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Journal

ISSN

Authors

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Publication Date

DOI

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Peer reviewed

Trace chemical measurements from the northern midlatitude lowermost stratosphere in early spring: Distributions, correlations, and fate

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Abstract. In situ measurements of a large number of trace chemicals from the midlatitude (37-57°N) lower stratosphere were performed with the NASA DC-8 aircraft during March 1994. Deepest penetrations into the stratosphere (550 ppb O_3, 279 ppb N_2O, and 350 K potential temperature) corresponded to a region that has been defined as the "lowermost stratosphere" (LS) by *Holton et al.* [1995]. Analysis of data shows that the mixing ratios of long-lived tracer species (e. g. CH_4, HNO_3, NO_y, CFCs) are linearly correlated with those of O_3 and N_2O. A $\Delta NO_y/\Delta O_3$ of 0.0054 ppb/ppb and $\Delta NO_y/\Delta N_2O$ of -0.081 ppb/ppb is in good agreement with other reported measurements from the DC-8. These slopes are however, somewhat steeper than those reported from the ER-2 airborne studies. We find that the reactive nitrogen budget in the LS is largely balanced with HNO_3 accounting for 80% of NO_y, and PAN and NO_x together accounting for 5%. A number of oxygenated species (e. g. acetone, H_2O_2) were present and may provide an important in situ source of HO_x in the LS. SO_2 mixing ratios were found to increase in the stratosphere at a rate that was comparable to the decline in OCS levels. No evidence of particle formation could be observed. Ethane, propane, and acetylene mixing ratios declined rapidly in the LS with Cl atoms likely playing a key role in this process. A number of reactive hydrocarbons/halocarbons (e. g. C_6H_6, CH_3I) were present at low but measurable concentrations.

Introduction

PEM-West (B) was an airborne experiment performed in the February/March of 1994 to primarily study the composition and chemistry of the troposphere over the western/central Pacific in the northern hemisphere (NH). The DC-8 airborne platform was instrumented to measure important reactive nitrogen species (NO_x, NO_y, PAN, HNO_3), O_3, C_1 to C_7 hydrocarbons, sulfur species, peroxides, organic acids, chemical tracers (CO, N_2O, halocarbons), and meteorological parameters [*Hoell et al.*, 1996a]. Due to the relatively low mean tropopause heights at northern midlatitudes in this season and the presence of stratospheric intrusions, it was frequently possible to sample air from the lower stratosphere at a level of detail that has not been possible before. The design of the experiment was such that all of the stratospheric sampling

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occurred in March. Here we present these data and provide a comparison with previously available information when possible. Measurement methods are not described here as these can be found in the published literature [*Hoell et al.*, 1996a, b and references there in; *Kondo et al.*, 1996a].

Results and Discussion

To focus on the stratosphere, PEM-West (B) data were selected for conditions of frost point < -60°C and O_3 > 100 ppb. Potential temperature of 310-350 K would place these measurements in the region defined by *Holton et al.* [1995] as the "lowermost stratosphere" (LS). All of the data were from 37-57°N latitudes and 8-12 km altitudes over the Pacific. Tropopause levels north of 40° were in the vicinity of 7-9 km. This subset captured all of the stratospheric data including the upper troposphere (UT)/LS transition. Deepest stratospheric penetrations corresponded to 550 ppb O_3 and 279 ppb N_2O. Data were plotted and interpreted as a function of O_3 and N_2O;
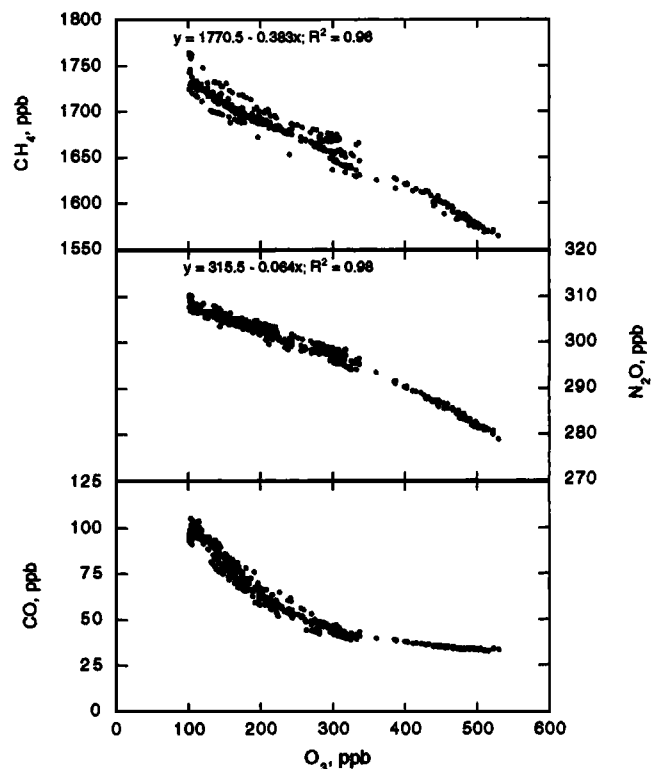
Figure 1. Methane, N_2O, and CO mixing ratios as a function of O_3 in the lowermost stratosphere. In this and subsequent figures data were selected for conditions of frost point < -60 °C and O_3 > 100 ppb. Linear fits of mixing ratios noted in the Y-axis (y) as a function of O_3 (x) are listed where appropriate.

