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

Meghna Soni$^{1,2}$, Narendra Ojha$^{1,*}$ and Imran Girach$^{3}$

$^1$Space and Atmospheric Sciences Division, Physical Research Laboratory, Ahmedabad 380 009, India
$^2$Indian Institute of Technology, Gandhinagar 382 424, India
$^3$Space Physics Laboratory, Vikram Sarabhai Space Centre, Thiruvananthapuram 695 022, India

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 (NOx), 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...
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 O3 variations. The model has a highly detailed treatment of gas-phase chemistry by including about 2000 chemical species participating in about 5000 reactions. 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.

In this study, three reference simulations have been performed, as summarized in Table 1. Observational values of CO, nitric oxide (NO), nitrogen dioxide (NO2) 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 O3, CO, NOx (NO, NO2) 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. Further details on measurement techniques, calibrations and data filtering are available elsewhere. As O3 production occurs through the photolysis of NO2, we have constrained the diurnal variations of NO2 in model based on observations (Figure 1) during the lockdown and pre-lockdown. Additionally, model is initialized with typical values of methane and C2–C5 non-methane hydrocarbons, formaldehyde, etc. based on earlier studies for the pre-lockdown simulation. For lockdown simulation, as discussed earlier also, input NOx 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 O3 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, NO2, CO and O3 observed at Maninagar station in Ahmedabad during pre-lockdown and lockdown periods. NO2 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 noon-time. In contrast, O3 mixing ratios are observed to be highest during the noon-time (40–60 ppbv) and lowest during the night time (5–10 ppbv). Night time O3 observations were not available for most of the days before the lockdown, and therefore here we focus only on daytime O3 build up. Lower NO2 but higher O3 during noon-time is manifestation of typical urban chemistry as reported from several stations including Ahmedabad. Such a strong O3 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

| Simulation | Brief description |
|------------|------------------|
| 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 |
Figure 1. Diurnal variations in surface NO₂, O₃, NO, and CO observed at Maninagar station in Ahmedabad during pre-lockdown and lockdown periods. O₃ shows stronger daytime build-up during the lockdown, in contrast with CO, NO and NO₂. Error bars show 1-sigma standard deviation.

Figure 2. Percentage change in mean values of CO, NO, NO₂, and daytime (1100–1700 h IST) O₃ 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 NO₂ 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, NO₂, and daytime (1100–1700 h IST) O₃ during the lockdown compared to the pre-lockdown period. The reductions are observed to be stronger in case of NO and NO₂ (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 O₃ precursors exhibited sharp decline, as expected. However, daytime O₃ mixing ratios showed an enhancement by 39%. We analyse this enhanced O₃ build-up in detail based on the photochemical box modelling.

Figure 3 shows a comparison of daytime mean O₃ between the pre-lockdown and lockdown conditions from observations and model simulations. As discussed earlier too, the model only simulates chemistry and therefore absolute O₃ levels can be different, nevertheless, model does show an enhancement (by ~41%) in O₃ during the lockdown in agreement with enhancement seen in the observations (by ~39%). Higher reduction in NO as compared to NO₂ caused enhancement in NO₂/NO ratio from 2.6 (pre-lockdown) to 3.3 (lockdown), increasing net O₃ production. Net enhancement (%) derived from additional sensitivity simulations is given in Table 3. Since during the lockdown NOₓ levels are constrained to lower values based on observations, this result suggests that reductions in VOCs would be required to reduce O₃ pollution in this environment. In addition, meteorological conditions have changed from pre-lockdown to lockdown, which could also contribute to the O₃ 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 NO₂, 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 O₃ 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, O₃ enhancement is simulated to be significantly lower (only 25% as compared to 41%). This shows that the enhancement in O₃ was caused by both chemistry and meteorological changes. Figure 5 b and c shows influence of 40% and 50% reductions in VOCs on O₃ 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.

