ТЕХНОЛОГИИ ЗА ОПАЗВАНЕ НА ОКОЛНАТА СРЕДА / ENVIRONMENTAL TECHNOLOGY / ТЕХНОЛОГИИ ОХРАНЫ ОКРУЖАЮЩЕЙ СРЕДЫ

MODELS OF AIR POLLUTION WITH NITROGEN DIOXIDE AND NITROGEN MONOXIDE IN ROMANIAN - BULGARIAN BORDER AT TURNU MAGURELE AND ALEXANDRIA

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Abstract: *The results of original research in the levels and dependencies of air pollution on the Romanian territory in the county of Teleorman are presenseted. At firstit is defined the indicators of pollution with nitrogen dioxide and monoxide. A database of two measuring points in Turnu Magurele and Alexandria is created. The data is processed by appropriate software, summarizing the results and drawing conclusions for hourly and daily average concentrations.*

Key words: *nitrogen oxides, pollution, air*

1. Introduction

The problem with the air pollution in Romanian-Bulgarian border is relevant for both the countries. Concentrations of air pollutants within the border areas are not known, because in March 2008 it was stopped the exchange of information between the environmental agencies. Therefore the pollution in recent years is studied and analyzed intensively.

In our studies [1] it was established the dynamics of the change in the maximum concentrations of nitrogen oxides in the Romanian and Bulgarian sections. The maximum values do not describe sufficiently the processes concentrations changes. Furthermore, the arithmetic averages for the relevant periods are used, which are not sufficiently adequate indicator. Average value is obtained based on a number of experimental values received and is only an approximation to the mean.

Nitrogen oxides concentration should be analyzed as random variables. Each concentration is completely determined by the probabilistic terms with the laws of distribution. That is why in [1] it is proved the necessity to establish the theoretical models and empirical statistical distributions in order to derive the numerical characteristics. The average value as a numerical characteristic defining the position of the random variables, such as concentrations and it can be determined only on the basis of the distribution laws.

The purpose of the paper is to derive the theoretical and empirical distributions of hourly (average hourly concentration-AHC) and daily average concentrations (DAC) of nitrogen dioxide (NO_2) and nitrogen monoxide (NO). To achieve this purpose, four main tasks must be solved: 1. Determination of the laws of statistical distribution for which the hypothesis for compliance must be tested; 2. Creation of a data sampling from measured values of the AHC in Turnu Magurele and Alexandria; 3. Computer processing of the measurement results; 4. Determination of the theoretical models and empirical distributions of the concentrations of nitrogen oxides.

2. Models of air pollution with nitrogen dioxide and nitrogen monoxide

AHC is taken as the main indicator of the pollution. It is derived from more than 300 discrete values measured hourly in the station TR1 and TR2 in Alexandria and Turnu Magurele using remote optical - absorption spectroscopy.

The created presentative samples are results measured during the spring season of the year from 20.03.2014 until 06.21.2014. The samples consist the data for the measurements taken during the spring period between 20.03.2014 to 21.06.2014. The data for the average hourly concentration of nitrogen dioxide has 1976 values and 2005 in TR1 and TR2, respectively and 2010 and 2084 values for nitrogen monoxide.

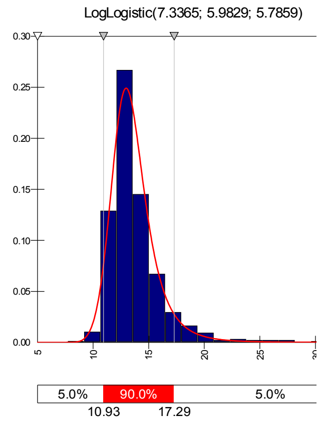
The values selected meet the requirements for validity presented in Ordinance №12 [2].

Based on these samples were obtained the distributions during the day hour by hour, respectively, 82 values for NO_2 and 85 values for NO in TR1 and TR2. These samples are used to calculate the DAC distribution.

A verification of the hypothesis of the 16 laws of statistical distributions of continuous random variables is made: probability law of uniform distribution (Uniform); gamma distribution (Gamma), a normal distribution (Normal); triangular distribution (Triang); log-normal disribution (LogNormal); exponential distribution (Expon), logistic distribution (Logistic); log-logistic distribution (LogLogistic), invariant Gaussian distribution (InvGauss); distribution of Gumbel, Weibull distribution (Weibull), distribution of Rayleigh (Rayleigh); distribution of Pearson (Pearson); distribution of Erlang (Erlang), distribution of the extreme value (ExtValue) - distribution of Wald. The verification is performed by the χ^2 criterion of Pearson. Computer data processing is made on specialized software - Risk 4.5 [3].

