Scientific
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Day Time Seasonal Variation of Ozone and Its Association with Methane at Different Pressures over Barrow, Alaska

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Abstract

This study has explored the seasonal day time variations of the two most important trace gases involved in global warming *i.e.*, Methane (CH_4) and Ozone (O_3). Since solar activities also play a vital role in the formation of ozone, and hence solar flux data is also consulted in the present paper. Here we have discussed, day hours seasonal variation of O_3, solar flux and CH_4 at different pressures for four different seasons *i.e.*, winter, summer, autumn and spring. We have evaluated the correlation between O_3, solar flux and CH_4 over an American station "Barrow, Alaska" for a period of 18 years and conclude that in every season of the year, CH_4 shows linear increment with a good significance level above 95%. The autumn season shows a good correlation between solar flux and O_3 with a maximum value of 0.53 in October and a minimum value of 0.34 in November month. In the winter season, CH_4 shows linear increment with a significance level above 95% at every pressure height. We also conclude that O_3 shows an increment trend in March and April months, but its negative trend is found in May month of the spring season.

Keywords

Surface Ozone, Methane, Solar Flux, Climate and Season

1. Introduction

Climate change is one of the major challenges for mankind and nature, which is affecting our lives [1]. The change in climate has been categorized as various seasons of the year. A season is a period of the year that is classified by special climate conditions. Each has its own temperature and weather patterns that repeat yearly, but this variation depends on many factors. Changes in the climate

badly affect the earth's atmosphere and hence have a severe impact on humans [2]. The lifespan of the earth is becoming smaller day by day due to human pollution [3]. In recent years, global surface temperatures are generally increasing which gave rise to many studies [4] [5] [6]. Methane (CH_4) and ozone (O_3) are the two most important gases involved in global warming [7], after carbon dioxide (CO_2). The concentrations of both of these gases have increased substantially during the industrial era [8]. Many studies have been done on ozone seasonal variation [9] [10]. Oxidation of methane is responsible for the large amount of ozone formation in the troposphere, which shows that both the gases are relatable to each other [11]. Methane data trends have developed many studies [12] and hence developed our interest too. This shows that correlation between the ozone and methane is an important aspect [13]. The chemically active climate gases ozone and methane are responsible for changes in the current climate and will affect the future climate also [14] [15]. Methane is one of the well-mixed green house gases; however, small regional variations in the atmospheric methane concentrations occur throughout the atmosphere. The source of it is divided into two categories *i.e.*, natural and anthropogenic sources. Most of the world's methane emissions come from natural sources, such as wetlands and lakes. The remaining is derived from anthropogenic activity. Global background surface ozone concentrations have roughly doubled since preindustrial times [16], because of increases in emissions of nitrogen oxides (NO_x) and methane [17], and are projected to continue to increase [18] [19]. One of the research work estimated that the reduction of about 20% of current global anthropogenic methane emissions, will reduce ozone mixing ratios globally by about 1 ppbv and prevent almost 30,000 premature mortalities globally in 2030 and about 370,000 mortalities between 2010 and 2030.

It is well known that solar ultraviolet (UV) radiation plays an important role in ozone generation [20]. Changes in solar activity influences climate, weather, seasons and other atmospheric properties. The photochemistry is driven by solar radiations [21]. Nearly all the earth's energy derives from the sun, and it is therefore natural to study about links between variations in the sun's irradiance and changes in the atmosphere [22] [23] [24]. The 10.7 cm solar radio flux (F10.7) is one of the most frequently used indices of solar activity, and it is expressed in solar flux units (sfu) [25]. In reference [26], observed that there is a declining trend in total column ozone at Karachi and Mt. Abu with a significance level of over 95%. They also observed on the basis of long term data set of 25 years that there is a higher magnitude of 4 to 10 DU per decade in September to December months, and a lower magnitude of 2 to 4 DU per decade in pre summer months.

The carbon monoxide and ozone show an increasing trend over the maximum months of the year (1980-2015) in "Tutuila", whereas the sun spot number shows decreasing trend throughout the year. It was found that the ozone shows an increasing trend and its value is found to be maximum in the month of December, whereas in November month, the value was found to be negative [27]. In the present paper, we have discussed ozone, solar flux and methane and the

correlations with each other.

