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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosols in the CALIOPE air quality modelling system: validation and analysis of PM levels, optical depths and chemical composition over Europe" *by* S. Basart et al.

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On behalf of all the co-authors I would like to thank the referee #1 for his/her constructive comments on the manuscript. Overall, the referee recognizes the interest of the manuscript in the particulate matter (PM) evaluation of the CALIOPE modelling system over Europe. Modelling data for 2004 has been compared with experimental data (observations) of PM10 and PM2.5 concentrations and chemical composition and with aerosol optical depth data (AOD). The manuscript has been revised after the referee's comments in order to introduce the suggestions for improving the quality of the paper. A revision of the manuscript has already been sent to the Editorial Office. Please find

hereafter an item-by-item response following to all the statements of the referee.

Referee #1: The number of stations with data of chemical speciation available is high for sulphate (53 sites across Europe) and nitrate (27 sites). For other compounds, the number of stations providing experimental data is low. For the case of OC and EC, only data from two stations across Europe, have been used. I do not really think that any conclusion about the suitability of the model can been reached with comparison with only two stations across Europe. Something similar occurs with ammonium in Spain. No data of this compound from Spain have been used and this difficult the interpretation of the origin of the discrepancies between the model and experimental data of sulphate and nitrate (see details below). I know that there are several research groups that have been producing chemical speciation data of ammonium in many sites across Spain during the last years, including 2004. CALIOPE is a worthy system, and this is a very interesting article. In my opinion, ammonium should also be validated in Spain. Also try to find some OC and EC data from more sites in Europe. To include these data will sure improve the validation and identification of some questions of the system. It will also help to understating how key features of nitrate changes across Europe.

Authors: As the reviewer indicates, the experimental data for some chemical compounds is low, particularly for carbonaceous matter. Unfortunately, a detailed investigation of the organic aerosol cannot be done for the present study since there are only very few measurements available that cover a longer time, therefore OC and EC could only be evaluated at Birkenes (NO01) and Melpitz (DE44) in 2004 on an annual basis. Here, the modelling system underestimates the measurements by a factor of 4 (DE44: measured mean (OC+EC) 3.21 μg m-3, modelled 0.66 μg m-3; NO01: measured mean (OC+EC) 0.97 μg m-3, modelled 0.23 μg m-3). This cannot be said more precisely because measurements were missing at the other sites. As indicate in P. 20590, l 14, Matthias (2008) also found that modelled OC+EC concentration were underestimated by a factor of 3 at Birkenes using CMAQ over Europe. This factor is lower

than that obtained with the CALIOPE system partly because carbonaceous aerosols from biomass burning emissions were taken into account in the aforementioned study. The limitations derived from the scarcity of these data are explicitly discussed in the manuscript. We also note that the assumption of underestimation of carbonaceous matter at ground-levels in the larger domain is supported by the results obtained in the evaluation with AERONET column-integrated measurements as shown in the Section 3.3 and other previous modelling studies. Therefore it is assumed that we can infer an adjustment factor from the results of these two stations. With respect to ammonium data we acknowledge the suggestion of the reviewer. We are aware of the existence of additional ammonium data in Spain. The objective of this contribution is to evaluate the behaviour of the European domain of the CALIOPE modelling system at 12km x 12km resolution. Our aim is to evaluate the ability of the model to represent the regional background using EMEP rural background stations. The Spanish network is mostly composed by sites located in sub-urban and industrial areas which are not representative of the regional background. In a complementary study (Pay et al., 2011, Atmos. Environ. Accepted) these data have been used for a detailed evaluation of a higher resolution (4 km x 4 km) nested domain of the CALIOPE modelling system centered over the Iberian Peninsula.

Referee #1: Section 2.1.1. In this section authors describe how the system (CMAQ) considers sulphate and nitrate present as ammonium salts. I suggest describing that other potential forms of sulphate and nitrate, such as salts linked to the reaction of acid pollutants with dust (calcium nitrate or calcium sulphate) or sea salt (sodium nitrate, or sodium sulphate)?. Some of these species may play a key role when comparing the model versus experimental data results (details below).

Authors: We agree with the reviewer that calcium and sodium salts coated with sulphate and nitrate are important when comparing with measurements. The aerosol module of CMAQv4.5 (AERO4, Binkowski and Rossell, 2003) considers aerosols in the coarse mode as dry and inert. The coarse fraction includes the unspeciated an-

thropogenic mass and the marine contribution as sodium (Na+), sulphate (SO42-) and chloride (Cl−). On the other hand, the desert dust contributions from the BSC-DREAM8b are added off-line to the modelled aerosol from CMAQ without any chemical speciation and interaction between them. We included in the manuscript the following text: P. 20587 Line 13: "The modelled coarse fraction includes the contribution of unspeciated anthropogenic mass, sea salt and desert dust. One source of uncertainty in the PM10 comparison comes from the fact that the aerosol module of CMAQv4.5 (AERO4) considers coarse mode aerosols as dry and inert. Several studies in Spain and the Mediterranean regions (e.g. Rodriguez et al., 2002; Querol et al., 2004; Querol et al., 2009) suggest that from mid-spring to mid-autumn most of nitrate is present as Ca and/or Na salts in the 2.5 – 10 μm fraction. Other potential forms of nitrate and sulphate, such as salts linked to the reaction of acid pollutants with dust (Rodriguez et al., 2002; Querol et al., 2004; Querol et al., 2009) are not considered in the simulated PM10."

