

The Examination of the Effects of Relative Humidity on the Changes of Tropospheric Ozone Concentrations in the Ciuc Basin, Romania

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As ozone is a secondary polluting substance, its oxides of nitrogen (NO_x) play a significant role as precursors. Their existence is influenced by climatological and meteorological parameters, as well as other air pollutants (SOA, VOC). At present, alongside with various meteorological parameters (temperature, wind speed, relative humidity, sun intensity), other air pollutants (oxides of nitrogen, carbon monoxide, benzene) and other physical phenomena (dry deposition, meteoric stability) mostly the indirect effects of relative air humidity was examined in relation with the evolution of tropospheric ozone concentration. Our aim was, to examine the closed experiment of Jia and Xu (2014) (smog chamber), under atmospheric conditions, according to which in the case of high relative humidity the formation of ozone falls if benzene and ethylbenzene are added. According to the results, relative humidity has an increasing effect on water radical reactions and the hydration of glyoxal, while the concentration of the ozone changes as a result. At the same time, it can be observed that the higher the value of relative humidity is, the higher are also the values of ONO_x , benzene and CO, whereas the concentration of O_3 decreases. The reactions caused by the relative humidity of the air and VOC concentration in the experiment of Jia and Xu (2014) produced relatively adversary demonstrations in natural environment, because the experiment had been carried out at room temperature, whereas temperature and other parameters are subject to constant change in the natural environment.

Keywords: secondary organic aerosol, volatile organic compounds, relative humidity, principal component analysis, tropospheric ozone

From the volatile aromatic hydrocarbons, primarily the photo-oxidation reactions of ozone and of secondary organic aerosols (SOA) play an important role in air pollution [1]. At the same time, in an urban environment, as much as 50-60% of the gas phase of polluted air is non-methane hydrocarbons, of which the concentrations of benzene and ethylbenzene stand out as the highest [2-4], originating mostly from motor vehicles and conifers [5, 6]. Ozone is a highly harmful secondary pollutant, which results from photochemical reactions, its primary source being industry and traffic [7, 8]. It is produced from anthropogenic precursors: volatile organic compounds (VOC) and oxides of nitrogen (NO_x) [8-10]. The ozone remains in the atmosphere for a short time only (for an average period of 22 days) [11], yet it is frequently accumulated in the troposphere, due to atmospheric conditions [12, 13]. The cold air cushion typical to the basin is a synoptic climatological characteristic in the course of which during the colder winter periods the colder air mass gets trapped near to the ground. The basin relief plays an important role in this phenomenon, as also does the fact that there is no horizontal or vertical mixing. This means that the phenomenon may persist for days, which on its turn limits the dilution of air pollutants in the basin.

Its dissociation can occur in various ways, the main mechanisms being in case of precipitation (wet phase) [2] and more frequently, photolytic decline, or deposition [8, 14, 15] etc. As previously, during the formation process of the ozone, various forms of nitrogen also prevail during its destruction process [16]. The water contents of the

atmosphere is also a determinant factor both in the destruction of the ozone, and the formation of SOA, primarily the presence of aromatic NO_x compounds [2].

Our aim is to examine the experiments described by Jia and Xu (2014) in a natural environment. In their experiment they studied the effect of RH on ozone dissociation and SOA formation during the feeding of benzene, done in a smog chamber.

The formation of ozone and benzene- NO_x irradiations was investigated under different levels of relative humidity (RH) in a smog chamber. The research shows that the increase in RH can greatly reduce the maximum O_3 by the transfer of NO_2 and ONO_2 -containing products into the particle phase [2]. An important precursor of benzene is glyoxal, thus RH probably has a great impact on SOA formation from benzene and VOC.

