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Monitoring the stratospheric chlorine budget during the past decades: the Montreal Protocol at work

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Abstract The study of series of ground-based solar observations performed within the frame of the NDSC indicates that the rate of increase of the atmospheric loading of inorganic chlorine has progressively slowed down, then stabilized around 1996-97, with a subsequent tendency towards a decrease. The investigation is based on total column abundances of HCl and $ClONO_2$ measured at the Jungfraujoch station in the Swiss Alps and on stratospheric columns of HCl derived from observations at Kitt-Peak National Observatory (Arizona, USA). The observed changes are compared with near-global observations of HCl around the stratopause by HALOE and with a global, best-case emission scenario of Cl-bearing ground-level source gases compiled by UNEP.

Introduction

In 1974, Molina and Rowland [1974] alerted the scientific community about the threat which chlorine-bearing source gases of anthropogenic origin (in particular the long-lived CCl_3F and CCl_2F_2) may represent for the stratospheric ozone layer once they get photo-dissociated above 20 km altitude and release their chlorine atoms. Their concerns were unambiguously verified with the observation and interpretation of the ozone hole over Antarctica [Farman et al., 1985; Solomon, 1990] and later erosion of the ozone layer at midlatitudes [WMO, 1999]. The Montreal Protocol (1987) and its key Amendments (1990 and 1992) have implemented phase-out scenarios for the most important halogenated source gases with large ozone depletion potentials, in order to stabilize then reduce the inorganic chlorine loading in the stratosphere. Monitoring of these scenarios has revealed that the tropospheric loading of chlorine from halocarbons peaked in early 1993 in the northern hemisphere and in early 1994, globally [Montzka et al., 1996]. Owing to the time it takes for tropospheric air to reach various geographic regions of the stratosphere, the maximum loading of inorganic chlorine was expected to occur later, and related monitoring experiments have been specifically watching for it.

Observational results

Based on near-global measurements of HCl concentrations with the HALOE instrument, Anderson et al. [2000] reported a steady decrease in the chlorine burden around 55 km altitude (stratopause) since the beginning of 1997 through May 1999. The ground-based measurements reported in Figures 1 and 2 add further information regarding the evolution of the stratospheric loading of inorganic chlorine.

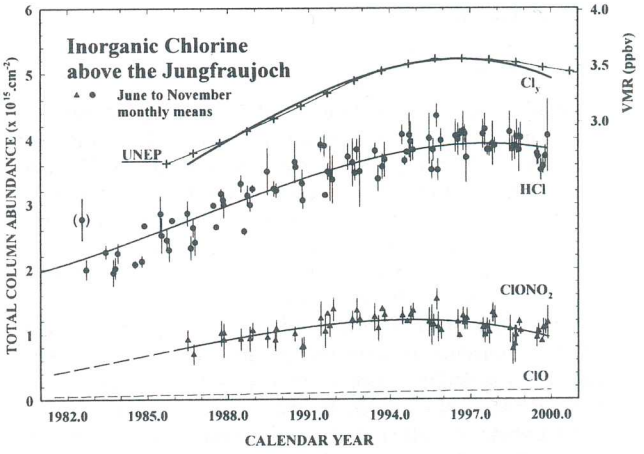

Figure 1. A subset of the time series of monthly mean column abundances of HCl and $ClONO_2$ measured above the Jungfraujoch for the months of June to November (to avoid significant variability occurring during winter and spring). The July 1982 column (between parentheses) appears to have been influenced by HCl injection from the 1982 El Chichón volcanic eruption [Mankin and Coffey, 1984]. Pre-1982 measurements of HCl have been reported by Zander et al. [1987]. The scale to the right is associated with the UNEP curve.

The curves fitted to the data points reported in Figure 1 and derived spectroscopically from infrared solar observations at the Jungfraujoch (Switzerland, 46.5°N, 8.0°E, 3.58 km asl) with the SFIT1 retrieval code [Rinsland et al., 1991], show peak occurrences for the total column abundances of HCl and $ClONO_2$

at times 1997.1 and 1994.8, respectively. At the time of this writing, we have no clear explanation for the early maximum occurrence of the $ClONO_2$ columns.

The curve labeled Cl_y results from the addition of the above curves, augmented by a ClO background estimated from UARS-MLS measurements at northern midlatitudes. Cl_y peaks in mid-1996, i.e., about 3.5 years later than the northern hemisphere maximum organic chlorine loading reported by Montzka et al. [1996]. The curve labeled UNEP represents a baseline scenario for the total tropospheric organic chlorine concentration [WMO, 1999]; its best fitting to the Cl_y maximum occurrence has requested a shift of 3.7 years.

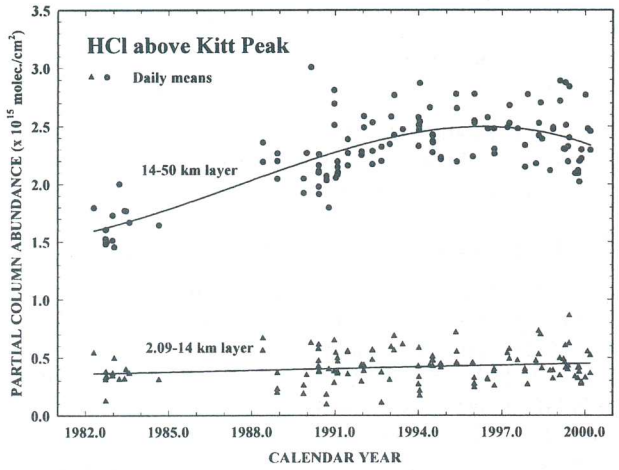

Figure 2. A subset of the time series of daily mean partial column abundances of HCl for the 2.09 to 14 km (mean troposphere) and 14 to 50 km layer (mean stratosphere) above Kitt Peak, as derived with the SFIT2 retrieval code described by Connor et al. [1998]. Pre-1982 measurements of HCl have been reported by Rinsland et al. [1991].

The data points displayed in Figure 2 have been derived spectroscopically from infrared solar observations made at the Kitt Peak National Solar Observatory Tucson, AZ (USA; 31.9°N, 111.6°W, 2.09 km asl). While the tropospheric HCl loading appears to have increased quasi-linearly by about 20% between 1982 and 2000, the stratospheric column of HCl (which is the most important surrogate of the inorganic chlorine loading in the stratosphere) reached a maximum at time 1996.3, slightly earlier than observed for the total HCl column above the Jungfraujoch. The post-1996.3 stratospheric column decrease above Kitt Peak is statistically significant at the 95% confidence level.

Conclusions

While the HCl total column abundances observed above the Jungfraujoch and Kitt Peak had been on the rise since the mid-1970s, a progressive slowing of their rates of increase during the early 1990s followed by a leveling off around 1996-97 and subsequent signs of a decrease are indicative of the effectiveness of the Montreal Protocol and its Amendments in controlling the major man-made perturbation of the stratospheric ozone layer. In contrast to the sharp Cl peak inferred from the HALOE measurements at 55 km [Anderson et al., 2000], the turnover in the HCl rates of change above the Jungfraujoch and Kitt Peak is smooth and relatively broad; consequently, more precise turnover times occurrences will require additional measurements during the coming years. The data base of the $ClONO_2$ loading above the Jungfraujoch has also experienced a maximum, but its occurrence during 1994 remains to be understood. This, as well as better evaluations of peak HCl and $ClONO_2$ occurrences at additional sites affiliated to the NDSC, consistent re-analyses using the new SFIT2 retrieval code, and comparisons with model calculations will be subjects to be undertaken in a near future.

Acknowledgements

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