

Spatial and Temporal Impacts of Chlorine Chemistry on Ozone Formation in Southeastern Texas

Submitted to

The Texas Natural Resource Conservation Commission
12100 Park 35 Circle
Austin, Texas 78711

Contract No. 9880077600-18

Prepared by:

Sunghye Chang
Elena C. McDonald-Buller
Yosuke Kimura
Matthew M. Russell
Paul L. Tanaka
David T. Allen

Center for Energy and Environmental Resources
The University of Texas
10100 Burnet Rd., MS R7100
Austin, Texas 78758

January 2002

Executive Summary

Recent evidence has demonstrated that chlorine radical chemistry can enhance tropospheric VOC oxidation and has the potential to enhance ozone formation in urban areas. In order to investigate the regional impacts of chlorine chemistry in Southeastern Texas, a series of sensitivity studies was conducted using the Comprehensive Air Quality Model with extensions (CAMx). The objectives of the project were to examine the spatial and temporal sensitivity of ozone and a unique marker species for chlorine chemistry, 1-Chloro-3-methyl-3-butene-2-one, to molecular chlorine emission estimates and to large point source releases of ethylene or paraffins alone or in conjunction with emissions of nitrogen oxides and molecular chlorine.

Based on current estimates of molecular chlorine emissions in Southeastern Texas, the results of the sensitivity studies demonstrated that chlorine chemistry has the potential to enhance ozone mixing ratios by 11-16 ppbv in the industrial areas of Houston and by 5-7 ppbv within and north of the Houston urban area. Impacts varied temporally with cooling towers primarily responsible for a morning enhancement in ozone mixing ratios and residential swimming pools for an afternoon enhancement. Maximum enhancement in CMBO mixing ratios ranged from 59-69 pptv. Temporal variations in CMBO mixing ratios observed during the TexAQS-2000 field study in Southeastern Texas were replicated by the model.

A 5000 lb/hr release of ethylene in the Houston Ship Channel area resulted in greater ozone formation, 3-6 ppbv versus 0.3-0.9 ppbv, than a 5000 lb/hr release of paraffins in the same location. The magnitude of the enhancement increased when the hydrocarbon releases were accompanied by a 100 lb/hr release of molecular chlorine. Releases of ethylene or paraffins with nitrogen oxides result in less ozone production than releases with molecular chlorine. The maximum enhancement in CMBO mixing ratios occurs when the hydrocarbon releases are accompanied by releases of both nitrogen oxides and molecular chlorine.

Chapter 1: Introduction

1.1 Background and Objectives

Ground-level ozone (O_3) in urban atmospheres is formed when volatile organic compounds (VOCs) are oxidized in the presence of nitrogen oxides (NO_x) and sunlight. Although hydroxyl radical ($OH\cdot$) is considered to be the most important oxidant in urban areas, Tanaka et al. (2002) recently demonstrated that chlorine radical ($Cl\cdot$) chemistry enhances tropospheric VOC oxidation and has the potential to enhance ozone formation in an urban area. The first direct evidence of chlorine radical ($Cl\cdot$) chemistry in the urban troposphere was based on the quantification of two products unique to the $Cl\cdot +$ isoprene reaction in Houston, Texas: 1-Chloro-3-methyl-3-butene-2-one (CMBO) and chloromethylbutenal (CMBA). The results suggested that reducing chlorine emissions should be considered during the development of ozone attainment strategies.

Regional photochemical models, such as the Comprehensive Air Quality Model with extensions (CAMx), are typically used to evaluate the effectiveness of proposed emission control strategies in ozone non-attainment areas (ENVIRON, 2000). However, CAMx and other photochemical models currently do not account for emissions and reactions of Cl_2 and other precursors of $Cl\cdot$. Tanaka et al. (2001), under contract to the TNRCC, modified the Carbon Bond IV chemical mechanism within CAMx to account for the dominant features of the urban, tropospheric $Cl\cdot$ chemistry. Two sources of $Cl\cdot$ were included in the mechanism: photolysis of molecular chlorine and photolysis of hypochlorous acid.

The Texas Natural Resource Conservation Commission (TNRCC) also contracted with the University of Texas to develop a preliminary emission inventory that could be used with CAMx to examine the regional impacts of $Cl\cdot$ chemistry in Southeastern Texas. Preliminary estimates of atmospheric releases of molecular chlorine and hypochlorous acid (referred to as atomic chlorine, $Cl\cdot$, precursors) were developed for the following sources:

- Point source releases of molecular chlorine reported through the Toxic Release Inventory (TRI) and the TNRCC's Point Source Database (PSDB).
- Point source releases of atomic chlorine precursors associated with the use of biocides in cooling towers
- Point source releases of atomic chlorine precursors associated with water and wastewater treatment
- Area sources of atomic chlorine precursors associated with disinfection of swimming pools
- Area sources of atomic chlorine precursors associated with marine sources, possibly reactions of chlorides in sea salt aerosol
- Area sources of atomic chlorine precursors associated with tap water use
- Area sources of atomic chlorine precursors associated with reactions of chlorinated organics in the atmosphere

The preliminary estimates indicated that emissions from cooling towers and swimming pools accounted for 47% and 39%, respectively, of the total inventory of molecular chlorine (Chang et al., 2002).

The objectives of the current study were to use the newly developed emission inventory for atomic chlorine precursors and modified chemical mechanism with CAMx to examine the spatial and temporal sensitivity of O₃ and CMBO formation to Cl₂ emission estimates and to large point source releases of ethylene or paraffins alone or in conjunction with emissions of NO_x and Cl₂ in Southeastern Texas.

1.2 Sensitivity Studies

The Comprehensive Air Quality Model with Extensions developed by ENVIRON International Corporation (2000) was used for all sensitivity studies. This model is currently used by the State of Texas in attainment demonstrations and for air quality planning. Impacts were evaluated for Southeastern Texas, shown in Figure 1.1, which included the ozone nonattainment areas of Beaumont/Port Arthur and Houston/Galveston. Two 1993 modeling episodes were available for Southeastern Texas: August 16 through 20 and September 6 through September 11, respectively. Sensitivity studies were performed using both episodes, however, the majority of these studies were performed using the September episode. The September episode is currently being used in ozone attainment demonstrations for the Houston/Galveston area and has been used by the State of Texas to evaluate regional emission control strategies. It has undergone rigorous performance evaluation and scrutiny by the State of Texas and the U.S. Environmental Protection Agency. A summary of the sensitivity studies is presented in Table 1.1.

Figure 1.1 Southeastern Texas nested regional/urban 16km/4km photochemical modeling domain.

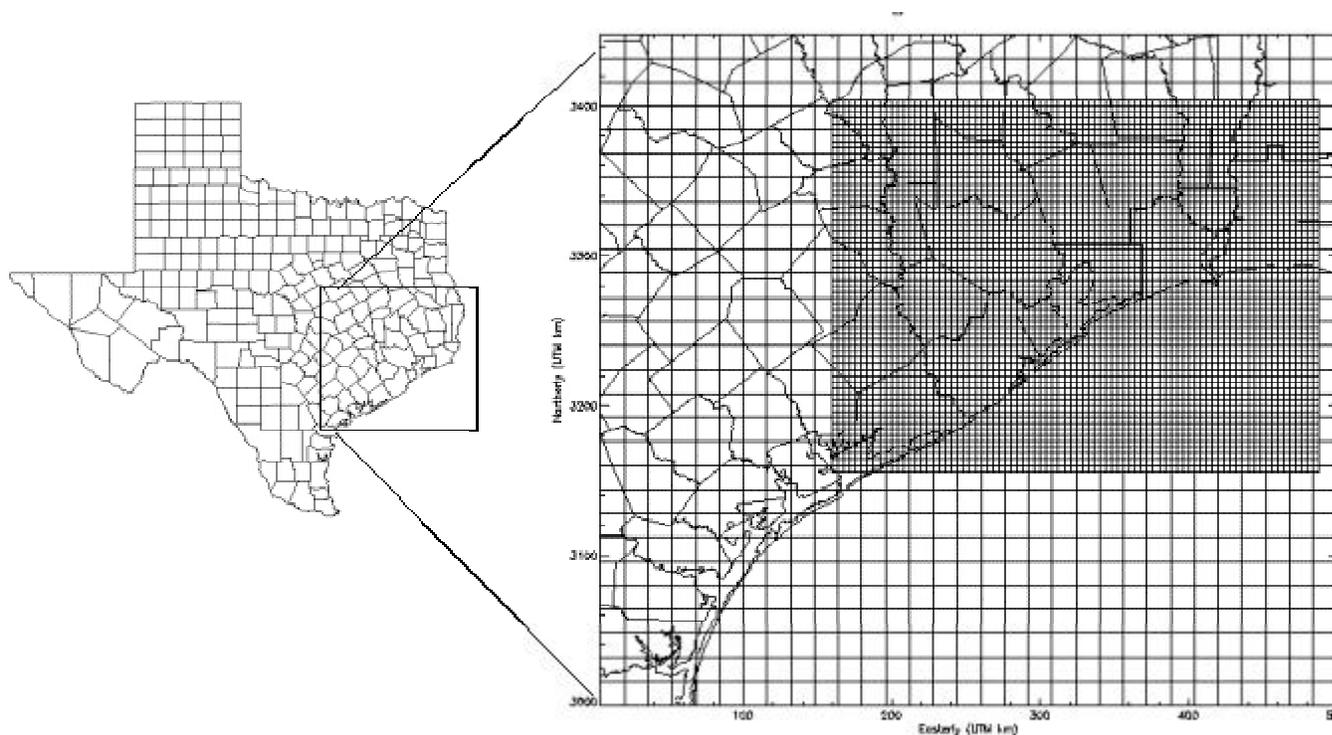


Table 1.1 Summary of sensitivity studies. All studies performed with CB-IV mechanism modified to include Cl·

Modeling Episode	
September 6-11, 1993	August 16-20, 1993
Basecase (no Cl ₂ or HOCl emissions)	Basecase (no Cl ₂ or HOCl emissions)
Basecase with all emissions assumed to be in the form of Cl ₂	Basecase with all emissions assumed to be in the form of Cl ₂
Basecase with emissions assumed to be in the form of Cl ₂ except for emission from cooling towers and swimming pools which are in the form of HOCl	
Double Cl ₂ emissions from cooling tower	
Double Cl ₂ emissions from swimming pools	
Double Cl ₂ emissions from point sources	
Increase Cl ₂ emissions from sea salt/marine aerosol by a factor of ten	
Increase Cl ₂ emissions by 2 tons/day at a large refinery in the Ship Channel	
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor	Release of 5000 lb/hr of ethylene from 1300-1400 in grid cell with Clinton monitor
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor without any emissions of Cl· precursors.	Release of 5000 lb/hr of ethylene from 1300-1400 in grid cell with Clinton monitor without any emissions of Cl· precursors
Release of 5000 lb/hr of paraffins from 0700-0800 in grid cell with Clinton monitor	Release of 5000 lb/hr of paraffins from 1300-1400 in grid cell with Clinton monitor
Release of 5000 lb/hr of paraffins from 0700-0800 in grid cell with Clinton monitor without any emissions of Cl· precursors.	Release of 5000 lb/hr of paraffins from 1300-1400 in grid cell with Clinton monitor without any emissions of Cl· precursors.

Release of 5000 lb/hr of ethylene and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	
Release of 5000 lb/hr of paraffins and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	
Release of 5000 lb/hr of ethylene and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	
Release of 5000 lb/hr of paraffins and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	
Release of 5000 lb/hr of ethylene, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	
Release of 5000 lb/hr of paraffins, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	

Chapter 2: Modeling Methodology

2.1 Emission Inventory for Atomic Chlorine Precursors

Emissions of atomic chlorine precursors for the following sources were estimated in a previous study conducted by the University of Texas at Austin under contract (No. 9880077600-18) to the TNRCC (Chang et al, 2001):

- Point source releases of molecular chlorine reported through the Toxic Release Inventory (TRI) and the TNRCC's Point Source Database (PSDB).
- Point source releases of atomic chlorine precursors associated with the use of biocides in cooling towers
- Point source releases of atomic chlorine precursors associated with water and wastewater treatment
- Area sources of atomic chlorine precursors associated with disinfection of swimming pools
- Area sources of atomic chlorine precursors associated with reactions of chlorides in sea salt aerosol
- Area sources of atomic chlorine precursors associated with tap water use
- Area sources of atomic chlorine precursors associated with reactions of chlorinated organics in the atmosphere

A summary of sources of Cl_2 emissions and their spatial and temporal distributions incorporated into the photochemical modeling inventory is presented in Table 2.1. Chlorine emissions from point sources were obtained from U.S. Environmental Protection Agency's (U.S. EPA) Toxic Release Inventory (TRI) and the TNRCC's Point Source Database (PSDB). When reported emissions from the two data sources did not match, higher values were selected as a conservative approach. Temporal distribution of emissions followed the reported schedule for each point source; hourly molecular chlorine emissions from most point sources were constant throughout the day. Total emissions from industrial point sources in the region were 1.416 tons/day.

Molecular chlorine emissions from cooling towers were assumed to be co-located with the fifty point sources, excluding electric generating units, with the largest NO_x emissions in the region. It was assumed that hourly emissions of molecular chlorine or hypochlorous acid during shock chlorination from 0700-1200 were twice the level of hourly emissions from 1200-1700. Emissions of molecular chlorine from cooling towers in the region were 6 tons per day (8 tons per day as HOCl).

Total chlorine emissions (as either Cl_2 or HOCl) from residential swimming pools were 5.04 tons per day. Emissions from swimming pools were spatially allocated according to households with annual incomes greater than \$50,000 based on 1990 U.S. Census data. Hourly emissions were assumed to be constant from 1200-2000.

Total chlorine emissions from the marine/sea salt aerosol component were estimated to be 0.4 tons per day. Because ozone is necessary to convert chloride from sea salt/ marine aerosol to molecular chlorine, sea salt emissions were spatially allocated among the two grid cells adjacent

to the Gulf of Mexico coastline and all grid cells covering Galveston Bay. Emissions were assumed to occur from 0600-1800.

Cooling towers were the largest source of molecular chlorine and represented 47% of the total inventory. Molecular chlorine emissions from swimming pools, point sources, and sea salt represent 39 %, 11%, and 3%, respectively, of the total inventory. Other sources of atomic chlorine precursors (i.e., water and wastewater treatment, tap water use) were neglected in the photochemical modeling inventory because total emissions from these sources were small.

The emission inventory for atomic chlorine precursors was processed using the Emissions Preprocessor System (EPS) Version 2.0 (U.S. EPA, 1992) to obtain a format suitable for input to CAMx. Two model-ready emission files were developed: one that assumed emissions from all sources were in the form of molecular chlorine and another that assumed emissions from swimming pools and cooling towers were in the form of HOCl. Each model-ready file for atomic chlorine precursors was merged with the September 6-11, 1993 basecase inventory for elevated point sources obtained from ENVIRON. Only the model-ready file with atomic chlorine precursor emissions in the form of molecular chlorine was merged with August 16-20, 1993 basecase inventory for elevated point sources obtained from ENVIRON. The merge operation was accomplished using the FORTRAN program PTSMRG developed by ENVIRON.

2.2 Application of Masking Factors for Sensitivity Studies

Emission inventories must be modified to conduct sensitivity studies that examine, for example, the impacts of doubling emissions or adding large point source releases of hydrocarbons. Although in some cases the modifications were conducted by changing the “raw” emission inventory and reprocessing it through EPS 2.0 to obtain a new model-ready file, in most cases the model-ready files were actually modified. The process of modifying model-ready files by applying factors to emissions in selected grid cells is referred to as “masking”. Masking was performed using the FORTRAN program ELMASK, developed by UT. A summary of modeling runs and masking factors is presented in Table 2.2. Table 2.2 also gives the internal UT reference identification for each modeling run. Results of modeling runs are available upon request from UT using this reference identification.

2.3 Meteorological Data and Other Model Inputs

Meteorological data files and other CAMx inputs including landuse characterization, boundary and initial conditions, gridded ozone column, albedo and turbidity files for each episode were obtained from ENVIRON.

2.4 Modified Chemical Mechanism

Tanaka et al. (2001), under contract to the TNRCC, modified the Carbon Bond IV chemical mechanism within CAMx (Mechanism 3) to account for the dominant features of urban, tropospheric Cl[·] chemistry. Two sources of Cl[·] were included in the mechanism: photolysis of molecular chlorine and photolysis of hypochlorous acid respectively. A summary of the

modified Cl₂ chemical mechanism and a copy of the modified *chemparm* file used in CAMx are presented in Appendix A.

2.5 Processing of Model Output

Several types of post-processing procedures were performed on CAMx output files as appropriate to the sensitivity study.

2.5.1 Evaluating Spatial and Temporal Impacts of Cl₂ Chemistry on O₃ and CMBO Formation

The Package for Analysis and Visualization of Environmental Data (PAVE) developed by the Microelectronics Center of North Carolina (MCNC) was used to create difference maps of one-hour averaged O₃ and CMBO concentrations between a given scenario and the basecase or other scenarios. PAVE was used to examine hourly differences as well as to generate maps of maximum differences in each grid cell on each day of the episode.

2.5.2 Peak Daily Ozone Concentrations and Area of Exceedance Above a Threshold Ozone Concentration

The Fortran program FINDMAX, developed by UT, was used to find peak predicted daily O₃ concentrations and their time and location in the 4km x 4km nested grid (11-county region) for each scenario. It was also used to find the area of exceedance above a 100 ppbv threshold O₃ concentration.

2.5.3 Impact of Cl₂ Chemistry on Model Performance

Model performance is typically evaluated using U.S. EPA-established graphical and statistical criteria. Model performance was compared for three scenarios: the Basecase without Cl₂ or HOCl emissions, the Basecase with all emissions assumed to be in the form of Cl₂, and the Basecase with emissions assumed to be in the form of Cl₂ except for emission from cooling towers and swimming pools which are in the form of HOCl.

Four programs were used to process the model output into a format suitable for evaluating model performance. CAMxtract, developed by ENVIRON, was used to extract 1-hour averaged O₃ concentrations from the binary model output. UAMpost and COMBINE, developed by ENVIRON, temporally and spatially paired observed and predicted ground level concentrations and combined the paired data for each episode day into a single file that can be used to create time series plots. TIMESERIES.PRO, a routine developed by UT for use with PV-WAVE software, and Microsoft Excel were used to generate time series plots for each ambient monitor in the 11-county region.

The output of UAMpost is used by another FORTRAN program, UAMstat to obtain statistical analyses of model performance. EPA has established guidance for the following statistical metrics: Unpaired accuracy of the peak domain maximum ($\pm 15-20\%$), normalized bias ($\pm 5-15\%$), and gross error (30-35%).

Table 2.1 Sources of Cl₂ emissions incorporated into the photochemical modeling inventory.

Source	Total Emission Rate (tpd)	Percent of Total Cl₂ Inventory (%)	Temporal Distribution	Spatial Distribution	Stack Parameters
Cooling Tower	6	46.7	0700-1200 at a constant fraction of 0.1333/hr 1200-1700 at a constant fraction of 0.0666/hr	Co-located with “top 50 point sources” of NO _x emissions excluding EGU	Height = 20m Diameter = 5m Temperature = 294K Stack gas velocity =1 m/s
Swimming Pool	5.04	39.2	1200-2000 (hourly emissions evenly distributed)	Center of each grid cell based on population and income distribution	Height = 3m Diameter = 0.2m Temperature = 294K Stack gas velocity =0.5m/s
Industrial Point Sources	1.416	11.0	0-2400 (hourly emissions evenly distributed)	Latitude and longitude provided in State of Texas PSDB	From State of Texas PSDB. Otherwise, default parameters applied: Height = 3m Diameter = 0.2m Temperature = 294K Stack gas velocity =0.5 m/s
Sea Salt	0.4	3.1	0600-1800 (hourly emissions evenly distributed)	Center of reach of two grid cells adjacent to the Gulf coast and Galveston Bay	Height = 3m Diameter = 0.2m Temperature = 294K Stack gas velocity =0.5 m/s

Table 2.2 Masking factors applied to modify emissions for sensitivity studies.

September 6-11, 1993		
Scenario	UT Internal Identification	Masking Factor (s) ** (Location of Application)
Basecase (no Cl ₂ or HOCl emissions)	Cl.noemiss.newphoto	NA
All emissions assumed to be in the form of Cl ₂	Cl.basecase.newphoto	NA
Emissions assumed to be in the form of Cl ₂ except for emission from cooling towers and swimming pools which are in the form of HOCl	Cl2+HOCL.basecase.newphoto	NA
Double Cl ₂ emissions from cooling tower	Cl.cool2.newphoto	1 (11-county region)
Double Cl ₂ emissions from swimming pools	Cl.pool2.newphoto	1 (11-county region)
Double Cl ₂ emissions from point sources	Cl.point2.newphoto	1 (11-county region)
Increase Cl ₂ emissions from sea salt/marine aerosol by a factor of ten	Cl.seasalt10.newphoto	2 (Gulf of Mexico coastline and Galveston Bay)
Increase Cl ₂ emissions by 2 tons/day at a large refinery in the	Cl.crown.2tpd.	Emissions of Cl ₂ from Crown Central Petroleum increased by 2 tons/day

Ship Channel		using EPS 2.0.
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor	Clinton.eth.sep.CL	3 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor without any emissions of Cl ⁻ precursors.	Clinton.eth.sep.regular	3 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of paraffins from 0700-0800 in grid cell with Clinton monitor	Clinton.para.sep.CL	4 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of paraffins from 0700-0800 in grid cell with Clinton monitor without any emissions of Cl ⁻ precursors.	Clinton.para.sep.regular	4 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of ethylene and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	Clinton.cl2.100pph.eth	3,5 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of paraffins and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	Clinton.cl2.100pph.para	4,5 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of ethylene and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	Clinton.cl2.NO _x _700pph.eth	3,6 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)

Release of 5000 lb/hr of paraffins and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	Clinton.cl2.NO _x _700pph.eth	4,6 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of ethylene, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	Clinton.cl2_100pph.NO _x _700pph.eth	3,5,6 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
Release of 5000 lb/hr of paraffins, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	Clinton.cl2_100pph.NO _x _700pph.para	4,5,6 (grid cell with Clinton Drive monitor; UTM coordinates 281.736, 3291.160)
August 16-20, 1993		
Basecase (no Cl ₂ or HOCl emissions)	Cl.noemiss.aug	NA
Basecase with all emissions assumed to be in the form of Cl ₂	Cl.basecase.aug	NA
Release of 5000 lb/hr of ethylene from 1300-1400 in grid cell with Clinton monitor	Clinton.eth.aug.CL	3
Release of 5000 lb/hr of ethylene from 1300-1400 in grid cell with Clinton monitor without any emissions of Cl ₂ precursors.	Clinton.eth.aug.regular	3

Release of 5000 lb/hr of paraffins from 1300-1400 in grid cell with Clinton monitor	Clinton.para.aug.CL	4
Release of 5000 lb/hr of paraffins from 1300-1400 in grid cell with Clinton monitor without any emissions of Cl ⁻ precursors.	Clinton.para.aug.regular	4

**1: Masking Factor (MF) = 2.0

2: MF = 10.0

3: Masking factor for ethylene in the grid cell with the Clinton ambient air monitoring site was based on total ethylene emissions in the basecase. Basecase emissions in the cell were 261.767 moles per hour. Therefore, the ethylene masking factor was: $MF = 5000 \text{ lb/hr} / [(261.767 \text{ mole/hr})(1\text{hr})(32\text{g/mole})(\text{lb}/454\text{g})] = 271$.

4: Basecase paraffin emissions in the cell were 1288.267 moles per hour. Paraffin masking factor was: $MF = 5000 \text{ lb/hr} / [(1288.267 \text{ mole/hr})(1\text{hr})(16\text{g/mole})(\text{lb}/454\text{g})] = 110.13$.

5: Cl₂ emissions in the grid cell were 104.259 moles per hour. Cl₂ masking factor was: $MF = 100 \text{ lb/hr} / [(104.259 \text{ mole/hr})(1\text{hr})(71\text{g/mole})(\text{lb}/454\text{g})] = 6.126$.

6: Basecase NO_x emission rate was 2604.669 mole/hr. Based on the NO molecular weight of 30g/mole, the masking factor was: $MF = 700 \text{ lb/hr} / [(2604.669 \text{ mole/hr})(1\text{hr})(30\text{g/mole})(\text{lb}/454\text{g})] = 4.06$.

Chapter 3: Ozone and CMBO Enhancement due to Chlorine Chemistry and Effects on Model Performance

3.1 Objectives

Spatial and temporal impacts of Cl[·] chemistry on ozone and CMBO formation were examined by comparing three modeling scenarios for the September 6-11, 1993 episode:

- 1) The Basecase without chlorine emissions (Cl.noemiss.newphoto)
- 2) Emissions from all sources in the form of Cl₂ (Cl.basecase.newphoto)
- 3) Emissions assumed in the form of HOCl except for emissions from swimming pools and cooling towers which are in the form of HOCl (Cl₂+HOCL.basecase.newphoto).

Two scenarios were compared for the August 16-20, 1993 episode:

- 4) The Basecase without chlorine emissions (Cl.basecase.aug)
- 5) Emissions from all sources in the form of Cl₂ (Cl.noemiss.aug)

Predicted differences between the Basecase without chlorine emissions and the scenario with emissions in the form of Cl₂ represent the enhancement of O₃ and CMBO formation due to chlorine chemistry and emissions. Because photolysis of Cl₂ and HOCl occur at different rates (ref. Appendix A), a third scenario with emissions from swimming pools and cooling towers in the form of HOCl was conducted with the September episode to examine the impacts of uncertainties in the chemical form of atomic chlorine precursors.

Results were analyzed using software tools described in Chapter 2. Spatial and temporal impacts between scenarios were examined using PAVE animations as well as by time series generated at locations where peak predicted differences were observed. Peak predicted ozone concentrations and the area of exceedance above a 100 ppbv threshold were determined for each scenario using FINDMAX.

The effects of Cl[·] chemistry on model performance were examined for the September episode because this episode is currently being used for SIP demonstrations in the Houston/Galveston ozone non-attainment area. Model performance was evaluated using time series of predicted and observed concentrations at ambient monitors and statistical metrics described in Chapter 2.

3.2 Results

3.2.1 O₃ and CMBO Enhancement due to Cl[·] Chemistry and Cl₂ Emissions

Including chlorine emissions and chemistry enhanced ozone formation by 12-16 ppbv in the morning between 0800 and 1000 in the Freeport and Houston Ship Channel areas throughout the September 6-11, 1993 episode. The maximum ozone enhancement during the September episode of 16 ppbv shown in Figure 3.1 occurred on September 11, 1993 at 0800 in the Freeport area near a large industrial point source. A time series of predicted differences in ozone concentrations at the location of the Freeport maximum is also shown in Figure 3.1. The impacts exhibited strong temporal variations throughout the episode. A secondary maximum of 5 ppbv to 7 ppbv was typically observed within and north of the Houston urban area in the afternoon at 1700.

CMBO formation, which is a marker for chlorine chemistry, exhibited the same spatial and temporal trends as O₃ formation during the September episode. CMBO mixing ratios at 0800 and 1700 on September 11 are shown in Figure 3.2. The maximum CMBO enhancement was 59 pptv on September 11 at 0800 slightly north of the location of the maximum O₃ enhancement.

CMBO mixing ratios were determined during the TexAQS-2000 field campaign (Tanaka et al., 2002). Although CMBO mixing ratios predicted by the model for September 11, 1993 cannot be quantitatively compared with the summer 2000 ambient monitoring data, morning increases in CMBO mixing ratios observed during the field campaign were replicated by the model. The maximum predicted CMBO mixing ratio is a factor of two lower than the highest mixing ratios detected during ambient measurements.

Ozone formation was enhanced by 11-13 ppbv between 1000 and 1100 in the Freeport and Houston Ship Channel areas throughout the August 16-20, 1993 episode. The maximum ozone enhancement during the August episode of 13 ppbv shown in Figure 3.3 occurred on August 19, 1993 at 1000 in the Freeport area near a large industrial point source. The locations of the maximum enhancement during the August and September episodes were within one grid cell of each other, but occurred two hours apart; the maximum enhancement during the August episode occurred at grid cell (27,13) at 1000 slightly north of grid cell (27,12) where the maximum enhancement occurred at 0800 during the September episode.

A time series of predicted differences in ozone mixing ratios at the location of the maximum enhancement during the August episode is shown in Figure 3.3. Similar to the September episode, a secondary maximum of 6-7 ppbv was observed within and north of the Houston urban area in the afternoons at 1700. Predicted differences in the afternoons were higher and more widespread in the urban area during the August episode than during the September episode.

Maximum CMBO enhancement during the August episode exhibited different temporal patterns than during the September episode. The maximum CMBO enhancement did not coincide with the day or time of the maximum ozone enhancement during the August episode. The maximum enhancement was 69 pptv and occurred on August 20 at 1700 in the Houston urban area, whereas the predicted maximum ozone enhancement occurred on August 19 at 1000 in the Freeport area when the maximum ozone enhancement was predicted. CMBO mixing ratios on both August 20th and 19th are shown in Figure 3.4 and Figure 3.5, respectively. The maximum enhancement occurred at 1700 throughout the August episode, and a secondary maximum was observed at 0800. These results are in contrast to those predicted for the September episode when the maximum CMBO enhancement consistently occurred during the morning in the Freeport area. Isoprene mixing ratios were higher during the August episode than during the September episode and peak mixing ratios tended to occur during the afternoon within and north of the Houston urban area. Isoprene mixing ratios at 0800 and 1700 on August 20th and September 11 are shown in Figures 3.6 and 3.7, respectively.

3.2.2 Impacts of HOCl Emissions from Swimming Pools and Cooling Towers

Photolysis of HOCl is slower than photolysis of Cl₂. Therefore, changes in the form of the emissions of atomic chlorine precursors were expected to lead to changes in the spatial and temporal distribution of the predicted O₃ and CMBO enhancements. The maximum predicted enhancement when emissions from cooling towers and swimming pools were in the form of HOCl was 10 ppbv at 1100 on September 11, 1993 in the urban core of Houston shown in Figure 3.8. The magnitude of the enhancement when emissions from swimming pools and cooling towers were in the form of HOCl was smaller than if they were in the form of Cl₂. Ozone mixing ratios each day increased by 6.5 ppbv – 10 ppbv between 1000 and 1200 relative to the basecase. Mixing ratios typically decreased steadily throughout the day, except for slight increases on September 8th and 10th at 1600.

The maximum CMBO enhancement was 17 pptv on September 11 at 0800 shown in Figure 3.9 in the Freeport area. Maximum increases in CMBO mixing ratios ranged from 8 ppbv to 17 ppbv each day, but the locations varied throughout the episode. Maximum enhancements occurred in the Beaumont/Port Arthur area on September 8th and 9th and in the Houston urban area on the 10th. Secondary maximums of 8 pptv to 10 pptv were observed in the Beaumont/Port Arthur area between 1600 and 1700 each day.

