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# Analysis and characterization of the predominant pollutants in the Catania's air quality monitoring stations.

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**Abstract**

It is useful to know about whether one or more pollutants predominate in different parts of a city and contributes to evaluating the efficacy of a variety of counter-measures for lowering pollutants in urban areas. This paper compares Catania (Italy) air quality measured in 2003 with that in 2012. The investigation was carried out at four monitoring stations of the city's Air Quality Monitoring Network (AQMN). The monitoring station locations had not changed from 2003 to 2012.

The impact of the city's primary and secondary pollutants was estimated from analyses of the daily concentrations of CO, $SO_2$, $PM_{10}$, $NO_2$ and$O_3$, and then by assembling the data into classes by applying Sturge's rule which provides the optimal number of intervals (or classes). Each class provides frequency density to make comparable intervals with different amplitudes. By analysing the frequency density intervals, the prevalence of a pollutant class could be highlighted and consequently linked to a range of representative concentrations in each urban area for each year analysed. Thus, after a decade, the decrease, stability or increase in a given pollutant could be defined providing a general overview of air quality traits in Catania and giving guidelines for pollution control policies.


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*Keywords:* Air quality, urban area, $NO_2$,$O_3$,$PM_{10}$

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## 1. Introduction

Continuous atmospheric monitoring for potential human health and ecosystem risks is critically important [1]. Increasing traffic pollutant concentrations are proportional to the increasing number of vehicular traffic. Measures taken in the last ten years especially those norms relating to fuel quality and the emissions of newly registered vehicles have had clearly positive effects regarding CO, $C_6H_6$ and $SO_2$. This partial improvement is above all perceived in those cities where the predominant source of pollution is vehicular.

The city of Catania falls into this category having one of the highest motorization indices in Italy at 700 vehicles per 1000 inhabitants.Furthermore, many of these vehicles are old in Euro class 0, registered prior to 1993. Moreover, added to this is the huge number of scooters and motorcycles abetted by the warm climate, the traffic congestion and the shortage of parking [2]. Factors such as domestic heating (abetted by the warm climate) are insignificant as are the emissions from industrial production. Time studies of air pollution concentrations in Catania [3,4] reveal how $PM_{10}$ concentrations have remained at acceptable levels even in the most congested areas, daily levels of 50μg/m$^3$ occasionally being verified when air currents bring in dust from the Sahara. In these same areas the most critical air quality criteria is $NO_2$ above all in urban centres [5,6]. Despite not having reached hourly concentration peaks of 200 μg/m$^3$, during most congestion and least wind concentrations of over 100 μg/m$^3$ have been measured as well as annual means above the baseline of 40μg/m$^3$ (EU Directive 2008/50). The critically high levels of $NO_2$ in many cities have not been remedied as they have for other pollutants [7,8].

These analyses identified the pollutants characteristic of the main urban conglomerations of Catania city. The pollutant concentration data were monitored in four monitoring stations in the Air Quality Monitoring Network (AQMN) of the city council. The station locations remained the same between 2003 and 2012 allowing a comparison over ten years of the pollutant concentrations to which the inhabitants had been exposed.

The data population used in this analysis is from the daily average pollutant concentrations in each monitoring station. The pollutants considered were carbon monoxide (CO), nitrogen dioxide ($NO_2$), nitrogen oxide (NO), sulphur dioxide ($SO_2$), the particulate ($PM_{10}$) and ozone ($O_3$).

To compare the pollutant concentrations measured over the two years were grouped into classes. The subdivisions into classes were carried out as per H.A. Sturges [9,10], which takes into account sample size and provides the optimum interval number (classes). Each class provides a frequency density so intervals with various amplitudes can be compared. The classes with greater frequency densities helped identify the associated concentration interval (CI). By iterating the calculation for each pollutant at the monitoring station, the prevalent pollutant concentration range characteristic for each station could be found and tied to the associated urban conglomeration.

