

Determination of the personal, indoor and outdoor exposure levels of inorganic gaseous pollutants in different microenvironments in an industrial city

Zehra Bozkurt **D** · Güray Doğan · Demet Arslanbaş · Beyhan Pekey · Hakan Pekey • Yetkin Dumanoğlu • Abdurrahman Bayram • Gürdal Tuncel

Received: 18 February 2015 /Accepted: 19 August 2015 / Published online: 27 August 2015 \odot Springer International Publishing Switzerland 2015

Abstract We measured SO_2 , NO_2 and O_3 concentrations during the summer and winter in Kocaeli, Turkey. The sampling was carried out indoors and outdoors at homes, schools and offices. Personal samplers were also used to determine personal exposures to these pollutants. High $NO₂$ and $SO₂$ concentrations were observed in outdoor samples collected close to locations characterized by heavy urban traffic. Concentrations of O_3 , on the other hand, were higher in rural areas around the city due to ozone distillation. For both sampling periods, the concentrations of outdoor SO_2 and O_3 were higher than for indoor and personal samples; however, the $NO₂$ concentrations were higher in indoor and personal samples, indicating that outdoor sources significantly

Z. Bozkurt (\boxtimes)

Department of Environmental Engineering, Düzce University, Düzce 81620, Turkey e-mail: zehrabozkurt@duzce.edu.tr

G. Doğan Department of Environmental Engineering, Akdeniz University, Antalya, Turkey

D. Arslanba^ş : B. Pekey : H. Pekey Department of Environmental Engineering, Kocaeli University, Kocaeli, Turkey

Y. Dumanoğlu : A. Bayram Department of Environmental Engineering, Dokuz Eylül University, İzmir, Turkey

G. Tuncel

Department of Environmental Engineering, Midle East Technical University, Ankara, Turkey

contribute to indoor SO_2 and O_3 levels and that indoor $NO₂$ concentrations are primarily modulated by sources within buildings. Seasonal variations in pollutant concentrations showed statistically significant differences. Indoor and outdoor concentrations of $NO₂$ and $SO₂$ measured in the winter were higher than the levels measured in the summer; O_3 concentrations, on the other hand, exhibited the opposite trend. Active-topassive concentration ratios for $NO₂$, $SO₂$ and $O₃$ were 0.99, 1.08 and 1.16, respectively; the corresponding outdoor ratios were 0.95, 0.99 and 1.00.

Keywords $NO_2 \cdot SO_2 \cdot O_3 \cdot$ Indoor air \cdot Outdoor air. Personal exposure

Introduction

Air pollution is a serious human health problem, notably in urban areas. The probable causes of air quality problems in urban areas include rapid and unplanned urbanization, increasing urban populations and industrialization (Mayer [1999](#page-15-0); Lawrence and Fatima [2014\)](#page-15-0). Organic and inorganic pollutants detected in urban environments originate from sources such as traffic, industry, power centres and commercial and domestic fuels (Schindler and Caruso [2014;](#page-15-0) Wei et al. [2014;](#page-16-0) Mraihi et al. [2015](#page-15-0)). An analysis of the pollutants originating from the atmosphere is crucial for formulating effective policies to reduce pollution and protect human health (Mavroidis and Ilia [2012\)](#page-15-0).

People in urban areas spend more than 80 % of their time in indoor environments, such as at home, work, and public and private places (schools, restaurants, etc.) (Norhidayah et al. [2013;](#page-15-0) Uchiyama et al. [2015](#page-15-0)). Indoor air quality is a basic determinant of the quality of life within a building. There are two main sources of indoor air pollution: substances present in the domestic environment and its activities (e.g. burning cooking fuels, construction materials and toxic gas emissions from household equipment) and outside pollutants entering the indoor environment (Jones [1999;](#page-15-0) Szczurek et al. [2015](#page-15-0)). For some pollutants, contributions from outdoor sources can significantly affect concentration levels indoors (Barraza et al. [2014;](#page-14-0) Demirel et al. [2014](#page-15-0); Rivas et al. [2015\)](#page-15-0), depending on the location of the building within the city (Jones [1999;](#page-15-0) Challoner and Gill [2014\)](#page-14-0). In buildings close to industrial areas or streets where traffic is heavy, the outdoor environment can be a significant source of indoor pollutants.

The primary sources of $NO₂$ and $SO₂$ in the atmosphere are industrial emissions, combustion processes and vehicle traffic (Langer and Bekö [2013](#page-15-0); Sudalma et al. [2015\)](#page-15-0). Previously, ambient concentrations of $SO₂$ appeared to arise completely from domestic heating; however, in recent years, as a result of the reduction in fuel consumption except for natural gas, diesel vehicles have currently become a significant source of $SO₂$ in Turkey (Genç et al. [2010\)](#page-15-0). Another air pollutant, ozone, is a secondary pollutant in the troposphere and is formed via photochemical reactions of NO_x and volatile organic compounds (VOCs) (Helaleh et al. [2002;](#page-15-0) Nopmongcol et al. [2014](#page-15-0)).

We measured the indoor and outdoor concentrations of SO_2 , NO_2 and O_3 in residences, offices and schools in the city of Kocaeli in north-western Turkey, a city of 1.7 million inhabitants, and we used active and passive sampling techniques in two campaigns during the summer and winter seasons. We measured the exposure to $SO₂$, $NO₂$ and $O₃$ using volunteers wearing personal samplers. The purpose of our study is twofold: (1) to relate the personal exposure of residents to the indoor and outdoor concentrations of SO_2 , NO_2 and O_3 and (2) to identify the indoor and outdoor sources of these pollutants that affect their indoor levels.

Materials and methods

Study area

Kocaeli is located in the most important industrial region in Turkey. Approximately 45 % of Turkey's manufacturing industries are located between Kocaeli and Istanbul. Kocaeli is also located on a corridor connecting Europe to the Middle East via Anatolia. The population density of the city is 445 people per square kilometre. Hence, both indoor and outdoor air quality in residential areas are heavily influenced by emissions from industries and traffic.

The sampling was carried out in 15 homes, 10 offices, and 3 schools in the city. The sampling was sequential between locations, i.e. the samplers were transported from one location to another. However, the indoor, outdoor and personal samplings were performed simultaneously at each location. Both active and passive sampling techniques were used in parallel during the indoor and outdoor sampling.

