NO_2 measurements at the bus station area in a big tourist city in Argentina

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Abstract

Ambient air concentrations of Nitrogen dioxide (NO_2) were monitored, together with the main meteorological parameters, at Mar del Plata's bus station. This city is located in the southeast of Buenos Aires province, in Argentina, and by the sea. Nitrogen dioxide was selected because its effects on health are particularly critical and it is considered a hazardous substance.

The standard sample analysis method for nitrogen dioxide was used, which is under the jurisdiction of ASTM committee (ASTM Designation: D 1607-76(1), 1979), based on the Griess-Saltzman reaction, and the IRAM 29268 (Argentina norm). Sampling was carried out in a fritted-tip bubbler. The absorbing device was installed at the places where people wait for the buses and at approximately 60 cm from the floor.

The concentrations measured were considerably higher than those corresponding to other urban sites. However, the resulting NO_2 levels were always below the existing air quality standards. Moreover, the results obtained may alert and guide the development of future controls and may be applied in the evaluation of air quality models. It is also an important step towards improving the knowledge of driver and passenger exposure in the urban area.
Keywords: bus emissions, air pollution, air quality, nitrogen dioxide, urban area, Griess-Saltzman method.

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1 Introduction

Mar del Plata is the main city of General Pueyrredón district, placed in the southeast of Buenos Aires province and by the argentine sea, Atlantic Ocean. It is possible to appreciate a precise descriptive location in Figure 1. Its coordinates are 38º 00' S and 57º 33' W. It is the most important tourist centre of Argentina, with a population of about 600.000 inhabitants that considerably increases during summertime and winter vacation.

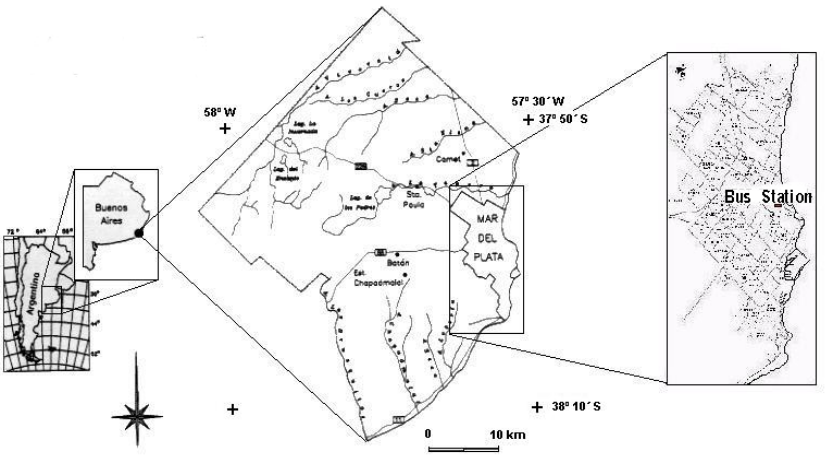


Figure 1: Mar del Plata city location.

The city extends throughout a region where the coast advances into the sea and hence it is exposed to the effect of the winds, principally those from the northeast, the east and southeast.

The atmosphere is composed primarily of nitrogen, oxygen and several noble gases, whose concentrations have remained almost constant over time. However, the atmosphere is actually a dynamic system; its constituents are being modified by vegetation, oceans and biological organisms. Only a small amount of nitrogen oxides is determined, such gases can be considered non-accumulative or quasi-equilibrium gases. This situation can be affected by the pollutant emission from different anthropogenic sources.

Different air pollutants have different toxicities per unit mass; hence the emissions should be rated by effect, so that more sensible priorities can be set in control research and regulation. As an example, carbon monoxide is far less harmful than nitrogen oxides at the same concentration, so, the effect factors should be based on the health effect [1].

For this study, nitrogen dioxide is selected because its effects on health are more critical than those of other vehicular pollution gases. NO_2 can irritate the lungs and lower resistance to respiratory infection. Sensitivity increases for people with asthma and bronchitis. In relation to environmental aspect, NO_2 can

chemically transform into nitric acid and consequently contribute to water or soil acidification, effect called acid rain. It damages trees and crops resulting in substantial health and economical losses.

