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DETERMINANTS OF SEASONAL VARIATIONS IN SURFACE OZONE – A STUDY IN VISAKHAPATNAM CITY OF ANDHRA PRADESH, INDIA

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ABSTRACT

Ozone is an important constituent of the atmosphere. It is a variable gas and even a minute changes in its composition in the vertical profile of the atmospheric gases can cause far reaching implications vis-à-vis warming of the earth and other effects. About 90% of Ozone is found in the stratosphere up to 50km the majority of which is in the height range of 10-16 km. The stratospheric ozone protects the earth from the harmful effects of the Ultraviolet (UV) radiation and hence it is known as 'good ozone'. The remaining 10% of ozone in the atmosphere hovers in the troposphere and resides on the ground which is a pollutant that is harmful to plants, animals, and humans. This is bad ozone. Hence, Ozone is metaphorically referred to as, "Good up high but bad down below". The paper attempts to analyze the seasonal variation in concentration of ozone at the surface. The role of precursors that help in formation and destruction are studied. The study shows correlation of concentration of surface ozone with precursors. The statistical inferences show an irrefutable influence of meteorological parameters on the concentration of ozone.

KEY WORDS : Ozone, Precursors, VOC, NOx, Surface ozone, Visakhapatnam

INTRODUCTION

Ozone present in the air can be good or bad. Good ozone is naturally present in the upper atmosphere, which shields us from harmful UV rays emanating from the Sun. Bad ozone forms near the surface due to the chemical reaction of primary pollutants from industries, refineries, power plants, etc.,under sunlight. Sunlight is the driving force for most atmospheric chemical reactions. A shorter wavelength of light with higher energy oxidizes primary pollutants into secondary pollutants, such as ozone(O_3).

Surface ozone (O_3) is a secondary pollutant that forms because of the photochemical reaction of primary pollutants - CO, VOCs, and NO_Xin the presence of sunlight. NO_x (NO_x= NO+NO_2) plays a vital role in the formation and reduction of O_3. NO_2 helps in the formation, while NO in NO_X reduces it. Another primary pollutant, SO_2, also acts as a precursor, as it helps form HO_2, a free radical on which O_3 formation is dependent. In addition to precursors, meteorological parameters such as relative humidity, temperature, wind speed, and direction significantly influence the concentrations of O_3. The variation in concentrations also depends on topography and the season of the year.

The seasonal variation of ozone exhibits different patterns across regions in India. At a semi-arid rural site, Anantapur (in the southern part of India) the highest seasonal ozone variation was recorded in (Reddy *et al.,* 2012). In rural parts of western India, the concentrations are high in summer due to anthropogenic activities (Debaje and Kakade, 2008).

In contrast, in Jabalpur, an urban place of India, the variations werehigher in autumn in 2013 and winter in 2014 due to low solar radiation and elevated concentrations of O_3precursors (Sarkar Champa, 2013). The city of Delhi also recorded highest concentrations in the winter, as reported by Singh *et al.* At a high-altitude site, Mt Abu, meteorological parameters influenced the diurnal and seasonal variations of O_3 and maximum concentration was reported in winter (Naja *et al.*, 2003). Thus, most of the studies reported highest Ozone concentrations in the summer and winter seasons. On the contrary, a survey carried out by Marathe and Murthy, (2015), observed the highest surface ozone concentrations in the post-monsoon season in the coastal city of Mumbai.

Against this backdrop, the present study aims to analyze the seasonal variations in surface ozone in the coastal city of Visakhapatnam, Andhra Pradesh, India, for the year 2020-21.

Data and Methodology

The study area is the largest city on the east coast of India in Andhra Pradesh. Visakhapatnam is located between the eastern ghats and the shore of the Bay of Bengal. Apart from being a port city, it is primarily an industrial city with large industries like steel plant, Hindustan shipyard, power plants, and many smaller industries. It also has refineries such as Hindustan Petroleum Corporation (HPCL), Bharat Petroleum Corporation Limited (BPCL), and Indian Oil Corporation (IOC).

