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Statistical Processing and Correlations Between Concentrations of Some Atmospheric Pollutants in Suceava and Botosani Counties

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Abstract: *The abundance of some pollutants from the air depend on the geographic area, the human activities intensity, the climate, the season and even on the hour within a day. The nitrogen oxides are the most abundant and most dangerous toxic species from the air, and these emissions are tightly connected to human polluting activities. Therefore, in our work, the first part is assigned for a wide literature search concerning the incidence of the keywords "nitrogen oxide" and searching the connections with other significant related terms and formulas, investigated by the researches worldwide. Then, a statistic approach was applied trying to correlate the values of the concentration in air of nitrogen monoxide, nitrogen dioxide, carbon monoxide, sulfur dioxide, benzene and particulate matter PM10, all of these being generated to a large extent from the exhaust gases from different automotives. The data were collected from the official site of the National Network of Air Quality Monitoring from Romania, and processed by statistical methods, using specific software and methods, in order to find significant differences between the pollutants concentrations values in two neighbor counties (Suceava and Botosani), with relatively similar climate conditions, but different social wealth. The findings of these statistical processing indicate that the PM10 values do not present significant differences between the two locations, neither the time within a day, while the other parameters exhibit distinctions between the values of the other pollutants concentrations in different seasons (summer and winter) and hourly intervals within a day (night, morning, afternoon and evening). 250 words*

Keywords*: air pollutants, nitrogen oxide, statistical processing*

1. Introduction

The chemistry of the atmosphere, in the sense of highlighting the role of different pollutants, is a major preoccupation for the environmental scientists, climate change specialists, medical doctors, political deciders, as well as for simple people. The chemists are asked to bring their competence to investigate the complex mechanisms involved in the emergence of various toxic gas species and particles in the troposphere. There are numerous undesired effects of the anthropogenic emissions on the breathable air, as well as on the upper layers of the atmosphere, therefore solutions to diminish these destructive human actions on the quality of the global environment are searched by scientists[1,2].

Several species resulting from the combustion processes occurring either in the large scale power plants production by using fossil fuels or solid combustible waste, or resulted from the automotive engine working (nitrogen oxides, sulfur dioxide, carbon monoxide, benzene and particulate matter) are responsible for acid rains, deforesting, soil deterioration, intensive corrosion and architecture damaging, agricultural production decrease, as well as for the initiation of various human and animal serious diseases (especially respiratory problems and carcinogenic effects) [3-5]. Therefore, the authorities have the obligation of monitoring the air quality, communicate the results in real time to the community, emit alerts when necessary and eventually establish activity restrictions and/or special fees in the urban agglomerations, aiming to reduce the number and density of mobile emitters of toxic gases and particles.

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These regulations aim to avoid exceeding the highest acceptable limits established by international conventions and detailed accordingly by the national legislations, in connection with human activities. The limit values and the exposure conditions to various atmospheric pollutants in Europe are filed in the 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 [6]. The limit values depend on the exposure time: daily and annual values are defined, together with the specification of the maximum number of times per year when exceeding the daily exposure concentrations are exceptionally permitted. The values of the limit concentrations are displayed in Table 1.

Table 1. Limit values of the toxic gases concentration in air [6]

Species and measure unit	Concentration values for pollutants		
	Value	Times per year of exceeding accepted	One day
SO_2 (µg/m3)	350	24	125
NO_2 (µg/m3)	200	18	40
CO (mg/m3)	10*	-	-
PM_{10} (µg/m3)	50	35	40

*value for 8 hours

The transportation by using vehicles equipped with gasoline and Diesel fuel accounts for almost one half of the NOx emissions in the atmosphere[7]. Therefore, the monitoring and the concern for reducing the amounts released is a priority for the European and national authorities.

In the present work, data concerning the air quality in Botosani and Suceava neighbor counties were collected from the official site of the National Network of Air Quality Monitoring [8], from June 2017 to May 2018, and statistically processed in order to investigate the similarities and/or differences concerning the air quality between: the two locations, cold season (winter) or warm season (summer) and dependence on the hour in a day. Although these two sites are near each other, Suceava is basically considered a developed region, mainly due to the tourism intensity at old medieval sites and wealth connected to forest exploitation, while Botosani has a relatively poor economic development, a high rate of unemployment, which defines a rather poor region [9]. The vehicles bring an important contribution to the air pollution with toxic gases and particulate matter (more than 45%). Therefore, the rate of second hand vehicles, with low performance exhaust gas cleaning systems is supposed to have an important influence on the air quality. According to economic statistics [10], this rate is higher in Botosani than in Suceava.

