Five years surface ozone behaviour in a semi-rural location at Mohal-Kullu in the north-western Himalaya, India

Jagdish Chandra Kuniyal (jckuniyal@gmail.com)
Govind Ballabh Pant Institute of Himalayan Environment and Development https://orcid.org/0000-0002-3365-0478

Sheetal Choudhary
Govind Ballabh Pant National Institute of Himalayan Environment and Sustainable Development

Priyanka Sharma
Govind Ballabh Pant National Institute of Himalayan Environment and Sustainable Development

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Abstract

Surface ozone is one of the most important Green House Gases (GHGs). Five years (2011–2015) measurements of surface ozone (O_3) and one of its precursors- oxides of nitrogen (NO_x) were carried out at a semi-rural location, Mohal (77.12°E, 31.91°N, 1154 m amsl) in the north-western Indian Himalaya. The concentration of O_3, NO, NO_2 and NO_x was measured maximum 74.6 ± 23.2 ppb in 2013, 27.5 ± 7.5 ppb in 2013, 51.8 ± 13.2 ppb in 2013, and 60.8 ± 13.2 ppb in 2012, respectively. Seasonally, O_3 concentration was highest during summer while lowest in monsoon. The O_3 concentration shows unimodal peak while its precursors show bimodal peaks. A reasonable decrease in percent change was found in terms of O_3 (-13), NO_2 (-6), and NO_x (-3) due to imposing regulations imposed by local government in compliance with the order of Hon'ble National Green Tribunal (NGT) of the country in 2015. However, NO (9) is increasing due to vehicular activities in the nearby area which is one of the famous tourist spots. Washout effect due to increasing rainfall by 8% might have also affected O_3 concentrations. Biomass burning for heating and cooking purposes and forest fire for tender livestock forage and transported gaseous pollutants from the Middle East countries and Indo-Gangetic Plain (IGP) could be major contributors of surface ozone and its precursors. HYSPLIT air-mass back trajectories drawn for external ozone sources showed the maximum air masses reached the study location either with the western desert countries or IGP polluted regions.

1. Introduction

Surface ozone (O_3) and changing climate are closely linked to each other. Surface ozone in climate change perspective primarily indicates changes in temperature. Air parcels having more ozone may absorb more heat through absorption of sun's ultraviolet radiation and upwelling infrared radiation from the troposphere. The more ozone in the air masses, the more it retains heat. According to the Intergovernmental Panel on Climate Change (IPCC 2001), O_3 in the atmosphere is the third most powerful greenhouse gas after CO_2 and CH_4.

In many parts of the northern hemisphere, the concentration of O_3 near the surface has been found to be increasing (Nair et al. 2002; Naja and Lal 2002). The meteorological parameters such as sunlight, temperature, and wind speed were the main parameters on which surface ozone concentration depends. From the polluted regions, ozone rich air-masses could be transported (Lal et al. 2014) and may affect nearby other remote places (Chand et al. 2001; Naja et al. 2004; Kumar et al. 2013; Lal et al. 2013). Due to increasing anthropogenic activities, the surface ozone produced by photochemical reactions is increasing rapidly (Lal et al. 2017). At high altitude, its maximum concentration is normally found in May, while minimum was in August due to conversion of its precursors (Sanchez et al. 2005; Kumar et al. 2010) due to washout effect or other atmospheric dynamism. In the southern and central Asia of the developing countries, there is continuous increase in the emission of O_3 precursors due to higher emissions and weaker legislative policies (Ghosh et al. 2018). Lower concentration of surface O_3 was measured in Paris due to poor layer formation of pollutants in morning, which develops due to daytime boundary (Klein et

al. 2019). Also, it shows significant seasonal and regional variations which mainly depends upon the stratospheric intrusion (Tiwari and Agarwal 2018). In the North Atlantic Ocean, the long-term trend gives the influence of European regional NO_x and VOC emissions which decrease in winter time and increase in summer time while episodic peaks reduce continuously (Derwent et al. 2018).

While in India especially at low altitudinal rural site, maximum O_3 concentration was found in summer and winter but minimum in rainy season (Debaje and Kakade 2006; Reddy et al. 2011). The temporal variation of NO_x concentration is highest in winter (Kumar et al. 2015) and shows seasonal variability with high NO and CO during summer but low in summer rains or monsoon (Tiwari et al. 2015). Also, it shows highest diurnal variation during afternoon hours and lowest in morning hours (Gaur et al. 2014). In Delhi, high level of variation occurs in O_3 concentration due to pollutants and intense solar flux across Indo-Gangetic Plain (Singh et al. 1997; Jain et al. 2005). Statistically, in Punjab and southern Sindh, the temporal increase raised the ozone columns which are consistent to high population, urbanization, and extensive anthropogenic activities (Noreen et al. 2018). Among all the O_3 precursors such as NO_x had shorter lifetime and also considered to be rate-limiting precursor in the atmosphere (Liu et al. 1980; 1987). The result of daytime gas phase (OH with NO_2) recombination reaction leads to the emissions of NO_x with significant increase in tropospheric O_3 which mainly promotes the HNO_3 formation (Finlayson-Pitts and Pitts 2000). In the lower troposphere, O_3 concentrations increased significantly (Naja and Lal 1996) and long-term measurement of O_3 and its precursors are actively involved in various groups (Lal et al. 2000; Naja and Lal 2002; Naja et al. 2003; Jain et al. 2005; Reddy et al. 2008; Kumar et al. 2010; David and Nair 2011; Singla et al. 2011; Nishanth et al. 2012). With increasing emissions of anthropogenic pollutants, ozone levels are likely to increase in this region in future (Wild et al. 2012; Stevenson et al. 2013). Long term ozone behaviour is studied in the Central Himalaya at Nainital (Kumar et al. 2010) and northwestern Himalaya at Kullu, Manali and Kothi (Kuniyal et al. 2007; Sharma et al. 2013). At Anantapur (Andhra Pradesh), it shows a significant positive correlation with ambient air temperature and negative correlation with both wind speed and relative humidity (Reddy et al. 2012). In the western and southern Indian region, O_3 concentration during summer was influenced by transported pollutants from backward air-mass trajectories, meteorological parameters and high insolation, while it is highly influenced during late autumn and winter (Lal et al. 2000; Naja and Lal 2002; Nair et al. 2002; Beig et al. 2007; Mittal et al. 2007; Sharma et al. 2013). Overall, high nitrate levels were associated with anthropogenic causes, whereas meteorological conditions were associated with sulphate concentrations as against to gaseous emissions (Si et al. 2019). By using the stable orbits, satellites will be able to check quality for climate issues, reference locations and meteorological radiometers (Keckhut et al. 2018).

2. Site Description And General Meteorology

The simultaneous measurements of O_3, NO_x ($NO + NO_2$) and other meteorological parameters were carried out at Mohal-Kullu (31.9°N, 77.19°E, 1154 m amsl) in India from January 2011 to December 2015. The sampling site is about 5 km south-south west to Kullu town and its distance from National Highway NH-21 is about 228 m (Fig. 1). It is mainly located in the campus of G.B. Pant National Institute of

Himalayan Environment (NIHE), Himachal Regional Centre, Mohal-Kullu (H.P.). The observation site is surrounded by hills of considerable height in a range 3,000–5,000 m in the Kullu valley and is far away from the snowline (Sharma et al. 2009). The famous River Beas flow in a middle of the Kullu valley extends up to 80 km long from north to south and, on average, is 2 km wide. It begins from Largi (957 m amsl) in the lower Beas basin and stretches up to Rohtang Pass (3978 m) and Rohtang Crest (4,038 m amsl) in the upper Beas basin (Kuniyal et al. 2009). Due to a bowl shaped valley, cooling occurs as the valley traps cold air in winter due to inversion of temperature. It settles close to a valley floor during night time and further leads to build-up pollutants. Heating by solar radiation destabilizes surface air due to movement against gravitational pull which results in dispersion of trapped pollutants.

On the basis of meteorological conditions, it is suggested that this region's climate has four distinct seasons, namely, winter (December to March) is associated with heavy snowfall and rain during summer (April to June). The air mass flow appreciably influences the pollutant concentrations from the western and south-eastern directions. The monsoon season (July to September) also receives heavy rain. While the autumn season (October to November) characterised with average temperature and unusual and torrent rainfall (Kuniyal et al. 2007; Sharma et al. 2011).

