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Air Pollution by Sulphur Dioxide and Nitrogen Oxides during the Tourist Season at the Bulgarian Black Sea Coast

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Air Pollution by Sulphur Dioxide and Nitrogen Oxides during the Tourist Season at the Bulgarian Black Sea Coast. *The aim is to identify the level of air pollution along the Bulgarian part of the Black sea. A database is established and the average hourly concentrations of sulphur dioxide, nitrogen dioxide and nitrogen monoxide defined at the fixed stations in Varna, Nessebar and Burgas are assessed; 2. The dependency of concentrations on weather by the hours in the day, by days and months of the active tourist season and by years is determined. The concentrations are of Mathematical modeling.*

Key words: *air pollution, concentration, sulfur dioxide, nitrogen oxides, Black sea Coast .*

INTRODUCTION

Tourism is a specific economic activity, the results of which depend on a series of anthropogenic and natural factors. Natural, urbanized and social-economic environment are a conventional feature of tourism. The influence of the social-economic and urbanized environment has been researched by a number of authors [4,5]. Natural environment is analyzed mainly in terms of geomorphology, landscape, zones of specific flora and fauna, meteorological conditions and climate, natural phenomena. No research was found on air quality and more specifically on the pollution dynamics during the tourist season.

The aim of this work is to identify the level of air pollution along the Bulgarian part of the Black sea. The main tasks to be solved are: 1. Establishing a data base, computer processing and assessment of the average hourly concentrations of sulphur dioxide, nitrogen dioxide and nitrogen monoxide defined at the fixed stations in Varna, Nessebar and Burgas; 2. Determining the dependency of concentrations on weather by the hours in the day, by days and months of the active tourist season and by years; 3. Determining the statistical patterns of concentrations of sulphur dioxide, nitrogen dioxide and nitrogen monoxide occurrence. 4) Mathematical modeling of concentrations.

EXPOSITION

1. Method of research.

A database is established from the researches made by the Bulgarian Executive Environment Agency for the period 2007 – 2013. The number of the data is different, as the validity requirements set in Ordinance №12 are taken into account [1]. They vary due to failures in the measuring units, organizational interruptions adjustment of equipment and other similar reasons.

Table 1. Mathematical models of concentrations by hours of the day measured at “Batak” automated measuring station

Year	Mathematical model	Coefficients of Pearson
2013	$Con_{NO} = 1E^{-06}T^2 - 0.0028\ T + 4.248$	R2 = 0.2965
2013	$Con_{NO2} = 0.0012\ T + 18.455$	R2 = 0.4375
2013	$Con_{SO2} = 2E^{-06}\ T^2 - 0.0092\ T + 10.59$	R2 = 0.7465
2012	$Con_{NO} = 1E^{-06}\ T^2 - 0.0028\ T + 3.9043$	R2 = 0.4245
2012	$Con_{NO2} = 5E^{-06}\ T^2 + 0.0025\ T + 6.66$	R2 = 0.3989
2012	$Con_{SO2} = -1.0422Ln(T) + 14.341$	R2 = 0.5141
2011	$Con_{NO} = -1E^{-07}\ T^2 + 0.0012\ T + 2.89$	R2 = 0.6321
2011	$Con_{NO2} = -3E^{-06}\ T^2 + 0.005\ T + 18.87$	R2 = 0.4056
2011	$Con_{SO2} = -0.0014\ T + 9.3877$	R2 = 0.3045
2010	$Con_{NO} = -3E^{-06}\ T^2 + 0.0042\ T + 8.27$	R2 = 0.3189
2010	$Con_{NO2} = -6E^{-06}\ T^2 + 0.0098\ T + 20.4$	R2 = 0.2278
2010	$Con_{SO2} = -2E^{-06}\ T^2 + 0.0042\ T + 1.31$	R2 = 0.3168

In the processing of the measurement data are applied the methods of probability theory and mathematical statistics. The reason for choosing this approach is that the pollutant concentrations are random variables. This is proved in a series of researches [4,5]. The theoretical and empirical distributions of the concentrations are determined. 11 numerical characteristics are used: 1) absolute and relative levels of change (*Left X, Left P, Right X, Right P*), 2) amplitude*, Diff. P*), 3) minimum, maximum and mean values (*Minimum, Maximum, Mean*), 4) mode (*Mode*), 5) median (*Median*), 6) standard deviation (*Std. Deviation*), 7) variance (*Variance*), 8) skewness (*Skewness*), 9) kurtosis (*Kurtosis*), 10) time series *C(T)* and 11) trend of measurement *Tr*. The numerical characteristics are used to recreate the average hourly concentrations at the sites of the measurements.

A two-dimensional analysis is used for the time series. 24 levels of time of measurement of the concentrations and three levels based on the feature “day of the month” are adopted – Fig.1. The trends are derived (Fig.2) and the correlation of the concentration and time is analyzed.

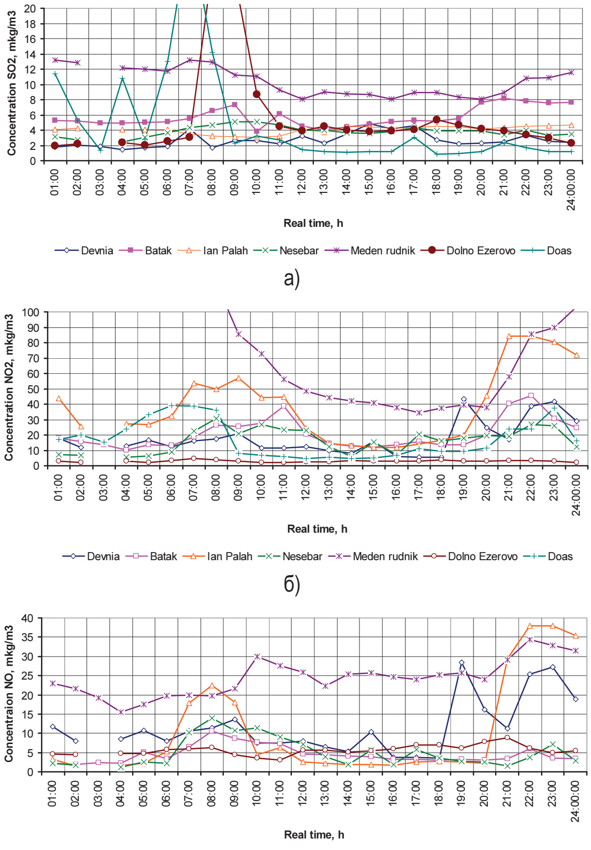

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Fig.1. Time series of the concentrations: a) sulphur dioxide, b) nitrogen dioxide, c) nitrogen monoxide measured in June 2011.

