Reply to the comments of Anonymous Referee #3

We thank Referee#3 for the comments provided to our manuscript. Here we try to reply to the comments at our best, indicating the changes we are going to make in the revised version of the manuscript. With "GC" indicate general comment, while with "SC" specific comment.

GC: "**The authors examine particle size distributions from about 0.3 um to 5 um diameter using two optical particle counters (OPC) located in Milan and on Oga-San Colombano at 2250 msl. They use a skewness-kurtosis plane based on the statistics of the measured size distributions to consider several possible statistical distributions that are commonly used to represent aerosol particle size distributions. They show that the Johnson SB (and SU) are capable of representing relatively complex distributions over the size range of the OPC (0.3-5 um) depending on factors that control total number concentrations, including wind speed and precipitation. This paper offers a new (to me) and interesting approach to contrasting particle size distributions, although it would have been more interesting had the size distributions covered sizes down to 20 or 30 nm, rather than starting at 300 nm. The work appears to be targeted towards models that use modal representations, but the skewness-kurtosis plane with separation by total number concentration seems like it has potential as a tool for analysis of size distributions. The paper is well organized, and the figures are well done, but a careful editing of the paper for grammar is required as misinterpretations are possible. The figure captions could use some additional detail**."

We thank Referee#3 for your kind and well-focused comment to our manuscript. In this manuscript, we would like to introduce this kind of analyses to PSD data, which could suggest other investigations including other diameter ranges (i.e. 20 or 30 nm) or other pollutants. In the revised version of the manuscript we will make a careful editing of the paper to avoid misinterpretations.

Specific comments:

SC1. "**Page 3, lines 4-5 – You first say the PNSD pattern does not change, and then you say that it varies by site and season. Please clarify. Also, clarify "In this case": winter?**"

Many thanks for this comment. Here we mean that PNSD pattern (i.e. the domain where the sample points are in the skewness-kurtosis plane) is well represented by the Johnson SB domain, except for the urban winter data. So, the PNSD pattern does not change, even if we change the site or the season with the exception mentioned above. We will clarify the point in the revised version of the manuscript in order to avoid misinterpretations.

SC2. "**Page 3, line 10 – What do you mean by "background"? Its meaning in this context needs to be clarified**."

We use the term "background" to identify a site that is not directly affected by local traffic emissions and is representative of the urban area. To clarify the site characteristics, the paragraph is modified as follows:

"The data have been collected in two sites: the urban site located in Milan at Pascal-Città Studi (45°28'42"N, 9°13'54"E, 120 m a.s.l.) and the rural high altitude site at Oga-San Colombano (46°27'40"N, 10°18'07"E, 2290 m a.s.l.). The urban site is representative of "urban background" conditions and is not direct affected by local traffic emissions (Vecchi et al., 2004)."

The following reference is added:

R. Vecchi, G. Marcazzan, G. Valli, M. Ceriani, C. Antoniazzi, The role of atmospheric dispersion in the seasonal variation of PM1 and PM2.5 concentration and composition in the urban area of Milan (Italy), Atmospheric Environment, 38(27), 2004, 4437-4446.

SC3. "**Page 4, line 1 – What model number? Did you use two counters, one at each site, or was one counter transported between sites? If two counters, were they the same model at both sites? If two counters, how were they compared and validated to determine possible differences associated with the counters rather than the sites? It is not uncommon for these types of counters to have large uncertainty in the smallest nominal size. Was the lowest size evaluated in any way**?"

Many thanks for this comment. The code related to the winter site of Oga San Colombano cited in page 4, line 1, is SC1. We used two code prefixes, "MI" for Milan-Città Studi and "SC" for Oga-San Colombano, followed by a counter (from 1 to 8 for Milan,1 and 2 for San Colombano) which has been associated to the datasets ordered chronologically. This code has been introduced in order to distinguish in an easier way the ten different datasets. The lowest site was 0.3 μg/m3 for all the datasets.

SC4. "**Page 4, lines 17 and 19 – do you mean ug/m3?**"

Many thanks for this comment. Yes, it is μg/m3. We fix it in the revised version of the manuscript.

