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Transport of Pollutants by the Sea Breeze in São Paulo under the South Atlantic High

Transporte de Poluentes pela Brisa Marítima em São Paulo sob a Alta do Atlântico Sul

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Resumo: A circulação de brisa marítima e continental tem importância expressiva na Região Metropolitana de São Paulo (RMSP), influenciando a direção predominante do vento na escala diurna e podendo ocasionar transporte de poluentes. No verão de 2014, houve ultrapassagem do Padrão de Qualidade do Ar da CETESB por ozônio em 43 dias, quando a Alta Subtropical do Atlântico Sul se fortaleceu sobre a região Sudeste do Brasil. Buscou-se compreender como a brisa marítima e continental influenciaram o transporte dos poluentes CO, NO, NO_2 e O_3 na área de estudo, utilizando o modelo WRF/Chem, no período 28/01-01/02/2014. Foram construídos dois cenários: CTRL – emissões veiculares baseadas em inventários atuais de emissão de poluentes, e SENS – retirada de cerca de 75% das emissões na RMSP. A análise dos resultados, por meio de mapas com a distribuição espacial dos poluentes no domínio, demonstrou a importância da circulação de brisa para o transporte de poluição. A análise do campo de divergência mostrou-se útil para a identificação das frentes de brisa. Concentrações de O_3 mais altas foram simuladas na região pré-frontal devido à estagnação e acúmulo de poluentes trazidos das áreas mais poluídas por onde a frente de brisa passou, ocasionando o transporte de ozônio para áreas distantes a noroeste durante a tarde. Ocorre também transporte de poluentes para sul durante o início da manhã com a brisa continental. O movimento ascendente do ar na região pré-frontal ocasionado pela convergência propicia o transporte vertical de ozônio durante a tarde.

Palavras-Chave: Poluição Urbana; Circulação de Brisa; Transporte de Poluição; Região Metropolitana de São Paulo; Química Atmosférica; WRF.

Abstract: *The land-sea breeze circulation is important for the Metropolitan Region of São Paulo (MRSP), influencing predominant wind direction during the night and day, and so, the transport of pollution in the local scale. In the summer of 2014, there were 43 exceedances of the state air quality by ozone, when the South Atlantic Subtropical High strengthened over southeast Brazil. We aimed to study how the land-sea breeze circulation influenced the transport of the pollutants CO, NO, NO_2 and O_3 in the study area using the WRF/Chem model in the period 28/01-01/02/2014. Two scenarios were considered: CTRL – vehicular emissions based on current emission inventories and SENS – removing 75% of emissions in the MRSP. Results were analysed through maps with the spatial distribution of pollutants in the domain and showed the importance of the land-sea breeze circulation for the transport of pollution. Analysis of the divergence field proved useful for identifying the sea breeze front. Higher O_3 concentrations were simulated in the prefrontal convergence line, due to stagnation and accumulation of pollutants brought by the passage of the sea breeze over polluted areas, resulting in the transport of ozone and other pollutants to distant areas northwest during the afternoon and evening. There was also transport of pollutants to the south in the early morning caused by the land breeze. Upward air motion due to the convergence in the prefrontal region caused vertical transport of ozone during the afternoon.*

Keywords: *Urban Air Pollution; Sea Breeze Circulation; Transport of Pollution; Sao Paulo Metropolitan Region; Atmospheric Chemistry; WRF.*

1. Introduction

Atmospheric pollution in the Metropolitan Region of São Paulo (MRSP) currently represents a complex environmental issue which translates, among other externalities, into the deterioration of public health (MIRANDA *et al.*, 2012). Several factors contributed for this Megacity to become the urban area with the highest emission of pollutants in Brazil. With 21 million inhabitants (2010 IBGE Census – Brazilian Institute for Geography and Statistics), and with an estimated fleet of more than 7 million vehicles (CETESB, 2014), it is also one of the most important industrial areas in Brazil. Currently, according to the 2016 emission inventory published by the environmental agency of the São Paulo state CETESB (CETESB, 2017), light and heavy-duty vehicles are the main sources of air pollution in the MRSP, accounting for about 80% of the emission of nitrogen oxides (NOx) and hydrocarbons (HC), and 97% of the emission of carbon monoxide (CO).

Besides emitting primary pollutants, vehicular pollution also increases surface ozone concentration in the urban environment, by the emission of precursor pollutants which form ozone in the atmosphere. In these locations, ozone formation occurs due to the photodissociation of NO_2 in the presence of volatile organic compounds (VOCs). The photodissociation produces nitrogen monoxide (NO) and atomic oxygen (O), which in turn reacts with molecular oxygen (O_2) to form O_3 (Haagen-smit, 1952). O_3 can be destroyed by NO to form nitrogen dioxide (NO_2) and oxygen. VOCs are important because they react with NO, oxidizing it to NO_2 in a series of reactions (BRASSEUR, 1999), so they contribute to increase NO_2 concentrations in the atmosphere, which results in a net increase of surface ozone in urban areas. Other factors, such as VOCs reactivity and the NOx/VOCs ratio are also relevant for determining ozone concentrations (ALVIM *et al.*, 2017). Just as well, VOCs may also lead to ozone destruction (e.g., via the OH radical). The intensive use of ethanol as fuel, either added to gasoline or used on its own, contributes to high VOCs emission and concentrations in the MRSP.

Because the MRSP is relatively close to the coast (about 50 km), it is frequently under the influence of the sea-land breeze secondary circulation (CARRERA and SILVA DIAS, 1990; DIAS *et al.*, 1995). This type of local circulation stems from the differential heating of nearby surfaces which present different thermal capacities, such as land and water, resulting in remarkably different thermal amplitudes through the day. The sea breeze occurs when the land is warmer than the ocean, therefore, a lower pressure area forms over land and induces winds flowing from the ocean to the continent on surface level, with a return circulation observed at higher altitudes (MUSK, 1988). This is observed from midday onwards into the afternoon and early night hours, after continental and maritime surfaces have heated differently along the day. The opposite is observed at night and early morning, when the ocean is warmer than land due to having lost less heat during the night, generating the land breeze, when winds flow from the higher pressure over the colder continent to the less cold ocean.

This thermodynamic process is important to determine wind direction in the diurnal scale over coastal areas, or close to large water bodies, such as lakes. Several studies have investigated the occurrence of the sea breeze in this region, either using observed data (CARRERA and SILVA DIAS, 1990; OLIVEIRA *et al*., 2003) or using numerical atmospheric modelling (DIAS *et al.*, 1995). The effects of the sea breeze in the local weather and climatic conditions of the MRSP have also been considered (AZEVEDO and TARIFA, 2001; ALVES and GALVANI, 2017). Other works investigated pollutant dispersion associated to the sea breeze circulation in this area (BISCHOFF-GAUß, 1998 *et al.*, FREITAS et al., 2007). In these works, the authors verified that pollutants emitted in closer municipalities, such as Cubatão (located halfway between the MRSP and the coast), can be transported to the MRSP by the sea breeze circulation, or overseas by the land breeze. Oliveira *et al.* (2003) used observational data to study wind patterns and the effect of orography because it also interferes with the heating patterns. Freitas and collaborators (2007) showed the interaction between the urban heat island and the sea breeze, in which greater heating leads to an increase in convection, and so, causes the pressure to decrease in downtown São Paulo. This eventually increases the velocity in which the sea breeze reaches the area. Silva Júnior (2009) studied the influence of the boundary layer characteristics on pollution dispersion with the WRF/Chem model, showing that the height of the boundary layer is important to determine pollutant concentrations locally and its vertical transport. Sánchez-Ccoyllo *et al.* (2006) studied the transport of pollution in the MRSP to regions further inland, and others have used backward trajectory models to study the recirculation of pollutants to the MRSP after being transported to the sea (SILVA, 2013; SILVA, 2017). However, there is an increasing need to investigate the impacts of the land-sea breeze on air quality in the MRSP under different synoptic and local atmospheric conditions and their interaction with vehicular emission patterns, and also, to comprehend the vertical transport of pollution in the area due to local convergence caused by the sea breeze front.

