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ORIGINAL ARTICLE

DOAS AS AN ANALYTICAL TOOL FOR EFFECTIVE AIR POLLUTION MANAGEMENT

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Abstract:

Long–path differential optical absorption spectroscopy is one of the best–suited monitoring techniques for the initialization and validation of photo chemical grid models. This technique has proven to be useful as well for tracking pollution episodes and for long-term monitoring of criteria and non-criteria air pollutants. DOAS is a highly specific, non-invasive technique particularly appropriate for the detection of very reactive species, such as fonmaldehyde, nitrous acid, nitrate and hydroxyl radicals. In addition, once a DOAS system is furnished with the appropriate reference spectra, it requires no further gas calibration in the field.

KEYWORDS:

DOAS, Photochemical pollution, & Air Pollution .

INTRODUCTION

The degradation of air quality is a major environmental problem that affects many urban and industrial sites and the surrounding regions worldwide. Air pollution can reach levels where it significantly influences human health, diminishes crop yield, and destroys infrastructure and patrimony.

The phenomena involved in air pollution are complex. Once emitted into the atmosphere, primary pollutants are transported by wind, turbulence and diffusion, they can undergo chemical reaction, change phase and finally are removed from the atmosphere by dry and wet deposition. Finally, in any attempt to improve air quality, the solutions need to take into account socioeconomic feasibility constraints.

One should be aware of the fact that the health and environmental impacts of secondary pollutants, i.e. those formed in the atmosphere, can be more severe than those of their emitted precursors. This is the case of ozone and other photochemical pollutants such as peroxyacetil nitrate (PAN) and possibly also secondary particles produced in the atmosphere. Photochemical pollution is a non-trivial problem because of the non-linearity of its response to changes in precursor emission

The Air Quality Management System (AQMS) approach is probably the most effective approach toward continuous improvement of air quality, particularly when targeting regional problems (see Figure 1). An AQMS involves continuous, long-term measurement of emissions, meteorology and pollutant concentration. These measurements are used to feed and validate deterministic simulation models that support the making of decisions toward air quality improvement.

Due to the complexity of the atmospheric phenomena, the devising, of cost-effective arid technically feasible air pollution abatement strategies requires the application of computational models able to simulate the dynamics of air pollution in the spatial domain being investigated, In its turn, if reliable simulation results are to be expected, the selected computational models have to be initialized and validated with the appropriate meteorological and air pollutant measurements. As shown in this paper, differential optical absorption spectroscopy (DOAS) is a simple and reliable monitoring technique whose measurements of primary and secondary pollutants are particularly well suited to the requirements of computational models, as well as for surveillance of local air pollution standard enforcement and measurement of long-term trends.

OVERVIEW OF THE DOAS TECHNIQUE

This spectroscopic monitoring technique uses a modification of the well-established Beer–Lambert–Bouger (BLB) law for determining the average concentration of atmospheric trace gases along a light path As light (from a natural or artificial source) passes through an air mass, several light attenuation processes take place. In general, Rayleigh (attenuation mainly due to O_2 and N_2) and Mie (attenuation due to particles) scattering contribute more to the total attenuation than molecular absorption. A raw, open-air spectrum will thus contain the imprint not only of molecular absorption but also of all other occurring light extinction process. In principle, this would prevent the application of the BLB law for determining air pollutant concentrations. Nevertheless, a mathematical subtraction procedure allows extracting the narrow spectral transitions ascribed to molecular absorption contained in the spectrum. The subtraction procedure is based on the fact that the decrease in light intensity due to the Mie and Rayleigh scattering in the optical path is much less wavelength dependent in many cases that the molecular absorption features of the pollutant gases. This extracted molecular absorption spectrum can be then fitted to reference (laboratory) spectra, which allows calculating the concentration of the light-absorbing species present in the observed air mass.

A typical DOAS system consists of a light emitter that collimates the light from a suitable light source, a telescope that collects the attenuated light beam, a spectrograph, a scanner-single- channel or multichannel light detection system and a computer for hardware control, data acquisition and processing (see Figure 2). A retroreflector, usually a multiple corner-cube mirror, can be interposed into the light beam to fold the optical path (monostatic configuration). In contrast to bistatic systems, monostatic DOAS systems are easier to install and align and require power at one end of the optical path only.

