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The Ground Ozone Variations with UV Radiation during Winter and Spring Seasons in 2007 over Makkah.

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Abstract. This study has measured the incident solar UV radiation and the concentrations of three pollutants of O_3, NO_2 and NO in atmosphere of Makkah, Saudi Arabia (322m altitude, 21^o.24 N, 39^o.51E) during to different seasons of winter and spring in 2007. A moderate bandwidth filter radiometer (GUV-2511) that has six channels in the UV region with centre wavelengths at 305, 313, 320, 340, 380 and 395nm and bandpass functions of approximately 10 nm was used to measure the incident UV radiation. The concentrations of O_3 and NOx were measured by two ambient Monitors of APOA-360 and APNA-360 respectively. The two periods of measurements were from 8^{th} to 17^{th} of Zul-Hijah 1427L (from 28/12/2006 to 6/1/2007) for winter time and between 21/4 and 1/5/1428L (8 -17/5/2007) for spring season. It was found that the highest concentrations of approximately 135, 200 and 365 mg/m^3 were recorded for O_3, NO_2 and NO pollutants respectively with maximum incident UV radiation at midday of 210 mW/cm^2 during winter time (Zul-Hijah 1428L). However, in spring season, the maximum recorded values for O_3, NO_2 and NO species were approximately 147, 100 and 95 mg/m^3 respectively with largest incident UV radiation at midday of 300 mW/cm^2. The ozone concentration may significantly increases if two factors (high vehicles emission and large incident solar UV radiation) combined together, which could occur when the hajj month synchronizes with spring or summer seasons in the coming few years. As a result, a big challenge of air quality in Makkah and hence pilgrims health problems will be encountered, otherwise new means of transportation and air quality controlled are required.

Introduction

Ozone is present in the troposphere and can play a significant role in the chemical processing of trace gases, pollutants and natural. Although concentrations of stratospheric ozone have declined in Polar Regions and in the Antarctic spring in particular[1], the concentration of tropospheric ozone (the ground ozone) has increased, especially in the mid-latitude Northern Hemisphere[2]. Therefore there are two very different, clearly marked and largely unrelated problems of atmospheric ozone. Tropospheric ozone represents only 10% of the total O_3 content of the atmospheric column. However, its concentration and its evolution are important for the Earth's biosphere. Ozone can be a powerful green house gas, contributing 18% to the global greenhouse effect[3]. Moreover, ozone can contribute to the oxidizing capacity of the troposphere since it is an oxidant, which, via photodissociation and the subsequent reactions of its photoproducts, leads to the formation of hydroxyl radical (OH), a very efficient oxidising agent in the troposphere. The ground ozone is produced through photochemical processes from the oxides of nitrogen ($NOx=NO_2+NO$) and volatile organic compounds (VOCs) in the presence of solar ultraviolet (UV) radiation ($200 \leq \lambda \leq 400$ nm).

Ozone is a very reactive and toxic gas and the most irritant of the common air pollutants. Its effects on both human health and plant life have been established as deleterious. At low concentrations, it can induce an inflammatory response in the lung[4]. On penetration into the respiratory system ozone can react strongly with a wide range of organic molecules. Ozone is such a reactive molecule that it is unable to penetrate for any distance through the system without undergoing reaction [5]. In the USA it has been observed that the long-term exposure to ozone, at average concentrations, was associated with a chronic decline in lung function. The World Health Organisation (WHO) reported that the air quality recommended level for ozone concentration is ranging between 150-200 $\mu g/m^3$ per h or between 100-120 $\mu g/m^3$ per 8 h[6, 7]. However, the relationship between daily emergency admissions for lower respiratory disorders and fixed 8-h mean ozone concentrations was examined in London from April 1987 to February 1992[8]. They found indications of a threshold value for a fixed 8-h mean in ozone in London in the range of 80-100 $\mu g/m^3$. Other studies have demonstrated that ozone levels in London are associated with changes in daily mortality rates[2]. They reported that the WHO has summarised a large number of studies from North America as well as Europe and presented exposure response relationship. The WHO advice was that in using the linear exposure-response relationship, no threshold should be assumed[2]. An impact of ozone on vegetation in the UK has also been demonstrated. Experimental evidence points out that current level of ozone in the UK, in certain summers, strongly affect crop yield, tree physiology and growth, and species composition of plant communities[2].

The ground ozone level concentration is very dependant on the sources such as vehicles and industries as well as the solar UV radiation. Some studies showed that increasing industrialization in the northern hemisphere has led to an increase in tropospheric ozone in this hemisphere[9-11]. In the troposphere there were significant spatial variations in the trends with largest increases found over Europe at two stations (Hohenpeissenberg and Payerne)[11]. These stations showed increases of about 2%yr^{-1} below 10km (300 mbar) for 1970-1991[11]. However, there was no long-term change in ozone over Canada where the small increase of ozone (<1%yr^{-1}) has occurred in summer[11]. In the southern hemisphere, mainly covered by oceans, the trend is not yet well established because it is based on few stations measurements such as the world meteorological organisation's baseline station at Cape Point (34°S, 18°E) in South Africa [12-14]. Perhaps because the majority of the observing stations are located in the northern hemisphere, where most of the emissions of the trace constituents (CO_2, O_3, CH_4, N_2O, CFCs and CO) are taking place. In the USA observations of ozone and O_3 precursors taken from aircraft flights over Houston showed that high concentrations of reactive volatile organic compounds (VOCs) in the Houston atmosphere have resulted in O_3 exceeding 500μg/m^3, the highest value observed in the USA from 1997 to 2002[15]. However, recent study has calculated ozone production rates and their sensitivity to NOx and VOCs in the same city, using observed concentrations as inputs to a steady state box model[16]. They found that the ozone production rates varied from nearly zero to 310 μg/m^3 per hour. They confirm that the differences in ozone production was depending on precursor concentrations, namely, radical sources, NOx and VOCs. Under conditions where the ozone production rates was greater than 50 μg/m^3 per hour, there was a potential to produce enough same-day O_3 to transform a typical regional background into a severe O_3 episode[16]. They reported that six times such cases were observed, in Nashville, Philadelphia, and Houston, with elevated O_3 concentrations in the afternoon (260-422μg/m^3) following a morning in which ozone production rates was between 50-280 μg/m^3 per hour. Moreover, high ozone production rates occurred when NOx concentrations were between 9-45 ppb and OH-VOC reactivity was above 5s^{-1}[16].