3. Material And Methods

Observation of surface O_3 and its precursors, i.e., nitrogen dioxides ($NO + NO_2$) were carried out in a bowl shaped valley (1154 m amsl) in an Environmental Observatory at Mohal. Here, different online analyzers and equipment are functional. Among these are UV photometric Ozone Analyzer (Thermo Fischer Model, 49i), and NO_x Analyzer (Thermo Fischer, Model 42i), etc.

Surface Ozone (O_3) measurement is based on the absorption of ultraviolet radiation by ozone molecules at 253.7 nm (Singla et al. 2011). The radiation source is a UV-lamp and zero air (clean air without any pollutants) and the sample itself is alternately measured in cells. The minimum detection limit is 0.5 ppb and precision is ± 1 while its flow rate is 0.5 slpm. Calibration of the instrument is done regularly by the built-in ozonator (ozone generator) and zero air generators. The online analysers were operated every day continuously for 24 h. Simultaneously, measurement of nitrogen oxides (NO, NO_2 and NO_x) is based on the chemiluminescence effect which forms peaks at 630 nm radiation. NO_2 is measured by the thermal conversion method from NO_2 into NO. The molybdenum converter is found to have higher sensitivity with 100% conversion efficiency (Winer et al. 1974; Finlayson-Pitts and Pitts 1986). The actual concentration of NO_2 is low as a result NO_x may also be lower. The minimum detection limit and precision of NO_x analyser is 0.4 ppbv and 1 ppbv, respectively.

The analog signal of gases data is converted into digital values through data acquisition system and stored in the computers by using ENVIDAS software. The raw files are then extracted and separated into individual series. The measurements of O_3 and NO_x ($NO + NO_2$) were available from January 2011 to December 2015. Hourly averaged data were used to perform statistical analysis. The data have been used to investigate the diurnal and seasonal patterns of trace gases and their interdependence of these

two chemical species. The major pollution sources near the study site are local traffic, biomass burning and use of coal in restaurants and hotels for heating and cooking purposes. In the present study, NO_x is the most crucial precursor of O_3.

The pollutants being contributed from external sources were also examined by drawing seven-days back trajectories using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT-4). This model is available with NOAA Air Resources Laboratory that has been utilized in both operational and research applications to enhance understanding of atmospheric chemical transport, dispersion, and deposition. The trajectories were calculated at 0700 UTC at 1000 m height. These trajectories show their origin, route or direction of the air masses to the present site. Additionally, the HYSPLIT trajectory model can be run both forward and backward depending on required time, and is therefore useful for source-receptor applications. Relevant to this work, HYSPLIT has been applied in studies of East Asian dust and pollution transport to both Mauna Loa Observatory (MLO) (e.g. Rinsland et al. 1999) and the Western United States (e.g. Weiss-Penzias et al. 2006). Calculations in HYSPLIT are based on a hybrid combination of Eulerian and Lagrangian frameworks (Draxler et al. 1998). Eulerian models focus on a specific location in space and calculate both advection and diffusion on a fixed spatial grid while Lagrangian models are applied to an air parcel moving through space, therefore calculating advection and diffusion separately (Draxler et al. 1998). HYSPLIT utilizes the Lagrangian method for calculating advection and diffusion while chemical concentrations are calculated using an Eulerian fixed grid (Draxler et al. 1998). For this study, HYSPLIT was used only for particle trajectory calculations without application of the dispersion or diffusion models. The HYSPLIT model can be run using a variety of available model meteorology datasets that have been processed into the format required by the model. These datasets include the metereological parameters like wind, temperature, etc. from which backward trajectories represent more accurate air masses motion in atmosphere (Nguyen et al. 2016). Concentrated Weighted Trajectory (CWT) also gives direction in concentrated ratio which helps to get the significant source of O_3 values for air masses in a concentrated form (Sharma et al. 2017).

4. Results And Discussion

During the study period (2011–2015), the average high concentration of surface ozone was observed in the year 2013 measuring maximum as 74.6 ± 23.2 ppb, on the other hand its minimum values stood to be 16.0 ± 5.6 ppb in 2015 (Fig. 2). Diurnal variation of O_3 concentration at Mohal in the Kullu valley from 2011 to 2015 showed uni-modal peak during mid of a day at 15:00 hrs (IST). This is mainly due to a strong process of photo-oxidation in presence of sunshine and its precursors. While O_3 values were found low in early morning and late evening due to absence of sunlight. The concentration of O_3 was found to be increasing gradually after sunrise (07:00–08:00 hrs IST), attaining maximum concentration during afternoon (14:00–16:00 hrs IST). Thereafter, it showed a gradual decrease. Annual maximum concentration of NO was found 27.5 ± 7.5 ppb in 2013, NO_2 51.8 ± 13.2 ppb in 2013 and NO_x 60.8 ± 13.9 ppb in 2012. These precursors of ozone are mainly considered to be produced due to anthropogenic activities such as vehicular emission and biomass burning; as a result these are considered to be primary

pollutants. The percentage change in O_3 concentration with its precursors (NO, NO_2, NO_x) shows the highest increase with 244.25% during 2011-13. Analysis of meteorological data in context to O_3 showed its high concentration days associated with a large-scale stagnation, intense solar radiation, and minimum rainfall. Among meteorological parameters, rainfall has a negative correlation with O_3. Its best example was observed from 2012 to 2015 when rainfall took place more as compared to remaining years. These precursors are mainly considered to be emitted in the present study sites due to primarily anthropogenic activities such as vehicular emission and biomass burning.

Figure 3 shows the seasonal averaged diurnal pattern of NO_x. The diurnal cycle shows two peaks during morning and evening traffic hours and valley during afternoon hours. The night-time concentration stayed relatively flat between the bowl - shaped valley's peak and gentle slope. This phenomenon can be attributed to the day-night differences in the chemical removal of NO_x via photo oxidation reactions and height of the mixing layer. The diurnal variation of NO_x did not show a clear fluctuation during monsoon. Further, the difference in peak magnitude of NO_x between winter and pre-monsoon season was about two-folds, which possibly indicate the vertical mixing as an important factor for the observed diurnal variations as photo-chemical loss is much lower in winter than that of the pre-monsoon season. The surface ozone, NO, and NO_2 show a significant diurnal variations at an urban site at Delhi (Sharma et al. 2016). The concentration of NO_x shows highest magnitude in winter season followed by post-monsoon, pre-monsoon and monsoon season. Lowest concentration of NO_x was observed during afternoon hours when O_3 showed a peak. This clearly illustrates the production of O_3 via photo-chemical oxidation of carbon like compounds by their reaction with OH radicals in presence of NO_x. The daytime O_3 concentration builds up is a pronounced feature of urban polluted sites (Lal et al. 2000). The largest diurnal peak concentration was observed in summer (61.1 ppb), followed by winter (45.7 ppb), monsoon (27.1 ppb), autumn (35.6 ppb) and pattern is similar to that of other locations in India (Pulikesi et al. 2006; Reddy et al. 2010; Ahammed et al. 2006; Beig et al. 2007). But unlike the Northern China (Meng et al. 2009), O_3 concentrations were lowest in monsoon season. The larger variability in monthly averaged NO_x was noticed during the winter season indicating larger anthropogenic sources near-surface and evolution of boundary layer height. On the other hand, the mean concentration of O_3 shows higher variability in summer season when photochemistry in presence of precursors and strong sunlight remains at peak. At this time, the process of O_3 production is faster than the process of destruction. The intercept shows low value during winter season, which are probably attributed to less active photochemistry (Table 1).

Table 1
Regression parameters for O_3 during 2011–2015 at Mohal.

