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STATISTICAL ANALYSIS OF AIR POLLUTION WITH SPECIFIC REGARD TO FACTOR ANALYSIS IN THE CIUC BASIN, ROMANIA

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ABSTRACT. In the present study, the changes of the concentration of air pollutants were examined, based on air pollution, meteorological and climatologic data gathered over an interval of two years (2012-2013) by the regional measuring station located in the basin, as well as the sources of the air pollutants were studied with the help of factor analysis. Biomass burning, traffic and photochemistry were characteristic regarding the source of air pollutants. This was also confirmed by the correlations between pollutants. Furthermore, the increasingly busy car traffic in the cold season and the atmospheric stability characteristic for it are also important observations with regard to the sources of air pollutants.

Keywords: *air pollution, factor analysis, air quality, atmospheric stability, environment and human originated ozone sources*

INTRODUCTION

Air pollution is an important factor affecting health and life quality. Road traffic and biomass burning can produce substantial increases in the concentrations of carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOC), particulate matter (PM), sulphur oxides (SO_x), ozone (O_3) [1], [2]. Nitrogen oxides may also cause adverse effects on vegetation and contribute to the formation of secondary inorganic PM and O_3 with associated effects on health, ecosystems and climate [3]. Sulphur dioxide is a precursor in the formation of PM and damages forests and terrestrial ecosystems, affecting the human respiratory system [4]. Carbon

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monoxide can reduce the oxygen-carrying capacity of blood [5]. In the atmosphere, CO slowly oxidizes into carbon dioxide or ozone [3].

In Europe, emissions of many air pollutants have decreased since the 1970s [3]. Despite regulations, the emission concentrations observed in Romania indicate air pollution levels exceeding European Union standards. In the last few years, air pollution concentrations decreased in Romania too, except $PM_{2.5}$ and VOC [6]. In 2012, the $PM_{2.5}$ concentrations were higher than the target value threshold at several stations in Romania. Furthermore, in Romania there are more than 500 premature deaths a year due to ozone exposure [3]. $PM_{2.5}$ mitigation measures reduced the premature deaths by 5 to 6 premature deaths annually per 10 000 people [7].

The present paper includes an analysis of the above described air pollution variations in the Ciuc basin in 2012 and 2013. Furthermore, air pollution factor analysis has been carried out using the measurements from the monitoring stations.

The Ciuc basin is a bowl-shaped basin in the Eastern Carpathian Mountains, Romania [8], characterized by a special microclimate, with significantly different changes of air pollutant concentrations, in comparison with other regions. In the cold season inversion periods occur and pollutants get trapped in the atmosphere of the basin [9]. Their accumulation causes frequent exceedances of limit values [10]. Emitted air pollutants can cause serious damage not only from the perspective of global warming, but also on the level of local conditions, with regard to the entire environment (e.g. acid rains, respiratory and cancerous diseases, plant ageing, damages of buildings etc) [11].

Solutions to global problems can be mitigated by local solutions, thus the exploration of the air pollution problems in the Ciuc basin can also play a significant role in the development of specific atmosphere protection policies.

RESULTS AND DISCUSSION

Air pollution variations and correlations

In order to decrease the extent of air pollution, the European Union has determined certain limit values in the case of the various pollutants. Air quality data collected in the Ciuc basin between 2012 and 2013 is shown in Table 1 in relation to these values.

Sulphur dioxide: Sulphur dioxide concentrations are almost insignificant, falling within the threshold values determined by the EU. Levels of sulphur dioxide have decreased in most of Europe [12]. The main sources of sulphur dioxide are fossil combustibles, which are less used in the basin.