SC5. "**Page 4, line 20 – Similar to 'background', how do you define pristine?**"

We would like to thank the Referee to point out the use of the "pristine" adjective. We apologize for the confusion. As reported in the site presentation, Oga San Colombano is a rural site. We rephrased the sentence as follows:

"The different characteristics of the aerosol number size distributions at Milan (urban site) and Oga-San Colombano (rural site) are shown in Fig. 1."

The adjective pristine is replaced throughout the manuscript.

SC6. "**Page 4, Line 23 – What are low aerosol levels**?"

Thanks for the request. In the revised manuscript we will clarify this issue. We would like to add the mean annual value of PM10 6 $\mu g/m^3$ and its standard deviation 5 $\mu g/m^3$. In addition, we would like to specify that during the summer (JAS) the mean seasonal value of PM10 12 $\mu g/m^3$ and its standard deviation 9 $\mu g/m^3$.

SC7. "**Page 4, lines 25-29 – This tells us nothing other than you have measured some other things (NOx and meteorological quantities). Perhaps that is what you intended, and there is simply a grammar issue? Otherwise, is there a reference for the "influence" investigation? NOx may be considered a component of the aerosol, but it is not an "aerosol compound"**."

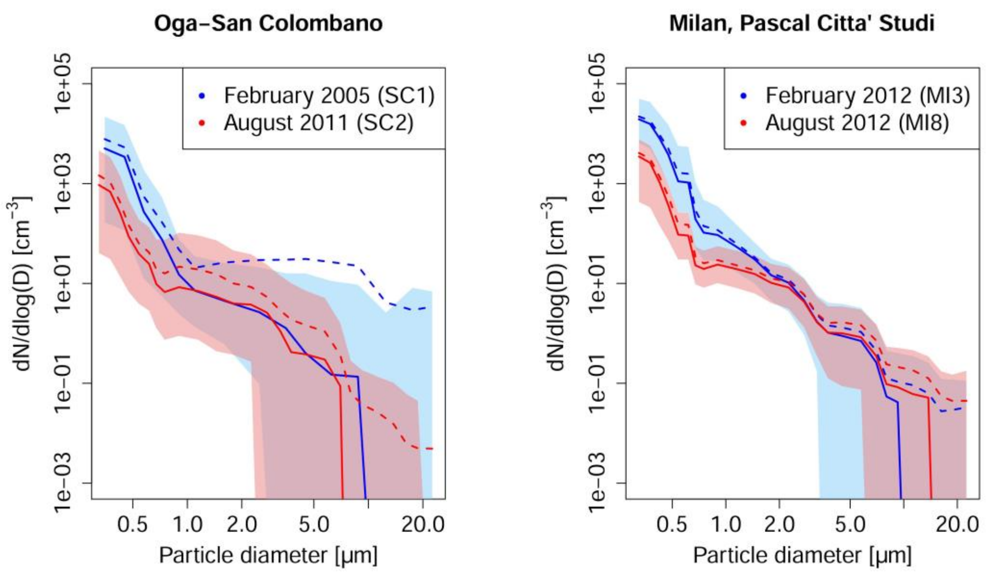
Many thanks for this comment. Yes, there is a grammar issue here, we have just measured some other things (NOx and meteorological quantities). We clarify this point in the revised version of the manuscript.

SC8. “**Figure 1 – Why did you choose August 2012 (MI8) rather than August 2011 (MI6) that is at the same time as SC2?**”

We decided to show the results for MI8 because the PNSD samples in MI8 are more in number (41945) respect to MI6 (28715). In this way we considered a greater statistical basis and thus a lower uncertainty in the calculation of the statistical quantities, such as mean and average.

SC9. “**Page 5, lines 6-8 - Figure 1 – The inflections in the distributions between about 0.4 um and 0.8 um are present at both sites, but particularly evident in the Milan results. Rather than “droplet mode particles”, the inflections may be a symptom of ambiguities in the scattering function for the particular angle of the OPC, sometimes referred to as Mie ambiguities. Some of the peaks and valleys above 1 um may also be due to this potential problem. The exaggerated inflections in the Milan PNSD relative to the SC PNSD may be due to differences in the index of refraction or the apparently less steep Milan distributions from 0.3 to 0.7 um compared with the SC distributions. You should look at the scattering function versus particle diameter for the counters. If ambiguities are present (i.e. a similar amount of light scattered into the collection angle by particles of different sizes), the common solution is to average across the bins covering the ambiguity size range**.”

