The 1992 measurements provide evidence that volcanic aerosol does play a major role in ozone depletion, presumably through the heterogeneous chlorine chemistry that occurs on the additional surface area from the volcanic aerosol or by acting as a nucleation site for additional growth of PSCs. The decay of the volcanic aerosol in the stratosphere will reduce the number of concentrations for the 1993 season but may continue to have an impact on ozone depletion.

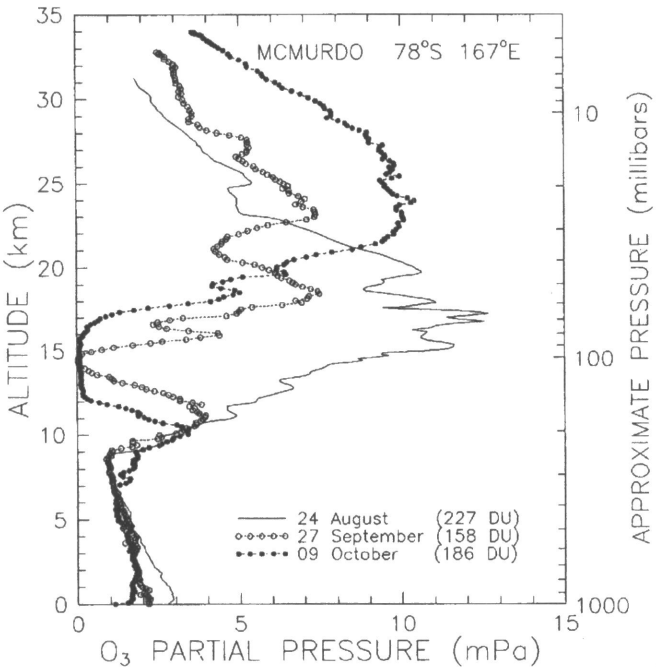

Figure 2. The initial ozone profile observed on 24 August compared with the minimum total ozone profile (27 September). On 9 October a record low of 17 Dobson Units ozone was measured in the 12–20-km layer. Ozone concentrations are in units of millipascals (mPa).

One of the essential areas of research related to the chemistry of the ozone hole lies in understanding the growth and composition of PSCs. Plans for future balloon flights, to provide further information on PSCs, include flying particle counters in conjunction with a nitric acid detector from the University of Denver and with a balloonborne lidar from the Italian lidar group at McMurdo.

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Field observations of stratospheric trace gases in support of the upper atmospheric research satellite mission during the antarctic spring of 1992

R.L. DE ZAFRA, *Physics Department* and *Institute for Terrestrial and Planetary Atmospheres, State University of New York, Stony Brook, New York 11794*

L.K. EMMONS, M. REEVES, D. SHINDELL, *and* C. TRIMBLE, *Physics Department, State University of New York, Stony Brook, New York 11794*

This research is intended to provide correlative data in support of instruments on the National Aeronautic and Space Administration's (NASA's) upper atmospheric research satellite (UARS), as well as to gather independent data pertaining to ozone loss during the antarctic spring season. We are particularly concerned with measurements of stratospheric chlorine monoxide (ClO), which is the direct product of ozone destruction by chlorine. Chlorine liberated by photolysis from chlorofluorocarbons has been shown by direct measurement to be the main cause of the springtime "ozone hole" over Antarctica (de Zafra et al. 1987, 1989; Barrett et al. 1988; Anderson, Brune, and Proffit 1989). The microwave limb sounder (MLS) instrument on board UARS also measures ClO. Both our ground-based instrument and the MLS detect rotational emission from ClO molecules in the millimeter-(mm-) wavelength spectral region.

Due to the early, seasonal nature of ozone loss over Antarctica, this research must be carried out during the winter fly-in period at McMurdo Station: that described here began in late August 1992. Following an initial period of setting up and debugging equipment, we carried out observations almost continuously from 9 September until 10 October. The troposphere was unusually cold at McMurdo Station during much of September 1992 (ground-level temperatures

steadily below –30°C, often below –35°C), and essentially no storms of any consequence occurred, so we were able to get an unusually large amount of useful data. (Tropospheric water vapor absorbs signals strongly in the spectral range of our experiment, and cold weather dries the troposphere.)

We used an improved mm-wave receiver for this work, having about half the intrinsic receiver noise as we have used previously (de Zafra et al. 1987, 1989), and this improvement cut the integration time needed to detect weak signals by about a factor of four. Therefore, we were able to get good data in as little as 2 hours in very cold, clear weather and to follow for the first time stratospheric changes taking place over short (approximately 1 day) periods.

McMurdo Station was well inside the polar vortex through early and mid-September. In the latter part of September and persisting well into October, the polar vortex was pushed away from McMurdo Station by a strong and persistent high-pressure region lying south of New Zealand. These conditions gave us a good opportunity to measure ClO both inside and outside of the vortex region, as well as to monitor the transition, which occurred over a period of a couple of days.

We again measured a ClO mixing ratio greater than or equal to 1.5 parts per billion in the lower stratosphere, peaking at around 18–19 kilometers altitude, during the earlier part of September when McMurdo Station was within the vortex region. This high a mixing ratio is enough to ensure rapid ozone destruction (Barrett et al. 1988), and balloonborne ozonesondes flown at McMurdo Station by the University of Wyoming indeed showed rapid destruction. Ozone depletion in the 1992 austral spring in fact surpassed that of any prior year. This was probably a consequence of additional lower-altitude processing of chlorine on aerosols persisting from the explosion of Mount Pinatubo in June 1991, as well as chemical processing on ice and nitric acid trihydrate particles composing polar stratospheric clouds.

We have a good record of the cycle of diurnal change for ClO, and we are comparing these data with the predictions of a photochemical model that we have recently constructed, paying particular attention to the characterization of solar flux at very large solar zenith angles. With the aid of this model and our observed rates of diurnal change, we believe it should be possible to place narrower limits on the rate of dissociation for the ClO dimer (Cl_2O_2) as a function of temperature than it has been possible to obtain from laboratory studies as a function of temperature (for example, Cox and Hayman 1988).

Comparisons are being carried out between our ground-based data and data from the MLS on UARS. The latter samples limited regions at particular times of day, and some care must be taken when comparing data: too small a temporal or geographical limit produces a small MLS data set with poor statistics, and a larger temporal or geographical range risks averaging over data that should not be compared with our own fixed-location data. Thus far, comparisons generally show very good agreement, allowing for some exceptions we are looking into.

At this writing (July 1993), we are preparing to return to McMurdo Station at winter fly-in for another series of correlative measurements under a continuation of the same National Science Foundation grant.

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