The regression models of concentrations are determined. Ten models are used: 1) Multiplication model: $y_i = b_o x_i^{b_i}$, where $b_o > 0, b_i > 1$. 2) Model of increase: $y_i = exp(b_o + b_i x_i)$, where $b_i > 0$. 3) Quadratic model: $y_i = b_o + b_1 x_i + b_2 x_i^2$, where $b_1 > 0, b_2 > 0$. 4) Cubic model: $y_i = b_o + b_1 x_i + b_2 x_i^2 + b_3 x_i^3$, where $b_3 > 0$. 5) Exponential model: $y_i = b_o x_i^{b_i}$, where $b_o > 0, b_i > 0$. 6) Logarithmic model: $y_i = b_o + b_i \ln x_i$, where $b_i > 0$. 7) S-curve: $y_i = exp\left(b_o + \frac{b_i}{x_i}\right)$, where $b_i > -b_o$. 8) Degree model: $y_i = b_o b_1^{x_i}$, where $b_o < 0, b_1 > 0$. 9) Inverse model: $y_i = b_o + \frac{b_1}{x_i}$. 10) Logistic model: $y = \frac{1}{\frac{1}{u} + b_o b_1^{x_i}}$, where u is the ordinate of the upper asymptote of y.

Verified are the hypotheses of 18 laws of continuous random variables – the concentrations of the air pollutants: 1) The law of equal probability (*Uniform*). Its parameters are *min* and *max*, with min < max. The functions of the law are $f(x) = \dfrac{1}{max - min}$, $F(x) = \dfrac{x - min}{max - min}$. 2) Beta distribution (*Betta*). Parameters of the position are α_1 and α_2 ($\alpha_1 > 0$, $\alpha_2 > 0$), and the critical parameters are *min* and *max* ($min < max$). The density of distribution and the cumulative function of distribution are $f(x) = \dfrac{(x - min)^{\alpha_1 - 1}(max - x)^{\alpha_2 - 1}}{B(\alpha_1, \alpha_2)(max - min)^{\alpha_1 + \alpha_2 - 1}}$, $F(x) = \dfrac{B_z(\alpha_1, \alpha_2)}{B(\alpha_1, \alpha_2)} \equiv I_z(\alpha_1, \alpha_2)$, where $z \equiv \dfrac{x - min}{max - min}$, B - beta function, B_z - incomplete beta function [2,3]. 3) Gamma - distribution (*Gamma*). The distribution has two parameters. The first one α is of the position, and the second β is of the scale of the values of the average hourly concentrations ($(\alpha > 0, \beta > 0)$). The functions of distribution $f(x) = \dfrac{1}{\beta\Gamma(\alpha)}\left(\dfrac{x}{\beta}\right)^{\alpha - 1} e^{-x/\beta}$, $F(x) = \dfrac{\Gamma_{x/\beta}(\alpha)}{\Gamma(\alpha)}$, where Γ is the gamma function, and Γ_x - incomplete gamma function [2,3]. 4) Normal distribution (*Normal*). The normal distribution (*Normal*) has density and cumulative function of the type $f(x) = \dfrac{1}{\sqrt{2\pi\sigma}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$, $F(x) \equiv \Phi\left(\dfrac{x - \mu}{\varpi}\right) = \dfrac{1}{2}\left[erf\left(\dfrac{x - \mu}{\sqrt{2}\sigma}\right)\right]$, where Φ is the integral of Laplace-Gauss, μ - parameter of location, σ - parameter of the scale of concentrations. 5) Triangular distribution (*Triang*). The distribution of the average hourly concentrations is by functions [2] $f(x) = \dfrac{2(x - min)}{(m.likely - min)(max - min)}$, where $min \le x \le m.likely$, $f(x) = \dfrac{2(max - x)}{(max - m.likely)(max - min)}$, where $m.likely \le x \le max$, $F(x) = \dfrac{(x - min)^2}{(m.likely - min)(max - min)}$, where $min \le x \le m.likely$, $F(x) = \dfrac{(max - x)^2}{(max - m.likely)(max - min)}$, where $m.likely \le x \le max$. What is specific is that the parameters are the maximum value of the concentration max, the minimum value min and the mode of the average hourly concentration $m.likely$. 6) Logarithmic-normal distribution (*LogNormal*). The function of the distribution density and the cumulative function are $f(x) = \dfrac{1}{x\sqrt{2\pi\sigma'}} e^{-\frac{1}{2}\left[\frac{\ln x - \mu'}{\sigma'}\right]^2}$, $F(x) = \Phi\left(\dfrac{\ln x - \mu'}{\sigma'}\right)$, where α and β are parameters of the law, Φ - cumulative function of the normal distribution, $\mu' \equiv \ln\left[\dfrac{\mu^2}{\sqrt{\sigma^2 + \mu^2}}\right]$, $\sigma' \equiv \sqrt{\ln\left[1 + \left(\dfrac{\sigma}{\mu}\right)\right]}$. 7) Exponential distribution (*Expon*). The distribution is with functions $f(x) = \dfrac{e^{-x/\beta}}{\beta}$, $F(x) = 1 - e^{-x/\beta}$, where β is a parameter of the distribution, reflecting the scale of magnitude of concentration. 8) Logistic distribution (*Logistic*). The distribution is with parameters - α of the location and β of the scale of the magnitude of concentration values. The concentration values range within $-\infty < x < +\infty$. The functions of the distribution are $f(x)=\dfrac{sec\,h^2\left[\dfrac{1}{2}\left(\dfrac{x-\alpha}{\beta}\right)\right]}{4\beta}$, $F(x)=\dfrac{1+tanh\left[\dfrac{1}{2}\left(\dfrac{x-\alpha}{\beta}\right)\right]}{2}$, where *“sech”* and *“tanh”* are hyperbolic functions [2]. The average value equals the parameter α, while the variation of the concentrations can be defined through the ratio $\pi^2\beta^2/3$. 9) Logarithmic-logistic distribution (*LogLogistic*). The distribution has three parameters: γ-of the location, β-of the scale of magnitude of concentration values (β>0), and α of the form of distribution (α>0). The functions of the distribution are $f(x)=\dfrac{\alpha t^{\alpha-1}}{\beta\left(1+t^{\alpha}\right)}$, $F(x)=\dfrac{1}{1+\left(\dfrac{1}{t}\right)^{\alpha}}$, where $t\equiv\dfrac{x-\gamma}{\beta}$. The average value equals $\beta\theta\,csc(\theta)+\lambda$, where $\theta\equiv\pi/\alpha$ at $\alpha>1$. 10) Inverse Gaussian distribution (*InvGauss*) – Gumbel distribution. The density of distribution and the cumulative function [12] are $f(x)=\sqrt{\dfrac{\lambda}{2\pi x^3}}e^{-\left[\frac{\lambda(x-\mu)}{2\mu^2 x}\right]}$, $F(x)=\Phi\left[\sqrt{\dfrac{\lambda}{x}}\left(\dfrac{x}{\mu}-1\right)\right]+e^{2\lambda/\mu}\Phi\left[-\sqrt{\dfrac{\lambda}{x}}\left(\dfrac{x}{\mu}+1\right)\right]$, where μ and λ are parameters of distribution and are bigger than zero. 11) Weibull distribution (*Weibull*). The distribution has two parameters - α and β. The first is an indicator of the position of the distribution, and the second of the scale of the values. Its functions are $f(x)=\dfrac{\alpha x^{\alpha-1}}{\beta^{\alpha}}e^{-(x/\beta)^{\alpha}}$, $F(X)=1-e^{-(x/\beta)^{\alpha}}$. 14) Rayleigh distribution (*Rayleigh*). There is only one parameter b, and $0 \le x < +\infty$. Different are the functions of density of distribution and the cumulative function $f(x)=\dfrac{x}{b^2}e^{-\frac{1}{2}\left(\frac{x}{b}\right)^2}$, $F(x)=1-e^{-\frac{1}{2}\left(\frac{x}{b}\right)^2}$. 15) Pearson distribution (*Pearson*). Its density of distribution is $f(z)=\dfrac{1}{\beta\Gamma(\alpha)}.\dfrac{e^{-\beta/x}}{(x/\beta)^{\alpha+1}}$, where α is the parameter of the position of distribution, and β - the scale of magnitude of concentration values. 16) Erlang distribution (*Erlang*). The integral parameter is m, which is bigger than 0. The parameter of the scale of concentration values is β, and the variable x ranges within $0 \le x < +\infty$. The functions of the distribution are $f(x)=\dfrac{1}{\beta(m-1)!}\left(\dfrac{x}{\beta}\right)^{m-1}e^{-\frac{x}{\beta}}$, $F(x)=1-e^{-\frac{x}{\beta}}\sum_{i=0}^{m-1}\dfrac{(\frac{x}{\beta})^i}{i!}$. 17) Extreme value distribution (*ExtrValue*) – Wald distribution. The extreme value distribution (*ExtrValue*) has parameters a of position and β of the scale of concentration values $-\infty < x < +\infty$ [2]. Different are the functions of distribution density and the cumulative function $f(x)=\dfrac{1}{b}\left(\dfrac{1}{e^{z+exp(-z)}}\right)$, $F(x)=\dfrac{1}{e^{exp(-z)}}$, where $z\equiv\dfrac{(x-a)}{b}$. 18) Pareto distribution *(Pareto)*. The Pareto distribution *(Pareto)* has two parameters. The first one is θ and is an indicator for the position of the distribution of the random variables, and the second one is

