

Determination of nitrogen dioxide, sulfur dioxide, ozone, and ammonia in ambient air using the passive sampling method associated with ion chromatographic and potentiometric analyses

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Abstract Concentrations of nitrogen dioxide (NO₂), sulfur dioxide (SO₂), ozone (O₃), and ammonia (NH₃) were determined in the ambient air of Al-Ain city over a year using the passive sampling method associated with ion chromatographic and potentiometric detections. IVL samplers were used for collecting nitrogen and sulfur dioxides whereas Ogawa samplers were used for collecting ozone and ammonia. Five sites representing the industrial, traffic, commercial, residential, and background regions of the city were monitored in the course of this investigation. Year average concentrations of ≤ 59.26 , 15.15, 17.03, and 11.88 $\mu\text{g}/\text{m}^3$ were obtained for NO₂, SO₂, O₃, and NH₃, respectively. These values are lower than the maxima recommended for ambient air quality standards by the local environmental agency and the world health organization. Results obtained were correlated with the three meteorological parameters: humidity, wind speed, and temperature recorded during the same period of time using the paired *t* test, probability *p* values, and correlation coefficients. Humidity and wind speed showed insignificant effects on NO₂, SO₂, O₃, and NH₃ concentrations at 95% confidence level. Temperature showed insignificant effects on the concentrations of NO₂ and NH₃ while significant effects on SO₂ and O₃ were observed. Nonlinear correlations ($R^2 \leq 0.722$) were obtained for the changes in measured concentrations with changes in the three meteorological parameters. Passive samplers were shown to be not only precise (RSD ≤ 13.57) but also of low cost, low technical demand, and expediency in monitoring different locations.

Keyword Nitrogen dioxide · Sulfur dioxide · Ozone · Ammonia · Determination · Ambient air · Ion chromatography · Potentiometry · Ion selective electrode

Introduction

The weather in Al-Ain city is tropical, deficient in rainfall, and characterized by two distinctive seasons; a dry hot spring–summer (April–November) with average temperature of 35°C, and a warm autumn–winter (December–March) with slight rainfalls and average temperature of 20°C. The city contains impressive number of parks and palms. Traffic congestion, cement, fertilizers and paint factories, and degradation processes of plants and sand dunes surrounding the city are the main sources for nitrogen dioxide, sulfur dioxide, ozone, and particulate matters (Yagoub 2004). The 2004 UAE Ministry of Health annual statistical report stated that out of 149,484 patients treated at Al-Ain public health clinics, 134,699 (90.1%) were suffering from allergic rhinitis, diseases of the upper respiratory tract, chronic bronchitis, asthma, and other diseases of respiratory system. This number represented around 46% of patients treated at public health clinics in the whole country (380,932 patients). As there were no reported data about the quality of the ambient air in the city, we have been motivated to measure NO₂, SO₂, O₃, and NH₃ in air as possible causes for such high incidence of respiratory diseases in the city. Concentration values of 14.82–27.86, 16.58–43.43, and 18.25–35.80 $\mu\text{g}/\text{m}^3$ were reported for NO₂, SO₂, and O₃, respectively, in some adjacent cities of Kuwait and Oman (Bouhamra and Abdul-Wahab 1999).

Passive samplers are small, silent, and reliable; do not need electricity; and are less expensive. They can be used for indoors and outdoors monitoring in rural, urban, arctic,

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and tropical environments where they can provide exposure profiles with high quality (Gorecki and Namiesnik 2002). Samplers do not need field calibration, air volume measurements, and technical demands at the sampling site. They are suitable for determining spatial distribution of gases and establishing atmospheric monitoring networks (Carmichael et al. 2003; Cox 2003; Cruz et al. 2004).

Passive samplers simplify the analytical procedure at the sampling step and minimize sample decomposition during transport and storage. Although its low sampling rates necessitate long sampling times at low concentrations, the time-weighted average concentrations of the analytes produced by the samplers are more useful in assessing long-term impacts of pollutants. Analytical results obtained by passive sampling can be affected by temperature, humidity, and air velocity. Detection limit is dependent on the sampling rate, time, and sensitivity of the detection systems used (Namiesnik et al. 2005).

Since the first sampler described by Palmes for collecting sulfur dioxide (Palmes and Gunnison 1973), several samplers developed by the Swedish Environmental Research Institute, Rupprecht and Patashnick Company (USA), Laboratory of Aerology in Toulouse (France), CSISRO (Australia), Radiello, and others. They generally rely on diffusion of contaminant molecules across concentration gradients defined by Fick's first law of diffusion. Diffused contaminants are trapped on filters impregnated with reagents consisted of NaOH, triethanolamine, Na₂CO₃, tetrachloro-mercurate, TEA, NaI + Na₂CO₃, citric acid, or phosphoric acid for trapping SO₂, NO₂, or NH₃ (Lan et al. 2004).

The IVL passive sampler was designed to avoid the effects of wind, temperature, humidity, interferences, and losses during storage. It was verified against established continuous measurement techniques. Accredited IVL samplers were used in the global atmospheric watch program (GAW) conducted by the World Meteorological Organization to measure SO₂, NH₃, and O₃ into 50 stations in Asia, Africa, South America, and Europe (Carmichael et al. 2003).

Ogawa passive samplers have been extensively used in monitoring SO₂, NO_x, O₃, and other gases by the American Environmental Protection Agency and Harvard School of Public Health. They were used in monitoring urban O₃ in national parks (Ray 2001), NO₂ emissions from highway traffic (Gilbert et al. 2003), and NO₂ in some Mexican–USA border cities. Good agreements between results from Ogawa's samplers and continuous gas analyzers were obtained (Mukerjee et al. 2004). Samplers developed by Warashina were applied to monitor SO₂, NO₂, NO, NH₃, HCl, HNO₃, HCOOH, and CH₃COOH concentrations in air (Lan et al. 2004).

Harvard samplers were used to measure outdoor, indoor, and school children's personal exposure of ozone. Weekly average outdoor concentrations of 0.011–0.030, 0.015–

0.042, and 0.0013–0.0064 ppm were reported for urban, suburban areas, and personal exposures, respectively. Air-conditioned homes displayed very low indoor O₃ concentrations relative to homes using open windows and fans for ventilation (Lee et al. 2004).

