Development of an updated chlorine mechanism and assessment of the effect of industrial chlorine emissions on ozone predictions in the western United States

Golam Sarwar and Deborah Luecken
Atmospheric Modeling Division
National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711, USA

Greg Yarwood
ENVIRON International Corporation
101 Rowland Way, Suite 220
Novato, CA 94945-5010, USA

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ABSTRACT

An updated chlorine mechanism combined with the CB05 mechanism was incorporated into the Community Multiscale Air Quality modeling system. The combined chemical mechanism was used to evaluate the effect of industrial chlorine emissions on ozone in the western United States for a summer month. Chlorine emissions affected ozone in two geographic areas in the western United States: the Great Salt Lake area and the Oklahoma City area. Chlorine emissions increased the daily maximum 1-hr and 8-hr ozone mixing ratios by up to 10 and 8 ppbv, respectively, near the Great Salt Lake area. However, they also decreased ozone mixing ratios near the Great Salt Lake area. The largest decrease in daily maximum 1-hr and 8-hr ozone mixing ratios were both 6 ppbv near the Great Salt Lake area. The largest increase in daily maximum 1-hr as well as 8-hr ozone mixing ratios was less than 0.5 ppbv near the Oklahoma City area.

1. Introduction

Reactions of hydroxyl radical (OH) and volatile organic hydrocarbons (VOCs) play an important role in producing ozone (O_3) in the atmosphere. Chlorine atoms (Cl) can also react with VOCs at rates generally faster than OH and provide an alternate route to O_3 production. However, chlorine emissions and chemistry are usually not included in air quality models because of uncertainties in the sources of chlorine and gaps in our understanding of the associated chemical reactions. The ability of air quality models to reliably predict O_3 mixing ratios is essential for understanding and controlling high O_3 mixing ratios. Thus, it is important that we understand whether or not molecular chlorine (Cl_2) emissions need to be included in air quality models for tropospheric ozone. Molecular chlorine is also a hazardous air pollutant

(USEPA, 1990) and reacts with mercury (Hedgecock *et al*., 2005; Lin *et al*., 2006) which provide additional reasons for better understanding the atmospheric chemistry of chlorine.

Recent studies provide evidence that chlorine chemistry might indeed enhance O_3 formation in coastal and industrial areas of the United States (Chang *et al*., 2002; Knipping and Dabdub, 2003; Chang and Allen, 2006; Sarwar and Bhave, 2007). Chang *et al*. (2002) studied the effect of chlorine emissions and concluded that industrial chlorine emissions can increase O_3 mixing ratios by up to 16 parts-per-billion (ppbv) in the Houston area of Texas. Chang and Allen (2006) evaluated the impact of chlorine emissions on O_3 mixing ratios for a photochemical episode in 2000. They used 1-chloro-3-mehtyl-3-butene-2-one (CMBO), a reaction product of isoprene and Cl, as a unique tracer species to evaluate chlorine emissions and chemistry in southeast Texas and demonstrated that predicted CMBO levels are in reasonable agreement with observed data. Predicted O_3 mixing ratios increased by as much as 72 ppbv during the morning hours when chlorine emissions were included in the model. However, the effects of chlorine emissions on O_3 mixing ratios decreased during the later hours of the day and were generally less than 10 ppbv at the time of daily maximum ozone. Since chlorine emissions can also potentially affect O_3 control strategies, they also evaluated the effect of chlorine emissions on the effectiveness of VOC and nitrogen oxides (NO_x) emissions reductions. They demonstrated that greater reductions in VOC and NO_x emissions are needed to achieve target O_3 mixing ratios when chlorine emissions are included in the model.

Knipping and Dabdub (2003) studied the impact of sea-salt derived chlorine emissions on coastal urban O_3 and reported that chlorine released via heterogeneous reactions can increase daily maximum 1-hr O_3 mixing ratios by up to 4 ppbv in the Los Angeles area of California.

Sarwar and Bhave (2007) studied the effects of chlorine emissions on O_3 over the eastern United States using the Community Multiscale Air Quality (CMAQ) modeling system for July 2001. They reported that chlorine emissions can increase O_3 mixing ratios in the Houston and New York/New Jersey areas. The daily maximum 1-hr and 8-hr O_3 mixing ratios in the Houston area increased by up to 12 ppbv and 8 ppbv, respectively. In the New York/New Jersey area, the daily maximum 1-hr and 8-hr O_3 mixing ratios increased by up to 6 ppbv and 4 ppbv, respectively.

While these studies suggest chlorine may affect O_3 mixing ratios in specific geographic areas, little is known about the importance of the chlorine mechanism beyond these areas. In the current study, we present an updated chlorine mechanism that can be used in conjunction with the Carbon Bond (CB05) mechanism and examine the effects of industrial Cl_2 emissions on O_3 mixing ratios in the western United States.

