Tropospheric ozone temporal variations and relationship to atmospheric oxidation in Ciuc basin

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Abstract. This study summarizes the results of a continuous measurements of gaseous pollutants, NO, NO_2, NO_x and O_3 in the ambient air of Ciuc basin. The main objectives of this report were to characterize the concentration and temporal variations of ozone and its precursors in Ciuc basin; to discuss the relationship between ozone and atmospheric oxidation OX (OX = NO_2+O_3). The highest concentration and highest amplitude of diurnal variation in OX throughout the four seasons were observed during summer. OX maintained a relatively low concentration during autumn. The concentration of ozone was highest in the spring, interesting is the relative higher concentration in winter. The major component of surface O_3 variation, both inter-annual and seasonal, is its annual cycle, which is primarily controlled at macro level by solar insulation and temperature cycle, in-situ production and transport. In this context, the diurnal ozone cycle consists of four phases: overnight carryover of ozone precursors; inhibition of ozone formation during the morning due to titration with NO; accumulation of ozone from the end of the inhibition period to the time ozone reaches its maximum; and post ozone maximum, which is characterized by increased vertical mixing and horizontal advection, declining actinic flux, and titration of ozone by fresh NO_2 emissions during the afternoon.

Key Words: tropospheric ozone, atmospheric oxidation, air quality, Ciuc basin, air pollution.

Introduction. In the course of constantly renewing and accelerating technology development, a setback in the protection of the environment occurred. Over the past few decades, the environmental problems have accumulated, and have been increasingly emphasized in the debates of world leaders. The emitted air pollutants discussed in this study can cause serious damages not only in the terms of global warming, but also to the local environment. These damages are: acid rains, respiratory diseases, cancer, plant aging, etc. (EPA 2015). Thus, the prediction of air pollution is becoming more and more important. According to previous studies, air pollution is a major concern both in terms of life and property protection (Mészáros et al 2015).

The damaging impact of ozone is caused by the high oxidizing effect of the gas molecule, which oxidizes the bond between the two fatty acids in the human and animal lungs, causing various diseases (Pönkä & Virtanen 1994). In the case of vegetation, ozone is assimilated by the plant through photosynthesis, leading to energy development, which accelerates the aging process of the plant (Emberson et al 2001; Szép et al 2016a). Ozone is the product of a series of complex photochemical reactions, in the presence of heat and sunlight (Figure 1).

In Romania, ozone concentration limits are regulated by the 104/15.06.2011 legislative act: one-hour moving average maximum is 240 μg m^{-3}; eight-hour moving average maximum value is 120 μg m^{-3}; the maximum value for vegetation (AOT40) is 18000 μg m^{-3} (May - July); long-term health limit: eight-hour moving average daylight maximum is > 120 μg m^{-3}; long-term limit for vegetation (May - July): 6000 μg m^{-3} h^{-1} (AOT40). In the studied area, particulate matter and ozone concentrations are greater than the limit values in the above mentioned European Directives (Korodi et al 2017).

The aim of this paper is to study the tropospheric ozone in the Ciuc basin, Eastern Carpathians, Romania, which is the main constituent element of the photochemical smog and plays a significant role in the atmosphere's oxidative environment.

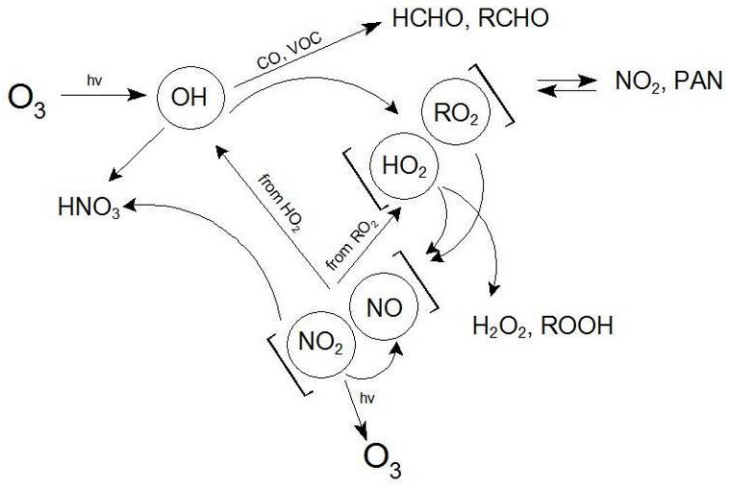

Figure 1. The photolysis of ozone (Calvert et al 2015).

