Examining the impact of heterogeneous nitryl chloride production on air quality across the United States

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Abstract. The heterogeneous hydrolysis of dinitrogen pentoxide (N\(_2\)O\(_5\)) has typically been modeled as only producing nitric acid. However, recent field studies have confirmed that the presence of particulate chloride alters the reaction product to produce nitryl chloride (ClNO\(_2\)) which undergoes photolysis to generate chlorine atoms and nitrogen dioxide (NO\(_2\)). Both chlorine and NO\(_2\) affect atmospheric chemistry and air quality. We present an updated gas-phase chlorine mechanism that can be combined with the Carbon Bond 05 mechanism and incorporate the combined mechanism into the Community Multiscale Air Quality (CMAQ) modeling system. We then update the current model treatment of heterogeneous hydrolysis of N\(_2\)O\(_5\) to include ClNO\(_2\) as a product. The model, in combination with a comprehensive inventory of chlorine compounds, reactive nitrogen, particulate matter, and organic compounds, is used to evaluate the impact of the heterogeneous ClNO\(_2\) production on air quality across the United States for the months of February and September in 2006. The heterogeneous production increases ClNO\(_2\) in coastal as well as many in-land areas in the United States. Particulate chloride derived from sea-salts, anthropogenic sources, and forest fires activates the heterogeneous production of ClNO\(_2\). With current estimates of tropospheric emissions, it modestly enhances monthly mean 8-h ozone (up to 1–2 ppbv or 3–4 %) but causes large increases (up to 13 ppbv) in isolated episodes. This chemistry also substantially reduces the mean total nitrate by up to 0.8–2.0 \(\mu\)g m\(^{-3}\) or 11–21 %. Modeled ClNO\(_2\) accounts for up to 6 % of the monthly mean total reactive nitrogen. Sensitivity results of the model suggest that heterogeneous production of ClNO\(_2\) can further increase O\(_3\) and reduce TNO\(_3\) if elevated particulate-chloride levels are present in the atmosphere.

1 Introduction

Recent studies suggest that chlorine chemistry affects air quality in coastal and industrial areas of the United States (Chang et al., 2002; Knipping and Dabdub, 2003; Tanaka et al., 2003b; Chang and Allen, 2006, Sarwar and Bhave, 2007; Simon et al., 2009). These studies have evaluated the effects of naturally- and anthropogenically-derived chlorine on ozone (O\(_3\)). First, Knipping and Dabdub (2003) reported that chlorine released via heterogeneous reactions on sea-salt particles can increase daily maximum 1-h O\(_3\) by up to 4 parts-per-billion (ppbv) in the Los Angeles area of California. Chang et al. (2002) and Chang and Allen (2006) concluded that industrial chlorine emissions increase O\(_3\) by up to 10–16 ppbv in the Houston area of Texas. Finally, Sarwar and Bhave (2007) found that anthropogenic chlorine emissions increase daily maximum 8-h O\(_3\) by up to 4 ppbv in New York/New Jersey and 8 ppbv in the Houston areas.

In the past few years a new chlorine-containing species, nitryl chloride (ClNO\(_2\)), has been implicated as a major pathway for the production of reactive chlorine. Photolysis of ClNO\(_2\) generates chlorine atoms (Cl) and nitrogen dioxide (NO\(_2\)); each can alter atmospheric chemistry and air quality. Finlayson-Pitts et al. (1989) first suggested that ClNO\(_2\) could be an intermediate between aqueous-phase chloride and gas-phase chlorine radicals, but measurement technology did not exist to confirm this hypothesis in the ambient atmosphere. In the 2006 TEXAQS-II field study, Osthoff et al. (2008) measured atmospheric ClNO\(_2\) for the first time. They reported a peak value of greater than 1.0 ppbv near Houston. Results of several other recent field campaigns also suggested the presence of relatively high levels of ClNO\(_2\) in coastal as well

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as in-land areas (Thornton et al., 2010; Mielke et al., 2010, 2011). These studies suggest that the main formation pathway for CINO₂ is heterogeneous hydrolysis of dinitrogen pentoxide (N₂O₅) in the presence of particulate chloride. Simon et al. (2009) investigated the impact of measured CINO₂ concentrations on O₃ in Houston using the Comprehensive Air quality Model with extensions (CAMx) and reported that it can enhance O₃ by up to 1.5 ppbv. While the Simon et al. (2009) study suggests CINO₂ can modestly affect O₃ in Houston, little is known about the importance of CINO₂ in other areas and seasons. In the current study, we examine the impacts of the heterogeneous CINO₂ production on air quality in the United States using state-of-the-science knowledge about chlorine chemistry and a detailed inventory of chlorine emissions.

2 Methodology

2.1 Model framework

This study uses the Community Multiscale Air Quality (CMAQ) modeling system (version 5.0; beta version) (Binkowski and Roselle, 2003; Byun and Schere, 2006; Foley et al., 2010) to simulate air quality. This version of CMAQ includes several updates to the aerosol treatment including tracking of trace metals in fine particles and an updated inorganic partitioning module, ISORROPIA 2.1 (Fountoukis and Nenes, 2007). ISORROPIA 2.1 calculates equilibrium partitioning of inorganic compounds (chlorine, ammonia, nitrate, and water) between the gas and particle phases. This partitioning is dependent on ionic concentrations in the particles of Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, SO₄²⁻, and NO₃⁻ and gas-phase concentrations of NH₃, HNO₃, and HCl. Evaluations for the CMAQ modeling system against ambient measurements have shown that CMAQ has considerable skill in simulating O₃ and fine particles (PM₂.₅) (Eder and Yu, 2006; Appel et al., 2007; Foley et al., 2010). The modeling domain covers the entire United States and consists of 299 x 459 horizontal grid-cells with a 12-km resolution (see Fig. 1). The model contains 34 vertical layers with a surface layer height of approximately 40-m. Model simulations were performed for February and September in 2006. Boundary conditions were generated from the GEOS-CHEM model (Bey et al., 2001) results. CMAQ results from a previous model simulation are used as initial conditions for this work. To further minimize the impact of initial conditions on predicted results, the model simulation started five days prior to the actual simulation periods. Meteorological fields were obtained from the Weather Research and Forecasting (version 3.3) model (Skamarock et al., 2008).

2.2 Emissions

The 2005 National Emissions Inventory (http://www.epa.gov/ttn/chief/net/2005_nei_point.pdf) is used to generate model-ready emissions using the Sparse Matrix Operator Kernel Emission (SMOKE) (Houyoux et al., 2000). The Biogenic Emissions Inventory System (version 3.14) is used to compute biogenic emissions from soil and vegetation (Schwede et al., 2005). Emissions of molecular chlorine (Cl₂) and hydrochloric acid (HCl) are included in the 2005 National Emissions Inventory. In addition, the fine-particulate emissions are specified into the standard suite of compounds and trace elements (Reff et al., 2009). The largest sources of anthropogenic particulate chloride include paved and unpaved road dust, agricultural soil, wildfires, agricultural burning, coal/wood combustion, and diesel exhaust (Reff et al., 2009). Coarse particulate matter is also specified to include particulate chloride. Road salt, one potentially important source of particulate chloride, is missing in the inventory. Fine and coarse sea-salt emissions (both open-ocean and surf-zone) are calculated in-line in CMAQ (Kelly et al., 2010).