a - for the scale of the concentrations $a \le x < +\infty$. The density of distribution is $f(x) = \frac{\theta a^{\theta}}{x^{\theta+1}}$, and the cumulative function is $F(x) = 1 - \left(\frac{a}{x}\right)^{\theta}$. The average value is $a\theta / \theta - 1$ [2]. Testing of the hypothesis is carried out through Pearson χ^2 criterion. In the computer processing of the data are used the programmes Risk 4.5 and SPSS 17.0.

2. Results and disscution.

The time series are determined. Fig 1. presents the time series by hours of the day for a specific date in the months June, July, and August. Results from the measurements in the measurement stations “Izvorite” – Devnya, in Varna – “Batak”, “Jan Palach”, “Angel Kunchev” Secondary School, in Nessebar, in Burgas – “Meden Rudnik”, “Dolno Ezerovo”, and DOAS are used.

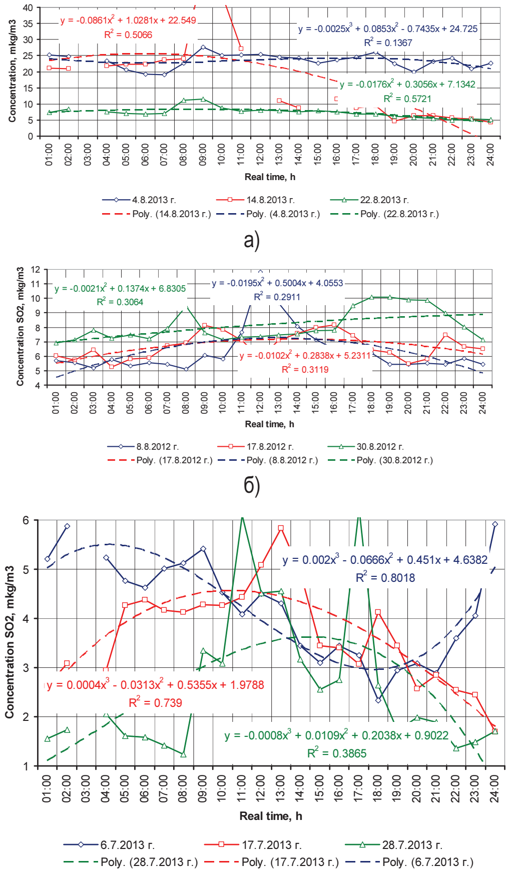

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Fig.2. Time series (——) and trends (- - - -) of sulphur dioxide concentrations measured at a) Dolno Ezerovo AMS, b) Jan Palach AMS; c) Nessebar AMS

The sampling is of about 70000 concentration values Con. The data is systemized by time features T in order to precisely identify their distributions.

The time series are graphically illustrated. Part of them is presented in Fig. 1 and 2. They allow for approximate determination of the patterns of change, the minimum and maximum values throughout the day. Notable is an increase in the concentrations in the interval between 7 and 11 o’clock and in the interval 17-18 o’clock. It is at most visible in the measuring stations situated near road arteries with high traffic intensity. For example, at “Jan Palach” measuring station in Varna – Fig. 1 and 2. It cannot be said that there are patterns of change of sulphur dioxide, nitrogen dioxide and nitrogen monoxide concentrations on.

the territory of the settlements, where the measuring stations are located. Each location is characterized by specific conditions and circumstances of the pollutants emissions distribution. Therefore it is not right to look for summarized patterns but the concentrations should be analyzed locally by measuring stations. The results obtained in such a way are to be juxtaposed, on one hand, with the normative values and, on the other hand, among the measuring stations.

