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"**."

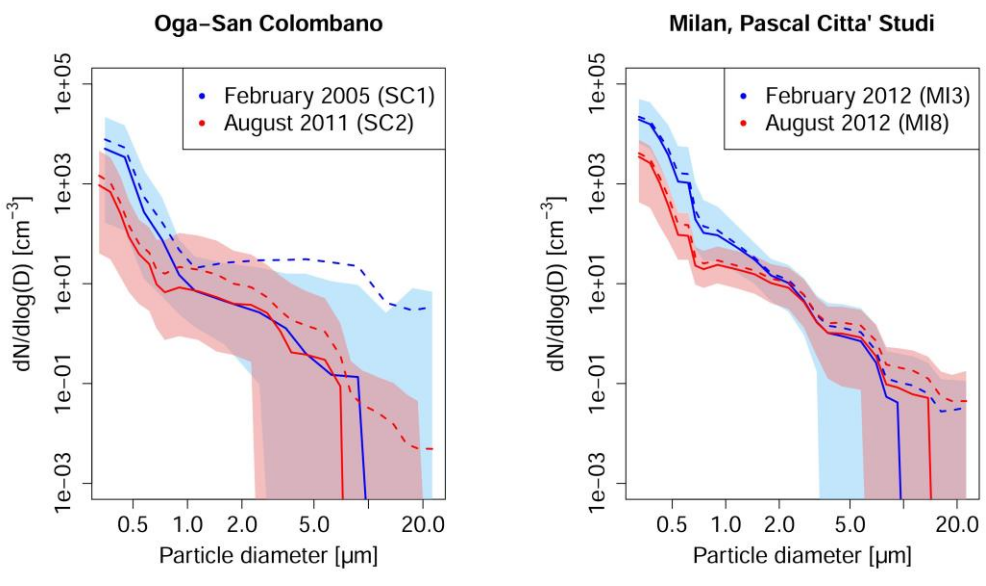
Many thanks for this comment. Yes, there is a grammar issue here, we have just measured some other things (NOx and meteorological quantities). We clarify this point in the revised version of the manuscript.

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*:*

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

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 $[\xi, \xi+\lambda]$ 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."

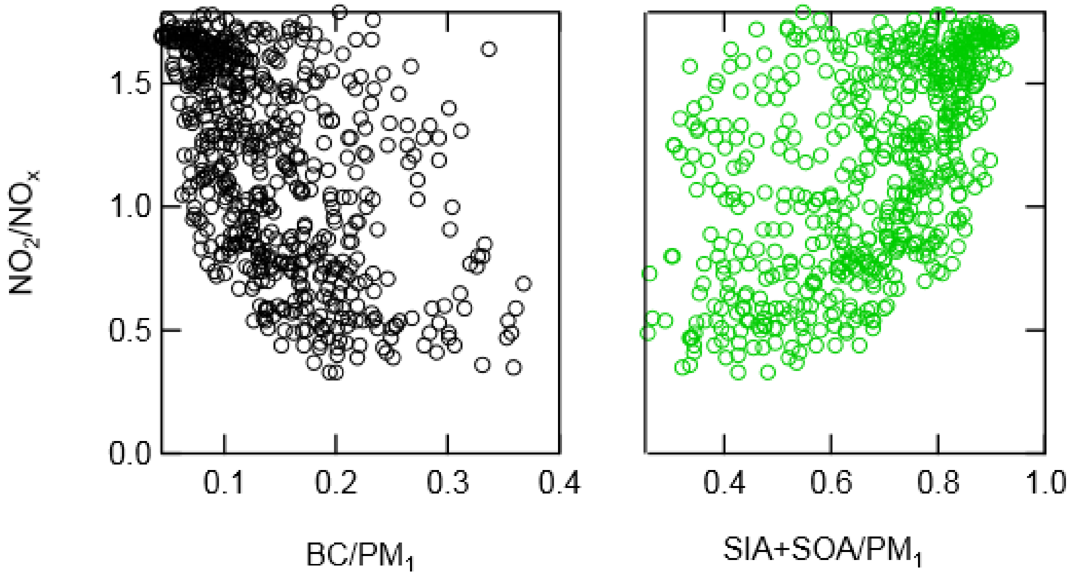


Figure 1. Dependency of the NO2 to NOx ratio on the chemical composition of submicron aerosol in Milan urban background site during winter 2014. BC/PM1 indicates the black carbon mass fraction, while SIA+SOA/PM1 indicates the secondary inorganic and organic mass fraction (secondary organic aerosol was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

Reply to the comments of Anonymous Referee #4

We thank Referee#4 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 "MC" minor comment.

GC1: "**This manuscript describes the applicability of the Johnson SB distribution for fitting particle size distributions measured by optical particle counters operated at two sites in Italy. The paper first focuses on assessment of the merits of the expression form by examining the fraction of measurements that lie within the region on the skewness-kurtosis plane that is bounded by the Johnson SB envelope of possible solutions. The patterns of data point clusters on that plane are then linked with meteorological and environmental conditions to suggest the more general use in describing the sources and processing responsible for an observed size distribution. The manuscript is reasonably well-written but would require some editing prior to publication**."

We thank Referee#4 for this kind and general comment to our manuscript.

GC2: "**I have identified several specific concerns I have with the manuscript below. More generally though, this simply does not seem to be appropriate for ACP. The dataset described is very limited and rather uninteresting when not complemented by other aerosol and trace gas measurements. More importantly, the dataset is not really the focus of the paper, but rather the technique to describe the dataset is. Thus, in its current form this would be more appropriate for a journal such as AMT. If the authors chose to shift the emphasis more toward the size distributions I still feel that because of the limitations of the dataset this would be better suited for another journal**."

We thank Referee#4 for this comment. Here we want to clarify that in this work we want to propose a new methodology of analysis of PNSD data, based on the skewness-kurtosis plane and the Johnson SB domain, which can be used also to summarize statistically the aerosol dynamics under meteorological conditions. We used two datasets to illustrate the methodology. The methodology is quite general, and with general implications for the assessment of aerosol dynamics. We intend to apply this to other datasets in the near future, as explained in the next point. In this work, we have mainly focused on physical issues, rather than chemical issues, influencing the variability of PNSD. We will investigate chemical issues in a further study. In the revised version of the manuscript, we clarify this issue to improve the presentation of our work. We think that, for the wide breath of the work, ACP is the proper editorial place.

GC3: "**It could be that collaboration with researchers involved in more comprehensive measurement campaigns could be valuable for evaluating the utility of the techniques described here for understanding influences on size distributions. It seems the authors have considerable experience with statistical methods and data analysis, but not with air quality. The relevance of this is that there is far too much text describing rather fundamental details about aerosol sources and sinks and meteorology**."

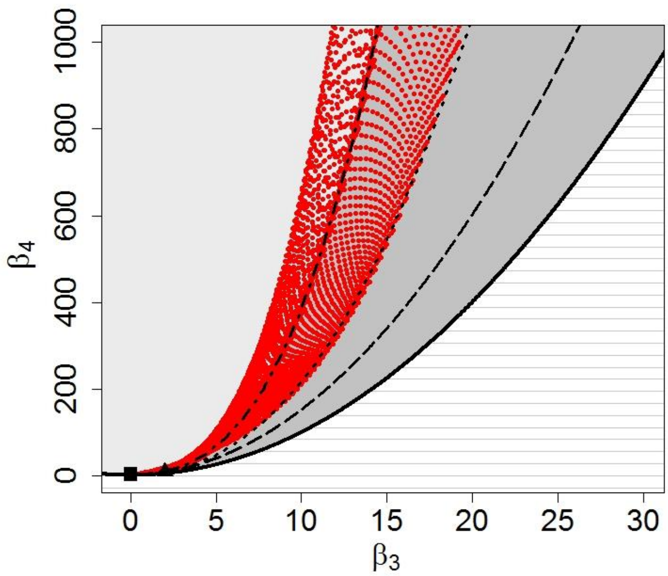
Thanks for this suggestion. We are planning to continue the collaboration with researchers belonging to Institute of Atmospheric Sciences and Climate –ISAC, National Research Council, Italy. They are regularly involved in comprehensive field campaigns (see e.g. activities documented at the website http://actris-cimone.isac.cnr.it/) measuring aerosol dynamics from the physical and chemical point of views, in addition to meteorological conditions. So, in the near future, we intend to analyze the data of existing comprehensive field campaigns in order to confirm and extend the results obtained in this work.

GC3: "**The averaged and example size distributions shown in Figures 1 and 3 reveal a common characteristic of distributions measured by OPCs - erroneous peaks and troughs that are often linked with features in the scattering intensity vs. size relationship for the optical geometry of the instrument. The fact that they are retained in the distributions suggests the authors didn't invest much time in calibration of the instruments and processing of the data. But more relevant for this paper, those features will influence any fit of the distributions and the location on the S-K diagrams. There is no discussion of these features or their impact**."

