Comparative ozone production sensitivity to NO$_x$ and VOCs in Quito, Ecuador and Santiago, Chile: ~~implications for control strategies in times of climate action~~

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Abstract. Amid the current climate and environmental crises ~~crisis~~, cities are being called to reduce levels of ~~levels of~~ atmospheric pollutants that ~~are~~ also act as short-lived climate forcers, ~~(SLCF)~~ such as ozone and PM$_{2.5}$. This endeavor presents new challenges, ~~s~~ especially in understudied regions. ~~in terms of control strategies.~~ Here, we use a chemical box model to investigate the ozone production sensitivity to NO$_x$ and VOCs in Quito, Ecuador and Santiago, Chile. We present ozone production rates (P(O$_3$)) calculated using VOC measurements taken in Santiago, along with VOC vs. CO linear regressions (LRs), and complementing the analysis with Monte Carlo (MC) simulations. In Quito, VOC measurements are unavailable for which we simulated a range of concentrations using LRs and MC simulations. We modeled P(O$_3$) in March 2021 and for typical conditions per season in 2022. We calculated a range of P(O$_3$) in Quito of 15-50 ppbv h^{-1} year-round. In Santiago, we found that P(O$_3$) is 23-50 ppbv h^{-1} in the ozone season. Although the P(O$_3$) magnitudes were found to be comparable, Santiago has a well-established ozone season, unlike Quito, where concentrations are lower. From sensitivity experiments, alkenes and aromatics contribute 50% to P(O$_3$) in Santiago and could reach 70-90% in Quito (noon and afternoon). Aldehydes and ketones contribute 30-40% in Santiago and about 20% in Quito (noon and afternoon). We estimate the isoprene contribution to be 20% in Santiago and 10% in Quito. VOC reduction experiments generally lowered P(O$_3$) in both cities. In Santiago, NO$_x$ reductions increased the morning P(O$_3$).

~~Here, we scrutinize the ozone production sensitivity to NO$_x$ and VOCs in Quito, Ecuador and Santiago, Chile, and we discuss the implications for precursor controls. To this end, we use a chemical box model constrained with VOCs, meteorological, and air quality data. Comparable ozone production rates (P(O$_3$)=15-35 ppbv h^{-1}) were found to influence both cities, which lead to a well-established ozone season in Santiago, but not in Quito. A partial explanation to this difference is the distinct mixing conditions in both cities. Alkenes and aromatics contribute 60-90% to ozone production in Quito and 50-60% in Santiago. Aldehydes and ketones contribute an additional 20-30% in Santiago. Isoprene contributes 10% in Quito and 20% in Santiago. Any isolated measure to reduce NO$_x$ alone would impact both cities negatively. For example, a 75 % reduction in NO$_x$ causes a 30% increase in peak P(O$_3$) in Quito and a 54% increase in Santiago. In contrast, equal reductions in NO$_x$ and VOCs would have a beneficial effect. For example, a 75% decrease in both precursors would cut the peak P(O$_3$) by more than half in both cities. Therefore, only parallel controls on NO$_x$ and VOCs in both cities have the potential of curbing ozone from the simultaneous perspective of public health and climate action.~~

1. Introduction

Tropospheric ozone bears a dual nature of a serious air contaminant and a short-lived climate forcer (SLCF). At the ground level, ozone negatively impacts ~~the health of~~ human health and ~~non-human populations~~vegetation due to its oxidative nature that

affects the respiration function in living beings (Fleming et al., 2018; Gaudel et al., 2018; Karlsson et al., 2017; ~~Madden and~~ ~~Hogsett, 2001~~; Malley et al., 2017; Soares and Silva, 2022). Furthermore, tropospheric ozone is the third largest anthropogenic climate forcer (Anon, 2014; Checa-Garcia et al., 2018; Skeie et al., 2020), and it deters carbon sinks as it is a limiting factor to carbon capture in vegetation (Mills et al., 2016; Zhang et al., 2022). Hence, mitigating the ozone abundance in the ambient air is an action that simultaneously protects public health while it combats climate change. For this reason, cities are currently called to take this action (Intergovernmental Panel on Climate Change (IPCC), 2023). In most cities across the world, ozone is considered one of the criteria air pollutants and thus is regulated by local and national legislation (Lyu et al., 2023). However, ozone continues to be a major air quality concern in many regions of the world despite decades of studying the complex and non-linear nature of its production chemistry. This complexity imposes tailoring control strategies appropriate for each city that carefully consider the local ~~makeup~~ composition of the ambient air.

The mitigation of ozone to benefit in parallel air quality and climate presents a new challenge in devising efficient controls on ozone precursors at the urban level. This need is particularly pressing in understudied regions that are highly vulnerable to climate change and that still struggle with poor air quality, such as cities in South America (SA) (Cazorla et al., 2022). In this work, we ~~scrutinize~~ investigate the sensitivity of ozone production to its precursors ~~the chemistry of ozone production and its~~ ~~sensitivity to its precursors~~ (NO$_x$ and VOCs) in a comparative fashion between Quito (Ecuador) and Santiago (Chile) during time periods in 2021 and 2022. To this end, we use a constrained photochemical box model, namely the F0AM (Framework for 0-D Atmospheric Modeling) (Wolfe et al., 2016). We present ozone production rates (P(O$_3$)) calculated using VOC measurements taken in Santiago, along with VOC vs. CO linear regressions (LRs), and complementing the analysis with Monte Carlo (MC) simulations. In Quito, in situ measurements of VOCs are not available. Hence, we used MC simulations to generate an array of VOC inputs to the model. We present the results as a series of sensitivity model runs. We discuss the impact of changing the precursor proportion on the chemistry of ozone production in both cities. ~~we present a unique set of VOC measurements taken in~~ ~~Santiago in March 2021. We use VOC vs. CO correlations from measurements in Santiago to scale CO and estimate VOCs in~~ ~~Quito. We incorporate VOCS, meteorological, and air quality data into a detailed photochemical box model using the F0AM~~ ~~(Framework for 0-D Atmospheric Modeling) (Wolfe et al., 2016). We present a discussion about the impact of changing~~ ~~precursor proportion on the chemistry of ozone production at both cities that could result from actions meant to curb ozone as an~~ ~~air pollutant and a SLCF.~~

A recent ozone trend study in South America demonstrated that the short- and long-term ozone exposure in tropical cities Quito and Bogota are lower than those encountered at extratropical cities Santiago and São Paulo (Seguel et al., 2024). This regional distribution of ozone exposure seems somewhat counterintuitive, given year-round solar radiation at high altitudes over tropical Andean cities combined with their intense traffic emissions. Previous work showed that a VOC-limited environment constrained ozone production in Quito, but rates of ozone production were not compared to other cities in the region (Cazorla, 2016). On the other hand, Santiago has been dealing with over two decades of ozone pollution and seasonal exceedances that are worsening in time due to an increased frequency of extreme heat and wildfire events (Seguel et al., 2020, 2024). ~~In this work~~Here, we compare the ozone production chemistry between both cities to gain insight into mechanisms that can lead to ozone ~~accumulation~~ formation in the ambient air.

An important angle to consider is the effect that a shift in precursors would have on ozone production rates. ~~An important angle~~ ~~to this work is investigating what would be the effect of applying control measures to reduce levels of air pollutants that are~~

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SLCFs on ozone production rates. For example, many cities in SA, including Quito and Santiago, have a seasonal high $PM_{2.5}$ problem (Gómez Peláez et al., 2020). As with ozone, reducing levels of $PM_{2.5}$ in cities protects public health while it is an effective climate action ((Szopa et al., 2023)Intergovernmental Panel on Climate Change (IPCC), 2023). A direct way of cutting down levels of $PM_{2.5}$ is reducing diesel-based traffic emissions, which in turn lowers NO_x levels. This beneficial outcome was observed during the COVID-19 pandemic confinements, when primary pollutants and $PM_{2.5}$ decreased immediately as a direct consequence of mobility restrictions. However, the effect on ozone was the opposite. Research conducted in Quito, Santiago and other South American cities proved showed that NO_x reductions increased ozone production rates and ambient groud-level ozone due to a shift in the production chemistry from a VOC-limited towards a more NO_x-limited regime (Cazorla et al., 2021b; Seguel et al., 2022; Sokhi et al., 2021). Meanwhile, in the free troposphere ozone generally decreased (Putero et al., 2023). Another example worth-noting is a modeling study in the city of Cuenca, Ecuador, that showed how the sole measure of replacing the diesel-based public transportation by electric means would decrease $PM_{2.5}$ and NO_2, but the levels of ambient ozone would increase (Parra and Espinoza, 2020). These eye-opening results impose a need to assess the impact of shifting the composition of precursors on the ozone forming chemistry that could arrive from applying controls on individual contaminants. It follows that assessing combined changes in both sets of precursors (NO_x and VOCs) is critical, which we present in this work.

With the above motivations, we employ a comparative sensitivity approach to the chemistry of ozone formation in Quito and Santiago to address the following research questions:

a) How do the typical magnitudes of ozone production rates compare between Quito and Santiago? Thus, what are likely reasons that explain ozone levels in the ambient air in both cities?
b) What chemical groups of VOCs contribute the most to ozone production in each city?
c) What would be the effect on ozone production if drastic reductions in NO_x, VOCS or both were appliedenforced in each city?

In the Methods section, we briefly describe ozone chemistry and the way we calculate ozone production and loss rates as well as radical production rates. Furthermore, we provide details of the study sites, time periods, and data sets. In addition, we give a full explanation of model details, constraints, and runs. In the Results and Discussion section, we compare pollutant levels, magnitudes of ozone production rates, radical abundances, and radical production rates between both cities. In addition, we quantify the contribution of different VOC groups to ozone production, and we discuss ozone production rates under different sensitivity scenarios of NO_x and VOCs. In the Conclusions section we present the main findings., and we emphasize the adverse or favorable implications of adopting specific control strategies on ozone precursors at both cities.

2. Methods

2.1 Ozone and radical production and losses

The abundance of ozone in the ambient air is the result from a balance between chemical production, chemical loss, dry deposition, and ozone transport due to advection (Seinfeld and Pandis, 2016). Sometimes, stratospheric intrusions could also contribute to the ozone budget (Archibald et al., 2020). The net chemical production rate, denoted as $P(O_3)$ in this study, (instantaneous chemical production minus chemical loss), is a direct source of ozone in the ambient air. Under stable atmospheric stability conditions, $P(O_3)$ is the main factoreulprit for ozone accumulation within the mixing layer. The chemistry of ozone production has been studied extensively for several decades (Gery et al., 1989; Haagen-Smit and Fox, 1956; Kleinman,

2005a; Logan et al., 1981; Thornton et al., 2002a). A simplified mechanism is depicted in reactions R1-R8. The hydroxyl radical, OH, oxidizes VOCs and leads to the formation of the hydroperoxyl radical, HO_2, and other peroxy- radicals, RO_2 (R1). The latter two react with fresh emissions of NO, which produces NO_2 (R2, R3). From these reactions, OH and other organic radicals (RO') are formed. The photolysis of NO_2 with daylight splits the molecule into ground state oxygen, O, and reforms NO (R4). Subsequently, O rapidly reacts with O_2, and ozone is formed (R5). Depending on the proportion of VOCs to NO_x, both sets of precursors compete to react with OH. Hence, OH and HO_2 radicals very rapidly cycle in a catalytic fashion to feed the mechanism with new NO_2 that undergoes photolysis and forms ozone. The titration of NO by ozone (R6) is not a real ozone sink during daytime due to the rapid NO_2 photolysis. From this mechanism, the rate equation for the instantaneous chemical production of ozone (p) is derived from reactions R2 and R3, as is depicted in equation (1) (Ren et al., 2013; Seinfeld and Pandis, 2016; Shirley et al., 2006; Thornton et al., 2002b).

$OH + VOC \rightarrow HO_2, RO_2 + H_2O + O_2$ (R1)

$HO_2 + NO \rightarrow NO_2 + OH$ (R2)

$RO_2 + NO \rightarrow NO_2 + RO'$ (R3)

$NO_2 + h\nu \rightarrow O + NO$ (R4)

$O + O_2 + M \rightarrow O_3 + M$ (R5)

$O_3 + NO \rightarrow NO_2 + O_2$ (R6)

$OH + NO_2 + M \rightarrow HNO_3 + M$ (R7)

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (R8)

$p = k_{HO2+NO}[NO][HO_2] + \sum k_i[NO][RO_2]_i$ (1)

$OH + VOC \rightarrow HO_2, RO_2 + H_2O$ (R1)

$HO_2 + NO \rightarrow NO_2 + OH$ (R2)

$RO_2 + NO \rightarrow NO_2 + RO$ (R3)

$NO_2 + h\nu \rightarrow O + NO$ (R4)

$O + O_2 \rightarrow O_3$ (R5)

$O_3 + NO \rightarrow NO_2 + O_2$ (R6)

$OH + NO_2 + M \rightarrow HNO_3 + M$ (R7)

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (R8)

$p = k_{HO2+NO}[NO][HO_2] + \sum_i^n ki\,[NO][RO_2]_i$ (1)

Meanwhile, ozone loss is driven by reactions that deplete radicals. In urban environments, the reaction of OH and NO_2 to form nitric acid (R7) is a main mechanism of ozone loss (Seinfeld and Pandis, 2016; Sillman, 1995; Thornton et al., 2002b). Other ozone losses are O_3 photolysis, the reaction of O_3 with HO_2, the reaction of alkenes (ALK) and O_3, and the reaction of RO_2 radicals with NO to produce organic nitrate, $P(RONO_2)$. Thus, the net ozone production rate, $P(O_3)$, can be calculated using equation (2), where k_i represents reaction rate constants, J_{O3} is the frequency of photolysis for ozone (R9), and species abundance is depicted within brackets. In the Quito and Santiago NO_x-rich environments R7 dominates in magnitude as we demonstrate in the Results section. Other ozone losses, such as the reaction of O_3 with HO_2 or the reaction of alkenes and O_3, yield loss rates

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two orders of magnitude lower than the loss to nitric acid, while the reaction of O^1D with water vapor yields rates an order of magnitude lower. Hence, for practical purposes, we calculate the net ozone production rate $P(O_3)$ using (2).

$P(O_3) = k_{HO2+NO}[NO][HO_2] + \sum(k_i[NO][RO]_i) - k_{OH+NO2+M}[OH][NO_2][M] - J_{O3}[O_3] - k_{HO2+O3}[HO_2][O_3] - \sum(k_i[O_3][ALK]_i) - P(RONO_2)$ (2)

$P(O_3) = k_{HO2+NO}[NO][HO_2] + \sum_{i}^{n} ki\,[NO][RO_2]_i - k_{OH+NO2+M}[OH][NO_2][M]$ (2)

In a VOC-limited regime, HO_x radicals are lost due to reactions with NO_x with R7 being a well-known chemical fate (Kleinman, 2005a; Kleinman et al., 2001a; Sillman, 1995). In addition, the production of organic nitrate can also be an important loss (Schroeder et al., 2017). In a NO_x-limited regime, reactions between HO_x radicals (collectively OH and HO_2) have been identified as an important chemical loss. For example, the reaction between two HO_2 radicals produces hydrogen peroxide, H_2O_2 (R8). The equations to quantify these two radical losses are depicted as L_{NOx} and L_{ROx} in equations (3) and (4).