2. Methodology

a. Model description

All simulations for this study were performed by using the CMAQ modeling system (version 4.6) (Binkowski and Roselle, 2003; Byun and Schere, 2006) for July 2001. Model performance evaluations for the CMAQ modeling system have been conducted by comparing model predictions to measured ambient pollutants (Eder and Yu, 2004; Yu, Dennis, and Eder, 2004; Appel et al., 2007). The horizontal modeling domain for the western United States (Figure 1) consisted of 217 x 196 grid-cells with 12-km grid spacings and 14 vertical layers of varying thickness between the surface and 100 mb. The surface layer thickness was approximately 36 meters. The CMAQ chemical transport model was configured to use the mass continuity scheme to describe advection processes, the Asymmetric Convective Model (version 2) (ACM2) (Pleim, 2007) to describe vertical diffusion processes, the multiscale method to describe horizontal diffusion processes, and an adaptation of the ACM algorithm for convective cloud mixing. Aqueous chemistry, aerosol processes, and dry and wet deposition were also included. The meteorological driver for the CMAQ modeling system was the PSU/NCAR MM5 system (version 3.5) (Grell *et al.,* 1994). Boundary conditions for this study were obtained from a larger model domain consisting of 148 x 112 grid-cells with a 36-km grid spacing for the continental United States. A seven-day spin-up period was used to minimize the effect of initial conditions on model predictions. The 2005 version of the Carbon Bond mechanism (CB05; Yarwood *et al.,* 2005; Sarwar *et al.,* 2008) was combined with the chlorine mechanism (discussed later) and used in this study. Two model simulations were performed for this study using the combined chemical mechanism. The first simulation included emissions that are typically used in CMAQ modeling system which includes emissions of VOCs, NO_x, sulfur dioxides, ammonia, carbon monoxide, and aerosols but not the Cl_2 emissions. For the second simulation, Cl_2 emissions in addition to the other emissions described in the first simulation was used in the study. The 1999 National Emissions Inventory (version 3) was used to generate model-ready emissions using the Sparse Matrix Operator Kernel Emission (SMOKE) (Houyoux et al., 2000). The Biogenic Emissions Inventory System (version 3.13) was used to prepare biogenic emissions for the study (Schwede et al., 2005). Chlorine emissions were obtained from the 1999 National Emissions Inventory for hazardous air pollutants. The chlorine emission inventory includes industrial sources but not other potential sources such as swimming pools or sea salt aerosol reactions.

b. Gas-phase chlorine chemistry

Gery *et al*. (1989) developed the Carbon Bond (CB-IV) mechanism in late 1980's. Yarwood *et al.* (2005) recently modified and extended the CB-IV mechanism into an updated Carbon Bond (CB05) mechanism consisting of 156 chemical reactions involving 52 chemical species. Tanaka *et al*. (2003) developed a chlorine mechanism consisting of 13 chemical reactions for use with the CB-IV chemical mechanism. Here, we update, modify, and extend the chlorine mechanism of Tanaka *et al.* (2003) for use with the CB05 mechanism. Rate constants for the updated chlorine mechanism were updated using the latest recommendations from the International Union of Pure and Applied Chemistry (IUPAC) (Atkinson *et al.*, 2005).

Similar to the chlorine chemistry of Tanaka *et al.* (2003), the updated chlorine mechanism contains two sources of Cl: photolysis of Cl_2 and HOCl (reaction nos. 1-2). Normalized photolysis rates of these reactions were used by Tanaka *et al*. (2003). In the updated chlorine chemistry, photolysis rates of Cl_2 and HOCl (hypochlorous acid) are calculated using quantum yield and absorption cross-section data from IUPAC (Atkinson *et al.*, 2005).

$Cl_2 = 2\ Cl$; photolysis (1)

$HOCl = OH + Cl$; photolysis (2)

where, Cl is atomic chlorine and OH is hydroxyl radical.

The reaction of Cl with O_3 (reaction no. 3) did not change compared to those of Tanaka *et al.* (2003); only the rate constant of the reaction was updated.

$$Cl + O_3 = ClO + O_2;\ k = 2.3 \times 10^{-11}\ e^{(-200/T)} \quad (3)$$

where, O_2 is oxygen, ClO is chlorine oxide, k is rate constant, and T is temperature.

The self-reaction of ClO (reaction 4) is added to account for situations where intense sources of ClO (e.g., high Cl_2 emissions) exceed the availability of NO or HO2 to act as sinks for ClO. The products of the ClO self-reaction are highly condensed to approximate the final products under tropospheric conditions. Similar to chlorine chemistry of Tanaka *et al.* (2003), the reaction of ClO with NO and HO2 (reaction nos. 5-6) are included; only the rate constants of the reactions were updated.

$$ClO + ClO = 0.3\ Cl_2 + 1.4\ Cl + O_2;\ k = 1.63 \times 10^{-14} \quad (4)$$

$$ClO + NO = Cl + NO_2\ ;\ k = 6.4 \times 10^{-12}\ e^{(290/T)} \quad (5)$$

$$ClO + HO2 = HOCl + O_2\ ;\ k= 2.7 \times 10^{-12}\ e^{(220/T)} \quad (6)$$

where, NO is nitric oxide, NO_2 is nitrogen dioxide, and HO2 is hydroperoxy radical.

Methane (CH_4) is an explicit species in the CB05 mechanism. However, the reaction of CH_4 with OH was revised in the CB05 mechanism to include methylperoxy radical (MEO2) as an explicit product. The reaction of CH_4 with OH proceeds via the hydrogen atom abstraction pathway producing MEO2 and H_2O (in the presence of oxygen). The reaction of CH_4 with Cl also proceeds via the hydrogen atom abstraction pathway and produces hydrochloric acid (HCl) and MEO2 (reaction no. 7).

$CH_4 + Cl = HCl + MEO2; k = 6.6 \times 10^{-12} e^{(-1240/T)}$ (7)

Unlike the CB-IV mechanism, ethane (ETHA) is an explicit species in the CB05 mechanism. Its reaction with Cl is also included. The reaction between ETHA and OH proceeds via the abstraction pathway and produces (in the presence of oxygen) ethyl peroxy radical and H_2O. The reaction of ethyl peroxy radical with NO can proceed via two different pathways. In one pathway, it converts NO into NO_2 and leads to acetaldehyde (ALD2) and HO2 (99.1%). In the other pathway, the reaction leads to nitrate formation (0.9%). The reaction of ETHA with Cl also proceeds via the hydrogen abstraction pathway. With the exception of HCl rather than H_2O, its reaction products are same as the products of the reaction between ETHA and OH (reaction 8).