We would even note, that the results cannot be used for assessing the pollution level in the quarters, where the measuring stations are located, since they have big and heterogeneous territories. By analyzing the determined time series the conclusion can be drawn, that the concentration values are lower than the normative which are regulated by Ordinance №12 [1]:

- sulphur dioxide – the average hourly norm for protection of human health is 350 µg/m3, with tolerance of 150 µg/m3 (43 %), while the average daily one is 125 µg/m3, which should not be exceeded more than three times within one calendar year. The norm for protection of the natural ecosystems is 20 µg/m3 but it is not applied in the immediate vicinity of sulphur dioxide sources;

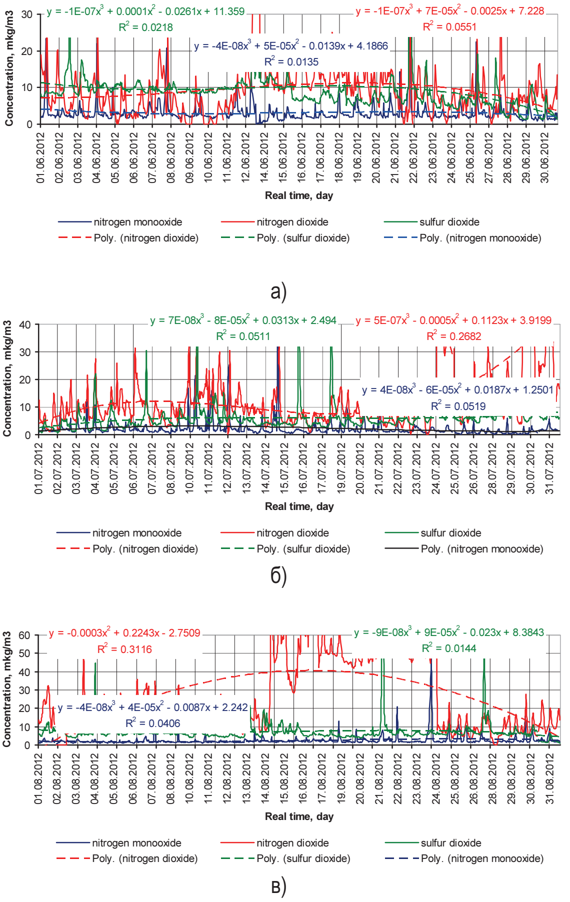

Fig.3. Time series (—) and trends (- - - -) of sulphur dioxide, nitrogen dioxide and nitrogen monoxide concentrations measured at Batak AMS in the months of June, July, and August 2012.

- nitrogen dioxide and nitrogen oxides – the average hourly norm for protection of human health is 200 µg/m3, which should not be exceeded more than 18 times within one calendar year. The norm for protection of the natural ecosystems is 30 µg/m3 for nitrogen dioxide plus nitrogen monoxide but it is not applied in the immediate vicinity of their sources.

It is found that this conclusion is valid both for the absolute values and for the number of exceedances. Increased content of pollutants is found only regarding the impact upon the ecological systems in the settlements but not upon the population health. Besides, it cannot be stated that they are close to the sources.

Particularly impressive is the increased dynamics of concentration change by days from the months of the active tourist season along the Bulgarian Black sea coast. Rare are the cases of low frequency of change. It is usual for the frequency to be within the range of 1/20 to 1/24. This is visible from the illustrations presented on Fig. 1 and 2. They confirm that the chosen approach for using the probability theory and the mathematical statistics is suitable for analyzing the concentrations of the research air pollutants.

The high frequency of concentrations change in time imposes this approach to be developed and they should be analyzed as random processes. This means that the methods of statistical dynamics should be applied. Therefore the processes of concentrations change should be reviewed as random processes. They require the usage of specific numerical features, which determine the correlation among them and the distribution in different frequency bands of appearance – Fig. 3 and 4.

The presented time series are forms of presenting the meanings of the statistical set or parts of it when the dynamics change. Each statistical line of concentrations has a title, ground and terms. The title presents the content of the time series. The ground shows what the adopted approach for the grouping is. The terms of the time series – the values of the concentrations, are numerical values, which can be absolute, relative and mean values. The current research uses absolute values. In methodological aspect the total change of the concentrations includes tendency Tr_i; seasonal fluctuations - S_i; cyclic fluctuations - Z_i; random fluctuations - E_i.

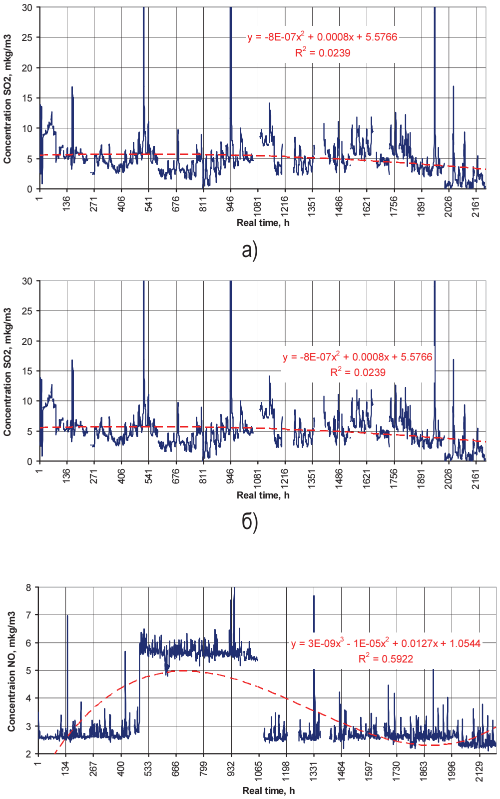

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Fig.4. Time series (—) and trends (- - -) and mathematical models of concentrations during the tourist season of 2011 measured at “Jan Palach” AMS: a) sulphur dioxide, b) nitrogen dioxide, c) nitrogen monoxide

At this stage of the research only the tendency is found, i.e. the so-called trends as written above. The study of the development tendency is researched through the models of the connection between the pollutant concentrations Con and the time T as independent variable. The checked 11 regression models show that most often the concentrations changes are approximated by a quadratic or cubic model – Fig. 2, 3 and 4. The linear models cannot be applied due to the specifics of concentrations change in time. Part of the concentrations models by hours of the day and for the entire tourist season, encompassing the months of June, July, and August are presented in Tables 1, 2 and 3. They are for the concentrations measured at the automated measuring stations – “Batak” and “Jan Palach”. For the remaining measuring stations “Izvorite” – Devnya, “Angel Kunchev” Secondary School – Varna, in Nessebar, in Burgas – “Meden Rudnik”, “Dolno Ezerovo”, and DOAS, the measurements of which are used in this research, the mathematical models are also mainly polynomials of third and second series.

A particularly important focus in this research are the theoretical models and the empirical statistic models of concentrations distribution by measuring stations and respectively in function of time – hours of the day, by months and by tourist seasons including data from the months of June, July, and August. The determined distribution law can be used for determining the concentration values that may appear in time. On the other hand, through them are found the values of the probabilities of concentrations occurring in certain ranges of change. The probabilities allow the calculation of air pollution risks along the Black sea coast. These risks can be used in the entire information-analytical activity, in the development of business projects, for assessing the security level of tourist activity and in many other fields.