The above–mentioned light attenuation processes are mathematically described by the following extension of the BLB law:

$$in\left[\frac{I_0(\lambda)\cdot A(\lambda)}{I(\lambda)}\right]=\left[\varepsilon_R(\lambda)+\varepsilon_M(\lambda)+\sum_j \sigma_j(\lambda)\cdot C_j\right]$$

Where:

λ	:	Wavelength
I_0	:	In: Emitted light intensity (initial, before attenuation)
I	:	Received light intensity (after travelling along the optical path, after attenuation)
A	:	System transmission function (wavelength-dependent transmission of the optical system)
ε_R	:	Rayleigh extinction coefficient ($\sim\lambda^{-4}$)
ε_M	:	Mie extinction coefficient ($\sim\lambda^{-\alpha}$, $\alpha\sim 1$–4)
σ_j	:	Absorption cross section of the J^{th} gaseous species
c_j	:	Path-averaged concentration of the J^{th} gaseous species
L	:	Optical path length

APPLICATIONS OF THE DOAS TECHNIQUE

Air Pollution Monitoring

The differential optical absorption spectroscopy (DOAS) technique, first introduced by J.F. Noxon in 1975 and U. Platt in 1979, has evolved during the last two decades from a laboratory instrument to a commercially available monitoring technique. Its applications range from the routine monitoring of criteria compounds (O_3, SO_2, NO_2,) to the detection of trace gases present in extremely low concentrations, such as NO_3, Hg and OH

DOAS measurements have the advantage over conventional point monitors in spatial rcpresentativencss, and are competitive in terms of time resolution. This applies in Particular to the relatively difficult to measure non-criteria compounds, such as BTEX, formaldehyde, nitrous acid and nitrate radical. In addition, when several compounds are targeted, a DOAS instrument is more economic and easier to operate than a set of point monitors.

Specificity is another advantage of DOAS. This is in particular the case of the measurement of NO_2, a criteria air pollutant often monitored with chemiluminescence detectors (CLD). Since many other reducible nitrogen-containing species (NO_y) are present in the atmosphere, particularly during strong photochemical smog episodes, nitrogen dioxide measurements by CLD depend on the specificity of the high-temperature reduction catalyzer used. Since this specificity to NO_2 is never 100%, CLD measurements of nitrogen dioxide can be in overestimation, as exemplified in Figure 5 due to the presence of NO_Y species. The spatial resolution is another reason of the discrepancies reported between path-integrated and point measurements of nitrogen dioxide carried out during the PIPAPO field campaign in the Milan area (Italy) in 1998 On the contrary, an almost perfect agreement is seen between DOAS and point measurements of ozone, a purely secondary pollutant, expected to he more homogeneously distributed in space. Figure 5 shows the capability of DOA S to track a Photochemical smog event: ozone peak concentrations measured at Seregno (Milan area) were over 100% in excess of the World Health Organization (WHO) recommended limit (60 ppb, 8 hours averaging time).

More significant discrepancies can be found between path-integrated and point measurements near to emission sources. This was the case of BTEX measurements performed in a wastewater treatment plant in Lausanne (Switzerland) in 1999 (see Figure 6). It was found that fugitive emissions of BTEX in the sludge management area remain stagnant at ground level until the convective air movement mixes them up and transports them upwards into the DOAS light beam.

DOAS measurements have been demonstrated to be perfectly applicable and useful for long-term air quality measurements as well. As seen on Figure 7, the ambient concentration of nitrogen dioxide in the Lausanne area shows an overall-decreasing trend over the last 10 years.

VALIDATION OF SIMULATION MODELS

Air quality models are used as the most powerful and the most scientifically relavant tool fur identifying effective strategies to improve air quality. For example, a mesoscale eulerian model may simulate pollutant dynamics over region like Athens, Milan or a region with high traffic load in central Switzerland Simulation models are aimed at providing technical guidance to air quality management agencies. The eulerian model resolution is around 1 .5 km on the horizontal scale, with a vertical resolution of some 10 meters for the first layer of the model and up to 500 m for the top layer. The maximum height of the model domain is located in general at 1-2 Km above ground level. For calculating pollutant dynamics, the model explicitly solves for each grid cell a set of equations that define the time evolution of all chemical species included. This equation set takes into account the primary emissions, the effect of transport and dilution due to the wind, photochemistry, and dry deposition. A typical base case simulates some days, i.e. the typical duration of a photochemical smog event. Before the model can be used with confidence, it must be validated against field measurements of similar spatial and time resolution.

