



Sensitivities of NO_x transformation and the effects on surface ozone and nitrate

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Abstract. As precursors to tropospheric ozone and nitrate, nitrogen oxide (NO_x) in the present atmosphere and its transformation in response to emission and climate perturbations are studied by using the CAM-Chem model and air quality measurements from the National Emissions Inventory (NEI), Clean Air Status and Trends Network (CASTNET), and Environmental Protection Agency Air Quality System (EPA AQS). It is found that NO_x transformations in present atmospheric conditions show different sensitivities over industrial and non-industrial regions. As a result, the surface ozone and nitrate formations can be divided into several regimes associated with the dominant emission types and relative levels of NO_x and volatile organic compounds (VOC). Ozone production in industrial regions (the main NO_x emission source areas) increases in warmer conditions and slightly decreases following an increase in NO_x emissions due to NO_x titration, which is opposite to the response in non-industrial regions. The ozone decrease following a temperature increase in non-industrial regions indicates that ozone production in regions that lack NO_x emission sources may be sensitive to NO_x transformation in remote source regions. The increase in NO_2 from NO_x titration over industrial regions results in an increase rate of total nitrate that remains higher than the increase rate of NO_x emissions. The presented findings indicate that a change in the ozone concentration is more directly affected by changes in climate and precursor emissions, while a change in the nitrate concentration is affected by local ozone production types and their seasonal transfer. The sensitivity to temperature perturbations shows that a warmer climate accelerates the decomposition of odd nitrogen (NO_y) during the night. As a result, the transformation rate of NO_x to nitrate decreases. Examinations of the

historical emissions and air quality records of a typical NO_x -limited area, such as Atlanta and a VOC-limited area, such as Los Angeles further confirm the conclusions drawn from the modeling experiments.

1 Introduction

Surface ozone and particulate matter (PM) are two major pollutants that affect US air quality (Blanchard and Hidy, 2003; Jacob and Winner, 2008) and that have a deleterious effect on the human respiratory system and health in general. Concentrations of surface ozone and PM-related secondary aerosols (nitrate, sulfate, and ammonium) are influenced by the precursor emission and transformation rate (Spicer, 1983). Since nitrogen oxide (NO_x) is a common precursor for ozone and nitrate aerosols, changes in NO_x emissions or the climate-induced change in related chemical reactions thus affect the concentrations and partitioning of pollutants in the air (Seinfeld and Pandis, 2006).

Previous modeling studies have aimed to diagnose air quality change due to anthropogenic emission change, biogenic emission change, and climate change under different scenarios (Wu et al., 2008; Pye et al., 2009; Lei et al., 2013). However, while these studies emphasize the possible long-term changing scenarios and status, they do not adequately account for the sensitivity of pollutants under present pollution conditions, which is actually more meaningful for air quality change on present status (Jacob et al., 1999). Considering the vital role played by NO_x in ozone and nitrate production, the sensitivities of NO_x transformation to

ozone/nitrate need to be examined in response to emission and climate perturbations for present air quality.

In addition, long-term air quality measurements and well-established emission inventories have yielded detailed information on air quality change in the past decade. For example, records from the Environmental Protection Agency Air Quality System (EPA AQS) have been used to examine the spatial and temporal variation of pollutants in the United States (Wu et al., 2008; Lin et al., 2008; Choi et al., 2012; Lei et al., 2012). The National Emissions Inventory (NEI) has also been used to determine the contributions of emission sources to the concentrations of PM and gases over the southeastern US (Tao et al., 2007; Blanchard et al., 2012). Based on these measurements and inventories, we can assess the changes in the concentrations of surface ozone and total nitrate under present atmospheric conditions and further examine their production associated with NO_x emissions.

In this study, we have analyzed the sensitivities of NO_x transformations in the present atmosphere through numerical experiments and diagnoses of observational air quality data. First, a set of experiments is conducted to evaluate the sensitivities of the NO_x transformation pathway to emission and climate perturbations. Experiments to exam emission perturbations are designed by 25% increase or decrease of global NO_x emissions, while climate perturbations are simulated by 1 °C increase or decrease of temperature. The changing rates of product concentration in the NO_x -to-ozone and NO_x -to-nitrate pathways are then analyzed. The results presented in this paper shed light on how emissions or climate change affect the production of ozone and nitrate – particularly how the surface ozone formation interacts with the nitrate formation. To test validity of the modeling experiments, the historical air concentrations of ozone and total nitrate as well as the historical emissions of NO_x and volatile organic compounds (VOC) over two typical US cities are diagnosed. The observational evidences confirm the air quality change processes and NO_x transformation pathways suggested by the numerical experiments. Finally, a summary discussion of NO_x sensitivity and its pivotal roles in ozone and nitrate productions is provided.

2 Methods

In order to evaluate the sensitivities of the NO_x transformation pathway in present atmospheric conditions, reproductions of the present concentrations of surface ozone and nitrate by using the CAM-Chem (climate–chemistry) model (as described and evaluated by Lamarque et al., 2012) are evaluated against observations from the EPA AQS and the Clean Air Status and Trends Network (CASTNET). Then, two pairs of perturbation experiments are conducted for emission and climate perturbations. As shown in Fig. 1, the chemical transformation of NO_x includes daytime and nighttime processes, which are both influenced by climate and

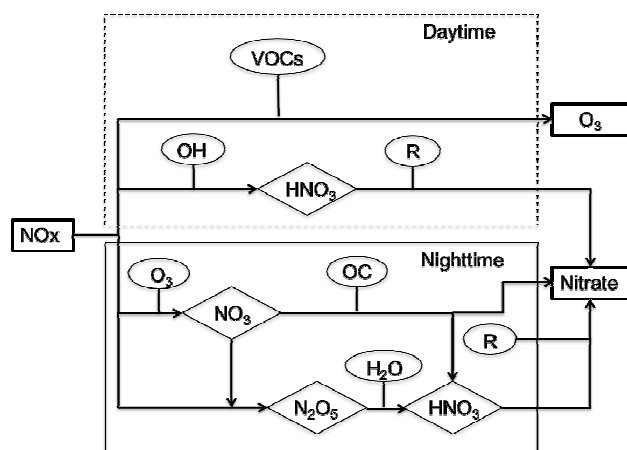


Fig. 1. Schematic diagram of the major NO_x transformation pathways to ozone or nitrate. Within the dashed line are the major chemical processes for the daytime. Within the solid line are the major chemical processes for the nighttime. The reversible reactions in the diagram only show the transformation to ozone or nitrate. The chemicals in rectangles are initial emissions or final products. Oval items are environmental chemicals (OC: organic compounds, R: compounds to neutralize nitric acid). Rhombuses are medial products.

emission changes. While climate perturbations may change the rates of chemical reactions, a shift in total emissions can result in nonlinear changes in product partitioning since chemical reactions interact (Monks et al., 2009).