Material and Method. The Ciuc basin (~600 m elevation - Figure 2) is located in the eastern Carpathians, limited to the south by mountains with 1000-1800 m altitude (Kristó 1994). The average temperatures of the basin are very low (Bogdan & Niculescu 2004). Furthermore, fog and thermal inversions are characteristic during cold periods (Kristó 1994).

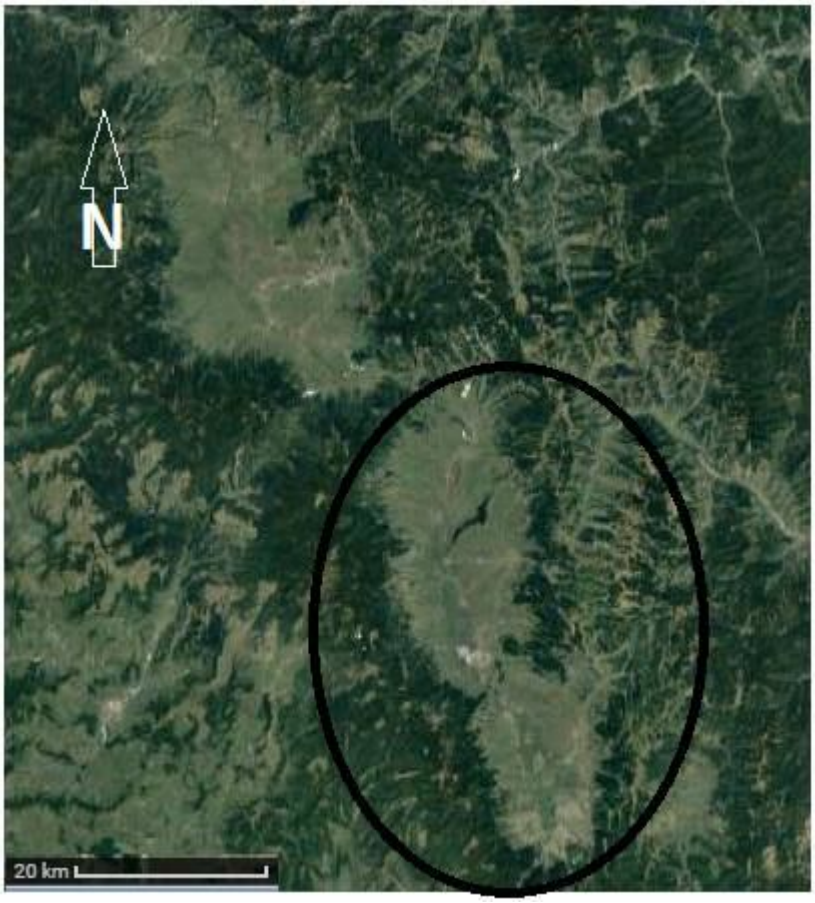

Figure 2. Sampling site, Ciuc basin, Eastern Carpathians, Romania.

The meteorological and air pollution data was collected in 2012 by a regional meteorology station (HR01) located in the Ciuc basin. The year of 2012 was the driest and the warmest during the past decade. In periods of drought and under high temperatures the ozone formation is more effective.

Nitrogen oxides were collected by a nitrogen oxide analyzer (ME9841B Monitor Europe, US EPA, RFNA1292-090) and ozone by an ozone analyzer (ME9810B Monitor Europe, Photometric UV, US EPA, EQOA0193-091). The air temperature was measured by a TS Thermometer sensor (measuring range: -30° C to +50°C) located two meters above ground, relative pressure and relative humidity detected by BP-S and RH-S Orion instruments. The speed of the wind is detected by a spoon wind speed detector at a height of 10 m (WS-S Orion).

Results and Discussion

Hourly, daily and seasonal variation data. In the studied atmosphere, the hourly and daily ozone variation is influenced by the meteorological conditions (temperature, day-intensity) and the NOx level. These near-surface ozone concentration variations are explained by the solar radiation, ambient temperature and NO_x concentrations. The inverse correlations with ozone formation and its precursors can be observed in the correlation table of annual mean daylight hours (Table 1) (Szép et al 2016b).