When using an artificial light source (usually a high pressure Xe lamp) the DOAS path, i.e. the separation between emission and reception, is typically some hundred meters to some kilometers. An Eulerian model cell is typically 1–5 Km long. Since both measured and calculated concentrations are spatially averaged over similar distance ranges, DOAS measurements are better suited than point measurements to initialize and validate eulerian models. In addition, since a DOAS instrument allows analyzing several air pollutants simultaneously, some of them hardly measurable by other techniques, additional pollutant concentration time series are available for initialization of and comparison with euleriari model calculations, making model initialization and validation more complete and robust.

Figure 8 shows that the photochemical grid model used for simulating air pollutant dynamics during PIPAPO is able to reproduce the afternoon ozone peak as measured by DOAS and a point monitor but unable to reproduce the early morning peak. This is probably due to an overestimation of the emissions of NO during in the morning period. Figure 9 shows a 2D plot of ozone over the simulation domain (Milan area).

CONCLUSIONS

In this paper, the DOAS (Differential Optical Absorption Spectroscopy) technique has been developed into one of the practical high performance techniques, based on the U V-visible molecular absorption of atmospheric gases. DOAS is a spectroscopic technique well suited for a simultaneous detection of many atmospheric trace gases including the criteria compounds, NO_2, SO_2, and O_3. Furthermore, the DOAS technique is based on the optical absorption of gases over long path lengths ranging from some hundreds of meters up to several kilometers long. Thus the DOAS values, in the case of non- folded optical paths, give in general pollutant concentrations averaged over relatively large distances, thus avoiding large local perturbations that can be observed in point measurements.

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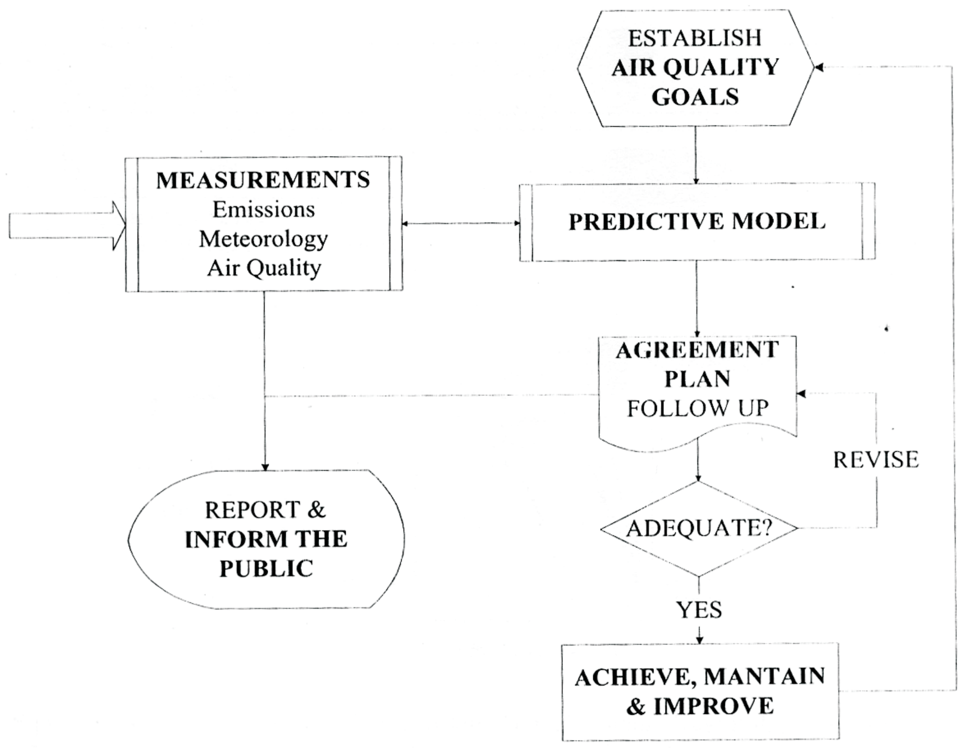

Figure 1. Air Quality Management System (AQMS): Tasks and information flow diagram.

