

# Numerical simulation of nocturnal ozone increase in Metropolitan Area of São Paulo

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**Abstract:** In large cities, pollution can not only cause deaths and illnesses due to exposure of people to it, but it can also reduce visibility on days of high atmospheric stability and high emission of pollutants, which can even result in vehicular accidents. Ozone is an atmospheric oxidizing gas that forms in minimal amounts naturally. People's health can be affected by the ozone present in the air they breathe, even in low concentrations, which can worsen preexisting diseases and increase hospital admissions for respiratory diseases, especially in babies, after episodes of high pollutant levels. An increase in secondary peaks during the night of this atmospheric pollutant occurs in several parts of the world, but its formation depends on the local condition. In this sense, this work aims to study the regional atmospheric characteristics for the nocturnal ozone formation in the Metropolitan Area of São Paulo (MASP). For this, the Simple Photochemical Module (SPM) coupled to the BRAMS (Brazilian Developments of Regional Atmospheric Modeling System) will be used to simulate this condition for the urban region. The results showed that the secondary nocturnal maximum of ozone concentrations in MASP is related to vertical transport of this pollutant from higher levels of the atmosphere to the surface.

**Keywords:** nocturnal ozone; air quality modeling; simple photochemical modeling

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## 1. Introduction

Pollutants are naturally present in the atmosphere due to fires, volcanic eruptions and biogenic emissions; but the greatest contribution is currently associated with anthropic activities. In Latin America, urban centers are in constant development and growth, generating numerous problems associated with the effects of pollution [1]. In large cities, pollution can not only cause deaths and illnesses due to exposure of people to it but can also reduce visibility on days of high atmospheric stability and high emission of pollutants, and can even result in vehicular accidents [2–4]. Several studies have shown that the meteorological condition has a great influence on the concentrations of pollutants [5–9].

Ozone (O<sub>3</sub>) is an atmospheric oxidizing gas that forms in very small amounts naturally. This secondary photochemical pollutant is formed in the atmosphere by photo dissociation of nitrogen dioxide (NO<sub>2</sub>) by ultra-violet light. For being an oxidant pollutant, ground-level ozone concentration can affect people health (especially children, elderly and people in outdoor activities), worsen pre-

existent diseases and increasing the number of hospitalizations by respiratory diseases in risk groups [10]. Also, ozone exposure can be related to morbidity and mortality by cardiopulmonary diseases [11]. In United States, ozone contributes to increase the mortality rate associated to respiratory diseases, being that an increment of 10 ppb in ground-level concentrations increase in 3% death risk associate to exposure [12]. Climatic change could be responsible by increase in ozone concentrations and, consequently, in the number of hospital admissions and deaths associated to ozone exposure [4]. Since, change in ozone concentrations are, in part, consequence of changes in the atmospheric system, it is important to know which synoptic patterns are associated to singular conditions of ground-level ozone concentrations.

During night, at very stable situations, especially under anticyclonic conditions, the increase of this contaminant has been observed with a well-defined behavior [13]. In cyclonic conditions, NO<sub>x</sub> can have low due to increased ventilation, and affect O<sub>3</sub> concentration [14]. The magnitude and frequency of nocturnal ozone peaks are generally observed in summer time, and can be associated with horizontal transport processes [15]. Also, in China, the nocturnal O<sub>3</sub> concentration is higher in suburban areas than in urban areas before it increase, reduced under the effect of vertical transport [16].

