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Investigation of gaseous pollutants in residential-industrial area: Ambient levels, temporal variation and health risk assessment

Ahmad Tarassoli, Abbas Esmaili Sari*, Nader Bahramifar

Department of Environment, Faculty of Natural Resources and Marine Science, Tarbiat Modares University, Imam Reza Street, Noor, Mazandaran, Iran

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CORRESPONDING AUTHOR:

esmaili@modares.ac.ir
Tel: (+98 12) 26253101
Fax: (+98 12) 26253101

ABSTRACT:

Introduction: The purpose of the current study was to investigate the ambient concentration levels of ground-level ozone (GLO), nitrogen dioxide, and sulfur dioxide with temporal variations and to determine the risk of exposure to their pollutant on public people living in this area.

Materials and methods: In the present study, GLO, NOx and SO_2 concentrations were monitored using an ambient analyzer during the period of April to September 2018.

Results: The obtained results demonstrated that the average concentrations of SO_2, NO_2 and GLO in the INZ station was significantly greater than the two other evaluated stations (i.e. SHV and CMC). The corresponding values for the measured parameters in INZ station was almost 8.9, 7.2 and 11.9 times higher than those in SHV station, however, 4.8, 5.3 and 2.9 times greater than of ones in CMC station, respectively. The average values of SO_2 and NO_2 concentrations in the INZ varied from 97.2 to 128.1 μg/m^3 in the evening hours and from 50.2 to 62.3 μg/m^3 in the morning hours respectively. Also, the lowest concentration of NO_2 was observed during afternoon hours when GLO showed a peak. The maximum pikes of GLO concentration were observed at 13:00 PM with 249.3 μg/m^3. Results of human health risk assessment indicated acceptable risk (hazard quotient (HQ) values< 1) for non-carcinogenic adverse health effect.

Conclusion: The findings in the present study can be useful in developing control-based strategies for primary pollutant emissions, and also GLO formation, improve air quality and reducing possible risks on human health. Policymakers should enforce the limits on the release of pollutants into the atmosphere in the study area by strengthening existing legislation.

Introduction

Gaseous pollutants due to the effects on atmospheric chemistry and the health of living organisms have been one of the most important challenges of the past few decades. The sources of air pollution are natural such as forest fires, volcanic, wetland, and salt spray or manmade such as industrial production, the burning of fossil fuels and transport modes [1].

The increasing activities of oil and gas refineries and petrochemical industry are the major causes of environmental air pollution. The dominant pollutants emitted from this industry into the environment are volatile organic compounds (VOCs),

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nitrogen oxide (NOx) and sulfur dioxide (SO_2), particulate matter (PM), carbon monoxide (CO), etc., that are listed as criteria pollutants in most of the country's air quality standards [2, 3]. Ground level ozone (GLO) is an important oxidant in the troposphere that is created through chemical reactions between NOx and VOCs in the presence of sunlight. The GLO can be considered as an indicator of manmade pollution in megacities or industrious areas [4]. Previous studies have shown that exposure to gaseous pollutants such as NO_2, SO_2, and GLO can result in short-term effects such as eye inflammation, throat, and upper respiratory tract infections, hospital admissions and long-term health effects such as lung cancer, heart disease, damage to the nerves or brain and death [5, 6]. Generally, the effect level usually depends on the concentration of chemicals, the duration of exposure, the gender and age of the person [7]. South Pars gas field is the world's largest gas field which is located on the border line between Iran and Qatar in the Persian Gulf [8]. For this reason, extensive equipment of the natural-gas refining and a large number of petrochemicals has been developed in the area. Naturally, the activities of these industries are accompanied by the release of various air pollutants. The pollutants released from these industries can not only create a problem in the vicinity of these sources, but can also travel long distances. The purpose of this study were to investigate the ambient concentrations of NO_2, SO_2, and GLO, temporal distribution, the relationship between measured pollutants and meteorological factors and finally, to determine the health risks of exposure to pollutants at three age groups (up to 6, 6-12, and >12 years).