ETHA + Cl = HCl + 0.991 ALD2 + 0.991 XO2 + 0.009 XO2N + HO2;

$k = 8.3 \times 10^{-11} e^{(-100/T)}$ (8)

where, XO2 is NO-to-NO_2 operator, XO2N is NO-to-nitrate operator.

The products of the reaction between Cl and paraffinic carbon chains (PAR) are updated to be consistent with the reaction between OH and PAR in the CB05 mechanism. The reaction of PAR with OH proceeds via the hydrogen atom abstraction pathway and produces ALD2, ALDX (propionaldehyde and higher aldehydes), H_2O, and other products. The reaction of PAR with Cl also proceeds via the hydrogen abstraction pathway. Its reaction products are same as the products of the reaction between of PAR and OH with the exception of HCl rather than H_2O

(reaction 9). The rate constant for reaction 9 is an average over the absolute rate constants of the alkanes listed in Tanaka *et al*. (2003).

PAR + Cl = HCl + 0.87 XO2 + 0.13 XO2N + 0.11 HO2 + 0.06 ALD2 - 0.11 PAR
+ 0.76 ROR + 0.05 ALDX; k = 5.00 x 10^{-11} (9)

where, ROR is secondary organic oxy radical.

Similar to the CB-IV mechanism, ethene (ETHE) is an explicit species in the CB05 mechanism. Thus, its reaction with Cl is also included (reaction 10). However, its reaction products did not change compared to those in Tanaka *et al*. (2003); only the rate constant is updated.

ETHE + Cl = FMCl + 2.0 XO2 + HO2 + FORM; k = 1.07 x 10^{-10} (10)

where, FMCl is formyl chloride, FORM is formaldehyde.

Terminal olefins (alk-1-enes) are represented by the species OLE with two carbons. Reaction products assume that reaction with the carbon-carbon double bond proceeds by addition and that the Cl ends up in a carbonyl compound, represented by FMCl as a surrogate. The rate constant for the reaction between Cl and OLE (reaction no. 11) is an average over the absolute rate constants for the alkenes presented in Tanaka *et al*. (2003).

OLE + Cl = FMCl + 0.33 ALD2 + 0.67 ALDX + 2.0 XO2 + HO2 – PAR;
k = 2.5 x 10^{-10} (11)

IOLE is a new species in the CB05 mechanism representing internal olefins (alk-*n*-enes with *n*>1) and has four carbons. The reaction of Cl and IOLE (reaction no. 12) is added to the mechanism. The rate constant for reaction 12 is estimated as the rate constant for Cl reacting with OLE + 2 PAR. 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. The products for Cl addition pathway are assumed to be FMCl + 0.65 ALD2 + 0.35 ALDX + 2 XO_2 + HO2. FMCl serves as a surrogate for all products where chlorine is incorporated into a chlorocarbonyl after an addition reaction. The purpose is to account for sequestration of Cl in an organic molecule (chlorocarbonyl) allowing for the Cl to return later as a Cl atom after the chlorocarbonyl reacts with OH or photolyses. The products for hydrogen atom abstraction pathway are assumed to be HCl + ALDX + OLE + XO_2 + HO2.

$$\begin{aligned} \text{IOLE} + \text{Cl} = {} & 0.3\ \text{HCl} + 0.7\ \text{FMCl} + 0.45\ \text{ALD2} + 0.55\ \text{ALDX} + 0.3\ \text{OLE} \\ & + 0.3\ \text{PAR} + 1.7\ \text{XO2} + \text{HO2};\ k = 3.5 \times 10^{-10} \end{aligned} \qquad (12)$$

The reaction between Cl and isoprene (ISOP) is revised from Tanaka *et al.* (2003). The goal of Tanaka *et al.* (2003) was to track a unique marker for the reaction between Cl and isoprene to permit comparison with ambient data. The goal for this mechanism is to track the fate of Cl and carbon in isoprene. The HCl and FMCl yields reflect the balance between hydrogen atom abstraction and addition pathways of 15% and 85% (Fan and Zhang; 2004). FMCl acts as a surrogate for the fate of all Cl addition pathways. The lumped isoprene oxidation product (ISPD) from the CB05 mechanism accounts for the carbon containing products. FMCl serves as a surrogate for all products where chlorine is incorporated into a chlorocarbonyl after an addition reaction (reaction 13).

ISOP + Cl = 0.15 HCl + XO2 + HO2 + 0.85 FMCl + ISPD; $k = 4.3 \times 10^{-10}$ (13)

To account for the loss of FMCl via atmospheric chemistry, the reaction of FMCl with OH and its photolytic reaction are included (14-15). The reaction of FMCl with OH proceeds via hydrogen abstraction pathway and produces H_2O, CO (carbon monoxide), and Cl atom. The photolysis of FMCl produces HO2, CO, and Cl. The photolysis rate of FMCl is calculated using quantum yield and absorption cross-section data from IUPAC (Atkinson *et al.*, 2005).

FMCl + OH = Cl + CO + H_2O; $k = 5.00 \times 10^{-13}$ (14)

FMCl = Cl + CO + HO2; photolysis (15)

The updated mechanism also includes reactions of Cl with FORM, ALD2, ALDX (reaction nos. 16-18). The reactions of FORM, ALD2, and ALDX with Cl are similar to their reactions with OH. The only exception is that the reaction with Cl produces HCl compared to H_2O produced from reactions with OH. The products of the reaction between ALDX and Cl are uncertain because there may be hydrogen atom abstraction at the paraffinic carbon atoms of higher aldehydes.

