Study of Air Pollution and Atmospheric Stability in Ciuc Basin - Romania

ROBERT SZEP[1], REKA KERESZTES[1], ATTILA KORODI[1,2], SZENDE TONK[3], MIHAELA EMANUELA CRACIUN[4]*

[1]Sapientia Hungarian University of Transylvania, Faculty of Technical and Social Sciences, 1 Liberty Market, 530104, Miercurea Ciuc, Romania,

[2]Bucharest University of Economic Studies, Romanã Market no. 6, 010374, Bucharest, Romania

[3]Sapientia Hungarian University of Transylvania, Faculty of Science and Arts, 4 Calea Turzii, 400193, Cluj Napoca, Romania

[4]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, no. 1-7 Gheorghe Polizu Str. , 011061, Bucharest, Romania

The atmospheric stability plays an important role in the accumulation of air pollutants and greatly influences their degradation, dispersion and deposition. These atmospheric qualities can be determined with various methods (Richardson number, Monin - Obukhov length, SRDT method) and the pollutant concentration increase demonstrates the atmospheric stability. In this study the cold periods were the most stable as well the PM_{10} and CO pollutants had high concentrations. Between these two pollutants the correlation is high because their sources are the same: transport and biomass burning. The study of hourly averages highlighted the importance of traffic intensity since the concentration variation follows the traffic intensity. An increase in the wind speed in the basin results in the pollutants concentrations decrease, the negative correlation with the temperature indicating the importance of the photochemical processes.

Keywords: atmospheric stability, Monin - Obukhov length, Richardson number, SRDT method, particulate matter, carbon monoxide

The stable boundary layer is long known for causing increasing concentration of pollutant [1-3] and plays the most important role in the transport and dispersion of air pollutants [4,5]. When the atmosphere is stable near the surface, pollution builds up, since air parcels cannot accelerate out of the stable layer to disperse the pollution, and when the atmosphere is unstable, emitted pollutants accelerate vertically, decreasing their concentration near the surface [6]. Many researchers studied the atmospheric stability and associated variation of ambient pollution concentrations [7,8]. In this paper the studied gaseous pollutants are CO (carbon monoxide) and PM_{10} (particulate matter with size smaller than 10 μm). The atmospheric stability can be determined with theoretical and empirical methods, including the Richardson number, Monin-Obukhov length, Pasquill-Gifford stability classification, Turner method, SRDT method [9-12]. These are based on the relative importance of convective and mechanical turbulence in atmospheric motion.

The pollutant concentration in the atmosphere is particularly important also taking into account the limit values set in the European Union by the First Daughter Directive to the Air Quality Framework Directive, which addresses both the annual average concentration of PM_{10} (40μg/m^3) and its daily average concentration (50 μg/m^3), to be exceeded no more than 35 times a year). In the European Union, the current target value for carbon monoxide concentration is measured as a maximum daily mean of 8 h averages is 1000 μg/m [13-14].

One study showed the concentration of PM_{10} in Rome is often higher, particularly during the winter season: in 2005 the yearly average of PM_{10} concentration the number of daily accidences was between 90 and 130 μg/m^3 [15]. The pollutants high concentrations and the atmospheric stability intensity are in positive correlation [6, 16]. Another study established that the wind speed is insignificant when the atmosphere is stable or neutral and also the PM_{10} concentration is high [10]. High levels of pollution throughout most of the year as well as high PM_{10} levels in winter and high O_3 levels in summer were reported in Santiago city [17]. Some researchers shown that the stable atmosphere in the winter and spring seasons exhibits also high concentration of PM_{10}

Furthermore in summer and autumn seasons the PM_{10} pollutant has low concentration.tg. The source of CO pollutant mainly derives from traffic, whereas in the winter season the biomass burning contributes to the CO emissions [18]. Other studies revealed that the CO pollutants accumulate if the atmosphere is stable [14].

