THE TROPOSPHERIC POLLUTION AND THE SOLAR **ULTRAVIOLET RADIATION**

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A comparison between the historic and present records of the surface ozone concentration at three European locations has been performed. The conclusion that increased photochemical pollution acts as a filter to deplete the solar ultraviolet radiation at the surface has been substantiated.

1. INTRODUCTION

It is well known that the transfer of solar ultraviolet radiation in the atmosphere is mainly affected by Rayleigh scattering, atmospheric ozone absorption, both scattering and absorption by aerosols and clouds. Assuming that solar elevation angle, cloud amount, and turbidity remain constant, the ultraviolet radiation in the wavelength range 280 to 315 nm (UV-B) is strongly affected by ozone changes. As a rule, these ozone changes are of an opposite sign in the stratosphere (a decrease) and in the troposphere (an increase).^{1,2} Increase in tropospheric ozone may have decreased the levels of the solar ultraviolet radiation both in rural and urban areas by amount comparable to the increase induced from stratospheric ozone depletion.^{3,4}

This paper presents a detailed analysis for the estimation of the UV-B reduction due to the dramatic increase of the tropospheric ozone over Southern Europe since the last century.

2. DISCUSSION AND RESULTS

A. Temporal increase in surface ozone concentration

Bojkov⁵ based on the surface ozone data from several European stations for the second half of the nineteenth century, found that the average daily maximum ozone mixing ratio was between 17 and 23 ppbv, or about one-half of the surface ozone concentration in recent years at the same geographic locations.

Bozo and Weidinger⁶ recently analyzed the surface ozone concentration measurements carried out at two meteorological observatories in Hungary (Buda and Szeged) during the second half of the last century. They discovered that higher values of the ozone concentration were detected in Szeged (the averages for 1853-1861 are 26.4 ppbv for day-time and 25.7 ppbv for the night-time) than in Buda (the averages for 1865-1873 and 1877-1887 are 18.2 ppbv for day-time and 16.8 ppbv for nighttime). They also have made a comparison of the historic surface ozone data with those currently measured at the air pollution monitoring station in K-puszta (since 1990). According to the recent surface ozone data for Hungary, the day-time mixing ratio is as high as 38 ppbv while the night-time is 24.3 ppbv. Figure 1 illustrates the monthly averages of the day—time surface $\,$ ozone mixing ratio measured in Buda during 1865-1888 and in K-puszta during 1990-1992. Inspection of Figure 1 shows that the 1990-1992 K-puszta record is characterized by higher ozone values as compared with the 1865-1888 Buda record. For instance, in July there is a secular increase in surface ozone mixing ratio from 20 ppbv to 55 ppbv. Such large differences may be attributed to the increase in the concentration of the

ozone precursors stimulating photochemically the formation of tropospheric ozone.

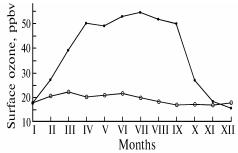


FIG. 1. Average monthly day-time mixing ratios of surface ozone in Buda (1865-1888) and K-puszta (1990-1992): •**__**•, Buda; **•**__•, K-puszta.

Anfossi et al. 7 analyzed a 26-year (1868–1883) data series of daily surface ozone mixing ratios obtained in Moncalieri, near Turin, in Nothern Italy. According to their results, the ozone concentration has increased by more than twice, not only at the surface, but also in the free troposphere, in comparison to one century ago. Figure 2 shows the average monthly surface ozone mixing ratios obtained in Moncalieri during 1868-1893 and Po valley, Ispra (1986-1989).

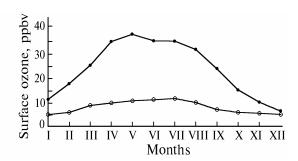


FIG. 2. Average monthly surface ozone mixing ratios in Moncalieri (1868–1893) and Ispra (1986–1989): ∘_ Moncalieri; •—•, Ispra.

It is obvious from Figure 2 that the July surface ozone level observed one century ago (12 ppbv) differs strongly from

the values measured in the recent years (35 ppbv). Such an increase is very likely to be related to the photochemical production of ozone because of the increased emission of such precursors as NO_x and hydrocarbons.

