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Atmospheric
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Interactive comment on "Size-segregated aerosol mass closure and chemical composition in Monte Cimone (I) during MINATROC" *by* J.-P. Putaud et al.

J.-P. Putaud et al.

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[12pt]article

First of all, we would like to thank both the Anonymous Referee #1 and Dr. F. Dulac for their compliments and comments to our manuscript.

0.1. Reply to comments by Anonymous Referee #1 (RC S1442):

This manuscript is part of a series of papers describing and discussing the results of a big 1 month-long field experiment. It does not pretend to lead to important or original conclusions by itself, but rather to provide other members of the project with aerosol chemical data, thoroughly analyzed for their uncertainties, which can be used in conjunction with others, for e.g., further aerosol optical properties calculations.

Replies to specific comments:

1. Regarding Figure 1, more explanations have been added in the text body to make it more explicit. We specified:

“Numerous parameters such as relative humidity, CO_2 concentration and standard deviation, aerosol absorption coefficient (B_{abs}) indicate that during the Minatroc campaign, MTC was reached from about 8:00 to 21:00 UTC by air masses coming from low altitude and therefore possibly affected by local pollution. For instance, average CO_2 concentration dropped while CO_2 standard deviation increased during daytime (Fig. 1), indicating that MTC was reached by air masses subjected to the vegetation CO_2 sink. This is due to the summertime development of surface thermal winds causing up-slope flows that transport low altitude air to MTC.”

2. The sentence describing the calculation of the sea salt fraction was indeed inaccurate. We actually calculated the sea salt fraction **from** the sum of Na^+, Mg^{2+}, and Cl^-, i.e. using Na^+ as a sea salt tracer and a standard sea water composition to account for the marine fraction of K^+, Ca^{2+}, and SO_4^{2-}. The relative piece of text was rephrased as:

The sea salt fractions of K^+, Ca^{2+} and SO_4^{2-} were calculated from the measured Na^+ concentrations and a standard sea water composition. They were added to the sum of Na^+, Mg^{2+}, Cl^- to calculate the sea salt component. Cl^- was not calculated from Na^+ to account for possible losses of Cl^- with respect to sea salt due to the reaction with acidic species. The sea salt fractions of K^+, Ca^{2+} and SO_4^{2-} were subtracted to the measured concentrations of K^+, Ca^{2+} and SO_4^{2-}, respectively, to get the non-sea salt fraction of these species ($nssK^+$, $nssCa^{2+}$ and $nssSO_4^{2-}$).

3. The correlation between dust and Ca^{2+} is indeed poor out of the Saharan dust

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periods. This is reflected by the large uncertainty in the regression slope (5.6 ± 2.1), which was taken into account in the uncertainty calculations.

4. Although we discussed the contribution of carbonaceous components to the various particle size fractions, Figure 6 was showing concentrations in μg/m^3, providing the readers with an additional piece of information, from which contributions could be easily derived. However, to be more consistent with the text body, and according to Referee #1's suggestion, we modified Figure 6 to show aerosol component contributions (in %) instead of concentrations (in μg/m^3).

5. It is absolutely true that we do not have any strong evidence to demonstrate that interactions between SO_2 and dust occurred or not in the Saharan dust plume we observed. This is indeed what we wrote in the conclusions, as highlighted by Referee 1. To get this results (that interaction between dust and SO_2 could not be demonstrated), we compared the SO_4^{2-}/Ca^{2+} ratio measured in coarse atmospheric particles with the SO_4^{2-}/Ca^{2+} ratio measured in fine Saharan sand grains AND results obtained by Schwikowski et al. We apologize for quoting the paper from Schwikowski et al., 1995, which was not relevant. We wanted instead to refer to Schwikowski et al., 1999, which presents Alpine ice-core data. These data show a linear regression between nssSO_4^{2-} and nss Ca^{2+} concentrations observed for pre-industrial times, with a slope of 0.42 (g/g) "determined by samples with high concentrations of nssCa^{2+}, indicating the presence of a significant amount of mineral dust." The reference has been corrected accordingly.

0.2. Reply to comments #1 by F. Dulac (SC S1436):

We agree with F. Dulac that "the scientific community has still to work on reconciling optical and chemical measurements of the super-μm aerosol fraction". This is indeed what we demonstrated by showing that mass closure could not be reached for this aerosol fraction: all the (random and systematic) errors affecting the determination of the super-μm aerosol fraction could not be accounted for.

Replies to specific comments:

1. The OPC used during this campaign was quite new and had been calibrated by the company before delivery less than 1 year before the campaign.

2. The time resolution for OPC measurements was 1 min. OPC measurements covered on average 96% on the impactor sampling time (median 99%, 10% percentile 81%). There are no cars at Monte Cimone, and spikes in OPC data were anyway eliminated from the data set. Volume size distributions were calculated from each number size distributions and averaged over the impactor sampling time afterwards.

