Evolution of Tropospheric Ozone and Relationship with Temperature and NOx for the 2007-2016 Decade in the Ciuc Depression

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This paper presents the evolution of ozone concentration for the 2007-2016 decade and a comparison with key values related to human and vegetation health. As temperature is one of the main factors influencing ozone concentration in this area, the most significant changes of air temperature and extreme temperature indices for the 2007 - 2016 decade were evaluated, in retrospect to temperature measurements for the 1961-1990 reference period. The relationship between temperature and ozone concentration was also overviewed, by means of climate penalty factor. The influence of NOx concentration on ozone concentration was studied in order to compare the impact of climate changes with the impact of changes determined by anthropogenic emission.

Keywords: air temperature, extreme temperature indices, tropospheric ozone, climate penalty factor, SOMO35

Climate started to intrigue scientists' centuries ago, academic societies from Eastern Europe financed the publication of scientific works on climate since the 19th century [1]. Global-scale observations from the instrumental era began in the mid-19th century for temperature and other variables, with more comprehensive and diverse sets of observations available starting with 1950 [2]. The growing concern about climate changes and their effects on human health and welfare led to intensified research and communication. Several recent studies are assessing the global [3, 4], regional [5-7] and local evolution of the climate [8]. Science shows with certainty that human activity is the dominant cause of observed warming since the mid-20th century. Many of the observed changes are unprecedented over decades to millennia: warming of the atmosphere and the ocean, diminishing snow and ice, rising sea levels and increasing concentrations of greenhouse gases. Each of the last three decades has been successively warmer at the Earth's surface than any preceding decade since 1850 [2].

Air pollution results from the combination of high emissions and unfavorable weather, one of the air pollutants of most concern for public health is surface ozone [9, 10]. Observational and modeling evidence indicates that locally higher surface temperatures in polluted regions will trigger regional feedbacks in chemistry and local emissions that will increase peak levels of ozone [2]. The climate change alone will increase summertime surface ozone in polluted regions by 1-10 ppb over the coming decades, with the largest effects in urban areas and during pollution episodes [11]. The increase in surface ozone as a result of future climate change represents a *climate change penalty* or climate penalty factor [12, 13]. Temperature is considered as the main factor influencing ozone concentrations [10, 11, 13-15]. Therefore, the evolution of key temperature values (yearly and monthly averages, variation) for the 2007-2016 timeframe is very important. The specificity of the climate is highlighted by the occurrence frequency of days with significant characteristics of air temperature. Severe cold days, winter days, frost days, summer days and hot days, known as extreme temperature indices, are affecting air quality in many ways [16]. Analyzing the intensity and frequency of these extreme events is important since human and natural systems may be especially affected by changes of extreme climate events [17-19]. Subsequently, the calculation of climate penalty factor is due to verify how climate change will likely impact the effectiveness of current emission reduction strategies.

Surface O_3 will be affected by warmer average surface temperatures, shifts in global circulation patterns, changes in the frequency of heat waves and frontal passages, altered surface mixed-layer depths and variations in cloud cover, precipitation, and convection. Climate change will likely also modify patterns in fires, vegetation, and land use, which are all large sources of O_3 precursors to the atmosphere [20]. There are several studies establishing air quality models that quantified the change in O_3 due to a prescribed temperature perturbation but did not refer to this sensitivity by a specific name [21, 22]. However, the name O_3-climate penalty became frequently used for it, with varying definitions presented in the literature. Some consider the climate penalty to represent either the additional decreases in NOx emissions to counter any climate driven increase in O_3 (assuming NOx is the limiting precursor), or the reduced benefits of emissions controls due to the increase in O_3 due to a warmer climate [12]. Another approach is that the *ozone-climate penalty factor* can be calculated as the slope of the best fit line between long-term observational measurements of O_3 and temperature [15]. Other studies identified the relationship between NOx emissions and temperature as a contributor to trends in ozone [20], or quantified the dependence of NOx emissions on temperature in the context of the climate penalty factor for O_3 production [23]. There are works that employ the temperature perturbation approach. They refer to the direct increase in O_3 concentrations due to increasing temperatures as the *O_3-climate penalty* or *climate penalty*, reporting it to be highly dependent of differing chemical and meteorological environments that

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influence O_3 formation [21, 24]. The aggregate effects that make up the total derivative $d[O_3]/dT$ include more components. The association between stagnant air masses and warm temperatures will facilitate the accumulation of the precursors of O_3 [13]. The increase in chemical reaction rates, including the thermal decomposition of alkyl nitrates (AN) and subspecies peroxyacetyl nitrate (PAN), will supply NOx and HOx at low temperatures [14]. Temperature dependent variations in biogenic emissions of VOCs act as a source of precursors for O3 formation under high-NOx conditions and tend to increase with temperature [13]. Beside volatile organic compounds (VOCs), in polluted environment ozone formation is promoted by photochemical oxidation of the unburned hydrocarbons in automobile exhaust gases, which requires the presence of nitric oxide and nitrogen dioxide as catalysts [25].