Varotsos and Cartalis⁸ evaluated the mixing ratio of surface ozone in Athens, based on 40—years record of measurements obtained at the National Observatory of Athens (1901—1940). They found that the daily average surface ozone mixing ratio was approximately 20 ppbv or about one—half of the surface ozone concentration in recent years. Figure 3 provides the monthly averages of the mean day—time surface ozone mixing ratios in Athens for the periods 1901—1941 and 1987—1990 (Varotsos et al.⁹). A close inspection of Figure 3 shows that the daily average surface ozone mixing ratio in July during 1901—1940 was about one third of the surface ozone mixing ratio in July during 1987—1990. It should be noted in this connection that Varotsos et al.¹⁰ suggested the physicochemical explanation for this dramatic increase in tropospheric ozone content over Athens.

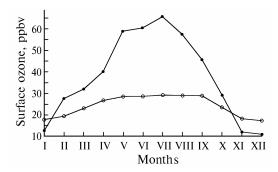


FIG. 3. Monthly averages of the mean daily surface ozone mixing ratios in Athens: •____, 1901–1990; •______, 1987–1990.

B. Estimated decrease in UV-B

Bruhl and Crutzen¹¹ pointed out that the scattering of UV—B light reaching the lower troposphere significantly changes the mean path length of the radiation through tropospheric ozone. Assuming that the solar zenith angles are less than 60°, the path lengths of the diffuse light are generally longer than those of the direct solar beam. Hence, for locations and seasons having solar zenith angles less than 60°, tropospheric ozone absorbs UV radiation more effectively than stratospheric ozone.

According to the above discussion concerning the dramatic increase of the surface ozone concentration at many sites over Europe (see paragraph A), it is of great importance to estimate relevant decrease in the biologically active ultraviolet radiation reaching the ground. For doing so, it is safe to assume that the ozone mixing ratio is constant from the surface to 10 km height, at least for middle latitudes. ¹² As an illustration, in Figure 4 the sensitivity of DNA daily dose rates of tropospheric ozone is presented, assuming a constant ozone mixing ratio in the troposphere between 0 and 10 km, for 40°N (see Refs. 3 and 13). Table I summarizes the results obtained from the comparison of the surface ozone mixing ratios at three European locations during the historic and recent periods, as they have been deduced from the discussion in paragraph A.

Using the information of Table I to assess the daily DNA dose in accordance with Figure 4 data, one can get the percentage in the DNA dose.

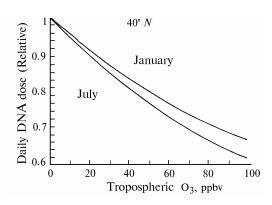


FIG. 4. Effect of tropospheric ozone on daily UV-B dose for DNA damage by tropospheric ozone, calculated assuming a constant ozone mixing ratio from sea level to 10 km height.

TABLE I. Mean daily surface ozone mixing ratio for July, during historic and recent years.

Location	Period	O ₃ ,	Period	O ₃ ,	DNA
		ppbv		ppbv	dose, %
Moncalieri	1868 - 1893	12	1986 - 1989	35	10.6
Athens	1901 - 1940	28	1987 - 1990	65	19.1
Buda	1865 - 1888	20	1990 - 1992	55	17.5
(K-puszta)					
Hungary					

An inspection of Table II shows that the solar ultraviolet radiation at the surface in the urban area of Athens is characterised by a larger decrease rate, comparing with semi—urban areas of Moncalieri and Buda. Thus, the hypothesis that increased levels of photochemical pollution may act as a filter to the transfer of solar ultraviolet radiation to the surface, is further supported.

TABLE II. Percentage decrease in the daily DNA dose for the entire comparison period and percentage decrease per decade.

Location	decrease in	decrease in DNA dose
	DNA dose, %	per decade, %
Moncalieri (Italy)		
	10.6	0.9
Buda (Hungary)	17.2	1.4
Athens (Greece)	19.1	2.0

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