



DE GRUYTER
OPEN

DOI 10.2478/pesd-2018-0041

PESD, VOL. 12, no. 2, 2018

THE EVALUATION OF THE TROPOSPHERIC OZONE VARIABILITY IN THE MUNICIPALITY OF SUCEAVA FROM THE METEOROLOGICAL PERSPECTIVE

Dumitru Mihăilă¹, Andrei-Emil Briciu², Gina Ursul

Key words: meteorological parameters, Pearson correlation coefficients, wavelet analysis, weekend effect

Abstract: The daily, monthly and annual variations of the tropospheric ozone in the area of Suceava municipality are described and explained by using the correlations between the ozone concentration and the local meteorological parameters. The meteorological parameters are as follows: the air temperature, the air humidity, the sunshine duration, the wind speed and direction. All parameters represent hourly datasets recorded in the interval 2004-2007. The Pearson correlation coefficients and the linear regressions were obtained for daily, monthly and yearly scales. Significant positive correlations between the O₃ and the temperature and strong negative correlations between the O₃ and the air humidity were found, especially between 11 a.m. and 8 p.m., during the warm season. The sunshine duration and the wind speed and direction were found to have weaker, but good positive correlation with the O₃ during the same hourly interval. The weekend effect of the ozone exists in the City of Suceava too, as the reduced road traffic during the weekend causes higher concentrations of ozone. The wavelet analyses were conducted in order to further explain the variability of the ozone.

Introduction

The ozone (O₃) plays an important role in the troposphere because of its impact upon the oxidation capacity of the atmosphere, upon the quality of the air in general, but also through its contribution to the greenhouse effect (Matthes et al. 2007). While the stratospheric O₃ protects the Earth from the UV solar radiations, the tropospheric ozone is the third important gas with greenhouse effect, after CO₂ and CH₄; concomitantly, it is one of the most phytotoxic pollutants, affecting not

¹ Assoc. prof. Department of Geography, University „Stefan cel Mare” of Suceava: dumitrum@atlas.usv.ro

² Ph.D. student Department of Geography, University „Stefan cel Mare” of Suceava and Regional Meteorological Centre of Moldova, National Meteorological Administration of Romania: petricabistricean@gmail.com

only the human health, but also the vegetation and materials (Vandermeiren et al. 2009). By comparing the average global concentrations of the tropospheric ozone with the ones measured over a century ago, an increase of about two times was observed, as a consequence of the developed anthropogenic emissions from the last century (Vandermeiren et al. 2009). The increased emissions of methane, carbon monoxide, volatile organic compounds (VOCs), mostly produced through the combustion of the biomass and fossil fuels, determined the meaningful growth of the ozone concentration in the industrial era (Voltz and Kley 1988; Thompson 1992; Marenco et al. 1994). By evaluating 30 years of measurements in Europe, Seinfeld and Pandis (1998) indicated a growth of the background ozone concentrations of 1-2% per year, which demonstrates the fact that the pollution of the air is not limited to a regional scale (Bauer and Langmann 2002). Some scenarios indicate the possibility of further increase of the ozone concentrations during this century. The simulations for the period 2015-2050 project an increase of 20 to 25% of the tropospheric ozone (Vandermeiren et al. 2009). The NO_x , CO and VOC present in the atmosphere act as precursors of the tropospheric ozone, by forming free radicals which finally contribute to the ozone net production (Matthes et al. 2007). The complexity of the chemical processes from the troposphere, as well as the variations of the meteorological parameters and the emissions of the pollutants involved in some chemical reactions in atmosphere can determine changes from a system to another in short periods of time (Finlayson-Pitts et al. 2007).

The air temperature, the wind, the solar radiation and the atmospheric humidity affect both the ozone precursors' emissions and the net ozone production (Parry et al. 2007). Two recent studies made on the tropospheric ozone in Europe (Ordonez et al. 2005) and in the USA (Camalier et al. 2007) show systematic correlations between the ozone and the meteorological variables at a regional scale. The first study, made in 12 areas of Switzerland, has identified the temperature, the solar radiation during the morning and the number of days from the last frontal passage that generated thunderstorms as dominant predictive variables for the summer time ozone. The second study highlighted the fact that up to 80% from the variability of the daily maximum values of the 8 hours averages in the east of the USA can be explained by a linearly generalized model, with the temperature (positive correlation) and with the relative humidity (negative correlation) as two of the most important predictive variables. The wind speed and direction are important only for a small number of ozone monitoring sites, according to another study (Jacob and Winner 2009).

The present work investigates the intensity of the correlations existent between the meteorological elements and the ozone concentrations, for each calendar month and for each day, on the basis of the hourly values measured in the

interval 2004-2007 in Suceava municipality. The main objective of this study is to analyze to what extent the variability of these meteorological conditions explains the variability of the ozone concentrations during an average year, but also during an average day. The second objective is to discover if in the studied area exist periodicities in the ozone concentrations, other than the daily and the annual ones.

1. Study area

Suceava City is located in the North-Eastern Romania. It is considered a medium-large city within the Romanian urban network, having a total population of 114000 inhabitants in 2011. Suceava City had moderate emissions of ozone precursors during 2004-2007 and the hourly ozone concentrations did not exceed the information threshold (Tab. 1, Fig. 1), but there were recorded daily maximum values of the 8 hours averages that were close to or even exceeded the long term target (in 2006). This thing means a warning signal and seems to register itself in the actual trend of the increasing O₃ background concentrations. In the Member States of the European Union (including Romania), the long term target (2020) is set to a concentration of 120 µg/m³ O₃ as daily maximum value of the 8 hours average (EU Environmental Agency, 2009).