In this study it is showed the Ciuc basin atmosphere stability with theoretical and empirical methods (Richardson number, Monin-Obukhov length, SRDT method), respectively the pollutants relationship between CO and PM_{10} in the atmosphere, meteorological parameters (wind speed, temperature) as well the atmospheric stability in one year period.

Experimental part

The Ciuc basin is situated in the center region of the East Carpathians, where the tectonic valley occupies the South section of this Carpathians has 60 km length and is 10-12 km large, that is 680 km^2 large area, respectively it has the following coordinates: latitude 46°30' N - 46°10' N, longitude 25°40' E - 26°00' E [19]. The bowl-shaped basin has a unique microclimate [20]. The sampling place is Miercurea Ciuc (latitude: 46°21'28.80'' N and longitude: 25°48'14.40" E; altitude: 662 m) and its suburb, Jigodin (latitude: 46°20'22.79" N and longitude: 25°48'26.95" E; altitude: 717 m).

The studied period was from 21 March 2012 till 20 March 2013, the data were provided by two measuring stations of Harghita County Environmental Agency, an urban-type measuring station in Miercurea-Ciuc and regional

* *email: me_craciun@yahoo.com*

background pollutants automatic measuring station in Jigodin.

The PM_{10} sampled using an Automatic analyzer $LSPM_{10}$ 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 C hourly data was recorded by the MONITOR EUROPE-ML 9830B. The air temperature is measured with the TS Thermometer sensor, which is able to detect temperature between -30 and +50 °C. This device is placed two meters above the ground and the solar radiation data is recorded by ORION – Mod SR-S sensor. 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). The processed data were validated by the Harghita County Environmental Agency.

Results and discussions

Kinematic turbulent flux changes

The atmospheric turbulence is composed of the mechanical and thermal turbulence, whose initial source is the surface roughness and the atmospheric stability conditions.

In the surface layer, kinematic turbulent ûux is often evaluated by Monin–Obukhov similarity theory [21-22]. Monin- Obukhov length is a length scale (m) proportional to the height above the surface at which buoyant production of turbulence first dominates mechanical (shear) production of turbulence[12,21,23]. Mathematically,

$$L = -u_*^3 \frac{\rho_a \cdot Cp_a \cdot T}{k \cdot g \cdot q_H} \qquad (1)$$

$$u_* = k \cdot u \left[\ln\left(\frac{z-d}{z_0}\right) - \psi_m\left(\frac{z-d}{L}\right) + \psi_m\left(\frac{Z_0}{L}\right)\right]^{-1} \qquad (2)$$

where u* is the friction wind speed, ρ_a is the air density, Cp_a is the specific heat at constant pressure, T is the air temperature, K, k =0.4 is the von Karman constant, g = 9.80665 m s^{-2} is the acceleration of gravity, q_H is the sensible heat flux and $\psi_m(\xi)$ is the integral from of universal stability correction functions for the momentum.

The non-iterative method is the Richardson number, and this is used for practical application in meteorological modeling [6]. This is a turbulence indicator and also an index of stability which is defined as [24]:

$$Ri = \frac{g\left(\frac{\Delta\theta}{\Delta z}\right)}{T\left(\frac{d\bar{u}}{dz}\right)^2} \qquad (3)$$

where, g is the acceleration of gravity, $\frac{\Delta\Theta}{\Delta z}$ is the potential temperature gradient, T is the temperature and $\frac{d\bar{u}}{dz}$ is the wind speed gradient.

And this can be expressed as a function of *z/L* as

$$Ri = \frac{z}{L}\frac{\Phi_h\left(\frac{z}{L}\right)}{\Phi_m^2\left(\frac{z}{L}\right)} \qquad (4)$$

In stable conditions, Φ_h and Φ_m are expressed as linear function of *z/L* [25] Golder's curves are based on the relation:

$$\Phi_m = \Phi_h = 1 + \beta\frac{z}{L} \qquad (5)$$

where β is a constant and $\psi_m = \psi_h$.