Several types of samplers have been used for monitoring ambient ozone in Europe (Blum et al. 1997; Bytnerowicz et al. 2002), North America (Brace and Peterson 1998; Cox and Malcolm 1999; Ray 2001; Bytnerowicz et al. 2001; Frączek et al. 2003), and at a global scale (Carmichael et al. 2003). Ogawa samplers have been the most commonly used in USA (Koutrakis et al. 1993). Correlation between ozone concentrations measured by Ogawa samplers and UV continuous monitoring gave linear correlations up to a dose of 52,500 ppb O₃×h with R²=0.9949. The reliability of the samplers for long time monitoring of O₃ (477 h at 110 ppb) was confirmed. The samplers have also shown very high precision with relative standard deviation of 4.8% (Bytnerowicz et al. 2004).

Several types of SO₂ passive samplers have been described. A comparison between SO₂ passive and active samplers at both urban and remote sites in Sweden demonstrated close agreement between the two methods within ±15% (Ferm and Svanberg 1998). Passive samplers' performances in determining SO₂ concentrations in tropical environment were compared with active methods (Cruz et al. 2004).

A poorly sensitive spectrophotometric method for determining NO₂ in air based on converting NO₂ into nitrite ions which was subsequently coupled with azodyes was reported (Pandurangappa and Balasubramanian 1996). Chemiluminescence sensitive methods based on catalytic reduction of NO₂ to NO which was subsequently reacted with ozone or luminal were also reported (Robinson et al. 1999; Mikuska and Vecera 2000). Laser-induced fluorescence detection was used in determining NO₂, but its high cost prevented it from popular use (Thornton et al. 2000; Matsumoto et al. 2001). NO₂ was also determined using optical sensors (Do and Shieh 1996), electrochemical sensors (Shimizu et al. 2000), and passive sampling methods (Yanagisawa and Nishimura 1982).

Sulfur dioxide in atmosphere is associated with adverse health effects, including respiratory and cardiovascular diseases. SO₂ exposure daily levels not exceeding 125.00 µg/m³ and mean annual levels below 50.00 µg/m³ are the maxima recommended by the World Health Organization guidelines (World Health 2000). Spectrophotometric (Segundo and Rangel 2001), chemiluminescence (Wu et al. 1998), ion chromatographic (Yang et al. 2007), spectrofluorometric (Yang et al. 2002), potentiometric (Ibrahim et al. 1996), and amperometric (Carballo et al. 2003) methods were reported for determining SO₂ in atmosphere. Online determinations of SO₂ in air based on sample collection using chromatomembrane cells or gas permeation denuders fol-

lowed by spectrophotometric flow injection analyses were also reported (Sriharathikhun et al. 2004; Guo et al. 2003). A method based on passive samplers was also used in monitoring of SO₂ (Yang et al. 2007).

Spectrophotometric, chemiluminescence, potentiometric, amperometric, and passive sampling methods were reported for determining ozone in ambient air (Eipel et al. 2003; Huang and Dasgupta 1997; Shiavon et al. 1990).

Colorimetric methods based on Nessler and Indophenol blue reagents are the most common methods for determining NH₃ (Stern 1968). The use of mercury or cyanide ions included in the two reagents make these methods hazardous. Methods based on potentiometry (Egan and Dubois 1974), ion chromatography (Kifune and Oikawa 1979), chemiluminescence (Demmers et al. 1998), denuders (Leuning et al. 1967), gas scrubbers (Fehsenfeld 1995), spectrophotometry (Przybylko et al. 1995), and remote detection using near infrared transmission (Christie et al. 2003) were reported. Direct readings of ammonia in atmosphere using bilayer lipid membrane sensor (Thompson et al. 1983), gas-sensitive semiconductor capacitor (Winquist et al. 1984), fiber-optic fluorescing sensor (Sellien et al. 1992), gas-sensitive electrode (Hjuler and Dam-Johansen 1993), and amperometric sensors (Strehlitz et al. 2000) were also reported.

As there are no reported data about the air quality of Al Ain city before the date of this study, this work aimed to determine the average concentrations of NO₂, SO₂, O₃, and NH₃ in the city ambient air. The second aim of this study was to find a probable cause for the relatively high incidences of acute respiratory attacks reported by the ministry of health annual statistical report in 2004. This report stated that around 46% of the patients treated at the public health clinics in the country suffered from acute respiratory diseases and were from the city inhabitants. Passive sampling extraction technique associated with ion chromatographic and potentiometric analyses have been used for this investigation.

Experimental

Materials and reagents

Analytical grade chemicals were used throughout. Sodium hydroxide, potassium hydroxide, sodium iodide, sodium nitrite, potassium carbonate, triethanolamine, hydrogen peroxide, citric acid, ammonium chloride, and EDTA were purchased from Sigma–Aldrich (St. Louis, MO, USA) or Merck (Darmstadt, Germany). Deionized water was used throughout.

Standard solutions

Standard solutions ranging from 1.0–20.0 ppm in nitrite, nitrate, and sulfate were prepared using 100 ppm stock

standard solution consisted of a mixture of nitrite, nitrate, and sulfate purchased from Dionex (Titan Way Sunnyvale, CA, USA).

A standard solution prepared by mixing 7.90 g NaI with 0.88 g NaOH into 100.0 ml methanol and stirred in ultrasonic bath was used as impregnation solution for the NO₂ samplers' filters.

A standard solution prepared by dissolving 5.60 g KOH into 50.00 ml methanol and mixed with 10.00 ml glycerol. The solution was made up to the 100 ml by methanol and used as impregnation solution for SO₂ samplers' filters.

A standard solution prepared by dissolving 0.3 g NaNO₂, 0.28 g K₂CO₃, and 1.00 ml glycerol into 100.00 ml of deionized water was used as impregnating solution for ozone samplers' filters.

A standard solution prepared by dissolving 2.00 g citric acid and 1.0 ml glycerol into 50.00 ml deionized water. The solution was made up to 100.00 ml by ethanol and used as impregnating solution for ammonia samplers' filters.

A 10⁻³-M triethanolamine and 0.3% hydrogen peroxide were used as extracting solutions for nitrite and sulfate ions, respectively, whereas deionized water was used for extracting nitrate and ammonium ions.

Apparatus

IVL passive samplers (Swedish Environmental Research Institute, Stockholm, Sweden) were used for collecting NO₂ and SO₂ from air. The sampler consisted of a bottom-lead, impregnation filter, passive sampler tube, Teflon filter; steel net, and front lead (Fig. 1a). The steel net and the Teflon membrane filter (Millipore filters, 1.0 μm pore size and 25 mm pore diameter) are used to prevent particles collection, turbulence inside the sampler, and to facilitate laminar diffusion inside the sampler tube. A Whatman-40 filter paper (Springfield Mill, Maidstone Kent, UK) was used as impregnating filters.