During the dry season (from April to September, austral winter), low humidity and atmospheric stability influence the climate in the MRSP, leading to higher overall pollutant concentrations. Thus, most studies are not usually performed during summer, when conditions are generally more favourable for pollutant dispersion. In 2014, however, there were 43 days on which the state air quality standard for ozone were exceeded, many of them during January and February (austral summer), when the South Atlantic Subtropical High (SASH) influenced southeast Brazil (CETESB, 2015). Due to higher air pressure, intense positive anomalies of solar radiation and air temperature occurred in the region (RIBEIRO *et al.*, 2015), blocking the passage of synoptic frontal systems and inhibiting precipitation regionally (according to the agrometeorological bulletin of the national institute of meteorology, January 2014). Therefore, the objective of this work is to comprehend how the sea and land breezes influenced the transport of the pollutants CO, NO, NO_2 and O_3 in the study area, during an episode of strengthening of the SASH during summer, using the WRF/Chem atmospheric model.

2. Methodology

The Weather Research and Forecasting model coupled with Chemistry (WRF/Chem) is a dynamic numeric physical model of the atmosphere with added atmospheric chemistry. Using a complex set of equations, it simulates the atmospheric behaviour and its influence on particles and gases, through the chemical module. It has a myriad of applications focused on regional air quality simulations, including the emission, transport, mixing, and chemical transformation of pollutants (GRELL *et al.*, 2005). However, since it is focused on regional air quality, it is not appropriate for micro-environment simulations. As with any atmospheric model, accuracy is improved by an appropriate set of initial conditions and simulation time depends largely on the computational power available.

The simulation for this analysis was performed for the period 28/01/2014 00Z to 01/02/2014 00Z, when favourable conditions for the concentration of pollutants were observed, particularly for surface ozone. WRF/Chem version 3.2.1 was used according to the scheme described in the work of Andrade *et al.* (2015), with emission estimates based on tunnel studies and in emission factors published by CETESB (2010) and VOCs chemical speciation performed specially for the local ethanol-fuelled vehicle fleet. Pollutant emission is proportional to total road length in each 1-km^2 grid cell. Initially, a control simulation (CTRL) was performed representing the "business as usual" pollutant emission in the MRSP according to the aforementioned criteria. An adjustment was made to the CTRL simulation to maintain emissions in downtown urban areas higher than in the suburbs, by lowering emissions in 20% outside the urban centre of São Paulo and in 80% on non-highway roads outside the urbanized area of the MRSP. After that, a sensitivity scenario (SENS) was built, in which about 75% of the emissions in the MRSP were removed (**Figure 1**), and the total number of vehicles in the domain were decreased from 8 to 2 million. This remarkable change in emissions made it easy to perceive the transport of air pollutants across the domain. After both simulations were performed, results were validated and analysed.

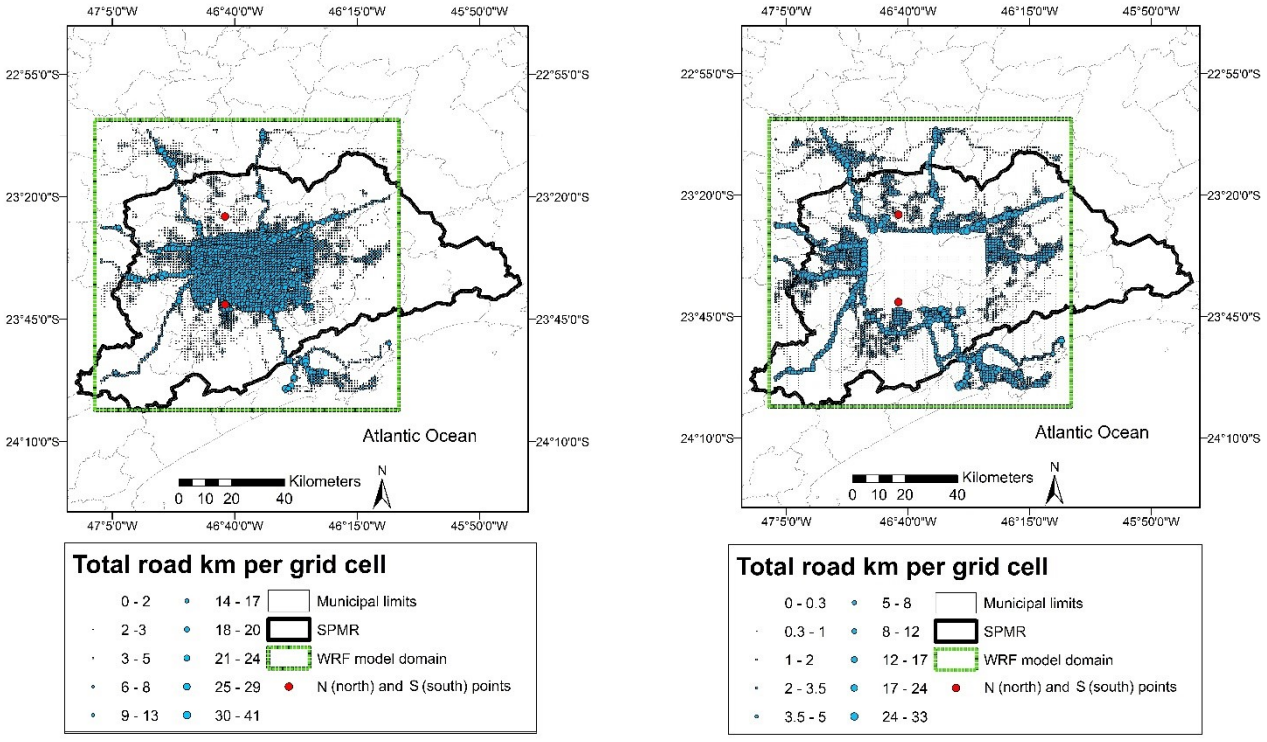


Figure 1: Total road length (km) in each of the 1-km^2 grid cells in the WRF/Chem model domain, in the CTLR (A - Left) and (B - Right) SENS scenarios. Pollutant emission is proportional to road length. In the SENS scenario, all emission was removed from the most urbanized area. The red dots indicate the points N (North) and S (South) used for temporal analysis.

To validate the simulation, pollutant data were obtained from three CETESB monitoring stations: Pinheiros (from which air temperature and wind speed data were also obtained), Capão Redondo and Ibirapuera. They are located in the MRSP in a varying degree of urbanization and direct impact of sources (from more to less urban and impacted: Pinheiros-> Capão Redondo-> Ibirapuera). The chosen points in the domain for comparison, also in order of urbanization and impact from sources, were: Central (densely urbanized in downtown São Paulo),

southwest (close to CETESB station Capão Redondo, suburban) and background (located in a rural area of the MRSP). The location of the validation points in the domain are shown in Annex 1.

