## **REFERENCES AND NOTES**

- G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, *Appl. Phys. Lett.* 40, 178 (1982); G. Binnig and H. Rohrer, *IBM J. Res. Dev.* 30, 355 (1986), and references therein.
- 2. M. Amrein, A. Stasiak, H. Gross, E. Stoll, G. Travaglini, *Science* 240, 514 (1988).
- 3. D. M. Eigler and E. K. Schweizer, *Nature* **344**, 524 (1990).
- See, for example, H. K. Wickramasinghe, Ed., volume 241 of the AIP Conference Proceedings (American Institute of Physics, New York, 1991).
- N. M. Amer, A. Skumanich, D. Ripple, *Appl. Phys. Lett.* 49, 137 (1986).
   P. H. Cutler, T. E. Feuchtwang, T. T. Tsong, H.
- P. H. Cutler, T. E. Feuchtwang, T. T. Tsong, H. Nguyen, A. A. Lucas, *Phys. Rev. B* 35, 7774 (1987).
- 7. R. J. Hamers and D. G. Cahill, Appl. Phys. Lett.

57, 2031 (1990); J. Vac. Sci. Technol. B9, 514 (1991).

- 8. M. R. Freeman and G. Nunes Jr., Appl. Phys. Lett., in press.
- L. Arnold, W. Krieger, H. Walther, *ibid.* 51, 786 (1987).
- G. P. Kochanski, *Phys. Rev. Lett.* 62, 2285 (1989).
  R. Möller *et al.*, *J. Vac. Sci. Technol.* B9, 506 (1991).
- 12. J. G. Simmons, J. Appl. Phys. 34, 238 (1963).
- 13. D. H. Auston, Appl. Phys. Lett. 26, 101 (1975).
- A. S. Hou, F. Ho, D. M. Bloom, *Electron. Lett.* 28, 2302 (1992).
- S. Weiss et al., Appl. Phys. Lett. 63, 2567 (1993).
  We thank N. M. Amer, S. von Molnar, R. S. Germain, and R. M. Feenstra for careful readings of the manuscript.

2 August 1993; accepted 28 September 1993

# Evidence for Large Upward Trends of Ultraviolet-B Radiation Linked to Ozone Depletion

# J. B. Kerr\* and C. T. McElroy

Spectral measurements of ultraviolet-B radiation made at Toronto since 1989 indicate that the intensity of light at wavelengths near 300 nanometers has increased by 35 percent per year in winter and 7 percent per year in summer. The wavelength dependence of these trends indicates that the increase is caused by the downward trend in total ozone that was measured at Toronto during the same period. The trend at wavelengths between 320 and 325 nanometers is essentially zero.

In 1974 it was proposed (1) that the continued use of chlorofluorocarbons (CFCs) would lead to a decrease in the amount of stratospheric ozone. This prediction led to concerns about possible detrimental effects on human health and other biological systems that might follow from the increased levels of ultraviolet-B (UV-B) radiation at the Earth's surface because of the decrease in the stratospheric ozone column. The first conclusive evidence for a downward trend in ozone levels was reported (2) in 1985 where springtime values of ozone over the Antarctic were observed to have declined by 40% between 1975 and 1984. More recently, negative trends in ozone levels at other locations have been reported (3-5) and their seasonal and geographical dependencies have been determined. Extensive field studies in the Antarctic (6) and Arctic (7) have associated the loss of ozone with high levels of chlorine in the stratosphere.

Definitive measurements of a long-term trend in UV-B radiation as a result of the decline in ozone levels at mid-latitudes have been difficult to obtain. Measurements have shown that short-term, dayto-day fluctuations of UV-B radiation vary as expected with changes in column ozone amount both in the Northern (8) and Southern (9) hemispheres as well as under the Antarctic ozone hole (10, 11). However, attempts to detect long-term trends in UV-B radiation from existing data records have been inconclusive and controversial. For example, an analysis (12) of data from a network of broad-band Robertson-Berger meters in the United States showed a negative trend in UV-B radiation levels at a time when ozone levels were known to be decreasing.

