Ozone destruction and production rates between spring and autumn in the Arctic stratosphere


Abstract. In situ measurements of radical and long-lived species were made in the lower Arctic stratosphere (18 to 20 km) between spring and early autumn in 1997. The measurements include O3, ClO, OH, HO2, NO, NO2, N2O, CO, and overhead O3. A photochemical box model constrained by these and other observations is used to compute the diurnally averaged destruction and production rates of O3 in this region. The rates show a strong dependence on solar exposure and ambient O3. Total destruction rates, which reach 19%/month in summer, reveal the predominant role of NOx and HOx catalytic cycles throughout the period. Production of O3 is significant only in midsummer air parcels. A comparison of observed O3 changes with destruction rates and transport effects indicates the predominant role of destruction in spring and an increased role of transport by early autumn.

Introduction

Measurements of a wide range of reactive and long-lived species were obtained in the lower stratosphere using the NASA ER-2 high-altitude research aircraft as part of the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) project in 1997. POLARIS was designed to explore the decrease of O3 that occurs between spring and autumn at northern high latitudes [Newman et al., 1999; Fahey and Ravishankara, 1999]. Ozone destruction and production rates in sampled air masses are calculated using a photochemical box model constrained by the available in situ and remote observations.

O3 destruction and production processes

Stratospheric O3 abundances represent a balance between destruction and production processes and transport. The reactions listed in Table 1 represent the principal chemical processes controlling O3 production and destruction in the lower summer stratosphere [Nevison et al., 1999; Lary et al., 1997]. Ozone is destroyed in catalytic cycles involving nitrogen, hydrogen, chlorine, and bromine species and in reaction with O atoms. Ozone production occurs primarily through oxygen photolysis (R14). Production terms from CO and CH4 oxidation are small and are neglected here. The destruction and production terms associated with the processes in Table 1 are grouped in Table 2. The grouping by reactive family is not unique since some catalytic cycles involve reactive species from more than one family. The terms use [X] for the concentration of species X, ki for the kinetic rate coefficient of R i, and Ci for branching terms. The O3 destruction and production rates for an air parcel are obtained by integration of the terms in Table 2 over a diurnal cycle. In addition to rate coefficients and pressure, the integration requires the diurnal abundances of 12 species: OH, HO2, NO, NO2, ClO, BrO, ClONO2, BrONO2, O, O2, O3, and CO.

Observed and derived parameters

Measurements provided by instruments on board the ER-2 aircraft are used directly and indirectly to constrain a photochemical box model and the integration of diurnal O3 change. Those used here are NO, NO2, OH, ClO, CIO, O3, NOy, N2O, halon-1211, CFC-11, SF6, surface area (SA) of background sulfate aerosol, overhead O3 column, effective surface reflectivity, pressure (P), temperature (T), latitude, longitude, and measurement time. The source and uncertainty for most of these in situ measurements are described elsewhere [Del Negro et al., 1999; Gao et al., 1997; Herman et al., 1999]. An air parcel is defined by a 100s average measurement along the flight track when the solar zenith angle (SZAs) is less than 83ø. The full diurnal dependences of OH and CIO are estimated for each air parcel by scaling the SZA relationships in Wennberg et al. [1994] to the respective air parcel measurement.

Photolysis rate coefficients for an air parcel are available from two independent calculations [Salawitch et al., 1994; Swartz et al., 1999]. Both calculations use a spherical, isotropic multiple-scattering model of the atmospheric radiation field, incorporating photolysis cross-sections, observed overhead O3 (column amount above the aircraft), and surface reflectivity. Changes in overhead O3 vary from climatological values along the flight track, significantly affecting the local radiation field. The j values calculated for POLARIS generally show good agreement (+15%) with each other [Del Negro et al., 1999]. Values of j15, O3, and pressure are combined to calculate the diurnal dependence of O atoms using the steady state relation [O] = j15[O3]/[K15(O3)[M]]

A diurnal photochemical box model is used here to calculate the diurnal dependence of NO2, HO2, ClONO2, BrONO2, and
Table 1. Reactions used in diurnal integration of O3 change.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant</th>
</tr>
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<tbody>
<tr>
<td>OH + O3 → HO2 + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>H2O + O3 → HO2 + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>ClO + O3 → Cl + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>BrO + O3 → Br + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>NO2 + O3 → NO + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>NOx + O3 → NO + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>Cl + O3 → ClO + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>Br + O3 → BrO + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>NO2 + O3 → NO + O2</td>
<td>1.0</td>
</tr>
<tr>
<td>NOx + O3 → NO + O2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

BrO. The model includes the NOx interconversion reactions as used by Guo et al. [1999] to simulate the NOx/NOy ratio in POLARIS. All rate coefficients are from DeMore et al. [1997] except for the Cl + O3 reaction. The model is constrained by measured ClO, the diurnal dependence of OH, and constant values of O3, SA, Br, and T. The model is initialized with measured NO and NOy and with approximate steady state values of NO2, CINO2, HNO3, HO2, and BrO. Good agreement has generally been found between measured and steady state values of NO2, CINO2, and HO2 in the lower stratosphere [Del Negro et al., 1999]. Diurnally averaged destruction rates increase with SE as shown in Figure 2 for the data in Figure 1. The positive correlation of the rates with O3 at constant SE is intriguing feature of the entire POLARIS data set. A similar correlation is also found separately in each phase. Underlying this correlation are the overall positive correlations of the day-to-night SE changes with those in the more extensive satellite data sets [Rosenlof, 1999]. Continuous exposure of stratospheric air parcels causes NO2 production to cease because NO3, the intermediate in the production of NO2, is rapidly photolyzed.

