Responses to Comments of Reviewer 1

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 black) and the corresponding changes in the manuscript follow each comment of the reviewer (in blue).

Specific comments

(2) The paper focuses on May 2008 as the period during which online observations of PM_1 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 PM_1 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 PM_1 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 a brief 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 error in Figure 6a with the nitrate diurnal variation shown for Cabauw. The data shown corresponded to another area in the modeling domain. This 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 added Figure S7 in the SI showing the comparison of the predicted and observed diurnal profiles. We have also added a brief discussion of the organonitrate fraction in the revised paper. The model predicts only inorganic nitrate, therefore the comparisons with observations should be based also on the inorganic nitrate.

(3) The introductory summary of observed aerosol pH (page 2 line 62 – page 3 line 89) 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. (2020) that includes a detailed survey of such measurements. This review includes tables so there is no reason to repeat them in this 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.

(6) Page 7 line 225: What does "both" refer to in this context?
We replaced "both" with "most" 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. Unfortunately, most of the available measurements during the simulated period focused on fine PM. We have added a few sections discussing the predicted nitrate size distributions and their comparison with the available measurements in Finokalia.

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

Responses to Comments of Reviewer 2

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 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 black) and the corresponding changes in the manuscript follow each comment of the reviewer (in blue).

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).

The recommended reference has been 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 sub-micrometer marine aerosol is several units lower than that of the super-micrometer 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.
The typo was corrected.

(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 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 reference has been added in the revised manuscript.

(10) Page 5 line 154: Do you assume stable or metastable aerosols for the present study?
We assumed metastable 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 $CaSO_4$ 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 in internally mixed, therefore all particles in that size range have the same composition. However, particles in the same section can contain both insoluble material and soluble. Therefore, the insoluble $CaSO_4$ 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 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 domain average ground-level pH is 2.05 for PM_1, 2.65 for $PM_{1-2.5}$, 3.2 for $PM_{2.5-5}$ and 3.35 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 PM_1. 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 super-micrometer 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 period. 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. S8). 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 NH_3 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.

(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 actually 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 with the RH profiles 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 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 NOx and NH_3 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 modest effect depicted here is due to the dust both from emissions inside the modeling domain but also from the boundary conditions (long range transport from outside the domain).

(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 PM_1 when dust is present increases by 0.1 units or so over continental Europe (Fig. 7a). We have rewritten this sentence to avoid confusion.

(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 a non-negligible change in the pH (around 0.2 units) and cause an increase of the fine nitrate of 20-30% (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. The effect is consistent with that of the dust overall suggesting the importance of calcium and of the dust composition. This point is made now in several points in the revised paper.

Size-resolved aerosol pH over Europe during summer

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Abstract. The dependence of aerosol acidity on particle size, location and altitude over Europe during a summertime period is investigated using the hybrid version of aerosol dynamics in the chemical transport model PMCAMx. The pH changes more with particle size in northern and southern Europe owing to the enhanced presence of non-volatile cations (Na, Ca, K, Mg) in the larger particles. Differences of up to 1-4 pH units are predicted between sub- and super-micron particles, while the average pH of $PM_{1-2.5}$ can be as much as 1 unit higher than that of PM_1. Most aerosol water over continental Europe is associated with PM_1, while ~~$PM_{1.-2.5–2.5-5}$ and $PM_{2.5-55-10}$~~coarse particles dominate the water content in the marine and coastal areas due to the relatively higher levels of hygroscopic sea salt. Particles of all sizes become increasingly acidic with altitude (0.5-2.5 units pH decrease over 2.5 km) primarily because of the decrease in aerosol liquid water content (driven by humidity changes) with height. Inorganic nitrate is strongly affected by aerosol pH with the highest average nitrate levels predicted for the $PM_{1-2.5}$~~$_{2.5-5}$~~ range and over locations where the pH exceeds 3. Dust tends to ~~to increase and decrease aerosol water levels,~~ increase aerosol pH for all particle sizes and nitrate concentrations for supermicron range~~all~~ particles~~ sizes~~. This effect of dust is quite sensitive to its calcium content. The size-dependent pH differences carry important implications for pH-sensitive processes in the aerosol.

1. Introduction

Acidity is an aerosol property of central importance driving gas-particle partitioning and heterogeneous chemistry (Pye et al., ~~2019~~2020). pH affects the formation of semi-volatile particulate matter and the nitrogen cycle by modulating HNO_3/NO_3^- and NH_3/NH_4^+ gas-particle partitioning (Meskhidze et al., 2003; Guo et al., 2017; Nenes et al., 2019). Aerosol acidity can influence pH-dependent heterogeneous atmospheric processes, like oxidation of SO_2 to sulfate, formation of secondary organic aerosol and uptake of N_2O_5 on particles (Huang et al., 2011) and also influences aerosol hygroscopicity (Hu et al., 2014). Deposition of acidic particles causes damage on building materials, forests, and aquatic ecosystems (Xue et al., 2011). Aerosol pH can change the solubility of metals, such as iron and copper, which have been linked to aerosol toxicity, and at the same time affects nutrient distributions with impacts on photosynthesis productivity and ocean oxygen levels (Meskhidze et al., 2003; Nenes et al., 2011). Adverse health outcomes have been linked to aerosol acidity, including respiratory diseases (Raizenne et al., 1996), oxidative stress (Fang et al., 2017) and lung and laryngeal cancers (Hsu et al., 2008).

The nitrate partitioning to the aerosol phase is favored when pH exceeds a threshold value (between 1.5 and 3) that depends logarithmically on liquid water content and temperature (Meskhidze et al., 2003; Guo et al., 2016; Nenes et al., 2019). If aerosol pH is high enough (typically above 2.5 to 3), aerosol nitrate formation is favored, as most of the total nitrate formed from NO_x chemistry resides in the aerosol phase. For lower pH values (below 1.5 to 2), formation of aerosol nitrate is not favored and remains in the gas phase as HNO_3. Between these pH value limits, a sensitivity window (of 1 to 1.5 pH units) exists in which nitrate can be found either as gas or as aerosol (Vasilakos et al., 2018; Nenes et al., 2019). Atmospheric aerosol has often pH values inside this sensitivity window, for which pH errors could translate to importance biases in aerosol composition (Bougiatioti et al., 2016; Guo et al., 2015, 2017; Vasilakos et al., 2018).

Aerosol acidity and partitioning of semi-volatile species, like nitrate, can be modulated by the presence of soluble inorganic cations of sea salt and mineral dust, such as Na^+, K^+, Ca^{2+} and Mg^{2+} (Vasilakos et al., 2018). These non-volatile cations (NVCs) tend to reside in the coarse mode of ambient aerosol (sea salt, dust), with much lower concentration in smaller particles (Seinfeld and Pandis, 2006). Chemical transport models tend to overpredict aerosol inorganic nitrate levels in both US and Europe (Yu et al., 2005; Pye et al., 2009; Fountoukis et al., 2011; Tuccella et al., 2012; Heald et al., 2012; Walker et al., 2012; Im et al., 2015; Ciarelli et al., 2016; Bian et al., 2017; Zakoura and Pandis, 2018~~; Zakoura and Pandis, 2019~~). One of the reasons for these errors is that these models do not simulate properly the aerosol acidity introducing errors in gas-particle partitioning of semi-volatile species, often affecting predictions of inorganic nitrate (Vasilakos et al., 2018).

The effect~~impact~~ of amines and organic acids on pH~~H$^+$~~ is usually neglected in efforts to simulate aerosol~~model~~ pH (Pye et al., 2020). In areas with high organic aerosol concentrations and relatively low inorganic ion levels, organics could play a non-negligible role in determining particle pH ~~Nevertheless, acidic organics together with other water-soluble organic compounds in the particulate phase could affect the aerosol water content~~ (Bougiatioti et al., 2016~~; Pye et al., 2020~~). The aerosol pH has been estimated combining field measurements and aerosol thermodynamic models. Katoshevski et al. (1999) predicted that the pH of the submicrometer marine aerosol is several units lower than that of the super-micrometer particles ~~estimated the aerosol pH in the marine boundary layer using the thermodynamic model ISORROPIA and found that it ranged between -0.5 to 9 for particle diameters smaller than 1 μm up to 10 μm~~. pH was estimated to be 0 to 2 for the accumulation mode and 2-5 for the coarse mode particles using aerosol and gas phase data collected over the Southern Ocean in combination with the EQUISOLV II model (Fridlind and Jacobson, 2000). Keene et al. (2004) calculated mean pH, ranging from 2.6 to 3.9, for 0.75-25 μm particles based on measurements by an impactor for aerosols and Teflon filters for gases in New England during summer. PM$_{2.5}$ pH was calculated with ISORROPIA II in Beijing during all seasons in 2016-2017 with values ranging from 3.8 to 4.5 (Ding et al., 2019). ~~PM$_{2.5}$ particles are strongly acidic in Hong Kong, China ([H$^+$]=103 nmol m^{-3} for spring of 2001) (Pathak et al., 2003). PM$_{2.5}$ particles during different seasons at an urban site in Guangzhou, China were generally acidic (average [H$^+$] ~ 70 nmol m^{-3}) (Huang et al., 2011).~~ Guo et al. (2015) estimated that PM$_1$ particle pH varied from 0.5 to 2 in the summer and 1 to 3 in the winter in the Southeastern US. PM$_1$ pH was estimated for the northeastern US and its mean value was 0.77 (Guo et al., 2016). PM$_{2.5}$ pH values of 0-2 were estimated combining ISORROPIA II and data collected at a rural southeastern US site during summer 2013 (Weber et al., 2016). Based on impactor measurements in Atlanta, GA during the spring of 2015, Fang et al. (2017) calculated a mean pH value of 3.5 for the coarse mode particles using the ISORROPIA II model. Guo et al. (2017) calculated PM$_1$ and PM$_{2.5}$ pH (equal to 1.9 and 2.7) from measurements during the CalNex study in combination with ISORROPIA II. An average PM$_1$ pH equal to 2.2 was estimated in a rural southeastern US site using ISORROPIA II (Nah et al., 2018). Vasilakos et al. (2018) used the three-dimensional chemical transport model, CMAQ, along with ISORROPIA II, to predict the annual average PM$_{2.5}$ pH over the Eastern US for 2001 and 2011 (pH equal to 1.6 and 2.5, respectively). Bougiatioti et al. (2016) calculated PM$_1$ pH (between -0.97 and 3.75) using ISORROPIA II in the eastern Mediterranean. Squizzato et al. (2013) estimated a mean PM$_{2.5}$ pH value equal to 3.1 over Po Valley, Italy during 2009 based on filter measurements using the E-AIM thermodynamic model. A comprehensive survey of pH studies to date including observation-based aerosol pH estimates in sites around the world can be found in Pye et al.~~,~~ (~~2019~~2020).

