Distribution of NO_2 and O_3 Concentration in Around an Oil Refinery: A Case Study in Golaghat District, Assam

Devolakshi Handique[1] and Krishna G. Bhattacharyya[2]

[1,2]Department of Chemistry Gauhati University, Guwahati 14
E-mail: [1]handiquedevolakshi@gmail.com, [2]kgbhattacharyya@gmail.com

Abstract—*Concentrations of ambient ozone (O_3) and nitrogen oxides (NO_2) were measured continuously for a period of 24 months in the Numaligarh, Golaghat district from June 2013 to May 2015. Meteorological parameters like wind speed, temperature, and relative humidity were also monitored. Concentrations of ground O_3 were found to be highly dependent on the NOx diurnal cycle and wind speed. The sampling showed an average concentration of NO_2 of 8 μg/m^3 (maximum 12.52 μg/m^3) in winter, and 6.2 μg/m^3 (maximum 10.06 μg/m^3) in summer. The maximum ozone concentrations were 44.32 μg/m^3 in summer and 36.91 μg/m^3 in winter. The results showed that NO_2 and O_3 concentrations near the refinery and the highway areas were higher compared with the residential and forest areas in both summer and winter. The measurements did not indicate any significant impact of the refinery on ambient air quality with respect to NO_2, and O_3. The seasonal variations of O_3 were more distinct than those of NO_2. However from result of two year observation the O_3 concentration increases 10-15% in summer and 5-10% in winter. The results of this work have helped in an understanding of the air quality in an ecologically fragile area.*

1. INTRODUCTION

Air pollution has become a world problem. Mostly all the developing nations are affected by atmospheric pollution in terms of human health [1], in terms of climate change [2] and loss of bio-diversity [3]. In 21st century air pollution is a great challenge to be considered. Gaseous pollutants, like O_3, NOx and SO_2 and particulate matter (PM), have been recognized as key environment problem in many cities around the world. Air Quality in cities, mainly affected by photochemical oxidants [4]. The presence of ozone (O3) in the troposphere is understood to arise from two basic processes: tropospheric / stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere; and production of ozone from photochemical reactions occurring within the troposphere [5–9]. Ozone is produced in the troposphere as a consequence of interaction of meteorological conditions, sunlight, nitrogen oxides (NOx), O_2 and volatile organic compounds (VOCs) [5, 8–10]. The relation between ozone and its two main precursors, NOx (NO and NO_2) and volatile organic compounds (VOC), represents one of the major scientific challenges associated with urban air pollution [11]. The formation of ground level ozone depends on the intensity of solar radiation, the absolute concentrations of NOx and VOCs, and the ratio of NOx and VOCs [12, 13]. The formation of ozone in the troposphere begins with NO_2 photolysis, after which the NO product quickly reacts with ozone to regenerate the NO_2.

Therefore, the ozone remains in a stationary state that depends on the speed of NO_2 photolysis and on the NO_2/NO ratio. If there were no other processes that transform NO into NO_2, the concentration of ozone would not increase significantly [14]. However, in the presence of VOCs, the ozone concentration increases after NO is converted to NO_2 due to the formation of radicals [15]. NOx is Produced formed in the atmosphere from both natural and anthropogenic sources, involving naturally occurring nitrogen and volatile organic compounds (VOCs) by the action of lightning [16]. However, NOx emissions from anthropogenic sources exceed natural sources [17]. Increased combustion of fossil fuels and exhaust fumes may be extremely pervasive, causing serious environmental degradation, illnesses and deaths [18, 19].

According to the literature, various methods have been reported for the detection of ozone, including spectroscopy and chemiluminescence procedures [21]. Passive sampling has become a widely accepted technology throughout the world for environmental sampling as evidenced by many regulatory guidelines, manuals and protocols published by various environmental standard policy makers worldwide. Passive sampling for nitrogen dioxide and troposphere ozone has become a well developed method for the last decade. Various trapping reagents have been used for absorbing O_3, like 1,2-di(4-pyridyl)-ethylene [22,23], potassium iodide [22-25], nitrite [22-27], 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol [23-24] and p-acetamidophenol [23]. Trapping reagent for absorbing NO_2 is sodium arsenite.