We thank Referee#4 for this comment, also pointed out by Referee#3 (see SC9). In the revised version of the manuscript we will fix this issue, i.e., the inflections in the distributions between about 0.4 um and 0.8 um, due to ambiguities in the scattering function for the particular angle of the OPC. We will operate an averaging across the bins, as suggested by Referee#3. So, in the revised version of the manuscript we will report the new figures (1 and 3), and remake the representation of data in the skewness-kurtosis plane.

GC4: "**The authors argue that the Johnson SB distribution is more appropriate for fitting the particle size distributions than more commonly used forms such as the lognormal. But they neglect to discuss the utility of the lognormal because of the direct connection of the parameters describing it with physically meaningful elements of the aerosol distribution (i.e., N, Dp_mean, SD) and the ability to describe variation of those parameters accompanying things such as atmospheric processing. Furthermore, the manuscript largely dismisses lognormals based on the difference between the data points and the single lognormal point on the S-K diagrams. But does the representation as a point presume that only one lognormal is used to fit the distribution? In practice, multiple lognormals are almost always used**."

We thank Referee#4 for pointing at our attention this interesting comment. In the revised version of the manuscript, we would like to address this issue by reporting in the skewness-kurtosis plane, the domain of a mixture of two lognormals (indicated with red dots). According to the OPC size particle classes, a mixture of two distributions is sufficient to keep the modes of the analyzed datasets. We have compared the Johnson SB domain (in dark grey) with the domain of a mixture of two lognormals, as reported here in the figure. This is an original issue never investigated in the literature and we are happy to deal it in the revised manuscript.



In the revised manuscript, we plan to add an appendix where we describe how we have calculated the β3-β4 domain of the mixture. From the figure, it is possible to see that the Johnson SB distribution has a wider domain respect to the mixture of two lognormals, indicating that the Johnson SB distribution is more versatile respect to the mixture of two lognormals in representing the OPC data.

Minor issues:

MC1: "**Page 4, line 1: Grimm model what**?"

The GRIMM model used at Oga San Colombano is "GRIMM 107 Environcheck" as well as at Pascal-Città Studi. We will specify this in the revised manuscript.

MC2: "**Page 4, line 7: What is the basis for the assertion that the composition is different between the two sites. It undoubtedly is, but this still needs some support**."

In the revised version of the manuscript, we will add some support to this sentence. Specifically, we would like to write "Oga San Colombano shows a higher relative contribution of organic aerosol, likely of secondary origin, as suggested by a higher organic to elemental carbon ratio (Sandrini et al., 2014). In addition, Milano shows a higher nitrate to sulfate ratio, in agreement with a stronger impact from combustion sources, such as traffic and industrial emissions (Perrone et al., 2012")."

Perrone M.G. (2012). Sources of high PM2.5 concentrations in Milan, Northern Italy: Molecular marker data and CMB modelling, Science of the Total Environment 414, 343–355.

Sandrini S. et al. (2014). Spatial and seasonal variability of carbonaceous aerosol across Italy, Atmospheric Environment, 99, 587-598.

MC3: "**Page 4, line 26: Nitrogen dioxide and nitric oxide are not aerosol compounds**."

We acknowledge the Referee for pointing out the mistake. The sentence in modified as follows:

"The influence of primary aerosol sources and meteorology on PNSD has been investigated for the site of Milan. To study the effect of pollutant concentration we have used nitrogen dioxide (NO2) and nitrogen oxide (NO) measurements collected with a chemiluminescence technique following the requirements of European Standard EN 14211: 2005: Ambient Air Quality".

MC4: "**Page 6, line 24: Total particle count is meaningless to readers. I assume the authors simply need to divide this by the product of flow rate and sample time to report it in concentration. Additionally, it seems there is confusion about the upper threshold value because it is written both as 10ˆ4 and as 100000 (=10ˆ5)**."

Thank you for the comment. There was an error in Table 2: the threshold value is 10^5 (100000) and not 10^4. Regarding the total particle count, we think that this statistical and physical measure is not meaning less, because it allows the readers to have a direct and simple measure of the load of aerosol particles that can be recorded in a minute and to compare the different cases, changing season and/or site.

MC5: "**Page 10, top: The NO2 to NOx ratio will be largely dependent on time of day, which will confound the interpretation of its influence on the patterns in the S-K diagrams**."

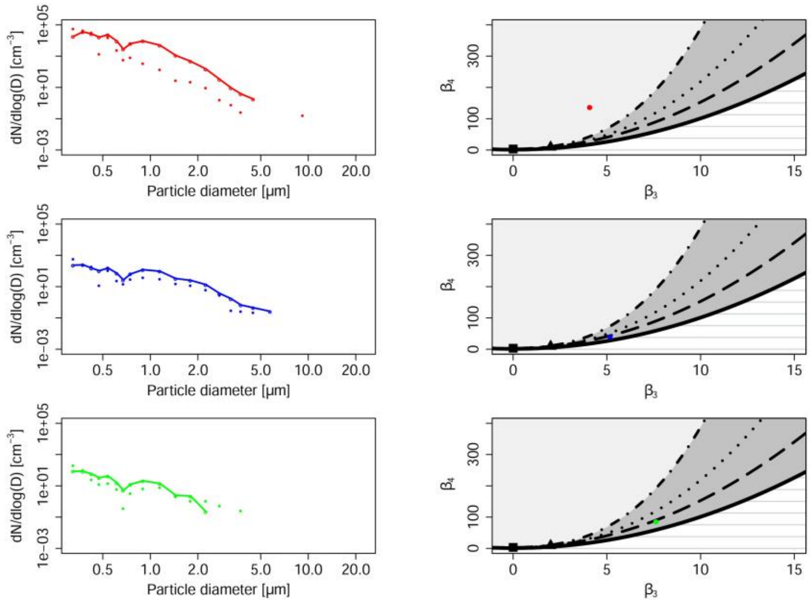
We agree with the Referee that the NO2 to NOx ratio depends on the time of the day, as primary emissions from traffic do as well. In addition, previous measurements at the urban site here investigated show that the NO2 to NOx ratio anti-correlates with black carbon to PM1 ratio (a marker of primary traffic emissions in this area) and correlates with the ratio of secondary to primary aerosol species (i.e. secondary organic and inorganic aerosol to black carbon plus primary organic aerosol ratio). Unfortunately, during the presented experiment no data on aerosol chemical composition was available to direct evaluate the contribution of primary and secondary components. Thus, we decided to use the NO2 to NOx ratio as a proxy of polluted air mass ageing. To improve clarity, 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). In addition, measurements 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 (β_3, β_4) couples in the skewness-kurtosis plane."

MC6: “**Figure 3: The use of an unnecessarily large y-axis range obscures the information in the distributions and the quality of the fits**.”

Thank you for the comment. We will modify Fig.3 following your suggestion.



MC7: “**Figure 4: The differences among these graphs are pretty modest**.”

In our opinion, the difference between the graphs are not so modest. The discrepancies are highlighted by the numbers showed in the legends and by the explanation of Paragraph 4.2.

Reply to the comments of Anonymous Referee #5

We thank Referee#5 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" we indicate the general comments.

GC1: "**The manuscript proposes that the skewness-kurtosis plane (the size distribution projected into the third and fourth moments) can be used to follow changes to the particle number size distribution (PNSD), and that four-parameter Johnson SB (JSB) distribution as being sufficient for observing changes to the PNSD in a way that maps to the skewness-kurtosis plane. The authors present PNSDs from four measurement campaigns under different NOx and meteorology conditions. This manuscript includes a few interesting ideas that are less well-known to the broader ACP community, and has potential for novelty and impact**."

We thank Referee#5 for this kind and encouraging comment to our manuscript.

GC2: "**However, at present time the manuscript is strongly recommended for revision and re-submission. The reason for this is recommendation that each of these ideas introduced are not fully developed. As a result, the reader is mostly left with an impression that what is demonstrated is that the size distribution changes when there are changes in meteorology or emission sources, which could be characterized more informatively using traditional approaches (number concentration, modes, etc.)**."

We thank Referee#5 for the comment. In the revised version of the manuscript will improve both the analyses and the presentation. In this manuscript we want to propose a new methodology of analysis of PNSD data, based on the skewness-kurtosis plane and the Johnson SB domain, which can be used also to summarize statistically the aerosol dynamics under meteorological conditions. We want to provide a tool to describe statistically and quantitatively the PNSD variation with meteorological conditions and emission sources. We used two datasets to describe the performance of such a tool. We will improve the presentation of our work, and add additional analyses as explained in the next point.

