

Evaluation of air quality by passive and active sampling in an urban city in Turkey: current status and spatial analysis of air pollution exposure

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Abstract Concentrations of air pollutants, nitrogen dioxide (NO₂), sulfur dioxide (SO₂), ozone (O₃), particulate matter (PM_{2.5} and PM₁₀), trace metals, and polycyclic aromatic hydrocarbons (PAHs) were measured in 2008 and 2009 in the city of

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Eskişehir, central Turkey. Spatial distributions of NO₂, SO₂, and ozone were determined by passive sampling campaigns carried out during two different seasons with fairly large spatial coverage. A basic population exposure assessment was carried out employing Geographical Information System techniques by combining population density maps with pollutant distribution maps of NO₂ and SO₂. It was found that 95 % of the population is exposed to NO₂ levels close to the World Health Organization guideline value. Regarding SO₂, a large proportion of the population (83 %) is exposed to levels above the WHO second interim target value. Concentrations of all the pollutants showed a seasonal pattern increasing in winter period, except for ozone having higher concentrations in summer season. Daily PM₁₀ and PM_{2.5} concentrations exceeded European Union limit values almost every sampling day. Toxic fractions of the measured PAHs were calculated and approximately fourfold increase was observed in winter period. Copper, Pb, Sn, As, Cd, Zn, Sb, and Se were found to be moderately to highly enriched in PM₁₀ fraction, indicating anthropogenic input to those elements measured. Exposure assessment results indicate the need for action to reduce pollutant emissions especially in the city center. Passive sampling turns out to be a practical and economical tool for air quality assessment with large spatial coverage.

Keywords Air pollution · Exposure assessment · Nitrogen dioxide · Sulfur dioxide · Ozone · Particulate matter · Polycyclic aromatic hydrocarbons · Geographical Information System

Introduction

Ambient air quality is one of the major concerns in developing countries. Due to rapid and irregular urbanization, pollutant

concentrations may increase and this situation may adversely affect people's health living in those areas. Assessment of air quality and health risk due to air pollution in a certain geographical location is not a simple issue. There exist ambient air quality stations operated by government networks in most of the developed countries. In Turkey, there are ambient air quality monitoring stations at all 81 provinces at which nitrogen oxides (NO_x), particulate matter (PM₁₀), and sulfur dioxide (SO₂) are continuously measured by online instruments operated by Ministry of Environment and Forestry. Establishment of air quality stations at more than one place is usually not feasible due to operational costs in developing countries. Even so micrometeorology, street canyon effects, existence of different pollutant sources may result in uneven distribution of air pollutants spatially even in a small city (Taseikoa et al. 2009; Nejadkoorki et al. 2011).

In order to develop effective risk assessment strategies, concentrations of pollutants and populations under risk should be accurately determined. In general, pollutant concentrations obtained from limited monitoring sites are extrapolated to larger areas to estimate pollutant concentrations in areas where no air pollution data exists. This approach has limitations such as the assignment of the same and sometimes lower concentrations for relatively large number of people. Geostatistical techniques have been used recently to overcome this problem but there is also a problem for using stationary monitoring data which may not be representative for the surrounding area (Vienneau et al. 2009). As passive samplers are relatively easy to use, they can be used in a large number of locations. Therefore the passive sampling methodology can provide the necessary information on the spatial concentration distribution to evaluate ambient air quality in a certain geographical area with a considerable spatial resolution (De Santis et al. 1997; Bush et al. 2001; Buffoni 2002; Namiesnik et al. 2005; Lin et al. 2011).

A project was carried out in Eskişehir, an urban city in Turkey, to assess the effect of air pollution on children's respiratory health by measuring lung function parameters of 2,000 primary school children between the years of 2008–2010. This study presents the evaluation of ambient air quality before and during the health survey. A preliminary passive sampling campaign for the measurement of NO₂, SO₂, and ozone was carried out in 65 points to identify lower and higher pollution sites. Based on the results of this campaign, schools for the measurement of lung function parameters were selected. Lung function tests were carried out in two seasons (summer and winter) and air quality parameters were determined by passive and active methodologies simultaneously. The mentioned project, some results of which are presented in this paper, also aimed at the preparation of the Clean Air Plan for the city of Eskişehir. Within the framework of a major change in the environmental legislation in Turkey, the By-law on the Assessment and

Management of Air Quality came into force in June 2008. According to the By-law, every province should carry out air quality evaluation practices with a deadline of the end of the year 2013 and prepare Clean Air Plans for the control of certain or all air pollutants. The evaluation realized in the project and presented in this paper was one of the rare practices in Turkey and the Clean Air Plan prepared for the city of Eskişehir was the first province-level plan in Turkey, already serving as a model for other provinces.

The objectives of this study were to (1) determine spatial distribution of NO₂, SO₂ and ozone in the study area thereby to identify lower and higher pollution sites where lung function parameters of children have been measured living in those areas, (2) measure and evaluate concentrations of particulate matter (PM_{2.5} and PM₁₀), polycyclic aromatic hydrocarbons (PAH), and trace metals during the health survey study, and (3) estimate the number of people under risk by using geographical information systems (GIS) and pollutant concentrations (NO₂ and SO₂) measured by passive samplers.

Materials and methods

Study area and sampling locations

Eskişehir is located in the Central Anatolian Region of Turkey, on a crossway from the Marmara region to Central Anatolia which represents also a major change in climatic conditions. Natural topography of Eskişehir, consisting of plains surrounded by mountains, causes the major change of the warmer climate of the neighboring Marmara Region to a continental climate dominant in Eskişehir. Day-time and night-time temperatures differ significantly, especially in winter. The dominant wind directions are easterly in winter and westerly in summer. The population of the city is well over the average of Turkish cities. The total population is 725,000 more than 600,000 living in the metropolitan center in which this study has been carried out. Coal usage in residential heating has been gradually replaced with natural gas since 1996. However, 50 % of the residences were still using coal for heating in winter time by 2008 (Özden et al. 2008). Coal use in the industry was phased out with the introduction of the natural gas in 1990s and all the industrial plants have been using natural gas since mid-1990s. Apart from a cement factory to the west of the city and a sugar factory which has stayed within the residential zone within the years, most of the industrial plants are located in an organized industrial zone located at the east of the city. The energy demand of the industrial zone is supplied from a natural gas-fired power plant inside the zone.

For the preliminary assessment of air quality in Eskişehir, a passive sampling campaign including 65 points was carried

out between 9th and 23rd of January 2008 to represent parts of the city with different characteristics and also to have good spatial coverage. The study area covered was approximately 120 km². Passive samplers were delivered to the sampling points and collected back 1 week later. The previous results on passive sampling of pollutants showed that very short sampling times, like 24 h, are not adequate for the detection limits of the method for locations with low levels of pollutants. Besides the analytical reasons, there were also practical limitations to carry out daily simultaneous sampling at 65 sampling locations distributed over the whole city. Second set of passive samplers were deployed to the same points to be collected 1 week later so that two weekly integrated samples were available from each point. The air pollution relevant characteristics of the selected points were registered such as the type of the dominating heating system within several hundred meters of the sampling point, traffic and vegetation density, distance to the closest road, the existence of major roads and traffic lights, presence of tall buildings, parking lots, petrol station, and industrial activities. Passive samplers were delivered to the nearest primary schools since the school location can be considered as a representative location for the air that the children breathe.

Summer (27 May–13 June 2008) and winter (27 February–13 March 2009) passive sampling campaigns were carried out to observe the seasonal changes of the levels of pollutants and to provide exposure data for the screened children. Sixteen primary schools (eight schools from higher pollution areas, eight schools from lower pollution areas) were selected and four active monitoring stations were set up to represent urban (E-1), urban-traffic (E-2), and suburban (E-3, E-4) areas according to the results of the preliminary passive sampling campaign. All the passive and active sampling locations are shown in Fig. 1. The classification of “higher” and “lower” pollution zones was made depending on the relative high and low values of NO₂ and SO₂ within the data set. Ozone was not included in this classification due to its secondary formation in the atmosphere. The reasons for the exclusion of ozone are also discussed in the following sections on the mapping and exposure assessment. For the choice of the “higher” and “lower” sampling locations, measured NO₂ and SO₂ values were first separately sorted from highest to lowest values and classified into three groups as high/moderate/low values of the data set. Locations in both high classes of NO₂ and SO₂ (in general those points coincide with relatively higher traffic density and high population density), or in high class of one and moderate class of the other were classified as “higher pollution locations.” Since NO₂ and SO₂ are both pollutants with primary health effects individually, points with high levels of either NO₂ or SO₂ were also classified as higher pollution. For example, in winter season, relatively higher SO₂ concentrations were measured at localities where coal is used for heating purpose. In this case such a point is classified as

“higher” pollution location because of its high SO₂ concentration accompanied by a moderate value of NO₂. Locations in both low classes of NO₂ and SO₂, or in low class of one and moderate class of the other were classified as “lower pollution locations.” The reason for choosing 8 points from each region was to have a total number of 1,000 students in each region. Among 2,000 children screened in the health survey, half were from lower pollution areas and the rest was from higher pollution areas.

