Anonymous Referee # 1

Response to reviewer comments for the paper "Effect of local and remote sources and new particle formation events on the activation properties of cloud condensation nuclei in the Brazilian megacity of São Paulo".

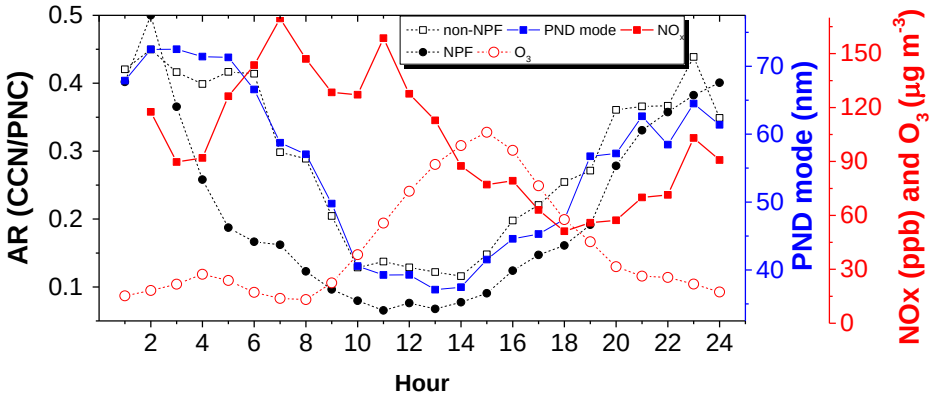
We thank the reviewer for valuable suggestions to improve our manuscript. We agree with the comments and made all the suggested modifications to our revised manuscript. Our responses to each of the comments (in black color) are provided below in blue color. We have highlighted the newly added text with a yellow color in the revised manuscript.

1. A major conclusion of the work is "local traffic emissions showed higher influence on activation parameters than remote sources". However, from Fig 8 to 11, I cannot see any data/information related to traffic source. From Fig 11, I will even conclude that remote sources (sea salt /biomass burning) had more significant influence on AR and Dact. These lead to a more serious problem of this work: the influencing sources of CCN were not clearly classified and many terms were used arbitrarily: diurnal, nocturnal, sea salt, biomass burning, NPF, non-NPF and traffic, the scopes of which overlap with each other. For example, in fig 11 and 10, why are diurnal/nocturnal and sea salt/biomburn put in the same figure? I think "diurnal" aerosols also received contributions from sea salt and biomass burning. Does "diurnal" here include both NPF and non-NPF? In Fig 11a, Fig 8b: "average" of what?

I strongly suggest the authors to state clearly which period (day or night) was dominated by which source. This could be possibly added in Table 1, since there are only 14 observation days. Then CCN properties should be calculated again according to the classification of influencing sources.

Response: In fact,we did not show information related to vehicular traffic in the figs. 8 to 11; hourly NOx average concentrations were added in figs. 9b and 1010, while NOx and CO mean in fig. 12b. The NOx and CO were measured by CETESB in a monitoring station at Marginal Tietê main road, which is distant about 4Km from the sampling site. The variability of NOx in this station is mainly associated with vehicular traffic, once fuel combustion of vehicles is the predominant source in this region. As can be seen in figs. 9b and 10c, NOx increase occurred during a first rush hour in the morning, which is clearly related with a decrease of particles diameter mode and AR (fig. 9b), and also with the increase of activation diameter (fig. 10c). Although the NOx decrease after midday is not associated with the decrease of traffic but with photochemical reactions and O_3 formation, briefly commented in Section 3.2, which contribute for secondary aerosol production. Therefore, NOx data corroborate the discussion presented in the next paragraph and included on page 15 in lines 13-19, which associated decrease and lower AR values during the day with vehicular traffic and secondary aerosol nucleation mainly.
The variability in NOx and CO concentrations measured at the Marginal Tietê is mainly associated with vehicular traffic, because fuel combustion is the predominant source of such pollutants in the MASP.As can be seen in Fig. 9b and Fig. 10c, an increase in NOx occurred during the morning rush and was clearly related to the decrease inAR and particle diameter mode (Fig. 9b), as well as to the increase in Dact (Fig. 10c). The NOx decrease after midday was not associated with the decrease in traffic volume but with photochemical reactions and secondary formation of pollutants, as previously discussed. We believe that

the NOx and O3 variability corroborates our assumption, explaining the decrease in AR values during the



diurnal period in the presence of high vehicular traffic volume and secondary aerosol formation.

Figure 9.(b) - Mean hourly AR (at a supersaturation of 0.4%) on days with and without NPF events, plotted together with particle size mode, nitrogen oxides (NO_x) and O_3 in order to evaluate the effect of vehicle emissions on particle size and AR. The AR values for nocturnal and diurnal showed clear differences, whereas days with NPF events presented slightly lower values than did days without. Two processes contribute to particle size and AR decrease, namely primary aerosol from vehicular traffic (NO_x) and secondary NPF formed in the afternoon. PND – particle number distribution.

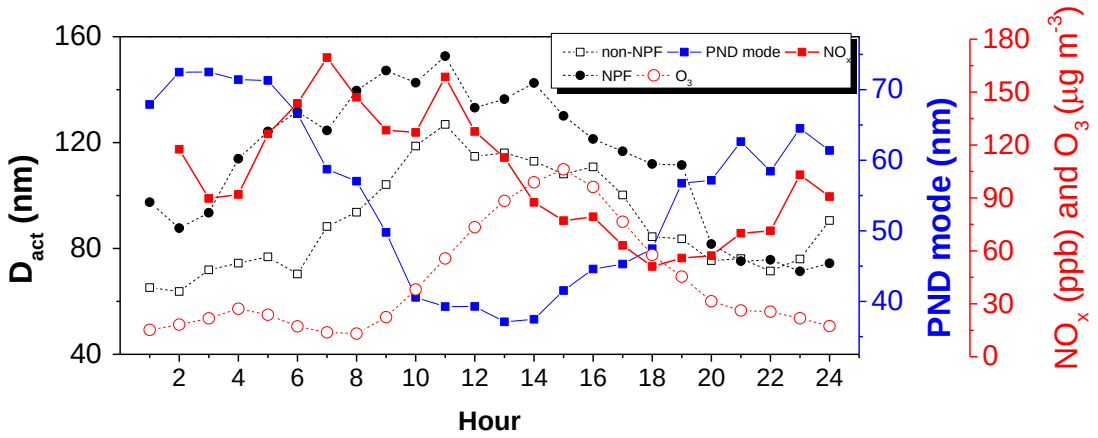


Figure 10. (c) - Time series of D_{act} on days with and without new particle formation (NPF) events, plotted together with particle size mode, NO_x and O_3. The D_{act} values were calculated for supersaturationof 0.4%. Biom burn – biomass burning; PND – particle number distribution.