FORM + Cl = HCl + HO2 + CO; $k = 8.2 \times 10^{-11} e^{(-34/T)}$ (16)

ALD2+ Cl = HCl + C2O3; $k = 7.9 \times 10^{-11}$ (17)

ALDX + Cl = HCl + CXO3; $k= 1.3 \times 10^{-10}$ (18)

where C2O3 is acetylperoxy radical, CXO3 is higher acylperoxy radicals.

The reactions of methanol (MEOH) and ethanol (ETOH) with Cl are also included (reaction nos. 19 and 20). The reaction of MEOH with Cl produces HO2, FORM, and HCl. The reaction of ETOH with Cl forms mainly acetaldehyde (with glycolaldehyde a minor product) and the products are HO2, ALD2, and HCl (Atkinson *et al.*, 2005).

MEOH + Cl = HCl + HO2 + FORM; $k = 5.5 \times 10^{-11}$ (19)

ETOH + Cl = HCl + HO2 + ALD2; $k = 8.2 \times 10^{-11}\ e^{(45/T)}$ (20)

Reactions of TOL, XYL, or TERP with Cl atoms are not included because the reaction products are too uncertain. Omitting these reactions may not greatly alter the fate of Cl atoms because Cl atoms react rapidly with all VOCs. For example, the global background for CH_4 of about 1.8 ppm (Oum *et al.*, 1998) provides a significant "universal" sink for Cl atoms because Cl atoms react quite rapidly with CH_4.

HCl is a toxic air pollutant and its reaction with OH is relatively slow in the atmosphere. However, the reaction may be important in polluted coastal areas (Keene et al., 2007). To account for the degradation of HCl in the atmosphere, its reaction with OH is included (reaction 21).

HCl + OH = Cl + H_2O; $k = 6.58\text{x}10^{-13}\ (T/300)^{1.16}\ e^{(-58/T)}$ (21)

In the updated chlorine chemistry, photolysis rates, J, (min^{-1}) are directly calculated using the following general equation (Finlayson-Pitts and Pitts, 2000):

$$J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda)\phi(\lambda)F(\lambda)d\lambda \tag{22}$$

where, is $\sigma(\lambda)$ 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}), λ is the wavelength (nm).

The reaction of 1,3-butadiene with Cl produces a unique tracer species. To account for the unique tracer species, two additional reactions related to 1,3-butadiene were included in the mechanism by Tanaka *et al.* (2003). Since 1,3-butadiene is not an explicit species in the Carbon Bond mechanism, these reactions have been eliminated from the updated mechanism.

Chlorine atoms can react with NO_2 to form either $ClNO_2$ or CLONO (Atkinson *et al.*, 2005) but these reactions are not included in the mechanism because photolysis will rapidly convert the products back to the reactants. This is an important difference between Cl and OH radical because the rapid reaction of OH with NO_2, combined with slow photolysis of HNO_3 back to the reactants, means that high concentrations of NO_2 strongly inhibit OH initiated degradation of VOCs (Finlayson-Pitts and Pitts, 2000). In contrast, high NO_2 concentrations have little or no inhibiting effect on the Cl initiated degradation of VOCs.

Chlorine chemistry can affect O_3 primarily via two competing pathways that consume and produce ozone. It can directly consume O_3 via reaction 3. It can also affect O_3 via reactions initiated by Cl and VOCs. Chlorine chemistry can enhance the oxidation of VOCs which then can produce additional peroxy radicals (HO2 and RO_2). The reaction of NO with HO2 and RO_2 converts NO into NO_2 and cause O_3 production when NO_2 is photolyzed (Finlayson-Pitts and Pitts, 2000):

$HO2 + NO \rightarrow HO + NO_2$ (23)

$NO_2 + hv \rightarrow NO + O(^3P)$ (24)

$\underline{O(^3P) + O_2 \rightarrow O_3}$ (25)

$HO2 + O_2 \rightarrow OH + O_3$ (net result of 23 to 25)

$RO_2 + NO \rightarrow RO + NO_2$ (26)

If additional O_3 production via reactions 23 and 26 exceeds O_3 consumption via reaction 3, O_3 mixing ratios will increase; otherwise O_3 mixing ratios may decrease or be unchanged.

3. Results and discussion

When chlorine emissions were included in the model, they changed O_3 mixing ratios in many grid-cells when compared with the results without chlorine emissions. However, most changes were less than 2.0 ppbv; thus, these small changes are not discussed further. The inclusion of chlorine emissions affected O_3 mixing ratios by more than 2.0 ppbv in two geographical areas in the western United States: the Great Salt Lake and the Oklahoma City areas.

The number of days when O_3 mixing ratios with chlorine emissions compared to those without the chlorine emissions exceeded 2.0 ppbv is shown in Figure 1. The instantaneous O_3 mixing ratios near the Great Salt Lake area increased by up to 17 ppbv; however, the impact of chlorine emissions on the daily maximum 8-hr O_3 mixing ratios was smaller. The largest increase in the daily maximum 8-hr O_3 mixing ratios near the Great Salt Lake was 8 ppbv when chlorine emissions were included in the model. The largest increase in the daily maximum 1-hr O_3 mixing ratios near the Great Salt Lake was 10 ppbv with chlorine emissions. These increases were localized and varied from day to day. The Great Salt Lake area contained the largest industrial Cl_2 emissions source in the United States with annual emissions of 22,000 tons based on the 1999 National Emission Inventory. The emissions from this source have a low VOC/NOx ratio and consequently O_3 production downwind of the source would tend to be inhibited by high NO_2 in the absence of Cl_2 emissions. The increases in O_3 mixing ratios occurred mostly over the Great Salt Lake showing that Cl_2 emissions were most effective at promoting O_3 formation when the source plume was transported into the relatively shallow boundary layer over the Lake. The shallow boundary layer concentrated emissions and enhanced the inhibiting effect of NO_2 on O_3 production, and therefore also enhanced the effectiveness of Cl_2 emissions in promoting O_3 formation.