Materials and methods

Sites description

South Pars is located Southeastern province of Bushehr, Iran. This location is limited to the village of Shirino at the western point, from the east to the city of Chah-Mobarak, from the south to the Persian Gulf, and from the north to the foothills of the Zagros Mountains [9]. The three target locations were selected in South Pars zone: Shirino village (SHV), Industrial zone (INZ) and Chah-Mobarak city (CMC).The details regarding the monitoring locations and their characteristics are shown in Table 1. The industrial zone ranges of longitude 52º 32′ to 52º 42′ and latitude 27º 28′ to 27º 34′ and includes 8 gas refineries and 12 petrochemical complex. Fig. 1 shows the geographical location to the study location.

Measurement techniques and instruments

Ambient concentrations of gaseous pollutants SO_2, NO_X and GLO were measured during a six month period (from April to September 2018). The SO_2 pollutant was monitored continuously using an ambient analyzer (model EC9852 Sulfur Compound analyzer). The EC9852 analyzer is an ultraviolet (UV) fluorescence spectrometer designed to continuously measure low concentrations of various sulfur compounds in an ambient air through switch cycling. NO_X pollutants were monitored using an ambient analyzer (model EC9841 nitrogen oxides). This analyzer uses

Table 1. Description of monitoring locations and its characteristics

Stations	Abbreviation	Latitude, Longitude	Altitude	Position relative to the industrial zone	Distance to industrial zone
Shirino village	SHV	27º 38′10″ N, 52º 27′32″E	5 m	Northwest	10 km
Chah-Mobarak city	CMC	27º 21′ 59″ N, 52º 47′46″ E	26 m	Southeast	18 km
Industrial zone	INZ	27º 32′01″ N, 52º 33′56″ E	4 m		

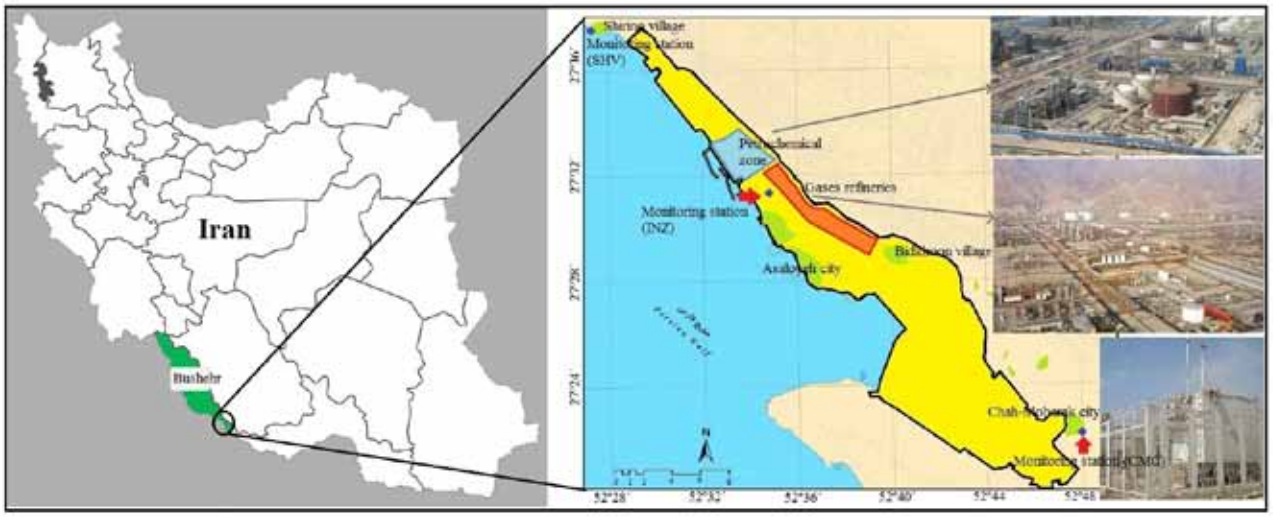


Fig. 1. Geographical location of the study area.

gas-phase chemilluminescence detection to perform continuous analysis of nitrogen oxides. For EC9852 and EC9841 analyzers, sampling flow rate was 640 mL/min and the detection limit was less than 0.5 ppb [10, 11]. GLO was monitored with an automatic ozone analyzer (model EC9810 series O_3) operated on the principle of a non-dispersive ultraviolet (UV) photometer which alternately switches a selective ozone scrubber in and out of the measuring stream and computes the ratio of transmitted light giving an accurate and reliable measure of ozone concentration in the presence of common atmospheric compounds. Sampling flow rate and detection limit were 0.5 L/min and ≤ 0.5 ppb, respectively [12, 13]. All equipment were made by Ecotech P/L in Australia. The instruments were placed at 2 m from the ground level. Instrument maintenance was done by following the manufacturer guidelines and calibration was done every two months.

