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RELATIONSHIP OF TOTAL OZONE AMOUNT, UV RADIATION INTENSITY, AND THE GROUND-LEVEL OZONE CONCENTRATION AT RURAL LITHUANIAN SITES

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The ultraviolet radiation intensity, the total ozone amount, and the ground-level ozone concentration are the three essential factors having impact on the vegetation, materials, the human health, and the atmospheric chemistry. The analysis of the relationship among these parameters was made for the obtained data under Lithuanian rural conditions. UVB radiation intensity and ground-level ozone concentration were measured at the Rūgšteliškės monitoring station and total ozone data were obtained from the Kaunas meteorological station during 2002–2003. Cloudless or slightly cloudy days of the period were chosen for the analysis. The results showed a strong dependence ($R = 0.73$ for 2002 and $R = 0.75$ for 2003) between the UVB radiation intensity and the ground-level ozone concentration. The photochemical ozone generation at the Rūgšteliškės station, located in the unpolluted forest area, is related to the reaction between natural volatile organic compounds emitted from the vegetation at low nitrogen oxide level. A more pronounced relationship between the UVB radiation intensity and the ground-level ozone concentration was found in 2003 and it could be related to specific meteorological conditions of the summer of 2003. A negative correlation ($R > -0.86$) was determined during cloudless days between the UVB radiation and the total ozone.

Keywords: ground-level ozone concentration, monitoring data, total ozone, ultraviolet radiation

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1. Introduction

Ozone content variations in the stratosphere lead to variations in the biologically active ultraviolet (UV) radiation. A major concern regarding a decrease in stratospheric ozone is the consequential increase of solar UV radiation passing through the atmosphere and reaching the Earth's surface [1]. According to current evaluations, a decline of the ozone layer thickness by 1% is approximately equivalent to the increase of UVB radiation intensity by 2% [2]. One of the main biological impacts of UV exposure on plants is reduction of the photosynthesis rate. This can have a direct effect on the plant primary productivity and, since different species may vary in their sensitivity to UV exposure, may eventually affect biodiversity. Apart from direct biological consequences, indirect effects may cause changes in atmospheric chemistry. Increased UVB will alter photochemical reaction rates in the lower atmosphere that are important for generation of ground-level ozone under smog conditions. Consequently, changes of UVB radiation, e. g., due to changes of the stratospheric ozone amount, could alter the concentration of reactive tropospheric gases, including ozone [3]. The solar ultraviolet radiation plays an important role in tropospheric photochemistry since it determines the rate of ozone photolysis $J(\mathrm{O}\,^1\mathrm{D})$ and a subsequent formation of OH radicals. The impact of UV radiation change on troposphere oxidation and on tropospheric ozone trends has been studied in several simulation experiments, which suggest that the impact of stratospheric ozone depletion on tropospheric ozone is different at different altitudes and in different chemical regimes [4].

Increased UV radiation intensity enhances photochemical activity in the troposphere [5, 6]. The photochemical effect of increased UV radiation intensity has a seasonal character. The increase of ground-level ozone due to reduced stratospheric ozone on a long term is expected to be the highest in spring [5]. The influence of the UV changes could also be relevant to the regional scale air quality, since it could alter the concentrations of photo-oxidants in the boundary layer on the time scale of episodes as well as on a long term.

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The spectrum of the ultraviolet radiation, by evaluating its impact on health, is grouped into UVA and UVB radiation according to the wavelengths. The UV radiation from 315 to 400 nm wavelength is called UVA. UVB radiation is in the interval from 290 to 315 nm wavelength and it damages the main block of life – deoxyribonucleic acid (DNA). UVB radiation that is damaging to all live organisms takes the least part of the spectrum and comprises ∼1% of the total radiation affecting the surface of the Earth. Such grouping is standardized by the International Commission on Illumination, however some scientists use different grouping by extending the UVB radiation interval from 315 nm to 320 nm [7].

The intensity of both UVA and UVB radiation exhibits a pronounced annual cycle. UV radiation varies markedly through the year – it is noticeably more intense from April to September. In winter, UV radiation intensity is low but can still be significant, especially at extended exposure and / or reflection off fresh snow. The seasonal variations of the total ozone show that at northern mid-latitudes ozone amounts are larger in winter and early spring and smaller in summer and fall, i. e., the ozone distribution varies by latitude, with different seasonal cycles at different locations [8].

