



Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.



Increased ozone levels during the COVID-19 lockdown: Analysis for the city of Rio de Janeiro, Brazil

Bruno Siciliano^a, Guilherme Dantas^a, Cleyton M. da Silva^{a,b,*}, Graciela Arbilla^a

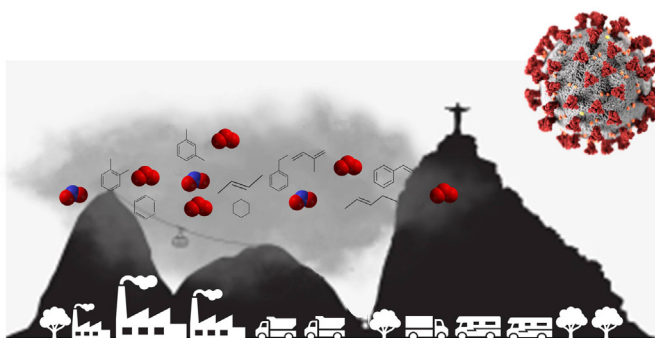
^a Institute of Chemistry, Federal University of Rio de Janeiro, Brazil

^b Veiga de Almeida University, Maracanã Campus, Rio de Janeiro, Brazil

HIGHLIGHTS

- Primary atmospheric pollutant concentrations decreased during the lockdown.
- Ozone levels increased during lockdown in many cities of the world.
- Ozone levels were related to the increase in NMHC/NO_x ratios in a VOC-controlled scenario.
- Air masses from the industrial areas contributed to ozone increase.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 May 2020

Received in revised form 24 May 2020

Accepted 26 May 2020

Available online 28 May 2020

Keywords:

COVID-19

Lockdown

Ozone

Nitrogen dioxide

Non-methane hydrocarbons

ABSTRACT

The first COVID-19 case in Brazil was confirmed on February 25, 2020. Partial lockdown measures came into force in the city of Rio de Janeiro, Brazil, on March 23. While CO and NO₂ levels showed significant reductions, PM₁₀ levels were only reduced in the first partial lockdown week. By contrast, ozone levels increased in all studied locations. In this study, the factors leading to this behavior were analyzed. Monitoring data obtained at two automatic monitoring stations showed higher ratios between non-methane hydrocarbons and nitrogen oxides (NMHC/NO_x) during the partial lockdown (up to 37.3%). The increase in ozone concentrations during the social distancing measures could be attributed to the increase in NMHC/NO_x ratios since atmospheric chemistry in Rio de Janeiro is under VOC-controlled conditions. However, the increase was higher when air masses arrived from the industrial areas, not only because of the higher NMHC/NO_x ratios, but also because the reactivity of VOC was highly increased by these air masses, which are rich in aromatic compounds.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Since December 31, 2019, SARS-CoV-2 virus has spread all over the world: in Africa, Asia, America, Europe and Oceania (Johns Hopkins, 2020). COVID-19 was characterized as a pandemic on March 12, 2020

(WHO, 2020) and, as the number of cases increased, most of the countries adopted some kind of measures in order to halt the spread of the virus: encouragement of social distancing, prohibition of public events, closure of schools, universities and non-essential business, lockdowns, closures of external borders and significant reduction of train, bus and

* Corresponding author at: Veiga de Almeida University, Maracanã Campus, Rio de Janeiro, Brazil.

E-mail address: cleyton.silva@uva.br (C.M. da Silva).

air travel. The containment measures had a huge impact in the daily life of the citizens, but they also had a positive impact on air quality (Dantas et al., 2020a; Saadat et al., 2020; Tobias et al., 2020).

In Brazil, COVID-19 was declared a public health emergency on February 3 (Croda et al., 2020) and São Paulo and Rio de Janeiro, the two most populated states of the country, were the first to step up social restrictions (Dantas et al., 2020a). In Rio de Janeiro, the first measures were implemented on March 16, when schools and universities were closed, public events were canceled and work at home was recommended. On March 19, a new decree determined a partial lockdown from March 21–23: bars, restaurants, beaches, shopping centers and commerce in general (except for food and medicines) were closed and public transport within the city was limited, as well as part of the passenger's transport within states. Industrial and construction activities were not suspended, as well as those related to health and basic services (Dantas et al., 2020a; DOERJ, 2020).

As discussed by Dantas et al. (2020a), as a consequence of the partial lockdown, CO and NO₂ levels showed significant reductions, 30.3–48.5% and 16.8–53.8%, respectively, while PM₁₀ levels were only reduced in the first couple of partial lockdown weeks. By contrast, ozone concentrations increased up to 67% during the same period. Similar trends were observed in São Paulo (CETESB, 2020; Nakada and Urban, 2020), Barcelona (Tobias et al., 2020), London (London, 2020) and many cities of India (Mahato et al., 2020; Sharma et al., 2020). The increase in ozone levels was explained as a consequence of the decrease in nitrogen oxides concentrations (NO_x = NO₂ + NO).

As noted by Wang and Su (2020), NO₂ decrease received extensive attention from the international community and the media, as an indicator of the improvement of air quality. Satellite images of the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) showed the clear decrease of NO₂ levels in China, Italy, Spain, France and other areas of the world (Copernicus, 2020; NASA, 2020; Muhammad et al., 2020; Wang and Su, 2020). The decrease in NO₂ and other primary pollutants (particulate matter and CO), in spite of being local and short-term consequences of the decrease in traffic and economic activities, was really positive for the environment and public health. By contrast, the increase of ozone received less attention. Health risks of ozone, for both short- and long-term exposures, are well known, such as lung damage, respiratory symptoms, chronic obstructive pulmonary disease, increased morbidity and mortality, independent of other air pollutants. These effects are worse in people with lung diseases, e.g. asthma (WHO, 2008, 2016; US EPA, 2020). Then, for many urban centers and when considering all criteria pollutants, air quality parameters had only a partial improvement.

According to the European Union (EU) Air Quality Directive and the WHO Guidelines, the target values for the maximum daily 8-hour mean ozone concentration are 120 and 100 µg m⁻³, respectively (EU, 2017; WHO, 2005). National Ambient Air Quality Standards in the United States set a maximum 8-hour value of 0.070 ppm (equivalent to 137 µg m⁻³ annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years) (NAAQS, 2020). In Brazil, the 8-hour maximum is 140 µg m⁻³, with the perspective of reducing this value to 100 µg m⁻³ (target value) in the future (CONAMA, 2018). Some recent studies have suggested that short- and long-term exposures to ozone were significantly associated with increased risk of mortality at levels below these standards, indicating that these values may need to be reevaluated (Di et al., 2017a, 2017b).