Figure 2. Distribution of reactive nitrogen species as a function of O_3 in the lowermost stratosphere. NO_x is defined as the sum of NO (measured) and NO_2 (calculated).

two traditional reference coordinates for the stratosphere [*Loewenstein et al.*, 1993; *Murphy et al.*, 1993]. Linear relationships between mixing ratios of long-lived chemicals as a function of N_2O (Table 2) and O_3 (Figures 1-4) have been explored. A summary of the measured concentrations of a large number of chemicals in the LS is provided in Table 1, and in order to exclude the UT transition region a more stringent cut off ($O_3 > 200$ ppb; frost point $< 60°C$) is used.

Methane, N_2O and CO

To provide some reference to previously published data, we show a plot of CH_4, N_2O and CO mixing ratios as a function of O_3 in Figure 1. Both CH_4 and N_2O show linear decline ($R^2=0.96$) as a function of O_3 as expected for long-lived species [Plumb and Ko, 1992]. The CH_4-N_2O slope (ppb/ppb) of 5.9 can be compared with slopes of 4.7-5.3 reported in the literature (Table 2). O_3 vs. N_2O correlations have been studied extensively based on data collected from the high altitude (≤ 21 km) ER-2 platform [*Proffitt et al.*, 1992; *Murphy and Fahey*, 1995; *Volk et al.*, 1996] and with the DC-8 in the Arctic when the tropopause is very low [*Collins et al.*, 1993]. Based on a number of DC-8/ER-2 measurements, typical O_3-N_2O slopes (ppb/ppb) are in the range of -20 to -23 [*Collins et al.*, 1993; *Volk et al.*, 1996]. However, *Collins et al.* [1993] report a slope of -15.8 for the month of March during AASE II and
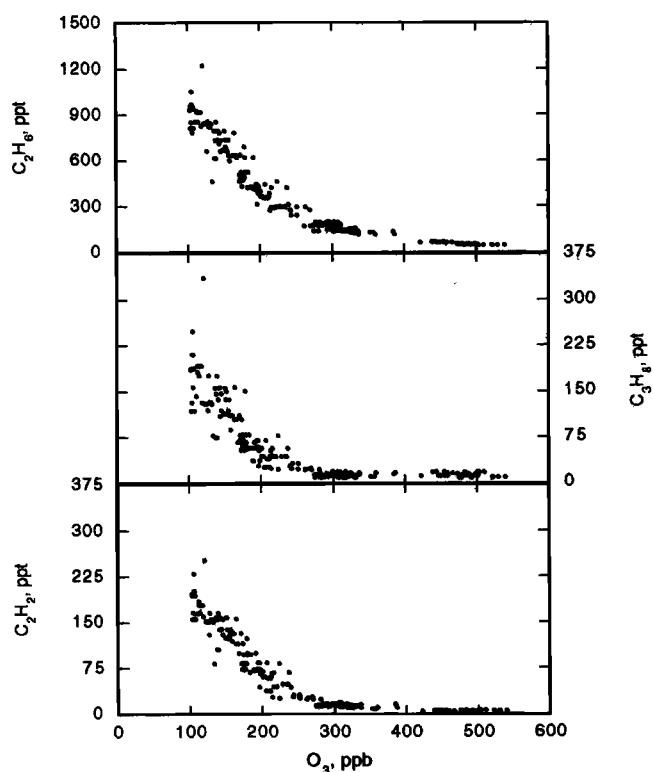
attribute this change to O_3 loss in the Arctic stratosphere. A comparable March slope of -15.3 found in this study (Table 2), implies that such depletions may influence the atmosphere all the way to the midlatitudes. An alternate explanation is that the air in this LS region is mixed with air from the tropical UT that contains much less O_3 relative to N_2O [*Holton et al.*, 1995].

