and southern hemispheres, this ratio varied between 0.79–1.40 and 0.82–1.22, respectively.

In addition to variations in emissions, the observations reflect all dynamical and chemical factors which determine the concentration of a species. Our simulations considered only constant emissions throughout the year in addition to the monthly changes in the interhemispheric exchange rate and OH concentration. Therefore the calculated deviation in values of S/O for C₂Cl₄ from 1.0 should arise from the model's inability to accurately generate the seasonal variations in OH concentration in both hemispheres and interhemispheric exchange. In general, the model has reproduced the general features of OH distributions which, in addition to transport features, have been shown to simulate the observed distributions, north-south gradients, and trends of CFC-11, CFC-12, and MCF. Because both of these factors, that is, seasonal variations in OH concentration in both hemispheres and interhemispheric exchange, are equally applicable to C₂Cl₄ and light NMHCs, the calculated deviation in S/O for C₂Cl₄ from 1.0, which will have most contribution due to seasonal variations in OH because of its short lifetime (more than 3 times smaller) as compared to the model interhemispheric exchange time, can be used for each month to normalize the S/O ratios for light NMHCs. This normalization of S/O for light NMHCs with respect to S/O of C₂Cl₄ will cancel the effects of both the factors mentioned before. Therefore any deviation in these normalized ratios for light NMHCs from 1.0 will reflect the seasonality in their sources. This approach should be the most accurate for the NMHCs whose atmospheric lifetime is closest to that of C₂Cl₄, that is, C₂H₆, and semiquantitative for other NMHC species. Figure 14 shows the monthly variations in surface source strengths of light NMHCs obtained after multiplying their monthly source strengths with their respective normalized S/O ratios. The calculation shows that emissions of C₂H₆ should be higher than average for the months of August–January in the NH and for July–November in the SH, with maximum amounts during September (0.9 Tg for NH and 0.2 Tg for SH). Emissions of C₂H₂ should be higher than average for the months of September–March in the NH and for August–January in the SH, with maximum amounts during November (0.9 Tg) for the NH and during September (0.2 Tg) for the SH. Similarly, C₂H₂ emissions should be higher than average for the months of September–January in the NH and for August–February in the SH, with maximum amounts during November (0.3 Tg) for the NH and during December (0.1 Tg).

**Table 5.** Ratio (S/O) of Hemispherically Averaged Simulated Steady State Surface Concentrations of Light NMHCs and C₂Cl₄ Using Equal Surface Sources Throughout the Year to Their Corresponding Observed Concentrations.

<table>
<thead>
<tr>
<th>Month</th>
<th>C₂Cl₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₂H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH</td>
<td>SH</td>
<td>NH</td>
<td>SH</td>
</tr>
<tr>
<td>Jan.</td>
<td>0.82</td>
<td>0.91</td>
<td>0.81</td>
<td>0.94</td>
</tr>
<tr>
<td>Feb.</td>
<td>0.79</td>
<td>0.97</td>
<td>0.82</td>
<td>1.02</td>
</tr>
<tr>
<td>March</td>
<td>0.82</td>
<td>0.95</td>
<td>0.90</td>
<td>1.04</td>
</tr>
<tr>
<td>April</td>
<td>0.92</td>
<td>0.87</td>
<td>1.03</td>
<td>1.04</td>
</tr>
<tr>
<td>May</td>
<td>1.00</td>
<td>0.82</td>
<td>1.16</td>
<td>1.07</td>
</tr>
<tr>
<td>June</td>
<td>1.07</td>
<td>0.88</td>
<td>1.19</td>
<td>1.07</td>
</tr>
<tr>
<td>July</td>
<td>1.17</td>
<td>1.04</td>
<td>1.16</td>
<td>1.03</td>
</tr>
<tr>
<td>Aug.</td>
<td>1.40</td>
<td>1.22</td>
<td>1.22</td>
<td>0.95</td>
</tr>
<tr>
<td>Sept.</td>
<td>1.37</td>
<td>1.22</td>
<td>1.10</td>
<td>0.90</td>
</tr>
<tr>
<td>Oct.</td>
<td>1.07</td>
<td>1.03</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>Nov.</td>
<td>0.92</td>
<td>0.89</td>
<td>0.78</td>
<td>0.88</td>
</tr>
<tr>
<td>Dec.</td>
<td>0.86</td>
<td>0.84</td>
<td>0.78</td>
<td>0.88</td>
</tr>
</tbody>
</table>