Knowing the various criticalities of city areas in relation to their characteristic pollutants is useful for evaluating pollutant reduction measures and mitigation in urban environments and avoiding less efficient and often useless procedures [11,12].

**Nomenclature**

| | |
|---|---|
| $N°_{2003}$ | Number of Samples for 2003 year [ - ] |
| $N°_{2012}$ | Number of Samples for 2012 year [ - ] |
| $\mu_{max}$ | Daily maximum mean [μg/m$^3$] or [mg/m$^3$] |
| $\mu_{min}$ | Daily minimum mean [μg/m$^3$] or [mg/m$^3$] |
| C | Optimal number of classes [ - ] |
| $h$ | Amplitude of the classes [ - ] |
| CI | Concentration interval [ - ] |

## 2. Description of the monitoring network

The city of Catania has had an air quality monitoring network since 1992. From 2009 to 2010 the whole network was re-organised substantially reducing the number of monitoring stations and up-grading as per EU Directives 50/2008 and D.Lgs 155/2010. To date the network consists of four monitoring stations: Parco Gioeni(S1), Piazza A. Moro (S2),Viale V. Veneto (S3),Librino(S4)whose characteristics are reported in table 1. Each station has a series of analysers which conform to UNI EN and are inter-independent. They can measure $SO_2$, $PM_{10}$, CO, $O_3$ or a family of $NO_2$, NO, $NO_X$, BTX. The analysers are calibrated automatically and periodically re-calibrated with certified gasses. The basic data acquired by these devices is processed on-board and stored as per-hour averages for each parameter. Subsequently, the station data is up-loaded to the central computer, validated and archived.

Table 1. Air quality monitoring station characteristics.

| Station | ID | Description | Altitude (m) | Pollutants measured |
|---|---|---|---|---|
| Parco Gioeni | S1 | Urban-background | 135 | NO, $NO_x$, $NO_2$, $O_3$, $SO_2$, CO, BTX, $PM_{10}$ |
| Piazza A. Moro | S2 | Medium traffic | 76 | NO, $NO_x$, $NO_2$, CO, $PM_{10}$ |
| Viale Veneto | S3 | Heavy traffic | 38 | NO, $NO_x$, $NO_2$, $SO_2$, CO, BTX, $PM_{10}$ |
| Librino | S4 | Light traffic | 71 | NO, $NO_x$, $NO_2$, $O_3$, CO, $PM_{10}$ |

## 3. Data analysis

### 3.1. Data Organization

The pollution concentration data was obtained hourly so it was thought better to summarise the daily data with a representative average for 24h being $\mu_{i,j}$(the pollutant, the station). The data was grouped by intervals or classes using Sturges law (1):

$$C = 1 + \frac{1}{log2}(logN)(1)$$

Equation (1) is based on the sample number (N); the more data the less influence casual fluctuations. C is rounded to the nearest whole number. In this study equation 1 has been adapted for the *i-pollutant* measured at *j-station* obtaining an optimum number of classes:

$$C_{i,j} = 1 + 3{,}322(logN)_{i,j}$$

(2

where$(N)_{ij}$is the number of data acquisition days. The ideal condition would be $N_{ij}$= (1,…, 365 or 366)generating a $C_{ij}$value approximated to 9; this condition is not always satisfied since the measuring equipment may malfunction so $(N)_{ij}$may vary. This variability is significant when $(N)_{i,j}<185$, whereas for $(N)_{i,j}\geq 185$ the optimum number of classes remains the same. The pollutants in this study are grouped into 9 classes when $(N)_{i,j}>185$. To compare the two reference years, amplitude *h* was calculated for the classes of *i-pollutant* and *j-station* using (3):

$$h_{i,j} = \frac{[\mu_{(max)}]_{i,j} - [\mu_{(min)}]_{i,j}}{C_{i,j}} \ (3)$$

where $\mu_{(max)i,j}$ and $\mu_{(min)i,j}$ are the average daily maximum and minimum concentrations for*i-pollutant* and *j-station* measured during the two reference years. Table 2 summarises the sample number for each pollutant, the classes, amplitudes, average maximums and minimums relative to the concentration values of the pollutants measured at the monitoring stations during 2003 and 2012.