Increases in O_3 and decreases in VOC mixing ratios with chlorine emissions compared to those obtained without the chlorine emissions are shown as time series in Figure 2 for a grid-cell located near the northern shore of the Great Salt Lake. Increases in O_3 mixing ratios started in the morning and continued until late afternoon hours. Mixing ratios of VOCs with chlorine emissions were lower than those obtained without chlorine emissions because reactions of VOCs with Cl depleted VOCs. Increases in O_3 were associated with additional loss of VOCs.

The largest increases in O_3 mixing ratio for this grid-cell occurred on July 23. Daytime O_3 mixing ratios with and without Cl_2 emissions for this grid-cell are shown in Figure 3. O_3 mixing ratios with chlorine emissions were greater than those without the chlorine emissions. Reaction rates for reactions 3, 23, and 26 with and without chlorine emissions are also shown in Figure 3. Chlorine emissions increased O_3 mixing ratios since reaction rates for reactions 23 and 26 were greater with chlorine emissions than those without chlorine emissions. Reaction rates for reaction 3 were small and did not significantly impact the resulting O_3 mixing ratios.

The number of days when O_3 mixing ratios with chlorine emissions compared to those without the chlorine emissions decreased by more than 2.0 ppbv is shown in Figure 4. These decreases were also localized and varied from day to day. While the instantaneous O_3 mixing ratios near the Great Salt Lake area decreased by up to 47 ppbv, the impact of chlorine emissions on daily maximum 1-hr and 8-hr O_3 mixing ratios were much smaller. The largest decreases in daily maximum 1-hr and 8-hr O_3 mixing ratios near the Great Salt Lake were 6 and 6 ppbv, respectively, when chlorine emissions were included in the model. The decreases in O_3 mixing ratios occurred mostly over the southern shore of the Great Salt Lake.

Decreases in mixing ratios of O_3 and VOCs with chlorine emissions compared to those obtained without the chlorine emissions are shown in Figure 5 for a grid-cell located near the southern shore of the Great Salt Lake. Mixing ratios of VOCs with chlorine emissions were lower than those obtained without the chlorine emissions. Despite the oxidation of additional VOCs with chlorine emissions, O_3 mixing ratios decreased in this grid-cell.

The largest decreases in O_3 mixing ratio for this grid-cell occurred on July 24. Daytime O_3 mixing ratios with and without Cl_2 emissions for this grid-cell are shown in Figure 6. O_3 mixing ratios with chlorine emissions were lower than those without the chlorine emissions. Reaction rates for reactions 3, 23, and 26 with and without chlorine emissions are also shown in Figure 6. Chlorine emissions lowered reaction rates for reaction 23. Mixing ratios of HO2 increased with chlorine emissions. However, the inclusion of chlorine emissions decreased the NO mixing ratios to a low level (~7 pptv); thus reaction rates for reaction 23 were lower. The inclusion of chlorine emissions increased RO_2 mixing ratios as well as reaction rates for reaction 26. Reaction rates for reaction 3 were significant and played an important role in lowering the O_3 mixing ratios.

Model performance near the Great Salt Lake area for O_3 is shown in Table 1. Ambient O_3 from monitoring stations located near the Great Salt Lake area and model results obtained without the chlorine emissions were used for this purpose. The model was biased low for daily maximum 1-hr O_3 and high for daily maximum 8-hr O_3. Overall, the model results agree with the observed data in the Great Salt Lake area. Results obtained with chlorine emissions did not alter the model performance for O_3 in this area. All monitoring stations used in the analysis are located outside the areas where chlorine emissions affected O_3 mixing ratios. Thus, the predicted effect of chlorine emissions on O_3 near the Great Salt Lake area cannot be corroborated by comparing these model predictions with the available observed data.

Cl_2 emissions increased O_3 mixing ratios near the Oklahoma City area by up to 7 ppbv; however impacts on daily maximum 1-hr and 8-hr O_3 mixing ratios were much smaller than for the Great Salt Lake area. Industrial Cl_2 emissions near the Oklahoma City area increased the daily maximum 1-hr and 8-hr O_3 mixing ratios by less than 0.5 ppbv near the Oklahoma City area. The source emitted about 480 tons of emissions based on 1999 National Emissions Inventory. Similar to the Great Salt Lake area, increases in O_3 mixing ratios near the Oklahoma City area also started in the morning. The O_3 increases were correlated with additional loss of VOCs. Reaction rates for reactions 23 and 26 with Cl_2 emissions were greater than those without the Cl_2 emissions; thus O_3 mixing ratios increased. Reaction rates for reaction 3 were negligible.

Chlorine chemistry can also affect O_3 via reactions 10-13 since these reactions can consume ethene, terminal olefin, internal olefin, and isoprene which could otherwise react with O_3. However, the impacts of these reactions on O_3 were small.

4. Summary

Atmospheric chemical reactions of chlorine for use with the CB05 mechanism have been developed. The results of this study suggest that industrial Cl_2 emissions affect O_3 by more than 2.0 ppbv in two areas in the western United States: the Great Salt Lake area and the Oklahoma City area. The largest impact occurred near the Great Salt Lake area where Cl_2 emissions affected O_3 mixing ratios due to the presence of a large industrial Cl_2 emissions source. Industrial Cl_2 emissions also increased O_3 mixing ratios near the Oklahoma City area. However, impacts of

Cl_2 emissions on O_3 near the Oklahoma City were smaller than those near the Great Salt Lake area.