2.3 Gas-phase chlorine chemistry

This study expands the CB05TU chemical mechanism (Whitten et al., 2010) to include additional chlorine chemistry. CB05TU builds on earlier work by Gery et al. (1989) and Yarwood et al. (2005) and includes 60 chemical species. These chemical mechanisms have been previously evaluated in the CMAQ model (Sarwar et al., 2008, 2011). Tanaka et al. (2003a) developed a chlorine mechanism consisting of 13 chemical reactions for use with an earlier version of this chemical mechanism. Here, we modify, and extend the chlorine mechanism of Tanaka et al. (2003a) for use with the CB05TU mechanism. Atmospheric reactions in the updated chlorine mechanism are shown in Table 1 (Reactions C1–C125). Rate constants for these reactions were updated using the recommendations from the International Union of Pure and Applied Chemistry (IUPAC) (Atkinson et al., 2005).

The new chlorine mechanism updates the chemistry developed by Tanaka et al. (2003a) in several ways. First, the chemistry is adjusted to new chemical species in the CB05TU mechanism. For example, the earlier mechanism grouped all aldehydes into a single lumped species, but the CB05TU mechanism splits acetaldehyde out from higher aldehydes. Similarly, the older mechanism included one olefin species, while the current mechanism separates compounds with internal carbon-carbon double bonds from those with a terminal carbon-carbon double bond (alk-1-enes). The new chlorine chemistry has been adjusted to account for these and other new species definitions.

The reactions of formaldehyde, acetaldehyde, and higher aldehydes with Cl are similar to their reactions with OH. The only exception is that the reaction with Cl produces HCl compared to H₂O produced from reactions with OH. The products of the reaction between higher aldehydes and Cl are
First order rate constants are in units of s\(^{-1}\). Temperatures (T) are in Kelvin. Rate constants for Reaction (7) is described by the falloff expression of the form \( k = (k_0/M)/(1 + k_{\infty}/Zk_0T)^{0.5} \), where \( Z = (T/N) + (k_{\infty}/k_0T)^{2} \), where \( M \) is the total pressure in molecules cm\(^{-3}\), and \( k_0, k_\infty, F, N, k_\infty \) are indicated in table.

Ref: b = Atkinson et al. (2005); c = Bryukov et al. (2006); d = Fan and Zhang, 2004; e = Smith et al. (2002); f = Wallington et al. (1988).

### Table 1. Reactions in the chlorine mechanism for use with the CB05 mechanism.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactants</th>
<th>Products</th>
<th>Rate expression(^a)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11</td>
<td>Cl + CH(_4)</td>
<td>HCl + MEO2</td>
<td>(6.6 \times 10^{-12} \ e^{(-1240/T)})</td>
<td>b</td>
</tr>
<tr>
<td>C12</td>
<td>Cl + ETHA</td>
<td>HCl + 0.991<em>ALD2 + 0.991</em>XO2 + 0.009*XO2N + H2O</td>
<td>(8.3 \times 10^{-11} \ e^{(-100/T)})</td>
<td>b</td>
</tr>
<tr>
<td>C13</td>
<td>Cl + PAR</td>
<td>HCl + 0.87<em>XO2 + 0.13</em>XO2N + 0.11<em>HO2 + 0.06</em>ALD2 - 0.11<em>PAR + 0.76</em>ROR + 0.05*ALDX</td>
<td>(5.00 \times 10^{-11})</td>
<td>b</td>
</tr>
<tr>
<td>C14</td>
<td>Cl + OLE</td>
<td>FMC1 + 2.0*XO2 + H2O + FORM</td>
<td>(1.07 \times 10^{-10})</td>
<td>b</td>
</tr>
<tr>
<td>C15</td>
<td>Cl + IOLE</td>
<td>0.3<em>HCl + 0.7</em>FMC1 + 0.45<em>ALD2 + 0.55</em>ALDX + 0.3<em>OLE + 0.3</em>PAR + 1.7*XO2 + HO2</td>
<td>(3.5 \times 10^{-10})</td>
<td>b</td>
</tr>
<tr>
<td>C16</td>
<td>Cl + ISOP</td>
<td>0.15<em>HCl + XO2 + H2O + 0.85</em>FMC1 + ISP</td>
<td>(4.3 \times 10^{-10})</td>
<td>b,d</td>
</tr>
<tr>
<td>C17</td>
<td>OH + FMC1</td>
<td>Cl + CO + H2O</td>
<td>(5.0 \times 10^{-13})</td>
<td>b</td>
</tr>
<tr>
<td>C18</td>
<td>FMC1</td>
<td>Cl + CO + H2O</td>
<td>Photolysis</td>
<td>b</td>
</tr>
<tr>
<td>C19</td>
<td>Cl + FORM</td>
<td>HCl + HO2 + CO</td>
<td>(8.2 \times 10^{-11} \ e^{(-34/T)})</td>
<td>b</td>
</tr>
<tr>
<td>C20</td>
<td>Cl + ALD2</td>
<td>HCl + C2O3</td>
<td>(7.9 \times 10^{-11})</td>
<td>b</td>
</tr>
<tr>
<td>C21</td>
<td>Cl + ALDX</td>
<td>HCl + C2O3</td>
<td>(1.3 \times 10^{-10})</td>
<td>b</td>
</tr>
<tr>
<td>C22</td>
<td>Cl + MEOH</td>
<td>HCl + HO2 + FORM</td>
<td>(5.5 \times 10^{-11})</td>
<td>b</td>
</tr>
<tr>
<td>C23</td>
<td>Cl + ETOH</td>
<td>HCl + HO2 + ALD2</td>
<td>(8.2 \times 10^{-11} \ e^{(45/T)})</td>
<td>b</td>
</tr>
<tr>
<td>C24</td>
<td>Cl + TOL</td>
<td>HCl + 0.88<em>XO2 + 0.88</em>HO2 + 0.12*XO2N</td>
<td>(6.1 \times 10^{-11})</td>
<td>e</td>
</tr>
<tr>
<td>C25</td>
<td>Cl + XYL</td>
<td>HCl + 0.84<em>XO2 + 0.84</em>HO2 + 0.16*XO2N</td>
<td>(1.2 \times 10^{-10})</td>
<td>f</td>
</tr>
</tbody>
</table>

\(^a\) First order rate constants are in units of s\(^{-1}\), second order rate constants are in units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Temperatures (T) are in Kelvin. Rate constants for Reaction (7) is described by the falloff expression of the form \( k = (k_0/M)/(1 + k_{\infty}/Zk_0T)^{0.5} \), where \( Z = (T/N) + (k_{\infty}/k_0T)^{2} \), where \( M \) is the total pressure in molecules cm\(^{-3}\), and \( k_0, k_{\infty}, F, N, k_{\infty} \) are indicated in table.
uncertain because there may be hydrogen atom abstraction at the paraffinic carbon atoms of higher aldehydes.

