NO_2 SEASONAL AND INTERANNUAL VARIABILITY IN UKRAINIAN INDUSTRIAL CITIES

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ABSTRACT

The paper aims to define the main features and principles of seasonal and interannual NO_2 variations in Ukrainian industrial cities. Using ground-based measurements for 15-year period, it shows weak NO_2 seasonal variability that could intensify in case of three regularities. These regularities depend on impact of natural conditions during anthropogenic emissions growth and redistribution between emission sources. Most industrial cities are characterized by positive trends even if stationary industrial emissions fall. NO_2 interannual changes forms under variety of fluctuations. However, 6.2- and 9.3-year periods have the biggest impact and might be explained by low-frequent lunar tidal forces through its influence on meteorological conditions.

Keywords: NO_2 emissions, industrial cities, seasonal variability, interannual variability, trend

1 INTRODUCTION

Nitrogen dioxide (NO_2) is one of the most dangerous atmospheric compounds for human health [1]. Huge anthropogenic role in NO_2 content increasing is the reason of great society attention to its temporal and spatial distribution [2, 3]. NO_2 seasonal variations do not coincide in different areas [4, 5, 6, 7, 8, 9, 10], thus analysis of seasonality formation helps to understand the main reasons of maximal values emergence. The biggest influence that drive NO_2 seasonal dynamics has combustion of fossil fuels (industry and traffic) [11]. Biomass burning [12], lightning, microbiological activity [12, 13] and other natural sources are not determinative. Temporal distribution and power of each emission source could cause different NO_2 seasonal variations. The study presents analysis of seasonal NO_2 dynamics in industrial cities with regularities that indicate seasonality smoothing or emergence.

Interannual variability forms under changes in meteorological conditions [14]. However, periodicity of nitrogen oxides changes still is controversial question, because of short life-time [15,16] and considerable spatial heterogeneity, especially in big industrial cities and regions with large anthropogenic emissions [6, 17]. The study aimed to define spectrum of significant NO_2 interannual fluctuations that observed in Ukrainian industrial cities. Knowledge about interannual periodicity allow to find regularities of NO_2 distribution on global scale, its chemical feedbacks and interaction between atmospheric air composition and meteorological parameters.

The most investigated interannual changes connected with NO_2 trends, which rapidly grow in urban areas [6, 8, 9, 19]. Permanent changes of anthropogenic emission sources in industrial cities cause difference in NO_2 tendency and have to be analyzed unceasingly. It will help to delimit areas with high pollution level or areas with high probability of natural changes which are favorable of nitrogen oxides accumulation.

2 DATA AND METHODOLOGY

Monthly ground-based NO_2 data involved for analysis and were averaged in 14 industrial cities rather even distributed on the territory of Ukraine (Fig. 1). Denser distribution selected for regions with high pollution level. Total period in research cover 15 years from 2000 till 2014, which allowed to divide on three five-year' periods (2000 – 2004, 2005 – 2009, 2010 – 2014) and make analysis of short-term variations within them.

