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)."

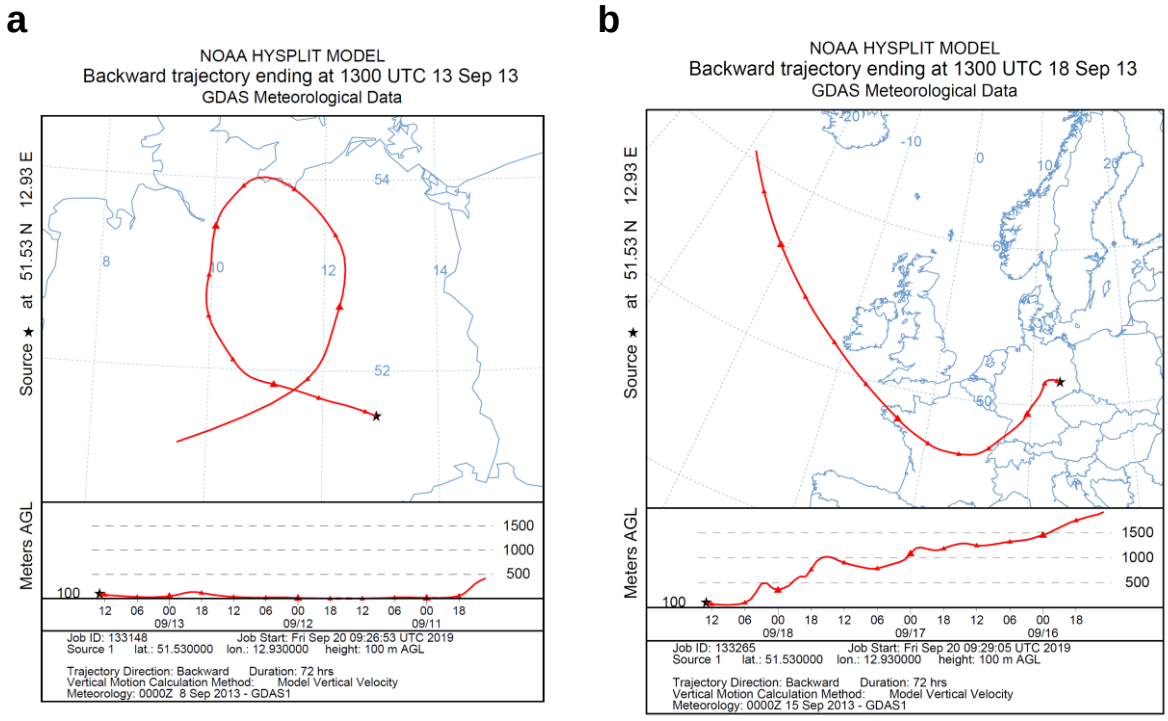

Fig. S1. Three days back-trajectories for Melpitz, Germany. (a) *13 September 2013, representing continental period;* ***(b)*** *18 September 2013, representing marine period. The back-trajectories are calculated by Hysplit (https://www.ready.noaa.gov/HYSPLIT.php).*

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 ($1^o \times 1^o$ 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.