Table 2. Pollutant data monitored at the stations

| | | NO | $NO_2$ | $O_3$ | CO | $PM_{10}$ | $SO_2$ |
|---|---|---|---|---|---|---|---|
| S1 | $N°_{2003}$ | 301 | 301 | - | 338 | - | 362 |
| | $N°_{2012}$ | 241 | 241 | - | 240 | - | 229 |
| | $C$ | 9 | 9 | - | 9 | - | 9 |
| | $h$ | 17.25 | 11,35 | - | 0,50 | - | 0,90 |
| | $\mu_{max}$ | 156.70 | 111,82 | - | 4,90 | - | 8.52 |
| | $\mu_{min}$ | 1.29 | 9,56 | - | 0.12 | - | 0,18 |
| S2 | $N°_{2003}$ | - | - | 330 | 265 | 203 | - |
| | $N°_{2012}$ | - | - | 213 | 361 | 340 | - |
| | $C$ | - | - | 9 | 9 | 9 | - |
| | $h$ | - | - | 10,25 | 0,30 | 6.40 | - |
| | $\mu_{max}$ | - | - | 96,76 | 3,05 | 61.30 | - |
| | $\mu_{min}$ | - | - | 4,24 | 0,21 | 3.40 | - |
| S3 | $N°_{2003}$ | 268 | 268 | - | 301 | 274 | 296 |
| | $N°_{2012}$ | 359 | 359 | - | 242 | 342 | 362 |
| | $C$ | 9 | 9 | - | 9 | 9 | 9 |
| | $h$ | 17.00 | 11,65 | - | 0,45 | 10,90 | 2.80 |
| | $\mu_{max}$ | 158,88 | 132,48 | - | 4,13 | 100,35 | 26.05 |
| | $\mu_{min}$ | 5,94 | 27.33 | - | 0.14 | 2,2 | 0,91 |
| S4 | $N°_{2003}$ | 255 | 255 | 313 | 312 | 273 | - |
| | $N°_{2012}$ | 352 | 352 | 347 | 349 | 308 | - |
| | $C$ | 9 | 9 | 9 | 9 | 9 | - |
| | $h$ | 4,35 | 8.20 | 11.35 | 0,25 | 6,85 | - |
| | $\mu_{max}$ | 40,66 | 76,91 | 104.72 | 2,39 | 66,13 | - |
| | $\mu_{min}$ | 1.17 | 3.15 | 2,25 | 0,12 | 4,25 | - |

Having obtained the optimum number of classes, the frequency $(f_{k,i,j})$ andthe $n^{th}$ class relative to *i-pollutant* measured at *j-station* was calculated using (4):

$$f_{k,i,j} = \frac{n_{C_k}}{N_{i,j}} \qquad (4)$$

where$n_{Ck}$ is the sample number in the $n^{th}$ class; $N_{ij}$ is the total sample number of *i-pollutant* measured at *j-station.*

### 3.2. Frequency density

Considering that each class $(C_{i,i})$ has a different amplitude, the frequency density$(d_{k,i,j})$ of the $n^{th}$ class relative to the*i-pollutant* measured at the *j-station* was used to compare the frequencies. The frequency of an $n^{th}$ class member is influenced by class amplitude so using the frequency density gets round the problem by providing distribution data which is uninfluenced by amplitude. In this work, frequency density is the ratio between frequency $(f_{k,i,j})$ and the respective amplitude of the $n^{th}$ class relative to the *i-pollutant* measured at the *j-station* (5):

$$d_{k,i,j} = \frac{f_{k,i,j}}{h_{i,j}} \qquad (5)$$

The frequency density of a class can be considered as a more frequent concentration range during a specific timeinterval in an urban conglomeration. Tables 3, 4, 5, and 6 show the frequency density for each class and the pollutant and monitoring station over the two reference years.

