Response to Referees' comments

Angel Vara-Vela, M. F. Andrade, Prashant Kumar, R. Y. Ynoue, and A. G. Muñoz

We are attaching a new version of the manuscript trying to answer all the questions that were presented. We would like to thank both referees for all the suggestions that we believe improved the quality of the work clarifying the objectives and conclusions.

Anonymous Referee #1

Specific comments

Abstract

P.14173,L.9-10: the beginning of the sentence "The study period... " is unclear, please reword. Suggestion: The simulation has been performed on a 1 month period (7 August-6 September 2012) to cover the availability of experimental...

The sentence was reworded to "The simulation has been performed for a one month period (7 August – 6 September 2012) to cover the availability of experimental…".

P.14173,L.13-16: the sentence "Results show that the emissions... in the downtown SPMA." is ambiguous and should be reword. State more clearly that 20-30% of the PM2.5 mass is due to secondary aerosols.

The sentence was reworded to "Results show that the emission of primary gases, mostly from vehicles, led to a production of secondary particles between 20 and 30% in relation to the total mass concentration of $PM_{2.5}$ in the downtown SPMA".

P.14173,L.16-17: Dust and sea salt contributed to 40-50% of the PM10 mass. Why not giving a percentage of the PM2.5 mass, in order to be able to compare it to the contribution of secondary aerosols ? Alternatively, contribution of secondary aerosols could be given as a percentage of PM10.

The percentage of the $PM_{2.5}$ mass was added in the text.

P.14173,L.23-24: "which simulates feedbacks...chemical species". This part of the sentence has no link with the following. It would better fit a the beginning of the abstract (L. 5-6).

That sentence was moved to the beginning of the abstract.

Introduction

P.14174,L1: the introduction should starts by a general paragraph describing the general context in which this study take place, e.g., why is it important to study

PM2.5, ozone, SOA,... ? What are the impacts of vehicular emissions on air quality and climate, generally ?.

The introduction was modified including two paragraphs describing the general context of emissions and their impacts on air quality in SPMA.

"The Sao Paulo Metropolitan Area (SPMA), in the southeast region of Brazil, is considered a megalopolis comprised of Sao Paulo city and more 38 municipalities. One of the main concern in the SPMA is the occurrence of violations of air quality standards for ozone and fine particles at different air quality stations from the Sao Paulo Environmental Agency (CETESB). The air pollutant emissions in the SPMA are related to the burning of the fossil fuels: ethanol, gasohol (gasoline with 25% ethanol) and diesel. Recent work of Carvalho et al. (2014) reported a substantial increase in number of road vehicles from 1 million in 2000 to almost 7 million in 2014, together with an overwiev of the pollutants concentration, fuel use in the SPMA and the relationship between the emissions and the improvement in the air quality in past years.

They constitute the main cause of impairment to air quality in the SPMA, but the number of air quality standard violations has decreased for almost all pollutants with the exception of $PM_{2.5}$ and O_3. Both these pollutants are impacted by the vehicular emissions and have experienced an increase in the number of violations of local air quality standards as discussed in detail by Carvalho et al. (2014). Pérez-Martínez et al. (2015) have analyzed the monthly mean values for the regulated pollutants from 2000 to 2013 for the air quality stations in the SPMA. They found a decrease in the average concentration of NOx, CO and PM_{10} by 0.65, 0.37 and 0.71 % $month^{-1}$, respectively, although the sales of the fuels (gasoline, ethanol, and diesel) had increased by 0.26, 1.96 and 0.38 % $month^{-1}$, respectively".

P.14174,L.8-26: To support this significant part of the introduction, the authors referred to a report written by the Sao Paulo Environmental Protection Agency (CETESB) in Portuguese. At least a part of this information should be support by peer-review material – few papers in the reference list adequately match this scope.

Some references published in peer-review journals were added, bringing studies regarding the air quality in SPMA: Carvalho et al. (2014) and Pérez-Martínez et al. (2015).

P.14174,L.15-18: It is claimed that "SPMA has a significant fleet... gasoline and ethanol).". In this section, informations on these specific fuels should be given – Are emitted pollutants the same as for classical fuel ? Does previous studies exist ?.

Additional references discussing the role of emissions in SPMA were added in this part of the introduction

"To date, many studies assessing the impact of biofuels on the air quality have been performed in Brazil. For example, Anderson (2009) conducted a review concerning the use of ethanol fuel in Brazil. His work highlighted that the atmospheric concentrations of acetaldehyde and ethanol are much higher in Brazil in comparison with the other areas of the world. Costa and Sodré (2010) showed that exhaust emissions of hydrous ethanol reduced CO and Hydrocarbons (HC), but increased CO_2 and NOx levels.".

P.14175,L.14-15: "One of the most important aspect of this work is the quantitative analysis of the formation of PM2.5 and ozone". Please add a paragraph introducing ozone formation mechanisms and explaining why it's relevant in the context of your study. In addition, the statement that "primary pollutants have rather increased in the past years" is vague and should be support by a reference.

A paragraph to reinforce the relation between ozone and aerosol particles was added in the text.

P.14175,L.26-29: More specific informations needed, how many measurement sites ? Is there a reference describing the NUANCE-SPS project and/or the field campaigns. Also, the sentence "In order to achieve these goals, aerosol measurements were taken..." don't fit with the previous sentence in which a numerical simulation is mentioned... this part should be reword and reorganized in order to provide a clear message to the reader.

The paragraph was better reorganized. An additional NUANCE-SPS reference was also given.

<u>Methodology</u>

P.14176,L.14-15: The beginning of this sentence should be reword, e.g.: "Aerosol observation datasets used in this work were collected using..." If you really want to keep mentioning the PM2.5 and PM2.5-10 acronyms, please define PM2.5-10.

The sentence was reworded to "Aerosol observation datasets used in this work were collected using a dichotomous sampler (Wedding et al., 1980) and a Micro-Orifice Uniform Deposit Impactor (MOUDI, model 100; MSP Corporation – Marple et al., 1986).".

P.14176,L.15-16: Please provide references which describe the dichotomous sampler and the MOUDI impactor used in the study. If references doesn't exist,

more detailed descriptions of the instrument measurement techniques, as well as their efficiency in collecting particles is necessary.

The reference was added in the text.

P.14176,L.18-19: the expression "after filter" is rather vague and should be replace by a more specific one.

The expression was replaced by "subsequent stage" in the text.

P.14176,L.19: "The collected filters and substrates". It is unclear so far, where filters and substrates are coming from ? Are filters from the MOUDI impactor and substrates from dichotomous sampler ? Such informations should be stated clearly when instruments are described.

A sentence to clarify where filters and substrates come from was added in the text.

"The samples collected with the MOUDI impactor were deposited on a polycarbonate membrane filter with 0.4 µm porous and for the Dichotomous sampler the substrate was a teflon membrane filter with 2 µm porous. The after-filter in the MOUDI impactor is a 33 mm teflon membrane filter, which was not submitted to the reflectance analysis.".

P.14176,L.20-24: To which samples (filters, substrates, both ?) X-ray, gravimetric, reflectance and thermo analysis were applied ? Ion chromatography is applied to material collected "on the membrane filters". Are membrane filters the same as filters mentioned above ? In addition, the analysis techniques should be support with references.

The text was clarified. The filters and membrane filters are related to the same material.

P.14177,L.7-12: The sentence "The WRF-Chem model (Grell et al. 2005) is an online mesoscale meteorological model ...." is incomplete. WRF-Chem is a fully coupled (as mentioned later in the text) online meteorological and chemical transport model and this information should appear first in this section. Then, the WRF acronym should have been define earlier (p. 14176, L. 1).

The sentence was reworded to "The WRF-Chem model is a fully coupled online meteorological and chemical transport model (Grell et al., 2005), supported by…around the world".

P.14178,L.6 and 18-19: "It is parametrized in WRF-Chem..." Such parametrisation is not included in all the WRF-Chem aerosol scheme, thus WRF-Chem should be replace by MADE-SORGAM. The same applies for "The primary organic aerosol (POA) in WRF-Chem...".

The WRF-Chem was replaced by MADE in both statements.

P.14178,L.22-27: In which category would SPMA fit the best ? Low amount of SA formation or area with a significant wood smoke influence ? What would be the expected OM:OC ratio in SPMA ?.

The formation of secondary aerosols in SPMA is very high, and thus, a high OM:OC ratio, probably higher than 1.54, is expected.

P.14179,L.1: Indicate the model version.

The model version was included in the text.

P.14179,L.16-23: This paragraph is inconsistent with Table 4, at least anthropogenic aerosol emissions are not mentioned in the text. Or, does the model feed with dust and sea salt only as primary aerosols ? This paragraph needs to be clarified.

The beginning of the paragraph was reworded to “WRF-Chem simulation with coupled primary aerosol (dust, sea salt and anthropogenic) and gas (biogenic and anthropogenic) emission modules,…”.

P.14179: Model description: The spin-up period used to initiate the model should be given somewhere in this section.

The statement “The first seven days of each simulation were not analyzed and used for model spin-up.” was added in this section.

P.14180,L.3-9: Is the LAPAt model able to differentiate, e.g., light vehicles as basic cars and heavy duty trucks ? The answer to that question should be given in the text in addition to an explanation of how the difference is made or why the model can't differentiate the different vehicles.

Yes, it is. In order to differentiate light and heavy vehicles, the LAPAt model applies the total fleet distribution to the total number of vehicles in each grid point within the domains. The total number of vehicles in each grid point of both domains is calculated from the normalization of the sum of individual intensities at each point (i.e. total road length for the 3 km modelling domain and night-time light for the 15 km modelling domain) by the total fleet, so that emissions in urban areas are mainly represented by emissions coming from their vehicles. A better explanation was added to the text.

P.14180,L.23-28: This paragraph is confusing and needs clarification. “...areas inside both grid cells”, do you mean in both domains ? What are the others metropolitan areas ? How many inhabitants vs SPMA ? Where are they located in the 3 and 15 km domains ? Where does “the number of vehicles in each one of the main urban areas” comes from ?.

Yes, I do. The expression “grid cells” was replaced by “modelling domains” throughout the manuscript. Basically, each grey stain on Fig. 2 (3 km modelling domain) represents an urban area, e.g., the second largest grey stain represents the Campinas Metropolitan Area (CMA). The number of vehicles comes from DENATRAN (see P.14180.L.13-15). There were 3 metropolitan areas in Sao Paulo State until 2012. They were: Metropolitan Area of Sao Paulo (19683975 inhabitants in 2010 Census), Campinas (2797137) and Baixada Santista (1664136). In 2012, the MA of Vale do Paraíba e Litoral Norte was created and, in 2014, the MA of Sorocaba.

P.14181,L.14-17: Does the sentence “Furthermore, due to the complexity... for distributing the emissions during the day in both grid cells.” means that a constant value has been used for vehicle emissions during the day ? If true, why not applying a diurnal cycle as observed in many megacities ?.

No, it doesn’t. We have applied a diurnal cycle at all grid points where emissions have values greater than zero. The calculation of that diurnal cycle follows the approach used by Fast et al. (2006) in which gas and particle emission profiles were calculated from median diurnal variations on weekdays and weekends.

P.14181: anthropogenic emissions section: The authors choose to force the model with vehicle emissions only. However, one would expect the presence of other anthropogenic emissions, e.g., industrial activities, able to impact SOA formation and PM concentrations. Have these emissions been evaluated ? How this lack is addressed in the study ? There is no mention of the emission used for the 75 km domain, please provide this information.

Other anthropogenic emissions have not been considered because this study focuses on the impact of on-road vehicle emissions on the concentration of fine particles. The statement “Anthropogenic emissions were not considered in the 75 km modelling domain.” was added in the text.

P.14182,L.5: Update the MEGAN reference to Guenther et al. (2006)

We used the Guenther scheme (default option) which is based on Guenther et al. (1993; 1994).

P.14182: Other emissions section: No fire emissions are used in this study. However, as visible on online tools (e.g., https://firms.modaps.eosdis.nasa.gov/firemap/), and as claimed in this study (section 3.2 and Fig. 5), important fires occur in Brazil at the period of this study. The validity of the back-trajectory presented in Fig. 5 is discussed further in this

review, but missing fire emissions may induce important bias in the model outputs and thus in this study results.

New back-trajectories were calculated using the suggestion on P.14184,L.21-25. Results suggest that aerosols from either forest fires or biomass burning areas can be advected to SPMA impacting, somehow, on the concentration of aerosol particles over this region.

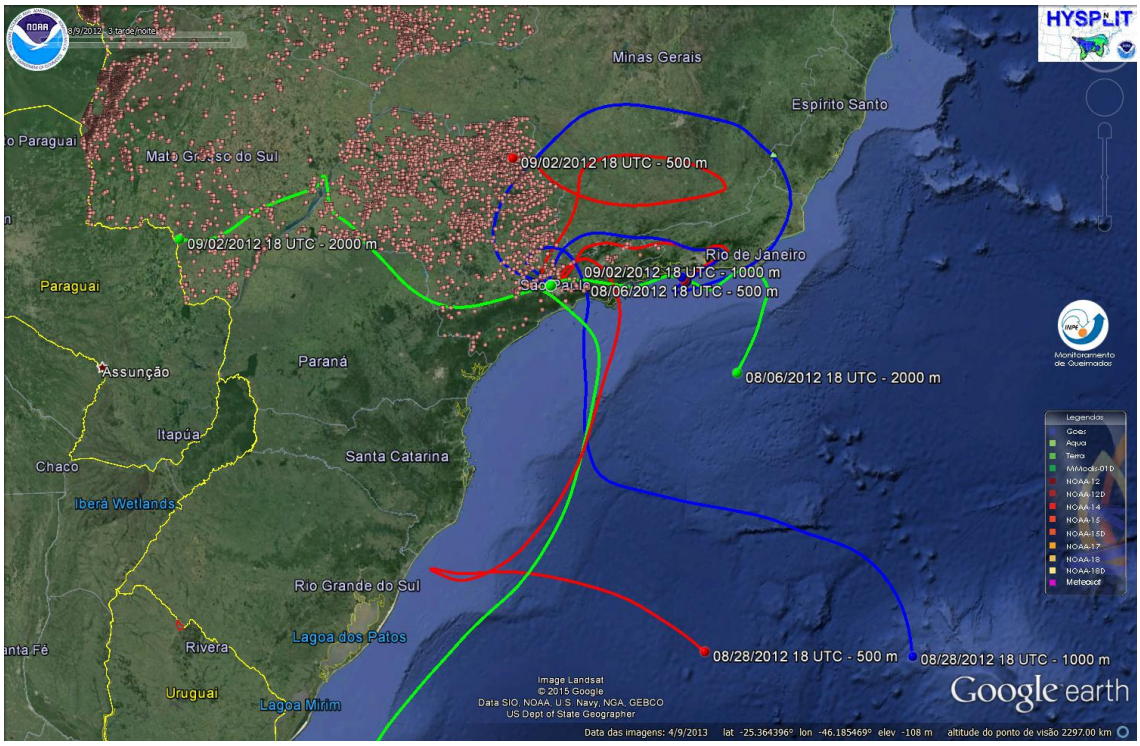

Figure 4. HYSPLIT three-day backward trajectories and locations of fires in Sao Paulo State and part of central-west region of Brazil. Pink markers represent the observed fire locations during the study period considering different satellite products (GOES, AQUA, TERRA, NOAA). The backward trajectories starting at IAG-USP were calculated for the days 9 and 31 August and 5 September 2012 at three different altitudes: 500 m (red lines), 1000 m (blue lines), and 2000 m (green lines).

Results and discussions

P.14183,L.3-6: "According to the climate reports... intensification of the South Atlantic Subtropical high (SASH)". How much observed precipitation rates are lower than climatological values ? A reference is necessary to support the statement that SASH is responsible for precipitation anomalies. Which impact, if any, such precipitation anomalies would have on the study ?

In SPMA, the observed precipitation rate was 38.6 mm lower than the climatological value for that month (August). This information is based on GrEC (2012a). The impact of negatives anomalies, in terms of aerosols, implicates a less efficient removal of particles and gases which are able to form new particles.

P.14183,L.7: "These conditions established an easterly wind anomaly pattern at the 850 hPa level". Where this information comes from ? Which kind of anomaly ?

This information also comes from GrEC (2012a).

P.14183,L.17-19: "Figure 3 shows the accumulated daily precipitations and humidity". It looks like precipitation are not daily accumulated, please check and reword accordingly. In addition, the (relative ?) humidity is presented in Fig. 3 but not discussed in the text.

The statement has been reworded to "Fig. 3 shows the hourly accumulated precipitation and relative humidity observed at the IAG-USP's climatological station".

P.14184,L.1-2: "Part of the unexplainable concentration is related to the water content of aerosols". "remaining mass" should be used instead of "unexplainable concentration". What do you mean by "water content of the aerosols" ? Is the remaining mass water ? Please be more specific and support this assumption with a reference.

Yes, water content of aerosols means the remaining mass water. The expression "unexplainable concentration" was replaced by "remaining mass". A reference was added in the text.

P.14184,L.3-9: "On the other hand... SASH system is moved away from the continent." Why is the semi-stationary front situation not described in section 3.1 ? The main information from this paragraph is that the meteorological situation is the main driver of the PM concentration, how is it compatible with this study ? It is claimed that an aerosol increased could be due to "an increase in relative humidity", however, such increase of relative humidity in not noticeable in the observed relative humidity time series in Fig. 3. Is there another reason which could explain it ?

Another possible reason could be the transport of aerosol particles produced by forest fires in the central-west region of Brazil and the Sao Paulo State (see new Fig. 4).

P.14184,L.9-10: "Aerosols coming from forest fires... during this period." This sentence belongs to the short discussion on forest fires (L. 21-24).

The paragraph (including the statement) was reorganized.

P.14184,L.19: “AQUA_M-T” M-T needs to be defined. More informations on the satellite and the product(s) used to detect fire locations should be provide, as well as references. In Fig. 5 legends, it appears that an other satellite was used (Terra), as well as MODIS and NOAA products.

The statement (including the expression) was removed. The new caption of Fig. 4 (ex Fig. 5) mentions the forest fire products displayed in the legend.

P.14184,L.21-25: “Figure 5 shows... reaching the measurement site.” First a reference to the back-trajectory model, i.e. HYSPLIT, should be given (as requested on the HYSPLIT website). On how many days the back-trajectory has been calculated ? How would be back-trajectories for other peaks ? As mentioned previously, important fires occurred in Brazil during the study period and it is crucial to be sure that fire emissions can be ignored.

The HYSPLIT reference was added in the text. Fig. 4 shows three-day backward trajectories of air masses for the days 9 and 31 August and 5 September 2012, when increases in the OC and EC concentrations were observed at IAG-USP. It is possible to note that some of trajectories have crossed forest fire areas before they come to SPMA, impacting on the concentration of aerosol particles over SPMA.

P.14184,L.26-29: “The increasing organic matter...efficient formation of secondary particles.” The statement on a possible impact of PBL height on a “more efficient formation of secondary particles” must be supported by references. The expression “high vehicular emission events” is unclear and should be reworded.

The increasing organic matter may have two possible explanations. First, it should be noticed that the diurnal cycle of emissions is the same for every day, but sometimes there are traffic incidents which may rise the emissions. These specific incidents were not taken into account in the simulations. Second, if there are no traffic incidents, the increase of aerosol particles is only due to different meteorological scenarios. High-pollution episodes occur when winds are light and the PBL height is low and these meteorological conditions are met under post-frontal anticyclonic influence.

The expression “high vehicular emission events” was replaced by “traffic incidents which may raise the emissions”. Additionally, a reference regarding the aerosol – meteorology relation was added in the text.

P.14185,L.15-16: The correlation coefficient between model results and observations are not very high, especially for temperature. Is the model nudge in the boundary layer with NCEP FNL data ? How the rather low correlation

coefficient would impact the simulation of PBL and pollutant concentrations ? An additional figure showing the T, RH, WS, WD time series would help a lot in understanding where and why the model partly fails in reproducing observations.

