CHAPTER -II

MEASUREMENT OF SURFACE OZONE IN
VARIOUS PLACES OF TAMIL NADU

2.1 Introduction

In recent years, O\textsubscript{3} chemistry has received considerable attention in Asia owing to rapid economic and industrial development, accompanied by its increasing air pollutant emissions. India and China are most populous countries in the world and also they are one of the top energy consuming countries. The temporal variations of O\textsubscript{3} have been reported at many sites including rural, urban, coast and mountain sites in India [1-6], China [7-8]. The tropospheric ozone changed dimensions about fifteen years ago, when it was realized that the increased surface ozone is not only a local urban problem but also a global increase of surface rural ozone concentration, especially in the northern hemisphere. This was observed during the 20\textsuperscript{th} century, which has been attributed to photochemical production [9-12]. Measurements during the second half of the last century at many sites show that the present levels of ozone have raised more than double their levels [13]. Estimations made using the chemical transport model showed that on increasing the anthropogenic emissions, ozone production efficiency was maximum over the Indian region followed by Japan and China. This can be explained on the basis of an increase in OH peroxy radicals [14].

Over the globe, especially in southern Asian countries, a few scared surface measurements of ozone are being carried out based on ozone sensors. Hence it demands to measure the surface ozone and other influenced meteorological parameters studies are very important in regional level. In this chapter study sites,
data measurement, statistical analysis and model performance evaluation also discussed.

2.2 Study area

Table 2.1 shows the details of major study sites. Fig2.1 refers geographical location of study stations of Tamil Nadu State. This study aspire to asses distribution of the surface zone concentration, characteristics of hourly and daily mean surface ozone with different climatic parameters, such as temperature, relative humidity, and wind speed over Tamil Nadu. Measurement was carried out at 11-stations (except this study no data is made available) having different weather conditions during the period from 8th June to 7th July of the year 2011. In each place, the measurement was done every hour from 08:00 am to 5:00 pm. We were the first researchers visited most of the district of Tamil Nadu state and measured surface ozone. Among the 11 cities Chennai surface ozone was taken for studies from the period 2011 to 2012. For total ozone and rainfall, we were considered Kodaikanal data.

Table- 2.1 Details of major study sites

<table>
<thead>
<tr>
<th>S. No</th>
<th>Measurement places</th>
<th>Description of measurement Stations</th>
<th>Latitude, Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Kanyakumari</td>
<td>Coastal area, More Brick kiln industry.</td>
<td>8º 04’ N   77º 33’ E</td>
</tr>
<tr>
<td>2</td>
<td>Myladuthurai</td>
<td>Continental area – Town, Villages</td>
<td>11º 06’ N   79º 42’ E</td>
</tr>
<tr>
<td>3</td>
<td>Tirunelveli</td>
<td>a Stretch of Western Ghats and lowland plains, scenic waterfalls, sandy soil and fertile alluvium, Beach Minerals Factory, Vehicles</td>
<td>8º 44’ N   77º 44’ E o</td>
</tr>
<tr>
<td>S. No</td>
<td>Measurement places</td>
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<td>Latitude, Longitude</td>
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<tr>
<td>4</td>
<td>Madurai</td>
<td>Continental area – Big Town rubber producing centers, Numerous textile and chemical industries, Granite industries, Brick kiln industry in villages</td>
<td>9° 58’ N 78° 10’ E</td>
</tr>
<tr>
<td>5</td>
<td>Tuticorin</td>
<td>Medium seaport (Artificial), Industrial coal, copper concentrate, fertilizer, timber logs, iron ore, pearl fishery</td>
<td>8° 48’ N 78° 11’ E</td>
</tr>
<tr>
<td>6</td>
<td>Vellore</td>
<td>Continental area with more industrialization surrounded by plains, low rocky hills, tropical wet and dry climate</td>
<td>12° 55’ N 79° 11’ E</td>
</tr>
<tr>
<td>7</td>
<td>Kanchipuram</td>
<td>Thriving hand loom industry, Continental area - Surrounded Village</td>
<td>12° 50’ N 79° 45’ E</td>
</tr>
<tr>
<td>8</td>
<td>Chennai</td>
<td>Eastern Coastal plains, a tropical wet and dry city, automobile industry, leather exports, more polluted city.</td>
<td>13° 04’ N 80° 17’ E</td>
</tr>
<tr>
<td>9</td>
<td>Coimbatore</td>
<td>A Stretch of Western Ghats, textile and manufacturing hub</td>
<td>11° 00’ N 77° 00’ E</td>
</tr>
<tr>
<td>10</td>
<td>Trichy</td>
<td>Alluvial soil, a belt of cretaceous rock, Layers of archaean rocks, granite and gneiss, thin bed of conglomeratic laterite, Cauvery delta</td>
<td>10° 50’ N 78° 46’ E</td>
</tr>
<tr>
<td>11</td>
<td>Cuddalore</td>
<td>Coastal area with less industrialization</td>
<td>11° 43’ N 79° 49’ E</td>
</tr>
</tbody>
</table>
2.2.1 Study area -1 Chennai:

The study site is located at 13.04°N 80.17°E on the southeast coast of India and in the northeast corner of Tamil Nadu. Chennai is capital of Tamil Nadu state. Chennai lies on the thermal equator and on a flat coastal plain, which prevents extreme variation in seasonal temperature. It is the biggest industrial, commercial center, and a major cultural, economic and educational center in South India. The weather is hot and humid. The Chennai include elevations up to 6 meters above sea level. Though surface ozone is a secondary pollutant; Tamilnadu Pollution Control Board located in Chennai was not measuring surface ozone along with other pollutants. The purpose of this study is to understand the temporal variations of surface ozone at this site. Since this ozone data has not been measured and analyzed previously, the study will consider the climate effects of this area and find correlations with ozone.

2.2.2 Study area- 2 Kodaikanal:

The study site is located at 10.13°N 77.28°E. It referred to as the "Princess of Hill stations" and popular tourist destination. The town of Kodaikanal sits on a plateau above the southern escarpment of the upper palani Hills at 2,133 metres (6,998 ft) above sea level. The Kodaikanal Observatory of the Indian Institute of Astrophysics is located in the beautiful palani range of hills in Southern India. According to the Köppen climate classification, Kodaikanal has a monsoon-influenced subtropical highland climate. The temperatures are cool throughout the year due to the high elevation of the city. The purpose of this study is to understand the temporal variations of total ozone column and rainfall at this site. Since total ozone column and rainfall data had been collected from Indian Metrological
Department and analyzed, the study considered the correlations between total ozone and rainfall.

![Geographical location of study stations](image)

**Fig2.1- Geographical location of study stations**

### 2.3 Method of data measurement

Surface ozone concentration along with wind speed, temperature and relative humidity were measured. A portable Aeroqual series S200 ozone monitor was used.

A gas sensitive semiconductor (GSS) type sensor is described in
www.aeroqual.com. Wind speed is calculated using AM-4201 digital Anemometer. Measurement in range 0.4 – 3 m/s has resolution 0.1 m/s of accuracy ± (2% + 0.2 m/s). The ambient temperature and humidity are measured by Thermo Hydrometer. Temperature accuracy ± 0.1°C and humidity accuracy ± 5%. Sampling was carried out August 2011 to July 2012. Total Ozone Column data of Kodaikanal for the period from 1995 to 2005 were collected from India Meteorological Department, New Delhi. The rainfall data of Kodaikanal from 2000 to 2010 were collected from India and the Regional Meteorological Center, Chennai.

2.4 Mathematical Methods used in this study

Most of the knowledge about ozone and total column ozone relationships is based on empirical observations and data analysis. Therefore, it is important to have a basic understanding of the statistical concepts employed to understand the significance of the relationships. The Pearson’s linear correlation analysis, regression techniques like method of least squares and regression analysis have been used in this study. The performance of the models has been evaluated using statistical error parameters like Mean Bias Error (MBE), Root Mean Square Error (RMSE), and Mean Absolute Percentage Error (MAPE).

