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 CO₂, CH₄, CO, N₂O, NOₓ and NO. The photolysis of nitrogen dioxide (NO₂) directly leads to the formation of ozone (O₃) in the lower atmosphere. This work is an attempt to estimate the level of ground level ozone (GLO) and NO₂ concentrations in the atmospheric surface layer of a rural area dominated by traditional brick kiln industries. A portable monitor with O₃ and NO₂ 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 NO₂ 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 (NOₓ) such as nitric oxide (NO) and nitrogen dioxide (NO₂). NOₓ 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 NOₓ-VOC reactions in sunlight involving naturally occurring oxides of nitrogen and hydrocarbons or CO (Seinfeld & Pandis, 2006; Salve et al., 2007).

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 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 CO₂, CH₄, N₂O, NOₓ 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 NO₂ concentrations in a rural area where a large number of traditional brick kilns are active.
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 1.00 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 µg/m³. The operating temperature range is from 5°C to 50°C, relative humidity limits are 5% and 95%. Similar kind of NO₂ 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 NO₂ 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 NO₂ 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.

| Month   | 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 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 (NOx 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 NO₂

The NO₂ emission from the brick kilns has a major role in the formation of ozone. The presence of NO₂ is very important because NO₂ can be the only potential source of ozone in the study area. If there is a fractional amount of NO₂ 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).

\[ \text{NO}_2 + h\nu (\lambda < 424 \text{ nm}) \rightarrow O(3P) + \text{NO} \]  
\[ O(3P) + O_2 \rightarrow O_3 \]  

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).

\[ O_3 + NO \rightarrow NO_2 + O_2 \]

But with the presence of any hydrocarbons in the atmosphere, NO will be transformed to NO₂ by peroxyl radicals such as RO₂ and hydroxyl-radicals HO₂ as indicated in eq. (4) and (5) (Tang, 2009).

\[ \text{NO} + \text{HO}_2^* \rightarrow \text{NO}_2 + \text{OH}^* \]  
\[ \text{NO} + \text{RO}_2^* \rightarrow \text{NO}_2 + \text{RO}^* \]

The RO₂* and HO₂* radicals originate in the oxidation of the VOCs. Hence no ozone is consumed for the NO oxidation and the concentration of O₃ is no longer constant, but increases. NO₂ 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 NO₂ concentration is shown in Fig. 3. The mean concentration of NO₂ 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 NO₂ indicates that the diurnal variation of ozone depend on photochemical reactions during day time. The low NO₂ concentration observed during day time may be due to the photochemical reaction taking place for ozone production using NO₂ as a fuel. The maximum of GLO at noon is related to the highest photolysis rate of NO₂ at noon.

Thus NO₂ acts as a precursor of ozone. After sunset, the intensity of photochemical reaction reduces and hence NO₂ concentration builds up. Table 3 shows the observed minimum and maximum values of GLO and NO₂ during the study.

Comparison of GLO & NO₂ concentrations

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

Analyzing the comparative diagram (Fig. 4) of GLO and NO₂ concentration the relationship between the two trace species in a monthly scale could be obtained. The two gases, one as a precursor (NO₂) and
**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**
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 NO₂ 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 NO₂ 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 & NO₂ (in ppb)

| Month  | GLO Minimum | GLO Maximum | NO₂ Minimum | NO₂ 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 NO₂ and hence ozone. June 2009 mostly had cloudy and rainy days. Hence lower concentrations of GLO and NO₂ 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 NO₂ 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, CO₂ and NOₓ. 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 NO₂ levels were within the permissible limits of both national and international air quality standards. The monthly average values were found to be explicitly dependent on natural and anthropogenic emissions as well as the photochemical mechanism.

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