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Quick and Economic Spatial Assessment of Urban Air Quality

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1. Introduction

The main sources of urban air pollution are transport and heating influenced by the background air pollution of the major area. Transport includes emissions from the road traffic, particle resuspension, petrol and gas stations, as well as emissions from ships and harbour traffic, in case of a city harbour. Heating includes emissions from oil or gas incinerators to provide central heating, which operate in houses and other buildings. Oncoming air pollution from any kind of emissions of the major area forms the background levels of the urban air pollution. These emissions may be originated from either anthropogenic or natural sources. Anthropogenic sources include activities of transport (airports, highways and ship emissions), power generation, oil refineries, waste incineration, industries and agriculture. Natural emissions come from area sources (sea, ocean, countryside land, forests) and point sources (volcanoes and territorial cracks). Air pollutants emitted from all these sectors include mainly the primary air pollutants of sulphur dioxide (SO_2), carbon monoxide (CO), oxides of nitrogen (NO_x), ammonia (NH_3), volatile organic compounds (VOC) and particulate matter (PM). Most of the traffic-related emissions are in the fine particulates range, i.e. $PM_{2.5}$ or of smaller size. Many of the primary air pollutants are deposited, but some of them interact with other air pollutants and form new secondary air pollutants, such as the photochemical air pollutants of ozone (O_3), aerosols, nitrogen dioxide (NO_2) and other. Although airborne particulates and ozone concern mostly human health, all aforementioned air pollutants (primary and secondary) affect adversely human health, ecosystems biodiversity, crops and forests, built environment, materials and cultural heritage. Besides the cost regarding general environmental damage, the death cost is huge. Several hundreds of thousands of premature deaths, increased hospital admissions, extra medication and millions of lost working days occur each year in Europe. Many developing countries, as China, are taking actions against air pollution. The Chinese policies to reduce SO_2 and NO_x emissions are similar to those of the European Union (EU). The developed countries, like USA and Japan, are not expected to cause any risk in competiveness to EU countries, because they have similar or more stringent air pollution policies than EU countries (Commission of the European Communities [CEC, 2005]). And of course there are other sources of potential pollutants, like noise causing annoyance to citizens, viruses causing human infections, and radioactive aerosols emitted due to probable failure episodes of nuclear reactors of power plants causing major impacts on major areas even globally

(Chernobyl of Ukraine in 1986 and, very recently in 2011, Fukushima of Japan). These pollutants need specific monitoring ways incompatible to the proposed methodology.
Cities of moderate or large population are facing air pollution problems and, therefore, a well organized monitoring program becomes mandatory to assess urban air quality and take decisions in the context of an air pollution abatement strategy. The first EU Council Directive regarding air pollution was the 80/779/EEC European Communities [EC, 1980]. That Directive in Article 6, partially kept in force up to 19 July 2001, had stated that SO_2 sampling stations might be located at sites where pollution is thought to be greatest and where the measured concentrations are representative of local conditions. The successor EU Council Directive 85/203/EEC (EC, 1985) in Annex III, which was kept in force up to 1 January 2010, gave among other specifications similar suggestions for the selection of NO_2 measurement points. A decade latter, the EU Council Directive 96/62/EC (EC, 1996) had enacted a common strategy on ambient air quality assessment and management, as well as measures and requirements to be adopted by Member States. The more recent EU Council Directive 1999/30/EC (EC, 1999), which has partially replaced the EC (1985), has established limit values and alert thresholds for concentrations of SO_2, nitrogen dioxide (NO_2) and NO_x, PM and lead (Pb) in ambient air. In addition, the latter EU Directive has specified common methods and criteria to assess concentrations for SO_2, NO_2 and NO_x, PM and Pb in ambient air and to obtain adequate information and maintain or improve ambient–air quality. It provides also lower and upper thresholds for determining the appropriate zones and the minimum number of sampling points for fixed measurement of the above pollutant concentrations. Interest is focused in zones where air pollution levels are higher than the lower thresholds or exceeding upper thresholds in contrast to zones where the levels are lower than the lower thresholds. The above directive forces Member States, which do not have representative measurements of the levels of pollutants for all zones, to undertake series of representative measurements, surveys or assessments in order to have the data available in time for implementation of the proposed legislation. For simplicity reasons, clarity and administrative efficiency, the five EU Directives 96/62/EC, 1999/30/EC, 2000/69/EC and 2002/3/EC, regarding air pollution issues have recently been replaced by the last EU Council Directive 2008/50/EC (EC, 2008). This Directive particularly seeks to promote the integration into the policies of the EU of a high level of environmental protection and the improvement of the environmental quality in accordance with the principle of sustainable development. This means that EC (2008) targets to reduce pollution to levels which minimise harmful effects on human health, paying particular attention to sensitive populations, and the environment as a whole, to improve the monitoring and assessment of air quality including the deposition of pollutants and to provide information to the public. Regarding urban air pollution monitoring, the Directive gives the criteria to establish an adequate network of pertinent monitoring stations installed at fixed locations where pollutants have to be measured, for taking either continuous measurements or measurements by random sampling. Managing a major city network, its high cost and need for reliable performance require convenient design and optimization based on a prior knowledge of the spatial and temporal concentration distributions of the city air pollution. Information from fixed measurements may be supplemented by modelling techniques and/or indicative measurements to enable spatial distribution of concentrations. In addition, the EC (2008) Directive allows the use of supplementary techniques of assessment, because they may reduce the required minimum number of fixed sampling points, contributing to economic monitoring networks and cost-effective air pollution abatement strategies.

In general, monitoring requires expert and assisting personnel, a network of rather permanent stations equipped by special analyzers and considerable funds on a yearly basis. Although such a network provides temporal concentration distributions of air pollutants at specified city locations, it is unable to give detailed spatial concentration distributions covering all the city areas. It is also unable to provide information on the apportionment of sources contribution to receptors. The latter information is necessary for taking appropriate measures in the application of the air pollution abatement strategy. However, knowledge of spatial concentration distributions of specific pollutants during rush hours may be necessary for the design of an optimised control of traffic (road and/or harbour traffic) and better the air quality of the city. It may be also important to obtain spatial concentration distributions for other atmospheric emissions coming from either urban sources (i.e. central heating) or rural and industrial sources; or it may be significant to identify the city locations and zones vulnerable to high pollution levels. Finally, short period measurements of spatial concentration distributions may contribute to the validation of models predicting urban air quality and assisting the apportionment of sources' contribution to the prescribed receptors.
This chapter describes an economic and quick methodology, which combines the determination of the spatial concentration distribution of air pollutants with suitable model predictions leading to source contribution for several urban receptors. For the determination of spatial concentration distribution, the bag sampling technique is used in conjunction with laboratory measurements performed by pertinent analysers (Yannopoulos, 2007a). The data obtained are then statistically analysed to get approximately spatial distribution of 1-h mean concentrations of specific air pollutants. For the model predictions of the same air pollutants, the USEPA integral dispersion models are employed (Yannopoulos, 2007b). In addition, this methodology may be employed to perform a preliminary spatial assessment of a city's air quality with the purpose to identify locations and zones susceptible to high pollution levels.
The advantages of the proposed methodology are the following:

a. Demand of limited personnel and small numbers of specialized sampling equipment and procedures. Only one analyzer per pollutant monitored may be used, since it involves the transfer of samples collected in the field to the laboratory for measurement and additional statistical treatment.
b. No need of permanent stations monitoring air pollution and, thus, flexibility in selecting the sampling sites.
c. Short sampling times in a rather restricted monitoring period lasting one to three months.
d. Satisfactory spatial coverage of urban air quality with measurements, which are adequate to further determine iso-concentration contours for each prescribed air pollutant.
e. Concentration results are characterized by mean probable errors less than around 25%.
f. Alternative usage of source emissions in predicting concentrations at the receptor locations and, thus, the ability to determine the contribution of each source. Note that this is unachievable by only using measurement data.
g. Possibility for a sporadic evaluation and harmonization of a network, which is used for continuous monitoring of the urban air quality, according to the needs of the air pollution abatement strategy of the city.
h. Possibility for prediction and assessment of the environmental impacts due to the city's development, which demands the installation of new infrastructure works or the

relocation of existing infrastructure (highways, bridges spanning rivers or sea narrow passages, underground railway, harbour, airport, industrial area e.t.c.).

While the proposed methodology has the following disadvantages:

a. The technique cannot be applied for all kinds of air pollutants, as for PM and aerosols that may sink during the time lag in the walls of the sampling bags. However, PM and aerosols are also difficult to predict using Gaussian models.
b. The time lag of air samples must be conveniently restricted and precautions must be taken, as the use of special bags (Teflon or Tedlar), depending on chemical properties of pollutants, and the daylight protection of samples, to avoid wall sinks and gas reactions. The conditions (a) and (b) bound the use of a laboratory for a prescribed city area satisfying limited time intervals to reduce the risk of pollutant alterations and reduction of their concentrations.
c. A small car in size or a monocycle must be available to enable visiting the city locations for air sampling and the quick transport of samples to the laboratory for immediate analysis.

The proposed methodology is applied for the air pollutant of SO_2. Mobile and stationary sources that use oil as a fuel (oil–engine cars, central heating and ships) constitute main sources of SO_2. For street level monitoring, SO_2 concentrations are mainly influenced by the traffic and therefore it is expected that the correlation coefficient should reflect the traffic-originated SO_2 emissions. In coastal cities where traffic presents important SO_2 emissions and the mixing height is reduced during rush hours due to the sea proximity, the street-level SO_2 concentrations monitored will be strongly correlated to traffic flow rates. This event obviously justifies the relatively high value 0.74 of the correlation coefficient reported by Jackson (2005). In contrast, in interior–land cities (without a harbour) the SO_2 concentrations are well correlated to particulate matter concentrations (Turalioğlu, 2005). Further on, cities are usually "hot spots" for certain atmospheric pollutants including SO_2 that may still affect large parts of forest ecosystems, particularly those under the immediate influence of pollutant sources (Smidt, 1998; Puxbaum et al., 1998; Herman et al., 2000). Therefore, it is interesting to give more light on spatial pollution levels in cities as the city sources may contribute significantly to increased regional levels. This implies that the reduction of emissions in city sources may effectively reduce the average of all emissions (Klemm and Lange, 1999).

2. Analytical description of methodology

The proposed methodology is a combination of the two alternatives already proposed by Yannopoulos (2007a, b), the air sampling bag alternative and the Gaussian modelling alternative. These are described step-by-step in the following.

2.1 Air sampling bag alternative

Plastic bags of various sizes (0.5 l to 100 l of volume) made by Tedlar, Teflon or aluminized Tedlar, have been used for air sampling, because they are simple in use and inexpensive. They can be easily cleaned by repeatedly filling the bag with pure nitrogen or zero air of high purity and evacuating it applying small under pressure. Leaving them filled with zero air overnight, they can be checked for leaks (Kumar & Viden, 2007). United States Environmental Protection Agency's [USEPA] Method 18 for the measurement of gaseous organic compound emissions by gas chromatography suggests the use of Tedlar bags

(USEPA, 1987). Some environmental agencies and specialized laboratories have established instrumented monitoring standards, which allow provision for bag sampling where direct measurement is difficult (Kennedy et al., 1995; USEPA, 1996; McGinley, 2002) or unsafe (Stewart, 1999). The air sampling bag method has been applied for both indoor and outdoor air quality measurements, regarding carbon dioxide (CO_2), methane (CH_4), non methane hydrocarbons (NMHC), ammonia (NH_3), nitrous oxide (N_2O), SO_2, NO, NO_2, CO and O_3 sampled with Tedlar sampling bags (Li et al., 2007; Lee, 1997; Lee and Chang, 2000; Li et al., 2001; Tsai et al., 2000). Although not valid in general, volatile organic compounds (VOC, Benzene) can be sampled and stored in Tedlar bags, because Tedlar bags present very little tendency to sorb organic compounds (Wang et al., 1996; Leong et al., 2002). Tedlar bags have been also used for sampling of odour characteristics and polycyclic aromatic hydrocarbons (PAH), analysing the samples within 24 h after sampling (Tsai et al., 2009). The losses from breath samples 52 h after filling the Tedlar bags were less than 10% (Steeghs et al., 2007). The losses from NO, NO_x and SO_2 air samples were about 15% 90 h after sampling, while CO didn't show any actual loss in Tedlar bags. The maximum losses have been observed from O_3 samples in Tedlar bags. They were more than 45% 90 h after sampling and more than 30% immediately after filling the bag (Chen, 2002). Alternatively, Teflon bags and sampling accessories are more inert than Tedlar, but they are more expensive and sensitive to punch and they need more care. Teflon bags can be used for air pollutant sampling and transport for analysis, in conjunction with all possible precautions taken to eliminate any potential errors in pollutant concentrations due to chemical transformations and wall sinks during the time lag in the sampling bags (Yannopoulos, 2007a; Kim et al., 2006).

2.1.1 Defining the study area

The first action to be made is the determination of the study area of the city. Information regarding population densities, sectors of the City Plan, iso-altitude contours, building heights, prevailing climatic conditions, location of air pollutant sources, dispersion conditions and previous measurements or indications of air pollution hot sports of the city under examination may be very useful in order to define the zones or agglomerations in conjunction with the legislation valid. It is worth to mention that each analyser in conjunction with the maximum time allowed from sampling and up to analysing the samples are the critical parameters to determine the size of the city zone, thus defining the general features of the area (number of maximum sampling points, personnel for sampling, necessary maximum time for the transportation of samples from the site to the laboratory for analysis).