This and other recent studies suggest that chlorine emissions can affect O_3 mixing ratios in some areas in the United States. Cl_2 emissions from the 1999 National Emissions Inventory were used in this study. Chang et al. (2002) suggest that cooling towers and swimming pools are also significant sources of chlorine emissions. However, the chemical forms of chlorine emissions from these sources are not certain; they may be emitted as Cl_2 or HOCl or as a combination. The chemical form of chlorine emissions is important. Both Cl_2 and HOCl photolyze in the atmosphere; however, their photolysis rates are different. Thus, it can affect the release of Cl atoms and subsequently O_3 mixing ratios in the atmosphere. Thus, future studies should focus on better characterizations of chlorine emissions from these and other sources. Chlorine emissions from sea-salts can also potentially affect O_3 in some areas in the western United States. Effects of such emissions have not been accounted for in this study. Future studies should also include the impact of sea-salt derived chlorine emissions on O_3.

Disclaimer

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Figures

Figure 1: Number of days when O_3 mixing ratios with chlorine emissions increased by more than 2.0 ppbv compared to those obtained without the chlorine emissions

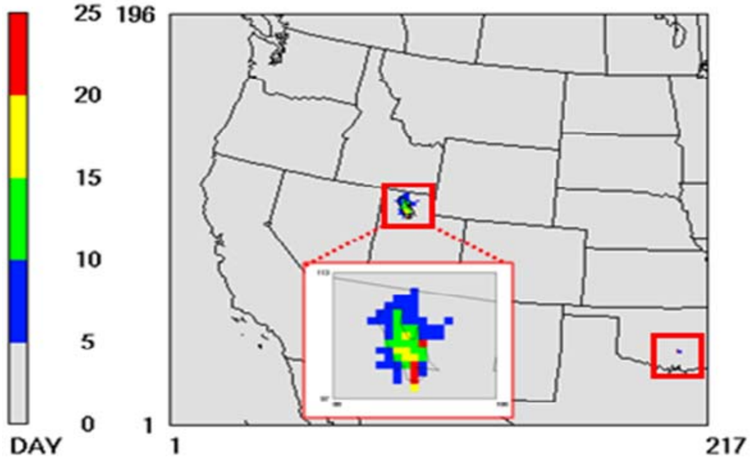


Figure 2: Increases in O_3 (ΔO_3) and decreases in VOC mixing ratios ($-\Delta VOC$) with and without chlorine emissions from a grid-cell located near the northern shore of the Great Salt Lake (local time)

