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Geospatial and Ground Based Monitoring of Gaseous Air Pollutants to Understand Their Environmental Chemistry and Relationship with Meteorological in a Semi Urban Environment at Third Pole †

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Abstract: The Third pole which includes the Himalayas has experienced significant environmental changes over the last five decades. Indian Himalayan region (IHR) is one of the most fragile ecosystems on this planet. The present study deals with the study of gaseous air pollutants such as SO_2,NO_2,CO,O_3 and NO_2 at Mohal Kullu to understand the seasonal behavior of pollutants and there atmospheric reaction with meteorological parameters. Gaseous air pollutants was monitored using Thermo fisher Scientific gas analyzer at ground level and by using SENTINEL-5P data using Google earth engine. The results revealed that SO_2 showed highest concentration of 2.12±0.03ppb in winter at ground level and lowest concentration 0.81±0.02 ppb in monsoon the reason being low availability of OH radical in winter. NO_2 and O_3 showed highest concentration in summer followed by autumn and lowest concentration in monsoon due to high rate of photochemical chain reaction in summer when compared to monsoon. Similar results were obtained using SENTINEL-5P data. The present study will help the researchers to understand the environmental chemistry and seasonal atmospheric behavior of gaseous air pollutants in Indian Himalayan Region.

Keywords: Air pollutants; Indian Himalayan Region; meteorological; SENTINEL-5P

1. Introduction

Pollution is defined as the introduction of substances that are hazardous to people and other living organisms into the environment. Pollutants are toxic solids, liquids, or gases that are created in higher-than-normal concentrations and degrade our environment's quality (Manisalidis et al., 2020) Air pollution has become a serious problem worldwide Air pollution not only leads to climate change but also have serious impact on human health. Air pollution is defined as the presence of one or more substances in the atmospheric air at concentrations and duration above the natural limits (Sienfield et al., 1998). Ozone (O3), airborne lead (Pb), carbon monoxide (CO), sulphur oxides (Sox), and nitrogen oxides (NOx) are examples of such gases (Nemmar et al., 2013). Air quality is degrading slowly in Indian Himalayan region.Continous satellite monitoring and ground level monitoring of pollutants must be done to understand the pattern of these pollutants in this region. Further regular monitoring of pollutants with meteorological parameters will help to understand the background values and environmental chemistry of these pollutants in the region.The present study deals with the study of gaseous air pollutants such as SO_2,NO_2,CO,O_3 and NO_2 at Mohal Kullu to understand the seasonal behavior of pollutants and there atmospheric reaction with meteorological parameters.The present study

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will help the researchers to understand the environmental chemistry and seasonal atmospheric behavior of gaseous air pollutants in Kullu Himachal Pradesh a semi urban location in Indian Himalayan Region.

2. Study Area

Kullu district is located between the Pir Panjal and the Dhaula Dhar mountain ranges at 31.91° North and 77.12° East, at an elevation of 1154 metres (Fig. 1) .The valley is U Shaped Valley and Beas River which is originated from Rohtang pass flows through it. The Kullu valley extends up to 80 km long from south to north and is 2 km wide, which begins from Largi (957 m amsl) in the lower Beas basin and stretches up to Rohtang Crest (4,038 m amsl) in the upper Beas basin (Kuniyal et al., 2009). The surrounding mountains of the Kullu valley have considerable height in the range of 3,000-5,000 m (Sharma et al., 2009). This part of the Indian Himalaya is topographically very fragile and ecologically very delicate. The high altitude with extreme diurnal variation in solar radiation leads to the formation of the inversion layer that can last for several days, particularly during the winter season. The valley is a bowl-shaped which during winter, traps cold air from higher peaks and/or produced by substantial nighttime cooling. The cold dense air settles to the valley floor and suppresses the vertical exchange of low-level air. The suppression leads to a buildup of pollutants. Solar heating destabilizes the surface air and the resulting vertical motion disperses the trapped pollutants.

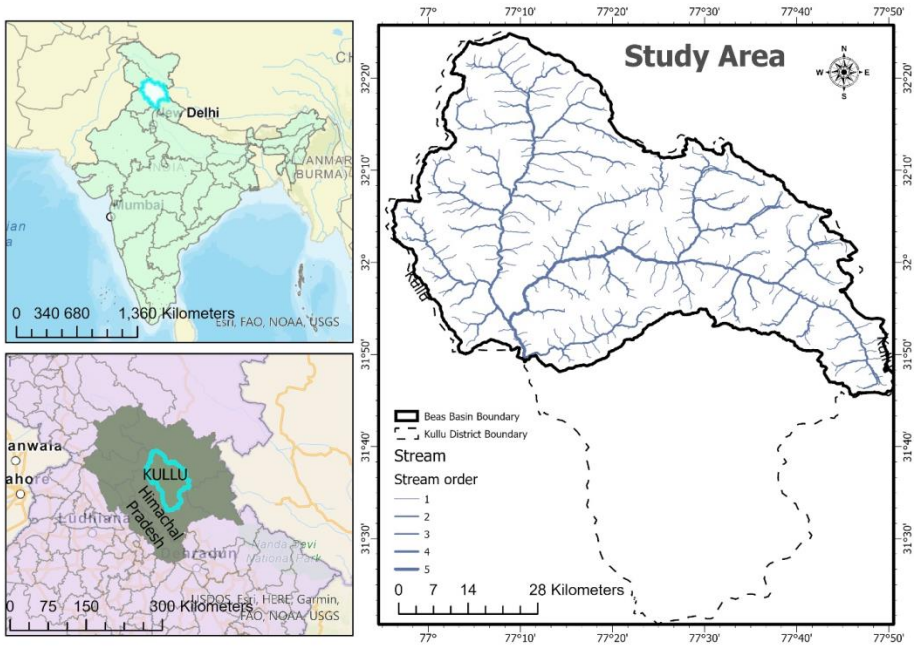


Figure 1. Study area.