E-1 was established in the backyard of the Provincial Directorate of Environment and Forestry quite close to the city center. Bursa–Ankara highway, mechanical facilities of Turkish Railways Foundation and some residences around the station can be considered as important pollutant sources close to the point. The sampling station was established near the air pollution monitoring station of the Ministry of Environment and Forestry. PM₁₀, SO₂, and meteorological parameters are being monitored continuously in this location by The Provincial Directorate of Environment and Forestry Office staff. E-2 was established in the city center, in the garden of a museum. This point is a typical urban-traffic sampling point just 2 m away from a main road. The road is usually used by local busses and has a busy traffic especially in morning and evening hours, with a traffic count of 50,000 vehicles per day. Moreover, in winter season, many of the surrounding houses of the sampling point use coal for domestic heating, resulting in high PM and gaseous organic and inorganic pollutant emissions. E-3 (suburban station-1) was located in the garden of a municipal service building. There was neither any important pollution source around the sampling location nor heavy traffic flow in sampling periods. The major pollutant source of the location is a group of houses around the station. E-4 (suburban station-2) was located at the backyard of a house in a district very close to the Bursa–Ankara Highway. This station was chosen as a polluted location since there is a busy highway nearby, and in this neighborhood many people use coal for heating in winter season. Pollution here might be caused by heating in wintertime, traffic, and road dusts in summer since not all the roads are paved. Mass concentrations of PM were measured at all four stations, while PAHs and trace metals together with PM were measured at only two stations (E-1 and E-2). During summer and winter passive sampling campaigns, passive and active samples were also collected from those four monitoring stations.

Sampling and analysis

Cyclones and impactors connected to low volume pumps (SKC Inc., USA) were used for the sampling of PM_{2.5} and PM₁₀ on Teflon filters. Air was sucked with a flow rate of 3.5 Lmin⁻¹ through the 37 mm aluminum cyclone (SKC Inc. USA) over a pre weighed Teflon[®] filter to determine

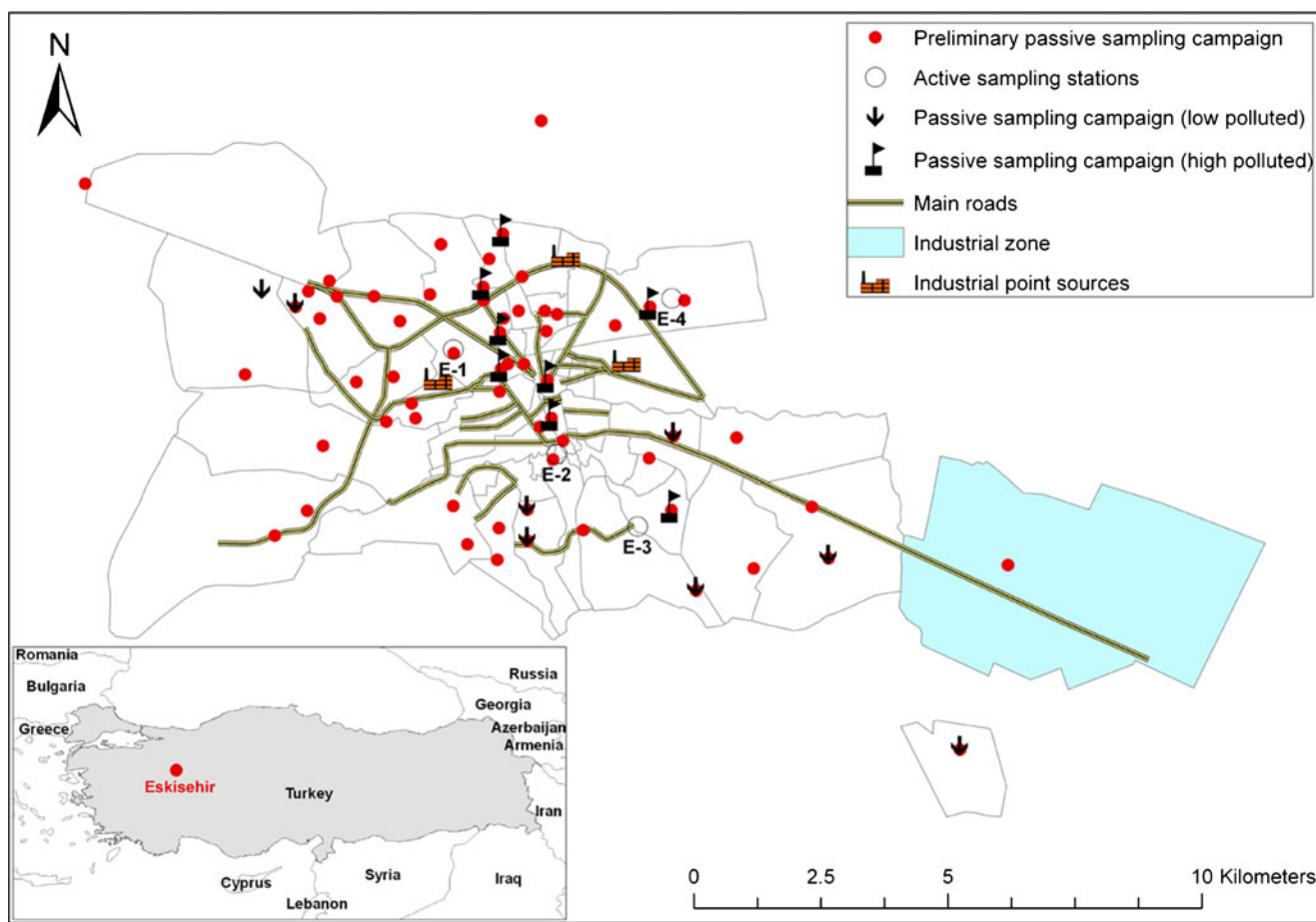


Fig. 1 Passive and active sampling locations

the $PM_{2.5}$ mass concentration. A PM_{10} single stage impactor (SKC Inc., USA) with a flow rate of 4 L min^{-1} was used for measuring the PM_{10} mass. Flows were measured before and after each sampling period with calibrated rotameters. Filters were double weighed using a microbalance at the beginning and end of each sampling period. Twenty-four-hour time integrated $PM_{2.5}$ and PM_{10} concentrations were measured at four stations during winter and summer sampling campaigns.

PM_{10} samples for trace metal analysis were collected by a Thermo High Volume PM_{10} Sampler. Two samplers were used simultaneously in urban (E-1) and urban-traffic (E-2) stations. Samples were collected on pre-conditioned and pre-weighed rectangular quartz fiber filters (QFFs) with dimensions of $20.3 \times 25.4 \text{ cm}$. A quarter part of each filter cut by a ceramic scissor was digested in a microwave oven with an acid mixture of 1:3 HNO_3 and HCl and analyzed by Perkin Elmer DV2100 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

Twenty-four-hour gaseous and particulate-phase samples were collected by a Thermo GPS 2 PUF sampler with an airflow rate of $0.225 \text{ m}^3 \text{ min}^{-1}$ to determine ambient concentrations of PAHs. A certified solution of a standard

mixture (Dr. Ehrenstorfer, Germany) containing 13 PAHs were used for the calibration of the gas chromatography–mass spectrometry (GC-MS) system: fluorene (Flu), phenanthrene (Phe), anthracene (ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3c,d*]pyrene (Ind), dibenzo[*a,h*]anthracene (DahA), and benzo[*g,h,i*]perylene (BgP). Details of analytical procedures for the extraction of polyurethane foam (PUF) plugs and glass fiber filters (GFFs) and analysis were described elsewhere (Gaga and Ari 2011). Briefly, glass fiber filters and PUF cartridges (used for the collection of particle and gas phase samples, respectively) were Soxhlet extracted with a mixture of petroleum ether and dichloromethane (1:4) and analyzed by GC-MS. PUF samplers were placed near to the high volume samplers at two stations.

Ambient NO_2 , SO_2 and ozone concentrations were determined by using passive samplers. Two different types of passive samplers developed and produced at Anadolu University were used for the sampling studies. Technical and analytical details of the passive samplers can be found elsewhere (Özden et al. 2008; Gül et al. 2011; Özden and Döğeroğlu 2012). NO_2 and SO_2 were collected in the same

sampler manufactured from Polytetrafluoroethylene while O_3 was collected in passive samplers made from delrin. The samplers have been derived from ANALYST® type passive sampler and comprise a plastic body with the dimensions of 2.5 cm length and 2.0 cm inner diameter, filter paper placed at the bottom, plastic ring, and stainless steel mesh barrier. Whatman GF/A glass fiber filter paper impregnated with 20 % TEA aqueous solution was used for the collection of NO_2 and SO_2 , and filter paper impregnated with 1 % $NaNO_2$ +2 % Na_2CO_3 +2 % glycerol aqueous solution was used for the collection of ozone. The filter papers were dried and placed at the bottom of the sampler and fixed with the 5 mm ring. The inlet ends were then closed with a plastic cap. Filter papers were removed from the samplers and extracted with a mixture of 10 mL deionized water (18 M Ω) and 0.04 mL 30 % H_2O_2 for 15 min for simultaneous determination of NO_2 and SO_2 . Glass fiber filters in the ozone passive samplers were extracted with 10 mL deionized water for 15 min. All the extracts were analyzed by using DIONEX 2500 ion chromatograph equipped with GP 50 gradient pump, LC 25 column oven and a conductivity detector. Atmospheric concentrations of the components were then determined by using Fick's first law of diffusion.

Mapping and exposure assessment

Pollutant maps of NO_2 , SO_2 , and ozone were created using ArcGIS 9.2. The concentration values were interpolated over the city by using the natural neighborhood method. As explained later, Kriging was also used for the air pollution exposure analysis but natural neighborhood was preferred in the preparation of the pollutant distribution maps for avoiding any extrapolation outside the sampling locations and also because one of the first aims was to determine regions with different pollution levels in order to categorize the schools for later lung function tests of children, which also did not require any extrapolation outside the sampling locations.

A basic exposure assessment was carried out employing GIS techniques. The two pollutants chosen for the assessment were NO_2 and SO_2 as good indicators of pollution originating from traffic and residential heating, respectively. Ozone values were not included in the assessment because of the very different trends of ozone compared to SO_2 and NO_2 , and also because the statistically reliable number of measurements (65 points) was present only during a winter campaign as explained before. Wintertime ozone measurements would not be very meaningful in the assessment.

A detailed spatial distribution of population was available through the use of GIS and population records on district level. Population data from 65 districts of Eskişehir were digitized on GIS and then converted to population density.