Reactive Nitrogen

Figure 2 shows a plot of the distribution of key reactive nitrogen species as a function of O_3. This is the first time that most of the major reactive nitrogen component species have been simultaneously measured in the stratosphere. The linearity of the NO_y vs. O_3 (and N_2O) is well known in the stratosphere. The NO_y-O_3 slope of 0.0054 ppb/ppb (Figure 2) and NO_y-N_2O slope of -0.081 ppb/ppb (Table 2) is in good agreement with the DC-8 measurements from the Arctic [*Weinheimer et. al.*, 1993]. However, these are steeper than the corresponding slopes of 0.003-0.004 and - 0.06-0.07 that have been reported from a variety of ER-2 studies [*Murphy et al.*, 1993; *Loewenstein et al.*, 1993; *Kondo et al.*, 1996b; *Volk et al.*, 1996]. Recent unpublished data from STRAT (M. Loewenstein, private comm., 1996) show that at midlatitudes these slopes are virtually unchanged with season. Although the ER-2 measurements extend deeper into the stratosphere, an inspection of these data suggest that the slope is unchanged when restricted to the LS only. Thus differences in altitudes sampled is not a main cause of these disagreements. Instrument
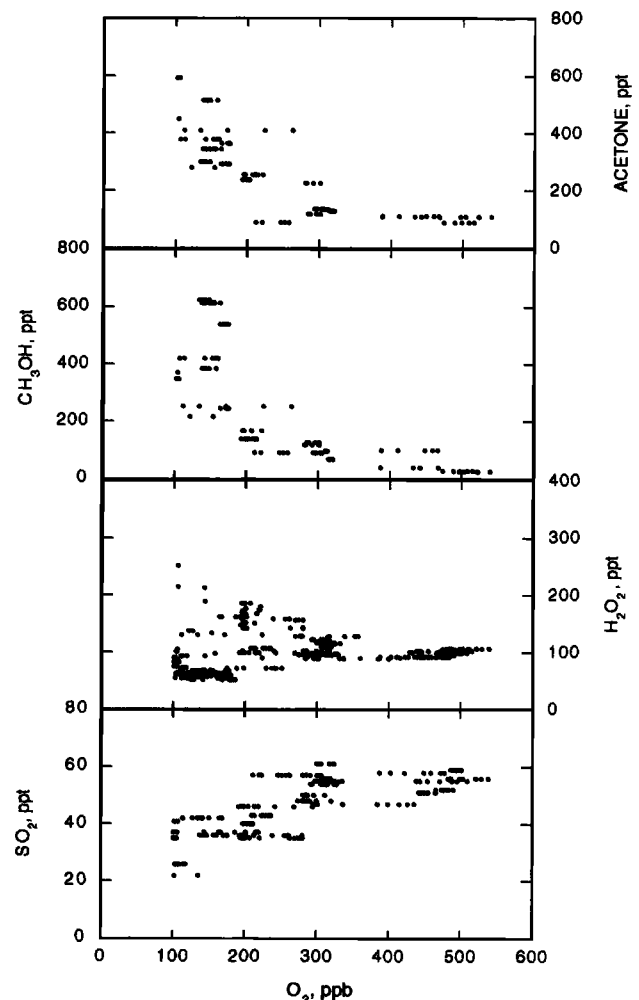
Figure 3. Distribution of acetone, CH_3OH, H_2O_2 and SO_2 as a function of O_3 in the lowermost stratosphere.