3. Methodology

3.1. Ground Based Measurement

Gaseous air pollutants such as SO_2, NO_2, NOx, CO,CO_2, and surface ozone was monitored using online gas analyzers manufactured by Thermo fisher Scientific .All the gaseous air pollutants were monitored simultaneously for 1 hour and the data was recorded using ENVIDAD-FW software for PC.

3.1.1. Oxides of Nitrogen

Simultaneous measurements of nitrogen oxides (NO, NO_2 and NO_x) were carried out using NO_x analyzer (Thermo Fischer, Model 42i). The NO_x analyzer is based on the chemiluminescence effect of NO_2 produced by oxidation of NO with O_3 molecules, which peak at 630 nm. In this analyzer, NO_2 is measured by the conversion of NO_2 into NO using the thermal conversion (heated molybdenum) method. The molybdenum converter is found to have higher sensitivity and 100% conversion efficiency (Winer *et al.*, 1974; Finlayson-Pitts and Pitts, 1986) but it has been realized that molybdenum converter also converts other species such as PAN, HNO_3, other organic nitrates and nitrites into NO (Winer *et al.*, 1974). However, these concentrations may be very small at surface level. Thus, the actual concentration of NO_2 is low as a result NO_x also remains lower.The minimum detection limit and precision of NO_x analyzer are 0.4 ppb and 1 ppb, respectively. Calibration of NO_x analyzer is performed by using standard NO gas. The instrument is operated every day continuously for 24 h. Air samples were collected through Teflon inlet tubes with a particulate filter to prevent the entry of particles into the instrument. The filter is replaced once every two weeks.

3.1.2. Sulphur Dioxide

For Sulphur Dioxide, the online analyzer used is Thermo scientific Model 43i.This model operates on the principle that SO_2 molecule absorbs U.V light and become excited at one wavelength , then decay to lower energy state emitting U.V light at different wavelength, specifically (Fluorescence) (Lv et al.,2018).

$$SO_2 + hv_1 \text{----}> SO_2^{*\text{-------}} SO_2 + hv_2 \quad (1)$$

Its measurement concentration varies from 50 ppb-1000 ppb with average time period 100-300 seconds with flow rate 0.5 -1.0 L/min.

3.1.3. Surface ozone (O_3)

Surface ozone (O_3) was monitored through Thermo scientific Model 49i and operates on the principle that ozone molecule absorbs UV light at wavelength of 254nm. (Singla et al., 2011; Ojha et al., 2012; Kumar et al., 2010).The degree to which the U.V. light is absorbed is directly related to ozone concentration as described by Beer-Lambert law.

$$I/I_{0=}e^{-klc} \quad (2)$$

Where

k= molecular absorption coefficient, $308cm^{-1}$(at $0^{o}C$ and 1 atmosphere)

L=length of cell, 38cm

C=concentration of ozone

I =Ultraviolet light intensity of Sample with ozone (sample gas)

I_0=Ultraviolet Light intensity of sample without ozone (reference gas)

The measurement concentration of Ozone Analyzer ranges from 50 ppb to 1000 ppb and averaging time 10 to 300 seconds with flow rate 1 to 3 L/min. (Thermo scientific model 49i manual).

3.1.4. Carbon dioxide

The Model 410i operates on the principle that carbon dioxide (CO_2), the sample is drawn into the Model 410i through the sample bulkhead. Sample passes easily via optical bench. An optical wheel rotates while sample and reference filters are alternately used to pass chopped-up infrared radiation through. The radiation then moves onto the optical bench, where the sample gas is absorbed. After leaving the optical bench, the infrared light strikes an infrared detector. The alternating of the filters modulates the chopped detector signal with an amplitude correlated to the CO_2 concentration in the sample cell. Due to the non-linear nature of infrared absorption measurement, The fundamental analyzer

signal must be converted into a linear output. The Model 410i accurately linearizes the instrument output throughout any range up to a concentration of either 10000 ppm (Standard) or 25 percent using an internally stored calibration curve (High Level). The CO_2 concentration is output by the Model 410i to the front panel display, analogue outputs, as well as making the information accessible over a serial or Ethernet connection.

3.2. Monitoring using Google Earth Engine and SENTINEL-5P data.

Gaseous air pollutants were monitored using SENTNEL-5P data through Google Earth engine and were further analyzed in ArcGs 10.8.

4. Results and Discussion

4.1. Monitoring of Pollutants at Ground level

4.1.1. Sulphur Dioxide

Sulphur Dioxide was monitored and hourly data (1 hr) was analyzed. Fig.4a. shows diurnal variation of SO_2 throughout the year. Sulphur Dioxide showed highest average concentration of 2.12±0.03ppb in the month of October 2022 followed by 2.0±0.02 in September 2022, while SO_2 showed lowest average concentration of 0.57±0.02 ppb in June 2022 and 0.81±0.02 ppb in July 2022 (Fig.2a) Diurnal Variation of Sulphur Dioxide showed high concentration in the mid-night night and beginning of morning while the least Concentration occurs in the afternoon.

4.1.2. Nitrogen Oxide (NO)

Nitrogen oxide showed high average concentration of 1.66±0.06 ppb in the month of September followed by 1.53±0.03 ppb in July and showed lowest concentration 1.27±0.13 ppb in November 2022**.** (Fig.2b)Nitrogen Oxide (NO) showed a bimodal peak which peaked during morning and evening hours probably because of the increased traffic during these hours The NO Shows more dominant peak in morning with little to no evening peak in spring/rain while the evening peaks are more pronounced in autumn and winter (Kendrick et al., 2015).

4.1.3. Nitrogen Dioxide (NO_2)

Diurnal variation of Nitrogen Dioxide showed bimodal peak. Nitrogen Dioxide also showed bimodal peak during early morning and evening hours when there is heavy traffic. Nitrogen dioxide showed high average concentration of 6.86±0.54 ppb in June 2022 followed by 6.85±0.54 ppb in May 2022.Nitrogen Dioxide showed lowest average concentration of 2.20±0.25ppb in October 2022 (Fig.2c).

