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Phase-wise analysis of the COVID-19 lockdown impact on aerosol, radiation and trace gases and associated chemistry in a tropical rural environment

Chaithanya D. Jain *, B.L. Madhavan, Vikas Singh, P. Prasad, A. Sai Krishnaveni, V. Ravi Kiran, M. Venkat Ratnam

National Atmospheric Research Laboratory, Gadanki, 517 112, India

ARTICLE INFO

Keywords:
COVID-19
Lockdown
Air quality
Aerosol
Radiation
Trace gases
Chemistry

ABSTRACT

Phase-wise variations in different aerosol (BC, AOD, PM$_{1}$, PM$_{2.5}$ and PM$_{10}$), radiation (direct and diffused) and trace gases (NO, NO$_{2}$, CO, O$_{3}$, SO$_{2}$, CO$_{2}$ and CH$_{4}$) and their associated chemistry during the COVID-19 lockdown have been investigated over a tropical rural site Gadanki (13.5° N, 79.2° E), India. Unlike most of the other reported studies on COVID-19 lockdown, this study provides variations over a unique tropical rural environment located at a scientifically strategic location in the Southern Indian peninsula. Striking differences in the time series and diurnal variability have been observed in different phases of the lockdown. The levels of most species that are primarily emitted from anthropogenic activities reduced significantly during the lockdown which also impacted the levels and diurnal variability of secondary species like O$_{3}$. When compared with the same periods in 2019, short-lived trace gas species such as NO, NO$_{2}$, SO$_{2}$ which have direct anthropogenic emission influence have shown the reduction over 50%, whereas species like CO and O$_{3}$ which have direct as well as indirect impacts of anthropogenic emissions have shown reductions up to 10%. Long-lived species (CO$_{2}$ and CH$_{4}$) have shown negligible difference (<1%). BC and AOD have shown reductions over 20%. Particulate Matter (1, 2.5 and 10) reductions have been in the range of 40 to 50% when compared to the pre-lockdown period. The changes in shortwave downward radiation at the surface, diffuse component due to the scattering and diffuse fraction have been +2.2%, 4.1% and -2.4%, respectively, in comparison with 2019. In contrast with the studies over urban environments, air quality category over the rural environment remained same during the lockdown despite reduction in pollutants level. All the variations observed for different species and their associated chemistry provides an excellent demonstration of rural atmospheric chemistry and its intrinsic links with the precursor concentrations and dynamics.

1. Introduction

COVID-19 pandemic has been a catastrophe for mankind around the world. It has been first detected in Wuhan, China during late 2019 and has since spread to other countries across the globe. COVID-19 has induced unprecedented containment strategies to stop its spread. Lockdown of the cities or entire countries to restrict the people’s movement has been one among them, which on the other hand temporarly resulted in air quality improvement (Nakada and Urban, 2020; Navinya et al., 2020; Sharma et al., 2020; Singh et al., 2020; Xu et al., 2020a). Two major sources of anthropogenic emissions viz., industrial set-ups and transport (public as well as private) have been restricted only to the essential services and that resulted in significant reduction of emissions. Globally China first started the lockdown to contain the spread followed by Japan, Singapore, South Korea, European countries, USA and other countries including India as the virus spread globalized (Jain and Sharma, 2020). India went to a complete lockdown starting on 25 March 2020 for 21 days (Phase I) and then extended the lockdown until the end of May in 3 additional phases namely, 15/04 to 03/05 (Phase II), 04/05 to 17/05 (Phase III) and 18/05 to 31/05 (Phase IV) (MHA, 2020). More details on India lockdown in Supplementary Table S3.

In the recent years air pollution has become a global concern and there are many negative impacts of air pollution on public health (Manisalidis et al., 2020). Most of the countries irrespective of their socio-economic status are facing the air quality management challenges. More often it is the tradeoff between development and environmental protection policies. Majority of the megacities around the world are...
reported to be having poor air quality levels (Gulia et al., 2015; Singh et al., 2020). On the other hand, the health conditions associated with the air pollution have been reported to be conducive for the COVID-19 infection and its increased risk of severity (Bashir et al., 2020; Ogen, 2020) however more research is required to establish this relation (Pisoni and Van Dingenen, 2020). The lockdown due to COVID-19 crisis has provided a unique scenario to assess the impact of developmental and social economic activities on the air quality. Even though this scenario is completely temporary but has demonstrated its effect on air quality across the globe. For example, China in general reported to have poor air quality (Wang and Hao, 2012) in its megacities but many studies reported from China have shown the significant improvement in air quality during the COVID-Lockdown (Shi and Brasseur, 2020; Xu et al., 2020a, 2020b). Three major cities in the central China’s Hubei Province, Wuhan, Jingmen and Enshi showed a major reduction in the emissions of pollutants and improvement in their Air Quality Index (AQI) by 32.2%, 27.7%, and 14.9%, respectively, during the lockdown period (Xu et al., 2020a, 2020b). In a more broader study taking data from 1641 China National Environmental Monitoring Centers across China, Shi and Brasseur (2020) have reported a decrease of 29 ± 22% and 53 ± 10% in PM$_{2.5}$ and NO$_2$ respectively and an increase of O$_3$ concentrations by a factor 2.0 ± 0.7. Similar study from Spain (Europe) reported a reduction of PM$_{10}$ (28 to 31.0%), BC and NO$_2$ (45 to 51%) and an increase of O$_3$ (33% to 57%) in Barcelona (Tobías et al., 2020). Another study from Brazil (South America) has also shown the concentration decrease in NO (up to ~77.3%), NO$_2$ (up to ~54.3%), and CO (up to ~64.8%) and contrastingly an increase of O$_3$ concentrations by ~30% over São Paulo (Nakada and Urban, 2020).

The lockdown effects on mega cities over Indian sub-continent have also been reported in many studies. In a comprehensive study over India, Singh et al. (2020) estimated the changes in the six criteria air pollutants during the full lockdown (25-March to 3-May) across India at 134 sites in different regions of India. They reported significant decline for PM$_{2.5}$ and PM$_{10}$ (40–60%); NO$_2$ (40–70%) and CO (20–40%); mixed behavior for SO$_2$ and O$_3$. They found decline in PM$_{2.5}$, PM$_{10}$ and NO$_2$ throughout the day whereas O$_3$ has been found to decrease during the day but increase in the night over Indo Gangetic Plain (IGP). Sharma et al. (2020) after analyzing the data from 22 cities covering different regions of India reported an overall 43%, 31%, 10%, and 18% reduction in PM$_{2.5}$, PM$_{10}$, CO, and NO$_2$ observed during lockdown period resulting in improvement of AQI by 44, 33, 29, 15 and 32% in north, south, east, central and western India, respectively. Another study covering five megacities of India; Delhi, Mumbai, Chennai, Kolkata, and Bangalore (Jain and Sharma, 2020) has also highlighted a statistically significant decline in all the pollutants except for O$_3$. The concentrations of PM$_{2.5}$, PM$_{10}$, NO$_2$ and CO have been declined by ~41, ~52, ~51 and ~28%, respectively, during the lockdown phase. One more study focusing on megacity Delhi also showed similar results with the reduction of PM$_{10}$ and PM$_{2.5}$ as high as about 60% and 39% respectively (Mahato et al., 2020). Among other pollutants, NO$_2$ (~52%) and CO (~30%) have also been reduced over Delhi during lockdown phase. About 40–50% improvement in AQI has been observed just after four days of start of the lockdown Phase 1. Satellite based observations have also shown a significant reduction in the tropospheric NO$_2$ vertical column densities (VCDs), mainly over the urban areas of India (Biswal et al., 2020). Similar reductions in NO$_2$ and SO$_2$ are also reported by Ratnam et al. (2020) using satellite measurements covering complete India. Interestingly they also showed reduction of 50–60% in AOD over north part of India covering IGP region but significant increase over Central India and attributed this to the natural processes.