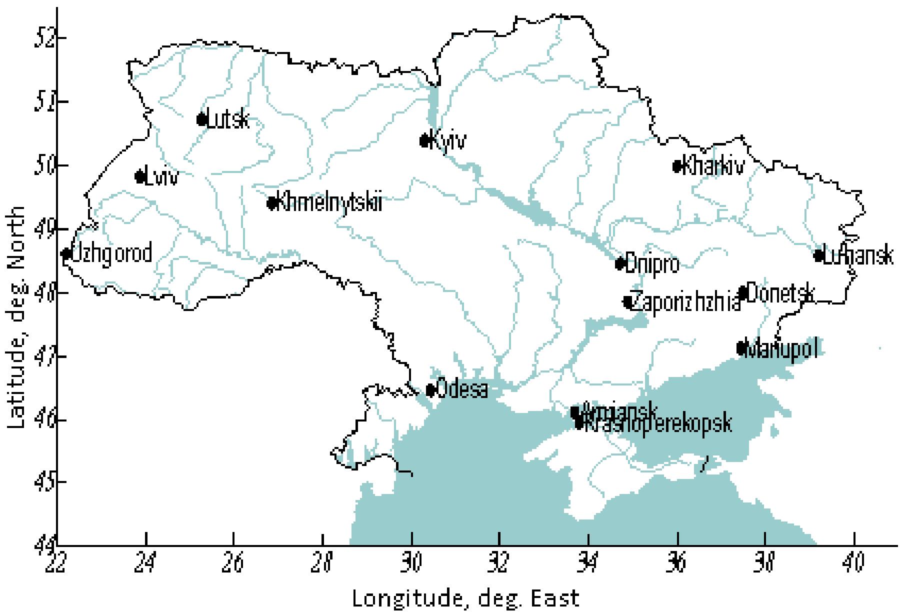

Figure 1. Spatial distribution of cities involved in research

Seasonal variations were calculated as sum of first five significant harmonics obtained from Fourier analysis (1), where Fourier coefficients defined using least squares method.

$$f(t) = \sum_{n=1}^{5} A_n \cos(\omega_n t - \varphi_n) \tag{1}$$

where

A_n - amplitude,

ω_n - frequency, and φ_n - phase of *n*-harmonic,

t – time.

Conclusion about harmonic's significance made using Student test with $\alpha = 0.05$. However, seasonal variations are considered as weak, if determination coefficient R^2 do not exceed 0.50; and absent in case of $R^2<0.5$ with insignificant Student test.

Trends and interannual variations were analyzed on residuals of seasonal variations after average values removal from time series. Interannual variations were also calculated using Fourier analysis for 130 equally distributed frequencies. The most significant separate variation had been calculated and its impact removed from the residuals. After this procedure Fourier analysis applied again while any significant fluctuation exists.

3 RESULTS AND DISCUSSION

Understanding the role of different emission sources in NO_2 dynamics is not easy for Ukrainian industrial cities. The main problem lies in quality of anthropogenic sources inventory. For stationary sources, e.g. factories, fossil-fuel power stations etc., inventory reports in Ukraine rather well reflect air pollution [20], but there are no such quality inventories for traffic emission.

To cope with this problem, preliminary analysis for Kyiv city was made. Kyiv has the biggest air pollution measurement network and consist of 16 stations. It was found, that maximal values in winter – early spring are typical for all stations with high traffic pollution. Summer maximal values observed on two stations in rather clean areas (Hydropark and Nauky Avenue), which are typical for natural NO_2 changes [9, 10]. It means that meteorological conditions and land cover type on quite clean territories within cities could change seasonal variability. Six stations in Kyiv have both of these maximal. Therefore, distribution of anthropogenic sources within industrial cities cause different types of seasonality.

Seasonal variability

NO_2 seasonal variations in cities are absent and determination coefficients usually do not exceed R^2=0.10. Therefore, availability of seasonal variations in NO_2 fluctuations evokes particular interest. For general period 2000 – 2014 statistically significant seasonal variations observed only in Kharkiv with R^2=0.47 and could be considered as weak (Fig.2). First harmonic (1-year period) has the biggest influence with 83% impact on total dispersion. The highest concentration observed in late spring, and phase falls on 149th Julian day.

Figure 2. Average NO_2 seasonal variations in Kharkiv for 2000 – 2014

Despite Kharkiv is big city with approximately 1.5 million inhabitants, the average NO_2 concentration is only 0.03 mg/m^3 compared with 0.12 mg/m^3 in Donetsk or 0.09 mg/m^3 in Kyiv. On one hand, it is possible to make assumption that power of anthropogenic emissions is the main reason of seasonality smoothing in industrial cities. On the other hand, in Luhansk seasonal variations are absent with R^2=0.04, but average NO_2 concentrations are also low (0.03 mg/m^3). Therefore, NO_2 seasonality formation in industrial cities is more complicated than only dependence from the power of anthropogenic emissions.