Reaction products for terminal olefins with chlorine assume that reaction with the carbon-carbon double bond proceeds by addition, leading to cleavage of the double bond producing an acyl chloride (represented by formyl chloride) and an aldehyde (represented as 33 % acetaldehyde and 67 % higher aldehydes). The rate constant for the reaction between Cl and terminal olefins, Reaction (Cl14), is an average over the absolute rate constants for the alkenes presented in Tanaka et al. (2003a). The rate constant for the reaction of chlorine with internal olefins, Reaction (Cl15), is estimated as the rate constant for Cl reacting with a terminal olefin bond and two paraffin bonds. The products assume that reaction proceeds 70 % by Cl addition to the C=C bond and 30 % by hydrogen atom abstraction from attached alkyl groups. Cl addition leads to cleavage of the double bond producing an acyl chloride (represented by formyl chloride) and an aldehyde (represented as 65 % acetaldehyde and 35 % higher aldehydes). The products for hydrogen atom abstraction pathway are assumed to be HCl, higher aldehydes, and terminal olefins.

Second, the new chlorine chemistry includes more reactions of chlorine radicals with organic species including methanol, ethanol, aromatics, aldehydes, and ethane. In addition, the products from the existing reaction with chlorine and isoprene were modified to more explicitly track the fate of Cl and carbon from isoprene. The HCl and formyl chloride yields reflect the balance between hydrogen atom abstraction and addition pathways of 15 % and 85 % (Fan and Zhang, 2004). Formyl chloride serves as a surrogate for all products where chlorine is incorporated into a chlorocarbonyl after an addition reaction. Reaction of terpenes with Cl atoms is not included because the reaction products are too uncertain. Omitting the reaction may not greatly alter the fate of Cl atoms because Cl atoms react rapidly with all VOCs. For example, the global background for CH4 of about 1.8 ppm (Oum et al., 1998) provides a significant “universal” sink for Cl atoms because Cl atoms react quite rapidly with CH4.

The next major update to the Tanaka et al. (2003a) work is the inclusion of new reactions that lead to the formation of chlorine radicals including OH oxidation of HCl, Reaction (Cl14), and photolysis and oxidation of formyl chloride, Reactions (Cl18) and (Cl17). The new chemistry also includes both the gas-phase formation of ClNO2, Reaction (Cl19), and its subsequent photolysis, Reaction (Cl13), as described by (Atkinson et al., 2005). In total, the updated chlorine mechanism contains five sources of reactive gas-phase Cl: photolysis of Cl2, HOCl, and ClNO2, reaction of HCl with OH, and the self-reaction of ClO, Reactions (Cl1)–(Cl4) and (Cl16).

Normalized photolysis rates were used by Tanaka et al. (2003a). In the updated chlorine chemistry, photolysis rates, \( J \), (min\(^{-1}\)) are directly calculated using the following general equation (Finlayson-Pitts and Pitts, 2000):\[ J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda) \phi(\lambda) F(\lambda) \, d\lambda \] where, \( \sigma(\lambda) \) is the absorption cross section (cm\(^2\) molecule\(^{-1}\)), \( \phi(\lambda) \) is the quantum yield (molecules photon\(^{-1}\)), \( F(\lambda) \) is the actinix flux (photons cm\(^2\) min\(^{-1}\)), \( \lambda \) is the wavelength (nm). Quantum yield and absorption cross-section data from the recent IUPAC recommendations are used in the mechanism (Atkinson et al., 2005). Photolysis of ClNO2 can produce Cl and NO2 in the presence of sunlight via Reaction (Cl13).

Finally, rate constants for several reactions described by Tanaka et al. (2003a), have been updated to meet the latest recommendations of IUPAC (Atkinson et al., 2005): the reaction of Cl with O3, Reaction (Cl15); the reaction of ClO with NO and HO2 (Reactions Cl17–Cl18).

Chlorine chemistry affects O3 primarily via two competing pathways that consume and produce O3. It directly consumes O3 via Reaction (Cl15). It also affects O3 via reactions initiated by Cl and VOCs. Chlorine chemistry can enhance the oxidation of VOCs which then produce additional peroxo radicals (HO2 and RO2); Reactions (Cl10)–(Cl16) and (Cl18)–(Cl25). The reaction of NO with HO2 and RO2 converts NO into NO2 and cause O3 production when NO2 is photolylized (Finlayson-Pitts and Pitts, 2000):

\[ \text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2 \] \[ \text{R} \text{O}^3(\text{P}) + \text{O}_2 \rightarrow \text{O}_3 \] \[ \text{HO}_2 + \text{O}_2 \rightarrow \text{OH} + \text{O}_3 \] \[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]

If additional O3 production via Reactions (R1) and (R5) exceeds O3 consumption via Reaction (Cl15) O3 will increase.

### 2.4 Heterogeneous reaction

Although ClNO2 can be formed in the gas phase through Reaction (Cl19), the high nighttime ClNO2 concentrations observed in recent field campaigns are predominantly formed from reactions of N2O5 on particle surfaces. Current versions of CMAQ treat this heterogeneous N2O5 chemistry as producing only nitric acid, Reaction (R6).

\[ \text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(aq) \rightarrow 2 \times \text{HNO}_3(g) \]

CMAQv5.0 calculates the rate constant of Reaction (R6) \( k_{\text{N}_2\text{O}_5,\text{het}} \) on fine PM using Eq. (2).

\[ k_{\text{N}_2\text{O}_5,\text{het}} = \frac{d}{2D} + \frac{4}{c\gamma} \]
In Eq. (2), $\bar{d}$ represents the effective diameter, $D$ represents the diffusivity of N$_2$O$_5$ in air (as a function of temperature and pressure), $\bar{c}$ is the mean molecular velocity of N$_2$O$_5$ (a function of temperature), $A$ is the aerosol surface area concentration, and $\gamma$ is the reactive uptake coefficient defined as the probability that a collision between a N$_2$O$_5$ molecule and an aerosol particle will result in a reaction. The derivation of this equation is discussed in more detail elsewhere (Jacob, 2000). The CMAQ model calculates $\gamma$ as a complex function of temperature, relative humidity, particle composition, and phase state (Davis et al., 2008).

The recent studies of Bertram and Thornton (2009) and Roberts et al. (2009) show that when particles contain chloride, ClNO$_2$ is also formed as a product, Reactions (R7)–(R10).

\[
\begin{align*}
N_2O_5(g) & \leftrightarrow NO_3^-(aq) + NO_2^+(aq) \quad (R7) \\
NO_3^-(aq) + H^+ & \rightarrow HNO_3(g) \quad (R8) \\
NO_2^+(aq) + H_2O & \rightarrow HNO_3(g) + H^+ \quad (R9) \\
NO_2^+(aq) + Cl^- & \rightarrow ClNO_2(g) \quad (R10) \\
N_2O_5 + H_2O & \rightarrow Y \times (HNO_3 + ClNO_2) + 2 \times (1-Y)HNO_3 \quad (R11: \text{net result of R7–R10})
\end{align*}
\]

The yield of ClNO$_2$ ($Y$) represents the likelihood of NO$_2^+$ (aq) reacting via Reaction (R9) versus Reaction (R10). This yield depends on the molar concentrations of Cl$^-$ (aq) present in the particle and has been parameterized by Bertram and Thornton (2009) and Roberts et al. (2009). Both suggested a similar correlation (Eq. 3):

\[
Y = \frac{1}{1 + \frac{k_9[H_2O(l)]}{k_{10}[Cl^-]}} \quad (3)
\]

where H$_2$O(l) = particle liquid water, Cl$^-$ = particulate chloride, and $k_9$ and $k_{10}$ are the rate constants for Reactions (R9) and (R10). Bertram and Thornton (2009) derived a value of 483 for $k_{10}/k_9$ while Roberts et al. (2009) derived a value of 485 for $k_{10}/k_9$. The formation of ClNO$_2$ in place of HNO$_3$ has implications for the reactive nitrogen budget since HNO$_3$ deposits quickly while ClNO$_2$ does not. Consequently, an increase in $Y$ leads to increased availability of NO$_x$ which participates in photochemical O$_3$ production outlined in Reactions (R1)–(R5).

