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Surface Ozone Measurements in Southernmost Tip of Peninsular India

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Abstract:

Surface Ozone pollution is one of the largely ignored problems of many countries of the world. It can have very toxic effects to biotic and abiotic factors. It is a potential oxidant and a radical which can react readily with other materials. Measurements of surface ozone concentration were carried out for the first time in Kanyakumari (8°4'33''N and 77°32'53'' E), one of the beautiful tourist spots in India, for a period of three years from March 2010 – February 2013.No air quality studies were done in the study area during the past, even though the place of study is of geographical importance. Surface ozone concentration varied between 11 ppb and 55 ppb. The daily average values lied between 20.17 ppb and 36.35 ppb. A clear diurnal cycle following the global pattern was observed with minimum values during early morning hours and maximum at afternoon hours. Summer season recorded the highest surface ozone concentration and north east monsoon with the lowest concentration. The seasonal average of diurnal amplitude of surface ozone concentration for the entire three years was found to lie between 23.50 ppb and 30.82 ppb. During the entire period of study, surface ozone was found to be positively correlated with temperature and negatively correlated with relative humidity .A neural network model was performed to forecast the peak hour ozone concentration. The improved model yielded a good correlation between the actual and predicted data points.

Keywords: Biotic, Correlation, Diurnal Variation, Neural Network, Oxidant, Ozone, ppb, radical

1.0 Introduction:

Our atmosphere has a specific composition, structure and life sustaining cycles of nature in its lower reaches. It comprises of a mixture of gases exposed to the electromagnetic spectrum of the sun (**Nandita and Iyer, 2005**).The gases which are in low quantities play a vital role in our atmospheric chemistry and radiation budget. Ozone (O_3) is a two-faced gas. High in stratosphere, it acts as a protective layer and closer to the surface, it is a pollutant. This tropospheric ozone is also known as Surface Ozone (SOZ) or Ground Level Ozone (GLO).Surface ozone is a secondary pollutant formed by photochemical reaction of primary pollutants like oxides of nitrogen (NO_X), carbon monoxide and volatile organic compounds. High concentration of SOZ can cause potential damage to biotic and abiotic factors. Epidemiological and toxicological studies indicate that higher concentration of ozone is harmful to biological health (**Avol et al., 1998**).Inhalation of ozone irritates the lining tissues of human airways leading to respiratory diseases. Exposure to SOZ can reduce the volume of air and cause shortness of breath. Evidence for the chronic effects of ozone is supported by human and experimental information. Animal data and some autopsy studies indicate that chronic exposure of SOZ induces significant changes in airways at the level of terminal and respiratory branchioli (**Markus et al., 2008)**.The presence of SOZ and its effects on crops are often not visible in contrast with other yield reducing factors. Ozone pollution poses a growing threat to global food security even under optimistic scenario of future ozone precursor emissions (**Avnry et al., 2011**). Hence efforts to raise awareness about the ozone pollution is very important and the most direct way to obtain accurate air quality information is from measurements made at particular study regions.

At present, ozone is measured in few cities in India and very few in TamilNadu. Surface ozone measurements were made in Pune and analyzed diurnally, seasonally and annually by Kaushar Ai et

al., 2012. They found that there was a decreasing trend in SOZ concentration at Pune and no significant trend was observed in Delhi. Suresh Kumar Reddy *et al.,* 2012 analyzed the diurnal and seasonal behaviour of surface ozone at Anantapur and found that the highest mean was observed in April and lowest in August. Debaje and Kakade (2006) carried out surface ozone measurements in Joharapur and observed that the annual average diurnal variation of O3 showed that maximum O3 concentration was 29.9 ± 5.7 ppbv at noon and minimum 7.0 ± 3.4 ppbv in the morning with 1 σ standard deviation. Surface ozone measurements were made in Chennai by Pulikesi *et al*., 2006.According to their observations; the maximum hourly ozone reached 69 ppb during April 2006. Elampari and Chithambarathanu (2011) showed that the highest average seasonal concentration in Nagercoil was observed in summer and lowest in north east monsoon. The interesting fact is that rural areas often show high ozone concentration than cities. This study is aimed to access the amount of SOZ concentration at Kanyakumari (8°4'33''N and 77°32'53'' E) .It lies in the southernmost tip of peninsular India and it is the place where the Indian Ocean, the Arabian Sea and the Bay of Bengal meet. Kanyakumari is one of the important traffic prones of the district with high mobile tourist population almost the entire year and no considerable studies have been made on air quality in the past.

1.1 Photochemical production of SOZ:

Surface ozone is produced from photochemical oxidation of CH_4, VOCs and carbon monoxide (CO) in the presence of NO_x. During daylight hours nitrogen dioxide (NO_2) is photolytically converted to nitric oxide (NO) leading to the formation of ozone.

