Regional NO$_2$ emission inversion through four-dimensional variational approach using SCIAMACHY tropospheric column observations

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Abstract

Significant reductions of tropospheric NO$_2$ columns over the Ohio valley region in USA have been revealed by the SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric CHartographY) satellite observations. In this paper, the NO$_x$ emission scaling factors applied over 2001 National Emissions Inventory (NEI) are estimated through a four-dimensional variational (4D-Var) approach. In this “top-down” approach, summer 2004 SCIAMACHY measurements are assimilated into a regional chemical transport model (CTM), STEM, using different assimilation set-ups. In one setup, NO$_x$ emissions are adjusted by assimilating SCIAMACHY NO$_2$ columns. In another setup, initial O$_3$ concentrations are allowed to be adjusted along with the NO$_x$ emissions. The optimal emission scaling factors obtained from the test cases agree well with each other. The spatial distribution of the emission

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scaling factors that reflect the recent emission changes confirms the reduction of the NO$_x$ emissions by power plants in the eastern United states. In the end, we explore a more general setup of emission inversion that not only allows control variables of initial conditions and emissions to be adjusted at the same time, but also allows assimilating observations of different species and of different nature. A test case that assimilates both NO$_2$ columns and ozone measurements from various platforms yields results mostly consistent with previous cases.

Key words: NO$_2$ column, NO$_x$ emission, Adjoint, Emission inversion, Assimilation

1. Introduction

As the most important ozone precursor and contributing to the local air pollution itself, nitrogen dioxide (NO$_2$) is one of the key species in atmospheric chemistry of earth’s troposphere. The NO$_2$ measurements by satellite instruments GOME (Global Ozone Monitoring Experiment, from August 1995 to June 2003 (Burrows et al., 1999)) and SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric CHartographY, since August 2002 (Bovensmann et al., 1999)) provide continuous global coverage of NO$_2$ columns. Richter and Burrows (2002) presented a technique using the Differential Optical Absorption Spectroscopy (DOAS) to retrieve the tropospheric NO$_2$ from the GOME satellite measurements. By applying the technique to GOME and SCIAMACHY measurements from 1995 to 2004, Richter et al. (2005) found significant reductions of tropospheric NO$_2$ over parts of Europe, and over the Ohio valley region in USA. An upward trend of tropospheric
NO$_2$ over the years was observed over parts of China and in the northeast of the USA.

To a first approximation, the changes of tropospheric NO$_2$ columns reflect the NO$_x$ emission changes. However, transport and photochemical reactions that affect NO$_2$/NO$_x$ partitioning have to be taken into account in order to trace back the emission sources. The nonlinear relationship between NO$_x$ emissions and NO$_2$ columns was demonstrated by Stavrakou et al. (2008). Using the IMAGES global CTM and its adjoint with GOME/SCIAMACHY observations, they showed that the inferred emission growth rate in Beijing region from 1997 to 2006 as $\approx 9\%/\text{year}$ in both summer and winter although there is dramatic differences in the growth rate of the observed NO$_2$ columns between the two seasons ($5.3\%/\text{year}$ in summertime and $11.8\%/\text{year}$ in wintertime). Therefore, to infer the emission of NO$_x$ via the “top-down” approach, it is important to fully take advantage of the CTMs which have our best understanding of the physical and chemical processes thoroughly implemented.

Emission inversion problems have drawn a lot of attention in recent years. For instance, Pétron et al. (2002) constrained the global emissions of carbon monoxide (CO) by using a three-dimensional (3-D) inverse modeling scheme with the IMAGES model. Palmer et al. (2003) and Wang et al. (2004) used aircraft and surface station observations of CO and NO$_y$ during the Transport and Chemical Evolution Over the Pacific (TRACE-P) mission in combination of an optimal estimation inverse model to constrain the regional CO and NO$_x$ emission of different sources. Recently, some CTMs and their adjoints have been utilized in the “top-down” emission estimations. The IMAGES global
CTM and its adjoint were used to invert CO and NO$_x$ emissions with both surface and satellite observations (Müller and Stavrakou, 2005; Stavrakou and Müller, 2006; Stavrakou et al., 2008). The STEM regional CTM and its adjoint model were developed for emission inversion problems and were applied to analyze the black carbon (Hakami et al., 2005) and mercury (Pan et al., 2007) emission inventories using the observations during the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia). Henze et al. (2008) developed inverse modeling for PM2.5 precursor emissions using the adjoint of GEOS-Chem.

In this study, we use the SCIAMACHY tropospheric NO$_2$ columns during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) (Singh et al., 2006) operations in the summer of 2004 and the STEM regional CTM to deduce time-independent scaling factors applied to grid-based NO$_2$ emissions generated using 2001 U.S. EPA National Emissions Inventory (NEI). In the emission inversion, two separate sets of emission scaling factors are applied to surface and elevated NO$_x$ emissions, respectively. A general setup of emission inversion that also allows the adjustment of initial concentrations of chemical species is also tested. In addition, the effect of assimilating ozone observations from various platforms is also discussed.

