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Surface Ozone Measurement with Meteorological Parameters at an Urban Site and Neural Network Modeling, Perumalpuram, Tirunelveli, Tamil Nadu, India.

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ABSTRACT
The surface ozone acts as a secondary pollutant, which depends on regional topography and climate. Ozone (O_3) is a reacting oxidant gas produced naturally in trace amounts in the earth's atmosphere. The surface ozone measurement was carried out for the first time for a period of two years from Nov - 2016 to Sep - 2018 at Perumalpuram (8.773°N, 77.7°E) an urban site of India, which is located at the southern Tamil Nadu. The variation of surface ozone concentration with various meteorological parameters were studied. The seasonal variation was also recorded. From this measurements, it was recorded that the relative humidity shows a negative correlation with surface O3. But temperature shows a positive correlation with surface O3. The wind speed shows a positive correlation with surface O3 except during winter season. A clear diurnal variation pattern was obtained for surface O3 in the site. Irrespective of the season the maximum ozone concentration was recorded in the afternoon and minimum value was recorded in the early morning. The maximum value of surface O3 obtained was 47.88ppb during summer and the minimum value obtained was 6.46ppb during winter. Annual increase of 0.71 ppb was reduced from (2016-17) to (2017-18). This shows and increasing trend of SOZ concentration in the site. The ozone variation in summer is very high, winter is low and for monsoon it is very low.

KEY WORDS : *Surface ozone, Diurnal variation, Seasonal variation, Air Quality, Meteorological parameters.*

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I. INTRODUCTION :

There is an alarming awareness in understanding the pollution arises naturally and by anthropogenic activities globally. The main reasons being the tremendous increase in the population and the unpredictable industrial revolution. Environmental imbalance is caused by the various anthropogenic activities. The increasing population gives multi dimensional disturbance and the environmental stress is the end product. The radiative forcing for the tropospheric ozone changes due to emission of pressures (NO & CO) with the order of (+0.25 to 40.65) wm $^{-2}$ (Soloman et al . 2007)[1] . Ozone is an important trace gas in stratosphere and also in troposhere. The variation of ozone concentration is due to the topography and season of the region. The meteorological parameters (temperature, relative humidity, wind speed) fluctuates the ozone concentration rapidly, Combustion is one of the principal process which emit trace gases and aerosols into the atmosphere (Khare 2012) [2]. Various meteorological parameters may also influence urban air pollution (Akpinar et al . 2008) [3]. Tropospheric ozone has two main source namely stratospheric intension affecting surface ozone and in-situ production via photochemical oxidation of Carbon like compound (CO, CH4& VOC's) in presence of NOx[4]. Tropospheric ozone has a detrimental effect on human health and ecosystem productivity[5].

It is proved that the concentration of stratospheric ozone is decreasing while that of troposphere is increasing. The rate of increase recorded is 0.32% per yea[6].

The diurnal and seasonal variation of surface ozone and its pressure NOx at a semi-Arid rural site in South India was carried out by (Reddy et al.,) [7]. The study reported the O3 concentration was high in April (56.1+ 9.9 ppbv) and lowest in August (28.5+ 7.4 ppbv). A review has given by T. sakthivel and K.K. Sivakumar Reddy[8]. The paper reviewed on the origin, causes, mechanism and bio-effects of ozone layer depletion and vanishing of their protective measures. In future, the ozone behaviour will be changing due to the changes in NOx, water vapour and climate. In the selected site Tirunelveli, Southern most part of India, nearby Kanyakumari the surface ozone measurement was carried out in the first time. The seasonal and annual variations of surface ozone were measured along with the variation of main precursor of ozone NO2. The surface ozone variation with meteorological parameters were also recorded.

II. SITE DESCRIPTION AND GENERAL METEOROLOGY

The site in which the surface ozone measurement was carried out is situated at Tirunalveli district of Tamil Nadu. The selected site is Perumalpuram (8.773°N, 77.7°E) Near to Tirunelveli. The climate of Tirunelveli is hot and humid. The average temperature during summer ranger from 25°C - 41°C and during rest of the year it is 18°C - 29°C. The average rainfall is 680 nm (whether undergrounds.com). The month may is generally hottest in the interior part of the district and the maximum temperature reaches upto 42°C. The seasons are classified as winter, summer and monsoon. The wind speed is moderate in the study site.

Fig.1 Location of Study site

III. MONTHLY AVERAGE VARIATIONS OF METEOROLOGICAL PARAMETERS

The monthly average variations of relative humidity wind speed maximum temperature, minimum temperature and rainfall are shown in figure 2. The maximum temperature recorded was at the month of April (41°C) and the minimum temperature recorded was at the month of November (21°C). Relative humidity was highest in the month of August (76%) and lowest in July (52%). Wind speed is maximum in August (20.52 km/h) and minimum in November (2.99 km/h). Maximum rainfall was noted in the month of November and October.

