Numerical study of variational data assimilation algorithms based on decomposition methods in atmospheric chemistry models

Alexey Penenko¹², Pavel Antokhin³

¹Institute of Computational Mathematics and Mathematical Geophysics SB RAS, ICM&MG SB RAS, prospect Akademika Lavrentyeva 6, 630090, Novosibirsk, Russia
²Novosibirsk State University, NSU, Pirogova Str. 2, 630090, Novosibirsk, Russia
³V.E. Zuev Institute of Atmospheric Optics SB RAS, IAO SB RAS, Academician Zuev square 1, 634055, Tomsk, Russia

aleks@ommgp.sscc.ru

Abstract. The performance of a variational data assimilation algorithm for a transport and transformation model of atmospheric chemical composition is studied numerically in the case where the emission inventories are missing while there are additional in situ indirect concentration measurements. The algorithm is based on decomposition and splitting methods with a direct solution of the data assimilation problems at the splitting stages. This design allows avoiding iterative processes and working in real-time. In numerical experiments we study the sensitivity of data assimilation to measurement data quantity and quality.

1. Introduction
Forecasting of chemical weather is a challenge for researchers due to the nonlinear, multiscale and dynamic character of the corresponding transport and transformation processes in the atmosphere. It becomes even more challenging when the emission data are not exact. The aim of data assimilation algorithms is to improve the quality of model forecasts with measurement data arriving in the course of calculations. High dimensional atmospheric chemistry problems impose strict requirements on the numerical efficiency of the algorithms. We study the performance of an algorithm that is able to work without any iterative processes. It is achieved by using independent data assimilation procedures at the splitting stages. Overviews of chemical data assimilation can be found in [1, 2, 3].

We consider a scenario where the unknown emission data are estimated with indirect concentration measurements. The algorithm is used to reconstruct the emission effects of a substance with measurements of the other substances. We evaluate the sensitivity of data assimilation to the quality and quantity of measurement data.

2. Data assimilation algorithm

2.1. Transport and transformation model
Let us consider a horizontally homogeneous domain
bounded by \( \partial \Omega = \partial \Omega \times [0,T] \). In the domain we consider the atmospheric chemistry transport and transformation model

\[
\frac{\partial \phi_l(z,t)}{\partial t} + \text{div}(w \phi_l(z,t) - \mu(z,t) \text{grad} \phi_l(z,t)) = S_l(\phi(z,t)) + f_l(z,t) + r_l(z,t), \quad (z,t) \in \Omega_T. 
\]

\[
\mu(z,t) \frac{\partial \phi_l(z,t)}{\partial \hat{n}} + \beta(z,t) \phi_l(z,t) = g_l(z,t), \quad (z,t) \in \partial \Omega_T, 
\]

\[
\phi_l(z,0) = \phi^0_l(z), \quad z \in \Omega. 
\]

Here \( \phi(z,t) \) is the state function. It has the physical meaning of the field of concentrations at point \( (z,t) \in \Omega_T \), e.g. \( \phi(z,t) \) corresponds to the concentration of \( l\)-th substance at point \( (z,t) \). Here \( l = 1, \ldots, N_c \), \( N_c \) is the total number of substances considered, \( w(z,t) \) denotes the "wind speed", \( \mu(z,t) \) is the diffusion coefficient, \( S : \mathbb{R}^{N_c} \rightarrow \mathbb{R}^{N_c} \) is the transformation operator, \( \hat{n} \) is the boundary outer normal direction, \( f(z,t) \), \( g(z,t) \), \( \phi^0(z) \) - a priori data from the sources and the initial data, \( r(z,t) \) is the control function (uncertainty). It is introduced in the perfect model structure to assimilate the data. Each entry of \( f(z,t) \), \( g(z,t) \), \( r(z,t) \), \( \phi^0(z) \) vectors corresponds to a quantity attributed to \( l\)-th substance at point \( (z,t) \). The transformation operator \( S \) is defined by a chemical kinetics system of 22 reacting species from [4,5] augmented with a \( SO_2 \) reaction taken from a model called CMAQ [6]:

\[
\begin{align*}
NO_2 + \text{hv} & \rightarrow NO + O_3P \\
HCHO + \text{hv} & \rightarrow CO + 2H_2O \\
O_2 + O_3P & \rightarrow O_3 \\
O_1D + O_3 & \rightarrow O_2 + O_1P \\
HO_2 + NO & \rightarrow NO_2 + OH \\
NO + RO_2 & \rightarrow HCHO + HO_2 + NO_2 \\
HC + OH & \rightarrow H_2O + RO_2 \\
NO_2 + OH & \rightarrow H_2O + NO_3 \\
H_2O + 2HO_2 & \rightarrow H_2O_2 + H_2O_2 + O_2 \\
2RO_2 & \rightarrow \text{Pr od} \\
\end{align*}
\]

\[
\begin{align*}
hv + O_3 & \rightarrow O_1D + O_2 \\
HCHO + \text{hv} & \rightarrow CO + H_2 \\
N_2 + O_1D & \rightarrow N_2 + O_3P \\
H_2O + O_1D & \rightarrow 2OH \\
NO + O_3 & \rightarrow NO_2 + O_2 \\
CO + OH & \rightarrow CO_2 + HO_2 \\
HCHO + OH & \rightarrow CO + H_2O + HO_2 \\
2HO_2 & \rightarrow H_2O_2 + O_2 \\
HO_2 + RO_2 & \rightarrow O_2 + ROOH \\
OH + SO_2 & \rightarrow HO_2 + Sulf \\
\end{align*}
\]

The reaction rates are taken from [5]. They depend on time, i.e. photochemistry is considered. This kinetics system can be presented in production-destruction operator form:

\[
S_l(\phi(z,t)) = -P_l(\phi(z,t))\phi_l(z,t) + \Pi_l(\phi(z,t)), \quad l = 1, \ldots, N_c \quad (4)
\]

\[
P_l, \Pi_l : \mathbb{R}^{N_c}_+ \rightarrow \mathbb{R}_+, \quad (5)
\]

where \( P_l \) is the destruction rate functional and \( \Pi_l \) is the production functional.
**Direct problem:** Given \( \tilde{f}(z,t), \tilde{g}(z,t), \tilde{r}(z,t), \tilde{h}(z) \), determine \( \tilde{\phi}(z,t) \) from equations (1)-(3). The exact solution \( \tilde{\phi} \) is the solution of the direct problem corresponding to the «unknown» emissions \( \tilde{r} \).

We assume all the functions and model parameters to be smooth enough for the solutions to exist and the transformations to be valid.

For the numerical solution, let us introduce a uniform temporal grid \( \omega_t = \{ t^i \}_{i=1}^{N_t} \) on \( [0,T] \) with step size \( \tau \) and \( N_t \) points and a uniform spatial grid \( \omega_z \) with \( N_z \), grid points on \( \Omega \). Let \( Q(\omega_t) \) be the space of real grid functions on \( \omega_t \). The direct problem can be efficiently solved with a splitting method. Let us consider an additive-averaged splitting scheme (analogous to [7]) on the intervals \( t^i \leq t \leq t^{i+1} \). The splitting is done with respect to the physical processes of advection-diffusion and transformation. Finally, we have two parallel stages with a step partition \( \gamma_1 + \gamma_2 = 1 \) and sources partition \( \tilde{f} = \tilde{f}_1 + \tilde{f}_2 \).

- **The convection-diffusion process:**
  \[
  \gamma_1 \frac{\partial \tilde{\phi}_1}{\partial t}(z,t) + \frac{\partial}{\partial z} \left( w(z,t) \tilde{\phi}_1(z,t) \right) - \frac{\partial}{\partial z} \left( \mu(z,t) \frac{\partial \tilde{\phi}_1}{\partial z}(z,t) \right) = \tilde{f}_1(z,t) + \tilde{r}_1(z,t), \quad (z,t) \in \Omega \times \left[ t^{i-1}, t^i \right],
  \]

- **The chemical reaction processes:**
  \[
  \mu(z,t) \frac{\partial \tilde{\phi}_2}{\partial t}(z,t) + \beta(z,t) \tilde{\phi}_2(z,t) = \tilde{g}_a(z,t), \quad (z,t) \in \partial \Omega \times \left[ t^{i-1}, t^i \right],
  \]

  \[
  \tilde{\phi}_2(z,t^{i-1}) = \tilde{\phi}(z,t^{i-1}), \quad \tilde{x} \in \Omega,
  \]

where \( \partial \Omega = \{ z = 0, z = X_z \} \). This initial value problem can be approximated in implicit matrix form:

\[
\gamma_1 \frac{\tilde{\phi}_1^{i+1} - \tilde{\phi}_1^i}{\tau} + L_1 \tilde{\phi}_1 = \tilde{r}_1^i + \tilde{f}_1^i, \quad L_1(\tilde{\phi}) = \{ L_1(\tilde{\phi}) \}_{i=1}^{N_t}.
\]