The variations of ground-level ozone concentrations also depend on the season and on the measurement location. Therefore, it is very important to evaluate the extent of the influence of mentioned factors on the UV radiation intensity.

The aim of this study is to evaluate relationship among the UVB radiation intensity and the total and ground-level ozone under low polluted Lithuanian rural conditions and to estimate a varying UV effect on the ground-level ozone concentration.

2. Measurement sites and methods

Measurements of the ultraviolet radiation intensity and ground-level ozone concentration were carried out at the Rūgšteliškės monitoring station (55°26′ N and 26°04′ E, 170 m above sea level). The station is located at the unpolluted site in the eastern part of Lithuania, surrounded by a coniferous forest. The nearest point of the local pollution source is Utena town with approximately 36000 inhabitants, 25 km to the west from the station.

Sensors of the sun radiation are installed on the top of the meteorological tower at the height of 26 m. The UVB radiation was measured with the pyranometer SKU–430 in a range of 0–5 W/m^2, providing radiation registration in the wavelength interval from 280 to 315 nm. The sensor sensitivity was 150 $mV/(W/m^2)$, response error was less than 3%.

The ground-level ozone concentration was measured with a standard ultraviolet absorption ozone analyzer ML9811. The lowest detectable limit is 1 $\mu g/m^3$, linearity error is about 1%. The ozone analyzer operates continuously with the lag time less than 20 seconds. The obtained data were averaged over a 1 hour period. The ground-level ozone concentration and UVB radiation were measured continuously and hourly average values were used for the analysis.

The total ozone content was measured with the filter ozonometer M-124 at Kaunas meteorological station (54°53′ N and 23°50′ E, 77 m above sea level) of the Lithuanian Hydrometeorological Service at about 100 km to the south from the Rūgšteliškės station. The measurement error of total ozone is less than 4%. The total ozone data were taken from the webpage of World Ozone and Ultraviolet Radiation Data Centre [9].

3. Results and discussion

The continuous measurement data of the total ozone, UVB radiation intensity, and the ground-level ozone concentration during 2002–2003 were analysed. The changes of the total ozone, the daily maximum values of UVB radiation intensity, and the ground-level ozone concentration during the investigation period are presented in Fig. 1. As at the most stations in the Northern hemisphere, the highest UVB radiation intensity was observed at the Rūgšteliškės station from April to September.

The seasonal course of the total ozone, as at the other neighbouring [9] stations, showed the increase in spring and the decrease in winter. The highest values of 490 DU (Dobson units) and 495 DU were observed in April and the lowest values of 230 DU and 250 DU in January of 2002 and 2003, respectively.

The previous investigations [10] revealed two most often observed types of the ground-level ozone concentration changes in the annual course at the Lithuanian rural stations: with the value increase only in spring and their broad increase in spring and summer. The annual variations of the ozone concentration (Fig. 1) during the evaluated period can be attributed to both cases: with one broad peak in 2003 and two peaks in 2002. It should be noted that maximum concentrations were not very high and they exceeded 165 $\mu g/m^3$ and 142 $\mu g/m^3$ in 2002 and 2003, respectively.