The tropospheric ozone is a determinative key element in the atmosphere oxidative environment and it is the main component of photochemical smog, which affects the air quality in urban and regional levels [26]. The elevated concentrations of ground-level ozone have harmful effects on human health and on agricultural and natural vegetation [27]. Air pollution is a serious health concern in many parts of the world, life expectancy is reduced even in moderately polluted areas, by fine particles and ozone (O_3), the two air pollutants of most concern for public health [28]. Fine particles stay suspended longer in the atmosphere, due to their size, shape, and density, and can be easily inhaled in the humans' respiratory tract [29]. The US EPA, based on its review of the air quality criteria for ozone (O_3) and related photochemical oxidants and national ambient air quality standards (NAAQS) for O_3, revised the primary and secondary NAAQS for O_3 to 0.070 parts per million (ppm), and retained their indicators (O_3), forms (annual fourth-highest daily maximum, averaged across three consecutive years) and averaging times (eight hours) [30]. The European Union, through Directive 2008/50/EC, sets the current target value for ozone concentration to 120 $\mu g/m^3$ [31]. This value should not be exceeded by the daily maximum of eight-hour running averages on more than 25 calendar days per year. As a long-term objective, Directive 2008/50/EC requires a strict compliance with the 120 $\mu g/m^3$ limit, but without setting a deadline for compliance. The United Nations Economic Commission for Europe (UNECE) suggested a new indicator for the calculation of the adverse effects on health due to ozone. The indicator AOT60 (Accumulated excess concentration over the guideline value of 60 ppb – around 120 $\mu g/m^3$) has been replaced by the SOMO35 indicator as an annual estimate of human exposure to ozone [26].

Numerical simulations of ozone show a dependence on the values for NOx concentrations [32], previous findings suggesting that NOx emissions are the primary explanatory variable in the observed decreasing trend in the climate penalty factor [15]. However, recent works assert that ozone concentrations are influenced by the absolute concentrations of NOx and VOCs, and the ratio of NOx and VOCs too [33]. When NOx emissions are much greater than VOC emissions, ozone concentration decreases with increasing temperature so the climate penalty factor may become strongly negative [13]. Reducing NOx emissions, primarily emitted as NO, in a NOx saturated environment can exacerbate ozone pollution by both decreasing O_3 loss by NO titration and increasing the ratio of VOCs to NOx, favoring HO_2 and RO_2 formation, both of which propagate a reaction mechanism that produces ozone in the troposphere [34]. While NOx emission controls may be effective at decreasing the climate penalty factor in NOx-limited environments [35], further decreases in VOC emissions may be beneficial to reducing ozone pollution and may additionally be effective at minimizing the climate penalty factor. The main factor driving future air quality projections is air pollutant emissions, rather than climate change or intercontinental transport of pollution [36]. So even if climate penalty is a reality for ozone pollution, its magnitude compared to recent trends and expected emission projections should not discourage from implementing ambitious mitigation measures [37]. Therefore, we have to analyze daily, monthly and yearly values of temperature, ozone and NOx concentrations in order to find correlations and to investigate the impact of temperature variations and NOx concentration on climate penalty factor.

Study area

The Ciuc Depression is an inter-montane basin situated in the Eastern Carpathians, at an altitude of 600-700 m (fig. 1), Miercurea-Ciuc being the most important city in the studied basin. The area is characterized by a mountain climate, summers are chilly, with abundant precipitations, and winters are cold, with snow for long periods [38].

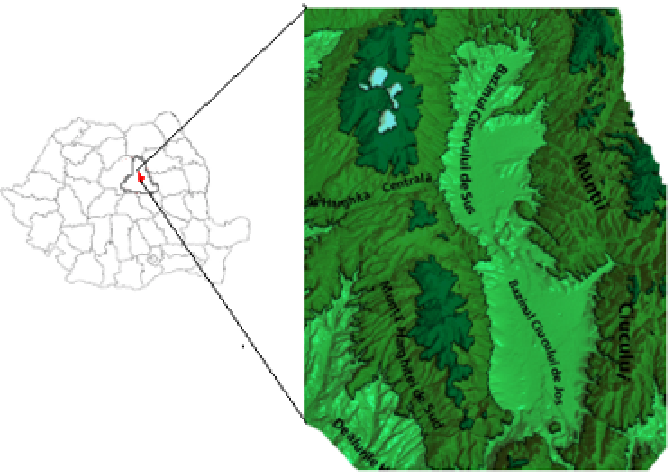

Fig. 1. Miercurea-Ciuc, Ciuc Depression, Eastern Carpathians

The main characteristics of the depression climate are low temperatures and high atmospheric stability [39], frequent and intense thermic inversions [40,41] which can fill the whole basin in the case of polar air invasion [39]. The local dominant wind direction is 180-270°, the characteristic wind speed being only 0 to 2 m/s [42]. In this area, one of the top priorities in the '70s and '80s consisted in drainage works, in order to obtain increasingly larger surfaces for extensive agriculture. These interventions caused significant changes of the climate of Ciuc Depression [43].The contribution of evapo-transpiration from local sources to the water cycle is vital. Its lowering due to groundwater drainage led to increasing static stability of the atmosphere, longer thermic inversion episodes and pollutant accumulation similar to those of urban agglomerations [44]. Groundwater drainage led to the degradation of peaty soils, changes in ecosystems and precipitation chemistry [26,43,45].

Experimental part

Materials and methods

Sampling

The National Meteorology Administration of Romania operates a network of ground-based automatic weather stations, one of them being situated at an altitude of 661 m, near the city of Miercurea-Ciuc, Ciuc Basin. The ground-based regional automatic background monitoring station HR-01, situated at an altitude of 710 m in Jigodin-Bai suburb of Miercurea-Ciuc, is operated by the National Environmental Protection Agency. The station started to operate in May 2007, thus we can analyze ozone concentration values for almost a decade. Both stations are sampling air temperature with an hourly time resolution, by similar -40^{0}C - +50^{0}C range TS Thermometer sensors installed at two meter above the ground. The NO, NO2 and NOx data were measured by a ME9841B Monitor Europe nitrogen dioxide analyzer using chemi-luminescence method, while O3 results were obtained with an ME9810B Monitor Europe ozone analyzer using UV absorption method. The equipment is installed two meter high from the ground. The data processing was realized with hourly values validated by the National Administration for Meteorology and by the Environmental Protection Agency of Harghita County.