There are no CETESB stations measuring CO directly under the impact of sources in downtown Sao Paulo close to the Central point, so we used CO observed at Pinheiros station for comparison, because it is also located in a densely urbanized area and is directly impacted by sources, and so, in a similar land use influence regarding pollutant emission. Ibirapuera station, located inside a city park, is not well represented at its domain location due to model constrains (such as the 1-km spatial resolution), so we used data simulated at the Background point in the domain for comparison, because it represents an urban background location, as for, example, inside an urban park (removed from the pollution sources). Only the Southwest point was used to compare observed O_3 and simulated O_3 in the same point. Furthermore, the Southwest and Background points are located to the west of the MRSP, so, downwind from the southeast sea breeze after it crosses the city, which was the focus of this study. BIAS values were calculated between the aforementioned pairs of points (Pinheiros-Central, Capão Redondo-Southwest, Ibirapuera-Background) and indicate the difference between simulated and observed values. In this study, it was calculated by the following formula (Eq. 1), in order to obtain percentage values.

$$BIAS = 100 * \left(\frac{S - O}{O}\right) \quad (1)$$

Where:

S: average of simulated values

O: average of observed values

2.1. Sea and Land Breezes

Based on the literature for the study region, the southeast winds, present from the beginning of the afternoon to the end of the evening, indicate the sea breeze (CARRERA and SILVA DIAS, 1990). As described in other works, the sea breeze is more intense than the land breeze, due to the greater contrast between the heating of continental and maritime surfaces compared to the cooling due to the differential heat loss at night (MAK and WALSH, 1976, BISCHOFF-GAUß *et al.*, 1998, CROSSMAN and HOREL, 2010). Complementary, we designated the N/NE winds, present from the middle of the night until the end of the morning, as the land breeze. Actually, their NE component suggests they were not purely the night-time response to the sea breeze circulation in the diurnal scale (which is usually NW), but rather a conjoined influence of the land breeze and the larger-scale SASH circulation. Either way, the simulated N/NE winds were certainly influenced by the local breeze circulation system as well.

Maps representing the spatial distribution of the concentration of CO NO, NO_2, O_3, along with wind speed and direction were used to represent the temporal evolution of these variables in both scenarios, at every three hours, for the day 01/02/2014. We chose to show results on the last day of simulation due to the model spin-up time and less interference from boundary and initial conditions. Vertical transport of O_3 was studied during the day, analysing convergence on surface level (which leads to vertical air motion) and O_3 at 1 km altitude, possibly at the top of the boundary layer. Time series are also shown, representing NO and O_3 concentrations of the two last simulation days, in two distinct points in the domain (N and S, shown in **Figure 1**) and correlation coefficients between the concentration of these pollutants in these locations and the V-wind vector were calculated, in order to analyse the relationship between north/south wind direction and pollutant concentrations in different locations.

3. Results

3.1. Simulation Validation

Data obtained in the Pearson's correlation test between simulated and observed data are shown in **Table 1.** Generally, the model reproduces the temporal series with good correlation. For ozone, correlations were higher in the points away from the urban core in the model (Southwest and Background), compared to the Central point. CO however, showed good correlation for the Central and Southwest points. BIAS revealed values very close to observed in Capão Redondo station for ozone (4%) with slight underestimation for CO in the Central point compared to Pinheiros station (-20%) and slight overestimation for ozone in the Background point compared to Ibirapuera station (22%). Correlations, on the other hand, were considered satisfactorily high (0.67, 0.69 and 0.72,

respectively) and nearly all were statistically significant (**Table 1**). Despite their distance in the model domain, comparing Ibirapuera station to the Background point (as explained in section 2), proved to be a good comparison, given the results shown in Table 1. This shows that land use and emission conditions impact pollutant concentrations significantly (since both Ibirapuera station and the Background point represent similar exposure conditions), but are not always correctly represented by atmospheric models, which stresses the need for improvements in their spatial resolution, in order to better represent fine intraurban variations of land use, emission conditions and air pollutants. Air temperature was simulated exceptionally well, presenting a correlation of 0.94 and a BIAS of 2%, when comparing values simulated at the Central point to the temperature observed in Pinheiros station. Since solar radiation incidence heats the surface (and is, therefore, strongly associated to air temperature), this suggests that solar radiation, which is paramount for ozone formation, was also well simulated, otherwise air temperature would have not behaved as closely to observations. Wind speed, however, was overestimated by the WRF model, indicating its known problems in simulating weak wind speeds close to the surface, particularly in urban areas, which was discussed in previous works such as Jiménez and Dudhia (2012) and Miao *et al.* (2015).

Table 1 - BIAS and Pearson's Correlation Coefficient between hourly CO data (ppm) obtained from Pinheiros station (PIN), and O_3 data (ppb) from Capão Redondo (CAPAO) and Ibirapuera (IBIRA) stations, and simulated data at the Central, Southwest and Background points in the domain (for CO and O_3); and between air temperature (TEMP (°C)) and wind speed (WS (ms^{-1})) between data from Pinheiros station and the Central point, for the whole period 28/01-01/02/2014. * indicates statistically significant correlations.

Correlation	**CO PIN**	**O_3 CAPAO**	**O_3 IBIRA**	**TEMP PIN**	**WS PIN**
Central	0.69*	0.55*	0.52*	0.94*	0.43*
Southwest	0.73*	0.67*	0.62*	-	-
Background	-0.09	0.75*	0.72*	-	-
BIAS	-20%	4%	22%	-2%	152%

3.2. Spatiotemporal distribution of pollutants and pollution transport

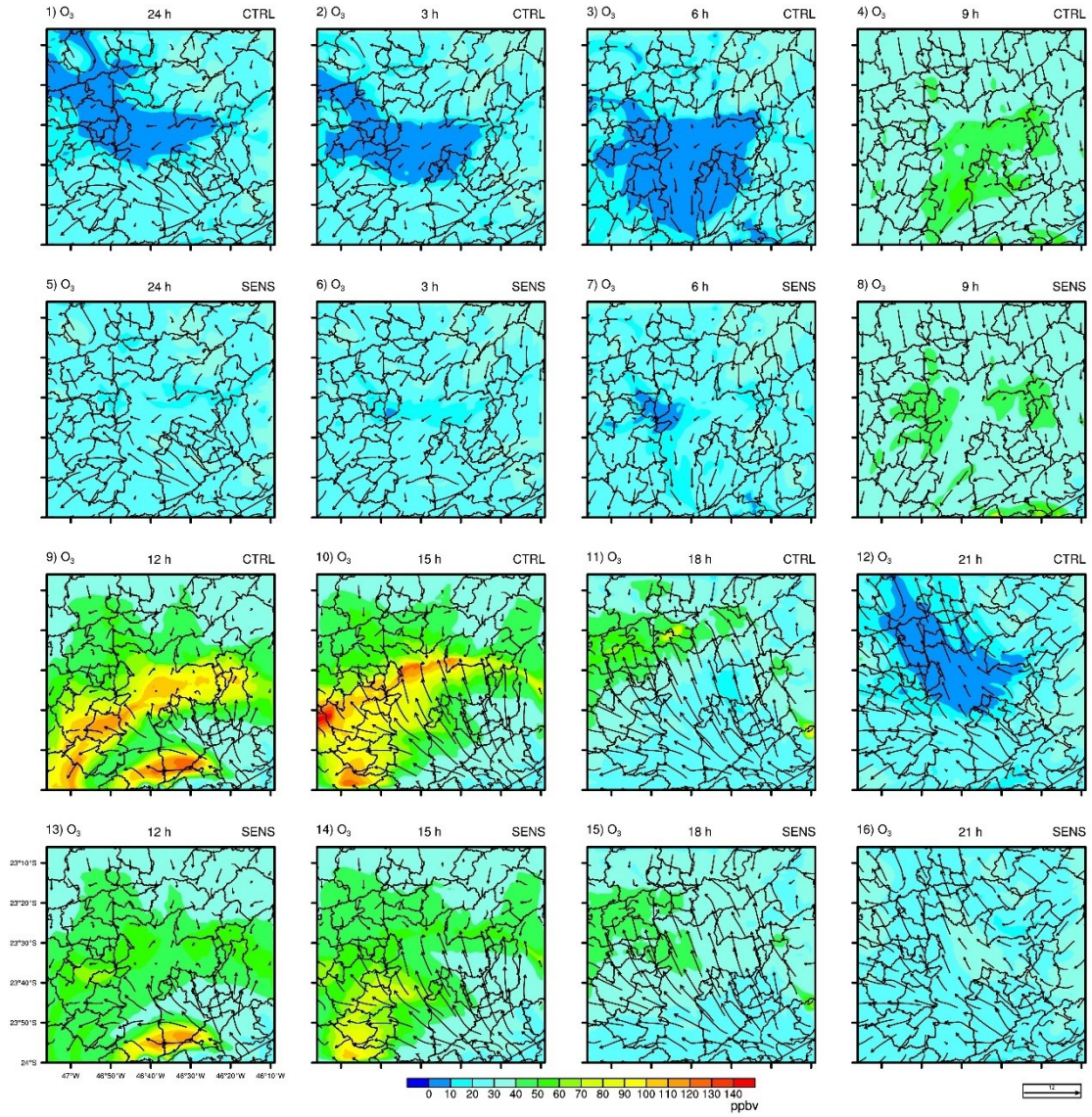
In view of the importance of solar radiation availability for ozone formation and the sea breeze circulation for pollution transport, we aimed to study the hourly temporal evolution of the concentrations of O_3, NO_2, NO and CO simulated in the CTRL and SENS scenarios, together with wind speed and direction, on the day 01/02/2014. Results are shown in **Figures 2.1** to **5.16**.