Meteorological parameters (temperature, humidity, solar radiation, wind speed, and direction) were continuously measured during the sampling campaign from the Asaloyeh airport meteorological location.

Health risk assessment method

For calculation of health risk people living in the investigated regions, the non-carcinogenic risk was evaluated according to the US Environmental Protection Agency protocol [14]. The general equation of the potential dose and the toxicological risk to SO_2, NO_2 and GLO are described Eq. (1).

$$I = C_A \times \frac{IR \times FR \times FA \times ET \times EF \times ED}{BW} \times \frac{1}{AT} \quad (1)$$

Non-carcinogenic hazards were determined using a term called hazard quotient (HQ). HQ is expressed as the probability of an individual suffering an adverse effect. An HQ ≤1 shows that adverse health effects are not likely to occur, and thus can be considered to have negligible hazard, even to a sensitive individual. An HQ >1 shows that there may be some risks to sensitive individuals as a result of exposure. HQ was calculated using Eq. (2).

$$HQ = \frac{I}{REL} \quad (2)$$

Reference exposure levels (RELs) is the dose at which adverse health impact will occur in exposed individuals when compared with the unex-

Table 2. The variables used in the calculation of exposure rate and risk assessment factors

Variable	Description	Value			Unit
		up to 6 y	6-12 year	>12 year (Adult)	
I	Pollutant intake dose		--		µg/kg/day
C	Contaminant concentration in ambient air		--		mg/m^3
IR	Inhalation rate	0.25	0.46	0.83	m^3/ h
BW	Body weight	16	29	70	kg
ED	Duration of exposure	5	6	58	year
ET	Exposure time	12	12	12	h/day
EF	Exposure frequency	365	365	365	day/year
AT	Averaging time for				
	- Noncarcinogenic	1825	2190	21170	days
FR [a]	Rate of retention factor of air inhaled	1	1	1	
FA [a]	Rate of absorption factor of air inhaled	1	1	1	
HQ	Hazard quotient				unitless number
REL [b]	Reference exposure level				
	O_3		18.0E+01		$\mu g/m^3$
	NO_2		47.0E+01		$\mu g/m^3$
	SO_2		66.0E+01		$\mu g/m^3$

[a] This value was assumed as 1 representing the worst-case scenario and potential impact on people's health.
[b] As adopted by the Office of the Environmental Health Hazard Assessment

posed individuals. RELs are designed to protect the most sensitive individuals [15, 16].

Statistical analysis

Statistical analysis was carried out using EXCEL (version 2007) and SPSS packaging (version 22). Nonparametric Spearman's rank correlation was used to measure the compounds and meteorological parameters. For the analysis of wind rose was done using the WRPLOT View from Environmental Lakes Inc.

Results and discussion

Meteorological data

Meteorological conditions may have a significant impact on the distribution of pollutants [17]. The average temperatures (T), relative humidity (RH), solar radiation (SR), and wind speed (WS) during the study periods are shown in Table 3. The climate of the study location is a hot semi-arid (BSh) matched Koppen climate classification system. T and SR exhibited the highest monthly averages in August (35.5ºC - 30.2 W/m^2) and the lowest in April (26.1ºC - 25.6 W/m^2) months, respectively. For RH, the highest and lowest monthly averages are in the months of September (57%) and May (45.5%), respectively. The WS showed the highest monthly averages in the month of July (7.6 m/s) and the lowest in the month of April (4.7 m/s). Wind rose for a period of six month was provided based on the meteorological data as shown in Fig. 2. During the measurement period, the dominant winds in the study location were

Table 3.The average (min-max) of T (ºC), SR (W/m2), RH (%), and WR (m/s) at the study period

	April	May	June	July	August	September
T	26.1 21.3 - 31.2	30.5 24.9-35.5	33.5 28.5-36.7	34.5 31.4-38.4	35.5 33.7-38.4	34.1 32.2-36.8
RH	54.2 31.0-72.5	45.5 28.5-59	51.7 33.5-70.5	52.0 37.5-62.5	55.9 39.5-67.0	57.0 40.0-73.0
SR	25.6 8.6-40.4	25.9 10.5-41.2	27.8 13.5-42.1	29.1 13.4-44.7	30.2 14.9-45.5	28.6 13.6-43.5
WS	4.7 2.9-6.5	4.9 3.4-6.4	5.7 4.1-7.3	7.6 4.1-11.2	6.1 3.5-8.8	5.3 2.8-7.9