Table 1. Concentration of pollutants in Ciuc basin during the study period (2012-2013) in relation to the European Union air quality standards set for the protection of human health [13]

		Limit value (μg/m^3)/number of allowed exceedances	**Measured concentration (μg/m^3)/number of exceedances**	
			2012	**2013**
SO_2	annual mean[1]	20	4.5	3.96
	max daily mean	125/3	18.82/0	16.53/0
	max hourly mean	350/24	35.97/0	24.91/0
NO_2	annual mean	40	7.78	25.96
	max daily mean	200/18	62.61/0	61.99/0
CO	annual mean	not applicable	0.32	0.32
	max 8-h mean	10 000	0.45	4.10
PM_{10}	annual mean	40	21.35	14.32
	max daily mean	50/35	21.31/0	**122.05**/13
$PM_{2.5}$	annual mean[2]	25	**37.19**	**28.03**
O_3	annual mean	not applicable	38.36	26.81
	daily max 8-h mean[3]	120/25	50.10/0	75.15/0
	max hourly mean[4]	180	107.92	89.34

[1]Protection of vegetation; [2]To be met by 2015; [3]Target value; [4]Information threshold

Carbon monoxide: The two annual cycles of air pollution concentrations began to increase at the beginning of November and reached their peaks at the end of January. This observation is best presented by PM_{10} and CO concentrations (Fig. 1). Biomass burning and traffic emissions significantly increase in the cold season, which have a great impact on air quality. In parallel atmospheric stability prevents the elimination of air pollutants like CO and PM_{10} from the basin [10], [14]–[18].

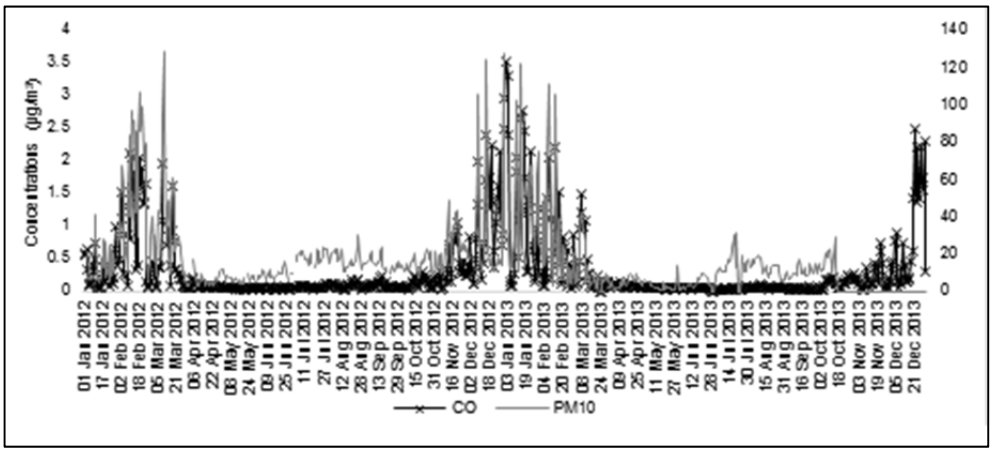

Figure 1. Daily CO and PM_{10} concentration in 2012-2013 period

Ozone and precursors: The lowest concentrations occurred between April and October (Fig. 2). During the same period, high ozone and precursors (NO_2, NO_x) concentrations show atmospheric stability conditions [14]. The tropospheric ozone was not consumed in reactions with exhaust gas NO and a small quantity was produced photochemically from NO_2. In this period air pollution is accumulated [15].

