Monitoring and study the effect of weather parameters on concentration of surface ozone in the atmosphere for its forecasting

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ABSTRACT. The surface ozone levels throughout the world have been on an increase for the last three decades. The present study has been conducted for five Indian cities viz., New Delhi, Pune, Nagpur, Kodaikanal and Thiruvananthapuram for a period of six to ten years between (2005 to 2015) to study the trends in surface ozone with respect to spatial, diurnal, monthly and annual variation. This surface ozone concentration which is measured in Dobson unit using electrochemical method (Brewer Bubbler ozone sensor) is analyzed for hourly, monthly and annual variations. This study reveals that New Delhi and Nagpur showing decreasing trend in annual maximum ozone concentration while Kodaikanal, Pune and Thiruvananthapuram showing increasing trend. Similarly, except Nagpur, all other four locations viz., New Delhi, Kodaikanal, Pune and Thiruvananthapuram showing increasing trend in annual mean surface ozone concentration. The influences of meteorological factors that affect ozone were investigated for these locations throughout the year with measurement analysis. It is found that there is close relation between meteorological factors and concentration of surface ozone. All five locations showed strong and positive correlation with maximum temperature. As temperature is rising (global warming), the levels of ozone will increase similarly.

It is well known that weather parameters influencing the emission rate of ozone precursors. An attempt has been made to check the possibilities to predict the ozone concentration using available weather parameters in absence of data related to ozone precursor gases like CH\textsubscript{3} and NO\textsubscript{x}. Ozone forecasting models were developed for all five locations using composite weather variables and the performance of the model in predicting ozone at various locations is quite satisfactory.

Key words – Surface ozone, Stratospheric ozone, Ozone forecasting, Empirical model, Global warming.
1. Introduction

Ozone (O$_3$), one of the most powerful oxidants known, is a naturally occurring allotrope of oxygen. Ozone is the life preserving gas naturally present in atmosphere that absorbs ultra violet rays but at high levels in the troposphere it is phyto-toxic as well as cyto-toxic. One of the most important minor constituents of air is triatomic oxygen or ozone. But in past few decades, troposphere O$_3$ has been identified as a most important air pollutant of rural areas. Air pollutants produce reactive oxygen species (ROS), which adversely affect biochemical processes of plants and reduce their tolerance capacity to other stresses also. From the meteorological point of view, the close connection between ozone and weather processes enables the study of ozone to serve as an indirect method for the exploration of the atmosphere.

Vukovich (1994); Sillman & Samson (1995) and Walcek & Yuan (1995) their finding stated that temperature has direct impact on the O$_3$ production rate. Similarly higher temperatures also increase the emission rate of ozone precursors (Valente and Thornton, 1993).

Central Road Research Institute conducted study at seven sites in Delhi showed that 8 hours O$_3$ concentration during day exceeded the WHO standard of 51 to 102 ppb by 10 to 40% [Singh et al., 1997]. According to Prather et al., 2003, O$_3$ may rise to 20% over the next 50 years due to likely three fold increases in NOx and CH$_4$ emissions. Climate change can further exacerbate the situation since it has been shown to increase O$_3$ in many regions of the world [Horowitz, 2006].

1.1. Impacts of ozone on plants

Surface ozone gas causing many detrimental effects on plants. Menut et al., 2000 observed that ozone interferes with the ability of green plants to convert sunlight into useful energy and causes damage to agricultural crops, commercial timber and natural forest ecosystems, ornamental plants and other natural flora.

According to Krupa et al., 1998; Morgon et al., 2006, Long-term exposure to high concentration of surface O$_3$ damages vegetation with substantial reduction in crop yields and crop quality. Varshney and Aggarwal (1992) showed ground level O$_3$ concentrations between 9.4 - 128.3 ppb in Delhi. In a proteomic analysis conducted in-vivo condition on rice seedlings exposed to O$_3$ (40, 80, 120 ppb for 6 h d$^{-1}$ for 9 d), reduction in expression of Rubisco large sub-unit (LSU) and small sub-unit (SSU) was reported (Feng et al., 2009).

