

Increase in levels of stratospheric chlorine and fluorine loading between 1985 and 1992

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Mixing ratios of 3.44 ppbv (parts per billion by volume) and 1.23 ppbv for HCl and HF above 50 km have been measured by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment on a March 1992 flight of the Space Shuttle. Compared to the measured values obtained on a 1985 flight, these correspond to a 37% and 62% increase for HCl and HF, respectively. The derived trend in HCl is in good agreement with the model-predicted increase in chlorine loading of 0.13 ppbv year¹. We attribute the main source of this change to the release of man-made chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) whose production and use are now controlled by international agreement in the Montreal Protocol² and its subsequent revisions, London and Copenhagen. Model calculations based on these measured levels predict the growth and subsequent decline of atmospheric chlorine to span several decades before returning to the critical value of below 2 ppbv at which the Antarctic ozone "hole" is believed to have been initiated. Future measurements of HCl and HF can be used as an accurate measure of chlorine loading, and will help monitor what kind of chemicals are being used to replace the CFCs.

The ATMOS instrument is designed to operate on board the Space Shuttle from where it obtains high resolution infrared solar observations during orbital sunrises and sunsets³. These data are used to infer the vertical concentration profiles of a large number of atmospheric constituents, including HCl, HF, and other major chlorine and fluorine bearing gases^{4,5} (both organic source molecules and their degradation products). The

ATMOS measurements of these gases obtained during the Spacelab 3 (SL-3) shuttle mission of March 29- April 6, 1985, together with measurements from other instruments for those gases which were below the detection limits of the ATMOS instrument, have been used to study the partitioning of chlorine- and fluorine-containing gases as a function of altitude from about 10 to 60 km⁶. This study demonstrated that the mixing ratios of HCl and HF above 50 km are approximately equal to the mixing ratios of total chlorine and fluorine respectively. The HCl volume mixing ratio at this height represents an upper limit on the mixing ratio of the inorganic chlorine available to participate in ozone removal chemistry in the lower stratosphere. It is thus a measure of the effective atmospheric chlorine loading, which is a good proxy for the ozone depletion potential,

During the 1985 SL-3 mission, ATMOS observations were limited to two latitudes centered at 30°N and 48°S. The mixing ratios of HCl and HF between 50 and 60 km were measured to be 2.55 ± 0.28 and 0.77 ± 0.10 ppbv, respectively⁵. The absolute concentrations of the gases above 60 km are too small to be detected. Between March 24 and April 2, 1992, ATMOS was flown for a second time as part of the Atmospheric Laboratory for Applications and Science (ATLAS- 1) shuttle mission. The more numerous observations made during this recent flight covered a broader range of latitudes, i.e. between 28°N and 54°S. HCl and HF profiles have been inferred from these data using analysis procedures and methods previously developed for the SL-3 dataset^{5,7}. From these new observations, no statistically significant latitudinal gradients were found in the distribution of HCl above 45 km, or above 50 km in HF; therefore, both halogen sink species appear well-mixed over these latitude and altitude ranges.

To provide a more precise estimate of the HCl and HF concentrations in the upper stratosphere, we have analyzed the spectra formed by averaging in 5 km altitude bins. It is clear from these average spectra that the concentrations of HCl and HF have increased sufficiently so as to make their spectral signatures evident at much higher altitudes. As they appear to retain a constant mixing ratio up to 70 km, this further suggests that there is no significant loss mechanism or sink for either of these gases in this upper height range. The mean concentrations derived from the ATLAS- 1 observations are 3.44 ± 0.30 ppbv for HCl, and 1.23 ± 0.12 ppbv for HF. The uncertainties quoted represent an estimated accuracy following the assessment provided originally in ref. 5 and then in ref. 8. The error estimates include the error of the mean in the observations, 5% for HCl and 6% for HF, combined with an estimated root-sum-square of systematic error sources of 7%.