Most of the previous studies focused on the average pH of a particular size range neglecting potential pH variation with particle diameter. There is evidence that pH may vary by as much as 6 units between particle diameters of 0.1 μm to 10 μm (Fang et al., 2017; Ding et al., 2019). The majority of previous work has focused on select locations in the US, Canada and Asia and there is still little information about Europe. Also, there is only one study that links aerosol acidity with altitude (Guo et al., 2016), indicating the need for further investigation.

The aim of our work is to investigate the size-dependent aerosol pH over Europe. For this purpose, the Particulate Matter Comprehensive Air quality Model with extensions, PMCAMx, including the thermodynamic model ISORROPIA II, was used. Europe is particularly interesting, owing to the large concentration of NH_3, nitrate, sulfate and dust across all sizes. The role of dust, Ca^{2+} and the variation of aerosol pH with altitude are analyzed in detail.

2. Model description

PMCAMx (Tsimpidi et al., 2010; Karydis et al., 2010) is based on the CAMx air quality model (Environ, 2003) to simulate the processes of horizontal and vertical advection, horizontal and vertical diffusion, wet and dry deposition, gas- and aqueous-phase chemistry. A sectional approach is used to dynamically track the evolution of the aerosol mass and composition distribution across 10 size sections covering a diameter range from 40 nm to 40 μm. ~~Addition of~~ T~~t~~he first 5 size bins represent the PM_1 fraction, while 3 size bins are used to describe the coarse PM_{1-10} fraction ($PM_{1-2.5}$, $PM_{2.5-5}$, PM_{5-10}). The model assumes that each size section is~~n~~ internally mixed, therefore all particles in that size range have~~s~~ the same composition. The aerosol components modeled include sulfate, nitrate, ammonium, sodium, chloride, calcium, potassium, magnesium, other inert crustal material, elemental carbon, water, primary and secondary organic species. The thermodynamics of inorganic aerosol species is simulated~~treated~~ using the ISORROPIA-II model (Fountoukis and Nenes, 2007), assuming that the aerosol exists only in liquid form and is therefore in a ~~(~~metastable equilibrium state at low relative humidity.~~).~~ The gas-phase chemical mechanism used in this application is based on the SAPRC mechanism (Carter, 2000; Environ, 2003). The version of SAPRC mechanism used here includes 237 reactions of 91 gases, 18 radicals and 37 aerosol species. ~~The thermodynamics of inorganic~~

~~species was simulated using the ISORROPIA II model (Fountoukis and Nenes, 2007).~~ Additional details regarding PMCAMx are provided in Fountoukis et al. (2011).

We use a~~a new~~~~the~~ hybrid approach to model inorganic aerosol mass transfer, where for particles with dry diameters less than 1 μm, bulk equilibrium is assumed. For larger particles, the mass transfer to each size section is simulated ~~by~~ using ~~a new version of~~ the Multicomponent Aerosol Dynamics Model (Pilinis et al., 2000) as extended by Gaydos et al. (2003) for metastable aerosol. –Two additional modifications have been made in this work –in the ~~to the multicomponent aerosol dynamics model of~~ Gaydos et al. (2003) algorithm. The first is that Ca^{2+}, K^+ and Mg^{2+} have been added to the various ionic balances in the algorithm and the corresponding mass transfer constraints. The second is that the mass transfer model now includes an explicit constraint that ~~This new version assumes that~~ nitric and hydrochloric acid~~s~~ do ~~n~~no~~'~~t condense when ammonia is condensing until the system equilibrates using the acidity as a drive force as described by Gaydos et al. (2003). ~~The second improvement has to do with the ionic balance used in order to calculate the hydrogen ion equilibrium concentration which can change at a rate as much as 10%/s. Now, dust components (Ca^{2+}, K^+, Mg^{2+}) are added in order to reach the proper equilibrium.Trump et al. (2015) used the hybrid approach over Europe to improve the simulation of coarse particle chemistry. They found that PM_1 nitrate overprediction in areas with high sea-salt levels was reduced with the hybrid approach due to the more accurate representation of the interaction of nitric acid and ammonia with coarse mode sea salt. These interactions result in reduction of fine nitrate and increase of nitrate in the coarse mode. Given the importance of pH on the partitioning of nitrate, the hybrid approach is essential for capturing the size-resolved variability of pH.~~

pH is calculated in this work for particles smaller than 1 μm, 1-2.5 μm, 2.5-5 μm and 5-10 μm, using a molal definition consistent with the pH_F definition of Pye et al. (2020~~19~~):

$$pH = -\log_{10}\left(\frac{1000[H^+]}{[W]}\right), \tag{1}$$

where $[H^+]$ and $[W]$ are the concentrations of particle hydronium ion and inorganic particle water in μg m^{-3}. -The water associated with organics is neglected in our study, as it has been shown that it~~s~~ has~~effects bears a~~ minor influence on the estimated pH~~ estimations~~ (Guo et al., 2015; Battaglia et al., 2019).

3. Model application

PMCAMx was applied over Europe, during the EUCAARI summer intensive campaign in May 2008 for which the model has been evaluated in previous work (Fountoukis et al, 2011). The domain covers a 5400×5832 km^2 region with 36×36 km grid resolution and 14 vertical layers extending up to 6 km. Inputs to the model include horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds and rainfall, all generated using the Weather Research and Forecast (WRF) meteorological model (Skamarock et al., 2005). Anthropogenic gas-phase emissions include land emissions from the GEMS dataset (Visschedijk et al., 2007) as well as international shipping emissions. Anthropogenic particulate emissions of organic and elemental carbon were obtained from the EUCAARI Pan-European Carbonaceous Aerosol Inventory (Kulmala et al., 2009). Industrial, domestic, agricultural and traffic emission sources are included in the two inventories. Biogenic emissions were based on MEGAN (Guenther et al., 2006), and sea-salt emission inventories were developed using the approach of O'Dowd et al. (2008). Urban dust emissions were based on the work of Kakavas et al. (2020), assuming that calcium, potassium, magnesium and sodium represented 2.4%, 1.5%, 0.9%, and 1.2% of the emitted mineral dust, respectively (Sposito, 1989). A reliable Saharan dust emissions inventory was not available; therefore the African region is excluded from the simulation analysis. Additionally, we focused on a period during which the impact of Saharan dust in Europe ~~is~~was minimal. The concentrations of d~~D~~ust and its components ~~concentrations~~ at the boundaries of the domain are considered constant ~~with typical small values~~ and invariant with height and along each boundary (Table S1). More information about the inputs of PMCAMx during the simulated period can be found in Fountoukis et al. (2011) and Kakavas et al. (2020).

Three simulations were performed. The first was the "base case" simulation and included all emissions described above. Two other simulations we~~a~~re carried out and compared with the "base case" to understand how non-volatile cations (NVCs) in dust affect water uptake and aerosol pH: one where dust lacks any non-volatile soluble cations ("inert dust" simulation) and one where we neglect calcium (~~the major NVC in dust~~"no calcium" simulation) from the "base case" simulation. Calcium is the major NVC in dust and ~~unique~~ compared to the other NVCs ~~in that~~ it can react with sulfate ions and form insoluble $CaSO_4$, which precipitates out of the aerosol aqueous phase and remains insoluble under subsaturated conditions - even for metastable aerosol (Fountoukis and Nenes, 2007). Particles in ~~the same~~ each size section can contain both insoluble ~~material~~ and soluble material. Therefore, the insoluble $CaSO_4$ is treated as such by ISORROPIA-II.~~-~~ This unique interaction implies that calcium~~Ca~~, if present in sufficient amounts, can reduce aerosol sulfate and reduce acidity, but at the same time reduce hygroscopicity that promotes acidity- in a way that is not obvious by just comparing the base case simulation with the “inert dust” simulation. In all simulations, the total dust mass emissions were the same and only its assumed composition varied.

4. Results and discussion

4.1 Size dependence of aerosol pH

The average ground ~~-~~level pH predictions for different size ranges are presented in Fig. 1. The domain average ground-level pH is 2.05 for PM_1, 2.65 for $PM_{1-2.5}$, 3.2 for $PM_{2.5-5}$ and 3.35 for PM_{5-10}. Higher pH values for all particle sizes are predicted over the Atlantic due to the presence of sea salt and the systematically higher RH and liquid water content – all of which act to reduce aerosol acidity. The acidity is higher over the Mediterranean, especially its eastern part, due to the higher sulfate and nitrate levels in that region. However, the fine particles over the Atlantic are also predicted to be quite acidic especially in the south. High pH is also predicted for parts of central and northern Europe due to the corresponding ammonia but also the effect of the alkaline dust particles.~~pH is higher over the sea for all particle sizes compared to continental regions due to the presence of sea salt and dust respectively,, lower NH_3 and the systematically higher RH and liquid water content – all of which act to reduce aerosol acidity.~~ The pH of marine aerosol increases with particle size, with the highest value equal to 4.5 for the 2.5-5 μm and 5-10 μm ranges, as sea salt is emitted mainly at the super-micron range and is the main aerosol component in these areas. Over the continental region, average PM_1 pH ranges between 1 to 3.5 with the highest values in the northern coastal parts of Europe and northern Italy; in these regions, acidity is reduced by the high levels of NH_3 present from agriculture and livestock emissions combined with high NO_x and RH levels (Guo et al., 2018; Masiol et al., 2019). $PM_{1-2.5}$ is less acidic with pH values from 1.5 to 4 over the continental region with the higher values in the northern coastal areas of Europe ~~(e.g., parts of the United Kingdom).~~extending from France to Denmark. The average pH increases further in the 2.5-5 μm range being equal to 2-3.5 over the continental regions and reaching values up to 4-~~4.~~5 in the ~~northern~~ coastal areas of the Netherlands,~~United Kingdom,~~ Belgium, France and Denmark~~Poland~~. Average PM_{5-10} pH increases ~~slightly decreases~~ over the continental region compared to $PM_{2.5-5}$, especially in ~~central~~ northern Europe, and the highest pH values (~~4-~~4.5-5) are predicted for the same regions. ~~The size-dependence of pH is stronger in the northern and southern parts of Europe, and weaker in central Europe, in which the average pH is in the 1.5-3.5 range for all particle sizes.~~ The largest pH changes across size occur for regions where fine-mode aerosol acidity is dominated by the NH_3-SO_4 system (i.e., relatively lower NH_3 levels – so that aerosol nitrate is low; Guo et al., 2018), and the largest sizes contain large amounts of NVCs from sea salt and dust.

