Impact of COVID-19 lockdown on surface ozone build-up at an urban site in western India based on photochemical box modelling

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Elevated ozone (O_3) near the earth's surface causes adverse impacts on human health and vegetation, besides impacting air chemistry and climate. Intense lockdown to contain the spread of Coronavirus disease 2019 (COVID-19) offered a rare opportunity to delineate the anthropogenic impact on urban O_3 build-up. In this regard, we incorporated observations of chemical species and environmental conditions into a photochemical box model (NCAR Master Mechanism) to study the O_3 changes at a semi-arid urban site in western India (Ahmedabad; 23°N, 72.6°E). In contrast with primary pollutants, daytime O_3 build-up is observed to be enhanced during the lockdown by ~39%. Model, driven by lower nitrogen oxides (NO_x) during the lockdown, also simulated enhanced O_3 (by ~41%) showing the role of nonlinear dependence of O_3 on NO_x. Further, a sensitivity simulation unravelled an important role of the meteorological changes in the O_3 enhancement (by ~16%) during the lockdown. The results highlight that the lockdown impacts can be modulated profoundly by the complex chemistry plus meteorological changes, offsetting the benefits of lower precursor levels in the context of O_3 pollution.

Keywords: Air quality, atmospheric chemistry, COVID-19, trace gases.

Introduction

IMPACTS of anthropogenic emissions on air pollution are generally understood through model calculations as it is impractical to remove them entirely and observe the reductions. Intense and long lockdowns to stop the spread of the Coronavirus disease 2019 (COVID-19) offered a rare and unique opportunity to study the role of man-made factors in the air quality variations. This is especially the case for short-lived climate forcing pollutants, such as ozone (O_3). O_3 in the troposphere plays a central role in atmospheric chemistry as the major precursor of the hydroxyl (OH) radical. Besides being an effective greenhouse gas, when present in elevated concentrations near the earth's surface, O_3 has adverse impacts on human health and crop yields[1–3]. In contrast with several primary air pollutants, O_3 is not emitted directly and instead gets produced in the atmosphere through chemistry of its precursors carbon monoxide (CO), oxides of nitrogen (NO_x), and volatile organic compounds (VOCs) emitted from various sources. Photochemical production of O_3 depends upon concentrations of precursors in a highly complex and nonlinear manner which also has a strong dependence on solar radiation and other meteorological conditions[4,5]. Considering these complexities, modelling is required to interpret the role of chemistry and meteorological conditions in observed O_3 variations.

The tropical Indian region experiences strong and diverse anthropogenic as well as natural emissions. Warmer climate with high water vapour content can favour ozone production, also through biogenic emissions[5–9]. Nevertheless, *in situ* measurements over this part of the world have been sparse and simulations from chemical transport models have shown significant biases[10–12]. The uncertainties in 3-dimensional models have been associated with input emissions and also with detailed chemistry of hydrocarbons[12]. Zero-dimensional photochemical box models can therefore be a valuable tool as these allow incorporating measured levels of chemical species in prescribed atmospheric conditions[11,13,14].

To stop the spread of COVID-19, India observed one of the most comprehensive and longest lockdowns of the world. This lockdown resulted in a near zeroing of various anthropogenic emissions except those associated with essential services. Assuming that natural and other factors remain similar, this unprecedented situation offers a rare opportunity to evaluate the air composition in a condition of minimal man-made emissions. Such studies would be valuable in designing emission reduction policies by knowing their potential impacts in given climatic conditions and chemical environments. Considering this, here, we incorporated measurements from ground-based monitoring station and satellite-based instruments into a photochemical box model. The study is conducted for

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Table 1. Different simulations performed in the study with brief descriptions

