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ASSESSMENT OF THE VALUE OF TROPOSPHERIC OZONE CONCENTRATION DEPENDING ON METEOROLOGICAL CONDITIONS AS EXEMPLIFIED BY THE WIDUCHOWA STATION (NORTH-WEST POLAND)

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Abstract

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The aim of the work was to find the temporal distribution of tropospheric ozone in connection with the course of meteorological conditions by night and daytime according to months, days and, next, hours and wind direction and to isolate a weather complex which was accompanied by the highest concentration of O3. The foundation of the study was hourly values of O_3 concentration in 2005–2008, and hourly data on five meteorological elements (total solar radiation, air temperature, relative air humidity, atmospheric pressure and direction and velocity of wind) in April 2006, from the Widuchowa station located at the Polish–German border in North-West Poland. The effect of meteorological conditions on ozone concentration values was determined with the use of Pearson's correlation analysis and cluster analysis. The highest mean concentration of ozone, out of the 48 analysed months in 2005–2008, was recorded in April 2006, by daytime, with the wind coming from westerly, easterly, south-westerly and southerly directions. The following weather situation was conducive to the highest O_3 concentrations, amounting, on average, to about 127 $\mu g.m^{-3}$: above-average mean total solar radiation (about 237 $W.m^{-2}$), above-average mean air temperature (11.5°C), below-average relative air humidity (about 52%), above-average atmospheric pressure (about 1016 hPa) and above-average mean wind velocity (2.4 $m.s^{-1}$).

Key words: air pollution, weather, wind direction, cluster analysis

Introduction

The occurrence of ozone in the closest to the Earth atmospheric layer is a result of both natural processes occurring in it and also has its origin in anthropogenic processes. Tropospheric ozone concentration can be characterized by distinct seasonal and day-to-day variability, dependent on latitude, the local lie of the land, distance from the emission sources of air pollution and time of their movement, but also on changeable meteorological conditions (Brace, Peterson, 1998; Monks, 2000; Treffeisen, Halder, 2000; Girgzdiene, Girgzdys, 2001; Kalbarczyk, Kalbarczyk, 2009; Turnipseed et al., 2009). The already existing publications demonstrated the existence of relation of changeable ozone concentration and many meteorological elements such as, e.g. solar radiation (Ośródka, Święch-Skiba, 1997; Wachowski et al., 2001), air temperature (Camalier et al., 2007; Kalbarczyk, Kalbarczyk, 2009), relative air humidity powietrza (Ośródka, Święch-Skiba, 1997; Elminir, 2005; Camalier et al., 2007; Barančoková, Barančok, 2008; Hosseinibalam et al., 2009), atmospheric pressure (Davis et al., 1998; Godłowska, Tomaszewska, 2006; Diem, 2009), wind velocity (Dueñas et al., 2002; Godłowska, 2004) and wind direction (Camalier et al., 2007).

The aim of the work was to find the temporal distribution of tropospheric ozone in connection with the course of meteorological conditions by night and daytime according to months, days and, next, hours and wind direction, and to isolate a weather complex which is accompanied by the highest concentration of O_3.

Material and methods

The foundation of the present study was hourly values of tropospheric ozone concentration (O_3, $\mu g.m^{-3}$) in 2005–2008 and hourly data on the following meteorological elements: mean total solar radiation (RAD, $W.m^{-2}$), mean air temperature (TP, °C), relative air humidity (RH, %), atmospheric pressure (PH, hPa), wind direction (N, NE, E, SE, S, SW, W, NW) and wind velocity (WS, $m.s^{-1}$) in April 2006. For ozone and each listed meteorological element, in the brackets there is its symbol and a unit, and in the case of wind direction the symbol of cardinal points. The input data used in the study were collected in the period from 1st January 2005 to 31st December 2006 for the Widuchowa station (14°23' E, 53°17' N, hs = 2 m a.s.l.), which is a part of the network of the State Environment Monitoring stations in Poland, located at the Polish–German border in North-West Poland (Fig. 1). The measurements of ozone concentration at the emission station

Fig. 1. Location of the immission and meteorological station in Widuchowa (North-West Poland).

in Widuchowa were conducted continuously every hour at the height of 2 m a.s.l. with the use of the MLU 400E analyser produced by Monitor Labs. The measurement was based on the phenomenon of UV radiation absorption by ozone in the length of the wave equal to 254 nm. On the other hand, the measurements of meteorological elements were carried out in accordance with the rules accepted by WMO (World Meteorological Organization).