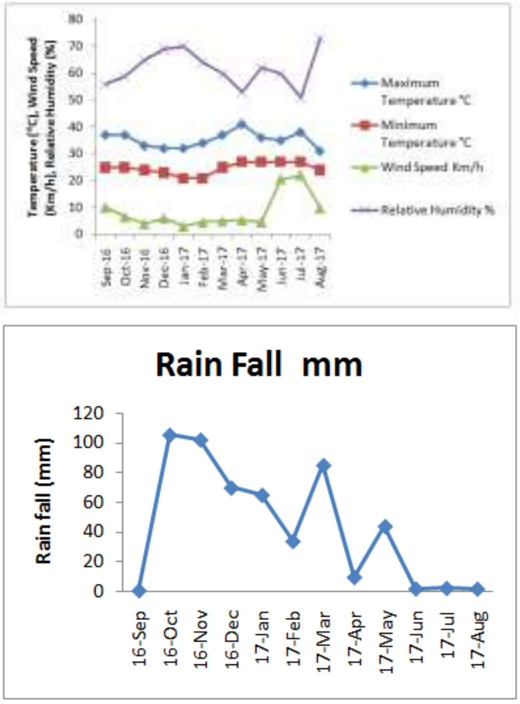

Fig.2 Monthly average variations of relative humidity, wind speed, maximum temperature, minimum temperature and rainfall

IV. INSTRUMENTATION AND METHOD.

The instrument used for measuring the surface ozone in the site is a portable gas sensitive aeroqual moniter S300. It is comparatively cheap and calibrated to measure the gas concentration directly. It is calibrated against a certified UV photometer. Surface ozone variation measurement is carried out for a period of two years (Nov-16 to Oct-18) in the site. The observation period covers totally six seasons. (for two years). The monitor has removable sensor heads for both O3 and NO2. It is a combination of smart measurement techniques and mixed metal oxide semiconductor sensor that exhibit an electrical resistance change in presence of the target gas. The concentration can be measured in ppm or in mg/m^3. The measurements are taken in all possible days of a month. The readings are taken from 5:30 am to next day 5.30 am. It comprises of 9 readings with an internal of 3 hrs. Figure 3 shows the Aeroqual S300 ozone monitor with O3 & NO2 sensing heads

Fig. 3 Aeroqual Ozone Monitor S300

V. RESULTS AND DISCUSSION.

This paper presents the two year continuous measurements of Og and NO2. The diurnal and seasonal variation of surface O3 are studied. Frequency distribution of ozone concentration for whole study period is also analyzed.

5.1. Frequency Distribution.

The number of observations within a given interval is called as frequency distribution. The following table 1 shows the frequency distribution for its whole study period of the site. The data points are divided into different concentration ranges known as bins. The minimum frequency is observed at (51-55) ppb[9]. The maximum frequency at (16-20) ppb i.e 22%. Nearly 69.9% of the data lies between (0-30) ppb. In the earlier studies it was reported as follows. In the Nagercoil site it was observed 70% of data lies between (5-25) ppb. In Kanyakumari, it was recorded that 60% of data lies between (11-30) ppb[10] From figure 4, it was noted as follows

i) 7% data lies in (0-10) ppb interval.
ii) 63% data lies in (11-30) ppb interval and
iii) 35% data lies in (31-55) ppb interval.

Table 1 : Frequency distribution of SOZ for the study site

Bins (ppb)	Frequency Distribution
0-5	1.97
6-10	4.92
11-15	14.49
16-20	22.08
21-25	13.92
26-30	12.52
31-35	11.39
36-40	11.95
41-45	3.53
46-50	2.67
51-55	0.56

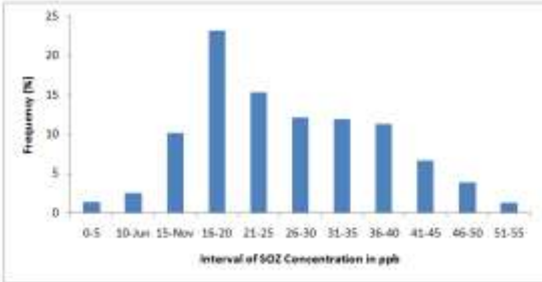

Fig. 4 Frequency distribution of SOZ for the study site

5.2 Diurnal variation of surface O3.

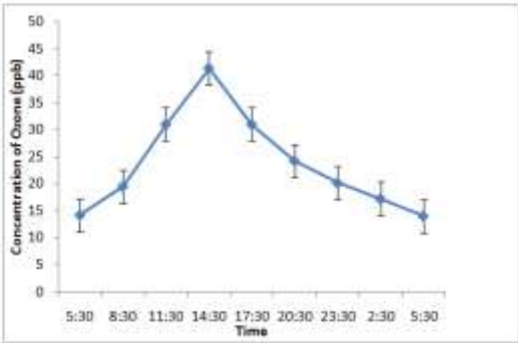

Fig. 5 Diurnal variation of the surface O3 during the period from Nov-16 to Oct18.