The distribution of the sampling locations in the city is shown in Fig. [1,](#page-2-0) and the general characteristics of these points are summarized in Table [1.](#page-2-0) Since the city of Kocaeli is located along the coast of Izmit Bay, all stations were influenced by the sea. Fifteen of the stations were located in residential areas away from industrial activities (8 of these 15 locations were houses, 6 were offices and 1 was a school). Nine of the stations were located in industrial areas (5 homes, 3 offices and 1 school), and four were located in rural areas (2 homes, 1 office, and 1 school) away from all anthropogenic activity. These remaining four stations were used as background sites.

Questionnaire study for personal exposure determination and comfort parameters

During the sampling, all sampled respondents (people who lived or worked in the sampled indoor microenvironments and carried personal samplers in each microenvironment) were asked to fill out a questionnaire about the environment they lived in and about the personal activities they performed during the sampling period. The determined characteristics were related to the sampled microenvironment. The amount of time that people spent indoors was a critical parameter. The time spent indoors and in other environments is provided in Table [2.](#page-3-0) On average, participants spent only 10 % of their time outdoors; they spent 85 % of their time indoors (70 % in a home indoor environment, 13 % in a business indoor environment and 17 % in other indoor environments) and 5 % of their time in other environments.

Fig. 1 Sampling locations in Kocaeli, Turkey

All of the sampled indoor environments were naturally ventilated without any air conditioning. The indoor and outdoor temperatures, relative humidity and CO and $CO₂$ concentrations during sampling are listed in Table [3](#page-3-0). The average indoor/outdoor temperatures in the summer and winter seasons were 24/25 and 20/ 9 °C, respectively. The similarity in indoor and outdoor temperatures in the summer is due to better ventilation via open windows in the summer, which generated similar trends in indoor/outdoor $CO₂$ (497/354 and 846/410 ppm, respectively) and CO (1.17 and 3.88 ppm, respectively) concentrations. The indoor CO2 concentration is an indicator of outdoor-to-indoor ventilation and comfort. If the $CO₂$ concentration is

above 1000 ppm, the indoor air quality may not be suitable from a health standpoint, given that the ventilation is poor. At the same time, a $CO₂$ concentration below 1000 ppm does not ensure healthy indoor air quality conditions (Menteşe et al. [2015\)](#page-15-0).

Sampling

We carried out the sampling using active and passive sampling methods at each location for 24 h. All sampling was started at 8 in the morning and each sampling point was continued until 8 the next morning. Two sampling campaigns, one between March 31 and June 29, 2006, and the other one between December

Table 1 General characteristics of sampled microenvironments

Summer	Winter				
March 31, 2006–June 29, 2006	December 16, 2006-January 20, 2007				
15 urban areas, 9 industrial areas, 4 rural areas					
$18 + 13$					
71 ± 40					
High or medium $(>24,000$ vehicles/day)	Low $(<24,000$ vehicles/day)				
2					
8	2				
10	5				

Table 2 Time spent in microenvironments by sampled respondents in different seasons (units are in hours)

SD standard deviation

16, 2006, and January 20, 2007, were conducted to determine seasonal differences in the concentrations of the measured parameters.

Passive sampling and analysis

Radial passive samplers produced by the Radiello Company (Italy) were used for sampling SO_2 , NO_2 and O_3 . The number of samplers used in indoor environments (homes, schools and offices) depended upon the variety of microenvironmental sources. The passive samplers used in homes were placed in three locations: living rooms, bedrooms and kitchens. In schools, the passive samplers were placed in two locations: classrooms and teachers' rooms. Finally, in offices, the passive samplers were placed in the interior of the central office. Special care was taken when placing the passive samplers. However, in all microenvironments, sampling was carried out in only one outdoor location. For indoor sampling, the samplers were placed at least 2 m from doors and windows, at a height of 1.5 m. We made sure that the active and passive samplers were placed in protected areas close to the selected microenvironment when performing the outdoor sampling.

Before and after exposure, the passive samplers were kept in airtight containers and stored in the refrigerator at 4 °C in the dark until sample processing. Nitrogen dioxide and O_3 concentrations were determined by using a UV-vis Varian 100 Spectrophotometer, and SO2 concentrations were determined by using a Dionex ICS-3000 ion chromatography system, as described in detail by Pekey and Özaslan [\(2013](#page-15-0)). The sample extraction process and the UV-vis method were applied according to the recommendations of the Radiello Company (Radiello [2015\)](#page-15-0). The mass of nitrite and O_3 in the cartridges was obtained by reference to a

Table 3 Sampled microenvironments' temperature, relative humidity, carbon monoxide and carbon dioxide levels of indoor and outdoor environments

linear calibration derived from the spectrophotometric analysis of standard solutions of sodium nitrite (for nitrite) and 4-pyridylaldehyde (for ozone).

The ion chromatography system consisted of an isocratic pump (Dionex isocratic single pump SP), a conductivity detector (Dionex CD), an anion selfregenerating suppressor (Dionex 4-mm selfregenerating II ASRS Ultra), an anion analytical column (Dionex IonPac AS9-HC 4×250 mm) and a guard column (Dionex IonPac AG9-HC 4×50 mm). Ten millimolars of Na_2CO_3 , 1 mL/min and 100 μL were used as the eluent, flow rate and sample size, respectively. Highpurity deionized water was used during sample dilution and the preparation of eluent and calibration standards. Calibration standards for the sulphate ion (Dionex seven anion standard, PART#57590) were prepared using deionized water, with concentrations ranging from 0.02 to 10 ppm.

Three samplers were used as field blanks and three samplers were used as laboratory blanks for each pollutant. A field blank is a sampler that is transported to the field in the same way as the samplers. At the sampling site, the plastic bag was opened and the cartridge taken from the box. After that, it was placed in the box and closed tightly again and the blank was taken back to the lab. Laboratory blanks were the unopened cartridges that were stored in the refrigerator until the analysis. All blanks were treated as environmental samples, and the average blank value was subtracted from the sample amount using the blank data set of each sampling period.