Here \( \tilde{\phi}_i^j \in Q(\omega_t)^{N_t} \) is the solution on the \( j \)-th time level, \( \tilde{r}_i^j \in Q(\omega_t)^{N_t} \) is the uncertainty on the \( j \)-th time level and \( L_1 : Q(\omega_t) \rightarrow Q(\omega_t) \) are the approximated advection-diffusion operators from equation (1) corresponding to the spatial dimensions.

- **The chemical reaction processes:**
  \[
  \gamma_2 \frac{\partial \tilde{\phi}_2(z,t)}{\partial t} + \text{diag} \left( \tilde{P}(\tilde{\phi}(z,t)) \right) \tilde{\phi}_2(z,t) = \Pi \left( \tilde{\phi}_2(z,t) \right) + \tilde{f}_2(z,t) + \tilde{r}_2(z,t),
  \]

  \[
  (z,t) \in \Omega \times \left[ t^{i-1}, t^i \right], \quad \tilde{\phi}_2(z,t^i) = \tilde{\phi}(z,t^i), \quad z \in \Omega,
  \]

Or, in entry form

\[
\gamma_2 \frac{\partial \phi_{2,l}(z,t)}{\partial t} + \tilde{P}_l \left( \tilde{\phi}_2(z,t) \right) \phi_{2,l}(z,t) = \Pi_l \left( \tilde{\phi}_2(z,t) \right) + f_{2,l}(z,t) + r_{2,l}(z,t),
\]

\[
(z,t) \in \Omega \times \left[ t^{i-1}, t^i \right], \quad l = 1, \ldots, N_c.
\]

In [8] a family of unconditionally monotonic schemes is constructed, from the first to fourth order of accuracy. One of the single stage schemes is equivalent to the well-known QSSA scheme [9]:

\[
\tilde{\phi}_{ij}^l = \tilde{G} \left( \tilde{\phi}^{i-1} \right) + \text{diag} \left( \tilde{W} \left( \tilde{\phi}^{i-1} \right) \right) \tilde{r}_{ij}.
\]

where
\[ G_{j}\left(\phi^{j-1}\left(\overline{p}\right)\right) = \phi^{j-1}_{i}\left(\overline{p}\right) e^{-P\left(\phi^{j-1}\left(\overline{p}\right)\right)^{2}} + \frac{1-e^{-P\left(\phi^{j-1}\left(\overline{p}\right)\right)^{2}}}{P_{j}\left(\phi^{j-1}\left(\overline{p}\right)\right)^{2}} \left( \Pi_{i}\left(\phi^{j-1}\left(\overline{p}\right)\right) + f_{i}^{j}\left(\overline{p}\right) \right), \]

\[ W_{j}\left(\phi^{j-1}\left(\overline{p}\right)\right) = \frac{1-e^{-P\left(\phi^{j-1}\left(\overline{p}\right)\right)^{2}}}{P_{j}\left(\phi^{j-1}\left(\overline{p}\right)\right)^{2}}. \]

The chemical splitting stage is calculated on a temporal grid \( \hat{t}_{j} \) that is \( iN_{t} \) times finer than the original temporal grid, i.e. every interval \( \left[t, t^{j+1}\right] \) is divided into \( iN_{t} \) subintervals.

- The next step approximation is

\[ \tilde{\phi}^{j} = \tilde{\phi}_{0}^{j} + \tilde{\phi}_{j}^{j}. \]  

An advantage of the scheme is that at each time step the individual processes are evaluated independently (in parallel).

2.2. Weakly coupled data assimilation algorithm

In order to assimilate the measurement data, we connect the measured quantities with the model variables. This is formally done with a measurement operator \( H : \)

\[ \tilde{I}(t) = H\left(t, \tilde{\phi}^{*}(t) + \tilde{\eta}(t)\right), t \in [0, T], \]  

where \( \tilde{I}(t) \) is the measurement data, \( \tilde{\phi}^{*}(t) \) is the «true» (or exact) solution, \( \tilde{\eta}(t) \) is the measurement data uncertainty.