The paper is organized as the following. A brief description of the STEM model and the emission inversion method using variational approach is given in Section 3. Section 4 presents the emission inversion results. A summary is given in Section 5.
2. SCIAMACHY Tropospheric Nitrogen Dioxide Observations

2.1. SCIAMACHY column data coverage

Although SCIAMACHY can provide global coverage of NO\textsubscript{2} columns, the region of our interest is only partially covered each day. Figure 1(a) shows the observed regions on July 20, 2004. The observing time is around 1030 local time. To eliminate the effect of clouds on the retrievals, a simple criterion, the normalized intensity < 0.15, was used to select cloud-free regions. Figure 1(b) shows the tropospheric NO\textsubscript{2} columns on July 20, 2004 after removing the cloud regions. The number of measurements is significantly reduced after the cloud removal. Hereafter, only data associated with the normalized intensity less than 0.15 are used.

For the NO\textsubscript{2} columns shown in Figure 1, not all the NO\textsubscript{x} emissions will be constrained if only such spatially incomplete samplings are incorporated in the emission inversion. To have a better constraint from the measurements in the “top-down” emission inversion, it is desirable to have a near complete sampling throughout the domain. Here we chose to merge the available NO\textsubscript{2} columns from July 1 to August 31, 2004 together by neglecting the daily variations.

Figure 2 shows the cloud-free measurements during the weekends and weekdays from July 1 to August 31, 2004, respectively. Even with the data of 18 different weekends stacked together, there are still significant blank regions. Merging the 44 weekdays generates a much better coverage of the domain, although there are still areas left without observations, e.g., middle Pennsylvania. However, these areas are well represented by the data during the weekends. Figure 2 also shows little contradictions between mea-
measurements from different days. Both weekday and weekend data sets show strong and similar spatial patterns revealing the various levels of anthropogenic activities at different locations. There are slight differences between the data sets of weekdays and weekends, but the differences are relative small compared with the spatial variations. In order to achieve a complete spatial coverage in the domain, we stacked both weekday and weekend data together. Such merging also helps to eliminate the effect of daily variation in NO$_x$ emission, which is not of our interest here. Our main objective is to infer the average NO$_x$ emissions in summer 2004 from the SCIAMACHY tropospheric NO$_2$ columns and compare that with the current 2001 NEI.

After stacking all the data together, we calculated the mean and standard deviation of the observations inside each grid cell. The standard deviation was then normalized by the local mean to indicate the variation of the observation in the two-month period. Figure 3 shows the distributions of the mean observations and normalized standard deviation in the computational domain. For most of the regions the normalized standard deviation is smaller than 50%. The areas with large daily variations during the two months are often associated with low NO$_2$ columns, except for the New York City area. As the daily variation is not of our interest here, we generate a pseudo-observation data set that has the two-month mean NO$_2$ column at each grid cell as the measurement value. The normalized standard deviation at each grid cell was assigned as the measurement uncertainty of the pseudo-observation. The average measurement time during the day was given for each pseudo-observation.
3. Method

3.1. Chemical transport model

In this study, the STEM-2K3 (Tang et al., 2004) regional chemical transport model is employed. It is a flexible regional-scale chemical transport model using SAPRC99 chemical mechanism (Carter, 2000) with on-line photolysis solver (Tang et al., 2003). Meteorological inputs to the model came from the fifth-generation Mesoscale Model (MM5) using NCEP (National Centers for Environmental Prediction) FNL (Final Global Data Assimilation System) analyzed data during post-analysis. A grid with a 60 km horizontal resolution (25 cells in longitude, and 22 cells in latitude) is used over the northeast US domain, as shown in Figure 3. Vertically the model had 21 layers, extending from the surface to 100 hPa using 0.999, 0.9965, 0.9925, 0.985, 0.97, 0.945, 0.91, 0.87, 0.825, 0.77, 0.71, 0.65, 0.59, 0.53, 0.47, 0.41, 0.35, 0.285, 0.21, 0.125, and 0.04 in sigma coordinates. The emissions inventory was based on the 2001 NEI, with updated large point source emissions (Frost et al., 2006). Upper troposphere lightning $NO_x$ emissions were added to the model based on the National Lightning Detection Network (NLDN), modulated by signal strength and multiplicity of flashes. Further information about the lightning emissions can be found in Tang et al. (2007). Biogenic emissions were estimated using Biogenic Emissions Inventory System 2 (BEIS2) which generates time-varied isoprene and monoterpene emissions driven by meteorological variables from MM5. Forest fires that occurred during the ICARTT period were largely outside the model domain (in Alaska and Northwestern Canada), therefore their influence was incorporated through lateral boundary conditions from MOZART global chemical model predic-
tions. The boundary conditions are provided by STEM-2K3 run over a bigger domain that covers the continental United States (see Tang et al. (2007) for detail).