Table 1

Spearman correlations table between O_3, NO, NO_2, NO_x, solar radiation and temperature

	Temp. (°C)	*NO ($\mu g\ m^{-3}$)*	*NO_x ($\mu g\ m^{-3}$)*	*NO_2 ($\mu g\ m^{-3}$)*	*Sol. Rad. ($W\ m^{-2}$)*	*O_3 ($\mu g\ m^{-3}$)*
Temp. (°C)	1	-0.33	-0.67	-0.68	0.50	0.39
NO ($\mu g\ m^{-3}$)	-0.33	1	0.67	0.46	-0.03	-0.36
NO_x ($\mu g\ m^{-3}$)	-0.67	0.67	1	0.95	-0.27	-0.57
NO_2 ($\mu g\ m^{-3}$)	-0.68	0.46	0.95	1	-0.30	-0.48
Sol. Rad. ($W\ m^{-2}$)	0.50	-0.03	-0.27	-0.30	1	0.47
O_3 ($\mu g\ m^{-3}$)	0.39	-0.36	-0.57	-0.48	0.47	1

The seasons are determined by temperature and precipitation. The seasons of this study period can be divided into spring (21 March - 21 June), summer (22 June - 22 September), fall (23 September - 21 December) and winter December 22 - March 21). Accordingly, ozone evolution is more effective during winter, spring and summer period. In winter, when the atmosphere exhibits high static stability ozone accumulation occurs, while in spring, the mixing with the stratospheric ozone and the presence of volatile organic compounds (VOC) increases the ozone formation (Szép et al 2017a, b). During summer when solar radiation and temperature is more intense (Petres et al 2017), and daylight hours are longer, photochemical reactions occur, hence, increasing the ozone concentration.

The measured values determine the air quality at a regional level. Observing the O_3 value, it can be noticed that its value is average during the whole year, except in the fall period. During spring, the values of NO, NO_2, NO_x decrease compared to the annual averages by 29.88%, 48.03% and 42.42%, respectively. In the summer period, the average value of the precursors also decreases in comparison with the annual values: NO - 1.97%, NO_2 - 60.37%, NO_x - 42.37%. In addition, the values in the fall season are higher than the annual hourly average values with17.51% for NO, 2.25% for NO_2 and 6.96% for NO_x.

During winter, this trend continues its growth compared to the annual average: with 15.10% in case of NO_2 and with 78.96% in case of NO_x. Between ozone and its precursors, inverse correlations can be observed. The increase compared to the annual average is 2.89% during spring, 10.25% during summer and 15.27% during fall. In the fall, this concentration decreases by 28.66% compared to the annual average.

The increase in the concentration of precursor gases during fall and winter periods is due to the decrease of intense solar radiation and high temperatures. At the same time, the increase is also caused by traffic emissions, biomass burning and static stability, which allows the accumulation of the precursors, thus the formation of ozone.

In addition, through examination of the variations of annual ozone concentrations, according to the eight – hour averages given in Figure 3, it is obvious that the concentration of ozone remains within the WHO limits (120 $\mu g\ m^{-3}$).

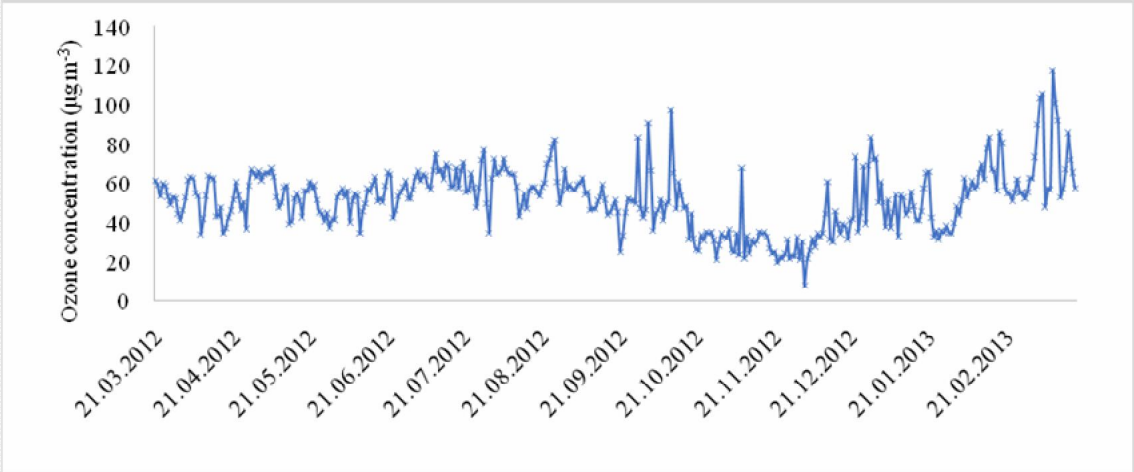

Figure 3. Annual eight – hour average ozone concentration diagram.

