



## Modeling the Effect of Chlorine Emissions on Ozone Levels over the Eastern United States

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### ABSTRACT

This paper presents model estimates of the effect of chlorine emissions on atmospheric ozone concentrations in the eastern United States. The model included anthropogenic molecular chlorine emissions, anthropogenic hypochlorous acid emissions from cooling towers and swimming pools, and chlorine released from sea-salt aerosols. The release of chlorine emissions from sea-salt aerosols was modeled using heterogeneous reactions involving chloride ions in aerosols and three gas-phase species. The gas-phase chlorine chemistry was combined with the Carbon Bond Mechanism and incorporated into the Community Multi-scale Air Quality modeling system. Air quality model simulations were performed for July 2001 and the results obtained with and without chlorine emissions were analyzed. When chlorine emissions were included in the model, ozone concentrations increased in the Houston, Texas, and New York–New Jersey areas. The daily maximum 1-h ozone concentrations increased by up to 12 parts per billion by volume (ppbv) in the Houston area and 6 ppbv in the New York–New Jersey area. The daily maximum 8-h ozone concentrations increased by up to 8 ppbv in the Houston area and 4 ppbv in the New York–New Jersey area. The monthly average daily maximum 1-h ozone concentration increased by up to 3 ppbv in the Houston area, but the increases in the monthly average daily maximum 1-h ozone concentration in the New York–New Jersey area were small. Chlorine emissions and chemistry enhanced the volatile organic compound oxidation rates and, thereby, increased the ozone production rate.

### 1. Introduction

Tropospheric ozone ( $O_3$ ) is produced by complex reactions involving volatile organic compounds (VOC), nitrogen oxides ( $NO_x$ ), and atmospheric oxidants in the presence of sunlight. Historically, chlorine emissions have not been included in photochemical models for air quality and, thus, the effects of such emissions on  $O_3$  have been neglected. The effect of chlorine chemistry on  $O_3$  has been studied as early as 1985 (Hov 1985). The author used a photochemical model that employed a chemical mechanism, including chlorine reactions, to

evaluate the effects of industrial emissions in Telemark, Norway. Industrial chlorine emissions were found to dominate the photochemical activity. Recent evidence further suggests that chlorine chemistry can enhance  $O_3$  formation by increasing the oxidation rates of VOC (Finlayson-Pitts 1993; Oum et al. 1998; Chang et al. 2002; Knipping and Dabdub 2003; Tanaka et al. 2003a; Chang and Allen 2006). Tanaka et al. (2003a) found this to be true in the Houston, Texas, area. They used 1-chloro-3-methyl-3-butene-2-one (CMBO) and chloromethylbutenal (CMBA), the reaction products of isoprene and the chlorine radical, as marker species to evaluate the effect of chlorine chemistry. The presence of CMBO and CMBA in the atmosphere on elevated  $O_3$  days suggested that chlorine chemistry enhanced  $O_3$  formation in that area. They also performed experiments in Houston using three environmental chambers with ambient air. The first chamber contained only ambient air. The second chamber contained ambient air and a known amount of propane. The third chamber contained ambient air and a known amount of propane and molecular chlorine ( $Cl_2$ ). They simultaneously ex-

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posed all three chambers to ambient sunlight in Houston. The  $O_3$  and CMBO formation rates were highest in the third chamber, suggesting that the chlorine chemistry enhanced the  $O_3$  formation rate.

Tanaka et al. (2003b) developed a gas-phase chlorine chemistry mechanism for use in the Carbon Bond IV (CB-IV) Mechanism. They added these reactions to the CB-IV Mechanism and implemented it into the Comprehensive Air-Quality Model with extensions (CAMx). Chang et al. (2002) used this model to study the effect of atomic chlorine precursor emissions in the 11-county  $O_3$  nonattainment area in southeastern Texas. They estimated atomic chlorine precursor emissions from industrial sources, cooling towers, swimming pools, and sea-salt aerosols, and conducted air quality simulations for 6–11 September 1993. They concluded that the atomic chlorine precursor emissions can increase  $O_3$  concentrations by 11–16 parts per billion by volume (ppbv) in southeastern Texas.

Knipping and Dabdub (2003) studied the effects of chlorine emissions from sea-salt aerosol on  $O_3$  concentrations in the south coast air basin of California (SoCAB). They added 83 gas-phase chlorine reactions to the California Institute of Technology (Caltech) Atmospheric Chemical Mechanism and implemented it in the Caltech Airshed Model. The model also included sea-salt emissions fluxes from the open ocean and coastal surf zone and several heterogeneous reactions leading to  $Cl_2$  formation. They conducted air quality simulations for 8–9 September 1993 and concluded that the sea-salt-derived chlorine emissions can increase morning  $O_3$  concentrations by a maximum of 12 ppbv in the coastal area and the peak  $O_3$  concentrations by a maximum of 4 ppbv.