Table 1

Hourly average concentrations of nitrogen dioxide in Turnu Magurele



Legend:
— - theoretical distribution;
■ - empirical distribution

Theoretical model / LogLogistic (7,3365; 5,9829; 5,7859)		Empirical distribution
Parameters		
g	7,3365	
b	5,9828	
a	5,7859	
Characteristics		
Left X	10,93	10,93
Left P	5,00%	2,81%
Right X	17,29	17,29
Right P	95,00%	92,75%
Diff. X	6,3556	6,3556
Diff. P	90,00%	89,94%
Minimum	7,3365	7,7606
Maximum	$+\infty$	31,1
Mean	13,6238	13,785
Mode	12,969	12.675
Median	13,3194	13,237
Std. Deviation	2,0988	2,45
Variance	4,4049	5,9936
Skewness	1,9265	2,4596
Kurtosis	16,4358	12,8667

The laws of distribution of the concentrations are regarded as theoretical models that approximate the experimental data. Their graphical interpretations were established (Table 1) as the parameters of the statistical distribution laws (Table 1-4).

Table 2

Hourly averaged concentrations of nitrogen monoxide in Turnu Magurele

Theoretical model Pearson (3.9143;5.9112)		Empirical distribution
Parameters		
m	15,38008	
l	1564,546	
Characteristics		
Left X	5,753	5,753
Left P	5,00%	4,35%
Right X	10,755	10,755
Right P	95,00%	95,65%
Diff. X	5,0025	5,0025
Diff. P	90,00%	91,30%
Minimum	7,2545	5,5215
Maximum	+∞	11,4412
Mean	8,1256	8,1256
Mode	7,9004	9.3469
Median	8,0504	8,0189
Std. Deviation	1,5249	1,5528
Variance	2,3253	2,3064
Skewness	0,2974	0,1349
Kurtosis	3,1475	2,2675

In parallel the empirical distributions were presented. They were illustrated with graphs together with the theoretical distributions - Table 1. 14 numerical characteristics, which define the position of the random variables, variance, and the degree of symmetry and sharpenss of the distribution were used: 1) left and right absolute boundary (Left X and Right X); 2) left and right relative boundary (Left P and Right P in%); 3)The absolute range (Diff. X); 4) relative range (Diff. P in%); 5) Minimum value (Minimum); 6) Maximum value (Maximum); 7) average (Mean); 8) mode (Mode); 9) median (Median); 10) standart deviation (Standart Deviation); 11) variance (Variance); 12) asymmetry (Skewness); 13) kurtosis (Kurtosis). Their values are presented in Tables 1-4.

The results of the concentration measurements are approximated with the corresponding theoretical models of the statistical distribution. They were displayed in measuring stations TR1 and TR2, for the pollutants- NO_2 and NO, on AHC, and DAC in real time and during the day.

Table 3

Daily averaged concentrations of nitrogen dinoxide in Turnu Magurele

Theoretical model Triang (12.1822;17.0544)		Empirical distribution
Parameters		
min	12,18222	
m. likely	12,18222	
max	17,05435	
Characteristics		
Left X	12,306	12,306
Left P	5,00%	13,33%
Right X	15,965	15,965
Right P	95,00%	96,67%
Diff. X	3,6593	3,6593
Diff. P	90,00%	83,33%
Minimum	12,1822	12,1822
Maximum	17,0544	16,6681
Mean	13,8063	13,7036
Mode	12,1822	13.7621
Median	13,6092	13,6692
Std. Deviation	1,1484	1,2051
Variance	1,3188	1,4037
Skewness	0,5657	0,7011
Kurtosis	2,4	2,7339

The theoretical model of AHC of NO_2 in Turnu Magurele is LogLogistic distribution (Table 1). Boundaries of the theoretical and empirical distribution did not differ significantly. The largest values of the minimum value of the empirical distribution are larger than 0,43 $\mu g/m^3$ compared to the theoretical. The maximum values (31,1 $\mu g/m^3$) are considerably smaller than norma. Average value 13,78 $\mu g/m^3$ is too small, and mode and median are very close each other. Variance of the results of theoretical and empirical distribution is approximately 18%. The biggest difference between them is in Variance - Table 1. Skewness and Kurtosis are positive. Distribution is sharper compared to the normal distribution.