**Data assimilation problem:** Determine \( \tilde{\phi}^{*}(t) \) for \( t > t^{*} \) with equations (1)-(3), (12) and functions \( \tilde{f}_{a}, \tilde{g}_{a}, \tilde{\phi}_{0}, \tilde{I} \) defined on \( 0 < t \leq t^{*} \).

We consider \( N_{m} \) in situ measurements at the domain grid points \( \{(z_{m}, t_{m})\}^{N_{m}}_{m=1} \subset \omega \times \omega_{t}. \) Hence the m-th measurement is defined by the vector

\[ \xi_{m} = \{(z_{m}, t_{m}, I_{m}, I_{m}, \sigma_{m}^{m})\}, m = 1, ..., N_{M}, \]

where \( z_{m} \) is the measurement point location, \( t_{m} \) is the measurement time point, \( I_{m} \) is the number of substances being measured, \( I_{m} \) is the resulting concentration and \( \sigma_{m}^{m} \) is the standard variation of the measurement. According to the data assimilation problem statement, at time \( t^{j} \) we can use only the measurements with \( t_{m} \leq t^{j} \). Let us define a set of indices

\[ \theta^{j} = \{1 \leq m \leq N_{M} | t_{m} = t^{j}\}. \]

The corresponding measurement operator and measurement data are defined by

\[ H^{j}\tilde{\phi} = \left\{ \phi_{m}^{j}\left(z_{m}^{m}, t_{m}^{m}\right)\right\}^{N_{m}}_{m=1}, I^{j} = \left\{\left(1 + \sigma_{m}^{m}\right)^{2} \xi_{m} \phi_{m}^{j}\left(z_{m}^{m}, t_{m}^{m}\right)\right\}^{N_{m}}_{m=1}, \sigma^{j} = \left\{\sigma_{m}^{m}\right\}^{N_{m}}_{m=1}. \]

We consider regular measurements in space and time which are defined by temporal \( \Delta t_{m} \) and spatial \( \Delta z_{m} \) gaps between the measurement points, \( \xi_{m} \) is a normally distributed random variable.

The variational data assimilation method provides a solution to the data assimilation problem as the minimum of a functional with constraints imposed by the model. The functional usually combines the measurement data misfit with the norm of the control variable:
where $\|\|$ is the norm of a Hilbert space over $Q(\alpha)^N$ and $\langle .. \rangle$ is the corresponding inner product, $\alpha$ is a regularization (assimilation) parameter which is selected to make the solution closer to the direct model solution or to the measurements. At $t'$ we update only the control variable $\tilde{r}^j$ for this time step. Under a weakly-coupled (or fine-grained) approach [10, 11, 12, 13] the same data are assimilated at the different splitting stages and the results are coupled afterwards. We seek for a minimum of the functional

$$J^j_j(\tilde{\phi}_j, \tilde{r}_j) = \alpha \| H \tilde{\phi} - \tilde{I}_j \|^2 + \| \tilde{r}_j \|^2,$$

under the constraints defined by equations (9), (10) with respect to the independent $\tilde{r}_j$. Using the method of Lagrange multipliers to solve minimization problems with equality constraints, we can construct the augmented functional

$$\bar{J}^j_j(\{\tilde{\phi}_j^i, \tilde{r}_j^i\}_{\beta \in \{z, x\}}) = \sum_{\beta \in \{z, x\}} J^j_j(\tilde{\phi}_j^i, \tilde{r}_j^i) + \left\{ \gamma z \frac{\tilde{\phi}_j^i - \tilde{\phi}_j^{i-1}}{\tau} - L_{z} \tilde{r}_j^i - \tilde{r}_j^i - \tilde{I}_j^i - \tilde{\psi}_j^i \right\} + \left\{ \tilde{\phi}_j^i - \tilde{G}_z \tilde{\phi}_j^{i-1} - \text{diag}(\tilde{\bar{W}}) \tilde{r}_j^i, \tilde{\bar{W}} \right\}.$$

The components of $\bar{J}^j_j(\{\tilde{\phi}_j^i, \tilde{r}_j^i\}_{\beta \in \{z, x\}})$ corresponding to the different $\beta$ are independent, hence the stationary point coordinates can be found independently.