4.1.4. Oxides of Nitrogen (NO_X)

Oxides of Nitrogen (NO_X) showed highest average concentration of 8.15±0.58 ppb in June 2022 followed by 7.93±0.61 ppb in May 2022.NOx showed lowest average concentration of 3.80±0.32 ppb in October 2022 (Fig.2d).Diurnal Variation of NO_X showed bimodal peak which peaked during heavy traffic hours.

4.1.5. Carbon Dioxide (CO_2)

CO_2 showed high concentration of 475.46±3.31 ppm in April 2022 followed by 462.53±4.98 ppm in March 2022 and lowest as 173.29±2.48 ppm in January 2022 (Fig.2e). The diurnal pattern of CO_2 remains high in the early morning and then steadily decreases due to increased photosynthetic activity and becomes minimum around 13:00.

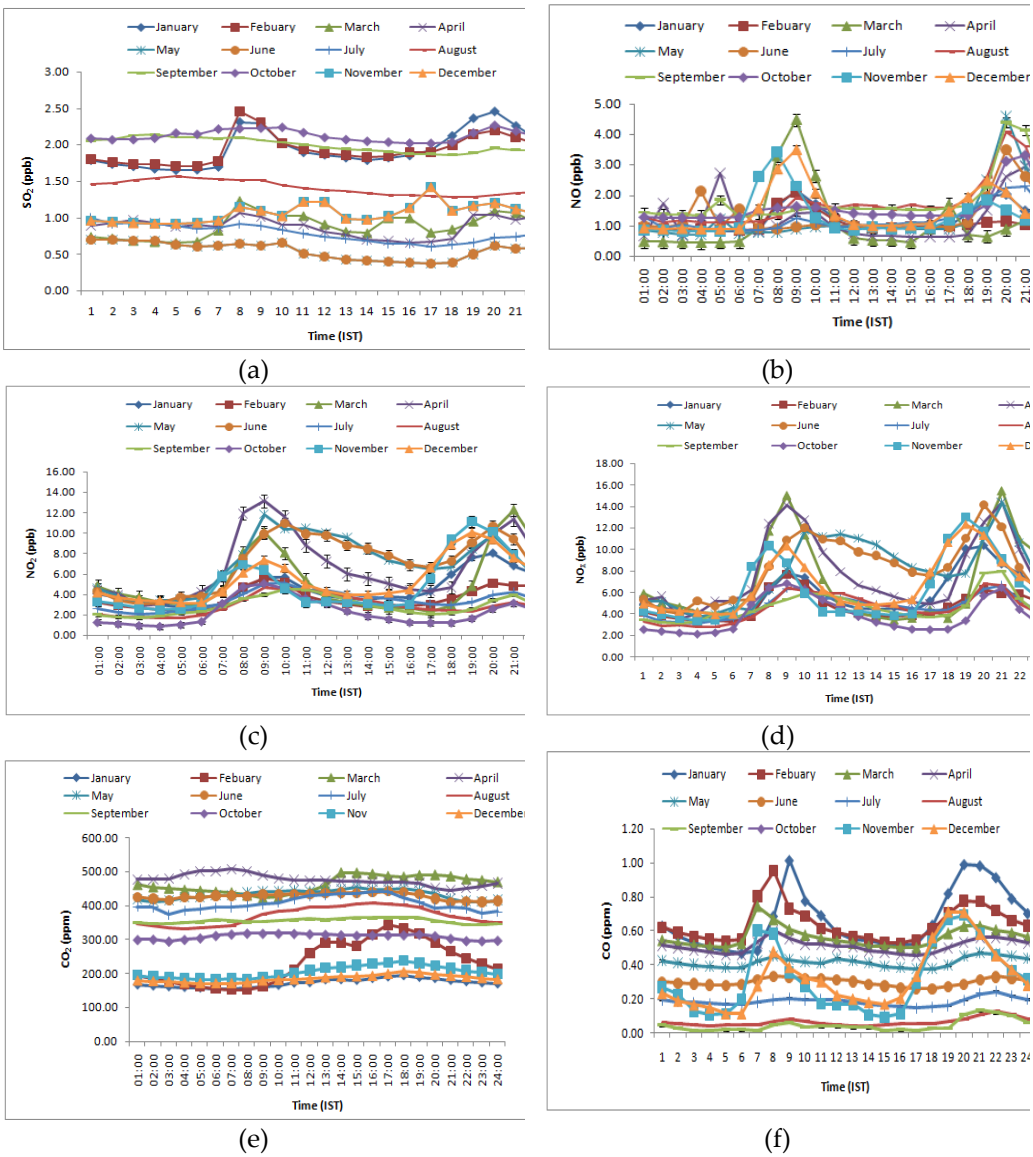


Figure 2. Yearly diurnal variation of **(a)** SO_2 **(b)** NO **(c)** NO_2 **(d)** NO_X **(e)** CO_2 and **(f)** CO at Mohal Kullu.

4.2. *Monitoring using SENTINEL-5P data*

4.2.1. Average values of the Criteria air pollutants (SO_X, NOx,O_3) using SENTINEL-5P data.

SENTINEL-5P data was analyzed in Arc Gis 10.8 for pollutants SO_2, NOx, CO and ozone to estimate the average value of pollutants in the year 2022 in the region. This satellite based measurement quantifies the amount of NO_2, O_3 etc in the whole of the troposphere. The average value of surface ozone varied from 0.128 mol/m^2 to 0.123mol/m^2, SO_2 varied from 0.0051 mol/m2 to -0.005 mol m^2 while the average value of CO ranged from 0.03 to 0.014 mol/m^2. (Fig 3a-d).

