# IN ACCORDANCE WITH FRAMEWORK DIRECTIVE 96/62/EC, DEVELOPMENT OF AN AIR QUALITY MONITORING NETWORK IN A CHINESE CITY.

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## ABSTRACT

In the framework of the Sino-Italian Program in which the Italian Ministry of Environment and Territory is participating, an Air Quality Monitoring System in the City of Suzhou (China) was implemented by the Institute for Atmospheric Pollution of the Italian National Research Council (CNR-IIA). As stated in Framework Directive 96/62/EC, preliminary assessment of air quality is a very important step in the identification of sites for fixed monitoring stations. To that end, 100 saturation stations, equipped with passive samplers for sulphur dioxide, nitrogen oxides, ozone, ammonia and BTX (benzene, toluene and xylene), were set up. The concentration values of these pollutants, coming from three campaigns carried out in Suzhou, were represented and explored by using a suitable software. With reference to each campaign, pollution maps related to each pollutant were produced. Moreover, during the preliminary assessment, a georeferenced mobile unit containing three electrochemical sensors was developed and characterized to determine carbon monoxide, sulphur dioxide and nitrogen dioxide. The data coming from the mobile unit are not local (like the ones from the saturation stations); they support the concentration values collected by means of saturation stations and allow for the production of distribution maps of the gas concentrations in the areas of interest. Moreover, the device provides information on vehicle emissions.

In addition, 20 of the 100 saturation stations were equipped with particulate matter samplers. The determination of fine particulate matter ($PM_{10}$) was carried out by means of the gravimetric method. Finally, preliminary assessment allowed for the creation of a map with the definitive siting of the fixed monitoring stations. After this phase, the Suzhou Air Quality Monitoring System was implemented consisting of 9 fixed stations and 20 saturation stations.

*Keywords: air quality monitoring system, fuel cells, electrochemical sensors for pollutant determination, passive samplers.*

## 1 INTRODUCTION

Air Quality is one of the areas in which Europe has been most active in recent years. The aim of the European Commission (EC) has been to develop an overall strategy through the setting of long-term air quality objectives. A series of Directives [1,2] has been introduced to control levels of certain pollutants, including sulphur dioxide, nitrogen dioxide, particulate matter, lead, ozone, benzene, carbon monoxide, polyaromatic hydrocarbons and metals, and to monitor their concentrations in the air. In 1996, the Environment Council adopted Framework Directive 96/62/EC [3] on ambient air quality assessment and management. This Directive covers the revision of previously existing legislation and the introduction of new air quality standards for previously unregulated air pollutants, setting the timetable for the development of Daughter Directives on a range of pollutants. The Framework Directive requires the

assessment of ambient air quality on the basis of common methods and criteria; to this purpose, the Commission prepared a Guidance report on Preliminary Assessment under EC Air Quality Directives [4] and a Guidance on Assessment under the EU Air Quality Directives [5].
In the framework of the Sino-Italian Program in which the Italian Ministry of Environment and Territory is participating, an Air Quality Monitoring System in the City of Suzhou (P.R. China) was implemented by the Institute for Atmospheric Pollution of the Italian National Research Council (CNR-IIA). The Framework Directive 96/62/EC states that preliminary assessment represents a very important tool for the identification of the sites for fixed monitoring stations. Location of such sites may result from model application or be decided upon according to information relating to type and intensity of emitting sources, distribution of polluting sources within the city, expected maximum concentration points in relation to the presence of human targets (population exposition), prevailing meteorological conditions, etc. In addition, the sampling sites should be representative of a sufficiently large surrounding area and/or representative of sites characterised by similar environmental conditions.

## 2 PRELIMINARY ASSESSMENT IN SUZHOU

In accordance with Framework Directive 96/62/EC, the preliminary assessment was carried out using three main approaches: passive samplers, supplemented by particulate measurements, a conventional mobile unit and a non conventional mobile unit for grid measurements.