In the first pair of experiments, NO_x emissions are increased or decreased by 25%. In the second pair, it is impossible to describe a climate perturbation in a numerical model exactly, since too many factors may be involved in a climate change process. However, temperature perturbations can be a good proxy of climate perturbations due to its key role in climate change, and similar method has been used in previous studies (IPCC, 2007; Aw and Kleeman, 2003). Tropospheric temperature is increased or decreased by 1 °C in order to isolate possible influences on the transformation rate. The outputs from both positive and negative perturbation runs, representing temperature increases and decreases, respectively, are then compared with the control results from run to examine anomalies. These results provide us with information on the tendency and stability of changes in pollutant levels. For instance, if the change in pollutant concentration induced by positive perturbations is larger than that induced by negative perturbations, the transformation tendency to that pollutant is accelerated by positive perturbations. Similarly, if a pair of experiments shows similar patterns for changes in pollution levels, the corresponding sensitivity to that perturbation is stable.

After the numerical experiments, the measurements of surface ozone and total nitrate concentrations over typical megacities are analyzed to assess their temporal variability.

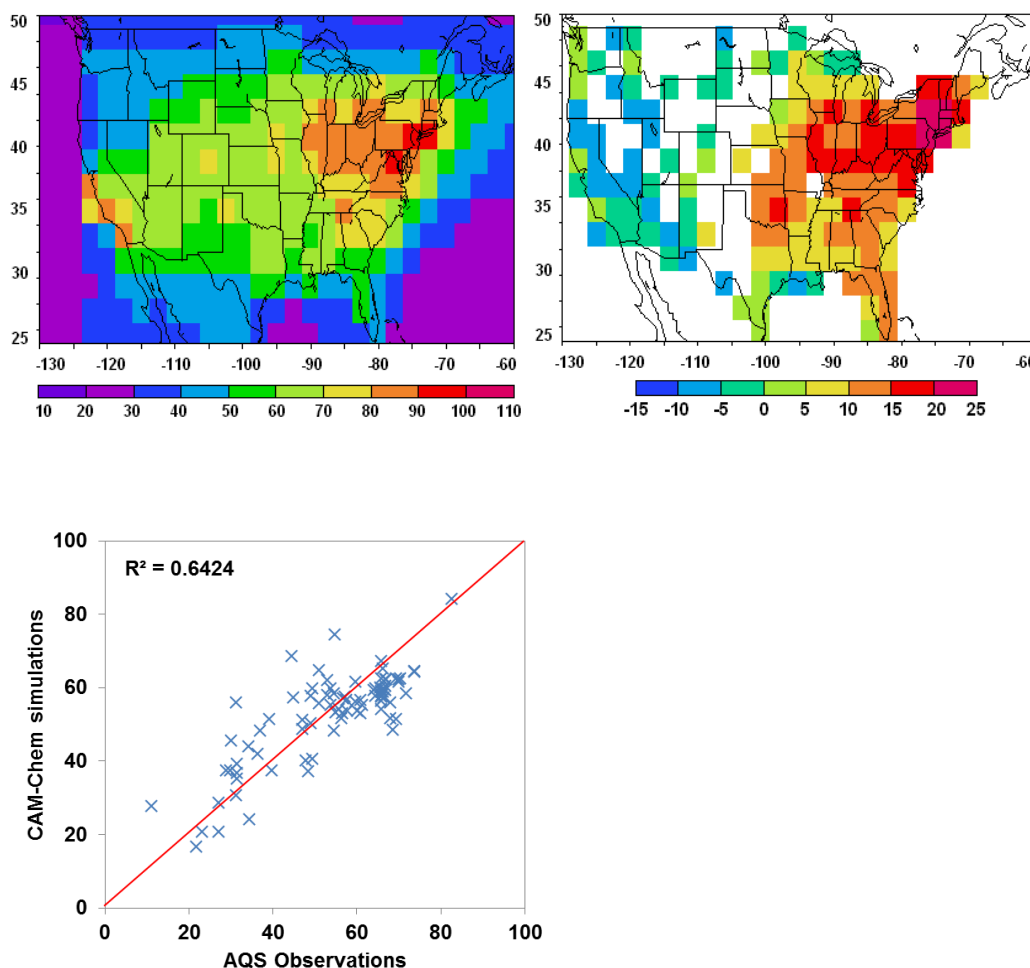


Fig. 2. Summer average DM8H surface ozone concentrations over the contiguous US during 1998–2002. The CAM-Chem-simulated results (left) and the comparison with the US EPA AQS site measurements (right). Unit: ppb; model-obs.

This variability, which is associated with the variation of NO_x and other precursor emissions, allows us to evaluate and better understand the conclusions drawn from numerical studies. Measurements of pollutants include the CASTNET observations of nitrate and EPA AQS records of surface ozone. The emissions analysis is based on the emissions budgets from the NEI.

The CAM-Chem model used in this study includes a simulation of O₃-NO_x-CO-VOC chemistry and the aerosol chemistry module. The ability of this model to reproduce global ozone and aerosol levels has been established in a suite of tropospheric ozone or aerosol studies (e.g., Tie et al., 2005; Murazaki and Hess, 2006; Emmons et al., 2010; Lei et al., 2012, 2013). Emissions of ozone precursors are based on the present-day inventory (for the year 2000) as described by Emmons et al. (2010). The meteorology data that drive the CAM-Chem model are derived from the National Centers for Environmental Prediction (NCEP) reanalysis II 1° × 1° fields from 1999 to 2002 (Kanamitsu et al., 2002). The six-hour interval data are re-gridded to a horizontal resolution of

1.9° latitude by 2.5° longitude and 26 vertical levels extending up to 0.01 hPa. The evaluation run and sensitivity experiments are performed over a four-year period. After one year's spin-up, the model result for the following three years is used in the analysis to perform inter-comparisons.

