

Modeling the impact of ClNO₂ on ozone formation in the Houston area

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[1] During the summer of 2006, nitryl chloride (ClNO₂) mixing ratios of over 1 ppb were measured in the Houston urban area. Nitryl chloride is potentially important to atmospheric chemistry in urban environments because its photolysis products include both NO₂ and chlorine atoms. Chlorine atoms have previously been shown to significantly increase ozone formation in urban Houston. Photochemical modeling was performed using the Comprehensive Air quality Model with extensions (CAMx) to estimate the effects of observed nitryl chloride concentrations on local chemistry in southeast Texas. CAMx was modified to include a formation mechanism for nitryl chloride as well as its photolysis reaction. Comparisons between model predictions and ambient measurements showed that the model-predicted ClNO₂ concentrations were within the range of observed data. Model simulations predict that ClNO₂ increases total reactive chlorine mass by 20–40% in the atmosphere of southeast Texas. Despite the high reactivity of chlorine, nitryl chloride caused only modest increases in ozone concentrations (up to 1.0–1.5 ppb when baseline 1-h average ozone concentrations were between 60 and 85 ppb). The chemistry and physical processes which affect ozone formation were further investigated using box model simulations and a Lagrangian process analysis tool (LPA) within the gridded photochemical modeling simulations. These analyses showed that vertical dispersion and local atmospheric composition moderated the effect of nitryl chloride on ozone mixing ratios.

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1. Introduction

[2] Understanding the physical and chemical processes that lead to ozone formation is essential to controlling ozone concentrations in urban areas. This is especially important in urban areas that are in nonattainment with EPA's National Ambient Air Quality Standards (NAAQS). Houston is currently classified as a moderate nonattainment area for ozone (U.S. Environmental Protection Agency, The Green Book Nonattainment Areas for Criteria Pollutants, 2007, <http://www.epa.gov/air/oaqps/greenbk/index.html>). Understanding the atmospheric chemistry in Houston poses a unique challenge due to the myriad pollution sources

specific to the area, including both typical urban emissions and large industrial emission sources. A substantial fraction of the nation's petrochemical facilities are located in southeast Texas and these sources release ozone precursors including nitrogen oxides (NO_x) and highly reactive volatile organic compounds (HRVOCs). In addition, Houston's atmosphere is influenced both by nearby emissions of biogenic volatile organic compounds and chemistry that occurs in the marine boundary layer.

[3] Radical concentrations in the atmosphere have an important effect on ozone formation and the overall photochemistry in urban environments. In the troposphere, O₃ is formed photochemically in the well-known HO_x and NO_x cycles. The key reactions are: oxidation of volatile organic compounds (VOCs) to organic peroxy radicals by radical species such as OH; reactions of organic peroxy radicals with NO, forming NO₂; and photolysis of NO₂ yielding atomic oxygen and subsequently ozone. Recent studies in Houston have shown that the chlorine radical may also play a role in ozone formation [Tanaka *et al.*, 2000, 2003a, 2003b, 2003c; Chang *et al.*, 2002; Sarwar and Bhawe, 2007]. These studies have identified a variety of factors that are important in determining the degree to which chlorine radicals enhance ozone formation. The composition of hydrocarbons in the atmosphere is important because the rates of chlorine radical reactions with some organic

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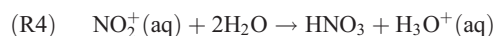
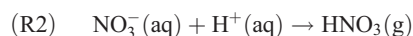
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compounds, specifically noncyclic alkanes, can be one to two orders of magnitude larger than reactions rates of hydroxyl radicals with the same compounds [Atkinson *et al.*, 1999; Sander *et al.*, 2006; Ragains and Finlayson-Pitts, 1997]. This means that Cl enhances ozone formation because it reacts quickly with compounds that do not readily react with OH radicals. Tanaka *et al.* [2000] demonstrated this point in chamber experiments which found that almost ten moles of ozone were formed for every mole of chlorine added when only pentane was present and the VOC/NO_x ratio was low. In contrast, only around five moles of ozone were formed for every mole of chlorine added when the VOC/NO_x ratio was higher and the VOC mixture included 56 different hydrocarbons (both alkanes and alkenes). In addition to VOC composition, it has also been shown the VOC/NO_x ratio impacts the effectiveness of Cl at enhancing ozone formation. Tanaka *et al.* [2003b] demonstrated this point using chamber experiments with Cl injections into ambient air and into air with increased NO_x concentrations.

[4] The chlorine radical sources studied by Tanaka *et al.* [2003a] included photolysis of Cl₂ and HOCl molecules. One source of atomic chlorine in Houston that has not been evaluated is the formation of nitryl chloride (ClNO₂) from sea salt and its subsequent photolysis. As part of a recent field campaign, the Texas Air Quality Study–Gulf of Mexico Atmospheric Composition and Climate Study (Tex-AQS-GoMACCS), tropospheric ClNO₂ was measured for the first time in an urban atmosphere aboard the R/V *Ronald H. Brown* [Osthoff *et al.*, 2008]. Measured nitryl chloride mixing ratios in the Houston Ship Channel reached over 1 ppb. Osthoff *et al.* [2008] linked nitryl chloride formation to uptake of N₂O₅ on chloride-containing aerosols as shown in reactions (R1)–(R4).



[5] The purpose of this paper is to estimate, using photochemical modeling, the effect of observed nitryl chloride concentrations on photochemistry, specifically ozone formation, in the Houston area. Comparisons of model predictions with ambient measurements were made, where possible, to evaluate the performance of the model.

2. Methods: Photochemical Modeling

[6] Modeling was performed using the Comprehensive Air Quality Model with extensions (CAMx) version 4.2 (ENVIRON International Corporation, <http://www.camx.com>). CAMx is a three dimensional Eulerian photochemical modeling program which simulates the effects of emissions, chemistry, advection, dispersion, and deposition on pollu-

tion concentrations. Several such models are readily available. CAMx was chosen for this work because the state of Texas uses it for their State Implementation Plan demonstrations. Therefore, modeling done with CAMx is most applicable to evaluating the implications of the chemistry considered in this work to regulatory decisions. In addition, previous modeling of chlorine chemistry in the Houston area was performed using CAMx [Chang *et al.*, 2002; Chang and Allen, 2006; Wang *et al.*, 2007]. Continuing to use CAMx facilitates comparisons with past studies.

[7] The modeling domain consisted of 3 nested grids: a large-scale grid with 36 km × 36 km cells covering most of the eastern United States, a regional grid with 12 km × 12 km cells covering large areas of Texas, Arkansas, Louisiana, and Mississippi, and a local grid with 4 km × 4 km cells focused on the Houston area. These grids are shown in Figure 1. The finest grid contained 28 vertical layers which spanned the lowest 15,000 m of the atmosphere. The layer closest to the ground was 34 m thick.

[8] The model runs simulated an episode that lasted from 30 August 2006 until 9 September 2006, one of the time periods when the R/V *Ronald H. Brown* traversed the Houston Ship Channel and Galveston Bay areas. The days 28 and 29 August were used as model spin-up days. Meteorological inputs for this time period were developed at the University of Houston using the Multiscale Nest-down Data Assimilation System (MUNDAS) [Ngan, 2008], which incorporates extensive meteorological observations with existing objective analysis and nudging tools in the Fifth-Generation PSU/NCAR Mesoscale Model (MM5) [Dudhia, 1993; Grell *et al.*, 1994]. The meteorological simulation results produce reasonable CO and ozone air quality simulation results as described by Byun *et al.* [2007].

[9] Emissions inputs were obtained from the Texas Commission on Environmental Quality (TCEQ) (Houston-Galveston-Brazoria 8-hour ozone SIP modeling, photochemical modeling data files, 2006, <http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb2.html>). The TCEQ has developed emissions inventories for ozone precursors as part of the modeling requirements for their State Implementation Plan for attaining the NAAQS for ozone (TCEQ, Houston-Galveston-Brazoria 8-hour ozone SIP modeling, photochemical modeling data files, 2006, <http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb2.html>). The emissions inventories were developed on the basis of data from the year 2000 and projected emissions for the year 2009. For this work, projected 2009 emissions were used since the only major difference between the 2009 emissions and the emissions at the time of the measurements (late 2006) would be reductions in vehicular emissions (both light and heavy-duty vehicles) due to fleet turnover and some increases in emissions due to population growth. In contrast, there were substantial differences between emissions in late 2006 and the emissions in the other comprehensive inventory, from 2000, due to significant emission reductions made as a result of Texas's State Implementation Plan. Emissions of NO_x from Houston area point sources, for example, were reduced by approximately 62% from 2000 to 2005 (2006 emission inventory reports are not yet available) (U.S. Environmental Protection Agency, Technology Transfer Network, Clearinghouse for Inventories and Emissions Factors, Criteria Pollutant Emissions

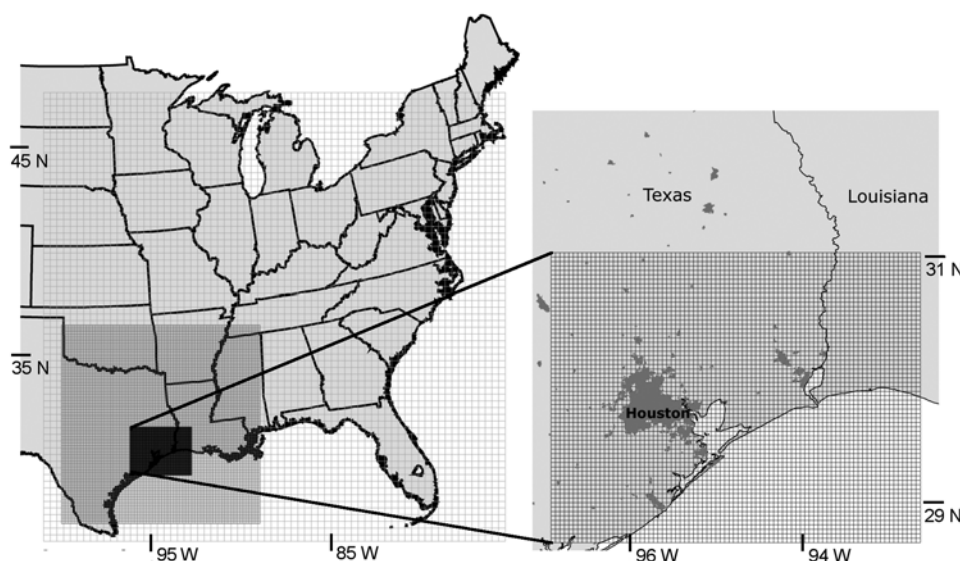
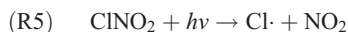


Figure 1. Nested domains used in CAMx modeling: 36 km × 36 km grid cells shown in light gray, 12 km × 12 km grid cells shown in medium gray, and 4 km × 4 km grid cells shown in dark gray.