Previous studies show that the formation of nitric acid (R7) or hydrogen peroxide (R8) can be used as indicators of the chemical regime of ozone production (Kleinman, 2005a; Kleinman et al., 2001a; Sillman, 1995). In a VOC-limited regime, HO_x radicals are lost due to reactions with NO_x with R7 being a well-known chemical fate. In a NO_x-limited regime, reactions between HO_x radicals (collectively OH and HO_2) have been identified as an important chemical loss. For example, the reaction between two HO_2 radicals produces hydrogen peroxide, H_2O_2 (R8). The equations to quantify these two main radical losses are depicted as L_1 and L_2 in equations (3) and (4).

$L_{NOx} = k_{OH+NO2+M}[OH][NO_2][M] + P(RONO_2)$ (3)

$L_1 = k_{OH+NO2+M}[OH][NO_2][M]$ (3)
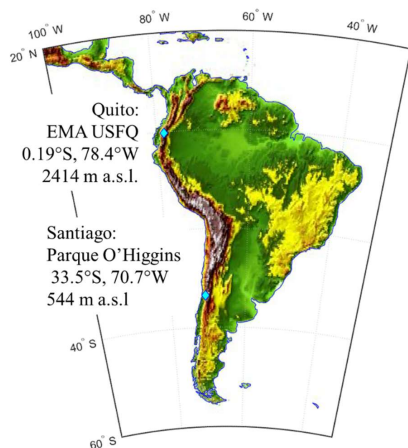
$L_2 = 2k_{HO2+HO2}[HO_2]^2$ (4)

In this work, we use the ratio $L_{NOX}/(L_{NOX}+L_{ROX})$ $L_1/(L_1+L_2)$ as an indicator of the chemical regime of ozone production (Kleinman, 2005b; Kleinman et al., 2001b). With this method Thus, ratios greater than t 0.5 indicate that radical losses to the production of nitric acid dominate, which takes place in a VOC-limited (NO_x-saturated) regime, while ratios below 0.5 indicate that reactions among radicals, such as R8, are important and mark a shift towards the NO_x-limited regime. According to (Schroeder et al., 2017), the 0.5 threshold should be revisited to 0.74 (or $L_{ROx}/L_{NOx} = 0.35$) by incorporating losses to the production of organic nitrate. Other useful indicators include the ratio of formaldehyde to reactive nitrogen $HCHO/NO_y$ for which a ratio below 1 is an indicative of a VOC-limited regime (Souri et al., 2020). Here, we used model output of this ratio to complement the analysis.

With respect to the production of HO_x, we examine include the main atmospheric sources of OH and HO_2 (independently from reactions R2 and R3, which are discussed in the ozone production section) to calculate radical production rates, $P(HO_x)$. Thus, reactions (R9) to (R11) briefly depict ozone photolysis followed by the reaction of O^1D with water vapor, which produces OH radicals (Levy, 1971). Other important sources of OH and HO_2 in the urban atmosphere are the photolysis of HONO and formaldehyde (R12 and R13) (Dusanter et al., 2009; Ren, 2003; Ren et al., 2013). Moreover, the reaction of ozone and alkenes (ALK) is known to produce OH and other radicals (R14). Therefore, equations (5) to (8 7) were used to quantify these rates.

$O_3 + hv \rightarrow O_2 + O^1D$ (R9)

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$O^1D + M \rightarrow O + M$ (R10)

$O^1D + H_2O \rightarrow 2OH$ (R11)

$HONO + hv \rightarrow OH + NO$ (R12)

$HCHO + hv \rightarrow 2HO_2$ (R13)

$ALK + O_3 \rightarrow OH + RO'$ (R14)

$P(HO_x)_1 = 2J_{O_3 \rightarrow O1D}[O_3] \, k_{(O1D + H2O)} \, [H_2O]/(k_{(O1D + M)}[M])$ (5)

$P(HO_x)_2 = 2J_{HCHO}[HCHO]$ (6)

$P(HO_x)_3 = J_{HONO}[HONO]$ (7)

$P(HO_x)_4 = \sum(ki[O_3][ALK]_i)$ (8)

$P(HO_x)_3 = J_{HONO}[HONO]$ (6)

$P(HO_x)_2 = 2J_{HCHO}[HCHO]$ (7)

2.2 Study sites and background information

A map with the location of the two study sites in Quito, Ecuador, and Santiago, Chile is shown in Fig. 1. Details of the stations chosen for the study as well as background information follow.

One of the sites is located at Universidad San Francisco de Quito's Atmospheric Measurement Station (EMA USFQ, Spanish Acronym) at coordinates 0.19°S, 78.43°W, and 2414 m a.s.l. Quito (2.78 million inhabitants) is an Andean city located at high altitude on the equator. In Quito, the typical UV index is greater than 11 on 40.0–76.1% of days per month, while the number of days per month with UV index greater than 16.0 varies between 0.7% and 32.0% (Parra et al., 2019). Particularly, intense insolation and UV index take place during the equinox months of March and September. In parallel, the times of the year with increased precipitation peak around March-April and November, while the drier months run from July to September (Cazorla et al., 2024), although conditions vary mildly within a year. A discussion on weather patterns that influence air quality in Quito can be found in previous work (Cazorla and Juncosa, 2018).

at high altitude where meteorological conditions fluctuate within rainy and dry seasons. The times of the year with increased precipitation peak around March and November, while the drier months run from July to mid-September (Cazorla et al., 2024). However, very sunny conditions can develop any time of the year in this equatorial city, especially during the March and September equinoxes. A discussion on weather patterns that influence air quality in Quito can be found in previous work (Cazorla and Juncosa, 2018).

Figure 1. Map of South America with location and coordinates of EMA USFQ station in Quito, Ecuador and Parque O'Higgins station in Santiago, Chile.

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In Santiago, we chose Parque O'Higgins station, located in the center of the city, at coordinates 33.46°S, 70.66°W, and 535 m a.s.l. This station is run by the Ministry of the Environment, and it typically represents the city's average conditions (Osses et al., 2013). Santiago, (8 million inhabitants) is a subtropical city ~~influenced by~~that exhibits four seasons. The warmest and sunniest months take place during the austral summer (December to February), but the high ozone season often extends until March.

240 ~~March~~This is an interesting month in terms of air quality in Santiago because high temperatures and insolation prevail, while anthropogenic emissions and ozone precursors increase as the school year starts and the flow of people into the city increases.

2.3 Study time periods

2.3.1 ~~March 2021~~Santiago

Ozone production was calculated for time periods in 2021 and 2022. A field campaign to measure VOCs in Santiago was
245 conducted in March 2021 (description in section 2.4.2 and Appendix A). Therefore, we performed detailed modeling of the chemistry of ozone production for sunny days during the month of March. We filtered out overcast days because photolysis frequencies were not measured and, thus, we rely on modeled actinic flux without cloud cover correction for the photolysis component of the model. March 2021 was mostly sunny in Santiago, so only 5 days were filtered out. Fig. S1 in the Supplement shows the time series of solar radiation overlapping mostly sunny days to all days.
250 To further explore ozone production under additional precursor conditions that are typically observed within a year, we run simulations for average conditions per season in 2022. Thus, we run the model for a typical sunny day in austral summer (February and March, data in January was not included because of poor quality), fall (April, May), winter (June to August), and spring (September to November). As in the previous case, we filtered out overcast days from the time series. Mean conditions were found by overlapping meteorological and air quality data (1-hour resolution) in 24-hour plots and finding the average for
255 every hour, namely the mean diurnal variation (MDV). These mean conditions were used as inputs to run the model. Model input variables are described in section 3.

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2.3.2 ~~Mean conditions by season (Santiago) or month-grouping (Quito) in 2022~~Quito

As in the case of Santiago, we performed detailed photochemical modeling for sunny days in March 2021 (11 overcast days were filtered out, Figure S1) and for typical sunny conditions in 2022. Thus, we run the model for typical conditions in January, often a sunny month; June-July, a time with low precursors due to summer vacation; September, an equinox month with increased precursors due to the return from summer vacation; and October-November, a time of transitioning into the rainy season. Mean conditions (sunny days only) for each period were found in a similar way as it was done for Santiago.

~~To further explore ozone production under additional precursor conditions that are typically observed within a year in each city, we run simulations for average conditions in 2022 by season (Santiago) or month-grouping (Quito). For Santiago, we run the model for a typical sunny day in austral summer (February only because data in January was of poor quality), fall (March to May), winter (June to August), and spring (September to November). Mean conditions were found by overlapping meteorological and air quality data (1-hour resolution) in 24-hour plots and finding the average for every hour, namely the mean diurnal variation (MDV). These mean conditions were used as model input to run the model. Model input variables are described in section 3.~~

~~In Quito, the amount of daylight as well as environmental conditions do not vary much within a year due to its equatorial latitude. Thus, we sampled average conditions in several months along 2022. We run simulations for a typical sunny day in January, often a sunny month; June-July, a time with low precursors due to summer vacation; September, an equinox month with increased pollution due to resuming school traffic; and October-November, a time of transitioning into the rainy season. Mean conditions for each period were found in a similar way as it was done for Santiago.~~

2.4 Data

2.4.1 Ozone, NO, NO$_2$, CO, and meteorological data

Santiago

Air quality data and meteorological conditions (1-hour) measured at Parque O'Higgins station were obtained from the Air Quality National Information System maintained by the Ministry of Environment (SINCA, Spanish acronym, https://sinca.mma.gob.cl/). From network information, ozone is measured with UV photometry, NO$_x$ with chemiluminescence, CO with infrared photometry, and published data complies with quality control standards according to national legislation (https://sinca.mma.gob.cl/index.php/documentos). Fig. S2 (Supplement) depicts a time series of measurements in March 2021. For comparisons with Quito, the time coordinate in all figures in this work are presented in UTC-5 (local and solar time in Quito and roughly solar time in Santiago).

All data described in this section are available as complete input files for the F0AM model for Quito (Cazorla et al., 2025a) and Santiago (Cazorla et al., 2025b), see also the Data Availability statement.

~~All data described in this section is available as complete input files for the F0AM model (see data availability statement).~~

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Ozone is measured at EMA USFQ with a Thermo 49i UV photometer. Measurements are periodically intercompared against a 2B-Technologies UV photometer. The agreement between measurements is better than 5%. A Teledyne 400 chemiluminescence instrument is used to measure NO-NO_2-NO_x. Calibration is done with a certified NO standard and zero air to prepare calibration mixtures. Uncertainty in measurements is better than 5% (Cazorla, 2016). The original rate of acquisition of ozone and NO_x measurements is 1-second. Meteorological measurements are also available at EMA USFQ with an original rate of acquisition of 30-second. CO is not measured at EMA USFQ. However, the car fleet is similar in the entire city. Hence, following previous work (Cazorla et al., 2021b), we used an average of CO measurements from three stations (Belisario, Centro and Tumbaco) run by the Quito Air Quality Network (Secretariat of the Environment, Quito, Ecuador) (https://aireambiente.quito.gob.ec/). Fig. S3 depicts a time series of Quito observations.

2.4.2 In situ measurements of VOCs in SantiagoVOCs
Santiago

VOC measurements in Santiago were taken from a fourth-story window at the Geophysics Department of Universidad de Chile (33.457 ºS, 70.662 ºW, 535 m a.s.l.) from 17 to 28 March 2021, corresponding to the late summer. The site is located at campus Beauchef, in downtown Santiago, at 770 m away from Parque O'Higgins station, where ozone, carbon monoxide, nitrogen oxides, and meteorological parameters are measured.

VOCs were measured using PTR-TOF-MS (proton transfer reaction time of flight mass spectrometry) at 1-secondminute resolution. The instrument used was an Ionicon Analytik GmbH, Model 1000. A detailed description of the sampling technique, technical operation of the PTR-TOF-MS instrument, calibration and mass discrimination methodology as well as the limit of detection of measured compounds is given in Appendix A. Table 1 shows the parent moleculesVOCs utilized in this study. Grouping was done for the practical purpose of organizing model runs, as explained in Section 2.5. The ISO nomenclature contains isoprene and monoterpenes also for practical reasons (isoprene contributes to $P(O_3)$ formation but the monoterpene contribution was found to be marginal). In Appendix B (Fig. B1), we present the time series of measured VOCs. Based on details in Appendix A, we estimate a conservative error of 30-40% in all VOC observations.

Previous studies conducted in numerous cities demonstrate that ambient measurements of VOCs, especially those whose source is fuel in vehicles, linearly correlate with CO, an anthropogenic tracer of combustion (Baker et al., 2008; Bon et al., 2011; Borbon et al., 2013; Brito et al., 2015). These correlations are useful as they can be used as emission ratios (Borbon et al., 2013). Thus, we obtained linear regressions between VOC and CO observations in Santiago for the campaign period. To this end, we linearly correlated the diurnal cycle of each VOC with the diurnal cycle of CO. We checked the results by correlating nighttime VOC and CO measurements and subtracting the background CO (noontime concentration) from the time series (Borbon et al., 2013; Brito et al., 2015). Both approaches yielded about similar slope values, but the determination coefficients were generally lower for the second approach. However, the determination coefficients improved for cresol, acetaldehyde, acetone, and isoprene. Thus, only for the latter compounds we used the linear fits obtained with the second approach. Table 1 shows the linear fit parameters used in this work. Table S1 contains the parameter regressions obtained with both approaches. Graphs for the VOC vs CO regressions for benzene and toluene can be found in Fig. S4 and S5. The entire compendium of regression figures (both methods) can be found in the link indicated in the Data Availability statement.

Compared to VOC/CO ratios (slope of linear fit in pptv/ppbv) reported for other cities in Latin America, namely Mexico City (Bon et al., 2011) and São Paulo (Brito et al., 2015), the slope we found for benzene (2.57) is about twice the value reported for Mexico City (1.21) and 2.5 times the value for São Paulo (1.03). For toluene, the slope in this study (7.54) is also higher than in Mexico City (4.2) and São Paulo (3.1). For C9 aromatics, we found a value of 3.64, close to what was reported in Mexico City (2.8). The Mexico City and São Paulo studies were done about a decade ago. Further work is needed regionally to better compare these ratios across cities, preferably with more recent measurements.