2.1.2 Defining the project duration

The definition of the project timing and the whole project duration follows. This is based on available previous measurements, if any, or, if not, on measurements of similar air pollutants in other areas having similar sources, activities and climate. For primary air pollutants it is usual that the most convenient season is the winter period. This is because during the year the lowest mixing heights that worsen dispersion of air pollutants are observed in winter, while the highest mixing heights in the summer that favour dispersion and moderate heights are common during spring and autumn (Yannopoulos 2007b). Within the prescribed time interval of the year, the most susceptible hours for primary air

pollutants are the morning hours or the evening hours of the working days, exempting the rainy workday hours. The determination of the project duration depends on the number of sampling points, the number of persons employed for simultaneous air sampling during each expedition and the statistically necessary revisits of each location for sampling in order to approximate hourly mean values. However, the maximum duration of the whole project should be less than the three months period, so as the project may be carried out entirely within a season of the year. If our purpose is the parallel run of a study of indicative measurements to a continuous monitoring network of stations, we have to design and apply four particular projects corresponding to the seasons of the year. According to the EC (2008) Directive, indicative measurements may have minimum time coverage 14% for air pollutants of SO_2, NO_2, NO_x, CO, benzene, $PM_{10}/PM_{2.5}$ and Pb, while more than 10% minimum time coverage during summer is required for O_3 and the related NO and NO_2. Therefore, the minimum duration of the whole project should be 13 working days for the winter months and 9 working days for the summer months, regarding the above air pollutants. A typically reasonable duration of a whole project of indicative air pollution measurements may be 1 to 2 months.

2.1.3 Defining the size and material of sampling bags

The size of the air sampling bags must be adequate to provide the necessary volume for analysing the sample by the analyser. The least volume of sample needed from the analyser to display the right value of the pollutant concentration depends on the rise time of the analyser and the pump discharge that the analyser uses. Therefore, the least sample volume can be calculated by multiplying the pump discharge by the rise time of the analyser employed. In case that more than one pollutant is going to be measured, the least sample volume must be the total sum of particular volumes needed for each analyser working independently. To save time during each sample analysis, all analysers have to be linked in parallel tubing with the bag. In such a case, the desired least volume should be calculated by multiplying the sum of discharges pumped from all analysers by the maximum rise time of the analysers employed. Indicative rise times of common analysers usually vary from 90 to 240 s, while their sampling rate varies from 0.2 to 1.0 l $minute^{-1}$. Sampling bags have to be filled up to 60-70% approximately for their protection by punch and leakage. This precaution is much more mandatory for Teflon bags than for Tedlar bags, because Teflon bags are more sensitive. Consequently, the least nominal capacity of each bag should be roughly 1.5 times larger than the volume of the sample needed for the analysis.

The bag material depends on the pollutant properties. For instance, even if a bag is made by a completely inert material, PM is adsorbed on the inner surface of bag in a more intensive way than a gaseous pollutant. O_3 is vulnerable to reactions with other air pollutants, thus it is reduced significantly during the time lag in the sampling bag, while CO indicates very good recovery rates when sampled in Tedlar bags. There are other air pollutants that may be absorbed by the wall material or may escape through the bag walls. All these restrictions bound the use of the bag sampling technique to only prescribed pollutants and bag materials.

Tedlar bags show low permeability in gases and they are chemically inert, causing minimal sample losses. They are also mechanically strong, reusable and cleanable. Teflon bags are ideal for unique applications, as they can withstand extreme temperature applications from -240°C up to 205°C. They are easily autoclavable and visually clear providing high

transmittance to UV light. They are non-wettable, non-charring and showing no electrical tracking. They can be cleaned up easily and they have antistick and low frictional properties. They are physico-chemically inert, non contaminating samples, with low permeability to liquids, gases, moisture and organic vapours, as well as solvent resistant to virtually all chemicals, except molten alkali metals, gaseous fluorine, complex halogenated compounds at elevated pressure and temperature. In the market, the capacities available for Tedlar and Teflon bags range from 0.6 to 100 l. Teflon bags are more expensive than Tedlar bags.

For the requirements of an air pollution study of the present type, a concentration recovery rate of more than 85% may be acceptable for no more than 90 minutes time spent from the start of sampling and up to integrating the sample analysis, i.e. the required time for completing an expedition. Selecting bags made by the most inert materials (Tedlar or Teflon), the most common gasses that may be measured using the bag sampling technique are CO_2, CO, SO_2, NO, NO_2, N_2O, NH_3, CH_4, NMHC, total hydrocarbons (THC), as well as some VOCs, odorants and PAHs.

2.1.4 Defining the suitable point for sampling at each particular location

Normally, a typical city location for sampling is a cross road that has four corners, alike this one shown in Fig. 1. The suitable point mainly depends on the wind speed and direction. Thus, care will be paid in order to check for these factors before collecting the sample of each time. When the atmosphere is calm, these precautions are not too compulsory to follow, since the pollutants are diffused around with a uniform way. In case of a detectable local wind speed, the suitable point for carrying out sampling is the downwind point of the

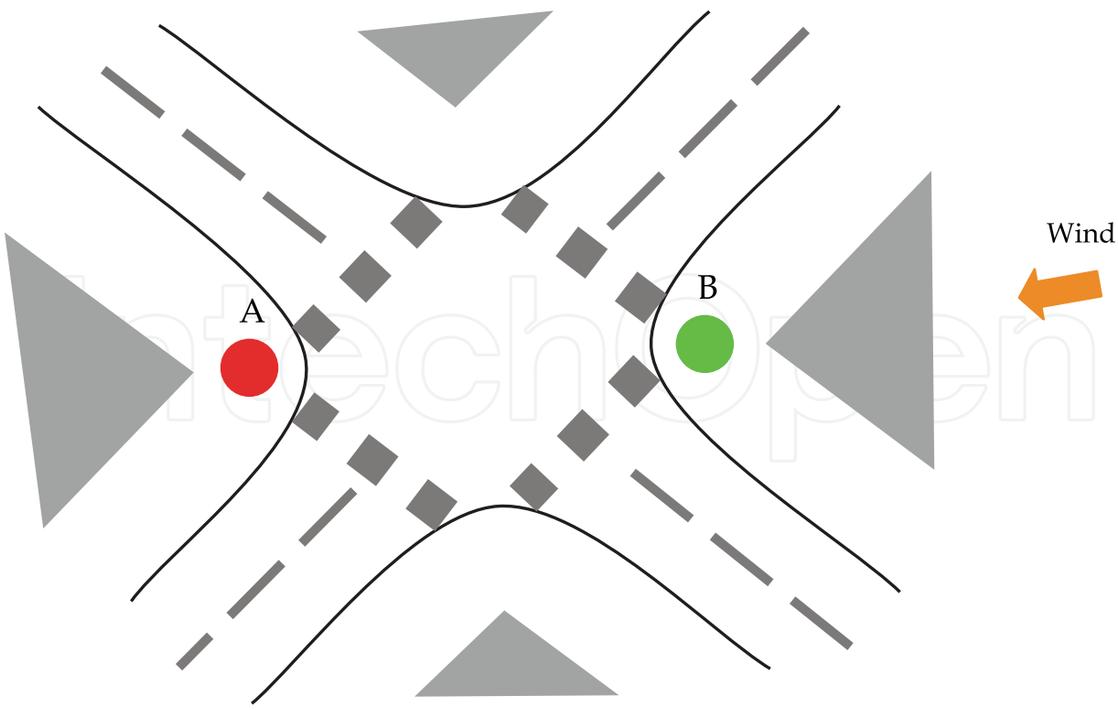


Fig. 1. A typical cross-road location where the downwind point A (red) and upwind point B (green) are shown

cross road with respect to traffic or other surrounding pollution sources. The data shown in Table 1 verify this argument. The results of two extra expeditions, including simultaneous sampling from two different positions of a junction, one upwind and another one downwind have been included in relation to the prevailing conditions. At each position five successive air samples were collected with 3–minutes duration per sample. Provided that the wind direction was detectable, data indicate that downwind points are mostly appropriate for peak concentration measurements, while this precaution becomes less important in a calm atmosphere. For instance, data given in Table 1 regarding Location 1 show that the wind conditions were calm to slight breeze with a rather well detectable direction. Thus, it is expected that the downwind point of the location would have higher impact from traffic than the upwind point, an event which is fully supported by the measurements presented in Table 1. In contrary, the measurements at Location 25 show approximately equal levels and this event is expectable due to unrecognised wind direction (calm atmosphere).

Point	A (red), Downwind						B (green), Upwind					
Sample No.	1	2	3	4	5	**Mean±σ_{n-1}**	1	2	3	4	5	**Mean±σ_{n-1}**
Location 1, Jan 7 1998, 10:27–10:45, clear sky, calm to slight breeze, traffic = 1658 vehicles/h												
SO_2	37	37	41	25	29	**34±7**	8	17	29	46	29	**26±14**
NO	326	237	455	227	268	**303±94**	62	75	72	102	265	**115±85**
NO_2	126	103	90	75	75	**94±22**	75	77	63	67	82	**73±8**
Location 25, Jan 7 1998, 12:20–12:40, clear sky, calm, traffic = 2011 vehicles/h												
SO_2	25	21	17	8	8	**16±8**	21	13	13	25	25	**19±6**
NO	266	175	291	137	131	**200±74**	168	40	26	195	203	**127±86**
NO_2	124	117	103	103	90	**108±13**	107	78	67	121	121	**99±25**

Table 1. Concentration measurements (μg m^{-3}) by simultaneous sampling at two points, one downwind (A) and another one upwind (B), taking five successive air samples of 3–minutes duration collected at each point

2.1.5 Estimating the maximum time lag of air samples in bags

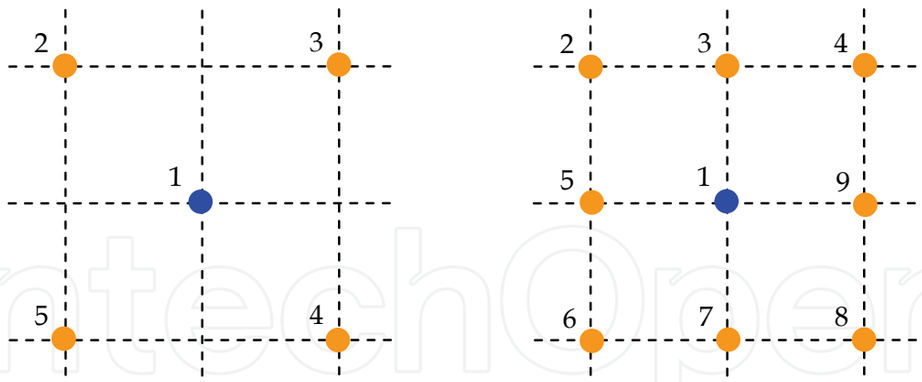
For the pollutant under examination, estimation of the maximum time lag during its remaining in the bag should be made. The site locations in the city are initially selected. These locations should be distributed in areas, where the prescribed pollutant levels are expected to be moderate or high. The number of locations must be adequate for pertinent statistical analysis. Teflon or Tedlar bags of volume larger than the volume of the normal sampling are selected. The bags of 24×36-in size and 47–l maximum volume may be a good choice. Air sampling is performed following exactly the procedure for normal samples, but with a sampling duration of approximately 20 to 30 minutes, using an air pump convenient

for sampling with such a flow rate as to fill the bag in the desired sampling duration time. Each sample collected in the bag is then transferred to the laboratory and measured without other delay. Then, the sample is preserved in its own bag enclosed in an opaque plastic sack in the room conditions. The measurement of the sample is repeated after two hours and then it may be useful to measure the sample after 12, 24, 48 and/or 72 hours. For all samples collected, the maximum losses per hour are calculated.

Having the possible recovery rate or the maximum rate of losses measured, the maximum allowed time lag for a smaller bag size may be estimated according to the following procedure (Yannopoulos, 2007a). It is considered that the wall losses are proportional to the internal wall surface of the sampling bag, S, or alternatively, the time lag is proportional to the air–sample height, h, defined as $h = V S^{-1}$, where V is the air volume sampled in the bag. For instance, taking that approximately 36–l and 3.6–l air volumes have been sampled using the 47–l and 4.7–l sampling bags, the corresponding air–sample heights are h = 3.23 and 1.94 cm. The hourly losses measured previously for 47–l bags correspond to losses during 36–minutes (1.94/3.23 h = 0.6 h) time lag for 4.7–l bags. Defining the allowed tolerance in recovery, which may be higher than 85%, it is then possible to determine the maximum time lag required for completing the entire process (sampling, transport and analysis) of each particular sample for normal sampling and analysis. Note that the time for the transport of samples depends on the distance between the city location and the laboratory in conjunction with the means for the transport. As mentioned previously, the use of small cars or motorcycles is preferable since they could be a good solution to minimise times, which may be critical to cost-effectively optimise the project area and site locations.

2.1.6 Estimating average air pollutant concentrations

The project may include measurements at the most critical hours of the day. According to previous experience described above, for measuring peaks of primary air pollution, the morning and evening hours from 08:00 to 10:00 and from 20:00 to 22:00, correspondingly, are the most suitable. The average concentration for all samples randomly picked at a particular location during morning or evening rush hours must be calculated separately for morning or evening hours and the average values are assigned initially at the nodes (sampling locations), using the point kriging method with a linear variogram model (Golden Software, 2002). All measurements used for the calculation of the above average concentration at each location have to pass the Q–test (Radojević and Bashkin, 1999). Thus, one grid matrix of average concentrations for each prescribed air pollutant for morning hours and another one for evening hours can be created. The next step is to filter each matrix using a low–pass linear convolution filter of 5-node averaging or, alternately, 9–node averaging with weights equal to 1 (moving average filter), as shown in Fig. 2. A number of four to five random measurements may be a good choice to carry out at each location, if a 9-node matrix for averaging is selected, while about the double random measurements are needed in case of selecting the 5-node averaging procedure for filtering. Thus, adopting the contribution of either 5-nodes or 9-nodes matrix in the calculation of the average value, which is assigned to the prescribed middle node of the group, the total number of samples is n, where $36 \leq n \leq 45$. After averaging the resulting matrices become smoother, as they are free of high frequency noise, and can be used to make the corresponding iso–concentration contour diagrams. The alternative use of Gaussian low–pass filter instead of the above will result in practically similar results with actually equal accuracy.