Season	Mean O_3	Intercept	Slope	Correlation (r)	Confidence level 95%	No. of days	No. of hourly sample
Winter (Dec-Mar)	20.94 ± 11.91	27.962	-0.030	-0.34	1.07	476	11424
Summer (Apr-Jun)	24.17 ± 12.66	26.170	-0.0025	-0.210	1.31	360	8640
Monsoon (Jul-Sep)	13.49 ± 9.54	14.206	-0.007	-0.084	0.99	360	8640
Autumn (Oct-Nov)	17.62 ± 10.25	18.155	-0.032	-0.175	1.46	192	4608

In contrast to NO_x as the secondary pollutant, O_3 exhibits a reverse seasonal pattern. It is mainly due to higher emissions related to heating and cooking, and photochemical production due to lower temperature and solar radiation. Surface ozone shows correlation coefficient of (-0.477*) with air temperature (Table 2). On average, the maximum vehicular inflow from Gulaba to Rohtang Pass (3978 m) in the year 2014 was recorded in the month of June (i.e., 44,588) and minimum in December (i.e., 13,696). Out of the total plying vehicles on the way to Rohtang Pass, majority of them were registered petrol operated vehicles followed by diesel operated. Petrol operated vehicles were recorded maximum in June (40,731), followed by October (24,300), whereas their minimum numbers stood in September (12,079). On the other hand, diesel operated vehicles were recorded maximum in August (4,195) and minimum in December (676) (Kuniyal et al. 2014). The vehicular activities reduced in the area only after the order of Hon'ble National Green Tribunal (NGT) wherein a regulation on diesel and petrol vehicles on Rohtang Pass area of Himachal Pradesh issued on 29th May, 2015. Here, total 1200 vehicles (i.e. 800 petrol and 400 diesel) were allowed in compliance to the NGT order. In between, there remains public resentment especially among the taxi operators because of limiting their livelihood options. In view of the same as well as accommodating more tourists, the previous limit was relaxed by NGT on June 19, 2017. At this point of time, daily limit increased from 1200 to 1300 (i.e. 60% petrol and 40% diesel) out of which 25% of the total were supposed to be reserved for the natives of Himachal State and 75% of the total allowed vehicles for the tourists outside Himachal Pradesh state. Daily 860 petrol, 440 diesel vehicles and up to 9 CNG buses are run to reduce the vehicular pollution activities in this ecologically sensitive and topographically fragile area.

Table 2
Correlation of O_3 with different parameters during 2011–2015 at Mohal.

Season	Parameters	Air temperature	Humidity	Ozone
Winter	Air temperature	1		
	Humidity	-0.215	1	
	Ozone	**-0.477***	0.385	1
Summer	Air temperature	1		
	Humidity	-0.210	1	
	Ozone	-0.160	0.063	1
Monsoon	Air temperature	1		
	Humidity	-0.221	1	
	Ozone	0.049	0.096	1
Autumn	Air temperature	1		
	Humidity	0.255	1	
	Ozone	-0.167	0.052	1
* Correlation is significant at the 0.05 level (1-tailed).				

The main reasons for high O_3 concentration are both- the local as well as external sources. The local sources are supposed to be from the immediate area or region, while the external pollution sources could be transported from outside the region. Figure 5 represents the back trajectory ending at study site at 1000 m altitude. From the pathways of air-masses, it is made clear from the trajectories that in all the seasons, north-west, south-west, and south-east winds were found to be dominant. Most of the times, air-masses passed through Saudi Arabia, Iran, Iraq, Thar desert, Sahara and sub-Saharan region and polluted regions of Pakistan, Punjab, Haryana and Delhi. During observational time, the air masses reaching at Mohal (present study site) in different seasons were from northwest and west direction in winter, north, northwest, west and southwest direction in summer, southwest and east to southeast direction in monsoon and north-western direction in autumn during observation years from 2011 to 2015. In a cluster analysis, 4 clusters were grouped into back trajectories (Fig. 6). From 2011–2015 years, most of the trajectories were corresponding to the western flows (regional) contributing to 38% of the total air masses followed by 33% from the south-eastern, 20% from the westerly moderately moving and 8.3% from the north-western directions. Mean concentration of ozone associated with fast moving westerly and southerly air masses are significant only in monsoon season compared to those observed for other clusters. The CWT analysis has indicated the heavy or pollution laden air mass flow from the Arabian and Middle East countries.

Surface ozone has been continuously monitored since 2007 under ISRO-GBP with Atmospheric Chemistry Transport and Monitoring (AT-CTM) programme throughout India. Its observations from year to year at different observational sites have been reviewed and compared with our location. The seasonal and diurnal variation of surface O_3 over Mohal shows a simple profile of a semi-rural area, which is changing season to season similar to other places of the country. Seasonally, O_3 concentration observed at Mohal-Kullu is lower than that of one of the hill station- Nainital which shows maximum O_3 during wintertime (Table 3). Similar observations having maximum in wintertime were also made at Kannur, Trivandrum and Delhi. On the other hand, Agra and Kanpur in summer and Udaipur, Jodhpur, Dibrugarh in pre-monsoon and Pantnagar, Nainital in springtime were observed with high o_3 concentration. The enhanced concentrations of O_3 in all the sites were predominant during winter season. The obstruction of O_3 from the free troposphere is its main reason for its increase at night-time hours in the Himalayan region. The enhanced O_3 concentrations during winter season are mainly due to higher local emissions of precursor gases, long-range transport of continental pollutants, and presence of a boundary layer height. Due to a reduced photochemical reaction, all the observational sites show low concentration of O_3 in monsoon season. Strong convective action, extreme rainfall, and air flow masses are the major causes of reduced photochemical activities in monsoon. From this, we conclude that the variations of surface O_3 at different locations mainly depend on the latitude/longitude variations, weather parameters, availability of solar radiation, concentrations of precursor gases, and degree of anthropogenic activities (Resmi et al. 2020). In winter, slow chemical loss is due to low temperature, minimal solar radiation and higher anthropogenic emissions from burning of fuel wood for cooking and heating in the surrounding villages. There has been a decrease in the percentage change of O_3 (-13) and NO_2 (-6), NO_x (-3), and BC (-14) during 2011–2015 (Table 4). However, as an exception, there has been increase in NO (9) concentration and rainfall (8) amount. These results may be due to washout effect of rainfall, anthropogenic activities, forest fires, automobiles, fuel and coal burning, etc.

Table 3
Maximum and minimum surface O_3 concentrations at Mohal-Kullu in comparison to other locations of India.

Sr. No.	Locations	Landscape category	Altitude (m amsl)	Period of observation	Daytime observed (ppbv)		Reference
					Maximum (season)	Minimum (season)	
1.	Nainital	High altitude Lesser / Central Himalaya	1958	2006–2008	67.2 ± 14.2, Late spring	24.9 ± 8.4, Monsoon	Kumar et al. 2010
2.	Mohal-Kullu	High altitude Lesser ? northwestern l Himalaya	1154	2011–2015	74.6 ± 3.3, Winter	15.8 ± 5.1, Monsoon	Present study
3.	Dibrugarh	North-Eastsub-Himalayan zone	111	2009–2013	42.9 ± 10.3, Pre monsoon	17.3 ± 7.0 Monsoon	Bhuyan et al. 2014
4.	Udaipur	Semi-arid, urban	598	2011–2012	46± 12.5, Pre-monsoon	26 ± 4.6, Monsoon	Yadav et al. 2016
5.	Jodhpur	Semi-arid, urban	250–300	2012–2013	47 ± 11.5, Pre-monsoon	27 ± 12, Monsoon	Pancholi et al. 2018
6.	Pantnagar	Semi-Urban IGP	231	2009–2011	48.7 ± 13.8, Spring	10.8 ± 12.1, Monsoon	Ojha et al. 2012
7.	Delhi	Urban IGP	218	2012–2013	38 ± 7, Winter	28 ± 6, Monsoon	Sharma et al. 2016
8.	Agra	Urban IGP	169	2012–2013	32.5 ± 19.3, Summer	8.74 ± 3.8, Monsoon	Saini et al. 2017
9.	Kanpur	Urban IGP	125	2009–2013	27.9 ± 17.8, Summer	10.5 ± 5.6, Monsoon	Gaur et al. 2014

Sr. No.	Locations	Landscape category	Altitude (m amsl)	Period of observation	Daytime observed (ppbv)		Reference
					Maximum (season)	Minimum (season)	
10.	Kannur	Rural, Western Coast	5	2013–2018	35.47 ± 10.5 Winter	13.5 ± 5.6, Monsoon	Resmi et. al. 2020
11.	Trivandrum	Coastal Site, Western Coast	3	2007–2009	40 ± 8.5, Winter	18 ± 5, Monsoon	Nair et. al. 2018

Table 4
Observed rate of percent change in different parameters for the year 2011–2015 at Mohal.