Temporal distribution of tropospheric ozone concentration in the consecutive years of the analysed period 2005–2008 was characterized by hourly measurements on the basis of which mean monthly and mean yearly values were then calculated, using basic statistical indexes: the mean, the minimum and maximum value, standard deviation and percentiles (from 10 to 90). In the case of 2006, when, out of all the four examined years, the highest mean yearly ozone concentration was recorded, measurements of O_3 and the examined meteorological elements were presented separately for daytime (from sunrise to sunset) and night (from sunset to sunrise), according to months and days, and, next, according to hours and wind direction. The influence of meteorological elements on the concentration of O_3 was investigated with the use of linear correlation analysis, but only in April 2006, that is, in the period when the highest mean concentration of O_3, out of the 48 analysed months in 2005–2008 was noted, separately for daytime and night (Sobczyk, 1998). The values of wind velocity, being an independent variable, had different than normal distribution. Therefore, the normalisation of this variable was conducted with the use of the function:

$$f(WS) = \ln(WS)$$

where: WS – the value of wind velocity. The conformity of independent variable WS with the normal distribution was examined with a Chi-square test with an assumed level of $P \leq 0.05$. The isolation of a weather complex which was conducive to the highest concentrations of O_3 was based on the method of generalised cluster analysis. Before the analysis both ozone concentration and the examined meteorological elements underwent normalization in accordance with the formula:

$$Z_j = \frac{X_j - Min(X_j)}{Max(X_j) - Min(X_j)}$$

where: $Max(X_j)$ and $Min(X_j)$ denote respectively the highest and the lowest j value of this variable. After such normalization, all variables (ozone concentration and meteorological elements) assumed values of the same interval (0; 1) (Dobosz, 2001). The division of all observations of the analysed meteorological elements into clusters was conducted by means of a non-hierarchical method of *k*-means, in which the Euclidean distance was used (Dobosz, 2001; Holden, Brereton, 2004). Grouping of the observations with the *k*-means method consisted in moving observations from cluster to cluster in order to maximise variance between particular clusters, with simultaneous minimization of variances within the examined clusters. The significance of differences between the isolated clusters was evaluated with the use of variance analysis, using the Fisher's test at a level of $P \leq 0.05$ (Dobosz, 2001).

Results and discussion

At the Widuchowa station, out of four analysed years: 2005, 2006, 2007 and 2008, the highest mean yearly concentration of tropospheric ozone was recorded in 2006 and was 12.8 $\mu g.m^{-3}$ higher than the lowest one amounting to 53.2 $\mu g.m^{-3}$, which was recorded in 2005 (Table 1). The absolute lowest hourly concentration of the gas being described, only 6.0 $\mu g.m^{-3}$, was recorded in 2005 and the absolute highest concentration, almost 142 $\mu g.m^{-3}$, in 2006. The highest changeability of the emission of O_3, described by standard deviation, was characteristic of 2006 (S = 27.1 $\mu g.m^{-3}$), and the lowest one of 2007 (S = 16.7 $\mu g.m^{-3}$). The highest values of percentiles of ozone concentration were determined for 2006 as well, with the exception of percentile 10 and 20; the lowest values occurred in 2005 (Fig. 2). For

T a b l e 1. Statistical characteristics of hourly concentrations of tropospheric ozone in the consecutive years 2005–2008 (Widuchowa).

Year	Characteristics [μg.m^{-3}]			
	mean	minimum	maximum	standard deviation
2005	53.2	6.0	108.1	22.3
2006	66.0	10.9	141.5	27.1
2007	59.4	15.2	113.2	16.7
2008	63.6	20.3	130.1	20.6

example, percentile 90 determined for 2006, amounted to 106.5 μg.m^{-3}, and for 2005 only 79.9 μg.m^{-3}. As presented in Fig. 3, out of 48 analysed months in 2005–2008, the highest

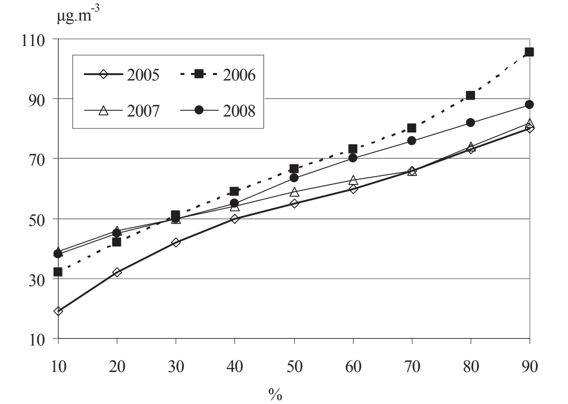

Fig. 2. Hourly course of tropospheric ozone concentrations based on percentiles in the consecutive years 2005–2008 (Widuchowa).

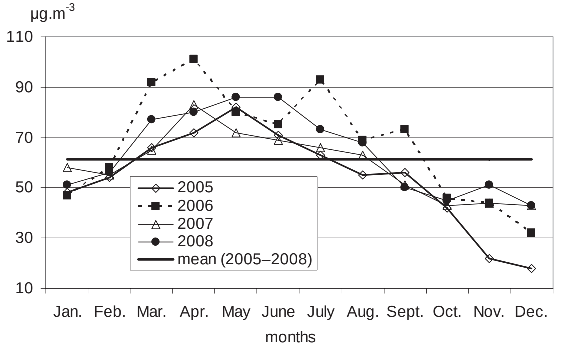

Fig. 3. Mean monthly concentration of tropospheric ozone in the consecutive years 2005–2008 (Widuchowa).

concentration of tropospheric ozone, equal to 101.1 $\mu g.m^{-3}$, occurred in April 2006 and the lowest one, equal to 17.9 $\mu g \cdot m^{-3}$, in December 2005.