Chang and Allen (2006) extended their earlier work to further study the effect of chlorine chemistry on  $O_3$  in southeast Texas for August–September 2000 using CAMx. The predicted CMBO compared reasonably well to the measured CMBO, validating the effect of chlorine chemistry in the Houston area. The investigators then applied the model to study the effect of chlorine emissions on  $O_3$  in southeast Texas. Chlorine emissions increased morning  $O_3$  concentrations by a maximum of 70 ppbv and the daily peak  $O_3$  concentrations by 10 ppbv. The aforementioned studies focused on the effect of chlorine emissions on  $O_3$  concentrations in relatively small geographic areas. The intent of the study described herein is to conduct a preliminary assessment of the effect of chlorine emissions on  $O_3$  concentrations in the eastern United States. The specific objective is to identify the regions in the eastern United States in which chlorine emissions may play a role in enhancing  $O_3$  concentrations.



FIG. 1. Modeling domain encompassing the continental (36-km grid spacing) and eastern (12-km grid spacing) United States. Results from grid cells marked “A” and “B” are presented in Figs. 3 and 5, respectively.

## 2. Methodology

### a. Model description

The U.S. Environmental Protection Agency’s (USEPA) Community Multiscale Air Quality (CMAQ) modeling system, version 4.5, was used for this study. Model performance evaluations for this modeling system have been conducted by comparing model predictions with measured ambient pollutants obtained from several measurement networks (Appel et al. 2007, manuscript submitted to *Atmos. Environ.*). As mentioned earlier, chlorine emissions are not typically included in photochemical models for air quality and the CMAQ model performance evaluations did not include any chlorine emissions. For this study, the horizontal domain of the model consisted of  $148 \times 112$  grid cells with a 36-km grid spacing for the continental United States and a nested one-way domain of  $213 \times 188$  grid cells for the eastern United States, with a 12-km grid spacing (Fig. 1). The model contained 14 layers in the vertical direction. The CMAQ chemical transport model was configured to use the mass continuity scheme to describe advection processes, the multiscale method to describe horizontal diffusion processes, the eddy method to describe vertical diffusion processes, and the asymmetrical convective model for cloud processes (see information online at [http://www.cmascenter.org/help/model\\_docs/cmaq/4.5/Science\\_Updates.pdf](http://www.cmascenter.org/help/model_docs/cmaq/4.5/Science_Updates.pdf)). Aqueous chemistry, aerosol processes, and dry and wet depositions were also included, but plume-in-grid treatment was not included. Dry and wet deposition losses for the chlorine species were included in the study. The CMAQ modeling sys-

tem currently includes three different gas-phase chemistry solvers—the Sparse-Matrix Vectorized Gear solver, the Rosenbrock solver, and the Euler Backward Iterative solver; the Rosenbrock solver was used for this study. The meteorological driver for the CMAQ modeling system was the fifth-generation Pennsylvania State University–National Center for Atmospheric Research Mesoscale Model (MM5) system, version 3.5 (Grell et al. 1994). Meteorological data obtained from the MM5 system were processed using the Meteorology–Chemistry Interface Program, version 2.3.

The predefined clean air vertical profiles for initial and boundary concentrations provided in the CMAQ modeling system were used in this study. The model was spun up for 7 days to minimize the effect of initial conditions on model predictions. Two model simulations were performed with the following two mechanisms for July 2001: 1) the Carbon Bond (CB05) mechanism, and 2) the combined CB05 and chlorine mechanism. The CB05 mechanism contains 156 chemical reactions involving 52 species; details of the mechanism can be found elsewhere (Yarwood et al. 2005; Sarwar et al. 2007).

#### b. Chlorine mechanism

A new chlorine mechanism was used in this study (Yarwood et al. 2005). The mechanism consists of 20 gas-phase reactions and includes reactions of the chlorine atom with organic and inorganic species. Reactions of chlorine atoms with the following organic species are included in the mechanism: methane, ethane, paraffin carbon bond, ethene, external olefinic bond, internal olefinic carbon bond, formaldehyde, acetaldehyde, higher aldehyde, isoprene, methanol, and ethanol. Four additional gas-phase reactions were added to the mechanism for simulating nitryl chloride ( $\text{ClNO}_2$ ) and chlorine nitrate ( $\text{ClONO}_2$ ), which are needed for the heterogeneous reactions described in the next section. Thus, a total of 24 chlorine reactions were used in this study; the combined mechanism included 180 chemical reactions.

#### c. Heterogeneous reactions

Recent studies suggest that  $\text{Cl}_2$  can be released from heterogeneous reactions of gaseous species with chloride ions in sea-salt particles (Oum et al. 1998; Spicer et al. 1998). In laboratory experiments, Oum et al. (1998) identified the release of  $\text{Cl}_2$  during the photolysis of  $\text{O}_3$  in the presence of aqueous salt particles. Spicer et al. (1998) measured atmospheric  $\text{Cl}_2$  at a New York coastal site and indicated that the concentrations

ranged from 10 to 150 parts per trillion by volume (pptv). They suggested that an unrecognized source of  $\text{Cl}_2$  exists in the marine boundary layer that may generate up to 330 pptv of  $\text{Cl}_2$  per day. Knipping and Dabdub (2003) identified three heterogeneous chemical reactions involving sea-salt particles and gaseous species that released  $\text{Cl}_2$  in the coastal areas of the SoCAB. These three heterogeneous reactions, involving gas-phase hydroxyl radical (OH), dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), and  $\text{ClONO}_2$ , with aerosol-phase chlorides, have been implemented in the CMAQ model.