Figure 4. Distribution of C_2H_6, C_3H_8 and C_2H_2 as a function of O_3 in the lowermost stratosphere.

appears that the LS reactive nitrogen budget is reasonably well balanced with HNO_3 accounting for nearly 80% of the NO_y.

Oxygenated Species

Figure 3 shows these distributions for several oxygenated species as a function of O_3. Acetone and H_2O_2 are important sources of HO_x in the UT/LS [Singh et al., 1995]. Acetone concentrations of about 100 ppt in the LS are in reasonable agreement with the data reported by Arnold et al. [1986], although substantial disagreement in the UT exist. Our model calculations suggest that 100 ppt of acetone in the LS ($\approx$12 km) can provide a HO_x source that is >5 times that due to the O (^{1}D) + H_2O reaction presently included in most models. We were unable to find any published H_2O_2 measurements from the LS, although concentrations at altitudes above 20 km have been deduced from satellite data [Park and Carli, 1991]. H_2O_2 LS mixing ratios of 100 ppt are probably an upper limit due to the possibility of positive interferences at high O_3 levels (B. Heikes, private comm.). Methylhydroperoxide was generally below its detection limit of 20 ppt. Formic and acetic acids were also measured with the former below its detection limit of 20-30 ppt (Table 1). Acetone photolysis followed by reaction of peroxyacetyl radicals with HO_2 ($CH_3CO_3+HO_2\rightarrow$ $CH_3COOH+O_3$) is a possible in situ source of the LS acetic acid.

uncertainties are a likely potential cause. The NO_y effective yield of 8% from N_2O is consistent with the notion that N_2O oxidation via reaction with O (^{1}D) is the major source of stratospheric NO_y and these correlations are dictated by stratospheric dynamics [Plumb and Ko, 1992]. Murphy and Fahey [1995] have used the NO_y-N_2O correlation to estimate the stratospheric flux of NO_y into the troposphere. This steeper slope would have the net effect of increasing this estimate by $\approx$25% thus bringing it more in line with other studies.

It is further evident from Figure 2 that independently measured HNO_3 behaves in a manner similar to NO_y with a HNO_3-O_3 slope (ppb/ppb) of 0.006. There are few such specific HNO_3 measurements available from the LS. In a recent winter Arctic study Bregman et al. [1995] report HNO_3-O_3 slopes that are comparable to this outside the polar vortex and nearly twice as large inside the vortex. In a subsequent study at midlatitudes in May 1996, Bregman and co-workers (private comm.) find HNO_3-O_3 slopes of 0.005-0.007, in excellent agreement with this study. PAN (peroxyacetyl nitrate) was present at relatively high concentrations in the UT ($\approx$ 200 ppt) and continued to decline approaching 20 ppt at the deepest stratospheric penetrations. NO_x [NO (measured) + NO_2 (calculated)] levels did not show a consistent trend and remained in the 25-100 ppt range. PAN has a relatively long lifetime in the LS because it reacts negligibly with OH and Cl and its photolysis is also slow. Diffusion from the UT and synthesis from acetone photolysis and ethane/propane oxidation likely provide the major source here [Singh et al., 1995]. Data from Table 1 shows that HNO_3, PAN and NO_x together can account for nearly 85% of the measured NO_y. Thus only about 15% ($\approx$300 ppt) of reactive nitrogen is unaccounted for. It is expected that HNO_4 levels of 25-50 ppt along with smaller quantities of N_2O_5 and $ClONO_2$ are probably present in the LS [Singh and Kasting, 1988]. In addition positive nitrile (HCN, CH_3CN) interferences of $\approx$20 ppt [Kondo et al., 1996a] and $\approx$80 ppt (J. Bradshaw; private comm.) may exist in the NO_y measurement. Thus it

Table 1. Mixing ratios of trace constituents in the lowermost stratosphere (O_3> 200 ppb; frost point < -60°C)