Mean yearly concentration of tropospheric ozone in 2006 in the Widuchowa station (North-West Poland) amounted to 66.0 $\mu g.m^{-3}$ and oscillated between 33.1 $\mu g.m^{-3}$ in December and 106.2 $\mu g.m^{-3}$ in April for daytime and, respectively, between 31.6 $\mu g.m^{-3}$ and 94.0 $\mu g.m^{-3}$ for night (Fig. 4a, b). Apart from April high ozone concentration was also recorded in July, during the daytime – 100.2 $\mu g.m^{-3}$, and in March at night – 87.9 $\mu g.m^{-3}$. Similar results concerning the size and temporal distribution of O_3 concentration at four measurement stations, situated in different regions of Poland were obtained by Bogucka (2006), according to whom the highest concentration of the analysed gas pollutant usually occurs in spring and summer. The occurrence of the spring maximum is characteristic of many locations of North-West Europe, and maximum values of O_3 concentrations in spring and summer are characteristic of the interior of the continent (Monks, 2000; Cristofanelli, Bonasoni, 2009). In the examined year in all months, higher ozone concentration was noted during the daytime, not at night. The biggest differences in the size of ozone concentration between daytime and night were noted in July (29.2 $\mu g.m^{-3}$), and, next, in June (26.9 $\mu g.m^{-3}$);

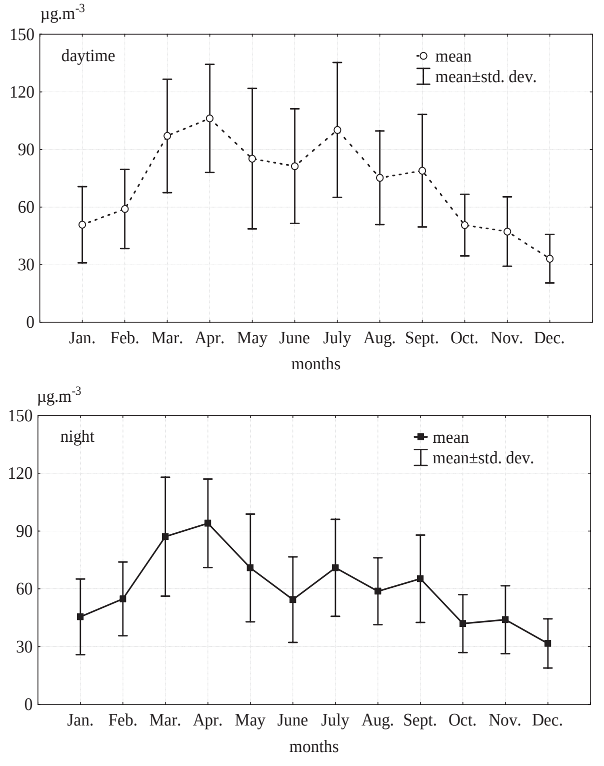

Fig. 4. Temporal distribution of tropospheric ozone concentration during the daytime (a) and at night (b) by months (2006, Widuchowa).

the lowest differences, on the other hand, in winter months (from 1.5 μg.m^{-3} in December to 5.4 μg.m^{-3} in January). A decrease in ozone concentration in night hours is caused by the disappearance of the photochemical conversion mechanism of primary NO into secondary NO_2, and the predominance of oxidation by the ozone accumulated during the daytime (Felzer et al., 2007). Figure 4a, b also shows that ozone concentration in the Widuchowa station was characterized by higher standard deviation during the daytime than in the night and amounted to, respectively, 34.7 and 27.9 μg.m^{-3}, while during the daytime it oscillated between 12.6 μg.m^{-3} in December and 36.6 μg. m^{-3} in May, and at night between 12.8 μg.m^{-3} in December and 30.8 μg.m^{-3} in March.

In April, i.e. the month with the highest recorded mean concentration of tropospheric O_3 at the Widuchowa station in 2006, the concentration of the investigated gas during the daytime oscillated between 85.0 μg.m^{-3} (24th April 2006) and even 127.5 μg.m^{-3} (26th April 2006), and at night between 57.8 μg.m^{-3} (13th April 2006) and 113.8 μg.m^{-3} (21st April 2006), whereas during the daytime the concentration was on average higher by 14.4 μg.m^{-3} than at night (Fig. 5a). Differences in ozone concentration occurring in April between daytime and night amounted to even over 30 μg.m^{-3} in the course of twenty-four hours; the biggest difference was noted on 17th April (46.3 μg.m^{-3}) and the next one on 18th April (32.1 μg.m^{-3}); in 13 days the differences did not exceed 10 μg.m^{-3}.

