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AIR POLLUTION ASSESSMENT IN SHIRAZ BY PASSIVE SAMPLING TECHNIQUES*

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Abstract – The air quality in Shiraz was assessed based on a one-week passive sampling campaign. During the first week of the summer 2003, about 400 passive samplers were used in groups of two and three, so that 187 sampling stations covered all of Shiraz. Pollutant gases including SO2, NO2 and BTX (benzene, toluene and xylene) were sampled by diffusive sampling tubes. Collected samples were analyzed and pollutant concentrations were determined by using ion chromatography, spectrophotometry and gas chromatography techniques. The result of the analysis shows that SO2 and NO2 concentrations exceed national and international standards in the central and southern parts of Shiraz. Weekly averaged concentrations of benzene, toluene and xylene at all sampling sites were 105, 206 and 123 $\mu g/m^3$, which exceed national and international standards.

Based on the results, more than 15% of Shiraz's population (180,000 out of 1.2 million people) were exposed to high levels of NO2 during this survey period.

Keywords – Urban air pollution, passive sampling, air quality, BTX concentration

1. INTRODUCTION

As with many developing countries, Iranian metropolitan cities are facing an increasing growth in air pollution sources. Industrial and traffic pollutants are the major contributors. The government has become aware of the problem and has acknowledged seven big metropolitan cities as having severe rates of air pollution. As one of the major metropolitan cities in southern Iran, Shiraz residents have been suffering from air pollution problems during past decades [1]. A Special budget plan has been set aside to control this problem, and several national legislative initiatives have also been put into law by the parliament.

Comprehensive air pollution reduction studies have been carried out for Tehran, Shiraz, Isfahan and Mashad [2], and various solutions have been proposed. An air quality control monitoring network is considered essential for these cities. To select the proper type and location of these stations, a detailed pollution map of the city is required.

The aim of this study was to design a pilot air quality monitoring system that could be used as a model for other large Iranian cities. The goal of the study was to evaluate the present conditions of Shiraz's air pollution, mainly for SO2-NO2 and BTX pollutants. The evaluation of the air quality of Shiraz was carried out using passive sampling tubes distributed in the urban and suburban areas.

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This method has been successfully carried out for big cities such as Boston and Rome, and also for the Swiss Alps and Poland [3-7]. Most recently, traffic-related air pollution in Paris and Northern California was estimated by passive sampling [7, 8]. The effects of meteorological factors on passive sampling measurements have been investigated by Plaisance [9].

2. METHODS

a) The diffusive sampling technique

The low cost and easy operation of the diffusive sampling technique makes it an ideal tool for large-scale air pollution surveys with a high spatial resolution. A diffusive sampler is a device capable of taking gas samples from the atmosphere at a rate controlled by molecular diffusion, and which does not require the active movement of air through the sampler. The diffusive sampler consists of a tube, with one end containing a sorbent that 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.

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 analysis. According to the type of device and the measured pollutant, analysis can be performed using different techniques such as colorimetry, ion chromatography and others. Maps of the pollutant concentrations over the area can be obtained by interpolation of the diffusive sampler measurements. Diffusive samplers are, today, available for a large number of gaseous pollutants such as SO2, NO2, O3, CO and benzene.

This technique is particularly suited to determine the pollutant distribution over a large area, and to assess integrated concentration levels over long periods of time (up to two weeks). Short-term limit values can be derived from statistical data by comparison with extended and time resolved measurement series from similar measurement locations. The proposed methodology can be used to determine areas of maximum concentration and combined with the use of a mobile laboratory. In addition, it may support the optimization of monitoring networks.

Table 1 gives an overview of the existing diffusive samplers and their analytical principles.

Table 1. Analytical Principles for different pollutants

Pollutant	**Analytical principle**
SO_2	Chemical absorption + colorimetry / ion chromatography
NO_2	Idem
NO_X	Idem (same as for NO_2 + oxidation layer)
O_3	Chemical absorption + colorimetry
CO	Chemical absorption + colorimetry
BENZENE	Chromatographic adsorbent + GC analysis

It should be noted that the principle of molecular diffusion does not adapt to particulate matter, and that the diffuse sampling technique is therefore not applicable for PM10 (i.e. Particulate Matter with $D \leq 10\ \mu m$) or heavy metals (plants have been used as passive samplers for some of these substances, but this is a surrogate for deposition rather than for concentration measurements).