Summary Files, 2008, <http://www.epa.gov/ttn/chief/net/critsummary.html>; TCEQ, 2005 Point Source Emissions Inventory, 2008, <http://www.tceq.state.tx.us/implementation/air/indusdei/psei/psei.html>). The lack of a specific 2006 emissions inventory does introduce uncertainty into the modeling results because of the fact that Cl impacts are affected by the NO_x/VOC ratio in ambient air. However, sensitivity analyses reported in this paper address that uncertainty. Finally, the inventory for direct, primary emissions of chlorine (as opposed to secondary chlorine formation due to the reactions of ClNO₂) developed by *Chang et al.* [2002] was used. The chlorine inventory included Cl₂ sources from cooling towers, industrial point sources, and swimming pools.

[10] The chemistry was modeled using Mechanism 1 of CAMx's Carbon Bond IV (CB IV) chemical mechanism [Gery *et al.*, 1989]. This mechanism includes chlorine chemistry but does not currently include nitryl chloride or any of its chemistry. Modifications were made to the source code to include nitryl chloride and its photolysis reaction (the dominant loss mechanism of this compound) (reaction (R5)).



[11] Photolysis rates for ClNO₂ were initially calculated by summing the product of quantum yield, absorption cross section, and actinic flux values across all wavelengths for several different zenith angles. Actinic flux values were estimated using NCAR's quick TUV calculator (available at http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/). Absorption cross section and yield values were taken from *Sander et al.* [2006]. On the basis of these calculations it was determined that nitryl chloride photolysis rates could be calculated within CAMx by using a scaling factor to the photolysis rate of formaldehyde. This scaling was done to simplify the execution of the model. Under standard conditions (ozone column of 300 Dobson units, albedo of 0.06,

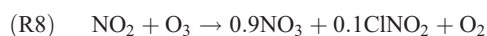
and a measurement height of 640 m), calculations at zenith angles of 0, 10, 20, 30, 40, 50, 60, 70, 78, and 86 degrees showed that scaling factor values had a standard deviation of less than five percent of the mean value. The scale factor used for this simulation was $j\text{ClNO}_2 = 10.05 \cdot j\text{Formaldehyde}$. Another possible loss mechanism is the recently discovered potential conversion of ClNO₂ to Cl₂ on acidic chloride-containing aerosols [Roberts *et al.*, 2008]. This loss pathway has not been explored here, but may be important to include in future modeling studies.

[12] In addition to photolysis, a formation mechanism for nitryl chloride was added to the model. There is considerable uncertainty in the yield rates and reactive uptake coefficients for the heterogeneous formation mechanism outlined in reactions (R1)–(R4). In addition, there are currently multiple versions of the CB IV chemical mechanism implemented in CAMx. One version includes gas-phase chlorine chemistry and a second version includes aerosol chemistry. There is no version that includes both aerosol and gas-phase chlorine chemistry, so it was not possible to use existing mechanisms to simultaneously simulate heterogeneous ClNO₂ formation and its effects as a gas-phase chlorine radical source. Therefore a gas-phase surrogate reaction was used to approximate ClNO₂ formation reactions in the model. The form and stoichiometry of this surrogate reaction were based on observational data. Measurements made aboard the R/V *Ronald H. Brown* of continental pollution plumes during TexAQS-GoMACCS showed that between 10% and 60% of the NO₃ formed by the reaction of NO₂ with ozone (reaction (R6)) is converted (via N₂O₅) to nitryl chloride [Osthoff *et al.*, 2008]. For simplicity, nitryl chloride formation was added to the model chemistry as a product of the reaction between NO₂ and O₃ (reaction (R8) replaces reaction (R6) below). It should be noted that reaction (R8) is not a balanced reaction, since it does not include as a reactant the aerosol chloride that is

Table 1. Maximum 1-h Average Ground Level Concentrations of ClNO₂ Predicted in the Initial Modeling Runs

Date	Maximum Concentration (ppt)	Time of Maximum Concentration (LT)
30 Aug	321	1200
31 Aug	313	2300
1 Sep	551	0400
2 Sep	719	0400
3 Sep	188	2100
4 Sep	197	0300
5 Sep	254	2200
6 Sep	416	2100
7 Sep	478	2300
8 Sep	563	0100
9 Sep	235	0100

involved in the formation of ClNO₂; the reaction in essence acts as a chlorine emission source.



[13] Reaction (R8) was only used in the 4 km and 12 km domains since the purpose of this study was to investigate the effects of local ClNO₂ production. The formation of ClNO₂ occurs mainly at night since N₂O₅ formation is suppressed during the daytime. In addition, reaction (R3) will only occur if chloride is present in the ambient aerosol. Generally this is true for aerosol that has a marine origin. Therefore, for initial test case simulations, the model was run so that reaction (R8) was only turned on at night over marine and shoreline grid cells (in all vertical layers). Shoreline grid cells covered the 4 km closest to the shore in the local grid and the 12 km closest to the shore in the regional grid. There is some uncertainty as to whether chlorine concentrations in ambient aerosols are high enough to lead to ClNO₂ formation further inland and aloft. Thus, the sensitivity of the model predictions to the horizontal and vertical extent of ClNO₂ was evaluated. In addition, sensitivity analyses examined the response of the model to changing other assumptions concerning the formation of ClNO₂.

[14] The assumptions regarding ClNO₂ production made here are simplistic and based on the limited information currently available about this chemistry. A more complete model would include the spatial distribution (both horizontal and vertical) of total aerosol surface area and chloride concentrations in the super and sub micron aerosol across the domain, as well as the production efficiency for ClNO₂ from N₂O₅ uptake to these aerosols as a function of chloride content. The lack of information on these parameters (particularly the chloride content and ClNO₂ yield) limits the accuracy of the current prediction. However, the assumption of a constant yield relative to the NO₂ + O₃ reaction over a limited spatial area along the coast provides a reasonable, if simplified, starting point for assessing the impact of ClNO₂ production on ozone formation in the

Houston area. Tests of these assumptions against the limited measurements of ClNO₂ that were available from the 2006 campaign are described below.

3. Results

3.1. Accuracy of the Surrogate Nitryl Chloride Formation Reaction

[15] The gas-phase surrogate reaction (reaction (R8)) is not intended to exactly replicate the mechanism of nitryl chloride formation, but instead is intended to represent the overall conversion of oxides of nitrogen into nitryl chloride over the modeling domain. To assess whether this approach was reasonable, simulated nitryl chloride concentrations were evaluated and compared to measured values. Daily maximum 1-h average ground level concentrations of ClNO₂, in the 4-km domain, predicted by the model, are shown in Table 1 for each of the eleven days of the episode. The model predicted that daily maximum 1-h average ClNO₂ concentrations ranged from 188 ppt to 719 ppt. All of these values are less than the maximum 60 s average ClNO₂ concentration measured aboard the R/V *Ronald H. Brown* (slightly more than 1300 ppt). However, the model predictions are in line with measured values when the measurements are averaged over a 1-h period. The maximum 1-h average measured ClNO₂ concentration ranged from 40 to 533 ppt during the time period from 30 August to 9 September 2006.

[16] The modeled horizontal extent of nitryl chloride concentrations depended on the day, but generally followed the path of urban and industrial plumes emitted from Houston, Texas, Beaumont, Texas, and Lake Charles, LA. Figure 2 shows the extent of ClNO₂ concentrations predicted in the 4 km grid on 1 and 8 September 2006.

[17] It is difficult to make exact comparisons between R/V *Ronald H. Brown* measurements and model predictions of nitryl chloride concentrations. Instruments on board the research vessel made measurements at a single point, while the model predicts average concentrations over 4 km × 4 km grid cells. However, comparisons of the median and range of concentrations can show whether model predictions are reasonable. Separate comparisons were made for nights during which the R/V *Ronald H. Brown* remained exclusively in the Houston ship channel (1–2, 6–7, and 7–8 September) and for nights during which the R/V *Ronald H. Brown* remained exclusively in the Gulf of Mexico (31 August to 1 September and 2–3, 3–4, and 4–5 September). Figure 3 shows the area defined as the ship channel in the model (black box). Comparisons between measurements and model predictions are shown in Figures 4 and 5. The median ClNO₂ concentration value for these four data sets (measured ship channel values, modeled ship channel values, measured Gulf of Mexico values, modeled Gulf of Mexico values) are indicated in Figures 4 and 5 by an asterisk. First and third quartile values are shown by the gray boxes and the whiskers extend to the minimum and maximum values. All four data sets show that the vast majority of ClNO₂ concentration values are low (below 200 ppt), with occasional peaks. The peaks in measured values are somewhat lower than modeled maxima (22% lower in the ship channel and 55% lower in the Gulf of Mexico). However, as discussed above, measurements were

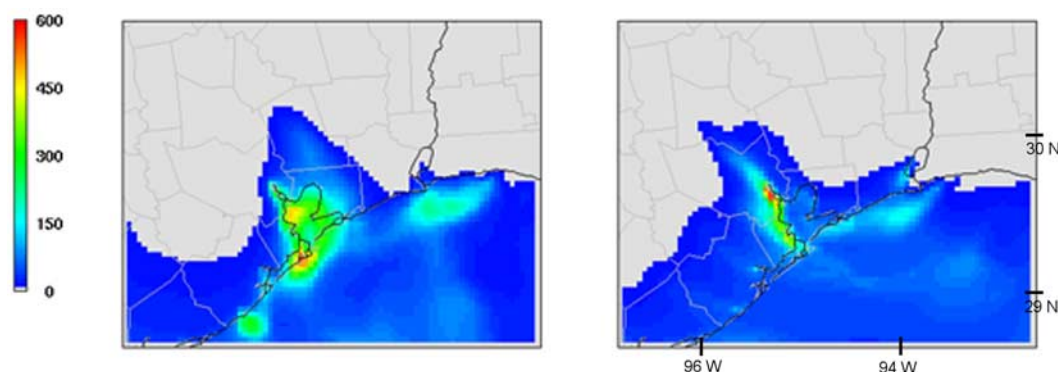


Figure 2. Predicted CINO₂ concentrations (ppt) (left) at 0400 LT on 1 September 2006 and (right) at 0100 LT on 8 September 2006.

at the location of the ship while the model was evaluated for all 4 km grid cells in the region of interest (Houston Ship Channel or Gulf of Mexico). It is likely that the ship did not intersect all of the plumes that contained the high CINO₂ concentrations. For example, in the Gulf of Mexico, some of the highest concentrations were predicted immediately adjacent to the shoreline and the R/V *Ronald H. Brown* generally traveled somewhat further out to sea where model predictions were lower. These differences in spatial averaging may contribute to the lower measured CINO₂ peaks. However, Figures 4 and 5 show that modeled CINO₂ values were generally within the range of observed CINO₂ concentrations. In addition, peak instantaneous ship measurements did show concentrations higher than the peak hourly CINO₂ concentrations predicted by the model.

