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NO_2 concentration analysis in urban area of Catania

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Abstract

The recent scientific researches have revealed principal causes and trend of Nitrogen dioxide (NO_2), a chemical gas very dangerous for the human respiratory apparatus. The generation of this gas is principally associated to the high temperature combustion processes such as those in internal combustion engines and thermal power plants. In the urban area of Catania there are not thermal power plants so, the most important NO_2 generation is related to the increasing use of vehicles. It is also demonstrated that NO_2 is correlated with other pollutants such as PM_{10} and $PM_{2,5}$. The city of Catania is provided by an air quality monitoring network made up of five fixed stations. The principal monitored pollutants are: NO_2, CO, BTX, PM_{10}, O_3, SO_2. This paper focuses on the analysis of the big amount of NO_2 data recorded by instrument "Philips model 42" in the urban area of Catania. This data has been validated and analysed in order to conduct a multivariate statistical analysis. The Principal Component Analysis (PCA) and Cluster Analysis (CA), have been developed related to the atmospheric parameters (Wind velocity, Air Temperature, Precipitation, Relative humidity, Global Solar Radiation) in the period between 2009 and 2012. This multivariate analysis has been applied to the investigation process about the linear dependence of NO_2 to these parameters. Another important aim of this paper has been to study the trend of NO_2 concentration and the number of times this value has overtook the limits imposed by the Air Quality Directive 2008/50/EC.

Keywords: Air quality, multivariate analysis, NO_2, urban area;

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1. Introduction

In the mediterranean area the effect of climate changes is very dangerous for the human health. The anthropic impact is one of the most principal causes of air pollution. NO_2 (Nitrogen dioxide) is a typical gas that contributes to modify the standard air quality and climate [1]. Oxides of nitrogen (NO_X) is the combination of nitric oxide (NO) and nitrogen dioxide (NO_2). NO_X is produced by fuel combustion processes occurring in the engine. NO is produced spontaneously in the human respiratory system, it is not harmful to health at the usual concentrations presented in the atmosphere. NO_2 instead, causes damages to health and environment. NO_2 is usually converted to nitric acid over a period of approximately 24 hours. It is removed from the atmosphere by two processes: direct deposition to the ground or in the form of acid rain. In a urban area with massive vehicles traffic and restricted dispersion of air pollutions, C_{NO2} exceeds the allowed threshold. As reported by EEA 2012 annual report [2], 22 of the 27 EU Member States recorded exceedances of the limit value at one or more stations and people living close to traffic zones are much more exposed to high C_{NO2} than those in urban background zones. The main causes of NO_2 and NO_X are the emissions by vehicles, combustion of fuel in industry and power Plants. In the last years there was an increase of NO_2 emissions by vehicles due to the use of oxidative catalytic converters in diesel vehicles and the increased ratio of diesel vehicles as compared to petrol vehicles [3]. It is well-known that in urban zones a percentage of about 70-75 % of NO_X emissions is usually related to vehicular sources. A focusing on physical and chemical fate of NO_X released in the atmosphere from vehicles is reported in [4].

Nomenclature

T	Air Temperature [°C]
P_{RC}	Precipitation [mm]
H_R	Relative Humidity [%]
R	Global Solar Radiation [MJ/m^2]
V_w	Wind Velocity at [m/s]
C_{NO2}	Concentration of Nitrogen Dioxide [μg/m^3]
M	Mean [-]
StD	Standard Deviation [-]
$S_{\%}$	Percentage of Samples [%]
N°	Number of Samples [-]
M*d*	Median [-]
A_m C_{NO2}	Annual Mean of concentration of Nitrogen Dioxide [μg/m^3]
Max	Maximum [μg/m^3]
$V_{M\%}$	Percentage of valid measurements [%]
E	Eigenvalue [-]
D_{EA}	Euclidean Average Distance [-]
$N°_{T200}$	Number of Times C_{NO2} is greater than 200 μg/m^3 [-]

2. Area of study

The metropolitan area of Catania is about 180.88 km^2 with a density of 1600 pop/km^2 and a total population of 291274 according last studies by Italy's National Statistics Institute (ISTAT). Catania is populated especially in the northern part, while its southern part is manly an industrial and commercial zone. It is one of the fifteen biggest metropolitan cities of Italy. It is characterized by a massive commuting toward the center of the city with a chaotic traffic caused especially by a disorganized urban development. The peak of the traffic is ranged between 07:00 and 09:30 while another important peak is concentrated in the late afternoon, and during summers even until 21:00. The climate is typically Mediterranean with high temperatures during the whole year (Average high Temperature up to 23/24 °C) and few precipitations with values usually between 450 mm and 550 mm per year.