3. Phantom counts can be observed in any device counting large particles. It is difficult to distinguish between these phantom counts and a few real super-μm particles. We estimated that phantom counts might account for up to 10% of the super-μm aerosol volume during the Saharan dust episodes. During clean conditions, phantom counts might dominate the super-μm aerosol volume. This possible inaccuracy is again reflected by the fact that mass closure was not reached for this aerosol size fraction. However, 1hour-averaged size distributions did not present any strange feature. A paper presenting in details the measurements of the aerosol physical properties during this field campaign will be shortly submitted to ACP (Van Dingenen, R., Putaud, J.P. and Raes, F. Physical aerosol properties and their relation to air mass origin at Monte Cimone (Italy) during the first MINATROC campaign).

4. The upper 50% aerodynamic cut-off diameter of the Berner low-pressure impactor we used is 10 μm. There is unfortunately no efficiency curve available for upper stage of this impactor (see point 6). However, field sampling of coarse particle has been observed to be affected by e.g. high wind velocity. This is again one more possible source of error that made the mass closure experiment fail for the super-μm aerosol fraction. There is no simple way of assessing in the filed the actual cut-off of a sampler,

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and specially of an impactor.

5. There was no other instrument counting and sizing sub-μm particles during the Minatroc experiment at Monte Cimone. A comparison between the OPC used during the Monte Cimone field campaign and an aerodynamic particle sizer (APS) was carried out afterwards at an urban site. The agreement between the two instruments is reasonable. However, this comparison may not be valid in the free troposphere. The aerosol physical characteristics during the Saharan dust episode are discussed in detail in “Physical aerosol properties and their relation to air mass origin at Monte Cimone (Italy) during the first MINATROC campaign”, by Van Dingenen et al. (to be submitted shortly to ACP). As a preliminary information, the coarse mode of the volume size distribution derived from the OPC measurements was indeed observed for Dp = about 4 μm, in agreement with what was observed during the desert dust outbreak at Izaña during ACE-2.

6. Data collected during the Saharan dust episode were indeed excluded from Figure 4b and 5b because the super-μm aerosol mass observed during this period was much larger than out of this period, and above all because obvious loss of material on the walls of the impactor was observed, which was attributed to the non-sticky character of the Saharan dust particles. This has been specified in Fig. 4 and Fig. 5 captions.

The aerodynamic cut-off diameter of the impactor stage 4 is actually 1.2 μm, which corresponds on average to 1.05 μm geometric diameter. Furthermore, a minimum in the particle volume size distribution was observed around 1μm, so that a slight error in the “1 μm” limit for integrating the volume size distribution has a minor impact on both the sub- and super-μm aerosol volume.

As already mentioned in Point 4, the efficiency curves for the impactor used in this work are available for stage 1 and 2 only. This prevents from inverting the whole mass size distribution obtained with the impactor. Considering the efficiency curve for stage 2 and a particle volume size distribution really observed during the Monte Cimone field campaign, we calculated an aerosol mass 1.13 as high as considering a perfectly sharp cut at the nominal cut-off diameter. However, this cannot be extended to stage 4 (1.2 μm aerodynamic cut-off), and once again, the fact that the particle volume size distributions present a minimum around 1 μm would minimize the effect of a not perfect cut on the calculation of the sub- and super-μm aerosol volume.

To calculate the particle volume size distribution in the super-μm size fraction, we used the geometric mean diameter of each OPC size bin. Fitting the observed volume size distributions with a log-normal distribution, we estimated that this approximation leads to errors < 2 % in the super-μm volume estimated from the OPC measurements.

0.3. Reply to comments #2 by F. Dulac (SC S1440):

1. The discussion of Figure 1 has been modified as described in the reply to Anonymous Referee #1, Point 1.

2. It is likely that Na^{+} is a component of Saharan dust. However, we did not observe any significant change in the Na^{+} / Mg^{2+} ratio during the Saharan dust episode. This shows that or the Na^{+} / Mg^{2+} ratios in sea water and Saharan dust are equal, or sea spray was the main source of both Na^{+} and Mg^{2+} even during the Saharan dust episode. We did not have any means to distinguish Na^{+} from marine origin from and from Na^{+} from Saharan origin.

3. No chemical analysis was carried out on Hi Vol samples and therefore no comparison between samplers was possible.

4. As pointed out in reply (3) to Anonymous Referee #1, the low significance of the regression between nssCa^{2+} and dust was taken into account through the uncertainty of the regression slope. As described in the manuscript, we actually considered that Ca^{2+} has a sea salt source as well. We used Na^{+} as a sea salt tracer because the regression (correlation and slope) between Na^{+} and Mg^{2+} suggested that both mainly

originate from sea spray. As mentioned in point 2, we could not assess the non-marine fraction of Na^+.