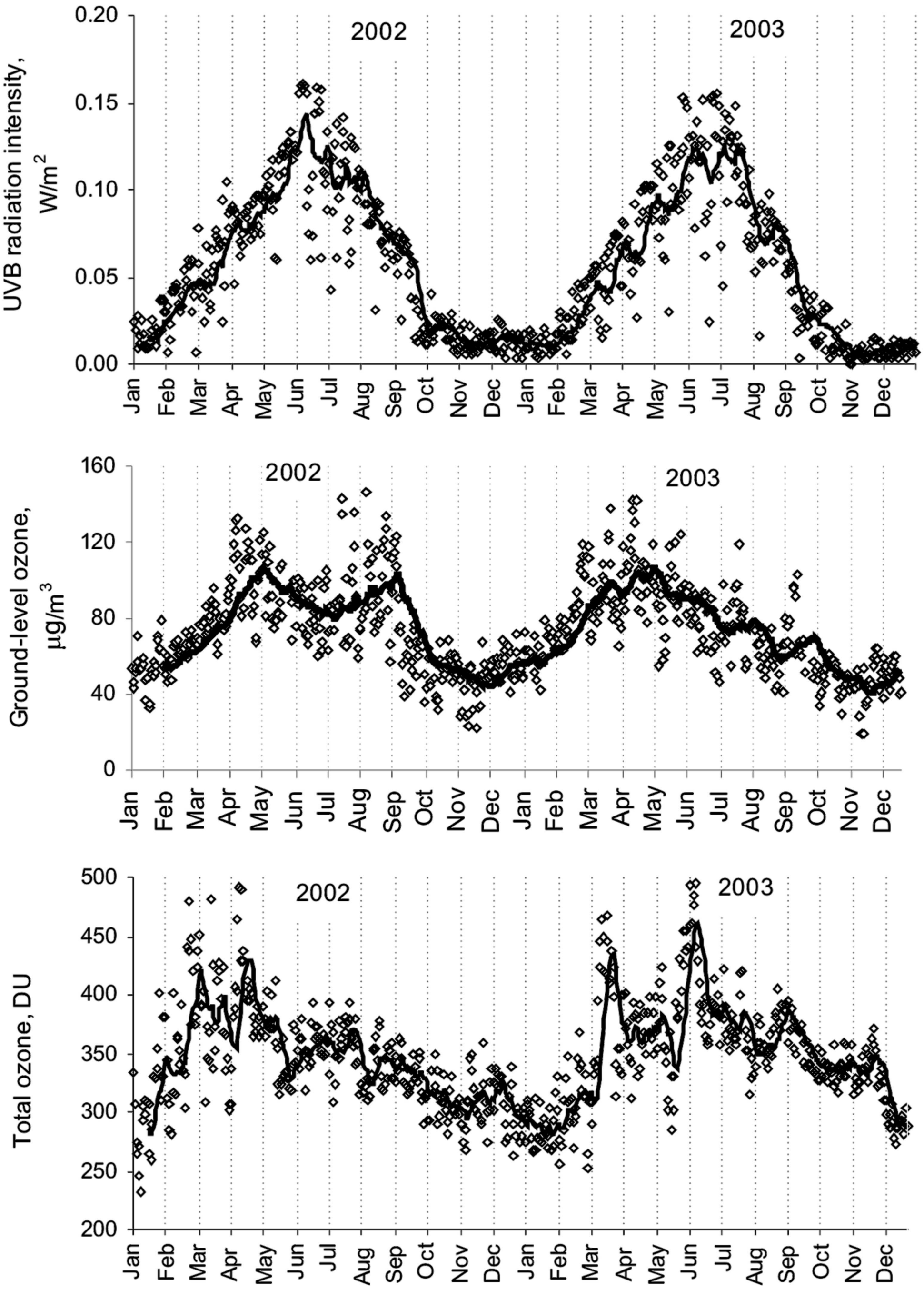

Fig. 1. Variations of the daily maxima of UVB radiation intensity, the total ozone, the ground-level ozone concentration, and their 31-day moving average.

It is known that the solar irradiance at the earth's surface varies greatly depending on factors such as latitude, time of a day, time of year, and the cloud cover. In the case of the UV radiation, additional factors are ozone, cloud cover, elevation above sea level, solar zenith angle, surface albedo. Therefore, the UVB radiation intensity was analysed during different months of the investigation period. The investigations revealed insignificant changes of the radiation intensity during these years; the maximum and minimum values were close. For example, the performed analysis of the UVB radiation variations during the cloudless days in July of 2002 and 2003 revealed that maximum radiation intensity values were 0.15 and 0.14 $\mathrm{W/m^2}$, respectively. It is necessary to note that the average values were also close to each other, 0.10 $\mathrm{W/m^2}$, in these months. On particular days of July 2002 (1, 5, 12, 21, 23) and July 2003 (4, 6–11, 14, 23) low UVB radiation intensity