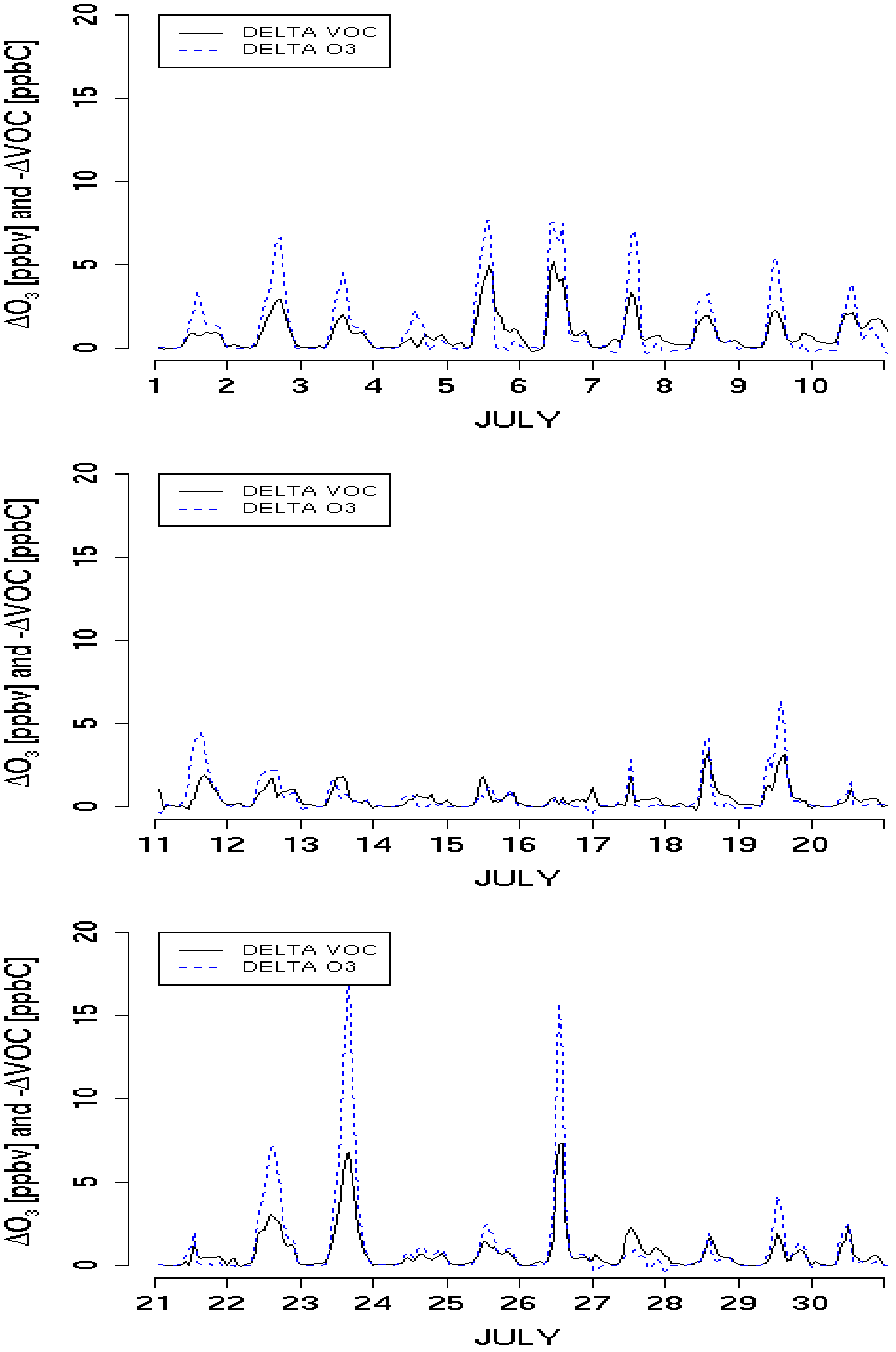


Figure 3: Daytime ozone mixing ratios and selected reaction rates (averaging time: 8 am to 6 pm) with and without chlorine emissions for a grid-cell near the northern shore of the Great Salt Lake on July 23 (a) ozone mixing ratios (b) reaction rates

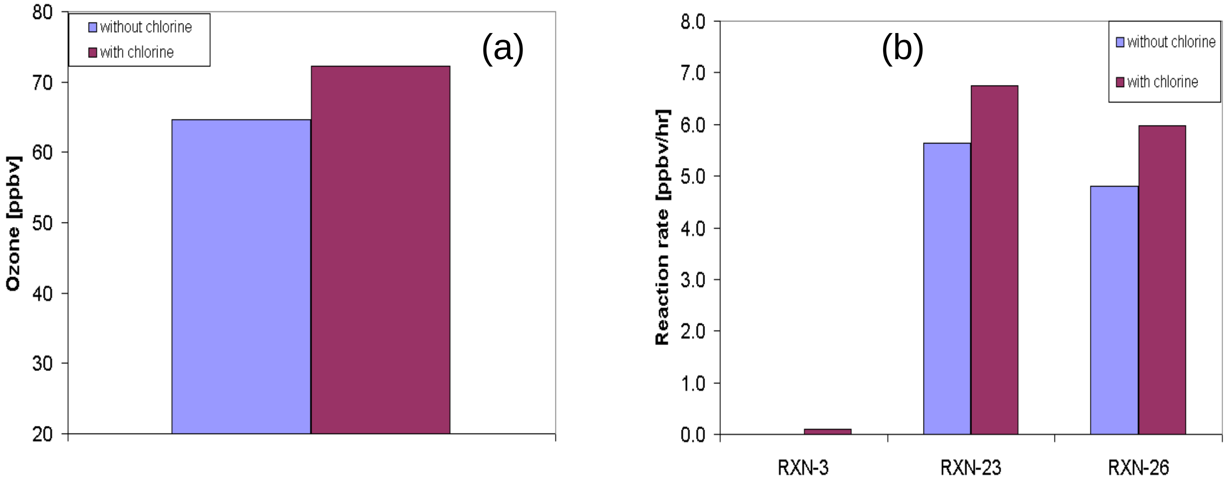


Figure 4: Number of days when O_3 mixing ratios with chlorine emissions decreased by more than 2.0 ppbv compared to those obtained without the chlorine emissions

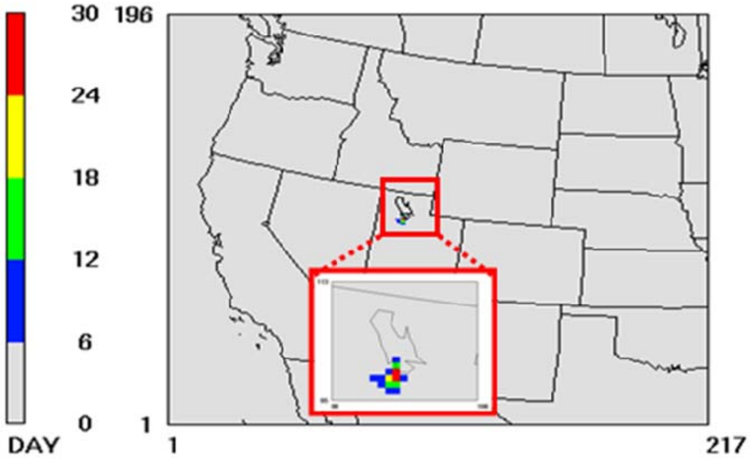


Figure 5: Decreases in O_3 (ΔO_3) and VOC ($-\Delta VOC$) mixing ratios with and without chlorine emissions for a grid-cell located near the southern shore of the Great Salt Lake (local time)