In order to present an algorithm of finding a stationary point for the convection-diffusion stage, we need further elaboration of the operator $L$. We use approximations of equation (6) that produce the tridiagonal matrix systems

$$-a_i \phi_{i+1}^j + b_i \phi_i^j = \phi_i^{j+1} + \tau r_i^j + \tau f_i^j, \quad i = 0, 1, \ldots, N,$$

$$-a_i \phi_{i+1}^j + b_i \phi_i^j - c_i \phi_i^{j+1} = \phi_i^{j-1} + \tau r_i^j + \tau f_i^j, \quad i = 1, \ldots, N - 1,$$

$$b_i \phi_{i+1}^j - c_i \phi_i^{j+1} = \phi_i^{j-1} + \tau r_i^j + \tau f_i^j, \quad i = N.$$

Here the assimilated state is the solution of the minimization problem

$$J(\phi^j, r^j) = \alpha \sum_{i=0}^{N} \left( \frac{\phi_i^j - I_i^j}{\sigma_i} \right)^2 + \sum_{i=0}^{N} (r_i^j)^2 \tau,$$

under the constraints defined by equations (13)-(15) where $M_i^j$ is a spatial-temporal measurement mask (i.e. $M_i^j$ is equal to 1 if there is a measurement at point $(z_i, t^j)$ and to 0 otherwise), $I_i^j$ is the measurement data at point $(z_i, t^j)$ (if there is a measurement) and $\sigma_i$ is the measurement device standard deviation of the measurement at point $(z_i, t^j)$ (if there is a measurement). Introducing Lagrange multipliers, we obtain the augmented functional

$$\bar{J}_j(\phi^j, r^j, \psi^j) = J(\phi^j, r^j) + \sum_{i=0}^{N} (-a_i \phi_{i+1}^j + b_i \phi_i^j - c_i \phi_i^{j+1} - \phi_i^{j-1} - \tau r_i^j - \tau f_i^j) \psi_i^j.$$
Equating the first variations of the augmented functional to zero, we obtain the following tridiagonal matrix equation [10, 11, 12]:

$$-A_i \Phi_i + B_i \Phi_i = F_i, i = 0,$$

$$-A_i \Phi_i + B_i \Phi_i - C_i \Phi_i = F_i, i = 1, ..., N - 1,$$

$$B_i \Phi_i - C_i \Phi_i = F_i, i = N,$$

where

$$A_i = \begin{pmatrix} a_i & 0 \\ 0 & c_{i+1} \end{pmatrix}, \quad B_i = \begin{pmatrix} b_i & -\tau \\ 2\alpha M_i \tau & b_i \end{pmatrix}, \quad C_i = \begin{pmatrix} c_i & 0 \\ 0 & a_{i-1} \end{pmatrix}, \quad \Phi_i = \begin{pmatrix} \phi_i \\ \psi_i \end{pmatrix}, \quad F_i = \begin{pmatrix} f_i \phi_i + \tau f_i \\ 2\alpha M_i \tau I_i \end{pmatrix},$$

which can be solved by a direct Gaussian elimination method.

At the transformation stage the algorithm is the same for any grid point \( \bar{p} \in \omega \). For brevity let \( \bar{\phi} = \Phi_i(\bar{p}) \in \mathbb{R}^N \), \( \bar{r} = r_i(\bar{p}) \in \mathbb{R}^N \), \( \bar{\psi} = \psi_i(\bar{p}) \in \mathbb{R}^N \) and the result is sought-for as a stationary point of the augmented functional

$$J(\bar{\phi}^i, \bar{r}^i) = \alpha \sum_{l=1}^{Nc} \left( \frac{\phi_i^l - I_i}{\sigma_i} \right)^2 M_i + \sum_{l=1}^{Nc} (r_i^l)^2 + \sum_{l=1}^{Nc} \left( \phi_i^l - G_i(\phi_i^{l-1}(\bar{p})) - W_i(\phi_i^{l-1}(\bar{p})) \right) r_i^l \psi_i^l,$$

where \( M_i \) is equal to 1 if the l-th substance is measured at point \( \bar{p} \) at moment \( t^i \) and zero otherwise. This minimum is given by the interpolation formula

$$\phi_i^l = \frac{1}{1 + Z_i^l} G_i(\phi_i^{l-1}(\bar{p})) + \frac{Z_i^l}{1 + Z_i^l} I_i, \quad Z_i^l = \frac{\alpha M_i}{\sigma_i^2} W_i(\phi_i^{l-1}(\bar{p})).$$

The next step is evaluated as in the direct problem:

$$\bar{\phi}^i = \bar{\phi}^i + \bar{\phi}^i.$$

Note that the resulting algorithm can be implemented without iterations. This allows using it in real-time for large chemical transformation models.