### 2.1 Passive samplers

The Italian National Research Council (Institute for Atmospheric Pollution) has developed, patented and certified a new passive device, known as *Analyst*, which collects pollutants over a very long time span. The *Analyst* was tested for a relatively long period of time and its performance documented in many scientific publications [6,7,8]. The low cost and easy operation of the *Analyst* makes it an ideal tool for large scale air pollution surveys with high spatial resolution. The *Analyst* diffusive sampler consists of a cylinder with a sorbent at one end which fixes the pollutant. The pollutant is sampled onto the sorbent at a rate controlled by the molecular diffusion of the pollutant gas in the air, without requiring any pump or electrical power [9,10,11]. The rate at which a pollutant is absorbed on the sorbent is - under specific conditions - a fixed constant (the uptake rate). After exposure of the samplers over periods varying from a few days to a few weeks, the tubes are closed and returned to the laboratory for solvent extraction and analysis by appropriate analytical techniques. This device can be used for the determination of BTX, $NO_2$, $SO_2$, $O_3$ and $NH_3$ and also as an extraction vial. Accuracy, precision and long exposure times make *Analyst* the best choice for the preliminary assessment of pollutants. 100 saturation stations, equipped with *Analyst* passive samplers for sulphur dioxide, nitrogen dioxide, ozone, ammonia and BTX (benzene, toluene and xylene) and with a particulate matter electronic sampler were used to preliminarily assess air quality in Suzhou. Three campaigns were carried out in Suzhou between August and October 2003 (first campaign, from the $1^{st}$ to the $15^{th}$ of August; second campaign, from the $15^{th}$ to the $30^{th}$ of August; third campaign from the $15^{th}$ to the $30^{th}$ of October). Maps of the pollutant concentrations in the area were obtained by interpolation of the diffusive sampler measurements. This preliminary assessment made it possible to site the fixed station and, thus, produce a map with their definitive locations. The analyses were carried out between

September and December 2003 in the IIA-CNR laboratories. For the organic samples 300 gas chromatographic analyses were done and for the inorganic samples ($SO_2$, $NO_x$, $O_3$, $NH_3$) 1020 ionic chromatographic analyses.

### 2.2 Conventional mobile unit

It is used as a preliminary assessment method in order to verify whether a zone is in exceedance or near-exceedance of the limit values and to determine the ongoing assessment regime that will be required.
Mobile laboratories or transportable measurement stations used for stationary measurements at fixed sites, usually combine the advantages of automated measurement methods (continuous, time-resolved measurements) with mobility or flexibility. The location of maximum concentration levels in a zone were chosen taking into account the source distribution, local meteorological conditions and orography. Indeed the types of sources present in an area are very important when choosing a measuring site. For example, the impact from elevated point sources is often difficult to measure at one point at ground level because both wind direction and wind speed and their variation with height is important for the location of the maximum ground level impact. Furthermore for monitoring the pollution from roads, the impact will decrease with the distance from the road and the level of pollution will on average be proportional to the volume of traffic.

The goal was to create a predictive model of air pollution values from the ones measured in the conventional mobile unit and in the 100 saturation stations during the three campaigns. A suitable software was used.
The project database contained the saturation station sites with relative GPS coordinates and a table with the concentration values from each saturation station, together with the values coming from the mobile unit.
For each monitoring campaign, distribution maps relative to each interpolation and each pollutant were produced. Figure 1 shows the distribution map (IDW, *Inverse Distance Weighting*) relative to sulphur dioxide in the first campaign.

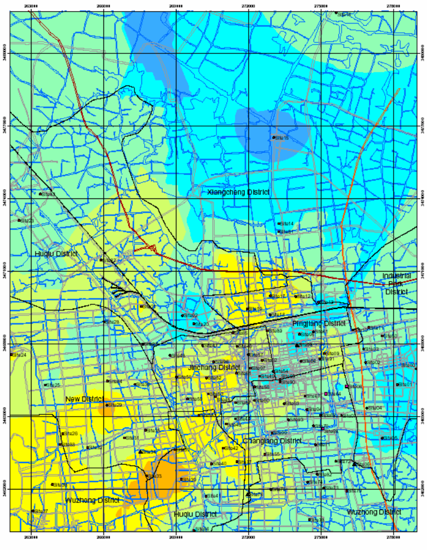


Figure 1. First campaign: Sulphur dioxide distribution map.

## 2.3 Non conventional mobile unit

Further to the assessment of pollution levels in areas of maximum concentrations, a non conventional mobile unit was used. This methodology is very useful when a limited number of measurements is required (small agglomerations) or when other kinds of screening techniques are not available. Unfortunately the method is not suitable to characterize air quality hot spots, for which additional sampling should be carried out. During the preliminary assessment in Suzhou, a georeferenced mobile unit (Eco–Explorer), equipped with sensors for atmospheric pollutants (carbon monoxide, sulphur dioxide and nitrogen dioxide) was used to:

1. construct a grid over the area under investigation;
2. prepare the measurement schedule, by choosing randomly over the year, the dates and hours for the measurements in such a way that they are evenly distributed over the months, the days of the weeks and the hours of the day, taking care that no neighboring intersections are measured on the same day;
3. make a graphical presentation of the pollutant distribution.

