SPRINGTIME SURFACE OZONE FLUCTUATIONS AT HIGH ARCTIC LATITUDES AND THEIR POSSIBLE RELATIONSHIP TO ATMOSPHERIC BROMINE

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At high Arctic stations such as Barrow, Alaska, springtime near-surface ozone amounts fluctuate between the highest and lowest values seen during the course of the year (Oltmans, 1981). Episodes when the surface ozone concentration is essentially zero last up to several days during this time of year (Fig. 1). In the Arctic Gas and Aerosol Sampling Program (AGASP-I and AGASP-II) in 1983 and 1986, it was found that ozone concentrations often showed a very steep gradient in altitude with very low values near the surface (Herbert et al., 1988; Bridgman et al., 1988). The cold temperatures, and snow-covered ground make it unlikely that the surface itself would rapidly destroy significant amounts of ozone.
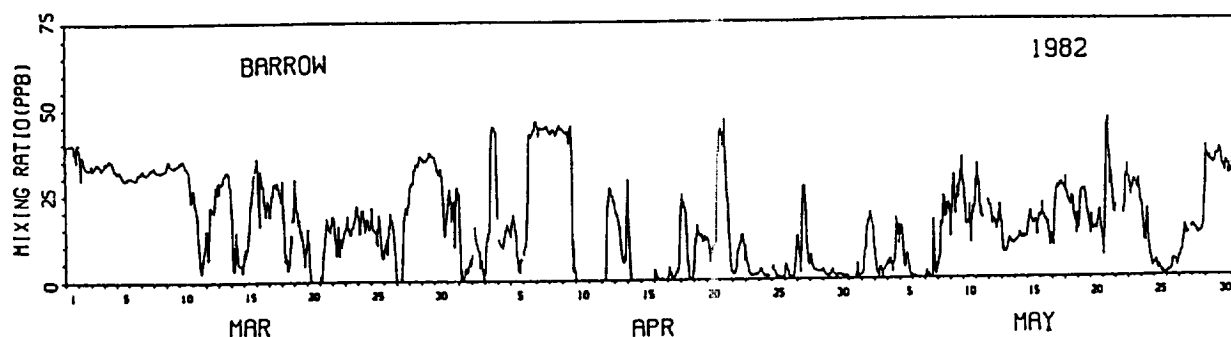

Fig. 1. Hourly surface ozone concentrations at Barrow for Mar-May 1982 showing large fluctuations and periods of near-zero values.

Fifteen years of ozone observations near the surface at Barrow, Alaska (71°N, 157°W) show (Fig. 2) a late autumn and winter maximum, a sharp springtime drop; a modest recovery to a secondary maximum in June; a small dip during the summer; followed by rising concentrations during autumn. Although ozone concentrations in Fig. 2 show a great deal of variability which ranges in scale from days to years, the pattern described above is in evidence each year. A very similar pattern is seen in the ozonesonde record at Resolute, NWT (75°N) for observations near the surface. Such a seasonal pattern is unique to the high Arctic and is not seen at other relatively high latitutde stations (e.g. Churchill at 59°N) outside the Arctic Basin. Ozonesonde observations at both Barrow and Resolute show that this behavior is confined to the boundary layer.

The AGASP aircraft measurements that found low ozone concentrations in the lowest layers of the troposphere also found that filterable excess bromine (the amount of bromine in excess of the sea salt component) in samples collected wholly or partially beneath the temperature inversion had higher bromine concentrations than other tropospheric samples. Of the four lowest ozone minimum concentrations, three of them were associated with the highest bromine enrichments. Surface measurements of excess filterable bromine at Barrow (Berg et al., 1983) show a strong seasonal dependence with values rising dramatically early in March, then declin-

ing in May. The concentration of organic bromine gases such as bromoform (Fig. 3) rise sharply during the winter, and then begin to decline after March with winter and early spring values at least three times greater than the summer minimum (Cicerone et al., 1988). Recently Barrie et al. (1988) found that at Alert, NWT (82°N), ozone mixing ratios during April 1986 were anticorrelated at a level of better than 0.95 with filterable bromine concentrations.
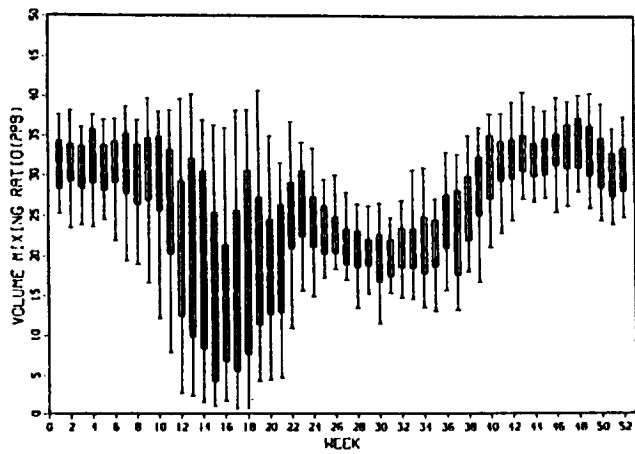