Ozone concentration limits, SOMO35 and AOT40

The Romanian legislation is in accordance with the EU directive. The ozone concentration, expressed as a daily maximum value of eight-hour running averages, should not exceed the 120 μg/m^3 limit on more than 25 days (averaged across three consecutive years) [46]. It also provides that the minimum amount of data necessary for valid data, when three-year consecutive results are not available, is a valid one-year data set. A yearly data set is valid if there are 75% or more available daily maximum values of eight-hour running averages, both for April-September and for January-March and October-December periods respectively, for annual average, or if there are five valid months out of six in the April-September period for number of limit breeches and annual maximum value calculations. The limit for the vegetation is set to 18000 h*μg/m^3 (AOT40, May - July), the long-term target being 6000 h*μg/m^3 (AOT40, May - July) [46].

By definition, SOMO35 means the sum of means over 35 ppb (daily maximum 8 h) for ozone [47], and is calculated with the formula:

$$SOMO35 = \sum_i Ov_i \qquad (1)$$

where

$$Ov_i = M_i - 70 \; with \; M_i \geq 7 \qquad (2)$$

represents the excesses of ozone concentrations over 70μg/m^3 and M$_i$ is the daily maximum value of eight-hour running averages of ozone concentrations for day i [26].

AOT40 is defined as the accumulated excess of hourly ozone concentrations above 80μg/m^3 between 8:00 and 20:00 CET in the months of May, June and July [31]. According to the Romanian regulations, if not all of the hourly values were measured, AOT40 can be estimated with the formula:

$$AOT40_e = AOT40_m * \frac{possible\ nr.of\ values}{nr.of\ values\ measured} \qquad (3)$$

where AOT40$_e$ is the estimated accumulated excess, and AOT40$_m$ is the accumulated excess determined from existing hourly values [46].

Results and discussions

The evolution of the temperature during the 2007-2016 decade

All recent studies, concerning both global [2-4] and regional [6,7] evolutions, conclude that air temperature values are higher than the average for the 1961-1990 reference period. In the Ciuc Depression, the average temperature for the 1961-1990 reference period was 5.5°C [40], and even lower, 5.2°C for the 1983-1992 decade [48]. This value increased to 6.5°C for the 2006-2015 period [8]. If we analyze the data collected during 2007-2016, the average will be even higher, 6.62°C. Thus, the difference to the reference value is more than +1.1°C. Yearly average values present an ascending trend (fig. 2), all of them being well above the average of the reference period.

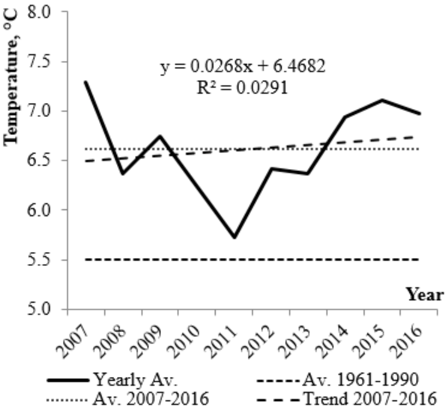

Fig. 2. Yearly average values for air temperature between 2007 and 2016 (°C)

There are important changes in the monthly averages of temperature (fig. 3), the differences between monthly averages for the 2007-2016 decade and the 1961-1990 reference period being significant.

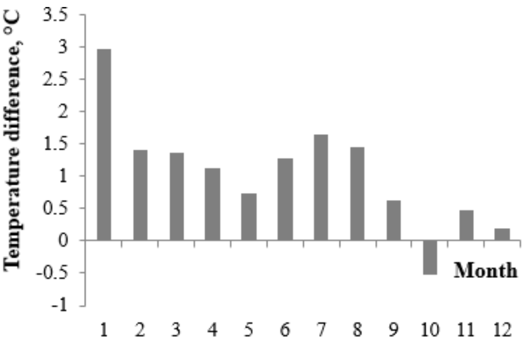

Fig. 3. Differences of monthly average air temperature values between 2007-2016 and 1961-1990 (°C)

Excepting January, the highest differences, of 1.3-1.6°C, were found for June, July and August, the warmest months of the year.

Temperature variations became more pronounced. *The annual average of monthly mean* amplitude increased from 24.5°C for the 1961-1990 reference period [39] with more than 20%. The alteration is so sharp that, in fact, the average of minimum monthly amplitudes for the 2007-2016 timeframe (24.3°C) is just 0.2°C *lower than the average of monthly mean* amplitude for the 1961-1990 reference period. These results emphasize that the basin's climate is seriously altered.

The most prominent changes in extreme temperature indices for the 2007-2016 period are the increases in the number of summer days (SU) and the number of hot days (Tx30GE, when temperature raises above 30°C).

In the studied period, the first appearance of summer days (when temperature raises above 25°C) within the year became possible in April, instead of May as in the reference period. The biggest part of the rise of the SU index from around 46.6 days [39] to 57.1 days is given by the warmer temperatures during the summer (fig. 4). October is the last month of the year with summer days recorded. The number of hot days (with temperatures above 30°C) increased even more during the 2007-2016 decade, from 3-4 days [39] in the 1961-1990 reference period to an average of 10.5 days. The occurence period during the year is June-September, annual variations in the 2007-2016 decade being very high, from 1 day in 2011 to 36 days in

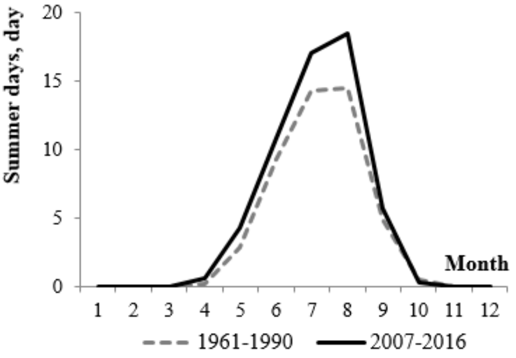

Fig. 4. Monthly average of the number of summer days (SU) for 1961-1990 and 2007-2016 periods

2012. July remains the warmest month of the year, but partly due to the lower intensity of night cooling processes, as warming-related extreme temperature indices for August are higher.