Ogawa passive sampler (Ogawa, Pompano Beach, FL, USA) was used for collecting O₃ and NH₃. The sampler consisted of a solid Teflon cylinder with two open, unconnected sides. Each side contains an impregnating cellulose filter mounted between two stainless steel screens (0.152 cm² open area, 0.02 cm thick) and situated behind a diffusion-barrier end cap containing 25 holes (0.785 cm² open area, 0.6 cm thick). The sampler body (6) has outer diameter of 2 cm and length of 3 cm. Two independent cavities, 1.4 cm inner diameter contain diffusive barrier end-caps (1), reactive filters (3) between the inner and outer stainless steel screens (2) and retainer rings (4) over base pads (5; Fig. 1b).

An ICS-90 ion chromatograph (Dionex, Titan Way Sunnyvale, CA, USA) supported with an AS9-SC anion analytical column and anion micro-membrane suppressor

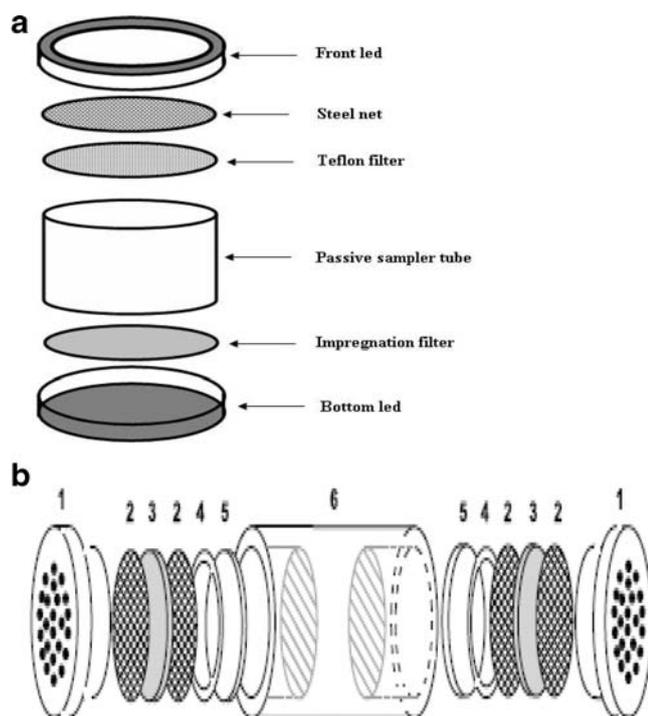


Fig. 1 Components of **a**: The IVL passive sampler used for collecting nitrogen dioxides and sulfur dioxide. **b**: The Ogawa passive sampler used for collecting ozone and ammonia: (1) Diffusive barrier end-caps, (2) inner and outer stainless steel screens, (3) reactive filters, (4) retainer rings, (5) over base pads, (6) sampler body

was used for measuring nitrite, sulfate, and nitrate ion concentrations. An ammonia ion selective electrode model IS 570-NH₃ (PHILIPS, Hamburg, Germany) was used for potentiometric measurements of ammonium ion.

Procedures

Sites selection

Sites represent the industrial, traffic, commercial, residential, and background regions of the city were selected for this study.

Impregnation

Samplers were cleaned with methanol and deionized water. IVL filters were placed on the sampler's bottom lids, and Ogawa filters were placed on Erlenmeyer flasks. Filters were impregnated using 50.0- μ l portions of any of the impregnation solutions given in "Standard solutions" and left to dry at 100°C for 30 min. The samplers were then mounted and placed in the transport boxes until deploying.

Deploying

Samplers were mounted on shielding plates (10 \times 15 cm², 5-cm rims) with their open sides oriented downwards to

protect them from direct exposure to sunlight, wind, dust, and rain falls. A double-sided adhesive tape and clips were used to mount the IVL and Ogawa samplers, respectively. Exposure times of 14 days were applied for all samplers, after which samplers were transferred to the lab for analyses. Blank samplers were treated similarly and kept in the laboratory during the sampling period.

Extraction

Samplers exposed to ambient air were collected; its filters were taken out using clean forceps and then immersed into 10.0-ml extraction solutions placed in clean plastic vials ("Standard solutions"). The vials were then closed and shaken carefully to extract the ions from the filters. The vials were then stored in a refrigerator at 4°C until analyses.

Analyses

Ion chromatography: Nitrite, sulfate, and nitrate ions were determined using IC. Dilute sulfuric acid was used as a regenerant and 1.8 mM sodium carbonate was used as mobile phase. Flow rate of 1.0 ml/min with 20 μ l injection volume and conductivity detector were used. Calibration graphs of integrated areas versus concentrations were constructed using standard solutions described in "Standard solutions." Samplers' extracts were measured under the same conditions.

Ion selective electrode: Calibration of ammonia ion selective electrode was done using standard ammonium chloride solutions in the concentrations range 10⁻⁴–10⁻¹ M. A 10.0-ml standard NH₄Cl solution was mixed with 1.0 ml of standard alkaline EDTA solution (0.1 M EDTA in 1.0 M NaOH). The solution was stirred for 1.0 min to release the ammonia gas and the potential was measured using the ammonia ISE electrode versus a calomel reference electrode. Calibration curve of potential in mV versus log concentration was plotted. Linear graphs with average slopes ranging from 52 to 55 mV were obtained; 5.0 ml portions of the extracts were put in the cell, mixed with 0.5 ml portions of alkaline EDTA solution, and stirred for 1.0 min. Potential were then recorded, and concentrations were determined from the calibration curve.

Calculations

Calculation of NO₂ concentration in air: Concentration of NO₂ was calculated using Eq. 1, given by the IVL protocol (Royset and Sivertsen 1998).

$$C_{(\text{NO}_2)} = \frac{m(\text{NO}_2^-) \times v}{t \times 0.0323} \quad (1)$$

where $C_{(\text{NO}_2)}$ is the concentration of the sampled gas in units of microgram per cubic meter, $m(\text{NO}_2^-)$ is the concentration of NO_2^- determined in the extract in the units of microgram per milliliter, v is the extraction volume of the filter and equals 5.0 ml for the IVL samplers used, t is the time of exposure in days (i.e., 24 h units) and 0.0323 is the sampler uptake rate for NO_2 in units of cubic meter per day.