Tropospheric ozone is a secondary atmospheric pollutant formed by the interaction of sunlight with NO_x and volatile organic compounds (VOC). The chemistry associated to ozone formation and consumption is complex and, as previously discussed (Dantas et al., 2019, 2020b), the relationship between ozone, VOC and NO_x is driven by nonlinear photochemistry and the sensitivity of O₃ formation to VOC and NO_x is subject to many uncertainties. In general, at high VOC/NO_x ratios (typically >12), the chemistry of the air masses is NO_x-limited, and NO_x control is the more effective way of reducing ozone levels. These scenarios

are typical of suburban and rural areas. In urban centers, the typical situation is low VOC/NO_x ratios (in general, equal to or lower than 6). These systems are VOC-controlled, and reducing NO_x at constant VOC leads to an increase in ozone concentrations (Silva et al., 2018; Dantas et al., 2020b). In fact, in these scenarios, ozone concentrations are sensitive to both VOC speciation and reactivity (Finlayson-Pitts and Pitts, 2000; Dantas et al., 2019). However, other factors should be considered such as the origin and aging of air masses and the role of biogenic hydrocarbons. These factors become more important in cities with a complicated pattern of emission sources or in special events, such as lockdowns, when the contribution of emissions sources is highly altered (Dantas et al., 2019, 2020a).

Considering the health risks associated to ozone and its complex chemistry, the main goal of this work is to discuss the impact of the partial lockdown on the ozone levels in the city of Rio de Janeiro, Brazil, as a consequence of the decrease in the concentrations of primary pollutants, VOC and NO_x, as well as the changes in the main emission sources.

2. Material and methods

2.1. Studied area

The city of Rio de Janeiro has approximately 6.5 million people and is part of the Metropolitan Region of Rio de Janeiro (MRRJ), the second largest urban center in Brazil, with approximately 12 million inhabitants (IBGE, 2020). The city is the capital of the state of Rio de Janeiro and is located on the western shore of Guanabara Bay. Its climatic condition is Atlantic tropical (Aw), characterized by being megathermal, with an average annual temperature of 16 °C, and a dry season from April to September (Bezerra et al., 2018). The city is divided by the Tijuca Massif in the southern and northern regions. The south, by the Atlantic coast, is a typical urban area with predominance of vehicular emission sources. The north of the city is characterized by higher temperatures and several emissions sources: local vehicular emissions and air masses passing through several avenues, expressways and also through the main industries in the MRRJ (Santa Cruz, Campo Grande, Belford Roxo, Nova Iguaçu and Duque de Caxias).

Santa Cruz and Campo Grande districts (with metallurgical and steel industries) are located in the western area of the city of Rio de Janeiro and the cities of Belford Roxo and Nova Iguaçu (with pharmaceutical, chemical, plastic and metallurgical industries), in the northern area of the MRRJ. The city of Duque de Caxias, in the northeastern zone, has >800 industries in several sectors, such as chemistry, petrochemistry, oil refining, plastic and metallurgy, power generation, gas production and fuel storage, which are important VOC emission sources (Dantas et al., 2020a, 2020b; INEA, 2016).

In this study, data obtained by the automatic monitoring stations in the districts of Irajá and Bangu, located, respectively, in the northern and western areas of the city (Fig. 1), were analyzed. These stations were selected because they are the only Rio de Janeiro stations for which the concentrations of non-methane hydrocarbons (NMHC) are available. These districts frequently receive the air transported from the industrial and petrochemical areas and show ozone pollution episodes. The monitoring station of Irajá is located approximately 100 m away from two main streets with high flux of light and heavy-duty vehicles, close to a taxi station, a supermarket with high flux of trucks, a cemetery and a square where several leisure, cultural and sports events take place (Mendes et al., 2020; Tsuruta et al., 2017). The monitoring station of Bangu is located in an area with moderate vehicular flow, surrounded by the Gericinó (altitude 970 m) and Pedra Branca (altitude 1020 m) mountains, which are natural barriers for air circulation, and frequently receives air masses from the west and east (Geraldino et al., 2020; Tsuruta et al., 2017).

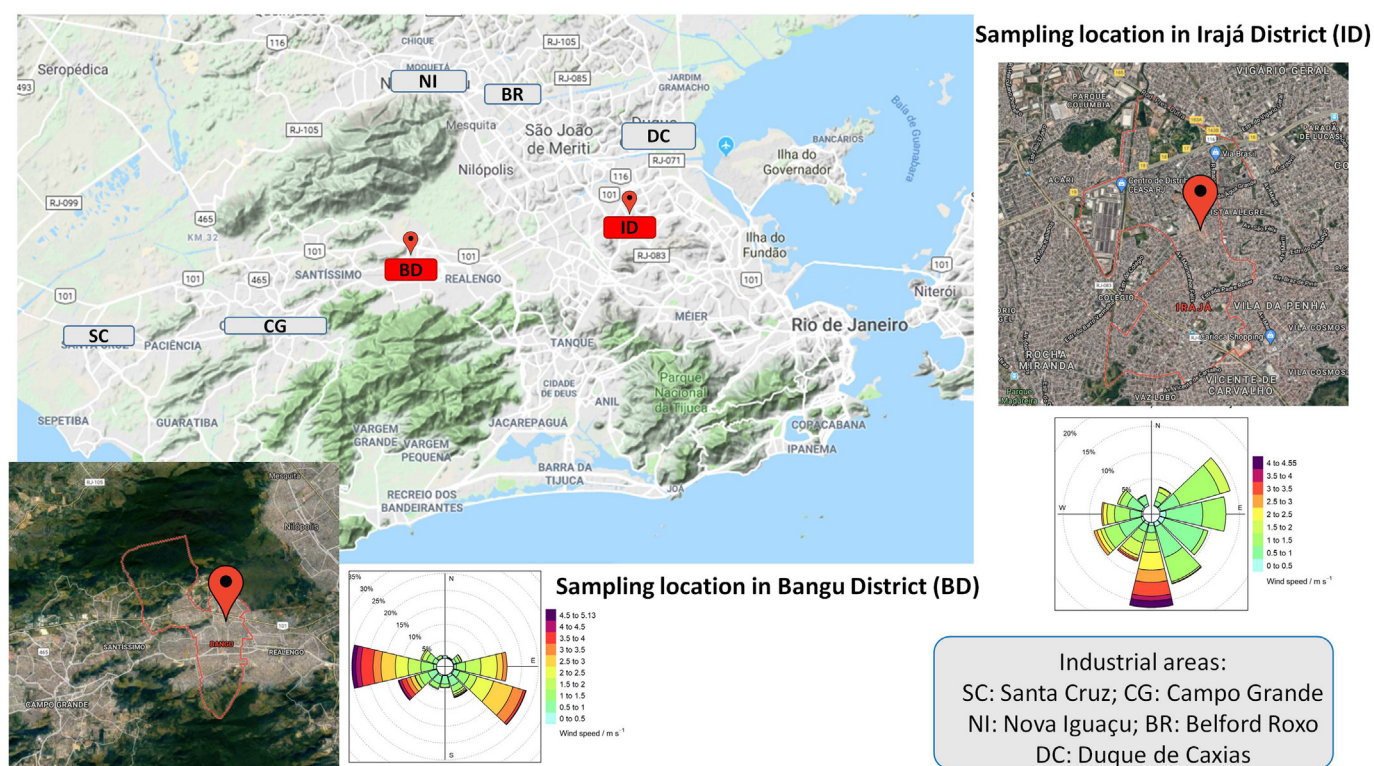


Fig. 1. Localization of the monitoring stations in districts of Irajá (ID) and Bangu (BD), as well as the industrial areas of Campo Grande (CG, western area), Santa Cruz (SC, western area), Belford Roxo (BR, northern area), Nova Iguaçu (NI, northern area) and Duque de Caxias (DC, northeastern area). Wind roses, calculated for both locations, from March 1 to April 16, 2020, are also shown. Wind roses were calculated from 6:30 to 20:30 h (local time BRT).