Squizzato et al. (2013) calculated PM$_{2.5}$ pH equal to 2.3 and Masiol et al. (2019) equal to 2.2 in the Po Valley, Italy during the summer of 2009 and 2012, respectively. The predicted pH by PMCAMx is a little higher and equal to approximately 3.3. ~~predictions tends to overpredict PM$_{2.5}$ pH for this area according are in good agreement with these studies, as PM$_{2.5}$ pH is predicted to be equal to 3.3~~2.4~~.~~ Guo et al. (2018) estimated that the PM$_{2.5}$ pH was equal to 3.3 in Cabauw, Netherlands during the summer of 2013, based on measurements and thermodynamic modeling. PMCAMx predicts a~~overunderpredicts~~ PM$_{2.5}$ pH by ~~0.58 units (~~equal to 3.8~~2.5)~~ in this area during the summer. T~~Part of t~~hese~~is~~ discrepancies~~y~~ could be partially due to the different periods compared as~~and~~ the aerosol pH can be sensitive to small changes in composition but also to meteorology (e.g., relative humidity). Nonetheless, these comparisons, even if they involve different years, suggest that the model predictions are reasonable. ~~Therefore our goal is to investigate if our model predicts reasonable pH values compared to the values calculated based on measurements and thermodynamic models for similar periods.~~ Bougiatioti et al. (2016) determined through thermodynamic analysis of observations with ISORROPIA-II that the PM$_1$ pH in Finokalia, Crete is equal to 1.3 which agrees ~~within 0.4 units~~ with our predictions~~ (equal to 1.7)~~.

The pH of PM$_{2.5}$ has often been the focus of previous measurement studies, due to the availability of the corresponding filter samples. However, the pH in the 1-2.5 range can be quite different from that in the sub-micrometer range (Fang et al., 2017; Ding et al., 2019). This difference may have important implications for aerosol toxicity, metal solubility, nitrate partitioning and other processes. The difference of average ground level aerosol pH predictions between PM$_{1-2.5}$ and PM$_1$ is shown in Fig. 2. The pH of these size ranges can differ up to 1.2 units over the continental region ~~owing~~due to the effect of NVCs from dust~~-~~ in the PM$_{1-2.5}$~~levels~~. This difference is predicted to be ~~even higher~~smaller over most ~~the ocean sea part of Europe~~marine areas (up to 1 ~~.4~~ unit~~s~~).~~,~~ ~~owing to the effect of NVCs from sea-salt levelsand the biggest one is observed in northern Atlantic and southern Mediterranean.~~

Particle water concentrations for the different particle sizes are shown in Fig. 3. PM$_1$ has the most water, compared to the other size fractions over the continental region. The coarse particles in PM$_{1-2.5}$~~$_{2.5-5}$~~ and PM$_{2.5-5}$~~$_{5-10}$~~ have the most water ~~over sea~~in the marine areas ~~owing~~ because of the~~to~~ sea salt, which is found in higher levels in these particles, and exhibits the highest hygroscopicity – compared to all other inorganic salts found in aerosol. Water levels for all particle sizes are higher at areas closer to the sea, owing to the relatively high dry aerosol mass concentration combined with the high RH typically associated with the marine environments; in just the 2.5-5 μm size range alone, water content exceeds 20 μg m^{-3}.

Northern Scotland is predicted to have lower pH values compared to the rest of Great Britain for all size ranges during the simulated period. 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. S8). The lower aerosol water content and lower dust concentrations lead to more acidic particles in Northern Scotland for all size ranges according to PMCAMx.

4.2 Temporal evolution of pH~~H~~

To study the temporal evolution of pH, eight sites (Fig. S1) with different characteristics were selected based on their different type, location and dust/sea salt levels (Table ~~S1~~S2). ~~Iza, in Ukraine~~Finokalia, has the lowest PM_1 pH of all examined locations with a value equal to 1.3~~0.25~~ (Fig. S2). During most of the time the PM_1 pH in that area in the eastern Mediterranean is predicted to be within 0.1-0.2 units of its average even if there are limited periods with both very low (pH=0.3) and high (pH=7.7) hourly average pH (not shown). The predicted pH for larger particles is higher, but remains the lowest of the examined group of sites due to the high sulfate levels in the area. ~~The pH is predicted to vary between -0.35 and 7.71.4 (on an hourly basis).~~ This site is affected by both relatively dry air masses with continental aerosol characteristics ~~(low pH)~~ and by air masses with relatively high sea-salt and dust levels as well as biomass burning influences (~~higher pH;~~ Bougiatioti et al., 2016). ~~in this region of Eastern Europe that is characterized by high sulfate levels. Mace Head~~Cabauw, on the other hand, has the highest average PM_1 pH (3.0~~1.7~~) with hourly average values ranging between 1.5~~0.9~~ and 4.5~~2.3~~. ~~Finokalia has the most variable PM_1 pH with a range covering 4 units. This site is affected by both relatively dry air masses with continental aerosol characteristics (low pH) and by air masses with relatively high sea-salt and dust levels as well as biomass burning influences (higher pH; Bougiatioti et al., 2016).~~ The distribution of pH values of the 1-2.5 μm diameter particles moves to higher values (less acidic particles) for all sites compared to the sub-micrometer particles. The pH values of all sites for the 2.5-5 μm range are similar to those in the 5-10 μm range and higher than the fine aerosol pH values.

The pH diurnal profiles for Cabauw, Melpitz, Paris, Finokalia are shown in Fig. 4. These sites were selected based on their different type, location and dust/sea salt levels (Table S2~~1~~) – and because ambient pH data is available for ~~both~~ most of them (Pye et al., ~~2019~~2020). pH follows ~~the same~~ similar trends for all particle sizes in each of the four sites. Cabauw is characterized by lower PM$_1$ and PM$_{1-2.5}$ pH during the afternoon and relatively constant average diurnal P$_{2.5-5}$ and PM$_{5-10}$ pH with slightly higher values early in the morning. The average ~~hourly~~ pH ~~is a lot more variable~~ in Melpitz is characterized for all particle sizes by early morning and an evening peaks and a strong afternoon minimum. The behavior in Paris is similar to that in Melpitz, but the variation in PM$_{1-2.5}$ is predicted to be stronger than in other size ranges due to the combined effects of photochemistry, relative humidity and urban dust emissions. The average ~~and Paris, with a peak early in the morning for Melpitz (up to 5.2)3.5 for Melpitz and a peak in the evening 3.8 for Paris (up to 5.8)). For both sites pH is, and then decreasing values decreasing during the day reaching a minimum in the afternoon. The~~ pH ~~diurnal profile is different~~ in the remote site of Finokalia~~, since pH~~ has the lowest variability of all four sites. It has a little higher values during the night and lower during the day. ~~its peak (up to 23.96) at noonearly in the morning (between 15-616 UTC time) and then starts to decrease.~~ These variations are caused by a variety of factors including the relative humidity (that is higher during the early morning, leading to higher liquid water content and higher pH), the temperature (which tends to evaporate nitrate) and mixing height variation (which in turn tends to affect precursor concentrations). The aerosol pH diurnal profiles in the four examined sites of our study follow the same pattern as the corresponding RH diurnal profiles, underlying the importance of RH as a driver of these average variations (Fig. S3).

4.3 pH variation with height

All the results presented so far are for the ground level (lowest 50 m). The predicted aerosol water content for all size ranges decreases with altitude (Fig. ~~S3~~S4). This is mainly due to the decrease of the relative humidity and aerosol concentrations with altitude (Mishra et al., 2015; Wang et al., 2018). As height increases, pH values for all particle sizes decrease, due to the reduction of aerosol water per unit mass of dry aerosol, with height (Fig. 5) – which is exclusively an effect of relative humidity decrease. A secondary effect is that the lower concentration of aerosol tends to drive partitioning of semi-volatile species (nitrate, ammonium) to the gas phase (Nenes et al., 2019). As a result, particles of all sizes that are acidic at ground level become more acidic when they move higher in the atmosphere.

For PM$_1$, in the less acidic areas over Europe the pH decreases from 3~~2~~-3~~2~~.5 near the ground to around 2~~1.5~~-2.5 at 2.5 km altitude. For PM$_{1-2.5}$, the reduction is even larger, since the pH values decrease from 3.5-4.0~~3.5~~ at the ground to 1.5-2.~~2~~ 0 at 2.5 km (the larger drop in pH is a result of the evaporation of nitrate aerosol and the decrease of liquid water content). Similar decreases of 2~~1~~-2~~1~~.5 pH units are predicted for the coarse particles in the first 2.5 km of the atmosphere in areas over land. The predicted decrease in aerosol water content and pH for the super-micrometer particles is even more pronounced in the marine atmosphere and coastal areas due to the high levels of sea-salt near the ground. This reduction of pH with altitude is smaller for the PM$_1$ size range in the marine atmosphere. A comparison of the average vertical profiles for the inorganic aerosol components is shown in Fountoukis et al. (2011). The measured reduction of PM$_1$ nitrate levels over central and northern Europe from their maximum near the ground to close to zero at 3-4 km was reproduced well on average by PMCAMx.

4.4 Effect of aerosol pH on inorganic nitrate

The model predicts significant concentrations of inorganic nitrate both in c~~C~~entral Europe and in parts of n~~N~~orthern and s~~in S~~outhern Europe (Figure S5). ~~The area around~~ PMCAMx does not simulate the concentrations of organonitrates. The high ammonia levels together with the high NO$_x$ emissions and photochemistry over Belgium, the Netherlands and the UK ~~have high ammonia levels and together with the high NO$_x$ emissions and photochemistry,~~ according to PMCAMx ~~the model,~~ result in high levels of nitrate both in the -fine and coarse particles in these areas~~nitrates~~. In parts of s~~S~~outhern Europe, the relatively high sea-salt concentrations result ~~ed~~ in ~~relatively higher~~modest levels of coarse nitrate in areas with very low or zero levels of fine nitrate. ~~The~~ H~~h~~igh~~est~~ average nitrate levels are predicted in several areas in which the pH exceeds 2.5 ~~(0.77 μg m^{-3}) in Italy~~ are predicted for the 1-2.5~~-5~~ μm size range (Fig. ~~S4~~S5)~~ for the whole domain~~. ~~This size range is characterized by an the highest average pH (with a value of 3.52.63).~~ Nitrate partitioning to the aerosol phase is favored at these higher pH ~~when the aerosol pH is higher than 2.5~~ (Guo et al., 2016; Vasilakos et al., 2018). At the same time, the mass transfer of the produced nitric acid ~~in~~ to the ~~gas~~ aerosol phase is faster for the particles in the 1-2.5~~-5~~ μm range compared to those in the PM$_{2.5-5}$ and PM$_{5-10}$ range also contributing to higher concentration. Finally, the removal of the larger particles from the atmosphere is faster adding one more reason for the maximum of the nitrate size distribution. Modest nitrate levels are predicted in central Europe during this period because both nitric acid and ammonia levels were modest and the temperature was relatively high.