$NO_2 + h\nu$ ($\lambda <= 430nm$) → NO + O (1)

$O + O_2$ → O_3 (2)

Studies reveal that the most important source of anthropogenic NOx emissions on the global scale is road transport followed by combustion in power plants and industries. Some global emissions come from international maritime shipping, from non-road vehicles and from aircraft. Open burning of biomass due to forest fires, savannah burning and agricultural practices account for approximately 15% of global anthropogenic emissions and natural sources include soils and lightning. Ozone precursor emissions are expected to change significantly as a result of population growth, economic development, technological progress and uptake, control measures, varying land use, climate and other environmental changes

2.0 Study Area:

The measurements were made in and around Kanyakumari and considering the coherence of readings, the major study area was chosen as Kanyakumari town(8°4'33''N and 77°32'53'' E) because of its geographical importance. The district has a varied topography with sea on three sides and the mountains of the Western Ghats bordering the northern side. Kanyakumari is at the tip of Indian Peninsula and the climate is almost tropical. The climate of the district is divided into four seasons. The town witness its summer season from March to May followed by southwest monsoon (SWM) that extends from June to September. Northeast monsoon (NEM) is from October to December followed by winter season during January and February. The average summer temperature is around 32°C and average annual rainfall is 1456mm. Humidity and temperature of this place remain comparatively high all through the year. High solar intensity, prevailing sea breeze and increased vehicular activity paved the way to choose Kanyakumari as the study area for surface ozone and its precursor measurements.Figure.1 shows the study area where measurements were made.

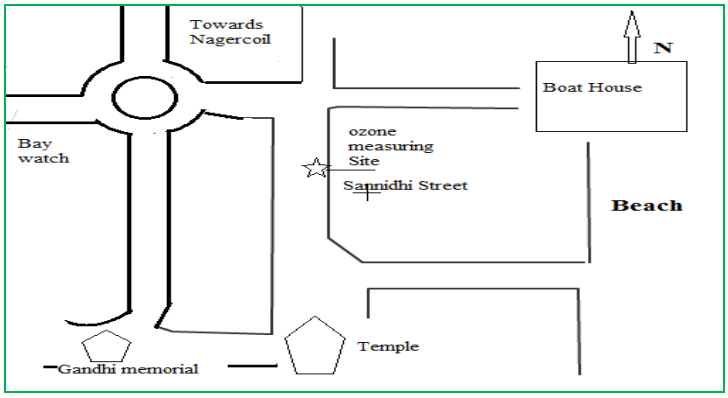

Fig.1.Study Area


Fig.2.Aeroqual S500 gas monitor

2.1 Data Collection:

Measurements of SOZ were made for a period of three years from March 2010 to February 2013. Measurements were carried out using Aeroqual monitors S500 & S300 employing various GSS sensor heads. This particular instrument was chosen for its simplicity and reliability in operation, ease of handling, and quickness in obtaining the gas concentration directly. The measurement units are in ppm or µg/m^3. The ozone sensor was calibrated against a certified UV photometer .At sampling site located near traffic, the monitor was placed a few metres from the closest road or parking lot in order to minimize perturbations from vehicular exhaust and the monitor was placed in an open space. Aeroqual ozone monitors were used for the measurement of ozone and nitrogen dioxide by Akram Ali, 2008, Su Lee and Shih-Wei Tsai, 2008. Aeroqual Series ozone monitor was used to calculate ozone deposition on snow and ice surfaces at Scott Base in Antarctica by a research team from Auckland University in New Zealand (http://www.aozp.co.uk).Nine readings were taken for SOZ concentration per day starting from morning 0530 hrs to next day morning 0530 hrs LT.

Temperature, relative humidity (RH), wind speed and wind direction are the key meteorological parameters measured at the site. Figure .2 shows the Aeroqual monitor S500.

3.0 Results and Discussions:

The observed SOZ data was analyzed on the basis of diurnal, seasonal and annual variations. All hourly values are used to analyze diurnal variability and daily average values are used to analyze the day-to-day variability.

3.1 Frequency Distribution:

The frequency distribution of SOZ concentration is given in table 1.From the observed data points, around 60 % of the data lies between 11 ppb and 30 ppb. The maximum distribution of the data is between 16 ppb and 20 ppb. No data points were recorded between 5 ppb and 10 ppb. The frequency distribution is clearly shown in figure 3.