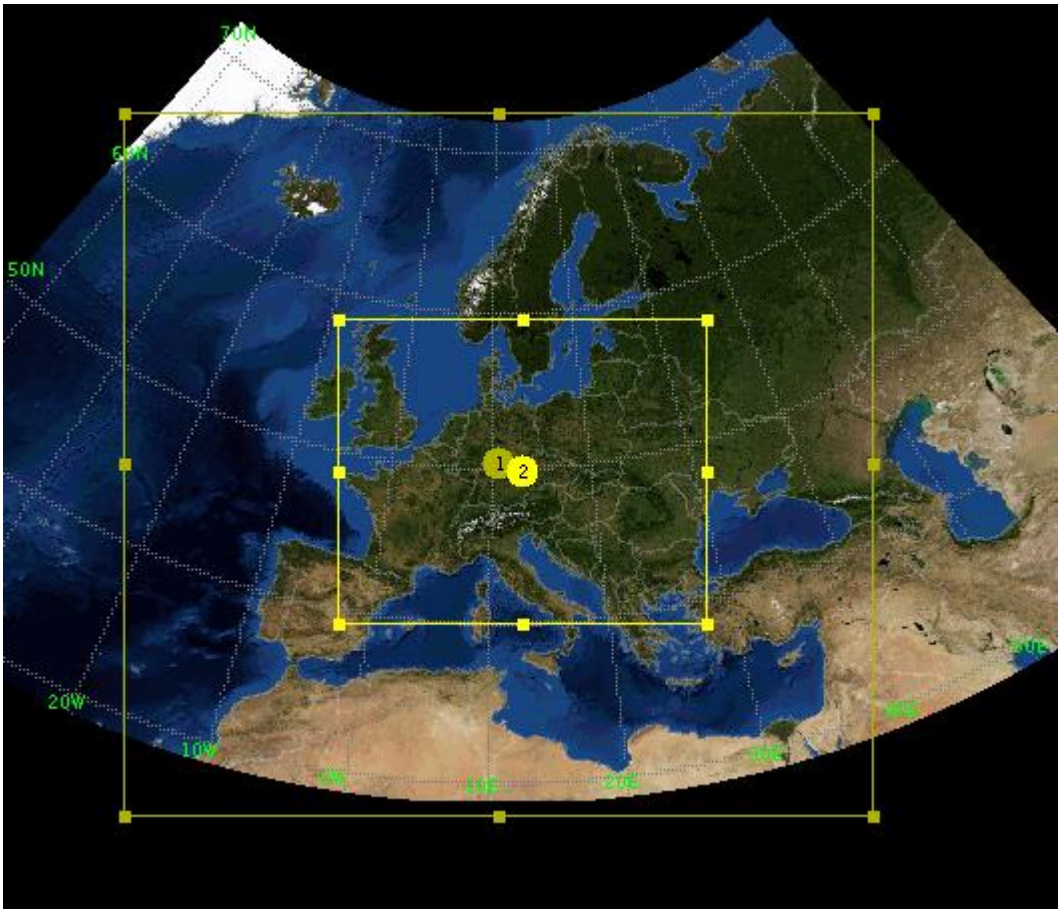

Fig. S2. *Domain setting of WRF-Chem European case.*

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)."