Ozone concentration variability in the closest to the Earth atmospheric layer is dependent, to a large extent, on meteorological conditions, which significantly affect it (Ośródka, Święch-Skiba, 1997; Davis et al., 1998; Treffeisen, Halder, 2000; Dueñas et al., 2002; Elminir, 2005; Godłowska, Tomaszewska, 2006; Shan et al., 2009). Figure 5 clearly shows that in April the course of concentration of tropospheric O_3 depended on meteorological conditions: the higher total solar radiation, air temperature, atmospheric pressure, wind velocity and the lower relative air humidity were, the higher O_3 concentration. During the daytime (from sunrise to sunset), on which the highest ozone concentration was recorded, namely 26th April, also the highest total solar radiation was noted (by 49.7 W.m^{-2} higher than average that month), as well as the highest air temperature (by 8.1 °C higher than monthly average), one of the lowest in April relative air humidity (by 15.3% lower than monthly average), higher atmospheric pressure (by 3.1 hPa higher than average in April) and slightly higher wind velocity (by 0.1 m·s^{-1} higher than the monthly average) (Fig. 5b, c, d, e, f). Apart from the presented figures, the correlation analysis also confirmed theses dependences. The strongest relation between O_3 concentration during the daytime and meteorological elements was proved for relative air humidity ($r_{d\ RH;O3} = -0.77$, $P < 0.01$) and for total solar radiation ($r_{d\ RAD;O3} = 0.65$, $P < 0.01$), and, next, for atmospheric pressure ($r_{d\ PH;O3} = 0.50$, $P < 0.01$); at night similarly: for relative air humidity ($r_{n\ RH;O3} = -0.58$, $P < 0.01$) and for wind velocity ($r_{n\ WS;O3} = 0.45$, $P < 0.05$), which had similar force also during the daytime (Fig. 5b, c, d, e, f). According to Ośródka and Święch-Skiba (1997), an increase in air humidity may cause the elimination of ozone from the atmosphere through the reaction of this gas with water. In Elminir's research (2005), the highest mean ozone concentration was noted with low relative air humidity ≤ 40%; a decrease in ozone concentration with an increase in relative humidity was also confirmed by the research of Camalier et al. (2007) and Barančoková

