A comprehensive review of tropospheric ozone in Brazilian urban areas

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ABSTRACT

This study presents a literature review on tropospheric ozone (O_3) formation and the influence of emission sources on its concentrations in urban regions of Brazil. It was conducted within the scope of the project "Estudo do impacto e da contribuição das fontes das emissões veiculares, de fontes fixas e de distribuição de gasool na formação do ozônio troposférico no eixo São Paulo-Belo Horizonte".

High O_3 concentrations are frequently recorded in various urban regions and their surroundings in Brazil, including the areas covered by this study: the Metropolitan Region of São Paulo (MRSP) and the Metropolitan Region of Belo Horizonte (MRBH). In these regions and their surroundings, the heavy vehicular traffic, the number of fuel production and distribution sources, and other fixed sources play a relevant role in O_3 concentrations, besides other atmospheric pollutants.

The review revealed that, although O_3 in Brazil has been studied for many years through experiments, data analysis, and modeling, the literature still lacks clarity regarding the contributions of the various emission sources that collectively influence ambient O_3 concentrations in Brazilian urban areas, including the São Paulo–Belo Horizonte corridor.

INTRODUCTION

Tropospheric ozone (O_3) is a secondary pollutant generated in the atmosphere by photochemical reactions from its mainly precursors – Volatile Organic Compounds (VOCs) and nitrogen oxides (NOx), which are emitted by several sources. Especially during spring and summer seasons higher concentrations are observed across many urban and surrounding areas in Brazil. For example, in MRSP, in September 2024, presented 22.7% of days with bad air quality for O_3 (> 130 µg m^{-3}, 8-hour moving average), considering the monitoring performed by CETESB.

This review aims to provide an overview of studies on tropospheric ozone in Brazilian urban areas and their relationship with emission sources, to assess the current state of knowledge on the subject in Brazil.

METHODOLOGY

The research was performed in the Consensus free tool, which is an academic search engine, powered by AI. The tool, based on research phrases, synthetizes the papers published by title and provided a study snapshot. The research phrase used was "atmospheric pollutant ozone and emission sources in Brazilian urban areas". The period of research included papers published since 2000 and all types of study (e.g., observational study, modeling, literature review etc).

The analysis of results consisted in: i) verified the veracity of papers directly in the periodic; ii) download the paper; iii) Based on title and study snapshot papers without the scope of research were excluded; iv) The load of results was interrupted when the papers listed was out of scope. The main results were synthesized to build a view about atmospheric pollutant ozone and emission sources in Brazilian urban regions.

RESULTS

Overall, ninety papers were found and after careful analysis of scope, forty-one were excluded. The papers excluded are less adherent, repeated, or not for Brazilian urban areas. Ten papers are mainly focused on emissions from vegetation and their influence on tropospheric ozone, as well as their benefits in mitigating air pollution, which the main results are not presented here. Finaly, five papers were included since during the analysis were identified as relevant for research.

The primary focus of five of the forty-four papers analyzed in greater depth was on emissions. Among them, Ibarra et al. [1], Kawashima et al. [2], and Hoinaski et al. [3] specifically addressed emission inventories for Brazil. The main findings of these studies are summarized in Table 1.

Table 2 presents the main studies found related to main focus of research review, totalizing 39.

Some studies, although excluded from table 2, brought information about the Ambiental concentrations and vehicular emissions of VOCs in urban areas (e.g., Martins et al. [4], Martins et al. [5], Nogueira et al. [6], Dominutti et al. [7], Nogueira et al. [8], Pereira et al. [9]).

DISCUSSION AND REMARKS

Most of the studies were conducted in the regions of São Paulo, Rio de Janeiro and Belo Horizonte. This can be attributed to the fact that these urban areas are part of the country's main economic region and, consequently, among the most impacted by air pollution. Furthermore, these areas are home to prominent universities, which contribute significantly to the volume of research conducted there.

Only five studies were found published in periodic addressing emission inventory for Brazil or urban areas. Although official reports that could provide state-level emission inventories were not considered, there remains a significant gap in atmospheric emission data in Brazil to support deeper air quality studies. The global emission inventories usually lack the spatial resolution and are inaccurate and/or not represent many important local emission sources.