Tab 1. The annual average and maximum concentrations (calculated on the basis of the hourly concentrations) of the ozone (µg/m ³) in Suceava city during 2004-2007.					
	2004	2005	2006	2007	2004-2007
Average hourly concentration	47	43.9	49.3	45.7	46.5
Maximum hourly concentration	122	122	146	118	146
Maximum value of the highest daily averages of 8 hours	111.8	112.8	139.5	106.3	139.5

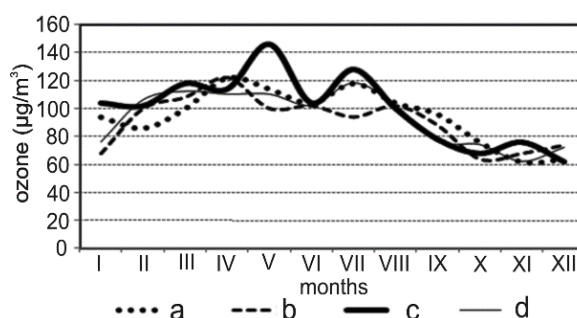


Fig. 1. The annual evolution of the ozone hourly maxima of each month in Suceava city during 2004-2007: a-2004, b-2005, c-2006, d-2007

The information level was set to an hourly concentration of 180 µg/m³ of O₃, while the alert level was set to an hourly value of 240 µg/m³ of O₃ (European

Environmental Agency 2009). In the urban areas of the EU Member States, almost 45 % from the monitoring stations do not respect the target values of the O₃ for the human health protection (Mol et al. 2008).

2. Data and methods

The hourly ozone data are provided by the Environmental Protection Agency (E.P.A.) Suceava. This parameter was continuously monitored during the period analysed in this study (2004-2007). The ambient ozone analyser used by the E.P.A. Suceava is a GUX-113 model, made by DKK TOA Japan, having as measuring principle the UV photometry (which is the European Union reference method, SR EN 14625:2005 - „Ambient air quality. Standard method for the measurement of the concentration of ozone by ultraviolet photometry”). The measuring range is 0 to 1 ppm (with self-scaling). The detection limit of the method is 0.5 ppb (Ursul and Nicu 2008).

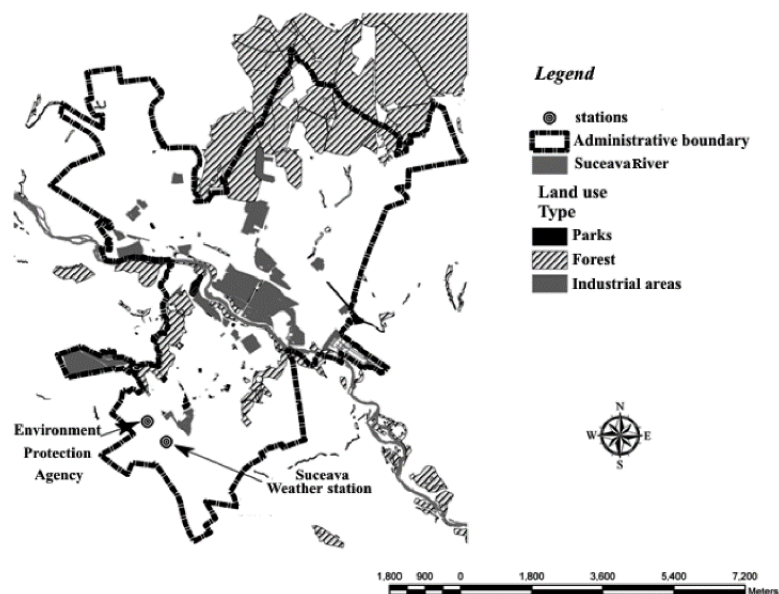


Fig. 2. Map of the study area

The E.P.A. measuring point is located in the suburbs of Suceava City (47°38'N, 26°13'E, 366 m above the sea level, Fig. 2), thus meeting the requirements of the European Union directives of being placed out of the significant local sources of ozone precursors. The industrial sources of ozone precursors are located in the following areas: the Suceava River Valley (which

divides the city) and the Șcheia industrial area (Fig. 2). The mobile sources consist of the vehicles transiting the European route E85 (crossing the city) and the urban and rural road traffic. The data from the measurements comply with the quality requirements regarding the data capture from continuous measurements of the O_3 in fixed points, set by the EU Directive no. 2002/3/EC.

The hourly data regarding the meteorological parameters used in this study for the 2004-2007 period (the air temperature - T , the air relative humidity - Rh , the sunshine duration - S , the wind speed - Ws - and the wind direction - Wd) were

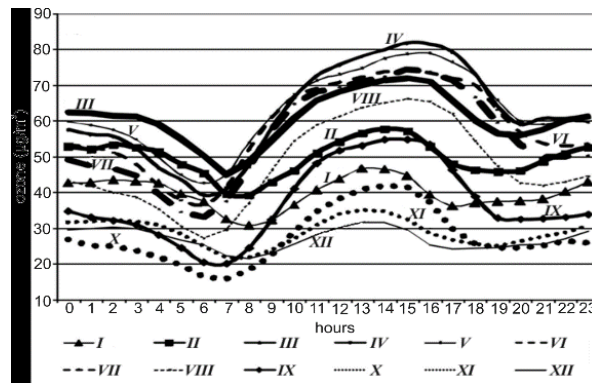


Fig. 3. The diurnal variation of the O_3 monthly hourly average concentrations in Suceava city during 2004-2007

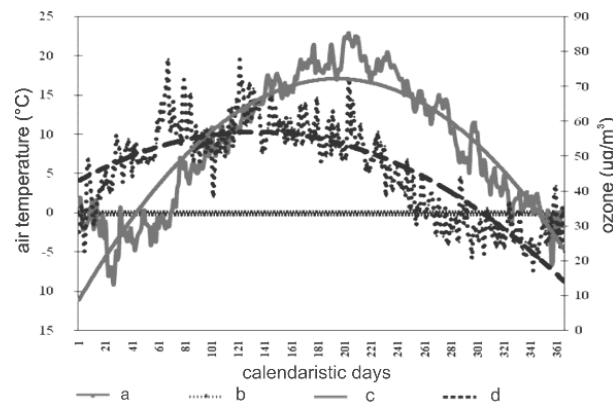


Fig. 4. The annual evolution of the diurnal values of the air temperature and tropospheric ozone during 2004-2007: a-average daily temperatures, b-average daily ozone concentrations, c-6th degree polynomial of the average daily temperatures, d-6th degree polynomial of the average daily ozone concentrations

obtained from Suceava Meteorological Station (47°37'N, 26°14'E, 359 m above the sea level), which is located close (0.7 km) to the ozone monitoring station (Fig. 2). The hourly wind direction data are continuous and 0 was used to indicate no direction, while values from 1 to 37 were used to replace the cardinal directions with their degree equivalent divided by 10. When calculating correlations and linear regressions including the Wd, the 0 values of the wind directions were excluded.