Bertram and Thornton (2009) also suggested that the presence of particulate chloride can alter $\gamma$N$_2$O$_5$ and developed a correlation (Eq. 4).

\[
\gamma_{N_2O_5} = AK_{1f}^{\gamma} \left(1 - \frac{1}{k_9[H_2O(l)]/k_{10}[NO_3^-]} + \frac{K_{10}[Cl^-]}{K_{10}[NO_3^-]}\right) \quad (4)
\]

where H$_2$O(l) = particle liquid water, NO$_3^-$ = particulate nitrate, Cl$^-$ = particulate chloride, $k_9/k_{10} = 6 \times 10^{-2}$, $k_{10}/k_{7b} = 29$, $A = 3.2 \times 10^{-8}$, and $k_{1f}^{\gamma}$ is calculated as follows:

\[
k_{1f}^{\gamma} = \beta - \beta e^{-[\delta[H_2O(l)]]} \quad (5)
\]

where $\beta = 1.15 \times 10^{-6}$, and $\delta = 1.3 \times 10^{-1}$ (Bertram and Thornton, 2009).

In this study, we replace Reaction (R6) with Reaction (R11) in CMAQ. The yield and reaction rates are calculated separately for coarse and fine particles and use the chloride and water contents in the appropriately-size particles. The yield for Reaction (R11) is calculated with Eq. (3) on fine and coarse particles separately. Reactive uptake ($\gamma$N$_2$O$_5$) is calculated based on Davis et al. (2008) for fine particles (as is done in the base version of CMAQ) and is calculated based on Eq. (4) (using $k_{10}/k_9$ from Bertram and Thornton, 2009) for coarse particles. To conserve mass of chlorine, particulate chloride mass is reduced by the amount of chlorine in ClNO$_2$ formed via the heterogeneous reaction on fine as well as coarse particles. Equilibrium between particulate chloride and gas-phase HCl is achieved quickly through the use of ISORROPIA 2.1 (Fountoukis and Nenes, 2007) in CMAQ, so the formation of ClNO$_2$ can affect ambient concentrations of both particulate chloride and HCl. If no particulate chloride is present, then $Y = 0$ according to Eq. (3) and no ClNO$_2$ is formed.

### 2.5 Simulation details

To evaluate the impacts of heterogeneous ClNO$_2$ formation on air quality, two different simulations were completed. The base simulation was conducted with $Y = 0$. Thus, only gas-phase reactions produced ClNO$_2$. The other simulation was conducted with yield calculated from Eq. (3) so that the heterogeneous hydrolysis of N$_2$O$_5$ produces HNO$_3$ and ClNO$_2$. Both the gas-phase and heterogeneous reactions produced ClNO$_2$. Differences in the results obtained with the two simulations are attributed to the heterogeneous production of ClNO$_2$.

### 3 Results and discussion

#### 3.1 Model performance without heterogeneous ClNO$_2$ production

Model performance statistics for the base simulation without the heterogeneous ClNO$_2$ production for 8-h daily maximum O$_3$ and 24-h average PM$_{2.5}$ are shown in Tables 2 and 3. Ambient monitoring data from the United States Environmental Protection Agency’s Air Quality System (AQS) are used to evaluate 8-h O$_3$. We show statistics both for all 8-h max O$_3$ concentrations and for observed values above 65 ppbv to show how the model performs during high pollution episodes. The model captures observed 8-h O$_3$ data.

\[ \text{www.atmos-chem-phys.net/12/6455/2012/} \]
Table 2. Model performance statistics for 8-h daily maximum O$_3$.

<table>
<thead>
<tr>
<th></th>
<th>AQS</th>
<th>AQS (obs $&gt;$ 65 ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>February</td>
<td>September</td>
</tr>
<tr>
<td>Number of observations</td>
<td>14873</td>
<td>20019</td>
</tr>
<tr>
<td>Mean modeled (ppbv)</td>
<td>39.5</td>
<td>49.8</td>
</tr>
<tr>
<td>Mean observed (ppbv)</td>
<td>36.4</td>
<td>40.5</td>
</tr>
<tr>
<td>Median modeled (ppbv)</td>
<td>40.8</td>
<td>48.8</td>
</tr>
<tr>
<td>Median observed (ppbv)</td>
<td>37.1</td>
<td>39.2</td>
</tr>
<tr>
<td>NMB (%)</td>
<td>8.5</td>
<td>22.9</td>
</tr>
<tr>
<td>NME (%)</td>
<td>17.5</td>
<td>26.4</td>
</tr>
<tr>
<td>MB (ppb)</td>
<td>3.1</td>
<td>9.2</td>
</tr>
<tr>
<td>ME (ppb)</td>
<td>6.4</td>
<td>10.7</td>
</tr>
</tbody>
</table>

NMB = Normalized Mean Bias, NME = Normalized Mean Error, ME = Mean Error, MB = Mean Bias

Table 3. Model performance statistics for 24-h average PM$_{2.5}$.

<table>
<thead>
<tr>
<th></th>
<th>AQS FRM Sites</th>
<th>IMPROVE</th>
<th>CSN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>February</td>
<td>September</td>
<td>February</td>
</tr>
<tr>
<td>Number of observations</td>
<td>9553</td>
<td>5998</td>
<td>1348</td>
</tr>
<tr>
<td>Mean modeled ($\mu$g m$^{-3}$)</td>
<td>15.2</td>
<td>11.9</td>
<td>5.7</td>
</tr>
<tr>
<td>Mean observed ($\mu$g m$^{-3}$)</td>
<td>11.6</td>
<td>9.7</td>
<td>4.4</td>
</tr>
<tr>
<td>Median modeled ($\mu$g m$^{-3}$)</td>
<td>12.7</td>
<td>10.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Median observed ($\mu$g m$^{-3}$)</td>
<td>9.8</td>
<td>8.3</td>
<td>2.9</td>
</tr>
<tr>
<td>NMB (%)</td>
<td>31.1</td>
<td>22.8</td>
<td>33.2</td>
</tr>
<tr>
<td>NME (%)</td>
<td>52.6</td>
<td>38.9</td>
<td>56.1</td>
</tr>
<tr>
<td>MB ($\mu$g m$^{-3}$)</td>
<td>3.8</td>
<td>2.2</td>
<td>1.4</td>
</tr>
<tr>
<td>ME ($\mu$g m$^{-3}$)</td>
<td>6.1</td>
<td>3.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>

FRM = Federal Reference Method

reasonably well. Model mean values are slightly greater than the observed values both in February and September. Ambient monitoring data from the AQS are used to evaluate daily mean PM$_{2.5}$ levels measured by the Federal Reference Method (FRM). In addition, daily mean PM$_{2.5}$ levels from the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network and the Chemical Speciation Network (CSN) are also used to evaluate the model results. The model captures observed PM$_{2.5}$ levels at all monitoring networks both in February and September. Model performance statistics are similar to or better than those for the previous versions of the model (Eder and Yu, 2006; Appel et al., 2007; Foley et al., 2010).