Comparing these characteristics to those used in [1] there are significant differences. The use of theoretical models and empirical statistical distributions is more accurate and presents the real level of contamination.

Table 4

Daily averaged concentrations of nitrogen monoxide Studies in Turnu Magurele

Theoretical model LogLogistic (6.7083; 0.4314)		Empirical distribution
Parameters		
a	6,708361	
b	0,431493	
Characteristics		
Left X	5,438	5,438
Left P	5,00%	0,00%
Right X	7,979	7,979
Right P	95,00%	93,33%
Diff. X	2,541	2,541
Diff. P	90,00%	93,33%
Minimum	-∞	5,573
Maximum	+∞	8,305
Mean	6,70836	6,7577
Mode	6,70836	6.2629
Median	6,70836	6,6204
Std. Deviation	0,78264	0,74325
Variance	0,61253	0,534
Skewness	0	0,4726
Kurtosis	4,2	2,2358

For the pollution in Turnu Magurele NO similar laws are seen. The maximum concentrations and average values are lower than the standards for nitrogen oxides. Concentrations are modeled by the law of Pearson. The values of numerical characteristics are more similar compared to NO_2. Larger gap (close to 2 μg/m^3) is only set at the minimum values of the theoretical and empirical distribution.

In Alexandria (TR1) the theoretical model for NO2 concentrations is LogNormal with parameters m = 14,231 and s = 4,4192. Numerical characteristics of the empirical distribution are: LeftX=12,14 μg/m^3, LeftP=3,01%; RihtX=26,28 μg/m^3; RightP=94,99%; Diff.X=4,13 μg/m3; Diff.P=91,98%; Minimum=7,51 μg/m^3; Maximum=42,80 μg/m^3; Mean=18,13 μg/m3; Mode=14.158 μg/m^3; Median=17,43 μg/m^3; Std.Deviation=4,56 μg/m^3; Variance=20,78 μg/m^3; Skewness=1,33 μg/m^3; Kurtosis=6,3 μg/m^3.

Comparing the results with the characteristics of Turnu Magurele in (Table 1) it is seen that the left and right boundaries are larger, and as a result the difference Diff.X is larger. The maximum value is higher (42,80 μg/m^3) and average is below the normal (18,13 μg/m3), and they are comparable. The standard deviation is higher and more significant here is the difference in variance (4-5 times). This is an indicator of instability and shows wide variability of the concentrations. It turns out that the level of air pollution in the urban area of Alexandria is greater than in the industrial zone of Turnu Magurele, located 7-8 km from the town of Nikopol

Table 3 and 4 shows that the theoretical models for DAC for NO_2 and NO in Turnu Magurele differ significantly from the AHC.

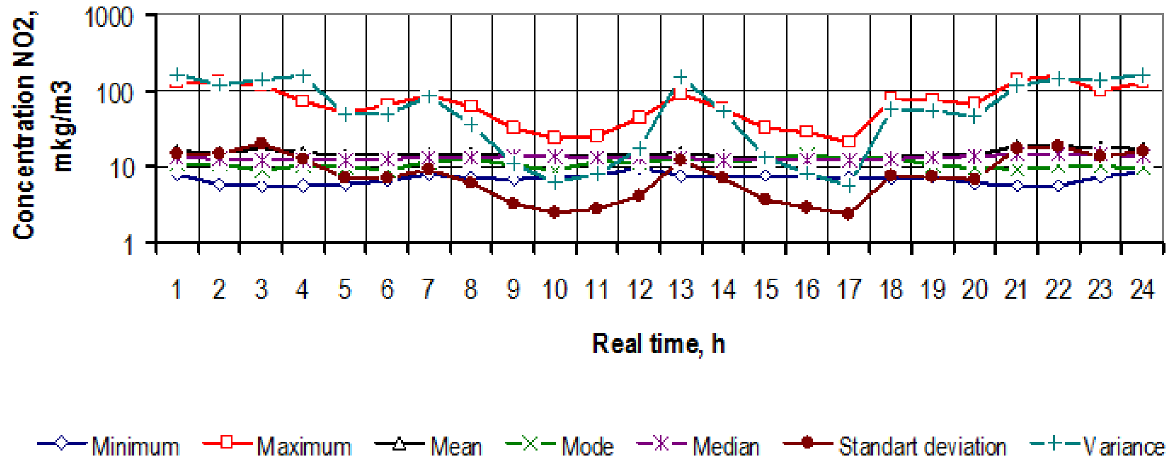
They has respectively triangular distribution Triang (parameter min=12.18; m. likely=18.22; max=17.05) and logistic distribution Logistic (with parameters a=6,7083, b=0,4314). The minimum value of t e DAC of NO_2 is 12,1822 μg/m^3 and is greater than the AHC until the maximum of the averages is lesser 16,66 μg/m^3 (Table 3). The average values for NO_2 are closer. Mode and median are similar. Standard deviation and variance of the average hourly concentration were increased, since the distribution is based on a number of different experiments.