2.2. Experimental data

Data were obtained by the automatic monitoring stations of the Municipal Department of the Environment (SMAC), using standard methods and equipment according to Brazilian legislation (CONAMA, 2018). The concentrations of NO_2 , NO , O_3 and NMHC were obtained at 10-minute intervals. Ecotech analyzers (Melbourne, Australia) were used to monitor nitrogen oxides- NO and NO_2 (Serinus® 40 model), ozone- O_3 (EC 9810 and Serinus® 10 model), and non-methane hydrocarbons-NMHC (Synspec Alpha 115 model). The detection limits (LOD) for O_3 , and NO_x were $0.01 \mu\text{g m}^{-3}$ and for NMHC, 0.01 ppm. Meteorological parameters (temperature, relative humidity, solar radiation, rainfall, wind speed and direction) were also determined at 10-minute intervals and were used in the interpretation of air pollutant concentration data.

Experimental data were analyzed using standard methods and free software (Openair, 2020; R, 2020). For the quantitative comparison of the results obtained in different days, medians were used instead of mean and standard deviation values, because data are not necessarily parametric (Dantas et al., 2020a). General trends were also analyzed using locally weighted polynomial regression (LOESS) with a confidence interval of 95%.

3. Results and discussion

Experimental results (NO_2 , NO , O_3 and NMHC) were obtained from March 1, 2020 to April 16, 2020 at the monitoring stations of Irajá and Bangu. Since PM_{10} and CO trends were fully discussed by Dantas et al. (2020a), they are not presented in this study. For each day, 1-hour means, from 6:30 to 20:30 h (local time BRT), were calculated. January and February were not considered in this study because during those months, ozone concentrations are highly impacted by the rainfalls, high temperature and solar radiation typical of summer (Alerta Rio, 2020) and primary pollutants are impacted by the high flux of tourists,

due to holidays and the celebration of Carnival. Hourly temperatures, solar radiation and rainfall, from March 1 to April 16, are shown in Fig. S1 (Supplementary material), wind roses are shown in Fig. 1 and, in more detail, in Figs. S2 and S3 (Supplementary material).

The obtained results for O_3 concentrations and the NMHC/ NO_x ratios are shown in Figs. 2 and 3, respectively, for the two studied locations. In these figures the daily 1-h means, from 6:30 to 20:30 h (local time BRT), were plotted as boxplots. Results for NO_x and NMHC are shown in Figs. S4 and S5, in the Supplementary material section. In these figures, three periods of time are shown: before the partial lockdown (03/01/2020–03/22/2020); partial lockdown (03/23/2020–04/05/2020); relaxed partial lockdown (04/06/2020–04/16/2020). As previously mentioned, during the partial lockdown shopping centers, restaurants and fitness centers were closed, educational activities, cultural and sporting events were canceled, and public transport was reduced. Since social distancing was recommended, but not mandatory, the response of the population varied within the different areas of the city and was reduced in April, mainly in the period from 04/06/2020 to 04/16/2020.

As a general trend, ozone concentrations and NMHC/ NO_x ratios increased during the partial lockdown. High temperatures and solar radiation favor ozone formation. Nevertheless, the increase in ozone levels cannot be attributed to these factors since, as shown in Fig. S1, values during the partial lockdown were within the general trend for the previous period, except from March 17 to March 22, when rainfalls contributed to lower temperatures and sunlight. As shown in Figs. S4 and S5 and previously discussed by Dantas et al. (2020a), primary pollutants (NMHC and NO_x) concentrations showed a decrease in the first days of the partial lockdown. Clearly if the emission sources of both primary pollutants were the same, the ratio should have remained constant. The increase in the NMHC/ NO_x ratios, determined at both monitoring stations, indicates different inputs. According to the MRRJ emission inventory (INEA, 2016), vehicular emissions contribute with 67.5 and 66.5% of hydrocarbons and NO_x emissions, respectively. Moreover, the main vehicular sources of NO_x are diesel-fueled vehicles (buses and trucks)

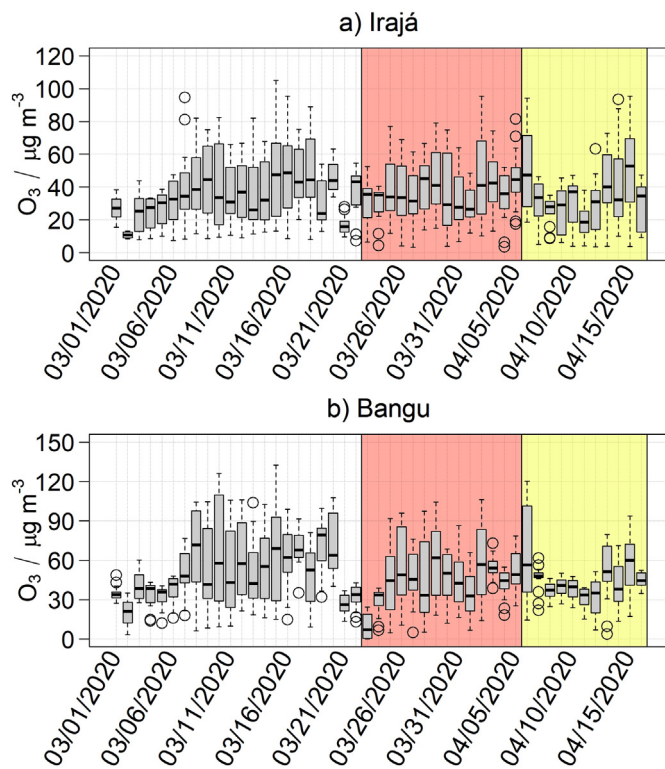


Fig. 2. Ozone concentration values ($\mu\text{g m}^{-3}$) determined at a) Irajá monitoring station; b) Bangu monitoring station from March 1 to April 16, 2020. The periods of time are indicated in different colors: before the partial lockdown (03/01/2020–03/22/2020); partial lockdown (03/23/2020–04/05/2020); relaxed partial lockdown (04/06/2020–04/16/2020).

which contribute with approximately 91% according to the national vehicular inventory, while NMHC are primarily due to light-duty vehicles (46%) and motorcycles (25%) (NEL, 2014). During the partial lockdown, the fleet of buses was partially reduced, while trucks continued to run since industrial and construction activities were maintained, as well as the transport of food and cargo in general. The circulation of passengers' cars had a 70–80% decrease in the first two weeks (03/23–04/05) and then raised to approximately 50% (Cyberlab 2020; Fiocruz, 2020). Then, when considering vehicular emissions, a higher decrease in NMHC should be expected. This fact suggests that other sources significantly contributed to NMHC levels.