Locally, the first study investigates the ground ozone level during hajj period from 12th to 15th in 1399L (1979) in Mina valley (412 m altitude, 21°.25 N, 39°.52 E), the holy place for pilgrimages, in Makkah in Saudi Arabia, was performed by the Hajj research centre (The Custodian of the Two Holy Mosques Institute of Hajj Research, new name)[17]. They found that the highest ozone concentration of 82μg/m^3 on 15th of Zul-Hijah due to the municipality cleaning works after pilgrims leaving on 13th of Zul-Hijah. They also reported that the ozone concentration decreased to 74 μg/m^3 on 12th and 13th of Zul-Hijah. However, their measurements were constrained to two periods only from 06:30

to 07:30 and from 14:00 to 14:30 with interval of 30 minutes. Therefore, it might be that ozone concentration was higher than the recorded values at different time especially on 9th of Zul-Hijah when pilgrims move from Mina valley to Arafat. Nevertheless, recent extended study measured the ground level concentration of N_O, NO_2 and O_3 in Mina valley every day during hajj period from 6th of Zul-Hijah to 18th in 1424L (28/1-9/2/2004) with interval of one hour average[18]. He used Mobile Pollutants monitoring Station (MPDS) with UV Photometric Ozone Analyses for O_3 detection and Chemiluminescent NOx Analysis for NO_2 and NO detection. It was found that the maximum hourly recorded concentrations of O_3, NO_2 and NO species were approximately 86 mg/m^3, 184 mg/m^3 and 626 mg/m^3 respectively, which is within the recommended levels by WHO[18].

The present study measures the concentrations of O_3, NO_2 and NO species with relation to the incident solar UV radiation on two different seasons of winter and spring at Al-Izaiziah area (which is very close to Mina valley just 1 km in between) in Makkah, Saudi Arabia (322m altitude, 21°.24N, 39°.51E). During Hajj period (the pilgrimage to Makkah), which comes in winter season nowadays, more than 2.5 million persons gathered in Makkah to perform the rites of Hajj and the number of vehicles and buses increases causing an ideal diurnal cycle of local ozone formation. Nowadays, hajj month comes in winter season where the incident solar UV radiation is lower in comparison to that in spring or summer seasons. Due to the hajj month is following the lunar months, consequently, in the coming several years hajj month is simultaneous with spring and summer seasons and hence more ozone formation is expected. This study tries to focus the light in this matter.

Equipment

GUV-2511 Radiometer

The GUV-2511 multichannel radiometer measures UV radiation in six channels covering the UVB and UVA with central wavelengths of 305, 313, 320, 340, 380 and 395 nm and bandwidths of approximately 10 nm. The GUV-2511, (Biospherical Instruments Inc., San Diego) is temperature stabilized at 50°C and designed for low maintenance operation. The optical part of a multichannel filter instrument consists first of a transmitting Teflon cosine response diffuser (flat plate diffuser) above six photosensitive detectors or diodes (*i.e.* one detector for each channel), each of which are coupled to an amplifier. Interference filters in front of each diode, give bandwidths of 7±1 nm at 305 nm, 11±1 nm at 313 and 320 nm, and 10±1 nm at 340, 380 and 395 nm. The GUV-2511 is installed from 25th of October 2004 to the present time, on the roof of the custodian of the two holy mosque institute of hajj research at Umm Al-Qura university in Al-Izaiziah (322 m altitude, 21°.24 N, 39°.51 E), for

monitoring the solar UV spectral irradiance. It has a 2πfield of view with a virtually uninterrupted flat horizon. Data from all channels is sampled at approximately 2-3 Hz and 10-minte averages stored between 04:00 and 20:00 (UTC) daily. Prior to this study the GUV radiometer was calibrated for irradiance against a Reference GUV by Biospherical Instruments Inc., in San Diego, by simultaneous measurement of solar irradiance.

Ambient Ozone Monitor APOA-360

The APOA-360 is an ozone concentration monitor for ambient air and also known as UV Photometric Ozone Analyser, which uses the non-dispersive UV absorptiometry. This analyser measures ozone continuously in unit of ppm that can be transformed to mg/m^3.

Ambient NOx Monitor APNA-360

The APNA-360 has been designed for measuring the concentration of nitrogen oxide in ambient air based on the chemiluminescence method (CLD method) and hence it is also known as Chemiluminescent NOx Analyser. This analyser continuously measures NO, NO_2 and NOx ($NO+NO_2$). The concentration of NO_2 is calculated from the concentrations of NO and NOx and is then output.

Both ambient monitors (O_3 and NOx analysers) are developed and calibrated by the Horiba, Ltd. Company in Japan. In order to obtain stable and accurate data, the calibration procedure need to be carried out when starting measurements and at regular intervals. Both analysers were installed since 28th of December 2006 until now, on the roof of the custodian of the two holy mosque institute of hajj research very close (10 m in between) to the GUV-2511 radiometer for monitoring O_3 and NOx. Measurements of O_3 and NOx were recoded every 10 minutes and averaged hourly during 24 h.

Methodology

The reaction with NO is an important removal process for O_3 (reaction 11). The ozone lifetime may vary from 2 to 5 days in the tropical boundary layer to several months in the middle troposphere[19]. Hence ozone concentrations in the troposphere show a highly spatial and temporal variability, which needs to be taken into account in any attempt to evaluate the ozone greenhouse effect. The detailed tropospheric chemical cycle, involving ozone production and loss and interactions with other atmospheric species, is summarised here.

