Tropospheric Ozone Concentrations - Seasonal and Daily Analysis and its Association with NO and NO_2 as a Function of NO_x in Ciuc Depression – Romania

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This paper summarizes the results of a yearlong continuous measurements of gaseous pollutants, NO, NO_2, NO_x and O_3 in the ambient air of Ciuc Depression. Measured concentration of the pollutants in study area is a function of time. NO, NO_2 and O_3 peak occurred in succession in presence of sunlight. At the time of maximum O_3 concentration most of the NO_x are utilized. The diurnal cycle of ground level ozone concentrations, revealed mid-day peak with lower nocturnal concentrations and inverse relationship exists between O_3 and NO_x, which are evidences of photochemical O_3 formation. Particular emphasis is placed on establishing how the level of "oxidant", OX (taken to be the sum of O_3 and NO_2) varies with the level of NO_x, and therefore to gain some insight into the atmospheric sources of OX. The analyses indicate that the level of OX at a given location is made up of NO_x – independent and NO_x – dependent contributions. The former is effectively a regional contribution which equates to the regional background O_3 level, whereas the latter is effectively a local contribution which correlates with the level of primary pollution. Increased values can be also observed for more periods of the year; this fact for the depressional case of Ciuc are due to the particular case represent by stable boundary layer conditions (high static stability conditions in term of Brunt - Vaisala frequency) which are long known for causing increasing concentration of pollutant concentrations.

Keywords: tropospheric ozone, static stability, weekend effect, seasonal variation, mixing ratio

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 [1,2]. The elevated concentrations of ground-level ozone have harmful effects on human health and on organisms and different materials as well [3] (Monteiro et al., 2012). According with the US EPA, susceptible people can be adversely affected by ozone levels as low as 40nmol/mol [4-6]. In the EU, the current target value for ozone concentrations is 120μg/m³ which is about 60nmol/mol. This target applies to all member states in accordance with Directive 2008/50/EC [7]. Ozone concentration is measured as a maximum daily mean of 8 h averages and the target should not be exceeded on more than 25 calendar days per year, starting from January 2010. Whilst the directive requires in the future a strict compliance with 120μg/m³ limit, there is no date set for this requirement and this is treated as a long-term objective (Directive 2008/50/EC).The Agency's scientists and advisory board had recommended lowering the standard to 60nmol/mol–120μg/m³ (for no more than 8 h) [5]. Many public health and environmental groups also supported the 60nmol/mol standard [8] and the World Health Organization recommends 51nmol/mol. This value 120μg/m³ is based on studies carried out on restricted groups of exposed populations for effects other than cancer or odor/annoyance. The same limit has been adopted by current European legislation on ozone, in Directive 2002/3/EC, as a reference value for the protection of human health. The United Nations Economic Commission for Europe (UNECE, 2004) and Task Force on Health have recently suggested a new indicator for the calculation of the adverse effects on health due to ozone. The indicator "accumulated excess concentration over the guideline value of 60ppb [120μg/m³]" (AOT_{60}) has been replaced by the $SOMO_{35}$ indicator as an annual estimate of human exposure to ozone (UNECE, 2004).

In 2009, Bloomer was able to quantify the relationship between ozone and temperature using a measure that he calls the "climate penalty factor (CPF)." This factor (CFP) is the slope of the DM8H O_3 and DMT relationships [9]. It was found that the decrease in NOx emissions also led to a decrease in the climate penalty factor.

The mentioned ground-level ozone transformation is a series of complex photochemical reactions, NO_x and volatile organic compounds (VOC) are formed in presence of heat and sunlight. This transformation depends on the intensity of solar radiation, on NO_x and VOCs absolute concentration and on NO_x and VOCs rate [10, 11]. The relatively high values observed indicate that the ozone concentration increases as the effect of solar radiation intensity and temperature [11-13].

The recent studies suggest that the stratospheric ozone is increasingly transported into the troposphere ozone layer, which results an increased circulation between the troposphere and stratosphere ozone particularly during spring months [13, 14]. The photochemical life time of O_3 in the winter in the mid-latitude is approximately 200 days. This long lifetime allows anthropogenically produced O_3 to accumulate and contribute substantially to the

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observed spring maximum that is usually attributed to stratospheric intrusion [15]. By emanation of toxic gases (NO, NO_2, NO_x, CO) the penetration of stratospheric ozone in troposphere increases, as a core sequence certain meteorological changes are possible. This fact may bring changes to certain parameters as are the humidity, temperature, cloud formation or the dynamics of atmosphere [16-18]. These manifestations may be more enhanced in depressions where the static stability and/or the presence of anticylons also have a role, even if there is no increase of originating gases. The most important day to day variations can be observed in late winter and early spring, beyond summer periods [13]. In this case the ozone concentration will be higher in troposphere relative to the rest of the year. In late winter, or early spring the cold whether may influence the presence of ozone precursors and it is also related to biomass burning [19]. In the rest of the year especially in autumn and winter one may also find the enhancement mainly due to boundary layer conditions where are long known for causing increasing concentration of pollutant [20].