Table 2 Mathematical models of concentrations by hours of the day measured at "Jan Palach" automated measuring station

Year	Mathematical model	Coefficients of Pearson
2012	$Con_{NO} = 1E^{-06} T^{2} - 0.0009 T + 3.7322$	R2 = 0.3149
2012	$Con_{NO2} = 3E^{-09} T^{3} - 1E^{-05} T^{2} + 0.0127 T + 1.047$	R2 = 0.5933
2012	$Con_{SO2} = -8E^{-07} T^{2} + 0.0008 T + 5.5766$	R2 = 0.4239
2011	$Con_{NO} = 5E^{-09} T^{3} - 2E^{-05} T^{2} + 0.0192 T + 2.3955$	R2 = 0.2263
2011	$Con_{NO2} = 7E^{-09} T^{3} - 3E^{-05} T^{2} + 0.0278 T + 20.17$	R2 = 0.6122
2011	$Con_{SO2} = -2E^{-0}8 T^{3} + 5E^{-05} T^{2} - 0.0448 T + 20.9$	R2 = 0.5196
2010	$Con_{NO} = 3E^{-09} T^{3} - 7E^{-06} T^{2} + 0.002 T + 6.3015$	R2 = 0.4265
2010	$Con_{NO2} = -1E^{-06} T^{2} + 0.0008 T + 25.502$	R2 = 0.3033
2010	$Con = 2E^{-06} T^{2} - 0.0035 T + 5.9186$	R2 = 0.1444
2009	$Con_{NO} = 7E^{-09} T^{3} - 2E-05 T^{2} + 0.0141 T + 10.57$	R2 = 0.0529
2009	$Con_{NO2} = 6E^{-06} T^{2} - 0.0094 T + 27.415$	R2 = 0.4234
2009	$Con_{SO2} = 8E^{-10} T^{3} - 2E^{-06} T^{2} - 0.0003 T + 6.0548$	R2 = 0.2745
2008	$Con_{NO} = 2E^{-07} T^{2} - 0.004 T + 12.798$	R2 = 0.4768
2008	$Con_{NO2} = -9E^{-06} T^{2} + 0.0164 T + 24.984$	R2 = 0.2305
2008	$Con_{SO2} = 0.0053 T^{2} + 5.4937$	R2 = 0.0564
2007	$Con_{NO} = -3E^{-06} T^{2} + 0.0057 T + 9.0784$	R2 = 0.1088
2007	$Con_{NO2} = -1E^{-06} T^{2} + 0.0018 T + 23.062$	R2 = 0.3007
2007	$Con_{SO2} = 2E^{-06} T^{2} - 0.0039 T + 7.6167$	R2 = 0.2316

Table 3 Mathematical models of concentrations measured at "Jan Palach" automated measuring station by tourist seasons

Year	Mathematical model	Coefficients of Pearson
2012	$Con_{NO} = 3E^{-09} T^{3} - 1E^{-05} T^{2} + 0.0127 T + 1.0544$	R2 = 0.5922
2012	$Con_{NO2} = 1E^{-06} T^{2} - 0.0009 T + 3.7416$	R2 = 0.0149
2012	$Con_{SO2} = -8E^{-07} T^{2} + 0.0008 T + 5.5766$	R2 = 0.0201
2011	$Con_{NO} = 5E^{-09} T^{3} - 2E^{-05} T^{2} + 0.019 T + 2.4399$	R2 = 0.0259
2011	$Con_{NO2} = 7E^{-09} T^{3} - 3E^{-05} T^{2} + 0.0276 T + 20.23$	R2 = 0.1612
2011	$Con_{SO2} = -2E^{-08} T^{3} + 5E^{-05} T^{2} - 0.044 T + 20.91$	R2 = 0.1196
2010	$Con_{NO} = 3E^{-09} T^{3} - 7E^{-06} T^{2} + 0.002 T + 6.3027$	R2 = 0.0265
2010	$Con_{NO2} = -4E^{-09} T^{3} + 1E^{-05} T^{2} - 0.0107 T + 27.5$	R2 = 0.1052
2010	$Con_{SO2} = 2E^{-09} T^{3} - 4E^{-06} T^{2} + 0.0023 T + 4.84$	R2 = 0.1478
2009	$Con_{NO} = 7E^{-09} T^{3} - 2E^{-05} T^{2} + 0.0141 T + 10.574$	R2 = 0.0529
2009	$Con_{NO2} = 6E^{-06} T^{2} - 0.0093 T + 27.365$	R2 = 0.0234
2009	$Con = 8E^{-10} T^{3} - 2E^{-06} T^{2} - 0.0003 T + 6.0548$	R2 = 0.074
2008	$Con_{NO} = 2E^{-07} T^{2} - 0.004 T + 12.795$	R2 = 0.0768
2008	$Con_{NO2} = -9E^{-06} T^{2} + 0.0162 T + 25.091$	R2 = 0.0303
2008	$Con_{SO2} = 0.0053 T + 5.4937$	R2 = 0.056
2007	$Con_{NO} = -1E^{-09} T^{3} + 2E^{-06} T^{2} + 0.0021 T + 9.65$	R2 = 0.1099
2007	$Con_{NO2} = -1E^{-06} T^{2} + 0.0021 T + 22.899$	R2 = 0.1007
2007	$Con_{SO2} = 2E^{-06} T^{2} - 0.0039 T + 7.6167$	R2 = 0.0316

The models of statistical distribution are very different. Part of them for the automated measurement stations "Batak" and "Jan Palach" are presented in Tables 4, 5 and 6.

Table 4. Features of the theoretical and empirical distributions of sulphur dioxide concentrations measured at the automated measurement stations “Batak” and “Jan Palach” by hours of the day during the tourist seasons of 2010 - 2012.