This study was undertaken in order to fulfil this gap of knowledge, and to describe the key observation of seasonal variation of ambient O_3 and its precursor NOx and their variation with meteorological parameters in Numaligarh. Moreover, we attempted in the present study to collect enough and significant data to estimate air quality trends in Numaligarh and Kaziranga atmosphere. Different metrological parameters (ambient temperature, relative humidity and wind speed and direction) and their influence on the air quality were also considered in the discussion of the results.

2. METHODOLOGY

2.1. Study Area

Numaligarh is a town in the Golaghat district of Assam, India. It is situated at the distance of 32 km from Golaghat town ($26^0$38'N$93^0$45'E). It has well established traffic networks because here a medium oil refinery is situated, resulting in high population density as well as dense urban and infrastructural network. At aerial distance of 10 km Kaziranga national park is situated which is famous for one horned rhinoceros.

There were four monitoring locations chosen along transect representing different levels of pollution in order to have a comprehensive study of spatial distribution of O_3 and NO_2. The gradient extended over a distance of approximately 10 km within the boundaries of the city. In the 10 km study area around the Numaligarh refinery, the ambient air quality was monitored in two years in 4 sampling stations. The GPS locations are given in **Table 1** below. The selection of parameters and the sampling techniques were as per Ministry of Environment & Forests (MoEF) / Central Pollution Control Board guidelines.

Table 1: Location of monitoring station

S/N	Location	Direction	Distance (km)	Latitude (N)	Longitude (E)
S1	Close to the front gate of the Refinery	--	0	26º35′2.3″	93º46′42.7″
S2	NRL township [The Butterfly Park]	N	2	26º35′31.5″	93º44′41.5″
S3	Raw water intake point, the Dhansiri River	E	2	26º35′25.7″	93º48′25″
S4	Near NH39 bypass (Rangbang Village)	S	4	26º33′42.1″	93º46′36″

2.2. Climate Characterization

Numaligarh town is located in the Golaghat district of Assam. This town has also a tropical climate, seasonally humid with maritime influence. There are two climatic periods, the summer period from April to June and winter period from November till January. In this town, the annual daily average temperature is 23 °C. The daily average temperature peaks in the summer period in June at around 28.3 °C and reaches its minimum of 13.2°C in December. The relative humidity is high; its average value is ranges from 36-87%. During summer due to monsoon climate humidity is more. It lies around 60-74%. During winter the values lies around 40-52%. The prevailing wind direction is north north eastern and second prevailing is south eastern. The average wind speed is around 2.1 m/s - 5.7 m/s throughout the year.

2.3. Sampling of O_3 and NOx

Sampling campaign was conducted from 2013-15 in Numaligarh area and done twice in a week and eight times in a month. The sampling periods are summer and winter respectively. Summer period sampling was done in month of April, May and June where as winter in the month of November, December and January.

Sampling was done by means of Envirotech dust sampler APM 460 NL for both ozone and NO_2.

2.4. Analytical procedure for O_3 and NO_2

For ozone potassium iodine is taken as absorbing solution. The iodine is determined spectro photo metrically by measuring the absorption of tri-iodide ion at 352nm. Ambient nitrogen dioxide is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion produced during sampling is determined calorimetrically by reacting the nitrite ion with phosphoric acid, sulphanilamide, and N-(1-naphthyle)-ethylenediammine dihydrochloride (NEDA) and measuring the absorbance of the highly coloured azo dye at 540 nm.