YEAR	O_3 (ppb)	NO (ppb)	NO_2 (ppb)	NO_x (ppb)	Rainfall (mm)
2011-12	-32	60	73	71	-12
2012-13	15	115	-7	11	31
2013-14	-7	-72	-62	-65	9
2014-15	-20	48	26	34	7
2011-15	-13	9	-6	-3	8

5. Conclusions

During reporting period (2011–2015), higher concentration of surface ozone was observed in the year 2013 indicating maximum as 74.6 ± 23.2 ppb, while its minimum values remained 15.8 ± 5.1ppb in 2015. Diurnal cycle of O_3 concentration at Mohal in the Kullu valley showed a unimodal peak during mid of a day at 15:00 hrs IST. This is mainly due to relatively a process of photo-oxidation in presence of strong sunshine and its precursors. While O_3 values were found low in early morning and late evening due to absence of sunlight. Concentration of O_3 was found to be increasing gradually after sunrise (07:00–08:00 hrs IST), attaining maximum concentration during afternoon (14:00–16:00 hrs IST). These gaseous pollutants, as considered to be primary pollutants, are mainly attributed to be produced due to anthropogenic activities such as vehicular emission and biomass burning. The percentage change of NO concentration shows its highest values up to 244.25% in 2011-13. There is a decrease in percentage change of O_3 (− 13), NO_2 (-6), and NO_x (-3) from 2011 to 2015. At contrary, it is only NO that has shown a reasonable increase (9) due to vehicular activities and washout effect as rainfall increased by 8%. Analysis of meteorological data in context to O_3 showed its higher concentration days associated with a large-scale stagnation, intense solar radiation, and minimum rainfall. Among meteorological parameters, rainfall has a negative correlation with O_3. In addition, the region has also a long range transport sources

outside the region such as the Indo-Gangetic Plain and Middle East countries. Nevertheless, such long-term continuous measurement of trace gases and meteorological variables are crucial to better understand the surface ozone behaviour for half a decade in the areas which are still considered to be having limited information on the subject and are considered to be more prone to climate change.

Declarations

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Conflict of Interest

The authors declare no conflict of interest.

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Authors' Contribution

The principal author Jagdish Chandra Kuniyal prepared a draft and finalised the manuscript, while other two authors Sheetal Chaudhary and Priyanka Sharma had taken the observations, analysed the data and helped the principal author in preparing the manuscript.

References

Ahammed YN, Reddy RR, Gopal KR, Narasimhulu K, Basha DB, Reddy LSS, Rao TVR (2006) Seasonal variation of surface ozone and its precursor gases during 2001-2003, measured at Anantapur (14.62 N), a semi-arid site in India. Atmospheric Research 80, 151-164

Beig G, Gunthe S, Jadhav DB (2007) Simultaneous measurements of ozone and its precursors on a diurnal scale at a semi urban site in India. Journal of Atmospheric Chemistry 57 (3): 239-253

Bhuyan PK, Bharali C, Pathak B, Kalita G (2014) The role of precursor gases and meteorology on temporal evolution of O_3 at a tropical location in northeast India. Environmental Science and Pollution Research 21: 6696–6713

Chand D, Modh KS, Naja M, Venkataramani S, Lal S (2001) Latitudinal trend in O_3, CO, CH_4, SF_6, over the Indian Ocean during the Index IFP- 1999 ship cruise. Current Science 80:100-104

David LM, Nair PR (2011) Diurnal and seasonal variability of surface ozone and NOx at a tropical coastal site: association with mesoscale and synoptic meteorological conditions. Journal of Geophysical Research 116(10): 1029, 4-14

Debaje SB, Kakade AD (2006) Weekend effect over rural and urban site in India. Aerosol Air Quality Research 6: 322-333

Derwent RG, Manning AJ, Simmonds PG, Spain TG, Doherty SO (2018) Long-term trends in ozone in baseline and European regionally-polluted air at Mace Head, Ireland over a 30-year period. Atmospheric Environment 179: 279-287

Draxler RR, Hess GD (1998) An Overview of the HYSPLIT-4 Modelling System for Trajectories, Dispersion, and Deposition. Australian Meteorological Magazine 47:295-308

Finlayson-Pitts BJ, Pitts JN (1986) Formation of sulfuric and nitric acids in acid rain and fogs. Atmospheric chemistry: Fundamental and experimental techniques, John Wiley, New York 702-705

Garg S, Shukla P, Bhattacharya S, Dadhwal V (2001) Sub-region (district) and sector level SO_2 and NOx emissions for India: assessment of inventories and mitigation flexibility. Atmospheric Environment 35:703-713

Gaur A, Tripathi SN, Kanawade VP, Tare V, Shukla SP (2014) Four-year measurements of trace gases (SO_2, NO_x, CO, and O_3) at an urban location, Kanpur, in Northern India. Journal of Atmospheric Chemistry 71: 283-301

Ghosh A, Singh AA, Agarwal M, Agarwal SB (2018) Ozone toxicity and Remediation in crop plants. Sustainable Agriculture Reviews 27: 126-169.

IPCC (2001) Climate Change 2001: Impacts, Adaptation and Vulnerability, Intergovernmental Panel on Climate Change (IPCC), Working Group II, Intergovernmental Panel on Climate Change, Working Group Science, Cambridge Univ. Press, pp. 1-1015.

IPCC (2007) Climate Change 2007: The Physical Science Basis. Cambridge Univ. Press, Cambridge, p. 506.

Jain AK, West T, Yang X, Post W (2005) Assessing the impact of changes in climate and CO_2 on potential carbon sequestration in agricultural soils. Journal of Geophysical Research Letter 32: L19711

Keckhut P, Claud C, Funatsu B, Hauchecorne A, Maury P, Khaykin S, Pichon AL, Steinbrecht W (2018) Temperature trends observed in the middle atmosphere and future directions. Infrasound monitoring for Atmospheric Studies 805-823

Klein A, Ravetta F, Thomas JL, Ancellet G, Augustin P, Wilson R, Dieudonné E, Fourmentin M, Delbarre H, Pelon J (2019) Influence of vertical mixing and nighttimes transport on surface ozone variability in the morning in Paris and the surrounding region. Atmospheric Environment 197: 92-103

Kumar A, Singh D, Singh BP, Singh M, Anandam K, Kumar K, Jain VK (2015) Spatial and temporal variability of surface ozone and nitrogen oxides in urban and rural ambient air of Delhi-NCR, India. Air quality, Atmosphere & Health 8(4): 391-399

Kumar R, Naja M, Pfister GG, Barth MC, Brasseur GP (2013) Source attribution of carbon monoxide in India and surrounding region during wintertime. Journal of Geophysics Research 118 (4): 1981-1995

Kumar R, Naja M, Venkataramani S, Wild O (2010) Variations in surface ozone at Nainital: A high altitude site in the central Himalayas. Journal of Geophysical Research 115:1-12

Kuniyal JC, Rao PSP, Momin GA, Safai PD, Tiwari S, Ali K (2007) Trace gases behaviour in sensitive areas of the northwestern Himalaya-a case study of Kullu-Manali tourist complex, India. Indian Journal of Radio Space Physics 36: 197-203

Kuniyal JC, Sharma P, Kumar K (2014) Assessment of Environmental impacts in and around the Rohtang Pass (3978 m) and its snow capped areas – A report. Hon'ble National Green Tribunal, GBPNIHESD, Kosi-Katramal, Almora, Uttarakhand, pp. 14-15

Kuniyal JC, Thakur A, Thakur HK, Sharma S, Pant P, Rawat PS, Moorthy KK (2009) Aerosol optical depths at Mohal-Kullu in the northwestern Indian Himalayan high altitude station during ICARB. Journal of Earth System Science 118 (1): 41-48

Lal S, Naja M, Subbaraya BH (2000) Seasonal variations in surface ozone and its precursors over an urban site in India. Atmospheric Environment 34: 2713-2724