The continuous wavelet transform (CWT) was applied to the analysed parameters by using the methodology described by Labat (2010) in order to obtain scalograms. On scalograms, the thick black contour indicates the 0.95 confidence level against red noise of AR1 type (specific to the climatological data). The confidence level is calculated by using the Monte Carlo test, according to the methodology described by Grinsted et al. (2004). A cone of influence appears as a result of the finite time series, which are affected by edge effects when a wavelet analysis is performed (Torrence and Compo 1998). The edge effects decrease the statistical relevance of the periods identified in scalograms, but their influence is clearly marked by the lighter shade applied to the colors of the power spectrum.

The wavelet coherence (WTC) analysis was applied to the analysed parameters by using the methodology of Grinsted et al. (2004). The phase arrows on the WTC scalograms suggest the relationship between the periods identified among the compared time series (the arrows pointing right indicate an in-phase relationship; left: anti-phase; down: series 1 leads series 2 by 90°), but their interpretation is difficult (Grinsted et al. 2004). Both wavelet analyses (CWT and WTC) used the Morlet wavelet as mother-wavelet. The Morlet wavelet is a sinusoid with the wavelength modulated by a Gaussian function (Morlet et al. 1982).

3. Results and discussions

Between 2004-2007, the annual profile of the ozone had the highest hourly concentrations in the spring-summer period, especially in April-May. During a day time, the critical hourly interval in which the ozone has the highest values is 11 a.m.–8 p.m. in the spring-summer season and 11 a.m.–6 p.m. in the rest of the year (Fig. 3). We took into consideration both the complete diurnal cycle and the main critical diurnal interval (11 a.m.–6 p.m.), when the O₃ values are the highest throughout the year. But, for the comparability of the results of all parameters, we use the same hourly intervals, regardless of the month of the year.

During an average year, between the evolution of the air temperature and that of the ozone concentration (Fig. 4), there can be observed many similarities, but also some differences.

The maximum values of the annual temperature, those from the interval July-August, are in a time gap of over two months when compared to the annual ozone

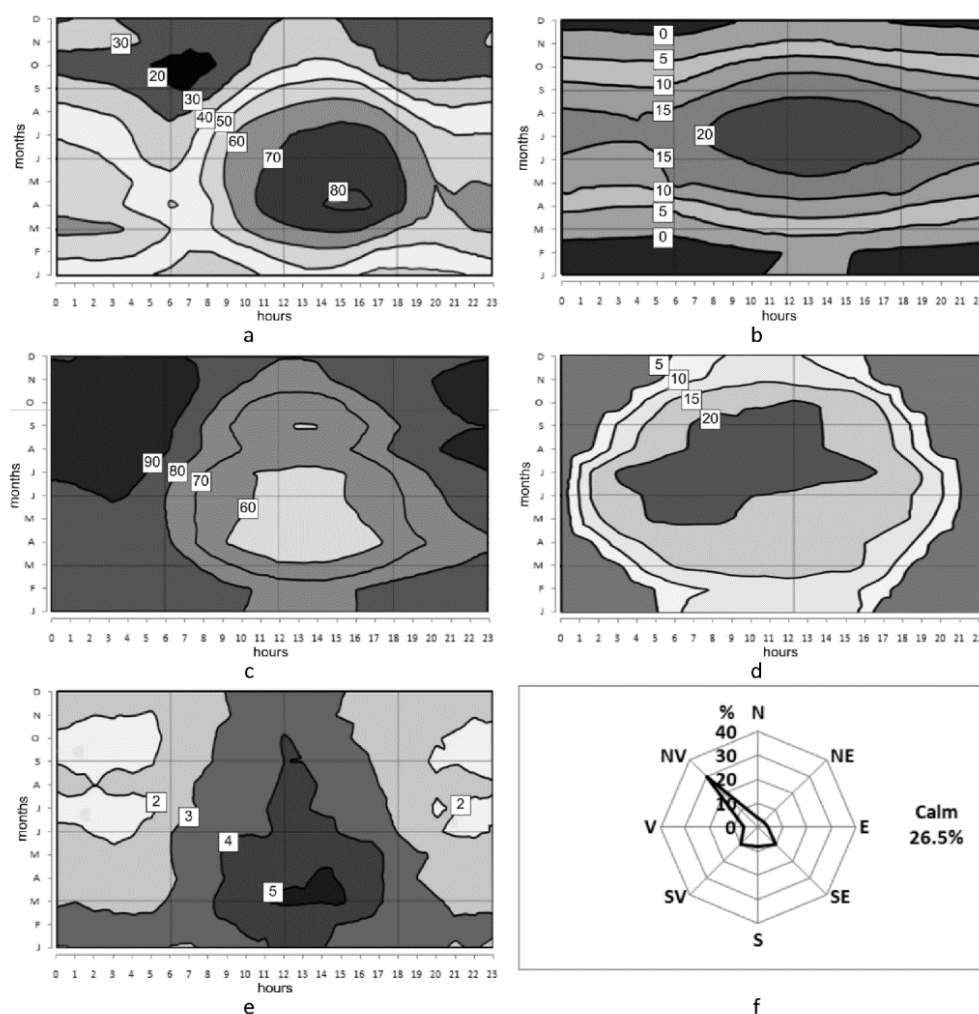


Fig. 5. Contour plots of the analysed parameters (2004-2007, Suceava city): a-O₃ (μg/m³), b-T, c-Rh, d-S, e-Ws; f-radar chart of the yearly wind directions

concentration maximum. The producing of the annual temperature minimum, at the end of January, occurs with almost a month and a half later than the annual ozone concentration minimum. The contour plots of the O₃ and T show a relatively good overlap of the two parameters (Fig. 5.a, b) from 10-11 a.m. until 7-8 p.m.,

approximately for each month of the year, but especially during March-September. In these intervals of similarities, to the domain with O_3 concentrations higher than the annual average (approximately $>50\mu\text{g}/\text{m}^3$) largely corresponds the domain with temperatures $>15\text{-}20^\circ\text{C}$.

During an average year, the monthly average values of the Pearson correlation coefficients calculated on the basis of the hourly values of the O_3 and the temperature show very good positive correlations (0.65-0.86) during March-October, but low correlations (0.38-0.46) for the cold period of the year (November-February) (Fig. 6.a). Taking into account the inter-monthly evolution of the Pearson correlation coefficients calculated for different hourly intervals of the day (Fig. 7.a), the strongest correlations for the entire year are those between the ozone measured during 11 a.m.-8 p.m. and the temperatures recorded one hour before, namely those from the interval 10 a.m.-7 p.m.