We agree that sources of CCN was not clearly described, in order to improve the figs. 11 and 12, and show the influence of each remote source contribution, predominant in different periods, was marked in Table 1 the days under remote source and NPF events, based on sections 3.3 and 3.2 respectively. Local sources represented by vehicular emission, industrial and other sources were not showed on the table 1,

because this source present daily emission, being a background condition for urban aerosol at SPMA, consequently local sources apportionment were not discriminated in this study.

Table 1. Diurnal data for meteorological parameters(temperature, relative humidity and rain), particle number concentration and cloud condensation nuclei during the period evaluated (19 August to 3 September, 2014). Peak diameter was calculated by size distribution mode. The last column, represent periods with NPF events and remote sources influence on MASP atmosphere.

Day		Date	Temperature (ºC)	RH (%)	Rain	PNC (cm^{-3})		Dp (nm)	Cloud Condensation Nuclei (mean ± SD)					Remote Source* and NPF	
			mean (range)	mean (range)	(mm)	mean ± SD	(range)		SS = 0.2%	SS = 0.4%	SS = 0.6%	SS = 0.8%	SS = 1.0%	Diurnal	Nocturnal
1	Tue	8/19/14	15 (11 - 20)	83 (64 - 96)	0.0	7654 ± 4582	1874 - 16607	50	1688 ± 569	1809 ± 624	2270 ± 830	2555 ± 965	2811 ± 1029		
2	Wed	8/20/14	16 (11 - 23)	80 (43 - 98)	0.0	13086 ± 8242	3335 - 35398	45	2240 ± 780	2385 ± 961	2969 ± 1191	3431 ± 1371	3770 ± 1611		
3	Thu	8/21/14	18 (13 - 27)	70 (32 - 95)	0.0	14133 ± 7647	3360 - 27144	54	2683 ± 1019	3082 ± 1451	3726 ± 1715	4201 ± 1831	4562 ± 1933		
4	Fri	8/22/14	19 (12 - 28)	62 (30 - 92)	0.0	15921 ± 7935	5529 - 35508	73	3368 ± 2664	2487 ± 1034	3208 ± 1512	3699 ± 1766	3960 ± 1890		
5	Sat	8/23/14	20 (13 - 28)	58 (28 - 87)	0.0	15923 ± 7644	5595 - 32061	72	3889 ± 752	4708 ± 1309	5633 ± 1588	6296 ± 1800	6860 ± 1894		
6	Tue	8/26/14	19 (16 - 23)	76 (48 - 96)	1.3	13091 ± 4965	5758 - 26105	92	2765 ± 411	5135 ± 1908	5961 ± 2242	6343 ± 2336	6678 ± 2522		
7	Wed	8/27/14	15 (10 - 20)	79 (55 - 93)	0.1	8627 ± 4965	1924 - 20416	50	1103 ± 549	1444 ± 954	1822 ± 1304	2229 ± 1405	2507 ± 1592		
8	Thu	8/28/14	13 (10 - 18)	84 (62 - 96)	0.0	11313 ± 6449	4920 - 25556	42	1432 ± 438	2103 ± 1181	2672 ± 1388	3117 ± 1536	3538 ± 1702		
9	Fri	8/29/14	13 (12 - 16)	85 (74 - 91)	0.0	9873 ± 3751	5170 - 17513	37	1609 ± 275	2201 ± 529	2747 ± 723	3146 ± 823	3444 ± 861		
10	Sat	8/30/14	16 (12 - 22)	80 (48 - 94)	0.0	12601 ± 8315	4486 - 30528	53	1945 ± 384	3144 ± 1142	3856 ± 1380	4304 ± 1632	4734 ± 1743		
11	Sun	8/31/14	18 (14 - 30)	83 (30 - 96)	2.2	7078 ± 4543	2781 - 18794	63	1573 ± 679	2144 ± 998	2525 ± 1159	2800 ± 1277	3036 ± 1366		
12	Mon	9/1/14	19 (15 - 26)	75 (48 - 95)	0.1	11014 ± 8580	2196 - 31674	38	782 ± 661	1315 ± 1011	1959 ± 1273	2336 ± 1263	2757 ± 1510		
13	Tue	9/2/14	19 (14 - 27)	79 (46 - 96)	3.6	14842 ± 10075	2294 - 32152	67	2138 ± 661	3861 ± 1564	4718 ± 1922	5281 ± 2073	5757 ± 2135		
14	Wed	9/3/14	18 (15 - 25)	80 (57 - 96)	2.2	7713 ± 7303	1347 - 26928	29	609 ± 328	727 ± 428	981 ± 580	1237 ± 701	1523 ± 834		
Mean	-	-	**17 (10 - 30)**	**79 (28 - 98)**	**0.9**	**11634 ± 3077**	**1347 - 35508**	**55**	**1987 ± 942**	**2610 ± 1264**	**3218 ± 1435**	**3641 ± 1512**	**3996 ± 1572**		

RH – relative humidity; PNC – particle number concentration; Dp – peak diameter; NPF – new particle formation; SS – supersaturation; SD – standard deviation.

* Emissions from local sources (vehicular traffic, industrial activity, etc.) occur daily, primarily during the diurnal period, and such sources were therefore excluded.