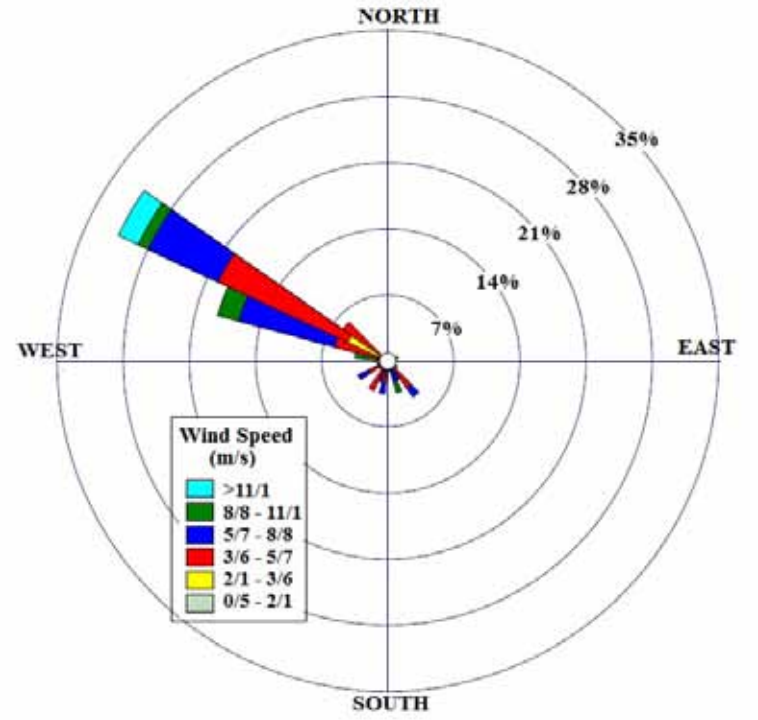


Fig. 2. Influence of geographical location and wind direction on air pollutants at the study period (from April to September 2018)

from the northwest to the southeast.

Concentration of pollutants

The concentration average of SO_2, NO_2, and GLO (µg/m^3) at the three stations are shown in Table 4. The highest average SO_2 concentrations were recorded in the INZ station during the month of June (the average concentration of 102.9 µg/m^3) and July (the average concentration of 99.4 µg/m^3). While, the highest average SO_2 concentration was observed in the CMC and SHV locations with 21.3 and 11.4 µg/m^3 in the months of June and May, respectively. With regard to the dominant wind direction from northwest to the southeast, the concentration of SO_2 pollutants in CMC point was higher than SHV point. The main sources that contribute to the emission of SO_2 are power generators fueled by coal and nat-

ural gas processors [18]. In this study, the highest concentration levels in the INZ location could be explained through the low efficiency of sulfur recovery unit (SRU) and the burning sour gas in refineries flares. SRU in the refinery converts H_2S extracted through sweetening units to sulfur. The results of a study at industrialized zone in Turkey showed that the average concentration for SO_2 in petroleum refinery and petrochemicals complex was 54.0 μg/m^3 [19]. The results of studies conducted in Puertollano, Spain, showed that the maximum SO_2 concentration in the winter season was 34.4 μg/m^3 [20].The average SO_2 concentration in three megacities (Beijing, Shanghai, and Guangzhou) from April 2014 to March 2015 was 15.5, 17.9, and 16.0 μg/m^3, respectively [21].

SO_2 diurnal variations of all the three air quality monitoring locations are as shown Fig. 3. The highest concentrations of SO_2 were recorded during the evening time in the INZ location. The results show that the average values of SO_2 concentrations in the INZ location varied from 83.1 to 104.8 μg/m^3 in the morning hours. Similarly, the average values of SO_2 concentrations varied from 72.5 to 102.6 μg/m^3 in the day-time, and from 97.2 to 122.1 μg/m^3 in the evening time.