NOx compounds are by-products of any combustion process. Both stationary and mobile sources contribute to NOx pollution. It is important also to consider the photochemical chain reaction where ozone and nitrogen oxides are involved. Ozone reacts with NO to regenerate both oxygen and NO_2, which is split again by sun radiation and the process is repeated over and over. A steady state between NO_2 and NO, which is referred to as the photo stationary state, determines the concentration of ozone and nitrogen oxides [2]. Although NO is the primary form, the conversion to dioxide is relatively rapid in the troposphere. The background concentrations of nitrogen oxides and ozone are increasing [3]. The large increases in ozone exposure predicted for 2060 and 2100 will have significant implications due mainly to the effects on vegetation [4].

To do an effective control of NOx emissions from vehicles it is necessary the use of three-way catalytic converters. In addition to platinum-palladium catalysts that oxidizes CO and hydrocarbons, these converters contain a rhodium compound that reduces NOx to nitrogen (N_2). Different traps are used, consisting of barium carbonate or a packed bed of sodium-yttrium (Na-Y) zeolite [5, 6].

The objective of this work is to characterize the air quality in Mar del Plata city, specifically in the most affected area, the bus station, taking NO_2 as studied reference gas. Other expected result of this study is to collect the information of the meteorological and climatic variations.

2 Experimental

The pollutant concentrations were determined by mean of the standard test method for nitrogen dioxide, which is under the jurisdiction of ASTM committee (ASTM designation: D 1607-76 (1), 1979), based on the Griess-Saltzman reaction [7], and also constitute the argentine norm IRAM 29268.

Sampling was carried out in a fritted-tip bubbler type B, and this absorbing device was placed at 60 cm from the floor, just where people wait for buses. The sampling period was 60 minutes and the flow rate ranged 0.4-0.8 l/min. The method reproducibility was about 5%.

All the reagents used were of analytical grade. Working standard solutions were prepared by dilution from stock standard solutions immediately before use. Bidistilled water, free of nitrites in order to avoid erroneous results, was used.

This method covers the determination of nitrogen dioxide (NO_2) in the atmosphere in the range from 0.002 to 5 ppm. Blank measurements were carried out at a suburban area, where a mean value of 4 ppb was obtained.

Sampling was conducted at the bus station during one-hour period, once a week and on a different day each turn, during the hours with the highest vehicles densities.

Spectrophotometric measurements were performed in Shimadzu UVPC-2101 equipment. The meteorological parameters were obtained by means of standard device constituted by temperature, atmospheric pressure and humidity registers

and the winds data, velocities and frequencies, were extracted from daily climate local information of the district.

3 Results and discussion

As it was mentioned in the introduction section, several compounds are present in the atmosphere arising from different contamination sources. Once emitted, some species can be converted at various rates into substances generally characterized by higher chemical oxidation states than their parent substances. Frequently these oxidative transformations are accompanied by an increase in polarity and hence, water solubility or other physical and chemical changes from the precursor molecule. Nitrogen oxides constitute an example of these species; they can be converted to nitric acid, inorganic nitrate salts, organic nitrates, etc. [2].

In the following scheme, it is possible to observe the hydrolysis reaction of nitrogen dioxide and the dissociation equilibrium of dinitrogen tetraoxide, which were thoroughly studied and investigated [8, 9].

$$2\ NO_2 + H_2O \ \Rightarrow\ HNO_2 + HNO_3$$

$$N_2O_4 \ \Leftrightarrow\ 2NO_2$$

The nitrogen oxides also participate in the reaction of NO with peroxy radicals, which are atmospheric radicals arising from the hydrocarbons.

$$NO + RO\text{-}O \ \Rightarrow\ NO_2 + RO$$

$$NO_2 + OH \ \Rightarrow\ HNO_3$$

Therefore, in this work, the focus was placed in the nitrogen dioxide because it is a primary gas emitted from the vehicular sources, and participates in several reactions in the atmosphere.

The meteorological parameters: temperature, pressure and relative humidity, were registered at the moment when the nitrogen dioxide measurements were carried out, in the bus station area. This is very important because these parameters were indispensable for the calculations needed to achieve the concentration values in the method used.

Figure 2 shows the meteorological parameters all along two consecutive months of measurements, December 2002 and January 2003. In December, the mean temperature was 24.3 ºC, with a maximum of 29.0 ºC on the 26th day and a minimum of 16.0 ºC on the 2nd . The relative humidity reached a mean value of 52%, with a minimum value of 32% registered on day 23rd. With regards to the atmospheric pressure, the mean value was 1016 hPa, with a minimum of 1003 hPa and a maximum of 1022 hPa. During January the temperatures resulted generally higher than December with lower values of humidity and pressure.

