

Modeling heterogeneous ClNO_2 formation, chloride availability, and chlorine cycling in Southeast Texas

H. Simon ^{a,b,*}, Y. Kimura ^a, G. McGaughey ^a, D.T. Allen ^a, S.S. Brown ^c, D. Coffman ^d, J. Dibb ^e, H.D. Osthoff ^{f,1}, P. Quinn ^d, J.M. Roberts ^c, G. Yarwood ^g, S. Kemball-Cook ^g, D. Byun ⁱ, D. Lee ^h

^a Center for Energy and Environmental Resources, University of Texas at Austin, 10100 Burnet Road, Bldg. 133, R7100, Austin, TX 78758, USA

^b National Exposure Research Laboratory, U.S. Environmental Protection Agency, 109 T.W. Alexander Dr., Research Triangle Park, NC 27711, USA

^c NOAA/ESRL Chemical Sciences Division, 325 Broadway, Boulder, CO 80305, USA

^d NOAA/OAR Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115, USA

^e University of New Hampshire, Climate Change Research Center, Morse Hall Rm 361, Durham, NH 03824, USA

^f NOAA/ESRL Chemical Sciences Division, 325 Broadway, Boulder, CO 80305, USA

^g Environ International Corp, 773 San Marin Drive, Suite 2115, Novato, CA 94998, USA

^h Department of Earth and Atmospheric Sciences, University of Houston, 312 Science & Research 1, Rm #312, Houston, TX 77204-5007, USA

ⁱ Air Resources Laboratory, OAR, NOAA, 1315 East West Highway, Silver Spring, MD 20910, USA

ARTICLE INFO

Article history:

Received 30 March 2009

Received in revised form

10 August 2009

Accepted 3 September 2009

Keywords:

Nitryl chloride

Chlorine

CAMx

Urban air pollution

Houston

GoMACCS

TexAQS II

Heterogeneous chemistry

ABSTRACT

Nitryl Chloride (ClNO_2) mixing ratios above 1 ppbv have been measured off the coast of Southeast Texas. ClNO_2 formation, the result of heterogeneous N_2O_5 uptake on chloride-containing aerosols, has a significant impact on oxidant formation for the Houston area. This work reports on the modeling of ClNO_2 formation and describes the sensitivity of ClNO_2 formation to key parameters. Model sensitivity analyses found that: (1) Chloride availability limits the formation of nitryl chloride at ground level but not aloft; (2) When excess particulate chloride was assumed to be present at ground level through sea salt, ClNO_2 concentrations increased in some locations by a factor of 13, as compared to cases where sea salt chloride was assumed to be limited; (3) Inland formation of ClNO_2 seems feasible based on chloride availability and could have a large impact on total ClNO_2 formed in the region; and (4) ClNO_2 formation is quite sensitive to the assumed yield of ClNO_2 from N_2O_5 uptake. These results demonstrate that there is a need for further field studies to better understand the geographic extent of ClNO_2 formation and the atmospheric conditions which control partitioning of chloride into the particle phase. In addition, this work examined the role of ClNO_2 in the cycling of chlorine between chloride and reactive chlorine radicals. The modeling indicated that the majority of reactive chlorine in Texas along the Gulf coast is cycled through ClNO_2 , demonstrating the importance of including ClNO_2 into photochemical models for this region.

Published by Elsevier Ltd.

1. Introduction

Ambient measurements of Nitryl Chloride (ClNO_2) were made for the first time during the TexAQS II/GoMACCS field campaign in 2006 (Osthoff et al., 2008). ClNO_2 mixing ratios measured on board the Research Vessel *Ronald H Brown* reached over 1 part per billion by volume (ppbv) off the coast of southeast Texas. This compound is potentially significant for several reasons. First, ClNO_2 serves as a NO_x reservoir at night which prevents nitrogen from being lost to inactive forms such as nitric acid. Second, ClNO_2 represents a largely

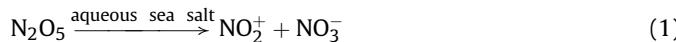
unstudied form of chlorine in the atmosphere that may be a key step in a pathway that converts particulate chloride into reactive chlorine radicals. The effect of this chemistry on both NO_x and chlorine cycling has the potential to increase ozone production in regionally polluted areas (Simon et al., 2009; Osthoff et al., 2008).

Finlayson-Pitts et al. (1989) first suggested that ClNO_2 could form from heterogeneous reactions between N_2O_5 and aqueous sea salt aerosols. Osthoff et al. (2008) showed strong temporal correlations between ClNO_2 and N_2O_5 concentrations measured in the Gulf of Mexico. Their results make a compelling case that the dominant mechanism for nitryl chloride formation is this heterogeneous pathway. Studies that have investigated heterogeneous ClNO_2 formation in the laboratory suggest that the mechanism is the same as that of heterogeneous N_2O_5 hydrolysis [Reaction (1)] (Behnke et al., 1997; Schweitzer et al., 1998).

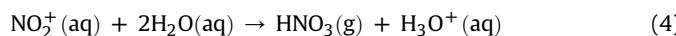
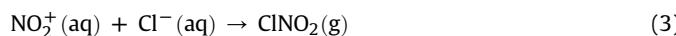
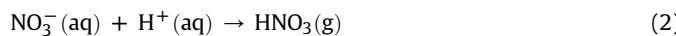
* Corresponding author. Tel.: +1 919 541 1803; fax: +1 919 541 1379.

E-mail address: simon.heather@epa.gov (H. Simon).

¹ Present address: University of Calgary, Department of Chemistry, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada.



The Cl^- ions in aqueous aerosol compete with H_2O to react with NO_2^+ . Therefore the reaction can either result in 2HNO_3 or $\text{ClNO}_2 + \text{HNO}_3$ as shown in Reactions (2)–(4).



The yield of nitryl chloride from this reaction [i.e. the fraction of NO_2^+ ions that proceed to Reaction (3) instead of Reaction (4)] is strongly dependent on the chloride ion concentration in the aerosol (Behnke et al., 1997; Roberts et al., *in press*; Schweitzer et al., 1998; Thornton and Abbott, 2005). Yields close to 1 at high molarities (1 M) suggest that Cl^- ions outcompete H_2O as discussed in Section 3.2.3. In fact, both Behnke et al. (1997) and Roberts et al. (*in press*) report nitryl chloride formation on aerosols as dilute as 0.01 M. Most laboratory studies are in relative agreement on their measurements of reactive uptake coefficients for N_2O_5 on chloride aerosols (0.01–0.03) (Behnke et al., 1997; Schweitzer et al., 1998; Thornton and Abbott, 2005).

Previous articles have described the impact of ClNO_2 , once formed, on ozone formation (Simon et al., 2009; Osthoff et al., 2008). The work presented here incorporated heterogeneous ClNO_2 formation on ambient aerosol, as well as other related heterogeneous N_2O_5 chemistry, and investigated the sensitivity of ClNO_2 formation to various model parameters. Specifically, this work studies the dependence of ClNO_2 formation on available chloride and its sensitivity to the assumed yield of ClNO_2 . Finally, the implications of this chemistry for chlorine cycling and the total reactive chlorine budget in Southeast Texas are investigated.

2. Methods

2.1. Photochemical simulations

Photochemical modeling was performed using the Comprehensive Air quality Model with extensions (CAMx) version 4.2 (Environ,

2008). This program is a three-dimensional Eulerian model which calculates the effects of emissions, chemistry, deposition, advection, and dispersion on chemical concentrations in the atmosphere. A full description of the model treatment of these processes as well as the nesting schemes and numerical solvers can be found in the CAMx User's Guide (Environ., 2008). Evaluations of CAMx model performance have been carried out by Tesche et al. (2006) and Morris et al. (2005). CAMx was chosen for this work to facilitate comparison with previous studies of chlorine and nitryl chloride in the Houston area (Chang and Allen, 2006a,b; Wang et al., 2007; Simon et al., 2009).

The modeling domain consisted of three two-way nested grids, as shown in Fig. 1. The two largest of these grids had cells with horizontal dimensions of 36 km by 36 km and 12 km by 12 km. These two grids have 17 vertical layers covering the lowest 15 km of the atmosphere. The finest of the grids, which was centered over the Houston area, had cells with horizontal dimensions of 4 km by 4 km and 28 vertical layers covering the lowest 15 km of the atmosphere. The layers are more finely divided at lower altitudes, with 12 of the 28 layers in the lowest 1000 m. A full description of the thickness of each vertical layer is described by the Texas Commission on Environmental Quality for their SIP mid-course review modeling (http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb1_camx_domain.html). The model simulation was run for the dates of August 30, 2006 through September 9, 2006, one of the time periods when the *R.V. Ronald H. Brown* was taking measurements in the Houston area. August 28 and 29 were used as model spin-up days. Meteorological inputs for the modeled days were developed at the University of Houston (Ngan, 2008), as described by Simon et al. (2009) and in the supplemental information.

Emissions inputs for ozone precursor compounds (NO_x and VOCs) are described by Simon et al. (2009). In addition, emissions of anthropogenic Cl_2 , primary particulate matter (PM), SO_2 , and ammonia were included in the modeling. A full description of these emissions and the associated boundary conditions can be found in the supplemental information.

2.2. Updated model chemistry

Current versions of the CAMx software include a standard CB IV chemical mechanism (Gery et al., 1989), and two enhanced mechanisms: one with added chlorine chemistry described in Tanaka et al.

