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The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations

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Abstract Volume mixing ratio (VMR) profiles of the chlorine-bearing gases HCl, $ClONO_2$, CCl_3F, CCl_2F_2, $CHClF_2$, CCl_4, and CH_3Cl have been measured between 3 and 49° northern- and 65 to 72° southern latitudes with the Atmospheric Trace MOlecule Spectroscopy (ATMOS) instrument during the ATmospheric Laboratory for Applications and Science (ATLAS)-3 shuttle mission of 3 to 12 November 1994. A subset of these profiles obtained between 20 and 49°N at sunset, combined with ClO profiles measured by the Millimeter-wave Atmospheric Sounder (MAS) also from aboard ATLAS-3, measurements by balloon for HOCl, CH_3CCl_3 and $C_2Cl_3F_3$, and model calculations for COClF indicates that the mean burden of chlorine, Cl_{TOT}, was equal to (3.53 ± 0.10) ppbv (parts per billion by volume), 1-sigma, throughout the stratosphere at the time of the ATLAS 3 mission. This is some 37% larger than the mean 2.58 ppbv value measured by ATMOS within the same latitude zone during the Spacelab 3 flight of 29 April to 6 May 1985, consitent with an exponential growth rate of the chlorine loading in the stratosphere equal to 3.3%/yr or a linear increase of 0.10 ppbv/yr over the Spring-1985 to Fall-1994 time period. These findings are in agreement with both the burden and increase of the main anthropogenic Cl-bearing source gases at the surface during the 1980s, confirming that the stratospheric chlorine loading is primarily of anthropogenic origin.

Introduction

The ATMOS experiment is a multi-mission, shuttle-based project designed for regular, detailed remote soundings of the Earth's middle atmosphere [*Farmer*, 1987; *Gunson et al.*, 1996].

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During its first mission of 1985, ATMOS demonstrated the capability of establishing the budget of and partitioning among the nitrogen, chlorine and fluorine "families" [*Russell et al.*, 1988; *Zander et al.*, 1992] through infrared remote sensing from space. Subsequently, ATMOS was selected as a core instrument of the ATLAS program, performing additional missions in 1992, 1993 and 1994 [*Gunson et al.*, 1996].

In this Letter, we report VMR profiles for the 7 most important Cl-bearing gases derived from a subset of ATMOS/ATLAS-3 sunset occultations observed at northern latitudes comparable to those covered during ATMOS/Spacelab-3 in 1985. By complementing these with profiles of 4 additional, non-negligible chlorinated species measured by other experiments, and the COClF contribution from model calculations, we evaluate the 1994 stratospheric Cl budget and derive its rate of change between 1985 and 1994.

Data base and analysis

The main absorption features used for VMR retrievals of the chlorine-bearing target molecules observed by ATMOS are primarily those reported in Table 1 of *Zander et al.* [1992]. This involves analyzing the ATMOS observations with the filters # 12 (600-1400 cm^{-1}), # 9 (600-2450 cm^{-1}) and # 3 (1580-3420 cm^{-1}) which were used alternately during the ATLAS-3 mission in predetermined sequences during 68 sunset occultations that occurred between 20 and 49°N. In order to appraise the latitudinal dependence of the VMR profiles, we subdivided this range into "midlatitude" (49 to 35°N) and "subtropical" (35 to 20°N) zones. The molecules HCl and CH_3Cl are studied in filter 3 occultations, while all other ATMOS-retrieved gases are from Filter 9 and 12 events; to eliminate any biasing arising from the sampling of the ensembles of the filter 3 or the filter 9 and 12 occultations, we used N_2O as a dynamical tracer to register HCl and CH_3Cl profiles on the same vertical scale as the other gases.

The VMR profiles were retrieved with the ODS (Occultation Display Spectra) onion-peeling retrieval algorithm developed at JPL and described by *Norton and Rinsland* [1991]. The input data to the code and parameters necessary to retrieve consistent composition of the atmosphere are discussed by *Gunson et al.* [1996].

The adoption of temperature-dependent absorption cross-sections for a number of heavy molecules such as CCl_2F_2, CCl_3F, $CHClF_2$ and $ClONO_2$, instead of more subjective parameters used before [*Zander et al.*, 1987; *Brown et al.*, 1987] greatly improved the absolute quality of related ATMOS retrievals used here [*Brown et al.*, 1996].