The evolution of the chemical constituent concentration vector $c$ in time $(t)$ can be described as

$$\frac{\partial c}{\partial t} = -u \cdot \nabla c + \frac{1}{\rho} \nabla \cdot (\rho K \cdot \nabla c) + \frac{1}{\rho} f + E$$

(1)

Here we denote by $u$ the wind field vector, $\rho$ the air density, $K$ the turbulent diffusivity tensor, $f$ the chemical transformation rate, and $E$ the emission rate.

3.2. Emission inversion via 4D-Var

In this study, the emission inversion problem is solved via the STEM 4D-Var system (Sandu et al., 2005; Chai et al., 2006, 2007). The discrepancy between the available observations and model counterparts is built into a cost functional. Optimal solutions of model parameters such as the NO$_x$ emissions are obtained by finding new parameters which minimize the cost functional. To solve the minimization problems efficiently, the sensitivity of the cost functional with respect to the control variables (parameters to be adjusted) need to be calculated. Adjoint models provide the most efficient way to calculate the gradients of a large number of control variables (Elbern et al., 2000; Schmidt and Martin, 2003).

The cost functional $J$ is defined as

$$J = \frac{1}{2} [\epsilon - 1]^T E^{-1} [\epsilon - 1] + \frac{1}{2} [c_0 - c_b]^T B^{-1} [c_0 - c_b] + \frac{1}{2} [y - h(c)]^T O^{-1} [y - h(c)].$$

(2)
$E$, $B$, and $O$ are error covariance matrices for emission scaling factors, initial states (background), and observations in discrete spaces, respectively. $h$ is a projection operator, calculating the observation vector $y$ from the model space $c$. In the current study the control variables can include both initial states $c_0$ and emission rates. The subscript “0” is used to denote variables at the instant $t = 0$. Assuming that the operator $h$ is linear, $h(c)$ can be written as $h(c) = H \cdot c$. In our application, $H$ reflects vertical integration and linear interpolation in time when constructing model counterparts of the $NO_2$ columns.

A larger-scale bound-constrained limited-memory quasi-Newton code, L-BFGS-B (Zhu et al., 1997) is used for the minimization. The maximum number of iterations is set to be 25. The initial $O_3$ background error covariance $B$ were estimated using both NMC and observational methods. Truncated singular value decomposition (SVD) regularization is used for the inversion of $B$ matrix (see Chai et al. (2007) for detail). Assuming uncorrelated emission scaling factor errors in space, the uncertainty of emission scaling factor $\epsilon$ was chosen as 0.5 uniformly. The upper and lower bounds of $\epsilon$ during the minimization with L-BFGS-B subroutine were assigned as 10 and 0.1, respectively. The observation errors of $NO_2$ pseudo-columns were given by the standard deviations at individual grid cells during the two-month period. Following Chai et al. (2007), the observation errors of $O_3$ were set to be 8 ppbv everywhere. Errors of $NO_2$ pseudo-columns and $O_3$ observations were assumed uncorrelated among themselves and between each other.

The assimilation time window is chosen to be 24 hours for the following emission inversion cases. We first started our emission inversion tests by
only adjusting the NO\textsubscript{x} emission rates. Later we included the initial ozone
conztrations as control variables as well. It is designed to eliminate the
effect of the notable errors in the initial ozone states. The most recent work
by Elbern et al. (2007) studied the effect of combining both emission rate and
initial state as control variables. Also note that we chose emission scaling
factors $\epsilon$ instead of the emission rates as control parameters (see Hakami
et al. (2005); Pan et al. (2007) for detail).

Appendix A illustrates the association between emission sensitivity and
adjoint variables through the “continuous adjoint” approach. In our applica-
tion, the “discrete adjoint” approach is implemented to assure consistency.
This is briefly described in Appendix B. More discussion on “continuous
adjoint” and “discrete adjoint” can be found in Sandu et al. (2005).