The highest and lowest average concentration was observed for NO_2/(NOx) in the INZ location to be 50.8/(71.6) and 39.5/(53.2) μg/m^3 in the months of May and August, respectively. Gas turbines and steam boilers were important emission contributor source of the NOx pollutants in the South Pars zone. With an increase in distance from the main sources, the concentrations at SHV and CMC locations are low. The highest values reached in the SHV and CMC locations are 7.1/(12.4) and 9.5/(12.1) μg/m^3 in the months of May and June, respectively.

The concentration of NO_2 in the INZ location is higher than in the Puertollano of Spain (27.0 μg/m^3) [22], at a heavily industrialized region in Western Turkey (20.0 μg/m^3) [19], and in an industrial location in Incheon City, Korea (0.03 μg/m^3) [23]. The average NO_2 concentrations for the diurnal cycle from April to September, 2018 are as shown in Fig. 4. During the study period in the INZ location, the average values of NO_2 concentrations varied from 50.2 to 62.3 μg/m^3 in the morning hours. Similarly, the average values of NO_2 concentrations varied from 22.3 to 53.8 μg/m^3 in the day-time, and from 27.5 to 53.6 μg/m^3 in the evening time. This phenomenon can be attributed to the day-night differences in the chemical removal of NOx via photo-oxidation reactions.

Table 4. The concentration average (standard deviation) of the inorganic pollutants (μg/m^3) in the study period.

locations	pollutants	April	May	June	July	August	September
SHV	SO_2	10.4±0.6	11.4±0.7	10.4±0.8	11.1±0.5	10.7±0.5	10.9±0.8
	NO_2	6.6±1.6	7.1±1.7	6.8±1.2	6.7±1.1	6.7±1.5	6.5±1.8
	GLO (8h)	8.1±1.3	9.6±2.2	8.4±1.6	10.2±2.1	10.9±2.1	10.5±2.7
INZ	SO_2	97.4±17.7	85.9±10.7	102±11.4	99.4±13.0	98.6±4.4	97.7±8.0
	NO_2	40.7±11.2	50.8±12.1	48.7±12.9	50.7±10.7	39.5±4.0	45.0±9.1
	GLO (8h)	57±12.4	59.9±19.0	75.8±16.3	129.5±39.6	119.9±37	106.8±34.5
CMC	SO_2	19.4±2.6	20.9±3.0	21.3±2.7	20.2±3.3	20.1±2.7	18.4±3.3
	NO_2	7.6±1.7	7.4±2.1	9.5±1.2	9.1±1.0	7.8±1.5	7.7±2.4
	GLO (8h)	32.5±7.7	33.5±7.7	42.0±10.2	44.9±11.5	43.1±9.5	44.1±9.4