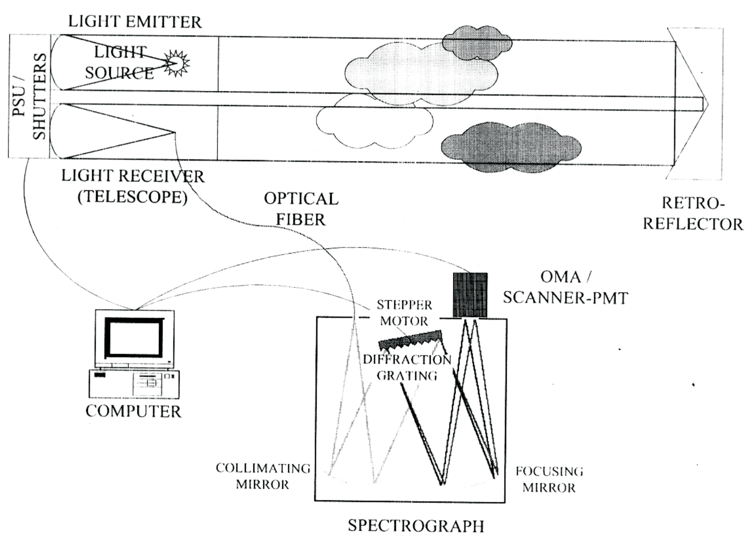

Figure 2. Schematic diagram of a monostatic DOAS system. Key: PSU, power supply unit; OMA, optical multichannel analyzer; PMT, photomultiplier tube.

