

## Review Article

# Impact of NO<sub>2</sub> on Ground-Level Ozone and Prediction using Neural Network Model

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## Abstract

Surface ozone or Ground level ozone has a vital role in the radiative and chemical processes in the atmosphere and poses as a potential problem to all developing countries. Measurements of surface ozone and NO<sub>2</sub>, one of the precursor for ground level ozone production has been carried out for the first time in karaikal (10.9327 °N and 79.8319 °E), a coastal region along the South eastern India for a period from October 2013 to September 2014. The results obtained in this study show a clear dependence of ozone on NO<sub>2</sub> levels. The results further shows a positive correlation between O<sub>3</sub> and NO<sub>2</sub> (r<sup>2</sup>=0.3073) on a monthly scale. A neural network model has been developed for short term prediction of Ground level ozone. The model can predict the mean surface ozone levels based on the parameters like Nitrogen-di-oxide, temperature and wind speed. The model exhibits a good correlation between the actual and predicted data points.

**Keywords:** Ground level ozone concentration; NO<sub>2</sub>; Neural network; Short term prediction

## Introduction

Surface or ground level ozone (O<sub>3</sub>) plays a very vital role in atmospheric oxidation processes and hence subsequently in air quality and its increase enhances the greenhouse effect in the free troposphere [1]. O<sub>3</sub> is regarded as the third most powerful greenhouse gas in the atmosphere after CO<sub>2</sub> and CH<sub>4</sub> with a radiative forcing of +0.35 Wm<sup>-2</sup>. Each molecule of O<sub>3</sub> added in the atmosphere proves to be about 1200-2000 times more powerful in global warming than an addition of CO<sub>2</sub> molecule [2]. O<sub>3</sub> is also a major component of photochemical smog and is a well known hazardous element for human health. It has been well proven that human exposure to ozone leads to respiratory problems [3]. Ground level ozone is not directly emitted into the atmosphere. It occurs as a result of photochemical reactions between oxides of nitrogen and volatile organic compounds in the presence of sunlight [4]. Nitrogen Oxides (NOx) and Volatile Organic Compounds (VOCs), well known precursors of ground level ozone have various anthropogenic and biogenic sources and exhibit non-linear effects on ozone production.

Several studies have been conducted aiming to develop tools and methods capable to achieve a short-term forecast of ozone levels [5,6]. The analysis often aims on investigating whether or not a threshold condition is exceeded. However, this means of analysis can often be exploited by environmental and medical authorities in issuing public warnings.

The most common method widely used for developing prediction models is to correlate meteorological and pollution data with the concentration of a certain pollutant. In this aspect, it has been shown that neural network technique can be employed for short term prediction.

Neural network techniques have recently become the focus of much attention as they can handle the complex and non-linear

problems much better than the conventional statistical techniques. It is a simple mathematical input-output model which learns the relationship (linear or non-linear) between the input and output during the training period. Neural network model brings out the maximum information available within the data during the training period and reflects these in the independent period.

In this paper, an attempt has been made to study the impact of NO<sub>2</sub> on Ground level ozone at Karaikal, a part of the union territory of Puducherry, a coastal region located along the south eastern side of the Indian Peninsula. Ground level ozone measurements have been carried out for the first time in this study region.

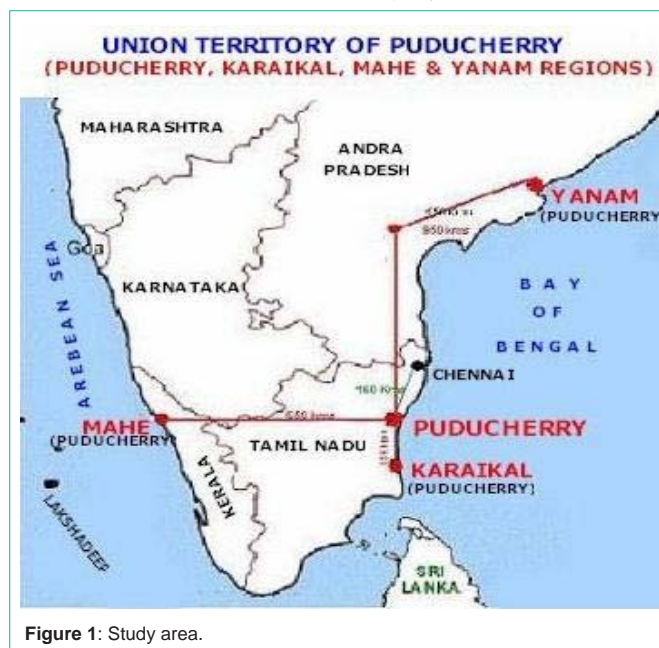


Figure 1: Study area.