An extensive bibliometric study performed in the preamble of this work helped us to establish several connections between the main keywords used in the air quality characterization. This analysis gives an image of how the effects of different pollutants have changed in the priority lists of the scientists, since the pollution of the atmosphere has a strong effect on the entire population state of health [1-5]. In this respect, the weight of practical studies versus pure theoretical approach increased in the period of four years.

2. Bibliometric maps

2.1. Theoretical background on bibliometric approach. The VOS method [11]

In our globalized world, the information flows a lot faster and its content is denser than a few decades ago. Hence, the requirements for more complex graphic representations led to the appearance of bibliometric maps [12]. The VOS viewer application is an example in this sense; its literal meaning relates to the phrase ”visualization of similarities”. The VOS application [13] had been developed for representing a couple of "objects" (seen without reference to their physical perception), between which the distance reflects their "likeness". The application’s principle assesses that the higher "resemblance" between two "objects" means they are closer to each other.

In principle, the application minimizes the weighted sum of squares of Euclidean distances between all elements of a matrix of n*m type, where n is the number of "objects" and m is the size of the space used to write the coordinates of the objects between 1… n. The VOS method is different from MDS (Multidimensional Scaling) [14]. This latter has another quantitative significance concerning the distance values between "objects", compared to VOS. In MDS, the creation of a two-dimensional space is chosen, so as the elements (objects) 1… n are placed such as the distance between the components of any pair {i, j} to reflect as much as possible the "similarity" among them. The above-mentioned pair of objects is named a VOS solution, conventionally denoted as X(VOS). This procedure is entitled Sammon mapping [13]; the notation X(S) is adopted, equivalent to VOS, for a Sammon solution. The relation between VOS and Sammon modes of representation can be depicted in a simplifying way through the discussion about the similarities, starting from the fact that in VOS, the objects (the elements) being more "similar", will be placed, in a two-dimensional representation, as close as possible to each other, while those "less similar" will be placed as far away as possible from each other.

The graphical representations of elements (objects) ordered in a two-dimensional space were made by the SPSS software application [15]; this is one of the most popular computer software for descriptive statistics. When the display of a large number of objects is required, VOS is superior to SPSS, especially due to the clarity that VOS brings in the two-dimensional representations.

In brief, we could assert that under specific conditions, VOS is the equivalent of the weighted variant of multidimensional scaling, MDS. According to the literature dedicated to mapping data processing, in most cases VOS and MDS produce bibliometric maps with very different appearance.

2.2. VOS method application for identifying the links between the literature terms, regarding nitrogen oxides between 2015-2018

Our research aiming to find if there are correlations between the pollutants in air with the location, season and time within a day. However, in the preamble we gathered information about the article literature, using the most important parameters of our study, the *nitrogen oxides*, for a longer duration, before and after the target period of our work (2015-2018). Nitrogen oxides arise to an important extent from the transportation, resulting from the reaction between oxygen excess used in the work function of Diesel engines and the nitrogen from air in the harsh conditions from the engine cylinders (high temperatures and pressure). The oxygen excess is one of the simple technical solutions to avoid the formation of particulate matter (PM) rich in carbon, usually named soot [16, 17]. Thus, the formation of nitrogen oxides result from the engine operation following the reduction of PM; their obtaining trend is inversely proportional. The interest paid to the nitrogen oxides is due to their very aggressive effect on the environment, since they are acid anhydrides, partly responsible for the acid rains [18].

Therefore, a package of literature data taken from Clarivate database using *nitrogen oxides* as keywords was gathered and the connection between these words and other terms often met in the papers were searched, in order to have an idea about the importance given by the scientists to thus a practical aspect concerning an important air pollutant. The abstracts of the corresponding papers were collected and counted on the basis of the occurrence of certain terms related to the fore-mentioned keywords. Two types of bibliometric maps were created, namely, ”network” and ”density”, reflecting the connections intensity between the frequencies of the chosen terms (their importance). The mapping parameters of the maps made by VOS software, namely "Attraction" and "Repulsion", were set to the default values 2, respectively 1. The range of assigned colors in the maps varies from blue (meaning small item densities) through green, to yellow (corresponding to the high item densities). The yellow color corresponding to the density of the items on the diagrams displays a maximum intensity for the density of the items (terms), not for the clusters in which these items are organized.