All these pollutants species are short-lived species and have a direct linkage to the traffic and other anthropogenic emissions. There are other studies (Le Quéré et al., 2020; Safarian et al., 2020) which have predicted a reduction in the emissions of long-lived greenhouse gas species (impact on climate change) like CO$_2$ by 7% for the year 2020 as a result of COVID19-Lockdown. Along with the reduction in emissions the meteorological parameters like boundary layer, temperature and humidity also play an important role in deciding the concentration variability of these species (Ratnam et al., 2020).

Most of the studies summarized above have concentrated on the quantitative effects of lockdown in urban environments considering the restriction of public and to the best of our knowledge there are no studies which focused on the impact of the COVID-19 lockdown over the rural environment in India. It should be noted that there are differences in the tropospheric chemistry of urban and rural environments (Harrison, 2018) which has intrinsic links with reactive species concentrations and dynamics. For example, O$_3$ levels are higher in rural areas than in cities because O$_3$ can be scavenged by the compounds (NO$_x$) by which it is also formed. This scavenging occurs more often in cities than in rural areas, because there is more NO in cities (National Research Council, 1992). Therefore, the impact of lockdown on O$_3$ chemistry in rural environments may be different when compared to the urban environment. Such differences in urban and rural environments motivated to look at the lockdown effects (in a tropical rural site Gadanki) on the quantitative changes in trace gases, greenhouse gases, aerosols, and surface radiation, their diurnal variability and their chemical reactivity. Some of the observed data sets have also been inter-compared with the satellite measurements for the same time period.

2. Site description, measurements and data sets

2.1. Observation site

NARL, situated at Gadanki (13.5°N, 79.2°E, 375 m asml), specializes in atmospheric research on various topics starting from the surface to the ionosphere. A wide variety of sophisticated instruments used in atmospheric probing are collocated under the same strategic location (Jayaraman et al., 2010). Gadanki is a tropical rural site (Gadhavi et al., 2015; Jain et al., 2019; Ravi Kiran et al., 2018; Renuka et al., 2014) located far from urban influence in the Southern Indian peninsula. The site is nearer to the Eastern Ghats with ~100 km distance from Bay of Bengal coast. Two major metropolitan cities of southern India viz., Bengaluru and Chennai are at ~250 and ~150 km distance from the site, respectively. The outline map of the observation site is shown in Supplementary Fig. S1. While the site has minimal influence of the urban sources, there exist a significant number of paddy fields and animal husbandry around Gadanki. The activities of biomass burning of agricultural residue, wood burning, and forest fires are occasionally observed in the nearby villages (Jain et al., 2018, 2019). Moderate to heavy traffic on the adjacent highway (~500 m west of observation site, connecting Chittoor and Tirupati) with a considerable portion being heavy-duty trucks are common. Winds at the site are mostly north-easterly during the winter season (December-January-February) and, south-westerly and south easterly during the summer season (March–April-May) (Ratnam et al., 2008).

2.2. Measurement data

Trace gases (NO, NO$_2$, CO, O$_3$ and SO$_2$) have been measured by Trace Gas Analyzers; Green House Gases (CH$_4$ and CO$_2$) have been measured by a Cavity Ring-Down Spectrometer (CRDS), PM$_1$, PM$_{2.5}$ and PM$_{10}$ have been measured by PM sensor, Black Carbon (BC) by Aethalometer. Radiation parameters (Global Horizontal Irradiance - GHI and Diffuse Horizontal Irradiance – DHI) have been obtained by Pyranometer and Aerosol Optical Depth (AOD) has been obtained by Sky Radiometer. Supplementary Table S1 lists the percentage availability of all the data sets (daily data) during different phases considered for the present study.

Detailed description of the instrumentation used in this study has been given in the supplementary section S1. Briefly it can be put here as; Trace gas analyzers use non dispersive absorption spectroscopy technique for the continuous measurements of the respective species, CRDS
is based on the adaptation of Lambert Beer law using an optical cavity to see the decay of the light in it. PM sensors use light scattering method and are able to detect the particles with aerodynamic diameter of 0.3–10 μm. They can infer the real time mass concentrations of PM1, PM2.5, PM10 based on the confidential proprietary algorithm (Kelly et al., 2017). Aethalometer works on the principle of measuring the attenuation of the transmitted light at seven wavelengths (viz., 370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm and 950 nm) through a quartz fiber filter tape loaded with aerosol particles on it. Pyranometer is a thermopile based sensor used for the measurement of global radiation received from the sun. Pyranometer uses the Sun tracking system consisting of a shading ball assembly for the shortwave incoming radiation measurements. Sky radiometer is an automatic ground-based radiometer measuring the direct solar radiation at 1 min interval and diffuse sky radiance with a 1° field-of-view with respect to the Sun at 10 min interval. Both the direct and diffuse sky radiances are used to retrieve the aerosol optical depth at 5 wavelengths, viz., 400, 500, 675, 870 and 1020 nm. AOD is retrieved using the SKYRAD package (SKYRAD.PACK, version 5.0) as detailed in Nakajima et al. (1996).

All the above instruments have been calibrated against the NIST traceable standards following the recommended procedures. The calibration factors have been applied on the measured data to ensure the data quality before going ahead with the analysis and interpretation. A consolidated list of all the different instruments used in the present study along with the salient specifications and further references to get more details are given in Table 1.

Daily mean MODIS AOD at 550 nm (MOD08_D3 C6 Level 3) and OMI Tropospheric Column NO2 (OMNO2d v003) over Gadanki region (12.5°-14.5° N, 78.5°-80.5° E) during 2019 and 2020 have been obtained from NASA’s Giovanni portal (https://giovanni.gsfc.nasa.gov/).

2.3. Meteorological data

Meteorological parameters such as Temperature (T), Relative Humidity (RH), Wind Speed (WS) and Atmospheric Boundary Layer (ABL) height have been taken from ERA5 Global reanalysis data sets (Hersbach et al., 2020) with a grid resolution of 0.25° x 0.25° keeping Gadanki at the centre. The European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalysis provides global atmospheric parameters covering the time period from 1979 to present with 1-h temporal resolution, ~31 km spatial resolution (0.25° x 0.25°) and 137 vertical pressure levels with a top level at 0.01 hPa.

2.4. Data period and methodology

In this study, the data period has been considered from 1-February-2020 to 31-May-2020. However while calculating the pre-lockdown averages, only five weeks prior to start of the lockdown has been used in order to minimize the meteorological impacts as the transition from winter to summer season occurred during the same time at Gadanki. Therefore the time period categories used in this study fall as pre-lockdown (15/02 to 21/03) and lockdown Phase I (25/03 to 14/04), Phase II (15/04 to 03/05), Phase III (04/05 to 17/05), Phase IV (18/05 to 31/05) and whenever it is mentioned lockdown it means total lockdown period (25/03 to 31/05). Some period data sets from 2019 have been used for the inter-comparison with 2020 to better understand the variations. Data sets of 22–24 March have been excluded in the study to avoid the impacts of partial lockdown and relaxations (22 March had been a voluntary lockdown across India, whereas during 23–24 March there had not been any lockdown).

The percentage changes in 2020 for different atmospheric parameters when compared with 2019 have been calculated by taking the difference between the 2019 and 2020 in respective time periods (Pre-lockdown, Phase I, Phase II and Phase IV). However for PM, data has not been available for 2019 and the changes have been calculated with respect to the pre-lockdown period. Diurnal variations of meteorological and atmospheric parameters have been compared (between 2019 and 2020) after taking the difference between pre-lockdown and lockdown period in the respective years.