3 Results and discussion

3.1 Evaluation of the current atmosphere and emissions

To evaluate CAM-Chem's ability to reproduce surface ozone and total nitrate concentrations, we compare the model-derived concentrations over the contiguous US around 2000 with EPA AQS site measurements. The model is driven by the NCEP reanalysis II meteorology, and its run for 2000–2002 is compared with the observations for the same period of time using averaged three-year data. All measurements, which include at least a 75 % record of valid operations at rural sites during the whole comparison period, are

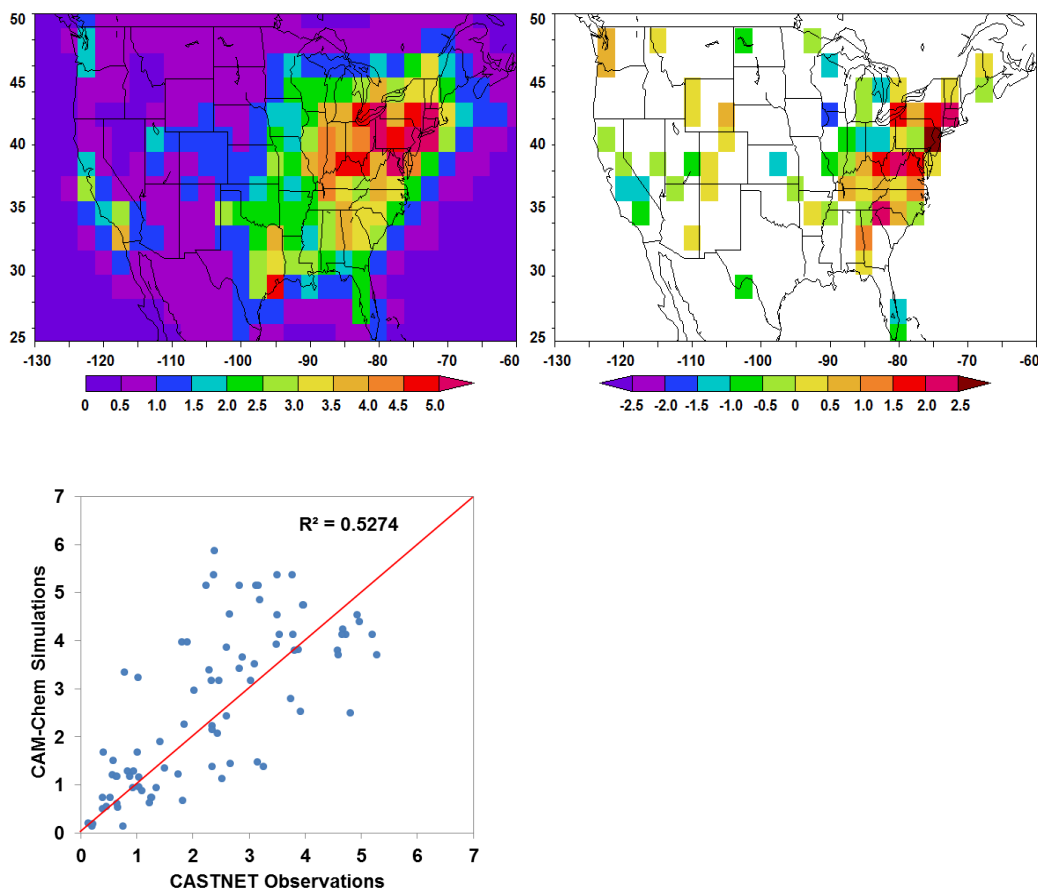


Fig. 3. Annual average total nitrate concentrations over the contiguous US in 2002. The CAM-Chem-simulated results (left) and the comparison with the CASTNET site measurements (right). Unit: $\mu\text{g m}^{-3}$.

selected within a given model grid cell. Then, the selected measurements are averaged to ascertain a grid cell mean value that can be directly compared with the modeled value for that grid cell.

Since summer is the active period for ozone production and the availability of ozone measurements is the best in summer, we compare the summer daily maximum eight-hour (DM8H) surface ozone concentrations in order to evaluate the model performance. Figure 2 shows the CAM-Chem-derived DM8H ozone concentration over the contiguous US and the corresponding errors from EPA AQS observations. We find that the model is able to reproduce summer ozone concentrations over most of the contiguous US, with overall biases smaller than 20 ppb. The comparison based on the grid cell average shows an R-squared value of 0.6424, which passes the 95 % confidence test. Similar spatial patterns and values of biases in the comparison of ozone concentrations over the contiguous US were previously reported by Lei et al. (2012).

Nitrate is the direct product of NO_x oxidations. Furthermore, it is transformed into other nitrate chemicals that exist in the atmosphere in various phases and forms. The measure-

ments of total nitrate, including all forms of nitrate chemicals, can be a good indicator of the NO_x transformation to nitrate. The CASTNET observations have systematically recorded the nitrate deposition over the past decade and derived total nitrate concentrations based on this amount. Therefore, we compare the simulated total nitrate (nitrate aerosols + nitric acid) concentrations with the CASTNET concentration map in order to evaluate CAM-Chem simulations. Figure 3 shows the CAM-Chem-simulated (right) annual mean concentration of total nitrate ($\mu\text{g m}^{-3}$) and the error from the CASTNET measurements (left) over the contiguous US between 2000 and 2002. Generally, the CAM-Chem model captures the pattern of total nitrate concentrations. The model biases mainly fall within the range of $+1 \mu\text{g m}^{-3}$. The detailed comparison based on the grid cell average shows an R-squared value of 0.5274, which passes the 95 % confidence test and thereby confirms the ability of the CAM-Chem model to be used in the subsequent sensitivity experiments.

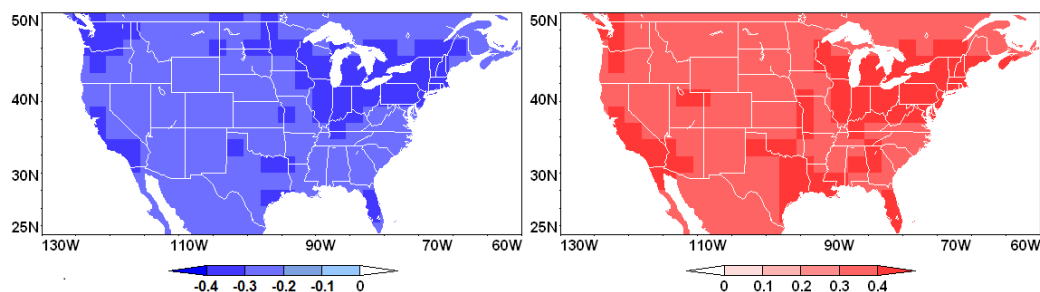


Fig. 4. Annual mean change ratio of the surface total nitrate concentration ((experiment–control run)/control run, left: result of the 25 % NO_x emissions decrease; right: result of the 25 % NO_x emissions increase).