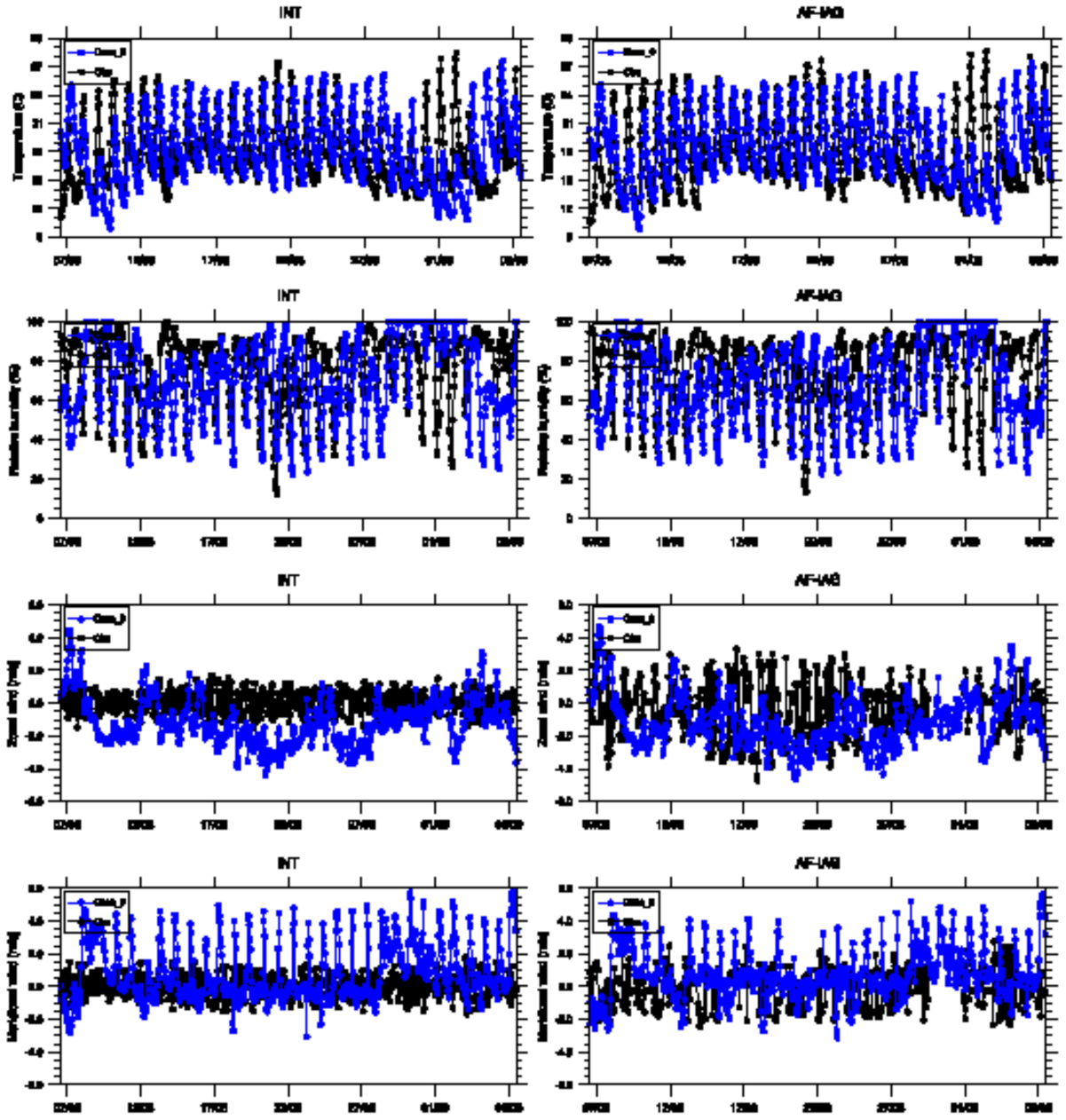

Figure 18. The observed and predicted hourly variations of temperature, relative humidity, and zonal and meridional wind components at INT and AF-IAG for the 3 km modelling domain.

We don't have PBL height observations to compare and evaluate the model performance. Mismatches in temperature and wind may lead to either underestimating or overestimating the PBL height calculation, increasing or decreasing, consequently, the amount of pollutants within this layer.

P.14185,L.17: "temporal variations" is not an appropriate expression to describe average wind and temperature fields. The period on which the fields have been averaged should be given.

The statement was reworded to "Fig. 6 shows the predicted average of wind vectors at 10 m and temperature at 2 m for the whole study period in the 3 km modelling domain".

P.14185,L.19: "(i.e 17.7°C at AF-IAG and 17.8°C at INT)" How does these values compare with observations ?

The values 17.7 and 17.8 °C are the observed average temperatures at AF-IAG and INT, respectively. These values are close to the predicted averages which range between 16 and 17 °C according to Fig. 6.

P.14185,L.20: "the predicted wind direction was easterly in SPMA" this sentence is in contradiction with the sentence p. 14184, L. 25-26 "The predicted average surface wind was predominantly from southeast (see Fig. 6)". Please modify the wrong sentence. How this wind direction compares with observations ?

The wrong statement has been removed.

P.14186,L.2: What is the term "point sources" uses for ? More specific words are expected here.

The term "point sources" was replaced by "industry".

P.14186,L.3-5: "The high concentration of PM2.5, ... establishment of lower PBL heights". There is no higher ozone concentration neither at the beginning or at the end of the study period (as seen in Fig. 9). "reasonably well captured" is vague and certainly don't apply to the PM time series presented in Fig. 7 and 8 where simulation can miss up to 50% of the observed PM concentrations. Why "the emission of high aerosol loadings" and "lower PBL height" would happened ? Emission rates and PBL height are available parameters, emissions because the authors created them and PBL heights because it's a basic output of the model (it can alternatively be calculated with basic meteorological parameters). Why not showing variations of such parameters as a figure to support these statements ?

The paragraph was modified. Traffic incidents may raise the emissions of aerosols

(aerosol loadings) in the atmosphere. Lower PBL heights are commonly observed under post-frontal situations.

P.14186,L.6-7: In relation with the previous comment, the PBL height value given here is not sufficient. To support the reasoning, it should be completed with PBL height of the beginning and ending periods as well as informations on the origin of this value (from the model ? Observations ?).

The paragraph was modified, indicating the predicted average PBL height at the beginning and ending periods. All values of PBL height provided in this study come from model outputs.

P.14186,L.13-18: Figures 11 and 12 are not described nor used as support for discussions. However, high concentration patterns are visible on both figures, between the coast and SPMA and at the west edge of the domain. Are such patterns expected ? What are their origins ?

Aerosol particles between the coast and SPMA are expected to have high concentrations because of the influence of the ocean (sea salt aerosols) in addition to any coastal urban areas like Baixada Santista, whereas at the west edge, this contribution mainly comes from the biogenic emission and forest fires.

P.14186,L.18-20: A high PM2.5/PM10 ratio, meaning that most of the mass is due to particles with diameter smaller than 2.5 µm, would be expected in high vehicular emission areas, why isn't it the case ? Impact of vehicular emissions is the main focus of this study, in that regard discussions should be focusing on it.

From Fig. 13, higher $PM_{2.5}/PM_{10}$ ratios over offshore continental areas may be associated with a more efficient formation of fine particles from oxidation of biogenic VOCs as well as primary emission of biogenic POA, mostly small particles. Furthermore, it should be noticed that there is no other relevant sources of primary aerosols over these areas. Otherwise, at places where there is a high impact of resuspended soil, it is possible to observe that the coarse fraction explains most of the PM_{10} concentrations.

P.14187,L.11-13: **Why only focusing on 16 days instead of the entire simulation period ?**

We have focused only on the days for which there are measurements of aerosol mass size distribution.

P.14187,L.22: “around 55 and 40%” please remove around and give the exact values.

The statement was reworded to "...mass with contributions of 55 and 40%, respectively".

P.14188,L.5: Rename the section as "Contribution of dust and sea salt to PM concentration" or approaching since this is more relevant to describe the actual content of the section.

The section was renamed to "Contribution of dust-sea salt and coarse anthropogenic aerosols to PM concentration".

P.14188,L.8-9: "The simulated average ratio...concentration is shown in Fig. 17b." This sentence is redundant with the previous one. On which period the average is calculated ?

The second statement was reworded to "The simulated average ratio between dust–sea salt aerosols and the total PM_{10} mass concentration is shown in Fig. 17b.". The average is calculated for the whole study period.

P.14188,L.15: How can forest fires be involved in emissions if they are not provided as input ?

Although forest fires are not directly involved in the emission, it's important to indicate that MOZART's gas and particle background concentrations used as initial and boundary chemical conditions in the simulations were previously calculated using a biomass burning emission global inventory (FINNv1).

P.14188,L.18-24: this paragraph has no connexion with the purpose of the section, it should be move elsewhere, or the section should be renamed.

The section was renamed to "Contribution of dust-sea salt and coarse anthropogenic aerosols to PM concentration".

P.14189,L.7-8: "But for the SPMA, the importance of SOA... transport sector was noted." A reference is needed to support that statement.

The reference was added in the text.

P.14190,L.2-6: Since it's the focus of the study, OC time series in Fig. 14 should be discussed in this paragraph.

A statement discussing OC and EC concentration peaks was added in the text.

P.14190,L.17-19: Is it an average or at a given time (16:00 LT) ?

It's an average for a given time, in this case 16:00 h (local time).

P.14190,L.22-24: How aerosols impact ozone formation in the SPMA morning ? How does it compares to Li et al. (2011a) ?

According to model results, in downtown SPMA, aerosols have a less expressive impact

on ozone photochemistry during the morning (~-1%), but can impact positively in other SPMA regions range between -1 – +1 %.

P.14191,L.5-7: There is no link between shortwave and longwave radiation, this sentence should be removed.

Even though there is no link between shortwave and longwave radiation, this statement reinforces the fact that inclusion or neglect of the direct effect of aerosol particles can impact the predicted downward longwave radiation, impacting consequently on the predicted surface temperature.

P.14191,L.11-16: Results from this study should be compared to these from the references given, otherwise, if references are given to acknowledge previous work, they belong to the introduction section.

The paragraph "The impact of the fine particles has been discussed in previous works, with evaluation of the scattering and absorbing effects of the aerosol (e.g. Li et al., 2005; Real et al., 2011). Vehicular emissions of particulate matter (PM) in the SPMA have a high percentage of BC (Brito et al., 2013), which after emitted to the atmosphere can enhance the absorption coefficient and thus the attenuation rates" was moved to introduction section.

Summary and conclusions

P.14191,L.27: Ozone concentrations are not lower than observations, at least, this is not obvious on Fig. 9. This statement should be reinforced with numbers or modified adequately.

As mentioned in the section 3.3, mean biases for $PM_{2.5}$, PM_{10} and O_3 concentrations were -8.84 μg m^{-3}, -14.13 μg m^{-3} and -0.85 ppb, respectively (see Table 5). So, the paragraph was reworded to "However, the predicted concentrations of $PM_{2.5}$, PM_{10} and O_3 (but in minor intensity) were lower than observed values.".

P.14192,L.10-12: The 2% might be higher when looking at the morning values ? The afternoon context should anyway be given in the text.

The statement was reworded to "...O_3 concentration by around 2% in the afternoon (16:00 h; local time) when the aerosol-radiation feedback..."

Tables and figures

Table 5: define UB (in "RMSE_UB")

$RMSE_{UB}$ is the RMSE after a constant bias is removed. The Appendix A describes all the statistics used in this work to assess the model skill.

Figure 1: Is topography from the model ? Add the information in the caption.

Replace “with information of ...” by “with information on ...” twice in the caption.

The caption was reworded to “Downtown area of the 3 km modelling domain (d03) showing the locations of measurement sites and WRF topography in the vicinity of SPMA. Red dots represent sites with information on O_3 and PM. Yellow dots represent only sites with information on PM. Blue dot represents the location of the IAG-USP's climatological station.”.

Figure 2: Is this figure for a week day or a week-end day ?

In our emission model, the emissions have the same diurnal cycle for every day, which was calculated from median diurnal variations on weekdays and weekends.

Figure 3: This doesn't seem to be daily precipitation data, please check and modify the caption accordingly.

The caption was reworded to “Hourly accumulated precipitation and relative humidity observed at the IAG-USP's climatological station during the study period.”.

Figure 4: The meaning of the 6 panels should be describe in the caption. The 4 bottom panels are not discussed within the text. Remove “some” or replace it by the list of aerosol constituents.

The figure 4 in the earlier version of the manuscript is the figure 5 now. The caption of this figure was reworded to “Daily (top), diurnal (bottom), and nocturnal (middle) mean concentrations for EC, OC, PM_{10}, $PM_{2.5-10}$, $PM_{2.5}$ (left panels), and Na, Fe_2SO_3, SiO_2, K_2O, and S (right panels). The $PM_{2.5-10}$ aerosol variable is defined as particulate matter with aerodynamic diameter between 2.5 and 10 μm. The grey line indicates the WHO air quality standard for $PM_{2.5}$ (25 $\mu g/m^3$).”.

Figure 5: Mention the sources of fire back-trajectory data.

The figure 5 in the earlier version of the manuscript is the figure 4 now. The caption of this figure was reworded to “HYSPLIT three-day backward trajectories and locations of fires in the Sao Paulo State and part of central-west region of Brazil. Pink markers represent the observed fires locations during the study period considering different satellite products (GOES, AQUA, TERRA, NOAA). The backward trajectories starting at IAG-USP were calculated for the days 9 and 31 August and 5 September 2012 at three different altitudes: 500 m (red lines), 1000 m (blue lines), and 2000 m (green lines).”.

Figure 6: Mention the period on which data are averaged. This not surface temperature and wind but 2 m temperature and 10 m wind speed and direction, please modify the caption accordingly.

The caption was reworded to “The predicted average of wind vectors at 10 m and temperature at 2 m from the baseline simulation (Case_0) for the whole study period in the 3 km modelling domain. Blue dots represent the locations of the measurement sites, whereas cyan numbers represent the observed average temperature in those sites: 17.7 ^{o}C in AF-IAG and 17.8 ^{o}C in INT.”.

Figure 9: This is obviously not daily data, please modify the text accordingly.

The caption was reworded to “The observed and predicted hourly variations of O_3 concentrations at six sites in SPMA for the 3 km modelling domain.”.

Figure 10: A reference to the Taylor (2001) paper should be given, either here or in the text.

The reference was added in the text.

Figure 11-12-13: Mention the period on which the data are averaged.

The captions were reworded to “The predicted average surface distribution of $PM_{2.5}$ concentrations for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on $PM_{2.5}$, whereas cyan numbers represent the observed average $PM_{2.5}$ concentration in those sites: 23.4 µg m^{-3} in IPEN-USP, 21.3 µg m^{-3} in IAG-USP, and 22.2 µg m^{-3} in CON.”, “The predicted average surface distribution of PM_{10} concentrations for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on PM_{10}, whereas cyan numbers represent the observed average PM_{10} concentration in those sites: 49.5 µg m^{-3} in IAG-USP and 38.7 µg m^{-3} in CON.”, and “The predicted average surface distribution of the $PM_{2.5}/PM_{10}$ ratio for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on both $PM_{2.5}$ and PM_{10}, whereas cyan numbers represent the observed average $PM_{2.5}$:PM_{10} ratio in those sites: 0.43 in IAG-USP and 0.57 in CON.” for the figures 11, 12, and 13, respectively.

Figure 15: Mention in the caption that no model data are available for > 1µm, as well as the intruments used to measure the concentrations.

The caption was reworded to “The observed and predicted average aerosol mass size distribution for SO_4, NO_3, NH_4, Na, Cl, and other PM_{10} constituents at IAG-USP. The observed aerosol distributions were collected in ten size classes using a rotated impactor (MOUDI) and joined adequately according to the three modes used by the MADE aerosol scheme: Aitken (<0.1 µm), accumulation (0.1–1 µm) and coarse (>1 µm). The five inorganic ions carried in MADE are only calculated for the Aitken and

accumulation modes. The WRF's PM_{10} aerosol variable does not include neither OC nor EC for this comparison.”.

Technical comments

Introduction

P.14174,L.10: Corrected.

P.14174,L.11: Corrected.

P.14174,L.12: Corrected.

P.14175,L.14: Corrected.

P.14176,L.1: The acronym was defined in the text: “...the Weather Research and Forecasting with Chemistry (WRF-Chem) model...”.

Methodology

P.14176,L.9: Corrected.

P.14176,L.13: Corrected.

P.14176,L.16: Corrected.

P.14177,L.13-14: Corrected.

P.14178,L.23: SD (Standard Deviation)

P.14179,L.11: Corrected.

P.14179,L.12: Corrected.

P.14179,L.12: The acronym was added in the text: “...the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4; Emmons et al., 2010)”.

P.14180,L.28: Corrected.

P.14181,L.11: Corrected.

P.14181,L.26: Corrected.

P.14181,L.26: Corrected.

P.14182,L.16: Corrected.

Results

P.14182,L.25: Corrected.

P.14183,L.4: Corrected.

P.14183,L.7: Corrected.

P.14183,L.8: “comes” was replaced by “coming”

P.14183,L.9: Corrected.

P.14183,L.11: “western State” was replaced by “western Sao Paulo State”.

P.14183,L.11-12: “Precipitation areas” has been replaced by “Precipitation events”.

P.14183,L.12: Corrected.

P.14184,L.16: Corrected.

P.14184,L.25: The sentence has been removed.

P.14185,L.12: Corrected.

P.14185,L.13: Corrected.

P.14185,L.21: Corrected.

P.14187,L.6: Corrected.

P.14187-14188,L.29-1: Yes, it means. The sentence has been reworded to "...Tuccella et al. (2012) found simulated SOA:OM ratios in the 5-40% range against the observed range of 50-80%...".

P.14188,L.13: Corrected.

P.14189,L.2: Corrected.

P.14189,L.16: Corrected.

P.14190,L.14: Corrected.

P.14190,L.18-19: Corrected.

P.14190,L.19-20: Corrected.

P.14191,L.1: Corrected.

P.14191,L.9-11: The statement was reworded to "...ground level O_3 concentrations in a few ppb.".

P.14191,L.15: Corrected.

Summary and conclusions

P.14192,L.8: Corrected.

P.14192,L.8: Corrected.

Anonymous Referee #2

Comments

1) The introduction should be extended with more background in general regarding traffic and its impacts on aerosol levels and the radiative impacts of the aerosols on photochemistry. The motivation and the aim of the study should be more clear and can be organized in a paragraph rather than scattering throughout the introduction section.

The introduction was modified including two paragraphs describing the general context of emissions and their impacts on air quality in SPMA.

"The Sao Paulo Metropolitan Area (SPMA), in the southeast region of Brazil, is considered a megalopolis comprised of Sao Paulo city and more 38 municipalities. One

of the main concern in the SPMA is the occurrence of violations of air quality standards for ozone and fine particles at different air quality stations from the Sao Paulo Environmental Agency (CETESB). The air pollutant emissions in the SPMA are related to the burning of the fossil fuels: ethanol, gasohol (gasoline with 25% ethanol) and diesel. Recent work of Carvalho et al. (2014) reported a substantial increase in number of road vehicles from 1 million in 2000 to almost 7 million in 2014, together with an overwiev of the pollutants concentration, fuel use in the SPMA and the relationship between the emissions and the improvement in the air quality in past years.

They constitute the main cause of impairment to air quality in the SPMA, but the number of air quality standard violations has decreased for almost all pollutants with the exception of $PM_{2.5}$ and O_3. Both these pollutants are impacted by the vehicular emissions and have experienced an increase in the number of violations of local air quality standards as discussed in detail by Carvalho et al. (2014). Pérez-Martínez et al. (2015) have analyzed the monthly mean values for the regulated pollutants from 2000 to 2013 for the air quality stations in the SPMA. They found a decrease in the average concentration of NOx, CO and PM_{10} by 0.65, 0.37 and 0.71 % $month^{-1}$, respectively, although the sales of the fuels (gasoline, ethanol, and diesel) had increased by 0.26, 1.96 and 0.38 % $month^{-1}$, respectively".

2) Omission of anthropogenic emissions other than the traffic sources should be mentioned clear in the Emissions section. Additionally, the anthropogenic emissions used in the coarser domains should be described clearly.

Anthropogenic emissions of trace gases and particles in both 3 and 15 km modelling domains were considered to include emissions only coming from on-road vehicles through the use of a vehicular emission model developed by the IAG-USP's Laboratory of Atmospheric Processes (LAPAt). Anthropogenic emissions were not considered in the 75 km modelling domain.

3) As the on-road vehicular emissions are emitting on the surface, a vertical distribution is not necessary. However, the authors should explain if they have used any vertical distribution for the emissions in the coarser domains. The impact of these missing sources on the model results and related discussions on the impact of traffic on air quality levels should be discussed.

There was no vertical distribution for emissions in all domains, since only on-road vehicles emissions is considered. A vertical distribution would be important for industrial sources and biomass burning. This last source is somewhat regarded due to

the boundary conditions. Inside the urban area, the vehicular source is the most important one, but in rural areas upwind urban regions, these missing sources would result in lower air pollutant concentrations.

4) What are the spatial and temporal resolutions of the boundary conditions?.

The initial and boundary meteorological conditions are from the National Center for Environmental Prediction's Final Operational Global Analysis with 1º of grid spacing, 26 vertical levels and are available every six hours: 00, 06, 12 and 18 UTC (http://rda.ucar.edu/datasets/ds083.2/). The chemical initial and boundary conditions are from MOZART at a horizontal resolution of 1.9ºx2.5º, 56 vertical levels and are also available every six hours.

5) The HYSPLIT configuration should be described in the methodology section with a reference to the model.

The HYSPLIT configuration and reference were added in the text.

6) Section 3.1: While it is true that the behavior of the main meteorological systems should be analyzed in order to understand the spatial and temporal variability of aerosols, the authors lack to discuss how these conditions would affect the levels. As the measurements would have a temporal variability, the authors could compare the measurements with the meteorology to show how meteorology (e.g. precipitation) can influence aerosol levels.

The Figure 18 (page 11) shows comparisons between measurements and WRF outputs for temperature, relative humidity, and zonal and meridional wind components at INT and AF-IAG measurement sites. In general, both wind components were overestimated on intensity, what may have led to a dilution of aerosol particles in SPMA.

7) Section 3.2: Page 14, line 28: As the WRF model calculates wind speeds and PBL height, it would be straightforward to show if low PBL heights or wind speeds caused the high levels of PM.

The model results show that overall the predicted PBL heights have a regular diurnal variation in the downtown SPMA with averaged daily values around 500 m at both the beginning and the end of the study period, when higher concentrations of aerosols were observed, whereas values of up to 700 m in the middle of the study period, when lower concentrations of aerosols were observed. In addition, aerosol particles transported from other regions (e.g. biomass burning areas; see Fig. 4) may have led to an increase of aerosol concentrations in SPMA.