3.2.3 Peak Ozone Mixing Ratios and Area of Exceedance

Peak 1-hour ozone mixing ratios in the 11-county region and the area of exceedance above 100 ppbv in the basecase are summarized in Table 3.1. The peak predicted 1-hour ozone mixing ratio for the September basecase without Cl₂ emissions was 200 ppbv on the 11th. The peak predicted 1-hour ozone mixing ratio for the August basecase without Cl₂ emissions occurred on the 18th and was 133 ppbv. Cl· chemistry increased peak mixing ratios by at most 3 ppbv during the September episode and 1 ppbv during the August episode, but had minimal effects on the time and geographic location of the peaks. Cl· chemistry increased the area of exceedance above a 100 ppbv threshold in the 11-county area during both episodes. Increases ranged from 40 to 400 km²hr relative to the basecase and were greatest when all emissions were in the form of Cl₂.

3.2.4 Impacts of Cl· chemistry on Model Performance

Statistical metrics of model performance for the September episode, currently being used for air quality planning purposes in the Houston/Galveston non-attainment area, are summarized in Appendix B. Time series comparing observed ozone mixing ratios at ambient monitors in the region with predicted mixing ratios from the basecase without Cl₂ emissions, the simulation with all emissions in the form of Cl₂, and the simulation with emissions from cooling and towers and swimming pools in the form of HOCl are given in Appendix C. Emission of atomic chlorine precursors and Cl· chemistry had minimal impacts on model performance during the September episode. The addition of Cl· chemistry increased peak domain-wide ozone mixing ratios by 1 to 2 ppbv, which on the 8th and 9th tended to improve the unpaired peak predicted accuracy slightly relative to the basecase. However, the opposite trend was observed on the 10th and 11th. Cl· chemistry did not improve the bias and gross error metrics. Conclusions regarding the effects of Cl· chemistry on model performance should be drawn with caution because ambient monitors were not dense in the Freeport area where the largest enhancement occurred.

Figure 3.1 Predicted enhancement in O₃ formation due to Cl₂ emissions and chemistry at a) 0800 and b) 1700 on September 11, 1993. The maximum predicted enhancement in O₃ formation occurred on this episode day. A time series at the location of the maximum predicted enhancement (Freeport) is shown in c).

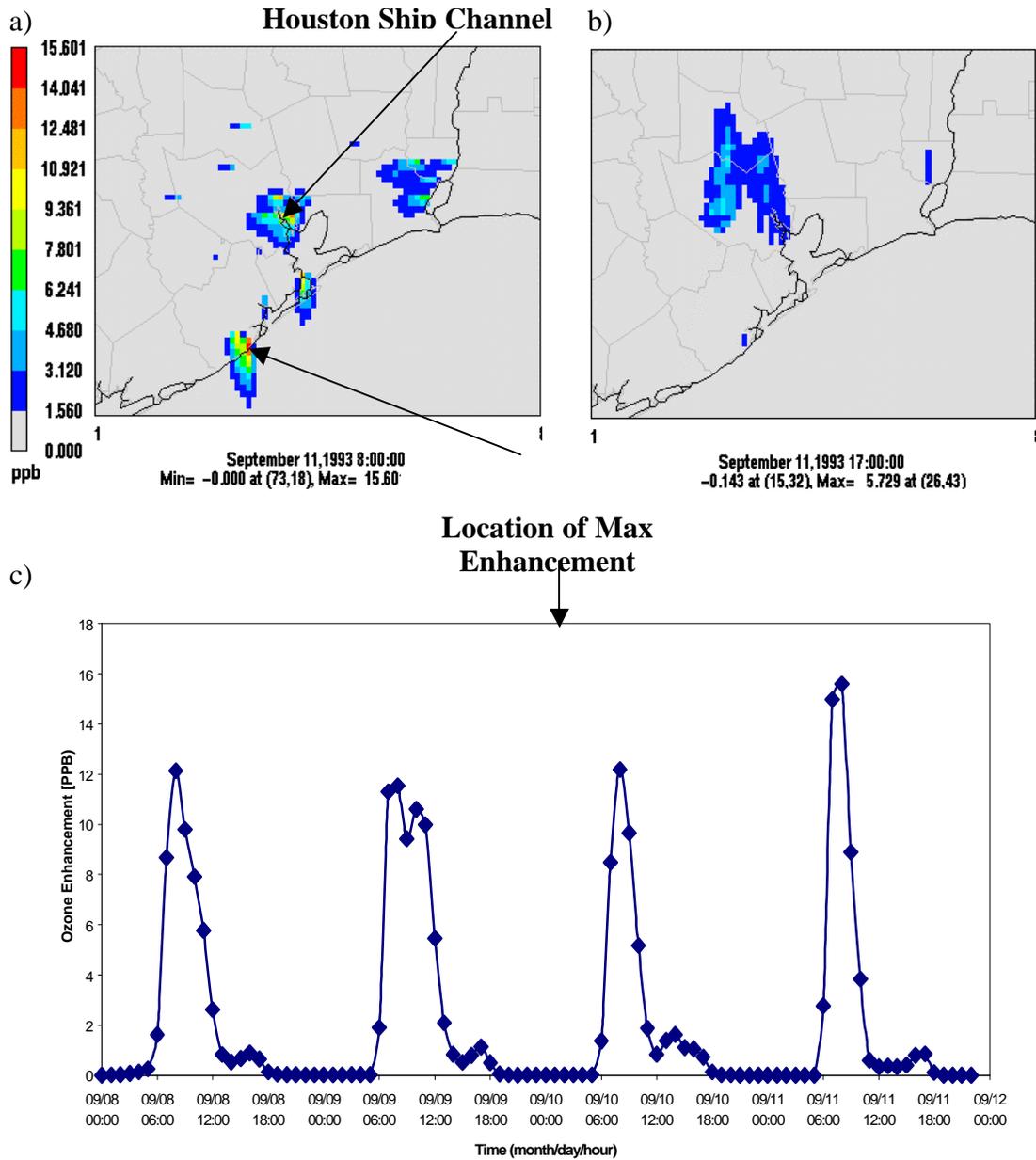


Figure 3.2 CMBO formation at a) 0800 and b)1700 on September 11, 1993.

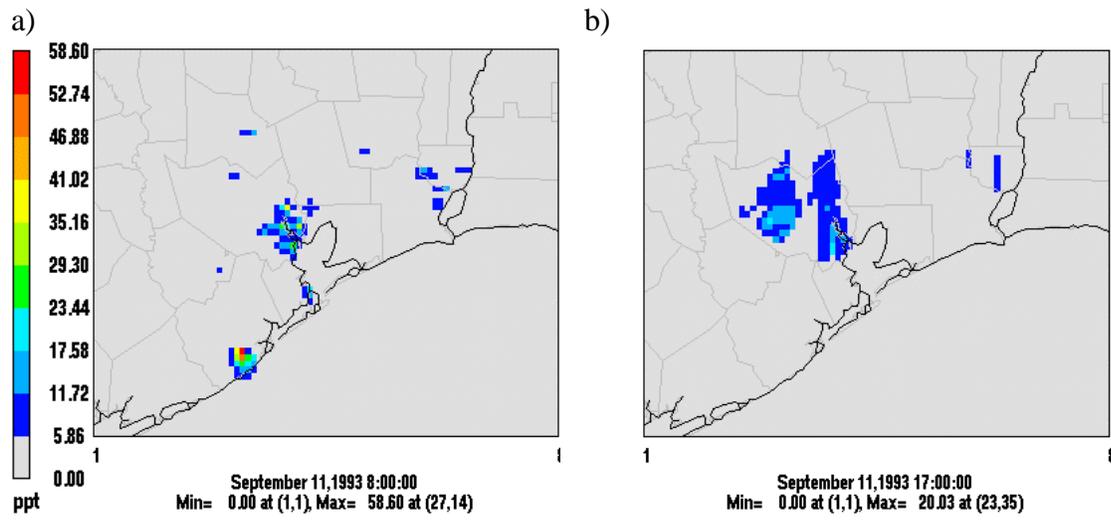


Figure 3.3 Predicted enhancement in O₃ formation due to Cl₂ emissions and chemistry at a) 1000 and b) 1700 on August 19, 1993. The maximum predicted enhancement in O₃ formation occurred on this episode day. A time series at the location of the maximum predicted enhancement (Freeport) is shown in c).

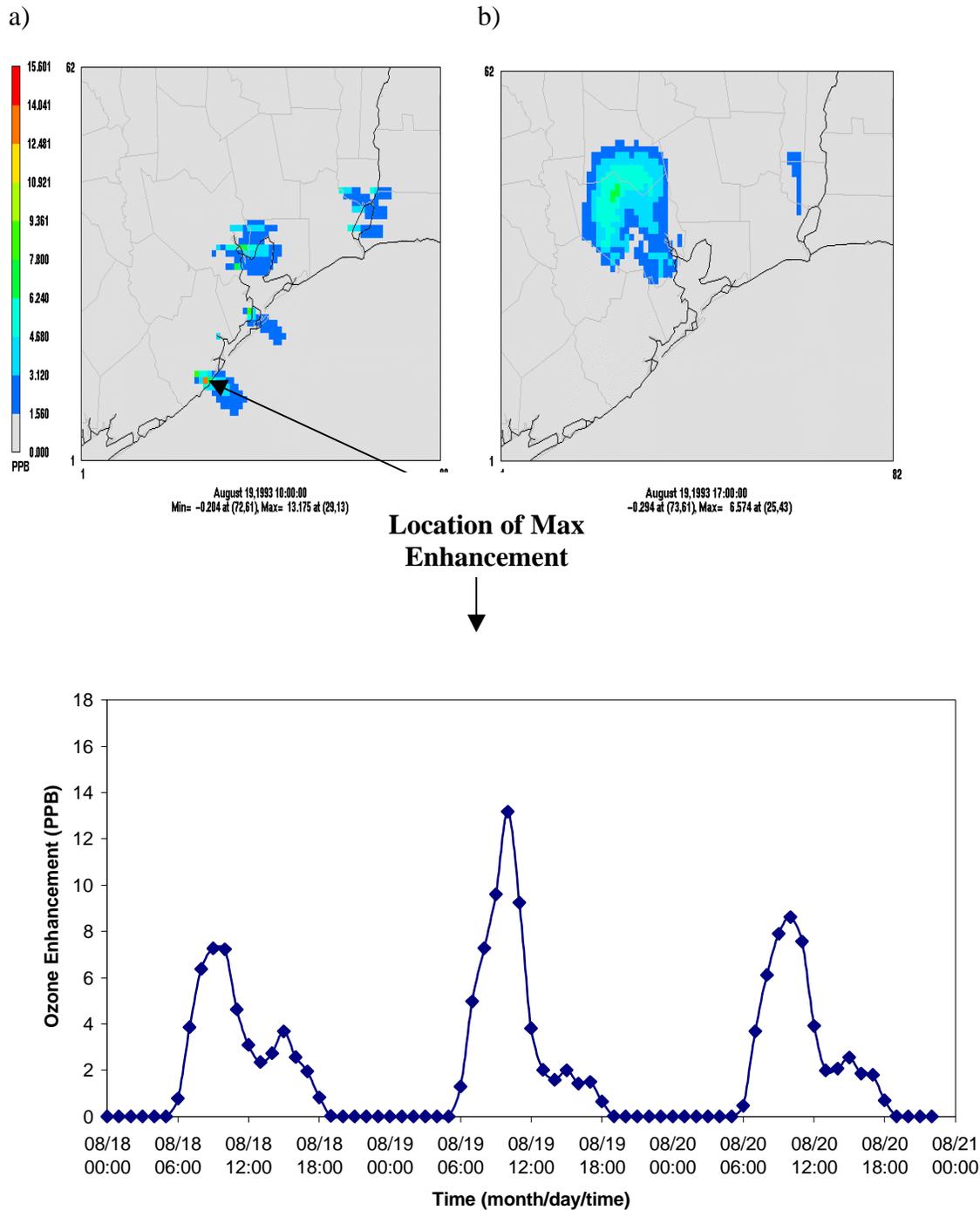
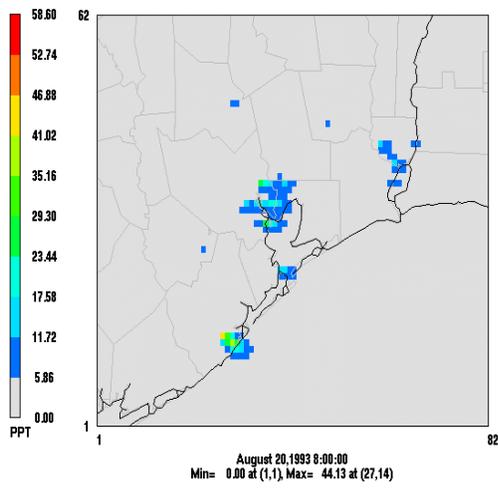


Figure 3.4 CMBO formation at a) 0800 and b) 1700 on August 20, 1993.

a)



b)

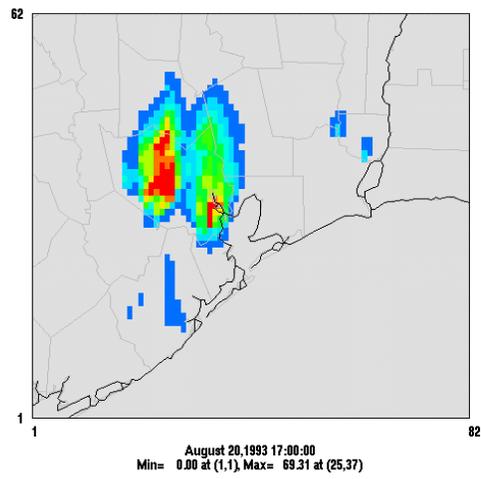


Figure 3.5 CMBO formation at a) 0800 and b) 1700 on August 19, 1993.

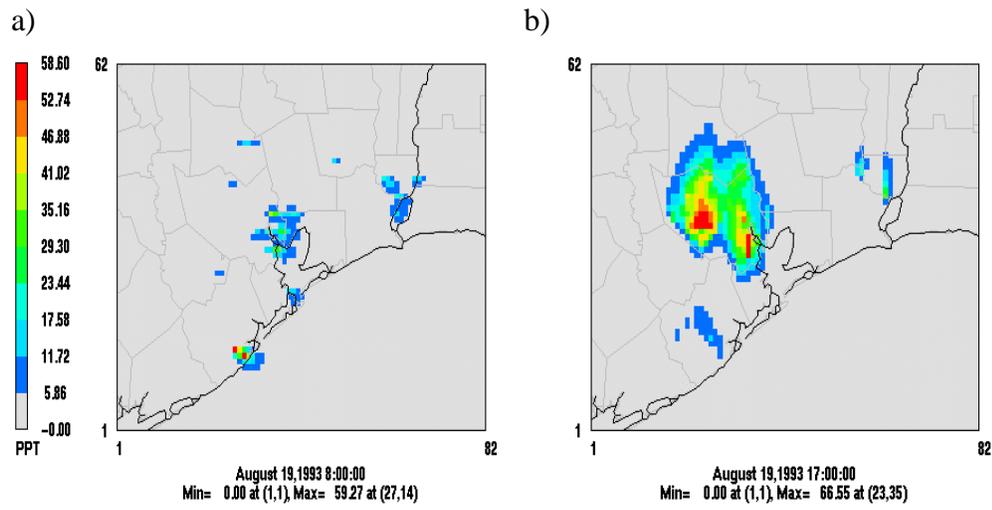


Figure 3.6 Isoprene mixing ratios at a) 0800 and b) 1700 on August 20, 1993.

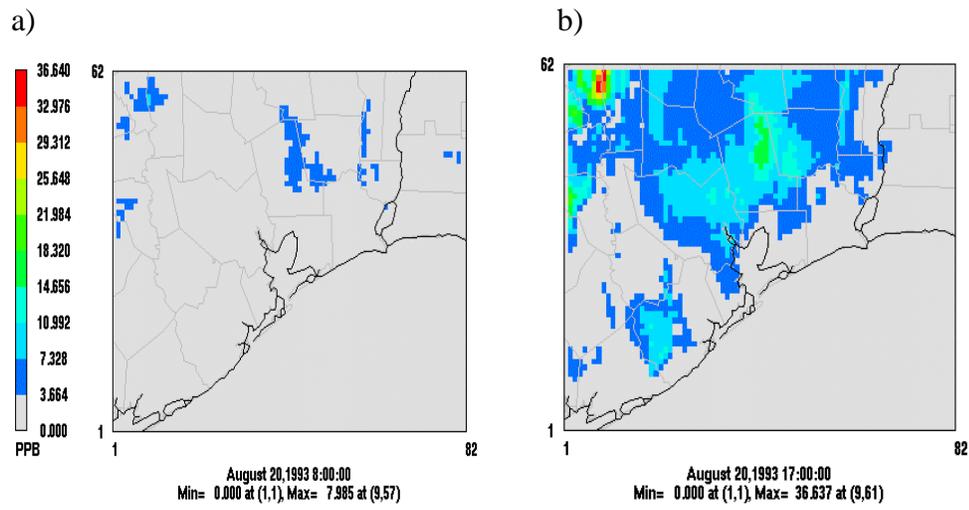


Figure 3.7 Isoprene mixing ratios at a) 0800 and b) 1700 on September 11, 1993.

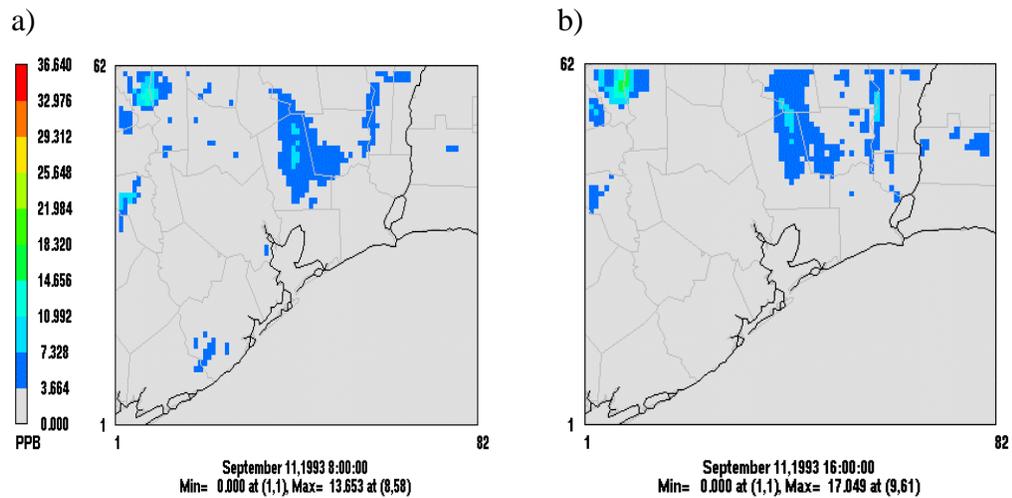


Figure 3.8 Predicted enhancement in O₃ formation due to Cl₂ emissions from industrial point sources and sea salt aerosol and HOCl emissions from cooling towers and swimming pools on September 11, 1993. The maximum predicted enhancement in O₃ formation occurred on this episode day.

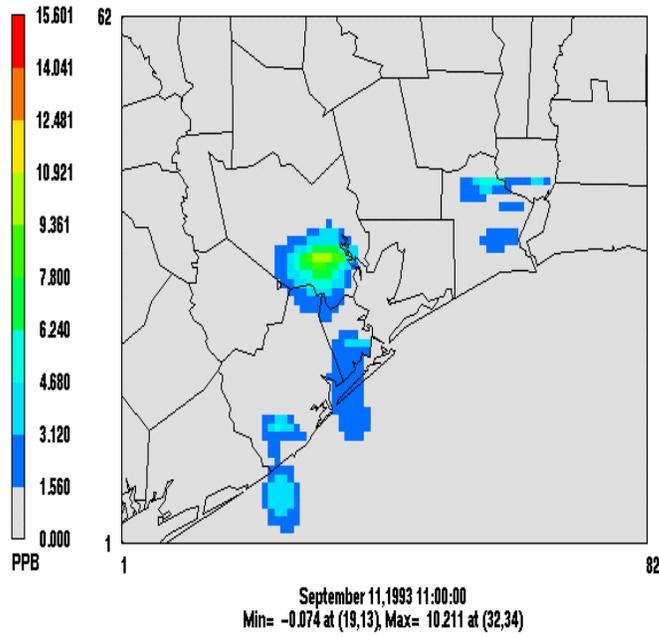
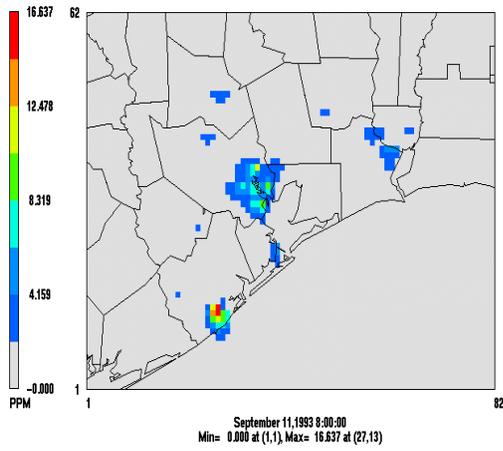


Figure 3.9 CMBO formation at a) 0800 and b) 1600 on September 11, 1993.

a)



b)

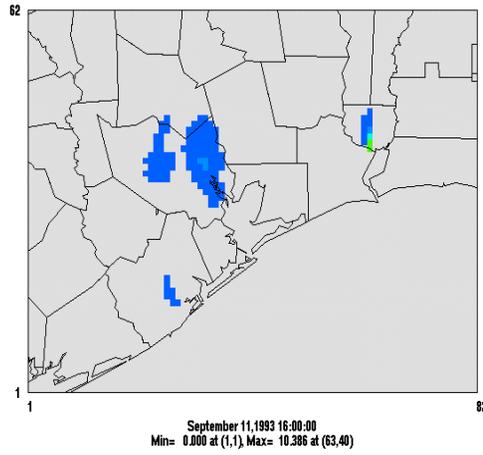


Table 3.1 Peak predicted ozone mixing ratios in 11-county region and area of exceedance above a 100 ppbv threshold ozone concentration for a) September episode and b) August episode. County Number: (1) Brazoria (2) Chambers (3) Fort Bend (4) Galveston (5) Hardin (6) Harris (7) Jefferson (8) Liberty (9) Montgomery (10) Orange (11) Waller.

a)

Scenario	Day	Peak Predicted Ozone Mixing Ratio (ppb)	Time of Peak	County of Peak	Location of Peak	AOE (area of exzceedance) km ² hr
Basecase with emissions in the form of Cl ₂	9/8/1993	200.99	16:00	3	(25, 30)	6912
	9/9/1993	194.39	16:00	4	(48, 45)	9872
	9/10/1993	194.84	16:00	3	(48, 45)	17840
	9/11/1993	202.58	16:00	9	(32, 26)	n/a
Basecase (no Cl ₂ or HOCl emissions)	9/8/1993	199.67	16:00	3	(25, 30)	6880
	9/9/1993	192.22	16:00	4	(48, 45)	9760
	9/10/1993	192.76	16:00	3	(48, 45)	17792
	9/11/1993	200.41	16:00	9	(32, 26)	n/a
Basecase with emissions in the form of Cl ₂ except for emission from cooling towers and swimming pools which are in the form of HOCl	9/8/1993	201.31	16:00	3	(25, 30)	6896
	9/9/1993	194.97	16:00	4	(48, 45)	9840
	9/10/1993	194.91	16:00	3	(48, 45)	17840
	9/11/1993	203.55	16:00	9	(32, 26)	n/a

b)

Scenario	Day	Peak Predicted Ozone Mixing Ratio (ppb)	Time of Peak	County of Peak	Location of Peak	AOE (area of exceedance) km ² hr
Basecase with emissions in the form of Cl ₂	8/18/1993	133.6	16:00	9	(28, 45)	4272
	8/19/1993	131.38	16:00	9	(24, 48)	5200
	8/20/1993	132.77	16:00	9	(28, 49)	n/a
Basecase (no Cl ₂ or HOCl emissions)	8/18/1993	133.6	16:00	9	(28, 45)	4272
	8/19/1993	131.38	16:00	9	(24, 48)	5200
	8/20/1993	132.77	16:00	9	(28, 49)	n/a

Chapter 4: Sensitivity of Ozone Formation to Chlorine Emission Estimates

Two types of studies were conducted to examine the impacts of Cl₂ emission estimates on regional O₃ formation:

1. Comparison of the impacts of Cl₂ emission sources on the spatial distribution of O₃ formation by doubling Cl₂ emissions from cooling towers, swimming pools, and point sources, respectively, and increasing Cl₂ emissions from sea salt by a factor of ten.
2. Assessment of the impacts of a 2 tpd release of Cl₂ from a Houston Ship Channel refinery on O₃ and CMBO formation.

4.1 Effects of Emission Estimates on the Spatial and Temporal Distribution of O₃ Formation

The relative impacts of chlorine emissions sources on the spatial distribution of O₃ are shown in Figure 4.1. The results are presented in the form of maps showing maximum predicted differences in O₃ mixing ratios between modeling simulations with Cl₂ emissions from an individual source doubled, or in the case of sea salt aerosol multiplied by a factor of 10, and the simulation with base Cl₂ emissions described in the previous chapter. It is important to recognize that the maps show maximum predicted mixing ratios in each grid cell for the entire episode.

Cooling towers and swimming pools had the largest impacts on ozone mixing ratios in the region. Maximum ozone enhancement from cooling towers was 15 ppbv in the Freeport and Houston Ship Channel areas. Although not shown in Figure 4.1, impacts from cooling towers occurred primarily in the morning between 0700 and 1000. Peak ozone enhancement from swimming pools is 7 ppbv in the Houston urban area. The enhancement from pools occurred in the afternoon around 1700. Industrial point sources and sea salt aerosol had negligible impacts on O₃ mixing ratios in the Houston area. CMBO mixing ratios followed similar spatial and temporal trends to those of O₃.

Peak domain-wide ozone mixing ratios and the area of exceedance above a 100 ppbv threshold are summarized in Table 4.1. Doubling emissions of Cl₂ from cooling towers, swimming pools, industrial point sources, and increasing sea salt aerosol emissions by a factor of ten, respectively, increased peak domain-wide ozone mixing ratios by at most 3 ppbv relative to the simulation with base Cl₂ emissions. Geographic locations (counties) of peak mixing ratios did not change except when emissions from swimming pools were doubled. In this case, peak mixing ratios were observed in the densely populated area of Harris County on the 8th and 10th of September instead of in Fort Bend County. The area of exceedance above a 100ppbv threshold tended to increase slightly in conjunction with the increase in emissions again with the exception of swimming pools. Doubling emissions from swimming pools increase the area of exceedance by as much as a factor of four on two days of the episode.

The results of the emission sensitivity studies suggest that reducing uncertainties associated with estimates from cooling towers and swimming pools should be focal points of future research.

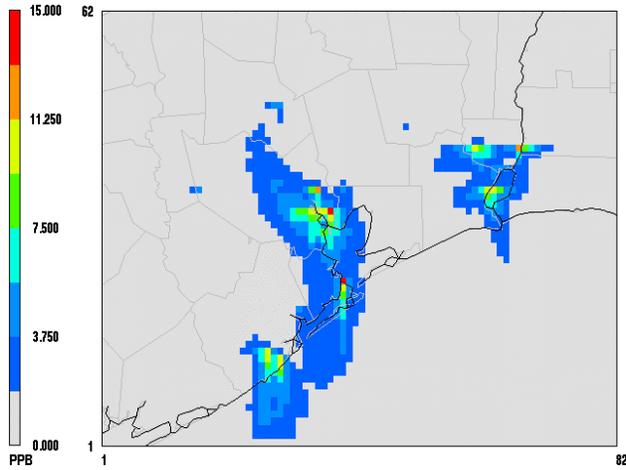
Future studies should specifically address (1) characterization of the spatial distribution of cooling towers and identification of facility practices associated with chlorination, and (2) comparison of spatial surrogates for residential pools and quantification of the rate of chlorine volatilization.

4.2 Impacts of a Point Source Release of Cl₂ on O₃ and CMBO Enhancement

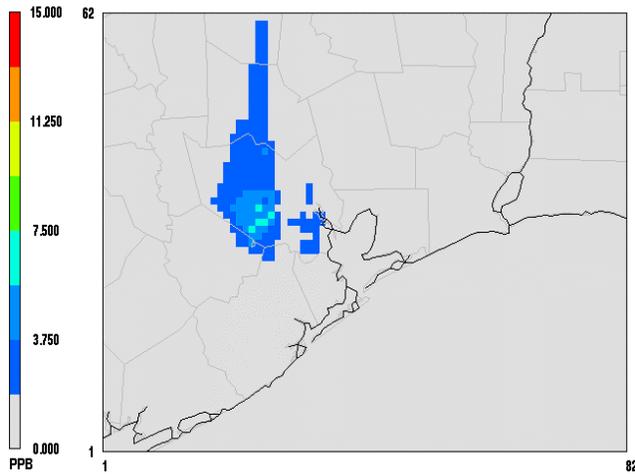
Hourly chlorine emissions for the episode from industrial point sources were calculated based on reported annual average emissions. In order to examine the potential impacts of a large release of chlorine from an industrial point source, emissions of Cl₂ from the second largest point source in the Houston Ship Channel were increased by 2 tpd. Maximum predicted differences in O₃ and CMBO mixing ratios, respectively, relative to the base simulation with Cl₂ emissions are shown in Figure 4.2. The maximum predicted ozone enhancement is 20 ppbv. Large point source releases of Cl₂ within an industrial area have the potential to cause localized enhancement of O₃.

Figure 4.1 Comparison of maximum predicted impacts on the spatial distribution of O₃ for September 1993 episode from the following emission sources: a) cooling towers, b) swimming pools, c) industrial point sources, and d) sea salt aerosol.

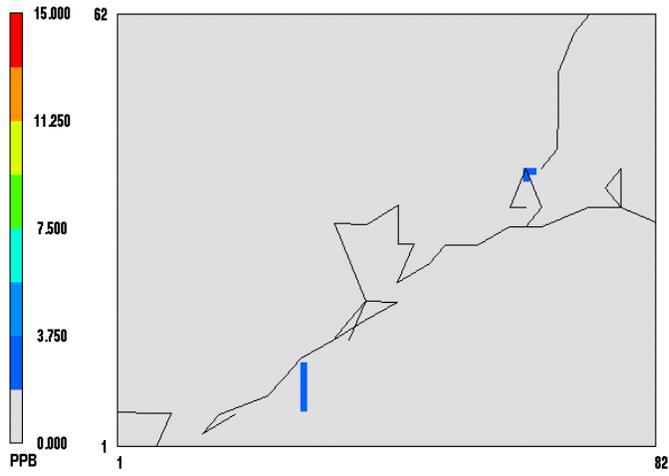
a)



b)



c)



d)

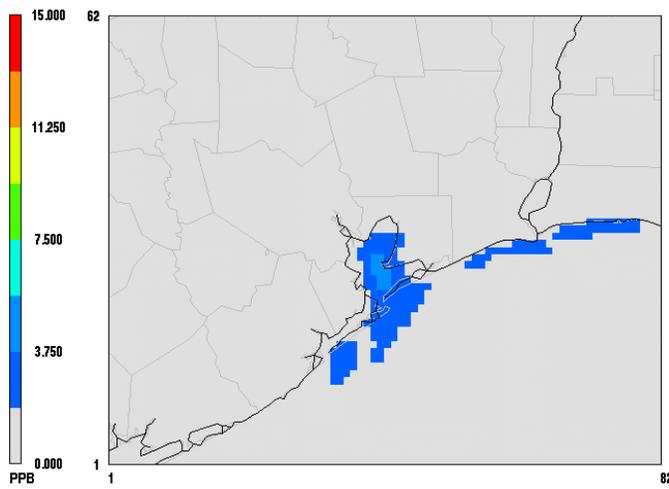
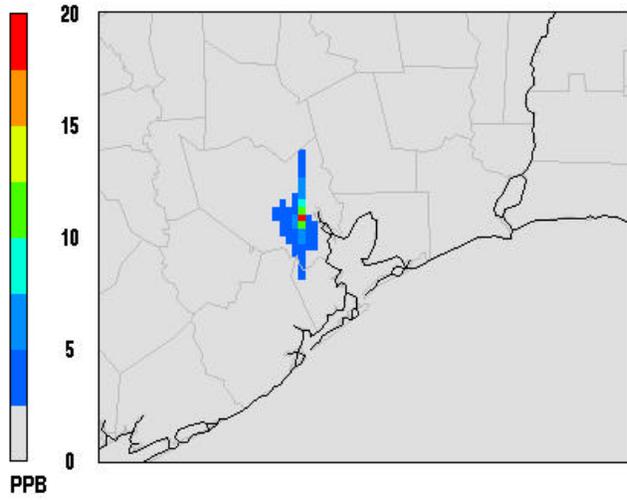


Table 4.1 Effects of uncertainties in Cl₂ emission estimates on peak predicted ozone mixing ratios in 11-county region and area of exceedance above a 100 ppbv threshold ozone concentration for September episode. County Number: (1) Brazoria (2) Chambers (3) Fort Bend (4) Galveston (5) Hardin (6) Harris (7) Jefferson (8) Liberty (9) Montgomery (10) Orange (11) Waller.