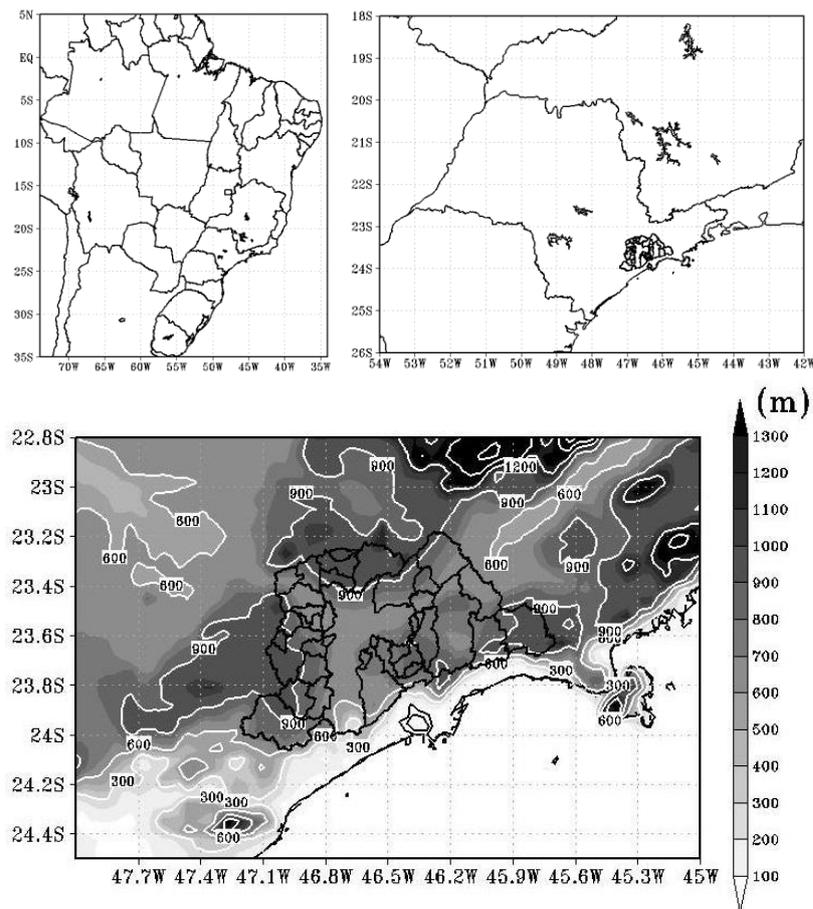
Given the importance and the elements that influence the magnitude and frequency of nocturnal ozone, this work aims to study the regional characteristics of the atmosphere of the Metropolitan Area of São Paulo in the formation of secondary ozone peaks during the night. For this, regional numerical modeling coupled with a chemical module will be used.

## **2. Methodology**

### *2.1. Study Area*

The Metropolitan Area of São Paulo (MASP) is located in southeastern Brazil, in a region of rugged topography (Figure 1), in which the city of São Paulo is located in the most central region coinciding with the valleys of the Tietê and Pinheiros rivers, between Serra do Mar and Serra da Cantareira, the latter, with elevations above 1000 m. The MASP comprises 39 municipalities and concentrates almost half of the state's total population (approximately 20 million inhabitants), covering an area of 8051 km<sup>2</sup> [17].

Given the proximity of the MASP to the coast, the surface extension of the urban area, and the heat island effect seen in it make this type of thermal origin generate a significant influence on the flow patterns [18] in the dispersion of pollutants. The passage of the sea breeze creates a favorable condition for the dispersion of pollutants in this urban region, while days with extreme heat island events generate a more stable condition on the RMSP, which may favor the accumulation of pollutants[9]. In winter and early spring, there is a greater frequency of days with the influence of high-pressure systems that hinder the passage of cold fronts, favoring the formation of a high-intensity heat island, which generates more appropriate conditions for the occurrence of high pollutant concentration events [19].



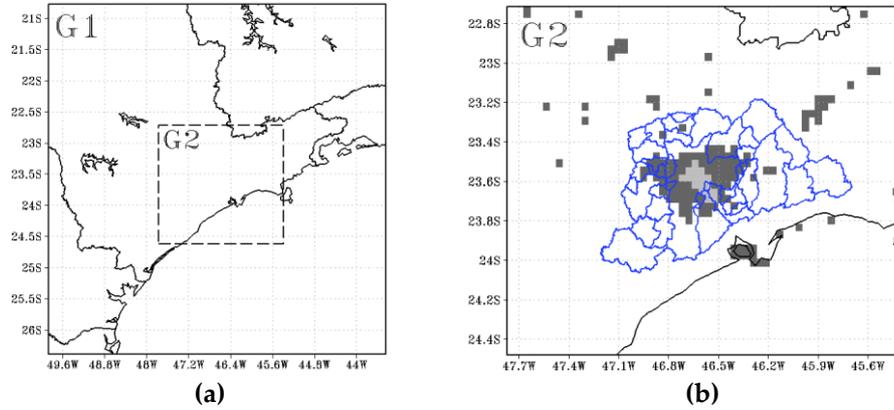
**Figure 1.** Location and topography map of the MASP. Scale color bar in meters.

## 2.2. SPM-BRAMS

In this work, the version 3.2 of the BRAMS model (*Brazilian Development on Regional Atmospheric Modeling System*, [20]) was used, which is based on the Regional Atmospheric Modeling System (RAMS, [21]). The model allows simulating several spatial scales, integrating the microscale with the larger scales. The system of equations that governs the atmospheric state is solved using second-order finite difference schemes, both in time and space. The conservation of mass, moment, and energy in the model is guaranteed since the advection terms of these equations are treated in flow. Numerical instability is minimized by using smaller time steps in solving equations in higher resolution grids. Atmospheric physical processes not explicitly resolved by the model are parameterized. The model has a multiple grid scheme that allows the simultaneous resolution of the equations. The interaction processes between the surface and atmosphere are carried out at BRAMS using the LEAF-3 model (Land Ecosystem-Atmosphere Feedback model version 3, [22]) for vegetated areas and with TEB (Town Energy Budget, [23]) for urban areas.