3. Data sources

The air quality in Catania is monitored by Ecological Department of Municipality of Catania since 1992.The monitoring system is constituted by five stations. The pollutants recorded are: Nitrogen dioxide (NO_2), Sulphur dioxide (SO_2), Carbon monoxide (CO), Ozone (O_3), Particulate matter (PM_{10}), Benzene (C_6H_6). Four of these stations provide to measure C_{NO2} hourly, and they are located in traffic ("Viale V. Veneto"), residential ("Piazza A. Moro" and "Librino") and background sites ("Parco Gioeni"). NO_2 measurements are implemented by the instrument "Philips model 42" using the chemiluminescence principle. The period of study of this work was from 2009 and 2012.

Table 1. Characteristics and locations of stations.

Station	Description	Latitude/Longitude	Altitude (m)	Variable measured
Viale V. Veneto	Heavy traffic	37° 30' 83" / 15° 05' 26"	38	C_{NO2}
Piazza A. Moro	Medium traffic	37° 31' 95" / 15° 05' 95"	76	C_{NO2}
Librino	Light traffic	37° 29' 47" / 15° 02' 70"	71	C_{NO2}
Parco Gioeni	Urban-background	37° 31' 44" / 15° 41' 99"	135	C_{NO2}
Meteorological station	Industrial zone	37° 26' 36" / 15° 04' 7"	10	T, P_{RC}, H_R, R, V_W

The meteorological data come from Sicilian agrometeorological information service (SIAS). The meteorological station is located at the industrial zone of Catania and is provided by the following instrumentations: an anemometer for V_W (m/s) and its direction, a pyranometer for R (MJ/m^2), a pluviometer for P_{RC} (mm), a thermometer for T (°C) and a hygrometer for H_R (%). All these instrumentations are installed at 2 m of altitude. In this work all data recorded were hourly. A brief description of these stations is in Table 1.

4. Methodology

A statistical analysis was chosen and applied in the present work. First of all, the big amount of data was analyzed and treated separately. Data from air quality monitoring systems stations needed to be validated and a great quantity of them were discarded because presented ambiguous values. Data from Meteorological station were treated as well but few samples were discarded. Once the two validations were performed, a database with all of them was build and each record consisted of meteorological variables and C_{NO2} for the four stations of the Air quality monitoring system. A statistical analysis followed a scheme that can be summarized in three steps:

- A basic statistical analysis
- Principal Component Analysis (PCA)
- Cluster Analysis (CA)

4.1. Basic statistical analysis

The data were analysed separately. The samples concerning C_{NO2} were treated considering the four stations. Basic indices such as N°, M, M*d*, Max, $V_{M\%}$ and $N°_{T200}$ were calculated to better understand C_{NO2} trend. The same analysis was made for meteorological variables. C_{NO2} was characterized respect both the four years and a division in diurnal hours (07:00/18:00) and nocturnal hours (19:00/06:00). It was also calculated the number of times C_{NO2} overtook the limit imposed the Air Quality Directive 2008/50/EC. In order to better characterize the evolution of C_{NO2}, EMMA index [5] was used. It was important to consider the reference temporal periods and values [5]. In order To better define the scale many reference standards [2] and C_{NO2} trends of previous years were consulted. According to this index, 7 classes were defined in Table 2.

Table 2. Classes of C_{NO2} according EMMA index.