(a) (b)

Fig. 2. Groups of matrix locations where averaging is applied: (a) Five-node matrix; (b) nine-node matrix

It can be shown that the final grid used above for contouring approximates mean concentrations of longer time interval at the specified locations. For this reason a confidence level 95% and the Student *t*–distribution are assumed. We define as probable error the percentage of the half–length of the confidence interval of the mean concentration for the specified level of confidence divided by the mean concentration at the particular location. This is expressed as a percentage of the mean concentration, i.e. $\pm 100 t_{n-1,\,a} n^{-1/2} \mathrm{CV}$ (%), where $t_{n-1,\,a}$ is the Student *t*–distribution parameter for n-1 degrees of freedom and a confidence level p; $a=(1-p)/2$; CV is the coefficient of variation defined as the standard deviation divided by the mean value. The mean probable error made for each final grid matrix of average concentrations can be calculated and tabulated. As we can see in Chapter 3, the maximum values of mean probable errors were around 25% and they depend on the parameter measured (Yannopoulos, 2007a).

The ratio of peak to mean concentrations at the ground level depends on the stability of the atmosphere and the type of terrain that the pollutant is passing over. Studies have also shown that the aforementioned ratio depends on the sampling time or averaging time, according to the following relationship (Turner, 1994; Schnelle and Dey, 2000)

$$C_t = C_s \left(\frac{s}{t} \right)^p \tag{1}$$

where s, t are the shorter and longer averaging times (in minutes), for t longer than 10 minutes and up to 24 h; C_s, C_t are the mean concentrations for averaging times s, t; power p ranges from 0.17 to 0.75, but the most usual values are between 0.17 and 0.20 (Turner, 1994). Schnelle and Dey (2000) suggest the value p=0.17. Values of the ratio of peak to mean concentrations, C_t/C_s, for p=0.17 or 0.20, s=3 minutes and t=3 minutes, 10 minutes, 20 minutes, 1 h, 6 h and 24 h, are calculated using equation (1) and shown in Table 2. These values can be compared to the corresponding values coming from the measurements. For the locations designed, we get the maxima of concentrations for the typical sampling time and, for the average values calculated by applying the procedure described above, the ratio C_t/C_3 is computed. According to the procedure described above, the time t that corresponds to the common ratio C_t/C_3 reflects the approximate averaging time. As we can see below,

this time approaches 1 h. In case that this procedure would give different averaging times than the desired time, the solution would be the revision of either the grid of sampling locations or the total number of visits for sampling at each location. For instance, making a denser grid, the averaging time would be decreased. The same result could be succeeded with the alternative procedure of collecting more samples randomly picked at each particular location during rush hours, with visits dispersed within workdays of the whole project period and using only 5-node averaging instead of 9-node averaging. A rarer grid of sampling locations, combined with increased number of nodes that participate in the group for the calculation of the average concentration of the middle node of the group, would lead to longer averaging times. Another way to get longer averaging times can be managed by increasing sampling time from 3 minutes to 5, 10, 15 or more minutes in relation to the desired result of the averaging time and simultaneously decreasing the total number of nodes or number of nodes participating in groups for the averaging procedure.

Averaging time or sampling time, t	C_t/C_3 (for p = 0.17)	C_t/C_3 (for p = 0.20)
3 minutes	1.000	1.000
10 minutes	0.815	0.786
20 minutes	0.724	0.684
30 minutes	0.676	0.631
1 h	0.601	0.549
6 h	0.443	0.384
24 h	0.350	0.291

Table 2. Values of the ratio of calculated concentration to 3-minutes concentration, C_t/C_3

If sampling intervals at the same location start at different times dispersed within the typical morning or evening sampling periods, it is expected that the aforementioned average concentrations will reflect mean levels of much greater time intervals than the 3 minutes, approaching the related typical morning or evening sampling periods. This assumption can be supported by additional expeditions organised within the program period, according to which simultaneous air sampling with 50-l and successive 5-l sampling bags at the same location must be performed, as indicated by the following case-study. Starting at the same time, the successive sampling of ten 5-l bags, each one filled with approximately 3.5-l air sample, lasted approximately 25 minutes, an equal time for a continuous collection of 30-40 l with a 50-l bag. The bag air samples were collected by four different locations of the central part of downtown Patras area and the concentrations measured for three air pollutants in regard to the conditions recorded are given in Table 3. The number of locations corresponds to that given in Fig. 5. A careful observation of data implies that the 25-minutes mean concentration (50-l bag) could be approximated fairly well by random picking of four to five 3-minutes concentration values (5-l bags).

Finally, the above procedure results in getting iso–concentration contour diagrams for average concentrations of a specified pollutant longer than the sampling time, within typical rush hours of the program period. These diagrams in conjunction with the probable errors encountered in iso–concentrations affect the determination of the boundaries of the high pollution zones and the mean displacements can be estimated.

Bag type	5 l											50 l
	1	2	3	4	5	6	7	8	9	10	**Mean**	**Mean**
	Location 2, Nov 26 1997, 10:35-11:00, cloudiness < ⅜, weak NE wind, traffic rate = 2682 veh h^{-1}											
SO_2	16	16	16	16	19	23	8	16	27	19	**17**	**24**
NO	192	202	172	134	201	157	137	134	242	193	**176**	**178**
NO_2	88	80	75	84	92	80	77	84	99	86	**85**	**104**
	Location 16, Dec 10 1997, 10:50-11:15, cloudiness < ⅜, calm, traffic rate = 1746 veh h^{-1}											
SO_2	8	8	12	32	12	16	20	20	8	4	**14**	**21**
NO	45	50	69	216	109	100	140	162	75	82	**105**	**100**
NO_2	61	67	71	134	78	73	82	84	67	61	**78**	**114**
	Location 22, Jan 14 1998, 10:45-11:10, cloudiness < ⅜, weak SW wind, traffic rate = 2328 veh h^{-1}											
SO_2	25	17	17	4	13	13	13	8	13	13	**13**	**20**
NO	147	82	106	24	55	21	49	17	64	40	**61**	**52**
NO_2	33	94	105	98	80	75	73	69	82	82	**79**	**106**
	Location 26, Jan 14 1998, 13:40-14:05, cloudiness < ⅜, weak SW wind, traffic rate = 1872 veh h^{-1}											
SO_2	8	8	8	4	4	8	8	8	4	13	**8**	**8**
NO	51	16	41	26	35	64	46	80	25	158	**54**	**25**
NO_2	77	59	55	65	55	75	75	78	59	94	**69**	**87**

Table 3. Concentration measurements (in μg m^{-3}) by simultaneous sampling at each selected location downtown of the city of Patras, using 10 successive 5-l and one 50-l Teflon air sampling bags

2.1.7 Correlating average air pollutant concentrations with traffic rates

Data regarding air pollution concentrations, measured within different rush-hour intervals of the project period, should present statistically insignificant concentration differences in order to be considered as belonging in a common group. If this statistical check is positive, then all concentration data can be considered suitable to be used for either calculating overall average pollutant concentrations or being correlated with traffic rates. Otherwise, the therapy would be to leave out concentrations measured at locations having a local effect that makes a different influence. Then, the rest data have to present statistically insignificant concentration differences and they can be used for the correlation with traffic rates. It must be noticed that data showing statistically insignificant concentration differences may be regarded as belonging in a common group and they can be used as an entity for the calculation overall average pollutant concentrations.

2.2 Gaussian modelling alternative

2.2.1 Gaussian model description

The USEPA Industrial Source Complex Long-Term model (ISCLT3) or/and Industrial Source Complex Sort-Term (ISCST3) model (http://sdi.odu.edu/air/isc3/) can be used to predict the dispersion of prescribed pollutants on a period basis in a city's atmosphere. These models provide options to model emissions from a wide range of sources. They use

the straight-line, steady-state Gaussian sector-average plume equation for modelling pollutant emissions on either a long-term basis (month, season, and year) or a short-term basis (hour and day). Both models use the Gaussian plume equation with some modifications to account for simple point source emissions from stacks, emissions from stacks that experience the effects of aerodynamic downwash due to nearby buildings, isolated vents, multiple vents, storage piles, conveyor belts, and other sources of similar types. Emission sources are grouped into four basic types (point, volume, area, and open pit sources); the volume source and the area source may also be used to simulate line sources. The models are equipped with suitable algorithms to manipulate each source type and calculate dry or wet deposition for simple terrain (elevations below the release height). They use input meteorological data that have been summarized into joint frequencies of occurrence for particular wind speed classes, wind direction sectors, and stability categories (http://sdi.odu.edu/air/isc3/, USEPA 1995, Schnelle and Dey 2000, Turner 1994). In particular, the ISCLT3 model uses input meteorological data that have been summarized into joint frequencies of occurrence for particular wind speed classes, wind direction sectors, and stability categories. These summaries are called STAR summaries for STability ARray and may include frequency distributions over a monthly, seasonal or annual basis. The long term model can be used to calculate concentration or dry deposition values for each separate STAR summary input and/or for the combined period covered by all available STAR summaries. Since the wind direction input is the frequency of occurrence over a sector, with no information on the distribution of winds within the sector, the ISC long-term model uses a Gaussian sector-average plume equation as the basis for modelling pollutant emissions on a long-term basis. On the other hand, the ISCST3 model accepts hourly meteorological data records to define the conditions for plume rise, transport, diffusion, and deposition. The model estimates the concentration or deposition value for each source and receptor combination for each hour of input meteorology, and calculates user-selected short-term averages. For deposition values, either the dry deposition flux, the wet deposition flux, or the total deposition flux may be estimated. The total deposition flux is simply the sum of the dry and wet deposition fluxes at a particular receptor location. The user also has the option of selecting averages for the entire period of input meteorology.

The newer model systems AERMOD (http://www.epa.gov/scram001/dispersion_prefrec.htm) introduced by the American Meteorological Society/Environmental Protection Agency Regulatory Model Improvement Committee (AERMIC) can be also used to predict the dispersion of prescribed pollutants on a period basis in a city's atmosphere. The modelling system, AERMOD, has incorporated air dispersion based on planetary boundary layer turbulence structure and scaling concepts, including treatment of both surface and elevated sources, and both simple and complex terrain. There are two input data processors that are regulatory components of the AERMOD modelling system: AERMET, a meteorological data pre-processor that incorporates air dispersion based on planetary boundary layer turbulence structure and scaling concepts, and AERMAP, a terrain data pre-processor that incorporates complex terrain using USGS Digital Elevation Data. Other non-regulatory components of this system include: AERSCREEN, a screening version of AERMOD; AERSURFACE, a surface characteristics pre-processor, and BPIPPRIME, a multi-building dimensions program incorporating the GEP technical procedures for PRIME applications. The reader may visit the relevant USEPA site given above for further details on these model systems.

2.2.2 Defining model conditions

For the application of a model to predict the air quality levels on an area, the first action is the geographical definition of the area. Then, the characterisation of the area type (city, rural area, etc.), in conjunction with its morphological and physiological properties, as well as the area relations to the neighbouring areas and activities is required. It follows the collection of the necessary information from available sources regarding geographical data, meteorological data and information for all main sources of air pollution, which may affect the air quality of the area, either within or outside it. As the area that the model is going to be applied concerns a city, for the requirements of the present chapter, data regarding emissions from central heating, traffic and harbour are necessary. In many cases, it is important to carry out individual project studies in order to produce suitable data for the model input using the available raw information collected from the data sources. For instance, one may find available traffic rate measurements for some roads of the city in the municipal authorities, but they may realise that the data refer to periods other than the period of interest or they are not complete and they need to be completed and updated.

For air pollution studies, meteorological data concerning wind speed and direction are needed in order to group wind speed into categories. For the present work and concerning prescribed wind directions, the following seven classes of the wind speed measured in m s^{-1} are taken: WS-1 (0 – 1), WS-2 (1 – 2), WS-3 (2 – 3.5), WS-4 (3.5 – 5.5), WS-5 (5.5 – 6.5), WS-6 (6.5 – 8) and WS-7 (> 8). The number of prescribed wind directions may be at least four and at most sixteen depending on the study's requirements. Typical examples for classification and nomination of wind directions are shown in Fig. 3.