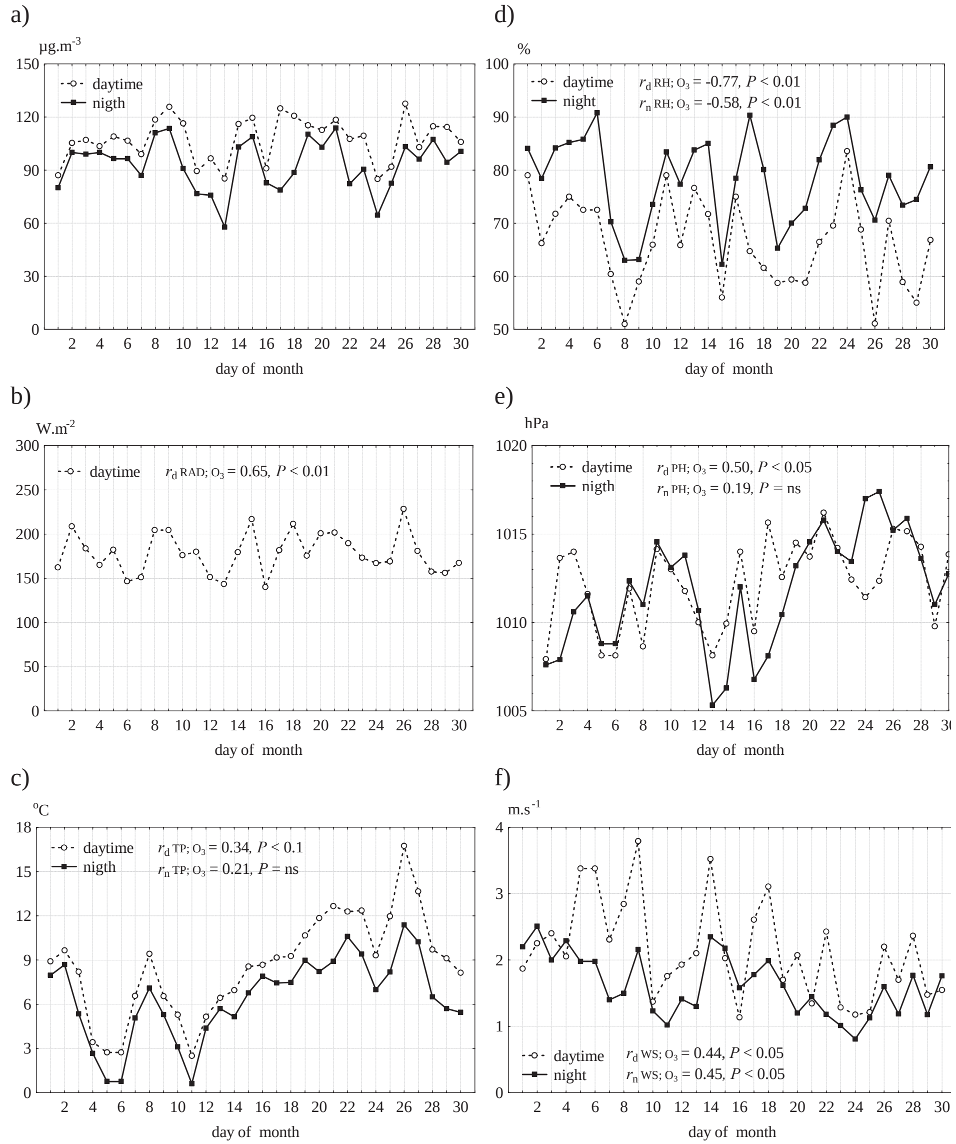

Fig. 5. Course of tropospheric ozone concentration during the daytime and at night by consecutive days (a) against meteorological conditions: total solar radiation (b), air temperature (c), relative air humidity (d), atmospheric pressure (e) and wind velocity (f) (April 2006, Widuchowa).

and Barančok (2008). According to Ośródka and Święch-Skiba (1997) and Wachowski et al. (2001), as a result of the effect of solar radiation – and to be more precise, a part of its spectrum of the wave-length smaller than 400 nm due to photolysis – there occurs nitrogen dioxide decay, which in consequence leads to the formation of ozone. In turn, strong relations of ozone concentration with anti-cyclone weather were shown by, e.g. Davis et al. (1998) and Godłowska and Tomaszewska (2006), according to whom an increase in atmospheric pressure in warm six months may be conducive to an increase in ozone concentration level. Under conditions of anti-cyclone synoptic situation with a stable balance of air masses, there often occurs photochemical smog, which is accompanied by high air temperatures, low relative air humidity and cloudless sunny weather during the daytime (Kalbarczyk, Kalbarczyk, 2008). On the other hand, an increase in mean O_3 concentrations, with an increase in wind velocity, may be caused by the fact that pollution sources located at a certain distance from a measuring station have significant influence on recorded ambient air pollutant concentration (Treffeisen, Halder, 2000; Walczewski, 2000). It results also from the analyses by Dueñas et al. (2002) and Godłowska (2004) that, in the warm half year, an increase in wind velocity determines higher O_3 concentration. The highest ozone concentrations occur in suburban areas and more distant rural areas without local emission sources of nitrogen, located on the lee side of main emission sources of ozone precursors; when air is transported with wind, NO_2 is photolysed and eventually in the troposphere, there occurs formation of ozone (Godłowska, 2004; Godłowska, Tomaszewska, 2006).

Ozone concentration in the troposphere is characterized not only by distinct seasonal variability (Figs 4 and 5), but also day-to-day, determined by latitude, the local lie of the land, meteorological conditions and a distance from emission sources of air pollutants and time of their movement (Brace, Peterson, 1998; Cooper, Peterson, 2000; Treffeisen, Halder, 2000). Fig. 6a points to the occurrence of distinct day-to-day variability of ozone concentration in April in the Widuchowa station area (North-West Poland). The highest concentration values of the described gas pollutant, even exceeding 120 $\mu g.m^{-3}$, were recorded between 1 p.m. and 6 p.m., with the maximum occurring at 4 p.m. (127.6 $\mu g.m^{-3}$); the lowest values, below 80 $\mu g.m^{-3}$, between 5 a.m. and 7 a.m. with the minimum at 7 a.m. (75.0 $\mu g.m^{-3}$). Similar day-to-day distribution of ozone concentration was proved by Brace and Peterson (1998) in the Mount Rainier National Park Region (U.S.A.), according to whom the highest concentrations in the summer season are recorded between 3 p.m. and 6 p.m. On the other hand, Hosseinibalam et al. (2009) in 2001 and 2002 in Tehran noted the highest concentration of O_3 between midday and 2 p.m., and the lowest between midnight and 1 a.m.

In the hours when the highest ozone concentration was noted – at the same time also one of the highest values of air temperature – atmospheric pressure and wind velocity and one of the lowest values of relative air humidity were recorded (Fig. 6c, d, e, f), and the highest total solar radiation took place around noon (Fig. 6b), that is, several hours before the maximum concentration of tropospheric ozone.

In April in the Widuchowa station area, wind came during the daytime most often from a southerly direction (30.6%), and, next, from a south-westerly direction (25.5%), and the least frequently from a northerly direction (0.7%); at night, respectively, from a south-

