Final Report

IMPACT OF CHLORINE ON OZONE MODELING FOR THE HOUSTON AREA

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1. INTRODUCTION

The TNRCC is responsible for developing a State Implementation Plan (SIP) for ozone in Houston/Galveston and Beaumont/Port-Arthur (HGBPA) ozone nonattainment areas (the Houston area). The TNRCC's SIP relies upon photochemical modeling to relate atmospheric ozone concentrations to emission levels for ozone precursors. The most recent modeling was performed using the Comprehensive Air Quality Model with extensions (CAMx) and considered emissions of volatile organic compounds (VOCs), nitrogen oxides (NOx) and carbon monoxide. However, recent studies have suggested that reactive chlorine compounds may play a significant role in ozone formation in the Houston atmosphere. The purpose of this study was to update the CAMx model to include reactive chlorine chemistry and evaluate the potential impact of reactive chlorine emissions in the Houston area.

Evidence for the importance of chlorine comes from recent studies at the University of Texas at Austin (UT) published by Tanaka, et al. (2000). This research was further developed through atmospheric measurements in Houston performed by UT during the Texas Air Quality Study (TexAQS) in the summer of 2000 (personal communication from David Allen, UT). The chlorine compounds that could most influence urban ozone are compounds that can photolyze rapidly to produce chlorine atoms (Cl) such as molecular chlorine (Cl_2) and hypochlorous acid (HOCl) but not chlorine containing organics such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Chlorine atoms are highly reactive toward many hydrocarbons and initiate VOC oxidation via reaction pathways that are generally similar to OH radical reactions. However, unlike OH radical, chlorine atoms are not scavenged by high NOx levels. Thus chlorine atoms may be particularly effective in initiating photochemical reactions in urban areas with high levels of both VOC and NOx. The reactions of chlorine atoms are not accounted for in the Carbon Bond 4 (CB4) chemical mechanism that is used for the HGBPA SIP modeling. UT has developed a simplified mechanism to describe the main features of chlorine reactions for ozone modeling in a format compatible with the CB4 mechanism (Tanaka and Allen, 2001).

Objectives

The objectives of this study were as follows:

1. Develop an improved version of CAMx that can be used to investigate the role of reactive chlorine emissions and, if appropriate, integrate chlorine emissions into future ozone control strategy modeling for the Houston area.

2. Test the improved CAMx using current TNRCC modeling databases for the Houston area and the best available chlorine emissions estimates to confirm that CAMx is ready to model chlorine impacts in a regulatory setting.

3. Use the model results from (2) to evaluate the potential impact of reactive chlorine emissions on ozone formation in the Houston area.

Limitations

The model development and application objectives (1 and 2) were successfully achieved by this study. However, after the photochemical model runs had been completed (objective 2) an error was discovered in the emission inventory for reactive chlorine compounds provided for the study. Briefly, a major source of chlorine emissions in the inventory is injection of chlorine into large cooling towers as an algaecide. An error in the spatial distribution of these emissions underestimated chlorine emissions in Harris County and overstated emissions elsewhere. *Consequently, the modeling results presented in the figures and tables of section 3 of this report should not be used to quantitatively evaluate the potential impacts of chlorine emissions in the Houston area.*

2. TECHNICAL APPROACH

This section of the report documents the Houston ozone modeling databases that were utilized, describes the reactions that were added to the CB4 mechanism to describe chlorine, discusses the calculation of photolysis rates for chlorine reactions, and describes the implementation and testing of the chlorine reactions in CAMx.

CAMx MODELING DATABASES

The TNRCC has developed CAMx modeling databases for ozone episodes that occurred in 1993 during the COAST field study. The episode periods are September 6-11 and August 16-20, 1993. Several concerns have been raised about the performance of these databases, and the TNRCC did not use the August episode in the HGBPA SIPs (the TNRCC is currently developing new modeling episodes). However, the effects of chlorine were evaluated for both episodes to include a wider range of conditions for the model testing and evaluation. The area covered by the CAMx model for the COAST domain is shown in Figure 2-1. The COAST domain has an outer 16 km grid with an inner 2-way nested 4-km grid. The grid is defined in UTM zone 15 coordinates and has 8 vertical layers between the surface and 3.03 km. The surface layer is 20 meters deep. The TNRCC has also performed Houston modeling over a much larger area referred to as the SuperCOAST domain, but since this study focused on the effect of chlorine emissions in just the Houston area it was decided that the smaller COAST domain would be adequate to meet the study objectives.

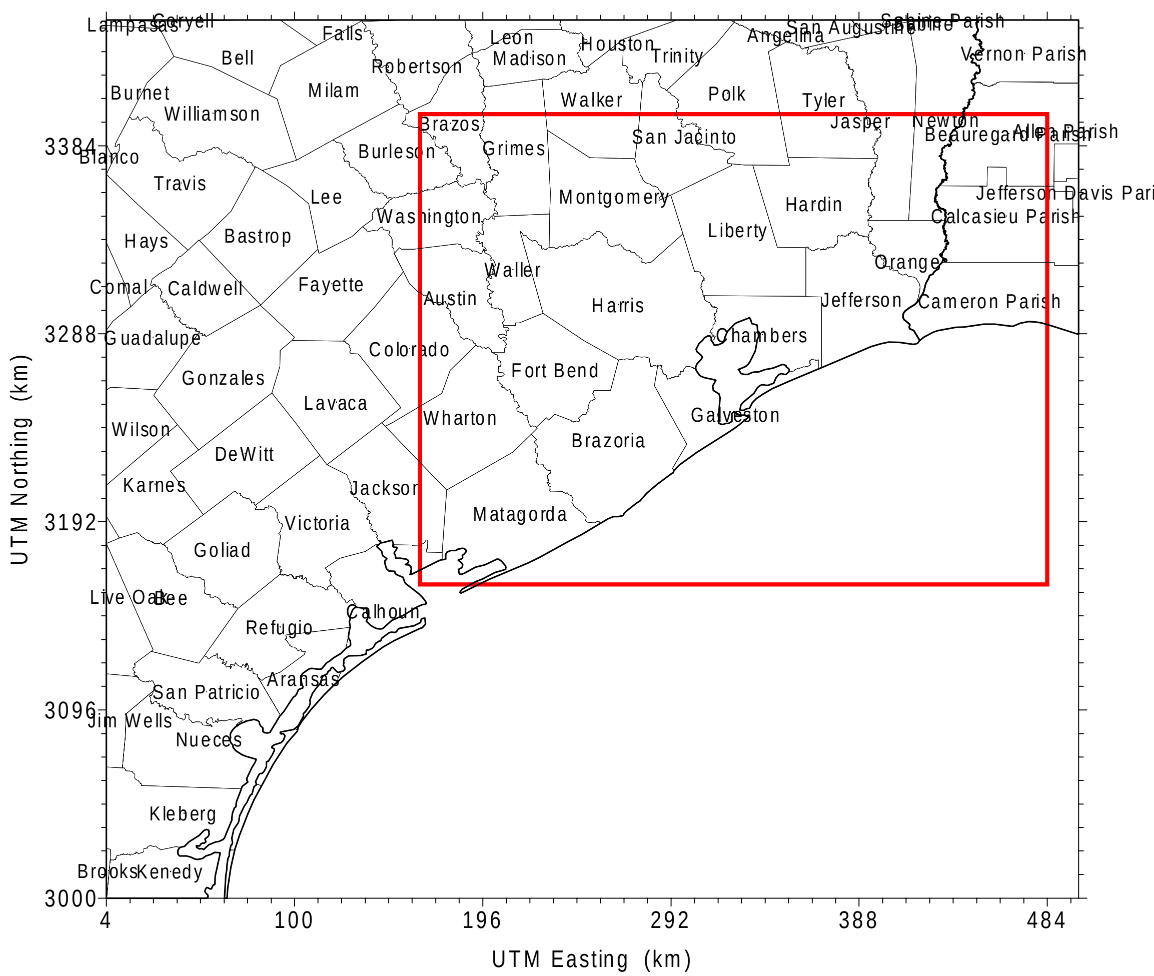
The COAST domain meteorological fields for both the August and September 1993 episodes were developed using the SAIMM hydrostatic meteorological model with data assimilation (Kessler and Douglas, 1992). SAIMM was applied with relatively strong assimilation of wind data in an attempt "nudge" the model into reproducing the timing and magnitude of the land/sea breezes Lolk et al., (1995). This has raised some concerns that the strength of the nudging may have compromised the consistency of the meteorological fields (Yocke et al., 1996). A recent study developed alternate meteorological fields for the September Episode using the Regional Atmospheric Modeling System (RAMS) at 4 km resolution (Emery et al., 2001). A current study (ENVIRON and MRC, 2001) is developing additional alternate meteorological fields using the PSU/NCAR Mesoscale Model version 5 (MM5) at 4 km resolution, and investigating meteorological modeling at very fine resolution (1.33 km) using RAMS and MM5. These studies may result in more realistic meteorological fields and improved photochemical model performance for the September 1993 episode.

The emission inventories were developed by the TNRCC and have undergone continual upgrades to include the latest information. The inventories for the September episode are more updated than for the August episode because the September episode continues to be used for SIP modeling. For example, the biogenic emissions were updated based on new local surveys and the latest emission factors as described in Yarwood et al., (1999). The biogenic emission inventories were prepared using the GLOBEIS model (http://www.globeis.com). The anthropogenic emission inventories were prepared using SMOKE (http://envpro.ncsc.org/products/smoke/).

Boundary conditions are important for the COAST domain, particularly along the eastern boundary close to BPA. TNRCC ran a regional scale model (Yocke et al., 1996) to develop initial conditions (ICs) and boundary conditions (BCs) for the COAST domain, i.e. one-way nesting of the COAST model into the regional model.

The modeling presented here was performed using the latest version (version 3.01) of the Comprehensive Air Quality Model with extensions (CAMx - http://www.camx.com). The only modification from the public version of CAMx3.01 was the implementation of additional chemical reactions for chlorine species as described below.

The TNRCC provided the CAMx input files for the September and August 1993 episodes. To document the input data that were used, the CAMx control files for the first day of the September 1993 and August 1993 episodes are shown in Figures 2-2 and 2-3, respectively.



16 km COAST domain: 31 x 28 16 km cells from (4, 3000) to (500, 3448)

4 km HGBPA domain: 80 x 64 4 km cells from (164, 3160) to (484, 3400)

Figure 2-1. Map of the COAST domain showing the location of the 4-km HGBPA nested grid.

```
CAMx verson         |VERSION3
Run message         |CAMx COAST: HG/BPA 4x4km subgrid, 930906; Cl.emiss.linux
Root output name    |../output/Cl.emiss.linux/CAMx3.930906.Cl.emiss.linux
Start yr/mo/dy/hr   |93 09 06    0.
End   yr/mo/dy/hr   |93 09 06 2400.
dtmx,dtin,dtem,dtou|0.5 1. 1. 1.
nx,ny,nz            |31  28  8
Coordinate ID       |UTM
xorg,yorg,dx,dy     |4. 3000.  16.  16. 15
time zone           |6
PiG parameters      |2000. 12.
Avg output species  |26
                    |O3        NO        NO2       PAN       NTR       HNO3
                    |PAR       OLE       TOL       XYL       FORM      ALD2
                    |ETH       ISOP      MEOH      ETOH      CO        H2O2
                    |CL2       HOCL      FMCL      HCL       ICL1      ICL2
                    |BCL1      BCL2
# nested grids      |1
nest grid params    |11 30 11 25 8 4
SMOLAR or BOTT?     |SMOLAR
Chemistry solver    |CMC
Restart             |false
Chemistry           |true
Dry dep             |true
Wet dep             |false
PiG submodel        |true
Staggered winds     |false
Treat area  emiss   |true
Treat point emiss   |true
1-day emiss inputs  |false
3-D average file    |false
Source Apportion    |false
Chemparam           |../common/CAMx3.chemparm.3.cl
Photolysis rates    |../common/uamv_photorate.930906-930911.isop
Landuse             |../common/uamv_landuse.coast_16km
Height/pressure     |../met/uamv_zp.930906.coast_16km
Wind                |../met/uamv_wind.930906.coast_16km.CAMx2
Temperature         |../met/uamv_temp.930906.coast_16km.CAMx2
Water vapor         |../met/uamv_hum.930906.coast_16km
Cloud cover         |
Rainfall            |
Vertical diffsvty   |../met/uamv_kv.930906.coast_16km
Initial conditions  |../bc-ic-tc/1993/uamv_ic.930906.uamv124_reg
Boundary conditions|../bc-ic-tc/1993/uamv_bc.930906.uamv124_reg
Top concentration   |../bc-ic-tc/1993/uamv_tc.clean
Albedo/haze/ozone   |../common/uamv_aho.930906-930911.coast_16km+hgbpa_04km
Point emiss         |../ei/1993/uamv_el_ei.930906.93.base.chlorine.a0
Area emiss          |../ei/1993/uamv_lo_ei.930906.coast_16km.93.base.regular
Landuse          #1 |../common/uamv_landuse.hgbpa_04km
Height/pressure #1 |../met/uamv_zp.930906.hgbpa_04km
Wind             #1 |../met/uamv_wind.930906.hgbpa_04km.CAMx2
Temp             #1 |../met/uamv_temp.930906.hgbpa_04km.CAMx2
Vertical diff    #1 |../met/uamv_kv.930906.hgbpa_04km
Area emiss       #1 |../ei/1993/uamv_lo_ei.930906.hgbpa_04km.93.base.regular
```

Figure 2-2. CAMx control file (CAMx.in) for the first day of the September 1993 episode.

```
CAMx verson         |VERSION3
Run message         |CAMx COAST: HG/BPA 4x4km subgrid, 930816; Aug.Cl.emiss
Root output name    |../output/Aug.Cl.emiss/CAMx3.930816.aug.Cl.emiss
Start yr/mo/dy/hr   |93 08 16    0.
End   yr/mo/dy/hr   |93 08 16 2400.
dtmx,dtin,dtem,dtou|0.5 1. 1. 1.
nx,ny,nz            |31  28  8
Coordinate ID       |UTM
xorg,yorg,dx,dy     |4. 3000.  16.  16. 15
time zone           |6
PiG parameters      |2000. 12.
Avg output species  |26
                    |O3        NO        NO2       PAN       NTR       HNO3
                    |PAR       OLE       TOL       XYL       FORM      ALD2
                    |ETH       ISOP      MEOH      ETOH      CO        H2O2
                    |CL2       HOCL      FMCL      HCL       ICL1      ICL2
                    |BCL1      BCL2
# nested grids      |1
nest grid params    |11 30 11 25 8 4
SMOLAR or BOTT?     |SMOLAR
Chemistry solver    |CMC
Restart             |false
Chemistry           |true
Dry dep             |true
Wet dep             |false
PiG submodel        |true
Staggered winds     |false
Treat area  emiss   |true
Treat point emiss   |true
1-day emiss inputs  |false
3-D average file    |false
Source Apportion    |false
Chemparam           |../common/CAMx3.chemparm.3.cl
Photolysis rates    |../common/uamv_photorate.930816-930820.isop
Landuse             |../common/uamv_landuse.coast_16km
Height/pressure     |../met/uamv_zp.930816.coast_16km
Wind                |../met/uamv_wind.930816.coast_16km.CAMx3
Temperature         |../met/uamv_temp.930816.coast_16km.CAMx3
Water vapor         |../met/uamv_hum.930816.coast_16km
Cloud cover         |
Rainfall            |
Vertical diffsvty   |../met/uamv_kv.930816.coast_16km
Initial conditions  |../bc-ic-tc/1993/uamv_ic.930816.uamv124_reg
Boundary conditions|../bc-ic-tc/1993/uamv_bc.930816.uamv124_reg
Top concentration   |../bc-ic-tc/1993/uamv_tc.clean
Albedo/haze/ozone   |../common/uamv_aho.930816-930820.coast_16km+hgbpa_04km
Point emiss         |../ei/9308/uamv_el_ei.930816.93.base.chlorine
Area emiss          |../ei/9308/uamv_lo_ei.930816.coast_16km.93.base.regular
Landuse          #1 |../common/uamv_landuse.hgbpa_04km
Height/pressure #1 |../met/uamv_zp.930816.hgbpa_04km
Wind             #1 |../met/uamv_wind.930816.hgbpa_04km.CAMx3
Temp             #1 |../met/uamv_temp.930816.hgbpa_04km.CAMx3
Vertical diff    #1 |../met/uamv_kv.930816.hgbpa_04km
Area emiss       #1 |../ei/9308/uamv_lo_ei.930816.hgbpa_04km.93.base.regular
```

Figure 2-3. CAMx control file (CAMx.in) for the first day of the August 1993 episode.