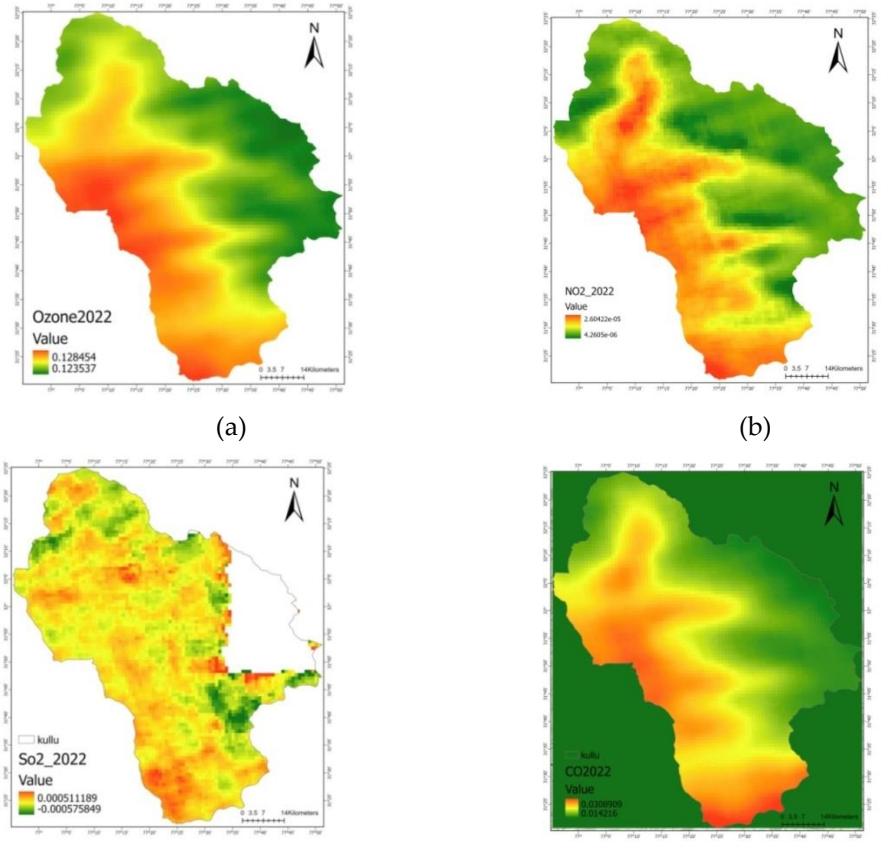
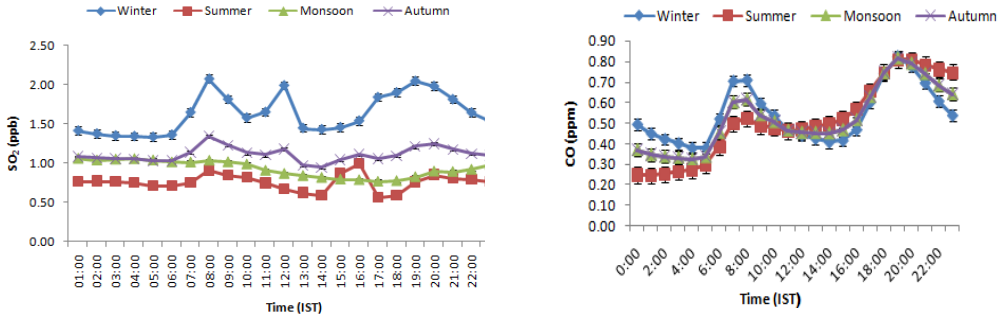


Figure 3. (a-d) Average values of the Criteria air pollutants (SO_x, NOx, O_3) using SENTINEL-5P data.

4.3. Seasonal Variability of pollutants using ground based and SENTINEL 5P measurement at Mohal Kullu Himachal Pradesh

Seasonal Variability of gaseous air pollutants was measured at ground level.SO_2 and CO showed highest concentration in winter season while the lowest in monsoon and summer(Fig 4a & 4b).CO_2,NOx and O_3 showed highest concentration in summer season.CO_2 showed lowest concentration in winter while NOx and surface ozone showed lowest concentration in monsoon (Fig 4c,4d &4e).