Station “Batak” 2010 г.			Station “Batak” 2011 г.			Station “Batak” 2012 г.		
Characteristics	Theoretical model LogLogistic(-2.5497; 8.5715; 3.8159)	Empirical distribution	Characteristics	Theoretical model LogLogistic(-0.94412; 7.3096; 4.2909)	Empirical distribution	Characteristics	Theoretical model BetaGeneral (0.67092; 3.6626; 0.0000; 23.946)	Empirical distribution
g	-2.5497		g	-0.9441		a1	0.6709	
b	8.5714		b	7.3095		a2	3.6625	
a	3.8158		a	4.2909		min	0	
						max	23.9460	
Left X	1.4	1.4	Left X	2.7	2.7	Left X	0.07	0.07
Left P	95.00%	92.46%	Left P	95.00%	94.73%	Left P	95.00%	95.02%
Right X	16.0	16.0	Right X	13.6	13.6	Right X	11.57	11.57
Right P	5.00%	4.13%	Right P	5.00%	4.54%	Right P	5.00%	0.18%
Diff. X	14.5803	14.5803	Diff. X	10.8377	10.8377	Diff. X	11.5017	11.5017
Diff. P	90.00%	88.32%	Diff. P	90.00%	90.19%	Diff. P	90.00%	94.84%
Minimum	-2.5497	0.0000	Minimum	-0.94412	0.64000	Minimum	0.0000	0.0000
Maximum	+Infinity	317.66	Maximum	+Infinity	264.23	Maximum	23.946	23.440
Mean	7.0725	7.8222	Mean	7.0618	7.3561	Mean	3.7074	3.8192
Mode	4.8972	0.0000	Mode	5.5998	4.2500	Mode	0.0000	0.0000
Median	6.0218	6.2600	Median	6.3655	6.2400	Median	2.4626	1.9500
Std. Deviation	5.3606	13.514	Std. Deviation	3.8195	8.6976	Std. Deviation	3.7507	3.4638
Variance	28.7362	182.54	Variance	14.5885	75.614	Variance	14.068	11.993
Skewness	5.0566	12.4534	Skewness	3.4952	19.8213	Skewness	1.3918	0.6193
Kurtosis		212.1615	Kurtosis	110.8510	520.1619	Kurtosis	4.6913	2.2223
Station “Ian Palah” 2010 г.			Station “Ian Palah” 2011 г.			Station “Ian Palah” 2012 г.		
Characteris	Theoretical	Empirical	Characteris	Theoretical	Empirical	Characteris	Theoretical	Empirical

tics	model LogLogistic (-0.42; 4.61; 4.0399)	distribution	tics	model Pearson 5(2.20; 14.85)	distribution	tics	model LogLogistic (1.51; 3.33; 2.3768)	distribution
g	-0.4239		a	2.2093		g	1.5144	
b	4.6170		b	14.8496		b	3.3304	
a	4.0399					a	2.3767	
Left X	1.80	1.80	Left X	1.5	1.5	Left X	2.5	2.5
Left P	95.00%	92.59%	Left P	95.00%	97.15%	Left P	95.00%	93.52%
Right X	9.15	9.15	Right X	32.2	32.2	Right X	13.0	13.0
Right P	5.00%	3.70%	Right P	5.00%	7.56%	Right P	5.00%	1.85%
Diff. X	7.3420	7.3420	Diff. X	30.6385	30.6385	Diff. X	10.5306	10.5306
Diff. P	90.00%	88.89%	Diff. P	90.00%	89.59%	Diff. P	90.00%	91.67%
Minimum	-0.42395	1.0300	Minimum	-1.3905	0.0000	Minimum	1.5145	1.8300
Maximum	+Infinity	14.450	Maximum	+Infinity	93.380	Maximum	+Infinity	159.20
Mean	4.6935	4.6188	Mean	10.889	10.413	Mean	6.0568	6.4191
Mode	3.6500	2.8700	Mode	3.2366	0.0000	Mode	3.7978	5.4300
Median	4.1931	4.1100	Median	6.4814	5.7000	Median	4.8450	5.2950
Std. Deviation	2.6400	2.2098	Std. Deviation	26.839	11.081	Std. Deviation	6.3838	11.351
Variance	6.9696	4.8606	Variance	720.352	122.739	Variance	40.7533	128.25
Skewness	4.1519	1.0265	Skewness		2.0019	Skewness		11.7545

Table 5 Features of the theoretical and empirical distributions of nitrogen monoxide concentrations measured at the automated measurement stations "Batak" and "Jan Palach" by hours of the day during the tourist seasons of 2010 - 2012.

Station "Batak" 2010 г.			Station "Batak" 2011 г.			Station "Batak" 2012 г.		
Characteristics	Theoretical model Lognorm (6.5730; 21.231)	Empirical distribution	Characteristics	Theoretical model LogLogistic (-0.62; 5.3807; 2.3613)	Empirical distribution	Characteristics	Theoretical model InvGauss (4.4529; 1.7353)	Empirical distribution
m	6.5730		g	-0.6262		m	4.4529	
s	21.2307		b	5.3807		l	1.7353	

			a	2.3612				
Left X	0.07	0.07	Left X	0.9	0.9	Left X	0.3	0.3
Left P	95.00%	89.04%	Left P	95.00%	92.61%	Left P	95.00%	92.73%
Right X	25.3	25.3	Right X	18.1	18.1	Right X	16.8	16.8
Right P	5.00%	2.28%	Right P	5.00%	6.09%	Right P	5.00%	4.75%
Diff. X	25.1868	25.1868	Diff. X	17.1774	17.1774	Diff. X	16.4347	16.4347
Diff. P	90.00%	86.76%	Diff. P	90.00%	86.52%	Diff. P	90.00%	87.99%
Minimum	-0.0771	0.0000	Minimum	-0.62624	0.0000	Minimum	-0.063001	0.030000
Maximum	+Infinity	99.430	Maximum	+Infinity	99.480	Maximum	+Infinity	95.980
Mean	6.4959	4.7716	Mean	6.7444	6.7462	Mean	4.3899	4.3899
Mode	0.092899	0.0000	Mode	3.0432	0.01000	Mode	0.50599	0.2600
Median	1.8668	2.5000	Median	4.7545	4.6250	Median	1.9558	1.9500
Std. Deviation	21.2308	7.4736	Std. Deviation	10.5966	7.7070	Std. Deviation	7.1331	7.9244
Variance	450.7453	55.828	Variance	112.2873	59.370	Variance	50.8813	62.764
Skewness	43.3877	4.4347	Skewness	N/A	4.3288	Skewness	4.8057	5.3387
Kurtosis	20462.6286	33.4350	Kurtosis	N/A	31.9690	Kurtosis	41.4910	42.9631