Division of general period on three five-year intervals (2000 – 2004, 2005 – 2009, 2010 – 2014) and analysis of seasonal variations within them allowed to find features in NO_2 seasonality formation. Number of cities, where seasonal variations are significant, have been increased. During 2000 – 2004 there were no cities with clear seasonal fluctuations. The highest determination coefficients reached R^2=0.36 in Kharkiv, R^2=0.32 in Lutsk and R^2=0.30 in Lviv. Average concentrations varied from 0.03 mg/m^3 in Kharkiv, Lviv and Luhansk to 0.08 mg/m^3 in Kyiv and Donetsk.

During 2005 – 2009 significant variations appeared in Kharkiv with R^2=0.58. Average concentrations increased in 8 cities to 0.09–0.13 mg/m^3.

Seasonality significance had been increased during 2010 – 2014 period. Weak seasonal variations observed in Kyiv, Odesa, Kharkiv, Lutsk and Donetsk, but determination do not exceed R^2=0.50. Average concentration in Donetsk reached 0.14 mg/m^3.

Such abrupt seasonality emergence caused by three main regularities which depend on NO_2 content. First regularity exists for cities with strong anthropogenic emissions. Seasonality appears if average concentrations are high and constantly increase. It is well observed in Kyiv where concentrations changed from 0.08 to 0.10 mg/m^3, Lutsk – from 0.05 to 0.09 mg/m^3 and Donetsk – from 0.08 to 0.14 mg/m^3. If NO_2 content is not so high, any increasing does not entail changes in seasonality.

In case of low or moderate NO_2 concentrations, an opposite effect is observed, and thus the second regularity acts – seasonality appears if concentrations continue to decrease constantly. In Odesa average concentrations fell from 0.07 mg/m^3 (2000–2004) to 0.05 mg/m^3 (2010–2014) and determination coefficient increased from R^2=0.07 to R^2=0.49. Slight changes in NO_2 content in Kharkiv possibly coincide with R^2 changes.

Both regularities represent the same idea: seasonality become stronger if prevailing anthropogenic emission source become more powerful: in highly polluted industrial cities with NO_2 content increasing and in less polluted cities with NO_2 concentrations decreasing.

The third regularity is connected with redistribution of emission sources. In this case, amplitudes or average values may not change. The best indicator of such type changes is phases shift. Of course, phases shift does not exist in polluted industrial cities with high NO_2 content. In Kharkiv with concentrations less than 0.033 mg/m^3 phases constantly shift on 14 days every 5 years (from 121 to 149 Julian day) which coincide with seasonality emergence. In Lviv with concentrations less than 0.047 mg/m^3 phases shifted from 227th day to 107th day and determination coefficient decreased from R^2=0.30 to R^2=0.07. Three curves on Fig. 3 represent NO_2 seasonal variations for 3 five-year' intervals based on first harmonic. Phase shift coincides with amplitude decreasing and seasonality smoothing, which relates to redistribution of NO_2 emission. With average values increasing it is possible to make conclusion about intensification of definite anthropogenic emission and its preponderance in comparison to other sources. If anthropogenic emissions become more powerful, maximal values shifts from summer to winter-spring.