3. Results

3.1. Meteorological parameters during lockdown

Fig. 1 (a) shows the mean diurnal variations of the meteorological parameters and their differences during pre-lockdown and lockdown taken from ERA5 data sets for the years 2019 and 2020. Diurnal variations show a strong influence of solar irradiation during the day time.
Fig. 1. (a) Diurnal variations of the meteorological parameters (averaged) at Gadanki obtained from ERA5 for the pre-lockdown (15/02 to 21/03) and lockdown (25/03 to 31/05) periods for 2019 and 2020. Differences represent the changes between the pre-lockdown and lockdown periods for the corresponding years. Shaded area represents the standard error. (b) Changes in the pre-lockdown and lockdown when compared to 2019.
(typical for a tropical hot and humid rural location). As a result Temperature (T), Wind Speed (WS) and Atmospheric Boundary Layer (ABL) height all show the daily maximum (late in the afternoon ~16:00 IST) whereas, Relative Humidity (RH) shows the daytime minimum and night time maximum. The diurnal variation in temperature follow similar variations during the pre-lockdown and lockdown periods in 2019 and 2020 except in 2020 night time temperature during the lockdown period has been cooler compared to 2019. ABL evolution too followed similar trends like T, however 2019 ABL evolution in the morning has been much sharper and the peak ABL height has been higher than 2020. ABL height has been comparatively higher during the lockdown period in both the years which is the result of higher temperatures compared to pre-lockdown period. This higher ABL height would contribute to the reduction in surface concentrations of aerosols and trace gases besides the local emissions. WS showed the minimal difference in its diurnal variation when compared between 2019 and 2020. Diurnal variation in RH during 2020 showed increase in both pre-lockdown and lockdown periods. In 2019, between the pre-lockdown and lockdown, there has been constant negative bias (owing to the diurnal temperature increase from pre-lockdown to lockdown) in RH during complete diurnal cycle except for a short period (around the peak temperature time of the day) in the late afternoon where it came close to the pre-lockdown value. Whereas in 2020, the variation in RH has been slightly different. It has been very close to pre-lockdown and during the night and the difference gradually increased during the day time as the temperature increased.

When compared quantitatively between 2019 and 2020 (Fig. 1(b)), T, ABL height and WS have shown decrease from 2019 to 2020 in both pre-lockdown and lockdown periods. All the comparative differences with the mean values for different parameters have been summarized in Table 2. Considering the fact that these are model reanalysis data sets (with significant uncertainty), and the observed changes falling within the standard deviation (Table 2) it can be assumed that meteorological conditions have been comparable in spite of differences between 2019 and 2020. Comparable meteorological parameters have also been reported by other studies during COVID-19 lockdown over India (Navinya et al., 2020; Sharma et al., 2020; Singh et al., 2020).

### 3.2. Impact of lockdown on trace gases (NO, NO₂, CO, O₃, SO₂, CO₂ and CH₄)

Fig. 2 shows the phase-wise statistical distribution of observed trace gas concentrations for the years 2019 and 2020. Time series of the trace gases (for 2019 and 2020) during the measurement period has been shown in Supplementary Fig. S2. In general most of the trace gas species have shown significant reduction during the lockdown period. In the pre-lockdown period the differences (compared to 2019) for NO, NO₂, CO₂ and CH₄ have been comparable with 2019 (~<3% change) except for CO, O₃ and SO₂. CO has shown an increase (~9%) whereas O₃ has shown slight decrease (~5%) and SO₂ has shown substantial decrease (~40%). In the Phase I (when strict restrictions on all the non-essential activities have been on) all the other trace gases except CO₂ and CH₄ have shown a significant decrease. Quantitatively the reductions for NO, NO₂ and SO₂ have been in excess of 50%, for CO and O₃ have been in excess of 8% while CO₂ and CH₄ have shown the increase of 1–2%. Similar trend continued NO, NO₂, SO₂, CO₂ and CH₄ in the Phase II but CO reduced by 3.8%, whereas O₃ increased by 9.8%. O₃ showed a substantial increase in its concentration. Phase III has seen the decrease in all the trace gases. Even though CO₂ and CH₄ decreased but the decrease has been negligible. In the Phase IV, when many relaxations have been allowed, the concentrations of most of the gases (except NO, SO₂) increased, leading to reduction in the percentage difference. Overall, during the lockdown all the short lived species (dominated by anthropogenic emissions) have shown the substantial reduction in their concentration while long lived more stable species such as CO₂ and CH₄ have shown minimal difference.

NO₂ concentrations obtained over the Gadanki region from the Aura OMI satellite have also shown similar variations. Supplementary Fig. S3 (a) shows the statistical variations of OMI NO₂ for the years 2019 and 2020 during pre-lockdown and at different lockdown phases (I-IV). The changes from 2019 to 2020 in OMI NO₂ data have been ~–18.9%, –33.6%, –30.2%, –28.5%, –39.2% and –30.2% for pre-lockdown, Phase I, Phase II, Phase III, Phase IV and lockdown period, respectively. It is worth to recall that both these independent observations show similar decreasing trends in the concentrations. Satellite measurements of NO₂ cannot be compared directly with ground measurements, as the former is the area averaged concentration for the complete tropospheric altitudes whereas the latter is for the surface. Further, the discrepancies between the surface measurements and satellite observations can be expected due to the differences in the way they are obtained. Thus, only qualitative comparison has been made. All the observed quantitative changes in trace gases have been summarized in Table 3.

#### 3.3. Impact of lockdown on aerosol parameters (PM₁₀, PM₂.₅, PM₁₀, BC and AOD)

Fig. 3 shows the phase-wise changes in PM₁₀, PM₂.₅, PM₁₀, BC and AOD. Time series of BC, AOD (for 2019 and 2020), and PM (only 2020) during the measurement period has been shown in Supplementary Fig. S4. There have been significant reductions in BC, AOD, and PM during the lockdown period in 2020. When compared with 2019 (phase-wise), BC showed the changes in the range of –65% to +24%. There has been an increase for BC in the pre-lockdown period but during lockdown BC has reduced. Like in trace gases, BC also showed the maximum decrease in Phase III of the lockdown and the difference decreased in the Phase IV. AOD obtained from the sky radiometer measurements showed the decrease in all phases. Phase-wise AOD changes have been in the range of –5% to –55%; AOD has also shown the maximum change in Phase III of the lockdown and difference reduced significantly in the Phase IV. Supplementary Fig. S3 (b) shows the comparison of AOD obtained for the Gadanki region from the MODIS satellite during 2019 and 2020. The variations have been different from the surface measurements in different phases. The changes at different phases have been in the range from –49% to +23%. Trend in Phase I, III, IV and lockdown has been similar like surface measurements (negative) but pre-lockdown period

### Table 2

Summary of changes in meteorological parameters during the pre-lockdown and lockdown period and, comparison of the same with 2019.