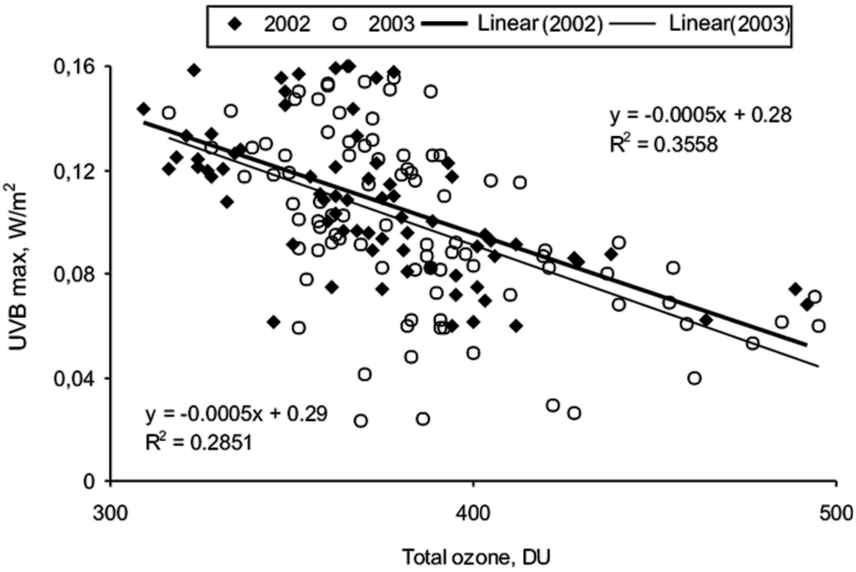

Fig. 2. UVB daily maximum versus total ozone during April–June of 2002 and 2003.

values of 0.06 W/m^2 were registered. This could be a consequence of the increased nebulosity because clouds can reduce UVB radiation at the surface down to just 10% [11]. Low UVB values were measured on days with precipitation. The precipitation amount varied from 0.3 mm on July 5 (UVB radiation intensity 0.085 W/m^2) to 2.6 mm on July 21 (UVB radiation intensity 0.1 W/m^2) in 2002, and from 0.3 mm on July 7 (UVB radiation intensity 0.04 W/m^2) to 6.8 on July 23 (UVB radiation intensity 0.02 W/m^2) in 2003.

It is known that the total ozone is the major factor controlling the solar UVB radiation reaching the ground surface [12]. The UV radiation is strongly anticorrelated with the total ozone, and some investigators explain 70% variability of UV by a varying total ozone [13]. The relation between the total ozone and UVB was estimated. The obtained results revealed the analogous tendency in 2002 and in 2003: higher total ozone values were registered simultaneously with the lower UVB intensity (Fig. 2) but the relationship was weak, statistically not significant. Consequently, clear-sky conditions were chosen for the further investigation of the relationship between UVB and total ozone. All continuous measurements were reconsidered and only data during the days with UVB radiation intensity courses being very close to bell-shaped curves were selected. Those cases were observed in 54% and 48% of all days during April–June of 2002 and 2003, respectively. As expected, the tighter relationship between these variables was determined right during these days (Fig. 3). A negative correlation between the total ozone and UVB intensity was determined and the coefficient R was -0.87 and -0.86 during 2002 and 2003, respectively. According to [14], for the data corresponding to cloudless days the regression curve may be satisfactorily described both by exponential and linear dependence.

As mentioned above, the UVB radiation plays an essential role in the photochemistry of the troposphere. The highest ground-level ozone concentration is measured in summer. The solar energy is intensive enough to trigger the photochemical reaction necessary for the ground level ozone formation involving NO_x and volatile organic compunds (VOCs) generation. For this reason, UVB radiation changes resulting from ozone variations in the stratosphere can change the concentration of the reactive gas, including ozone, in the troposphere. For the relationship between the ground-level ozone concentration and UVB radiation intensity estimation, a period from April to June was chosen, because it was during these months that high values of both variables were observed. The ground-level ozone concentrations in the daytime when UVB radiation intensity reached maximum were used for this study. The scatter plot of UVB radiation intensity and ground-level ozone concentration, presented in Fig. 4, does not show a significant relationship between these parameters during the investigated period. The presumption was made that this relationship could be insignificant, because the maximum values of those parameters were observed in different months (Fig. 1): UVB radiation intensity in May and the ground-level ozone concentration in April. To eliminate this phenomenon, the UVB and ozone data of different months were normalized to the adequate monthly maximum values (Fig. 5). It could be noted that the obtained results reveal a