The box containing Eco–Explorer was set on a low speed vehicle (an electric bicycle) able to support the device. The measurements were performed by the mobile unit 4 times per day (between 8 am and 18 pm) covering 30 km. The map of the mobile unit route is showed in figure 3.

Figure 2 shows the trends of the gas average concentrations. The measurements were carried out between the 14$^{th}$ and the 21$^{st}$ of May 2004 in a central area of Suzhou.

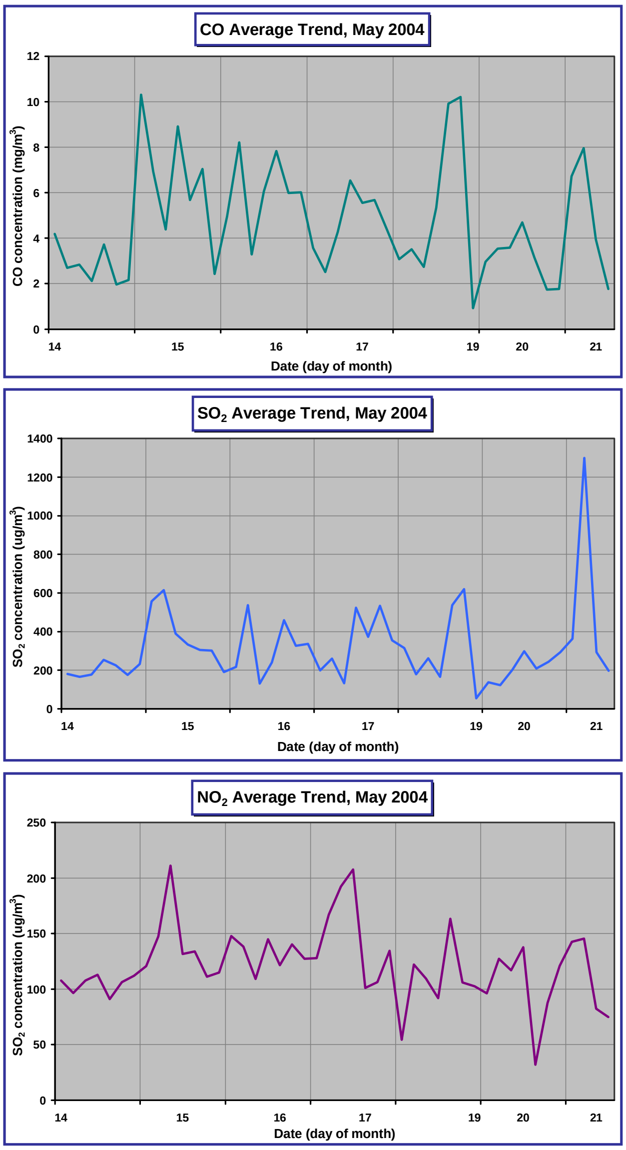


Figure 2. Gas average trend by means of fuel cells.

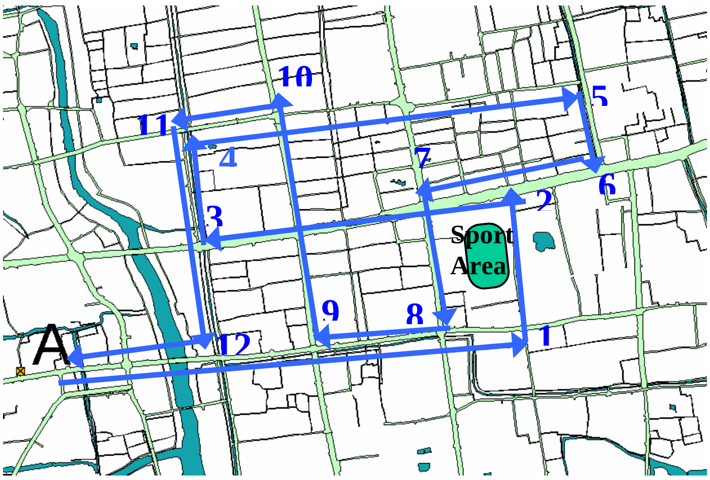


Figure 3. Map of the distance covered by the device.