CHLORINE EMISSIONS

The chlorine emission inventory was prepared by UT and is described in detail elsewhere (Tanaka and Allen, 2001). Briefly, the inventory included following source types:

- Point sources included in the TNRCC's point source database (PSDB) and the Toxic Release Inventory (TRI).
- Emissions from chlorinating swimming pools.
- Emissions from chlorinating large cooling towers.
- Formation of chlorine from sea salt reactions in the atmosphere.

There is uncertainty whether emissions from cooling towers and swimming pools are in the form of molecular chlorine (Cl_2) or hypochlorous acid (HOCl), or both. For this study, UT recommended assuming that all emissions are in the form of Cl_2 (personal communication from David Allen, UT).

The chlorine emission estimates provided by UT were processed using the emissions preprocessor system version 2 (EPS2) and formatted for CAMx. For simplicity, UT represented all emissions as point sources (e.g., area source emissions such as swimming pools were broken out by grid cell and represented as a single point source released at the surface in the center of the appropriate grid cell). Thus, only the point source emission file for CAMx was modified by the inclusion of chlorine sources – the area source emission files did not change from the base case. The chlorine point sources were merged with the VOC, NOx and CO point sources for the COAST domain.

The Cl_2 emission inventory was the same for each day modeled and totaled 12.6 tons of Cl_2. The magnitude of the Cl_2 emissions varied by hour. The spatial distribution of emissions at hour 12 (mid-day) is shown in Figures 2-4 and 2-5. The geographic extent and scale in Figure 2-4 were chosen to show all areas that were influenced by chlorine emissions. Figure 2-4 confirms that chlorine emissions were only modeled for counties around Houston and Beaumont and just offshore (sea salt related emissions) of these counties. Figure 2-5 is designed to show the location of larger sources in just the Houston/Beaumont area. For reference, an emission rate of 100 moles/hour is equivalent to 0.19 tons/day of Cl_2. These figures show smaller but widespread Cl_2 emissions from swimming pools and/or sea salt with isolated larger emissions from point sources and/or cooling towers.

Limitations of the Chlorine Emission Inventory

After the ozone modeling had been completed using the chlorine emissions described above, a significant error was identified in the emissions calculations for cooling towers. Cooling towers in Harris County (which contains Houston) were omitted from the spatial allocation of cooling tower emissions. The result is that emissions of reactive chlorine were understated in Harris County and overstated in other areas.

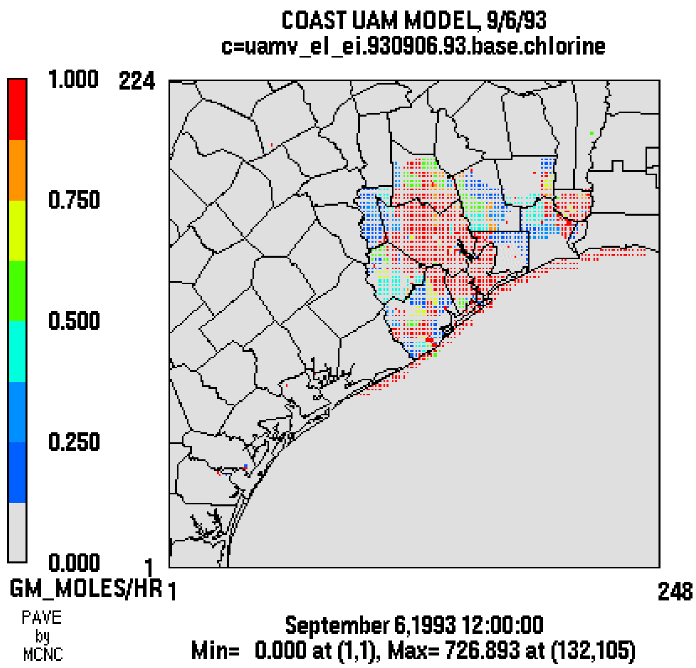


Figure 2-4. Emissions density plot for molecular chlorine emissions over the whole COAST domain. Emissions scale maximum set at 1 mole/hour/grid cell.

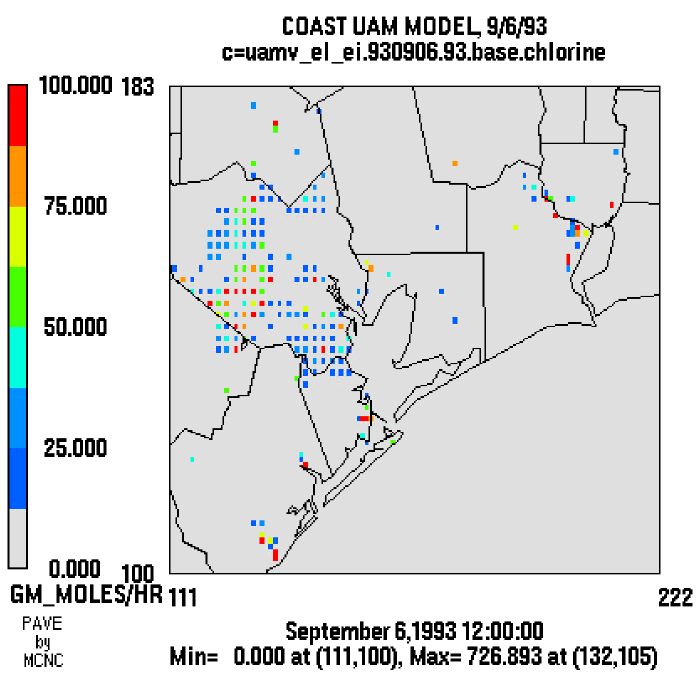


Figure 2-5. Emissions density plot for molecular chlorine emissions in the Houston/Beaumont area. Emissions scale maximum set at 100 moles/hour/grid cell.

CHLORINE REACTION MECHANISM

The CB4 mechanism in CAMx was modified by adding 13 reactions for chlorine species, as shown in Table 2-1. The base CB4 mechanism is listed in the CAMx User's Guide (http://www.camx.com).

Table 2-1. Chlorine reactions added to the CB4 mechanism.

	Reactants			Products			k(298) ppm^{-1} min^{-n}
97	CL2		=	2 CL			0.295 * JNO2
98	HOCL		=	1 OH	1 CL		0.0295 * JNO2
99	CL	O3	=	1 CLO	1 O2		17790
100	CLO	NO	=	1 CL	1 NO2		24491
101	CLO	HO2	=	1 HOCL	1 O2		7314.4
102	CL	PAR	=	1 HCL	0.87 XO2	0.13 XO2N	93834
				0.11 RCHO	0.76 ROR	-0.11 PAR	
103	CL	OLE	=	1 FMCL	1 RCHO	2 XO2	840000
				1 HO2	-1 PAR		
104	CL		=	1 HCL	1 XO2	1 FORM	281.57
				1 HO2			
105	CL	ETH	=	1 FORM	2 XO2	1 FMCL	150190
				1 HO2			
106	CL	ISOP	=	0.15 HCL	1 XO2	1 HO2	664200
				0.28 ICL1			
107	OH	ICL1	=	1 ICL2			28044
108	CL	BUTA	=	1 XO2	1 HO2	0.7 BCL1	619920
109	OH	BCL1	=	1 BCL2			53136

The following points should be noted in reading Table 2-1:

- Reactions 97 and 98 are photolysis reactions. Detailed photolysis rates were calculated for these reactions using the latest cross-section and quantum yield data identified by Tanaka and Allen (2001) and the TUV radiative transfer model (http://www.acd.ucar.edu/TUV/). Based on these calculations, simple ratios to the NO_2 photolysis rate (JNO2) were developed as shown in Table 2-1. The photolysis rate calculations are further described in Appendix 1.

- Rate constants for the thermal reactions 99-109 were specified using the temperature and/or pressure dependent expressions recommended by Tanaka and Allen (2001). For simplicity, the rate constant at 298 K and 1 atmosphere is shown in Table 2-1 in concentration units of ppm and time units of minutes.

- The Cl + O3 reaction (99) was added to permit sensitivity studies to investigate the importance of this reaction. Theoretical analysis suggests that this reaction (and subsequent reactions of CLO) has negligible impact (Tanaka and Allen, 2001).

- Reaction 104 accounts for reaction of Cl atoms with methane assuming a background methane concentration of 1.75 ppm.

- The reactions of 1,3-butadiene were included because they provide a potentially unique marker product for Cl-atom reactions in the atmosphere (Tanaka and Allen, 2001). At this time, the emission inventories do not include 1,3-butadiene so this capability can not be used yet.

- Ten new species are added to the CB4 mechanism, as listed in Table 2-2.

Table 2-2. Species added to the CB4 mechanism to describe chlorine reactions.

CB4 Name	Description
CL2	Molecular chlorine
CL	Chlorine atom
CLO	Chlorine monoxide radical
HOCL	Hypochlorous acid
FMCL	Formyl chloride - HC(O)Cl
HCL	Hydrochloric acid
ICL1	Reaction product 1 from Cl + Isoprene
ICL2	Reaction product from Cl + ICL1
BUTA	1,3-Butadiene
BCL1	Reaction product 1 from Cl + 1,3-Butadiene
BCL2	Reaction product 1 from Cl + BCL1

Quality Assurance: Verifying the implementation of the Chlorine mechanism in CAMx3

Several steps were taken to ensure that the correct reactions were implemented in CAMx. The CAMx chemistry solver uses a chemical mechanism compiler (CMC) to generate model code which minimizes the potential for typographical errors. The reaction listing and rate constant values shown in Table 2-1 were output from the CMC and CAMx, so these are the exact reactions and rate constants modeled. The information shown in Table 2-1 was compared to Allen and Tanaka (2001) to ensure correct implementation.

The next step was to check the accuracy of the CAMx chemistry solver with chlorine reactions against a reference numerical method (LSODE). This procedure is the same as the evaluation of the standard CB4 chemistry solver in CAMx described in the CAMx User's Guide. The CAMx chemistry solver predictions agreed well with the LSODE Gear solver predictions, as shown in Appendix 2.

The final step was a comparison of CAMx simulation results for the "chlorine chemistry" version of CAMx3 to the standard CAMx3.01 result when there are no sources of chlorine. With no input of chlorine, we expect to get identical model predictions from the versions of CAMx with and without the chlorine reactions. The maximum differences in predicted ozone concentrations were on the order 10^{-5} ppm, which is very small and on the order of single precision numerical round-off. Differences for other species were similarly small.

Based on the results of these quality assurance steps we are satisfied that the chlorine reactions were correctly implemented in CAMx for this study.

3. CAMx RESULTS

Ozone modeling was performed for the Houston area (COAST domain) using an improved version of CAMx3, as described in section 2. The modeling used existing databases prepared by the TNRCC with reaction chlorine emission estimates from UT and the simple chorine reaction mechanism developed at UT. As discussed in section 2, an error in the spatial distribution of the chlorine emissions underestimated chlorine emissions in Harris County and overstated emissions elsewhere. *Consequently, the modeling results presented in the figures and tables in this section should not be used to quantitatively evaluate the potential impacts of chlorine emissions in the Houston area.*

CAMx simulations successfully completed for two episode periods: September 6-11 and August 16-20, 1993. When no chlorine emissions were input to the modified version of CAMx3 the predicted ozone levels were the same as from the publicly released version 3.01 of CAMx. Based on these results and the quality assurance findings presented in section 2 we conclude that the version of CAMx with chlorine chemistry is ready to be used in a regulatory setting. This satisfies first two objectives of this study listed in section 1.

The ozone modeling results for the September and August 1993 COAST domain episodes are presented in series of tables and figures in Appendices 3 and 4. Model spin-up days were generally excluded and so the results focus on September 8-11 and August 17-20, 1993. The presentation of results also focuses on 4-km grid area (Figure 2-1). The following results are presented for each episode:

- Tables of 1-hour ozone model performance statistics with and without chlorine emissions.
- Isopleth plots of daily maximum 1-hour ozone with observations for simulations including chlorine emissions.
- Isopleth plots of the difference in daily maximum 1-hour ozone due to chlorine emissions.
- Time series of hourly 1-hour ozone observations and predictions with and without chlorine emissions.
- Isopleth plots of daily maximum 1-hour chlorine (CL2).
- Isopleth plots of daily maximum 1-hour hydrochloric acid (HCL).
- Isopleth plots of daily maximum 1-hour formyl chloride (FMCL).

Discussion of Results

The impact of chlorine emissions in the Houston area can be discussed using just a few of the model results. Table 3-1 shows the peak 1-hour ozone concentrations for each episode day with and without chlorine emissions. Depending upon the day, the impact of chlorine emissions on the peak ozone ranged from zero to 1.9 ppb. The magnitude of the impact depends upon the geographic relationship between the chlorine emissions and the location of the ozone peak on each day. Table 3-1 also shows the largest impact of chlorine on the daily maximum 1-hour ozone in any 4-km grid cell on each day, which ranged from 6 to 17 ppb. Chlorine emissions had little impact on the EPA model performance statistics (see Appendices 3 and 4) because the impacts on peak ozone were small and larger impacts away from the peak were highly localized and frequently did not coincide with the monitor locations used in the statistical calculations.

Table 3-1. Impact of chlorine emissions on the peak predicted 1-hour ozone and the largest impact on daily maximum 1-hour ozone in any 4-km grid cell on each day.

Episode Day	Peak Ozone without chlorine (ppb)	Peak Ozone with chlorine (ppb)	Impact of chlorine on peak ozone (ppb)	Largest impact of chlorine on daily maximum ozone (ppb)
17-Aug-93	137.9	138.5	0.6	8
18-Aug-93	139.6	139.6	0.0	9
19-Aug-93	130	131.2	1.2	6
20-Aug-93	131.1	132.7	1.6	7
8-Sep-93	199.7	200.6	0.9	10
9-Sep-93	192.2	193.2	1.0	17
10-Sep-93	192.8	194.7	1.9	9
11-Sep-93	200.4	201.5	1.1	12

Figure 3-1 shows four isopleth plots for September 9th: the difference in maximum ozone, maximum chlorine (CL2), maximum hydrochloric acid (HCL) and maximum formyl chloride (FMCL). The largest ozone increase on this day was 17 ppb near Texas City on the west side of Galveston Bay. This increase coincides with several point sources of chlorine emissions. *Note that the magnitude of the chlorine emissions and concentration impacts at this location are overstated due to the emission inventory error described in section 2.* However, the model results for this day can be used to describe the qualitative response of the model to chlorine emissions for an industrial area near Houston. Figure 3-2 shows a time series of hourly ozone concentrations at this location (no observations are shown because this location does not coincide with a monitor). The time series show that the chorine emissions accelerated ozone formation in the morning through about mid-day but had less impact on afternoon ozone levels. This is consistent with morning ozone formation being limited by the availability of radicals to initiate reactions (a condition where ozone formation is also VOC sensitive). Since chlorine emissions provide additional radical sources, morning ozone formation is accelerated and ozone levels are increased when chlorine is added to the model simulation. The smaller impact of chlorine emissions in the afternoon could be due to several reasons: (1) the diurnal profile used for the chlorine emissions at this location had higher emissions in the morning than the afternoon by a factor of two; (2) ozone formation may be less radical limited in the afternoon; (3) greater atmospheric mixing in the afternoon than the morning dispersed the impact of the chlorine emissions. Additional modeling could be performed to identify the relative importance of these processes, such as using the Process Analysis diagnostic capability recently developed for CAMx.