Calculation of SO_2 concentration in air: The air concentration of SO_2 was calculated using Eq. 2, given by the IVL protocol (Royset and Sivertsen 1998).

$$C_{(\text{SO}_2)} = \frac{m(\text{SO}_4^{2-}) \times v \times 0.667}{t \times 0.0277} \quad (2)$$

where $C_{(\text{SO}_2)}$ is the concentration of the sampled gas in the units of microgram per cubic meter, $m(\text{SO}_4^{2-})$ is the concentration of SO_4^{2-} determined in the extract in the units of microgram per milliliter, v is the extraction volume of the filter in ml and equals 5.0 ml, 0.667 is the conversion factor from SO_4^{2-} to SO_2 , t is the time of exposure in days (24 h units) and 0.0277 is the uptake rate for SO_2 in units of cubic meter per day.

Calculation of O_3 concentration in air: The air concentration of O_3 was calculated using Eq. 3, given by Ogawa protocol (Harvard School of Public Health, Department of Environmental Health 2001).

$$C_{(\text{O}_3)} = \frac{m(\text{NO}_3^-) \times v \times 18.09}{t} \quad (3)$$

where $C_{(\text{O}_3)}$ is the concentration of the sampled gas in the units of microgram per milliliter, $m(\text{NO}_3^-)$ is the concentration of NO_3^- determined in the extract in units of microgram per milliliter, v is the extraction volume of the filter in ml, t is the time of exposure in minutes, 18.09 is the constant includes conversion factor from NO_3^- to O_3 and the uptake rate for O_3 (21.8 ml/min).

Calculation of NH_3 concentration in air: The air concentration of NH_3 was calculated using Eq. 4, given by Ogawa protocol (Yokohama City Research Institute for Environmental Science 2005, 2006).

$$C_{(\text{NH}_3)} = \frac{m(\text{NH}_3) \times v \times \alpha}{t} \quad (4)$$

where $C_{(\text{NH}_3)}$ is the concentration of the sampled gas in units of microgram per cubic meter, $m(\text{NH}_3)$ is the concentration of NH_3 determined in the extract in the unit of ng/ml, v is the extraction volume of the filter in ml and equals 8.0 ml, t is the time of exposure in minutes, and $\alpha=43.8$ ppb.min/ng.

Results and discussion

Ion chromatograms of the standard Dionex solutions consisted of nitrite, sulfate and nitrate ions at different concentrations were measured using 20.0 μl injection volumes, sodium carbonate ($1.8 \times 10^{-3}\text{M}$) as mobile phase and a flow rate of 1.0 ml/min. The peaks at 7.99 ± 0.10 ($n=4$), 12.99 ± 0.14 ($n=4$), and 18.59 ± 0.28 ($n=4$) minutes were assigned to nitrite, nitrate, and sulfate ions, respectively. Calibration graphs were obtained by plotting the integrated areas versus concentrations. Linear dynamic ranges from 0.5 to 100 ppm were obtained for the three investigated ions with detection limits of 0.1, 0.05 and 0.05 ppm, respectively.

Passive samplers deployed in different city sites were collected after 14 days exposure time intervals. A total of 26 batches of measurements over 52 weeks were carried out. NO_2^- , SO_4^{2-} , and $\text{NO}_3^- \text{NH}_4^+$ ions were extracted from the samplers and analyzed using ion chromatography or ion selective electrodes. Concentrations of the corresponding gas pollutants were calculated using Eqs. 1–4 (“Calculations”) The results obtained were correlated with the humidity, wind speed, and temperature meteorological parameters recorded by the local Weather Forecast Department during the same period of time.

Nitrogen dioxide

Nitrogen dioxide diffused through the sampler filter reacts with iodide ions and converted into nitrite ion according to equation (5)



Nitrite ions were extracted into 10^{-3}M triethanolamine and its concentrations were measured using IC. Atmospheric NO_2 concentrations were calculated using Eq. 5. Variations in NO_2 concentrations during the period Feb 2005 to Feb. 2006 for the industrial, traffic, commercial, residential, and background regions are shown in Fig. 2. NO_2 concentrations in ($\mu\text{g}/\text{m}^3$) and its descriptive statistical analysis are given in Table 1. Average concentrations from $35.50 \mu\text{g}/\text{m}^3$ in residential to $59.26 \mu\text{g}/\text{m}^3$ in traffic regions were obtained. Median concentrations between $34.12 \mu\text{g}/\text{m}^3$ (in commercial) and $60.15 \mu\text{g}/\text{m}^3$ (in the traffic) regions were obtained. High NO_2 concentrations at the traffic site can be attributed to traffic congestion caused by the large numbers of vehicles releasing NO_2 . The background concentrations varied from 1.0 to $7.03 \mu\text{g}/\text{m}^3$. Concentration values in the ranges of 9.18–55.44, 43.25–80.90, 26.03–51.38, and 26.46–52.32 $\mu\text{g}/\text{m}^3$ were obtained in industrial, traffic, commercial, and residential regions, respectively. These values generally lie below the air quality standards recommended by the local environmental agency— $150 \mu\text{g}/\text{m}^3$

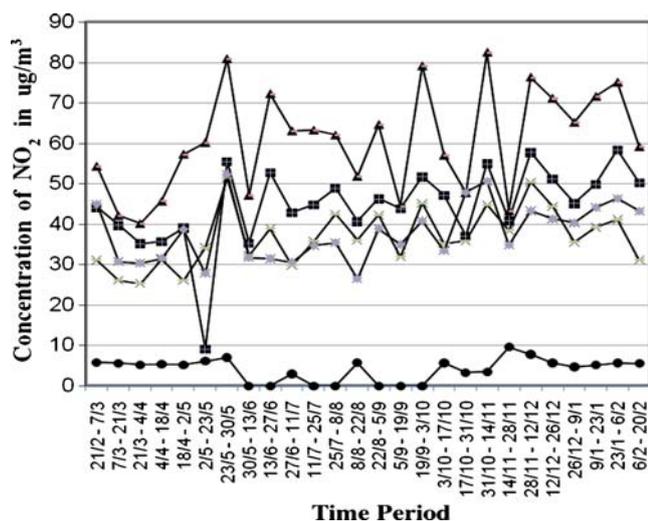
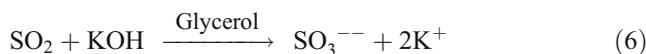


Fig. 2 Concentrations of NO_2 in ($\mu\text{g}/\text{m}^3$) at different sites versus time in the period from 21st Feb. 2005 to 20th Feb. 2006. Measurements were done in 26 batches each of which lasted 14 days exposure interval. (filled diamonds) background area, (filled squares) industrial area, (filled triangles) traffic area, (ex marks) commercial area and (asterisks) residential area

as 24-h average—and the WHO (Environmental Agency Abu 2004).