In urban areas, the spatial variation for primary pollutants such as NO, CO, Pb, PAH's (Polycyclic Aromatic Hydrocarbons) and benzene is mainly determined by their emissions from automotive traffic. As a result of this, one single pollutant representative of the emissions from automotive traffic may be used as an indicator for the other pollutants when determining areas of maximum concentrations. However this "indicator approach" is valid only if large industrial sources with low level emission heights are not present in the area. In particular, for Pb, PAH or benzene, this cannot be taken for granted, nor is this approach acceptable for secondary pollutants such as NO2.

b) Data quality

When performing diffusive sampling campaigns, the following data quality requirements are proposed. These data quality objectives are only indicative, and may be strengthened where possible.

1. Maximum uncertainty of the measurements: ±30% (for single measurements and a 95% confidence interval averaged over the reference period and at the level of the limit value, taking into account errors of calibration, sampling efficiency, analytical performances and the effect of environmental parameters). The measurements should be supported by an adequate QA/QC program during the period of the campaigns, and the quality of the measurements fully documented [10, 11]. It should be noted that the diffusive sampling technique is still coping with a lack of harmonized validation data. The current state of the art of the technique however has shown that the required uncertainty level (± 30%) can be met for SO2 and NO2, provided that the measurements are supported by an adequate QA/QC program. Several studies have shown that diffusive sampling tubes have a good repeatability (coefficient of variation < 4%) and an uncertainty of 20% [7, 10, 12, 13].
2. Time coverage: to have a good assessment of pollution in the studied area, the ideal is to do two 2 week campaigns corresponding to the seasons with maximum and minimum pollution levels (typically during winter and summer periods).
3. Minimum data capture: 90% of the time of the campaigns, allowing for a failure (leakage, theft, vandalism, presence of insects) of the diffusive samplers during 10% of the time.

c) Use modalities

When applying this methodology in the case of a preliminary assessment, the following steps were proposed:

1. Establish the location of the main emission sources from an assessment of emission sources.
2. Construct a grid over the area under investigation (that surrounds the main area of interest) with a density of sampling sites defined according to emission sources.
3. For each cell of the grid select a location representative of the background pollution level in that cell, which is not directly influenced by local pollution sources. (in remote and homogeneous areas, we may reduce the number of sampling to one for two cells)
4. If necessary, select additional sampling sites in the vicinity of important pollution sources (hot spots such as roads with heavy traffic and industrial sources).
5. Install the samplers over the area and expose them over a representative time period.

6. In support of the QA/QC of the measurements, it is recommended to install duplicate/triplicate samplers in a limited number of sites in order to assess the reproducibility of the measurements. Unexposed samplers should be kept during the period of exposure for assessing the sampler blank value.
7. Perform the analysis of the diffusive samplers in the laboratory and calculate the pollution levels for each particular site.
8. Calculate the distribution of the pollution levels by interpolation methods according to the measurements made in each grid cell.
9. Make a graphical presentation of the pollutant in map form.

d) Application to Shiraz

Shiraz is a large city of some 1.2 million inhabitants. It has only recently come into development. The population has tripled since 1988. This increase has put a heavy load on the infrastructure, and traffic is sometimes chaotic.

Where the city is located in a valley between two mountain ranges of east-west orientation, its development has occurred on the mountain slopes and toward the east for housing (green areas) and west for industrial developments. Old chemical and petrochemical plants are located in the north beyond the mountains in a large and fertile valley bordering the river.

Some industries are still located in the city or its immediate vicinity, one in particular, a cement plant on the west side.

The prevailing winds are oriented west- east, with many days of very stable air conditions. In winter the number of days with temperature inversions is growing, as the number of rainy days is decreasing.

This situation is not favorable to the quality of the atmosphere, and a growing pollution is noted.

I. Sampling campaign for Shiraz

The purpose of the study was to have an assessment of the global air pollution level in the city of Shiraz prior to the localization of automatic monitoring stations. Cost, efficiency and the large area covered by passive sampling made us choose this technology to assess Shiraz's air pollution level.

Due to the limitations of passive sampling, only SO2, NO2 and BTX sampling was taken into consideration. Previous air pollution studies have also shown a high concentration of these pollutants in Shiraz [14, 15].