If one compares the values of concentration on the days of the week, a kind of weekend effect of ozone one may also find. The phenomena occurs when concentration of the ozone precursors (NO_x and VOC) are relatively low [13, 21, 22]. Such reports has been realized in certain parts of America [13, 23-25], 2006), in Japan [13, 26] [13], in Nepal [13] and in China [27].

Experimental part

Materials and methods

Study area

The thermal profile (sampling site) is situated in Jigodin suburban area of the Miercurea Ciuc town (latitude 46°21'0''N, longitude 25°48'0''E).

The geographical position of the Ciuc depression - situated mostly in the shelter of the orographic dam determined by the limitrophic mountain frame of the Eastern Carpathians - is similar to a (depressional) groove in which thermal inversions are remarkable [28]. Formation of fog and thermal inversion is characteristic especially during winter [29].

In the Ciuc Depression, the average temperature is just with 0.2 grades smaller than on the Limitrophic Mountains with the height of 1800 m latitude, but with 1-2 grades smaller than on the slopes with 1200-1400 m, which stays warmer [28].

Because of this fact the inversion can be very intense, and it may occupy the whole topoclimatic space, having a width of 500-600 m. On the other hand in case of polar air invasion determined by Eastern European anticyclone this may expand up to 1200 m [28.The main wind direction is westerly and north-westerly [29].

Sampling

The data of NO, NO_2, NO_x and O_3 are under observation in the period March the 21st 2012 and March the 20th 2013, at the Jigodin HR01 background measurement station and at APM measuring station of the Environmental Agency at Miercurea Ciuc. The measuring instruments have been the nitrogen oxide analyzer (ME9841B monitor Europe, US EPA, nr. RFNA-1292-090) and the ozone analyzer (ME9810B Monitor Europe, Photometric UV, US EPA, reference no. EQOA-0193-091). The nitrogen analyzer continuously measured NO, NO_2 and NO_x values, using chemical luminescent method (in case of the Miercurea Ciuc station in the examined period only the NO_2 values have been disponible), while the ozone analyzer measured the O_3 values in the air by the UV absorption techniques. The air temperature values have been sampled by a TS Thermometer sensor with measuring range between -30^0C and $+50^0$C installed at standard 2 meter above the ground, and the solar radiation with ORION – Mod SR-S sensor.

Regarding data processing we have used values validated by the Environmental Agency, the eventual wrong data have been filtered. The evaluations are based on hourly measured values of NO, NO_2, NO_x, and O_3.

Results and discussions

Hourly, diurnal and seasonal changes

In the study area, hourly and day-to-day variations of Ozone are strongly influenced by meteorological conditions (temperature, solar radiation) and prevailing levels of NO_x. Solar radiation, ambient temperature, and NO_x together can explain the variation in measured ground level ozone concentration. From the table of annual daily correlation one can see a kind of inverse proportionality relation between ozone formation and measured precursor gases (table 1).The formation of ozone is more accentuated during the winter and spring at high static stability; and summer, when the intense solar radiation and longer day lengths, stimulate the photochemistry, resulting high concentration of ozone.

	Annual mean daytime correlation for Jigodin Ciuc Station						Annual mean daytime correlation for Miercurea Ciuc Station			
	Temp.	NO	NO_x	NO_2	Solar rad.	Ozone	Temp.	NO_2	Solar rad.	Ozone
Temp.	1	***-0.33***	***-0.67***	***-0.68***	***0.50***	***0.39***	1	***-0.62***	0.19	***0.66***
NO	*-0.33*	1	**0.67**	***0.46***	-0.03	***-0.36***	---	---	---	---
NO_x	*-0.67*	*0.67*	1	***0.95***	-0.27	***-0.57***	---	---	---	---
NO_2	***-0.68***	***0.46***	***0.95***	1	-0.30	***-0.48***	***-0.62***	1	***-0.39***	***-0.46***
Solar rad.	***0.50***	-0.03	-0.27	-0.30	1	***0.47***	0.193	***-0.39***	1	-0.11
Ozone	***0.39***	**-0.36**	**-0.57**	**-0.48**	***0.47***	1	***0.66***	***-0.46***	-0.11	1

Table 1
THE VALUE OF SPEARMAN CORRELATION BETWEEN O_3, NO, NO_2, NO_X, THE SOLAR RADIATION, AND TEMPERATURE

If we study the hourly values during a year determined by the monitoring station of air quality we can see that values of O_3 over the annual average may occur in all seasons except the autumn. The values of NO, NO_2 and NO_x during the spring usually are lower NO -29.88%, NO_2 - 48.03% respective NO_x - 42.42%.