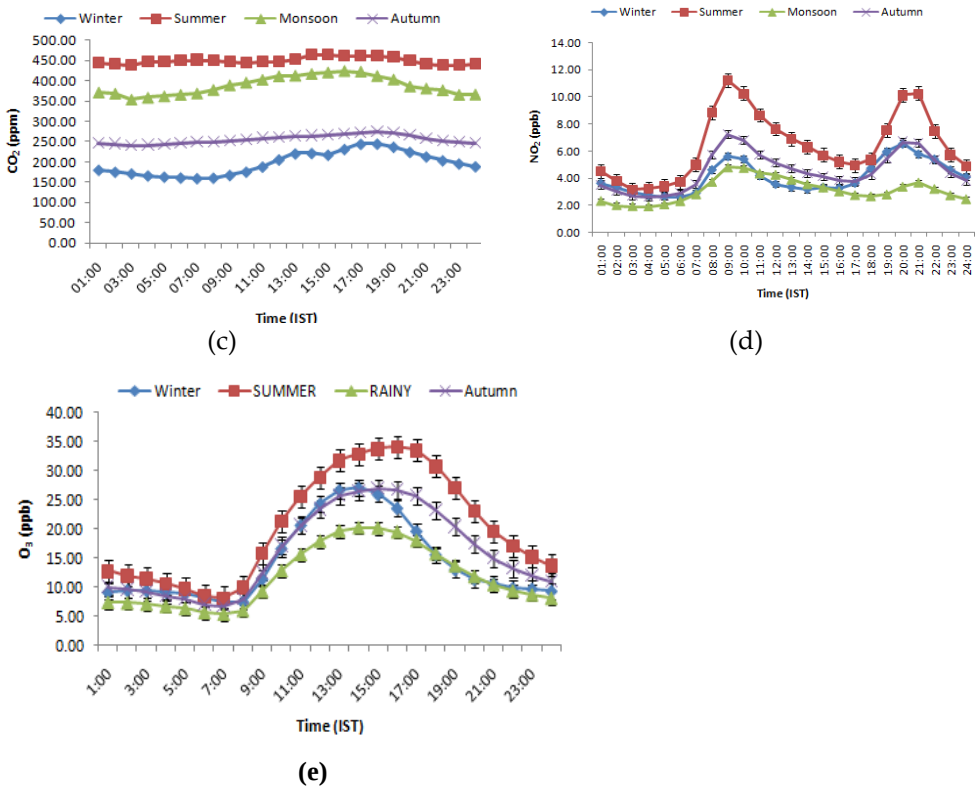
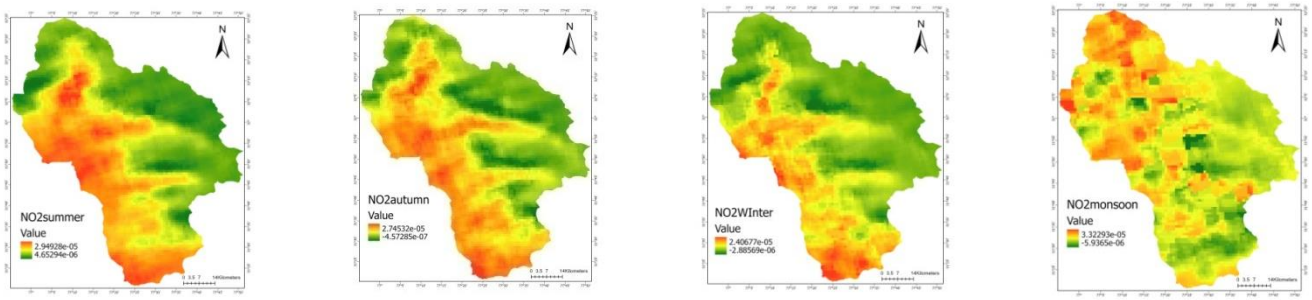


Figure 4. (a-e) Seasonal Variability of gaseous air pollutants based on ground based measurement.

4.4. Seasonal trend of atmospheric pollutants using SENTINEL-5P data

4.4.1. Seasonal Variability of NO_2

Seasonal Variability of NO_2 showed highest concentration in summer followed by autumn and lowest concentration in monsoon (Fig5 a-d). Similar results were observed in ground level measurement of these pollutants.



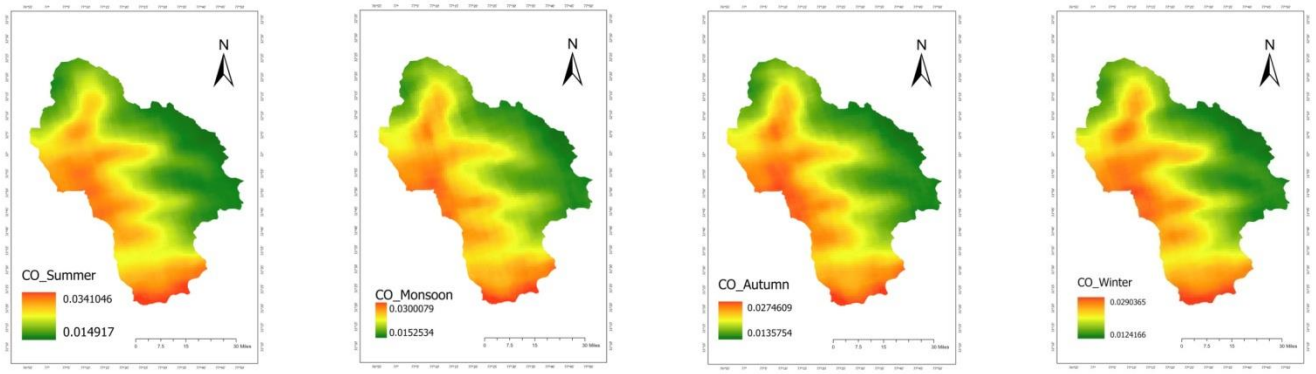
(a) (b) (c) (d)

Figure 5. (a-d) Seasonal Variability of NO_2 in Kullu Himachal Pradesh using SENTINEL-5P data.

4.4.2. Seasonal Variability of CO

Seasonal Variability of CO using SENTINEL-5P data showed highest concentration in winter followed by autumn and lowest concentration in monsoon (Fig 6a-d). Similar results were observed in ground level measurement of these pollutants. High levels of CO were seen in winter as conversion of CO into O3 is a photochemical chain reaction initiated by sunlight and OH radical.

$$CO + 2O_2 + hv \quad \text{-----} > \quad CO_2 + O_3 \qquad (3)$$

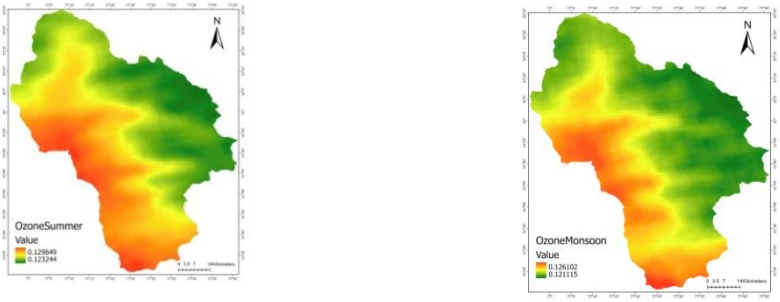


(a) (b) (c) (d)

Figure 6. (a-d) Seasonal Variability of CO in Kullu Himachal Pradesh using SENTINEL-5P data.

4.4.3 Seasonal Variability of Ozone.

Seasonal Variability of O_3 showed highest concentration in summer and lowest concentration in monsoon (Fig 7a-b). Similar results were observed in ground level measurement of these pollutants.



(a) (b)

Figure 7. (a-b) Seasonal Variability of O_3 in Kullu Himachal Pradesh using SENTINEL-5P data.