The analytical quality control procedures was carried out using calibration linearity and field and laboratory blanks to check for artefacts and calculate the detection limit. The limit of detection for each pollutant (for a 1-day exposure) was calculated as three times the standard deviation of the blank values, and was 0.41 μg (2 μg/m³) for NO₂, 0.06 μg (1.7 μg/m³) for O₃ and 0.24 μ g (1.4 μ g/m³) for SO₂. The linearity of the calibration standards was calculated by regression analysis with values greater than 0.99 (r^2) for NO₂, O₃ and SO₂ by spectrophotometry and ion chromatography.

Active sampling

All parameters were also measured using automated active monitors to generate short-term (hourly) data. All active samples within the scope of the study were taken simultaneously in one location for both indoor and outdoor microenvironments. For the measurements of NO, $NO₂$ and NO_x , we used Thermo model 42C and Environment S.A. AC model $31M NO_x$ analyzers. Two Environment S.A. AC model 21M analyzers were used for the active monitoring of SO_2 . Measurements of active O_3 were carried out using Environment SA O_3 model 41M O₃ analyzers. Active monitoring in indoor environments was performed in the communal areas of the sampling locations (such as in living rooms or classrooms). In the outdoor environment, the samplers were placed close to the selected microenvironment.

Thermal comfort parameters (temperature and relative humidity) were measured simultaneously using a Langan Model L76n Indoor Air Quality Measurer (Langan Products, Inc., CA, USA) to produce a general profile of both indoor and outdoor air. The 24-h average values of temperature and relative humidity were obtained from measurements recorded using a data logger during each sampling event.

Statistical analysis

Statistical analyses were performed using SPSS 21 software (SPSS Inc., Chicago, IL, USA) for Windows. The data were log-normally distributed in a Kolmogorov-Smirnov statistical test, which was employed to assess the normality of the data. The distribution of indoor air quality data and air pollutants was generally found to be typical (Baek et al. [1997\)](#page-14-0). Since the concentrations of the measured pollutants were not normally distributed, we used a nonparametric Friedman test to determine whether there were significant differences among urban, industrial and rural areas' outdoor microenvironments and between summer and winter measurements. Statistical significance was set at $P<0.05$ (95 % confidence level).

Results and discussion

Temporal variations in NO_2 , SO_2 and O_3 concentrations

We used active and passive sampling methods in our study. The results that we obtained from the simultaneously performed measurements were compared and the ratios were close to 1. The correlation coefficient values (r) for the concentrations of NO₂, SO₂ and O₃ obtained by active and passive sampling were between 0.82 and 1.00 ($P < 0.01$; 99 % confidence interval). The r values, which were close to 1, indicate that the passive samplers can be used reliably to monitor spatial changes in air quality or health risks. Furthermore, these passive samplers were both economical and easy to handle.

The average seasonal concentrations and range of concentrations observed at different microenvironments for NO_2 , SO_2 and O_3 with passive sampling are provided in Table [4](#page-6-0). Considering all the sampling points, the NO2 concentrations were 1.3–4.3 times higher in winter than in summer. The higher winter concentrations were mainly due to burning fossil fuels for space heating and transportation. Furthermore, the higher $SO₂$ concentrations observed in winter were almost all in microenvironments. In the residential parts of the city, fossil fuels with significant sulphur content, such as coal, yielded high $SO₂$ levels. The major sources of $SO₂$ pollution in the other parts of the city included vehicles using diesel fuel and industries. In recent years, heating in Kocaeli was carried out using natural gas. Therefore, compared with previous years, we observed a serious decrease in $SO₂$ concentration based on the transition from using coal to using natural gas.

Tropospheric O_3 is formed by photochemical production processes, including reactions of VOCs and NO_x in the presence of solar radiation. We observed higher O_3 concentrations during the summer period in outdoor environments, which makes sense since solar radiation is much higher in the summer than in the winter. However, higher $O₃$ concentrations were also measured in the summer than the winter in indoor environments, despite indoor environments not having any sources of O_3 . This finding can be explained by the increase in pollutant transport from outdoor environments to indoor environments because of ventilation, an effect that persists more in summer than in winter.

Seasonal variations in $NO₂$ and $SO₂$ levels likely arise from source variation, meteorology and limited vertical mixing in the atmosphere during the winter. Seasonal variations in O_3 levels are caused by limited or decreased photochemical reactivity in $O₃$ levels during the winter.

We prepared a daily change chart to better understand the changes in the sampled contaminants. The diurnal variations of the active sampling results for different microenvironments in outdoor (a) summer and (b) winter are shown in Fig. [2](#page-7-0). These data were obtained by taking the average of all outdoor microenvironments' concentrations for the summer and winter seasons. The diurnal cycle of pollutants for different microenvironments in the indoor locations (a) home, (b) office and (c) school in summer and (d) home, (e) office and (f) school in winter is shown in Fig. [3](#page-8-0). These data were also obtained by taking the separate averages of home, office and school indoor concentrations for the summer and winter seasons. The effect of the sources can be determined more easily depending on sudden increases or decreases in $NO₂$, $SO₂$ and $O₃$ concentrations on the day of the measurement by evaluating the time-dependent changes in the pollutants in the various microenvironments.

In summer, the outdoor SO_2 and O_3 concentrations increased during daylight hours, when anthropogenic activities were at high levels. Maximum values were observed in the morning and in the evening at rush hour for $NO₂$ $NO₂$ $NO₂$ in Fig. 2; this finding is a typical pattern of traffic for $NO₂$. However, the variation of $NO₂$ concentration was low throughout the day, possibly due to the following two reactions among NO, $NO₂$ and $O₃$ in the troposphere (Mavroidis and Chaloulakou [2011;](#page-15-0) Stranger et al. [2008](#page-15-0)):

$$
NO + O_3 \rightarrow NO_2 + O_2 \tag{1}
$$

$$
NO2 + hv + O2 \rightarrow NO + O3
$$
 (2)