The finding of studies (table 2) indicates that most of studies have employed measurements with statistical analyses, and modeling. The use of satellite products is still less frequent, likely due to limitations in representing surface-level conditions. Integrating multiple approaches, including conventional monitoring stations, low-cost sensors, satellite data, statistical analyses, and air quality models could be helpful to enhance the understanding of atmospheric pollution.

Further, vehicular emissions are pointed out as the dominant source of air pollution in major urban areas, with light-duty flex-fuel vehicles and motorcycles contribute significantly to ozone pollution. In the truck driver strike in São Paulo, in 2018, led to a drop in primary pollutants (CO, NO) but a rise in ozone. This real-world experiment occurred emphasizing the role of traffic and chemical regime ($VOCs/NO_X$) on ozone, which was also observed during COVID-19 lockdown. The photochemical models highlight the importance of VOCs/NOx ratios and the influence of meteorological conditions on ozone concentrations. Finally, the results for MRSP (variations in usage occurred between 2010-2013) indicate that ethanol use increase ozone levels and decrease ultrafine particles compared to gasoline.

The contribution of sources to ozone formation varies by region, influenced by local and regional emissions, as well as the transport of ozone and its precursors. Figure 1 provides an overview of this interactions of sources, meteorological conditions and chemical regime for tropospheric ozone.

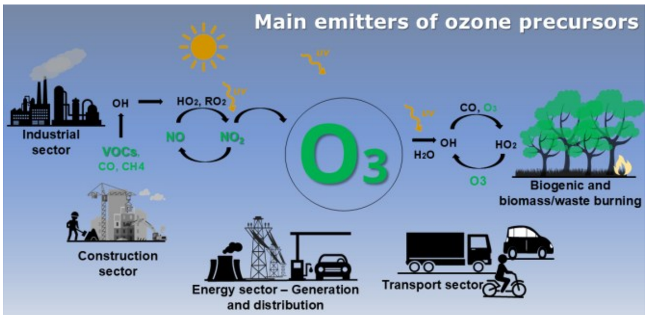

Figure 1: Schematic representation of tropospheric ozone (O_3) formation and the main sources of its precursors.

Table 1: Main scientific papers reviewed on atmospheric emission inventories, with key findings.

Ref.	Main results
[1]	The VEIN v0.2.2 model provides high-resolution vehicular emissions inventories for various fields, aiding in atmospheric models, health studies, air quality standardizations, and decision-making.
[10-11]	In Belo Horizonte, Brazil, 75 chimneys contribute to regulated air pollutant emissions, with 305, 235, 234, 224, 206, 180, and 63 t $year^{-1}$ for NO_X, CO, TSP, PM_{10}, $PM_{2.5}$, SO_2, and VOC, respectively. Vehicular air pollutant emissions in Minas Gerais, Brazil, are mainly influenced by exhaust, tire and brake wear, and road surface wear, with light commercial vehicles and ethanol cars contributing significantly.
[2]	This study developed a spatialized atmospheric emission inventory for Brazil's main industrial sources, revealing that NOx emissions were slightly lower than vehicular emissions, SOx emissions were 300 times greater, CO 17 times greater than vehicular emissions, and PM 360 times greater than vehicular emissions.
[12]	The Brazilian top-down vehicle emission inventory (VEI) of 2012 is a reliable and representative source for modeling air quality in urban areas, with vehicles being the main contributor to particulate matter emissions.
[3]	The Brazilian Atmospheric Inventories (BRAIN) is a comprehensive database of air quality and its drivers in Brazil, providing valuable data for developing air quality policies and research.

Table 2: Summary of the reviewed scientific articles, including publication year, authorship, main results, and type of study.