We can conclude that the average temperature of the Ciuc Depression is more than 1.1°C warmer than in the 1961-1990 reference period, and the four-season characteristic of the local climate is altered, shifting to a two-season type of climate.

Climate penalty factor

For the evaluation of the penalty factor we used the temperature interval 19-37°C, we selected 3°C interval length groups and we evaluated percentile values, which gives the proportion in that interval. The scaling goes from the lowest value (α= 0) up to the highest value (α = 1), α = 25% meaning the quartile and μ = 50% the median value. The average of the slopes (5, 25, 50, 75, 95%) yields the climate penalty factor [10,49].

The average slope for the 2008-2010 years is 1.967μg/m^3/°C, slightly lower than the value reported for 2012-2013, 2.05μg/m^3/°C [10]. For the year 2015 (fig. 5), the average slope was 2.014 μg/m^3/°C. For the year 2016 (fig. 6), the average slope was 1.517 μg/m^3/°C. All values are similar to the values which one finds in literature [15, 49]. The mean value for the entire 2007-2016 period will be around 1.9 μg/m^3/°C.

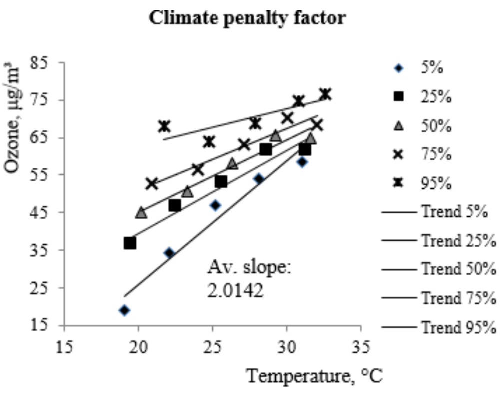

Fig. 5. The climate penalty factor for HR-01 regional station for 2015

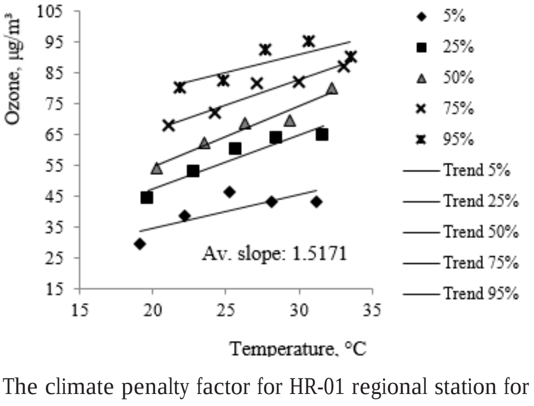

Fig.6. The climate penalty factor for HR-01 regional station for 2016

One can see that the slopes for the 95 percentile values are lower than those for smaller percentiles, and, more important, that above 30°C, the increase of the ozone concentration with the temperature is less steep. The results for the climate penalty factor indicates that a 1°C increase in temperature can lead to an increase of around 1.9 μg/m^3 of the ozone concentration. Therefore, at relatively high ozone concentrations in the Ciuc Depression, the increasing temperature can cause further concentration increments, accumulations with harmful effects on human and vegetation health.

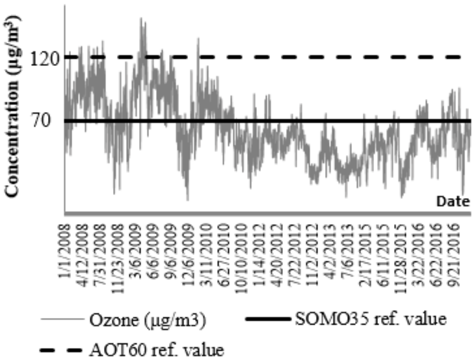

Fig.7. Daily maximum values of eight-hour running averages of O_3 for 2007-2016 at HR-01 regional station

Tropospheric ozone concentrations in Ciuc Depression for the 2007-2016 period

Using the hourly data for ozone concentration, we analyzed the evolution of daily maximum value of eight-hour running averages (fig. 7).

Regarding the 120 μg/m³ limit, there were 9 breeches in 2008, equally spread in the February-August period. 2009 was a special year, with 26 daily maximum values over the limit, 19 of them being recorded in April. The month of April 2009 was one with average April temperatures, but the driest in the 2007-2016 period. The total rainfall in April 2009 was 23.3 mm, less than half of the average rainfall in April (46.8 mm). The monthly average of NOx concentration in April 2009 was also the highest for a month of April in that decade, almost 50% higher than April averages. For the rest of the year, 7 exceedances were noted, from March to September. Year 2010 (3 breeches in January) was the last year with recorded daily maximum values of eight-hour running averages over 120 μg/m³. We can conclude that ozone concentration in the Ciuc Depression is within the acceptable limits as far as EU and national regulations are concerned.

The results are different when we compare the ozone concentration values with the 70 μg/m³ SOMO35 reference value. More than 71% of the daily maximum values of eight-hour running averages for 2008 and 2009 are above the 70 μg/m³ mark, virtually all the March-September (2008) and March-October (2009) figures exceeding it. For 2010, the rate of breeches decreased till 45%, and the period of the year with all values beyond the reference value diminished to March-April. 2012, 2013 and 2015 presented much lower ozone concentrations, just 1-5% of the daily maximum values of eight-hour running averages were above 70 μg/m³, the months with breeches being February-April and July-September. 2016 had the ratio increasing to 22.5%, with exceedances in every month excepting January and February. April-May and August-September were by far the periods with most breeches.