The primary emission from a combustion source is NO. The NO in the atmosphere reacts with readily available O_3 and generates NO_2 . When there is sufficient solar irradiance, the $NO₂$ that is formed decomposes into NO and O_3 . The concentration of NO₂ increases either when there is too much NO and O_3 in the atmosphere or when there is insufficient solar irradiance. The accumulation of $NO₂$ in the atmosphere is a result of the domination of Eq. 1 over Eq. 2. In the early morning hours, when there is excess NO and $O₃$ in the atmosphere and the solar irradiance is insufficient, Eq. 1 dominates the system. As a result, $NO₂$ increases in the atmosphere. As the solar irradiance impinging upon the troposphere increases at midday, however, Eq. 2 begins to dominate, $NO₂$ decomposes into NO and the $O₃$ concentration increases. In the studies conducted by Castellano et al. [\(2009\)](#page-14-0), Mavroidis and Ilia [\(2012\)](#page-15-0), and Notario et al. ([2013](#page-15-0)), a similar $NO₂-O₃$ relationship was observed. Therefore, when the $NO₂$ concentration decreases, the O_3 concentration increases. In winter, the outdoor concentrations of $NO₂$ and $SO₂$ increased during daylight hours when anthropogenic activities were Table 4 The average value intervals and seasonal changes of the $NO₂$, $SO₂$ and $O₃$ concentrations for the different microenvironments

S/W summer/winter

at high levels (Fig. [3\)](#page-8-0). On the other hand, winter O_3 concentrations did not vary with time and were lower than in the summer. This finding can be explained by the lower levels of solar irradiance reaching the ground in Kocaeli in the winter. As given by Eq. [2,](#page-5-0) the decrease in solar irradiance reaching the troposphere in winter decreases ozone formation and hence allows $NO₂$ to accumulate in the atmosphere.

In indoor home environments, the concentration of NO2 increases early in the morning, primarily due to cooking activities. The influence of outdoor emissions might also play a role because the indoor concentrations of NO2 increased along with the outdoor concentrations.

In indoor office environments, $NO₂$ concentrations increase in the morning hours of the summer season. The concentrations of $NO₂$ started to decrease after midday and the SO_2 and O_3 concentrations increased, just as in outdoor environments. This finding shows that office environments in summer are not completely isolated from the outdoors; the intrusion of outdoor air decreases $NO₂$ concentrations and increases $SO₂$ and $O₃$ concentrations. In winter, the variations in the concentrations of inorganic gases were almost the same as in summer, except for O_3 , which was not produced in indoor environments.

During the summer, the concentrations of inorganic gases in schools' indoor environments started to increase after 8:00. Later, however, each pollutant exhibited different diurnal variation patterns. The concentrations of SO_2 increased until 10:00, remained almost constant throughout the day and decreased after 18:00. The $NO₂$ concentrations exhibited a bimodal diurnal variation, peaking both at 12:00 and at 19:00. The maximum O_3 concentration was observed at 15:00, when the $NO₂$ concentrations were at their lowest levels in the daytime. The diurnal variations of these gases were generally due to ventilation of the school rooms. While the first peak in the $NO₂$ concentration at 12:00 could be due to outdoor to indoor $NO₂$ transition, the second peak in the $NO₂$ concentration at 19:00 was likely the result of the reaction of O_3 with NO to form $NO₂$, as shown in Eq. [1.](#page-5-0) In winter, the school environment was ventilated poorly to ensure heat isolation. Although this poor ventilation lets less SO_2 and NO_2 penetrate from the outdoor environment, pollutants can be accumulated in the indoor air due to higher outdoor concentrations than in summer.

Spatial variations in $NO₂$, $SO₂$ and $O₃$ concentrations

Based on Table [4](#page-6-0), which lists the range of concentrations of $NO₂$, $SO₂$ and $O₃$ observed in different microenvironments, we can conclude several findings. In summer, the highest $NO₂$ concentrations in indoor environments were observed in homes (kitchens). Our findings reveal that natural gas and liquefied petroleum

Fig. 2 Diurnal cycle of the active sampling mean results for $NO₂$, $SO₂$ and $O₃$ in outdoor environments: a summer; b winter

Fig. 3 Diurnal cycle of the active sampling mean results for NO₂, SO₂ and O₃ in indoor environments: a home, b office, c school (summer); d home, e office, f school (winter)

gas (LPG) usage as a heating source in kitchens is a major source of $NO₂$ pollution in indoor environments. In office and school environments, the outdoor air is a possible source of $NO₂$ (Wichmann et al. [2010](#page-16-0); Jovanovic et al. [2014](#page-15-0)). The highest winter concentrations for $NO₂$ were measured in schools' outdoors, followed by the outdoors of homes and offices. Furthermore, high $NO₂$ concentrations were observed in the indoor environments of schools, followed by homes (kitchens) and offices.

The highest outdoor levels of $SO₂$ concentrations were obtained in schools, followed by offices and homes, in both summer and winter. These findings can be explained by the proximity of the sampled outdoor environment to pollution sources. Sulphur dioxide concentration levels were low and similar to each other in all of the indoor environments. As a result, we can state that there were no significant differences in the indoor environments of homes, offices and schools in terms of $SO₂$ concentrations. Furthermore, the same situation holds true for O_3 concentrations. Ozone is an outdoor

pollutant, so its concentrations change not only due to the type of microenvironment but also depending on the position of the sampling point in the area, the season and the state of ventilation.

To determine the effect of industry, traffic and space heating on the levels of the pollutants outdoors, we collected samples in urban, industrial and rural areas. The statistical values of these samples are listed in Table [5](#page-9-0). The higher concentrations of $NO₂$ and $SO₂$ in outdoor environments in urban areas suggest that traffic emissions are the most important source of $NO₂$ and $SO₂$ in the area. Likewise, $NO₂$ concentrations measured in outdoor environments in industrial areas are higher than the concentrations in outdoor environments in rural areas. The same effects were also observed for SO_2 ; in the summer, the high concentration of SO_2 in urban areas, compared with other areas, supports our hypothesis that motor vehicles burning diesel fuels could be responsible for this effect. The urban $SO₂$ concentration described in Table [5](#page-9-0) was higher in summer than in winter. The key point here is that the values

in Table 5 express the average of all urban points at which the study was carried out. When the comparison is made separately for the sampling points, it was observed that there were only some points for summer that increased the average, and at the other points, winter concentrations were higher than summer concentrations. Additionally, the points where the summer concentrations were higher than the winter concentrations were on the street and central points that were close to the traffic; the traffic is heavier at these points in summer than in winter. Therefore, it can be said that one of the most important sources that determine the $SO₂$ concentrations in summer is traffic.