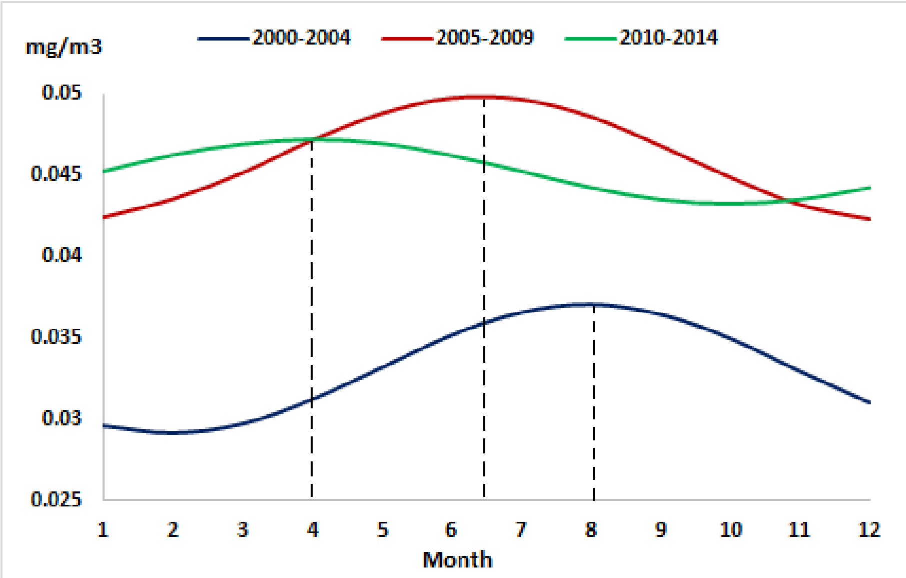

Figure 3. Phase shifts and seasonal NO_2 variability in Lviv for 3 five-year' intervals

Redistribution between emissions usually observed in case of low concentrations. With NO_2 content increasing such regularity lose its power. In case of high concentrations, caused by anthropogenic emission, phases shift connected only with adding or cessation of separate industrial sources, e.g. factory building in cities with high NO_2 emission from transport. Direction of phase shifts show the intensification/ weakness of anthropogenic sources.

Trends

Almost all industrial cities in Ukraine have significant trends of NO_2 concentrations. Fisher test showed tendency absence in Mariupol, Uzhgorod and Luhansk. Most trends are positive, even if emission from stationary sources decreased [20]. It means that traffic emissions have crucial impact on NO_2 distribution in Ukrainian industrial cities.

There are two negative trends: in Odesa and Kharkiv with values -0.01 mg/m^3 per decade. Determination coefficients are R^2=0.18 and R^2=0.21 respectively (Fig. 4). The highest positive trend reached 0.07 mg/m^3 per decade in Donetsk city with R^2=0.48 (Fig. 5). For other industrial cities values vary from 0.01 to 0.03 mg/m^3 per decade with determination within R^2=0.05…0.55 interval.