Class	Limit
Good	$C_{NO2}<C_{AM}$
Moderate	$C_{AM}<C_{NO2}<C_{IV}$
Poor	$C_{IV}<C_{NO2}<C_{AV}$
Critical	$C_{AV}<C_{NO2}<C_{TV}$
Bad	$C_{TV}<C_{NO2}<C_{LL}$
Severe	$C_{LL}<C_{NO2}<C_{UL}$
Extreme	$C_{NO2}>C_{UL}$

These classes were defined as follow:

- C_{AM} represents the annual mean of C_{NO2} concentration according European standards.
- C_{TV} represents the current limit value imposed by the Directive 2008/50/EC.
- C_{UL} represents the upper protection limit. It was set according European Standards.
- C_{LL} represents the lower protection limit and was set as half the value of C_{UL}.
- C_{IV} represents the intermediate value between C_{AM} and $C_{TV.}$
- C_{AV} represents the alert concentration and was set equal more or less the 85% of $C_{TV.}$

4.2. Multivariate Analysis

After the data were treated and analyzed separately, a multivariate analysis was used to relate meteorological patterns and C_{NO2} in different stations and considering diurnal and nocturnal hours. First a PCA was conducted and results of it were used as support for a following CA. In previous studies, these two approaches were combined to explore significant information from the origin data for different air pollutants [6-8].

4.3. Principal Components Analysis

PCA is a statistical technique that transforms the original set of inter-correlated variables into a new set of an equal number of independent uncorrelated variables or principal components that have linear combinations to the original variables. This technique was used to analyze the whole set of data composed by atmospheric variables and C_{NO2}, normalizing them because of their different units of measurement. In order to have robust results, only principal components with E greater than 1 were considered because only these samples can be considered statistical significant [9]. For the same reason only linear correlation coefficients with absolute values greater than 0.50 were selected [10]. This analysis was useful to highlight principal components and to exclude variables that do not give a significant contribution to the set of data.

4.4. Cluster Analysis

CA is used to group objects based on the similarity between them. In this study, a no-hierarchical agglomeration algorithm for clustering was applied. It was used K-means clustering of observations. This procedure uses non-hierarchical clustering of observations according to MacQueen's algorithm [11]. The variables were standardized in order to minimize the effect of scale differences because of their different units. K-means procedures work best when you provide good starting points for clusters [12] and for this reason the classification by EMMA index was used to initialize the clustering process. Only Clusters with a $S_{\%}$ greater than 20% and D_{EA} less than 1.3 were considered. StD, M and other parameters of each variable were considered to better understand the trend of these clusters.

5. Results and discussions

Table 3 shows basic statistical indices that were calculated considering the four air quality monitoring stations. Station "Librino" presents C_{NO2} values lower than the others stations because it is placed in a zone with light traffic. Its values decreased from 34.78 μg/m^3 in 2009 up to 16.07 μg/m^3 in 2012. The station of "Viale V. Veneto" presents the highest values in terms of C_{NO2} and the peak is 70.11 μg/m^3 in 2010. Concerning "Piazza A. Moro" station, it has to be mentioned that there were insufficient data in 2010 and 2011. "Parco Gioeni" station presents an important decrease of C_{NO2} from 74.97 μg/m^3 in 2009 up to 17.22 μg/m^3 in 2012. According parameters imposed by the European Directive 2008/50/EC it was highlighted that all stations present for all the years a C_{NO2} overtaking the limit of 200 μg/m^3 less times than 18 (number of allowed exceedances) with the exception of the station "Parco Gioeni" in 2009. It is also important to notice that the station "Parco Gioeni" never gets the minimum percentage of valid measurements imposed by the same law (70%).

Table 3. Basic statistical indices

		2009	2010	2011	2012
LIBRINO	N°	7626	5631	6875	7489
	A_mC_{NO2}	34.78	28.56	16.72	16.06
	M*d*	31.22	22.46	11.96	10.77
	$N°_{T200}$	0	0	0	0
	Max	128.75	176.93	122.24	119.03
	$V_{M\%}$	98.83	67.08	81.89	88.96
Parco GIOENI	N°	4315	\	3770	5176
	A_mC_{NO2}	74.97	\	28.18	17.22
	M*d*	66.37	\	20.15	10.76
	$N°_{T200}$	66	0	0	0
	Max	289.33	\	194.44	114.73
	$V_{M\%}$	51.4	\	44.91	61.49
Piazza A. MORO	N°	6331	\	\	7791
	A_mC_{NO2}	37.41	\	\	34.44
	M*d*	28.35	\	\	28.03
	$N°_{T200}$	1	0	0	0
	Max	210.41	\	\	177.75
	$V_{M\%}$	75.41	\	\	92.55
Viale V. VENETO	N°	6552	6389	8276	8147
	A_mC_{NO2}	67.14	70.68	71.32	65.73
	M*d*	66.16	70.11	69.79	65.22
	$N°_{T200}$	10	0	3	0
	Max	285.18	182.53	214.15	182.77
	$V_{M\%}$	78.04	76.1	98.58	96.78