Linear fits for compounds associated with traffic (10 cases) show $R^2>0.83$ and correspond to alkenes, aromatics, and some oxygenated compounds (methanol, ethanol, and phenol). Some of the latter compounds could also have a biogenic origin, but finding exact proportions from each source was not within the scope of this study. The determination coefficient is less good for other oxygenated compounds, namely acetaldehyde, acetone, and acetic acid ($R^2\sim0.61$), which can be attributed to the secondary nature of these compounds. As expected, the linear fit for isoprene is less good ($R^2 = 0.56$) due to its combined anthropogenic and biogenic origin. In contrast, monoterpenes correlate well ($R^2=0.82$), for which we associate these compounds with traffic sources in addition to biogenic sources as observed in other cities (Borbon et al., 2023).

Table 1. VOCs measured in Santiago from 17 to 28 March 2021 and linear regressions of VOCs vs. CO in ppbv.

Group	Compound	VOC regressions (ppbv)		
		Slope x 10^{-3}	Intercept	R^2
ALK	Propene	7.46	-2.467	0.87
	Butene	9.66	-3.07	0.84
ARO	Benzene	2.57	-0.85	0.86
	Toluene	7.54	-2.95	0.9
	Ethylbenzene	15.73	-6.44	0.83
	Styrene	0.96	-0.24	0.87
	C9 Aromatics	3.64	-1.47	0.9
OXY	Methanol	19.59	-5.10	0.87
	Ethanol	4.87	-2.23	0.87
	Phenol	0.98	-0.16	0.84
	Cresol	0.29	0.27	0.45
ALD	Acetaldehyde	8.05	3.35	0.62
	Acetone/Propanal	8.57	3.33	0.61
	Butanone/Butanal	4.70	-1.30	0.73
	Methacrolein/MVK	0.88	0.21	0.74
	Acetic acid/Glycolaldehyde	14.70	-2.06	0.59
ISO	Isoprene	0.88	0.58	0.56
	Monoterpenes	0.66	-0.14	0.82

2.4.3 Monte Carlo perturbations on VOCs in Santiago

Direct measurements of VOCs were not available in Santiago on all days of March 2021 or on typical days per season in 2022. In addition, the available measurements were subject to methodological limitations, as previously discussed. Given the error in measurements and the uncertainty of applying regressions in Table 1 to derive VOCs at times other than the campaign period, we run ten thousand Monte Carlo (MC) simulations within +/- 35% of the known values to find an array of inputs to the F0AM

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355 model. Thus, we run individual MC simulations for 22 compounds (Table 1). From the bulk of each MC simulation, we extracted percentiles 10 to 90, which cover the simulation range. Fig. S6 depicts the flow diagram followed to generate MC simulations. In Fig. S7, we present the MC simulations for benzene (time series and percentile distribution as diurnal cycles). The entire compendium of MC simulation figures for all VOCs are accessible through the link provided under Data Availability.

360 ### 2.4.4 Simulations of VOCs in Quito

Measurements of VOCs are unavailable in Quito. For this reason, we used a Monte Carlo approach to simulate VOCs and to find an array of inputs to the model. VOCs in Quito could be derived from CO provided suitable emission ratios were available (Borbon et al., 2013). Given the lack of experimental data, we generated VOCs using CO measurements in Quito and the regressions in Table 1. Subsequently, we perturbed these data ten thousand times within +/-50% through Monte Carlo

365 simulations. This conservative factor was applied based on the observation that CO in Quito varies from CO in Santiago in about +/- 25% at noon, but during rush hours this variability could be up to +/-50%. From the bulk of the simulations, we extracted percentiles 10 to 90. This process was applied to all time periods analyzed in this study. In Fig. S8, we present the flow diagram followed to generate VOCs.

In Quito, 98% of ambient CO is a primary emission that comes from on-road traffic (Hernandez and Mendez, 2020; Parra, 2017;

370 Vega et al., 2015). Hence, alkene and aromatic compounds such as propene, butene, benzene, toluene, xylenes as well as C8 and C9 aromatics are expected in the Quito environment. Fuel options such as gasoline mixtures with ethanol are not currently commercialized in Quito, but they are available in some other cities, mainly in the coast of Ecuador. Thus, we included ethanol and methanol to investigate the potential effect if these types of fuels were available. In addition, methanol can also be present from biogenic sources. Aldehydes and ketones are usually present in an urban environment as they are byproducts of oxidation

375 and photolysis reactions.

We present MC simulations for benzene in Fig. S9. The entire compendium of MC simulation figures for all VOCs for Quito can be found in the link provided under Data Availability.

Measurements of VOCs were linearly correlated to CO observations and these correlations were used to derive VOCs in

380 Santiago for the days of March when VOCs were not measured. The same technique was used to derive VOCs for a typical day per season in 2022. Linear correlations were obtained with 1-hour data. Table 1 shows the correlation parameters of the linear fit. Correlations for compounds associated to traffic (10 cases) show $R^2>0.83$ and correspond to alkenes, aromatics, and some oxygenated compounds (methanol, ethanol, and phenol). Some of the latter compounds could also have a biogenic origin, but finding exact proportions from each source was not within the scope this study. High correlation between traffic-borne VOCs

385 and CO has also been reported in previous studies (Bon et al., 2011). The correlation is less good for other oxygenated compounds, namely acetaldehyde and acetic acid ($R^2=0.61$). R^2 is the lowest for formaldehyde and acetone ($R^2=0.34$ and 0.35), which we attribute to the secondary nature of these compounds. As expected, isoprene does not correlate well ($R^2=0.47$) for being a biogenic compound. However, monoterpenes do ($R^2=0.82$), for which we partially associate these compounds with traffic sources in addition to biogenic sources. Thus, in the case of compounds that do not relate directly to CO, determination

390 coefficients are low. However, we use the same scaling technique to derive the abundance of these compounds on days when measurements were not available until better estimates become available.

Quito

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Measurements of VOCs are unavailable in Quito. Thus, we scaled local CO observations using the linear correlations found at Santiago (Table 1). In previous work (Cazorla et al., 2021b), VOCs for Quito were estimated from VOC/CO ratios extracted from previous work conducted in Mexico City (Jaimes-Palomera et al., 2016). The VOC/CO ratios (slope of linear fit) found at Santiago for propene is similar (0.008) to the one found at Mexico City (0.0076), but greater for toluene by 34% (0.0076 vs. 0.005), benzene by 53.7% (0.0026 vs. 0.0012), and ethylbenzene by 97% (0.0159 vs 0.00045). These are the only coincident compounds between both studies. We regard the current VOC estimations for Quito as an improvement because the Santiago measurements are more recent, have a more complete set of compounds, and because of our direct access to data and methodology. Nevertheless, we acknowledge the uncertainty of estimating VOCs and the need for a new iteration of this study whenever in situ measurements of VOCs become available in Quito. From the available information (differences with the Mexico study and the error in the Santiago measurements), we estimate a conservative uncertainty of 50-60% for VOCs in Quito, but further studies need to refine this estimate.

Table 1. VOCs measured in Santiago from 17 to 28 March 2021 and linear correlations of VOCs vs. CO in ppbv .

Group	Species	Slope × 10^{-3}	Intercept	R^2
Aromatic compounds traffic-associated	Benzene	2.60	-0.88	0.86
	Toluene	7.61	-3.02	0.89
	Ethylbenzene	15.93	-6.65	0.83
	Styrene	0.97	-0.25	0.86
	C-9 Aromatics	3.67	-1.50	0.89
Alkenes traffic-associated	Propene	7.56	-2.56	0.87
	Butene	9.78	-3.19	0.83
Biogenic	Isoprene	0.81	0.31	0.47
Biogenic or traffic-related	Monoterpenes	0.65	-0.14	0.82
Oxygenated Alcohols	Methanol	19.87	-5.35	0.86
	Ethanol	4.89	-2.26	0.86
	Phenol	0.99	-0.02	0.84
	Cresol	0.20	0.22	0.27
Oxygenated Aldehydes and ketones	Formaldehyde	0.95	1.06	0.34
	Acetaldehyde	12.65	-1.47	0.61
	Acetone	5.38	2.34	0.35
	Butanone	4.78	-1.41	0.72
	Methacrolein_MVK (Methyl Vinyl Ketone)	0.90	0.19	0.74
	Acetic Acid	15.16	-2.54	0.61

2.5 Model details

We used the F0AM (Wolfe et al., 2016) to model ozone formation chemistry in Quito and Santiago in ~~the time periods indicated~~ in Section 2.3.~~March 2021 and for average conditions per season (Santiago) or month-grouping (Quito) in 2022.~~ The chemical mechanistic information was taken from the Master Chemical Mechanism, MCM v3.3.1 (Bloss et al., 2005; Jenkin et al., 1997, 2003, 2015; Saunders et al., 2003), via website: www.mcm.york.ac.uk. The F0AM is a model that runs in MATLAB (https://la.mathworks.com/). We used MATLAB R2024a licensed to USFQ. We provide open data sources for model input (see Data Availability). Details of model settings, and simulations follow.

2.5.1 Model input and options

Time step

The time step for the March 2021 model runs for Santiago and Quito was 10 minutes. To this end, the original Quito data were integrated into 10-minute resolution. The same was done with Santiago 1-minute VOC data. Regarding air quality and meteorological observations in Santiago, 1-hour data were interpolated to generate 10-minute time series. In contrast, the 2022 runs were done using 1-hour data for average conditions in a season (Santiago) or month-grouping (Quito).

Model constraints, boundary layer depth, and dilution constant

We constrained the model with ozone, CO, and meteorological observations from both cities. VOCs (obtained as described in the previous section) were also used to constrain the model. NO and NO_2 were not constrained but the NO_x sum was conserved (constrained). Following model recommendations, background concentrations were set to zero to avoid buildup of secondary species (Wolfe, 2023).

For boundary layer depth (PBLh) we used results from previous work done in Quito and Santiago. For Quito, we used the empirical model published by (Cazorla and Juncosa, 2018) that was inferred from balloon-borne measurements of PBLh and surface observations between 2014 and 2017. This approach was used to obtain PBLh in March 2021 and for the 2022 runs. For Santiago, we used results from the EMEP MSC-W model that is an offline chemical transport model (Simpson et al., 2012) as recently applied in Santiago and other South American cities (Pachón et al., 2024). For the seasonal runs in 2022, we scaled the March 2021 PBLh with an empirical factor using as reference previous work (Muñoz and Undurraga, 2010). Thus, we used 1/3 of the summertime values for winter PBLh and 2/3 for the fall. Fig. S10 shows PBLh for Quito and Santiago in March 2021. As stated in the F0AM model documentation, dilution is treated as a first order sink (Wolfe, 2023). Thus, we calculated a first order constant of dilution (kdil in the model) for each city by relating the time evolution of the PBL (m/s) to PBLh (m) at every step of the run. The bottom panels in Fig. S10 show kdil for both cities.

VOC input

For the VOC input, compounds were distributed among explicit VOCs available in the MCM using weighing factors indicated in Table S2 in the Supplement. For example, compounds measured as butanone/butanal were distributed as 50% butanone and 50% butanal. These correspond to MCM notations MEK and C_3H_7CHO, respectively. Thus, a total of 36 VOCs were input to the model resulting in 9189 reactions. Compound-grouping and notation used in this study, along with all input species are depicted in Table 2.

Table 2. VOCs measured in Santiago, Chile in March 2021 and used as model input.

Group	Compounds
ALK	1-butene, cis-butene, trans-butene, propene

ARO	benzene, toluene, styrene
	ethylbenzene, o-xylene, m-xylene, p-xylene
	propylbenzene, isopropylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene
OXY	methanol, ethanol, phenol, cresol
ALD	acetaldehyde, acetic acid, glycolaldehyde
	acetone, propanal, methacrolein, methyl vynil ketone, butanone, butanal
ISO	isoprene
	alpha-pinene, beta-pinene, limonene

Frequencies of photolysis ozone column and albedo

Frequencies of photolysis were modeled using the MCM option in the F0AM for both cities. In the Results section we compare the mean diurnal variation of JNO_2 and JO^1D between both cities and with previous studies. For the ozone column and albedo, we used 1-hour area-averaged MERRA-2 (Modern-Era Retrospective analysis for Research and Applications, Version 2) data sets for Quito and Santiago (Global Modeling and Assimilation Office (GMAO), 2015a, b). This data selection was based on previous work that showed good performance of MERRA-2 products for total column ozone in the region (Cazorla and Herrera, 2022). Table S3 contains a summary of options chosen in the F0AM for model runs.

2.5.2 Sensitivity runs

We run a series of experiments to investigate the individual contribution of VOC groups to $P(O_3)$ as well as the sensitivity of $P(O_3)$ to different combinations of VOC and NO_x levels.

For determining the contribution of VOC groups to $P(O_3)$, we run the model starting with alkenes (ALK) and adding one VOC group at the time until completion of all groups (ALK, ARO, OXY, ALD, and ISO). From these runs, we determined the percentage contribution of each group to $P(O_3)$ in each city. For the last group (ISO), the percentage contribution refers to isoprene because adding monoterpenes essentially did not cause change.

We tested the sensitivity of $P(O_3)$ to VOC levels P10, P50, and P90 (percentiles 10, 50 and 90 from MC simulations) under observed NO_x concentrations, 25% NO_x reductions, and 75% NO_x reductions in each city. VOC level P10 (P90) corresponds to a 30% decrease (increase) from P50 in Santiago and 40% in Quito. The group contribution runs were done using P50. In addition, we performed seasonal runs in 2022 for the entire VOC range (P10, P50, and P90) under observed NO_x levels in each city. Thus, we present the results from a total of 50 model runs (25 per city).

We constrained the model with ozone, NO, NO_2, CO, and meteorological observations from both cities. VOC observations in Santiago and estimations in Quito were also used to constrain the model. The time step for the March 2021 model runs was 10 minutes. To this end, original Quito data were integrated into 10-minute resolution. The same was done with Santiago 1-minute VOC data. Regarding air quality and meteorological observations in Santiago, 1-hour data were linearly interpolated to generate 10-minute time series. In contrast, the 2022 runs were done using 1-hour data for average conditions in a season (Santiago) or month-grouping (Quito).

For the VOC input, measurements were distributed among primary VOCs available in the MCM using equal weighing for all compounds. For example, compounds measured as butanone/butanal were distributed as 50% butanone and 50% butanal. These correspond to MCM notations MEK and C_3H_7CHO, respectively. Table S1 in the Supplement shows all VOC compounds

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organized by chemical groups with the measurement nomenclature and with the weighting factors attributed to explicit MCM compounds. Thus, a total of 35 VOCs were input to the model. Compound-grouping and notation used in this study, along with all input species are depicted in Table 2.

Table 2. VOCs measured in Santiago, Chile in March 2021 and used as model input.