In Turnu Magurele the difference for NO (Table 4) is twice narrowed. Minimum and maximum values are close to hourly averaged values. The average value is smaller, as the dispersion - standard deviation and variance.

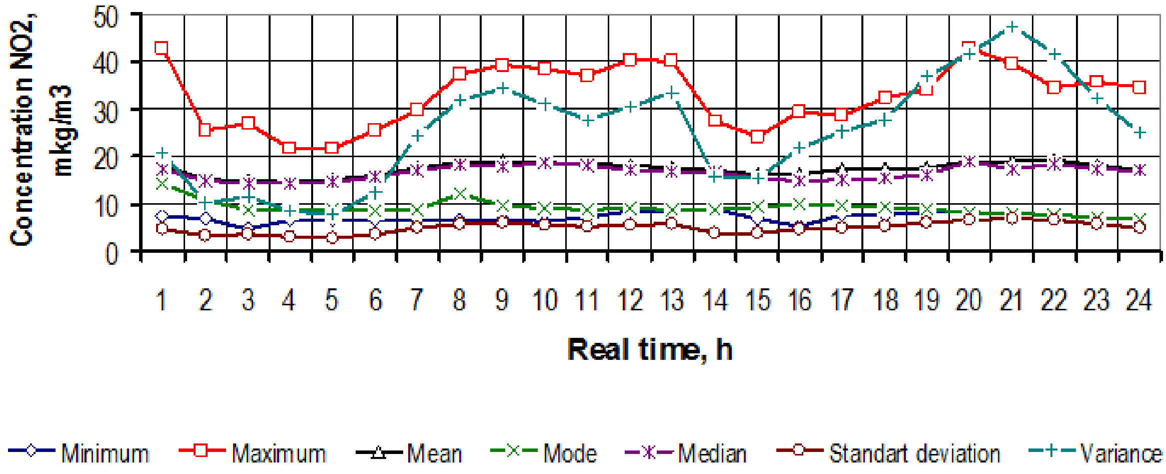
It was found that NO for DAC in Alexandria are Invariant Gauss distribution InvGauss with parameters m=10,388 and l=157,36. The numerical characteristics are: minimum 3,995 μg/m^3; maximum 24,815 μg/m^3, average 18,067 μg/m^3; mode 16.578 μg/m^3; median 17,739 μg/m^3; standard deviation 2,7002 μg/m^3; variation 6,9741 μg/m^3.

Therefore, the concentrations are higher compared to those in Turnu Magurele.

Daily average concentrations of NO_2 in Alexandria also have different than those in Turnu Magurele - InvGauss (m = 3.2457; l = 3.3333), as for the NO. Numerical characteristics are also larger: Minimum 5,5215 μg/m^3; Maximum 11,4412 μg/m^3; Mean 8,1256 μg/m^3; Mode 9.3469 μg/m^3; Median 8,0189 μg/m^3; Standard deviation 1,5528 μg/m^3; Variance 2,3064 μg/m^3.



a)



b)