Predicted mean fine-particulate chloride levels in the base simulation are shown in Fig. 1a–b. Fine particulate chloride concentrations are highest in coastal areas and the mid-west. In addition, fine particulate chloride is present in the entire eastern half of the United States in February and in Idaho in September. The fine particulate chloride in the eastern United States is largely derived from anthropogenic sources (mostly fugitive dust), while fine particulate chloride in the coastal areas comes mostly from sea salt. The high modeled levels in Idaho in September are due to particulate chloride emissions from a large wildfire. While the magnitudes of predicted concentrations are greater in September, predicted particulate chloride in February is present over a larger geographical area. Predicted mean coarse particulate chloride levels without the heterogeneous ClNO$_2$ production are shown in Fig. 1c–d.

Predicted fine particulate chloride levels averaged across all measurement sites in the United States are compared to the observed data from IMPROVE in Fig. 1e–f. With the exception of a few days in early February, average predictions are in good agreement with average observed data. Previous studies using the Tanaka et al. (2003a) chlorine chemistry and no ClNO$_2$ formation also showed reasonable performance of particulate chloride predictions. Kelly et al. (2010) compared CMAQ predictions to size resolved (both fine and coarse particles) particulate chloride observations from three coastal monitoring sites in Florida and reported good agreement between the model predictions and the observed data. Bhave and Appel (2009) compared CMAQ predictions to size resolved (both fine and coarse particles) particulate chloride observations from multiple monitoring sites in the United States.
Fig. 1. Predicted mean fine particulate chloride (µg m\(^{-3}\)) without the heterogeneous ClNO\(_2\) production in (a) February and (b) September. Predicted mean coarse particulate chloride (µg m\(^{-3}\)) without the heterogeneous ClNO\(_2\) production in (c) February and (d) September. A comparison of predicted fine particulate chloride with observed data from the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network in (e) February and (f) September.
United States and also reported good agreement. These results suggest model predicted fine and coarse particulate chloride levels are in good enough agreement with observed data to be used to examine the impact of heterogeneous ClNO$_2$ production on air quality.

3.2 Impact of heterogeneous ClNO$_2$ chemistry on model performance statistics

The heterogeneous production of ClNO$_2$ marginally affects model performance statistics for daily maximum 8-h O$_3$. For example, it changed the Normalized Mean Bias (NMB) (Eder and Yu, 2006) from $-20.2\%$ to $-18.8\%$ in February and $0.1\%$ to $0.4\%$ in September for observed values above 65 ppbv. These changes which are mapped in Fig. S1 show that improvements and degradations in model performances do not have a noticeable geographic pattern. The inclusion of heterogeneous ClNO$_2$ formation also changed Normalized Mean Error (NME) (Eder and Yu, 2006) both in February and September by similar margins.

Predicted weekly average total nitrate (TNO$_5$) is compared with observed data from the Clean Air Status and Trends Network (CASTNet). Predicted TNO$_5$ without the heterogeneous production is greater than the observed data with NMB of $61.1\%$ in February and $89.5\%$ in September. Previous studies also reported over-predictions of nitrate (Foyle et al., 2010). The over-predictions may be partially due to the $\gamma_{N_2O_5}$ parameterization used in the model. Brown et al. (2006) measured $\gamma_{N_2O_5}$ values in the eastern United States and reported the values to be much lower than those derived from current $\gamma_{N_2O_5}$ parameterizations available in the peer-reviewed literature. Coatings of particles by organic materials have been suggested to lower $\gamma_{N_2O_5}$ values (Anttila et al., 2006; Chang et al., 2011). However, the effect of organic particles on $\gamma_{N_2O_5}$ is not included in the current CMAQ model. The heterogeneous production of ClNO$_2$ reduced the NMB to $57.1\%$ in February and $85.9\%$ in September for TNO$_5$ in the CASTNet. The heterogeneous production of ClNO$_2$ reduced the NMB from $64.2\%$ to $61.2\%$ in February and $42.1\%$ to $36.4\%$ in September for 24-h average PM$_{2.5}$ nitrate in the IMPROVE network. It also reduced the NMB from $44.8\%$ to $41.7\%$ in February and $67.7\%$ to $60.5\%$ in September for 24-h average PM$_{2.5}$ nitrate in the CSN. These improvements are shown in Fig. S2, S3, S4, and S5 and are most pronounced in the eastern US in February where observed total nitrate concentrations are highest.

3.3 Predicted $Y$, ClNO$_2$ levels, and comparison with observed ClNO$_2$

Predicted mean values of $Y$ on fine and coarse particles with the heterogeneous ClNO$_2$ production are presented in Fig. 2. As might be expected from Eq. (3), calculated yield is largest in areas in which particulate chloride concentrations are highest. Modeled yields on fine particles reached values above 0.7 in some coastal and in-land areas. Yield values on coarse particles reached 1.0 over the Gulf and the Oceans and ranged between 0.5 and 0.8 in coastal and between 0 and 0.4 for in-land areas. These modeled yields suggest that the presence of particulate chloride can efficiently activate the heterogeneous ClNO$_2$ production pathway throughout large areas of the United States. Thornton et al. (2010) calculated annual average ClNO$_2$ yield over the contiguous US by using a coarse grid-resolution ($10^\times10^$) and constraining their predictions with observations from the IMPROVE and the National Atmospheric Deposition Program. We calculate monthly averaged values for fine as well as coarse particles over the contiguous US by using a finer grid-resolution ($12^{-}\times12^{-}$km). Thus, these values cannot be directly compared, so a qualitative comparison of these yields is made. Our predicted values are consistent with the calculation of Thornton et al. (2010) over the coastal areas; both studies suggest relatively higher values over the coastal areas in the US. While our study suggests values can be high in the entire eastern US in February (fine particles), Thornton et al. (2010) calculates higher values only in the southeastern US. Thornton et al. (2010) also suggests higher values throughout the western US while our study finds higher values over much of the West, but very low yields in the desert southwest.

Modeled mean of daily maximum ClNO$_2$ levels in the base simulation that included only the gas-phase formation pathway (no heterogeneous ClNO$_2$ production) were negligible (generally $<5$ pptv) and are not discussed further. Heterogeneous production enhanced ClNO$_2$ levels both in February and September. The predicted monthly mean of daily 1-h ClNO$_2$ maximum and the highest daily maximum ClNO$_2$ levels with the heterogeneous production are presented in Fig. 3. ClNO$_2$ formed where particulate chloride and NO$_x$ concentrations are prevalent. The highest mean daily maximum ClNO$_2$ was found in the Los Angeles area both in February ($\sim1.0$ ppbv) and in September ($\sim1.5$ ppbv). Monthly average of daily maximum ClNO$_2$ concentrations also reached values of 0.24 to 0.48 ppbv in portions of the northeast during both September and February. While predicted values reached higher concentrations in September, predicted levels are more spatially distributed in February. The maximum hourly predicted value in February reached almost 3.0 ppbv in Los Angeles and 2.0 ppbv in the Midwest. High hourly ClNO$_2$ concentrations in September were found in Idaho (4.5 ppbv maximum) and in Los Angeles (4.0 ppbv maximum). Predicted ClNO$_2$ levels were consistently high in Los Angeles both in February and September. Available chlorine to produce ClNO$_2$ in coastal areas comes from seasalt emissions and in the Midwest comes from anthropogenic chloride emissions. In addition, chlorine available to enhance ClNO$_2$ over the eastern half of the United States in February is due to anthropogenic emissions and over Idaho is due to chlorine emissions from the forest fires in September 2006.