The isopleth plot of ozone impacts (Figure 3-1) shows a rapid decrease in the impact of chlorine on maximum ozone moving away from point source locations. This is due to dispersion of the chlorine emissions and the excess ozone formed from the chlorine emissions. The location of the ozone impacts is closely related to the location of the largest point sources in the emission inventory used for this study. This suggests that the widely dispersed area sources of chlorine in the inventory (swimming pools and formation from sea salt aerosol) had very little impact on maximum ozone levels. Because of the error in spatially allocating chlorine emissions from cooling towers the distribution and magnitude of the ozone impacts shown in Figure 3-1 may be misleading.

Figure 3-1 also shows the daily maximum concentrations for chlorine (CL2) and the main chlorine containing reaction products hydrochloric acid (HCL) and maximum formyl chloride (FMCL). The largest CL2 impacts are localized near to emission sources because of dispersion and rapid chemical reaction of chlorine during the daytime. The highest CL2 concentrations occur in the early morning due to combination of factors: (1) the diurnal emissions profile used for chlorine emissions from major sources has low emissions at night, high emissions during the morning, moderate emissions in the afternoon; (2) low mixing and dispersion in the morning concentrates emissions near the surface; (3) the chemical lifetime of CL2 against photolysis is longer at low sun angles and shortest in the middle of the day.

The main chlorine containing reaction products in these simulations were HCL and FMCL. The concentration isopleth plots for these compounds in Figure 3-1 show a close relationship between maximum HCL/FMCL concentrations and CL2 concentrations. This is consistent with CL2 reacting rapidly in the atmosphere so that HCL and FMCL were formed close where the CL2 was emitted. Near the coastline of the Gulf of Mexico several plumes are apparent in the HCL and FMCL isopleth plots and the plumes are oriented offshore. This is because the maximum HCL and FMCL concentrations occur in the early morning (shortly after sunrise) and there was an offshore land breeze near the Gulf coast on September 9th, 1993. The locations of the maximum chlorine product impacts (HCL and FMCL) do not necessarily coincide with the locations of maximum ozone impacts because they occur at different times of day when the winds may have different directions.

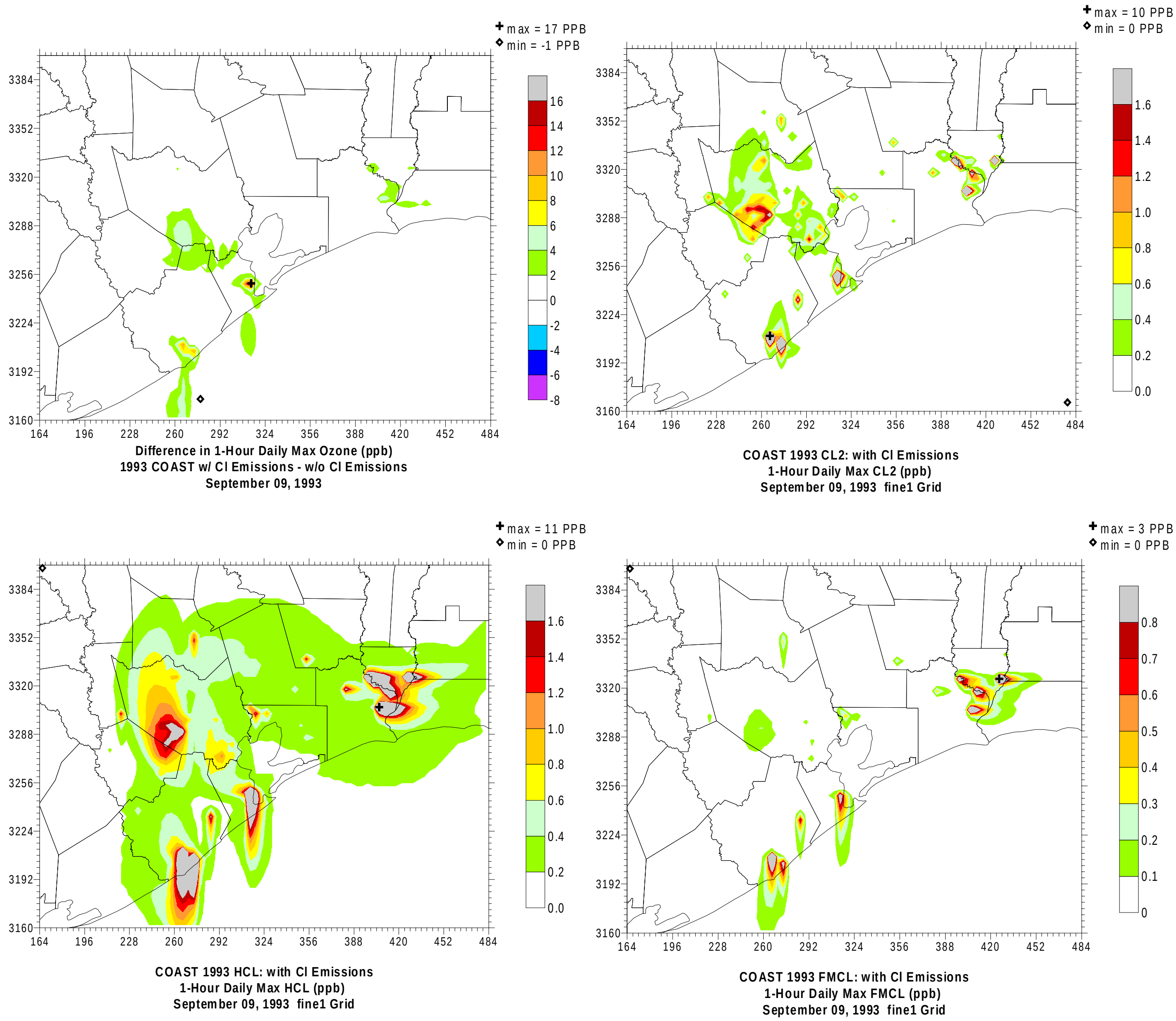


Figure 3-1. Isopleth plots for September 9th, 1993: The difference in daily maximum ozone due to chlorine, maximum chlorine (CL2), maximum hydrochloric acid (HCL) and maximum formyl chloride (FMCL).

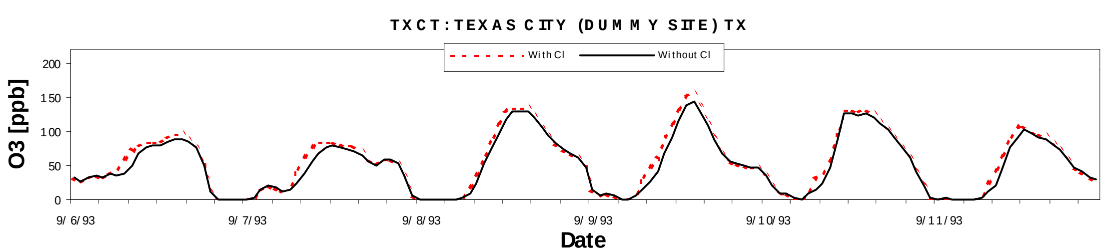


Figure 3-2. Time series of hourly ozone concentrations at the location of the maximum ozone impact in Figure 3-1 (no observations are shown because this location does not coincide with a monitor).

4. CONCLUSIONS

The main conclusion from this study is that CAMx has been successfully modified to include the simple chlorine reaction mechanism developed by Tanaka and Allen (2001) providing a modeling tool that is ready to be used in a regulatory setting. *This study also provides ozone model results for two episodes in the Houston area, but these must be interpreted with caution because of an error in the spatial distribution of cooling tower emissions which underestimated chlorine emissions in Harris County and overstated emissions elsewhere.* With this caveat in mind, the following points are drawn from the ozone modeling results:

- Depending upon the day, the impact of chlorine emissions on the peak ozone ranged from zero to 1.9 ppb. The magnitude of the impact depends upon the geographic relationship between the chlorine emissions and the location of the ozone peak on each day. The largest impact of chlorine on the daily maximum 1-hour ozone in any 4-km grid cell ranged from 6 to 17 ppb depending upon the day.

- Chlorine emissions had little impact on the EPA model performance statistics for ozone because the impacts on peak ozone were small and larger impacts away from the peak were highly localized and frequently did not coincide with monitor locations used in the statistical calculations.

- Chorine emissions accelerated ozone formation in the morning through about mid-day but had less impact on afternoon ozone levels.

- The locations of the ozone impacts were closely related to the location of the largest point sources in the chlorine emission inventory used for this study. This suggests that the widely dispersed area sources of chlorine in the inventory (swimming pools and formation from sea salt aerosol) had very little impact on maximum ozone levels. *Because of the error in spatially allocating chlorine emissions from cooling towers the distribution and magnitude of the ozone impacts shown in Section 3 may be misleading*.

- The highest modeled concentrations of chlorine and chlorine-containing reaction products occurred in the early morning hours soon after sunrise.

- The locations of the maximum chlorine-containing reaction products (hydrochloric acid and formyl chloride) do not necessarily coincide with the locations of maximum ozone impacts because they occur at different times of day when the winds may have different directions.

5. REFERENCES

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Appendix 1

Calculation of photolysis rates using the TUV model

ENVIRON

MEMORANDUM

To: David Allen and Paul Tanaka, UT Austin

cc: Jim Neece, TNRCC

From: Greg Yarwood

Date: 13 June 2001

Subject: Treatment of Chlorine Photolysis Reactions in CAMx Modeling

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We are preparing to model the impact of chlorine reactions on ozone formation in the Houston area using CAMx. The chlorine mechanism is described in a report by Allen and Tanaka dated April 4, 2001. The mechanism includes photolysis reactions for Cl_2 and HOCl and recommends ratios for these photolysis rates to the NO_2 photolysis rate. Specifying photolysis rates for one reaction as a ratio to another reaction is a useful simplification for CAMx modeling. In choosing a suitable surrogate reaction (e.g., NO_2 photolysis), the main concern is that the two species (e.g. Cl_2 and NO_2) should photolyse over similar regions of the solar spectrum so that the ratio is near constant over a wide range of conditions.

Photolysis rates for CAMx are usually prepared using a preprocessor called TUV (http://acd.ucar.edu/models/UV/TUV/index.html and http://www.camx.com). We have added the absorption cross-section and quantum yield data identified by Allen and Tanaka for Cl_2 and HOCl to the CAMx version of TUV so that photolysis rates for these species can now be calculated in the same way as any other photolysis reaction in CAMx. To test the implementation in TUV, photolysis rates were calculated for some typical conditions:

Zenith angles: 0, 10, 20, 30, 40, 50, 60, 70, 78, 86 degrees
Elevation: 640 m above ground
Ozone column: 300 Dobson Units
UV surface albedo: 0.06
Optical depth due to haze: 0.1

Ratios of photolysis rates to NO_2 averaged over the 10 zenith angles are shown in the table below. The ratios calculated by TUV are similar to Allen and Tanaka's values. Differences are likely due to different underlying assumptions for the solar spectral distribution.

	Allen and Tanaka Ratio	TUV Ratio	TUV Ratio Std. Dev. (% of mean)
Cl2/NO2	0.295	0.264	8.1
HOCl/NO2	0.0295	0.0262	18.7
HOCl/ISPD	--	143	6.4

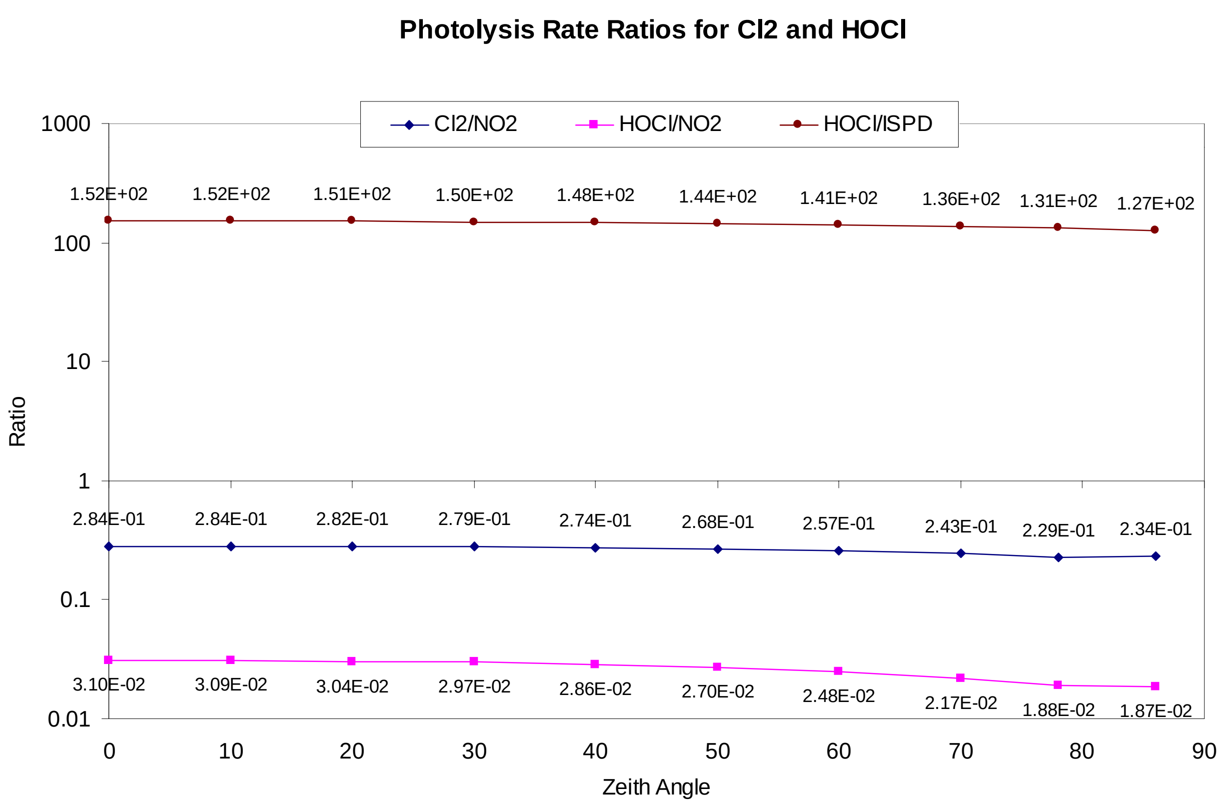
In addition to showing the average photolysis rate ratio over the 10 zenith angles, the standard deviation of ratio is shown as a percentage of the mean. This gives a measure of the variability in the ratio with zenith angle. The actual ratios are shown in the figure below. The ratio of Cl_2 to NO_2 photolysis rates does not vary greatly with zenith angle because these two molecules photolyze in similar regions of the solar spectrum. However, the ratio of HOCl to NO_2 photolysis rates varies by nearly a factor of 2 between high (zero degrees) and low (86 degrees) sun angles suggesting that NO_2 is not an ideal surrogate for HOCl photolysis. Several other photolysis reactions are available in CAMx for use as a surrogate for HOCl photolysis. The most suitable surrogate is the photolysis of the lumped isoprene oxidation product (ISPD) which is based on acrolein photolysis. The ratio of HOCl to ISPD photolysis rates is quite stable with zenith angle, as shown in the table and figure.

