# MONITORING OF AIR QUALITY FOR NITROGEN DIOXIDE, NITROGEN OXIDES AND BENZENE IN SELECTED ZONES OF THE LOMBARDY REGION BY DIFFUSIVE SAMPLING

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## ABSTRACT

Diffusive sampling has been used to study the spatial distribution of $NO_2$, $NO_x$, and benzene in selected zones of the Lombardy Region, Italy, during winter and summer 2001. Three different categories of sampling sites (roadside, residential and background) were studied. In total, 315 sites distributed over four differently characterised zones of about 1000 $km^2$ were monitored. The results were evaluated on the basis of the limit values found in the European Directives.

## INTRODUCTION

Air pollution is highly variable both geographically and over time. Concentration differences between urban and rural areas vary from one pollutant, and one area, to another. Depending on where people spend their time, how long and when they spend in any place, exposures to air pollution may greatly differ. These variations depend on many different factors: on the distribution and activity of emission sources (i.e. the geographic patterns of emission sources); on the reactions and transformations that affect the pollutant during transport; on air mixing and transport. Under the European Framework Directive 96/62/EC [1], the Member States are required to assess the spatial concentration distribution of air pollutants throughout their territory by using screening techniques and large scale surveys. There is a need to devise monitoring techniques that can help in organising the plans and programmes that have to be drafted under the Directive when certain air quality thresholds have been exceeded. The use of diffusive sampling provides an answer to this problem. In principle, passive sampling represents a perfect tool in the light of the new Directive to map a particular area for a given pollutant and to characterise those areas where the limit values are expected to be exceeded. In fact, compared with the pump-dependent active sampling procedure, main advantages of the method are cost effectiveness, simplicity and the potential for large-scale measurements carried out at the same time. In addition, the passive device is not constrained to sites where electrical power is available.

In this work, diffusive sampling has been used to study the spatial distribution of $NO_2$, $NO_x$, and benzene in selected zones of the Lombardy Region, Italy, during winter and summer 2001. In total, 315 sites distributed over four differently characterised zones, each of about 1000 $km^2$, were monitored. The results were evaluated on the basis of the limit values found in the European Directives.

## EXPERIMENTAL

Analyst diffusive monitors (Marbaglass, Rome, Italy) were used in this study. Since the Analyst development and use has been described fully in previous publications from this

laboratory [2-6] only essential aspects will be given here. The body of the sampler is a cylindrical vial with a threaded cap at one end and an adsorbent or a reactive pad, held in position by a net and/or a stainless steel ring, placed at the bottom. The collecting pad for benzene, toluene and xylenes consists of a layer of active carbon [2] whereas for $NO_2$ the pad is a suitable filter coated with a specific chemical which acts as a sink for the pollutant under investigation [3-6]. In the sampler for $NO_x$ the capability of measuring NO as well as $NO_2$ in the same sampler is reached by using an oxidising surface placed at the bottom of the sampler and held in position by a stainless steel ring. On this ring is placed a polyethylene disc having three small bulges that supports the collecting pad, which faces the oxidising surface. A second stainless steel ring is used to hold the disc in position [6]. Sampling was carried out by mounting the Analyst samplers under a protective shelter with their open ends down to exclude dust, at heights of approximately 2.0-2.5 m above ground level. As a quality check, for all measured pollutants 8 additional samplers to be used as "field blanks" were deployed during each exposure period. At the end of sampling, samplers and blanks were collected, placed in airtight bags and stored at 4°C until analysis by colorimetry for $NO_2$ and NOx, and by gas chromatography for BTX, following the procedure available through the manufacturer.

In order to have an estimate of the yearly average levels, the study included a winter campaign from 20/01/01 to 03/03/01 and a summer campaign from 09/06/01 to 21/07/01. Both campaigns were divided into three fortnightly periods. The sampling protocol was based on methods and approaches described in the EC document of guidance on preliminary assessment in relation to the Framework Directive [7]. To this purpose, a grid over the areas under investigation was constructed and for each cell of the grid a location as much as possible representative and not influenced by very local pollution sources, was chosen. Contour charts for the monthly mean concentrations were constructed using SURFER (Golden Software, USA) with sampling sites entered as Gauss-Boaga co-ordinates.