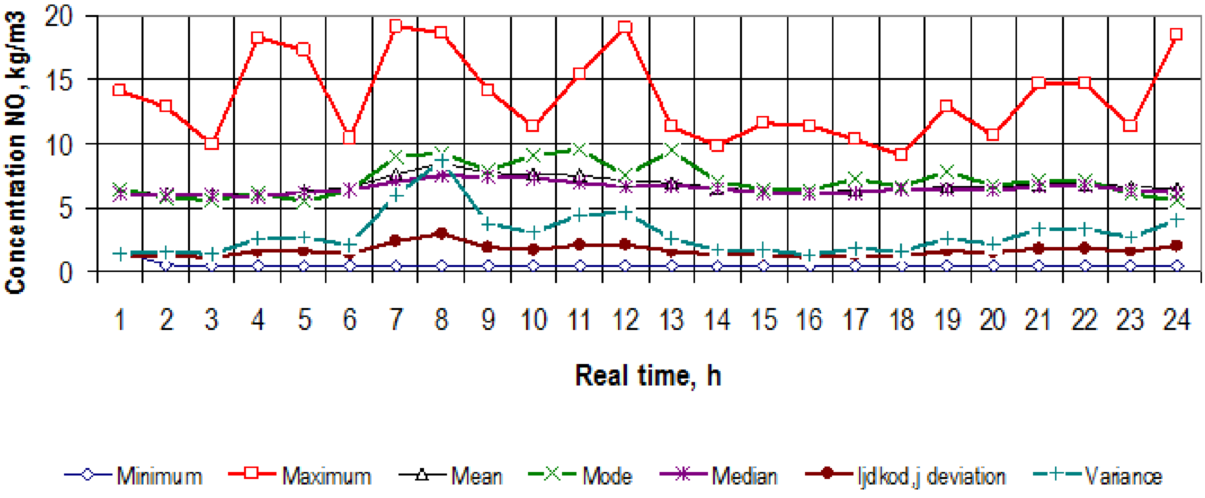
Fig.1. Numerical characteristics of hourly averaged concentrations of nitrogen dioxide in real time during the day at: a) Turnu Magurele; b) Alexandria

Theoretical models and empirical distributions in real time show the dynamics in the statistical characteristics of the pollution. It was found that in Turnu Magurele NO_2 concentrations between the hours from 1 to 16 h., 18-22 hrs., and in 24 h. were distributed in LogLogistic distribution with parameters g from 2.98 to 9.13, b from 4.07 to 10.37 and from a form 3.10 to 13:02. In 17 h. The distribution is Logistic distribution with parameters a = 12.3087 and b = 1.2184, and for 23 h. the distribution is extreme value ExtValue a = 14.1428 and b = 5.4295.

Theoretical models of the concentrations of NO in Turnu Magurele in real time have two types. The first law is Logistic (2, 3, 6, 9, 10, 13-17, 20, 22-24 hrs.) with parameter a from 6.60 to 6.88 and b from 0.47 to 0.88. The second law of distribution at 1, 4, 5, 7, 8, 11, 12 and 19 h. of the day is LogLogistic.

In Alexandria theoretical models of NO_2 differ significant in real time. The distributions, adopted are following: at 1 h - LogLogistic (14.231; 4.4119); 2 h. - LogLogistic (-31.98; 7.00; 27.24); 3 h. - LogLogistic (-33.067; 47.698; 27); 4 h. - Logistics (14.5352, 1642); 5 h. - Logistic (14.9862; 2.8056); 6 h. - LogLogistic (-15.136; 30.896; 16.512); 7 h. - ExtValue (15.0991; 4.5694); 8 h. - Pearson (25.657; 665.48); 9 h. - Logistic (18.3705; 3.1102); 10 h. - Logistic (13.9, 1.4835); 11 h. - LogLogistic (-6.9594; 24.918; 9.2651); 12 h. - LogLogistic (1.2194; 16.134; 5.8654); 13 h. - ExtValue (15.1122; 4.4594); 14 h. - ExtValue

(15.1417; 3.7308); 15 h. - ExtValue (14.3089; 3.6611); 16 h. - ExtValue (14.1184; 4.1618); 17 h. - Triang (7.0888; 14.158; 30.053); 18 h. - Triang (7.0103; 13.513; 33.279); 19 h.-Weibull (1.6964; 11.339); 20 h.-Logistic (18.549; 3.4188); 21 h. - ExtValue (16.0565; 5.4844); 22 h. - Logistic (18.1549; 3.7247); 23 h. - Gamma (16.717; 1.3867); 24 h. - Pearson (92.503; 4328.3).