#### d. Emissions for the study

Anthropogenic emissions of criteria pollutants from version 3 of the 1999 National Emissions Inventory (NEI) were used in this study (see information online at <http://www.epa.gov/ttn/chief/net/1999inventory.html>). Biogenic emissions were generated using the Biogenic Emissions Inventory System, version 3.13 (Schwede et al. 2005). Sea-salt emission fluxes from the open ocean are based on the parameterization of Gong (2003) and are adjusted to ambient relative humidity using the polynomial expressions of Zhang et al. (2005). The resulting fluxes are fit to a bimodal size distribution and injected into the accumulation and coarse modes of the CMAQ model. Sea-salt emissions from the coastal surf zone are currently not included in the CMAQ model and are, therefore, not considered in the present study. Sea-salt emissions from the coastal surf zone can be higher than those from the open ocean; thus, the effect of chlorine emissions on  $\text{O}_3$  in the coastal area may be underestimated somewhat in this study. Chlorine emissions are described in the next sections.

#### 1) ANTHROPOGENIC MOLECULAR CHLORINE EMISSIONS

Molecular chlorine emissions were obtained from version 3 of the 1999 NEI for hazardous air pollutants (NEI99HAP), which included an annual total of about 33 000 tons (short tons) of  $\text{Cl}_2$  emissions nationwide. Point sources contributed about 26 980 tons, area sources about 5780 tons, and nonroad mobile sources about 290 tons. Nonroad mobile  $\text{Cl}_2$  emissions were modeled as area sources. Source-segregated inventories of point source  $\text{Cl}_2$  emissions are presented in Table 1. Primary metal production was the dominant point source category and emitted approximately 22 370 tons of  $\text{Cl}_2$ , representing about 83% of all point source emissions. Industrial solid waste disposal and incineration, and miscellaneous manufacturing industries were the second and third highest point source categories in the

TABLE 1. Point source chlorine emissions by source classification codes (SCC) in the United States. Estimates have been rounded off to the nearest 10 (only top 10 emissions categories are included).

| No. | SCC        | Short descriptions                                    | Tons yr <sup>-1</sup> |
|-----|------------|---|-----------------------|
| 1   | 0030399999 | Primary metal production                              | 22 370                |
| 2   | 0050300501 | Industrial solid waste disposal and incineration      | 1020                  |
| 3   | 0039999999 | Miscellaneous manufacturing industries                | 980                   |
| 4   | 0030700114 | Pulp and paper and wood products (bleaching reactors) | 180                   |
| 5   | 0030300908 | Steel manufacturing                                   | 170                   |
| 6   | 0030700199 | Pulp and paper and wood products (others)             | 130                   |
| 7   | 0030400103 | Aluminum, smelting furnace/reverberatory              | 120                   |
| 8   | 0030101101 | Hydrochloric acid; by-product process                 | 110                   |
| 9   | 0030500606 | Cement manufacturing (dry process); kilns             | 100                   |
| 10  | 0039001299 | In-process fuel use; solid waste; general             | 100                   |

United States, respectively. The Sparse Matrix Operator Kernel Emission (SMOKE) modeling system was used to process NEI99HAP and generate a model-ready Cl<sub>2</sub> emissions file. All Cl<sub>2</sub> emissions were assumed to occur at a constant rate. Plume rise calculations were performed for point sources in the SMOKE model.

## 2) ANTHROPOGENIC HYPOCHLOROUS ACID EMISSIONS

Because hypochlorous acid (HOCl) is not considered a hazardous air pollutant by the USEPA, NEI99HAP does not include its emissions. Chlorine emissions from cooling towers and swimming pools in the United States were estimated using the procedures described in Chang et al. (2002). Chang et al. (2002) suggested that chlorine from these sources may be emitted either as Cl<sub>2</sub> or HOCl. The chemical form of chlorine emissions is important because it directly affects the production of the chlorine atom. The photolysis rate of Cl<sub>2</sub> is greater than that of HOCl; therefore, Cl<sub>2</sub> is expected to produce chlorine atoms at a greater rate than HOCl. Chang et al. (2002) studied the effect of chlorine emissions on O<sub>3</sub> in the Houston area by using chlorine emissions in the form of Cl<sub>2</sub>. In this study, chlorine emissions from cooling towers and swimming pools were used in the form of HOCl. The results presented in this article are likely to represent the lower bound of the effect of chlorine emissions on O<sub>3</sub> concentrations.

### (i) Hypochlorous acid emissions from cooling towers

Chlorine is often added to cooling towers to control the buildup of microorganisms. Chlorine is removed from the system via the following three different mechanisms: 1) flash off, 2) blow down, and 3) reactions with contaminants present in the system (Chang et al.