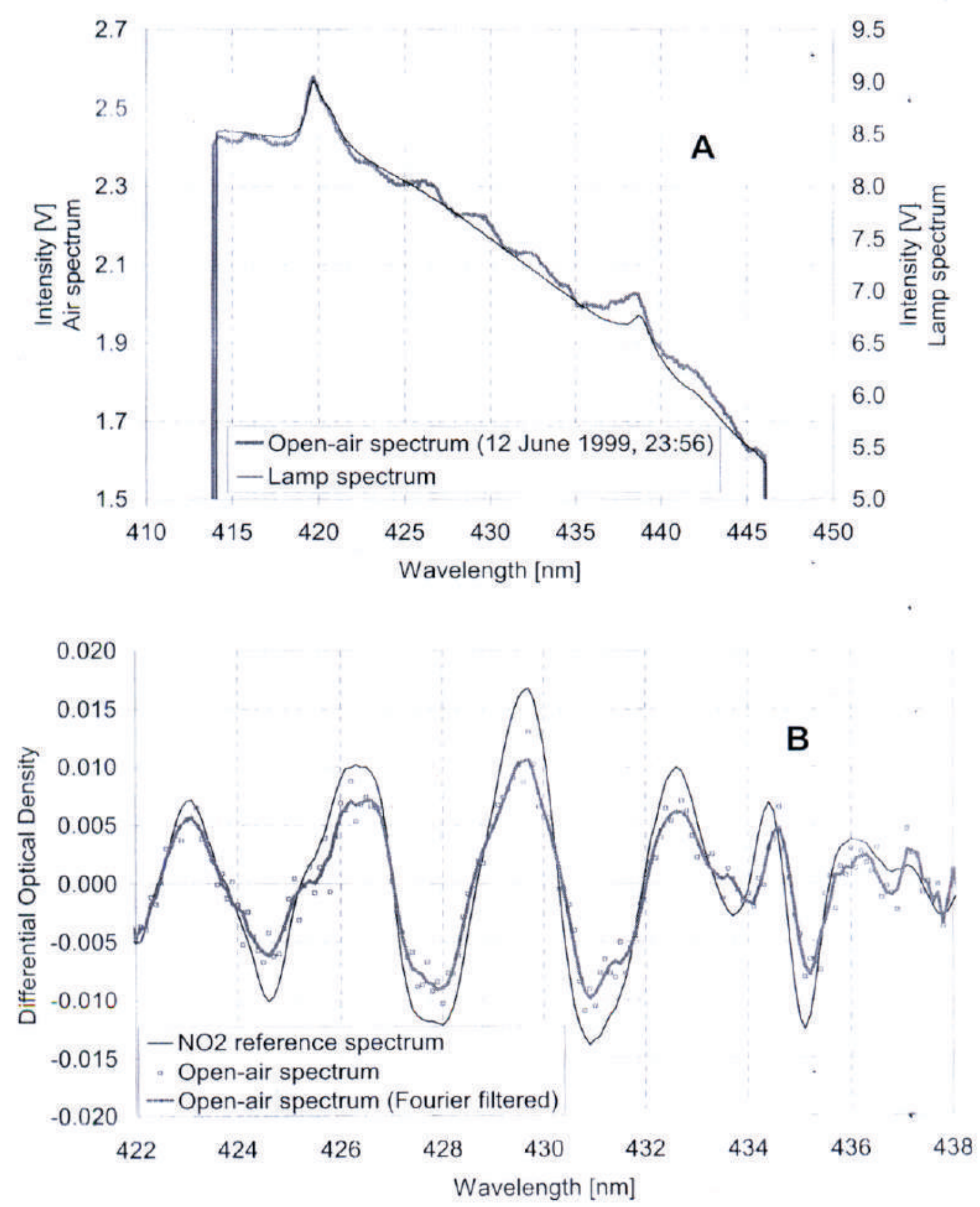

Figure 3. Visible spectrum taken in downtown Lausanne

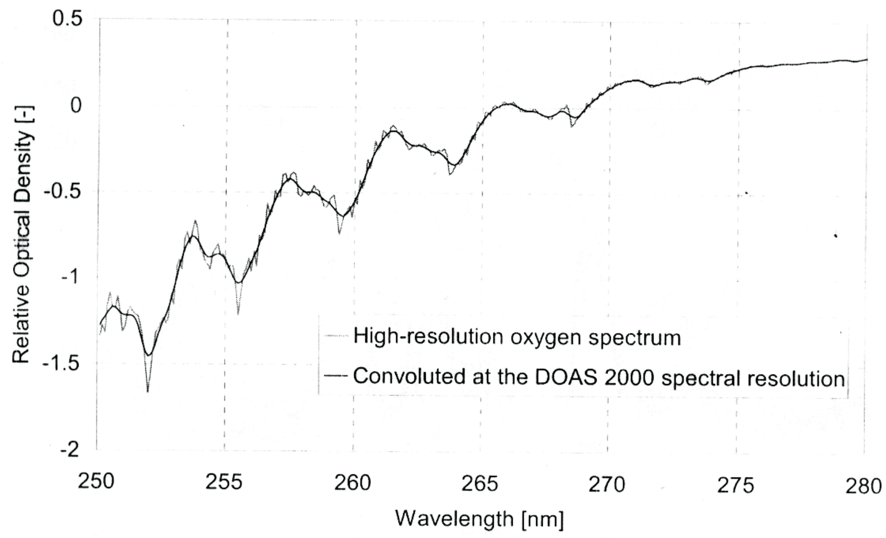

Figure 4. Spectra of oxygen (1.8.10^{24} molecules/cm^2 column density)

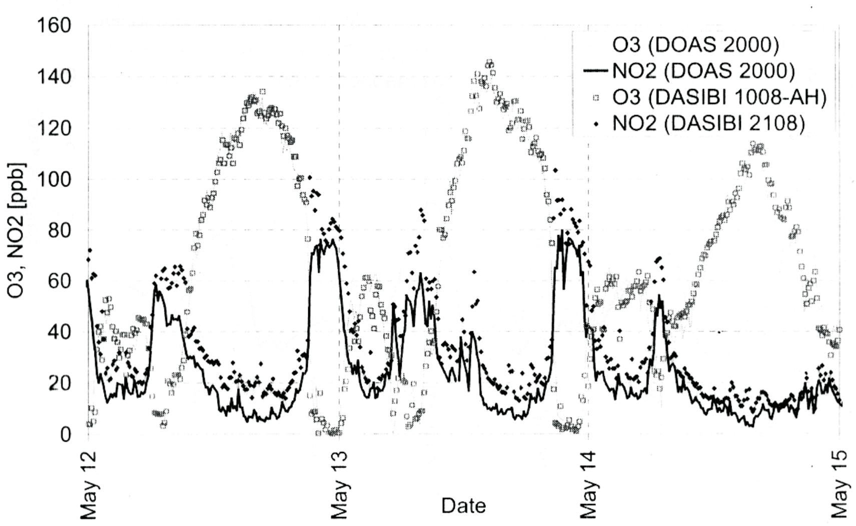

Figure 5. Ozone and nitrogen dioxide measurements by DOAS and point monitors carried out at during a photochemical smog