According the use of the EMMA index, the frequency of occurrence of C_{NO2} was calculated in respect to the reference years (Figures 1-4) and diurnal (Figure 5) and nocturnal hours (Figure 6). The trend of C_{NO2} is almost the same with a most frequency of the Bad class both for years and hours. The station of "Viale V.Veneto" presents a frequency of occurrence of the Bad class very high, especially in the years 2011 (75%) and 2012 (79.7%). All stations present almost the same trend in diurnal hours and nocturnal hours. Even if it is supposed a drastic decrease of C_{NO2} from diurnal hours to nocturnal hours, it does not happen in the urban area of Catania because of the intensive traffic during the late afternoon caused by the daily commute to home.

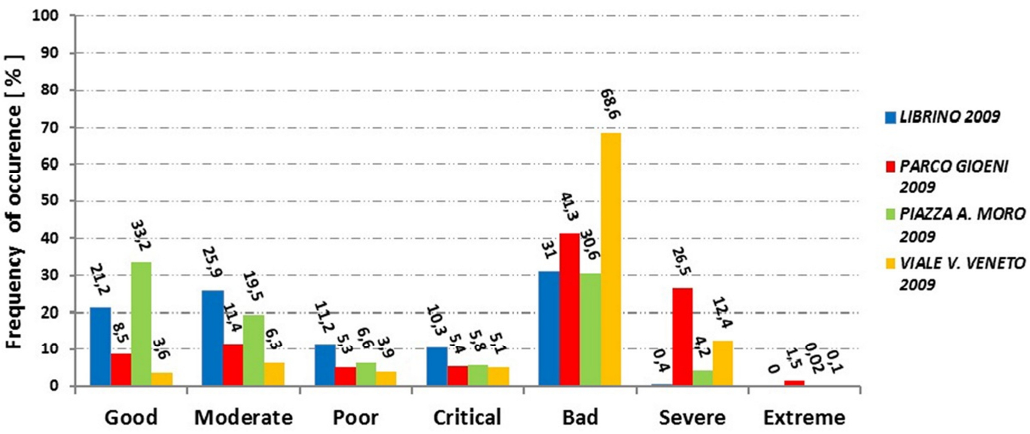

Fig 1. C_{NO2} trend in the four stations in 2009.

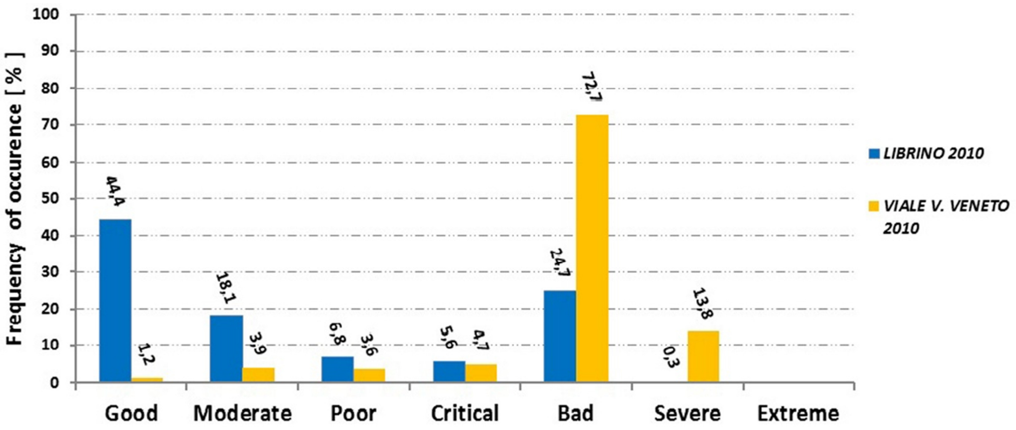

Fig 2. C_{NO2} trend in the two stations in 2010.