The search in Web of Science database supposed the use of default keywords *nitric oxide* in the corresponding abstracts of the papers; the search was restricted for the specified year; document type considered: article; subarea (domain): chemistry; language of publication: English.

Following this algorithm, the papers package from 2015 contained 1,026 articles. The overall frequency of the keywords *nitric oxide* occurrence was 28,996 times. In 3,877 thereof, a minimum frequency of 5 occurrences of the mentioned keywords was found. The minimum number of other keywords connected to our keywords is 1,000. Under these conditions, the frequencies of the first 3 specific terms for the chosen domain (*range*, *emission* and *removal*, found for 2015) and the number of connections between them and the terms with relative high frequencies from the selected articles, are, respectively, in descending order: *article* / 2,168 / 63,003; *nitric oxide* 2,494 / 56,785; *controlled study* 1,513 / 49,068.

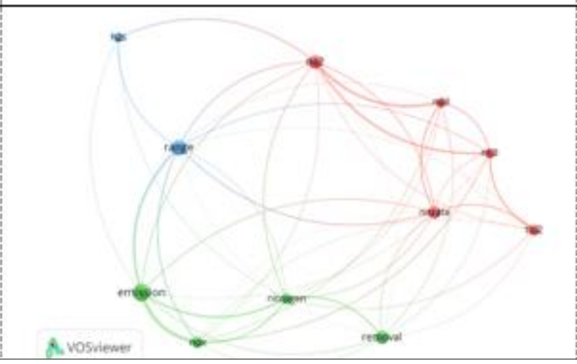
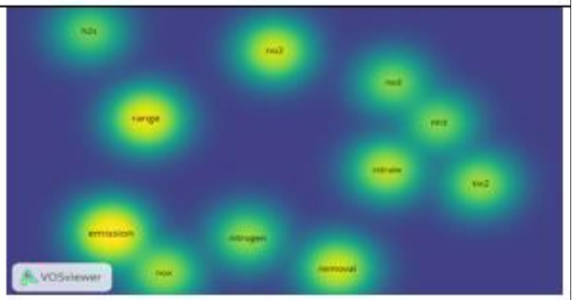
Similar approaches for years 2016, 2017 and 2018 were collected. The data are gathered in Table 2.