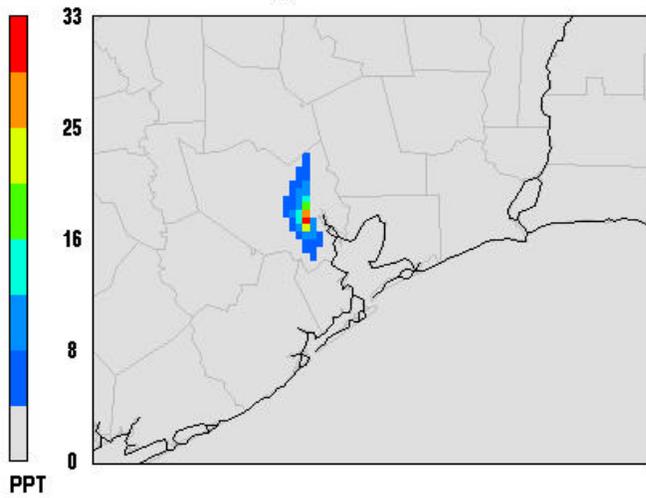
Scenario Run Description	Day	Peak Predicted Ozone Mixing Ratio (ppb)	Time of Peak	County of Peak	Location of Peak	AOE (area of exceedance) km²hr
Basecase with Cl ₂ emissions	9/8/1993	200.99	16:00	3	(25, 30)	6912
	9/9/1993	194.39	16:00	4	(48, 45)	9872
	9/10/1993	194.84	16:00	3	(48, 45)	17840
	9/11/1993	202.58	16:00	9	(32, 26)	n/a
Double emissions from cooling towers	9/8/1993	201.4	16:00	3	(25, 30)	6928
	9/9/1993	195.54	16:00	4	(48, 45)	9904
	9/10/1993	194.98	16:00	3	(48, 45)	17840
	9/11/1993	203.6	16:00	9	(32, 26)	n/a
Double emissions from pools	9/8/1993	202.39	16:00	6	(25, 31)	23280
	9/9/1993	195.14	16:00	4	(48, 45)	9904
	9/10/1993	197.2	16:00	6	(42, 38)	31184
	9/11/1993	203.49	16:00	9	(32, 26)	n/a
Double emissions from point sources	9/8/1993	201.03	16:00	3	(25, 30)	6912
	9/9/1993	194.49	16:00	4	(48, 45)	9872
	9/10/1993	194.85	16:00	3	(48, 45)	17840
	9/11/1993	202.66	16:00	9	(32, 26)	n/a
Increase sea salt emissions by a factor of ten	9/8/1993	201	16:00	3	(25, 30)	6912
	9/9/1993	194.44	16:00	4	(48, 45)	9936
	9/10/1993	194.84	16:00	3	(48, 45)	17840
	9/11/1993	202.6	16:00	9	(32, 26)	n/a
Increase Cl ₂ emissions by 2 tons/day at a large refinery in the Ship Channel	9/8/1993	201.45	16:00	3	(25, 30)	6912
	9/9/1993	195.35	16:00	4	(48, 45)	9872
	9/10/1993	194.98	16:00	3	(48, 45)	17840
	9/11/1993	203.3	16:00	9	(32, 26)	n/a

Figure 4.2 Comparison of maximum predicted impacts on a) O₃ and b) CMBO formation for September 1993 episode from a 2 tpd point source release of Cl₂ in the Houston Ship Channel.

a)



b)



Chapter 5: Impacts of Large Point Source Releases of Ethylene or Paraffins Alone or in Conjunction with Emissions of NO_x and Cl₂

The nature of high ozone events in Houston has been the subject of recent scrutiny. It has been recognized that many of the highest events are transient in nature. High ozone mixing ratios occur with the greatest frequency in the vicinity of the Houston Ship Channel and near Texas City. In order to examine the potential impacts of emissions from upsets at industrial point sources in the Ship Channel area, a series of sensitivity studies was conducted that focused on large releases of ethylene and paraffins alone or in conjunction with upsets of NO_x and Cl₂ emissions. Unless otherwise specified, the releases were added to the base Cl₂ emissions case. The releases occurred from the grid cell containing the Clinton Drive ambient monitor. The following simulations were conducted with the September episode:

1. 5000 lb ethylene released between 0700-0800 (no emissions of Cl₂ precursors)
2. 5000 lb ethylene released between 0700-0800 (with emissions of Cl₂ precursors)
3. 5000 lb ethylene, 100 lb Cl₂ released between 0700-0800
4. 5000 lb ethylene, 700 lb NO_x released between 0700-0800
5. 5000 lb ethylene, 700 lb/hr NO_x, 100 lb/hr Cl₂ released between 0700-0800
6. 5000 lb paraffins released between 0700-0800 (no emissions of Cl₂ precursors)
7. 5000 lb paraffins released between 0700-0800 (with emissions of Cl₂ precursors)
8. 5000 lb paraffins, 100 lb/hr Cl₂ released between 0700-0800
9. 5000 lb paraffins, 700 lb/hr NO_x released between 0700-0800
10. 5000 lb paraffins, 700 lb/hr NO_x, 100 lb/hr Cl₂ released between 0700-0800

The following sensitivity studies were conducted with the August episode:

1. 5000 lb ethylene released between 1300-1400 (no emissions of Cl₂ precursors)
2. 5000 lb ethylene released between 1300-1400 (with emissions of Cl₂ precursors)
3. 5000 lb paraffins released between 1300-1400 (no emissions of Cl₂ precursors)
4. 5000 lb paraffins released between 1300-1400 (with emissions of Cl₂ precursors)

5.1 Impacts of an Ethylene Release in the Absence of Cl₂ Chemistry

Enhancement in O₃ mixing ratios from a large, elevated ethylene release in the Ship Channel was examined by comparing predicted mixing ratios from the September Basecase to predicted mixing ratios after the addition of 5000 lb of ethylene at 0700-0800 each day in the grid cell with the Clinton monitor. The analysis was repeated for August episode, but the time of the release was changed to 1300-1400 each day. Results are presented in the form of maps showing maximum predicted differences in O₃ mixing ratios and in the form of a table with peak predicted mixing ratios and the area of exceedance above a 100 ppbv threshold for each scenario.

Ozone formation was enhanced by 2-5 ppbv between 1100 and 1300 each day of the September episode and between 1400 and 1500 each day of the August episode. The maximum enhancement, shown in Figure 5.1, was 5 ppbv at 1100 on September 9th southwest of the Ship Channel. The maximum enhancement during the August episode was 5 ppbv on the 18th at 1400.

As shown in Table 5.1, the ethylene release increased peak predicted ozone mixing ratios by 1 to 5 ppbv during the September episode, but did not change the geographic location or time of the peak. The area of exceedance increased by 50 km²hr due to the ethylene release during the September episode. Peak predicted mixing ratios during the August episode increased by at most 1 ppbv.

5.2 Impacts of an Ethylene Release with Base Cl₂ Precursor Emissions and Chemistry

Enhancement in O₃ mixing ratios from a 5000 lb elevated ethylene release in the Ship Channel was examined by comparing predicted mixing ratios from the following two scenarios: (1) the September Basecase with Cl₂ emissions and (2) the release of 5000 lb/hr of ethylene at 0700-0800 in the grid cell with Clinton monitor in conjunction with September Cl₂ Basecase emissions. The comparison was repeated for the August episode, but ethylene was released at 1300-1400. Ozone formation was enhanced by 2-5 ppbv between 1100 and 1200 each day of the September episode and between 1400 and 1500 each day of the August episode. The maximum enhancement during the August episode, shown in Figure 5.2, was 5 ppbv on the 18th at 1400. The maximum enhancement during the September episode was 5 ppbv at 1100 southwest of the Ship Channel. These results were consistent with the enhancement from an ethylene release in the absence of Cl₂ chemistry, i.e., enhancement from an ethylene release in the absence and presence of base Cl₂ precursor emissions and chemistry are 5.18 ppbv and 5.41 ppbv, respectively, during the September episode. Enhancement was slightly greater in the presence of base Cl₂ precursor emissions and chemistry, which is likely due to the additional free radical source (Cl₂). CMBO mixing ratios, shown in Figure 5.3, decreased by 0.6 - 0.9 pptv at 0800 each day of the September episode and by 0.3 - 0.4 pptv between 1300 and 1700 each day of the August episode, indicating competition between ethylene and isoprene for Cl₂.

The ethylene release increased peak predicted ozone mixing ratios by 1-2 ppbv during the September episode, but did not change the geographic location, time of the peak, or area of exceedance relative to the Cl₂ Basecase. Peak predicted mixing ratios during the August episode increased by less than 1 ppbv.

5.3 Impacts of an Ethylene Release Alone or with Simultaneous Releases Cl₂ and/or NO_x

A series of runs with the September episode compared the predicted enhancement in ozone mixing ratios when the ethylene release from 0700 to 0800 in the grid cell with the Clinton monitor occurred in conjunction with large releases of Cl₂ and/or NO_x. It is important to note that the base Cl₂ and/or NO_x emissions throughout the rest of the 4km domain remained the same. The results were then compared with the Cl₂ basecase to determine if the 'upset' releases led to increases in predicted ozone mixing ratios.

The release of 5000lb/hr of ethylene in conjunction with 100 lb of Cl₂ increased ozone mixing ratios by 3-6 ppbv each day relative to the Cl₂ basecase, as shown in Table 5.2. The maximum enhancement, shown in Figure 5.4, occurred on September 9th at 1100 southwest of the Ship Channel. The peak predicted ozone mixing ratio in the 11-county region, shown in Table 5.1, increased by 1 to 2 ppbv during the September episode, but its geographic location and timing relative to the Cl₂ Basecase were unchanged. The area of exceedance was also unchanged.

The maximum CMBO enhancement on the 9th, also shown in Figure 5.4, was smaller than on other days. Enhancement of CMBO mixing ratios each day coincided with the time of Cl-precursor release (0700) and ranged from 2-4 pptv. The maximum CMBO enhancement for the episode occurred on September 11th in the same geographic location as on the 9th.

A 700 lb NOx release in conjunction with the ethylene release at 0700 in the grid cell with the Clinton monitor did not increase ozone mixing ratios as much as if ethylene was released in conjunction with Cl₂ alone. After an initial decrease in ozone mixing ratios due to titration by NOx immediately after the release, ozone formation was enhanced by 2-4 ppbv between 1100 and 1300 each day, as shown in Table 5.2. The maximum enhancement, shown in Figure 5.5, occurred on September 9th at 1100 southwest of the Ship Channel. CMBO mixing ratios decreased by 0.6 to 0.9 pptv between 0800 and 0900 each day of the September episode. The simultaneous release of ethylene and NOx had negligible effects on the area of exceedance and peak predicted ozone mixing ratios or their geographic location and time relative to the Cl₂ Basecase.

The simultaneous release of 5000 lb of ethylene, 100 lb of Cl₂, and 700 lb of NOx increased ozone mixing ratios by 2 to 5 ppbv between 1100 and 1200 each day of the episode. The maximum enhancement was lower than in the scenario when ethylene was released with Cl₂ alone, but higher than when ethylene was released with NOx alone. The maximum enhancement, shown in Figure 5.6 occurred on September 9th at 1100. The simultaneous release of ethylene, NOx, and Cl₂ had negligible effects on the area of exceedance and peak predicted ozone mixing ratios or their geographic location and time relative to the Cl₂ Basecase. CMBO mixing ratios were enhanced by 2-4 pptv at 0700 each day of the episode. The maximum enhancement, shown in Figure 5.6, occurred on September 11th. The simultaneous release of ethylene, Cl₂, and NOx produced a greater enhancement in CMBO mixing ratios than the release of ethylene with either Cl₂ or NOx alone.

5.4 Impacts of a Paraffin Release

The sensitivity studies described above were repeated with a 5000 lb release of paraffins from 0700 to 0800 in the grid cell with the Clinton monitor instead of ethylene. Tile plots showing maximum predicted differences in O₃ and CMBO mixing ratios for each scenario are presented in Figures 5.7 through 5.12, respectively. Peak predicted ozone mixing ratios and the area of exceedance above a 100 ppbv threshold for the 11-county region are given in Table 5.3. Maximum predicted daily difference in O₃ and CMBO mixing ratios and the time of occurrence are summarized in Table 5.4.

Several trends emerged from comparing the results of the ethylene and paraffin releases. A 5000 lb/hr release of paraffins produced less ozone (0.27-0.86 ppbv enhancement) during these particular episodes than a 5000 lb/hr release of ethylene (2-5.4 ppbv enhancement). These results were independent of the presence of base Cl₂ emissions and chemistry. Large releases of either ethylene or paraffins alone or simultaneously with Cl₂ and/or NOx increased the peak predicted ozone mixing ratios for the 11-county region by at most 1-2 ppbv with no or minimal impacts on the time and geographic location of the peak mixing ratios and the area of exceedance above a 100 ppbv threshold.

Maximum enhancement in ozone mixing ratios (3-6 ppbv) occurred when a 100 lb of Cl₂ was simultaneously released with ethylene or paraffins. Enhancement in ozone mixing ratios from ethylene and paraffin releases tended to occur in the same geographic location. However, the time of maximum enhancement from the paraffin release was 0800 versus 1100 from the ethylene release, respectively.

Emissions of NO_x have an important role both in the magnitude and timing of the enhancement of ozone mixing ratios. When paraffins or ethylene were released simultaneously with NO_x, ozone mixing ratios tended to decrease initially following the release and to increase in the late morning to mid-afternoon. Although reaction of paraffins with Cl· was rapid, ozone was titrated by NO. Thus, the timing of the maximum enhancement shifted from 0800 when paraffins and Cl₂ were released simultaneously, to early afternoon (1300-1400) when NO_x was included in the release. The release of ethylene or paraffins with NO_x resulted in a lower daily maximum enhancement in ozone mixing ratios than the release of ethylene or paraffins with Cl₂. Simultaneous releases of the hydrocarbons with NO_x and Cl₂ reduced NO_x disbenefits in the morning and resulted in greater ozone production than if NO_x were released with the hydrocarbons alone.

Maximum enhancement in CMBO ratios tended to occur within the first two hours following the release, independent of the scenario. Less CMBO was formed relative to the Cl₂ basecase when ethylene or paraffins were released alone because of competition with isoprene for Cl·. However, CMBO formation was enhanced by 2-4 pptv when the hydrocarbon release was accompanied by a 100 lb release of Cl₂. Release of ethylene or paraffins and NO_x slightly mitigated the effects of competition between isoprene and ethylene/paraffins for Cl·. The maximum enhancement in CMBO mixing ratios (4-4.4 pptv) occurred when ethylene or paraffins were released simultaneously with NO_x and Cl₂.

Figure 5.1 Predicted enhancement in O₃ mixing ratios at a) 1100 on September 9, 1993 and b) 1400 on August 18th, 1993 due to 5000 lb ethylene release in the Ship Channel (Clinton Drive). The maximum predicted enhancement in O₃ formation occurred on these episode days.

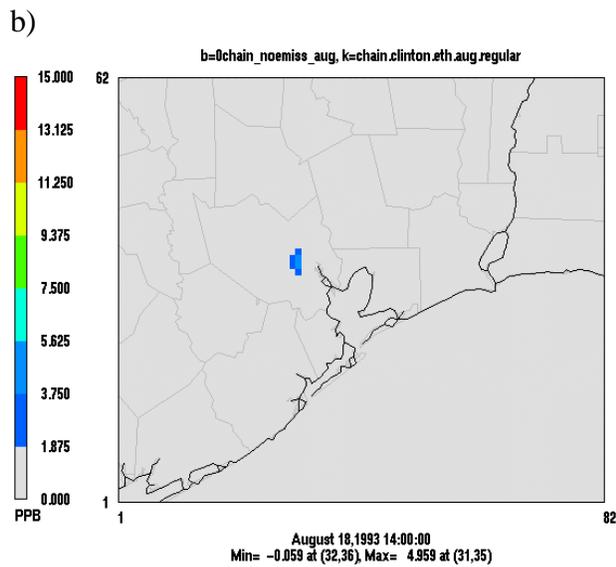
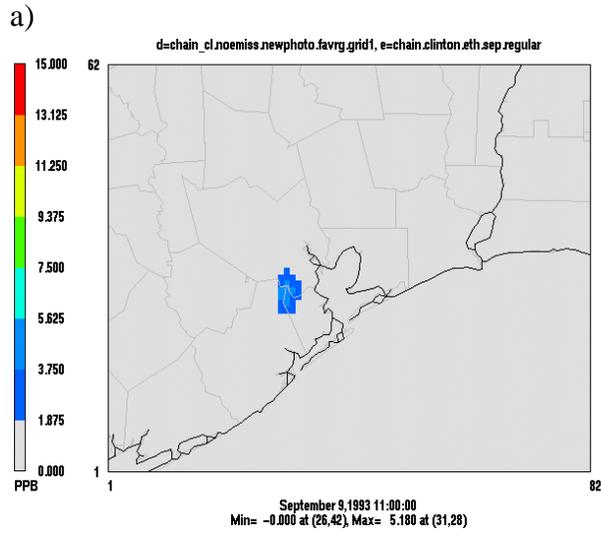
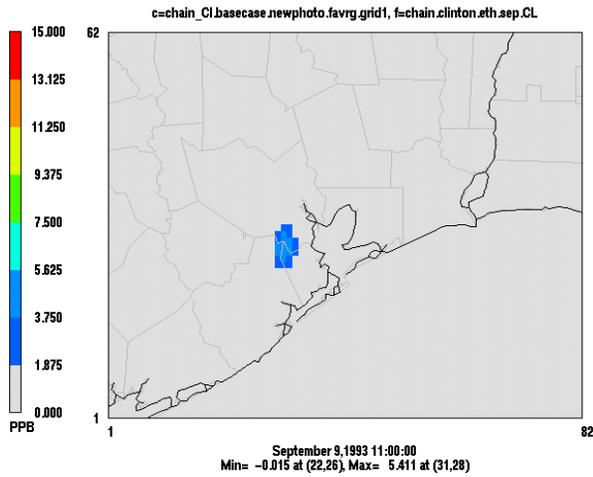


Figure 5.2 Predicted enhancement in O₃ mixing ratios at a) 1100 on September 9, 1993 and b) 1400 on August 18th, 1993 due to 5000 lb ethylene release in the Ship Channel (Clinton Drive) with base Cl⁻ precursor emissions and chemistry. The maximum predicted enhancement in O₃ formation occurred on these episode days.

a)



b)

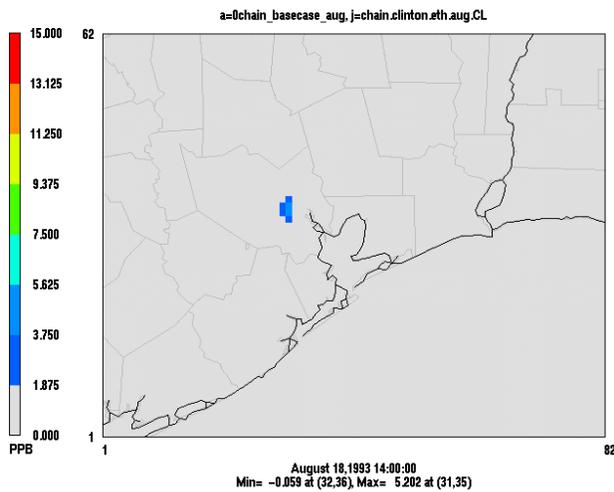


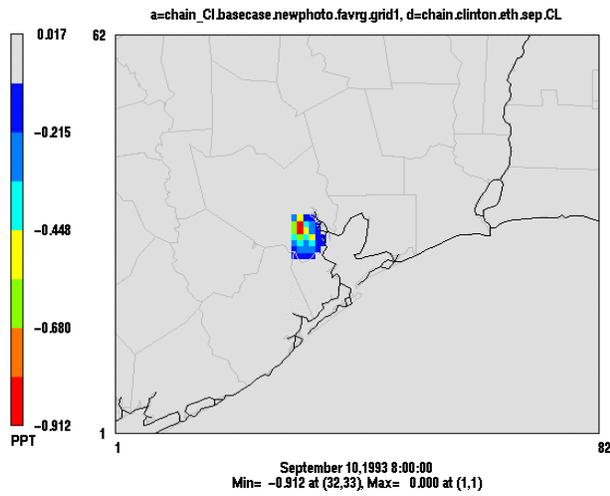
Table 5.1 Effects of 5000 lb ethylene release alone or in conjunction with releases of NO_x and/or Cl₂ in the grid cell with the Clinton monitor on peak predicted ozone mixing ratios in 11-county region and area of exceedance above a 100 ppbv threshold ozone concentration for the September and August episodes. County Number: (1) Brazoria (2) Chambers (3) Fort Bend (4) Galveston (5) Hardin (6) Harris (7) Jefferson (8) Liberty (9) Montgomery (10) Orange (11) Waller.

Scenario Description	Day	Peak Predicted Ozone Mixing Ratio (ppb)	Time of Peak	County of Peak	Location of Peak	AOE (area of exceedance) km ² hr	
Basecase	9/8/1993	199.67	16:00	3	(25, 30)	6880	
	9/9/1993	192.22	16:00	4	(48, 45)	9760	
	9/10/1993	192.76	16:00	3	(48, 45)	17792	
	9/11/1993	200.41	16:00	9	(32, 26)	n/a	
	August Episode						
	8/18/1993	133.6	16:00	9	(28, 45)	4272	
	8/19/1993	131.38	16:00	9	(24, 48)	5200	
8/20/1993	132.77	16:00	9	(28, 49)	n/a		
Basecase with Cl ₂ emissions	9/8/1993	200.99	16:00	3	(25, 30)	6912	
	9/9/1993	194.39	16:00	4	(48, 45)	9872	
	9/10/1993	194.84	16:00	3	(48, 45)	17840	
	9/11/1993	202.58	16:00	9	(32, 26)	n/a	
	August Episode						
	8/18/1993	133.6	16:00	9	(28, 45)	4272	
	8/19/1993	131.38	16:00	9	(24, 48)	5200	
8/20/1993	132.77	16:00	9	(28, 49)	n/a		
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.24	16:00	3	(25, 30)	6912	
	9/9/1993	195.59	16:00	4	(48, 45)	9872	
	9/10/1993	194.86	16:00	3	(48, 45)	17840	
	9/11/1993	204.33	16:00	9	(32, 26)	n/a	
	August Episode						

	8/18/1993	133.76	16:00	9	(28,45)	4288	
	8/19/1993	131.41	16:00	9	(24,48)	5216	
	8/20/1993	132.79	16:00	9	(28,50)	n/a	
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor without any emissions of Cl precursors	9/8/1993	199.93	16:00	3	(25, 30)	6880	
	9/9/1993	193.49	16:00	4	(48, 45)	9760	
	9/10/1993	192.79	16:00	3	(48, 45)	17792	
	9/11/1993	202.22	16:00	9	(32, 25)	n/a	
	August Episode						
	8/18/1993	133.17	16:00	9	(28,45)	4064	
	8/19/1993	130.06	16:00	9	(24,48)	4896	
	8/20/1993	131.33	16:00	9	(28,50)	n/a	
Release of 5000 lb/hr of ethylene and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.25	16:00	3	(25, 30)	6912	
	9/9/1993	195.63	16:00	4	(48, 45)	9872	
	9/10/1993	194.86	16:00	3	(48, 45)	17840	
	9/11/1993	204.39	16:00	9	(32, 26)	n/a	
Release of 5000 lb/hr of ethylene and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.22	16:00	3	(25, 30)	6912	
	9/9/1993	195.55	16:00	4	(48, 45)	9872	
	9/10/1993	194.86	16:00	3	(48, 45)	17840	
	9/11/1993	204.22	16:00	9	(32, 26)	n/a	
Release of 5000 lb/hr of ethylene, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.23	16:00	3	(25, 30)	6912	
	9/9/1993	195.58	16:00	4	(48, 45)	9872	
	9/10/1993	194.86	16:00	3	(48, 45)	17840	
	9/11/1993	204.27	16:00	9	(32, 26)	n/a	

Figure 5.3 Peak predicted difference in CMBO mixing ratios at a) 0800 on September 10, 1993 and b) 1700 on August 18th, 1993 due to 5000 lb ethylene release in the Ship Channel (Clinton Drive) with base Cl⁻ precursor emissions and chemistry. The maximum predicted enhancement in O₃ formation occurred on these episode days.

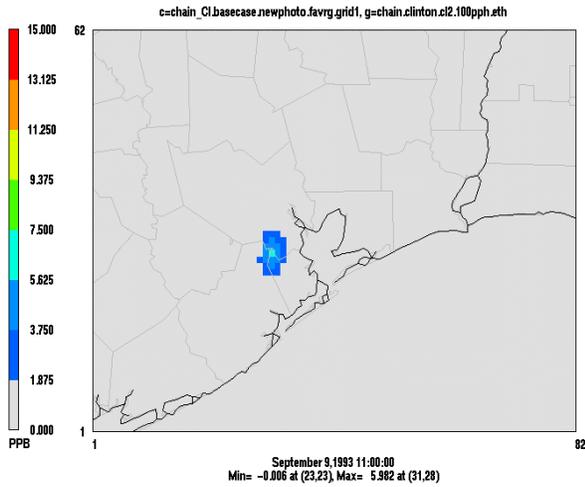
a)



b)

Figure 5.4 Predicted enhancement in a) O₃ mixing ratios at 1100 and b) CMBO mixing ratios at 0700 on September 9, 1993 due to 5000 lb ethylene and 100 lb molecular chlorine release in the Ship Channel (Clinton Drive). The maximum predicted enhancement in O₃ formation occurred on this episode day.

a)



b)

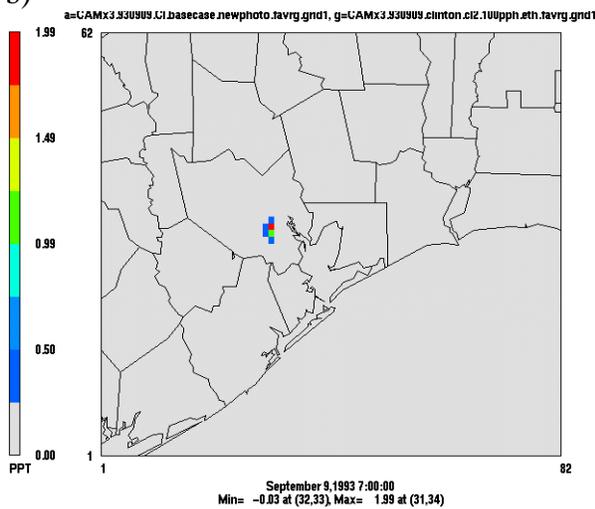


Table 5.2 Maximum predicted daily difference in O₃ and CMBO mixing ratios due to ethylene release alone or in conjunction with Cl₂ and/or NO_x emissions relative to the Cl₂ basecase: [O₃(scenario) – O₃(Cl₂ basecase)] and [CMBO(scenario) – CMBO(Cl₂ basecase)].

Scenario Description	Day	Maximum Daily Ozone Enhancement Relative to Cl₂ Basecase (ppbv)	Time	Maximum Daily CMBO Difference Relative to Cl₂ Basecase (ppbv)	Time
Release of 5000 lb/hr of ethylene from 0700-0800 in grid cell with Clinton monitor	9/8/1993	3.87	1100	-0.89	0800
	9/9/1993	5.41	1100	-0.60	0800
	9/10/1993	2.44	1100	-0.91	0800
	9/11/1993	3.98	1200	-0.76	0800
Release of 5000 lb/hr of ethylene and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	4.18	1100	3.30	0700
	9/9/1993	5.98	1100	1.99	0700
	9/10/1993	2.63	1100	3.84	0700
	9/11/1993	5.42	0800	4.38	0700
Release of 5000 lb/hr of ethylene and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	9/8/1993	3.31	1200	-0.86	0800
	9/9/1993	4.31	1100	-0.58	0800
	9/10/1993	2.10	1200	-0.88	0800
	9/11/1993	3.40	1300		0800
Release of 5000 lb/hr of ethylene, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	3.52	1200	3.33	0700
	9/9/1993	4.86	1100	2.01	0700
	9/10/1993	2.21	1100	3.87	0700
	9/11/1993	3.63	1200	4.44	0700

Figure 5.5 Predicted enhancement in O₃ mixing ratios at 1100 on September 9, 1993 due to 5000 lb ethylene and 700 lb NO_x release in the Ship Channel (Clinton Drive). The maximum predicted enhancement in O₃ formation occurred on this episode day.