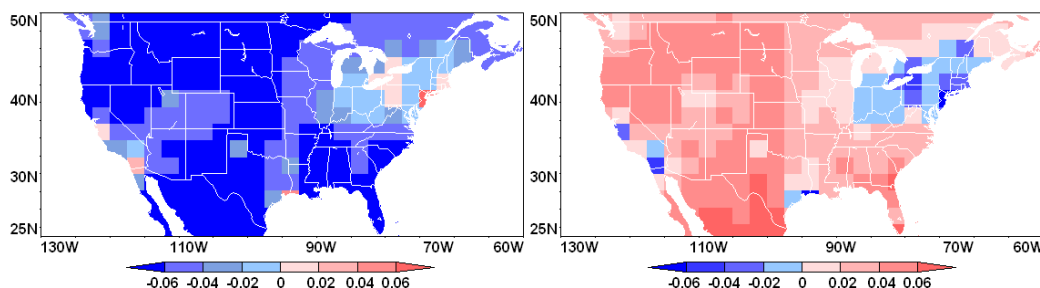


Fig. 5. Annual mean change ratio of the surface ozone concentration ((experiment–control run)/control run, left: result of the 25 % NO_x emissions decrease; right: result of the 25 % NO_x emissions increase).

3.2 Transformation rate change response to emission perturbations

Figure 4 shows the annual mean change ratio of the surface total nitrate concentration simulated from the experiment with a 25 % increase (or decrease) in global NO_x emissions. The patterns are found to be similar between the two experiments, which indicates a consistent sensitivity (symmetric results show that the sensitivity is consistent, namely that the system is not on a point of inflection) in response to emission perturbations. By comparing the magnitudes of the two diagrams in Fig. 4, it is clear that the tendency of transformation from NO_x to nitrate increases as NO_x emissions increase. In the industrial regions of the US (the east, the coastal area of Texas, and southern California), the change rate of nitrate is greater than 0.4, generally higher than the rate (0.3) over the majority of the non-industrial area. The overall change rate is above the change rate of NO_x emissions.

For the transformation pathway from NO_x to ozone, Fig. 5 shows the annual mean change ratio of the surface ozone concentration. Over the major industrial regions of the eastern US, the ozone concentration decreases in response to an increase in emissions, which means less active NO_x is transformed. The hydrocarbon-limited surface ozone production regime and associated NO_x titration are responsible for the converse relationship in industrial regions. For the US, the overall change rate of ozone is also considered to be very

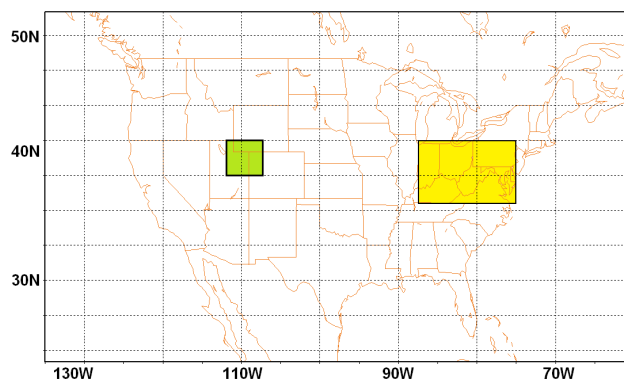


Fig. 6. The shaded rectangular regions are the sensitivity regions used for the analysis. The yellow sensitivity region (over 36° – 42° N; 90° – 75° W) stands for the industrial region, while the green sensitivity region (over 38° – 42° N; 112° – 107° W) is the non-industrial/mountainous region. Surface aerosol concentrations are averaged over these areas.

low in comparison with the 25 % change rate in NO_x emissions, which is attributable to the limitation of hydrocarbons (Ying et al., 2009).

In order to examine the seasonal variation in these sensitivities, monthly changes in ozone or total nitrate levels are analyzed. Figure 7 shows the monthly change ratio of surface total nitrate and ozone over the selected industrial region defined in Fig. 6. For the NO_x –nitrate pathway, the

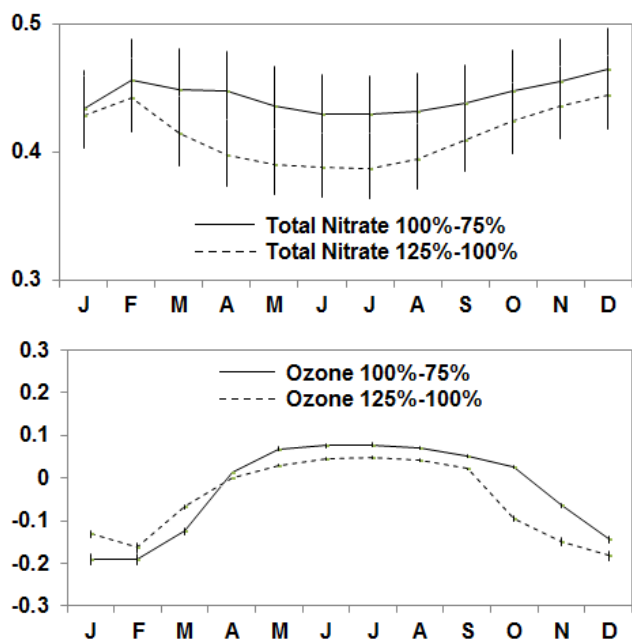


Fig. 7. Monthly mean change ratio of surface total nitrate and ozone over the industrial region. Top: nitrate change ratio; bottom: surface ozone change ratio.

efficiency of the transformation (represented as the ratio of incremental percentage change of nitrate to NO_x) shows a significant increase (above 0.3), which agrees with the results presented in Fig. 4. The solid line shows a higher efficiency than the dashed line, especially in summer, which indicates reduced sensitivity at high emission levels. The bars show the uncertainty range according to the model-simulated daily change each month, which does not affect the trends of the change ratios in Fig. 7. On the pathway of NO_x transformation to ozone, the surface ozone concentration decreases in all seasons except summer, in response to an increase in NO_x emissions. This finding indicates that surface ozone production over industrial regions is generally of the hydrocarbon-limited type, except in the growing season when an abundance of hydrocarbon emissions from biogenic sources and ozone production becomes the NO_x -limited type. Overall, the transformation efficiency (represented as the ratio of incremental percentage change of ozone to NO_x) is below 1.