Lower O_3 concentrations in residential and industrial areas, compared with rural areas, are usually reported in environmental studies. Ozone occurs in the presence of NO_x in the environment as a result of the photochemical reaction of hydrocarbons and CO (Chameides and Walker [1973](#page-14-0); Crutzen [1973](#page-15-0)). In places where photochemical reactions are completed, the concentration of $O₃$ is expected to be higher. Therefore, the concentration of O_3 in urban centres is lower than in rural areas because O_3 is consumed by NO (Brunekreef and Holgate [2002\)](#page-14-0). The results of O_3 observed in the study area are consistent with the mechanism explained in Eqs. [1](#page-5-0) and [2.](#page-5-0) The data in Table 5 verify that O_3 levels were low in places where $NO₂$ levels were high. Likewise, the data confirm that where $NO₂$ levels were low, O_3 levels were high.

We found that in winter there were higher concentrations of $NO₂$ and $SO₂$, as in the summer season. This effect held true not only in the outdoor environments of urban areas but also in all microenvironments. Therefore, one cannot suggest that emissions from

traffic are the most important source of $NO₂$ and $SO₂$. High concentration levels were measured in urban areas, even those far from industry and traffic. Additionally, winter concentrations for $SO₂$ in rural areas dramatically increased compared to the summer concentrations. This finding is explained by the effect of fossil fuels (fuel oil, coal) used for heating. The use of fossil fuels for heating, particularly in residential areas, adds to the emissions from motor vehicles in the city in winter; they are also the main cause of the increase in the levels of $NO₂$ and SO2 pollutant concentrations in winter. Fossil fuels are also used for purposes other than domestic heating; they are used in industry for heating or for the production of energy in cogeneration facilities. Employees in industry are allowed to go on holiday in the summer; this time is also when the annual maintenance activities are performed due to the reduction in production capacity. Increasing manufacturing activities in the winter correlates with increased use of fossil fuels. This rise, paired with traffic emissions and the combustion of fossil fuels, is responsible for the observed high levels of $SO₂$ and $NO₂$.

The concentration of O_3 in outdoor environments in winter was low in urban and industrial areas, just as in the summer; however, in rural areas far from pollution sources, the concentrations of O_3 were high. It is important to note that this trend was not as apparent as in the summer season.

The active sampling results for NO_2 , SO_2 and O_3 in outdoor environments in urban, industrial and rural areas of homes, offices and schools are shown in Fig. [4](#page-10-0) in hourly slices. These data were obtained by taking the average of all environments for the summer and winter seasons. Nitrogen dioxide concentrations

Fig. 4 Diurnal cycle of the active sampling mean results in the urban, industrial and rural areas. a NO₂, b SO₂, cO₃ in summer; d NO₂, e SO_2 , **f** O_3 in winter

increase more dramatically in summer than in winter in urban areas. On the other hand, the increase was more pronounced in winter than in summer in rural areas due to the burning of fossil fuels for heating purposes. Similarly, when we analysed the $SO₂$ diurnal results, we clearly found that urban areas exhibited a remarkable increase in $SO₂$ concentrations in the summer; however, rural areas showed similar results in winter, which indicates that the main source of $SO₂$ is traffic emissions in summer and fossil fuels in winter. Ozone showed the highest diurnal levels in rural areas, both in summer and winter (Fig. 4), as expected.

Ratios and correlations

To determine the influence of indoor and outdoor environment concentrations on personal exposure to pollutants, the ratios and correlation coefficient (r) were calculated for the concentrations obtained in the following environments: personal exposure/indoor environment (P/I) , personal exposure/outdoor environment (P/O) and indoor environment/outdoor environment (I/O).

The average of the ratios and the correlation coefficients are presented in Table [6.](#page-11-0)

The P/I ratios of the examined pollutants were in the ranges of $0.92-1.81$ and $0.57-1.83$ in summer and winter, respectively. The P/I ratios were lower in winter than in summer, on average. This finding shows that personal exposure levels are similar to the outdoor environment concentrations in summer and indoor environment concentrations in winter, because people spend more time indoors in winter than in summer.

Despite some of the seasonal differences, the fact that the P/I ratio is above 1 in some cases indicates that the influence of outdoor sources on the examined inorganic pollutants, in terms of personal exposure, was as strong as the influence of the indoor pollutants. The P/O ratios were in the ranges of 0.19–1.61 and 0.14–1.49 during summer and winter, respectively. The P/I and P/O ratios obtained for $NO₂$ were typically greater than 1; however, the rates obtained for SO_2 and O_3 were above 1 and below 1 for P/I and P/O , respectively. This situation points out the contribution of both indoor and outdoor environments to $NO₂$ exposure levels and the

Components	Summer					Winter						
	Home	Office	School	Home	Office	School	Home	Office	School	Home	Office	School
	Personal indoor correlation coefficients		Personal/indoor		Personal indoor correlation coefficients		Personal/indoor					
NO ₂	$0.7*$	$0.9*$	$1.0*$	1.0	1.0	1.8	$0.8*$	$0.9*$	$1.0*$	1.1	1.1	1.0
SO ₂	$0.9*$	$0.9*$	$1.0*$	1.2	0.9	1.4	$0.8*$	0.2	0.1	1.2	1.8	0.6
O ₃	$1.0*$	$1.0*$	0.7	1.6	1.6	1.3	0.4	0.6	0.6	1.3	1.0	0.9
	Personal outdoor correlation coefficients		Personal/outdoor		Personal outdoor correlation coefficients		Personal/outdoor					
NO ₂	0.4	$0.8*$	1.0	1.6	1.2	1.5	$0.5*$	0.3	1.0	1.1	1.5	0.8
SO ₂	0.4	0.2	0.6	0.5	0.4	0.3	0.1	-0.2	0.9	0.6	0.5	0.1
O ₃	0.5	0.6	0.1	0.2	0.2	0.2	-0.0	-0.4	$-1.0*$	0.7	0.5	0.6
	Indoor outdoor correlation coefficients		Indoor/outdoor		Indoor outdoor correlation coefficients		Indoor/outdoor					
NO ₂	0.5	$0.7*$	1.0	1.57	1.2	1.4	0.3	0.2	1.0	1.1	1.3	0.9
SO ₂	0.5	0.3	0.7	0.39	0.5	0.2	0.0	0.5	-0.3	0.6	0.3	0.4
O ₃	0.4	0.5	0.8	0.13	0.1	0.2	0.0	$0.7*$	-0.5	0.6	0.5	0.7

Table 6 Personal exposure/indoor environment, personal exposure/outdoor environment and indoor/outdoor environment ratios and correlation coefficients

 $*P<0.05$

contribution of outdoor environments to the exposure levels of SO_2 and O_3 .