The size-dependent average nitrate diurnal profiles for Cabauw, Melpitz, Paris, and Finokalia, are shown in Fig. 6. In Cabauw, predicted total nitrate levels start to increase early in the morning and peak around 9:00. Lower values are predicted during midday and early afternoon, with fine nitrate starting to increase in the early evening. ~~and have their peak early in the morning, have their peak at noon or afternoon and then start to decrease during the afternoon and early evening.~~ Most of this variation is due to the formation of ammonium nitrate in the PM_1 size range. The increase in PM_1 nitrate is accompanied by an increase in the ammonium levels (Fig. S6~~5~~) in this area that is characterized by high ammonia concentrations. Predicted s~~S~~upermicrometer ~~The morning increase in the PM_{5-10}~~ nitrate levels are less variable (in absolute terms) ~~is due to the formation of sodium nitrate and calcium nitrate remaining almost constant~~ during the day~~time~~. In Cabauw, ~~all super-micron~~coarse particles have on average pH above 2~~2~~.5 throughout the day (Figure 4a), favoring the partitioning of nitrate to the aerosol phase forming also coarse ammonium nitrate. The predicted average PM_1 nitrate diurnal variation is in very good agreement with the measurements in that site during the EUCAARI campaign (Figure S7).

In Melpitz, the predicted behavior of nitrate is ~~quite different than in~~almost the same as in Cabauw, but with lower fine nitrate levels ~~due to the differences in the pH behavior~~ (Fig. 6~~4~~). PM_1 nitrate peaks early in the morning with peaks in coarse nitrate a few hours later. The peak in fine nitrate is at the same period as the pH in this range, while for the coarse particles it is a few hours later due to the delays in mass transfer to the larger particles. Nitrate levels in all size ranges are predicted to decrease during the afternoon with nitrate reaching a minimum in the late afternoon. The predicted diurnal pattern is the same as the observed values but the model tends to overpredict nitrate in this area by approximately 0.5 μg m^{-3}. The behavior of nitrate in the fine and coarse particles in Paris is quite similar as in Melpitz reflecting the similarity in the behavior of pH. Nitrate in all size sections peaks in the early morning and has a minimum in the afternoon. The main difference in this case is that there is more nitrate in the coarse particles due to the higher predicted levels of dust in this megacity. In Finokalia, the predicted fine nitrate is quite low reaching a peak of approximately 0.2 μg m^{-3} at 11:00 UTC. These very low levels are consistent with the corresponding measurements of very low fine nitrate (approximately 0.1 μg m^{-3}) in this area during this summertime period. The nitrate in the coarse particles is significantly higher and peaks a few hours later. increases gradually in all sizes during the morning, reaches its maximum values in the afternoon and then gradually decreases. These higher levels of coarse nitrate exceeding 1 μg m^{-3} are consistent with the 1-2 μg m^{-3} of coarse nitrate measured in Finokalia during this EUCAARI campaign. So PMCAMx reproduces well the size distribution of nitrate in this area, with practically all of the mass in the super-micrometer range.

4.5 Effect of dust composition on particle pH

The impact of the NVCs from dust on pH can be quantified comparing the results of the simulation in which the dust was assumed to be inert with the base case simulation. The NVCs in dust affect directly and indirectly the a~~A~~erosol water content for both the fine and coarse particles ~~levels are highervary in all particle sizes for the base case simulation~~ (Fig. ~~S6~~S8~~7~~) ~~compared to the inert dust simulation, as result of the water uptake associated with the NVCs~~. The predicted dust concentrations are shown in Fig. S9 and their effects on aerosol water in the different size sections are predicted to be both positive and negative. This complex picture is due to series of effects of the dust NVCs on the particle composition. In general, the the presence of dust causes an increase in coarse nitrate and a reduction in fine nitrate. At the same time, there is increase water absorption by the coarse particles. These effects, dominate near the sources of dust, but at the same there an increase in removal rates of the nitrates leading to reductions further downwind of their sources. The result of these processes are reductions in fine nitrate in most areas of continental Europe (Fig. S10) accompanied by a reduction in fine aerosol water. However, there are some reductions of PM$_1$ water due to the presence of the NVCs in marine areas. On the other hand, for the larger coarse particles the presence of the dust NVCs leads to an increase in aerosol water practically everywhere. For the particles in the intermediate size ranges (PM$_{1-2.5}$ and PM$_{2.5-5}$) the effects of dust NVCs on aerosol water are mixed, with both increases and decreases predicted due to changes in the total concentrations and size distributions of the water-soluble aerosol components. These results highlight the complex effect of the coarse dust particles on aerosol water and its size distribution.

~~Dust is predicted to cause an increases and decreases of 1.2-2 μg m^{-3} in aerosol water concentration even for the submicrometer particles over Europe with the highest changes in the northern areas. The water deincreases for PM$_1$, PM$_{1-2.5}$ and PM$_{2.5-5}$ in the continental due to dust varies from 1 to 2.5 μg m^{-3} over continental region. The effect, as expected, is higher fFor PM$_{52.5-510}$ water increases reaching up to 3 1.5 μg m^{-3} in areas like Paristhe Po Valley in Italy and even higher for PM$_{5-10}$ ranging between 1 and 6 μg m^{-3}. The highest differences in aerosol water levels between the two simulations are predicted for areas that combine relatively high values of RH and relatively high values of dust (Fig. S7S8) during the simulated period.~~

The predicted aerosol pH is lower in all particle sizes for the inert dust case compared to the base case simulation (Fig. 7). The soluble NVCs in dust tend to increase pH, ~~as~~ because due to their lack of volatility they irreversibly neutralize ~~bi~~sulfates ions~~ that are generated by the NH_3/NH_4^+ equilibrium, and therefore elevate aerosol pH~~. NVCs also tend to elevate aerosol water in a way that leads to ~~–~~pH increase, directly through their hygroscopicity and indirectly, through promoting the condensation of aerosol nitrate ~~(~~and its associated water content (~~;~~ Guo et al., 2018). PM$_1$ is ~~also~~ slightly affected, ~~due to~~because ~~even though~~ it contains small amounts of dust. The average PM$_1$ ~~, as its~~ pH changes ~~increase~~due to dust by less than ~~approximately by~~ 0.05~~1~~ units~~ or so over parts of continental Europe~~. The corresponding pH increase is around~~s with diameter by~~ 0.1~~5~~ units for PM$_{1-2.5}$, 0.2-~~almost~~ 1 ~~0.8~~ units~~s~~ for PM$_{2.5-5}$ and 0.3-1~~.4~~ units~~s~~ for PM$_{5-10}$.

The effects of dust on pH and aerosol water ~~is~~ are reflected on the predicted aerosol nitrate. Nitrate in the submicron range increases and for bigger ~~in all~~ particle sizes decreases when dust is assumed to be inert (Fig. ~~S8~~S10~~9~~)~~. due to mass transfer, as the corresponding pH reduction (for cases when pH < 2.5) does not favor the partitioning of nitrate to the aerosol phase.~~ The average effect of dust on submicrometer nitrate is negligible in ~~most~~ several areas, but there ~~is still an~~are significant effects in the Netherlands and the surrounding areas~~ (Fig. S8S9)~~. The dust is predicted to cause average increases of PM$_{1-2.5}$, PM$_{2.5-5}$ and PM$_{5-10}$ nitrate up to 0.01~~5~~ μg m^{-3}, 0.1~~1.3~~ μg m^{-3} and 0.08~~1.2~~ μg m^{-3}, respectively in parts of northern Europe with higher dust levels and also Italy. This nonlinear impact of relatively minor amounts of NVCs from dust occurs because relatively small changes in aerosol pH, when occurring in the "pH sensitivity window" of nitrate partitioning can lead to large responses in nitrate uptake (Vasilakos et al., 2018).

If only calcium is neglected in the simulation, aerosol pH decreases for all particle sizes compared to the base case simulation (Fig. 8). This decrease varies from 0.01 to 0.03 units for PM$_1$, 0.05-0.1 units for PM$_{1-2.5}$, 0.1-0.7 for PM$_{2.5-5}$ and 0.4-0.7 for PM$_{5-10}$ over continental Europe. The highest pH differences are predicted for the coarse particles, consistent with that the coarse particles are richest in calcium. Considering the possible effects calcium can have on soluble sulfate and water uptake, the simulations suggests that the primary effect of calcium is through its action as a soluble ion.

~~4.5.1 The role of calcium~~

~~Predicted aerosol water levels increase in the PM$_{1-2.5}$, PM$_{2.5-5}$ fractions and decrease in the PM$_1$, PM$_{5-10}$ fractions over the continental region in the absence of calcium compared to the base case simulation (Fig. S9S10). The increase change of aerosol water concentration caused by the calcium ranges between 0.028-0.1 μg m^{-3} for PM$_1$ and, 0.8-1.1 μg m^{-3} for PM$_{1-2.5}$, 0.08-01.2 μg m^{-3} for PM$_{2.5-5}$ and 0.087-0.1.37 μg m^{-3} for PM$_{5-10}$ over continental Europe. The effect is more significant in the coarse particles where most of the calcium is found. Considering the possible effects calcium can have on soluble sulfate and water uptake, the simulations suggests that the primary effect of calcium is through its action as a soluble ion. If calcium is neglected in the simulation, aerosol pH decreases for all particle sizes compared to the base case simulation (Fig. 8). This decrease varies from 0.012 to 0.033 units for PM$_1$, 0.0525-0.14 units for PM$_{1-2.5}$, 0.31-0.5 7 for PM$_{2.5-5}$ and 0.46-0.78 for PM$_{5-10}$ over continental Europe. The highest pH differences are predicted for the coarse particles, consistent with that the coarse particles are richest in calcium.~~

5. Conclusions

The size-dependent aerosol pH was simulated over Europe during an early summer period. We find that fine mode aerosol is persistently more acidic than coarse mode particles. The size-dependence of pH is strongest in northern and southern Europe, where the difference can be as large as ~~4~~ 2 units between submicron and 10 μm particles. This difference is reduced over other continental regions, but can still be as large as 1 pH unit -between PM$_1$ and PM$_{1-2.5}$. PM$_1$ has the most water over continental areas, while ~~PM$_{2.}$~~$_{1-2.5}$~~$_{-5}$ and PM$_{5-10}$~~$_{2.5-5}$coarse PM has~~ve~~ the most water in ~~the~~ marine and coastal areas.

Particles of all sizes become increasingly acidic with altitude owing to the reduction of aerosol water levels with height and volatilization of particulate ammonium and nitrate due to dilution. The highest pH decrease between the ground and 2.5 km altitude is 1~~0.5~~-1.5 units for PM$_1$, 2~~1.5~~-2.5 units for PM$_{1-2.5}$, ~~and~~ PM$_{2.5-5}$ and~~, 1.3 units for~~ PM$_{5-10}$. The largest drop in pH is observed for the PM$_{1-2.5}$ fraction, because it coincides with where aerosol nitrate resides most – hence its evaporation with altitude tends to have a larger impact on pH than reductions of liquid water from the RH effect alone.