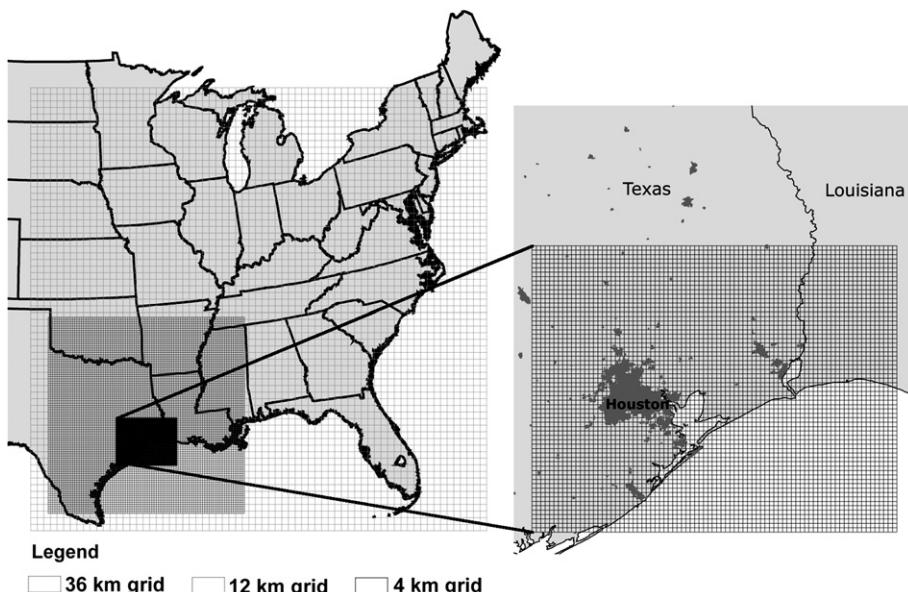


Fig. 1. Nested domains used in CAMx modeling.

(2003) and one with added aerosol chemistry based on work by Pandis et al. (1993), Nenes et al. (1998), and Yarwood et al. (2005). The aerosols in this model are categorized into 16 main species (sulfate, nitrate, ammonium, water, 9 secondary organic aerosol species, sodium, chloride, primary organic matter, elemental carbon, and 4 non-reactive species) and 4 size bins (0.039–0.156 μm ; 0.156–0.625 μm ; 0.625–2.5 μm ; and 2.5–10 μm). Since this study entails modeling processes that interact both with chlorine and with aerosols, the chlorine and aerosol chemistry were linked in a single mechanism.

To correctly model the heterogeneous conversion of N_2O_5 to ClNO_2 , there are several key factors that must be properly accounted for: the formation of NO_3 from $\text{O}_3 + \text{NO}_2$, the strongly temperature-dependant reversible inter-conversion of NO_3 and N_2O_5 , and the relative magnitudes of NO_3 and N_2O_5 losses. The formation and destruction reactions of NO_3 are handled in CAMx's standard CB IV chemical mechanism. The reactions of N_2O_5 are also, for the most part, included in the standard chemical mechanism. A major uncertainty in the N_2O_5 chemistry in CAMx is the loss mechanisms for N_2O_5 (both homogeneous and heterogeneous). Field measurements suggest that gas-phase reactions of N_2O_5 are not a significant loss pathway in the lower troposphere in southeast Texas (Brown et al., 2006, 2009; Simon, 2008), so gas-phase hydrolysis of N_2O_5 was not included in the model simulations. Changes to the heterogeneous chemistry used in this modeling are discussed below.

The heterogeneous loss rate for N_2O_5 was calculated using Equation (5) and the heterogeneous formation rate of ClNO_2 was calculated using Equation (6),

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5] = \frac{\gamma\omega A}{4}[\text{N}_2\text{O}_5] \quad (5)$$

$$\frac{d[\text{ClNO}_2]}{dt} = Yk[\text{N}_2\text{O}_5] = \frac{Y\gamma\omega A}{4}[\text{N}_2\text{O}_5] \quad (6)$$

where k (s^{-1}) is the first order rate constant for the heterogeneous reaction, Y is the yield of ClNO_2 for each molecule of N_2O_5 reacted, γ is the reactive uptake coefficient (the probability that a molecule

of N_2O_5 which impacts a particle will react), ω (m s^{-1}) is the mean molecular speed of the N_2O_5 , and A ($\text{m}^2 \text{ m}^{-3}$ of air) is the total aerosol surface area. For each time step, the total aerosol surface area was calculated based on model predictions of speciated aerosol mass in each grid cell. For this calculation, particles were assumed to be spherical with species-specific densities given by Simon (2008). The assumption of spherical particles is reasonable since previous studies in Texas have shown aerosol to be predominantly in a deliquesced state (Santarpia et al., 2004). Mean particle diameters were taken as the geometric mean for each of four PM size bins used. It should be noted that Equations (5) and (6) represent the change in N_2O_5 and ClNO_2 concentrations from this specific chemistry and not the full differential equation with all source and loss terms.

The reactive uptake coefficient is a complex function of aerosol composition and relative humidity (Davis et al., 2008; Evans and Jacob, 2005). A recent study of N_2O_5 reactivity in Texas showed that parameterization of $\gamma(\text{N}_2\text{O}_5)$ based on laboratory studies are systematically larger than direct determinations from aircraft measurements taken over inland areas during night flights (Brown et al., 2009). However, N_2O_5 and ClNO_2 data from ship based measurements in Galveston Bay and other location along the Gulf Coast were consistent with relatively larger $\gamma(\text{N}_2\text{O}_5)$, in the range of 0.02–0.03 (Osthoff et al., 2008). On the basis of these empirical observations, geographic location was used as a surrogate for $\gamma(\text{N}_2\text{O}_5)$ in this study. Heterogeneous chemistry was only included in the 4 and 12 km modeling domain, since the focus of this modeling is to evaluate chemistry in Southeast Texas. Because model parameters were based on local ambient measurements, the chosen modeling setup may not be applicable to other areas of the country. The 4 and 12 km domains were split into 3 regions (see Fig. 2): region 1 covered all marine and coastline grid cells, region 2 covered the Houston Ship Channel, and region 3 covered all other terrestrial grid cells. Although region 2 is small in area it was treated as a distinct region because it includes a large number of industrial sources. Heterogeneous N_2O_5 uptake was modeled using Reactions (7)–(9) for regions 1, 2, and 3 respectively. It should be

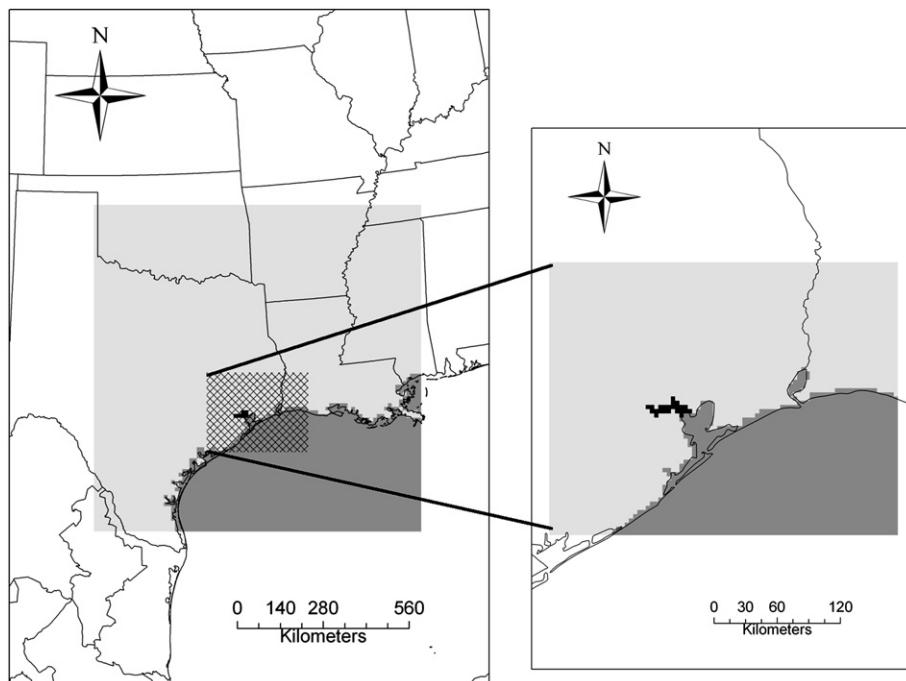
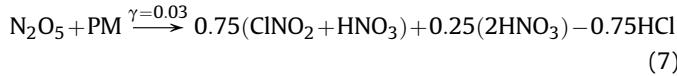


Fig. 2. Regions used to define heterogeneous N_2O_5 reaction rate parameters. Region 1 is shown in dark gray, region 2 is shown in black, and region 3 is shown in light gray.

noted that water as a reactant is implied in these reactions, but is not explicitly shown.



Aldener et al. (2006) reported a reactive uptake of 0.03 from ambient measurements taken in the marine boundary layer. In addition, Osthoff et al. (2008) modeled data using a $\gamma(\text{N}_2\text{O}_5)$ value of 0.025 for the TexAQS 2006 episode. Based on these two studies, the reactive uptake coefficient for Reaction (7) was set to 0.03. Reaction (7) represents a 75% yield of ClNO_2 with respect to N_2O_5 uptake. Osthoff et al. (2008) reported yields from measurements in the Gulf of Mexico of between 18% and 100%. The 75% yield is an intermediate value; however, the sensitivity of the model to this value is tested in this work. Reaction (7) was added as a loss mechanism for HCl, since one chlorine atom is required to form each ClNO_2 molecule. Given that CAMx calculates a rapid equilibrium between gas-phase HCl and particle-phase chloride, removing the HCl from the gas phase is essentially equivalent to removing it from the particle phase. Reaction (7) was shut off [and N_2O_5 chemistry switched to Reaction (9)] when HCl mixing ratios dropped below 0.5 parts-per trillion by volume (pptv) to prevent creation of chlorine mass. This threshold was taken as 0.1% of a typical HCl concentration for the Houston area (0.5 ppbv) as reported by Chang and Allen (2006b) and is assumed to be a lower bound for the concentration of chloride required to form ClNO_2 . This will give an upper-bound on the amount of ClNO_2 formed since the model uses a constant yield until HCl concentrations reach this threshold, while actual yields decrease at lower particulate chloride concentrations. The uncertainties due to this assumption and the assumption of a constant 75% yield are discussed in more detail below.

