Response to Editor:

Dear ACP Editor Dr. Pedro Jimenez-Guerrero,

We would like to thank the two referees for their helpful comments, which have been fully taken into account upon manuscript revision. A point-by-point response to all the comments and a change-tracked revised version are shown below.

Best Regards,
Ying Chen

Response to comments of referee #1: Dr. Daniel Neumann

General comments

The submitted manuscript describes the impact of sea salt aerosol on atmospheric nitrate concentrations. The presence of sea salt aerosol leads to a mass-enhancement of nitrate in the particle phase but also to a re-distribution of nitrate from fine to coarse particles modes. However, the two processes increase and decrease the absolute value of nitrate direct radiative forcing, respectively, and, hence, are in competition to each other. In theory, the considered impact of particulate sea salt on the size distribution of particulate nitrate and the resulting change of the DRF is well understood. Practically, however, we do not have exact numbers on how strong the impact is. The authors evaluate this competition for certain environmental conditions and spatial scales. The manuscript is well written and structured. The scientific aim is clearly formulated. The main manuscript provides the relevant information as brief as possibles, whereas an extended presentation of the model description and results are provided in the supplement. I appreciate the quite detailed supplementary text and the additional figures. I have several comments on the manuscript. However, these are no critical aspects. In summary, I recommend the manuscript for acceptance after minor revision.

Many thanks to Dr. Neumann for the careful reading and the helpful comments and suggestions. We have improved the manuscript accordingly. Please find a point-by-point response below. Please refer the order of figures to the revised version.

Major comments:

1) What are the statistics of the sea-salt-over-continent-transpor events in Europe? Do they take place sufficiently often and/or do they persist over a sufficient long time period in order to have relevant impact on the annual mean $DRF_{nitrate}$?

Marine air masses influence Europe quite frequently. In a previous long-term observation-based study (Birmili et al., 2001), they classified the air masses influencing Central Europe as 'Maritime Character', 'Continental Character' and 'Mixed-Type Character'. They performed a statistical study with observations of more than one year and reported that the frequency of

'Maritime Character' and 'Mixed-Type Character' air masses are 46.6% and 33.3%, respectively (see the Table 1b of Birmili et al. 2001). Therefore, the marine air masses influence Europe with a total frequency of about 90%, and are expected to have impact on the annual mean DRF$_{nitrate}$ by such a high frequency. We have modified the summarization of the frequency in section 3.1 to make it clearer, as shown below.

"Marine air masses frequently (~90%) approach Central Europe (Birmili et al., 2001). The interaction between anthropogenic pollutants and sea-salt aerosol commonly happens in the atmosphere."

Changed to:

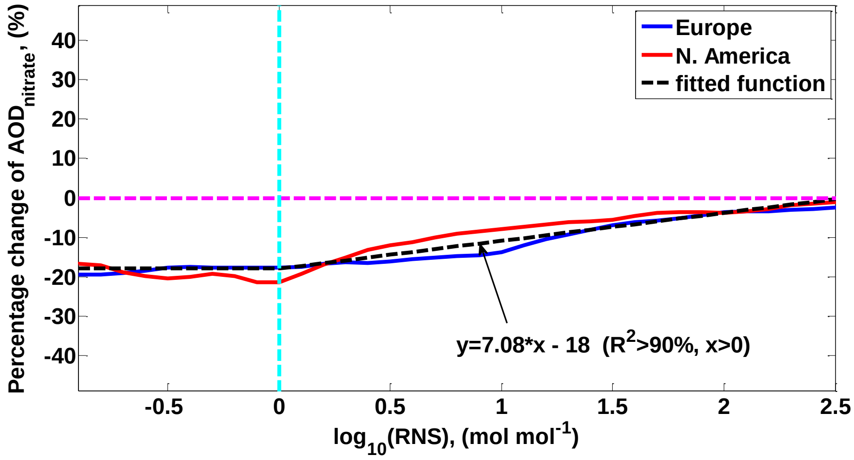
"Marine air masses frequently, up to 90% of days in a year, influence Central Europe (Birmili et al., 2001). The interaction between anthropogenic pollutants and sea-salt aerosol commonly happens in the atmosphere."

2) For the European modeling period a time frame containing a strong sea-salt-transport event was choosen. For the US example, an arbitrary time period was choosen. How far are both modeling cases – Europe and US – comparable?

There are similarities and differences between the European case and the US case.

The difference. For Europe case, a sea-salt event was chosen, we see a strong 're-distribution effect'. This leads to a reduction of 10-20% in AOD$_{nitrate}$ over European polluted regions, such as northern polish region, and a clear reduction of AOD$_{nitrate}$ over most of European continent (see Fig. 5a). For US case, we see outflows bring continental pollutants to marine and a clear 're-distribution effect' leading to reduction of AOD$_{nitrate}$ over oceanic regions, such as the Gulf of Mexico; but, there is much weaker 're-distribution effect' over the N. American continent (see Fig. 8a). This difference between the European and US cases indicates that 're-distribution effect' happens wherever natural sea-salt and anthropogenic nitrate mixed, no matter over continental or oceanic regions. Lots of big cities are along coast globally with high NOx (precursor of nitrate) emissions, offshore and onshore wind patterns can both induce the 're-distribution effect' and reduce AOD$_{nitrate}$.

The similarity. Although we see different spatial patterns of the 're-distribution effect' in the European and US cases, the relationships between AOD$_{nitrate}$ reduction and RNS (molar ratio *between nitrate and sodium) are quite consistent in these two cases. As suggested by the Reviewer#2, we show this relationship as a first-order approximation, given in the newly added Fig. 9b. Later on, we adopt this generalized relationship combined with EMAC global model results to estimate the potential changes of* $AOD_{nitrate}$ *associated with 're-distribution effect' on a global scale.*



Newly added Fig. 9b. *The median possibility of the percentage change of* $AOD_{nitrate}$ *as a function of RNS.*

3) On p.4 l.116 the authors state that they found in previous studies that – using the Gong emission parameterization – modeled sea-salt concentrations overestimated measurements by a factor of 10. However, the sea salt emissions estimated by the Gong parameterization are not necessarily 10x as high as the real world sea salt emissions are. Processes that lead to lower atmospheric sea salt concentrations might be underestimated in the used model – e.g. underestimated deposition. Or, the particle size distribution of the Gong sea salt emissions might not be appropriate for the model setup. Therefore, please add ". . . using WRF-Chem . . . " or something similar to the sentence – e.g. in the end of the sentence.

We have modified the context as suggested.

4) In the first paragraph on page S9 in the supplement, the authors discuss that nitrate concentrations are overestimated by several models in Europe. Vivanco et al. (2017, DOI: https://doi.org/10.1016/j.atmosenv.2016.11.042) evaluated several air quality models and found that most considered models underestimate the nitrogen deposition in Europe (The

EMEP model performed best). WRF-Chem was not partof the latter evaluation. However, too high atmospheric nitrate concentrations may point to issues in the deposition parameterizations. This wouold also explain why the Gong parameterization apparently lead to considerably overestimated atmospheric sea salt concentrations. Could the authors comment on that?

This is a good point, thanks for the suggestion. We have added a comment in the last paragraph of section 3.4, as shown below.

"The uncertainty in deposition parameterizations could be one reason of this overestimation, as suggested by the overestimation of sea-salt particles as well (Chen et al., 2016a) and the underestimation of nitrogen deposition over Europe in many models (Vivanco et al., 2017)."

5) Evaluating the mass concentration of sea salt aerosol is reasonable to evaluate the coarse sea salt emissions. The contribution of fine sea salt to the total sea salt mass concentration is very low. Hence, the strong overestimation of sea salt mass concentrations documented in previos studies does not necessarily indicate that the fine particulate sea salt was overestimated as well. The black bars in Fig. S3 rather indicates that fine sea salt might be underestimated in some episodes. Please briefly describe this uncertainty in the Materials & Methods or in the Discussion section.

Good point. We have added discussion of this uncertainty in the Materials & Methods, section 2.2, as shown below.

"The sea-salt emissions computed with the modified Gong scheme (Gong, 2003) were reduced to 10% in the 'Case_SeasaltOn', because a previous study (Chen et al., 2016) has shown that the original Gong scheme overestimates the sea-salt mass concentrations by a factor of ~10 over the coastal regions of Europe using WRF-Chem model. We note that although the mass of coarse sea-salt particles is certainly overestimated, it might not necessarily indicate overestimation in fine sea-salt particles related to their minor contribution to the total mass."

6) p.6 l.165-168 "In addition, a one-year simulation with global model (EMAC) was carried out for analysis of the potential impact of 're-distribution effect' on a global scale, although the fully dynamic mass transfer between particle sizes is not considered in EMAC (four size modes

rather than eight size bins as applied in the WRF-Chem model).” Why is EMAC neverthelss applicable for the used purpose?

Here, we did not directly use EMAC model to estimate the impact of ‘re-distribution effect’. We generalized a relationship between the impact of ‘re-distribution effect’ and RNS (molar ratio between nitrate and sodium) from the European and US cases, and then used this relationship combined with the RNS values from EMAC model to investigate the potential impact of ’re-distribution effect’ on a global scale. Please also see the ‘The similarity’ part of the response in point-2. We have modified the context to make it clearer, as shown below.

“In addition, a one-year simulation with global model (EMAC) was carried out for analysis of the potential impact of ‘re-distribution effect’ on a global scale. Although the fully dynamic mass transfer between particle sizes is not considered in EMAC (four size modes rather than eight size bins as applied in the WRF-Chem model), we adopt a parameterization derived from WRF-Chem simulations to estimate the potential impact (details given in section 3.5).”

7) “Sea-salt is emitted into the marine planetary boundary layer (PBL) as coarse particles [. . .]” (p.7 l.183). Aren’t it coarse and fine particles? Depending on the considered moment of the particle size distribution the fine or the coarse mode dominates: the number distribution is dominated by the fine mode; the volume/mass distribution is dominated by the coarse mode. Please clarify this in the text.

Yes, the reviewer is right that it has to be precise. We have clarified this, as shown below.

“Sea-salt is emitted into the marine planetary boundary layer (PBL) with mass concentration dominated by coarse particles…”

8) The authors mention the importance of vertical transport of sea salt aerosol into the continental free troposphere followed by the horizontal transport of it over land and refer to their previous studies (p.7 l.186-190). This transport mechanism seems to be very important. However, vertical transport/convection is not necessarily well represented by all meteorological models – depending on grid resolution and parameterization. This study’s

WRF-Chem model simulations probably reproduce this vertical transport of sea salt? Do the other used models reproduce it as well?

The vertical transport of sea-salt particles to free troposphere can increase their lifetime and facilitate their inland transport, therefore, it could be important for the 're-distribution effect' over the deeper inland regions. This vertical transport and the associated land inward transport are reproduced well in our high-resolution simulation using WRF-Chem, as shown in our previous study (Chen et al., 2016). However, as the reviewer concerned, this vertical transport may not be well reproduced in other models with lower resolutions. But, this does not necessarily mean that sea-salt cannot transport further inland in other models. The long-range transport of sea-salt to inland regions also depends on the deposition scheme (which might be underestimated as pointed out by the reviewer in the point-4), the vertical mixing rate, the parameterizations for marine boundary layer and continental boundary layer and etc. These can be different model-by-model and case-by-case, and the discussion of these differences go beyond the scope of this study.

But, I think the vertical transport might not be such important for the coastal regions, where lots of big cities with high NOx emissions are located, especially for China and N. America with many large and the most developed cities along the coast. This is because no matter offshore or onshore wind patterns both mix sea-salt with anthropogenic nitrate and induce the 're-distribution effect', as discussed in the point-2.

9) In chapter 3.3 (p.10 l.281-290), the authors mention the aim to 'generalize' the results. To 'generalize' something has a quite broad meaning and can be interpreted differently. The benefit of calculating the RNS and of including Fig. 5 did not become clear for me in chapter 3.3 – but, later in chapter 3.4 it became obvious. Please clarify the motivation in chapter 3.3.

We have modified the corresponding sentence and clarify the motivation in section 3.3, as shown below.

"To compare the relative importance of the sea-salt-induced 're-distribution effect' and 'mass-enhancement effect' on anthropogenic nitrate cooling…"

10) Classification of RNS: Currently, we have the situations “RNS < 1”, “1 < RNS < 30” and “30 < RNS”. I know that these are rough classifications. Nevertheless, please also cover “RNS == 1” and “RNS == 30” to be mathematically correct.

Thanks for the carefulness. We have corrected it as suggested.

Comments on figures:

1) Figure 1: I like the intention of Fig. 1. All relevant aspects are shown. However, on the first view, the reader might not recognize the particle size distribution plot as such. At least I did not recognize it first. I am not sure how to improve the Figure. Possibly, a y-axis on the left of the plot might help. Their are no issues when the figure is printed in grey-scales (see my comments to the other figures below).

We have added a y-axis in Fig. 1. It does make the particle size distribution plot clearer. Thanks.

2) Figure 2, 6, 8 and 9: Please consider using a color scale, which is recognizable in black-and-white and readable by color blind people (not “jet” or “rainbow”). Examples for such a color scale are “viridis” and “magma”.

We have changed the color scales of Fig. 3, Fig. 7, Fig. 9 and Fig. 10 (Fig. 2, Fig. 6, Fig. 8 and Fig. 9 in the original version) to make them recognizable in grey-scales.

3) Figure 4 and 7: Printed in grey scales it is hard to distinguish whether values are negative or positive. However, alternative color scales would make the full-color plots difficult to interprete. Therefore, it might be reasonable to keep the blue-white-red colorscale.

We did not find a proper color-scales fit in the grey-scales perfectly, and also clearly show the trends. Agree with the reviewer, it is better to keep it as it is.

4) Figures 3: Please add information to the plot that nitrate is plotted. It is written in the caption but it would be nice to also have this information in the plots. The colors in this figure are fine.

Done. 'Nitrate' has been added in the y-axis.

5) Figures 5: The colors in this figure are fine. Figure S6: Maybe exchange panels (a) and (b). For me it would have made the figure easier to understand. I would consider adding Figure S6 to the main manuscript.

Thanks. As suggested, we have moved the Fig. S6a (original) to Fig. 7c (revised), and Fig. S6b (original) to Fig. 7b (revised).

<u>Minor Comments:</u>

p.4 l.117: consider to replace "for both with and without sea-salt presence respectively" by "for both sea salt emission cases"

p.5 l.123: remove "and" in ". . . assumption and taking . . . "

p.5 l.136: "and part of North Africa" → "and the northern part of North Africa"

p.5 l.142 "1/8_ × 1/16_" → space between "×" and "1/16"

p.5 l.147 "In the 'Case SeasaltOn' (with sea-salt emission) of European simulation" → "In the European 'Case SeasaltOn' simulation (with sea-salt emission)", suggestion

p.5 l.148 "over coastal region" → "over coastal regions", added plural-s

p.6 l.149/150 "with a factor (and correlation coefficient) of 0.85 (0.67), 1.16 (0.80) and 0.83 (0.87) respectively for Bilthoven, Kollumerwaard and Vredepeel (Fig. S2)" → "with a factor (and correlation coefficient) of 0.85 (0.67), 1.16 (0.80) and 0.83 (0.87) for Bilthoven, Kollumerwaard and Vredepeel, respectively (Fig. S2)", moved 'respectively' p.6 l.154 “over coastal, German low lands (Melpitz) and northern Poland regions” → “over coastal, German low land (Melpitz) and northern Polish regions”, remove ’s’ from lands because we have “coastal regions”, “German low land regions” and northern Polish regions”

p.6 l.162 “concentration of nitrate was” → “concentrations of nitrate were”

p.6 l.164 “covers US, the Gulf of Mexico and part of Pacific and Atlantic oceans” → “covers the US, the Gulf of Mexico and parts of Pacific and Atlantic oceans”, ’the’ in front of ’US’ and ’s’ added to ’part’

p.6 l.171 “1.1 by 1.1 degrees” → “1.1^{o} × 1.1^{o}”, formatting consistent with p.5 l.142

p.6 l.161 “boarder” → “broader”

p.6 l.177 “approach Central Europe, and the interaction” → “approach Central Europe.

The interaction”

p.7 l.179 “a typical sea-salt transport event”; maybe ’sea salt transport event’ in italics

p.7 l.182 “originated” → “originating”

p.7 l.187 “long-range transport, see the figure 11 of Chen et al. (2016a)” → “long-range transport (see Fig. 11 of Chen et al. (2016a))”

p.8 l.212: “the northern Poland region” → “a region in northern Poland”

p.8 l.220: “,thus ” → “, thus, ”

p.8 l.227: “Over the northern Poland region” → “Over the region in northern Poland”

p.8 l.231-234: “being slightly . . . in the offline calculation” – Please consider writing this sentence outside of the brackets. It improves the readability.

p.9 l.241-242: “with increasing AOD with [NO3-]” → “of increasing AOD with increasing [NO3-]”; I am not sure about it but for me it sounds better.

p.9 l.242: “would result by neglecting the ’re-distribution effect”’ → “would result when the ’re-distribution effect’ was neglected” p.9 l.242-244: “For example, instead of a decrease by 29

p.9 l.245: remove “also”

p.9 l.245: “. . . increases and there is . . . ” → “. . . increases. There is . . . ”

p.9 l.248: “and thus shorter” → “and, thus, shorter”

p.9 l.251: “and hence further moderate” → “further moderating”

p.9 l.254: “, therefore fasten” → “fastening”

p.9 l.255: “oxygenated nitrogen” → maybe “oxidized nitrogen”?

p.9 l.257: “which result” → “which resulted”

p.9 l.258-263: This has been mentioned previously. Although, this is important motivation for performing another simulation without deposition, I would like to suggest shortening these sentences considerably.

p.10 l.265-266: “as the simulations with aerosol dry deposition” → “as in the simulations with aerosol dry deposition turned on”; corresponds better with l.263-264 stating “. . . with aerosol dry deposition turned off”

p.10 l.289: “due to” → “because”; ’due to’ does not allow a verb (’are’)

p.11 l.319-320: “Myhre et al. (2006), where a similar . . . aerosol was evaluated but the simplification . . . ” → “Myhre et al. (2006). They evaluated a similar . . . aerosol. But, their simplification . . . ”; split into two or three individual sentences;

p.12 l.332: “and thus reduces” → “and, thus, reduces”

p.12 l.337: “presented” → “present”

p.12 l.342-343: “that sea-salt transport (May et al., 2018) and impact AODnitrate further inland over North America.” → “that sea-salt is transported further inland over North America und impacts AODnitrate there (May et al., 2018).”

p.13 l.352-356: Please refer to Fig. 9 (maybe I overlooked the reference).

p.13 l.360: “and hence lower” → “and, hence, lower”; I would consider splitting the sentence into two sentences at this ’and’.

p.13 l.369: “if only consider” → “if we only consider” or passive form

p.13 l.374: “. . . when RNS is lower than 1” → Formulation is ambiguous in this context: the dominance could take place when RNS < 1 OR the mass-enhancement effect could be associated with RNS < 1. It know (and probably most readers) know that the latter is meant. However, I would suggest to reformulate this part. The same for the next sentence (“. . . when 1 < RNS < 30“).

Many thanks for the careful reading, helping correct the typos and improving the language. We have improved the manuscript as suggested. Please find details in the change-tracked revised manuscript.

References:

Birmili, W., Wiedensohler, A., Heintzenberg, J., and Lehmann, K.: Atmospheric particle number size distribution in central Europe: Statistical relations to air masses and meteorology, Journal of Geophysical Research, 106, 32005-32018, DOI: 10.1029/2000JD000220, 2001.

Chen, Y., Cheng, Y., Ma, N., Wolke, R., Nordmann, S., Schüttauf, S., Ran, L., Wehner, B., Birmili, W., van der Gon, H. A. C. D., Mu, Q., Barthel, S., Spindler, G., Stieger, B., Müller, K., Zheng, G. J., Pöschl, U., Su, H., and Wiedensohler, A.: Sea salt emission, transport and influence on size-segregated nitrate simulation: a case study in northwestern Europe by WRF-Chem, Atmos. Chem. Phys., 16, 12081-12097, 10.5194/acp-16-12081-2016, 2016.

Gong, S. L.: A parameterization of sea-salt aerosol source function for sub- and super-micron particles, Global Biogeochemical Cycles, 17, 10.1029/2003GB002079, 2003.

Vivanco, M. G., Bessagnet, B., Cuvelier, C., Theobald, M. R., Tsyro, S., Pirovano, G., Aulinger, A., Bieser, J., Calori, G., Ciarelli, G., Manders, A., Mircea, M., Aksoyoglu, S., Briganti, G., Cappelletti, A., Colette, A., Couvidat, F., D'Isidoro, M., Kranenburg, R., Meleux, F., Menut, L., Pay, M. T., Rouïl, L., Silibello, C., Thunis, P., and Ung, A.: Joint analysis of deposition fluxes and atmospheric concentrations of inorganic nitrogen and sulphur compounds predicted by six chemistry transport models in the frame of the EURODELTAIII project, Atmospheric Environment, 151, 152-175, https://doi.org/10.1016/j.atmosenv.2016.11.042, 2017.

Response to comments of referee#2

General comments:

This is a well-written paper that highlights an interesting topic that I had not previously thought about, but makes a lot of sense conceptually and could have important implications for anthropogenic aerosol radiative forcing on a global scale. I have one comment which questions some of the methods used in the experiment, which I am not expecting the authors to address in this paper but could be the subject of further discussion or future work. Beyond that, I just have a few minor comments I think the authors should

Many thanks to the reviewer for the insightful comments and suggestions. We have improved the manuscript accordingly. Please find a point-by-point response below. Please refer the order of figures to the revised version.

Main comments:

My main comment is that the main purpose of this paper is to investigate the sensitivity of the nitrate aerosol radiative forcing to the process that redistributes it from fine modes when associated with ammonium to course modes when associated with sodium. The authors have tested this by turning off sea salt emissions in the sensitivity simulation and seeing how this changes nitrate aerosol size distribution, which is perfectly valid but does limit what they can investigate in some ways because removing sea salt emissions will have many other changes to total aerosol AOD, CCN and aerosol-radiation/aerosol-cloud interactions that go beyond the redistribution effect they are investigating. I would have thought a better experiment would have been to turn off the association between NO3 and Na in MOSAIC in the sensitivity simulation, and have sea-salt emissions in both, thereby having a “clean” experiment where the only change is to the exact process you are investigating. A key benefit of this approach is that you would then be able to test the impact of this process on both total aerosol AOD/DRF (not just the NO component), and how it effects the aerosol-cloud interactions (ACI).

On both a local and global scale, my gut says that the influence of the redistribution effect on (ACI), particularly the Twomey or first- indirect effect, would be greater that the DRF. I would expect shifting nitrate from subnitrate modes to coarse modes would slightly increase the number of low-supersaturation CCN, whilst massively decreasing the number of high-supersaturation CCN. This could in turn have a large impact on the activated cloud droplet number, cloud optical depth and therefore climate. Unfortunately, the current methodology cannot address this as any impact from the redistribution effect would be likely overwhelmed by the lack of sea salt aerosol in the sensitivity simulation. This is a shame, as without investigating the aerosol-cloud interactions we are only seeing part of the impact of this process on the climate.