Year/Ref.	Main results	Type of study
2025 [13]	It suggests, in Vitória, Brazil, that both anthropogenic sources (such as solvent use, industrial processes, vehicle emissions, and fuel combustion) and biogenic sources (notably isoprene and other plant emissions) significantly contribute to VOCs with high potential for ozone and SOA formation, and accurate source apportionment requires accounting for photochemical loss and intraday variability to effectively target pollution control strategies.	Observational
2024 [14]	Ethanol biofuel use in Brazil may increase toxic aldehydes and ozone levels, potentially threatening air quality and human health in urban areas.	Observational
2024 [15]	In the metropolitan area of Belo Horizonte, vehicular, industrial, and mining emissions contribute to poor air quality, with fire outbreaks significantly contributing to air pollution.	Observational
2023 [16]	It was reviewed 29 air quality modeling studies performed over the MASP published between 2001 and 2023. Air quality modeling in the São Paulo metropolitan area shows good performance for ozone, but needs further research on climate change, emissions, and satellite data.	Review - modeling
2023 [17]	Brazilian urban centers have high levels of air pollutants, with SO_2, NO_2, formaldehyde, and benzene exceeding WHO recommendations, influenced by factors such as temperature, solar radiation, and wind direction. 16 gaseous pollutants/contaminants (SO_2, O_3, NO_2, NOx, NO, NH_3, BTEX, HCOH, CH_3COH, HCl, HNO_3, HCOOH and CH_3COOH) were evaluated in 5 large Brazilian urban centers (São Paulo, Salvador, Rio de Janeiro, Londrina and Rio de Janeiro) using passive sampling.	Observational
2023 [18]	Brazilian urban centers have high levels of HCHO and CH_3COH, with vehicle emissions being the main source, and these compounds pose a health risk due to their carcinogenic properties. It was investigated São Paulo, Belo Horizonte, Salvador, Rio de Janeiro, and Londrina.	Observational
2023 [19]	Under RCP 4.5, peak ozone concentrations in São Paulo's metropolitan area could be higher in urban areas than under RCP 8.5, due to increased temperatures, higher surface radiation, and reduced cloudiness.	Modeling
2023 [20]	The WRF-Chem model accurately simulates air quality in southeastern Brazil, with ozone being the best simulated pollutant for temporal variability and trends.	Modeling
2023 [21]	Current Brazilian national legislation is outdated, leading to multiple exceedances of WHO Air Quality Guidelines 2021, with 62% of São Paulo stations	Observational

	showing increasing ozone trends and 85.7%) showing decreasing trends in Rio de Janeiro.	
2021 [22]	Biomass burning and the metropolitan area of São Paulo emissions contribute to up to 80% of surface ozone pollution in communities over 200 km away in Brazil.	Observational
2021 [23]	Urban mobility restrictions in Rio de Janeiro, Brazil, showed that controlling both stationary and mobile sources is crucial for improving air quality, with vehicular emissions being the main source of pollutants.	Observational
2021 [24]	The nocturnal maximum of ozone concentrations in the Metropolitan Area of So Paulo is related to vertical transport from higher levels of the atmosphere to the surface, not synoptic condition.	Modeling
2021 [25]	Near a petrochemical complex in São Paulo, Brazil, there is a significant presence of aromatic hydrocarbons, with vehicular emissions being the main source, and industrial sources also contributing to the formation of secondary pollutants.	Observational
2021 [26]	Light-duty flex-fuel vehicles contribute significantly to ozone formation in the Rio de Janeiro metropolitan area, with propene being the main contributor.	Observational
2020 [27]	Vehicles significantly affect air quality in Aracaju-SE, Brazil, with CO concentrations exceeding standards and NO_2 concentrations exceeding standards, mainly due to heavy vehicles and light vehicles.	Observational
2020 [28]	Vehicular emissions are the main source of BTEX compounds in Salvador, Bahia, Brazil, with lower concentrations in dry periods due to higher temperatures and solar radiation favoring photochemical reactions.	Observational
2020 [29]	Ozone episodes in the Irajá district of Rio de Janeiro depend on the ratios of volatile organic compounds to	Observational