1.2. Meteorological conditions conducive to ozone formation

1.2.1. Days when solar radiation is high

\[ NO_2 + h\nu \rightarrow k \rightarrow NO + O \]

Solar radiation is an important factor because of ozone formation reactions. Solar radiation is highest during cloudless, summer days.

1.2.2. Days with low wind speed

Low wind speeds lead to poorer dispersion and generally result in increased concentration of ozone and ozone precursors within a smaller area. However, areas affected by long-range transport can experience high ozone concentrations during periods of moderate wind speeds.

Although many factors influence ozone concentration, diurnal meteorological variations are the one that clearly explain diurnal variation of ozone concentrations. The most important meteorological parameters which influence ozone concentration are solar irradiation (influencing the speed and amount of photochemical production of ozone), temperature (controlling, influencing the speed and amount of photochemical production of ozone), vertical temperature gradient (influencing the vertical mixing in the atmosphere and thereafter the ozone concentration near the ground), surface winds (controlling the formation of the diurnal pattern of surface ozone concentrations in mountain valleys and coastal areas), aloft winds (responsible for the transport of ozone and its precursors), precipitation (decreasing the ozone concentration by means of wet deposition) and relative humidity (chemically controlling the ozone concentration) (Alexandrov et al., 2005).

1.3. Measurement of surface ozone using electrochemical concentration cell

The surface ozone measurement system is successfully operating from the five stations using Electrochemical Concentration Cell, e.g., New Delhi, Pune, Kodaikanal, Thiruvananthapuram and Nagpur. Brewer Bubbler measures the surface ozone. The bubbler ozone sensor is based on electrochemical reaction of ozone with potassium iodide solution. A glass bubbler containing about 3 ml of buffered potassium iodide solution is surrounded by a reservoir of the same solution. A small hole at the bottom of bubbler allows the solution from the reservoir to enter the chamber. Air is aspirated
TABLE 1
Details of stations used during study

| Station name     | Altitude (a.m.s.l.) in meters | Average annual maximum temperature | Average annual minimum temperature | Data used for the years                      |
|------------------|-------------------------------|-----------------------------------|-----------------------------------|---------------------------------------------|
| New Delhi        | 227                           | 31 °C                             | 19 °C                             | 2005, 2007, 2009, 2010, 2011, 2013 and 2014 |
| Pune             | 559                           | 32 °C                             | 18 °C                             | 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014 and 2015 |
| Kodaikanal       | 2133                          | 18 °C                             | 11 °C                             | 2005, 2006, 2007, 2010, 2012, 2013, 2014 and 2015 |
| Thiruvananthapuram | 10                           | 31 °C                             | 23 °C                             | 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013 and 2014 |
| Nagpur           | 310                           | 34 °C                             | 20 °C                             | 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013 and 2014 |

through the bubbler using a suction pump. When ozone enters the sensor, iodine is formed in the cathode half-cell. The cell then converts the iodine to iodide, a process during which electrons flow in the cell’s external circuit.

Titration of ozone in a potassium iodide (KI) solution according the redox reaction:

$$2KI + O_3 + H_2O \rightarrow I_2 + O_2 + 2KOH$$

The iodine makes contact with a platinum cathode and is reduced back to iodide ions by the uptake of 2 electrons per molecule of iodine:

$$I_2 + 2e \text{ on Pt} \rightarrow 2I^- \text{ (cathode reaction)}$$

By measuring the electron flow (i.e., the cell current) and the rate at which ozone enters the cell per unit time, ozone concentrations can be calculated.

2. Materials

In order to carry out this study hourly ozone data and daily weather data of 6 to 10 years collected for New Delhi, Nagpur, Pune, Kodaikanal and Thiruvananthapuram locations. These stations cover a range of altitude between 10 meters to 2133 meters above mean sea level (a.m.s.l.) so that air masses from the near sea surface to the lower free troposphere are sampled.

The data required for analysis is acquired from National Data Centre, Pune, overlapping years of data for the stations was chosen. Hourly surface ozone data which is measured using electrochemical concentration cell method (Brewer bubbler ozone sensor) as well as daily weather data measured in respective meteorological observatories were collected for these locations from National Data Centre, India Meteorological Department, Pune.