Another point that is clear from Fig. 7 is the tendency for improved transformation efficiency in response to an increase in emissions. For the NO_x -to-nitrate pathway, the change in transformation efficiency caused by a 25% increase in NO_x emissions is smaller than that created by a 25% reduction in NO_x , which indicates that transformation efficiency may decrease when NO_x emissions increase. The limitation on base nitrate precursors may be a reason for this result. For the NO_x -to-ozone pathway, the absolute change in transformation efficiency caused by a 25% increase in NO_x emissions is smaller than that caused by a 25% re-

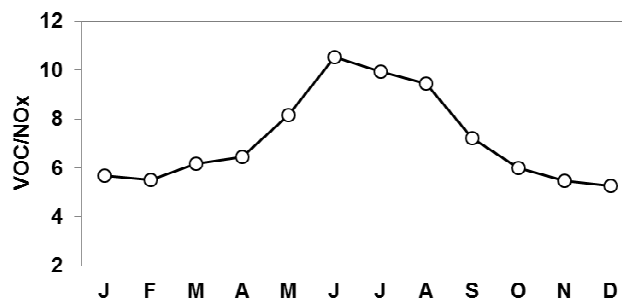


Fig. 8. Seasonal variation in the ratio (VOC/NO_x) over the industrial region under current conditions. All active hydrocarbons are unified based on ozone productivity compared with carbon monoxide.

duction in NO_x emissions for most of the year except for January, February, and March. In particular, there exist two transitions between ozone production transformation types, as indicated by the change from positive to negative tendencies – one around April and the other around September. For the September transition, the positive-to-negative switch of tendency for the NO_x emission increase ones is around one-month earlier than that for the emission reduction ones. In contrast to the April transition, both switches of tendency from negative to positive are almost on the same time. In summary, an increase in NO_x emissions results in an earlier transfer to a hydrocarbon-limited type. This pattern results from the variation in hydrocarbon emissions, which has strong seasonality. The relative level of hydrocarbon (defined as hydrocarbon/ NO_x) determines the ozone production type and thus affects the transfer time in each case.

Figure 8 shows the ratio of total volatile organic carbon to NO_x . Different hydrocarbons are unified based on their ozone productivity compared with that of carbon monoxide in the calculation of total active hydrocarbon. Moreover, the hydrocarbon concentration in summer is high. According to ozone production regime studies (Seinfeld and Pandis, 2006; Madronich et al., 2011), a VOC/NO_x ratio below 10 indicates a typical VOC-limited ozone production regime. In most months except June and July, in which the biogenic emissions of VOC are strong, the ratio remains below 10. The lowest ratio occurs in winter when biogenic sources are small, indicating a deep VOC-limited ozone production regime. In the summer, VOC/NO_x ratios are approximately 10, which implies a weak NO_x -limited regime. As a result, an increase in NO_x emissions reduces the ratio, leading to a VOC-limited regime after a small increase in ozone production.

According to the nitrate concentration change described above, a decrease or small increase in the ozone concentration in response to an increase in emissions means that more active NO_x participated in nitrate formation (through $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$; $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$). Moreover, a large amount of OH will be taken by nitric acid

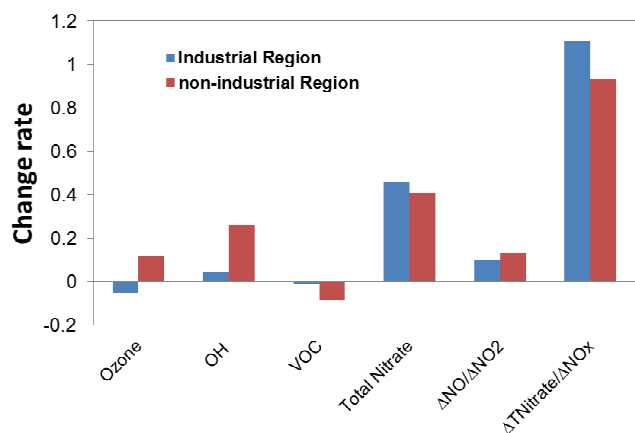


Fig. 9. Change rates of surface ozone, OH, VOC, and total nitrate concentrations, and rates of change in NO_2 and change in total nitrate/change in NO_x in response to a 25% NO_x emissions increase. Industrial regions and non-industrial regions are defined as the sensitivity regions in Fig. 6. VOC includes total active hydrocarbons, which are unified based on ozone productivity compared with carbon monoxide.

formation since OH plays an important role in the initial reaction of ozone formation ($\text{VOC} + \text{OH} + \text{O}_2 \rightarrow \text{RO}_2 + \text{H}_2\text{O}$). The removal of OH will thus further prohibit ozone formation. As a result, the increase rate of total nitrate is greater than the emissions increase ratio. Figure 9 presents the rates of change in major surface species and key ratios, showing a surface ozone decrease in industrial regions and an increase over mountainous regions. More VOC is consumed in mountainous regions than in industrial regions, where OH is mainly removed by nitrate acid formation. Similar results are shown by Madronich (2013), who refers to this situation as OH collapse.

Owing to the ozone titrate ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$), the ratio of change in NO to change in NO_2 over industrial regions is less than that over non-industrial/mountainous regions. As a result, total nitrate increases more in industrial regions than in mountainous regions. The ratio of change in total nitrate to change in NO_x over industrial regions is more than that over non-industrial regions. Although the relatively high ammonia emissions over agricultural regions increase the formation of nitrate aerosol (Becker and Graves, 2004) and thus increase the efficiency of NO_x transformation to nitrate, NO_x titration improves the efficiency of NO_x transformation to total nitrate in industrial regions.

3.3 Transformation rate change in response to temperature perturbations

Figure 10 shows the annual mean change ratio of the surface total nitrate concentration from a temperature increase or decrease of 1°C . Generally, total nitrate concentration over the US decreases in response to a temperature increase

at the current emission level. An increase in temperature tends to repress the chemical and physical processes relevant to nitrate formation and thus decrease the nitrate concentration. These results can be explained by the temperature impact on N_2O_5 formation. Warmer temperatures tend to accelerate the decomposition of NO_y ($\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ and $\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$), resulting in less nitrate production (Seinfeld and Pandis, 2006). The sensitivity over non-industrial regions shows a more sensitive response to temperature changes.

For the temperature impacts on the NO_x –ozone transformation pathway, Fig. 11 shows the annual mean change ratio of the surface ozone concentration. Surface ozone production is directly affected by the climate and precursor emission change due to the rapid photochemical reactions for ozone formation (Seinfeld and Pandis, 2006). The ozone concentration increases generally over the contiguous US, except over mountainous regions and northern border areas where the NO_x concentration is affected by the exchange and transport from remote sources. Since higher temperatures tend to increase ozone production efficiency, more NO_x is involved in ozone production over source regions.