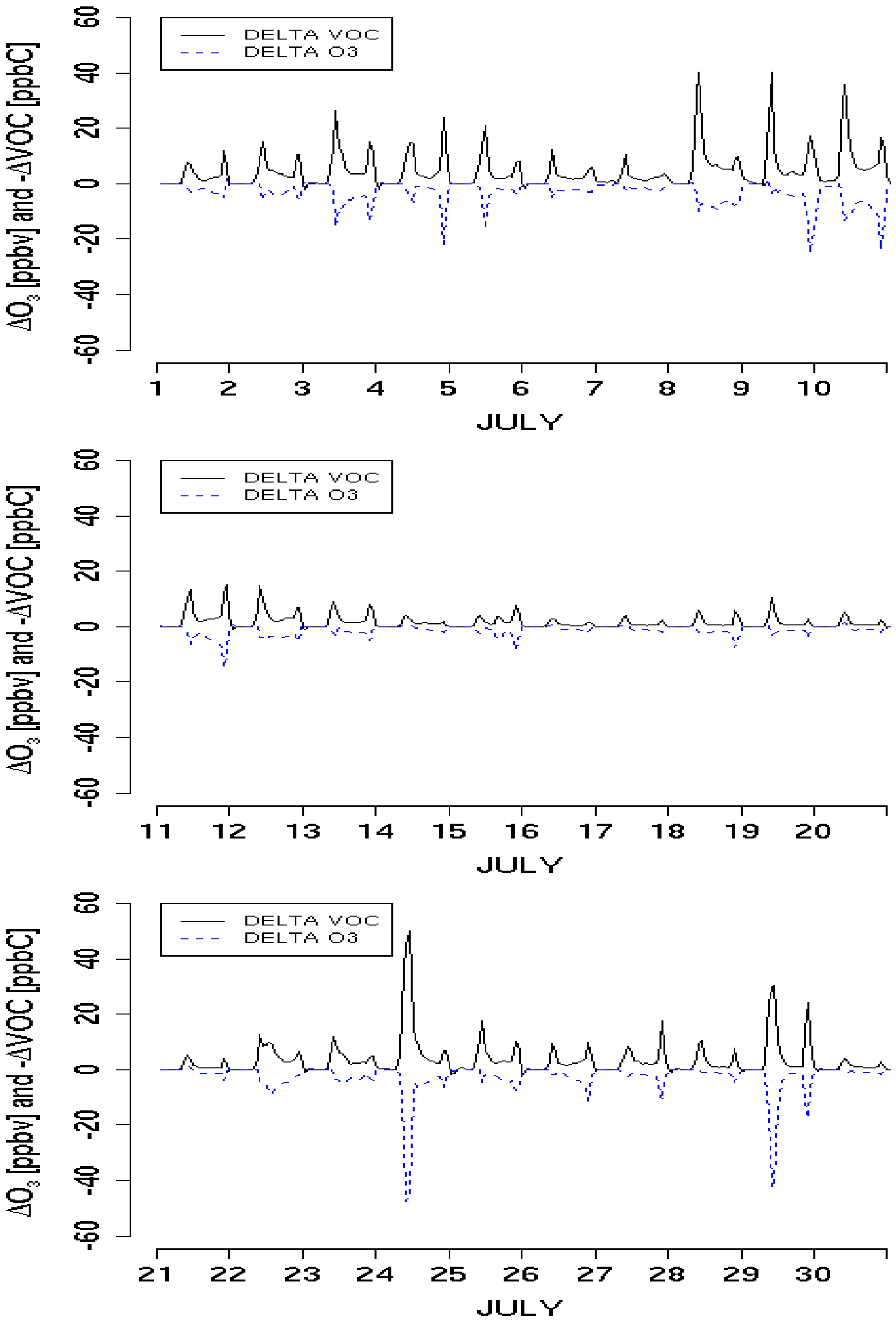
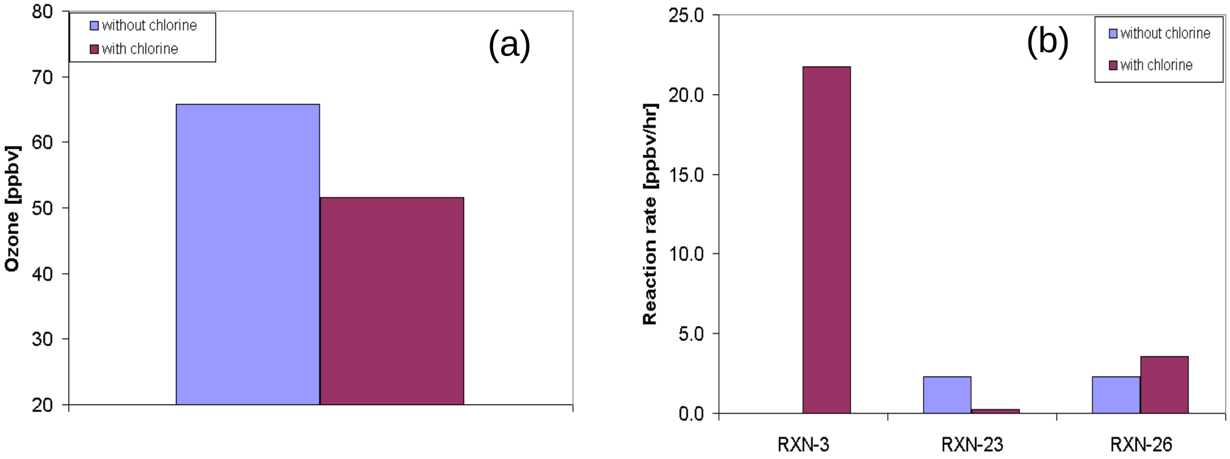


Figure 6: Daytime ozone mixing ratios and selected reaction rates (averaging time: 8 am to 6 pm) with and without chlorine emissions for a grid-cell near the southern shore of the Great Salt Lake on July 24 (a) ozone mixing ratios (b) reaction rates



Tables

Table 1: Model performance statistics for O_3 in Great Salt Lake area during July 2001

Metric	1-hour maximum O_3	8-hour maximum O_3
Number of Observations	321	304
Mean Modeled (ppbv)	67.2	63.9
Mean Observed (ppbv)	68.7	61.4
Mean Bias (ppbv)	-1.5	2.5
Mean Error (ppbv)	8.7	7.1
Normal Mean Bias (%)	-2.1	4.1
Normal Mean Error (%)	12.7	11.6
Index of Agreement	0.63	0.65
Root Mean Square Error (ppb)	12.1	8.9