2.5. Reagents

All the reagents used are of analytical grade. For making chemical solution and dilution, de ionised water having conductivity less than 0.15 mS cm^{-1} was used throughout the experiments. The extraction solution for nitrogen dioxide was prepared by mixing 4 gm of sodium hydroxide (avantor performance materials, India) and 1 gm of sodium arsenite (lobal chemie, India). For ozone by mixing 13.6 g of potassium dihydrogen phosphate (Merck Mumbai), 14.2 g of disodium hydrogen phosphate (loba chemie, India) and 10 g of potassium iodide(RFCL limited India) and make up to 1 L. Accurate weighing of chemical was performed on Kern electronic balance model type ABS 220-4 no WB 1110567.

3. RESULTS AND DISCUSSION

3.1. Nitrogen dioxide concentration in the winter and summer season and the impact of meteorological condition

NO_2 ground level concentrations (GLC) in the winter were between 2.2-12.5 µg/m^3 (table 2). These concentrations do not exceed both the target level of 80 mg/m^3 given in the NAAQS. In the summer, on the other hand, ambient air NO_2 levels varied between 1.1 and 10.1 µg/m^3 (Table 3). The winter levels were higher than the summer levels for all the sampling points.

The results obtained for NO_2 are originate mainly from the combustion of fossil fuels and have similar sources including vehicles, residential heating, chemical processes, etc. Due to the small area and population

Table 3: Temporal and site specific variation of no2 in winter season with meteorological data

Month	Nov1	Dec1	Jan1	Nov2	Dec2	Jan2
avgS1	7.3	5.3	5.9	10.5	12.5	7.5
avgS2	2.1	3.5	3.4	6.1	8.1	4.2
avgS3	2.2	2.9	2.6	3.8	4.8	3.1
avgS4	5.5	3.3	4.8	6.1	7.0	5.1
Tem (0C)	140	130	150	160	160	180
WS	3.8	3.9	4.3	3.9	4.1	4.5

Nov1, Dec1 is for year 2013, Jan1 for 2014, Nov2, Dec2 for 2014 and Jan2 for 2015. WS - wind speed. Concentration unit is µg/m^3.

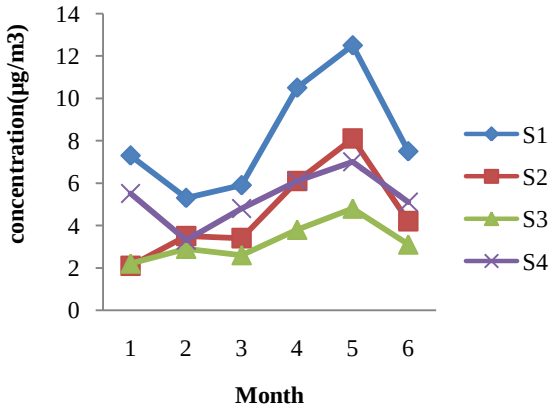

Fig. 1: Average concentration of NO2 in winter season

density, the large amount of traffic (5,000 vehicles/day on S4 highway, 3,000 vehicles/day on S2 highway, and 2,401 vehicles/day on S1 highway) has led to residential areas being near the heavy traffic and industrial fields in Numaligarh. NO_2 concentrations are high not only in the areas close to the highways of S2 and S4 , but also in the S3 point, proving that the traffic emissions and the industrial activities are the most important sources determining the NO_2 levels measured in the study area. Chemical reactions, dispersion, and dilution processes result in spatial and temporal variations in concentrations of air pollutants. Due to its short life-time, the distribution of NO_2 is strongly heterogeneous with highest abundances in industrial areas [27]. As a result of which the increasing concentration was observed in the refinery and the bypass area. It is shown that the natural gas combustion in the industrial plants is the most significant source of NOx pollution [28]. Among the industrial sectors, petroleum refining, power generation, petrochemical and chemical industries, and tire industry have been found to be the major NOx sources. Concentration of NO2 increases slightly from year 2013-2014 to 2014-2015. Such yearly variations might be due to local variations in the climate pattern.