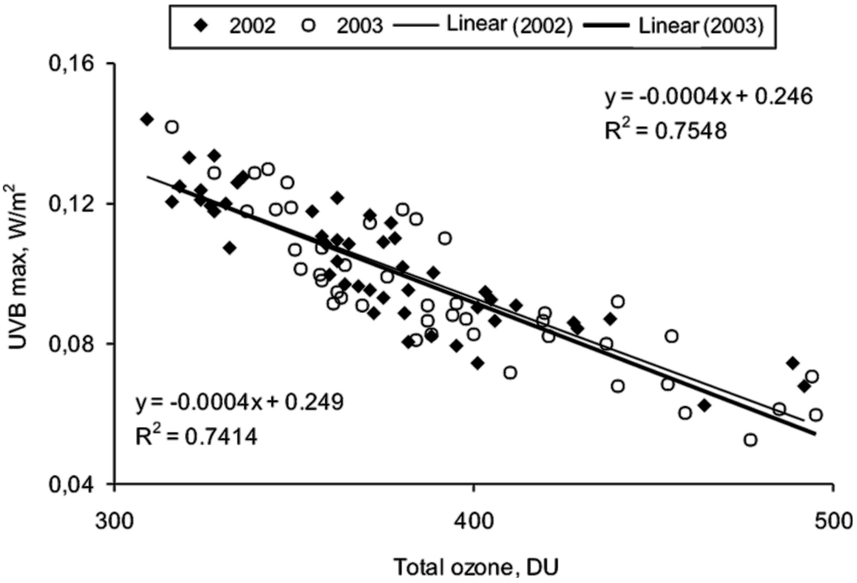

Fig. 3. UVB daily maximum versus total ozone under clear-sky conditions during April–June of 2002 and 2003.

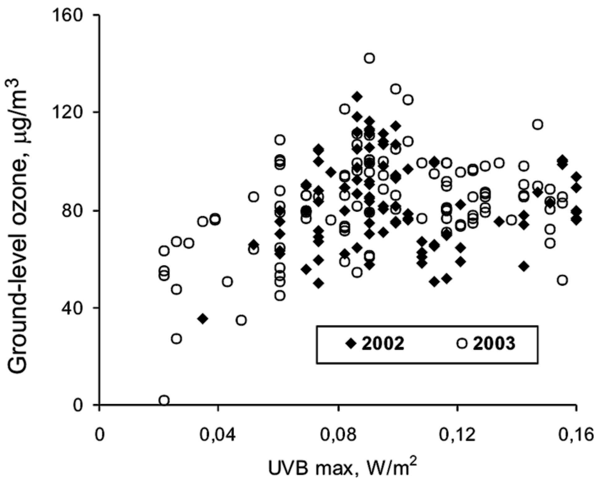

Fig. 4. Scatter plot of maximum UVB radiation intensity and ground-level ozone concentration in April–June of 2002 and 2003.

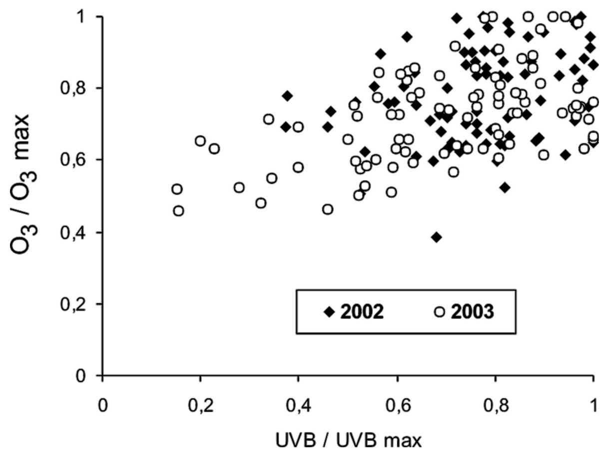

Fig. 5. Scatter plot of normalized UVB radiation intensity and the ground-level ozone concentrations in April–June.

pronounced tendency: the higher ground-level ozone concentrations are observed at the higher UVB intensity values.

