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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 "Anonymous Referee #1" S. Rodríguez srodriguez@inm.es Author Comment on behalf of all Co-Authors (AC)

We first want to thank the constructive comments raised by Referee #1. Specially because some of these comments allow defining more clearly some concepts. Moreover, some suggestions of the referee contribute to make more clear interpretation of data. These comments definitively contribute to improve the manuscript. 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 (C1). On his first comment, Referee #1 asked, "What exactly meant when we use the term new particle formation (NPF) in this work". Reply (C1): The term NPF used in this work includes two concepts: i) nucleation of the initial cluster, and ii) activation of such cluster resulting in particle growth (by coagulation and/or condensation) to detectable sizes ($\geq$3nm). This is already defined in the current version of the manuscript (please read paragraph 3 in the introduction). We understand that this is a proper way to interpret the 3-10nm particle number concentration. Referee#1 also points to this idea and in fact we agree with his comments about this. For example, the referee said "The physics and specific chemical compounds involved in these two processes may be different". This is already included in the manuscript, e.g. in the introduction (line27, pag10915 and line 1-2 pag10916: "It is believed that nucleation and cluster and particle growth may frequently be decoupling processes" and pag 10916, line 5-7: "...condensation of organic vapours onto the cluster/particles may also result in growth processes...") and in the data discussion (pag 10927, line 20-24). Reword (C1). In order to remove any uncertain about the definition of NPF event used for studying N3-10 data, we have add the following sentence at the end of the first paragraph of section 4.3 (3-10 nm particle events): The formation of a 3-10nm particle is understood as a result of two processes (as defined above in the introduction): nucleation of an initial cluster and activation of such cluster resulting in particle growth to detectable sizes ($\geq$3 nm).

Comment 1(C1a). In pag 10927, we proposed that organic compounds may contribute to N3-10 concentration. Then referee asked: "What does particle formation mean in this case? Can it be stated from this data set that compounds, such as organic species contributed to the process of homogeneous nucleation, or was the role in a condensational growth process?". Reply (C1a): The term NFP used here is that defined above and in the introduction (includes two steps, initial cluster formation and subsequent

growth to $\geq$3nm). In our opinion, the potential contribution of organic compounds to N3-10 is already described by using this definition of NPF (including the two steps, initial cluster formation and subsequent growth to $\geq$3nm). See pag 10927, line 1-24. More specifically (lines 20-23): In this air mass, organic compounds may contribute to N3$-$10 by "nucleation and condensation of pure organic substance" or by "condensation of organic compounds onto sulphuric acid droplets or clusters".

Comment 1(C1b). Referee said: An example of an implication of this is the effect of temperature discussed in the paper in Section 4.4.4. Is the temperature effect mainly playing a role in either the homogeneous nucleation process, as stated in the paper (e.g., sulfuric acid +water +whatever else), or in the condensational growth of a newly formed stable particle (e.g. partitioning of some oxidized organic), or both?. Reply (C1b): In section 4.4.4., we described how the slope of N3-10 versus SO2 concentrations increased when temperate decreased, and how this indicates that low temperate increased the NPF rates. The term NPF used here (section 4.4.4) is that defined above and in the introduction (includes two steps, initial cluster formation and subsequent growth to $\geq$3nm). With our results and our data set, we cannot identify if such increase in the NPF rates is caused by an increase in the "homogenous nucleation (i.e. initial cluster formation)" rates or by an increase in the "condensation" rates. Point to any of these processes with our data set would, in principle, be purely speculative. However, we can keep in mind some recent results obtained by Kulmala and co-workers (see the references that appears in the third paragraph in the introduction). According to these studies, "homogenous nucleation" (step-1 in the NPF) and "cluster and particle growth" (step-2 in the NPF) may be decoupled processes. In a set of field measurements campaigns, Kulmala and co-workers (Kulmala et al., 2005; Kulmala and Tammet, 2007) observed that the clusters necessary for the initial steps seem to be always present in the atmosphere. Thus, NPF events (as define above and in the introduction) would occur when clusters are activated and they grow to detectable sizes ($\geq$3 nm). By keeping this in mind, we could make the following interpretation of our results: the increase in the N3-10 versus SO2 slope we observe (Type I events, section 4.4.4) suggest that

cluster activation and growth (condensation) is favored by temperature decreases. Reword (C1b). By taking into account this comment of the referee, we have performed the following slight modification in section 4.4.4, lines 16-21 were reworded as: These results fit with those found by Eastern and Peters (1994), who showed that the NPF rates due to binary H2SO4-H2O nucleation and condensational growth (which is 20 considered an important NPF mechanism in the free troposphere; Kulmala and Kerminen, 2008) increased when the temperature decreased. If, as suggested by Kulmala and co-workers (Kulmala et al., 2005; Kulmala and Tammet, 2007), it is assumed that stable clusters are always present in the atmosphere, then, the increase we observe in the "N3-10 versus SO2" slope, would indicate that clusters activation and growth is favored by decreases in temperature.