Results

The mean HCl VMR value obtained by averaging all individual measurements made during the ATLAS-3 mission near and above 50 km altitude, and over the 3 to 49°N latitude zone was found equal to (3.52 ± 0.10) ppbv. Sub-binnings performed over the northern midlatitude and subtropical zones identified here indicate no statistically significant difference with respect to that mean, thus confirming that HCl is well mixed at the hemispheric level near and above the stratopause. Previous ATMOS missions also demonstrated that the VMR measurement of HCl in the vicinity of the stratopause is a good surrogate for total stratospheric chlorine loading [*Zander et al.*, 1992; *Gunson et al.*, 1994]. Therefore, the value of (3.52 ± 0.10) ppbv for HCl near 50 km should represent the mean stratospheric loading of chlorine for the Fall-1994 time.

To corroborate this, we evaluated the burden of chlorine, Cl_{TOT}, at various pressure levels by summing measured VMRs of the largest possible set of Cl-bearing gases (sources, sinks and reservoirs combined) weighted by the number of Cl atoms bound in each of them. For the ATLAS-3 time period, we performed the following summation:

$$Cl_{TOT} = [HCl] + [ClONO_2] + 4x[CCl_4] + 3x[CCl_3F] + 2x[CCl_2F_2] + [CHClF_2] + [CH_3Cl] + \{ClO\} + 3x\{CH_3CCl_3\} + 3\{C_2Cl_3F_3\} + \{HOCl\} + \{\{COClF\}\}$$

where the brackets indicate the VMRs of the seven important chlorinated constituents measured by ATMOS, and the 4 braces referring to VMRs of additional, non-negligible chlorine contributors not retrieved by ATMOS but by other experiments. In particular, the ClO data were derived from the MAS (Millimeter-wave Atmospheric Sounder) experiment [*Croskey et al.*, 1992] which was also part of the ATLAS-3 payload; details about the ClO data analysis have been reported by *Aellig et al.* [1996]. The VMR profiles for CH_3CCl_3 and $C_2Cl_3F_3$ were derived from in situ measurements during a balloon flight performed by the Jülich group (A. Engel, private communication) in Aire-sur-l'Adour, France, on 7 October 1994, i.e., about one month prior to the ATLAS-3 mission. The HOCl profile was obtained from the analysis of sunset spectra recorded with the Mark IV FTIR during a balloon flight in September 1993 near 32°N (G.C. Toon, private communication), scaled by a 3% increase per year to represent the HOCl loading at the time of the ATLAS-3 mission. The double braced COClF VMRs were extrapolated from model calculations by *Kaye et al.*, [1991], assuming a 3%/yr increase between their 1990 evaluations and 1994.

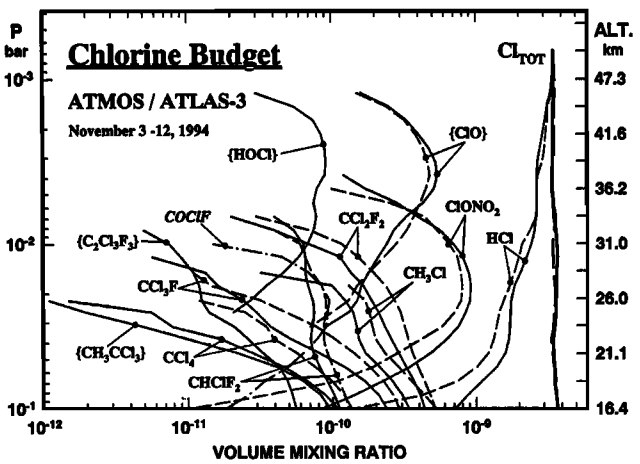

Figure 1. Graphical representation of the individual volume mixing ratio profiles included in the evaluation of the 1994 stratospheric Cl-loading for the northern midlatitude (35 to 49°N; thin full lines) and subtropical (20 to 35°N; thin dashed lines) zones. The thicker full and dashed lines display the corresponding Cl budgets throughout the stratosphere, sources, sinks and reservoirs combined. While all subtropical profiles experience uplifting, opposite relative contributions to Cl_{TOT} are noticeable between sources on one hand, and sinks and reservois on the other hand. For details, see text.

Table 1. Numerical values (in ppbv) for Cl_{TOT} and CCl_y at northern mid- and subtropical latitudes in November 1994

P, mbar	Approx. Alt., km	Midlatitudes Cl_{TOT}	Midlatitudes CCl_y	Subtropics Cl_{TOT}	Subtropics CCl_y
0.68	50.2	3.52		3.50	
1.00	47.3	3.49		3.52	
1.47	44.4	3.47		3.51	
2.15	41.6	3.46		3.55	
3.16	38.9	3.45		3.48	
4.64	36.2	3.43	0.02	3.39	
6.81	33.6	3.49	0.08	3.58	0.06
10.00	31.0	3.65	0.22	3.41	0.31
14.68	28.5	3.64	0.44	3.43	0.53
21.54	26.0	3.62	0.69	3.57	0.98
31.62	23.6	3.55	0.90	3.50	1.37
46.42	21.2	3.49	1.34	3.43	1.86
68.13	18.8	3.55	2.19	3.62	2.74
100.00	16.4	3.74	2.92	3.72	3.56
	Mean :	3.54 ± .09		3.52 ± .09	

Figure 1 displays the profiles of the individual gases included in the present evaluation for both the midlatitude (thin full lines) and the subtropical (thin dotted lines) zones, as well as the corresponding total Cl profiles labeled Cl_{TOT} displayed as thicker lines. For CH_3CCl_3, $C_2Cl_3F_3$, HOCl and COClF, the same profiles were used in both binnings, because of unavailable measurements for the two latitudinal zones.