Table.1.Frequency distribution of SOZ concentration

Range (ppb)	No. of Data points	Distribution (%)
5-10	0	0.00
11-15	178	6.55
16-20	657	24.17
21-25	439	16.15
26-30	326	11.99
31-35	353	12.99
36-40	314	11.55
41-45	282	10.38
46-50	134	4.93
51-55	35	1.29

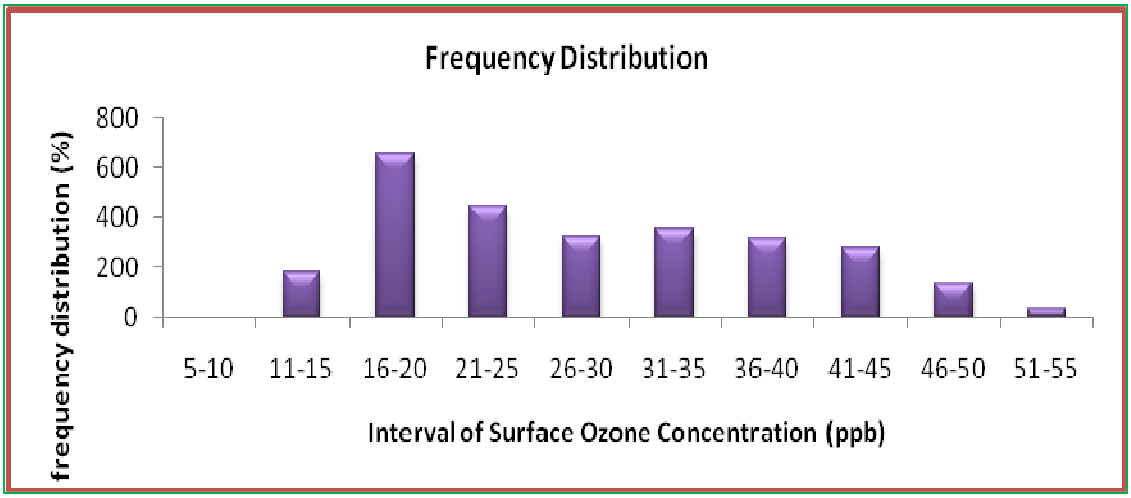

Fig.3. Frequency Distribution

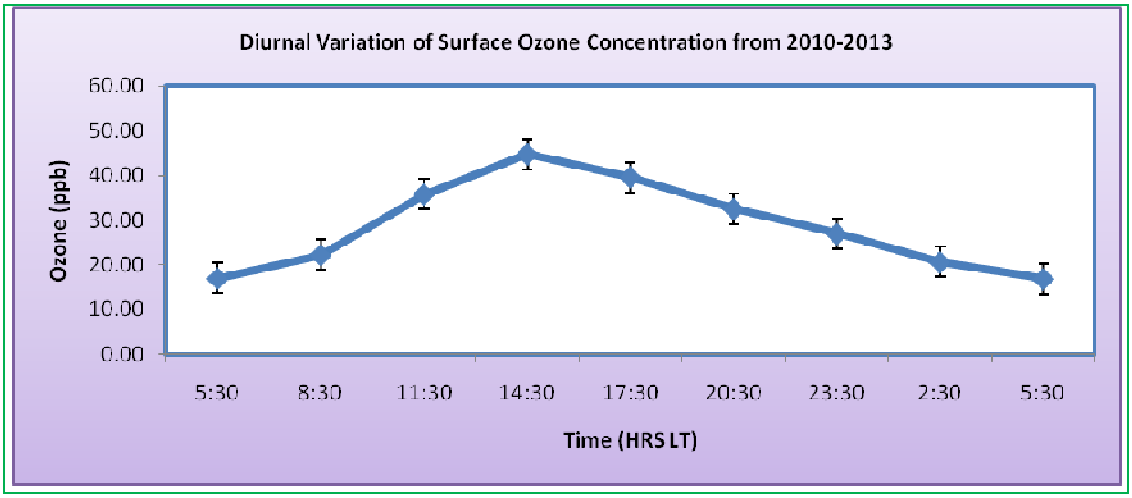

Fig.4.Diurnal variation of SOZ

3.2 Diurnal Variation of SOZ Concentration:

The diurnal variation of SOZ is important to understand the different processes responsible for o formation and destruction at the particular location. The overall mean diurnal variation of SOZ for the entire study period is represented in Figure 4.

During the entire study period, the SOZ concentration varied from 11 ppb to 55 ppb. The diurnal cycle of ozone showed a universal pattern and was characterized by the minimum ozone concentration in the early hours of the morning (05:30 hrs) and maximum ozone concentration in the afternoon (14:30 hrs). A gradual decrease was observed in the evening hours (17:30 hr). After sunset, the concentration declined further. This clearly shows the relationship between the build-up of ozone precursor gases in the morning hours and the photochemical formation of ozone in the daytime. Also this low concentration of ozone during night and early morning time could be a result of its deposition and surface chemical reaction (**Renuka et al., 2008**).The increase of SOZ concentration during daylight is attributed to the photolysis reactions of NO_2 and photo oxidation of VOCs, CO, hydrocarbons and other O_3 precursors. It is also attributed to the downward transport of ozone by the vertical mixing, due to convective heating, which takes place during daytime hours (**Tyson et al., 1998**). In the evening, ozone concentration decreases steadily because the night inversion layer is formed and once it is formed, no great changes occur (**Sillman, 1995**).The rate of photolysis increases due to intense solar radiation. Generally a well marked diurnal variation occurs in

relatively unpolluted air during calm weather (**Donald Allen Widen, 1960**).Apart from the role of photochemistry, boundary layer meteorology and dynamics also play a key role in ozone variability (**White *etal.*, 2002**).