Chemical (Mixing ratio unit)*	Mixing ratios mean±σ (median, n)
CH_4 (ppb)	1642.3±39.7 (1656.2, 255)
O_3 (ppb)	334.4±96.5 (306.8, 301)
N_2O (ppb)	294.1±7.0 (297.2, 252)
CO (ppb)	44.5±9.1 (43.4, 254)
NO_y (ppt)	1883.3±532.8 (1736.6, 244)
NO (ppt)	27.2±18.6 (21.0, 244)
NO_x (ppt)	52.1±31.5 (40.7, 95)
HNO_3 (ppt)	1511.2±677.9 (1266, 226)
PAN (ppt)	42.3±19.2 (38.7, 145)
Acetone (ppt)	152.9±73.6 (130, 61)
CH_3OH (ppt)	94.2±49.2 (97, 61)
H_2O_2 (ppt)	107.8±20.1 (103, 241)
CH_3COOH (ppt)	25.4±26.3 (28, 267)
C_2H_6 (ppt)	170.3±102.8 (146.4, 136)
C_3H_8 (ppt)	19.0±13.4 (13.2, 136)
C_2H_2 (ppt)	19.9±18.1 (13.3, 133)
C_2H_4 (ppt)	4.5±1.6 (3.8, 127)
C_6H_6 (ppt)	2.9±2.1 (3.6, 136)
SO_2 (ppt)	50.4±7.7 (54, 193)
OCS (ppt)	429.8±4.8 (427, 45)
Aerosol (#/cm³)	84.5±33.1 (74.1, 183)
CH_3Cl (ppt)	493.4±37.0 (496, 123)
CH_3Br (ppt)	8.9±1.9 (9.3, 100)
CH_3I (ppt)	0.05±0.02 (0.04, 129)
CH_2Cl_2 (ppt)	6.4±3.0 (6.1, 86)
$CHCl_3$ (ppt)	4.0±1.5 (4.1, 42)
CCl_4 (ppt)	92.3±9.1 (98.9, 31)
CH_3CCl_3 (ppt)	101.3±11.7 (108.0, 31)
C_2HCl_3 (ppt)	0.4±0.2 (0.5, 46)
C_2Cl_4 (ppt)	1.4±0.6 (1.2, 53)
CF_2Cl_2 (ppt)	483.7±14.1 (486.2, 136)
$CFCl_3$ (ppt)	236.2±16.5 (236, 112)
$C_2F_3Cl_3$ (ppt)	76.3±4.8 (79.1, 42)
$C_2F_4Cl_2$ (ppt)	9.6±0.5 (9.6, 115)
CHF_2Cl (ppt)	107.2±8.7 (108.6, 111)
$CBrF_3$ (ppt)	2.1±0.1 (2.1, 136)
$CBrClF_2$ (ppt)	2.5±0.3 (2.5, 123)

*Several chemicals were below the detection limit of measurements. These are: DMS, C_3H_6, butanes, toluene <2ppt; CH_3OOH, HCOOH and C_2H_5OH <20 ppt. H_2O_2 and C_2H_4 are probably upper limits due to possible artifacts.

Regression equations based on the present data set*	Mean slopes from literature (Ref.)**
$[CH_4] = -96.7 + 5.92 [N_2O]$; $R^2 = 0.97$	4.7-5.3 (1-2)
$[O_3] = 4830.2 - 15.30 [N_2O]$; $R^2 = 0.98$	-15 to -23 (1-3)
$[NO_y] = 25726 - 81.17 [N_2O]$; $R^2 = 0.94$	-60 to -80 (2-6)
$[HNO_3] = 27934 - 90.18 [N_2O]$; $R^2 = 0.93$	
$[OCS] = -160.9 + 1.97 [N_2O]$; $R^2 = 0.60$	
$[CH_3Cl] = -992.6 + 5.06 [N_2O]$; $R^2 = 0.87$	3.4 (7)
$[CH_3Br] = -51.4 + 0.21 [N_2O]$; $R^2 = 0.73$	
$[CCl_4] = -163.8 + 0.87 [N_2O]$; $R^2 = 0.80$	0.9 (2), 0.5 (7), 1.0 (8)
$[CH_3CCl_3] = -231.9 + 1.13 [N_2O]$; $R^2 = 0.75$	0.8 (2), 1.4 (7)
$[CF_2Cl_2] = -146.4 + 2.14 [N_2O]$; $R^2 = 0.96$	2.4 (2), 1.6 (7), 2.1 (8)
$[CFCl_3] = -388.5 + 2.13 [N_2O]$; $R^2 = 0.91$	1.8 (2), 1.5 (7), 1.6 (8)
$[C_2F_3Cl_3] = -69.9 + 0.49 [N_2O]$; $R^2 = 0.62$	0.5 (2), 0.2 (7)
$[C_2F_4Cl_2] = -4.6 + 0.048 [N_2O]$; $R^2 = 0.57$	0.03 (7)
$[CHF_2Cl] = -121.7 + 0.775 [N_2O]$; $R^2 = 0.59$	
$[CBrF_3] = -3.6 + 0.019 [N_2O]$; $R^2 = 0.86$	0.007 (7)
$[CBrClF_2] = -8.3 + 0.037 [N_2O]$; $R^2 = 0.87$	0.043 (2), 0.015 (7)