Figure 2: Aeroqual S500 gaseous monitor.

Table 1: Sensor head specifications.

Sensor Gas	Sensor	Range (ppm)	Lowest Detection Limit (ppm)	Resolution (ppm)	Response Time T90	Operational Range	
						Temperature	RH
Ozone (O <sub>3</sub> ) 0-0.015 ppm	GSS	0.0-0.150	0.001	0.001	<70s	-5-40°C	5-95%
Nitrogen Dioxide (NO <sub>2</sub> ) 0-0.2 ppm	GSS	0.0-0.200	0.001	0.001	<180s	0.40°C	30-70%

**Measurement site and methodology**

Karaikal (10.9327 °N, 79.8319 °E), is situated in the eastern coast of India (Figure 1).

The Ground level ozone was continuously monitored from October 2013 to September 2014 at a major traffic thoroughfare in the karaikal region. The gaseous measurements were taken by using a portable sensitive gaseous monitor Aeroqual S500. This instrument is the advanced version of the S200 series utilized by [7,8]. The Aeroqual S500 gaseous monitor utilized for this study (Figure 2). The sensor specification for ozone and NO<sub>2</sub> is given in (Table 1). Ground level ozone and NO<sub>2</sub> was measured every hour. The hourly data were averaged to obtain the daily averaged value. The meteorological parameters were obtained from IMD and weather underground Inc.

**Neural network technique**

Neural Networks are a family of statistical learning models inspired by biological neural networks (the central nervous systems of animals, in particular the brain) and are used to estimate or approximate functions that can depend on a large number of inputs and are generally unknown. Artificial neural networks are generally presented as systems of interconnected “neurons” which exchange messages between each other. The connections have numeric weights that can be tuned based on experience, making neural nets adaptive to inputs and capable of learning.

For regression, we assume a functional form first, such as linear or exponential and then we find the coefficients that minimize some measure of errors whereas for neural networks, the method itself extracts the functional form from the data.

As input to the model, the meteorological data and NO<sub>2</sub> dataset is used, whereas the output, ozone concentration is predicted by the model (Figure 3). The network is trained with the past data. By proper choice of training sets, after the learning process, the trained network is capable of predicting the ozone concentrations as an

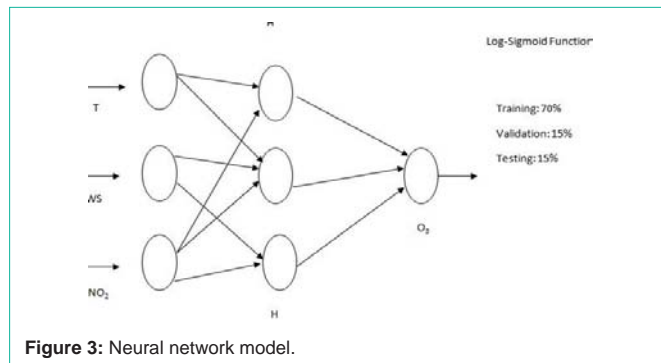


Figure 3: Neural network model.

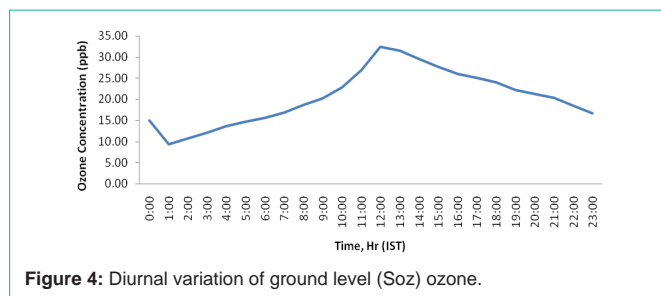


Figure 4: Diurnal variation of ground level (Soz) ozone.

output according to the inputs and internal structure of the network established during the learning period.

In the present study, for predicting ozone concentration using neural network, Matlab R2014a has been utilized.

**Results and Discussion**

**Diurnal variation of ground level ozone**

Analysis of the diurnal variation of Ground level ozone is very essential in order to understand the various mechanisms responsible for the formation and destruction of ozone at a particular region. The overall mean diurnal variation of Ground level ozone (Figure 4) for the entire study period is as shown.