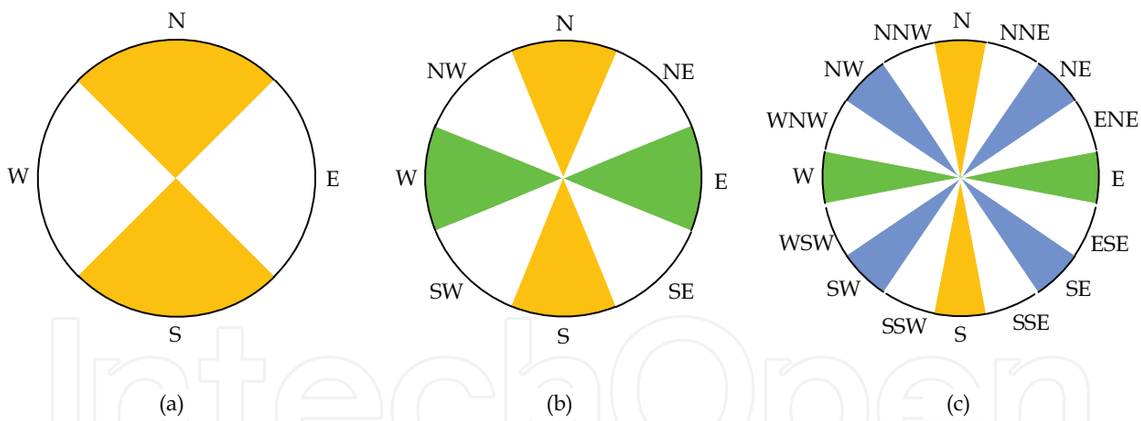


Fig. 3. Classification of wind directions in: (a) four sectors; (b) eight sectors; (c) sixteen sectors

The simplest four directions classification utilises the following sectors of equal angles, measured clockwise from the north direction in deg: N (-45 to 45), E (45 to 135), S (135 to 225) and W (225 to 315). The usual eight divisions for the classification of the wind direction include the following sectors: N (-22.5 to 22.5), NE (22.5 to 67.5), E (67.5 to 112.5), SE (112.5 to 157.5), S (157.5 to 202.5), SW (202.5 to 247.5), W (247.5 to 292.5) and NW (292.5 to 337.5). The most complete classification is in sixteen sectors as: N (-11.25 to 11.25), NNE (11.25 to 33.75), ENE (33.75 to 56.25), E (56.25 to 78.75), ESE (101.25 to 123.75), SE (123.75 to 146.25), SSE (146.25 to 168.75), S (168.75 to 191.25), SSW (191.25 to 213.75), SW (213.75 to 236.25), WSW (236.25 to 258.75), W (258.75 to 281.25), WNW (281.25 to 303.75), NW (303.75 to 326.25) and NNW (326.25 to 348.75).

In general, it must be noticed that available raw data regarding wind information for extended periods (years or decades) are very useful for the production of wind rose diagrams. These diagrams provide useful information for deciding and creating pertinent scenarios of prevailing winds, when air quality in adverse atmospheric conditions is claimed to predict. A very simple wind rose diagram is shown in Fig. 4. This diagram concerns a special period, which may be a month, year or any other defined period, and shows the wind occurrences per direction (thick line) for wind speeds within a prescribed range. Wind occurrences are given in frequency percentages 0, 5, 10 … (%), which include calm occurrences shown in red colour in the rose centre.

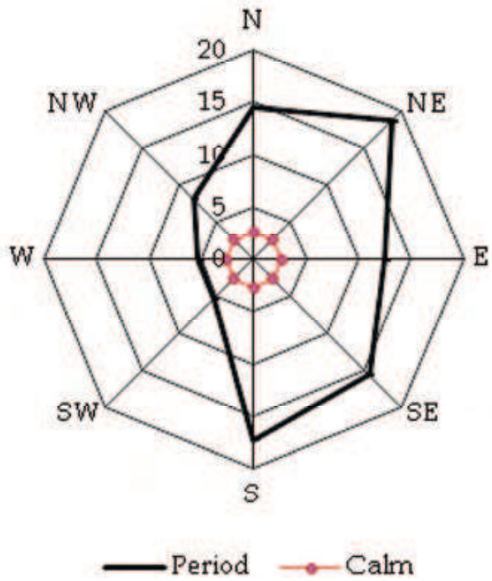


Fig. 4. A simple wind rose diagram showing the wind frequencies per direction for a prescribed speed range of winds

Another important magnitude to be defined is the atmospheric stability, which depends mainly on the convective and mechanical eddies. Classification is based on the assumption that stability at the near ground layers depends on the incoming solar radiation (insolation), which contributes to the production of convective eddies, and on wind speed, mainly responsible for the production of mechanical eddies. The high levels of incoming solar radiation in conjunction with low wind speed occurrences contribute to unstable atmospheric conditions. Conditions for a neutral atmosphere are probable when the sky is cloudy or with occurrences of high speed winds. The stable conditions occur when the net radiation index (NRI) gets negative values. The classification system followed herein is the Turner' system, which is based on hourly meteorological observations and Pasquill-Gifford's work (Turner 1994; Schnelle and Dey 2000). According to Schnelle and Dey (2000), Turner has classified atmospheric stability into the following seven categories:

1. Extremely unstable
2. Unstable
3. Slightly unstable
4. Neutral
5. Slightly stable

6. Stable
7. Extremely stable

The determination of the stability class is enabled by data given in Table 4, where the stability class number is given as a function of the class of the wind speed and the NRI. Schnelle and Dey (2000) has given some recipes regarding the correct choice of the stability class. The most important criteria are the following:

- Irrespective of day or night for complete cloudy sky (10/10) and ceiling less than 2000 m, the zero value for the net radiation index is suggested, NRI = 0.
- For night hours and small cloudy sky occurrences (less than 4/10), the value of NRI = -2 is recommended, while NRI = -1 for heavier cloudy sky occurrences (more than 4/10).
- For day hours, NRI is related to the insolation class number (ICN), which indicates the incoming net solar radiation. ICN depends on the angle that solar rays fall on the location of interest, called solar altitude a, as well as for the atmospheric conditions affecting insolation. The recommended values of ICN are:
  ICN = 1 for $a < 15$ deg (weak insolation)
  ICN = 2 for $15 < a < 35$ deg (slight insolation)
  ICN = 3 for $35 < a < 60$ deg (moderate insolation)
  ICN = 4 for $a > 60$ deg (strong insolation)
- For day hours and small to moderate cloudy sky occurrences (less than 5/10), the recommendation is to consider equality between NRI and ICN. Thus, for prescribed daylight conditions, the value of ICN can be determined as above and consequently the NRI value. Then, the value of Atmospheric Stability Class (ASC) can be determined from the data given in Table 4, using NRI = ICN and the class of the prevailing wind speed.
- For day hours and heavier cloudy sky occurrences (more than 5/10), NRI is determined by a modified ICN according to the procedure: NRI = ICN – 2 for ceiling less than 2000 m; NRI = ICN – 1 for ceiling between 2000 m and 5000 m; NRI = ICN – 1 for complete cloudy sky and ceiling higher than 2000 m.
- In cases when the modified ICN is found less than 1, then the value NRI = 1 is recommended.

Wind speed (WS) class	Net radiation index (NRI) of the area to the sunlight exposure (insolation)*						
	4 (strong)	3 (moderate)	2 (slight)	1 (weak)	0	-1	-2
WS-1	1	1	2	3	4	6	7
WS-2	1	2	2	3	4	6	7
WS-3	1	2	3	4	4	5	6
WS-4	2	3	3	4	4	4	5
WS-5	3	3	4	4	4	4	4
WS-6	3	4	4	4	4	4	4
WS-7	3	4	4	4	4	4	4

* Positive values indicate that radiation is directed toward the ground, while negative values indicate radiation directed away from the ground.

Table 4. Atmospheric stability class (ASC) as a function of the wind speed class and the net radiation index

It must be noticed that data in Table 4 have taken into consideration the effect of retaining heat by buildings and pavements after sunset. During the night hours this heat is re-radiated away from the earth. Due to more reflection conditions met in cities compared to rural areas, the city surfaces and buildings become warmer than the surfaces in rural areas and, therefore, they help the production of more convective eddies affecting ASC.

2.2.3 Determining source characteristics

The most significant sources for the study have to be defined. A source classification may help the knowledge of expected characteristics, using literature. Data regarding source location, emission inventories and other related information are very useful for producing emission loads or updating them, according to the prescribed procedure of the model. Always a pertinent preparation of data for the model input is requisite. It is needed either a slight data treatment or severe manipulation of data to become suitable for the model input. There are cases that input data has to be constructed by existing raw measurements. For instance, the central heating and ship emissions can be modelled as area sources, while traffic as a line source divided in segments of a prescribed length.

The calculation of the emission from each source category is based on the legislation in force and existing data. As an example, according to the USEPA data, the SO_2 central heating emissions are considered to be 852 mg l^{-1} per fuel mass consumed and varied with respect to the sector of the City Plan. The traffic emissions in a European country can be determined using the Computer Programme to calculate Emissions from Road Transport [COPERTIII] of the European Environmental Agency (http://vergina.eng.auth.gr/mech/lat/copert/copert.htm) or a newer version, in conjunction with the fuel quality characteristics for the period of interest. Traffic loads (cars per day or month), as well as the car types (conventional, catalytic passenger cars, light-duty and heavy-duty vehicles) and their percentages must be determined for the city's main streets and probably harbour and other significant areas. Both the average car speed and the average trip distance regarding the particular urban areas have to be defined. In addition, the daily or monthly ship and vehicle emissions due to a probable harbour, affecting the air quality of the city areas under examination, have to be calculated according to the model requirements. In most of cases, the raw data regarding traffic, central heating and harbour need laborious treatment efforts in order to create the suitable data for the model input.

2.2.4 Locating receptors

The city locations of special interest (downtown central points, traffic-jam street points, cross-roads with high traffic loads, parking lots, central squares etc.) may be defined as receptors. These locations may be any suspected points or points indicated by previous studies for probable high pollution levels. The locations, where measurements are available to be used for model validation or comparisons, should be also included in the list of receptors. Finally, receptors may be all locations where output values have to be provided by the model, for either direct comparison with existing measurements or plotting iso-concentration contour diagrams that can be used for several types of studies of the future development of the city.

3. Application and evaluation

3.1 The case-study area

The central part of the city of Patras is selected for the application of the methodology proposed. Patras, the third largest city of Greece, after Athens and Thessaloniki, is built on

the NW coast of Peloponnese and today has a population of around 200,000 inhabitants. The population is further increased during summertime, festivals and working days, because of tourists and other visitors. Patras is the western gate of the country with a busy harbour due to many links to Ionian Greek Islands and Italy. The study area includes Sectors A, B, C, D, E and F of the City Plan, as shown in Fig. 5, which gives a general view of Patras highlighting areas of interest. The City Plan Sectors are included between the streets described in Table 5, where some important information is also given. For simplicity reasons, the town planning sectors included in the area of the present study have been grouped in regard to their common characteristics given in the City Plan of Patras: (a) Allowed Building Coefficient (ABC) defined as the area of all floors of a building that is allowed to be built, divided to the area of plot; (b) Allowed Cover Coefficient (ACC) defined as the maximum area of plot that is allowed to be covered by a building, divided to the area of plot. In addition, the storey number of buildings, an estimated range of building heights and useful remarks attaining in each sector part are given. Up to 1970's the coastal zone of Sectors A and D, in Akti Dymeon Street south of Papaflessa Street, constituted the old

City Plan Sector	ABC[a]	ACC[b]	Building Height (m)	Short description
A	2.4	0.70	15–28	Flat area, with most of the old buildings being rehabilitated. It has intensive traffic and business activities especially in main streets.
B	2.1	0.70	8–12	It includes the old flee Market and the area around the Odeum, built during the Roman Colony. The traffic and business activities are considerable mainly in the streets of boundaries.
C	1.6	0.60	8–21	Both parts are built in flat areas and there are intensive business activities and traffic, mainly in main streets.
D	1.2	0.70	8-24	It has parts of small plots in hilly old areas built rather disorderly and parts with plots having gardens of normal or big size. It has also a downgraded part with normal or big size plots and gardens. The traffic rates are intensive in main streets and low to moderate in secondary roads. The new harbour, which extends west of Sector D, is going soon to be in operation.
E	0.8	0.70	4–12	It is built on a hill having steep slopes and small plots, but it has a part built on a flat area with normal or big size plots and gardens. The traffic rates are low to moderate.
F	0.6			A small hilly area presenting moderate to high traffic rates in Alsiliou Str.

[a] Allowed Building Coefficient; it denotes the area of all floors of a building that is allowed to be built, divided by the plot area.
[b] Allowed Cover Coefficient; it denotes the maximum area of plot allowed to be covered by a building, divided by the plot area.

