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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric nanoparticle observations in the low free troposphere during upward orographic flows at Izaña Mountain Observatory" *by* S. Rodríguez et al.

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Reply to comments of "F. Costabille (Referee)" S. Rodríguez srodriguez@inm.es

We thank very much the review and comments performed by this referee. These suggestions allow improving the manuscript by performing a more specific analysis that may contribute to generalize the results and conclusions of this study. The replies to the referee's questions are listed below. Most of suggestions have been introduced in the manuscript and will appear in the final version.

Comment-1(a). Referee said ". . .. .I suggest to build up one single dataset, including all data observed - including one year, night and day data and excluding only cases when available data are below the detection limit. . ...".

Reply: We have done this analysis as suggested the referee. Results are shown in Table 1. In PC1 an association between N3-10 and nitrogenous compounds is observed. In PC4, an association between SO2 and N3-10 is also observed. This result was also obtained in the month-by-month analysis we performed initially. However, other important results that were found in the month-to-month analysis are not observed in the single PCA (1-year). For example, the significant negative association between N3-10 and temperature we observed in summer (July) is not observed in this new PCA. Other example, the significant negative association between N3-10 and PM10 (Saharan dust) we observed in summer (July) is not observed in this new PCA. Other example, the association between N3-10 and direct-radiation observed in July PCA is not observed with the 1-year PCA. This happens because the PCA performed in a "month-to-month basis" and with "the whole data set ($\sim$1year)" are complementary (not equivalent). As pointed by one of the referee in the fast review step, results obtained in the PCA are strongly dependent on many factors (e.g. type of variables, eigenvalues, maximum number of factors allowed, data set length, etc. . .). An example of this was discussed, in previous studies on aerosol chemistry, by Rodríguez et al. (2002, Journal of Geophysical Research, 107, 4777-4790) and Rodríguez et al. (2004, Science of The Total Environment, 328, 95-113). In these 1-year studies it was shown how the highest concentration of nitrate were recorded in the two coldest month of the year (January and February) due to the condensation of ammonium-nitrate (in the rest of the year low concentrations of nitrate were due to calcium and sodium nitrate). However, in a PCA performed with the "1-year data" set the association between nitrate and ammonium was not observed (even if ammonium-nitrate accounted for the highest concentrations of nitrate). In contrast, the seasonal PCAs showed a strong association between ammonium and nitrate in winter, but not in the other seasons. The analysis of the seasonal evolution of the score factors (proposed by the referee) is suitable if the

principal components identified in the PCA allows a detailed identification of the processes affecting the studied variable. However, shown in Table 1 and explained above, this is not the case. In summary, the result of the PCAs performed with the whole data set is complementary to that performed in a month-by-month basis. The 1-year PCA allows identifying the general relationships between N3-10 and other variables (SO2 and nitrogenous compounds in this case). However, a month-to-month PCA for provides more details on the role of for seasonal specificities (temperature, dust as condensation sink, etc. ...). Reword. The results obtained in the PCA performed with the whole data set will be included or discussed in the final version of the manuscript. This allowed identifying the general relationships between N3-10 and other variables (SO2 and nitrogenous compounds in this case). We sincerely consider that this is an interesting analysis, but complementary to the month-by-month PCA.

Comment-1(b). Referee said ". . .. .The results of this statistical analysis can be misleading for two major reasons: Data availability varies a lot with the months . . . From a statistical perspective, the number of cases does not guarantee for every month a statistically representative dataset. As the major consequence, the resulting principal components (PCs) extracted are difficult to investigate. (E.g., it is difficult to understand the meaning of PC3 calculated in Nov 2007, tab.2.)".

Reply: In table 3, it can be observed how the number of days with available data is equal or higher than 22 during 8 month (over 12 months). It means that the data availability accounts for at least the 73% of the period of each month (22 days). In our modest opinion this is a suitable "minimum data availability" of the month, i.e. the results of a PCA performed with $\geq$73% of the days/month should not differ significantly to that obtained with the 100% of the days/month. Although it was not said in the manuscript text, no PCA was performed in June because the low number of available days. Reword: The suggestion of the referee is important, it is necessary to declare clearly in the manuscript that monthly PCA were performed only on month with a enough high data availability. For this reason, a short sentence has been added to the first para-

graph of section 4.3.1: "PCA were only performed when the data availability was $\geq$22 days/month". PC3 in Nov 2007: the association between PM10, T and P is due to Saharan dust transport. These events are more frequent in summer, although they may also occur at any period of the year. Transport of Saharan dust air masses occurs in autumn-winter under high pressures over North Africa and Canary Islands (high P values) and result in increases in temperature and PM10 concentrations at Izaña (see details in Viana et al., 2002, Atmospheric Environment, 36, 5861-5875; Alonso-Pérez et al., 2007; Atmospheric Environment, 41/40, 9468-9480). This is the origin of PC3 in Nov 2007.