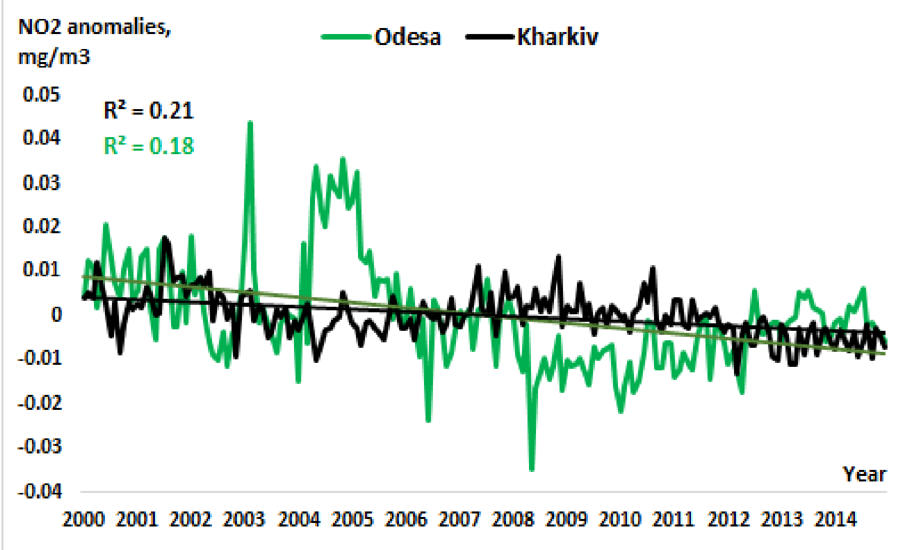

Figure 4. NO_2 negative trends in Odesa and Kharkiv

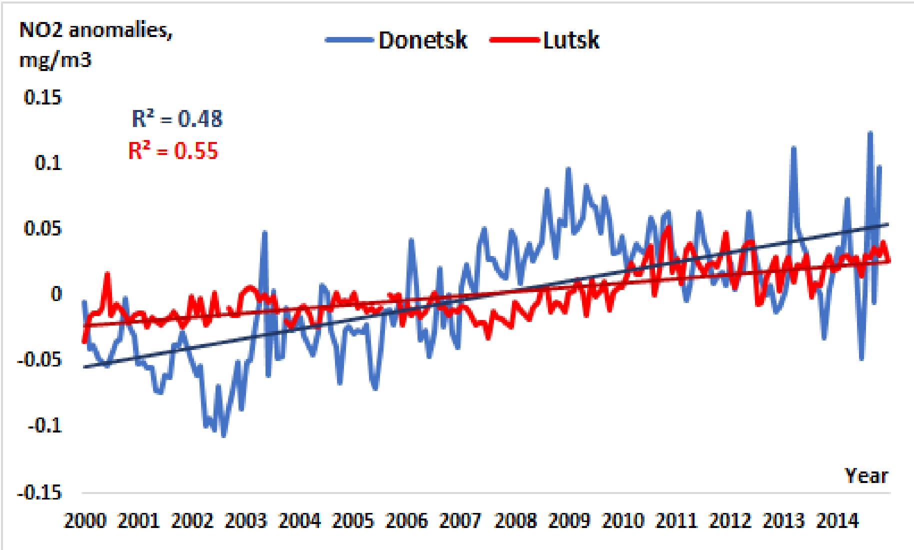

Figure 5. NO_2 positive trends in Donetsk, with the highest trend value, and Lutsk, with the highest trend determination coefficient

Trends existence for each month (monthly trends) is typical for cities with high positive trends. In Lutsk and Donetsk every month is characterized by a constant NO_2 increase. In Donetsk maximal monthly trend observed in August with 0.10 mg/m^3 per decade. The lowest reached 0.05 mg/m^3 per decade during autumn months. In Lutsk monthly trends vary from 0.02 to 0.05 mg/m^3 per decade.

In Lviv, Zaporizhzhya and Krasnoperekopsk monthly trends show significance for 10 months. Trends values are higher in Zaporizhzhya and Krasnoperekopsk (0.02 – 0.03 mg/m^3 per decade) and lower in Lviv (0.01 – 0.02 mg/m^3 per decade). There are no trends for August and September in Lviv, for May and June in Zaporizhzhya, for October and November in Krasnoperekopsk.

In Kharkiv and Odesa monthly trends are negative as its general trends. Significant monthly trends in Odesa observed from November till April and vary from -0.01 mg/m^3 per decade to -0.02 mg/m^3 per decade. In Kharkiv monthly trends are significant in June, December and February – April with values -0.01 mg/m^3 per decade.

Despite most industrial cities have trends, there are no dependence and regularities in monthly trends. It means that tendency of NO_2 emissions in industrial cities is unique for each city and depend on the processes within it.

Interannual variability and spectrum of fluctuations

According to slight seasonality, interannual variability is the only changes connected with natural forces. Significant interannual variations explain from 29 to 61% of residuals dispersion, however, there are no dependence withNO_2 content. The highest determination coefficients of interannual dynamics reached 0.61 in Lviv, 0.60 in Dnipro (Fig. 6) and 0.55 in Armyansk. Less clear interannual variations observed in Zaporizhzhia, Uzhgorod and Krasnoperekopsk with R^2=0.29…0.31.