Zou studied about the seasonal variation in total ozone over the Tibetan Plateau and found the low ozone concentrations over the large scale topographies of the Tibetan Plateau, the Rocky Mountains, and the Andes Mountains. The total ozone in Tibet was found to be lowest in October and highest in March month. On the basis of zonal mean total ozone, the largest ozone deficiency over Tibet was found in the month of May, while smallest deficiency during November to January months. Also it was found that the ozone deficiencies are negatively correlated to the heat flux from the surface to the air in Tibet and the correlation coefficient was −0.97 [28].

The same type of study of surface ozone and its precursor gas was done at Anantapur, a semi-arid region. In this study the ozone levels were found to be highest during the winter and summer period and lowest during the monsoon period. The increment rate of ozone was found to be highest around the local time 09:00 hour, and it is about 4.7 ppbv/h, and the maximum rate of decrement was observed during the evening time and this rate of decrement was observed to be about −3.0 ppbv/h [29].

The study about the seasonal variation in surface ozone and its precursor gases was also done at Ahmedabad, India, which is an urban site. This study showed the diurnal variations of Ozone, NO_x and CO. In this study the high levels of ozone were observed, and it exceed to 80 ppbv. It was found that the day time ozone production is basically due to the photo-oxidation of the precursor gases. The boundary layer processes and meteorology also play an important role in the variability of these gases. The study showed that increment in the average amount of ozone is larger during daytime than the night time. The diurnal variations in NO_x and CO are due to combined effects of local emissions. It was found that the annual variation in average ozone concentrations varies from August to November month. The minimum value 12 ± 2 ppbv is found in August month to a high value of about 30 ± 3 ppbv during November. Also the concentration of ozone concentrations was observed to be maximum during autumn and winter months and this higher value is due to higher amounts of precursor gases. Also during these months, the solar radiation was minimum. Actually, the higher levels of precursors during these two seasons are due to large scale transportation from the continents and lower boundary layer heights. They also try to correlate the ozone and precursor gases and found that both are anti-correlate with each other [30].

2. Dataset and Site Description

As in the present study we try to establish a relation between solar flux, ozone and methane so we required sufficient data of any station, therefore we chose an American station "Barrow, Alaska". A sufficient ground base satellite ozone data for this station was available on https://www.noaa.gov/ and hence we have retrieved it from there. The ESRL Global Monitoring Division measures surface

ozone at several global locations starting at Barrow, Alaska and Mauna Loa, Hawaii in 1973. The Barrow Atmospheric Baseline Observatory (BRW) was established in 1973. This observatory is located at the northern most side of U.S., having coordinates 71.3230˚N, 156.6114˚W. It is now the longest continuously operating atmospheric data observatory in the Arctic with a record of accurate measurements that exceeds all others in this region of the globe.

The CH_4 data for the current study is downloaded from https://giovanni.gsfc.nasa.gov/. Giovanni is a medium that displays earth science data from NASA satellite directly on the internet, which can be easily accessed. Here in this study we have selected the time series, area-averaged data of American station Barrow; it is the same station for which ozone data was collected. For a comparative study of O_3 and CH_4 at different pressure height we have downloaded the CH_4 data on five different pressure heights *i.e.*, 100, 200, 300, 400 and 500 hPa for same period of about two decades ranging from 2003 to 2020. Here the data source which we used is MERRA-2 model. Also F10.7 data was downloaded from https://lasp.colorado.edu/home/.

3. Methodology

For the comparative study and for analyzing the data, we have selected the appropriate station and downloaded O_3 data for the years 2003 to 2020 from the above-mentioned site. This data includes every day hourly (24 hours) ground base O_3 data. For comparative study, CH_4 data at different pressures and solar flux data were also downloaded for the same period of the same station from their respective sites. Since UV rays are involved in formation and destruction of O_3 so we have collected solar flux data for the better comparative study. All the raw data downloaded was in text file containing 24 hours of a particular day. We extract the first half data of each day covering the time from 00:00 hours to 12:00 hours and we call this data as a daytime data. After it, we determine the mean of this day time data. In this way we got a single data for each day. This process is done from each day for entire period of study. Further, we have calculated the monthly mean for every year and got 12 values *i.e.*, one for each month. Now we arrange all these data in grid form *i.e.*, in table form so we can plot it as per our requirement. After it, we have plotted the monthly mean values of all the seven substituent (O_3, CH_4 at 100, 200, 300, 400 and 500 hPa and lastly solar flux data) against the years, so that the variation in all the seven substituent can be easily concluded. The results obtained from each graph, *i.e.* the slope, the correlation coefficient and P value for each month are collected and maintained in tabulated form. In below Figures 1-4 we have divided data into four seasons of the year *i.e.*, winter, spring, summer and autumn.