Until recently, there has been some question as to whether significant amounts of HCl are injected into the stratosphere following volcanic eruptions which would contribute to some of the observed changes. While the ATLAS- 1 mission followed 9 months after one of the largest volcanic eruptions of this century, that of Mount Pinatubo in June 1991, measurements of the total column burden of HCl before and immediately after this eruption indicate that little HCl reached the stratosphere ^{9,10}. This observation is further supported by a recent model study which suggests that HCl is successfully scavenged from volcanic plumes and removed in solution by condensing supercooled water¹¹. Thus, the increase in stratospheric chlorine is almost wholly related to the continued build up of industrial halocarbons rather than to any natural events. Much stronger evidence of this is found in the increase in HF for which there are no known significant natural sources,

Historical and future stratospheric chlorine and fluorine levels can be modeled based on release and use of CFCs and their replacements as set out in the Montreal Protocol and its subsequent amendments (Figure 1), The ATMOS measurements of HCl and HF match the modeled growth in Cly and Fy data as surrogates for this change in total stratospheric chlorine and fluorine. Similar measurements in the future will reflect the phase out and replacement policy adopted after 1996 for the CFCs, and the exact mix of HCFCs (hydrochlorofluorocarbons) with HFCS (hydrofluorocarbons) used as substitutes. However, the modeled chlorine loading suggests some leveling off and reduction in stratospheric levels by the end of the century.

The future for stratospheric fluorine levels is more uncertain, as this will depend more critically on the exact mix of HCFCs and HFCs. Current understanding indicates that inorganic fluorine does not play a significant role in the catalytic destruction of ozone; its primary interest is as a measure of the destruction of the precursors. To date, the rapid growth in HF remains the strongest indicator that the source of active chlorine in the stratosphere is the photolysis of CFCs. As reductions in future chlorine loading is achieved, the primary environmental concern will shift from issues related to stratospheric ozone loss, to the global warming potential of halocarbons^{1 2}. The changes observed in HF in the next decades will be an indicator of the mix of HCFCs and then HFCS which will be present in the atmosphere. Continued measurements of the stratospheric concentrations of HCl and HF through a series of planned flights of the ATMOS instrument on board the Space Shuttle will provide a better prognosis of future stratospheric trends.