High levels of SOZ concentration were recorded in summer season followed by almost same levels during southwest monsoon and winter seasons. Low levels of SOZ were recorded during northeast monsoon. The highest mean concentration of SOZ during summer was 49.67 ppb and lowest value was 18.67 ppb. Since the study area usually receives more rainfall during northeast monsoon, the highest and lowest values of SOZ during this season were 39.20 ppb and 17.85 respectively. The diurnal variation of SOZ concentration for different seasons throughout the entire period is clearly depicted in figure 5.

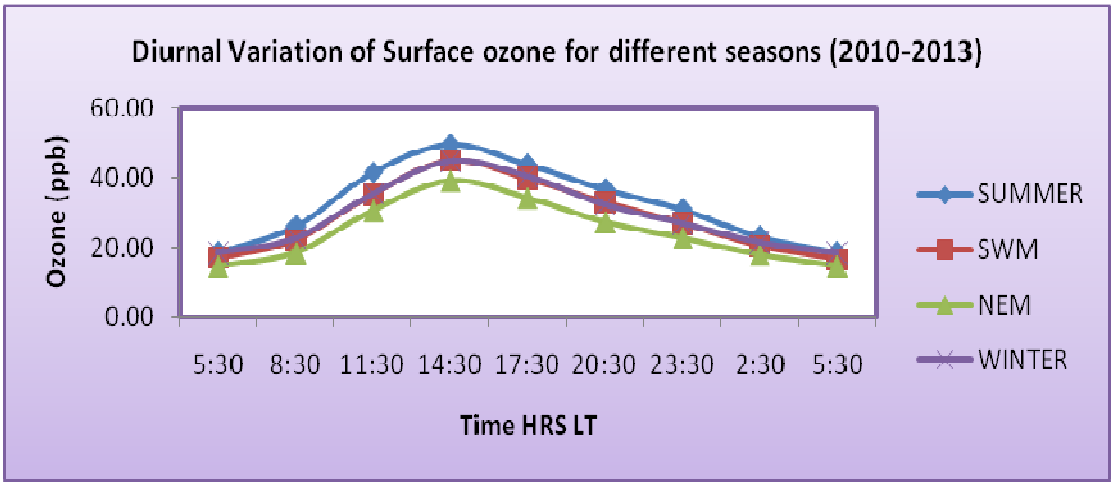

Fig.5.Diurnal variation of SOZ for different seasons.

3.3 Seasonal Variation of Surface Ozone:

A proper seasonal variation of SOZ concentration was observed at the study area. For all the three years summer season recorded the maximum concentration of surface ozone. This was primarily due to the availability of solar flux and its intensity during this season. High temperatures, heat waves accelerate the ground-level O_3production (**EEA, 2009**).Elevated levels of ozone had frequently observed during summer months. The formation of ozone in the troposphere depends upon several meteorological factors (Supriya Tiwari *etal.,* 2008).Southwest monsoon (SWM) receives less rainfall than Northeast monsoon (NEM).Also SWM is characterised by monsoon winds that play active role in the transport of pollutants.NEM recorded the lowest values for all the three years. The low values recorded during this season was mainly due to heavy rainfall which usually will not allow the pollutants to settle down or accumulate rather it will wash away the pollutants. Moreover during this season there was absence of clear sky conditions, the sky was almost cloudy during most of the days and thus leading to insufficient sunshine for photolysis .Winter 2011-12, recorded high levels of SOZ concentration than SWM and the reason being the accumulation the pollutants due to increased cloudiness, prevailing wind patterns and ozone titration in the study area. The increase in relative humidity to a level that produces more free OH radicals is involved in the photochemical processes of the day time ozone production and hence, among the two moderate ozone ranges, the winter records a slightly higher range of ozone concentration over the NEM .The seasonal average diurnal variation is given in table 2.