Sulfur dioxide

Sulfur dioxide diffused through the sampler filter reacts with KOH resulting in the formation of sulfite ions according to equation (6)

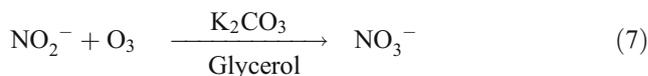


Sulfite ions produced were extracted into 0.3% hydrogen peroxide to be converted into sulfate ions whose concentrations were measured using IC. Atmospheric SO_2 concentrations were calculated using Eq. 6. Variations in SO_2 concentrations are shown in Fig. 3 for the industrial, traffic, commercial, residential, and background regions. SO_2 concentrations ($\mu\text{g}/\text{m}^3$) and its descriptive statistical analysis are given in Table 1. Average concentrations varying between $11.82 \mu\text{g}/\text{m}^3$ (in residential) and $15.15 \mu\text{g}/\text{m}^3$ (in traffic) regions were recorded. The median concentrations varied from $10.36 \mu\text{g}/\text{m}^3$ in residential to $142.47 \mu\text{g}/\text{m}^3$ in traffic regions. SO_2 concentrations in different sites were generally found close to each other (11.82 – $15.15 \mu\text{g}/\text{m}^3$). This might be attributed to the fact that sulfur dioxide originates from nonpoint sources scattered in the city such as aerosols, fertilizer, and emissions from plant degradation. The maximum SO_2 emission in the city was found during the summer time (July–August) where the temperature reaches 45 – 50°C (Fig. 3). The average SO_2 concentrations in all sites were found two to three times higher than the average background concentrations ($5.92 \mu\text{g}/\text{m}^3$). These values are

generally below the air quality standards recommended by the local environmental agency $150 \mu\text{g}/\text{m}^3$ as 24-h average (Environmental Agency Abu 2004) and the WHO.

Ozone

Diffused ozone through the passive sampler's filter oxidizes NO_2^- on the filter to NO_3^- according to equation (7).

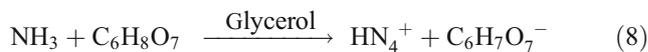


Nitrate ions produced were extracted into deionized water and determined using IC. Variations in O_3 concentrations in the period April 2005 to April 2006 are shown in Fig. 4 for the industrial, traffic, commercial, residential, and background regions. Table 2 shows the obtained O_3 concentrations ($\mu\text{g}/\text{m}^3$) and its descriptive statistical analysis. Average O_3 concentrations varying from $8.56 \mu\text{g}/\text{m}^3$ (in the traffic) to $17.03 \mu\text{g}/\text{m}^3$ (in the background) regions were obtained. The median concentrations varied from $7.82 \mu\text{g}/\text{m}^3$ (in the traffic) to $15.52 \mu\text{g}/\text{m}^3$ (in the background) regions. The highest ozone concentration was found in the background site ($17.03 \mu\text{g}/\text{m}^3$). The reason can be attributed to what is called “urban quenching.” Ozone concentrations are generally lower in urban areas than in rural areas because urban areas are having higher levels of nitrogen oxides. The latter react with ozone and resulting in decreasing its concentration (De Leeuw et al. 1999). Negative correlations between ozone and NO_2 concentrations can be deduced from data shown in Tables 1 and 2 as well as from Figs. 2 and 4.

Ozone in the industrial, traffic, commercial, and residential regions showed concentrations in the ranges of 6.85 – 21.26 , 4.67 – 18.77 , 7.75 – 17.61 , and 8.66 – $20.71 \mu\text{g}/\text{m}^3$, respectively. These values are generally below the air quality standards recommended by the local environmental agency; $120 \mu\text{g}/\text{m}^3$ as 8-h average and the WHO (Environmental Agency Abu 2004).

Ammonia

Ammonia gas diffused through the sampler's filter impregnated with citric acid is converted into ammonium ions as given in equation (8).



Ammonium ions produced were extracted into deionized water and potentiometrically determined using the ammonia gas ion selective electrode.

Variations in ammonia concentrations over the period April 2005 to April 2006 for the industrial, traffic, commercial, residential, and background regions are shown in Fig. 5. Concentrations in $\mu\text{g}/\text{m}^3$ and its descriptive

Table 1 Average concentrations in $\mu\text{g}/\text{m}^3$ and descriptive statistical analyses of nitrogen and sulfur dioxides in air at different city sites in the period 21st Feb. 2005 to 20th Feb. 2006

Sampling no.	Time period	Nitrogen dioxide					Sulfur dioxide				
		Background area	Industrial area	Traffic area	Commercial area	Residential area	Background area	Industrial area	Traffic area	Commercial area	Residential area
		1	21/2–7/3	5.81	44.12	54.28	31.05	44.90	3.40	5.83	8.62
2	7/3–1/3	5.60	39.70	42.10	26.00	30.70	2.80	6.40	7.60	6.10	4.00
3	21/3–4/4	5.20	35.20	40.10	25.30	30.30	2.70	5.50	6.40	5.30	3.80
4	4/4–18/4	5.35	35.72	45.66	31.23	31.55	4.24	4.63	5.78	6.01	3.47
5	18/4–2/5	5.21	39.05	57.27	26.03	38.68	5.58	12.78	12.36	11.86	14.53
6	2/5–16/5	6.16	9.18	60.15	34.12	27.75	3.95	8.43	14.83	7.64	5.88
7	16/5–30/5	7.03	55.44	80.90	51.38	52.32	8.74	15.17	18.53	11.87	10.36
8	30/5–13/6	<1.00	35.27	47.10	32.34	31.64	9.32	8.42	17.25	11.12	10.30
9	13/6–27/6	<1.00	52.71	72.22	38.91	31.40	13.07	17.20	22.02	14.45	26.32
10	27/6–11/7	2.93	42.88	63.07	29.79	30.58	12.34	11.90	15.90	13.29	13.38
11	11/7–25/7	<1.00	44.77	63.23	35.81	34.69	2.54	12.35	14.02	13.08	10.90
12	25/7–8/8	<1.00	48.91	61.98	42.42	35.40	3.54	16.99	10.79	17.78	12.12
13	8/8–22/8	5.74	40.65	51.80	36.03	26.46	25.27	30.55	35.08	29.70	30.08
14	22/8–5/9	<1.00	46.25	64.59	42.26	38.81	5.45	12.09	14.47	13.18	11.89
15	5/9–19/9	<1.00	43.84	44.30	31.94	34.91	3.98	10.44	12.56	11.41	10.18
16	19/9–3/10	<1.00	51.68	79.09	45.13	40.73	5.59	11.65	15.88	11.73	9.57
17	3/10–17/10	5.64	47.16	56.98	35.20	33.40	5.43	7.44	10.49	10.42	6.32
18	17/10–31/10	3.28	37.04	47.75	35.84	47.86	7.83	11.52	13.16	11.87	9.29
19	31/10–14/11	3.47	54.94	82.47	44.76	50.66	2.59	9.15	7.94	5.44	3.45
20	14/11–28/11	9.62	40.86	43.27	38.46	34.85	7.20	7.90	9.10	7.50	5.40
21	28/11–12/12	7.81	57.69	76.32	50.48	43.27	7.50	9.10	12.30	6.80	6.10
22	12/12–26/12	5.70	51.20	71.10	44.40	41.30	6.90	8.50	10.70	6.60	6.00
23	26/12–9/1	4.74	45.12	65.16	35.54	40.28	6.18	7.63	8.94	6.58	5.92
24	9/1–23/1	5.20	49.80	71.56	39.21	44.11	5.52	6.84	8.02	5.92	5.39
25	23/1–6/2	5.69	58.33	75.09	41.17	46.37	5.13	5.66	5.52	5.52	4.21
26	6/2–20/2	5.53	50.26	59.11	31.16	43.22	4.14	4.30	8.93	3.98	6.33
Mean		2.96	42.07	59.26	35.73	35.50	5.92	12.39	15.15	12.33	11.82
Median		2.93	43.84	60.15	34.12	34.69	3.95	11.90	14.47	11.86	10.36
SD		1.52	7.01	12.88	6.95	7.17	4.71	3.62	3.70	3.32	5.02
Minimum		<1.00	9.18	43.25	26.03	26.46	<1.00	4.63	5.78	4.93	3.47
Maximum		7.03	55.44	80.90	51.38	52.32	25.27	30.55	35.08	29.70	30.08