Simulation	Brief description
Reference simulations	
Pre-lockdown	Chemical and meteorological inputs set as to pre-lockdown mean conditions
Lockdown	Chemical and meteorological inputs set as to lockdown mean conditions
Chem_effect	Lockdown simulation but meteorological inputs same as that during pre-lockdown conditions
Sensitivity simulations	
sens_0.40*voc_lock	Similar to simulation – Lockdown, except that VOCs reduced to 40% of pre-lockdown conditions
sens_0.50*voc_lock	Similar to simulation – Lockdown, except that VOCs reduced to 50% of pre-lockdown conditions
sens_0.40*voc_chem_eff	Chemical inputs as in sens_0.40*voc_lock and meteorological inputs same as that during pre-lockdown
sens_0.50*voc_chem_eff	Chemical inputs as in sens_0.50*voc_lock and meteorological inputs same as that during pre-lockdown

a semi-arid urban environment in the western India (Ahmedabad; 23°N, 72.6°E). Pre-lockdown and lockdown periods are considered as 1–21 March 2020 and 24 March–10 May 2020 respectively. We performed sensitivity simulation to delineate the effects of reduced levels of precursors versus a change in the meteorology from pre-lockdown to lockdown.

Modelling and input datasets

The study utilizes the NCAR's Master Mechanism model – version 2.5 for simulating the surface O_3 variations. The model has a highly detailed treatment of gas-phase chemistry by including about 2000 chemical species participating in about 5000 reactions[13]. Time evolution of air parcel initialized with known chemical composition can be simulated by the model in absence of further emissions, dilution or transport effects. Therefore, the model is a tool to probe the effects of changing chemistry in prescribed atmospheric conditions; however, absolute levels of trace gases could differ significantly than measurements since the transport effects are not simulated. Further details and successful applications of this model over the Indian region can be found elsewhere[11,14].

In this study, three reference simulations have been performed, as summarized in Table 1. Observational values of CO, nitric oxide (NO), nitrogen dioxide (NO_2) and meteorological conditions (temperature and relative humidity) have been included from the ground-based monitoring station – Maninagar, Ahmedabad available from the Central Pollution Control Board (CPCB). Measurements of O_3, CO, NO_x (NO, NO_2) are based on the absorption of ultraviolet radiation, non-dispersive infrared spectroscopy and chemiluminescence respectively. Observational datasets have been screened prior to the analysis for abnormal values, such as the data points beyond 3-sigma (standard deviation), and recurring values as described in earlier studies analysing these type of datasets[7,15]. Further details on measurement techniques, calibrations and data filtering are available elsewhere[16,17]. As O_3 production occurs through the photolysis of NO_2, we have constrained the diurnal variations of NO_2 in model based on observations (Figure 1) during the lockdown and pre-lockdown. Additionally, model is initialized with typical values of methane and C_2–C_5 non-methane hydrocarbons, formaldehyde, etc. based on earlier studies[18–21] for the pre-lockdown simulation. For lockdown simulation, as discussed earlier also, input NO_x was set (reduced) according to observational data. Following upon a series of sensitivity simulations (Table 1), VOCs were reduced in the model by 45% compared to the level during pre-lockdown. The key environmental conditions included in the model are summarized in Table 2. Solar irradiance in the simulations is based on the Tropospheric Ultraviolet Visible (TUV) radiative transfer model for Ahmedabad location in prescribed atmospheric conditions. The values of surface albedo and O_3 column are based on the Modern-Era Retrospective Analysis for Research and Application – version 2 (MERRA-2) model. Aerosol Optical Depth (AOD) and Ångstrom coefficient are from the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite. Model is run for three days and the output for the third day has been used for the analyses.