3. Numerical experiments

In the numerical experiments, we take a realistic scenario corresponding to August 8, 2013. The turbulence diffusion coefficient \( \mu(z,t) \) is calculated from ground heat flux measurements and the friction stress, and from vertical wind profiles based on the k-theory. The vertical speed \( w(z,t) \) and \( \mu(z,t) \) are presented in figure 1. Realistic initial conditions are considered. The grid parameters are \( N_z = 30, X_z = 3000m, T = 75600s, N_t = 281, iNt = 10^4 \).
Figure 1. Turbulent diffusion coefficient $\mu(z,t)$ (a) and vertical speed $w(z,t)$ (b).

We compare three configurations for the numerical experiments:

- **NoDA** (Background solution): Direct problem solution that is driven by initial and boundary conditions only.
- **«Truth»** (Exact solution): Direct problem solution that is driven by both initial and boundary conditions and by an «unknown» source of $NO_2$ «on the ground» ($z=0$). The emission rate is chosen to provide a 100% relative difference between «true» and background solutions. The scenario models traffic emissions.
- **DA** (Data assimilation solution): The result of data assimilation algorithm. In this case, the initial and boundary conditions are the same as for NoDA and «true» solutions. The source is absent as in the NoDA case but there are $NO$ and $O_3$ concentration measurements available for the data assimilation system. In the experiments $\sigma_m^m = 1$, $\alpha = 10^{10}$.

The results are presented for three groups of substances: a substance whose measurement data is assimilated (figure 2), a substance that is emitted in the «true» solution (figure 3) and a substance that is neither emitted nor assimilated (figure 4). In the experiment $\sigma = 0$, $\Delta z_m = 500$ m, $\Delta t_m = 135$ min.

Figure 2. Comparison of «true» solution (a), solution without data assimilation (b) and data assimilation results (c) for a substance whose concentrations are assimilated.
Figure 3. Comparison of «true» solution (a), solution without data assimilation (b) and data assimilation results (c) for a substance that is emitted.

Figure 4. Comparison of «true» solution (a), solution without data assimilation (b) and data assimilation results (c) for a substance that is neither assimilated nor emitted.

From these figures we can conclude that for these substances the data assimilation algorithm was successful at least qualitatively. In the following experiments we will study the sensitivity of the results to measurements data. The results for the substances affected by the emissions (NoDA relative error > 0.5%) are presented in tables 1-3.

Experiment 1: Sensitivity to vertical gaps in data. $\Delta z_m$ is varied with a fixed $\sigma = 0$, $\Delta t_m = 269 \text{ min}$.

Table 1. Relative error of DA versus vertical gaps in measurement points.

| Vertical gap $\Delta z_m$ | H2O2 | HC  | HCHO | HNO3 | HO2 | NO  | NO2 |
|--------------------------|------|-----|------|------|-----|-----|-----|
| 500 m                    | 0.01 | 0.01| 0.07 | 0.63 | 0.25| 0.79| 0.95|
| 1000 m                   | 0.01 | 0.01| 0.07 | 0.65 | 0.26| 0.83| 0.96|
| 1500 m                   | 0.01 | 0.01| 0.08 | 0.66 | 0.27| 0.84| 0.97|
| NoDA                     | 0.01 | 0.03| 0.32 | 0.76 | 0.53| 0.99| 1   |

Experiment 2: Sensitivity to temporal gaps in data. $\Delta t_m$ is varied with a fixed $\sigma = 0$, $\Delta z_m = 500 \text{ m}$.
### Table 2. Relative error of DA versus temporal gaps in measurements.