4. Results

4.1. Results without assimilation

First we included all the measurements and assumed the two-month ob-
servations were measured on July 20, 2004. Figure 4 shows the compari-
son between the SCIAMACHY NO\textsubscript{2} columns and the “model counterparts”
on July 20, 2004. It is seen that the model mostly overestimates the low
NO\textsubscript{2} column values ($< 10^5$ molecules/cm\textsuperscript{2}). Then we considered the pseudo-
columns which were generated by averaging multiple observations during the
two-month period at each grid cell. Figure 4 shows a good agreement be-
tween such pseudo-observations and their “model counterparts”. Note that
the low NO\textsubscript{2} column values were effectively removed after the averaging for
the pseudo-observations.
Figure 5 shows model predictions of SCIAMACHY $NO_2$ pseudo-columns on July 17 (Saturday), 18 (Sunday), 19 (Monday), and 20 (Tuesday), respectively. Note that the current emission inventory differentiates Saturdays and Sundays from weekdays, i.e. it has 3 different temporal daily profiles. Since the $NO_2$ columns are dominated by the lower level $NO_2$ concentrations, the different $NO_x$ daily emission profiles generated significantly different $NO_2$ columns. It is shown in Figure 5 that $NO_2$ predictions on July 17 and 18 are dramatically different from those predicted during the weekdays. The differences between July 19 and 20 predictions are relatively small, albeit apparent. The distribution of $NO_2$ column predictions on the weekdays resemble that of the SCIAMACHY observations shown in Figure 3. Table 1 shows that the model overestimates the $NO_2$ columns for all four days. Predictions on July 20, 2004 gives the best overall agreement with the SCIAMACHY observations, showing a small bias of $6.7 \times 10^{14}$ molecules/cm$^2$, and correlation coefficient as 0.673.

4.2. Assimilation results

The emission inversion tests are listed in Table 2. In all four tests, the $NO_x$ emission scaling factors are adjusted. Considering the different nature of the two major $NO_x$ sources, transportation and power plants, we adjust the surface and elevated (above the first level) $NO_x$ emissions with two different sets of emission scaling factors. No temporal variation is assumed for the scaling factors. That is, the diurnal variations of the original emissions are preserved. In the emission inversion, the valid range of the emission scaling factors is set to be between 0.1 and 10.0.

In case EM01, $NO_2$ columns are assimilated on July 20, 2004 with a
24-hour time window. The distributions of the $NO_x$ emission scaling factors at the surface and upper levels are shown in Figure 6. In most of the domain there is little $NO_x$ emission adjustment, indicated by the regions with the emission scaling factors close to one. Close to the area where the states of Ohio, West Virginia, and Pennsylvania join each other hereinafter referred as the OWP area, both surface and elevated emissions show downward adjustment to alleviate the model overestimation (see Figure 3 and Figure 5). Similar emission reductions are found at Detroit and Washington DC areas for both surface and elevated emissions as well. At the surface, there are several other locations with $NO_x$ emissions adjusted up or down. However, these locations are often not associated with large $NO_x$ emission sources. To show the overall emission adjustment in the domain, we multiply the emission scaling factors with their base emission rates. The results are shown in Table 3. It shows that the elevated emissions are reduced by 12.9% and the surface emissions are reduced by only 6.6%. Combined together, the total $NO_x$ emissions are reduced by 8.0% after assimilating the SCIAMACHY data. After the emission adjustment, the model results of $NO_2$ columns improve significantly. As shown in Table 1 and Table 3, the bias is reduced from $6.7 \times 10^{14}$ molecules/cm$^2$ to $0.561 \times 10^{14}$ molecules/cm$^2$, and root-mean-square (RMS) error is reduced from $33.4 \times 10^{14}$ molecules/cm$^2$ to $12.188 \times 10^{14}$ molecules/cm$^2$. The correlation between the model and observation also improves, with correlation coefficient increased from 0.673 to 0.819.

The setup of case EM02 is same as case EM01, except that the assimilation time window is shifted one day earlier. Note that there are not only
changes in the meteorological fields, but also differences in the atmospheric chemistry states. The distributions of the $NO_x$ emission scaling factors at the surface and upper levels are shown in Figure 7. Emission reductions are seen around the OWP area and Washington DC in both surface and upper levels, similar as case EM01 shown in Figure 6. However, the emission reduction in the OWP area for case EM02 is greater than that in case EM01. For the surface $NO_x$ emissions, there are differences in the direction of the adjustments at several locations, such as the northeast and northwest corners of the domain. For the elevated emissions, results of the two cases resemble each other except for slight differences in northern Virginia and western Erie lake areas. The emission changes over the whole domain after the adjustment for case EM02 are very close to case EM01, especially for the emissions at the upper levels, with both cases showing a 12.1% reduction over the domain.

In cases EM01 and EM02, only the $NO_x$ emissions are adjusted to fit the model predictions of the SCIAMACHY $NO_2$ columns. This approach assumes that the only source of error is the emission, thus it attempts to minimize the model prediction errors by adjusting emissions only. With significant uncertainties in many other parameters, such as initial and boundary conditions, reaction rates, and meteorological fields, the emission adjustments may yield faulty results due to the errors in the other model parameters. In cases IE01 and IE02 which are listed in Table 2, we extend the emission inversion to include the simultaneous adjustment of additional parameters. As $NO_2$ is short lived, its initial concentrations will have little effect in model predictions. We chose to add initial ozone concentrations as control variables because of the key role of the $NO_x$ emissions in ozone
chemistry and ozone being the major concern in the troposphere chemistry.