The detection of a long-term change of UV-B radiation is considerably more difficult than the measurement of the long-term decline of ozone levels. One reason is that the intensity of UV-B radiation at the Earth's surface depends on many factors other than stratospheric ozone, including clouds, aerosols, haze, pollutants and ground albedo. Periodic or long-term changes of any of these variables will influence trend results derived from the analysis of UV-B measurements. It is essential that instruments making the measurements be well characterized and that a good calibration of instrumental response be maintained for a long period of time. Because of the difficulty of the measurement, UV-B data are sparser, available for a shorter time interval, and are poorer in quality than the ozone record, making trend analysis uncertain.

In this paper we report spectroradiometric UV-B measurements made at Toronto (44°N, 79°W) between 1989 and 1993. Our results are from Brewer instrument number 14, one of the triad of independently calibrated instruments maintained at Toronto as the Canadian total ozone reference. The Brewer instrument measures the intensity of UV-B radiation falling on a horizontal diffusing surface. Measurements are made at wavelength intervals of 0.5 nm between 290 and 325 nm with a resolution of about 0.5 nm. Each spectral measurement consists of the average of a forward and backward wavelength scan, which takes about 8 min to complete. Measurements are made between once and twice each hour throughout the day from sunrise to sunset.



**Fig. 1.** Record of daily ozone measurements between 1989 and 1993. The straight lines are the best-fit linear trends through the winter (December to March; -4.1% per year) and summer (May to August; -1.8% per year) data points with the annual cycle removed.

Environment Canada, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Canada M3H5T4.

<sup>\*</sup>To whom correspondence should be addressed.

SCIENCE • VOL. 262 • 12 NOVEMBER 1993

### REPORTS

Fig. 2. Record of integrated daily total radiation at (A) 324 nm and 300 nm. The (**B**) straight lines are linear regressions through winter and summer data points with the annual cycle removed. The trends at 300 nm where ozone absorption is stronger (35% per year in winter; 6.7% per year in summer) are significantly larger than those at 324 nm (-0.4% per year in winter; -0.1% per year in summer). The light intensity at 300 nm is about 1% of that at 324 nm; the difference is mostly a result of ozone absorption.



The spectral responsivity of the instrument to UV-B radiation is routinely monitored by measuring the spectral irradiance from a set of lamps whose specific intensities are traceable to calibrations made at the U.S. National Institute of Standards and Technology (NIST). Analysis of the calibration records is a useful means to determine relative uncertainties in the measurement of UV-B as a function of time both in the short-term (month-to-month) and the long-term (several years). The calibration records indicate that the instrument responsivity varied by  $\pm 2.7\%$  at 300 nm and ±2.5% at 325 nm between 1989 and 1993. These variations are representative of the overall uncertainty of the calibration process including instrument variability with time and differences in calibration set-up that may occur from one calibration to another. Also, the trend of instrument responsivity was measured as -0.3%  $(\pm 0.6\%)$  per year at 300 nm and  $\pm 1.0\%$  $(\pm 0.5\%)$  per year at 324 nm. This trend



**Fig. 3.** Absorption spectrum (*18*) of ozone at 226 K for wavelengths between 298 and 325 nm at 0.5-nm intervals smoothed to the 0.5-nm resolution of the Brewer instrument.

was seen using several lamps and is believed to be mostly a result of instrument change with time. The data have been adjusted to account for both short-term and long-term changes in instrument sensitivity.

Our results are for winter months (December to March) and summer months (May to August) as defined in previous reports (3, 4). These seasons are of prime interest because winter is the time of year when maximum ozone depletion is observed and summer is the time of maximum intensity of UV-B incidence. The minimum ozone depletion occurs during fall (September to November) and the trends in UV-B radiation at this time of year are yet to be assessed.

The record of daily total ozone levels measured over Toronto between 1989 and 1993 (Fig. 1) shows that ozone levels decreased 4.1% per year in winter and 1.8% per year in summer. These rates of decline are significantly larger than those seen throughout the 1980s (3) and are enhanced by record low total ozone values in 1993 (13, 14). Based on ozonesonde data (13), 90% of the observed total ozone change over the period likely occurred in the lower stratosphere. The record includes data over a period of five summer seasons and four winters and is for direct sun measurements only. The winter of 1991-92 is not included because the instrument was out of service for a calibration trip to Mauna Loa Observatory, Hawaii.

The UV-B radiation data are given as integrated daily flux values taken routinely under all types of weather and turbidity conditions and only from days with complete data sets (that is, measurements from sunrise to sunset with no intervals exceeding 2 hours). It is important to assess these

SCIENCE • VOL. 262 • 12 NOVEMBER 1993

daily measurements because they represent the total UV-B energy dose received by biological systems at the Earth's surface.