3.2. Comparison With Ambient Measurements of a Chlorine Chemistry Tracer

[18] 1-chloro-3-methyl-3-butene-2-one (CMBO) is a unique product of isoprene and chlorine radicals and has been previously used as a molecular marker of chlorine chemistry [Ragains and Finlayson-Pitts, 1997; Reimer, 2001; Tanaka et al., 2003c; Chang and Allen, 2006]. Chang and Allen [2006] evaluated the accuracy of the Houston anthropogenic Cl₂ inventory by comparing model predictions of CMBO concentrations to measured values from the summer of 2000 at the LaPorte airport (location is shown in Figure 3). The modeling period spanned from 22 August to 6 September 2000. The model included isoprene emissions from both biogenic and industrial sources, although biogenic sources dominate in this area. Both modeled and measured values showed sharp increases in CMBO mixing ratios at ground level in the early morning. Measured peaks were over twice as high as model predictions, but daily average CMBO concentrations from model predictions were comparable to measured values.

[19] Since no previous chlorine evaluations have included nitryl chloride, it was of interest to repeat the analysis done by Chang and Allen [2006] with the inclusion of nitryl chloride. Maximum predicted CMBO concentrations in the 44 km × 44 km region centered at the LaPorte Airport (the same region used by Chang and Allen [2006] in their comparisons) were evaluated in modeling runs with and without nitryl chloride chemistry included. The two runs used ozone precursor emissions and meteorological inputs

developed by TCEQ for 23–30 August 2000 (TCEQ, Houston-Galveston-Brazoria 8-hour ozone SIP modeling, photochemical modeling data files, 2006, <http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb2.html>). The days 23 and 24 August were used as model spin-up days, so concentrations for those 2 days were not evaluated. These inputs are similar to those used by Chang and Allen [2006], who also used inputs developed by the Texas Commission on Environmental Quality. However, the TCEQ continually updates and improves on its model inputs, so the current files, specifically the meteorological inputs, are not identical to inputs from Chang and Allen

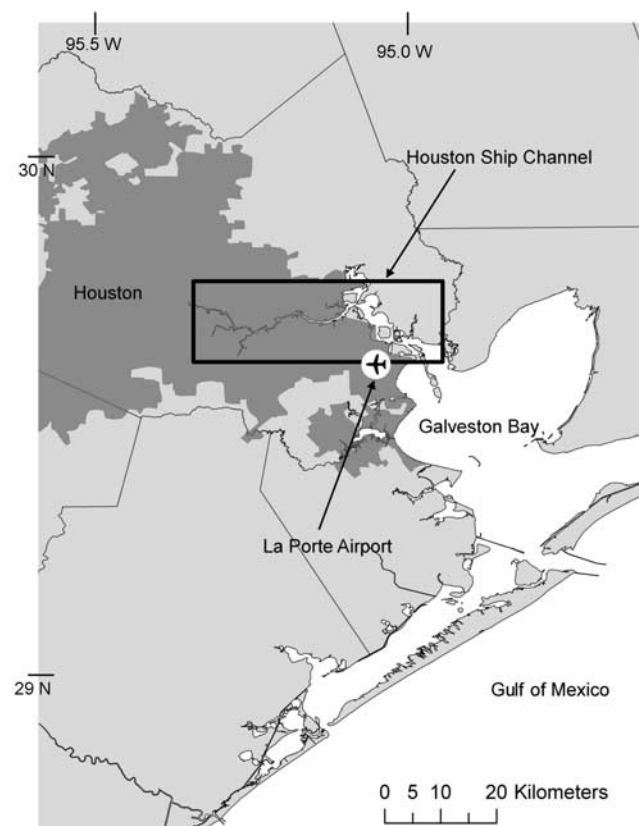


Figure 3. Ship channel location in the modeling runs (black box) and LaPorte Airport location (white circle).

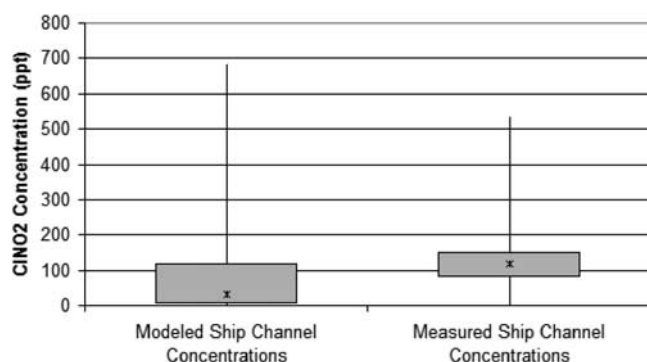


Figure 4. Box and whisker chart comparison of measured and modeled CINO₂ concentrations (ppt) in the Houston Ship Channel on the nights of 1–2, 6–7, and 7–8 September. Concentrations from model predictions are 1-h averages for individual grid cells. Concentrations from ship measurements are also 1-h averages.

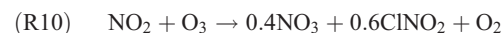
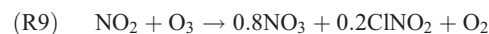
[2006]. The base case run used the standard CAMx CB IV chemical mechanism which includes chlorine and the chlorine emissions inventory used was developed by *Chang and Allen* [2006]. The nitryl chloride run used the nitryl chloride chemistry described above as an additional source of chlorine radicals. Figure 6 shows predicted CMBO concentrations in the simulations as well as CMBO increases (in percent) in the simulation including CINO₂ chemistry. The base case results look qualitatively similar to those reported by *Chang and Allen* [2006], however, predicted peak concentrations are about 1.5 to 2 times lower. This is due to updates in meteorological input files made by the TCEQ, which increase the extent of vertical mixing, and therefore decrease ground level concentrations of isoprene and atomic chlorine precursors, which are emitted at ground level. As seen in Figure 6, including CINO₂ in the analysis only increased CMBO concentrations by 0.5 to 1.5% for this episode. This is likely due to the fact that CMBO is a reaction product of chlorine radicals and isoprene, and isoprene is highly concentrated near biogenic ground-level sources while CINO₂ is concentrated in areas where NO_x plumes meet the marine atmosphere. In addition, isoprene emissions peak in the late afternoon while most CINO₂ is converted into chlorine radicals within a few hours after sunrise. Therefore, even though CINO₂ may contribute significantly to the total mass of reactive chlorine in the boundary layer, it has a minor impact on CMBO formation. Since the biogenic source of isoprene does not coincide either spatially or temporally with CINO₂ sources, CMBO is not the best indicator for CINO₂ formation processes. The observed CMBO concentrations do indicate a substantial ground level atomic chlorine source, but that source is unlikely to be a nighttime reaction involving N₂O₅ and sea salt.

3.3. Sensitivity of CINO₂ Concentrations to Model Assumptions

3.3.1. Sensitivity to Branching Ratio

[20] While the surrogate formation reaction being used to create CINO₂ in the model simulations provides reasonable estimates of atmospheric concentrations, there is uncertainty

in the branching ratio for the formation reaction. The current modeling assumes that the molar ratio of CINO₂ to NO₃ in reaction (R8) is 1:9. This is equivalent to a 10% yield for CINO₂ with respect to the NO₃ produced from the reaction of NO₂ and O₃ (the lower end of observed yields). Measurements from the R/V *Ronald H. Brown* show that this ratio can be higher under some circumstances. An aged marine pollution plume from an unknown source was measured east of the Florida coast. In this plume the yield of CINO₂, relative to NO₃ produced from NO₂ + O₃, was over 60% [Osthoff et al., 2008]. The exact conditions that lead to such a large percentage of NO₃ being converted into CINO₂ (emission of the plume into a relatively clean marine environment where uptake of N₂O₅ to sea salt should not compete with other N₂O₅ and NO₃ loss mechanisms) is not typical of the Houston area. It is uncertain whether such high yields are found in the Houston atmosphere as researchers had difficulty assessing CINO₂ yields in the Houston area because of the presence of local NO_x and ozone sources. Therefore the sensitivity of the model to the branching ratio used in this calculation was tested. Two additional model runs were performed in which the CINO₂ formation reactions were changed from reaction (R8) to reactions (R9) and (R10). Again, it should be noted that reactions (R9) and (R10) are not balanced and therefore act as chlorine sources.



[21] The effects of doubling the CINO₂ yield (using reaction (R9) instead of reaction (R8)) on CINO₂ and ozone concentrations were linear. CINO₂ concentrations doubled consistently throughout the 4 km domain. In addition, the ozone increases in the run using reaction (R9) compared to the base case run with no CINO₂ formation were almost exactly double those from the initial nitryl chloride run (using reaction (R8)) compared to the base case run. This

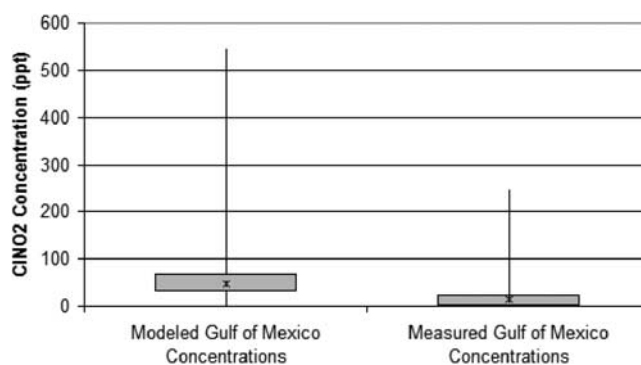


Figure 5. Box and whisker chart comparison of measured and modeled CINO₂ concentrations (ppt) in the Gulf of Mexico on the nights of 31 August to 1 September and 2–3, 3–4, and 4–5 September. Concentrations from model predictions are 1-h averages for individual grid cells. Concentrations from ship measurements are also 1-h averages.