2002). Holzwarth et al. (1984a,b) have studied the fate of chlorine in cooling towers and performed on-site measurements in a refinery in 1981. Flash off is believed to be the most significant mechanism removing chlorine from the system. Chang et al. (2002) estimated emissions for a cooling tower that used 1.44 million gallons of water per day (MGD). By combining the flash-off factor and the chlorine feed rate, they estimated that the 1.44 MGD cooling tower emits 18.4 Kg of Cl<sub>2</sub> per day. They also estimated the number of cooling towers in the 11-county area by assuming that 1 gallon of cooling water is needed to produce each pound of commodity products. The amount of cooling water needed to produce the nation's 300 million tons of commodity products is 1643 MGD. Assuming that each cooling tower emits the same amount of chlorine whether it is in the form of Cl<sub>2</sub> or HOCl, the HOCl emissions from cooling towers in the United States are about 35 tons day<sup>-1</sup> (12 640 tons yr<sup>-1</sup>).

Having computed a national total of HOCl emissions from cooling towers, a method was needed to spatially allocate these emissions into model grid cells. Because NEI99HAP includes some Cl<sub>2</sub> emissions from cooling towers, the spatial distribution of these emissions was used as a surrogate for HOCl emissions from cooling towers. The total estimated cooling tower HOCl emissions were apportioned to each source according to the ratio of Cl<sub>2</sub> emissions from that source to the total Cl<sub>2</sub> emissions from all cooling towers. Note that we have implicitly assumed that the spatial distribution of cooling tower Cl<sub>2</sub> emissions in NEI99HAP is accurate. The SMOKE model was used to generate a model-ready emissions file using the HOCl emissions inventory for cooling towers, which were treated as point sources. Using this approach, Texas was the highest contributor to the cooling tower HOCl emissions in the United States, with 73% of the total emissions. California emitted about 9%, New Mexico 6%, Louisiana 5%, and

Colorado 4%. Cooling towers were assumed to emit HOCl at a constant rate. Plume rise calculations for the cooling tower sources were performed in the SMOKE model.

(ii) *Hypochlorous acid emissions from swimming pools*

Recent estimates suggest that approximately 7.3 million residential and 700 000 public swimming pools exist in the United States (information online at [ftp://ftp.epa.gov/EmisInventory/finalnei99ver3/haps/documentation/nonpoint/nonpt99ver3\\_aug2003.pdf](ftp://ftp.epa.gov/EmisInventory/finalnei99ver3/haps/documentation/nonpoint/nonpt99ver3_aug2003.pdf)). Chang et al. (2002) estimated atomic chlorine precursors from swimming pools in southeastern Texas by three different methods. The first method involved the mass balance of sodium hypochlorite (NaOCl), which led to an estimate of approximately 17 000 kg of NaOCl emissions per day from swimming pools. The second method involved the use of an overall mass transfer coefficient of 10–100  $\mu\text{g m}^{-2} \text{min}^{-1}$  for HOCl and the average swimming pool surface area, and it led to an estimate of 90–900 kg of HOCl emissions per day. The third method involved the use of a residual chlorine concentration and the volume of each swimming pool, and led to an estimate of 16 000 kg of chlorine emissions per day. Because these methods produce diverse estimates of chlorine emissions, the second method that produces the lowest estimates of chlorine emissions was adopted in this study to represent the lower bound of the effect of chlorine emissions on  $\text{O}_3$  concentrations. An overall mass transfer coefficient of 100  $\mu\text{g m}^{-2} \text{min}^{-1}$  for HOCl was used. The average surface area of residential and public swimming pools in the United States is 48 and 200  $\text{m}^2$ , respectively. Thus, the total HOCl emissions from residential and public swimming pools in the United States are approximately 20 000 and 8100  $\text{tons yr}^{-1}$ , respectively. Annual chlorine production in the United States is approximately 11 million  $\text{tons yr}^{-1}$  (Ayres 1997). The amount of chlorine used in swimming pools is not readily available. However, 5% of the annual chlorine production is used for water disinfection (Ayres and Ayres 1997). Thus, approximately 550 000 tons of chlorine are used annually for water disinfection in the United States. Total HOCl emissions estimated from swimming pools in the United States are approximately 28 100  $\text{tons yr}^{-1}$  (approximately 18 700  $\text{tons yr}^{-1}$  of chlorine). Thus, the estimated chlorine emissions from swimming pools represent about 3% of the total chlorine usage for water disinfection in the United States. This percentage appears to be reasonable given the high solubility of chlorine in water, thus lending some credibility to the chlo-

TABLE 2. Summary of anthropogenic chlorine emissions in the United States. Estimates have been rounded off to the nearest 10 (only top 5 states are listed).

| State | Tot $\text{Cl}_2$ emissions<br>(tons $\text{yr}^{-1}$ ) | State | Tot HOCl emissions<br>(tons $\text{yr}^{-1}$ ) |
|-------|---|-------|--|
| UT    | 22 430  | TX    | 10 890   |
| CA    | 5220  | CA    | 4600   |
| OK    | 490   | NY    | 2140   |
| TX    | 430   | FL    | 1410   |
| MI    | 410   | IL    | 1270   |

rine emissions inventory for swimming pools developed in this study.

