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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.

Anonymous Referee #1

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Overview This manuscript presents the results of the validation of the CALIOPE air quality 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 AOD data. Chemical speciation in the modelling includes sulphate, nitrate, ammonium, organic carbon, elemental carbon, sea salt and mineral dust. 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.

Major issues Point-1 Section 2.1.1 In this section authors describe how the system (CAMQ) 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).

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 ni-

trate is present as Ca and/or Na salts in the 2.5 – 10 μm fraction (Querol et al., 2004, Speciation and origin ofPM10 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.

Minor issues I suggest writing PM10 and PM2.5 using subscripts in 10 and 2.5, as already authors used for AOD-fine and AOD-coarse.

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