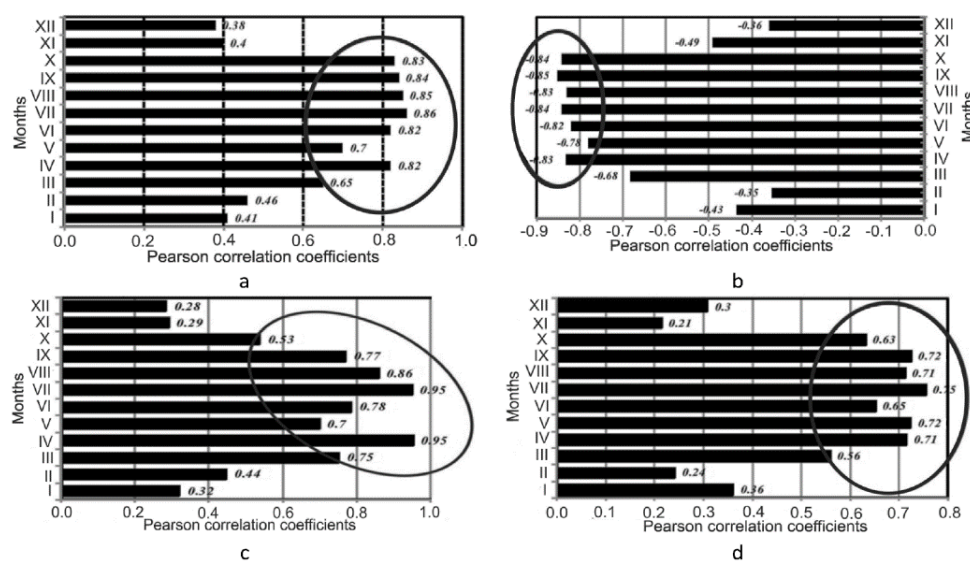


Fig. 6. The average annual evolution of the monthly values (calculated by averaging the hourly values of each day) of the Pearson correlation coefficients for: a- O_3 and T, b- O_3 and Rh, c- O_3 and S (O_3 -11 a.m.-8 p.m., S-8 a.m.-5 p.m.), d- O_3 and Ws

Strong and even very strong positive correlations for the cold period (November-February) are also being obtained when taking into account only the ozone-temperature sets of values from the hourly intervals 11 a.m.-8 p.m. of the day, while smaller hourly intervals, 11 a.m.-7 p.m. and respectively 10 a.m.-6 p.m., presented much weaker correlations for the hot months. Good correlations also exist between the hourly ozone concentrations and the values of the temperature

recorded 2 hours before the recording of the ozone (Fig. 7.a), but only for the period March-October, these correlations being weaker during the cold months.

The solar radiation (mainly the UV radiation) is the determining factor for the ozone generating process, even in a greater extent than the temperature itself, and the high T-O₃ positive correlation is determined by the big values of the radiation which correspond to the big values of the temperature.

But it is possible the temperature to be involved indirectly by favoring the natural VOC emissions (foliar emissions) as determinant agent in the ozone formation, especially during the hot periods.

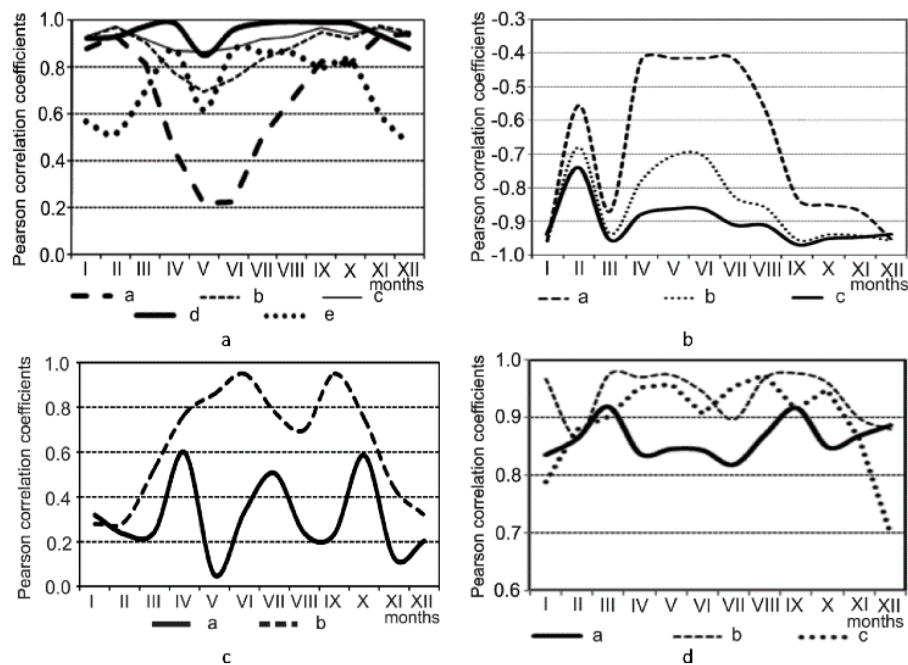


Fig. 7. The average annual evolution of the monthly values of the Pearson correlation coefficients during different hours: a-O₃ and T (a. 10 a.m.-6 p.m., b. 11 a.m.-7 p.m., c. 11 a.m.-8 p.m., d. 11 a.m.-8 p.m. with an interval gap of 1 hour, e. 11 a.m.-8 p.m. with an interval gap of 2 hours), b-O₃ and Rh (a. 10 a.m.-6 p.m., b. 11 a.m.-7 p.m., c. 11 a.m.-8 p.m.), c-O₃ and S (a. 11 a.m.-8 p.m., b. O₃-11 a.m.-8 p.m. and S-8 a.m.-5 p.m.), d-O₃ and Ws (a. 11 a.m.-8 p.m., b. 11 a.m.-8 p.m. with an interval gap of 1 hour, c. 11 a.m.-8 p.m. with an interval gap of 2 hours)

The delay of the ozone concentration (observed when compared to the values of the temperature) can be caused by the delay in the VOC emission by the vegetation from the surrounding areas of the city (a major importance representing

the Adâncata and Dragomirna forests from the Northern and respectively the North-Western hills from nearby).

