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Examining the variations of ground level ozone and nitrogen dioxide in a rural area influenced by brick kiln industries

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Abstract

Burning of biomass fuels is responsible for the emission of both trace and non-trace greenhouse gases such as CO_2, CH_4, CO, N_2O, NO_X and NO. The photolysis of nitrogen dioxide (NO_2) directly leads to the formation of ozone (O_3) in the lower atmosphere. This work is an attempt to estimate the level of ground level ozone (GLO) and NO_2 concentrations in the atmospheric surface layer of a rural area dominated by traditional brick kiln industries. A portable monitor with O_3 and NO_2 sensor heads was employed for the measurement of the trace gases from May 2009 to July 2009. The GLO concentration showed a clear diurnal cycle with higher values in the daytime and notably lower values at night time. The concentration of GLO during the period of study varied from a minimum value of 7 ppb around 0530 h to a value of 48 ppb around 1430 h. The lowest mean day time value of NO_2 was 2.52 ppb and the highest mean night time value was 5.83 ppb.

Keywords: Brick kilns, biomass, diurnal variation, ozone precursor, photochemical reaction, ground level ozone

Introduction

Ozone is an important trace species present in the atmosphere. It is produced photochemically in the lower atmosphere from reactions involving a variety of volatile organic compounds (VOCs) composed mainly of non- methane hydrocarbons in the presence of sufficient sunlight and nitrogen oxides (NO_x) such as nitric oxide (NO) and nitrogen dioxide (NO_2). NO_x are emitted from a variety of natural and anthropogenic sources (Al-Khalaf, 2006). Ozone is the most important gas in the photochemistry of the atmosphere and is the primary constituent of photo-oxidative smog. Thus, it can be considered as an indicator of the overall burden of the atmospheric oxidants. The physical and chemical processes of this GLO directly depend on the local precursor emission levels and meteorological factors. In the ambient air even a micro level variation in the concentration of GLO brings lethal effects on the biological and material systems (Ravishankar & Rao, 2002; Moller, 2004). Ozone in the troposphere has been steadily increasing at the rate of 0.5-2% per year (Vingarzan, 2004) over the past few decades. Thus, abundance of GLO concentration is increasing at many sites over the globe and expected to rise significantly above the threshold limit set for human (hourly average of 80 ppbv set by World Health Organization) throughout the 21st century (WHO, 2000; IPCC, 2001). Further increase of tropospheric ozone is anticipated under likely scenarios of increasing regional and global emissions of ozone precursor compounds (Seinfeld, 1991). The two sources of ozone in the natural troposphere are: a) Injected from stratosphere and b) Photochemical production via NO_x-VOC reactions in sunlight involving naturally occurring oxides of nitrogen and hydrocarbons or CO (Seinfeld & Pandis, 2006; Salve *et al.*, 2007). Studies show that apart from the industrial and vehicular exhausts, fumes from brick kilns also contribute to the increase in the level of local ozone at surface levels (Pudasainee *et al.,* 2006). Using biomass fuels in traditional brick industries is responsible for the emission of both trace and non-trace gases such as CO_2, CH_4, N_2O, NO_X and NO and also toxic fumes containing suspended particulate matters rich in carbon particles and high concentration of carbon monoxides and oxides of sulphur (SOx) (Alam, 2006). Therefore, brick making industries can be considered as one of the important sources of greenhouse gases.

The objective of this study is to determine the level of GLO and its precursor NO_2 concentrations in a rural area where a large number of traditional brick kilns are active.

Study area

The study area Chenbagaramanputhur (8°15'1" N, 77°29'19" E) is a rural place in Kanyakumari district and is about 12 km from Nagercoil town (Fig. 1). Brick production is one of the traditional crafts of the people in this village and is a valuable source of employment. There are approximately 300 conventional brick kilns around this study place. These kilns are heavily utilized during dry season since the wet weather in other seasons prevents the bricks from setting hard. In this brick kilns, firewood is used as the main fuel and approximately 1,000 bricks need 45 kg of fire wood.