In our paper we firstly examine the relationship between ozone and the different meteorological parameters (temperature, wind speed, relative humidity, sun intensity), other air pollutants (oxides of nitrogen, carbon monoxide, benzene) and physical phenomena (dry deposition, meteoric stability), using the statistical method of principal component analysis, respectively the indirect effects of relative air humidity based on the phenomena studied and described by Jia and Xu (2014), according to which RH has an influence upon the concentration of the ozone resulting from aromatic NO_x by photo-oxidation. This research aims to investigate the behavior of the laboratory result values obtained by Jia and Xu (2014) under natural conditions, where, unlike in laboratory environments,

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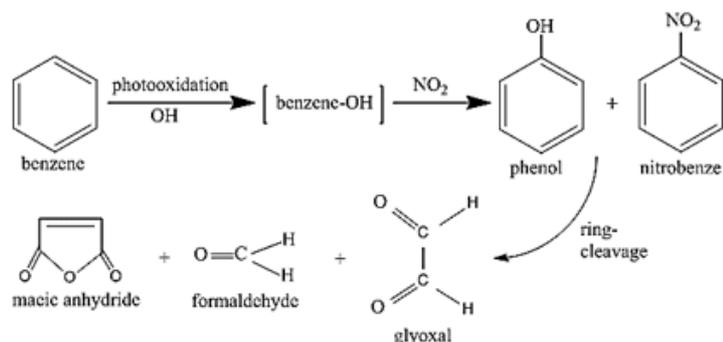


Fig. 1. Reaction of benzene photooxidation

conditions are not controlled but may be influenced by various factors.

Experimental part

Study area

The studied area is the Ciuc Basin, a 60 km long, prolonged bowl-shaped basin within the Eastern Carpathian Mountains. Its average altitude is 600 m, while its highest mountains reach 1000-1800 meters. The average temperature is only 0.2 grades lower than on the limitrophic zones of these mountains, yet by 1-2 grades lower than on the 1200-1400 m high slopes, which stays warmer [17]. Fog and meteoric stability are characteristic for the cold season, frequently resulting in inversion. The inversion can be very intense, and it may occupy the whole topoclimatic space, having a width of 500-600 m [18]. On the other hand in case of polar air invasion determined by the Eastern European anticyclone, this may expand up to 1200 m [17]. The main wind direction is westerly and north-westerly [18].

The climatic and environmental characteristics of the sample area we have studied are defined by two factors: its geographical position and its specific natural features. Romania is situated in the central part of Europe, therefore it has a transitional character from the point of view of the climate because the western, wet oceanic effects and the dry continental, eastern effects can be felt simultaneously. The Eastern Carpathians, which cut the country in two parts in northern-southern direction, are the peculiarities of Romania. In the same time this chain of mountains forms an orographic blocking in the way of the masses of air coming both from the Atlantic Ocean and from Siberia.

The different parts of the Eastern Carpathians surround the Ciuc basin stretching along an axes of northern-western direction. The western border of the basin is formed of volcanic mountains while the Easter of folded mountains. This intermountain basin is situated at the meeting fronts of different climatic effects, it is completely closed and it has some special climatic features like thermic inversion, climatic stability and high humidity.

Sampling

Pollutants and meteorological data are gathered in the basin by a regional-type measuring station. The collected data in our case are the hourly data of the period between 2012-2013.

The nitrogen oxide analyzer (ME9841B monitor Europe, US EPA, no. RFNA-1292-090) measures NO, NO₂ and NO_x values, using the chemi-luminescence method, and the ozone analyzer (ME9810B Monitor Europe, Fotometric UV, US EPA, no. of reference EQOA-0193-091 measures O₃ in the air using the UV absorption method. We measured temperature using a TS Thermometer sensor (detecting values between -30 and +50 °C) and the level of sun intensity was registered by an Orion-Mod SR-S sensor. Wind speed was measured by the Orion-Mod WS-S sensor, 10

meter aloft. The CO (carbon monoxide) hourly data was recorded by MONITOR EUROPE-ML 9830B and benzene data by a BTX2000 sensor.