Since the sampling points were not evenly distributed, pollutant distribution maps were created by the Kriging technique, after a series of optimization procedures. For a broader spatial coverage, Kriging was chosen among the interpolation alternatives. Kriging is an interpolation technique that depends on the minimization of error of predicted values through the use of semivariograms (Nejadkoorki et al. 2011). One of the important differences of the Kriging technique from other interpolation techniques is that it takes into account only certain neighboring measurement points rather than all the measurement points. Two methods (ordinary Kriging and prediction maps methods) were used to predict the concentrations derived by interpolation of the monitoring data. The semivariogram models were determined by spherical, Gaussian and exponential functions and Kriging parameters were selected by trial and error to minimize the root mean square prediction error (the minimum number of contributory sites was set to 4 and the maximum to 8). Owing to the better spatial coverage of the Kriging method, only a very small portion of the study remained outside the interpolation boundaries and the number of people with "unknown" degree of exposure was quite small.

Quality control/quality assurance (QC/QA)

Field blanks were taken and analyzed regularly to determine any contamination during the transportation of samples to the sampling site. Blank levels were subtracted if the concentration of the blank was more than 10 % of the analyte for all kinds of the analyses. Since the amounts of analytes in the collected samples were very low, strict quality assurance procedures were followed.

Mass concentrations of PM_{10} and $PM_{2.5}$ were determined by pre and post weighing. Teflon® filters were placed in the conditioning room for at least 24 h before and after sampling to be weighed by a microbalance. Each filter was weighed twice (with some time in between the two measurements) and if the two weighed values differed more than 0.005 mg, the two measurements were considered false and repeated. All post and pre weights were checked for whether the difference between first and second weights exceeded 0.005 mg or not. Only for filters that meet this requirement the data was used. The gained weights (post minus pre weights) were calculated and then the acquired data was corrected for the field blank weights.

Certified multi-element standards (ICP-MS, High Purity Standards, USA) were used for calibration of ICP-OES. Daily calibration checks were performed by using check verification standard (CCV-1) purchased from High Purity Standards, USA. Accuracy of the method including digestion and measurement was evaluated by using a certified reference material (SRM 1648, urban dust NIST, Gaithersberg, MD).

Certified reference material was digested and analyzed using the same digestion and measurement procedure. Recoveries of metals from the certified reference material were in the range of 96 % (Al) and 112 % (Zn). The limit of detection (LOD) was estimated as the concentration corresponding to three times the standard deviation (3σ) of the blank signals obtained from a set of reagent blanks. LOD values were found in the range of 0.05 (Sr) and $3.89 \mu\text{g L}^{-1}$ (Al).

Deuterated surrogate standards were added prior to extraction of the samples to correct recoveries of each PAH from the sample matrix. The average recoveries were $73 \%\pm 19$ for Acenaphthene-d10 (Ace-d10), $83 \%\pm 21$ for Phenanthrene-d10 (Phe-d10), $83 \%\pm 16$ for Chrysene-d12 (Chr-d12), and $88 \%\pm 19$ for Perylene-d12 (Per-d12) for PUF samples and $60 \%\pm 15$, $72 \%\pm 17$, $79 \%\pm 12$ and $86 \%\pm 26$ for the GFFs, respectively. Limit of detection (LOD) values were calculated by sequential injections of diluted standard solutions by using a signal-to-noise (S/N) ratio of 3. LOD values for PAH compounds varied between 0.006 (chrysene) and 0.02 ng m^{-3} (benzo[*b*]fluoranthene).

The accuracy of the passive samplers for NO_2 was previously determined by comparison with a Thermo 42i chemiluminescence NO_x (NO and NO_2) Continuous Automatic Gas Analyzer and percent relative error was found to be lower than 15 % (Özden 2005). LOD of the passive sampler was estimated as three times of the standard deviation of the field blanks and found as $1.00 \mu\text{g m}^{-3}$ for a 1-week sampling period. For the ozone passive samplers, the accuracy of the sampler was determined by comparison with O_3 42 M UV Photometric Environnement S.A. continuous automatic analyzer and percent relative error was lower than 15 % (Özden 2005; Özden and Döğeroğlu 2012). Detection limit for a 1-week sampling period was $2.42 \mu\text{g m}^{-3}$. For the SO_2 passive samplers, during the study period, SO_2 concentrations were compared with the reference acidimetric (H_2O_2) method which was included in the Turkish ambient air monitoring network operated by the Ministry of Health. The average obtained value of percent relative error was lower than 19 %. The LOD for the sampler was approximately $3.00 \mu\text{g m}^{-3}$ for a 1-week sampling period.

Results and discussion

Passive sampling campaigns

Preliminary weekly passive sampling of NO_2 , SO_2 , and ozone was carried out at 65 points during 9–23 January of 2008. Measured concentrations of NO_2 , SO_2 , and ozone were mapped using Arc GIS and shown in Fig. 2. Since the main source of NO_2 in the atmosphere is traffic, the highest NO_2 concentrations ($\sim 76 \mu\text{g m}^{-3}$) were obtained in the city center while there was a decrease in the

concentration levels far away from the city center. Higher SO_2 levels were generally associated with highly populated districts close to the city center. Sulfur dioxide concentrations in the regions where coal was used for domestic heating were at higher levels than those in the regions with natural gas use. This result indicated that SO_2 is a seasonally varying pollutant. Contrary to NO_2 , ozone concentration values were higher in the locations far from the city center. The low ozone levels in the center are related to the high NO_2 levels. Figure 2 shows a typical opposing relationship between NO_2 and ozone concentrations measured in this study.

Ozone formation is a highly nonlinear process regarding its interactions with NO_x and volatile organic compounds. Nonlinear and reverse relationship between NO_2 and ozone concentrations obtained in this study and shown in a different way in Fig. 3 is also confirmed by the studies conducted by Sillman (1999) and Yay (2006). Ozone formation reactions are not instantaneous but take place over several hours or days depending on the precursors. Also, once ozone has been produced, it may persist for several days and travel for long distances. Therefore, maximum concentrations generally occur downwind of the source areas of the precursor pollutant emissions.

Based upon the results of the preliminary passive sampling campaign, the sampling locations were classified as relatively lower/higher pollution locations depending on NO_2 and SO_2 levels. The 16 schools were selected for lung function screening and the passive samplers were deployed to those schools in summer and winter sampling campaigns. Sampling points 1–8 were located in lower pollution areas while sampling points 9–16 were located in higher pollution areas. The total number of the schools (16) was enough to provide 2,000 students (1,000 from high and 1,000 from low pollution area schools) necessary for the health survey. Also, 4 monitoring stations where active PM, PAH, and trace metals measurements were carried out (sampling points 17–20) were included in the sampling studies. In total, 20 sampling points were included in both summer and winter sampling campaigns. The sampling campaigns were carried out during 2 weeks with 1-week periods for passive sampling.

Average summer and winter concentrations of all pollutants measured in this study are shown in Fig. 4. This figure facilitates the observation of spatial and temporal distribution of these pollutants over the city. The average temperatures were $4.6 \text{ }^\circ\text{C}$ and $16.6 \text{ }^\circ\text{C}$ during winter and summer campaigns and westerly winds were prevalent in both sampling periods.

Summer average NO_2 concentration of the schools located in low polluted areas was $7.63\pm 1.85 \mu\text{g m}^{-3}$, while it was $11.38\pm 5.85 \mu\text{g m}^{-3}$ for the schools located in high polluted areas. Also, for the winter season, the average concentration

Fig. 2 SO₂, NO₂, and ozone concentration distributions obtained in preliminary passive sampling campaign