Higher ozone concentrations were simulated during the day, and particularly in the afternoon. During the night, under more stable conditions, there is less ozone variation (particularly in the early hours). After 9 hours, with greater availability of shortwave solar radiation and precursor pollutants emitted by traffic, the concentration of ozone starts to increase while wind direction is weaker and not influenced directly by any breeze type (**Figure 2.4**). At 12 hours, after a few hours of heating, the wind pattern changes and is influenced by the southeast winds of the sea breeze, which prevail and intensify in the afternoon, lasting through the evening, until at around 21 hours (**Figure 2.16**).

Under these conditions, in the CTRL simulation, ozone produced in the afternoon (peaking at 140 ppb) is transported to the northwest of the MRSP, far from downtown as much as 80 km, more evidently at 15 and 18 hours (**Figures 2.9, 2.10**, **2.11**). In Portugal, Monteiro *et al.* (2016) found that ozone was transported from the coast to the continent by the sea breeze and reached areas as far as 30 km away from the emission of the precursors. In the evening, with the absence of solar radiation, ozone is consumed by NO and VOCs emitted by the vehicles, while the sea breeze keeps influencing the wind direction, resulting in the transport of air containing less ozone (than its surroundings) from downtown to west and north-western regions (**Figures 2.12, 2.1, 2.2**). During most of the early hours, more stable conditions prevail, but after 3 hours, the N/NE wind intensifies and transports the air with lower ozone concentrations from downtown to the south of the MRSP, a similar spatial dynamic simulated as in the work of Silva (2017) (**Figures 2.2, 2.3**).

O_3 simulation in the SENS scenario showed much different results due to the complex interactions involved in its formation and destruction. Compared to the CTRL scenario, lower values are observed in the urban core, at around 80 ppb. The air parcel originated on the coast, however, is still under the influence of local emission in the SENS scenario, and so, ozone remains high in this parcel during the day (120 ppb, **Figure 2.13**). This demonstrates

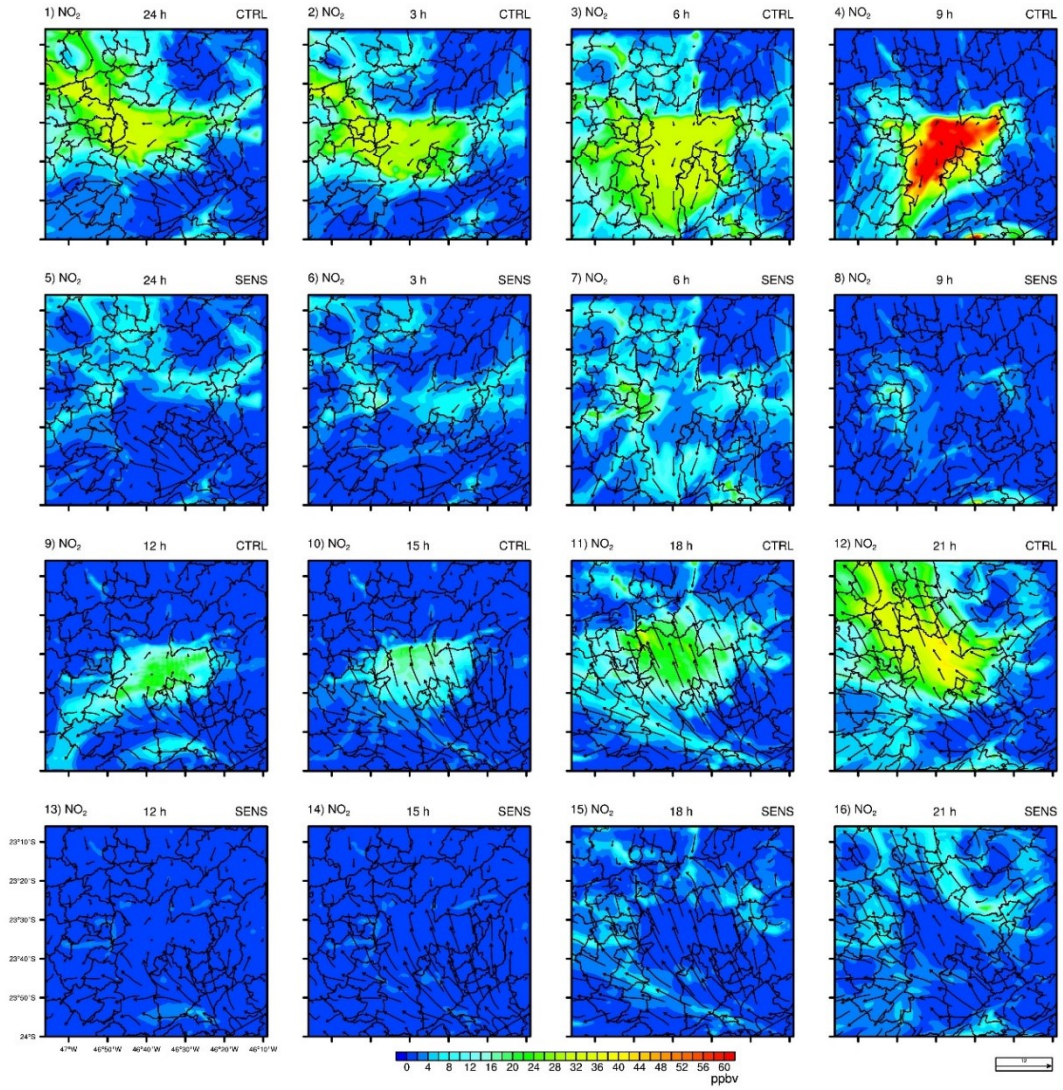
that the southwest of the MRSP undergoes ozone transport from the coastal areas nearby (e. g., the metropolitan region of Santos) via the sea breeze, leading to high ozone in the south of the MRSP even in the absence of emissions in the MRSP. Some ozone transport to the west/northwest in the afternoon was also simulated in the SENS scenario (**Figures 2.14, 2.15**), but in a much lesser magnitude than in the CTRL scenario (**Figures 2.10, 2.11**). After 18 hours, concentrations stabilize at around 30 ppb in the SENS simulation, and do not decrease at night in the centre of the domain, due to the absence of ozone consuming by NOx and VOCs, leading to an increase in night-time ozone compared to the CTRL simulation (**Figures 2.16, 2.5, 2.6**). This excess of ozone is then transported northwest by the sea breeze after 18 hours, and to the south by the land breeze, at around 3 and 6 hours (**Figures 2.6 and 2.7**), leading to an ozone increase at night in areas far from the urban core (opposite to the CTRL scenario, where an air parcel with less ozone was transported). Chiquetto *et al.* (2016) also observed a net O_3 increase to the south of the MRSP at night after changing land use and emissions in a much smaller area. At 9 hours, photodissociation increases surface ozone concentrations again – but in a lesser proportion compared to the CTRL simulation.