Table 5. Important details and short description of the City Plan Sectors shown with similar colours as in Fig. 5

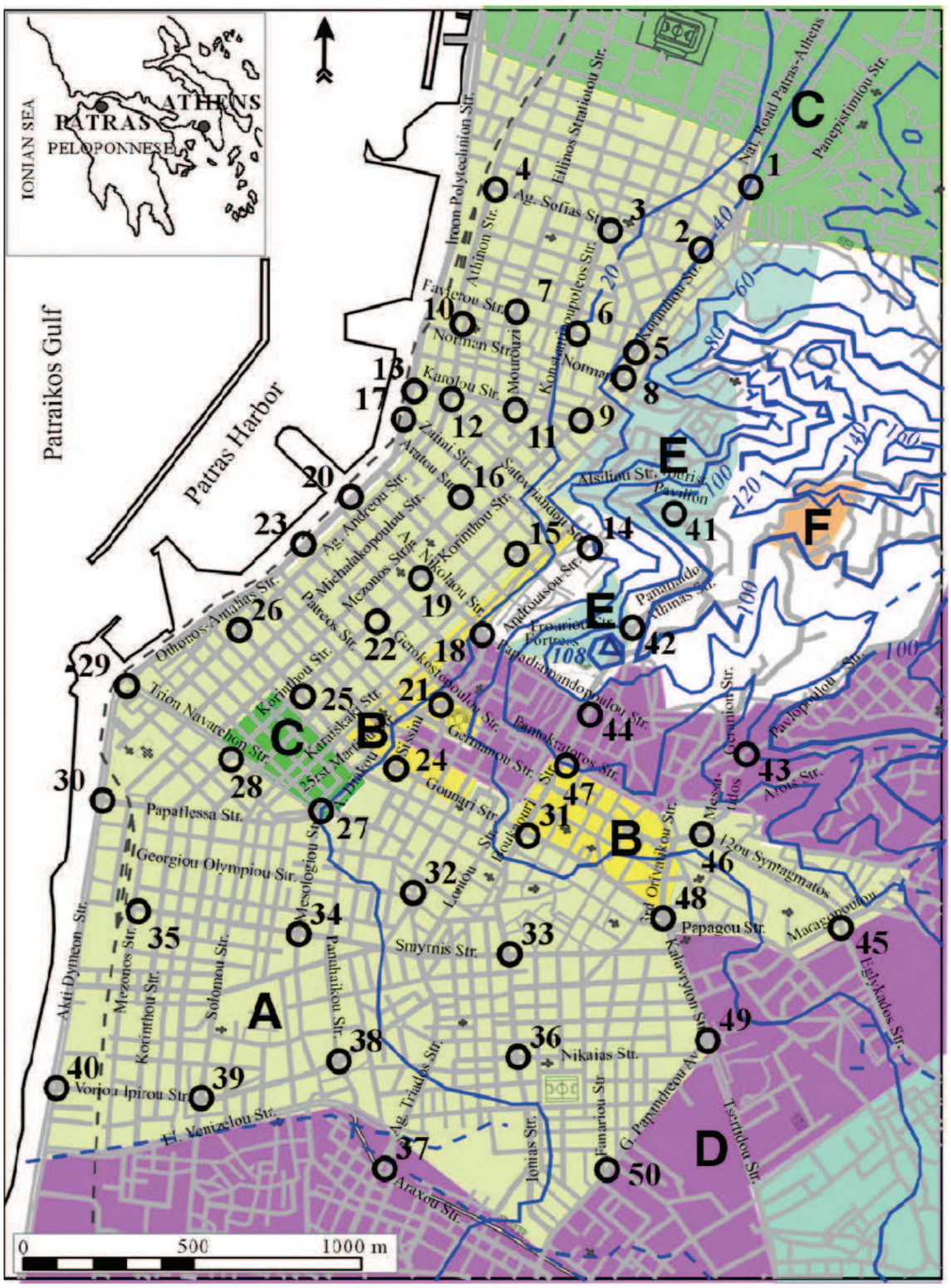


Fig. 5. A map showing interesting Patras areas, the City Plan Sectors A, B, C, D, E, F and the sampling locations 1-50

industrial area of Patras, but last years the industries - one by another - either ceased to operate or were removed in the new industrial area located at a distance of 17 km approximately towards SW of Patras. In now a day, some of the abandoned buildings and industrial structures have been modified to house municipal authorities or offer modern entertainment and shopping.

The marine Mediterranean climate is prevailing in the major Patras area, having relatively high humidity (annual mean 67%) and prolonged and sunny warm periods. As shown in Fig. 6, the NE and SW winds prevail during the actual program period with comparable frequencies (Yannopoulos and Skokaki, 2003). Frequencies (%) and directions of prevailing winds concern the period 1955-1988 and have been recorded by the station of the Hellenic National Meteorological Service (HNMS) at Akti Dymaion Str. of Patras. In addition, during the program periods, air temperatures varied between -6 and 31ºC, with monthly mean values from 10 to 15ºC. The annual mean precipitation is approximately 747 mm, with 52% occurrences during November, December and January; during these months, the monthly mean relative humidity is around 72 to 73%. During the program period a mean number of 45 cloudy days over 199 annually corresponds. Tables 6 and 7 include local climatic

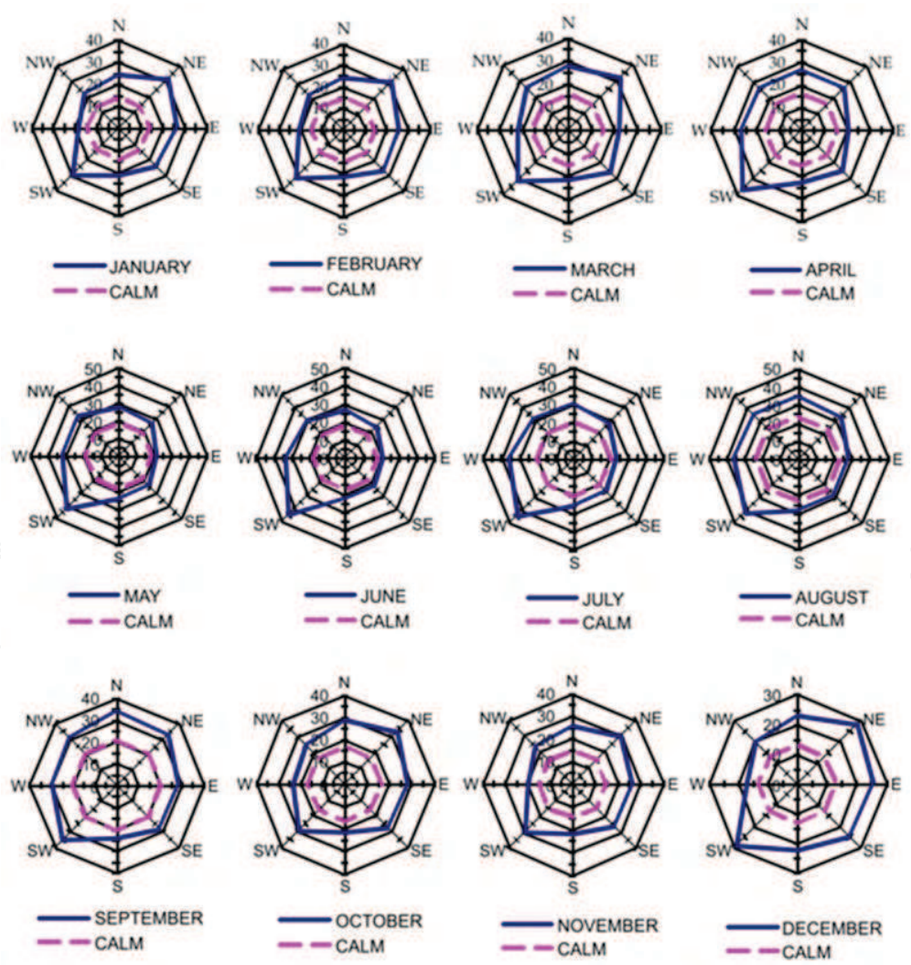


Fig. 6. Wind rose diagrams for Patras during months of a typical year

conditions recorded during the sampling period. Wind data in Table 7 show that calm or light winds were the most frequent weather conditions during sampling hours. Winds with very low velocity and rather detectable direction constitute suitable conditions for air sampling, since it is possible to define the downwind point for sampling performance. As for many other Mediterranean cities of moderate size and similar activities with Patras and apart of sporadic emissions due to industrial and service enterprises and background pollution due to probable remote sources, air pollution in Patras originates from the classic sources of harbour, traffic and central heating. More details and a thorough review for the actual air quality data for the city of Patras have been given by Yannopoulos and Skokaki (2003), Yannopoulos (2008) and Bloutsos & Yannopoulos (2011).

Month	Dates with cloudiness occurrences	Dates with rainfall occurrences
Nov 1997	13^{e}, 14, 17, 18, 19, 20^{e}, 21^{e}, 24^{m}, 25 ^{e}, 26, 27^{me}, 28	13, 17, 18, 19, 20, 21, 24
Dec 1997	2, 4, 5, 8, 10, 11, 12, 16^{m}, 19^{me}, 22^{m}	2, 4, 12, 16, 19, 22
Jan 1998	13^{e}, 14, 15, 16^{e}, 20, 22^{e}, 23	20, 23

Note: Superscript m denotes cloudiness more than ⅜ in the morning- and e in the evening-sampling period. The absence of an index denotes cloudiness less than ⅜ but not clear sky.

Table 6. Dates with cloudiness and rainfall occurrences during the project period

Date	Wind condition		Date	Wind condition		Date	Wind condition	
	08:30-09:30	20:30-21:30		08:30-09:30	20:30-21:30		08:30-09:30	20:30-21:30
Nov 13		S^{M}	Dec 2		NE	Jan 7	Calm	
14	SW	S	4		SW^{M}	8	Calm	Calm
17	Calm or S		5	Calm	NE	9	Calm	NE
18	Calm or N	Calm or NE	8	NE		12	Calm	
19	Calm or N		9	NE	Calm	13	Calm	Calm
20		Calm	10	Calm		14	Calm	
21		Calm	11	Calm	NE	15		Calm
24	NE^{G}		12	SE	SE	16		Calm
25	NE	NE	16	Calm	Calm	20		W
26	NE		19	Calm	NE^{M}	22		Calm
27	Calm	NE	22	SW^{M}		23		Calm
28	NE	NE						

Note: Superscript M denotes moderate- and G Gusty-wind speed. Index absence denotes slow wind, nearly calm.

Table 7. Local weather conditions prevailing during morning and evening sampling periods

3.2 Site dispersion conditions

Pollution rates and dispersion conditions present spatial and temporal differences. Dispersion conditions depend upon local and temporal characteristics and a measure of dispersion quality is the mixing height. In general, the mixing height over land is low during the morning, evening and night hours daily, when inversion effects occur, and increases significantly during the early afternoon hours (Schnelle and Dey, 2000). An

indicator of its daily persistence is the percentage of calm frequency, which is 14% during program period and increases gradually from winter to summertime (Yannopoulos and Skokaki, 2003). Annually, the lowest mixing heights giving the worst dispersion conditions are observed in winter (usually in December), the highest with the best dispersion in summer (usually in July) and moderate values are common during spring and autumn. The diurnal variation of the mixing height depends mainly on the hour of day, the ground level conditions (roughness, thermal capacitance, reflection, radiation and altitude) and the weather conditions (cloudiness, prevailing winds, relative humidity e.t.c.). Coastal sites are more influenced by the higher thermal capacitance and the lower roughness height of the seawater than any other interior locations. Computations of the spatial variation of the mixing height over the whole Europe with land-sea distinction have shown that the mixing height becomes high (around 750 m) over Ionian Sea and small (around 50 m) over the land of Greece after midnight at 04:00 UT, while the opposite holds true in the afternoon at 16:00 UT (Delobbe et al., 2001). For Patras, a coastal city adjacent to Ionian Sea, it is evident that sea proximity will influence the actual mixing heights, which, over the sampling locations, are expected to increase with the distance from the shoreline (Hanna, 1987). Thus, in the typical hour of morning samplings, a small enough mixing height (around 50 m) prevailed over the sea and a higher one over the interior land, in contrast to the typical hour of evening samplings when the mixing heights over the sampling locations were decreased with the distance from the sea, up to a distance of ten times the interior land mixing height, i.e. around 500 m. Consequently, in the mornings, an improvement of the dispersion conditions occurred from sea towards interior locations, while the opposite in the evening (Yannopoulos, 2007b). It is evident that the influence of the harbour and the city emissions should be more important for sites located downwind. Therefore in the mornings, when breeze blows from sea towards land, a higher influence is expected to occur in the city locations downwind of the harbour, and a lower or none influence in the evenings when wind direction is reversed. Note that calm or winds of very low speed and rather detectable direction (light winds) were the most frequent during sampling hours, as shown in Table 7.

3.3 Air sampling bag alternative

3.3.1 Design characteristics of the study area

The study area of Patras has been defined to include the most critical parts of the city centre and its surroundings, as it is shown in Fig. 5. A number of 50 locations cover the most significant cross-road points and they are distributed over the area of interest as shown by numbered open circles. The program of air sampling and analysis started on the 13rd of November 1997 and finished on the 23rd of January 1998, in such a way to meet monthly peaks for primary air pollutant concentrations. It included 24 morning expeditions for sampling and an equal number of evening expeditions. Requiring getting nearly the critical situation for primary air pollutant concentrations, as for SO_2, morning and evening samplings were scheduled to be carried out during open market hours on working days, between 08:30 to 09:30 and 20:30 to 21:30, correspondingly. These hours of day were considered appropriate since SO_2 emissions are maximized due to peak-hour activities in conjunction with the low mixing heights (systematic daily radiation inversions). In order to minimise the duration of each expedition, a couple of students were used simultaneously, each one collecting 5 samples of short duration, of 3 minutes time approximately. Thus, ten air bag samples were normally collected, covering equal number of predefined city locations.

Sampling locations are shown in Fig. 5, where the City Plan Sectors A, B, C, D, E and F have been also plotted. The main characteristics of these sectors useful for model validations are given in Table 5 and Section 3.1.

3.3.2 Sampling equipment and procedure

Each air sample had a volume of about 3.5 to 4 l and was collected in a 5-l Teflon air-sampling bag (type 12×12in on/off) by using a small volume pump (model PM11/2 12VDC STD, Charles Austen Pumps Ltd.), which was operating for about 3 minutes. A small glass funnel (approximately 5-cm face diameter) fixed to face in front the pump followed by its standard filter resulted the pump intake. Sampling was performed 0.80 m above ground level on foot pavement, few meters far from the nearest kerbside and obstacles, depending on actual space availability. The knowledge of pollution levels at this altitude may be significant for assessing health effects on drivers and children since their nose is almost at 0.80 to 1.00 m above ground. Each sampling process was associated by a 3-minutes traffic recording and the recordings of useful local conditions (start time of sampling, wind and weather conditions as cloudiness and rainfall occurrences). Although not always feasible, care was paid for performing expeditions in nearly calm weather conditions and without drizzling or raining. The actual wind direction was considered in selecting the correct downwind position on the road junction with respect to the surrounding pollution sources, as justified above performing extra expeditions and the results are given in Tables 1 and 3.