3. Method

Fisher (1924) and Hendrick and Scholl (1943) used small number of estimated parameters for taking care of distribution pattern of weather over the crop season. It assumed that the ozone concentration is not depending on single variable but in combination of many variables. Hence, same model is used for estimation of ozone as a dependent variable on many weather variables as independent parameter. The main aim of this project is to identify some trend in the values of ozone over Indian cities viz., New Delhi, Pune, Nagpur, Kodaikanal and Thiruvananthapuram so that we get an idea of the ozone concentration scenario over the tropical Indian sub-continent.

From the hourly ozone data and daily weather data was selected on the basis of availability of data. Finally comparison of ozone concentration was made using graphs with respect to varying hours, months and years to know the trend of ozone concentration. Step wise regression method used to analyze the effect of weather variables on the amount of tropospheric ozone.

3.1. Models using composite weather variables

$$Y = A_0 + a_0 \sum_{w=1}^{n} X_w + a_1 \sum_{w=1}^{n} w^1 X_w + a_2 \sum_{w=1}^{n} w^2 X_w + e$$
where, $X_w$ denotes value of combination of weather variable under study, $n$ is the number of weather variables and $A_0$, $a_0$, $a_1$ and $a_2$ are the model parameters. This model was extended to study combined effects of weather variables and an additional variate $T$ representing the year for time trend.

Weather variables used for these models are:

- **MAX** = maximum temperature (in degree C),
- **MIN** = minimum temperature (in degree C),
- **AW** = average wind speed (in kilometers per hour),
- **EVP** = evaporation (in mm) in 24 hours ending 0830 hours IST,
- **SN** = weather day with snow,
- **DRNRF** = duration of rainfall in 24 hours in hours and minutes,
- **SSH** = duration of sunshine in hours,
- **HA** = weather day with hail,
- **DS** = weather day with dust-storm,
- **TSQ** = total number of squalls,
- **TS** = weather day with thunder.

4. Results and discussion

4.1. Variation of annual maximum ozone concentration

Fig. 1(a) shows the variation of annual maximum ozone concentration in parts per billion (ppb) for New Delhi. And it is decreasing with the rate of 4.48 ppb per year (approx.).

Fig. 1(b) shows the variation of annual maximum ozone concentration in parts per billion (ppb) for Kodaikanal. And it is increasing with the rate of 4.44 ppb per year (approx.).

Fig. 1(c) shows the variation of annual maximum ozone concentration in parts per billion (ppb) for Nagpur. And it is decreasing with the rate of 0.39 ppb per year (approx.).

Fig. 1(d) shows the variation of annual maximum ozone concentration in parts per billion (ppb) in for Pune.
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Figs. 2(a-e). Annual mean ozone at (a) New Delhi (b) Kodaikanal (c) Nagpur (d) Pune and (e) Thiruvananthapuram

And it is increasing with the rate of 2.2 ppb per year (approx.).

Fig. 1(e) shows the variation of annual maximum ozone concentration in parts per billion (ppb) for Thiruvananthapuram. And it is increasing with the rate of 4.24 ppb per year (approx.).

Except New Delhi and Nagpur other three locations viz., Kodaikanal, Pune and Thiruvananthapuram showing increasing trend in annual maximum ozone concentration. Highest decreasing rate of annual maximum ozone concentration i.e., 4.48 ppb per year was found at New Delhi station while highest increasing rate i.e., 4.44 ppb per year was found observed at Kodaikanal station.

4.2. Variation of annual mean ozone concentration

Fig. 2(a) shows the variation of annual mean ozone concentration in parts per billion (ppb) for New Delhi. And it is increasing with the rate of 1.64 ppb per year (approx.).

Fig. 2(b) shows the variation of annual mean ozone concentration in parts per billion (ppb) for Kodaikanal. And it is increasing with the rate of 3.06 ppb per year (approx.).

Fig. 2(c) shows the variation of annual mean ozone concentration in parts per billion (ppb) for Nagpur. And it is slightly decreasing with the rate of 0.24 ppb per year (approx.).