Table.2.Seasonal Average diurnal Variation of SOZ Concentration

Season	Average O_3 concentration in ppb								
	5:30	8:30	11:30	14:30	17:30	20:30	23:30	2:30	5:30
SUMMER 2010	18.13	25.55	40.78	48.95	43.80	37.38	31.43	22.27	18.19
SWM 2010	16.97	21.35	34.79	44.33	39.39	31.75	25.91	19.43	16.12
NEM 2010	14.16	17.69	29.58	37.66	33.22	27.00	22.56	17.73	14.19
WINTER 2010	18.55	22.74	35.68	45.08	41.73	33.39	27.62	21.61	18.14
SUMMER 2011	18.92	26.18	42.09	50.65	44.78	37.81	31.59	23.65	18.71
SWM 2011	16.61	21.78	35.60	44.60	39.01	33.64	27.29	21.09	16.78
NEM 2011	15.04	18.56	31.04	39.76	34.27	27.84	22.75	18.11	15.22
WINTER 2011	18.75	22.55	35.78	45.08	39.62	31.96	26.88	21.53	18.87
SUMMER 2012	18.96	26.53	42.02	49.40	43.28	35.37	30.08	23.59	19.06
SWM 2012	16.91	22.81	35.53	46.19	41.04	33.66	27.52	20.64	16.92
NEM 2012	14.50	19.06	31.07	40.18	35.28	26.96	22.68	17.72	14.48
WINTER 2012	18.06	22.44	34.76	44.52	40.29	31.58	26.17	21.06	18.04

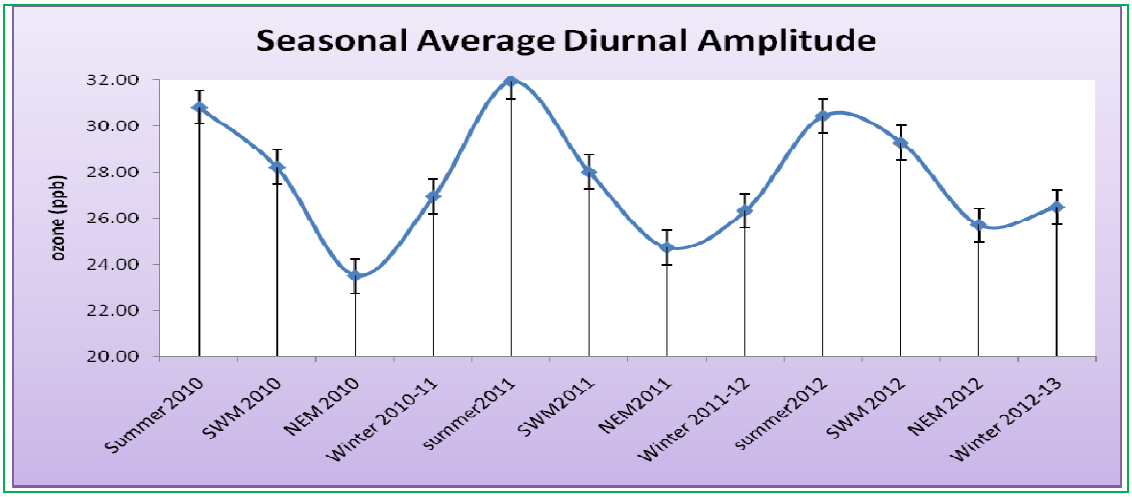

Fig.6.Diurnal Amplitude of SOZ concentration.

3.4 Seasonal Average Diurnal Amplitude of SOZ:

Diurnal amplitude is the difference between the minimum and maximum values of daily surface ozone values. The seasonal average of diurnal amplitude for the entire three years was found to lie between 23.50 ppb and 30.82 ppb. From this it is clear that under favourable conditions, SOZ can build up to a value of around 30 ppb in a day and in less ozone active days it can go up to 23 ppb in the study area. The diurnal amplitude of SOZ is shown in fig 6.

3.5 Variation of SOZ with Meteorological Factors:

The variation of SOZ concentration not only depends on its precursor emissions but also on the various meteorological parameters like temperature ,rh, wind speed, wind direction, cloud cover and

precipitation. Clear skies, warm temperature, solar radiation and soft winds are believed to have a great influence on surface ozone concentration (**Lennartson and Schwartz, 1999**).The variation of SOZ along with temperature is depicted in figure 7.

From the statistical analysis it was found that the temperature and SOZ were positively correlated (r=+ 0.5048).So it is evident that temperature plays a major role in the formation of ozone. The ozone concentration fluctuation follows the relative temperature variation, especially during the daytime, when the highest values of ozone are observed because of the high values of solar radiation and of the high concentrations of ozone precursors.Figure.8. shows the variation of SOZ with RH and wind speed. The correlation between SOZ and RH was found to be negative (r = -0.40) .SOZ and wind speed were positively correlated (r = 0.04). Wind speed is very important factor influencing the NOx and ozone concentration in the urban landscape. Higher wind speeds act to dilute NO_2 due to stronger dispersion, but also lead to an enhanced vertical transport of ozone, which produces NO2through oxidation of NO. The details regarding various levels of wind speeds in different wind directions observed in the study area is given in table 3 and figure 9 shows the wind rose pattern.