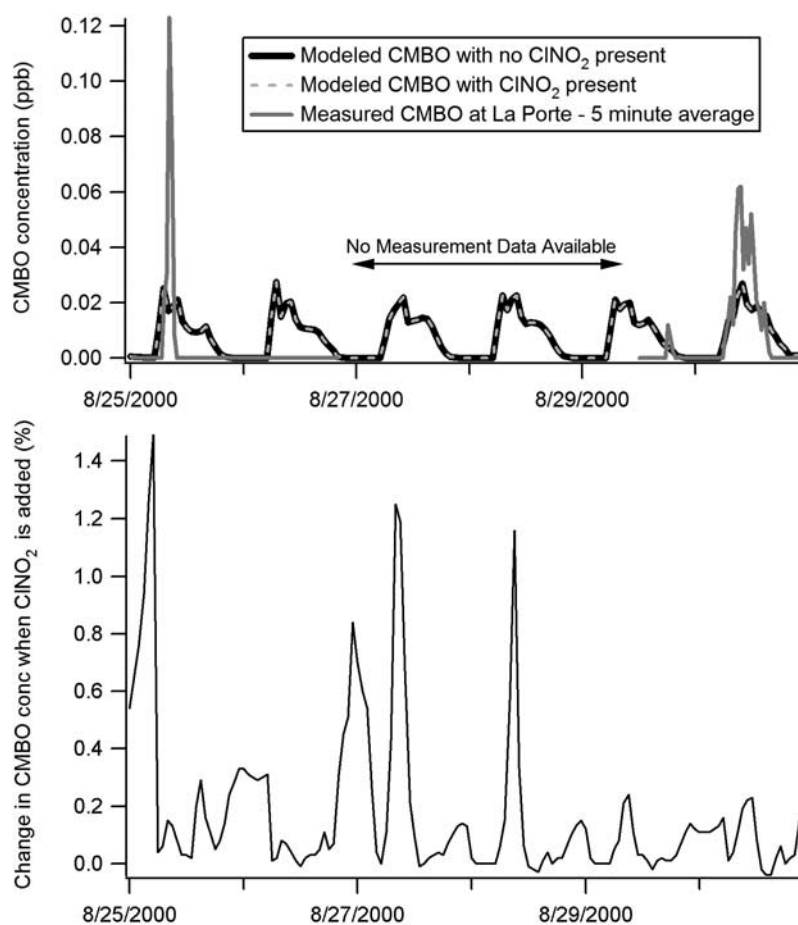


Figure 6. (top) Modeled and measured CMBO concentrations at La Porte and (bottom) changes in CMBO due to addition of CINO₂. Modeled values represent the maximum concentration predicted in the 11×11 grid cell area centered on La Porte.

too was consistent throughout the entire 4 km modeling domain and throughout the entire modeling episode. The effect of multiplying the branching ratio by 6 (using reaction (R10) instead of reaction (R8)) was also essentially linear. There was slightly more variation than in the doubling case, but in general both the CINO₂ and ozone responses increased by a factor of 6 ± 0.6 . The fact that ozone formation had a linear response to increased CINO₂ concentrations indicates that the atmosphere during this pollution episode was radical limited.

3.3.2. Sensitivity to Variations in CINO₂ Formation With Height

[22] An additional assumption made in the analysis was that the same CINO₂ formation process occurred at all elevations. This would be a reasonable assumption if aerosol surface area concentrations and aerosol composition were similar at ground level and aloft. If, however, either of these factors is significantly different at higher elevation, then the formation mechanism for CINO₂ may not be the same at all heights.

[23] A first step in assessing the potential importance of changes in CINO₂ formation reactions with height is to determine the extent to which formation varies with height in the current model formulation. The model predicts that nitryl chloride concentrations decrease with height. However, the rate at which this decrease occurs varied significantly

from day to day. The maximum concentration decreased more rapidly in the first 500 m of atmosphere in cases where the maximum ground level concentrations were highest. Evaluations of the maximum concentration in each vertical grid layer were made at the hour when ground level concentrations were greatest for each day. The height at which the maximum concentration in the 4 km domain dropped below 50% of the maximum ground level concentration ranged from 257 m to 1847 m. The height at which the maximum concentration in the 4 km domain dropped below 10% of the maximum ground level concentration ranged from 928 m to 3026 m. Figures 7 and 8 show how the maximum CINO₂ concentration in the 4 km domain varied with height.

[24] While maximum concentrations are important, it is also important to characterize the total amount of CINO₂ present. Figure 9 shows the total mass of nitryl chloride present in the 4 km domain at or below each height. This gives a more complete picture of how much total nitryl chloride is predicted to be present aloft. Again, with this metric there is variation from day to day. Generally the height below which 50% of the mass is predicted to be present ranges from 450 to 700 m and the height below which 90% of the mass is present ranges from 1200 to 2300 m. It should be noted that the predicted vertical distribution of CINO₂ is based on the model calculation of CINO₂

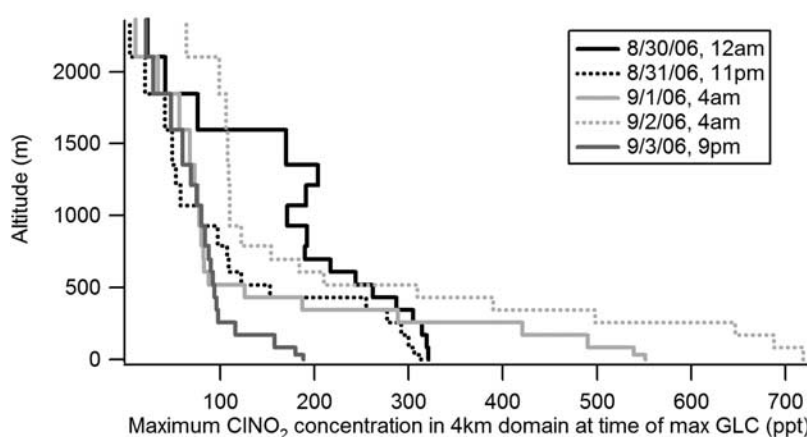


Figure 7. Vertical distribution of maximum CINO₂ concentrations in the 4 km domain: 30 August to 3 September.

formation from reaction (R8). Therefore, the model predictions are based on NO₂ and O₃ concentrations, but not on aerosol chloride concentrations as these are not explicitly included in the model. Therefore these predictions rely on the assumption that in marine environments CINO₂ formation is not limited by particulate chloride availability.

[25] These data show that the model predicts significant chlorine mass from nitryl chloride formation. Figure 9 indicates that total CINO₂ in the nighttime atmosphere ranges from about 4000 to 9000 kg in the 4 km domain. This translates to about 1700 to 4000 kg of reactive chlorine mass in the form of nitryl chloride. Previous emissions inventories for chlorine in the Houston area reported that Cl₂ and HOCl sources released about 10,000 kg of reactive chlorine per day concentrated at ground level [Chang and Allen, 2006]. Therefore these model runs predict that nitryl chloride would increase total tropospheric reactive chlorine mass by 20 to 40% in southeast Texas.

[26] A sensitivity run was performed to evaluate the implications of the assumption that CINO₂ formation occurs at all heights. In this simulation, the formation of CINO₂ was shut off at elevations greater than 600 m. This sensitivity analysis was performed because chloride in aerosols primarily originates from sea salt. Since the source is at ground level, aerosols at higher elevations may not contain

enough chloride for nitryl chloride formation to proceed. Ground level concentrations of CINO₂ and ozone in the 4 km domain were compared for the original case (CINO₂ formation at all elevations) and for the case in which formation only occurred below 600 m. In the case where there was no formation above 600 m, CINO₂ concentration decreases in a single grid cell were up to 46 ppt. On most simulation days, the decrease in the maximum ground level concentration of CINO₂ was less than 1%. The two exceptions were on 4 September 2006 (model predicted a 9.6% decrease in maximum ground level concentration from 197 to 178 pptv) and 9 September 2006 (model predicted a 1.7% decrease in maximum ground level concentration from 235 to 231 pptv). The effects of turning off CINO₂ formation aloft were more significant for ozone formation. In the case where there was no CINO₂ formation above 600 m, ground level ozone concentration increases due to CINO₂ were decreased by up to 0.4 ppb in a single grid cell. The maximum ground level ozone increases caused by CINO₂ were decreased by 2–28% depending on the day. To date, no measurements of CINO₂ have been made aloft. In the future it will be important to make these measurements in order to accurately represent CINO₂ formation and its effect on ozone formation at ground level.

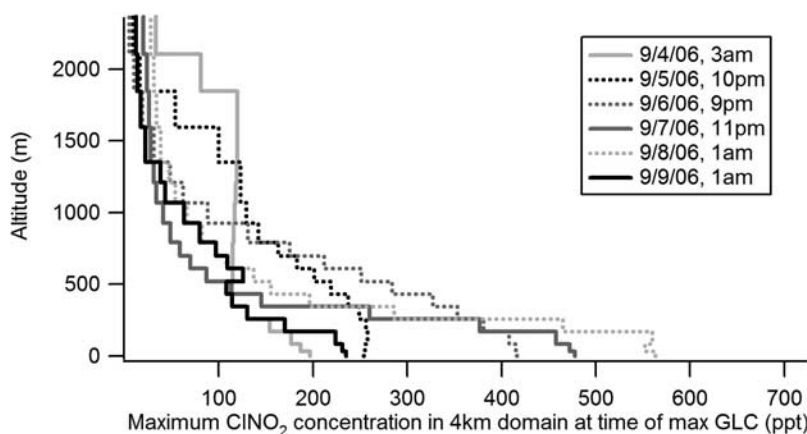


Figure 8. Vertical distribution of maximum CINO₂ concentrations in the 4 km domain: 4–9 September.