Figures 2.1 to 2.16: O_3 concentrations (ppb) and wind speed and direction ($m.s^{-1}$) at every three hours, simulated from 00 to 21 hours on 01/02/2014. The CTRL scenario is shown in the first line (figures 2.1 to 2.4) and in every other line. The SENS scenario is shown in the second line (figures 2.5 to 2.8), and every other line. On top of each figure, the pollutant, hour and scenario are displayed. The bottom right arrow length corresponds to 10 $m.s^{-1}$ wind speed.

CO, NO and NO_2 show higher concentrations in the early morning and evening, and lower in the afternoon. In general, NO_2 concentrations present similar behaviour to O_3, such as the transport by the sea breeze to the northwest. Daily maximum hours are different, however, with highest NO_2 concentrations in the morning (about 80 ppb at 9 hours, **Figure 3.4**, when much of the NO has been converted into NO_2) and lower NO_2 concentrations in the afternoon (when most of NO_2 has been converted into O_3). CO shows a similar pattern, with peaks ranging from 1.4 to 2 ppm between 6 and 9 hours (**Figure 5.3** and **5.4**), although the lower concentration in the afternoon might also be attributed to the expansion of the boundary layer, since it is not as reactive as NOx and O_3. Similar results were obtained for the MRSP by Silva Júnior (2009). NO undergoes little transport during the day, due to its reactivity, and is more directly influenced by local vehicular emission, with a maximum of 120 ppb at 6 hours (**Figure 4.3).** It remains low throughout the day, save for a slight increase due to the evening rush hour. From 0 to 9 hours, however, it is transported southward by the land breeze (**Figures 4.1, 4.2, 4.3** and **4.4**). These NO concentrations over São Paulo influence ozone concentrations in the CTRL scenario, keeping them lower under conditions of no solar radiation availability, via the removal of O_3 by NO.

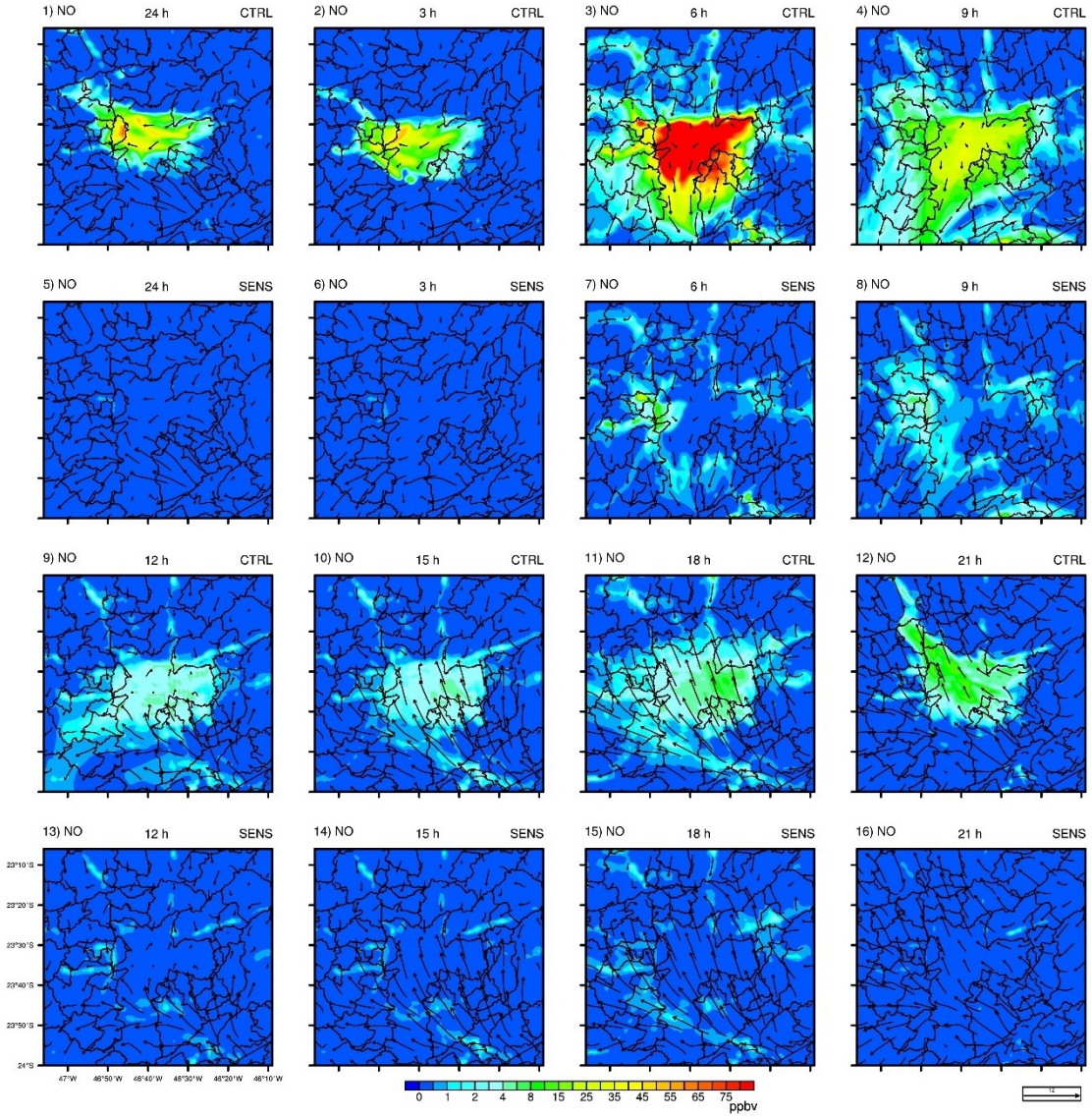
In the SENS scenario, CO, NO, and NO_2 were simulated in much lower concentrations, due to the removal of emissions (as shown in **Figures 1a** and **1b**), reaching peaks of 0.6 ppm, 15 ppb and 28 ppb, respectively. The spatiotemporal behaviours of NO_2 and CO in the SENS simulation were different than in the CTRL scenario. The transport of these pollutants by the sea breeze, however, shifts to more northern areas of the MRSP in the evening (**Figure 3.16** and **5.16**), due to the emissions of highways north of São Paulo, instead of being transported to the west/northwest as in the CTRL simulation (when most emission takes place in the urban centre). Morning transport of NO_2 by the land breeze is not as evident, and it remain closer to the vicinity of highways, similarly to NO (**Figures 3.5** and **3.6**). NO and CO showed near zero concentrations in the SENS scenario in late night and early morning hours.