The site has a tropical climate. The driest month is March. May is the warmest month,and the coldest month happens to be January. Precipitation peaks in August. The city experiences maximum temperatures with high humidity in the summer months, making the climate sultry and uneasy. The winter months record the lowest temperatures ranging between 15 °C to 18 °C, with the maximum being 32 °C. The city is under the spell of southwest monsoon from June to September and northeast

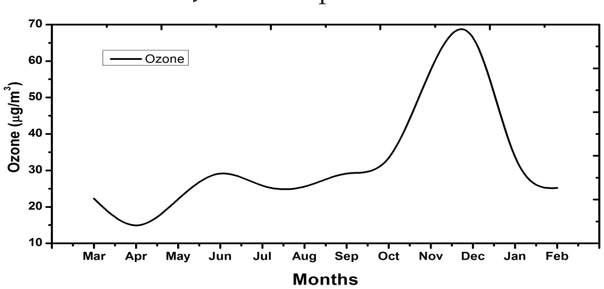

Fig. 1. Monthly Variations of O_3 during the study period

monsoon sets in October. June has the maximum daily hours of sunshine at this location.

Analysis of seasonal variations is carried out using the hourly average values of O_3, precursors, and meteorological parameters data obtained from the website (https://app. cpcbccr.com/)during March 2020 -Feb 2021. The acquired data is grouped into four seasons for seasonal analysis – summer, monsoon, post-monsoon, and winter.

The precursors and meteorological parameters considered are NOx, NO, NO_2, SO_2, CO, solar radiation, temperature, relative humidity, and wind speed. Pearson correlation and regression tests are carried out to delineate the influence of precursors and meteorological parameters in ozone formation.

RESULTS AND DISCUSSION

Table 1. gives a statistical summary of variables, and Table 2. presents the Pearson correlation test results carried out on the data set.

Monthly variations of O_3 for the study period are represented in Figure 1. It is evident from the figure that the amplitude of O_3peaked in December and it is the lowest in April. A sudden and steep increase in amplitude of O_3 from October onwards could be attributed to seasonal changes in wind patterns. The seasonal mean of O_3 recorded the highest value (44.90±21.04 µg/m³) in post-monsoon and registered lowest value (19.93±10.18 µg/m³) in summer.

The maximum and minimum hourly values are 92.98 µg/m³ and 6.78 µg/m³ recorded in the winter and summer months, respectively. Also, It may be seen from Figures 2(a) & (b) that exceptionally in 4 % of observations in winter the 8-hr. permissible limit is exceeded with a maximum of 126.94 µg/m³ at the present site.

Meteorological parameters

The chemical reactions in ozone formation generally involve hydrocarbons and nitrogen oxides. The changes in meteorological conditions favor ozone-producing reactions or reactions that destroy ozone. In this aspect, the variations in the parameters and their correlation with $O_3$are analyzed. Figures 3(a) to (d) depict meteorological variables' monthly variation for the reference year.

Negative correlation of O_3 with relative humidity isobserved in all seasons. Monsoon season recorded the highest RH mean value (76.53±3.37%) and lowest is registered in winter period (70.26±4.88 %).RH's monthly mean values peaked in August

Table 1. Statistical profile of various parameters considered in the present study