According to the air quality report (SMAC, 2020), the highest 8-hour ozone concentrations during the partial lockdown were registered on 03/29/2020 (62.4 and $80.0 \mu\text{g m}^{-3}$ in Irajá and Bangu, respectively) and during the relaxed lockdown, on 04/06/2020 (69.3 and $85.8 \mu\text{g m}^{-3}$ in Irajá and Bangu, respectively) and on 04/15/2020 ($>65 \mu\text{g m}^{-3}$ in both locations). It may be noted that maximum 1-hour means were still higher, for example on 04/06/2020 a value of $120.3 \mu\text{g m}^{-3}$ was registered in Bangu, and on 04/15/2020 a value of $95.5 \mu\text{g m}^{-3}$ was determined in Irajá. On 04/02/2020, 1-hour means were also high: 95.5 and $106.3 \mu\text{g m}^{-3}$ in Irajá and Bangu, respectively (Figs. S6 and S7, Supplementary material). During those days, NMHC/ NO_x ratios were also slightly higher than the median for the period of time. Air masses arriving at the studied locations were simulated using the dispersion model Hysplit implemented by the Air Resources Laboratory - NOAA e Australian Bureau of Meteorology (Hysplit, 2020; Rolph et al., 2017). A backward dispersion model was used to simulate air masses arriving at 12:00 (local time, BRT) for four representative days: two days with relatively high O_3 concentrations and two days with relatively low levels (Fig. 4). On 03/29/2020 and 04/06/2020, when the 8-hour means for ozone concentrations were $>80 \mu\text{g m}^{-3}$ in Bangu, air masses

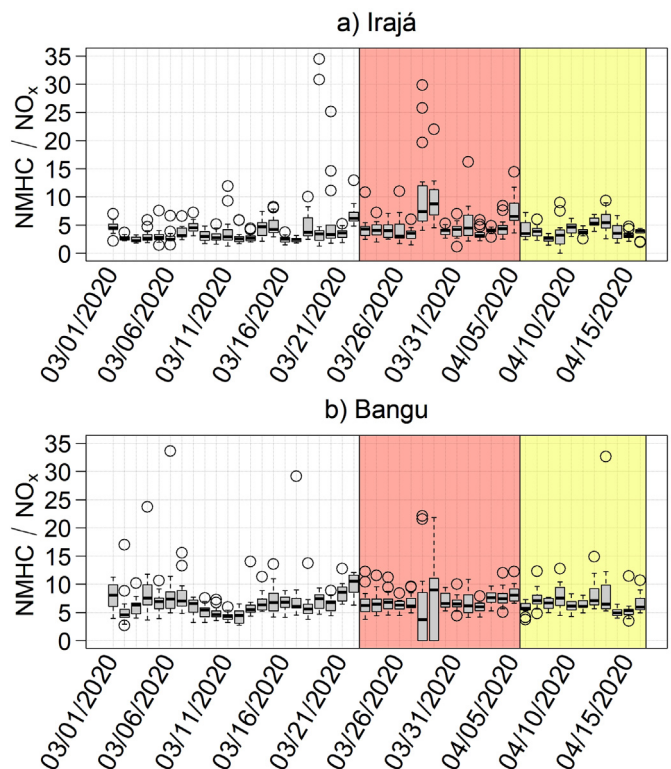


Fig. 3. NMHC/ NO_x concentration ratios (calculated using ppmC and ppm units for NMHC and NO_x , respectively) determined at a) Irajá monitoring station; b) Bangu monitoring station from March 1 to April 16, 2020. The periods of time are indicated in different colors: before the partial lockdown (03/01/2020–03/22/2020); partial lockdown (03/23/2020–04/05/2020); relaxed partial lockdown (04/06/2020–04/16/2020).

trajectories, from north and northeast passed through the industrial areas of Duque de Caxias, Nova Iguaçu and Belford Roxo and over the main highways BR-101 and 116, several avenues and the expressways Linha Vermelha and Avenida Brasil, with intense traffic of both light and heavy-duty vehicles. These winds from the north and northeast favored the transport of pollutants, in particular hydrocarbons, to Irajá and Bangu. On 04/06/2020, the air mass trajectory also passed over the Gerico-nó Mendanha Massif, covered with tropical rainforest, an important source of biogenic volatile organic compounds, such as isoprene, which, in general, have a high ozone forming potential (Silva et al., 2018). By contrast, on 03/23/2020 (the first partial lockdown day) and 04/09/2020, when air masses arrived from the south (Atlantic ocean) and passed through the urban area, ozone concentrations (8-hour means) were lower ($<42 \mu\text{g m}^{-3}$) and NMHC/ NO_x ratios were within the median value for the period.

Then, the increase of ozone concentrations during the social distancing measures could be attributed to the increase in NMHC/ NO_x ratios since atmospheric chemistry in Rio de Janeiro is under VOC-controlled conditions. The increase of ozone formation was higher when air masses arrived from the industrial areas, not only because of highest NMHC/ NO_x ratios, but also because of the VOC mixture reactivity, which is highly increased by industrial air masses rich in aromatic compounds (such as alkyl-substituted benzene and xylene isomers) (Dantas et al., 2020b).

A qualitative analysis is presented in Figs. 5 and 6, which show the changes in hourly average NO_x , NMHC, NMHC/ NO_x ratio and O_3 at the monitoring stations of Irajá and Bangu, respectively, from March 1 to April 16, 2020. The green, red and blue lines show the hourly trends before the partial lockdown (03/01/2020–03/22/2020), during the partial lockdown (03/23/2020–04/05/2020) and after the relaxing of the lockdown (04/06/2020–04/16/2020). During the partial lockdown, hourly averages of NO_x and NMHC were reduced, both in Irajá and Bangu.