Between the air humidity and the tropospheric ozone concentrations there is a strong annual relation of inverse proportionality. During the period of the year in which Rh reaches the lowest values (April-May), the O₃ concentrations reach their maximum. In the months with the highest relative humidity (November-January), the O₃ concentrations reach the lowest rates. From the contour plot representations of the ozone (Fig. 5.a) and those of the relative humidity (Fig. 5.c) can be observed a relatively good overlap of the hourly intervals from 10-11 a.m. to 7-8 p.m. To the annual and diurnal interval with concentrations of the O₃ higher than the multiannual average (approximately >50 µg/m³) largely correspond the annual and diurnal intervals with relative humidity < 70 %. The increased humidity has a general effect upon the decreasing of the O₃ concentration from the air, the O₃-Rh relationship being negative.

By analysing the annual regime of the Pearson correlation coefficients (Fig. 6.b) we have noticed that the negative correlation between O₃ and humidity is strong in April-October (between -0.78 and -0.853), moderate in March (-0.682) and weak in November (-0.492) and during the winter months (between -0.355 and -0.436). The analysis of the inter-monthly evolution of the O₃-Rh Pearson correlation coefficients, calculated for different times of the day (Fig. 7.b) shows that the 11 a.m.-8 p.m. hourly interval presents the strongest negative correlations (stronger than -0.8).

The first explanation which targets the relations established between the air humidity and the O₃ is that the O₃ is removed from the air by the presence of the water droplets (aerosols) through absorption on the water drops. Moreover, during the periods with high humidity (in the evening, night and morning, especially in the cold season), with pronounced cloudiness and rainfalls, the intensity of the sunlight (especially the UV) also decreases, this reducing the photochemical processes of the O₃ production and decomposition. The humidity itself has, during these periods, a relevant impact on the O₃ level, thus resulting strong negative O₃-RH correlations.

Within a year, in Suceava City the inter-diurnal evolutions of the sunshine duration and the tropospheric ozone concentrations are positively and strongly correlated. By comparing the contour plots of the sunshine duration (Fig. 5.d) and the ozone, there can be observed only a weak overlap of the analysed parameters, although it was expected an obvious correlation.

The diurnal maximum of the sunshine duration occurs most frequently when the Sun crosses the meridian of the place or immediately post-meridian (12 p.m.-1 p.m.), with approximately 3-4 hours before the maximum of the ozone, which is usually recorded during the afternoon hours (4-5 p.m.). The sunshine duration

during 8 a.m.-5 p.m. correlates best with the O_3 recorded during 11 a.m.-8 p.m. The monthly Pearson correlation coefficients (calculated on the basis of the correlation between the sunshine duration from the diurnal interval 8 a.m.-5 p.m. and those of the ozone concentration from the diurnal interval 11 a.m.-8 p.m.) are strongly positive (0.955-0.860) in the months of April and July-August (when the wind speed, the air temperature, the relative humidity and the share of the UV radiation act in the same direction).

The correlations are relatively good in March, May, September and October (0.786-0.539), but are weak during November-February (cold, nebulous, humid months - 0.285-0.448). The inter-monthly evolution of the O_3 -S correlation coefficients shows a good relationship for the common hourly interval 11 a.m.-8 p.m., too (fig. 7.c).

The correlations set between the O_3 and the sunshine duration are significant during the warm season of the year and during the afternoons of this season. The weaker correlations could be explained by certain inertia of the reactions of the O_3 formation under the impulse of the UV rays and also by other factors (the air temperature, the wind speed and the hourly variation of its direction).

The analysis of the annual evolution of the O_3 and Ws has shown that the highest diurnal speeds of the wind (specific to the months of April-May) correspond to a period with diurnal maximum of the tropospheric ozone concentration. During the periods with the lowest wind speeds (e.g. September), the ozone concentrations decrease significantly. Between the Ws and the O_3 , in annual profile, there is established an obvious positive correlation. The analysis of the ozone concentration and wind speed contour plots (Fig. 5.e) allowed us to ascertain a weaker overlap of them (comparatively with those of the temperature and humidity, but more relevant than in the case of the O_3 concentration versus the sunshine duration), especially at low values of the two variables, finally resulting weaker correlations between the two parameters.

Yet, to the diurnal and annual intervals with higher average values of the wind speed (>4 m/s) correspond, with some precision, intervals with bigger concentrations of the O_3 (>60 $\mu\text{g}/\text{m}^3$), in this case resulting the visible and relevant positive correlations. The average wind speed correlates positively with the O_3 concentration on the complete diurnal cycle in the months March-October.

The monthly average values of the Pearson correlation coefficients range between 0.560 and 0.755 (Fig. 6.d). There are weak correlations in the interval November-February (0.215-0.361), which is characterized by low concentrations of O_3 . By analysing the inter-monthly evolution of the Pearson correlation coefficients, calculated for different temporal intervals from the day (Fig. 7.d), there can be observed that in the case of the hourly interval 11 a.m. – 8 p.m. exist

strong positive correlations of the ozone and the average wind speed recorded one hour before the O₃ measurements (≥ 0.9 in 10 months of the year).

The most probable cause of the positive correlation between the two parameters is the transport of the ozone precursors from the local industrial sources of NO_x and VOC - Burdujeni industrial platform - and from the natural sources of VOC – Adâncata and Dragomirna forests. The natural sources are placed at only

Tab. 2. The hourly values of an average daily evolution of the analysed parameters.