The Richardson number is related with the dynamic stability and turbulence, i.e., when the value of Richardson number increases, the atmosphere will become more stable and when it decreases, the atmosphere will become unstable [26].

Other empirical measures of atmospheric stability are the Pasquill-Gifford stability class and the solar radiation/ delta temperature (SRDT) method [27]. The Pasquill-Gifford method is an early scheme for classifying stability from very unstable (A) to neutral (D) and very stable (G) based on wind speed and cloud cover at night, as well as wind speed and incoming solar radiation during the day [9, 27]. Daytime stability classes were determined by wind speed and solar radiation, with incoming solar radiation defined as slight for flux values <300 W/m^2 and strong for values >600 W/m^2. Nighttime stability classes were determined from wind speed and cloud cover [9]. Pasquill-Gifford stability was also determined using the SRDT method. This method uses wind speed and solar radiation for daytime stability, and wind speed and vertical air temperature gradient for nighttime stability [27].

The Monin-Obukhov length analysis highlighted that the atmosphere is unstable in 28.81%, stable in 29.60% and extremely stable in 41.52%. The atmospheric stability varies as follows: in the colder months (November-March) it is unstable, but in warmer months (April-October) it is stable. Richardson number stability classification schemes have been developed based on Businger-Hicks formula [28]. Resulting 14.39% are unstable, 58.36% neutral and 27.25% stable. Monthly stability classes are distributed relatively equal during the studied year, although in the colder months (October-February) slight increase in stability can be observed (fig. 1).

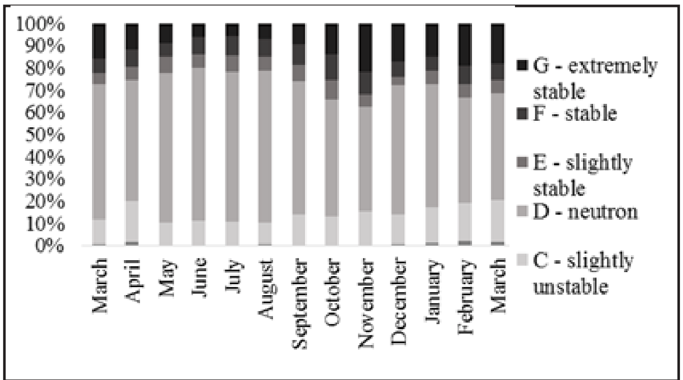

Fig.1. Monthly variation of Richardson number

The empirical methods divide the data to day and night categories, i. e., the atmospheric stability is highly unstable (convective) and neutral at daytime, whereas it is neutral or stable at night. This is an obvious difference between the theoretical and empirical methods mentioned before. The fact that in the daytime the stable stratification is impossible should be rejected.

In the case of Monin-Obukhov length, the daytime stratification is 27.59% unstable, 28.39% stable and 44.02%, extremely stable while for the Richardson number method the atmosphere is 0.73% unstable, 68.69% neutral and 30.58% stable. With the SRDT method the stratification is 9.99% extremely unstable, 27.79% moderately unstable, 2.25% unstable and 59.66% neutral. The Monin-Obukhov length method leads to the night stratification an in 30.89% unstable atmosphere, 31.89% stable and 37.28% extremely stable, while the Richardson number indicates 2.65% instability, 92.3% neutral stratification and 5.05% stable. The empirical methods analysis resulted stable atmosphere, on the base of the SRDT method the

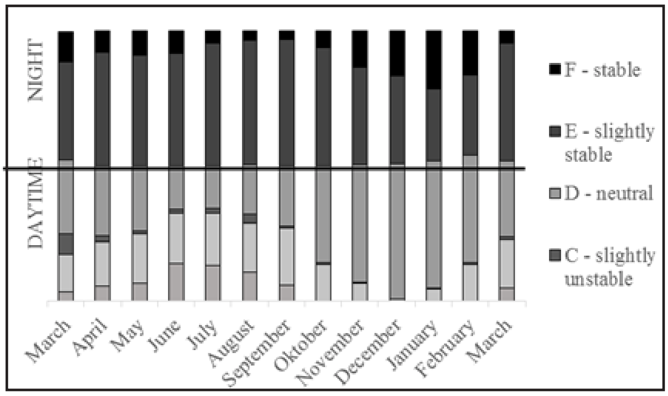

Fig.2. Daily and nightly stability variation on the basis of SRDT method

stratification is 78.69% stable, 19.91% extremely stable and 1.37% neutral (fig.2).