During spring, very high levels in the ozone concentration can observed in the hourly changes (Figure 3). This is due to the movement of the stratospheric ozone in the troposphere and its mostly characteristic in the months of February and March.

The influence of wind on the development of ozone concentration. The value of the concentration of near-surface ozone is affected by the wind strength measured at the given time and its direction. The wind strength measured by the regional station is between 0 and 6 m s^{-1}. For the statistical analysis, the data was sorted according to the Beaufort scale. Then, the correlations between ozone, its precursors and meteorological parameters are examined in accordance with the degrees. By the examination of the local dominant wind direction (180-270°), the characteristic wind speed is established, being only 0 to 2 m s^{-1}.

The 83.5% of the data can be classified in the windless category (0 grade), which has little influence on the correlation between the ozone concentrations and its precursors, meteorological parameters and the atmospheric stability.

The relationship between the distribution of the ozone concentration and the wind direction, according to which higher concentrations correlate with low wind strength, is further proof to the presence of atmospheric stability conditions.

Furthermore, the eight – hour moving average represented in Figure 4, shows that the ozone concentration exceeding harmful to human health is concentrated in the 0-2 m s^{-1} windspeed zone.

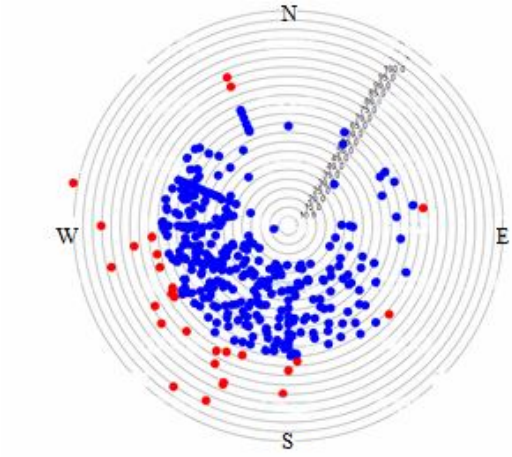

Figure 4. Distribution of the daily average ozone concentration related to wind direction. The values marked in red exceed the permitted eight-hour moving average limit (70 µg m^{-3}).

Oxidative effect of the atmosphere. Conversion to O_3, NO and NO_2 under atmospheric conditions is usually dominated by the following reaction (Auvray & Bey 2005; Han et al 2011):

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

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

Where: M may designate any atmospheric element as a catalyst. Ozone can thus be transformed and decomposed by reacting with NO:

$$O_3 + NO \rightarrow NO_2 + O_2$$

Data from Figure 5 shows that at lower levels NO is the main component of NO_x and where NO_2 dominates there is a higher mixing rate. Figure 6 shows daytime O_3 and NO_2 data on the linear NO_x scale, where the internal transformation between O_3 and NO_2 can be seen as a function of NO_x, but it is also shown that NO_2 levels are constantly increasing as a function of NO_x, which almost completes the O_3 degradation.