8) As the statistics are made for all the sites, can the authors also comment on how

the model performance differs among individual stations? For example correlation coefficients and Normalized mean biases (NMB) can be shown for each station in Figures 7-9.

Individual statistics are shown in Fig. 10. In general, most of evaluated WRF-Chem parameters present good correlation coefficients (mainly those for PM_{10}), but with negative biases (except for O_3 at NSO and PDP) and standard deviations lower than those for observations.

9) Section 3.3: It would be good to see more discussion on Figure 15 as I think it is an important figure showing the size distribution capability of the model for the different aerosol species. For instance, while the model underestimates SO4, it over estimates NO3 and NH4, meaning that the model simulates more NH4NO3 aerosols compared to (NH4)2SO4 aerosols. Correlation coefficients of observed and simulated NH4 and SO4 levels can give important information on why the model behaves as such (see for example Im et al., AtmEnv, 2012 and references therein).

Correlation coefficients for both chemical species show a good WRF-Chem simulation performance, especially for SO4.

Abstract

Line 9: Remove "during a month,"

The expression was removed.

Lines 21-27: I would move this part to line 9, before the sentence starting with "The study period. . ."

The statement was adequately relocated.

Introduction

Page 5, Line 16: Add a reference for the increase in PM2.5 and O3.

The reference was added in the text.

Section 2.1: More detail (urban/traffic/background etc. . .) is needed for the characterization of the sampling site in the NUANCE_SPS project.

The following sentence "All these samplings were performed on the roof of the main building of the Institute of Astronomy, Geophysics and Atmospheric Sciences of the University of Sao Paulo (IAG-USP) (hereafter also referred as IAG-USP measurement site or simply IAG-USP), which is inside a small green-park (approximately 7.4 km^2), with local traffic during the day and surrounded by major roads with intense traffic by light and heavy-duty vehicles (Nogueira et al., 2014)." was added in the text.

Section 3.1:

Page 13, Line 4: Change “lesser” to “lower”.

Corrected.

Page 13, Line 8: Change “comes” to “coming”.

Corrected.

Section 3.2:

Figure 4: The figure caption of Figure 4 should be more explanatory.

The caption was reworded to “Daily (top), diurnal (bottom), and nocturnal (middle) mean concentrations for EC, OC, PM_{10}, $PM_{2.5-10}$, $PM_{2.5}$ (left panels), and Na, Fe_2SO_3, SiO_2, K_2O, and S (right panels). The $PM_{2.5-10}$ aerosol variable is defined as particulate matter with aerodynamic diameter between 2.5 and 10 µm. The grey line indicates the WHO air quality standard for $PM_{2.5}$ (25 µg/m^3).”.

Figure 10: The figure caption of Figure 10 should be more explanatory, showing that these statistics are for the individual 11 stations for example.

The caption was reworded to “Taylor diagram showing the individual correlation coefficients, biases, and normalized standard deviations for the $PM_{2.5}$, PM_{10}, and O_3 concentrations.”.

Figures 11-13: The figure caption of Figure 11-13 should explain what red dots and cyan numbers are although they are described in the text. This comment goes for all relevant figures in the manuscript.

The captions were reworded to “The predicted average surface distribution of $PM_{2.5}$ concentrations for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on $PM_{2.5}$, whereas cyan numbers represent the observed average $PM_{2.5}$ concentration in those sites: 23.4 µg m^{-3} in IPEN-USP, 21.3 µg m^{-3} in IAG-USP, and 22.2 µg m^{-3} in CON.”, “The predicted average surface distribution of PM_{10} concentrations for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on PM_{10}, whereas cyan numbers represent the observed average PM_{10} concentration in those sites: 49.5 µg m^{-3} in IAG-USP and 38.7 µg m^{-3} in CON.”, and “The predicted average surface distribution of the $PM_{2.5}/PM_{10}$ ratio for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on both $PM_{2.5}$ and PM_{10}, whereas cyan numbers represent the observed average $PM_{2.5}$:PM_{10} ratio in those sites: 0.43 in IAG-USP and 0.57 in CON.” for the figures 11, 12, and 13, respectively.

Section 3.5:

Page 20, Line 2: Change to “. . .and measurements at IAG-USP shown in Figure 14 include the Case_1 simulation.

Corrected.

Impact of vehicular emissions on the formation of fine particles in the Sao Paulo Metropolitan Area: A numerical study with the WRF-Chem model

Angel Vara-Vela[1], M. F. Andrade[1], Prashant Kumar[2,3], R. Y. Ynoue[1], and A. G. Muñoz[4,5]

[1]Department of Atmospheric Sciences, Institute of Astronomy, Geophysics and Atmospheric Sciences, University of Sao Paulo, Sao Paulo, Brazil

[2]Department of Civil and Environmental Engineering, Faculty of Engineering and Physical Sciences (FEPS), University of Surrey, Guilford GU2 7XH, United Kingdom

[3]Environmental Flow (EnFlo) Research Centre, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford GU2 7XH, United Kingdom

[4]International Research Institute for Climate and Society (IRI), The Earth Institute, Columbia University, NY, USA

[5]Centro de Modelado Científico (CMC), Universidad del Zulia, Maracaibo, Venezuela

Corresponding author: A. V. Vela (angel.vela@iag.usp.br)

Abstract

The objective of this work is to evaluate the impact of vehicular emissions on the formation of fine particles ($PM_{2.5}$; ≤2.5 μm in diameter) in the Sao Paulo Metropolitan Area (SPMA) in Brazil, where ethanol is used intensively as a fuel in road vehicles. The Weather Research and Forecasting with Chemistry (WRF-Chem) model, which simulates feedbacks between meteorological variables and chemical species, is used as photochemical modelling tool to describe the physico-chemical processes leading to

[1] Comentário: The phrase was moved to the beginning of the abstract (comment P.14173,L.23-24 from Referee#1)

evolution of number and mass size distribution of particles through gas-to-particle conversion. A vehicular emission model based on statistical information of vehicular activity is applied to simulate vehicular emissions over the studied area. The simulation has been performed for a one month period (7 August - 6 September 2012) to cover the availability of experimental data from the NUANCE-SPS (Narrowing the Uncertainties on Aerosol and Climate Changes in Sao Paulo State) project that aims to characterize emissions of atmospheric aerosols in the SPMA. The availability of experimental measurements of atmospheric aerosols and the application of the WRF-Chem model made it possible to represent some of the most important properties of fine particles in the SPMA such as the mass size distribution and chemical composition, besides allowing us to evaluate its formation potential through the gas-to-particle conversion processes. Results show that the emission of primary gases, mostly from vehicles, led to a production of secondary particles between 20 and 30 % in relation to the total mass concentration of $PM_{2.5}$ in the downtown SPMA. Each of $PM_{2.5}$ and primary natural aerosol (dust and sea salt) contributed with 40-50% of the total PM_{10} (i.e. those $\leq$10 μm in diameter) concentration. Over 40% of the formation of fine particles, by mass, was due to the emission of hydrocarbons, mainly aromatics. Furthermore, an increase in the number of small particles impaired the ultraviolet radiation and induced a decrease in ozone formation. The ground level O_3 concentration decreased by about 2% when the aerosol-radiation feedback is taken into account.

[2] Comentário: The phrase was reworded (comment P.14173,L.9-10 from Referee#1)

[3] Comentário: The statement was adequately relocated (comment "Abstract-Lines21-27" from Referee#2)

[4] Comentário: The statement was reworded (comment P.14173,L.13-16 from Referee#1)

[5] Comentário: The statement was reworded (comment P.14173,L.16-17 from Referee#1)

1. Introduction

The Sao Paulo Metropolitan Area (SPMA), in the southeast region of Brazil, is considered a megalopolis comprised of Sao Paulo city and more 38 municipalities. One of the main concern in the SPMA is the occurrence of violations of air quality standards

for ozone and fine particles at different air quality stations from the Sao Paulo Environmental Agency (CETESB). The air pollutant emissions in the SPMA are related to the burning of the fuels: ethanol, gasohol (gasoline with 25% ethanol) and diesel. Recent work of Carvalho et al. (2014) reported a substantial increase in number of road vehicles from 1 million in 2000 to almost 7 million in 2014, together with an overview of the pollutants concentration, fuel use in the SPMA and the relationship between the emissions and the improvement in the air quality in past years.

They constitute the main cause of impairment to air quality in the SPMA, but the number of air quality standard violations has decreased for almost all pollutants with the exception of $PM_{2.5}$ and O_3. Both these pollutants are impacted by the vehicular emissions and have experienced an increase in the number of violations of local air quality standards as discussed in detail by Carvalho et al. (2014). Pérez-Martínez et al. (2015) have analyzed the monthly mean values for the regulated pollutants from 2000 to 2013 for the air quality stations in the SPMA. They found a decrease in the average concentration of NOx, CO and PM_{10} by 0.65, 0.37 and 0.71 % $month^{-1}$, respectively, although the sales of the fuels (gasoline, ethanol, and diesel) had increased by 0.26, 1.96 and 0.38 % $month^{-1}$, respectively.

A recent report from CETESB (CETESB, 2013) highlighted that, in 2012, the vehicles contributed with about 40% of the total PM_{10} mass concentrations through direct emissions. If we consider the secondary aerosols, which were about 25% of PM_{10} as estimated by CETESB (2013), these were mainly found to be formed by chemical reactions between gases released from exhaust of vehicles.

The implementation of the Program for the Control of Vehicular Emission (PROCONVE) established by the Brazilian Government in the 80's, enforcing measures such as use of catalytic converters and ethanol as additive to gasoline in substitution of

[6] Comentário: The paragraph was added in the text (comments P.14174,L.1 from Referee#1 and Comment(1) from Referee#2)

[7] Comentário: The paragraph was added to support the comment P.14174,L.8-26 from Referee#1 and also the comments P.14174,L.1 from Referee#1 and Comment(1) from Referee#2)

[8] Comentário: Reference to support the comment "Introduction-Page5-Line16" from Referee#2

[9] Comentário: The paragraph was added to support the comments P.14174,L.1 and P.14174,L.8-26 from Referee#1 and Comment(1) from Referee#2

tetraethyllead, led to decrease in emissions of CO and VOCs and hence their ambient concentration. Although the emissions have been controlled by regulations, the number of vehicles has increased substantially and faster than the replacement of the old vehicles by the new ones (Pérez-Martínez et al., 2014). According to CETESB (2013), the road vehicles contributed up to about 97, 87 and 80% of CO, VOCs and NOx emissions in 2012, respectively.

To date, many studies assessing the impact of biofuels on the air quality have been performed in Brazil. For example, Anderson (2009) conducted a review concerning the use of ethanol fuel in Brazil. His work highlighted that the atmospheric concentrations of acetaldehyde and ethanol are much higher in Brazil in comparison with the other areas of the world. Costa and Sodré (2010) showed that exhaust emissions of hydrous ethanol reduced CO and Hydrocarbons (HC), but increased CO_2 and NOx levels.

[10] Comentário: The paragraph was added in the text (comment P.14174,L.15-18 from Referee#1)

A number of past studies has shown the significant participation of the carbonaceous compounds in the concentration of fine particles in the SPMA (Albuquerque et al., 2011; Miranda and Andrade, 2005; Ynoue and Andrade, 2004; Castanho and Artaxo, 2001). Studies conducted on ambient air pollution in the SPMA have also shown that black carbon (BC) explains 21% of mass concentrations of fine particles ($PM_{2.5}$; ≤2.5 μm in diameter) compared with 40% of organic carbon (OC), 20% of sulfates, and 12% of soil dust (Andrade et al., 2012). Most of the observed ambient $PM_{2.5}$ mass concentration usually originates from precursors gases such as sulphur dioxide (SO_2), ammonia (NH_3), nitrogen oxides (NOx) and volatile organic compounds (VOCs) as well as through the physico-chemical processes such as the oxidation of low volatile hydrocarbons noted above transferring to the condensed phase (McMurry et al., 2004; Heal et al., 2012). Since these processes are often photo-

chemically driven, the resultant aerosol usually falls into the category of secondary photochemical pollutant (Jenkin and Clemitshaw, 2000). Oxidation of VOCs can produce species of sufficiently low vapor pressure to be condensable, leading to the formation of secondary organic aerosol (SOA) (Kroll and Seinfeld, 2008). Fine particles in SPMA have a great participation on its composition of SOA, formed from the emissions of VOCs, which have the same origin of the primary compounds involved in the formation of ozone, from the burning of fuels. The participation of the biogenic emission is considered to be small in the formation of particles in the metropolitan area of the city according to previous studies of Martins et al. (2006).

The impact of the fine particles has been discussed in previous works, with evaluation of the scattering and absorbing effects of the aerosol (e.g. Li et al., 2005; Real et al., 2011). Vehicular emissions of particulate matter (PM) in the SPMA have a high percentage of BC (Brito et al., 2013), which after emitted to the atmosphere can enhance the absorption coefficient and thus the attenuation rates.

One of the most important aspects of this work is the quantitative analysis of the formation of $PM_{2.5}$ and ozone (O_3) in the SPMA. Photolysis of O_3 by ultraviolet light in the presence of water vapor is the main source of hydroxyl radical (OH), the most important radical in the atmosphere in terms of reactivity (Monks, 2004). At the same time, OH levels in the atmosphere directly determine the oxidation rate of the precursors of secondary aerosols. Oxidation products of VOCs and semi-VOCs by OH are the most important precursors of SOA (Li et al., 2011a). Although VOCs and NOx are precursors of both O_3 and a fraction of atmospheric PM (NO_3^- and secondary organics) while they influence indirectly the formation of the rest of the secondary PM components like $SO_4^=$, their control strategies that are optimal for O_3 controls may even increase $PM_{2.5}$ concentrations (McMurry et al., 2004). Such an analysis is important to

[11] Comentário: The paragraph was moved to introduction section (comment P.14191,L.11-16 from Referee#1)

[12] Comentário: The paragraph was added in the text (comment P.14175,L.14-15 from Referee#1)

evaluate the contribution of the vehicular fleet using different kind of fuels to the concentration of fine particles. In this sense, a numerical study with an adequate physical approach, representing particles in the modelling system, is important to understand the formation of secondary aerosols from primary emission of gases in a metropolitan area where the composition of fuel in vehicular fleet has changed significantly over the past years. Therefore, the goal of the present study is to evaluate the impact of vehicular emissions on the formation of fine particles in the SPMA, focusing especially on the potential formation of secondary particles from the primary emission of gases coming from on-road vehicles. The impact of aerosol particles on the ozone photochemistry is also examined by means of numerical simulations. Measurements were performed to provide input data to evaluate the modelling performance and estimate the vehicular emission factors. Aerosol measurements were taken from field campaigns that were carried out as part of the Narrowing the Uncertainties on Aerosol and Climate Changes in Sao Paulo State (NUANCE-SPS) project (http://nuance-lapat.iag.usp.br/). These campaigns took place between July and September 2012. An online-coupled meteorology and chemistry model, i.e., the Weather Research and Forecasting with Chemistry (WRF-Chem) model, has been used to characterize and describe the physico-chemical processes involved in both the formation and growth of new particles over the SPMA in southern Brazil. The details of the experimental campaigns, WRF-Chem model and emissions are described in Section 2. Results from modelling experiments and comparison with measurements are presented in Section 3. Finally, the summary and conclusions are given in Section 4.

[13] Comentário: NUANCE-SPS reference (comment P.14175,L.26-29 from Referee#1)

[14] Comentário: Full form + acronym (comment "Technical-comments-P.14176,L.1" from Referee#1)

2. Methodology

2.1. Observational datasets

The study period starting from 7 August until 6 September 2012 was selected for comparison with the modelled results (Section 2.2) due to the availability of experimental data from the NUANCE-SPS project. The aim of NUANCE-SPS was to evaluate the impact of emissions in the SPMA on the air quality and changing climatic conditions, and feedback mechanisms between climatic perturbations produced by both primary and secondary emissions and urban atmospheric processes. Aerosol observation datasets used in this work were collected using a Dichotomous sampler (Wedding et al., 1980) and a Micro-Orifice Uniform Deposit Impactor (MOUDI, model 100; MSP Corporation - Marple et al., 1986). The MOUDI impactor collected particles in 10 size classes with nominal 50% cut-off diameters: 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.06 µm. Particles smaller than 0.06 µm were collected in a subsequent stage or after-filter. The samples collected with the MOUDI impactor were deposited on a polycarbonate membrane filter with 0.4 µm porous and for the Dichotomous sampler the substrate was a teflon membrane filter with 2 µm porous. The after-filter in the MOUDI impactor is a 33 mm teflon membrane filter, which was not submitted to the reflectance analysis. The collected membrane filters sampled with the Dichotomous and MOUDI samplers were analyzed to the identification of trace elements of mass through X-ray diffraction analysis, mass concentration through gravimetric analysis, and black and organic carbon through reflectance and thermo analysis using a thermal-optical transmittance (TOT) (Sunset Laboratory Inc. – Birch and Cary, 1996). Ion concentrations were evaluated through the ion chromatography analysis of the soluble material collected on the membrane filters (sulphate, nitrate, ammonium, sodium, and chloride). All these samplings were performed on the roof of the main building of the Institute of Astronomy, Geophysics and Atmospheric Sciences of the University of Sao Paulo (IAG-USP) (hereafter also referred as IAG-USP measurement site or simply

[15] Comentário: The statement was reworded (comments P.14176,L.14-15 and P.14176,L.15-16 from Referee#1)

[16] Comentário: The statement was reworded (comment P.14176,L.18-19 from Referee#1)

[17] Comentário: The paragraph was added in the section to support the comment P.14176,L.19 from Referee#1

[18] Comentário: The paragraph was reworded (comment P.14176,L.20-24 from Referee#1)

IAG-USP), which is inside a small green-park (approximately 7.4 km^2), with local traffic during the day and surrounded by major roads with intense traffic by light and heavy-duty vehicles (Nogueira et al., 2014). Table 1 lists the aerosol instrumentation deployed roughly at the IAG-USP measurement site. In addition, ambient data from the CETESB's air quality monitoring network and the IAG-USP's climatological station (hereafter also referred as AF-IAG) were also considered for evaluation of numerical simulations. The locations of measurement sites are depicted in Fig. 1 whereas geographic coordinates and the list of pollutants and meteorological parameters monitored at each site is available in Table 2.

[19] Comentário: The paragraph was reworded (comment Introduction-Section2.1 from Referee#2)

2.2. WRF-Chem model

The WRF-Chem model is a fully coupled online meteorological and chemical transport model (Grell et al., 2005), supported by National Center for Atmospheric Research (NCAR) of the USA and several other research institutions around the world. This model is a system of two key components. The WRF-Chem meteorological component, the Weather Research and Forecasting (WRF), is a system configured for both research and operational applications. The dynamical core used in this study is the Advanced Research WRF (ARW). Model's equations into ARW are solved to non-hydrostatic conditions on a fully compressible atmosphere. Further details on the modelling system can be found on the WRF model website (http://www.wrf-model.org). On the other hand, the WRF-Chem chemical component treats chemical processes such as dry deposition, gas-phase chemistry, photolysis rates, and aerosols chemistry. A detailed description of the WRF-Chem model can be found on its website (http://ruc.noaa.gov/wrf/WG11). Since both meteorological and chemical components are fully coupled, the transport of all chemical species is on-line. The gas-phase

[20] Comentário: The statement was reworded as suggested by the Referee#1 (comment P.14177,L.7-12)

chemistry and aerosol modules employed in this study are the Regional Acid Deposition Model, version 2 (RADM2) (Chang et al., 1989) and the Modal Aerosol Dynamics Model for Europe - Secondary Organic Aerosol Model (MADE - SORGAM) (Ackermann et al., 1998; Schell et al., 2001), respectively. The inorganic species included in the RADM2 mechanism are 14 stable species, 4 reactive intermediates, and 3 abundant stable species (oxygen, nitrogen and water). Atmospheric organic chemistry is represented by 26 stable species and 16 peroxy radicals. The RADM2 mechanism represents organic chemistry through a reactivity aggregated molecular approach (Middleton et al., 1990). Similar organic compounds are grouped together in a limited number of model groups through the use of reactivity weighting. The aggregation factors for the most emitted VOCs are given in Middleton et al. (1990).

On the other hand, the most important process for the formation of secondary aerosol particles is the homogeneous nucleation in the sulfuric acid-water system. It is parameterized in MADE, following the method of Kulmala et al. (1998). Aerosol growth by condensation occurs in two steps: the production of condensable material (vapor) by the reaction of chemical precursors, and the condensation and evaporation of ambient volatile species on aerosols. The inorganic chemistry system, based on the Model for an Aerosol Reacting System (MARS) (Saxena et al., 1986) and its modifications by Binkowski and Shankar (1995), calculates the chemical composition of a sulphate-nitrate-ammonium-water aerosol according to equilibrium thermodynamics. The organic aerosol chemistry is based on the SORGAM, which assumes that SOA compounds interact and form a quasi-ideal solution (Grell et al., 2005). The SOA formation in SORGAM follows the two-product approach (Odum et al., 1996) where the oxidation of hydrocarbons produces two types of modelled semivolatile compounds that are partitioned between the gas and particle phases after

[21] Comentário: Replaced by "MADE" (comment P.14178,L.6 from Referee#1)

considering the absorptive partitioning theory (Pankow, 1994a; b). The primary organic aerosol (POA) in MADE is calculated from the primary anthropogenic emission of OC. Then, one may calculate the predicted OC concentration from the sum of both SOA and POA. The concurrent organic matter (OM) can be obtained from the OC concentration by application of a conversion factor. Brown et al. (2013) showed that the average OM:OC ratio was 1.54 (with a standard deviation of 0.2) for sites with low amount of secondary aerosol formation. It is important to note that this ratio can change from one place to another. In areas impacted by biomass burning the ratio can be higher. Gorin et al. (2006) assumed a ratio of 1.6 for the conversion from OC to OM over an area that experiences a significant wood smoke influence.