During the summer the average values of the precursor gases decreases in comparison with the annual average value -1.97%, NO, -60.37% NO_2, -42.37% NO_x. Beginning with autumn these values increases, exceeding quite often the average annual values by 17.51% NO, 2.25% NO_2 and 6.96% NO_x. During the winter, this increasing tendency is maintained at 15.10% for NO_2 108.31% forNO_x 78.96% above the average annual value. The behavior of ozone is somehow contrary to the precursor gases. The increase relative to the annual hourly average is 2.89% in spring, 10.25% in summer and 15.27% in winter. During autumn a decrease by 28.66% occurs relative to the average.

The increase of precursor gases during the autumn and winter is due to the decrease of intensity of solar radiation and of temperature. The increased concentrations of ozone during winter are rather caused by the static stability of air mass from the neighborhood of soil.

Analyzing the hourly variation of ozone concentration, the hourly concentrations exceeds the allowed values in spring period is partly caused to the movement of stratospheric ozone to lower levels producing a kind of mixture of tropospheric ozone [14, 15, 30]. Increased values one may also observe in more periods of the year; this fact for the depressionar zone of Ciuc is due to a particular case represented by stable boundary layer conditions (high static stability conditions in term of Brunt -Vaisala frequency) (table 2) which are long known for causing increasing concentration of pollutant concentrations [20].In our situation, in case of a stable stratification the flow of background layer cannot be determined owing to the fact that the consolidated uniformly stratified free flow waves extend to the convection field of the whole basin. Since the extension of the stable stratified flows is limited with a *z* upper limit which is the height of the ascending inversion, the stability of the flow can be described making use of frequency Brunt-Vaisala N^2, which presents at zero the most instable stratification [31].

The density of moist air [32] has been determinate from measurements of air pressure, temperature, humidity and (and in our case because is required a high accuracy) carbon dioxide concentration using an equation [33, 34] Davis, 1992) recommended by the „Comité International des Poids et Mesures"(CIPM) derived by Giacomo and modified by Davis.

The average Brunt–Vaisala frequency can be well estimated in a medium with a depth of *z*, between the top and bottom of which $\Delta\rho$ is the minor difference in density. Since the average density gradient here is $\Delta\rho/z$, with regard to the Brunt–Vaisala frequency one can state with a good approximation that [35].

$$N^2 = -\frac{g}{\rho_0}\frac{d\rho}{dz} \qquad (1)$$

N– Brunt–Vaisala frequency (Hz)

$\Delta\rho$- difference in density measured at two measuring stations (kg/m^3)

Δz- elevation difference between the two measuring stations (m)

g- gravitational acceleration (m/s^2)

$\rho_0 \equiv \rho(z_0)$ density measured at the $z_0$level.

Table 2

SPEARMAN CORRELATION BETWEEN THE STATIC STABILITY IN TERMS OF BRUNT - VAISALA FREQUENCY AND THE HOURLY DAYTIME CONCENTRATION OF O_3

N^2\Ozone	Spearman correlation for daytime hours
Annual data	0.468
Spring	0.492
Summer	0.476
Autumn	0.358
Winter	0.409

From the values of table 2 one can observe a semnificative positive correlation of daytime hours with the static stability, for all seasons. The lowest, but still semnificative correlation one can observe in autumn, when the atmospheric nebulosity in general is higher.

The data from table 1 show the connection between static stability and ozone concentrations. This correlation may occur in the following way: because of high values of the Brunt - Vaisala frequency a higher quantity of ozone is much closer to ground level where the precursors have been emitted.

The instability periods - mainly in autumn - results in a decrease of correlation values. The cold periods which even may go beyond the winter in the Ciuc Depression, and the relatively high value of atmogeochimic background of ozone determine higher correlations in spring.

Analyzing the daily averages, it shows that observed average ozone concentrations are within WHO guideline values of 120μg/m^3. Based on EPA classification and European Union Air Quality Standards, during the study period, daily-h ozone concentration remained healthy for all the time.

The UNECE Task Force on Health has recently suggested a new indicator for the calculation of the adverse effects on health due to ozone. The indicator "accumulated excess concentration over the guideline value of 60ppb [120μg/m^3]" (AOT_{60}) has been replaced by the $SOMO_{35}$ indicator as an annual estimate of human exposure to ozone (UNECE, 2004). For every day *i*, $SOMO_{35}$ is calculated, in line with the metric used in the health studies to derive the summary estimate [36]. It uses 24-hourly running averages, from 00:00 (midnight) to 23:00, as follows:

$$\mathbf{A_{v_i} = average(h, h-1 \ldots, h-6, h-7)} \qquad (2)$$

with h = 0 to 23.

For every day i, the maximum average is then considered:

$$\mathbf{M_i = Max(A_{v_i})} \qquad (3)$$

For data validation, the so-called 75% rule has been applied: an 8-hour running average (Equation Avi) was considered valid if at least 75% of its hourly values (6 of 8) were available, while every daily maximum 8-hour running average (equation M_i) was considered valid if at least 75% of the 8-hour running average values (18 of 24) on that day were available.