The tropospheric photochemical reactions can produce various radicals that exert a substantial influence on the atmospheric composition. OH is the dominant tropospheric oxidant and is mainly responsible for controlling many of the anthropogenic pollutants in the troposphere. Its concentration in the

troposphere is usually between $3 \cdot 10^5$ and $5 \cdot 10^6$ molecules cm^{-3}[20]. Although its concentration is low, its high reactivity enables it to be an important player in tropospheric chemistry. The most important photochemical reaction source of free radicals is related to the UV photodissociation of ozone producing the $O(^1D)$ radical (reaction 1). The latter initiates in turn the production of hydroxyl radicals (through its reaction with water vapour) as follows:

$$O_3 + hv\ (\lambda \leq 310nm) \rightarrow O(^1D) + O_2(a\ ^1\Delta_g) \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (2)$$

Approximately 10% of the $O(^1D)$ formed from reaction 1 can react with water vapour to produce two hydroxyl radicals. The reminder (90%) is deactivated to the total ground state, $O(^3P)$, which recombines with O_2 to produce O_3. Each photolysed ozone molecule in reaction 1 can lead to approximately 20% OH molecules[20]. The highest levels of OH are predicted to occur in the tropics, where high humidity and actinic flux can lead to faster production of OH from ozone photolysis. The molecular products of these reactions that produce OH in the atmosphere are called reservoirs where the possibility of OH regeneration via thermal decomposition or photolysis often occurs. The lifetime of these reservoirs is very variable and is a strong function of time and location (*i.e.* temperature, pressure and solar intensity). As a result of this the OH lifetime in the troposphere is highly variable.

In the absence of NOx the main two sinks of the OH radical in the troposphere are the reaction with carbon monoxide, CO, and methane, CH_4 to produce organic peroxy radicals, RO_2, such as the hydro peroxy radical, HO_2, and the methyl peroxy radical, CH_3O_2 as follows:

$$OH + CO \rightarrow H + CO_2 \quad (3)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (4)$$

$$OH + CH_4 \rightarrow CH_3 + H_2O \quad (5)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (6)$$

Reactions 4 and 6 are extremely fast while 3 and 5 are rate-limiting steps in the production of peroxy radicals HOx. The chemical lifetimes of OH and HO_2 in clean atmospheric conditions (when there is no NOx) are as short as 1 s and 150s respectively and cycling between the two species is rapid[21]. At low concentrations of NOx, HO_2 can react with ozone resulting in an increase in destruction of ozone via a chain sequence involving the production of hydroxyl radicals (see reactions 7 and 8).

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (7)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (8)$$

The alternative reactions that occur in the absence of NOx, are the peroxy radical self-reactions (with the same peroxy radical) or cross-reactions (with another sort of the peroxy radicals)[22].

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (9)$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \quad (10)$$

The formed hydrogen peroxide (H_2O_2) and methyl peroxide (CH_3OOH) can then act as additional effective reservoirs for both OH and HO_2, where their photolysis and reaction with OH leading to more free radicals production[21]. They also are soluble (in practice H_2O_2) and subject to rainout.

However, in more polluted conditions where a concentration of NOx is high, which is our case here in Makkah, the conversion between NO and NO_2 can take places in troposphere. Under most tropospheric conditions the dominant NO and NO_2 conversion route is the reaction of NO with O_3 as the following:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (11)$$

In general about 40% of the global emissions result from the combustion of fossil fuel that almost exclusively leads to emission directly into the planetary boundary layer, mainly in the form of NO production, while a small fraction (≤10%) might be released as NO_2[2]. The lifetime of NO_2 with respect to the photolysis rates in the boundary layer is dependent on latitude, season and time of day. However, during daylight NO_2 is converted back to NO by photolysis (see reaction 12) that leads to regeneration of O_3 by the following:

$$NO_2 + h\nu \rightarrow NO + O \quad (12)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (13)$$

This is the only reaction producing ozone in the atmosphere and reaction 12 is very fast so reaction 11 is a rate-limiting step. Thus, reactions 11, 12 and 13 constitute a cycle with no net chemistry. In the absence of competing interconversion reactions, this cycle leads to a photostationary state. Other daytime chemical reactions interconverting the NOx species generally involve free radicals such as organic peroxy radicals, RO_2, the methyl peroxy radical CH_3O_2 and the hydro peroxy radical, HO_2. Both the RO_2 and the HO_2 radicals can provide additional NO and NO_2 conversion routes to supplement reaction 11 (see reactions 14 and 15).

$$HO_2 + NO \rightarrow OH + NO_2 \quad (14)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (15)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \quad (16)$$

In urban areas where there are many pollutants the OH radical can undergo similar reactions with a variety of Non-Methane Hydrocarbons (NMHCs). HO_2 can also be recycled back to OH in the presence of ozone as in reaction 7. The photolysis of formaldehyde, CH_2O (or HCHO), represents an important free radical production rate in the troposphere (reactions 17 to 19) and dominates radical production under urban conditions, when the concentration of O_3 is suppressed by reaction with NO (reaction 11)[2]. The HCHO is elevated due to high local emissions from combustion sources such as transport. It is also formed via the oxidation of most biogenic and anthropogenic hydrocarbons (reaction 16).

$$HCHO + hv \rightarrow H + HCO \quad (17)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (18)$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad (19)$$

The HCHO represents an important bridge between OH and HO_2 in the presence of O_2 in the following route:

$$HCHO + OH + O_2 \rightarrow HO_2 + H_2O + CO \quad (20)$$

$$HCHO + hv + 2O_2 \rightarrow 2HO_2 + CO \quad (21)$$

Note here reaction (21) represents the net reactions from 17 to 19 and it presents an important contribution for OH. As HCHO is photolysed at much longer wavelength ($302 \leq \lambda \leq 356$nm) than O_3, it is a big source of OH if the light levels are lower. Furthermore, many hydrocarbons produce HCHO when react with O_3. Alternative reactions with the free radicals OH and HO_2 can take place in the presence of NOx[21]:

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M \quad (22)$$

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (23)$$

$$OH + NO + M \rightarrow HONO + M \quad (24)$$

The formed nitric acid (HNO_3) is most likely to diminish via deposition resulting in permanent loss of radicals[21]. However, nitrous acid (HONO) is very effectively photolysed under both summertime and wintertime conditions, and is a potentially important free radical source (reaction 25), although being present at very small concentrations during daylight period[2].

$$HONO + hv \rightarrow OH + NO \quad (25)$$

The importance of the atmospheric NOx concentration is in its ability to determine whether there is a net production or destruction of tropospheric ozone. It was reported that ozone production exceeded destruction at NO concentrations of 55±30ppt (0.07±0.04 mg/m^3) at Mace Head during late

spring[23]. Below this threshold, the HO_2 reaction with ozone dominates in net ozone destruction as in reaction (7). However, above this threshold, HO_2 and RO_2 convert NO to NO_2 via reactions 14 and 15 and then NO_2 photolysis via reactions 12 and 13 leads to enhancement of ozone concentration. In the present study it was found that the lowest recorded NO concentration in Makkah was 0.2 mg/m^3, which is 3 times of the reported threshold by last study[23].

Result and Discussion

The UV radiation and O_3, NO_2 and NO concentrations were measured through two different seasons of winter and spring. The measurements were selected from 8th to 17th of Zul-Hijah (8 -17/12) in 1427L as lunar calendar (from 28/12/2006 to 6/1/2007) for winter time with the lowest midday SZA of 44^o and between 21st of Rabie Thani and 1st of Jumada Al-Aula (21/4 to 1/5) in 1428L (8 -17/5/2007) for spring season with SZA the largest midday SZA of approximately 4^o (Fig. 1). Figure shows that SZA reaches to decimal digits (<1^o) twice a year in spring and summer time at midday. This means that there are very high amount of solar UV radiation is received by surface in Makkah during spring and summer (Fig. 1).

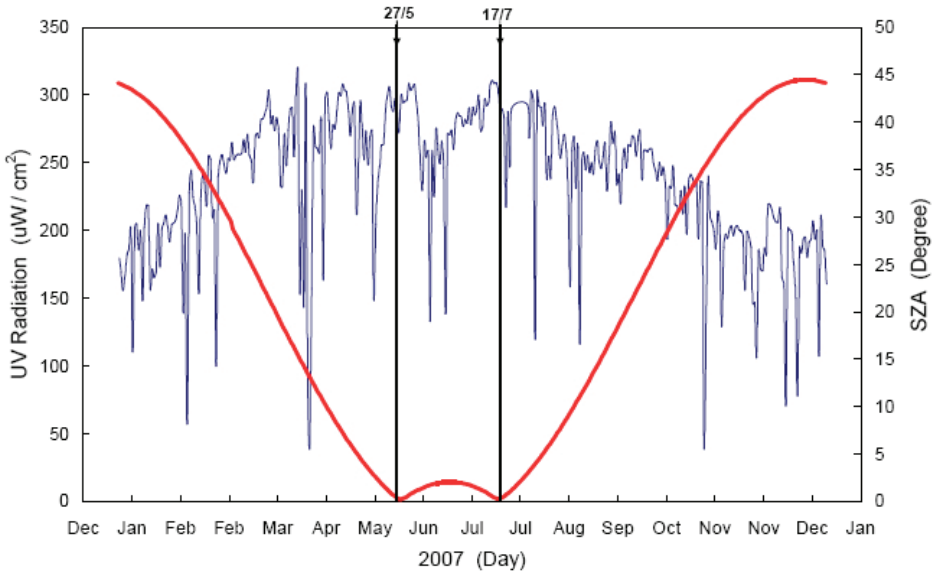

Fig. 1. The Incident Solar UV Radiation with SZA Variations at local noon midday in 2006.

Winter Season Measurements

The measured UV radiation and the concentrations of O_3, NO_2 and NO from 8th to 17th of Zul-Hijah, 1427L were presented in Fig. 2. It is clear that the UV

radiation has the maximum values at midday due to the lowest attenuation for the incident solar UV radiation by absorption, reflection and refraction in the atmosphere due to the smallest SZA. The highest incident solar UV intensity (70%) was concentrated around local noon (from 09:00 to 15:00) and then decreases towards either the morning or the evening, which confirms the findings of last studies[18]. In general, the incident UV radiation has similar intensity during the selected period, where its maximum values at midday were varies between 170 mW/cm^2 on 11th of Zul-Hijah and 210 mW/cm^2 on 8th of Zul-Hijah at midday with SZA within 44^o. However, there were some fluctuations in some days such as 16th and 17th of Zul-Hijah, which is due to the presence of some clouds passing through during the scanning time. This fluctuation is due to the attenuation that caused to the incident UV radiation by clouds, which confirms other studies[24-26]. The ultraviolet radiation levels depend on cloud type, thickness, height, amount, and microphysical properties[27]. Although, clouds have reduced the incident UV radiation on 16th and 17th of Zul-Hijah, some relative higher UV values of 200 mW/cm^2 occurred for short time in the same days.

Figure 2, which might be due to the UV enhancement by clouds under specific conditions. This is consistent with the previous works[28-30] that is under some specific broken cloud conditions, a short-term enhancement in surface UV irradiance of up to 20%[31, 32] might occurred due to reflection of the incoming solar radiation from sides of the clouds toward the ground.