GC3: "**The conclusion that the JSB can be used to represent PNSDs does not appear to be well-supported by the material that is presented. As one of the other reviewer notes, PNSDs can be multimodal, and representing each of these modes well is in itself a challenge. There is no indication regarding the modality or quality of fit permitted by JSB. What is presented seems to be that the range of skewness and kurtosis in observed PNSDs fall within the range that can be represented by the JSB distribution except at high concentrations. Furthermore, it is not demonstrated that JSB outperforms other parametric distributions for representing PNSDs (except for the reason of having four fitting parameters), and the authors even note in the conclusions that the other parametric representations may be adequate**."

Thanks again for this comment, also raised by Referee#4 (GC4). We know that the lognormal or the mixture of lognormals are generally used in the literature to represent the PNSD data. We agree with the Reviewers that it is a nice idea to compare JSB distribution with those commonly used in the literature, in order to see if the JSB outperforms (or not) other parametric distributions in representing PNSDs. We have analyzed this topic and in the revised version of the manuscript, we would like to address this issue.

Lets consider a mixture of two lognormals. According to the OPC size particle classes, a mixture of two lognormals is sufficient to keep the modes of the analyzed datasets. Let assume that X follows a mixture of two lognormal distributions. Its density $f_X(x)$ is

$$f_X(x) = \sum_{i=1}^{2} \pi_i f_i(x)$$

Where $f_i(x)$ and π_i are respectively the (lognormal) density and the weight of the i-th component. The k-th order moment respect the origin of the mixture

$$E[X^k] = \mu^{(k)}$$

has been calculated as

$$\mu^{(k)} = \sum_{i=1}^{2} \pi_i \mu_i^{(k)}$$

where $\mu_i^{(k)}$ is the k-th order moment respect the origin of the i-th component. $\mu_i^{(2)}$, $\mu_i^{(3)}$, $\mu_i^{4)}$ can be written in terms of mean $\mu_i^{(1)}$, standard deviation σ_i, skewness β_3 and kurtosis β_4 of the i-th component as

$$\mu_i^{(2)} = \sigma_i^2 + (\mu_i^{(1)})^2 \quad (1)$$

$$\mu_i^{(3)} = \beta_{3_i}\sigma_i^3 + 3\mu_i^{(1)}\sigma_i^2 + (\mu_i^{(1)})^3 \quad (2)$$

$$\mu_i^{(4)} = \beta_{4_i}\sigma_i^4 + 4\mu_i^{(1)}\beta_{3_i}\sigma_i^3 + 6(\mu_i^{(1)})^2\sigma_i^2 + (\mu_i^{(1)})^4 \quad (3)$$

The skewness β_3 and kurtosis β_4 of the mixture are respectively

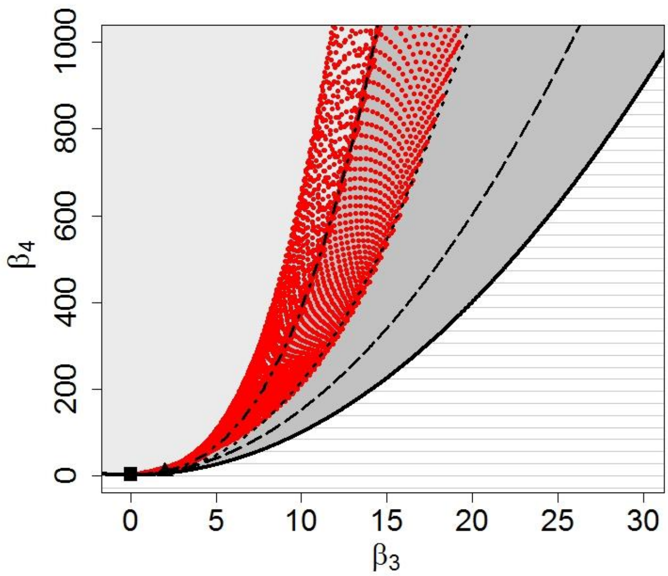
$$\beta_3 = \frac{\mu^{(3)} - 3\mu^{(1)}\mu^{(2)} + 2(\mu^{(1)})^3}{(\mu^{(2)} - (\mu^{(1)})^2)^{3/2}} \quad (4)$$

$$\beta_4 = \frac{\mu^{(4)} - 4\mu^{(1)}\mu^{(3)} + 6\mu^{(2)}(\mu^{(1)})^2 - 3(\mu^{(1)})^4}{(\mu^{(2)} - (\mu^{(1)})^2)^2}. \quad (5)$$

Substituting Eq.s (1-3) into Eq.s (6,7), it is possible to express skewness and kurtosis of the mixture as a function of mean, standard deviation, skewness and kurtosis of each component.

In the skewness-kurtosis plane, the domain of a mixture of two Lognormal distributions has been determined numerically through a Montecarlo simulation by simulating couples of lognormal distributions with parameter μ in the range (-10:0.1:10), parameter σ in the range (0:0.1:10) and weight π in the range (0:0.1:10). The skewness and the kurtosis can be calculated by using equations (4,5).

We compared the Johnson SB domain (in dark grey) with the domain of a mixture of two lognormals (indicated with red dots), as reported here in the figure. This is an original issue never investigated in the literature and we will be happy to deal it in the revised manuscript.



As shown in the figure, the Johnson SB distribution has a wider domain respect to the mixture of two lognormals, indicating that the Johnson SB distribution is more versatile respect to the mixture of two lognormals in representing the OPC data.

GC4: "**Regarding the use of the skewness-kurtosis (S-K) plane, does it provide more information that cannot be achieved by examining other parameters of the PNSD conventionally used (e.g., first and second moments of lognormally transformed data)? Given the long history of modeling PNSDs, the mode gives some indication of whether the dominant source is likely anthropogenic or biogenic; the geometric standard deviation may be related to the extent of atmospheric dispersion. It is not clear from the results presented whether 1) changes in PSNDs in the S-K plane cannot be detected in a conventional parameter space, and 2) any approximate delineations can be proposed that link physical processes to regions in S-K that could demonstrate its usefulness**."

Thank you for this comment, we will improve the description of the skewness-kurtosis plane in the revised manuscript, accordingly.

The S-K has been used here as a powerful and easy-to-use statistical tool for the identification of the statistical distributions which best represent the PNSDs. The peculiarity of the S-K moment-ratio diagram is that every theoretical distribution occupies a specific domain in the plane, that can be a point, a line or an area. Thus, this plane can be used as a diagnostic tool for the identification of distributions able to model given datasets, comparing the domain of the theoretical distributions and the sample variability. For these reasons we can state that the use of this plane provides different information respect the examinations of other statistical parameters, conventionally used for the analysis of PNSDs. In the manuscript we have described our first tentative to study the changes in PNSDs pattern in the S-K plane related to physical processes, in particular the influence of primary and secondary aerosol particles. In the future, we would like to examine more in depth this very interesting and, in our opinion, very promising analysis.

On the functional form of particle number size distributions: influence of particle source and meteorological variables

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Abstract. Particle number size distributions (PNSDs) have been collected periodically in Milan urban area, Italy, during 2011 and 2012 in winter and summer months. Moreover, comparable PNSD measurements were carried out in the rural mountain site of Oga-San Colombano (2250 m a.s.l.), Italy, during February 2005 and August 2011. The aerosol data have been measured through the use of Optical Particle Counters in the size range $0.3 - 25$ μm, mainly belonging to the coarse mode (PM_{coarse}), with a time resolution of one minute. The comparison of the PNSDs collected in the two sites has been done in terms of total number concentration, showing higher numbers in Milan (often exceeding 10^3 cm^{-3} in winter season) compared to Oga-San Colombano (not greater than $2 \cdot 10^2$ cm^{-3}), as expected. The skewness-kurtosis plane has been used in order to provide a synoptic view, and select the best distribution family describing the empirical PNSD pattern. The four-parameter Johnson SB (JSB) distribution has been tested for this aim, due to its great flexibility and ability of assuming different shapes. The PNSD pattern has been found to be generally invariant under site and season changes. Nevertheless, several PNSDs belonging to Milan winter season (generally more than 30 %) clearly deviate from the standard empirical pattern. The seasonal increase of the concentration of primary aerosols due to combustion processes in winter and the influence of weather variables, such as precipitation and wind speed, throughout the year, could be considered plausible explanations of PNSD dynamics.