The reactive uptake coefficients in Regions 2 and 3 were based on measurements made by Brown et al. (2009) and Brown et al. (2006). The reactive uptake coefficient for region 2, an area characterized by non-neutralized sulfate aerosols, was set at the upper end of the ambient measured values (0.01). The reactive uptake coefficient for region 3, whose aerosol is composed of neutralized ammonium sulfate and secondary organic aerosol, was set at the lower end of the measured range (0.001). It is assumed that over terrestrial grid cells, chloride availability is low and a negligible

amount of ClNO_2 will form in these locations. However, the sensitivity of the model to this assumption is evaluated below.

The final change made to the chemical mechanism in CAMx was the addition of the photolysis of ClNO_2 to form NO_2 and Cl^{\bullet} as described in Simon et al. (2009).

3. Results

3.1. Model predictions of N_2O_5 , ClNO_2 , and HNO_3 mixing ratios

Maximum and average hourly ground-level mixing ratios of N_2O_5 , ClNO_2 , and HNO_3 in the 4 km domain are shown in Table 1. The values were calculated for each night in the simulation for the hours of 10pm–5am. Average values for ClNO_2 mixing ratios are reported only over marine grid cells where formation occurs in the model. Maximum predicted ClNO_2 mixing ratios ranged from 256 pptv to 1210 pptv on different nights. The maximum 1-min average ClNO_2 mixing ratio measured aboard the Research Vessel *Ronald H Brown* during the TexAQS II/GoMACCS field study was just above 1300 pptv, similar to the maximum ClNO_2 concentrations in the model. More detailed comparisons between model predictions and ambient measurements for PM surface area, N_2O_5 , HNO_3 , and ClNO_2 mixing ratios are given in the supplemental information. These comparisons show that predicted values using this modeling scheme are generally consistent with measured values, except in the Houston Ship Channel, where ClNO_2 concentrations are consistent with measurements and N_2O_5 is over-predicted. Inaccuracies in this region are likely due to uncertainties in the emissions inventory or sub-grid cell phenomena associated with localized plumes.

Fig. 3 shows the spatial distribution of the species on the night of Aug 30–Aug 31, 2006. The spatial distribution of N_2O_5 depends on the location of NO_x in urban and industrial plumes. The major NO_x plumes on every night originated from Houston, TX, Beaumont, TX, and Lake Charles, LA. PM surface area was also highest in these three urban/industrial areas. The spatial distribution NO_3 and N_2O_5 mixing ratios were the same, which is expected since there is rapid inter-conversion between these two compounds in the model. HNO_3 and ClNO_2 follow the same spatial patterns as N_2O_5 except for the fact that ClNO_2 was mostly restricted to marine and near-marine grid cells. For the Houston area, it appears that the NO_x and aerosol surface area are highest in the source region, while N_2O_5 , ClNO_2 , and HNO_3 are highest downwind. This pattern is to be expected at night since NO_2 reacts with ozone to form NO_3 and eventually N_2O_5 . Therefore the NO_2 is generally observed in fresh plumes and the N_2O_5 and its reaction products reach peak concentrations several hours downwind of the source region.

Table 1

Average and Maximum ground-level concentrations for N_2O_5 , ClNO_2 , and HNO_3 for nights in the modeled episode in the 4 km domain.

Night of:	N_2O_5 (pptv)		ClNO_2 (pptv)		HNO_3 (pptv)	
	Average	Maximum	Average ^a	Maximum	Average	Maximum
Aug 30–Aug 31	78	3885	14	419	719	3338
Aug 31–Sep 1	280	8526	85	1034	1519	6297
Sep 1–Sep 2	304	8016	81	1210	1830	9675
Sep 2–Sep 3	189	8906	37	362	1000	6286
Sep 3–Sep 4	191	7362	51	256	1039	6113
Sep 4–Sep 5	92	4565	31	400	677	4415
Sep 5–Sep 6	18	2235	17	276	459	1946
Sep 6–Sep 7	199	6215	101	1002	937	7260
Sep 7–Sep 8	316	8165	97	911	1995	16 025
Sep 8–Sep 9	333	13 547	161	882	2620	13 964

^a Average values for ClNO_2 were only calculated for marine grid cells.

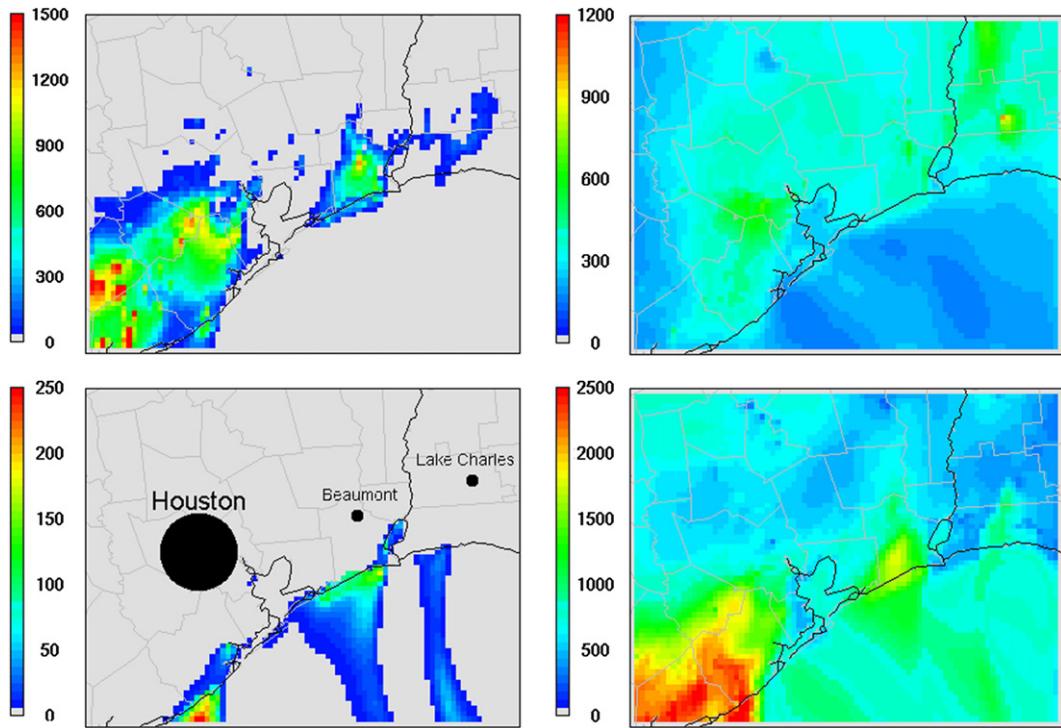


Fig. 3. Pollutant concentrations at 4am on Aug 31, 2006: N_2O_5 (pptv) at upper left, aerosol surface area ($\mu\text{m}^2 \text{cm}^{-3}$) at upper right, ClNO_2 (pptv) at lower left, HNO_3 (pptv) at lower right.

3.2. Evaluation of chloride availability and its effect on ClNO_2 production

Even with data from measurements taken during TexAQS II, there is still a great deal of uncertainty about parameters used to model heterogeneous N_2O_5 chemistry. One key uncertainty is the availability of chloride. This can affect the ClNO_2 yield from heterogeneous N_2O_5 uptake and the geographic extent of these reactions. A set of sensitivity runs was performed to further evaluate the assumptions about chloride availability that were made in this model simulation.

3.2.1. Effect of using the HCl switch

The methods described above include techniques implemented to account for the depletion of HCl due to ClNO_2 formation and for the fact that heterogeneous uptake will not result in ClNO_2 formation unless there is particulate chloride present. The two elements of this technique were 1) the loss of an HCl molecule for every ClNO_2 molecule formed [see Reaction (7)] and 2) an “HCl switch” (based on the assumption that gas-phase and particulate chloride are rapidly exchanged). When the gas-phase HCl, and therefore total chloride, concentration dropped below a minimum level (0.5 pptv) all ClNO_2 formation was turned off. Further evaluation of the sensitivity of the model to this “HCl switch” chemistry can give insight into how chloride limitation is affecting the heterogeneous N_2O_5 chemistry. Two sensitivity runs are used to evaluate this dependency further.

3.2.1.1. ClNO_2 formation in the presence of excess chloride. In this sensitivity run, ClNO_2 formation was modeled as if it were not dependent on chloride availability. To do this, the “HCl switch” was always on. There was no loss of HCl when ClNO_2 formed and ClNO_2 formation depended solely on location (ClNO_2 formation was still restricted to marine grid cells), surface area concentration, and N_2O_5 mixing ratio, and not on the predicted HCl mixing ratio.

Results from this run indicate how much ClNO_2 would form if there were a surplus of chloride present in the atmosphere.

This run shows significant increases in HCl mixing ratios in areas where ClNO_2 is present. Fig. 4 shows the predicted HCl mixing ratios on September 1, 2006 at 5am in the base case simulation and the predicted increases in HCl caused by eliminating HCl loss due to ClNO_2 formation. In regions where HCl mixing ratios were essentially zero in the main run, HCl mixing ratios increase by up to 0.4 ppbv in this run. Fig. 4 demonstrates that the model predicts ClNO_2 formation will almost completely deplete chloride concentrations in the locations where it occurs. The fact that ClNO_2 formation continues to occur throughout the night in the base case simulation is likely due to sea salt emissions, which act as a continual source of chloride.