	Summer				Monsoon				Post Monsoon				Winter			
	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min
Ozone ($\mu g/m^3$)	19.93	10.18	59.15	6.78	27.38	8.19	66.39	15.03	44.90	21.04	91.56	15.43	42.35	21.84	92.98	9.25
NO($\mu g/m^3$)	6.48	5.47	22.17	0.65	7.18	6.81	38.64	0.72	18.51	14.79	76.28	1.63	34.05	35.05	136.79	1.49
NO_2($\mu g/m^3$)	26.92	10.25	59.15	10.58	32.55	9.78	65.66	12.28	30.21	17.30	92.76	9.26	40.40	19.63	89.44	6.96
NO_x(ppb)	19.32	8.49	46.44	6.34	22.80	9.06	61.05	6.83	30.94	15.67	77.43	10.87	49.27	29.30	129.71	14.75
SO_2($\mu g/m^3$)	8.25	2.31	18.82	3.87	8.92	2.61	18.01	3.80	9.34	3.76	19.25	3.20	13.48	4.81	39.84	2.45
CO(mg/m^3)	0.35	0.35	1.17	0.11	0.50	0.20	1.64	0.22	0.57	0.25	1.25	0.16	0.94	0.45	2.07	0.01
RH(%)	72.11	3.93	80.65	52.97	76.53	3.37	87.24	66.46	71.93	7.87	83.49	54.32	70.26	4.88	85.00	59.24
Temp(^oC)	32.57	2.58	40.69	27.77	31.31	2.01	36.74	27.32	28.05	2.44	41.15	24.73	28.92	1.02	34.68	27.18
WS(m/s)	2.25	0.57	3.48	0.96	2.21	0.64	3.70	0.76	1.71	0.78	4.44	0.42	1.62	0.44	2.62	0.80
SR(W/mt^2)	167.43	38.79	262.52	6.20	122.37	43.88	195.65	26.10	103.65	36.00	157.28	8.53	114.18	26.39	205.39	6.00

(77.22%) and recorded the lowest in December (68.71%).

On the other hand, temperature exhibited a positive and weak correlation with O_3 in Summer, Monsoon, and Winter, and negatively correlated in the post-monsoon season. Month-wise mean values showed the highest (33.2^{o}C) in March and lowest in November (27.5^{o}C). The maximum seasonal mean recorded in summeris 32.57± 2.58 ^{0}C.

Monthly ($1.41 \leq Ws \leq 2.64\ ms^{-1}$) and seasonal ($0.44 \leq Ws \leq 2.25\ ms^{-1}$) wind speed mean values showed calm winds prevailing at the site throughout the study period. A weak positive correlation of O_3 with wind speed is recorded during the post-monsoon and winter seasons.

Figure 3(d) depicts the mean solar radiation received during the study period. The maximum monthly mean is observed in April (176.75 Wm^{-2}), and the minimum is recorded in August (98.84 Wm^{-2}). Summer recorded a maximum mean of 167.43±38.79 Wm^{-2} and a minimum (103.65±36 Wm^{-2}) in the post-monsoon period. The solar radiation exhibited a positive correlation with O_3 except in winter season. The magnitude of the correlation is highest in the Monsoon period.

Among the considered variables, relative humidity exhibited negative correlation with O_3 for the reference period. A strong negative correlation of O_3 with relative humidity is observed in the post-monsoon season.

Precursors

Surface ozone is a secondary pollutant not emitted directly from anthropogenic sources but forms due to photochemical reactions of NO_X and VOCs. The anthropogenic sources of its precursors can increase O_3 concentrations when higher concentrations of its precursors coincide with favorable meteorological conditions, such as low wind speed. The following equations given below give a better understanding of the role of precursors in ozone formation:

$$SO_2 + OH + h\upsilon \rightarrow HOSO_2 \quad ...(1)$$

$$HOSO_2 + O_2 + h\upsilon \rightarrow SO_3 + HO_2 \quad ...(2)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad ...(3)$$

$$OH + CO \rightarrow H + CO_2 \quad ...(4)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad ...(5)$$

Summer recorded the lowest concentrations of precursors, while the highest values are observed in the winter months as evident from Figure 4. The average hourly mean values of NO, NO_2, NOx, SO_2, and CO recorded in winter are 34.05 ± 35.05 $\mu g/m^3$,