1 Introduction

High suspended aerosol concentration in low atmosphere causes short-term health effects and increases the possibility of contracting serious chronic respiratory and cardiovascular diseases (Pope III and Dockery, 2006; Pope III et al., 2011; WHO, 2013). In addition, atmospheric aerosols reduce the visibility (Schwartz, 1996) and alter the Earth's radiation balance (Solomon et al., 2007; Stocker et al., 2013) are two additional environmental issues. In particular, aerosol size distribution is a climate relevant variable, able to modify the optical properties of particles and their cloud forming potential as well (Stocker et al., 2013)

Number concentrations of aerosol particles are generally very high in urban and kerbside environments, compared to rural and pristine areas, due to the proximity to pollution sources (Van Dingenen et al., 2004). Urban particle number concentration (in the range 10 nm - 800 nm) is usually above 10^4 cm^{-3} during the cold season, while at regional background site it do not exceed 10^3 cm^{-3} (Van Dingenen et al., 2004; Asmi et al., 2011). In urban environment the most important sources of atmospheric aerosols are combustion processes (mainly related to traffic, residential heating, and energy production), road dust re-suspension, and formation of secondary aerosols from gas and particulate phase precursors. While combustion emissions and secondary aerosol contributes mainly to fine particles (below 1 μm), road re-suspension and part of the traffic emissions contribute to the coarse particle mode (Seinfeld and Pandis, 2006; Fuzzi et al., 2015). In pristine areas aerosols are mainly composed by secondary aerosol (fine particles) and re-suspended soil dust (coarse particles). Source and removal processes determine season and spatial variability of particle size distribution.

Models can describe particle number size distribution by two different approaches. In the sectional approach, particles are distributed into size bins, or sections. Such approach is computationally expensive, but does not require any assumptions about the functional form of the particle size distribution. More computationally efficient models represent aerosol with a limited number of modes, described by mathematical equations. This scheme requires to know the mathematical function that better describes the multimodal distribution of ambient aerosol. In the literature, different probability distribution functions have been used to represent particulate size distributions. The first one is the classic Normal distribution, that was soon discarded because of its symmetry (Liu and Liu, 1994). Other distributions have been used in limited specific applications: Deirmendjian (1964, 1969) proposed the modified-gamma distribution for describing the particulate size distribution of marine or coastal particles for studying the light scattering phenomena; Brown and Wohletz (1995) employed the Weibull distribution to fit the aerosols generated from fragmented rocks; Rosin and Rammler (1933) introduced a new mathematical form, derived from the Weibull distribution, the so called Rosin-Rammler, to model the evolution of atmospheric aerosol. Later, Barndorff-Nielsen (1977, 1978) introduced firstly the Hyperbolic, and secondly the Generalized Hyperbolic distribution to represent the statistical variability of sand grading. Other authors (Junge, 1963; Clark and Whitby, 1967; Pruppacher and Klett, 1980) proposed the Power-Law distribution to model atmospheric aerosol number size distribution. This is mathematically simple to compute, compared to other used functional forms, but it is accurate only over a limited size range, beyond which significant errors can arise (Leaitch and Isaac, 1991). Above all, the most used distribution to describe PNSDs is the lognormal (Jaenicke and Davies (1976); Whitby (1978), among others). This functional form is mathematically simple, easy to apply and allows a good match with a wide variety of empirical data, even if a theoretical justification for its widespread use does not exist, neither it has been identified to be superior to others in a general sense (Seinfeld and Pandis, 2006; Hinds, 2012).

Here, the four-parameter Johnson SB distribution is considered for modelling PNSD data, in addition to the classical mixture of (two) lognormals, widely used in the literature (Butcher and Charlson, 1972; Hinds, 1982; Seinfeld and Pandis, 2006). The great flexibility and versatility of Johnson SB, together with its boundedness (which matches the physical limitations of the analysed aerosol particles) make it a good candidate for this purpose. The use of this distribution has also been inspired by Cugerone and De Michele (2015); D'Adderio et al. (2016); Cugerone and De Michele (2017), where the Authors have recently demonstrated the accuracy of Johnson SB in modelling the number size distribution of drops (DSD) at the ground, a particular case of PNSD. Furthermore, the outcomes of this study are in accordance with the works of Yu and Standish (1990) and Liu and Liu (1994), in which JSB was firstly proposed for this aim. In order to statistically prove the adequacy of this distribution, we use the skewness-kurtosis moment ratio diagram (S-K plane), the locus of the couples skewness (β_3) and kurtosis (β_4), as diagnostic tool (Vargo et al., 2010). The availability of a great number of PNSD data makes possible to plot a great amount of empirical couples (β_3, β_4) on S-K plane. In this way, the general PNSD empirical pattern and in parallel a consistent theoretical distribution family can be individuated.

In the next, we present the results of the analysis of a great amount of PNSD data, collected with Optical Particle Counters in two different sites: the urban site of Milan and the mountain rural site of Oga-San Colombano. By using the skewness-kurtosis plane, we shows the existence of a unique PNSD empirical pattern, which seems not to change, varying the site and the season, with the exception of the urban winter data.For these cases, the 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. In other words, the PNSD pattern does not change, even if we change the site or the season with the exception mentioned above. In winter In this case, the pattern seems to be altered, probably by the influence of the aerosols punctual sources, which cause an increase of the total particle counts. In order to give our interpretation of these trends, we used the S-K plane to summarize, from the statistical point of view, the aerosol dynamics due to anthropogenic and also meteorological forcings.

2 Datasets and instrumentation

The data have been collected in two sites: the urban site located in Milan at Pascal-Città Studi (45°28'42", 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 data have been collected in two sites: the urban background site located in Milan at Pascal-Città Studi (45°28'42"N, 9°13'54"E, 120 m a.s.l.) and the rural mountain site at Oga-San Colombano (46°27'40"N, 10°18'07"E, 2290 m a.s.l.). The former is an urban background site, while the latter was a temporary experimental high altitude site. Tab. 1 provides details about the period of observation considered in this analysis and the number of minutes. We would like to point out that the analysed time ranges have been selected also according to the availability of the aerosol PNSD datasets, which were kindly provided by ARPA Lombardia.

Aerosol particle number concentrations were measured using an Optical Particle Counter (OPC), Grimm 107 Environcheck model, with a time resolution of 1 minute. The measured size distributions range from 0.3 to 25 μm subdivided in 26 size bins for all the analysed months and sites. The only exception is the winter dataset of Oga-San Colombano collected in February 2005 (SC1), characterized by size distributions between 0.3 and 25 μm, subdivided in 15 size bins. The OPC measurements allow the quantification of a portion of fine mode particles (between 300 nm and 1 μm) and the coarse mode particles (above 1 μm). The instrument is based on the quantification of the 90° scattering of light by aerosol particles.

The two sites present very different characteristics regarding the magnitude, the distribution and the composition of the aerosol fraction and the climatic characteristics. In particular, Oga San Colombano shows a higher relative contribution of organic aerosol, likely of secondary origin, as suggested by a higher organic to elemental carbon ratio, Sandrini et al. (2014). Milano shows a higher nitrate to sulfate ratio, in agreement with a stronger impact from combustion sources, such as traffic and industrial emissions, Perrone (2012). Milan has a humid subtropical climate (Cfa), according to the Köppen climate classification (Kottek et al., 2006). Milan's climate, as the all Valpadana valley, the Northern Italy's inland plain, is influenced by the natural barrier of the mountains (the Alps in the North and the Apennines in the South) which obstruct and prevent inflows from North, South and West. Winters and summers are usually dominated by high pressure, while autumns and springs are characterized by alternation between high and low pressure. These conditions cause usually high moisture levels in the low atmosphere and air stagnation, especially during high pressure seasons. Furthermore, Milan climatic conditions can be considered a typical example of urban climate: urbanization has evidently changed the form of the landscape, and has also produced changes in the area's air. According to the European directive 2008/50/CE, all the European Countries must respect the standard limits related to the air quality (European Commission, 2008). In particular, the maximum daily levels of PM10 do not have to exceed 50 μm/m^3μg/m^3 (for more than 35 days per year), while the annual limit is 40 μm/m^3μg/m^3 (which should not be overcome on a yearly average). During 2011 (2012), the maximum daily limit in Milan was passed 122 (97) times, during the winter period, and the average yearly level was 47 (43) μm/m^3μg/m^3.

On the contrary, San Colombano is a mountainous pristinerural site, characterized by the typical Alpine climate (Dfb, according to the Köppen climate classification) with warm summers and long, cold and snowy winters. In the specific, the analysed site is located far away from higher mountains, and for this reason is not often shaded. Typically, San Colombano presents free air circulation and stagnation of cold air during winters. These characteristics allow low aerosol levels (the average annual value of PM10 is 6 μg/m^3 with standard deviation of 5 μg/m^3), mostly consisting in particles produced far away and transported locally by the wind and thus good air quality all over the year.

The influence of primary aerosol sources and meteorology on PNSD has been investigated for the site of Milan. To do so,

Table 1. List of sites with indication of season, date of measurement and number of minutes.