Days with NPF events

Remote source apportionment

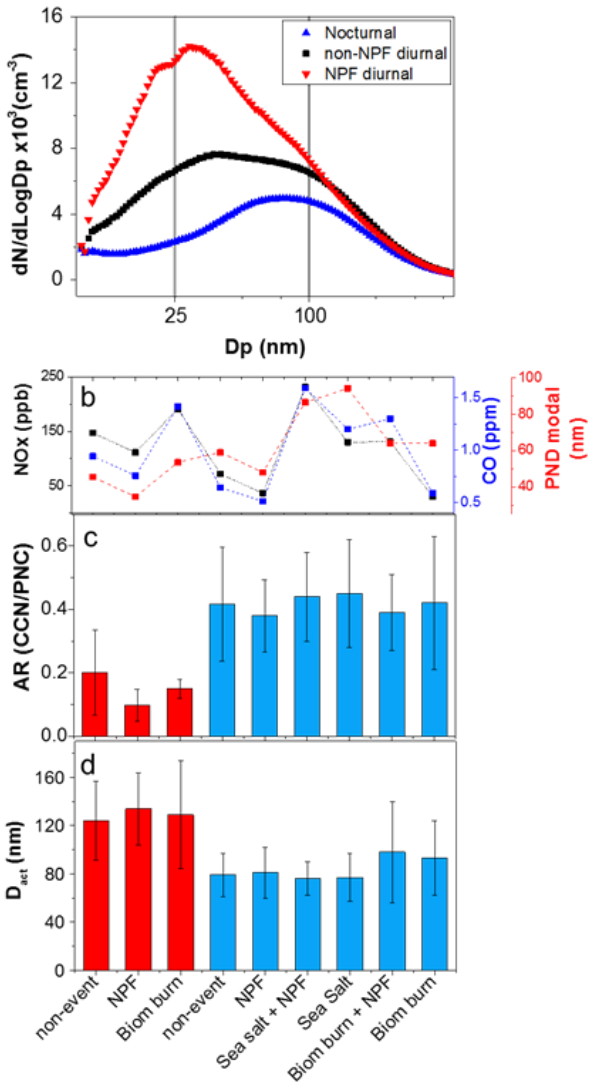
Sea salt **Biomass burning**

Based on days with and without the NPF as well as remote source events, CCN activation properties were recalculated, as shown in figs. 12c and d. The CCN activation properties related to event and non-event days were calculated for diurnal and nocturnal periods and represented in red and blue colors respectively. In addition, were separated means of nocturnal periods after NPF and non-NPF days, in order to evaluate the effects of particles formed during NPF after growth and also exclude this possible effect during biomass burning and sea salt events. Another, information is related to vehicular traffic variability, which was represented by NO_x and CO in Fig. 12b. New discussion related to Fig.12 was included on page 4 in lines 6-26 and also showed on the next two paragraphs.

On the basis of our data for diurnal and nocturnal periods with and without NPF and remote source events, we calculated the mean AR and Dact for specific periods (Fig. 12c and Fig. 12d), in order to identifythe influence thatdifferent events have onCCN activation. The CCN activation properties related to event and non-event days were calculated for the diurnal and nocturnal periods. The variability for diurnal and nocturnal periods was taken into account, and the events were calculated for each period. In addition, we calculated the mean AR and Dactvalues fornocturnal periods after NPF and non-NPF days,in order to evaluate the effects of NPF on CCN activation. Another important information is the variability in the volume of vehicular traffic, asestimated from the meanNOx and CO values(Fig. 12b), which was previouslyassociated with decreasedCCN activation. The overestimation of the volume ofvehicular traffic can result in the underestimation of effects of remote source events onCCN activation.

As can be seen in Fig.12c, diurnal periods with NPF showed lower AR values than did biomassburning and non-event days. However, AR values were similar among nights after NPF with those non-event and sea salt influence nights and also biomass burning after NPF events. The nocturnal increase in AR after NPF events was related to particle growth (Fig. 12c). Lower AR for nocturnal periods with sea-salt influence after NPF can be attributed to smaller particle size, whereas sea-salt events in these nocturnal periods occurred after low-O3 NPF events (on days 7 and 8). As previously discussed, low-O3 NPFevents were characterised by the formation ofparticles that were smaller than those formed during high-O3NPFevents. The effect of another sea-salt event (day 4) onCCN activation might have been underestimated due tohigh traffic volume during thenocturnal period, as indicated by high concentrations of NOx and CO. The AR values were slightly lower during diurnal and nocturnal periods with biomass burning plumes only (i.e. without NPF events) than during those with non-events. In addition, during the nocturnal periods, the biomass-burning events promotedslightly higher Dact values than did NPF and sea salt, which is attributable to lower particle hygroscopicity. Although there was a lack of statistical significance, weobserved atendency forbiomass burningaffected air masses arriving at the MASP to decrease the activation properties.

Figure 12. (a) Average diurnal and nocturnal particle size.Average of CO, NOxand modal particle size(b), theactivated ratio (c) and diameter activation (d) for diurnal and nocturnal periods, as well during NPF, biomass burning and sea salt events.The diurnal period is showed in red and nocturnal in



blue.Average for event-NPF were calculated for nights after NPF events.

2. The current source apportionment is not persuasive and could be a weakness of this work. Three sources were identified: biomass burning, seasalt, and vehicle emission. Industrial source was mentioned a few times in the manuscript, but was omitted in the data analysis. Then the “diurnal” is equivalent, by the authors, to local vehicular emission. It is not shown in the text what elements were analyzed with X-ray Fluorescence. Will these elements together with BC allow a more precise source apportionment?

Response: Some paragraphs were rephrased in section 3.3 in order to improve discussion, additionally title of this session was changed to **apportionment of biomass burning and sea salt remote sources,** to state more clearly the objectives of this section, related to the identification of biomass burning and sea-salt influence associated with local pollution sources for MASP aerosol.

In the next two paragraphs follow examples of reviewed paragraphs of section 3.3.

A combination of lidar, HYSPLIT trajectory and size-distributed chemical composition(Na, Ca, Ti, K, Cl P, Fe, Mn, Pb, Cu, Zn, S and BC) analyses were used in order to apportion the contribution of sea-salt and biomass burning withinthe air masses arriving at the MASP. Over the past 30 years, variousstudies conducted in the MASP have employed receptor modelling and aerosol chemical composition analysis in order to identify the main sources of atmospheric pollutants (Bouéres and Orsini, 1981; Andrade et al., 1994; Castanho and Artaxo, 2001; Sanchez-Ccoyllo and Andrade, 2002; Sanchez-Ccoyllo et al., 2008; Andrade et al., 2012). Those studies have determinedthat vehicle emissions account for 50–60% of fine particles, thus constitutingthe main source, followed by oil boilers (accounting for 20–40%), road dust (accounting for 10–30%), industrial emissions(accounting for 10–20%), biomass burning (accounting for 10–20%) and construction activities (accounting for ~10%). Some studies carried on in the MASP evaluated the elemental profiles of the principal urban pollution sources, characterising observed elements such as Mn, Pt, Ni, Cu, Pb, Cr and Zn as markers of gasoline and alcohol emissions (Silva et al.,2010). Diesel burning byheavy-duty vehicles is associated mainlywith BC and S. Suspended road dust, characterised inside and outside road tunnels, has been found to becomprise BC, Si, Al, Fe, Ca, Mg, K, Ti and S, which denotes a mixture of soil, pavement abrasion, tire wear, brakewear and vehicular emission (Hetem and Andrade 2016). In a general approach, other studies found BC to be related to biomass burning;Na and Cl to be related to sea-salt contribution; and Fe, Cu, Zn, Cr, Pb and Ni to be related to industrial emissions (Bzdek et al., 2012; Calvo et al., 2013; Taiwo et al., 2014).

Local pollution sources presents acontinuous contribution to atmospheric aerosol, functioning as background toMASP aerosol, emission of which are higher emission during the diurnal period and lowerduring nocturnal period, as demonstrated by the PNC variability (Fig. 2). The objective of this study was not todiscriminate amongthe main local sources but rather to identify periods during which remote sources were detectable, in order to evaluate how CCN activation properties are affected by such sources, in association with local sources, which cannot be excluded during urban aerosol measurements.