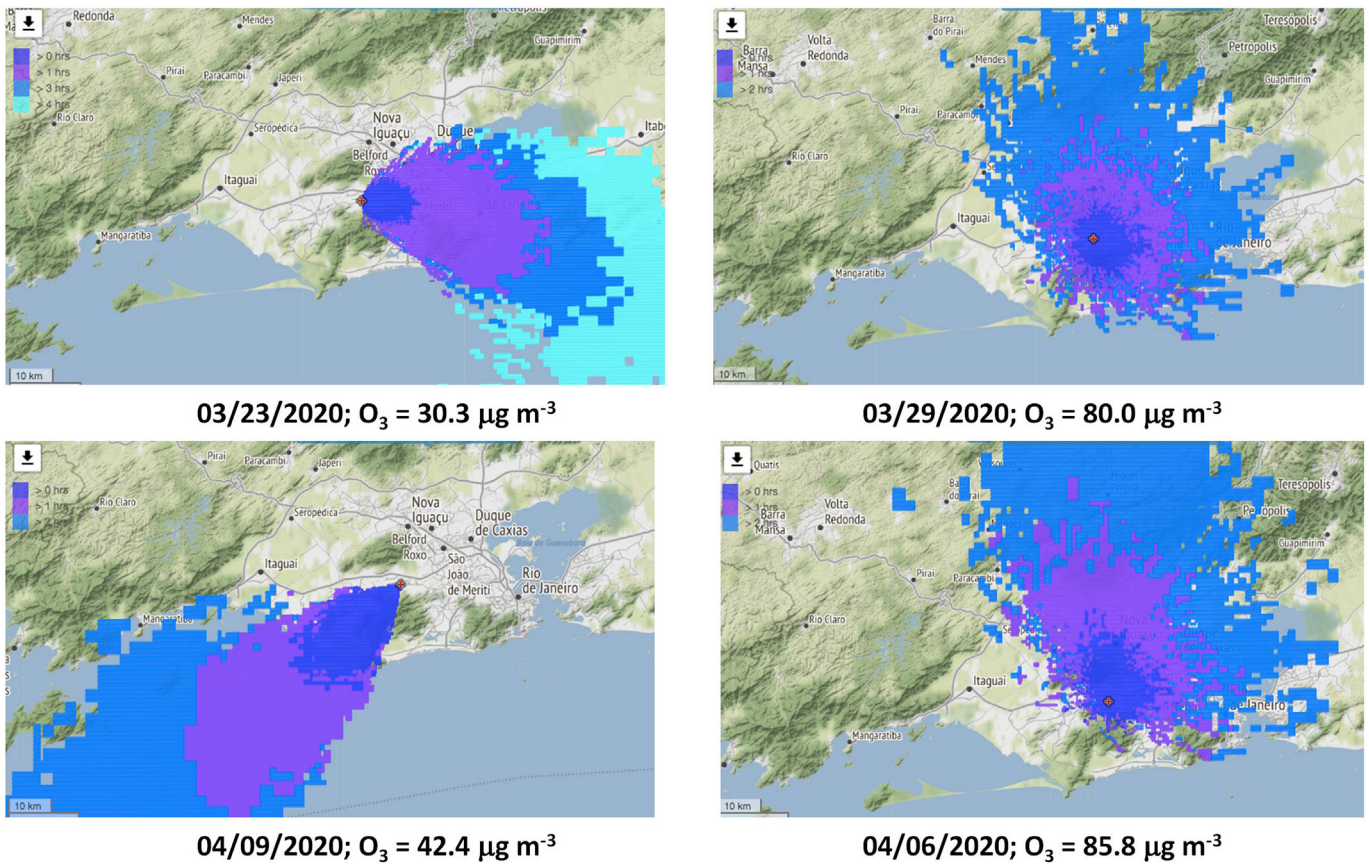


Fig. 4. Dispersion plume with the air masses arriving in Bangu on 03/23/2020 (top left), 03/29/2020 (top right), 04/09/2020 (bottom left) and 04/06/2020 (bottom right). Results obtained using HYSPLIT (NOAA). Maximum 8-hour ozone concentrations, determined at Bangu monitoring station, are also indicated (SMAC, 2020).

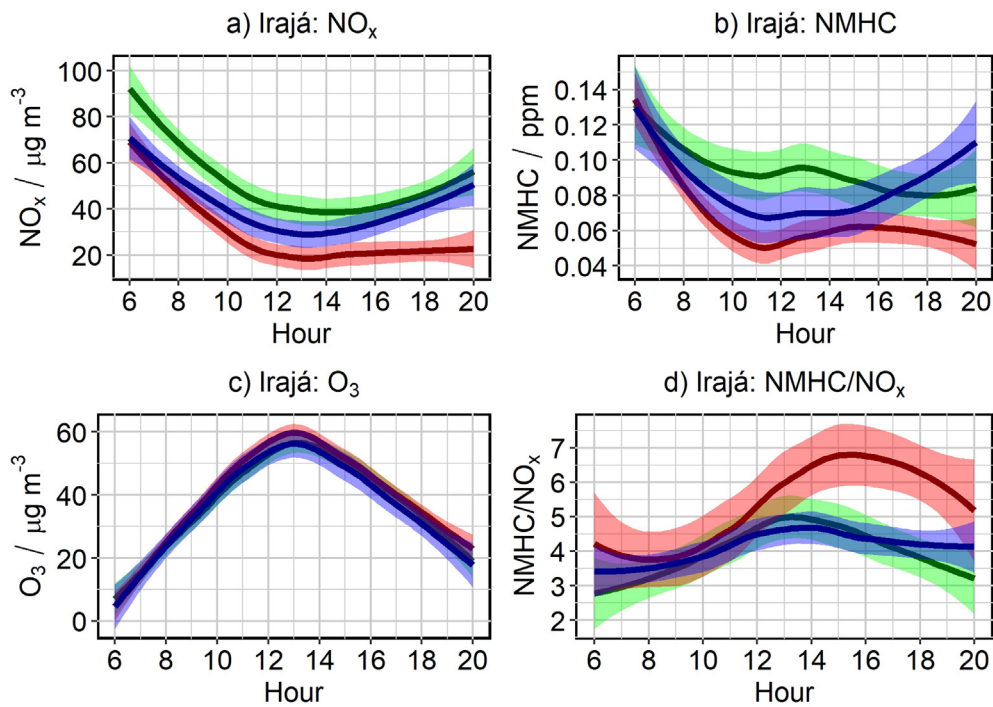


Fig. 5. Changes in hourly averages of NO_x , NMHC, NMHC/ NO_x ratio and O_3 at the monitoring station of Irajá, from March 1 to April 16, 2020. The green, red and blue lines show the hourly trends before the partial lockdown (03/01/2020–03/22/2020), during the partial lockdown (03/23/2020–04/05/2020) and after the relaxing of the lockdown (04/06/2020–04/16/2020).