Recommendations for CAMx Modeling

1. Use photolysis rate ratios calculated with TUV to improve consistency with other CAMx photolysis reactions

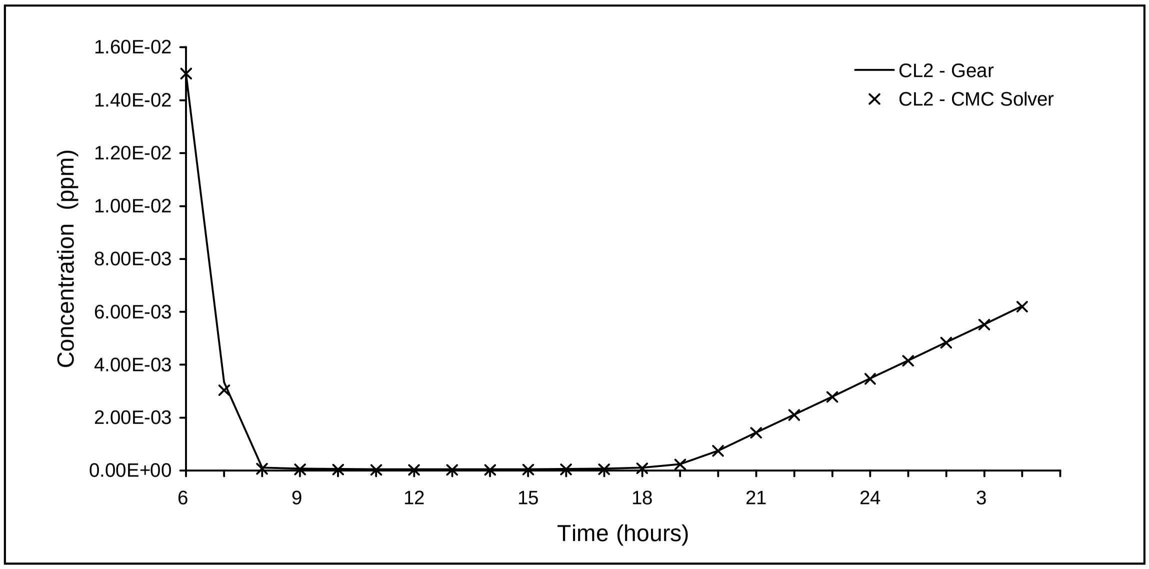
2. Set Cl_2 photolysis as a ratio to NO_2 photolysis as recommended by Allen and Tanaka, but using a revised ratio of 0.264.

3. Set HOCl photolysis as a ratio to ISPD photolysis, different from Allen and Tanaka's recommendation, using a ratio of 143.



Appendix 2

Evaluation of the numerical implementation of the chlorine reactions in the CAMx chemistry solver: Comparison against the LSODE Gear solver in a chemistry box model.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Concentration (ppm)
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18
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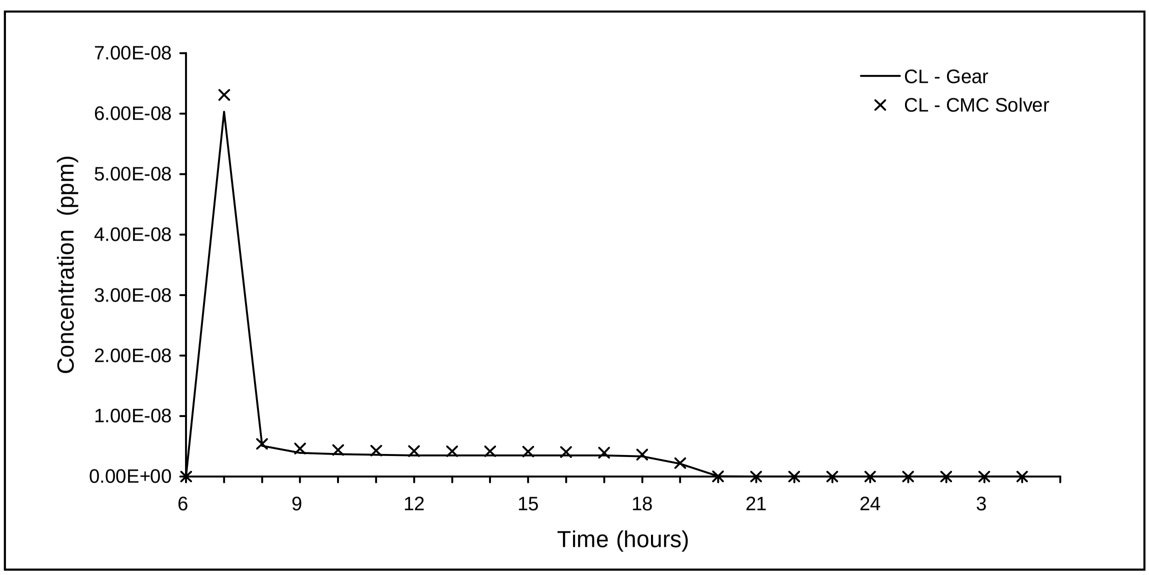
24
3
Time (hours)
CL2 - Gear
CL2 - CMC Solver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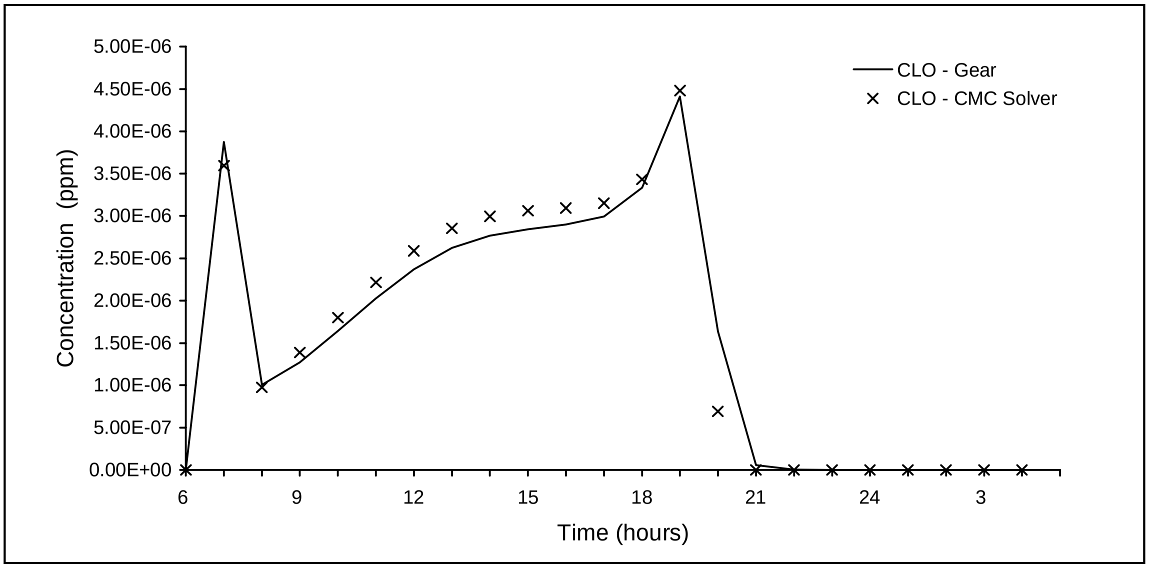
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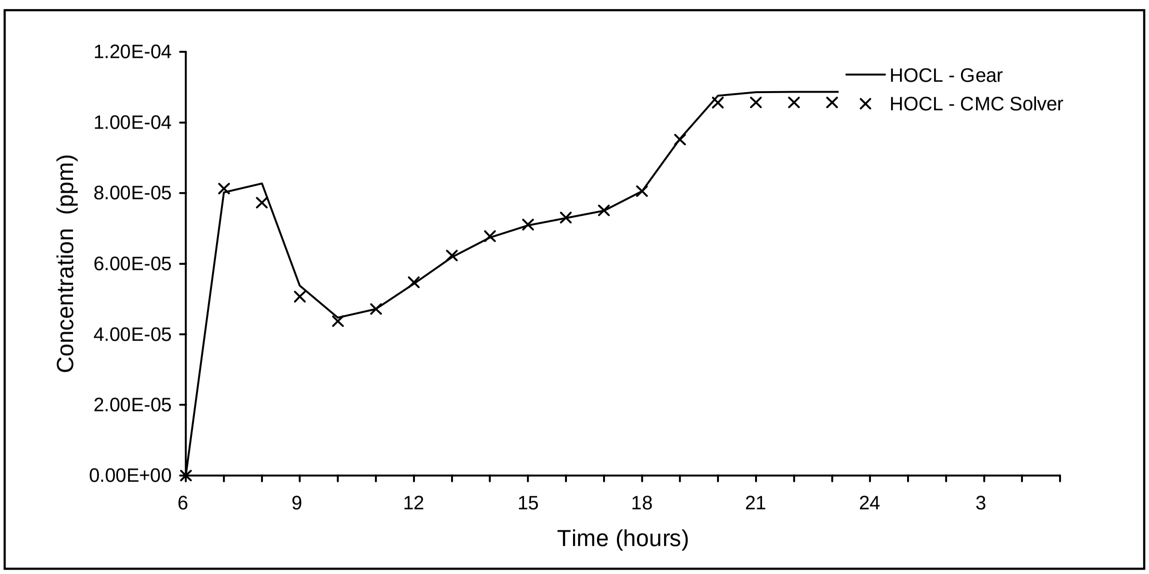
Time (hours)
CLO - Gear
CLO - CMC Solver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24
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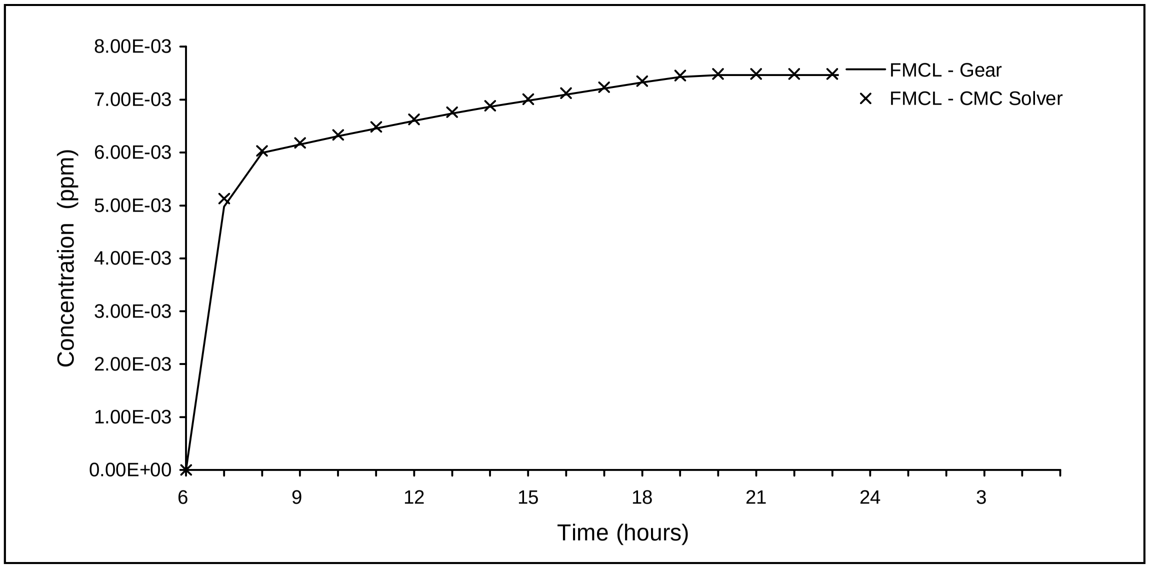
Time (hours)
HOCL - Gear
HOCL - CMC Solver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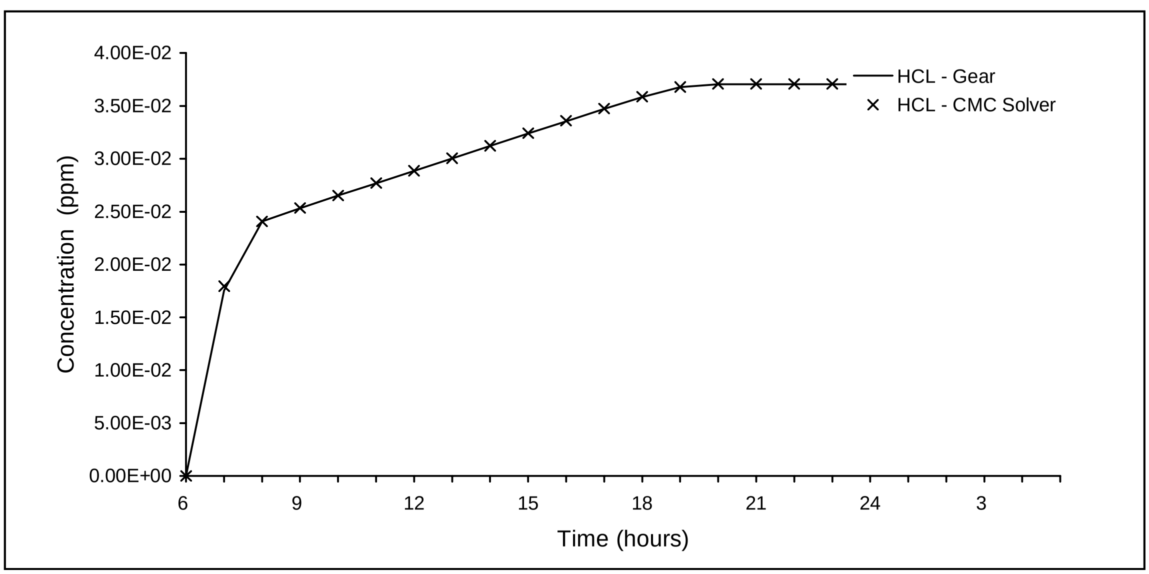
Time (hours)
FMCL - Gear
FMCL - CMC Solver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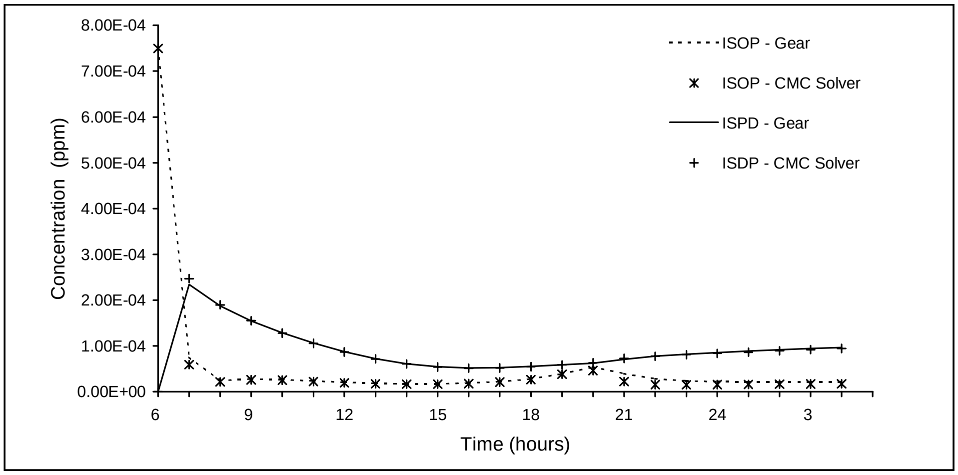
3
Time (hours)
HCL - Gear
HCL - CMC Solver