Effect of lockdown on chemistry is further analysed by computing the O₃ production and loss rates for the three reference simulations: pre-lockdown, lockdown and chem_effect (Figure 6). O₃ production rates are based on the HO₂ + NO and RO₂ + NO reactions, whereas the loss rates are determined using the O(1D) + H₂O, OH + O₃, and HO₂ + O₃ reactions, as described in the literature. In all the three cases, O₃ 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 O₃ loss rates are also maximum during the noon hours (1.7–3 ppbv h⁻¹). This supports the discussion on observed and modelled O₃ diurnal variations that O₃ build up in this environment is dominated by the local photochemistry. Here, it is clearly seen that the O₃ 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 O₃ 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 O₃ 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 O₃ air quality can get offset by chemistry and meteorology. Our findings suggest that these effects should be considered while planning to curb O₃ 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 O₃ (%) during lockdown based on reference and sensitivity simulations

| Simulation                      | O₃ 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 O₃ 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 O₃ 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, O₃ 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 O₃ production in lower NOₓ conditions of lockdown. Meteorological changes, most importantly higher solar irradiance, contributed to more intense photochemistry during the lockdown. Model derived net O₃ 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 O₃ 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 O₃ pollution in future by considering the effects of chemistry and atmospheric conditions in this semi-arid urban environment.

1. Lelieveld, J. et al., The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature, 2015, 525, 367–371; https://doi.org/10.1038/nature15371.
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2. Ghude, S. D. et al., Premature mortality in India due to PM2.5 and ozone exposure. Geophys. Res. Lett., 2016, 43, 4650–4658; doi:10.1002/2016GL068949.

3. Sharma, A., Ojha, N., Pozzer, A., Beig, G. and Gunthe, S. S., Revisit the crop yield loss in India attributable to ozone. Atmos. Environ., 2019, X, 110008; doi:https://doi.org/10.1016/j.atmosenv.2019.100008

4. Jacob, D., Introduction to Atmospheric Chemistry, Princeton University Press, New Jersey 1999; doi:10.2307/ctt768h

5. Coates, J., Mar, K., Ojha, N. and Butler, Tim., The influence of temperature on ozone production under varying NOx conditions—a modelling study. Atmos. Chem. Phys., 2016, 16, 11601–11615; 10.5194/ACP-16-11601-2016.

6. Akimoto, H., Global air quality and pollution. Science, 2003, 302(5651), 1716–1719; doi:10.1126/science.1092666.

7. Ojha, N. et al., On the widespread enhancement in fine particulate matter across the Indo-Gangetic Plain towards winter. Sci. Rep., 2020, 10, 5862; https://doi.org/10.1038/s41598-020-62710-8.

8. Gunthe, S., Beig, G. and Sahu, L., Study of relationship between daily maxima in ozone and temperature in an urban site in India.Curr. Sci., 2016, 110, 1994–1999; 10.18520/cs/v110/i10/1994-1999.

9. Sahu, L., Tripathi, N. and Yadav, R., Contribution of biogenic and photochemical sources to ambient VOCs during winter to summer transition at a semi-arid urban site in India. Environ. Pollut., 2017; doi:10.1016/j.envpol.2017.06.091.

10. Kumar, R., Naja, M., Pfister, G. G., Barth, M. C., Wiedinmyer, C. and Brasseur, G. P., Simulations over South Asia using the weather research and forecasting model with chemistry (WRF-Chem): chemistry evaluation and initial results. Geosci. Model Dev., 2012, 5, 619–648; https://doi.org/10.5194/gmd-5-619-2012.

11. Ojha, N. et al., Variabilities in ozone at a semi-urban site in the Indo-Gangetic Plain region: Association with the meteorology and regional processes. J. Geophys. Res., 2012, 117, D20301; doi:10.1029/2012JD017716.

12. Sharma, A., Ojha, N., Pozzer, A., Mar, K. A., Beig, G., Lelieveld, J. and Gunthe, S. S., WRF-Chem simulated surface ozone over south Asia during the pre-monsoon: effects of emission inventories and chemical mechanisms. Atmos. Chem. Phys., 2017, 17, 14393–14413; https://doi.org/10.5194/acp-17-14393-2017.

13. Madronich, S., Chemical evolution of gaseous air pollutants down-wind of tropical megacities: Mexico City case study. Atmos. Environ., 2006, 40, 6012–6018; 10.1016/j.atmosenv.2005.08.047.

14. Girach, I. A. et al., The changes in near-surface ozone and precursors at two nearby tropical sites during annular solar eclipse of 15 January 2010. J. Geophys. Res., 2012, 117, D01303; http://dx.doi.org/10.1029/2011JD016521.

15. Schnell, J. L. et al., Exploring the relationship between surface PM2.5 and meteorology in Northern India. Atmos. Chem. Phys., 2018, 18, 10157–10175; https://doi.org/10.5194/acp-18-10157-2018.

16. Technical Specifications for Continuous Ambient Air Quality Monitoring (CAAQM) Station (Real Time), 2019; https://cpceb.nic.in/report.php

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