As I said above, I'm not expecting the authors to do reruns with this change as it is a substantial amount of work and, to my knowledge, their current paper is already the first I know of to look into this problem in detail and already contributes significantly to the field. But I would be interested in hearing their response and any follow up studies that look into this further – this discussion could be included in the revised paper.

Thanks for the positive comments on the scientific meaning of this study and insightful suggestions. We agree with the reviewer that turning off the association between NO3 and Na in MOSAIC can be an optional to produce 'clean' sensitivity experiments for investigating the influence of re-distribution on radiative forcing (RF). I think the method we used in this study also generates the 'clean' experiments for the influence of re-distribution on direct $RF_{nitrate}$*, although the review's suggestion can be a better way for investigating ACI and indirect* $RF_{nitrate}$*.*

What we did in this study is not simply turn off the sea-salt emissions and compare the AOD between simulations with and without sea-salt. As correctly pointed out by the reviewer, this would include lots of noise from the changes of sea-salt. Alternatively, we performed four sensitivity simulations (cases 01-04) to derive the 'clean' influence of nitrate re-distribution on $AOD_{nitrate}$*, which was provided in the Method (line: 127-130 in the change-tracked version). Nitrate AOD and DRF (direct RF) with 're-distribution effect' is calculated as: differences between with (case 01) and without (case 02) the anthropogenic emitted gas phase precursor NOx in the simulations with sea-salt emissions turned on. Nitrate AOD and DRF without 're-distribution effect' is calculated as: differences between with (case 03) and without (case 04) the anthropogenic emitted gas phase precursor NOx in the simulations with sea-salt emissions turned off. This calculation method is in line with IPCC and previous studies (IPCC, 2013;Xu and Penner, 2012). For the impacts of the 're-distribution effect', we calculate the differences between nitrate AOD/DRF with 're-distribution effect' (case01-case02) and nitrate AOD/DRF* *without 're-distribution effect' (case03-case04). In this approach, the influences of changes in sea-salt on AOD and DRF were ruled out.*

But, we agree with the reviewer that our method can not rule out the noise of sea-salt influence on ACI and IRF (indirect RF). Therefore, in this study, we only analyzed the results which are marked as cloud-free (i.e. cloud optical depth equals to zero, see Method section in line 130-131 of the change-tracked version) in cases 01-04. In this study, we only focus on the influence of 're-distribution effect' on the direct radiative forcing of nitrate. However, we agree with the reviewer that the influences on ACI and IRF is another important impact of the 're-distribution effect' and might be even larger. This question needs to be investigated in further studies, possibly with the method suggested by the reviewer. We have added the discussion about this point at the end of the section 4, as shown below.

"This study demonstrates the suppression of AOD and DRF of particulate nitrate by the 're-distribution effect'. In addition, the 're-distribution effect' may also reduce the number of cloud condensation nuclei (CCN) by lowering the nitrate concentration in fine particles which are the main contributors to CCN number. The hygroscopicity of coarse sea-salt particles could also be reduced by associating with nitrate, which might suppress cloud droplet activation (Xu and Penner, 2012). Further studies are needed to investigate the influences of 're-distribution effect' on aerosol-cloud interaction and indirect radiative forcing."

Minor comments

1) Ln 40-41: Under what kinds of emission scenarios are we expecting the aerosol radiative cooling to increase by this much?

According to the provided references, there are a series of different emission scenarios used in the projection, such as IPCC SRES (Special Report on Emission Scenarios) A2 emission Scenario in Adams et al. (2001), RCP8.5 (Representative Concentration Pathways) in Bellouin et al. (2011) and RCP CMIP5 (Climate Model Intercomparison Project) emission scenarios in Hauglustaine et al. (2014).

2) Ln 76: Please explain acronym for HOPE-Melpitz campaign

We have modified the sentence as shown below.

"The HOPE campaign (HD(CP)2 Observational Prototype Experiment, (Macke et al., 2017) at Melpitz, Germany"

3) Ln 82: "which represent continental period and marine period" Is this based from back trajectories? Please explain better.

Yes, it is based from back-trajectories. We have added this information in the context and the back-trajectories in the supplementary information Fig. S1. As shown below.

"which represent the continental period and marine period, respectively (see back-trajectories in Fig. S1)."

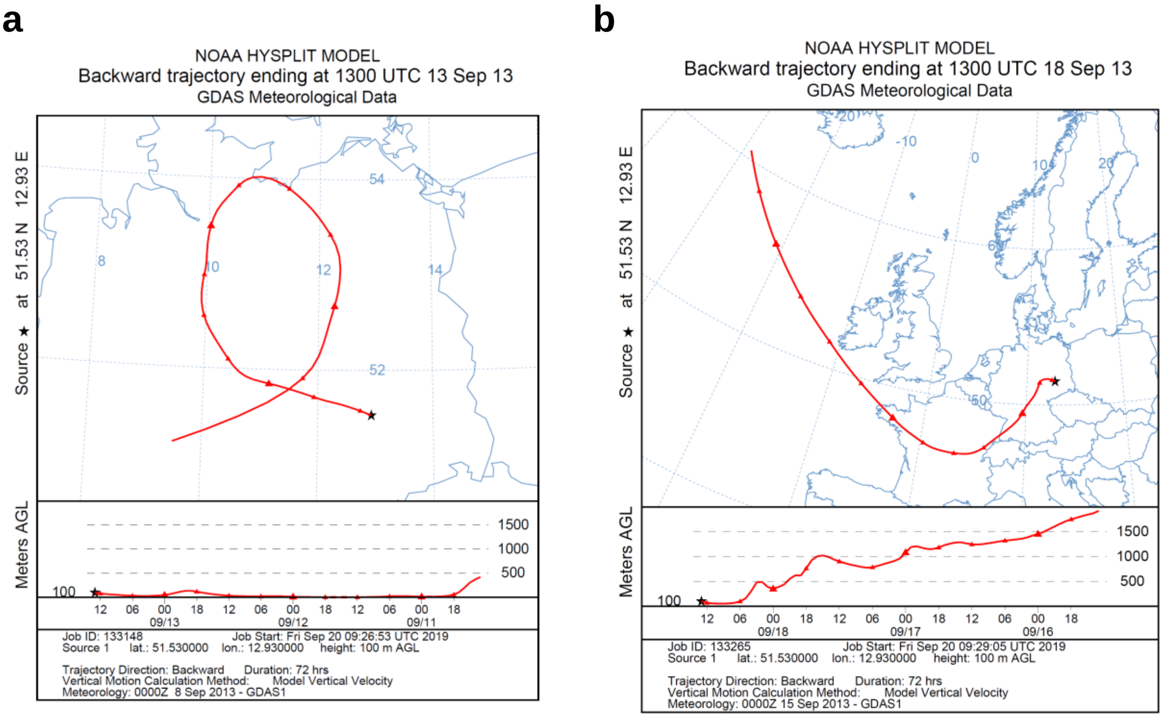


Fig. S1. Three days back-trajectories for Melpitz, Germany. (a) *13 September 2013, representing continental period;* ***(b)*** *18 September 2013, representing marine period. The back-trajectories are calculated by Hysplit (https://www.ready.noaa.gov/HYSPLIT.php).*

4) Section 2.2 Model Description: this section is missing some important information. Firstly, I couldn't find anywhere a description of how the MOSAIC mechanism describes the chemical uptake of HNO3 onto aerosol via NH4+ or Na+ channels. A short (onetwo sentences) here describing that process and how it is parameterised in MOSAIC would be welcome.

We have added a brief summary in section 2.2 to introduce that how the MOSAIC describes the chemical uptake of HNO_3 *onto aerosol via* NH_4^+ *and* Na^+ *channels. As shown below.*

"In MOSAIC, NaCl reacts irreversibly with nitric acid with its equilibrium surface vapor pressure of zero; and a gas-particle partitioning approach ASTEM (Adaptive Step Time-Split Euler Method) is coupled with a thermodynamic module (MESA-MTEM, Multicomponent Equilibrium Solver for Aerosols – Multicomponent Taylor Expansion Method) to dynamically calculate the equilibrium vapor pressure and condensation rate of semi-volatile ammonium nitrate, details are given in the section 4 of (Zaveri et al., 2008)."

5) Please can you add what meteorology data you are using to drive the model and if you are nudging, or if it freerunning (with or without feedbacks). Some of this information is in the supplement.

We have added this information in the supplement Section S2, as shown below.

"The WRF-Chem model was driven by NCEP reanalysis data (1° × 1° resolution and provided every 6 hours), including the Final Analysis Operational Global Analysis (http://rda.ucar.edu/datasets/ds083.2/) and the sea surface temperature datasets (http://polar.ncep.noaa.gov/sst/). The first two days were spin-up runs for simulations in this study. The nudging is carried out in every 6 hours for meteorological conditions, including wind, temperature and moisture."

6) Finally, are you running with N2O5 heterogeneous chemistry? This is relevant for a point later on in the paper, plus in WRF-Chem the Bertram and Thornton (2009) parameterization does have a channel for uptake via Cl-, so provides another mechanism for nitrate to be taken up to course modes that is modulated by the presence of sea salt (Archer-Nicholls et al., 2014).

Bertram, T. H., & Thornton, J. A.,Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride. Atmospheric Chemistry and Physics, 9(4), 15181–15214. https://doi.org/doi:10.5194/acp-9-8351-2009, 2009.

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., et al., Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem. Geoscientific Model Development, 7, 2557– 2579. https://doi.org/10.5194/gmd-7-2557-2014, 2014

In this work, we did not consider N_2O_5 *hydrolysis with NaCl, we focus on the uptake of* HNO_3 *because this process makes fine mode nitrate particles shift to the coarse mode, i.e., the 're-distribution effect'. The* N_2O_5 *reaction is important during night. Due to the topic of radiative forcing in this study, we are mainly focusing on the daytime period. But, we agree with the reviewer that* N_2O_5 *hydrolysis with NaCl is an important pathway of particulate nitrate in coarse mode, the considering of this process may make the 're-distribution effect' stronger. We have added this comment in section 2.2, as shown below.*

"We note that heterogeneous hydrolysis of N_2O_5 *with NaCl is an important chemical pathway of particulate nitrate in coarse mode during nighttime (Bertram and Thornton, 2009; Archer-Nicholls et al., 2014). This process may enhance the 're-distribution effect', however it is not considered in this study."*

7) Ln 110: Is the version of MOSAIC being used with or without aqueous chemistry?

The version of MOSAIC is being used with some aqueous chemistry, as described in Zaveri et al. (2008). However, N_2O_5 *hydrolysis and the oxidation of* SO_2 *in aqueous aerosols are not included.*

8) Ln 137: Please include figure of outer and inner domains, here or in supplement.

We have added a map of the outer and inner domains in the supplement Fig. S2.

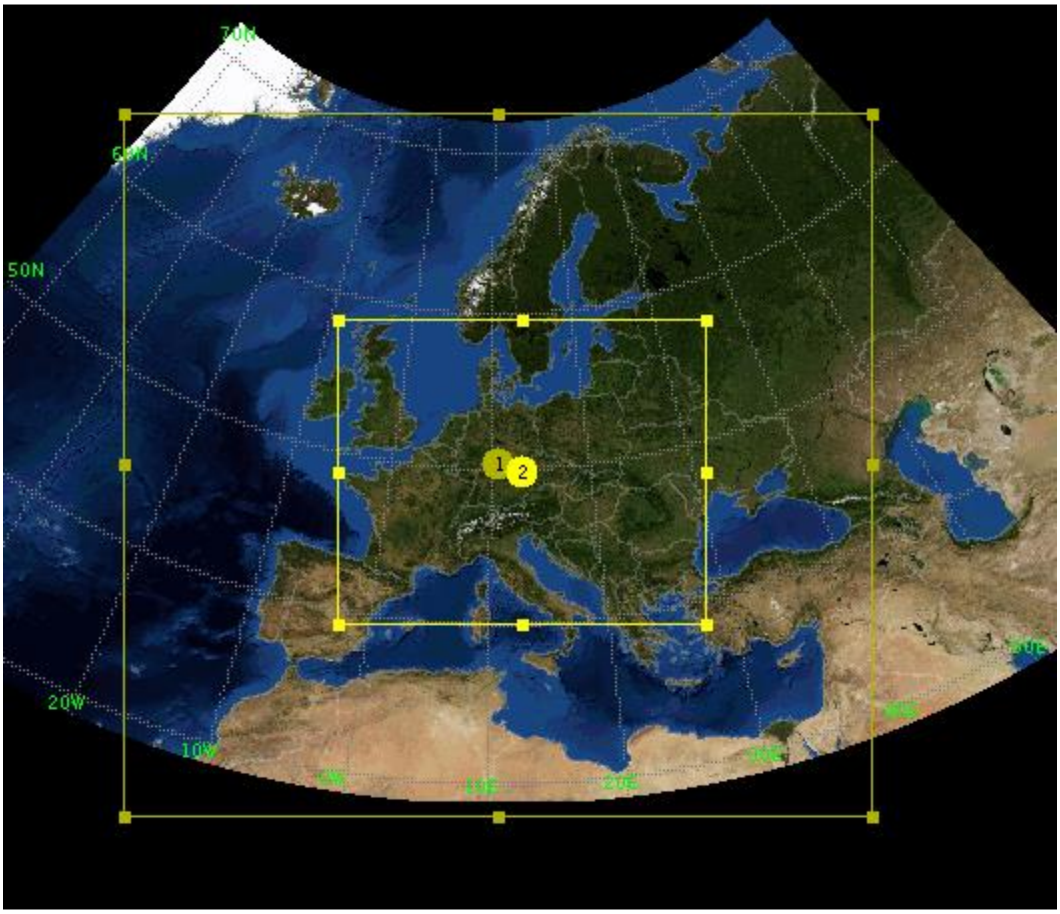


Fig. S2. *Domain setting of WRF-Chem European case.*

9) Ln 249: In terms of lifetime of nitrate radical (i.e. gas phase NO3), I would have thought this has more to do with the uptake of N2O5 to aerosol enhanced by Cl- rather than the HNO3 process you discuss in this paper. I'm not sure if it is quite relevant with the discussion here, which is more about the lifetime of aerosol NO3- when it is in different aerosol size modes. Please clarify.

Thanks for the comment. We agree with the reviewer that the discussion here might be more relevant with the uptake of N2O5 to NaCl rather than the lifetime of particulate nitrate in different aerosol size modes. We therefore removed the discussion here to make the point clearer.

10) Ln 336-347: Would it be possible to show a map of RNS over Europe and North America from the WRF-Chem model for comparison? You've only done this for the global EMAC

model, which by the sounds of things has lower values for RNS over most of the US compared to WRF-Chem (essentially nowhere in North America has RNS > 30 in the EMAC model, whereas this regime dominate continental North America in the WRf-Chem simulations). The figures currently given make it hard to follow the logic in this paragraph. In general, I think this section can be improved by outlining the conclusions that can be drawn from the evidence given, rather than speculating on what we might expect the effects to be if sea salt is transported further inland.

We have provided the map of RNS (molar ratio between nitrate and sodium) over Europe and North America from the WRF-Chem model as below (Fig. R1). The reviewer is right that RNS values from WRF-Chem cases are generally higher than the values from EMAC global model. However, these results are not directly comparable, because the EMAC global model provides the information of annual average but WRF-Chem provides results of a short period. In this paper, we would like to generalize a relationship between RNS and changes of $AOD_{nitrate}$ *due to the 're-distribution effect' from WRF-Chem results; and then estimate the potential impact of the 're-distribution effect' on a global scale, by adopting this relationship combined with RNS values from EMAC global model (as correctly pointed out by the reviewer in the next comment). Therefore, we prefer not to include Fig. R1 in the manuscript, because it is not directly comparable with the results of the EMAC model and does not clearly show the relationship. Alternatively, we have added a Fig. 9b to clearly show the relationship between RNS and changes of* $AOD_{nitrate}$ *as a first-order estimate, as suggested by the reviewer in the next comment. This makes the discussion clearer.*

Thanks for the suggestion about how to improve the logic of this paragraph. We have re-written this paragraph as suggested, and moved the discussion of differences between Europe and North America and further transport of sea-salt to the next paragraph, as shown below.

"The statistical analysis of the 're-distribution effect' over North America (Fig. 9a) shows a similar pattern as over Europe (Fig. 7a), and a first-order approximation ($R^2 > 90\%$) *is derived from the European and North American results of WRF-Chem model to parameterize the relationship between RNS and the changes of* $AOD_{nitrate}$ *associated with the 're-distribution effect' (Fig. 9b). In general, the impact of the 're-distribution effect' on* $AOD_{nitrate}$ *decreases as RNS increases. Only considering the 'mass-enhancement effect' but ignoring the 're-*

distribution effect' may lead to an overestimation of $AOD_{nitrate}$ *by about 20% when RNS < 1, by about 10-20% when 1 ≤ RNS ≤ 30 and by less than ~10% when RNS > 30.*

On a global scale, the potential influence of the 're-distribution effect' on $AOD_{nitrate}$ *is estimated by using the above first-order approximation combined with a one-year RNS simulation with the EMAC (Klingmüller et al., 2014;Pringle et al., 2010) chemistry-climate model (Fig. 10). The global distributions of percentage changes of* $AOD_{nitrate}$ *and surface nitrate concentration are given in Fig. S8. In line with the WRF-Chem results, a significant 're-distribution effect' is expected over North America and Europe, especially over the coastal regions with high nitrate loading and RNS values around 1 (Fig. 10b). As shown in Fig. 10c, the impact over Europe is stronger than over North America. The oceanic influence dominates over western Europe whereas over North America the predominantly more continental air masses (Kottek et al., 2006) may be a possible reason of this. It leads to less interactions of sea-salt with anthropogenic nitrate in North America, and more significant reduction of* $AOD_{nitrate}$ *over Europe. This result is consistent with a previous study (Myhre et al., 2006). Nevertheless, it is still possible that sea-salt is transported (May et al., 2018) further inland over North America and impacts* $AOD_{nitrate}$ *there. The coastal and offshore regions of Asia with 1 ≤ RNS ≤ 30 may experience strong reductions of* $AOD_{nitrate}$*, where the 're-distribution effect' is expected to overwhelm the 'mass-enhancement effect', such as coastal and outflow regions of China. The influence of sea-salt aerosol becomes negligible over inland Asia where marine air mass influence is small (RNS > 30). For the open sea regions with RNS < 0.01 (white background), nitrate climate effect is not important, due to very limited nitrate loading contributing to* $AOD_{nitrate}$ *(Fig. 10a)."*

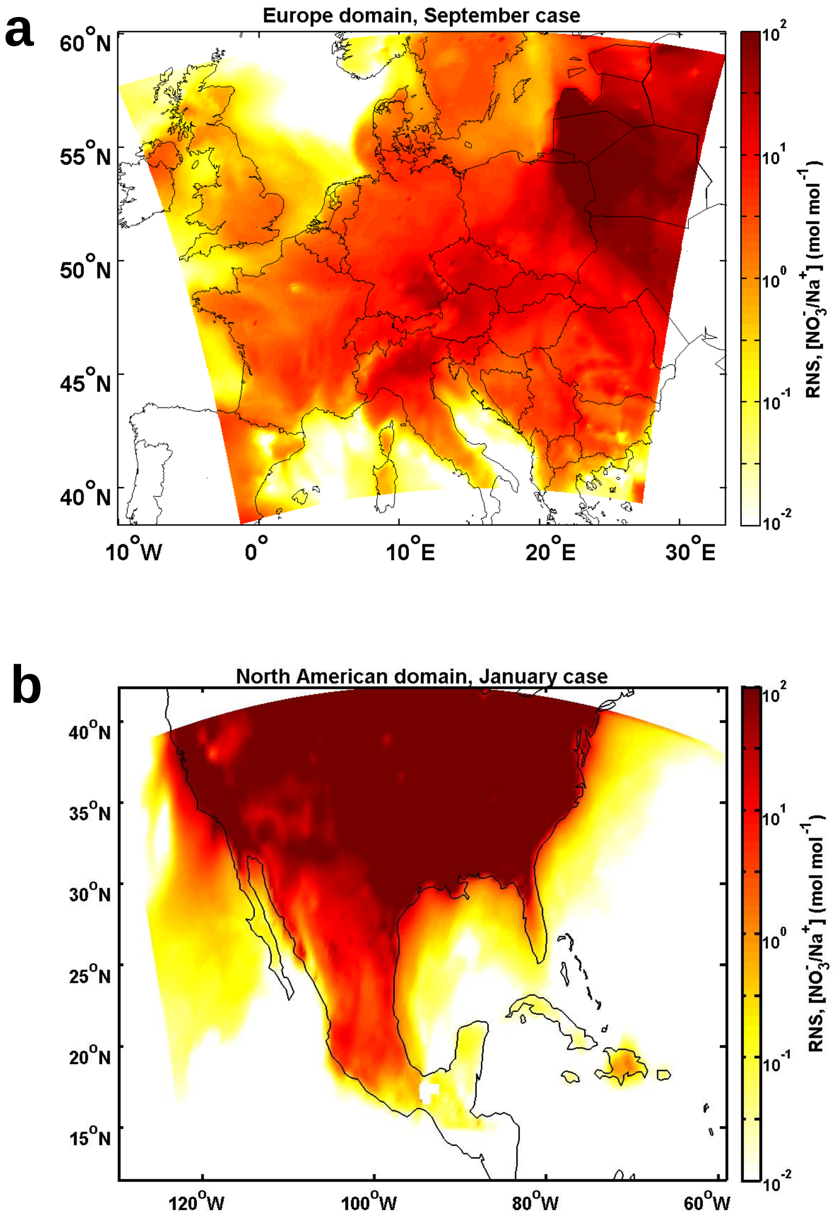


Figure R1. *Map of RNS (molar ratio between nitrate and sodium) in the European case (a) and the North American case (b) from the WRF-Chem simulation. Note that the color-scales have been changed to grey-scale friendly style, as suggested by the Reviewer#1.*