Ground-level nitryl chloride mixing ratios increased significantly in this sensitivity analysis. On some days, the maximum ground-level nitryl chloride mixing ratio increased by more than a factor of three. The ClNO_2 mixing ratio in a single ground-level grid cell increased by up to 3200 pptv (more than a tenfold increase). In addition, some decreases in ClNO_2 mixing ratios occurred in this sensitivity run. The maximum decrease was almost 300 pptv. These decreases may be caused by faster depletion of N_2O_5 when the ClNO_2 formation is not limited by chloride availability. Fig. 5 shows the ClNO_2 mixing ratio in the base case heterogeneous chemistry run at 5am on September 1, 2006 as well as the changes in ClNO_2 mixing ratios that occurred in the simulation with no chloride limitations. The spatial distribution of the changes in ClNO_2 mixing ratios is similar to the distribution of depleted HCl mixing ratios shown in Fig. 4. Also, the spatial extent of the ClNO_2 did not change significantly, only the magnitude of the mixing ratios. Table 2 summarizes the changes that occurred in ground-level HCl and ClNO_2 mixing ratios in this simulation versus the base case simulation.

In addition to the ground-level mixing ratio, vertical profiles were also evaluated for this simulation. Figs. 6 and 7 show the vertical profile of maximum and average ClNO_2 mixing ratios in the 4 km domain at 1am for 4 nights. These figures show that on many nights

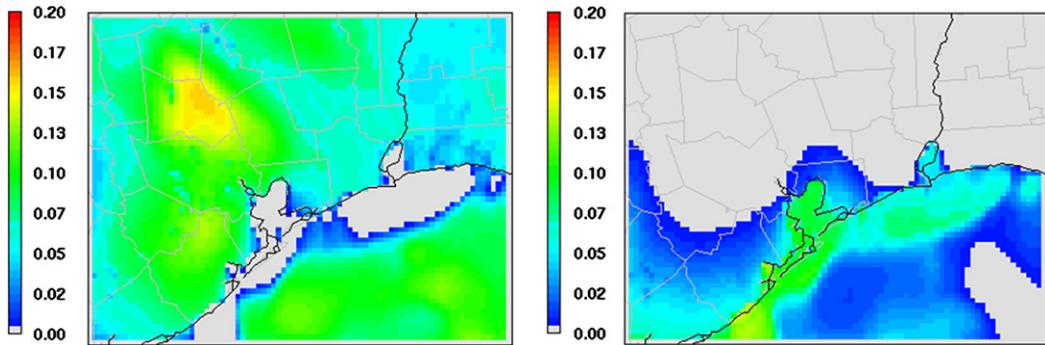


Fig. 4. HCl mixing ratio (ppbv) in base case run on September 1, 2006 at 5am (left). Change in HCl mixing ratio (ppbv) caused by not depleting HCl when ClNO_2 is formed on September 1, 2006 at 5am (right).

ClNO_2 mixing ratios above 1000 m are virtually identical in the base case heterogeneous chemistry run and in the sensitivity run: August 31 (shown), September 1 (shown), September 2 (shown), September 3 (not shown), September 5 (not shown), and September 9 (not shown). On those nights, marine chloride availability appears to play no role in limiting ClNO_2 formation above 1000 m. Since most chloride is emitted at ground-level, it might be expected that chloride would be most concentrated at lower altitudes and that this would be a main limiting factor for ClNO_2 formation aloft. However, these results suggest that the opportunity for interaction between N_2O_5 and particle surfaces is the limiting factor for ClNO_2 formation aloft.

Based on this simulation, marine chloride availability greatly affected the magnitude of ClNO_2 mixing ratios at ground-level (by up to a factor of 13), but not aloft. In addition, horizontal spatial distributions were not affected within the marine grid cells. The sensitivity run described in the next section tests the chloride availability inland and gives insight into whether sufficient chloride is present over terrestrial regions to lead to significant ClNO_2 formation.

3.2.1.2. Allowing ClNO_2 formation at inland locations. In this sensitivity run, the “HCl switch” was used for the entire 4 km and 12 km domains instead of just for the marine grid cells. ClNO_2 formation (Reaction (7)) proceeded wherever HCl mixing ratios were sufficiently high (above 0.5 pptv) regardless of whether the location was marine or terrestrial. The reactive uptake and yield used were the same as described above. When HCl dropped below 0.5 pptv, Reaction (8) was used in the Houston Ship Channel grid cells and Reaction (9) was used in all other cells. Previous modeling limited the geographic extent of ClNO_2 formation based on the assumption that it would only occur in a marine environment where sea salt emissions are prevalent. This run eliminated that constraint, so that

ClNO_2 could form inland wherever HCl mixing ratios were high enough. There have been no inland measurements of ClNO_2 in the Houston area, so model results cannot be compared at this time with ambient data.

Fig. 8 shows comparisons of ClNO_2 mixing ratios in the base case run and in the sensitivity run which allowed formation at inland locations on the evening of September 4, 2006. This figure shows that the model predicts sufficient concentrations of chloride inland to form ClNO_2 . In this sensitivity run, ClNO_2 mixing ratios were often above 400 pptv over the city of Houston. ClNO_2 mixing ratios over land that was within 50 km of the shoreline were often as high as mixing ratios over marine grid cells. On some days, ClNO_2 mixing ratios above 100 pptv were predicted at locations more than 100 km inland.

Table 3 summarizes changes in domain-wide maximum ground-level ClNO_2 mixing ratios and domain-wide ClNO_2 mass at 5am. On some days the maximum ClNO_2 mixing ratio was greater in the base case heterogeneous chemistry run and on some days the maximum mixing ratios were greater in this sensitivity run. It appears that when mixing ratios were greater in the base case heterogeneous chemistry run, the maxima usually occurred where a NO_x plume first came in contact with marine grid cells. In the sensitivity run where ClNO_2 formation could occur over land, the N_2O_5 in the NO_x plume became partially depleted over land so the ClNO_2 mixing ratios were lower but covered a greater area. In contrast, in the base case heterogeneous chemistry run the NO_x plumes stayed relatively concentrated over land and when these plumes suddenly contacted the marine environment, a great deal of ClNO_2 was formed all at once, causing intense peaks over small areas. This was due to the fact that the model predicted a lower reactive uptake coefficient over terrestrial grid cells when no chloride was present (0.001) versus when sufficient chloride is available to form ClNO_2 (0.03).

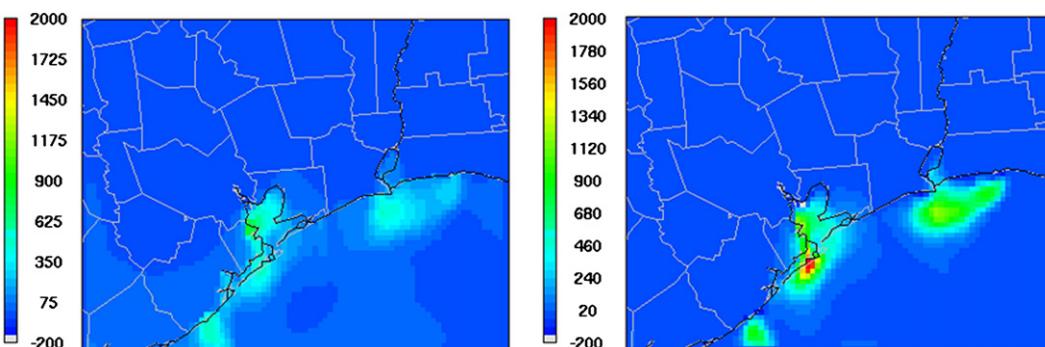


Fig. 5. ClNO_2 mixing ratio (pptv) in base case run on September 1, 2006 at 5am (left). Change in ClNO_2 mixing ratio (pptv) when excess chloride is present on September 1, 2006 at 5am (right).

Table 2Summary of changes in ClNO_2 and HCl concentrations when excess chloride is present.

Night of:	Max ClNO_2 concentration in main run (pptv)	Max ClNO_2 concentration with excess chloride (pptv)	Max ClNO_2 increase in a single grid cell ^a (pptv)	Max ClNO_2 increase in a single grid cell ^b (%)	Max change in HCl in a single grid cell ^c (ppbv)
Aug 30–31	419	928	630	210	0.2
Aug 31–Sep 1	1034	2606	2020	670	0.1
Sep 1–2	1210	3733	3244	1110	0.3
Sep 2–3	362	800	500	220	0.1
Sep 3–4	256	817	615	470	0.4
Sep 4–5	400	996	616	200	0.1
Sep 5–6	276	397	242	280	0.2
Sep 6–7	1002	1716	1115	610	0.2
Sep 7–8	911	2535	2216	1270	0.3
Sep 8–9	882	1343	901	390	0.4

^a Change in ClNO_2 concentration calculated as concentration in sensitivity run simulation (excess chloride) minus concentration in base case run.^b Percent increases only calculated for grid cells in which the ClNO_2 concentration was greater than 50 pptv in the sensitivity run simulation.^c Calculations done between the hours of 8pm and 5am.