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Concentration (ppm)
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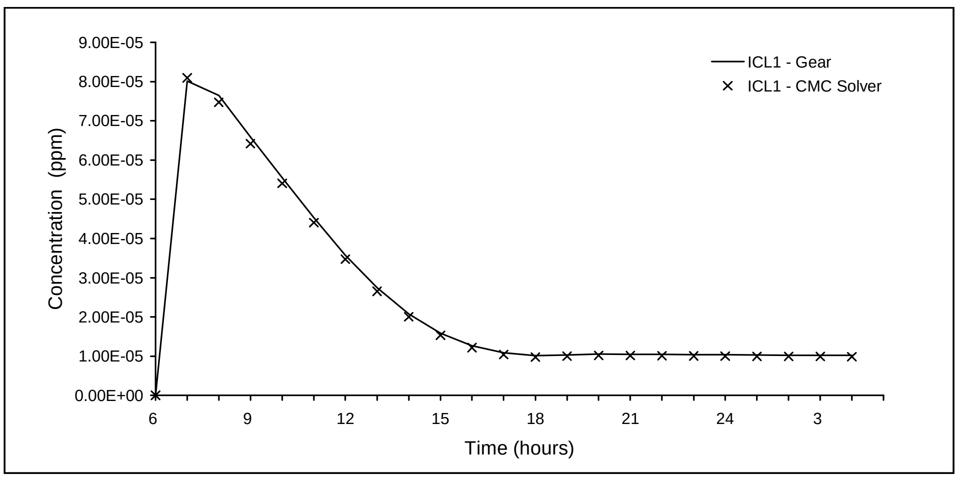
3
Time (hours)
ISOP - Gear
ISOP - CMC Solver
ISPD - Gear
ISDP - CMC Solver



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3
Time (hours)
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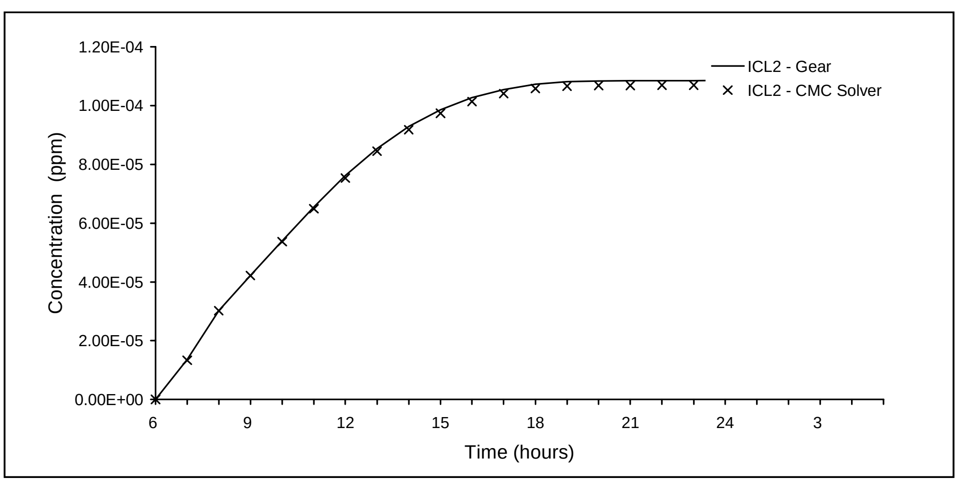
ICL1 - CMC Solver



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9
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15
18
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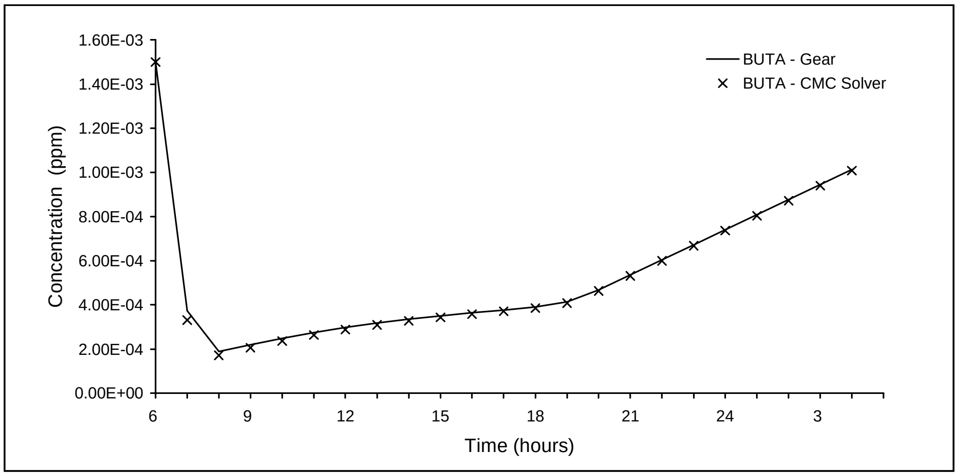
3
Time (hours)
ICL2 - Gear
ICL2 - CMC Solver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0.00E+00
6
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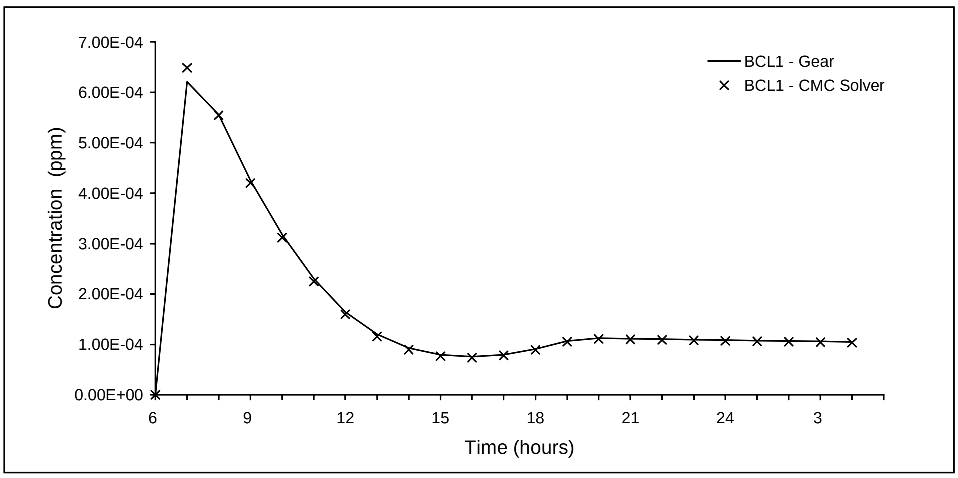
18
21
24
3
Time (hours)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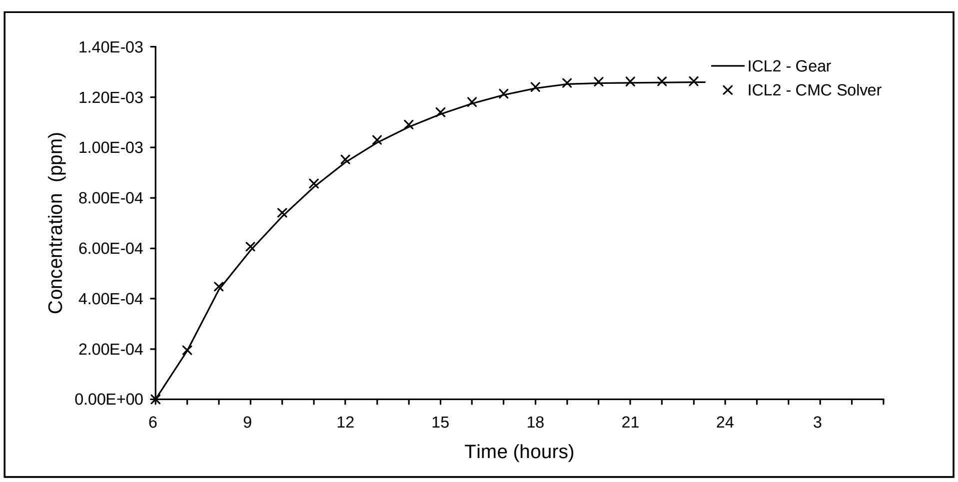
Time (hours)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4.00E-04
2.00E-04
0.00E+00
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3
Time (hours)

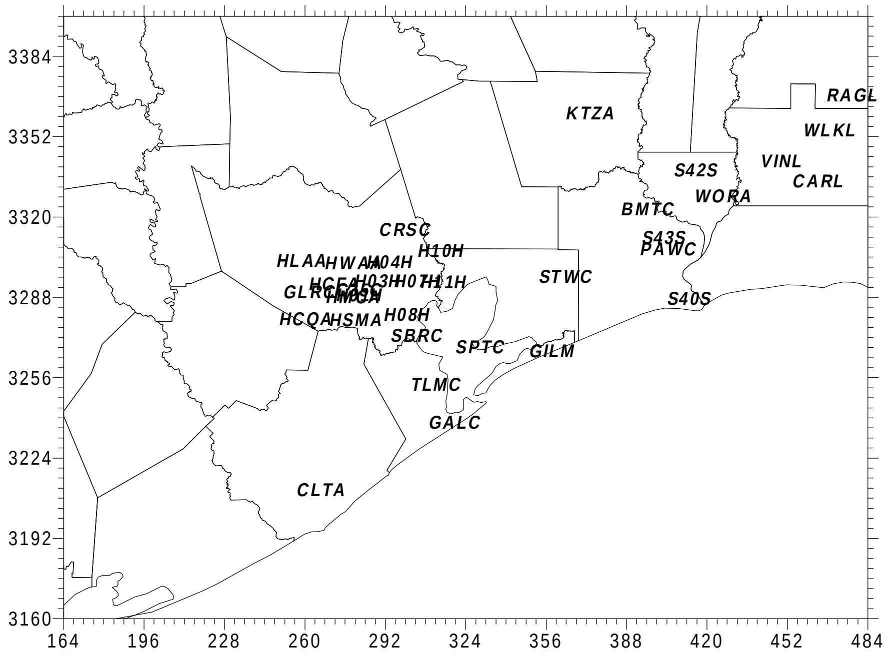
Appendix 3

CAMx results for the September 6-11, 1993 episode

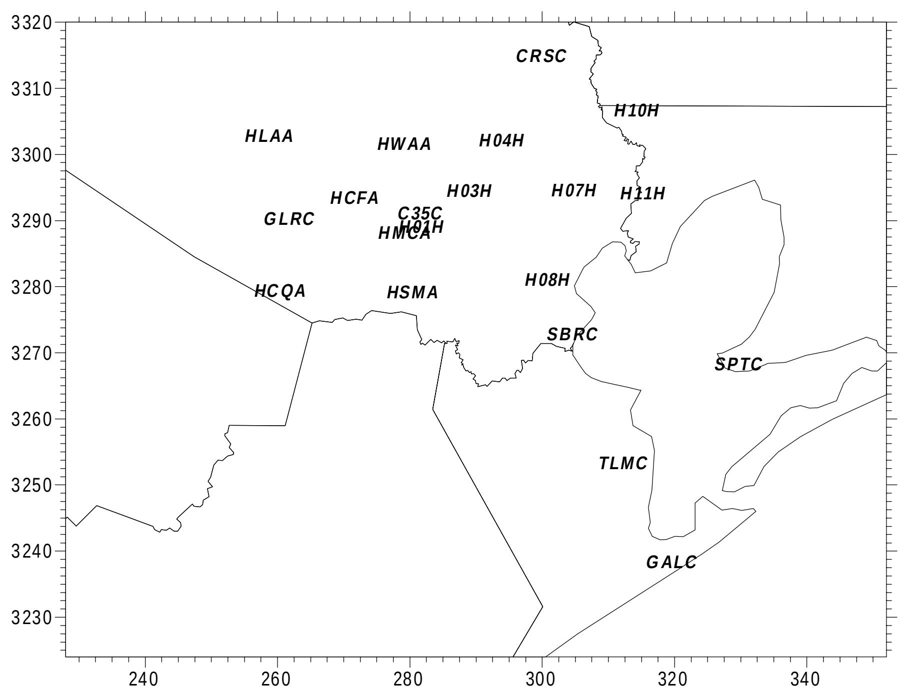
Table 1. Comparison of CAMx 1-hour ozone model performance statistics with and without Cl emissions.

	EPA Goal	8-Sep	9-Sep	10-Sep	11-Sep
Observed Peak (ppb)		214.0	195.0	162.0	189.0
			Without Cl Emissions		
Modeled Peak (ppb)		199.7	192.2	192.8	200.4
Unpaired Peak (%)	≤ ±20	-6.7	-1.4	19.0	6.0
Normalized Bias (%)	≤ ±15	17.3	16.7	2.9	11.7
Normalized Error (%)	≤ 35	27.7	28.9	25.9	22.2
			With Cl Emissions		
Modeled Peak (ppb)		200.6	193.2	194.7	201.5
Unpaired Peak (%)	≤ ±20	-6.3	-0.9	20.2	6.6
Normalized Bias (%)	≤ ±15	18.3	17.5	3.8	12.8
Normalized Error (%)	≤ 35	31.1	29.3	26.2	22.9

Statistical measures were calculated for valid data pairs with observed values > 60 ppb at 37 stations



Location of monitoring sites in 4-km grid



Location of monitoring sites in Houston area

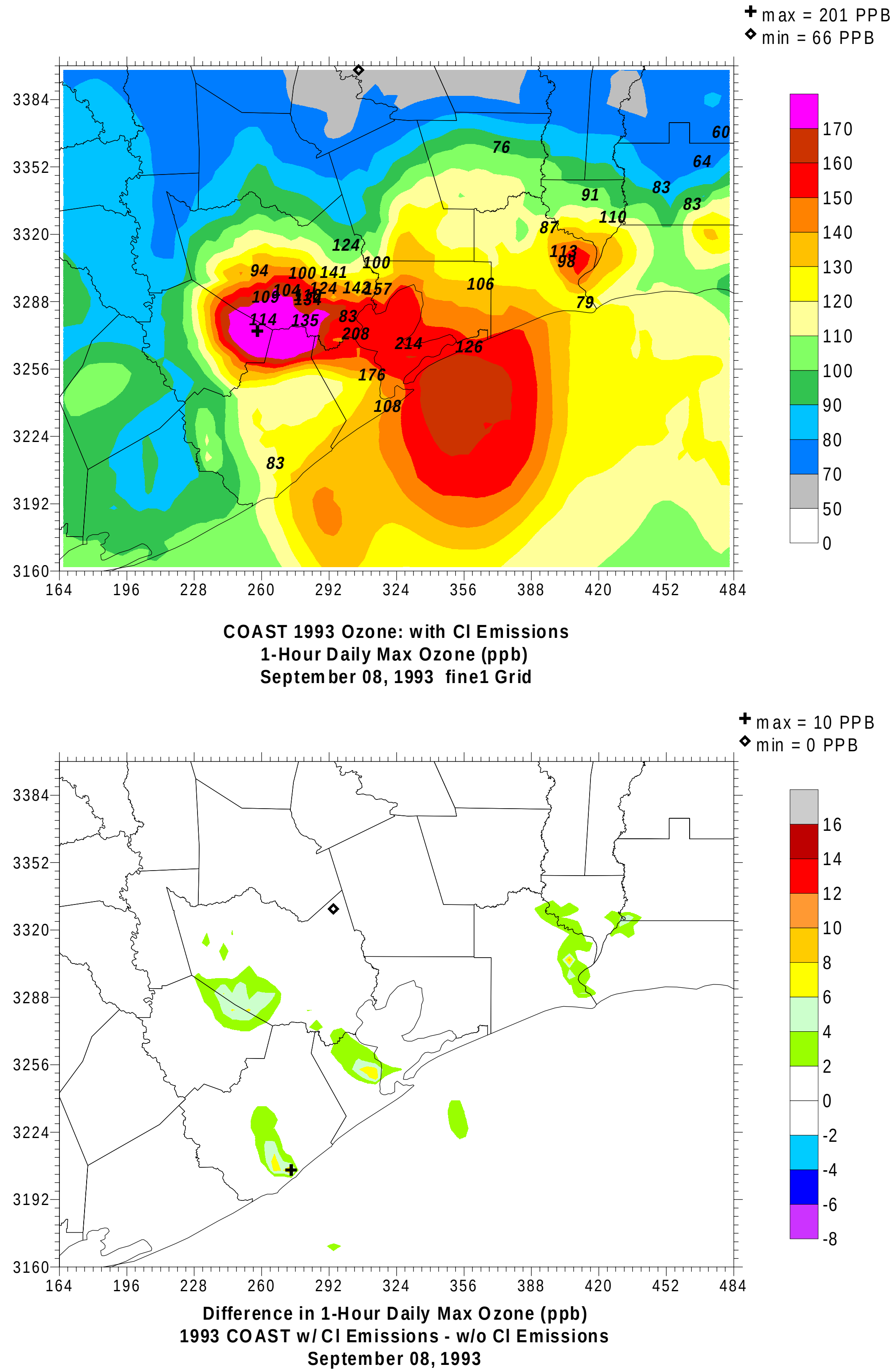


Figure 1. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results with Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.