Figure 2 presents the nesting grids used in the simulations centered at MASP ( $-23.60^\circ$ ,  $-46.65^\circ$ ). The horizontal spacing grid of both domains is 16 and 4 km, from lower to the higher resolution. For the topography, files with spacing between 1 km grid points provided by the United States Geological Survey (USGS) were used. For the sea water surface temperature, weekly mean values corresponding to the simulated periods were used as input data, without considering the update of these files during the rounds. As input meteorological data, the Global Forecasting System (GFS) global model's outputs with a horizontal spacing grid of  $1^\circ$  were used. For all analysis of the results, the simulations were run one day before the nocturnal event, and we reject the first 24 hours to avoid the spin-up effect [24] of the meteorological part of the model and to allow the model to accumulate more realistic amounts of pollutants in the atmosphere. The first level of the model output considered is 33.4 m

above the surface. The model physics and land use parameterization configuration are the same as Morais et al. [25].



**Figure 2.** Grid domains used in the simulation. (a) Lower resolution domain (G1), and (b) higher resolution. Lighter gray color represents the dense urban area since dark gray is the suburban area (similar to Morais et al. [25]).

The Simple Photochemical Module (SPM, [26]) was inserted in the BRAMS model to generate operational forecasts of ozone concentrations and other constituents for the MASP with only 15 chemical reactions. Ozone formation was represented without considering hydrocarbon speciation. These equations were selected from the chemical mechanism SAPRC-99, which in turn is used in the CIT photochemical model (Caltech Institute of Technology, [27]). Volatile organic compounds are considered in a single category to simplify the numerical scheme and reduce the calculation time. The emissions module consists of an Eulerian dispersion model integrating the mass conservation equation, which distributes the emission. For vehicular emission, the emission is still distributed in space and time within the grid following a daily cycle based on in a Gaussian pair to represent the times with the highest flow vehicular. The module also makes an adjustment to consider variations in emissions during the week and on weekends. The same parameterization solves the terms of advection and turbulent transport of pollutants as the model.

### 2.3. Model Evaluation

In this work, two statistical indices were used to assess the proximity of the result generated by the model with the observed values of  $O_3$  in the MASP. The Bias (or mean error) measures the model's tendency to underestimate or overestimate the value of a variable with its observed value and is defined by the expression,

$$BIAS = \frac{1}{N} \sum_{i=1}^N (S_i - O_i), \quad (1)$$

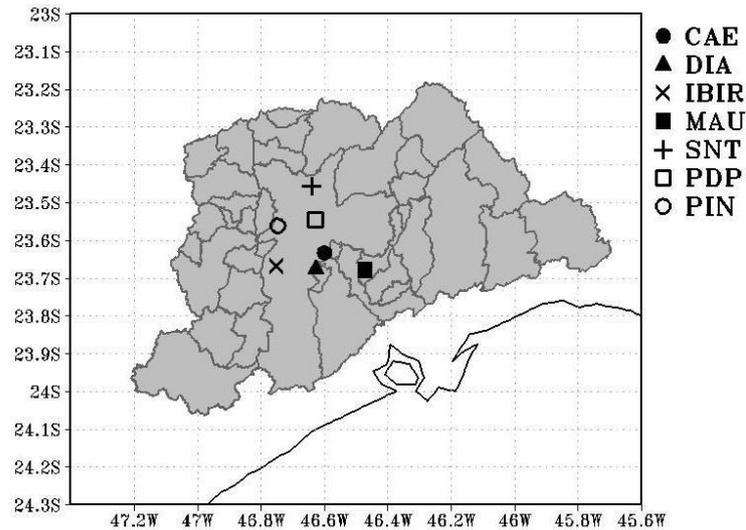
where  $S_i$  corresponds to the  $i$ -th value of the simulated, and  $O_i$  for the same observed variable.  $N$  is the number of data.

The Root Mean Square Error (RMSE) is used to express the accuracy of the numerical results and is given by the following equation

$$RMSE = \frac{1}{N} \sum_{i=1}^N \sqrt{(S_i - O_i)^2}, \quad (2)$$

where  $S_i$  corresponds to the  $i$ -th value of the simulated, and  $O_i$  for the same observed variable.  $N$  is the number of data.

Some representative points of CETESB's pollutant monitoring stations were chosen to assess the model's performance in representing the concentration at levels close to the surface. The location of these points is shown in Figure 3. For meteorological variables, the model was extensively validated by Morais et al. [25,28].