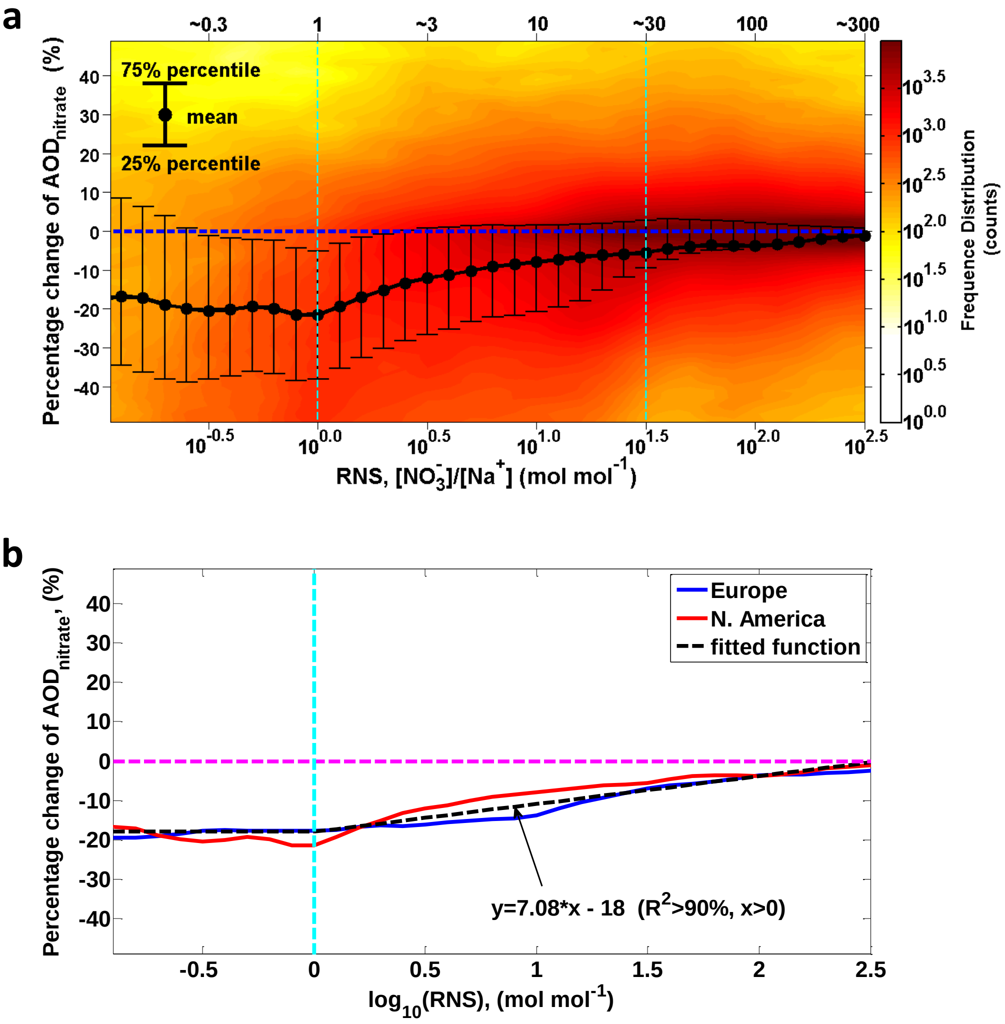


Fig. 9. Intensity of 're-distribution effect' as a function of molar ratio between surface fine nitrate and total sodium (RNS). (a) *The intensity of 're-distribution effect' over North American domain, similar as Fig. 7a, calculated as the difference in percentage between* $AOD_{nitrate}$ *and* $AOD^{*}_{nitrate}$ *in the 'Case_SeasaltOn'.* $AOD^{*}_{nitrate}$ *indicates the* $AOD_{nitrate}$ *calculated by re-allocating nitrate mass into different size bins according to the normalized nitrate particle mass size distribution simulated in 'Case_SeasaltOff' (i.e., without 're-distribution effect'). The black dots indicate the mean values; the upper and lower error bars indicate the 75% and 25% percentile, respectively. The colour indicates the frequency distribution (i.e., how many counts) of the hourly model results over entire North America domain during 10-17 January 2015.* ***(b)*** *The median possibility of the percentage change of* $AOD_{nitrate}$ *as a function (first-order approximation) of RNS.*

11) Ln 348-350: Would it be possible to plot a first-order estimate of what the change to nitrate AOD would be from this effect, using a function based on the relation between RNS and [NO3-] derived from the WRF-Chem model simulations?

This is a good point. We have plotted the first-order approximation in the newly added Fig. 9b, provided the estimated change of nitrate AOD associated with the 're-distribution effect' in the Fig. 10c, and added the corresponding discussions in the last two paragraphs of section 3.5. Please find details in the response to the last comment. This does make the discussion clearer. Thanks for your suggestion.

12) Ln 364: "(_90%)" – what is this referring to exactly?

We have modified the description to make this clearer, as shown below.

"up to 90% of the days in a year"

13) Ln 390-394: This last section is confusing what you can derive from the results of this study (modulation to nitrate DRF from sea-salt aerosol) from that speculated from other related chemical interactions (sulfur, dust etc.). Please rewrite to clearly separate the conclusions drawn from your results from speculations/highlight topics for future research.

We have re-written the context in the last section to clearly separate the conclusions drawn from this study from highlight topics for future research, as shown below.

"This study highlights the impact of the 're-distribution effect' on moderating nitrate cooling and altering the nitrogen deposition efficiency by interacting with natural sea-salt aerosols (Fig. 1) … All these previous studies imply the possibility that natural particles (sea-salt aerosol and very likely dust as well) moderate the DRF of anthropogenic aerosols and alter the nitrogen and sulfur deposition efficiency. We highlight the importance of further study of the inter-actions between natural and anthropogenic aerosols."

Figures:

1) Please promote Fig S1 into the main paper, I think it really clearly shows how the redistribution effect changes the aerosol chemical size distribution.

Modified as suggested.

2) Fig 9. Please can you include a subplot with this showing [NO3-]? You need this with RNS to get an understanding of where the redistribution impact is likely to be strongest.

We have added the map of [NO_3^-] in the Fig. S8b, as shown below. Please also see detailed discussion in the Minor Comment-10.

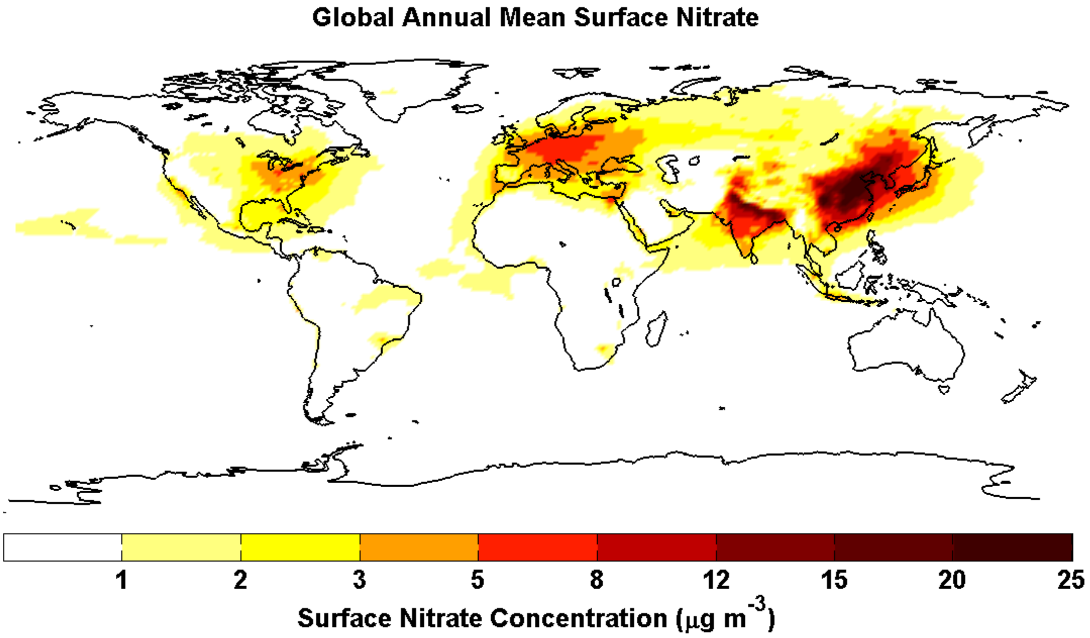


Fig. S8b. *Global distribution of percentage changes of surface nitrate concentration. The results are from EMAC model.*

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Natural sea-salt emissions moderate the climate forcing of anthropogenic nitrate

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Abstract. Natural sea-salt aerosols, when interacting with anthropogenic emissions, can enhance the formation of particulate nitrate. This enhancement has been suggested to increase the direct radiative forcing of nitrate, called ‘mass-enhancement effect’. Through a size-resolved dynamic mass transfer modelling approach, we show that interactions with sea-salt shift the nitrate from sub- to super-micron sized particles (‘re-distribution effect’), and hence lower its efficiency for light extinction and reduce its lifetime. The re-distribution effect overwhelms the mass-enhancement effect and significantly moderates nitrate cooling; e.g., the nitrate associated aerosol optical depth can be reduced by 10-20% over European polluted regions during a typical sea-salt event, in contrast to an increase by ~10% when only accounting for the mass-enhancement effect. Global model simulations indicate significant re-distribution over coastal and offshore regions world-wide. Our study suggests a strong buffering by natural sea-salt aerosols that reduces the climate forcing of anthropogenic nitrate, which had been expected to dominate the aerosol cooling by the end of the century. Comprehensive considerations of this re-distribution effect foster better understandings of climate change and nitrogen deposition.

1. Introduction

Particulate nitrate (NO_3^-) is one of the most important anthropogenic aerosol components that exert a climate cooling effect (IPCC, 2013;Haywood and Schulz, 2007). On a global scale, its average direct radiative forcing (DRF) has been estimated to span over a relatively wide range from -0.08 to -0.19 W m^{-2} (Liao et al., 2004;Liao and Seinfeld, 2005;IPCC, 2013;Xu and Penner, 2012;Haywood and Schulz, 2007;Myhre et al., 2013;Forster et al., 2007;Adams et al., 2001;Bauer et al., 2007;Jacobson, 2001;Streets et al., 2013;van Dorland et al., 1997). It is projected to reach up to about -0.4 to -1.3 W m^{-2} and dominate the aerosol cooling by the end of the century (Adams et al., 2001;Bellouin et al., 2011;Hauglustaine et al., 2014). Although the gaseous precursors of nitrate, e.g., NOx (= NO + NO_2) and HNO_3, are mainly of anthropogenic origin, globally about 35-50% of the nitrate mass is associated with natural sea-salt aerosol (Xu and Penner, 2012;Myhre et al., 2006). This is because sea-salt aerosol can be transported over industrialized regions, interacts with anthropogenic precursors of nitrate and enhances the total nitrate column loading in the atmosphere through heterogeneous uptake of HNO_3 and its precursors (Liao et al., 2004;Liao and Seinfeld, 2005;Seinfeld and Pandis, 2006;Xu and Penner, 2012;Ravishankara, 1997;Lowe et al., 2015). Such sea-salt-induced nitrate mass increase is believed to strengthen the DRF and climate cooling of nitrate (Liao and Seinfeld, 2005), called the ‘mass-enhancement effect’.

However, not only the mass concentration but also the particle mass size distribution (PMSD) are essential for evaluating the direct radiative forcing of nitrate ($DRF_{nitrate}$) (IPCC, 2013;Murphy et al., 1998;Kok et al., 2017). Besides leading to the increase of total nitrate mass, interactions with sea-salt aerosol also have a ‘re-distribution effect’ on nitrate PMSD which shifts nitrate from sub- to super-micron sizes (e.g., Chen et al., 2016a, see also Fig. 1). Because sea-salt aerosol is mainly present as super-micron (coarse) particles (Murphy et al., 1998;O'Dowd et al., 1997;Ravishankara, 1997), chemical equilibrium favors the formation of thermodynamically stable sodium nitrate in the coarse mode, which inhibits the formation of semi-volatile ammonium nitrate in the sub-micron size (fine mode) through competitive consumption of gaseous precursors and change of gas-particle equilibrium (Chen et al., 2016a;Zaveri et al., 2008;Myhre et al., 2006). Compared to the fine particles, coarse particles have a significantly lower extinction efficiency in the visible part of the spectrum (IPCC, 2013;Murphy et al., 1998), the sea-salt-induced ‘re-distribution effect’ thus tends to weaken $DRF_{nitrate}$, which counteracts the ‘mass-enhancement effect’. The competition between these two effects will ultimately determine the net impact of sea-salt aerosol on anthropogenic $DRF_{nitrate}$. To the best of our knowledge, this sea-salt-induced ‘re-distribution effect’ is neglected in most global models, due to the computationally expensive calculations of fully dynamic mass transfer between size-resolved particulate nitrate (Adams et al., 2001;Myhre et al., 2006); for more details see Supplementary Information Section S1.

To explore the competition between the sea-salt-induced ‘mass-enhancement effect’ and ‘re-distribution effect’ and the impact of the ‘re-distribution’ process on the nitrate cooling of climate, we conducted a series of sensitivity studies with and without sea-salt aerosol emission for a typical sea-salt event over Europe and North America, using a regional atmospheric chemistry model (WRF-Chem) with a fully dynamic mass transfer approach (Zaveri et al., 2008); see ‘Data & Methods’ for details. A one-year simulation with the EMAC (ECHAM5/MESSy Atmospheric Chemistry) model is used to demonstrate the importance of the ‘re-distribution effect’ on a global scale (Jöckel et al., 2010).

2. Data & Methods

2.1 Observations

The HOPE~~-Melpitz~~ campaign (HD(CP)^2 Observational Prototype Experiment, Macke et al., 2017) at Melpitz, Germany, was carried out during 10-20 September 2013 at Melpitz (12.93°E, 51.53°N, 86 m a.s.l.). Melpitz represents the regional background of central Europe (Spindler et al., 2012), with flat surrounding topography over an area of hundreds of square kilometers, ranging 100-250 m a.s.l.

Size-segregated measurements of particles composition were carried out on 13 September and 18 September, which represent the continental period and marine period, respectively (see back-trajectories in Fig. S1~~8~~). A five-stage Berner impactor (Hauke, Austria, 0.05-0.14 μm, 0.14-0.42 μm, 0.42-1.2 μm, 1.2-3.5 μm, and 3.5-10 μm; Berner and Luerzer, 1980) was operated to segregate particles onto ring-like pre-baked (350 °C) aluminium foils with a sampling period of 24 h (00:00-24:00, local time) for detailed chemical analyses (Spindler et al., 2012). The isokinetic inlet for particles with an aerosol dynamic diameter smaller than 10 μm was installed 6 meters above the ground. To compare with modelling results, we use the sum of the particle mass at stage 1-3 ($PM_{1.2}$, aerosol dynamic diameter smaller than 1.2 μm) to represent fine mode particles and the sum of the mass at stages 4-5 ($PM_{1.2-10}$, aerosol dynamic diameter smaller between 1.2 and 10 μm) to represent coarse mode particles. The gravimetric mass of the pre-heated aluminium foils was weighted respectively before and after the sampling process, by a microbalance (UMT-2, Mettler-Toledo, Switzerland). Before each weighting, the aluminium foils were equilibrated for at least 72 hours in a strictly controlled environment with a temperature of 20±1 °C and a relative humidity of 50±5%. After an aqueous extraction of foil aliquots, the main water-soluble cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were quantified by standard ion chromatography (Neusüß et al., 2000). Likewise, capillary electrophoresis (Neusüß et al., 2000) was carried out to quantify the anions (NO_3^-, SO_4^{2-} and Cl^-). A carbon analyzer (Behr Labor-Technik, Germany) was used to separate and measure the sampled organic and elemental carbon with a two-step thermographic method (modified VDI method 2465 part-2, Spindler et al., 2012). Organic carbon was vaporized at 650 °C for 8 minutes under N_2 and catalytically converted to CO_2; the remaining elemental carbon was combusted for another 8 minutes with O_2 at 650 °C. Generated CO_2 was then quantitatively determined using a non-dispersive infrared detector.

2.2 Model description

We performed regional model simulations with the 'online coupled' air quality model Weather Research and Forecasting/Chemistry model (WRF-Chem V3.5.1, Grell et al., 2005). WRF-Chem enables more detailed investigation of aerosol-radiation interaction over specific regions at higher horizontal resolution compared with global models, and has been broadly used for investigating aerosol radiative forcing in previous studies (e.g., Archer-Nicholls et al., 2019;Fast et al., 2006;Saide et al., 2012;Gao et al., 2018;Yao et al., 2017;Huang et al., 2015). To investigate the impact of 're-distribution effect' on PMSD and climate effect of nitrate, the fully dynamic aerosol module MOSAIC (Zaveri et al., 2008) was utilized with eight discrete size bins (39-78 nm, 78-156 nm, 156-312 nm, 312-625 nm, 625-1250 nm, 1.25-2.5 μm, 2.5-5 μm, 5-10 μm; see also Fig. 2~~S1~~), with the online coupled CBMZ (Carbon-Bond Mechanism version Z) gas chemistry scheme (Zaveri and Peters, 1999). In MOSAIC, NaCl reacts irreversibly with nitric acid with its equilibrium surface vapor pressure of zero; and a gas-particle partitioning approach ASTEM (Adaptive Step Time-Split Euler Method) is coupled with a thermodynamic module (MESA-MTEM, Multicomponent Equilibrium Solver for Aerosols – Multicomponent Taylor Expansion Method) to dynamically calculate the equilibrium vapor pressure and condensation rate of semi-volatile ammonium nitrate, details are given in the section 4 of Zaveri et al. (2008). We note that heterogeneous hydrolysis of N_2O_5 with NaCl is an important chemical pathway of particulate nitrate in coarse mode during nighttime (Bertram and Thornton, 2009;

Archer-Nicholls et al., 2014). This process may enhance the 're-distribution effect', however it is not considered in this study. The sea-salt emissions computed with the modified Gong scheme (Gong, 2003) were reduced to 10% in the 'Case_SeasaltOn', because a previous study (Chen et al., 2016a) has shown that the original Gong scheme overestimates the sea-salt mass concentrations by a factor of ~10 over the coastal regions of Europe using WRF-Chem model. We note that although the mass of coarse sea-salt particles is certainly overestimated, it might not necessarily indicate overestimation in fine sea-salt particles ~~due~~related to their minor contribution to the total mass. The sea-salt emission was turned off in the 'Case_SeasaltOff' simulation. We calculate the DRF and aerosol optical depth of anthropogenic nitrate at the top of the atmosphere for both ~~with and without~~ sea-salt ~~presence respectively~~emission cases, based on the difference in the net incoming radiative flux with and without the anthropogenically emitted gas phase precursor NOx (IPCC, 2013;Xu and Penner, 2012). Only the model results during daytime (07:00-16:00, local time) and under clear-sky condition (cloud optical depth equals to zero) were used for the analyses of DRF in this study.

WRF-Chem calculated aerosol optical depth (AOD) and direct radiative effect of total aerosols based on the internal mixture assumption ~~and~~ taking the hygroscopicity into account. In order to calculate the light extinction coefficient and optical depth for individual aerosol species, we performed the following off-line calculation. The AOD of each species is calculated by integrating light extinction coefficient (σ_{ex}) over all vertical layers. The σ_{ex} of sea-salt (NaCl) and particulate nitrate were calculated with Mie theory, based on their PMSD. Different from the WRF-Chem calculation of total aerosol AOD, external mixture was assumed for nitrate and sea-salt particles when calculating their respective contributions on σ_{ex} or AOD. Hygroscopic growth was also considered, following the κ-Köhler theory (Köhler, 1936;Petters and Kreidenweis, 2007).

2.3 European simulation

The European simulations focus on the HOPE-Melpitz campaign period of 10-20 September 2013, during which a sea-salt event that influenced most part of Europe was captured. The simulations are defined by two nested domains with horizontal resolutions of 54 km and 18 km respectively, and 39 vertical layers with model top at 50 hPa. The coarse domain (D01~~, 30º N – 71.5º N, 30º W – 46º E~~) covers the North Sea, the European continent and the northern part of~~ North~~ Africa; ~~. T~~the inner domain (D02~~, 38º N – 60º N, 8º W – 28º E, see Fig. 2~~) covers most of the North Sea and the European continent (Fig. S2~~9~~). The European anthropogenic emission inventories are provided by TNO (www.tno.nl) from the AQMEII project (Air Quality Model Evaluation International Initiative) for $PM_{2.5}$, $PM_{2.5-10}$, NOx, SO_2, CO, NH_3, and non-methane volatile organic compounds (Pouliot et al., 2012;Chen et al., 2018b), and from the EUCAARI project (European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions) for particulate organic carbon and elemental carbon (Kulmala et al., 2011). The inventories are with a spatial resolution of 1/8° × 1/16° longitude-latitude. We excluded the point source emissions of elemental carbon in EUCAARI inventory over Germany, since a previous study (Chen et al., 2016b) reported large uncertainty of them. More details about emissions, meteorological and chemical initial/boundary conditions can be found in the Supplementary Information Section S2. Detailed information about the model configuration is given in Table 1.

In the European ‘Case_SeasaltOn’ simulation (with sea-salt emission)~~ of European simulation~~, modelled $[Na^+]$ showed good agreement with measurements over coastal regions from European Monitoring and Evaluation Programme (EMEP, http://www.emep.int), with a factor (and correlation coefficient) of 0.85 (0.67), 1.16 (0.80) and 0.83 (0.87) ~~respectively~~ for Bilthoven, Kollumerwaard and Vredepeel (Fig. S3~~2~~), respectively. Compared with ground-based measurements at Melpitz and radio-sounding measurements across Europe, the meteorological conditions were well captured by the model (Chen et al., 2016a). Vertical structures of potential temperature and wind speed were realistically reproduced, with correlation coefficients between simulation and measurement results of ~0.9 over coastal, German low land~~s~~ (Melpitz) and northern Polish~~and~~ regions (Chen et al., 2016a). In line with previous studies (Xu and Penner, 2012;Li et al., 2013), the modelled AOD agreed reasonably well with the AERONET observations (AErosol RObotic NETwork, http://aeronet.gsfc.nasa.gov). The spatial distribution of AOD can be generally captured by the model (R=0.64), although model may overestimate AOD by a geometric mean bias of 70% (see Supplementary Information Section S3 for details).

2.4 North America and global simulations

To investigate the significance of the ‘re-distribution effect’ in a broa~~r~~der spatial scale, we also conducted WRF-Chem simulation over North America, where high concentrations of nitrate were~~as~~ usually observed. We focus on the period of 10-17 January 2015, when strong continental outflow interacted with marine air masses over the Gulf of Mexico. The North American domain covers the US, the Gulf of Mexico and parts of Pacific and Atlantic oceans, with a horizontal resolution of 36 km. In addition, a one-year simulation with global model (EMAC) was carried out for analysis of the potential impact of 're-distribution effect' on a global scale.~~,~~ ~~a~~Although the fully dynamic mass transfer between particle sizes is not considered in EMAC (four size modes rather than eight size bins as applied in the WRF-Chem model), we adopt a parameterization derived from WRF-Chem simulations to estimate the potential impact (details given in section 3.5). More details of EMAC model and its aerosol module are described in our previous work (Pozzer et al., 2012;Klingmüller et al., 2014;Pringle et al., 2010). The global simulation was run at T106L31 resolution, corresponding to a quadratic Gaussian grid of approximately 1.1º ~~by~~× 1.1º ~~degrees~~ (in latitude and longitude) and with 31 levels in the troposphere. The global emission inventory EDGAR (V4.3, 2010, http://edgar.jrc.ec.europa.eu) was used in the North American and global simulations.