Figures 3.1 to 3.16: NO_2 concentrations (ppb) and wind speed and direction ($m.s^{-1}$) at every three hours simulated from 00 to 21 hours on 01/02/2014. The CTRL scenario is shown in the first line (figures 3.1 to 3.4) and in every

other line. The SENS scenario is shown in the second line (figures 3.5 to 3.8), and every other line. On top of each figure, the pollutant, hour and scenario are displayed. The bottom right arrow length corresponds to 10 m.s^{-1} wind speed.

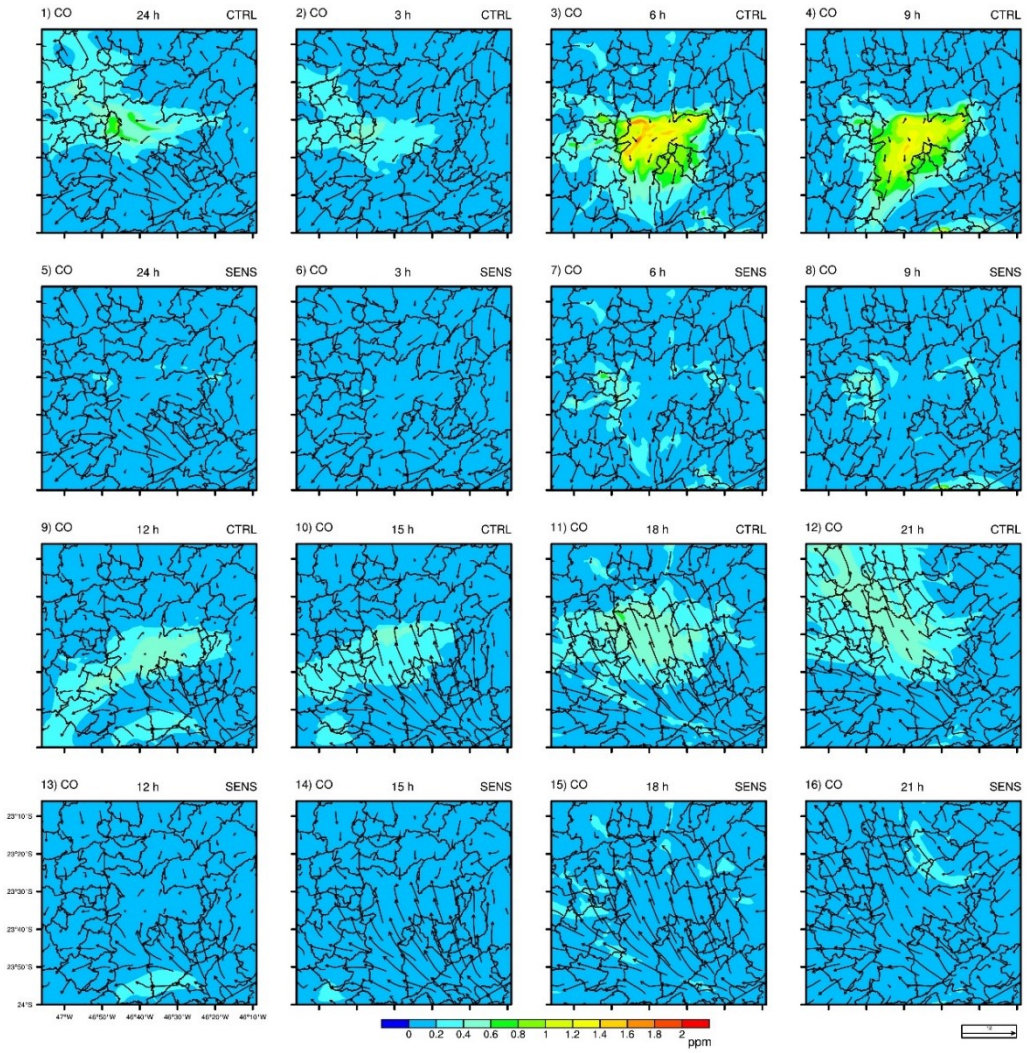
In both scenarios, higher ozone concentrations in the afternoon were simulated at the edge of the sea breeze influence over land (**Figures 2.9, 2.10, 2.11, 2.13, 2.14, 2.15**), where the southeast winds converge with the more stagnant air present over the urban centre. This leads to a local convergence zone in the shape of a front (the blue stripe in **Figures 6e** and **6h**), the sea breeze front (SBF) (KINGSMILL, 1995). As the SBF moves through the MRSP, it transports ozone from SE to NW, accumulating this pollutant in the region characterized by calm winds right before the passage of the SBF in the afternoon. Since convergence leads to upward air movement, this suggests a possible vertical transport from the SBF region upwards, which was verified in our analysis.



Figures 4.1 to 4.16: NO concentrations (ppb) and wind speed and direction (m.s^{-1}) at every three hours simulated from 00 to 21 hours on 01/02/2014. The CTRL scenario is shown in the first line (figures 4.1 to 4.4) and in every other line. The SENS scenario is shown in the second line (figures 4.5 to 4.8), and every other line. On top of each figure, the pollutant, hour and scenario are displayed. The bottom right arrow length corresponds to 10 m.s^{-1} wind speed.

At 10 hours, photochemical activity produces surface ozone and there is a convergence zone north of the São Paulo municipality, possibly generated by the contrast between the larger scale northern circulation (SASH) and the more stagnant air in the urban core. At 1 km altitude, ozone concentrations are stable and wind directions are from E/SE. At 14 hours, surface ozone concentration increases drastically in the urban centre, its hotspots shaped by the sea breeze front which crosses the MRSP (characterized by the convergence zone in **Figure 6e** and also possible to