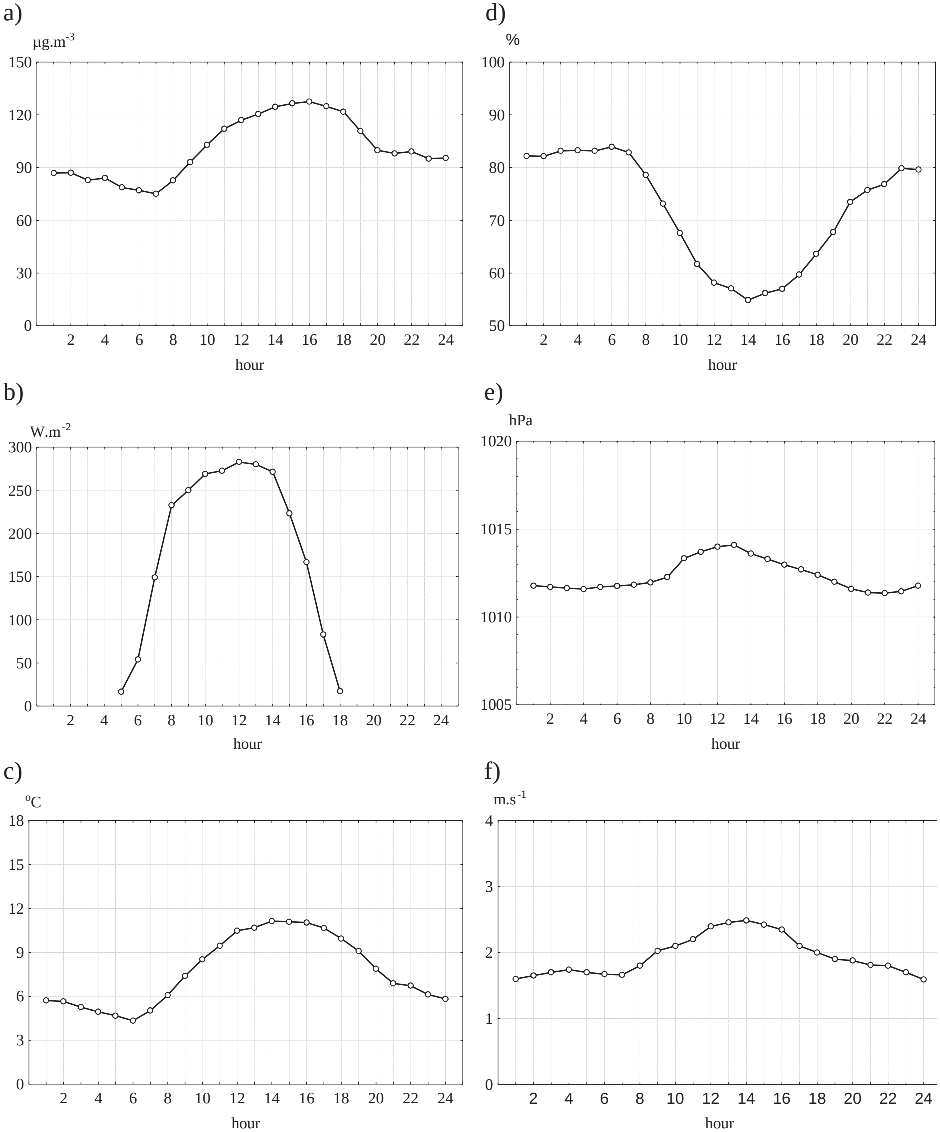

Fig. 6. Day-to-day course of tropospheric ozone concentration (a) against meteorological conditions: total solar radiation (b), air temperature (c), relative air humidity (d), atmospheric pressure (e) and wind velocity (f) (April 2006, Widuchowa).

westerly direction (24.7%) and from an easterly direction (21.7%), the least frequently from a northerly direction (3.4%) (Fig. 7), which means that the size of tropospheric ozone concentration recorded at the Widuchowa station depends on gas pollutants coming not only from Poland, but also from Germany.

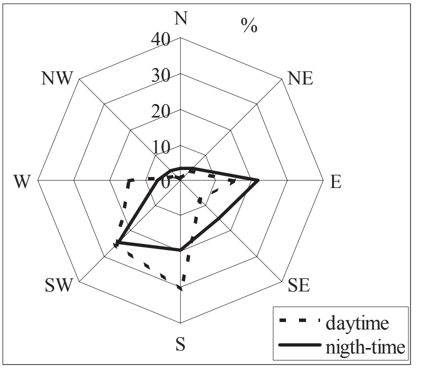

Fig. 7. Wind-rose (April 2006, Widuchowa).

Analysing the amount of ozone concentration in April depending on wind direction, one can state that, irrespective of the type of circulation, higher values, on average by 10.9 μg.m^{-3}, were noted during the daytime than at night; similar predominance was earlier found on the basis of the analysis of temporal distribution according to months, days and hours (Figs 4, 5 and 6). The biggest differences in the size of O_3 concentrations between the daytime and night were recorded with a southerly circulation (15.9 μg.m^{-3}), and the smallest with a north-westerly one (5.0 μg.m^{-3}) (Fig. 8a). During the daytime, the highest ozone concentration was recorded with the following winds: westerly (114.2 μg.m^{-3}), easterly (113.4 μg.m^{-3}), south-westerly (111.6 μg.m^{-3}) and southerly (110.1 μg.m^{-3}). In April 2006, during the daytime, with a westerly circulation, i.e. when the highest mean tropospheric ozone concentration was noted, at the Widuchowa station the following weather conditions were observed: above-average solar radiation – 206.5 W.m^{-2}, average air temperature – 9.2 °C, below-average relative air humidity 65.8%, average atmospheric pressure – 1012.4 hPa and slightly above-average wind velocity – 1.8 m.s^{-1} (Fig. 8b, c, d, e, f).