Lal S, Venkataramani S, Chandra N, Cooper OR, Brioude J, Naja M (2014) Transport effects on the vertical distribution of Tropospheric ozone over western India. Journal of Geophysics Research atmosphere 119: 10012-10026

Lal S, Venkataramani S, Naja M, Kuniyal JC, Mandal TK, Bhuyan PK, Kumari KM, Tripathi SN, Sarkar U, Das T, Swamy YV, Gopal KR, Gadhavi H, Kumar MKS (2017) Loss of crop yields in India due to surface

ozone: an estimation based on a network of observations. Environment Science and Pollution Research 24: 20972-20981

Lal S, Venkataramani S, Srivastava S, Gupta S, Mallik C, Naja M, Sarangi T, Acharya YB, Liu X (2014) Transport effects on the vertical distribution of tropospheric ozone over the tropical marine regions surrounding India. Journal of Geophysics Research 118:1513-1524

Mallik S, Lal S, Venkataramani S (2015) Trace gases at a semi- arid urban site in western India: variability and inter-correlations. Journal of atmospheric Chemistry 72:143-164

Meng ZY, Xu XB, Yan P, Ding GA, Tang J, Lin WL, Xu XD, Wang SF (2009) Characteristics of trace gaseous pollutants at a regional background station in Northern China. Atmospheric Chemistry and Physics 9(3): 927-936

Mittal ML, Hess PG, Jain SL, Arya BC, Sharma C (2007) Surface ozone in the Indian region. Atmospheric Environment 41: 6572-6584

Monks PS (2005) Gas-phase radical chemistry in the troposphere. Chemical Society Reviews 34(5): 376-395

Nair PR, Chand D, Lal S, Modh KS, Naja M, Parameswaran K, Ravindran S, Venkataramani S (2002) Temporal variations in surface ozone at Thumba (8.6N, 77E), a tropical costal site in India. Atmospheric Environment 36: 603-610

Nair PR, Kumar RSA, David LM, Girach IA, Mottungan K (2018) Decadal changes in surface ozone at the tropical station Thiruvananthapuram (8.542◦ N, 76.858◦ E), India: Effects of anthropogenic activities and meteorological variability. *Environmental Science* and *Pollution* Research 25:14827–14843

Naja M, Chand D, Sahu L, Lal S (2004) Trace gases over marine regions around India. Indian Journal of Geo-Marine Sciences 33(1): 95-106

Naja M, Lal S (1996) Changes in surface ozone amount and its diurnal and seasonal patterns, from 1954-55 to 1991-93, measured at Ahmedabad (23N), India. Journal of Geophysical Research 23(1): 81-84

Naja M, Lal S (2002) Surface ozone and precursor gases at Gadanki (13.5°N,79.2°E), a tropical rural site in India. Journal of Geophysical Research 107(14): 8-13

Naja M, Lal S, Chand D (2003) Diurnal and seasonal Variabilities of surface ozone at a high altitude site Mt Abu (24.6°N, 72.7°E, 1680m amsl) in India. Atmospheric Environment 37(30): 4205-4215

Nguyen DL, Kim, JY, Shim SG, Ghim YS, Zhang XS (2016) Shipboard and ground measurements of atmospheric particulate mercury and total mercury in precipitation over the Yellow Sea region. Environmental Pollution 219: 262-274

Nishanth T, Satheesh KMK, Valsaraj KT (2012) variations in surface ozone and NOx at Kannur: a tropical, coastal site in India. Journal of Atmospheric Chemistry 69(2): 101-126

Noreen A, Khokhar MF, Zeb N, Yasmin N, Hakeem KR (2018) Spatio-temporal assessment and seasonal variation of tropospheric ozone in Pakistan during the last decade. Environment Science and Pollution Research 25: 8441-8454

Ojha N, Naja M, Singh KP, Sarangi T, Kumar R, Lal S, Lawrence MG, Butler TM (2012) Variabilities in O3 at a semi-urban site in the Indo-Gangetic Plain region: Association with the meteorology and regional processes. Journal of Geophysical Research 117: D20301

Pancholi P, Kumar A, Bikundia DS, Chourasiya S (2018) An observation of seasonal and diurnal behaviour of O_3-NOx relationships and local/regional oxidant (OX = O_3 + NO_2) levels at a semi-arid urban site of western India. Sustainable Environment Research 28: 79–89

Pulikesi M, Baskaralingam P, Rayudu VN, Elango D, Ramamurthi V, Siveanesan S (2006) Surface ozone measurements at urban coastal site Chennai in India. Journal of Hazardous Material 137(3): 1554-1559

Reddy BSK, Kumar KR, Balakrishnaiah G, Gopal KR, Reddy RR, Ahammed YN, Narasimhulu K, Reddy LSS, Lal S (2010) Observational studies on the variations in surface ozone concentration at Anantapur in southern India. Atmospheric Research 98: 125-139

Reddy BSK, Kumar KR, Balakrishnaiah G, Gopal KR, Reddy RR, Sivakumar V, Lingaswamy AP, Arafath SM, Umadevi Kumari SP, Ahammed YNK, Lal S (2012) Analysis of Diurnal and Seasonal Behaviour of Surface Ozone and its Precursors (NOx) at a Semi-Arid Rural Site in Southern India. Aerosol and Air Quality Research 12: 1081–1094

Reddy BSK, Reddy LSS, Cao Jun-Ji, Kumar KR, Balakrishnaiah G, Gopal KR, Reddy LSS, Narasimhulu K, Lal S, Ahmmed YN (2011) Simultaneous measurement of surface ozone at two sites over the southern Asia: a comparative study. Aerosol and Air Quality Research 11: 895-902

Reddy RR, Gopal KR, Reddy LSS, Narasimhulu K, Kumar KR, Ahammed YN, Reddy CVK (2008) Measurements of Surface ozone at semi-arid site Anantapur (14.62 N, 77.65 E, 331 m amsl) in India. Journal of Atmospheric Chemistry 59:47-59

Resmi CT, Nishanth T, Kumar SMK, Balachandramohan M, Valsaraj KT (2020) Long-Term Variations of Air Quality Influenced by Surface Ozone in a Coastal Site in India: Association with Synoptic Meteorological Conditions with Model Simulations. Atmosphere 11, (193):16-17

Saini R, Taneja A, Singh P (2017) Surface ozone scenario and air quality in the north-central part of India. Journal of Environmental Science 59: 72–79

Sanchez ML, de Torre B, Garcia MA, Perez I (2005) Ozone concentrations at a high altitude station in the central massif (Spain). Chemosphere 60: 576-584

Sharma A, Mandal TK, Sharma SK, Shukla DK, Singh S (2017) Relationships of surface ozone with its precursors, Particulate matter and meteorology over Delhi. Journal of Atmospheric chemistry 74: 451-474

Sharma A, Sharma SK, Mandal TK (2016) Influence of ozone precursors and particulate matter on the variation of surface ozone at an urban site of Delhi India. Sustainable Environment Research 26: 76–83

Sharma A, Sharma SK, Pathak U, Gupta NC, Mandal TK (2016) Study on surface ozone and its precursors at an urban site of Delhi, India. Indian Journal of Radio and Space Physics 45: 95-100

Sharma A, Sharma SK, Rohtash, Mandal TK (2016) Influence of ozone precursors and particulate matter on the variation of surface ozone at an urban site of Delhi, India. Sustainable Environment Research 26: 76-83

Sharma NL, Kuniyal JC, Singh M, Negi AK, Singh K, Sharma P (2009) Number concentration characteristics of ultrafine aerosols (atmospheric nanoparticles/aitken nuclei) during 2008 over western Himalayan region, Kullu-Manali, India. Indian Journal of Radio and Space Physics 38: 326-337

Sharma NL, Kuniyal JC, Singh M, Sharma M, Guleria RP (2011) Characteristics of Aerosol Optical Depth and Angstrom Parameters over Mohal in the Kullu Valley of Northwest Himalayan Region, India. Acta Geophysica 59: 334-360

Sharma P, Kuniyal JC, Chand K, Guleria RP, Dhyani PP, Chauhan C (2013) Surface ozone concentration and its behaviour with aerosols in the northwestern Himalaya, India. Atmospheric Environment 71: 44-53