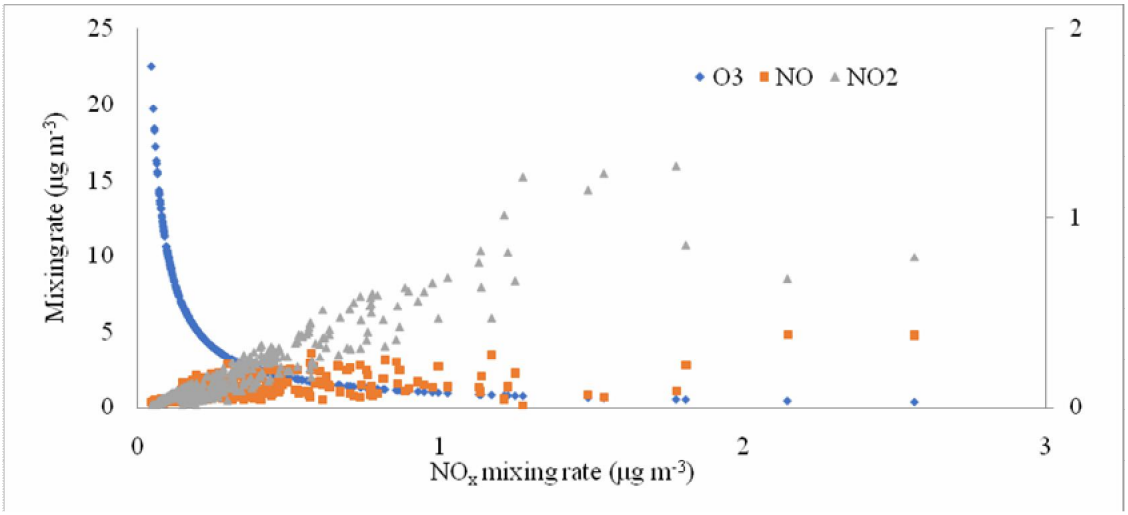

Figure 5. The ratio of the regional O_3, NO and NO_2 mixture to the NO_x level (Data shows the study period for each day).

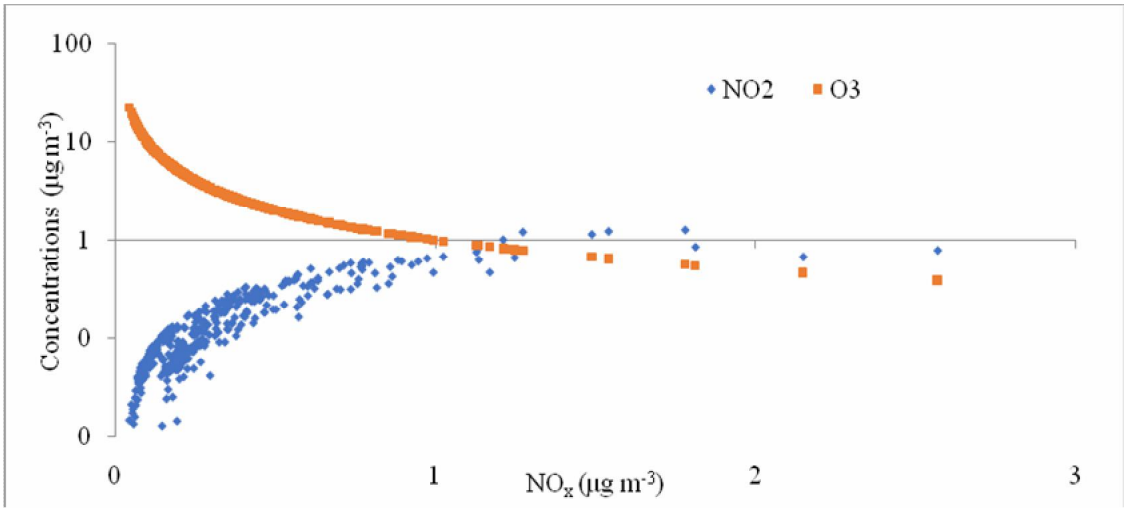

Figure 6. Logarithmic diagram of daytime average mixing rate changes for regional O_3 and NO_2 elements, as a function of NO_x level. Data obtained by determining the molar fraction and the mixing rate.

The basins natural ozone base value is higher (38.12 µg m^{-3}) than other values measured in Europe (Auvray & Bey 2005). This is due to the natural volatile organic compounds (VOC), having the vegetation as source (Constable et al 1999), primarily the conifers, which are characteristic for the studied area. VOCs released from vegetation are mainly

terpenes, which are highly reactive with ozone precursors and are also more active by the effects of strong solar radiation and high temperatures, and this is a favorable condition for ozone formation (Figure 7) (Szép & Mátyás 2014; Szép et al 2016b, 2016c, 2016d).

