The Variability of Surface Ozone Concentration Over Different Localities of Delhi And the Correlation of It With the Emission of Precursor Gases Like Nox, Sox and the Amount Of Solar Radiation

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INTRODUCTION

Atmosphere is a gaseous envelops hanging over the earth's surface. It is composed of different types of gases mixed in a distinct proportion. Some of them are constant in their proportion, while others are variable in characters over space and time. Nitrogen, Oxygen, CO₂, Argon, Ozone, Water vapor, Neon, Hydrogen, Helium etc. is the some among them. Each of these gases is plying a prominent role in the structuring of the earth's biosphere and vice versa. It is this distinct composition making the earth different from other planets and makes the life possible on it.

Of these gases Ozone is one of the most distinct one. Because ozone plying double role (bad vs. good ozone) at different locations. Ozone has a capacity to absorb the UV radiation coming from the Sun; it causes various kinds of skin diseases to the human beings. At the same time it's higher concentration at or near the surface has some hazardous effect on the human as well as the plants health. Various studies have been showed that the increased concentration of surface ozone (tropospheric ozone) causes asthma in human and also affect the growth of the plants.

The concentration of ozone is mainly found within an altitude of 10 to 23 Km from the earth's surface. But its concentration is very high in the Stratosphere ¹ (higher concentration with in a height ranges between 22 to 23 Km).

Ozone (O_3) is a gas composed of three oxygen atoms. It is not usually emitted directly into the air, but at ground-level is created by a chemical reaction between oxides of nitrogen (NOx) and volatile organic compounds (VOC) in the presence of sunlight. The stratospheric ozone is formed due to Chapman cycle, which represents the production and subsequent annihilation of ozone by solar UV radiation.

¹ Stratosphere is the second layer of the Earth's atmosphere, lies above the troposphere at an altitude ranges between 15 to 50 km from the surface.

Chapman Cycle:

 $O_2 + \text{light} \rightarrow 2O (120 - 210 \text{ nm})$ $O + O_2 + M \rightarrow O_3 + M^* \text{ (generates heat)}$ $O_3 + \text{light} \rightarrow O_2 + O (220 - 320 \text{ nm})$ $O_3 + O \rightarrow 2O_2$

At the surface, since the amount of UV is insufficient for the Chapman cycle to operate, so tropospheric ozone arises in different ways:

- 1. Intermittent intrusion of stratospheric ozone, chiefly near thunderstorms with overshooting cloud tops,
- 2. Lightning, and
- 3. Urban air pollution.

Lightning-induced ozone is produced in the same way as in the stratosphere: the high-energy radiation from a lightning stroke dissociates oxygen (and water vapor), and the resulting radicals (O and HO⁻) quickly combine with oxygen to produce ozone.Pollution-related ozone results from reactions involving oxides of nitrogen (NO and NO₂), carbon monoxide, organic compounds of the kind found in car exhausts, water vapor and hydroxyl radicals (HO⁻). Especially important is the photochemical decomposition of NO₂. Then ozone itself photodissociates to produce energetic oxygen atoms that in turn produce HO⁻ radicals following reaction with water vapor. If organic molecules are present, these radicals react to form HO₂ and other organic-peroxy radicals, which are able to react with NO to generate NO₂ for further production of ozone (Hales, J. 1996). The nitrogen oxides and the organic compounds including carbon monoxide, sulfur dioxide, are called precursors of ozone formation.

The identification of an ozone hole at Halley Bay, Antarctica in 1982 with the help of an American satellite brought Ozone for a serious and controversial talk not only among the scientist but also among the politicians and the common people.

In this term paper I would like to study the variability in the concentration of bad ozone (surface ozone) and its correlation with the precursor gases, over the national capital of India, one of the emerging third world countries. This study focuses on the seasonal and daily variability of surface ozone at different places with in Delhi.

REVIEW OF LITERATURE

Ozone is one of the most important constituent of the earth's atmosphere. It is formed through the process of photochemical reaction in the presence of solar radiation. The stratospheric ozone act as an umbrella, by protecting the lives on the earth from the UV radiation from the Sun. Thus it acts as a life saver. But now as a result of increased emission of CFC gases etc. this stratospheric ozone is under a great threat of depletion. At the same time, with the rapid rate of urbanization and modernization the amount of surface ozone called as the tropospheric ozone is increasing recently. This conditions have multitude of impacts on the earth's climate, composition of atmosphere and ultimately on the lives on this planet. Ozone is a secondary air pollutant and is a green house gas too. The presence of O_3 beyond a certain level can affect the growth and productivity of plants (Krupa and Manning, 1988). Some studies also shows that this increased presence of O3 became a serious threat to the human health (the illness of asthma is being attributed by it). Ozone is an oxidizing agent, an increasing concentration of which can modulate the oxidizing capacity of the atmosphere and in turn can affect climate (Portmann et al. 1997). That is why the concentration of surface ozone became a topic study for a number of researchers and academicians at the same time when people are discussing the ozone holes over Antarctica. Ozone is not a problem but where it located is a problem.