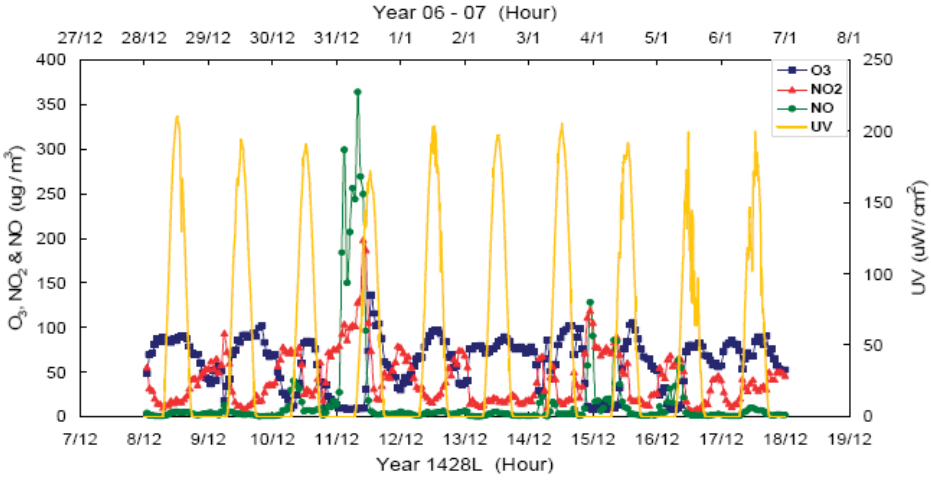

Fig. 2. Average Hourly Variations of O_3, NO_2 and NO concentrations with UV radiation during Zul-Hijah 1427L (28/12/06-6/1/07).

Moreover, the diurnal variation of O_3, NO_2 and NO concentrations were observed. In general, similar behaviour was presented by each pollutant for each day during the selected period of the study. However, only one day of 11th of Zul-Hijah (31/12/06), different behaviour was observed where the pollutant concentrations sharply increased. The largest O_3, NO_2 and NO concentrations of approximately 135, 200 and 365 mg/m^3 were recorded respectively on 11th of Zul-Hijah. This might be related to the transfer of the NO and NO_2 pollutants from the central area around Al-Masjed Alharam (the holy mosque in Makkah) via the north west (NW) wind Fig. 3 towards Al-Izaiziah leading to NO and NO_2 concentration enhancement.

Figure 3 shows that the dominant average daily wind direction in Makkah during the study was generally between N and NW, while the average daily wind speed (WS) was approximately ranging between 1 to 4.5 m/s and these findings are agreed with another studies by Naser Allah in 2005[33]. The reason of the large concentration of NO and NO_2 in the central area on 11th of Zul-Hijah, might be related to high traffic jam of transportation in the rood from Al-Masjed Alharam to Mina valley from the night on 10th to the early morning on 11th of Zul-Hijah. On both days, pilgrims spent long time (from 22:00 on 10/12 to 02:00 on 11/12/1428L) to arrive their camps in Mina valley due to the transportation difficulties in the rood. The distance from central area to Al-Izaiziah area is about 5 km and the WS was about 2 m/s on 11th of Zul-Hijah, therefore only less than one hour is required for trace gases to reach Al-Izaiziah area and that is agreed with the beginning of the NO concentration increasing at 03:00.

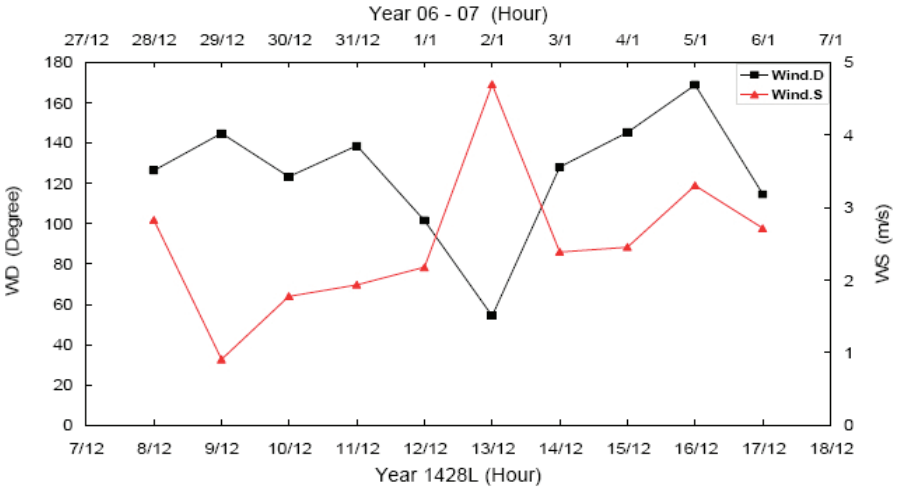

Fig. 3. Average Daily Variations of wind direction (WD) wind speed (WS) during Zul-Hijah 1427L (28/12/06-6/1/07).

Figure 2, In term of NO_2 pollutant it is expected that some of NO pollutant was converted to NO_2 through the reactions of 14 and 15 when the NW wind was moving towards Al-Izaiziah area on 11th of Zul-Hijah. This NW wind could continue bringing and accumulating more NO and NO_2 pollutants to Al-Izaiziah area during night and as soon as sunlight starts most of NO_2 is photolysed by UV radiation to produce the ground ozone pollutant, which explains the increase of ozone concentration after 09:00 on 11th of Zul-Hijah to its highest levels.

Another explanation for this higher NO and NO_2 concentrations at early morning (03:00) on 11th of Zul-Hijah could be related to the possibility of inversion occurring. In the presence of inversion the temperature decreases towards the ground instead towards the atmosphere resulting in bringing the atmospheric pollutant towards the ground. In the morning of the previous day of 10th of Zul-Hijah (day of celebration, Eid, and sacrificing), the majority of pilgrims move from Mina valley to Al-Masjed Alharam passing through Al-Izaiziah area to perform Tawaf Alifadah (one of the most important hajj rites). Later on in the evening they move back to Mina valley to stay two or three nights in their camps there. As a result, more vehicle emissions of NO and NO_2 pollutants to the atmosphere can occur during the transportation. Consequently, it is expected that, the accumulated NO and NO_2 pollutants in the atmosphere during 10th of Zul-Hijah come down towards the surface causing high NO and NO2 concentration.