Results and discussions

Figure 1 shows the diurnal variations in surface NO, NO_2, CO and O_3 observed at Maninagar station in Ahmedabad during pre-lockdown and lockdown periods. NO_2 mixing ratios show double peaks, one during the morning hours (0800–0900 h IST) and other during the evening (2000–2100 h); whereas lowest levels are seen during the noontime. In contrast, O_3 mixing ratios are observed to be highest during the noontime (40–60 ppbv) and lowest during the night time (5–10 ppbv). Night time O_3 observations were not available for most of the days before the lockdown, and therefore here we focus only on daytime O_3 build up. Lower NO_2 but higher O_3 during noontime is manifestation of typical urban chemistry as reported from several stations including Ahmedabad[19,22–24]. Such a strong O_3 build-up during noon hours over urban stations is attributed to the photochemistry involving precursors emitted from local-regional sources. CO and NO mixing ratios show stronger variabilities as reflecting from higher sigma values (standard deviations), nevertheless, the mean values are observed to be lower during the

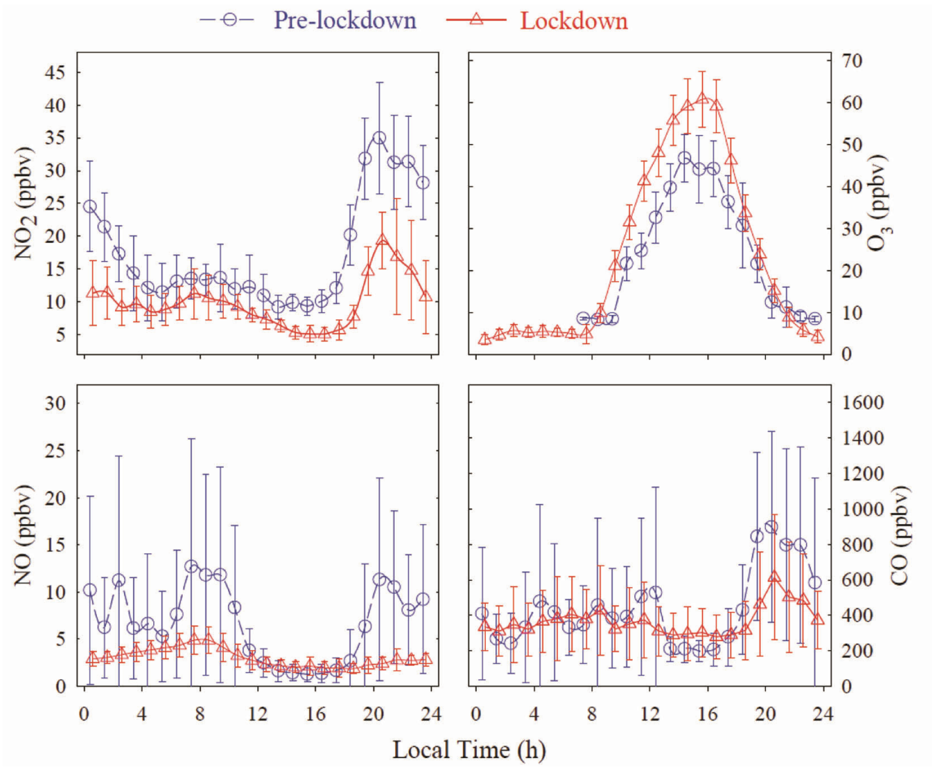

Figure 1. Diurnal variations in surface NO_2, O_3, NO, and CO observed at Maninagar station in Ahmedabad during pre-lockdown and lockdown periods. O_3 shows stronger daytime build-up during the lockdown, in contrast with CO, NO and NO_2. Error bars show 1-sigma standard deviation.

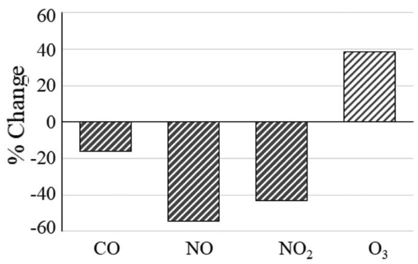

Figure 2. Percentage change in mean values of CO, NO, NO_2, and daytime (1100–1700 h IST) O_3 during the lockdown compared to the pre-lockdown period.