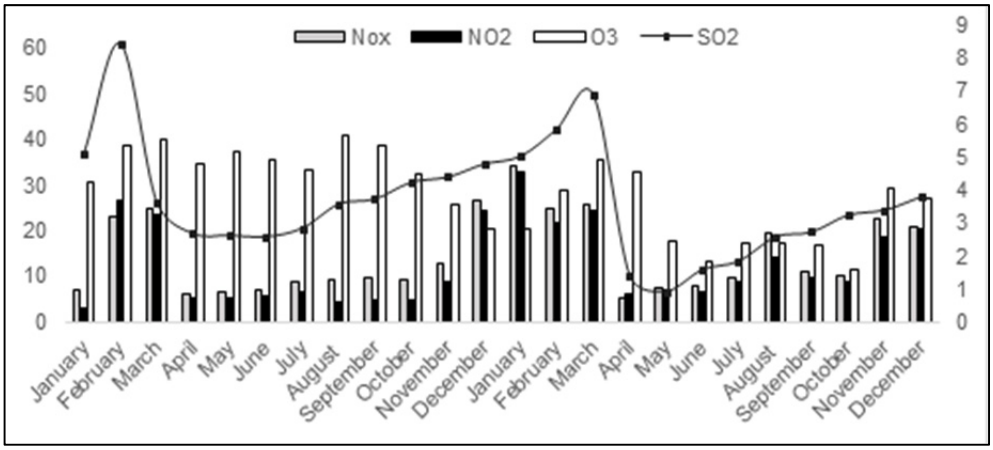

Figure 2. Monthly O_3, NO_x, NO_2 and SO_2 concentration in 2012-2013 periods

High ozone concentrations can cause major diseases, both for humans and to the vegetation. Because of their considerable oxidative effect, they influence the radical reactions of the organisms. In winter, human organisms

are even more prone to illnesses, thus accumulated air polluting ozone is a further stress factor that can cause disease in the human body. As a consequence of the frequent fog (and of the stable atmospheric conditions) in the cold season, pollution remains constantly in the air. The only market-town of the Ciuc basin (Miercurea Ciuc), from an air pollution perspective contributes to poor air quality only in a smaller degree; the climatology and the terrain of the basin are much more the cause of such poor air quality.

Particulate matter: The daily concentrations of PM_{10} (122.03 μg/m^3 in 2013) exceeded the limit value (50 μg/m^3), while the annual mean concentration of $PM_{2.5}$ were higher than the limit value (25 μg/m^3). The ratios between these PM pollutions are stable, approximately 0.67 and r=0.95 in 2013, but in 2012 no correlations can be observed between PM_{10} and $PM_{2.5}$, as these behaved differently in the atmosphere. They differ in size and in time, being present in the atmosphere, under different properties, such as atmospheric distribution and electrostatic character etc.). In the case of PM, we are talking about solid pollutants that can easily be eliminated from the atmosphere by sedimentation. The air pollutants are traffic induced dust and floating dust from the increased biomass burning in the cold season. The quantity of dust from traffic, settles down more easily due to its larger size and lower position, whereas the floating dust originating from smoke at higher altitudes is formed from tinier particles, which are mostly only eliminated from the air by precipitation. Thus, in the stable periods of the cold season, their concentration gets significantly higher, just as the concentration of ozone.

Air pollution correlations

In the case of other air pollutants, significant correlation could be observed in 2012, between CO and NO_x (r=0.938), CO and NO_2 (0.936), NO_2 and NO_x (r=0.992), NO and SO_2 (r=0.585), NO_x and SO_2 (r=0.505), NO_2 and SO_2 (r=0.635), PM_{10} and SO_2 (r=0.650), and in 2013 between PM_{10} and CO (r=0.725), SO_2 and CO (r=0.477), NO_2 and NO_x (r=0.908). In the case of correlations of air pollutants with meteorological parameters significant correlations could be observed in 2012 between RH and O_3 (r=-0.766), temperature and CO (r=0.692) temperature and SO_2 (r=-0.560), and in 2013 between RH and O_3 (r=-0.745), temperature and CO (r=0.699), temperature and SO_2 (r=-0.392). The listed correlations are significant at the 0.01 level (2-tailed). These correlations support the reactions that occur in the atmosphere:

$$CO + NO_2 \rightarrow CO_2 + NO \qquad (1)$$

The ozone then decays, and redevelops:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2)$$

During its development, solar radiation with a wavelength of less than 0.41 μm dissociates the nitrogen dioxide into nitric monoxide and atomic oxygen [19]:

$$NO_2 + hv \rightarrow NO + O \quad (3)$$

Then, atomic oxygen combines with one molecular oxygen in the presence of a third molecule (M), forming ozone:

$$O_2 + O + M \rightarrow O_3 + M \quad (4)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (5)$$