The Eco-Explorer device contains three electrochemical sensors for the determination of carbon monoxide, sulphur dioxide and nitrogen dioxide. These sensors are micro fuel cells, designed to be maintenance-free and stable for long periods. The signal results in a direct response to volume concentration. In general, a fuel cell produces electricity through an electrochemical process. Unlike a standard battery, a fuel supply continuously replenishes the fuel cell. The power is generated as long as the reactants are fed into the fuel cell reactor. No part of the fuel cell is consumed during the process, so the cell should be everlasting. This is not true, indeed the cell lasts approximately 3 or 4 years.
As shown in figure 4, the central feature of the design is the gaseous diffusion barrier, which limits the gas flow to the sensing electrode. The electrode is therefore able to react with all the target gas that reaches its surface. After the reaction occurs, the electrode still maintains a residual electrochemical activity, which ensures its long life and temperature stability.

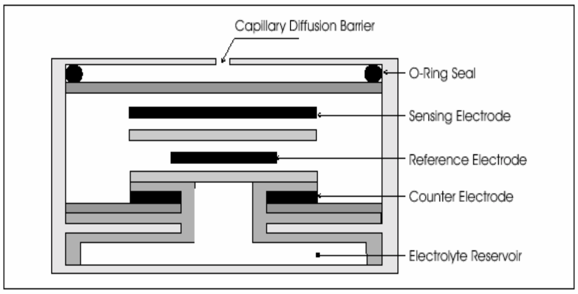


Figure 4. Four electrode sensor.

The diffusing gas occurs oxidation (carbon monoxide and sulphur dioxide) or reduction (nitrogen dioxide) at the sensing electrode. With respect to carbon monoxide, for example, the oxidation reaction is:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

The counter electrode balances the reaction at the sensing electrode. If oxidation occurs (carbon monoxide) at the sensing electrode, oxygen will be reduced to water at the counter electrode.

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Instead if the sensing electrode reaction is a reduction, water will be oxidized at the counter electrode.
The two chemical equations can be combined and simplified to give an overall cell reaction:

$$2CO + O_2 \rightarrow 2CO_2$$

Both the fuel and the product are gases, thus the sensor is merely a reaction catalyst and it is not directly consumed. The electrochemical reaction produces current (uA, detected by means of a digital multimeter) which is linearly proportional to the gas concentration in air. The sensors were designed to be highly specific and the effect caused by cross-interfering gases was minimized by:
1) developing a specific electrode catalysts;
2) controlling the operating potential of the sensing electrode;
3) using chemical filters to remove interfering gases selectively;
4) using a fourth electrode.
To achieve maximum accuracy, these sensors were calibrated using a gas mixture in the range where most measurements were made.

Calibration normally is carried out by exposing the sensing face of the sensor to the gas for a relatively short period, thus a calibration gas should not contain oxygen (the needed amount is supplied for a limited period of time by certified standard air). In most cases, a five minute exposure time is sufficient to achieve a stable calibration signal.
At first, specific tests were carried out to check the trend of the gas concentration signal vs temperature (temperature range: 10– 45°C). Both the span signal and the baseline (zero gas current) were affected by temperature. With respect to the three sensors, the span signal was only slightly affected by temperature, while the baseline signal varied with temperature exponentially. The baseline approximately doubled for every 10°C increase.

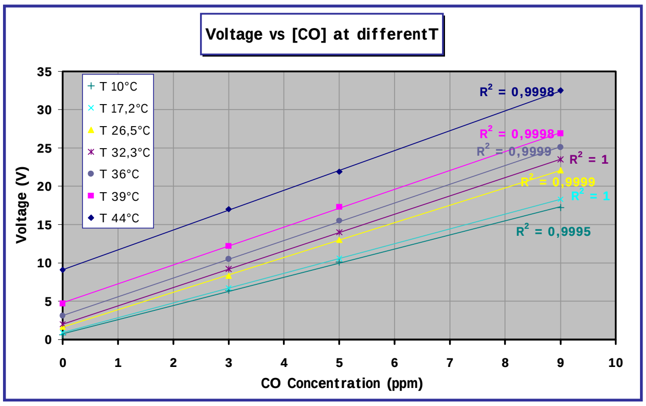


Figure 5. CO. Scatter plot of output signal vs gas concentration.