4. Result and Discussion

4.1. Variation in Winter Season

The variations in mean value of O_3 and CH_4 for five different pressures 100, 200,
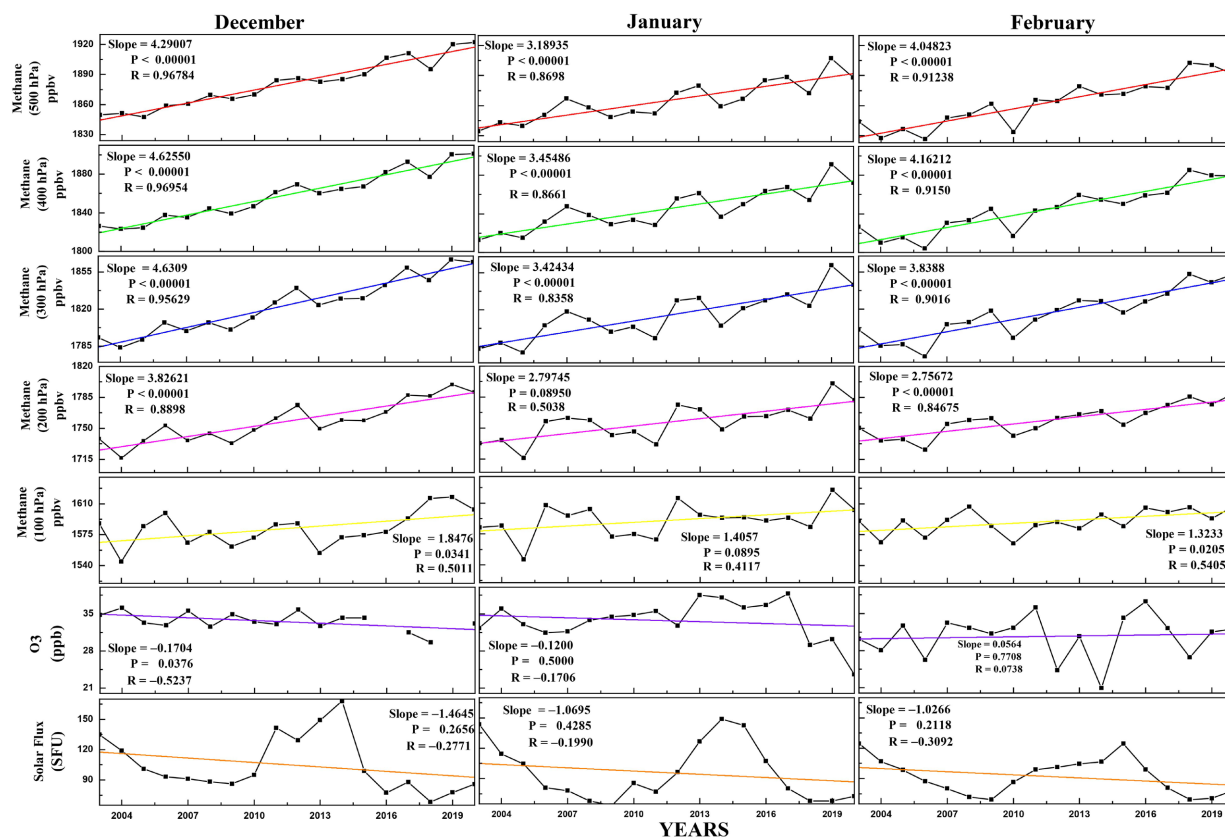
Figure 1. Day hours seasonal data variation of Ozone, Solar flux and CH$_4$ at different pressures for winter season.