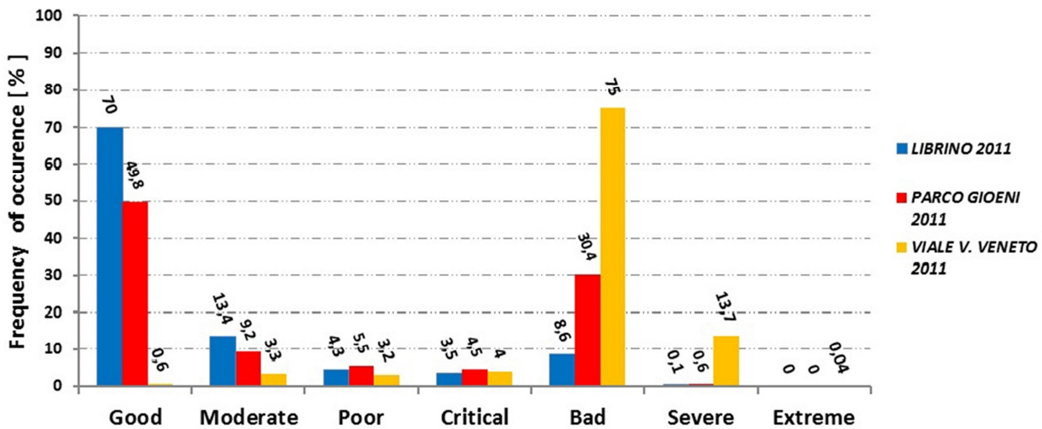

Fig 3. C_{NO2} trend in the three stations in 2011.

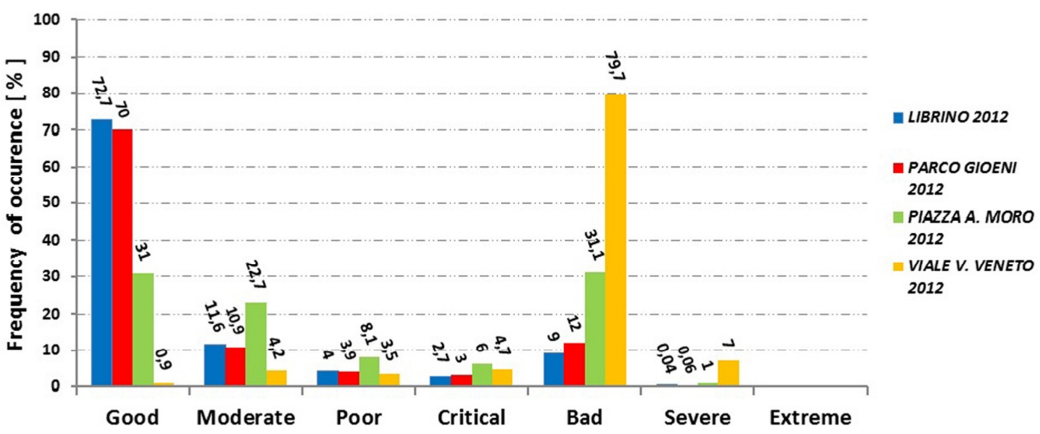

Fig 4. C_{NO2} trend in the four stations in 2012.

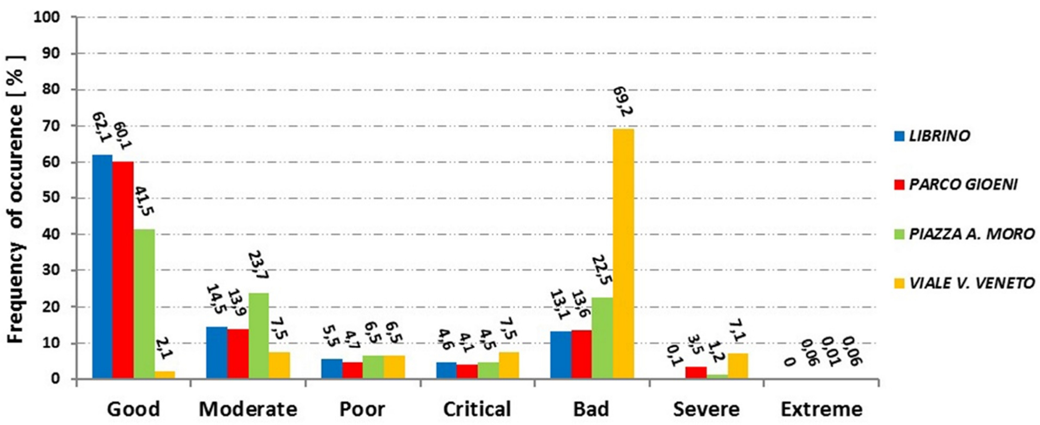

Fig 5. C_{NO2} trend in the four stations during diurnal hours.