We next examined Pearson correlation coefficients (r). In general, we found stronger correlations in both the summer and winter seasons $(P<0.05, 95\%$ confidence interval) between personal exposure and the indoor environment pollutant concentrations than between personal exposure and the outdoor environment pollutant concentrations. The exposure concentration of the sampled people and the concentration of the indoor environment were more strongly related in homes than in offices and schools. This finding is related to people who were sampled at home and spent more time in an environment where the sampling took place, in contrast to people sampled in offices or schools. However, the sampled people were not only affected by the pollutant concentration of the indoor environment but at the same time affected by the pollutant concentration of the outdoor environment as well. When analysing the correlation coefficients between the concentration of the outdoor environment and the concentration of personal exposure, a relationship was observed between them.

In Table 6, we show the relationship between indoor environment and outdoor environment, which we attempted to determine for the compounds examined in the sampled schools, offices and homes by calculating the ratios of I/O and the correlation coefficients.

If the I/O ratio exceeds 1, we can infer the presence of a strong indoor environment source of the investigated pollutant. When evaluating the I/O environment ratios of the investigated pollutants collectively, we recovered values in the ranges of 0.13– 1.57 during the summer and 0.33–1.34 during the winter. While the I/O ratio was above 1 for $NO₂$, it was less than 1 for SO_2 and O_3 . In the sampled environments, the indoor air $NO₂$ concentrations were higher than the outdoor concentrations. This finding clearly demonstrates that $NO₂$ pollution was primarily due to indoor activities, rather than outdoor activities, in the indoor environments. Despite some seasonal differences, the fact that the I/O environment ratios of SO_2 and O_3 were between 0.13 and 0.66 demonstrates that the examined inorganic pollutants were more often derived from outdoor environments. The low indoor O_3 concentration levels were due to low solar irradiance in indoor environments and the very fast reaction between O_3 and indoor surfaces or alkenes (Stranger et al. [2007;](#page-15-0) Jovanovic et al. [2014](#page-15-0); Waring and Wells [2014](#page-15-0)). When looking at the Pearson correlation coefficient (r) given in Table 6, in both summer and winter, a stronger general correlation was observed between the concentrations measured in homes and offices than in schools.

Comparison of the results with guidelines and the literature

The levels of the inorganic pollutants examined in this study were compared with national and international guideline values to obtain information about the level of pollution in the area of study. Due to the absence of regulations regarding indoor limit values on pollutants in Turkey and other countries, we assessed the outdoor environment pollution levels between this study and national and international limit values (Table 7). While all data obtained in the study were evaluated regarding the limit values given in the regulations, they were compared with the annual limit value by calculating the average of the outdoor environment data obtained from the summer and winter samplings.

The values for $SO₂$ obtained from our study are far below the limit values given by the Air Quality Assessment and Managements Regulations (AQAMR), the European Union (EU) and the United States Environmental Protection Agency (US EPA); the SO_2 concentrations in the area exceeded only the guideline values given by the World Health Organization (WHO). Due to the recent widespread use of natural gas in the region, both for domestic heating purposes and for industrial uses, the $SO₂$ levels were much lower than most of the limit values. However, the sulphur content of diesel fuels and some industrial activities still results in higher $SO₂$ levels than the limit values given by the WHO guidelines. In addition, the sulphur content of coal combustion in rural environments increases $SO₂$ concentrations during the winter. Alternative energy sources must be proposed to rural parts of the province to decrease $SO₂$

levels. The $NO₂$ concentrations obtained in this study were also below the limit values given in every guideline.

Despite lacking a direct evaluation, because the national and international limit values for O_3 are provided only per hour or on an 8-h basis, we can conclude that the pollution levels of O_3 were generally low.

We compared the indoor, outdoor and personal exposure levels of the area with similar studies from other parts of the world. In Table [8,](#page-13-0) we list the results obtained in this study and in other similar studies for inorganic gaseous pollutants $(NO₂, SO₂ and O3)$ that are widely studied in the literature. $NO₂$ concentration was determined in most of the indoor air pollutant studies because important indoor sources, other than the outdoor sources, affect indoor $NO₂$ concentrations. The indoor and outdoor $NO₂$ concentrations determined in Kocaeli were in the concentration range obtained from the literature (indoors $31-65 \text{ µg/m}^3$; outdoors $31-71 \text{ µg/m}^3$). The concentrations obtained from personal samplers for NO2 in summer and in winter were the lowest and highest concentrations obtained in the literature, respectively. The difference between the summer and winter season concentrations indicates that space heating in winter has the largest influence on $NO₂$ concentrations in Kocaeli.

Studies related to the determination of $SO₂$ levels, particularly studies of indoor air quality, are limited. The lowest and the highest indoor concentrations of $SO₂$ in the literature were 5 and 265 μ g/m³, respectively, in Hong Kong, China. The indoor $SO₂$ concentrations in Kocaeli were comparable to the numbers from most of the studies; however, excluding the study conducted in Taiyuan, China, the outdoor $SO₂$ concentrations were

	This study $(\mu g/m^3)$	$AQAMR^a (\mu g/m^3)$	EU guideline b $(\mu g/m^3)$	US EPA guideline c $(\mu g/m^3)$	WHO guideline ^d $(\mu g/m^3)$
SO ₂	Summer 19.1 Winter 23.2	225 (daily) 20 (annual)	125 (daily) 20 (annual)		20 (daily)
NO ₂	Summer 31.4 Winter 63.5	58 (annual)	40 (annual)	100 (annual)	40 (annual)
O ₃	Summer 40.1 Winter 7.1	120(8 h)	120(8 h)	147(8 h)	100(8 h)

Table 7 Comparison of outdoor average concentrations of this study with national and international guidelines

^a Turkish AQAMR (Air Quality Assessment and Management Regulations)

^b European Union (EU). Council Directive 1999/30/EC. 2002/3/EC

^c United States Environmental Protection Agency (US EPA), <http://www.epa.gov/ttn/naaqs/>

^d World Health Organization (WHO), <http://www.who.int/peh/>

Table 8 Comparison of the results with similar studies

^a Numbers in parentheses indicate the number of observations

slightly higher than the values reported in the literature. This fact could arise due to the use of high sulphurcontent coal and diesel fuel in the region.