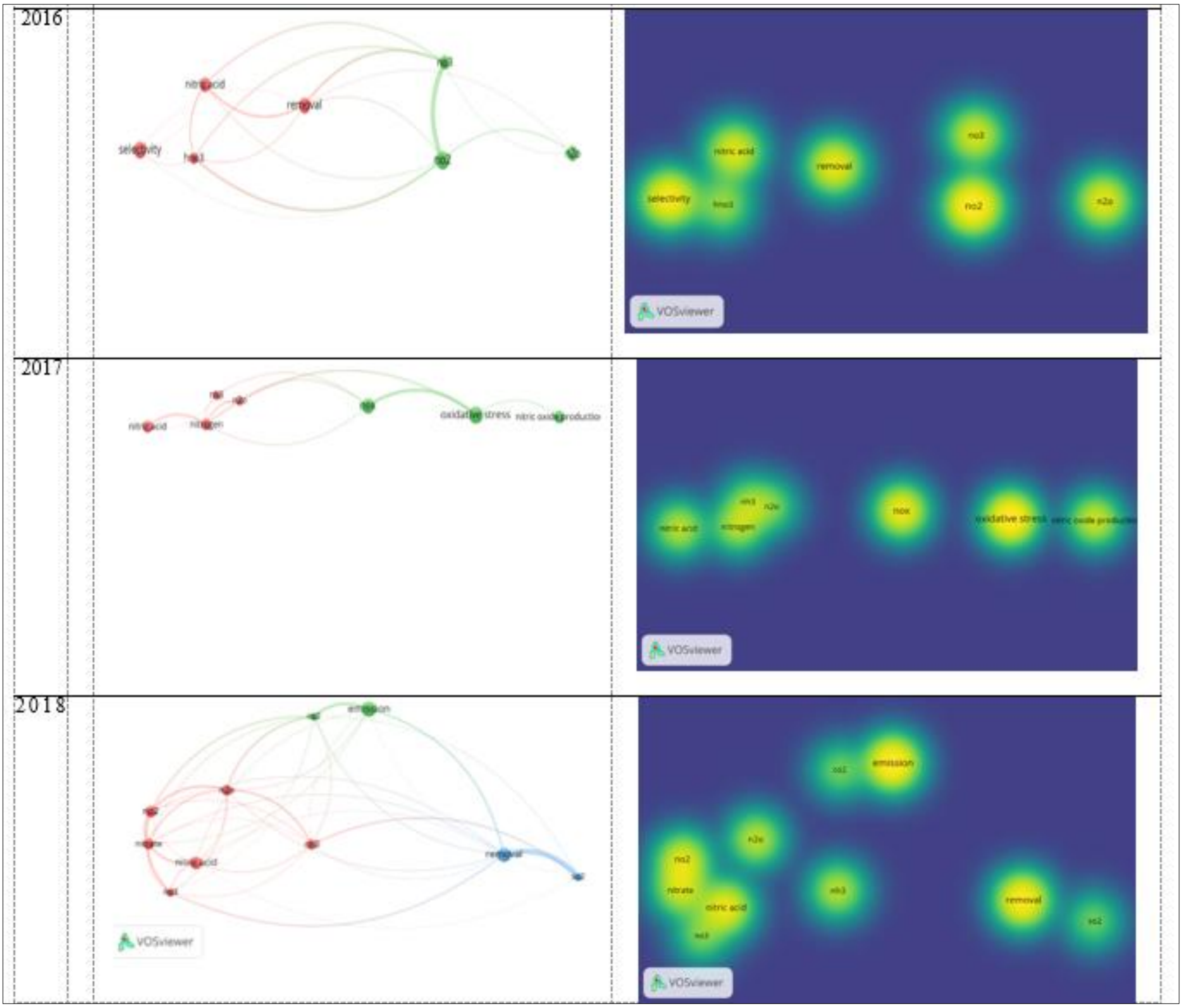
Table 2. Literature data concerning the occurrence of *nitric oxide* keywords

Year	Number of papers	Overall keywords frequencies	More than 5 repetitions of the keywords	**Three keywords most frequently used** / Frequencies of terms / Number of connections with other frequently used words
2015	1026	28,996	3,887	**Range, Emission, Removal** *article* / 2,168 / 63,003 *nitric oxide* 2,494 / 56,785; *controlled study* 1,513 / 49,068
2016	989	12,223	1,020	**NO_3, NO_2, removal** *nitric oxides* 710/16.042 *article* 516/15,580 *chemistry* 399/12,327
2017	993	13,409	1,160	**NOx, oxidative stress, nitric oxide production** *article* 568/17,829 *nitric oxide* 700/17,086 *chemistry* 424/13,974
2018	1064	13,747	1,152	**Removal, emission, CO_2** *nitric oxide* 742 *article* 542

The connections network between terms (or chemical formulas) and the density (frequency) of the terms included in the connection networks for the years 2015-2018 have been gathered in Table 2, as network connections, for the keywords and related terms peculiar to each year, and by presenting the density of the network items, as shown in Table 3. The number of papers dealing with the chosen keywords varies around 1000 per year and the most frequently used keywords connected to *nitric oxide* were clearly connected to terms dealing with environment investigation, as: emission, removal, oxidative stress, nitric acid.

Table 3. Graphical representation of the details corresponding to VOS method data processing concerning the terms ”nitric” and ”oxide

Year	Network connections for the keywords and related terms	Density of the network items/terms (literature)
2015		



3. Distribution of atmospheric pollutants in the Moldova area. A Case Study

The values of the pollution parameters processed in this study are provided by the official site of the Ministry of Environment, Water and Forests, from the urban automated stations from two cities from the North-East Development Region, Botoșani and Suceava. The positions of the measurements points are established by the reponsible authorities in a manner so they can evaluate the influence of extended human settlements on the air quality for representative areas with radius of 1-5 km, without being directly influenced by traffic or industry (not very near main routes from agglomerated cities). The sites for measurements are chosen so that the level of monitored pollution to be influenced by the integrated contributions from all sources, in the opposite direction of the wind, in open spaces situated in residential and commercial areas such as educational facilities [19]. In this respect, the data were collected from the stations SV-1 (Suceava) and BT-1 (Botosani), as defined in [19]. The data were noted twice per month, keeping broadly two weeks between two consecutive collections.