3. Results and Discussion

3.1 Sea-salt-induced 're-distribution effect'

Marine air masses frequently, ~~(~~ ~up to 90% of the days in a year,~~)~~ ~~approach~~ influence Central Europe (Birmili et al., 2001).~~, and t~~ The interaction between anthropogenic pollutants and sea-salt aerosol commonly happens in the atmosphere. In this study, we performed a series of numerical sensitivity experiments during a typical *sea-salt transport event* from 10 to 20 September 2013 during the HOPE-Melpitz campaign. During the campaign, Central Europe was dominated by continental air masses before 15 September. Subsequently marine air masses started travelling over land on 17 September, and sea-salt aerosol originating~~ed~~ from the North Sea and the Baltic Sea was transported to northern Poland and dominated Central Europe on 19 September (Fig. 3~~2~~). Sea-salt is emitted into the marine planetary boundary layer (PBL) with mass concentration dominated by~~as~~ coarse particles, usually with a short lifetime and a limited transport range. Previous studies showed that the special PBL thermodynamic structure over coastal regions (Ding et al., 2004) can bring sea-salt from the marine PBL to the continental free troposphere, therefore prolonging its lifetime and favoring long-range transport~~,~~ (see the figure 11 of Chen et al. ~~(~~2016a). Afterwards, the sea-salt aloft could be mixed down to surface layer by the fully developed PBL (Chen et al., 2009;Chen et al., 2016a) and interact with anthropogenic nitrate. Therefore, this transport mechanism broadens the sea-salt-induced 're-distribution effect' on nitrate to a larger spatial scale.

As shown in Fig. 4~~3~~a and 4~~3~~b, the 'Case_SeasaltOn' simulation successfully reproduces the 're-distribution effect' of nitrate when the dominating air mass changed from a continental to marine type at the Central Europe background site Melpitz. Measurements and model results both show an ~10 times increase of sodium concentration ([Na^+], indicator of sea-salt aerosol) in the coarse mode when marine air masses approached (Fig. S4~~3~~). While the nitrate mass fraction in the coarse mode was enhanced by a factor of ~5.5, its concentration ([NO_3^-]) in the fine mode was lowered by ~20% (Fig. 4~~3~~b). A clear re-distribution of particulate nitrate from fine to coarse mode is found when introducing sea-salt in the 'Case_SeasaltOn', with negligible changes in other particulate species except sea-salt (Fig. 2~~S1~~). Conversely, without introducing sea-salt aerosol, the 'Case_SeasaltOff' did not capture the 're-distribution effect', and the nitrate mass in the fine mode (~97%) dominated in both continental and marine air masses (Fig. 4~~3~~c).

3.2 Moderation of nitrate cooling by the 're-distribution effect'

Figure 5~~4~~ shows the strong impact of the 're-distribution effect' on nitrate cooling when marine air mass transported further inland and predominated over Europe on 19 September. Although sea-salt aerosol leads to an overall enhancement of nitrate column loading (~1 mg m^{-2}, Fig. S5~~4~~) compared to the 'Case_SeasaltOff', the nitrate associated aerosol optical depth ($\mathrm{AOD}_{\mathrm{nitrate}}$) decreases significantly over the relatively polluted continental regions (Fig. 5~~4~~a), leading to a strongly weakened cooling effect of nitrate in those regions (positive change in $\mathrm{DRF}_{\mathrm{nitrate}}$ in Fig. 5~~4~~b). We find that the regions of reduced $\mathrm{AOD}_{\mathrm{nitrate}}$ co-locate with the regions of reduced fine mode [NO_3^-] (bluish colored areas in Fig. 5~~4~~a and 5~~4~~c). Over a large area of the European continent, the 're-distribution effect' shifts the nitrate PMSD from the fine to the coarse mode (Fig. 5~~4~~c, 5~~4~~d), resulting in much less efficient light scattering of nitrate aerosol with a reduced cooling effect. The box with a solid black frame in Fig. 5~~4~~ marks a region in ~~the~~ northern Poland~~ region~~, where sea-salt aerosol strongly interacted with anthropogenic precursors of nitrate during the studied sea-salt event. In this region, 're-distribution effect' leads to a decrease of column nitrate loading in the fine mode by ~2.9 mg m^{-2} (Fig. 5~~4~~c) accompanied by an increase of ~3.7 mg m^{-2} in the coarse mode due to the 'mass-enhancement effect' (Fig. 5~~4~~d). Consequently, the anthropogenic $\mathrm{AOD}_{\mathrm{nitrate}}$ is significantly reduced by up to ~30% with an average reduction of ~22% (~0.05 in absolute AOD value, Fig. 5~~4~~a), despite of a ~0.8 mg m^{-2} net increase in total nitrate loading. This results in a 5-70% reduction of nitrate cooling, on average by ~26% (Fig. 5~~4~~b). Our results demonstrate that the sea-salt-induced 're-distribution effect' overwhelms the 'mass-enhancement effect' over polluted regions, thus moderating the anthropogenic nitrate cooling.

The resulting decrease of nitrate cooling is non-linear with respect to the sea-salt aerosol loading due to the competition between sea-salt-induced ‘mass-enhancement effect’ and ‘re-distribution effect’. To investigate the net impact of this competition, we performed a series of sensitivity simulations with different sea-salt aerosol emission scaling factors (0, 0.5, 1, 2, 3, 4, 5, 6, 8, and 10, the ones with scaling factors of 0 and 1 being our ‘Case_SeasaltOff’ and ‘Case_SeasaltOn’, respectively). As a surrogate of aerosol DRF, the AOD of nitrate and sea-salt aerosol was calculated offline based on the simulated PMSD (see ‘Data & Methods’). Over the region in northern Poland~~ region~~ (box with solid frame in Fig. 5~~4~~), total [NO$_3^-$] (green dashed line in Fig. 6~~5~~a) increased continuously as a function of [Na$^+$], which is in line with previous estimates and clearly shows the ‘mass-enhancement effect’ (Liao and Seinfeld, 2005). However, the ‘re-distribution effect’ overwhelms the ‘mass-enhancement effect’ in this region, and the AOD$_{nitrate}$ drops significantly by ~29% (red solid line in Fig. 6~~5~~a) when the scaling factor of sea-salt aerosol is 1 (‘Case_SeasaltOn’), Noting that this is~~being~~ slightly higher than the average ~22% from the on-line calculation, due to the difference in aerosol mixing state, i.e., internal mixing of aerosol compositions in the on-line calculation; and external mixing in the offline calculation~~)~~. The reduction of AOD$_{nitrate}$ reaches a maximum of ~50% (~0.09 in absolute AOD value) when [Na$^+$] is ~2.5 μg m^{-3} or higher, which level of sea-salt aerosol has been often observed in Central Europe (Fig. 6~~5~~c, Gustafsson and Franzén, 2000;Neumann et al., 2016;Gantt et al., 2015). A similar net reduction of AOD$_{nitrate}$ is also found for Central Europe (marked in Fig. 3~~2~~), where the overall moderation is ~13% compared to the ‘Case_SeasaltOff’ (Fig. S6~~5~~a). To further demonstrate the influence of the ‘re-distribution effect’ on nitrate cooling, we calculate the ΔAOD$_{nitrate}$ by re-allocating nitrate mass into different size bins according to the normalized nitrate PMSD simulated in the ‘Case_SeasaltOff’, i.e., by neglecting the ‘re-distribution effect’ (ΔAOD$^*_{nitrate,}$ pink dashed line in Fig. 6~~5~~a). A distinct opposite trend, of~~with~~ increasing AOD$^*_{nitrate}$ with increasing [NO$_3^-$] (green dashed line), would result when~~ by neglecting~~ the ‘re-distribution effect’ was neglected. For example, instead of a decrease by 29%, the AOD$^*_{nitrate}$ over the region of northern Poland increases by ~8% from the ‘Case_SeasaltOff’ to the ‘Case_SeasaltOn’.

It is~~ also~~ noteworthy that the increase rate of [NO$_3^-$] decreases as [Na$^+$] further increases.~~ and t~~There is even a slight decrease of [NO$_3^-$] when [Na$^+$] exceeds ~5 μg m^{-3} (Fig. 6~~5~~a). This is mostly due to the consumption of nitrate precursor and stronger deposition of particulate nitrate by ‘re-distribution’ toward larger particles sizes and, thus, shorter lifetimes. ~~This result is consistent with previous studies showing that~~

~~lifetime of nitrate radical is significantly reduced in the presence of sea-salt aerosols (Rudich et al., 1998;Ravishankara, 1997).~~ The lifetime of nitrate particles can be shortened from about a week to one day by shifting from the fine to the coarse mode (Croft et al., 2014;Chen et al., 2016b) ~~and hence~~ further moderate nitrate cooling effect. Moreover, coarse mode nitrate associated with highly hygroscopic sea-salt enhances its water uptake (Chen et al., 2018a) and cloud condensation nuclei activation (Xu and Penner, 2012;Wang and Chen, 2019), ~~therefore~~ fastening its deposition and scavenge rate. Itahashi et al. (2016) reported that oxidized~~ygenated~~ nitrogen deposition can be enhanced by 1.6-2.2 times over ocean regions in East Asia by including sea-salt associated nitrate. Liao and Seinfeld (2005) implied a similar enhancement for sea-salt/dust associated sulfate deposition, which resulted in a decrease in sulfate concentrations in the downwind regions. Our study implies the enhancement of nitrate deposition. As one can see in Fig. 6~~5~~a, nitrate concentration (green dashed line) firstly increases with increasing sea-salt and then slightly declines when the amount sea-salt (represented by sodium) exceeds a certain level. An inflection point is observed when sodium concentration approached 5.5 μg m^{-3} (sea-salt emission factor = 8), the nitrate starts to decrease as sodium further increases (sea-salt emission factor = 10). The enhancement of nitrate deposition should be the reason of this phenomenon. To demonstrate this, we conducted a sensitivity simulation with aerosol dry deposition turned off. We found that nitrate concentration kept increasing from 10.91 to 11.02 μg m^{-3} when sea-salt emission factors increased from 8 to 10, instead of showing a decreasing trend as in the simulations with aerosol dry deposition turned on. This indicates an enhanced deposition of nitrate by interaction with sea-salt which shortens nitrate lifetime and can further reduce nitrate cooling.

3.3 Competition between 're-distribution effect' and 'mass-enhancement effect'.

As a result of competition between the sea-salt-induced 're-distribution effect' and 'mass-enhancement effect', clear spatial inhomogeneity can be found in Fig. 5~~4~~. The 're-distribution effect' decreases AOD$_{\text{nitrate}}$ over the polluted continental regions; while the 'mass-enhancement effect' increases AOD$_{\text{nitrate}}$ mostly over marine areas (Fig. 5~~4~~a), although the absolute enhancement is rather small due to the low [NO_3^-] in this environment. For example, over the Mediterranean Sea (marked by the box with a dashed black frame in Fig. 5~~4~~), the AOD$_{\text{nitrate}}$ increases by ~0.01 and the cooling effect of nitrate is amplified by ~0.54 W m^{-2} (negligible without introducing sea-salt aerosol). Sensitivity study also shows a monotonic increase of AOD$_{\text{nitrate}}$ with [Na^+] over the Mediterranean Sea (Fig. 6~~5~~b), indicating a dominant role of the 'mass-enhancement effect' over regions with limited anthropogenic influence.

Thus, abundant sea-salt aerosol and pre-existing fine mode nitrate (as if no sea-salt aerosol influence in the 'Case_SeasaltOff') favor an efficient 're-distribution effect' that reduces $AOD_{nitrate}$ and moderates nitrate cooling. To ~~generalize the net impact~~compare the relative importance of the sea-salt-induced 're-distribution effect' and 'mass-enhancement effect' on anthropogenic nitrate cooling, we conducted statistical analysis of the molar ratio between fine nitrate in the 'Case_SeasaltOff' and total sodium in the 'Case_SeasaltOn' (RNS = $[NO_3^-]/[Na^+]$ in mol mol^{-1}) with relation to the percentage change of nitrate AOD (surrogate of $DRF_{nitrate}$) between the two cases, i.e., $(AOD_{nitrate\ Case\_SeasaltOn} - AOD_{nitrate\ Case\_SeasaltOff})/AOD_{nitrate\ Case\_SeasaltOn}$,. We found that the 're-distribution effect' tends to be strong enough to overwhelm the 'mass-enhancement effect' when the RNS value is in the range of about 1 to 30, corresponding to ~70% of the data points in the European domain, as detailed in Supplementary Information (Fig. ~~S~~7~~6a~~c and Section S4). Note that only the surface concentrations were used for calculating the RNS, because fine mode ammonium nitrate is mostly limited in the surface layer ~~due to~~ because emissions of NH_3 are in surface layer. The sea-salt (or sodium) aloft during transport process (as discussed in section 3.1) did not exert the 're-distribution effect' before being mixed down to surface layer, and should not be included in the analysis. Therefore, we carried out a statistical analysis with surface nitrate and sodium concentrations, to draw a more robust conclusion. When the 're-distribution effect' is sufficiently strong, the net reduction of $AOD_{nitrate}$ may even counteract the AOD enhancement contributed by the additional sea-salt aerosol loading and lead to an overall reduction of total AOD in many regions in Europe (Supplementary Information Fig. S6~~5~~b and Section S5).

3.4 The 're-distribution effect' over Europe

Due to the frequent interactions between sea-salt aerosol and polluted air masses (Myhre et al., 2006;Xu and Penner, 2012), the moderation of nitrate cooling is expected to be common over Europe, where the lower atmosphere is characterized by RNS values between 1 and 30 (Fig. 7~~6~~). As discussed above (Fig. 6~~5~~a and Fig. S6~~5~~), considerable moderation is expected over inland and Central Europe, where $[Na^+] > 2.5\ \mu g\ m^{-3}$ is observed frequently (Gustafsson and Franzén, 2000, also see Fig. 6~~5~~c). Such moderation could be even more relevant over coastal and continental outflow regions of North America and South/East Asia (discussed in the next section), where high loadings of nitrate were observed and found to be significantly associated with sea-salt aerosol (30-90% of total nitrate) (Xu and Penner, 2012).

To quantify the possible overestimation of nitrate radiative forcing when only the sea-salt-induced 'mass-enhancement effect' was treated but not the 're-distribution effect', similar statistical analysis (Fig. 7ab~~6~~) is conducted for the percentage change of nitrate AOD between the $AOD_{nitrate}$ in the 'Case_SeasaltOn' and the corresponding $AOD^{*}_{nitrate}$, i.e. ($AOD_{nitrate} - AOD^{*}_{nitrate}$)/$AOD_{nitrate}$. As described before, $AOD_{nitrate}$ stands for the case where both 'mass-enhancement' and 're-distribution' effects have been accounted for the 'Case_SeasaltOn', while only the 'mass-enhancement effect' is accounted for $AOD^{*}_{nitrate}$. Fig. 7b~~cS6b~~ shows that the $AOD^{*}_{nitrate}$ could increase by 5-30% when introducing sea-salt and only the 'mass-enhancement effect' is considered. Conversely, the statistics show that the 're-distribution effect' tends to significantly reduce the nitrate AOD by 10-20% when there is abundant sea-salt interacting with anthropogenic nitrate (RNS < ~30, Fig. 7ab~~6~~). Note that this estimation of percentage reduction in $AOD_{nitrate}$ is robust (may be slightly conservative), despite of the overestimation of particulate nitrate over Europe (Supplementary Information Section S6). The uncertainty in deposition parameterizations could be one reason of this overestimation, as suggested by the overestimation of sea-salt particles as well (Chen et al., 2016a) and the underestimation of nitrogen deposition over Europe in many models (Vivanco et al., 2017). The upper limit of our result is comparable to a previous estimate of 25% reduction of $AOD_{nitrate}$ by sea-salt aerosol on a global scale by Myhre et al. (2006).~~,~~ They evaluated ~~where~~ a similar 're-distribution effect' of sea-salt aerosol. ~~was evaluated b~~But the simplifications of the mass transfer between fine and coarse modes may lead to overestimation of the reduction (Supplementary Information Section S1). The 're-distribution effect' becomes rather weak (limited within 10%) as RNS further increased (RNS > ~30) when marine air masses are transported further inland.

3.5 The 're-distribution effect' over North America and on a global scale

An additional simulation over North America confirms our findings. Similar as over Europe, the sea-salt-induced 're-distribution effect' predominates and reduces $AOD_{nitrate}$ over industrialized and outflow regions of the North America domain (Fig. 8~~7~~). Generally, similar reduction of $AOD_{nitrate}$ is found over North America due to the sea-salt-induced 're-distribution effect'. A monotonous decrease (increase) of column fine (coarse) nitrate loading is observed all over North America and oceanic regions (Fig. 8~~7~~c and Fig. 8~~7~~d). This sea-salt-induced 're-distribution effect' ~~overwhelmes~~overwhelms the 'mass-enhancement effect' over most regions and, thus, reduces $AOD_{nitrate}$ (Fig. 8~~7~~a) and cooling effect of nitrate especially over the Gulf of

Mexico (Fig. 8~~7~~b), although the total nitrate column loading increases significantly (Fig. S7). This is because the high concentration of nitrate in the continental outflow from North and Central America strongly interacts with sea-salt over the Gulf (Xu and Penner, 2012).

The statistical analysis of the 're-distribution effect' over North America (Fig. 9a) shows a similar pattern as over Europe (Fig. ~~8~~7a~~ba~~), and a first-order approximation ($R^2 > 90\%$) is derived from the European and North American results of WRF-Chem model to parameterize the relationship between RNS and the changes of AOD$_{nitrate}$ associated with the 're-distribution effect' (Fig. 9~~8~~b).~~. Meanwhile, different from Europe, there is large fraction of the model results presented in the RNS > 30 regime in North America, indicating less regions over North America experience a strong 're-distribution effect'. The oceanic influence dominates over western Europe whereas over the North America the more continental air masses (Kottek et al., 2006) may be a possible reason of this. It leads to less interactions of sea-salt with anthropogenic nitrate in North America, and more significant reduction of AOD$_{nitrate}$ over Europe. This result is consistent with a previous study (Myhre et al., 2006). However, there are still chances that sea-salt is transported (May et al., 2018) further inland over North America and impacts AOD$_{nitrate}$ there. On average,~~ In general, the impact of the 're-distribution effect' on AOD$_{nitrate}$ decreases as RNS increases. O~~ o~~nly considering the 'mass-enhancement effect' but ignoring the 're-distribution effect' may lead to an overestimation of AOD$_{nitrate}$ by about~~more than~~ 20% when RNS < 1,~~ and~~ by about 10-20% when 1 ≤~~<~~ RNS ≤~~<~~ 30 and by less than ~10% when RNS > 30. ~~This RNS range encompasses most of the coastal and offshore regions of North America and favors 're-distribution effect'.~~

On a global scale, the potential influence of the 're-distribution effect' on ~~DRF$_{nitrate}$~~ AOD$_{nitrate}$ is estimated by using the above first-order approximation combined with a one-year RNS simulation with the EMAC (Klingmüller et al., 2014;Pringle et al., 2010) chemistry-climate model (Fig. 10~~9~~). The global distributions of percentage changes of AOD$_{nitrate}$ and surface nitrate concentration are given in Fig. S8~~10~~. In line with the WRF-Chem results, a ~~strong~~ significant 're-distribution effect' is expected over North America and Europe, especially over the coastal regions with high nitrate loading and RNS values around 1~~.~~ (Fig. 10~~9~~b). As shown in Fig. 10~~9~~c, the impact over Europe is stronger than over North America. The oceanic influence dominates over western Europe whereas over ~~the~~ North America the predominantly more continental air masses (Kottek et al., 2006) may be a possible reason of this. It leads to less interactions of sea-salt with anthropogenic nitrate in North America, and more significant reduction of AOD$_{nitrate}$ over

Europe. This result is consistent with a previous study (Myhre et al., 2006). ~~However, there are still chances~~Nevertheless, it is still possible that sea-salt is transported (May et al., 2018) further inland over North America and impacts AOD$_{nitrate}$ there. The coastal and offshore regions of Asia with 1 $\leq$~~$<$~~ RNS $\leq$~~$<$~~ 30 may experience strong reductions of AOD$_{nitrate}$, where the 're-distribution effect' is expected to overwhelm the 'mass-enhancement effect', such as coastal and outflow regions of China. The influence of sea-salt aerosol becomes negligible over inland Asia where marine air mass influence is small (RNS > 30). For the open sea regions with RNS < 0.01 (white background), nitrate climate effect is not important, due to very limited nitrate loading contributing to AOD$_{nitrate}$ (Fig. 10~~9~~a).

4. Summary and Discussion

The interaction between natural sea-salt aerosols and anthropogenic nitrate leads to the 're-distribution effect', which can shift the particulate nitrate from sub- to super-micron sizes. ~~and hence~~This effect lowers its mass light extinction efficiency and shorten its lifetime. This 're-distribution effect' can significantly moderate nitrate cooling.

The interaction between natural sea-salt aerosols and anthropogenic nitrate happens frequently over Europe (up to ~~∼~~90% of the days in a year). We performed a series of sensitivity studies during a typical sea-salt event over Europe, using WRF-Chem model with fully dynamic aerosol mass transfer treatment online-coupled. The 're-distribution effect' of nitrate is observed by field measurements and well captured by the 'Case_SeasaltOn' simulation. Over the highly polluted northern Poland region, our sensitivity modelling results show that the 're-distribution effect' can reduce AOD$_{nitrate}$ by about 20-30%, or even up to ∼50% when the sea-salt event is sufficiently strong. Conversely, if we only consider the increase of nitrate mass by introducing sea-salt ('mass-enhancement effect') and ignore the 're-distribution effect', nitrate AOD could increase by ∼8% or even up to ∼30% in a strong sea-salt event. We propose a single parameter, RNS ([NO$_3^-$]/[Na$^+$] in mol mol^{-1}), to describe the competition between sea-salt-induced 're-distribution effect' and 'mass-enhancement effect'. In general, (1) the sea-salt-induced 'mass-enhancement effect' is dominant over oceanic regions and tends to increase AOD$_{nitrate}$~~.~~; the dominance of 'mass-enhancement effect' could take place when RNS is lower than 1; (2) the sea-salt-induced 're-distribution effect' on nitrate PMSD can decrease AOD$_{nitrate}$ by about 10-20% and overwhelm the 'mass-enhancement effect' resulting in a net reduction of AOD$_{nitrate}$~~.~~; this could take place when ~~1 < RNS < 30~~RNS is in the range between 1 and 30; and

(3) the influence of sea-salt aerosol is not significant when RNS is higher than 30. These findings are further confirmed by the sensitivity simulations over North America. The impact of ‘re-distribution effect’ on a global scale is estimated using global simulation of RNS~~, as shown in Fig. 9~~. Significant ‘re-distribution effect’ is expected over Europe, the Gulf of Mexico, Eastern Asia, coastal and offshore regions world-wide, may resulting in reduction of $\mathrm{AOD}_{\mathrm{nitrate}}$ by about 10-20%. This study demonstrates the suppression of AOD and DRF of particulate nitrate by the ‘re-distribution effect’. In addition, the ‘re-distribution effect’ may also reduce the number of cloud condensation nuclei (CCN) by lowering the nitrate concentration in fine particles which are the main contributors to CCN number. The hygroscopicity of coarse sea-salt particles could also be reduced by associating with nitrate, which might suppress cloud droplet activation (Xu and Penner, 2012). Further studies are needed to investigate the influences of ‘re-distribution effect’ on aerosol-cloud interaction and indirect radiative forcing.