The diurnal pattern of Ground level ozone gives a clear picture of the ozone status in Karaikal region. It is observed that (Figure 4), ozone levels start increasing gradually in the morning hours with its maximum value seen in the noontime. After the noontime, ozone levels show a decreasing trend. As seen from the (Figure 4), the rise in ozone levels during the morning hours is observed to be fast as compared to the decreasing trend seen in the evening hours. This is due to the increase in solar radiation which in turn aids in the photochemical production. It can also be due to the effect of the downward transport of ozone caused due to the downward movement of ozone through vertical mixing, as a result of convective heating [9]. Low concentration in the evening hours could be as a result of its deposition and surface chemical reactions [10]. Lower concentration level seen in the evening hours is also attributed to the fact that the night inversion layer is formed and this formations aid in no change in the atmosphere [11]. It is seen that for the entire study period, the ozone levels varied between 20 ppb to 32 ppb. It can be seen that the diurnal cycle of ozone exhibit pattern in concurrence with the universal pattern with minimum levels seen in the morning hours and maximum ozone levels in the afternoon (between 12 hrs to 14 hrs). Generally, one can observe a well noticeable diurnal variation

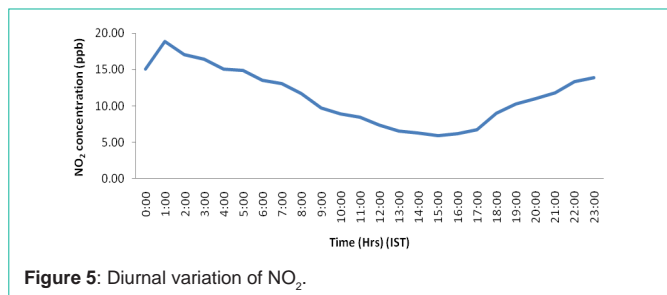


Figure 5: Diurnal variation of NO<sub>2</sub>.

pattern in a relatively unpolluted air during calm weather [12].

### Diurnal variation of NO<sub>2</sub>

24 hours surface level NO<sub>2</sub> concentration averages measured from October 2013 to September 2014 are presented (Figure 5). This diurnal cycle of NO<sub>2</sub> is as a result of the photochemical, transport and emission processes and their strengths vary between day and night.

The morning high values of NO<sub>2</sub> concentration in the study area is mainly due to the increase in traffic flow. This is also associated with weak winds besides atmospheric stability which is the characteristic of the 'nocturnal stable boundary layer that still persists in the first hours of the morning. The decrease in NO<sub>2</sub> in the late morning hours (from 8.00 hrs) coincides with the appearance of ozone in the atmosphere. Ozone now accumulates and reaches a maximum in the afternoon hours and then gradually declines during the following several hours. The concentration of NO<sub>2</sub> usually declines from its peak as the ozone builds up and NO<sub>2</sub> concentration reaches its minimum level in the afternoon, at which the production of ozone is maximum. Eventually, after sunset, the photochemical reaction stops and hence ozone concentration decreases while NO<sub>2</sub> concentration increases in the complex nighttime chemistry of the atmosphere.

### Relationship between ground level ozone and NO<sub>2</sub>

As NO<sub>2</sub> is one of the well known precursor of Ground level ozone, it is essential to analyze the relationship between the two in the study area.

The monthly averaged NO<sub>2</sub> and Ground level ozone concentration values (Figure 6) have been plotted in time series to analyze their relationship.

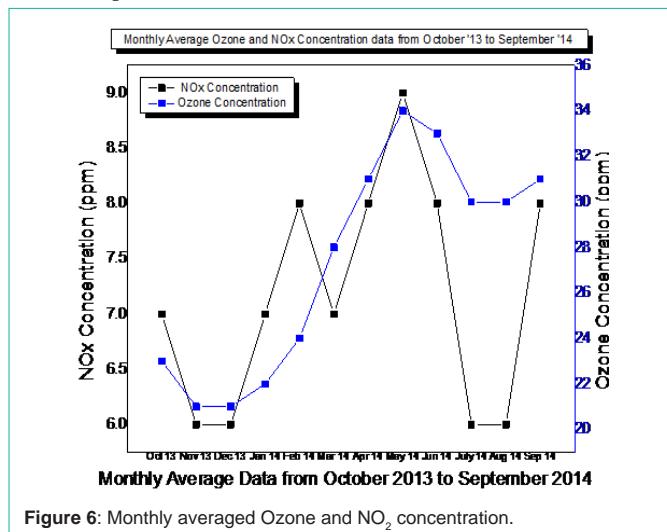


Figure 6: Monthly averaged Ozone and NO<sub>2</sub> concentration.