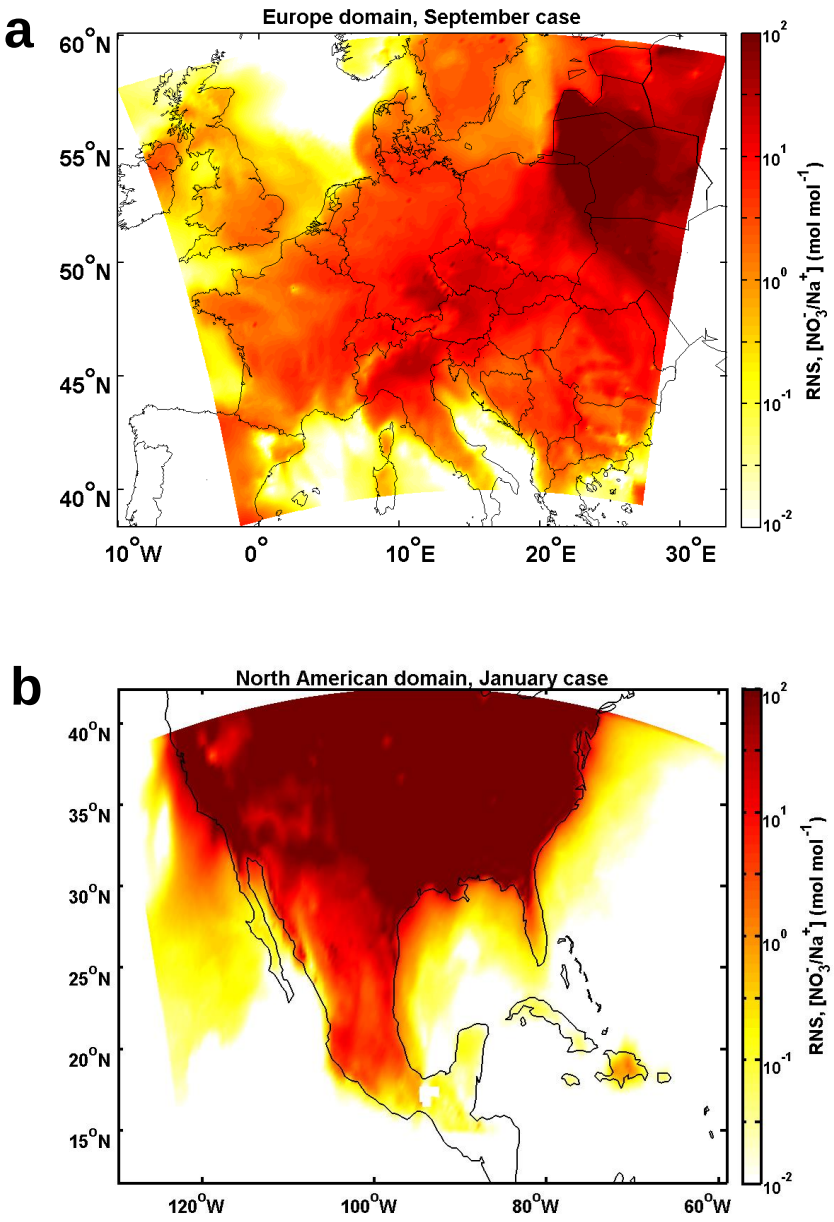

Figure R1. *Map of RNS (molar ratio between nitrate and sodium) in the European case (a) and the North American case (b) from the WRF-Chem simulation. Note that the color-scales have been changed to grey-scale friendly style, as suggested by the Reviewer#1.*