3. Some judgments made in the abstract are not well supported and probably biased. “weak effects of sea-salt and biomass burning aerosols could be observed on activation parameters as sea-salt showed a positive feedback” "vehicular traffic presented most negative effect on CCN activation." “NPF events showed a negative feedback to CCN activation.

First, it was not defined in the text what is negative feedback or positive feedback?
compared with what? second, from the Figures I would say sea salt has significant feedback on CCN parameters , but why is the effect claimed to be “weak”? third, it is generally accepted that NPF will eventually has positive contribution to CCN number. it is thus misleading to say NPF showed negative feedback to CCN activation.

Response: The abstract was rewritten in order to correct some not well supported or biassed information as follow.

Atmospheric aerosol is the primary source of cloud condensation nuclei (CCN). The microphysics and chemical composition of aerosols can affect cloud development and the precipitation process. Among studies conducted in Latin America, only a handful have reported the impact of urban aerosol on CCN activation parameters such as activation ratio (AR) and activation diameter (Dact). With over 20 million inhabitants, the Metropolitan Area of São Paulo (MASP) is the largest megacity in South America. To our knowledge, this is the first study to assess the impact that remote sources and new particle formation (NPF) events have on CCN activation properties in a South American megacity. The measurements were conducted in the MASP between August and September 2014. We measured the CCN within the 0.2–1.0% range of supersaturation, together with particle number concentration (PNC) and particle number distribution (PND), as well as trace-element concentrations and black carbon (BC). NPF events were identified on 35% of the sampling days. Combining TEC and BC data with an aerosol profile from Lidarand HYSPLITmodel analyses allowed us to identify the contribution of sea salt and biomass burning from remote regions on 28% and 21% of the sampling days, respectively. The AR and Dact parameters showed distinct patterns for diurnal and nocturnal periods. For example, CCN activation was lower during the diurnal periods than during the nocturnal periods, a pattern that was found to be associated mainly with local road traffic emissions. A decrease in CCN activation was observed on the NPF event days, mainly due to high concentrations of particles with smaller diameters. We also found that aerosols from sea salt and biomass burning had minor effects on Dact. For example, nights with biomass burning showed slightly higher Dactvalues than did non-event nights. Our results show that particulate matter from local pollution sources, mainly local road traffic emissions, has a greater effect on CCN activation parameters than those from remote sources.

4. Activation Ratio is discussed in this work and shown to have a negative "feedback". But what about CCN number increase/enhancement due to a NPF event? how is it when compared to non-NPF or local/remote episodes?

Response: In order to account CCN number enhancement during NPF, days were plotted CCN number mean for NPF and non-NPF days in Figure S2, which was included on Supplementary Information. Could be observed the enhancement of CCN number at nights after NPF events (Fig. S2), caused by th growth of high particle number formed during NPF, being this observation supported by previous studies by experimental measurements or modelling (Sihto et al., 2011). These new text was included in the discussions (page 14, lines 17-21) as follow.

In the present study,the AR increased substantially after each NPF event,although it was still lower than that observed on thenon-event days. In addition, weobserved increase in the number of CCN during thenocturnal periods after NPF events, as showed in Supplementary Information (Fig. S3), attributed tothe high rate of growth amongtheparticlesformed during NPF, an observation that is supported by previous studies (Sihto et al., 2011; Yue et al., 2011; Peng et al., 2014).

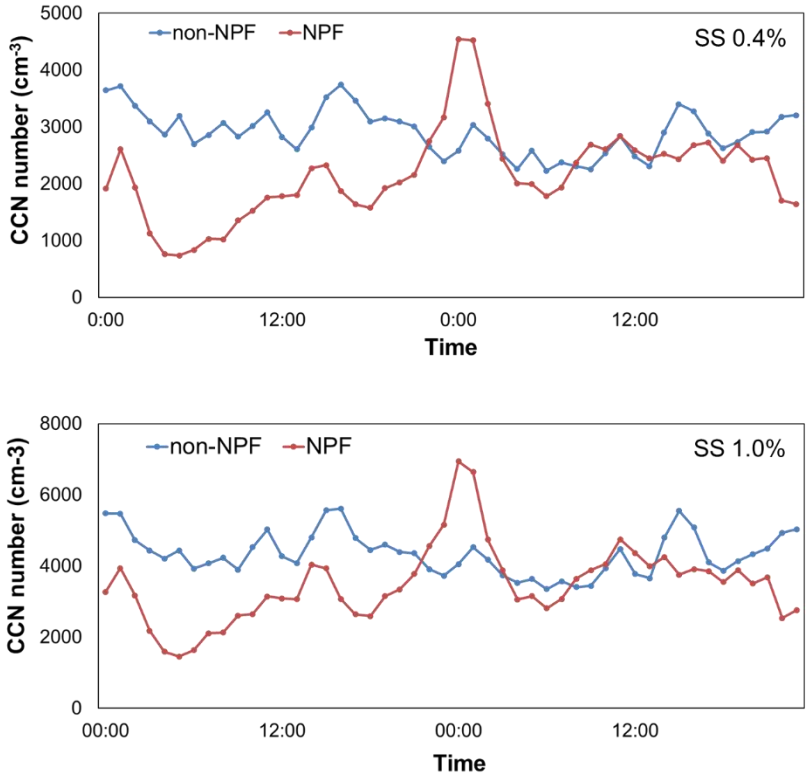


Figure S2. CCN number concentrations during NPF and non-NPF days. CCN averages were calculated for the48h period, being the first day select as NPF or non-NPF, while the second day was not considerate in this classification. During NPF days the CCN number is lower than non-NPF days in agreement with theprevious discussion about AR showed in Fig. 8. In this figure can be seen clearly the enhancement of CCN number for NPF days in comparison with non-NPF followed by similar values on the second day.

5. Other specific comments include:

1. There are many very short paragraphs in the text (like in Section 3.1 and 3.3). They should be reorganized.

2. Some terminology may not be used correctly: “Diurnal” or “daytime”? Page 2 line 26: hygroscope compounds Page 4 line 18: alcohol vapour Page 10 line 2: “frequency of hourly PNCs in three modes”, "frequency" or “percentage"?

3. Page 4 line 25-29: is the correction factor 1.3 or 1.15?

4. Some literature citations should be moved to Introduction section, like page 8 line 24-28.

5. Page 15 line 20: “It can be observed that nocturnal samples are most related with water soluble species as (NH4)2SO4, SOA, NO3- and marine air than the diurnal aerosol.”——— This is obviously not your observation.

6. There are many other typo- or grammar mistakes in the manuscript.

Response: Other specific comments:

1. The short paragraphs were reorganized improving the text structure.

All the specific comments as well as rewrite or new paragraphs are plotted in yellow crosshatch in the paper revised version.