	O ₃ µg/m ³	T °C	Rh %	S hrs	Ws m/s	Wd °/10
0	45.43	6.84	88.56	0.00	2.39	25.62
1	44.82	6.51	89.34	0.00	2.31	25.64
2	44.14	6.28	89.84	0.00	2.21	26.04
3	42.77	6.03	90.52	0.00	2.21	26.17
4	39.74	5.91	90.57	0.01	2.22	26.31
5	36.18	6.29	89.81	0.16	2.34	26.28
6	33.29	6.97	87.46	0.28	2.69	25.41
7	32.80	7.87	83.66	0.40	2.96	25.23
8	36.98	9.00	78.83	0.50	3.24	24.91
9	43.02	10.13	74.10	0.55	3.63	24.26
10	48.94	11.08	70.62	0.57	3.92	23.6
11	53.35	11.74	67.35	0.56	4.00	22.72
12	55.96	12.23	65.41	0.57	4.24	22.21
13	57.90	12.37	65.02	0.53	4.22	22.07
14	59.03	12.26	65.16	0.51	4.10	21.98
15	59.03	11.80	67.01	0.38	3.91	22.08
16	56.85	11.10	69.92	0.24	3.61	22.61
17	53.31	10.42	73.19	0.11	3.25	23.25
18	49.69	9.67	77.05	0.02	2.94	24.29
19	45.67	8.84	80.41	0.00	2.60	24.37
20	43.42	8.40	82.97	0.00	2.44	24.76
21	43.50	7.88	85.00	0.00	2.37	25.31
22	44.52	7.48	86.37	0.00	2.28	25.31
23	45.55	7.25	87.36	0.00	2.27	25.54

~7 km and, respectively, ~10 km away from the O₃ measuring station. In general, the horizontal air displacement can create significant changes of the ozone concentration in urban or non-urban areas (Kim et al. 2006). The parallelism

between the Suceava River Valley and the wind direction favours the transport of the ozone precursors on the dominant direction from NW to SE or from the inverse secondary direction (Fig. 5.f). Both wind directions bring air masses from the previously mentioned local sources of VOC. The strong wind usually generates a high intensity of the horizontal transport of the air masses, causing the dispersion of some ozone precursors from the sources.

The average daily evolutions of all parameters analysed indicate that there is a temporal gap between the ozone and the other parameters, the ozone maximum occurring later or in anti-phase (Fig. 9). The temporal gap supports the idea that the temporal position of the ozone maximum is an effect of the meteorological factors.

As far as concerning the wind-derived parameters, the higher wind speed during the daytime influences the ozone maximum by bringing air masses from the nearby woods (poor in NO_x and rich in VOCs). The daily O_3 -Wd is an apparently anti-phase relationship. In fact, the maximum average daily values of Wd represent a WSW direction (26) which is the NW direction (32-33) diminished by random wind directions. During the daytime, the air turbulence is higher, especially above the built area, due to the increased heating of the urban surfaces, the dominant (and average) direction of the wind being more altered than during night. The sunshine duration has a higher than proved correlation with the ozone at daily, monthly or annual scales (Tables 2 and 3), but the analysis is limited because the lower limit of the sunshine duration cannot be below 0.

In conditions of polluted air, the water vapours from the atmosphere may act, on the one hand, through the formation of the OH radicals in the terms of the regeneration of the O_3 previously decomposed photochemically and, on the other hand, in the terms of the O_3 reduction by consuming the OH radicals in the concurrent reaction of the HNO_3 formation (if the NO_2 concentrations are high). In this case, the OH radicals will no longer react with the VOCs in order to resume the cycle of the O_3 (Lelieveld et al. 2004). The anthropogenic emissions, such as road traffic (Matthes et al. 2007), also induce cyclicity in the ozone concentrations.

Tab. 3. Daily and yearly relationships established between the analyzed parameters.

	Daily - average hours basis		Yearly - average days basis	
	R	linear regression	R	linear regression
T	0.80	$\text{O}_3 = 2.775\text{T} + 21.70$	0.34	$\text{O}_3 = 0.609\text{T} + 41.07$
Rh	-0.80	$\text{O}_3 = -0.663\text{Rh} + 99.16$	-0.71	$\text{O}_3 = -1.316\text{Rh} + 151.0$
S	0.31	$\text{O}_3 = 10.14\text{S} + 44.20$	0.48	$\text{O}_3 = 59.07\text{S} + 33.18$
Ws	0.68	$\text{O}_3 = 7.168\text{Ws} + 24.87$	0.39	$\text{O}_3 = 6.007\text{Ws} + 28.39$
Wd	-0.86	$\text{O}_3 = -4.519\text{Wd} + 156.8$	-0.02	$\text{O}_3 = -0.066\text{Wd} + 48.07$

A weekly periodicity of the urban O_3 exists, with the O_3 being in negative correlation with the anthropogenic NO_x gases, which are strong ozone sweepers in the urban areas; high ozone concentration during Saturday-Sunday are expected as a result of the reduced road traffic (Shutters and Balling 2006).

The ozone concentrations show the same behaviour in Suceava City, with only Saturdays and Sundays' values above the daily average ($45.892 \mu g/m^3$) and the hourly average, too ($46.495 \mu g/m^3$); Sundays have the maximum values, while Saturdays, Mondays and Tuesdays represent transitions to the mid-weekly concentrations (Fig. 8).

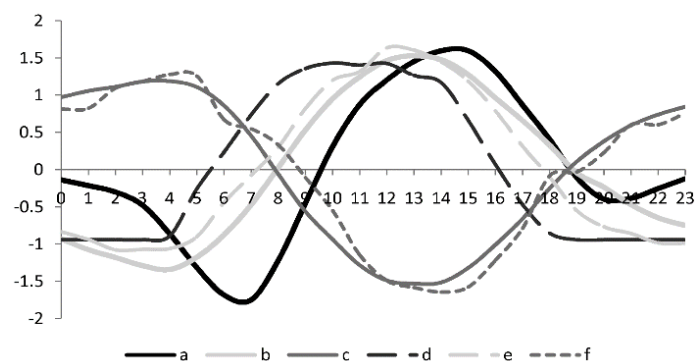


Fig. 8. The weekly profile of the ozone concentration: a-daily averages, b-the mean value of the daily averages, c-hourly average

The strategies of the air quality control based on the pollutants emissions control are usually directed to the regulation of the nitrogen oxides (NO_x) and volatile organic compounds (VOC) emissions, originated from various stationary sources of emissions. In many urban areas, the mobile sources are still responsible for the majority of the NO_x and VOC emissions.

Therefore, the policies that determine the reduction of the emissions from mobile sources can lead to substantial benefits for the human health, the ecosystems and the climate (Zavala et al. 2009). Although, as a result of these control strategies, the emissions of the O_3 precursors fell with almost 40% in the States Members of the European Union during 1990-2005 (Leeuw 2002), the O_3 concentrations do not present the same tendency, but, on the contrary, there is even an increasing tendency of the O_3 in the urban air. This may be due to a reduced decomposition of the O_3 due to the decreasing of the NO_x emissions. Yet, the net values of the O_3 are the resultant of a complex of factors and processes which take place at the same time in atmosphere: the growth of the background level in the Northern hemisphere, the more reduced dry deposition of the O_3 due to the

prolonged periods of drought in the summer months, the growth of the O_3 production due to the higher temperatures and the decrease of the O_3 production due to the NO_x emissions reduction.