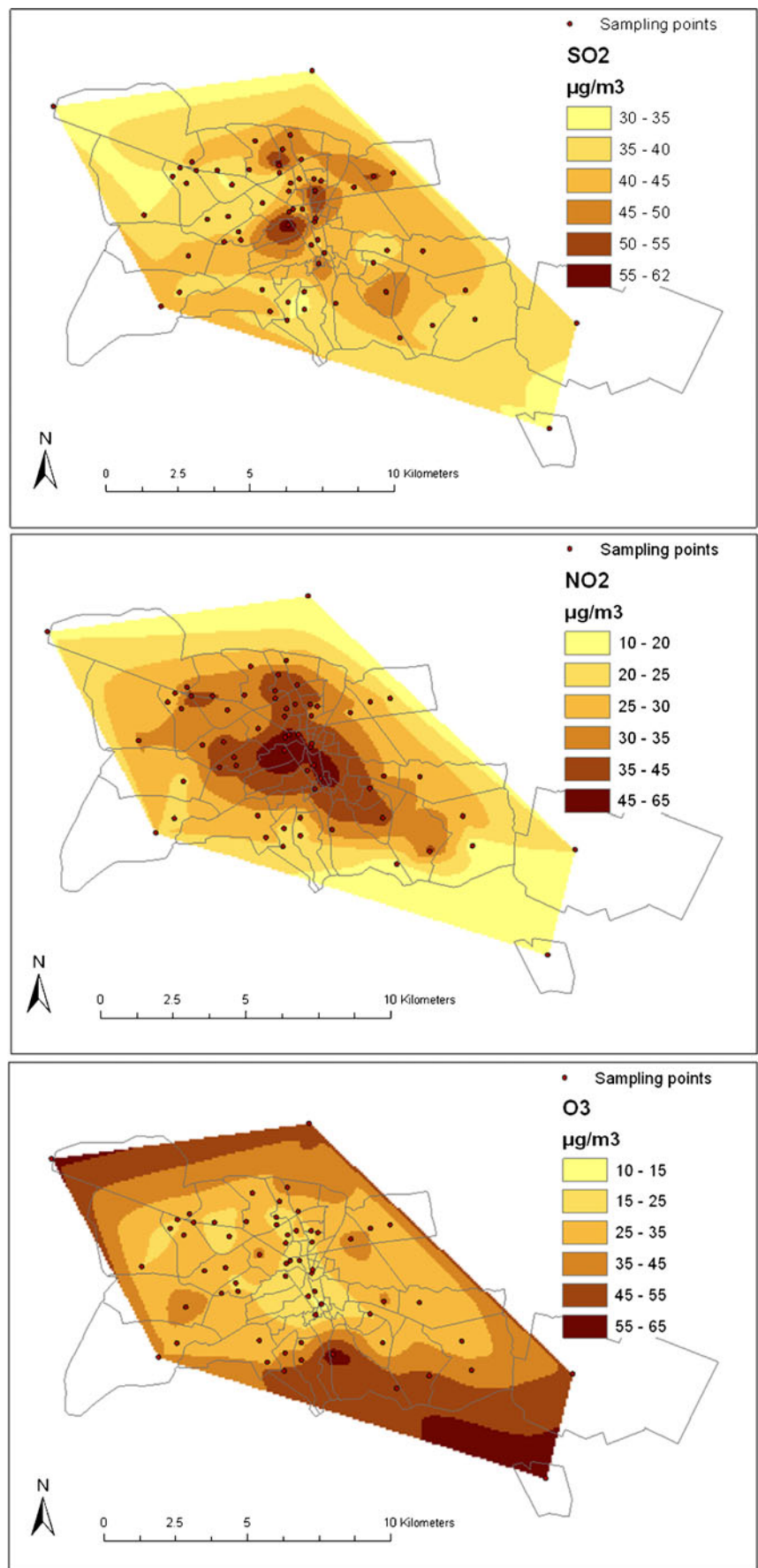
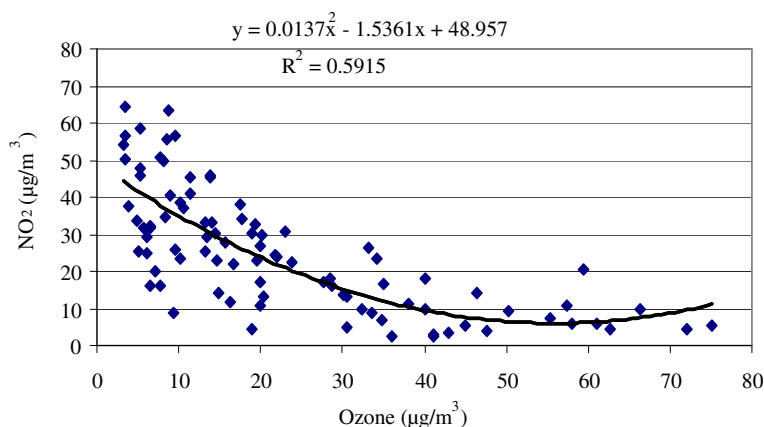


Fig. 3 Nonlinear and reverse relationship between atmospheric NO₂ and ozone concentrations measured in Eskişehir



was $19.13 \pm 7.77 \mu\text{g m}^{-3}$ in low polluted areas and $35.38 \pm 7.89 \mu\text{g m}^{-3}$ around schools located in high polluted areas. As observed also in Fig. 4, the concentrations in winter season were higher than summer concentrations (*t* test, $p < 0.001$). Winter average NO₂ concentration including monitoring stations was 2.8 times higher than the summer average concentration probably due to higher traffic density and fuel combustion for residential heating. Especially emissions of SO₂ and NO_x from residential heating exhibit a seasonal difference owing to the hard winter conditions in Eskişehir with much lower winter average temperatures as mentioned before. The seasonal dependency of atmospheric PAHs also support the conclusions related to the effect of combustion activities in Eskişehir in a previous study (Gaga and Ari 2011). Lower NO₂ levels in summer may also be due to its destruction by photochemical reactions. Since the main source of NO₂ in the atmosphere is traffic, the highest NO₂ concentrations were obtained in the city center while there was a decrease in the concentration levels far away from the city center. A possible contribution of the varying mixing heights to the seasonality of the concentrations was investigated by Yay (2010) and the differences between average mixing heights alone did not explain the seasonal differences. Previously explained day–night temperature differences seem to cause summer early morning mixing heights close to those during winter. The cloud cover present during the winter sampling campaign also probably prevented stable conditions and neutral atmospheres were observed more frequently during the winter campaign nights.

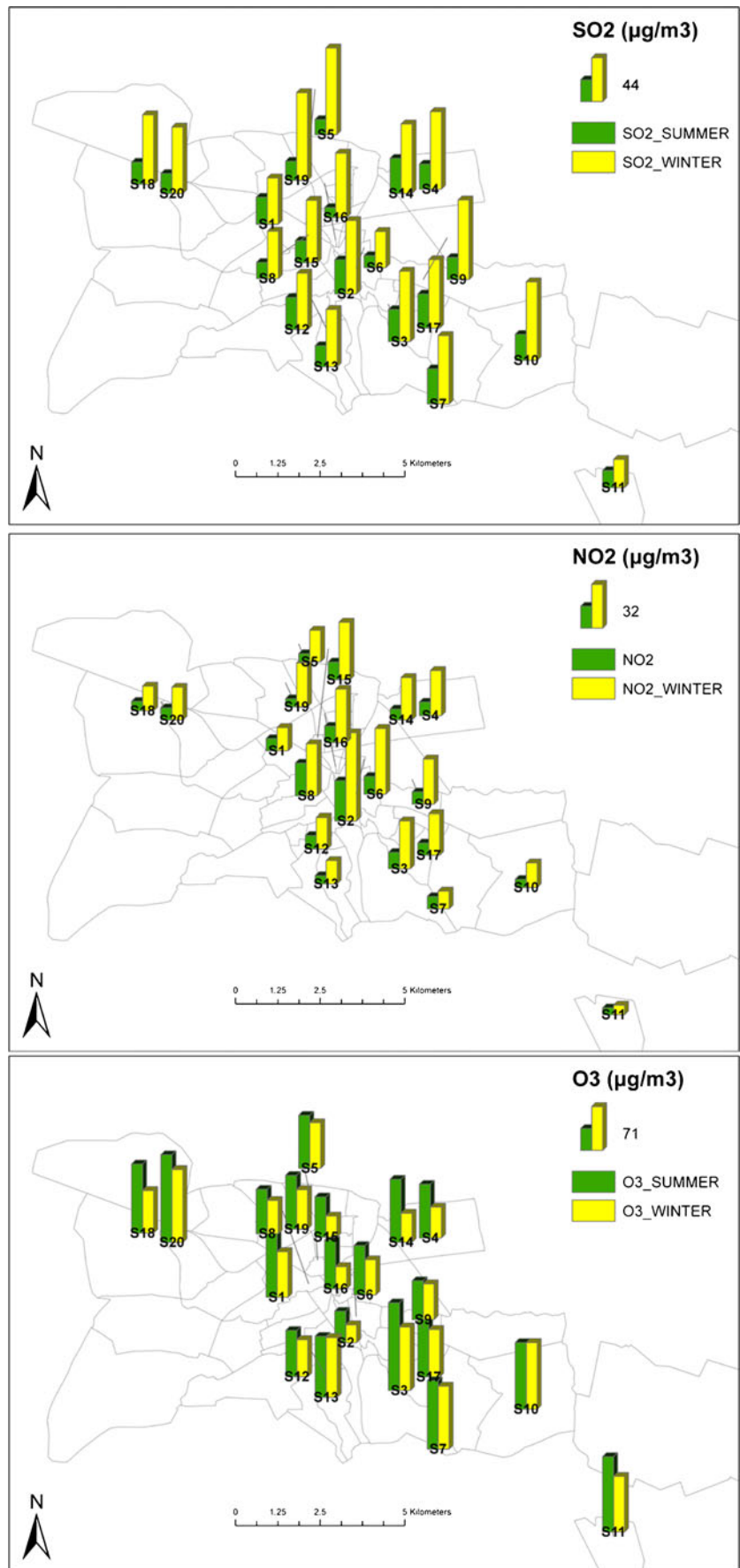
Average summer SO₂ concentration of the schools located in low polluted areas was $24.38 \pm 6.21 \mu\text{g m}^{-3}$, while the concentration was $20.38 \pm 9.49 \mu\text{g m}^{-3}$ for the schools in higher pollution areas. From these results, it can be concluded that there is no difference between low and high pollution area concentrations in summer. Also, the same conclusion can be made for the winter season since the average SO₂ concentration was $62.63 \pm 16.30 \mu\text{g m}^{-3}$ in the schools in lower pollution areas while it was $64.88 \pm 17.42 \mu\text{g m}^{-3}$ around higher pollution areas. Especially, around the

schools (sampling points 2, 3) which were classified as lower pollution areas, high SO₂ concentrations were obtained in winter. This very small difference between low and high pollution areas in winter may be linked to the increase of the natural gas price. After the introduction of natural gas in the 90s, the city planning based on the creation of new settlements (settlements which are generally lower pollution areas at the outer parts of the city) with the promotion of the use of natural gas while many settlements at the older districts, generally closer to the current city center, were allowed to continue to use coal. After the natural gas price changes, some buildings located in low pollution areas also started to switch back to coal for domestic heating. Therefore this switch back to coal was more effective in the low pollution areas. There is a seasonal trend for both low and high pollution areas. Including the monitoring stations, average summer SO₂ concentration was 2.7 times lower than winter concentration.

Temporal and seasonal differences were observed in ozone concentrations. Average summer concentration in lower pollution areas (most of them are far away from the city center) was 104.00 ± 25.20 and $83.75 \pm 12.58 \mu\text{g m}^{-3}$ around higher pollution areas (most of them being in the city center). For winter, the concentration was $87.75 \pm 22.76 \mu\text{g m}^{-3}$ in lower pollution areas, while it was $55.38 \pm 16.02 \mu\text{g m}^{-3}$ in higher pollution areas. The average ozone concentration in summer ($93.88 \pm 21.90 \mu\text{g m}^{-3}$) was significantly higher (*t* test, $p < 0.001$) than winter average concentration ($71.56 \pm 25.32 \mu\text{g m}^{-3}$). Contrary to NO₂, ozone concentration values were higher in the locations far from the city center. This is generally caused by the depletion of ozone by NO in the city center, particularly in areas with high traffic density as the main source of NO_x.