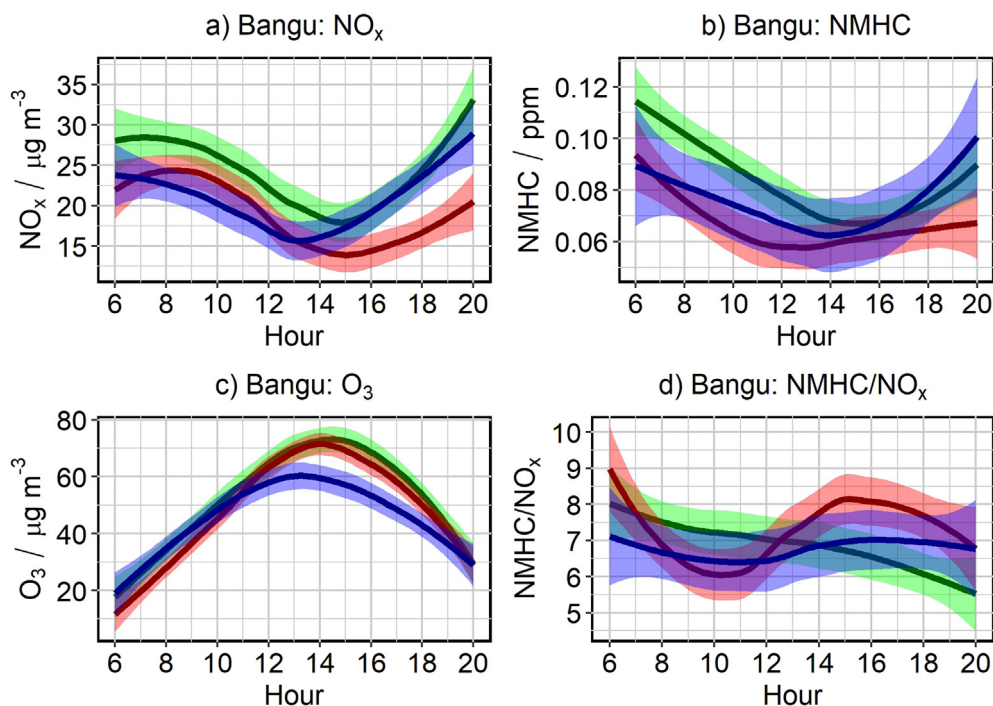


Fig. 6. Changes in hourly averages of NO_x , NMHC, NMHC/ NO_x ratio and O_3 at the monitoring station of Bangu, from March 1 to April 16, 2020. The green, red and blue lines show the hourly trends before the partial lockdown (03/01/2020–03/22/2020), during the partial lockdown (03/23/2020–04/05/2020) and after the relaxing of the lockdown (04/06/2020–04/16/2020).

There was an additional reduction of NO_x after 14 h (BRT local time). In Irajá, NMHC/ NO_x ratios increased, mainly after 14 h, while in Bangu the increase was only observed in the afternoon. Ozone levels had a slight increase, mainly in Irajá, as will be discussed in detail later. After the relaxing of the lockdown, the reduction of primary pollutants, NO_x and NMHC, was small, with a clear increase in the afternoon, and ozone levels remained similar to those before the partial lockdown.

Maximum 1-hour concentrations for NO_x , NMHC and O_3 , as well as wind speed and directions, are also shown in Figs. S6 and S7 (Supplementary material), confirming that the highest O_3 levels are associated with winds from the north-northeast direction.

In order to clarify these results, data were organized in boxplots for each period, as shown in Figs. 7 and 8 for O_3 concentrations and NMHC/ NO_x ratios and in Figs. S8 and S9 (Supplementary material) for NMHC and NO_x . As shown in Fig. 7, 1-hour O_3 concentration values $> 80 \mu\text{g m}^{-3}$, were frequently determined. In Rio de Janeiro, according to the Municipal Department of the Environment, for values between 81 and $160 \mu\text{g m}^{-3}$ the Air Quality Index (AQI) is considered >50 and informed to the public as “Moderate” (SMAC, 2020).

In Table 1, median values of O_3 , NO_x and NMHC concentrations and NMHC/ NO_x ratios are shown for the three periods. In Table S1 (Supplementary material), values calculated for weekdays are presented. Also, in Figs. S10–S13 the boxplots for weekdays are displayed. In Irajá, results showed the same trend, both on weekends and during weekdays, and larger increases were observed for ozone concentrations and NMHC/ NO_x ratios, mainly from 03/23/2020 to 04/05/2020. In Bangu, the decrease in NMHC and NO_x levels was lower and the raise in ozone concentrations and NMHC/ NO_x ratios was moderate from 03/23/2020 to 04/05/2020 and nearly zero after 04/06/2020. In part, lower ozone concentrations in both locations, in April, were due to sparse rainfall and low solar irradiances, from April 6 to April 12 (Fig. S1), which favored the decrease in ozone levels. Anyway, NMHC and NO_x higher levels (in comparison to the previous two weeks) were due to the relaxing of the partial lockdown. During the weekend (April 4 and 5), an increase in vehicular flux was observed. As fully published in media, in April, some gatherings were registered in

supermarkets, banks and other public places, in part due to the payment of salaries, and also by the lack of consensus about the importance and need of social distancing and lockdown. As previously stated, during the first two weeks the adherence to the social mobility restrictions was 70–80%, while in April it was only approximately 50%, mainly in the western area of the city (such as Bangu, Campo Grande and Santa Cruz indicated in Fig. 1).

The dependence of ozone levels with NMHC/ NO_x ratios and VOC speciation is a difficult challenge to air quality policies. Ozone levels are a major concern in tropical cities, such as Rio de Janeiro, where high temperatures and solar irradiation favor the atmospheric processes leading to O_3 formation. It is also the least well-controlled pollutant due to its non-linear dependence with emission sources. These results showed that the reduction of transportation by personal automobiles, in spite of contributing to lower emissions of primary pollutants (NO_2 ,

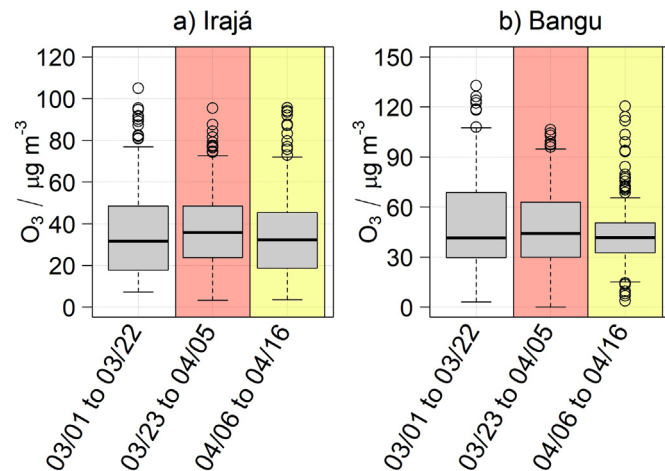


Fig. 7. Concentration values of O_3 ($\mu\text{g m}^{-3}$) determined at Irajá and Bangu monitoring stations from March 1 to April 16, 2020.

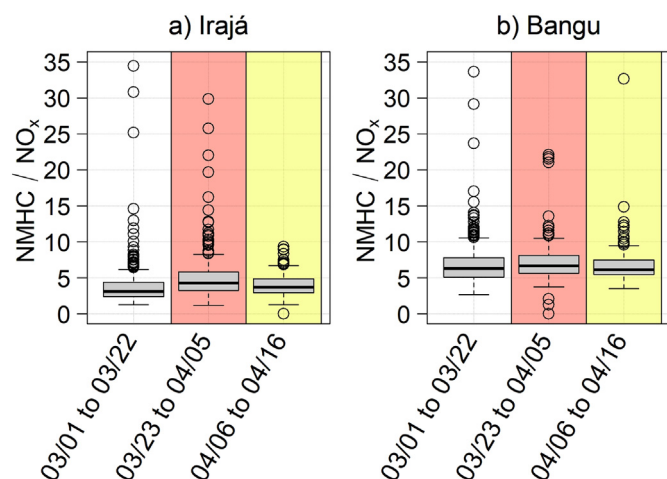


Fig. 8. NMHC/NO_x ratios (calculated in units of ppmC and ppm for NMHC and NO_x, respectively) determined at Irajá and Bangu monitoring stations from March 1 to April 16, 2020.

particulate matter, hydrocarbons) and greenhouse gases, would not be able to cut down ozone concentrations. More difficult tasks should be considered, such as the composition of fuels and the control of industrial emissions to reduce both the emissions and the reactivity of the air masses.