Comment-2. Referee said "I suggest a deeper investigation of the - common and odd - sources of NO, NOy, SO2, and PM10 concentrations affecting the measurements at Izana Mountain Observatory (E.g.: Weekly cycles may be investigated to separate anthropogenic emission sources from biogenic contributions). The different evolution of NO and NOy–NO concentrations can be analyzed to identify fresh emissions sources, and aged air masses. The decoupling of SO2 and PM10 sources can clarify the negative association with N3$-$10 not shown in PC3 of Nov07, tab.2.) Particularly, the understanding of the reasons causing the higher concentrations of the nitrogen compounds during Type II events has probably the potential to elucidate mechanisms still unknown. . .. .

Reply: In our opinion, the role of the most important sources and processes that affect NO, NOy, SO2, and PM10 is already discussed in the manuscript. When performing the data treatment we did many other analyses that are not described in the current version of the manuscript for the sake of brevity. For example, the role of fresh emissions and the weekly cycles suggested by the referee. Izaña is a Global Atmospheric Watch station (http://gaw.empa.ch/gawsis/reports.asp?StationID=7). There are no fresh anthropogenic emissions in the area that many result in weekly cycles of gases of particles. Please, see Figure 1. The suggestions of the referee for assessing the role of fresh emissions (by analyzing the weekly cycles) is suitable for urban and nearby

sites, but not for a background site such as Izaña (in fact we have done the type of analysis suggested by the referee in previous studies in urban air, e.g. Rodriguez and Cuevas, Journal of Aerosol Science, 38, 1207 – 1219, 2007; Rodriguez et al., Atmospheric Chemistry and Physics, 7, 2217-2232, 2007; Rodriguez et al., Atmospheric Environment, 42, 6523-6534, 2008). About the sources of particles and gases: PM10 particles. Saharan dust is the only source of particles that may result in significant PM10 concentrations. During non Saharan dust events PM10 concentrations at Izaña are extremely low, <3 ug/m3 most of time. This is also supported by our data on PM10 chemical composition (2002-2008), that shows that mineral dust accounts for 94% of PM10 (still unpublished data; Rodriguez et al., 2009, paper in preparation). Because PM10 is due to Saharan dust transport, it does not shows any significantly marked daily cycle related to upward transport (observe in Figure 1 how PM10 "hourly averages" do not shows any specific weekly cycles). Under no-Saharan dust conditions, PM10 concentrations are very low and experiences very small night-to-daylight increases ($\sim$1 μg/m3; Figure 6 in the manuscript) as a result of upward orographic flows. The PC3 observed in Nov 2007 is due to some dust events (as described above). NO, NOy-NO and SO2. Is associated with aged air that reaches the observatory by the upward orograpic flows (as described in section 4.1). As shown in Figure 1, there are no weekly cycles in the amount of NOy, NO, SO2 and particles that reaches Izaña. About the slight higher levels of NOy during events Type II. This suggests a role of photochemistry as described in the reply to Comment C2 of referee#1 and in section 4.3.2. This role of photochemistry is described in more detail in the final version of the manuscript.

Comment-3. Referee said "With the aim to generalize the results and conclusions of the manuscript, I suggest to summarize in a separate section (paragraph, table, etc.) the comparison with similar previous works from other stations in the remote troposphere. This can also make the overall presentation clearer. As well, the readability can be improved by adding a table summarizing the temporal data coverage of the whole dataset (i.e., particles number and mass, gaseous compounds and meteorology), and the PM10 values in Figure 5. . . ..