**Figure 3.** Location of CETESB's monitoring network stations in the Metropolitan Region of São Paulo (in gray) used for this study, where CAE corresponds to São Caetano do Sul station, DIA to Diadema station, IBI to Parque do Ibirapuera station, MAU to Mauá station, SNT to Santana station, PDP to Parque Dom Pedro II station and PIN to Pinheiros station.

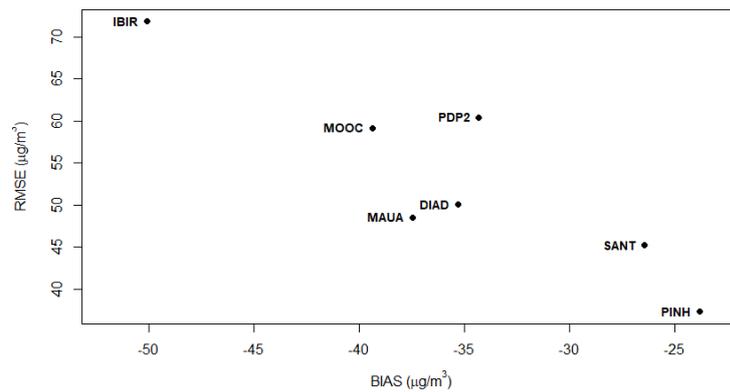
#### 2.4. Experimental design

Two different periods were considered to study the local meteorological factors that influence the increase in nocturnal ozone concentration. The first one corresponds to the condition where the nighttime ozone increase was recorded in all stations (case 7E), which was occurred on 25<sup>th</sup> December 2010. The second was considered a period where it was not recorded nocturnal ozone in any of the selected stations (case 0E). The last one was on 22<sup>nd</sup> January 2005. The discussion was done analyzing the  $O_3$  evolution in each station and by an average nocturnal concentration map. After, a vertical profile of the ozone is done, considering the latitude of MASP.

### 3. Results and Discussions

#### 3.1. Model Evaluation

Figure 4 shows a scatter plot of the RMSE and BIAS of the ozone concentration for all air quality stations in MASP. By BIAS, it appears that the model tends to underestimate the values of  $O_3$ . The absolute value of these indices is related to the order of magnitude of the variable. However, it appears that the values are like those obtained by other authors [6,29]. Besides, it is noted that the Ibirapuera park station has the worst rates, which may be related to the intense presence of green areas in the place, needing to improve this type of representation in the model [30].