5. Implication

This study highlights the impact of the ‘re-distribution effect’ on moderating nitrate cooling and altering the nitrogen deposition efficiency by interacting with natural sea-salt aerosols (Fig. 1). A similar ‘re-distribution effect’ may apply to the heterogeneous reaction and consumption of gaseous organic compounds, sulfuric and nitric acids on natural desert dust (Usher et al., 2003;Ponczek and George, 2018;Dupart et al., 2012;Ravishankara, 1997), although non-volatile particulate sulfate does not shift from fine to the coarse mode aerosols. Uptake of acids by dust particles can shorten their lifetimes and reduce their radiative forcing (Liao and Seinfeld, 2005;Harris et al., 2013;Karydis et al., 2016;Abdelkader et al., 2015), which could be significant over inland areas where sea-salt aerosol is lacking. All ~~this~~these previous studies~~Our results~~ imply the possibility that natural particles (sea-salt aerosol and very likely dust as well) moderate the DRF of anthropogenic aerosols and alter the nitrogen and sulfur~~(very likely sulfur also)~~ deposition efficiency~~ (Fig. 1)~~. We highlight the importance of further study of the inter-actions between natural and anthropogenic aerosols. More comprehensive modelling studies with fully dynamic aerosol mass transfer treatment are needed for improving the assessment of aerosol climate effect accounting for the ‘re-distribution effect’ on a global scale.

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Author contributions

Y. F. C. led the study. Y. F. C. and Y. C. conceived and design the study. Y. C. performed the WRF-Chem model simulations and processed the data. N. M. supported the optical calculation. C. W. supported the kinetic part of the model simulation and result analyses. A. P. and J. L. provided the EMAC global simulation. G. S. carried out the aerosol chemical composition observations at Melpitz. Y. C., Y. F. C. and H. S. interpreted the results. All co-authors discussed the results. Y. C. and Y. F. C. wrote the manuscript with inputs from all co-authors.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Data availability

WRF-Chem model code and FINN fire emissions are openly available for download from the website www2.acom.ucar.edu. NCEP reanalysis data is openly available for download from the website https://rda.ucar.edu/. AERONET and aerosol observational datasets are openly available for download from the websites https://aeronet.gsfc.nasa.gov/ and http://ebas.nilu.no/default.aspx. The European emission inventory is available from AQMEII project (http://aqmeii.jrc.ec.europa.eu/) and EUCAARI project (https://www.atm.helsinki.fi/eucaari/?q=node/3). The global emission inventory is available from EDGAR project (http://edgar.jrc.ec.europa.eu). The results of EMAC global model is available from https://dx.doi.org/10.17635/lancaster/researchdata/297. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supporting Information. Additional data related to this paper should be addressed to and Y.F.C and Y.C.

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Table 1. Configurations of WRF-Chem

Physics	**WRF options**
Micro physics	Lin scheme (Lin, 1983)
Boundary layer	YSU (Hong, 2006)
Surface	Rapid Update Cycle (RUC) land surface model
Shortwave radiation	Goddard shortwave (Chou et al., 1998)
Longwave radiation	New Goddard scheme
Cumulus	Grell 3D
Urban	3-category UCM
Chemistry and Aerosol	**Chem options**
Aerosol module	MOSAIC with 8 bins (Zaveri et al., 2008)
Gas-phase mechanism	CBMZ (Zaveri and Peters, 1999)
Photolytic rate	Fast-J photolysis scheme (Wild et al., 2000)
Sea salt emission	Gong scheme (Gong, 2003)

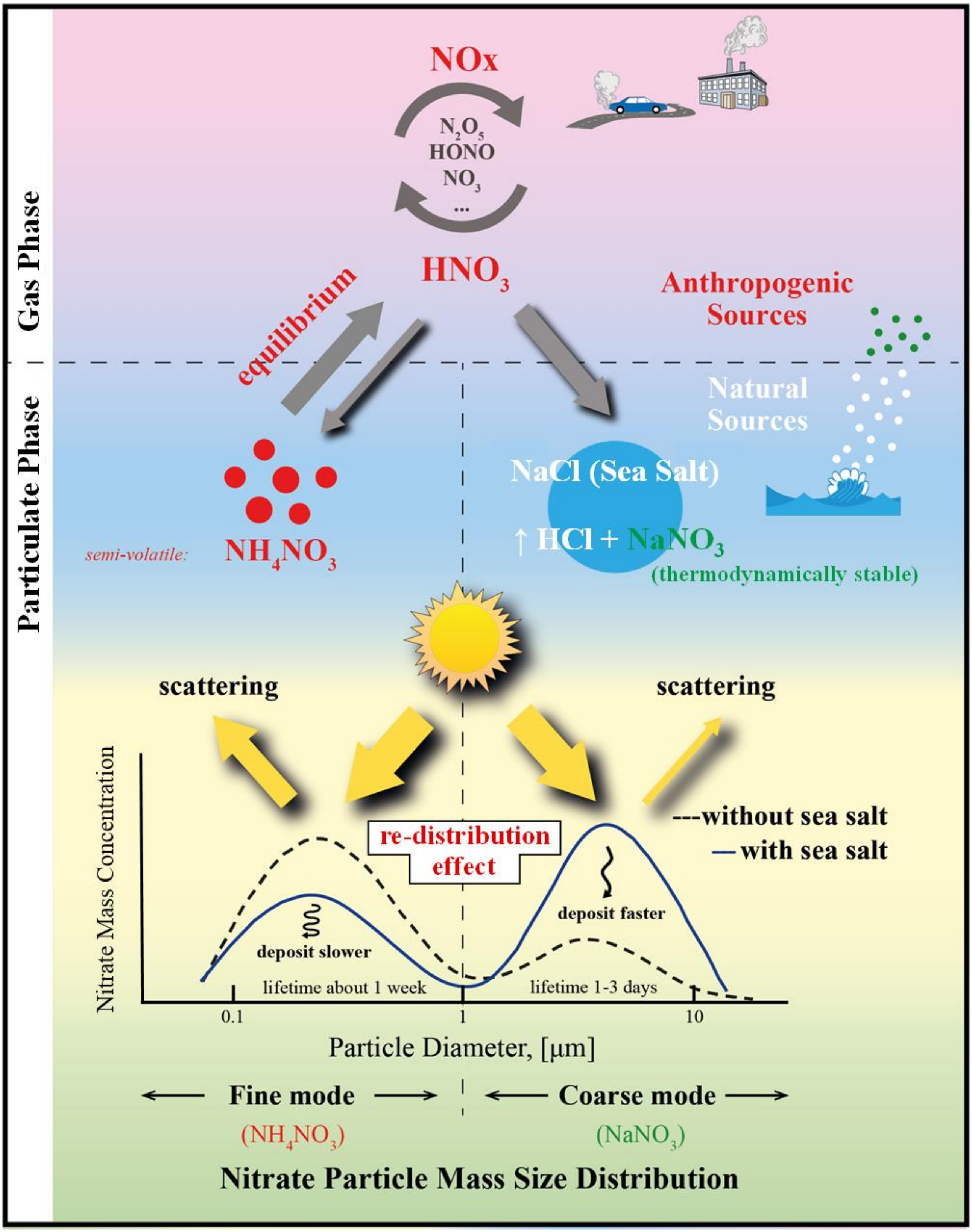


Fig. 1. Concept of the sea-salt aerosol induced 're-distribution effect'.

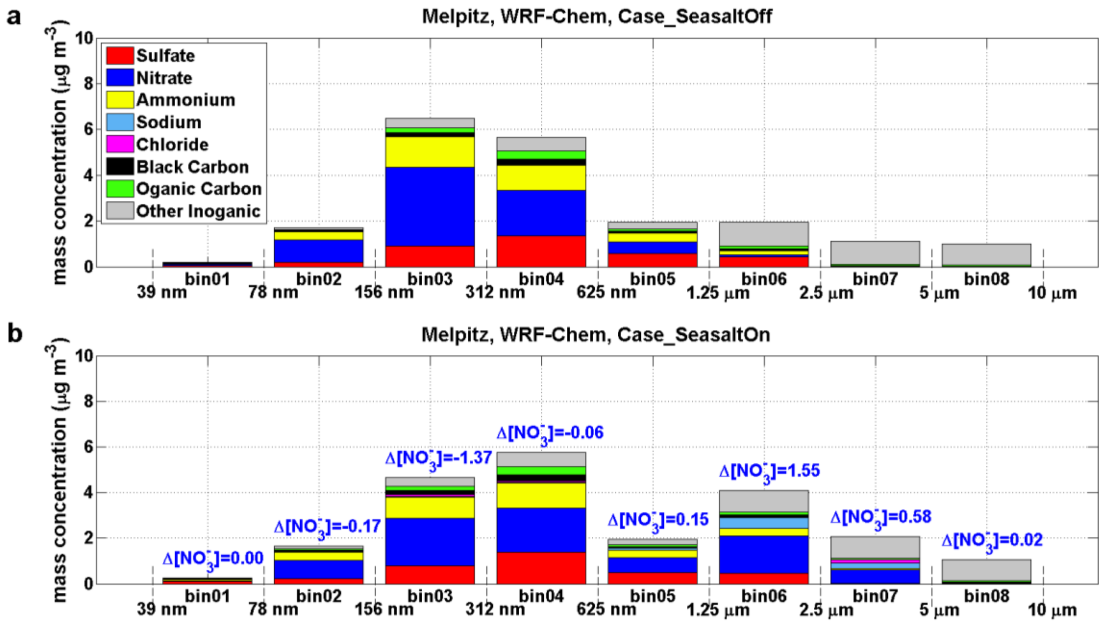


Fig. 2~~S1~~. Model results of mass concentration of each chemical compounds in eight size bins at Melpitz. The results showed here are averaged during 17 September 2013 when marine air masses started approaching Melpitz. Sodium is used as an indicator of sea-salt aerosol. **a**, Result of the ‘Case_SeasaltOff’ (without sea-salt emission). **b**, Result of the ‘Case_SeasaltOn’ (with sea-salt emission). The differences of particulate nitrate mass concentration (Δ[NO_3^-]) in each size bin are marked.

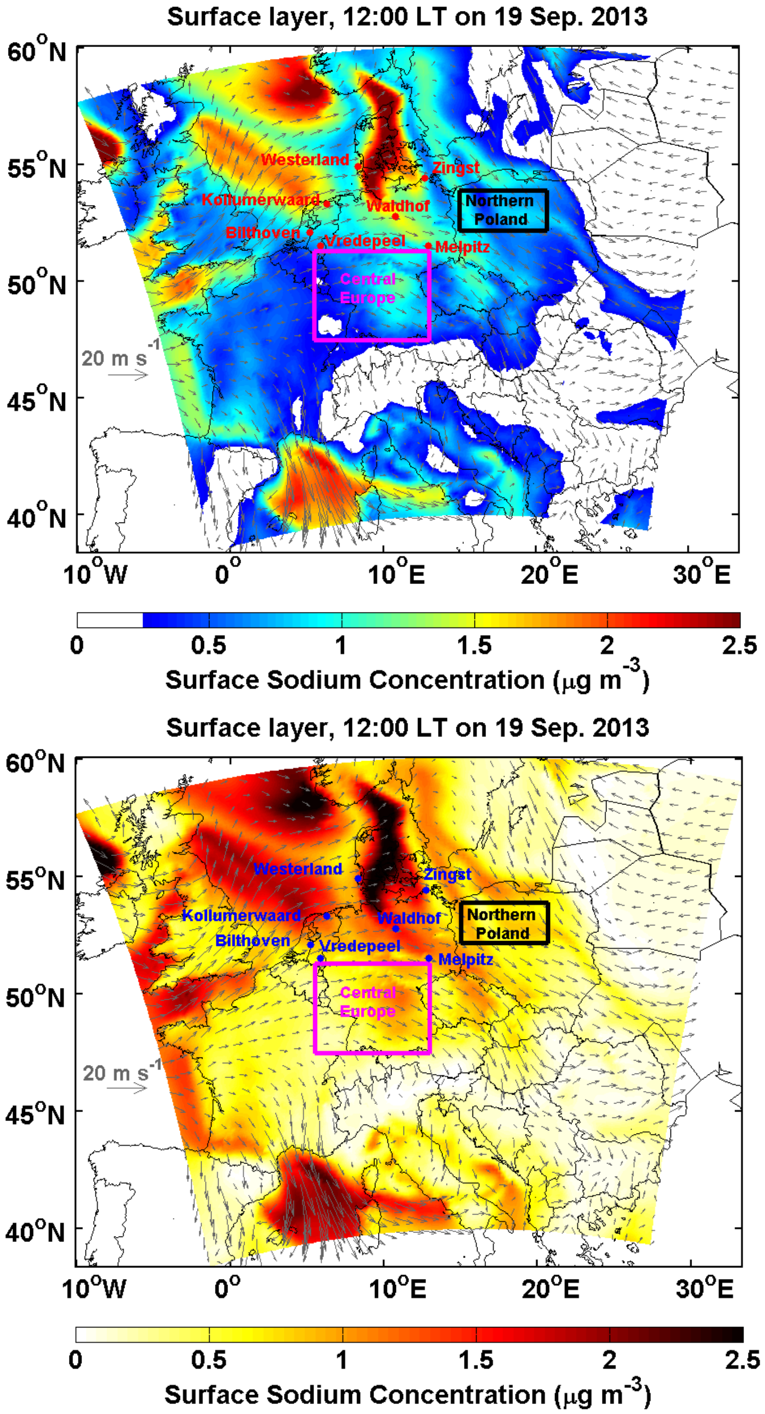


Fig. 3~~2~~. Surface sodium mass concentration over Europe domain at 12:00 local time (LT) on 19 September 2013. The 10-meter wind is indicated by the grey arrows. The results are based on the 'Case_SeasaltOn'. Westerland, Waldhof, Zingst, Bilthoven, Kollumerwaard, Vredepeel, Melpitz, Central Europe and the northern Poland regions are marked.

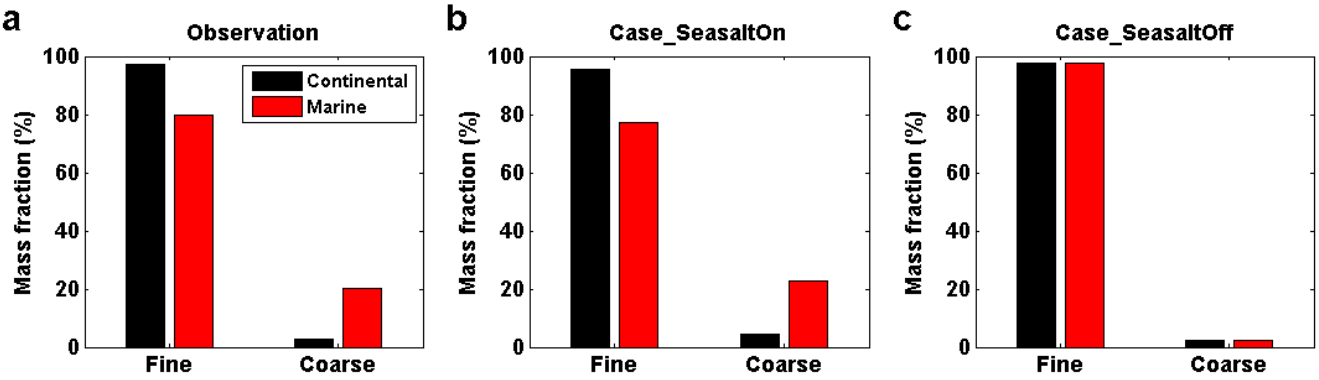


Fig. 4~~3~~. Observed and simulated mass fraction of particulate nitrate in fine and coarse modes at Melpitz, Germany. **a**, Observation based on the Berner impactor measurements. **b**, WRF-Chem 'Case_SeasaltOn' simulation, i.e., with sea-salt emission. **c**, WRF-Chem 'Case_SeasaltOff' simulation, i.e., without sea-salt emission. The results are grouped into continental (black bar) and marine (red bar) air mass types, respectively. According to the size-cuts of the Berner impactor, the size ranges of the fine and coarse mode particles are defined as PM$_{1.2}$ (particles with an aerodynamic diameter smaller than 1.2 μm) and PM$_{1.2\text{-}10}$ (particles with an aerodynamic diameter larger than 1.2 μm and smaller than 10 μm), respectively.

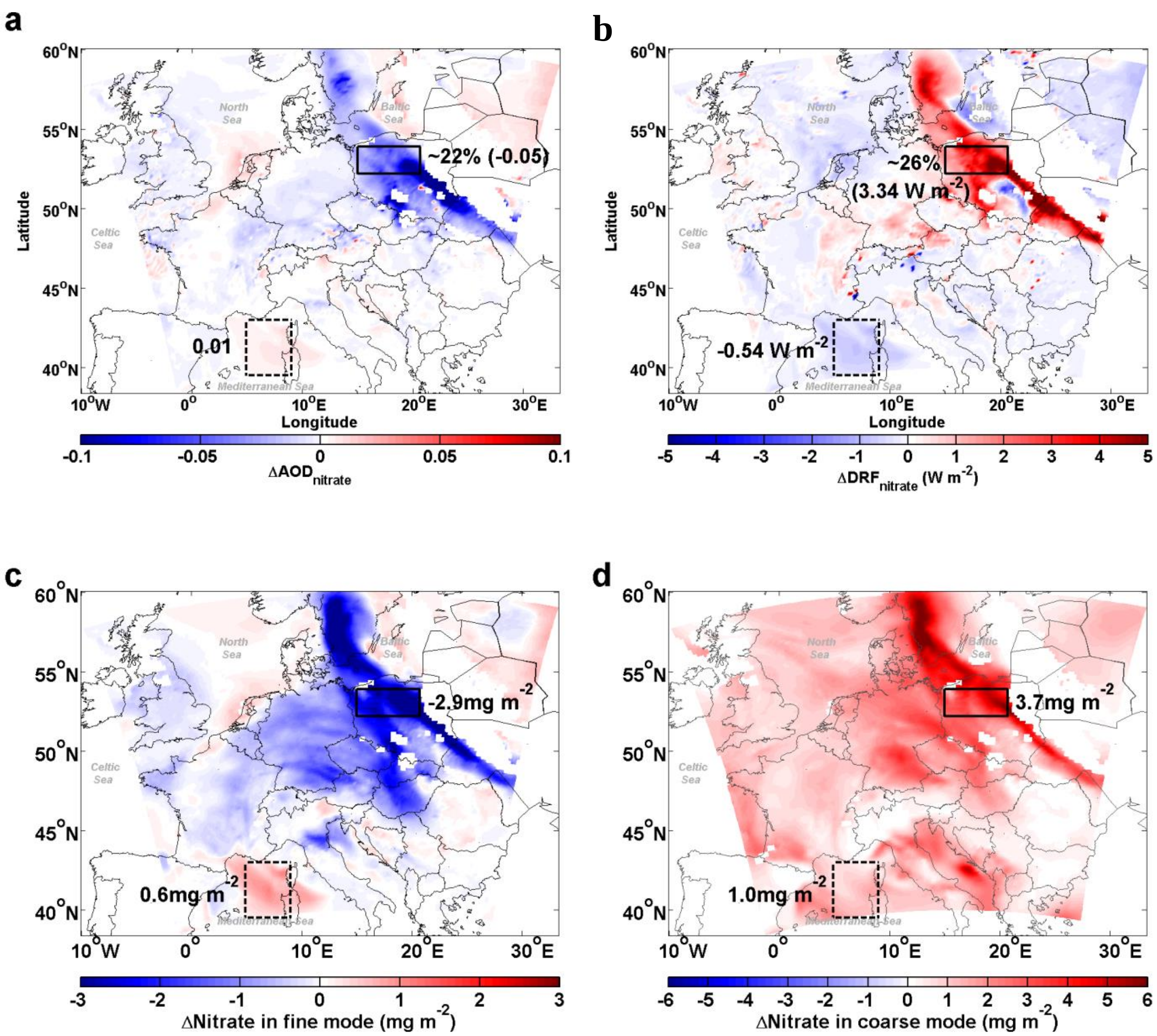


Fig. 54. Influence of sea-salt on the abundance and direct radiative forcing of nitrate. Differences ('Case_SeasaltOn' – 'Case_SeasaltOff') between simulations with and without sea-salt emission in aerosol optical depth (ΔAOD$_{nitrate}$, **a**), direct radiative forcing (ΔDRF$_{nitrate}$, **b**), and column loading of nitrate (ΔNitrate) for the fine (**c**) and coarse (**d**) mode particles, during daytime, i.e., 07:00-16:00 local time (LT) on 19 September 2013. The northern Poland and Mediterranean regions are marked by boxes with solid and dashed black frames, respectively.