26 batches, 14 days each, of measurements were done

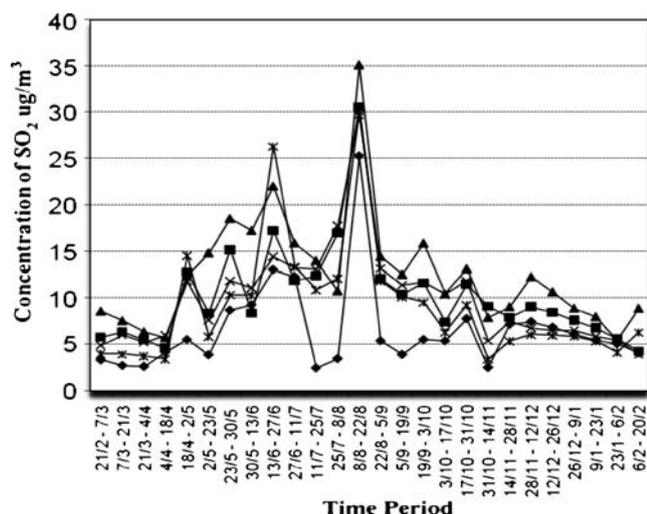


Fig. 3 Concentration of SO_2 in ($\mu\text{g}/\text{m}^3$) at different sites versus time in the period from 21st Feb. 2005 to 20th Feb. 2006. Measurements were done in 26 batches each of which lasted 14 days exposure interval. (filled diamonds) background area, (filled squares) industrial area, (filled triangles) traffic area, (ex marks) commercial area and (asterisks) residential area

statistical analysis are shown in Table 2. Average NH_3 concentrations varied from $7.81 \mu\text{g}/\text{m}^3$ (in the industrial) to $11.88 \mu\text{g}/\text{m}^3$ (in the traffic) regions were obtained. The median concentrations varied from 3.23 to $10.26 \mu\text{g}/\text{m}^3$ in the same regions. The highest year average for ammonia's concentration was found in the traffic site ($11.88 \mu\text{g}/\text{m}^3$). Variations in NH_3 concentrations in all sites were found generally similar, 0.69 – 38.67 , 1.80 – 43.93 , 0.71 – 41.24 , and 0.16 – $53.74 \mu\text{g}/\text{m}^3$ in industrial, traffic, commercial, and residential regions, respectively. The reason can be attributed to the fact that ammonia gas is produced from ammonia-containing fertilizers and wastewaters produced from the municipality treatment plant and used in irrigating parks and streets' green areas. This rationale can be supported by the observed maximum year average concentrations ($10.61 \mu\text{g}/\text{m}^3$) detected in the green background region outside the city. Ammonia detected in all sites were less than, the $350 \mu\text{g}/\text{m}^3$ as 1 h average, the standard recommended by the local environmental agency (Environmental Agency Abu 2004) and the WHO.

Statistical evaluation and effect of meteorological factors on pollutant levels

Average relative standard deviations in the ranges of 3.64 – 12.24 , 4.30 – 13.57 , 1.09 – 5.92 , and 3.39 – 13.23 ppm were obtained for the determinations of NO_2 , SO_2 , O_3 , and NH_3 , respectively. Year average standard deviations in the ranges of 2.99 – 12.88 , 3.32 – 5.02 , 3.60 – 4.50 , and 4.65 – 8.94 were, respectively, obtained for determined NO_2 , SO_2 , O_3 , and NH_3 . Standard deviation values obtained for NO_2 and NH_3

were shown relatively higher than SD values obtained for SO_2 and O_3 (Tables 1, 2).

Since meteorological parameters play an important role in the dispersion of emitted pollutants in atmosphere, the effects of humidity, wind speed, and temperature on the concentrations of studied gases were evaluated using the multiple regression analysis implemented in the SYSTATE software package. Table 3 shows the effects of the three parameters on the average concentrations of determined gases at different sites and on the overall averages.

The paired t test was applied to evaluate the correlations between changes in concentrations of measured gases and changes occurred in the three meteorological parameters during the time interval of this investigation; $t \leq 1.483$, 0.390 , 1.950 , and 0.998 were obtained for the effects of humidity on NO_2 , SO_2 , O_3 , and NH_3 concentrations, respectively. Changes in wind speed revealed $t \leq 1.452$, 1.175 , 1.829 , and 1.385 on NO_2 , SO_2 , O_3 , and NH_3 concentrations, respectively. These t values are less than the critical values indicating insignificant effects for humidity and wind speed on the concentrations of measured gases at 95% confidence level; $t \leq 1.609$, 1.414 , 4.165 , and 3.379 were respectively obtained for the effect of temperature on NO_2 , NH_3 , SO_2 , and O_3 . These values indicate that temperature had insignificant effects on NO_2 and NH_3 and significant effects on SO_2 and O_3 concentrations at 95% confidence level.