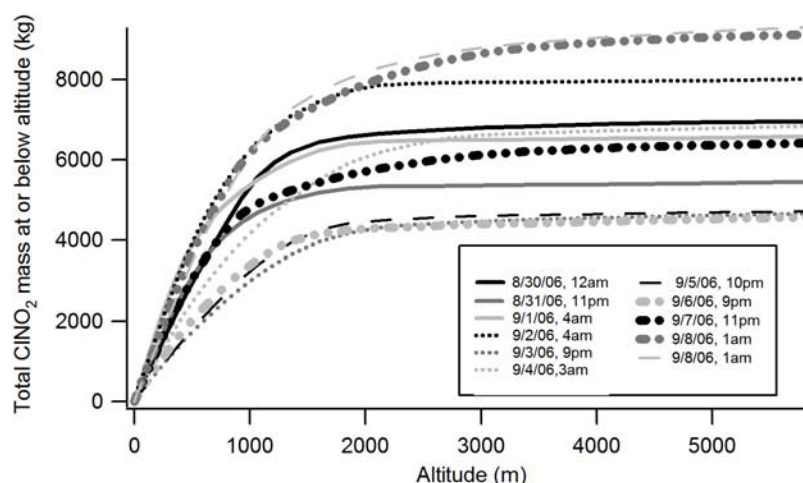


Figure 9. Vertical distribution of nitryl chloride mass in the 4 km domain.

3.4. Effects of CINO₂ on Ozone Concentrations

3.4.1. Increases in Ozone Concentrations

[27] Model predictions of maximum ozone concentration increases caused by the nitryl chloride are summarized in Tables 2 and 3. Time series of ozone increases for 1 and 8 September 2006 are shown in Figures 10 and 11. The maximum hourly increase during the model run was 1.5 ppb on 2 September 2006. The maximum increase over land was 0.9 ppb which occurred on 1, 7, 8, and 9 September. These increases in ozone are modest. However, it should be noted that this modeling is based on the observation that the yield of CINO₂ from the reaction between NO₂ and O₃ at night (reaction (R8)) was 10% off the southeast Texas coast. As noted previously, observations in other locations suggested that under some conditions as much as 60% of the NO₃ could be converted to CINO₂ and that the response of ozone formation to this yield is linear. Therefore, there may be conditions under which ozone increases per mole of N₂O₅ reacting to form CINO₂ might be six times higher than predicted by this modeled episode (up to 10 ppb). However, since the concentrations of CINO₂ used in this work were consistent with ambient observations (Figures 4 and 5), the changes in ozone concentrations due to the observed CINO₂ concentrations are likely to be only a few ppb.

3.4.2. Incremental Reactivity

[28] One approach for estimating the potential of CINO₂ to contribute to ozone formation is the use of incremental reactivities. *Carter* [1994] first introduced the concept of

Incremental Reactivity (IR) as a metric for measuring the importance of VOC emissions for ozone formation. Incremental reactivity is typically calculated on the basis of results from a box model which simulates atmospheric chemistry, time-varying emissions, and a changing boundary layer height. The box model does not include advection, dispersion, or deposition. Two simulations are performed: a base case simulation with standard VOC and NO_x concentrations and a test case simulation in which extra VOC is emitted. *Carter* used a standard VOC and NO_x mixture which was based on an average from measurements made in 39 U.S. cities on high ozone days [*Carter*, 1994]. The incremental reactivity is calculated as the total extra ozone mass created in the test run (at the time of the daily maximum concentration) divided by the total excess mass of VOC that was emitted in the simulation. This provides a measure of how effective the added VOC is at creating ozone and different values are obtained for different VOCs. In addition, incremental reactivities depend on the NO_x/VOC ratio. There are a variety of incremental reactivities including Maximum Incremental Reactivity, Equal Benefit Incremental Reactivity, and Maximum Ozone Incremental Reactivity (see *Carter* [1994] for definitions). While no previous values have been reported for incremental reactivities of CINO₂, *Carter* [2001] has reported a Maximum Incremental Reactivity (MIR) of chlorine (24 g of excess ozone formed per g of chlorine added) in a typical urban atmosphere, where MIR is the incremental activity at a

Table 2. Summary of Maximum Ozone Increases Caused by Addition of CINO₂ to the Model

Date	Time of Maximum Ozone Increase (LT)	Maximum Ozone Increase Caused by CINO ₂ (ppb)	Approximate Base Case Ozone Concentration at Location of Maximum Ozone Increase (ppb)	Typical Widespread Ozone Increase at Time of Maximum (ppb)	Number of Hours With Ozone Increases Above 1 ppb
30 Aug 2006	1200	0.7	50	0.4	0
31 Aug 2006	1700	0.3	60	0.1	0
1 Sep 2006	1000	1.0	60	0.8	2
2 Sep 2006	1000	1.5	80	0.9	3
3 Sep 2006	1500	1.3	85	1.1	8
4 Sep 2006	1300	0.9	70	0.3	0
5 Sep 2006	1000	0.5	70	0.4	0
6 Sep 2006	1000	0.3	65	0.1	0
7 Sep 2006	1300	1.3	70	0.8	6
8 Sep 2006	1100	0.9	85	0.7	0
9 Sep 2006	1200	0.9	55	0.8	0

Table 3. Summary of Maximum Onshore Ozone Increases Caused by the Addition of ClNO₂ to the Model

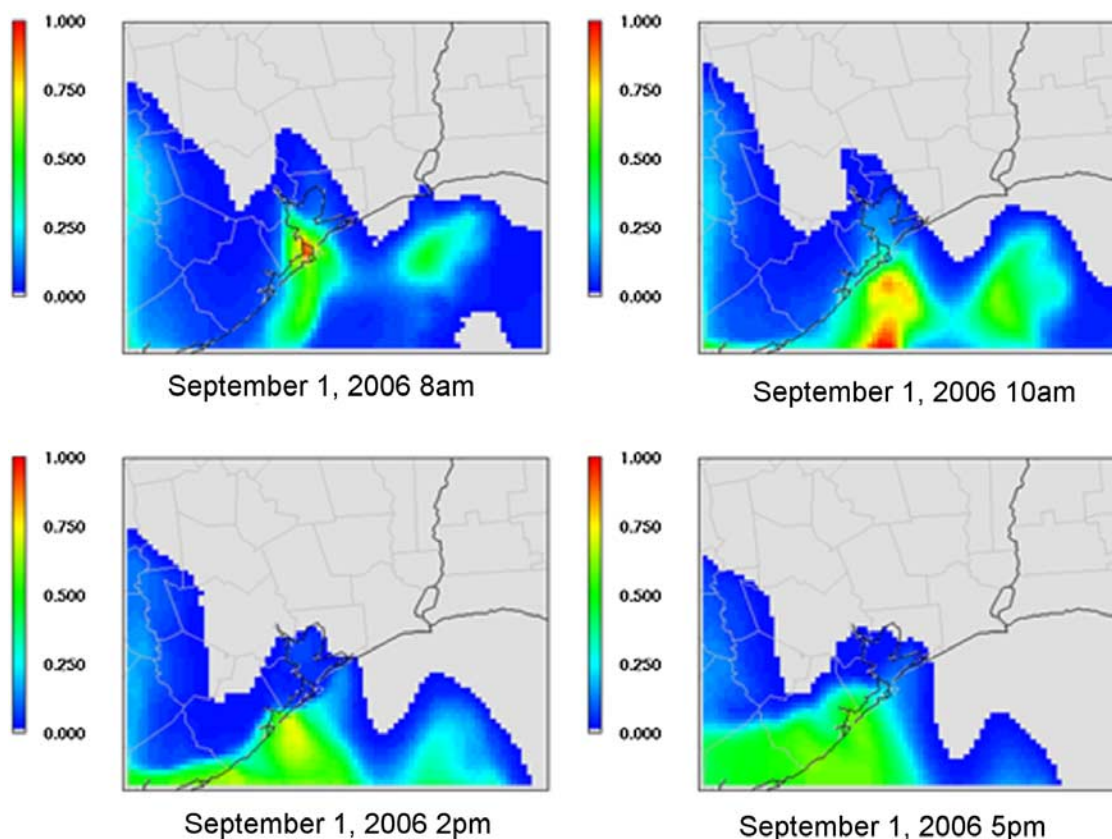
Date	Time of Maximum Onshore Increase (LT)	Maximum Onshore Ozone Increase (ppb)	Base Case Ozone Concentration at Maximum Onshore Increase (ppb)
30 Aug 2006	1200	0.4	40
31 Aug 2006	1700	0.3	60
1 Sep 2006	0800	0.9	60
2 Sep 2006	0800	0.8	65
3 Sep 2006	1000	0.3	70
4 Sep 2006	0900	0.2	75
5 Sep 2006	1000	0.1	45
6 Sep 2006	1000	0.1	50
7 Sep 2006	1600	0.9	70
8 Sep 2006	1100	0.9	85
9 Sep 2006	1100	0.9	60

NO_x/VOC ratio that results in the highest incremental reactivity value. This gives an upper bound for how much ozone could be formed from the chlorine in ClNO₂.

3.4.3. Box Model Incremental Reactivity Results

[29] A box model was used to perform incremental reactivity calculations for ClNO₂ using Houston conditions. The box model only simulated chemistry and did not include any emissions, advection, dispersion, or deposition. The mixing height was adjusted throughout the day on the basis of profiler data which measured the wind field aloft in the Houston area. All air above the boundary layer was assumed to contain no pollutant mass. Four sets of scenarios were examined. The initial concentrations of pollutants for these four scenarios are shown in Table 4. One set of simulations used as input the initial VOC and NO_x mixture based on canister measurements made at the La Porte

Airport (industrial area of Houston) in 2000 [Faraji *et al.*, 2008]. A second set of simulations used initial VOC and NO_x concentrations based on measurements from the R/V *Ronald H. Brown* that were taken on the morning of 8 September 2006 near the Houston Ship Channel. The instruments and methods used to obtain the VOC data have been described elsewhere [Goldan *et al.*, 2004; Herndon *et al.*, 2007]. The final two sets of simulations set initial concentrations of VOCs and NO_x in the box model to average modeled values in the first 350 m of atmosphere from the 1 September CAMx simulation at 0800 LT. One of these sets initialized VOC and NO_x concentrations to average values in the smallest rectangular area that encompassed the entire Houston ship channel, an area that is dominated by industrial emissions. The other set initialized VOC and NO_x concentrations to the average values in the