After NO2, HO2 cycles are the next largest contributor (20 – 40%) to O3 destruction rates in all phases. The largest contributions are from the Cl/Br and O cycles which sum to about 20% in the spring and midsummer and slightly more in early autumn. The average mixing ratios of HO2, CINO2, and BrO are all less than 0.03 ppbv and significantly less than NO2 values (panel G – I). The largest absolute values of the HO2 and Cl/Br radicals and their largest contribution to O3 destruction occur in early autumn. This is consistent with minimum values of NO2 observed in late summer because NO2 moderates the abundance of these species [e.g. Nevison et al., 1999; Wennberg et al., 1994].

Forced increases in NO2 at constant NO do not proportionately increase modeled O3 loss in the high-latitude summer stratosphere because of the NO3 moderating effect on the other loss cycles [Nevison et al., 1999]. Continuous exposure of stratospheric air parcels causes NO2 production to cease because NO3, the intermediate in the production of NO2, is rapidly photolyzed.

The decrease in O3 values in the POLARIS aircraft data set (60 – 70°N, 18-20 km) are very consistent (absolute values and month-to-month changes) with those in the more extensive satellite data sets [Rosenlof, 1999] and with the sondes/satellite climatology for 1988 to 1996 [Logan and McPeters; 1999]. Average O3 values for 18 – 20 km for the month pairs April-May, June-July, and August-September are 2.6, 2.1, and 1.9 parts per million by volume (ppmm), respectively, from POLARIS and 2.4, 1.9, and 1.8 ppmm, respectively, from the climatology. The O3 decreases in the aircraft data set are proportionately similar to...
Phase 1, April 22 - May 13
Phase 2, June 26 - July 7
Phase 3, September 8 - 23

Figure 1. Observational data and results of the photochemical box model calculations as a function of northern latitude for the three phases of POLARIS. The total destruction rate is offset by the production rate to obtain the net destruction rate. Data are averages of sampled air parcels found in 5° latitude bins for ambient pressures between 50 and 80 hPa (~ 18 – 20 km). The number of flights and 100s data points included in each phase are, respectively, 9 and 600; 4 and 590; 6 and 530. More than one-half of the data points are obtained between 60°N and 70°N latitude in each phase. The lines in panels (D-F) are the calculated 1-day (thick-dashed) and 5-day (thin-dashed) solar exposure (SE) factors. Panels (D-F) represent the fractional contribution of the destruction processes in Table 2 to the total destruction rates. Panels (G-I) show the calculated daytime average mixing ratio of key radical species as used in the box model. Panels (J-L) show average observed O₃ and NOy. The vertical bars show the sample variance in each latitude bin for the respective parameters. Ozone values are expressed as parts per million by volume (ppmv).

decreases in the associated O₃ column amounts [Newman et al., 1999].

The net chemical destruction rates in Figure 1 for 60 – 70°N have been compared with observed O₃ changes and those inferred from modeled transport terms [Rosenlof, 1999]. In spring and midsummer the net destruction rates and observed rates of change (%/month) are very similar. In early autumn the net chemical destruction rate exceeds the observed rate of change. Transport processes are found to increase O₃ more strongly in early autumn than spring. A quantitative comparison indicates that spring and midsummer O₃ changes are dominated by chemical destruction whereas transport dominates in early autumn. Independent evidence for the predominant role of chemically induced O₃ changes in spring and summer comes from analysis of the O₃/HF column abundance ratios [Toon et al., 1999] and fractal analysis of the O₃ data time series [Tuck et al., 1999].

Summary and conclusions
In situ observations of radical and long-lived species made in the lower Arctic stratosphere (18 – 20 km) between spring and autumn of 1997 were combined with a photochemical box model to calculate total and net O₃ destruction rates. The rates are 10 – 20%/month in spring and midsummer, decreasing to near 5%/month in early autumn. Production of O₃ plays a significant role only in the Arctic summer period. The results show the predominance of the NOx catalytic cycle over the HOx and ClO/BrO cycles, arising from enhanced solar exposure. The

Figure 2. Total O₃ destruction rates from Figure 1 plotted versus observed O₃ in ppmv. The data points are 100s averages with the 1-day SE value indicated by the color legend.
destruction rates increase with solar exposure and ambient O_3 throughout the data set. A comparison with transport calculations show that chemical O_3 destruction predominates over transport effects in spring and that transport and chemical O_3 changes are more comparable in late summer/early autumn. Ozone destruction rates and transport processes are both altitude dependent. Hence, the results presented here may not be generalized to lower or higher altitudes. These results provide an observationally based reference point for the continued evaluation of observed spring/summer O_3 changes and of atmospheric models used to calculate present and future abundances of stratospheric O_3.

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References


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