| Temporal gap, $\Delta t_m$ | H2O2 | HC  | HCHO | HNO3 | HO2 | NO  | NO2 |
|-----------------------------|------|-----|------|------|-----|-----|-----|
| 135 min                    | 0.00 | 0.00 | 0.05 | 0.55 | 0.18| 0.69| 0.9  |
| 269 min                    | 0.01 | 0.01 | 0.07 | 0.63 | 0.25| 0.79| 0.95 |
| 404 min                    | 0.01 | 0.01 | 0.14 | 0.69 | 0.35| 0.88| 0.97 |
| NoDA                       | 0.01 | 0.03 | 0.32 | 0.76 | 0.53| 0.99| 1.0  |

| Temporal gap, $\Delta t_m$ | O1D | O3  | O3P | OH  | RO2 | ROOH | Prod |
|-----------------------------|-----|-----|-----|-----|-----|------|------|
| 135 min                    | 0.55| 0.52| 0.87| 0.22| 0.2 | 0.15 | 0.15 |
| 269 min                    | 0.63| 0.59| 0.93| 0.3 | 0.27| 0.22 | 0.22 |
| 404 min                    | 0.69| 0.64| 0.96| 0.5 | 0.38| 0.31 | 0.3  |
| NoDA                       | 0.76| 0.7  | 1   | 0.87| 0.57| 0.5  | 0.48 |

Experiment 3: Sensitivity to measurement noise. $\sigma$ is varied with a fixed $\Delta t_m = 269$ min, $\Delta z_m = 500$ m.

### Table 3. Relative error of DA versus standard deviation of measurement noise.

| Measurement noise, $\sigma$ | H2O2 | HC  | HCHO | HNO3 | HO2 | NO  | NO2 |
|-----------------------------|------|-----|------|------|-----|-----|-----|
| 0                           | 0.01 | 0.01| 0.07 | 0.63 | 0.25| 0.79| 0.95 |
| 0.1                         | 0.01 | 0.01| 0.07 | 0.64 | 0.26| 0.81| 0.95 |
| 0.5                         | 0.01 | 0.01| 0.09 | 0.67 | 0.29| 0.85| 0.96 |
| 1                           | 0.01 | 0.01| 0.12 | 0.71 | 0.34| 0.9 | 0.98 |
| 2                           | 0.01 | 0.02| 0.1  | 0.74 | 0.42| 0.94| 1.04 |
| 3                           | 0.01 | 0.02| 0.2  | 0.75 | 0.41| 0.96| 1.22 |
| NoDA                        | 0.01 | 0.03| 0.32 | 0.76 | 0.53| 0.99| 1    |

| Measurement noise, $\sigma$ | O1D | O3  | O3P | OH  | RO2 | ROOH | Prod |
|-----------------------------|-----|-----|-----|-----|-----|------|------|
| 0                           | 0.63| 0.59| 0.93| 0.3 | 0.27| 0.22 | 0.22 |
| 0.1                         | 0.64| 0.6  | 0.93| 0.31| 0.28| 0.24 | 0.23 |
| 0.5                         | 0.68| 0.63| 0.95| 0.36| 0.31| 0.28 | 0.27 |
| 1                           | 0.72| 0.67| 0.97| 0.45| 0.37| 0.34 | 0.33 |
| 2                           | 0.75| 0.71| 1   | 0.67| 0.45| 0.41 | 0.39 |
| 3                           | 0.76| 0.74| 1.03| 0.67| 0.44| 0.42 | 0.4  |
| NoDA                        | 0.76| 0.7  | 1   | 0.87| 0.57| 0.5  | 0.48 |

The quantitative efficiency of the data assimilation can be studied by comparison of the NoDA results and the results of data assimilation (DA). The small error in both DA and NoDA cases for a substance means that the emissions do not affect the dynamics of its concentrations (as it is for HC and H$_2$O$_2$). The less error for the DA cases compared to NoDA means that the data assimilation...
is efficient. In the numerical experiments with high noise levels ($\sigma = 2, 3$), the DA becomes inefficient for some substances. In all DA cases the more (smaller gaps) and the better (less noise) data are available the better are the reconstructions.

4. Conclusions
The combination of splitting and direct variational data assimilation schemes at the splitting stages allows constructing computationally efficient algorithms for data assimilation of in situ concentration measurements in the convection-diffusion-reaction models. The algorithm performance was evaluated in a series of numerical experiments with indirect measurements. In the numerical experiments, the data assimilation algorithm was efficient in all the experiments except for ones with large noise levels. For all the data assimilation cases, the smaller gaps and less noise in data, the better the reconstruction results. We conclude that in the numerical experiments the data assimilation algorithm was able to partially substitute the missing emission inventories with additional concentration measurements.

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