Both for NO₂ and SO₂, winter/summer (w/s) ratios in higher pollution areas were higher than lower pollution areas. For NO₂, average w/s value was 2.49 ± 0.77 for low pollution areas while it was 3.52 ± 1.03 in high pollution areas. For SO₂, average w/s value was 2.64 ± 0.75 for low pollution areas while it was 3.68 ± 1.69 in high pollution

Fig. 4 Average summer and winter concentrations of SO₂, NO₂, and ozone obtained from passive and active sampling points



areas. Higher values of w/s ratios for both pollutants in high polluted areas are due to the higher winter concentrations obtained in these areas. The opposite situation was obtained for ozone. Average w/s value obtained from low pollution areas was 0.85 ± 0.13 and it was 0.66 ± 0.16 in high pollution areas. This is because the low-high pollution region classification was done depending only on NO_2 and SO_2 concentrations and ozone was ignored during this classification. This fact caused higher w/s ratios in the so-called low pollution areas.

Mapping and exposure assessment

Overlaying of the population density data and the pollutant distribution data allowed for a classification of the number of people exposed to certain intervals of pollutant levels. The classification of the pollution levels were adopted from a study by Thepanondh and Toruska (2011) and from Scoggins et al. (2004). The approach is to take certain percentages of the limit values as critical break values. Pollutant concentrations over the limit value are regarded as the threshold for “need for action,” the limit value for “alert condition,” two thirds of the limit value for “levels of some concern,” one third of the limit value for “good condition,” and 10% of the limit value for “excellent condition.” The limit values were taken from WHO Air Quality Guidelines rather than the national air quality standards, regarding the fact that the main concern is the health effect of pollutants (WHO (World Health Organization) 2006). Since the passive sampling lasted for one week, the most suitable SO_2 WHO guideline for comparison was the second interim target of $50 \mu\text{g m}^{-3}$ as the 24-h average value. The WHO air quality guideline value of $20 \mu\text{g m}^{-3}$ was not used since it would be too challenging for a city like Eskişehir where all wintertime measurements are above this value. The choice of a 24-h SO_2 guideline value was obligatory because there is no weekly guideline value for SO_2 while the sampling has to be weekly because of the mentioned detection limit problems for low levels. Because of these practical reasons, it was not possible to see if the exceedances are valid for each individual day or not.

Regarding NO_2 , there is no weekly or 24-h WHO guideline but there is an annual guideline value of $40 \mu\text{g m}^{-3}$. Therefore, the NO_2 values first needed to be converted to annual averages. In order to realize this, previous NO_2 multi-point measurements from Eskişehir were used. There were two datasets available. One was the winter and summer campaigns from the same project (still with a fair spatial distribution but not as detailed as this study), and the other data set had a very good temporal resolution (two whole-year measurements with one or two week sampling periods) but a lower spatial resolution (Özden et al. 2008). Winter to whole-year ratios of both datasets yielded almost the same

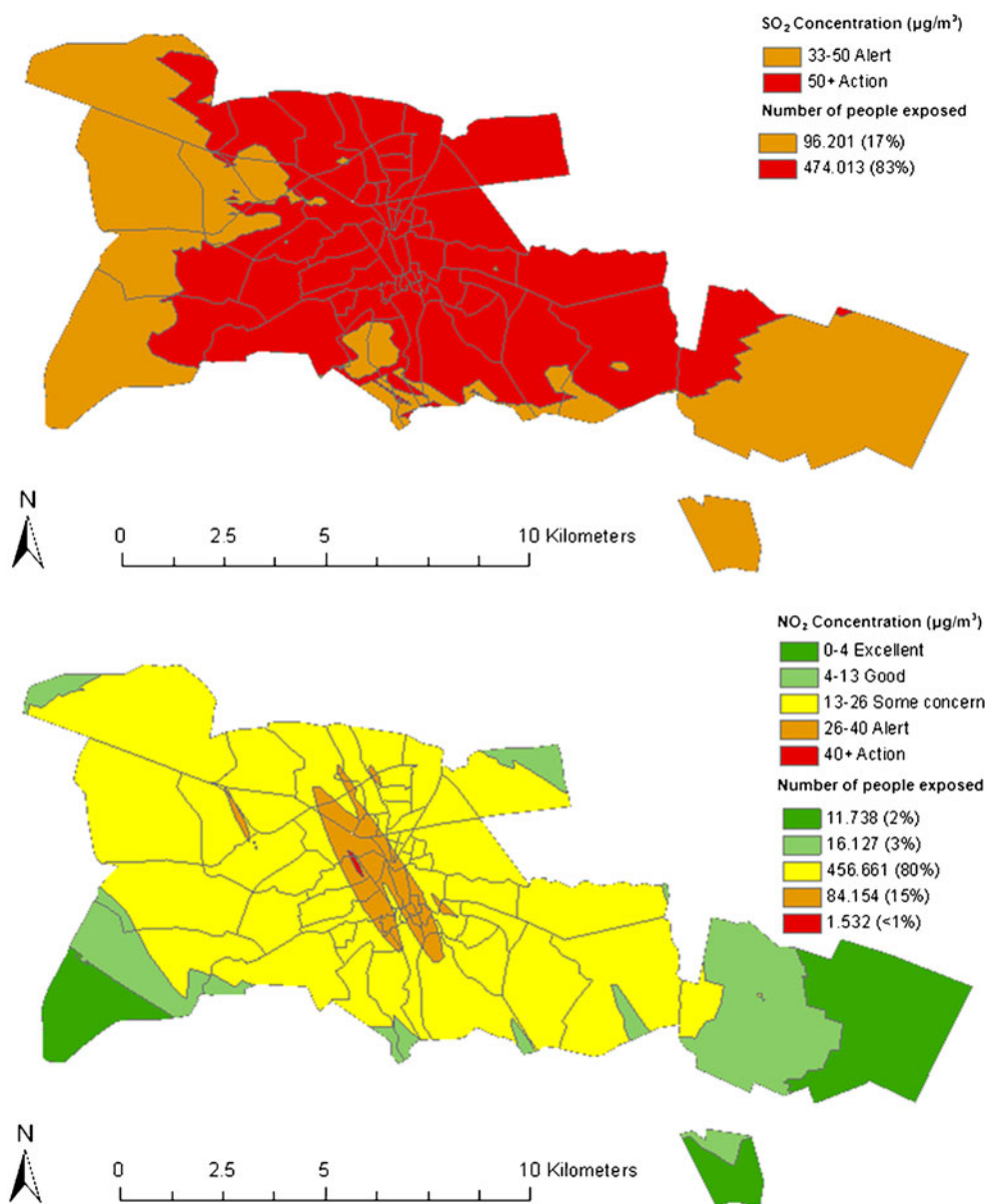
result. It was found that the average ratio of winter NO_2 values to whole-year values was 4/3. Using this factor, the winter NO_2 values from the extensive measurement campaign were converted to annual averages and these values were used in the exposure assessment. The overlaying of the population and pollution was done with a series of GIS tools. The pollutant distribution maps were first reclassified according to the mentioned designations like “alert,” “levels of some concern,” etc. and the population density maps were combined (using the “union” tool in ArcGIS) with this reclassified dataset in order to determine the population in each category by making use of the rectified original maps which contain the area of each reclassified population zone. The population falling within each classified pollution zone was determined with the “resolve” tool to sum all subpopulation zones during the union of the layers. The exposure assessment necessarily depended on the residential addresses of the population which may lead to some uncertainty because of the mobility of the population within the city for various reasons like work, travel, recreation, etc. and also because of varying indoor exposures to certain types of pollutants.

Figure 5 shows the spatial distribution of ambient pollutant concentrations in the study area and the number of people exposed in each category of air pollutant.

As seen in Fig. 5, most of the population (80 %) is exposed to NO_2 levels classified as “levels of some concern”; and around 15 % in the very urban center is exposed to levels close to the guideline value. Regarding SO_2 , the exposure seems to be a more important problem, since a great portion of the population (83 %) is exposed to levels above the WHO guideline value, classified as “alert condition.” The rest of the city is also exposed to levels close to the limit value. There seems to be no part of the city that can be classified as “excellent,” “good,” or “some concern” with respect to exposure to SO_2 during winter. Another point of concern is that except for the population numbers depending on residential addresses shown in the maps, many people work or spends several hours in the city center where there is a lot of commercial and bureaucratic activities and therefore is exposed to critical pollutant levels.

A buffer analysis carried out in GIS also confirmed the relationship between NO_2 and traffic. Buffer zones were created around the “main roads” or “arteries” (as defined by the municipality) and the multiple ring buffers had distances of 100, 300, 500, 1,000, 2,000, and 5,000 m from the main roads. This buffer layer was overlaid on the NO_2 pollution class map explained before and the results are shown in Fig. 6 and Table 1. As seen in the table, 38 % of the areas classified as “alert” and 75 % of the areas classified as “action” are within only the first 100 m distance to the main roads while the percentage for the same distance for “excellent” areas is below 1 and it is only 1 % for the

Fig. 5 Spatial distributions of ambient SO₂ and NO₂ concentrations in the study area and the number of people exposed in each category of air pollutant



“good” areas. All “alert” areas are within 1,000 m to the main roads and all “action” areas are within 300 m to the main roads. Overlaying of the “high” and “low” polluted sites on the buffer zones also indicate that the high pollution sites are covered by the zones closer to the roads (all covered within 1,000 m) while the coverage of the low pollution sites has a more spread distribution (the whole coverage spread till the outermost zone of 5,000 m).