From equation A_i, the excesses of ozone concentrations over 70μg/m^3 were calculated as follows:

$$\mathbf{O_{v_i} = M_i - 70 \text{ if} M_i \geq 70;} \qquad (4)$$

$$O_{vt} = O \text{ otherwise}$$

from which the $SOMO_{35}$ indicator is:

$$SOMO_{35} = \frac{\sum_i O_{v_i}}{N} \qquad (5)$$

$SOMO_{35}$ is the sum of these excesses divided by N, the number of valid days –that is, the number of days for which a valid maximum 8-hour running average is available.

For so-called valid days with ozone concentrations above 70µg/m^{3}as the maximum 8 h running average, only the increment exceeding 70µg/m^3 contributes to the estimation of the impact on health. No adverse effects on health for ozone concentrations below 70µg/m^3 are considered, as shown in figure 1. The largest contribution to $SOMO_{35}$ obviously comes from the late winter and spring months but also in the summer months (fig.1.) when one can identify exceeds of limits corresponding to this indicator. This approach is conservative, as it effectively involves the equivalent to a relatively high counterfactual value. It is motivated, however, by the uncertainties about the shape of the concentration-response function at very low concentrations and reflects seasonal cycles [36].

Much of the inter-annual variation in ozone can be attributed to variations in meteorological conditions that control ozone accumulation more exactly by the photo-dissociation of NO_2 [37, 38].

It's about an inter-conversion of O_3, NO and NO_2 under atmospheric conditions [39] is generally dominated by the following reactions [40]:

$$NO_2 + h\nu(\lambda < 410nm) \rightarrow NO + O(^3P) \qquad (R. 1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (R. 2)$$

where: M denotes any atmospheric element acting as catalyzer. The ozone thus generated can be removed by the titration with NO as:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (R.3)$$

In the process of transformation NO_2 the proportion of participants in reaction changes. One possibility to show the presence of different components might be the mole fraction:

$$\frac{n_i}{n_{tot}} \qquad (6)$$

where, n_i is the number of moles for component i, and n_{tot} is the total mole number of all participants in reactions.Although in such cases a more adecvate parameter to present which participant becames dominant is the mixing ratio:

$$r_i = \frac{n_i}{n_{tot} - n_i} \qquad (7)$$

The effect of reaction (R. 1) and (R. 2) which constitute a cycle with is no net chemistry. The overall effect of reaction (R_1) is the reverse of reaction (R. 3). These reactions represent a closed system which has the overall effect of partitioning NO_x between its component forms of NO and NO_2, and oxidant (OX) between its component forms of O_3 and NO_2 (the sum of O_3 and NO_2), but leaving the total mixing ratio of both NO_x and OX unchanged [37].The data in figure 2 indicate that at lower levels, NO is the major component of NO_x, whereas NO_2 dominates at higher mixing ratios. Figure 3 show the same daylight data for O_3 and NO_2 on a linear NO_x scale.

This clearly shows the inter-conversion of O_3 and NO_2 as a function of NO_x, but also indicates that NO_2 levels continue to increase with NO_x when O_3 is almost completely removed. Particular emphasis is placed on establishing how the level of "oxidant", OX (taken to be the sum of O_3 and NO_2) varies with the level of NO_x, and therefore to gain some insight into the atmospheric sources of OX, particularly at polluted urban locations to understanding of their chemical coupling. Correspondingly we will use a kind of mixing ratio, which reflects the presence of one component relative to the others.

In the figure 4 shows that the total OX appears to increase linearly with NO_x over the entire range considered, such that the level of OX at a given location has a NO_x-independent contribution, and a NO_x - dependent contribution [37]. The former is effectively a regional contribution which corresponds to the regional background O_3 level, whereas the latter is effectively a local

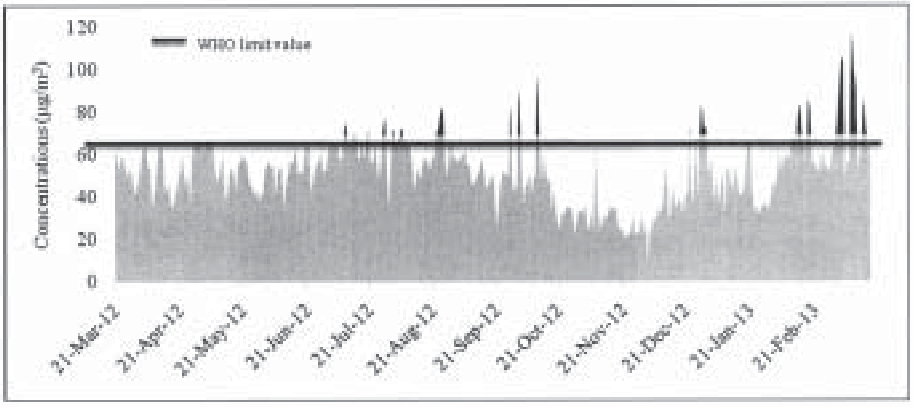


Fig.1. Diagram for $SOMO_{35}$ values for the station Jigodin Ciuc. The horizontal line shows the level above which the values pass the WHO limit.