4. Conclusions

These results, as well as several reports across the world, showed that in the short term, concentrations of primary pollutants were reduced due to traffic restrictions and the decreasing in economic activities. However, from a wider point of view, it should be noted that levels of ozone, a major concern secondary pollutant, increased or remained unchanged. A detailed analysis of NMHC/NO_x ratios and trajectories of air masses in the city of Rio de Janeiro, showed that the relatively high ozone concentrations were a consequence of higher ratios (due to a sharper decrease in NO_x than for hydrocarbons) and also to the possible increase in the reactivity of the VOC mixture. Although these are local results, related to the particular topographical and climatic conditions of the city, as well as the input of industrial emissions in the surrounding area, similar situations may be applicable to other metropolitan areas.

The general conclusion, supported by several scientific publications and the media, that air quality was improved during the lockdown should be carefully considered in order to include all pollutants which have an impact of human health. The reduction in particulate matter and NO₂ levels is, certainly, a positive consequence of the social

Table 1

Variations (%) of median values for NMHC/NO_x ratios and the concentrations of O₃ (μg m⁻³), NMHC (ppmC) and NO_x (μg m⁻³) during the partial lockdown (03/23/2020–04/05/2020) and relaxed lockdown (04/06/2020–04/16/2020) relative to the period before the partial lockdown (03/01/2020–03/22/2020).

	Partial lockdown	Relaxed lockdown
Irajá monitoring station		
NMHC/NO _x	+37.3	+18.5
O ₃ (μg m ⁻³)	+12.9	+1.8
NMHC (ppmC)	-25.0	-12.5
NO _x (μg m ⁻³)	-46.1	-9.2
Bangu monitoring station		
NMHC/NO _x	+5.21	-3.0
O ₃ (μg m ⁻³)	+6.3	+0.1
NMHC (ppmC)	-14.3	0
NO _x (μg m ⁻³)	-24.4	-13.8

distancing and lockdown measures, but other negative environmental impacts should be considered.

Finally, these results suggest the importance of NMHC monitoring and speciation. The possibility of including NMHC in air quality standards seems an interesting suggestion for future discussions.

CRedit authorship contribution statement

Bruno Siciliano: Software, Data curation, Validation, Formal analysis, Investigation, Writing - review & editing. **Guilherme Dantas:** Software, Data curation, Validation, Formal analysis, Investigation, Writing - review & editing. **Cleyton M. da Silva:** Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **Graciela Arbilla:** Conceptualization, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Resources, Supervision.

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.

Acknowledgments

The authors acknowledge financial support from the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), the National Council for Scientific and Technological Development (CNPq, 409930/2018-0) and Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ, E26/010.001798/2019). GA, GD and BS acknowledge research scholarships from CNPq and CMS a research scholarship from FUNADESP. The authors also gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model through the READY website (<http://www.ready.noaa.gov>) used in this publication and the Municipal Department of the Environment (SMAC) for providing the data obtained in the monitoring stations.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.139765>.

References

- Alerta Rio, 2020. Sistema Alerta Rio da Prefeitura do Rio de Janeiro. <http://alertario.rio.rj.gov.br/>, Accessed date: 2 May 2020.
- Bezerra, C., de Carvalho, N., Geraldino, C., da Silva, C.M., Arbilla, G., 2018. Air quality in the Maracanã and Deodoro Zones during the Rio 2016 Olympic Games. *J. Braz. Chem. Soc.* 29, 2020–2232.
- CETESB, 2020. São Paulo. Governo do Estado. Qualidade do ar. <https://cetesb.sp.gov.br/ar/boletim-diario/>, Accessed date: 30 April 2020.
- CONAMA, 2018. Resolução CONAMA 491/2018. <http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=740>, Accessed date: 30 April 2020.
- Copernicus, 2020. <https://directory.eoportal.org/web/eoportal/satellite-missions/c-missions/copernicus-sentinel-5p>, Accessed date: 30 April 2020.
- Croda, J., Oliveira, W.K., Frutuoso, R.L., Mandetta, L.H., Silva, D.C.B., Brito-Sousa, J.D., Monteiro, W.M., Lacerda, M.V.G., 2020. COVID-19 in Brazil: advantages of a socialized unified health system and preparation to contain cases. <https://doi.org/10.1590/0037-8682-0167-2020>.
- Cyberlab, d. Dados de contagem veicular. https://twitter.com/cyberlabsai?ref_src=twsrc%5Egoogle%7Ctwcamp%5Eserp%7Ctwgr%5Eauthor, Accessed date: 20 April 2020.
- Dantas, G., Siciliano, B., Freitas, L., Seixas, E.G. de, da Silva, C.M., Arbilla, G., 2019. Why did ozone levels remain high in Rio de Janeiro during the Brazilian truck driver strike? *Atmos. Pollut. Res.* 10, 2018–2029.
- Dantas, G., Siciliano, B., França, B., da Silva, C.M., Arbilla, G., 2020a. The impact of COVID-19 partial lockdown on the air quality of the city of Rio de Janeiro, Brazil. *Sci. Total Environ.* 729, 139085. <https://doi.org/10.1016/j.scitotenv.2020.139085>.
- Dantas, G., Siciliano, B., da Silva, C.M., Arbilla, G., 2020b. A reactivity analysis of volatile organic compounds in a Rio de Janeiro urban area impacted by vehicular and industrial emissions. *Atmos. Pollut. Res.* 11, 1018–1027.
- Di, Q., Dai, L., Wang, Y., Zanobetti, A., Choirat, C., Schwartz, J.D., Dominici, F., 2017a. Association of short-term exposure to air pollution with mortality in older adults. *JAMA* 318, 2446–2456.