Methods

The relations between air pollutants and meteorological and climatological parameters were studied with Principal Component Analysis (PCA), Spearman rank correlation, touching upon the changes of and connections among relative humidity, ozone, carbon monoxide, oxides of nitrogen.

Principal component analysis (PCA) is a multivariate data analysis method. With the help of the analysis, the most characteristic patterns among the data sets are identified. PCA processes data in the form of a matrix using the method of the least squares model, and makes use of eigenvectors of the correlation matrix [19]:

$$B[iv, is] = \frac{A[iv, is] - \bar{A}[iv]}{\sigma[iv]}, is = 1: S; iv = 1: V \quad (1)$$

where:

A[V, S] is the input matrix;

B[V, S] is the split normalized input matrix;

V is the normalized matrix and S=E*. B is score matrix;

E* is the coefficient matrix.

Eigenvectors with eigenvalues less than 1 are usually discarded, so that only p (<V) factors are retained. The absolute PCA method rotates the E[V, p] matrix with a scheme called *varimax* to reach a final coefficient matrix E*, and calibrates the corresponding PC score matrix, S to reach the absolute PC score matrix X, as shown in formula [19]:

$$X[ip, is] = S[ip, is] + \sum_{iv=1}^p E^* \frac{\bar{A}[iv]}{\sigma[iv]}, is = 1: S; ip = 1: p \quad (2)$$

In order to demonstrate the experiment carried out by Jia and Xu (2014) we investigate the ozone formation, firstly with the above described method of principal component analysis (PCA), and the connections between benzene and ozone and oxides of nitrogen, respectively the connections between RH and the same pollutants.

The characteristic features of the mentioned basin was part of our research method, the atmospheric stability [15, 20, 21], which plays an important role in the accumulation of polluting materials, as well as in the occurrence of the periods when the concentration of air pollutants exceeds allowed limit values.

Results and discussions

The processed data of year 2012 were grouped in three different ways applying the method of independent variables. Group one includes: O₃, NO, NO₂, benzene, temperature, solar radiation; group two consists of: O₃, NO, NO₂, benzene, RH, dry deposition, atmospheric stability and group three consistent of: O₃, NO, NO₂, benzene, RH, dry deposition, wind speed. Division into groups has been

done by a combined method, according to which the precursors, the primary sources of ozone, as well as the meteorological and climatological parameters that directly influence them were included in group one, whereas in group two and three, besides precursors, secondary influencing parameters also appear (dry deposition, atmospheric stability, wind speed).

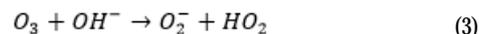
During PCA, following varimax rotation, we receive again the correlation of components, whereby the first components of the one group based on factor loading, the solar radiation (0.860) and ozone (0.825) were the strong contributors [22]. The two group based on factor loading, the ozone (-0.918), relative humidity (0.880) and in the three group strong contributors to the first component were the ozone (-0.903) and relative humidity (0.899).

Jia and Xu (2014) studied the effects of RH on the evolution of ozone concentration under the circumstances of decreasing benzene-NO_x, according to which the formation of O₃ and CO and consumption of NO₂ were much faster in the first hour at a 96% RH than at a 5% RH; but the measured maximum concentrations of O₃ and CO were greatly reduced under high RH conditions. In order to confirm similar phenomena and reactions in nature we examined correlations between air pollutants, under different RH conditions (RH 40-60%, 61-80%, 81-100%). In the first case (RH 40-60%) there were significant correlations ($p > 0.05$; significant level 0.197) between ozone and NO (-0.287), CO and NO (+0.558), benzene and NO (+0.426), and benzene and NO₂ (-0.370). In the second case (RH 61-80%) significant correlations were found ($p > 0.05$) between NO and NO₂ (-0.395), NO and O₃ (-0.267), NO and CO (+0.376), and NO and benzene (+0.621). In the last case (RH 81-100%) significant correlations were found ($p > 0.05$) between NO and O₃ (-0.278), NO and benzene (+0.409), NO₂ and O₃ (-0.278), NO₂ and CO (0.768), NO₂ and benzene (0.356), and CO and benzene (0.665). The correlation of benzene with NO₂ in low and increased RH is (-0.370; 0.356) can be linked to the aromatic nitro compounds originating from the photo-oxidation of benzene (fig. 1). Highly likely depending on how much NO₂ is consumed or produced during the photooxidation process of the benzene, the correlation of NO₂ with benzene can be either positive or negative. In case of 40-60% value, the correlation of NO₂ with benzene is negative (-0.370), which is explained by the fact that during photooxidation more NO₂ is consumed than produced. However, with higher RH values (81-100%) the correlation is positive because more NO₂ is produced than what had been consumed previously by the reaction.