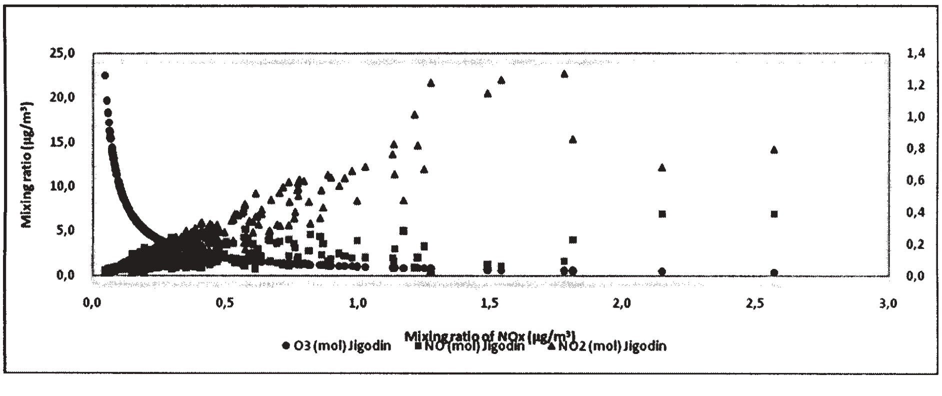


Fig .2. Mixing ratios of O_3, NO and NO_2 with the level of NO_x. Data are presented for each day of studied period. In the right side – secondary axes for NO and NO_2

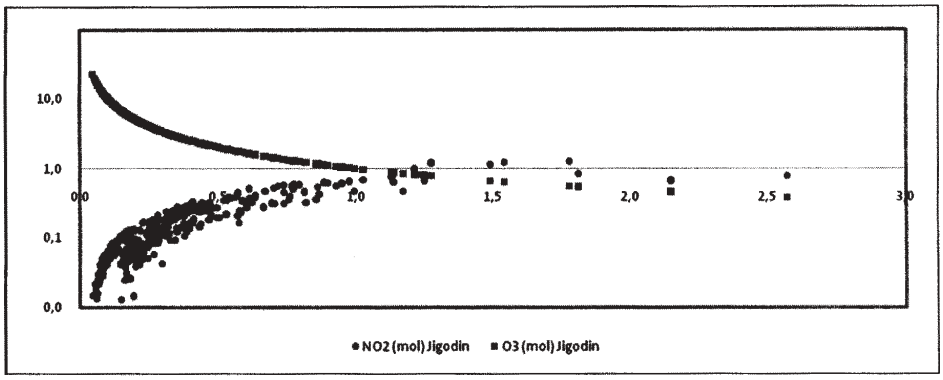


Fig. 3. Semi-logarithmic diagram of variation of daylight average mixing ratios of O_3 and NO_2 with the level of NO_x,. The lines were calculated with the mixing theory by mole fraction

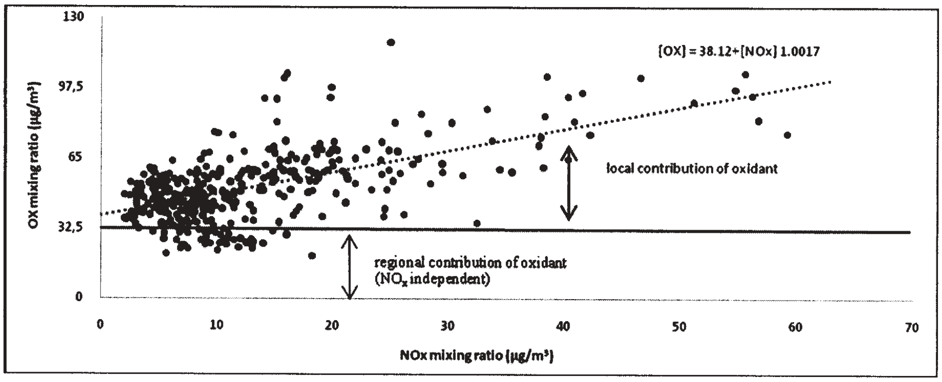


Fig. 4. Variation of annual daylight average mixing ratios of oxidant (OX) with the level of NO_x. Data are presented for each day of studied period. The line was defined by regression analysis

contribution which correlates with the level of primary pollution.

One of the most important European results about ozone primary (natural, historical) background level has been reported by [42, 42] and it have also been reviewed and summarized by Atmospheric Composition Change Network of Excellence funded by the European Community [43]. These studies used in the present work too, found background ozone concentrations in the range 25 to 40ppb.

The natural components - nitrogen oxides are naturally emitted from soils, as a consequence of microbial processes occurring in the soil, and may also be produced by lightning and by forest fires (many of which are started by lightning strikes).

If one analyze figure 3, one can observe that the values of natural background are higher (38.12µg/m^3)relative to the one determineted for some parts of Europe (e.g 37µg/m^3 [40], 30µg/m^3 [44], 30 to 35µg/m^3 [43].