The nitrate concentration tends to peak a few hours later than the pH in ~~all examined~~ most sites due to the time required for the production of nitric acid and its partitioning to the aerosol phase. If aerosol pH becomes low enough to impede fine mode nitrate formation, its preferential condensation to larger sizes tends to increase the pH difference between fine and coarse particles~~across size~~.~~ The highest average nitrate levels over Europe are predicted for the 2.5-51-2.5 μm range for which the average pH is equal to 3.52.6 during the simulated period.~~

The water soluble components of d~~D~~ust have a rather complex effect on aerosol water causing both~~es~~ increases and decreases of the aerosol water levels~~ in all particle sizes~~. The average increase in water levels ranges from 0.1 to 1.5~~6~~ μg m^{-3} with the highest change for PM$_{5-10}$ in parts of northern Europe. ~~with relative high concentrations of dust. ~~Dust ~~also ~~causes an increase in aerosol pH for all particle sizes with higher effects in the coarse particles. This effect can be more than 1 pH unit. This increase in pH is accompanied by increases in aerosol nitrate.~~,~~ ~~which can be as large as 2.50.1 μg m^{-3}.~~ This effect of dust is mainly due to its calcium content, suggesting the importance of simulating accurately not only the dust concentration, but also the calcium levels. This study focused on periods during which the impact of Saharan dust on Europe was minimal and the predicted dust was dominated by local sources. The effect of Saharan dust on the aerosol pH of Europe is expected to be even more important than our results indicate and will be the topic of future work.

This study ~~clearly ~~shows that aerosol acidity and liquid water content changes considerably across size, location, time and height over Europe. These changes will impact aerosol formation and its response to emissions controls, solubility of aerosol trace metals and deposition. With this realization, aerosol pH and liquid water content emerge as powerful aerosol state variables (Nenes et al., 2019) that could help elucidate the complex impacts of aerosol on public health, ecosystems and climate.

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Code and Data availability. Simulation results are available upon request.

Competing interests. The authors declare that they have no conflicts of interest.

Author contributions. SK extended the hybrid module in the revision stage of the paper, repeated all simulations, analyzed the revised results and wrote the final version of the paper. He also contributed the dust emissions and NVC scheme. DP assisted in the extension of the hybrid module and the development and implementation of the final pH calculation scheme and the analysis of the final results. MZ developed and implemented the original pH calculation scheme in PMCAMx, carried out the initial simulations and was responsible for the first draft of the paper. ~~MZ,~~ SN and AN conceived and led the study and helped in the writing of the paper.~~.~~ ~~SK, AN, SN and MZ developed and implemented the pH calculation scheme in PMCAMx, carried out the simulations. MZ, SN and AN and wrote the first draft of the paper, with considerable edits by SK. SK contributed the dust emissions and NVC scheme.~~ ~~MZ, AN and SP~~All authors were involved in the scientific interpretation of the simulations, ~~. All authors~~ provided feedback on the analysis approach and extensively commented on the manuscript.

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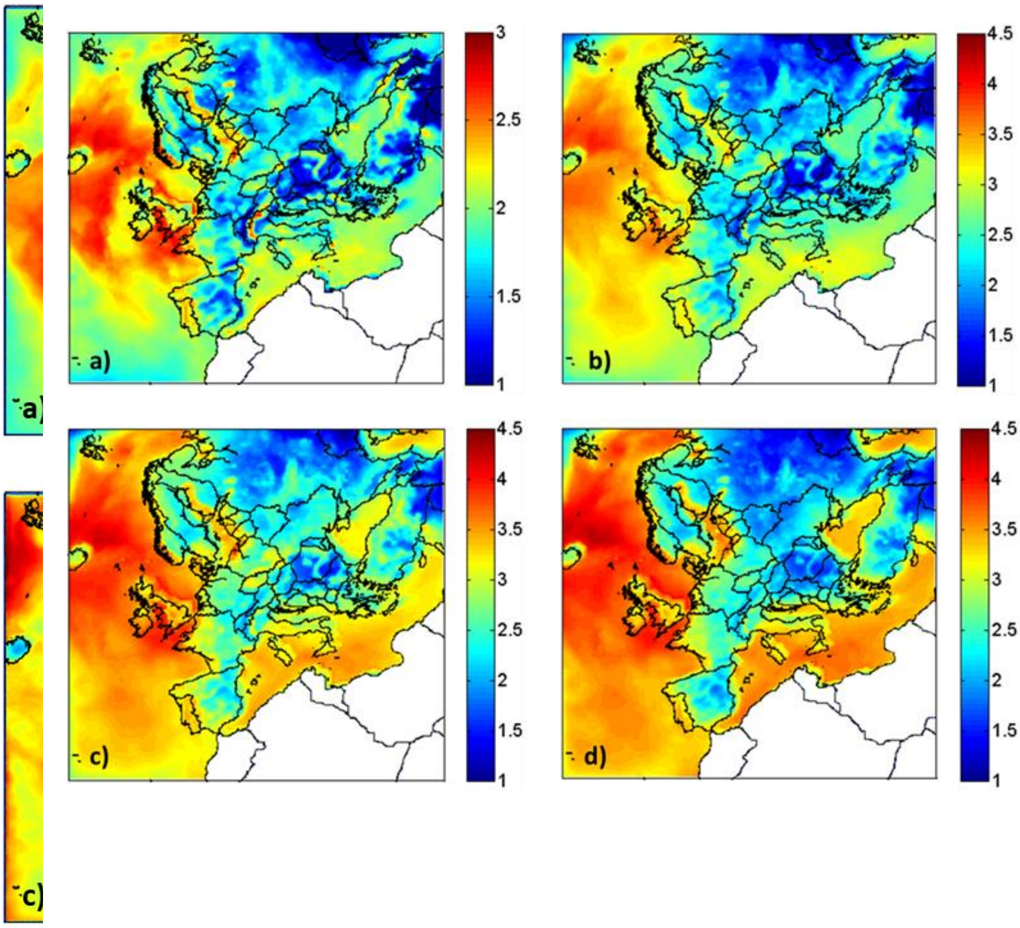

a)
3
2.5
2
1.5
1
b)
4.5
4
3.5
3
2.5
2
1.5
1
c)
4.5
4
3.5
3
2.5
2
1.5
1
d)
4.5
4
3.5
3
2.5
2
1.5
1
a)
c)

Figure 1. Average ground level aerosol pH predictions for **a)** PM_1, **b)** $PM_{1-2.5}$, **c)** $PM_{2.5-5}$ and **d)** PM_{5-10} for the base case simulation over Europe during May 2008.

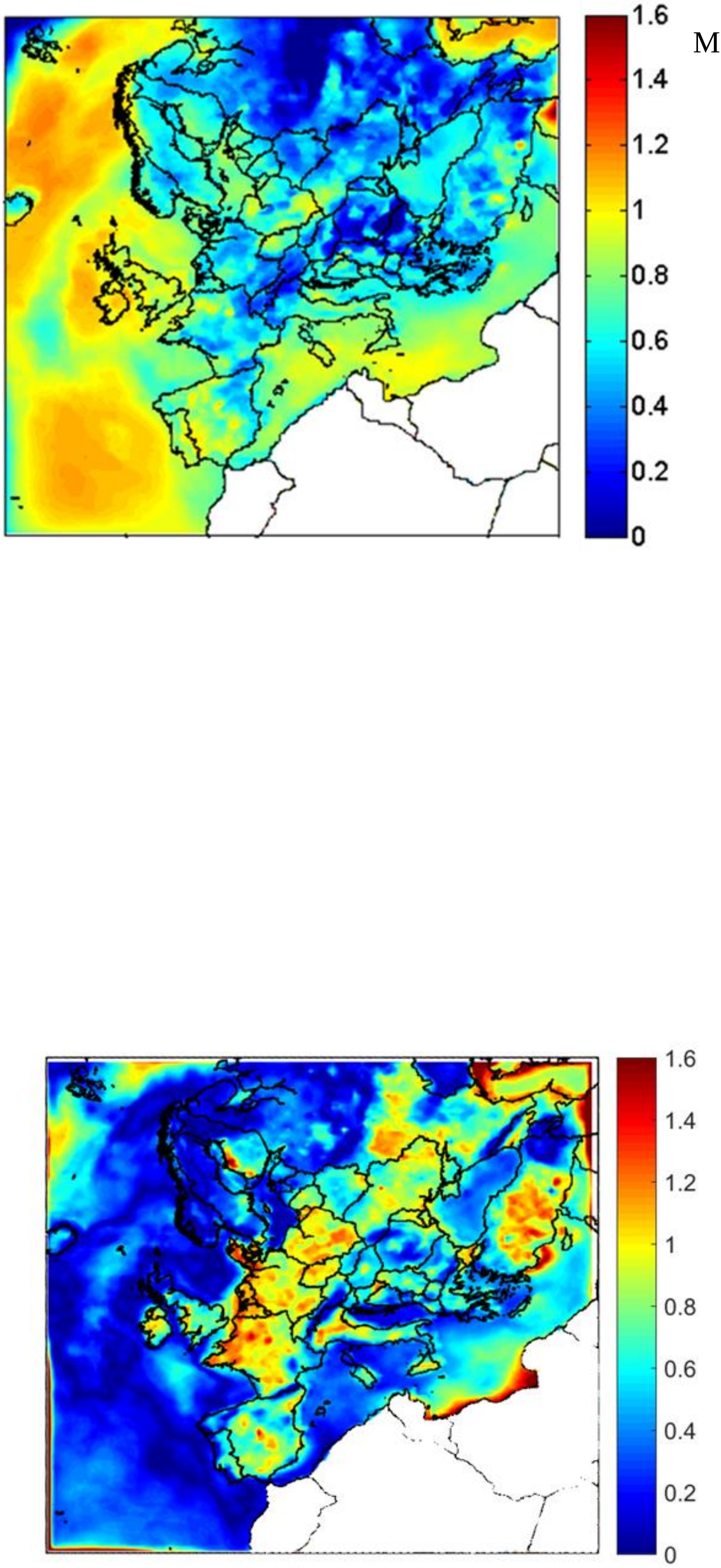
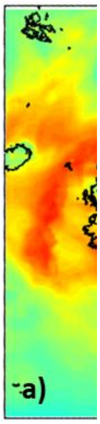
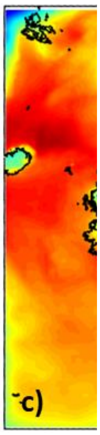