Group	Notation	Compounds
Alkenes	ALK	1-butene, cis-butene, trans-butene, propene
Aromatics	ARO	benzene, toluene, styrene
		ethylbenzene, o-xylene, m-xylene, p-xylene
		propylbenzene, cumene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene
Oxygenated	OXY	methanol, ethanol, phenol, cresol
	ALD	formaldehyde, acetaldehyde, acetic acid
		acetone, propanal, methacrolein, methyl ethyl ketone, butanal
Biogenic	ISO	isoprene
		alpha-pinene, beta-pinene, limonene

Frequencies of photolysis were modeled using the MCM option in the F0AM for both cities. In the Results section we compare the mean diurnal variation of JNO_2 and JO^1D between both cities and with previous studies.

For the ozone column and albedo inputs in the F0AM, we used 1-hour area-averaged MERRA-2 (Modern-Era Retrospective analysis for Research and Applications, Version 2) data sets for Quito and Santiago (Global Modeling and Assimilation Office (GMAO), 2015a, b). This data selection was based on previous work that showed good performance of MERRA-2 products for total column ozone in the region (Cazorla and Herrera, 2022a).

Table S2 contains a summary of options chosen in the F0AM for model runs.

2.5.2 Model runs and scenarios

The model components to this study consist of a base run, VOC sensitivity runs, anthropogenic precursor scenario runs, and isoprene scenario runs (Table 3). These simulations were done comparatively for both cities with the March 2021 data. Table 3 presents details of the model runs, notation, and factors applied to precursor concentrations in each case. Notation is consistent with VOC groups in Table 2. The base run includes all measured VOC compounds. Subsequently, for the VOC sensitivity portion, we computed the individual percentage contribution to ozone production by each VOC group. Furthermore, we run sensitivity scenarios decreasing NO_x alone and together with VOCs by 75%, 50% and 25%. The purpose of running these scenarios is to evaluate the impact of applying potential isolated controls on NO_x versus applying simultaneous controls to NO_x and VOCs. In addition, we run isoprene scenarios, which are relevant from the perspective that isoprene is emitted by vegetation as a protection to biotic and abiotic stresses, a mechanism that might be enhanced in a drying and warming climate (Arneth et al., 2010). This aspect is of particular relevance for Santiago given the expected impacts of climate change in this region (Boisier et

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Table 3. Model runs and factors used to modify precursor concentrations

Study Component	Notation	Factors used on precursor concentrations							
		NO	NO$_2$	CO	ALK	ARO	OXY	ALD	ISO
Base run	ALK+ARO+OXY+ALD+ISO	1	1	1	1	1	1	1	1
VOC Sensitivity	ALK	1	1	1	1	0	0	0	0
	ALK+ARO	1	1	1	1	1	0	0	0
	ALK+ARO+OXY	1	1	1	1	1	1	0	0
	ALK+ARO+OXY+ALD	1	1	1	1	1	1	1	0
Anthropogenic Precursor Scenarios	75% NO$_x$ decrease	0.25	0.25	1	1	1	1	1	1
	50% NO$_x$ decrease	0.50	0.50	1	1	1	1	1	1
	25% NO$_x$ decrease	0.75	0.75	1	1	1	1	1	1
	75% NO$_x$&VOCs decrease	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1
	50% NO$_x$&VOCs decrease	0.50	0.50	0.50	0.50	0.50	0.50	0.5	1
	25% NO$_x$& VOCs decrease	0.75	0.75	0.75	0.75	0.75	0.75	0.75	1
Isoprene Scenarios (*)	100% Isoprene increase	1	1	1	1	1	1	1	2
	50% Isoprene decrease	1	1	1	1	1	1	1	0.50
	100% Isoprene increase & 50% NO$_x$ decrease	0.50	0.50	1	1	1	1	1	2

(*) Only isoprene was modified.

3 Results and discussion

3.1 March 2021

3.1.1 Air pollutant levels

Ozone maxima in Santiago ranged between 30 to below 70 ppbv in March 2021, as shown by percentiles 10 and 90 of diurnal profiles obtained with 1-hour ~~data~~ observations in Fig. 2a. Looking at the entire data set, half of the days in the month had ozone higher than 50 ppbv and there was a day with a maximum of 100 ppbv on March 4 (the school year started on March 1). Unlike Santiago, Quito does not have a well-established ozone problem or season, despite equatorial solar radiation at high altitude and urban emissions. Usually, 1-hour data remain below 50 ppbv. For example, in March 2021, ozone maxima during mostly sunny days ranged between 30 to 50 ppbv for percentiles 10 and 90 as depicted in Fig. 2a. In previous years, high ozone in Quito (~~usually~~ up to 80 ppbv) has been recorded episodically and has been associated with wildfires in the surrounding forests, usually during the month of September (Cadena et al., 2021). During the study time period, PM$_{2.5}$ levels (24-hour mean) were 17.6 µg m^{-3} in Quito and 22 µg m^{-3} in Santiago.

Regarding levels of NO$_x$, ambient concentrations of NO and NO$_2$ in Santiago in March 2021 were larger than in Quito by a factor of 3 for the maximum at the 50th percentile, as depicted in Fig. 2b and 2c. However, levels of CO at the 50th percentile from the mid-morning to noon were about similar (Fig. 2d), although data dispersion is within +/-25%. During the rush hours CO can differ in +/-50%.were similar (Fig. 3d). The CO and NO diurnal profiles show strong traffic signatures of the morning and

evening rush hours over Quito. In contrast, the morning rush hour in Santiago stands out more, while the evening signature is delayed and less prominent. These features are associated with the urban activity and work habits of citizens in both cities. In Santiago, work hours extend into the evening and night, often past the work schedule, and citizens take a long time to return to their homes. In Quito, citizens usually leave work before dark and usually do not extend the eight-hour work schedule.
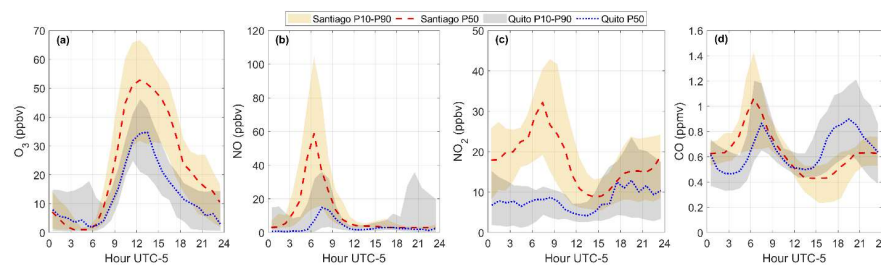
Figure 2. Diurnal variation of a) ozone, b) NO, c) NO$_2$, and d) CO for observed in Santiago and Quito in March 2021. The red dashed line is the diurnal variation for Santiago at the 50th percentile and the dotted blue line is the same but for Quito. The oOrange shadow is limited at the bottom and top by the 10th and 90th percentile diurnal variations of every variable for Santiago. The gray shadow is the same but for Quito.

The diurnal NO$_2$/NO$_x$ ratio is an indicator of photochemical activity. It involves nitric oxide (NO) reacting with hydroperoxyl (HO$_2$) and alkyl peroxy (RO$_2$) radicals to form NO$_2$. The shape of the diurnal cycle of this ratio is similar between Quito and Santiago. However, Santiago's photochemical activity starts earlier than in Quito as given by an earlier increase of NO$_2$/NO$_x$ (Fig. 3) right after the rush hour dip (due to increased NO$_x$ from traffic emissions). This is related to the earlier start in traffic in Santiago as seen in NO and CO (Fig. 2b and d), which in turn leads to a distinct NO$_2$ morning maximum that is not present in

Quito (Figure 2c). At noon and in the afternoon, NO$_2$/NO$_x$ at the 50th percentile (observations) is about similar in both cities, which indicates similar photochemical activity.

The diurnal NO$_2$-to-NO$_x$ ratio shows some similarities between the two cities, particularly between noon and 15:00 (Fig. 3). This ratio is a good indicator of photochemical activity involving nitric oxide (NO) reacting with hydroperoxyl (HO$_2$) and alkyl peroxy radicals (RO$_2$), leading to the production of NO$_2$. However, in Santiago, this ratio increases one and a half hours earlier

than in Quito, which indicates active photochemistry since the early morning in Santiago that continues into the afternoon.
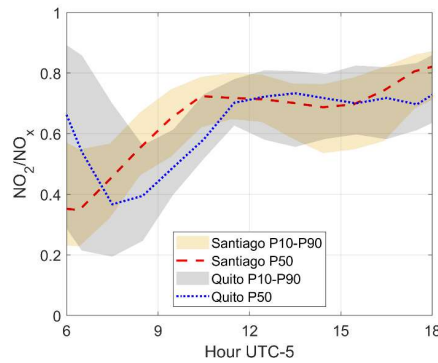
Figure 3. Diurnal variation of the NO_2/NO_x ratio at the 50th percentile from observations in~~or~~ Santiago (red dashed line) and Quito (blue dotted line) in March 2021. Shadows depict limits at the 10th and 90th percentiles at Santiago (orange) and Quito (gray).

3.1.2 ~~Base run~~Model Output

JO^1D and JNO_2

Photolysis reactions are key to radical and ozone production during daylight hours. Being Quito and Santiago located on the equator and in the subtropics, respectively, the magnitude of frequencies of photolysis are different due to the intensity of solar radiation at both locations. From model output, the diurnal variation at the 50th percentile of frequencies of photolysis of ozone (towards the production of O^1D) and NO_2 in March 2021 are presented in Fig. 4. As expected, both quantities are greater in Quito than in Santiago due to~~for~~ its equatorial location and high altitude. Previous work on the oxidation capacity of the Santiago air reported direct measurements of JO^1D and JNO_2 taken during a field campaign in March 2005 (Elshorbany et al., 2009a). These measurements for diurnal maxima in Santiago were $JNO_2 \sim 0.008$ and $JO^1D \sim 2.5 \times 10^{-5}$ s^{-1}, which are similar to mean values obtained through modeling in this work ~~(Fig. 4)~~.

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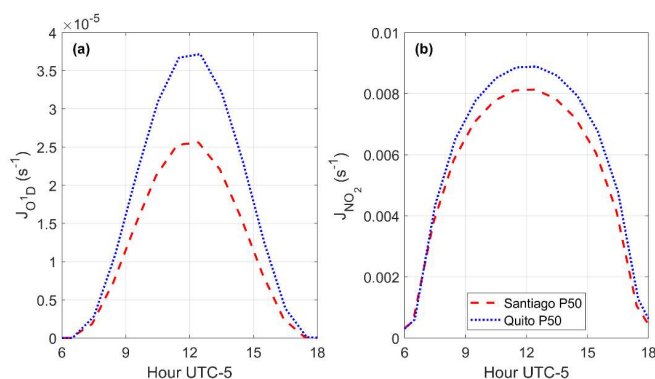
Figure 4. Comparison between the diurnal variation of frequencies of photolysis a) JO^1D and b) JNO_2 in Quito and Santiago at the 50th percentile from model output.

Ozone production and loss

Ozone production rates were modeled for a range of VOC inputs and so are discussed in terms of ranges bounded by percentiles P10 and P90 obtained from the VOC distribution in each city (Fig. 5a). For Santiago, the range represents the uncertainty in the $P(O_3)$ simulation given the uncertainty in VOC measurements. Thus, the best estimation of $P(O_3)$ for Santiago is represented by P50 in Fig. 5a. The uncertainty was determined from the mean percentage difference of the upper and lower boundaries from percentile 50 and corresponds to +/- 32% (Fig. S11). For Quito, P10 and P90 set the boundaries of the possible range of $P(O_3)$ magnitudes expected for Quito calculated to the best of our knowledge from a distribution of VOC inputs. Due to a lack of in situ measurements we deal with the entire range when discussing Quito and we only present P50 curves in a referential way. The mean variability from percentile 50 is +/- 42% (Fig. S11).

The range of net ozone production rates at both cities at noon are comparable (22-45 ppbv h^{-1}), but in the mid-morning values could be higher for the upper boundary in Quito (up to 55 ppbv h^{-1}) (Fig. 5a). Further below we show that in Quito the HO_2 and RO_2 abundance is greater when compared to Santiago (Fig. 9), but NO levels are lower (Fig. 2b). Thus, there is a compensating effect in the levels of HO_2 and NO in both cities in a way that application of equation (1) yields about similar ozone production rates. Previous work that determined net ozone production rates in Santiago from measurements and model calculations in 2005, reported substantially higher values for the mean $P(O_3)$ diurnal maximum (160 ppbv h^{-1}) (Elshorbany et al., 2009b). Such high value is outside of our calculation range, although it is possible that after almost twenty years of reassessing $P(O_3)$ in Santiago, conditions changed. $P(O_3)$ maxima presented in Fig. 5a for percentiles 50 of the distributions in both cities are consistent with values obtained in previous studies. For example, direct measurements of $P(O_3)$ in Houston in 2009 were about 30 ppbv h^{-1} on average (Cazorla et al., 2012). Another example is a recent sensitivity study of ozone production to NO_x and VOCs in New York city that found $P(O_3)$ within 26-37 ppbv h^{-1} from modeling work with the F0AM (Sebol et al., 2024).

Losses to nitric acid are higher in Santiago than in Quito (Fig. 5b). This is consistent with higher NO_x levels present in the Santiago ambient air. Meanwhile, losses to hydrogen peroxide are higher in Quito, but the magnitude of this loss is one order of magnitude lower that the loss to nitric acid (Fig. 5c). Other losses are presented in Fig. S12 (Supplement). The loss due to ozone photolysis and the reaction of ozone with HO_2 are two and one orders of magnitude lower than the loss to nitric acid,

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respectively. The reaction of ozone with alkenes is also an order of magnitude lower than the loss to nitric acid, but this is higher than the loss to hydrogen peroxide. The upper boundaries of the loss to alkyl nitrates ($P(RONO_2)$) approach a digit and become important along with the loss to nitric acid in both cities.

NO and NO_2 were unconstrained in the model, but the NO_x sum was constrained. A comparison of measured and modeled NO/NO_2 ratio is presented in Fig. S13. From the mid-morning to the early afternoon values are about similar.
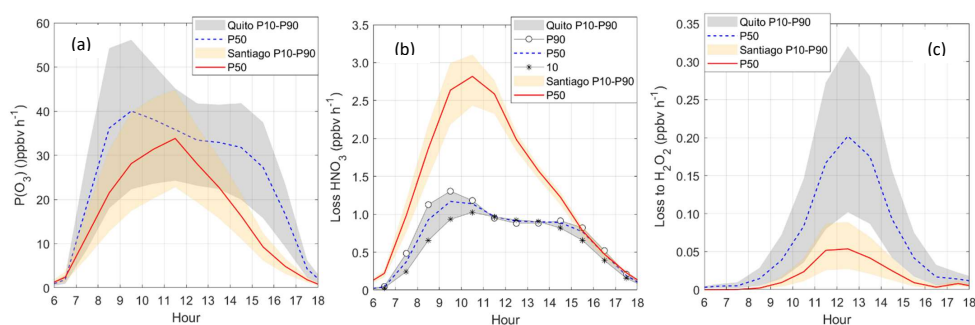
Figure 5. Diurnal variation of a) Net ozone production, b) Loss to nitric acid, and c) Loss to hydrogen peroxide in Quito and Santiago. Shadows correspond to boundaries obtained with VOC levels P10 (10th percentile) and P90 (90th percentile) from Monte Carlo simulations (orange for Santiago and gray for Quito). Results obtained at the VOC level P50 (50th percentile) are given by the solid red line for Santiago and blue dashed line for Quito in each graph.