Materials and methods

Ground level ozone concentration and nitrogen dioxide measurements were carried out in the rural site Chenbagaramanputhur. A portable Aeroqual series S200 ozone monitor similar to that of Aeroqual S300 used by Dovile (2009) was used for the measurement. An Aeroqual series 200 ozone monitor is constructed to measure low and high ozone levels. Its ultra low concentration ozone head measures the ozone concentration from 0.000 to 0.500 ppm and a high

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concentration ozone head measures the ozone concentration from 0.50 to 20.00 ppm. Accuracy of a low concentration ozone head is +/- 0.010 ppm (from 0 to 0.100 ppm); +/- 10% (0.100 to 0.500 ppm), while that of a high concentration ozone head is +/- 10% (from 0.20 to 2.00 ppm); +/- 15% (from 2.00 to 20.00 ppm), the measurement units being either ppm or $\mu g/m^3$. The operating temperature range is from 5°C to 50°C, relative humidity limits are 5% and 95%. Similar kind of NO_2 sensor has been used for nitrogen dioxide measurement. A gas sensitive semiconductor (GSS) type sensor is described in www.aeroqual.com. Sampling was carried out for three months from May 2009 to July 2009. For ozone seven readings were taken per day starting from 0530 h to 2330 h with 3 h interval. For NO_2, only two readings were taken one at day time (1430 h) and the other at night time (2330 h).

Results and discussion

The results of surface ozone and NO_2 levels observed during the present study are given below.

Diurnal variation of GLO

The observed mean values of GLO and nitrogen dioxide are shown in Table 1 & 2. The GLO concentration showed a clear diurnal cycle with higher values in the daytime and notably lower values at night time. This diurnal pattern is shown in Fig. 2. It can be seen that the ozone concentration was low at the early morning hours (0530 h), it slowly picked up in the forenoon and then built up faster and ultimately reached the maximum value in the afternoon. A gradual decrease was observed in the evening and a sudden fall was recorded after the sunset.

Table 1. Monthly mean GLO concentration (in ppb)

Month	Time						
	5:30	8:30	11:30	14:30	17:30	20:30	23:30
May 2009	20.40	26.40	32.40	44.60	33.60	30.20	27.40
June 2009	10.00	15.17	23.67	31.33	28.00	20.67	18.00
July 2009	19.33	23.83	30.00	36.67	34.33	27.83	23.67

The diurnal variation of GLO is helpful to understand the different processes responsible for ozone formation and destruction at this particular location. Chemical and atmospheric dynamic processes regulate the diurnal ozone concentration. The maximum value of GLO was observed around post noon which indicates that there exists a direct coincidence of GLO variation with the surface temperature. The photochemical production of ozone depends on the concentration of its precursor gases and meteorological parameters. The variation in these parameters changes the diurnal magnitude of ozone concentration. The lower levels of GLO observed during night time may be due to chemical loss of ozone (NO_x titration) and also due to the ozone loss at the surface of the earth, as there is no production of ozone during night hours (Debaje *et al.*, 2003). The concentration of GLO during the period of study varied from a minimum value of 7 ppb around 0530 h to a value of 48 ppb around 1430 h whereas the monthly mean concentration of GLO varied from 10 ppb to 44.60 ppb. May 2009 recorded the maximum and June 2009 recorded the minimum values of GLO.

Behaviour of NO_2:

The NO_x emission from the brick kilns has a major role in the formation of ozone. The presence of NO_x is very important because NO_2 can be the only potential source of ozone in the study area. If there is a fractional amount of NO_x in the troposphere, it receives solar radiation and the ozone is formed as indicated by the following reactions in eq. 1 and 2 (Tang, 2009).

$NO_2 + h\upsilon\ (\lambda < 424\ nm) \rightarrow O\ (^3P) + NO$ (1)

$O\ (^3P) + O_2 \rightarrow O_3$ (2)

Where, O (^3P) represents the oxygen atom in the ground state. However if those are the only reactions, then the ozone concentration would attain a steady state and does not reach to high value because the reaction (3) will occur in which ozone will be destroyed by NO produced in the reaction (1).

$O_3 + NO \rightarrow NO_2 + O_2$ (3)

But with the presence of any hydrocarbons in the atmosphere, NO will be transformed to NO_2 by peroxyl radicals such as RO_2^* and hydroxyl-radicals HO_2^* as indicated in eq. (4) and (5) (Tang, 2009).