Figure 2. Absolute difference of average ground level pH between $PM_{1-2.5}$ and PM_1 for the base case simulation during May 2008.


a)


c)

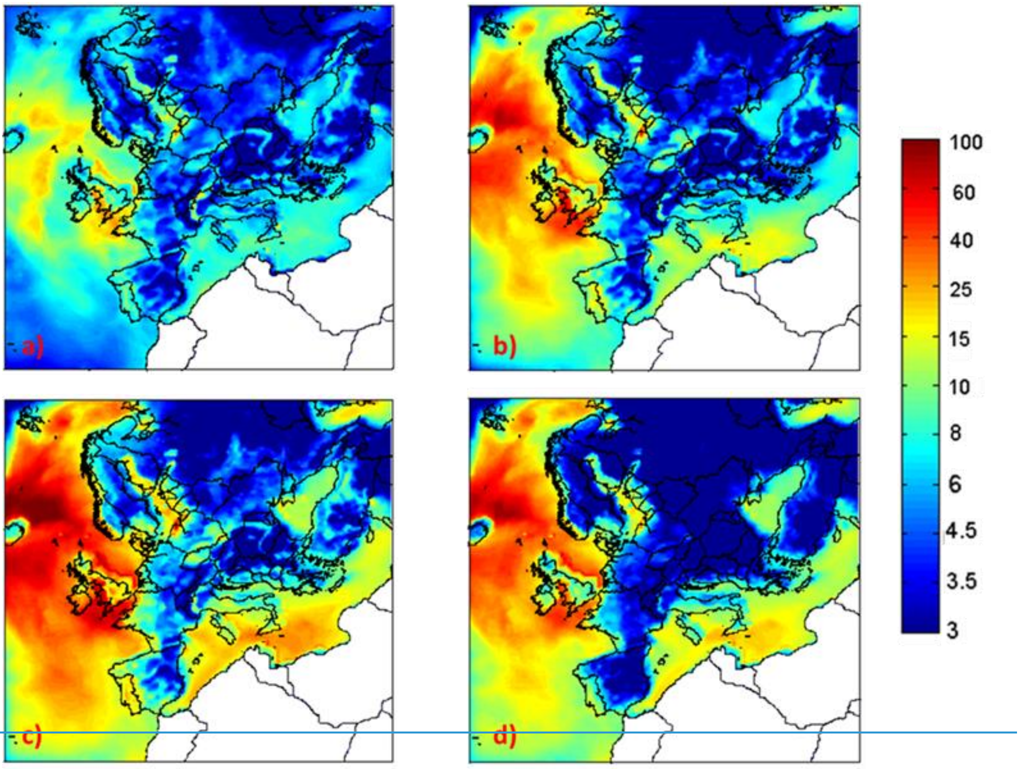

a)
b)
c)
d)
100
60
40
25
15
10
8
6
4.5
3.5
3

Figure 3. Average ground level aerosol water predictions (in μg m^{-3}) for **a)** PM_1, **b)** $PM_{1\text{-}2.5}$, **c)** $PM_{2.5\text{-}5}$ and **d)** $PM_{5\text{-}10}$ for the base case simulation over Europe during May 2008.

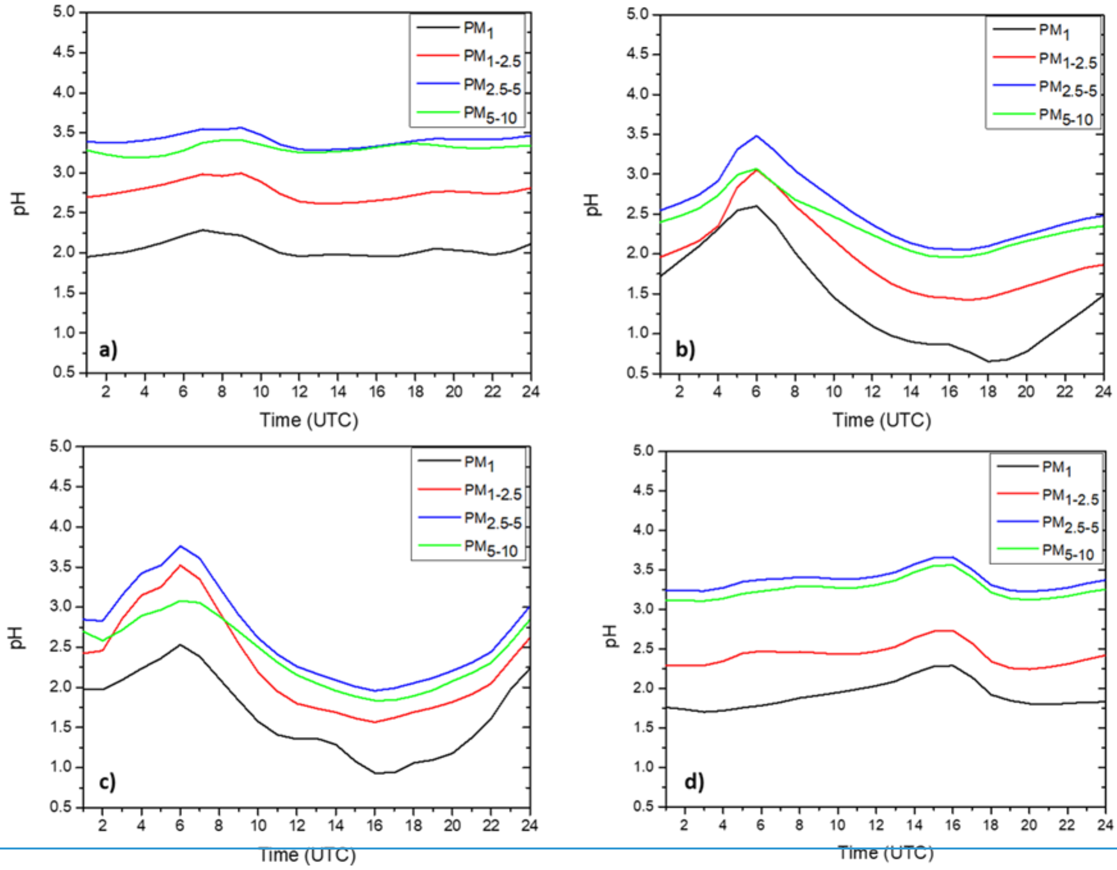
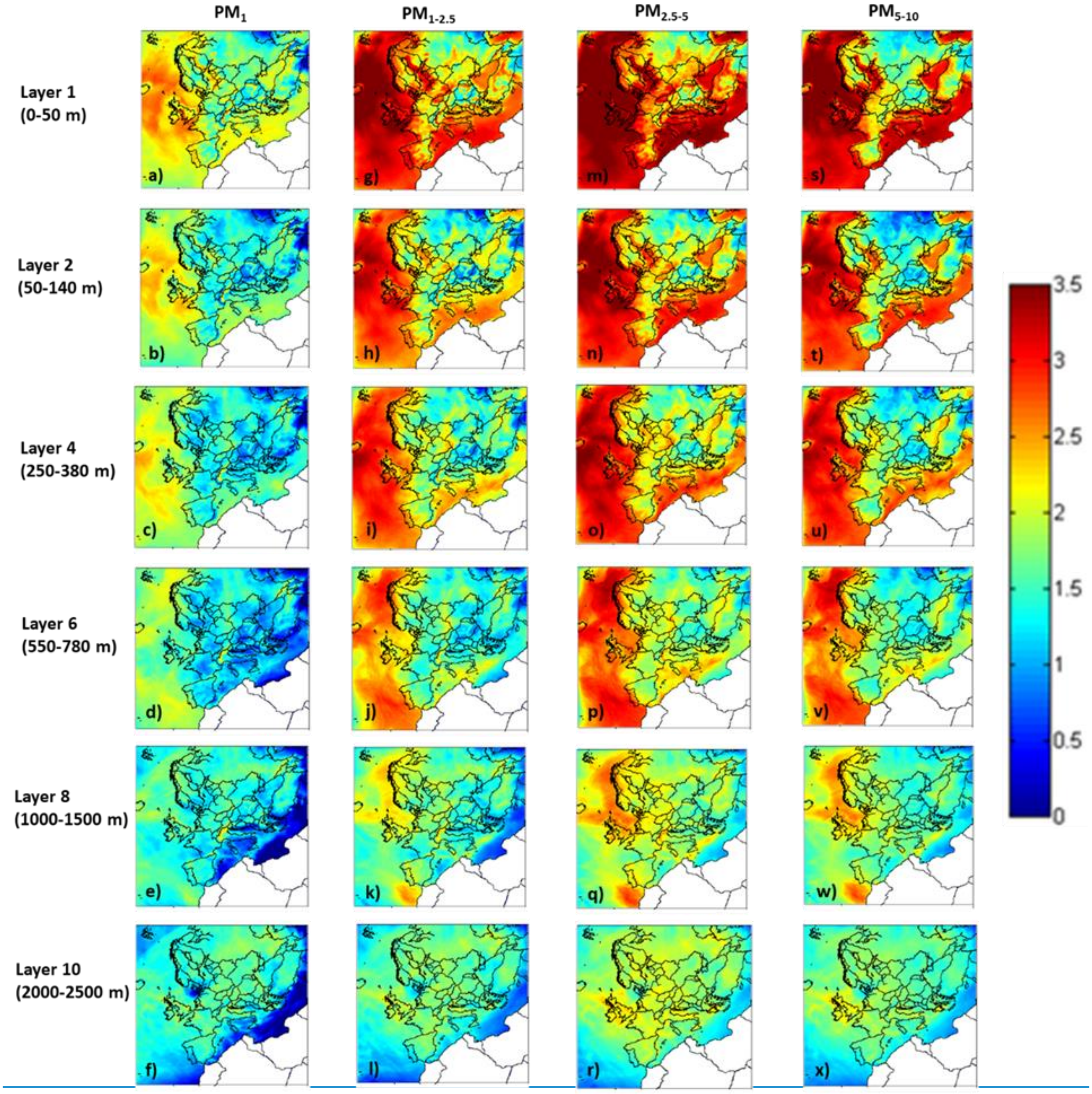

a)
b)
c)
d)
PM1
PM1-2.5
PM2.5-5
PM5-10
pH
Time (UTC)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
2
4
6
8
10
12
14
16
18
20
22
24

Figure 4. Average pH diurnal profiles for **a)** Cabauw, Netherlands, **b)** Melpitz, Germany, **c)** Paris, France and **d)** Finokalia, Greece for the four particle size ranges for the base case simulation during May 2008.