In order to examine the complex relationship between changes in ozone and nitrate production, the changes in associated pollutants caused by a temperature increase over industrial and non-industrial/mountainous regions (as defined in Fig. 6) are shown in Fig. 13. By keeping the emissions and meteorology unchanged, we can see that the NO_x , O_3 , and OH concentrations in the surface layer over mountainous regions all decrease in response to a temperature increase, whereas they increase over industrial regions. Furthermore, total nitrate decreases in both regions. Although the main reason for these changes is the temperature impacts on the NO_y chemistry, ozone production may also contribute to the change in total nitrate. VOC over both regions increases due to the increased biogenic emissions (Guenther, 1997), which caused more NO_2 to transform into NO through ozone production, and also caused there to be less NO_2 for total nitrate production. As a result, the partitioning of NO_x over total nitrate moves to the NO_x side. In mountainous (and non-industrial) regions, the ozone decrease under a VOC-increasing condition can be explained by the decrease in NO_x . Since global total emissions of NO_x are unchanged, the missing NO_x in mountainous regions can only be attributed to the exchange with surrounding regions. More NO_2 and VOC consumed in industrial regions will modify the gradients of NO_x and VOC, leading to a decrease in the NO_x level in the sensitive mountainous regions after air transport and exchange. Conversely, this may enhance the transport of hydrocarbons to industrial regions by increasing the gradient of hydrocarbon concentrations. According to the change in the total nitrate concentration, increased NO_x involvement in ozone production results in less active NO_x available for nitrate formation (affecting HNO_3 and N_2O_5 formation),

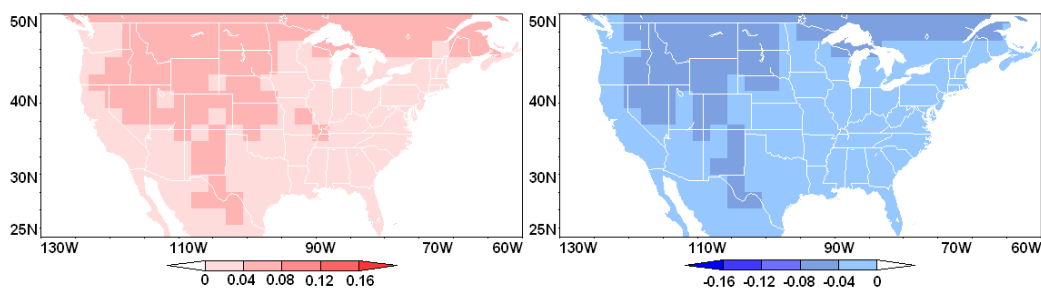


Fig. 10. Annual mean change ratio of the total surface nitrate concentration ((experiment–control run)/control run, left: result of the 1 °C temperature decrease; right: result of the 1 °C temperature increase).

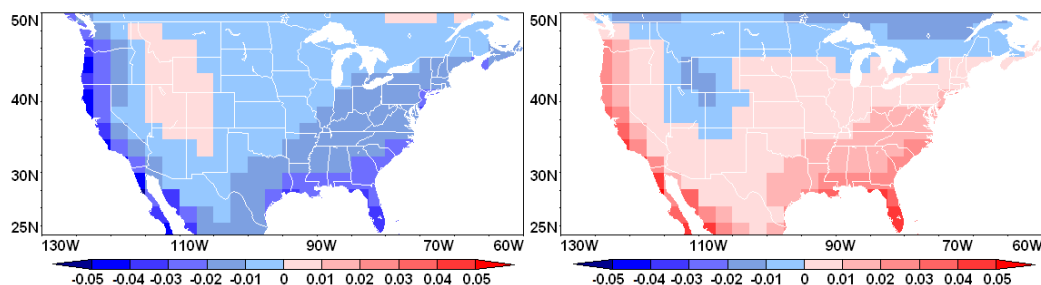


Fig. 11. Annual mean change ratio of the surface ozone concentration ((experiment–control run)/control run, left: result of the 1 °C temperature decrease; right: result of the 1 °C temperature increase).

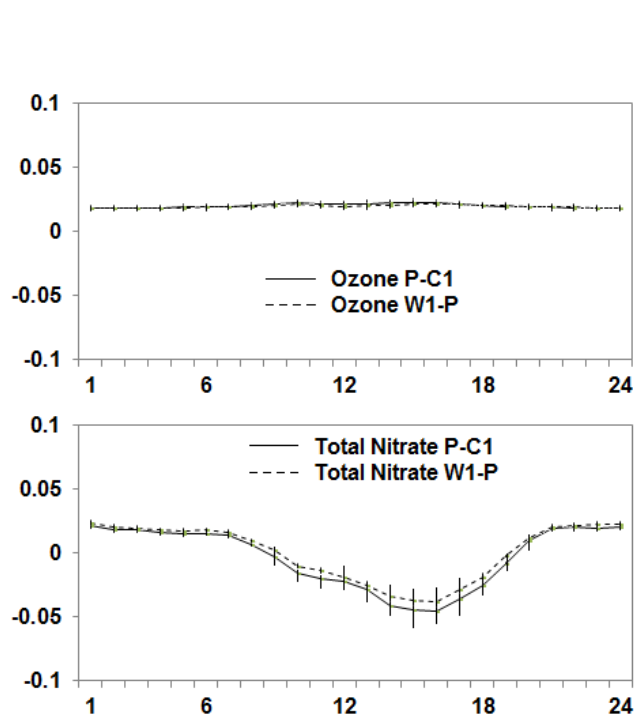


Fig. 12. Annual mean diurnal cycles of ozone and total nitrate change ratios averaged over the industrial region. Top: surface ozone change ratio; bottom: surface nitrate change ratio.

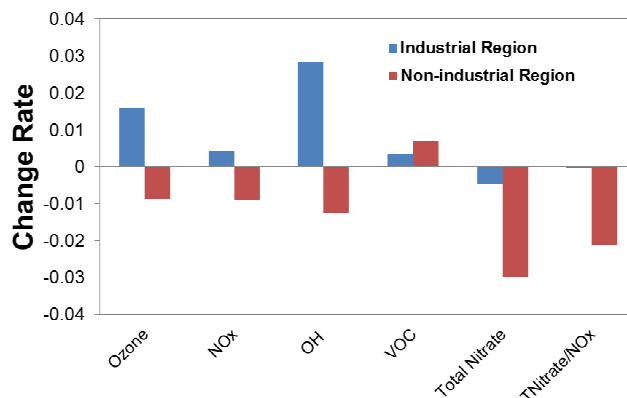


Fig. 13. Change rates of surface ozone, NO_x , OH, VOC, and total nitrate concentrations, and rates of total nitrate/ NO_x in response to the 1 °C temperature increase. Industrial regions and non-industrial regions are defined as the sensitivity regions in Fig. 6. VOC includes total active hydrocarbons, which are unified based on ozone productivity compared with carbon monoxide.

which contributes to the decrease in NO_x /nitrate partitioning.