The diurnal variation of surface ozone is studied by many researchers locally and globally. The minimum value of surface ozone was found to be 12.87ppb.

The maximum value recorded was 42-92 ppb. In general the diurnal variation stands for the ozone fluctuations that occur during each day. The diurnal variation is characterized by gradual increase in the morning after sun rise, a peak in the noon and a wide minimum in the night time [11]. The diurnal variation is a measure of overall budget of production and loss rate of O3. The same characteristic of SOZ variation is obtained in the study site. The maximum concentration of ozone in the day time is due to the high photochemical production by the precursor of ozone [12]. The ozone variation is characterized by the meteorological parameters[13]. The minimum value of SOZ concentration during morning hours and night hours is due to the accumulation of precursor gases in huge concentration without photolysis[14]. The low concentration of SOZ observed in the morning is due to the lower boundary layer height which reduces the mixing process between ozone rich stratosphere and ozone poor troposphere the mixing ratios increases gradually from morning and reaches the maximum in the local noontime[15]. The ozone variability is determined by boundary layer meteorology apart from the role of photochemistry[16]. The transport mechanism is another main factor that determines the SOZ concentration.

The O3 from stratosphere travels to troposphere by transport mechanism. It is achieved by vertical mining due to convective heating. At night there would not be any radiation and no photolysis and there is no photochemical reaction and hence the O3 concentration is reduced. It is noted remarkably that the production rate of O3 in the morning is higher than the destruction rate O3 in the evening.

Boundary layer attains maximum height during afternoon hours due to the increase of surface heating. It was noted that the trace species gets vigorously mixed and thus farmed a convective mixing layer. During the observation period, it was noted that a maximum O3 concentration of 49.32 ppb during summer and minimum of 6.16 ppb SOZ concentration were recorded. The increase of SOZ concentration during day time is attributed to the photolysis of NO2 and photo oxidation of VOC's, CO, hydro carbon and other ozone pressures. The downward transport of surface O3 is by vertical mining due to convective Heating[17]. The O3 concentration decreases as the night inversion layer is formed in the evening. During night time there wound be any radiation & hence no photochemical reaction lakes place and its O3 concentration declines.

5.3. Seasonal Variation of O3.

The seasonal observation for the variation of SOZ concentration is observed for two years (6 season). From the continuous study, it was revealed that the maximum SOZ concentration was recorded in the summer season followed by monsoon and then winter. Whether plays a vital role in the variation of SOZ concentration. While analyzing the variation of SOZ concentration in the summer, the variation is high as the temperature is maximum and hence the photolysis process is dominant and conversion of SOZ from its pressure is in the peak. The high temperature has a direct influence on chemical kinetic rate and the mechanism leads to O3 production[18].

In a previous research carried out at Kanpur in North India, it was revealed that the concentration of SOZ was found to be maximum in summer and minimum during monsoon (Attitude Gaur et al 2014) [19]. The SOZ concentration is maximum during summer due to high solar fluctuation, High temperature, more sunshine hours and accumulation of pollutants. During NEM season, the SOZ concentration is low due to heavy rainfall and low anthropogenic emission (R.K. Sharma 2018) [20].

Relatively low level of ozone during winter might be due to greater atmospheric stability and an increased incidence of nocturnal (night time) inversion [21]. The formation of ozone in the troposphere depends upon several meteorological factors such as temperature, sunshine hours, wind velocity and relative humidity [22]. The overall peak value of SOZ during summer was 45.26ppb and the minimum SOZ concentration was observed during winter (29.13). During winter season, the cloudy skies reflect back the radiation into the stratosphere and the precursors are reduced by the rain. Due to the low temperature, the internal decomposition of O3 precursors is reduced[23].