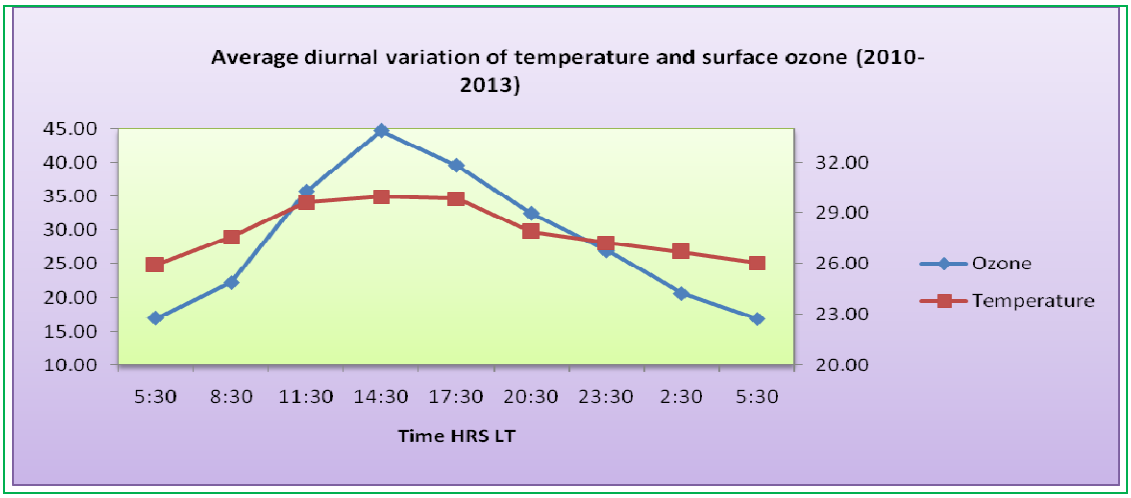

Fig.7.Variation of SOZ with Temperature

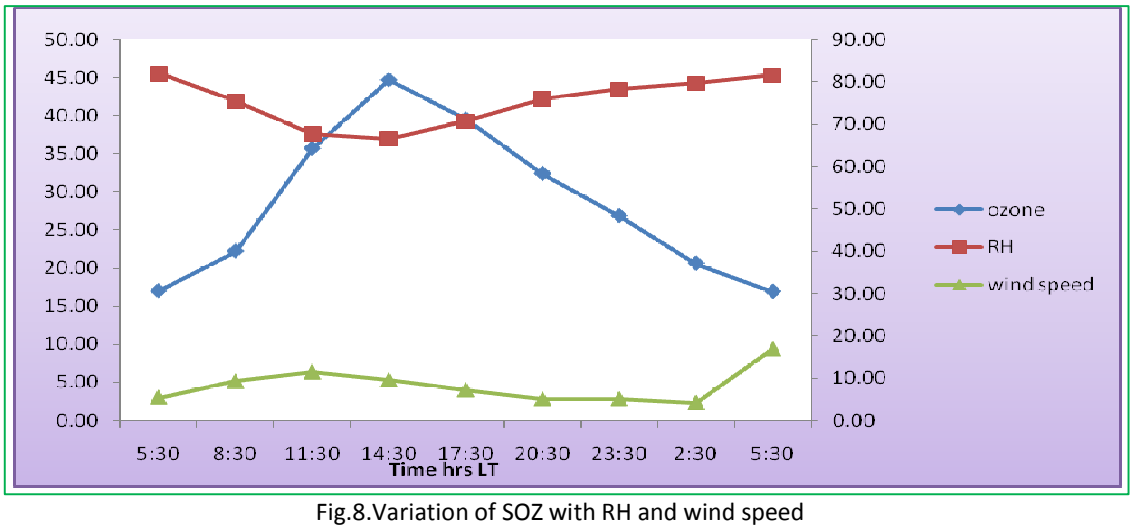

Fig.8.Variation of SOZ with RH and wind speed

Table.3.Observed wind speed in different directions

Wind direction	Wind speed (m/s)							
	0-1	1-2	2-3	3-4	4-5	5-6	6-7	No. of events
N	513	251	286	148	74	20	1	1293
NNE	8	10	9	6	1	1	0	35
NE	1	5	2	5	2	1	0	16
ENE	2	4	3	2	0	0	1	12
E	6	5	3	3	2	1	0	20
ESE	3	1	3	2	1	0	0	10
SE	0	0	1	0	0	0	0	1
SSE	3	0	0	1	1	0	0	5
S	8	2	4	0	1	1	0	16
SSW	6	3	3	2	2	0	0	16
SW	23	10	15	8	3	0	0	59
WSW	23	12	13	4	6	0	1	59
W	72	52	40	14	11	1	3	193
WNW	115	53	41	41	13	1	0	264
NW	149	83	97	51	21	2	1	404
NNW	53	48	38	28	11	12	0	190