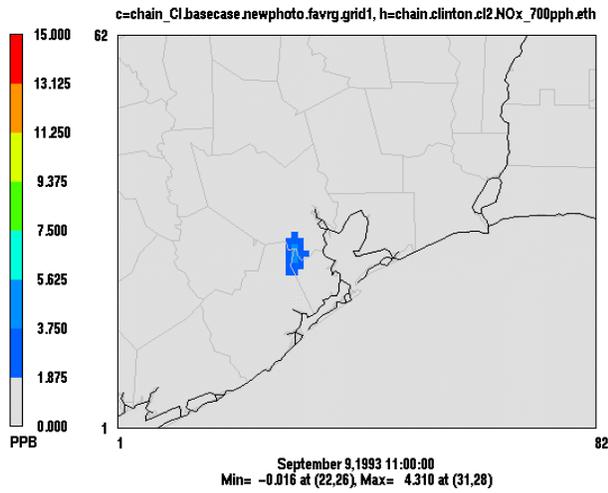
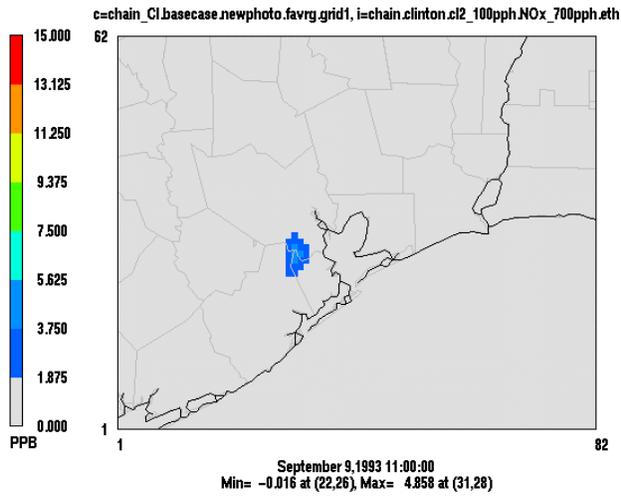


Figure 5.6 Predicted enhancement in a) O₃ mixing ratios at 1100 on September 9, 1994 and b) CMBO mixing ratios at 0700 on September 11, 1993 due to simultaneous release of 5000 lb ethylene, 100 lb Cl₂, and 700 lb of NO_x in the Ship Channel (Clinton Drive). The maximum predicted enhancement occurred on these episode days.

a)



b)

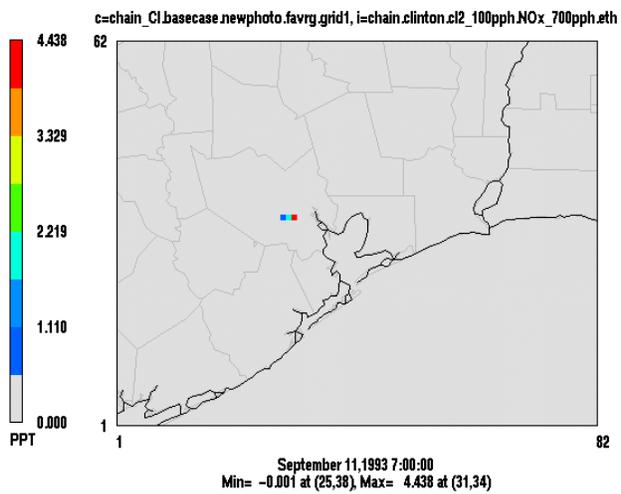
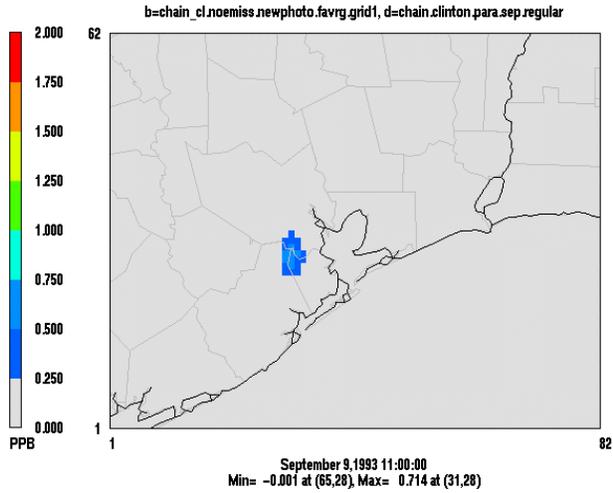


Figure 5.7 Predicted enhancement in O₃ mixing ratios at a) 1100 on September 9, 1993 and b) 1400 on August 18th, 1993 due to 5000 lb paraffin release in the Ship Channel (Clinton Drive). The maximum predicted enhancement in O₃ formation occurred on these episode days.

a)



b)

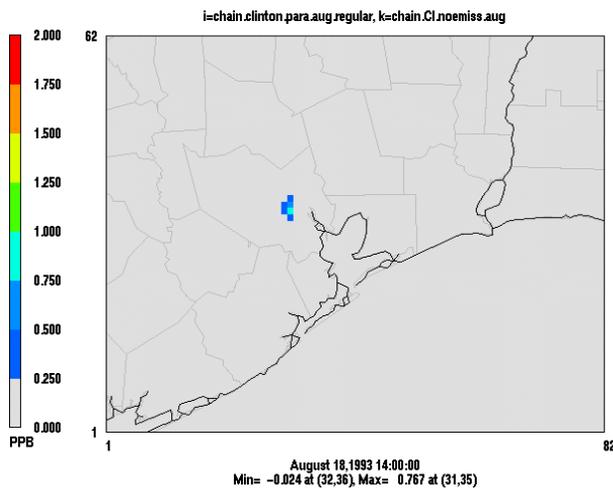
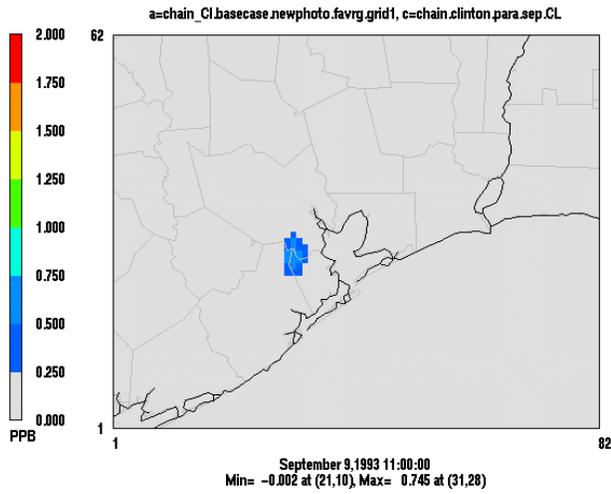


Figure 5.8 Predicted enhancement in O₃ mixing ratios at a) 1100 on September 9, 1993 and b) 1400 on August 18th, 1993 due to 5000 lb paraffin release in the Ship Channel (Clinton Drive) with base Cl⁻ precursor emissions and chemistry. The maximum predicted enhancement in O₃ formation occurred on these episode days.

a)



b)

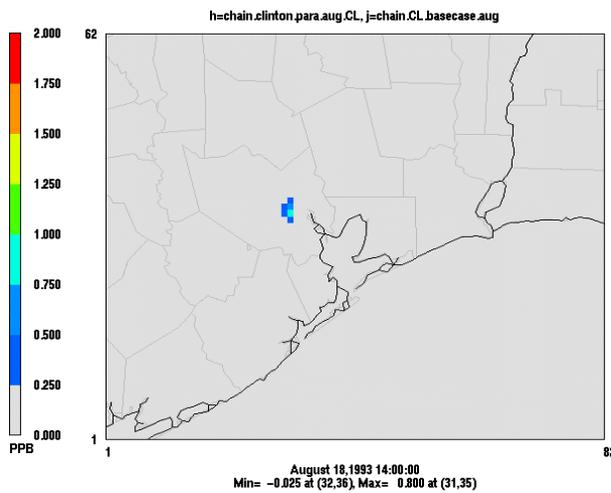
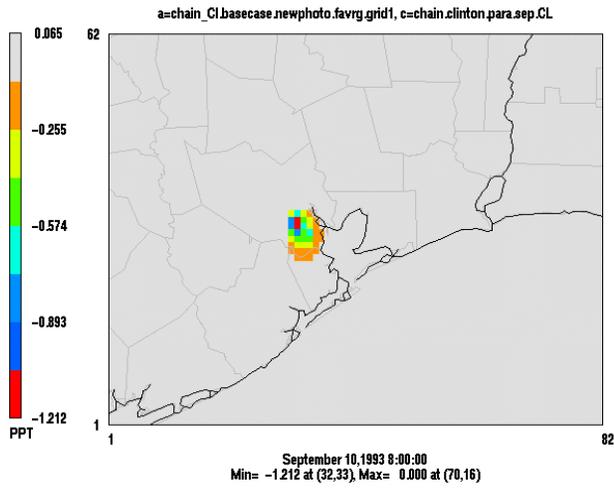


Figure 5.9 Peak predicted difference in CMBO mixing ratios at a) 0800 on September 10, 1993 and b) 1700 on August 19th, 1993 due to 5000 lb paraffin release in the Ship Channel (Clinton Drive) with base Cl⁻ precursor emissions and chemistry. The maximum predicted enhancement occurred on these episode days.

a)



b)

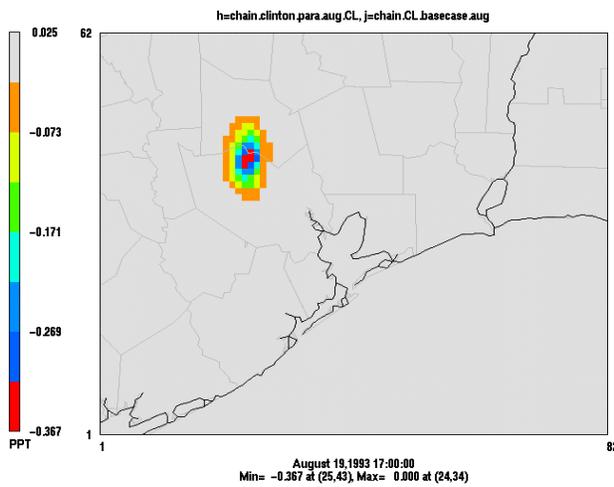
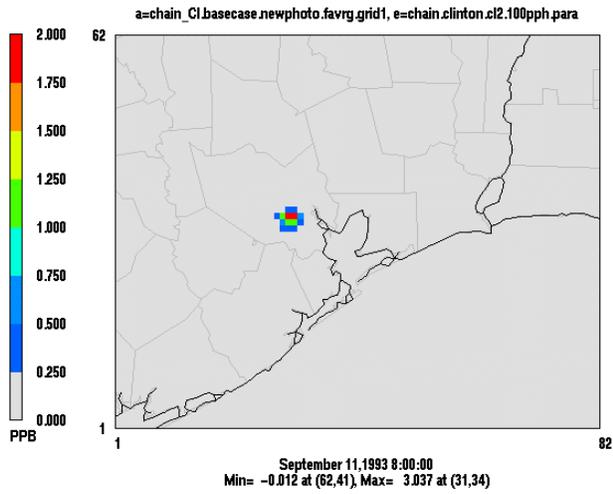


Figure 5.10 Predicted enhancement in a) O₃ mixing ratios at 0800 and b) CMBO mixing ratios at 0700 on September 11, 1993 due to 5000 lb paraffin and 100 lb molecular chlorine release in the Ship Channel (Clinton Drive). The maximum predicted enhancement occurred on this episode day.

a)



b)

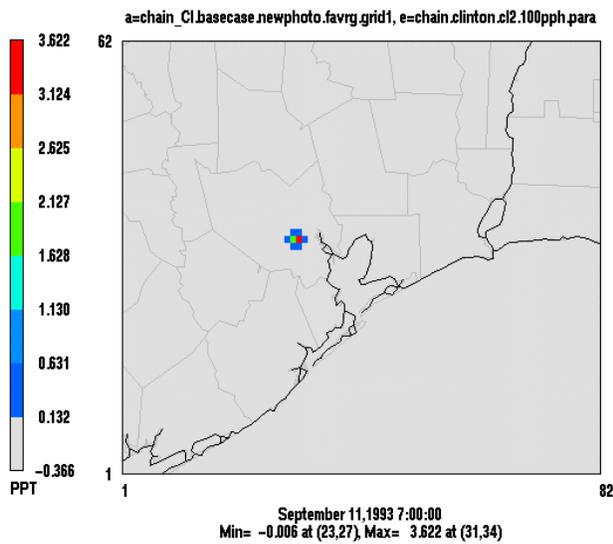


Figure 5.11 Predicted enhancement in O₃ mixing ratios at 1400 on September 10, 1993 due to 5000 lb paraffin and 700 lb NO_x release in the Ship Channel (Clinton Drive). The maximum predicted enhancement in O₃ formation occurred on this episode day.

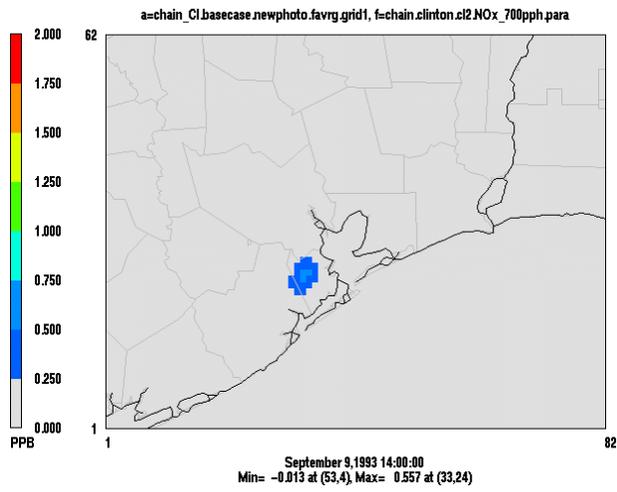
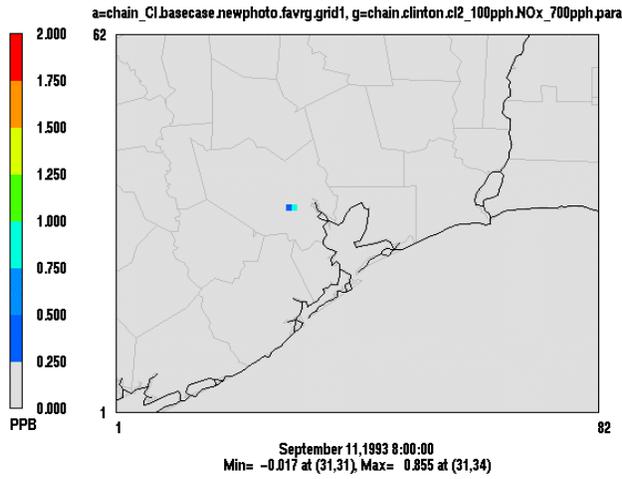


Figure 5.12 Predicted enhancement in a) O₃ mixing ratios at 0800 and b) CMBO mixing ratios at 0700 on September 11, 1993 due to simultaneous release of 5000 lb/hr ethylene, 100 lb/hr Cl₂, and 700 lb/hr of NO_x in the Ship Channel (Clinton Drive). The maximum predicted enhancement occurred on this episode day.

a)



b)

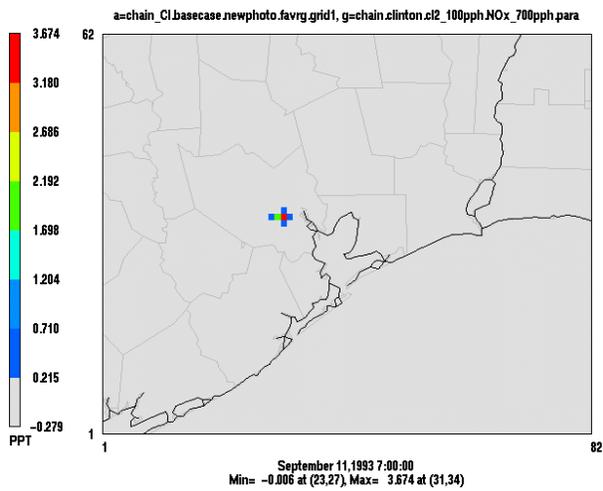


Table 5.3 Effects of 5000 lb/hr paraffin release alone or in conjunction with releases of NOx and/or Cl₂ in the grid cell with the Clinton monitor on peak predicted ozone mixing ratios in 11-county region and area of exceedance above a 100 ppbv threshold ozone concentration for the September and August episodes. County Number: (1) Brazoria (2) Chambers (3) Fort Bend (4) Galveston (5) Hardin (6) Harris (7) Jefferson (8) Liberty (9) Montgomery (10) Orange (11) Waller.

Scenario Description	Day	Peak Predicted Ozone Mixing Ratio (ppb)	Time of Peak	County of Peak	Location of Peak	AOE (area of exceedance) km ² hr	
Basecase	9/8/1993	199.67	16:00	3	(25, 30)	6880	
	9/9/1993	192.22	16:00	4	(48, 45)	9760	
	9/10/1993	192.76	16:00	3	(48, 45)	17792	
	9/11/1993	200.41	16:00	9	(32, 26)	n/a	
	August Episode						
	8/18/1993	133.6	16:00	9	(28, 45)	4272	
	8/19/1993	131.38	16:00	9	(24, 48)	5200	
8/20/1993	132.77	16:00	9	(28, 49)	n/a		
Basecase with Cl ₂ emissions	9/8/1993	200.99	16:00	3	(25, 30)	6912	
	9/9/1993	194.39	16:00	4	(48, 45)	9872	
	9/10/1993	194.84	16:00	3	(48, 45)	17840	
	9/11/1993	202.58	16:00	9	(32, 26)	n/a	
	August Episode						
	8/18/1993	133.6	16:00	9	(28, 45)	4272	
	8/19/1993	131.38	16:00	9	(24, 48)	5200	
8/20/1993	132.77	16:00	9	(28, 49)	n/a		
Release of 5000 lb/hr of paraffin from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.04	16:00	3	(25, 30)	6912	
	9/9/1993	194.64	16:00	4	(48, 45)	9872	
	9/10/1993	194.85	16:00	3	(48, 45)	17840	
	9/11/1993	202.92	16:00	9	(32, 26)	n/a	
	August Episode (release from 1300-1400)						

	8/18/1993	133.63	16:00	9	(28,45)	4272
	8/19/1993	131.39	16:00	9	(24,48)	5200
	8/20/1993	132.77	16:00	9	(28,49)	n/a
Release of 5000 lb/hr of paraffin from 0700-0800 in grid cell with Clinton monitor without any emissions of Cl precursors	9/8/1993	199.72	16:00	3	(25, 30)	6880
	9/9/1993	192.47	16:00	4	(48, 45)	9760
	9/10/1993	192.77	16:00	3	(48, 45)	17792
	9/11/1993	200.75	16:00	9	(32, 25)	N/a
	August Episode (release from 1300-1400)					
	8/18/1993	133.04	16:00	9	(28,45)	4272
	8/19/1993	130.03	16:00	9	(24,48)	5200
	8/20/1993	131.32	16:00	9	(28,49)	N/a
Release of 5000 lb/hr of paraffin and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.05	16:00	3	(25, 30)	6912
	9/9/1993	194.67	16:00	4	(48, 45)	9872
	9/10/1993	194.85	16:00	3	(48, 45)	17840
	9/11/1993	202.97	16:00	9	(32, 26)	n/a
Release of 5000 lb/hr of paraffin and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.02	16:00	3	(25, 30)	6912
	9/9/1993	194.59	16:00	4	(48, 45)	9872
	9/10/1993	194.85	16:00	3	(48, 45)	17840
	9/11/1993	202.8	16:00	9	(32, 26)	n/a
Release of 5000 lb/hr of paraffin 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	201.03	16:00	3	(25, 30)	6912
	9/9/1993	194.62	16:00	4	(48, 45)	9872
	9/10/1993	194.85	16:00	3	(48, 45)	17840
	9/11/1993	202.85	16:00	9	(32, 26)	n/a

Table 5.4 Maximum predicted daily difference in O₃ and CMBO mixing ratios due to paraffin release alone or in conjunction with Cl₂ and/or NO_x emissions relative to the Cl₂ basecase: [O₃(scenario) – O₃(Cl₂ basecase)] and [CMBO(scenario) – CMBO(Cl₂ basecase)].

Scenario Description	Day	Maximum Daily Ozone Enhancement Relative to Cl₂ Basecase (ppbv)	Time	Maximum Daily CMBO Difference Relative to Cl₂ Basecase (ppbv)	Time
Release of 5000 lb/hr of paraffin from 0700-0800 in grid cell with Clinton monitor	9/8/1993	0.503	1200	-1.130	0800
	9/9/1993	0.745	1100	-0.756	0800
	9/10/1993	0.362	1200	-1.212	0800
	9/11/1993	0.560	1300	-0.946	0800
Release of 5000 lb/hr of paraffin and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	1.23	0800	2.70	0700
	9/9/1993	1.93	0800	1.61	0700
	9/10/1993	1.01	0800	3.22	0700
	9/11/1993	3.04	0800	3.62	0700
Release of 5000 lb/hr of paraffin and 700 lb/hr of NO _x from 0700-0800 in grid cell with Clinton monitor	9/8/1993	0.217	1400	-1.11	0800
	9/9/1993	0.557	1400	-0.73	0800
	9/10/1993	0.320	1400	-1.18	0800
	9/11/1993	0.271	1600	-0.915	0800
Release of 5000 lb/hr of paraffin, 700 lb/hr of NO _x , and 100 lb/hr of Cl ₂ from 0700-0800 in grid cell with Clinton monitor	9/8/1993	0.271	1400	2.72	0700
	9/9/1993	0.612	1400	1.63	0700
	9/10/1993	0.356	1300	3.24	0700
	9/11/1993	0.855	0800	3.67	0700

Chapter 6: Conclusions and Recommendations

The first direct evidence of chlorine chemistry in an urban atmosphere was provided by quantification of a unique marker species (CMBO) in southeastern Texas (Tanaka et al., 2001). In order to examine the regional impacts of chlorine chemistry on ozone and CMBO formation, the State of Texas sponsored the development of an emissions inventory and chemical mechanism that could be used with the CAMx photochemical grid model. The objectives of the current study were to examine the spatial and temporal sensitivity of O₃ and CMBO formation to Cl₂ emission estimates and to large point source releases of ethylene or paraffins alone or in conjunction with emissions of NO_x and Cl₂ in Southeastern Texas.

The major findings of the study include the following:

- Chlorine chemistry has the potential to enhance ozone mixing ratios by 11-16 ppbv in the industrial areas of Houston and by 5-7 ppbv within and north of the Houston urban area based on the current emission inventory.
- The impacts of chlorine chemistry exhibited strong temporal variations in accordance with the emission inventory for Cl· precursors. Cooling towers were primarily responsible for the morning peak in ozone mixing ratios, while swimming pools were responsible for the afternoon peak.
- The maximum enhancement in CMBO mixing ratios ranged from 59-69 pptv. The location and timing of the CMBO enhancement did not always correspond to the location of the maximum O₃ enhancement, but was associated with the spatial distribution of isoprene.
- Although CMBO mixing ratios predicted by the model cannot be quantitatively compared with the summer TexAQS-2000 ambient monitoring data, morning increases in CMBO mixing ratios observed during the field campaign were replicated by the model. The maximum predicted CMBO mixing ratio was within a factor of two of the highest mixing ratios detected during ambient measurements.
- Changes in the form of the emissions of atomic chlorine precursors led to changes in the spatial and temporal distribution of O₃ and CMBO enhancements. The magnitude of the enhancements with swimming pool and cooling tower emissions were in the form of HOCl was smaller and occurred later in the morning than in the form of Cl₂.
- Chlorine chemistry increased peak ozone mixing ratios for the 11-county region by 1-3 ppbv with minimal effects on time and geographic location of the maxima. Cl· chemistry increased the area of exceedance above a 100 ppbv threshold in the 11-county area from 40 to 400 km²hr .

- Emission of atomic chlorine precursors and Cl· chemistry had minimal impacts on model performance. However, conclusions should be drawn with caution because monitors there were no monitors at the locations of maximum ozone enhancements.
- A large elevated point source release of 2 tpd of Cl₂ in the Ship Channel has the potential to cause localized enhancement of 20 ppbv ozone mixing ratios.
- A 5000 lb/hr release of paraffins from the grid cell with the Clinton monitor produces less ozone (0.27-0.86 ppbv enhancement) than a 5000 lb release of ethylene (2-5.4 ppbv enhancement) in the same location.
- The maximum enhancement in ozone mixing ratios (3-6 ppbv) occurred when Cl₂ was released simultaneously with ethylene or paraffins. The maximum enhancement occurred earlier in the day after the paraffin release than after the ethylene release.
- Emissions of NO_x have an important role both in the magnitude and timing of the enhancement in ozone mixing ratios. Releases of ethylene or paraffins with NO_x result in less ozone production than releases with Cl₂ due to NO_x titration.
- Release of NO_x, alone or in conjunction with Cl₂, and ethylene or paraffins tends to slightly mitigate the effects of competition between isoprene and ethylene/paraffins for Cl·. The maximum enhancement in CMBO mixing ratios (4-4.4 pptv) occurs when ethylene or paraffins are released simultaneously with NO_x and Cl₂.

The following studies are recommended:

- Reducing uncertainties associated with estimates from cooling towers and swimming pools should be focal points of future research. Future studies should specifically address (1) characterization of the spatial distribution of cooling towers and identification of facility practices associated with chlorination, and (2) comparison of spatial surrogates for residential pools and quantification of the rate of chlorine volatilization.
- The analysis should be repeated using a modeling episode during the Tex-AQS 2000 time period in order to better assess the impacts of chlorine chemistry on model performance and to evaluate the ability of the model to replicate observed CMBO ratios.
- The impacts of chlorine chemistry during ‘upsets’ or non-routine releases should continue to be assessed as these events become better characterized both spatially and temporally.

References

- Chang, S.; Tanaka, P.L.; McDonald-Buller, E.C.; Allen, D.T. "Emission inventory for atomic chlorine precursors in southeast Texas", Report on Contract 9880077600-18 between the University of Texas and the Texas Natural Resource Conservation Commission, Center for Energy and Environmental Resources, University of Texas, Austin, Texas, August 24, 2001.
- ENVIRON International Corporation, User's Guide: Comprehensive Air Quality Model with extensions, version 3.00, 2000.
- Tanaka, P.L. and Allen, D.T. "Incorporation of Chlorine Reactions into the Carbon Bond-IV Mechanism: Mechanism Updates and Preliminary Performance Evaluation", Report on Contract 9880077600-18 between the University of Texas and the Texas Natural Resource Conservation Commission, Center for Energy and Environmental Resources, University of Texas, Austin, Texas, April 4, 2001.
- Tanaka, P. D.D.; Reimer, D.D.; Chang, S.; Yarwood, G.; McDonald-Buller, E.C.; Apel, E.C.; Orlando, J.J.; Neece, J.D.; Mullins, C.B.; and Allen, D.T. "Direct Evidence for Chlorine Chemistry and Ozone Enhancement in Urban Air", in preparation for submission to Atmospheric Environment, 2002.

Appendix A: Chlorine Mechanism and CAMx Chemparm File

The 13-step mechanism consists of the following reactions:

- (97) $\text{Cl}_2 = 2\text{Cl}$
- (98) $\text{HOCl} = \text{OH} + \text{Cl}$
- (99) $\text{Cl} + \text{PAR} = \text{HCl} + 0.87*\text{XO}_2 + 0.13*\text{XO}_2\text{N} + 0.11*\text{HO}_2 + 0.11*\text{RCHO} + 0.76*\text{ROR} - 0.11 \text{ PAR}$
- (100) $\text{Cl} + \text{OLE} = \text{FMCL} + \text{RCHO} + 2 \text{XO}_2 + \text{HO}_2 - 1*\text{PAR}$
- (101) $\text{Cl} = \text{HCl} + \text{XO}_2 + \text{FORM} + \text{HO}_2$
- (102) $\text{Cl} + \text{ETH} = \text{FORM} + 2 \text{XO}_2 + \text{FMCL} + \text{HO}_2$
- (103) $\text{Cl} + \text{ISOP} = 0.15 \text{HCl} + \text{XO}_2 + \text{HO}_2 + 0.28 \text{ICL1}$
- (104) $\text{OH} + \text{ICL1} = \text{ICL2}$
- (105) $\text{Cl} + \text{BUTA} = \text{XO}_2 + \text{HO}_2 + 0.70 \text{BCL1}$
- (106) $\text{OH} + \text{BCL1} = \text{BCL2}$
- (107) $\text{Cl} + \text{O}_3 = \text{ClO} + \text{O}_2$
- (108) $\text{ClO} + \text{NO} = \text{Cl} + \text{NO}_2$
- (109) $\text{ClO} + \text{HO}_2 = \text{HOCl} + \text{O}_2$

CAMx Chemparm File: Chlorine Reactions Bolded

```

CAMx Version      |VERSION3
Mechanism ID     |3
Description      |CBM-IV / updated rad-rad/ Carter 1 product ISOP mech
w/ Cl chemistry/corr 97&98
No of gas species |34
No of aero species |0
No of reactions  |109
Prim photo rxns  |6 1 38 39 9 45 95
No of sec photo rxn |8
ID, prim ID, scale |8 1 0.053
                  |14 1 33.9
                  |23 1 0.1975
                  |34 39 0.189
                  |69 38 9.04
                  |74 38 9.64
                  |97 1 0.264
                  |98 95 143.0
    
```

Species Records

	Gas Spec	lower bnd	H-law	T-fact	Diffirat	Reactivty
1	NO	1.00E-15	1.90e-03	-1480.	1.29	0.0
2	NO2	1.00E-09	1.00e-02	-2516.	1.60	0.1
3	O3	1.00E-09	1.10e-02	-2415.	1.63	1.0
4	PAN	1.00E-09	3.60e+00	-5910.	2.59	0.1
5	NXOY	1.00E-12	3.20e+04	-8706.	2.45	0.1
6	OLE	1.00E-09	5.00e-03	0.	1.80	0.0
7	PAR	1.00E-04	1.00e-03	0.	2.00	0.0
8	TOL	1.00E-09	1.20e+00	0.	2.26	0.0
9	XYL	1.00E-09	1.40e+00	0.	2.43	0.0
10	FORM	1.00E-09	6.30e+03	-6492.	1.29	0.0
11	ALD2	1.00E-09	6.30e+03	-6492.	1.56	0.0
12	ETH	1.00E-09	1.00e-02	0.	1.25	0.0
13	CRES	1.00E-09	2.70e+03	-6492.	2.45	0.0
14	MGLY	1.00E-09	2.70e+03	-6492.	2.00	0.0
15	OPEN	1.00E-12	2.70e+03	-6492.	2.47	0.0
16	PNA	1.00E-09	2.00e+04	-5910.	2.09	0.0
17	CO	1.00E-04	1.00e-10	0.	1.25	0.0
18	HONO	1.00E-09	5.90e+01	-4781.	1.62	0.1
19	H2O2	1.00E-09	7.40e+04	-6643.	1.37	1.0
20	HNO3	1.00E-09	2.00e+05	-8707.	1.87	0.0
21	ISOP	1.00E-09	1.00e-02	0.	1.94	0.0
22	MEOH	1.00E-09	2.20e+02	-4932.	1.33	0.0
23	ETOH	1.00E-09	2.20e+02	-4932.	1.60	0.0
24	ISPD	1.00E-09	6.30e+03	-6492.	1.97	0.0
25	NTR	1.00E-09	9.40e+03	-8706.	2.72	0.0
26	CL2	1.00E-12	1.82e-02	0.	1.98	0.0
27	HOCL	1.00E-12	6.62e+02	0.	1.71	0.0
28	FMCL	1.00E-12	1.50e+01	0.	1.89	0.0
29	HCL	1.00E-12	4.72e+01	0.	1.42	0.0
30	ICL1	1.00E-12	1.50e+01	0.	2.09	0.0
31	ICL2	1.00E-12	1.50e+01	0.	2.09	0.0
32	BUTA	1.00E-12	1.00e-02	0.	1.73	0.0
33	BCL1	1.00E-12	1.50e+01	0.	2.41	0.0
34	BCL2	1.00E-12	1.50e+01	0.	2.41	0.0

Reaction Records

```

Rxn Typ Parameters (1 to 10, depending upon Typ)
 1 1 0.0000E+00
 2 2 4.3233E+06 -1.1750E+03
    
```