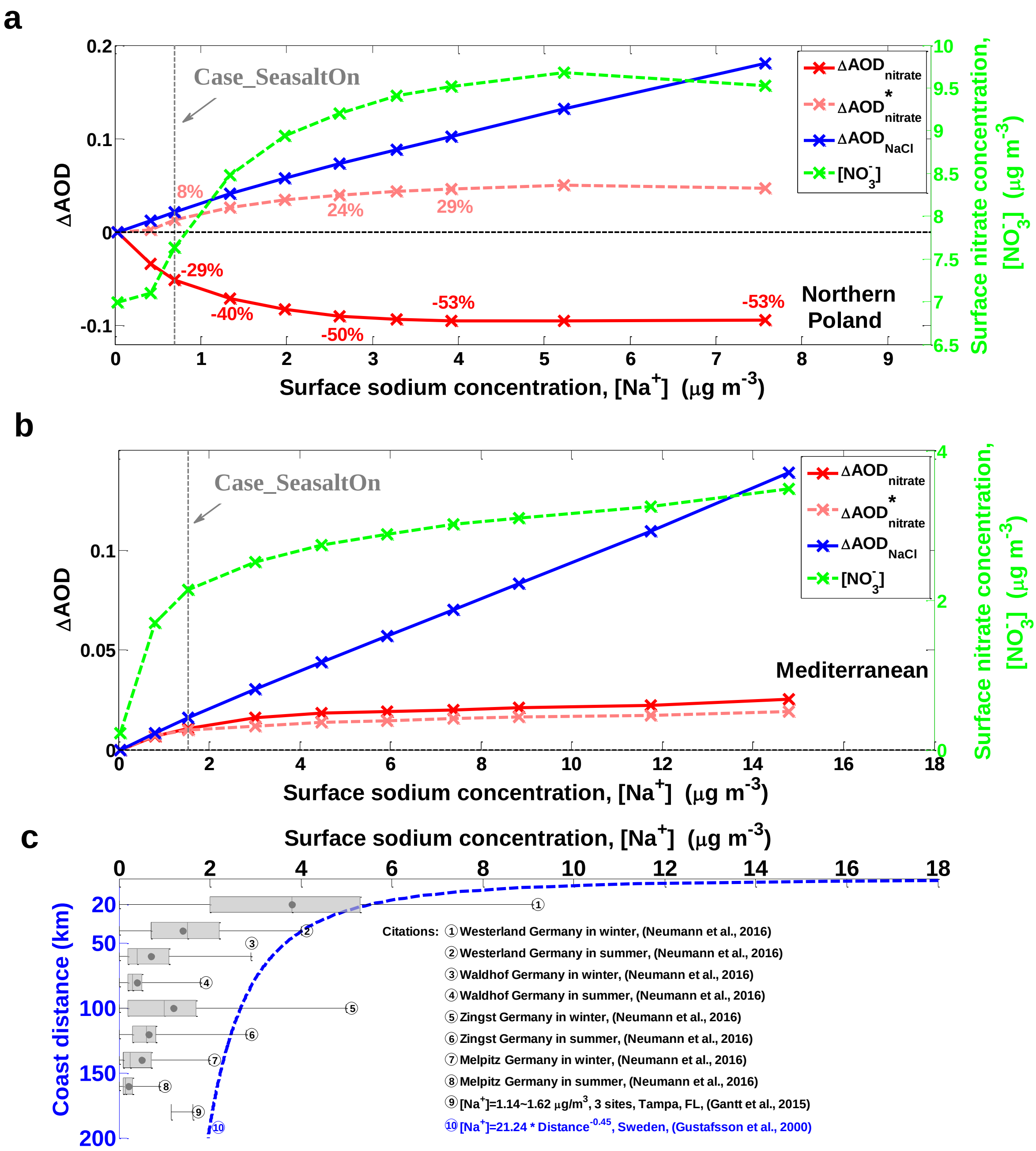


Fig. 6~~5~~. Sensitivity of aerosol optical depth (ΔAOD) as a function of sodium mass concentration ($[Na^+]$). Differences between the 'Case_SeasaltOff' and sensitivity cases (sea-salt emission with different scaling factors) for different aerosol components, i.e., nitrate ($\Delta AOD_{nitrate}$) and sea-salt (ΔAOD_{NaCl}): ΔAOD (sensitivity case – ' Case_SeasaltOff') versus $[Na^+]$ over northern Poland (**a**) and Mediterranean regions (**b**), respectively. The model results shown here are averages over a sea-salt event during daytime (07:00-16:00 LT) on 19 September 2013. The results of surface $[NO_3^-]$ are indicated by the green dashed line. Here, the 'Case_SeasaltOff' is the reference case and the 'Case_SeasaltOn' is marked. Note: $\Delta AOD^*_{nitrate}$ (pink dashed line) indicates the ΔAOD of nitrate calculated by re-allocating nitrate mass into different size bins according to the normalized nitrate particle mass size distribution simulated in 'Case_SeasaltOff' (i.e., without 're-distribution effect'). **c,** The measured $[Na^+]$ at different sites over Sweden as a function of coast distance, and in Germany (marked in Fig. 3~~2~~) and US. The box-whisker plots of the references ①-⑧ indicate the median, mean (black dot), 25% percentile, 75% percentile, maximum and minimum. The error bar of the reference ⑨ indicates the range. The blue dashed line of the reference ⑩ indicates the statistically empirical function of $[Na^+]$ with the distance from coast, based on the network measurements of 16 sites in Sweden.

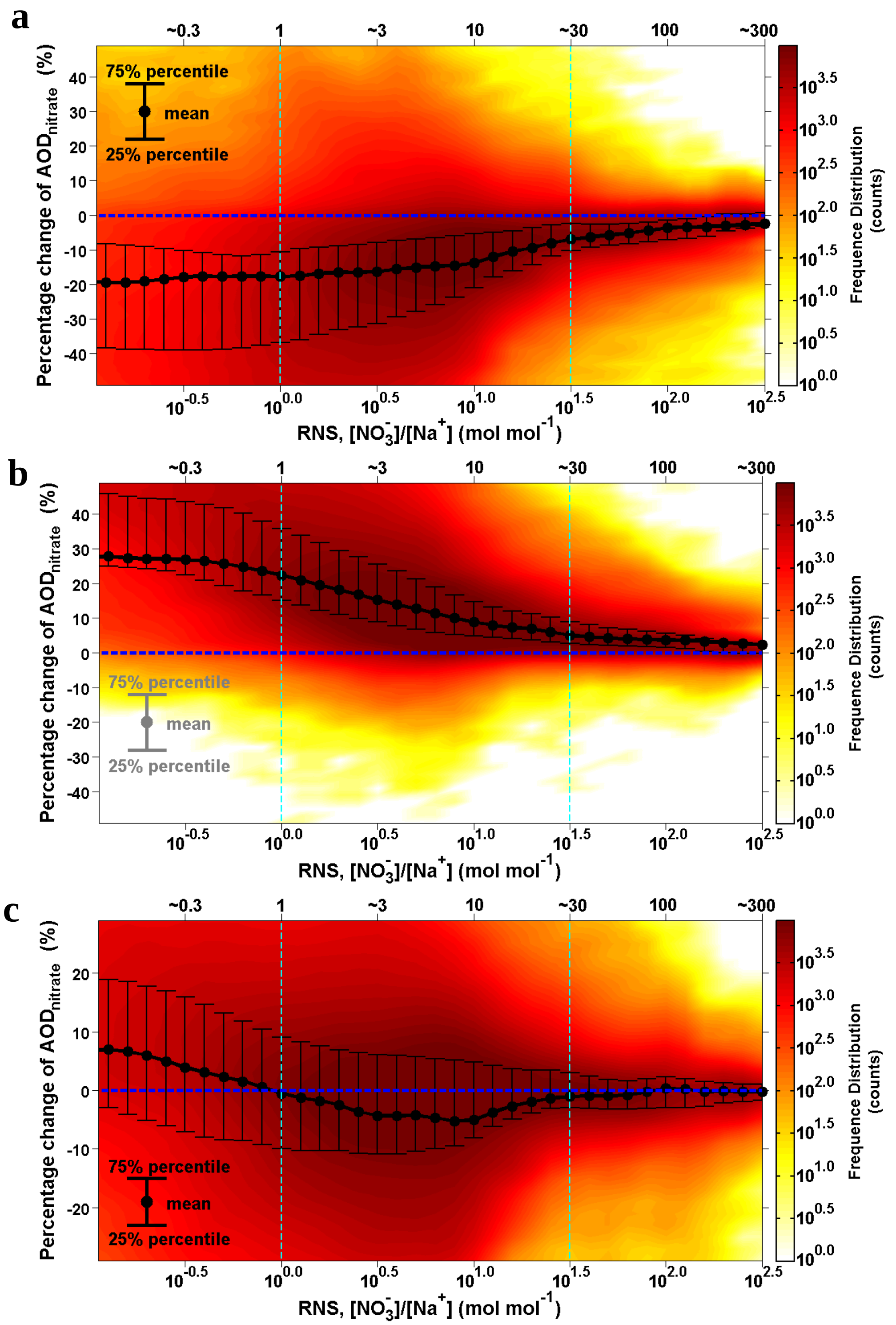


Fig. 7. Intensity of 're-distribution effect' as a function of molar ratio between surface fine nitrate and total sodium (RNS) over European domain. (a) The intensity of the 're-distribution effect' is calculated as the difference in percentage between $AOD_{nitrate}$ and $AOD^*_{nitrate}$ in the 'Case_SeasaltOn'; **(b)** the intensity of 'mass-enhancement effect'. The black dots indicate the mean values; the upper and lower error bars indicate the 75% and 25% percentile, respectively; and **(c)** the net effect of 'mass-enhancement' and 're-distribution';The colour indicates the frequency distribution (i.e., how many counts) of the hourly model results over entire Europe domain during 16-20 September 2013. The coverage of model results between the two light blue dashed lines is ~70%.

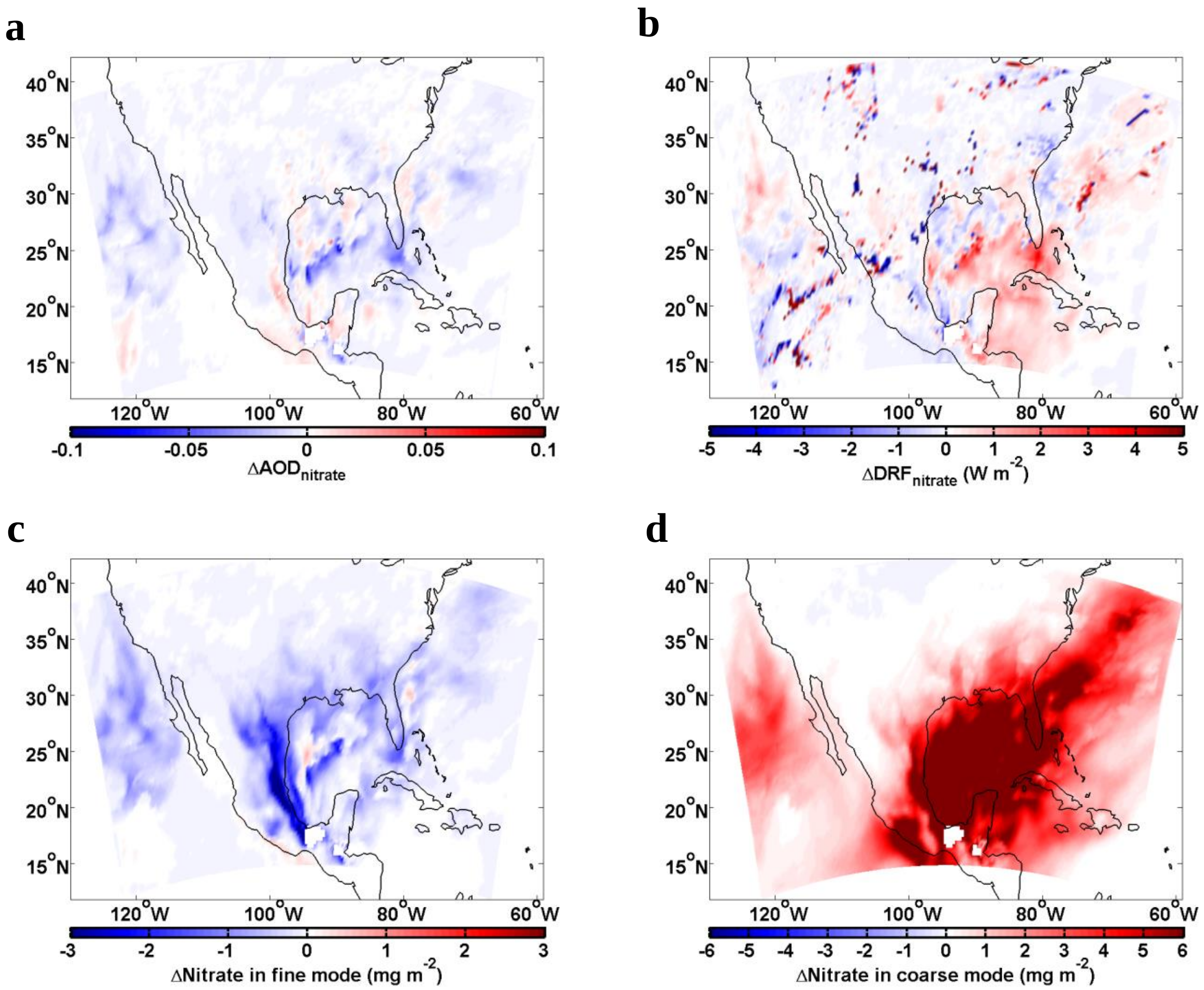
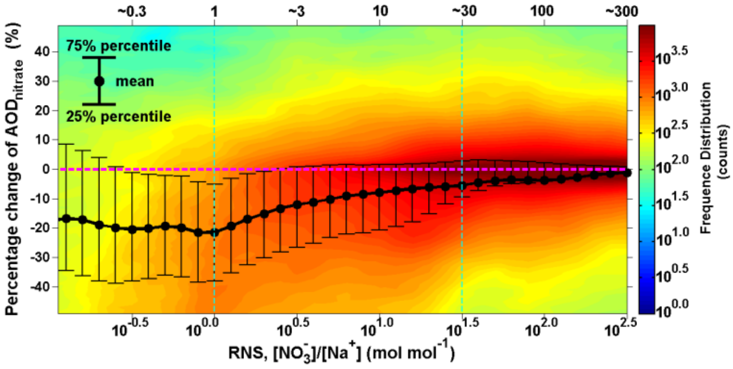


Fig. 8~~7~~. Influence of sea-salt aerosol on the abundance and direct radiative forcing of nitrate (similar as Fig. 5~~4~~). Differences (‘Case_SeasaltOn’ – ‘Case_SeasaltOff’) between simulations with and without sea-salt emission in aerosol optical depth ($\Delta AOD_{nitrate}$, **a**), direct radiative forcing ($\Delta DRF_{nitrate}$, **b**), and column loading of nitrate (ΔNitrate) for the fine (**c**) and coarse (**d**) mode particles. The modelled results showed here are averaged during daytime over North America domain, i.e., 16:00-22:00 (UTC) on 10-17 January 2015.



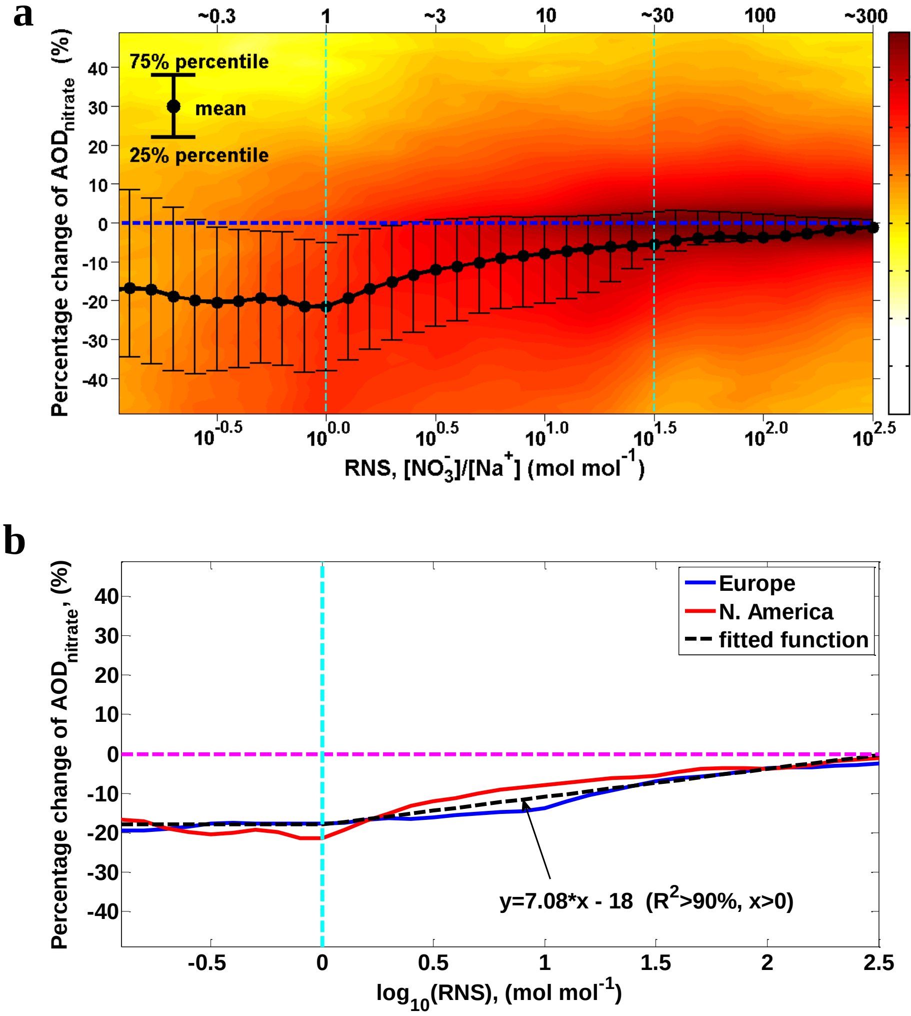
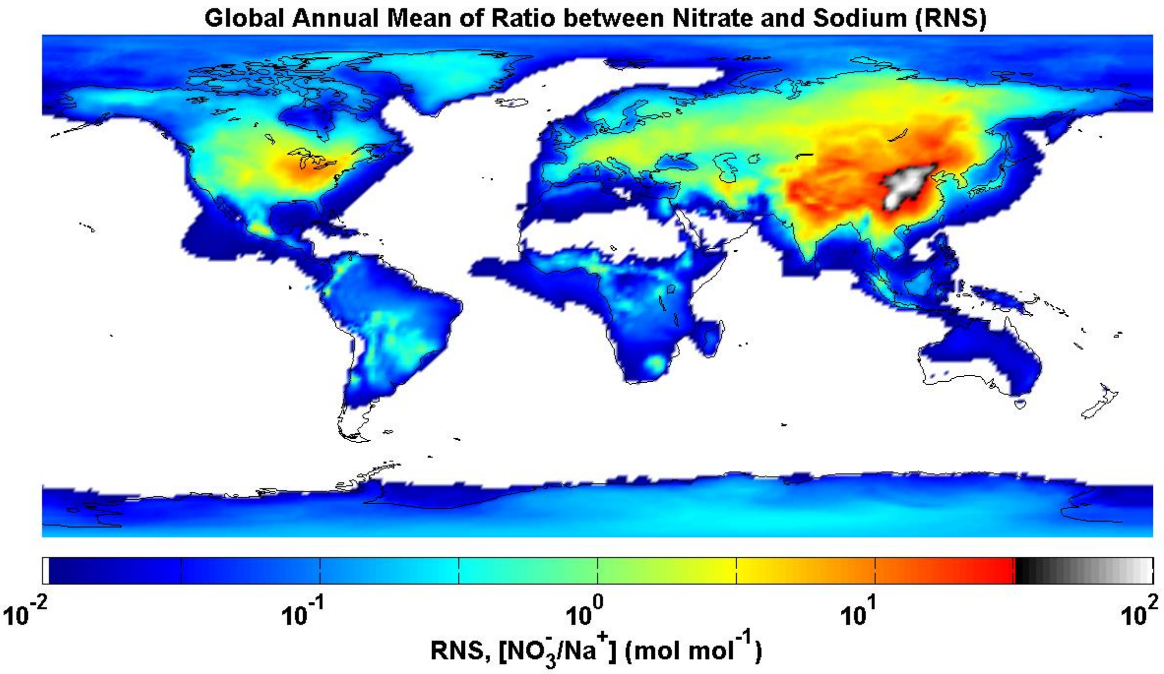


Fig. 9~~8~~. Intensity of 're-distribution effect' as a function of molar ratio between surface fine nitrate and total sodium (RNS). (a) The intensity of 're-distribution effect' over North American domain, similar as Fig. ~~6~~7~~b~~a, ~~. (a) The intensity of 're-distribution effect' is~~ calculated as the difference in percentage between $AOD_{nitrate}$ and $AOD^*_{nitrate}$ in the 'Case_SeasaltOn'. $AOD^*_{nitrate}$ indicates the $AOD_{nitrate}$ calculated by re-allocating nitrate mass into different size bins according to the normalized nitrate particle mass size distribution simulated in 'Case_SeasaltOff' (i.e., without 're-distribution effect'). The black dots indicate the mean values; the upper and lower error bars indicate the 75% and 25% percentile, respectively. The colour indicates the frequency distribution (i.e., how many counts) of the hourly model results over entire North America domain during 10-17 January 2015. (b) The median possibility of the percentage change of $AOD_{nitrate}$ as a function (first-order approximation) of RNS.



~~**Fig. 9. The global distribution of annual mean RNS, simulated with the EMAC model.** The regions with RNS smaller than 0.01, i.e., negligible particulate nitrate loading, are white.~~

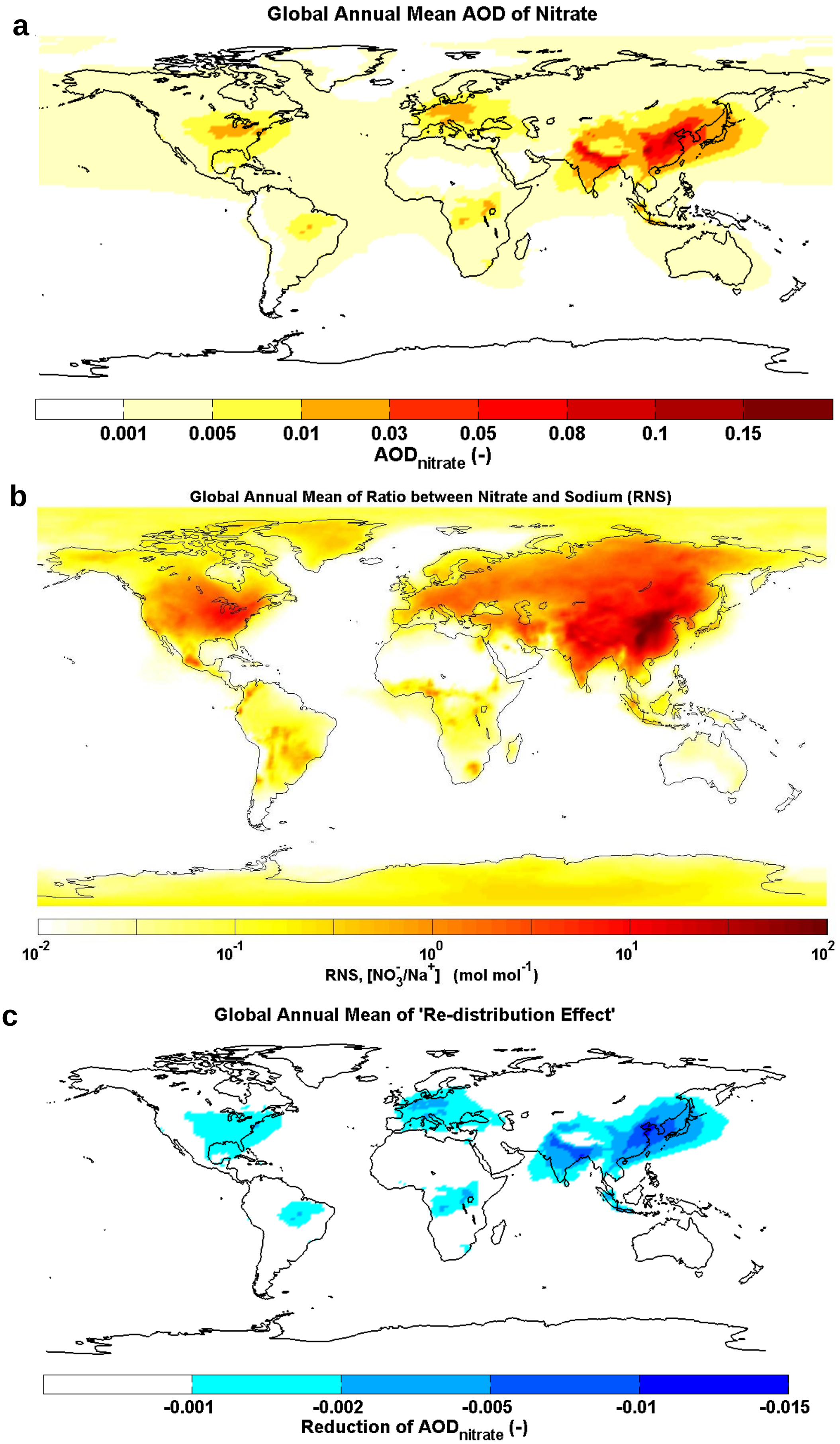


Fig. 10~~9~~. The global distribution of annual mean AOD$_{nitrate}$ (a), RNS (b) and reduction of AOD$_{nitrate}$ associated with the 're-distribution effect' (c). The results of (a, b) are simulated with the EMAC model, the results of (c) are estimated from the first-order approximation in Fig. 9~~8~~b.