The article entitled 'Observational Study of Surface Ozone at New Delhi, India' by S.L. Jain et al., appeared in the International Journal of Remote Sensing (Vol. 26, No. 16, 20 August 2005, Pp 3515-3524) focuses on the tropospheric ozone's photochemical air pollution in Delhi, the capital city of India. This study analyzes the variability of surface O3 by seasonal as well as daily basis for a period of 1997-2003. It shows an increasing trend of surface O3 concentration over time and according to the researchers the increased number of vehicle played a crucial role for this trend. Besides these

anthropogenic factors the meteorological factors such as sunny warm weather, stagnant wind pattern, low humidity, anti-cyclonic condition etc also influences these high ozone episodes. Like other studies, this work also shows that the O3 concentration is maxima at dry summers (April and June) and minima during Monsoon periods. The diurnal O3 concentration is higher at day times and lowers at night times. But in winter season the reverse is happening, i.e., night time surface O3 concentration is higher as a result of mechanical turbulence mixing up of O3 rich upper air to the ground by low level jets, according to them. One of the serious concern that this study shares us, 'on a large number of days (83, 39, 113, 158, 112, 111 days during 1997, 1998, 1999, 2001, 2002, 2003 respectively) the surface ozone value at Delhi exceeds the WHO ambient air quality standards (hourly average of 80 ppb) for ozone'.

The article 'Surface Ozone in the Indian Region' by Moti L. Mittal, Peter G. Hess, S.L. Jain, B.C. Arya and C. Sharma, published in the Journal of Atmospheric Environment (41. 2007. Pp 6572-6584) is the first comprehensive attempt to study the spatial and temporal variation of O3 concentration in the surface air across the Indian Subcontinent. The data used for the whole region is not primary in nature, but is estimated on the basis of the observation and measurement of ozone at various corners of the subcontinent such as Ahmadabad, Delhi, Mount Abu in India and Koshidhoo in Maldives and from Arabian Sea MBL. And these all data are combined and then the whole region of the Indian Subcontinent is divided in to various grids and their surface Ozone level is estimated with the help of 'HANK Model'. One of their finding is that the higher O3 concentration move from south to north and east to west from February. In May high O3 concentration has been observed over parts of Afghanistan and Pakistan, but in February it is quite higher over Arabian Sea and Bay of Bengal than the nearby coastal areas, by March it became reversed (higher over the coastal areas). This study also shows that there is a substantial temporal and spatial variation in the concentration of O3 due to different meteorological and topographic conditions. This article concludes with a serious remark that, the surface ozone is much above critical levels, as AOT40 is greater than 3000 ppbh at most places in the Indian region. It is of significant concern for agricultural productivity and an agricultural economy like India.

The research article by the scholars of Indian Institute of Tropical Meteorology, Pune including L.T. Khemani, G.A. Momin, P.S.P. Rao, R. Vijayakumar and P.D. Safai, titled *'Study of Surface Ozone Behaviour at Urban and Forested Sites in India'* (Atmospheric Environment Vol. 29, No. 16, 1995, Pp. 2021-2024) is a comparative study of the spatial variation in the concentration of surface Ozone between two different environments, say urban environment of Pune and forested areas of Bandipur, a core zone of Nilgiri Biosphere Reserve Forests in the Tamil Nadu Karnataka border. It points out that

the dynamics of place also influences the level of surface Ozone over that place. This study also shows an interesting fact that the diurnal variation of O3 in the forested area is different from that of at Pune. That is there is a high level of O3 concentration at early morning (5.00 am) and a decreasing trend by evening as compared to Pune (urban area).

All these works are different both in their scope and area of referring. But commonly we can see there are some uniformity in their content and results, i.e. the surface ozone concentration is a serious threat to the lives both climatically and for their health. There are a lot of factors affecting the surface O3 concentration such as meteorological conditions, dynamics on the earth mainly by humans and the topography of the area. There is a general trend of high surface O3 during summers and at day times. Ozone plays a key role in biogeochemical cycles, air quality, and global change. As a pollutant and greenhouse gas, O3 should be brought under effective control, but the variability of its natural background level in the boundary layer makes difficult the definition of the concentration above which it becomes a pollutant (Y.N. Ahammed et al.).

Through this term paper I would like to focuses on the variability of surface ozone concentration over different localities of Delhi and the correlation of surface O3 with the emission of precursor gases like NOx and the amount of solar radiation. It would be a first and an important attempt since Delhi is one of the most populous cities of the world and the capital of a country like India. The data is available for the last one year (2010), which is quite insufficient though help us to understand the seasonal as well as the diurnal variations and its correlation with other factors.