5.4. Variation of SOZ with meteorological parameters.

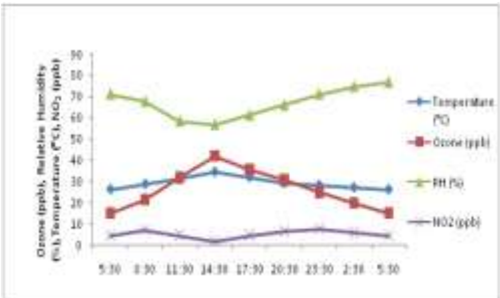

Fig. 7 Variation of SOZ with temperature, RH and NO2

The meteorological parameters play a remarkable role in the fluctuation of SOZ concentration. The variation of SOZ with various meteorological parameters observed in the site is discussed in the following sections.

5.4.1. Correction between SOZ and temperature

There is a direct relationship between SOZ concentration temperature. The mean temperature of air at any place depends on many factors like altitude, latitude, proximity to the sea and so. (Rao et al, 1972). Temperature and long term urban warming have a serious impact on urban pollution, resulting in higher concentration, as heat accelerates the chemical reaching in the atmosphere (Waleck and Yuvan, 1999). The ozone concentration reaches its peak value when the temperature is maximum. This shows that the there exists a direct relationship between the temperature and SO concentration the temperature varies from season to season and throughout the day also. Invariably in all seasons it was observed that maximum temperature was attained around 14:30 hrs. There exists a positive correlation between temperature and SOZ. The overall correlation co-efficient between temperature and SOZ is positive (r= +0.70).

Table-2 shows the correlation between Og and T average.

Season	Correlation Co-efficient	P-Value
Winter	0.74	4×10^{-20}
Summer	0.62	3×10^{-16}
Monsoon	0.76	5×10^{-19}

5.4.2. Correlation between relative humidity and SOZ.

The moisture content of the atmosphere influences the correlation action of the air pollutants. Relative humidity is used very often in the air pollution studies. When the humidity is high, the major photochemical path for removal of ozone will be enhanced. Hence the surface ozone is depleted by deposition as water droplets. There exists a negative correlation between RH and SOZ in all season. The overall correlation co-efficient between relative humidity and SOX is -0.5621.

Table-3 Correlation between O3 average and RH average.

Season	Correlation Co-efficient	P-Value
Winter	-0.4358	0.0063
Summer	-0.6973	0.0001
Monsoon	-0.5532	0.0032

5.4.3 Correlation between wind speed and SOZ

The wind plays an important role in the transport of O3 from stratosphere. The O3 precursors are transported from region to region by wind. The land breeze can transport the photo chemically produced ozone and its precursors over the sea. The accumulated ozone over the sea will be returned to the land by sea breeze. This kind of transport tends to contribute significantly to high ozone episodes in clean coastal and mountain regions (time et al, 2002).

Table 5 : Correlation between W_{avg} and $O_{3\ avg}$

Season	Correlation Co-efficient	P-Value
Winter	-0.2566	0.0210
Summer	0.6543	0.0042
Monsoon	0.5521	0.0112

There exists the positive correlation between wind speed and SOZ in summer and Monsoon but a negative correlation in winter season.

VI. NETWORK MODELING.

In order to give the correlation between actual and predicted values of surface ozone, neural network model was developed. Generally, neural networks are simple mathematical technique. This technique uses a set of nodes similar to neurons in the brain. These nodes are inter connected and they are exposed to the date that they can identify pattern in data. Neural networks in different arrangements perform various tasks as pattern recognition, data mining, classification and process modeling.

This model is developed using feed forward back propagator multilayer perception. this model is carried out in matlab using levenberg marquadrt algorithm.

The artificial Neural Network (ANN) researchers believe that the human capabilities in real-time unusual perception speech understanding and intelligent decision making are formed with the base from organizational and computational principles exhibited in the complex neural network of the human brain. Eve n neural network has a perception (neural node) which is the counter part of neuron nucleus in the brain. Then we have the hidden layer which is perception. The collective operation of the connected neurons provides powerful learning capacity.

5.4.1. Model biasing

The following fig. 4 shows the model biasing. The input signals are applied to the node through input connection.

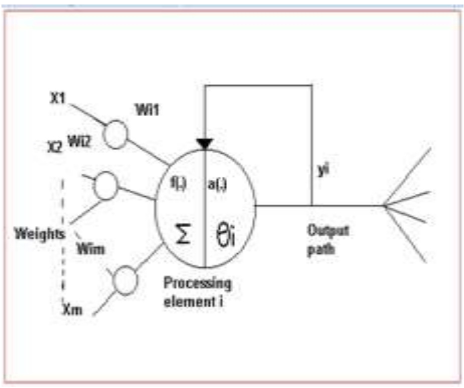

Fig.5.1 Model biasing

In this neural networks, the strength of the connections are referred to as weights. This weights will excite or inhibit the transmission of the incoming signed. These incoming signals are multiplied by the value of the corresponding weights. At the perception, all weights are summed as in the above figure. This value is passed to the scaling function. The selection of the scaling function is the part of the neural network design.