An interesting point to investigate in the future is the connection between ozone production rates and ambient ozone, whose budget not only depends on atmospheric chemistry but also on meteorological and circulation factors. From our calculations, the range of $P(O_3)$ in both cities is similar, but ambient ozone is higher in Santiago. This city has a year-round influence of the Subtropical Pacific High that determines a strong subsidence inversion, which is often strengthened by low-level lows and occasionally disrupted by passing synoptic disturbances (Gallardo et al., 2002; Garreaud et al., 2002; Huneeus et al., 2006; Muñoz and Undurraga, 2010). Such meteorological condition is known to be the cause of pollutant accumulation in the boundary layer in Santiago. In contrast, Quito is not affected by a similar high-pressure system. In our simulations, we used information of the boundary layer evolution in both cities. The boundary layer in Quito can often grow up to 2200 m a.g.l. (Fig. S10) (Cazorla and Juncosa, 2018). Under such conditions, the first order dilution constant in the model reached up to 2.5×10^{-4} - 5.8×10^{-4} s^{-1}. Meanwhile in Santiago, the boundary layer can reach up to 1500 m and dilution constants usually stay below 2.5×10^{-4} s^{-1} (Fig. S10). Additional research that uses a chemical transport model is needed to explain ambient ozone levels.

Ozone production regime

The chemical regime of ozone production in Santiago is strongly VOC-limited as indicated by the ratio $LNO_x/(LNO_x+LRO_x)$ being very close to one for the entire range of the model output as depicted in Fig. 6a. This indicator is consistent with the

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620 formaldehyde to reactive nitrogen ratio (HCHO/NO$_y$) being well below 1 (Fig. 6b), and with the losses to nitric acid being substantial (Fig. 5b).
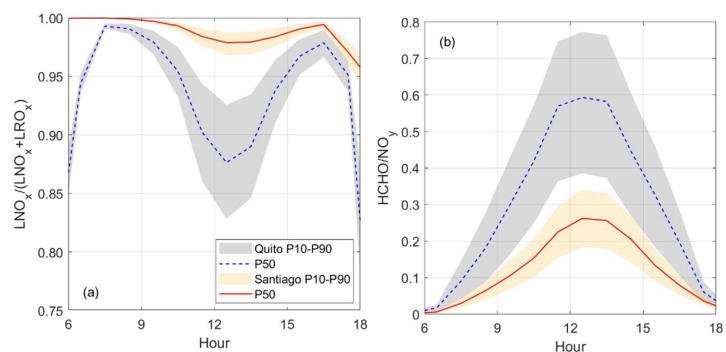
Figure 6. Indicators of the chemical regime of ozone production: a) Ratio LNO$_x$/(LNO$_x$+LRO$_x$) (defined by Eq. 3 and 4), b)
625 Ratio HCHO/NO$_y$ (formaldehyde to reactive nitrogen). Shaded area indicates model output boundaries obtained with the 10th and 90th percentiles (P10 and P90) of the VOC Monte Carlo distribution (orange for Santiago and gray for Quito). The solid red line and dashed blue lines correspond to model output at the 50th percentile (P50) for Santiago and Quito, respectively.

For the Quito runs, LNO$_x$/(LNO$_x$+LRO$_x$) points to a VOC-limited regime as this indicator is above suggested thresholds of 0.5
630 (Kleinman, 2005c; Kleinman et al., 2001a) or revisited 0.74 (Schroeder et al., 2017). Meanwhile, the HCHO/NO$_y$ ratio is still below 1 for the entire range (VOC-limited), but the upper boundary approaches one digit. This indicates that with a higher VOC content, the Quito environment is more prone to transitioning towards a more NO$_x$-limited regime. At the moment, a lack of in situ measurements constrains our ability to define how close the Quito environment is from the transition region. Even though from our calculations both cities are in the VOC-limited chemical regime, this character is noticeably more intense in Santiago
635 from the indicators in Fig. 6. This finding illustrates that within the VOC-limited and NO$_x$-limited categories of ozone production lay a range of intensities that depend on the unique conditions that surround every urban area.

VOC group contribution to P(O$_3$)

The percentage contribution to P(O$_3$) caused by every chemical group (Table 2) during daylight hours in both cities is depicted in
640 Fig. 7a (Quito) and 7b (Santiago). For the Quito simulations, alkenes and aromatics combined (blue and cyan in Fig. 7a) contribute with 45% of ozone formation around the morning rush-hour, 70% at noon, and up to 90% in the afternoon. Meanwhile, the contribution of these two groups to P(O$_3$) in Santiago is under 50% throughout the day. The contribution of aldehydes and ketones is substantial over Santiago, which combined with alkenes and aromatics adds up to 80-90% of P(O$_3$) during daylight hours (magenta in Fig. 7b). In Quito, aldehydes and ketones are important in the morning, between 07h00-08h00,
645 when the percentage contribution could be up to an additional 40-50%, while at noon and in the afternoon this contribution is

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about 20%. Isoprene contributes an additional 10-20% in Santiago and becomes increasingly important towards the afternoon. In Quito, we estimate that his contribution is about 10%. It must be noted that Central and Southern Chile suffered a longstanding drought between 2010 and 2022 (Garreaud et al., 2020) that likely caused an increase in isoprene emissions by vegetation due to hydrological stress (Jiang et al., 2018). The contribution of oxygenated compounds in both cities is marginal (black in Fig. 7).
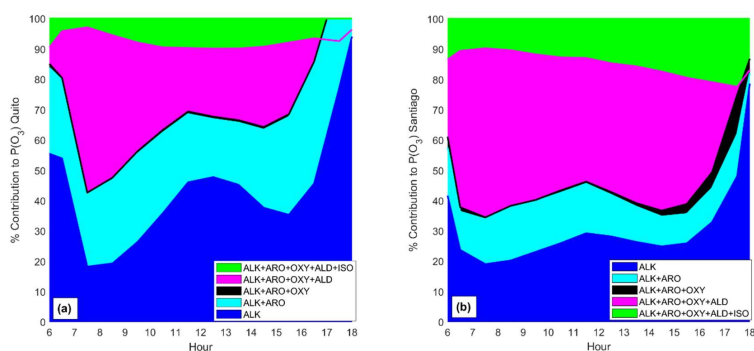
Figure 7. Percentage contribution to P(O$_3$) by chemical groups in a) Quito and b) Santiago obtained with model output at the 50th percentile from VOC Monte Carlo simulations.

Radical production and abundance

The main sources of radical production are depicted in Fig. 8 and correspond to the photolysis of ozone followed by the reaction of O^{1}D with water vapor (Fig. 8a), the photolysis of formaldehyde (Fig. 8b), the photolysis of HONO (Fig. 8c), and the reaction of ozone with alkenes (Fig. 8d). The first contribution has the largest magnitude in both cities. Computing this rate does not depend on VOC abundance for which percentile boundaries are absent in Fig. 8a. Thus, the curves depict the mean diurnal cycles whose maxima are about 1 pptv s^{-1} in both cities, on average. However, within the month, variaibility in Santiago (0.5-1.75 pptv s^{-1}) is somewhat greater than in Quito (0.75-1.5 pptv s^{-1}). From meteorological data, the water vapor content at solar noon in Quito and Santiago is about similar (10 vs 9 g kg^{-1}) but solar radiation does not vary much on the equator while in Santiago daylight progressively lowers as the season advances towards the autumn.
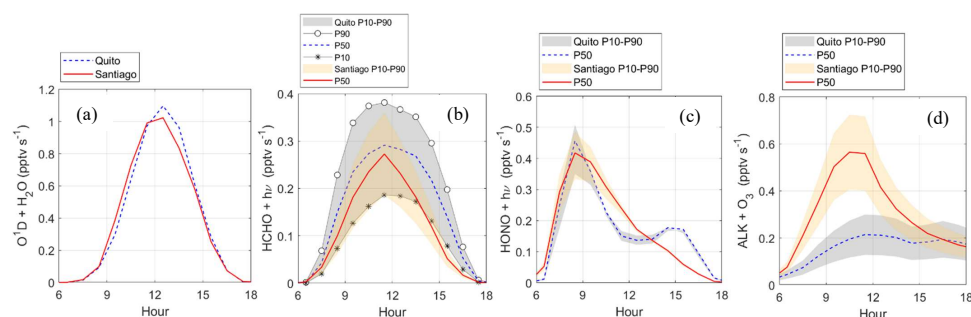
$P(HO_x)$ production from formaldehyde photolysis in Quito and Santiago is comparable (0.18-0.35 pptv s^{-1}) (Fig. 8b). Overall, this contribution is 2-3 times lower than the first source. In the morning, radical production from the photolysis of HONO is equally important in Santiago and in Quito (0.35-0.5 pptv s^{-1}), as indicated in Fig. 8c, which is expected given the high abundance of NO_x in the morning. However, the contribution from this radical source gradually decreases from the mid-morning into the afternoon. The contribution from the reaction of alkenes and ozone is higher in Santiago (Fig. 8d), which is consistent with higher ozone levels. Previous work determined $P(HO_x)$ from different sources in Santiago (Elshorbany et al., 2009a). They found rates of HO_2 production from formaldehyde photolysis of 0.15 ppt s^{-1}, on average, and rates of OH production from HONO photolysis of 0.4 ppt s^{-1}. Our calculations are consistent with these findings. However, rates of OH production reported by Eshorbany et. al. in 2009 from ozone photolysis are substantially lower (0.27 ppt s^{-1}, on average) . It is important to remark that this study only considers gas phase chemistry and urban emissions following previous work (Elshorbany et al., 2009b, a; Ren, 2003; Ren et al., 2013).

Radical abundances in both cities during the study time period are illustrated in Fig. 9. With higher frequencies of photolysis, the OH abundance in Quito for the entire simulation range (0.33-0.38 pptv) is overall greater than in Santiago (0.23 pptv) (Fig. 9a). The order of magnitude of radical abundances is similar to those found in other studies (Cazorla et al., 2021; Dusanter et al., 2009; Ren et al., 2013). Given the greater OH availability in Quito, reactions with VOCs yield HO_2 and RO_2 abundances that at noon in Quito are about three times greater than in Santiago (Fig. 9b and 9c). From the magnitudes in the latter figures, HO_2 and RO_2 are equallly important, which is consistent with previous work (Bottorff et al., 2023; Dusanter et al., 2009; Elshorbany et al., 2009a).

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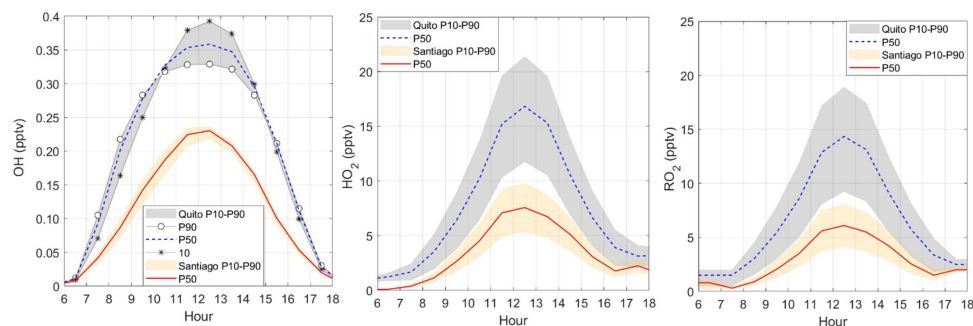
Figure 9. Diurnal variation of a) OH, b) HO_2, and RO_2 in Quito and Santiago. Shaded area indicates model output boundaries obtained with the 10th and 90th percentiles (P10 and P90) of the VOC Monte Carlo distribution (orange for Santiago and gray for Quito). The solid red line and dashed blue lines correspond to the output with the VOC 50th percentile (P50) for Santiago and Quito, respectively.

3.1.3 NO_x and VOC scenarios

In this section we explore the effect on $P(O_3)$ due to changes in NO_x and VOCs that could arrive from potential actions intended to improve air quality and help reduce SLCF. As stated before, diesel-based public transportation in South American cities is an important source of $PM_{2.5}$ and NO_x. It follows that a relevant scenario to consider is the effect on ozone production if this type of transportation were replaced, as it is often included in air quality and climate mitigation planning. Notice that Santiago's public transport bus fleet has roughly 10% of electric buses, a fraction that is expected to increase in the future. This type of action would significantly lower ambient NO_x (and $PM_{2.5}$), although VOCs would also decrease. Another relevant scenario is exploring changes in VOCs. For example, applying changes in the quality of fuels to reduce the content of aromatic compounds would influence $P(O_3)$. Here, we explore some sensitivity scenarios, but additional research is needed to precisely determine the proportion in precursor reduction associated to specific environmental actions.

The effect on $P(O_3)$ with different combinations of NO_x and VOCs is quantified in Fig. 10. The scenarios investigated were those of current NO_x levels, NO_x reductions by 25%, and NO_x reductions by 75% at VOC levels P10, P50 and P90. For the latter, the percentage decrease (or increase) from P50 to P10 (or to P90) is 30% in Santiago and 40% in Quito. In Santiago and Quito, lowering the levels of VOCs would result in lower ozone production rates at all tested levels of NO_x as presented by the progression of panels in Figs. 10a to 10c (Quito) and 10d to 10f (Santiago). This feature is expected in VOC-limited environments. For example, at the current NO_x Quito levels, reducing VOCs by 40% from the P50 level reduces the maximum $P(O_3)$ in 37%. In Santiago, a 30% decrease in VOCs would result in a 32% decrease in the maximum $P(O_3)$.

At lower levels of VOCs in Quito (P10), a 25% decrease in NO_x causes a slight $P(O_3)$ increase in the morning and almost no change in the afternoon (Fig. 10a), while a 75% NO_x reduction modestly raises the morning $P(O_3)$ but causes a drop at noon. As VOC levels increase (P50 and P90), a 25% reduction in NO_x causes a modest decrease in $P(O_3)$, but a 75% decrease causes the noon $P(O_3)$ to decrease by half. This result indicates that at higher VOC levels in Quito the ozone production chemistry is prone to transitioning towards a more NO_x-limited regime, especially at noon and in the afternoon. This aspect underscores the

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necessity of implementing in situ measurements of VOCs in Quito to accurately determine how close the Quito environment is to the transition region.