Due to solar radiation, the newly formed nitrogen dioxide is decomposed again into nitrogen monoxide and atomic oxygen:

$$NO_2 + hv \rightarrow NO + O \quad (6)$$

The reason of the high correlation between NO_x and NO_2, respectively CO is a similar source of pollution (traffic) [20]. According to the researchers, the correlation between RH and O_3 results from a shift in the soil moisture-atmosphere coupling regime, because the condition of the photochemical formation of ozone is the oxidation of the carbon-hydrates by the hydroxyl radical (OH), in the presence of nitrogen-oxides (NO_x) and sunlight [21]. The high relative humidity is often associated with fog and rain events. Thus, in both cases drifting ozone is removed from the atmosphere through humid precipitation.

The explanation of the connections between CO and PM_{10} can also be traced back to their common origins, as in both cases biomass burning and traffic can be considered their main originators [6] [22].

Result of the factor analysis

During factor analysis for the sake of more accurate results the hourly series of data from 2012 and 2013 were organised in one data block on which the analysis was carried out. In the case of $PM_{2.5}$ the measuring station only detects daily data; therefore, this data block was not included in the factor analysis. Factor analysis (FA) summarizes the correlation patterns. According to the results of the analysis in the case of two factors the eigenvalue is higher than in the case of one factor (Table 2). These values are 4.763 and 2.260, while the value of total cumulated variance is 70.234%.

Eigenvalues can be influenced by various factors. The characteristics of highlighted eigenvalues in Table 2 are shown by the component matrix in Table 3.

Factor 1 is composed of NO_x, NO_2, CO, SO_2, PM_{10}, and temperature. According to Table 2 their cumulative variation is 47.635%. The highest factor

loadings of NO_x in table 3 reach 0.916, followed by temperature (-0.898), CO (0.896), NO_2 (0.876), PM_{10} (0.780) and SO_2 (0.700). NO_x is an important indicator of air pollution and is emitted by vehicles, biomass burning and industrial emissions [23]. Statistical analysis shows that a high percentage of CO, NO_2 and PM_{10} in the atmosphere is emitted from households [16]. The SO_2 is mainly produced from the combustion of fuel containing sulphur, energy production and households [11].

Table 2. Factor analysis and variances

Components	Initial Eigenvalues		
	Total	**% of Variance**	**Cumulative %**
1	**4.763**	47.635	47.635
2	**2.260**	22.599	70.266
3	0.750	7.504	77.738
4	0.637	6.365	84.103
5	0.509	5.094	89.197
6	0.418	4.180	93.377
7	0.279	2.788	96.164
8	0.210	2.096	98.260
9	0.156	1.562	99.822
10	0.018	0.178	100.000
Extraction Method: Principal Component			

Table 3. Component matrix of air quality factor loadings

Pollutants	Factors	
	1	**2**
NO_X	**0.916**	0.191
NO_2	**0.876**	0.167
O_3	-0.197	**0.830**
CO	**0.896**	0.102
SO_2	**0.700**	0.250
PM_{10}	**0.780**	0.359
Wind speed	-0.295	**0.680**
Temperature	**-0.898**	-0.005
Relative humidity	0.382	**-0.760**
Solar radiation	-0.421	**0.515**
Extraction Method: Principal Components.		

In conclusion, pollutants of Factor 1 sources are biomass burning and car transport. Biomass smoke contains the oxide of nitrogen, carbon monoxide, oxide of sulfur and particle matter [24].

Factor 2 is characterized by O_3 and meteorological components (wind speed, relative humidity, solar radiation), with a cumulated variance of

22.599%. The O_3 value of the factor is 0.830. Ozone is a secondary pollutant, resulting from photochemical reactions. Because factor 2 is only constituted by ozone, it can be said that factor 2 is the “factor of photochemistry”.