2.4.1 Karl Pearson’s correlation analysis

Many different statistical and mathematical methods exist to detect, describe, quantify and evaluate correlations between two variables. This method can be used to measure the strength of association between two variables [15]. If the change in one variable affects the other variable, the variables are said to be correlated. If two variables deviate in the same direction, correlation is said to be direct or positive. If
two variables deviate in the opposite direction, correlation is said to be diverse or negative [16].

Correlation coefficient between two random variables X and Y denoted by $r(X, Y)$ is a numerical measure of linear relationship between them is defined as

$$r(X, Y) = \frac{\text{Cov}(X, Y)}{\sigma_X \sigma_Y}$$  \hspace{1cm} (2.1)$$

Where Cov (X, Y) is the covariance of the variables of X and Y given by

$$\text{Cov}(X, Y) = \frac{1}{n} \sum (x_i - \bar{x}) (y_i - \bar{y})$$  \hspace{1cm} (2.2)$$

$$\sigma_x = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}$$  \hspace{1cm} (2.3)$$

$$\sigma_y = \sqrt{\frac{\sum (y - \bar{y})^2}{n-1}}$$  \hspace{1cm} (2.4)$$

Where $\bar{x}$ and $\bar{y}$ are the average values of x and y, n is the number of observations.

2.4.2 Linear Regression method

One of the most common methods is linear regression method to estimate the best-fit linear relationship between two or more quantities. Regression is used to assess the contribution of one or more explanatory variables called independent variables to one response or dependent variable. It can also be used to predict the value of one variable based on the values of other. When there is only one independent variable and when the relationship can be expressed as a straight line this is called single linear regression.

2.4.3 Least Squares Linear Regression

Least Squares Linear Regression is a method for predicting the dependent variable Y based on the value of an independent variable X. The dependent variable
Y has a linear relationship to the independent variable X. To verify this plot XY scatter plot is linear and that the residual plot shows a random pattern.

The population regression line is:

\[ y = b_0 + b_1 x \]  \hspace{1cm} (2.5)

Where \( b_0 \) is a constant, \( b_1 \) is the regression coefficient, \( x \) is the value of the independent variable, and \( y \) is the value of the dependent variable.

If the sample is random, the population regression line is given by \( \hat{y} = b_0 + b_1 x \)

Where \( b_0 \) is a constant, \( b_1 \) is the regression coefficient, \( x \) is the value of the independent variable, and \( \hat{y} \) is the predicted value of the dependent variable.

\[ b_1 = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sum(x_i - \bar{x})^2} \]  \hspace{1cm} (2.6)

\[ b_1 = r \frac{\sigma_y}{\sigma_x} \]  \hspace{1cm} (2.7)

\[ b_0 = y - b_1 \times x \]  \hspace{1cm} (2.8)

Where \( r \) is the correlation between \( x \) and \( y \), \( x_i \) is the \( x \) value of observation \( i \), \( y_i \) is the \( y \) value of observation \( i \), \( x \) is the mean of \( x \), \( y \) is the mean of \( y \), \( \sigma_x \) is the standard deviation of \( x \), and \( \sigma_y \) is the standard deviation of \( y \).

The coefficient of determination \( (R^2) \) is interpreted as the proportion of the variance in the dependent variable that is predictable from the independent variable. The coefficient of determination ranges from 0 to 1. An \( R^2 \) of 0 means that the dependent variable cannot be predicted from the independent variable. An \( R^2 \) of 1 means that the dependent variable can be predicted without error from the independent variable. An \( R^2 \) between 0 and 1 indicates the extent to which the dependent variable is predictable.
The coefficient of determination \( R^2 \) for a linear regression model with one independent variable is:

\[
R^2 = \left\{ \frac{1}{N} \sum \left[ (x_i - \bar{x})(y_i - \bar{y}) / (\sigma_x \sigma_y) \right] \right\}^2
\]

(2.9)

where \( N \) is the number of observations used to fit the model, \( \Sigma \) is the summation symbol, \( x_i \) is the x value for observation \( i \), \( \bar{x} \) is the mean x value, \( y_i \) is the y value for observation \( i \), \( \bar{y} \) is the mean y value, \( \sigma_x \) is the standard deviation of x, and \( \sigma_y \) is the standard deviation of y.