lockdown. Higher sigma values are suggested to be due to significant day-to-day variations in the local anthropogenic emissions in this urban environment, besides the effects of meteorological variations. Additionally, the morning and evening time peaks in NO and NO_2 are seen to be less pronounced during the lockdown compared to the pre-lockdown condition. Figure 2 shows the percentage change in the mean mixing ratios of CO, NO, NO_2, and daytime (1100–1700 h IST) O_3 during the lockdown compared to the pre-lockdown period. The reductions are observed to be stronger in case of NO and NO_2 (by ~43 to 55%) compared to that in CO (by ~16%). Larger reduction in NO is attributed to the strongly impacted transportation sector in Ahmedabad due to stringent restriction on road traffic during the lockdown. Due to minimal anthropogenic emissions during the intense lockdown, the mixing ratios of O_3 precursors exhibited sharp decline, as expected. However, daytime O_3 mixing ratios showed an enhancement by 39%. We analyse this enhanced O_3 build-up in detail based on the photochemical box modelling.

Figure 3 shows a comparison of daytime mean O_3 between the pre-lockdown and lockdown conditions from observations and model simulations. As discussed earlier too, the model only simulates chemistry and therefore absolute O_3 levels can be different, nevertheless, model does show an enhancement (by ~41%) in O_3 during the lockdown in agreement with enhancement seen in the observations (by ~39%). Higher reduction in NO as compared to NO_2 caused enhancement in NO_2/NO ratio from 2.6 (pre-lockdown) to 3.3 (lockdown), increasing net O_3 production. Net enhancement (%) derived from additional sensitivity simulations is given in Table 3. Since during the lockdown NO_x levels are constrained to lower values based on observations, this result suggests that reductions in VOCs would be required to reduce O_3 pollution in this environment. In addition, meteorological conditions have changed from pre-lockdown to lockdown, which could also contribute to the O_3 enhancement. Besides other meteorological variables such as temperature and relative humidity (Table 2), solar irradiance is seen to have played most important role. Noontime solar irradiance is higher by 58–132 Wm^{-2} during the lockdown compared to the pre-lockdown (Figure 4). Slightly stronger (by 0.5–1 ms^{-1}) and more frequent northerly local winds were observed during the lockdown, as compared to the pre-lockdown. By incorporating the observed variations in CO, NO and NO_2, model simulations account for the effects of this change in local dynamics on these species. The relative effects of change in precursor levels and meteorological conditions have been studied further using the model simulations (Figure 5).

Figure 5 shows a comparison of the three reference simulations which are described in Table 1. As discussed earlier also, model shows most pronounced O_3 build up during the lockdown conditions with a daytime enhancement by 41%, compared to the pre-lockdown simulation. Interestingly, when reduced levels of chemical input are implemented but meteorology (solar radiation, temperature, etc.) is kept the same as that during the pre-lockdown period, O_3 enhancement is simulated to be significantly lower (only 25% as compared to 41%). This shows that the enhancement in O_3 was caused by both chemistry and meteorological changes. Figure 5 *b* and *c* shows influence of 40% and 50% reductions in VOCs on O_3 for lockdown and pre-lockdown conditions. These additional simulations suggest that this interplay of chemistry and meteorology remains important even if levels of VOCs are slightly higher (or lower) than that considered in the reference simulations.

Table 2. Environmental conditions opted for pre-lockdown and lockdown conditions in the model

Parameter	Pre-lockdown	Lockdown
Temperature	303 K	305 K
Relative humidity	38.5%	33%
Total O_3 column	284.1 DU	283.8 DU
Aerosol optical depth at 550 nm	0.25	0.19
Ångstrom coefficient	0.75	1.141

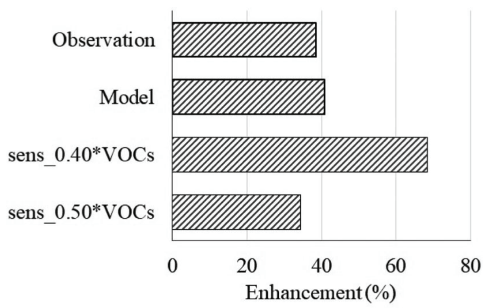

Figure 3. Enhancement in daytime mean (1100–1700 h IST) O_3 during the lockdown as compared to pre-lockdown based on observation and model. Results from two additional sensitivity simulations with varying VOCs, as described in the Table 1, are also shown.