The Richardson number as well as the empirical methods in the colder months (November-February) resulted the same, the atmosphere is extremely stable at night.

Changing of the PM_{10} and CO concentrations

The annual daily average PM_{10} and CO diagram shows that in the colder periods the pollutants concentration are high (fig. 3). This specific property is proved on the seasonal averages diagram (fig. 4), where the PM_{10} and CO pollutants concentration are high in autumn and winter seasons, in spring and summer seasons the concentrations are lower [29]. This is an effect of biomass burning which plays an important role of the pollutants concentration increases [30].

In morning hours the PM_{10} pollutant hourly averages concentration shown increase and between 09:00 and 11:00 h reaches the maximum value. The concentration in the afternoon is decreasing slightly and around 19:00 h can be observed a moderate increase. In the nightly hours the measurements had shown a steady concentration. The CO pollutant has the same behaviour: the maximum values are between 07:00 and 09:00 h , then decreases rapidly until 15:00 when it start a steep increase and over the night is steady [31] (fig. 5).

The correlation between the PM_{10} and the CO concentration is very high (annual: 0.77), which suggests that they are also related to the same traffic source [32]. Incomplete combustion in vehicle engines leads to higher CO and particle emissions [33]. The biomass burning causes on increase in the concentration of this pollutants, so they have a positive correlation [30, 34, 35]. CO and the PM_{10} pollutant concentration negative are in correlation with the wind speed (-0.363 and -0.184), which fact shows the next: the wind speed increase results in a dilution of the pollutants.

The temperature and the pollutant concentration are in negative correlations: in the case of the CO is -0.43, while for PM_{10} is -0.328. The photochemical reactions play an important role in the changes of the pollutant