Station “Ian Palah” 2010 г.			Station “Ian Palah” 2011 г.			Station “Ian Palah” 2012 г.		
Characteristics	Theoretical model Lognorm (6.5730; 21.231)	Empirical distribution	Characteristics	Theoretical model LogLogistic (-0.62; 5.3807; 2.3613)	Empirical distribution	Characteristics	Theoretical model InvGauss (4.4529; 1.7353)	Empirical distribution
m	6.5730		g	-0.6262		m	4.4529	
s	21.2307		b	5.3807		l	1.7353	
			a	2.3612				
Left X	0.07	0.07	Left X	0.9	0.9	Left X	0.3	0.3
Left P	95.00%	89.04%	Left P	95.00%	92.61%	Left P	95.00%	92.73%
Right X	25.3	25.3	Right X	18.1	18.1	Right X	16.8	16.8
Right P	5.00%	2.28%	Right P	5.00%	6.09%	Right P	5.00%	4.75%
Diff. X	25.1868	25.1868	Diff. X	17.1774	17.1774	Diff. X	16.4347	16.4347
Diff. P	90.00%	86.76%	Diff. P	90.00%	86.52%	Diff. P	90.00%	87.99%
Minimum	-0.0771	0.0000	Minimum	-0.62624	0.0000	Minimum	-0.063001	0.030000
Maximum	+Infinity	99.430	Maximum	+Infinity	99.480	Maximum	+Infinity	95.980
Mean	6.4959	4.7716	Mean	6.7444	6.7462	Mean	4.3899	4.3899
Mode	0.092899	0.0000	Mode	3.0432	0.01000	Mode	0.50599	0.2600

Median	1.8668	2.5000	Median	4.7545	4.6250	Median	1.9558	1.9500
Std. Deviation	21.2308	7.4736	Std. Deviation	10.5966	7.7070	Std. Deviation	7.1331	7.9244
Variance	450.7453	55.828	Variance	112.2873	59.370	Variance	50.8813	62.764
Skewness	43.3877	4.4347	Skewness		4.3288	Skewness	4.8057	5.3387
Kurtosis	20462.6286	33.4350	Kurtosis		31.9690	Kurtosis	41.4910	42.9631

Table 6. Features of the theoretical and empirical distributions of nitrogen dioxide concentrations measured at the automated measurement stations "Batak" and "Jan Palach" by hours of the day during the tourist seasons of 2010 - 2012.

Station "Batak" 2010 г.			Station "Batak" 2011 г.			Station "Batak" 2012 г.		
Characteristics	Theoretical model InvGauss (29.750; 71.476)	Empirical distribution	Characteristics	Theoretical model BetaGeneral (1.70; 23.79; 2.98; 351.26)	Empirical distribution	Characteristics	Theoretical model InvGauss (1.42; 1.13)	Empirical distribution
a	5.8082		g	-0.2142	a	g	-0.9038	
b	169.4974		b	16.1417	b	b	11.8779	
			a	2.6515		a	2.0393	
Left X	3.2	3.2	Left X	5.1	5.1	Left X	1.9	1.9
Left P	95.00%	93.69%	Left P	95.00%	95.27%	Left P	95.00%	94.90%
Right X	54.8	54.8	Right X	48.8	48.8	Right X	49.4	49.4
Right P	5.00%	5.13%	Right P	5.00%	5.41%	Right P	5.00%	8.38%
Diff. X	51.6186	51.6186	Diff. X	43.6846	43.6846	Diff. X	47.5199	47.5199
Diff. P	90.00%	88.56%	Diff. P	90.00%	89.86%	Diff. P	90.00%	86.51%
Minimum	-13.340	0.0000	Minimum	-0.21420	0.97000	Minimum	-0.90381	0.0000
Maximum	+Infinity	118.76	Maximum	+Infinity	121.03	Maximum	+Infinity	132.34
Mean	21.912	21.835	Mean	20.429	20.005	Mean	17.402	16.761
Mode	11.556	0.0000	Mode	11.753	13.800	Mode	6.1145	0.0000
Median	17.599	17.550	Median	15.928	15.820	Median	10.974	10.920
Std. Deviation	18.064	17.148	Std. Deviation	21.423	15.338	Std. Deviation	82.668	18.214
Variance	326.31	293.91	Variance	458.944	235.16	Variance	6833.925	331.60
Skewness	2.7796	1.7587	Skewness		2.3753	Skewness		2.5131
Kurtosis	24.3168	7.3093	Kurtosis		10.8110	Kurtosis		10.7758
Station "Ian Palah" 2010 г.			Station "Ian Palah" 2011 г.			Station "Ian Palah" 2012 г.		

Characteristics	Theoretical model InvGauss (29.750; 71.476)	Empirical distribution	Characteristics	Theoretical model BetaGeneral (1.70; 23.79; 2.98; 351.26)	Empirical distribution	Characteristics	Theoretical model LogLogistic (-0.90381; 11.878)	Empirical distribution
m	29.7496		a1	1.7073				
l	71.4758		a2	23.7983		g	-0.9038	
			min	2.9882		b	11.8779	
			max	351.2637		a	2.0393	
Left X	4.5	4.5	Left X	6.5	6.5	Left X	1.9	1.9
Left P	95.00%	95.11%	Left P	95.00%	96.35%	Left P	95.00%	94.90%
Right X	62.0	62.0	Right X	59.3	59.3	Right X	49.4	49.4
Right P	5.00%	4.51%	Right P	5.00%	5.71%	Right P	5.00%	8.38%
Diff. X	57.5217	57.5217	Diff. X	52.8355	52.8355	Diff. X	47.5199	47.5199
Diff. P	90.00%	90.60%	Diff. P	90.00%	90.64%	Diff. P	90.00%	86.51%
Minimum	-5.0834	0.0000	Minimum	2.9883	2.9900	Minimum	-0.90381	0.0000
Maximum	+Infinity	109.23	Maximum	351.26	103.95	Maximum	+Infinity	132.34
Mean	24.666	24.666	Mean	26.302	26.297	Mean	17.402	16.761
Mode	11.415	0.0000	Mode	13.469	7.2600	Mode	6.1145	0.0000
Median	19.643	19.910	Median	22.444	21.750	Median	10.974	10.920
Std. Deviation	19.193	18.051	Std. Deviation	16.906	17.063	Std. Deviation	82.668	18.214
Variance	368.373	325.68	Variance	285.83	291.00	Variance	6833.925	331.60
Skewness	1.9355	1.2571	Skewness	1.2973	1.1294	Skewness	N/A	2.5131
Kurtosis	9.2433	4.6554	Kurtosis	5.2256	4.0309	Kurtosis	N/A	10.7758

The analysis of Table 4 shows that for the theoretical and empirical distributions of sulphur dioxide concentrations measured at the automated measurement stations “Batak” and “Jan Palach” the most typical is the logarithmic – logistic distribution.

The mean value (Mean) shows the best what the position of the random values of sulphur dioxide concentrations is – Table 4. It is the center, around which, to a different extend, are grouped the possible values of these concentrations. At “Batak” station the mean value gradually decreases and for 2012 reaches 3.8192 µg/m^3. At “Jan Palach” station is observed an initial increase in 2011 and then a distinctive decrease, which for 2012 is 6.4191 µg/m^3. Compared to the norms pursuant to Ordinance №12 [1] it is visibly manifold lower. The mode (Mode) od sulphur dioxide concentrations reflects the maximum of the distribution density. Table 4 shows that at “Batak” automated measuring station the minimum value is zero, while the maximum in 2011 is 4.2500 µg/m^3. At “Jan Palach” station the minimum is zero and is during the tourist season of 2011. The highest one is in 2012 - 5.4300 µg/m^3.