[22] Comentário: Replaced by "MADE" (comment P.14178,L.6 from Referee#1)

2.2.1. Model configuration

WRF-Chem version 3.5 was configured with three nested grid cells: coarse (75 km), intermediate (15 km) and fine (3 km). The coarse grid cell covered a big region of Brazil and also of the Atlantic Ocean. The intermediate grid covered the southeast Brazil while the fine grid cell covered barely the SPMA and metropolitan areas nearest to it. Fig. 1 shows the arrangement of measurement sites and topography in the downtown area of the 3-km modelling domain. The initial and boundary meteorological conditions are from the National Center for Environmental Prediction's Final Operational Global Analysis with 1^{o} of grid spacing, 26 vertical levels and are available every six hours: 00, 06, 12 and 18 UTC (http://rda.ucar.edu/datasets/ds083.2/). The initial and boundary chemical conditions for representing gases and aerosols background concentration were obtained from the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4; Emmons et al., 2010). This model was driven by meteorological inputs from the Goddard Earth Observing System Model,

[23] Comentário: The model version was indicated in the text (comment P.14179,L.1 from Referee#1)

[24] Comentário: The acronym was added (comment "Technical-comments-P.14179,L.12" from Referee#1)

version 5 at a horizontal resolution of $1.9^{o} \times 2.5^{o}$, 56 vertical levels that are also available every six hours. Table 3 lists the WRF-Chem configuration options employed by this study.

WRF-Chem simulation with coupled primary aerosol (dust, sea salt and anthropogenic) and gas (biogenic and anthropogenic) emission modules, together with the direct effect of aerosol particles turned on, is performed as the control simulation in order to evaluate the model performance (hereafter referred to as Case_0). For secondary aerosols, a simulation scenario (Case_1) with biogenic and anthropogenic gases emission is performed to evaluate its formation potential. An additional simulation (Case_2) is also performed to evaluate the impact of aerosols on ozone photochemistry. Notation and description of simulations are listed in Table 4. The first seven days of each simulation were not analyzed and used for model spin-up.

[25] Comentário: The phrase was reworded (comment P.14179,L.16-23 from Referee#1)

[26] Comentário: The statement was added in the text (comment P.14179:Model-description from Referee#1)

2.3. Emissions

2.3.1. Anthropogenic emissions

Anthropogenic emissions of trace gases and particles in both 3 and 15 km modelling domains were considered to include emissions only coming from on-road vehicles through the use of a vehicular emission model developed by the IAG-USP's Laboratory of Atmospheric Processes (LAPAt). Basically, this model considers the number of vehicles, vehicular emission factors, and average driving kilometers for vehicle per day as basic parameters for the calculation of exhaust emissions considering different vehicle types (light-duty vehicles, heavy-duty vehicles, and motorcycles) and different fuel types (ethanol, gasohol, combination of any proportion of gasohol and ethanol, and diesel) according to CETESB (2012). The details of this model are available in Andrade et al. (2015). In the case of VOCs, there are other two relevant

[27] Comentário: The statement was reworded (comment "Comments(2)" from Referee#2)

emissions (fuel transfer and evaporative processes) associated with the vehicles, besides the exhaust emissions. Because of the complexities in the spatial representation due to a numerous factors such as emissions at service stations, such emission sources are assumed to be emitted by exhaust of vehicles for the sake of simplicity. The vehicular fleet and intensity of use datasets are provided by the National Department of Traffic (DENATRAN) and the Sao Paulo Transporte (SPTrans), respectively. Emission factors for road vehicles for most pollutants were considered from previous studies performed inside the road tunnels (i.e. Janio Quadros, referred as JQ tunnel, and the tunnel 3 of the Rodoanel Mario Covas that is referred hereafter as RA tunnel) located within the SPMA (Pérez-Martínez et al., 2014; Nogueira et al., 2014). However, emission factors for VOCs are considered from dynamometer protocols (CETESB, 2010). VOCs and particulate matter speciation profiles used by pas-phase and aerosol chemical modules were also obtained from NUANCE-SPS experimental campaigns performed in 2011 (tunnel measurements) and 2012 (ambient data). It is important to note that due to the lack of information on vehicular emission factors and intensity of use for most of the other metropolitan areas inside both modelling domains (e.g. the Campinas Metropolitan Area, which is shown by the second largest grey stain in Fig. 2), the calculation of vehicular emissions for these urban areas was carried out on the basis of the parameters found for the SPMA. The number of vehicles in any modelling domain is calculated from the sum of the number of vehicles in each one of the main urban areas inside the modelling domain in question.

Spatial distribution of emissions for the 3 km modelling domain resolution was based on road density products compiled by the OpenStreetMap project and extracted from the Geofabrik's free download server (http://download.geofabrik.de). Urban areas were assumed to allocate high emissions since these concentrate a road density greater

[28] Comentário: The expression “grid cells” was replaced by “modelling domains” throughout the manuscript (comment P.14180,L.23-28 from Referee#1)

than other areas. In the case of the 15 km modelling domain, emissions are based on night-time lights data from the Defense Meteorological Satellite Program (http://ngdc.noaa.gov/eog/dmsp/downloadV4composites.html). These images are 30 arc second grids, spanning from -180^{o} to +180^{o} longitude and -65^{o} to +75^{o} latitude and contain the lights from cities, towns and other sites with persistent lighting, including gas flares. Cleaned up night-time light points with no ephemeral events such as forest fires are used to allocate emissions. To estimate the number of vehicles in each grid point of both domains, the sum of individual intensities at each point (i.e. total road length for the 3 km modelling domain and night-time light for the 15 km modelling domain) is firstly normalized by the total fleet, and then distributed uniformly using the total fleet distribution so that emissions in urban areas are mainly represented by emissions coming from their vehicles. Furthermore, due to the complexity involved in describing the temporal variation of emissions at each grid point, median values for vehicular traffic obtained from measurements inside the JQ and RA tunnels (Pérez-Martínez et al., 2014) were used for distributing the emissions during the day in both domains. This approximation followed the approach used by Fast et al. (2006) where emission profiles were calculated from median diurnal variations on weekdays and weekends. We have applied the same constant diurnal cycle at all grid points where emissions have values greater than zero. VOC and PM emission profiles were assumed to be the same as for CO and NOx emission profiles since these pollutants are also characteristic tracers of emissions of light-duty and heavy-duty vehicles, respectively. Fig. 2 shows the maximum hourly emission rates for aromatic VOCs in the 3 km modelling domain. Anthropogenic emissions were not considered in the 75 km modelling domain.

[29] Comentário: The statement was added in the text (comments P.14181:anthropogenic-emissions-section from Referee#1 and “Comment(2)” from Referee#2)

The Another Assimilation System for WRF-Chem (AAS4WRF) chemical emissions pre-processor developed by the Latin American Observatory (OLE2; Muñoz et al., 2010; 2012) was used to scale emission rates on WRF curvilinear coordinates. AAS4WRF is appropriate to write chemical emission rates from both surface and elevated sources in the proper WRF data file format, providing an alternative tailored way to assimilate emissions to WRF-Chem. The method is explained in the OLE2 Wiki pages in detail (http://www.cmc.org.ve/mediawiki/index.php?title=Calidad_de_Aire).

2.3.2. Other emissions

Biogenic emissions are calculated online based on the Guenther scheme (Guenther et al., 1993; 1994). The Guenther biogenic emissions model calculates the emission rates using temperature, photo-synthetically active radiation flux and land-use data as the U.S. Geological Survey (USGS) land-use cover system classification if coupled with the WRF model. However, as indicated in the WRF-Chem emissions guide (http://ruc.noaa.gov/wrf/WG11/Emission_guide.pdf), several key chemical species would have been representing relatively low emission rates because of the limited vegetation types in the simulation, and thus their impacts are anticipated to be much lower than those from vehicular emissions.

Dust and sea salt emissions are calculated online following the works of Ginoux et al. (2001) and Gong (2003), respectively. The calculation of Ginoux et al. (2001) for the uplifting of dust particles is based on the surface wind speed, wetness and information on soil characteristics. The model then solves the continuity equation including the emission, chemistry, advection, convection, diffusion, dry deposition, and wet deposition of each species. The parameterization of sea salt aerosol source function of Gong (2003) is an extended parameterization of Monahan et al. (1986), which scales

the generation of marine aerosols from mechanical disruption of wave crests by the wind and sea surface covered by whitecaps.

3. Results and discussion

3.1. Characterization of meteorological conditions

In order to study and understand the spatial and temporal variability of atmospheric aerosols, O_3, and other pollutants (i.e. CO, NOx) during the study period, it was first necessary to analyze the behavior of main meteorological systems acting on the atmospheric environment of the SPMA and surrounding areas.

According to the monthly climate reports from the IAG-USP's Climate Research Group (GrEC), the observed precipitation rates were lower than the climatological value in SPMA (anomaly of -38.6 mm) and larger part of the Sao Paulo State during August 2012. Negative anomalies on the precipitation were caused by the intensification of the South Atlantic Subtropical High (SASH). These conditions established an easterly wind anomaly pattern at the 850 hPa level. Conditions were unfavorable for relative humidity coming from the Amazon due to the Low Level Jet (LLJ) and less intense Alisian winds in the Tropical Atlantic (GrEC, 2012a). However, the action of frontal systems favored the rain accumulation in September 2012, mainly in western Sao Paulo State where the greater positive amount of anomalies was observed. Precipitation events were predominantly observed during the second half of the month. In this case, the wind pattern showed an opposite configuration to that observed in August 2012 as a result of the weakening of the SASH (GrEC, 2012b). The IAG-USP's climatological station recorded an accumulated precipitation of about 1.3 mm on three days of occurrence (28 August, 30 August and 4 September 2012) and an easterly wind pattern with a median intensity of 2 m s^{-1} during the period between 07 August and 06 September 2012. Fig. 3

[30] Comentário: The precipitation anomaly was added in the text (comment P.14183,L.3-6 from Referee#1)

[31] Comentário: Replaced by "coming" (comment "Technical-comments-P.14183,L.8" from Referee#1)

[32] Comentário: Reference to support the statement immediately above (comment P.14183,L.3-6 from Referee#1)

[33] Comentário: Replaced by "western Sao Paulo State" (comment "Technical-comments-P.14183,L.11" from Referee#1)

[34] Comentário: Replaced by "Precipitation events" (comment "Technical-comments-P.14183,L.11-12" from Referee#1)

shows the hourly accumulated precipitation and relative humidity observed at the IAG-USP's climatological station.

[35] Comentário: The statement was reworded (comment P.14183,L.17-19 from Referee#1)

3.2. Analysis of aerosol species

Aerosol analysis included species such as organic carbon (OC), elemental carbon (EC), sulphate, nitrate, ammonium, sodium and chloride in addition to other elemental constituent of PM. All the sampling for these species were performed at IAG-USP. Results showed that the major contributors to the concentration of fine particles are OM (55.7%; OM:OC ratio of 1.5 found by Brito et al. (2013)) and EC (15%), followed by sulphate (2.9%), ammonium (2.1%), sodium (1.9%), nitrate (0.5%) and chloride (0.3%). The remaining mass (21.6%) is calculated by determining of the difference between the total mass of $PM_{2.5}$ (from the gravimetric analysis) and the sum of the masses of 7 individual compounds, as noted above. Part of this remaining mass is related to the water content of aerosols (Andrade et al., 2012).

[36] Comentário: The expression "unexplainable concentration" was replaced by "remaining mass". Also, it was indicated a reference to support the statement (comment P.14184,L.1-2 from Referee#1)

On the other hand, $PM_{2.5}$, PM_{10} and size distribution of particles measured at IAG-USP show that the study period was characterized by a reduction in the concentrations up to the end of August 2012 when their minimum values were achieved. This reduction was related to the action of a semi-stationary front between the coasts of Sao Paulo and Parana States. After the passage of this system, aerosol concentrations have significantly increased what could be related to an increase in relative humidity once the SASH system is moved away from the continent, as well as the transport of aerosol particles produced by forest fires in the central-west region of Brazil and the Sao Paulo State. Several studies have shown the contribution of forest

fires on the atmospheric aerosol concentrations in SPMA (Vieira-Filho et al., 2013; Vasconcellos et al., 2010). One way to qualitatively evaluate the contribution of forest fires on aerosol concentrations is by using the air mass trajectories. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998) was used to calculate backward trajectories of air masses in order to identify atmospheric transport of air mass from forest fire areas. Fig. 4 shows the three-day backward trajectories of air masses starting at IAG-USP for the days 9 and 31 August and 5 September, when increases in the OC and EC concentrations were observed at IAG-USP. The pink markers on the map represent the observed fire locations during the study period considering different satellite products (GOES, AQUA, TERRA, NOAA).

Fig. 5 shows the concentration of OC, EC and some species of $PM_{2.5}$ during the study period at IAG-USP. We can observe eleven exceedances of $PM_{2.5}$ concentration with respect to the air quality standard of 25 µg m^{-3} (see grey line in Fig. 5a) established by the World Health Organization (WHO). These exceedances have mainly occurred at the beginning and at the end of the study period when an increase in the concentrations of OC and EC were observed. The increasing organic matter could be associated to traffic incidents which may raise the emissions, which in case of less favorable meteorological conditions (e.g. lower height of lower planetary boundary layer, PBL, or slow transport of air pollutants) may have led to a more efficient formation of secondary particles. Castanho and Artaxo (2001) analyzed the behavior of the aerosol composition in SPMA and showed the increase in the concentration of inorganic and organic material in the winter season compared to the summer season, explaining this behavior with the meteorological characteristics: dry conditions with low height inversion layer in the wintertime and a rainy summer.

[37] Comentário: The paragraph was added in the text (comments P.14184,L.21-25 from Referee#1 and Comment(5) from Referee#2)

[38] Comentário: The paragraph was reworded (comment P.14184,L.26-29 from Referee#1)

[39] Comentário: The paragraph was added in order to support the earlier one (comment P.14184,L.26-29 from Referee#1)

Size distributions of aerosol mass indicate that the majority of sulphate, ammonium and PM_{10} mass concentration is distributed in the size range with diameters between 0.1 and 1 µm, commonly known as accumulation mode particles (Kumar et al., 2010). In the cases of nitrate, sodium, and chloride, most part of mass was concentrated in particles with diameters greater than 1 µm.

3.3. Comparison of baseline simulation with observations

All the numerical results presented in this section, for the purpose of comparison with the measurements, were obtained from the baseline simulation (Case_0). The predicted temperature, humidity, and wind distribution have been compared to measurements from the AF-IAG and INT measurement sites. Overall, the model captured the diurnal variation of temperature, humidity, and wind directions reasonably well. However, the predicted wind speeds were slightly lower than the observed values. To evaluate the model performance in solving the meteorology and chemical species, we computed the statistics correlation coefficient (R), Bias (B), and root mean square error ($RMSE_{UB}$). The definitions of these statistics are given in the Appendix. Table 5 presents the summary of these statistics, showing comparisons between WRF-Chem predictions and observations. Fig. 6 shows the predicted average of wind vectors at 10 m and temperature at 2 m for the whole study period in the 3 km modelling domain. Blue dots represent the locations of AF-IAG and INT sites, while the numbers in cyan indicate the observed average temperatures (i.e. 17.7 °C at AF-IAG and 17.8 °C at INT). On an average, the predicted wind direction was easterly in SPMA, which has somewhat affected the spatial distribution of aerosol particles as examined later in this section. Likewise, a good agreement is found between the predicted $PM_{2.5}$, PM_{10} and O_3 concentration and measurements at most of the sites. Figs. 7, 8 and 9 show the observed

[40] Comentário: The term "temporal variations" was omitted. The average period was also indicated (comment P.14185,L.17 from Referee#1)

447 and predicted temporal variations of $PM_{2.5}$, PM_{10} and O_3 concentrations at 3, 10 and 6
448 sites in the SPMA, respectively, with some measurement sites sharing the same grid
449 point for comparisons due to the geographical proximity. These figures suggest that
450 predicted concentrations did not present any significant spatial variation in the
451 downtown SPMA and were generally underestimated when compared to measurements.
452 This under prediction could be associated with an underestimation on the vehicular
453 emissions as well as other emission sources (e.g. emissions coming from industry) that
454 are disregarded in this study, in addition to predicted surface winds more intense than
455 those observed, leading to a dilution of aerosol particles in SPMA. The high
456 concentrations of $PM_{2.5}$ and PM_{10} observed at the beginning and at the end of the study
457 period, whose variability and trends were reasonably well captured by the model, could
458 be related with the emission of high aerosol loadings due to traffic incidents as well as
459 the establishment of lower PBL heights, commonly observed under post-frontal
460 situations. The results for this simulation (Case_0) show that overall the predicted PBL
461 heights (not shown here) have a regular diurnal variation in the downtown SPMA with
462 averaged daily values around 500 m at both the beginning and the end, and of up to 700
463 m in the middle of the study period, when lower concentrations of aerosols were
464 observed. Statistics to quantify the model performance in the representation of $PM_{2.5}$,
465 PM_{10} and O_3 concentrations can be visualized along with the Taylor Diagram (Taylor,
466 2001) shown in Fig. 10. In general, most of evaluated parameters present good
467 correlation coefficients, mainly those for PM_{10}, but with negative biases and standard
468 deviations lower than those for observations. The mean biases for $PM_{2.5}$, PM_{10} and O_3
469 concentrations were -8.84 μg m^{-3}, -14.13 μg m^{-3} and -0.85 ppb, respectively (see Table
470 5).

[41] Comentário: Replaced by "industry" (comment P.14186,L.2 from Referee#1)

[42] Comentário: The statement was added in the text

[43] Comentário: The paragraph was reworded (comment P.14186,L.3-5 from Referee#1)

[44] Comentário: The paragraph was reworded (comment P.14186,L.6-7 from Referee#1)

[45] Comentário: Reference added in the text (comment "Figure 10" from Referee#1)

[46] Comentário: The statement was added in the text

Figures 11-13 show the predicted average surface distribution of $PM_{2.5}$, PM_{10} and $PM_{2.5}$:PM_{10} ratio for the 3 km modelling domain, respectively. Red dots and cyan numbers represent the locations and the observed mean PM concentrations (or mean PM concentration ratios) at the measurement sites, respectively. Major contributions of $PM_{2.5}$ on the total PM_{10} concentration were observed mainly over offshore continental areas (see Fig. 13). High $PM_{2.5}$:PM_{10} concentration ratios would be firstly associated with the transportation of fine particles and gases from upwind regions (see Fig. 6), followed by a production of fine particles from biogenic emissions. Additional comparisons between the observed and predicted concentrations of OC and EC at IAG-USP (the only site with measurements of OC and EC) are shown in Fig. 14. In addition to an underestimation of emissions, under predicted OC concentrations could also be associated with an underestimation of SOA probably due to the absence of oxidation of monoterpenes and a limited treatment of anthropogenic VOCs oxidation in the RADM2 mechanism, as discussed by Tuccella et al. (2012). The SORGAM aerosol module considers the formation of anthropogenic SOAs from the oxidation of alkane, alkene and aromatic VOCs as well as the biogenic SOA formation from the oxidation of alpha-pinene, limonene and isoprene VOCs. Recent studies coupling non-traditional SOA models (volatility basis set approaches) in WRF-Chem show improvements in the predicted SOA concentrations, although these are still lower than those observed (e.g. Li et al., 2011b; Ahmadov et al., 2012; Shrivastava et al., 2013).

On the other hand, measurements of mass size distribution were also made with a MOUDI impactor at IAG-USP, following the protocol describe in Miranda and Andrade (2005). Constituents of aerosol were subsequently determined by X-Ray fluorescence analysis and ion chromatography analysis. As previously indicated in this section, the main identified species are SO_4, NO_3, NH_4, Na and Cl. The observed

496 average aerosol composition is derived using measurements from both MOUDI
497 impactor and SUNSET analyzer. To perform the comparisons of mass size distribution,
498 we adequately joined the MOUDI bin sizes according to the three modes used by the
499 MADE aerosol module: Aitken (<0.1 μm), accumulation (0.1-1 μm) and coarse (>1
500 μm). The observed and predicted aerosol mass size distributions averaged over the same
501 sampling time period (16 days along the study period) are shown in Fig. 15. Over the
502 downtown SPMA, both the observed and predicted fine particles from accumulation
503 mode account for majority of the total $PM_{2.5}$ mass. Since the formation-growth
504 processes of aerosols in question are explicitly treated in the Aitken and accumulation
505 modes, the predicted concentrations for particles larger than 1 μm are assumed to be
506 zero. In this case, the mass of particles larger than 1 μm is allocated to the PM_{10} aerosol
507 variable (see Fig. 15). The comparison between the observed and predicted average
508 contributions for the main identified aerosol constituents at IAG-USP is shown in Fig.
509 16. Both the observed and predicted OC and EC make up the largest fraction of $PM_{2.5}$
510 mass with contributions of 55 and 40%, respectively. In addition, it was found that the
511 predicted SOA concentrations contribute 17% of the predicted total OC concentration at
512 this measurement site. Various global and regional scale SOA simulations have been
513 conducted using mass-based yield and partitioning coefficients, but they have
514 underestimated the SOA concentrations by roughly an order of magnitude, especially
515 over urban regions (Matsui et al., 2014). Using the same SOA formation approach
516 employed by this study and a conversion factor of 1.6 to convert the emissions of OC to
517 OM, Tuccella et al. (2012) found simulated SOA:OM ratios in the 5-40% range against
518 the observed range of 50-80%. Although the predicted average $PM_{2.5}$ concentration
519 (14.48 μg m^{-3}) was lower than observed (22.32 μg m^{-3}), the mean aerosol chemical
520 composition was reasonably well represented by the model (see Fig. 16).