Swimming pool emissions were modeled as area sources and, as with the cooling tower emissions, a method was needed to allocate the total emissions into model grid cells. NEI99HAP includes chloroform emissions from swimming pools. The same procedure that was used for allocating total HOCl emissions from cooling towers to model grid cells was used for swimming pools (i.e., the total estimated swimming pool HOCl emissions were apportioned to each source according to the fraction of chloroform emissions from swimming pools in each model grid cell). The SMOKE model was used to process the HOCl emissions inventory for swimming pools and generate a model-ready HOCl emissions file. Using this approach, California was the highest contributor to the total HOCl emissions from swimming pools in the United States, with about 12% of the total emissions. New York emitted about 8%, Texas 6%, Florida 5%, Illinois 4%, and Pennsylvania 4%. Swimming pools were assumed to emit HOCl at a constant rate. The model-ready  $\text{Cl}_2$  emissions files from NEI99HAP and the HOCl emissions files for swimming pools and cooling towers were combined with the standard emissions files required for the CB05 mechanism.

e. *Spatial distribution of chlorine emissions*

A summary of the chlorine emissions is presented in Table 2. The total  $\text{Cl}_2$  emissions represent the sum of point and area source emissions from NEI99HAP; the total HOCl emissions represent the sum of cooling tower and swimming pool emissions. The largest point source for  $\text{Cl}_2$  emissions, located near the Great Salt Lake in Utah, emitted about 22 350 tons of  $\text{Cl}_2$  in 1999. Overall, sources in Utah contributed the largest amount of total  $\text{Cl}_2$  emissions. Sources in California contributed the second largest amount of total  $\text{Cl}_2$  emissions, with area sources representing about 97% of the emissions. Sources in Texas contributed the largest amount of HOCl emissions, with cooling towers representing over 85% of the HOCl emissions. Sources in

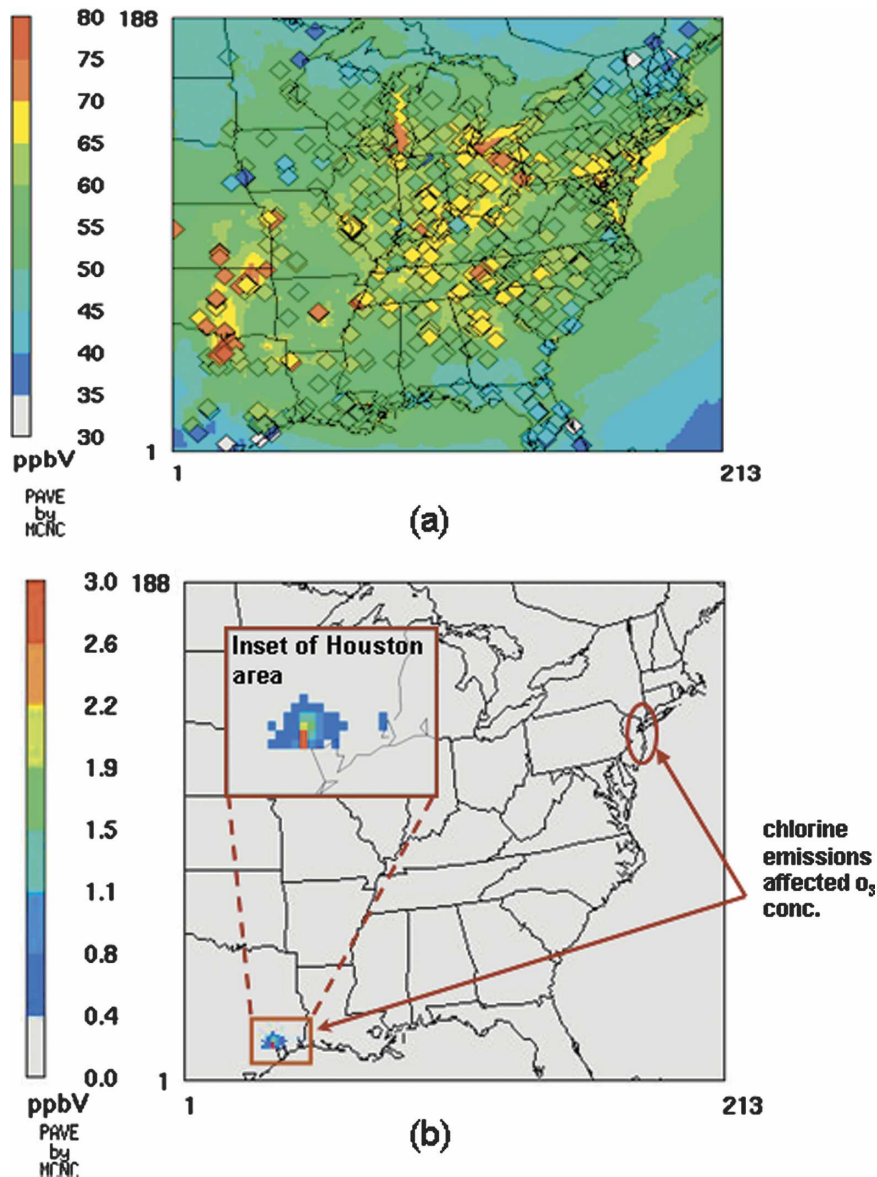


FIG. 2. Impact of chlorine emissions on O<sub>3</sub> concentrations in the eastern United States: (a) predicted and observed monthly average daily maximum 1-h O<sub>3</sub> concentrations without chlorine emissions, and (b) predicted increases in the monthly average daily maximum 1-h O<sub>3</sub> concentrations with chlorine emissions.