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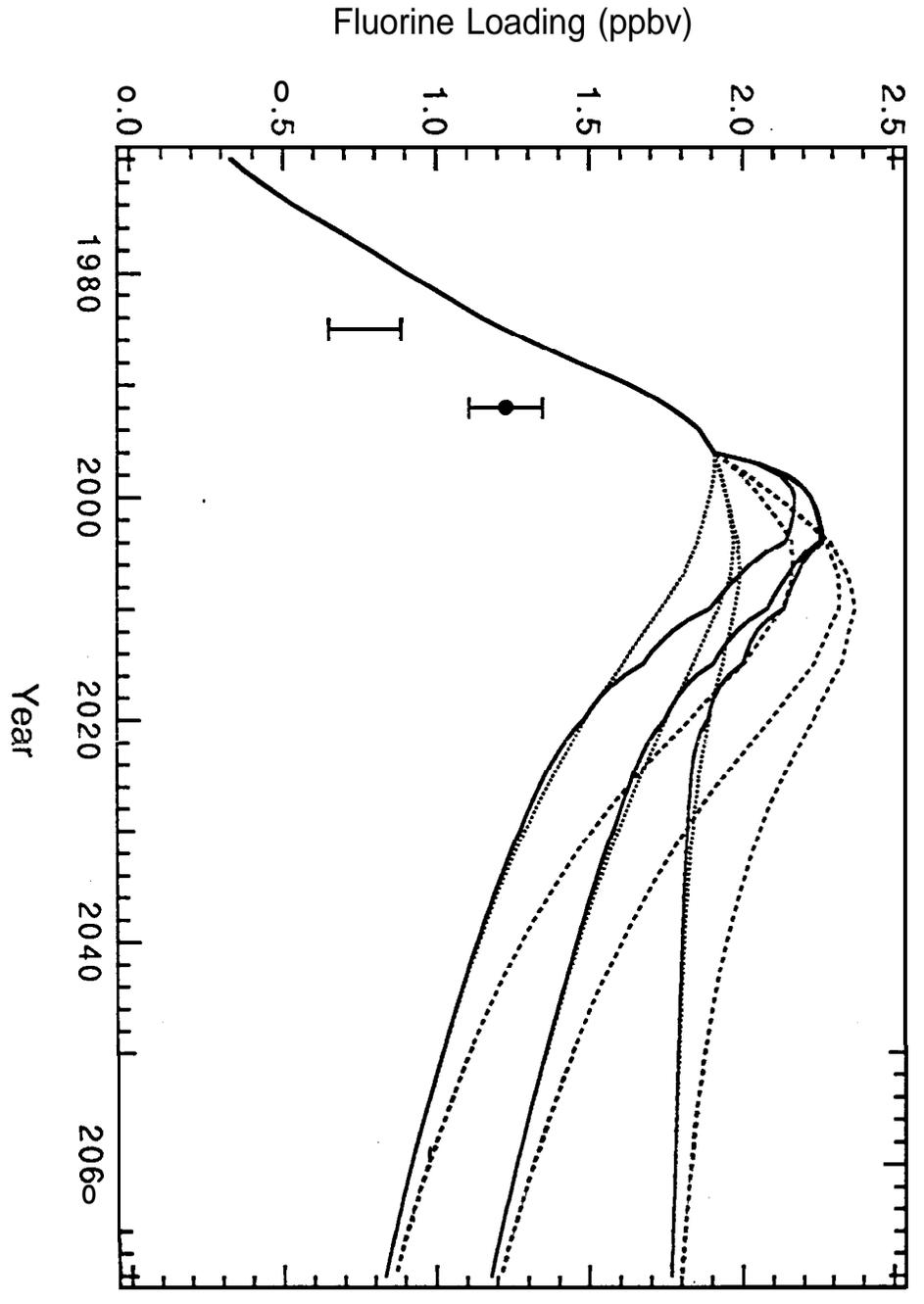
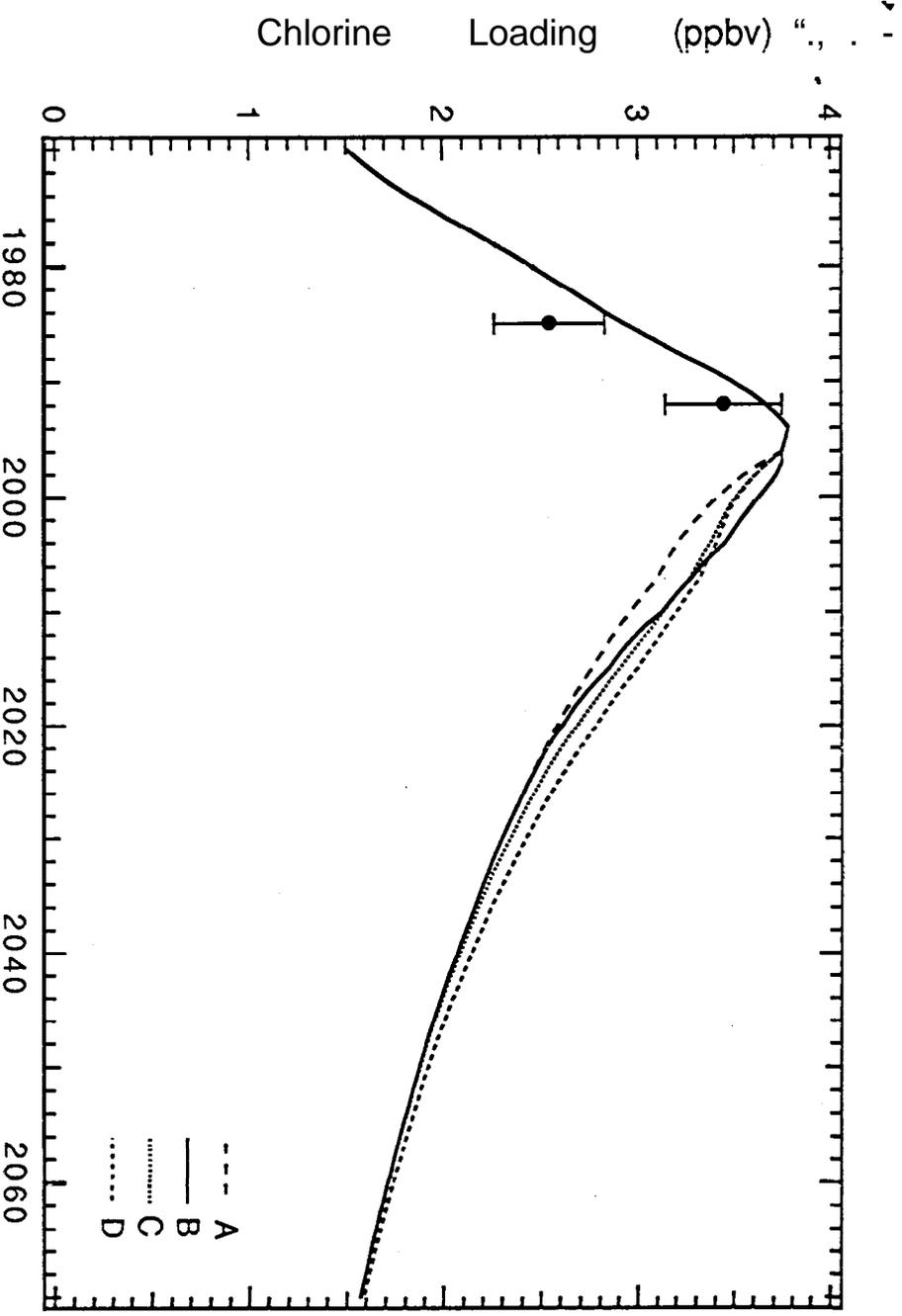
References:

- 1, Prather, M. J., Watson, R. T., *Nature*, 344, 729-733, (1990).
2. Montreal Protocol on Substances that Deplete the Ozone Layer, Final Act, UNEP (1987).
3. Farmer, C. B., *Mikrochim. Acts [Wien]*, 111, 189-214, (1987).
- 4, Zander, R., Rinsland, C. P., Farmer, C. B., Norton, R. H., *J. geophys. Res.*, 92, 9836-9850, (1987),
5. Zander, R., Gunson, M. R., Foster, J. C., Rinsland, C. P., Namkung, J., *J. geophys. Res.*, 95, 20519-20525, (1990).
6. Zander, R., Gunson, M. R., Farmer, C. B., Rinsland, C. P., Irion, F. W., Mahieu, E., *J. Atmos. Chem.*, 15, 171-186, (1992),
7. Norton, R. H., Rinsland, C. P., *Appl. Opt.*, 30, 389-400, (1991).
8. Gunson, M. R., Farmer, C. B., Norton, R. H., Zander, R., Rinsland, C. P., Shaw, J. H., Gao, B.-C., *J. geophys. Res.*, 95, 13867-13882, (1990).
9. Mankin, W. G., Coffey, M. T., Goldman, A., *Geophys. Res. Lett.*, **19**, 179-182, (1992).
- 10, Wallace, L., Livingstone, W., *Geophys. Res. Lett.*, **19**, **1209**, (1992).
- 11, Tabazadeh, A., Turco, R. P., *Science*, 260, 1082-1086, (1993),
12. Ko, M, K, W., N. D. Sze, G. Molnar and M, J. Prather, *Atmospheric Environment*, 27A, 581-587, (1993).

Figure Caption

Figure 1. Upper and lower panels represent modeled changes in total chlorine (Cl_y) and fluorine (F_y), respectively, from the present through the next century. Added to these are values reported in this paper of the ATMOS measurements of the upper stratospheric HCl and HF mixing ratios from 1985 and 1992. The modeled curves are calculated from the assumed emissions and lifetimes using the methods described in reference 1. Emissions for the HCFCs after 1992 follows the Copenhagen amendment of the Montreal Protocol with phase-out of CFCs in 1996, and gradual phase-out of the HCFCs starting in 2004 and terminating in 2030. The emissions of the HCFCs are limited to less than 3.1% of the total

Ozone Depletion Potential weighted production of the base year of 1989. The choice of substitutes depends on many factors. At present there is no clear indication which substitutes will be used. In the calculations, we have considered three substitutes, HCFC-123 (CF_3CHCl_2), HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$), and HCFC-142b (CH_3CClF_2) to illustrate the range of chlorine loading. Curve A in the upper panel corresponds to the case with no substitutes. Curve B, C, and D assume that HCFC-123, HCFC-141b, and HCFC-142b, respectively, are used exclusively. If a mixture of the three is used, the calculated chlorine loading will fall between these curves. There is no international agreement on the control of HFC emissions, In this calculation, we assume that 10% of the emissions in 1989 are replaced by HFCS starting in 1996. With a 50% substitution, this corresponds to an 80:20 split between HCFCs and HFCs¹². The HFC emission is assumed to continue indefinitely at this fixed rate. Three substitutes used to illustrate the range of expected fluorine loading are HFC-143a (CHF_2CH_3), HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$), and HFC-152a (CHF_2CH_3). The lower panel shows the calculated F_y for the three cases. The spread within each group of three curves represents the contribution from the mix of HCFCs used prior to 2030.



Gunson et al. - Figure 1