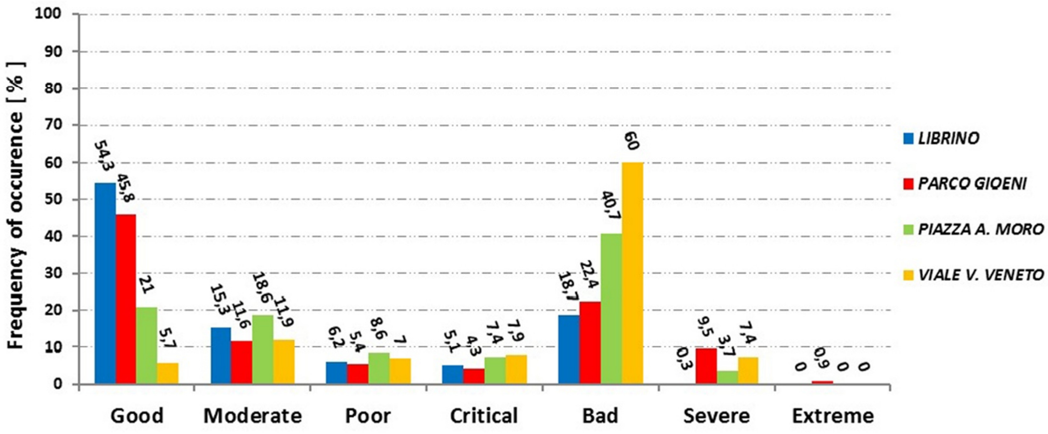

Fig 6. C_{NO2} trend in the four stations during nocturnal hours.

PCA was made in order to relate atmospheric data from the meteorological station with C_{NO2} of the four stations of the air quality monitoring system considering diurnal hours (Table 4) and nocturnal hours (Table 5). It is interesting how the first principal component is described almost ever by a strong correlation between T, H_R and R that characterize the typical Mediterranean climate. Moreover, it is shown that for both diurnal and nocturnal hours there is a strong linear dependence between V_w and C_{NO2}. The P_{RC} do not seem to give any significant contribution to the study of this set of data. For this reason, it was decided to exclude P_{RC} in the CA.

Table 4. Main results of PCA at all stations for diurnal hours.

	Librino		Parco Gioeni		Viale V. Veneto		Piazza A. Moro	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
T	**0.50**	0.29	**0.51**	0.24	**0.52**	0.10	**0.50**	0.22
P_{RC}	-0.18	0.23	-0.25	0.04	-0.19	0.29	0.18	-0.28
H_R	**-0.56**	-0.05	**-0.55**	0.17	**-0.57**	0.06	**-0.56**	-0.11
R	**0.54**	0.15	**0.57**	0.03	**0.56**	0.01	**0.55**	0.10
V_w	0.31	**-0.60**	0.18	**-0.69**	0.25	**-0.63**	0.27	**-0.64**
C_{NO2}	0.15	**0.70**	0.14	**0.66**	0.04	**0.71**	-0.16	**0.66**
E	2.29	1.30	2.18	1.33	2.26	1.19	2.25	1.21
Proportion	38.20%	21.60%	36.40%	22.20%	37.70%	19.90%	37.50%	20.30%
Cumulative	38.20%	59.80%	36.40%	58.60%	37.70%	57.60%	37.50%	57.80%

Table 5. Main results of PCA at all stations for nocturnal hours.

	Librino		Parco Gioeni		Viale V. Veneto		Piazza A. Moro	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
T	0.10	**0.66**	0.35	**0.52**	**0.62**	0.18	0.34	**-0.55**
P_{RC}	0.00	-0.28	-0.07	-0.25	-0.22	-0.17	0.01	0.40
H_R	**-0.56**	-0.39	0.32	**-0.66**	**-0.64**	0.29	**-0.66**	0.21
R	0.16	0.38	0.10	**0.47**	0.36	-0.15	0.27	0.28
V_w	**0.58**	-0.34	**-0.65**	0.13	0.00	**-0.72**	**0.49**	**0.54**
C_{NO2}	**-0.56**	0.26	**0.58**	0.08	0.17	**0.56**	-0.36	-0.36
E	1.65	1.40	1.72	1.33	1.49	1.40	1.51	1.37
Proportion	27.40%	23.30%	28.70%	22.20%	24.80%	23.40%	25.00%	22.80%
Cumulative	27.40%	50.70%	28.70%	50.90%	24.80%	48.20%	25.00%	47.80%