3	2	2.6640E+01	1.3700E+03
4	1	1.3750E+04	
5	2	2.3090E+03	-6.8700E+02
6	2	2.4380E+03	-6.0200E+02
7	2	4.7310E-02	2.4500E+03
8	1	0.0000E+00	
9	1	0.0000E+00	
10	2	4.2500E+10	-3.9000E+02
11	1	3.2600E+05	
12	2	1.0000E+02	9.4000E+02
13	2	2.9990E+00	5.8000E+02
14	1	0.0000E+00	
15	2	4.4167E+04	-2.5000E+02
16	2	5.9010E-01	1.2300E+03
17	2	1.8530E+03	-2.5600E+02
18	1	1.9000E-06	
19	2	2.7760E+00	1.0897E+04
20	2	1.5390E-04	-5.3000E+02
21	1	1.6000E-11	
22	2	9.7990E+03	-8.0600E+02
23	1	0.0000E+00	
24	1	9.7700E+03	
25	1	1.5000E-05	
26	2	1.6817E+04	-7.1300E+02
27	2	2.1790E+02	-1.0000E+03
28	2	1.2270E+04	-2.4000E+02
29	1	0.0000E+00	
30	1	0.0000E+00	
31	1	0.0000E+00	
32	2	4.1440E+03	-1.1500E+03
33	2	2.1810E-01	-5.8000E+03
34	1	0.0000E+00	
35	2	2.5200E+03	1.8700E+02
36	1	3.2200E+02	
37	1	1.5000E+04	
38	1	0.0000E+00	
39	1	0.0000E+00	
40	2	2.3700E+02	1.5500E+03
41	1	9.3000E-01	
42	2	6.3600E+02	9.8600E+02
43	2	2.4000E+04	-2.5000E+02
44	1	3.7000E+00	
45	1	0.0000E+00	
46	2	2.8200E+04	1.8000E+02
47	2	1.3700E+04	-3.8000E+02
48	2	2.5400E-02	1.3500E+04
49	1	3.7000E+03	
50	1	9.6000E+03	
51	2	2.1000E+01	1.7100E+03
52	1	1.2030E+03	
53	2	1.3710E+05	8.0000E+03
54	1	9.5450E+04	
55	1	2.2000E+04	
56	2	5.9200E+03	3.2400E+02
57	2	4.2000E+04	-5.0400E+02
58	2	1.8000E-02	2.1050E+03
59	1	1.1350E+01	
60	2	1.0800E+03	7.9200E+02
61	2	1.1920E+04	-4.1100E+02
62	2	2.7000E-03	2.6330E+03

63	2	9.1500E+03	-3.2200E+02		
64	1	1.2000E+04			
65	1	2.5000E+02			
66	1	6.1000E+04			
67	1	3.2500E+04			
68	1	2.0000E+04			
69	1	0.0000E+00			
70	1	4.4000E+04			
71	2	1.5000E-02	5.0000E+02		
72	2	3.6200E+04	-1.1600E+02		
73	1	2.6000E+04			
74	1	0.0000E+00			
75	1	5.3200E+04			
76	1	1.4760E+05			
77	1	1.9000E-02			
78	1	9.9600E+02			
79	1	1.2000E+04			
80	2	2.0000E+03	-1.3000E+03		
81	1	1.2000E+04			
82	2	1.1100E+03	-1.6000E+02		
83	1	8.1667E-05			
84	1	1.6000E+03			
85	2	4.3000E+03	-1.7600E+02		
86	2	8.9000E+03	-1.3000E+03		
87	2	8.9000E+03	-1.3000E+03		
88	2	2.0000E+03	-1.3000E+03		
89	2	4.0000E+03	-1.3000E+03		
90	2	1.6260E+05	-2.5000E+02		
91	1	2.7778E-04			
92	1	4.9667E+04			
93	1	1.0500E-02			
94	1	1.4780E+00			
95	1	0.0000E+00			
96	1	2.2000E-04			
97	1	0.0000E+00			
98	1	0.0000E+00			
99	3	4.2569E+04	-2.6000E+02	0.0000E+00	3.0000E+02
100	3	9.1010E+03	2.9500E+02	0.0000E+00	3.0000E+02
101	3	6.7523E+02	7.1000E+02	0.0000E+00	3.0000E+02
102	1	9.3834E+04			
103	2	8.4000E+05	-5.0400E+02		
104	3	1.8060E+04	-1.2400E+03	0.0000E+00	2.7300E+02
105	2	1.5019E+05	-4.1100E+02		
106	1	6.6420E+05			
107	1	2.8044E+04			
108	1	6.1992E+05			
109	1	5.3136E+04			

Appendix B: Model Performance Statistics

Scenario	Episode Date	Number of Monitors	All Data Pair with Obs > 60.0 ppb		Domain Maximum							
			Normalized Bias	Normalized Gross Error	Unpaired Accuracy	Predicted				Observed		
			± 15 %	± 30 %	± 20 %	ppb	Xcell	Ycell	Hour (CST)	ppb	Site	Hour (CST)
Cl2.Basecase	09/08/93	38	18.3	28	-6.1	201	25	30	16:00	214	SMITH	14
	09/09/93	38	17.5	29.2	-0.3	194.4	34	26	16:00	195	SMITH	12
	09/10/93	38	3.9	26.2	20.3	194.8	20	34	16:00	162	GALVESTON	14
	09/11/93	38	13.2	29.2	7.2	202.6	24	49	16:00	189	HRM 1	12
Cl2.Noemiss	09/08/93	38	17.3	27.7	-6.7	199.7	25	30	16:00	214	SMITH	14
	09/09/93	38	16.7	28.9	-1.4	192.2	34	26	16:00	195	SMITH	12
	09/10/93	38	2.9	25.9	19	192.8	20	34	16:00	162	GALVESTON	14
	09/11/93	38	11.8	28.9	6	200.4	24	49	16:00	189	HRM 1	12
Cl2+HOCl.base	09/08/93	38	18.1	27.9	-5.9	201.3	25	30	16:00	214	SMITH	14
	09/09/93	38	17.5	29.2	0	195	34	26	16:00	195	SMITH	12
	09/10/93	38	3.7	26.1	20.3	194.9	20	34	16:00	162	GALVESTON	14
	09/11/93	38	13	29.2	7.7	203.6	24	49	16:00	189	HRM 1	12

Appendix C

Time Series of O₃ Mixing Ratios at Ambient Monitors in the 11-County Region Comparing Observed Data with Model Predictions from Three Scenarios:

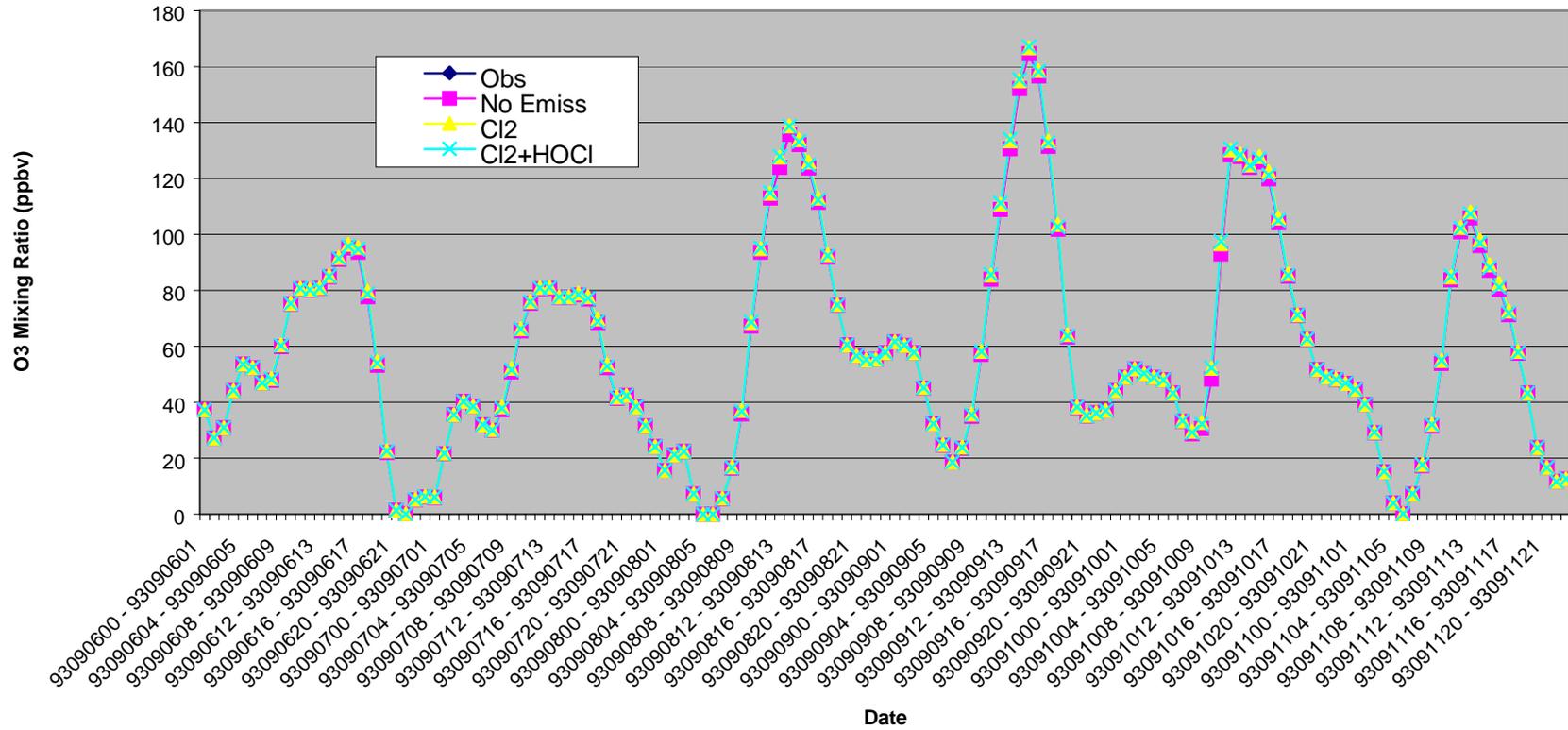
1. Basecase
2. Emissions of Cl₂ (all sources)
3. Emissions of Cl₂ (industrial point sources and sea salt aerosol) and HOCl (swimming pools and cooling towers)

Ambient Monitors

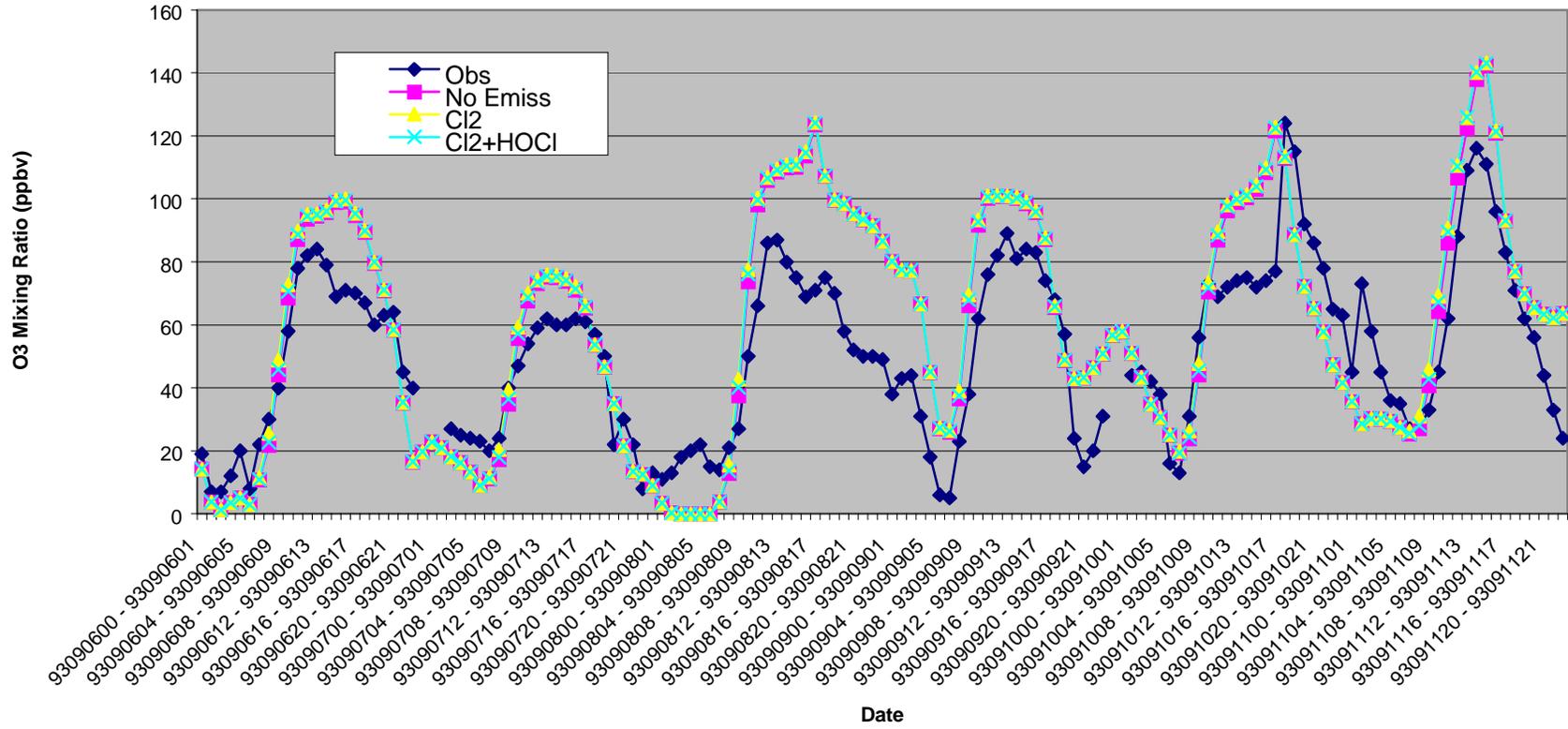
34ST	34TH ST, TEXAS CITY, TX
BMTC	BEAUMONT C02/JEFFERSON CO TX
C35C	CLINTON CGC / HARRIS CO TX
CLTA	CLUTE CAMS 11/BRAZORIA CO TX
CRSC	CROSBY AQ/MET SITE TX
GALC	GALVESTON AS SITE TX
GILM	GILCREST TX
GLRC	GALLERIA CGC SITE TX
H01H	HRM SITE 1 TX
H03H	HRM SITE 3 TX
H04H	HRM SITE 4 TX
H07H	HRM SITE 7 TX
H08H	HRM SITE 8 TX
H10H	HRM SITE 10 TX
H11H	HRM SITE 11 TX
HALC	ALDINE C8/HARRIS CO TX
HCFA	SITE T-19 CRAWFORD TX
HCQA	SITE T-18 CROQUET TX
HLAA	SITE T-26 LANG TX
HMCA	MANCHESTER C22 TX
HNWA	NORTHWEST HARRIS C26 TX
HSMA	SWISS&MONROE / HARRIS CO TX
HWAA	SITE S-13 N WAYSIDE TX
KTZA	KOUNTZE C85/HARDIN CO TX
PAWC	PORT ARTHUR WEST C28 TX
S40S	SETRPC SITE 40 TX
S42S	SETRPC SITE 42 TX
S43S	SETRPC SITE 43 TX
SBRC	SEABROOK C20 TX
SPTC	SMITH POINT AQ/MET SITE TX