**Figure 10.** Time series of ozone increases (ppb) caused by addition of ClNO₂ on 1 September 2006.

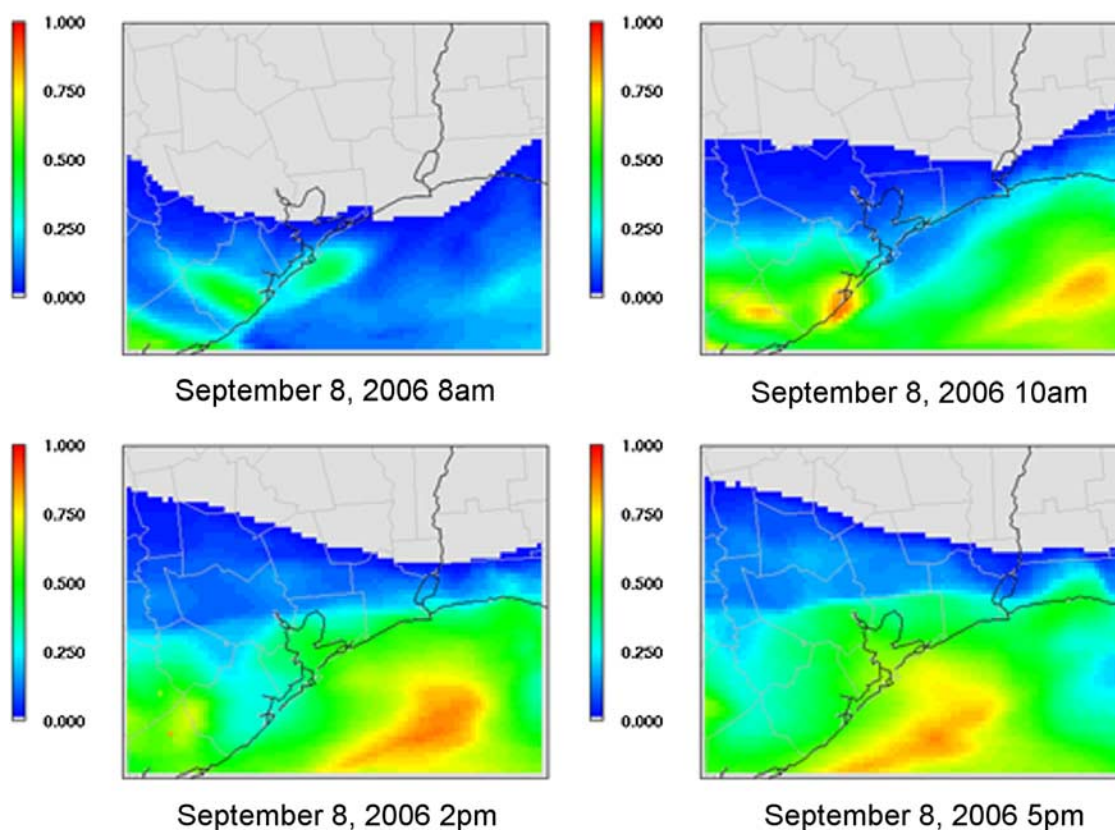


Figure 11. Time series of ozone increases (ppb) caused by addition of CINO₂ on 8 September 2006.

smallest rectangular area that encompassed all of Harris County (the county in which Houston is located), which is dominated by urban emissions. For each set of initial VOC and NO_x concentrations, a series of simulations were run with initial CINO₂ mixing ratios between 0 and 1.5 ppbv. These simulations used the same photolysis rate that was implemented in the CAMx simulation. Incremental reactivity based on maximum daily ozone values were calculated as the total mass of excess ozone at the time of the maximum daily ozone value divided by the mass of chlorine from nitryl chloride (equation (1)). This is similar to calculations described by Carter [1994, 2001], however, these incremental reactivity values are not MIR values because the NO_x/VOC concentrations have not been manipulated to obtain the maximum possible impact of CINO₂. The calculated box model values will be referred to as Maximum Daily Ozone Incremental Reactivity for Houston (MDOIR_H). In equation (1) $M_{O_3,max}$ is the mass of ozone present in the 4 km domain at the time when daily ozone concentration is maximum, the subscripts test and base refer to the test case run and the base case run respectively, and $M_{Cl,6am}$ is the mass of chlorine in the form of CINO₂ present in the 4 km domain at 0600 LT.

$$MDOIR_H = \frac{M_{O_3,max,test} - M_{O_3,max,base}}{M_{Cl,6am}} \quad (1)$$

[30] It is important to note that the MDOIR_H values can either be calculated on the basis of chlorine mass added to the model, or on the basis of total nitryl chloride mass added

to the model. Using chlorine makes this calculation comparable to Carter's values. However, sensitivity runs described below show that CINO₂ contributes to ozone formation not only as a chlorine source, but also as a NO₂ source. Therefore, it would be expected that Carter's MIR values would be higher for CINO₂ than for an equivalent mass of chlorine as Cl₂ because of the added ozone forming potential from the NO₂.

[31] The four sets of box model simulations predicted the effect of CINO₂ on ozone formation in an atmosphere that has VOC and NO_x concentrations representative of the Houston area. The values from the 2000 canister measurements and the 2006 R/V *Ronald H. Brown* measurements are important because they are based on the actual chemical composition of the atmosphere instead of emissions inventory and modeling estimates. Comparing these two simulations also gives insight into the change that has occurred in Houston's atmospheric chemistry in the past 6 years due to reductions of industrial NO_x emissions. However, it was also important to repeat the box model simulation using values from the 2006 modeling run because this provides an understanding of what is occurring in the regional photochemical model. The model allows evaluation of chemistry that occurs at times and locations for which no measurements are available. For instance, both the 2000 and 2006 measurements were taken in an area that is dominated by industrial emissions. Modeling is needed to evaluate the chemistry in areas that are dominated by urban emissions, since no current measurements are available at those locations.

[32] The MDOIR_H was calculated using a linear regression of data points plotted on a graph where the *y* axis

Table 4. Initial Conditions Used in the Box Model Simulations

Chemical Species	Concentrations From Canister Samples Taken in 2000 (ppb)	Concentrations Measured on Board the <i>Ronald H. Brown</i> (8 September 2006, 0700–0900 LT) (ppb)	Average Modeled Concentrations in the Ship Channel Area (ppb)	Average Modeled Concentrations in the Harris County Area (ppb)
Aromatic ring opening product	not measured	not measured	3.4×10^{-2}	6.3×10^{-3}
Carbon monoxide (CO)	335	263	479	305
Cresol and higher molecular weight phenols	not measured	not measured	0.17	0.057
Ethanol	not measured	4	1	1
Ethene	57	9	4	2
Formaldehyde	26	4	14	11
Higher molecular weight aldehydes	17	6	10	10
Hydrogen peroxide (H ₂ O ₂)	not measured	not measured	9	7
Isoprene	2.8×10^{-1}	3.0×10^{-2}	8.1×10^{-1}	2
Methanol	not measured	15	17	24
Methyl glyoxal and other aromatic products	not measured	not measured	1	8.5×10^{-1}
Nitric acid (HNO ₃)	not measured	not included	6	3
Nitric oxide (NO)	9	1	3	7.1×10^{-1}
Nitrogen dioxide (NO ₂)	52	27	16	4
Nitrous acid (HONO)	not measured	not measured	6.3×10^{-2}	1.6×10^{-2}
NO ₃	not measured	1.2×10^{-2}	4.9×10^{-3}	1.6×10^{-3}
Olefins	42	16	3	3
PAN	2	4.6×10^{-1}	3	3
Paraffins	501	677	152	94
Peroxy nitric acid (HNO ₄)	not measured	not measured	1.0×10^{-6}	1.0×10^{-6}
Toluene and other monoalkyl aromatics	3	3	1	3.2×10^{-1}
Xylene and other polyalkyl aromatics	2	2	1	5.8×10^{-1}

represents total mass of extra ozone created and the x axis represents the total mass of chlorine or ClNO₂ added. Results of these linear regressions are shown in Table 5. In each case the high R^2 value means that the incremental reactivity value is consistent over the entire range of added nitryl chloride concentrations. All of the MDOIR_H values are much lower than Carter's 24 g of ozone per g of chlorine added. This suggests that the NO_x and VOC mixtures typical of the Houston area not optimal for ozone formation with respect to chlorine. Carter [2001] reported that the chlorine MIR occurred at a ROG (Reactive Organic Gas)/NO_x ratio of around 3.5. He also reported that the incremental reactivity for chlorine decreased as ROG/NO_x ratios increased above 3.5 and dropped below 5 g of ozone per gram of chlorine added at an ROG/NO_x ratio of just below 6. The initial ROG/NO_x ratios for all four scenarios modeled here were well above 10, so it is to be expected that the incremental reactivity is much lower than Carter's MIR.

[33] The MDOIR_H value from the box model runs performed here varied with the initial conditions used. The run that used VOC and NO_x concentrations based on canister measurements from the year 2000 had the lowest MDOIR_H of 3.8, while the simulation that used initial conditions

based on 2006 ship channel measurements had an MDOIR_H of 4.9. This indicates that the potency of ClNO₂ in areas of the Houston atmosphere that are affected by industrial emissions has likely increased in the past 6 years as NO_x reductions have taken place. It should be noted that the MDOIR_H values based on measured and modeled 2006 industrial area emissions were similar (4.9 versus 5.4). The ratios of NO_x and VOC concentrations in these two runs were similar even though the absolute magnitude of the concentrations was different. This suggests that the reactivity of ClNO₂ is more dependant on the ratio of NO_x to VOC than on the absolute concentrations and that the modeled VOC and NO_x concentrations do a reasonable job of simulating the chemistry of ozone formation due to ClNO₂ that is occurring in this part of Houston.