California contributed the second largest HOCl emissions, with swimming pools representing about 75% of the HOCl emissions.

### 3. Results and discussion

When chlorine emissions were included in the model, O<sub>3</sub> concentrations increased in many grid cells relative to the case without chlorine emissions. Most of the increases were less than 4 ppbv, and these small increases

are not discussed further. Chlorine emissions enhanced O<sub>3</sub> concentrations by more than 4 ppbv in only two areas in the eastern U.S. 12-km domain: the Houston area and the New York–New Jersey area.

When chlorine emissions were included in the model, O<sub>3</sub> concentrations in the Houston area increased each day in July and affected both the daily maximum 1- and 8-h O<sub>3</sub> concentrations. The largest increases in the daily maximum 1- and 8-h O<sub>3</sub> concentrations in the Houston area were about 12 and 8 ppbv, respectively. The Hous-

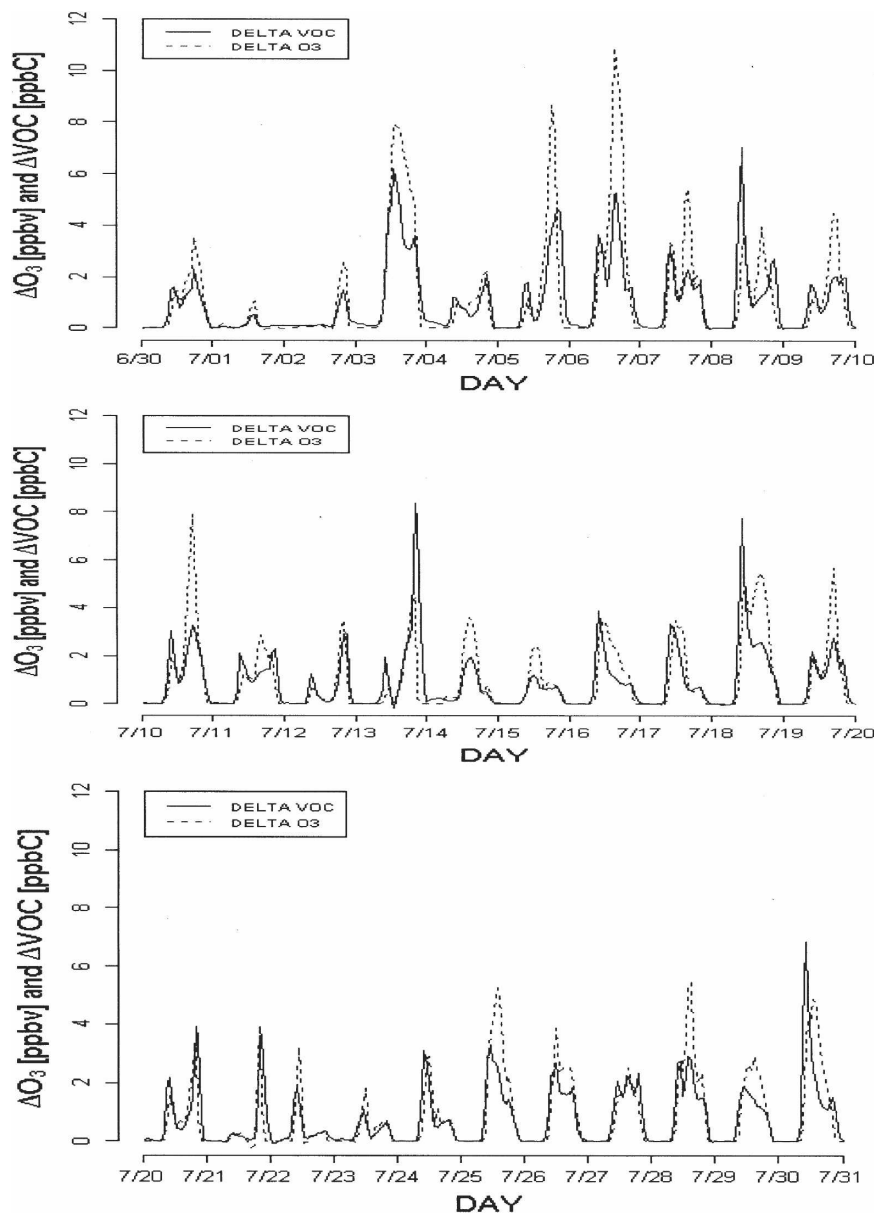


FIG. 3. Increases in O<sub>3</sub> concentrations ( $\Delta O_3$ ) and decreases in VOC concentrations ( $\Delta VOC$ ) between the cases with and without chlorine emissions from a grid cell near Houston.

ton area contained the largest amount of HOCl emissions; therefore, the most significant impact also occurred in this area.