Table 3. Frequency density for monitoring station S1.

| Pollutant | | Classes | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| NO | ***2003*** | 0,0129 | 0,0189 | 0,0083 | 0,0071 | 0,0052 | 0,0027 | 0,0013 | 0,0010 | 0,0006 |
| | ***2012*** | 0,0563 | 0,0017 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $NO_2$ | ***2003*** | 0,0003 | 0,0026 | 0,0129 | 0,0225 | 0,0284 | 0,0158 | 0,0038 | 0,0012 | 0,0006 |
| | ***2012*** | 0,0168 | 0,0190 | 0,0230 | 0,0154 | 0,0062 | 0,0051 | 0,0011 | 0,0011 | 0,0004 |
| CO | ***2003*** | 0,0237 | 0,3905 | 0,7278 | 0,4793 | 0,2485 | 0,0947 | 0,0237 | 0,0059 | 0,0059 |
| | ***2012*** | 1,4750 | 0,4917 | 0,0333 | 0 | 0 | 0 | 0 | 0 | 0 |
| $SO_2$ | ***2003*** | 0,5067 | 0,3785 | 0,1587 | 0,0305 | 0,0153 | 0,0092 | 0,0061 | 0,0031 | 0,0031 |
| | ***2012*** | 0,7424 | 0,2377 | 0,0534 | 0,0534 | 0,0146 | 0,0097 | 0 | 0 | 0 |

Table 4. Frequency density for monitoring station S2.

| Pollutant | | Classes | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| $O_3$ | ***2003*** | 0,0283 | 0,0118 | 0,0259 | 0,0189 | 0,0077 | 0,0038 | 0,0006 | 0,0003 | 0,0003 |
| | ***2012*** | 0,0046 | 0,0147 | 0,0229 | 0,0202 | 0,0137 | 0,0105 | 0,0069 | 0,0027 | 0,0014 |
| CO | ***2003*** | 0,6117 | 1,5231 | 0,7116 | 0,2996 | 0,0999 | 0,0125 | 0,0499 | 0,0125 | 0,0125 |
| | ***2012*** | 2,1855 | 0,9826 | 0,1377 | 0,0275 | 0 | 0 | 0 | 0 | 0 |
| $PM_{10}$ | ***2003*** | 0,0169 | 0,1062 | 0,0262 | 0,0023 | 0,0031 | 0,0015 | 0 | 0 | 0 |
| | ***2012*** | 0,0087 | 0,0201 | 0,0420 | 0,0425 | 0,0256 | 0,0096 | 0,0037 | 0,0023 | 0,0018 |

Table 5. Frequency density for monitoring station S3.

| Pollutant | | Classes | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| NO | ***2003*** | 0,0094 | 0,0158 | 0,0134 | 0,0108 | 0,0031 | 0,0035 | 0,0020 | 0,0002 | 0,0007 |
| | ***2012*** | 0,0234 | 0,0221 | 0,0092 | 0,0028 | 0,0011 | 0,0003 | 0 | 0 | 0 |
| $NO_2$ | ***2003*** | 0,0010 | 0,0022 | 0,0119 | 0,0250 | 0,0272 | 0,0138 | 0,0035 | 0,0010 | 0,0003 |
| | ***2012*** | 0,0010 | 0,0048 | 0,0285 | 0,0328 | 0,0143 | 0,0041 | 0,0007 | 0 | 0 |
| CO | ***2003*** | 0,0074 | 0,1255 | 0,5832 | 0,6792 | 0,4208 | 0,2510 | 0,1255 | 0,0221 | 0,0074 |
| | ***2012*** | 0,1469 | 1,6437 | 0,3949 | 0,0367 | 0 | 0 | 0 | 0 | 0 |
| $PM_{10}$ | ***2003*** | 0,0221 | 0,0459 | 0,0074 | 0,0030 | 0,0017 | 0,0030 | 0,0044 | 0,0027 | 0,0017 |
| | ***2012*** | 0,0030 | 0,0282 | 0,0467 | 0,0102 | 0,0030 | 0,0008 | 0 | 0 | 0 |
| $SO_2$ | ***2003*** | 0,2111 | 0,0941 | 0,0290 | 0,0121 | 0,0012 | 0,0048 | 0 | 0,0012 | 0,0036 |
| | ***2012*** | 0,3058 | 0,0306 | 0,0207 | 0 | 0 | 0 | 0 | 0 | 0 |