## RESULTS AND DISCUSSION

In total 315 sites were set up across four different areas to provide a spatial sampling scheme that indicates the extent of local variability within this part of the Lombardy Region. The four zones, of about 1000 $km^2$ each, and indicated with the Greek letters alpha, beta, gamma and delta, were chosen to be representative of long term exposure. The alpha and delta areas are the most and least affected from traffic, respectively. Each sampling site was placed into one of three categories: background i.e. a regional park (79 sites), roadside or near road (100 sites): facing directly onto a major road and intermediate in build-up places (82 sites). The remaining 54 sites were all located, in generally, open ground, typically not far from lightly travelled inner roads. The map in figure 1 shows the location of the selected 315 sites.

In order to test the measurement precision, sampling was replicated on some (12) selected sites belonging to the four zones. A relative standard deviation ranging from 6 to 13% for the three species determined was obtained. As a further quality assurance, an intercomparison campaign was organised exposing three samplers plus three blanks at the three monitoring stations of the City of Milan Department of Air Quality in *Viale Marche, Parco Lambro* and *Via Juvara*. The accuracy of the data collected is well within 20% of the actual value measured by the reference method and therefore the samplers meet the data quality goal requested by the first EU Directive 1999/30/EU [8] for these pollutants.


Figure 1: Map of the Lombardy Region. The Greek letters α β δ and γ indicate the zones.

Figure 2 shows the average concentrations measured over the three summer and winter periods respectively, whereas in figure 3 the estimated yearly averages are presented. The concentration levels for $NO_2$ ranges from 85.9 to 44.1 μg/m$^3$ at Alpha and Delta locations, respectively, during the winter campaign. During summer the corresponding values were 20.0 and 37.4, respectively. $NO_x$ was found to be variable between 163.7 and 87.7 μg/m$^3$. Lower concentrations, ranging from 41.7 to 63.0 μg/m$^3$ were found in summer. The concentration levels for benzene ranges from 10.9 to 8.3 μg/m$^3$ at alpha and delta locations, respectively, during the winter campaign. Toluene was found to be variable between 35.9 and 27.8 μg/m$^3$ whereas the xylenes were 19.1 and 14.8 μg/m$^3$ respectively. Lower concentrations were found in summer. The First Daughter Directive 1999/30/EC [8] provides two health targeted air quality standards for $NO_2$ with the objective of achieving compliance by 2010. The first applies to the annual mean concentration, which must not exceed 40 μg/m$^3$, the second applies to the hourly average $NO_2$ concentration, which must not exceed 200 μg/m$^3$ on more than 18 episodes per year. These are the "action" levels at which local authorities should establish air quality management zones aimed at reducing urban pollution. Annual limit values for $NO_x$ (30 μg/m$^3$) to protect ecosystems and vegetation have also been set in the First Directive. The second Daughter Directive [9] defines the Air Quality Objective for benzene as an annual average of 5 μg/m$^3$ to be achieved by 2010. Overall, the benzene levels found in this study are most likely comparable or much less than those observed in other urban sites and city centres [10]. It must be observed that of the four pollutants regulated by the First (1999/30/EC) and Second (2000/69/EC) Directives, only for NO2 hourly average concentrations are also set by legislation, whereas for NOx and benzene only annual average limit values have been defined. It is important to note that for the year 2001, the comparison should be made against the so-called "margin of tolerance". The margins decrease by a constant percentage year by year until the date for the attainment of the limit value. It is also

important to note that, differently from health based limit values which apply everywhere, the limit values for $NO_x$ aimed to ecotoxic effects, apply only in the rural background.

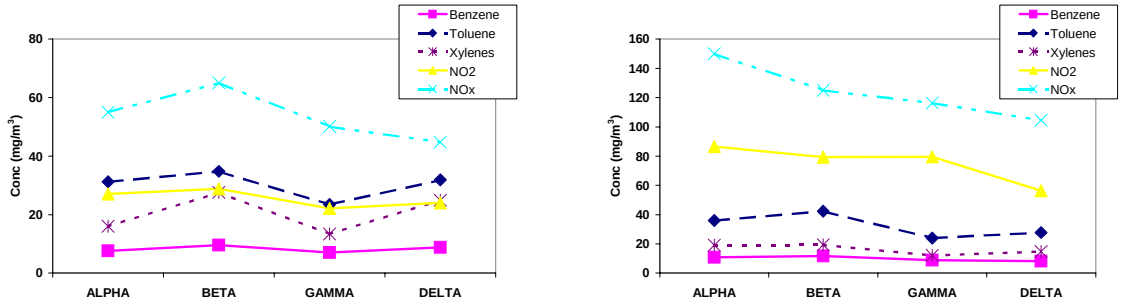


Figure 2: Average concentrations measured over the three winter and summer periods