II. Grid

For an intensive measurement campaign, 177 sampling stations were installed. The sampler density varied as a function of the emission sources configuration, and its density increased in the city center with respect to the outskirts. Additional samplers were installed to have a representative sample of hot spots, such as along busy roads and crossings, as well as in the surrounding areas of industrial pollution sources, particularly if they were likely to affect local pollution levels. A sampling grid of low density was installed at the periphery of the area under investigation (Shiraz itself), in order to assess the impact of adjacent areas and to have good limit conditions for the mapping.

All the sites were selected in accordance with the following constraints:

1. In order to be representative of the global pollution in the concerned grid's cell, the sampling sites should not be too close to an important traffic lane (at least 50m). More samplers were installed closer to the lanes in order to have the peak values, but only in addition to those already provided in the grid.

2. The sampling site must also be far from any known pollution source; no obstacle should prevent the pollutant diffusion; the site had ventilation to avoid accumulation phenomena.
3. Sampling tubes should be settled between 2 and 3 meters high to avoid vandalism (mostly on electric poles).

The sampling grid for Shiraz is illustrated in Fig. 1. Since this was the first such campaign in Shiraz, public awareness and involvement for the tubes security were essential. This was achieved by press interviews and directly talking to the people during the tubes installation campaign. Only 6% of the tubes were lost and 94% were collected after a week of sampling from the sampling stations.

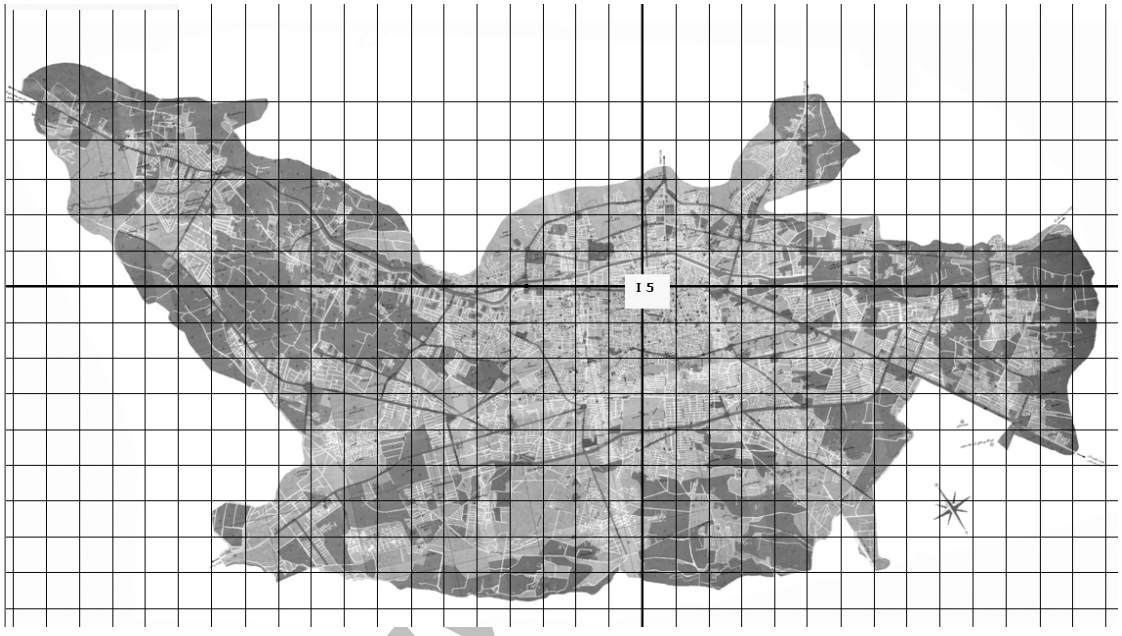

Fig. 1. Grid and sampling points for Shiraz

III. Logistic aspects

Once the grid was defined, all the sites were determined and referenced according to the following constraints:

1. Each site was precisely determined in advance; the box to protect the tubes was installed previously. The coordinates and precision of the locations were recorded and given to the persons responsible for the installation of tubes to save time. Photographs of the sites were included in the station file.
2. Tubes were labeled by the manufacturer; when installing and recollecting the tubes, these labels were recorded with the location, date and time. The tubes were stocked in a cool place (fridge) and protected from the sun before and after analysis.
3. The periods for installing and collecting the tubes were less than 4 hours: therefore, many persons and vehicles were requested at the same time for these operations.
4. To reduce measuring uncertainties, 2 to 3 tubes were installed at the same location for the same pollutant.