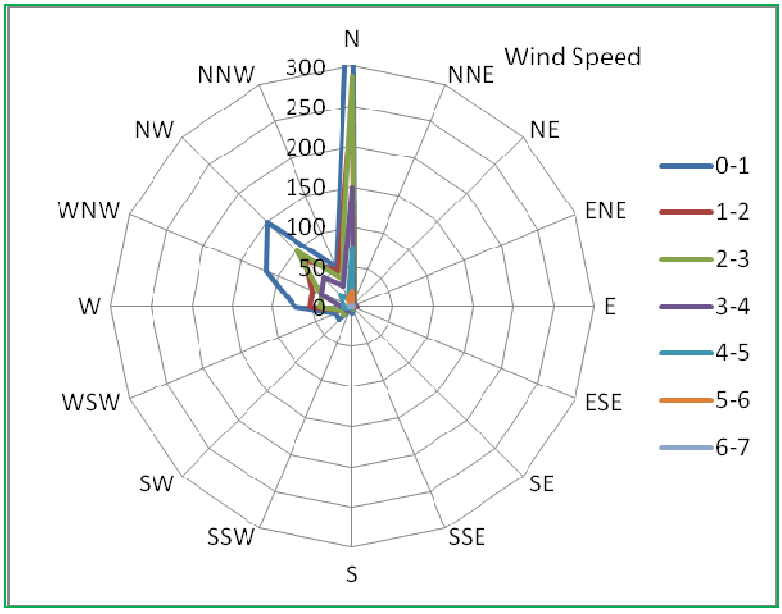

Fig.9.Wind Rose Diagram

3.6 Neural Network Model:

Neural network is one of the important tools used for predicting and forecasting. In this study, the peak ozone (1430hrs) was forecasted by using the inputs as temperature, RH and wind speed. The data set is randomly divided into three sets namely training, validation, testing. Training set is the largest set (70%) and the remaining sets are assigned to contain 15 % of the samples. The training set is a set of samples used to adjust or train the weights in the neural network to produce desired outcome. The validation set is used to find the best network configuration and testing set is to evaluate the fully trained networks. The most used computational function in air quality modelling is the Log-Sigmoid functionf(x) = 1/ (1+e-x) (**Seinfeld, 1998)**.The model was carried out using Levenberg Markquadrt algorithm. The neural network model is trained using all the input parameters. The model gives an R of 0.55438 for all the data points with MSE of 17.04.Figure .10. shows the regression of the above model.