Code	Season	Date	N° minutes	Site
MI1	Winter	January 2011	43409	Milan
MI2	Winter	February 2011	21777	
MI3	Winter	February 2012	29221	
MI4	Winter	January 2014	41760	
MI5	Summer	July 2011	36621	
MI6	Summer	August 2011	28715	
MI7	Summer	July 2012	42833	
MI8	Summer	August 2012	41945	
SC1	Winter	February 2005	40320	Oga
SC2	Summer	August 2011	44243	

~~we have used measurements of common aerosol compounds, in particular nitrogen dioxide (NO_2) and nitrogen oxide (NO), measured by ARPA Lombardia at Pascal-Città Studi.~~ To study the effect of pollutant concentration we have used nitrogen dioxide (NO_2) and nitrogen oxide (NO) measurements, collected with a chemiluminescence technique following the requirements of European Standard EN 14211:2005:Ambient Air Quality. While, meteorological variables, namely precipitation and wind speed, have been measured respectively with a tipping bucket rain-gauge and by an anemometer located at the ARPA station of Lambrate (45°29’46”N, 9°15’28”E, 120 m a.s.l.), which is around 3 km away from Pascal-Città Studi.

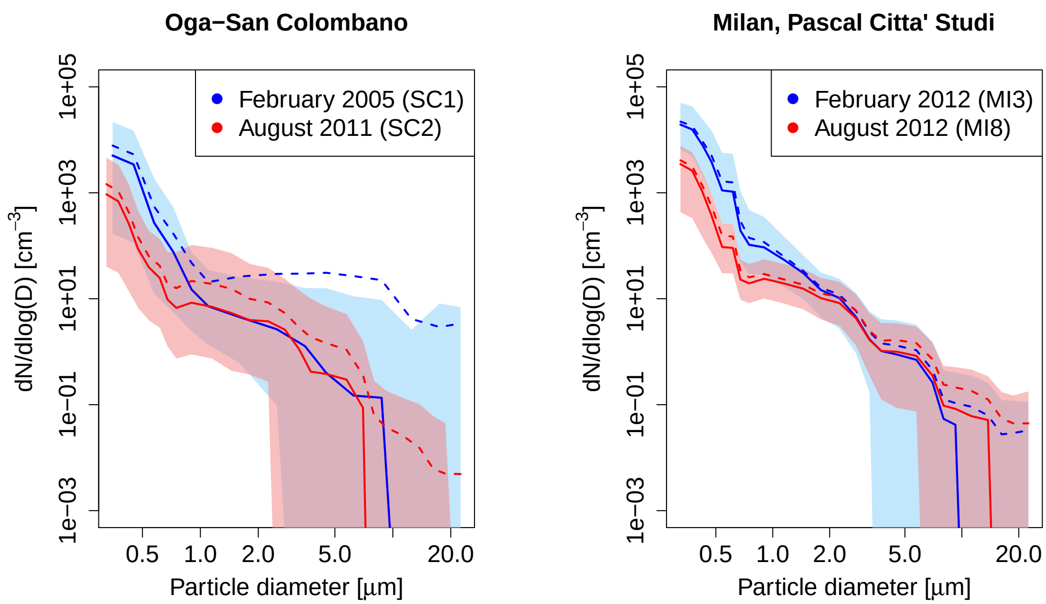

Figure 1. Median (solid lines) and mean (dashed lines) number size distributions for two selected winter and summer datasets of Pascal-Città Studi (MI3, MI8) and the two datasets of Oga-San Colombano (SC1, SC2). The coloured blue and red areas are limited below and above by the 5^{th} and the 95^{th} percentiles of the correspondent dataset.

3 Data analyses

The different characteristics of the aerosol number size distributions at Milan (urban site) and Oga-San Colombano (~~pristine~~rural site) are shown in Fig. 1. Here, median (solid lines) and mean (dashed lines) number size distributions for the two datasets of Oga-San Colombano (SC1, SC2 in the left panel) and two selected winter and summer datasets of Milan (MI3, MI8 in the right panel) are shown, together with the 95-confidence interval (coloured areas). Similar results can be obtained considering the other datasets of Milan. Median and mean number size distributions of all the datasets present a common decreasing trend inside the analysed size range, 0.3-25 μm, but also evident discrepancies. In particular, the coloured areas depicted in the plots denote a greater PNSD variability for SC1 and SC2 compared to MI3 and MI8. The distance between the

5^{th} and the 95^{th} percentiles of the latter is very small in the diameter range 0.3-3 μm, accumulation mode particles and smaller coarse mode particles, and is characterized by higher number concentrations (especially in winter) compared to Oga-San Colombano. Furthermore, a peak between 0.5 and 1 μm is clearly visible in the urban datasets, but not in Oga-San Colombano, corresponding to the droplet mode particles.

Looking at these plots, it is difficult to understand if a unique functional form is able to describe the variety of PNSDs. In order to clarify this issue, we propose the use of the skewness-kurtosis moment-ratio diagram as diagnostic tool. This plane was introduced by Craig (1936) and then updated by various authors, e.g. Balakrishnan et al. (1994); Cugerone and De Michele (2017). The skewness-kurtosis ($\beta_3 - \beta_4$) plane presents the skewness (Eq. 1), in abscissa, and the kurtosis (Eq. 2), in ordinate,

$$\beta_3 = E\left[\left(\frac{X-\mu_X}{\sigma_X}\right)^3\right] \tag{1}$$

$$\beta_4 = E\left[\left(\frac{X-\mu_X}{\sigma_X}\right)^4\right] \tag{2}$$

where X is the variable, $E[.]$ is the expected value, μ_X and σ_X are respectively the mean and the standard deviation of X. The Pearson limit curve $\beta_4 - \beta_3^2 - 1 \geq 0$ (Pearson, 1916) divides the theoretically impossible and possible areas, in which a couple (β_3, β_4) can be found. In this diagram, each theoretical probability distribution is represented by a domain, which can be a point, or a line, or an area, depending on the number of shape parameters involved. Therefore, this plane can be used as a diagnostic tool for the identification of distributions able to model given datasets, comparing the theoretical domain of the distributions and the sample variability of data. In Fig. 2, following Cugerone and De Michele (2015, 2017), we have reported the domain of some families of distributions including: normal, exponential, gamma, lognormal, Johnson SB and Johnson SU, and in addition, for the first time, a mixture of two lognormals. From Figure 2, it is possible to identify the following features:

- normal and exponential are represented by a single point. In particular, the square (0,3) represents the normal, and the triangle (2,9) the exponential;
- gamma (long-dashed line) and lognormal (dotted-dashed line) are distributions represented by a line;
- the Johnson SB is the upper and lower bounded family and occupies the area (medium grey region) limited below by the Pearson limit curve and above by the lognormal line. The Johnson SU is the unlimited family; it covers all the rest of the plane (light grey region) and is limited below by the log-normal curve
- the domain of a mixture of two lognormals (red dots area) is represented by an area embracing the lognormal line. The domain has been determined numerically by Montecarlo simulations as reported in Appendix A.

Given this, we use the skewness-kurtosis plane to search the best functional forms able to describe the sample PNSDs of Milan and Oga-San Colombano datasets and to analyse the effects of primary pollutants and weather variables, in order to clarify the dynamics of PNSD variations.

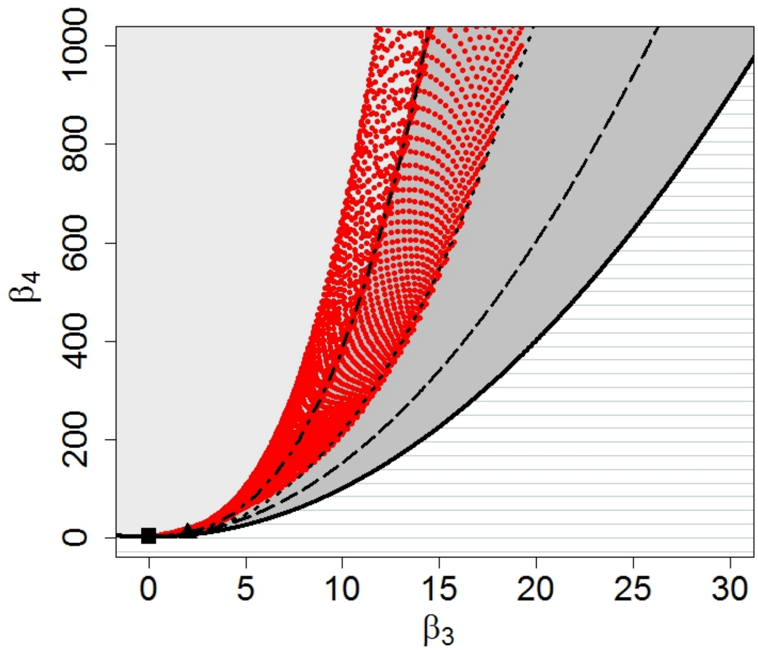

Figure 2. (β_3, β_4) domain of some families of distributions including: normal (square), exponential (triangle), gamma (dashed line), lognormal (dotted-dashed line), Johnson SB (medium grey area) and Johnson SU (light grey area), and a mixture of two lognormals (red dotted area).