| Parameter       | 2020       | 2019       | % Difference | 2019       | % Difference | % Difference when compared to 2019 |
|-----------------|------------|------------|--------------|------------|--------------|----------------------------------|
|                 | Pre Lockdown | Lockdown   | % Difference | Pre Lockdown | Lockdown     | % Difference in Difference (approx. %) |
| Temperature (°C) | 25.7 ± 1.6  | 28.7 ± 1.3 | +11.7        | 27.5 ± 1.5 | 31.3 ± 1.7  | +13.8                           | –6.5 | –8.3 | –2.1 |
| Relative Humidity (%) | 65.6 ± 7.9 | 62.4 ± 8.4 | –4.9         | 58.8 ± 1.2 | 53.5 ± 1.2  | –9.0                            | +11.6 | +16.4 | +4.1 |
| ABL height (m)   | 742.1 ± 163.2 | 778.2 ± 209.4 | +4.9       | 880.5 ± 214.0 | 952.9 ± 249.0 | +8.2                         | –15.7 | –18.3 | –3.3 |
| Wind Speed (m/s) | 2.13 ± 0.49 | 2.0 ± 0.62 | –6.2         | 2.35 ± 0.68 | 2.11 ± 0.81 | –10.2                           | –9.4 | –5.2 | +4.0 |
a little bit because NO concentrations have been very close to the detection limit of the instrument. There has been a significant change (qualitatively) but quantitative MODIS AOD retrieval (Kiran Kumar et al., 2013). Further, Sai Suman of Sky Radiometer AOD increases. This underestimation has been reported that the correlation between MODIS and Sky Radiometer AODs at Gadanki has improved significantly for different seasons and with different phases of the lockdown, PM1 changes have been in the range of −13% to −70%, PM2.5 showed the changes in the range −17% to −75% and PM10 in the ranges of −20% to −78%. Overall lockdown

and Phase II values from the satellite data showed an increase. Despite high accuracy of ground-based AOD measurements, the spatial coverage is only possible through satellite retrievals. Recently, Madhavan et al. (2021) reported that the correlation between MODIS and Sky Radiometer AODs at Gadanki has improved significantly for different seasons but with a systematic underestimation of MODIS AOD as the magnitude of Sky Radiometer AOD increases. This underestimation has been attributed to the usage of less absorbing type aerosol model in the MODIS AOD retrieval (Kiran Kumar et al., 2013). Further, Sai Suman et al. (2014) indicated that a more absorbing aerosol model could replicate the fine mode aerosols while less absorbing model with coarse sea-salt particles as appropriate for coarse mode aerosols towards reducing the uncertainty in MODIS retrievals over Southern India.

Particulate matter data for 2019 has not been available (started November 2019) for the study period. Therefore pre-lockdown period has been considered as the reference as adopted by other studies (Shi and Brasseur, 2020). When compared with the pre-lockdown period different phases of the lockdown, PM1 changes have been in the range of −13% to −70%, PM2.5 showed the changes in the range −17% to −75% and PM10 in the ranges of −20% to −78%. Overall lockdown

Fig. 2. Changes in the trace gas concentrations as the lockdown imposition extended from the first phase (Phase I, 25/03 to 14/04), to the second phase (Phase II, 15/04 to 03/05), third phase (Phase III, 04/05 to 17/05) and the IV Phase (Phase IV, 18/05 to 31/05). ‘Pre’ represents the pre-lockdown period (15/02 to 21/03).

Table 3
Summery of the observed concentration changes during the pre-lockdown and lockdown period and comparison of the same with 2019. *Differences in NO might vary a little bit because NO concentrations have been very close to the detection limit of the instrument. There has been a significant change (qualitatively) but quantitative uncertainty may be little high. **PM differences have been calculated by taking the reference of pre-lockdown period because of 2019 data unavailability.

| Sl. No. | Parameter       | % change when compared to 2019 |
|---------|----------------|-------------------------------|
|         | Dates ->       | Pre Lockdown | Phase I     | Phase II    | Phase III   | Phase IV    | Total       |
| 1       | *NO            | −0.6           | −63.6        | −72.4       | −37.6       | −48.1       | −55.4       |
| 2       | NO2            | −2.3           | −58.3        | −57.7       | −72.9       | −43.0       | −58.0       |
| 3       | NO3            | −2.4           | −58.9        | −60.7       | −68.1       | −40.5       | −57.0       |
| 4       | CO             | +9.2           | −8.2         | −3.8        | −26.6       | −1.8        | −10.1       |
| 5       | O3             | −5.0           | −9.4         | +9.8        | −34.3       | +5.4        | −7.1        |
| 6       | SO2            | −40.7          | −79.6        | −53.6       | −54.1       | −67.3       | −63.7       |
| 7       | CO2            | +0.9           | +1.4         | +0.9        | −0.1        | +0.9        | +0.8        |
| 8       | CH4            | +2.4           | +2.6         | +1.2        | −0.6        | +1.2        | +1.1        |
| 9       | BC             | +24.1          | −6.8         | −43.6       | −65.4       | −21.0       | −34.2       |
| 10      | AOD            | −6.2           | −5.2         | −21.3       | −55.2       | −9.7        | −22.9       |
| 11      | GHI            | −0.7           | +1.4         | +1.9        | +12.4       | −3.8        | +2.2        |
| 12      | DHI            | 0.0            | −6.6         | −19.0       | −7.6        | +17.7       | −4.1        |
| 13      | Diffuse Fraction | 0.0         | +9.7         | +18.2       | +17         | −20.9       | −2.4        |
| 14      | AOD (Modis)    | +22.6          | −17.3        | +12.1       | −49.2       | −12.8       | −16.8       |
| 15      | NO2 (OMI)      | −18.9          | −33.6        | −30.2       | −28.5       | −39.2       | −30.1       |
| 16      | PM1            | NA             | −13.0        | −45.0       | −69.9       | −35.0       | −40.9       |
| 17      | **PM2.5        | NA             | −16.7        | −52.0       | −75.5       | −42.7       | −46.7       |
| 18      | **PM10         | NA             | −19.7        | −56.3       | −78.2       | −47.2       | −50.4       |
Fig. 3. Changes in BC and PM concentrations along with the observed AOD as the lockdown imposition extended from the first phase (Phase I, 25/03 to 14/04), to the second phase (Phase II, 15/04 to 03/05), third phase (Phase III, 04/05 to 17/05) and the IV Phase (Phase IV, 18/05 to 31/05). ‘Pre’ represents the pre-lockdown period (15/02 to 21/03). PM data is not available for 2019.

Fig. 4. Changes in GHI, DHI, and diffuse fraction (i.e., DHI/GHI) as the lockdown imposition extended from the first phase (Phase I, 25/03 to 14/04), to the second phase (Phase II, 15/04 to 03/05), third phase (Phase III, 04/05 to 17/05) and the IV Phase (Phase IV, 18/05 to 31/05). ‘Pre’ represents the pre-lockdown period (15/02 to 21/03).
period the changes in PM concentrations when compared to pre-lockdown phase have been $-40.9\%$, $-46.7\%$, and $-50.4\%$ for PM$_1$, PM$_{2.5}$, and PM$_{10}$, respectively. There has been a substantial decrease in the concentrations compared to the pre-lockdown phase in all the 3 PM sizes. Like other atmospheric parameters Phase III has seen the highest decrease among the different phases. Phase-wise quantitative differences in aerosol parameters have been listed in Table 3.