$NO + HO_2^* \rightarrow NO_2 + OH^*$ (4)

$NO + RO_2^* \rightarrow NO_2 + RO^*$ (5)

The RO_2^* and HO_2^* radicals originate in the oxidation of the VOCs. Hence no ozone is consumed for the NO oxidation and the concentration of O_3 is no longer constant, but increases. NO_2 produced in the above reactions is then used to form ozone through reactions of eq. (1) and (2). As a result the concentration of ozone becomes high under the condition of strong solar radiation (Seinfeld & Pandis, 2006).

The observed levels of NO_2 concentration is shown in Fig. 3. The mean concentration of NO_2 at night was greater than that of day (i.e.,) 5.83, 4.56 and 4.77 ppb at night and 2.79, 2.64 and 2.52 ppb at day during the study period. This behavior of NO_2 indicates that the diurnal variation of ozone depend on photochemical reactions during day time. The low NO_2 concentration observed during day time may be due to the photochemical reaction taking place for ozone production using NO_2 as a fuel. The maximum of GLO at noon is related to the highest photolysis rate of NO_2 at noon.

Thus NO_2 acts as a precursor of ozone. After sunset, the intensity of photochemical reaction reduces and hence NO_2 concentration builds up. Table 3 shows the observed minimum and maximum values of GLO and NO_2 during the study.

Table 2. Monthly mean NO_2 concentration (in ppb)

Month	Day	Night
May 2009	2.79	5.83
June 2009	2.64	4.56
July 2009	2.52	4.77

Comparison of GLO & NO_2 concentrations

Analyzing the comparative diagram (Fig. 4) of GLO and NO_2 concentration the relationship between the two trace species in a monthly scale could be obtained. The two gases, one as a precursor (NO_2) and

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Fig.1. Location map of the observation site

Fig. 2. Mean GLO concentration for May, June & July 2009.