PM$_1$
PM$_{1-2.5}$
PM$_{2.5-5}$
PM$_{5-10}$
Layer 1
(0-50 m)
Layer 2
(50-140 m)
Layer 4
(250-380 m)
Layer 6
(550-780 m)
Layer 8
(1000-1500 m)
Layer 10
(2000-2500 m)
a)
b)
c)
d)
e)
f)
g)
h)
i)
j)
k)
l)
m)
n)
o)
p)
q)
r)
s)
t)
u)
v)
w)
x)
3.5
3
2.5
2
1.5
1
0.5
0

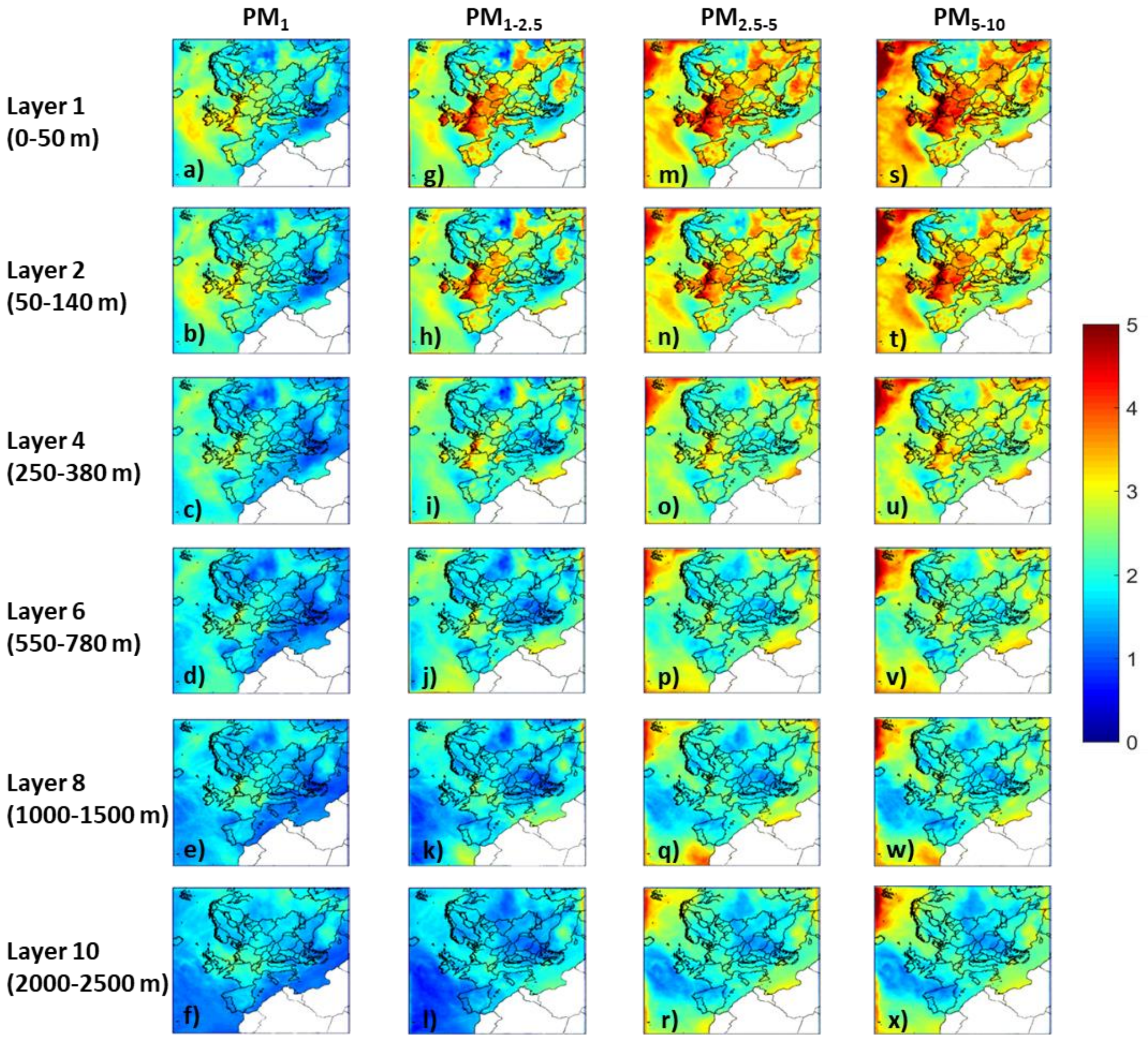
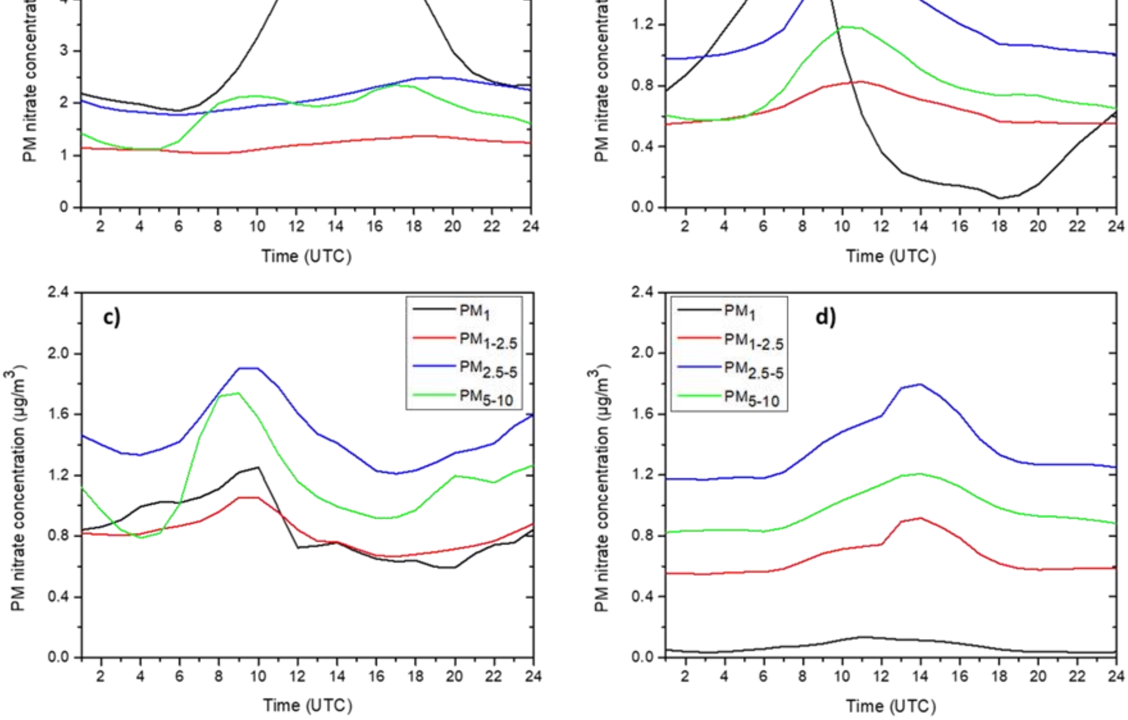
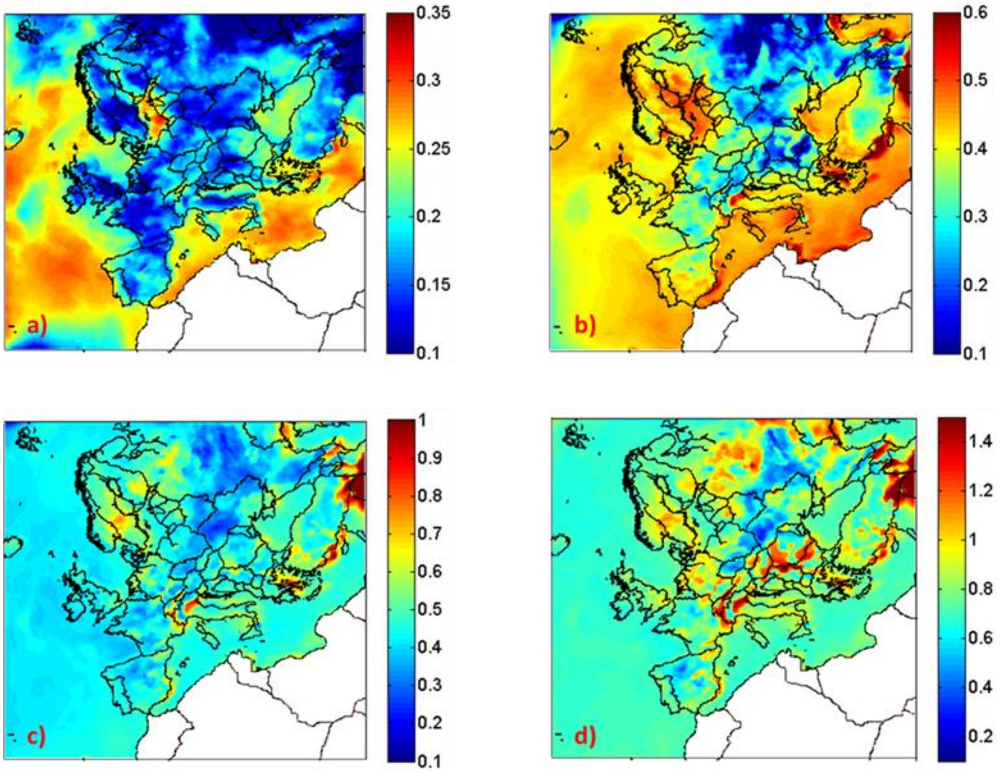


Figure 5. Average predicted aerosol pH as a function of size and altitude: **a), b)**, **c)**, **d)**, **e)**, **f)** for PM$_1$, **g), h)**, **i)**, **j)**, **k)**, **l)** for PM$_{1-2.5}$, **m)**, **n) o)**, **p)**, **q)**, **r)** for PM$_{2.5-5}$, **s)**, **t)**, **u)**, **v)**, **w)**, **x)** for PM$_{5-10}$ at 0-50 m, 50-140 m, 250-380 m, 550-780 m, 1000-1500 m, and 2000-2500 m for the base case simulation during May 2008.