Table 6. Frequency density for monitoring station S4.

| Pollutant | | Classes | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| NO | ***2003*** | 0,1861 | 0,0215 | 0,0081 | 0,0054 | 0,0027 | 0,0027 | 0,0009 | 0,0018 | 0,0009 |
| | ***2012*** | 0,1742 | 0,0458 | 0,0059 | 0,0033 | 0,0007 | 0 | 0 | 0 | 0 |
| $NO_2$ | ***2003*** | 0,0033 | 0,0067 | 0,0191 | 0,0258 | 0,0263 | 0,0220 | 0,0100 | 0,0057 | 0,0029 |
| | ***2012*** | 0,0412 | 0,0437 | 0,0274 | 0,0076 | 0,0014 | 0,0007 | 0 | 0 | 0 |
| CO | ***2003*** | 0,5513 | 2,2179 | 0,8974 | 0,1923 | 0,0641 | 0,0128 | 0,0256 | 0,0128 | 0,0256 |
| | ***2012*** | 1,0920 | 2,3678 | 0,4483 | 0,0920 | 0 | 0 | 0 | 0 | 0 |
| $PM_{10}$ | ***2003*** | 0,0128 | 0,0417 | 0,0337 | 0,0273 | 0,0171 | 0,0112 | 0 | 0 | 0,0011 |
| | ***2012*** | 0,0162 | 0,0338 | 0,0504 | 0,0309 | 0,0076 | 0,0033 | 0,0029 | 0,0010 | 0 |
| $O_3$ | ***2003*** | 0,0152 | 0,0273 | 0,0253 | 0,0138 | 0,0048 | 0,0008 | 0,0008 | 0 | 0 |
| | ***2012*** | 0 | 0 | 0,0041 | 0,0094 | 0,0181 | 0,0199 | 0,0188 | 0,0138 | 0,0041 |

Figures 1 and 2 graphically compare the frequency density trend of each class relative to the *i-pollutant* measured at the *j-station* during the two reference years (2003 & 2012) in the city of Catania. Each class represents a specific concentration interval and amplitude *($h_{i,j}$)*; as the class number grows, the concentration within the interval increases. The classes with greater frequency density represent the concentration range characteristic of the *i-pollutant* measured at the *j-station*. The pollutant concentration ranges measured for each class are reported in the appendix (table 7).