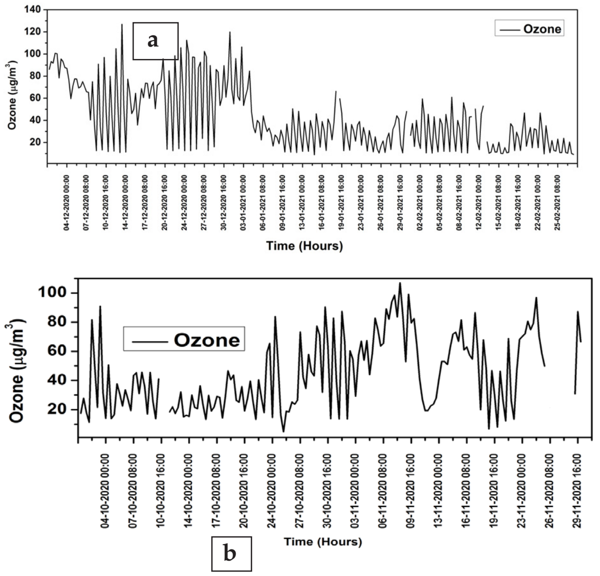

Fig. 2. (a) & (b). Seasonal Variations of O_3 (8hr.averaged values) during post monsoon and winter

40.40 ± 19.63 µg/m³, 49.27± 29.30 ppb, 13.48 ± 4.81 µg/m³, and 0.94 ± 0.45 mg/m³ respectively. In three out of four seasons, O_3 is positively correlated with NOx (except in post-monsoon) and SO_2 (except in winter). In contrast, the correlation of O_3 with other precursors is either positive or negative. A strong correlation of O_3 with its precursors is not observed during the study period. It is either low or moderate.

The exact magnitude of the impact of each independent variable (precursors and meteorological parameters) on O_3 is discerned using the multiple linear regression method.

The estimated regression equations are presented in Tables 3 to 6. It may be observed from Table 3 that the considered variables could only explain 22 percent of variation in O_3 in summer season. SO_2, SR and RH variables bear expected signs. SO_2 and RH are significant explanatory variables of O_3. In monsoon season (Table 4) 33 percent of variation is explained by the considered variables. NO_2 and SR exhibit expected signs, and other variables have negative signs. All the variables except RH are significant at one percent level. In case of post monsoon season, the considered variables explain 57 per cent of variation in O_3. Both the variables have negative signs and significant also. The chosen variables could explain 43 per cent of variation in O_3 in the winter season. NO and CO are positive, while NOx and RH are negative. All the variables are

Table 2. Pearson correlation Coefficients of O_3 with variables

Variables	Summer	Monsoon	Post Monsoon	Winter
NO	-0.074	0.090	-0.314	0.252
NOx	0.036	0.162	-0.275	0.079
NO_2	0.119	0.197	-0.066	-0.457
CO	-0.100	-0.076	0.271	0.344
SO_2	0.308	0.042	0.333	-0.048
RH	-0.373	-0.377	-0.725	-0.335
Temp	0.142	0.074	-0.161	0.087
SR	0.162	0.385	0.332	-0.129
WS	-0.155	-0.301	0.254	0.064

Table 3. Regression results for summer season

Dependent Variable	Intercept	Independent variables			R^2
		SO_2	SR	RH	
O_3	65.18	1.28*(3.09)	0.05(2.29)	- 0.90*(-3.73)	0.22

Note: Figures in brackets are t values
*Significant at 1 percent

Table 4. Regression results for monsoon season

Dependent Variable	Intercept	Independent variables					R^2
		NO_2	CO	SR	WS	RH	
O_3	64.16	0.31*(4.11)	- 10.09*(-2.88)	0.05*(2.93)	- 2.80*(-2.77)	- 0.55(-2.40)	0.33