For a typical expedition, the average time spent for the movement to the next sampling location was normally around 2 to 3 minutes and consequently the time needed to integrate 5-bags sampling was approximately 20 minutes. Finally, to protect bags against potential puncture and direct sunlight exposure and eliminate photochemical reactions and other sink losses on the sampling bag walls, the bags were placed immediately in thermally insulated and dark plastic sack. Then, they were transferred in the Environmental Engineering Laboratory (EEL) for the subsequent analysis without delay. A mean travel time of about 15 minutes was needed. The change of the pollutant concentration with time lag occurring in sampling bags was investigated. For seven locations distributed in downtown Patras with moderate to high pollution levels, specific air sampling using 50-l Teflon bags was made following exactly the procedure for normal samples. Subsequent analysis showed that negligible time lag effects encountered on the concentration measurement. The maximum SO_2 losses per hour were less than 0.5% and, since the maximum time lag required for completing the sampling and analysis process of each particular 5-l sample was always less than ¾ h, the procedure was proved appropriate. Note that each 50-l sample preserved in the laboratory in its Teflon bag entirely enclosed in a black sack.

The number of visits for sampling of each location was 4 to 5 mornings and equal evenings of different dates dispersed within the whole program period. The visits started at different times allocated within the typical morning or evening sampling hours. The target was to get an average pollutant concentration of the morning or evening measurements more or less unaffected of these conditions, demonstrating an average of the critical situation, as it is affected mainly by the sampling hour of day. Therefore, the sampling schedule proposed makes average concentrations rather free from local weather conditions, since they generally differ from sampling to sampling. In addition, as sampling intervals at the same location started at different times dispersed within the typical morning or evening sampling periods, the aforementioned average concentrations should reflect mean levels of much greater time

intervals than the 3 minutes, approaching the related typical morning or evening sampling periods. This assumption was supported by four additional expeditions within the program period, according to which simultaneous air sampling with 50-l and successive 5-l Teflon sampling bags at the same location were performed. The results are given in Table 3 along with the suitable justification and concluding remarks.

3.3.3 Laboratory equipment and measurement methods

The EEL is equipped with analyzers of continuous operation for SO_2 and other air pollutants. Regarding SO_2 the model 4108 of Dasibi Environmental Corp., USA, was available, designated by the USEPA as an equivalent method for the measurement of ambient air concentrations of SO_2. During the program period, indoor air temperatures varied from 13 to 24ºC being within the range 5-40ºC of the analyzers operating temperatures. The intake of SO_2 analyzer was linked through a "T" shaped connector to a common entrance pipe connector where the sampling bag was mounted; the length of the Tygon piping used was less than 1 m. The analyzer had its individual pumping system for air sampling and it was continuously operating during the whole program period. For the calibration, a standard mixture of 100 ppb SO_2 in pure Nitrogen (N_2) was used. An automatic zeroing of signals was systematically performed at 12-h intervals.

The analyzer uses the UV-fluorescence method with 1% linearity and 1% precision in the range 0-500 ppb. The sample flow rate is 0.5 l minute^{-1} and the rise time is 90-120 s with lower detectable limit less than 1 ppb in the range 0-1 ppm and noise at zero concentration less than 0.5 ppb. Therefore, the minimum air volume required for the sample analysis regarding SO_2 is approximately 1.0 l, which was less than the volume of each sample.

3.3.4 Treatment of measurements

For obtaining average concentration values at all locations of the study area of Patras, the procedure described above (Section 2.1.6) has been applied. All measurements at each location had passed the Q–test (Radojević and Bashkin, 1999). Thus, the average concentration of four or five 3–minutes samples randomly picked at a particular location during morning or evening rush hours was calculated separately for morning or evening hours and assigned initially at each node, using the point kriging method with a linear variogram model (Golden Software, 2002). Thus, two grid matrices of average concentrations for each air pollutant, one for morning hour and another for evening hour, were taken. Next, each of these matrices was filtered using a low–pass linear convolution filter of 9–node averaging with weights equal to 1 (moving average filter). The 9–node averaging is actually performed on a sample of n values, where $36 \leq n \leq 45$. For a confidence level 95% and using the Student t–distribution, the final grid used above for contouring is proved to approximate 1–h mean concentrations at the specified locations, as it will be shown in the following. The probable error defined in Section 2.1.6 is calculated and consequently the mean probable error made for each final grid matrix of average concentrations was determined and shown in Table 8. The mean error made for estimating SO_2 average concentrations was less than 23.2%, while the corresponding error for traffic rates was less than 1.4%.

For the dependence of concentration on averaging time, the relationship given above by Eq. 1 may be applied for p = 0.17 and s = 3 minutes and averaging times t = 25-60 minutes. The ratio of C_t/C_3 computed by the above equation varied in the range 0.601-0.697 with mean value 0.649. Using the data given in Table 3 concerning successive sampling with 5-l bags, $C_t/C_3 \pm \sigma_{n-1}$ is found to be 0.63±0.155. For examined Patras locations, the maxima for 3-

minutes and for morning or evening period averaging time that is roughly 1 h are given in Table 8 with respect to the location measured. Calculating again $C_t/C_3 \pm\sigma_{n-1}$, it is found to be 0.542 regarding the morning and evening SO_2 concentrations, while is 0.588±0.0562 based on an average value regarding SO_2, NO and NO_2 concentrations (Yannopoulos 2007a). All above findings support the conclusion that the morning- or evening-period average concentrations approximate 1-h mean values.

Pollutant	Averaging time	Mornings	Probable error	Evenings	Probable error
SO_2	3 minutes	81 (Location 30)*		108 (Location 25)	
	about 1 h	49 (Location 30)	±21.3%	56 (Location 19)	±23.2%
Traffic rate	3 minutes	3360 (Location 40)		721 (Location 26)	
	about 1 h	2920 (Location 2)	±1.4%	512 (Location 19)	±1.2%

* The locations where the peak value was observed are given in parentheses.

Table 8. Maximum values of 3-minutes and approximated 1-h average concentrations (in μg m^{-3}) for SO_2 and traffic rate (in veh h^{-1}) in the Patras area with regard to the locations where they have been measured

Finally, application of the procedure described above results in 1–h average values of SO_2 concentrations and traffic rates, within typical morning or evening hours of workdays during program period. Then, iso–concentration and iso–traffic contour diagrams are plotted and shown in Fig. 7 and 8, correspondingly. Each of these figures consists from two diagrams; (a) and (b) for morning and evening average values. It is noted that probable errors encountered in iso–concentrations may affect the determination of the boundaries of high pollution zones by mean displacements less than the mean spatial resolution (±360 m) regarding SO_2, approximately.

3.3.5 Evaluation of sulfur dioxide levels

According to Fig. 5 and 7(a), the 1–h SO_2 morning maxima found to be 40–45 μg m^{-3} and were located at the centre of downtown Patras around Vas. Georgiou Square (Locations 22, 23 and 25) and close to Ag. Andreas Church (Locations 29 and 30) on the main national road connecting Patras with the Western Peloponnese. Note that the numbered open circles in Fig. 5, 7 and 8 indicate locations. At Location 30, an extended municipal parking lot for citizen's cars was operating. These locations presented high rates of traffic (more than 2000 veh h^{-1}) as indicated in Fig. 8(a), while emission rates were augmented due to car stops controlled by traffic lights. The 1–h mean SO_2 concentrations are well correlated to the corresponding traffic rates. The correlation coefficient for all locations (n = 50) found to be r = 0.60, meaning that the SO_2 air pollution is a rather traffic oriented pollution. Note that Jackson (2005) has given r = 0.74. The fact that Locations 1, 2 and 49 were found less polluted by SO_2 concentrations, although they have comparable traffic rates, may be justified taking into consideration that the latter locations are far-off the centre of downtown Patras and belong in more open areas (near Sector A boundaries), which resemble more or less to suburbs with better dispersion conditions than other areas of downtown Patras. In addition, since these locations (being on the ground) are rather far from both harbour (traffic and ships) and central-heating (elevated) sources, more dilution is favoured compared to the nearby traffic sources, which were also free from long vehicles emitting SO_2, as such

vehicles were enforced to drive along the seaside roads. It is noted that the peripheral diversion highway was then under construction, thus all vehicles coming from Pyrgos and going to Athens and vice-versa passed through the city of Patras.

According to Fig. 5 and 7(b), the 1–h SO_2 evening maxima found to be 45–50 μg m^{-3} and were located around Locations 19, 22 and 25, in the central area of downtown Patras. However, SO_2 concentrations equal to or higher than 40 μg m^{-3} covered almost all the central area of Sector A and the central part of Sector C. Figure 8(b) shows that traffic rates were more than 1250 veh h^{-1} in most of this area. For all locations (n = 50) and evening hours, a lower correlation coefficient (r = 0.48) than that for morning hours and enough lower than Jackson's (2005) was found. If evening SO_2 concentrations are compared to morning ones (Fig. 7a and b), the differences observed might not be considered statistically significant. The values of the correlation coefficient for either morning or evening observations remained actually unchanged. Since for most samplings the wind conditions recorded and given in Table 7 indicate calm or light NE winds, the harbour traffic and ship emissions might not significantly affect the study area compared to the effect by the local traffic and central heating. The lower value of r computed for evening hours may be attributed to more intense contribution of central heating emissions in conjunction with probably lower mixing heights during evening hours than morning hours. Applying the statistical test with a significance level 0.005, for the acceptance or not of the hypothesis that morning measurements at each location have equal mean values to the corresponding evening measurements, indicated that the above hypothesis is acceptable. Therefore the SO_2–concentration differences can be considered statistically insignificant. Further on, the low enough correlation coefficient (r = 0.25) found denotes that the aforementioned small differences are rather weakly correlated to the corresponding differences of traffic rates. Consequently, evening and morning concentrations could be statistically considered as coming from similar populations.

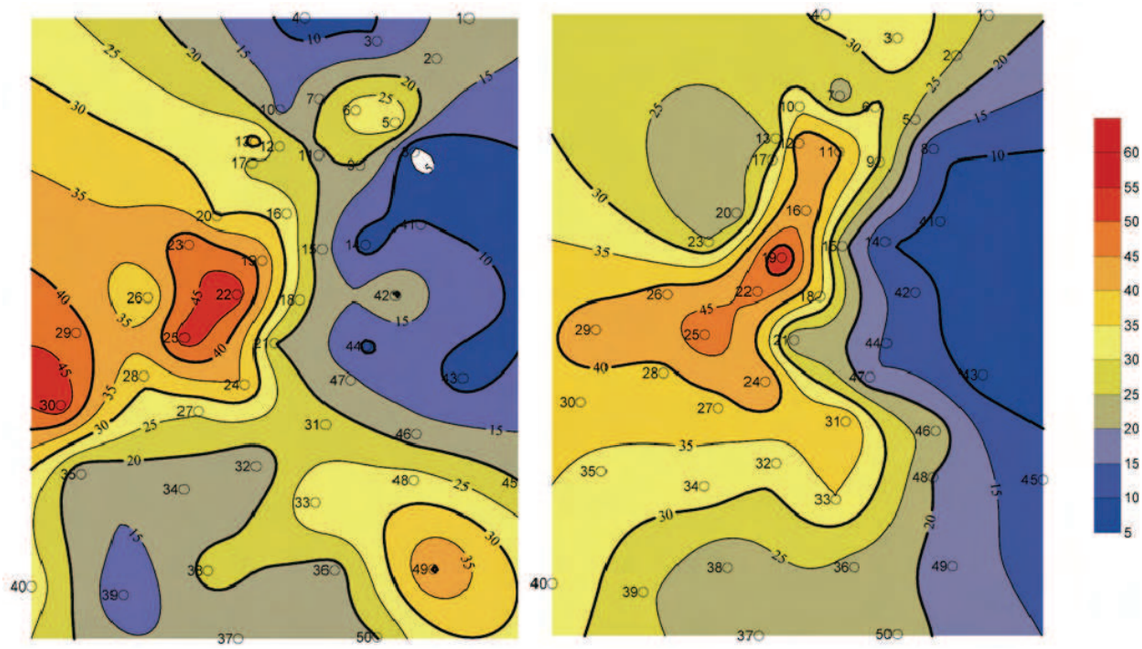


Fig. 7. Iso-concentration contours of 1-h mean SO_2 values (in μg m^{-3}) for (a) morning hours and (b) evening hours of a typical winter period (November 13 1997 – January 23 1998)

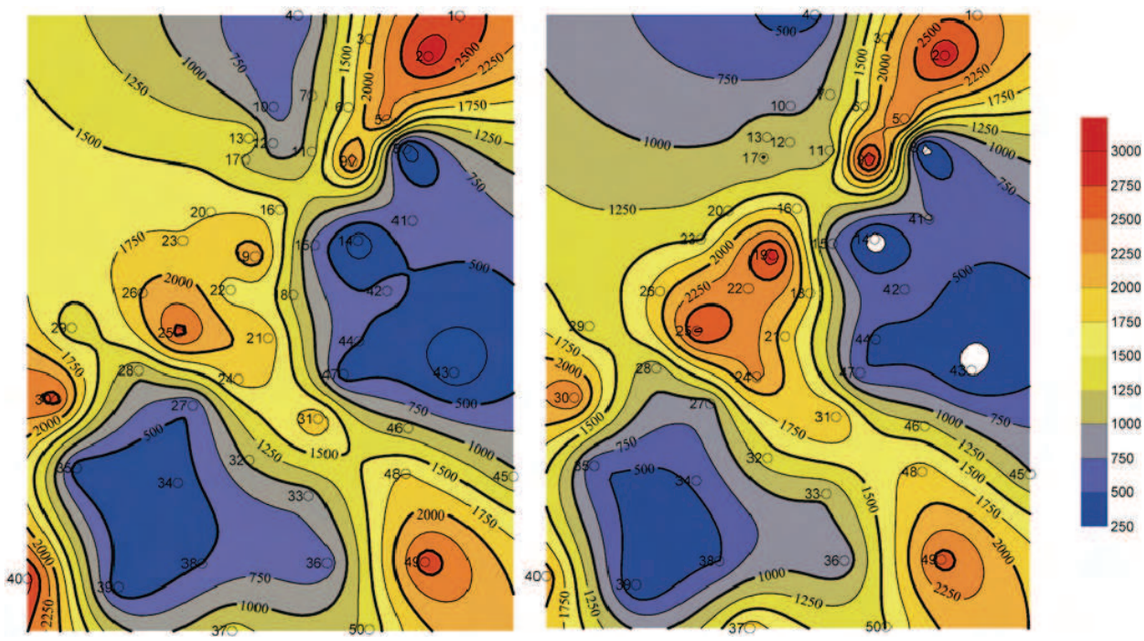


Fig. 8. Iso-traffic contours of 1-h mean traffic rates (in veh h^{-1}) for (a) morning hours and (b) evening hours of a typical winter period (November 13 1997 – January 23 1998)