300, 400 and 500 hPa, during daytime, for the corresponding years, covering a period of 18 years from 2003 to 2020, during winter season *i.e.*, December, January and February months are shown in **Figure 1**. It has been observed from the slopes of corresponding CH$_4$ data that for each set of different pressures, the value is showing linear increment with good significance level above 95% in every month of this season. In December month the maximum growth is found for CH$_4$ at 300 hPa pressure and minimum for CH$_4$ at 100 hPa pressure and the maximum and minimum values are 4.6309 and 1.8476 respectively. Similarly for January month the maximum increment is 3.4548 which is for CH$_4$ at 400 hPa pressure and minimum is 1.4057, which is for CH$_4$ at 100 hPa pressure. In the same way for February month the maximum and minimum value is found to be 4.1621 and 1.3233 corresponding to 400 and 100 hPa pressure. Hence for CH$_4$ we see that for each three months minimum increment is at the lowest pressure of 100 hPa. The variation of solar flux is also shown for winter season against the year in the same figure, and the observations show that the O$_3$ and solar flux slopes are decreasing for all three months of season and hence we get their negative slopes. O$_3$ shows minimum slope of −0.1704 in December month with a good significance level above 95% and maximum slope of 0.0564 in February month with a bad significance below 30%, whereas the slope of solar flux is found to be minimum having value of −1.4645 in December month with c lying between 70% - 75%.
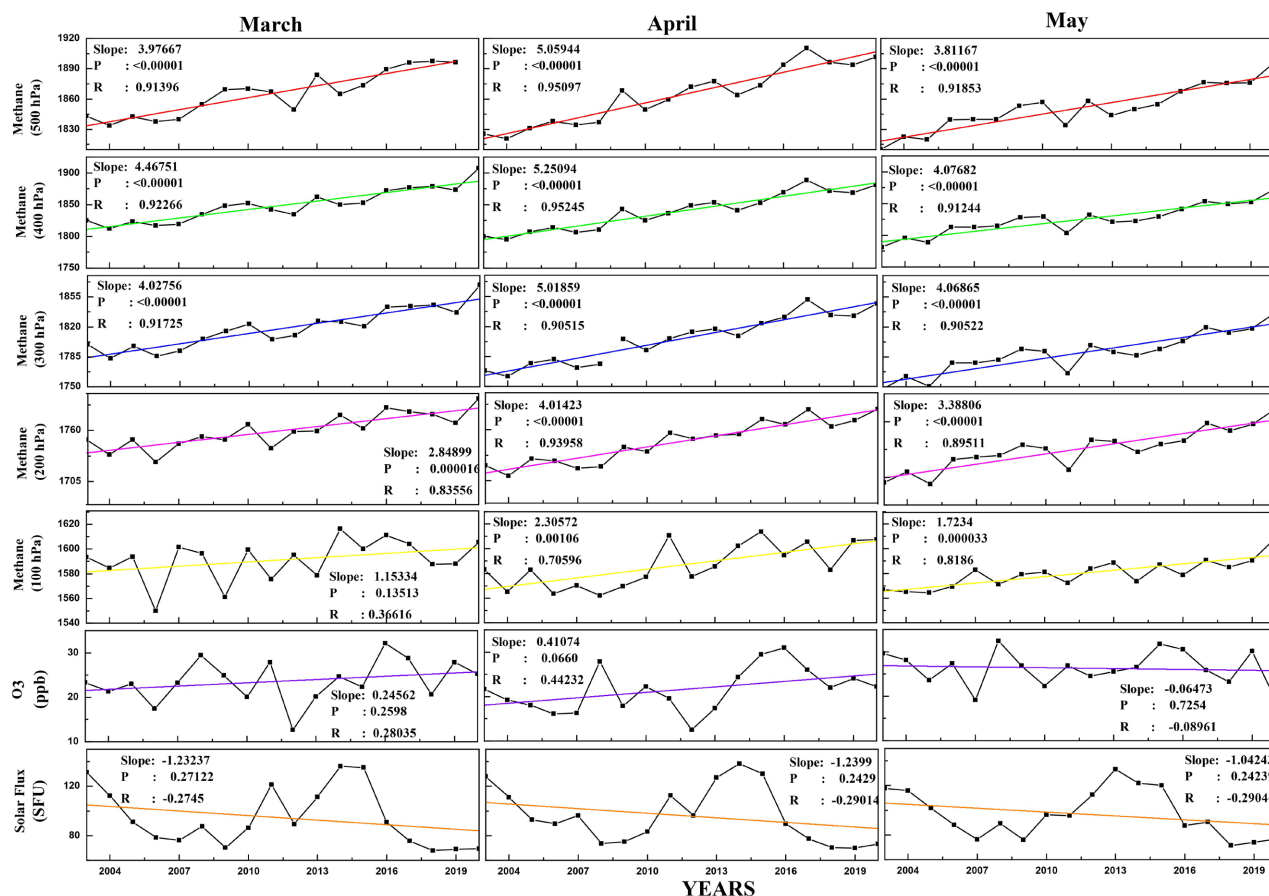
Figure 2. Day hours seasonal data variation of Ozone, Solar flux and CH_4 at different pressures for spring season.