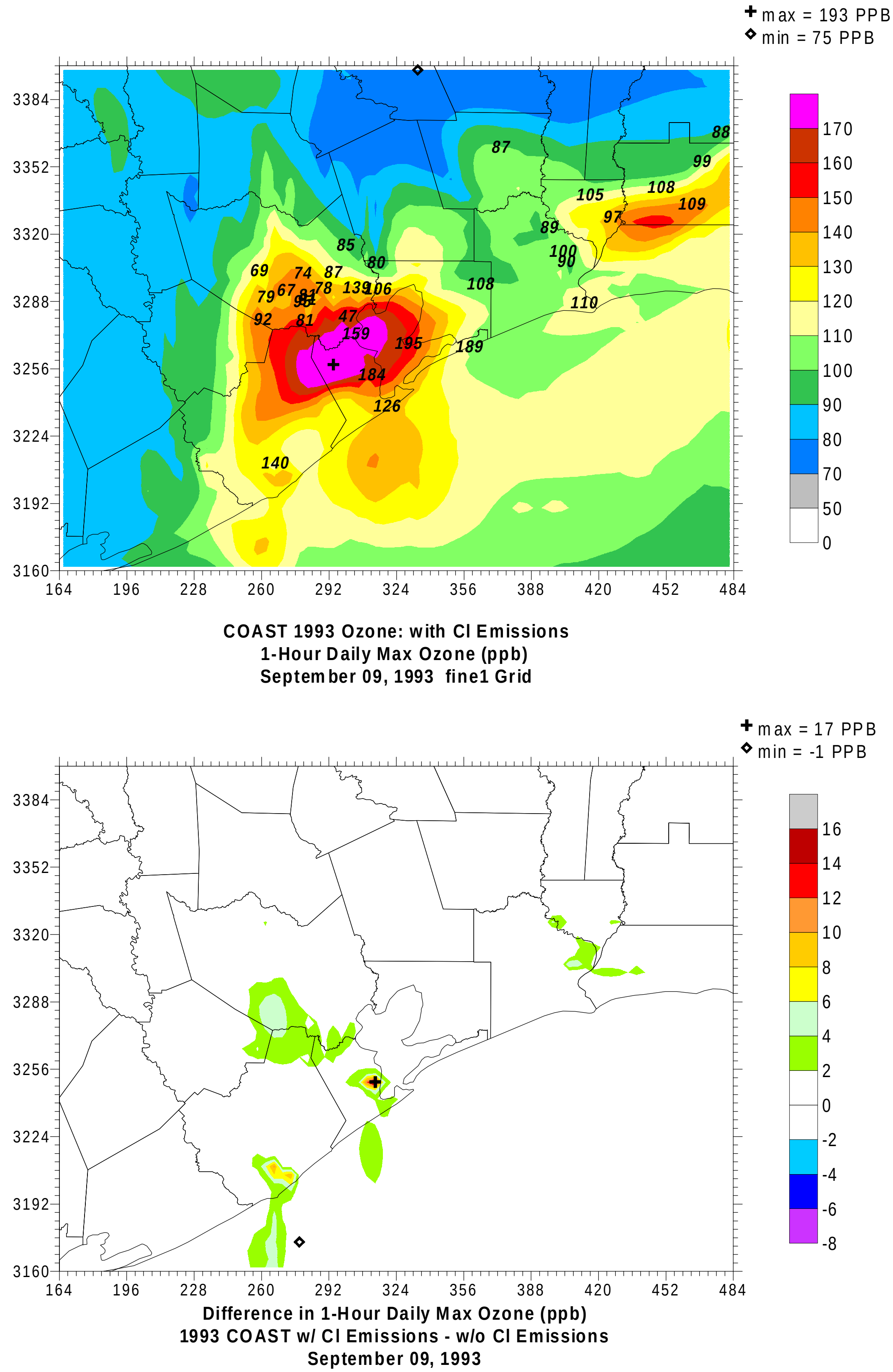


Figure 2. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results with Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.

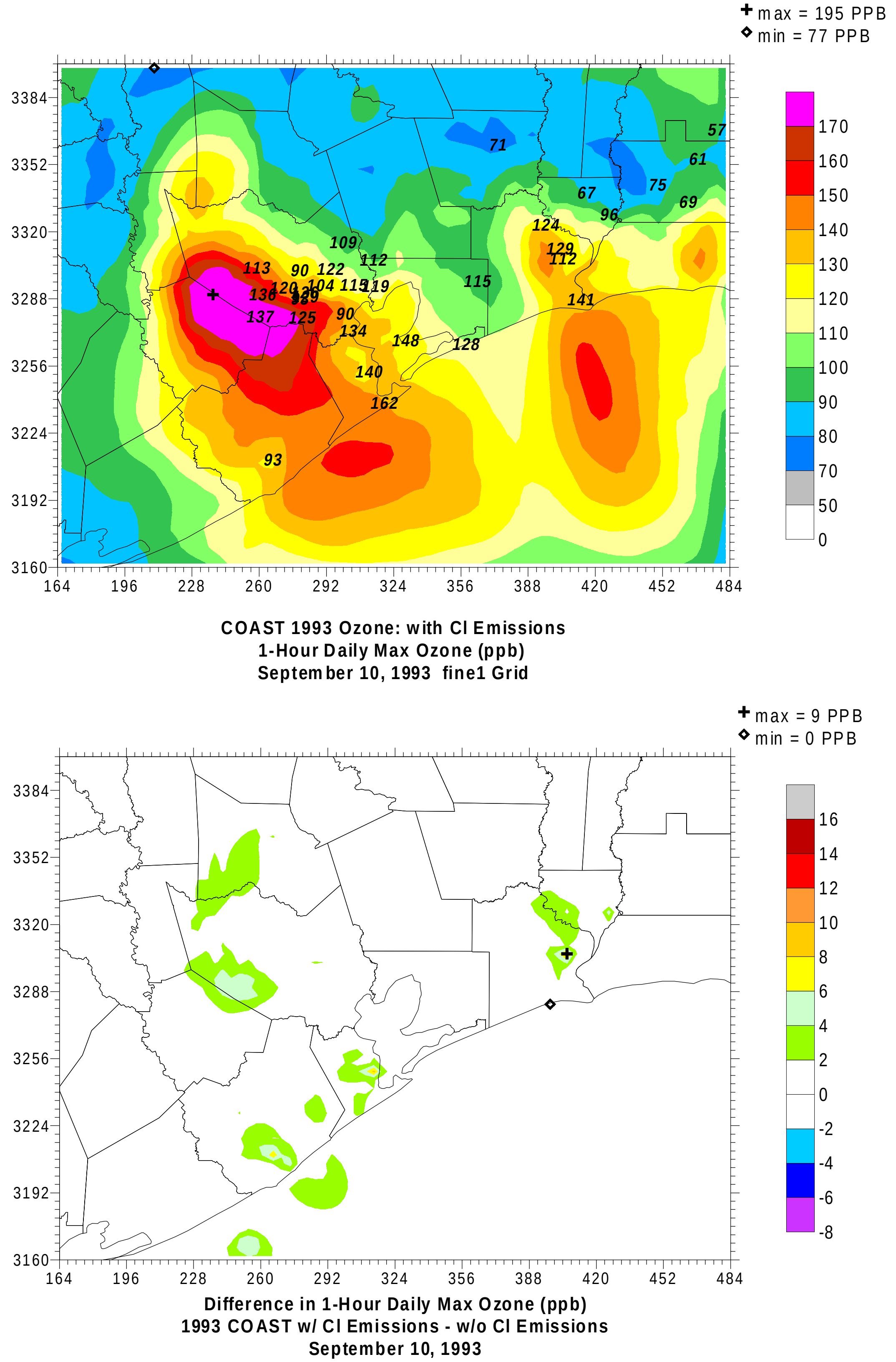
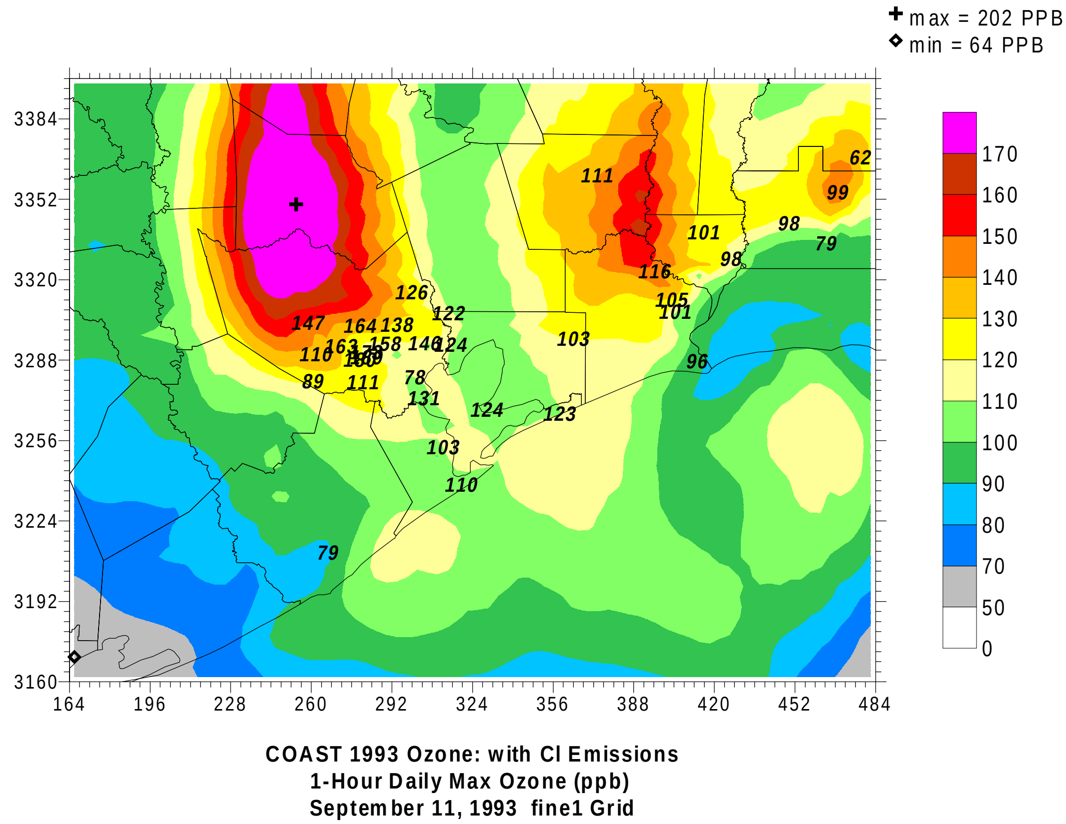


Figure 3. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results with Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.



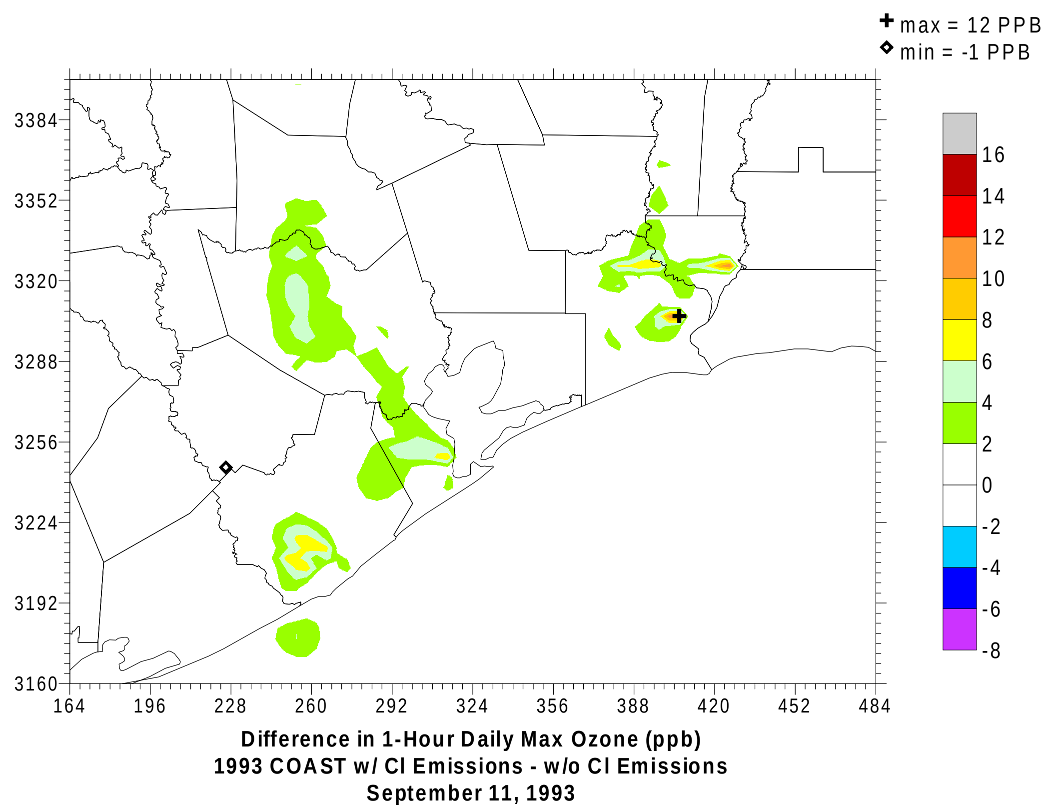
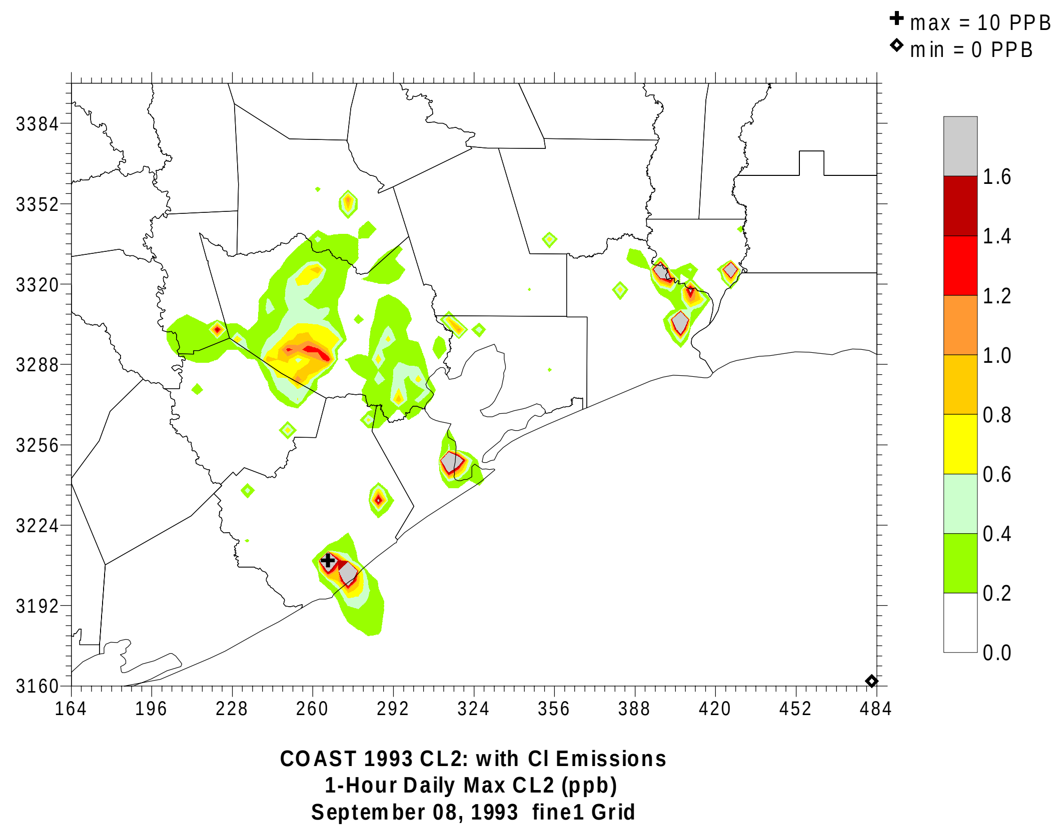