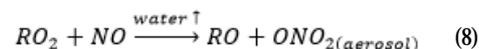
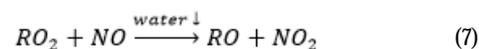
The significance of benzene photo-oxidation primarily resides in the formation of the mentioned aromatic NO_x and glyoxal. In the present case, the less significant CO has got a role in the genesis of carbon dioxide, while NO₂ is

released during the photo-oxidation of benzene, after it had been taken up in the first steps of photo-oxidation.

High RH has a positive impact on these photo-oxidation of benzene (fig. 1), as e.g. in the case of 81-100% RH the value of correlation between CO and benzene is 0.665, while at a RH of 61-80% this correlation is only 0.577, and at a RH 40-60% it is not significant any more (significant level 0.197). Jia and Xu (2014) related that the oxidation of benzene (and the hydrolysis of glyoxal within it) speeded up the establishment of C=O, C-O and C-OH bonds. They concluded that in the case of high RH values water radical reactions and the hydrolysis of glyoxal can be increased. The correlation result with RH and between O₃ ($r = -0.688$) refers to the increase in RH that can greatly reduce the maximum O₃ by the transfer of NO₂ by means of the reaction of ozone and watery steam [23] (fig. 2):



By Jia and Xu (2014) different from benzene, the ONO₂ group has a much better linear relationship with RH than the NO₂ group in ethylbenzene irradiations, which may be due to the hydrophobic ethyl group in ethylbenzene. Thus, the formation process of polar nitro (RNO₂) and nitrate (RONO₂) is also described by Jia and Xu (2014) as having a semiquantitatively decreasing ozone concentration, which explains the decrease of ozone concentration.



Tropospheric ozone is primarily formed from the photolytic dissociation of ambient NO₂ [25]. Thus, reaction (7) results in increasing ozone concentration and RH decrease, while during reaction (8) a decrease of RH and of ozone concentration can be observed. In the presence of benzene the formation of ONO₂ group (reaction 8) is more intensive, thus the destruction of ozone is more extensive, than its creation [2]. In our case the correlation between ozone and NO₂ is not significant ($r = 0.034$), whereas it shows a weak negative correlation with benzene ($r = -0.181$) and NO ($r = -0.164$) concentrations. According to these results, probably some ozone formed from NO₂ dissociation, yet in the case of high benzene and NO concentrations, the destruction of ozone can be observed.

As it can be observed on figure 2., in parallel with the decrease of ozone, NO₂ concentration increases with

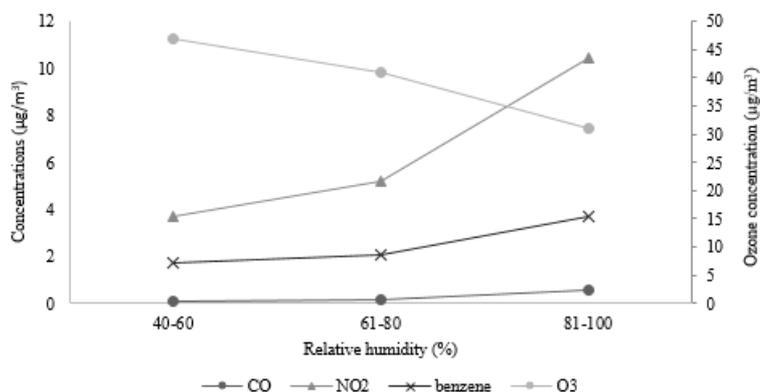
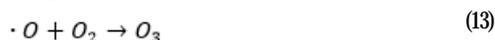
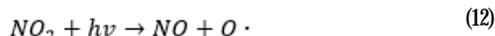
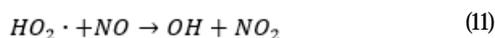
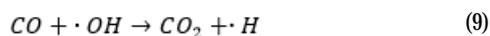