4.2. Variation in Spring Season

Figure 2 represents the variations in above mentioned data for spring season *i.e.*, during March, April and May months. In this season CH_4 shows linear increment at every pressure height with good significance level above 95% in each three month of the season. In the month of March the maximum slope is 4.4675 which is for CH_4 at 400 hPa pressure and minimum slope is 1.1533 and it is for CH_4 at 100 hPa pressure. Similarly for April month the maximum and minimum rate of increment is 5.2509 and 2.3057 for CH_4 at 400 hPa pressure and at 100 hPa pressure respectively. During the month of May the maximum slope is of 4.0768 which is for CH_4 at 400 hPa and minimum slope is 1.7234 at 100 hPa pressure. Further observations show that the O_3 data slope is positive for March and April month, but negative in May month and solar flux value is decreasing for all three months of spring season with negative slope. O_3 shows minimum value of −0.0647 in May month and maximum value of 0.4107 in April month with good significancy above 90%, whereas solar flux shows minimum value of −1.2399 in April month with significance level between 75% to 80%.

4.3. Variation in Summer Season

Figure 3 represents the respective data for summer season *i.e.*, during June, July
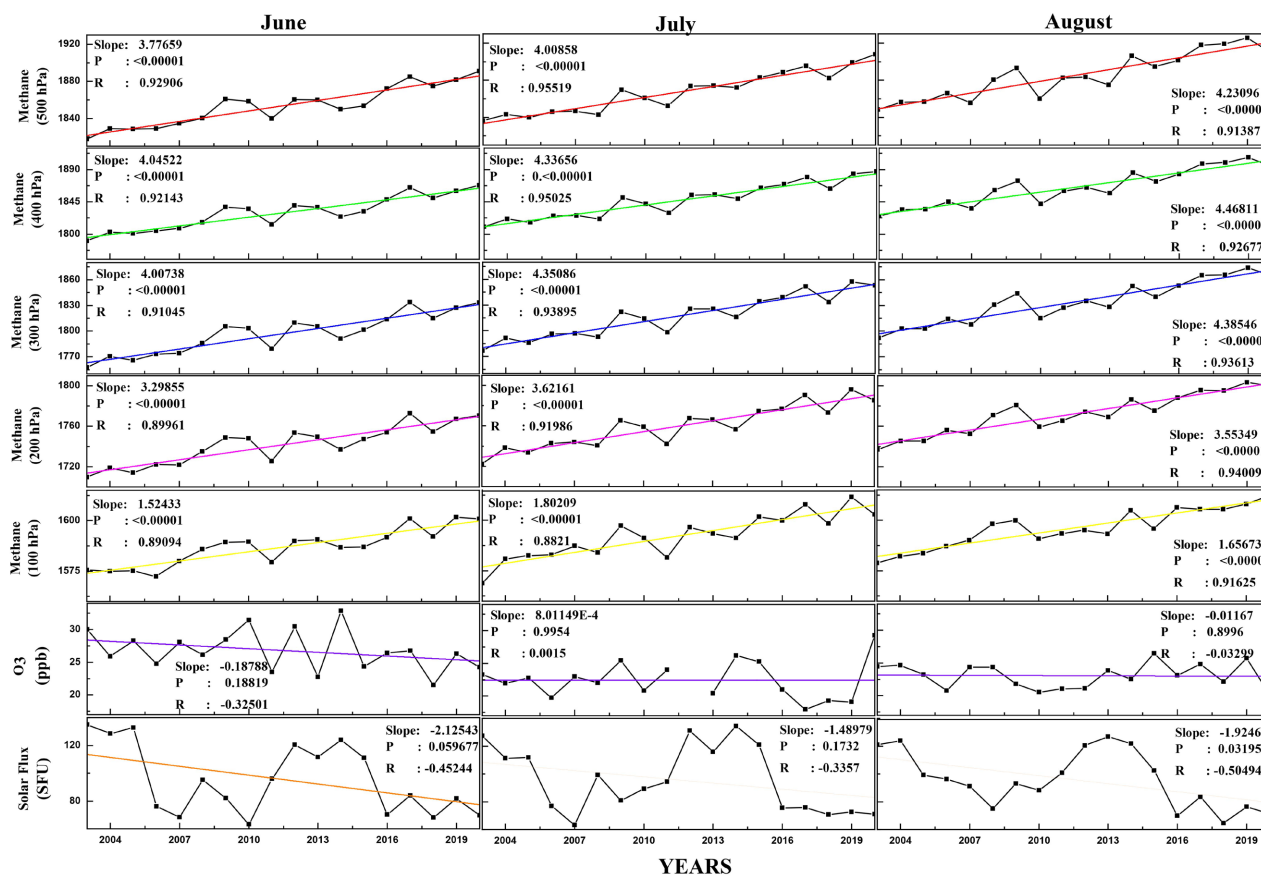
Figure 3. Day hours seasonal data variation of Ozone, Solar flux and CH$_4$ at different pressures for summer season.