The predominant source for natural VOC is vegetation [45], mainly caused by conifers wich are predominant in Ciuc Depresion and surroundings. Vegetative emitted VOC, mainly terpenes, are highly reactive in the formation of ozone, and the magnitude of their emissions increases with increased sunlight and temperature, in the conditions which favor ozone production [46]. Additional natural sources of VOC, mainly methane, are emissions from wetlands, peat bogs, and geological and geothermal leakage from underground deposits.

It is also possible for ozone to be formed directly in the atmosphere by lightning. Another source for naturally produced ozone in the troposphere is the stratosphere [19]. The local, NO_x-dependent contribution could result from a number of sources, the most obvious being direct emission of a proportion of NO_x in the form of NO_2. The dominant NO_x source in urban locations is road traffic [13-16].

The termolecular reaction of NO with molecular oxygen provides an additional thermal source of oxidant (R.4).

$$2NO + O_2 \rightarrow 2NO_2 \qquad (R.4)$$

The rate of this reaction is strongly dependent on the NO concentration, such that it is much more rapid at the elevated levels typical of those close to points of emission [37].

This reaction has certainly been postulated to make a major contribution to NO_2 formation in wintertime pollution episodes when a shallow inversion layer can lead to a combination of high NO_x levels and stagnant air for periods of a day or more [47]. Other NO_x - dependent sources of OX can derive from the concurrent emission of species which can lead to NO to NO_2 conversion.

It is well-established that the sunlight-initiated, free radical catalyzed degradation of VOC in the presence of NO_x leads to the oxidation of NO to NO_2 [48] (Atkinson, 1998; [49] Jenkin and Clemitshaw, 2000). In the Ciuc depression the local oxidant source has contributions from: direct NO_2 emissions, the thermal reaction of NO with O_2reaction (R.4) at high NO_x, and other common source emission of species which promote NO to NO_2 conversion.

From the analysis of figure 5 regarding the variation of daylight average of mixing ratios of oxidant (OX) with the level of NO_x, for the period 01 to 20 March, one can observe the contribution of tropospheric ozon and the beginning of vegetative period, which presents VOC production. This substance implicitly leads to high values of O_3 and to the increase of background concentration of OX with a value 31.1 µg/m^{3}relative to the variation of daylight average mixing ratios of oxidant (OX) with the level of NO_x.

If we analyze the evolution of annual average values for each hour we can observe a maximum around 07-11 o'clock for precursor gases while one can see a minimum for ozone for this time period (fig. 6). The correlation of annual average for each hour of ozone measured at the two stations is statistically significant (table 3). The seasons are quite influenced by temperature and rainfall and the present study is realized for the intervals: (Dec. 22. - March 20.) corresponds to a kind of period for winter, (Sept. 23.–Dec. 21.) for autumn, (March 21. - June 21.) spring and (June 22. - Sept 22.) summer. Because of the form of depression of Miercurea Ciuc, as one can also see for other depressions with bowl shape [13], a number of pollutants are captured.

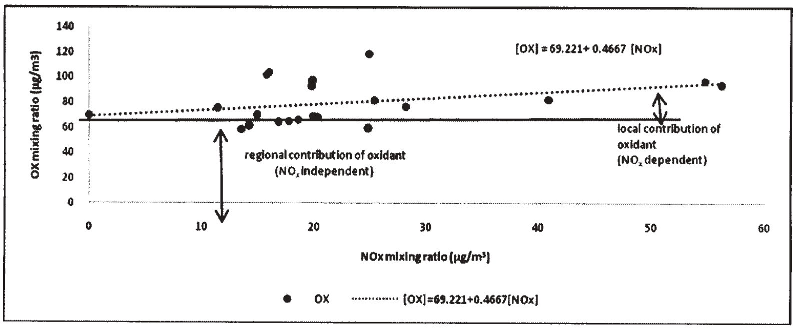


Fig. 5. Variation of daylight average mixing ratios of oxidant (OX) with the level of NO_x. Data are presented for each day from 01 to 20 March. The line was defined by regression analysis [37, 50].

Table 3

THE VALUE OF SPEARMAN CORRELATION OF O_3 BETWEEN - DAYTIME HOURLY VALUES.

O_3 Jigodin/O_3 Miercurea Ciuc	
Annual data	0.805
Spring	0.913
Summer	0.901
Autumn	0.719
Winter	0.719
March	0.742
Weekdays	0.821
Weekend	0.767

This fact occur usually in case of static stability conditions, by this we are able to claim, that this phenomenon is quite important beyond the other meteorological parameters, which influences the air quality at ground level. The anticorelational character is maintained relative to the precursor gases with specific variations for autumn and winter (fig. 7c, d). Relatively high seasonal averages of ozone concentrations can be seen in summer and winter (fig. 7b, c). In cold periods this is due to the increase of the traffic and of the domestic heating [51] (fig. 7 b, d), which implicitly leads to increase in concentration of precursor gases.