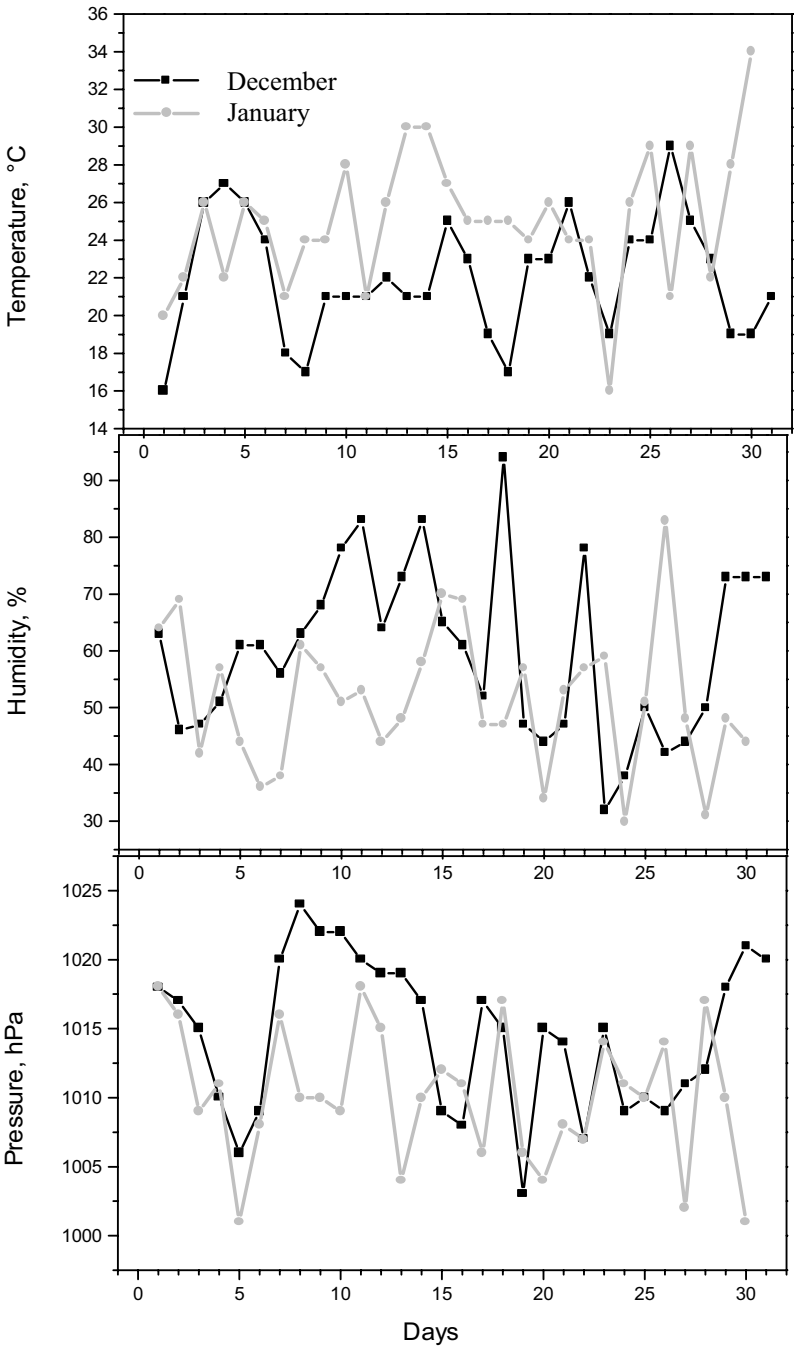
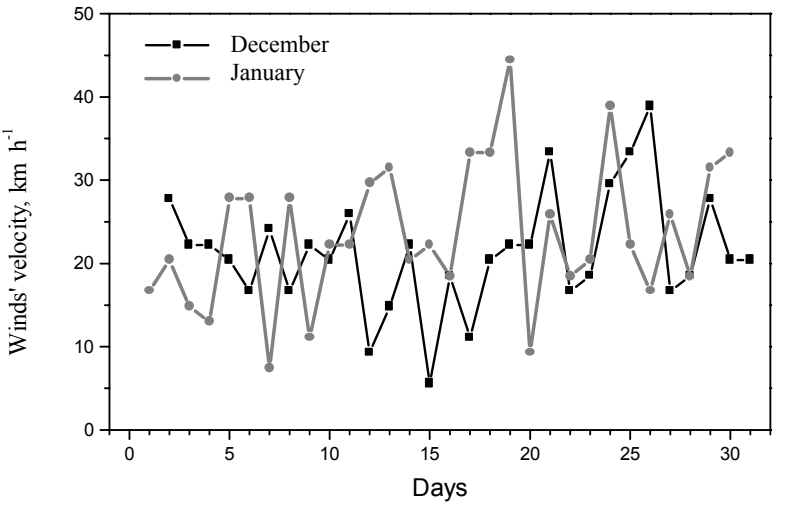
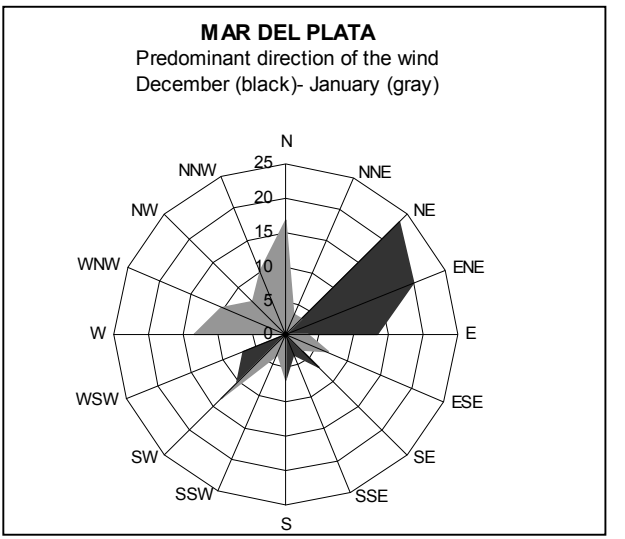