UV Radiation and O_3, NO_2 and NO Concentrations

The relationship between the incident solar UV radiation and the O_3, NO_2 and NO concentrations are presented separately and respectively in Fig. 4-6.

Figure 4, shows that as the solar UV radiation increases as the concentration of ozone becomes greater confirming the ozone dependence on UV intensity. This result confirms the presence of the reactions from 12 to 13. The linear regression was applied to study the correlation between the UV variation and ozone concentration values. The linear regression analysis generally shows symmetric distribution of both selected data (ozone and UV data here) and gives a best fit of both data and a correlation coefficient (R^2) level. The correlation coefficient between UV and ozone was 85% (R^2 = 85%) while the intercept is constrained to be zero and this high correlation between both data and it also agrees with the previous study[18]. However, in term of NO_2 pollutant, this correlation coefficient has diminished to 50%, which confirms the NO_2 photolysis by UV radiation (Fig. 5) and hence reaction 12 takes place during daytime. Furthermore, the correlation coefficient between UV and NO was approximately 13% and this is also consistent with the last findings[18]. This result gives an evidence of the weakly NO dependence on solar UV radiation.

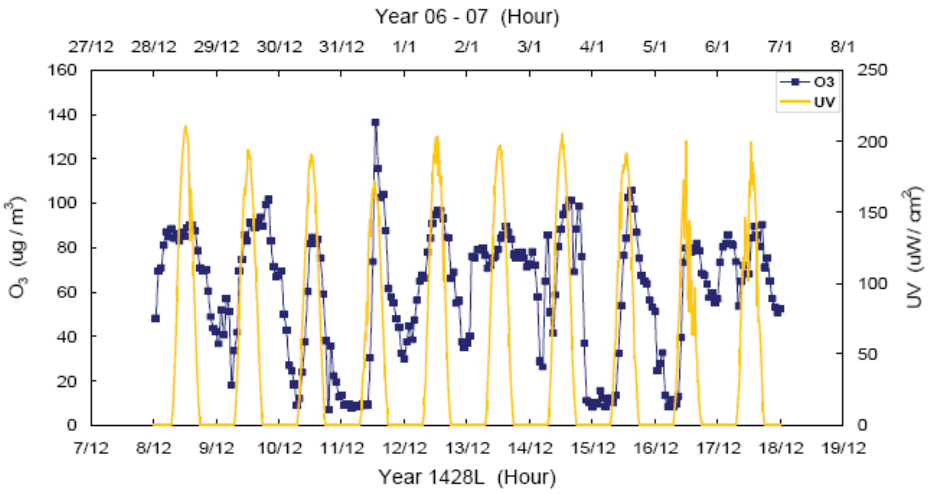

Fig. 4. Average Hourly Variations of O_3 concentrations with UV radiation during Zul-Hijah 1427L (28/12/06-6/1/07).

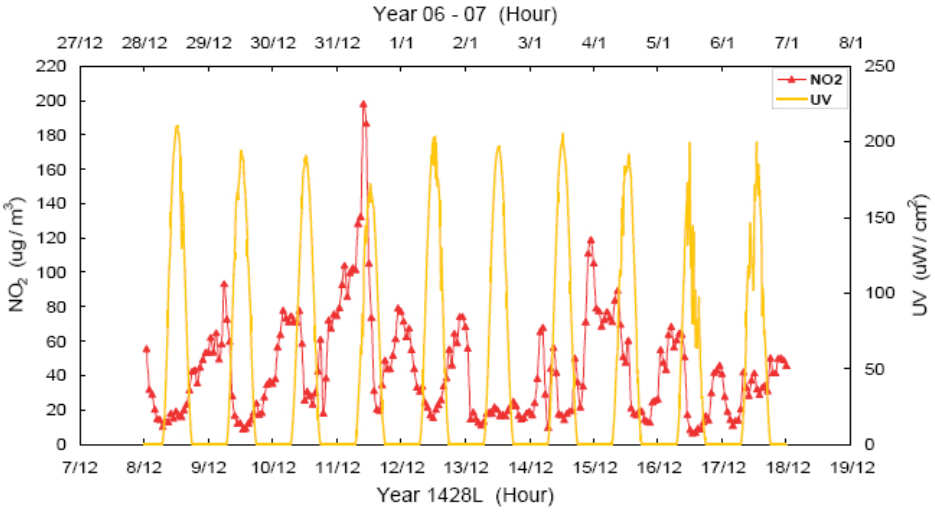

Fig. 5. Average Hourly Variations of NO_2 concentrations with UV radiation during Zul-Hijah 1427L (28/12/06-6/1/07).

Figure 6 also confirms that about 40%[34] of the global emission and largest single source for NO, is resulting from fossil fuels.

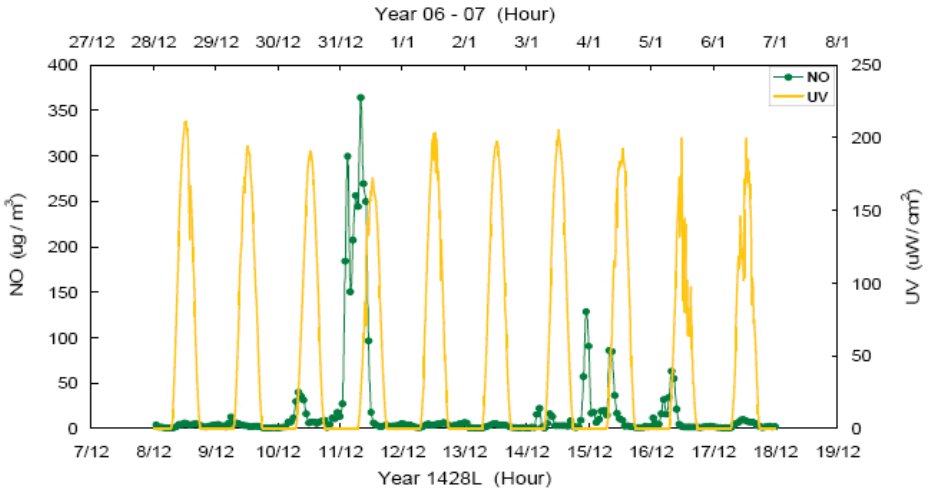

Fig. 6. Average Hourly Variations of NO concentrations with UV radiation during Zul-Hijah 1427L (28/12/06-6/1/07).