The diurnal evolution of the photo dissociation rates reflects in daylight duration (fig. 7) [52]. Analyzing the data from the two station, one can observe a similarity in diurnal change of the concentration of annual average for each hour of ozone (fig. 6) arriving to a minimum value for summer and spring (fig. 7 b, a) at 08 o'clock in the morning and for winter and autumn at 09 o'clock (fig. 7d, c). This prolongation of ozone built-up period follows that of duration of sunlight (and thus of the photolysis rates) indicating a photochemical origin in the changes of ozone during day [53]). The most semnificative difference between the two station is the fact that the hourly average values during the winter from the Jigodin station are much higher, exceeding sometimes in many cases the hourly concentrations during the summer (fig. 7d, c). This fact may be caused by an enhanced static stability during winter, which is reflected high values of oscillations of air layers in terms of Brunt - Vaisala frequency, which counterbalances the lack of solar radiation and of positive temperature in the process of ozone formation. This phenomenon - static stability - keeps the particles of precursor gases for longer time in the measuring zone, leading to formation and accumulation of ozone. These observations are also sustained by the literature, which suggest that the winter ozone is may be mostly derived from human activities as suggested by the modeling study of [15, 54]. This latter study concludes that the photochemical lifetime of tropospheric ozone in winter is of the order of 200 days, leading to the increase in surface ozone observed at remote locations. The photochemical lifetime of O_3 in the mid-latitude in winter is essentially the whole season, a significant accumulation of O_3 may occur even with a slow O_3 production. Slow photochemical activities allow the precursors of O_3 to build up to higher concentrations and to be transported over greater areas than those in summer that tends to compensate for the decreased photochemical activities [55]. At the station from Miercurea Ciuc, this phenomenon is not observed because of the urban microclimate due to domestic heating, which causes a decrease of the values of indicators of static stability and the precursor gases meet difficulties in leaving the measuring zone. For the station of Miercurea Ciuc the highest concentrations one meets for the spring and the summer period (fig. 7a, b).

Comparing the monthly average for each hour we can observe higher values which is due to the contribution of stratospheric ozon and emissions of VOC - more intense in March [19].

Ozone concentration during the week and on weekends

Measured ground level ozone concentrations are higher during weekend than weekdays (weekend effect) [56-58]. The mechanisms for the weekend effect on ozone formation are still not well understood [13].

According to the authors mentioned above this effect may be due by: day of week differences in timing of NO_x emissions; carryover of ozone and precursors on Friday and Saturday nights, and increased weekend emission. Marr et al.[59] proposed the theory of less absorption of sunlight due to lower fine particle's concentrations at weekend resulted enhanced ozone formation during weekend. In our case according with Pudasainee et al. [13], to some extent this can be explained by using destruction mechanism for ozone. Low values of NO, VOC emissions in weekend morning consume less O_3, and in daytime, it cannot be depleted further. Therefore, there is the variation of ozone. Table 4 presents the statistical detail of measured gaseous pollutants, NO, NO_2 and O_3 during

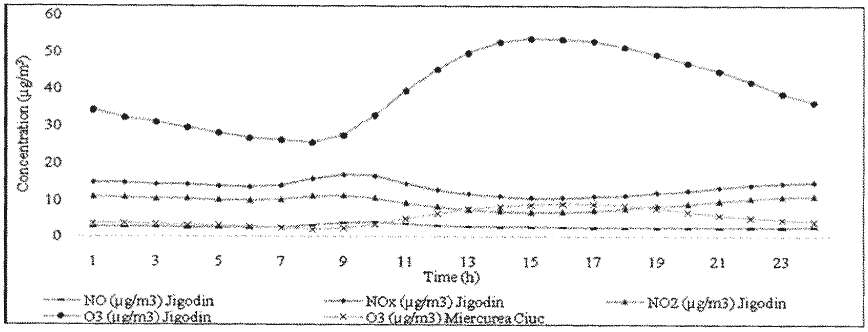
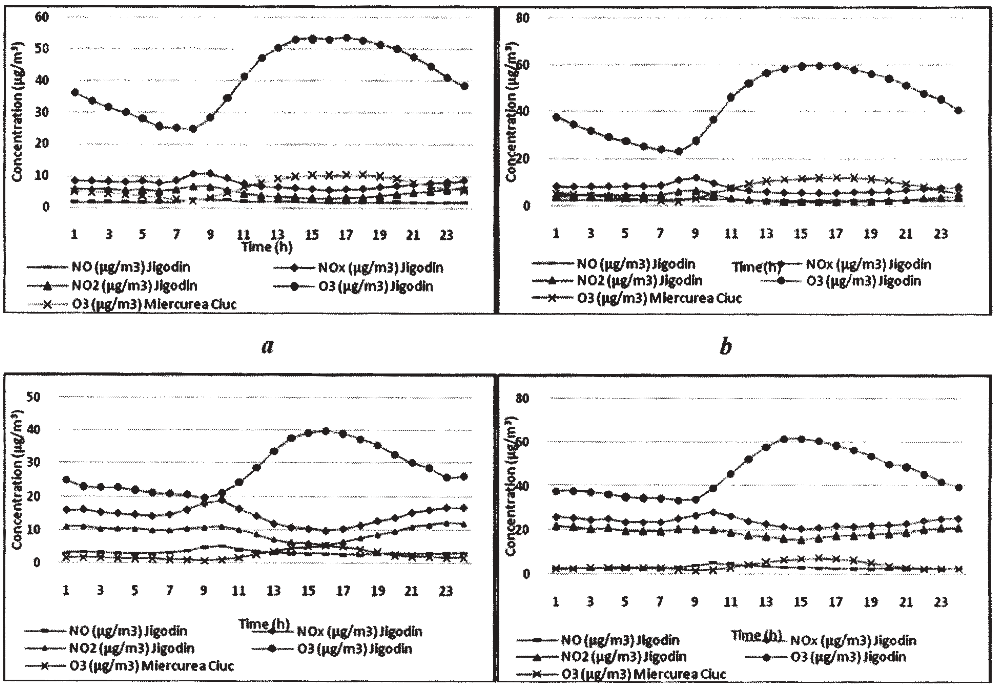