The impact of chlorine emissions on monthly average O<sub>3</sub> concentrations is shown in Fig. 2. Predicted and observed monthly average daily maximum 1-h O<sub>3</sub> concentrations without chlorine emissions for July are presented in Fig. 2a. Ambient monitoring data from the USEPA's Air Quality System were used for this purpose. Overall, the model results were in reasonable agreement with the observed O<sub>3</sub> concentrations in most

areas of the eastern United States. Increases in predicted monthly average daily maximum 1-h O<sub>3</sub> concentrations with chlorine emissions are shown in Fig. 2b. The inclusion of chlorine emissions increased the average daily maximum 1-h O<sub>3</sub> concentrations in the Houston area by up to 3.0 ppbv. Increases in the daily maximum O<sub>3</sub> concentrations did not always occur in the same grid cell. As a result, the increases in the monthly average daily maximum O<sub>3</sub> concentrations were lower than the increases in the daily maximum O<sub>3</sub> concentrations. Although not shown here, the inclusion of chlo-

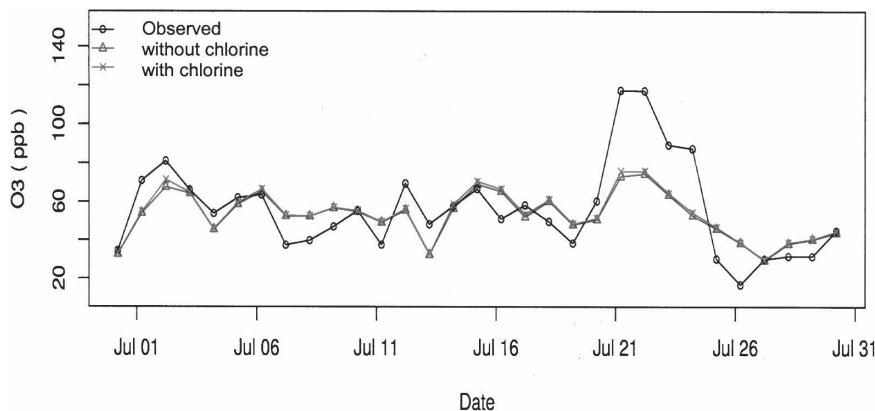


FIG. 4. Comparisons of Houston-wide average predicted and measured daily maximum 1-h  $O_3$  concentrations.

rine emissions increased the monthly average daily maximum 8-h  $O_3$  concentrations in the Houston area by up to 2.7 ppbv.

The concentrations of VOC decreased in the Houston area when chlorine emissions were included in the model. The increases in  $O_3$  concentrations were accompanied by corresponding decreases in VOC concentrations in these areas, as illustrated in Fig. 3 for a grid cell in the Houston area. This trend was also observed in other grid cells in the Houston area. This suggests that the additional VOC oxidation enhanced the  $O_3$  formation when chlorine emissions were included in the model.

Comparisons of Houston-wide average predicted and measured daily maximum 1-h  $O_3$  concentrations are shown in Fig. 4. It should be noted that the data in Fig. 4 represent the average daily maximum 1-h  $O_3$  concentrations for all monitoring sites in the Houston area for which measurements were available. The model (without chlorine emissions) captures the day-to-day variability of Houston area  $O_3$  concentrations for most days, except during 22–27 July. The inclusion of chlorine emissions increased the predicted Houston-wide average  $O_3$  concentrations by up to 3.7 ppbv, but it did not substantially improve the model results. Although not shown here, chlorine emissions increased the daily maximum 1-h  $O_3$  concentrations at one monitoring station in the Houston area by up to 9 ppbv. Results with chlorine emissions did not fully explain the elevated observed  $O_3$  concentrations during 22–25 July. Several investigators have attributed the high observed  $O_3$  concentrations to olefins that are underestimated in the Houston inventory (Kleinman et al. 2002; Ryerson et al. 2003). The chlorine emissions and chemistry may play some role on  $O_3$  production in the Houston area,

but they account for a small fraction of the model underestimates.

The largest increases in the daily maximum 1- and 8-h  $O_3$  concentrations in the New York–New Jersey area were about 6 and 4 ppbv, respectively. Unlike in Houston, the increases in  $O_3$  concentrations in the New York–New Jersey area did not occur each day and were lower than those in the Houston area. Consequently, the increases in the monthly average daily maximum 1- and 8-h  $O_3$  concentrations in the New York–New Jersey were small (less than 0.3 ppbv). Enhancements in  $O_3$  concentrations in the New York–New Jersey area appear to occur primarily due to the release of chlorine emissions from heterogeneous reactions with sea-salt particles. The increases in  $O_3$  and the corresponding decreases in VOC concentrations for a grid cell in the New York–New Jersey area are shown in Fig. 5. The largest increase in this grid cell occurred on 21 July, when the  $O_3$  concentration increased by about 4 ppbv. Consistent with the Houston area, these increases in  $O_3$  concentrations were accompanied by corresponding decreases in VOC concentrations. This reinforces the earlier explanation that the additional VOC oxidation enhanced the  $O_3$  formation when chlorine emissions were included in the model.

It should be noted that when chlorine emissions were included in the model,  $O_3$  concentrations at several grid cells also decreased when compared with the case without the chlorine emissions. However, these decreases were small and less than 2 ppbv.