In addition, the chemical reactions that occur during the night are important in aiding the transformation of NO_x into nitrate (Seinfeld and Pandis, 2006), since medium chemicals for nitrate formation are formed nocturnally (refer to Fig. 1). Temperature is an important factor that affects nocturnal

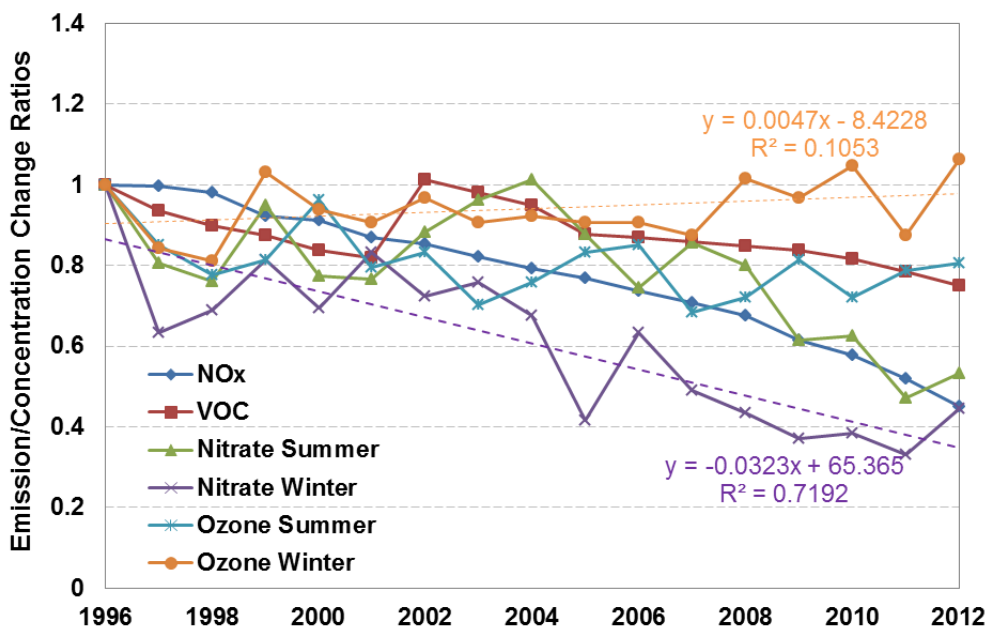


Fig. 14. Historical variations in emissions and pollutant concentrations in Los Angeles, CA between 1996 and 2012. The data for NO_x and VOC emissions are from the NEI data set. The change rates of total nitrate in summer and winter are calculated from the CASTNET measurements at site JOT403. The change rate of ozone is calculated from the DM8H concentrations of surface ozone, which are averaged from the EPA AQS records for the same county where site JOT403 is located. The change rate is calculated based on the first year concentration (e.g., 1996).

chemistry. Therefore, it is necessary to examine the diurnal change in the sensitivity of NO_x transformation pathways to temperature change. Figure 12 shows the diurnal cycle of the annual mean concentration changes averaged over industrial regions (as defined in Fig. 6). The solid line shows the response of hourly surface concentrations to a temperature increase, while the dashed line represents the results based on a temperature decrease. The bars show the uncertainty range according to model-simulated hourly change rates based on monthly variation. The ozone concentration increases by approximately 2% over the present value in response to a 1°C temperature increase. Although the change in the transformation rate is almost constant throughout the whole day, it is larger during the daytime. The limited uncertainty may not upset the trend. Nitrate concentration decreases during the day and sharply increases at night, with a change ratio from -0.2 to 0.3 . This also indicates that ozone production is less affected by nitrate production. The daytime decrease in nitrate is mainly caused by the accelerated NO_y decomposition as well as the increased consumption of active NO_x in ozone formation. During the night, ozone is consumed and this action contributes to nitrate formation (as shown in Fig. 1). As a result, the NO_x transformation to total nitrate is enhanced. However, nitrate aerosol formation is also influenced by other factors, including humidity, the availability of base precursors (e.g., ammonia), and the concentrations of other acids (e.g., sulfuric acid) (Lei and Wuebbles, 2013).

As a result, the potential responses of the nitrate aerosol concentration to a changing climate and emission scenario are complex. Observations and microphysical studies of its formation may further improve our understanding in this regard.

3.4 Evidence from observations

In order to ascertain evidence from the observations and confirm the findings drawn from the sensitivity experiments, we further examine the NO_x transformation in existing emissions and air quality records. These data sets include the NEI emissions data sets, CASTNET nitrate observations, and EPA AQS ozone observations. Two cities, Los Angeles and Atlanta, are selected to represent the two types of ozone production environments in the analysis. Los Angeles is a heavily polluted city where the ozone production type is strongly VOC-limited (e.g., Harley et al., 1993; Steiner et al., 2006). Specifically, nitrate observations from CASTNET for the site located in Los Angeles (JOT403) are used in the analysis. Ozone data in the surrounding area of site JOT403 are then averaged based on EPA AQS records. Ozone production in Atlanta is known to be NO_x -limited (Sillman et al., 1995). Similarly, we use data from CASTNET for the site located in the suburban area of Atlanta (GAS153) for our analysis.

Figure 14 shows the historical variations in emissions and pollutant concentrations in Los Angeles from 1996 to 2012 as well as the change rates of surface ozone and total nitrate across the study area. We choose total nitrate (nitrate aerosols