In general, this implies relatively similar justifications for both morning and evening SO_2 concentrations. Therefore, the entire dataset of 1–h SO_2 morning and evening concentrations (n = 50×2) may be fairly well correlated to the corresponding traffic rates, while be weakly correlated to other factors through the prevailing wind and mixing height conditions. For traffic-explained SO_2 concentrations, the following relationship is taken (Yannopoulos 2007a):

$$SO_2\ (\mu g\ m^{-3}) = 0.0076 \times (veh\ /\ h) + 15.55\text{, with } r\text{=}0.54 \tag{2}$$

The present findings can be verified once more by Yannopoulos and Skokaki's (2003) SO_2 concentration measurements. The measurements had been carried out for extended periods of year at Location 22 (former Location A), as well as at a location between the nearby Locations 12 and 17 (former Location B). The 1–h SO_2 levels determined in the present study at these locations during same year seasons and hours of the day were found close to the corresponding levels continuously monitored roughly two years earlier. Continuous measurements made by a Program of Achaia Prefecture during 1988–89, at a location between Locations 5 and 6 and at an elevation approximately 10 m above ground level, gave morning and evening maxima of 1–h mean SO_2 56 and 83 μg m^{-3} for the winter period (Yannopoulos and Amanatidis, 1993). According to Fig. 5, 7(a) and (b), the 1–h values of the present program for the above location were approximately 25 and 30 μg m^{-3}, which are less than the past concentrations. The higher levels recorded in 1988–89 than 1997–98 may be attributed mainly to the greater sulphur content of fuels in conjunction with the shorter distance of the monitoring site from central heating emission sources, since the fixed station had been installed on a building's roof. Yannopoulos (2007a) has given additional comparisons to available levels of other Greek and Mediterranean cities, as well as further details regarding NO, NO_2 and NO_x air pollutants and comparisons to air quality limits.

3.4 Gaussian modelling alternative

3.4.1 Application details of the model

The ISCLT3 model described above was used to simulate emissions from the sources affecting the Patras atmosphere. Besides background air pollution, these sources include mainly emissions from traffic, central heating and ships. The study area belonged in downtown Patras and had a magnitude of 3 km^2, approximately. It covered the central parts of Sector A, B and C of the Patras city plan. The main streets, which incorporated in this area, were Agias Sofias, Korinthou, Trion Navarhon, Agiou Andreou and Othonos Amalias Street (Fig. 5). These streets included in a polygon, which can be defined by Locations 2, 4, 29, 27, 31, 41 and 2. The necessary altitudes for the model input were available from the Municipality of Patras. In addition, the polygon included the two sites (receptors) where EEL had been carried out in the past continuous monitoring of air pollution. The site A coincides with the Location 22 at the Vas. Georgiou A' Square, while the site B is located in the junction of the streets of Ag. Andreou and Zaimi, between Locations 12 and 16.

The model input preparation was the first step. The central heating and ship emissions were modelled as area sources. Traffic is modelled as a line source and each main street was divided in 20-m length segments. Then, the emissions from the several types of vehicles were calculated according to globally acceptable methodologies and the European Union legislation. Primary data of traffic rates were available by previous EEL studies. To determine the emissions due to traffic, COPERTIII (http://vergina.eng.auth.gr/mech/lat/copert/copert.htm) was utilised. The fuel quality characteristics during the period of interest were considered according the European Union legislation. Due to the operation of the Patras harbour, increased traffic was observed in the main streets of each neighbourhood, i.e. Korinthou, Ag. Andreou and Othonos-Amalias. The monthly traffic loads applied were 524,960 vehicles. They consisted of 36% conventional type and 64% catalytic passenger cars. The light-duty vehicles were considered to be approximately equal to the heavy-duty vehicles and were taken 5% each. The traffic oil was considered to contain 0.3% sulphur by weight, while the petrol contained 0.2% and the oil consumed in central heating contained 0.2% by weight. To calculate traffic emissions, the average car speed was considered equal to 19 km h^{-1}, as usually taken for Greek urban areas, and applied to an average trip distance of 12 km. These assumptions imply that the final SO_2 emission load due to traffic was equal to 146 μg s^{-1}. In the neighbourhood of the harbour, the mean speed of vehicles was taken equal to 9 km h^{-1} with an average trip distance 1.5 km. Thus, the monthly emissions of ships and the vehicle traffic due to harbour are given in Table 9. The emissions of SO_2 due to central heating were based on the USEPA data. They were assumed to be 852 mg l^{-1} per fuel mass consumed, but varied with respect to the population density attained in the relevant sectors of the City Plan. Deposition of air pollutants and additional natural processes were not considered in this application.

As it was described above (Section 2.2.1), the wind speed was grouped in six categories and the atmospheric stability determined according to the Turner's classification system with respect to the incoming solar radiation and the wind speed class. During the winter, from October to March, 5 h of moderate insolation daily with slight insolation for the remaining 19 h was assumed. During summertime, from April to September, it was assumed that 5 h corresponded to strong insolation, 5 h to moderate insolation and 14 h to slight insolation.

The determination of the roughness height for downtown Patras and especially for the central parts of Sectors A and C was based on the average building height, which is among 15 to 28 m (Table 5). Thus, the roughness height was taken equal to 1.0 m.

One of the most important parameters for model calibration is the mixing height, which depends on the time during a day and the seasonal properties. The prevailing mixing height during a typical day for each season was determined on the basis of author's visual observations made during morning hours and agreed with predictions in coastal areas by applying the models proposed by Hanna (1987), Luhar (1998) and Delobbe et al. (2001), as well as according to computations made using the procedure provided by www.dar.csiro.au/pollution/MixHeight/botWindow.htm.

Month	Year 1994		Year 1995	
	Ships	Vehicles	Ships	Vehicles
January	12,311	63	11,303	55
February	10,571	55	9,102	61
March	12,362	63	9,255	61
April	12,126	63	10,739	58
May	12,043	63	11,229	65
June	14,690	78	14,609	62
July	13,308	71	14,932	72
August	15,136	78	14,780	51
September	15,157	78	14,634	56
October	14,102	71	13,541	75
November	11,978	63	11,975	76
December	12,268	63	12,248	76

Table 9. Monthly SO_2 emissions (kg month^{-1}) from ships and vehicles due to traffic in the Patras harbour

Then, according to the model requirements, the mixing height for the A stability class have to be equivalent to approximately 1.5 times the mixing height for stability classes B and C and double for the stability class D. Equal mixing heights have to be assigned for B and C classes of atmospheric stability. According to the analysis given above (Section 3.2), the lowest values of the mixing height assigned during the winter period and the highest values during summertime. For spring and autumn, the average of the corresponding values for winter and summer were taken.

3.4.2 Sensitivity analysis of the model

The most important feature of the model is the comprehension of its sensitivity with respect to input key parameters controlling the prediction behaviour. These parameters are the roughness height and the mixing height, which present in general the highest uncertainty. For the present case study, it was found that an increase of the roughness height from 1.0 to 3.0 m indicated insignificant effect (less than 1%) in concentrations and, therefore the mixing height of 1.0 m was used in the predictions. Since, the concentration is inversely related to the mixing height, a mixing height increase would cause a decrease of the concentrations. Giving a 10% increase in the mixing height of A-class and subsequent increase in the mixing heights of B-, C- and D-classes of atmospheric stability according to the aforementioned instructions, the average decrease in predicted concentrations was 2%. This test showed that the mixing height was the most critical parameter affecting the model predictions. Since neither measurements nor reliable estimations of the mixing height were available, the mixing height became the main key parameter for the model calibration aiming to obtain acceptable SO_2 predictions at the prescribed receptor locations. For simplicity reasons and a

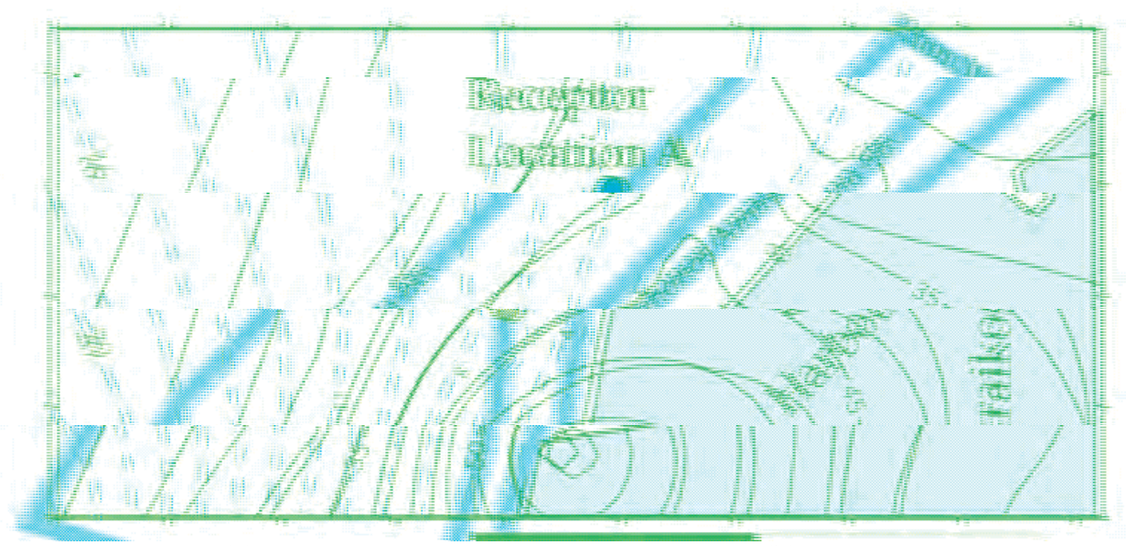
specified stability class, fixed values of mixing height were used during the same season, irrespective of the year with available concentration measurements. In Table 10 the values of mixing heights, which give the best model performance at the receptor Sites A and B, are shown. According to USEPA (1995), it is noted that the model assumes unlimited mixing heights for classes E and F of the atmospheric stability.

Class of Atmospheric stability	Mean seasonal mixing height (m)		
	Winter	Spring and Autumn	Summer
A	90	195	300
B, C	60	130	200
D	45	100	150

Table 10. Mean seasonal values of the mixing height (in m) for Patras city with respect to atmospheric stability class

3.4.3 Model predictions and discussion

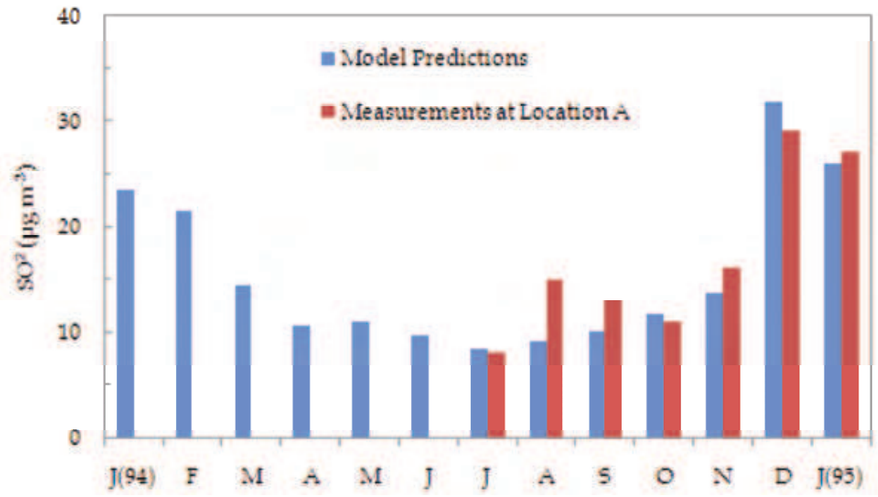
The model ISCLT3 was applied to predict the mean monthly SO_2 concentrations in the area of downtown Patras described above considering only emissions from the predefined human activities of traffic, central heating and harbour activities including ship emissions and related harbour traffic. The results were calculated using the aforementioned input values of the several model parameters. The background influence is introduced by superimposing the predicted SO_2 values on the actual ambient background levels. The spatial distribution of the mean monthly SO_2 concentrations is shown in Fig. 9, including two iso-concentration contour diagrams for (a) December 1994 and (b) December 1995. Note, that December is a month of the winter period where maxima of concentrations have occurred. The mean monthly SO_2 concentrations predicted at the receptor Locations A and B are compared with the related measurements at these sites and they are shown in Fig. 10.