The indoor, outdoor and personal concentrations of ozone in Kocaeli were found to be similar to the values reported in the literature.

Conclusions

The concentrations obtained for NO_2 , SO_2 and O_3 using both active and passive sampling techniques are similar to each other, which reveals that both sampling techniques can be used safely in sampling studies of indoor environments, outdoor environments and personal exposure.

When looking at the ratios of P/O and I/O in the entire data set for the assessment of the results obtained in both summer and winter sampling, the obtained rates for $NO₂$ are above 1 for both cases. On the other hand, the obtained rates for SO_2 and O_3 were found to be far below 1. This fact highlights the contribution of both indoor and outdoor environments to the $NO₂$ exposure levels of personal and indoor environments, and the contribution of outdoor environments to the exposure levels of SO_2 and O_3 . The fact that the P/I ratios are generally above 1 for each of the three pollutants shows that the indoor environment is not the only effect on the personal exposure concentrations.

The seasonal differences were found to be dependent on the type of pollutants and the levels of concentration. The concentrations of $NO₂$ and $SO₂$ measured in winter were higher than the levels measured in summer. The increase in the use of fossil fuels for heating purposes has a significant impact on the levels of $NO₂$ and $SO₂$. When analysing the seasonal differences of O_3 , the level of concentration measured in the winter due to the absence of photochemical reactions dependent on the intensity and duration of the sunlight was found to be significantly lower than in the summer.

When we analysed the concentration levels of NO2, SO2 and O3 pollutants in urban, industrial and rural areas, we obtained high concentration levels of $NO₂$ and $SO₂$ in the outdoor environment of urban areas in summer. The main reason for this finding relates to traffic emissions, because traffic is heavier in urban areas. The higher results of outdoor environment concentrations of $NO₂$ and $SO₂$ in industrial and rural areas in winter showed that using fossil fuels for heating purposes is the most significant emission source, together with traffic. We also recovered lower O_3 concentrations for residential and industrial areas, even though this same pollutant exhibited higher concentrations in locations far from its sources like rural areas.

Acknowledgments Financial support from the TÜBİTAK (The Scientific & Technological Research Council of Turkey) Grant (104Y275) is gratefully acknowledged.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

Informed consent Informed consent was obtained from all individual participants included in the study.

Ethical approval For this type of study, formal consent is not required.

This article does not contain any studies with animals performed by any of the authors.

References

- Baek, S. O., Kim, Y. S., & Perry, R. (1997). Indoor air quality in homes, offices and restaurants in Korean urban areas indoor/ outdoor relationships. Atmospheric Environment, 31, 529– 544.
- Barraza, F., Jorquera, H., Valdivia, G., & Montoya, L. D. (2014). Indoor PM_2 , in Santiago, Chile, spring 2012: source apportionment and outdoor contributions. Atmospheric Environment, 94, 692–700.
- Bracho, L. R., Suh, H. H., Oyola, P., & Koutrakis, P. (2002). Measurements of children's exposures to particles and nitrogen dioxide in Santiago, Chile. The Science of the Total Environment, 287, 249–264.
- Breysse, P. N., Buckley, T. J., Williams, D., Beck, C. M., Jo, S. J., Merriman, B., Kanchanaraksa, S., Swartz, L. J., Callahan, K. A., Butz, A. M., Rand, C. S., Diette, G. B., Krishnan, J. A., Moseley, A. M., Curtin-Brosnan, J., Durkin, N. B., & Eggleston, P. A. (2005). Indoor exposures to air pollutants and allergens in the homes of asthmatic children in inner-city Baltimore. Environmental Research, 98, 167–176.
- Brunekreef, B., & Holgate, S. T. (2002). Air pollution and health. Lancet, 360, 1233–1242.
- Castellano, M., Franco, A., Cartelle, D., Febrero, M., & Roca, E. (2009). Identification of NOx and ozone episodes and estimation of ozone by statistical analysis. Water, Air, and Soil Pollution, 198, 95–110.
- Challoner, A., & Gill, L. (2014). Indoor/outdoor air pollution relationships in ten commercial buildings: $PM_{2.5}$ and NO_2 . Building and Environment, 80, 159–173.
- Chameides, W., & Walker, J. C. G. (1973). A photochemical theory of tropospheric ozone. Journal of Geophysical Research, 78, 8751–8760.
- Chao, C. Y. H. (2001). Comparison between indoor and outdoor air contaminant levels in residential buildings from passive sampler study. Building and Environment, 36, 999-1007.
- Crutzen, P. J. (1973). A discussion of the chemistry of some minor constituents in the stratosphere and troposphere. Pure and Applied Geophysics, 106, 1385–1399.
- Demirel, G., Özden, Ö., Döğeroğlu, T., & Gaga, E. O. (2014). Personal exposure of primary school children to BTEX, $NO₂$ and ozone in Eskişehir, Turkey: relationship with indoor/ outdoor concentrations and risk assessment. Science of the Total Environment, 473–474, 537–548.
- Genç, D., Yeşilyurt, C., & Tuncel, G. (2010). Air pollution forecasting in Ankara, Turkey using air pollution index and its relation to assimilative capacity of the atmosphere. Environmental Monitoring and Assessment, 166, 11–27.
- Helaleh, M. I. H., Ngudiwaluyo, S., Korenaga, T., & Tanaka, K. (2002). Development of passive sampler technique for ozone monitoring. Estimation of indoor and outdoor ozone concentration. Talanta, 58, 649–659.
- Jones, A. P. (1999). Indoor air quality and health. Atmospheric Environment, 33, 4535–4564.
- Jovanovic, M., Vucicevic, B., Turanjanin, V., Zivkovi, M., & Spasojevic, V. (2014). Investigation of indoor and outdoor air quality of the classrooms at a school in Serbia. Energy, 77, 42–48.
- Langer, S., & Bekö, G. (2013). Indoor air quality in the Swedish housing stock and its dependence on building characteristics. Building and Environment, 69, 44–54.
- Lawrence, A., & Fatima, N. (2014). Urban air pollution & its assessment in Lucknow City—the second largest city of North India. Science of the Total Environment, 488–489, 447–455.
- Lee, S. C., & Chang, M. (2000). Indoor and outdoor air quality investigation at schools in Hong Kong. Chemosphere, 41, 109–113.
- Lee, H. S., Kang, B.-W., Cheongs, J. P., & Lee, S. K. (1997). Relationships between indoor and outdoor air quality during the summer season in Korea. Atmospheric Environment, 31(11), 1689–1693.
- Lee, K., Parkhurst, W. J., Xue, J. P., Ozkaynak, A. H., Neuberg, D., & Spengler, J. D. (2004). Outdoor/indoor/personal ozone exposures of children in Nashville, Tennessee. Journal of the Air and Waste Management Association, 54, 352–359.
- Mavroidis, I., & Chaloulakou, A. (2011). Long-term trends of primary and secondary NO2 production in the Athens area. Variation of the NO2/NOx ratio. Atmospheric Environment, 45, 6872–6879.
- Mavroidis, I., & Ilia, M. (2012). Trends of NOx, NO2 and O3 concentrations at three different types of air quality monitoring stations in Athens, Greece. Atmospheric Environment, 63, 135–147.
- Mayer, H. (1999). Air pollution in cities. Atmospheric Environment, 33, 4029–4037.
- Meng, Q., Williams, R., & Pinto, J. P. (2012). Determinants of the associations between ambient concentrations and personal exposures to ambient $PM_{2.5}$, NO_2 , and O_3 during DEARS. Atmospheric Environment, 63, 109–116.
- Menteşe, S., Mirici, N.A. Otkun, M.T., Bakar, C., Palaz, E., Taşdibi, D., Cevizci, S., Cotuker, O. (2015). Association