Because UVB radiation intensity depends on the nebulosity, for the further investigation, as in the case of the total ozone, only cloudless or slightly cloudy days of the period have been chosen. The daily maximum of the ground-level ozone concentration versus the UVB daily maximum radiation during these days of April and June is presented in Fig. 6. In this case, the results showed a strong dependence ($R = 0.73$ for 2002, and $R = 0.74$ for 2003) between the UVB radiation intensity and the ground-level ozone concentration, which means that during cloudless days the ozone formation takes place in the ground-level layer. Since the Rūgšteliškės station is located in an unpolluted forested area, the photochemical ozone generation can be mostly induced by the natural volatile organic compound emission from vegetation at a certain nitrogen oxide level. The similar investigations in the Czech Republic [15] showed a comparable relationship and the correlation coefficient R equal to 0.73.

The analysis of relationship between the UVB radiation intensity and the ground-level ozone concentrations revealed some variations during separate months (Table 1). The correlation coefficient between these variables was calculated from the daily UVB radiation intensity maximum and corresponding ground-level ozone concentration at the same hour. The probability value (p) given in Table 1 indicates the statistical validity of the correlation; only if the probability is less than 0.05, the relationship between variables can be assumed significant. The obtained results show

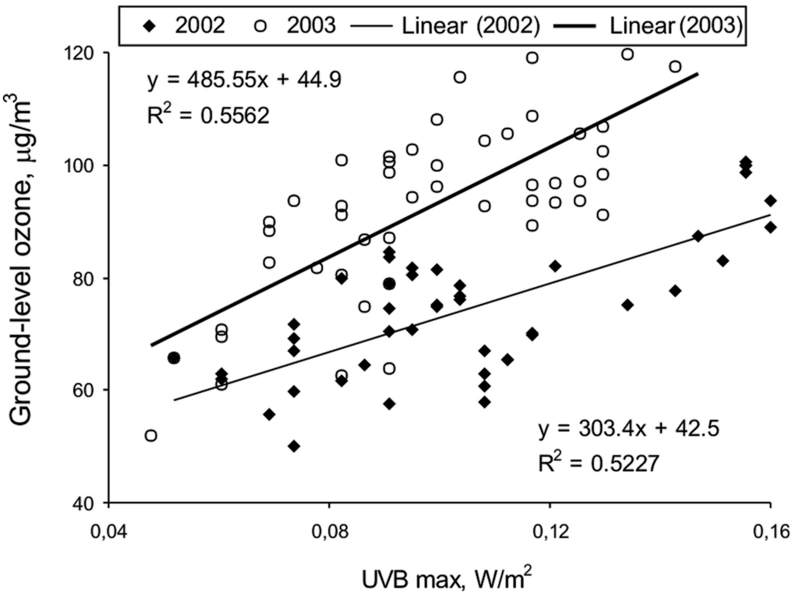

Fig. 6. UVB daily maximum versus ground-level ozone under clear-sky conditions during April–June of 2002 and 2003.

Table 1. Correlation coefficients between UVB radiation intensity and ground-level ozone concentration during different months in the 2002–2003 period.

Period	Correlation coefficient	95% confidence interval lower	95% confidence interval upper	p-value
January 2002	0.514	0.187	0.730	0.002
February	0.332	−0.051	0.624	0.083
March	0.307	−0.057	0.593	0.092
April	0.658	0.382	0.820	<0.0001
May	−0.170	−0.527	0.244	0.419
June	0.468	0.122	0.705	0.008
July	0.695	0.442	0.838	<0.0001
August	0.147	−0.208	0.464	0.417
September	0.167	−0.208	0.495	0.380
October	0.695	0.449	0.837	<0.0001
November	0.422	0.073	0.672	0.017
December	−0.137	−0.467	0.230	0.463
Whole 2002 year	0.699	0.641	0.747	<0.0001
January 2003	−0.231	−0.543	0.144	0.221
February	0.499	0.153	0.727	0.005
March	0.645	0.368	0.810	<0.0001
April	0.656	0.385	0.816	<0.0001
May	0.634	0.351	0.803	<0.0001
June	0.620	0.324	0.797	0.0002
July	0.767	0.563	0.877	<0.0001
August	0.288	−0.136	0.615	0.174
September	−0.075	−0.423	0.293	0.692
October	0.001	−0.402	0.404	0.994
November	0.194	−0.251	0.566	0.390
December	0.294	−0.130	0.619	0.164
Whole 2003 year	0.534	0.453	0.606	<0.0001
Whole period	*0.612*	*0.563*	*0.656*	*<0.0001*