Fig. 6. Hourly concentration diagram, realized by averaging of measurements at a given hour for the full year, and corresponding standard deviation.



a *b*

c *d*

Fig. 7. Seasonal average concentrations for each hour of ozone and precursors. Starting from the left upper corner (to right): a) spring b) summer c) autumn d) winter

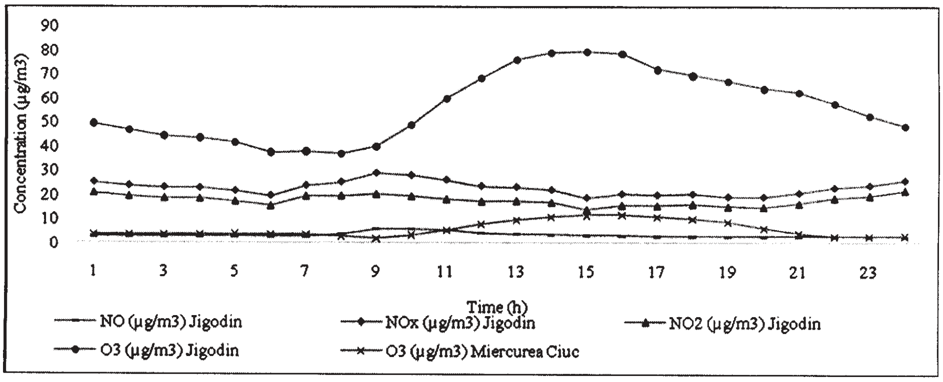


Fig. 8. Concentration diagram of March 2013 for each hour.

Table 4

MEAN VALUES OF CONCENTRATIONS OF NO, NO_2, NO_X, AND O_3 DURING THE WEEK AND IN WEEKEND RELATIVE TO THE MEAN ANNUAL VALUE

	NO	NO_2	NO_x	Ozone
total year mean	2.695	9.289	13.419	39.463
weekdays to year mean	+1.818	-0.194	+0.417	-0.522
weekends to year mean	-4.712	-0.517	-1.796	+1.191
weekend to weekdays	-6.414	-0.324	-2.204	+1.722

the studied period. The Ozone concentrations measured in the weekend are 1.191% higher than the average and 1.722% than weekdays.

Conclusions

Solar radiation, ambient temperature, and NO_x together can explain the variation in measured ground level ozone concentration in the study area. The formation of ozone is more during the winter and spring - at high static (which partly comes from a particularity of Depression of Ciuc deriving from its groove shape); and summer, when the intense solar radiation and longer day lengths, stimulate the photochemistry, resulting high concentration of ozone. The diurnal cycle of ground level ozone concentrations, revealed mid-day peak with lower nocturnal concentrations and inverse relationship exists between O_3 and NO_x, which are evidences of photochemical O_3 formation.

Ozone concentrations measured in weekend are higher than those at weekdays. Weekend effect can be in some extent explained by the destruction mechanism for ozone. In accord with scientific literature, the level of OX at the given location is made up of NO_x - independent and NO_x - dependent contributions. The former is effectively a regional contribution which equates to the regional background O_3 level, whereas the latter is effectively a local contribution which correlates with the level of primary pollution. All these are superimposed on a natural fund quite high due to coniferous vegetation and to the frequent inversion phenomena when cold air laden with VOC falls into the depression, where due to the photochemical processes it is converted into ozone. The $SOMO_{35}$ analysis identifies really short periods of time when we are facing exceedances of permissible limits for the indicators mentioned above and recommended by UNECE Task Force on Health. The mentioned phenomena in this paper draws a warning that should be taken into account by the local and environmental protection authorities when county land use plans, urbanism plans are elaborated or updated, when environmental permits and agreements are granted for some development projects which can lead to the increase of VOC and of other precursor gases in vulnerable areas in terms of the lower atmosphere dynamics.

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