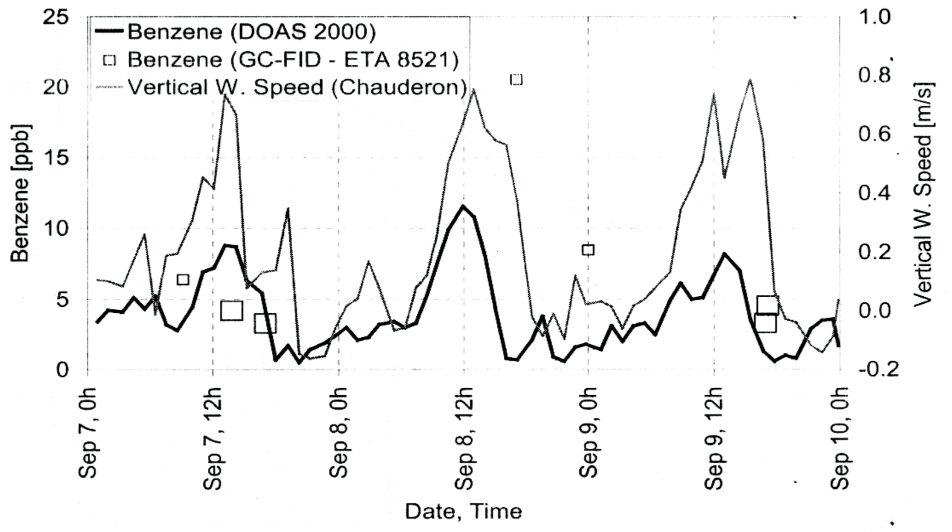

Figure 6. Outdoor concentration of benzene as measured by DOAS (220 m optical path length) and gas chromatography (GC-FID) over a wastewater sludge treatment facility (dewatering and incineration) at Lausanne (Switzerland) in 1999. Note that the discrepancy between path- integrated (DOAS) and point measurements (GC-FID) gets lower at higher vertical wind speeds due to increased vertical mixing

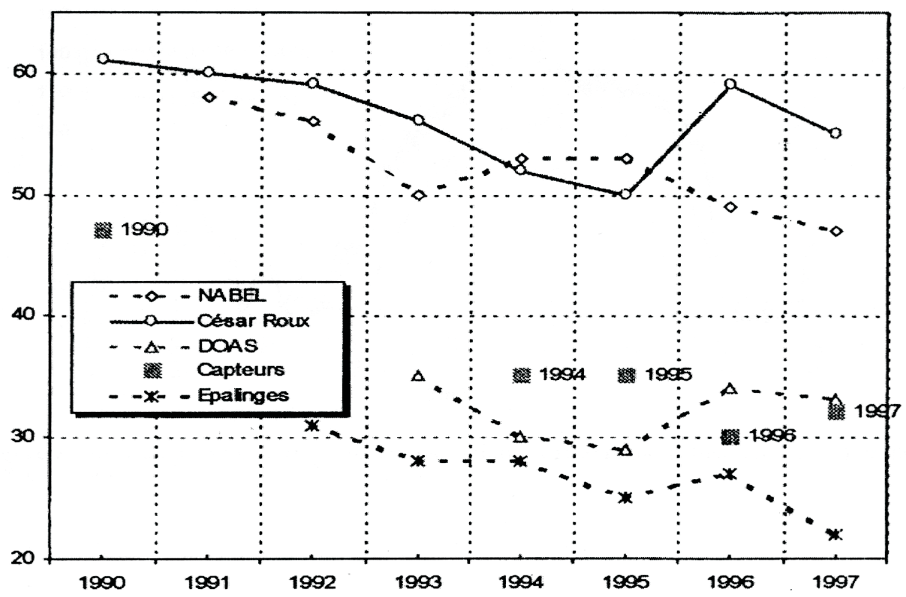

Figure 7, Long-term evolution of the ambient average concentration of nitrogen dioxide in the Lausanne area [16] Concentrations are in µg/m^3.