2.4.4 Model performance evaluation

A Statistical Analysis was conducted in order to evaluate the performance of each single model. Four statistical instruments were used to quantify the performance of the models [17].

2.4.4.1 Mean Bias Error (MBE)

There are different instruments that can quantify the error between the observed and the calculated values. The first is the Mean Bias Error which is the average deviation of the estimated values from the measured values. It is derived as follows

\[
MBE = \frac{1}{N} \sum_{i=1}^{N} (P_{cal}^i - P_{obs}^i)
\]

(2.10)

\( N \) is the total number of observations, and \( P_{obs} \) and \( P_{cal} \) are the \( i^{th} \) observed and measured values of p parameter. This test provides information on the long term performance. A low MBE is desired. A model would perfectly fit the observed data if the MBE is equal to zero that is the sum of pair wise negative and positive
deviations would also be zero\[18\]. A positive value gives the average amount of over-estimation in the calculated value or vice versa.

2.4.4.2 Root Mean Square Error (RMSE)

The RMSE provides information on the short term performance of the correlation by allowing a term-by-term comparison of the deviation between the calculated and observed values. The smaller the values, better the model perform and RMSE is a non-systematic error.

It is defined as:

\[
RMSE = \left( \frac{1}{N} \sum_{i=1}^{N} (P_{cal}^i - P_{obs}^i)^2 \right)^{1/2}
\]  

(2.11)

2.4.4.3 Mean Absolute Percentage Error (MAPE)

MAPE is an overall measure of forecast accuracy computed from the absolute differences between a series of forecasts and actual data observed, each absolute difference is expressed as a percentage of each actual data, then summed and averaged \[19\]. It is defined as:

\[
MAPE = \frac{100}{N} \sum_{i=1}^{N} \frac{P_{cal}^i - P_{obs}^i}{P_{obs}^i}
\]  

(2.12)

2.4.4.4 Mean Absolute Error (MAE)

It gives the absolute value of bias error and is a measure of the goodness of the correction.

It is defined as

\[
MAE = \frac{1}{N} \sum_{i=1}^{N} |P_{cal}^i - P_{obs}^i|
\]  

(2.13)
Fig 2.2 - Average value of Surface Ozone in different places of Tamil Nadu

Fig 2.3 - Hourly average of Ozone and Temperature over Tamil Nadu

Fig 2.4 - Hourly average of Ozone & wind over Speed over Tamil Nadu
2.5 Conclusion

The correlation coefficient between the surface ozone and meteorological parameters were calculated. The result indicated no major difference between the Hourly and daily average of the \( \text{O}_3 \) concentrations. And also it does not exceed the national ambient air quality standard (0.075 ppm). Fig.2.2 shows average value of surface ozone in different places of Tamil Nadu. Variations of surface ozone concentration in different places showed that, hourly and daily mean ground level ozone concentration in Tamil Nadu state was 0.0109 ppm and 0.0108 ppm. The highest ground level ozone concentration was observed at Kanyakumari which is the south most district of Tamil Nadu and its value is 0.0179 ppm. The next higher concentration of 0.0168 ppm was observed at Myladuthurai. The lowest ground level ozone concentration was noticed at Cuddalore (0.0038 ppm). Fig.2.3 gives the distribution of ozone and temperature over the entire day. It reveals that ground level ozone increases with temperature. This is due to the fact that ozone formation is enhanced by the temperature.
From Fig. 2.4, it is clear that the ground level Ozone is correlated with wind speed negatively to a certain extent. From Fig. 2.5 we can understand ozone & relative humidity are correlated negatively. Relative humidity decreases with increasing temperature. From the fig 2.6, the surface ozone concentration has shown a clear diurnal cycle, with highest value at around 1500 hours in the day time. Also, it has been observed that ozone concentration gradually increased at day time and decreased at night time. Thus, ozone level is positively correlated with temperature. The dependence of ground level Ozone concentration on meteorological parameters such as temperature, wind speed and relative humidity has been established. Results of this study have revealed that the surface ozone is positively correlated with temperature and inversely correlated with relative humidity and wind speed. Fourth coming chapters describe trend analysis and various forecasting methods.
References