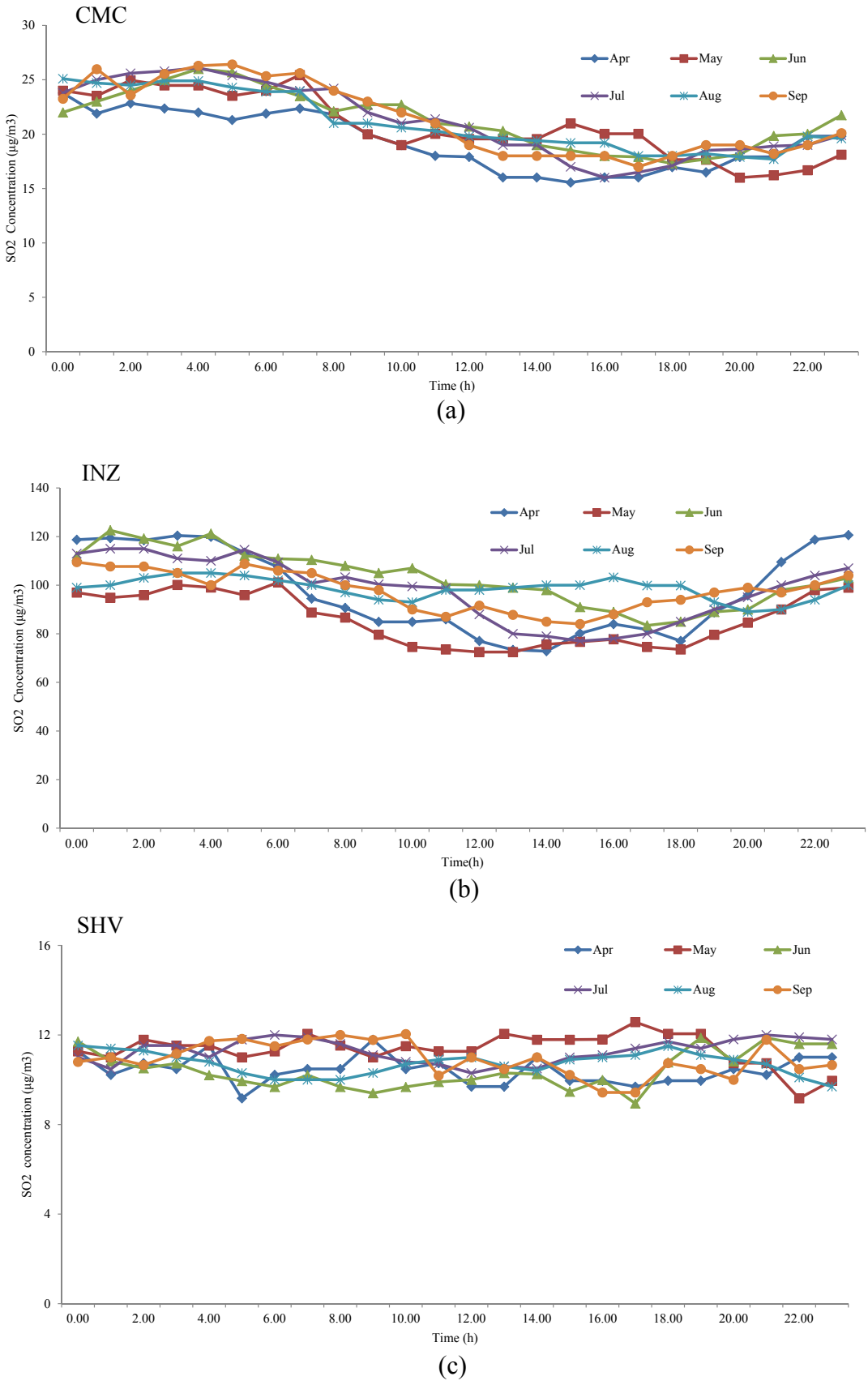


Fig. 3. Average daily variation of SO2 concentration for SHV (a), INZ (b) and CMC (c) locations

GLO diurnal variations of all the three air quality monitoring locations are as shown Fig. 5. The variation trend of GLO concentration in all the locations is similar. GLO concentration tends to increase from 08:00 AM in April to June, while tends to increase from 06:00 AM in June to September. In this study, the maximum pikes of GLO concentration were observed at 13:00 PM. The highest concentration (8 h) was observed in the month of July in CMC and INZ with 44.9 and 129.5 μg/m^3, while in SHV, the highest values are reached in the month of August with 10.9 μg/m^3 (Table 4). However, the maximum hourly value was registered in INZ location with 249.3 μg/m^3 in the month of June. While in CMC and SHV locations, the maximum hourly value was 82.1 and 13.8 μg/m^3 in the month of July and September, respectively. The lowest GLO concentration was recorded in the month of April in the three locations.

Relationship between measured pollutants and meteorological factors

Spearman's correlation coefficients of average measured pollutants and average meteorological parameters are shown in Table 5. This study showed significant negative correlation between SO_2 and NO_2 with temperature, solar radiation, and wind speed in each of the three locations at 0.01 levels. The concentration of SO_2 and NO_2 decreases with increase in temperature and solar radiation in these locations. Also, when wind speed is high in this location, pollutants are diluted by dispersion. GLO is known to be a secondary air pollutant and several studies have shown that the formation process mainly depends on the temperature, solar radiation, NOx emissions and ambient concentration of VOCs [24]. In this study, a negative correlation of NO_2 and GLO was found, while there was a significant positive correlation between GLO and temperature and solar radiation. This may be in line with the aforementioned titration effect, where NO reacts with GLO to give NO_2. During daytime, photolysis of NO_2 causes the formation of GLO using the following reactions:

$$NO_2 + h \rightarrow NO + O \qquad \lambda \leq 424 \text{ nm} \qquad (1.3.4)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2.3.4)$$