These results point to the fact that the traffic network should be optimized since the city center is already facing a critical condition for NO₂ exposure. The maps showing the SO₂ exposure are even more striking. In spite of the fact that there has been a considerable ratio of switch from coal to natural gas, there is still a SO₂ problem. Since the national policy of benefiting from local high-sulfur coal seems to be still effective in the near future, the measure for overcoming

the SO₂ problem, at least to some degree, should concentrate on the promoting of central residential heating systems rather than individual and non-professional combustion systems, like stoves.

Atmospheric gas and particle-phase PAHs

As it was mentioned before, daily samples were also collected during winter and summer seasons to determine atmospheric PAH and metal concentrations. Regarding PAHs, on the average, 73 % and 69 % of the PAHs were found in the gas phase in winter and summer season, respectively. Among the volatile species, Flu, Phe, Flt, and Pyr were the most abundant PAH compounds in two sampling stations, in both seasons. These compounds are most frequently detected species in urban locations (Tsapakis and Stephanou

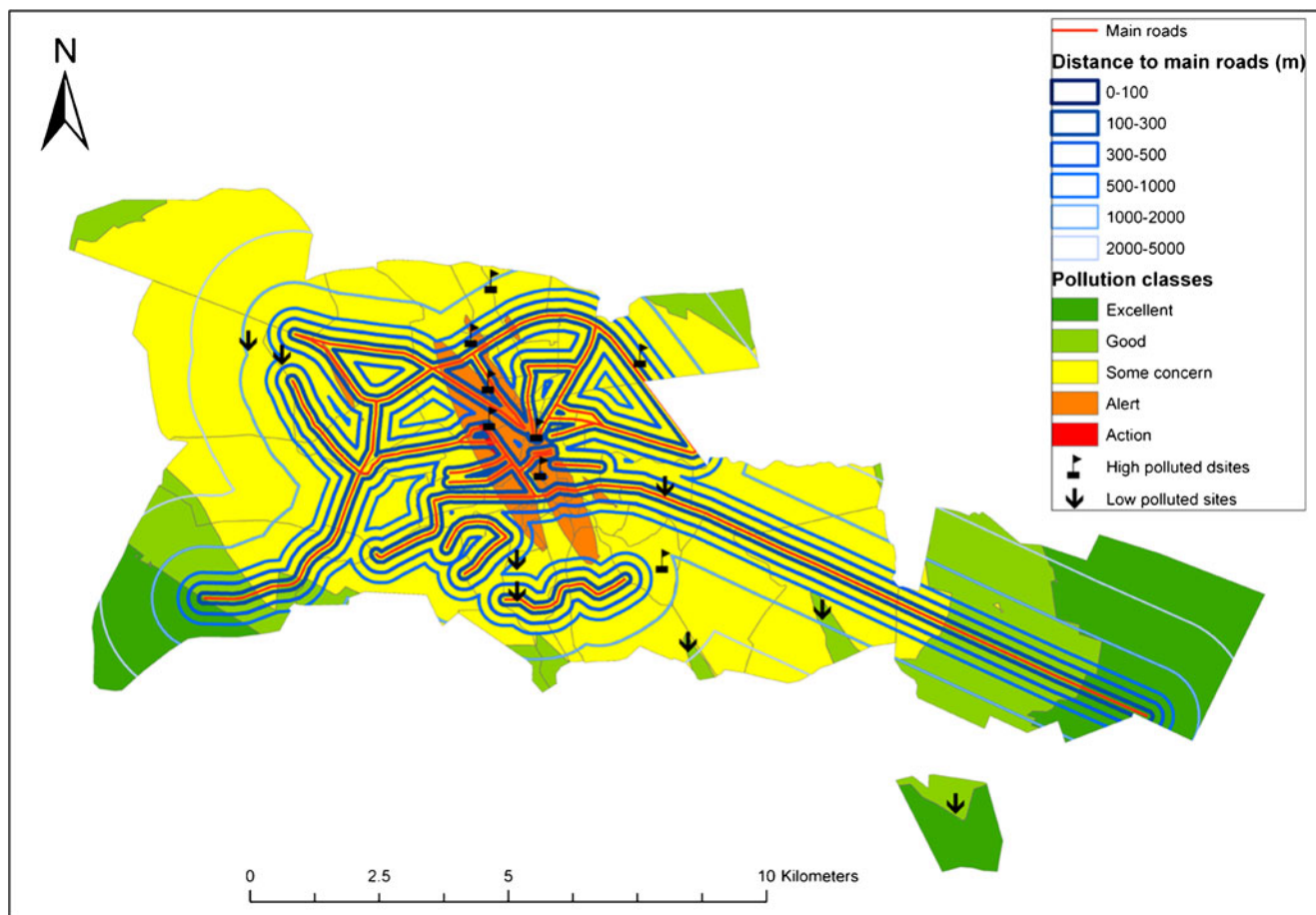


Fig. 6 Buffer analysis on the effect of traffic on NO₂

2005; Esen et al. 2006; Gaga and Ari 2011). Concentrations of 13 individual PAH compounds in gas and particulate

phases were found to be three to ten times higher during the winter period in both stations. This situation is usually

Table 1 Coverage of the pollution zones by the buffer zones around the main roads

Pollution class		Distance to the main roads					
		0–100	100–300	300–500	500–1,000	1,000–2,000	2,000–5,000
Excellent	Coverage ^a	0	1	1	4	14	79
	Total coverage	0	1	2	7	21	100
Good	Coverage	1	3	3	9	29	55
	Total coverage	1	4	7	16	45	100
Some concern	Coverage	9	16	12	19	24	20
	Total coverage	9	25	37	56	80	100
Alert	Coverage	38	42	9	11	0	0
	Total coverage	38	80	89	100		
Action	Coverage	75	25	0	0	0	0
	Total coverage	75	100				
Lower polluted sites	Coverage	0	25	25	25	12.5	12.5
	Total coverage	0	25	50	75	87.5	100
Higher polluted sites	Coverage	25	37.5	12.5	25	0	0
	Total coverage	25	62.5	75	100		

^aCoverage (%) is the percent covered by the buffer zone; total coverage (%) is the total percent covered starting from the road

attributed to the increased use of fossil fuels and adverse meteorological conditions (Gaga et al. 2009; Gaga and Ari 2011) and the effect of meteorological conditions during winter will be discussed later in the manuscript in detail.

In addition to increased fossil fuel consumption, lowered atmospheric mixing layer and decreased sunlight intensity, which is a major contributor to the degradation of PAH compounds in the atmosphere due to the photochemical reactions, might be the other reasons for the higher concentrations measured in the winter period (Park et al. 2002; Fang et al. 2004a, Morville et al. 2011). Lowering the ambient temperatures in winter months (4.6 °C average) is the most important reason of increasing fossil fuel combustion for space heating and increase of the combustion related emissions in Eskişehir. Summer average ambient temperature was about 16.6 °C and does not cause any space heating requirement. Lowering the atmospheric mixing height (1,300 m in winter and 2,500 m for summer average) and decrease in the sunlight intensity may result of decrease in the depletion rates of PAH compounds in atmosphere and stacking the pollutants into a smaller volume over the city.

Table 2 denotes the average concentrations of 13 individual PAH compounds (gas+particle) for each sampling period. Total concentration of 13 PAHs were found to be 39.2±14.0 and 140.5±60.5 ng m⁻³ for summer period samples in urban and urban-traffic stations, respectively. Total concentrations of PAHs increased to 235.7±153.0 and 788.4±324.5 ng m⁻³ for these stations in the winter period. A very similar trend was observed in a previous study carried out using the same urban traffic station indicating seasonal behavior of PAHs which has been partly linked to increased

use of fossil fuel combustion in winter period (Gaga and Ari 2011). Dense traffic flow including many diesel powered city busses might be one other reason of the pollution around the urban traffic station.

Toxicity assessment of individual PAHs can be made based on their BaP equivalent concentrations (BaP_{eqv}). Nisbet and LaGoy (1992) have established toxic equivalency factors (TEFs) for individual PAHs by using BaP as the reference compound. A TEF of 1.0 was assigned to the classified carcinogenic compounds and 0.001 to the noncarcinogenic ones (Nisbet and Lagoy 1992; Collins et al. 1998; Fang et al. 2006). Concentration of each PAH was converted to the benzo[*a*]pyrene equivalent (BaP_{eqv}) concentration by multiplying the concentrations of PAHs with the corresponding TEFs. BaP_{eqv} concentrations of PAHs at two sampling points are presented in Table 2. Higher toxic concentrations were measured both in the winter and summer periods at the urban-traffic sampling station. The sum of carcinogenic species in winter time is apparently higher than those in the summer period for both sampling stations. Contribution of higher molecular weight PAH compounds, BaP, BbF, BkF, and Ind to the toxic fractions is significant because of their higher TEFs. There is no limit value for the atmospheric BaP concentrations in Turkish Air Quality and Control Regulations. On the other hand, WHO proposed an annual limit value of 1 ng m⁻³ for BaP concentration. Benzo[*a*]pyrene limit value was exceeded at all times in urban traffic location (E-2) in both periods. The percent of days in which BaP concentration exceeded the WHO limit value were 64 % and 72 % in summer and winter period, respectively, in the urban

Table 2 Ambient and BaP_{eqv} toxic concentrations of PAHs (ng m⁻³)