4 Results and discussions

4.1 Urban vs rural sites

In order to analyse and compare PNSDs characterized by different ambient conditions and different seasons, we calculate the skewness and the kurtosis of each minute of the four datasets previously considered, SC1 (a), SC2 (b), MI3 (c), MI8 (d), and we report the sample couples (β_3, β_4) in the skewness-kurtosis plane, see Fig. 3. The sample couples (β_3, β_4) are divided in four classes and coloured as function of the total particle count (TP) of the related minute: cyan dots represent PNSDs with TP$<$25000, blue dots 25000$<$TP$<$62500, purple dots 62500$<$TP$<$100000 and magenta dots TP$>$100000.

Firstly, by analysing Fig. 3, we see that the great part of the couples are located inside JSB theoretical domain, see Tab 2. This is a four-parameter distribution characterized by a bounded domain, which is suitable for the particles diameter, being a finite variable. MI3, the Pascal-Città Studi dataset collected on February in midwinter, represents the only evident exception with the 29.6% of the data points outside the JSB domain. Fig. 3 indicates also the existence of a relation between the position of the dots and their colour, and thus between the functional form and the total particle count. In particular, the sample skewness-kurtosis couples tend to move left and to exit from the JSB domain with the increase of TP. This is again specially true for MI3, which is characterized by the 96% percentage of the data points belonging to the fourth class, with TP>100000, while for SC1, SC2 and MI3 the percentages are respectively 18%, 2% and 14%. To stress this point, let's consider only the data outside the JSB domain. The percentage of data outside JSB with TP>100000 is 73.2%, 33.3%, 99.5% and 95.5%, respectively for SC1, SC2, MI3 and MI8. The smaller percentage observed for SC2 is likely due to the limited number of data points characterized by large TP, and thus not statistically significant. We can conclude that, in case of very high number of aerosol particles, the Johnson SB cannot be considered anymore the most accurate distribution in describing PNSDs. From Fig. 3, it is possible to see that, the data points outside the JSB domain, are located within the domain of Johnson SU (light grey) and in some cases in the domain of the mixture of two lognormals, which seem good candidates to represent them, even if these distributions are

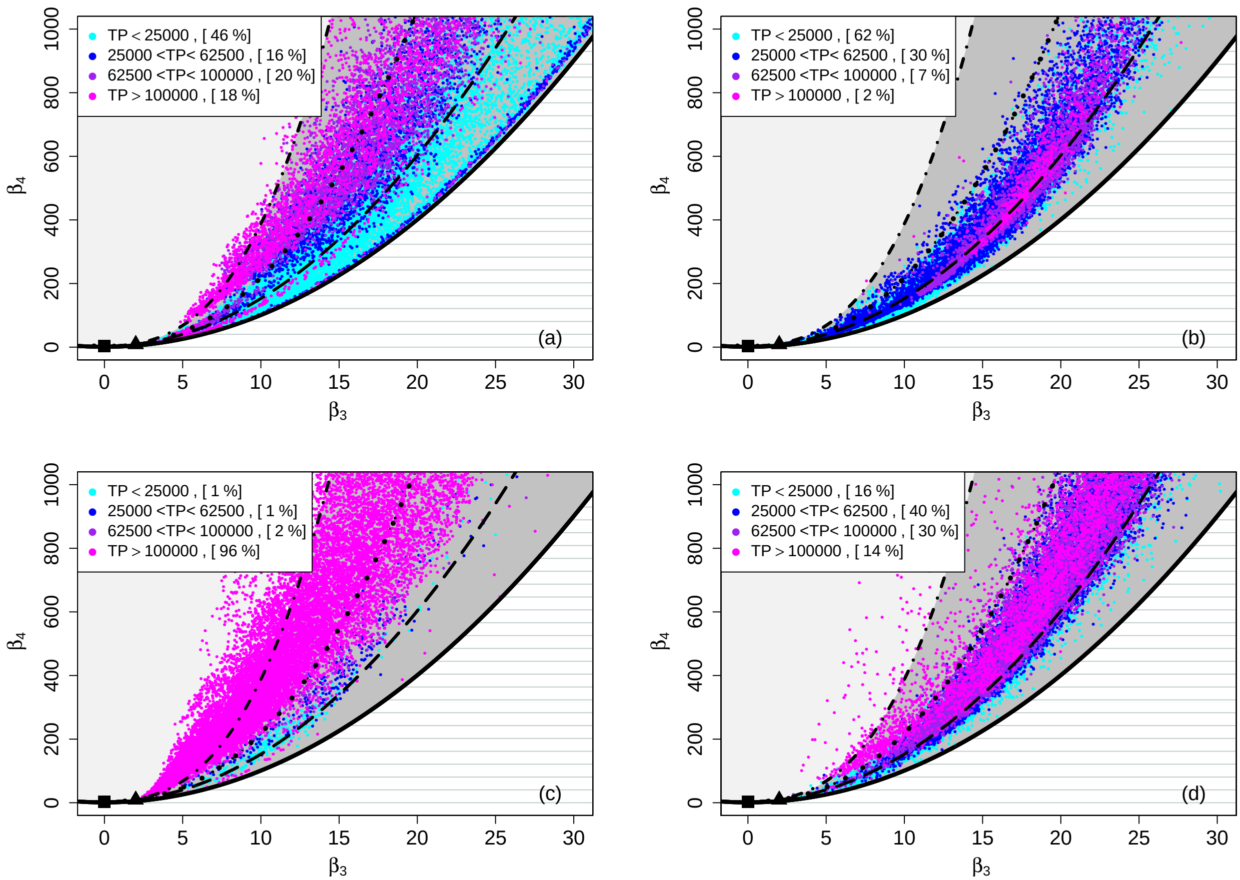

Figure 3. Location of the sample couples (β_3,β_4) from SC1 (a), SC2 (b), MI3 (c), MI8 (d) datasets in the skewness-kurtosis plane with theoretical distribution reference domains. Cyan dots represent PNSDs with TP<25000, blue dots 25000<TP<62500, purple dots 62500<TP<100000 and magenta dots TP>100000. The dotted-dashed line is the lognormal distribution, the dotted line is the Weibull distribution, and the dashed line is the gamma distribution.

not upper bounded, like the variable under investigation. Similar results have been obtained for the others Milan datasets, see Appendix B.

Table 2. Quantitative analysis of Fig. 3

(β_3,β_4)	SC1 [%]	SC2 [%]	MI3 [%]	MI8 [%]
with TP$>10^5$	18	2	96	14
outside JSB	1.1	0	29.6	0.4
with TP$>10^5$ outside JSB	73.2	33.3	99.5	95.5

As proof of this, we have fitted the JSB distribution to the measured PNSDs, using the Maximum Likelihood Method(, see Appendix C for more details). Fig. 4 shows the size distribution of particle number at the urban site MI3 in winter (red), at the urban site in summer MI8 (blue), and at the rural site SC2 (green), together with their corresponding position in the (β_3, β_4) space. The three PNSDs are representative of their own datasets. In particular, the MI3 PNSD collected at 9:57 pm (UTC) counts 1155778 particles, the MI8 PNSD collected at 4:34 pm (UTC) counts 9465 particles and the SC2 PNSD collected at 8:41 pm (UTC) counts 2755 particles. The JSB accurately fits PNSDs data in the last two cases, characterized by a lower total number of particles. The figure clearly illustrates that when the size distribution is efficiently described by the JSB parameterization, the corresponding distribution falls in the grey area, the JSB domain. The mixed lognormal distribution, represented in the skewness-kurtosis plane with dark grey dots, is not able to represent the PNSDs in none of the three cases.

4.2 Primary pollutants influence

The analysis of the skewness-kurtosis plane shows the existence of a PNSD pattern, which is generally under site and season changes, with the exception of the winter datasets. During winter seasons in urban environments, a significant change of the general PNSD pattern, consisting in a shift toward the centre of S-K plane, has indeed been observed. A plausible explanation of PNSD dynamics can be found in the recurrent winter increase of aerosol emissions (much more evident in urban sites), due to heating ignition and high traffic levels.