IV. Operation procedures

SO2/NO2 sites were chosen in every cell of the grid; some sites were cancelled in remote cells of homogeneous zones (suburban areas) to allow additive sampling in peak zones (city center).

BTX tubes were installed only at gas stations, and all industries in the studied area where benzene levels at these locations could be estimated.

e) Tube analysis

To be analyzed, tubes are turned over; the NO2 adsorbing capsule is then "in the bottom". The tap is then removed and a defined quantity of solution is introduced in the tube. This solution will make a reaction with the product formed during NO2 trapping. A nitrite solution is then formed that has a rose coloration. The intensity of the coloration depends on the NO2 quantity trapped.

Next, the absorbance of the solution is determined using a spectrophotometer. Absorbencies are then converted into mass equivalent, and according to the diffusion coefficient and the duration of the exposure, we can reach the average level of the pollutant. A similar procedure is performed for SO2 and BTX analysis. The solution specification is based on the manufacturer's recommendation and for the case of NO2; it consists of N-1 naphthylethylene-diamine dihydrochloride (NEDA), Sulfanilic acid, O-Phosphoric acid, nitrite standard and ultra high quality water (UHQ).

f) Pollutants mapping

For the purpose of mapping a pollutant, of which the concentration has been measured at different locations, an interpolation was done at the points of a grid that cover the studied area. In each point of this target grid, an estimation of the concentration was calculated using an algorithm that attaches weights to the concentrations measured at the sampling points.

There are several weighting algorithms, each one leading to a different estimate of the concentration, therefore, to a different pollutant map. The choice of the algorithm depends on how consistently it combines the experimental measurements and on how it integrates other information such as traffic density or meteorological conditions.

In order to always get the most representative map, the method used must also take into account the pollutant's specific spatial features (e.g. topography, roughness etc), and if available, auxiliary data to complement the information.

The next section contains the results found for this study with three different (and common) algorithms (with the same scale).

3. RESULTS AND DISCUSSION

The results of NO2 and SO2 analysis are shown in Figs. 2 to 5. NO2 and SO2 concentration data have been mapped using three different approximations. In Fig. 2, the inverse distance square method, in Fig. 3 the moving average method and in Fig. 4 the nearest neighbor method have been used. The SO2 concentration has been mapped using the inverse distance square method, and is shown in Fig. 5. As can be seen from NO2 maps, its concentration in the north and central parts of Shiraz is more than 100 $\mu g/m^3$, which exceeds the national and international levels in the north and central parts of Shiraz. At the same time, the SO2 concentration in the southern parts of Shiraz is over 80 $\mu g/m^3$, which exceed the standard levels.

The results of the BTX analysis are shown in Fig. 6. As can be seen, the benzene concentration exceeds the standard levels in all sampling stations which were chosen to be the gas stations and chemical process industries.

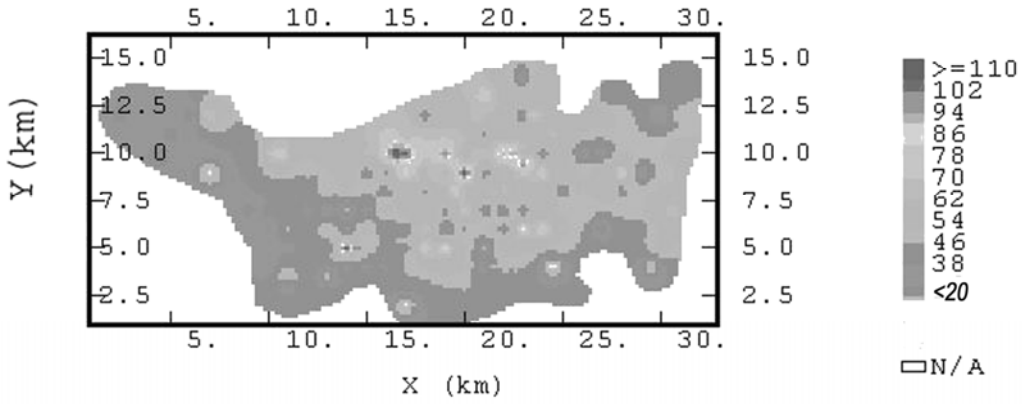

Fig. 2. NO2 concentration map in Shiraz (µg/m3) by the inverse distance squared method