Fig. 5. Diurnal variations (averaged) of trace gases observed at Gadanki for the pre-lockdown (15/02 to 21/03) and lockdown (25/03 to 31/05) periods for 2019 and 2020. Differences represent the changes between the pre-lockdown and lockdown period for the corresponding years. Shaded area represents the standard error.
3.4. Impact of lockdown on shortwave surface radiation

Shortwave downward radiation at the surface (or GHI) is a combination of direct solar beam component and diffuse component (or DHI) due to the scattering from atmospheric constituents and reflected from clouds. The statistical distribution of the daily mean GHI, DHI, and the diffuse fraction (i.e., DHI/GHI) for different time periods of 2019 and 2020 is shown in Fig. 4. It should be noted that the diffuse fraction is an indirect measure of the sky condition. Higher diffuse fraction (~1.0) refers to overcast sky condition while the lower values (~0.2) denote clear skies with stable background contribution representative of the observation location. Although the range of variability of GHI differs slightly, the median values have been observed to be comparable before the lockdown period for both 2019 (443 W m$^{-2}$) and 2020 (440 W m$^{-2}$). Similarly the range of variability and median values of DHI are found to be comparable before lockdown period for both 2019 (165 W m$^{-2}$) and 2020 (164 W m$^{-2}$). During the lockdown periods, the median values of GHI have been found to be higher by 7 W m$^{-2}$ (Phase I), 10 W m$^{-2}$ (Phase II), 51 W m$^{-2}$ (Phase III) in comparison with those in 2019. This is consistent with the observed decrease in DHI values by 10 W m$^{-2}$ (Phase I), 40 W m$^{-2}$ (Phase II), and 17 W m$^{-2}$ (Phase III) during 2020 in comparison with those in 2019. While the median of diffuse fraction has been the same (0.39) before lockdown period for both 2019 and 2020, there has been a considerable reduction of the diffuse fraction by 3% (Phase I), 8% (Phase II) and 9% (Phase III) in comparison with those in 2019. However, the phase IV lockdown period showed a reduction (~17 W m$^{-2}$) in median value of GHI during 2020 due to increased DHI (~35 W m$^{-2}$) and diffuse fraction (from 0.42 to 0.52). Further details on the observed relative change (%) in the GHI, DHI and diffuse fraction are given in Table 3.

3.5. Impact of lockdown on the diurnal variation of the pollutants

A more detailed diurnal analysis of the observed trace gases would help in better understanding of the changes occurred during the lockdown period. Most of the studies summarized in the introduction (of this article) focused on the overall changes in trace gas concentrations before and during the lockdown. However, there have been few studies which reported the diurnal changes too. To the best of our knowledge, there are two studies by Shi and Brasseur (2020) and Singh et al. (2020), where the authors have discussed the changes in the diurnal variations during the lockdown period in 2019. However, the phase IV lockdown period showed a reduction (~17 W m$^{-2}$) in median value of GHI during 2020 due to increased DHI (~35 W m$^{-2}$) and diffuse fraction (from 0.42 to 0.52). Further details on the observed relative change (%) in the GHI, DHI and diffuse fraction are given in Table 3.

The diurnal variation (2019) where the difference in the diurnal variations of pre-lockdown and lockdown period in 2019 was mostly positive (except CO, which has been always negative, indicating the overall decrease in CO concentration from the per-lockdown period to lockdown, starting from the post-midnight hours (01:00-02:00 IST) until early morning (10:00-11:00 IST). After that when the photochemistry and increased boundary layer height (Fig. 1) came into effect, the difference shifted towards subzero. During the summer season Gadanki experiences more solar radiation and hence the hot weather, which increases the photochemistry as well as boundary layer expansion when compared to the pre-lockdown period. This effect lasted until midnight. Such a scenario has been completely changed during the year 2020. The differences of these species before and during the lockdown time never became positive and always stayed negative (%). The impact of these variations has also been transferred on the secondary species such as O$_3$. In 2019 the O$_3$ experienced a sharp decline in its concentrations in the early morning hours but such decline has never been observed in 2020 diurnal variations instead, O$_3$ steadily increased throughout the night and peaked during the early morning hours.

On the other hand SO$_2$ showed enhanced daytime increase in the concentrations during the lockdown time window in 2019, which may depend on many factors like local emissions (Datta et al., 2010; Lin et al., 2012). However, that day time increase has been significantly low during the lockdown period in 2020. SO$_2$ concentration peaks have been entirely different in 2020. SO$_2$ also showed a steady increase throughout the night and showing an early morning peak that had not been there in 2019.

Other more stable and long lived gases such as CO$_2$ and CH$_4$ have not shown any significant differences between 2019 and 2020 diurnal variation for the pre-lockdown and lockdown periods. Their diurnal variability has been mainly driven by the photochemistry and boundary layer dynamics. CO$_2$ has shown positive diurnal variation difference between the pre-lockdown and lockdown in all the hours (for both 2019 and 2020), and this difference has been higher in 2020. Along with the reduction in temperature during 2020 the increased CO$_2$ concentration might have partially induced the RH increase (Fig. 1) as there are reports stating that the positive feedback mechanism works for the CO$_2$ and H$_2$O relationship (Held and Soden, 2000). CH$_4$ has shown slightly lesser values during the night hours in 2020, day time variations have been comparable.

Fig. 6 shows the diurnal variations of BC and PM (1, 2.5 and 10). The difference in BC diurnal variations has been straight forward decreasing during the lockdown period in 2020. During 2019 pre-lockdown and lockdown time windows, diurnal variation has shown minimum percentage difference (close to zero); however that has been increased significantly towards the negative side in 2020. Like trace gas variations, a fumigation peak has been observed (in the early morning hours) in BC at all the times. The diurnal variation in BC has mainly been driven by the boundary layer expansion during day time resulting in lower day time concentrations (Ravi Kiran et al., 2018). Diurnal variation in PM (only for 2020) also showed similar features like BC and the differences between the pre-lockdown and during the lockdown has been significant (well below zero %).
3.6. Impact of local and regional transport during the lockdown

To understand the local and regional transport impacts on the observed concentration changes during the pre-lockdown and lockdown periods, a three-day back trajectory clusters arriving at 500 m agl have been simulated using the NOAA global meteorological reanalysis data. After performing the cluster analysis, Concentration Weighted Trajectory (CWT) analysis has been performed using the TrajStat GIS based software extension to the HYSPLIT which is an useful tool for source identification (Wang et al., 2009). Results show that during the lockdown period local emission impacts have been more dominant compared to the transport. Therefore it may be inferred that the changes observed during the lockdown period at Gadanki have been induced by the changes in the local emission patterns. Fig. 7 shows an example CWT analysis for pre-lockdown and during the lockdown period performed on NO\textsubscript{x}. Concentration weighing has been done on the trajectory clusters by taking the average concentrations observed during the pre-lockdown period and lockdown period to see the potential transport impacts on NO\textsubscript{x}. A higher value in the average weighted concentration (color contour scale) of CWT implies that air parcels traveling over that particular trajectory cluster would be, on average, associated with high concentrations at the receptor (Wang et al., 2009).

4. Discussion

4.1. Composition changes

It is well understood that ambient concentrations of air pollutants are
greatly affected by meteorology with low wind speeds causing a build-up of pollutants. Regional transport of the pollutants from the nearby regions also impacts the observed concentrations. Even though there have been small discrepancies in the meteorological conditions between 2019 and 2020, but they have been comparable. Absolute change wise (for the lockdown period in 2020) Temperature, ABL height and Wind Speed all have decreased while Relative Humidity increased (Table 2). These changes indicated more settled meteorological conditions which might have resulted in more stable atmospheric conditions. Therefore the changes observed in the concentrations have been mainly impacted by the emission changes rather than the meteorology. An evidence for this would be the negligible changes that have been observed in the stable species such as CO₂ and CH₄ (Table 3).