STWC	STOWELL (WINNIE) AQ/MET TX
TLMC	TEXAS CITY / LA MARQUE TX
WORA	WEST ORANGE C9 TX

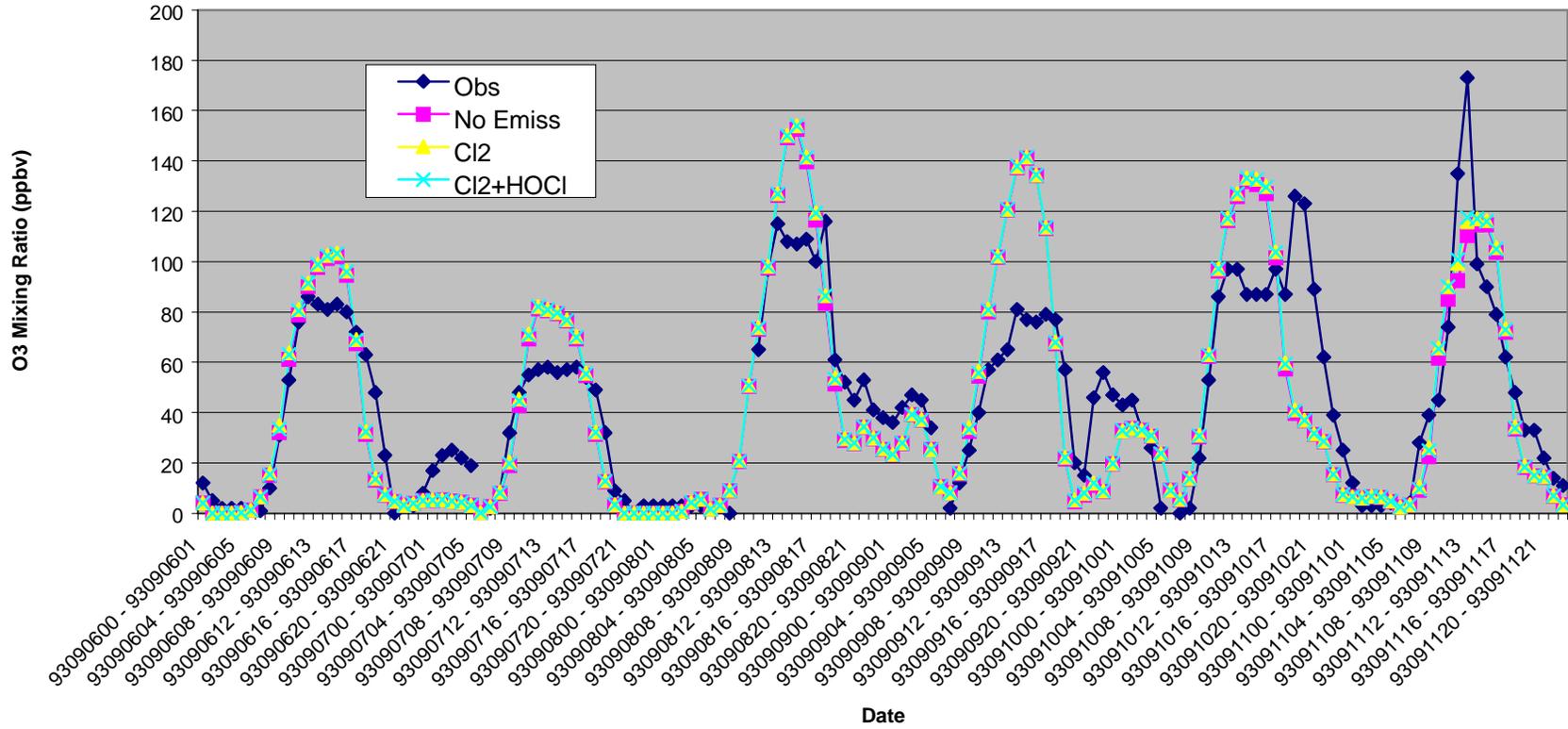
34ST



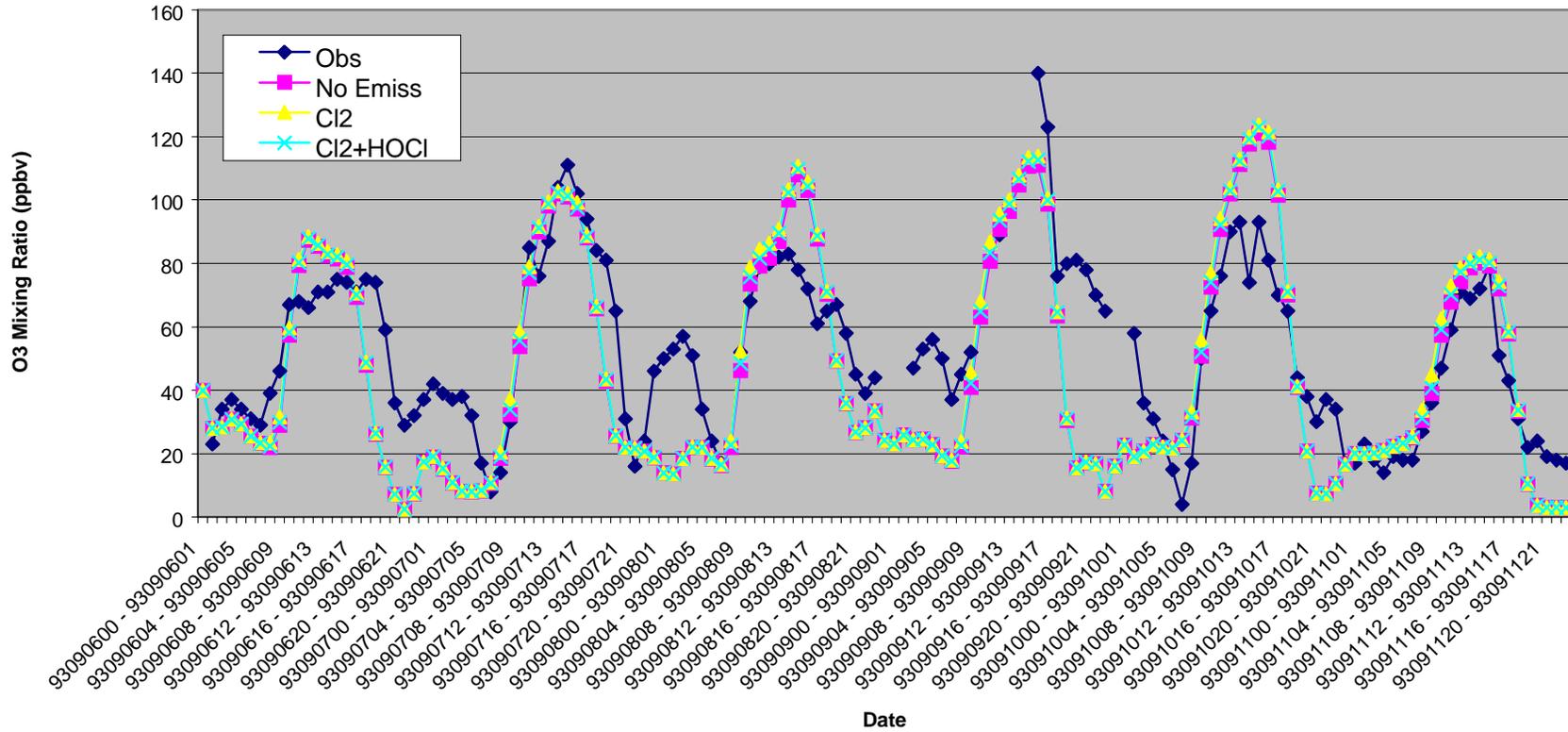
BMTC



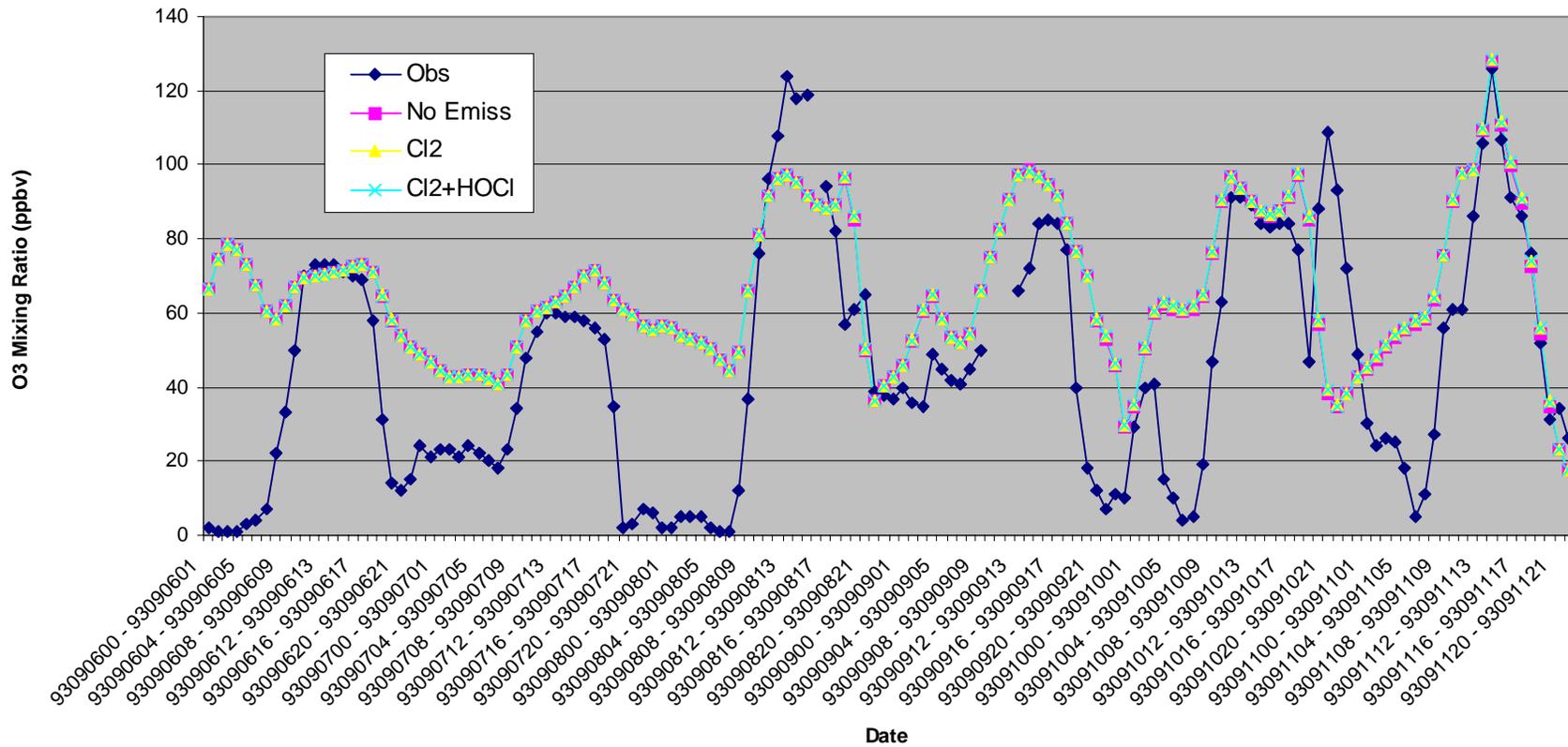
C35C



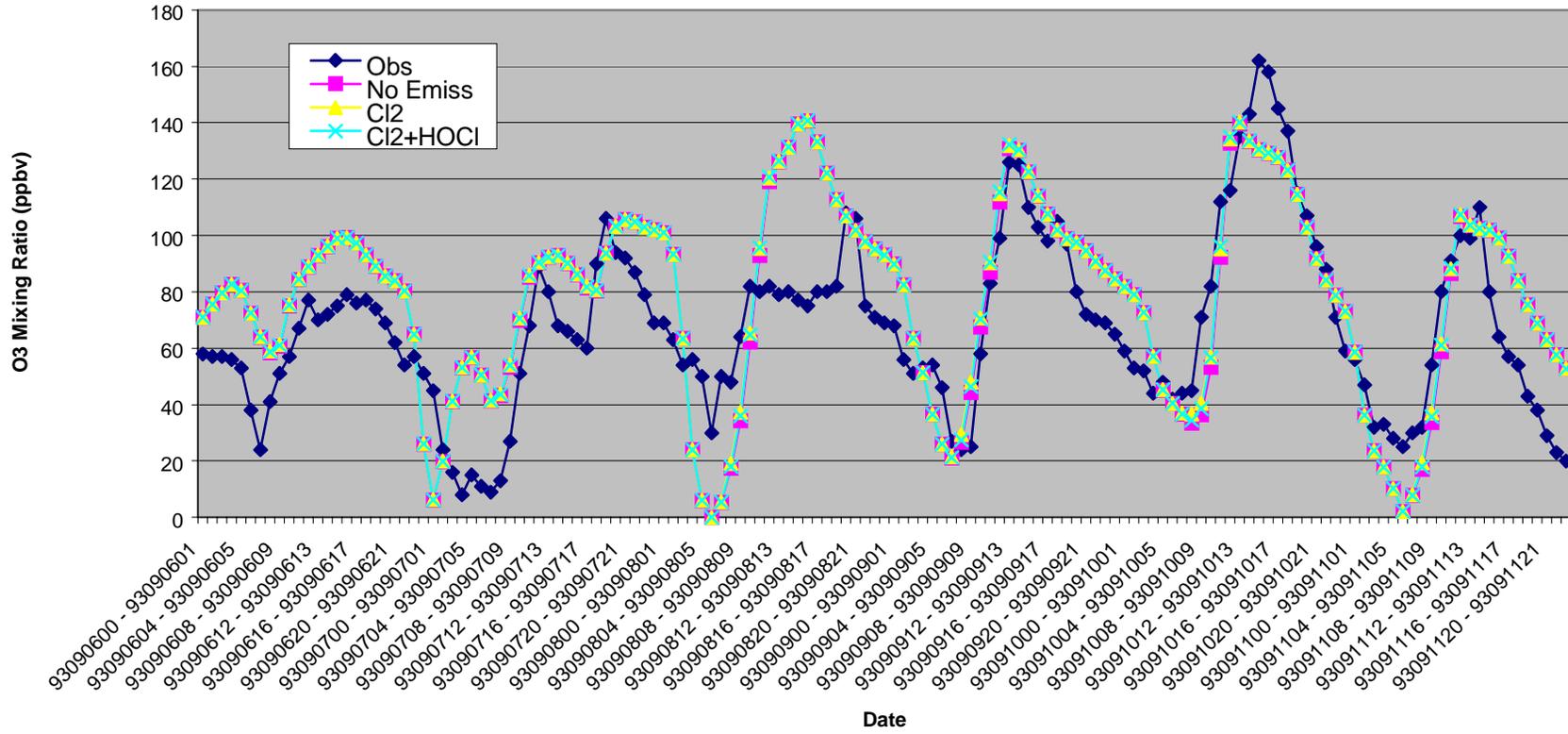
CLTA



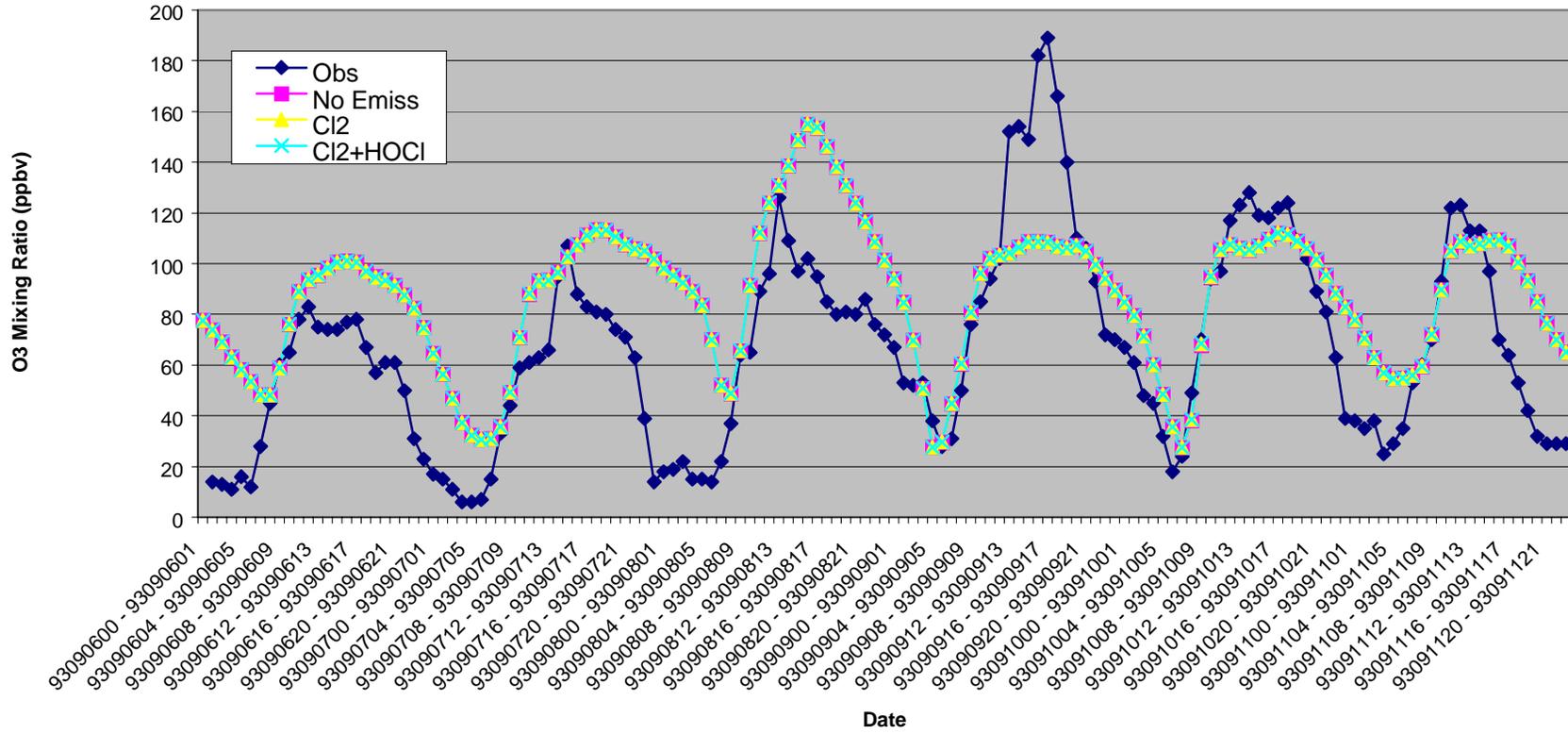
CRSC



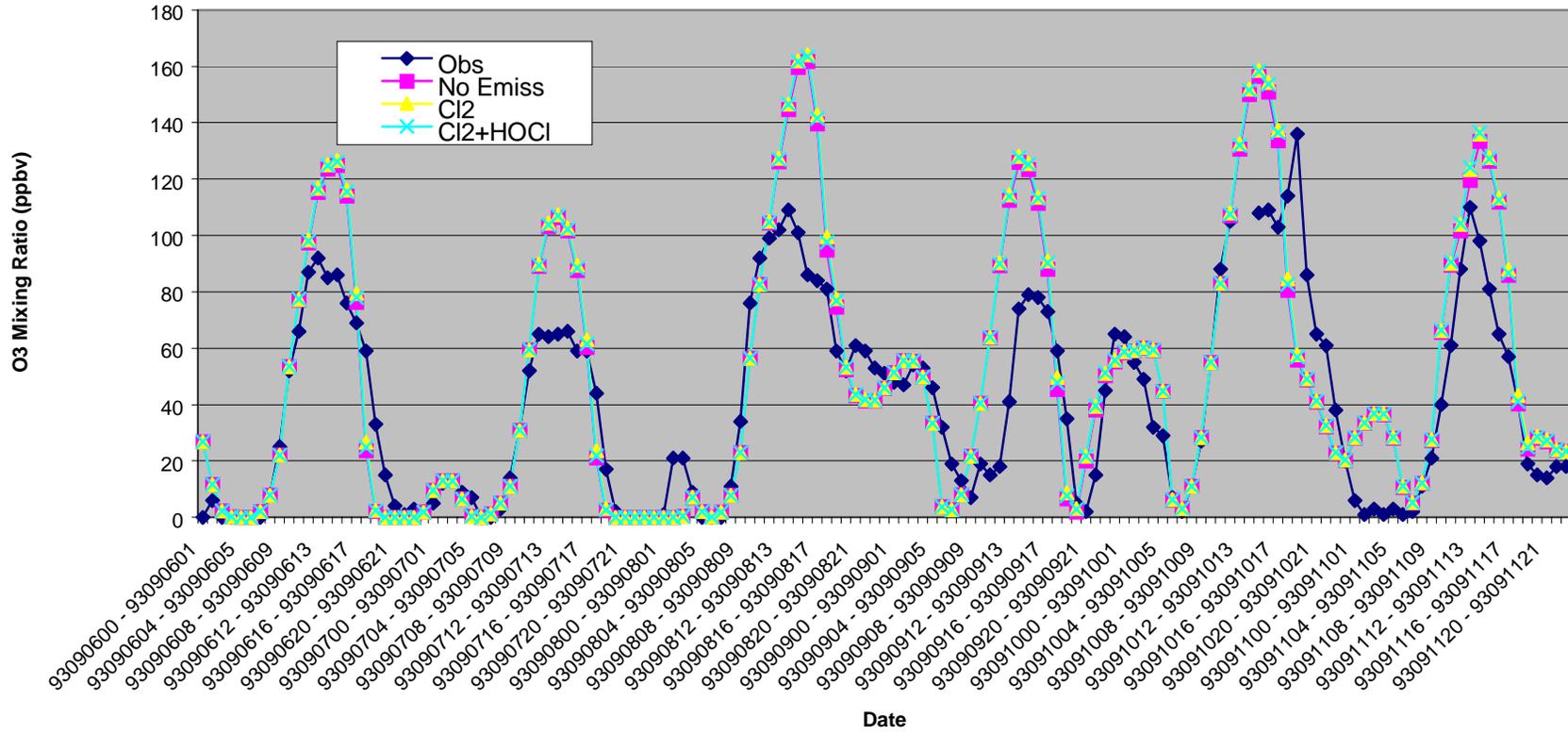
GALC



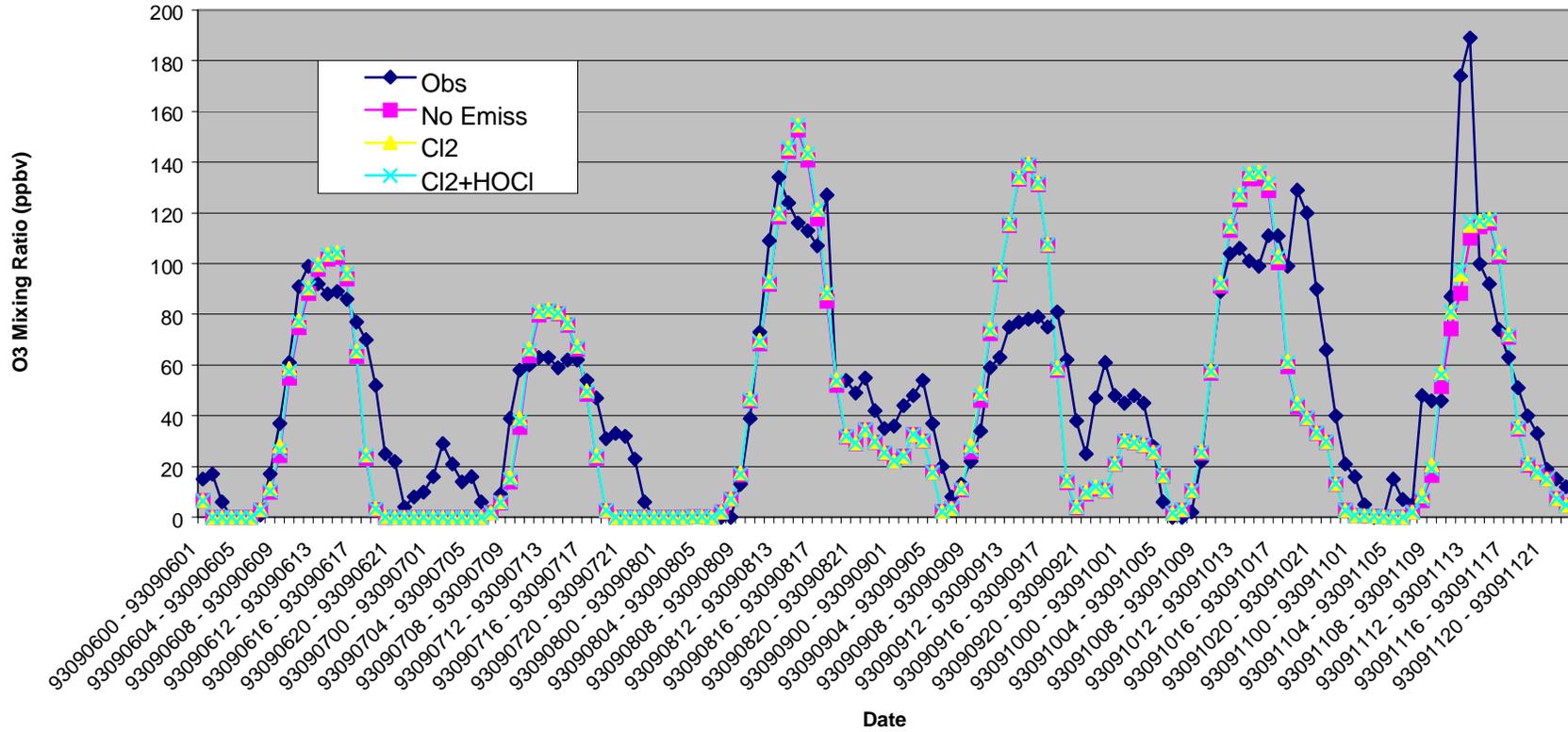
GILM



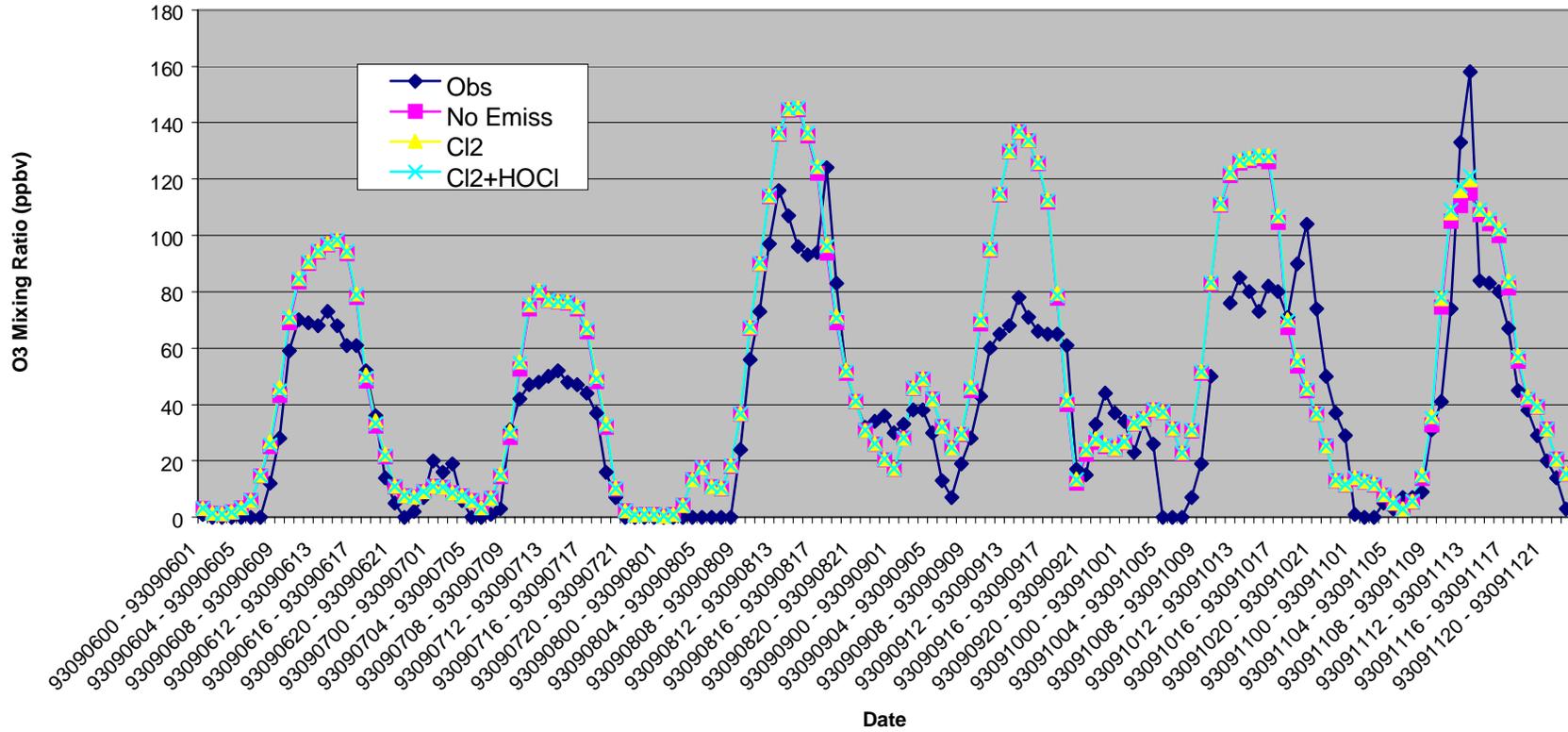
GLRC



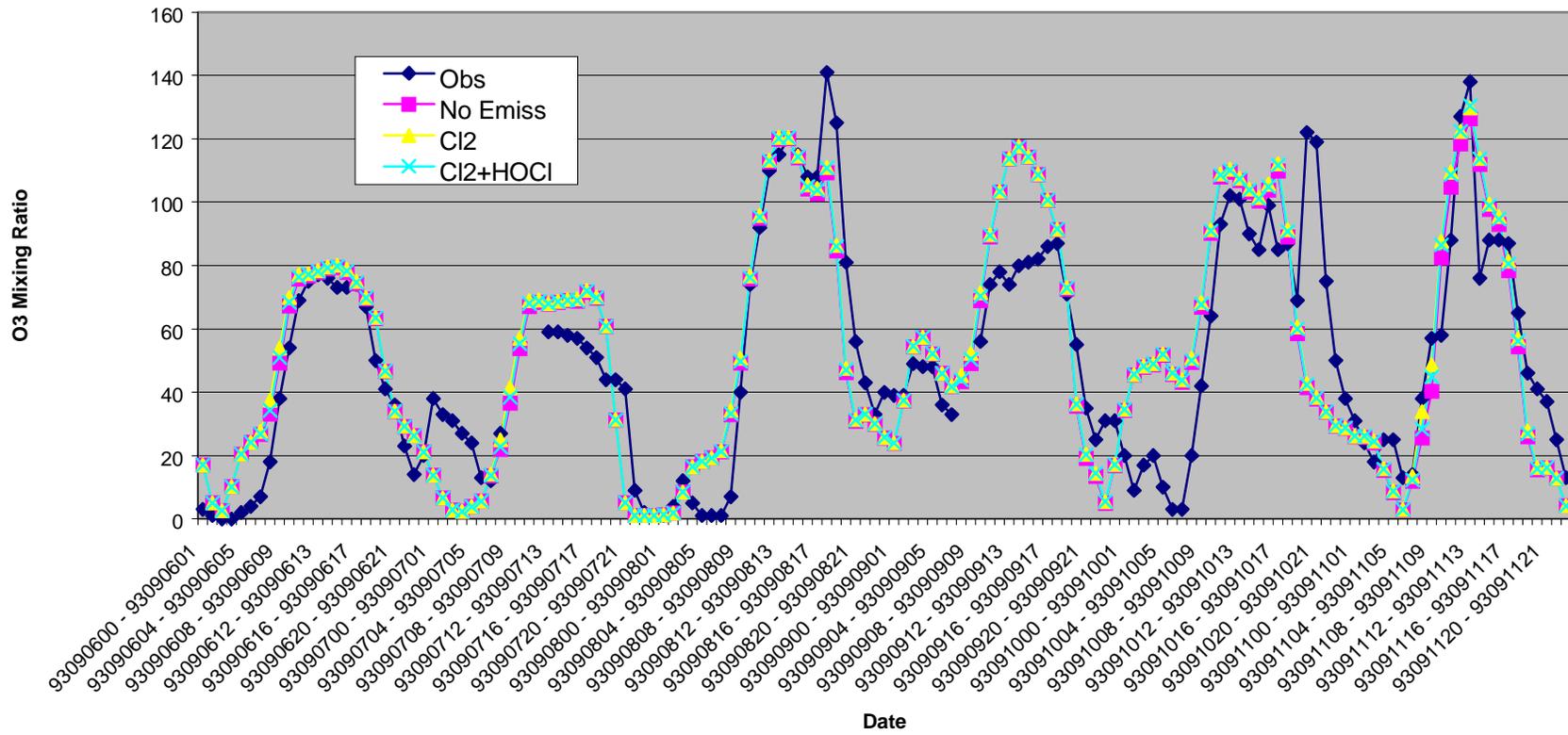
H01H