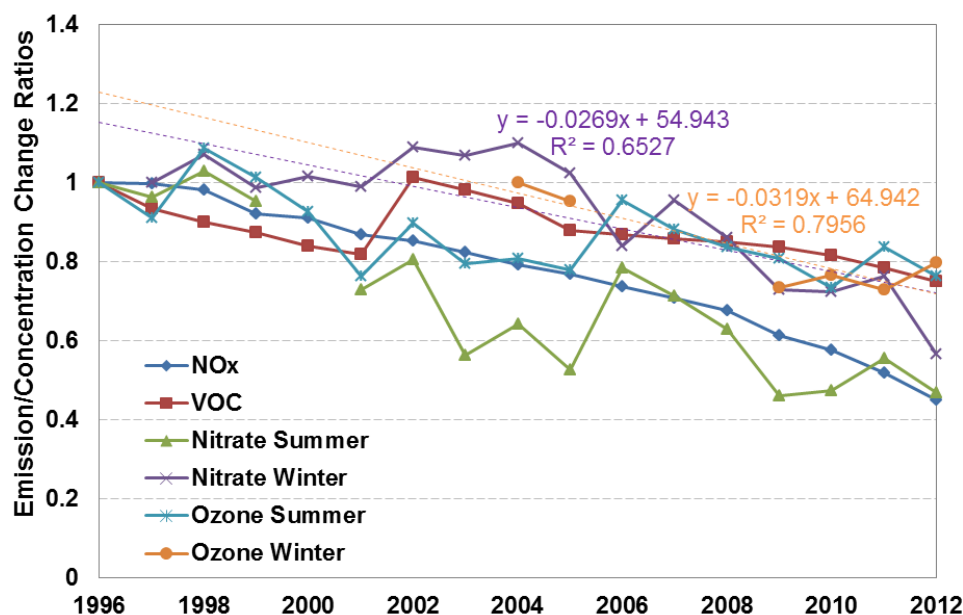


Fig. 15. Historical variations in the emissions and pollutant concentrations in suburban Atlanta, GA between 1996 and 2012. The data for NO_x and VOC emissions are from the NEI data set. The change rate of total nitrate for both summer and winter are calculated from the CASTNET measurements at site GAS153. The change rate of ozone is calculated from the DM8H concentrations of surface ozone, which are averaged from the EPA AQS records for the same county where site GAS153 is located. Winter ozone in this area was not recorded until 2009. The change rate is calculated based on the first year concentration (e.g., 1996).

+ nitric acid) for the presented analysis in order to avoid the influence of sulfate and the availability of ammonia on nitrate formation (Lei and Wuebbles, 2013); this means that the analyzed change can be expected to represent the specific effect of NO_x transformation.

We find that both NO_x and anthropogenic VOC emissions decrease slowly. The NO_x decrease rate is approximately 20 % by 2012. Considering the large amount of VOC emitted from biogenic sources in summer, the VOC decreasing rate may be less than is indicated by the trend in Fig. 14, which suggests that both the surface ozone concentration and the nitrate concentration in the summer show decreasing trends. The nitrate decrease rate is larger than that for the surface ozone, which echoes the results from the model sensitivity analysis (Fig. 7). Owing to the reduction of biogenic VOC emissions in winter, surface ozone production in Los Angeles is strongly VOC-limited. As a result, the total nitrate concentration decreases by as much as 60 % in response to a NO_x decrease with an R-squared value of 0.7192. This trend of total nitrate change shown in the figure passes the 95 % confidence test (*t* test).

The ozone concentration does not show a clear decreasing trend. According to the sensitivity analyses, more active NO_x can be produced for nitrate formation with a rate above the NO_x increase rate in a VOC-limited ozone production environment. In the same environment, the nitrate decrease rate is larger than the decrease rate of NO_x . This observational variability confirms the results of the analyses presented in

modeling sensitivity studies, indicating that a typical nitrate production type is associated with a high NO_x regime.

Ozone production in Atlanta is reported to be a typical NO_x -limited type (Sillman et al., 1995), and the analyses of the suburban regions of Atlanta confirm this (Pierce et al., 1998). Figure 15 shows the observational results from Atlanta. In the summer, nitrate and ozone both show decreasing trends in response to the reduction in NO_x emissions over the past decade. The trends are given in dashed lines. The nitrate change trend has an R^2 value of 0.6527, which passes the 95 % confidence test. As reported in previous studies (Blanchard et al., 2010) concerning relative VOC/ NO_x level (> 10), ozone production in suburban Atlanta is still under a NO_x -limited regime in winter. Therefore, the change rate of nitrate is much lower than the change rate in a VOC-limited environment (e.g., Los Angeles). Although wintertime ozone data are not abundant in the Atlanta area, the available data also show a clearly decreasing trend.

4 Conclusion

As precursors to tropospheric ozone and nitrate, NO_x and its transformation are heavily related to their concentrations and to total pollution level. Climate and emission changes are the two key factors that dictate NO_x transformation. In this study, the CAM-Chem model is used for simulations to study the sensitivity of NO_x transformations over the contiguous US in

response to emission and climate perturbations. In the emission perturbation experiments, the ozone concentration over industrial regions is relatively stable. The examination of the relative concentrations of hydrocarbon and NO_x indicates a weak VOC-limited regime for ozone production over the industrial regions of eastern US. A decrease or small increase in the ozone concentration in response to a large increase in NO_x emissions leads to more active NO_x for nitrate formation, which explains why the responded nitrate change ratio is larger than the emission change ratio. The seasonal transfer of ozone production type can also affect changes in surface ozone and nitrate levels.

In the climate perturbation experiments, a temperature increase was shown to accelerate the decomposition of odd nitrogen (NO_y) during the night. As a result, the total transformation rate of NO_x to nitrate decreases. Ozone production in industrial regions increases in warmer conditions and decreases with an increase in NO_x emissions, but it shows the opposite trends in non-source regions into which NO_x is primarily transported, indicating different regional sensitivities for the transformation rate of NO_x to ozone in response to climate change. The findings of the present study thus indicate that a change in the ozone concentration is more directly affected by changes in climate and precursor emissions, while a change in the nitrate concentration is sensitive to local ozone production types and their seasonal transfer.

Furthermore, our subsequent analyses of historical emissions and air quality observations from the NEI, CASTNET, and EPA AQS data sets confirm the results of the sensitivity studies. As a typical VOC-limited environment, the Los Angeles area shows a higher rate of change in total nitrate compared with the change in NO_x emissions. By contrast, the Atlanta area, as a typical NO_x-limited environment, shows close rates of change in both ozone and total nitrate in response to the change in NO_x emissions from 1996 to 2012. This observational evidence substantiates the results of the sensitivity studies and further confirms that nitrate change is associated with the relative levels of NO_x and VOC emissions in the local area.

It is noted that we focus our analysis on the processes of NO_x transformation and the subsequent production of nitrate and ozone as well as on how these processes respond to emission and climate perturbations. The perturbations in other factors associated with ozone/nitrate production are not discussed. Some of these factors may also seriously affect future surface ozone or nitrate change. For example, the biogenic emissions of hydrocarbons are sensitive to surface ozone production; the availability of ammonium and sulfate may limit nitrate aerosol production (Lei and Wuebbles, 2013); and humidity may affect the physical and chemical processes associated with both. An analysis of these factors is outside the scope of this study. However, studying the role of these factors in affecting the surface ozone or nitrate concentration would be a valuable topic to study in order to further understand the complicated processes associated with

ozone/nitrate formation as well as change on present pollution status.

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