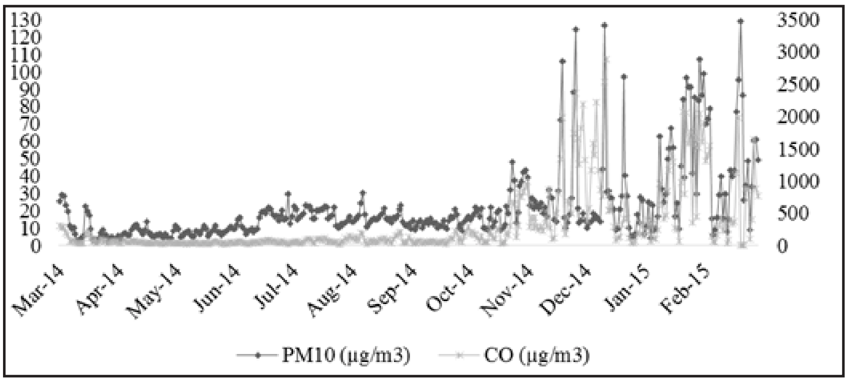

Fig.3. Daily averages of PM_{10} and CO concentrations

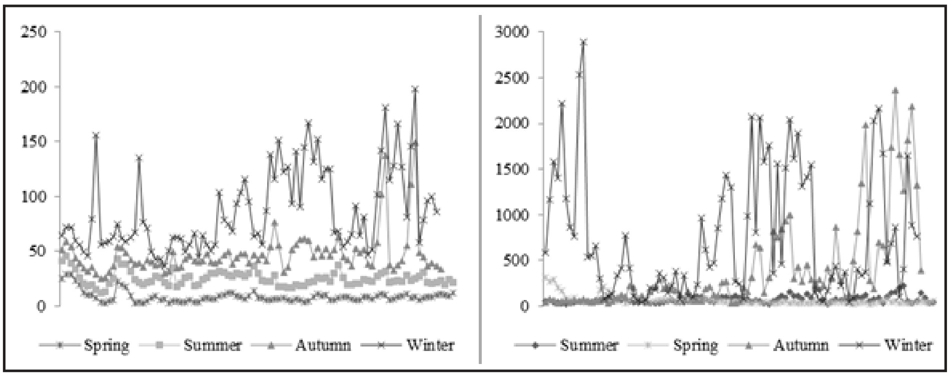

Fig. 4. Seasonal evolution of PM_{10} (left) and CO (right) concentration

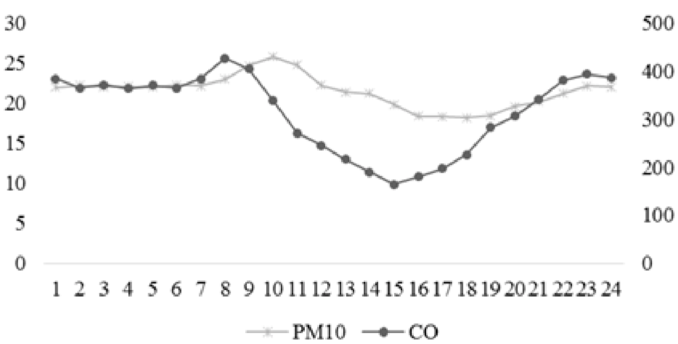

Fig.5. Hourly averages of PM_{10} and CO

concentrations [36]. Namely, major components of PM_{10} include sulfate, nitrate, organic carbon, elemental carbon, soil dust and sea salt [37]. Higher temperature can promote PM formation by increasing the oxidation rates, and the concentration of oxidants in the air. The low temperature contributes to increase of the pollutants especially in winter, when the atmospheric stability is the highest [36, 38].

The negative correlation (-0.43) between the temperature and CO is an effect of CO intensive reactivity which is influenced by the temperature [39]. This fact is also proved by CO and NO_2 positive correlation (0.607), determined Because CO can react with NO_2 as follow: [13]:

$$CO + NO_2 \rightarrow CO_2 + NO \quad (6)$$

The pollutant (CO, PM_{10}) concentration decrease is influenced by the meteorological conditions however, the wind and the low temperature conditions contribute to the atmospheric stability formation, and also to the pollutant concentration increase.

The NO agent resulted in the reaction given by equation (6) reacts further with the O_3 resulting NO_2 and O_2 (equation 7) which can enter in a new cycle, i. e., equations (8) and (9), when M represents a hydrocarbon [40-41]:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (7)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (8)$$

$$O_2 + O + M \rightarrow O_3 + M \quad (9)$$

The stable atmosphere determines its quality, because the atmospheric inversion and the low wind speed create the conditions for the accumulation of pollutants. The atmospheric conditions and the meteorological parameters contribute to the pollutants formation and dispersion. Furthermore, the pollutant emission is an important factor, however in this study the cold period showed that the biomass burning also leads to a higher pollutant concentration.

Conclusions

The PM_{10} and CO pollutant concentration evolution follows the daily vehicle traffic intensity and it was observed that the intensity of the wind influenced this concentration, the pollutants were diluted, and however, there were still high concentration values of PM_{10} and CO pollutants, because the reactions (formation, decomposition) also repeated within the basin microclimate. During the cold period the pollutants are trapped by the effect of stability so the PM_{10} and CO gradually accumulated in the Ciuc basin. The pollutants in the moderately stable and unstable periods continue to be produced and consumed by the influences of the environmental parameters, but no longer show outstanding high concentration values, therefore they are considered less dangerous to human health. In winter some PM_{10} concentrations reaches 120μg/m^3 as well, compared to 50μg/m^3 established threshold, while most of CO concentration values are also two to three times higher than 1000μg/m^3 limit.

