

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

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General comment

(1) In this work, Zakoura et al. used a chemical transport model to investigate aerosol acidity over Europe and its variations with particle size, altitude, and time. In addition, they emphasize on the central role of non-volatile mineral cations, notably calcium, on pH calculations and nitrate concentrations. This study is of definite interest to the ACP audience by contributing to one of the least understood atmospheric aerosol properties, the aerosol acidity. The manuscript is very well written, the methodology is scientifically sound, and the presentation is clear. However, I have one major comment regarding the omission of mineral dust emissions from the Sahara Desert. Overall, I

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recommend this study for publication. Below are a few comments to be considered prior to publication.

We appreciate the positive assessment of our work and the careful review of our work by the reviewer. Our responses (in regular font) and the corresponding changes in the manuscript follow each comment of the reviewer (in italics).

Major comment

(2) The authors mention that they have not included the dust emissions from the Sahara Desert. However, it is well known that dust particles from the Sahara can travel towards Europe and influence the air quality over Southern Europe but in some cases as far as the Central Europe. Given the importance of NVCs to aerosol pH calculations and aerosol nitrate formation, as vividly presented in this work, the authors should include the Saharan mineral dust and NVC emissions in their analysis. Mineral dust emissions can be calculated online from the WRF model that has been used here for meteorological inputs. Alternatively, there are available reliable emission inventories to be used offline such as the AEROCOM emission inventory (Dentener, 2006).

We agree with the reviewer about the interesting features of Saharan dust episodes and their impacts on both air quality and pH of aerosol over Southern Europe and even further north. We made the decision to focus first on periods during which the impact of Saharan dust in Europe is minimal. This is the majority of the time. Our plan is to investigate dust events in the next step of this work. We do need to address not only the dust emissions and transport but also the other rather uncertain anthropogenic emissions from Northern Africa. This is now explained in the revised paper.

Specific comments

(3) Page 2, lines 52-61: A reference to the AeroCom phase III study for aerosol nitrate can also fit in the discussion here (Bian et al., 2017).

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The recommended reference has added to the revised manuscript.

(4) *Page 2 line 64: The value of 9 for aerosol pH seems unrealistically high and certainly not in line with the results of your study.*

We have rephrased this sentence given that the major point here is that Katoshevski et al. (1999) predicted that the pH of the submicrometer marine aerosol is several units lower than that of the supermicrometer particles.

(5) *Page 4 line 112: Please change “was” with “is”.*

Done.

(6) *Page 4 Eq. 1: The [W] needs to be inside the log.*

Done.

(7) *Page 4 Eq. 1: Is this the water from ISORROPIA II only or do you also consider the water associated with the organics? If so, please discuss briefly how you calculate the aerosol water associated with the organics and state their hygroscopicity if needed.*

In Eq. 1, [W] represents the concentration of particle water calculated from ISORROPIA II. The water associated with organics is neglected in our study, since most of the time water concentrations associated with organics are about 1/10 of those associated with inorganic aerosol components (Bougiatioti et al., 2016). As a result, the error would be small in our first effort to simulate aerosol pH across particle size. The water associated with organics will be calculated and used for pH calculation in future study. This simplification is now explicitly stated at this point in the paper.

(8) *Page 4 Section 2: Based on the model description, I assume that you don't take*

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into account the impact of organic acids on aerosol pH. Can you briefly discuss the implications of such a simplification?

This is correct, the effect of the organic acids on aerosol pH is not considered in this study. A brief discussion of the literature regarding this effect has been added to the revised paper.

(9) *Page 5 line 144: Can you add a reference for these fractions?*

The requested references have been added in the revised manuscript.

(10) *Page 5 line 154: Do you assume stable or metastable aerosols for the present study?*

We assumed stable aerosols for the present study. This is now explained in the paper.