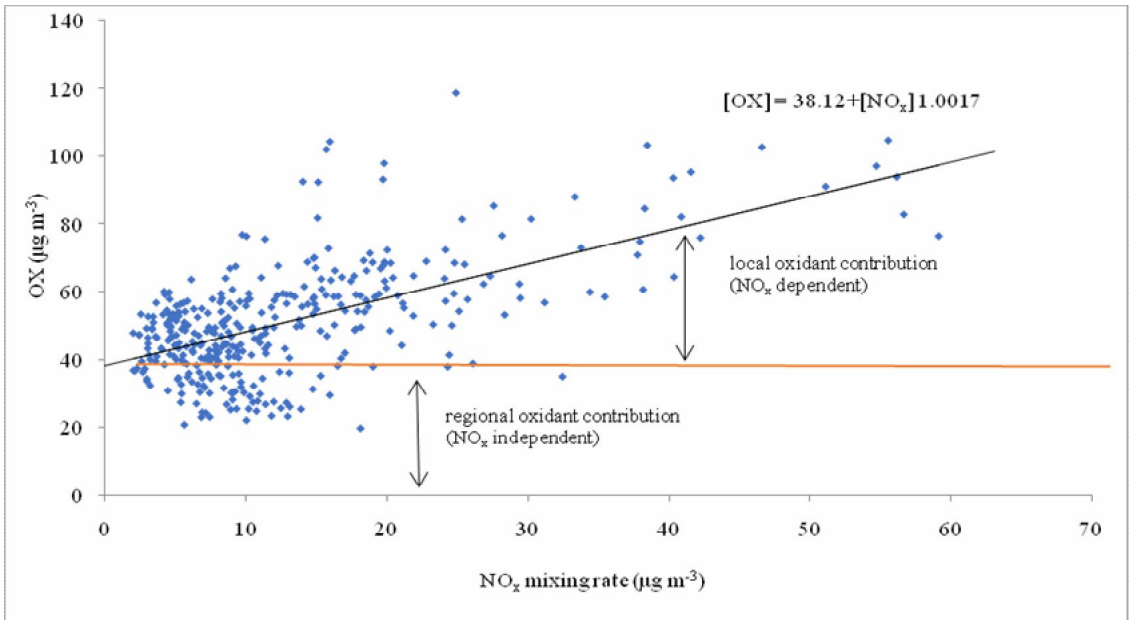

Figure 7. Average annual variations of the regional OX reaction rate according to the NO_x level (daily data).

Natural emissions include the release of nitrogen oxides from soils, as a consequence of microbial processes, as well as lightning and forest fires. Methane is emitted by the wet environment, such as swamps and geological, geothermal leaking. Another phenomenon that increases the concentration of natural ozone in the troposphere is the phenomenon that causes the above-mentioned stratospheric ozone to enter the troposphere (Collins et al 2003).

The local NO_x contribution is mostly composed of NO_2, which is emitted from the urban road traffic (Jenkin & Clemitshaw 2000). The reaction of NO with molecular oxygen provides the thermal oxidation source:

$$2NO + O_2 \rightarrow 2NO_2$$

This reaction depends on the NO concentration (Clapp & Jenkin 2001). This reaction certainly assumes that NO_2 formation is significantly contributed by wintertime impurities when a shallow inversion layer can be associated with the combination of high NOx levels and stagnant air periods for one or more days (Bower et al 1994).

The free radical decomposition of VOC by sunlight in the presence of NO_x produces NO, and then oxidizes NO_2 (Atkinson 1998). NO_2 emissions from vehicles are the source of the oxidizing effect in the Ciuc basin.

Conclusions. According to the terms of Brunt-Väisäla, used to examine the stability in the Ciuc basin, stable periods occur during the one-year period when the frequency of contamination between the air layers is very high. As a result, pollutants are continuously accumulating, and are released slowly from the air masses.

Further investigation of the pollutants has shown that the intensity of solar radiation, the temperature and the NO_x can explain the variations of the near-surface ozone concentrations in the given area. During winter, under high static stability conditions and in summer period, when daylight hours are longer and solar radiation is more intense, high ozone concentrations are produced from photochemical reactions.

The one-day ozone concentration cycle shows peak values during daytime, while at night a lower concentration is observed and an inverse relationship between O_3 and NO_x is shown, which proves the photochemical formation of O_3.

The 83.5% of the data can be classified in the windless category (0 grade), which has little influence on the correlation between the ozone concentrations and its precursors, meteorological parameters and the atmospheric stability. The relationship between the distribution of the ozone concentration and the wind direction, according to which higher concentrations correlate with low wind strength, is further proof to the presence of atmospheric stability conditions.

The basins oxidative effect is high, which is mainly due to its bowl shape and microclimate. Here, atmospheric stability and the inversion phenomena are often observed, causing pollutant accumulation. In some cases, the accumulated pollutant concentrations exceeded the threshold limits.

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