4.4.3. Seasonal Variability of SO_2

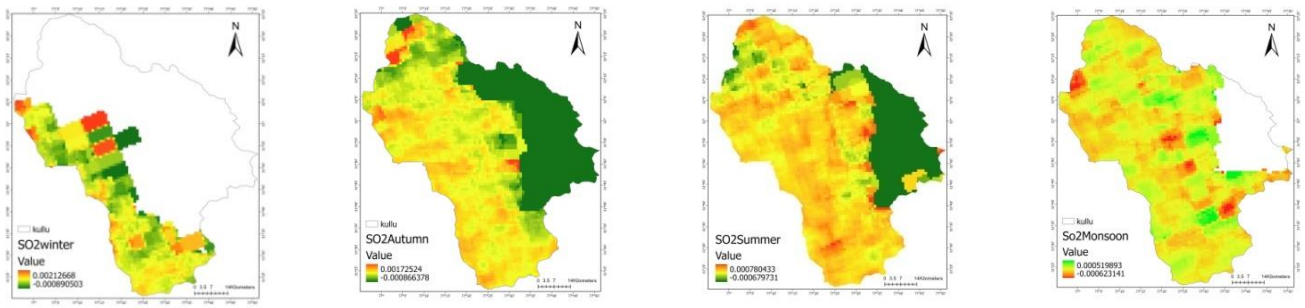
Seasonal Variability of SO_2 showed highest concentration in winter followed by autumn and lowest concentration in monsoon (Fig 8 a-d). Similar results were observed in ground level measurement of these pollutants.SO2 showed highest concentration in winter as in winter due to lack of OH radical the formation of SO_2 to $S04^{-2}$ slows down, leading to increased level of SO_2 in air.

$$\mathbf{SO_2 + H_2O \text{ ---> } SO_2H_2O}$$

$$\mathbf{SO_2H_2O \text{----> } H+ + HSO^{-3}}$$

$$\mathbf{HSO_3 \text{ ---> } H+ + SO^{-3}}$$

$$\mathbf{SO_3^{-2} + O_3 \text{ ---> } SO_4^{-2} + O_2}$$



(a) (b) (c) (d)

Figure 8. (a-d) Seasonal Variability of SO_2 in Kullu Himachal Pradesh using SENTINEL-5P data.

4.5. *Relationship between gaseous air pollutants and meteorological parameters*

4.5.1. Relationship between Nox (oxides of Nitrogen) and meteorological parameters

NOx (oxides of Nitrogen) showed a positive correlation with air temperature and relative humidity while wind speed and rainfall showed no significant correlation with NOx (Fig.9).

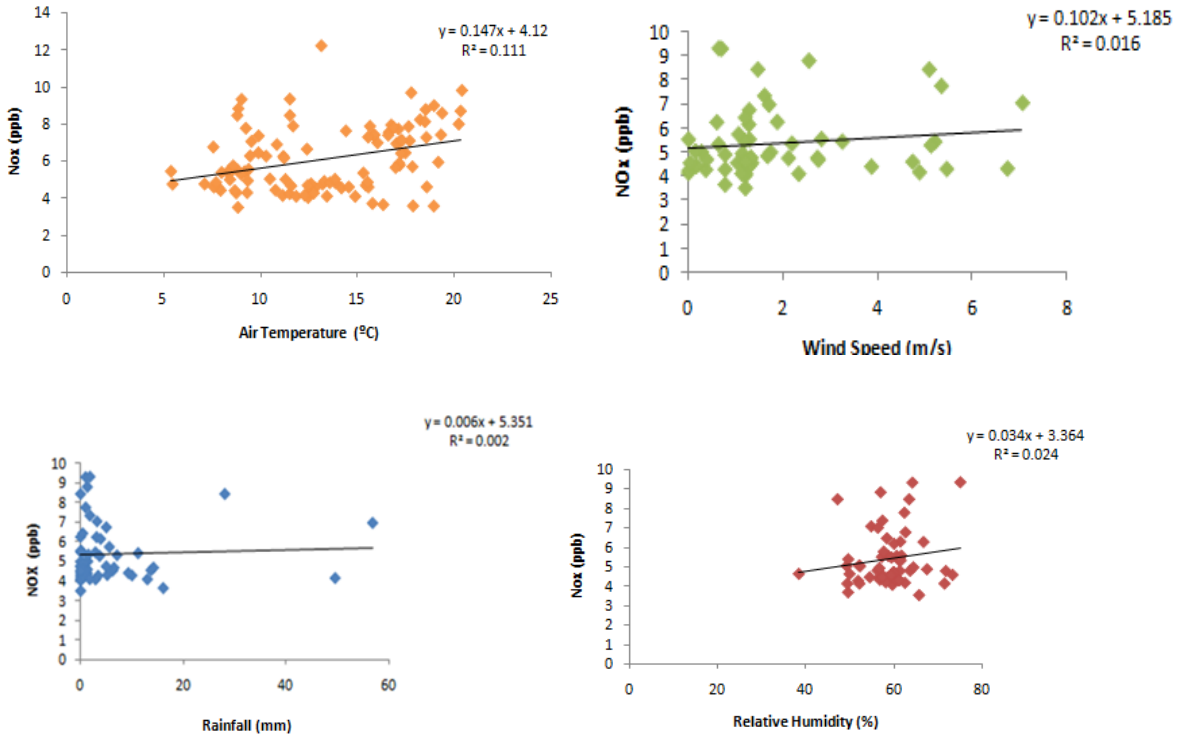


Figure 9. Correlation between NOx and meteorological parameters.

4.5.2. Relationship between CO (Carbon monoxide) and meteorological parameters

CO (Carbon monoxide) showed a negative correlation with air temperature and relative humidity while wind speed and rainfall showed no significant correlation with CO(Fig.10)..