that correlation coefficients were statistically not significant ($p > 0.05$) in February, March, May, August, September, December of 2002 and in January, August, September, October, November, and December of 2003. During other months, January, April, June, July, October, and November of 2002 and February, March, April, May, June, and July of 2003, the correlation coefficient was statistically significant ($p < 0.05$). The positive and statistically significant correlation coefficients between the UVB radiation intensity and the ground-level ozone concentration were established also for the period of 2002–2003 at the 95% confidence level. This indicates that photochemical ozone production is strongly related to the change of the UVB radiation intensity under rural Lithuanian conditions.

4. Conclusions

The investigations of the two-year continuous measurements of the total ozone, ultraviolet radiation, and the ground-level ozone concentration at the rural monitoring stations did not reveal significant changes in their course.

The relationship between the total ozone amount and the UVB radiation daily maximum intensity can be approximated using the linear regression. A strong negative correlation was determined between these variables during the cloudless days in April–June: the coefficients of the correlation were -0.87 and -0.86 in 2002 and 2003, respectively.

The relationship between daily maximum values of UVB radiation intensity and the ground-level ozone concentration can also be approximated using a linear regression. The correlation coefficient during different months varied: it was in the interval from -0.15 in May to $+0.73$ in July of 2002 and from -0.11 in January to $+0.77$ in July of 2003. A more pronounced relationship between the UVB radiation and the ground-level ozone was found in 2003, which could be related to specific meteorological conditions of the summer of 2003. It should be noted that a very high ozone level was characteristic of the year 2003 in Europe.

The increase of the UV radiation intensity could be one of the main reasons for the ground-level ozone concentration increase in future, and thereby ozone exposure, up to a dangerous level, for vegetation and living organisms in unpolluted forested regions.

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RYŠYS TARP BENDRO OZONO KIEKIO, ULTRAVIOLETINĖS SPINDULIUOTĖS INTENSYVUMO BEI PAŽEMIO OZONO KONCENTRACIJOS LIETUVOS KAIMO VIETOVĖSE

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Santrauka

Analizuotas ultravioletinės spinduliuotės intensyvumo ir bendro ozono kiekio bei pažemio ozono koncentracijos ryšys. Priklausomybė tirta panaudojant ultravioletinės spinduliuotės intensyvumo ir pažemio ozono koncentracijų matavimų Aukštaitijos ekologinės stebėsenos stotyje Rūgšteliškėse duomenis ir bendro ozono kiekio matavimų (M-124 tipo ozonometru) Lietuvos hidrometeorologijos tarnybos Kauno meteorologinėje stotyje duomenis, gautus 2002–2003 metų nenutrūkstamų matavimų metu. Ryšio tarp pažemio ozono lygio ir UVB spinduliuotės intensyvumo bei bendro ozono kiekio paieškai pasirinkti balandžio–birželio mėnesiai, kadangi kaip tik tuo laikotarpiu registruojamos didelės šių parametrų vertės. Statistiškai nagrinėjant tarpusavio ryšį, tarp bendro ozono kiekio ir UVB spinduliuotės intensyvumo nustatytas antikoreliacinis ryšys, stebimas tik giedromis dienomis; koreliacijos koeficientai 2002 ir 2003 metais atitinkamai buvo $-0{,}87$ ir $-0{,}86$. Nagrinėjant ryšį tarp UVB spinduliuotės ir pažemio ozono koncentracijos, nustatyta, kad UVB spinduliuotės ir pažemio ozono tarpusavio ryšys tampresnis giedromis dienomis; koreliacijos koeficientai 2002 ir 2003 metais atitinkamai 0,72 ir 0,75.