PM nitrate concentration
Time (UTC)
c)
d)
PM nitrate concentration (μg/m3)
PM1
PM1-2.5
PM2.5-5
PM5-10
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2
4
6
8
10
12
14
16
18
20
22
24


a)
b)
c)
d)
0.1
0.15
0.2
0.25
0.3
0.35
0.1
0.2
0.3
0.4
0.5
0.6
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0.2
0.4
0.6
0.8
1
1.2
1.4

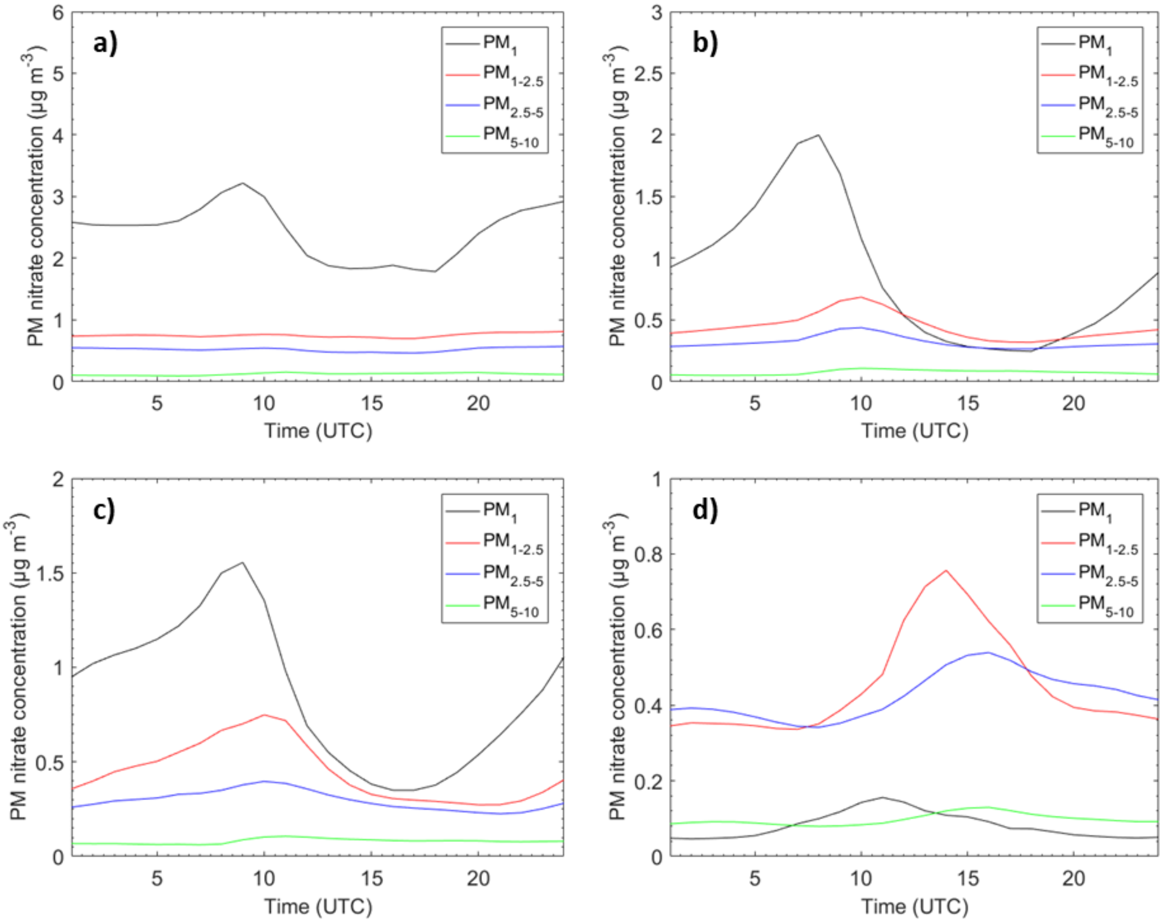


Figure 6. PM_1, $PM_{1\text{-}2.5}$, $PM_{2.5\text{-}5}$ and $PM_{5\text{-}10}$ nitrate diurnal profiles for **a)** Cabauw, Netherlands, **b)** Melpitz, Germany, **c)** Paris, France and **d)** Finokalia, Greece for the base case simulation during May 2008.

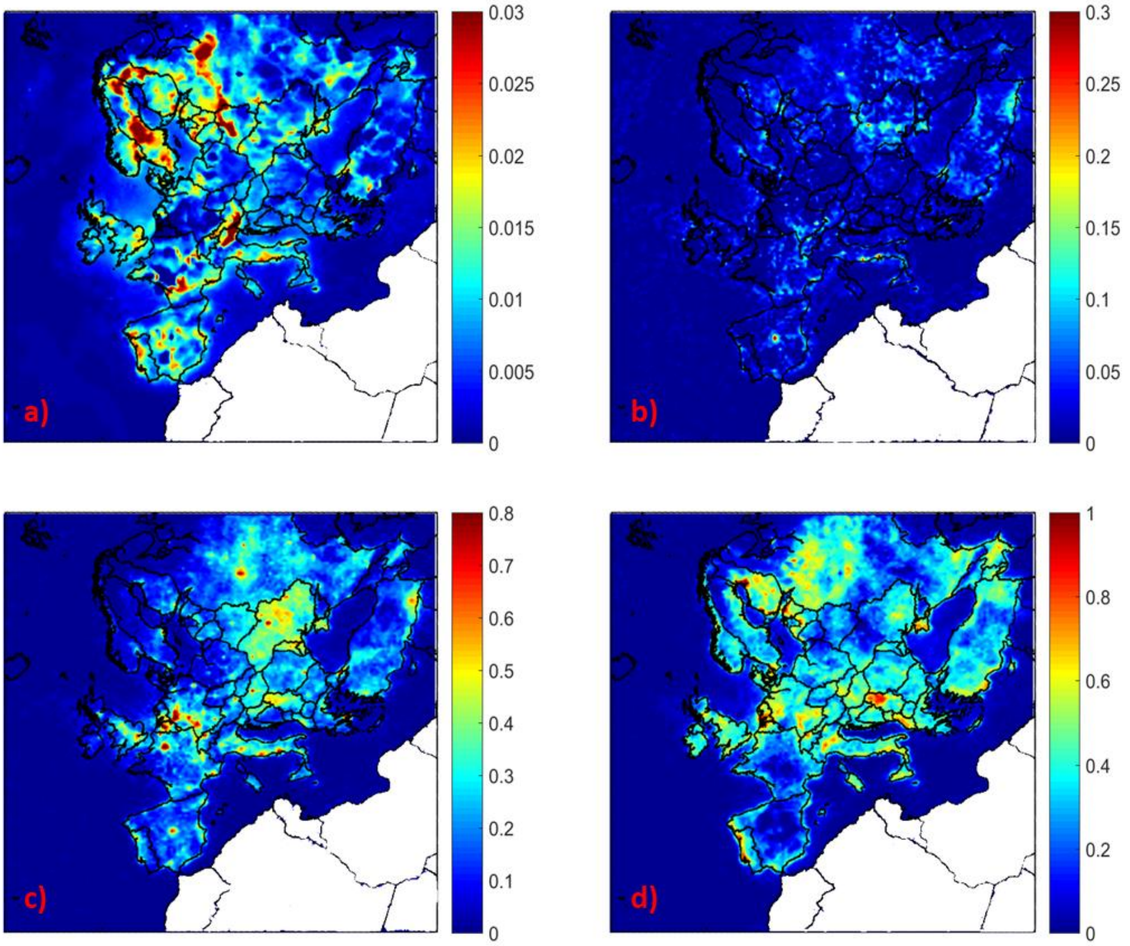

a)
0.03
0.025
0.02
0.015
0.01
0.005
0
b)
0.3
0.25
0.2
0.15
0.1
0.05
0
c)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
d)
1
0.8
0.6
0.4
0.2
0

Figure 7. Increase of average ground level aerosol pH for **a)** PM_1, **b)** $PM_{1-2.5}$, **c)** $PM_{2.5-5}$ and **d)** PM_{5-10} for the base case simulation compared to the inert dust case during May 2008.

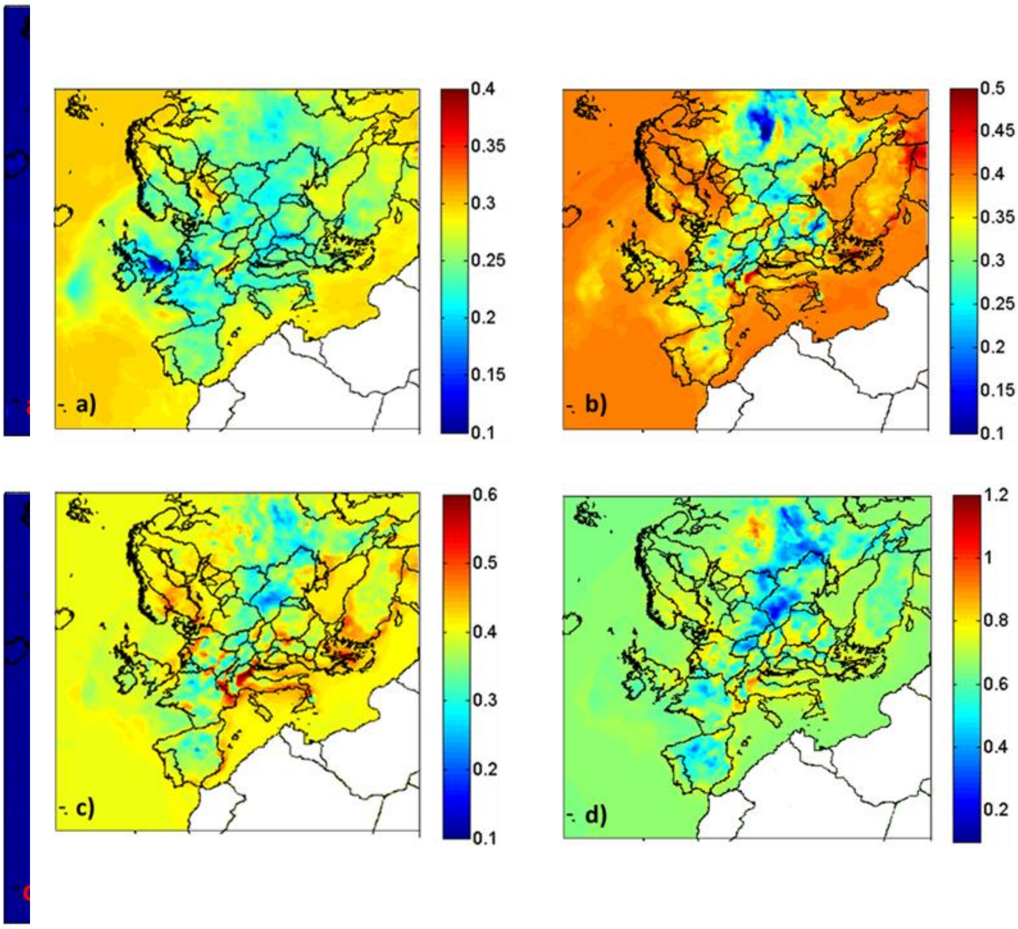

a)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
b)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
c)
0.6
0.5
0.4
0.3
0.2
0.1
d)
1.2
1
0.8
0.6
0.4
0.2

Figure 8. Increase of average ground level aerosol pH for **a)** PM_1, **b)** $PM_{1-2.5}$, **c)** $PM_{2.5-5}$ and **d)** PM_{5-10} for the base case simulation compared to the case when calcium is neglected during May 2008.