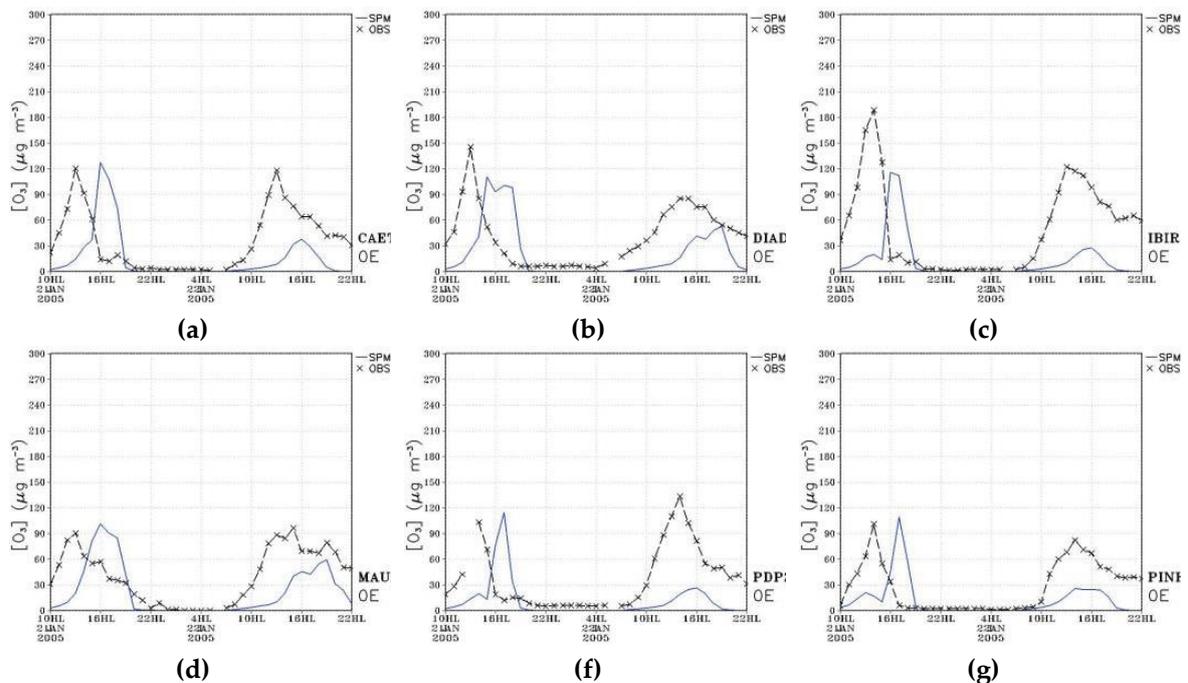


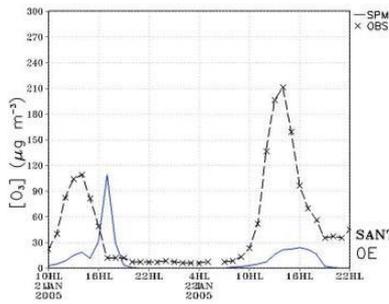
**Figure 4.** RMSE versus BIAS for ozone concentration. Each point represents an air quality station in the MASP: São Caetano do Sul (CAET), Diadema (DIAD), Ibirapuera Park (IBIR), Mauá (MAUA), Pq. D. Pedro II (PDP2), Pinheiros (PINH) and Santana (SANT).

### 3.2. Nocturnal Ozone experiments

#### 3.2.1. No increase in ozone concentration (0E)

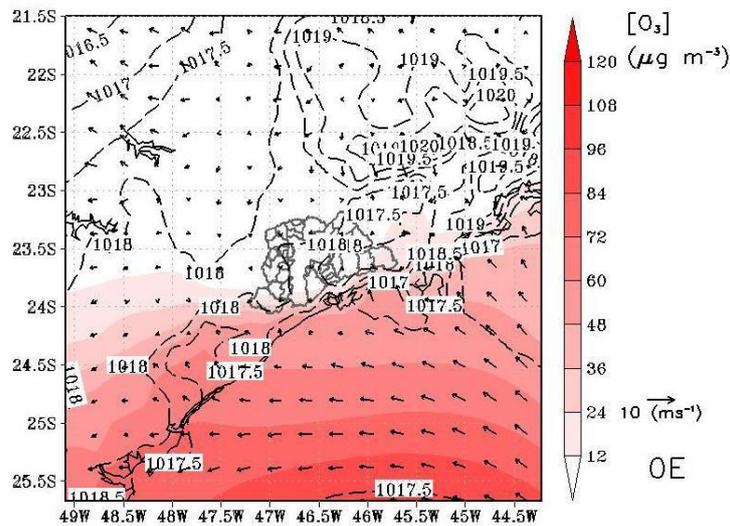
Figure 5 shows the concentrations simulated by the model for air quality stations in cases where no increase in ozone concentration was observed during the night (0E, left column). In the 0E case, the model represented the behavior of nocturnal concentrations relatively well, with the diurnal peak being underestimated, especially on the second day. The mean ozone field and reduced pressure at mean sea level (Figure 6) show an anticyclone located southeast of the simulation domain, which concentrates the core of maximum ozone concentration values. Values below  $36 \mu\text{g m}^{-3}$  are observed in almost the entire continental part. The pressure field tends to be homogeneous over the RMSF and the average wind in this period is weak.





(h)