3.1. Descriptive statistics for the hourly data set for Botosani and Suceava counties, on January 5 and August 25

The concentration values of 7 significant atmospheric pollutants (NO, NO_2, NO_x, benzene, SO_2, PM10 and CO) were collected from the Ministry of Environment, Water and Forests site. In this first approach, the values were statistically analyzed for two days, one in the cold season (January 5^{th}) and the other in the warm season (August 25th). The values of the pollutants concentrations (μg/m^3 for the fore-mentioned species, excepting CO, for which the unit is mg/m^3) values were collected for each hour in a day (24 values).

In Table 4 are displayed the values of the following indicators calculated from the individual values: number of values, arithmetic mean (Average) and limits of confidence range with a probability of 95% in the arithmetic mean. The ”Median” is the value from the middle of the string of values of a sample whose constituents are ascending or descending and the ”Modal” is the value from the sample appearing with the highest frequency.

Table 4. Descriptive data for Botoșani, Suceava, January 5th and August 25th, hourly values

Pollutant	Number of values	Average	Confidence range + 95.00%	Confidence range - 95.00%	Median	Modal
NO	96	26.384	16.043	36.725	11.145	5.240
NO2	96	37.041	32.534	41.547	32.720	Multiple
NOx	96	66.688	46.935	86.440	47.595	Multiple
Benzene	49	6.027	5.033	7.020	5.180	Multiple
SO2	96	10.666	9.863	11.469	10.060	Multiple
PM10	96	31.163	26.302	36.023	33.560	Multiple
CO	96	10.060	6.545	13.574	0.610	Multiple

The asymmetry and vaulting are the specific indicators for data distribution; the first describes the horizontal deformation of a Gaussian curve and the second shows the vertical deformation of the same Gaussian curve.

The asymmetry is calculated in function of the median with the relation:

$$C_{as} = \frac{3(\overline{x} - Me)}{\sigma} \quad (1)$$

The asymmetry values vary between –3 and +3; the values close to zero indicate a low asymmetry, while the high ones, near ±3, show pronounced asymmetry.

The vaulting is calculated with the relation:

$$\mu_4 = \frac{\sum (x_i - \overline{x})^4 n_i}{\sum n_i} \quad (2)$$

where μ_4 is the central moment of fourth order.

The standard errors for asymmetry, vaulting and the variation coefficient are displayed in Table 5.

Table 5. Calculated data for Botoșani, Suceava, January 5th and August 25th, hourly

Variable	Variation co-efficient	Standard error of the average	Asymmetry	Asymmetry standard error	Vaulting	Vaulting standard error
NO	193.447	5.209	5.176	0.246	33.447	0.488
NO_2	60.042	2.270	1.777	0.246	4.836	0.488
NOx	146.186	9.950	4.377	0.246	26.230	0.488
Benzene	57.388	0.494	-0.063	0.340	-1.656	0.668
SO_2	37.151	0.404	1.543	0.246	3.462	0.488
PM10	76.982	2.448	0.114	0.246	-1.153	0.488
CO	172.435	1.770	1.501	0.246	0.674	0.488

The variation coefficient, CV, measures the homogeneity of the sample, and is defined by the relation:

In the interpretation of the analytical data, a value over 17% of CV means a heterogeneous sample (Table 6).

$$CV = \frac{\sigma}{\bar{x}}[100] \quad (3)$$

Table 6. Minimum and maximum values and CV for the combined samples in Botosani and Suceava counties for both measurements days (January 5th and August 25th)

Variable	Number of values	Average	Minimum	Maximum	Standard deviation	CV
NO	96	26.384	3.400	405.910	51.039	**193.447**
NO_2	96	37.041	9.580	138.760	22.240	60.042
NOx	96	66.688	2.510	749.250	97.488	146.186
SO_2	96	10.666	5.140	26.480	3.963	**37.151**
PM10	96	31.163	0.130	81.520	23.990	76.982
CO	96	10.060	0.030	60.280	17.346	172.435

The lowest value of the CV is found for the SO_2, while the highest CV value corresponds to NO (values marked in bold face). The samples are heterogeneous or very heterogeneous, with a high variability of the values.