CONCLUSIONS

According to our earlier studies the determinant parameters of the air quality in the Ciuc basin are its relief and the emerging atmospheric conditions (atmospheric stability who induced high inversion periods). The decrease of temperature causes more frequent atmospheric inversions, which prevent the dilution of air pollutants in the basin’s atmosphere. These pollutants often accumulate. In the studied period between 2012 and 2013, the limit values defined by the EU were exceeded only by floating dust, still, an established fact is that in the cold season (November-January) the concentrations of air pollutants remain high.

In the Ciuc basin, according to the results of the factor analysis, the formation of pollutants can be classified in two major groups: environmental and anthropogenic. The environmental source strands for the photochemical formation of ozone, whereas the anthropogenic source can be divided into two main components: biomass burning and traffic emissions.

According to our observations, decreasing temperatures cause biomass burning and car traffic emission increase (walking and cycling are more frequent in the summer). In correlation with the above-mentioned fact, more air pollutants are produced, such as the precursors of ozone, from which ozone is created thru photochemistry. With the decreasing temperatures, the frequency of atmospheric stability increases and the concentration of polluting gases and substances increases. This process (the accumulation of air polluting substances) is highly dangerous for human health; and all air polluting gases and substances that accumulate to a degree that exceeds certain limits of concentration can cause numerous diseases.

EXPERIMENTAL SECTION

Sampling

The sampling site is situated in the Ciuc basin, in the shelter of the orographic dam determined by the limitrophic mountain frame of the Eastern Carpathians. The Ciuc basin is similar to a (depressional) groove in which thermal inversions are remarkable [25, 26].

The data of SO_2, NO_2, CO, PM_{10}, $PM_{2.5}$ and O_3 are under observation in the period of January the 1st 2012 and December the 31st 2013, at the Jigodin HR01 background measurement station.

The nitrogen analyser (ME9841B monitor Europe, US EPA, nr. RFNA-1292-090) continuously measured NO, NO_2 and NO_x values, using

chemical luminescent method, while the ozone analyser (ME9810B Monitor Europe, Photometric UV, US EPA, reference no. EQOA-0193-091) measured the O_3 values in the air by the UV absorption techniques. The PM_{10} were sampled with an Automatic analyser LSPM10 equipped with PM_{10} and $PM_{2.5}$ impactors, and Low volume gravimetric sampler for $PM_{10}/PM_{2.5}$ - lead analysis (FOX Pump and Sentinel). The CO (carbon monoxide) hourly data were recorded by the MONITOR EUROPE-ML 9830B.

The air temperature values have been sampled by a TS Thermometer sensor with measuring range between -30°C and +50°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 wind speed detector is placed above ten meters of the ground and it can measure wind speed between 0-60 m/s (ORION WS-S anemometer, CUP WHEEL sensor type).

Statistical analysis

The statistical analysis was carried out using IBM SPSS Statistics 22 programme, with the help of which Spearman rank correlation and factor analysis were performed. The latter was only used when we wanted to reveal which parts of the set of variables included common fluctuations.

Factor analysis starts from the pairwise covariance of the variables, searching for factors that doesn't correlate, and whose effects can be summed up, or by using a linear combination of them, "simple" variables can be shown. The number of factors is optimal if it is as small as possible, but this minimal number of factors still represents the pairwise covariance system. Factor weights (factor coefficients in linear combinations) can be deduced as to how close the linear relationship between a given "simple" variable and a factor is. The higher the factor weight, the closer the linear relationship is to the corresponding factor-variable pair, i.e. between the background context (factor) and the part content. An important difference between the main component analysis and between the factor analysis is that during the factor analysis, the meaning of the factors is also searched for.

During factor analysis, the data were rotated using the varimax method. The role of this method is to obtain final eigenvectors with the most representatives of individual sources of variation. The maximum varimax rotation is used to carry out orthogonal rotation, to explain the number characteristics of factors [26].

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