Many thanks for this comment and for the suggestion. Yes, in the revised version of the manuscript, we removed the ambiguity averaging across the bins. We have produced a new Figure 1.



SC10. “**Figure 2 – Indicate what the lines refer to in the caption**.”

Many thanks again for this comment. In the revised version of the manuscript, we will clarify in the caption of Figure 2 that the dotted-dashed line is the lognormal distribution, the dotted line is the Weibull distribution, and the dashed line is the gamma distribution.

SC11. "**Page 7, line 7 and Figure 3 – The fits in Figure 3 are very good considering the detail. Not being familiar with the JSB distribution, I would to see your fitting process discussed in a little more detail, including the Maximum Likelihood Method. The details could be added to the supplement.**

Thanks for this question. The details about the fitting method will be added to the supplement in the revised manuscript.
We would like to add the following text:
"The Johnson SB distribution is a four-parameter distribution characterized by a bounded domain and great flexibility in the shape. These features make JSB applicable to many fields like meteorology (Johnson, 1949; Tang and Lin, 2013), hydrology (Kottegoda, 1987; Wakazuki, 2013) and ecology (Rennolls and Wang, 2005). The four parameters of JSB are calculated here using a Maximum Likelihood method, applied to each minute of the dataset. The parameters are estimated by maximizing the log-likelihood function *L*:*

$$
\begin{aligned}
L^* &= N\ln(\gamma) + N\ln(\delta) + N\ln(2\pi)^{-1/2} - N\gamma^2/2 - \sum_{i=1}^{N}\ln(D_i - \xi) + \\
&- \sum_{i=1}^{N}\ln(\xi + \lambda - D_i) - \gamma\delta\sum_{i=1}^{N}\ln(D_i - \xi) + \gamma\delta\sum_{i=1}^{N}\ln(\xi + \lambda - D_i) + \\
&- (\delta^2/2)\sum\left[\ln(D_i - \xi) - \ln(\xi + \lambda - D_i)\right]^2
\end{aligned}
$$

where N is the sample size. To do this, we used the function "optim" of R language and the iterative process is controlled by setting specified initial values of location and scale parameters and the distribution constraints. In particular, being JSB a bounded distribution in the interval [ξ, $\xi+\lambda$] and the DSDs physically bounded by D_{min} and D_{max}, the initial values of ξ and λ are chosen sufficiently below and above D_{min} and D_{max}, respectively. Thus, ξ_{start} is set equal to ($D_{min} - \varepsilon_1$) and λ_{start} is set equal to ($D_{max} - \xi_{start} + \varepsilon_2$), where ε_1 and ε_2 are two arbitrarily small quantities. See Cugerone and De Michele, 2015 and Cugerone and De Michele, 2017 for more details. Alternatively, D'Adderio et al. (2016) used a Least Square method applied to theoretical and empirical third order moment to estimate the parameters of JSB."

SC12. **Page 10, lines 10-17 – Higher values of NOx/NO2 may indicate closer temporal proximity to sources. They also suggest the possibility of a greater fraction of particles from primary emissions, but it does not guarantee that primary particle emissions dominate over secondary. Also, it sounds like "These findings support our hypothesis that in urban sites during winter season the increase of primary aerosols emission by local sources causes an evident increase of primary aerosol compounds concentration." is saying that an increase of primary aerosol emissions causes an increase in primary**.

We would like to thank referee #3 to point out the need for clarity at the beginning of page 10. We agree with the referee that the higher NOx to NO2 ratio indicates a closer temporal proximity to sources.

In addition to support our interpretation of such ratio, we report here the results of aerosol chemical composition analysis performed at the Milan urban site during winter 2014 (a field experiment not discussed in the present manuscript). During such experiment we observed that the NO_2 to NO_x ratio decreases with the increase of black carbon mass fraction, i.e. a marker of primary emissions. At the same time the NO_2 to NO_x ratio increases when the contribution of secondary organic and inorganic aerosol increases (see attached figures).