Probability p values in the range of 0.10 – 0.896 were obtained for the effects of humidity and wind speed on

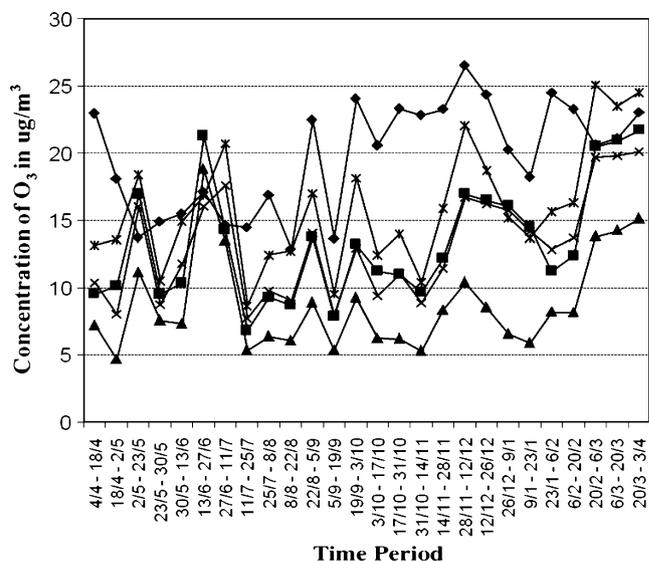


Fig. 4 Concentration of O_3 in ($\mu\text{g}/\text{m}^3$) at different sites versus time in the period 4th April 2005 to 3rd April 2006. Measurements were done in 26 batches each of which lasted 14 days exposure interval. (filled diamonds) background area, (filled squares) industrial area, (filled triangles) traffic area, (ex marks) commercial area and (asterisks) residential area

Table 2 Average concentrations in $\mu\text{g}/\text{m}^3$ and descriptive statistical analyses of ozone and ammonia in air at different city sites in the period 4th April 2005 to 3rd April 2006

Sampling No.	Time Period	Ozone					Ammonia				
		Background Area	Industrial Area	Traffic Area	Commercial Area	Residential Area	Background Area	Industrial Area	Traffic Area	Commercial Area	Residential Area
		1	4/4–18/4	22.92	9.57	7.16	10.37	13.15	5.81	2.02	11.89
2	18/4–2/5	18.10	10.15	4.67	8.04	13.57	8.83	8.32	8.94	0.73	
3	2/5–23/5	13.76	16.96	11.13	16.03	18.42	11.54	5.29	8.30	0.62	
4	23/5–30/5	14.91	9.53	7.57	8.76	10.54	1.51	38.67	41.24	53.74	
5	30/5–13/6	15.52	10.38	7.28	11.81	14.96	6.10	0.74	3.02	4.01	
6	13/6–27/6	17.14	21.26	18.77	16.05	16.82	3.05	4.06	10.20	< 1.00	
7	27/6–11/7	14.66	14.29	13.47	17.61	20.71	10.26	9.68	10.38	0.99	
8	11/7–25/7	14.49	6.85	5.34	7.75	8.66	4.33	21.36	3.57	< 1.00	
9	25/7–8/8	16.89	9.30	6.35	9.75	12.45	18.27	1.65	14.71	10.89	
10	8/8–22/8	12.86	8.71	6.04	9.08	12.72	11.02	10.47	7.87	8.18	
11	22/8–5/9	22.44	13.75	8.88	14.06	17.01	9.02	14.59	39.59	20.81	
12	5/9–19/9	13.67	7.87	5.33	8.01	9.54	50.91	24.33	15.38	13.40	
13	19/9–3/10	24.01	13.20	9.24	12.93	18.15	10.58	13.32	6.68	21.25	
14	3/10–17/10	20.57	11.22	6.22	9.40	12.44	3.67	14.30	3.26	0.54	
15	17/10–31/10	23.27	11.01	6.17	11.06	13.99	7.71	11.90	9.65	0.52	
16	31/10–14/11	22.80	9.67	5.29	8.88	10.40	4.83	2.04	1.32	0.50	
17	14/11–28/11	23.23	12.20	8.32	11.46	15.90	7.95	0.91	< 1.00	10.56	
18	28/11–12/12	26.46	16.97	10.38	16.69	22.06	4.41	0.69	1.31	4.01	
19	12/12–26/12	24.30	16.50	8.52	16.22	18.71	9.60	1.30	7.98	28.79	
20	26/12–9/1	20.24	16.08	6.55	15.75	15.19	13.92	2.41	13.34	1.08	
21	9/1–23/1	18.23	14.49	5.89	14.21	13.70	16.48	7.84	15.69	1.30	
22	23/1–6/2	24.45	11.22	8.18	12.86	15.66	8.47	1.06	11.98	14.87	
23	6/2–20/2	23.23	12.39	8.14	13.70	16.32	3.09	1.90	27.79	33.06	
24	20/2–6/3	20.57	20.48	13.79	19.68	25.06	14.25	1.11	1.11	4.91	
25	6/3–20/3	21.10	20.94	14.22	19.80	23.50	15.23	1.53	1.43	4.67	
26	20/3–3/4	23.00	21.70	15.10	20.10	24.51	14.93	1.62	0.90	5.35	
Mean		17.03	11.68	8.56	11.56	14.36	10.61	7.81	10.70	9.65	
Median		15.52	10.15	7.28	10.37	13.57	8.93	3.23	8.62	4.79	
SD		4.09	4.362	3.61	3.90	4.50	4.65	6.80	8.94	6.56	
Minimum		12.86	6.85	4.67	7.75	8.66	1.51	0.69	< 1.00	< 1.00	
Maximum		24.01	21.26	18.77	17.61	20.71	50.91	38.67	41.24	53.74	