Reply: This is a very good suggestion. We have done several comparisons with other studies along the manuscript (Jungfraujoch, Mauna Loa, Monte Cimone and Izaña in the Introduction; Mauna Loa in section 4.4.2). However, to give a brief overview by comparing with other mountain sites, in a separated section or within the summary and conclusion, is very interesting. This will be included in the final version of the manuscript. About PM10 in Figure 5. It was not included because it does not show any specific marked daily cycle (please see Figure 1C). As stated above, under no-Saharan dust conditions, PM10 concentrations are very low and experiences very small night-to-daylight increases ($\sim$1 μg/m3; Figure 6 in the manuscript) as a result of upward orographic flows. During dust events, PM10 do not exhibits any specific daily cycle and shows high concentrations.

Technical corrections

Comment-4. Referee said "The discussion of the negative association of the particle mass concentrations (PM10) with the nucleation mode particle number concentration (N3$-$10) presented in the paragraph 4.4.2 should clarify when only summer data are considered - e.g., PC3 in Nov07, tab.2, shows no negative correlation.

Reply: No distinction between summer and other season data have been performed in section 4.4.2, i.e. section 4.4.2 is based on the whole data set. The fact that a negative association between N3-10 and PM10 is observed in the whole data set is due to the predominant influence of the Saharan dust events, which mostly occurs in summer. The case of Nov 2007 is not suitable for studying the influence of the Saharan dust on the 3-10nm particle formation for two reasons: 1) it as an extraordinary short (2 days) event (most of the winter events occurs at altitudes below Izaña), and 2) gaseous precursos of 3-10nm particles were not transported upward to Izaña (SO2, NOy well below detection limit), i.e. no night-to-daylight increase was observed in N3-10, SO2, NOy and water vapor due to there was no significant increase in the u'pward orographic flows. In contrast, in summer Izaña remains within the Saharan Air Layer almost permanently and gaseous precursors of 3-10nm particles are present almost

every day. The fact that the negative correlation between N3-1 and PM10 is mostly due to summer dust events is described in section 4.4.2, pag 10930, lines 10-15.

Comment-5. Referee said “Caption of Figure 9: replace “1 October” with “15 December”.

Reply: done.

Comment-6. Referee said “Check for references missing, e.g.: Herman et al., 2003; Benson et al., 2008”.

Reply: done. References introduced.

Comment-7. Referee said “Par.3.1, pag.10919 line 2: replace “a electrostatic” with “an electrostatic”.

Reply: done .

Comment-8. Referee said “Page 10923, line 10: replace “dN/dogD” with “dN/dlogD”.

Reply: done.

Comment-9. Referee said “Pag10922 line 14: replace “de” with “the”.

Reply: done .

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10913, 2009.

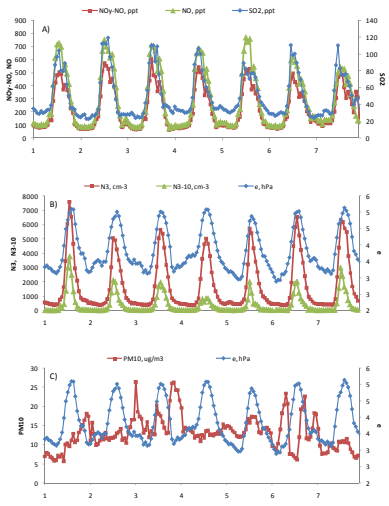

Figure 1. Hourly averaged concentrations of gases and particles for every day of the week (1=Monday,.....7=Sunday).

Fig. 1.

Table 1. PCA performed with the whole data set (described in the manuscript) recorded from Nov 2006 to December 2007.

	PC1	PC2	PC3	PC4
N3-10	**0.68**	0.13	-0.06	0.42
PM10	-0.15	0.00	**0.80**	0.06
SO2	0.27	0.03	-0.04	**0.69**
NOy-NO	**0.88**	0.03	-0.03	0.27
NO	**0.93**	-0.09	0.08	0.01
H2O	0.01	0.03	0.20	**0.80**
DF-RAD	0.30	0.20	**0.78**	-0.02
DI-RAD	0.25	**0.61**	**-0.46**	0.05
P	0.00	**0.79**	0.22	-0.13
T	-0.11	**0.75**	0.10	0.46
wind speed	-0.16	-0.03	0.09	-0.40
Var, %	22	15	14	15

Fig. 2.