While processing the data the daily average values of the surface one is forecastes by using the input parameters including temperature (T), wind speed and NO_2. The data is divided randomly into a) Training set (70%), b) validating set (15%) and c) Testing set (15%). The training set samples are used to train the weights in the network to produce desired outcome. The validation set finds the best network configuration and the testing set evaluate the fully trained networks. There are many computational functions. In air quality modeling, the most used function is the sigmaid function.

The log sigmaid function is given as, f(x) = 1/(1+e-x). This model is developed using feed-forward back propagation multilayer perception using four neuras in the hidden layer as in the fig 4.

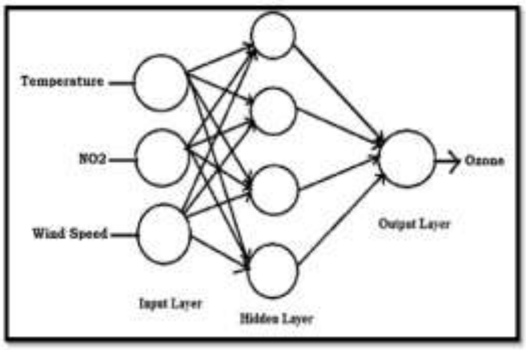

Fig. 5.2 Proposed neural network model for ozone

The model is carried out in matlab using Levenberg Marquadrt algorithm. The neural network model is trained using all the input parameters. In a previous study, through the neural network model, yielded a regression of R=0.8015 with MSE of 8.04 was obtained (Krishna Sharma, R., et al., 2013). The model gives R2 values of 0.635 for all the data points with MSE of 8.476. Fig ( ) shows the results of the model. Fig ( ) gives the correlation between the actual and predicted values of surface ozone.

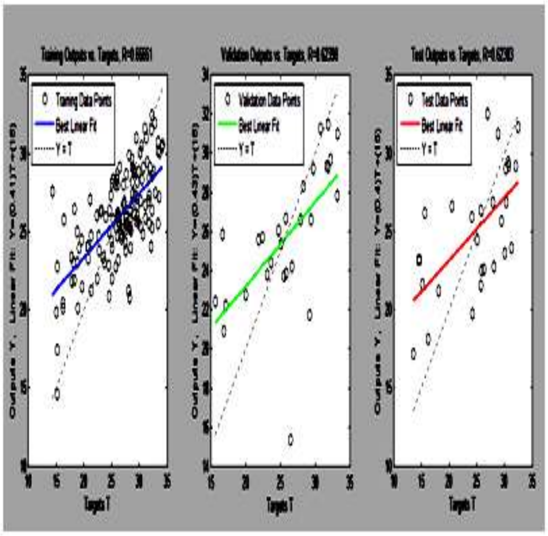

Fig. 5.3. Model Results

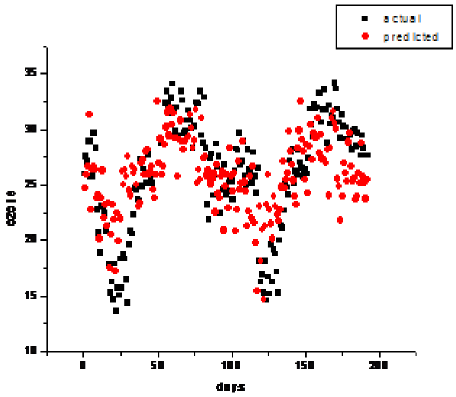

Fig.5.4. Actual and predicted values of ozone

VII. CONCLUSION

Continuous observation was carried out in the site for 2 years (6 seasons). The observed results are ,

- ❖ A clear diurnal pattern of variation of SOZ concentration was recorded. It shows its reliance on temperature and photochemical reactions.
- ❖ The meteorological parameters find strong dependence an SOZ variation. A positive correlation was recorded between SOZ and temperature. A negative correlation between SOZ & RH. Wind speed shows positive correlation except winter.
- ❖ From the frequency distribution, it was revealed that the SOZ concentration is comparatively low for most of the time in all days.
- ❖ The SOZ concentration was found to be maximum in the summer season and minimum in the winter season. It was noted an increase trend of annual variation of SOZ.
- ❖ The study site is an area in the city which has maximum network of transport of this produce the precursor emission which enhances the production of SOZ.
- ❖ The neural network model gives R2 value of 0.653 for all data points with MSE of 8.476. There is a good agreement between the actual and predicted values of surface ozone.

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