In order to clarify this point, measurements of two common atmospheric components, in particular nitrogen dioxide (NO_2) and nitrogen oxide (NO) collected at Pascal-Città Studi, have been considered. Nitrogen oxides (NO_x=NO+NO_2) can form naturally in the atmosphere by lightning and some is produced by plants, soil and water, but their major source in urban areas is the burning of fossil fuels, like coal, oil and gas (World Health Organization, 2000). NO_x are mainly produced by combustion processes. Nevertheless primary combustion emissions are dominated by NO over NO_2. NO_2 can then be formed through the oxidation of NO in the atmosphere. It follows that the NO_2 to NO_x ratio can provide a measure of the oxidative capacity of the

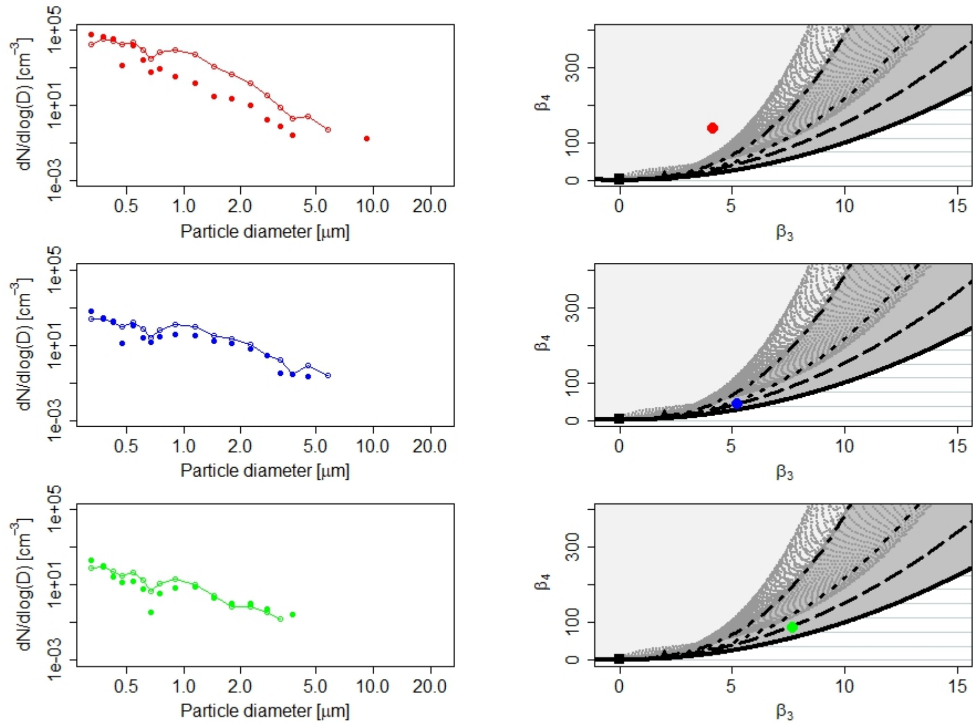

Figure 4. Comparison of empirical PNSDs (dots) and JSB fittings (lines) from MI3 (red), MI8 (blue) and SC2 (green), first column. Correspondent location of the (β_3, β_4) couples in the (S-K) plane, second column.

atmosphere (Rao and George, 2014; Fernández-Guisuraga et al., 2016) ~~and indirectly of the relevance of secondary pollutant formation over primary emissions.~~ and it is a measures 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. 5 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/NO_2 between 1 and 1.1 (red dots - strong prevalence of secondary aerosols), 1.1 and 1.5 (orange dots - ligh prevalence of secondary aerosols), 1.5 and 3 (yellow - light prevalence of primary aerosols), greater than 3 (green - strong prevalence of primary aerosols). 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/NO_2 greater than 3 are around 50 %, indicating a prevalence of the primary 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 aerosols emission by local sources causes an evident increase of primary

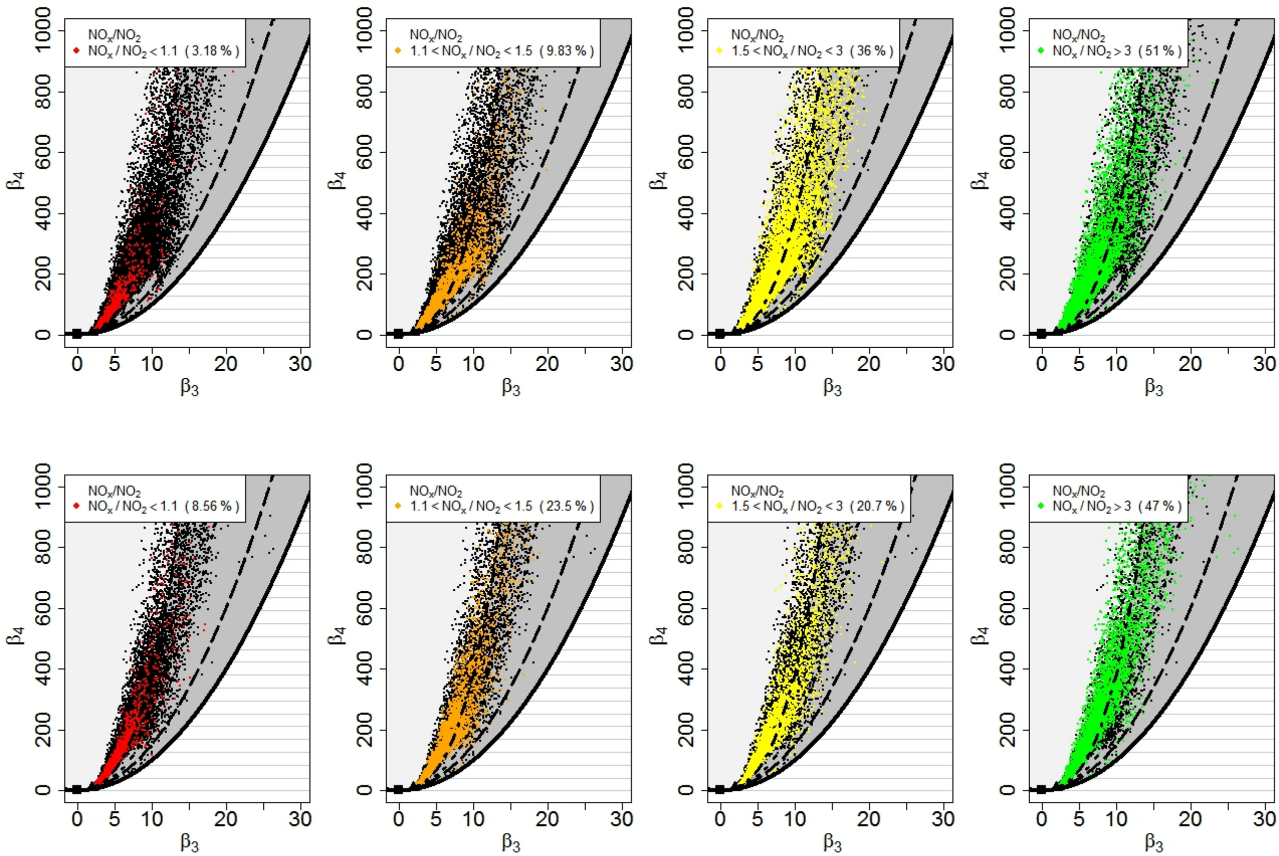

Figure 5. Location of the sample couples (β_3,β_4), black dots, from MI1 (upper panel) and MI2 (lower panel) in the skewness-kurtosis plane with theoretical distribution reference domains. Red dots represent PNSDs with ratio NOx/NO_2 between 1 and 1.1, orange dots 1.1<NOx/NO_2<1.5, yellow dots 1.5<NOx/NO_2<3 and green dots NOx/NO_2>3.

aerosol compounds concentration. This can be considered one of the cause of the location shifts of (β_3,β_4) couples in the skewness-kurtosis plane.

4.3 Weather variables influence

The aerosol concentration variation due to the increase of particles emissions in the atmosphere is not the only cause of PNSD shape changes. The occurrence of weather events, such as precipitation or high wind speed, indirectly causes a modification of the particle concentration, which often results in a decrease of number and mass of aerosol particles suspended in the low atmosphere. In particular, the aerosol wet removal during rain events, known as scavenging process, is caused by the vertical movement of the falling raindrops, which intercept the suspended aerosol particles and bring them to the ground (Seinfeld and Pandis, 2006). While, the blowing of high wind speeds in urban areas far away from the sea, like Milan, cleans the atmosphere by dispersing and diluting the aerosol particles and preventing local accumulations (Harrison et al., 2001). The visible effect of these phenomena in the skewness-kurtosis plane is described again by a shift of the position of the couples (β_3,β_4), but in the opposite direction (toward the right-side of S-K plane) respect to the one (toward the centre of S-K plane) caused by the influence of the high concentration of primary aerosol compounds. In other words, the couples (β_3,β_4) are forced to stay in the JSB theoretical domain. Therefore, looking at the skewness-kurtosis plane, the influence of the weather variables is visible only if the occurrence of high wind speed or significant precipitation events are foregone by particle size concentrations characterized by couples (β_3,β_4) outside JSB domain. These conditions generally occur in winter seasons in urban areas, as we have seen in the previous paragraph.