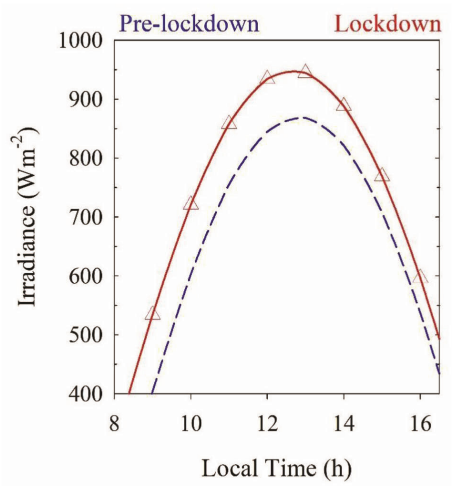

Figure 4. Hourly variation in solar irradiance at Ahmedabad during the pre-lockdown and lockdown condition driving the photochemistry in the model.

Effect of lockdown on chemistry is further analysed by computing the O_3 production and loss rates for the three reference simulations: pre-lockdown, lockdown and chem_effect (Figure 6). O_3 production rates are based on the $HO_2 + NO$ and $RO_2 + NO$ reactions, whereas the loss rates are determined using the $O(^1D) + H_2O$, $OH + O_3$, and $HO_2 + O_3$ reactions, as described in the literature[10,11,25]. In all the three cases, O_3 production rates increase in the morning to a maximum (8–10.2 ppbv h^{-1}) in the noontime (~13:00 h), before starting to decrease. Similarly, the O_3 loss rates are also maximum during the noon hours (1.7–3 ppbv h^{-1}). This supports the discussion on observed and modelled O_3 diurnal variations that O_3 build up in this environment is dominated by the local photochemistry. Here, it is clearly seen that the O_3 production rate is higher during the lockdown condition (up to 10.2 ppbv h^{-1}) in comparison with the pre-lockdown condition (up to 8 ppbv h^{-1}). When meteorological conditions are not changed and only chemical inputs are changed to the lockdown condition (Chem_effect simulation), the O_3 production rate is found to be higher than pre-lockdown (by up to 0.4 ppbv h^{-1}). Since, besides production, the loss rates have also been impacted by the chemistry and meteorology, the net production rates (production minus loss) have also been considered to see the overall effect. The net O_3 production rate is estimated to be higher during the lockdown than those during the pre-lockdown by up to 1.2 ppbv h^{-1}. The analyses highlight that while the lockdown had a remarkable impact in reducing levels of primary pollutants, any potential benefits in context of O_3 air quality can get offset by chemistry and meteorology. Our findings suggest that these effects should be considered while planning to curb O_3 pollution in this environment in the future.

Summary and conclusion

An intense and comprehensive lockdown implemented to minimize the spread of COVID-19 reduced anthropogenic

Table 3. Contribution of chemistry and meteorology in the enhancement of daytime O_3 (%) during lockdown based on reference and sensitivity simulations

Simulation	O_3 enhancement (%)	Contribution of chemistry (%)	Contribution of meteorology (%)
Lockdown	41	25	16
sens_0.40*voc_lock	68	48	20
sens_0.50*voc_lock	34	16	18