The estimated AOT40 values for 2008 and 2009 were above the 18000 h*μg/m³ mark, and below the long-term 6000 h*μg/m³ limit for the rest of the period (table 1).

Table 1
ESTIMATED VALUES OF SOMO35 AND AOT40 FOR VALID YEARS IN THE 2007-2016 PERIOD IN CIUC DEPRESSION

Year	SOMO35 (h*µg/m³)	$AOT40_e$ (h*µg/m³)
2008	5223.5	23985
2009	7260.5	24528
2010	2118.4	2997
2012	139.6	0
2013	6.8	0
2015	29.3	0
2016	645.8	418

We can conclude that the decreasing trend of ozone concentration values in Ciuc Depression led to conformation with actual European and Romanian requirements regarding human and vegetation health, but ozone concentration can easily increase above stricter SOMO35 limits.

Ozone concentrations, temperature and NOx concentrations in the 2007-2016 period

Ozone is produced by the photolysis of NO_2 (R1), where the resulting atomic oxygen recombines rapidly with molecular oxygen to produce ozone (R2). Normally, this reaction is counterbalanced by the reaction of NO with ozone, ending in NO_2 (R3) [50]:

$$NO_2 + h\vartheta \rightarrow NO + O \quad \text{(R1)}$$

$$O + O_2 \rightarrow O_3 \quad \text{(R2)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R3)}$$

Taken together, reactions (R1) and (R3) produce no net change in ozone. Each of these reactions occurs rapidly, in 200 s or less. Usually, the two major components of NOx adjust to establish a balance between reactions (R1) and (R3), except at nighttime, when there is always a net loss of ozone since photolysis rates are zero, reaction (R3) dominates over reaction (R1) [51].

The other situation in which these reactions become unbalanced is ozone production associated with daytime chemical processes involving NOx, VOC and CO. The ozone formation occurs through series of reactions involving VOC, CO and NOx, which result in the conversion of NO to NO_2 through processes other than reaction (R3). The conversion is followed by reaction (R1) and results in additional O_3. A typical sequence of reactions would be:

$$RH + OH \xrightarrow{[O_2]} RO_2 + H_2O \quad \text{(R4)}$$

$$CO + OH \xrightarrow{[O_2]} CO_2 + HO_2 \quad \text{(R5)}$$

followed by reactions of RO_2 and HO_2 radicals with NO:

$$RO_2 + NO \xrightarrow{[O_2]} R'CHO + HO_2 + NO_2 \quad \text{(R6)}$$

$$H_2O + NO \xrightarrow{[O_2]} NO_2 + OH \quad \text{(R7)}$$

Reactions (R6) and (R7) convert NO to NO_2, and their result is the formation of ozone when followed by reaction (R3). The directly emitted hydrocarbons and intermediate organics are collectively referred to as volatile organic compounds or VOC [51].

Previous studies show that in the Ciuc Depression, hourly and daily variations of ozone are strongly influenced by meteorological conditions (temperature, solar radiation) and NOx levels [26,42]. VOCs can occur naturally due to emissions from trees and plants. Anthropogenic sources of VOCs in Ciuc Depression include emissions from traffic and from organic solvents in small stationary sources. The main natural sources to atmospheric NOx are anaerobic biological processes and lightning. The main anthropogenic amounts of NOx originate from traffic and the combustion of fossil fuels in power plants and home heaters [43].

Daily profile

Ozone concentration (fig. 8) slowly decreases during the night, with a minimum value (28.34 µg/m³, 8 o'clock) in the early morning due to titration with NO, abruptly increases due to the usually growing solar radiation and temperature values, peaks in the middle of the afternoon (67.25 µg/m³, 4 o'clock), then starts to drop in the evening till a value close to the daily average (47.69 µg/m³, around 11 o'clock in the evening) because of increased vertical mixing, horizontal advection and titration by fresh NO_2 emissions [10].

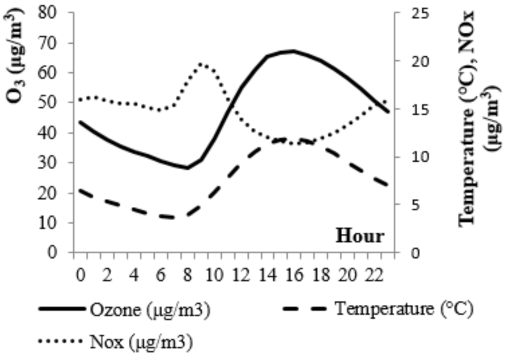

Fig.8. Daily temperature, O_3 and NOx concentration profiles at HR-01 regional station

Temperature variation presents the same pattern, with a minimum value just before sunrise (3.68°C, 7 o'clock), and a maximum between 3 and 4 o'clock in the afternoon (11.9°C). However, NOx concentration shows a completely different course. An intermediate maximum (16.25 µg/m³) occurs around midnight and a narrowly lower intermediate minimum (14.84 µg/m³), almost equal to the daily average value of 14.71 µg/m³, at 6 o'clock in the morning. Afterwards, home and industrial heating processes, as well as heavy traffic are leading to a sharp increase, with a maximum (19.73 µg/m³) at 9 o'clock in the morning, followed by a decrease that leads to a pronounced minimum value (11.35 µg/m³) at 4 o'clock in the afternoon. The late afternoon and the evening lead the curve back till midnight.