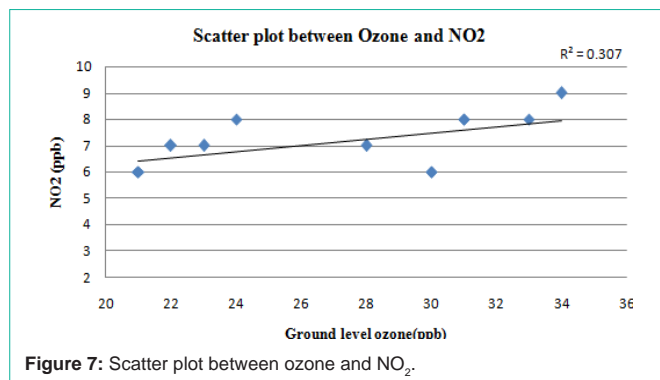


Figure 7: Scatter plot between ozone and NO<sub>2</sub>.

It can be seen (Figure 6) that Ground level ozone and NO<sub>2</sub> supplement each other well on a monthly scale while on a diurnal scale, they complement each other (Figure 4 and 5). It is seen that Ground level Ozone and NO<sub>2</sub> show similar patterns but in a different range on a monthly scale. Ground level ozone exhibits a positive correlation [8] (Figure 7) with NO<sub>2</sub> ( $r = 0.307$ ) on a monthly scale.

This is due to the fact that in the study area, the rise in NO<sub>2</sub> level is due to vehicular emissions. This rise in NO<sub>2</sub> triggers an increase in the ozone levels [15].

### Prediction of ground level ozone

Neural network is one of the vital tools utilized for forecasting or prediction. In this study, Ozone concentration was predicted or forecasted by using the meteorological parameters like temperature and wind speed along with one of the precursors of Ozone namely NO<sub>2</sub> as inputs. The data set is randomly divided into three sets namely training, validation and 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 used to evaluate the fully trained networks. The most commonly used computational function in air quality modeling is the Log-Sigmoid function  $f(X) = 1 / (1 + e^{-X})$  [16].

The model was carried out using Levenberg Markquadt algorithm. The neural network model is trained using all the input parameters.

The model gives an R of 0.90093 for all the data points. (Figure 8) shows the regression of the above model. The model exhibits a good correlation between the actual and predicted data points.

### Conclusion

Ground level ozone measurements were carried out for the first time at Karaikal, a coastal region along the south-eastern India. The diurnal variation of ground level ozone was found to be in concurrence with the observed global pattern. For the entire study period, ground level ozone was found to vary between 20 ppb to 32 ppb. Diurnal variation of NO<sub>2</sub> was also investigated. Daily variation of NO<sub>2</sub> was found to be quite similar to the daily variation of ozone. The average diurnal variation was found to be about 5 ppb to 10 ppb. Monthly averaged time series plot between Ground level ozone and NO<sub>2</sub> showed that an increase (decrease) in NO<sub>2</sub> leads to an increase (decrease) in the Ground level ozone. A positive correlation ( $r =$

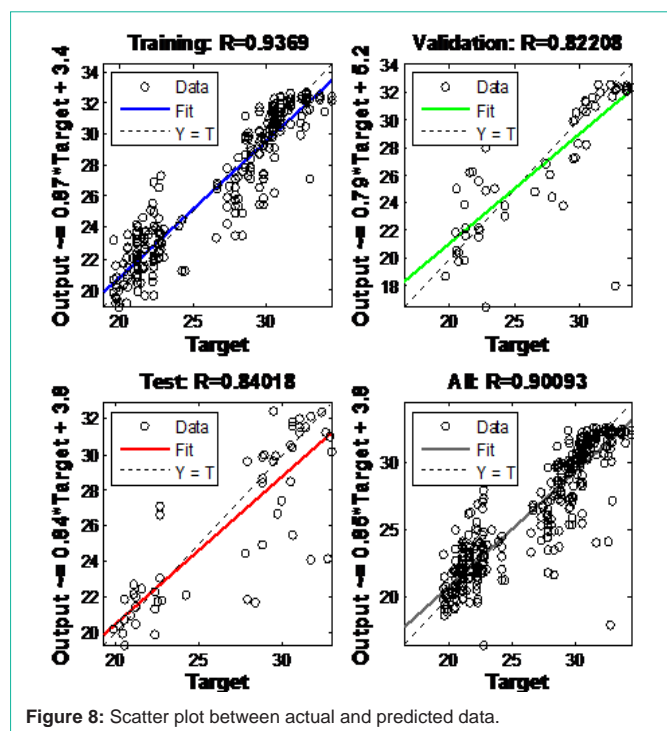


Figure 8: Scatter plot between actual and predicted data.

0.307) was found to exist between ozone and  $NO_2$ . Neural network model was performed to predict the Ozone concentration levels using various inputs. The study shows that the model exhibits a good correlation between the actual and predicted data points.

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