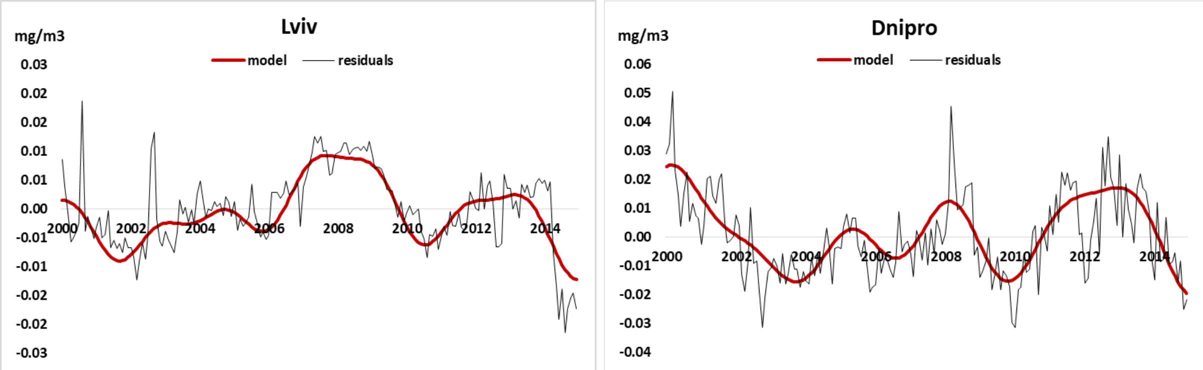

Figure 6. Interannual NO_2 variability in cities with the highest determination coefficients of models

Types of variations are rather different, but majority of them combine in separate groups. The most significant variations could be connected with tidal forces, because of the approximate periods of 6.2 and 9.3 years. These periods coincide with overtones of 18.6-year lunar nodal tidal cycle. 6.2-years fluctuations are the biggest in Uzhgorod (R^2=0.31), Dnipro (R^2=0.25) and Krasnoperekopsk (R^2=0.19) with 0.01 mg/m^3 amplitudes. In Lviv, Khmelnytskiy and Zaporizhzhya 6.2-year fluctuations have lower impact with R^2 less than 0.1. NO_2 interannual dynamics are characterized by maximum values in 2000 – 2001, 2006 – 2007 and 2012 – 2013 in all mentioned cities except Uzhgorod, where variations were opposite. First overtone (9.3 years) of lunar nodal tidal cycle has the biggest impact in Kyiv (R^2=0.31), Lutsk (R^2=0.29) and Odesa (R^2=0.25) with amplitudes from 0.01 to 0.02 mg/m^3. In this case NO_2 differ and maximal positive deviation observed in 2002 in Lutsk, 2004 in Odesa and 2005 in Kyiv. Surely, these forces do not act directly on the NO_2 concentrations. Interannual variability in wind and temperature distribution, connected with lunar nodal tidal cycle [21, 22, 23], caused changes in meteorological conditions and possibility to NO_2 accumulation in the atmosphere.

Another big group of variations is situated within higher frequency spectrum with approximately 2.6 – 3.4 years' period. Generally, 7 out of 14 researched cities have these fluctuations, but impact is lower with determination coefficients within R^2=0.05…0.14. The highest amplitude is 0.01 mg/m^3.

It was found another four groups of interannual fluctuations: with periods 2 – 2.2 years (4 cities), 3.8 – 4 years (3 cities), 4.3 – 4.5 (4 cities) years and 5.2 years (Lutsk and Donetsk only). The most powerful are variations 4.3 – 4.5 years with determination coefficients R^2=0.07…0.24. They observed in Odesa, Lviv, Mariupol and Armyansk. These fluctuations have the biggest impact in Mariupol and explain up to 20% in total dispersion. 3.8 – 4-year variations with 11–14% impact in total dispersion are typical for Dnipro, Luhansk and Krasnoperekopsk.