The diagram suggests a positive correlation between temperature and ozone concentration values, and a negative correlation between ozone and NOx concentration values, a presumption we verified through running a Spearman rank correlation test. According to the results (table 2), there is a very strong positive correlation (+0.988) between temperature and ozone concentration values, and a strong negative correlation (-0.777) between ozone and NOx concentration values.

Table 2
SPEARMAN CORRELATION BETWEEN TEMPERATURE, O_3 AND NO_X VALUES OF THE DAILY PROFILE

	Temp	O_3	NOx
Temp	1	0.988	-0.725
O_3	0.988	1	-0.777
NOx	-0.725	-0.777	1

Monthly average values

Autumn is the season with minimum ozone concentration values. With warmer September temperatures in the last decade, ozone concentration in September (47.1 µg/m³) is around the yearly average (46.95 µg/m³), but decreases due to the frequent autumnal instability periods [26], and reaches the minimum value (32.55 µg/m³) in November (fig. 9).

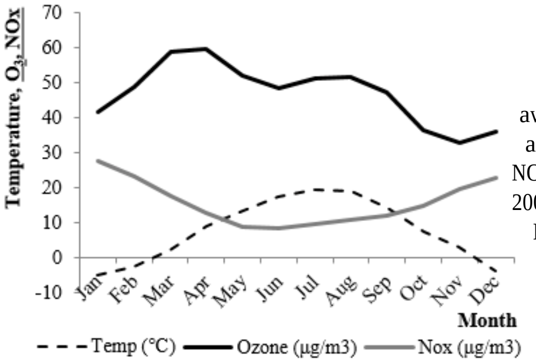

Fig.9. Monthly average values of air temperature, NOx and O_3 for the 2007-2016 period at HR-01 regional station

Frequent and very intense thermic inversion periods during the winter [41] and increased emissions of NOx by heating trigger raising ozone concentration in wintertime, February average values (48.85µg/m³) already exceeding the yearly average. High static stability [40], increasing solar radiation [39] and temperature values [8], together with still above or around average NOx values, are characteristic for the spring. Photochemical production resulting from increased solar radiation acting upon NOx and hydrocarbons accumulated during the winter period is the major cause of the growing concentrations of ozone [52]. March (58.73 µg/m³) and April (59.40 µg/m³) are the months presenting the maximum ozone concentration averages. At summer, when the intense solar radiation and longer day lengths stimulate the photochemistry [11], ozone concentration is still high (48.41-51.37 µg/m³).

NOx concentration has its maximum average value in January, the coldest month, but all winter values are below 20 µg/m³. March presents an average well above the yearly average value, then the concentration will drop till the minimum monthly average (8.52 µg/m³ in June). Later on, concentration starts to raise, passing the yearly average value in the autumn, in October or November.

The results for the Spearman rank correlation test for the monthly averages of temperature, ozone and NOx concentrations show that there is a positive correlation between temperature and ozone concentration, and a negative correlation between ozone and NOx concentrations (table 3).

Table 3

SPEARMAN CORRELATION BETWEEN TEMPERATURE, O_3 AND NOx MONTHLY AVERAGE VALUES

	Temp	O3	NOx
Temp	1	0.371	-0.909
O3	0.371	1	-0.427
NOx	-0.909	-0.427	1

We can conclude that there is an obvious influence of higher air temperatures on the measured ozone levels, and the limiting/facilitating effect of NOx values can also be clearly observed.

Yearly average values

The analysis of the values and trends for valid yearly averages of ozone and NOx concentrations during the 2007-2016 timeframe show that in the Ciuc Depression there is a decreasing trend of ozone concentrations (fig. 10), which can be explained by the decrease of the industrial activity [40] and changes in the heating system, thus NOx emission is also lower. In the same time emission due to the motor cars and the burn of biomass can contribute to a partial rise of NOx concentration [10].

The global climate change expectedly leads to the rise of the over ground temperature and aggravate the air pollution [11]. The results for the climate penalty factor led us to the conclusion that a 1°C increase in temperature can lead to an increase of around 1.9 µg/m³ of the ozone concentration. However, decreasing NOx concentrations caused decreased ozone levels, emphasizing the importance of controlling the NOx emission, which may lead to the decrease of photochemical smog and limit the effects of climate change. Our findings show that the impact of recorded and projected climate changes is of smaller magnitude than the changes determined by anthropogenic emission.

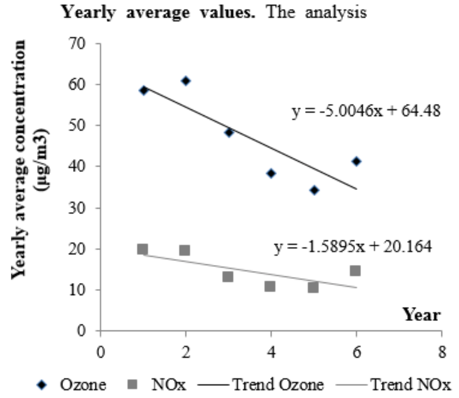

Fig.10.Yearly averages and trend for NOx and O_3 values at HR-01 regional station

Conclusions

The annual average values of temperature at Miercurea-Ciuc are on a growing trend, the difference between the average of the 2007-2016 decade and the mean value for the 1961-1990 reference period is 1.12°C. The differences for the average monthly temperatures of Summer months are above 1.3°C. As for the extreme temperature indices, the occurrence frequency of summer days has risen with 22.5%, and the number of tropical days from 3-4 to 10.5.

The calculation of the climate penalty factor showed that a 1°C growth in temperature can lead to a 1.9 µg/m³ increase of the concentration of tropospheric ozone in the atmosphere of Miercurea-Ciuc.