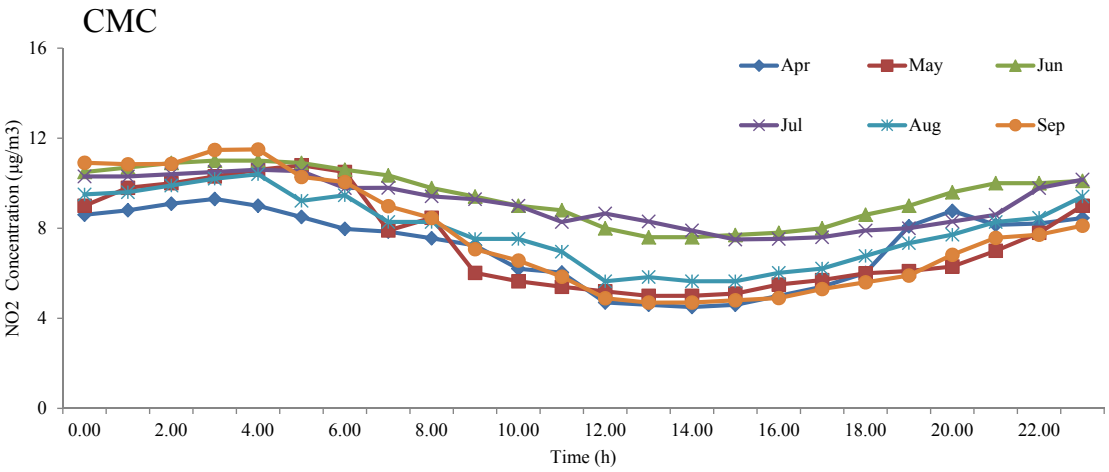
But during nighttime, the process of titration by NOx reduces the ozone levels:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (3.3.4)$$

In this study, there was a significant negative correlation between GLO and relative humidity. This phenomenon shows that high concentrations of water vapor eliminate part of the contamination from the atmosphere through chemical reaction (acid rain) or precipitation [25].

Health risk

SO_2 exposure causes mucus secretion and decrease in respiratory function of humans due to irritation and airway obstruction. Asthmatics in general are highly sensitive to SO_2 exposure at short time periods [26]. In this study, the highest concentration of SO_2 for 1 and 24 h was 128.1 and 114.7 μg/m^3, respectively in the INZ location. These values do not exceed the alert threshold set by the European Environment Agency as 1and 24 h value of 350 and 125 μg/m^3. Although, 24 h value was exceeded when compared with guideline values of 20 μg/m^3 established by the World Health Organization [27, 28].The estimation of risk for exposures to SO_2 in the INZ location showed that non-cancer risk lower than 1.0 (HQ<1.0) for up to 6 years (2×10^{-2}), 6-12 years



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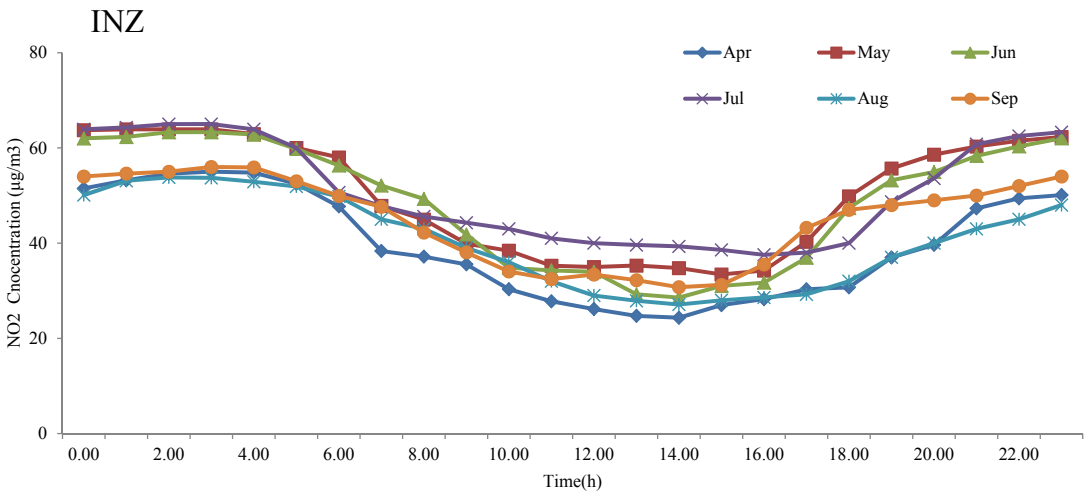