It is clear now that the lockdown has dramatically decreased the anthropogenic emissions and the impacts have been seen on the observed concentrations (Jain and Sharma, 2020; Mahato et al., 2020; Sharma et al., 2020; Shi and Brasseur, 2020; Singh et al., 2020; Wyche et al., 2021). As explained in section 3.1 and 3.2 most of the criteria pollutant concentrations responded negatively to the lockdown through their reductions. Allowed and restricted services/activities have been different during different phases of lockdown. Supplementary Table S3 lists all the services/activities that have been allowed or restricted in each phase of the lockdown (MHA, 2020). It is evident that Phase I and Phase II have been the strictest lockdowns and Phase III and Phase IV have seen various relaxations. Phase I and Phase II have seen maximum possible restrictions on traffic and industrial activities. These changes have been reflected in the observed concentrations but some of them have been delayed in response which extended to the Phase III and IV. Maximum changes (Table 3) have been in the Phase I and Phase II. Phase III also observed changes but there also have been rain events and the changes observed might have been the combined impacts. Most of the changes started reversing in Phase IV as more and more relaxations on anthropogenic activities have been given. Changes in the secondary species such as O₃ followed the NOx variation during different phases.

AOD, BC and PM have also shown similar trends. PM concentration changes have been calculated by taking the pre-lockdown as the reference. Even though the meteorological parameters changed from pre-lockdown to lockdown, the observed changes in PM found to be beyond the changes potentially induced by the meteorological changes. Similar changes have been observed in other parameters (in this study) and other locations (Singh et al., 2020). Therefore, it can be assumed that observed PM changes have also been directly linked to the emission changes and the results confirm the same. The absolute reduction in fine mode particles (PM₂.₅) has been higher (~18 μg/m³) compared to the coarse mode particles (PM₁₀PM₂.₅) (~1.8 μg/m³). Further, significant reductions in BC changes (2.5 μg/m³ → 1.2 μg/m³) have also confirmed that the reductions have been more on finer particles. These findings indicate that the changes observed might have been the result of the reductions in primary pollutant emissions (which have an intrinsic link with the Secondary Organic Aerosol (SOA) formation) due to lockdown anthropopause.

There has been an overall increase (~2%) in GHI and decrease in DHI (~4%). These changes can be significantly influenced by atmospheric aerosols, water vapour and clouds (e.g., Madhavan et al., 2017, 2016). Water vapour is highly variable in space and time with a strong absorption effect (mostly in the infrared beyond 0.9 μm) on the solar radiation components (GHI and DHI). Since water vapour is mainly concentrated in the lower atmosphere, it is considered as the second most important source of extinction of clear sky solar radiation after aerosols (Geyymard, 2014). Obręben et al. (2015) analysed the effect of water vapour content on the downward irradiance at the Earth’s surface, and found that shortwave GHI reaching the surface increases when the water vapour content decreases. In contrast, increase of water vapour in the atmosphere eventually enhances the formation of cloud condensation nuclei and clouds which are able to reflect more incoming solar radiation (i.e., increase in DHI) and thus allowing less energy to reach the Earth’s surface (i.e., decrease in GHI). Another possibility for increased DHI and diffuse fraction results from prevalence of the partly cloudy to overcast sky conditions. While clouds attenuate solar-radiation incidents on cloud shaded areas, sunlit ground surfaces may actually receive more GHI than under a clear sky due to light scattering and reflection from neighbouring clouds (i.e., broken cloud effect). Under thin high cloud conditions, GHI can be higher due to the dominance of DHI. Therefore, the temporal characteristics of GHI and DHI change significantly due to strong regional influences of changing cloud amounts, water vapour, and air quality (or emissions). Overall, it has been clearly evident that the observed increase in GHI and decrease in DHI and diffuse fraction have been a resultant of reduction in emission sources due to strict lockdown norms, decreased cloud cover, and intermittent rain events during Phases I, II and III. However the changes observed in the IV phase can be attributed to the increased cloudy conditions and possibly to the partial relaxation of the norms of the lockdown for essential services.

The changes observed at Gadanki have been within the range of changes reported by other studies. O₃ concentration changes have been mostly positive (up to 200%) (Lee et al., 2020; Nakada and Urban, 2020; Ottmani et al., 2020; Sharma et al., 2020; Shi and Brasseur, 2020; Tobias et al., 2020). However, some studies reported the decrease (ranging between ~39 and ~7.5%) in the north-west, central and southern India (Jain and Sharma, 2020; Singh et al., 2020) and Wyche et al. (2021) have reported the O₂ decrease (ranging from ~6% to ~3.3%) in two rural sites in the UK. Gadanki O₂ change has been ~7%. Other anthropogenic emission marker species like NOx, NO, CO, SOx, PM₂.₅ and PM₁₀ have also been in the range of changes observed in the above studies. A detailed comparison is given in the Supplementary Table S4.

4.2. Rural atmospheric chemistry

The atmospheric chemistry in the troposphere is driven by the two most powerful oxidants namely O₃ and OH radical (Prinn, 2003). They have close link among their formation and degradation in atmospheric conditions and both of them are controlled by solar radiation. O₃ is a secondary pollutant formed by its precursor’s viz., nitrogen oxides (NOx) and volatile organic compounds (VOC). Traffic is the main source (~50%) of O₃ precursors (Wayne, 2000). The formation mechanism for O₃ from nitrogen-dioxide (NO₂) (this is the most predominant way of its production in troposphere) can be given as,

\[
\text{NO}_2 + \text{h}(\lambda<420 \text{ nm}) \rightarrow \text{NO} + \text{O}(^1\text{P})
\]

R1

\[
\text{O}(^1\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

R2

where, M is a third body acting as an association complex stabilizer by collision. Above reactions are a part of cyclic reactions involved in the photochemical oxidation initiated by OH produced by O₃ and solar irradiation. On the other hand O₃ is also involved in the formation of OH via following reactions.

\[
\text{O}_3 + \text{h}(\lambda<320 \text{ nm}) \rightarrow + \text{O}(^1\text{D}) + \text{O}_2(\Delta_g)
\]

R3

\[
\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}
\]

R4

The OH radical chemistry in the troposphere is difficult to treat in isolation as it is closely associated with a reaction system involving HOx (OH and HO₂), NOx and O₃. In a relatively unpolluted environment (low NOx regimes, which is the case with Gadanki) (Jain et al., 2019) reactions with CO and CH₄ become the main sinks of OH radicals (Monks, 2005; Seinfeld and Pandis, 2006) as given in the following reactions.

\[
\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2
\]

R5

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}
\]

R6

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}
\]

R7
CH$_4$ + OH $\rightarrow$ CH$_3$ + H$_2$O \hspace{1cm} R8

CH$_3$ + O$_2$ + M $\rightarrow$ CH$_3$O$_2$ + M \hspace{1cm} R9

CH$_3$O$_2$ (or generally termed as organic peroxy radicals) regenerate the OH through a similar reaction like R7 and also produce NO$_2$ which further takes part in the O$_3$ formation via R1 and R2. Therefore O$_3$ formation is always decided by the availability of two precursor species NO$_2$ and VOCs. The ratio between them decides the formation of O$_3$ and if the ratio is imbalanced (generally explained by the O$_3$ isopleths (Seinfeld and Pandis, 2006; Wayne, 2000)) then it ends up with a situation called NO$_x$ limited regime (rural environments) or VOC limited regime (urban environments). Therefore, O$_3$ production is non-linear with the precursors (Chen et al., 2020; Renuka et al., 2014). In the environments where NO concentrations are high (urban environments), NO can act as the sink for O$_3$ via following reaction.

NO + O$_3$ $\rightarrow$ NO$_2$ + O$_2$ \hspace{1cm} R10

If the NO concentrations are low, one of the major sinks of O$_3$ is reduced and is the main reason for the observed higher O$_3$ concentrations in the rural environments. NO has a very short lifespan (a couple of minutes) and is immediately oxidized into NO$_2$ (Wayne, 2000), which has a longer lifespan of hours to even days, which allows it to be transported to different environments. Therefore any changes in NO$_x$ concentrations would directly impact the chemical transformations involving formation and degradation of O$_3$ through reactions R1 and R2, and also enhance the reactivity of CO with OH radicals.