PAHs	E-1 (Urban) Summer		E-1 (Urban) Winter		E-2 (Urban-Traffic) Summer		E-2 (Urban-Traffic) Winter	
	PAH conc. (ng m ⁻³)	BaP _{eqv} toxic conc.	PAH conc. (ng m ⁻³)	BaP _{eqv} toxic conc.	PAH conc. (ng m ⁻³)	BaP _{eqv} toxic conc.	PAH conc. (ng m ⁻³)	BaP _{eqv} toxic conc.
Flu	3.4±1.7	<0.01	30.5±22.3	0.03±0.02	11.9±6.4	0.01±0.01	100.6±59.9	0.10±0.06
Phe	13.0±5.7	0.01±0.01	63.1±33.9	0.06±0.03	44.3±18.3	0.04±0.02	220.2±90.5	0.22±0.09
Ant	0.5±0.5	0.01±0.01	14.1±23.2	0.14±0.28	2.5±2.1	0.03±0.02	40.3±21.7	0.40±0.22
Flt	4.5±2.4	<0.01	28.4±18.3	0.03±0.02	15.6±7.0	0.02±0.01	93.0±41.9	0.09±0.22
Pyr	2.6±1.7	<0.01	22.4±14.9	0.02±0.01	11.7±5.0	0.01±0.01	81.0±37.4	0.08±0.04
BaA	1.2±1.2	0.12±0.12	9.5±9.8	0.95±0.98	3.4±3.1	0.34±0.31	33.0±22.9	3.30±2.29
Chr	1.7±1.3	0.02±0.01	12.2±12.0	0.12±0.12	5.7±5.1	0.06±0.05	37.3±24.1	0.37±0.24
BbF	1.8±2.9	0.18±0.29	5.2±5.0	0.52±0.50	6.6±14.8	0.66±1.48	19.8±14.7	1.98±1.47
BkF	1.1±0.4	0.11±0.04	4.4±4.4	0.44±0.44	5.6±12.2	0.56±1.22	14.6±11.1	1.46±1.11
BaP	1.1±0.6	1.10±0.60	5.3±4.9	5.30±4.90	3.3±4.0	3.30±4.0	19.2±17.9	19.2±17.9
DahA	1.1±0.4	0.11±0.04	5.0±4.8	0.50±0.48	2.6±4.7	0.26±0.47	24.4±11.0	2.44±1.10
Ind	0.5±0.2	0.50±0.20	1.8±1.7	1.80±1.70	1.5±1.6	1.50±1.60	7.9±3.5	7.90±3.50
BgP	0.9±0.4	0.01±0.00	4.0±3.4	0.04±0.03	3.2±3.3	0.03±0.03	22.2±11.5	0.22±0.12
ΣPAH	39±14	2.2±1.3	236±153	10±9.5	141±61	6.8±9.2	788±325	27.8±28.2

station (E-1). It is necessary to take certain actions for reducing atmospheric PAH concentrations in the study area such as increasing natural gas use and optimizing traffic flow.

Diagnostic ratios of PAH compounds have been widely used to identify their possible emission sources (Rogge et al. 1993; Dickhut et al. 2000; Park et al. 2002; Lodovici et al. 2003; Ravindra et al. 2006; Gouin et al. 2010). Although they may not serve as very reliable tracers, some specific PAH compounds or a group of PAHs may indicate certain sources. However, it is known in the literature that overlaps and discrepancies may occur for different emission source categories. Among the several ratios, Ind/(Ind+BgP) ratio is used to indicate different types of combustion sources. Grimmer et al. (1983) suggested Ind/(Ind+BgP) ratio of 0.62 for wood burning, and Kavouras et al. (2000) used this ratio between 0.35 and 0.70 for diesel emissions. Some other researchers used the ratio of 0.56 for coal burning, and 0.18 for traffic emissions (Khalili et al. 1995; Guo et al. 2003; Fang et al. 2004b). In this study, Ind/(Ind+BgP) ratio was found between 0.50 and 0.56 in urban and urban-traffic sampling stations, in both two seasons (Table 3). Flu/Flu+Pyr ratio below 0.5 is interpreted by many researchers to indicate gasoline powered vehicle emissions, and above 0.5 for diesel powered vehicles (Khalili et al. 1995; Guo et al. 2003; Ravindra et al. 2006). In this study, Flu/Flu+Pyr ratio was found between 0.49 and 0.56 in both stations which may indicate traffic emissions. Higher ratios of BbF/BkF over 0.5 are in agreement with diesel emissions in literature (Pandey et al. 1999; Park et al. 2002). The ratio of BbF to BkF was found as 1.06 to 1.21 in the urban station and 1.13 to 1.30 in the urban-traffic station.

The ratio of BaP to BgP >1.25 indicates the effect of coal emissions. This ratio increased from 1.02 and 1.05 to 1.29 and 1.32 in both urban and urban-traffic stations in winter period samples, respectively. Higher ratios of Ind/BgP over 1 indicates the emissions from mixed combustion sources (Pandey et al. 1999; Park et al. 2002; Ravindra et al. 2006). This ratio was found to be above 1 in two stations in the winter period. In Eskişehir, many people use brown coal for residential heating in winter period. This situation affects the air quality adversely, especially in cold season. A previous emission inventory study carried out in Eskişehir indicated the respective contributions of domestic heating to SO₂ and

PM emissions as 70 % and 84 %, respectively (Çınar 2003; Özden et al. 2008). Based on the previous studies carried out in Eskişehir and diagnostic ratios, fossil fuel combustion and traffic emissions might be important reasons of high PAH concentrations measured in Eskişehir.

Atmospheric PM_{2.5}, PM₁₀, and heavy metal concentrations

Mass concentrations of PM_{2.5} and PM₁₀ and heavy metal content of PM₁₀ were also determined in this study. Measured mass concentrations of PM (PM_{2.5} and PM₁₀) and heavy metal concentrations of PM₁₀ samples are presented in Table 4.

Concentrations of PM_{2.5} and PM₁₀ were present in much higher concentrations in the urban-traffic sampling station as compared to other locations. Winter to summer ratios of measured PM_{2.5} concentrations increased about two times in all four sampling stations. From summer to winter, PM₁₀ concentrations decreased by 16 % in the urban station, and increased by 30 % and 15 % in the urban-traffic station (E-2) and the sub-urban station (E-3), respectively. PM₁₀ concentrations did not change in the sub-urban station (E-4) significantly. Since the roads are not paved completely around the sub-urban station (E-4), a constant high PM₁₀ background level was observed because of the road dust suspension in this station. PM₁₀ levels exceeded the European Union limit value of 50 µg m⁻³ (daily limit that should not to be exceeded more than 35 days in a year) at each station almost every day. Percent exceedances of PM₁₀ levels were in the range of 77 % to 100 % in both seasons. PM_{2.5}/PM₁₀ ratios increased in the winter period samples in all four sampling locations. The ratios changed from 0.24 (E-4, in summer period) to 0.55 (E-3, in winter). Increase in the ratio indicates an increase in the dominance of the PM_{2.5} on PM₁₀ concentrations, and mainly anthropogenic emissions are known to be the main source of those fine particles (Rodriguez et al. 2004; Hueglin et al. 2005; Chuersuan et al. 2008). Coal is widely used especially around the urban-traffic station and sub-urban stations (E-3, E-4). Doubling of the PM_{2.5} concentrations measured in these stations is an indication of coal consumption. Increased coal and wood consumption mainly in winter season may cause an increase in the PM_{2.5} concentrations in Eskişehir. Besides that, the

Table 3 Diagnostic ratios of PAHs

Diagnostic Ratios	Urban Summer	Urban Winter	Urban-Traffic Summer	Urban-Traffic Winter
Ind/(Ind+BgP)	0.52±0.16	0.50±0.16	0.52±0.05	0.56±0.08
Flu/(Flu+Pyr)	0.56±0.10	0.56±0.08	0.49±0.12	0.53±0.16
Phe/(Phe+Ant)	0.96±0.03	0.82±0.16	0.94±0.05	0.85±0.04
BbF/BkF	1.06±0.12	1.21±0.35	1.13±0.17	1.30±0.18
BaP/BgP	1.02±0.36	1.29±0.20	1.05±0.42	1.32±0.19
Ind/BgP	1.04±0.30	1.12±0.38	1.10±0.21	1.16±0.10

Table 4 PM_{2.5}, PM₁₀ and heavy metal concentrations (µg m⁻³)

Pollutant	E-1 (Urban) Summer	E-1 (Urban) Winter	E-2 (Urban-Traffic) Summer	E-2 (Urban-Traffic) Winter	E-3 (Suburban) Summer	E3 (Suburban) Winter	E-4 (Suburban) Summer	E-4 (suburban) Winter
PM _{2.5}	18.6±5.7	30.4±16.9	31.8±9.4	59.7±25.4	21.1±6.9	42.4±20.4	24.0±8.0	50.5±19.0
PM ₁₀	65.1±21.0	55.9±19.1	85.0±20.6	120.7±40.0	69.2±17.1	81.3±26.2	102.3±33.3	104.5±37.5
PM _{2.5} /PM ₁₀	0.30±0.10	0.35±0.10	0.38±0.07	0.44±0.12	0.30±0.07	0.55±0.18	0.24±0.07	0.52±0.24
Metals								
Al	494.1±204.7	451.4±585.0	706.7±293.5	1045.8±968.1	na	na	na	na
As	1.2±1.2	3.2±2.1	1.1±0.6	10.0±5.4	na	na	na	na
Ba	8.8±5.5	4.6±4.6	18.1±5.9	20.9±7.6	na	na	na	na
Cd	0.5±0.5	0.9±1.4	0.2±0.2	1.5±1.8	na	na	na	na
Co	0.4±0.5	0.2±0.2	0.5±0.3	0.7±0.3	na	na	na	na
Cr	13.4±15.1	4.0±3.3	8.8±5.6	7.3±7.6	na	na	na	na
Cu	25.2±11.2	67.8±41.8	21.7±11.0	25.2±8.6	na	na	na	na
Fe	511.3±219.3	326.0±432.3	766.7±306.0	972.2±532.2	na	na	na	na
Hg	nd	0.01±0.01	0.02±0.01	0.02±0.02	na	na	na	na
Mg	525.9±296.9	357.0±273.3	782.6±303.0	827.0±386.7	na	na	na	na
Mn	12.4±5.2	9.2±10.8	18.3±10.3	21.0±9.9	na	na	na	na
Ni	3.1±1.8	1.3±1.2	4.0±2.2	4.4±2.2	na	na	na	na
Pb	5.8±5.1	8.7±7.5	5.7±3.2	23.8±10.1	na	na	na	na
Sb	1.3±1.1	1.2±0.8	2.3±0.9	4.6±1.9	na	na	na	na
Se	0.6±0.2	0.6±0.5	0.6±0.2	1.2±0.7	na	na	na	na
Sn	2.2±3.0	2.2±3.4	3.2±1.8	7.7±3.1	na	na	na	na
Sr	4.7±2.6	4.0±4.6	7.3±2.8	11.1±6.1	na	na	na	na
V	1.9±0.9	3.4±2.1	2.8±1.3	3.6±2.0	na	na	na	na
Zn	41.1±26.8	40.1±37.8	70.1±45.4	94.9±55.4	na	na	na	na

na not available, nd not detected

contribution of road dust to PM₁₀ is decreasing due to wet surfaces in winter period.