As a guideline, a sampling point for fixed measurements for $NO_x$ should be sited in locations which are representative of air quality in a surrounding area of at least 1000 $km^2$ [8]. In the present study, all the sampling points are located at a much lesser distance than specified in the Directive and are representative of the air quality only on a local scale in a much less extended area. The sites are therefore to be considered representative of a "worst case" scenario. Considering the results obtained in this study, we can note that a direct comparison of the annual average estimated from diffusion samplers can be made with the annual average limit value as established in the Daughter Directive and shown in Figure 3. If we assume that the two periods used for this study allow an estimate of the yearly average, then we can directly compare the concentration measured here with the limit values prescribed by the Directive for $NO_2$ and benzene. The average concentrations found for $NO_2$ at background locations are 40.2 $\mu g/m^3$ in compliance to the limit that should be reached by the deadline of 1 January 2010. The levels measured at roadside and residential locations are somewhat higher but anyway lower than the reference value which applies at present if we consider the margin of tolerance (58 $\mu g/m^3$ by 2001).

The measured concentrations for $NO_x$ obviously exceed the reference level at the roadside and residential areas. This limit is essentially in compliance in the background sites.

As far as the hourly average concentrations is concerned, the limit value to be considered refers only to $NO_2$. Obviously, since diffusion samplers provide an integrated, average concentration for the pollutant over the exposure period, the measured value cannot be directly compared with a standard based on hourly sampling, as requested for $NO_2$ for health protection. However, it has been found that short term average estimates can be derived from statistical data, by comparison with extended and time resolved measurement series. This can be done using data deriving from automatic monitors placed in similar measurement locations. This procedure has already been applied in previous studies, carried out for $NO_2$ by using diffusive samplers, by investigating the relationship between the annual 98th percentile of hourly means and the annual average for checking the compliance to the EC Directive 85/203 [11]. The Directive 1999/30/EC requires that the $99.8^{th}$ percentile for $NO_2$ must not exceed 200 $\mu g/m^3$. By examining data from the monitoring stations of Corte dei Cortesi of the network of Lombardy Region for the year 2001 where hourly measurements are taken, the

average ratio between the 99.8$^{th}$ percentile and the annual mean is 3.52 [12]. Hence, if the annual average $NO_2$ concentration calculated from the diffusive technique is 200/3.52 = 56.8 µg/m$^3$ or greater, then the 99.8$^{th}$ percentile limit may most likely have been exceeded. If we consider the so called "margin of tolerance" that should be applied for the year 2001 the ratio becomes 290/3.52 = 82.38.

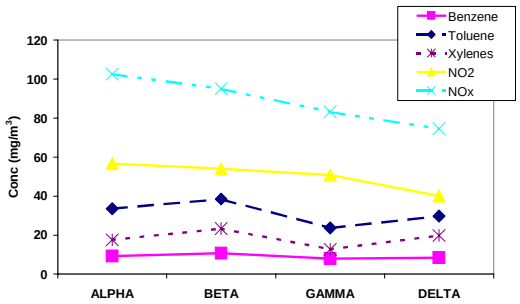


Figure 3: Average concentrations estimated in the four sampling zones

The average concentrations found at the four locations are essentially all below these values and therefore very likely in compliance of the 99.8$^{th}$ percentile parameter. The only exception is the Alpha zone which has an estimated yearly average of 86.5 which, however, is near to the limit requested by the Legislation.

## CONCLUSION

The main conclusions of this study were as follows:

- The results of the study indicate that the measured concentrations were essentially lower than the ambient air quality standard with the maximum concentrations being generally found much closer to diffuse emission sources. Pollutant parameters are determined through observation over one year period and are therefore less susceptible to characteristics of stochastic nature than are short time parameters as it is likely can occur when short term campaigns are performed.
- The monitoring method described here can be used to assess integrated concentration levels over long period of time and to the identify pollution "hotspots" where concentrations are likely to be consistently high. Identification of these hotspots may help to assess air quality and to focus proper action plans.

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