This phenomenon can be seen in the Lake Charles, LA plume in Fig. 8. The results reported here show that integrated ClNO_2 is larger in the sensitivity run, even though ClNO_2 mixing ratios may be lower in marine hotspots and that ClNO_2 formation becomes NO_x limited in the sensitivity run. On days when the maximum ClNO_2 mixing ratio was greater in the sensitivity run, it appears that the maximum occurred over land. This can be seen in Fig. 8, which shows ClNO_2 hotspots over Houston in the sensitivity run but not in the base case heterogeneous chemistry run. The total ClNO_2 mass in the 4 km domain was significantly greater (between a factor of 3 and 22 greater depending on the day) when ClNO_2 formation was allowed to occur over land. This indicates that ClNO_2 formation over land uses reservoirs of chloride that would not be accessed if ClNO_2 formation were restricted to marine cells and again supports the finding that integrated ClNO_2 is larger when inland formation is included in the simulation.

Overall, this sensitivity run predicts that inland chloride concentrations are indeed high enough to form ClNO_2 . Inland formation is important for correctly predicting the magnitude and extent of ClNO_2

mixing ratios. In addition, a great deal more chloride mass will be converted to ClNO_2 when inland formation is taken into account. Ambient measurements are still needed to verify these model results. It should be noted again that these results represent an upper-bound estimate for ClNO_2 formation since modeled yields were held constant at 75% but actual yields will decrease as HCl concentrations drop.

3.2.2. Sensitivity to changes in ClNO_2 yield

The modeling performed above used a ClNO_2 yield in Reaction (7) of 75%. As discussed previously, laboratory studies have shown that this yield depends on the chloride concentration in the aerosol (Behnke et al., 1997; Schweitzer et al., 1998; Roberts et al., in press). Measurements and modeling results reported by Osthoff et al. (2008), show that in the Gulf of Mexico this yield can range from 18% to 100%. Two further modeling runs were performed (one with a 100% yield and one with an 18% yield) to evaluate the upper and lower bounds of ClNO_2 yield for this region.

Table 4 shows the maximum ground-level mixing ratio changes in a single grid cell for ClNO_2 in the low and high yield sensitivity

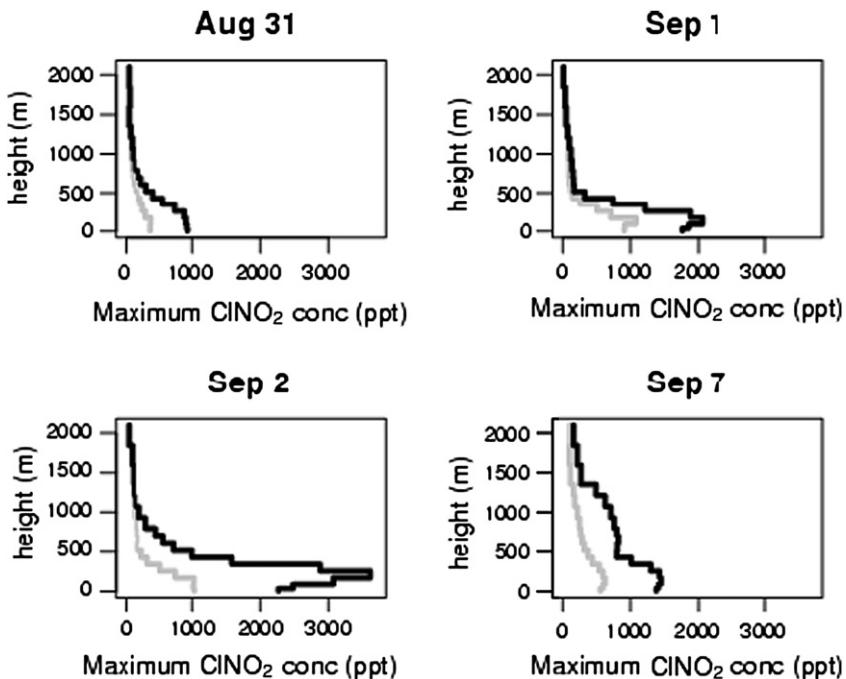


Fig. 6. Vertical profiles of maximum ClNO_2 mixing ratios (pptv) at 1am in the 4 km domain for the base case run (gray) and the sensitivity run with excess chloride (black). Maximum is reported as the maximum concentration at each height (this value may occur in different grid cells in different vertical layers).

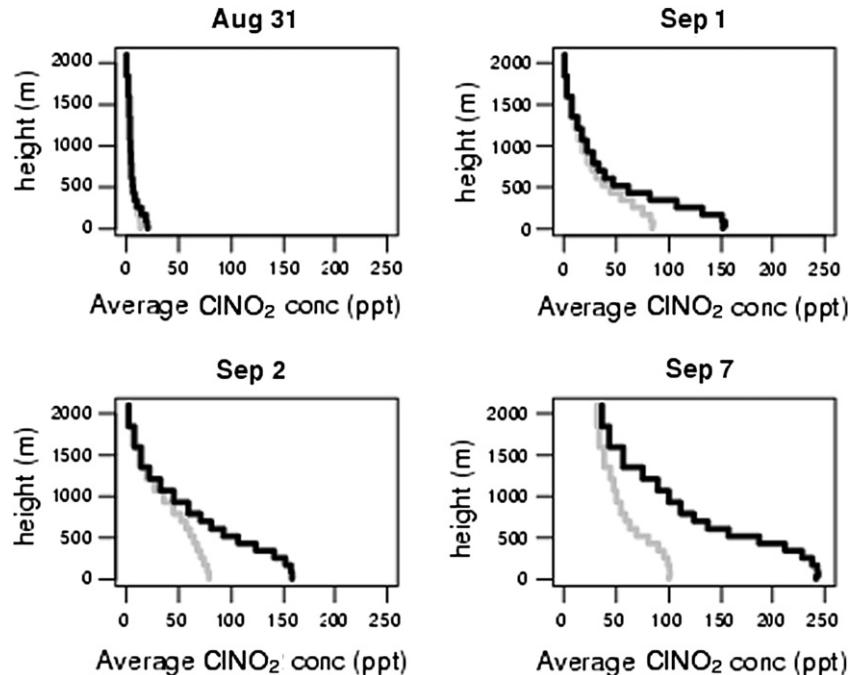


Fig. 7. Vertical profiles of average CINO_2 mixing ratios (pptv) at 1am in the 4 km domain for the base case run (gray) and the sensitivity run with excess chloride (black).

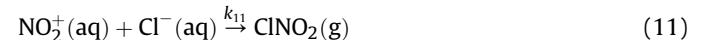
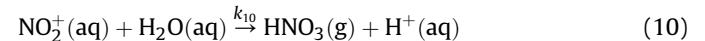
runs. Changes are calculated as the mixing ratio in the sensitivity run minus the mixing ratio in the base case run and are evaluated over the entire 4 km domain. As would be expected, there are large decreases in CINO_2 mixing ratios in the low yield run and large increases in CINO_2 mixing ratios in the high yield run.

These sensitivity runs bound the uncertainty in the magnitude of mixing ratio changes caused by the possibility of different yields. CINO_2 mixing ratios could be up to 85% lower or 70% higher if a different yield is used. These increase and decreases are upper- and lower-bounds based on observed yields in the Gulf of Mexico, but they show that the chemistry described in this work appears to be very sensitive to CINO_2 yield. It should also be noted that although the magnitude of CINO_2 mixing ratios changed with the yield, the spatial distribution of this compound remained essentially unchanged.

3.2.3. Explicit model representation of CINO_2 yield as a function of particulate chloride concentration

All of the uncertain parameters discussed above could be more explicitly modeled by parameterizing the CINO_2 yield as a function

of particulate chloride concentration. Studies by [Roberts et al. \(in press\)](#) and [Behnke et al. \(1997\)](#) have reported CINO_2 parameterizations based on laboratory data for Reactions (10) and (11).



Both [Roberts et al. \(in press\)](#) and [Behnke et al. \(1997\)](#) fitted their data to Equation (12), reporting k_{10}/k_{11} average values of 1/450 and 1/836 respectively.

$$y = \left\{ \left(\frac{k_{10}}{k_{11}} \right) \frac{[\text{H}_2\text{O}]}{[\text{Cl}^-]} + 1 \right\}^{-1} \quad (12)$$

In Equation (12), y is CINO_2 yield, (k_{10}/k_{11}) is the ratio of the rate constants for Reactions (10) and (11), $[\text{H}_2\text{O}]$ is the molar density of water (mol l^{-1}), and $[\text{Cl}^-]$ is the concentration of chloride in the aqueous phase (mol l^{-1}). [Table 5](#) shows the particulate chloride

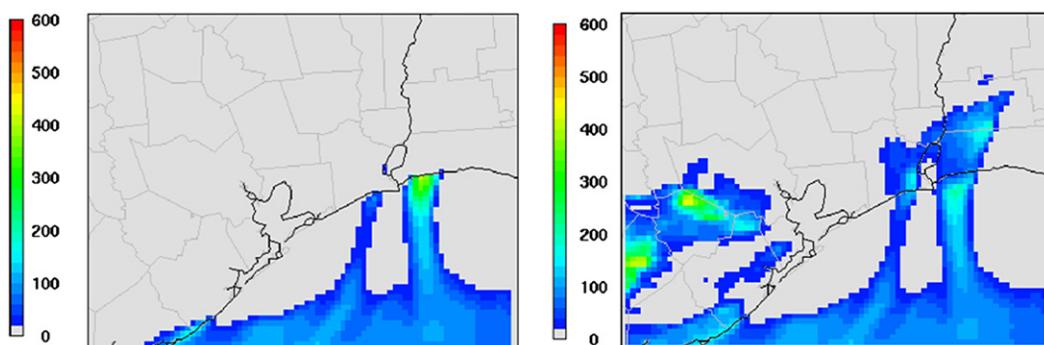


Fig. 8. Modeled CINO_2 mixing ratios (pptv) on September 4, 2006 at 8pm in the base case run (left) and in the sensitivity run which allowed inland CINO_2 formation (right).