Note: Figures in brackets are t values
*Significant at 1percent

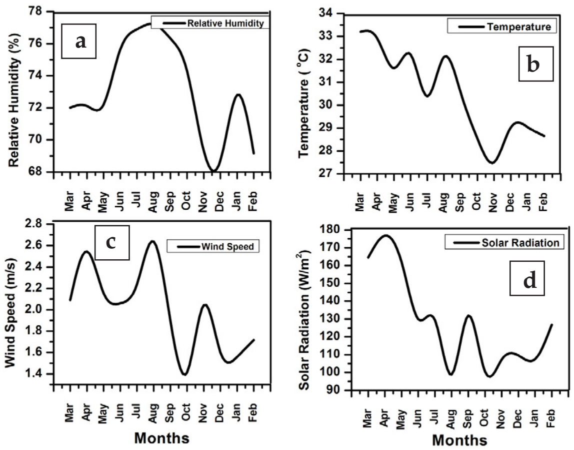

Fig. 3. Seasonal Variations in considered meteorological parameters

significant. It may be inferred that seeing R^2, the variables considered for post monsoon season, offered best explanation of variations in O_3. There may be other factors not taken in the present study that could be better determinants of O_3.

CONCLUSION

The study infers that the amplitude of Ozone in Visakhapatnam city is mostly within permissible limits, with seasonal variations. The influence of precursors on ozone formation can be constructive or destructive. The correlation of ozone with relative humidity is negative throughout the study, indicating that an increase in relative humidity

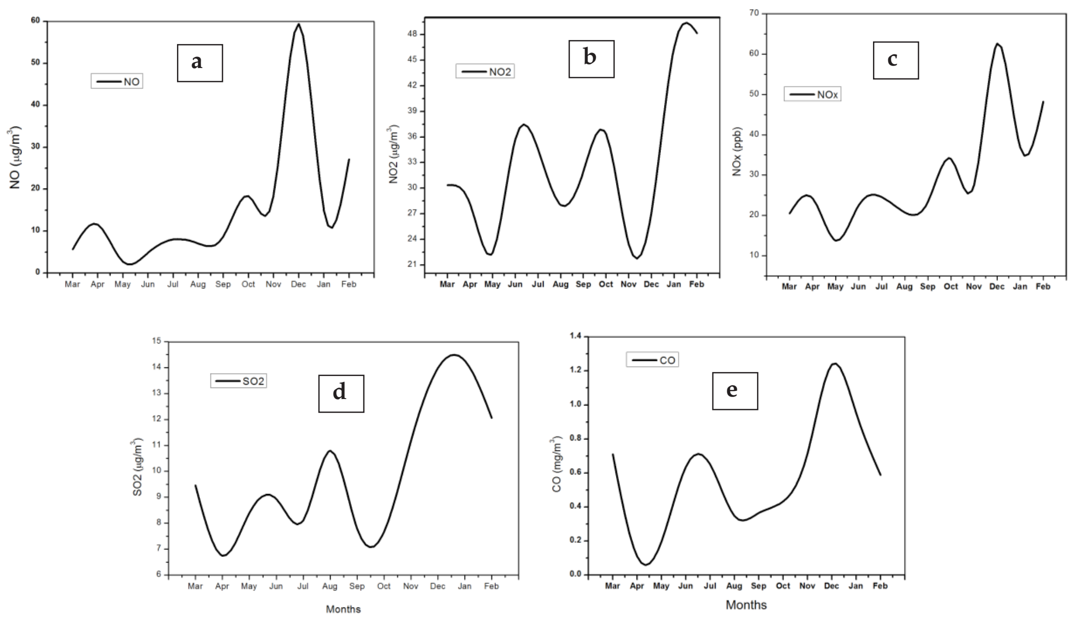

Fig. 4. Seasonal Variations in precursors concentrations

Table 5. Regression results for post monsoon season

Dependent Variable	Intercept	Independent variables		R^2
		NO_2	RH	
O_3	205.039604	-0.30*(-2.84)	- 2.09*(-8.86)	0.57

Note: Figures in brackets are t values
 * Significant at 1 percent

Table 6. Regression results winter season

Dependent Variable	Intercept	Independent variables				R^2
		NO_x	NO	CO	RH	
O_3	196.64	-1.09*(-6.4)	0.77*(5.33)	16.17*(3.30)	-2.01*(-5.05)	0.43

Note: Figures in brackets are t values
 * Significant at 1 percent

reduces ozone concentration. The average mean value of O_3 is high in the post-monsoon season because of a strong negative correlation of relative humidity with ozone compared to other seasons.

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