To clarify the meaning and interpretation of the NOx to NO2 ratio we would like to modify the manuscript as follows:

"It follows that the NO2 to NOx ratio can provide a measure of the oxidative capacity of the atmosphere (Rao and George, 2014; Fernández-Guisuraga et al., 2016) and it's a measure of the temporal proximity to emission sources. In addition, measurement performed in Milan during different field experiments show that NO2 and NOx ratio anti-correlates with black carbon to PM1 ratio, confirming that the NO2 to NOx in urban area is an indicator of the relevance of secondary pollutant formation over primary traffic emissions. In Fig. 4 we have again reported the skewness-kurtosis plane, where we have plotted in black the data points of MI1 (upper panel) and MI2 (lower panel). Then, we have selected the data points belonging to minutes characterized by values of the ratio NOx/NO2 between 1 and 1.1 (red dots – highly oxidizing atmosphere), 1.1 and 1.5 (orange dots – slightly oxidizing atmosphere), 1.5 and 3 (yellow – little oxidizing atmosphere), greater than 3 (green - no oxidizing atmosphere). Both the two datasets are characterized by high aerosol numbers and high percentages of data points outside JSB domain (74 % and 65% respectively). The percentages of data points characterized by a ratio NOx/NO2 greater than 3 are around 50 %, indicating a prevalence of the primary traffic aerosol contribution. If we select only the data points outside the JSB domain, the percentage of data points with ratio greater than 3 (strong prevalence of primary aerosols) is 56 % for MI1 and 50 % for MI2. While, the percentage of data points with ratio greater than 1.5 (light or strong prevalence of primary aerosols) is 88 % for MI1 and 67 % for MI2. These findings support our hypothesis that in urban sites during winter season the increase of primary traffic contributes to the shifts of (β3, β4) couples in the skewness-kurtosis plane."

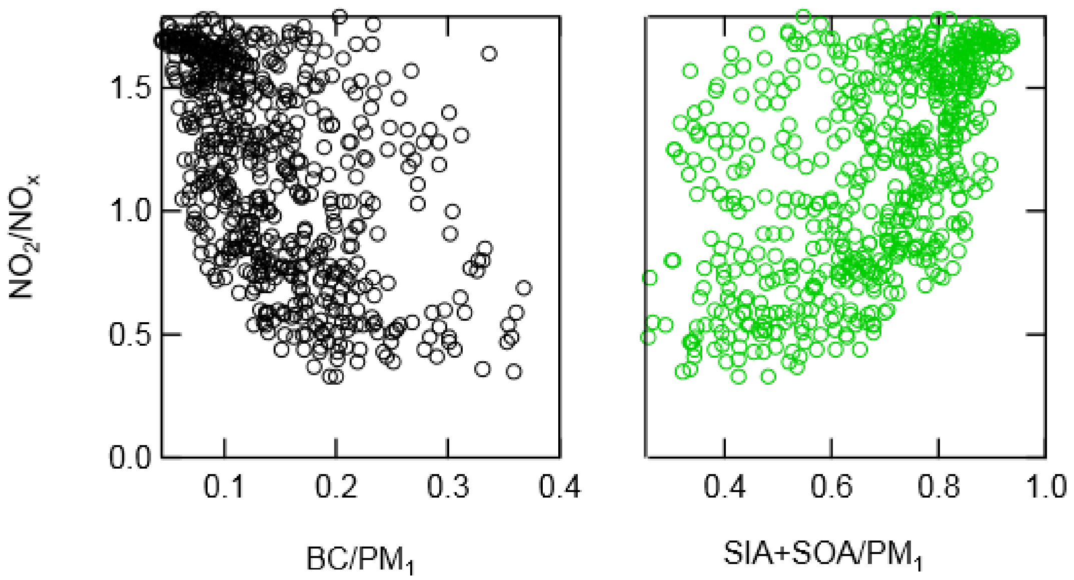


Figure 1. Dependency of the NO2 to NOx ratio on the chemical composition of submicron aerosol in Milan urban background site during winter 2014. BC/PM1 indicates the black carbon mass fraction, while SIA+SOA/PM1 indicates the secondary inorganic and organic mass fraction (secondary organic aerosol was quantified with positive matrix factorization analysis of organic aerosol mass spectra – data not published).