Vertical profiles of ClNO$_2$ and its main precursors (N$_2$O$_5$ and particulate chloride) are examined for one day before
Figure 2. (a) Predicted mean yield for ClNO$_2$ on fine particles in (a) February and (b) September. Predicted mean yield for ClNO$_2$ on coarse particles in (c) February and (d) September.

Sunrise in February and one day in September at a few locations with high ClNO$_2$ concentrations: Los Angeles and Indiana in February; Los Angeles and Idaho in September. The profiles shown in Fig. 4 are average concentrations over the identified regions and represent mean values over hundreds of square km. These vertical profiles reveal some interesting relationships between ClNO$_2$ and its precursors at these times and locations. All four instances shown in Fig. 4 display that ClNO$_2$ concentrations are highest at the surface. Variation in the nighttime boundary layer height by location and season is demonstrated by ClNO$_2$ being concentrated in the lowest 40 m of atmosphere in Los Angeles on 9 February 2006, but being mixed up to a height of 200–400 m in both locations on 12 September 2006. In contrast to ClNO$_2$, N$_2$O$_5$ appears to peak in the residual layer aloft at between 200 and 400 m depending on the location and season. The exception to this is the Idaho location on 12 September 2006, where N$_2$O$_5$ is mostly depleted at all heights. Since the Idaho ClNO$_2$ concentrations are associated with a large fire plume, it is possible that the loss of N$_2$O$_5$ by the end of the night was a result of large amounts particulate surface area available for hydrolysis reactions. In all four examples shown here, the vertical profiles of ClNO$_2$ appear to mirror the profiles of particulate chloride suggesting that chlorine probably limits ClNO$_2$ formation aloft, especially given the elevated N$_2$O$_5$ concentrations above the boundary layer. These plots also demonstrate that the chlorine may come from either fine or coarse particulate chloride since the Los Angeles profiles show very little fine chloride while the Indiana profile demonstrates a predominance of fine chloride over coarse chloride.

Ambient ClNO$_2$ levels are not routinely measured; these measurements are conducted only in specialized field campaigns. To our knowledge, four sets of measurements have been published in the peer-reviewed literature. A qualitative comparison of predicted ClNO$_2$ levels with these measurements is presented in Table 4. Osthoff et al. (2008) measured ClNO$_2$ in Houston in 2006 and reported a peak value of about 1200 pptv. Predicted peak ClNO$_2$ in Houston reached to 2000 pptv in February and 1500 pptv in September. Thornton
Fig. 3. Predicted mean of daily maximum ClNO$_2$ in (a) February, (b) September. Predicted hourly maximum ClNO$_2$ in (c) February, (d) September. It should be noted that the largest hourly value for each grid-cell in the entire month is shown in (c) and (d).

Table 4. A comparison of predicted nitryl chloride with observed data.

<table>
<thead>
<tr>
<th>Measurement location</th>
<th>Measurement time period</th>
<th>References</th>
<th>Peak measurement (pptv)</th>
<th>Peak prediction in February (pptv)</th>
<th>Peak prediction in September (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calgary, Alberta</td>
<td>4/16–4/21, 2010</td>
<td>Mielke et al. (2011)</td>
<td>250</td>
<td>500</td>
<td>300</td>
</tr>
</tbody>
</table>

et al. (2010) reported a peak value of 450 pptv in Boulder, Colorado in February 2009. The predicted peak value in Boulder was 300 pptv in February and 200 pptv in September. Mielke et al. (2011) reported a peak ClNO$_2$ value of 250 pptv in Calgary, Canada in April 2010. The predicted peak value in Calgary reached 500 pptv in February and 300 pptv in September. Mielke et al. (2010) reported a peak value of 2550 pptv in Los Angeles, California in June 2010. Predicted peak value in Los Angeles reached 2700 pptv in February and 4000 pptv in September. Predicted levels are similar to the observed values reported in the literature. It should be noted that measured and predicted values cannot be directly compared for several reasons. First, predicted values are hourly averaged while measurements are conducted at a much finer temporal resolution. Moreover, simulation and observed time periods are different (except for Houston, TX). Nevertheless, the model tends to slightly over-predict ClNO$_2$ compared to the observed data. Such over-predictions can be caused by several reasons including over-estimation of $\gamma_{N_2O_5}$ as indicated earlier. Based on these comparisons, the model
Figure 4. Vertical profiles of ClNO$_2$, N$_2$O$_5$, coarse Cl, and fine Cl for (a) Los Angeles on 9 February 2006 at 7 a.m. (note that coarse Cl is divided by 10 to fit on scale), (b) Los Angeles on 12 September 2006 (5 a.m.) (note that coarse Cl is divided by 10 to fit on scale), (c) Indiana on 9 February 2006 at 7 a.m., (d) Idaho on 12 September 2006 at 5 a.m. (note that fine Cl is divided by 10 to fit on scale). Units of ClNO$_2$ and N$_2$O$_5$ are in [ppb] while units of fine and coarse Cl are in [µg/m$^3$].

Parameterizations of yield and $\gamma_{N_2O_5}$ along with our emissions of NO$_x$ and gas and particle-phase chlorine compounds appear to do a reasonable job of replicating the chemistry that leads to ClNO$_2$ production.

3.4 Impact of the heterogeneous ClNO$_2$ production on selected gaseous and particle species

3.4.1 Monthly mean concentrations

Monthly mean O$_3$ levels in the base simulation and changes due to the heterogeneous production are presented in Fig. 5. Monthly mean O$_3$ levels between 30 and 50 ppbv in February and between 40 and 65 ppbv in September were modeled over most areas in the United States. The heterogeneous ClNO$_2$ production enhanced monthly mean O$_3$ by a maximum of 1.3 ppbv in February and 1.4 ppbv in September. On a percentage basis, the O$_3$ enhancement reached up to 4% and 3% in February and September, respectively. Enhancements in February occurred over a larger geographic area than those in September. Predictions of ClNO$_2$ occurred over a wider area in February; consequently enhancements also occurred over a larger geographic area. Although not shown here, the heterogeneous ClNO$_2$ production enhanced mean HO$_2$ and RO$_2$ by a few percent. These radicals increased primarily due to the oxidation of VOCs by Cl which is produced via the photolysis of ClNO$_2$. Enhancements of O$_3$ in the heterogeneous ClNO$_2$ formation simulation were due both to the increased HO$_2$ and RO$_2$ radicals and due to the increased availability of NO$_2$.

Monthly mean total nitrate (TNO$_3$) levels in the base simulation and changes due to the heterogeneous production are presented in Fig. 6. Here we define TNO$_3$ as the sum of gas-phase HNO$_3$ and fine and coarse particle nitrate. Mean TNO$_3$ levels of more than 4.0 µg m$^{-3}$ are predicted over most of the eastern United States and southern California in February and over parts of Midwest, southern United States, and southern California in September. The activation
of the heterogeneous CINO\(_2\) pathway reduced the production of HNO\(_3\) via the N\(_2\)O\(_5\) hydrolysis which then decreased TNO\(_3\) both in February and September. The mean decreases in February were up to 0.8 µg m\(^{-3}\) while the decrease in September reached 2.0 µg m\(^{-3}\). On a percentage basis, the reductions were up to 11% and 21% in February and September, respectively. Both high nitrate concentrations and large nitrate decreases covered a broader area in February than in September.