*Mixing ratios of CH_4, O_3 and N_2O are in ppb. All other mixing ratios are in ppt. Data as in Fig. 1

**References: 1. Collins et al. (1993); 2. Volk et al. (1996); 3. Chang et al. (1996a); 4. Loewenstein et al. (1993); 5. Weinheimer et al. (1993); 6. Kondo et al. (1996b); 7. NASA (1994); 8. Chang et al. (1996b).

Sulfur Species

SO_2 tended to increase into the stratosphere from about 30 ppt to 60 ppt (Figure 3). Corresponding OCS mixing ratios declined from 440 ppt to 410 ppt, potentially providing a sulfur source of comparable magnitude (≈ 30 ppt). This equivalence is consistent with the notion that OCS photolysis may be a major source of SO_2 in the stratosphere [Chin and Davis, 1995]. Although volcanic influences on SO_2 abundance can not be strictly ruled out, no recent major eruption could be uncovered. No particle formation resulting from SO_2 chemistry was evident as particle numbers (CN) continued to decline from about 350 cm^{-3} in the UT to 50 cm^{-3} in the stratosphere ($O_3 \approx$ 550 ppb). Lack of particle formation is not surprising at these relatively warm prevailing air temperatures (>210 K).

Nonmethane hydrocarbons (NMHCs)

Ethane, propane and acetylene declined rapidly as a function of O_3 (Figure 4). Assuming Cl and OH concentrations (molec cm^{-3}) in the LS of 10^3 and 5×10^5 respectively [Singh and Kasting, 1988], we estimate that 65% of ethane, 40% of propane and 15% of acetylene could have been oxidized by Cl atoms alone. While many other NMHCs were well below their detection limit of about 2 ppt, both benzene and ethylene were clearly detectable (Table 1). Ethylene mixing ratios should be considered an upper limit as positive sampling artifacts may exist (D. Blake, private comm.).

Halocarbons

Mixing ratios of a large number of halogenated species were also measured and are summarized in Table 1. Many of the CFCs have been routinely measured in the stratosphere (NASA, 1994) and only mean concentrations are stated here for reference. However, few measurements of reactive halogens (CH_2Cl_2, $CHCl_3$, C_2Cl_4, C_2HCl_3, CH_3I) have been reported in the literature. Methyl iodide is present at extremely low concentrations in the stratosphere (≤ 0.05 ppt) and is not likely to be a major player here except perhaps during periods of deep convection. In Table 2 we list the halocarbon-N_2O linear correlations measured in this study along with a comparison with previously published data. The published observations are almost exclusively derived from instruments from satellite, balloon or ER-2 platforms. The differences in slopes may be in part attributable to the fact that the present data represents only the lowermost portion of the stratosphere.

Conclusions

An instrumented DC-8 aircraft, designed for tropospheric chemistry research, has provided an opportunity to sample the midlatitude lower stratosphere at a level of detail not possible before. We have presented here data for reactive nitrogen species, NMHCs, oxygenated species, sulfur species, halocarbons and chemical tracers, in many cases for the first time. These data have been analyzed in light of lower stratospheric chemistry and dynamics and compared with existing measurements. The results should augment and support the existing body of information from the lower stratosphere.

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