between respiratory health and indoor air pollution exposure in Canakkale, Turkey. Building and Environment, 93(1), 72– 83.

- Mraihi, R., Harizi, R.,Mraihi, T., & Bouzidi,M. T. (2015). Urban air pollution and urban daily mobility in large Tunisia's cities. Renewable and Sustainable Energy Reviews, 43, 315–320.
- Nopmongcol, U., Emery, C., Sakulyanontvittaya, T., Jung, J., Knipping, E., & Yarwood, G. (2014). A modeling analysis of alternative primary and secondary US ozone standards in urban and rural areas. Atmospheric Environment, 99, 266– 276.
- Norhidayah, A., Chia-Kuang, L., Azharb, M. K., & Nurulwahida, S. (2013). Indoor air quality and sick building syndrome in three selected buildings. Procedia Engineering, 53, 93–98.
- Notario, A., Bravo, I., Adame, J. A., Díaz-de-Mera, Y., Aranda, A., Rodríguez, A., & Rodríguez, D. (2013). Variability of oxidants $(OX=O3+NO2)$, and preliminary study on ambient levels of ultrafine particles and VOCs, in an important ecological area in Spain. Atmospheric Research, 128, 35–45.
- Pekey, B., & Özaslan, Ü. (2013). Spatial distribution of SO2, NO2, and O3 concentrations in an industrial City of Turkey using a passive sampling method. Clean: Soil, Air, Water, 41, 423–428.
- Radiello the radial diffusive sampler, Italy. Available at [http://www.radiello.com.](http://www.radiello.com/) Accessed on 15 Feb 2015.
- Rivas, I., Viana, M., Moreno, T., Bouso, L., Pandolfi, M., Alvarez-Pedrerol, M., Forns, J., Alastuey, A., Sunyer, J., & Querol, X. (2015). Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in PM2.5 in schools. Atmospheric Environment, 106, 129–138.
- Schindler, M., & Caruso, G. (2014). Urban compactness and the trade-off between air pollution emission and exposure: lessons from a spatially explicit theoretical model. Computers, Environment and Urban Systems, 45, 13–23.
- Stranger, M., Potgieter-Vermaak, S. S., & Van Grieken, R. (2007). Comparative overview of indoor air quality in Antwerp, Belgium. Environment International, 33, 789–797.
- Stranger, M., Krata, A., Kontozova-Deutsch, V., Bencs, L., Deutsch, F., Worobiec, A., Naveau, I., Roekens, E., & Grieken, R. V. (2008). Monitoring of $NO₂$ in the ambient air with passive samplers before and after a road reconstruction event. Microchemical Journal, 90, 93–98.
- Sudalma, S., Purwanto, P., & Santoso, L. W. (2015). The effect of $SO₂$ and $NO₂$ from transportation and stationary emissions sources to SO_4^2 ⁻and NO₃⁻in rain water in Semarang. Procedia Environmental Sciences, 23, 247–252.
- Szczurek, A., Maciejewska, M., Teuerle, M., & Wyłomańska, A. (2015). Method to characterize collective impact of factors on indoor air. Physica A: Statistical Mechanics and its Applications, 420, 190–199.
- Uchiyama, S., Tomizawa, T., Tokoro, A., Aoki, M., Hishiki, M., Yamada, T., Tanaka, R., Sakamoto, H., Yoshida, T., Bekki, K., Inaba, Y., Nakagome, H., & Kunugita, N. (2015). Gaseous chemical compounds in indoor and outdoor air of 602 houses throughout Japan in winter and summer. Environmental Research, 137, 364–372.
- Waring, M. S., & Wells, J. R. (2014). Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals

in residential indoor air: magnitudes and impacts of oxidant sources. Atmospheric Environment, 106, 382–391.

- Wei, J., Guo, X., Marinova, D., & Fan, J. (2014). Industrial SO₂ pollution and agricultural losses in China: evidence from heavy air polluters. Journal of Cleaner Production, 64, 404–413.
- Wichmann, J., Lind, T., Nilsson, M. A. M., & Bellander, T. (2010). PM2.5, soot and NO2 indoor outdoor relationships at homes,

pre-schools and schools in Stockholm. Sweden Atmospheric Environment, 44, 4536–4544.

Zhao, Z., Zhang, Z., Wang, Z., Ferm, M., Liang, Y., & Norback, D. (2008). Asthmatic symptoms among pupils in relation to winter indoor and outdoor air pollution in schools in Taiyuan, China. Environmental Health Perspectives, 116, 90–97.