[47] Comentário: The statement was reworded (comment "Technical-comments-P.14187-14188,L.29-1" from Referee#1)

3.4. Contribution of dust-sea salt and coarse anthropogenic aerosols to PM concentration

The evaluation of the contribution of dust and sea salt aerosols on PM_{10} concentration is performed from the sum of their concentrations divided by the PM_{10} concentration. The simulated average ratio between dust–sea salt aerosols and the total PM_{10} mass concentration is shown in Fig. 17b. High concentration ratios have been observed over the ocean where sea salt emissions are by far the most important aerosols source. Unlike high concentration ratios over the ocean, lower concentration ratios are observed over the continent far away from the coast. In this region, the main sources of atmospheric aerosols would be the emission of primary biological aerosol, SOA formed from the emission of biogenic volatile organic compounds (BVOCs), and forest fires. However, particles could also be transported from remote areas. In addition, we can also observe that dust and sea salt aerosols have a contribution between 40 and 50% of the total PM_{10} concentration in the downtown SPMA. Furthermore, it is possible to estimate the contribution of all the other PM_{10} (i.e., the coarse anthropogenic aerosol) to the total PM_{10} mass concentration. It may be directly calculated from the model or estimated from the Figs. 13 and 17b once the sum of concentrations of $PM_{2.5}$, dust and sea salt, and coarse anthropogenic aerosol represents 100% of the total PM_{10} mass concentration. For example, we found that the coarse anthropogenic aerosol represents around 10% of PM_{10} in the downtown SPMA.

3.5. Evaluation of secondary aerosol formation

As described in Section 2.1, aerosol module employed by this study (MADE/SORGAM) includes the homogeneous nucleation in the sulphuric acid-water system. The sulphuric acid is the most significant condensable molecule formed in the atmosphere, which has also been long recognised as the most important molecule from

[48] Comentário: The section was renamed as suggested by the Referee#1 (comment P.14188,L.5)

[49] Comentário: The statement was reworded (comment P.14188,L.8-9 from Referee#1)

546 the point of view of the nucleation of new particles (Jenkin and Clemitshaw, 2000;
547 Seinfeld and Pandis, 2006). However, for the SPMA, the importance of SOA formed
548 from the anthropogenic emission of fuel used by the transport sector was noted (Salvo
549 and Geiger, 2014). According to the official emission inventory developed by the Sao
550 Paulo Environmental Protection Agency (CETESB, 2013), the SOA explains 51% of
551 the fine particle mass concentration, with the vehicular emission being its main source.
552 The subsequent growth processes involve aerosol growth by condensation of
553 condensable material onto existing particles, and by coagulation of particles to form
554 larger particles (Kumar et al., 2011; 2014). For example, particles in the accumulation
555 mode emerge through coagulation of particles from the Aitken mode (Kumar et al.,
556 2011). It is important to emphasize that the boundaries were updated with gas and
557 aerosol background concentrations coming from the 15 km modelling domain during
558 the whole simulation period. Thereafter, the impact of vehicular emissions on the
559 formation of fine particles was calculated from the predicted $PM_{2.5}$ concentration
560 considering an emission scenario (Case_1) in which only emission of gases from
561 vehicles and vegetation are taken into account to be emitted to the atmosphere from the
562 surface. The predicted average $PM_{2.5}$ (Case_1):$PM_{2.5}$ (Case_0) ratio is shown in Fig.
563 17a. A contribution between 20 and 30% in the predicted baseline $PM_{2.5}$ concentration
564 in downtown SPMA is found to correspond to the fine particles formation and
565 transportation processes. Higher concentration ratios over the SPMA surroundings (30-
566 50%) could be associated with more efficient biogenic emissions. Overall, it is observed
567 that the formation efficiency increases towards the northwest from the ocean. Deep red
568 areas in Fig. 17a could also be associated with the transportation of fine particles and
569 gases from other regions, in addition to having a more efficient production of fine
570 particles from biogenic emissions. For example, given the distribution of winds in Fig.

[50] Comentário: Reference to support the statement earlier (comment P.14189,L.7-8 from Referee#1)

[51] Comentário: The statement was added in the text

6, the northern boundary could represent the main source of particles and gases over this part of the simulation domain. Additionally, the comparison between the predicted and observed OC and EC concentrations at IAG-USP shown in Fig. 14 includes the Case_1 simulation in which only emission of primary gases is taken into account in the assessment of fine particles formation. The concentration peaks observed at the beginning and at the end of the study period may be associated with the transport of aerosol particles from both biomass and fossil fuel burning areas (see Fig. 4). Considering the Case_1 simulation, we can observe very low concentrations for EC (mean concentration of 0.01 μg m^{-3}), as expected. This is because these particles are not produced by photochemical processes in the atmosphere, but associated mainly with the diesel exhaust.

[52] Comentário: The phrase was reworded (comment "Section3.5-Page20-Line2" from Referee#2)

[53] Comentário: The statement was added to support the Fig. 14 (comment P.14190,L.2-6 from Referee#1)

3.6. Aerosol impact on O_3 photochemistry

Ozone photochemistry production mainly depends on the two key photolysis rates, as shown in Eqs. (1) and (2), i.e., shortwave radiation able to reach the surface to break molecules of O_3 and NO_2.

$$O3 + hv \rightarrow O2 + O(^1D)\ (\lambda < 320\ nm) \quad (1)$$

$$NO_2 + hv \rightarrow NO + O(^3P)\ (\lambda < 420\ nm) \quad (2)$$

Therefore, the impact of aerosols on O_3 photochemistry has been evaluated from the impact of aerosols on downward shortwave radiation. Attenuation (scattering and absorption) of downward shortwave radiation by aerosols may substantially modify the photolysis rates, and thereby affecting the ozone photochemistry production.

[54] Comentário: The paragraph was reorganized

The average percentage change in surface O_3 concentrations at 16:00 h (local time) with and without the aerosol-radiation feedback module turned on are shown Fig.

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17c. Overall O_3 is destroyed or formed (incoming transport from other regions) in small quantities between -1 and +1% in relation to its total concentration. In addition, it was observed that the surface O_3 concentration decreased by around 2% in the downtown SPMA. Li et al. (2011a) found that the impact of aerosols on O_3 formation in Mexico City was most pronounced in the morning with the O_3 reduction of 5-20%, but the reduction is less than 5% in the afternoon. Low reductions in the O_3 concentration in the downtown SPMA compared to results from other studies may be explained by the lower predicted PM_{10} concentrations, which can lead to a minor attenuation of the incoming solar radiation. Simulated mean downward shortwave fluxes at ground surface (not shown) were up to 5% higher for the Case_2 than for the Case_0 during the afternoon. The inclusion of the direct effect of aerosol particles was found to have small reductions in the surface temperature (changes by around 2%), presumably due to an increase in the number of atmospheric processes involving downward longwave fluxes over this area. Forkel et al. (2012) found an underestimation of predicted downward longwave radiation over the southern Baltic Sea when the direct effect of aerosol particles was neglected. Despite the highly non-linear behavior of tropospheric O_3, the reduction in the predicted O_3 concentrations indicates a high efficiency of aerosols to attenuate the downward shortwave radiation, what is plausible once it was found that low PM_{10} concentrations have a capability to reduce ground level O_3 concentrations in a few ppb.

[55] Comentário: The phrase was reworded (comment "Technical-comments-P.14191,L.9-11" from Referee#1)

4. Summary and conclusions

The WRF-Chem community model has been used to evaluate the impact of vehicular emissions on the fine particles formation in the SPMA. Three thirty-one day simulations, covering a period from 7 August to 6 September 2012, have been performed. The aims were to evaluate the impact of fine particles formation (both inorganic and SOA) from gases emitted by road vehicles as well as the aerosol impacts

on the ozone formation photochemistry. The results were compared with the measurements available from the NUANCE-SPS project.

The predicted temporal variations of meteorology, $PM_{2.5}$, PM_{10} and O_3 were found to agree well with the measurements at most of the sites during the entire simulation period. However, the predicted concentrations of $PM_{2.5}$, PM_{10} and O_3 (but in minor intensity) were lower than the observed values. This difference could be associated with an underestimation of the vehicular emissions and other emission sources such as industry, heating and cooking, which are not considered in this study. Wind speed and direction played an important role in the distribution of fine particles over the simulation domain. Backward trajectories analysis suggested that aerosol particles from biomass burning were transported to SPMA, impacting on the PM concentration over this region.

The baseline simulation (Case_0) showed that dust and sea salt aerosols made a contribution between 40 and 50% of the total PM_{10} concentration in the downtown SPMA. On the other hand, the Case_1, which represents simulations with gaseous emissions only, indicates that the emissions of primary gases coming mainly from vehicles have a potential to form new particles between 20 and 30% in relation to the baseline $PM_{2.5}$ concentration found in the downtown SPMA. Finally, the Case_2, which represents simulations with aerosol-radiation feedback turned on, reveals a reduction in the surface O_3 concentration by around 2% in the afternoon (16:00 h; local time) when the aerosol-radiation feedback is taken into account.

This study provides a first step to understand the impact of vehicular emissions on the secondary particles formation in the SPMA. Nevertheless, more experimental campaigns are recommended for future work in order to characterize aerosols in

[56] Comentário: The statement was reworded (comment P.14191,L.27 from Referee#1)

[57] Comentário: The statement was added in the text

[58] Comentário: The phrase was added in the text (comment P.14192,L.10-12 from Referee#1)

ambient air and to improve their emission estimates so that a better understanding of physical and chemical properties and their formation can be established. This study also evaluates the importance of the VOCs in the formation of not only O_3 but also of fine particles. These compounds play an important role concerning health impacts and climate change, and the control of their concentrations requires the description of their formation mechanisms.

Appendix A

[59] **Comentário:** An appendix with the definitions of used statistics was added

The statistics used in this study are defined as follows:

1. Correlation coefficient (R)

$$R = \frac{\sum_{i=1}^{N}(M_i - \overline{M})(O_i - \overline{O})}{\sqrt{\sum_{i=1}^{N}(M_i - \overline{M})^2}\sqrt{\sum_{i=1}^{N}(O_i - \overline{O})^2}}$$

2. Root mean square error UB ($RMSE_{UB}$)

$$RMSE_{UB} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}[(M_i - \overline{M}) - (O_i - \overline{O})]^2}$$

3. Bias (B)

$$B = \frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)$$

where

$\overline{O} = \frac{1}{N}\sum_{i=1}^{N} O_i$ and $\overline{M} = \frac{1}{N}\sum_{i=1}^{N} M_i$ are the average values of the individual observed and predicted values, O_i and M_i, respectively. N is the number of observations.

5. Acknowledgments

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890 Table 1. Description of aerosol sampling campaigns performed at IAG-USP.

Parameter	Sampling frequency	Period of sampling	Sampling device
Aerosol mass size distribution	24 hours	July-September	MOUDI impactor
$PM_{2.5}$ and PM_{10} concentration	12 hours	July-September	Dichotomous sampler
OC and EC concentration	12 hours	August-September	Sunset OC-EC analyser

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Table 2. Description of measurement sites.

Initials	Name	Latitude	Longitude	Measured species
NSO	Nossa S. do O	-23.4796	-46.6916	PM_{10}, O_3
SAN	Santana	-23.5055	-46.6285	PM_{10}
PDP	Parque D. Pedro	-23.5448	-46.6276	PM_{10}, O_3
MOO	Mooca	-23.5497	-46.5984	PM_{10}, O_3
CCE	Cerqueira Cesar	-23.5531	-46.6723	PM_{10}
IAG-USP	IAG-USP	-23.5590	-46.7330	PM_{10}, $PM_{2.5}$, OC, EC Aerosol mass size distrib.[a]
IPEN-USP	IPEN-USP	-23.5662	-46.7374	$PM_{2.5}$, O_3, NOx, CO
IBI	Ibirapuera	-23.5914	-46.6602	PM_{10}, O_3, NOx, CO
CON	Congonhas	-23.6159	-46.6630	PM_{10}, $PM_{2.5}$
AF-IAG	AF-IAG	-23.6500	-46.6167	T, RH, WS, WD[b]
SAM	Santo Amaro	-23.6545	-46.7095	PM_{10}
INT	Interlagos	-23.6805	-46.6750	PM_{10}, O_3, T, RH, WS, WD

[a]includes SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Cl^- and PM_{10}.

[b]T, RH, WS, and WD denote temperature, relative humidity, wind speed and wind direction, respectively.

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Table 3. Selected WRF-Chem configuration options.

Atmospheric Process	WRF-Chem option
Longwave radiation	RRTM
Shortwave radiation	Goddard
Surface layer	Monin-Obukhov
Land surface	Noah
Boundary layer	YSU
Cumulus clouds[a]	Grell 3D
Cloud microphysics	Lin
Gas-phase chemistry	RADM2
Aerosol chemistry	MADE/SORGAM
Photolysis	Fast-J

[a]Outer domains only

Table 4. Description of WRF-Chem simulations.

Label	Description
Case_0	Emission of gases
(Baseline simulation)	Emission of aerosols
	Aerosol-radiation feedback turned on
Case_1	Emission of gases
	No emission of aerosols
	Aerosol-radiation feedback turned on
Case_2	Emission of gases
	Emission of aerosols
	Aerosol-radiation feedback turned off

Table 5. Performance statistics for WRF-Chem predictions at all sites[a]

Index	$PM_{2.5}$	PM_{10}	O_3	NOx	CO	T	RH	U[b]	V[c]
R	0.73	0.72	0.63	0.42	0.54	0.71	0.62	0.48	0.44
B	-8.84	-14.1	-0.85	-8.75	-0.27	0.65	-5.74	-0.96	0.75
$RMSE_{UB}$	6.83	10.59	27.45	30.35	0.57	3.21	20.06	1.04	1.02

[a]Values are averaged from all the individual indexes found at the measurement sites. Individual indexes are calculated from both hourly observed and predicted values.

[b]Zonal wind component

[c]Meridional wind component

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Figure 1. Downtown area of the 3 km modelling domain (d03) showing the locations of measurement sites and WRF topography in the vicinity of SPMA. Red dots represent sites with information on O_3 and PM. Yellow dots represent only sites with information on PM. Blue dot represents the location of the IAG-USP's climatological station.

Figure 2. Emission rates for Aromatic VOCs at 19 UTC in the 3 km modelling domain.

Figure 3. Hourly accumulated precipitation and relative humidity observed at the IAG-USP's climatological station during the study period.

Figure 4. HYSPLIT three-day backward trajectories and locations of fires in Sao Paulo State and part of central-west region of Brazil. Pink markers represent the observed fire locations during the study period considering different satellite products (GOES, AQUA, TERRA, NOAA). The backward trajectories starting at IAG-USP were calculated for the days 9 and 31 August and 5 September 2012 at three different altitudes: 500 m (red lines), 1000 m (blue lines), and 2000 m (green lines).

Figure 5. Daily (top), diurnal (bottom), and nocturnal (middle) mean concentrations for EC, OC, PM_{10}, $PM_{2.5-10}$, $PM_{2.5}$ (left panels), and Na, Fe_2SO_3, SiO_2, K_2O, and S (right panels). The $PM_{2.5-10}$ aerosol variable is defined as particulate matter with aerodynamic diameter between 2.5 and 10 µm. The grey line indicates the WHO air quality standard for PM2.5 (25 µg m^{-3}).

Figure 6. The predicted average of wind vectors at 10 m and temperature at 2 m from the baseline simulation (Case_0) for the whole study period in the 3 km modelling domain. Blue dots represent the locations of the measurement sites,

[70] Comentário: The caption was reworded (comment "Figure 1" from Referee#1)

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[71] Comentário: The caption was reworded (comment "Figure 3" from Referee#1)

Formatado: Inglês (EUA)

[72] Comentário: The figure 5 in the earlier manuscript is the figure 4 in the present manuscript. The caption of this figure was also reworded (comment "Figure 4" from both referees)

Formatado: Inglês (EUA)

Formatado: Inglês (EUA)

[73] Comentário: The figure 4 in the earlier manuscript is the figure 5 in the present manuscript. The caption of this figure was also reworded (comment "Figure 5" from Referee#1)

Formatado: Inglês (EUA)

Formatado: Inglês (EUA)

whereas cyan numbers represent the observed average temperature in those sites: 17.7 °C in AF-IAG and 17.8 °C in INT.

Figure 7. The observed and predicted daily variations of $PM_{2.5}$ concentrations at three sites in SPMA for the 3 km modelling domain.

Figure 8. The observed and predicted daily variations of PM_{10} concentrations at ten sites in SPMA for the 3 km modelling domain.

Figure 9. The observed and predicted hourly variations of O_3 concentrations at six sites in SPMA for the 3 km modelling domain.

Figure 10. Taylor diagram showing the individual correlation coefficients, biases, and normalized standard deviations for the $PM_{2.5}$, PM_{10}, and O_3 concentrations.

Figure 11. The predicted average surface distribution of $PM_{2.5}$ concentrations for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on $PM_{2.5}$, whereas cyan numbers represent the observed average $PM_{2.5}$ concentration in those sites: 23.4 µg m^{-3} in IPEN-USP, 21.3 µg m^{-3} in IAG-USP, and 22.2 µg m^{-3} in CON.

Figure 12. The predicted average surface distribution of PM_{10} concentrations for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on PM_{10}, whereas cyan numbers represent the observed average PM_{10} concentration in those sites: 49.5 µg m^{-3} in IAG-USP and 38.7 µg m^{-3} in CON.

Figure 13. The predicted average surface distribution of the $PM_{2.5}$:PM_{10} ratio for the whole study period in the 3 km modelling domain. Red dots represent the locations of the measurement sites with information on both $PM_{2.5}$ and PM_{10}, whereas cyan numbers represent the observed average $PM_{2.5}$:PM_{10} ratio in those sites: 0.43 in IAG-USP and 0.57 in CON.

[74] Comentário: The caption was reworded (comment "Figure 6" from Referee#1)

Formatado: Inglês (EUA)

[75] Comentário: The caption was reworded (comment "Figure 9" from Referee#1)

Formatado: Inglês (EUA)

[76] Comentário: The caption was reworded (comment "Figure 10" from Referee#2)

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Formatado: Inglês (EUA)

Formatado: Inglês (EUA)

[77] Comentário: The captions were reworded (comments "Figure 11-12-13" from Referee#1 and "Figure 11-13" from Referee#2)

Formatado: Inglês (EUA)

Figure 14. The observed and predicted daily variations of OC and EC concentrations at IAG-USP.

Figure 15. The observed and predicted average aerosol mass size distribution for SO_4, NO_3, NH_4, Na, Cl, and other PM_{10} constituents at IAG-USP. The observed aerosol distributions were collected in ten size classes using a rotated impactor (MOUDI) and joined adequately according to the three modes used by the MADE aerosol scheme: Aitken (<0.1 µm), accumulation (0.1-1 µm) and coarse (>1 µm). The five inorganic ions carried in MADE are only calculated for the Aitken and accumulation modes. The WRF's PM_{10} aerosol variable does not include neither OC nor EC for this comparison.

Figure 16. The observed and predicted average contributions for the main identified constituents of $PM_{2.5}$ at IAG-USP.

Figure 17. The impact of (a) emissions of primary gases on the fine particles formation, (b) emissions of dust-sea salt aerosols on the PM_{10} concentration, and (c) aerosol direct effect on the ground level O_3 concentrations at 16:00 h (local time).