Afterwards, several tests were carried out to evaluate the interference caused by hydrocarbons (both aliphatic and olefins) mixtures. The mixture containing alkanes (n-butane, ethane, n-esane, methane, n-pentane and propane, total concentration 611 ppm) didn't affect the three sensors. The mixture containing alkenes (1-butene, ethylene, 1-esene, 1-pentene and propylene, total concentration 500 ppm) instead didn't affect the nitrogen dioxide sensor, affected slightly the sulphur dioxide sensor and highly the carbon monoxide sensor.
Finally, the influence of relative humidity on the sensor response was evaluated. To this end, a Humicon relative humidity generator was used to humidify the air (dilution gas) entering the cell. Only the nitrogen dioxide sensor showed significant response variations.
Once all the preliminary tests were carried out, the Eco-Explorer device (containing the three sensors) was positioned within a fixed monitoring station (Rome Municipality Air Quality Monitoring Network) in a medium-high traffic level area. This allowed for the comparison with the data coming from the automatic analyzers. The monitoring campaign took place from the 29$^{th}$ of December 2003 to the 7$^{th}$ of January 2004. The carbon monoxide and nitrogen dioxide sensors showed a trend comparable with the analyzer ones. Figure 4 shows the scatter plot with respect to the carbon monoxide sensor (notice the good correlation between the sensor measurements and the reference instrumentation: $R^2$ = 0.99).

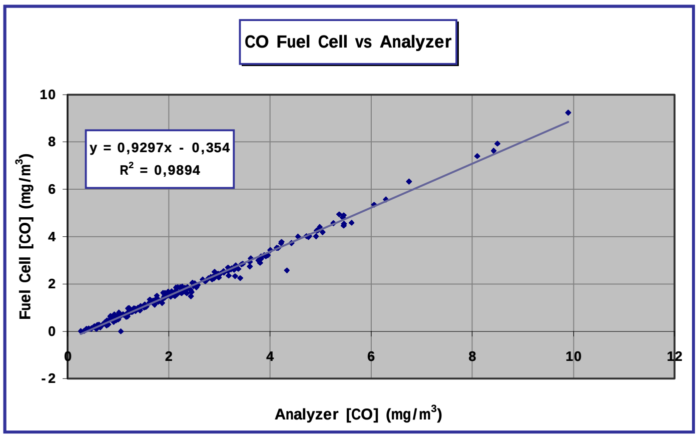


Figure 6. CO. Scatter Plot of fuel cell data vs analyzer data.

## 3 NETWORK DESIGN

The results of preliminary assessment were used as input for the network design [1,2,3,4,5] process, that is to say the procedure of macrositing fixed stations within a territory aimed at optimising the information on the spatial distribution of pollution levels within the territory. The essence of macrositing is not the assessment of concentrations at the monitoring site, but the optimisation of monitoring locations for translating the measured levels to other locations.
The step-wise process was along the following lines:
1. preliminary assessment of where in the zone monitoring may be needed to investigate how the spatial distribution of levels can best be assessed. An estimate was performed in order to classify at which type of location the relevant levels can be expected.
2. distribution of locations of monitoring stations. How a limited number of stations can be distributed over and within these location types to give the best description of the relevant levels in the territory was investigated. Out of the very large number of locations of a certain type to be assessed, one or more locations best suited to represent a larger set of relevant locations of this type were selected.
3. applying the data from the network in assessing the spatial distribution. Generalizing the results of measurements at individual locations, the measurement locations were finally determined.
The management and assessment requirements concerning a zone depend in principle on whether the pertinent thresholds are exceeded *anywhere* in the zone. Consequently the assessment of levels has to cover the entire zone and not only the spots where there is a fixed station. Therefore, a fixed saturation network was also designed in order to enlarge the spatial coverage of the AQMS assessment. Network design was completed in 2004: 9 fixed stations and 20 saturation stations were sited. Figure 4 shows the siting map of the fixed stations.

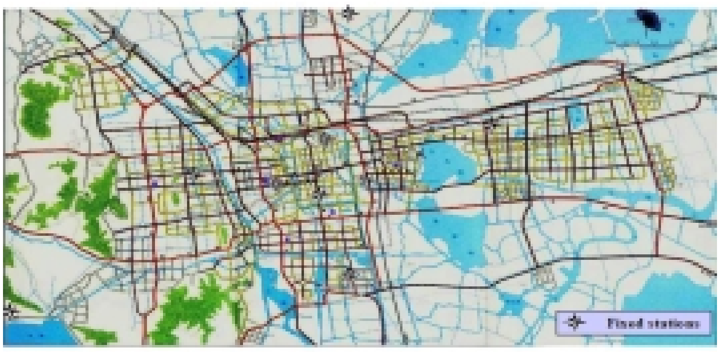


Figure 7. Siting of the fixed stations.