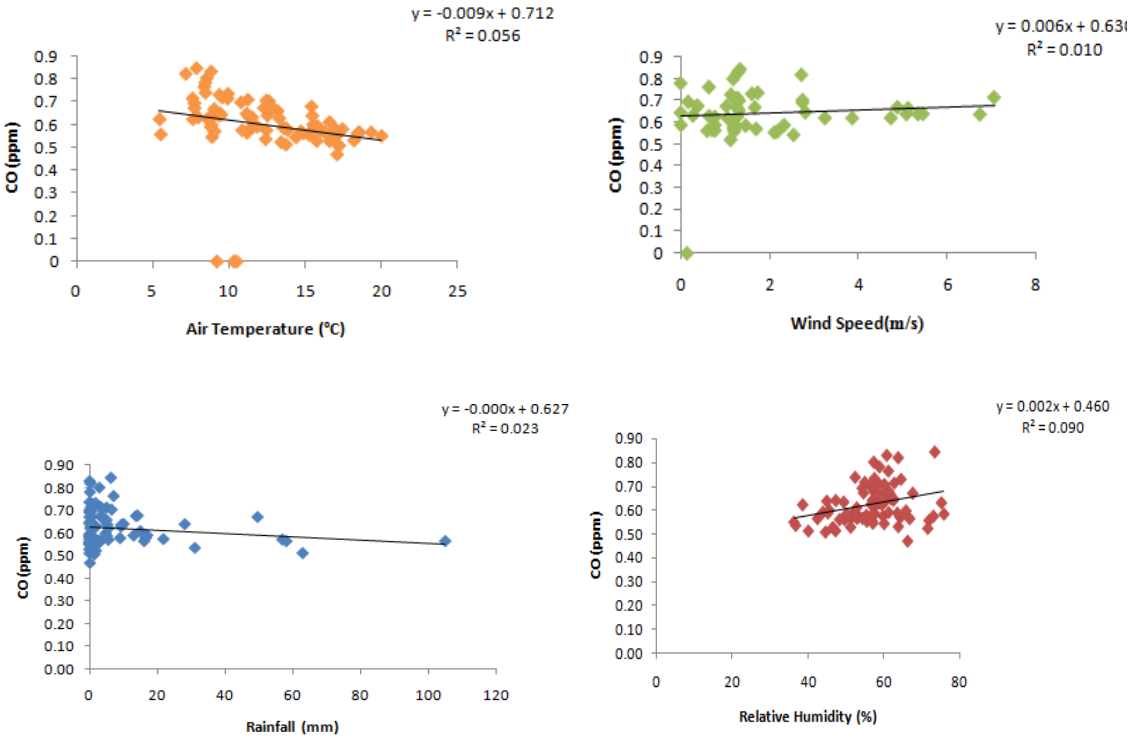


Figure 10. Correlation between CO and meteorological parameters.

4.5.3. Relationship between SO_2 (Sulphur Dioxide) and meteorological parameters

SO_2 (Sulphur Dioxide) showed a negative correlation with air temperature relative humidity while wind speed and rainfall showed no significant correlation with CO (Fig.11).

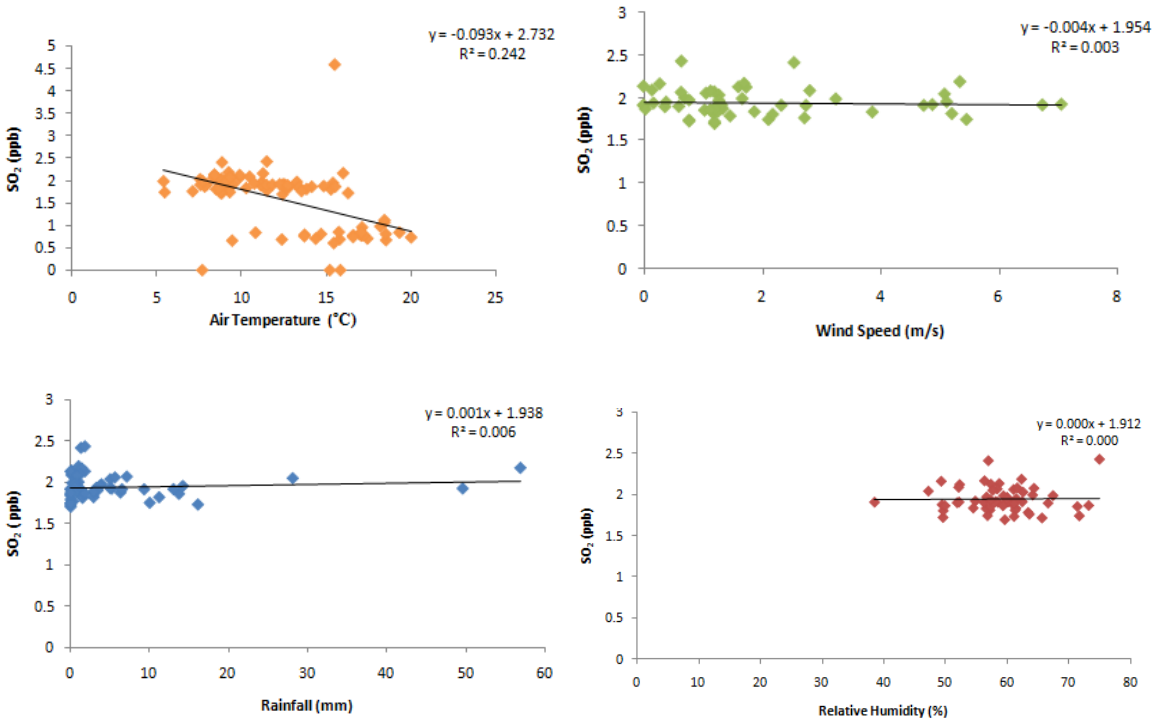


Figure 11. Correlation between SO_2 and meteorological parameters.