OBJECTIVES

- To know the vulnerability of air pollution over Delhi.
- ✤ To understand the seasonal as well as the daily variability in the surface ozone concentration.
- To identify the degree of correlation exists between O3 and the precursor gases and solar radiations.
- ✤ To understand the spatial variability in the concentration of surface O3 with in Delhi.
- ✤ To analyze the causes for such spatial and temporal variability with in region.

METHODOLOGY

Calculate the average monthly concentration of O3 over different stations; plot them with the help of a bar graph. With help of this bar graph find out the months and seasons which have high concentration of

surface O3. Then find out the correlation between O3 with NO2, SO2, CO and Solar Radiation. Plot the values of each of them in a line graph and compare their trend with the trend of O3 and the respective correlation. Calculate the coefficient of variance of O3 concentration for each station and each month, and identify the Stations and months of high variability. Likewise calculate the correlation among the O3, precursor gases and solar radiation for each day, and compare it with the monthly values. Compare the daily concentration of O3, CO, NO2, SO2 with the standard air quality index by CPCB, to understand the vulnerability of air pollution over Delhi.

DATA BASE

The Delhi Pollution Control Committee, New Delhi.

AREA OF STUDY

Delhi is the national capital territory of India located at the 28°36′36″N latitude and the 77°13′48″E longitude. It is the largest metropolis by area and the second-largest metropolis by population in India. It is the eighth largest metropolis in the world by population with 16.7 million inhabitants in the Territory at the 2011 Census. Delhi is spread over an area of 1,484 km² in the northern India on the banks of river Yamuna. The climate of Delhi is humid subtropical in nature. Mainly four seasons are predominant; summer (March-June), monsoon (June-September), autumn (October-November) and winter (December-February). Summers are long and extremely hot while winters are extremely cold due to its continental climate. It was one of the most densely populated and polluted cities of the world.

This study focuses on the ambient air qualities of five station in Delhi; Mandir Margh, Punjabi Bagh, RK Puram, IGI Airport and Civil Line. All of them are residential area except IGI Airport, located at different parts of the state.



RESULTS AND DISCUSSIONS

Seasonal Variations

The monthly pattern of ozone concentration shown in the figure, which shows that the surface O3 concentration is generally higher during the summer and autumn seasons, while it is minimum during the wet (monsoon) and winter seasons. While looking across each station, Mandir Marg, Panjabi Bagh and RK Puram recorded higher concentration of O3 in the month of October, but IGI Airport and Civil Line recorded high O3 concentration during May and December respectively. This seasonal variation shows that along with the anthropogenic causes of pollution the atmospheric conditions also influences the concentration of surface ozone. That is, the summer time maximum O3 concentration is mainly due to high degree of photochemical reactions with higher amount of solar radiation. The minimum ozone levels observed during the monsoon periods are may be due to non-availability of sufficient solar radiation and washout of pollutant as well as consumption of O3 by HOx radicals.

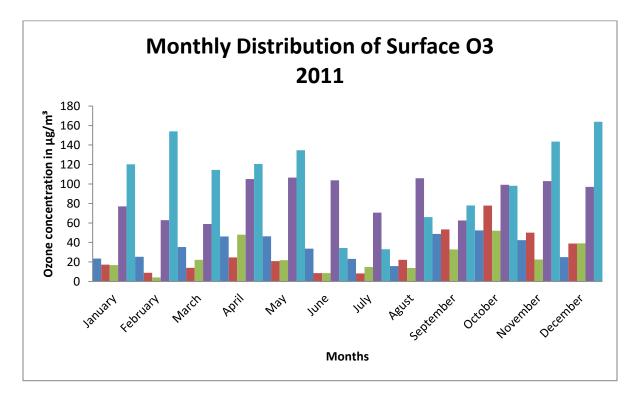


Figure 1. Average monthly O3 concentration at different stations in Delhi during 2011.

The variability of surface O3 concentration is higher at Punjabi Bagh and RK Puram. And it is comparatively lower at IGI Airport, Mandir Margh and Civil Line. Among these five stations IGI Airport having higher concentration of O3 throughout the year, while it is relatively lower at Mandir Marg. It may be because of high dynamism keep the level of ozone higher throughout the year in these two stations and thus lower variability. At IGI Airport the concentration of surface O3 is higher than the amount of precursor gases. It may be because of the mixing of upper O3 rich stratospheric air with the lower surface air during the landing and taking off of the airplanes.

Considering the months, the months of February and June have high variability in the concentration of surface O3. During the month of February and June RK Puram shows low level of O3 concentration of the year. In February the insufficiency of solar radiation was the major reason for lower ozone level, while in June the insufficiency of the precursor gases was the reason, though there was enough solar radiation. During June IGI Airport recorded higher O3 concentration, though the amount of the precursor gases was lower.