(9) *Page 5 line 152-156: Can you explain more here? How the insoluble CaSO₄ is removed from the particles? Do you have soluble and insoluble size sections in your model and you calculate the aerosol pH only for the soluble sections or do you have only one well mixed particle for each size section?*

The model assumes that each size section is internally mixed, therefore all particles in that size range has the same composition. However, particles in the same section can contain both insoluble material and soluble. Therefore, the insoluble CaSO₄ is treated as such by ISORROPIA-II. This information has also been added to the paper.

(10) *Page 6 Section 4: I found the map projection used in Fig. 1 and the rest of the manuscript quite confusing, making hard to follow the results. Can you use a different map projection (e.g., Mercator)?*

The map projection used in Fig. 1 as well as in the rest of the manuscript is the polar stereographic map projection that is actually used by PMCAMx in these simulations

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to cover most of Europe with fewer computational cells. Using other projections for the results is possible, but it results in empty areas in the graphs (those outside of the modeling domain) or in not showing all the modeling domain. For this reason, we prefer to maintain these maps.

(11) *Page 6 1st paragraph: Can you state the domain average (or the continental average) aerosol pH for each of the particle sizes?*

The continental average pH is 1.7 for PM₁, 2.2 for PM_{1–2.5}, 2.6 for PM_{2.5–5} and 2.5 for PM_{5–10}. This information is included in the revised manuscript.

(12) *Page 6 1st paragraph: Can you comment on why the tropical Atlantic Ocean in Figure 1a looks very acidic with pH values lower than 2? Also, Northern Scotland looks more acidic than the rest of the Great Britain.*

Figure 1a shows the average ground aerosol pH predictions for PM₁. Particles of this size range are predicted to contain relatively little sea-salt and significant concentrations of sulfates resulting in relatively low pH. Obviously the situation is quite different for supermicrometer particles in these regions. Northern Scotland is predicted to have lower pH values compared to the rest of Great Britain for all size ranges during the simulated. This happens because particles across all sizes have lower water content (Fig. 3) in this area. Also, the predicted dust concentrations are lower than the rest of Great Britain (Fig. S7). The lower aerosol water content and lower dust concentrations lead to more acidic particles in Northern Scotland for all size ranges. These observations and explanations have been added to the paper.

(13) *Page 6 line 167: Why lower NH₃ results in higher pH? Do you mean lower sulphate?*

This is a good point. We have deleted these two words. While this is the case, it does not contribute to higher pH but to lower pH values.

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(14) *Page 6 lines 181-184: Very interesting. You can also specifically comment on the Mediterranean Sea where the change of pH between sizes is large. Furthermore, over the Mediterranean, submicron aerosol nitrate is very low and super-micron nitrate very high, corroborating your hypothesis.*

We have followed the reviewer's suggestion and added a discussion of the behavior of the aerosol pH, fine and coarse nitrate over the Mediterranean Sea. We have added a discussion of the existing measurements of fine and coarse nitrate in the area that are consistent with the model predictions.

(15) *Page 7 line 225: Do you mean all of them (and not both)?*

We mean most of them. The correction has been made in the revised manuscript.

(16) *Page 8 lines 231-234: This is very interesting. Can you expand the discussion here? Do these diurnal profiles of aerosol pH correlate with any of the diurnal profiles of the variables stated here (e.g., RH, T, PBL)?*

The aerosol pH diurnal profiles in the four examined sites of our study follow the same pattern as the corresponding RH diurnal profiles. RH values are higher during the early morning, leading to higher liquid water content and higher pH values, for all sites except for Finokalia. RH and pH profiles follow each other in Finokalia too, but they peak at noon and then they start to decrease. This discussion has been added to the paper and the corresponding figure has been added to the supplementary information.