Spring Season Measurements

The measured UV radiation and the concentrations of O_3, NO_2 and NO from 21/4-1/5/1428L were presented in Fig. 7. The incident UV radiation has generally greater midday intensity than the recorded one during last hajj in 1427L. The maximum recorded UV values at midday were ranging between approximately 265mW/cm^2 on 28/4 (15/5/07) to 300mW/cm^2 on 27/4 (14/5/07), which is due to the very small SZA of 4^o. Therefore, the lowest recorded midday value of UV (265mW/cm^2), during the period of interest, in spring season was greater with about 55mW/cm^2, than the highest recorded one (210 mW/cm^2) during last hajj. Moreover, the highest recorded UV value (300 mW/cm^2) in spring season was over that in the last hajj (210mW/cm^2) with approximately 90mW/cm^2. In term of O_3, NO_2 and NO concentrations, the maximum recorded values for these species were approximately 147, 100 and 95mg/m^3 respectively. For a comparison, the maximum values of O_3, NO_2 and NO concentrations during two different selected periods (12/1427L and 4/1428L) were presented in Table 1.

Table 1. The maximum values of O_3, NO_2 and NO concentrations during two different selected periods (12/1427L and 4/1428L).

NO	NO_2	O_3	Date
365	200	135	12/1427L (12/06)
95	100	147	4/1428L (5/07)

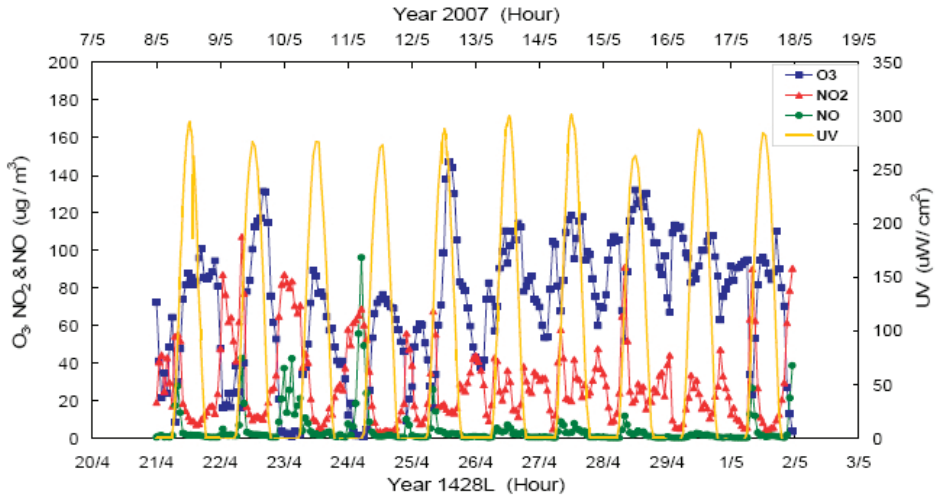

Fig. 7. Average Hourly Variations of O3, NO 2 and NO concentrations with UV radiation during Rabie Thani 1427L (1-15/5/07).

Table 1 shows that the highest O_3, NO_2 and NO concentrations in both period were within the recommended WHO values (150-200mg/m^3 1h for ozone and 400mg/m^3 for NO_2)[6, 7]. However, there no threshold was reported by WHO for NO concentration[6, 7]. Despite these concentrations are within the recommended levels by WHO, these concentrations or lower one (100-µg/m^3) may lead to some health problems particularly for children as reported by new WHO updated guidelines in 2005. It was reported that the severity of respiratory symptoms in asthmatic children is another approach to determining the acute health effects of ozone. In a study performed in the New Haven, Connecticut area, ozone was significantly associated with respiratory symptoms in asthmatic children; a 100-µg/m^3 increase per 1-hour ozone was associated with increased likelihood of wheeze (by 35%) and chest tightness (by 47%)[35]. In a cohort of children with asthma in 12 southern California communities, respiratory symptoms were associated with the yearly ozone variability (odds ratio=1.06 per 2µg/m^3)[35].

Moreover, some studies pointed that the magnitude of the risk for respiratory morbidity associated to an increase of 20µg/m^3 ozone ranged between none and 5%[35]. There is also some evidence of a threshold in the dose-response functions relating ozone to respiratory disease, the smallest effect level being around 150µg/m^3 of ozone concentration[35].

Nevertheless, these concentrations may significantly increases if two factors combined together, which is high vehicles emissions and large incident solar UV radiation, which what is going to be explained here.

From Table 1, it is clear that the O_3 concentrations in Zul-Hijah, 135 mg/m^3, (winter season) and in Rabie Thani, 147mg/m^3, (spring season) were similar only 12 mg/m^3 difference. This is very interesting result, where there is no a lot of transportation in Rabie Thani as that experienced during hajj period (more that 2.5 million pilgrims and a lot of traffic road) and despite that the ozone concentration was similar in both periods. It is known that there are two factors can effectively affect atmospheric ozone concentration; high vehicles emissions of the primary pollutants and high incident solar UV radiation. The reason of the highest ozone concentration in hajj period is more related to the relative high vehicles emissions of NO_2 and NO.

Figure 2, the incident UV radiation, due to the high transportation during hajj occasion. However, in Rabie Thani, the high incident UV radiation (300 mW/cm^2 compared to 210 mW/cm^2 in Zul-Hijah) is more dominant in ozone formation than the vehicles emissions of NO_2 and NO.