3.2. Inferential statistics for the hourly data in Botosani and Suceava, on January 5th and August 25th

3.2.1. Inferential statistics for the hourly data in Botosani and Suceava on January 5th

The t-tests (Student) [20] were applied to compare the samples with volumes (number of cases) in agreement with the factual literature data by noting, hour by hour, the values of the parameters corresponding to the concentrations of NO, NO_2, NO_x, SO_2, PM10, CO. The values are presented in Tables 7 and 8, for January 5th and August 25th.

Table 7. Comparison between average daily values (between 0-24 h), January 5th, Suceava and Botosani counties

Variable	Average Suceava	Average Botosani	t - Test value	Degrees of freedom (DF)	Statistical significance level	Number of valid dates Suceava	Number of valid dates Botosani
NO	*7.083*	*29.132*	*-4.402*	*46*	*0.000*	*24*	*24*
NO_2	*27.778*	*47.237*	*-4.671*	*46*	*0.000*	*24*	*24*
NOx	*3.384*	*89.705*	*-9.839*	*46*	*0.000*	*24*	*24*
PM10	*0.242*	*55.958*	*-21.542*	*46*	*0.000*	*24*	*24*
CO	*38.357*	*0.855*	*16.238*	*46*	*0.000*	*24*	*24*

Table 8. Comparison between average daily values (between 0-24 h), August 25th, Suceava and Botosani counties

Variable	Average Suceava	Average Botosani	t - Test value	Degrees of freedom (DF)	Statistical significance level	Number of valid dates Suceava	Number of valid dates Botosani
NO	*8.703*	*60.618*	*-2.807*	*46*	*0.007*	*24*	*24*
NO_2	*24.415*	*48.732*	*-3.561*	*46*	*0.001*	*24*	*24*
NOx	*37.396*	*136.265*	*-2.963*	*46*	*0.005*	*24*	*24*
PM10	*23.137*	*45.314*	*-6.261*	*46*	*0.000*	*24*	*24*
CO	*0.205*	*0.821*	*-4.536*	*46*	*0.000*	*24*	*24*

The significances of the data are:

1) Average - Suceava or Botosani - average values of the parameters measured in 24 hours, at the respective dates;

2) t-Test values, determined from the data processed by SPSS software;

3) Degrees of freedom assigned to the t-test, DF = N1 + N2 - 2, where N1, respectively N2 are the volumes of the samples (24 cases each);

4) Level of statistical significance, associated probabilistically following the test t, with the risk threshold $\alpha = 0.05$; any level of significance lower than the specified risk threshold gives the statistical significance of the test for the corresponding level of estimated statistical significance. The values in italic are statistically significant.

5) Number of valid data for each of the two counties, Suceava and Botosani.

The values of the level of statistical significance obtained by applying the t-test indicate that statistically significant differences exist between the arithmetic averages of the values for all the variables (NO, NO2, NOx, PM10, CO), collected by the mentioned procedure (same day, hour by hour, 24 values per variable), in both Suceava and Botoșani counties and both winter or summer conditions.

3.2.2. Inferential statistics for the data set based on 6 hours packages (Botosani and Suceava counties, January 5th and August 25th)

The investigation of the influence of the moment of the day when the values were collected was made by applying the one-way ANOVA test [21], on the selected pollutants. The results are shown in the table 8. The reason for using time packages of 6 hours comes from the possible time-related differences in the emissions. The 24 h daytime were divided in four segments, conventionally defined as: 0-6 = night; 6-12 = morning; 12-18 = afternoon; 18-24 = evening.

In all the situations in table 8, the ANOVA test was statistically significant, regardless of the 6-hour time package, for all six compounds, meaning that there are statistically significant differences between any of the considered 6-hour time intervals.