Table 6 and Table 7 show the results obtained by CA. Obviously the R was not considered for nocturnal hours. As expected, from the inter-conversion of Ozone, NO and NO_2 [13], there is a presence of high values of R and consequently high T, when there are low values of C_{NO2} for all clusters in Table 6. There is also a strong relation between low values C_{NO2} and high values of V_w and low values of H in clusters 1, 2, 3 and 4 (Table 6).

Table 6. Main results of CA at all stations for diurnal hours.

CLUSTER	T		H_R		R		V_w		C_{NO2}				Station
	M	StD	M	StD	M	StD	M	StD	M	StD	$S_{\%}$	D_{EA}	
1	27.70	4.03	46.14	11.42	2.57	0.51	2.07	0.58	10.25	8.71	23.00	1.26	Librino
2	29.25	2.89	43.84	10.85	2.62	0.53	2.00	0.64	21.99	9.92	23.72	1.16	Piazza A. Moro
3	27.66	3.58	49.17	10.36	2.57	0.51	2.14	0.57	44.02	15.19	22.53	1.23	Viale V. Veneto
4	27.75	2.95	46.50	10.16	2.56	0.57	1.84	0.55	24.03	16.22	19.83	1.18	Parco Gioeni

Table 7. Main results of CA at all stations for nocturnal hours.

CLUSTER	T		H_R		V_w		C_{NO2}				Station
	M	StD	M	StD	M	StD	M	StD	$S_{\%}$	D_{EA}	
5	25.59	2.97	75.92	6.58	0.70	0.43	18.21	11.87	29.93	1.08	Librino
6	20.27	3.43	83.21	7.02	0.42	0.39	32.12	14.59	24.29	1.07	Piazza A. Moro
7	10.32	3.43	83.76	7.25	1.03	0.47	43.06	15.85	26.66	1.14	Viale V. Veneto
8	19.64	3.30	81.76	6.30	0.56	0.41	33.04	22.70	20.69	1.05	Parco Gioeni

Figure 7 shows the prevailing Wind directions for the eight clusters. It shows as the typical direction of Wind for diurnal hours is North-East while for nocturnal hours is South-West.