2. Diurnal and Nocturnal periods are related to events occurred during daytime and night-time respectively. All other indicate corrections were made.

3. The correction factor employed was 1.3, additional test explaining this factor assurance has now been removed to avoid confusion. In addition, the paragraph was rephrased (page 5, lines 20-25) as follow.

Determining PNCs from the DMPS has been found to result in the undercounting of particles during ambient measurements, mainly due to lower DMA transfer probability or deviation in sampling and sheath flow rates (Almeida et al., 2014). Another deviation is related to the different diameter size range of particles measured by the DMPS (10–450 nm) and CCN (<10 µm), which can lead to overestimation of AR values, as calculated from the CCN/PNC ratio. A correction factor of 1.3 was applied to the entire data set in order to correct for undercounting during the measurement of PNCs and for overestimation of the AR. That factor was obtained by linear fitting of scatter plot data (CCN versus PNC) with AR values>1.

4. As suggested, some text and citations were moved for introduction section

5. As suggested, we have re-written this phrase (page 16, lines 28-31) as follow.

Our observations support the assumption that nocturnal samples typically comprise greater concentrations of water soluble species, such as (NH4)2SO4, SOA, NO3−, and of marine air than do diurnal samples. Our findings are also in keeping with those of other studies showing that aged aerosols present high hygroscopicity (Gunthe et al., 2011; Bougiatioti et al., 2011).

6. We have read the text of the manuscript to remove any grammaltical infelicities.

Anonymous Referee # 2

Response to reviewer's comments for the paper "Effect of local and remote sources and new particle formation events on the activation properties of cloud condensation nuclei in the Brazilian megacity of São Paulo".

We thank the reviewer for valuable suggestions to improve our manuscript. We agree with the comments and made all the suggested modifications to our revised manuscript. Our responses to each of the reviewer comments (in black color) are provided below in blue color. We have highlighted the newly added text with a green color in the revised manuscript.

Section 2 - I think that the methodology section is relatively well described. The only thing I am a bit skeptical is the discussion about the correction needed for DMPS measurements (lines 22-28 on page 4). Applying a correction factor appears justified due to potential undercounting of particles. However, the fact that the system does not measure particles larger than 450 nm in diameter is expected to have a negligible effect on this phenomenon (because the fraction of particle number at those size is very small). The authors might consider modifying the text a bit

Response: The text above about DMPS measurements corrections was rephrased in order to clarify the importance of correction related to AR overestimation.

The aerosol size distribution was measured in the 10–450 nm range, particles being scanned in 22 diameter size bins, with a 5-min time resolution. The gas sample and sheath flow rate were 1.0 and 6.0 L min^{-1}, respectively. Determining PNCs from the SMPS has been found to result in the undercounting of particles during ambient measurements, mainly due to lower DMA transfer probability or deviation in sampling and sheath flow rates (Almeida et al., 2014). Another deviation is related to the different diameter size range of particles measured by the SMPS (10–450 nm) and CCN (<10 µm), which can lead to overestimation of AR values, as calculated from the CCN/PNC ratio. A correction factor of 1.3 was applied to the entire data set in order to correct for undercounting during the measurement of PNCs and for overestimation of the AR. That factor was obtained by linear fitting of scatter plot data (CCN versus PNC) with AR values>1.

Section 3.1 The comparison of PNC and CCN concentrations to other studies should be made scientifically, not just reporting whether the concentrations observed in other studies had been higher or lower. I recommend that the numerical values of these concentrations, along with those obtained in other studies, will be collected in a Table. There no sense of giving all these numbers in text, rather the text should concentrated on analyzing the differences between this and other studies, and the meaning of these differences.

I understand that the authors compare their PNC data to the earlier Sao Paulo data, but I do not understand the comparison to the Vienna data. Why Vienna and no otherurban sites? Also, a reference to Vienna data is missing. I would like to see more urban sites in this PNC comparison.

The comparison needs some logic. There are apparently urban regions of different pollution levels. Is there any systematic pattern between the level of pollution and PNC or CCN concentration? There is enough information in the literature, the authors simply need to have a look at that.

Response: In order to improve the comparison of PCN and CCN values of this study, were selected recent studies conducted in urban regions. All values were showed in Fig. 2. Additional information about this regions and studies as well PCN and CCN numerical values, were collected in table S1 and included in the Supplementary information. The text about comparisons and discussion are showed in the follow paragraphs, which were included in the revised version of manuscript (page 8, lines 26-32 and page 9, lines 1-25).

To compare our PNC and CCN values with those of other studies, we plotted our results against the results of recent studies conducted in other urban regions (Fig. 3, Table S1 on Supplementary Information). The PNCs were higher during the diurnal period than during the nocturnal period, whereas, CCN concentrations were comparable between the two periods. The higher PNCs during the diurnal period were expected, given the increased emission of pollutants from local sources such as vehicular traffic. However, the fact that CCN concentrations did not vary significantly between the nocturnal and diurnal periods indicates that CCN formation was more efficient during the nocturnal period. In a study conducted in Beijing, Gunthe et al. (2011) reported similar behavior for fresh pollutant emissions and regional aged pollution, the latter presenting higher efficiency for CCN formation, as evidenced by lower PNCs and higher CCN concentrations. Those observations are supported by Köhler theory predictions, related to the greater efficiency of larger particles in CCN formation, which is extensively discussed in section 3.4.

The overall mean PNC and CCN values obtained in the present study were similar to those observed by Almeida et al. (2014) for the MASP during October 2012. However, our PNC values were lower than those reported for the MASP by Backman et al. (2012) for October 2010 and January 2011. This variability can be attributed to different meteorological conditions, seasonal differences and the decrease in SO_2 emissions associated with the recently mandated reduction in sulphur concentrations in diesel fuel (Kumar et al., 2016; CETESB, 2015). In a study conducted in Shanghai, Leng et al. (2013) reported PNC values similar to those obtained for the SPMA in the present study, although the CCN concentrations reported by those authors were higher; that might be related to the coastal environment, which increases the concentrations of most soluble compounds, such as ionic species (SO_4^{-2}, NO_3^-, Na^+, Cl^-, K^+), in the aerosol chemical composition. Our results showed PNC values similar to those observed for London and Madrid (Reche et al., 2011; Gómez-Moreno et al., 2011, respectively). In these three urban areas (London, Madrid and the MASP),transport emissions constitute the main pollution source and there are light industries around urban regions. London and Madrid have higher population densities than does the MASP. However, the vehicle fleet in the SPMA is larger than is that in any of the other urban regions evaluated, although Madrid has the highest vehicle/inhabitant ratio and the highest proportion of diesel-

powered vehicles (~50%). With a population of over 20 million, Mexico City is the largest megacity in North America. Although comparable to the MASP, the mean PNC for Mexico City in 2006 was double that reported for the 2012–2014 period in the MASP (Kalafut-Pettibone et al., 2011; Almeida et al., 2014; This study). Nevertheless, the mean PNC reported for Mexico City was similar to that observed for 2010 in the MASP (Backman et al., 2010). As previously mentioned, the lower PNCs in the MASP can be attributed to legislation that mandated a reduction in the concentration of sulphur in diesel fuel. The CETESB reported a ~10% reduction in the emission of particulate matter from diesel-powered vehicles between 2010 and 2015. In the MASP, such vehicles emitted 26% of all particulate matter attributed to anthropogenic sources during 2015 (CETESB 2016). In the case of Mexico City, 50% of all particulate emissions in 2006 were from diesel-powered vehicles (Kalafut-Pettibone et al., 2011).