The heterogeneous CINO\(_2\) production also enhanced sulfate by <0.1 µg m\(^{-3}\), decreased ammonium by <0.3 µg m\(^{-3}\), and increased anthropogenic and biogenic secondary organic aerosols by <0.003 µg m\(^{-3}\). These changes are due to shifts in the radical budget and NO\(_x\) availability and are not discussed further in this paper.

To evaluate the sensitivity of the model results to particulate chloride concentrations, two additional simulations were conducted with increased chlorine emissions [3.0 \(\times\) (anthropogenic particulate chloride, Cl\(_2\), HCl) emissions used for the previous two simulations] for 10 days in February. One simulation was conducted without the heterogeneous production of CINO\(_2\) and the other simulation was conducted with the heterogeneous production of CINO\(_2\). The additional chlorine emissions further increased CINO\(_2\) and O\(_3\) and further decreased TNO\(_3\). Heterogeneous CINO\(_2\) chemistry combined with the augmented chlorine emissions increased mean daily maximum CINO\(_2\) by up to 1.05 ppb compared to the value of 0.88 ppbv with the normal emissions. Similarly, heterogeneous CINO\(_2\) chemistry combined with the augmented chlorine emissions increased mean O\(_3\) by up to 2.1 ppb compared to the value of 1.2 ppbv with the normal emissions. Mean O\(_3\) in the northeast United States increased by 1.0–2.0 ppb with the augmented chlorine emissions, while mean O\(_3\) increased only by 0.6–1.0 ppbv with the base case emissions. The augmented chlorine emissions decreased mean TNO\(_3\) by up to 1.2 µg m\(^{-3}\) compared to the value of 0.9 µg m\(^{-3}\) with the normal emissions. In the Midwest, this decrease in mean TNO\(_3\) was 0.4–0.6 µg m\(^{-3}\).
compared to a value of 0.1–0.3 µg m$^{-3}$ with normal emissions. The impacts on ClNO$_2$, O$_3$ and TNO$_3$ were more pronounced with the enhanced emissions. These results suggest that the heterogeneous production of ClNO$_2$ can further increase O$_3$ and lower TNO$_3$ predictions if elevated chlorides are present in the atmosphere.

3.4.2 Day-to-day variation

Several areas were identified as having high modeled ClNO$_2$ concentrations in Sect. 3.3. Here we examine the temporally-resolved changes in ClNO$_2$, O$_3$, and TNO$_3$ in those areas. Time series of the changes in ClNO$_2$, O$_3$, and TNO$_3$ due to the heterogeneous production in Los Angeles, Indiana, and Idaho are shown Fig. 7. These values are averaged over each representative region and since ClNO$_2$ formation chemistry can occur in localized areas, this analysis does not show the maximum impact of that chemistry. Figure 7 shows that ClNO$_2$ concentrations increase every night in Los Angeles in both February and September. Predicted increases in ClNO$_2$ in February are lower than those in September in Los Angeles. Nightly concentrations averaged over the Los Angeles area range 0.15 ppbv to above 1.0 ppbv. These fairly routine ClNO$_2$ episodes are due to the constant source of particulate chloride from sea-salt and NO$_x$ from mobile sources. Ozone enhancements and TNO$_3$ decrease due to the ClNO$_2$ chemistry are predicted daily in Los Angeles and range from 0.3 to 3 ppb for O$_3$ and from 0.1 to 4.0 µg m$^{-3}$ for TNO$_3$. Anthropogenic particulate chloride emissions are responsible for the chlorine available for heterogeneous production in Indiana and enhanced ClNO$_2$ and O$_3$, and decreased TNO$_3$ on most days in February. Chloride and NO$_x$ emissions from a large wildfire in Idaho activated the heterogeneous production and increased ClNO$_2$ and O$_3$ up to 1 ppbv and 2.5 ppbv, respectively, and decreased TNO$_3$ by up to 2.5 µg m$^{-3}$ over a large portion of Idaho. The wildfire was active only during the first part in September and consequently the heterogeneous production during the second part in September is negligible. Thus, the heterogeneous ClNO$_2$ production is active on most
Figure 7: Time series of the absolute value of changes in ClNO$_2$, O$_3$, and TNO$_3$ at (a) Los Angeles in February, (b) Los Angeles in September, (c) Indiana in February, (d) Idaho in September. All $\Delta$ values are positive for O$_3$ and ClNO$_2$ and negative for TNO$_3$.

3.4.3 Diurnal variation of the impact

Figure 8 shows average diurnal changes in ClNO$_2$, O$_3$, TNO$_3$ in Los Angeles, Indiana, and northeastern United States due to the heterogeneous production of ClNO$_2$. Again, these changes are averaged over each representative area. ClNO$_2$ increased during the course of the night, reached peak levels in the early morning and then decreased due to the photolysis and dropped to its lowest level in the afternoon. The peak ClNO$_2$ levels in February occurred somewhat later in the morning than those in September due to the lower photolysis rate and late sun rise. The modeled diurnal pattern of ClNO$_2$ agrees well with observed profile reported by Thornton et al. (2010). The O$_3$ enhancement started in the morning and reached a peak value in the afternoon and then decreased. The time of peak O$_3$ increase varied by season; O$_3$ enhancements reached their peak around noon in September and later in the afternoon in February. So even though ClNO$_2$ photolysis released Cl radicals and NO$_2$ in the first several hours after sunrise, these model simulations predict that its effect on O$_3$ continues well into the day meaning that ClNO$_2$ production will have a noticeable impact of 8-h daily maximum O$_3$, the regulatory metric used to identify areas in violation with national air quality standards in the US. The decrease in TNO$_3$ followed the same diurnal pattern as the changes in ClNO$_2$ since the decrease of HNO$_3$ is a direct result of the heterogeneous N$_2$O$_5$ chemistry following the pathway of ClNO$_2$ formation (R10) rather than HNO$_3$ production (R9). Similar diurnal pattern of the changes in ClNO$_2$, O$_3$, TNO$_3$ were observed in other areas.

3.4.4 Impact on daily maximum 8-h O$_3$

Predicted mean 8-h daily maximum O$_3$ in the base simulation and enhancements due to the heterogeneous production are presented in Fig. 9. Predicted mean 8-h daily maximum O$_3$ without the heterogeneous production are greater than 46 ppbv in most of the United States in September while predicted values are lower than 46 ppbv in February. The heterogeneous production enhanced the monthly mean 8-h daily maximum O$_3$ by up to 1.7 ppbv in February and 1.9 ppbv in
September. On a percentage basis, the enhancement reached up to 4% and 3% in February and September, respectively. The largest monthly mean impact occurred in Los Angeles both in February and September. Predicted maximum changes in 8-h \( O_3 \) are also shown in Fig. 9 for February and September. The largest enhancement in daily maximum 8-h \( O_3 \) in any grid-cell was 13.3 ppb in February and 6.6 ppbv in September. On a percentage basis, the largest enhancement in daily maximum 8-h \( O_3 \) in any grid-cell was 43% in February and 10% in September. Although mean enhancements in maximum 8-h \( O_3 \) are modest, impacts on specific days can be quite large. The addition of \( \text{ClNO}_2 \) heterogeneous chemistry also increases the number of days any grid-cells exceed the National Ambient Air Quality Standards of 75 ppbv in Los Angeles and other areas (the maximum increase in any grid cell was 7 additional days in September).