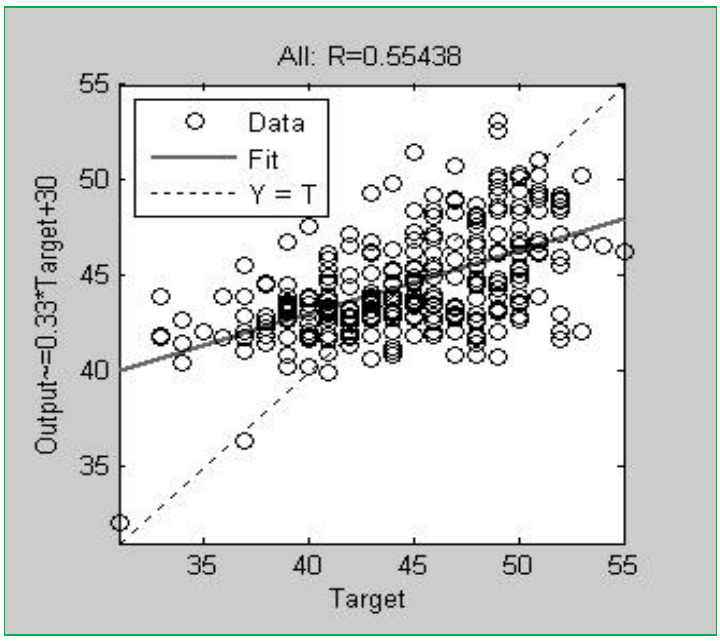

Fig.10.Scatter plot between actual and predicted data

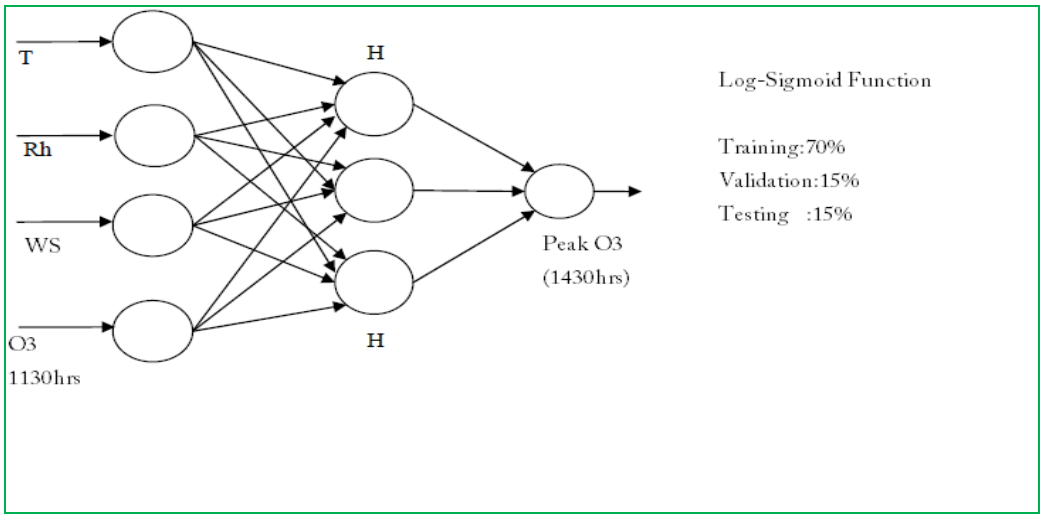

Fig.11.Neural Network Model

Now the model was improved by adding the SOZ values corresponding to 1130 hrs as one of the inputs. This was to check the influence of 1130 hrs SOZ concentration to the peak ozone. The model was found far better after the inclusion of 1130 hrs SOZ. Figure. 11 shows the neural network model. The improved model yielded a regression of R =0.8015 with MSE of 8.04.The scatter plot for the improved model is depicted in figure.12

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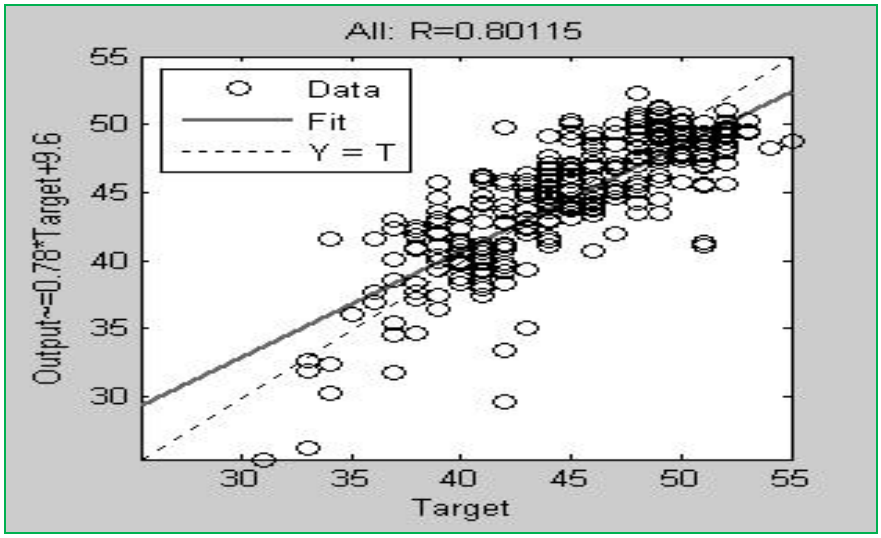

Fig.12.Scatter plot of the improved model

4.0 Conclusion:

Surface ozone measurements were made at Kanyakumari of southern Tamilnadu, India for a period of three years from March 2010 to February 2013.This study was an attempt to study the variation of potentially harmful SOZ concentration in a site where no previous studies had been made.

1. During the entire period of study, SOZ varied between 11 ppb to 55 ppb. The frequency distribution showed that around 60 % data points lied between 11 ppb and 30 ppb.
2. Only 35 data points lied between 51 ppb and 55 ppb. This shows that the study area has not experienced high concentration of SOZ during the three years of observations.
3. The diurnal variation of SOZ was systematic and it followed the universal pattern. It clearly indicated that the photochemical activity was predominant.
4. SOZ concentration was observed to be the highest during summer and lowest during north east monsoon.
5. SOZ was found to be positively correlated with surface temperature and negatively correlated with RH. Wind speed and its direction were also taken into consideration and wind speed was positively correlated with SOZ.
6.A Neural network model was performed to forecast the peak SOZ concentration using various inputs and then it was improved by adding SOZ concentration of 1130 hrs as one more input.

Even though the SOZ concentration was currently within the national standard in Kanyakumari, it has the potential to increase in near future. In order to understand the role of ozone in the atmospheric chemistry and climate dynamics measurements of SOZ along with its precursors like oxides of nitrogen, oxides of carbon and methane should be monitored and analysed. Knowing the current levels of these pollutants is very essential to bring awareness and mitigate them .So continuous monitoring is inevitable.

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