**Figure 14.** Calculated monthly variations in the hemispheric emissions of C₂H₆, C₃H₈, and C₂H₂ for case PC3A shown in Table 4.
for the SH. These conclusions were unaffected by uniformly changing the surface mixing ratio of C₂Cl₄ by ±25% and introducing the convective transport and repeating the same exercise. To some extent, these conclusions may be affected by the problems associated with background air sampling, the ways that the raw observed data were treated and the hemispheric averaging was performed, and by chromatographic artifacts.

8. Summary

In the present study, we have calculated the global surface removal rates and corresponding latitudinal distributions for CH₄, C₂H₆, C₃H₈, C₂H₂, and C₂Cl₄ using surface measurements from all seasons. The distribution of OH radicals, the primary sink of these hydrocarbons, is photochemically computed using detailed photochemical schemes. For the methane-only model (PC1) the global and annual average OH concentration is 1.0 x 10⁸ molecules cm⁻². Annually averaged OH concentrations are found to be higher in the SH which is consistent with some previous studies. Addition of soil sinks for CO and CH₄ and inclusion of NMHC chemistry to photochemical scheme PC1 have significant effects on the global and regional distributions of OH radical and its interhemispheric concentration ratios. Nighttime OH radical concentrations in the upper troposphere are explicitly due to the interhemispheric transport feature and not from effects of the upper stratosphere and lower stratosphere. Modeled increases in the upper troposphere are found to be only 40–80 times lower than the daytime maximum value. In the upper troposphere, nighttime OH concentrations drop to almost zero. This difference in diurnal variations in the OH concentration at different altitudes is due to the concentration of HO₂ radicals and their rapid recycling with O₃ and HO₂NO₂.

The annual surface emissions of CH₄, C₂H₆, C₃H₈, C₂H₂, and C₂Cl₄ calculated using the nonconvective scheme PC3 are 490 Tg, 10.4 Tg, 8.4 Tg, 3.1 Tg, and 432 kT, respectively. Inclusion of the convective scheme increased these emission estimates by 2.0, 4.0, 3.9, 4.1, and 3.7%, respectively. For NMHCs and C₂Cl₄ these emissions show distinct latitudinal variations. Because of their relatively short lifetimes compared to the 1 year interhemispheric exchange time, the calculated higher north to south ratios of total emissions of all three NMHCs (which range between 4.0 and 4.7) and C₂Cl₄ (7.5) clearly indicate that more than 80% of their global annual sources originated from the NH. Given the industrial emissions of C₂Cl₄ for the southern hemisphere, estimated by McCulloch and Midgley [1996], our calculations indicate that as much as 47 kT of additional southern hemispheric source of C₂Cl₄ is needed for 1989–1990 to attain its steady state mass balance in this region. Because of relatively long lifetimes, these NMHCs and C₂Cl₄ show significant presence in the upper troposphere and lower stratosphere. Modeled increases in southern tropical mixing ratios of these species with altitude in the upper troposphere are explicitly due to the interhemispheric transport feature and not from effects of the upper boundary condition. The calculated atmospheric distributions of NMHCs and C₂Cl₄ are shown to be strongly affected by convective transport.

With the use of C₂Cl₄, which has sources independent of season and also has similar atmospheric chemical sinks as those for NMHCs, the comparison of observed surface mixing ratios of NMHCs with the corresponding modeled surface mixing ratios (calculated using uniform surface emissions throughout the year as the lower boundary condition) indicates that the sources of these species may be seasonal in nature. Over a year, northern hemispheric emissions for C₂H₆, C₃H₈, and C₂H₂ for the months of August–January, September–March, and September–January, respectively, are more than the monthly average emissions.

In future studies we will use these calculated emissions of hydrocarbons to examine the effects of perturbations due to anthropogenic and natural sources of various gases on tropospheric chemical nonlinearity and on the distribution and budgets of key chemical species such as O₃, CO, NOₓ, HOₓ, and CH₄.

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