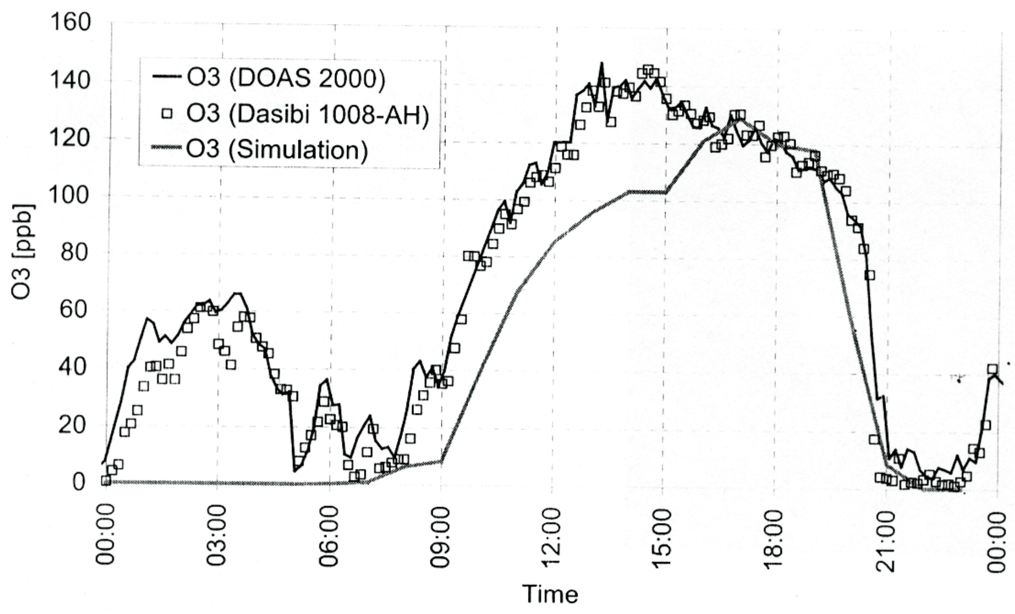

Figure 8. Measured and simulated ozone concentrations at Seregno

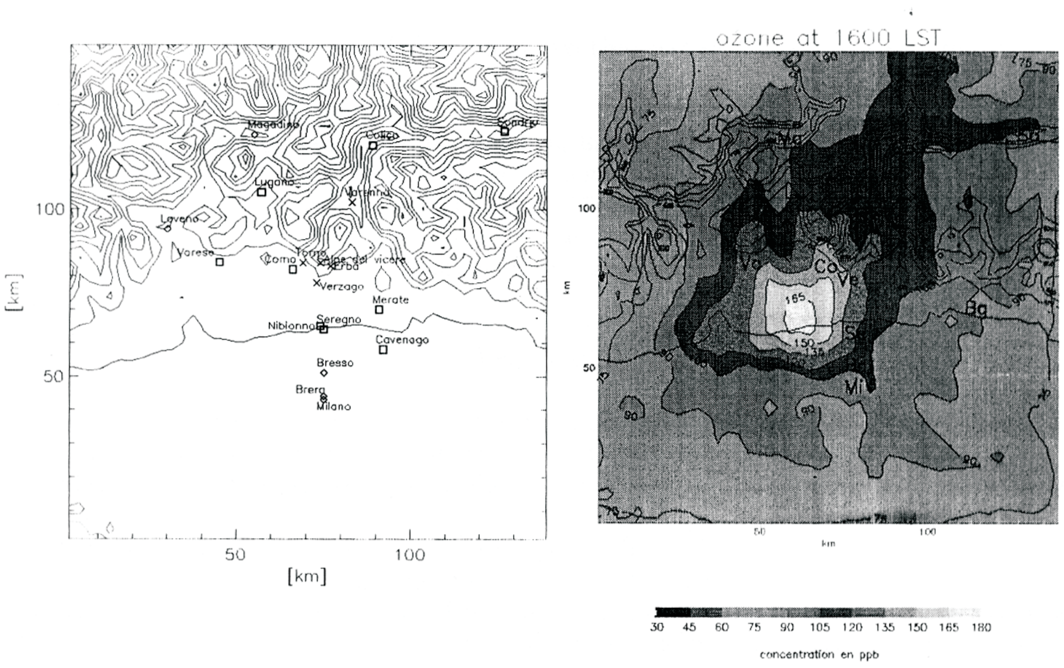

Figure 9. Simulated ozone plume over the Milan area on 13th May 1998. Left: Milan area (model domain) topography and measurement sites during the PIPAPO experiment. Right: 2D plot of ozone concentration (in ppb) at ground level over the model domain.