## 4 CONCLUSIONS

Full assessment of a monitoring system should include analysis of monitoring data, spatial distribution of concentrations and air pollution causes. The use of supplementary assessment methods, like passive samplers and non conventional mobile units, in legislation is new and needs considerable development in the next few years. The EU air quality Directives take advantage of advances in air quality science and introduce assessment methods and concepts that have not been used before in legislation. Preliminary air quality measurements are used to explore air quality, especially in those places where excesses are to be expected and/or emission information is inadequate.

This work shows that passive samplers are a valuable tool for determining the spatial distribution of pollutants over a large area and for preliminarily assessing integrated concentration levels over longer periods of time (long-term limit values). They can also be used to identify areas of maximum concentration and thus support the optimisation of monitoring networks.

Furthermore, data collected by the non conventional mobile unit, Eco–Explorer can be used to carry out grid measurements. This allows to obtain information on the relationship between the distribution of the studied pollutants from exhaust and the related traffic emissions. This kind of measurements can be made both, in urban and in rural areas.

Finally, air quality models are another way to improve the spatial coverage of assessment. They are by nature more suitable to provide complete coverage of the territory. They are essential tools in the development of action plans for improving air quality, which is the ultimate goal of local authorities. Another major advantage to be gained from using models in assessment and management of air quality is that they enhance the ability to map the spatial distribution of the pollutant concentrations. It is clear that modeling plays an important role in Preliminary Assessment. Knowledge of the spatial distribution of pollutant concentrations and emissions in a zone is required and models are appropriate tools for obtaining that information. Since a network in practice only has a limited number of stations and since monitoring is a part of the basis for assessing compliance and exposure, stations must represent other pollution/exposure situations in the zone. Data for a small set of locations needs to be translated into information on a much larger area (made up of similar locations). This is the essence of network design.

## References


[1] Council Directive 00/69/EC of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air, Official J. of European Communities, No L 313/12 – 13 December 2000.

[2] Council Directive 99/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, Official J. of European Communities, No L 163/41 – 29 June 1999.

[3] Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management, Official J. of European Communities, No L296/55 - 21 November 1996.

[4] Guidance Report on Preliminary Assessment under EC Air Quality Directives of January 1998, Project Manager Gabriel Kielland, European Environment Agency.

[5] Guidance on Assessment under the EU Air Quality Directives- Final Draft.

[6] De Santis,F., Vazzana,C., D'Angelo, B., Dogeroglu, T., Menichelli, S.& Allegrini, I. *Validation and use of a new diffusive sampler for ozone assesment in the Lazio Region, Italy*, In: Air Pollution X. C.A.Brebbia & J.F.Martin-Duque Eds., WIT Press, 2002, pp.371-380.

[7] De Santis,F., Dogeroglu, T., Fino, A., Menichelli, S., Vazzana, C. & Allegrini, I., *Laboratory development and field evaluation of a new diffusive sampler to collect nitrogen oxides in the ambient air*, Anal. Bioanal. Chem., Vol.373, 2002, pp.901-907; on-line: 3 Luglio 2002.

[8] Bertoni, G., Tappa, R.& Allegrini, I., *Assessment of a new passive device for the monitoring of benzene and other volatile aromatic compounds in the atmosphere*, Annali di Chimica, Vol.90, 2000, pp.249-263.

[9] Allegrini, I., Ianniello, A. & Costabile, F., Area Saturation Monitoring of atmospheric pollutants by means of passive samplers and diffusion denuders. *Proc. Of the 14th Int. Conf. on Air Quality – Assessment and Policy at local, Regional and Global scales*, Dubrovnik, Croatia, pp.300, 6-10 October 2003.

[10] Allegrini,I. & Costabile,F., A new approach for monitoring atmospheric pollution in urban environment. *Proc. Of the Int. Seminar Urban Air Quality Management* , 21st-23rd October 2002, Sao Paulo, Brazil.

[11] Brown, R.H., *The use of diffusive samplers for monitoring of ambient air*, Pure and Appl. Chem., Vol.65 (8), 1993, pp.1859-1874.