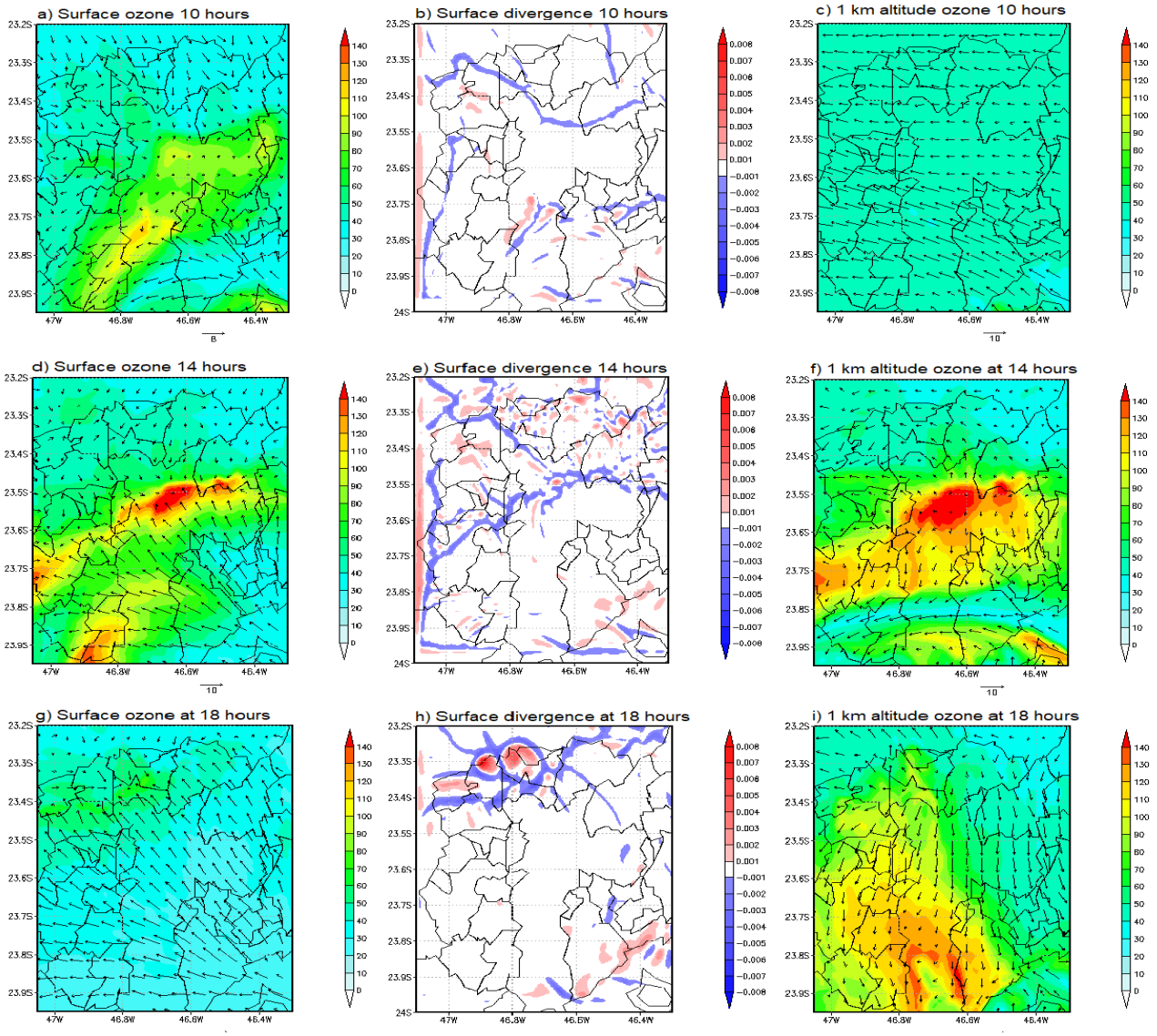
identify by the change in wind direction from **Figure 6a** to **Figure 6d**). At the altitude of 1 km, there is also a marked increase in ozone concentrations at 14 hours (**Figure 6f**). However, there is transport to the south, following the wind direction at these altitudes, the return flow of the 3-dimentional sea breeze circulation. At 18 hours, with the decrease in photochemical activity, surface ozone decreases (**Figure 6g**), and the SBF has crossed the MRSP almost entirely, reaching the far northwest of the domain (**Figure 6h**). However, at 1 km height, ozone which was transported upwards at the SBF convergence during the afternoon is transported towards the south, following the return altitude flow (**Figure 6i**). In the SENS scenario, with the removal of the majority of emissions in the urban core, there is little vertical transport of ozone (not shown). Finally, time series of the two points shown in **Figure 1** (located in the north and south of the domain) were evaluated on figure 7.



Figures 5.1 to 5.16: CO concentrations (ppb) and wind speed and direction (m.s^{-1}) at every three hours simulated from 00 to 21 hours on 01/02/2014. The CTRL scenario is shown in the first line (figures 5.1 to 5.4) and in every other line. The SENS scenario is shown in the second line (figures 5.5 to 5.8), and every other line. On top of each figure, the pollutant, hour and scenario are displayed. The bottom right arrow length corresponds to 10 m.s^{-1} wind speed.

In the CTRL simulation, NO concentration is higher in the S point, located inside the urbanized area (bottom left of figure 7), under the influence of local emissions, which is completely changed in the SENS scenario (bottom right of figure 7). The ozone peak was simulated in the last day, many hours after the NO peak. During the hours with high NO concentrations, there are northern winds, which might be associated to the transport of this pollutant from more central areas of the MRSP, as discussed previously (**Figure 2.1** to **Figure 5.16**). In both points, O_3 concentrations are more variable in the CTRL simulation (top and bottom left), with higher peaks during the day and lower minimums at night, also as observed in the spatial analysis. In the N point (top left of figure 7), O_3 concentrations are comparable to the S point (bottom left of figure 7), even without local emissions, particularly on the first day (31/01/2014), during the influence of the sea breeze in the afternoon, which probably indicates the pollution transport as discussed for **Figure 2**. The temporal variation of O_3 in both points tend to be more similar in

the SENS scenario (top and bottom right), moving towards concentration patterns observed in background locations (with slightly lower peaks and higher minimums), similar to results obtained in other studies (LEVY *et al.*, 2014).



Figures 6a to 6i: Ozone at surface level (left), air divergence at surface level (centre) and ozone at 1 km altitude (right) at 10 hours (top line), 14 hours (centre line) and 18 hours (bottom line), in the CTRL scenario. Ozone concentrations are in ppb, divergence and wind speed and direction are in $m.s^{-1}$.

The Pearson's correlation coefficient between V-wind and NO concentration was 0.23 in the N point, which suggests higher NO under the influence of southern winds. In the S point, this coefficient was -0.46, indicating higher NO under the influence of northern winds. Both results suggest the transport of NO from the urban centre of the MRSP towards the suburbs in the CTRL scenario. After removing the emissions, the correlations become weaker (-0.18 and 0.1, respectively). For O_3, correlations with V-wind did not present conclusive results, which might be attributed to the secondary nature of this pollutant and the complex environmental interactions involving other pollutants and the strong temporal correlation with solar radiation (CHIQUETTO and SILVA, 2010; SILVA, 2017), which might interfere with the correlation with wind direction in the diurnal scale.