Records of total daily radiation between 1989 and 1993 (Fig. 2) show that the energy measured as a function of time at 324 nm was relatively flat from year-toyear (winter trend of -0.4% per year and summer trend of -0.1% per year), whereas a distinct trend is seen at 300 nm. Light at 324 nm has little dependence on the amount of atmospheric ozone because the absorption coefficient at this wavelength is small (Fig. 3). Variations in the light intensity at this wavelength are a result mainly of other influences such as changes in cloud cover, haze, aerosol, pollution, and ground albedo. The large fluctuations of the many variables that affect radiation received at the Earth's surface appear to have been averaged out and do not contribute to a significant trend over a 5-year period. The lack of a trend at 324 nm is consistent with the hypothesis that the responsivity of the measurement system remained stable.

At 300 nm (Fig. 2B), where there is a relatively large amount of absorption due to ozone (Fig. 3), the data show increases in radiation of 35% per year for winter and 6.7% per year for summer. The difference between trends seen at 300 nm (Fig. 2B) and 324 nm (Fig. 2A) is because of the wavelength dependence of the absorption coefficient of ozone.

To confirm that the observed trends at 300 nm are a result of changes in ozone levels, we determined linear trends at all wavelengths between 280 and 325 nm (Fig. 4). Comparison of these trends with the ozone absorption spectrum shown in Fig. 3 shows that the observed, long-term trend in ozone has caused the observed increase in the level of UV-B radiation at Toronto. Some of the detailed structure of the ozone absorption spectrum (Fig. 3) is seen in these data (Fig. 4).

The temporal increase of UV-B radiation is also revealed by comparing the average total daily flux spectra measured at Toronto in 1993 to those made in 1989 (Fig. 5). It is apparent that recent measurements are larger than those made earlier for both summer and winter and that the increases are consistent with less absorption attributed to ozone.

The observed UV-B trends as a function of wavelength (Fig. 4) are consistent with those expected from the observed ozone trends (Fig. 1). Dividing the winter and summer trend values in Fig. 4 by 4.1 and 1.8, respectively, gives the wavelength dependencies of the percentage increase of UV radiation for a 1% decrease in ozone. Reasonable agreement is found when these values are compared with model calculations for winter and summer clear sky, noontime conditions at comparable latitudes (15).

We found that erythemally (16) active radiation levels increased by +5.3% per year in winter and +1.9% per year in summer after adjustment for effects not caused by changes in ozone levels by use of trends at wavelengths between 323 and 325 nm. Comparison of these values to the ozone trends shown in Fig. 1 give radiation amplification factors (RAFs) of 1.3 for winter and 1.1 for summer. These values are consistent with those seen when day-to-day fluctuations in erythemally active UV-B radiation are compared to variations in ozone levels (8, 9).

The winter and summer decreases in



**Fig. 4.** The winter and summer linear trends in UV-B radiation as a function of wavelength. There is striking similarity between the shapes and some detailed features of these curves with those of the ozone absorption spectrum shown in Fig. 3, establishing a link between the positive trend in UV-B and the negative trend in ozone both observed over the same period.

total ozone between 1989 and 1993 (Fig. 1) are about six times those measured at midlatitudes during the 1980s (3-5). Although there is evidence that the rate of decline in total ozone has increased in recent years (4), it is not likely that the values given in Fig. 1 are representative of time periods extending into the future. Trend results from a few years of data are influenced by natural cyclic variations with periods of a few years such as the Quasi Biennial Oscillation, El Niño, and the 11-year solar sunspot cycle. Also, the volcanic eruption of Mount Pinatubo in 1991 is likely to have temporarily reduced total ozone on a global scale (14). The UV-B trends (Fig. 4) may not be representative of longer term changes at mid-latitudes in the Northern Hemisphere and, therefore, should not be extrapolated to predict future UV-B conditions. The observed trends from the ozone data (Fig. 1) and UV-B data (Fig. 4) may be applied to the ozone trends determined from the longer data records in order to determine longer term spectral changes in UV-B radiation.

Our data were measured at a site in close proximity to a large urban center where several local changes could influence the measured UV-B radiation levels. The use of a spectroradiometric instrument is necessary in distinguishing between effects caused by changes in stratospheric ozone and those of other atmospheric variables such as clouds, haze, pollution, and volcanic aerosols. Model results (15, 17) indicate that the wavelength dependence of UV-B radiation on clouds and aerosols is relatively small.