Table 3Comparison of ClNO_2 concentration and mass in base case run and sensitivity run which allows inland ClNO_2 formation.

Night of:	Maximum ClNO_2 concentration in the base case run (pptv)	Maximum ClNO_2 concentration in sensitivity run (pptv)	ClNO_2 mass in the 4 km domain in base case run at 5am (metric tons)	ClNO_2 mass in the 4 km domain in sensitivity run at 5am (metric tons)
Aug 30–31	419	539	4.8	103.8
Aug 31–Sep 1	1034	630	9.7	113.6
Sep 1–2	1210	800	15.7	97.4
Sep 2–3	362	241	16.5	88.6
Sep 3–4	256	682	14.7	80.9
Sep 4–5	400	494	10.7	97.4
Sep 5–6	276	220	11.3	156.4
Sep 6–7	1002	1010	29.6	125.2
Sep 7–8	911	909	51.7	165.8
Sep 8–9	882	2051	52.2	197.5

concentrations needed according to these two parameterizations to achieve different ClNO_2 yields.

Roberts et al. (in press) reported that during the TexAQS II/GoMACCS field campaign submicron aerosols measured on board the *Research Vessel Ronald H. Brown* had a median chloride concentration of approximately 0.04 M and a maximum chloride concentration of 1 M. Super-micron aerosols measured at the same time had a median chloride concentration of approximately 2.5 M and a maximum concentration of 10 M. This means that in the Gulf of Mexico, a ClNO_2 yield between 29% and 40% would be expected on submicron aerosols and a yield between 95% and 97% would be expected on super-micron aerosols.

In order to add such a parameterization to a regional photochemical model it is important that predictions of the particulate chloride concentrations be accurate. This requires an accurate chlorine inventory, accurate partitioning between gas-phase HCl and particulate-phase chloride (including acid displacement of chloride in sea salt aerosols), and accurate determination of particulate water concentrations. Figs. S7–S9 (see supplemental information) show predicted nighttime gas-phase HCl mixing ratios, $[\text{Cl}^-]$ in $\text{PM}_{2.5}$, and $[\text{Cl}^-]$ in coarse PM (PM with a diameter between 2.5 and 10 μm) from a CAMx model simulation which did not include any ClNO_2 chemistry, but included the same emissions and meteorology of the model runs described above. The HCl and particulate chloride concentrations shown in these figures should be higher than would be predicted in a run that includes ClNO_2 chemistry since ClNO_2 formation depletes HCl/particulate chloride and cycles the chlorine into other forms. Dibb (2009) and Osthoff et al. (2008) report that HCl measurements made during TexAQS II in the Houston Ship Channel and at Moody Tower in downtown Houston rarely dropped below 0.1 ppbv. HCl mixing ratios for those areas show in Fig. S7 are generally less than this lower bound of 0.1 ppbv by a factor of two to ten. Since partitioning between HCl and particulate chloride heavily favors the gas-phase state, this

indicates that total chloride is being under-predicted in the model. This is likely due both to the large uncertainty in current anthropogenic chlorine emissions and the fact that the sea salt inventory used in this modeling included open-ocean, but not surf-zone emissions.

The $[\text{Cl}^-]$ concentrations shown in Figs. S8 and S9 can be compared to the submicron and super-micron concentrations reported by Roberts et al. (in press), although it should be noted that $\text{PM}_{2.5}$ concentrations will include some super-micron particles and coarse PM will not contain all super-micron particles. The comparison shows that on one night (August 30, 2006) $[\text{Cl}^-]$ concentrations in fine PM are over-predicted since the median concentration in marine regions is around 1 M and the maximum concentration is above 10 M. The plot from September 5 shows $[\text{Cl}^-]$ in the range of that reported by Roberts et al. However the plots from September 2 and September 8 show very low concentrations of $[\text{Cl}^-]$, with median values less than 0.01 M. ClNO_2 formation on such particles would be negligible. The $[\text{Cl}^-]$ concentration in coarse PM is greater than the range reported by Roberts et al. (in press), with median values above 10 M on several nights. The inaccuracy of model predictions for particulate chloride concentrations may be a result of under-predicted chlorine emissions, inaccurate gas/particle partitioning of HCl (specifically the movement of chloride out of coarse aerosol through reactions with HNO_3), or inaccurate particulate water content predictions.

The uncertainty in the model's ability to correctly predict particulate chloride concentration in both coarse and fine PM means that explicitly representing ClNO_2 yield as a function of particulate chloride concentration in the current model could lead either to significant under-predictions or significant over-predictions of ClNO_2 formation. Over-predictions of chloride at high concentrations (above 1 M) will not have a dramatic effect on the ClNO_2 formation rate since the yield at 1 M is already close to 100%. For example, at 2.5 M ClNO_2 yield from N_2O_5 uptake is above 95%. If the chloride concentrations were

Table 4Changes in ground-level ClNO_2 concentrations in the low and high ClNO_2 yield sensitivity runs in the 4 km domain. All changes in ClNO_2 concentrations are defined as (concentration in sensitivity run) – (concentration in base case run).

Night of:	ClNO_2 Yield = 0.18		ClNO_2 Yield = 1.00	
	Max decrease in ClNO_2 (pptv)	Max decrease in ClNO_2 (%)	Max increase in ClNO_2 (pptv)	Max increase in ClNO_2 (%)
Aug 30–31	–332	–86	137	68
Aug 31–Sep 1	–706	–85	289	67
Sep 1–2	–896	–85	373	60
Sep 2–3	–273	–79	122	63
Sep 3–4	–200	–78	85	45
Sep 4–5	–322	–81	137	61
Sep 5–6	–194	–76	72	54
Sep 6–7	–808	–83	355	65
Sep 7–8	–579	–80	232	57
Sep 8–9	–654	–80	285	44

Table 5

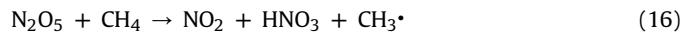
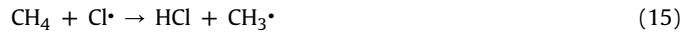
ClNO_2 yield parameterized by $[\text{Cl}^-]$ using k_{10}/k_{11} values reported by Behnke et al. (1997) and Roberts et al. (in press).

ClNO_2 yield (%)	Required $[\text{Cl}^-]$ (M) from Roberts et al. (in press)	Required $[\text{Cl}^-]$ (M) from Behnke et al. (1997)
1	0.001	0.001
10	0.014	0.007
50	0.123	0.066
75	0.370	0.199
90	1.111	0.598

over-predicted by a factor of 10 (25 M), then the yield would be above 99% (only a 4% increase). Consequently over-predictions of coarse PM chloride concentrations are not a serious concern. In contrast, either an over-prediction or an under-prediction of $[\text{Cl}^-]$ in fine PM will significantly affect ClNO_2 formation rates. As mentioned above, at 0.05 M the expected yield is between 29% and 40%. A tenfold over-prediction in chloride concentration (0.5 M) would cause a yield of between 80% and 88%. A tenfold under-prediction in chloride concentration (0.005 M) would cause a yield of between 4% and 7%. Thus the ClNO_2 yield is particularly sensitive to chloride concentration in the range of values found in submicron aerosols.

3.3. The role of ClNO_2 in atmospheric chlorine cycling

In this model simulation, chlorine is emitted into the atmosphere in two forms: particulate chloride from sea salt emissions and Cl_2 from anthropogenic sources. The anthropogenic Cl_2 photolyses to form chlorine radicals which proceed to participate in chemical reactions; HCl is a dominant product. This HCl can then partition into the particle-phase to form particulate chloride (the reverse phenomenon also occurs in which particulate chloride can partition to form gas-phase HCl). The particulate chloride and HCl reservoirs can be treated as one chloride reservoir since the model simulates that rapid equilibrium will be reached between gas and particle-phase chloride. Once chlorine is converted to HCl it can then react further to form ClNO_2 , which in turn photolyzes to create chlorine radicals. As previously stated, the chlorine radicals (whether from the photolysis of Cl_2 or ClNO_2) react to form HCl and other products. Because ClNO_2 acts both as a source and a sink for HCl, it forms a key step in chlorine cycling. Reactions (13)–(15) show an example of how this chlorine cycling can occur leading to net Reaction (16).



N_2O_5 does not react directly with gas-phase HCl. Instead, Reaction (13) is a representation of the net process that occurs when N_2O_5 reacts with particulate chloride and then HCl partitions into the particle form to replenish the loss of particulate chloride [essentially the same as Reaction (7)]. Reactions (13)–(15) provide a path by which chlorine may be continually cycled and reused in the atmosphere. It should also be noted that Reaction (15) is shown as one example of how $\text{Cl}\cdot$ can be transformed into HCl; there are a variety of other $\text{Cl}\cdot$ reactions in the CB IV chemical mechanism that also lead to the formation of HCl. However, without the inclusion of ClNO_2 , there is no pathway in the chemical mechanisms used in current air quality models for non-reactive chloride (in the form of HCl or particulate chloride) to be quickly transformed back into reactive chlorine. The reaction of OH radicals with HCl to form a Cl radical and water has the potential to also cycle chlorine, but is not included in the CB IV chemical mechanism and was not considered here. In addition, it is important to note that Reaction (16) acts as a net radical source, while the $\text{OH} + \text{HCl}$ reaction simply converts a HO_x radical into a chlorine radical.

To quantify the amount of ClNO_2 that results from the cycling described above, two more simulations were performed. These simulations modeled ClNO_2 as a chlorine sink. Photolysis was simulated using Reaction (17) instead of Reaction (14).