A final stage of the study was selecting a weather complex occurring in April (in 2006), but only during the daytime and chosen atmospheric circulations: E, S, SW and W, i.e., when the highest, above 110 μg.m^{-3}, mean tropospheric ozone concentration was noted. On the basis of cluster analysis, two groups of observations of meteorological elements were isolated characterising different aerosanitary situations which were conducive to high and low concentrations of ozone in the Widuchowa station area (North-West Poland). Cluster 1 was characterized by high ozone concentration and, at the same time, high total solar radiation, high mean air temperature, high atmospheric pressure, high wind velocity and low relative air humidity; Cluster 2 – exactly the reverse in comparison with Cluster 1 (Fig. 9). It results from variance analysis that all the investigated meteorological elements statistically significantly, at a level of $P \leq 0.01$, differentiate the isolated clusters, i.e., significantly determine different size of ozone concentration – the direction of their influence was the same as it was shown earlier by the correlation analysis, without the division into atmospheric circulations (Fig. 5). The biggest differences between the examined elements describing two different weather complexes concerned relative air humidity, and the smallest differences pertained to atmospheric pressure (Fig. 9).

As it can be seen in Table 2, Cluster 1 encompassed 183 observations, and Cluster 2 – 171 observations. Higher mean ozone concentration recorded during the daytime with the circulations: E, S, SW and W was calculated for Cluster 1 and amounted to 126.6 μg.m^{-3}, and for Cluster 2 lower concentration – 91.2 μg.m^{-3}. Values of meteorological elements in Cluster

1 amounted to: mean total solar radiation – about 237 W.m^{-2}, mean air temperature – 11.5 ^{o}C, relative air humidity – 51.7%, atmospheric pressure – about 1016 hPa and mean wind

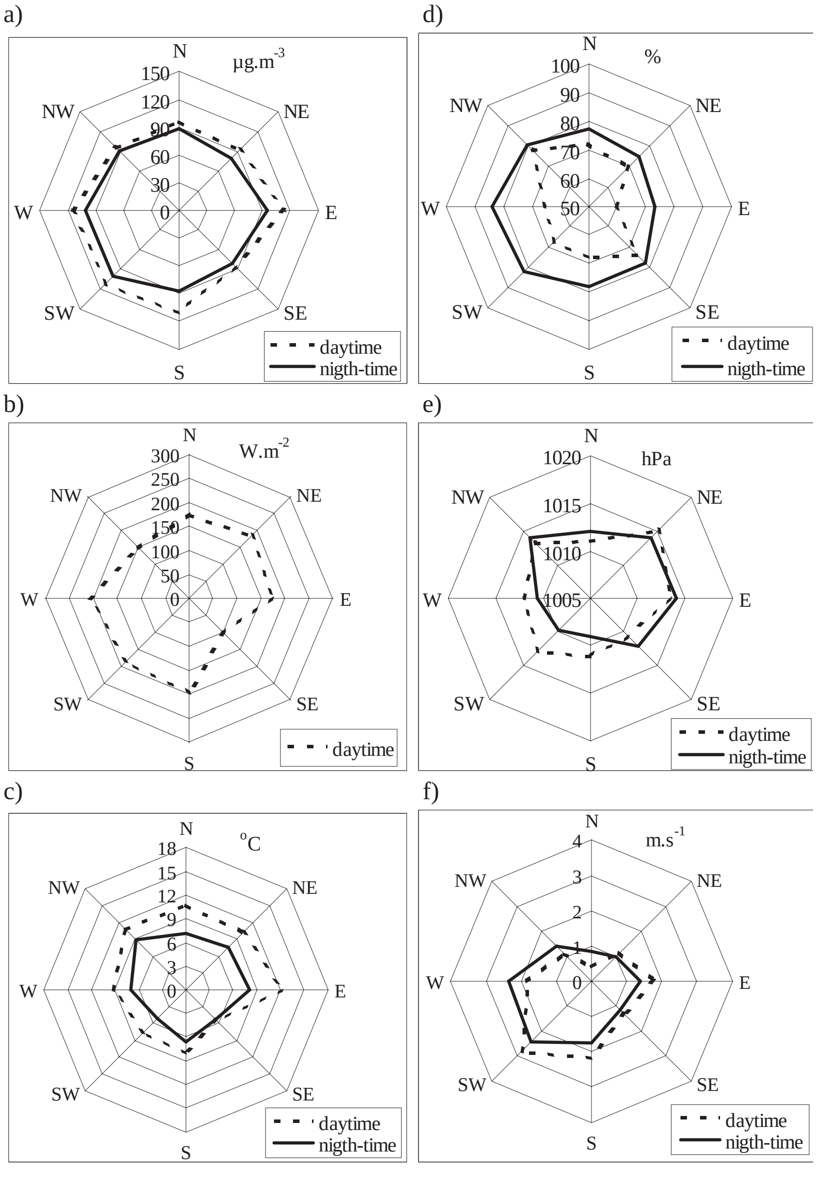

Fig. 8. Distribution of tropospheric ozone concentration by wind direction (a) against meteorological conditions: total solar radiation (b), air temperature (c), relative air humidity (d), atmospheric pressure (e) and wind velocity (f) (April 2006, Widuchowa).