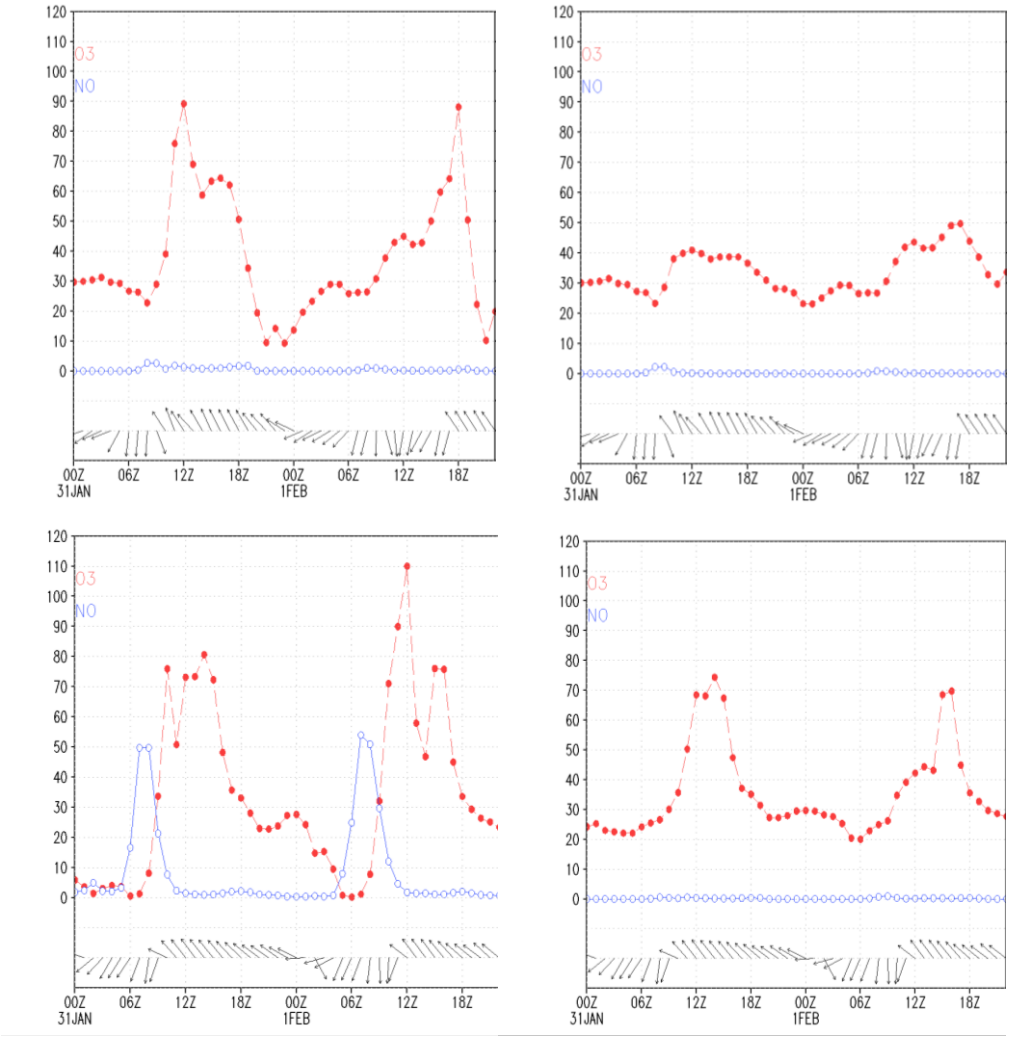


Figure 7: Time series of ozone (red) and NO (blue), simulated for 31/01/2014 and 01/02/2014, at the points N (top) and S (bottom), displayed in Figure 1, for the CTRL (left) and SENS (right) scenarios. Wind direction is shown by the arrows at the bottom of the figures.

4. Conclusions

This study focused on the interactions between the sea-land breeze circulation and the transport of pollution in the greater São Paulo area, during the summer of 2014, under the strong influence of the South Atlantic Subtropical High. The WRF/Chem model was used to analyse two scenarios: control (CTRL, normal emission) and sensitivity (SENS, removal of most emissions from the urban area). Results showed that the sea-land breeze circulation in the area has a strong influence over air pollutants concentration.

During the afternoon, the SE winds of the sea breeze transport NO_2, CO and O_3 to the west/northwest of the MRSP, driving the pollution hotspots to these areas and decreasing concentrations downtown. NO reacts rapidly and does not undergo much transport in the MRSP. In the SENS scenario, concentrations of all pollutants are much lower during the afternoon, due to the emissions removal. However, in the evening and at night, O_3 concentrations increase in the SENS scenario in many parts of the domain, due to the absence of ozone-consuming pollutants – leading to an increase of ozone in the urban core in the evening and transport of higher ozone concentrations to the northwest at these hours. Therefore, the removal of emissions changes the hour of the day on which the transport of the O_3 hotspots occurs to downwind areas by the sea breeze: during the afternoon (CTRL), or during the evening (SENS). Also, during the early morning hours, an excess of ozone remains over the urban core when there is no emission. This excess of surface ozone is transported southward by the land breeze in the SENS scenario. The upwards air motion generated by convergence at the sea breeze front, during the afternoon, leads to an increase in O_3 at 1 km altitude (possibly at the limit of the boundary layer) in the CTRL scenario. Ozone transported upwards at the sea breeze front is then transported to areas far south of the MRSP by the return circulation of the sea breeze at 1 km altitude.

The detailed analysis of the secondary sea-land breeze circulation, its interaction with vehicular emission patterns and with the complex ozone photochemistry are of vital importance to understand air quality in the diurnal scale and the pollution transport in the MRSP, both horizontally and vertically, in finer temporal and spatial scales.

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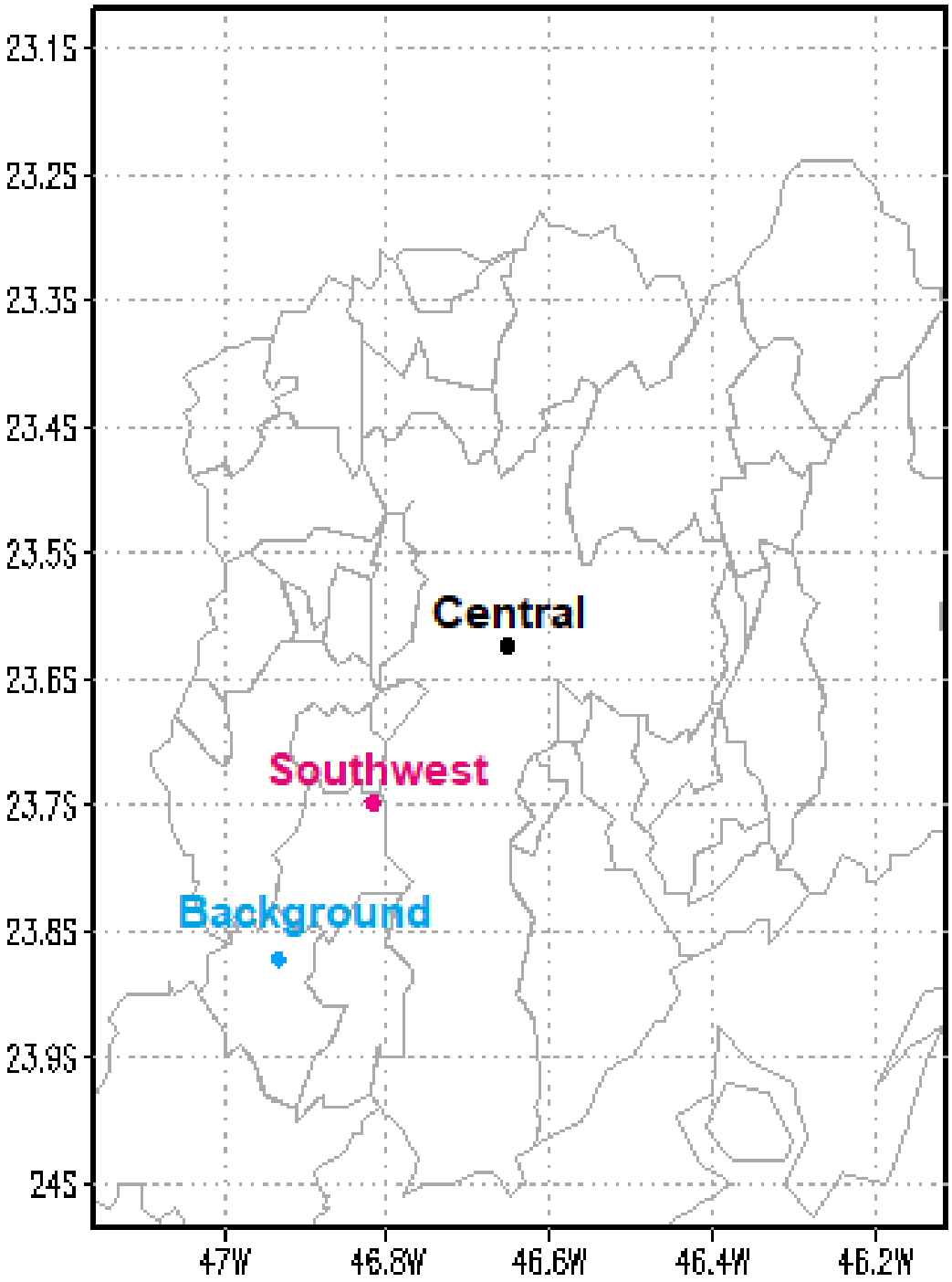
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