Figure 8 shows the distributions of the $NO_x$ emission scaling factors from case IE01. Great similarity is found between Figure 6 and Figure 8, especially for the elevated emissions. At the surface, the magnitude of the emission adjustment tends to be smaller than for the case EM01 in most regions. As listed in Table 3, the total emission reduction at surface over the computational domain (2.7%) is less than half of case EM01 (6.4%). The emission reduction for IE01 at the upper levels (12.4%) is close to the result of case EM01 (12.1%). By allowing additional parameters to be adjusted, the model predictions of $NO_2$ are slightly better than case EM01, as indicated by model bias, RMS error, and correlation coefficient as listed in Table 3.

In case IE01, it is found that allowing the $NO_2$ column observations to impact both the emission scaling factors and the initial $O_3$ improves the $NO_2$ predictions. We also explored whether assimilating additional observations would improve the results. In case IE02, ozone observations from various platforms on July 20, 2004 (see Chai et al. (2007) for details) are added to the observation set assimilated. Same as case IE01, both the emission scaling factors and the initial $O_3$ concentrations are treated as control variables. Figure 9 shows the distributions of $NO_x$ emission scaling factors yielded from case IE02, which are quite different from the previous cases. However, the emission reduction in the OWP area and DC area are consistent with the previous tests. Case IE02 results show that the $NO_x$ emissions at several grid cells need to be doubled in order for the model to match the additional ozone observations. After integrating over the computational domain, we see little change in the $NO_x$ emissions at the surface (0.8% in reduction).
the upper levels, the emission reduction of 8.9% over the domain is close to
the previous cases. Compared with cases IE01 and EM01 (see Table 3), IE02
generates NO₂ predictions with worse bias (3.631 \times 10^{14} \text{ molecules/cm}^2),
larger RMS error (15.098 \times 10^{14} \text{ molecules/cm}^2), and smaller correlation
coefficient (0.794). This suggests that the additional O₃ observations does
not help constraining the NOₓ emissions. It is probably due to the high
uncertainty in other parameters involved in the ozone chemistry, such as the
emissions of volatile organic compounds (VOCs).

If we simply adjust the NOₓ emissions by the ratio of the SCIAMACHY
NO₂ columns versus the predicted NO₂ columns at each grid point, we will
get an increase of 24.6% in total NOₓ emission (31.8% increase for the surface
emission and 2.9% for the elevated emission). This result clearly contradicts
to the fact that the actual NOₓ emissions were less than what is given in
NEI 2001. Such contradiction is mainly caused by the over-simplification, i.e.
assuming linear relationship between the NOₓ emissions and NO₂ columns
without taking account of transport or photochemical reactions that affect
NO₂/NOₓ partitioning. As also demonstrated by Stavrakou et al. (2008), it
is important to include the physical and chemical processes in the “top-down”
approach to infer the NOₓ emissions.

5. Summary

In a “top-down” approach, SCIAMACHY NO₂ column data in the sum-
mer of 2004 are assimilated into a chemical transport model (CTM), STEM.
We demonstrate that the four-dimensional variational (4D-Var) approach al-
allows a more general framework in emission inversion. In this general setup,
more uncertain model parameters can be adjusted in addition to the emission fields. Observations of different species in various format can also be used to constrain the inverse problem.

The test cases show that the emission inversion results are sensitive to the problem setup. Emission scaling factors from the last case where both ozone observations and NO2 column data are assimilated while allowing initial ozone and NOx emissions to be adjusted are very different from the other cases. It is probably not beneficial to add ozone observations to constrain the NOx emissions because of the great uncertainties associated with VOCs.

When only NO2 column data are assimilated, adding initial ozone concentrations as control variables to be adjusted generates less adjustment in NOx emissions, especially for the surface emissions. All the cases show consistent results over the Ohio valley region and Washington District of Columbia area, revealing the NOx emission reduction. With emission at surface and upper levels adjusted separately, we found the results at upper levels are quite robust. The elevated NOx emission reduction results from four test cases range from 8.9% to 11.4%, indicating the power plant NOx emission reduction from 2001 to 2004. Stavrakou et al. (2008) reported their inferred posterior NOx emissions are decreased by 35% between July 1997 and 2006 in the Ohio River Valley, with annual change rate of $-0.47\%/year$ in summertime. This agrees well with our results.

While SCIAMACHY satellite observations provide more than adequate data for global model emission inversion, their temporal and spatial resolutions are lacking for a regional model application to resolve detailed grid-based emission inversion. Ignoring the daily variability, we stacked together
the $NO_2$ columns in two months to generate a pseudo-observation set that has the two-month mean at each grid cell. While our main focus here is on the formulating of the emission inversion problem, we plan to apply such pseudo-observations as well as the original data over a larger domain for an extended time period in the future. The emission inversion results will be able to complement the “bottom-up” emission inventories.

