

Interactive comment on “Size-resolved aerosol pH over Europe during summer” by Maria Zakoura et al.

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General comment

(1) The paper describes results on size dependent pH in aerosol from the PMCAMx chemical transport model and analyses sensitivity of modeled pH with regard to non-volatile cations. Considering the importance of aerosol pH for aerosol public health, ecosystem and climate effects, the topic is relevant for this journal and this reviewer recommends publication after the following major comment have been addressed.

We appreciate the positive assessment of our work and the careful review of our work by the reviewer. We have tried to address all comments of the reviewer and to improve the paper accordingly. Our responses (in regular font) and the corresponding changes

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in the manuscript follow each comment of the reviewer (in italics).

Specific comments

(2) The paper focuses on May 2008 as the period during which online observations of PM₁ composition are available through the EUCAARI intensive campaign at the sites discussed in more detail. While some of the model performance was evaluated in the paper cited (Fountoukis et al., 2011), aspects such as the representation of nitrate diurnal concentration (Figure 6) were not shown before. The diurnal variation of PM₁ nitrate shown in Figure 6 does not seem to be in accordance with observed diurnal variation (see e.g. Mensah et al., ACP 2012). Considering the link to aerosol pH, it is critical in the context of this paper to show in detail the performance of the model with respect to aerosol composition. This reviewer therefore requests a detailed analysis of the model ability to simulate particle composition, specifically particulate nitrate. Accounting for the high fraction of organic nitrate in PM₁ across Europe (Kiendler-Scharr et al., 2016), this analysis should take into consideration organic nitrate.

We have followed the suggestion of the reviewer and added an analysis of the model performance for nitrate. Overall, the results are quite similar to the previous applications of PMCAMx for this period (including the Fountoukis et al., 2011 study). The model does capture the observed nitrate diurnal variation in the corresponding sites. There was an unfortunate error in Figure 6a with the nitrate diurnal variation shown for Cabauw and we thank the reviewer for noticing it. The data shown corresponded to another area in the modeling domain. This figure has been corrected. The model does predict, consistent with the observations in Cabauw, that the fine nitrate peaked on average in the early morning. We have also added a discussion of the organonitrate fraction in the revised paper. The model predicts only inorganic nitrate, therefore the comparisons with the AMS results should be based also on the inorganic nitrate.

(3) The introductory summary of observed aerosol pH (page 2 line 62 – page 3 line 89)

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is not suitable to provide an overview as is. Switching between reported units (from pH to $[H^+]$ in nmol m^{-3}) and listing values without obvious systematic should be avoided and the material structured into e.g. a table or figure to provide an overview.

We have rewritten this section of the introduction focusing on the pH and the existing information about its size dependence. We also discuss briefly the recently published review of Pye et al. (2019) that includes a detailed survey of such measurements. This review includes tables so we do not repeat them in the present study.

(4) Page 5 Lines 148ff: *When introducing abbreviated names for simulations, apply this to all including the simulation that neglects calcium.*

We have followed the reviewer's suggestion and now use the abbreviated name "no calcium" for the simulation where we neglect calcium.

(5) Page 6 Lines 188: *Are the two periods for Cabauw (summer 2013 and May 2008) similar in aerosol composition and source, i.e. should one expect the same pH value? If not, why make a comparison and state that PMCAMx under predicts $PM_{2.5}$ pH by 0.8 units (line 190)?*

The aerosol pH can be sensitive to small changes in composition but also to meteorology (especially relative humidity). These differ seasonally so differences from year to year are expected that can be easily as much as 0.5 pH units. So while it is expected that the early summer period (May 2008) in our study and the summer 2013 period studied by Guo et al. (2018) do not have major differences concerning the emissions and meteorology, it is dangerous to reach quantitative conclusions comparing the corresponding pH values. Our goal here was to investigate if our model predicts reasonable pH values compared to the values calculated based on measurements and thermodynamic models for similar periods. We have added a brief discussion of this point in the revised manuscript.

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(6) Page 7 line 225: *What does "both" refer to in this context?*

We replaced "both" with "all" in the revised manuscript.

(7) Page 8 Line 246: *Show comparison of observed and modeled size distribution of nitrate where available.*

Please note that this section in the paper focuses on the vertical distribution of nitrate. The overall agreement of PMCAMx predictions with the airborne data is encouraging. The ability of the model to reproduce the high time resolution airborne measurements at multiple altitudes and locations is quite similar to its ability to capture the ground level (hourly) observations. A comparison of the average vertical profiles for the flights of EUCAARI is shown in Figure 8c of Fountoukis et al. (2011). A brief discussion has been added. We have also added a paragraph discussing the predicted nitrate size distributions and their comparison with the available measurements.

(8) Page 8 Line 261: *If kinetics of mass transfer is critical here, discuss for full size distribution. It is unclear why only the difference between two size ranges is discussed here.*

PMCAMx uses a sectional scheme for the description of the aerosol size-composition distribution. There is one size bin extending from 2.5 to 5 μm and one from 5 to 10 μm . This is the reason that the discussion in this point focuses on the differences between the two size ranges that cover the coarse mode above 2.5 μm . There is no other information to show about the size distribution in this size range. This discussion is trying to address the factors affecting the nitrate distribution in the coarse particles. We have added a reminder to the reader at this point about the size resolution used by the model to avoid confusion.

(9) Page 9 Line 264: *Compare average diurnal profiles of nitrate with observed data (see also major point above).*

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We have followed the reviewer's suggestions and added comparisons of the diurnal variation of the predicted nitrate with the available observations. Overall the model is successful in capturing the corresponding patterns.

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