Regarding the limits for human and vegetation health protection, there were few exceedances of the 120 µg/m³ mark, and none after 2010, ozone concentration in the Ciuc Depression is within the acceptable limits as far as EU and national regulations are concerned. The results are the same for the AOT40 indicator. Things are different when we refer to the stricter SOMO35 indicator, where the best three years regarding ozone concentration exceedances, still present 1-5% breeches of the 70 µg/m³ mark, the last recorded year (2016) being just below the average of the decade with 22.5% of daily values above limit.

The decreasing trend of NOx concentration implied a decrease of ozone concentration, showing that the impact of anthropogenic factors is larger than the one due to temperature raises. Thus, we realize the necessity of the control of NOx emission, in order to mitigate climate change effects.

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References

1. HELLER, A., The weather (Az idojaras), Termeszettudomanyi Konyvkiado-Vallalat & Magyar Tudomanyos Akademia, Hungary, 1888, pp 1-408.

2. STOCKER, T. F., QIN, D., PLATTNER, G., TIGNER, M., ALLEN, S., BOSHUNG, J., NAUELS, A., XIA, J., BEX, V., MIDGLEY, P., Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, 2013.

3. *** WMO (2016) Provisional WMO Statement on the Status of the Global Climate, https://public.wmo.int/en/media/press-release/provisional-wmo-statement-status-of-global-climate-2016, 14.11.2016.

4. *** WMO (2017) WMO Statement on the State of the Global Climate in 2016, https://library.wmo.int/opac/doc_num.php?explnum_id=3414, 2017.

5. *** NAM 2008 Climate of Romania, Editura Academiei Romane, ISBN 978-973-27-1674-8, National Meteorology Administration of Romania.

6.PONGRACZ, R., BARTHOLY, J., SZABO, P., GELYBO, GY., Int. J Global Warm., 1, 2009, pp 238-252.

7.MACHIDON, O., APOSTOL, L., MACHIDON, D., BURUIANA, D., Annuals of DAAAM for 2012 & Proceedings of the 23rd International DAAAM Symposium, DAAAM International, vol. 23, No. 1, 2012, pp 0689-0692.

8.PETRES, S., KORODI, A., KERESZTES, R., SZEP, R., Applied and Environmental Geophysics, SGEM 2017 Conference Proceedings, 17(14), 2017a, pp 445-452.

9. SZEP, R., KERESZTES, R., KORODI, A., TONK, SZ., NICULAE, A.G., BIRLOIU, A.M., Rev. Chim. (Bucharest), **67**, no. 10, 2016, p. 1914

10. SZEP, R., KERESZTES, R., CONSTANTIN, L., Rev. Chim. (Bucharest), **67**, no. 3, 2016, p. 408

11.JACOB, D.J., DARREL, A.W., Atmos. Environ., 43, 2009, pp 51-63.

12.WU, S., MICKLEY, L. J., LEIBENSPERGER, E., JACOB, D., RIND, D., AND STREETS, D., J Geophys. Res., 113, 2008, pp 1-12.

13. RASMUSSEN, D.J., HU, J., MAHMUD, A., KLEEMAN, M.J., Environ. Sci. Technol., vol. 47 (24), 2013, pp 14258–14266.

14. SILLMAN, S., SAMSON, F.J., J. Geophys. Res.-Atmos., vol. 100, 1995, pp 11497-11508.

15. BLOOMER, B.J., STEHR, J.W., PIETY, C.A., SALAWITCH, R.J., DICKERSON, R.R., Geophys. Res. Lett., 36, L09803, 2009.

16. BARTHOLY, J., PONGRACZ, R., Glob. Planet. Change, vol. 57, (2007), pp 83–95.

17. KLEIN TANK, A.M.G., KONNEN, G.P., J. Climate, vol. 16, 2003, pp 3665–3680.

18. SHEPHERD, T.G., Nature, vol. 522 (7557), 2015, pp 425-427.

19. MORABITO, M., CRISCI, A., MESSERI, A., MESSERI, G., BETTI, G., ORLANDINI, S., RASCHI, A., MARACCHI, G., Atmosphere (Basel), vol. 8(7), 115, 2017, pp 1-20.

20.PUSEDE, S. E., STEINER, A. L., RONALD, C., Chem. Rev., vol. 115 (10), 2015, pp 3898-3918.

21. MAHMUD, A., TYREE, M., CAYAN, D., MOTALLEBI, N., KLEEMAN, M.J., J. Geophys. Res., 113, D21103, 2008.

22.ABEL, D., HOLLOWAY, T., KLADAR, R.M., MEIER, P., AHL, D., HARKEY, M., PATZ, J., Environ. Sci. Technol., vol. 51 (10), 2017, pp 5838–5846.

23. HE, H., HEMBECK, L., HOSLEY, K.M., CANTY, T.P., SALAWITCH, R.J., DICKERSON, R.R., Geophys. Res. Lett., vol. 40, 2013, pp 1-4.

24. FUJITA, E. M., CAMPBELL, D. E., STOCKWELL, W. R., LAWSON, D. R., J. Air Waste Manage. Assoc., vol. 63, 2013, pp 54-69.

25. SZEP, R., MATEESCU, E., NECHIFOR, C., KERESZTESI, A., Environ Sci Pollut Res 1-18. doi: 10.1007/s11356-017-0318-2, 2017

26. SZEP, R., MATYAS, L., KERESZTES, R., GHIMPUSAN, M., Rev. Chim. (Bucharest), **67**, no. 2, 2016, p. 205

27. LAGZI, I., MESZAROS, R., HORVATH, L., TOMLIN, A., WEIDINGER, T., TURÁNYI, T., ACS, F., HASZPRA, L., Atmos. Environ., 38, 2004, pp 6211-6222.

