ABSTRACT

Ground level atmospheric ozone (O_3) is a criteria air pollutant and a major component of photochemical smog. Its formation depends on the chemistry of the precursors, viz., oxides of nitrogen (NOx = NO_2+ NO), volatile organic compounds(VOC), and related species like carbon monoxide(CO), and prevailing meteorological conditions like solar radiation, air temperature, and wind [1-9]. Ozone in the lower atmosphere is termed as 'bad' O_3 for its adverse effects on health and environment. It was termed as lung irritant soon after its discovery [10]. Rising concentration of ambient O_3 has negative effect on natural ecosystem, agricultural crops and forests [11-12].

There has been limited literature addressing O_3 from India. There are a few studies on the ground level atmospheric O_3 from the Brahmaputra Valley region [13-16]. The proposed work has been envisaged to understand all factors influencing ozone formation over mid-Brahmaputra region with the following objectives:

- To characterize ambient ozone and it's selected precursors over mid-Brahmaputra region.
- To investigate the relationship of ozone with its dominant precursor compounds.
- To quantify the role of atmospheric transport on local ozone concentration.

The entire thesis is divided into chapters as per the following:

Chapter 1: It constitutes of a brief introduction on ambient ozone and its precursors, sink of ozone, its effect on health and environment and the effects of meteorology on ambient O_3. The importance and scope of the study, research hypotheses and objectives are discussed in this chapter.

Chapter 2: It comprises of the history of discovery of O_3 and the current trends on O_3 modelling. Moreover, O_3 trends in the Northern hemisphere, trends in Europe and trends in India were also discussed in this chapter. Extensive literature survey has been done on the relationship among the Precursor compounds and ambient O_3, measurements of ambient O_3 along with its precursors and on ambient O_3 and its meteorological interactions. Night time chemistry of ambient O_3, Ozone trends during different festivals and transportation of ambient O_3 and possible source regions of O_3 concentrations were also incorporated elaborately in this chapter.

Chapter 3: It explains the different experimental methods used for carrying out the present work. The study site and the climatic condition of the study area have been discussed here. The measurement techniques used for analyses of O_3 and its precursors are explained. The data was obtained from an automated instrument known as Combined Ambient Air Quality Monitoring Station (CAAQMS) installed in the Department of Environmental Science, Tezpur University under the MAPAN (Monitoring of atmospheric pollution and Networking) project in collaboration with Indian Institute of Tropical Meteorology (IITM), Pune and Ministry of Earth Sciences (MOES) and Government of India (GOI). The Meterological parameters were also recorded simultaneously with a mechanized weather tracking system installed as a part of CAAQMS. Ambient O_3 concentrations were measured using a Serinus 10 ozone analyzer. This analyzer uses non-dispersive ultraviolet (UV) absorption technology to measure ozone to a sensitivity of 0.5 ppb in the range of 0-20 ppm. Continuous measurement of oxides of Nitrogen (NOx) were carried out using a Serinus 40 Oxides of Nitrogen analyzer that uses gas phase chemilluminescence detection to perform continuous analysis of Nitric Oxide (NO), total oxides of nitrogen (NO_X), and Nitrogen dioxide (NO_2). SPSS and Excel are used for plotting the concentrations of O_3 and NOx as well as their relationships with meteorological parameters and also the different seasonal and monthly trends. The R package, Openair [17-18] was used for analyses and illustrations and in computing the calendar plots, time variation plots and polar plots. The gbl files used for calculating back trajectories in PSCF and CWT analyses were obtained from NCEP/NCAR Reanalysis database available at ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis. Back trajectories were computed using NOAA HYSPLIT model. Reanalysis data were downloaded from gridded meteorological data archives. The direction of ambient O_3 local sources in Tezpur was computed by using pollution roses, Conditional probability function (CPF) and conditional bivariate probability function (CBPF) in an hourly interval time. The course and origin of the pollutant air masses transported over to the study area were detected by computing backward trajectories at 500 m above ground level by using the TrajStat software which uses NOAA HYSPLIT model to calculate back trajectories. PSCF and CWT calculations are done to analyze the regional contributions of ambient O_3 in Tezpur.

Chapter 4: It constitutes the result and discussion of the present study. The concentrations of O_3 and its precursors over mid-Brahmaputra valley were discussed elaborately. The maximum O3, NOx and OX concentrations were found to be 85 ppb, 19.2 ppb and 174 ppb respectively and the minimum concentrations are 11 ppb, 2 ppb and 0.9 ppb respectively.

The Comparison of ambient ozone and NOx measured at Tezpur station with different locations in India and other International Cities were also discussed here. The temporal variations with regard to seasonal, diel, monthly and annual trends of ambient O_3 and NOx were also described in this chapter.

The days of the week generally showed O_3 trends with single hump (maximum ozone) during the mid-day in all the four years. The O_3 distribution of the days of the week which however shows a mild rise in the concentrations mostly during midweek during the first three years but the rise in concentrations shifts towards weekends in the last year i.e. 2016-2017. The hourly variations of O_3 shows much clear 'bookish' hump around midday in all the four years [19-20].

The monthly distribution of O_3 clearly shows a peak during the month of April (spring) maximum of O_3 concentrations at this remote site like several earlier researchers reported in all the years except in the year 2014-2015 which shows a slight increase in concentrations during the month of February [15,20-22]. Least concentrations were observed mainly from June to December in all the years. The graph clearly shows pre-monsoon (Spring) maximum of O_3 concentrations in all the three years except in the year 2014-2015 where maximum O_3 concentration was seen during winter season at this remote site like several earlier researchers reported [15,20-22]. The mid-day maximum ozone concentrations of various seasons were different with the pre-monsoon season (springtime) showing the maximum mid-day O_3 compared to the other seasons, and the monsoon season showing the minimum mid day O_3.