Fig. 2(d) shows the variation of annual mean ozone concentration in parts per billion (ppb) for Pune. And it is increasing with the rate of 0.59 ppb per year (approx.).

Fig. 2(e) shows the variation of annual mean ozone concentration in parts per billion (ppb) for Thiruvananthapuram. And it is increasing with the rate of 1.43 ppb per year (approx.).

Except Nagpur, all other four locations viz., New Delhi, Kodaikanal, Pune and Thiruvananthapuram showing increasing trend in annual mean ozone concentration. Highest increasing rate of annual mean ozone concentration i.e., 3.06 ppb per year was found at Kodaikanal station while highest decreasing rate i.e., 0.24 ppb per year was found at Nagpur station.

4.3. Diurnal variation in ozone concentration

Figs. 3(a) show the diurnal variation in ozone concentration in Parts per billion, ppb for New Delhi.
Figs. 3(a-e). Diurnal variation in ozone concentration at (a) New Delhi (b) Kodaikanal (c) Nagpur (d) Pune and (e) Thiruvananthapuram

Figs. 4(a-e). Annual variation in ozone concentration at (a) New Delhi (b) Kodaikanal (c) Nagpur (d) Pune and (e) Thiruvananthapuram
Table 2

Empirical equations of ozone forecasting models for different locations

| Location      | Equation                                                                 | $R^2$ | Std. Error |
|---------------|--------------------------------------------------------------------------|-------|------------|
| New Delhi     | $Y = -2.66456 + 1.04093^* [\text{SUMPRODUCT} (\text{MAX}, \text{MIN}, \text{EVP}, \text{TSQ}, \text{SN}, \text{HA})]$ | 0.155 | 12.06      |
| Kodaikanal    | $Y = 6.259 + 1.805^* [\text{SUMPRODUCT} (\text{MAX}, \text{MIN}, \text{AW}, \text{HA})]$ | 0.126 | 9.90       |
| Nagpur        | $Y = -8.055 + 1.071^* [\text{SUMPRODUCT} (\text{MAX}, \text{AW}, \text{EVP}, \text{TS})]$ | 0.242 | 7.46       |
| Pune          | $Y = -3.421 + 0.241^* [\text{SUM} (\text{MAX}, \text{MIN}, \text{AW}, \text{EVP}, \text{DRNRF}, \text{TS})]$ | 0.231 | 4.97       |
| Thiruvananthapuram | $Y = -28.213 + (1.03^*\text{MAX}) + (0.006^*\text{DS})$ | 0.340 | 3.86       |

Fig. 3(b) shows the diurnal variation in ozone concentration in Parts per billion, ppb for Kodaikanal.

Fig. 3(c) shows the diurnal variation in ozone concentration in Parts per billion, ppb for Nagpur.

Fig. 3(d) shows the diurnal variation in ozone concentration in Parts per billion, ppb for Pune.

Fig. 3(e) shows the diurnal variation in ozone concentration in Parts per billion, ppb for Thiruvananthapuram.

There is a wave like pattern in the diurnal variation in hourly amount of ozone concentration for all years, in all five cities. Low amount of ozone concentration observed during morning, evening and night hours and high amount of ozone concentration observed in noon hour at New Delhi, Nagpur, Pune & Thiruvananthapuram locations while Kodaikanal witnesses lowest amount of ozone concentration during noon hours. According Chevalier et al. (2007) averaged ozone level strongly depends on altitude and varies from 25 to 53 ppb over the range 100-3500 m. From these results can be inferred that altitude plays an important role in influencing weather of particular location which ultimately affects the ozone (O3) concentration.

4.4. Annual variation in ozone concentration

Fig. 4(a) shows the annual variation in ozone concentration in Parts per billion, ppb for New Delhi.

Fig. 4(b) shows the annual variation in ozone concentration in Parts per billion, ppb for Kodaikanal.

Fig. 4(c) shows the annual variation in ozone concentration in Parts per billion, ppb for Nagpur.

Fig. 4(d) shows the annual variation in ozone concentration in Parts per billion, ppb for Pune.

Fig. 4(e) shows the annual variation in ozone concentration in Parts per billion, ppb for Thiruvananthapuram.