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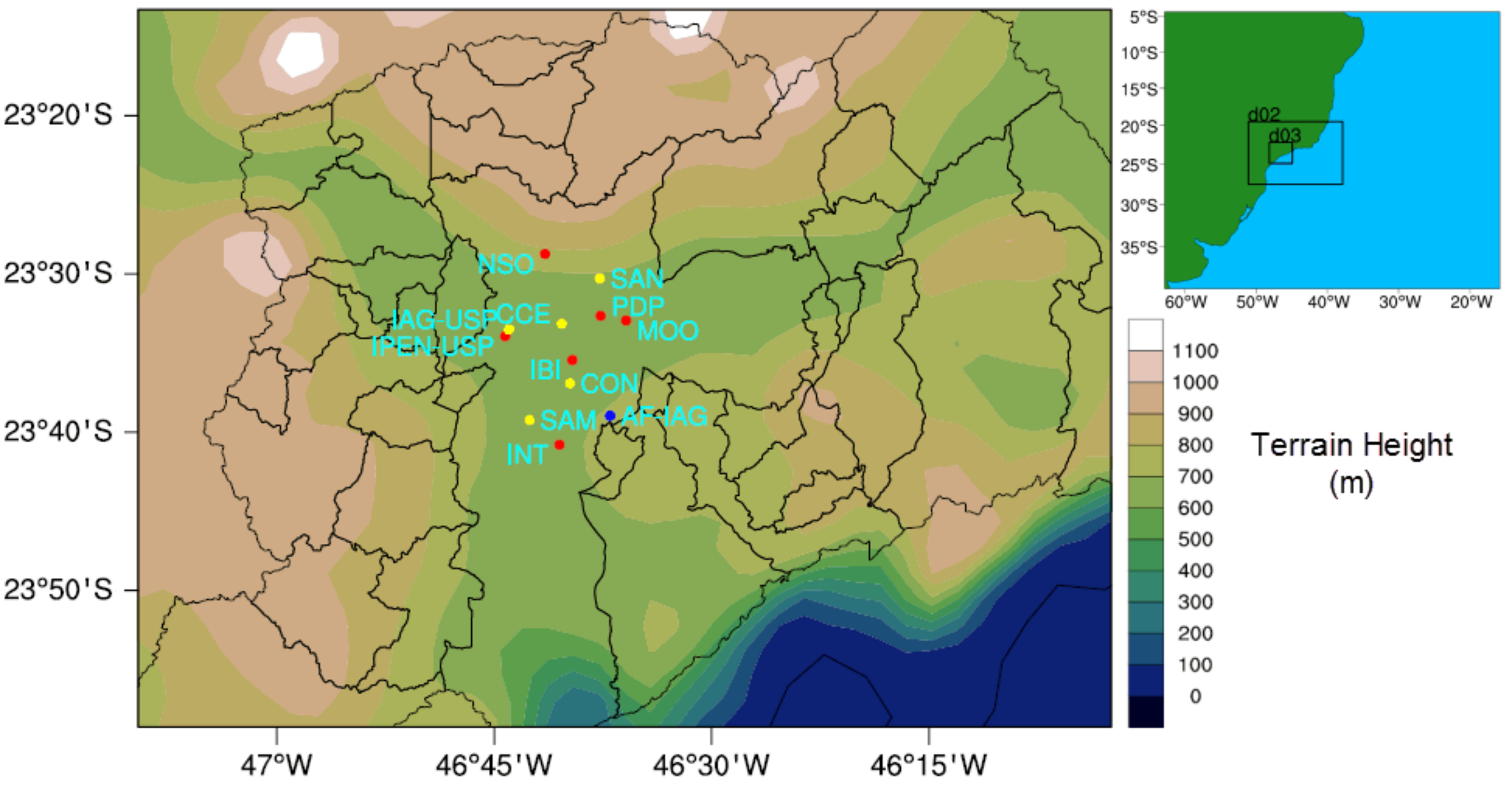
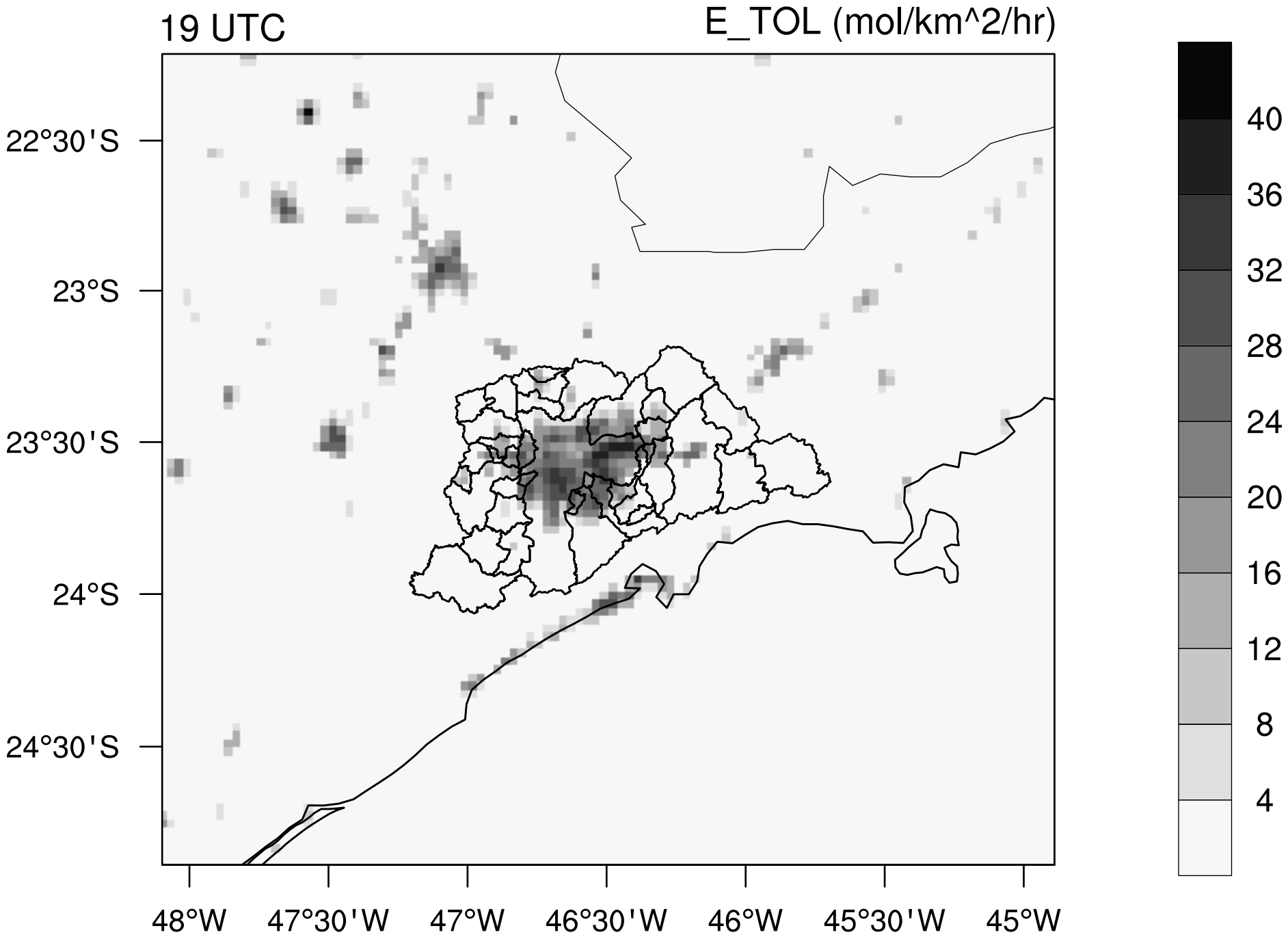
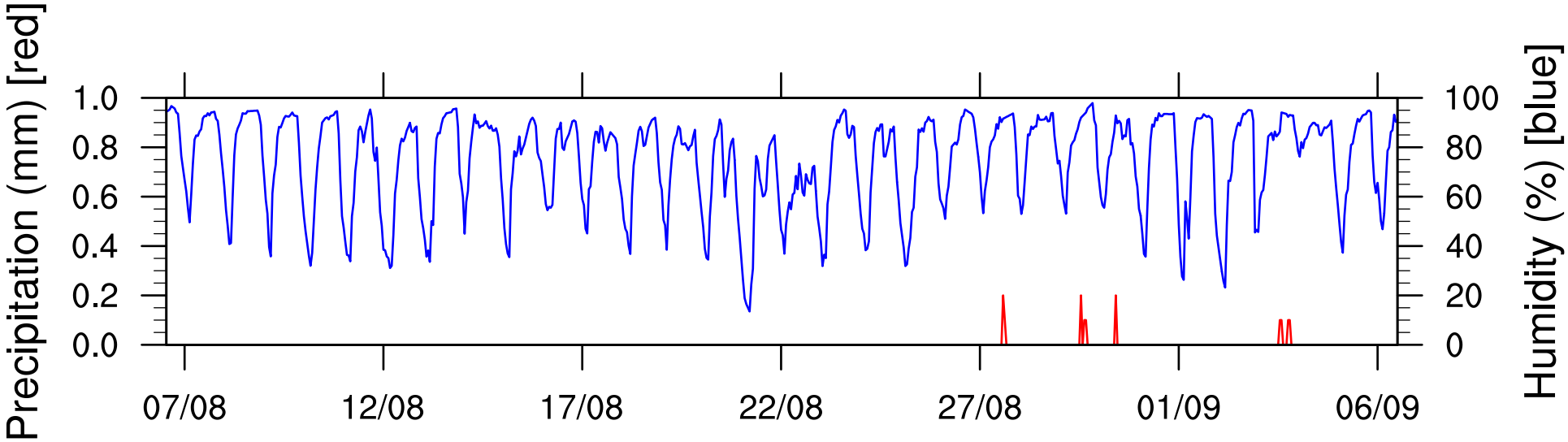
[78] Comentário: The caption was reworded (comment "Figure 15" from Referee#1)

Formatado: Inglês (EUA)


23°20'S
23°30'S
23°40'S
23°50'S
47°W
46°45'W
46°30'W
46°15'W
NSO
SAN
PDP
MOO
IAG-USP
CCE
IPEN-USP
IBI
CON
SAM
AF-IAG
INT
5°S
10°S
15°S
20°S
25°S
30°S
35°S
60°W
50°W
40°W
30°W
20°W
d02
d03
1100
1000
900
800
700
600
500
400
300
200
100
0
Terrain Height
(m)


19 UTC
E_TOL (mol/km^2/hr)
22°30'S
23°S
23°30'S
24°S
24°30'S
48°W
47°30'W
47°W
46°30'W
46°W
45°30'W
45°W
40
36
32
28
24
20
16
12
8
4


Precipitation (mm) [red]
1.0
0.8
0.6
0.4
0.2
0.0
100
80
60
40
20
0
Humidity (%) [blue]
07/08
12/08
17/08
22/08
27/08
01/09
06/09

8/9/2012 3 tarde/noite

HYSPLIT

Minas Gerais

Espírito Santo

Mato Grosso do Sul

09/02/2012 18 UTC - 500 m

09/02/2012 18 UTC - 2000 m

Rio de Janeiro

09/02/2012 18 UTC - 1000 m

08/06/2012 18 UTC - 500 m

08/06/2012 18 UTC - 2000 m

Paraguai

Assunção

Paraná

Itapúa

Chaco

Santa Catarina

Iberá Wetlands

Rio Grande do Sul

Lagoa dos Patos

Rivera

Uruguai

Lagoa Mirim

08/28/2012 18 UTC - 500 m

08/28/2012 18 UTC - 1000 m

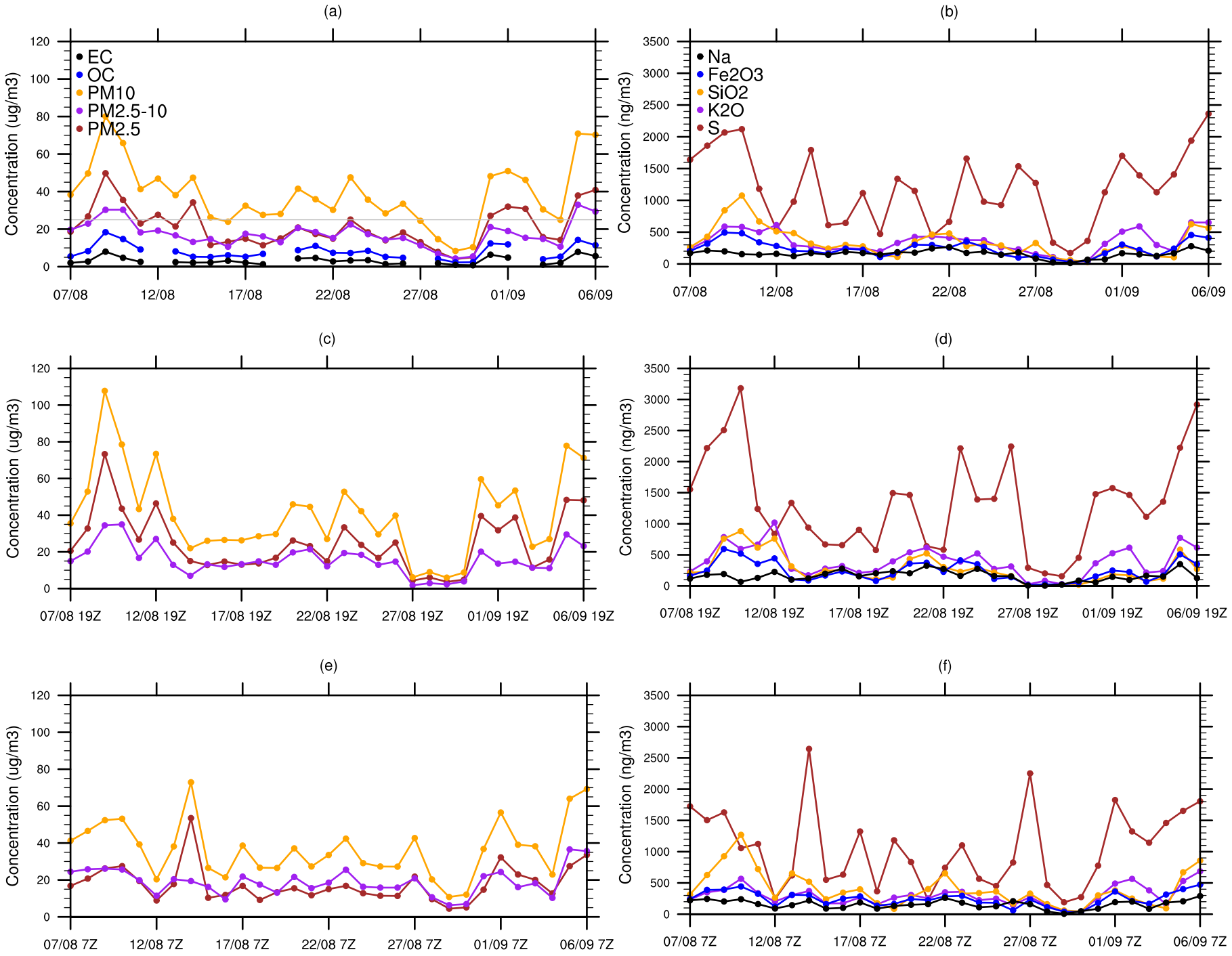
Monitoramento de Queimadas

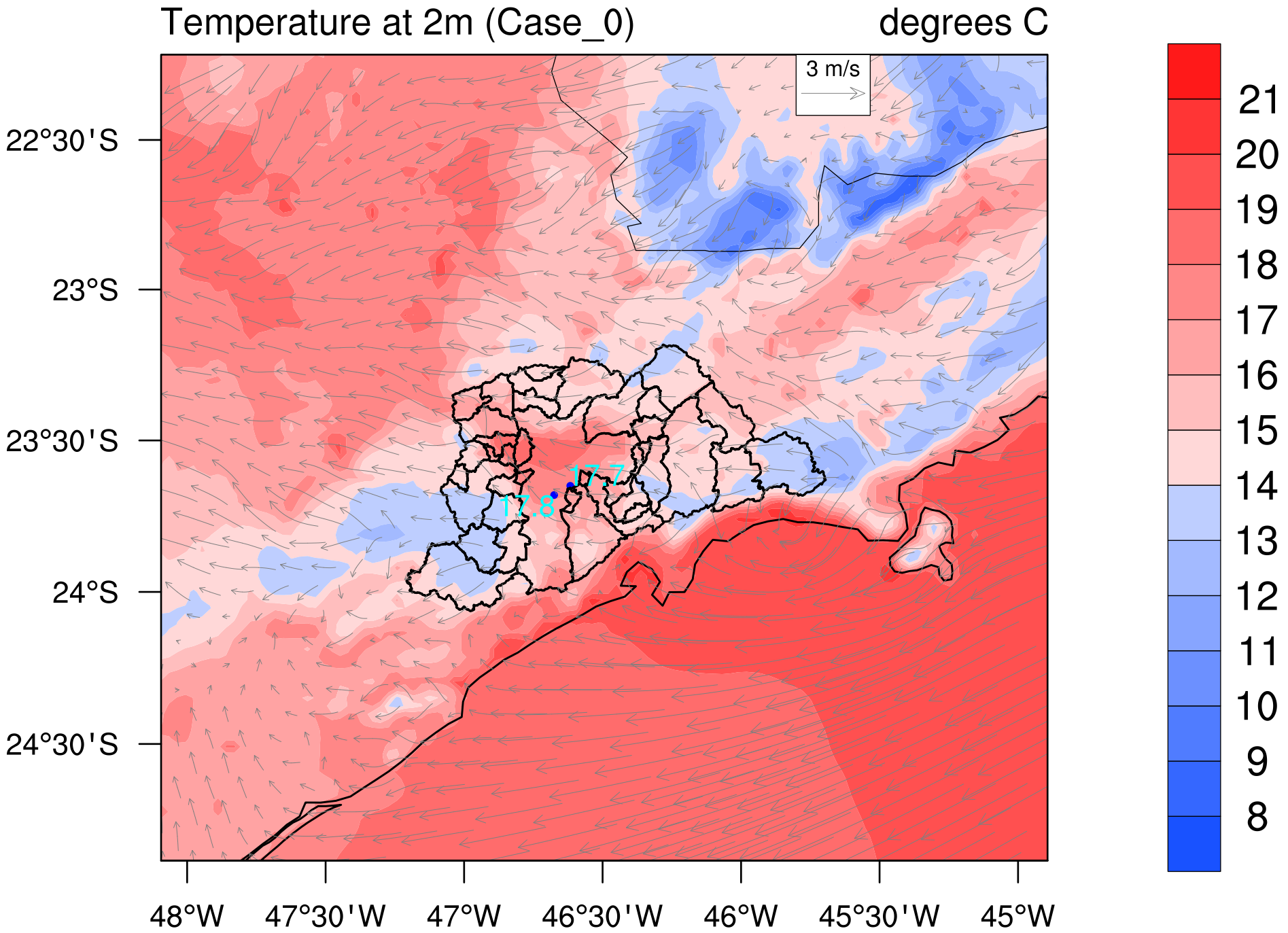
Legendas
- Goes
- Aqua
- Terra
- MModis-01D
- NOAA-12
- NOAA-12D
- NOAA-14
- NOAA-15
- NOAA-15D
- NOAA-17
- NOAA-18
- NOAA-18D
- Meteosat

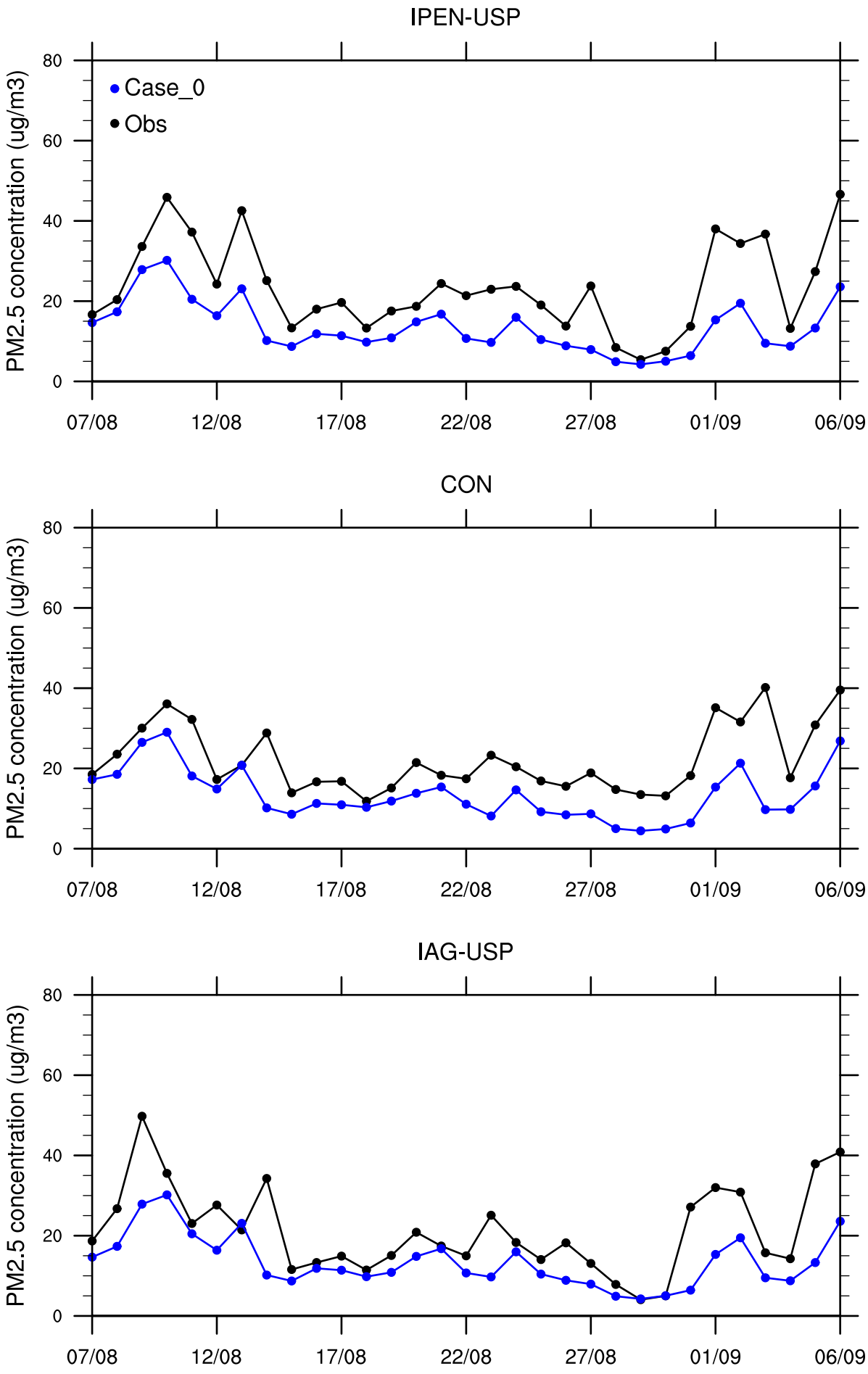
Image Landsat
© 2015 Google
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
US Dept of State Geographer