Figure 2: Meteorological parameters registered during vacation months. Values on the graphics correspond to 12:00 a.m.

In the period studied the winds were intense developing a mean value of 23 km h^{-1} and a maximum value of 44.4 km h^{-1} (Figure 3(a)). In Figure 3(b). it can be noticed that the predominant winds were from northeast-east quadrant in December, and from the north (N), west (W) and southwest (SW) in January, The former from the ocean and the latter from the continent (See Figure 1).



(a)



(b)

Figure 3: Velocities and predominant directions of the winds.

It is possible to relate the pollutant concentrations in areas such as city centres or bus stations with vehicular densities or people concurrence, but the climate and mainly the winds have considerable importance too because they are the principal actors in the contaminant diffusion processes.

Due to the particular geographic position the zone is reached by subtropical masses of air, from the north; by masses of air from the Pacific Ocean and by cold fronts from Antarctica. The region is described as having a subtropical marine climate without a very thermal summer and with a maximum precipitation in spring and autumn [10].

Figure 4 shows the results achieved during December 2002 and January 2003. The amount of NO_2 in the atmosphere was expressed as the mixing ratio, which is the amount of the pollutant related to the total air amount. This tendency graphic shows that during January the NO_2 levels were higher than those measured during December.

The relation in % terms between the busy days and the quiet days at the bus station was c.a. 33%. In relation to other weekdays considered with moderate vehicle movement this percentage was 67%. In the period studied, the maximum vehicle densities took place during the second and third week of January with an important vehicle number increase on the 15^{th} – 19^{th} period, which correspond to people semimonthly replace. Similar situation occurred on the last days of January. During these days fortunately the winds were strong.

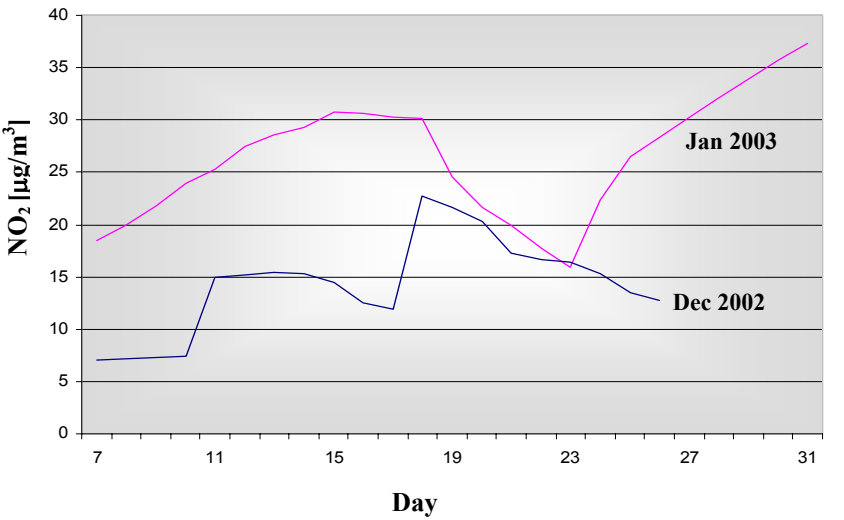


Figure 4: NO_2 levels during summer 2002-2003.