Gadanki is a rural site with a lot of vegetation around in the Eastern Ghats mountain range and agriculture fields. This means there is a VOC rich and NO$_x$ limited zone for O$_3$ formation. Any increase in the NO$_x$ should lead to the more O$_3$ production (up to the extent where the NO$_x$/VOC ratios cross over and NO becomes the sink for O$_3$) and any decrease in NO$_x$ would generally expect to impact the O$_3$ negatively (Wyche et al., 2021). The same has been observed during the lockdown period (Table 3). When the traffic emission reduced during the lockdown that resulted in the reduction of both NO and NO$_2$ (Fig. 2, Table 3), even in rural environment (Biswaal et al., 2020) leading to the reduction of O$_3$. This is in contrast with the other studies reporting the increase of O$_3$ in urban and polluted environments (Jain and Sharma, 2020; Mahato et al., 2020; Sharma et al., 2020; Shi and Brasseur, 2020; Singh et al., 2020; Xu et al., 2020a; Zambrano-Monserrat et al., 2020). In the urban environments which are NO$_x$ rich, reduction of NO would have decreased the O$_3$ scavenging via R10 (change in the sink), but in rural environments which are VOC rich and NO$_x$ limited any further reduction will only lead to the reduction of O$_3$ (change in the source) as shown by Singh et al. (2020) for southern part of India. Comparison of diurnal variations (Fig. 5) observed for O$_3$ and NO and NO$_2$ during the lockdown between 2019 and 2020 gives an excellent demonstration of the O$_3$ formation and degradation phenomenon observed at the site. In the 2019 case as the accumulation of the NO and NO$_2$ happened during the night (increased night time heavy duty vehicular traffic) and lack of photochemistry, the O$_3$ experienced a sharp decline in its concentrations when the NO and NO$_2$ concentrations have been at their highest (early morning hours). However, such decline has never been observed in 2020 diurnal variation, O$_3$ steadily increased throughout the night and peaked during the early morning hours. This demonstrates the lack of scavenging of O$_3$ by NO because of lower accumulation of NO during the night time when compared with the same period in 2019.

To understand the complete formation and loss processes of O$_3$ during the lockdown it may be required to have comprehensive non methane hydrocarbon (NMVOCs) data sets. Unfortunately VOC data sets have not been available for the study period and hence it is difficult to conclusively decide on the potential O$_3$ scavenging through VOC reactions. To have the O$_3$ scavenging through its reaction with VOCs, VOC/NO$_x$ ratio should decrease significantly (Stockwell et al., 2011).

Gadanki being a rural site (VOC rich environment) biogenic VOCs dominate the anthropogenic VOCs (Benzene, Toluene and Xylene etc.). Since the reductions observed during the lockdown have been mainly due to the anthropogenic emission changes, it can be assumed that, biogenic VOC concentrations remained the same during the lockdown even though the NO$_x$ concentrations reduced significantly. These changes would have increased the VOC/NO$_x$ ratio, and lead to the O$_3$ formation (Monks, 2005; Stockwell et al., 2011). However this increase would not have been dominant because the impact of NO$_x$ change was expected to be very small (owing to their overall low concentration - NO$_x$ limited regime). Therefore the changes observed in O$_3$ would go more with the NO$_x$ and NO$_2$ photo-stationary state ([O$_3$]=[NO$_2$/NO$_2$]x/k[NO]). Fig. 8 further confirms the photochemical repartition, total oxidant concentrations (O$_3$=NO$_2$+O$_3$) over the 2020 period have not been changed significantly as a result of the lockdown. The preservation of total O$_3$ species observed here is the result of well-known tropospheric NO$_x$-O$_3$ photochemistry (Monks, 2005; Stockwell et al., 2011) as explained above. O$_3$ reduced to its lowest when NO$_2$ concentration has been least (Phase III) and increased to the maximum in Phase II when observed NO concentration has been at its lowest.

HONO chemistry in the troposphere also plays an important role in the formation and removal of O$_3$ (Monks, 2005; Wyche et al., 2021). HONO is mainly formed by the heterogeneous reaction of water with NO$_2$ and a minor portion by the reaction of NO$_3$ on the particles (this could account only for maximum 10% of NO$_3$ loss). HONO can also be emitted in small quantities by automobiles (Wayne, 2000). When photolysed during the early morning hours it produces OH and NO and, would influence the NO$_x$ and OH budget (Jain et al., 2011a). However this pathway is significant only in polluted urban environments (could be up to 40-50% of the total OH formed) and insignificant in cleaner rural environments (could produce a maximum of 10%) like Gadanki. Therefore processes involving HONO might not have impacted much of the chemical changes observed during the lockdown at Gadanki.

Some studies (Li et al., 2019a, 2019b) have reported that particulate matter has the scavenging effect on HO$_3$ and NO$_x$ radicals (which would otherwise proceed to produce O$_3$ particularly in summer time. It has been observed that PM concentration too decreased significantly during the lockdown. This would go in favor of O$_3$ production. However, at Gadanki O$_3$ decrease because of non-availability of NO$_2$ looks to be the dominant path than the phenomena which are favoring production and sustainability (scavenging by NO) of O$_3$. Therefore, the net result observed has been the decrease of O$_3$. During the lockdown period in 2020 a slight increase (+2.2%) has been observed in GHI (Fig. 4, Table 3). Any increase in incoming shortwave radiation would increase
the efficiency of O₃ formation; however, the observed change has been very small and would not have induced significant changes in O₃ concentration.

Unlike 2019, 2020 lockdown period CO variations followed the NOₓ (Fig. 2) indicating that, when the NOₓ concentrations decreased CO became the main sink of OH through the reaction R5. This would add to the reduction of CO along with its reduced emissions because of lockdown restrictions. Therefore, net result has been enhanced reduction of CO during the lockdown and the effect would have also been transferred to the O₃ formation and degradation mechanisms.

A considerable decrease in SO₂ during 2020 when compared to 2019 has been observed both in pre-lockdown as well as the lockdown time. SO₂ primary sources are anthropogenic sources (Cox and Mulcahy, 1979; Garland, 1978; Wayne, 2000) and when the lockdown imposed most of the anthropogenic activities have been stopped resulting in the reduction of SO₂ emissions. However, SO₂ is also removed by both homogeneous and heterogeneous oxidation pathways in the boundary layer. All the removal processes convert SO₂ to H₂SO₄ (Jain et al., 2011b). Homogeneous oxidation linked with photochemistry is generally initiated with the reaction with OH radicals and then with H₂O to form H₂SO₄. However, OH production through O₃ photolysis is the dominant source of OH under study conditions and there has been a decrease of O₃ overall during the lockdown period. This should ideally reduce the photochemical sink of SO₂ and SO₄ should increase. Reactions involving other species such as peroxy radicals are rather slow and in polluted environments reaction with methyl peroxy (CH₃O₂) radical may become the significant sink. However, considering Gadanki is an unpolluted rural environment this pathway may not be accounted for SO₂ loss. O₃ reaction with SO₂ is also very slow and insignificant under the study conditions. Therefore, photochemical reduction which would be accounted for SO₂ change might not have been significant. Other dominating pathway of SO₂ removal in the boundary layer is through dry and wet deposition processes. Wet and dry deposition rates are 5-10 times higher than the homogeneous oxidation indicating the heterogeneous pathways are more dominating compared to homogeneous oxidation pathways (Wayne, 2000). Meteorological conditions such as RH, cloudiness and fog control the homogeneous and heterogeneous process. Higher RH enhances the oxidation rates indicating the more efficient removal of SO₂ (Liu et al., 2017). This could be one of the reasons along with anthropogenic emissions for the differences observed in 2020 because the RH has been higher by 11.5% during the pre-lockdown and 16.5% (Table 2) during the lockdown period. Higher relative humidity could have induced the faster removal process and hence the decrease in SO₂ concentrations. A study by Ye et al. (2018) reported the enhanced Secondary Organic Aerosols (SOA) formation from ozonolysis products of biogenic VOCs in SO₂ rich conditions. They have observed an enhancement in heterogeneous uptake of SO₂ at RH levels more than 50%. Additionally, recent studies also reported the enhanced SOA formation because of O₃ increase during the lockdown (Chatterjee et al., 2021). However, decrease in both O₃ and SO₂ have been observed at Gadanki. VOC data unavailability again makes it difficult to conclude the above path as one of the paths SO₂ removal and a source for secondary aerosols formation. However, it might have partially played a role in SO₂ reduction and hence SOA observed at Gadanki.