Acknowledgements: Particular thanks for the support of Environmental Protection Agency of Harghita for the meteorological and CO, PM_{10} data.

Reference

1. D. PERNIGOTTI, A. M. ROSSA, M. E. FERRARIO, M. SANSONE, A. BENASSI, Meteorol. Z., 16, no. 5, 2007, p. 505–511.
2. S. LEE, H. C. HO, G. Y. LEE, J. H. CHOI, K. C. SONG, Atmos. Environ., no. 77, 2013, p. 430–439.
3. LAZAR, G., CAPATINA, C., SIMONESCU, C.M., Rev. Chim.(Bucharest), **65**, no. 10, 2014, p. 1215
4. M. PIRINGER, A. BAKLANOV, D. K. RIDDER, J. FERREIRA, S. JOFFRE, A. KARPPINEN, P. MESTAYER, D. MIDDLETON, M. TOMBROU, R. VOGT, Bound. - Layer Meteor., vol. 124, no. 1, 2007, p. 3-24.
5. K. ASHRAFI, A. G. HOSHYAARIPOUR, World Acad. Sci. Eng. Technol., no. 2, 2008, p. 143–148.
6. M. Z. JACOBSON, Fundamentals of atmospheric modeling. New York: Cambridge University Press, 2005.
7. M. M. FREY, N. BROUGH, J. L. FRANCE, P. S. ANDERSON, O. TRAULLE, M. D. KING, A. E. JONES, E. W. WOLFF, J. SAVARINO, Atmospheric Chem. Phys., vol. 13, no. 6, 2013, p. 3045–3062.
8. C. D. WHITEMAN, S. W. HOCH, J. D. HOREL, A. CHARLAND, Atmos. Environ., vol. 94, 2014, p. 742–753.
9. M. MOHAN, A. T. SIDDIQUI, Atmos. Environ., vol. 32, no. 21, 1998, p. 3775–3781.
10. S. ZORAS, A. G. TRIANTAFYLLOU, D. DELIGIORGI, J. Environ. Manage., vol. 80, no. 4, 2006, p. 295–302.
11. M. F. YASSIN, Energy Build., vol. 62, 2013, p. 68–77.
12. A. I. PEREZ, A. M. GARCIA, B. TORRE, L. M. SANCHEZ, Ann. Geophys., no. 27, 2009, p. 339–349.
13. C. BAIRD, M. C. CANN, Environmental chemistry, 5th ed. New York: W.H. Freeman, 2012.
14. M. A. POHJOLA, M. RANTAMAKI, J. KUKKONEN, A. KARPPINEN, E. BERGE, Boreal Environ. Res., no. 9, 2004, p. 75–87.
15. C. PERRINO, M. CATRAMBONE, A. PIETRODANGELO, Environ. Int., vol. 34, no. 5, 2008, p. 621–628.
16.SZEP, R., REKA, K., GYORGY, D., TOBA, F., GHIMPUSIAN, M., CRACIUN,M.E., Rev. Chim.(Bucharest), **67**, no. 4, 2016, p. 639
17. E. GRAMSCH, F. CERECEDABALIC, P. OYOLA, D. VONBAER, Atmos. Environ., vol. 40, no. 28, 2006, p. 5464–5475.
18. R. VECCHI, G. MARCAZZAN, G. VALLI, Atmos. Environ., no. 41, 2007, p. 2136–2144.
19. A. KRISTO, An environmental assessment of the Ciuc Basin, Csiki Zold Fuzetek, 1994, p. 7–26.
20. O. BOGDAN, E. NICULESCU, Factors and pedogenetics processes from temperate area, 2004, p. 3–115.
21. S. A. MONIN, M. A. OBOKHOV, Contrib. Geophys. Inst. Acad., 1954, p. 163–187.
22. L. CVITAN, N. SINIK, Z. B. KLAIC, Meteorol. Appl., vol. 9, no. 4, 2002, p. 423–432.
23. *** EPA, „AERMOD Description of model formulation, EPA-454/R-03-004. Research Triangle Park, NC". 2004.
24. M. SHARAN, T. V. B. P. S. RAMA KRISHNA, J. PANDA, Atmos. Environ., vol. 39, no. 30, 2005, p. 5619–5623.
25. A. J. BUSINGER, C. V. WINGAARD, Y. IZUMI, F. E. BRADLEY, J. Atmos. Sci., no. 28, 1971, p. 181–189.
26. W. C. CHIANG, K. S. DAS, Y. C. LIN, B. J. NEE, H. S. SUN, W. H. CHIANG, J. M. YU, T. S. ZHANG, J. Atmospheric Sol.-Terr. Phys., no. 89, 2012, p. 40–47.
27. *** EPA, Meteorological Monitoring Guidance for Regulatory Modeling Applications. Reasearch Triangle Park, NC 27711, EPA-454/R-99-005, February, 2000.
28. L. SEDEFIAN, E. BENNETT, Atmos. Environ., no. 14, 1980, p. 741–750.
29. M. D. MARKOVICY, A. D. MARKOVIC, A. JOVANOVIC, L. LAZIC, Z. MIJIC, Atmos. Environ., no. 145, 2008, p. 349–359.
30. W. J. COLLINS, Effect of stratosphere-troposphere exchange on the future tropospheric ozone trend, J. Geophys. Res., vol. 108, no. D12, 2003.
31. V. GVOZDIC, E. ANDRIC-KOVAC, J. BRANA, Environ. Model Assess., no 16, 2011, p. 491–501.
32. P. E. SAIDE, G. R. CARMICHAEL, S. N. SPAK, L. GALLARDO, A. E. OSSES, M. A. MENA-CARRASCO, M. PAGOWSKI, Atmos. Environ., vol. 45, no. 16, 2011, p. 2769–2780.
33. W. WANG, F. CHAI, K. ZHANG, S. WANG, Y. CHEN, X. WANG, Y. YANG, Air Qual. Atmosphere Health, vol. 1, no. 1, 2008, p. 31–36.