26 batches, 14 days each, of measurements were done

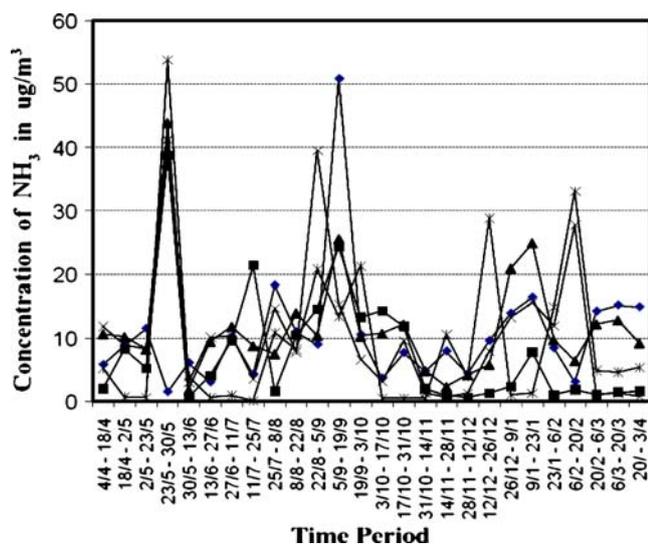


Fig. 5 Concentrations of NH_3 in ($\mu\text{g}/\text{m}^3$) at different sites versus time in the period 4th April 2005 to 3rd April 2006. Measurements were done in 26 batches each of which lasted 14 days exposure interval. (filled diamonds) background area, (filled squares) industrial area, (filled triangles) traffic area, (ex marks) commercial area and (asterisks) residential area

measured gas concentrations. These values indicated insignificant correlations between the two parameters and NO_2 , SO_2 , O_3 , and NH_3 concentrations at 95% confidence level. Temperature had shown insignificant correlations with SO_2 and O_3 concentrations as shown by the low probability p values obtained ($p=0.002$ – 0.016). The effects of temperature on NO_2 and NH_3 gave significant correlations as indicated by the p values of 0.122–7.47 obtained at 95% confidence level.

Average correlation coefficients between the four pollutants' concentrations and the three meteorological parameters are given in Table 3. Values between 0.200 and 0.722 were obtained indicating nonlinear correlations.

Conclusion

Concentrations of nitrogen dioxide, sulfur dioxide, ozone, and ammonia were determined over a year using the passive sampling associated with ion chromatographic and potentiometric detections. IVL samplers were used for collecting NO_2 and SO_2 whereas Ogawa samplers were

Table 3 Effects of temperature, humidity, and wind speed meteorological parameters on the average concentrations of gas pollutants at different sites and on the overall averages of all sites

Site	Temperature		Humidity		Wind Speed		R
	t test	P value	t test	P value	t test	P value	
Nitrogen dioxide							
Industrial	1.123	0.283	1.483	0.152	1.452	0.168	0.518
Traffic	0.469	0.644	0.679	0.504	0.536	0.597	0.249
Commercial	1.609	0.122	1.326	0.198	1.319	0.201	0.459
Residential	0.853	0.403	0.448	0.658	0.723	0.478	0.475
Overall Average	0.709	0.486	1.135	0.296	1.114	0.277	0.438
Sulfur dioxide							
Industrial	3.470	0.002	0.328	0.746	1.175	0.253	0.692
Traffic	2.943	0.008	0.225	0.824	0.261	0.797	0.659
Commercial	4.165	0.000	0.390	0.700	0.806	0.429	0.765
Residential	3.084	0.005	0.048	0.962	1.082	0.291	0.680
Overall Average	3.615	0.002	0.222	0.826	0.882	0.387	0.722
Ozone							
Industrial	2.724	0.012	0.715	0.482	1.065	0.298	0.556
Traffic	3.379	0.003	1.950	0.064	1.829	0.100	0.634
Commercial	2.605	0.016	0.678	0.505	0.558	0.582	0.544
Residential	2.737	0.012	0.939	0.358	0.869	0.394	0.541
Overall Average	3.004	0.007	1.087	0.289	1.107	0.280	0.575
Ammonia							
Industrial	1.414	0.171	0.133	0.896	0.701	0.491	0.471
Traffic	0.326	0.747	0.637	0.531	0.283	0.780	0.138
Commercial	0.415	0.682	0.998	0.329	1.385	0.180	0.299
Residential	0.608	0.549	0.272	0.788	0.463	0.648	0.159
Overall average	0.322	0.750	0.398	0.694	0.839	0.411	0.200

R correlation coefficient

used for collecting O₃ and NH₃. Five sites represent the industrial, traffic, commercial, residential, and background regions of the city were monitored in the course of this investigation. Concentrations lower than standards recommended for ambient air by the Local Environmental Agency and the World Health Organization were obtained. Detected concentrations were also found comparable to reported concentrations in some adjacent (Bouhamra and Abdul-Wahab 1999) and worldwide cities (Carmichael et al. 2003). Passive samplers were shown to be not only precise (RSD≤13.57) but also of low cost, low technical demand, and expediency in monitoring different locations.

Statistical evaluations of results obtained with meteorological parameters recorded during the same period of time were performed; *t* test revealed insignificant effects for humidity and wind speed on NO₂, SO₂, O₃, and NH₃ concentrations at 95% confidence level. Insignificant effects for temperature on NO₂ and NH₃ concentrations while as significant effects on SO₂ and O₃ concentrations were observed. The probability *p* values gave insignificant correlations between each of humidity and wind speed and concentrations of the four measured gases at 95% confidence level. Temperature showed significant correlations with SO₂ and O₃ and insignificant correlations with NO₂ and NH₃ concentrations. Nonlinear correlations ($R^2 \leq 0.722$) between the concentrations of the four measured gases and changes in the three meteorological parameters were obtained.

The low concentration of measured gases excluded them from being the possible cause for the high incidence rate of acute respiratory attacks reported in the city during the year 2004 (90.1% of patients treated at the city public health clinics). Therefore, the finger was pointed out towards particulate matters (PM) originated from sand dunes surrounding the city and those produced as a consequence of the second Gulf War occurred in 2003. Gas pollutants and PM measured in some gulf cities, by the US Army Environmental Hygiene Agency, 9 months after the first Gulf War in 1991, showed normal concentrations for the former and two to five times greater concentrations than the US standard (150 µg/m³) for the latter. PM consists of 75% calcium and silica (originated from sand) and 10–23% soot (originated from oil well fires and industrial sources) were obtained. This condition was most likely repeated in the region after the second Gulf War occurred in 2003. Particulate matters are known to penetrate the upper part of the airways and lung and can go deeply reaching the alveolar region. Sand and dust PM irritate skin and sensitive membranes of the eyes, nose, and throat and aggravate sinus and asthmatic conditions. Exposure to silica particulates can lead to cough, runny nose, shortness of breath, and the development of a benign, nonprogressive pneumoconiosis referred to as “Desert Lung Syndrome” (Winkenwerder 2002). Pollens and bacterial infections

could possibly be of minor contributions but unfortunately there are no reported statistical records about that.

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