Appendix A: Emission sensitivity via continuous adjoint

Here we first consider a simple one dimensional problem involving only one species. By assuming constant air density, and ignoring the advection and reaction terms, the transport equation is further simplified and becomes

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left( K \frac{\partial c}{\partial z} \right) + E(z, t) \tag{3}$$

where $c = c(z, t)$ and $z \in (0, L)$, $t \in (0, T)$. As we only aim to illustrate how the emission sensitivity associates with the adjoint variables, instead of cost functional in the least square form as in equation (2), we define a general response functional as

$$J = \int_0^L \int_0^T g(z, t) dt dz \tag{4}$$

To derive the adjoint equation, we introduce the Lagrange multiplier $\lambda_c(z, t)$. Multiply equation (3) with it and integrate over computational domain (a factor of $\frac{1}{L}$ is added). Subtract the result from equation (4), we get

$$J' = J - \frac{1}{L} \int_0^L \int_0^T \lambda_c \left[ \frac{\partial c}{\partial t} - \frac{\partial}{\partial z} \left( K \frac{\partial c}{\partial z} \right) - E(z, t) \right] dt dz \tag{5}$$
The variation of equation (5) yields

\[ \delta J' = \delta J - \frac{1}{L} \int_0^L \int_0^T \delta \lambda_c \left[ \frac{\partial c}{\partial t} - \frac{\partial}{\partial z} \left( K \frac{\partial c}{\partial z} \right) - E(z, t) \right] dtdz \]

\[ - \frac{1}{L} \int_0^L \int_0^T \lambda_c \left[ \frac{\partial \delta c}{\partial t} - \frac{\partial}{\partial z} \left( K \frac{\partial \delta c}{\partial z} \right) - \delta E(z, t) \right] dtdz \]

(6)

Integrating by parts gives

\[ \delta J' = \frac{1}{LT} \int_0^L \int_0^T \delta g(z, t) dtdz \]

\[ - \frac{1}{L} \int_0^L \int_0^T \delta \lambda_c \left[ \frac{\partial c}{\partial t} - \frac{\partial}{\partial z} \left( K \frac{\partial c}{\partial z} \right) - E(z, t) \right] dtdz \]

\[ - \frac{1}{L} \int_0^L \int_0^T \delta c \left[ - \frac{\partial \lambda_c}{\partial t} - \frac{\partial}{\partial z} \left( K \frac{\partial \lambda_c}{\partial z} \right) \right] dtdz \]

\[ - \frac{1}{L} \int_0^T \left[ - K \lambda_c \frac{\partial \delta c}{\partial z} + K \frac{\partial \lambda_c}{\partial z} \right] dt \]

\[ - \frac{1}{L} \int_0^L [\lambda_c \delta c] |_{t=T} dz \]

\[ + \frac{1}{L} \int_0^L [\lambda_c \delta c] |_{t=0} dz \]

\[ + \frac{1}{L} \int_0^L \int_0^T \lambda_c \delta E(z, t) dtdz \]

(7)

The second term on the right-hand side vanishes as the state variable satisfies equation (3). Combine the first and the third term and force that to vanish gives the adjoint equation

\[ \frac{\partial \lambda_c}{\partial t} = - \frac{\partial}{\partial z} \left( K \frac{\partial \lambda_c}{\partial z} \right) - \frac{1}{T} \frac{\partial g}{\partial \lambda_c} \]

(8)

The fourth term would vanish with proper boundary conditions (e.g., \( \lambda_c = 0 \) at Dirichlet boundaries). Forcing the fifth term to be zero gives the initial condition for the adjoint variable \( \lambda_c \) at \( t = T \) as

\[ \lambda_c(z, T) = 0 \]

(9)
Then equation (7) becomes

\[
\delta J' = \frac{1}{L} \int_0^L [\lambda_c \delta c] |_{t=0}dz + \frac{1}{LT} \int_0^L \int_0^T T \lambda_c \delta E(z, t) dt dz
\]  

(10)

This provides the variational sensitivity information for both the initial and emission functions.

\[
\frac{\delta J'}{\delta c(z, t = 0)} = \lambda_c(z, t = 0), \quad \frac{\delta J'}{\delta E(z, t)} = T \lambda_c(z, t)
\]  

(11)

If we introduce emission scaling factors \(\epsilon\) as

\[
\epsilon(z) = \frac{E(z, t)}{E_0(z, t)}
\]  

(12)

Note \(\epsilon(z)\) does not to vary in time. The last term in equation (7) would become

\[
\frac{1}{L} \int_0^L \left( \int_0^T \lambda_c E_0(z, t) dt \right) \delta \epsilon(z) dz
\]  

(13)

Thus, the sensitivity of the response function to the emission scaling factor has the following form

\[
\frac{\delta J'}{\delta \epsilon(z)} = \int_0^T \lambda_c E_0(z, t) dt
\]  