One of the simulations used the N_2O_5 chemistry from the base simulation and the other simulation used the N_2O_5 chemistry from the inland ClNO_2 formation sensitivity run. Comparisons of total ClNO_2 mass present before dawn (at 5am) each morning in the runs with chlorine cycling and in the new runs which do not cycle chlorine through ClNO_2 are shown in Table 6. Decreases in total ClNO_2 mass from the base case heterogeneous run to the simulation using Reaction (17) range from 28 to 56%. Decreases in total ClNO_2 mass from the original inland ClNO_2 formation run to the simulation using Reaction (17) range from 55 to 69%. The model simulations predict that a large portion of the ClNO_2 in Southeast Texas has cycled through ClNO_2 on previous nights.

This cycling is important because it means that greater amount of chlorine will be in a form that is easily photolyzed into chlorine radicals which have an important impact on urban ozone formation as discussed in Simon et al. (2009) and Chang and Allen (2006a). Figs. 9 and 10 show total photolabile chlorine mass in the simulations with and without cycling through ClNO_2 in the base case and inland formation simulations respectively. In these simulations the

Table 6

Decreases in ClNO_2 mass at 5am in the 4 km domain resulting from turning off chlorine cycling through ClNO_2 .

Date	Base case run			Inland Cl run		
	ClNO_2 mass: Cl cycling (metric tons)	ClNO_2 mass: no Cl cycling (metric tons)	Decrease in ClNO_2 mass (%)	ClNO_2 mass: Cl cycling (metric tons)	ClNO_2 mass: no Cl cycling (metric tons)	Decrease in ClNO_2 mass (%)
31-Aug	4.8	2.7	44	103.8	36.5	65
1-Sep	9.7	7.0	28	113.6	46.9	59
2-Sep	15.7	11.4	28	97.4	43.8	55
3-Sep	16.5	9.8	40	88.6	35.2	60
4-Sep	14.7	10.6	28	80.9	32.4	60
5-Sep	10.7	4.9	55	97.4	30.4	69
6-Sep	11.3	4.9	56	156.4	53.9	66
7-Sep	29.6	19.8	33	125.2	54.5	57
8-Sep	51.7	31.3	39	165.8	64.8	61
9-Sep	52.3	35.2	33	197.5	84.0	58

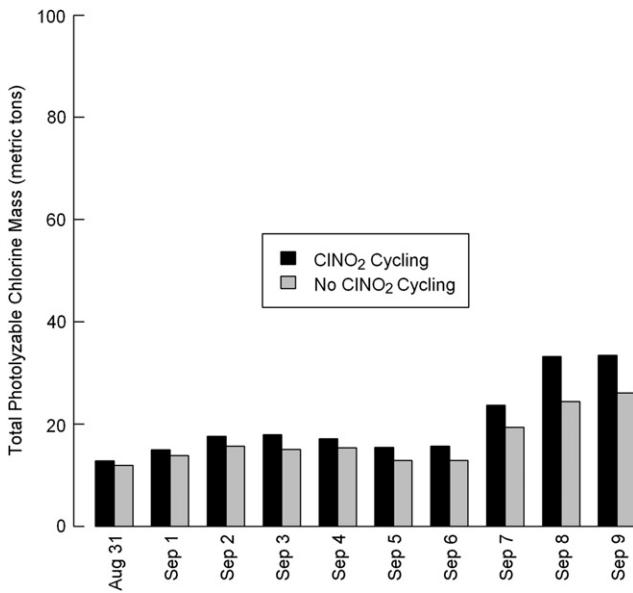


Fig. 9. Total daily photolabile chlorine mass present (Cl_2 and CINO_2) with and without cycling through CINO_2 for simulations that only allowed CINO_2 formation in marine grid cells.

majority of photolabile chlorine is in the form of Cl_2 and CINO_2 . Daily photolabile chlorine mass in Figs. 9 and 10 was calculated as total 24 h emissions of Cl_2 plus total CINO_2 mass present just before sunrise. These figures show that when cycling through CINO_2 is shut off, the total reactive chlorine mass in the atmosphere decreases significantly. On some days over two thirds of the reactive chlorine mass present in the atmosphere has been cycled through CINO_2 . Properly modeling this process will be important for properly simulating chlorine chemistry in regional photochemical models.

One additional factor must be considered when evaluating the impact of CINO_2 formation on chlorine cycling: deposition. HCl from the cycling pathway described above is mostly formed in the

first few hours after sunrise when CINO_2 photolyses. For CINO_2 to play a major role in chlorine cycling, this HCl must remain in the atmosphere through the day (at least 12 h) since the CINO_2 formation process occurs predominately at night. If the deposition lifetime of HCl were short (on the order of several hours), then the majority of HCl formed through Reaction (15) and similar reactions would be lost before it could react with N_2O_5 to form CINO_2 . CAMx models dry deposition based on the methods developed by Wesely (1989) which account for Henry's law, diffusion, reactivity, and surface resistance. An average deposition lifetime for the entire 4 km modeling domain (including the boundary layer and the free troposphere) was calculated as the total mass of HCl (moles) divided by the deposition rate of HCl (moles day⁻¹). During the modeling simulation this value was 16.8 days. The lifetime with respect to deposition within the boundary layer is considerably shorter and was calculated as the average dry deposition velocity (m s^{-1}) divided by the boundary layer height (m). The deposition lifetime for HCl during the simulation in the boundary layer was 3.1 days in marine areas and 0.74 days (17.8 h) in terrestrial areas. These deposition lifetimes for HCl are in the same range as the global deposition lifetime reported by Graedel and Keene (1995) for HCl: 1.44 days in the boundary layer and 73 days in the free troposphere. Even with the relatively short deposition lifetime of HCl in the boundary layer, reactions of particulate chloride with N_2O_5 lead to significant chlorine cycling. This process appears to compete effectively with deposition as a major loss/transformation process for HCl and particulate chloride.

Previous modeling studies have looked at other chlorine cycling pathways in the atmosphere. Notably, the reaction of OH radicals with HCl to form a Cl radical and water has the potential to also cycle chlorine (Pechtl and von Glasow, 2007). However, that reaction cycles a smaller amount of Cl than the heterogeneous N_2O_5 reaction pathway under the heavily polluted conditions encountered in this study. With a rate constant of $8 \times 10^{-13} \text{ cm}^3 \text{ molecule-s}^{-1}$, the reaction rate in heavily polluted conditions (HCl concentration of 1 ppbv and OH concentration of 0.5 pptv) is approximately 30 pptv h^{-1} during the day and much less at night when OH concentrations are small. Over the period of 12 h of sunlight, the $\text{HCl} + \text{OH}$ reaction could create approximately 360 pptv of $\text{Cl}\cdot$ with no dilution, much less than CINO_2 concentrations measured by Osthoff et al. (2008). Other chlorine cycling pathways (reactions of OH, ClONO_2 , and NO_3 on sea salt aerosols to produce Cl_2) have been modeled by Knipping and Dabdub (2003). They reported that the chemistry only led to maximum Cl_2 concentrations of 12 pptv in the late evening and pre-dawn. The CINO_2 concentrations measured by Osthoff et al. (2008) were two orders of magnitude greater than the Cl_2 concentrations from the Knipping and Dabdub modeling. Although these previous studies show that other chlorine cycling pathways may exist in the atmosphere, the ambient measurements made by Osthoff et al. (2008) are direct evidence that the CINO_2 pathway is an important chlorine cycling mechanism in a major urban area.

4. Conclusions

The work reported here examined the effect of chloride limitation on CINO_2 formation using a regional photochemical model. Modeling predicted peak CINO_2 concentrations of above 1 ppbv based on parameters specific to Southeast Texas, which were in line with measurements made in this region. These concentrations may not be applicable to other regions.

This work identified key uncertainties in the modeling of heterogeneous N_2O_5 chemistry including yield of CINO_2 and the availability of chloride at inland locations. Eliminating the dependence of CINO_2 formation on chloride availability caused increases in CINO_2 mixing ratios of up to a factor of 13. This suggests that chloride

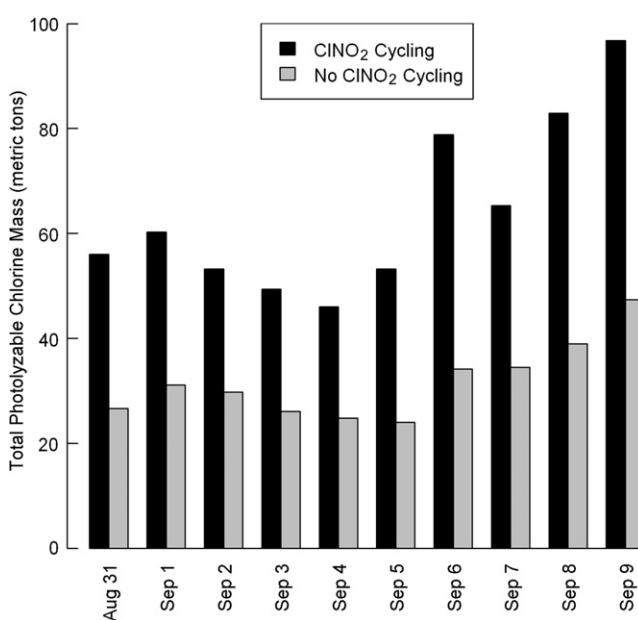


Fig. 10. Total daily photolabile chlorine mass present (Cl_2 and CINO_2) with and without cycling through CINO_2 for simulations that allowed CINO_2 formation both at marine and inland locations.

availability is a major limiting factor in this process at ground level. The sensitivity run which allowed ClNO_2 formation to occur at terrestrial locations predicted that chloride mixing ratios are high enough inland to cause significant ClNO_2 formation over the entire Houston area. Sensitivity runs showed that the modeled ClNO_2 concentration is very sensitive to yield. Although this parameter is highly uncertain, the yields used in this study are as accurate as any other in the absence of realistic model simulation for aerosol chloride molarity. Further work is suggested to increase model accuracy in predicting particulate chloride concentrations so that yield can be more accurately simulated in the future. In addition, there are two major areas for which field studies are needed to better understand the chemistry investigated in this work. First, no measurements of ClNO_2 have been made at inland locations. Further field work is suggested to verify the model prediction that significant ClNO_2 mixing ratios may occur over land. Second, more ambient measurements are needed to determine if parameterization of ClNO_2 yield based on laboratory data hold in the ambient atmosphere.