Table 3: Temporal and site specific variation of no2 in summer season with meteorological data

Month	Apl1	May1	Jun1	Apl2	May2	Jun2
avgS1	6.2	6.3	8.0	7.9	8.1	10.1
avgS2	3.5	2.3	3.2	3.3	3.6	4.2
avgS3	2.7	1.8	1.1	3.2	3.0	2.4
avgS4	4.8	2.1	4.3	6.7	6.5	4.3
Tem (0C)	280	290	300	290	300	300
WS	2.3	2.4	2.3	2.4	2.4	2.3

April1, May1 and June1 are for year 2014, April2, May2 and June2 for 2015. Concentration unit is µg/m^3.

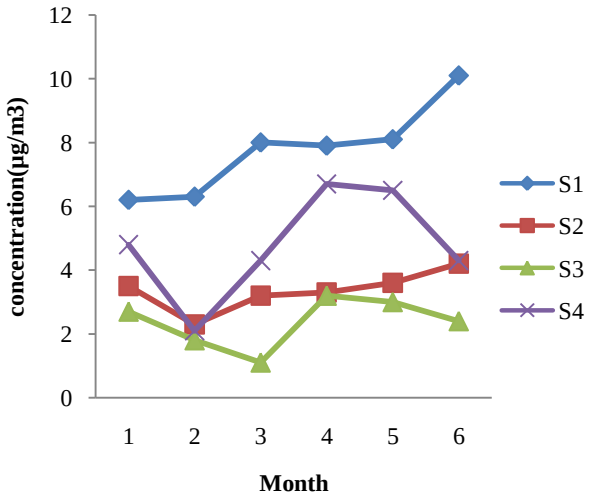

Fig. 2: Average concentration of NO_2 in summer season

3.2. Ozone concentration in the winter and summer season and the impact of meteorological condition

The lowest average GLC O_3 concentration in winter season was 4.5 µg/m^3 detected at the S3 sampling site, where the air exits the sampling zone and the highest value was 36.9 µg/m^3 measured at the S4 site, where the clean air arrives at this area(Table 2). As can be seen from these results, the O_3 could not be produced in this zone. The high concentrations observed at the S1 site can be due to the emission from refinery. Ozone

concentrations in all sites during winter were measured between 4.5 and 36.9 µg/m^3 (Table 2), which are below the limit values set for both human health and the development of the plants. It is known that the photochemical reactions occurring in the atmosphere play a significant role in ozone formation; therefore, ozone concentrations in summer are generally higher than those in winter due to the higher temperatures and light intensity promoting these reactions, making ozone as a typical summer pollutant [29, 30].

Table 4: Temporal and site specific variation of O3 in winter season with meteorological data

Month	Nov1	Dec1	Jan1	Nov2	Dec2	Jan2
avgS1	23.8	23.6	30.7	26.9	32.3	34.3
avgS2	7.6	17.8	29.2	35.8	29.6	35.9
avgS3	4.5	4.7	5.0	18.8	19.9	21.9
avgS4	12.5	22.7	30.1	34.5	36.0	36.9
Tem (0C)	140	130	150	160	160	180
WS	3.8	3.9	4.3	3.9	4.1	4.5

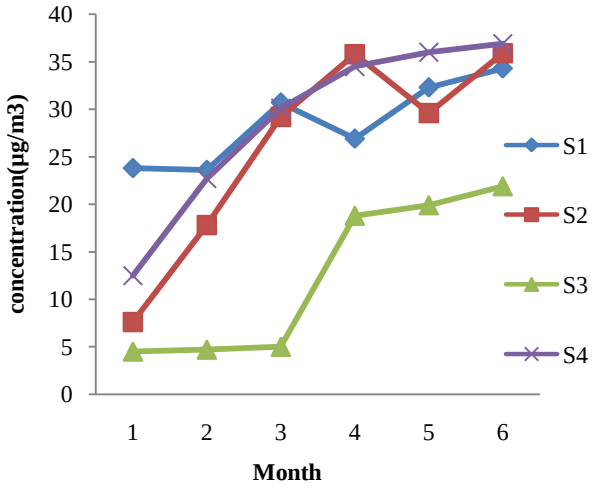

Fig. 3: Average concentration of Ozone in winter season

Table 5: Temporal and site specific variation of O3 in summer season with meteorological data