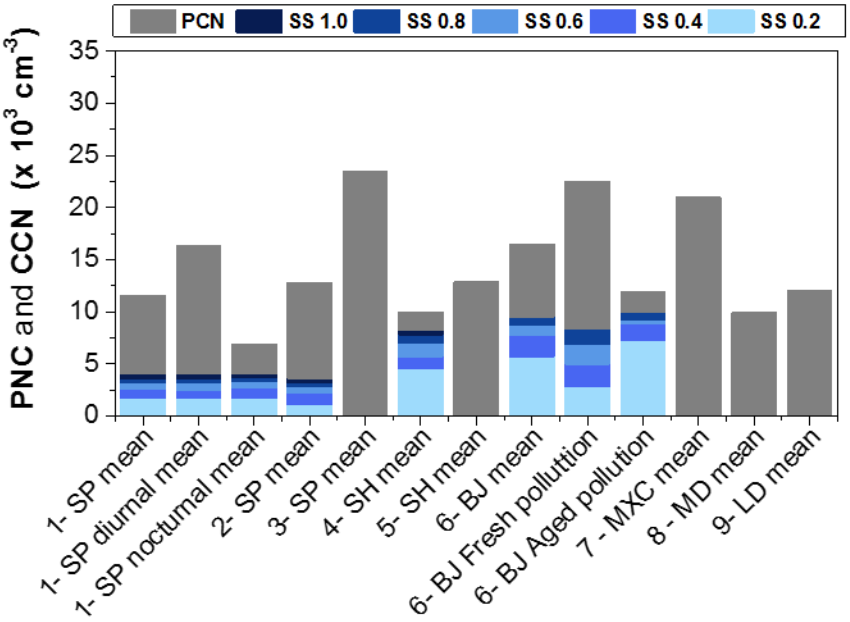


Figure 3. Comparison between particle number concentration (PNC) and cloud condensation nuclei (CCN) values obtained in this study and in previous studies. All studies were carried out at urban background monitoring sites, where measurements were made on rooftops of buildings located some kilometres from the downtown areas. In the case of Toronto, the measurements were carried in the downtown area of the city. Detailed information is available on Supplementary information in Table S1.

SP – São Paulo; SH – Shangai; BJ – Beijing; MXC – Mexico City; MD – Madrid; LD – London; 1 –the present study; 2 –Almeida et al. (2014); 3 –Backman et al. (2012); 4 –Leng et al. (2013); 5 – Peng et al. (2014); 6 –Gunthe et al. (2011); 7 - Kalafut-Pettibone et al. (2011); 8 – Gómez-Moreno et al. (2011); 9 –Reche et al. (2011).

Table S1 –Detailed information of studies, regions and values compared in Fig. 1.

Country	Sites	year / period	id	PCN ± SD (x 10^3 cm^{-3})	CCN (SS%) (x 10^3 cm^{-3})	Instrument	vehicle (million)	inhabitant (million)	Populational density (Km^{-2})	Sampling site	Reference
Brazil	São Paulo	2014 (Aug/Sep) 14 days	1.1 CCN and PCN mean 1.2 Diurnal mean 1.3 Nocturnal mean	11.6 ± 3.1 16.4 ± 7.9 6.9 ± 3.4	2(0.2), 2.6(0.4), 3.2(0.6), 3.6(0.8), 4(1.0) 1.7(0.2), 2.5(0.4), 3.2(0.6), 3.6(0.8), 4(1.0) 1.7(0.2), 2.7(0.4), 3.3(0.6), 3.7(0.8), 4(1.0)	DMT CCN-100 (SS 0.2 - 1.0%) DMPS (10- 450 nm)	7	20	2552.0	Rooftop of building (30m above groung) urban area	This study
	São Paulo	2012 (Oct - 15 days)	2 CCN and PCN mean	12.8 ± 5.4	1.1(0.2), 2.2(0.5), 2.8(0.7), 3.2(0.9), 3.6(1.1)	DMT CCN-100 (SS 0.2 - 1.0%) DMPS (10- 450 nm)	7	20	-	Rooftop of building (40m above groung) urban area	Almeida et al., 2014
	São Paulo	2010 Oct - 2011 Jan (79 days)	3 PCN mean	23.5	-	DMPS (6 - 800 nm)	7	20	-	Rooftop of building near urban area	Backman et al., 2012
China	Shangai	2010 - 2011 (1 year)	4 CCN and PCN continental air mean	10	4.5(0.2), 5.7(0.4), 7(0.6), 7.8(0.8), 8.2(1.0)	DMT CCN-100 (SS 0.07 - 2%) DMPS (20-800 nm)	2.2	24	3800	Rooftop of building (30m above groung) residential urban area	Leng et al., 2013
	Shangai	2010 (Apr/Jun)	5 PCN mean	12.9	-	DMPS (15-600 nm)	2.2	24	-	Roof six-floor building, urban residential and business areas	Peng et al., 2014
	Beijing	2006 (Aug/Sep)	6.1 CCN and PCN mean 6.2 Fresh city pollution 6.3 Aged regional pollution	16.5±9.0 22.5 ± 7.3 11.9 ± 2.8	5.7(0.26), 7.7(0.46), 8.7(0.66), 9.5(0.86) 2.9(0.26), 5.0(0.46), 6.8(0.66), 8.3(0.86) 7.3(0.26), 8.8(0.46), 9.2(0.66), 9.9(0.86)	DMT CCN-100 (SS 0.07 - 0.86%) DMPS (3-800 nm)	2.6	18.6	1300	Rooftop third-floor building in a suburban area	Gunther et al., 2011
Mexico	Mexico City	2006 (Mar)	7 PCN mean	21	-	DMPS (15 - 494 nm)	4	20	6000	Residential and light industrial area	Kalafut-Pettibone et al., 2011
Spain	Madrid	2007-2008	8 PCN mean	9.9	-	DMPS (15 - 1000 nm)	4	6	5325	Park inside metropolitan region	Gómez-Moreno et al., 2011
UK	London	2009	9 PCN mean	12.1 ± 5.8	-	DMPS (7 - 1000 nm)	2.6	13	5223	North Kensington, surrounded by a mainly residential area.	Reche et al., 2011

Section 3.2 This section has several serious problems that need to be fixed.