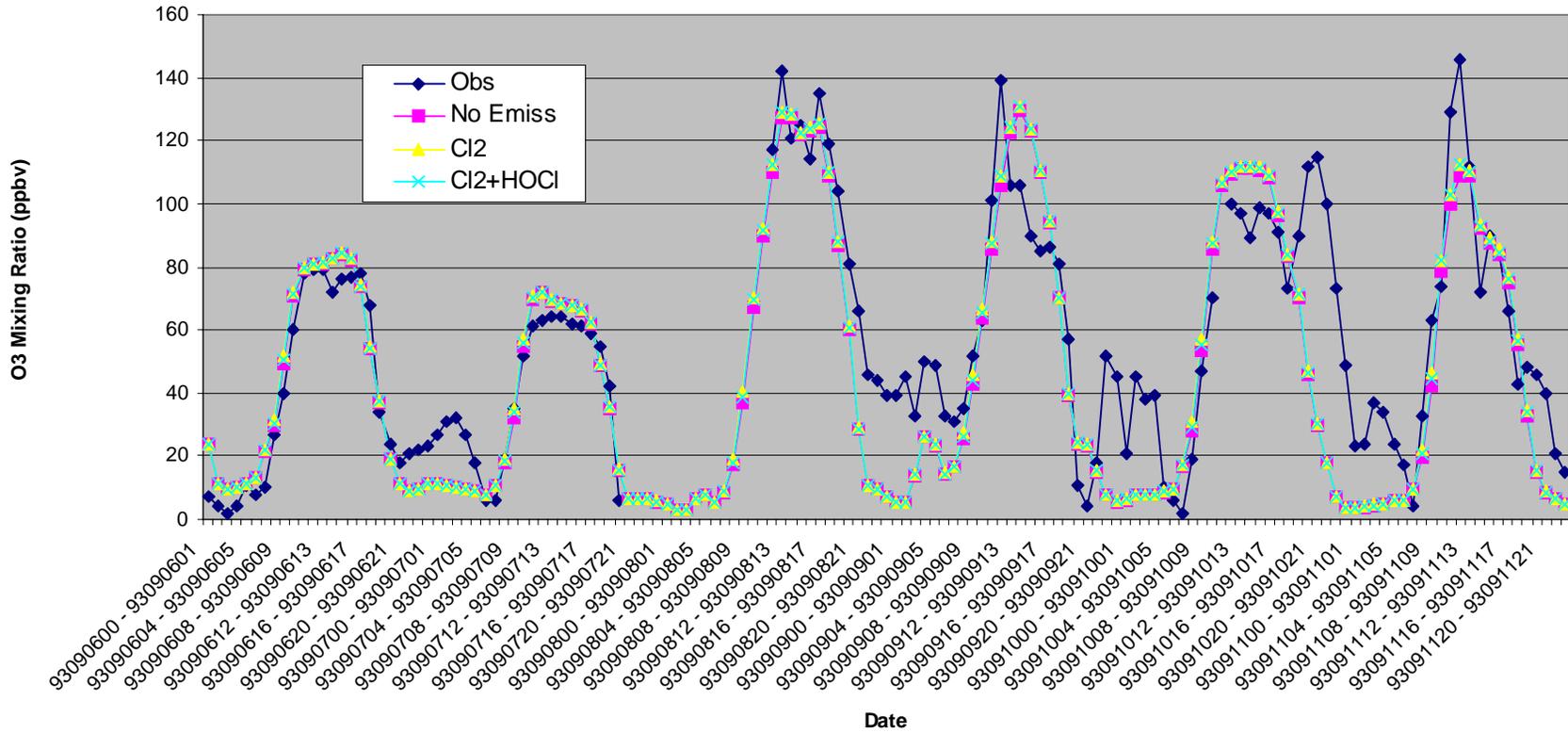
H03H



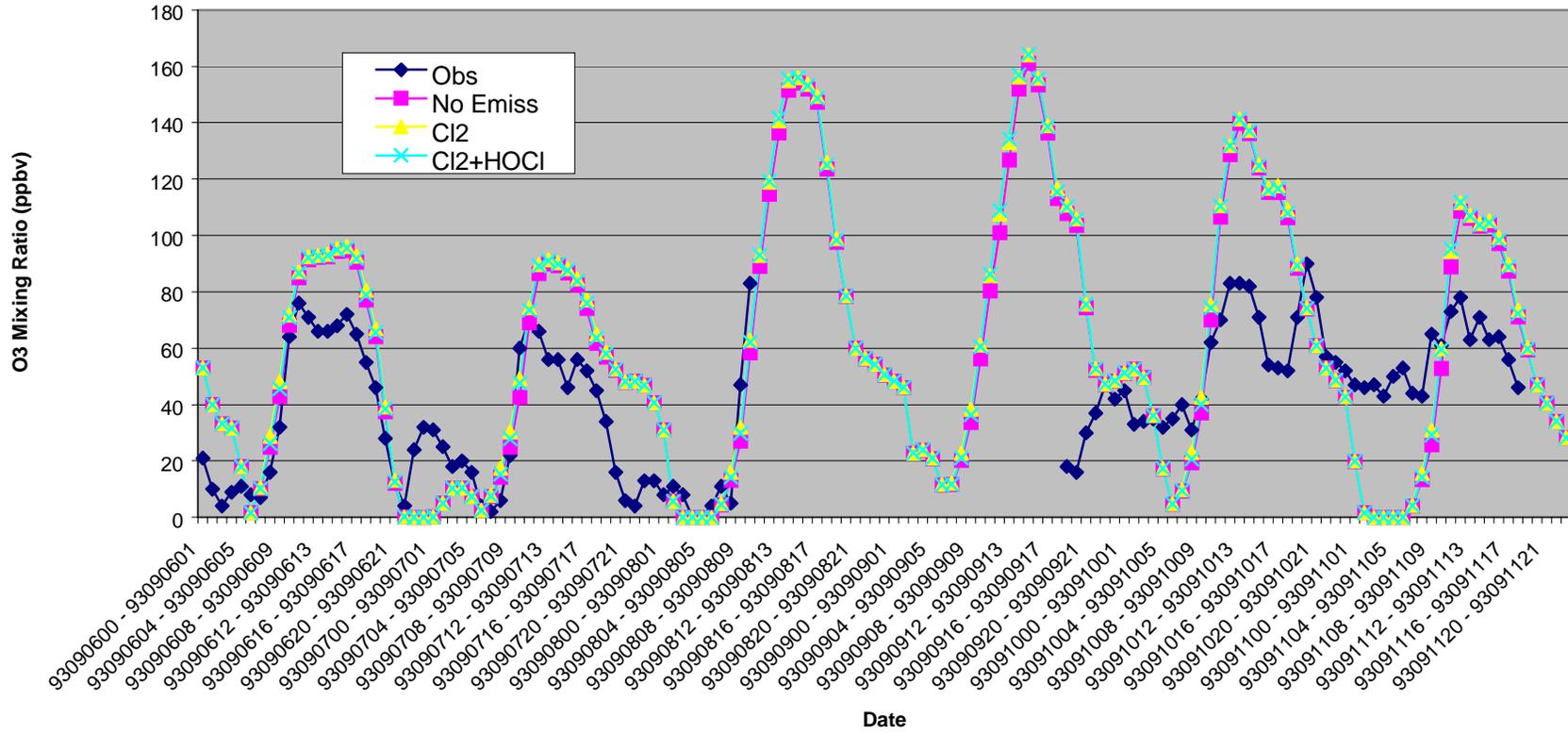
H04H



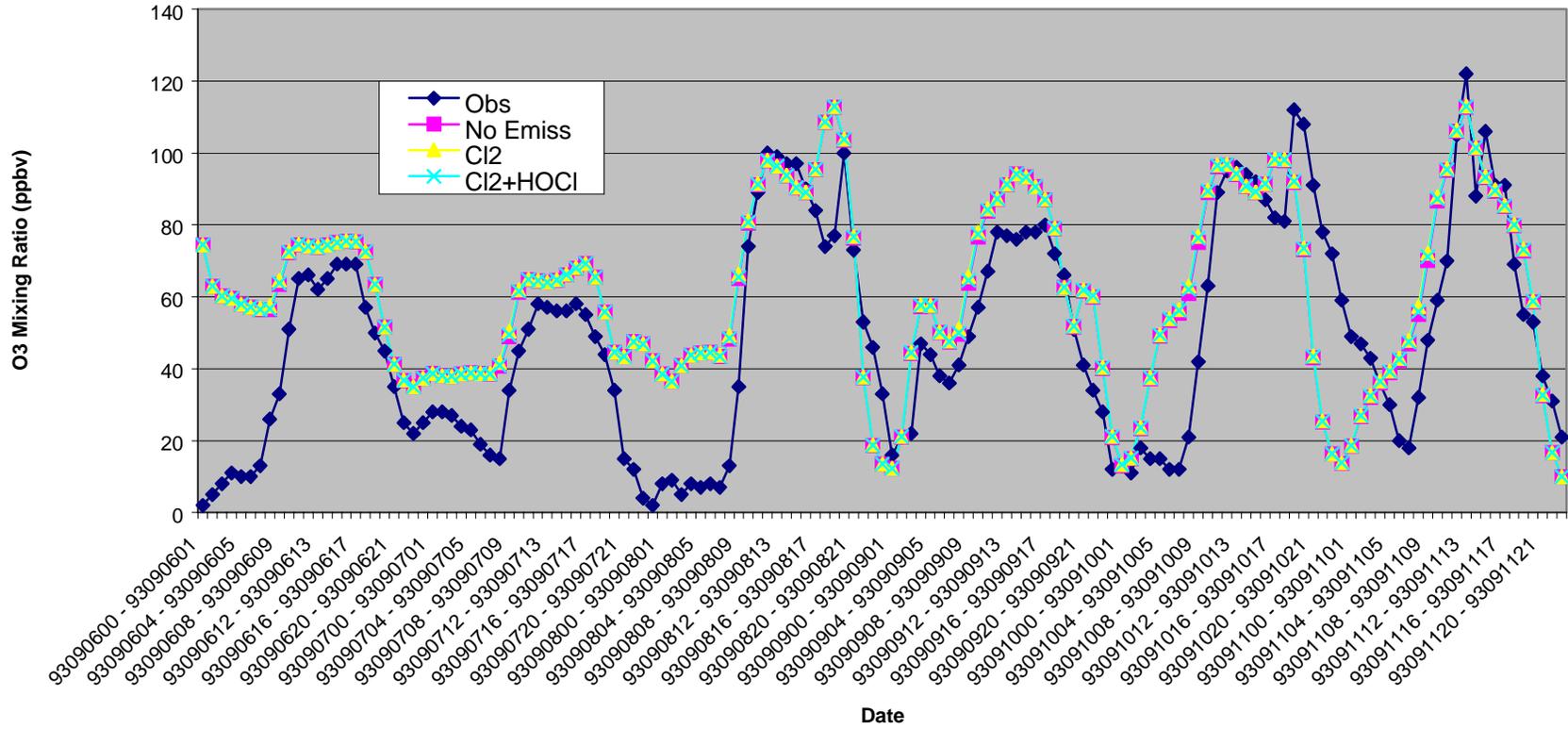
H07H



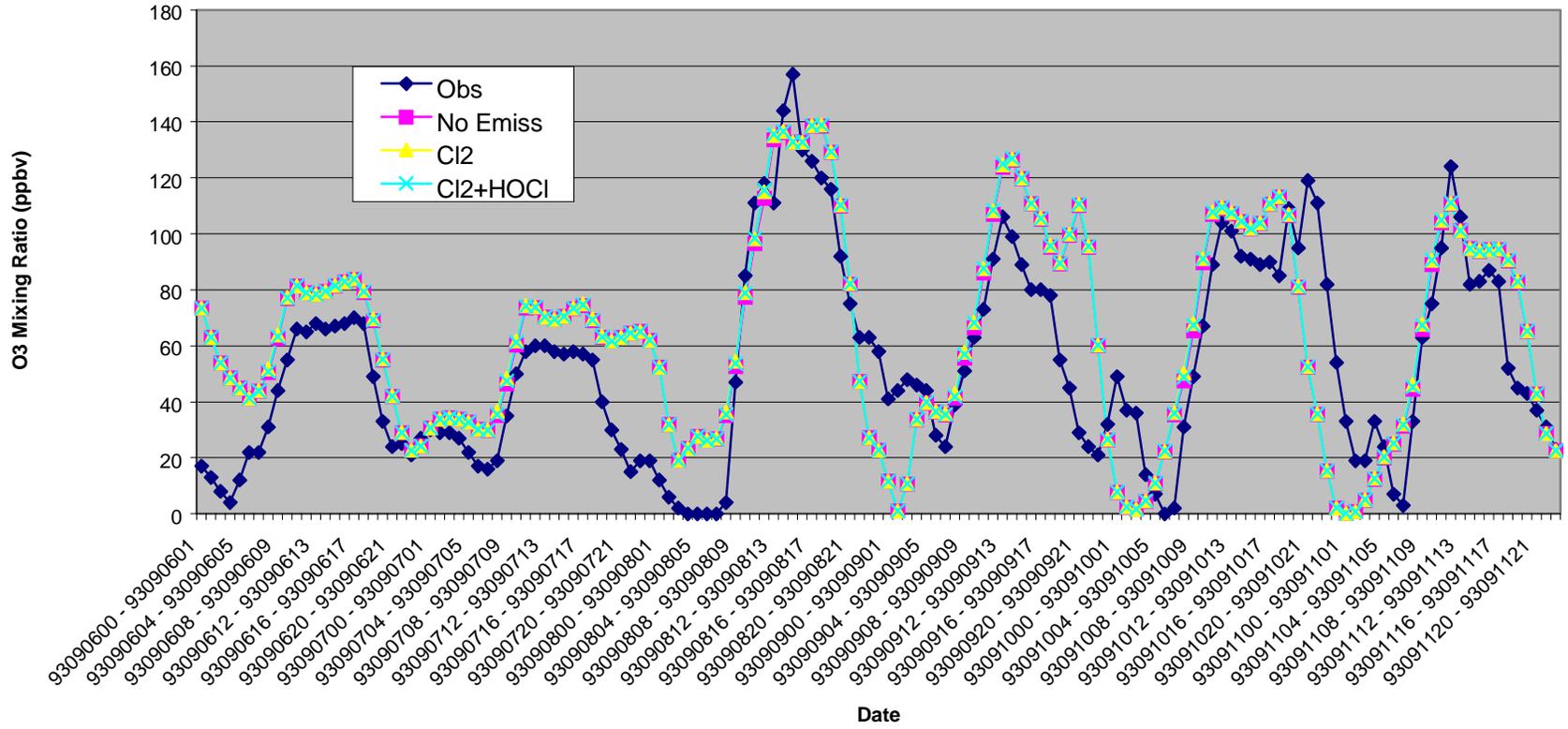
H08H



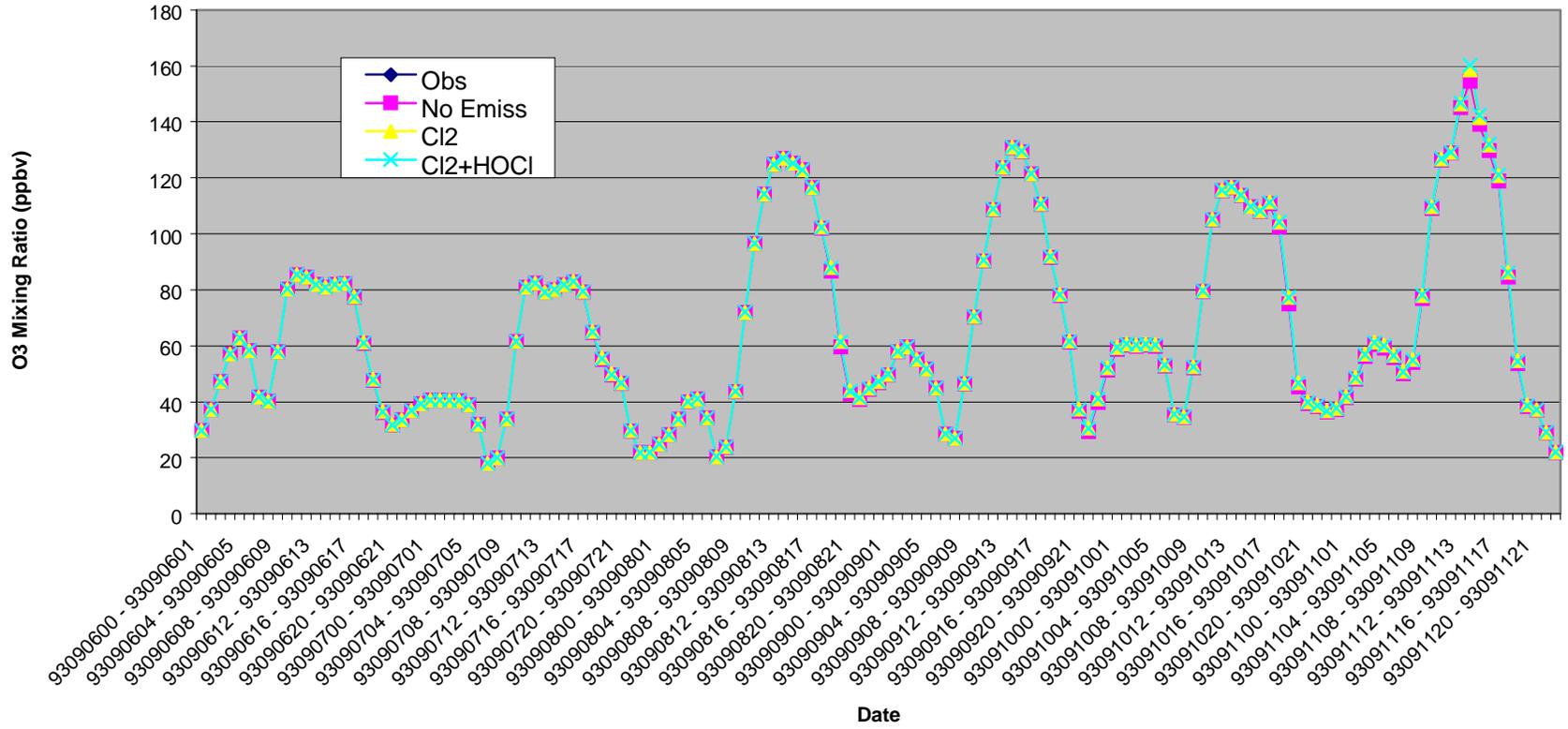
H10H



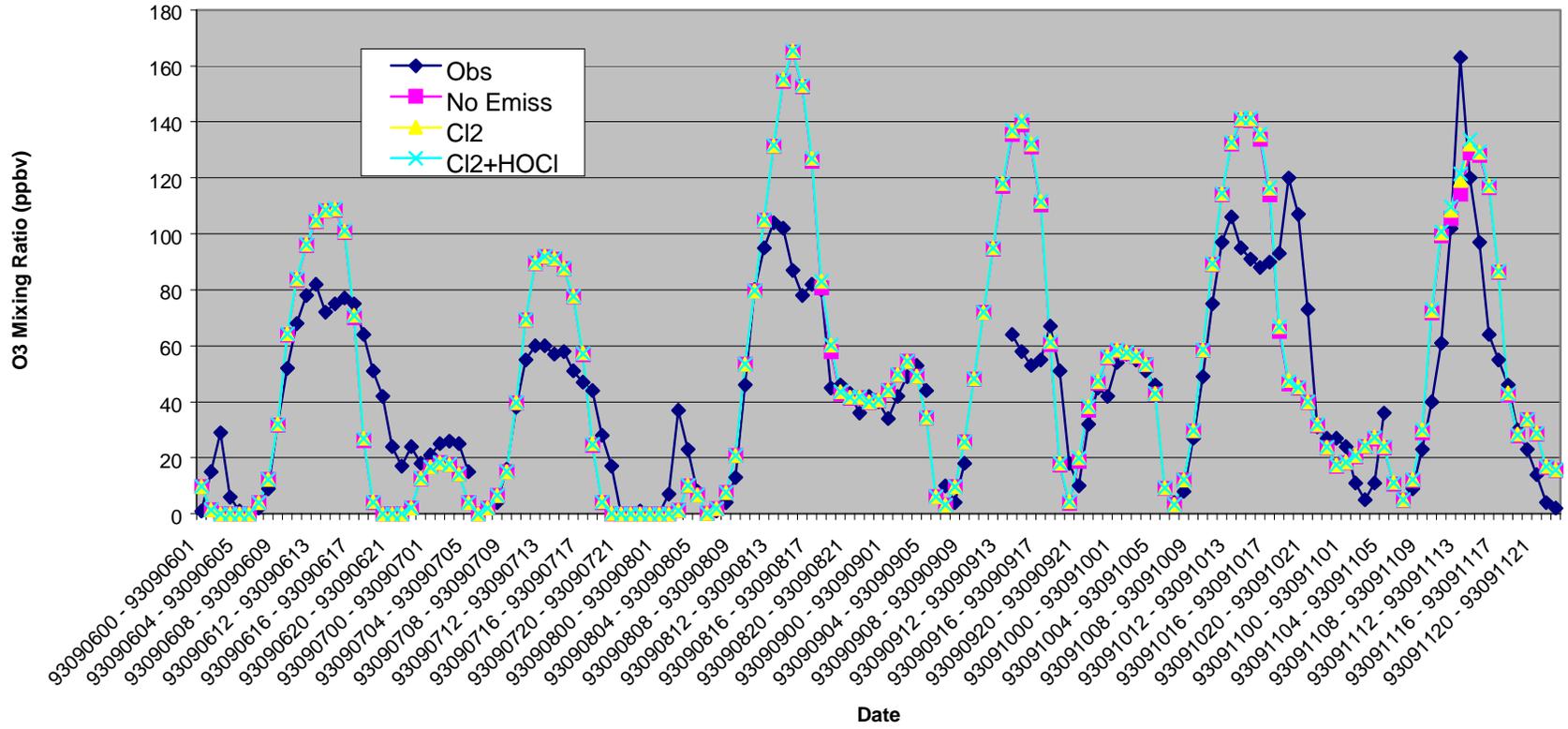
H11H



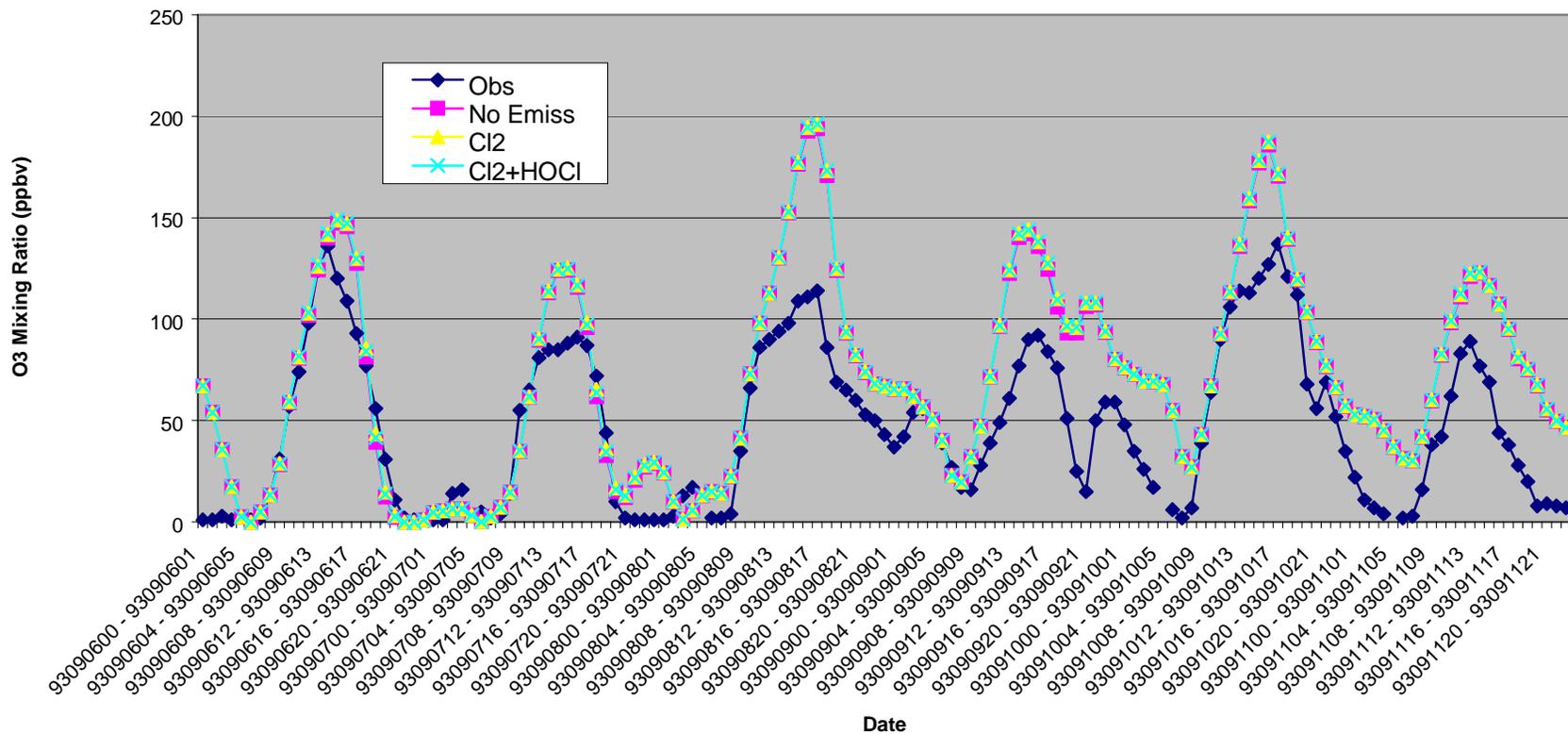
HALC



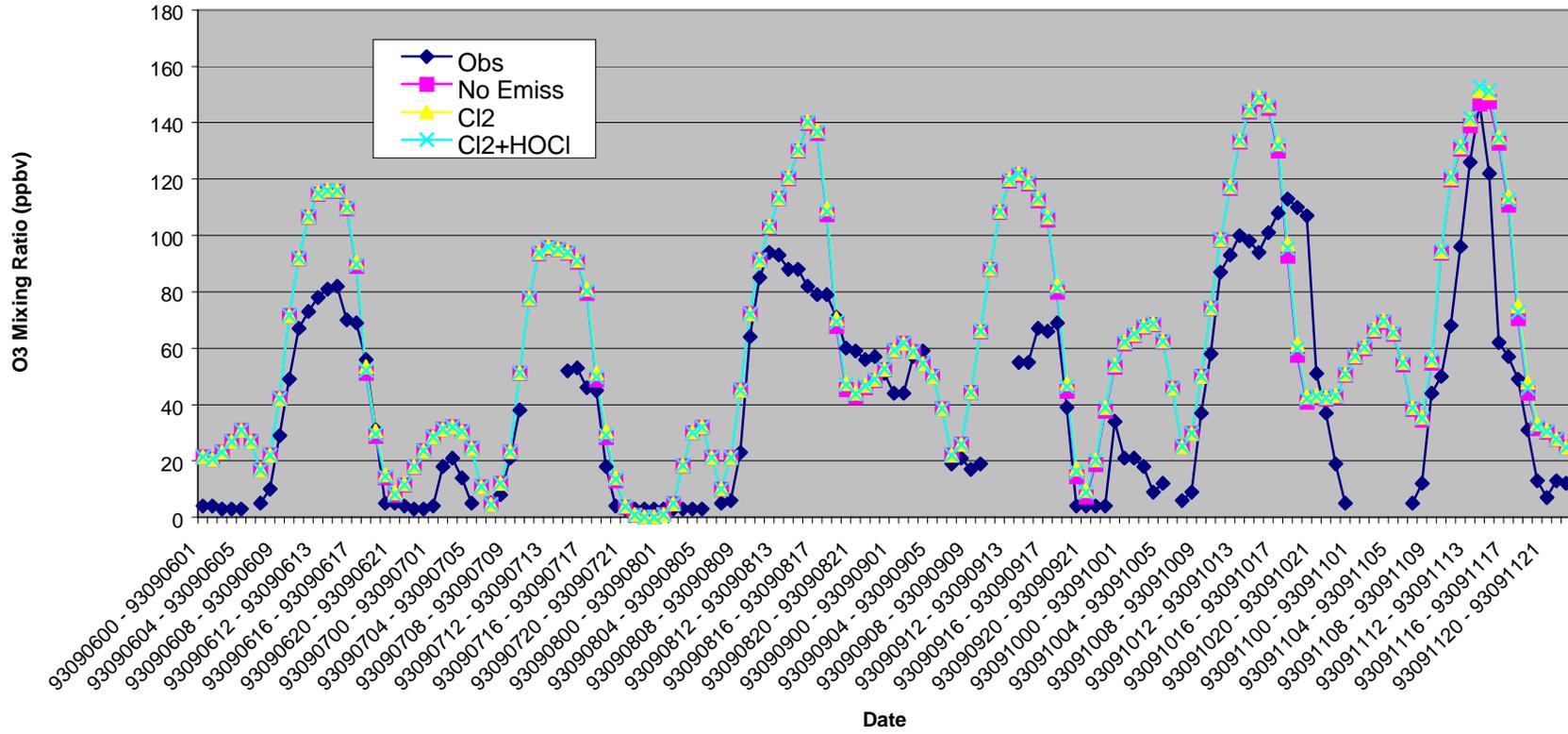
HCFA



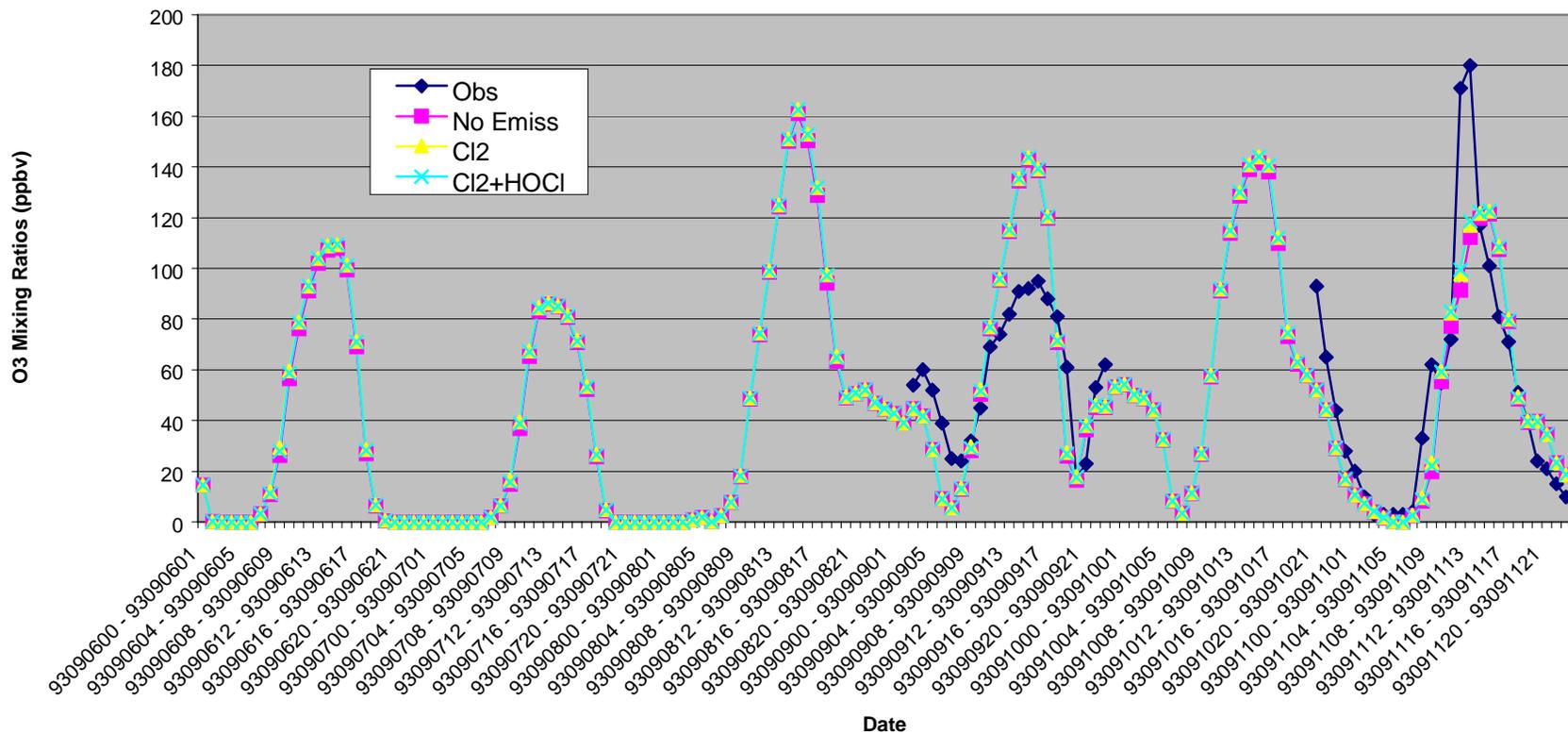
HCQA



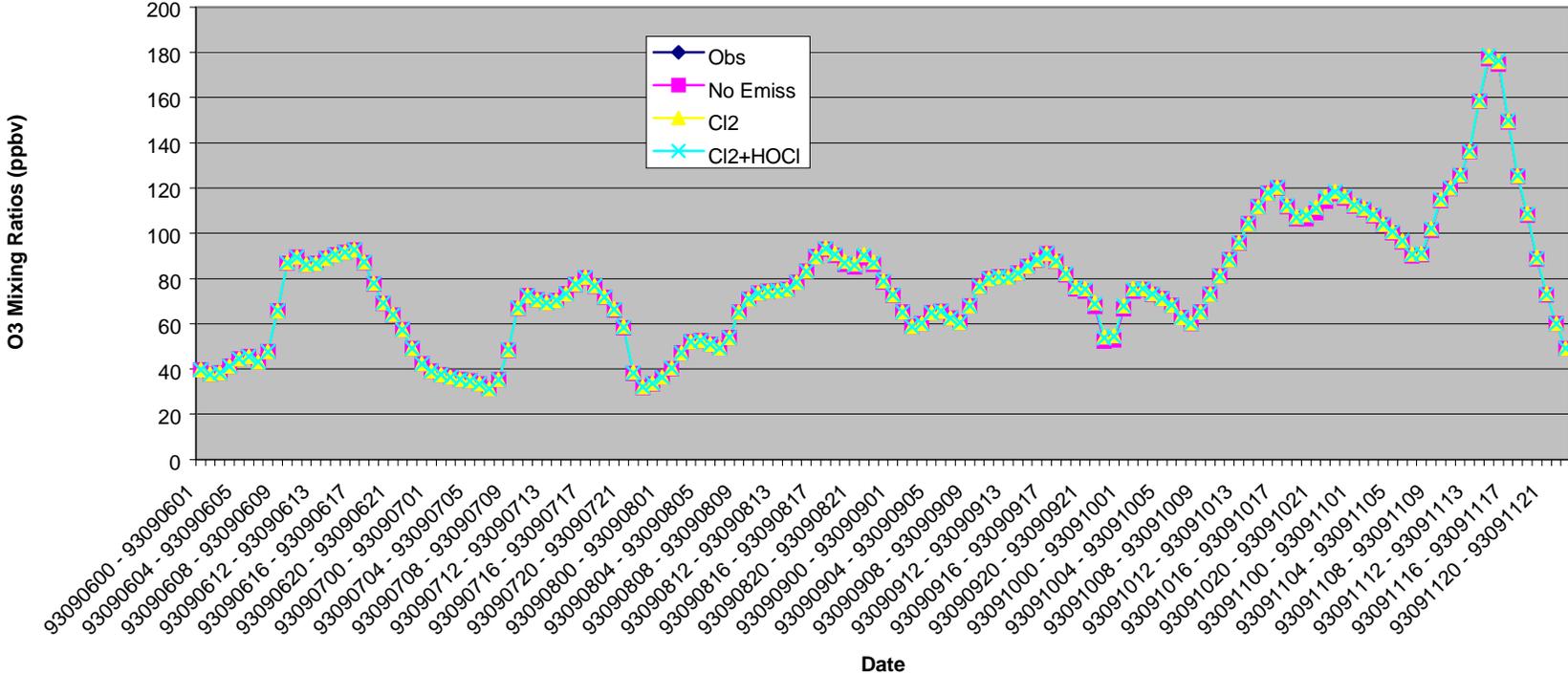
HLAA



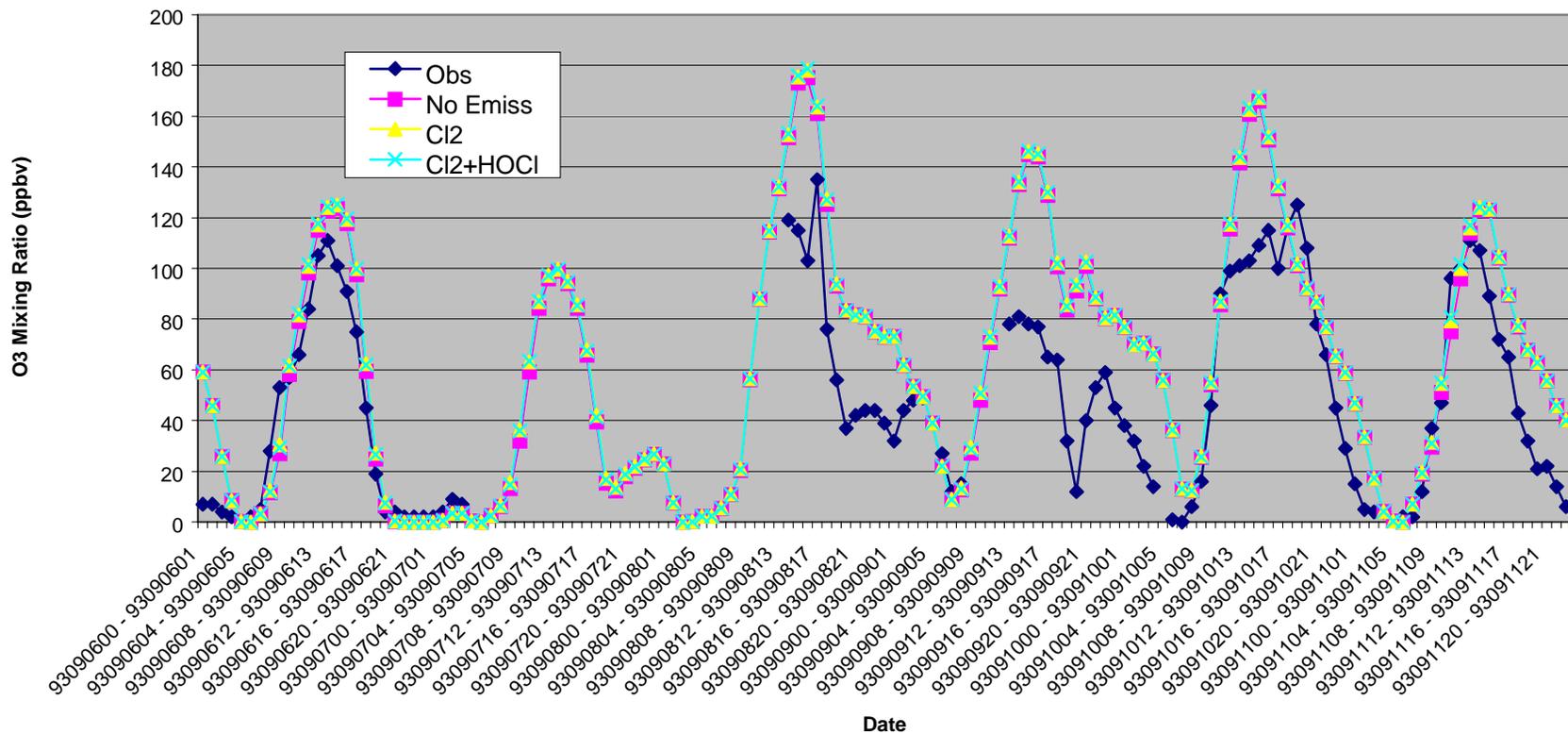