The diel variation of maximum concentration of NOx exhibited a slight morning and a prominent evening peak in all the four years. The rise in concentrations of NOx was generally seen around midweek i.e Wednesday and Thursday during the entire study period.

The monthly distribution of NOx clearly shows a peak during the month of January and February in all the three years except in the last year the peak was seen during March month. The first two years clearly shows winter maximum whereas for the next two years maximum concentration was seen during postmonsoon season at this remote site. Least concentration of NOx concentration was seen during monsoon season in all the four years.

The daily profile of OX was found to be sharply increasing during the morning hours to the mid-day. The maximum concentrations of OX were found during the pre-monsoon season mainly in the month of April.

Special O_3 days were observed in comparison to the normal days. Two special events Diwali and Solar eclipse was selected for this observation as there are very less study in India during this special events. Highest concentration of ambient O_3 was found during Diwali day in the year 2016. Moreover during the year 2014 and 2016 the effect of Diwali crackers on O_3 concentration during night time was found to be more prominent. During the year 2013 O_3 and NO_2 shows a strong relationship than the non-Diwali nights showing a poor relation. Same trend was also observed during the following years. The concentrations of O_3 were found to be decreasing during eclipse hours as compared to the normal days.

The polynomial fit curves for NO, NO_2, and O_3 against NOx of the remote rural location (Tezpur) were found NOT to follow the pattern of a highly polluted city (Delhi). O_3 concentrations tend to increase slowly with lower values of NO_2/NO ratio and gradually reaches a stable period which explains the photostationary state of O_3.

During daytime the concentration of O_3 is higher than the concentration of O_3 during nighttime while the concentration of NO is higher at nighttime than the concentrations during daytime. Also an inverse relation was seen during nighttime which indicates as NO increase during night O_3 concentration decreases. The maximum concentration of O_3 and NO_2 during daytime was found to be 75 ppb and 42.3 ppb respectively and during nighttime the concentrations were 63 ppb and 33.6 ppb respectively. A strong relation was seen between NOx and NO_2 during Daytime as compared to NO. So it can be said that NO_2 contributes more to O_3 buildup than NO during daytime.

OX and NO_2 have a linear relationship which inferred that as NO_2 concentration increases OX concentration also increases. A positive dependency of O_3 on temperature and an inverse relationship of O_3 with relative humidity are seen.

The n*et* O_3 (measured O_3 concentration) and J_1/k_3 (J_1 is a function of solar intensity so it includes a diel variability whereas k_3 is a function of temperature) were plotted against time of day for the different seasons to ascertain how the temporal variation of O_3 behaved relative to J_1/k_3. The *net* O_3 and J_1/k_3 attained a maximum during midday to the early afternoon hours and then both parameters declined as the day progressed.

During the pre-monsoon and monsoon seasons, the *net* O_3 and J_1/k_3 attained their maxima and were about equal during midday to afternoon. During post-monsoon and winter seasons, the *net* O_3 and J_1/k_3 peaked for a shorter duration. During the post-monsoon *net* O_3 and J_1/k_3 were nearly equal. However, during the winter, *net* O_3 and J_1/k_3 never became equal. During the peak hour, the levels of *net* O_3 were much higher than the J_1/k_3 during the winter month. During all seasons, the ratio (J_1/k_3) and *net* O_3 fell after the peak. The slopes of *net* O_3 and J_1/k_3 were not similar.

The maximum VC was experienced at ~9:00am in the morning and that is then there was steep rise in the winter period concentration of *net*O_3. Through the seasons, high O_3 concentrations were found to accompany high wind speed, which suggests transport of O_3 to the site. Alternatively, higher concentrations of NO_2 were observed under lower wind speeds .Only moderate and low levels of NO_2 were associated with high wind speeds indicating that the NOx was locally emitted and dispersed under higher ventilation conditions.

Higher concentration of ambient O_3 concentration was dominant towards southeasterly direction in all the seasons. The Conditional Probability Function and Conditional Bivariate Probability Function results signify extreme ambient O_3 episodes under the influence of wind from south-easterly directions. The regional to local contribution was 1:1 over mid Brahmaputra Valley.

The PSCF maps were also plotted to study the impact of continental and marine air masses on ambient O_3 and NO_2 concentrations at Tezpur by calculating 3 days back trajectory during winter, premonsoon, monsoon and postmonsoon season for the year 2014-2017 using meteoinfo and trajstat software.

HYSPLIT air mass trajectories for four years (2014-2017) together reaching the site was weighted with the concentrations of O_3 and NO_2 and the CWTs were computed. In all the four years it was seen that highest concentrations of O_3 were originated from regions like Bangladesh, West Bengal, Guwahati etc and least concentrations of O_3 were originated from the areas like Myanmar, New Delhi, Pakistan, Tajikistan etc. In case of NO_2 in all the four years it was seen that highest concentrations of NO_2 were originated from regions like Bangladesh, Patna, Jharkhand etc and least concentrations were originated from regions like Tajikistan, Dehradun, Bay of Bengal, Bhutan.

Chapter 5: It consists of the conclusion part with notable findings. The future scopes of the present study are also discussed in this chapter.

Key words: O_3, NOx, OX, photostationary state, long range transport, CPF, CBPF, PSCF and CWT.

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