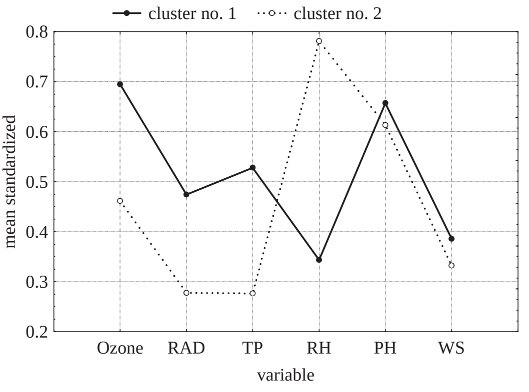

Fig. 9. Mean standardised values of O_3 concentration and meteorological elements occurring during the day with wind from the following directions: E, S, SW and W for each isolated cluster (April 2006, Widuchowa).

Notes: Ozone – mean ozone concentration, RAD – mean of total solar radiation ($W.m^{-2}$), TP – mean air temperature (^{o}C), RH – mean air humidity (%), PH – mean air-pressure (hPa), WS – mean wind speed ($m.s^{-1}$).

Table 2. Statistical characteristics of O_3 concentration and meteorological elements occurring by daytime with the wind from the following directions: E, S, SW and W for each isolated cluster (April 2006, Widuchowa).

Cluster number	Number of observations	Characteristics	Ozone concentration	Element				
				RAD [$W.m^{-2}$]	TP [^{o}C]	RH [%]	PH [hPa]	WS [$m.s^{-1}$]
		minimum	73.0	8.0	3.3	29.0	999.0	0.3
1	183	maximum	173.0	497.0	21.8	75.0	1020.0	5.7
		mean	126.6	237.2	11.5	51.7	1015.8	2.4
		std. dev.	19.9	105.5	3.8	9.8	3.3	1.2
		minimum	21.0	3.0	-0.1	58.0	996.0	0.2
2	171	maximum	131.0	353.0	13.9	95.0	1019.0	4.7
		mean	91.2	140.2	6.0	80.6	1009.7	1.8
		std. dev.	19.8	107.4	30	8.4	4.1	0.9
		minimum	21.0	3.0	-0.1	29.0	996.0	0.3
1-2	354	maximum	173.0	497.0	21.8	95.0	1020.0	5.7
		mean	109.5	190.3	8.8	65.6	1012.3	2.2
		std. dev.	26.6	116.8	4.4	17.1	3.8	1.0

Notes: RAD – mean of total solar radiation, TP – mean air temperature, RH – mean air humidity, PH – mean air-pressure, WS – mean wind speed.

velocity -2.4 $m.s^{-1}$. As it is illustrated in Table 2, Cluster 1 was most frequently characterized by higher standard deviation, which concerned 3 out of the 5 considered meteorological elements: air temperature, relative air humidity and wind velocity. In the case of absolute maximum values of meteorological elements it was stated that they mainly occurred in Cluster 1, with exception of relative air humidity (in Cluster 1 there occurred its minimum value), and in the case of minimum values – in Cluster 2.

Conclusion

In the Widuchowa station area located in North-West Poland at the Polish–German border, the highest mean yearly concentration of O_3, out of the four analysed years 2005–2008 was recorded in 2006 when temporal distribution of the examined gas pollutant displayed distinct seasonal and day-to-day structure. In April 2006, the size of O_3 concentration was three times higher than in December and amounted to 100.1 $\mu g.m^{-3}$. In 2006, higher, on average by 12.1 $\mu g.m^{-3}$, ozone concentration was recorded during the daytime than at night, while the biggest differences were seen in June (26.9 $\mu g.m^{-3}$) and July (29.2 $\mu g.m^{-3}$). In April, in the course of twenty-four hours, the highest values, even exceeding 120 $\mu g.m^{-3}$, of concentration of the analysed gas were recorded between 1 p.m. and 6 p.m.; the lowest values, not exceeding 80 $\mu g.m^{-3}$, between 5 a.m. and 7 a.m. The highest mean ozone concentration was recorded in April during the daytime with the following winds: easterly, southerly, south-westerly and westerly, and the following aerosanitary situation was conducive to them: above-average mean total solar radiation (about 237 $W.m^{-2}$), above-average mean air temperature (11.5 °C), below-average relative air humidity (51.7%), above-average atmospheric pressure (about 1016 hPa) and above-average mean wind velocity (2.4 $m.s^{-1}$).

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