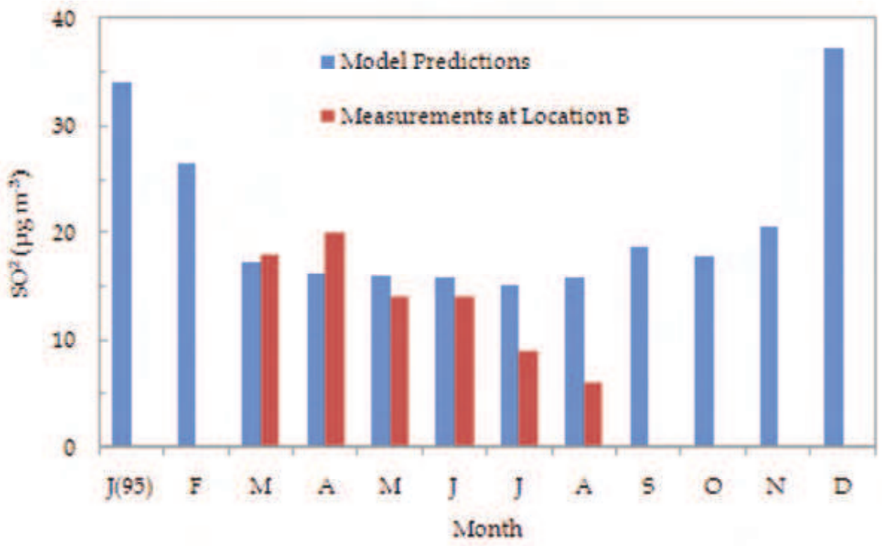
(a) (b)

Fig. 9. Predicted mean monthly SO_2 iso-concentration contours (in μg m^{-3}) for (a) December 1994 and (b) December 1995

The SO_2 concentrations monitored at the W boundaries of the University of Patras Campus, a low activity outskirt, were considered equal to the ambient air background levels, which had been measured equal to 5.5 μg m^{-3}, according to Yannopoulos and Skokaki (2003). As shown in both diagrams of Fig. 9, the harbour areas that concentrate the most frequent ship calls are affected by high levels of pollution. Regarding the higher SO_2 concentration levels predicted in 1994 than 1995 (Fig. 9), it is believed that the concentration differences were due to somewhat different weather conditions and emission rates. As justified by the results shown in Fig. 10 and the following statistical analysis, the model performance is satisfactory in estimating both anthropogenic SO_2 levels and period pattern.



(a)



(b)

Fig. 10. Predicted and measured mean monthly SO_2 concentrations (in μg m^{-3}) at the receptor locations; (a) Location A and (b) Location B

For the statistical analysis, the paired t-test method is applicable (Kreyszig, 1999, p. 1125-1126), since two samples of the same size are available; the sample of observations and the sample of predictions. Each value of the sample of observations corresponds precisely to one value of the sample of predictions. Consequently, the sample of differences of corresponding values can be formed and tested. The test hypothesis is that the population corresponding to the differences should have a zero mean. As data lead definitely to the hypothesis acceptance with a significance level of 0.05 for a two-sided test, it is concluded that the two samples have statistically the same mean values.

Then, the contribution of the emissions from each source to the air pollution at the receptor Locations A and B has been computed and shown in Fig. 11 on a seasonal and an annual basis. It is obvious that the yearly average SO_2 contribution of ship emissions to both sites is around 60% and therefore significant, compared to all other sources, which show approximately equal contributions to each other, being around 20%. Although during winter the harbour contribution decreases to 39 and 57% at the receptor Locations A and B, respectively, it remains the dominant source for site B with central heating contributing to 22% of the SO_2 emissions. Central heating contributes 46% in SO_2 emissions at site A, with the harbour contributing less SO_2 than central heating. During summertime, the harbour contribution is maximised becoming 72 and 77% at the receptor locations A and B, respectively. An increased contribution of the traffic was found during summertime with the percentages of 27 and 28% than during winter, where contribution was 15 and 20% at the receptor Locations A and B, respectively.

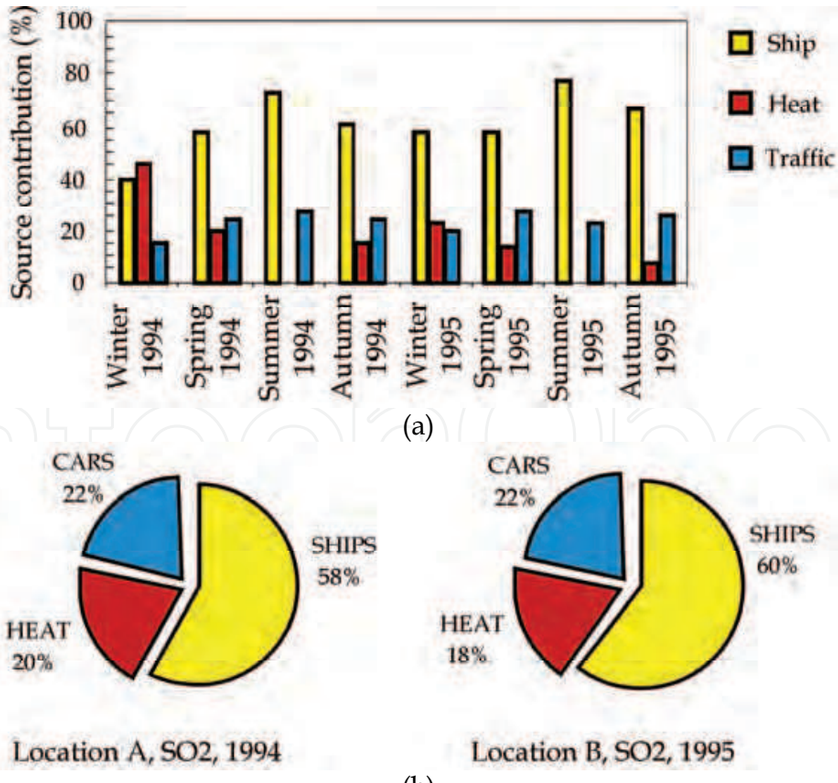


Fig. 11. Mean contribution of SO2 sources to air pollution at receptor locations A and B; (a) seasonal and (b) annual

3.5 Indicative cost analysis of methodology and comparison to custom monitoring

The cost of application of the proposed methodology in the city of Patras included the particular cost of the two alternatives increased by an extra cost for the evaluation and dissemination of results and preparation of the final report, as shown in Table 11. The Value Added Tax (VAT) is included in the particular item values. The cost of the air sampling bag technique can be analysed in the cost of suitable equipment, the necessary expenses for consumables, the labour cost of personnel needed for the collection, transfer and laboratory analysis of samples, as well as the transport and service expenses. The cost of equipment

Description	Unit	Quantity	Value per unit (Euros)	Partial cost (Euros)
A. Air sampling bag technique				
1. Equipment				
SO_2 analyser usage (1.5/36)×12,000.00	Item	1	500.00	500.00
Pump for air sampling (1.5/36)×900.00	Item	2	37.50	75.00
2. Consumables				
Calibration standard (100 ppb SO_2 in 10 l pure N_2 of 200 bar)	Item	1	200.00	200.00
Teflon air sampling bag of 5-l	Item	10	120.00	1,200.00
Teflon air sampling bag of 50-l	Item	1	300.00	300.00
Pump accessories (particulate filter, funnel, Tygon tubing, rechargeable battery and opaque plastic sack) and office consumables	Item	2	162.50	325.00
3. Labour				
Sampling and analysis of 450 samples	Person×months	3	2,000.00	6,000.00
Treatment of results	Person×months	0.5	3,000.00	1,500.00
4. Additional expenses				
Car or motorcycle rent for sample and personnel transport	Item	1	1,200.00	1,200.00
Calibration and service of the equipment	Item	1	500.00	500.00
Cost of A =				**11,800.00**
B. Gaussian modelling alternative				
1. Equipment				
Usage of a computer system (1.5/36)×4,800.00	Item	1	200.00	200.00
2. Labour				
Input data treatment, calculations and analysis of results	Person×months	2	3,000.00	6,000.00
Cost of B =				**6,200.00**
C. Evaluation and dissemination of results A and B and writing the final report	Person×months	1	3,000.00	**3,000.00**
Total cost of methodology application A+B+C=				**21,000.00**

Table 11. Indicative expenditure of methodology application in an urban area of Patras

included the cost proportion of the SO_2 analyser and the two sampling pumps to the 1.5-month project period, considering that the useful life of analyser and pump is 36 months. The cost of consumables included the SO_2 calibration standard for analyser calibration, 10 Teflon air sampling bags of 5-l nominal volume, 1 Teflon air sampling bag of 50-l nominal volume, accessories for two pumps (particulate filter, funnel, Tygon tubing, rechargeable batteries and opaque plastic sacks), as well as office consumables for preparing the report. The labour included the work for collecting the samples, transferring them and analysing in the laboratory, as well as the work for treatment of the results. There were additionally transport and service expenses, as the cost of renting a small car or motorcycle for the personnel and sample transport, as well as the analyser calibration and service expenses of the equipment. It is noted that the total distance covered for personnel and sample transport reached 2,200 km.
Since the total cost of methodology application was 21,000.00 Euros for 50 locations, the corresponding relative cost per location was **420,00** Euros.
The corresponding cost of measuring hourly mean concentrations of SO_2 using a permanent station, which constitutes the custom monitoring methodology, is difficult to account in a comparable way with the cost of the proposed methodology. The reason is the fussy determination of the area, where a permanent station could be considered representative for hourly mean concentration measurements. In my opinion, the best way to define this area is the consideration of a common mean spatial resolution. Thus, defining 360-m spatial resolution, comparable probable errors to the proposed methodology would be expected in plotting iso-concentration contours. Therefore, for the urban area of Patras of approximately

Description	Unit	Quantity	Value per unit (Euros)	Partial cost (Euros)
1. Equipment				
SO_2 analyser usage (1.5/36)×12,000.00	Item	1	500.00	500.00
Housing with network connections for power supply and communication (1.5/36)×6,000.00	Item	1	250,00	250.00
2. Consumables				
Calibration standard (100 ppb SO_2 in 10 l pure N_2 of 200 bar)	Item	0.1	200.00	20.00
Consumed electric power and office consumables	Item	0.02	500.00	10.00
3. Labour				
Treatment, evaluation and dissemination of results	Person×months	0.03	3,000.00	90.00
4. Additional expenses				
Calibration and service of the equipment	Item	0.02	6,500.00	130.00
Total cost of permanent station =				**1,000.00**

Table 12. Indicative expenditure of a permanent station in an urban area of Patras

6 km^2 covered by the 50 locations, a comparable number of permanent stations should be considered. Assuming that the corresponding cost of each permanent station for 1.5 months operation is as given in Table 12, it is evident that the proposed methodology has a considerable less cost than permanent station measurement. However, there is not a panache methodology that could substitute any other. The continuous monitoring using permanent stations is advantageous in getting direct mean values of any time interval at a location. Its disadvantage is the low flexibility in relocation of a permanent station, the difficulties encountered in finding suitable places for location with pertinent conditions being in agreement with installation standards, difficulties in the availability of power supply and network link, as well as the weakness in determining the contribution of a source to the pollution of a prescribed receptor location. As it has been already described, the proposed methodology has overcome all these disadvantages.

4. Conclusion

The proposed methodology combines the use of the air sampling bag technique and the Gaussian modelling alternative. The application in the city of Patras proved that the methodology is capable of evaluating cost effectively the spatial air pollution and detecting the city locations susceptible to high pollution levels needing more attention. The bag sampling technique allows measuring short time concentrations of specified air pollutants sampled at urban locations, using only one analyser per pollutant. The maximum mean errors made in the determination of hourly mean SO_2 levels were less than 25%. An acceptable prediction is also succeeded by employing the USEPA Gaussian models. The mean concentrations between predictions and measurements at two locations of Patras downtown showed statistically unimportant differences with a significance level of 0.05 for a two-sided test. Thus, the two samples have statistically the same mean values, a fact confirming the use of Gaussian modelling for air pollutant concentration predictions and therefore trusting the methodology application for estimating the seasonal and annual contribution of pollutant sources to prescribed receptor locations. The latter is extremely difficult or even impossible to be made using measurement stations only, because it is not practically feasible to stop emissions for long of a particular group of sources representing an activity, while monitoring continuously emissions from other activities. The disadvantages of the bag sampling technique concern air pollutants that show high enough chemical reactivity in the atmosphere and/or in the samples, like O_3, or they sink in the bag walls and generally present low enough recovery values, as for aerosols and particulates.

The future research may include use of available measurements and meteorological information for calibrating Gaussian models suitable for predicting the city air quality impact due to new activity installations and operations or activity relocations. The city of Patras needs such an air quality evaluation, because of the harbour relocation, which is going to start operating shortly, as well as an evaluation due to the construction and operation of the peripheral diversion highway and the Rion-Antirrion cable bridge. In general, the proposed methodology and its outcomes could be useful for the design and optimization of a city network of stations to monitor air quality, for environmental impact assessments, future reference and comparisons due to city development needs, and for validating dispersion models.

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Leading air quality professionals describe different aspects of air pollution. The book presents information on four broad areas of interest in the air pollution field; the air pollution monitoring; air quality modeling; the GIS techniques to manage air quality; the new approaches to manage air quality. This book fulfills the need on the latest concepts of air pollution science and provides comprehensive information on all relevant components relating to air pollution issues in urban areas and industries. The book is suitable for a variety of scientists who wish to follow application of the theory in practice in air pollution. Known for its broad case studies, the book emphasizes an insightful of the connection between sources and control of air pollution, rather than being a simple manual on the subject.

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