[34] The box model runs using modeled concentrations of VOC and NO_x from the Houston Ship Channel (industrial) and from Harris county (urban) had MDOIR_H values that differed by a factor of two from one another (5.4 for the Houston Ship Channel versus 10.5 for Harris County). This indicates that the effect that nitryl chloride has on photochemistry in southeast Texas will depend on its location within the modeling domain. Since Houston has distinct

Table 5. MDOIR_H From Box Model Runs Based Both on Chlorine Mass and on Nitryl Chloride Mass

Metric Used	Box Model Run Using Initial Concentrations From Canister Samples Taken in 2000	Box Model Run Using Initial Concentrations From Measurements on Board the <i>Ronald H. Brown</i> (8 September 2006, 0700–0900 LT)	Box Model Run Using Initial Concentrations From Modeled Averages in the Ship Channel Area	Box Model Run Using Initial Concentrations From Modeled Averages in the Harris County Area
MDOIR _H based on chlorine mass added	3.8	4.9	5.4	10.5
MDOIR _H based on nitryl chloride mass added	1.7	2.1	2.4	4.6
R^2 (same for both calculation methods)	0.9986	0.9996	1.0000	0.9996

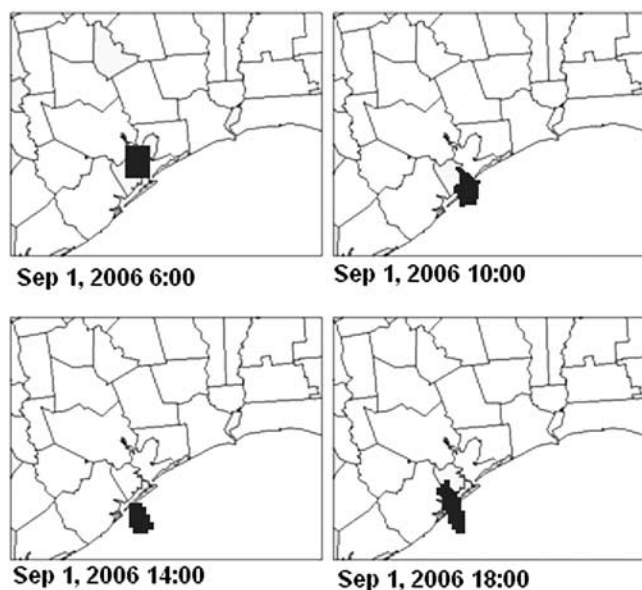


Figure 12. Location of LPA box throughout the day (0600, 1000, 1400, and 1800 LT) on 1 September 2006.

regions that are dominated by urban emissions and regions that are dominated by industrial emissions, the effect of nitryl chloride is quite heterogeneous. From the simulations performed here, nitryl chloride has a greater effect in the areas dominated by urban emissions rather than the areas dominated by industrial emissions.

3.4.4. Lagrangian Process Analysis Tool

[35] A tool called Lagrangian process analysis (LPA), recently developed by Kimura *et al.* [2008], was used to calculate the incremental reactivity of CINO₂ within the full CAMx modeling program which includes the effects of emissions, advection, dispersion and deposition. LPA was implemented for CAMx simulations on two of the days which had the highest onshore ozone concentration increases caused by CINO₂: 1 and 8 September 2006. LPA tracks the rates of both chemical and physical processes that affect pollutant concentrations in a set of grid cells that moves with a user selected parcel of air. This allows the analysis of discrete parcels of air and allows the evaluation of process rates within a plume. The LPA was set up so that the parcel of air could change shape as it moved, but the interior volume remained constant.

[36] On both of the evaluated days, the box was initially set at a location in the 4 km domain that had the greatest CINO₂ concentration at 0600 LT. Wind patterns on these days are demonstrated by the paths of the LPA box throughout the day (shown in Figures 12 and 13). On 8 September, the box was advected out of the 4 km domain by 1500 LT. As both days progressed, the plume changed shape as the boundary layer grew in the morning. Both plumes became narrower horizontally and taller vertically.

[37] Evaluation of the loss of a nonreactive tracer species shows that there is significant loss of pollutant mass from the air parcel via physical processes. LPA results show that 50% of the original tracer mass (at 0600 LT) was lost from the LPA box by 0858 LT on 1 September 2006 and by 0805 LT on 8 September 2006. 80% of the original tracer mass was lost from the LPA box by 1332 LT on 1 September 2006 and by 1032 LT by 8 September 2006. The processes which affect the overall physical loss of ozone were further analyzed. On average for both 1 and 8 September 2006, the physical loss of ozone from the LPA box was dominated by vertical dispersion. On 1 September, approximately 7% of the physical loss was due to advection, 23% was due to horizontal dispersion, 66% was due to vertical dispersion, and 4% was due to deposition. On 8 September, approximately 6% of the physical loss was due to advection, 7% was due to horizontal dispersion, 65% was due to vertical dispersion, and 22% was due to deposition. This finding that vertical dispersion is the dominant cause of dilution means that correctly modeling the vertical extent of the CINO₂ is much more important than correctly modeling the horizontal extent.

[38] Two types of incremental reactivity values were calculated for CINO₂ using Lagrangian process analysis. The first is the MDOIR_H that was discussed previously (equation (1)). The second type of value calculated will be called an Hourly Incremental Reactivity (HIR). This value was calculated every hour and is defined as the mass of excess ozone at the hour of interest divided by the mass of chlorine present at 0600 LT in nitryl chloride (equation (2)). The symbols in equation (2) are the same as those in equation (1) except that the subscript *t* (in place of *max*) represents that this value can be calculated at any time, *t*, during the day.

$$HIR = \frac{M_{O_3,t,est} - M_{O_3,t,base}}{M_{Cl,6am}} \quad (2)$$

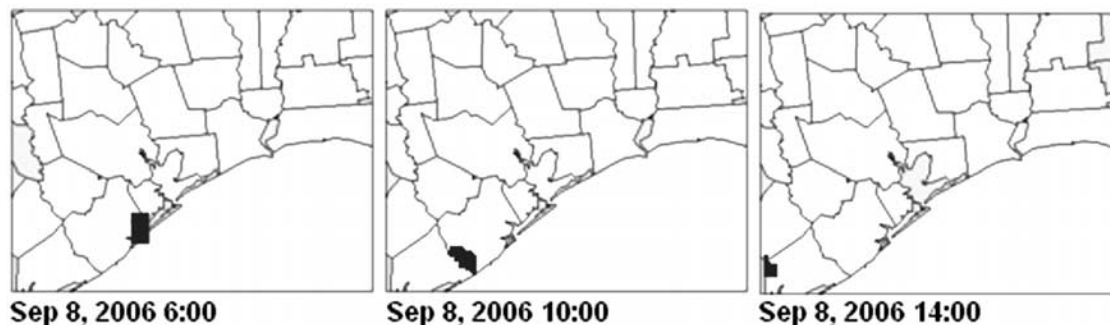


Figure 13. Location of LPA box throughout the day (0600, 1000, and 1400 LT) on 8 September 2006.

Therefore for each day, there is one MDOIR_H value and many HIR values. These two metrics were calculated in several ways. First they were calculated solely on the basis of mass of ozone and initial CINO₂ present in the LPA box. This method does not account for chlorine mass which is lost from the box via physical processes before it can react or for ozone mass which is created and then lost from the box. Method 1 can be thought of as an “apparent” MDOIR_H because in full-scale model runs both physical and chemical processes affect final ozone concentrations. Since physical loss affects pollutant concentrations in the actual environment, this method is likely to most accurately predict the increases in ozone concentrations caused by CINO₂. However, in order to isolate the effects of atmospheric composition on chemistry, a second method was used to calculate the incremental reactivity metrics (equation (3)). In the second method, the denominator was replaced with the total mass of Cl in the box that was created from the photolysis of CINO₂ over the entire period of time since sunrise. By doing this, all CINO₂ that was advected out of the box before it could react is ignored. Once the Cl radicals are formed, they react quickly enough that none are lost from the air parcel for which process analysis is performed. The numerator in the second method includes both ozone mass in the box and net ozone mass lost from the box, relative to the base case, via physical processes (advection, horizontal dispersion, vertical dispersion, and deposition). This second method therefore calculated the total amount of extra ozone formed and divides it by the total amount of extra chlorine reacted and should be most comparable to the box model results.

$$MDOIR_H(\text{method2}) = \frac{(M_{O_3, \text{max}, \text{test}} + M_{O_3, \text{PL}, \text{test}}) - (M_{O_3, \text{max}, \text{base}} + M_{O_3, \text{PL}, \text{base}})}{M_{Cl, 6 \text{am}} - M_{Cl, \text{PL}}} \quad (3)$$

Again, the symbols for equation (3) are essentially the same as those in equation (1) except that mass is summed within the LPA box instead of the entire 4 km domain. Also, additional symbols include $M_{O_3, \text{PL}}$ which represents the mass of ozone lost from the LPA box via physical processes since sunrise and $M_{Cl, \text{PL}}$ which represents the mass of chlorine in the form of CINO₂ that is lost from the LPA box via physical processes since sunrise. Tables 6 and 7 show the calculated incremental reactivities within the LPA box for 1 and 8 September 2006. The results are consistent with the results predicted by the box model runs which used initial conditions based on modeled Harris County VOC and NO_x conditions. That box model simulation predicted that the MDOIR_H would be 10.5, which is in the same range as the predictions made using method 2 in the LPA volume. The fact that incremental reactivity calculated via method 2 is three to four times higher than incremental reactivity calculated via method 1 highlights the fact that physical loss, especially vertical dispersion, decreases the apparent potency of CINO₂.

3.5. Sensitivity Analyses

[39] The standard chlorine chemistry in CAMx includes reactions of chlorine radicals with olefins and paraffins [Tanaka *et al.*, 2003a]. These reactions result in several products including aldehydes. However, the aldehyde prod-

ucts are not accounted for in the current implementation of the CAMx code. Simulations were performed with and without the production of aldehyde products. In general, the effect of including the aldehyde products was minor; ozone concentrations were generally changed by less than 2% when the aldehyde product was ignored.

[40] Additional sensitivity analyses were done to look at the effects of changing certain variables on HIR values for CINO₂. This is important since there are many assumptions made in this analysis including an accurate spatial extent of predicted CINO₂ values (both horizontal and vertical), meteorological conditions representative of 30 August to 9 September 2006, and a 2009 emissions inventory. Simulations for the sensitivity analysis were performed using a different method from previous simulations. Reactions (R8), (R9), and (R10) were turned off so that there was no CINO₂ formation through chemical processes. Instead, emissions of CINO₂ were injected into a small portion of the 4 km modeling domain between 0600 and 0700 LT each morning. This was done for several reasons. First, the effect of the nitryl chloride addition was limited to a small volume. This allowed an easy calculation of HIR values without using the LPA tool as long as the packet of air which contained the original CINO₂ is not advected outside of the 4 km domain. Second, this allowed us to investigate the sensitivity to the vertical and horizontal extent of the nitryl chloride. This is important since there are limited measurements available for CINO₂ concentrations, which makes it difficult to confirm that model predictions of CINO₂ concentrations are correct in large areas of the domain or aloft.