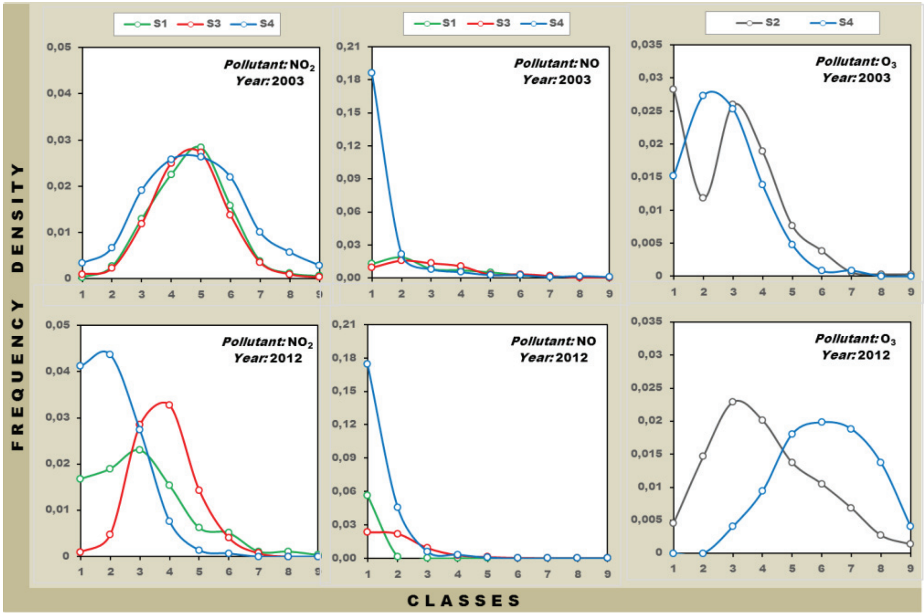


Fig.1- The frequency density distributions for $NO_2$, NO and $O_3$ during the two reference years

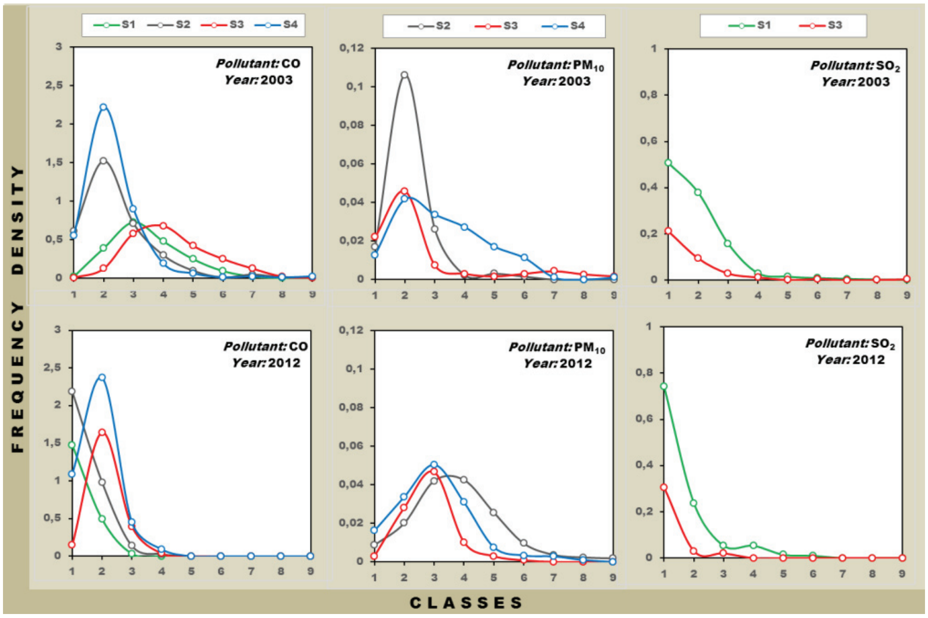


Fig.2 - The frequency density distributions for CO, $PM_{10}$ and $SO_2$ during the two reference years.

## 4. Results

### *4.1. Monitoring stations*

The frequency densities obtained at station (S1) show over ten years a reduction in pollutant concentrations. $NO_2$ has fallen from class 5 (CI 55.00–66.35μg/$m^3$) to class 3 (CI 32.28–43.63μg/$m^3$). Likewise NO has fallen from class 2 (CI 18.55–35.80μg/$m^3$ ) to class 1 (CI 1.29–18.54μg/$m^3$). CO has fallen from class 3 (CI 1.14–1.64mg/$m^3$) to class 1 (CI 0.12–0.62mg/$m^3$). Uniquely, $SO_2$ remains in class 1 with a very low concentration interval between 0,18 and 1,08 μg/$m^3$ a rise in frequency density for 2012 over 2003.

The frequency densities obtained at station (S2) show over ten years a partial increase in pollutant concentrations. $O_3$ has risen from class 1 (CI 4.24–14.49μg/$m^3$) to class 3 (CI 32.28–43.63μg/$m^3$ ). Likewise $PM_{10}$ has risen from class 2 (CI 9.81–16.21 μg/$m^3$) to class 4 (CI 22.63–29.03μg/$m^3$). CO has fallen from class 2 (CI 0.52–0.82mg/$m^3$) to class 1 (CI 0.21–0.51mg/$m^3$).