4.5.4. Relationship between CO_2 (Carbon Dioxide) and meteorological parameters

CO_2 (Carbon Dioxide) showed a positive correlation with air temperature and rainfall while negative with wind speed and showed no significant correlation with relative humidity. SO2 showed highest concentration in winter as in winter due to lack of OH radical the formation of SO_2 to $S04^{-2}$ slows down, leading to increased level of SO_2 in air,also it showed a negative correlation with temperature (Fig.12).

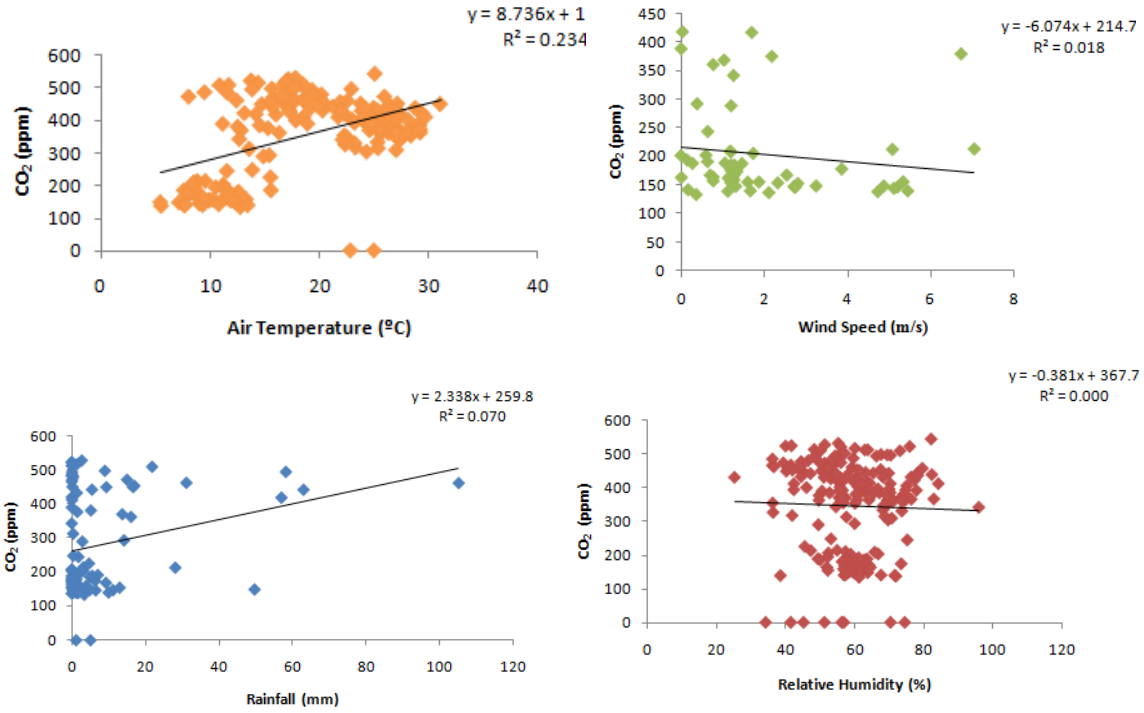


Figure 12. Correlation between CO_2 and meteorological parameters.

4.5.5. Correlation between surface ozone and its Precursors

Surface Ozone is a secondary pollutant and Nox and CO are its precursors. During the day time NOx and CO undergo photochemical chain reaction which lead to production of surface ozone. The equation below shows the atmospheric reaction of NOx and CO which lead to production of surface ozone (Fig.13).

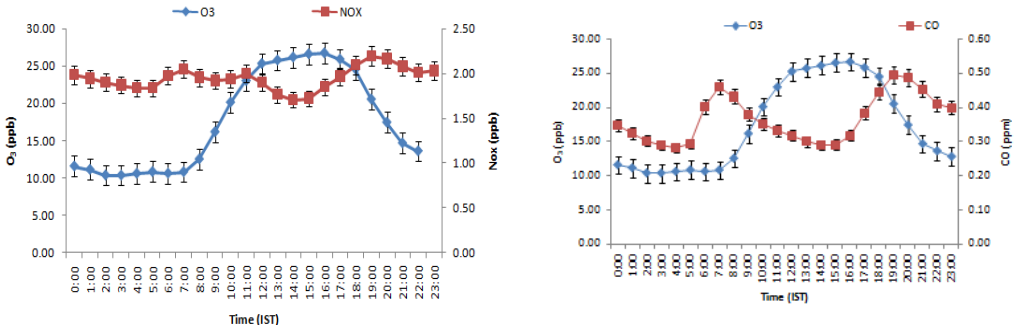
- Formation of Surface ozone from NOx

$NOx + radiations\ (>380nm) \rightarrow NO + O$

$O + O_2 \rightarrow O_3$

- Formation of Surface ozone from CO

$CO + 2O_2 + hv \rightarrow CO_2 + O_3$



(a) (b)

Figure 13. Correlation between surface ozone and its precursor (a) Nox (b) CO.

5. Conclusion

The concentration of pollutants was within prescribed standards as per NAAQS as per ground based and satellite based measurement.

- Seasonal Variability of NO_2 showed highest concentration in summer followed by autumn and lowest concentration in monsoon. Seasonal Variability of SO_2 showed highest concentration in winter followed by autumn and lowest concentration in monsoon.SO_2showed highest concentration in winter as in winter due to lack of OH radical the formation of SO_2 to $S0_4^{-2}$ slows down, leading to increased level of SO_2 in air.
- Seasonal Variability of O_3 showed highest concentration in summer and lowest concentration in monsoon.
- Surface Ozone is a secondary pollutant and Nox and CO are its precursors. During the day time NOx and CO undergo photochemical chain reaction which lead to production of surface ozone.
- Although all the gaseous air pollutants are within permissible standards as per NAAQS Still it is essential to understand the atmospheric chemistry of the pollutants and their correlation with meteorological parameters in order to understand the background values of pollutants in this region and to further suggest mitigating measures.

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