	nitrogen oxides, with transport of air masses playing a crucial role in ozone levels.	
2017, 2020 [30-31]	High ozone levels in Bangu, Rio de Janeiro, are mainly caused by pollutant transport and low NOx levels, with photochemical activity, and mountain ranges contributing to increased surface temperatures and pollution accumulation.	Observational
2019 [32]	The BEP-WUDAPT parameterization improves meteorological field representation, but not ozone surface concentrations, in the WRF-Chem model for the So Paulo metropolitan area.	Modeling
2019 [33]	Ozone concentrations in São Paulo, Brazil, show a significant correlation with fuel sales, with radiation and temperature being key factors in determining ozone levels.	Observational
2018 [34]	The WRF-SMOKE-CMAQ modeling system effectively represents meteorological and air quality conditions in So Paulo, Brazil, with some limitations in representing $PM_{2.5}$ concentrations.	Modeling
2017 [35]	Air quality in São Paulo has improved over the last 30 years, but controlling secondary pollutants like ozone and fine particles remains a challenge.	Review
2016 [36]	In a Brazilian city (Londrina), on-road traffic is the main source of black carbon during daytime, with local waste and biomass burning at night contributing to ozone. Both local and regional sources contributed to high ozone episodes.	Observational
2014, 2017 [37-39]	Increased ethanol uses in blended gasoline in São Paulo led to higher ozone levels. Not significant changes on $PM_{2.5}$ concentrations was observed, while for ultra fine particles it was found that the shifting from gasoline to ethanol leads to a one-third increase during morning hours, when traffic emissions are highest. The findings support that São Paulo's atmosphere is VOC-limited.	Observational study
2015 [40]	Air quality modeling in Southeastern Brazil helps predict pollutant concentrations, inform public policies, and study the impact of climate change on air quality and health. It was presented operational tools, developed using the WRF/Chem and BRAMS-SPM models as platforms, for forecasting pollutant	Modeling

	concentrations in the southeastern region of Brazil.	
2015 [41]	Brazil's emission control policies, particularly PROCONVE, have improved air quality in the So Paulo metropolitan area, except for ozone, with peaks during rush hours and different patterns for pollutants.	Observational
2014 [42]	The use of alternative fuels like ethanol and CNG in Brazilian cities leads to increased ozone formation, with the model revealing the influence of precursors, seasons, and weather conditions on photochemical smog formation.	*Modeling
2013 [43]	Motorcycles using gasohol in Brazilian cities contribute to urban ozone pollution, leading to ozone levels exceeding national limits within three years. Study conducted in Rio de Janeiro, Brazil.	Observational and Modeling
2010 [44]	Reducing VOC emissions can effectively decrease ozone concentrations in the São Paulo Metropolitan Area, while NOx reductions may increase ozone levels.	Observational and modeling
2010 [45]	Manaus City's urban plume contributes to strong photochemical ozone formation in the Amazon Green Ocean, with aerosol concentrations significantly enhanced and sensitivity to NOx emissions.	Observational
2009 [46]	Ozone concentrations in the So Paulo metropolitan region increase during weekends due to higher levels of volatile organic compounds and NOx, affecting air quality.	Observational
2008 [47]	Ozone concentrations in the Megacity of São Paulo are more sensitive to VOCs than to NOx, with the most important species being aromatics, olefins, ethene, and formaldehyde.	Modeling
2007 [48]	Implementing a control program for mobile emissions in São Paulo, Brazil, significantly reduces tropospheric ozone concentrations, improving air quality and protecting human health.	Modeling
2006 [49]	Reducing reactive hydrocarbon emissions could promote lower ozone concentrations in the São Paulo metropolitan area, with meteorological variables and ozone precursor limitations playing a role.	Modeling
2005 [50]	The simplified photochemical module was coupled with RAMS, which effectively forecasts ozone concentrations in the São Paulo metropolitan area, providing a useful tool for emission control strategies.	Modeling
2004 [51]	Using the official emissions inventory of vehicular emissions in simulations led to lower ozone values and overestimation of nitrogen oxide emissions in the São Paulo Metropolitan Area, Brazil.	Modeling

*Not published in journal.

CONCLUSION

Additional studies concerning tropospheric ozone in Brazilian urban regions, including the São Paulo–Belo Horizonte corridor, are necessary to better understand the contribution of specific sources and reactions. The lack of accurate atmospheric emissions inventory is a challenge since data from specific sectors are not publicly available, organized or even documented. Furthermore, the lack of air quality monitoring and the lack of transparency and the years-long delay in air quality data release, contribute to hinders the development and publication of scientific studies in many Brazilian urban areas.

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