The frequency densities obtained at station (S3) show different characteristics compared to the previous stations. Pollutants like $NO_2$ and CO highlight a reduction in concentrations. $NO_2$ has fallen from class 5 (CI 73.97 and 85.62μg/$m^3$) to class 4 (CI 62.31 and 73.96μg/$m^3$). CO has fallen from class 4 (CI 1.52–1.97 mg/$m^3$) to class 2 (CI 0,60–1,05 mg/$m^3$). Pollutants like NO and $SO_2$ were more stable leaving them in classes 2 (CI 22.95–39.95 μg/$m^3$)and 1 (CI 0.91–3.71μg/$m^3$) for the two reference years. $PM_{10}$ has risen from class 2 (CI 13.11–24.01μg/$m^3$) to class 3 (24.02–34.92μg/$m^3$).

The frequency densities for station (S4) over the ten years show concentration increases for $O_3$ (Class 2, CI 13.61–24.96μg/$m^3$,to Class 6, CI 59.05–70.40μg/$m^3$)and $PM_{10}$ (Class 2, CI 11.11–17.96μg/$m^3$ to Class 3, CI 17.97–24.82 μg/$m^3$) stability for CO (remains in Class 2) and NO (remains in Class 1) and a significant decrease for $NO_2$ (Class 5, CI 35.99–44.29μg/$m^3$, to Class 2, CI 11.36 –19.56μg/$m^3$).

### *4.2. Identifying predominant pollutant*

The four monitoring stations are located in urban conurbations with quite different characteristics and so a scenario was created which takes into account the pollutant types to which the inhabitants in each conurbation are exposed to. By comparing the frequency densities at the four monitoring stations for the two reference years, a characteristic pollutant was identified for each station.

The results show that for station (S1) nitrogen dioxide ($NO_2$) was the characteristic pollutant in both reference years, although in 2012 its concentration was lower than for 2003. Among the pollutants monitored at station (S2), $PM_{10}$ was the characteristic pollutant in both years with higher levels in 2012 compared to 2003. Like station (S1), $NO_2$ was the characteristic pollutant in both years being lower in concentration in 2012 compared to 2003. There was a change in trend for the pollutants monitored at station (S4). In 2003 the characteristic pollutant was $NO_2$ which changed in 2012 to $O_3$. For S4, $O_3$s in 2003 were quite low compared to the high $NO_2$s. This situation reversed in 2012. Considering that these are secondary pollutants and not from direct emissions, certain particular conditions are necessary for their formation. It is likely that in 2012, favourable photochemical conditions existed for the formation of $O_3$ over $NO_2$.

## 5. CONCLUSIONS

From data acquired by the Air Quality Monitoring Network of the city of Catania, the characteristic pollutants of the main urban conurbations were identified and compared for 2003 and 2012 to see if they had increased, decreased or remained stable. The data was grouped into intervals or classes(C). Identifying the pollutant and its persistence during the two reference years along with characterising the monitoring station was defined by taking into account a class prevalence for each pollutant.

The data highlighted ever-present $NO_2$ in two of the urban conurbations in both reference years. Considering the location of the two monitoring stations (S1, S3), the surrounding morphological conditions and the area proportion they represent, the high likelihood of parking with the resulting pollutant accumulation could produce such significant values as to entail long-term health risks for their inhabitants.Station (S2) identified $PM_{10}$ as the main characteristic pollutant for residents. The peculiarities of that area are such that there is reduced air circulation which favours parking and pollutant accumulation. S4's urban context is quite different to the others. Here the secondary pollutants have dominated during the two reference years. In 2003 the main pollutant was $NO_2$ whereas in 2012 it became $O_3$.In 2012, $O_3$ replaced $NO_2$ probably as a result of favourable photochemical conditions and intensely stable atmospheric phenomena.

Future developments for these analyses will concentrate on correlating the inhabitants state of health with the main pollutant to identify wherever possible illness onset or the specific symptoms associated.

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