Referee #1: Section 3.2 PM chemical composition Point-2 It is shown how the model underestimates sulphate, nitrate and ammonium concentrations. This under estimation is of about 18% for sulphate (assessed across Europe), of 50% for nitrate (assessed in most of Europe) and of 36% for ammonium (assessed only in Central and Eastern Europe). About nitrate. There are important underestimations in Eastern Spain, especially in summer. Moreover, correlations between the model and experimental data are rather low in summer in Spain. In their discussion on nitrate, authors have only considered ammonium-nitrate. Ca-nitrate and Na-nitrate accounts for a significant fraction of nitrate in Spain, mainly in summer, and this is not considered in the data discussion. Several studies in that region have shown that ammonium-nitrate is only formed in significant amounts in winter, whereas from mid-spring to mid-autumn most of nitrate is present as Ca and/or Na salts in the 2.5 – 10 μm fraction (Querol et al., 2004, Speciation and origin of PM10 and PM2.5 in Spain, J. Aerosol Science, 1151–1172; Rodriguez et al., 2002, Sources and processes affecting levels and composition of atmospheric aerosol in the western Mediterranean, J of Geophys Res, 107, 4777). The

fact that the formation of Ca nitrate and Na nitrate is not included in the model, may significantly contribute to the underestimation of nitrate concentrations. Again, this should be discussed in the manuscript. The presence of Ca sulphate and Na sulphate may also contribute to the under estimation in the modelling, with is much lower than that in nitrate because most of sulphate in ambient air is present as ammonium-sulphate. The key question here is that authors did not validate the model for ammonium in Spain. If authors include validation of ammonium in Spain, they could estimate what fraction of the under estimation in nitrate is due to under estimation in the formation of ammonium nitrate and underestimation due to the presence of Ca and Na nitrate not modelled. They should take into account the following issues: ammonium nitrate is usually dominant in winter whereas Ca and/or Na nitrate dominates in summer. Ammonium-nitrate mostly occurs in PM2.5, whereas Ca and/or Na nitrate mostly occurs in the coarse PM2.5-10 mode. They could also compare ability of the model to simulate sulphate and nitrate in the PM10 and PM2.5 fractions. This will help to understand what is the reason of the underestimation in the model, since ammonium-sulphate and ammonium-nitrate mostly occurs both in the PM2.5 fraction and Ca and Na sulphate and nitrate mostly occurs in the 2.5-10 μm fraction.

Authors: We agree with referee #1 that there are some evidences (Rodriguez et al., 2002; Querol et al., 2004) which demonstrate that nitrate is significantly present as calcium and/or sodium salts in the coarse fraction in eastern Spain, especially from mid-spring to mid-autumn. However, the formation of calcium nitrate and sodium nitrate is at present not included in the CMAQ aerosol module (AERO4) which significantly contributes to underestimate PM10 concentrations, specifically of coarse fraction, in summer in eastern Spain. As the reviewer suggests, this key question has been discussed in the revised manuscript. On the other hand, it is not possible to perform the comparison that the reviewer suggests between modelled sulphate and nitrate in the PM10 and PM2.5 fractions. The modelled nitrate and sulphate concentrations are found in the 2.5 μm fraction. However, the observed concentrations are available in total mass fraction without any discrimination of size. Consequently, this is another

source of underestimation that has been discussed in the revised manuscript. These evidences have been included in the manuscript as follows: P. 20589 Line 11: “One source of underestimation is related to the fact that CMAQv4.5 (AERO4) does not consider the formation of Ca(NO3)2 and NaNO3 salts in the coarse fraction which are significant in Spain from mid-spring to mid-autumn (Rodriguez et al., 2002; Querol et al., 2004, Querol et al., 2009). Ammonium-nitrate is usually dominant in winter whereas calcium- and/or sodium-nitrate dominate in summer (Rodriguez et al., 2002; Querol et al., 2004, Querol et al., 2009). Ammonium-nitrate mostly occurs in PM2.5, whereas calcium- and/or sodium-nitrate nitrate mostly occur in the coarse PM2.5-10 mode (Rodriguez et al., 2002; Querol et al., 2004, Querol et al., 2009). This could be related with the underestimations observed in Eastern Spain, particularly in summer (Fig. 3). Moreover, correlations between the simulated and the observed values are rather low in summer in Spain (Fig. 3).” P. 20594 Line 1: “In general, highest AODcoarse values are linked to the presence of DD. However, some coarse events in North-western and Eastern Europe are not captured by the modelling system (not show here). They are linked to the occurrence of the coarse sodium and calcium nitrate because high levels of sulphate neutralize ammonium (Querol et al., 2009).”

Referee #1: I suggest writing PM10 and PM2.5 using subscripts in 10 and 2.5, as already authors used for AOD-fine and AOD-coarse.

Authors: Amended.

References: Pay et al. (2011), "Spatio-temporal variability of concentrations and speciation of particulate matter across Spain in the CALIOPE modeling system" accepted in Atmospheric Environment.

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