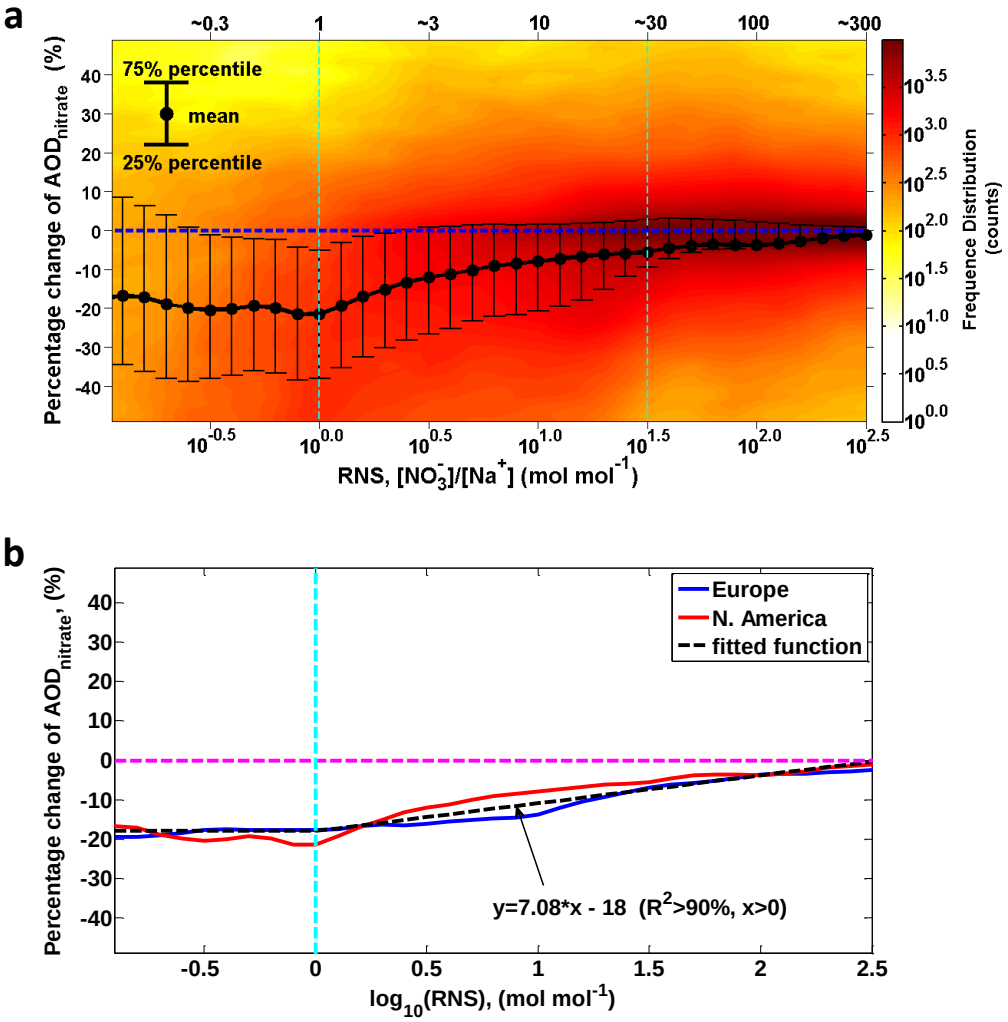

Fig. 9. Intensity of 're-distribution effect' as a function of molar ratio between surface fine nitrate and total sodium (RNS). (a) *The intensity of 're-distribution effect' over North American domain, similar as Fig. 7a, calculated as the difference in percentage between* $AOD_{nitrate}$ *and* $AOD^{*}_{nitrate}$ *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.

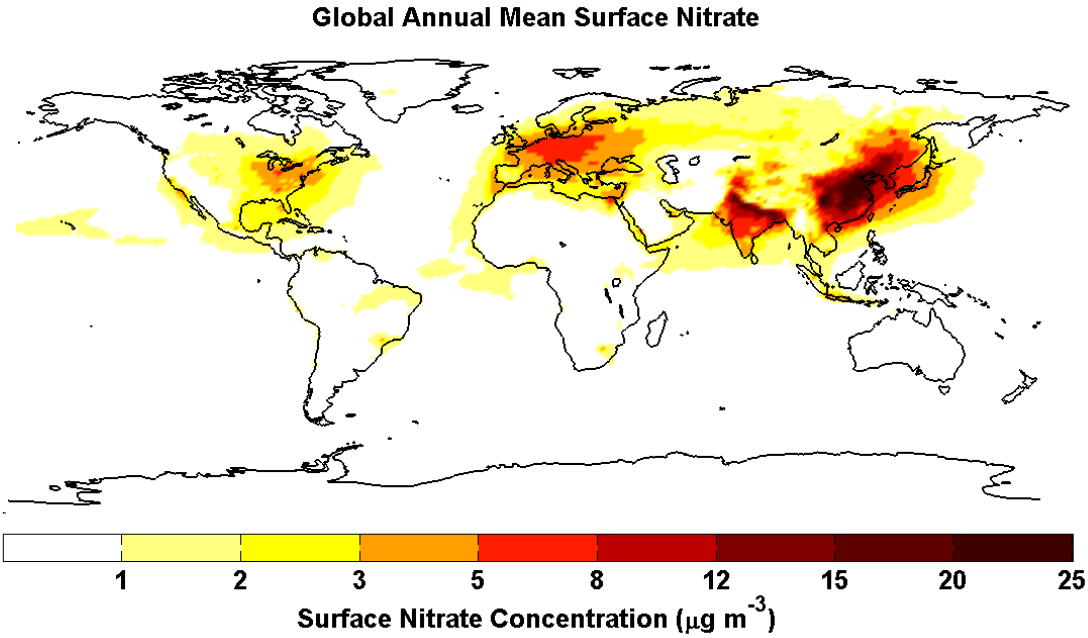

Fig. S8b. *Global distribution of percentage changes of surface nitrate concentration. The results are from EMAC model.*

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