Other variations do not form any group and distribute separately in spectrum. For some cities these separate fluctuations have the biggest impact up to 45% in Armyansk, 43% in Kharkiv, 34% in Donetsk, 30% in Khmelnytskii and Lviv, 15% in Luhansk.

4 DISCUSSION

NO_2 seasonal changes in industrial cities depend on predominant emission sources and clarity of fluctuations varies in time with emission changes. Maximal values are typical for winter in industrial regions and polluted areas, due to cold-started vehicles and residential heating [5, 9, 24], inversions and lower temperatures [5]. In more "clean" areas summer maximal is usual [9, 10, 18]. Our study finds three regularities of seasonality changes in industrial cities. However, maximal values on some territories may be observed in winter [6, 9, 17], summer [8, 9, 10, 17] and spring [7, 8].

NO_2 in most industrial cities increase, even if pollution from stationary sources decrease. This fact showed that traffic emission has crucial impact on NO_2 distribution. NO_2 positive trends observed in other urban areas [6, 8, 9, 18, 19] and dependence from vehicles were proved [6, 7, 8, 25]. NO_2 interannual variability caused by natural forces. Changing meteorology (winds, temperatures, humidity and clouds) on a global scale drive interannual variability of NO_2 [14]. As our research show, meteorological variations caused by low-frequent lunar tidal forces could be the reason of 6.3- and 9.2-year fluctuations, which have the biggest impact on interannual NO_2 variability.

CONCLUSIONS

Seasonal NO_2 variability in Ukrainian industrial cities is weak and usually there are no significant seasonality. However, it could appear if one of three regularities act. They are constant NO_2 content increasing in cities with high pollution level, constant NO_2 content decreasing in cities with low pollution level, and phases shift in case of low concentrations. All regularities act if prevailing emission source become more powerful or in case of its redistribution.

Positive NO_2 trends are typical for most cities, even if emission from stationary sources decreased. It represents crucial role of traffic emissions. The highest positive trend reached 0.07 mg/m^3 per decade. Trends for each month do not have any regularities, which reject any natural reasons of trends formation.

Spectrum maximal of interannual NO_2 fluctuations coincide with period of 6.2 or 9.3 years. It could be the reaction on meteorological changes under influence of lunar nodal tidal forces. Another significant variation combines in separate groups. In general, all interannual variability explains from 29 to 61% of residuals dispersion.

REFERENCES

[1] SOURKOVA, G. *Chemistry of the atmosphere*. Moscow: Moscow University Press, 2002, 210 p.

[2] DIRECTIVE 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. In *Official Journal of the European Union*, L 152, pp. 1-44. Available from: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0050&from=en

[3] WHO. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Summary of risk assessment. [online] 2005 [cited 2017-06-30]. Available from: https://apps.who.int/iris/bitstream/handle/10665/69477/WHO_SDE_PHE_OEH_06.02_eng.pdf;jsessionid=1561BBB0A3C888FF985E11EE9E1570B7?sequence=1

[4] DVORETSKA, I. et al. The main characteristics of nitrogen dioxide seasonal-latitude's distribution over the territory of Ukraine by ground-based and satellite measurements data. *Phisychna Geographia i Geomorfologia.* 2014, 76, pp. 81-87.

[5] HAGENBJORK A. et al. 2017. The spatial variation of O_3, NO, NO_2 and NO_x and the relation between them in two Swedish cities. *Environ. Monit. Assess*. 2017, 189(4), pp.161.

[6] KHOKHAR, M. et al. Detection of Trends and Seasonal Variation in Tropospheric Nitrogen Dioxide over Pakistan. *Aerosol and Air Quality Research.* 2015, 15, pp. 2508-2524.

[7] MULLA, E. et al. Seasonal variation of NO2 and SO2 concentrations in Tirana's Air. *J. Int. Environmental Application & Science.* 2013, Vol. 8, pp. 272-279.