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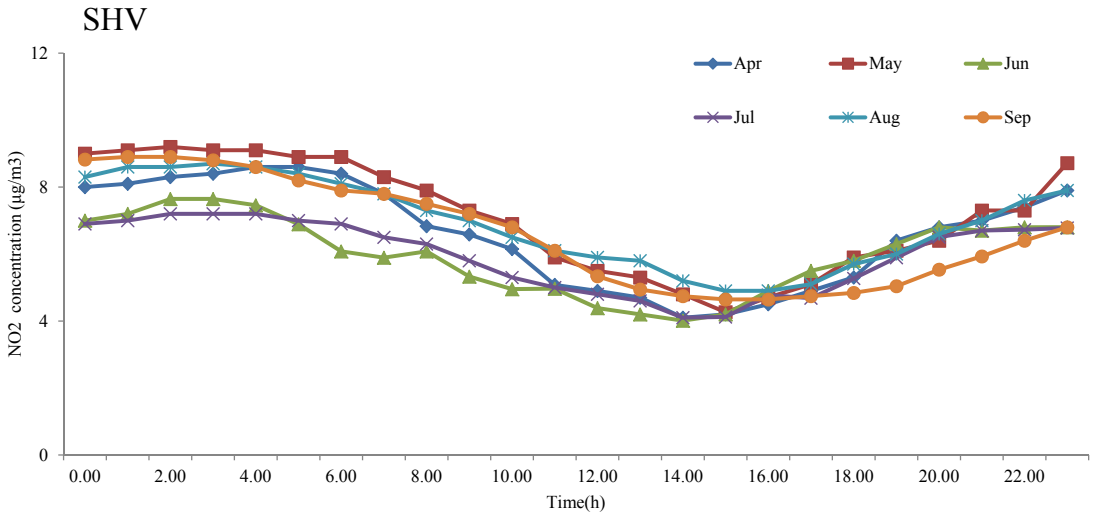

(c)

Fig. 4. Average daily variation of NO_2 concentration for SHV (a), INZ (b) and CMC (c) locations

(3×10^{-2}), and >12 years (2×10^{-2}).

The highest concentration of NO_2 for 1 h was 128.1 μg/m^3 in the INZ location. These values do not exceed the alert threshold set by the European Environment Agency and World Health Organization as 1 h value of 200 μg/m^3 [27, 28]. NO_2 exposure causes decrease in lung function and aggravate respiratory diseases. The estimation of risk for exposures to NO_2 in the INZ location showed that non-cancer risk is lower than 1.0 for up to 6 (2×10^{-2}), 6-12 (3×10^{-2}), and >12 (1×10^{-2}) years.

The highest concentration of GLO for 8 h average was 129.5 μg/m^3 respectively in the INZ location. These values exceeded the alert threshold set by the European Environment Agency and World Health Organization as the maximum daily 8 h average value of 120 and 100 μg/m^3, respectively[27, 28]. Estimation of risk for acute exposures to GLO in the INZ location showed that non-cancer risk lower than 1.0 for up to 6 (13×10^{-2}), 6-12 (14×10^{-2}), and >12 (11×10^{-2}) years.

Conclusion

In this study, analysis of measurements were presented for SO_2, NO_2 and GLO in the industrial zone (INZ) and two villages situated in the northwest (SHV) and southeast (CMC) of the INZ from April to September, 2018. The concentration levels of the measured pollutants at INZ location were higher than CMC and SHV locations. Some factors such as the geographic characteristics of this location are effective on weather conditions and prevent gas emissions. Therefore, the gas remained at the vicinity of the foot of the mountains; as a result, pollutants are concentrated on the surface of the location. In this location, because the dominant wind direction is from northwest to southeast, therefore, the concentration of pollutants in the city of Chah-Mobarak was found to be higher than the village of Shirino. The present results show that the GLO concentration slowly increases after the solar radiation rising, reaching a maximum value during the daytime and subsequently, decreases until the next morning. This is due to the photochemical formation of GLO. A correlation between GLO and NO_2/NO has been found. This result can be useful for the most appropriate prediction and control strategies of GLO formation. Health risk assessment based on the data estimated, showed that the HQ of non-carcinogenic risk for SO_2, NO_2 and GLO pollutants in all the locations was lower than 1 showing no concern of increased health risk.

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Competing interests

The authors declare that there are no competing interests.

Ethical considerations

Ethical issues (Including plagiarism, Informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

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