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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Sensitivities of NO_x transformation and the effects on surface ozone and nitrate" *by* H. Lei and J. X. L. Wang

H. Lei and J. X. L. Wang

hang.lei@noaa.gov

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We wish to express our appreciation to Reviewer 1 for the careful review. Your very careful comments and editing have significantly improved the quality of our draft. In the revised manuscript, we have incorporated your comments. In the response below, we address each of major comments and all specific comments. The Reviewer's comments are italicized and our responses immediately follow.

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This paper investigates the change of surface ozone and aerosol nitrate in response to the perturbation on chemical transformation of NOx in the atmosphere using both model simulations and ground station measurements. The authors conducted a series of experiments to examine the impact of NOx transformation due to increase and decrease of NOx emissions and of atmospheric temperature. Although the presented material is interesting and valuable and the topic of the paper is suitable for Atmospheric Chemistry and Physics, I believe a major revision is needed before it can be accepted for publication as explaining following.

#General Remarks: The major conclusion of the paper is that "the decrease or small increase in ozone concentrations over industrial regions result in the responded nitrate increasing rate staying above the increasing rate of NOx emissions" [Abstract lines 11-13 and page 21968 lines 1-4]. I do not think this conclusion can be inferred from Figures 4 and 5.

Revised: The original expression is concluded from Figure 7. It is talking about the change in summer time rates. In summer time, the increase rate over industrial regions is above the rate of NOx emission change. In the new manuscript, we replace all figures and expressions about nitrate aerosols change by total nitrate change. Since there are impacts of sulfate aerosols to nitrate aerosol formation, it is inappropriate to use it in understanding the sensitivities of NOx transformation. Thanks for your comments.

#Over major industrial regions such as Northeast U.S. and Los Angeles, the authors point out that there is less active NOx transformation in ozone chemistry due to ozone decrease in Figure 5 [page 21967 line22], so that more active NOx could be available for nitrate formation [page 21968 lines 1-3]. However, the increase of nitrate formation over these regions is less than the NOx emission increase rate as shown in Figure 4.

Revised: By using the total nitrate concentration to interpret NOx sensitivity in the new manuscript, both figures are clear to show the rates above 0.25. Originally, the figure 4 shows the result of annual average concentrations which smooth the seasonal variations. The change ratio are from the figure 7.

#Over the other contiguous states, both ozone and nitrate formations are increased with NOx emission increase. However, the ïňAgures give no information that indicates

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that the signiïňĄcant increase of nitrate formation resulted from the more active NOx due to the ozone increase.

Revised: We added further analysis on this part. The added plots and text further explain the linkage between ozone and nitrate formation.

#The paper needs further in-depth discussion. The authors show changes of surface ozone and nitrate under the various perturbations on NOx emission and atmospheric temperature. However, explanations of the changes are generally vague, without clear and detailed support. Many explanations are presented as hypotheses [i.e. Page 21967 lines 16-18, Page 21968 lines 11-12, Page 21968 lines 23-25, Page 21970 line 2]. The explanation is also incomplete without including the discussion of reduced nitrogen (i.e. NH3 and NH4) for the change of nitrate. For example, another hypothesis in explaining Figure 4 is that the availability of free atmospheric NH3 is the dominant factor for the pattern of nitrate change in response to NOx emission change. The authors should discuss the relative contribution to nitrate formation from ozone and NH3 chemistries.

Revised: We enhanced the analyses in this study. The conclusions in this study are further supported by added plots and text. We also cited recent studies on NOx sensitivity to clearly explain the results. In order to focus on the sensitivity of NOx transformation, we replace the nitrate aerosols by total nitrate in the revised manuscript. We also included some discussions on the possible effects on nitrate aerosol from the NOx transformation and NH3 aspects.

#SpeciïňĄc Comments: #Page 21962 lines 11-16: I do not see any support for these conclusions in the paper. The paper shows only the change of surface ozone and nitrate in response to the change of NOx emission. There is no clear and direct evidence in the paper to demonstrate that the change of ozone concentration is the driving reason for the rate of nitrate increase staying above the rate of NOx emission increase.

Revised: We add analyses to further interpret this part.