Fig. 2. The seasonal variation of ozone at Barrow, AK for 1973-1986. Box and whisker plots at weekly intervals are from daily means. The median (dot), the upper and lower quartiles (ends of the box) and upper and lower 5 percentiles (ends of lines are shown.
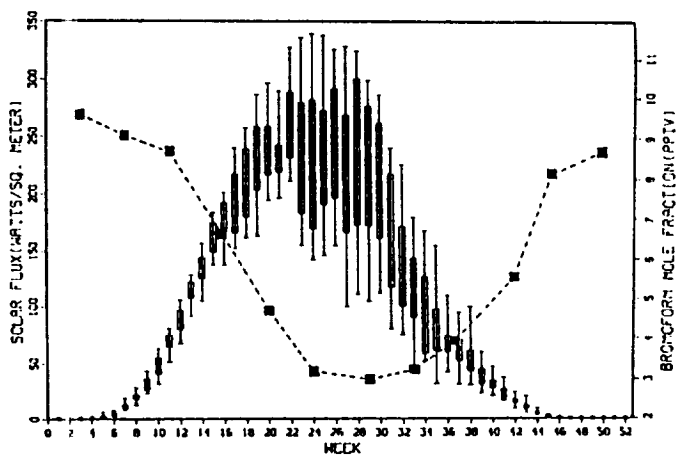
Fig 3. Total global flux of solar radiation at Barrow for 1976-1983, with box and whisker plots as in Fig. 2 and mean monthly bromoform mole fraction (from Cicerone et al., 1988).

The critical link between the presence of organic bromine gases and the large fluctuations in ozone near the surface is the appearance of sunlight in the spring. In early March at Barrow, the total global flux of solar radiation (Fig. 3) begins a rapid rise. March and April appear to be months with a number of days having relatively clear skies. Although the radiative input continues to climb through May, there is an increasing amount of cloudiness as 24-hour daylight approaches. If solar radiation is an important factor, then more northerly stations should show a later appearance of the spring peak in filterable bromine. This indeed does appear to be the case from data presented by Sturges and Barrie (1988) from stations ranging in latitude from 70°N to 82°N.

The springtime minimum in the seasonal cycle of surface ozone concentrations at high arctic latitudes appears to be linked to the destruction of ozone in the boundary layer by reactions with bromine compounds (Wofsy, 1975; Barrie et al., 1988). Organic bromine compounds emitted from the predominatly ice-covered ocean appear to react with ozone in the presence of adequate sunlight to destroy ozone and produce filterable bromine particles. During stable periods, bromine compounds appear to produce a rapid and thorough destruction of the ozone as seen in the Barrow surface ozone record. Simultaneous measurements of filterable bromine and ozone at the surface were made at Barrow during the spring of 1986. The broad features of the relationship between filterable bromine enrichment and ozone mixing ratio are shown in Fig. 4. A 60-hour running mean has been applied to these data to smooth out small scale fluctuations. Although the correlation is a modest -0.64 between these two quantities, there is a clear tendency for high bromide values to be associated with low ozone concentrations and vice versa. The long

series of ozone measurements combined with measurements of filterable bromine, bromine gases and solar insolation show that the pattern seen in 1986 is found each year at Barrow. Data from aircraft and from a number of other locations suggest that this is an important process over a broad region of the Arctic Basin.
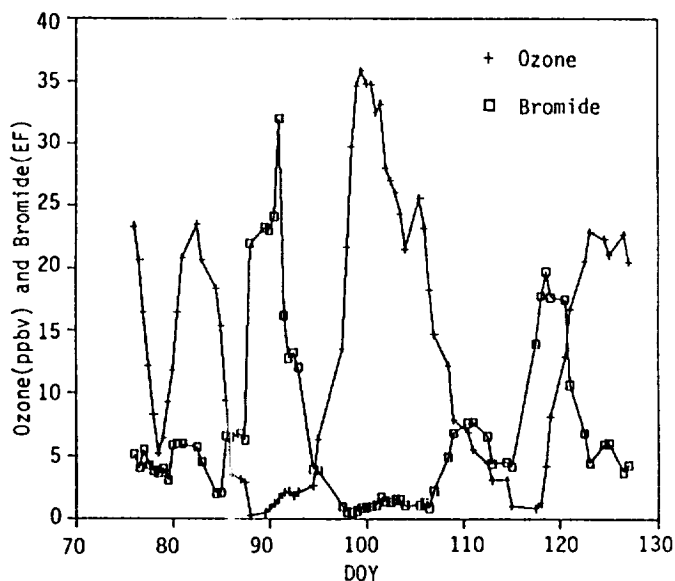

Fig. 4. Surface ozone mixing ratio (+) and filterable bromine enrichment factor (□) during Spring 1986 at Barrow, AK.

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