NO_3 radiacals are active during night time only, so it has very little to do with photochemistry.

The discussion about SOA formation and its connection with NPF is both outdated and partly erroneous, so should be entirely rewritten in light of more recent literature. SOA formation refers to the secondary production of organic particulate matter, while only a small fraction of SOA participates in NPF in any way (the least volatile of the gas-phase products). Furthermore, SOA formation itself is not dependent on NPF, since the aerosol volume of surface area needed for SOA formation is almost always dominated by particle larger than those in the nucleation mode. As a result, I see no justification for statements like that in lines 13-14 on page 8, or that in lines 18-19 on page 9.

This discussion about atmospherically-relevant nucleation mechanisms (lines 24-28 on page 8) is seriously outdated.

If mentioning banana and apple –type NPF events, they should be defined somewhere.

Response: The citation of NO_3 radical participation on photochemistry reactions was excluded of paragraph. This one was moved to introduction section, line 10 on page 3, as suggested by another reviewer.

Literature review and text about SOA, NPF and nucleation mechanisms were rewrite and references were updated as follow in the next paragraphs, this new text was included in the reviewed manuscript in lines 10 – 34 on page 3 in the section 1 (introduction).

The cited statements were removed from reviewed version of the manuscript.

Typically, nucleation events occur in clean air under high solar radiation conditions. Many authors have shown that sulphuric acid and precursor species (SO_2, hydroxyl, NH_3 and oxidised organic compounds) play important roles in the nucleation process (Yue et al., 2011; Andreae, 2013; Long et al., 2016). Reche et al. (2011) suggested that the occurrence of SO_2 peaks contributes to midday nucleation bursts as a

function of the sources. Kumar et al. (2014) discussed the different conditions for the secondary formation of particles over different types of urban areas. Recent studies have demonstrated the importance of oxidised organic vapors to drive NPF nucleation with H_2SO_4 and enhance secondary particle growth (Metzger et al., 2010; Donahue et al., 2013). Zhu et al. (2014) demonstrated the importance of SOA to particle growth over urban sites with different levels of pollution.

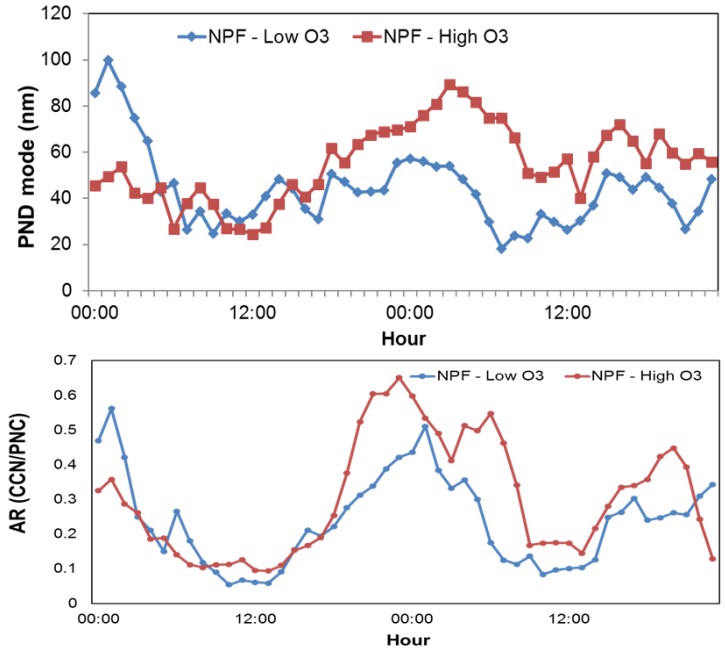
Volatile organic compounds (VOCs) constitute a fundamental precursor of secondary organic aerosols (SOA) and tropospheric ozone (O_3). Primary organic aerosols (POA) originate from biogenic sources (isoprene, terpenes, dimethylsulphide and dicarboxylic acids) and anthropogenic sources (biomass burning and traffic), thereafter being emitted directly into the atmosphere. Atmospheric species such as hydroxyl radicals and O_3 play a major role in VOC chemical degradation and the consequent formation of SOAs, which contain polar oxygenated functional groups (Hallquist et al., 2009). Recent studies have confirmed that the SOA yield is dependent on high concentrations of nitrogen oxides (NO_x), which explain the formation of certain SOAs, such as those derived from isoprene degradation (Shilling et al., 2013; Yuan et al., 2013). Another study, carried out in California, showed that vehicle emissions play an important role in the formation of urban SOAs (Ortega et al., 2016). In MASP, biofuels (ethanol and biodiesel) increase the emission of carbonyl compounds, which can be precursors of secondary oxygenated pollutants. In one study conducted in the MASP, Oyama et al. (2015) showed the emission factors for light-duty vehicles, which run on gasohol or ethanol, and for heavy-duty vehicles, which run on biodiesel. The authors found that oxygenated hydrocarbon compounds accounted for a major proportion of the aerosol composition. Those same authors also reported that, during biodiesel combustion, heavy-duty vehicles in the MASP emit greater quantities of volatile nitrogen compounds, which are associated with the NO_x chemistry, than light-duty vehicles in the MASP. Wallington et al. (2016) showed that engine calibration is a determinant of NO_x emissions, which are higher from biodiesel-burning vehicles. The use of biofuels has introduced new challenges for the description of atmospheric chemistry, by increasing the emissions of carbonyl and polycyclic aromatic hydrocarbons (PAHs, including those containing nitrogen and those that are oxygenated), as shown by Karavalakis et al. (2011).

In light of more recent literature about SOA formation and importance for NPF particle growth. The new discussion paragraph was write and included in lines 6-17 on page 11 (section 3.2), as follow.