Fig. 2. Changes of average concentrations of air pollutants (CO, NO₂, benzene, O₃) in the case of rising RH

higher RH, yet in our observation this is in contrast with the results of the laboratory experiments performed by Jia and Xu (2014). The explanation for that is that they had carried out their experiment at room temperature, while air pollution concentrations, alike to other parameters, continuously changes in the environment. In our case, if environmental temperature increases, the relative humidity of the air decreases, on the other hand photo-oxidation reaction become more intensive. Thus, benzene decline speeds up [25], or otherwise, under circumstances of growing RH and decreasing temperature it slows down, and as a consequence it can even accumulate in the environment, thanks to the characteristic features of the basin (atmospheric stability). Increasing NO₂ concentration is not directly significantly linked to the relative humidity of the air (r=0.085).

The behavior of CO concentrations is similar to the results of the Jia and Xu (2014) experiments, as concentrations increase depending on the values of relative humidity. The reason for is most probably connected to CO oxidation.



The oxidation of carbon monoxide linked to the photo-chemical mechanism of ozone formation also decreases together with the decrease of the photo-chemical reaction of ozone, respectively with the decrease of temperature and the increase of RH [26].

Conclusions

The experiment described by Jia and Xu (2014) was carried out in a smog chamber, with the aim of examining the effects on ozone formation/destruction in conditions of high relative humidity and the presence of benzene/ethylbenzene. This experiment was tested under atmospheric circumstances. We were curious to find out, whether the hypothesis of Jia and Xu (2014) partial work out in nature too. In our case, we studied the changes of ozone concentration only in the presence of benzene (in different RH threshold).

Our first conclusion determined that higher RH leads to decreasing ozone and carbon monoxide concentrations. As ozone is a secondary pollutant, the relative humidity of the air has got a stronger influence on its precursors, yet its reaction with water can also be observed, which also lowers its concentration.

In case the system also includes benzene, the decline of ozone intensifies even more, because the connection between benzene and high RH speeds up the formation of SOA, particularly of the ONO₂ group. During their formation the relative humidity of the air continues to rise, intensifying water radical reactions and the hydrolysis of glyoxal.

Summing it up, the reactions caused by the relative humidity of the air and VOC concentration in the experiment of Jia and Xu (2014) produced relatively adversary demonstrations in natural environment, because the experiment had been carried out at room temperature, whereas temperature and other parameters are subject to constant change in the natural environment. Thus, high RH induced low ozone concentration and increasing

benzene, as well as carbon monoxide concentrations. In the case of nitrous oxide there is no direct connection between the relative humidity of the air and the increase of NO₂ concentrations.