#### 4. Summary

The results of this study suggest that chlorine emissions do not affect atmospheric  $O_3$  concentrations in most areas of the eastern United States; they only affect



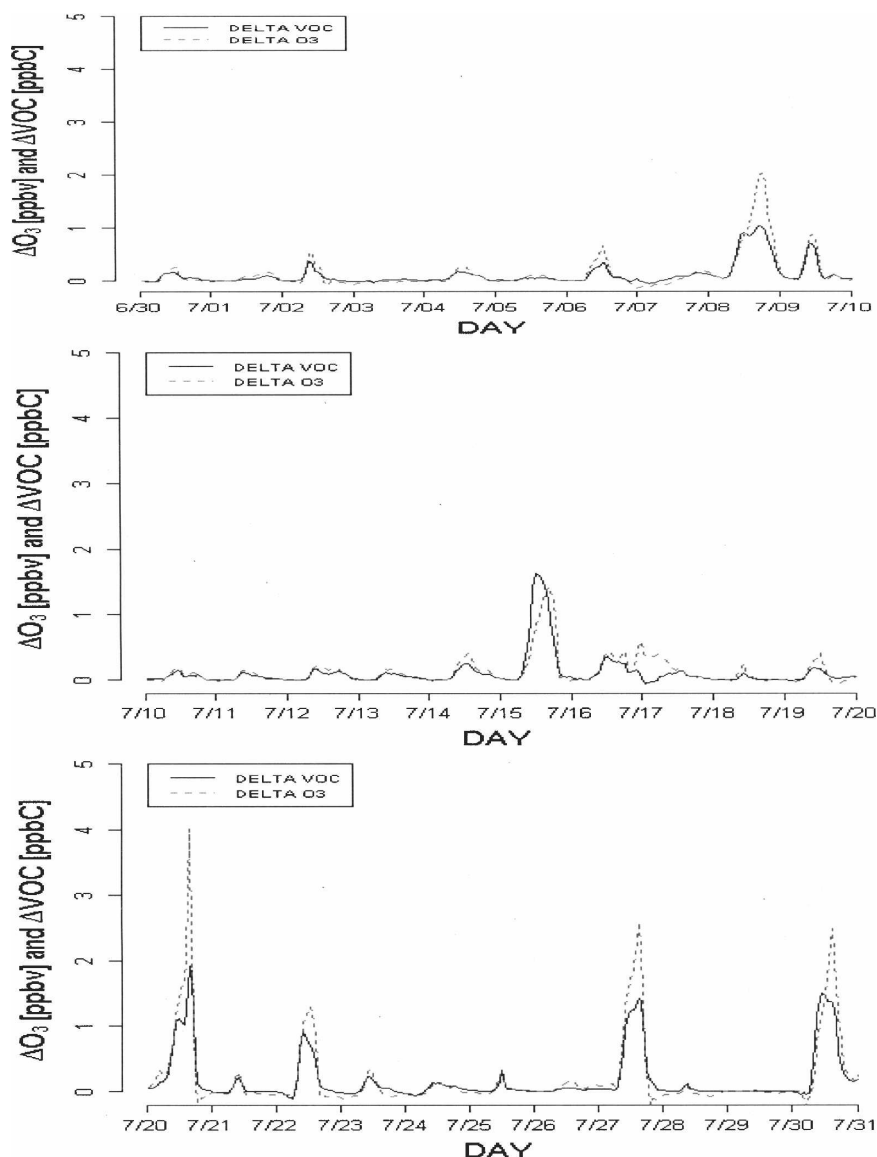


FIG. 5. Increases in  $O_3$  concentrations ( $\Delta O_3$ ) and decreases in VOC concentrations ( $\Delta VOC$ ) between the cases with and without chlorine emissions from a grid cell in the New Jersey–New York area.

$O_3$  in two areas by more than 4 ppbv—the Houston and New York–New Jersey areas. The largest impact occurred in the Houston area where chlorine emissions increased the daily maximum 1-h  $O_3$  concentrations by up to 12 ppbv due to chlorine emissions from industrial sources. Chlorine emissions increased the daily maximum 1-h  $O_3$  concentrations in the New York–New Jersey area by up to 6 ppbv, primarily due to the chlorine emissions released from sea-salt aerosols via heterogeneous reactions.

The results of this study compare favorably to those of Chang et al. (2002) and Chang and Allen (2006), who

concluded that chlorine emissions can potentially increase the peak  $O_3$  concentrations in southeastern Texas by a maximum of 7 and 10 ppbv, respectively. While the results of this study compares favorably to the results of Chang et al. (2002) and Chang and Allen (2006), it should be noted that they used 4-km grid spacings and we used 12-km grid spacings. Because the modeling domain covered the entire eastern United States, larger grid spacings were used in this study. Chlorine emissions used by Chang et al. (2002) and Chang and Allen (2006) are also different than those used in this study. The larger grid spacings and different

chlorine emissions may have affected the results presented herein.

Future studies should focus on improving the chlorine emissions inventory. The development of an accurate and reliable emissions inventory is a resource-intensive process. Despite the tremendous improvements made during the past years, emissions of O<sub>3</sub> precursors still contain large uncertainties (Placet et al. 2000; Sawyer et al. 2000; Werner et al. 2005). The chlorine emissions used in this study are preliminary in nature. Thus, these emissions are likely to contain large uncertainties and warrant further investigation. Additional assessments of the effects of chlorine emissions may be warranted as emissions estimates are improved. To improve the assessment of the effects of chlorine emissions on O<sub>3</sub>, uncertainties in the VOC emissions inventory also need to be reduced.

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