Table 4 shows an overview of the mean concentrations of the analyzed elements in PM₁₀ at two sampling stations in both seasons. Cu and Cr were found in higher concentrations in urban station samples. Mn and Fe were found at high concentrations in this location, too. The main train station of Eskişehir and a maintenance facility of Turkish State Railways are placed very close to this station, and these metals are usually related with railway emissions (Bukowiecki et al. 2007; Gehrig et al. 2007). Arsenic, Cd, Pb, Sb, Se, Sn, and Zn were found in higher concentrations in urban-traffic location samples. Concentrations of these elements increased significantly in the winter period. Heavy traffic both in summer and winter periods and coal usage in winter are suspected to be the main sources of these elements in this location. Some specific elements such as As, Cd, Pb, Sb, and Se had higher winter to summer period concentration ratios, varying between 2 (Sb) and 9.1 (As), and it is known in the literature that these elements are

strongly related with coal burning in urban atmospheres (Wang et al. 2001; Srinivasa Reddy et al. 2005; Wu et al. 2009). Additionally, another factor affecting the ambient concentrations of heavy metals is traffic. Ba, Cd, Cr, Fe, Mn, Ni, Pb, Sn, Sr, and Zn concentrations are strongly affected by traffic emissions (Sternbeck et al. 2002; Harrison et al. 2003; Shi et al. 2008; Verma et al. 2010).

Enrichment factors (EFs) of atmospheric heavy metals were calculated for indicating the relative contribution of natural and anthropogenic sources. The EF for an element analyzed on particles can be calculated using the equation:

$$EF(X) = (C_X/C_{Ref})_{aerosol} / (C_X/C_{Ref})_{crust} \quad (1)$$

where $(C_X/C_{Ref})_{aerosol}$ and $(C_X/C_{Ref})_{crust}$ represent the concentrations of an element X relative to a reference element in the aerosol and crust respectively (Taylor and McLennan 1995; Kaya and Tuncel 1997). Fe was chosen as the reference element to calculate EFs because of its low anthropogenic emissions and its high abundance in the earth's crust (Wu et al. 2009; Hieu and Lee 2010; Shridhar et al. 2010).

Values of EF between 1 and 10 suggest that crustal erosion is the dominant source of the relevant element and that its atmospheric concentrations are not significantly affected by the anthropogenic activities. Elements having EFs in the range of 10–100 are considered as moderately enriched and elements having EFs over 100 are considered as highly enriched (Shridhar et al. 2010).

The EFs calculated for the analyzed elements in PM at two sampling stations in two seasons are presented in Fig. 7 for all the samples.

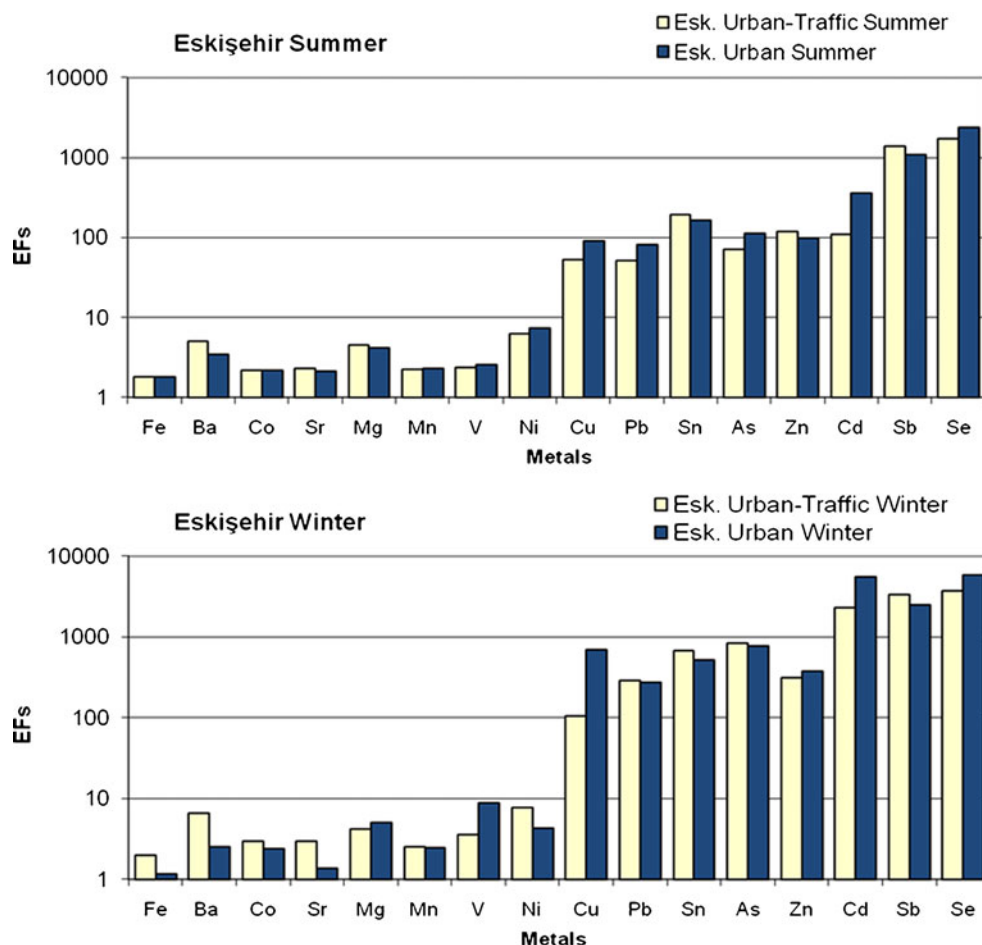
At both stations, the EF values of Ba, Fe, Co, Sr, Mg, Mn, Ni, and V were less than 10, indicating that these elements have originated mostly from soil, and not been affected by human activities significantly. Among the other elements, Cu and Pb at two sites were observed to be moderately enriched in both seasons. Arsenic, Cd, Sn, and Zn were enriched moderately in two stations only in summer period, but highly enriched in winter period samples. High level of enrichment of Sb and Se at two stations in both two seasons was apparent. Arsenic, Cd, Pb, Sn, and Zn showed higher enrichment in the winter period samples compared to the summer period. Coal and wood consumption for residential heating in winter are one of the most

important parameters which increase the enrichment of these elements in ambient air (Wang et al. 2001; Srinivasa Reddy et al. 2005; Pacyna et al. 2007).

Conclusions

One of the objectives of this study was the pre-assessment of the air quality in Eskişehir through an extensive passive sampling campaign. This first campaign which was carried out at 65 points in the city included NO_2 , SO_2 , and ozone measurements. Depending on the results of this assessment, some points were chosen for new campaigns to see the seasonal changes of the pollutants. Four other monitoring stations were also designed for including the measurements of PAHs, PM_{10} , and $\text{PM}_{2.5}$. The particulate matter (PM_{10}) was also analyzed for its chemical composition. According to the results, higher SO_2 values are associated with highly populated and central districts of the city. Nitrogen dioxide is generally attributed to the traffic; however the residential heating also plays an important role because of the terrestrial climate and hard winter conditions, indicated by almost a threefold increase in winter compared to summer levels.

Fig. 7 EFs of atmospheric metal concentrations



Ambient air quality measurement results were also used in a health survey in which 2,000 children living in the vicinity of the sampling locations were included.

The classification of the low and high pollution zones were based on SO₂ and NO₂ since residential heating and traffic are the primary sources of air pollution. However, such a classification may limit the assessments regarding ozone. Especially in cities with higher solar radiation, ozone should not be underestimated during the assessment of lower and higher pollution zones.

PAH and PM results points out that coal consumption is still of importance in spite of the gradual switch from coal to natural gas in the last 15 years.

Passive sampling provides a powerful and relatively easier and cheaper tool for the general assessment of urban air quality. Such an assessment has become a legal obligation in Turkey after the revision of the By-Law on Assessment and Management of Air Quality in 2008, depending mostly on the adaptation of framework and daughter European Union directives on air quality.

The results of the air pollution exposure analysis show that there is need for action to reduce the exposure to the pollutants especially at the populated city center.

Considering the results indicating that the levels of NO₂ and SO₂ are elevated in the densely populated districts, especially the city center, one perspective in the development of the city may be the promotion of new settlements with smaller population density. The population of the city is expected to have an increasing trend in the future according to the municipal strategic plan and other projections, therefore this new population should not be encouraged to settle in the already populated areas. The population living in the current high population density areas should also be encouraged to settle in new areas by the creation of new attraction centers. The current state of the city can be characterized as having a single attraction center, which is also the physical center of the metropolitan area. The topographic properties of the city are advantageous in this sense since it can be considered to be dominated by terrain flat compared to many other cities in Turkey. Recommendations on these and other air quality related issues were stated in the Clean Air Plan of the city (Anonymous, 2010), which was one of the main outputs of the same project.

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