Supplementary Information for

Natural sea-salt emissions moderate the climate forcing of anthropogenic nitrate

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Section S1. Modelling of particulate nitrate in global models

Nitrate is a major anthropogenic aerosol component exerts large radiative scattering (cooling) effect and is expected to dominate the aerosol cooling by the end of the century (Bellouin et al., 2011;Adams et al., 2001;Hauglustaine et al., 2014). However, in the IPCC estimation of climate change, nearly all CMIP5 (Coupled Model Intercomparison Project phase 5) global models (IPCC, 2013) and about half of ACCMIP (The Atmospheric Chemistry and Climate Model Intercomparison Project) global models (Shindell et al., 2013) did not take nitrate into consideration. Generally, models with a modal aerosol approach of M7 (an aerosol module, Vignati et al., 2004) or GLOMAP (Global Model of Aerosol Processes, Mann et al., 2010) do not consider nitrate, although some modified models might add nitrate in M7 and GLOMAP. For example, EMAC (ECHAM5/MESSy Atmospheric Chemistry model, Karydis et al., 2016) adopts an aerosol module similar as M7 and includes particulate nitrate (details below); the representation of nitrate is under developing for GLOMAP and waiting for activation in Hadley Centre Global Environmental Model (Bellouin et al., 2013).

The chemical and thermodynamic equilibrium of semi-volatile ammonium nitrate, i.e., its mass transfer between gas and particulate phases and partitioning in different sizes, appears to be crucial for modelling the size distribution and climate effect of particulate nitrate. Fully dynamic mass transfer approach, which considers the diversity of particulate chemical compositions and mass transfer flux across different particle sizes dynamically, is the best method to address this issue (Capaldo et al., 2000;Zaveri et al., 2008). However, it is computationally very expensive for the fully dynamic approach, due to the large difference in equilibrium time scale of different particle size bins, multicomponent and etc., see detailed description in the section 3 of Zaveri et al. (2008). The aerosol module MOSAIC (Model for Simulating Aerosol Interactions and Chemistry, Zaveri et al., 2008), was developed to address dynamic gas-particle partitioning in a relatively efficient way. It agreed well (Zaveri et al., 2008) with the benchmark equilibrium model AIM (Aerosol Inorganics Model, Wexler and Clegg, 2002) and was coupled into the regional chemical transport model WRF-Chem. Bulk equilibrium or ‘hybrid method’ (Capaldo et al., 2000) and other simplifications have been adopted for nitrate partitioning treatment in some global models for computational efficiency, but it is difficult for them to capture the ‘re-distribution effect’ of nitrate, as described following.

In the GISS (Goddard Institute for Space Studies) model (Liao and Seinfeld, 2005), the gas-particle transfer of ammonium nitrate is represented by a bulk equilibrium approach over land. To calculate nitrate direct radiative forcing (DRF), the bulk nitrate mass is distributed into different size bins with a pre-fixed lognormal distribution. They are thus only able to take into account the impact of enhanced total nitrate mass concentration, but not the competition for nitric acid between fine and coarse modes nor the dynamic impact on aerosol number/mass size distributions. For example, with GISS GCM II global model, Liao and Seinfeld (2005) reported that heterogeneous reactions on the surface of natural source aerosols (including sea-salt and dust) increase the column burdens of particulate nitrate by 30-50% and thus lead to an strengthening of anthropogenic nitrate DRF by 0-2 W m^{-2} over Europe.

Xu and Penner (2012) investigated nitrate global DRF with the IMPACT (Integrated Massively Parallel Atmospheric Chemical Transport) global model, by treating the gas-particle transfer with a ‘hybrid’ method (Capaldo et al., 2000). It firstly employed a bulk equilibrium method for fine mode followed by a dynamic mass transfer method for coarse mode. This approach has limitation in considering the competitive consumption of gaseous precursors between fine and coarse mode particles, and is difficult to capture the continuous dynamic evolution of particles size and compositions distributions (Zaveri et al., 2008). Xu and Penner (2012) showed that sea-salt associated nitrate is one of the most important chemical pathway for the secondary formation of particulate nitrate, especially over Europe, ocean and coastal regions; however they mainly focused on the indirect radiative forcing of nitrate, the DRF of sea-salt associated-only nitrate was not well investigated.

Myhre et al. (2006) identifies the deficiency in Liao and Seinfeld (2005) and pointed out that sea-salt aerosol will deplete HNO_3 and reduce AOD of fine mode nitrate. Myhre et al. (2006) used the Oslo CTM2, a global chemistry model off-line coupled with a meteorological module, to illustrate the impacts of sea-salt aerosol on fine mode nitrate and its AOD. The modelling study was based on state-of-the-art algorithms in 2006 and made some simplified assumptions to facilitate computational efficiency. For example, it was assumed that fine particles are entirely comprised by sulfate and coarse particles by sea-salt aerosol; the later on condensed fine mode ammonium nitrate was assumed to be externally mixed with a prefixed lognormal size distribution in optical calculation. This simplification improves computational efficiency but reduces the multicomponent level. The Equilibrium Simplified Aerosol Model (EQSAM, Metzger et al., 2002a;Metzger et al., 2002b) was implemented twice to solve the thermodynamic equilibrium firstly for fine mode and then followed by the coarse mode. However, to reduce the computational burden for a global model, the fully dynamic mass transfer between particle sizes was not considered in the study. With the bulk equilibrium method (EQSAM) and assuming an instant equilibrium for both fine and coarse mode particles, the ‘re-distribution effect’ of nitrate could be overestimated since the coarse mode needs extended time to reach equilibrium (Myhre et al., 2006). Myhre et al. (2006) evaluated that the depletion of HNO_3 by sea-salt aerosol may reduce 25% of $AOD_{nitrate}$ in fine mode on a global scale, which is consistent with the upper limit of our estimation for Europe.

ISORROPIA (an aerosol thermodynamic model, Nenes et al., 1998) is adopted in the GEOS-Chem global CTM model, which consider particles as a bulk for the equilibrium. The partitioned nitrate is then proportioned to each size bin according to sulfate mass (Yu and Luo, 2009). In INCA (Interaction with Chemistry and Aerosols) model, the nitrate irreversibly condenses on particle surface (Bauer et al., 2004), therefore no equilibrium between gas and particulate phases. There is only accumulation mode nitrate in HadGEN2 model (the Earth system model of the UK Met Office Hadley Centre, Bellouin et al., 2011). Therefore, the ‘re-distribution’ of pre-existing fine mode ammonium nitrate to sea-salt aerosol surface cannot be captured by these models.

EMAC adopts a modal aerosol approach similar to M7, with modification to include particulate nitrate (Karydis et al., 2016). It treats gas-particle partitioning with GMXe (Global Modal-aerosol eXtension, Pringle et al., 2010), and calculates the partitioning process in two stages. First, the amount of gaseous species which is able to kinetically condense on each mode is estimated, based on diffusion limited condensation. Second, ISORROPIA or EQSAM (choose either of them) is employed for thermodynamic calculation in each mode separately, assuming instant equilibrium between gas and particulate phase. The competition of existing nitric acid between fine and coarse modes can be partly considered in this treatment. However, ISORROPIA and EQSAM are both bulk approaches, and the diversity of components in different particle sizes is not considered. In the EMAC model, the association of nitrate with fine and coarse mode particles is considered separately. When abundant sea-salt aerosol mixes with a nitrate-rich air mass, the ambient gaseous precursors may not suffice for condensation. The evaporation of fine mode ammonia nitrate can complement the shortage of gaseous species, and a significant ‘re-distribution effect’ occurs. A fully dynamic mass transfer approach would provide more insight in the ‘re-distribution effect’.

Section S2. WRF-Chem simulation

The WRF-Chem model was driven by NCEP reanalysis data (1° × 1° resolution and provided every 6 hours), including the Final Analysis Operational Global Analysis (http://rda.ucar.edu/datasets/ds083.2/) and the sea surface temperature datasets (http://polar.ncep.noaa.gov/sst/). The first two days were spin-up runs for simulations in this study. The nudging is carried out in every 6 hours for meteorological conditions, including wind, temperature and moisture.

The inventory, provided by TNO for the EUCAARI project (Kulmala et al., 2011), was adopted for the elemental carbon anthropogenic emission, with exclusion of point sources over Germany due to their remarkable uncertainties (Chen et al., 2016b). The hourly Fire INventory from NCAR (FINN, Wiedinmyer et al., 2011), with a horizontal resolution of 1 km, was employed. Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2006) was on-line coupled to provide biogenic emissions.

In this study, dust emission was not considered, because of its negligible contribution to total particle mass concentration during HOPE-Melpitz (Chen et al., 2016a) campaign, and besides, large uncertainty was reported for the parameterization of the dust emission in WRF-Chem (Saide et al., 2012).

The 'Gong' sea-salt aerosol emission scheme (Gong, 2003) was adopted with total sea-salt aerosol emission been reduced to 10% in the 'Case_SeasaltOn' (Chen et al., 2016a). The modelled sea-salt mass concentrations were in good agreements with measurements over coastal region from European Monitoring and Evaluation Programme (EMEP, http://www.emep.int), with a factor (and correlation coefficient) of 0.85 (0.67), 1.16 (0.80) and 0.83 (0.87) respectively for Bilthoven, Kollumerwaard and Vredepeel (Fig. S3~~2~~).

Section S3. Comparison between AERONET measurement and modelled AOD results

The modelled aerosol optical depth (AOD) was evaluated against the AERONET dataset (AErosol RObotic NETwork, http://aeronet.gsfc.nasa.gov/, Level 2.0) over Europe. The direct (collimated) solar radiation observed by sun photometer was used to derive the AOD, which were pre- and post-field calibrated, manually inspected and automatically cloud cleared. The AOD at 550 nm wavelength was derived from the 500 nm wavelength data and the Ångström index in AERONET dataset. Please find more details about AERONET in http://aeronet.gsfc.nasa.gov/.

The simulated AOD (550 nm wavelength) of the ‘Case_SeasaltOn’ was validated with the AERONET AOD measurements over Europe during 10-20 September 2013. The comparison was made in the daytime under clear-sky condition, when AERONET measurements were available, the highest AOD was found in the inland European region by both simulated and measured AOD, followed by the coastal regions, whereas the lowest AOD was found over Alpine regions. Generally, the pattern of AOD spatial distribution can be captured by model (R=0.64), although it was overall overestimated with a geometric mean ratio (GMR) value of 1.7. Despite of some shortcomings of AOD modelling, the general performance is satisfactory and in line with previous studies (Li et al., 2013;Xu and Penner, 2012). The overestimation of AOD was reduced in our ‘Case_SeasaltOn’ (sea-salt emission in a factor of 1) compared with Chen et al. (2016a), which reported an overestimation of AOD with GMR of 2.3 (F-CASE, sea-salt emission in a factor of 10) and 1.8 (R-CASE, sea-salt emission in a factor of 0.5). The reduction of sea-salt aerosol contributes to the shrink of AOD when compare with the reported F-CASE, however, reduction of sea-salt aerosol should not be the reason of decreasing GMR when compare with the R-CASE. The ‘re-distribution effect’ of nitrate particle mass size distribution could be the reason for this.

Section S4. Competition between ‘re-distribution effect’ and ‘mass-enhancement effect’

The direct radiative forcing (DRF) of aerosol is strongly related with its aerosol optical depth (AOD) (Wang et al., 2014). During daytime on 19 September when marine air masses brought sea-salt aerosol to northern Poland, the nitrate AOD significantly decreased as a function of sea-salt mass concentration ($[Na^+]$), due to the sea-salt-induced ‘re-distribution effect’ on nitrate particle mass size distribution (PMSD, Fig. 5~~4~~

and 6~~5~~a). As shown in Fig. 7a~~b6~~, the ‘re-distribution effect’ can averagely reduce AOD of nitrate ($AOD_{nitrate}$) by ~20% when abundant sea-salt present with a molar ratio between particulate nitrate and sodium (RNS) smaller than 1, and reduce by 10-20% over regions where relatively high nitrate loading present with 1< RNS < 30. On the other hand, the sea-salt-induced increase of particulate nitrate mass concentration ([NO_3^-], ‘mass-enhancement effect’) may enhance $AOD_{nitrate}$ (Liao and Seinfeld, 2005). The $AOD_{nitrate}$ could increase by up to 30% averagely by introducing sea-salt if only ‘mass-enhancement effect’ is considered (Fig. 7b~~c~~~~S6b~~). Fig. ~~S6~~7~~a~~c shows the net effect as competition between the sea-salt-induced ‘re-distribution’ and ‘mass-enhancement’ effects. The clear-sky results over the entire European domain were used for the statistical analysis when sea-salt aerosol was transported over the European continent during 16-20 September. In sea-salt-rich air masses (RNS < 1), which mostly appear over the oceanic regions, the net effect tends to increase $AOD_{nitrate}$ (as shown in Fig. 5~~4~~a and Fig. 6~~5~~b). Conversely, the ‘re-distribution effect’ tends to overwhelm the ‘mass-enhancement effect’ resulting in a net effect with decreasing $AOD_{nitrate}$ when the RNS is higher than 1. This is because a considerable amount of particulate nitrate is shifted from the fine to the coarse mode (‘re-distribution effect’) by the heterogeneous reactions on the surface of sea-salt aerosol and change of gas-particle equilibrium (Fig. 1). The largest mean value of $AOD_{nitrate}$ net reduction over Europe was ~6% when RNS is ~10, with ~25% probability of $AOD_{nitrate}$ net reduction by more than 10% (Fig. ~~S6~~7~~a~~c). The mean value of reduction starts to decrease as RNS increases when RNS > 10. A possible explanation is that air masses with high [NO_3^-] are accompanied by a high level of anthropogenic NOx, and hence more sodium chloride is consumed by the sea-salt-induced ‘mass-enhancement effect’, outcompeting the ‘re-distribution’ of nitrate PMSD and thus decreasing $AOD_{nitrate}$. When RNS is higher than 30, there is no significant change in $AOD_{nitrate}$ (~50% probability for both increasing and decreasing), because of the very limited loading of sea-salt aerosol. In general, (1) the sea-salt-induced ‘mass-enhancement effect’ is dominant over oceanic regions and tends to increase $AOD_{nitrate}$ when RNS is lower than 1; (2) the sea-salt-induced ‘re-distribution effect’ on nitrate PMSD can decrease $AOD_{nitrate}$ by about 10-20% and overwhelm the ‘mass-enhancement effect’ resulting in a net reduction of $AOD_{nitrate}$ when 1 < RNS < 30; and (3) the influence of sea-salt aerosol is not significant when RNS is higher than 30.

Section S5. Moderating total aerosol cooling by the ‘re-distribution effect’ on nitrate

The reduction of nitrate AOD may even lead to a decrease of total aerosol radiative effect; however, it is non-monotonic with sea-salt aerosol loading due to competition between the increasing of sea-salt AOD and decreasing of nitrate AOD. As shown in Fig. S6~~5~~b, the total aerosol AOD (AOD_{total}, black line indicates the change of AOD_{total}) firstly decreases with increasing [Na^+] and reaches the largest reduction of 0.03 (~11%) when [Na^+] was about 0.4-0.6 μg m^{-3} in the ‘Case_SeasaltOn’. Later, with further enhanced sea-salt aerosol emissions, the increase of sea-salt AOD (AOD_{NaCl}) compensates the decrease of $AOD_{nitrate}$ and dominates the change of AOD_{total}, eventually leading to a slow increase of AOD_{total} up to ~10% with a sea-salt aerosol emission factor of 10. Our results indicate that the natural sea-salt aerosol may reduce the total light extinction when marine air masses mix with nitrate-rich air masses and sea-salt concentration is still relatively low. In view of Europe, this critical [Na^+] is estimated to be ~4-7 μg m^{-3}, see Fig. S6~~5~~b and similar results at Melpitz/Leipzig (not shown here). For more polluted regions, such as the North China Plain and India, the critical [Na^+] is expected to be higher. The measurements of [Na^+] in Germany (Neumann et al., 2016), Florida USA (Gantt et al., 2015), and Sweden (Gustafsson and Franzén, 2000), where considerable amounts of sea-salt associated nitrate (about 1-3 ppbv, about 35-90% of total nitrate) are found (Xu and Penner, 2012), are summarized in Fig. 6~~5~~c. Broadly speaking, the [Na^+] in these regions are in the range of 0-5 μg m^{-3}, with very rare exceptions at Westerland Germany (a coastal station) in winter. A similar level of sea-salt associated nitrate is reported by a regional model study over coastal regions of China and western Pacific Ocean (Li et al. 2018). This implies that the reduction of total aerosols light extinction due to sea-salt-induced ‘re-distribution effect’ may be commonly observed over the European continent, the coastal and outflow regions of US and China.

Section S6. Uncertainty in estimation of $\Delta AOD_{nitrate}$ resulted from 're-distribution effect'

Our 'Case_SeasaltOff' and 'Case_SeasaltOn' simulations overestimate particulate nitrate mass concentration by a factor of ~5 compared with filter measurements at Melpitz. Overestimation of particulate nitrate is a common issue of simulations over Europe. Lecœur and Seigneur (2013) performed a 9-year simulation over Europe using Polyphemus/Polair3D model, validated model results with observations from EMEP stations and compared their results with AQMEII models (including CHIMERE, CALIOPE-EU, WRF-Chem and CMAQ). They found that all models overestimate particulate nitrate over Europe. Polyphemus/Polair3D model overestimates by a factor of 1-3 during summer (Lecœur and Seigneur, 2013); WRF-Chem overestimates by a factor of 3-6 during September (Tuccella et al., 2012); CHIMERE performs the best among all models but still overestimates nitrate by a factor of 1.7 during September-November (Péré et al., 2010). Another recent study carried out European simulation over period of 1994-2014 using a regional climate model (ALADIN-Climate) and validated nitrate simulation with surface observations from 33 EMEP stations (Drugé et al., 2019). They found that, i) nitrate starts to play the most important role on aerosol radiative forcing over Europe since 2005; ii) their model is able to reproduce surface distribution of nitrate however generally overestimate nitrate by factors of 2-5. The above results indicate that nitrate simulation in our model is within a comparable range with previous studies.

The 're-distribution effect' on nitrate is captured well in our simulations (Fig. 4~~3~~), although particulate nitrate mass is overestimated. This overestimation can lead to a more conservative assessment of $\Delta AOD_{nitrate}$ (surrogate of $\Delta DRF_{nitrate}$), which is resulted from the 're-distribution effect' (see Fig. 7a~~b6~~). But, this overestimation of nitrate would not have significant influence on the assessment of percentage change in $AOD_{nitrate}$. Remarkable 're-distribution effect' occurs in the regime of $1 < RNS < 30$, where consists of ~70% European results and $AOD_{nitrate}$ is reduced by about 10-20% (Fig. 7a~~b6~~). The percentage change of $AOD_{nitrate}$ decreases very slowly as increase of RNS, which is proportional to nitrate mass concentration. A smaller $[NO_3^-]$ (or RNS) by a factor of 5 generally leads to a greater decreasing of $AOD_{nitrate}$ in percentage by less than 10% (Fig. 7a~~b6~~). Therefore, our assessment of moderation in $AOD_{nitrate}$ resulted from 're-distribution effect' is robust (slightly conservative) and not significantly influenced by nitrate overestimation in this study.

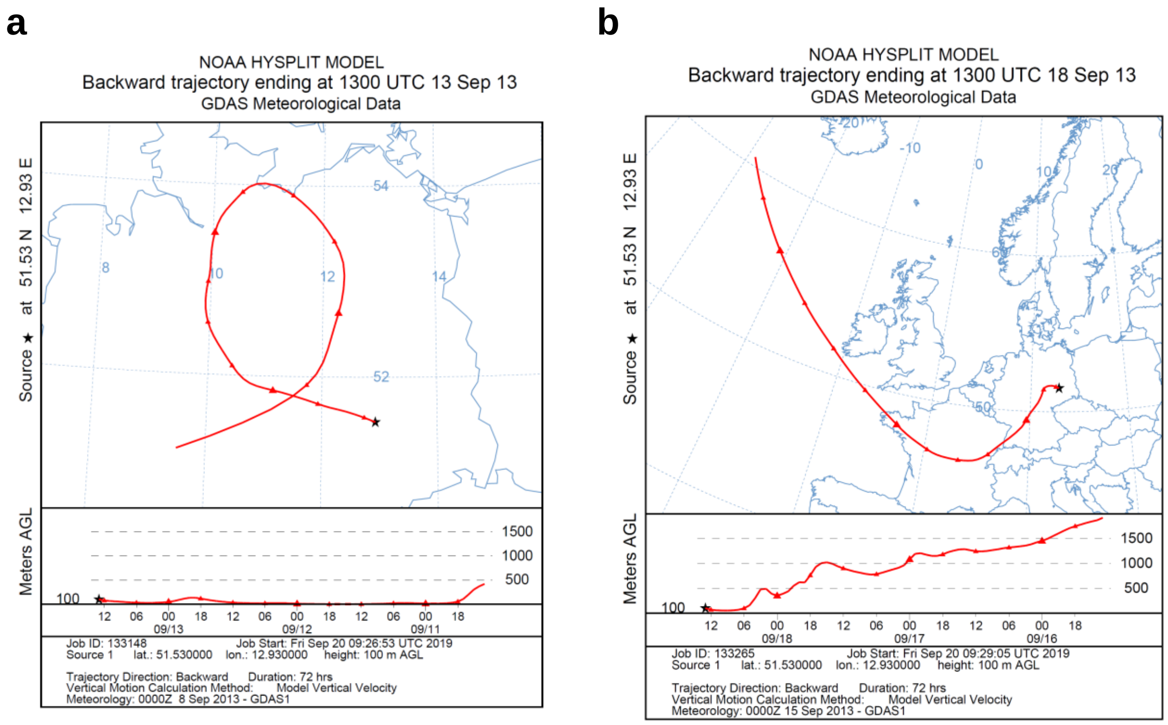


Fig. S1~~8~~. Three days back-trajectories for Melpitz, Germany. (a) 13 September 2013, representing continental period; **(b)** 18 September 2013, representing marine period. The back-trajectories are calculated by Hysplit (https://www.ready.noaa.gov/HYSPLIT.php).