In Santiago, at the current levels of VOCs and NO_x (P50), lowering NO_x increases ozone production rates, especially in the morning and mainly when the decrease is substantial (75%), but the change at noon and in the afternoon is modest. Thus, at 9 am $P(O_3)$ grows from 25 ppbv h^{-1} to 38 ppbv h^{-1} (Fig. 10e). Similar effects are observed at the lowest (P10) and highest (P90) VOC levels (Figs. 10d and 10f). Thus, $P(O_3)$ increases in the morning and either there is a modest change or a decrease from noon to the afternoon. Therefore, NO_x decreases cause the peak $P(O_3)$ to shift from noon to the morning.
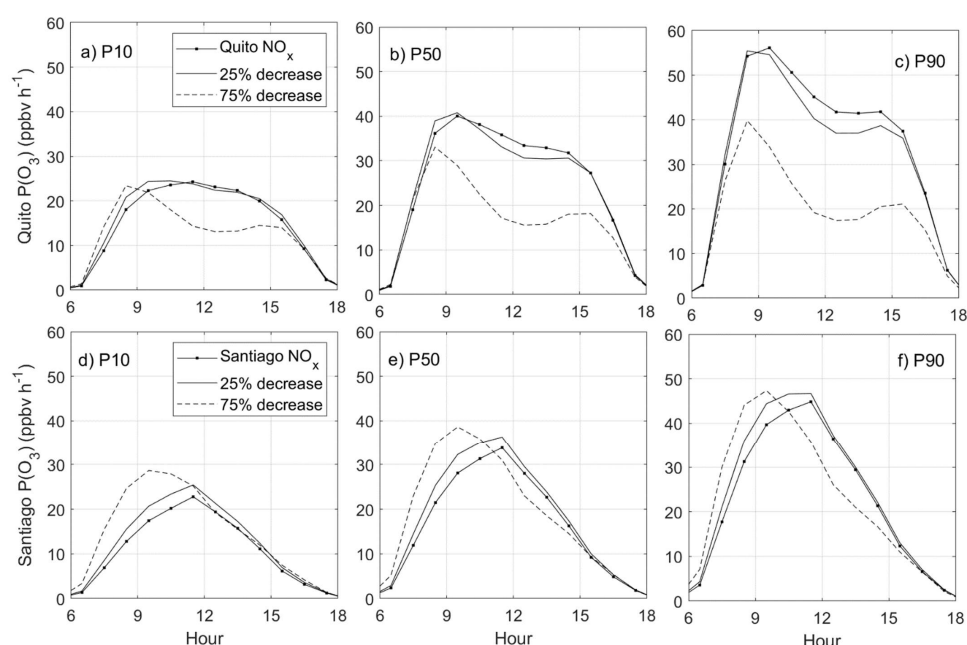
Figure 10. $P(O_3)$ sensitivity to changes in NO_x and VOCs in Quito (top panels) and Santiago (bottom panels) obtained with VOC levels P10, P50 and P90 from Monte Carlo simulations.

OH, HO$_2$, RO$_2$, and rates of radical production

Radical abundances in both cities during the study time period are illustrated in Fig. 5. With higher frequencies of photolysis, the OH abundance in Quito is overall larger than in Santiago (Fig. 5a). This is evident from the Quito diurnal profile at the 50th percentile in Fig. 5a and close packing of data within percentiles 10 and 90 that contrast with Santiago. Maximum abundances at the 50th percentile are 0.25 and 0.22 pptv in Quito and Santigo, respectively. The order of magnitude of radical abundances is similar to those found in other studies (Cazorla et al., 2021b; Dusanter et al., 2009; Ren et al., 2013).
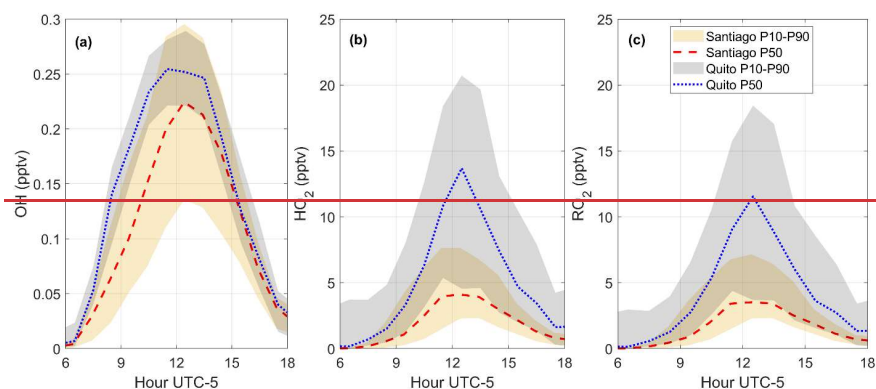
Figure 5. Diurnal variation of a) OH, b) HO₂, and RO₂ in Quito and Santiago at the 50th percentile (blue dashed line and red dotted line, respectively). Shadows indicate limits set by the 10th and 90th percentiles (orange for Santiago and gray for Quito).
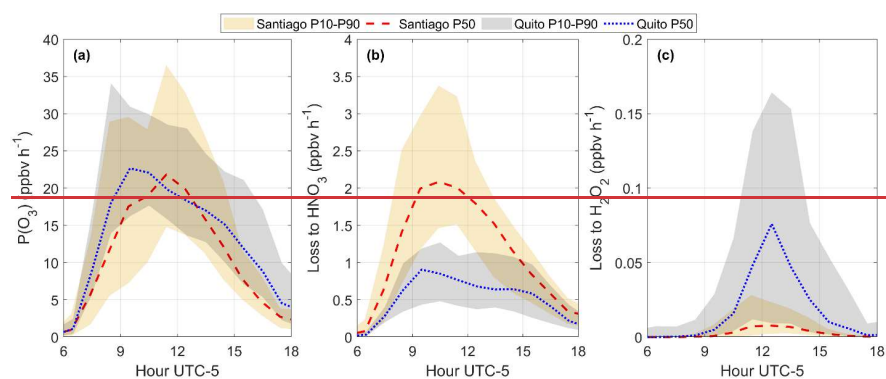
The main source of OH is the photolysis of ozone followed by the reaction of O^{1}D with water vapor. The diurnal maximum of radical production rate from this source (percentile 50) is about 1 pptv s^{-1} in both cities with Quito values being slightly larger (Fig. 6a). From meteorological data, the water vapor content at solar noon in Quito is about 10 g kg^{-1}, while in Santiago is about 9 g kg^{-1}, but JO^{1}D is greater in Quito. Due to high altitude, Quito is a city with rather low humidity in spite of its tropical latitude. Furthermore, at Santiago data scattering is larger than in Quito as it happens with the OH abundance. Given that the OH availability is larger in Quito, reactions with VOCs yield HO₂ and RO₂ abundances about three times greater in Quito than in Santiago (Fig. 5b and 5c). From the magnitudes in the latter figures, HO₂ and RO₂ are equallly important, which is consistent with previous work (Bottorff et al., 2023; Dusanter et al., 2009; Elshorbany et al., 2009a).

In the morning, radical production from the photolysis of HONO is equally important in Santiago and in Quito (0.28 pptv s^{-1}), as indicated in Fig. 6b, which is expected at rich NO$_x$ environments. However, the contribution from this radical source in Santiago gradually decreases from the mid-morning into the afternoon, while it drops sudenly at noon in Quito (Fig. 6b). This difference indicates higher photochemical activity in the morning in Quito and less in the afternoon. Formaldehyde photolysis as a source of radicals is greater in Santiago, especially at noon and in the afternoon (Fig. 6c). However, this is a less important source when its magnitude is compared to the magnituede of the two other sources. Previous work determined P(HO$_x$) from different sources in Santiago (Elshorbany et al., 2009a). Thus, Elshorbany et al. found rates of HO₂ production from formaldehyde photolysis that are about 60% higher (0.15 ppt s^{-1}, on average) than the magnitudes found in this study. Furthermore in the aforementioned study, rates of OH production from HONO photolysis are about 30% higher (0.4 ppt s^{-1}, on average), while rates of OH production from ozone photolysis are substantially lower (0.27 ppt s^{-1}, on average) . These differences are due to lower abundances of measured formaldehyde and modeled HONO in this study than the abundances reported in Elshorbany's 2005 study. For example, the latter reports mean HONO and formaldehyde levels up to 4 and 7 ppbv, respectively. Meanwhile, in this study, the diurnal maximum of formaldehyde is 2 ppbv (percentile 50, from measurements) and 0.4 ppbv for HONO (percentile 50, from model output).

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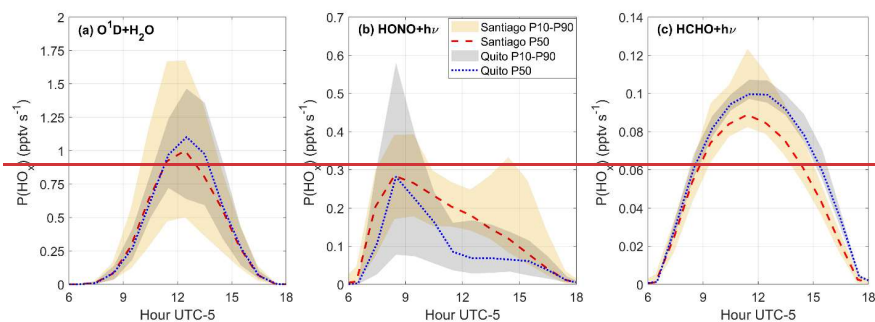
Figure 6. Diurnal variation of radical sources: a) ozone photolysis followed by O^{1}D + H$_2$O, b) HONO photolysis, and c) formaldehyde photolysis in Quito and Santiago at the 50th percentile (blue dashed line and red dotted line, respectively). Shadows indicate limits set by the 10th and 90th percentiles (orange for Santiago and gray for Quito).

Ozone production and loss

Magnitudes of ozone production rates at both cities are comparable for the 50th percentile diurnal profile (maximum of about 22-23 ppbv h^{-1}), but the time of the maximum shifts towards the morning over Quito (Fig. 7a and 7b). This is consistent with more active photochemical production of radicals, for example from HONO photolysis in the morning hours (Fig. 6b). The range of values within percentiles 10 and 90 (about 15 to about 35 ppbv h^{-1}) is also comparable. In Quito, the HO$_2$ and RO$_2$ abundance is greater when compared to Santiago, but NO levels are lower. Thus, there is a compensating effect in the levels of HO$_2$ and NO in both cities in a way that application of equation (1) yields about similar ozone production rates. Previous work that determined net ozone production rates in Santiago from measurements and model calculations in 2005, reported substantially higher values for the mean P(O$_3$) diurnal maximum (160 ppb h^{-1}) (Elshorbany et al., 2009b). This value seems high, although it is possible that after almost twenty years of reassessing P(O$_3$) in Santiago, conditions changed. However, the mean P(O$_3$) maximum presented in Fig. 7a is consistent with values of mean diurnal maximum of P(O$_3$) obtained from direct measurements and phothochemical modeling, for example in Houston in 2009 (~30 ppb h^{-1}) (Cazorla et al., 2012). Likewise, a recent sensitivity study of ozone production to NO$_x$ and VOCs in New York City (Sebol et al., 2024), that uses the F0AM model, reported a P(O$_3$) range of 26-37 ppb h^{-1}, which is similar to our results.

The chemical regime of ozone production in Santiago is strongly VOC-limited as indicated by the loss rate to the production of nitric acid, depicted in Fig. 7b. These rates are 2 to 3 times greater in Santiago than in Quito. This finding is consistent with the loss rate to the formation of hydrogen peroxide being greater in Quito than in Santiago (Fig. 7c), although the magnitude of this loss is an an order of magnitud lower than losses to nitric acid at both cities.

As stated earlier, the ratio L1/(L1+L2), where L1 is the loss to the formation of nitric and L2 is the loss to hydrogen peroxide, is a common way to assess the VOC-limited character of the chemistry of ozone production. In the case of Quito, the chemical regime is also VOC-limited as L1/(L1+L2) at the 50th percentile is between 0.9 and 1 as shown in Fig. 8a (solid black line). However, this chemical character is more intense at Santiago as this ratio lays very close to 1 (Fig. 8b). This finding illustrates

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Our model simulations indicate that at both cities high photolysis frequencies and sufficient precursor availability set the right conditions for comparable radical and ozone production rates. However, $P(O_3)$ of like magnitudes are associated to ozone levels in Quito that are lower than in Santiago. A partial explanation to this fundamental difference lays in the vertical mixing conditions that dominate both cities. Santiago has a year-round influence of the Subtropical Pacific High that determines a strong subsidence inversion, which is often strengthen by low-level lows and occasionally disrupted by passing synoptic disturbances (Gallardo et al., 2002; Garreaud et al., 2002; Huneeus et al., 2006; Muñoz and Undurraga, 2010). Such meteorological conditions are known to be the cause of pollutant accumulation in the boundary layer in Santiago. In Quito, circulation patterns that affect air quality are less studied and characterized, partially due to the topographic complexity of the region. However, there is experimental evidence of strong vertical mixing over the Quito region from the morphology of ozone vertical profiles studied over the past ten years (Cazorla, 2017; Cazorla et al., 2021a; Cazorla and Herrera, 2022b). Additionally, previous studies demonstrate that on sunny days in Quito, a deep convective boundary layer develops in connection with thermal and mechanical eddies that break the early morning thermal inversion (Cazorla and Juncosa, 2018; Muñoz et al., 2023). Thus, we propose that strong convection at this tropical area helps mix and dilute ozone produced at the surface in the vertical direction. Future studies need to incorporate chemical transport models to simulate ozone abundances under different vertical mixing scenarios. In addition, other chemical fates of ozone precursors that lead to photochemical fractions different from ozone need to be further explored.

In spite of limitations, from this modeling work we identified that average $P(O_3)$ magnitudes of 23 ppbv h^{-1} (or higher) combined with well-known meteorological conditions produce seasonally elevated levels of ambient ozone over Santiago. In contrast, the same average $P(O_3)$ magnitudes over Quito are associated to ambient ozone that usually meets the national air quality standard (51 ppbv). The question remains as per what magnitudes of $P(O_3)$ are high enough in Quito to power down mixing conditions and overshoot normal ambient ozone levels. Shifting ozone precursors permanently as a result of changes in environmental policy that controls atmospheric pollutants could cause unwanted changes towards higher ozone production rates. As countries and cities are urged to implement climate actions that curb fossil fuel use, changes in environmental policy are expected to happen at some point in the future. In upcoming sections we quantify the impact of changing ozone precursor abundance on the magnitude of ozone production rates.