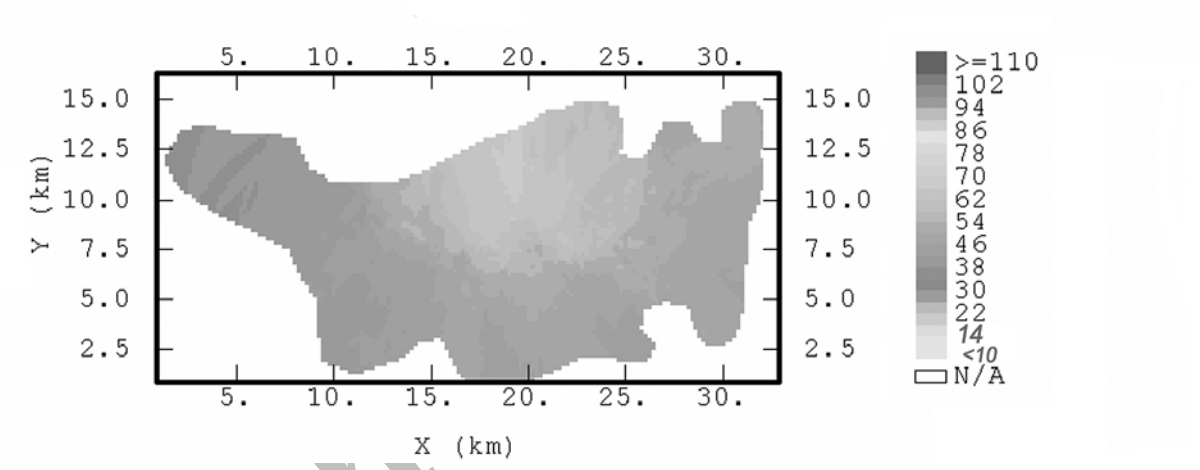

Fig. 3. NO2 concentration map in Shiraz (µg/m3) by a moving average method

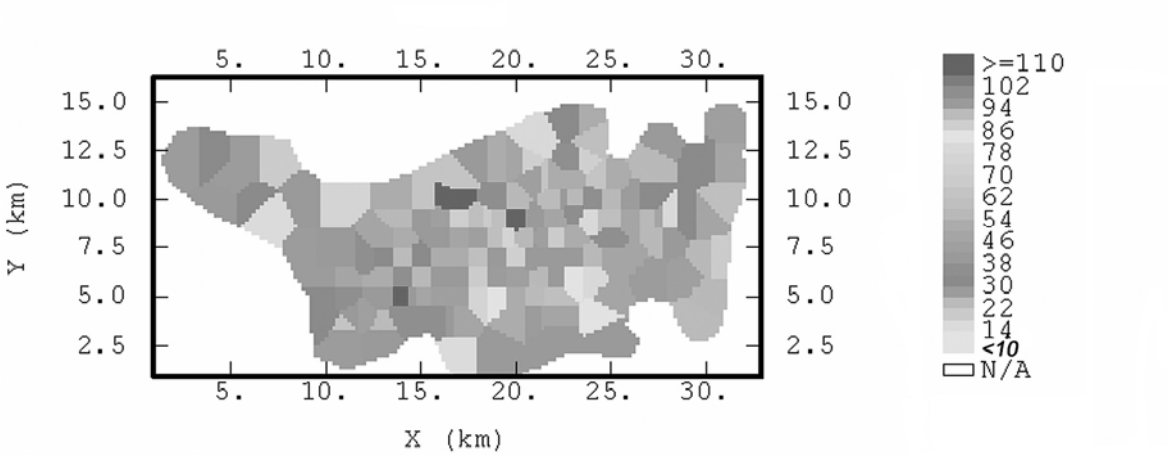

Fig. 4. NO2 concentration map in Shiraz (µg/m3) by a nearest neighbor method

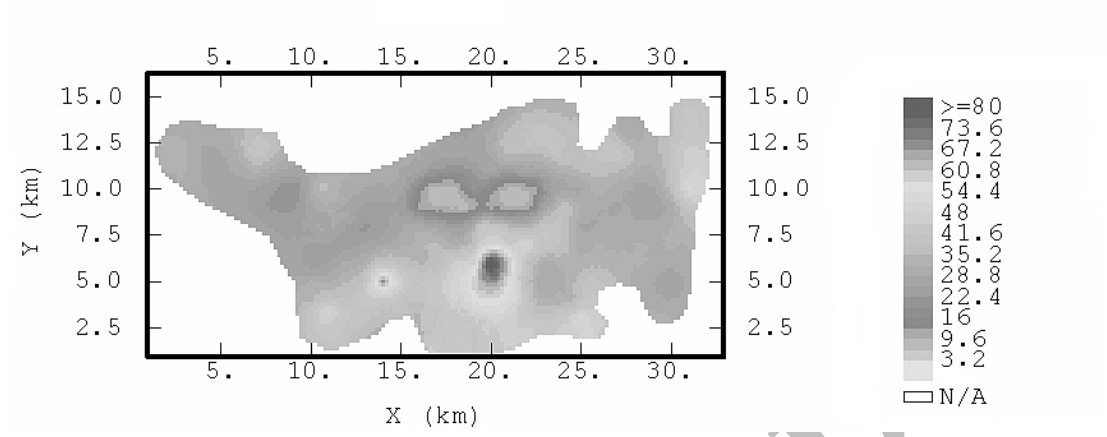

Fig. 5. SO2 concentration map in Shiraz (µg/m3) by the inverse distance squared method

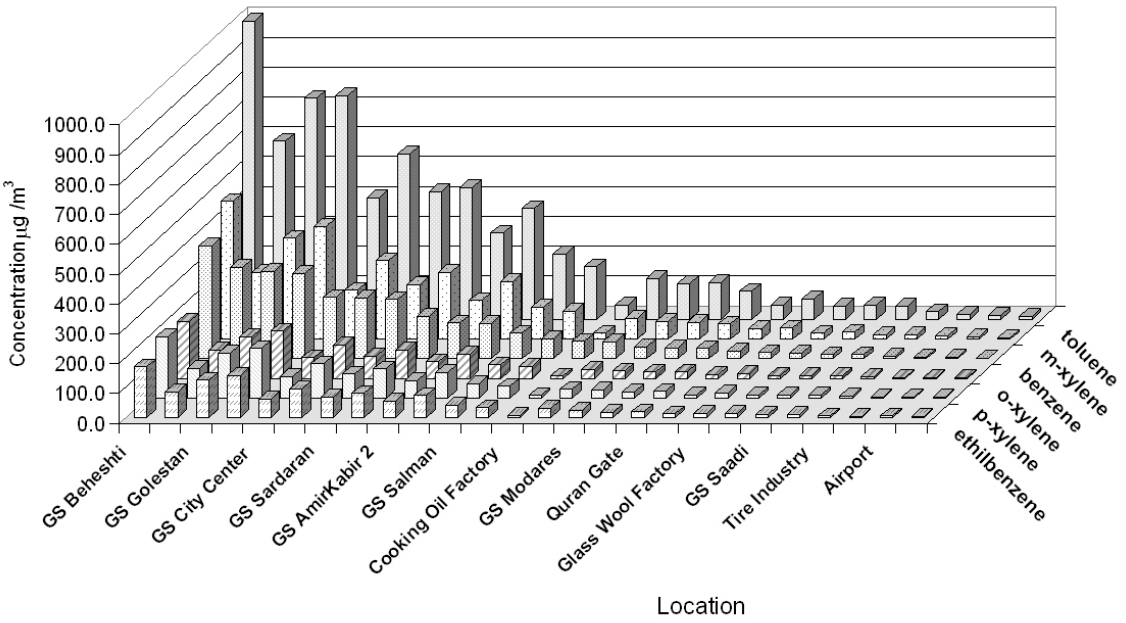

Fig. 6. Benzene, Xylene and Toluene concentration at all gas station and industries within the study area in Shiraz

High levels of NO2 pollution were expected in the central parts of Shiraz due to congested traffic and lack of annual emission inspections and controls. During this period of study, other sources of NO2 pollution (domestic and industrial sources) were not as decisive as the traffic source. The domestic sources are mainly from household burners and stoves and should be investigated thoroughly during the cold months in Shiraz. Due to the spread of big industries in Shiraz, their contribution to air pollution has been found minimal.