Si Y, Li S, Chen L, Yu C, Wang H, Wang Y (2019) Impact of precursor gases and meteorological variables on satellite-estimated near-surface sulfate and nitrate concentrations over the North China Plain. Atmospheric Environment 199: 345-346

Singh S, Sarin M, Sanmugam P, Sharma N (1997) Ozone distributions in the urban environment of Delhi during winter months. Atmospheric Environment 31(20): 3421-3427

Singla V, Satsangi A, Pachauri T, Lakhani A, Kumari KM (2011) Ozone formation and destruction at a sub-urban site in North Central region of India. Atmospheric Research 101: 373-385

Stevenson DS (2013) Tropospheric ozone changes, radiative forcing and attribution to emission in the Atmospheric Chemistry and Climate Model Inter-comparison Project (ACCMIO). Atmospheric chemistry Physics 13: 3063-3085

Tiwari S, Agarwal M (2018) Tropospheric Ozone Budget: Formation, Depletion and Climate Change. Tropospheric Ozone and its impacts on crop Plants, Springer International Publishing 31-64

Tiwari S, Dahiya A, Kumar N (2015) Investigation into relationships among NO, NO_2, NOx, O_3 and CO at urban background site in Delhi, India. Atmospheric Research 157: 119-126

Tyagi S, Tiwari S, Mishra A, Hopke PK, Attri SD, Srivastava AK, Bisht DS (2016) Spatial variability of concentrations of gaseous pollutants across the national capital region of Delhi India. Atmospheric Pollution Research 7(5): 808-816

Ugolnikov OS, Maslov IA (2019) Optical depths and vertical profiles of stratospheric aerosol based on multi-year polarization measurements of the twilight sky. Journal of Aerosol Science 127: 93-103

Wild O, Fiore AM, Shindell DT, Doherty RM, Collins WJ, Dentener FJ, Schultz MG, Gong S, Mackenzie I A, Zeng G, Hess P, Zuber A (2012) Modelling future changes in surface ozone: a parametrized approach. Atmospheric Chemistry and Physics 12: 2037-2054

Winer AM, Peters JW, Smith JP, Pitts JN (1974) Response of commercial chemiluminescent NO-NO_2 analyzers to other nitrogen-containing compounds. Environment Science and Technology 8: 1118-1121

Yadav R, Sahu LK, Beig G, Jaaffrey SNA (2016) Role of long-range transport and local meteorology in seasonal variation of surface ozone and its precursors at an urban site of India. Atmospheric Research 176: 96-107

Figures

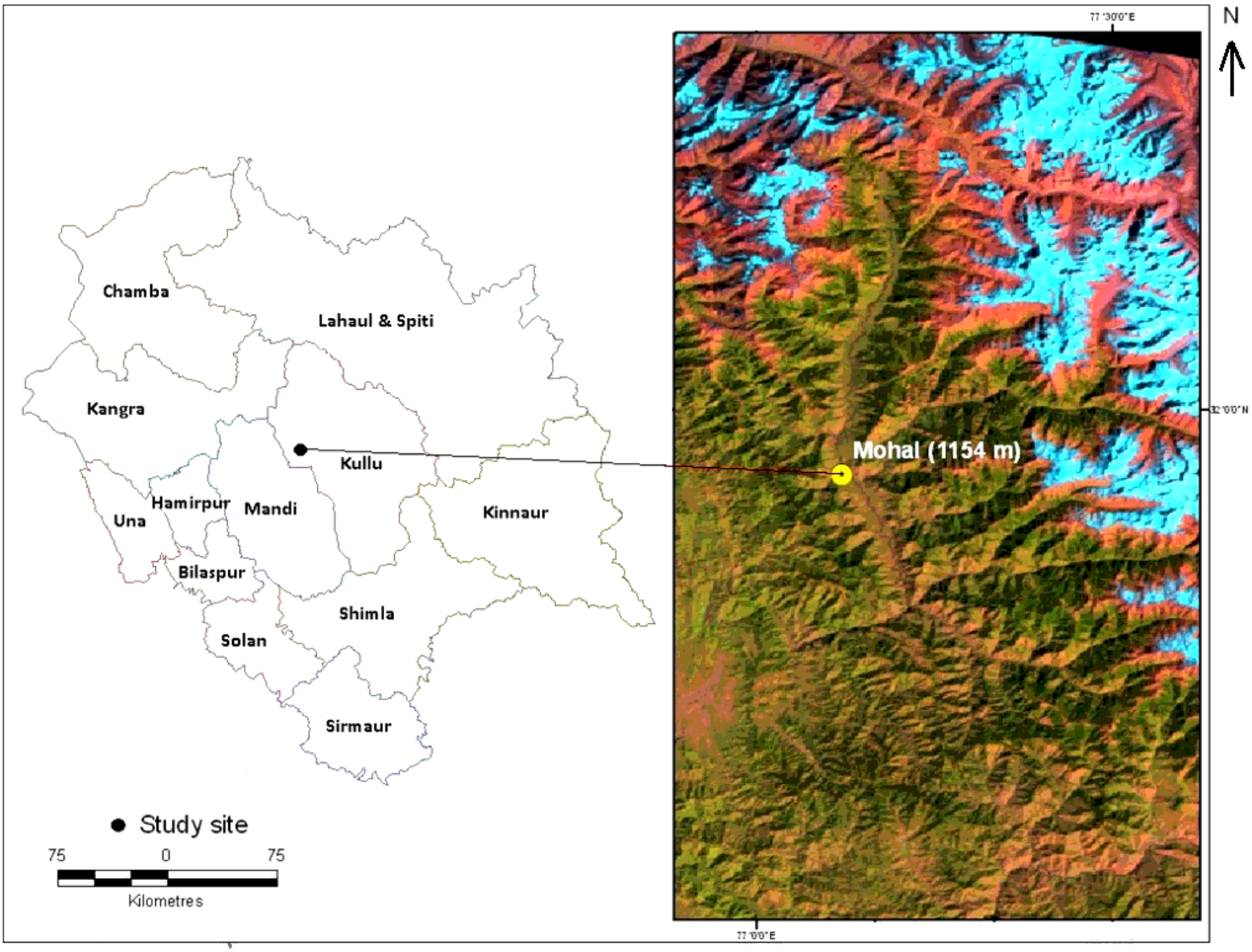

Figure 1

Study site- Mohal in the Kullu valley, north-western Indian Himalaya. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