Month	Apl1	May1	Jun1	Apl2	May2	Jun2
avgS1	40.9	37.1	10.2	46.3	33.5	42.3
avgS2	32.9	32.7	20.4	37.3	36.1	32.5
avgS3	20	27.9	19	28.3	29.3	27.8
avgS4	38.5	35.8	11.2	45.3	30.7	40.9
Tem (0C)	280	290	300	290	300	300
WS	2.3	2.4	2.3	2.4	2.4	2.3

In the study, ozone concentrations in summer varied between 10.13 and 54.33 µg/m^{3}as given in Table 5. All the ozone concentrations measured in the study was below the limit value of 120 µg/m^3 (as a daily average) given in NAAQs directives. Seasonal distribution diagram for ozone pollution in summer and winter in the study area are shown in Fig. 3, 4.

It is observed that the ozone levels are generally low in the residential i.e. S2 (township) and the S3 (intake) areas, and high in the S4 (bypass) areas. Additionally the concentration of Ozone in both seasons is increasing gradually (Figure. 3, 4) with increase of NO_2 concentration (Fig. 1, 2).

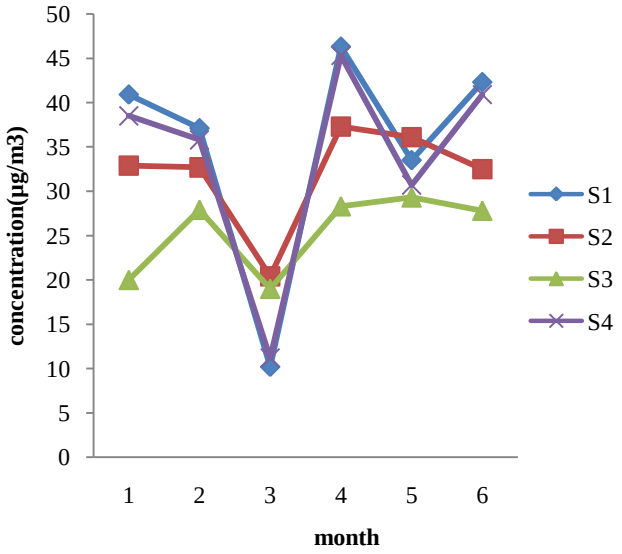

Fig. 4: Average concentration of ozone in summer season

The concentration of ozone is increases from year 2013-2014 to 2014-2015. NOx are required for formation of O_3 [24]. During the noon hours, the sun rays increased greatly and the photochemical processes that produce O_3 dominated, especially after the sunrise. Oxygen atoms produced in the photolysis of NO_2 could react with O_2 and to produce O_3 through the chemical reactions [31]. The reduction in O_3 level is mainly due to the decrease of solar radiation which then would lower the level of the photochemical production. During winter the intensity of solar light is less. Ozone concentration is less in the winter season than the summer.

4. CONCLUSION

The aim of this work is to determine the pollutant level of Nitogen dioxide and ozone in ambient air. This provides a good knowledge about the ground level concentration of the nitrogen dioxide as well as ozone. The concentration of nitrogen dioxide is found higher in winter than the summer whereas the ozone concentration is found high in summer than the winter. But the concentration of both the pollutant increases slightly from year 2013-2014 to 2014-2015. It can be seen that the maximum increase are all very minimal. If the seasonal average is considered then the increase are nearly negligible. The contour shows that in most of the study area, the increase in GLC of the pollutant is negligible. Only in some small packet, there is some marginal increase.

Ambient air pollutants NO_2 and O_3, have not exceeded the NAAQS and in most cases, their concentrations are much below the permissible limits. The results of this work will definitely help in expanding the knowledge base and in understanding air quality in an ecologically fragile area.

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