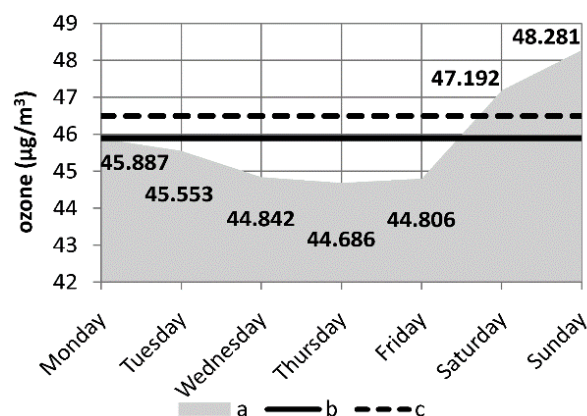


Fig. 9. The average daily evolution of the analyzed parameters: a- O_3 , b-T, c-Rh, d-S, e- W_s , f-Wd

The continuous wavelet analysis of the daily ozone concentrations shows weekly groups of high confidence areas approximately at 24 hours periodicity (Fig. 10.a).

Those small groups are far more frequent in the warm season than in the cold one, as results of the higher night-day contrast. The standard deviation of the October-March interval is with 5.14% higher than the standard deviation of the April-September months (the difference is calculated based on the average standard deviation of the seasons during each year because there is a great variation from one year to another: cold season – 19.94 $\mu\text{g}/\text{m}^3$, 20.83 $\mu\text{g}/\text{m}^3$, 24.99 $\mu\text{g}/\text{m}^3$ and 18.07 $\mu\text{g}/\text{m}^3$, warm season – 22.82 $\mu\text{g}/\text{m}^3$, 21.61 $\mu\text{g}/\text{m}^3$, 20.85 $\mu\text{g}/\text{m}^3$ and 21.5 $\mu\text{g}/\text{m}^3$ for 2004, 2005, 2006 and 2007).

The continuous wavelet analysis of the daily ozone concentrations shows weekly groups of high confidence areas approximately at 24 hours periodicity (Fig. 10.a). Those small groups are far more frequent in the warm season than in the cold one, as results of the higher night-day contrast. The standard deviation of the October-March interval is with 5.14% higher than the standard deviation of the April-September months (the difference is calculated based on the average standard deviation of the seasons during each year because there is a great variation from one year to another: cold season – 19.94 $\mu\text{g}/\text{m}^3$, 20.83 $\mu\text{g}/\text{m}^3$, 24.99 $\mu\text{g}/\text{m}^3$ and 18.07 $\mu\text{g}/\text{m}^3$, warm season – 22.82 $\mu\text{g}/\text{m}^3$, 21.61 $\mu\text{g}/\text{m}^3$, 20.85 $\mu\text{g}/\text{m}^3$ and 21.5 $\mu\text{g}/\text{m}^3$ for 2004, 2005, 2006 and 2007).

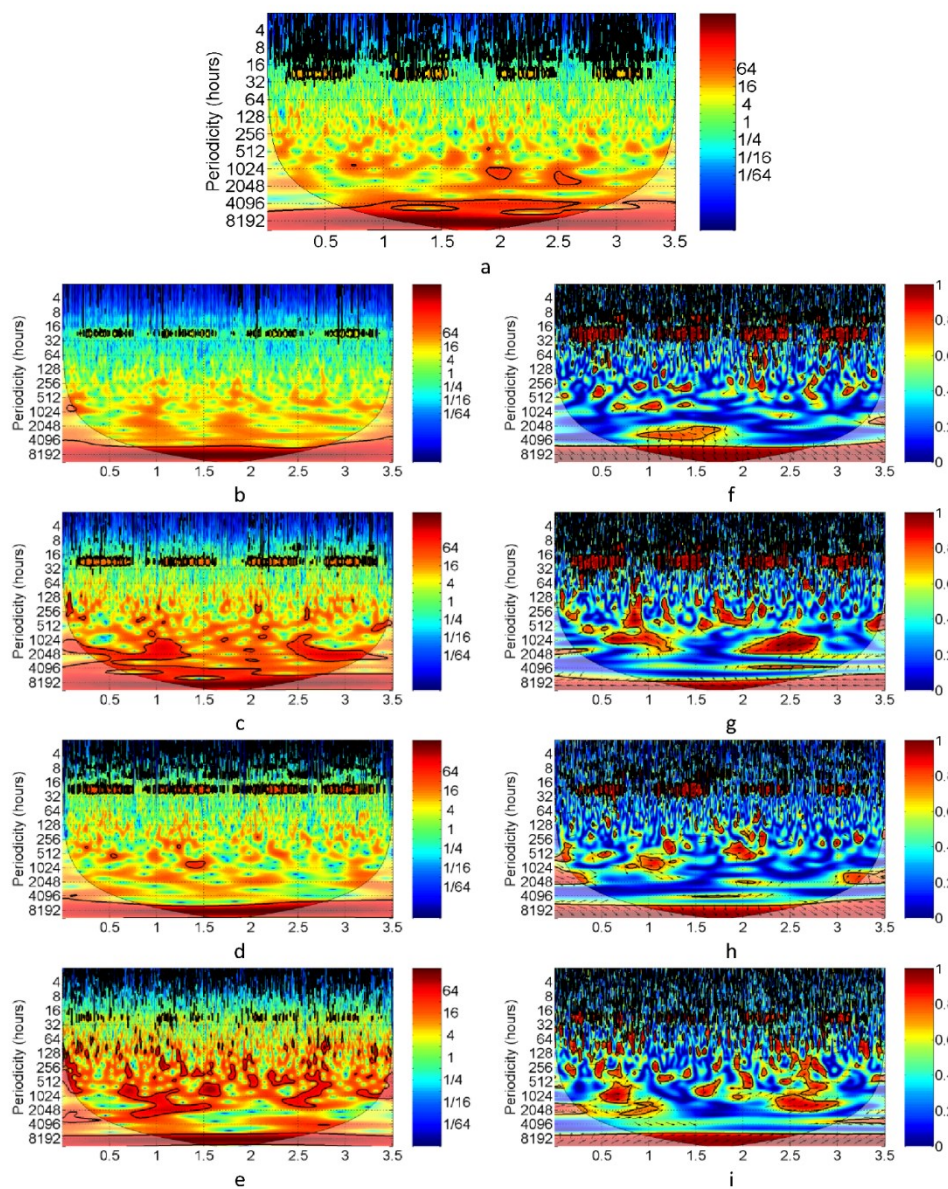


Fig. 10. Wavelet analysis of the analysed parameters: a-e. CWT of O_3 , T, Rh, S, Ws; f-i WTC of O_3 with T, Rh, S and Wd, respectively (the horizontal axes represent number of consecutive measurements/hours $\times 10^4$)