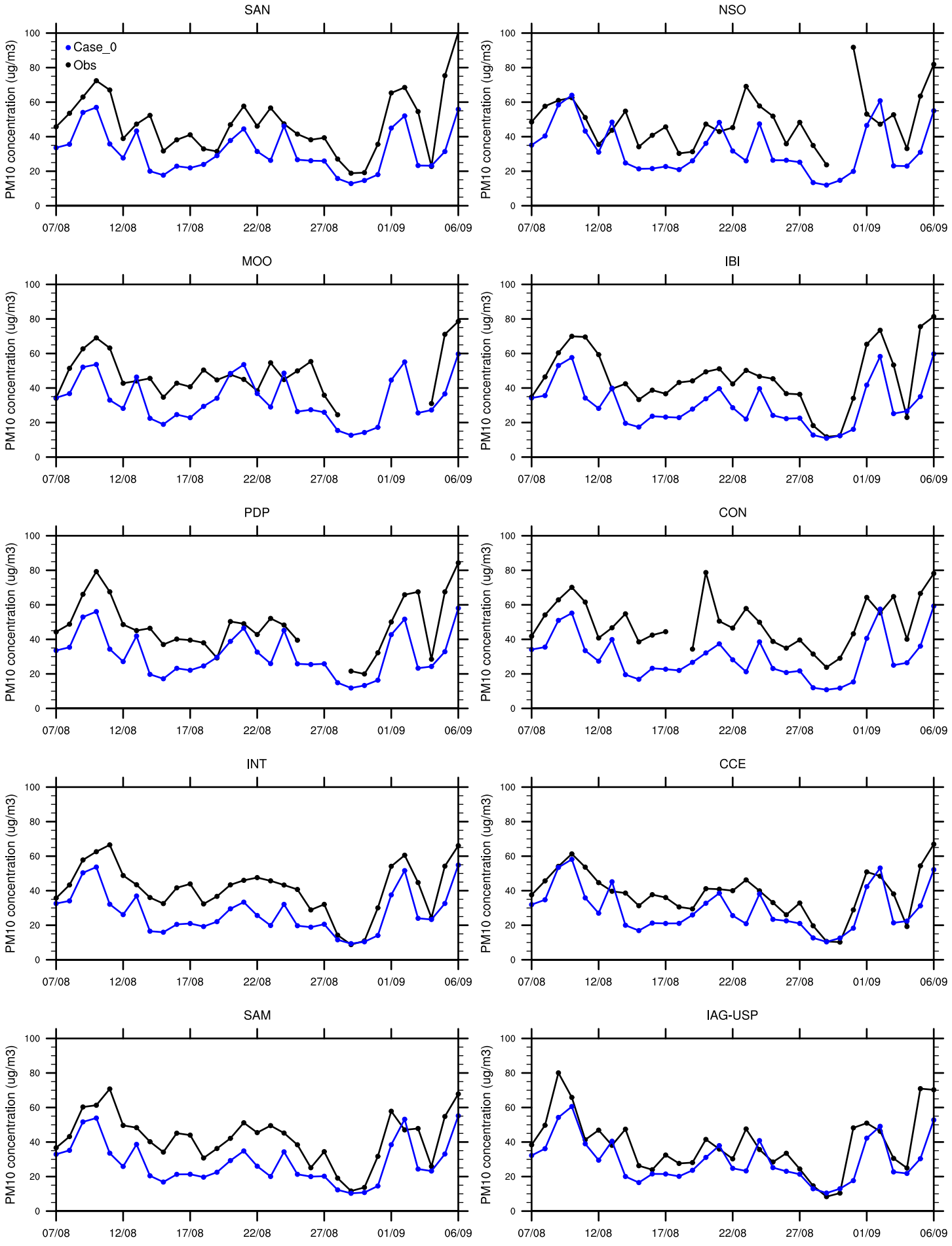
Google earth

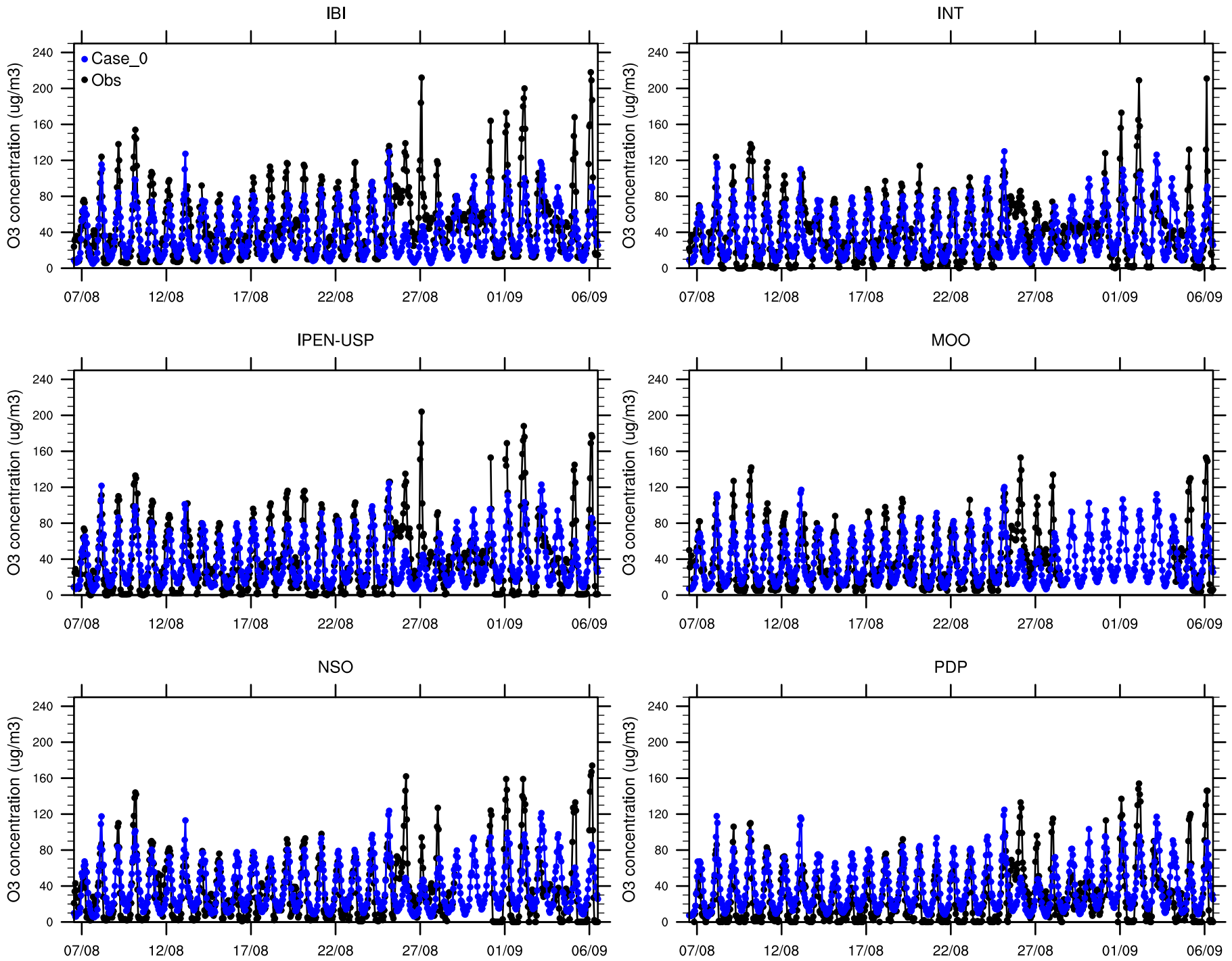
Data das imagens: 4/9/2013 lat -25.364396° lon -46.185469° elev -108 m altitude do ponto de visão 2297.00 km

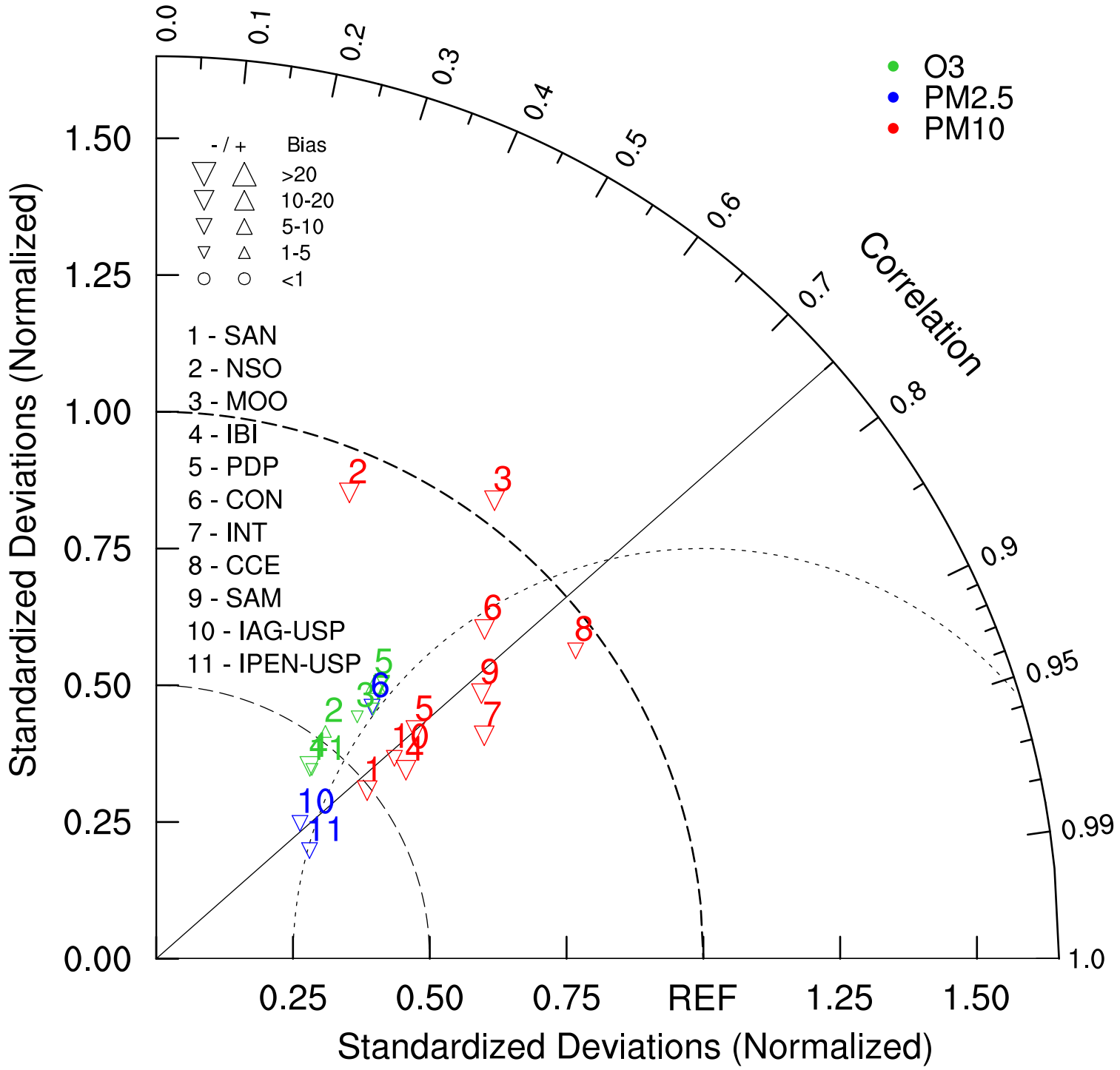

(a)
Concentration (ug/m3)
EC
OC
PM10
PM2.5-10
PM2.5
07/08
12/08
17/08
22/08
27/08
01/09
06/09
(b)
Concentration (ng/m3)
Na
Fe2O3
SiO2
K2O
S
(c)
Concentration (ug/m3)
07/08 19Z
12/08 19Z
17/08 19Z
22/08 19Z
27/08 19Z
01/09 19Z
06/09 19Z
(d)
Concentration (ng/m3)
(e)
Concentration (ug/m3)
07/08 7Z
12/08 7Z
17/08 7Z
22/08 7Z
27/08 7Z
01/09 7Z
06/09 7Z
(f)
Concentration (ng/m3)

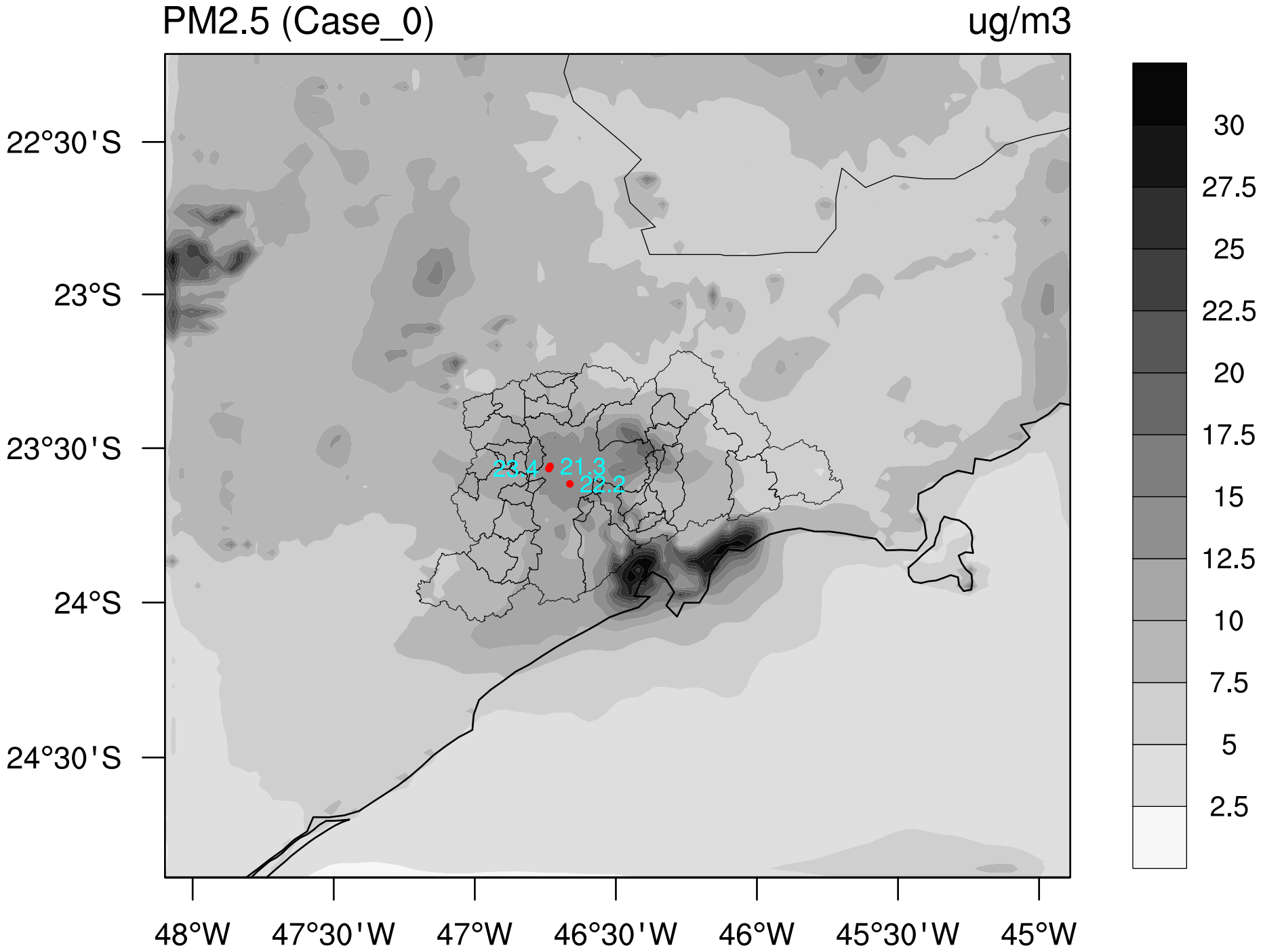

Temperature at 2m (Case_0)
degrees C
3 m/s
22°30'S
23°S
23°30'S
24°S
24°30'S
48°W
47°30'W
47°W
46°30'W
46°W
45°30'W
45°W
17.7
17.8
21
20
19
18
17
16
15
14
13
12
11
10
9
8

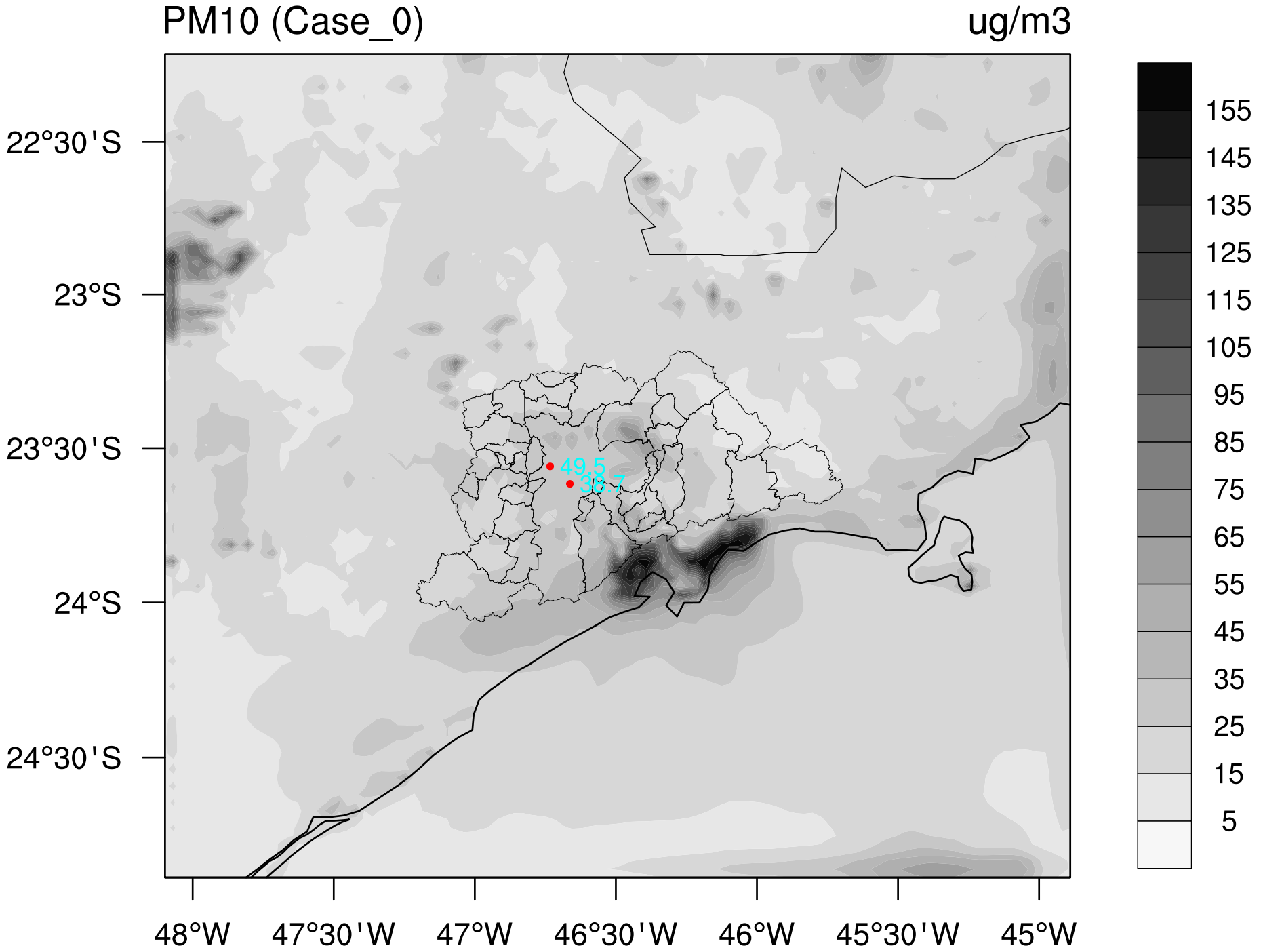

IPEN-USP
Case_0
Obs
PM2.5 concentration (ug/m3)
0
20
40
60
80
07/08
12/08
17/08
22/08
27/08
01/09
06/09
CON
PM2.5 concentration (ug/m3)
0
20
40
60
80
07/08
12/08
17/08
22/08
27/08
01/09
06/09
IAG-USP
PM2.5 concentration (ug/m3)
0
20
40
60
80
07/08
12/08
17/08
22/08
27/08
01/09
06/09