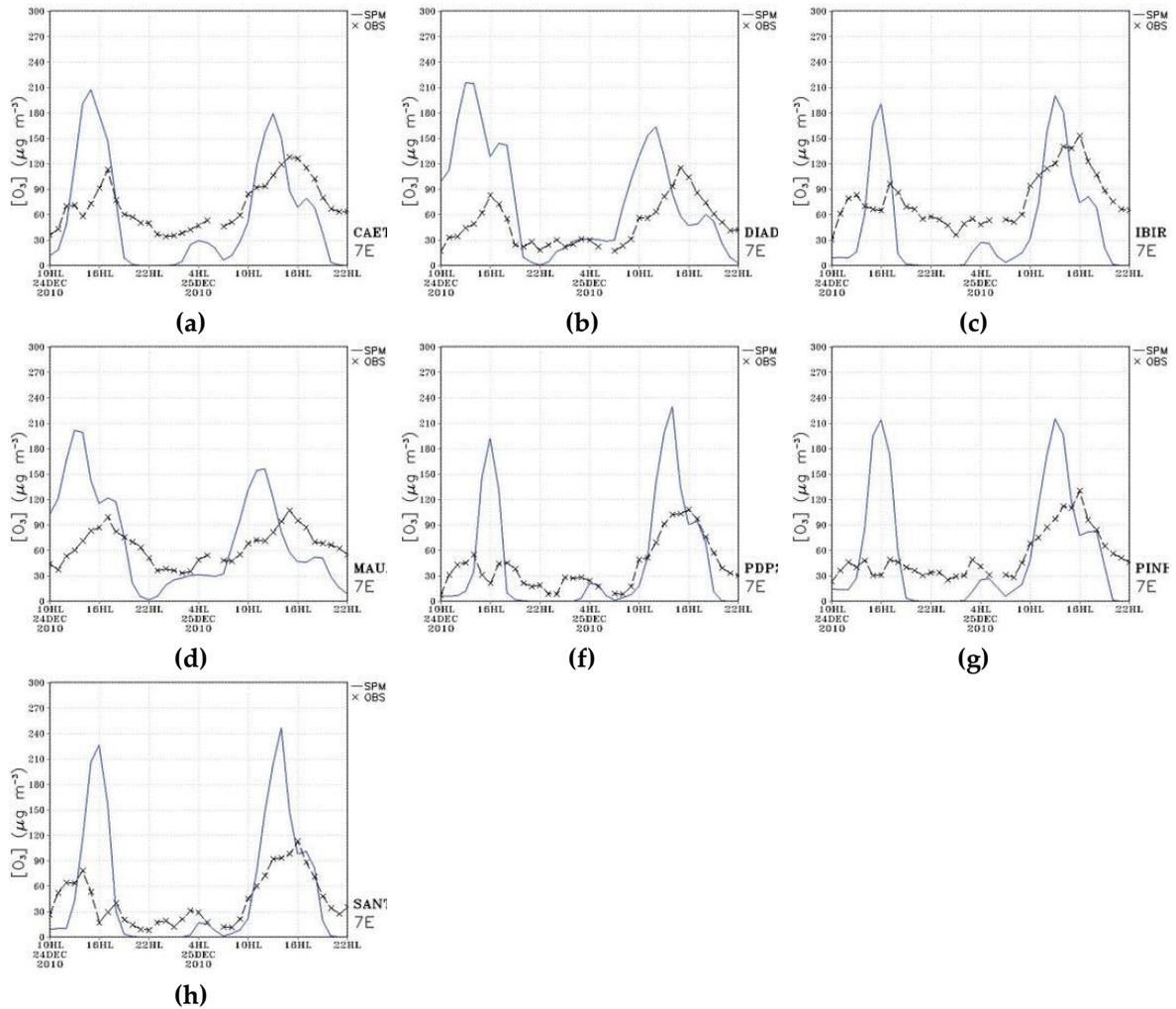
**Figure 5.** Ozone concentration (in  $\mu\text{g m}^{-3}$ ) measurement (OBS, with x black) and simulated (SPM, blue line) for (a) São Caetano do Sul (CAET), (b) Diadema (DIAD), (c) Ibirapuera Park (IBIR), (d) Mauá (MAUA), (e) Pq. D. Pedro II (PDP2), (f) Pinheiros (PINH) and (g) Santana (SANT).



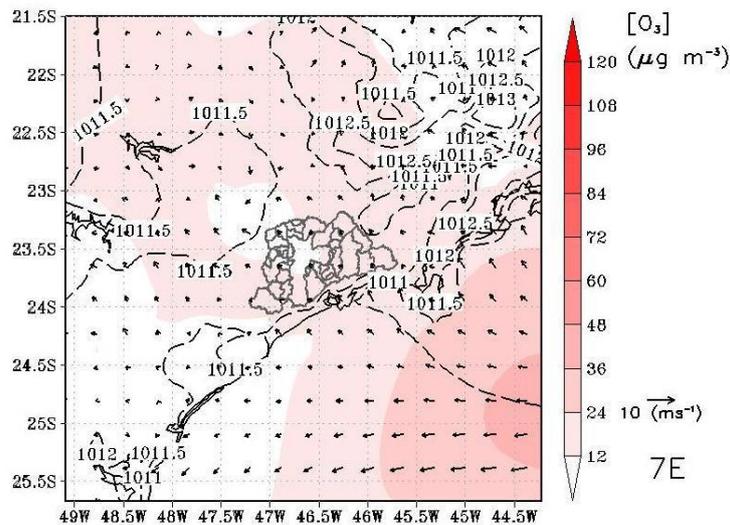
**Figure 6.** Average ozone concentration (color bar, in  $\mu\text{g m}^{-3}$ ), reduced pressure at average sea level (hPa), and average wind ( $\text{m s}^{-1}$ ) for the corresponding period between 22 HL and 10 HL (Local Time) at the first output level of the model.

### 3.2.2. Increase in ozone concentration (7E)

In the 7E case (Figure 7), the model represented the nocturnal increase in ozone, although, in most seasons, an underestimation occurred (difference of almost  $30 \mu\text{g m}^{-3}$ ). At Diadema and Parque Dom Pedro II stations, although the nocturnal increase in ozone has been represented, there is a lag in the model's concentration and that obtained in such stations. Regarding daytime maximums, there was an overestimation for both days at all points analyzed. The average ozone field for this simulation (Figure 8) showed values below  $24 \mu\text{g m}^{-3}$  in the continental part and a core of maximum values southwest of the domain, where the wind tends to have a higher average intensity when compared the rest of the study area.