High amount of ozone concentration observed during May and June month at New Delhi, Nagpur and Pune but in Kodaikanal witnesses highest amount of ozone concentration during March and October while during February and March in Thiruvananthapuram. Altitude of station is affecting the surface ozone concentration. According Chevalier et al. (2007) at high-altitude sites maxima may appear for summer months (June to September) in addition to the spring tropospheric maximum (April-May).

4.5. Model output and actual ozone concentration

The empirical equations of ozone forecasting models for different locations are shown in Table 2. All five stations showing strong and positive correlation with Maximum temperature. In case of minimum temperature, New Delhi, Pune showing positive correlation while Kodaikanal and Thiruvananthapuram showing negative correlation but there is no significant correlation found in case of Nagpur. Similarly for evaporation, New Delhi, Pune, Thiruvananthapuram showing positive correlation while Nagpur showing negative correlation but there is no significant correlation found in case of Kodaikanal.

Fig. 5(a) shows the model output ozone and actual observed in ozone concentration in Parts per billion, ppb for New Delhi.

Fig. 5(b) shows the model output ozone and actual observed ozone concentration in Parts per billion, ppb for Kodaikanal.
Figs. 5(a-e). Model output and actual ozone at (a) New Delhi (b) Kodaikanal (c) Nagpur (d) Pune and (e) Thiruvananthapuram

Figs. 6(a-e). Actual vs. forecasted ozone at (a) New Delhi (b) Kodaikanal (c) Nagpur (d) Pune and (e) Thiruvananthapuram
Fig. 5(c) shows the model output ozone and actual observed ozone concentration in Parts per billion, ppb for Nagpur.

Fig. 5(d) shows the model output ozone and actual observed ozone concentration in Parts per billion, ppb for Pune.

Fig. 5(e) shows the model output ozone and actual observed ozone concentration in Parts per billion, ppb for Thiruvananthapuram.

4.6. Forecasted and actual ozone concentration

Fig. 6(a) shows the forecasted ozone and actual observed in ozone concentration in Parts per billion, ppb for New Delhi.

Fig. 6(b) shows the forecasted ozone and actual observed in ozone concentration in Parts per billion, ppb for Kodaikanal.

Fig. 6(c) shows the forecasted ozone and actual observed in ozone concentration in Parts per billion, ppb for Nagpur.

Fig. 6(d) shows the forecasted ozone and actual observed in ozone concentration in Parts per billion, ppb for Pune.

Fig. 6(e) shows the forecasted ozone and actual observed in ozone concentration in Parts per billion, ppb for Thiruvananthapuram.

5. Conclusions

The present study is carried out to analyze the ozone data over 6 to 10 years (2005-2015) collected for 5 surface stations viz., New Delhi, Nagpur, Pune, Kodaikanal and Thiruvananthapuram. Surface ozone concentration analyzed for hourly, monthly and annual variations. Annual trends in maximum troposphere ozone level were first discussed. The highest increasing rate of annual maximum ozone concentration i.e., 4.44 ppb per year was found at Kodaikanal station. While highest decreasing rate i.e., 4.48 ppb per year was found at New Delhi station. Similarly highest increasing rate of annual mean ozone concentration i.e., 3.06 ppb per year was found at Kodaikanal station while highest decreasing rate i.e., 0.24 ppb per year was found at Nagpur station. It is found that the altitude plays an important role in influencing weather of particular location and which ultimately affecting the surface ozone (O₃) concentration. The main focus of the study was on the development of empirical surface ozone forecasting models. During this process simple and weighted weather indices are prepared for individual weather variables as well as for interaction of two variables at a time considering throughout the year. The performance of the model in predicting ozone at various locations is quite satisfactory. Except few days, ozone values of modeled output and actual observed ozone showing similar trends though out the 350 days of the year. Similarly, except few observations actual ozone was almost equal to forecasted ozone though out 15 days. The performance of these models in predicting ozone at various locations is quite satisfactory. Forecasted ozone values given by the models are acceptable. Further studies needed to develop more accurate ozone forewarning models. This study can be helpful to predict the possible effect of climate change on surface ozone.

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