Tabel 9. Analysis of Variance

Variable	SS Effect	DF Effect	MS Effect	SS Error	DF Error	MS Error	F	p
NO	*44723.9*	*7*	*6389.14*	*202747.8*	*88*	*2303.952*	*2.773*	*0.012*
ppo	*22900.9*	*7*	*3271.56*	*24086.8*	*88*	*273.713*	*11.952*	*0.000*
NO_x	*270769.6*	*7*	*38681.38*	*632099.1*	*88*	*7182.944*	*5.385*	*0.000*
SO_2	*730.3*	*7*	*104.33*	*761.4*	*88*	*8.652*	*12.059*	*0.000*
PM10	*39636.8*	*7*	*5662.40*	*15036.1*	*88*	*170.865*	*33.140*	*0.000*
CO	*8344.7*	*7*	*1192.10*	*20240.1*	*88*	*230.001*	*5.183*	*0.000*

SS-Sum of Squares; DF-Degree of freedom; MS-Mean of Squares; F- Value of Fischer tests; p-significance.

3.2.3. Influence of the PM10 concentrations on NOx concentrations

By using a General linear model (GLM), an equation of shape $y = f(x_1, x_2) + \varepsilon$ (ε being the error) was calculated considering the NOx concentration as the dependent variable and the PM10 or CO concentrations as independent variables, by using all 96 available collected values. The deduced prediction equation for this case is:

$$NOx = -46.4151 + 3.2354\ PM10 + 1.2204\ CO$$

Table 10. Validation attempt of the general linear model concerning the influence of the concentrations of two predictors on the dependent variable NOx

Case	SS	DF	MS	F	P
Intercept	29669.2	1	29669.2	5.4700	0.0215
PM10	297204.5	1	297204.5	54.7942	0.0000
CO	22111.5	1	22111.5	4.0766	0.0464
Error	504433.1	93	5424		

SS-Sum of Squares; DF-Degree of freedom; MS-Mean of Squares; F- Value of Fischer tests; p-significance.

The proposed linear regression model is statistically significant (p <0.05). However, the fit between the calculated values and the collected ones is not satisfactory for about one half of the data set. It means that the assumption that the PM10, CO and NOx concentrations could be correlated into a valid mathematical relation is not readily possible. This fact could be due on one part, to the different pollutants sources (other than fuels burning), and on another part, to their very different chemical reactivity (the PM10 are quite unreactive).

3.3. Searching extreme/aberrant values for the data set with hourly measurement, for Botosani and Suceava counties, on January 5 and August 25

The highlighting of extreme or aberrant values were tested by the Grubbs test [13], by applying it to each variable separately, respectively for NO (Table 11), NO_2 (Table 12), NO_x (Table 13), SO_2 (Table 14), PM10 (Table 15), and CO (Table 15).

The significance of the values in Tables 10-15 is: Average - Arithmetic mean of the individual values from the sample; SD-Standard deviation of the values; Grubbs test - value of the statistics corresponding to the Grubbs extreme / aberrant value detection test; Significance level - Risk associated with the determination by the Grubbs test. It is accepted that any risk below 5%, regardless of the test applied, is statistically significant [22].

In these tables, the values refer to the winter data package (January 5, line 1), summer data package (August 25, line 2) as well as between the two counties and both measuring days (line 3).

Table 11. Grubbs test for NO (Botoșani and Suceava, January 5th and August 25th, N=96

NC	Average	Number of values	SD	Grubbs test	Significance level
1	7.893	48	6.420	4.132	**0.000**
2	44.875	48	67.274	5.367	**0.000**
3	26.384	96	51.039	7.436	**0.000**

The Grubbs test applied for the NO case indicates that extreme values exist inside both Therefore, extreme values may occur, depending on the variable investigated.

The possible aberrant values given by Grubbs test concerning NO_2 are displayed in Table 11.

Table 12. Grubbs test for NO_2 (Botoșani and Suceava, January 5th and August 25th, N = 96

NC	Average	Number of values	SD	Grubbs test	Significance level
1	26.096	48	13.491	2.830	0.153
2	47.985	48	23.939	3.792	**0.002**
3	37.041	96	22.240	4.574	**0.000**

In what concerns NO_2, the Grubbs test shows that for the winter (January 5th), extreme values cannot be met. The values in bold indicate statistically significant values for the applied test.

The Grubbs test analysis results for NO_x are shown in Table 12.