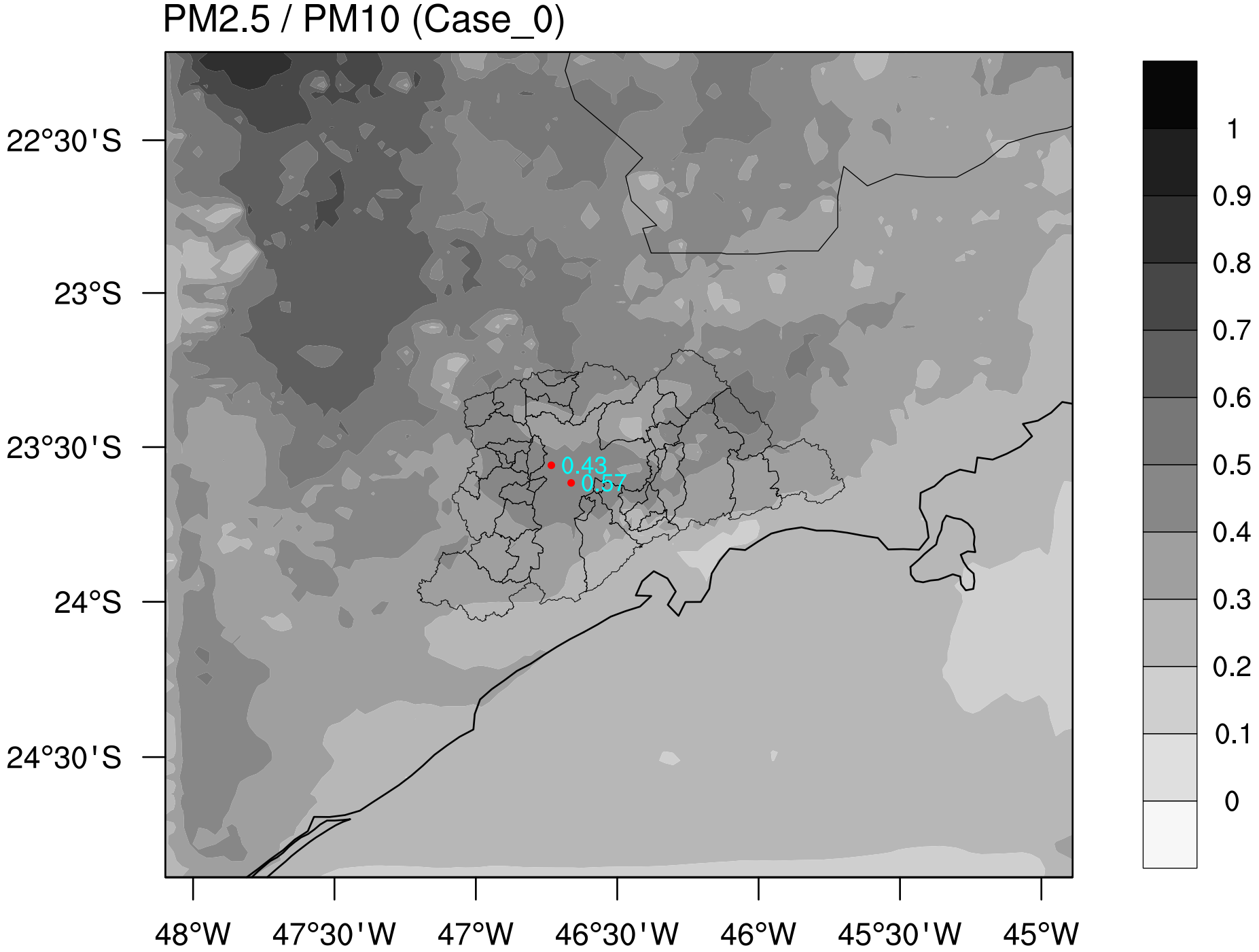

SAN
NSO
MOO
IBI
PDP
CON
INT
CCE
SAM
IAG-USP
Case_0
Obs
PM10 concentration (ug/m3)
0
20
40
60
80
100
07/08
12/08
17/08
22/08
27/08
01/09
06/09

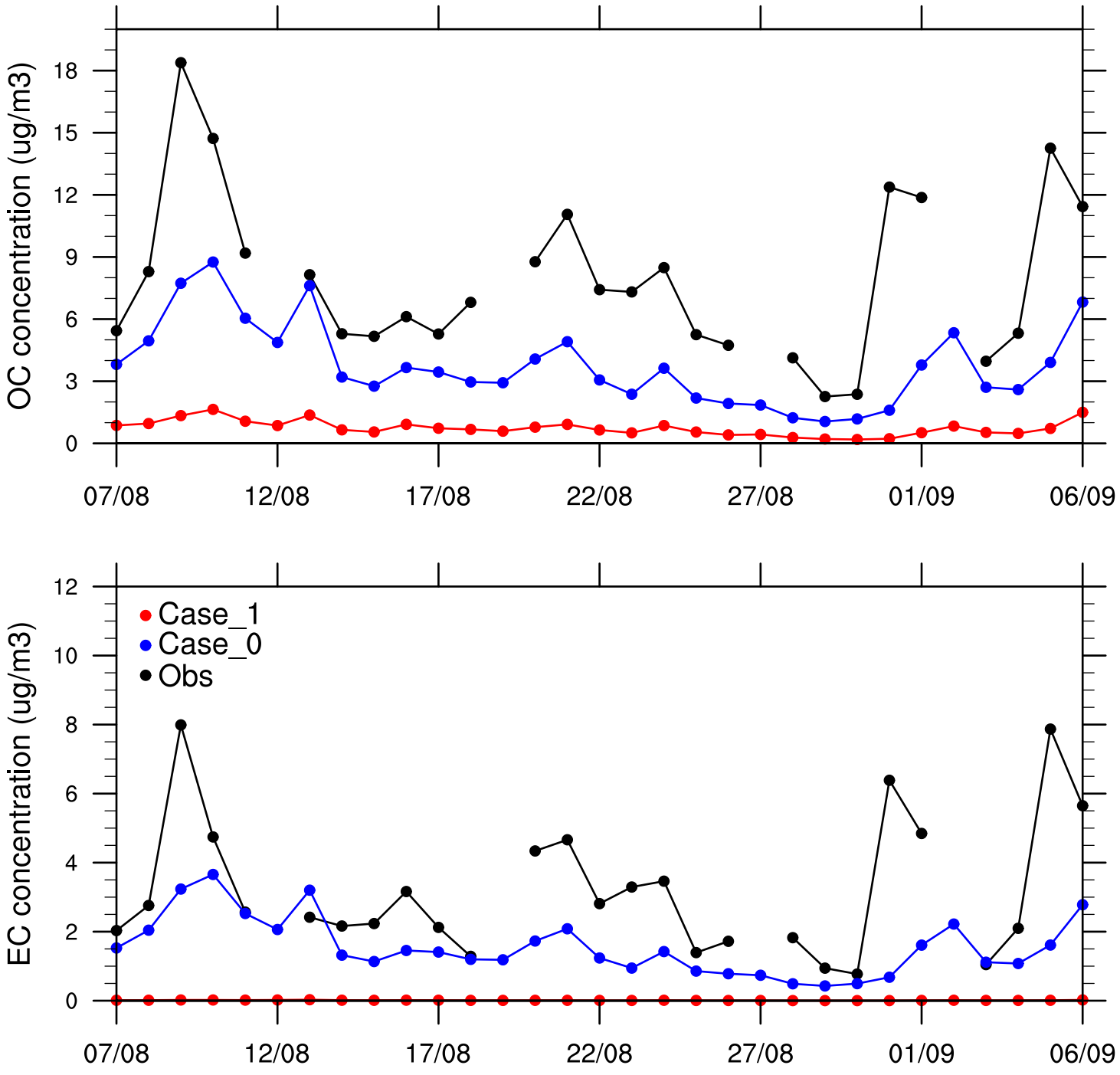

IBI
INT
IPEN-USP
MOO
NSO
PDP
Case_0
Obs
O3 concentration (ug/m3)
0
40
80
120
160
200
240
07/08
12/08
17/08
22/08
27/08
01/09
06/09

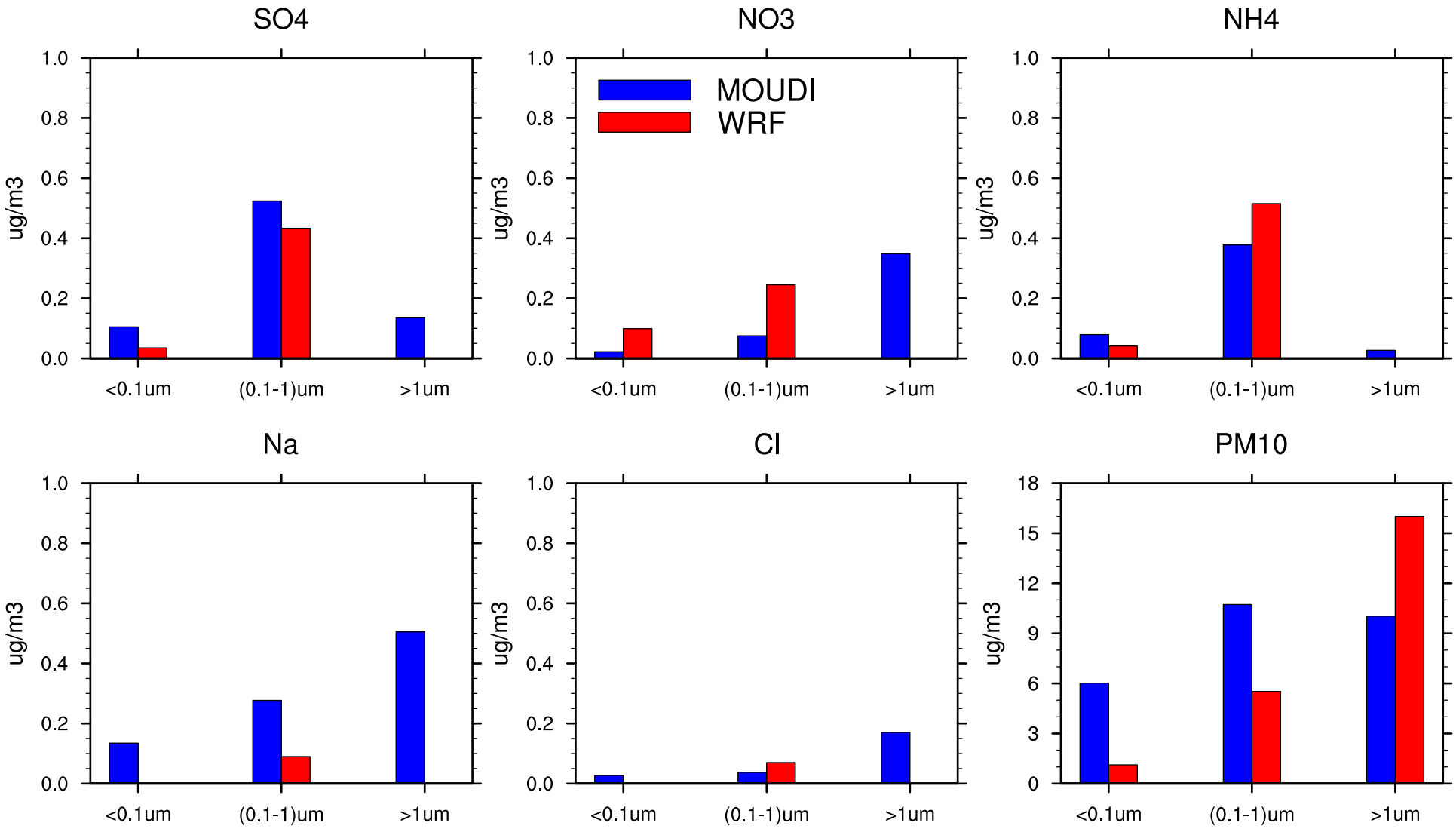

O3
PM2.5
PM10
- / + Bias
>20
10-20
5-10
1-5
<1
1 - SAN
2 - NSO
3 - MOO
4 - IBI
5 - PDP
6 - CON
7 - INT
8 - CCE
9 - SAM
10 - IAG-USP
11 - IPEN-USP
Correlation
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0.95
0.99
1.0
Standardized Deviations (Normalized)
0.00
0.25
0.50
0.75
1.00
1.25
1.50
REF
Standardized Deviations (Normalized)

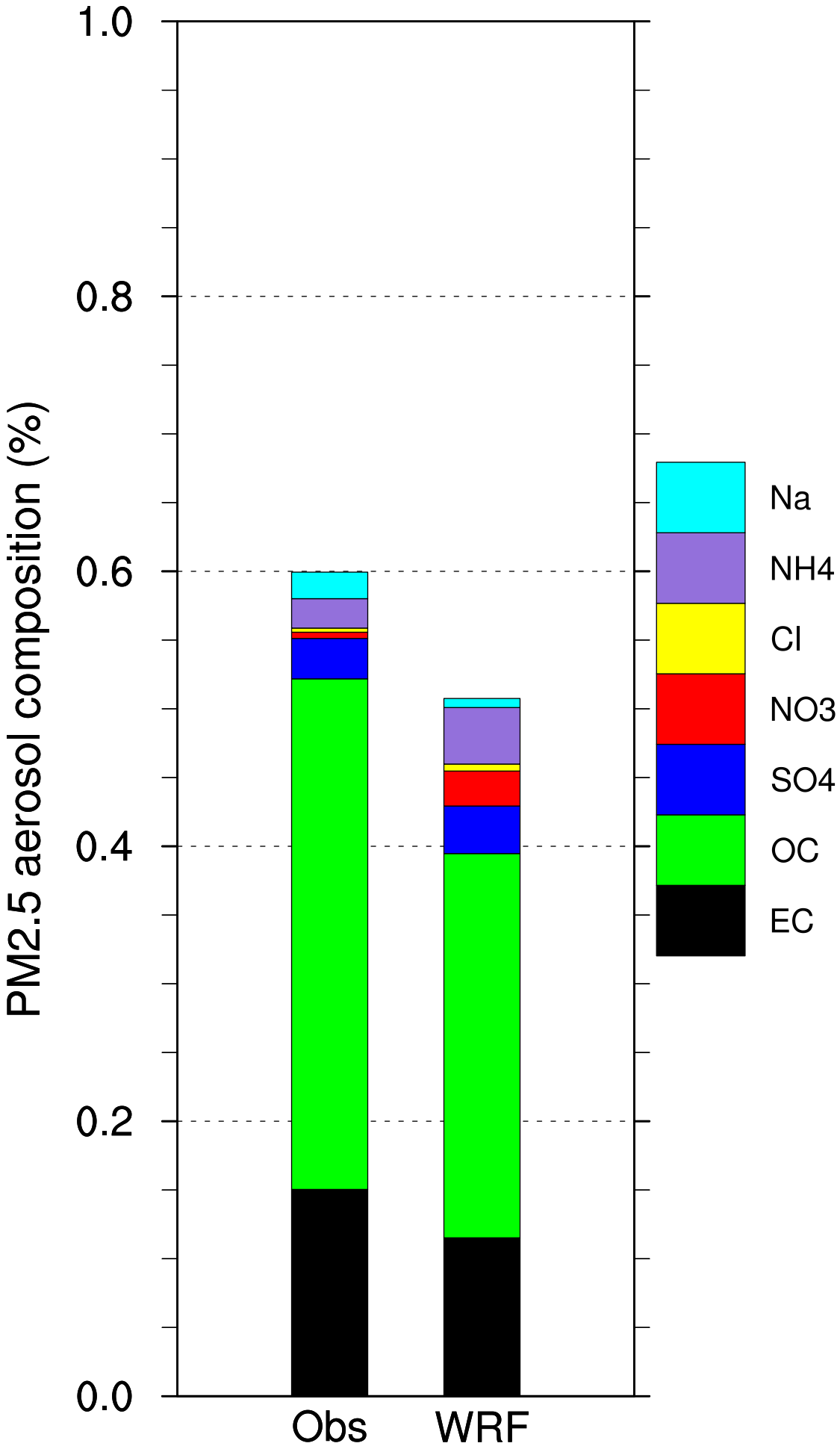

PM2.5 (Case_0)
ug/m3
22°30'S
23°S
23°30'S
24°S
24°30'S
48°W
47°30'W
47°W
46°30'W
46°W
45°30'W
45°W
23.4
21.3
22.2
30
27.5
25
22.5
20
17.5
15
12.5
10
7.5
5
2.5

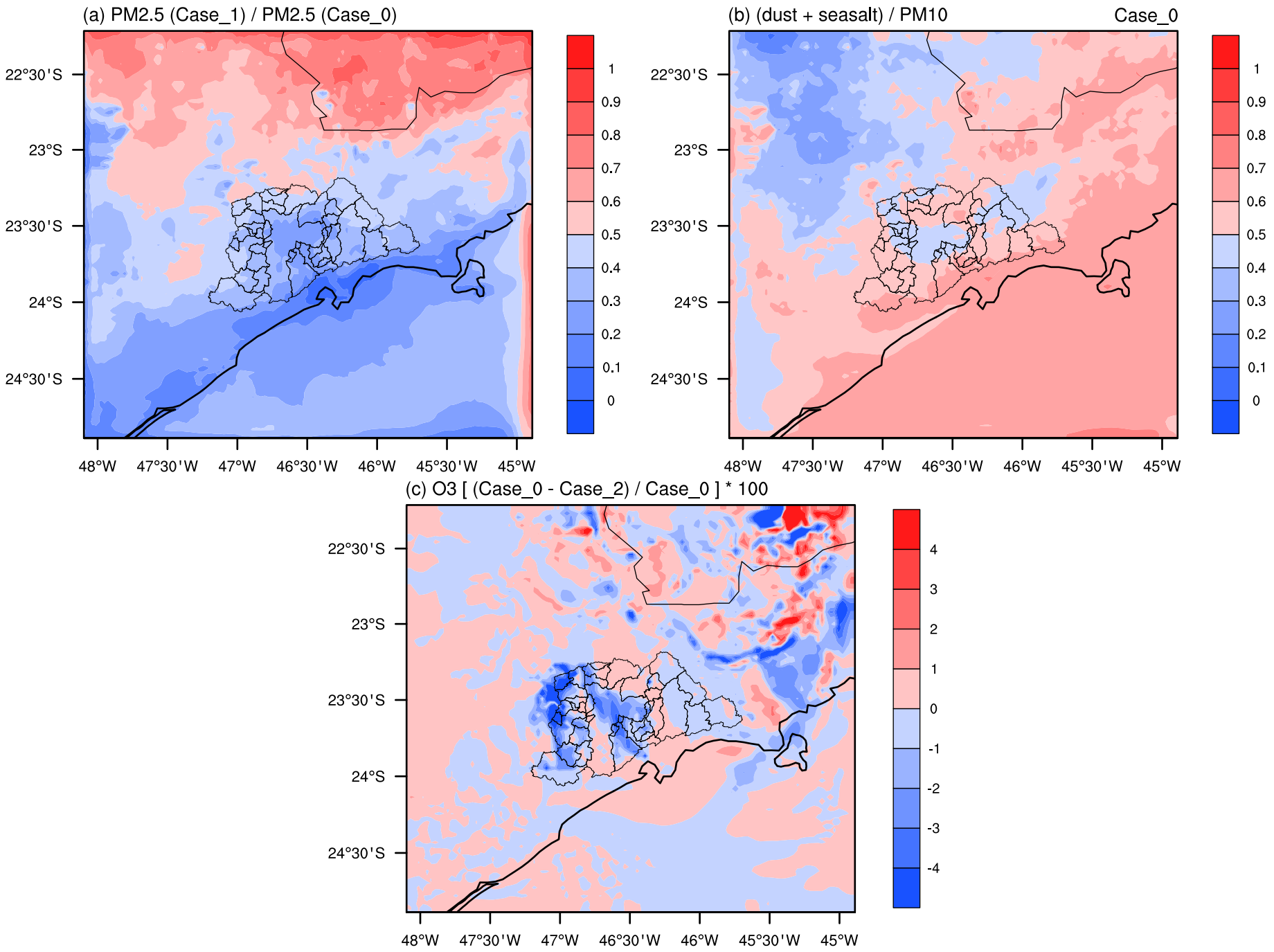

PM10 (Case_0)
ug/m3
22°30'S
23°S
23°30'S
24°S
24°30'S
48°W
47°30'W
47°W
46°30'W
46°W
45°30'W
45°W
49.5
38.7
155
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5


PM2.5 / PM10 (Case_0)
22°30'S
23°S
23°30'S
24°S
24°30'S
48°W
47°30'W
47°W
46°30'W
46°W
45°30'W
45°W
0.43
0.57
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0


OC concentration (ug/m3)
18
15
12
9
6
3
0
07/08
12/08
17/08
22/08
27/08
01/09
06/09
EC concentration (ug/m3)
12
10
8
6
4
2
0
Case_1
Case_0
Obs
07/08
12/08
17/08
22/08
27/08
01/09
06/09


SO4
NO3
NH4
Na
Cl
PM10
MOUDI
WRF
ug/m3
<0.1um
(0.1-1)um
>1um
0.0
0.2
0.4
0.6
0.8
1.0
0
3
6
9
12
15
18


1.0
0.8
0.6
0.4
0.2
0.0
PM2.5 aerosol composition (%)
Obs
WRF
Na
NH4
Cl
NO3
SO4
OC
EC


(a) PM2.5 (Case_1) / PM2.5 (Case_0)
(b) (dust + seasalt) / PM10
Case_0
(c) O3 [(Case_0 - Case_2) / Case_0] * 100
22°30'S
23°S
23°30'S
24°S
24°30'S
48°W
47°30'W
47°W
46°30'W
46°W
45°30'W
45°W
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4
3
2
1
0
-1
-2
-3
-4