and August months. It has been observed from the slopes of corresponding CH$_4$ data that in summer season value is showing linear increment with good significance level of above 95% in each three month of this season. In June month the maximum slope is 4.0452, which is for CH$_4$ at 400 hPa pressure and minimum slope is 1.5243 for CH$_4$ at 100 hPa pressure. Similarly in July month the maximum slope is 4.3365 for CH$_4$ at 400 hPa pressure and minimum slope is 1.8020, which is for CH$_4$ at 100 hPa pressure. August month shows the maximum slope of 4.4681, and minimum slope of 1.6567 for CH$_4$ at 400 hPa and 100 hPa pressure respectively. If we observe the variation of O$_3$ then it is found that the slope is negative in all three months of the summer season with significance level above 80% in June month. The variation of the solar flux is also negative for all three months with maximum slope −1.4897 in July month with significance above 80% and minimum slope −2.1254 in June month with good significance level above 90%.

4.4. Variation in Autumn Season

Figure 4 represents the variation of O$_3$, CH$_4$ and solar flux in the remaining season *i.e.*, in autumn season. It has been observed from the slopes of corresponding CH$_4$ data that for each set of different pressures the value is showing linear increment with good significance level above 95% in each three months of
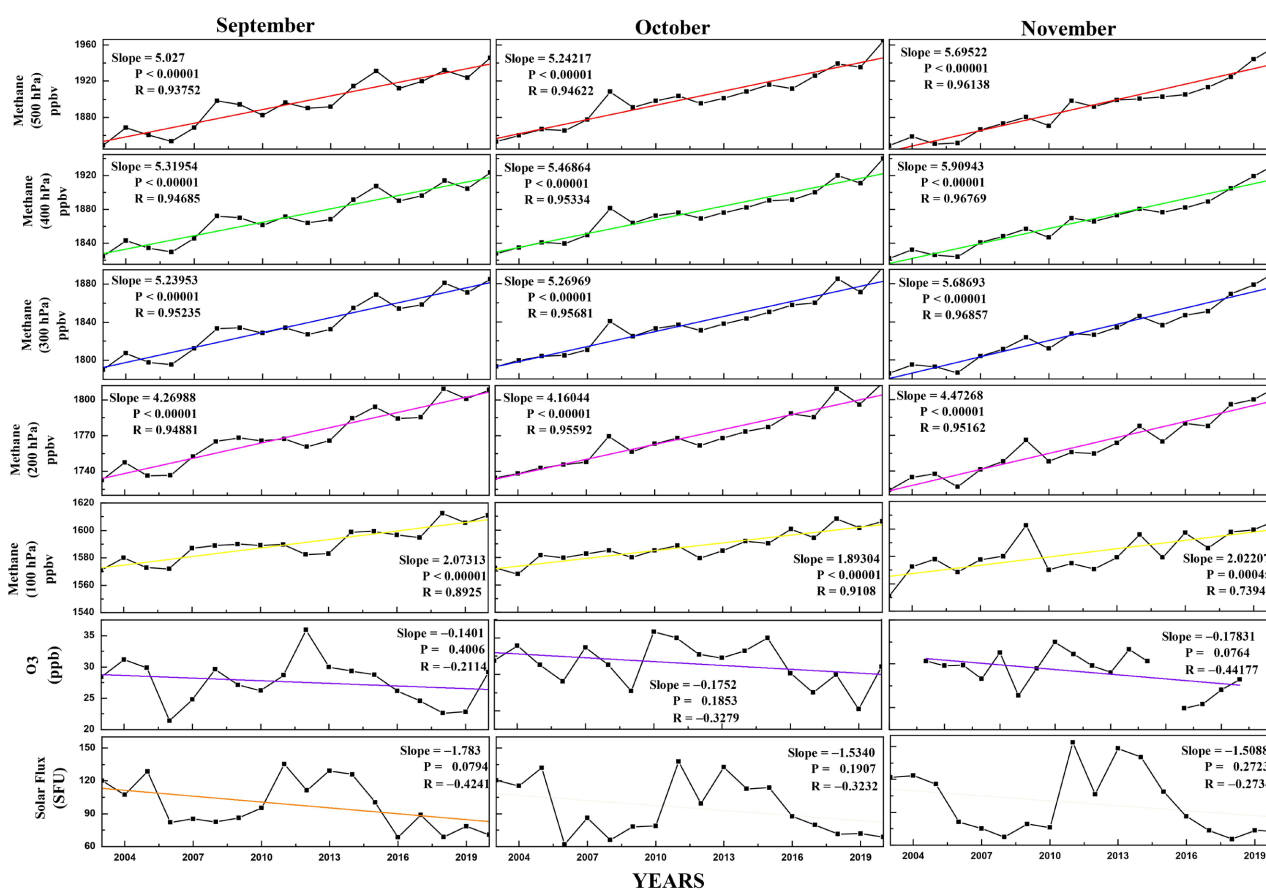
Figure 4. Day hours seasonal data variation of Ozone, Solar flux and CH_4 at different pressures for autumn season.