Figure 4. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results with Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.



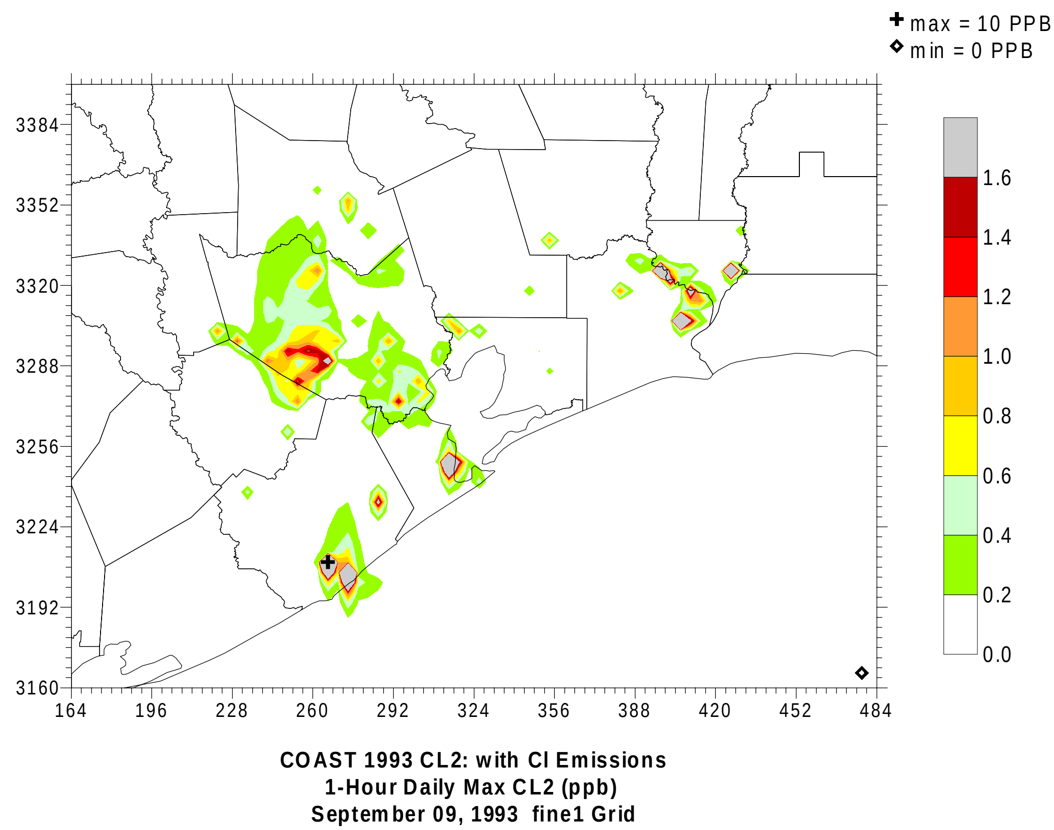
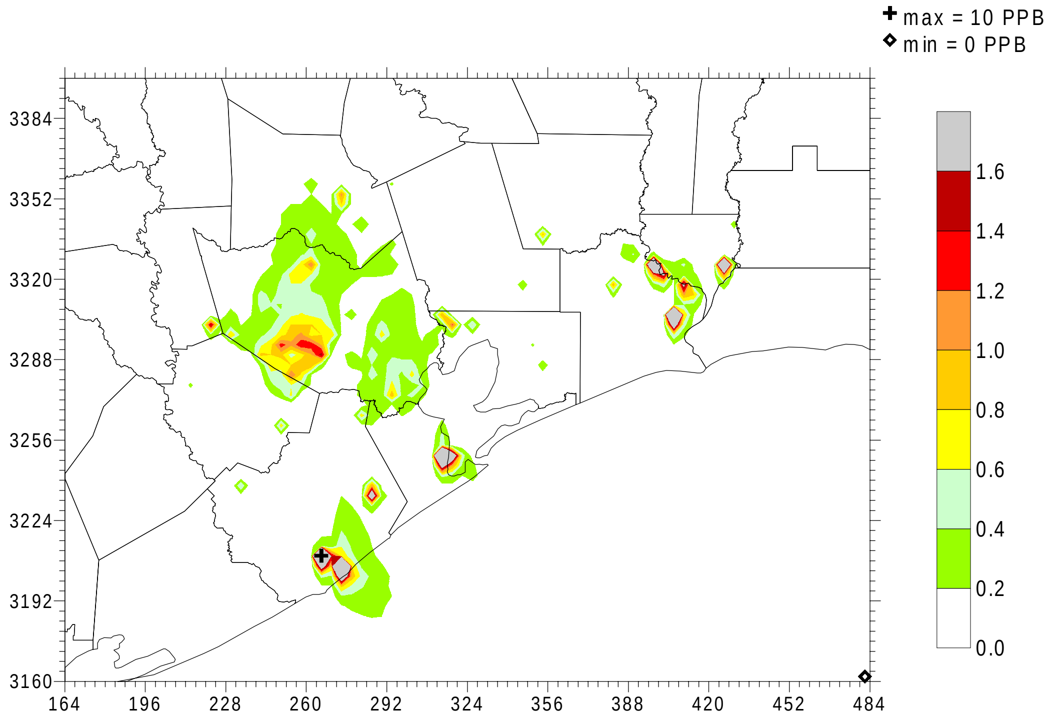
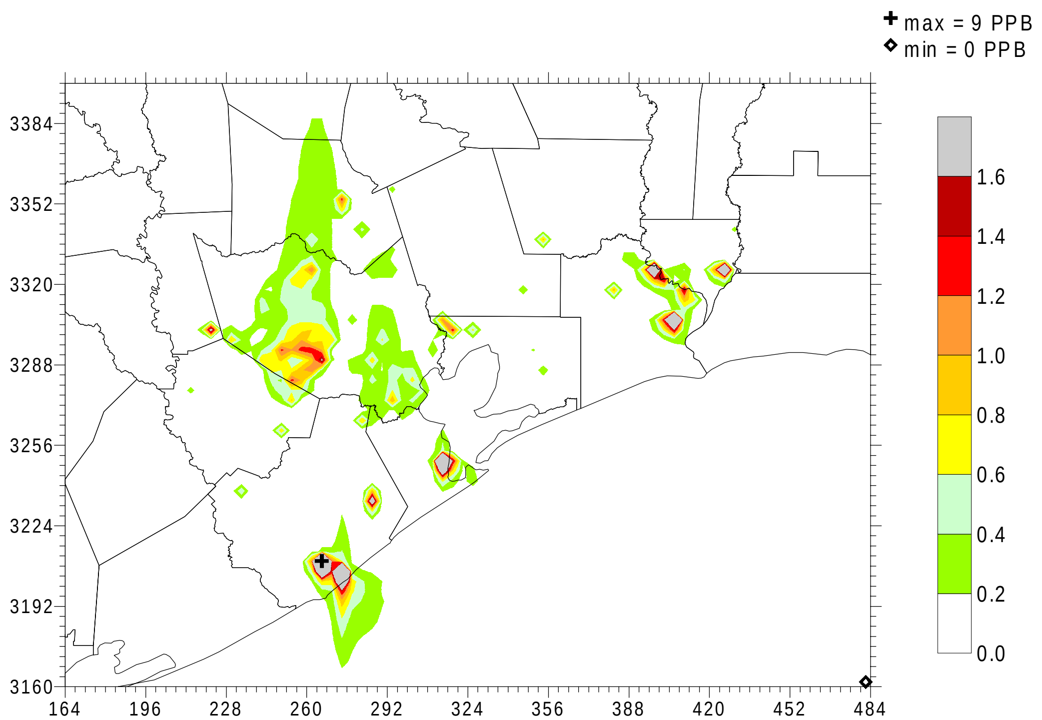


Figure 5. Daily maximum 1-hour CL2 plots showing CAMx results with Cl emissions.



COAST 1993 CL2: with Cl Emissions
1-Hour Daily Max CL2 (ppb)
September 10, 1993 fine1 Grid



COAST 1993 CL2: with Cl Emissions
1-Hour Daily Max CL2 (ppb)
September 11, 1993 fine1 Grid

Figure 6. Daily maximum 1-hour CL2 plots showing CAMx results with Cl emissions.

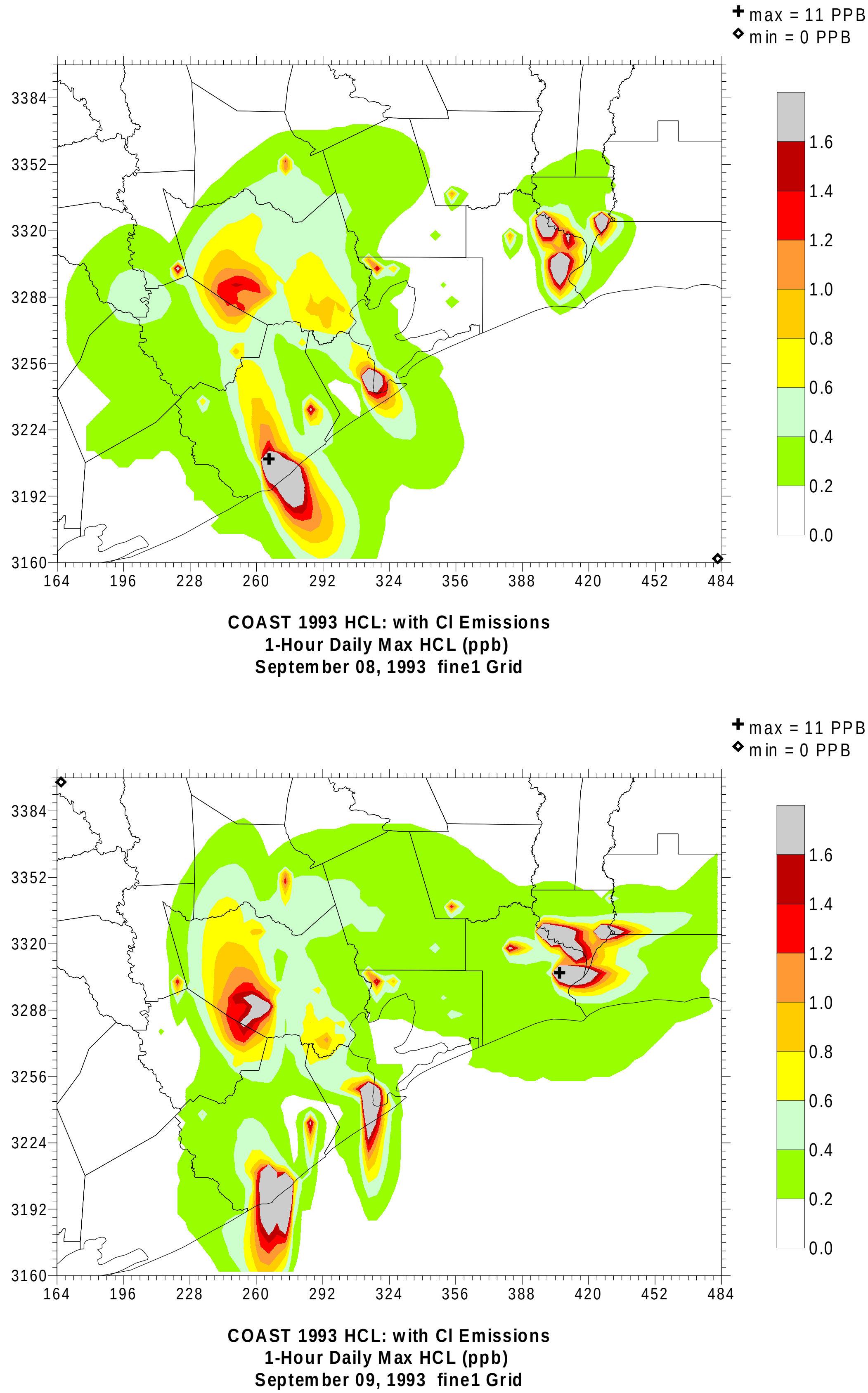
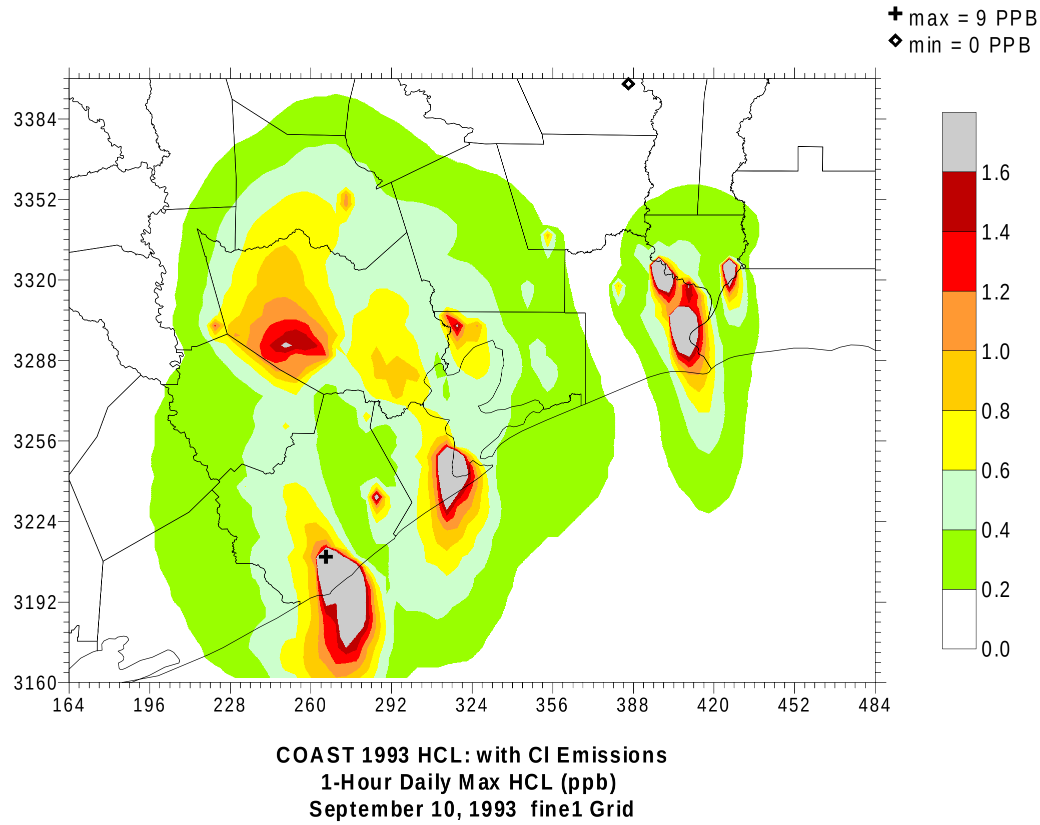


Figure 7. Daily maximum 1-hour HCL plots showing CAMx results with Cl emissions.