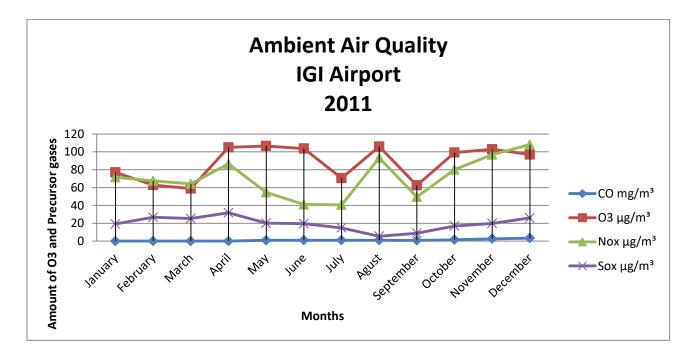


Figure2. Ambient air quality at IGI Airport, 2011.

While looking at the correlation of surface O3 concentration, it is clear that the correlation varies across the places. NO_2 and SO_2 are the major determinants of surface O_3 at Punjabi Bagh and Civil Line. While solar radiation is the chief determinant at Mandir Margh. At RK Puram and IGI Airport, CO and NO_2 are the major determinants of O_3 . In RK Puram there is a negative correlation between O3 and solar radiation shows that ozone is not only affected by the amount of solar radiation available but also on the amount of precursor gases in the near air. That is, the surface ozone is a product of both solar radiation and precursor gases.

Diurnal variation

The daily data tell us the alarming condition of the Delhi air. The analysis of daily averaged surface ozone data illustrates that on a large number of days the surface ozone values at different stations of Delhi exceeds the CPCB's ambient air quality standards for ozone (100 μ g/m³ for 8 hours); it is of serious concern because it has a greater impact on human health. The number of days registered O₃ concentration above 100 μ g/m³ for 8 hours were found to be 191, 114, 8,4, 0 at Civil Line, IGI Airport, Punjabi Bagh, RK Puram and Mandir Margh respectively, which shows the seriousness of ozone pollution over Delhi (figure 3). The highest numbers of elevated ozone episodes were recorded at Civil Line.

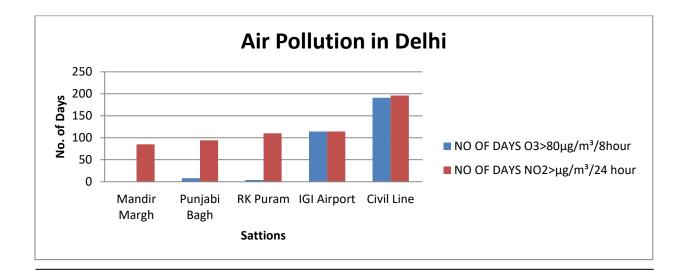


Figure 3. No of days the concentration of O3 and NO2 exceeded the National Ambient Air Quality Standard by CPCB (2011).

The nitrogen dioxide (NO₂) is also a major air pollutant, and can cause serious hazards to the human health. The condition of the concentration of the NO₂ is also too vulgar as the O₃. There are a large number of days the observed value of NO₂ exceeds the national ambient air quality standard by the CPCB (80 μ g/m³ for 24 hours). The figure3 shows that Civil Line is more vulnerably polluted areas of Delhi in terms of high concentration of both NO₂ and O₃.

CONCLUSION

This study throws lights on the alarming conditions of the air that we are breathing in our national capital. The condition of the Delhi is highly vulnerable due to high amount of air pollution. Though station under this study was all residential except one, the impact of pollution is different. The analysis shows that on a large number of days the surface ozone values at different stations of Delhi exceed the CPCB's ambient air quality standards for ozone (100 μ g/m³ for 8 hours), which has a serious impact on human health and is of serious concern. Because the high O₃ concentration in the air causes various kinds uncomfortability for the human such as eye, nose and throat irritation, risk of asthmatics etc. Moreover higher amount of NO₂ further worsen the situations.

Of this five stations studied the condition at Civil Line and IGI Airport are too bad. They have high concentration of O_3 even during winters and monsoon seasons. The variability in the concentration of surface O_3 is highly influenced by the amount of precursor gases, solar radiation, air circulations and the dynamism on the land. Such higher concentrations of O_3 not only affect the plants and animals but also could alter the earth's climate.Because, ozone is an oxidizing agent, an increasing concentration of it can modulate the oxidizing capacity of the atmosphere and in turn can affect the Earth's climate (Portmann et al. 1997). Therefore this condition should be taken as a serious challenge to the whole humanity and further actions should be taken to control this situation.

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