[41] In this sensitivity analysis the modeling episode, meteorological inputs, initial conditions, and emissions of NO_x, VOC, and Cl₂ are the same as described above. The initial test case consisted of emissions in a 36 km × 36 km area around the R/V *Ronald H. Brown* location on the morning of 8 September 2006 (Houston Ship Channel). Emissions were spread evenly over the lowest 344 m of the atmosphere. The mass emitted was enough to create a CINO₂ concentration of 555 ppt, similar to the value obtained in the original CINO₂ simulation using the surrogate formation reaction. Nine sensitivity runs were performed. Each run was identical to the main run except for one factor which was changed. Results from these runs are shown in Table 8. It is important to note that HIR and ozone concentration values should not be looked at as absolute results. The purpose of these runs is to see how changing specific variables affects the impact of CINO₂ on ozone.

[42] In sensitivity run 1, CINO₂ emissions were replaced with an amount of Cl₂ such that the total moles of Cl formed were the same. In this run the highest HIR value was only half as large as in the main run. Since both Cl₂ and CINO₂ photolyze quite rapidly, the main difference in these two runs is the presence of extra NO₂. It appears from the results of sensitivity run 1 that approximately half of the impact of CINO₂ is actually from the insertion of extra NO₂ into the domain. This is important when considering the hypothe-

Table 6. Incremental Reactivity Results From the LPA Analysis on 1 September 2006

Metric Used	Method 1 (g of Ozone Formed/g of Chlorine Added)	Method 2: Accounts for Loss of ClNO ₂ and Ozone via Physical Processes (g of Ozone Formed/g of Chlorine Added)
MDOIR _H	2.4	9.9
Maximum HIR	2.9	10.3
Time of maximum HIR (LT)	0900, 1200, 1300	1400

sized formation mechanism of ClNO₂. ClNO₂ forms from the heterogeneous uptake of N₂O₅ on aqueous aerosols if trace chloride concentrations are present. If ClNO₂ were not created, the nitrogen in some cases instead forms HNO₃, which is not reactive. Therefore, ClNO₂ is important not only as a chlorine source, but also as a reservoir which prevents loss of reactive nitrogen to nitric acid. This conclusion was also reached by *Osthoff et al.* [2008] on the basis of observational data.

[43] Sensitivity runs 2 and 3 further investigated the effect of ClNO₂ as a chlorine and reactive nitrogen source. In sensitivity run 2 ClNO₂ was replaced with equivalent amounts of Cl₂ and NO₂. The incremental reactivity calculated for this run was essentially the same as for the main test case run. This confirms that the importance of ClNO₂ comes from the products of its photolysis (Cl radicals and NO₂). In sensitivity run 3, ClNO₂ was replaced with an equivalent amount of NO₂ but no extra chlorine source was included. Incremental reactivity was not calculated for this run since the HIR in all other runs was calculated on the basis of total chlorine mass injected into the domain. Therefore an HIR calculated for sensitivity run 3 would not be comparable to those from other runs. However, maximum ozone concentration increases in this run reached approximately 80% of increases in the main run. This confirms that the NO₂ produced from ClNO₂ photolysis is indeed important for ozone formation.

[44] Sensitivity run 4 removed the Cl₂ emissions (sources of Cl other than ClNO₂) from both the base case and test case runs. This was done to investigate whether the effect of chlorine additions depended on the amount of chlorine already present in the atmosphere. This simulation showed that background Cl levels had little effect on the HIR of ClNO₂.

[45] Sensitivity run 5 replaced the 2009 emissions inventory with the 2000 emissions inventory in both the base case and the test case run. As mentioned previously, the composition of the Houston atmosphere is changing rapidly because of new control requirements for NO_x. This run shows that the HIR decreased by about 25% when using 2000 emissions. As shown in sensitivity run 1, the NO₂

from the ClNO₂ appears to have as much impact on ozone as the extra Cl radical. The reduced effect in sensitivity run 5 may be due to the fact that since NO_x emissions are significantly lower in the 2009 emissions inventory, the atmosphere in the initial test case is more NO_x limited. Therefore, ClNO₂ additions appear to have more effect on ozone in 2006 than they would have had in 2000. This is also consistent with the box model runs that showed a higher MDOIR_H when initial conditions were based on 2006 measurements rather than 2000 measurements.

[46] Sensitivity run 6 replaced the 8 September 2006 meteorological conditions with conditions developed for 25 August 2000. This day had stagnant conditions in the morning that were not observed in the 2006 episode. The stagnant conditions appear to have enlarged the total ozone concentration increase due to ClNO₂ by about 50%, however the HIR value was slightly lower. Therefore, even though the chlorine did not create any more ozone on this day, concentrations were increased because of stagnant conditions that did not dilute the ozone.

[47] Sensitivity runs 7, 8, and 9 all investigated the effect of changing the spatial extent of nitryl chloride emissions. In each of these runs, when the horizontal or vertical extent of emissions was changed, the total mass emitted was adjusted to keep the resulting concentration the same as in the initial test case ClNO₂ run. Quadrupling the horizontal area over which emissions occurred (sensitivity run 9) did not significantly change the HIR or the ozone concentration increase. This is consistent with results from the LPA simulations which suggested that changing the horizontal extent of ClNO₂ will not significantly affect the magnitude of ozone increases. Increasing the height of the ClNO₂ emissions above the top of the morning boundary layer (sensitivity run 8) also did not significantly change the HIR. However, lowering the height of the emissions so that they only occurred in the first 40 m of the atmosphere (sensitivity run 7) cut the HIR in half. This is likely due to significant vertical dispersion of the nitryl chloride, which would reduce its concentration and thus the reaction rates of Cl radicals with VOCs. This suggests that within the boundary layer, it is important to accurately represent ClNO₂ concen-

Table 7. Incremental Reactivity Results From the LPA Analysis on 8 September 2006

Metric Used	Method 1 (g of Ozone Formed/ g of Chlorine Added)	Method 2: Accounts for Loss of ClNO ₂ and Ozone via Physical Processes (g of Ozone Formed/g of Chlorine Added)
MDOIR _H	4.5	13.0
Maximum HIR	4.5	13.1
Time of maximum HIR (LT)	1200	1200, 1300

Table 8. Results From Sensitivity Study Investigating the Dependence of Ozone Increases on Model Assumptions

Sensitivity Run Number	Sensitivity Run Description	Highest HIR Value (g Ozone Formed/g Cl From CINO ₂)	Maximum Ozone Concentration Increase (ppb)	Time of Highest HIR Value (LT)	Time at Maximum Ozone Concentration Increase (LT)
Main run	-	7.1	1.1	1200	0800
Sensitivity run 1	Cl ₂ in place of CINO ₂	3.6	2.0	0800	0800
Sensitivity run 2	Cl ₂ + NO ₂ in place of CINO ₂	7.2	2.2	1200	0800
Sensitivity run 3	NO ₂ in place of CINO ₂	n/a	0.9	n/a	1000
Sensitivity run 4	no Cl ₂ emissions	7.2	1.3	1200	0800
Sensitivity run 5	2000 EI	5.4	1.3	1200	0900
Sensitivity run 6	2000 met	6.9	1.6	1000	0900
Sensitivity run 7	vertical extent of CINO ₂ = 40 m	3.6	0.6	1200	0800
Sensitivity run 8	vertical extent of CINO ₂ = 520 m	7.0	1.2	1200	0900
Sensitivity run 9	horizontal extent = 72 km × 72 km	7.7	1.4	1200	0800

trations aloft. It will be necessary in the future to make measurements aloft to verify whether formation rates are the same as at ground level.

4. Conclusions

[48] This paper is the first comprehensive photochemical modeling work to take CINO₂ measurements into account in the evaluation of urban ozone formation. The modeling evaluation found that CINO₂ did have an impact on ozone concentrations, increasing ozone mixing ratios by up to 1.5 ppb. This concentration increase is modest when compared to typical summertime levels in Houston (above 100 ppb on a 1 h average), but is significant in comparison to preindustrial levels of around 10 ppb.

[49] Sensitivity runs revealed several key factors that affect how CINO₂ interacts with the Houston atmosphere. NO_x and VOC conditions in the Houston area are not optimal for forming ozone from chlorine emissions and the modeled ozone increases were less than what would have been predicted on the basis of Carter's MIR values for chlorine. It appears that the presence of CINO₂ had less effect in modeled runs which used 2000 emissions versus 2009 emissions. This is likely due to the significant reductions in NO_x emissions in the Houston area (1005 tons per day in 2000 to 445 tons per day in 2009). As these reductions continue and the Houston atmosphere becomes more NO_x limited, the effect of CINO₂ may become more important. In addition to the importance of the local NO_x and VOC mixtures, the effect of CINO₂ on ozone mixing ratios was significantly reduced by vertical dispersion of both CINO₂ and the ozone that it formed. This is due in part to the fact that CINO₂ is mainly formed at night, so the air mass which contains it becomes diluted in the morning as the boundary layer rises. Although the vertical extent of CINO₂ greatly affected its impact, the horizontal extent did not. This finding suggest that even if CINO₂ formation were extended inland in the model, the magnitude of the effects on ozone formation would not be dramatically different than what is seen in the original modeling runs. However, the area over which this effect is seen would likely be greater.

[50] The results from these modeling runs were based on meteorological conditions specific to the pollution episode modeled. It is possible that under other meteorological conditions (particularly those in which the boundary layer does not rise quickly in the morning) CINO₂ may have a more significant impact on ozone mixing ratios. In addition, there may be cases in which total CINO₂ formation is

significantly greater than what was simulated in these model runs. Measurements show that in some cases, up to six times as much CINO₂ could form.

[51] This study has revealed several areas that will be fruitful for further research. First, it will be important to make measurements of CINO₂ aloft since properly predicting the vertical extent of this compound is essential to predicting its effects on ozone formation. In addition, further study is necessary to determine whether the Houston results are typical of other coastal urban areas. Explicitly incorporating the heterogeneous formation mechanism into photochemical models will be important for properly predicting its concentration over a wide geographic area and for fully understanding how CINO₂ affects chlorine cycling in the atmosphere. Finally, CINO₂ has the potential to impact the effectiveness of control strategies being implemented to meet the ozone NAAQS. Since nitrogen oxides (in the form of N₂O₅) convert chloride into reactive radicals, reducing NO_x emissions could potentially be more effective at reducing ozone than previously thought. Modeling studies will need to be performed in a variety of coastal urban areas to examine this phenomenon.

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