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).
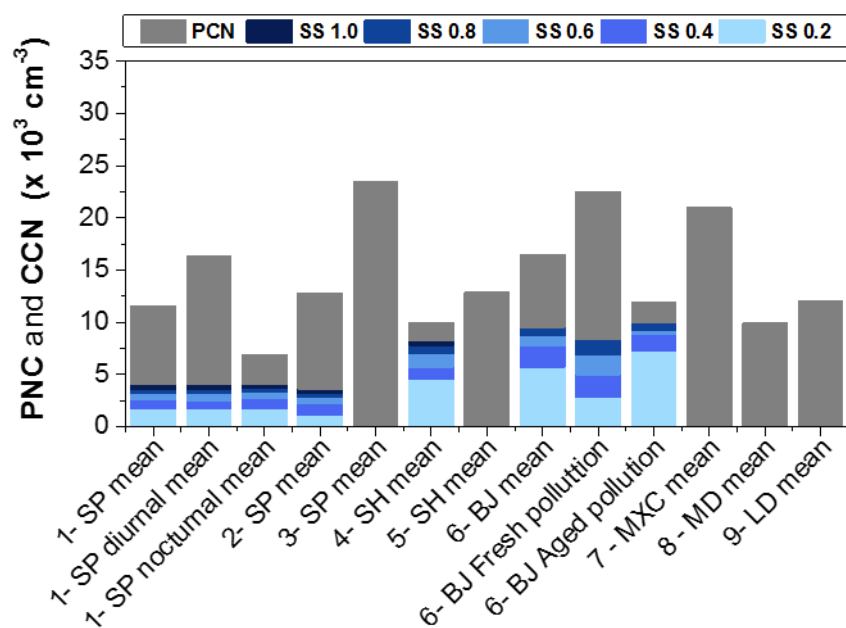

Figure 3. Comparison between particle number concentration (PNC) and cloud condensation nuclei (CCN) values obtained in this study and in previous studies. All studies were carried out at urban background monitoring sites, where measurements were made on rooftops of buildings located some kilometres 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 10³ cm³)	CCN (SS%) (x 10³ cm³)	Instrument	vehicle (million)	inhabitant (million)	Populational density (Km²)	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$_2$SO$_4$ 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)
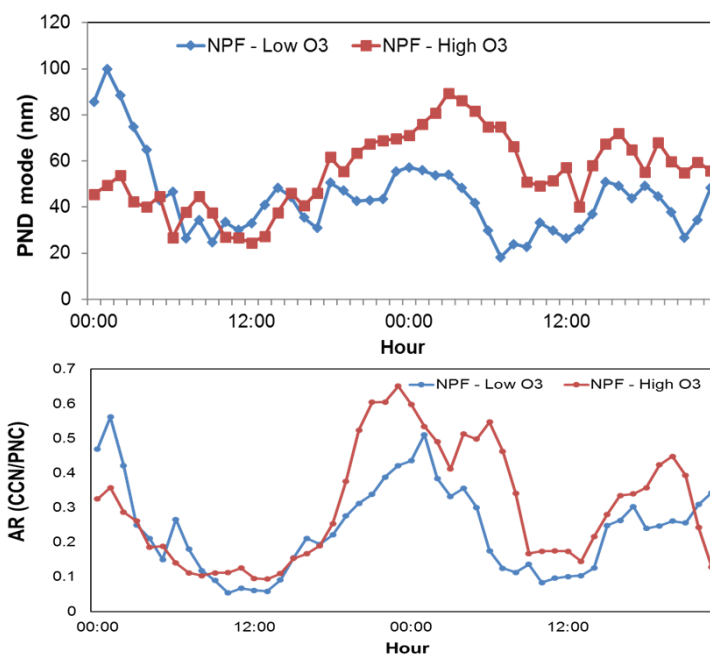

Figure S1. Hourly mode of particle diameter (PND mode) and AR (SS 0.4%) for NPF events with low and high O_3 concentrations. In order to evaluate particle increase were plotted the day after NPF event. The days after NPF-low O_3 showed low O_3 concentrations also, which can explain the lower diameter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