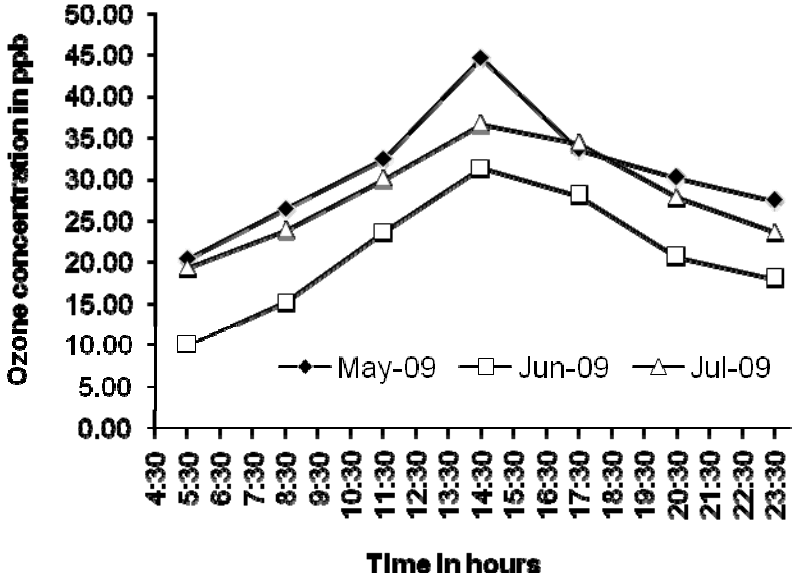


Fig. 3. Mean NO_2 concentration in May, June & July 2009

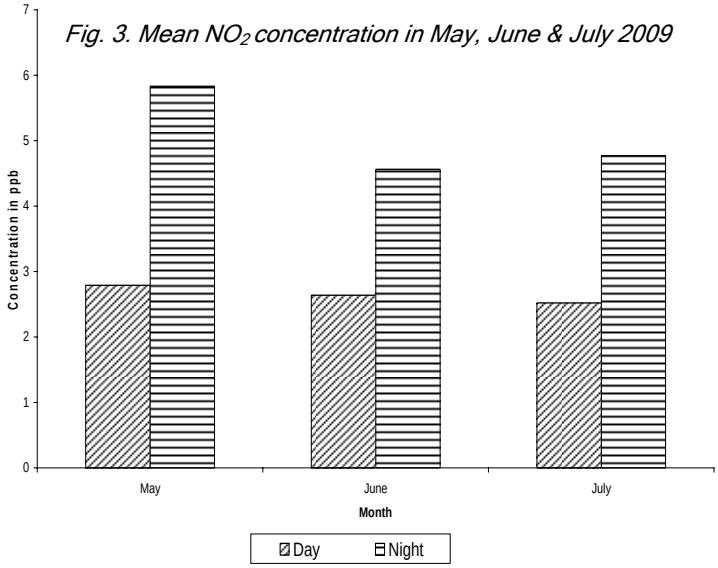
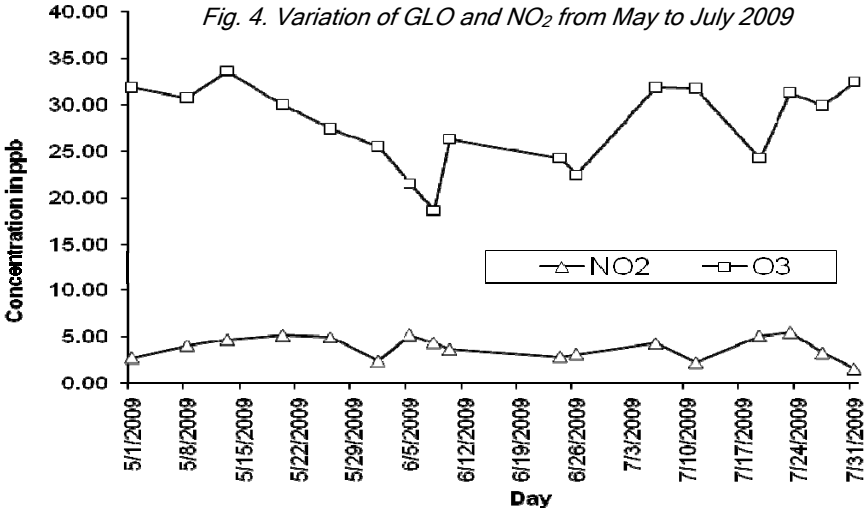


Fig. 4. Variation of GLO and NO_2 from May to July 2009



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the other as a product (GLO) vary in a similar way but with a different range of values throughout the period of observation. It clearly indicates that the role of photochemical process and emission rates at this observational location are significant. One more interesting inference from the fig. 4 is that the increasing or decreasing trend of NO_2 started first and then followed by ozone with the delay of at least a week's time. This is also helpful in substantiating the idea of NO_2 acting as a precursor emitted from both natural and man-made sources, for the photo chemical production of ozone (Ahammed *et al.,* 2006).

Table 3. The maximum and minimum concentrations of GLO & NO_2 (in ppb)

Month	GLO		NO_2	
	Minimum	Maximum	Minimum	Maximum
May 2009	18.00	48.00	2.35	7.25
June 2009	7.00	34.00	1.75	6.11
July 2009	10.00	40.00	1.26	7.47

The local meteorological factors and the activities involved in the brick kilns played a great impact on the observed pattern. In May 2009 with clear sky conditions and intense solar flux density marking the peak summer season at this place which provided a conducive atmosphere for the better production of NO_2 and hence ozone. June 2009 mostly had cloudy and rainy days. Hence lower concentrations of GLO and NO_2 were recorded than that of July 2009 and a similar condition was observed by Muralidharan *et al.* (1989). The recovery of background values of these gas concentrations in July 2009 may be due to the reversal of meteorological conditions from the previous month.

Conclusion

As a case study at Chenbagaramanputhur village, the ambient concentration of GLO and NO_2 and the relationship between these two generic species of gases has been revealed. Due to the improper construction of kilns large amount of fumes were released which may contain gases like CO, CO_2 and NO_X. Hence these brick kilns are acting as a point source of the precursor gases of ozone. During May, which is the crucial period for kiln works, large amount of fumes were released from kilns and hence maximum concentration of GLO was observed. Because of rain during June the activities were reduced and hence the values of GLO were comparatively lower than the other two months. Once again work was regained in July, which resulted into improved emissions and increased concentrations. The GLO and NO_2 levels were within the permissible limits of both national and international air quality standards. The monthly average values were found to be explicitly depended on natural and anthropogenic emissions as well as the photochemical mechanism.

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