this season *i.e.*, September, October and November. In September month of autumn season the maximum slope for CH_4 is 5.3195 at 400 hPa pressure and minimum slope is 2.0731 at 100 hPa pressure. Similarly for October month the maximum slope for CH_4 is 5.4686 at 400 hPa pressure and minimum slope is 1.8930 at 100 hPa pressure. For November month the maximum and minimum slope for CH_4 is 5.9094 and 2.0220 at 400 hPa 100 hPa pressure respectively. Observations also show that slope of O_3 is negative in all three months of the season with significance level above 80% in October month and above 90% in November month. Solar flux value is also found to be negative for all three months with maximum slope of −1.5088 in November month with significance level above 70% and minimum slope of −1.7834 in September month with good significance level above 90%.

In observing Table 1 we see that the correlation between solar flux and O_3 in February, March and April months is negative, while rest all the months of the year shows positive correlation with highest positive correlation coefficient of 0.53 in October month and lowest positive correlation coefficient of 0.11 in August. Correlation between solar flux and CH_4 in every season at different pressure levels is negative with significancy above 90% in August, September and October months. Also it is observed that the correlation between solar flux and O_3 for

Table 1. Correlation between the solar flux and O$_3$, and Solar flux and methane at different pressures for different months.

Years	Correlation between solar flux and					
	Ozone	Methane (100 hPa)	Methane (200 hPa)	Methane (300 hPa)	Methane (400 hPa)	Methane (500 hPa)
January	0.304182226	−0.107128077	−0.272329688	−0.297834959	−0.289798083	−0.277023968
February	−0.034681401	−0.308140286	−0.384958125	−0.342608853	−0.309598517	−0.285642827
March	−0.072217034	0.191954003	−0.200096648	−0.304995056	−0.328729438	0.339754354
April	−0.037391805	0.206881405	−0.155717573	−0.277312989	−0.319651566	−0.343089405
May	0.155888177	−0.307680826	−0.401400008	−0.453917725	−0.484750887	−0.502546475
June	0.282572661	−0.457412463	−0.501154037	−0.517043971	−0.530415919	−0.544129154
July	0.203307905	−0.402254747	−0.395564324	−0.375747420	−0.353997119	−0.327989808
August	0.111275693	−0.615193022	−0.566127617	−0.553434605	−0.541972770	−0.525089193
September	0.398708392	−0.537360915	−0.488165630	−0.465000071	−0.443330674	−0.419415202
October	0.530021467	−0.405981875	−0.425452204	−0.419473003	−0.416727303	−0.413612237
November	0.341826033	−0.368500090	−0.303837956	−0.266542721	−0.244843500	−0.226668196
December	0.373496272	−0.426930876	−0.293613530	−0.247859838	−0.255009531	−0.277476651

autumn season is positive with maximum value 0.53 in October and minimum value 0.34 in November month, and the whole season shows a good significance level above 95%.