However, due to the distribution of low-sulfur gas-oil among public transportation buses within Shiraz, SO2 concentration has not exceeded the threshold level. Meanwhile the heavy vehicle traffic in the southern part of Shiraz has raised the SO2 concentration beyond international standards.

Extremely high levels of BTX have been measured at all gas stations, which is due to evaporation of aromatics in gasoline during car refueling. The chemical processing industries within the study area did not comply with national and international standards.

Frequencies of NO2 concentration exceeding 100 μg/m^3 (Iranian standard), and 58 μg/m^3 (EU standard) are shown in Figs. 7 and 8. Based on this, 180,000 people in Shiraz are exposed to levels of NO2 exceeding EU standards.

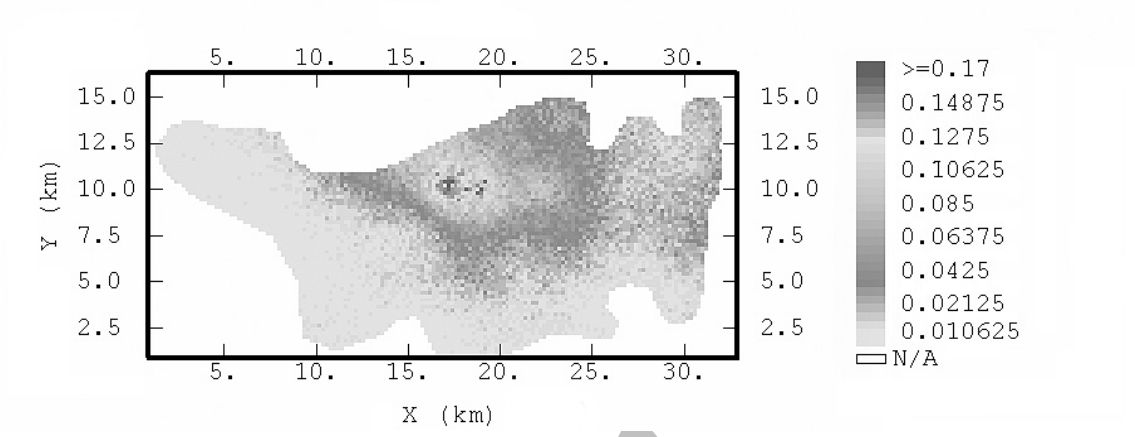

Fig. 7. Probability for NO2 to exceed 100 μg/m3 (annual Iranian standard) on a week

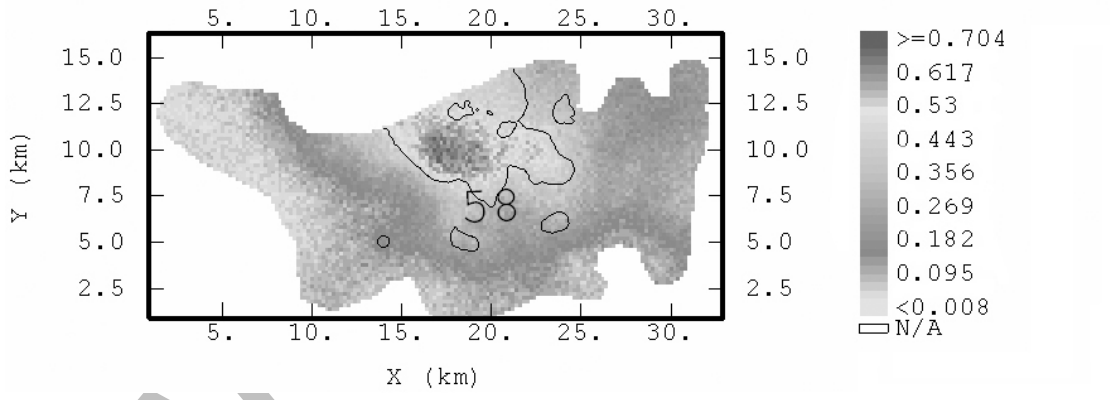

Fig. 8. Probability for NO2 to exceed 58 μg/m3 (annual European standard) on a week with 58 μg/m^3 isoline

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