(14)

Without detail, here we give the emission sensitivity for species \(i\) in a four-dimensional air quality model,

\[
\frac{\delta J'}{\delta \epsilon_i(x, y, z)} = \int_0^T \lambda_{c_i}(x, y, z) E_0(x, y, z, t) dt
\]  

(15)

In the current study, emission rates are adjusted separately using two sets of 2-D functions, \(\epsilon^s(x, y)\) for the surface and \(\epsilon^e(x, y)\) for higher levels.

\[
\frac{\delta J'}{\delta \epsilon^s_i(x, y)} = \int_0^T \lambda_{c_i}(x, y, z) \frac{q_0(x, y, t)}{\Delta z_1} dt
\]  

(16)
\[
\frac{\delta J'}{\delta e_i(x, y)} = \frac{1}{z_{\text{top}} - z_1} \int_{z_1}^{z_{\text{top}}} \int_0^T \lambda_i(x, y, z) E_0(x, y, z, t) dt dz
\]  
(17)

where \(\Delta z_1\) is the depth of the first layer. \(z_1\) and \(z_{\text{top}}\) are the height of the first and top layer, respectively. Note that the surface area emission \(q_0(x, y, t)\) includes the first level volume emission rate, i.e.

\[
q_0(x, y, t) = q_0^{\text{surface}}(x, y, t) + \int_{z_1}^{z_{\text{top}}} E_0(x, y, z, t) dz
\]  
(18)

**Appendix B: Emission sensitivity via discrete adjoint**

As operator-splitting technique is implemented in solving equation (1), the emission sensitivity is only directly associated with vertical transport. Using Crank-Nicholson time stepping for the concentrations and forward Euler for boundaries and the surface emissions, the forward discrete model evolving the concentration column vector \(C_i\) from time step \(n\) to \(n+1\) for vertical transport reads

\[
C_i^{n+1} = \left( I - \frac{\Delta t}{2} A (t^{n+1}) \right)^{-1} \left[ \left( I + \frac{\Delta t}{2} (t^n) \right) C_i^n + \Delta t \left( B(t^n) e_N + \sum_{j=2}^N E_j^i(t^n) e_j + \frac{q_i(t^n)}{\Delta z_1} e_1 \right) \right]
\]  
(19)

where matrix \(A\) depends on the wind field, the diffusion tensor, and the air density. \(B\) is a scalar that accounts for the top boundary. \(e_j\) is the \(j\)th column of the identity matrix. The adjoint sensitivity with respect to emission rates can be calculated as

\[
\frac{\partial J}{\partial q_i(t^n)} = \left( \frac{\partial C_i^{n+1}}{\partial q_i(t^n)} \right)^T \left( \frac{\partial J}{\partial C_i^{n+1}} \right) = \left( \frac{\partial C_i^{n+1}}{\partial q_i(t^n)} \right)^T \lambda_i^{n+1} = \frac{1}{\Delta z_1} e_1^T \left( I - \frac{\Delta t}{2} A^T (t^{n+1}) \right)^{-1} \lambda_i^{n+1} \Delta t
\]  
(20)

\[
\frac{\partial J}{\partial E_j^i(t^n)} = \left( \frac{\partial C_i^{n+1}}{\partial E_j^i(t^n)} \right)^T \left( \frac{\partial J}{\partial C_i^{n+1}} \right) = \left( \frac{\partial C_i^{n+1}}{\partial E_j^i(t^n)} \right)^T \lambda_i^{n+1} = e_j^T \left( I - \frac{\Delta t}{2} A^T (t^{n+1}) \right)^{-1} \lambda_i^{n+1} \Delta t
\]  
(21)
Since the vector \((I - \frac{\Delta t}{2}A^T(t^{n+1}))^{-1}\lambda_i^{n+1}\) is already computed during the update of \(\lambda\), there is little additional cost to calculate the emission sensitivity. If we choose the non-time-varying emission scaling factors \(\epsilon_i\) as control variables, their sensitivities can be written as

\[
\frac{\partial J}{\partial \epsilon_i^n} = \sum_{n=0}^{N_t-1} \left[ \frac{1}{\Delta z_1} e^T_1 \left( I - \frac{\Delta t}{2}A^T(t^{n+1}) \right)^{-1} \lambda_i^{n+1} q_{i0}(t^n) \Delta t \right] (22)
\]

and

\[
\frac{\partial J}{\partial e_i} = \sum_{n=0}^{N_t-1} \sum_{j=2}^{N_z} e_j^n \left( I - \frac{\Delta t}{2}A^T(t^{n+1}) \right)^{-1} \lambda_i^{n+1} E_{i0}^j(t^n) \Delta t \right] (23)
\]

where \(N_t\) and \(N_z\) are total number of time steps and vertical levels, respectively.

