

Air chemistry monitoring at Palmer Station

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The fourth and final year of operation of the Washington State University clean-air facility at Palmer Station concluded in December, 1985. Preliminary results from the first 2 years of sampling have been published (Robinson et al. 1984), and the set-up and operation of this system have been outlined in previous *Antarctic Journal* reports.

Trace gas measurements were made at Palmer Station to determine the ambient mixing ratios of methane, carbon monoxide, carbon dioxide, fluorotrichloromethane (CCl₃F/F-11), difluorodichloromethane (CCl₂F₂/F-12), methyl chloroform, carbon tetrachloride, and nitrous oxide. All of these measurements were made on an hourly basis using flame ionization and electron capture gas chromatography. Ozone sampling (by ultraviolet photometry) was done on a continuous basis. Additionally, meteorological information such as temperature, pressure, dew point, wind speed, and wind direction was collected as well as condensation nuclei counts, which were used to determine periods of contamination from Palmer Station power plant.

This extended data set of trace gas concentrations has a wide range of applications. Increases in the world background levels of these gases have significant implications for climatic changes. Although carbon dioxide is the best known of these for its potential in global heating, the other gases being sampled also contribute to the "greenhouse effect" (Ramanathan et al. 1985). Stratospheric ozone destruction due to interaction with fluorocarbons is also of primary concern (Farman, Gardiner, and Shanklin 1985). Seasonal cycles as well as concentration changes due to meteorological variables provide important insights into atmospheric transport. To provide more comprehensive data on the correlation of synoptic meteorology and trace gas variations, the sampling frequency was increased to twice per hour during the final 3 months of the program. The gas chromatograph calibration interval was changed from a 4-hour to a 2-hour cycle to improve the precision further during this time frame.

Before the clean-air facility was shut down, a series of continuous standards analyses was conducted to provide a final system check. The system precision as indicated by the standard deviation of the analyses ($20 \leq N \leq 44$) was as follows: methane—0.66 percent; carbon monoxide—2.5 percent; carbon dioxide—0.31 percent; F-11—0.36 percent; F-12—1.24 percent; methyl chloroform—0.78 percent; carbon tetrachloride—0.58 percent; nitrous oxide—0.67 percent. This series also revealed an inconsistency in the integration techniques used by the microprocessor to determine the mixing ratios of certain compounds during the final year of operation. Correction of these calculation errors is currently in progress and will reduce the noise seen in the preliminary data presented here for nitrous oxide, methyl chloroform, and carbon tetrachloride.

The secondary field standards used on site for the gas chromatography analyses have been shipped back to Washington State University for recalibration against the primary long-term

standards series maintained for this purpose. Mixing ratio changes within the field standards are not expected to be significant.

The preliminary results of the 4-year data set have been plotted and are presented in figures 1, 2, and 3. Figure 1 represents