The areas with high confidence values in the relatively compact groups of 24 hours periodicity also exist in all analysed parameters and in their WTC with the ozone (Fig. 10.b-i). The groups of the 24 hours signal are very strong during the warm season but almost absent during the cold one. The continuous red and high confidence area at the bottom of all scalograms in Fig. 10 represents the yearly periodicity of all parameters and the phase arrows within it confirm that the highest temporal gap between the minimums and the maximums of the parameters compared is the one for the O₃-Rh relationship.

Conclusions

The quality of the Suceava City air has been proper in the terms of the ozone concentration, without being recorded the exceeding of the public information or alert thresholds during the 4 years of monitoring. The long term objective was exceeded only once, but the daily maximum values of the 8 hour-averages achieved the European Union long-term objective of maximum O₃ production. Within a daytime, the correlation coefficients between the analyzed variables are more significant than within a year time. Many similarities with other urban sites exist (such as Pehnec et al., 2005, Shan et al., 2009, Hosseinibalam et al, 2010), but with local features. The high levels of the O₃ in Suceava City are usually correlated with decreases of the NO_x concentrations (the weekend effect), respectively with high solar radiation, temperatures, wind speeds, but with low air humidity.

Acknowledgment: Wavelet coherence software was provided by A. Grinsted

References

- Grigore Elena**, (2012) *Potențialul bioclimatic al Podișului Dobrogei de sud*, Editura Universității București;
- Bauer S.E. and Langmann B.** (2002), *Analysis of a summer smog episode in the Berlin-Brandenburg region with a nested atmosphere – chemistry model*, Atmospheric Chemistry and Physics, **2**, 259–270.
- European Environmental Agency** (2009), *Assessment of ground-level ozone in EEA member countries, with a focus on long-term trends*, EEA Technical report No 7/2009, ISSN 1725-2237, Office for Official Publications of the European Communities, Luxembourg.
- Finlayson-Pitts B.J. and Pitts Jr. J.N.** (1997), *Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles*, Science, **276**(5315), 1045-1051.

- Grinsted A., Moore J.C. and Jevrejeva S.** (2004), *Application of the cross wavelet transform and wavelet coherence to geophysical time series*, *Nonlinear Processes in Geophysics*, **11**, 561-566.
- Hosseinibalam F., Hassanzadeh S. and Alizadeh R.** (2010), *Analysis and assessment of ground-level ozone measured at two stations in Tehran*, *Environmental Monitoring and Assessment*, **165**(1-4), 275-281.
- Jacob D.J. and Winner D.A.** (2009), *Effect of climate change on air quality*, *Atmospheric Environment*, **43**, 51-63.
- Kim J.H., Lee H.J. and Lee S.H.** (2006), *The characteristics of tropospheric ozone seasonality observed from ozone soundings at Pohang, Korea*, *Environmental Monitoring and Assessment*, **118** (1-3), 1-12.
- Labat D.** (2010), *Cross wavelet analyses of annual continental freshwater discharge and selected climate indices*, *Journal of Hydrology*, **385**, 269-278.
- Lelieveld J., Dentener F.J., Peters W. and Krol M. C.** (2004), *On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere*, *Atmospheric Chemistry and Physics*, **4**, 2337-2344.
- Matthes S., Grewe V., Sausen R. and Roelofs G.J.** (2007), *Global impact of road traffic emissions on tropospheric ozone*, *Atmospheric Chemistry and Physics*, **7**, 1707-1718.
- Mol W.J.A., van Hooydonk P.R. and de Leeuw F.A.A.M.** (2008), *European Topic Centre on Air and Climate Change Technical paper 2008/1*. <http://air-climate.eionet.europa.eu/>. Accessed 1 July 2009.
- Morlet J., Arehs G., Fourgeau I. and Giard D.** (1982), *Wave propagation and sampling theory*, *Geophysics*, **47**, 203-221.
- Ordonez C., Mathis H., Furger M., Henne S., Huglin C., Stachelin J. and Prevot A.S.H.** (2005), *Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003*, *Atmospheric Chemistry and Physics*, **5**, 1187-1203.
- Parry M.L., Canziani O.F., Palutikof J.P., van der Linden P.J. and Hanson C.E.** (Eds.) (2007), *Climate change 2007 – Impacts, adaptation and vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on climate change*, Cambridge University Press, UK.
- Pehnec G., Vadjic V. and Hršak J.** (2005), *Measurements of ozone concentrations in Zagreb*, *Environmental Monitoring and Assessment*, **105** (1-3), 165-174.
- Shan W., Yin Y., Zhang J., Ji X. and Deng X.** (2009), *Surface ozone and meteorological condition in a single year at an urban site in central-eastern China*, *Environmental Monitoring and Assessment*, **151**(1-4), 127-141.
- Shutters S.T. and Balling Jr. R.C.** (2006), *Weekly periodicity of environmental variables in Phoenix, Arizona*, *Atmospheric Environment*, **40**, 304-310.
- Ursul L.G. and Nicu M.** (2008), *Aspects on the monitoring of tropospheric ozone in Suceava city*, *Innovative Materials and Processes, Proceedings of the National Conference Days of the Faculty of Chemical Engineering and Environmental Protection*, November 19-21 2008, 73-78.

-
- Vandermeiren K., Harmens H., Mills G. and De Temmerman L.** (2009), *Climate Change and Crops*, In: Impacts of Ground-Level Ozone on Crop Production in a Changing Climate (pp. 213-243), S.N. Singh (Ed.), Springer-Verlag, Germany.
- Zavala M., Lei W., Molina M. J. and Molina L. T.** (2009), *Modeled and observed ozone sensitivity to mobile-source emissions in Mexico City*, Atmospheric Chemistry and Physics, **9**, 39–55.