3.1.3 VOC sensitivity

Ozone production sensitivity to VOCs in both cities was evaluated by determining the contribution to $P(O_3)$ by individual chemical groups as defined in Table 2. Diurnal profiles of $P(O_3)$ at the 50th percentile, when one VOC group at a time is added to the model, are presented in Fig. 9a (Quito) and 9b (Santiago). With only alkenes, $P(O_3)$ maxima in Quito and Santiago reach 12 and 9 ppbv h^{-1}. Adding aromatic compounds more than doubles ozone production rates in the morning over Quito (from 7 to about 16 ppbv h^{-1} at 09h00). Also, there is a shift towards more active photochemistry earlier in the day as the $P(O_3)$ maximum is displaced from noon (12 ppbv h^{-1}) to the mid-morning (18 ppbv h^{-1}). In Santiago, the addition of aromatics increases the $P(O_3)$ maximum from 9 to 14 ppb h^{-1}, but there is no change in the time of peak $P(O_3)$. Oxygenated compounds (only alcohols and excluding aldehydes and ketones) practically do not cause an increase in ozone production rates in Santiago, while there is a negative effect over Quito mainly in the mid-morning. In contrast, adding aldehydes and ketones causes an additional increase in the morning $P(O_3)$ in Quito and shifts the maximum even earlier (up to 21 ppbv h^{-1}). In Santiago, this group increases $P(O_3)$ throughout the day and the maximum up to almost 19 ppbv h^{-1}. These results are consistent with previous findings in regard to alkenes, aromatics, and aldehydes being important contributors to ozone production (Bowman and Seinfeld, 1994; Calvert et al., 2000; Fanizza et al., 2014). Finally, the addition of isoprene causes an additional increase of $P(O_3)$ in Quito in the mid-morning

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to the early afternoon. Over Santiago, the effect of isoprene is important from the morning to the afternoon, bringing the P(O₃) maximum up to 22 ppb h⁻¹. This last run also contains monoterpenes, but they do not cause a visible effect in P(O₃) for which they are not shown as a separate curve.
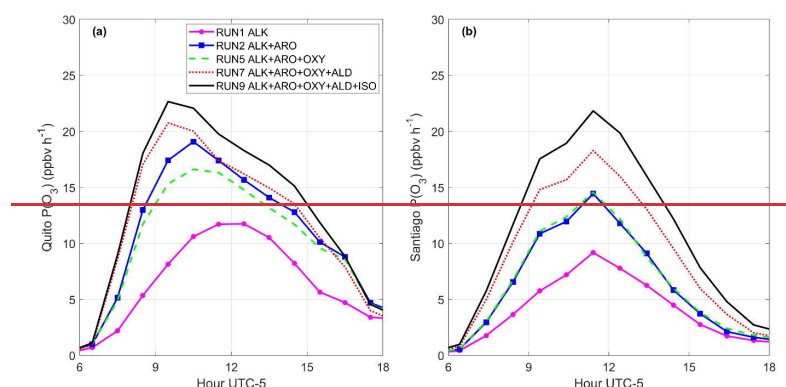
Figure 9. Diurnal variation of net ozone production at the 50th percentile when individual VOC groups are added to the model run according to grouping in Table 2 for a) Quito, and b) Santiago.

The percentage increase in P(O₃) caused by every chemical group during daylight hours at both cities is depicted in Fig. 10a (Quito) and 10b (Santiago). Alkenes and aromatics combined (blue and cyan in Fig. 10a) produce 60 to 90% of P(O₃) in Quito with the lower contribution at around 07h00 and the higher contribution mostly before noon and into the afternoon. Meanwhile, the contribution of these two groups to P(O₃) in Santiago is 50-60% throughout the day. The contribution of aldehydes and ketones is substantial over Santiago, which combined with alkenes and aromatics make up for 80-90% P(O₃) during daylight hours (magenta in Fig. 10b). In Quito, aldehydes and ketones are only important in the morning, between 07h00-08h00, when the percentage contribution could be up to 30%. Isoprene contributes an additional 10-20% in Santiago and becomes increasingly important towards the afternoon, while in Quito this contribution is about 10%. However, this contribution is affected by error as the isoprene abundance in Quito was estimated (CO scaling) as opposed to measured for which it needs further research. Oxygenated compounds (alcohols) only affect P(O₃) marginally in Santiago, while in Quito these compounds slightly lower P(O₃). As in the case of isoprene, this contribution could also be affected by greater error.

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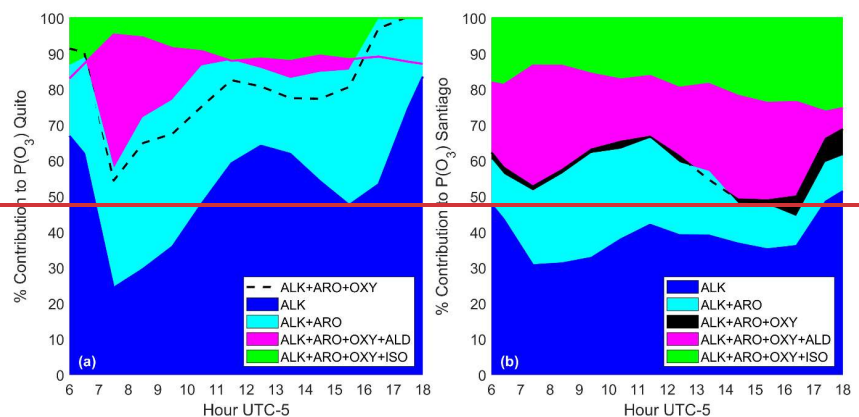
Figure 10. Percentage contribution to P(O₃) by chemical groups at a) Quito and b) Santiago.

3.1.4 NOx and VOC scenarios

Environmental action directed to improving air quality and climate demand applying control strategies to reduce levels of atmospheric pollutants. As stated before, diesel-based public transportation in South American cities is an important source of $PM_{2.5}$ and NO_x that, in turn, is also associated to the formation of $PM_{2.5}$. Having this in mind, we explore the consequences of reducing this type of transportation as it is often included in air quality and climate mitigation planning. Notice that Santiago's public transport bus fleet has roughly 10% of electric buses, a fraction that is expected to increase in the future.

The impact of applying controls only on NO_x are quantified in Fig. 11. The scenarios investigated were those of NO_x reductions in 25%, 50%, and 75%. In Quito, a 25% decrease in NO_x causes a modest P(O₃) increase in the morning (Fig. 11a), but a 50% reduction shifts faster ozone production rates before 09h00. A 75% decrease in NO_x causes a substantial increase in morning ozone production rates, but at noon the chemical regime shifts to NO_x-limited and ozone production drops. The evolution of the chemical regime shifting towards NO_x-limited in Quito from the first scenario (25% NO_x reduction) to the third (75% NO_x reduction) is illustrated in Fig. 8a. In the third scenario, the ratio L1/(L1+L2) drops below 0.5, which indicates that losses to hydrogen peroxide become increasingly important from before noon into the afternoon. Meanwhile in Santiago, the greater the NO_x reduction, the higher the ozone production rates during daylight hours (Fig. 11b). A 75% reduction in NO_x causes the ozone production maximum to increase by a factor of 1.8, while for the 50% reduction the factor is 1.4. In the third scenario, faster ozone production maxima shift before noon for both cases. With a 75% reduction in NO_x there is a visible departure of the ozone formation chemistry towards a less VOC-limited regime, although the L1/(L1+L2) ratio is still below 0.5 (Fig. 8b).

The former simulations demonstrate that lowering solely NO_x has a harmful effect in Santiago and Quito. As increased ozone production rates contribute to the overall ozone budget, this isolated measure should be avoided in both cities due to the potential risk of exceeding current ambient ozone levels.

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3.2 Mean conditions by season

As per additional conditions observed within a year in Quito and Santiago, Fig. 1$\underline{1}\underline{2}$ illustrates the range of mean levels of O$_3$, NO, NO$_2$, and CO that are typical in both cities (2022 data). In Quito, the daily ozone maxima progressively range from 30 to 45 ppbv, with higher ozone levels in September and lower in June-July (Fig. 1$\underline{1}\underline{2}$a). In contrast, Santiago data show clear seasonal differences in data distribution with mean summer peak ozone concentrations being more than 2.5 times higher than those of the winter (20 vs 55 ppbv) (Fig. 1$\underline{1}\underline{2}$b). The diurnal cycles shown in Fig. 1$\underline{1}\underline{2}$ are smoothed out when hourly data are averaged within

a season. However, when inspecting 1-hour time series, only on 1 day in 2022 ozone was higher than 60 ppbv in Quito. Meanwhile in Santiago, the peak ozone values were between 60-100 ppbv in 48 days. Table S43 shows statistics for 2022 data in both places.

Regarding NO, peak values in the diurnal cycle in Quito range between 30 to 55 ppbv, but there are times in the year when NO
910 spikes substantially in the rush hour (Fig. 12c). In 2022, this spike happened in October-November. In Santiago, NO is substantially higher in the winter months, when in addition to transportation and industry, residential sources become significant (Fig. 11d). (Fig. 12d). As temperatures are low, the mixing volume remains shallow and primary pollutants such as NO accumulate, while the actinic flux is not sufficient to activate photochemistry. In the 1-hour time series, 148 days in 2022 had NO higher than 100 ppbv in Santiago, while in Quito there were 31 days with morning NO of such magnitudes.

915 In Santiago, the winter-to-summer variability is also evident in the diurnal cycles of NO_2 and CO, with higher concentrations during the cold months (Fig. 112fe and 112hg). In contrast, the variability is small in Quito for NO_2, especially during daylight hours, and marginal for CO (Fig. 112ef and 11g2).
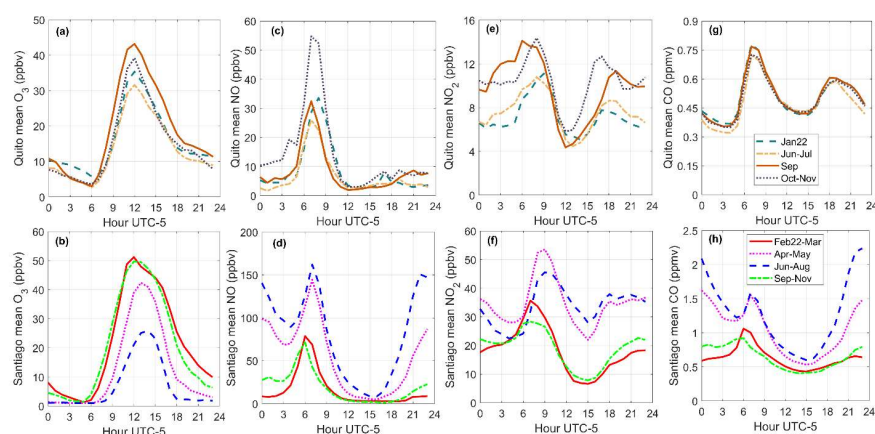
920 **Figure 112.** Air quality conditions observed within a year by season (Santiago) or month-grouping (Quito) presented comparatively for a) and b) ozone, c) and d) NO, e) and f) NO_2, and g) and h) CO.

With the range of conditions presented in Fig. 112, the range of ozone production rates expected on average in both cities is depicted in the top panels of Fig. 123a for (Quito) and 13b (at the bottom for Santiago). In Quito, the mean ozone production
925 rates roughly range from 15-40 ppbv h^{-1} year-round (Fig. 12a to d), although in September the upper boundary is right under 50 ppbv h^{-1}. These magnitudes of P(O_3) resemble ozone production rates during the ozone season in Santiago (February-March, Fig. 12e). The rest of the seasons, P(O_3) in Santiago is lower by 10-20 ppbv h^{-1}. Therefore, with the range of VOCs used in the model, ozone production rates during sunny days in Quito stay high most of the year. In contrast, ozone in Santiago is high only during the ozone season. However, ozone levels in Quito are generally lower than in Santiago.

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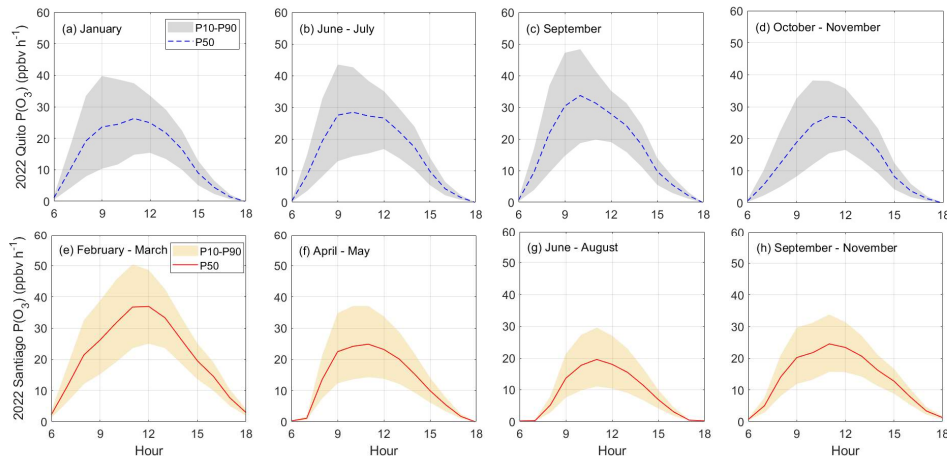
Figure 12. Comparison of the range of net ozone production rates observed in a year (2022) in Quito (top panels) and Santiago (bottom panels). Shaded area indicates model output boundaries obtained with the 10th and 90th percentiles (P10 and P90) of the VOC Monte Carlo distribution (orange for Santiago and gray for Quito). The solid red lines and dashed blue lines correspond to percentile 50 (P50) for Santiago and Quito, respectively.

Thus, over Quito the mean ozone production rates roughly range from 15-25 ppbv h^{-1} year-round, which is comparable to observed rates during the ozone season in Santiago (summer). However, differences in ambient ozone levels point to physical mixing conditions as a partial explanation. Other chemical paths for precursors, for example to the production of nitrate particles or PAN, need to be further explored in Quito as a potential chemical reason in addition to the physical explanation that we propose in this study.

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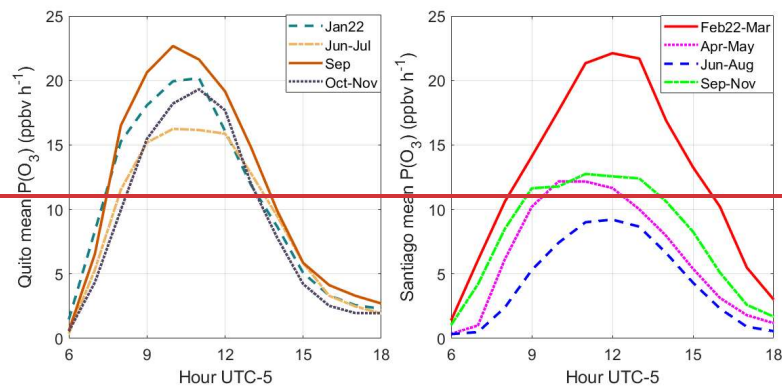
~~**Figure 13.** Comparison of the range of net ozone production rates observed in a year (2022) in a) Quito and b) Santiago.~~

4 Conclusions

Ozone production rates in Quito and Santiago (sunny days) were calculated using the F0AM (Framework for 0-D Atmospheric Modeling)~~, a chemical box model, constrained by a unique set of VOC measurements taken in Santiago in~~ for March 2021 and for mean conditions per season in 2022.