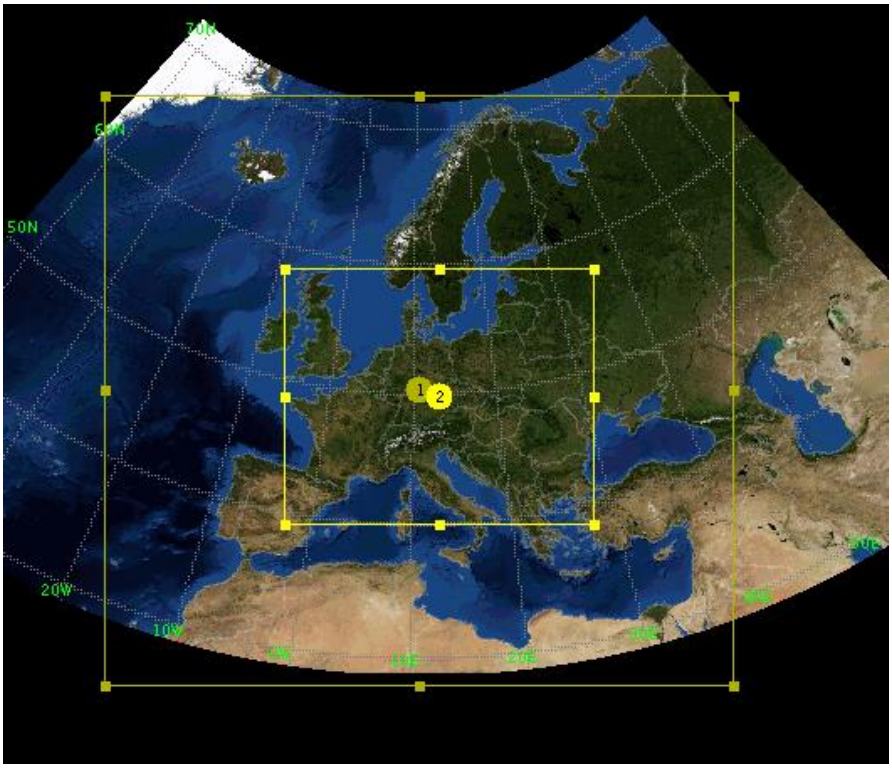


Fig. S2~~9~~. Domain setting of WRF-Chem European case.

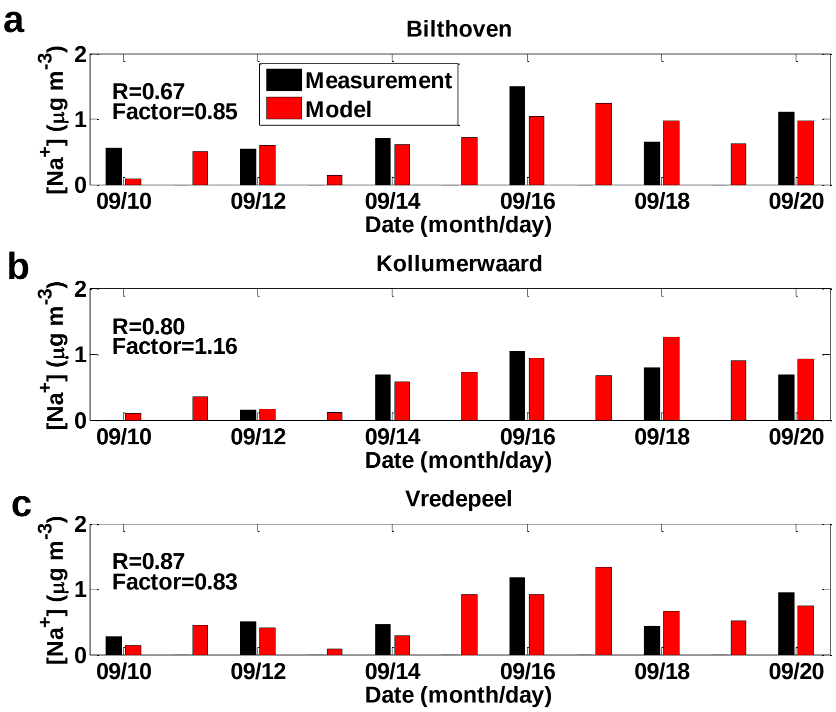


Fig. S3~~2~~. Comparisons of sodium mass concentration ([Na$^+$]) in PM$_{10}$. The filter sampler measurements at EMEP stations (Chen et al., 2016a) are in black bars, and the 'Case_SeasaltOn' model results are in red bars. **a,** Bilthoven. **b,** Kollumerwaard. **c,** Vredepeel. The locations of stations are shown in Fig. 3~~2~~.

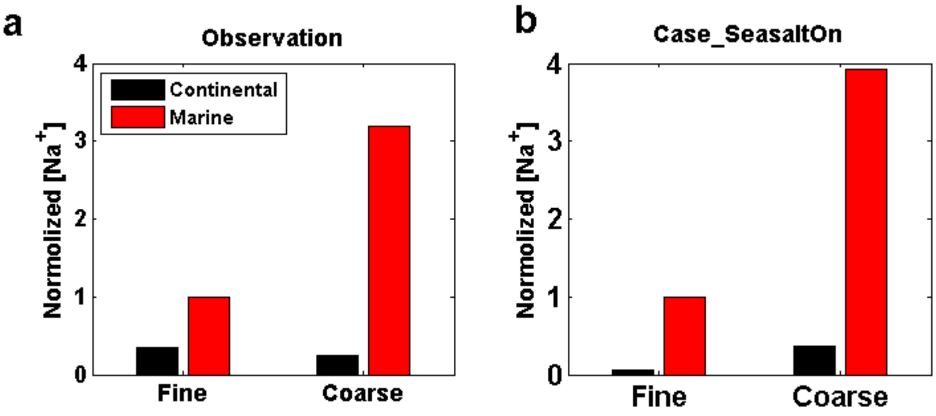
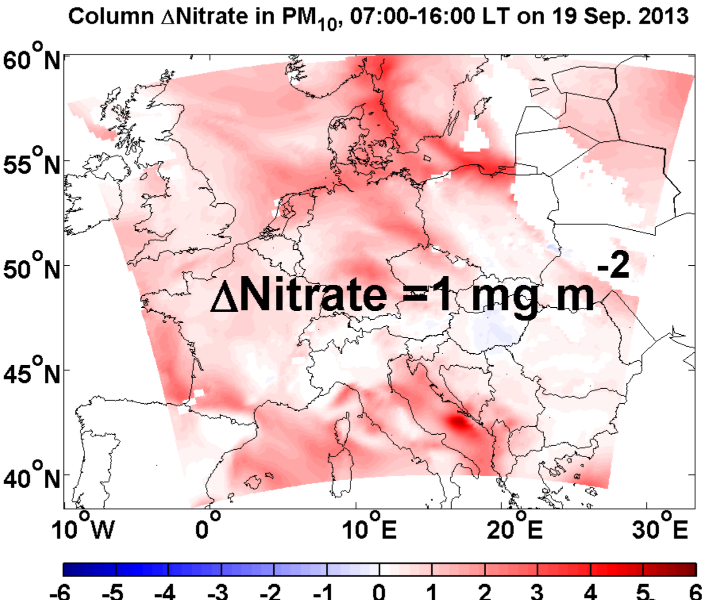


Fig. S4~~3~~. Sodium mass concentration ([Na$^+$]) normalized with the fine mode sodium concentration during the marine period. a, Berner impactor measurements. **b,** WRF-Chem 'Case_SeasaltOn', i.e., with sea-salt emission. The results are grouped into continental (black bar) and marine (red bar) air mass types, respectively. The fine and coarse mode particles are defined as PM$_{1.2}$ (particles with aerodynamic diameter smaller than 1.2 μm) and PM$_{1.2\text{-}10}$ (particles with aerodynamic diameter between 1.2 μm and 10 μm), respectively. Note: the sodium is negligible (< 0.5 μg m^{-3}) for the 'Case_SeasaltOff' simulated without sea-salt emission.



ΔNitrate in PM$_{10}$, ‘Case_SeasaltOn’ - ‘Case_SeasaltOff’ (mg m^{-2})

Fig. S5~~4~~. Influence of sea-salt aerosol on the simulated column nitrate loading in PM$_{10}$ (ΔNitrate). The simulated ΔNitrate between the ‘Case_SeasaltOn’ and ‘Case_SeasaltOff’ simulations showed here are averaged during daytime, i.e., 07:00-16:00 local time (LT) on 19 September 2013.

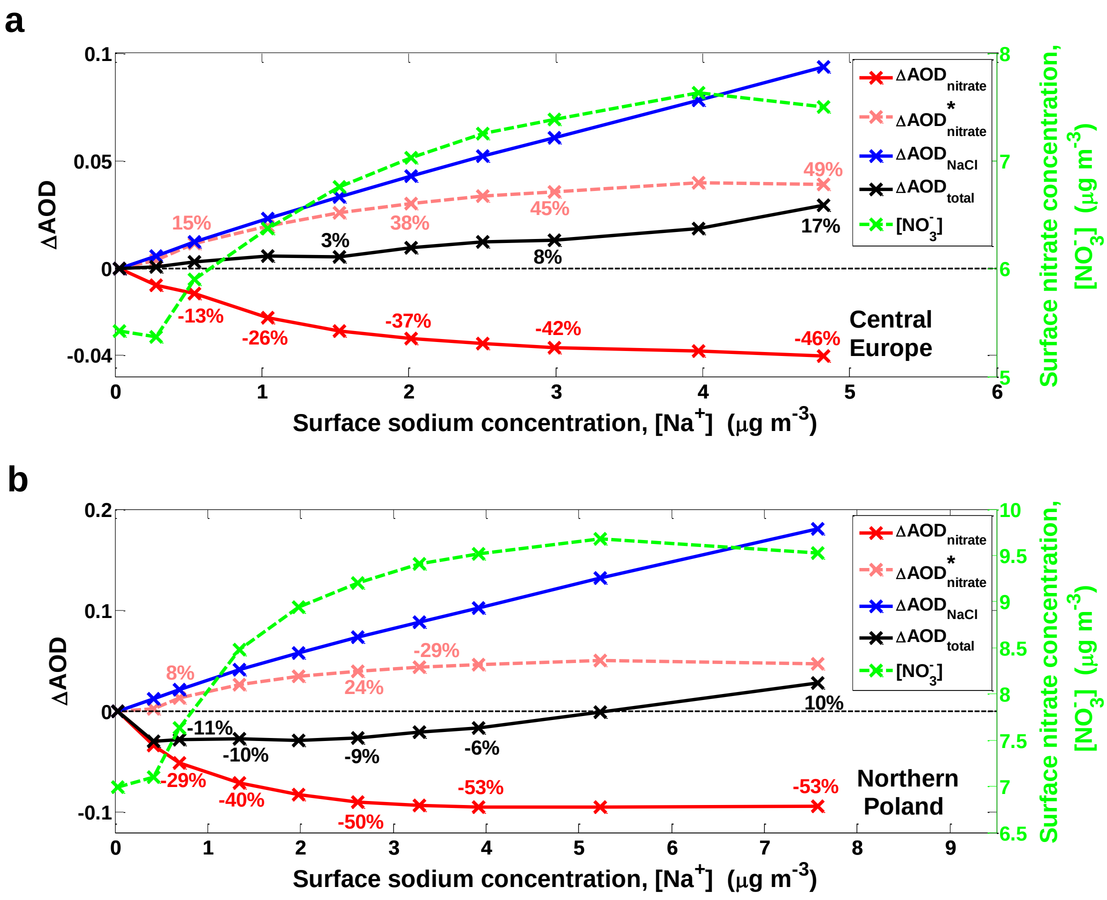
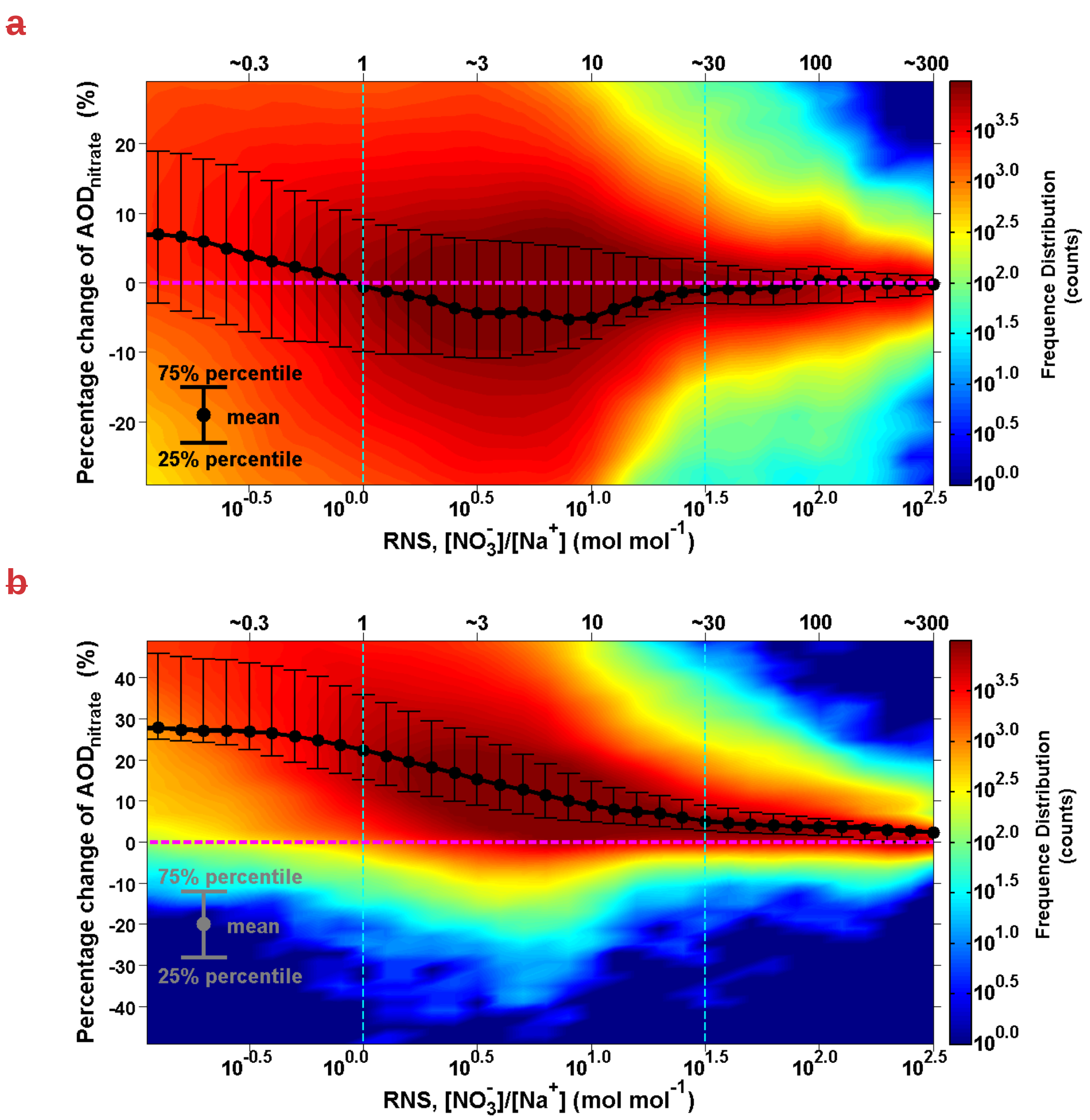


Fig. S6~~5~~. Similar as Fig. 6~~5~~. The additional black lines indicate the changes of total AOD (ΔAOD_{total}), including the reduction of nitrate AOD ($\Delta AOD_{nitrate}$) and the enhancement of sea-salt AOD (ΔAOD_{NaCl}). **a**, Central Europe region; **b**, Northern Poland region. The regions are marked in Fig. 3~~2~~.



~~**Fig. S6. Intensity of 'mass-enhancement effect' and its competition with the 're-distribution effect' as a function of molar ratio between surface fine nitrate and total sodium (RNS).** Percentage change of aerosol optical depth of nitrate (AOD$_{nitrate}$): **a,** net effect of 'mass-enhancement' (bottom panel) and 're-distribution' (Fig. 6). **b,** the intensity of 'mass-enhancement effect' is calculated as the difference in percentage between AOD$^{*}_{nitrate}$ in the 'Case_SeasaltOn' and AOD$_{nitrate}$ in the 'Case_SeasaltOff'. AOD$^{*}_{nitrate}$ indicates the AOD$_{nitrate}$ calculated by re-allocating nitrate mass into different size bins according to the normalized nitrate particle mass size distribution simulated in 'Case_SeasaltOff' (i.e., without 're-distribution effect'). The black dots indicate the mean values; the upper and lower error bars indicate the 75% and 25% percentile, respectively. The colour indicates the frequency distribution (i.e., how many counts) of the hourly model results over entire Europe domain during 16-20 September 2013.~~

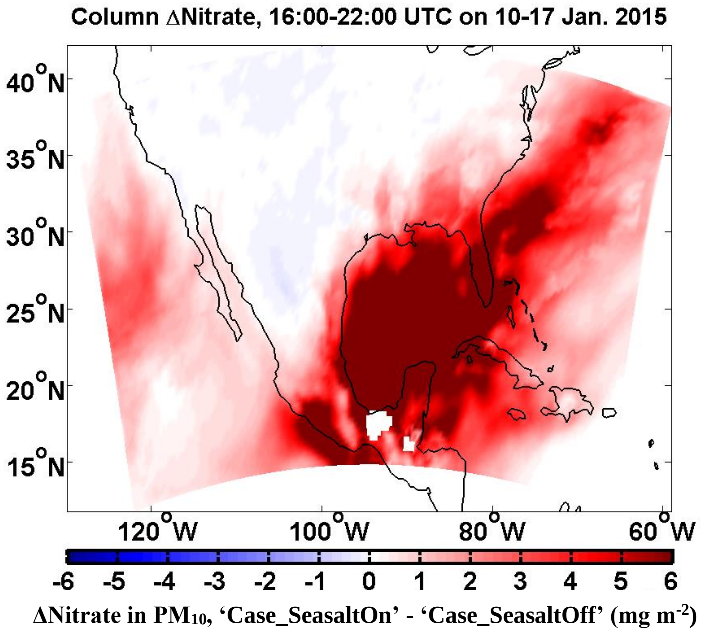


Fig. S7. Influence of sea-salt aerosol on the simulated column nitrate loading in PM_{10} (ΔNitrate). The simulated ΔNitrate between the 'Case_SeasaltOn' and 'Case_SeasaltOff' simulations showed here are averaged during the daytime over North America, i.e., 16:00-22:00 (UTC) on 10-17 January 2015.

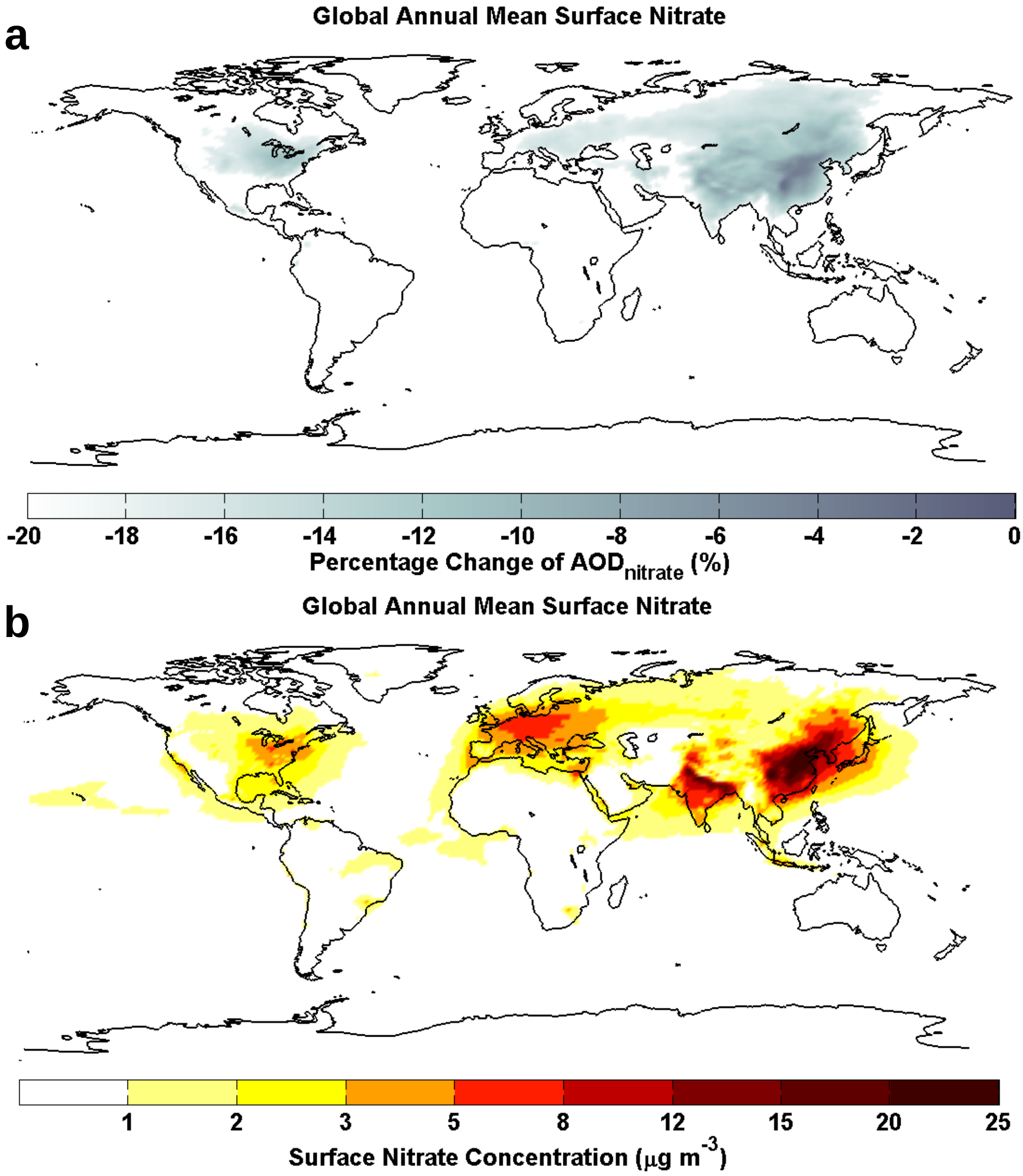


Fig. S8~~10~~. Global distribution of percentage changes of AOD$_{\text{nitrate}}$ (a) and surface nitrate concentration (b). The results are from EMAC model.

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