- Di, Q.M.S., Wang, M.S., Zanobetti, A., Wang, Y., Koutrakis, P., Choirat, C., Dominici, F., Schwartz, J.D., 2017b. Air pollution and mortality in the Medicare population. *N. Engl. J. Med.* 376, 2513–2522.
- DOERJ, 2020. Diário Oficial do Estado do Rio de Janeiro (DOERJ). Decreto N° 46.980 de 19 de março de 2020. <https://www.legisweb.com.br/legislacao/?id=391093>, Accessed date: 29 April 2020.
- EU, 2017. Air quality standards EU. <https://www.eea.europa.eu/downloads/6cbbc2402c194045a4ad7fcc26cdfc6e/1574331026/air-quality-standards.pdf>, Accessed date: 29 April 2020.
- Finlayson-Pitts, B.J., Pitts, J.N., 2000. *Chemistry of the Upper and Lower Atmosphere. Theory, Experiments and Applications*. Third edition. Academic Press, San Diego.
- Fiocruz, 2020. Agência Fiocruz. Monitora COVID-19 alerta para o aumento da circulação nas ruas. <https://agencia.fiocruz.br/monitoracovid-19-alerta-para-aumento-de-circulacao-nas-ruas>, Accessed date: 20 April 2020.
- Geraldino, C.G., Arbilla, G., da Silva, C.M., Corrêa, S.M., Martins, E.M., 2020. Understanding high tropospheric ozone episodes in Bangu, Rio de Janeiro, Brazil. *Environ. Monit. Assess.* 192, 156. <https://doi.org/10.1007/s10661-020-8119-3>.
- HYSPLIT, 2020. NOAA Air Resources Laboratory. <https://www.ready.noaa.gov/HYSPLIT.php>, Accessed date: 30 April 2020.
- IBGE, 2020. Brazilian cities. <https://cidades.ibge.gov.br/brasil/rj/rio-de-janeiro/panorama>, Accessed date: 17 April 2020.
- INEA, 2016. Inventário Emissões de Fontes Veiculares. <http://www.inea.rj.gov.br/wp-content/uploads/2019/01/Invent%C3%A1rio-de-Emiss%C3%B5es-de-Fontes-Veiculares.pdf>, Accessed date: 17 April 2020.
- Johns Hopkins, 2020. John Hopkins University of Medicine, 2020. Coronavirus Research Center. <https://coronavirus.jhu.edu/map.html>, Accessed date: 30 April 2020.
- London, 2020. Mayor of London. Estimation of changes in air pollution in London during the COVID-19 outbreak. https://www.london.gov.uk/sites/default/files/london_response_to_aqeg_call_for_evidence_april_2020.pdf, Accessed date: 28 April 2020.
- Mahato, S., Pal, S., Ghosh, K.G., 2020. Effect of lockdown amid COVID-19 pandemic on air quality of the megacity Delhi, India. *Sci. Total Environ.* 730, 139086. <https://doi.org/10.1016/j.scitotenv.2020.139086>.
- Mendes, D., Dantas, G., Da Silva, M.A., De Seixas, E.G., Da Silva, C.M., Arbilla, G., 2020. Impact of the petrochemical complex on the air quality of an urban area in the city of Rio de Janeiro, Brazil. *Bull. Environ. Contam. Toxicol.* 104, 438–443.
- Muhammad, S., Long, X., Salman, M., 2020. COVID-19 pandemic and environmental pollution: a blessing in disguise? *Sci. Total Environ.* 728, 138820. <https://doi.org/10.1016/j.scitotenv.2020.138820>.
- NAAQS, 2020. United States Environmental Protection Agency. Criteria air pollutants. <https://www.epa.gov/criteria-air-pollutants/naaqs-table>, Accessed date: 29 April 2020.
- Nakada, L.Y.K., Urban, R.C., 2020. COVID-19 pandemic: impacts on the air quality during the partial lockdown in São Paulo state, Brazil. *Sci. Total Environ.* 730, 139087. <https://doi.org/10.1016/j.scitotenv.2020.139087>.
- NASA, 2020. National Aeronautics and Space Administration. Earth Observatory <https://earthobservatory.nasa.gov/images/146362/airborne-nitrogen-dioxide-plummets-over-china>, Accessed date: 17 April 2020.
- NEI, 2014. Inventário Nacional de Emissões Atmosféricas por Veículos Automotores Rodoviários. http://www.antt.gov.br/backend/galeria/arquivos/inventario_de_emissoes_por_veiculos_rodoviarios_2013.pdf, Accessed date: 20 April 2020.
- Openair, 2020. The Openair Project. <http://www.openair-project.org/GettingStarted/Default.aspx>, Accessed date: 29 April 2020.
- R, 2020. <https://www.r-project.org/>, Accessed date: 15 April 2020.
- Rolph, G., Stein, A., Stunder, B., 2017. Real-time Environmental Applications and Display sYstem: READY. *Environ. Model. Softw.* 95, 210–228.
- Saadat, S., Rawtani, D., Hussain, C.M., 2020. Environmental perspective of COVID-19. *Sci. Total Environ.* 728, 138870. <https://doi.org/10.1016/j.scitotenv.2020.138870>.
- Sharma, S., Zhang, M., Anshika Gao, J., Zhang, H., 2020. Effect of restricted emissions during COVID-19 n air quality in India. *Sci. Total Environ.* 728, 138878. <https://doi.org/10.1016/j.scitotenv.2020.138878>.
- Silva, C.M., Corrêa, S.M., Arbilla, G., 2018. Isoprene emissions and ozone formation in urban conditions: a case study in the city of Rio de Janeiro. *Bull. Environ. Contam. Toxicol.* 100, 184–188.
- SMAC, 2020. Prefeitura da Cidade do Rio de Janeiro. Boletim da Qualidade do Ar. <http://jeap.rio.rj.gov.br/je-metinfosmac/boletim>, Accessed date: 29 April 2020.
- Tobias, A., Carnerero, C., Reche, C., Massagué, J., Via, M., Minguillón, M.C., Alastuey, A., Querol, X., 2020. Changes in air quality during the lockdown in Barcelona (Spain) one month into the SARS-CoV-2 epidemic. *Sci. Total Environ.* 726, 138540. <https://doi.org/10.1016/j.scitotenv.2020.138540>.
- Tsuruta, F., De Carvalho, N., Da Silva, C., Arbilla, G., 2017. Air quality indexes in the city of Rio de Janeiro during the 2016 Olympic and Paralympic Games. *J. Braz. Chem. Soc.* 29, 1291–1303.
- US EPA, 2020. United States Environmental Protection Agency. Health effects of ozone pollution. <https://www.epa.gov/ground-level-ozone-pollution/health-effects-ozone-pollution>, Accessed date: 29 April 2020.
- Wang, Q., Su, M., 2020. A preliminary assessment of the impact of COVID-19 on environment – a case study of China. *Sci. Total Environ.* 728, 138915. <https://doi.org/10.1016/j.scitotenv.2020.138915>.
- WHO, 2005. World Health Organization. Air quality guidelines-global update 2005. <https://www.who.int/airpollution/publications/aqg2005/en/>, Accessed date: 29 April 2020.
- WHO, 2008. Health risks of ozone from long-range transboundary air pollution. http://www.euro.who.int/__data/assets/pdf_file/0005/78647/E91843.pdf, Accessed date: 29 April 2020.
- WHO, 2016. World Health Organization. WHO Expert Consultation. Available evidence for future update of the WHO Global Air Quality Guidelines (AQGs) (2016). <http://www.euro.who.int/en/health-topics/environment-and-health/air-quality/publications/2016/who-expert-consultation-available-evidence-for-the-future-update-of-the-who-global-air-quality-guidelines-aqgs-2016>, Accessed date: 29 April 2020.
- WHO, 2020. World Health Organization. WHO Director-General's opening remarks at the media briefing on COVID-19 - 11 March 2020. <https://www.who.int/dg/speeches/detail/who-director-general-s-opening-remarks-at-the-media-briefing-on-covid-19-11-march-2020>, Accessed date: 29 April 2020.