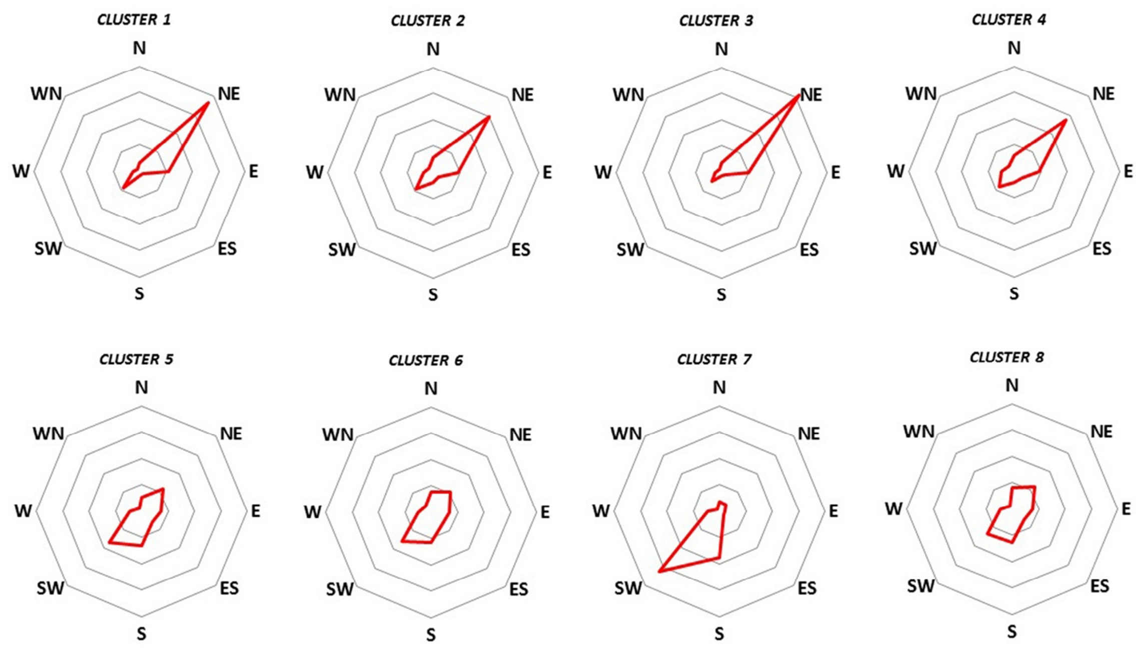

Fig 7. Prevailing Wind directions for the eight Clusters.

6. Conclusions

This work consists of a Statistical characterization of C_{NO2} in Catania. Data come from the four stations of the air quality monitoring system presented in this metropolitan area. While “Librino” station and “Parco Gioeni” station present light traffic, “Piazza A. Moro” station and especially “Viale V. Veneto” are characterized by heavy traffic. None of them are provided by meteorological instruments, and for this reason meteorological data were acquired and treated from the meteorological station of SIAS in the industrial zone. As expected after first analysis the highest values of C_{NO2} were found in the station of “Viale Veneto” while the station with le lowest values was “Librino”. After a basic statistical analysis a multivariate analysis was performed. This analysis showed that the lowest values of C_{NO2} were found when high V_w and low H_R occurred, and during diurnal hours they were also related with high T and R values. This methodology allowed to find some linear correlations between these parameters, nevertheless, the monitoring air system of Catania should be provided by meteorological instruments for each station to describe more accurately these correlations.

References

[1]Cantarel AM, Bloor JMG,Deltroy N,Soussana JF. Effects of Climate Change Drivers on Nitrous Oxide Fluxes in an Upland Temperate Grassland. Ecosystems 2011, 163: 51-9.
[2]EEA Report. Air quality in Europe - 2012 report. European Environment Agency. 2012.
[3]Keuken M, Roemer M, Van Den Elshout S. Trend analysis of urban NO2 concentrations and the importance of direct NO2 emissions versus Ozone/NOx equilibrium. Atmospheric Environment 2009, 43: 4780-4783.
[4]Shishir l, Patil RS. Monitoring of atmospheric behaviour of NOx from vehicular traffic. Environmental Monitoring and Assessment 2001, 68: 37-50.
[5]Kassomenos P, Skouloudis A, Lykoudis S, Flocas HA. Air quality indicators for uniform indexing of atmospheric pollution over large metropolitan areas. Atmospheric Environment 1999, 33: 1861-1879.
[6]Pires JCM, Sousa SIV, Pereira MC, Alvim-Ferraz MCM, Martins FG. Management of air quality monitoring using principal component and cluster analysis-Part I: SO_2 and PM_{10}. Atmospheric Environment 2008, 42: 1249-60.
[7]Pires JCM, Sousa SIV, Pereira MC, Alvim-Ferraz MCM, Martins FG. Management of air quality monitoring using principal component and cluster analysis-Part II: CO, NO_2 and O_3. Atmospheric Environment 2008, 42: 1261-74.
[8]Shah MH, Shaheen N. Annual and seasonal variations of trace metals in atmospheric suspended particulate matter in Islamabad, Pakistan. Walter Air Soil Pollut 2008, 190: 13-25.
[9]Yidana SM, Ophori D, Banoeng-Yakubu B. A multivariate statistical analysis of surface water chemistry data the Ankobra Basin, Ghana. J Environ Manage 2008, 86: 80-87.
[10]Jolliffe IT. Principal component analysis. New York: Springer; 1986.
[11]Johnson R, Wichern D. Applied Multivariate Statistical Methods. Fifth Edition. New Jersey: Prentice Hall; 2002.
[12]Milligan GW. An Examination of the Effect of Six Types of Error Pertubation on Fifteen Clustering Algorithms. Psychometrika 1980, 45: 325-342.
[13] Suqin H, Hai B, Yinchang F, Aixia L, Xiangjin L, Fang Z, Xiaoling Z. Analysis of Relationship between O_3, NO and NO_2 in Tianjin, China. Aerosol and Air Quality Research 2011, 11: 128-139.