### 3.5 Impact on the composition of total reactive nitrogen (\( \text{NO}_y \))

The monthly mean of daily maximum \( \text{ClNO}_2: \text{NO}_y \) ratios without the heterogeneous \( \text{ClNO}_2 \) production were negligible (<0.005). Heterogeneous \( \text{ClNO}_2 \) production increased monthly mean of daily maximum \( \text{ClNO}_2: \text{NO}_y \) ratios up to 0.06 in February as well as in September. Higher \( \text{ClNO}_2: \text{NO}_y \) ratios occurred over a larger geographic area in February than those in September. As \( \text{TNO}_3 \) concentrations decreased with the heterogeneous \( \text{ClNO}_2 \) production, so did their contribution to \( \text{NO}_y \). While the monthly mean \( \text{ClNO}_2: \text{NO}_y \) ratios were small, the maximum hourly \( \text{ClNO}_2: \text{NO}_y \) ratios are much greater and reached 0.34 in February and 0.17 in September. The contribution of \( \text{ClNO}_2 \) to \( \text{NO}_y \) was greater in February than in September; thus, the ratio was also generally higher in February. Our predicted maximum hourly \( \text{ClNO}_2: \text{NO}_y \) ratios agree well with the
Fig. 9. (a) Predicted monthly average of 8-h daily maximum $O_3$ in February, (b) changes in monthly average of 8-h daily maximum $O_3$ due to the heterogeneous production in February, (c) the largest changes in daily maximum 8-h $O_3$ due to the heterogeneous production in February, (d) predicted monthly average of 8-h daily maximum $O_3$ in September, (e) changes in monthly average of 8-h daily maximum $O_3$ due to the heterogeneous production in September, (f) the largest changes in daily maximum 8-h $O_3$ due to the heterogeneous production in September.

results of Thornton et al. (2010) who suggested up to 22\% of NO$_x$ may be cycled through ClNO$_2$.

3.6 Impact of $\gamma_{N_2O_5}$ parameterization on model predictions

The presence of particulate chloride can increase $\gamma_{N_2O_5}$ as described by Bertram and Thornton (2009). However particulate chloride is not explicitly accounted for in the $\gamma_{N_2O_5}$ which is described by Davis et al. (2008) and used in this work and in the current version of CMAQ. The Davis et al. (2008) parameterization accounts for PM concentrations of sulfate, nitrate, ammonium, and water, phase of the PM (ice versus aqueous) and temperature. However, it does not account for the effect of particulate chloride on $\gamma_{N_2O_5}$. Bertram and Thornton (2009) account for the effect of particulate chloride on $\gamma_{N_2O_5}$ but neglect the effects of temperature and PM phase. Both parameterizations account for decreasing $\gamma_{N_2O_5}$ with increased nitrate concentrations, but the Bertram and Thornton (2009) formulation is based on a mechanistic description of the nitrate inhibition effect while Davis et al. (2008) uses a linear relationship. To evaluate the sensitivity of the model results to $\gamma_{N_2O_5}$, two additional simulations were completed for a 10-day period in each month. The first simulation employed $\gamma_{N_2O_5}$ (Eq. 4) of Bertram and
Thornton (2009) on both fine and coarse particles and used $Y = 0$. The second simulation employed $\gamma_{N_2O_5}$ of Bertram and Thornton (2009) on both fine and coarse particles with $Y$ calculated using Eq. (3). The differences in results obtained with the two simulations are compared to those obtained with the previous two simulations employing $\gamma_{N_2O_5}$ of Davis et al. (2008) on fine particles and $\gamma_{N_2O_5}$ of Bertram and Thornton (2009) on coarse particles. While enhancements in hourly $O_3$ obtained with the two $\gamma_{N_2O_5}$ varied occasionally by 1–2 ppbv, the enhancements in mean 8-h $O_3$ obtained with the two $\gamma_{N_2O_5}$ formulations did not differ significantly ($<0.2$ ppbv). The decreases in mean $TNO_3$ obtained with the $\gamma_{N_2O_5}$ of Bertram and Thornton (2009) on both fine and coarse particles were greater than those obtained with the modeling simulations described in the main portion of this paper (Figs. S6 and S7). Thus, the use of $\gamma_{N_2O_5}$ of Bertram and Thornton (2009) on both fine and coarse particles can further reduce $TNO_3$ without further enhancement of $O_3$.

4 Summary

Heterogeneous ClNO$_2$ chemistry is successfully implemented into the CMAQ model along with a comprehensive inventory of chlorine and reactive nitrogen emissions. While the homogeneous production of ClNO$_2$ is negligible, the heterogeneous production can enhance ClNO$_2$ in coastal areas, the eastern half of the United States, and Idaho. Sea-salt derived particulate chloride enhances ClNO$_2$ in coastal areas while anthropogenic particulate chloride enhances ClNO$_2$ in the eastern half of the United States and chloride from forest fires enhances ClNO$_2$ in wildfire plumes. Mean of daily maximum ClNO$_2$ levels increase by up to 1.0 ppbv in February and 1.5 ppbv in September though the maximum hourly values are greater.

Predicted ClNO$_2$ enhances monthly mean 8-h $O_3$ modestly but enhances 8-h daily maximum $O_3$ concentrations quite substantially in some episodes. It can, however, decrease mean $TNO_3$ by larger margins and improve model performance statistics. Predicted ClNO$_2$ reaches its peak level in the early morning while the $O_3$ enhancement starts in the morning and reaches a peak value in the afternoon. The impact of the heterogeneous production occurs over a larger geographical area in February. The heterogeneous production of ClNO$_2$ changes the composition of NO$_3$; predicted ClNO$_2$ can account for up to 6% of the monthly mean NO$_3$ but up to 34% of NO$_3$ in some localized episodes.

The results of this study compare favorably to the findings of Simon et al. (2009) who reported that the heterogeneous ClNO$_2$ production can increase daily maximum 8-h $O_3$ in Houston by up to 1.5 ppbv. While the heterogeneous ClNO$_2$ production in this study enhances monthly mean 8-h $O_3$ by less than 0.2 ppbv in Houston, it enhanced the daily maximum 8-h $O_3$ on some days by levels similar to those reported by Simon et al. (2009). It should be noted that Simon et al. (2009) used 4-km grid resolution and this study uses 12-km grid resolution. Since the modeling domain covers the entire United States, a larger grid resolution is used in this study. Emissions of NO$_x$ and VOCs used by Simon et al. (2009) are also different than those used in this study. One large improvement over the modeling formulation presented in that work is that this modeling uses generalized parameterizations for reactive uptake and ClNO$_2$ yield while Simon et al. (2009) relied on local measurements to create fixed values for those variables. Our new model formulation has allowed for the investigation of the effects ClNO$_2$ chemistry over the entire continental United States and over multiple seasons. Our predicted yields in Houston are lower than the fixed 0.75 value used by Simon et al. (2009). Results of this study suggest that the effect of ClNO$_2$ production on air quality is more pronounced in several areas in the United States than it is in Houston. Field campaigns in those areas could validate the findings in this study.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/6455/2012/aep-12-6455-2012-supplement.pdf.

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