Almost all the studies on COVID-19 lockdown impact (Singh et al., 2020a, Bashir et al., 2020; Jain and Sharma, 2020; Mahato et al., 2020; Nair and Bashir Urban, 2020; Naviny et al., 2020; Sharma et al., 2020; Xu et al., 2020) reported a statistically significant improvement in the air quality during the COVID-19 lockdown. However, there has not been any change in the air quality category at Gadanki. Gadanki being a rural site the Air Quality Index (AQI) (Ranjan et al., 2015) generally stays in the category of good (0–50) to satisfactory (51–100) depending on the season of the year. AQI of Gadanki will be decided by O₃ sub-index owing to its observed higher concentration in comparison with the other criteria pollutants considered for the calculation of AQI. There has been a slight decrease of O₃ concentrations (8 h maximum for calculating the AQI) during the lockdown (2 ppbv) when compared with the 2019. This has induced a decrease of AQI by 4 from 93 to 89) but that would not change the AQI category, so it still stayed the same (satisfactory range) as 2019.

5. Summary and conclusions

Restrictions imposed to stop the spread of COVID-19 over India have given a unique opportunity to study the variations in different aerosol, radiation and trace gases and their associated chemistry at tropical rural environment Gadanki. A significant reduction has been observed during the COVID-19 lockdown in almost all the short lived species which are directly linked with the anthropogenic emissions. On the other hand, the effect has been minimal on the long lived more stable species such as CO₂ and CH₄. When compared phase-wise, Phase III had the highest reductions this may be partly due to the observed rain events that could have resulted in wet scavenging during that phase. Changes in the concentrations also had the significant impact on atmospheric chemistry focused on O₃. Chemical changes in the rural environment have given an excellent demonstration of formation and degradation mechanisms of O₃ in the tropical rural environment. The salient conclusions from the study can be drawn as.

a) Meteorological parameters obtained from ERA5 data for the study period have been comparable for 2019 and 2020 with slight differences. The absolute changes (observed for 2020) in T, ABL height, RH and WS have been −2.1%, +4.8%, −3.3% and +4.0% respectively.

b) Trace gases have shown a variation of −55.4%, −58.8%, −10.1%, −7.1%, −63.7%, +0.8% and +1.1% for NO, NO₂, CO, O₃, SO₂, CO₂ and CH₄ respectively, during the lockdown period when compared with 2019. Phase-wise changes have been at their maximum during the Phase III and the differences generally reduced in the Phase IV. NO₂ variations obtained from the OMI satellite have shown a difference of −30.2% during the lockdown period when compared to 2019.

c) Particulate matter (PM₁, PM₂.₅, and PM₄₀). Black carbon and AOD have also shown significant variations between 2019 and 2020. BC and AOD have shown 34.2% and 22.9% reductions during the lockdown period. Once again reduction has been its maximum in Phase III. PM data for 2019 has not been available hence the variations have been calculated taking the pre-lockdown period as reference. When compared with pre-lockdown period, PM₁, PM₂.₅, and PM₁₀ have shown a reduction of 40.9%, 46.7% and 50.4% during the lockdown period, respectively. AOD obtained from MODIS satellite data has also shown a reduction of 16.8% during the lockdown period when compared with 2019.

d) Similar reduction during the lockdown has been observed in both the ground-based observations and the satellite-borne measurements (in NO₂ and AOD) suggesting that latter can be used in absence of former observations.

e) Increase in GHI with decrease in DHI and diffuse fraction during the lockdown phases I, II and III is a resultant of reduction in emission sources due to strict lockdown norms along with the decreased cloud cover and intermittent rain events, while the vice versa during the phase IV lockdown period can be attributed to the increased cloudy conditions and possibly to the partial relaxation of the norms of the lockdown for essential services.

f) There have been striking differences in the diurnal variation of different atmospheric parameters. There has been a predominant steady increase in the concentrations throughout the night in 2019 but in 2020 the steady increase has been minimized. All the atmospheric parameters have shown the fumigation peak in the early morning hours. There has been a maximum impact on O₃ diurnal variation. During the lockdown period in 2019 there had been a
sharp decline in the early morning (dawn) O\textsubscript{3} concentrations when the NO\textsubscript{x} concentrations reached their maximum. Such decline in the O\textsubscript{3} concentrations has not been observed in 2020 showing the lack of NO scavenging effect on O\textsubscript{3}.

g) Variations observed are explained on the basis of known atmospheric chemistry of the rural environments. Rural environments are NO\textsubscript{x} limited zones and any further reductions in NO\textsubscript{x} would reduce O\textsubscript{3} concentrations and the same has been observed. This is in contrast with the other studies reported on urban environments. Phase-wise changes in O\textsubscript{3} followed the NO\textsubscript{x} concentrations. CO variations also demonstrated the known chemistry of the rural environment.

h) Although there have been significant reductions in all the pollutants they remained still in the same AQI category. Therefore, in contrast to the other reported studies over urban environments, there has not been any change in the air quality at Gadanki during the lockdown.

Overall, lockdown imposed to stop the spread of COVID-19 provided an excellent demonstration of rural atmospheric chemistry and its intrinsic links with precursor concentrations and dynamics.

Credit author statement

Chaithanya D. Jain: Conceptualization, Methodology, Visualisation, Data curation, Writing- Original draft preparation. B. L. Madhavan: Data Curation, Visualisation, Writing- Original draft preparation. Vikas Singh: Methodology, Visualisation, Data curation, Writing- Reviewing and Editing. Prasad: Data curation, Writing- Reviewing and Editing. A. Sai Krishnaveni: Data curation, V. Ravi Kiran: Writing- Reviewing and Editing and Ms. Venkat Ratnam: Resources, Visualisation, Supervision, Writing- Reviewing and Editing. I. A. Singh: Data curation, Writing- Reviewing and Editing and Ms. Renju Nanadan for acquiring the data during the lockdown project. We also thank research scholars of ARTG (NARL) Ms. Sindu S. Gueymard, C.A., 2014. Impact of on-site atmospheric water vapor estimation methods on the accuracy of local solar irradiance predictions. Sol. Energy 101, 74–82. https://doi.org/10.1016/j.solener.2013.12.027.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank the Department of Space, Government of India for the financial support during this work through the ISRO-GBP ATCTM project. We also thank research scholars of ARTG (NARL) Ms. Sindu S. and Ms. Renju Nanadan for acquiring the data during the lockdown period. We acknowledge the use of TrajStat/HYSPLIT models for CWT studies. We thank ECMWF-ERA5, NOAA-GRD, MODIS, OMI teams for the data used in the study. The data used in present study can be obtained on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2020.110665.

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