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References

1. M. E. JENKIN, E.M., CLEMITSHAW, C.K., Atmos. Environ., 34, nr. 16, 2000, p. 2499-2527
2. JIA, L., XU, Y., Aerosol Science Technol., 48, 2014, p. 1-12
3. CAPATANA, C., SIMONESNCU, C.M., Rev. Chim. (Bucharest), 63, no. 12, 2012, p. 1289
4. NENCIU, F., VAIREANU, D.I., Rev. Chim. (Bucharest), 65, no. 5, 2014, p. 565
5. REID, N., A Review of Background Ozone in the Troposphere, Transbound. Sci. Unit Ont. Minist. Environ., 2007.
6. YUAN, B., SHAO, M., LU, S., WANG, B., Atmos. Environ., 44, 2010, p. 1919-1926
7. STRUJS, J., DIJK, A., SLAPER, H., WIJNEN, H.J., VELDEERS, G.J.M., CHAPLIN, G., HUIJBREGTS, M.A.J., Environmental science & technology, 44, nr. 1, 2010, p. 204-209
8. DERVENT, R.G., UTEMBE, S.R., JENKIN, M.E., SHALLCROSS, D.A., Atmos. Environ., 112, 2015, p. 216-224
9. ABDUL-WAHAB, S.A., BAKHEIT, C.S., AL-ALAWI, S.M., Environmental Modelling & Software, 20, nr. 10, 2005, p. 1263-1271
10. BAYLON, P., JAFFE, D.A., WIGDER, N.L., GAO, L., HEE, J., Atmos. Environ., 109, 2015, p. 297-304
11. OGUNSEITAN, O., Green Health: An A-to-Z Guide. Sage Publications, 9, 2011
12. PUDADAINEE, D., SAPOKOTA, B., SHRESTHA, M.L., KAGA, A., KONDO, A., INOUE, Y., Atmos. Environ., 40, 2006, p. 8081-8087
13. SZEPE, R., MATYAS, L., KERESZTES, R., GHIMPUSIAN, M., Rev. Chim. (Bucharest), 67, no. 2, 2016, p. 205
14. GERASOPOULUS, E., KOUVARAKIS, G., VREKOUSIS, M., DONOUSIS, C., MIHALOPOULUS, N., KANAKIDOU, M., Atmos. Environ., 40, nr. 17, 2006, p. 3057-3069
15. SZEPE, R., KERESZTES, R., DEAK, GY., TOBA, F., GHIMPUSIAN, M., CRACIUN, E.M., Rev. Chim. (Bucharest), 67, no. 4, 2016, p. 639
16. BLANKINSHIP, D.J., A discussion of the spatial and temporal variability of ozone concentrations along the front range of Colorado. University of Colorado at Boulder, Program in Atmospheric and Oceanic Sciences, 1996
17. BOGDAN, O., NICULESCU, E., Aspecte climatice specifice ale depresiunilor Giurgiu, Ciuc, Brasov in Factori si procese pedogenetice din zonă temperata, 2004, p. 3-115.
18. KRISTO, A., Csiki Zöld Füzetek, 1994, p. 7-26
19. LIANG, J., Chemical Modeling for Air Resources: Fundamentals, Applications, and Corroborative Analysis. Academic Press, 2013
20. SZEPE, R., MATIAS, L., Carpathian J. Earth Environ. Sci., 9, nr. 2, 2014, p. 241-250
21. SZEPE, R., KERESZTES, R., DEAK, GY., BOBOC, M.G., RAISCHI, M., Study of Atmospheric Stability in Ciuc-Basin and of the Relationship between PM₁₀ and CO Pollutants, 1st International Conference on Sea and Coastal Development in the frame of Sustainability MACODESU 2015, Karadeniz Technical University in Trabzon, Turkey, p. 120.
22. AWANG, R.N., RAMLI, A.N., YAHAYA, S.A., ELBAYUMI, M., Atmospheric Pollut. Res., nr. 6, 2015, p. 726-734
23. CHAPLESKI, R.C., ZHANG, Y., TROYA, D., MORRIS, J.R., Chem Soc Rev, 2016.
24. FINLAYSON PITTS, B.J., PITTS, J.N., Chemistry of the upper and lower atmosphere: theory, experiments, and applications. San Diego: Academic Press, 2000
25. MOLLER, D., Chemistry of the climate system. Berlin; New York: De Gruyter, 2010.
26. MESZAROS, R., Budget and trend of atmospheric carbon monoxide in Europe. Theses of PhD dissertation, PhD School of Environmental Sciences, 2006.