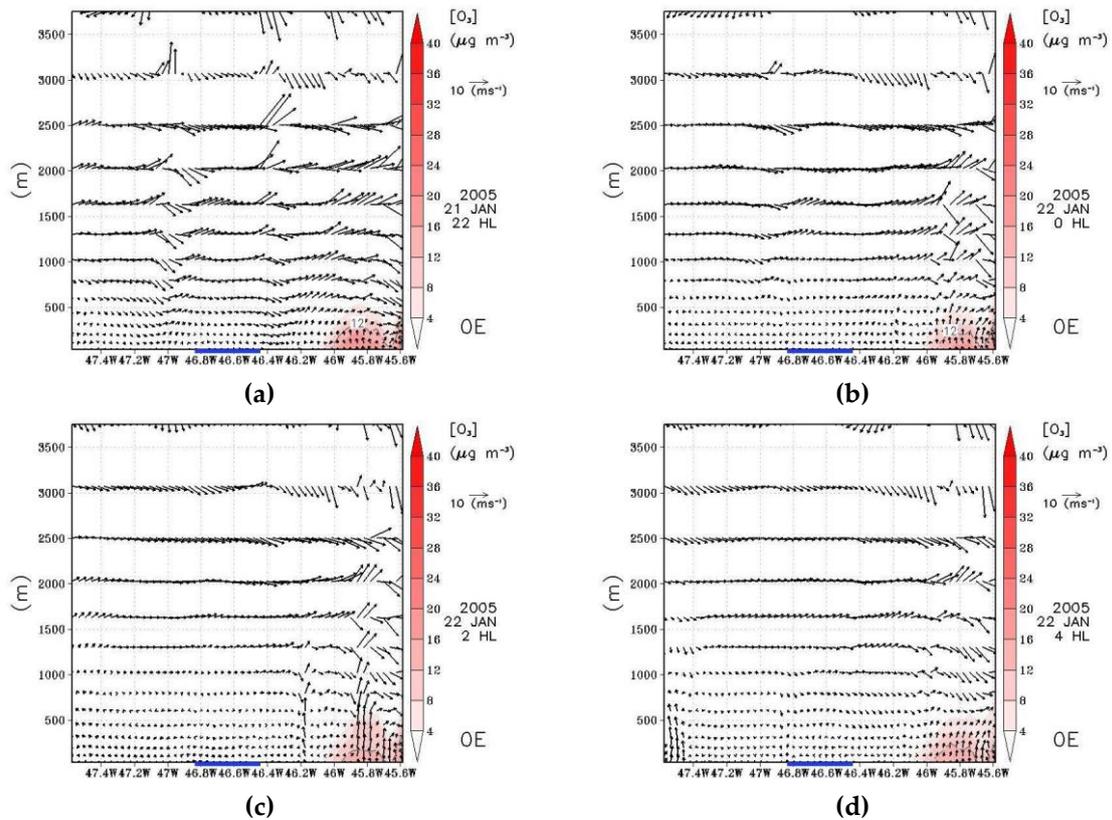
**Figure 7.** Ozone concentration (in  $\mu\text{g m}^{-3}$ ) measurement (OBS, with x black) and simulated (SPM, blue line) for (a) São Caetano do Sul (CAET), (b) Diadema (DIAD), (c) Ibirapuera Park (IBIR), (d) Mauá (MAUA), (e) Pq. D. Pedro II (PDP2), (f) Pinheiros (PINH) and (g) Santana (SANT).