5. Conclusions

The current study shows the seasonal variation in ozone and methane and on the basis of this study the following conclusions were carried out:

- In winter season we observed the linear increment with a good significance level above 95%. The maximum growth is found for methane at 300 hPa and minimum at 100 hPa during December. The maximum and minimum values are observed to be 4.6309 and 1.8476 respectively in this month. The maximum increment in methane is found to be 3.4548 at 400 hPa and minimum is 1.4057 at 100 hPa in January month. The February month shows the maximum value of methane is about 4.1621 and minimum value is 1.3233, and these maximum and minimum values are observed at 400 and 100 hPa respectively. Thus during winter season the minimum increment in methane is found to be at lowest pressure of 100 hPa. The graph of solar flux versus year and ozone versus year shows that during winter season the slopes of ozone and solar flux decrease in all three months of this season. The minimum slope of ozone and solar flux are −0.1704 and −1.4645 respectively, which we got in December months of winter season.

- In spring season, methane shows the linear increment at every pressure height in all three months of the season. In March the maximum slope of methane is 4.4675, and it is observed at 400 hPa, whereas the minimum slope is 1.1533 at 100 hPa. April month shows the maximum and minimum rate of

increment in methane at 400 hPa and 100 hPa respectively and these increments are 5.2509 and 2.3057, whereas May month shows the maximum slope in methane is 4.0768 at 400 hPa and minimum slope at 100 hPa, which is 1.7234. If observe the ozone data slope then it is found that the slope is positive for March and April month, but negative in May month. During spring, the solar flux value is decreasing in all three months. It was observed that the minimum and maximum values of ozone are −0.0647 and 0.4107, and these values are observed in the month of May and April respectively. The solar flux graph of this season shows minimum value is −1.2399 in April month and this value is observed with the significance level of 75% to 80%.

- On the basis of summer season of our study period, we observed that the methane in this season shows the linear increment with the significance level above 95%. In June month of summer the maximum slope in methane is observed at 400 hPa and minimum at 100 hPa and the maximum and minimum values are 4.0452 and 1.5243 respectively. In July month the maximum slope of methane is 4.3365 and minimum slope is 1.8020, and these values are observed for methane at 400 hPa and 100 hPa pressure respectively. August also shows the minimum slope in methane is observed at 100 hPa and maximum at 400 hPa. In this month the maximum and minimum slope in methane are 4.4681 and 1.6567 respectively. Also the ozone and solar flux graph which are plotted against year for summer season showing that the slope of both these data are negative in all three months of the summer season.

- The autumn season shows that the slope of methane increases linearly with a good significance level above 95% in whole season. In September month of it, the maximum slope in methane is 5.3195, observed at 400 hPa and minimum is 2.0731 at 100 hPa. October month shows that the maximum value of methane is 5.4686 at 400 hPa and minimum is 1.8930 at 100 hPa. The maximum and minimum slopes in methane are 5.9094 and 2.0220 at 400 hPa and 100 hPa in November months. The observations also show that the ozone decreases during whole autumn season and its significance is above 80% in October and November month. The solar flux values are found to be negative in this season, and the maximum slope of −1.5088 in November and minimum is −1.7834 in September month.

On the basis of above outcome, we conclude that, the minimum slope of CH_4 is at the lowest pressure of 100 hPa and it increases with an increase in pressure heights up to 400 hPa, but further starts decreasing at 500 hPa pressure *i.e.*, slope is increasing with increase in pressure height to some extent only, and also for each season slope is showing linear increment. It was also observed that the value of methane is found to be minimum in winter season and maximum in autumn season at every pressure height. Further we observe that in each season of the year significance level for CH_4 data is really good *i.e.*, above 95%. For ozone and solar flux we concluded that its value is decreasing with a negative slope for every season. Studying about every season for 18 years we conclude that autumn

season shows a good correlation between O_3 and solar flux with a significance level above 95% and also there is a good correlation between solar flux and CH_4 with a significancy above 90% in autumn season.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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