The median (Median) divides the area of the distribution of sulphur dioxide concentrations into two equal parts. Successively at the two measuring stations during the three years of observation it is 6.2600, 8.6976 and 3.4638 µg/m^3.

The standard deviation (Standard Deviation) of sulphur dioxide concentrations is respectively 13.514, 3.7507, 3.8195 µg/m^3 at “Batak” station and 2.2098, 11.081, 11.351 µg/m^3 at “Jan Palach”. Therefore, the dispersal is much higher and the differences between the measured concentrations are significant. The high values of the variances (Variance) are also due to this, since they are a result of the standard deviation.

The amplitude between the maximum value (Maximum) and the minimum value (Minimum) of sulphur dioxide concentrations follows almost the same sequence. These results are an additional indicator of the dynamics of the concentrations measured at both stations.

The skewness (Skewness) of the laws of the concentrations measured at both stations is positive, which shows that they have left asymmetry. The kurtosis of distributions is also positive. This means that the distributions of sulphur dioxide concentrations are sharper compared to the normal distribution.

Table 5 shows the theoretical and empirical distributions of nitrogen monoxide concentrations at “Batak” and “Jan Palach” automated measuring stations. Logarithmic – logistic distribution, logarithmic – normal distribution and inverse Gaussian distribution are found. The mean value (Mean) at “Batak” measuring station is the highest during 2011 but significantly lower than the norm both for human health protection and for impacts on the natural ecosystems. The mode is significantly lower compared to the sulphur dioxide. A similar conclusion can be made for the median too - 2.5000, 4.6250, 1.9500 µg/m^3. The dispersal of nitrogen monoxide is considerable. The standard deviation reaches up to 7.9244 µg/m^3, which corresponds to variance of 62.764 µg/m^3. The skewness (Skewness) and the kurtosis (Kurtosis) are positive, i.e. there is left asymmetry and bigger sharpness of the graph of the distribution functions.

At “Jan Palach” measuring station the characteristics of the concentrations are similar. In 2011 the values are the highest, which seems to be a tendency. The mean value (Mean) is 6.7462 µg/m^3, the median is 4.6250 µg/m^3, the standard deviation is 7.7070 µg/m^3 and the variance is 59.370 µg/m^3.

Table 6 reflects the distribution laws for nitrogen dioxide concentrations. Comparing them it is visible that the inverse Gaussian distribution tolerates in the values measured at “Batak” measuring station. Second is the beta distribution. There is a tendency for the mean values during 2010 and 2011 to be significantly higher – 24.666 and 21.750 µg/m^3 respectively. During 2012 it is 3.4965 µg/m^3, i.e. there is a decrease in pollution throughout the years. Unlike the other pollutants the standard deviation and the variance are much higher and reach values of 18.051 and 325.68 µg/m^3. These results completely confirm the graph illustrations presented in Fig.1-4.

At “Jan Palach” measuring station those patterns are similar. The mean values during the three tourist seasons of 2010, 2011 and 2012 are respectively 24.666, 26.297 and 16.761 μg/m^3. The medians are 19.910, 21.750 and 10.920 μg/m^3, the standard deviations are 18.051, 17.063 and 18.214 μg/m^3, and the variance - 325.68, 291.00 and 331.60 μg/m^3. The norms for human health protection are met but the norms for impact on the natural ecosystems are exceeded.

Summarizing the above-written the following conclusion can be drawn.

CONCLUSION

1. A sampling was raised up and the air pollution values were established for sulphur dioxide and nitrogen oxides along the Black sea coast. They are within the norms based on the absolute values and on the allowed accidences pursuant to the legislative base active in the country. They are manifold lower than the norm values of the concentrations and can be used in advertisement campaigns for tourism.

2. Determined are the patterns in the variation of the concentrations along the location of the measuring units. They show that when their values are processed it should be done as if dealing with random processes and it is not necessary to be analyzed only as random values. It is suitable to use features reflecting their dynamics – probability of exceeding certain values, frequency, correlation functions and spectral densities.

3. Obtained are the mathematical models of the time series of the concentrations, which reflect the patterns in different time dimensions – hours, days, months and years. The trends approximate with sufficient accuracy the actual concentration change processes. They can be used for pollution forecasting and be applied in the municipal programmes for environment protection parallel with licensed programme products. The models are suitable for developing and verifying business-projects in the field of tourism.

4. Determined are the statistical laws for the distribution of sulphur dioxide and nitrogen oxides concentrations, which can be taken as theoretical models of the appearance of concentration values.

They can be used to determine the probabilities of values occurring in certain ranges, as well as of the air pollution risk. When testing the hypotheses of the distribution laws it is suitable beside the Pearson criterion to be also used the criteria of Kolmogorov – Smirnov and Anderson – Darling. Experience shows that in many cases different results are obtained and therefore the application of each of the criterion should be justified.

5. The proposed experimental and mathematical approach is useful to be adopted by the experts in the system of the Executive Environment Agency. By means of it can be carried out objective and scientifically substantiated information - analytical work, which would assist the optimization of the entire measurement activity for air quality monitoring.

REFERENCES

[1]. Ordinance №12 of 15 July 2010 for norms of sulphur dioxide, nitrogen dioxide, particulate matter, benzene, carbon oxide and ozone in the air, promulgated in State Gazette 58/2010.

[2]. A Concise Summary of @RISK Probability Functions. Palisade Corporation, 798 Cascadilla St. Ithaca, NY USA 14850. www.palisade.com

[3]. Guide to Using @RISK Risk Analysis and SimulationAdd-In for Microsoft® Excel. Version 4.5. Palisade Corporation, 798 Cascadilla St. Ithaca, NY USA 14850. www.palisade.com

[4]. Vladimirov, L., N. Kovachev, P. Manev. Scenarios situations of transboundary environmental impacts in border areas. Svishtov, The D. A. Tsenov Academy of Economics, Department of International Economic Relations, Jubilee International Scientific Conference dedicated to the 20th anniversary of the establishment of the Department of International Economic Relations – “The future of integration, the

future of the European Union”,16-17 May 2013. Proceedings, pp.253-260. ISBN 978-954-23-0867-6.

[5]. Vladimirov, L., E. Babanova, N. Kovachev. Models of air pollution with nitrogen dioxide and nitrogen monoxide in Romanian - Bulgarian border at Turnu Magurele and Alexandria. Sustainable Development. International Journal, 2014, No 20, pp., ISSN 1314-4138 (in press).

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The report has been reviewed.