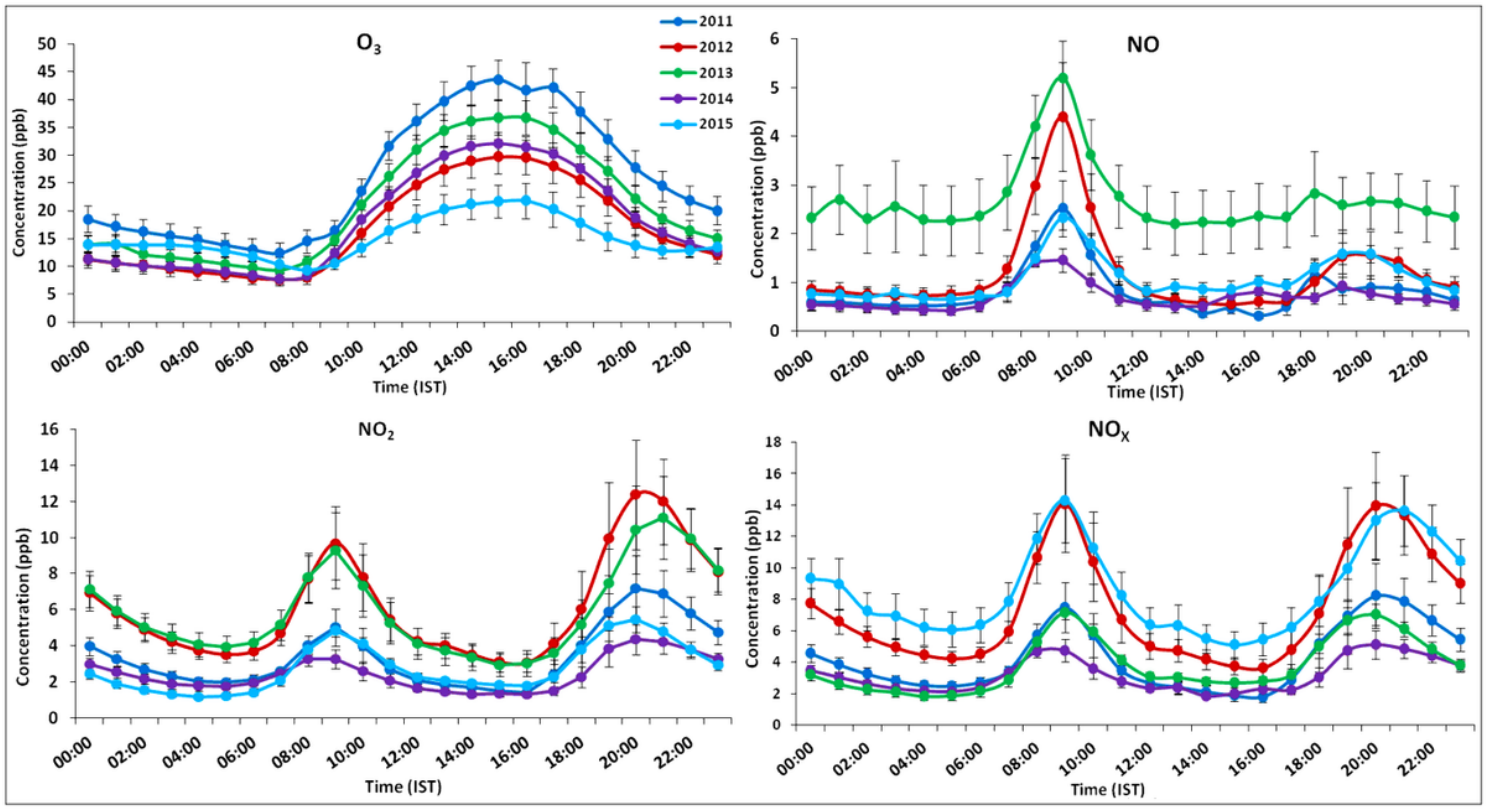

Figure 2

Diurnal variation of O3 and its precursors (NO, NO2, NOx) at Mohal in the north-western Indian Himalaya.

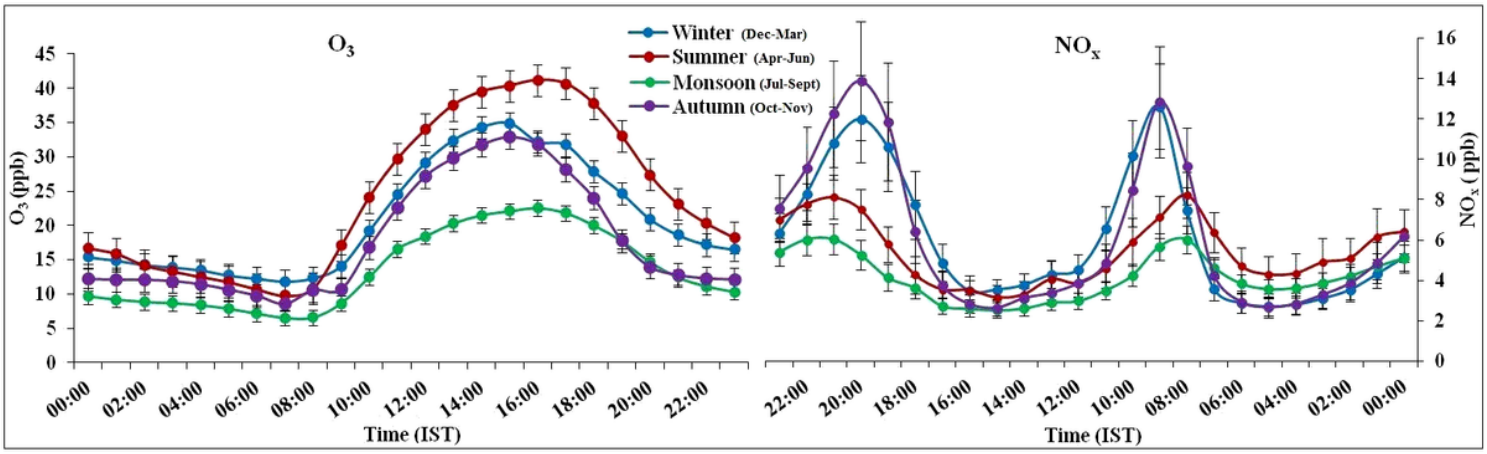

Figure 3

Diurnal variation of trace gases at Mohal in the north-western Indian Himalaya: (a) O3, and (b) NOx.

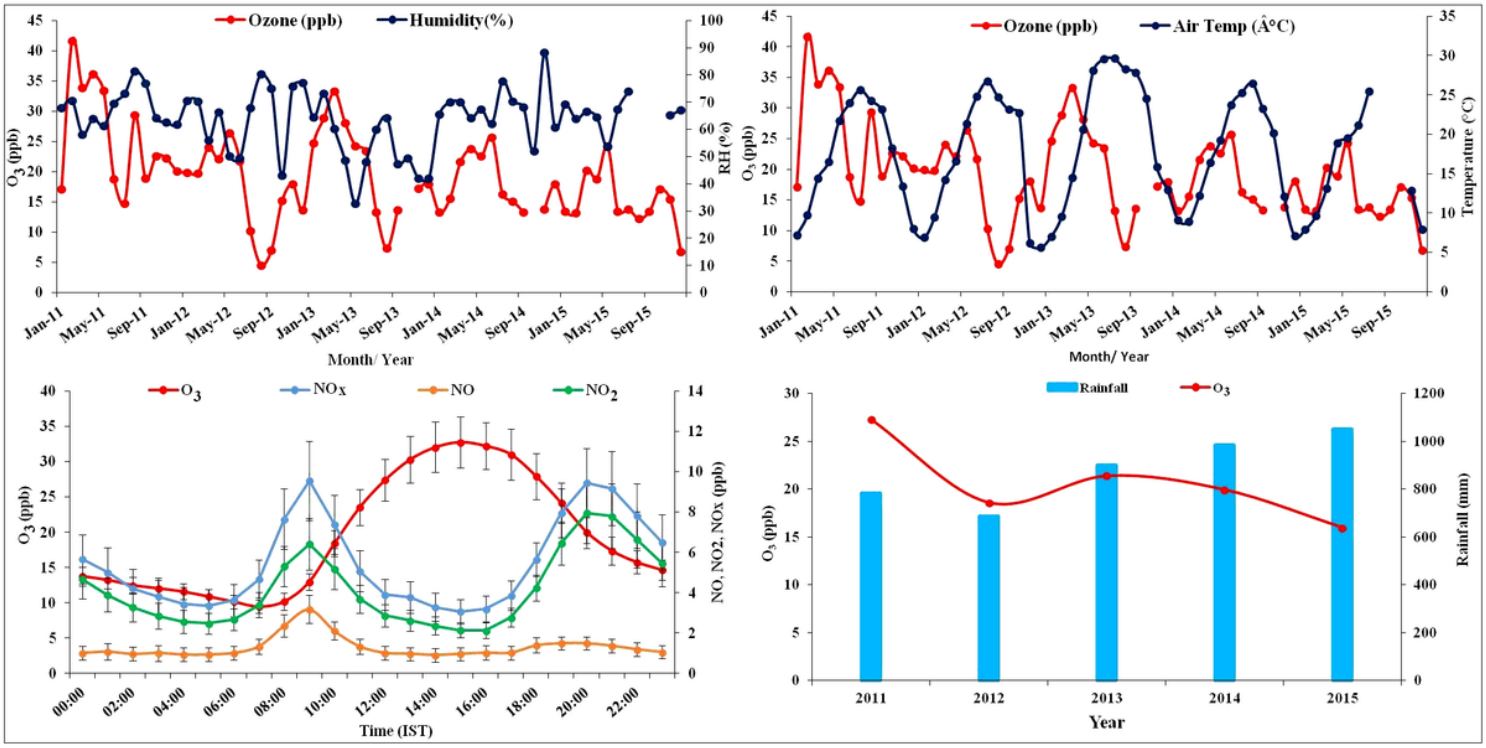

Figure 4

Surface ozone (O3) behaviour with meteorological parameters at Mohal: (a) humidity, (b) air temperature, (c) NO, NO2, NOx and (d) rainfall.