Table 13. Grubbs test for NO_x (Botoșani and Suceava, January 5th and August 25th, N = 96

NC	Average	Number of values	SD	Grubbs test	Significance level
1	20.390	48	26.655	3.588	**0.005**
2	112.985	48	118.834	5.354	**0.000**
3	66.687	96	97.488	7.002	**0.000**

As in the case of NO, when applying the Grubbs test for NOx, the calculated amount indicates that extreme values exist inside the package in winter, summer and between the two counties when using all collected values. The statistically significant values are also labeled with bold face.

The application of Grubbs test for SO_2 reveals a similar situation as in the case of NO_2, respectively the lack of extreme values in winter package (Table 13).

Table 14. Grubbs test for SO_2 (Botoșani and Suceava, January 5th and August 25th, N = 96

NC	Average	Number of values	SD	Grubbs test	Significance level
1	9.578	48	4.519	2.922	0.108
2	11.755	48	2.983	4.936	**0.000**
3	10.666	96	3.963	3.991	**0.003**

An interesting and different behavior is noticed when applying Grubbs test for the particulate concentration, PM_{10} (Table 14).

Table 15. Grubbs test for PM10 (Botoșani and Suceava, January 5th and August 25th, N = 96

NC	Average	Number of values	SD	Grubbs test	Significance level
1	11.689	48	14.302	2.912	0.112
2	50.636	48	13.570	2.276	0.948
3	31.163	96	23.990	2.099	1.000

In the case of the Grubbs test applied to PM10, extreme values are missing for both winter and summer, in Suceava and Botosani counties, neither when all data were processed in the case and this test does not deliver statistically significant values. In other words, the PM_{10} variable does NOT show extreme values in any context of the study.

Further, possible aberrant values were searched in the CO case. In Table 16, the values of the Grubbs test are given.

Table 16. Grubbs test for CO (Botoșani and Suceava, January 5th and August 25th, N = 96

NC	Average	Number of values	SD	Grubbs test	Significance level
1	19.281	48	20.84	1.968	1.000
2	0.838	48	0.58	3.854	**0.001**
3	10.060	96	17.35	2.895	0.300

In the case of the Grubbs test applied to CO values, extreme values are present only within the summer data package (August 25, line 2, Table 14) in both counties, but not in the winter data or in the 96 cases package, as shown by the values in bold face, which indicate statistically significant values for the analyzed test.

4. Conclusions

Due to the overwhelming importance of nitrogen oxide from the atmosphere in the characterization of the air quality, the information on the subject was searched in the scientific literature filed by Clarivate database and processed in the form of bibliometric maps. The information was collected for 4 years (2015-2018). The number of papers dealing with the chosen keywords varies around 1000 per year and the most frequently used keywords connected to *nitric oxide* were clearly connected to terms dealing with environment investigation, as: emission, removal, oxidative stress, nitric acid. Also, the highest density on the bibliometric of ”network” and ”density” types showed strong interactions between *nitric oxide* keyword and the mentioned words.

Six pollutants species (analytes) from the city air were selected to attempt finding correlations in between, namely: nitrogen oxide (NO), nitrogen dioxide (NO_2), carbon monoxide (CO), all nitrogen oxide species (NO_x), sulfur dioxide (SO_2) and particulate matter PM10. The concentrations of these species were collected from the official site of the Ministry of Environment, Water and Forests, between August 2017 – July 2018, in two locations (Botosani and Suceava). The collected data were used to make statistic comparisons between the two locations, the pollutants concentrations registered in cold and warm season and the variations within a day (morning, afternoon, evening and night).

The values of the descriptive statistical indicators for the concentrations of the mentioned atmospheric pollutant species were determined. The inferential statistics, such as the t test or ANOVA one way, showed certain differences between the concentrations of the pollutant gases and PM, for the two measuring points, the hour interval witin a day and the season of measurement.

The research of aberrant/extreme values shows that the PM10 values from the list of pollutants do not present extremes related to the season or to day time. For the other parameters, extreme values exist for the different locations, winter or summer seasoning or time measurement within a day, respectively. It means that the PM10 remanence in air is more constant that that of the toxic gases (NO_x, SO_2, CO) in the two locations, day-night or summer-winter changes. Thus, PM10 is a constant pollution source of the air from urban areas and their presence cannot be directly connected with the other pollutant species.

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