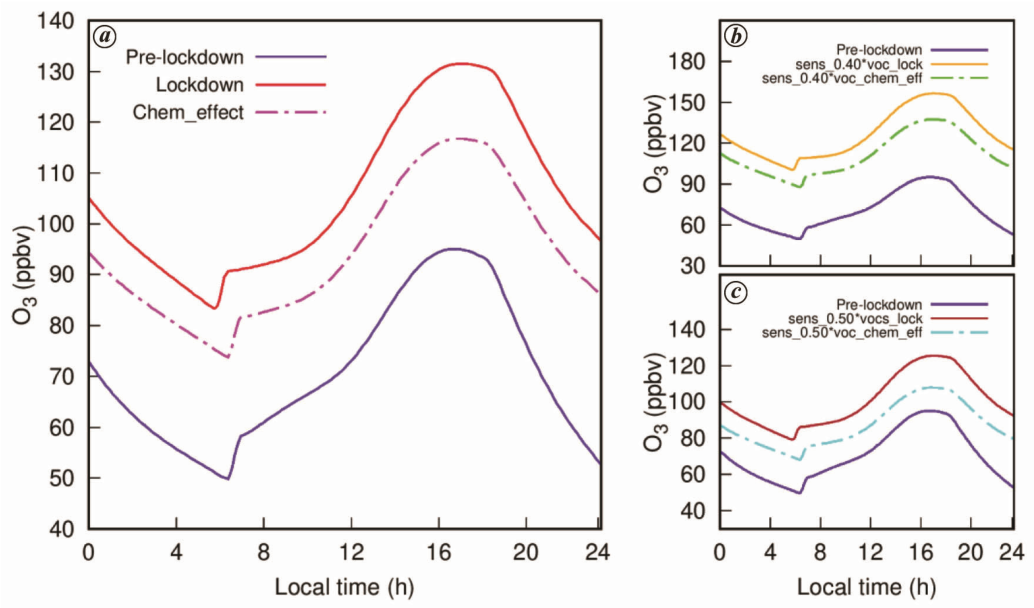

Figure 5. ***a***, Comparison of model simulated O_3 for pre-lockdown and lockdown conditions. Chem_effect is an additional simulation with chemical inputs of lockdown but meteorological inputs of pre-lockdown. ***b*** and ***c***, Results from two additional simulations with varying VOCs, as described in Table 1, are also shown.

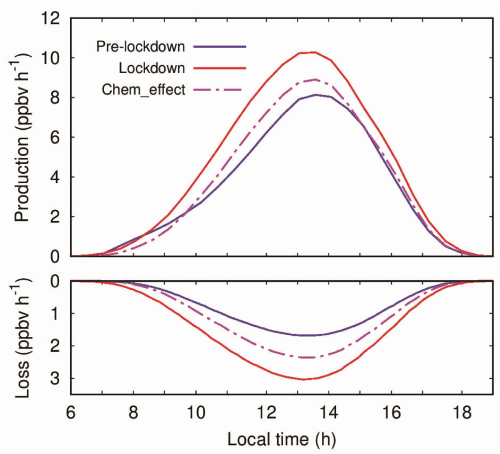

Figure 6. Diurnal variation in O_3 production and loss rates for pre-lockdown and lockdown conditions derived from model simulations. Chem_effect is an additional simulation with chemical inputs of lockdown but meteorology same as that during the pre-lockdown.

emissions across India drastically. Although this led to a remarkable improvement in the air quality in context of primary gases, O_3 pollution did not show a reduction instead showed more build up during the lockdown at an urban site in Ahmedabad. Model reproduced this feature of enhancement in daytime O_3 production in lower NO_x conditions of lockdown. Meteorological changes, most importantly higher solar irradiance, contributed to more intense photochemistry during the lockdown. Model derived net O_3 production rate was higher by up to 1.2 ppbv h^{-1} during the lockdown than that during the pre-lockdown. Sensitivity simulations were performed to quantify the relative effects of change in precursor levels and meteorological conditions. The analysis revealed that the meteorological changes enhanced O_3 by ~16% whereas additional 25% enhancement was due to chemistry. The study highlights that the effects of emission reductions could get modulated by complex chemical processes and meteorological variations and therefore intense lockdown might not have yielded anticipated reductions for some pollutants. The findings could prove valuable in planning strategies to curb O_3 pollution in future by considering the effects of chemistry and atmospheric conditions in this semi-arid urban environment.

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