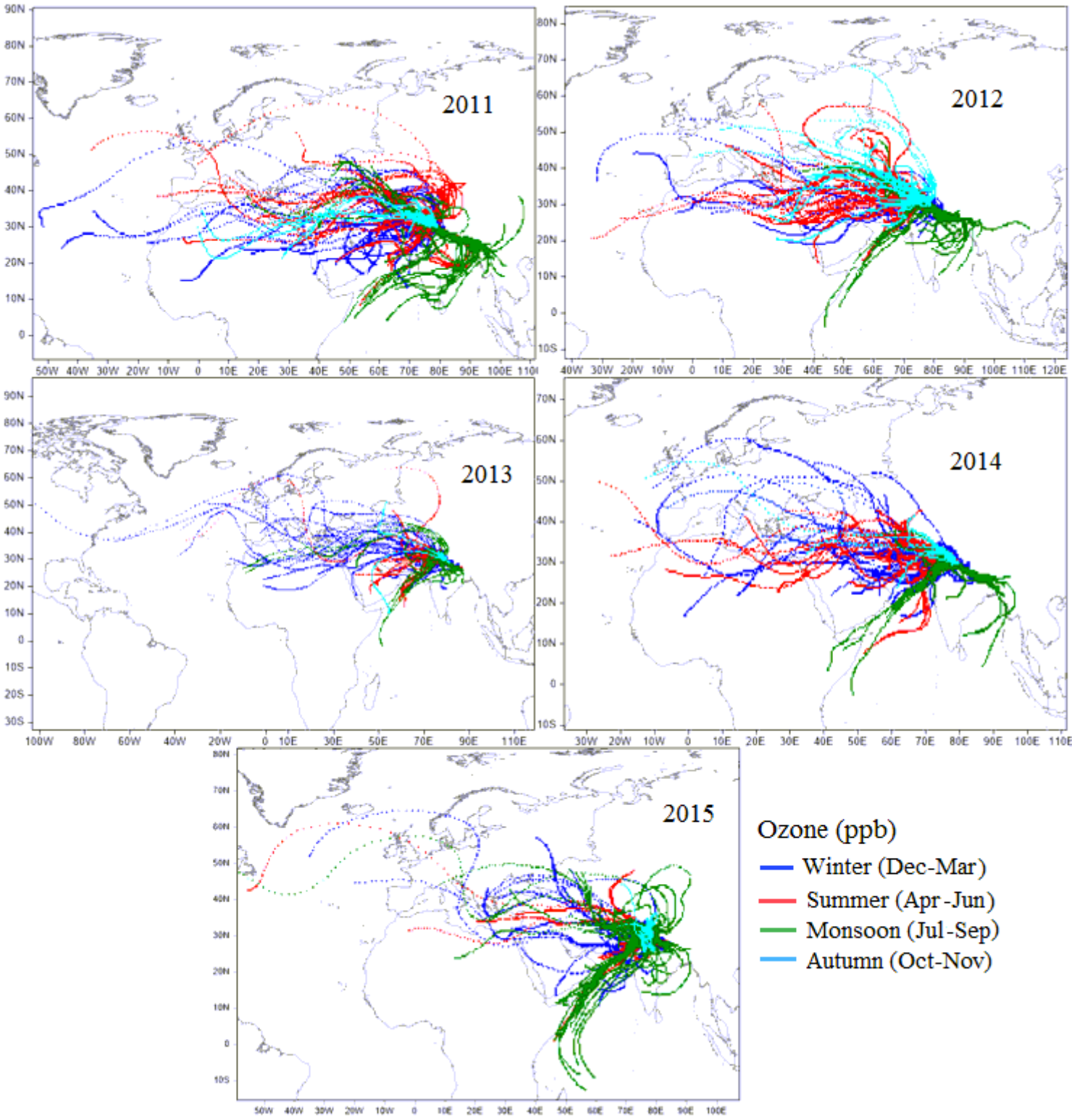

Figure 5

Concentrated Weighted Trajectory (CWT) analysis for identifying sources of surface ozone. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

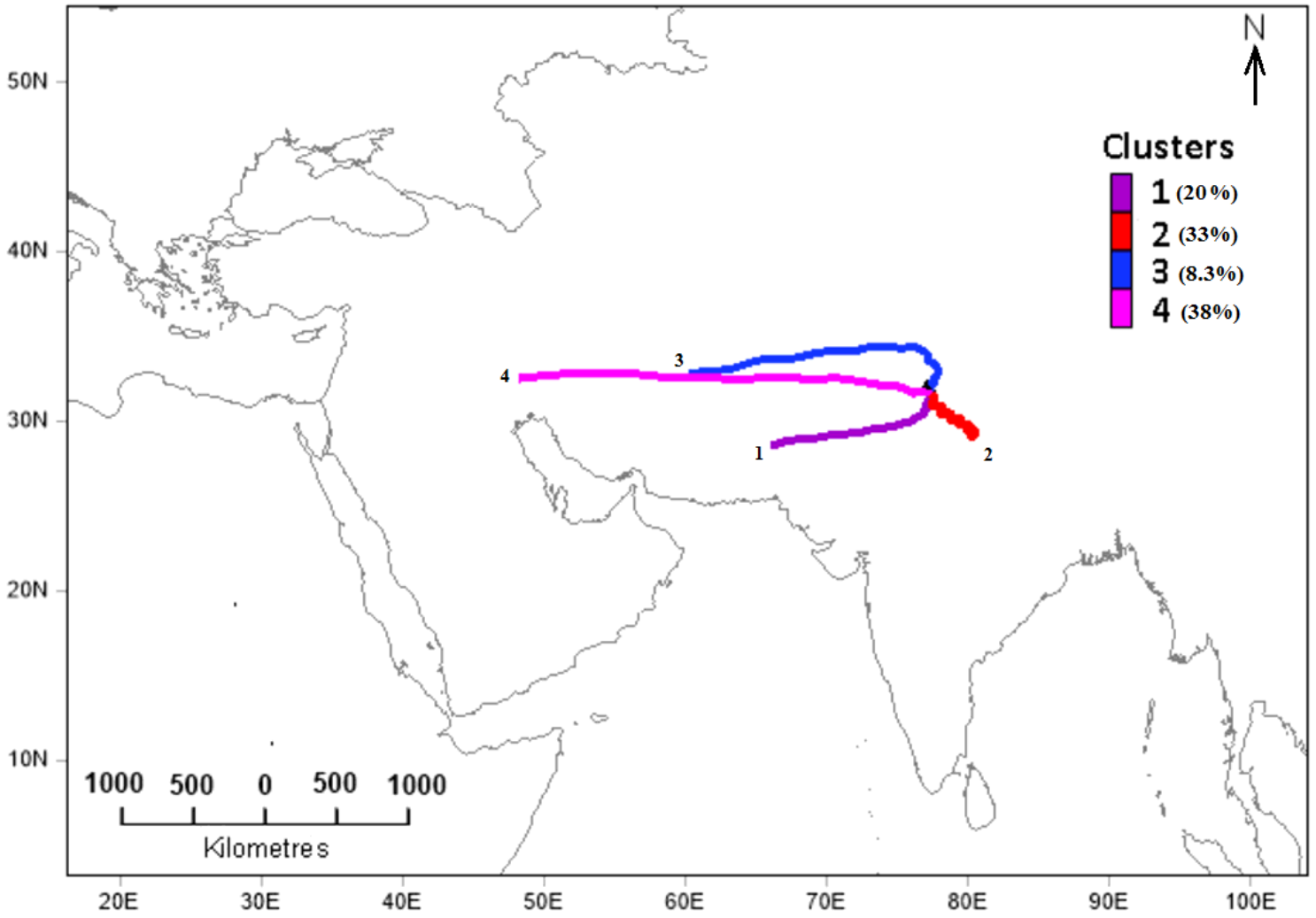

Figure 6

Cluster analysis of air mass at the receptor site- Mohal-Kullu for five years (January 2011 to December 2015). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.