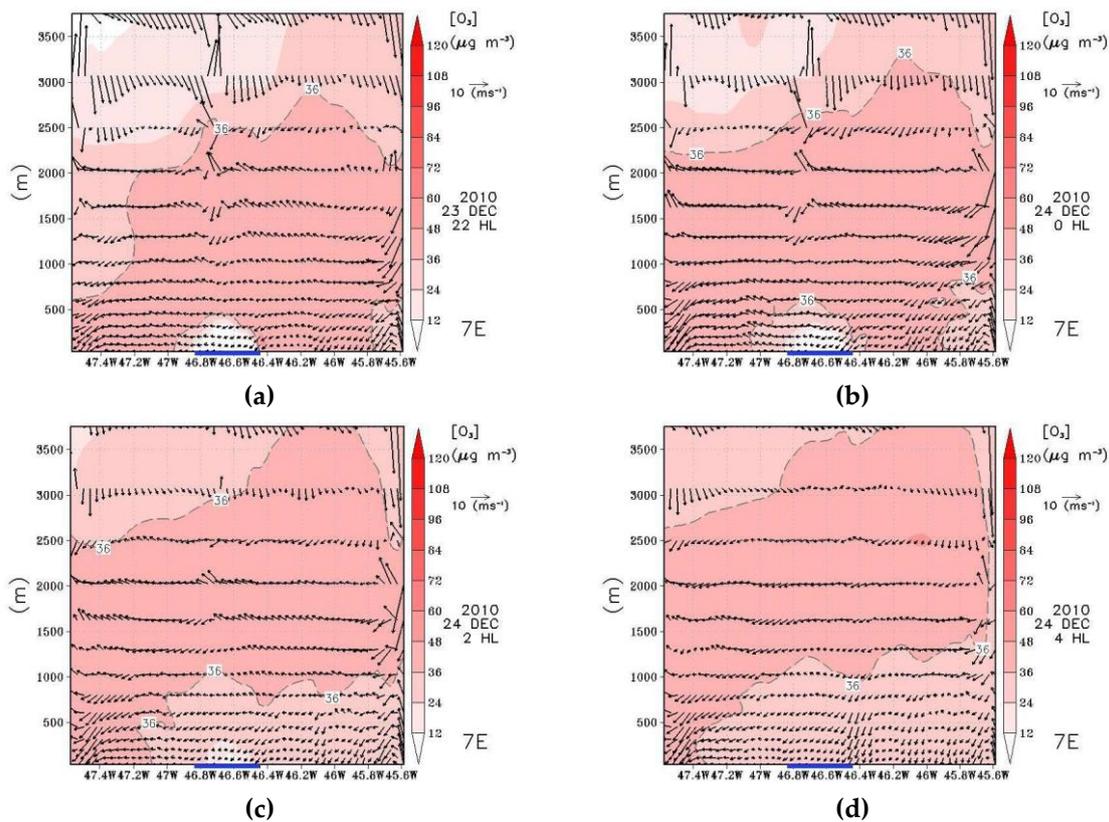
**Figure 8.** Average ozone concentration (color bar, in  $\mu\text{g m}^{-3}$ ), reduced pressure at average sea level (hPa), and average wind ( $\text{m s}^{-1}$ ) for the corresponding period between 22 HL and 10 HL (Local Time) at the first output level of the model.

### 3.2.3. Ozone vertical profile

In case 0E (Figure 9), the wind remains weak throughout the period, with a minimal vertical component. The atmosphere under the MASP is clean for all hours of the night. When an increase in the concentration of ozone is observed in all stations in the MASP (case 7E, Figure 10), the sub-wind component is more intense than when this phenomenon is observed in only a few stations. This result shows that, in the cases of the nocturnal peak, the vertical transport of ozone present in the residual layer has an essential contribution in the generation of increased concentration at levels close to the surface.



**Figure 9.** Ozone concentration ( $\mu\text{g m}^{-3}$ ) and vertical wind component ( $\text{m s}^{-1}$ ) with the zonal wind ( $\text{m s}^{-1}$ ) for a vertical view at  $23.616^\circ$  S latitude, for the case 0E. The blue line indicates the location of the MASP. Local Time is indicated in the corresponding figure.



**Figure 10.** Ozone concentration ( $\mu\text{g m}^{-3}$ ) and vertical wind component ( $\text{m s}^{-1}$ ) with the zonal wind ( $\text{m s}^{-1}$ ) for a vertical view at  $23.616^\circ$  S latitude, for the case 7E. The blue line indicates the location of the MASP. Local Time is indicated in the corresponding figure.

#### 4. Conclusions and Remarks

To study at a local level the characteristics that contributes to an increase in nocturnal ozone concentrations in the MASP, two cases were simulated, when no increase is observed (0E) and when the secondary peak is observed in all air quality stations (7E). In general, the model was able to better represent the nocturnal evolution of ozone concentrations close to the surface at stations located in the MASP. For daytime concentrations, the model simulated concentrations with the maximum values overestimated. The atmospheric condition resulting from the simulations for MASP was similar, confirming that the formation of nightly ozone peaks is not linked to the synoptic situation in this study region. In this case, the greatest influence resides in the amount of ozone that is trapped in the residual layer and the intensity of the subsiding currents over the urban area, as seen in the vertical sections for all cases.

**Author Contributions:** All authors have contributed equally. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors would like to thank the financial support of the Coordenação de Aperfeiçoamento de Pessoal de Nível (CAPES) and the São Paulo Research Foundation (#2011/01040-0).

**Conflicts of Interest:** The authors declare no conflict of interest.

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