The observed, large increases in UV-B radiation near 300 nm in winter are large fractional increases in small values. For this reason, it may not represent a significant increase in terms of its biological impact.



**Fig. 5.** Spectra of the average daily total UV-B energy flux for the 1993 and 1989 winter and summer seasons. The dependence of the increase of flux with wavelength is consistent with the decrease in ozone.

However, increases in UV-B in the late spring may have a disproportionately larger effect on some species if they occur at critical phases in their development.

Record low ozone values have been recorded at Toronto during 1993 (13). Measurements of UV-B radiation levels in 1993 were higher on several days than any measurements made in the previous four years for the same time of year (Fig. 2B). It is likely that past UV-B values have never reached the 1993 levels, at least since the beginning of the Toronto ozone record (1960). It is also quite reasonable to extend this conclusion based on the Toronto data (where record high UV-B readings were recorded in 1993) to other places because record low ozone values are also being reported elsewhere (13, 14).

#### **REFERENCES AND NOTES**

- 1. M. J. Molina and F. S. Rowland, *Nature* 249, 810 (1974).
- 2. J. C. Farman et al., ibid. 315, 207 (1985).
- 3. R. Stolarski, R. Bojkov, L. Bishop, C. Zerefos, J.
- Staehelin, J. Zawodny, *Science* 256, 342 (1992).
  World Meteorological Organization, WMO Global Ozone Research and Monitoring Project *Rep.* 25 (WMO, Geneva, 1992).
- 5. J. B. Kerr, J. Geophys. Res. 96, 20703 (1991).
- 6. A. F. Tuck *et al.*, *ibid.* **94**, 11181 (1989), and references therein.
- R. Turco, A. Plumb, E. Condon, *Geophys. Res.* Lett. 17, 313 (1990), and references therein.
- J. B. Kerr, C. T. McElroy, D. W. Tarasick, D. I. Wardle, in *Proceedings of Quadrennial Ozone Symposium*, R. D. Hudson, Ed. (University of Virginia, Charlottesville, 1992).
- R. L. McKenzie, W. A. Matthews, P. V. Johnston, Geophys. Res. Lett. 18, 2269 (1991).
- 10. D. Lubin et al., ibid. 16, 783 (1989).
- J. E. Frederick, P. F. Soulen, S. B. Diaz, I. Smolskaia, C. R. Booth, T. Lucas, D. Neuschuler, J. Geophys. Res. 98, 8891 (1993).
- 12. J. Scotto, G. Cotton, F. Urbach, D. Berger, T. Fears, *Science* 239, 762 (1988).
- J. B. Kerr, D. I. Wardle, D. W. Tarasick, *Geophys. Res. Lett.* 20, 1979 (1993).
- 14. J. F. Gleason et al., Science 260, 523 (1993).
- World Meteorological Organization, WMO Global Ozone Research and Monitoring Project, *Rep. 20* (WMO, Geneva, 1989).
- A. F. McKinlay and B. L. Diffey, in *Human Exposure to Ultraviolet Radiation: Risks and Regulations*, W. R. Passchler and B. F. M. Bosnajakovic, Eds. (Elsevier, Amsterdam, 1987), pp. 83–87.
- 17. S. Madronich, *Geophys. Res. Lett.* **19**, 37 (1992). 18. L. T. Molina and M. J. Molina, *J. Geophys. Res.*
- 91, 14501 (1986). 19. Single monochromators are subject to stray light
- 19. Single molecularity light intensity (>320 nm) contaminating measurements at wavelengths (<305 nm) with significantly less energy. This effect is minimized in the Brewer instrument with a band limiting filter which removes light at wavelengths >340 nm and by subtracting the stray light measured near 290 nm where there is negligible ground level radiation. Resulting errors are typically ~0 for wavelengths >302 nm, ~+5% at 300 nm and increase below 300 nm, depending on ozone amount and sun angle. Errors on the trends with wavelength are smaller.
- D. I. Wardle provided valuable scientific discussion. A. Asbridge, J. Bellefleur, W. Clark, and E. Wu provided routine instrumental operation, maintenance, and calibrations.

2 September 1993; accepted 15 October 1993

SCIENCE • VOL. 262 • 12 NOVEMBER 1993