28. LACRESSONNIERE, G., FORET, G., BEEKMANN, M., SIOUR, G., ENGARDT, M., GAUSS, M., WATSON, L., ANDERSSON, C., COLETTE, A., JOSSE, B., MARECAL, V., NYIRI, Á., VAUTARD, R., Clim. Change, vol. 136, 2016, pp 309–324.

29.RAISCHI, AN., SZEP, R., BALACEANU, CM., RAISCHI, M., DUMITRU, D., MONCEA, A., LASLO, L., DEAK, Gy., KERESZTESI, A, Ecoterra, 14(2), 2017, pp 70-77.

30.*** US EPA (2015) 2015 National Ambient Air Quality Standards (NAAQS) for Ozone, Ozone Standards Regulatory Actions, https://www.epa.gov/ozone-pollution/2015-national-ambient-air-quality-standards-naaqs-ozone.

31. *** EUR-Lex (2008) Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, EUR-Lex Access to European law, http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32008L0050.

32.CANTY, T.P., HEMBECK, L., VINCIGUERRA, T.P., ANDERSON, D.C., GOLDBERG, D.L., CARPENTER, S.F., ALLEN, D.J., LOUGHNER, C.P., SALAWITCH, R.J., AND DICKERSON, R.R., Atmos. Chem. Phys. Discuss., vol. 15, 2015, pp 4427–4461.

33.DERWENT, R., BEEVERS, S., CHEMEL, C., COOKE, S., FRANCIS, X., FRASER, A., HEAL, M.R., KITWIROON, N., LINGARD, J., REDINGTON, A., SOKHI, R., VIENO, M., Atmos. Environ., vol. 94, 2014, pp 249-257.

34. SEINFELD, J.H.; PANDIS, S.N., 2nd ed.; J. Wiley: Hoboken, N.J., 2006, p xxviii.

35. DUNCAN, B. N., YOSHIDA, Y., OLSON, J. R.;, SILLMAN, S., MARTIN, R.V., LAMSAL, L., HU, Y., PICKERING, K.E., RETSCHER, C., ALLEN, D.J., CRAWFORD, J.H., Atmos. Environ., vol. 44, 2010, pp 2213-2223.

36.COLETTE, A. , BESSAGNET, B., VAUTARD, R., SZOPA, S., RAO, S., SCHUCHT, S., KLIMONT, Z., MENUT, L., CLAIN, G., MELEUX, F., CURCI, G., AND ROUIL, L., Atmos. Chem. Phys., vol. 13, 2013, pp 7451–7471.

37.COLETTE, A., ANDERSSON, C., BAKLANOV, A., BESSAGNET, B., BRANDT, J., CHRISTENSEN, J.H., DOHERTY, R., ENGARDT, M., GEELS, C., GIANNAKOPOULOS, C., HEDEGAARD, G.B., KATRAGKOU, E., LANGNER, J., LEI, H., MANDERS, A., MELAS, D., MELEUX, F., ROUIL, L., SOFIEV, M., SOARES, J., STEVENSON, D.S., TOMBROU-TZELLA, M., VAROTSOS, K.V., YOUNG, P., Environ. Res. Lett., vol. 10, 084015, 2015

38. KERESZTESI, A., PETRES, S., GHITA, G., DUMITRU, FD., MONCEA, MA., OZUNU, A., SZEP, R., Rev. Chim. (Bucharest), **69**, no.1, 2018,p. 57

39.BOGDAN, O., NICULESCU, E., Specific climatic aspects of Giurgeu, Ciuc and Braºov depressions, Pedogenetic factors and processes in the temperate climatic zone, New series, Romania, vol. 2, 2004, pp 3-115.

40. SZEP, R., MATYAS, L., Carpath. J Earth Env., vol. 9., 2014, pp 241-250.

41. PETRES, S., BOGA, R., KERESZTESI, A., GHITA, G., ILIE, M., DEAK, G., Ecoterra, 14(2), 2017b, pp 60-69.

42. BOGA, R., KORODI, A., KERESZTESI, A., GHITA, G., ILIE, M., DEAK, G., Ecoterra, vol. 14(2), 2017, pp 44-51.

43. KORODI, A., PETRES, S., KERESZTESI, A., SZEP, R., Environmental Legislation, Multilateral Relations and Funding Opportunities, Vol. 17 (54), 2017, pp 387-393.

44.SZEP, R., KERESZTES, R., DEAK, G., TOBA, F., GHIMPUSAN, M., CRACIUN, E.M., Rev. Chim. (Bucharest), **67**, 2016, p. 408

45. KERESZTESI, A., KORODI, A., BOGA, R., PETRES, S., GHITA, G., ILIE, M., Ecoterra, 14(2), 2017, pp 52-59.

46. *** L.104/2011 (2011) Law no. 104/2011 on ambient air quality (Legea nr. 104/2011 privind calitatea aerului înconjurãtor), L.104/2011 – 09/11/2016 offered by LEX EXPERT software.

47. *** European Environment Agency, eea.europa.eu/help/glossary/eea-glossary/somo35

48.TAMAS, L., Miercurea-Ciuc - Geography of population and settlements (Csíkszereda nepesseg- es telepulesfoldrajza), M. Sc. Thesis, Janus Pannonius University Pecs, Hungary, 1997, pp 2-9.

49. BLOOMER, J. B., Air pollution response to changing weather and power plant emissions in the eastern United States, Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 2008.

50. SKALSKA, K., MILLER, J., LEDAKOWICZ, S., Sci. Total Environ., vol. 408 (19), 2010, pp 3976-3989

51. SILLMAN S., Atmos. Environ., vol. 33, 1999, pp 1821-1845.

52. VINGARZAN, R., Atmos. Environ., vol. 38, 2004, pp 3431-344

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