Two practical examples are taken from the dataset MI3 (February 2012). The first is related to precipitation (Fig. 6), the second to wind (Fig. 7). In both the two cases we represent the skewness-kurtosis plane and we track the movement of the couples (β_3,β_4) before, during and after the respective weather event. The dots are coloured according to the time window in which the PNSDs have been collected. Fig. 6 shows the location of the sample couples (β_3,β_4) in the skewness-kurtosis plane during the days 19-20-21 February 2012; each day is represented in a specific panel to visualize the movements of the couples precisely. On February 19$^{\rm th}$ the couples are stably located outside the JSB domain, as normally for urban site in midwinter, no precipitation occurs. In February 20$^{\rm th}$ between 9am and 5pm, a rainfall event with a maximum intensity of 1 mm/h and

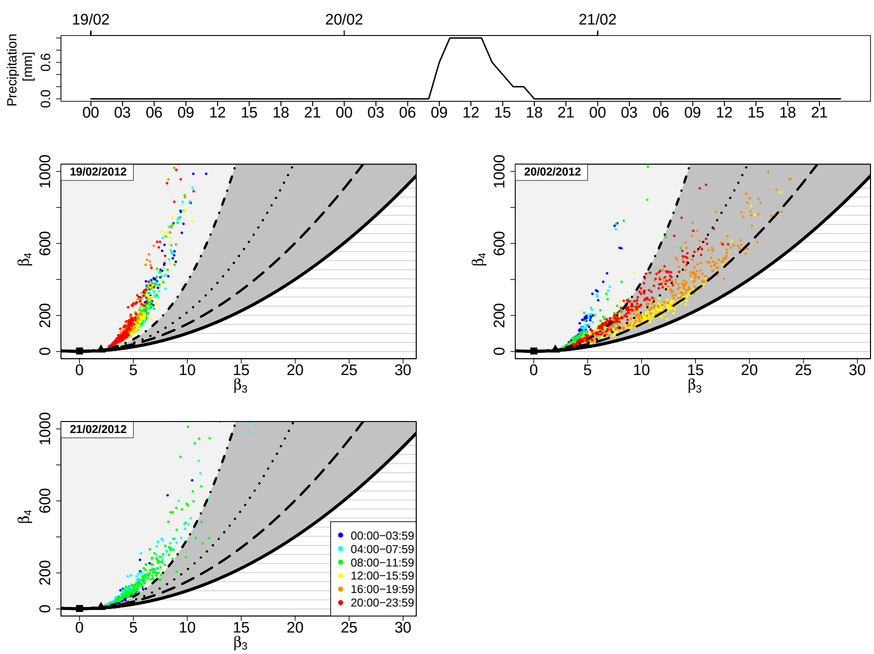

Figure 6. Location of the sample couples (β_3,β_4) in the skewness-kurtosis plane for the days 19-20-21/02/2012. The dots are coloured according to the time slot as explained in the legend. Between 9am and 5pm of February 20$^{\rm th}$, a precipitation event with a maximum intensity of 1 mm/h and average intensity of 0.6 mm/h occurred.

average intensity of 0.6 mm/h occurred. The influence of meteorological change is clearly reflected in the skewness-kurtosis plane: the dots related to PNSDs collected between midnight and 8 am (blue and cyan) on this day are still outside JSB area, but starting from 8 am until around 8 pm the dots (green, yellow and orange) move right and enter inside JSB domain, then after 8 pm they start to exit (red dots) and remain outside also during February 21^{th}.

Similarly, the effect of high wind speed is reported in Fig. 7, where the location of the sample couples (β_3,β_4) in the skewness-kurtosis plane during the days 14-15-16-17 February 2012 is shown. During these days, and in particular between February 15^{th} and February 16^{th}, relatively high wind speed with maximum of 3.8 m/s (recorded on 15/02 at 3pm) occurred. The increase of wind speed causes a movement to the right (inside JSB area) of the couples (β_3,β_4), but when the wind speed decreases the couples returns outside JSB domain fairly quickly.

In other words, the modifications of PNSDs shape (caused by increase or decrease of aerosol concentration by new emissions or weather events) result in movements of the sample (β_3,β_4) couples in the moment ratio diagram, and consequently in changes of the pool of distributions potentially able to describe the PNSDs. Inside this pool, the Johnson SB distribution seems the best, in case of ~~pristine or~~ low polluted conditions - achievable also after significant weather events, such as precipitation or high wind speed. Gamma, lognormal and Weibull can be considered accurate too, but for a limited number of times. Conversely, in case of high concentration, none of these distributions should be inserted into the pool: the PNSD shape changes because of the elevated increment of the fine particles, which shift the sample mode to the left and cause an increase of the number of

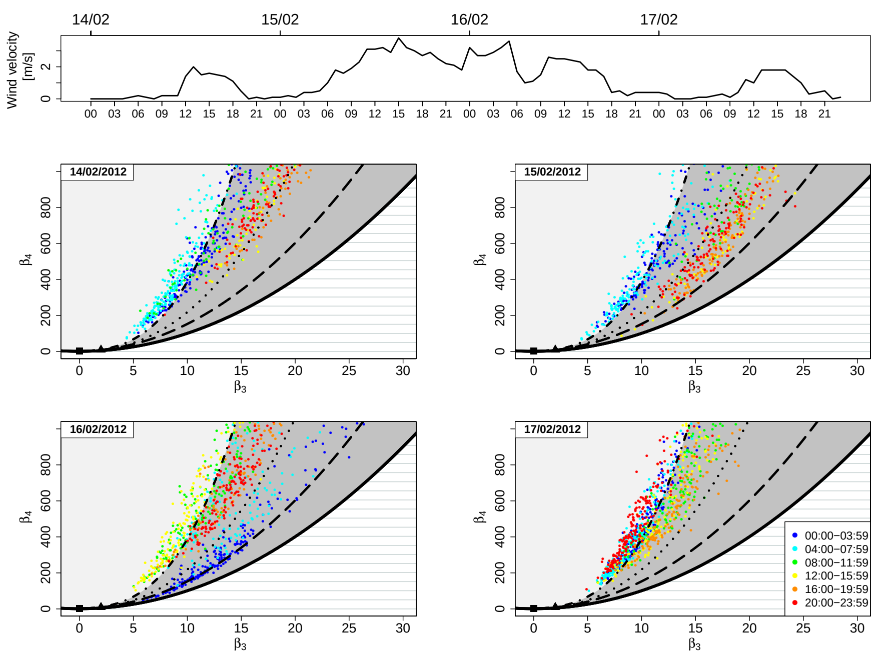

Figure 7. Location of the sample couples (β_3,β_4) in the skewness-kurtosis plane for the days 14-15-16-17/02/2012. The dots are coloured according to the time slot as explained in the legend. Between February 15^{th} and February 16^{th}, relatively high wind speed with maximum of 3.8 m/s (recorded on 15/02 at 3pm) occurred.

outliers. (β_3,β_4) couples are shifted into an area of the skewness-kurtosis plane belonging to unlimited distributions, such as the Johnson SU or the Generalized Hyperbolic. These distributions become the best suitable for PNSDs characterized by this kind of shape, despite the limited (above and below) nature of the variable under exam, the aerosol diameter.

5 Conclusions

In this work, OPC data, collected in two sites, one urban, Milan at Pascal-Città Studi, and one ~~pristine~~rural, Oga-San Colombano, have been analysed. The aerosol particle number concentrations present very different characteristics: the magnitude, the composition of the aerosol fractions and also the empirical distribution shape vary a lot within the dataset. These variations are caused both by the different nature of the measurement site (urban and polluted Pascal-Città Studi, rural ~~and pristine~~ Oga-San Colombano) and by the season of measurement. This likely suggests that a unique statistical distribution cannot be able to cover all of the PNSD forms.

In order to statistically identify the best distribution describing the empirical PNSD pattern, the skewness-kurtosis plane has been used as a synoptic tool. Our analyses show that the four-parameter Johnson SB, thanks to its flexibility, could be considered the most accurate distribution for representing the empirical PNSD forms, being able to describe the great majority of the PNSDs analysed, under conditions of low pollution level. Other distributions, such as gamma, Weibull, lognormal,and mixture of two lognormals could be considered adequate too, but for a much more limited portion of the datasets. Further work is needed to quantitatively describe the goodness of the JSB distribution, and the link between the fit parameters and aerosol sources and processes. Such analyses will be the subject of a future study.

The urban datasets, collected on January and February in midwinter, represent the only evident exceptions, since their PNSDs clearly deviate from the pattern generally found for the other datasets. The combined analysis of the skewness-kurtosis plane and the ratio between NOx and NO_2 suggested that the increase of the concentration of primary aerosol compounds, due to the seasonal winter increase of combustion processes from a countless number of punctual sources, can be considered a plausible explanation of PNSD empirical pattern dynamics. In particular, the increment of the fine particles shifts the sample mode to the left and causes an increase of the number of outliers. In these cases, distributions like the Johnson SU and the mixture of two lognormals can be good candidates. This important issue will be investigated in future works.

Nevertheless, also the occurrence of weather events, such as precipitation and high wind speed, by indirectly decreasing the aerosol concentrations, can have considerable influence in PNSD dynamics. The influence of these events is particularly evident in winter months, when the aerosol concentration is normally high and the PNSDs deviate from the general empirical pattern. Precipitation or high wind speed decrease the aerosol concentration, making the empirical PNSDs following again the general empirical pattern, even if for a limited time (more or less corresponding to the duration of the event itself).

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