(17) *Page 8, lines 244-245: This is also very useful result. Can the authors comment if this acidification of aerosols can affect their CCN activity and/or the pH of the formed cloud droplets?*

This is an interesting question that has a rather complicated answer. The lowering of the pH can drive nitric acid from the particles to the gas phase and lower the CCN

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activity of the particles. However, this nitric acid will be available for recondensation as the particle water is increasing during the activation process and may cancel this effect. We will try to look into this issue in future work simulating the detailed activation of such particle populations.

(18) *Page 8 Section 4.4: Why there is a nitrate-free zone between North and South Europe in Figure S4? I would expect that NO_x and NH₃ emissions are everywhere in central Europe. Furthermore, it looks like you have more nitrates over the oceans than over land.*

Please note that the model predicts significant concentrations of nitrate in Central Europe, it just predicts even more in parts of Northern and in Southern Europe. The area around Belgium, Netherlands and the UK had high ammonia levels and together with the high NO_x emissions and photochemistry, according to the model, resulted in high levels of both high and coarse nitrates. In parts of Southern Europe, the relatively high sea-salt resulted in relatively high levels of coarse nitrate. Central Europe had all the components but not in such high levels, so there was a minimum in predicted nitrate in that area. An explanation of this interesting behavior has been added to the paper.

(19) *Page 8 Line 260: Do you mean the mass transfer to the aerosol?*

Yes. The correction has been made in the revised manuscript.

(20) *Page 10 lines 296-304: Why the effect over oceans is so large in Fig. 7? What is the composition of sea salt emissions? Have you changed their composition here as well?*

The initial sea-salt composition has remained constant in this sensitivity test. Of course, the composition changes during the simulation as sulfuric and nitric acid may condense on the sea-salt particles, chloride may evaporate, etc. The effect depicted here is due

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to the dust both from emissions inside the modeling domain but also from the boundary conditions (long range transport from outside the domain). The model is predicting that the marine areas, having already a higher pH compared to the continental areas are more sensitive to the dust non-volatile cations. This is now explained in the revised paper.

(21) *Page 10 lines 296-304: The impact of NVCs on aerosol pH and nitrate is quite impressive, given that you only use urban dust emissions. This emphasizes the need to include Saharan emissions as well.*

Please note that some Sahara dust emissions are included in the model indirectly as boundary conditions in the south. However, these are constant and lead to moderate transport of dust to Europe and not to so called Sahara dust episodes. We agree with the reviewer that these are clearly important and we will focus on them in future work. This is now explained in the revised text.

(22) *Page 10 line 303: Do you mean by up to 0.5 units?*

No. The predicted pH for PM₁ when dust is present increases by 0.1 units or so over continental Europe (Fig. 7a). This is clarified in the revised text.

(23) *Page 10 line 308: This is not the case here. Over the northern coast of continental Europe and Southern England, the impact of NVCs on nitrate concentrations is significant despite the fact that the impact on pH is negligible. Why submicron aerosol nitrate has such a strong increase (almost twofold) in the presence of NVCs?*

This is a good point and it deserves additional discussion. The pH in this region is in the 2-3 range in which there is significant nitrate in both the gas and particulate phases. These values are inside the "sensitivity window" that we described in the introduction and nitrate is quite sensitive to changes in the cations. The NVCs cause

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a non-negligible change in the pH (around 0.2 units) and cause an increase of the fine nitrate of 20-30 percent (not twofold). Some of these changes are not entirely clear due to the color schemes used in the different maps. A brief discussion of the submicron nitrate in this area has been added to the paper.

(24) *Page 10 Section 4.5.1: Similar to NVCs, The impact of calcium on the pH all over the oceans is very strong. Does your sea salt contain any Ca? Can you comment why pH increases almost uniformly even over the remote oceanic locations of your domain?*

The calcium over the marine areas in these simulations is due to transport both from the continental areas but also from outside the domain (through the dust boundary conditions). These boundary conditions for dust are now shown in the Supplementary Information (Table S2). The emitted sea salt in our simulations has zero calcium. These once more stress the importance of dust for the pH of the marine atmosphere. This point has been added to the paper.

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