The model was constrained with ground station observations (air quality and meteorology) and VOCs. The latter were measured in Santiago during part of March 2021. When measurements were not available, VOCs were generated with experimental VOC vs. CO linear regressions and Monte Carlo simulations within 35% of error in the observed values. We estimate an uncertainty of 32% in P(O$_3$) calculations for Santiago. Measurements of VOCs in Quito are not available for which we simulated the entire set of VOCs. To this end, we scaled Quito CO using Santiago linear regressions, but we perturbed these values within 50% using Monte Carlo simulations. The percentage variability in the range of calculated P(O$_3$) for Quito is 42% from the mean.

Santiago is impacted by a well-established ozone season during the austral summer, which extends into March. In March 2021, the P(O$_3$) maximum was 32 ppbv h^{-1} (+/- 32% or 22-42 ppbv h^{-1}). During this period, there were 11 days in Santiago when 1-hour ozone observations were between 60-80 ppbv and one day when ozone was 100 ppbv. In the summer 2022, the peak P(O$_3$) was similar (37 ppbv h^{-1} +/-32%), while the rest of the seasons P(O$_3$) was 10-20 ppbv h^{-1} lower. Meanwhile in Quito, our calculations indicate that the P(O$_3$) range in March 2021 was 23-45 ppbv h^{-1} at noon, but in the mid-morning the upper boundary could reach 55 ppbv h^{-1}. From calculations in 2022 we found a range between 15-40 ppbv h^{-1} except in September when the upper boundary could reach 50 ppbv h^{-1}. However, ozone levels in Quito (1-hour) usually remain below 50 ppbv (only 1 day in 2022 was just over 60 ppbv). Therefore, we found that P(O$_3$) in Quito is comparable or possibly even higher than in Santiago (during the ozone season) but ambient ozone is generally lower. The air quality in Santiago is permanently impacted by the Subtropical Pacific High, which causes a strong subsidence inversion. In contrast, Quito is not influenced by a similar high-pressure system. Furthermore, we found that often a deep boundary layer of up to 2200 m develops over Quito and the model first order dilution constant reaches 2.5x10^{-4} - 5.8x10^{-4} s^{-1}. Meanwhile in Santiago, we found that the boundary layer depth reaches 1500 m and the dilution constant stays below 2.5x10^{-4} s^{-1}. These findings provide some indications of relevant physical factors but additional research using a chemical transport model is needed to explain ambient ozone levels and the ozone budget.

As per the chemical nature of VOCs that contribute the most to the formation of ozone, we found that alkenes in Quito contribute with 45% in the morning and 70-90% at noon and in the afternoon. In Santiago, the contribution of alkenes and aromatics is about 50% throughout the day. Aldehydes and ketones contribute with about 50% in the morning in Quito and with about 20% at noon and in the afternoon. In Santiago, aldehydes and ketones contribute with an additional 40%, which adds up to 90% of the contribution along with alkenes and aromatics. We estimate that isoprene contributes with about 10% in Quito and 20% in Santiago. The latter may be linked to the effects of a longstanding drought that affected Central and Southern Chile until 2022.

Ozone production rates of similar ranges in both cities result from a compensating effect in the magnitude of radical abundance relative to NO abundance. Thus, HO$_2$ and RO$_2$ radicals in Quito (HO$_2$: 12-22 pptv, RO$_2$: 9-18 pptv) are about twice the abundance in Santiago (HO$_2$: 6-9 pptv, RO$_2$: 4-8 pptv) but NO is two to three times higher in Santiago than in Quito. As in the case of ozone production rates, radical production rates from several sources are comparable in both cities. From ozone photolysis radical production rates are about 1 pptv s^{-1}; from formaldehyde photolysis 0.18-0.35 pptv s^{-1}; and from HONO

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photolysis 0.35-0.5 pptv s^{-1}. The contribution of ozone reactions with alkenes is greater in Santiago (0.4-0.7 pptv s^{-1}) than in Quito (0.12-0.3 pptv s^{-1}).

Indicators of the chemical regime of ozone production from model output, (LNO$_x$/(LNO$_x$+LRO$_x$ and HCHO/NO$_y$), point to Santiago being a strongly VOC-limited environment. This is confirmed by higher ozone losses to nitric acid than in Quito although losses to the production of organic nitrate are comparable in both cities. In addition, from sensitivity tests in Santiago, NO$_x$ reductions at all levels of VOCs lead to higher ozone production rates in the morning. In Quito, the two indicators also point to a chemical regime limited by VOCs. However, the value of HCHO/NO$_y$ (0.8) approaches 1 at higher percentiles of VOC abundance. At such VOC levels, NO$_x$ decreases cause a drop in ozone production especially at noon and in the afternoon, which indicates transitioning into a more NO$_x$-limited regime. However, a lack of in situ VOC measurements in Quito limits our ability to better determine these thresholds. From sensitivity tests, VOC reductions lead to a general decrease in P(O₃) in both cities.

Finally, our results remark the importance of implementing in situ measurements of VOCs in Quito and conducting more extended measurements in Santiago given the current conditions of environmental vulnerability and the need to implement policies that protect public health and climate.

For Quito, the model was constrained using VOCs derived by scaling CO with experimental VOC vs. CO linear correlations found in Santiago. From model results, Quito and Santiago are VOC-limited environments influenced by comparable rates of ozone production. On sunny days, these rates are about 23 ppbv h^{-1}, on average, but the range is 15-35 ppbv h^{-1}. However, these magnitudes of P(O₃) do not result in comparable ambient ozone at both cities as ozone is greater in Santiago. This result seems counterintuitive being Quito an equatorial city at high altitude with plentiful solar radiation and urban emissions. Santiago has a well-known ozone season that takes place in the austral summer (December to February) but extends into March. For example, in March 2021 there were 11 days in Santiago when 1-hour ozone observations were between 60-80 ppbv and one day when ozone was 101 ppbv. Meanwhile in Quito, 1-hour data stayed below 50 ppbv the entire month. In 2022, 13% of 1-hour observations in Santiago were between 60-90 ppbv, while in Quito only 1 day in 2022 surpassed 60 ppbv. We partially attribute this fundamental difference to physical reasons related to mixing conditions at both cities, but chemical reasons need to be further explored. Thus, it is well-documented that Santiago's air quality is permanently impacted by the Subtropical Pacific High, which causes a strong subsidence inversion. This circumstance, together with the magnitudes of ozone production rates identified in this work, lead to ozone accumulation in the ambient air. On the other hand, there is observational evidence that the vertical mixing is strong over Quito. Thus, we propose that although ozone is produced at fast rates in Quito, it quickly becomes mixed vertically at this highly convective tropical environment. Future studies need to verify this hypothesis with chemical transport models. Also, additional research is needed to explore other chemical fates of precursors to form photochemical fractions other that ozone in Quito.

As in the case of ozone production rates, radical production rates are comparable at both cities, on average. From ozone photolysis radical rates are about 1 pptv s^{-1}; from HONO photolysis 0.28 pptv s-1; and from formaldehyde photolysis 0.08 to 0.1 pptv s^{-1}. However, ozone production rates of like magnitudes result from a compensating effect in the magnitude of radical abundance relative to NO abundance. Thus, the abundance of HO₂ and RO₂ radicals is greater in Quito than in Santiago (about 13 pptv for each set of radicals versus 4 pptv, on average) but NO is two to three times greater in Santiago. Given the latter, the VOC-limited character of the ozone production chemical regime is much more intense over Santiago although the Quito environment is also VOC-limited.

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Appendix A: VOC measurements in Santiago, Chile

VOCs were measured by a PTR-TOF-MS (Ionicon Analytik GmbH, Model 1000). Ambient air was drawn with an external pump (KNF, N86KN.18) through a sampling line (1/8''). The sample air was injected into the PTR from a T-union via a polyether-ether-ketone (PEEK) capillary (1/16'') conditioned at 80 ºC. The ion source was supplied with a 15 cm^3 min^{-1} water vapor flow. The drift tube was operated at temperature, voltage and pressure of 353 K, 600 V and 2.3 mbar, respectively, corresponding to a reduced electric field strength (E/N ratio) of ~136 Td (Townsend) (1 Td =10-17V cm^2).

The mass scale was calibrated every 10 minutes using H_3O^+ isotope (21.0220), NO^+ (29.9970) and protonated acetone (59.0490), while the voltage of the multichannel plate detector was optimized weekly. The relative mass discrimination (transmission) was calculated before the campaign using a calibration gas standardthe sensitivity and known reaction rates. The limit of detection (LoD) was calculated as three times the standard deviation of the background signal from zero air measurements (ENVEA, Model ZAG7001). We use a certified gas standard (Airgas Specialty Gases) valid until 2023 traceable to NIST (National Institute of Standards and Technology) for calibration checks for benzene (79.054), toluene (93.070), and ethylbenzene+xylenes (107.086). The error for toluene, ethylbenzene+xylenes, and benzene wasere -1.23%, -34.615% and +27.240%, respectively.

PTR-TOF-MS provides several advantages, including mass range and high measurement frequency. However, this technique is susceptible to fragmentation that may interfere at a given m/z. The data used in this work resulted from a series of field campaigns aiming to optimize the measurements (e.g., E/N) and reduceknow the impact of fragmentation on benzene. We also used specific ion peaks in the mass spectrum collected by (Pagonis et al., 2019) in a public online library to identify reasonable VOC candidates in urban environments. Table A1 shows the protonated parent molecules detected in Santiago's atmosphere and the compound assigned by the monoisotopic m/z for identification. In general terms, PTR has been reported as a reliable way to measure species with higher proton affinities, such as aromatics (Table A1). However, m/z 107.086 produces fragments that interfere with m/z 79.054 (assigned to benzene), and therefore, conservative error of 35% should be considered for aromatics and up to 50% for small hydrocarbons without known molecular fragmentation.a conservative error of 50% should be considered for benzene without known molecular fragmentation. We also detected interferences with m/z 69.070 (assigned to isoprene) during the morning rush hours. On the other hand, reactive species such as acetaldehyde, with high levels in Santiago, should be interpreted considering the photochemistry of Santiago. Table 1 also includes m/z values assigned to more than one species reported in the literature.
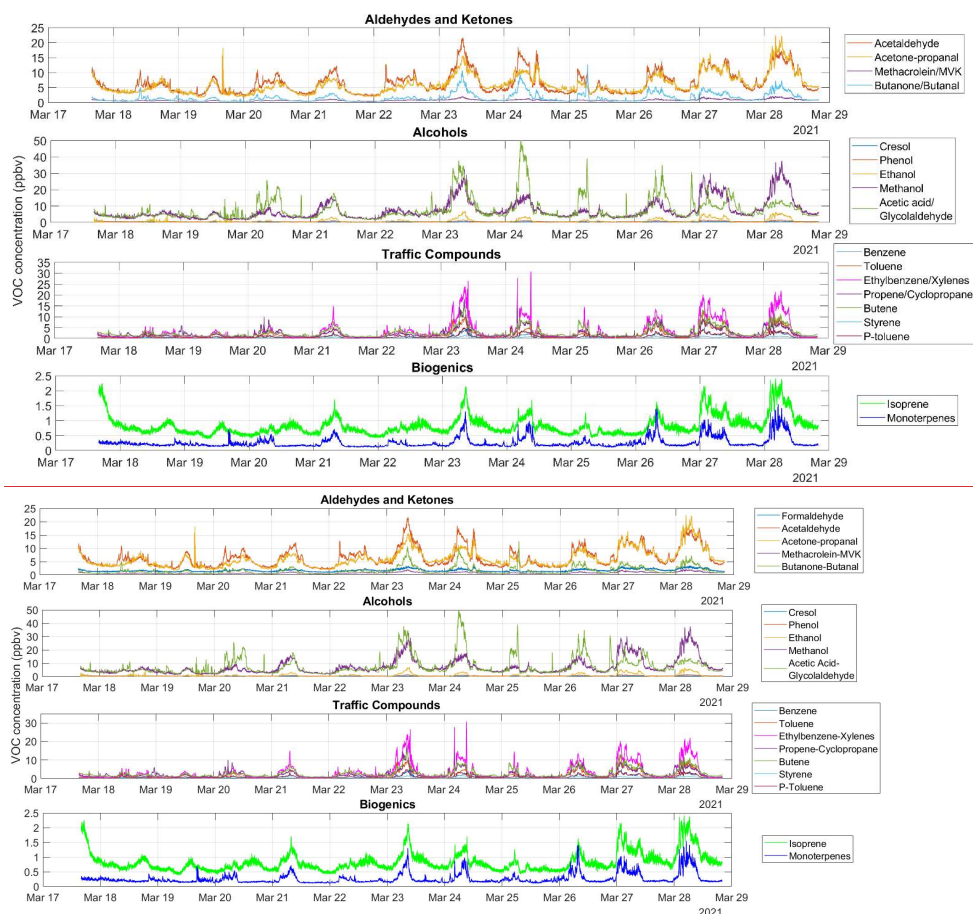
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Table A1. Protonated parent molecules utilized in this study and VOCs assigned according to literature. More details can be found in Pagonis et al (2019) and in the PTR library. The table indicates names, parent ions and proton affinity obtained from https://webbook.nist.gov/chemistry/ and limit of detection.

Compound assigned	m/z	Proton affinity (kJ/mol)	Limit of Detection (ppbv)
Formaldehyde	31.018	712.9	1.0
Methanol	33.034	754.3	0.5
Propene/Cyclopropane	43.054	751.6/750.3	0.2
Acetaldehyde	45.033	768.5	0.4
Ethanol	47.049	779.4	0.5
1-Butene/2-Butene	57.070	-----	0.3
Acetone/Propanal	59.049	812/786	0.3
Acetic acid/Glycolaldehyde	61.028	783.7/N.A. [1]	0.4
Isoprene	69.070	826.4	0.2
Methacrolein/Methyl vinyl ketone	71.049	808.7/834.7	0.2
2-Butanone/Butanal	73.065	827.3/792.7	0.2
Benzene	79.054	750.4	0.09
Toluene	93.070	784.0	0.2
Phenol	95.049	817.3	0.2
Styrene	105.070	839.5	0.08
Ethyl benzene/Xylenes	107.086	-----	0.09
Cresol	109.065	N.A.	0.1
C_9-Aromatics	121.101	-----	0.05
Monoterpenes	137.132	-----	0.08

[1]N.A.: Not Available

Appendix B: Time series of VOCs measurements taken in Santiago

Figure B1. Time series (1-minute data) of VOCs measurements taken in Santiago, Chile from 17 to 28 March.

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Supplement

Separate document

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