As previously mentioned, O_3 plays a fundamental role in SOA formation via VOC oxidation, its concentrations being indicative of the efficiency of the photochemical process (Sorribas et al., 2015). However, after the nucleation process, SOAs drive particle growth to larger sizes, primarily by condensation of non-volatile molecules (Pierce et al., 2012; Donahue et al., 2013). In addition, the particle growth rate is the most important factor in determining the extent to which new particles become CCN during NPF events (Leng et al., 2013). As can be seen in Figs. 4a and c, the NPF events observed on days 7 and 8 occurred at low O_3 concentrations, whereas those observed on days 10, 12 and 14 occurred at high O_3 concentrations. To assess the importance of photochemical activity and SOA production to particle diameter and to the AR, we plotted NPF events under low and high O_3 concentrations (Fig. S1, on Supplementary Information). As expected, particles formed during low-O_3NPF were smaller than were those formed during high-O_3NPF (Fig. 4c). In addition, the AR was higher for the particles formed during

high-O_3NPF than for those formed during low-O_3NPF. That is in agreement with the findings of studies predicting or demonstrating the efficiency of SOA condensation in inducing particles to become CCN (Pierce et al., 2012; Riipinen et al., 2011)

Figure S1. Hourly mode of particle diameter (PND mode) and AR (SS 0.4%) for NPF events with low and high O_3 concentrations. In order to evaluate particle increase were plotted the day after NPF event. The days after NPF-low O_3 showed low O_3 concentrations also, which can explain the lower diameter and AR for these days compared with days after NPF-high O_3.



The mention about banana and apple events was removed of discussion on revised manuscript.

Section 3.3 - The purpose of this section remains unclear after reading it. The authors discuss connections between a number of tracers and source types, but I have a hard time to catch where all this information is used for in the rest of this paper. I recommend shortening the discussion and summarizing the main findings relevant to the rest of this work in the last paragraph.

The sentence in lines 32-34 on page 10 does not make any sense.

Response: The discussions were shortened and a final paragraph was included with the conclusions of this section (lines 28-35, page 13) as follow.

In summary, sea-salt air masses arriving at the MASP were observed during the nocturnal period on three of the days evaluated. During the nocturnal period of days 4 and 7, 8, sea-salt events were observed by Lidar and trace-element concentration analysis, respectively. Throughout the year, sea breezes arrive at the MASP in the afternoon and evening (Oliveira et al., 2002; Freitas et al., 2007). In the present study, plumes generated from biomass burning

were detected by lidar on days 6 and 12, being associated with an increase in BC on those specific days. In Brazil, numerous biomass burning events occur every year from July to November, mainly in the central and northern regions of the country. However, many such events, associated with agricultural activities, occur within the state of São Paulo throughout the year (Kumar et al., 2016). All focus fire, as shown in figures 7a and 7b, were identified from Geostationary Operational Environmental Satellite images (GOES).

The sentence in lines 32-34 on page 10 was removed.

Section 3.4

3.41 The third paragraph (lines 18-22 on page 13) discusses AR values related many different environments, yet only two studies have been cited. The sources of all the information referred to here should be explicitly given.

3.42 The sentences in lines 23-24 on page 13 are very unclear. . . .increase of AR over SS? What has a diurnal period to do with a slope?

3.43 A statement like the one given in lines 3-4 on page 14 need a reference.

3.44 Lines 9-18 on page 14: The authors refer to studies mentioned in the introduction without specifying them. This is not a good scientific practice of citing other studies.

3.45 The sentence in lines 21-23 starts and ends with a different reference. It remains unclear which information refers to which of these two references.

3.46 The sentence in lines 33-34 on page 14 does not make any sense. Furthermore, a citation is missing.

3.47 The paragraph in lines 13-22 on page 15 is difficult to follow. The last statement needs a reference. Please rewrite this paragraph.

3.48 Finally, the text suffers from rather poor language. Without pointing out individual places in text, there are major problems with many individual sentences, and especially with the use of articles and prepositions (sometimes also with the tense.) After revising the scientific contents of the paper, the authors need be make a very thorough language check out of the text.

Response :

3.41 About the third paragraph, all the sources were included in the reviewed manuscript.

3.42 In fact the sentence was unclear, therefore we rewrite this one (lines 29-32, page14 and lines 1-6, page 15) as follow. The comparison between diurnal and nocturnal AR slope, showed in fig. 8a, was imprecise due the high deviation of average values, consequently this sentence was removed.

During the diurnal period, the mean AR values were similar to those observed in other urban areas, although not to those observed in coastal areas (Leng et al., 2013; Furutani et al., 2008), as indicated by

recent studies of fresh urban pollution conducted in the MASP, Vienna and Beijing (Almeida et al., 2014; Burkartet al., 2012; Gunthe et al., 2011). However, the AR reported for Beijing was twice that found for the MASP in the present study, considering entire campaign for both, although the PNC values were similar. In addition, the AR values observed for the SPMA in the present study are comparable to the fresh ship exhaust emissions reported in a study conducted along the coast of California (Furutani et al., 2008). The nocturnal AR values observed for the MASP were similar to those reported in a study conducted in a forest environment (Sihto et al., 2011) and in the coastal environments, although opposite those observed in others urban environments (Table 2). However, the mean nocturnal AR and PNC values were higher for aged pollution in Beijing than for the MASP.

3.43 The reference about the statement in lines 3-4 on page 14 was included.

3.44 All the references about mentioned studies in introduction were included.

3.45 In the case of sentence in lines 21-23 on page 14, the information refer to Frank et al.(2006), thus the other citation was excluded.

3.46 The sentence late in lines 33-34 on page 14 was rewrite and highlighted in yellow in the reviewed manuscript (now in lines 15-18, page 16), as follow. In addition, the reference was included.

The mean D_{act} values for diurnal period with biomass burning and NPF events were similar to those observed for non-event days. The D_{act} values for nocturnal periods after NPF or during sea-salt events were similar to those observed after non-event days, although the D_{act} values were slightly higher for nocturnal periods during which there were biomass burning plumes, mainly when the SS < 0.6%. At high supersaturation values, particles with different chemical composition and therefore hygroscopicity have only a weak effect on CCN activity (Sihto et al., 2011; Zhang et al., 2014).

3.47 The paragraph late in lines 13 – 22 on page 15 was rewrite, as follow. In the reviewed manuscript this paragraph is in lines 27 – 35 on page 16, as follow.

The efficiency of aerosol particles to act as CCN can be estimated on the basis of AR and D_{act} data. The AR is dependent on particle size and chemical composition, whereas D_{act} is dependent on chemical composition only (Furutani et al., 2008). As can be seen in Fig. 10b, the non-linear correlation between AR and D_{act} can be related to different chemical composition and size distribution of aerosol. During the diurnal period, the D_{act} was increased and the AR was decreased, whereas the inverse was true for the nocturnal period. In general, the diurnal period is associated with particles that are less hygroscopic and smaller, mainly emitted by vehicular traffic. However, the decreased D_{act} and increased AR were observed in the nocturnal period, being associated with larger and more hygroscopic particles. Our observations support the assumption that nocturnal samples typically comprise greater concentrations of water soluble species, such as $(NH_4)_2SO_4$, SOA, NO_3^-, and of marine air than do diurnal samples. Our findings are also in keeping with those of other studies showing that aged aerosols present high hygroscopicity (Gunthe et al., 2011; Bougiatioti et al., 2011).

3.48 We have read the text of the manuscript to remove any grammaltical infelicities and improve the language.