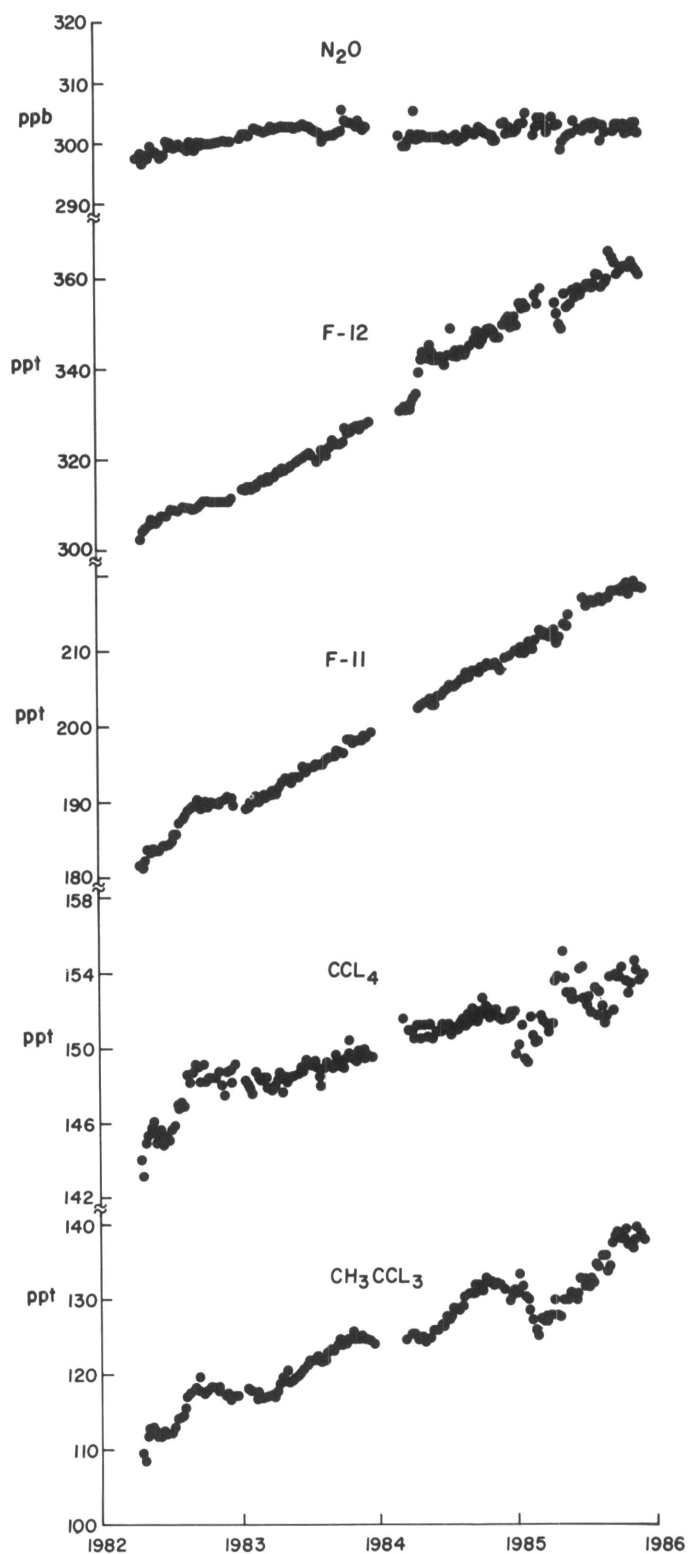


Figure 1. Weekly mixing ratios of nitrous oxide (N₂O), halocarbons (F-12 and F-11), methyl chloroform (CH₃CCl₃) and carbon tetrachloride (CCl₄). ("ppb" denotes "parts per billion" and "ppt" denotes "parts per trillion.")

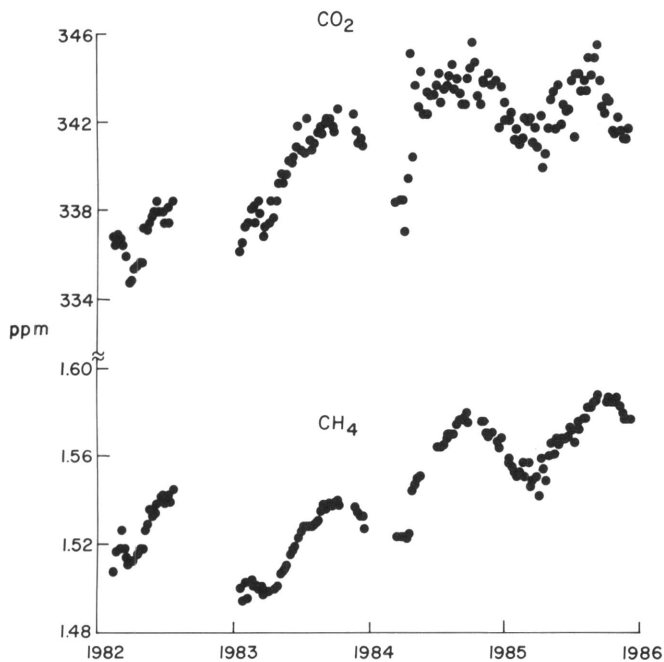


Figure 2. Weekly mixing ratios of carbon dioxide (CO₂) and methane (CH₄). ("ppm" denotes "parts per million.")

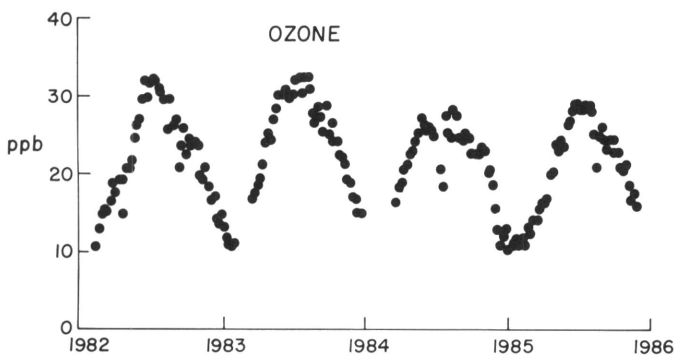


Figure 3. Weekly mixing ratios of ozone. ("ppb" denotes "parts per billion.")

the halocarbon and nitrous oxide preliminary weekly averages which show the following yearly increases over the sampling interval (based on a simple linear least-squares fit of the data): F-11—5.5 percent; F-12—5.3 percent; methyl chloroform—5.2 percent; carbon tetrachloride—1.3 percent; nitrous oxide—0.2 percent. Methane and carbon dioxide presented in figure 2, both exhibit a strong seasonal variation as well as an overall increase of 1.3 percent and 0.5 percent per year, respectively. (Carbon monoxide results are not presented at this time because further data reduction is needed. Data reduction for carbon monoxide is more time consuming because of the lower precision and lower ambient levels being measured.) In figure 3, the 4-year trend of weekly averaged ozone has been plotted, also showing a strong seasonal correlation. A more detailed analysis of these ozone trends is currently being done (Sheppard, Cronn, and Westberg in preparation). Gaps in these figures are due to times of equipment failure and periods of system retrofit and upgrade.

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References

- Farman, J.C., B.B. Gardiner, and J.D. Shanklin. 1985. Large losses of total ozone in Antarctica reveal seasonal C10_x/NO_x interaction. *Nature*, 315, 207.
- Ramanathan, V., R.J. Cicerone, H.B. Singh, and J.T. Kiehl. 1985. Trace gas trends and their potential role in climate change. *Journal of Geophysical Research*, 90, 5547.
- Robinson, E., W.L. Bamesberger, F.A. Menzia, A.S. Waylett, and S.F. Waylett. 1984. Atmospheric trace gas measurements at Palmer Station, Antarctica: 1982–1983. *Journal of Atmospheric Chemistry*, 2, 65.
- Sheppard, J., D. Cronn, and H. Westberg. In preparation. Astronomical influences on atmospheric photochemistry: Annual concentration cycles, global production rates and average OH concentration.