HMCA



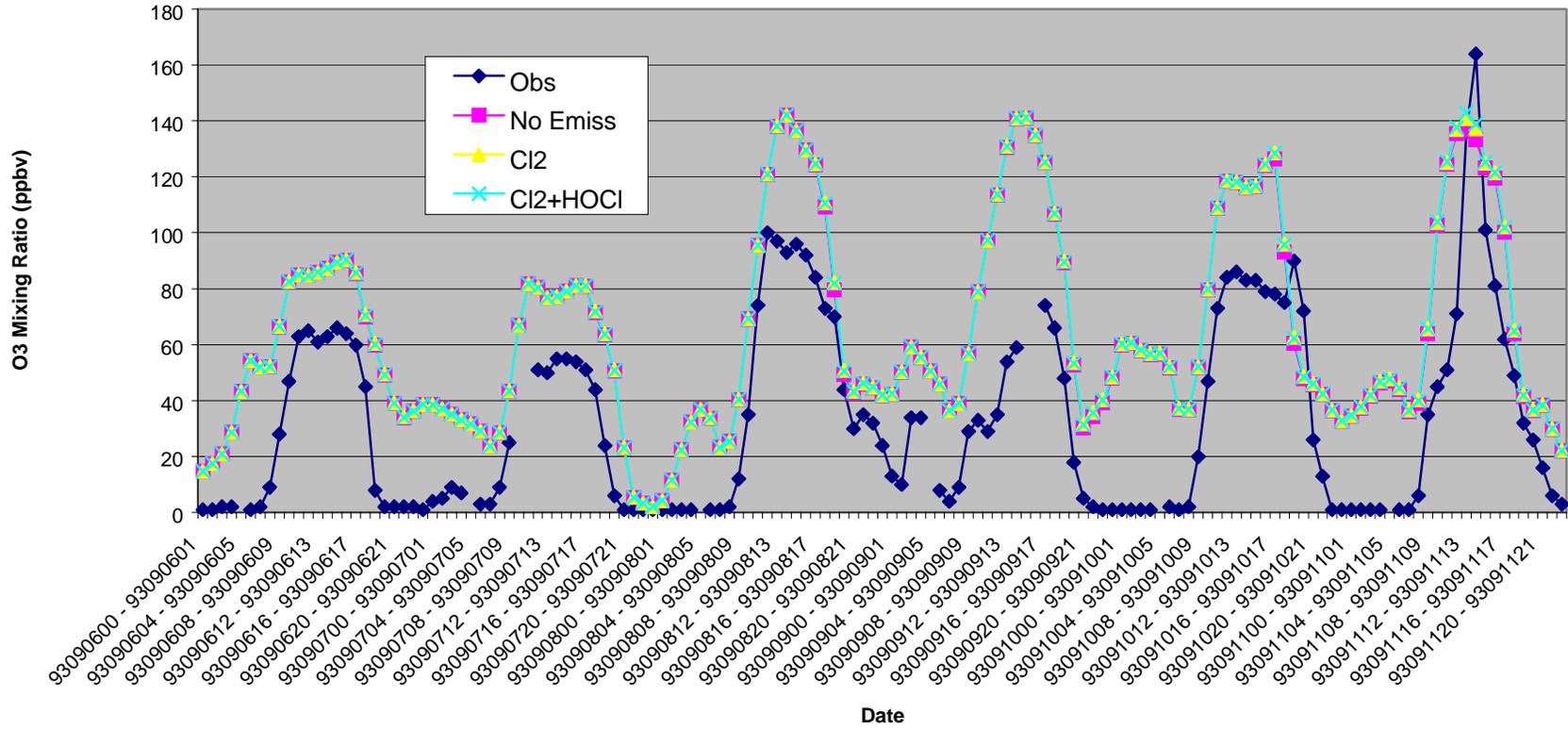
HNWA



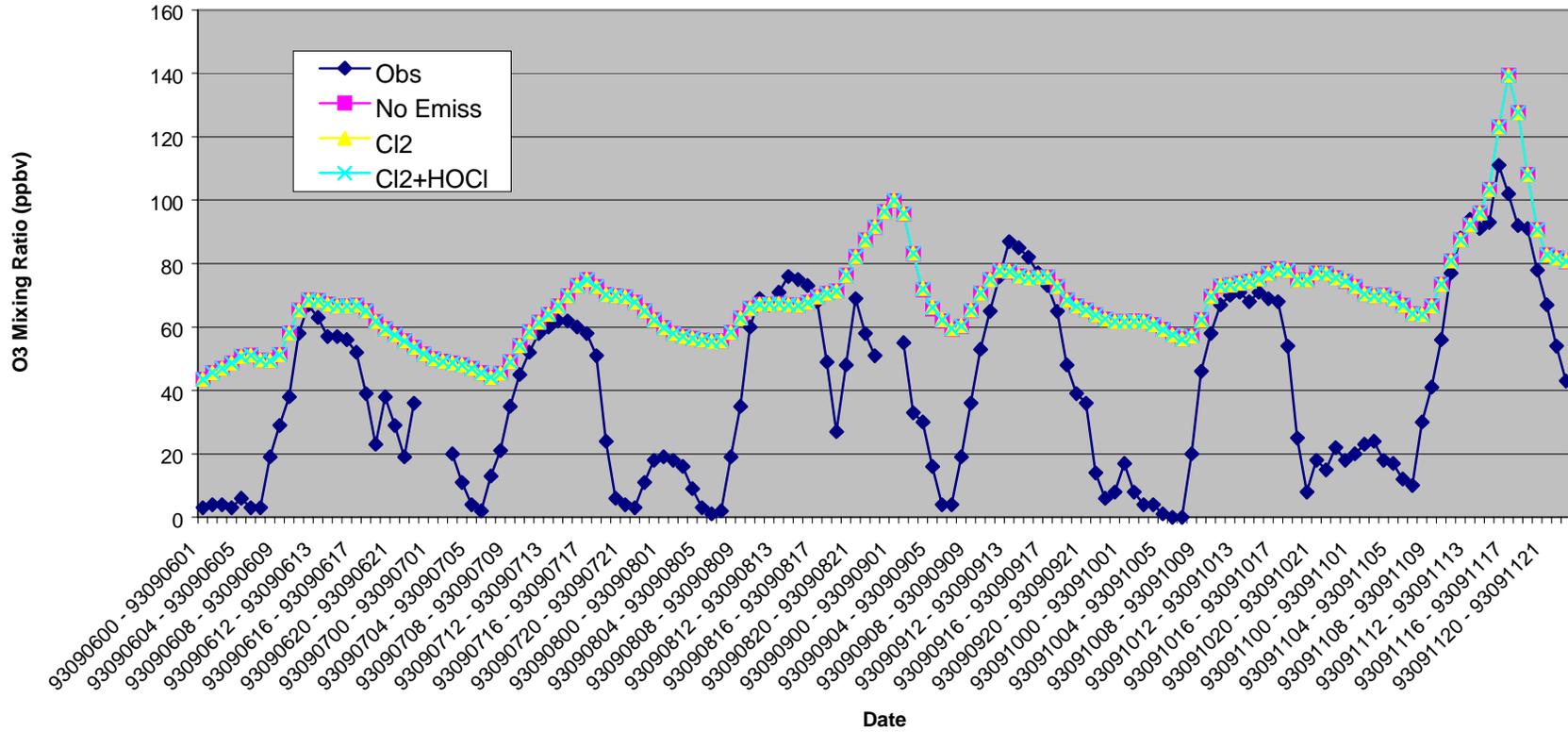
HSMA



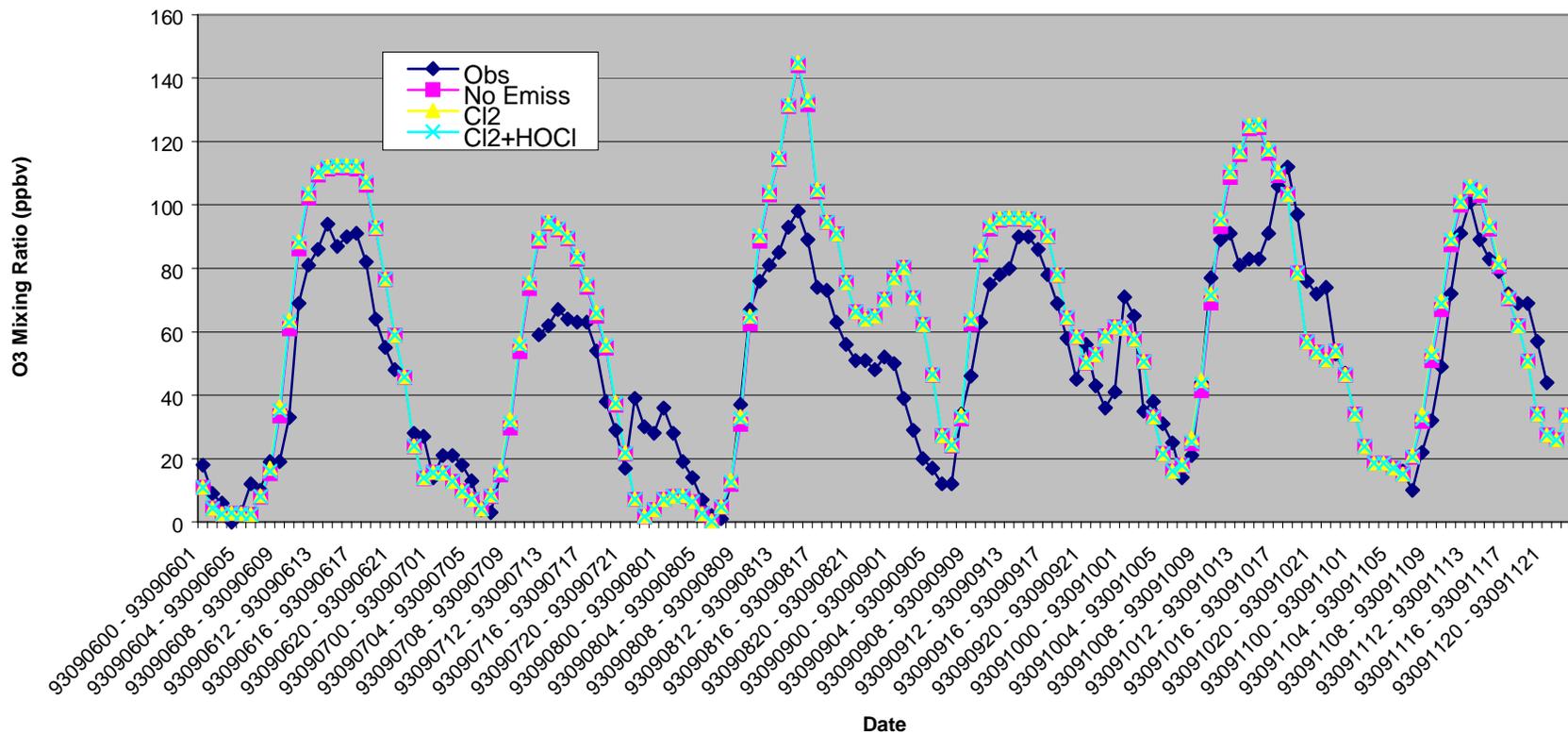
HWAA



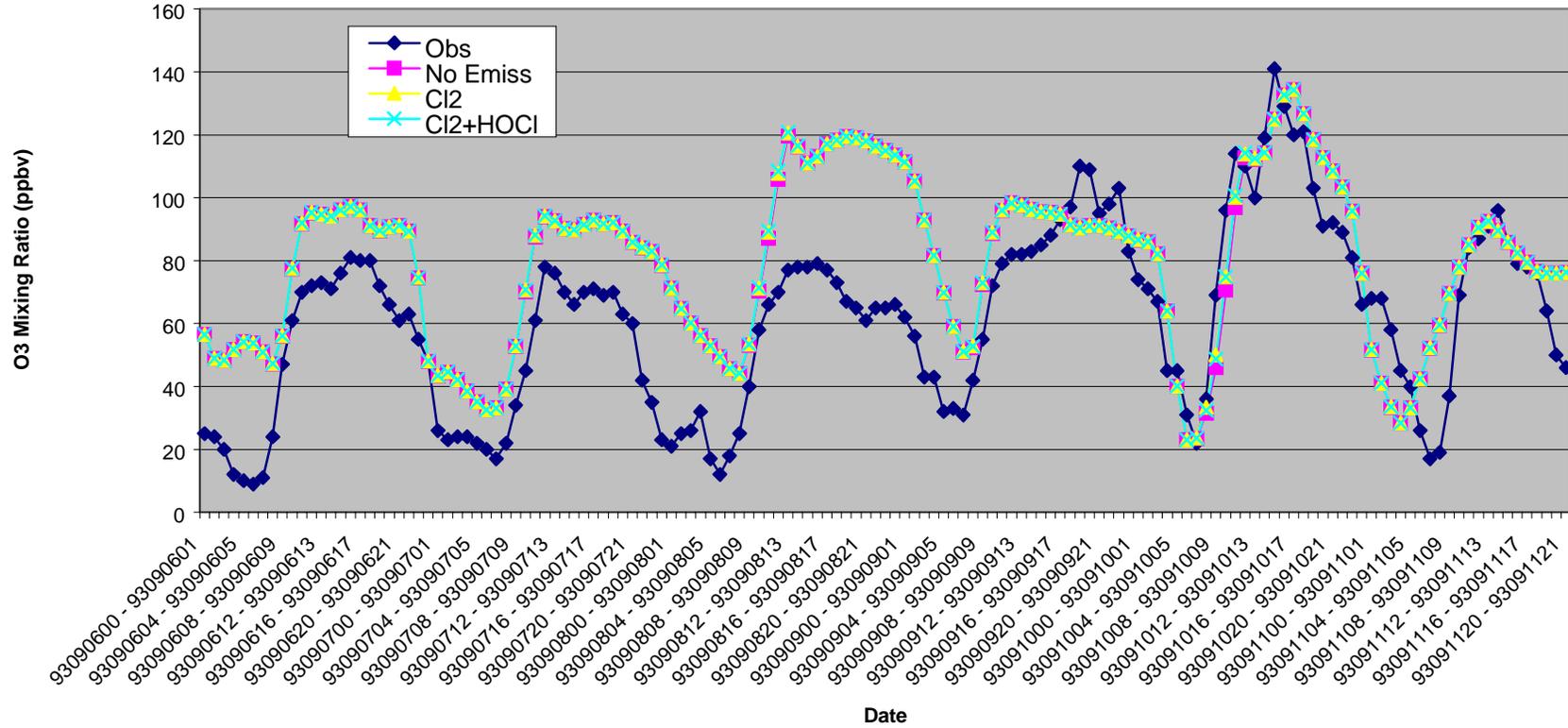
KTZA



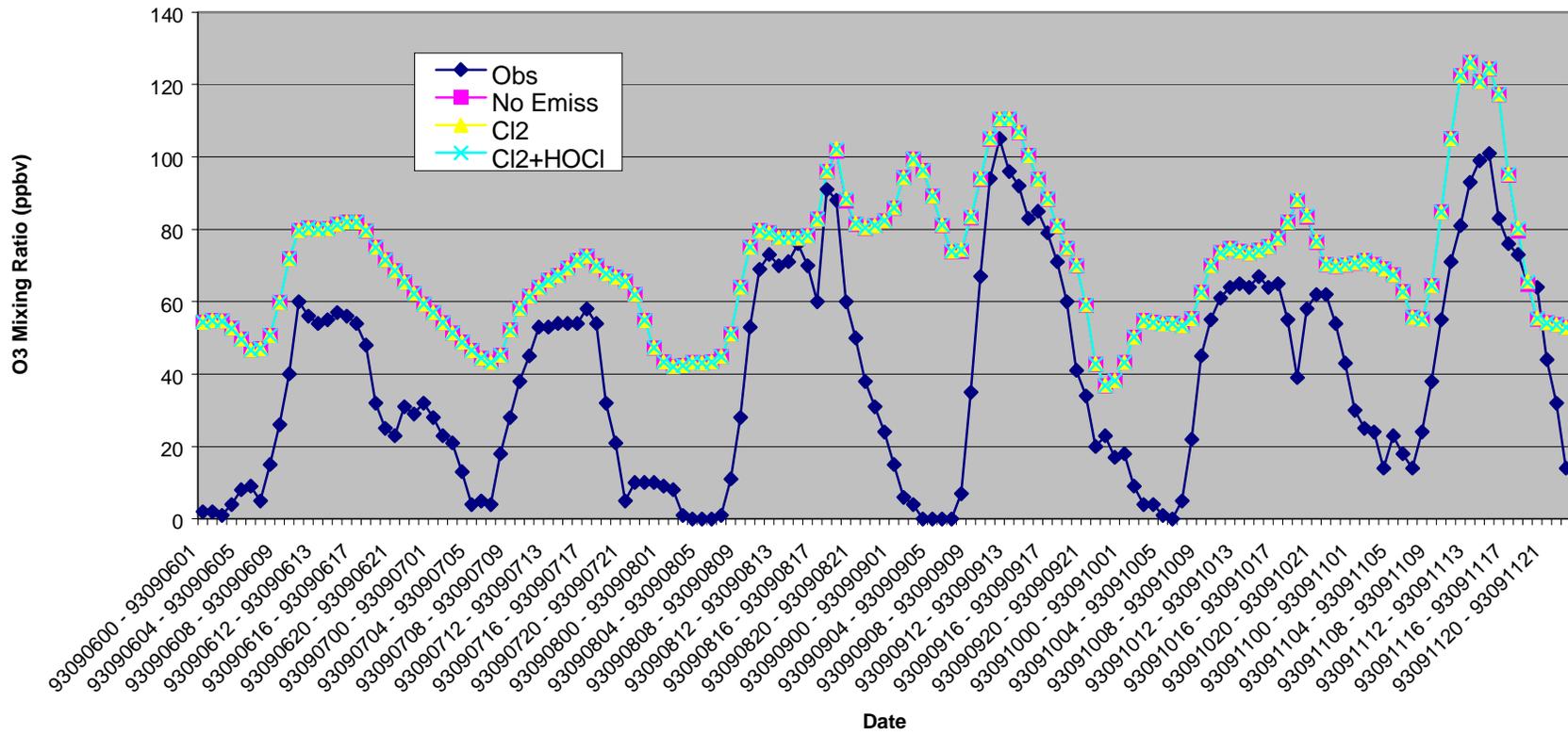
PAWC



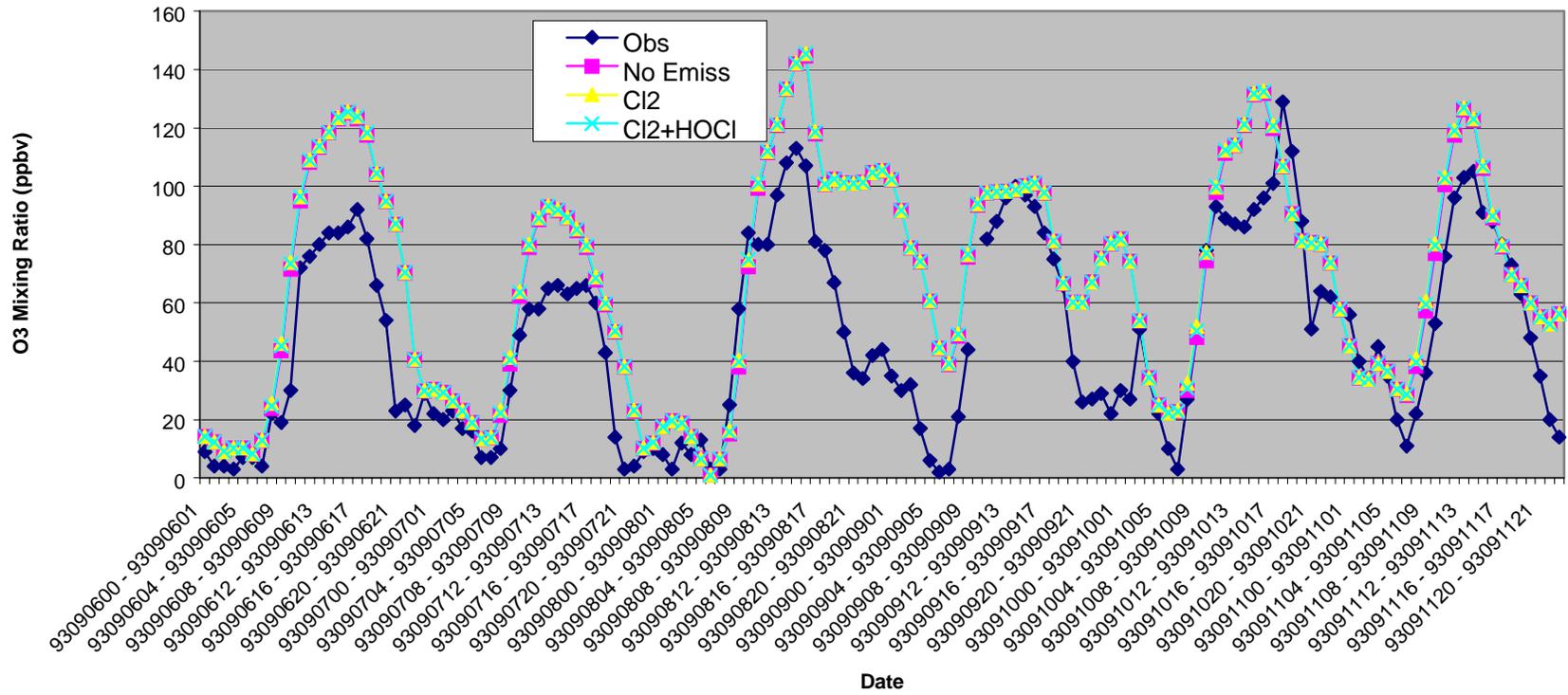
S40S



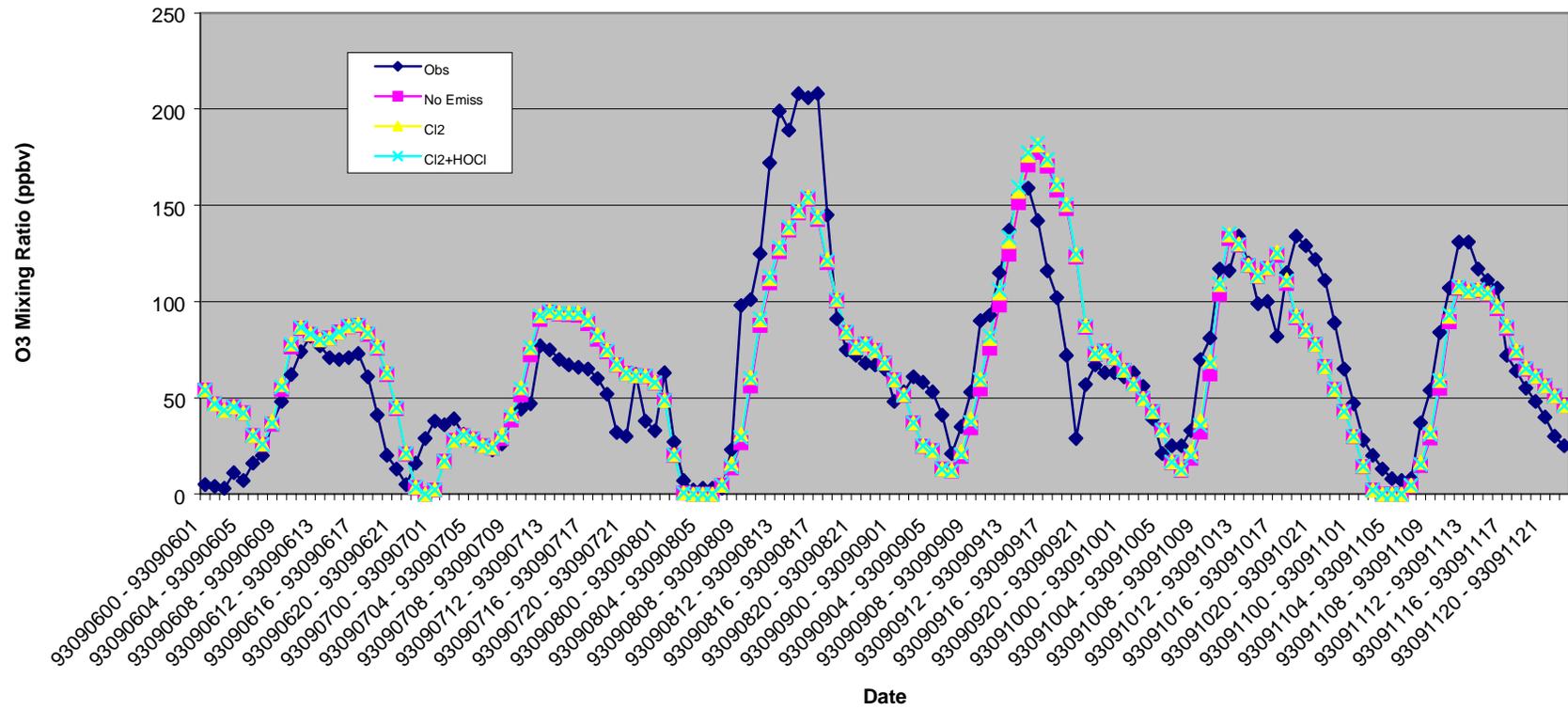
S42S



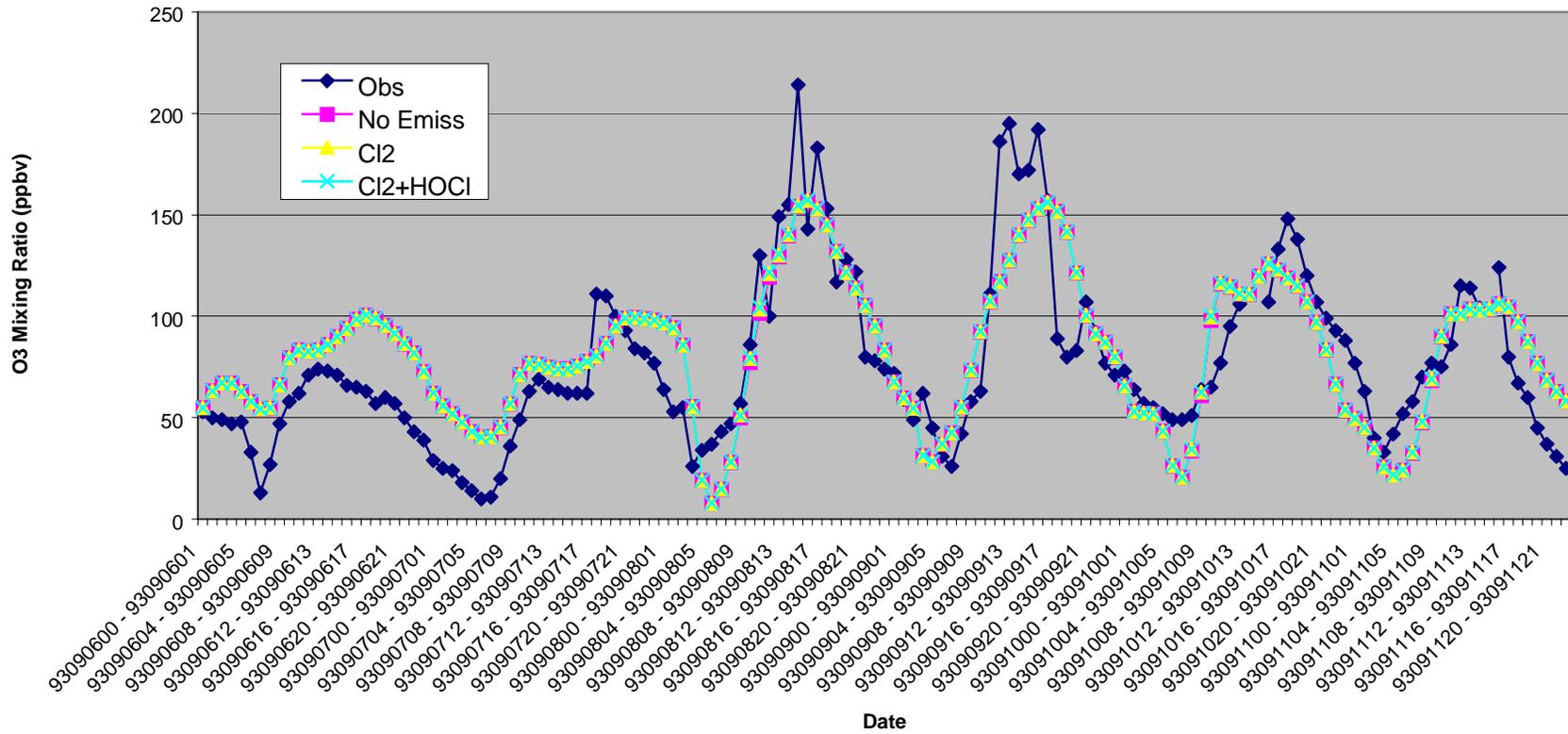
S43S



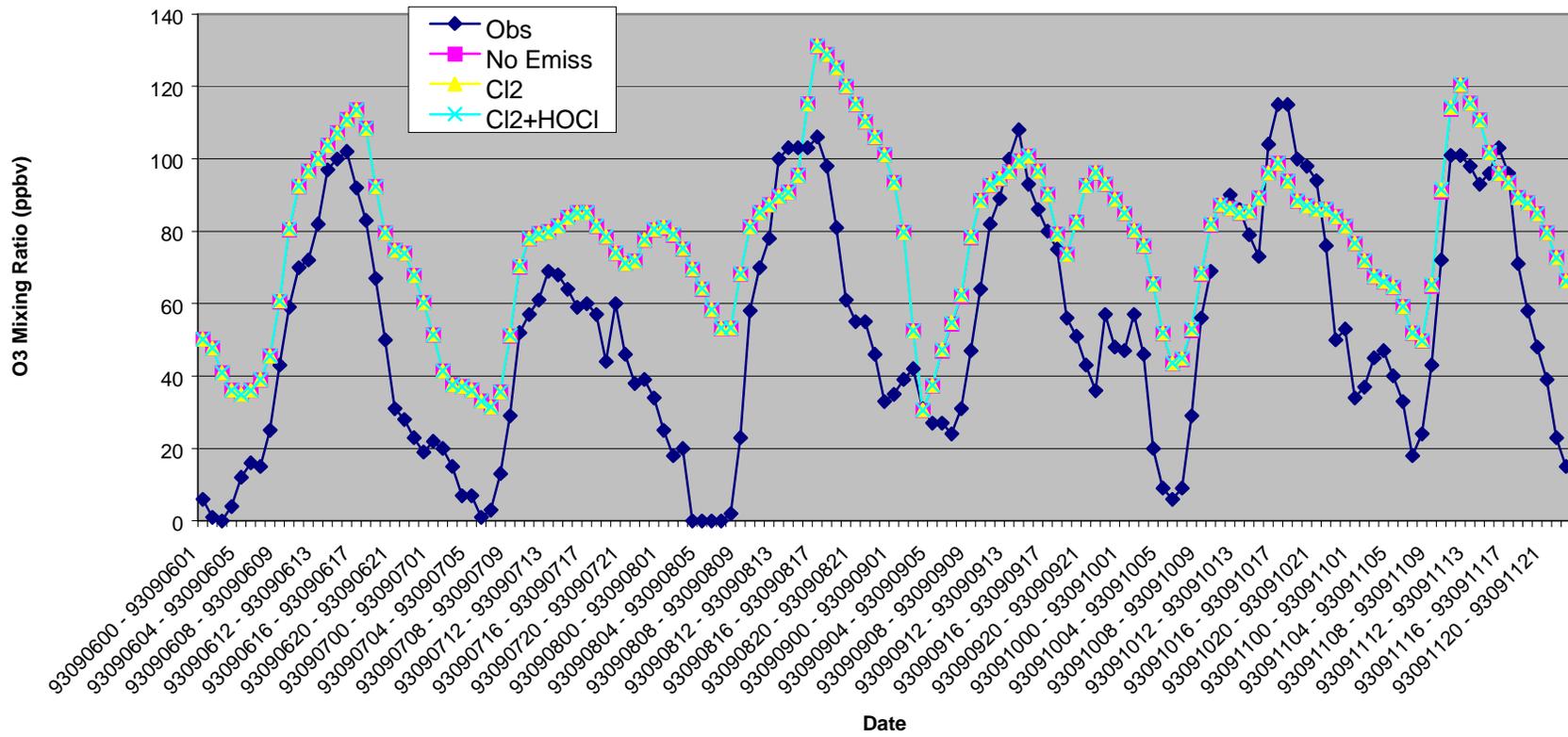
SBRC



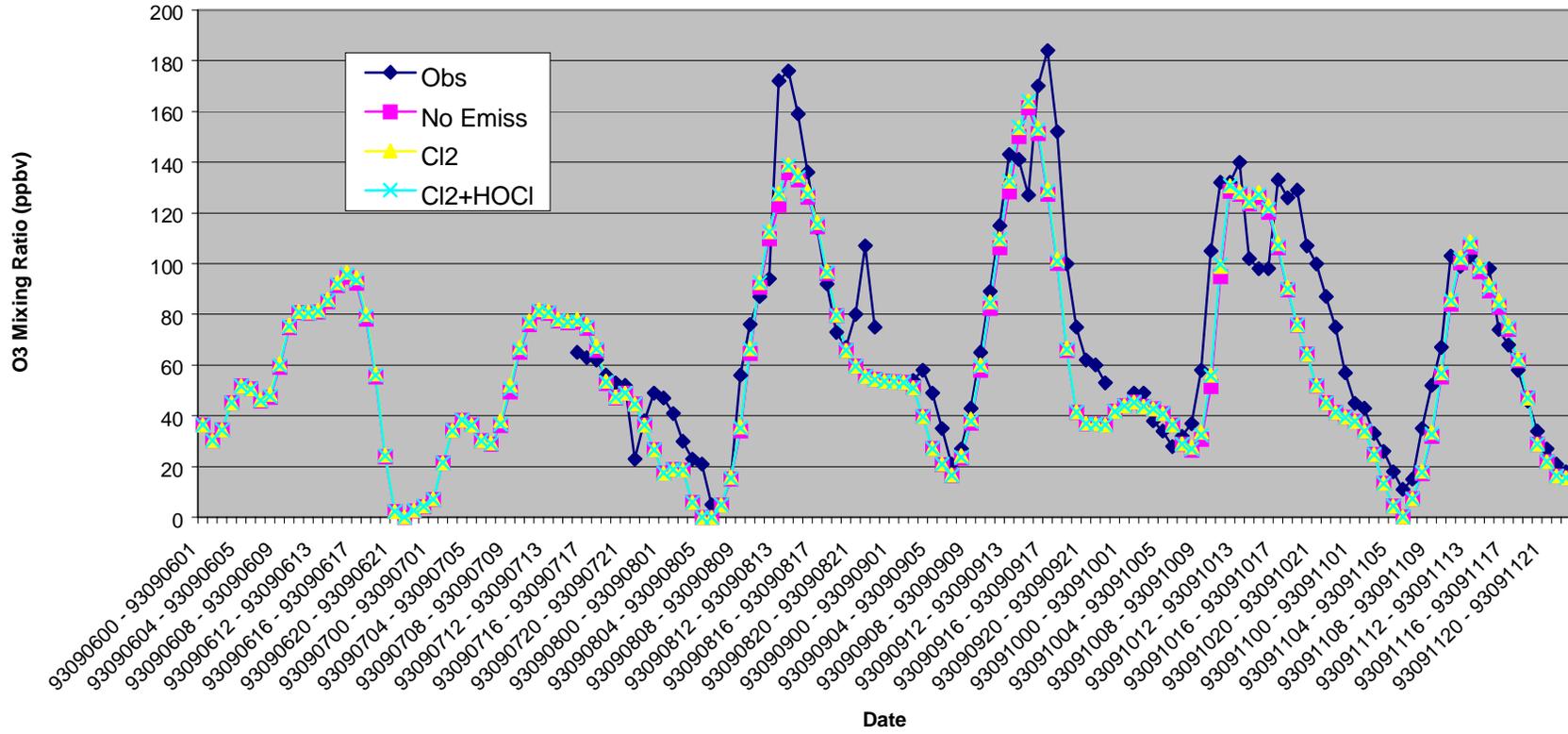
SPTC



STWC



TLMC



WORA