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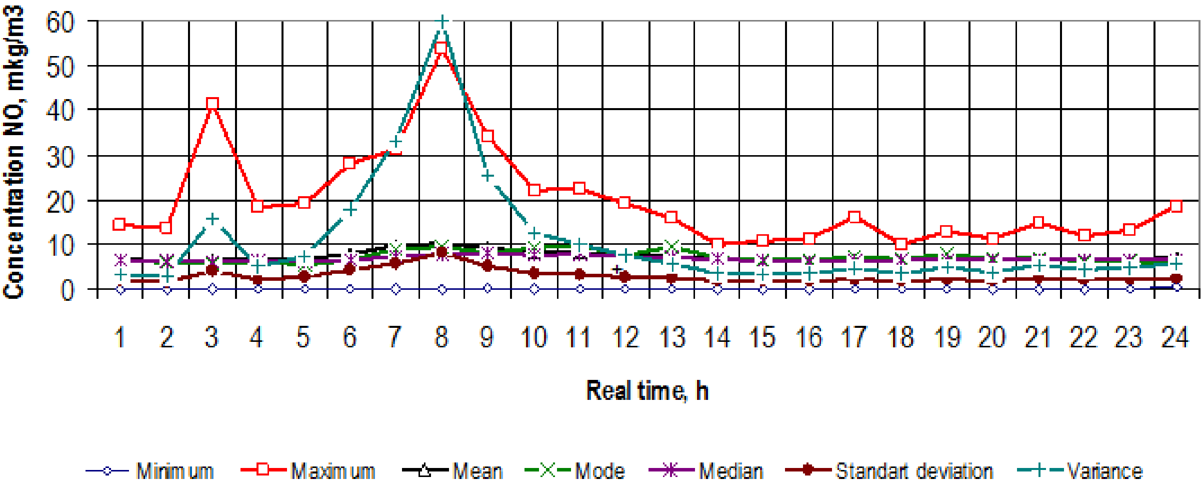

b)

Fig.2. Numerical characteristics of hourly averaged concentrations of nitrogen monooxide in real time during the day at: a) Turnu Magurele; b) Alexandria

For nitrogen monoxide the theoretical distributions from 1 to 24 hours. consecutively at each hour are: InvGauss (37.702; 16549.835); Logistic (6.19276; 0.77097); LogLogistic (-6.4012; 12.539; 13.694); Logistic (6.27665; 0.95708); LogLogistic (-9.2415; 15.668; 13.734); LogLogistic (-3.8946; 11.042; 6.159); LogLogistic (-2.8528; 11.164; 4.1976); LogLogistic (-2.4754; 11.039; 4.0763); LogLogistic (-4.9553; 13.329; 6); LogNormal (26.765; 3.4956); Logistic (7.8778; 1.5814); LogLogistic (-33.018; 40.462; 29.292); Logistic (7.1379; 1.2134); logistics (6.78658, 0.95265); Logistic (6.49048; 0.8885); Logistic (6.43578; 0.90093); Logistic (6.6356; 1.0501); Logistic (6.55193; 0.95997); Logistic (6.7812; 1.1526); Logistic (6.60603; 0.95749); Logistic (6.7933; 1.1506); Logistic (6.6886; 1.0132); Logistic (6.6307; 1.1005); LogLogistic (-7.7653; 14.433; 14.121).

The presented laws allow to simulate the appearance of each concentration in the tested range. They meet the exact numerical expressions to perform the simulation. In this manner, the numerical characteristics at every hour of the day are very important. Dependencies over the real time are shown at Figures 1 and 2. Their analysis reveals the some regularities. First, the maximum values and variations are greatest in range and frequency of change. There was a large coincidence between them. Second, the average value is closest to the median, indicating that the distributions are symmetric. Third, mode, reflecting the maximum probability of occurrence of a certain concentration is in a relatively narrow range and gradual change. Fourth, the standard deviation does not vary widely and has a substantially constant frequency. Fifth, in Turnu Magurele the maximum, standard deviations and variations and the average concentrations are higher for the individual values, which can be explained by the location of the measuring station in the industrial area of the city.

3. Conclusion

Summarizing, it can be argued that the goal is achieved.

The theoretical models and empirical distributions with the corresponding parameters and numerical characteristics were set. Certain dynamics and laws of alteration is defined. Adopted results allow modeling of the concentration levels of nitrogen oxides in ambient air at Turnu Magurele and Alexandria, and thus the probability for air pollution in border towns in the Bulgarian section of the Lower Danube - Nikopol and Svishtov

References: **1** Vladimirov, L., E. Babanova. Series of air pollution levels with nitrogen oxides in ambient air in Romanian - Bulgarian border at Teleorman County. Sustainable Development, 20, 2014 (in press). **2** Reg. №12 of 15 July 2010 on allowable concentrations for sulfur dioxide, nitrogen dioxide, particulate matter, lead, benzene, carbon monoxide and ozone in ambient air. prom. SG 58/2010 **3**. http://www.palisade.com.