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Page 21962 lines 16-18: Atmospheric temperature impacts not only NOy chemistry but also the partitioning of nitric acid between gas phase and aerosol phase. Page 21963 lines 6-9: No, other studies do account for the effects on the present condition, such as the studies of HTAP activity. Revised: Since we focus on the sensitivity of NOx transformation, the analysis in improved manuscript is for total nitrate. The information you suggested is also included in discussion part to discuss the possible effects on aerosol.

#Page 21964 lines 3-4: “Partitioning” is not an appropriate word to use here. Surface ozone and nitrate do not share a common source entirely.

Revised: revise the expression.

#Page 21965 lines 17-21: Please describe brieïňĆy the mechanism of nitrate simulation in the CAM-Chem model.

Revised: revise the text to describe the mechanism.

#Page 21966 lines 24-26: CASTNET does provide the measurement of dry depositions for aerosol nitrate and gas phase nitric acid separately. Please do model-observation comparison for aerosol nitrate directly since this paper investigates the change of aerosol nitrate, not oxidized nitrogen. Revised: We use CASTNET total nitrate data to further evaluate the model performance.

Page 21967 line 22: How do you know “less active NOx is transformed”? NOx titration reduces ozone concentration but do not change NOx volume mixing ratio.

Revised: NOx concentration is not changed. But the NO2 concentration increased, which will further foster the nitrate formation.

#Page 21968 lines 1-3: Figure 5 tells nothing about how NOx changes due to the change of ozone.Page 21968 lines 3-4: I do not think this conclusion can be inferred from Figures 4 and 5 as I discuss in the major comments. Page 21968 lines 6 and Figure 7: It would be more valuable to add the monthly change rate of surface NOx

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concentration in the ïňĄgure.

Revised: We revised figures and text to further interpret this.

#Page 21968 lines 8-10: Why does warmer climate cause higher nitrate formation? The relationship of nitrate formation and temperature change shown in Figure 8 does not support this conclusion. Meanwhile, I do not understand how “a response of the NOx-to-ozone pathway as mentioned above” supports the summer increase of nitrate formation. Page 21968 lines 25-28: The months are “January, February, and March”.

Revised: We improved the text to better interpret these question.

#Page 21969 lines 13-15: The change of surface nitrate in response to the temperature change shown in Figure 8 is partially attributed to the impact of temperature on the partitioning of total HNO3 between gas phase (nitric acid) and aerosol phase (nitrate). Since this paper investigates the impact on nitrate formation via perturbation on ozone chemistry, it would be valuable if the authors could explore how much of nitrate change is solely due to perturbation of NOy and ozone chemistry by temperature change. Page 21969 lines 18-19: How is active NOx concentration affected by the NOx-toozone transformation?

Revised: We revised the text by focus on the change in total nitrate. Through the NO2-NO cycle in ozone formation, the total nitrate concentration is affected.

#Page 21970 line 11-16 and Figure 10: What do the symbols “P-C1” and “W1-P” represent? Please change the scale of “change ratio” in the left panel so that the readers can tell the diurnal cycle of ozone change ratio. Page 21970 lines 16-17: Again cold temperatures also favor the total HNO3 partitioning toward aerosol nitrate. Page 21970 lines 17-22: How do you know that the NOy chemistry, and not the HNO3 partitioning, is the major reason for the daytime decrease of nitrate? Please check the other relevant tracers (i.e. NOx, gas phase nitric acid, etc) or design sensitivity experiments to conïňĄrm your conclusion.

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Revised: We revised caption of figures to clearly describe figures. Since the analysis focus on the sensitivity of NOx transformation, the analysis will focus on total nitrate.

#Page 21973 line 1: Please delete “further” since the authors do not provide any other reasons before. Technique Corrections Page 21963 line 14: Is it a typo of “processes”? The word of “progresses” makes more sense. Page 21964 lines 5-6: How about “Then, the air concentrations of ozone and nitrate aerosol and emissions of their precursors NOx and VOCs on several : : :”.

Revised: revised the corresponding text.

#Page 21966 line 6: Please spell out CCSM3. Page 21966 line 28: Please change “right” to “bottom” and “left” to “top”. Please do a similar change in the Figure 3. Figure 6: Please add “and ozone” after “Surface aerosol”. Page 21970line 23: Please add “For the experiment of temperature increase” before “The ozone: : :”.

Revised: We revised the text and correct some typo error in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 21961, 2013.