The following monthly mean values were calculated: 43 ppb, during January 2003 and 23 ppb during December 2002. The blank measurements carried out in a suburban area yielded a mean value of 4 ppb.

Some values registered during December 2001 showed similar behavior to December 2002, with a mean value of 22 ppb.

From all the results obtained in these analysis it is possible to conclude that the highest pollution levels take place during Wednesdays and Fridays, which is coincident with the highest densities of buses at the station.

Urban areas have large sources of NO_2 molecules and it takes several hours to convert them to other compounds. The diffusion of them is mainly controlled by the meteorological conditions, but an important role is joined by the buildings height and distribution in the area. So, the effects of nitrogen oxides emissions are expected to be local or regional depending on these factors. Seinfeld and Pandis [11] pointed out that in United States, NOx concentrations decrease sharply as one moves from suburban and urban areas (10-1000 ppb) to rural sites (0.2-10 ppb). They located the lowest levels of these compounds in remote areas such as the tropical forests (0.02-0.08 ppb) and over the oceans (0.02-0.04 ppb).

In Argentina, the environmental control organism in Buenos Aires Province, where Mar del Plata city stands, has fixed the annual arithmetic mean concentration, expressed as nitrogen dioxide, of 100 $\mu g\ m^{-3}$ or 53 ppb, and an hourly mean value of 200 ppb [12], following the values fixed by the Environmental Protection Agency (EPA) of United States, which correspond to temperature and pressure standard conditions. The same value is established by the NAAQS (National Ambient Air Quality Standards), also from USA.

If an annual arithmetic mean concentration inferior to or equal to 53 ppb is considered secure, without taking into account other parameters like wind, for example; so, it can conclude from this study, that the area in analysis may be considered secure in relation to the health standard levels. The density of the mobile sources (vehicles) due to vacation period is higher during January and December, so these months can be considered the most contaminated months. Although the registered levels were never very close to the hourly-established value, during periods of high winds velocities, this makes us wonder what may happen with these levels in similar situations when the wind is not blowing. The population exposure in that case may become dangerous and it is necessary to consider this fact as a warning.

It is important to mention that in Argentina a large number of vehicles have adapted their engines to work with compressed gas [13]. In Argentina the cost of compressed gas used as fuel is notably inferior to that of liquid fuels, which explains that transformation during the economic crisis suffered by the country during the 2000-2001 period. For example, to travel the same distance the money expense is six times lower if the vehicle uses compressed gas instead of liquid fuel. As it is known this kind of fuel is considered “friend” of the environment due to the lower contaminant concentrations that produces. It’s possible to compare the average emissions of compressed natural gas in relation to ones corresponding to traditional fuel [14]. So, values such as 7% CO, 5% HC, 37% NOx and a negligible concentration of particulate matter (PM_{10}) were established.

In the year 2005 Argentina registered 1,200,000 private vehicles with this system. The bus companies for short and long distance travel are carrying out

experiences with some of their units in order to try this gas system on buses for people transportation. So, it is expected that in the future, the present contaminants levels will diminish if the number of vehicles keeps constant.

4 Conclusions

It is important to do air quality controls in areas such as bus stations where the vehicular densities suffer a very important increase in several periods of the year.

From the studies carried out in this work it is possible to conclude that the quality of the air in the area where the passengers wait for buses in the bus station of Mar del Plata city is good, notwithstanding the high vehicular densities observed in the period studied, which corresponds to vacation time. This is probably due to the habitual presence of strong winds which provide suitable conditions so that the diffusion processes take place with higher velocities.

The maximum levels of the nitrogen dioxide pollutant were detected on days with the highest buses densities, which correspond to people semimonthly replace, Wednesdays and Fridays in this case.

The authors recommended to the municipal authorities to contact the bus companies and work together in order to get more homogeneous distributions of the vehicles along the day and the week, and to promote the transformation of the unit' engines to work to compressed natural gas. These actions may tend to keep the air quality in secure level.

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