Figure 6, This is also confirmed by the different concentrations of NO_2 and NO in two different periods (see Table 1). In Zul-Hijah 1427L, the concentration of NO_2 was double (200 compared to 100 mg/m^3) of that in Rabie Thani in 1428L, while NO in Zul-Hijah was more than three times (365 compared to 95 mg/m^3) of that in Rabie Thani. As a result, the higher relative emissions of NOx with small relative UV radiation have led to the highest ozone concentration in Zul-Hijah, in winter season. In contrast, the larger relative UV radiation and lower relative emissions of NOx have led to the highest ozone concentration in Rabie Thani, in spring season. The problem here is that what is the situation looks like in Makkah when the large NOx emissions conjoined with the high incident solar UV radiation?!! In aspect that the hajj month is annually following the Muslim calendar year (12 lunar months) that is less than the solar year with 11 days, consequently it is rounded through the different seasons of the 365day solar year. In the next few years, the month of pilgrimage is moving towards the spring and summer seasons, and as a result a big challenge of air quality in Makkah atmosphere is have to be encountered. Other wise, alternative means of transportation and vehicle emissions controlling are required to keep Makkah atmosphere clean and healthy and to protect pilgrims from potential air pollution episodes.

Conclusion

The incident solar UV radiation and the concentrations of three pollutants of O_3, NO_2 and NO in atmosphere of Makkah, Saudi Arabia (322 m altitude, 21^o.24 N, 39^o.51 E) were measured during two different seasons of winter and spring in 2007. GUV-2511 that has six channels in the UV region, was used to measure the incident UV radiation. The concentrations of O_3 and NOx were

measured by two ambient Monitors of APOA-360 and APNA-360 respectively. The measurements were selected for two different seasons of winter and spring. The highest concentrations of approximately 135, 200 and 365 mg/m^3 were recorded for O_3, NO_2 and NO pollutants respectively with maximum incident UV radiation at midday of 210 mW/cm^2 during winter season (Zul-Hijah 1428L). However these values were approximately 147, 100 and 95 mg/m^3 for O_3, NO_2 and NO respectively with largest incident UV radiation of 300 mW/cm^2 in spring season. The ozone concentration may significantly increases if two factors (high vehicles emissions and large incident solar UV radiation) combined together, which is might occur when the hajj month synchronizes with spring or summer seasons in the coming few years.

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تغيرات غاز الأوزون السطحي مع الأشعة فوق البنفسجية خلال فصلي الشتاء والربيع لعام ٢٠٠٧م بمكة المكرمة

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المستخلص. قامت هذه الدراسة بقياس الأشعة فوق البنفسجية الشمسية الساقطة وتركيزات ثلاث غازات: هي الأوزون السطحي، وثاني أكسيد النيتروجين، وأول أكسيد النيتروجين في أجواء مكة المكرمة، السعودية (على ارتفاع ٣٢٢ مترًا، ٢٤ َ ٢١° درجة شمالاً، ٥١ َ ٣٩° درجة شرقًا) خلال فصلي الشتاء والربيع لعام ٢٠٠٧م، وقد تم استخدام جهاز المقياس الطيفي للأشعة فوق البنفسجية ذو العرض الموجي المحدود رقم ٢٥١١ (GUV-2511) والذي يحتوي على ست قنوات في منطقة الأشعة فوق البنفسجية والتي تتمركز عند الأطوال الموجية التالية ٣٠٥، و٣١٣، و٣٢٠، و٣٤٠، و٣٨٠، و٣٩٥ نانومتر وذات عرض موجي قدره ١٠ نانومتر. ولقد تم قياس تركيزات غازات الأوزون السطحي وأكاسيد النيتروجين بواسطة اثنين من محطات الرصد الغازي موديل (أيه بي أو أيه رقم ٣٦٠) وموديل (أيه بي إن أيه رقم ٣٦٠) على الترتيب. وقد تم أخذ القياسات خلال فترتين الأولى من ٨–١٧ ذوالحجة لعام ١٤٢٧هـ (الموافق ٢٠٠٦/١٢/٢٨م – ٢٠٠٧/١/٦م) لفصل الشتاء، والفترة الثانية ٤/٢١ – ١٤٢٨/٥/١هـ (الموافق ٨–٢٠٠٧/٥/١٧م) لفصل الربيع، ولقد وصلت أعلى قيمة للتركيزات حوالي ١٣٥، و٢٠٠، و٣٦٥ ميكروجرام/م^{3} لكل من الأوزون السطحي وثاني أكسيد النيتروجين وأول أكسيد النيتروجين على الترتيب، وكانت القيمة العظمى التي

رصدها للأشعة فوق البنفسجية في منتصف النهار حوالي ٢١٠ ميكروواط/سم^{٢} خلال فصل الشتاء (شهر ذو الحجة عام ١٤٢٧هـ)، أما في فصل الربيع فقد كانت أعلى قيمة تم رصدها لغازات الأوزون السطحي، وثاني أكسيد النيتروجين، وأول أكسيد النيتروجين قرابة ١٤٧، و١٠٠، و٩٥ ميكروجرام/م^{٣} على الترتيب، وكانت أعلى قيمة رصدت للأشعة فوق البنفسجية عند منتصف النهار حوالي ٣٠٠ ميكروواط/سم^{٢} خلال هذه الفترة، وبالتالي فإن تركيزات غاز الأوزون السطحي يمكن أن ترتفع في حالة توفر عاملين هما: انبعاثات عالية من عوادم المركبات، وارتفاع في مقدار الأشعة فوق البنفسجية الساقطة والتي ممكن أن تحدث عندما يحل موسم الحج في فصلي الربيع أو الصيف في السنوات القليلة القادمة، نتيجة لذلك فإن هناك تحدٍّ كبير سنواجهه في جودة الهواء في مكة المكرمة والذي قد يؤثر سلبا على صحة الحجيج، مالم يتم استخدام وسائل نقل جديدة أكثر أمنا للبيئة وحفاظا على جودة الهواء.