[8] SNIZHKO, S. and O. SHEVCHENKO. *Meteorological Aspects of Air Pollution of Urban Areas*. Kyiv: Obrii Publishing House, 2011.

[9] VAN DER A., R.J. et al. Detection of the trend and seasonal variation in tropospheric NO2 over China. *Journal of Geophysical Research.* 2006, Vol. 111, D.12. Available from: https://doi.org/10.1029/2005JD006594

[10] VAL MARTIN, M. et al. Seasonal variations of nitrogen oxides in the central North Atlantic lower free troposphere. *Journal of Geophysical Research*, 2008, Vol. 113, D 17. Available from: https://doi.org/10.1029/2007JD009688

[11] OLIVIER, J. et al. Global Air Emission Inventories for Anthropogenic Sources of NO_x, NH_3 and N_2O in 1990. *Environ. Pollut*. 1998, 102, pp. 135-148.

[12] SEINFELD, J. and S. PANDIS. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. New York: Whiley, 2008.

[13] LEE, D. et al. Estimation of Global NO Emissions and their uncertainties. *Atmos. Environ.* 1997, 31, pp. 1735-1749.

[14] VOULGARAKIS, A. et al. Interannual variability of tropospheric composition: the influence of changes in emissions, meteorology and clouds. *Atmospheric Chemistry and Physics.* 2010, 10, pp. 2491-2506.

[15] CRUTZEN, P.J. The Role of NO and NO_2 in the Chemistry of the Troposphere and Stratosphere. *Annu. Rev. Earth Planet. Sci.* 1979, 7, pp. 443-472.

[16] LIANG, J. et al. Seasonal budgets of reactive nitrogen species and ozone over the United States and export fluxes to the global atmosphere. *J. Geophys. Res.* 1998, 103(D11), pp. 13435-13450.

[17] SHEVCHENKO, O., S. SNIZHKO and N. DANILOVA. Air pollution by nitrogen dioxide in Kiev city. *Ukr. Gidrometeorol. Zh*. 2015, 16, pp. 6 – 16.

[18] BASHTANNIK, M. et al. Air pollution state on the territory of Ukraine. *Naukovi pratsi UkrNDGMI.* 2014, Vol. 266, pp. 70-93.

[19] UNO, I. et al. Systematic analysis of interannual and seasonal variations of model-simulated tropospheric NO2 in Asia and comparison with GOME-satellite data. *Atmos. Chem. Phys. Discuss*. 2006, 6, pp. 11181-11207.

[20] Reports of Ministry of Ecology and Natural Resources of Ukraine. [online] 2017 [cited 2017-06-30]. Available from: URL: https://menr.gov.ua/en/timeline/?t=569&th=0&m=2&g=569&from=&till=

[21] BEST, C. and R. MADRIGALI. Observation of a tidal effect on the Polar Jet Stream. *Atmos, Chem. Phys. Discuss*. 2015, Vol.15, pp. 22701 – 22713.

[22] CURRIE, R. Evidence for 18.6-year signal in temperature and drought conditions in North America since A.D. 1800. *J. Geophys. Research.* 1981, Vol. 86, pp. 11055-11064.

[23] SAVENETS, M. et al. Long-term upper wind dynamics: variability and trends. In *Proceedings of the 14th International Conference of Young Scientists on Energy Issues, Kaunas, Lithuania, May 25-26*, 2017, pp. 94-101.

[24] BRALIC M. et al. Monthly and Seasonal Variations of NO_2, SO_2 and Black-Smoke Located Within the Sport District in Urban Area, City of Split, Croatia. *Croat. Chem. Acta.* 2012, Vol. 85, pp.139 – 145.

[25] CHEN, W. et al. Seasonal Variations of Atmospheric Pollution and Air Quality in Beijing. *Atmosphere.* 2005, 6, pp. 1753-1770.