Finally, this work not only evaluated the effect of chloride availability on ClNO_2 formation, but also investigated how this formation process may affect chlorine cycling in the atmosphere. Modeling analyses suggest that chemical cycling of chlorine through HCl and ClNO_2 is important and that on many nights the majority of photolabile chlorine present in the atmosphere goes through chloride/active chlorine cycling. Although modeling techniques here predict an upper-bound for the effect of ClNO_2 chemistry, this work shows that ClNO_2 plays an important role in chlorine cycling. Current photochemical air quality modeling programs do not include this cycling pathway for chlorine, so once Cl radicals react to form HCl there is no efficient pathway to convert the chloride back into reactive species. Other pathways not included in this modeling could also lead to chlorine cycling in the atmosphere (although to a lesser degree under conditions relevant to southeast Texas) and should be included in future modeling studies. The work described here has shown that in order to properly model atmospheric chlorine chemistry and its effects on urban air pollution in Southeast Texas, it will be essential to include this ClNO_2 formation pathway and chlorine cycling mechanism. Although this work used modeling parameterized specific to Southeast Texas, the general mechanism in which Cl cycles between HCl during the day and ClNO_2 at night may be more widely applicable and should be investigated more fully through modeling and measurement studies in other regions.

Disclaimer

The United States Environmental Protection Agency through its Office of Research and Development collaborated in the research described here. It has been subjected to Agency review and approved for publication.

Acknowledgements

Support for this work was provided by the Texas Air Research Center.

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2009.09.006.

References

Aldener, M., Brown, S.S., Stark, H., Williams, E.J., Lerner, B.M., Kuster, W.C., Goldan, P.D., Quinn, P.K., Bates, T.S., Fehsenfeld, F.C., 2006. Reactivity and loss mechanisms of NO_3 and N_2O_5 in a marine environment: results from in-situ measurements during NEAQS 2002. *Journal of Geophysical Research* 111, D23S73. doi:10.1029/2006JD007252.

Behnke, W., George, C., Scheer, V., Zetzsch, C., 1997. Production and decay of ClNO_2 , from the reaction of gaseous N_2O_5 with NaCl solution: bulk and aerosol experiments. *Journal of Geophysical Research – Atmospheres* 102 (D3), 3795–3804.

Brown, S., Ryerson, T., Wollny, A., Brock, C., Peltier, R., Sullivan, A., Weber, R., Dube, W., Trainer, M., Maegher, J., Fehsenfeld, F., Ravishankara, A., 2006. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. *Science* 311, 67–70.

Brown, S., Dube, W.P., Fuchs, H., Ryerson, T.B., Wollny, A.G., Brock, C.A., Bahreini, R., Middlebrook, A.M., Neuman, J.A., Atlas, E., Roberts, J.M., Osthoff, H.D., Trainer, M., Fehsenfeld, F.C., Ravishankara, A.R., 2009. Reactive uptake coefficients for N_2O_5 determined from aircraft measurements during the second Texas air quality study: comparison to current model parameterizations. *Journal of Geophysical Research* 114, D00F10. doi:10.1028/2008JD011679.

Chang, S., Allen, D.T., 2006a. Atmospheric chlorine chemistry in southeast Texas: impacts on ozone formation and control. *Environmental Science and Technology* 40, 251–262.

Chang, S., Allen, D.T., 2006b. Chlorine chemistry in urban atmospheres: aerosol formation associated with anthropogenic chlorine emissions in southeast Texas. *Atmospheric Environment* 40 (S2), S512–S523.

Davis, J.M., Bhave, P.V., Foley, K.M., 2008. Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium sulfate and nitrate. *Atmospheric Chemistry and Physics* 8, 5295–5311.

Jack Dibb, Research Associate Professor, Climate Change Research Center, University of New Hampshire, Durham, NH. Personal Communication, February 2009.

ENVIRON International Corporation, 2008. User's Guide to the Comprehensive Air Quality Model with Extensions, Version 4 Accessed at: <http://www.camx.com>.

Evans, M.J., Jacob, D.R., 2005. Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH. *Geophysical Research Letters* 32, L09813. doi:10.1029/2005GL022469.

Finlayson-Pitts, B.J., Ezell, M.J., Pitts Jr., J.N., 1989. Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and ClONO_2 . *Nature* 337, 241–244.

Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. *Journal of Geophysical Research* 94, 925–956.

Graedel, T.E., Keene, W.C., 1995. Tropospheric budget of reactive chlorine. *Global Biogeochemical Cycles* 9 (1), 47–77.

Knipping, E.M., Dabdub, D., 2003. Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. *Environmental Science and Technology* 37, 275–284.

Morris, R.J., Koo, B., Yarwood, G., 2005. Evaluation of multisectional and two-sectional particulate matter photochemical grid models in the western United States. *Journal of the Air and Waste Management Association* 55, 1683–1693.

Nenes, A., Pandis, S.N., Pilinis, C., 1998. ISORROPIA: a new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. *Aquatic Geochemistry* 4 (1), 123–152.

Ngan, F., 2008. Classification of Weather Patterns and Improvement of Meteorological Inputs for TexAQS-II Air Quality Simulations. Ph.D. dissertation. University of Houston.

Osthoff, H.D., Roberts, J.M., Ravishankara, A.R., Williams, E.J., Lerner, B.M., Sommariva, R., Bates, T.S., Coffman, D., Quinn, P.K., Dibb, J.E., Stark, H., Burkholder, J.B., Talukdar, R.K., Maegher, J., Fehsenfeld, F.C., Brown, S.S., 2008. High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nature Geosciences* 1 (5), 323–328.

Pandis, S.N., Wexler, A.S., Seinfeld, J.H., 1993. Secondary organic aerosol formation and transport II, predicting the ambient secondary organic aerosol size distribution. *Atmospheric Environment* 27A, 2403–2416.

Pechtl, S., von Glasow, R., 2007. Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: a model study. *Geophysical Research Letters* 34, L11813.

Roberts, J.M., Osthoff, H.D., Brown, S.S., Ravishankara, A.R., Coffman, D., Quinn, P., Bates, T., Laboratory studies of products of N_2O_5 uptake on Cl^- containing substrates, *Geophysical Research Letters*, 2009GL0400448, in press.

Santarpia, J.L., Li, R., Collins, D.R., 2004. Direct measurement of the hydration state of ambient aerosol populations. *Journal of Geophysical Research – Atmospheres* 109, D18209. doi:10.1029/2004JD004653.

Schweitzer, F., Mirabel, P., George, C., 1998. Multiphase chemistry of N_2O_5 , ClNO_2 , and BrNO_2 . *Journal of Physical Chemistry* 102, 3942–3952.

Simon, H., 2008. Heterogeneous N_2O_5 Chemistry in the Houston Atmosphere. Ph.D. dissertation. University of Texas at Austin. Available through the UT Libraries at: <http://www.lib.utexas.edu/etd/d/2008/simonh18695/simonh18695.pdf#page=3>.

Simon, H., Allen, D.T., Wittig, A.E., 2008. Fine particulate matter emissions inventories: comparison of emissions estimates with observations from recent field programs. *Journal of the Air and Waste Management Association* 58 (2), 320–343.

Simon, H., Kimura, Y., McGaughey, G., Allen, D.T., Brown, S.S., Osthoff, H.D., Roberts, J.M., Byun, D., Lee, D., 2009. Modeling the impact of ClNO_2 on ozone formation in the Houston area. *Journal of Geophysical Research* 114, D00F03. doi:10.1029/2008JD010732.

Tanaka, P.L., Allen, D.T., McDonald-Buller, E.C., Chang, S., Kimura, Y., Mullins, C.B., Yarwood, G., Neece, J.D., 2003. Development of a chlorine mechanism for use in the carbon bond IV chemistry model. *Journal of Geophysical Research – Atmospheres* 108 (D4), 4145.

Tesche, T.W., Morris, R., Tonnesen, G., McNally, D., Boylan, J., Brewer, P., 2006. CMAQ/CAMx annual 2002 performance evaluation of the eastern US. *Atmospheric Environment* 40, 4906–4919.

Thornton, J.A., Abbott, J.P.D., 2005. N_2O_5 reaction on submicron sea salt aerosol: kinetics, products, and the effect of surface active organics. *Journal of Physical Chemistry* 109, 10004–10012.

Wang, L., Thompson, T., McDonald-Buller, E.C., Webb, A., Allen, D.T., 2007. Photochemical modeling of emissions trading of highly reactive volatile organic compounds in Houston, Texas. 2. Incorporation of chlorine emissions. *Environmental Science and Technology* 41, 2103–2107.

Wesely, M.L., 1989. Parameterization of surface resistances to gaseous dry deposition in regional-scale numeric models. *Atmospheric Environment* 23, 1293–1304.

Yarwood, G., Whitten, G.Z., Rao, S., 2005. Updates to the Carbon Bond 4 Photochemical Mechanism. Prepared for the Lake Michigan Air Directors Consortium, Des Plaines, IL. Available at: http://www.ladco.org/reports/rpo/modeling/camx_cb4.pdf.