34. S. SAARIKOSKI, M. SILLANPÄ, M. SOFIEV, H. TIMONEN, K. SAARNIO, K. TEINILÄ, A. KARPPINEN, J. KUKKONEN, R. HILLAMO, Atmos. Environ., vol. 41, no. 17, 2007, p. 3577–3589.
35. S. SILLAPAPIROMSUK, S. CHANTARA, U. TENGJAROENKUL, S. PRASITWATTANASEREE, T. PRAPAMONTOL, Chemosphere, vol. 93, no. 9, nov. 2013. p. 1912–1919.
36. N. GALINDO, M. VAREA, J. GIL-MOLTO, E. YUBERO, J. NICOLAS, Water. Air. Soil Pollut., vol. 215, no. 1–4, febr. 2011, p. 365–372.
37. F. AMATO, M. PANDOF, M. VIANA, X. QUEROL, A. AlASTUEY, T. MORENO, Atmos. Environ., no. 43, 2009, p. 1650–1659.
38. M. AKYUZ, H. ÇABUK, J. Hazard. Mater., vol. 170, no. 1, 2009, p. 13–21.
39. D. D. EBBING, D. S. GAMMON, General Chemistry. Ninth Edition. Boston, 2007.
40. S.-B. LEE, Correlation between Light Intensity and Ozone Formation for Photochemical Smog in Urban Air of Seoul, Aerosol Air Qual. Res., 2010.
41. S. HAN, H. BIAN, Y. FENG, A. LIU, X. LI, Z. FANG, X. ZHANG, Analysis of the relationship betwen O_3, NO and NO_2 in Tianjin, China, no. 11, 2011, p. 128–139.

Manuscript received: 23.09.2016