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Table 1: Assessment of NO\textsubscript{2} column predictions on four different days (July 17-20, 2004) against the SCIAMACHY pseudo-columns. Units of bias, mean differences, and RMS differences are 10\textsuperscript{14} molecules/cm\textsuperscript{2}.

<table>
<thead>
<tr>
<th>Date</th>
<th>Bias</th>
<th>Mean Difference</th>
<th>RMS Difference</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 17, 2004</td>
<td>13.6</td>
<td>25.2</td>
<td>41.4</td>
<td>0.336</td>
</tr>
<tr>
<td>July 18, 2004</td>
<td>8.7</td>
<td>18.1</td>
<td>29.6</td>
<td>0.491</td>
</tr>
<tr>
<td>July 19, 2004</td>
<td>11.7</td>
<td>17.7</td>
<td>28.9</td>
<td>0.587</td>
</tr>
<tr>
<td>July 20, 2004</td>
<td>6.7</td>
<td>14.6</td>
<td>33.4</td>
<td>0.673</td>
</tr>
</tbody>
</table>

Table 2: Descriptions of data assimilation test cases. Init: initial.

<table>
<thead>
<tr>
<th>Case</th>
<th>Assimilation Window</th>
<th>Assimilated Observation</th>
<th>Control Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM01</td>
<td>0000-2400 UT, July 20, 2004</td>
<td>NO\textsubscript{2} column</td>
<td>NO\textsubscript{x} emission</td>
</tr>
<tr>
<td>EM02</td>
<td>0000-2400 UT, July 19, 2004</td>
<td>NO\textsubscript{2} column</td>
<td>NO\textsubscript{x} emission</td>
</tr>
<tr>
<td>IE01</td>
<td>0000-2400 UT, July 20, 2004</td>
<td>NO\textsubscript{2} column</td>
<td>Init O\textsubscript{3} + NO\textsubscript{x} emission</td>
</tr>
<tr>
<td>IE02</td>
<td>0000-2400 UT, July 20, 2004</td>
<td>NO\textsubscript{2} column, O\textsubscript{3}</td>
<td>Init O\textsubscript{3} + NO\textsubscript{x} emission</td>
</tr>
</tbody>
</table>
Table 3: Data Assimilation Results. Units of bias and RMS error for $NO_2$ columns are $10^{14}$ $molecules/cm^2$.

<table>
<thead>
<tr>
<th>Case</th>
<th>Surface</th>
<th>Elevated</th>
<th>Total</th>
<th>Bias</th>
<th>RMS error</th>
<th>Correlation Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM01</td>
<td>0.934</td>
<td>0.879</td>
<td>0.920</td>
<td>0.561</td>
<td>12.188</td>
<td>0.819</td>
</tr>
<tr>
<td>EM02</td>
<td>0.936</td>
<td>0.879</td>
<td>0.922</td>
<td>5.653</td>
<td>15.883</td>
<td>0.819</td>
</tr>
<tr>
<td>IE01</td>
<td>0.973</td>
<td>0.876</td>
<td>0.949</td>
<td>-0.873</td>
<td>12.108</td>
<td>0.832</td>
</tr>
<tr>
<td>IE02</td>
<td>0.992</td>
<td>0.911</td>
<td>0.972</td>
<td>3.631</td>
<td>15.098</td>
<td>0.794</td>
</tr>
</tbody>
</table>

Figure 1: SCIAMACHY $NO_2$ columns on July 20, 2004. Unit: $molecules/cm^2$. Original data shown on the left (a); data with the normalized intensity less than 0.15 shown on the right (b).
Figure 2: SCIAMACHY $NO_2$ columns from July 1 to August 31, 2004. Unit: molecules/cm$^2$. Left: accumulated data during the weekends. Right: accumulated data during the weekdays.

Figure 3: Mean (left, Unit: molecules/cm$^2$) and normalized standard deviation (right, STD/mean) of SCIAMACHY $NO_2$ columns from July 1 to August 31, 2004.
Figure 4: Comparison between SCIAMACHY $NO_2$ columns and “model counterparts”, before (left) and after (right) averaging in each grid cell. “Model counterparts” were generated by assuming all the observations were measured on July 20, 2004.
Figure 5: “Model counterparts” of SCIAMACHY NO$_2$ pseudo-columns. They were generated by assuming pseudo-columns were measured on July 17, 18, 19, and 20 respectively.
Figure 6: Distributions of $NO_x$ emission scaling factors from Case EM01. Left: surface; Right: upper levels.

Figure 7: Distributions of $NO_x$ emission scaling factors from Case EM02. Left: surface; Right: upper levels.
Figure 8: Distributions of $NO_2$ emission scaling factors from case IE01. Left: surface; Right: upper levels.

Figure 9: Distributions of $NO_2$ emission scaling factors from Case IE02. Left: surface; Right: upper levels.