Table 1 provides numerical values for Cl_{TOT} and CCl_y, for the two northern midlatitude and subtropical zones; the pressure levels were selected among standard values adopted by various experiments (including UARS) for date archiving.

The VMRs of the top and bottom pressure levels of the midlatitude Cl_{TOT} profile (thick continuous line in Fig. 1) are equal, respectively, to 3.52 and 3.74 ppbv, with a corresponding mean VMR and standard deviation over the entire altitude span equal to (3.54 ± 0.09) ppbv. The extremes are indicative of a 6.3% decrease of Cl_{TOT} which can be explained by the time delay for air to mix between 100 and 0.68 mbar (~16.5 to 50 km) levels.

The Cl_{TOT} profile for the subtropical latitudinal zone (thick dotted line in Fig.1) also indicates a decrease of 6.3% between bottom (3.72 ppbv) and top (3.50 ppbv) VMRs, with a corresponding mean mixing ratio and standard deviation equal to (3.52 ± 0.09) ppbv.

Figure 2 with its linear abscissa scale shows some details of the profiles of the key components which make up the Cl inventory for the northern midlatitude case (35 to 49°). In particular, we have reproduced the CCl_y curve corresponding

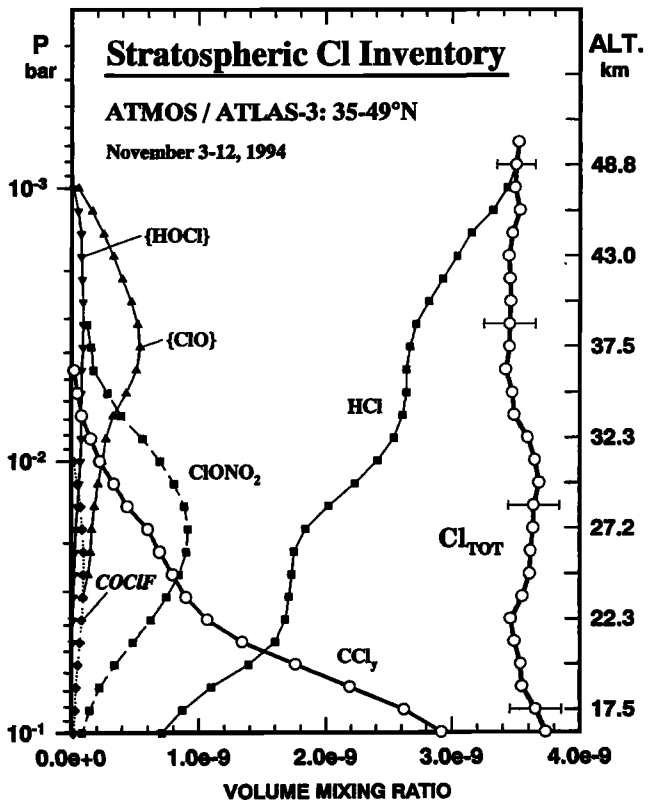

Figure 2. A linear-scale presentation of the key components entering in the total Cl-loading evaluation throughout the stratosphere at northern midlatitudes. The CCl_y curve refers to the total chlorine bound in all organic source gases listed in the text. Cl_{TOT} represents the summation over CCl_y, HCl, $ClONO_2$, ClO, HOCl and COClF.

to the sum of Cl atoms bound in all source gases considered here. By further summing over CCl_y and the inorganic compounds HCl, $ClONO_2$, ClO, HOCl and COClF also reproduced in Fig. 2, one obtains the thicker continuous curve which corresponds to the total chlorine loading Cl_{TOT}. Within the estimated uncertainty ranging from 4% at the top to 6% at the bottom of the Cl_{TOT} profile, the conservation of chlorine is properly demonstrated throughout the stratosphere. Within that uncertainty, however, we cannot rule out some missing, second order contributions from either reservoirs or sources not accounted for here. Some uncertainty in the spectroscopic parameters used to derive the profiles of the heavier molecules [see *Brown et al.*, 1996 and *Gunson et al.*, 1996] could also reflect in the lower altitude range.