Comment-2 (C2). Referee said: A general observation on Type I vs Type II events: Maybe a fundamental difference between Type I and Type II events is mainly photochemical age. If my understanding is correct, Type II occurred later in the day whereas Type I was in the morning. This would explain the high SO2 in Type I -less time to react away to sulfuric acid, and low SO2 in Type II -most SO2 converted to H2SO4, and also the slightly higher NOy in Type II. The authors also suggest that Type I involves NPF upwind of the site (lower elevations) and Type II as in situ. Does the size distribution data (DMA data) provide any evidence to support this? Reply (C2): We agree with the interpretation performed by the referee. In fact, is very similar to that we performed in pag 10926 and pag 10927, lines 1-10. The interpretation performed by the referee allows also explaining why SO2 concentrations are lower and NOy concentrations are higher in events Type II. This is a very interesting observation that supports the role of photochemistry in events Type II. This has been added to section 4.4.1. This is really a good comment that contributes to improve the data interpretation and the paper. Thanks. About the DMA data (C2). N3-10 data were collected during the period Nov 2006 – Dic 2007, whereas the size distribution data were collected from Jun to Sep 2008. Thus, there are no simultaneous "size distribution (13-1660)" and "N3-10" data. Nonetheless we have classified the events (Type I, II and III) according the correlation

of SO2 with N13-20 (instead of N3-10), as performed in the paper. The average size distribution during Type I, II and III events are plotted Figure 1 (below). Concentrations of nucleation particles are slightly higher during Type II events than during Type I events. This support the idea that nucleation particles during Type II events are fresher than during Type I events.

Comment-3 (C3). It might be worth discussing in more detail the clear linear relation between SO2 and N3-10 given that homogeneous nucleation via some mechanisms is very nonlinear in H2SO4. Could it be that the SO2 is just related to growth, which may be directly related to H2SO4 concentration. Reply (C3): Yes, we agree with the referee interpretation. The linear relationship between SO2 and N3-10 suggest that the linear relationship between N3-10 and SO2 is caused by cluster/particles growth due to sulpuric acid condensation, rather than to homogeneous nucleation. Even if homogeneous nucleation is occurring during these events, the interpretation of the N3-10 data requires the involvement of condensation processes, owing to we measure particles with a size >3 nm and condensation accounts for particle growth from 1 to 3 nm. Reword (C3). By following the referee suggestion we have reworded lines 23-25 (pag 10926), as: "The fact that the relationship between N3-10 and SO2 is linear, suggest that the N3-10 and SO2 correlation is caused by cluster/particle growth to $\geq$3 nm size due to sulpuric acid condensation. Fiedler et al. (2005)..." (follows as it is).

Comment-4 (C4). On the discussion on page 10929, second bullet, regarding the role of clouds and particle surface area. Don't the clouds need to be precipitating for a reduction in the aerosol particle surface area in an air mass passing through the cloud? Reply (C4): Yes, we agree with the referee. Foggy and rainy conditions prevail within the stratocumulus layer that is usually located between 800 and 2000 masl, i.e. below the altitude of Izaña (2367 masl). Cloud droplets in this cloud layer are removed by "precipitation" (rain, downward fall) and by "impaction of droplets with terrain (deposition forced by the air mass movement)". This is the main water supply to the forest of pines that surround the Island. The fact that a forest of pines surround the island

between 800 and 2000 masl (where the stratocumulus layer is located) evidence that there is a high transfer of droplets from cloud to terrain. This is favored by the fact that cloud condensation level is usually located between 800 and 2000 masl. A description of this scenario is already performed in section2 (meteorology and topography) pag 10917, line 21-26. Finally, it is important to highlight that the decrease in the aerosol surface area within the stratocumulus layer is a fact that we observe experimentally. This stratocumulus layer is usually located between 800 and 2000 masl. However, in winter this cloud layer is often lifted and is located at the altitude of Izaña (2367 masl). During these events a strong decrease in the aerosol surface area is observed. Please, see below (Figure 2) how high surface area concentrations are recorded under low relative humidity conditions (when Saharan dust events occurs), whereas surface area is rather low under high RH conditions.

Comment-5 (C5). Page 10930 lines 21 to 24, second last line: is it true that particle chemistry significantly matters in the uptake of H2SO4. That is, having an aerosol of equal surface areas, mineral dust will significantly scavenge more H2OS4 than say liquid drops? Reply (C5): Both mineral dust particles and water droplets scavenge significant amounts of H2SO4 and SO2. This is experimentally observed at Izaña. See in Figure 3 how under foggy (high relative humidity) and Saharan dust conditions (high PM10 concentrations), N3-10 and SO2 concentrations are low. This high capacity of water droplets to absorb SO2 and H2SO4 accounts for the fact that even under upslope wind regime, SO2 concentrations at Izaña are rather low (from tens to hundreds of ppt). This is due to the fact that water droplets within the stratocumulus clouds layer typically located below Izaña may absorb a significant fraction of the SO2 and H2SO4 that is transported upward during the daylight buoyant flow regime.

Minor editorial suggestions.

Comment-6 (C6). Page 10927 line 22, I would change: onto sulphuric acid droplets or clusters..... to onto sulphuric acid-containing droplets or clusters.... Reply (C6): We have performed this change.

Comment-7 (C7). In many cases I found the graphs difficult to read. Placing symbol labels within the graph may help. Reply (C7): We have performed this change.

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

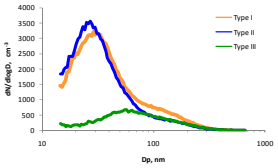

Figure 1. Size distribution during Type I events (when N13-20 and SO2 were correlated and N13-10 > 100 cm-3), Type II events (when N13-20 and SO2 were not correlated and N13-10 > 100 cm-3), and Type III events (N13-10 < 100 cm-3).

Fig. 1.

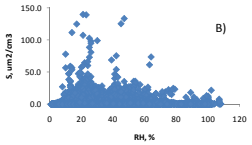

Figure 2. Surface area concentration versus RH at Izaña.

Fig. 2.

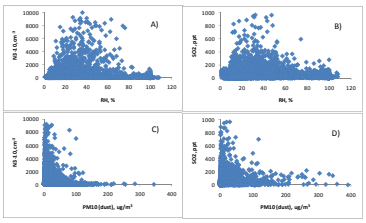

Figure 3. Hourly concentrations of N3-10 and SO2 versus PM10 and RH at Izaña.

Fig. 3.