Discussion and conclusions

The measurement of the budget of chlorine in the middle atmosphere involve a large number of Cl-bearing gases which cannot be studied by any one technique alone, and related investigations during the last years have sought approaches for its evaluation, based on a more limited number of measurements. These have generally invoked the work of *Plumb and Ko* [1992] who demonstrated that there exist compact correlations between the mixing ratios of long-lived atmospheric constituents, thus providing means of deriving the distribution versus altitude for some species, solely based on concentrations measured for others. The procedure has been applied in many cases [e.g., *Schmidt et al.*, 1994; *Woodbridge et al.*, 1995]. Among these, the application by *Schmidt et al.* [1994] is of relevance here; using CCl_2F_2 as the "reference" gas, they derived the function

$$[CCl_y] = 0.045 \times [CCl_2F_2]^{1.82} + 67.35$$

in which the brackets refer to the VMRs of the related compounds, expressed in units of pptv ($x10^{-12}$ ppv). Application of that formulation to the midlatitude mean CCl_2F_2 profile derived in 1994 by ATMOS produces results which match very well the CCl_y profiles obtained in this work, when accounting for the fact that *Schmidt et al.* [1994] sample species amounting to 95% of the total organic chlorine.

Model evaluations of the chlorine partitioning in the stratosphere as reported here for the ATLAS-3 mission are dealt with and discussed by *Michelsen et al.* [1996].

From the various independent results derived here, it can be concluded that the overall chlorine loading at the top of the stratosphere over the 20 to 49°N latitudinal zone was equal to 3.51 ppbv at the time of the November 1994 ATLAS-3 mission, with a 1-sigma uncertainty of 0.15 ppbv or 4%; this uncertainty represents an estimated accuracy assessed as in previous investigations [*Zander et al.*, 1990; *Gunson et al.*, 1990]. Throughout the stratosphere, the Cl_{TOT} VMR profiles combining the important sources, sinks and reservoirs display consistent values which suggest only second order local deficit and a mean slope reflecting the time for air to mix from the lower to the upper stratosphere.

When compared to the mean stratospheric chlorine VMR of 2.58 ± 0.10 ppbv derived from the 1985 ATMOS/Spacelab-3 mission [*Zander et al.*, 1992], the present mean stratospheric chlorine loading of 3.53 ppbv (see Table 1) corresponds to a 37% increase over the 9.5 years separating the two missions, i.e., an exponential rate of 3.3%/yr or a linear change of 0.10 ppbv/yr. The mean stratospheric Cl VMR derived from the ATMOS/Spacelab-3 mission was shown to be in excellent agreement with the corresponding 1980 Cl inventory in the lower troposphere [*Zander et al.*, 1992], indicative of a mixing time of about 5 years for free tropospheric air to be transported and mixed throughout the stratosphere. The upper stratospheric Cl loading derived here (3.51 ppbv) for the time of the ATLAS-3 mission of November 1994 mirrors precisely the tropospheric Cl content that prevailed in 1989-90 [*WMO Reports No. 25*, 1992 and *NASA Pub. 1339*, 1994], thus confirming the 4-5 year lag time between tropospheric and stratospheric chlorine loading identity. In addition, the rate of change of 3.3 %/yr deduced here agrees very well with the increase of the organic chlorine burden in the lower troposphere (i.e., 0.104 ppbv for a total of 3.18 ppbv in 1986 and 0.109 ppbv for a total loading of 3.46 ppbv in 1989; see *WMO Reports No. 18*, 1989 and *No. 25*, 1992).

As a consequence of the excellent agreement between the stratospheric chlorine loadings and rates of change derived from the ATMOS missions of 1985 and 1994 and the surface measurements of Cl-bearing gases some 4-5 years earlier, there remains no doubt that the bulk of stratospheric chlorine and its evolution are primarily associated with the release at the ground of chlorinated source gases produced industrially. As concluded by *Gunson et al.* [1994], this implies that natural sources of chlorine, in particular CH_3Cl and perhaps

CCl_4, and volcanic activity, have contributed negligibly to the changes in the burden of stratopheric Cl over the last decade or so.

The 1987 Montreal Protocol and its London and Copenhagen Amendments are intended to reduce the future levels of atmospheric chlorine by regulating the production and release in the atmosphere of the most important anthropogenic, Cl-bearing source gases at the ground, primarily the chlorofluorocarbons (CFCs).The successive ATMOS missions have provided, thus far, the most consistent and complete set of measurements needed to "watch" the timely chlorine loading and to model its impact on ozone depletion throughout the entire stratosphere. Similar measurements will become critical in the near future when the stratospheric loading is expected to start decreasing, to test the implementation of the Protocol and the validity of the model predictions.

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