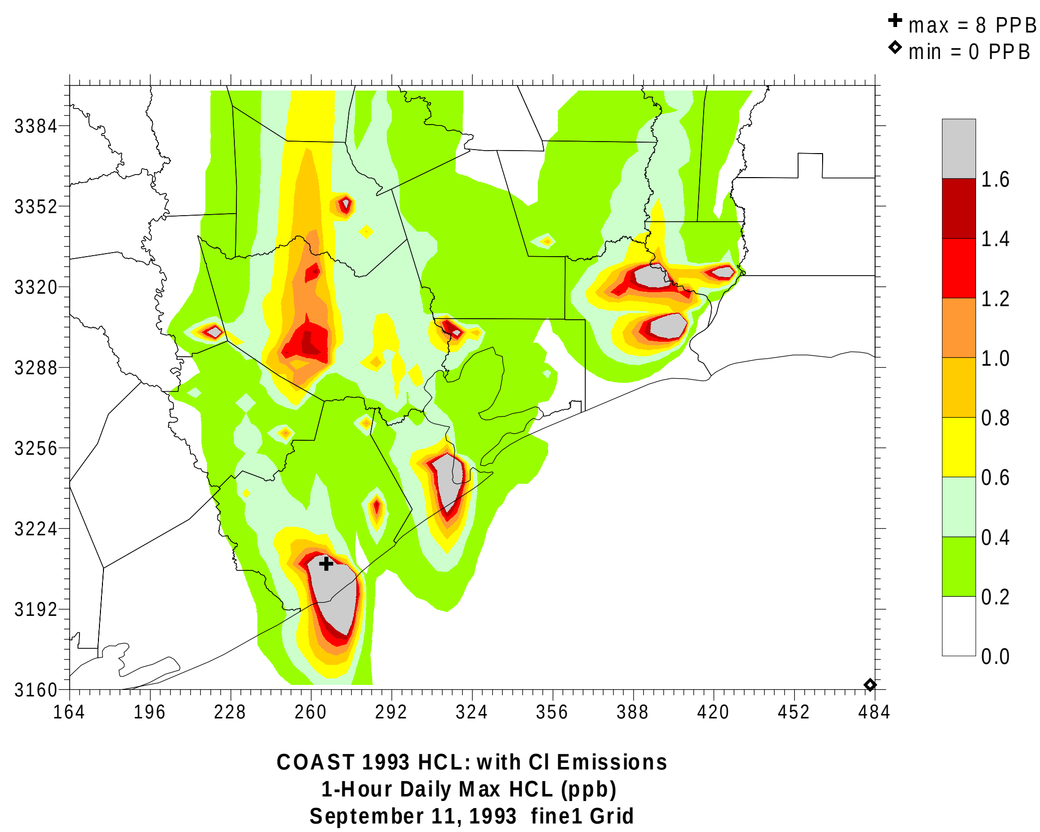
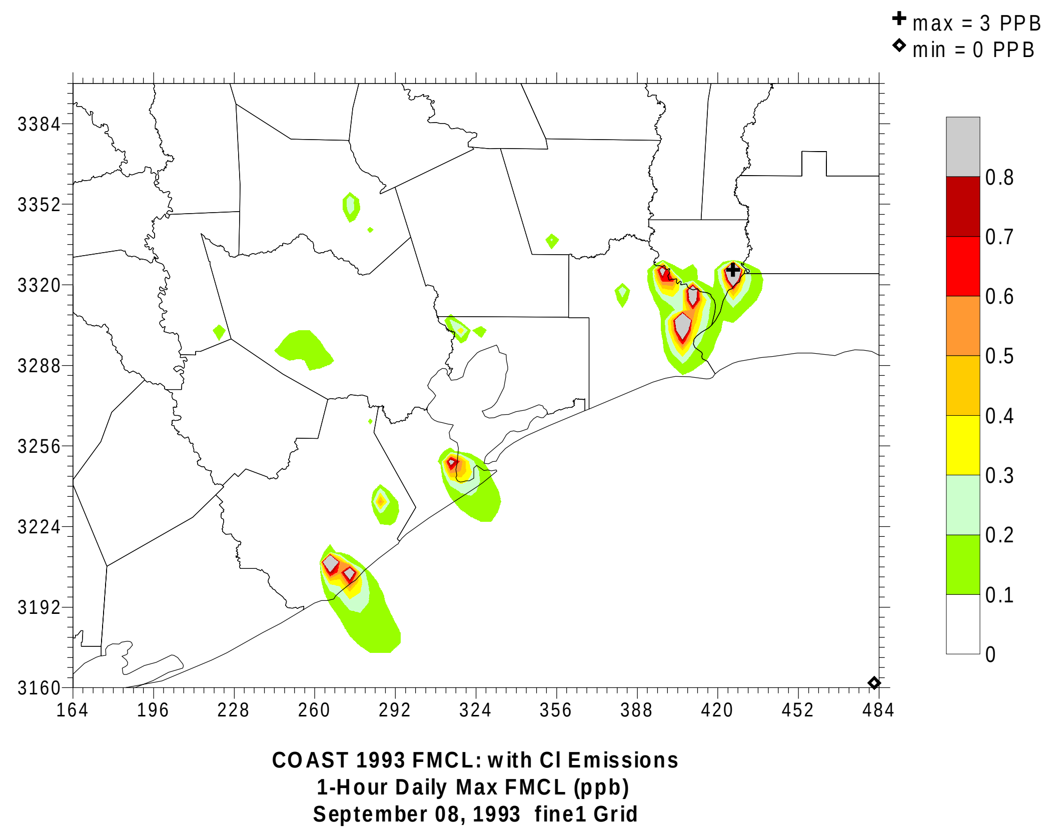


Figure 8. Daily maximum 1-hour HCL plots showing CAMx results with Cl emissions.



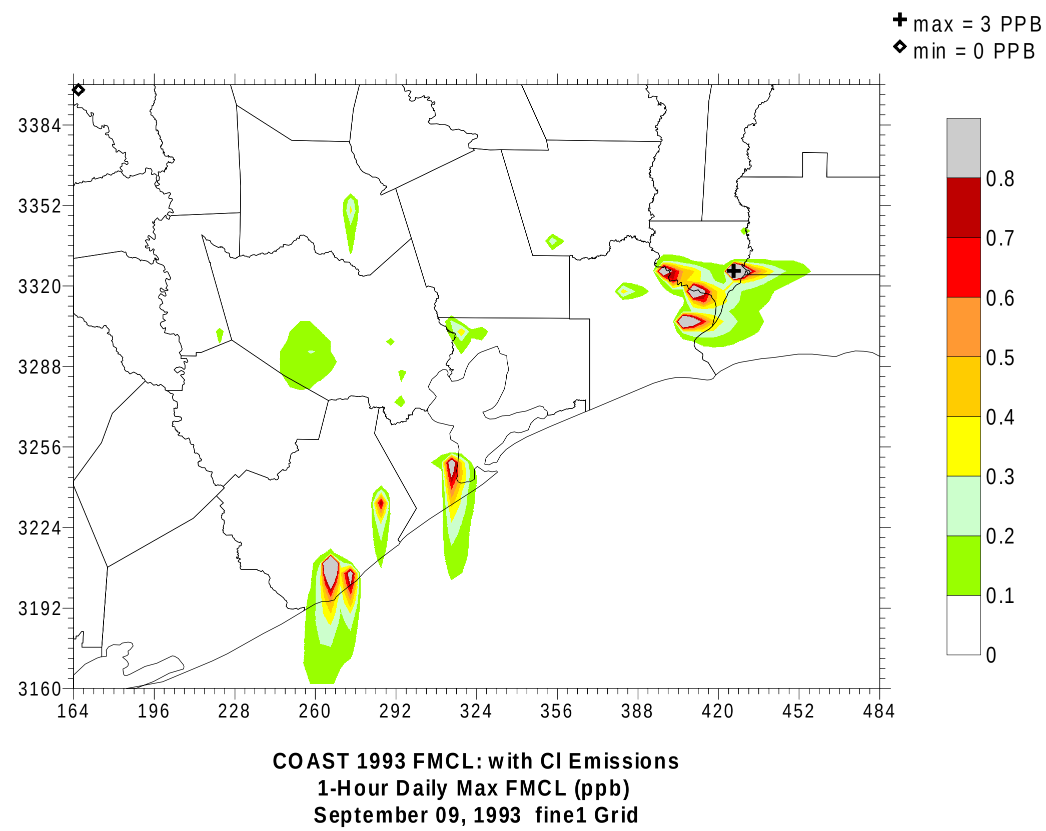
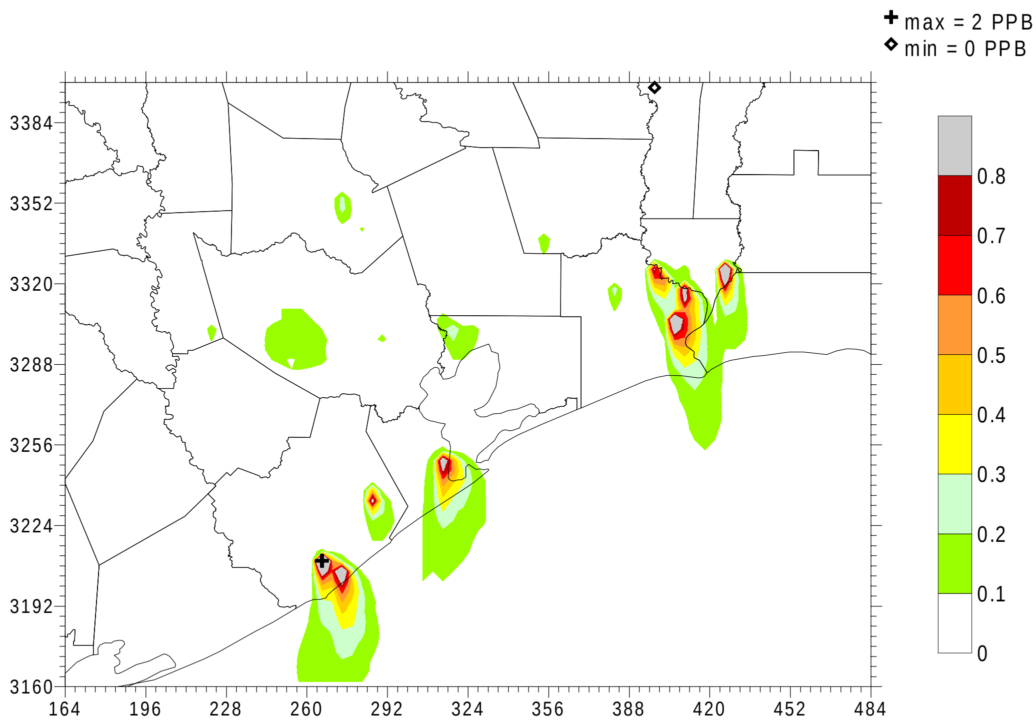
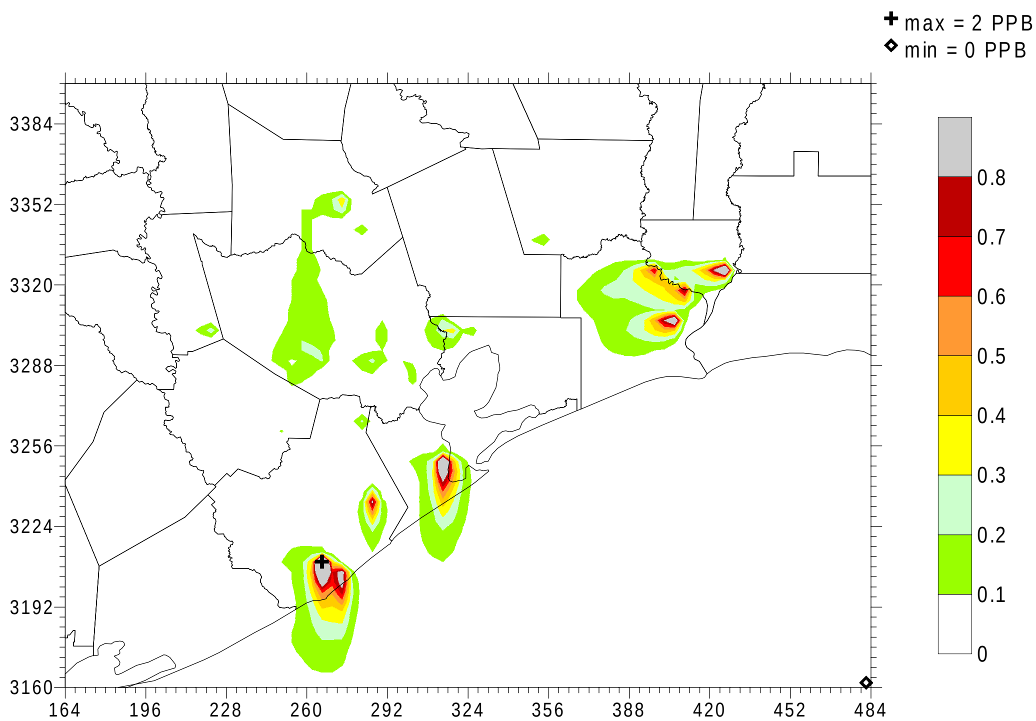


Figure 9. Daily maximum 1-hour FMCL plots showing CAMx results with Cl emissions.



COAST 1993 FMCL: with Cl Emissions
1-Hour Daily Max FMCL (ppb)
September 10, 1993 fine1 Grid



COAST 1993 FMCL: with Cl Emissions
1-Hour Daily Max FMCL (ppb)
September 11, 1993 fine1 Grid

Figure 10. Daily maximum 1-hour FMCL plots showing CAMx results with Cl emissions.

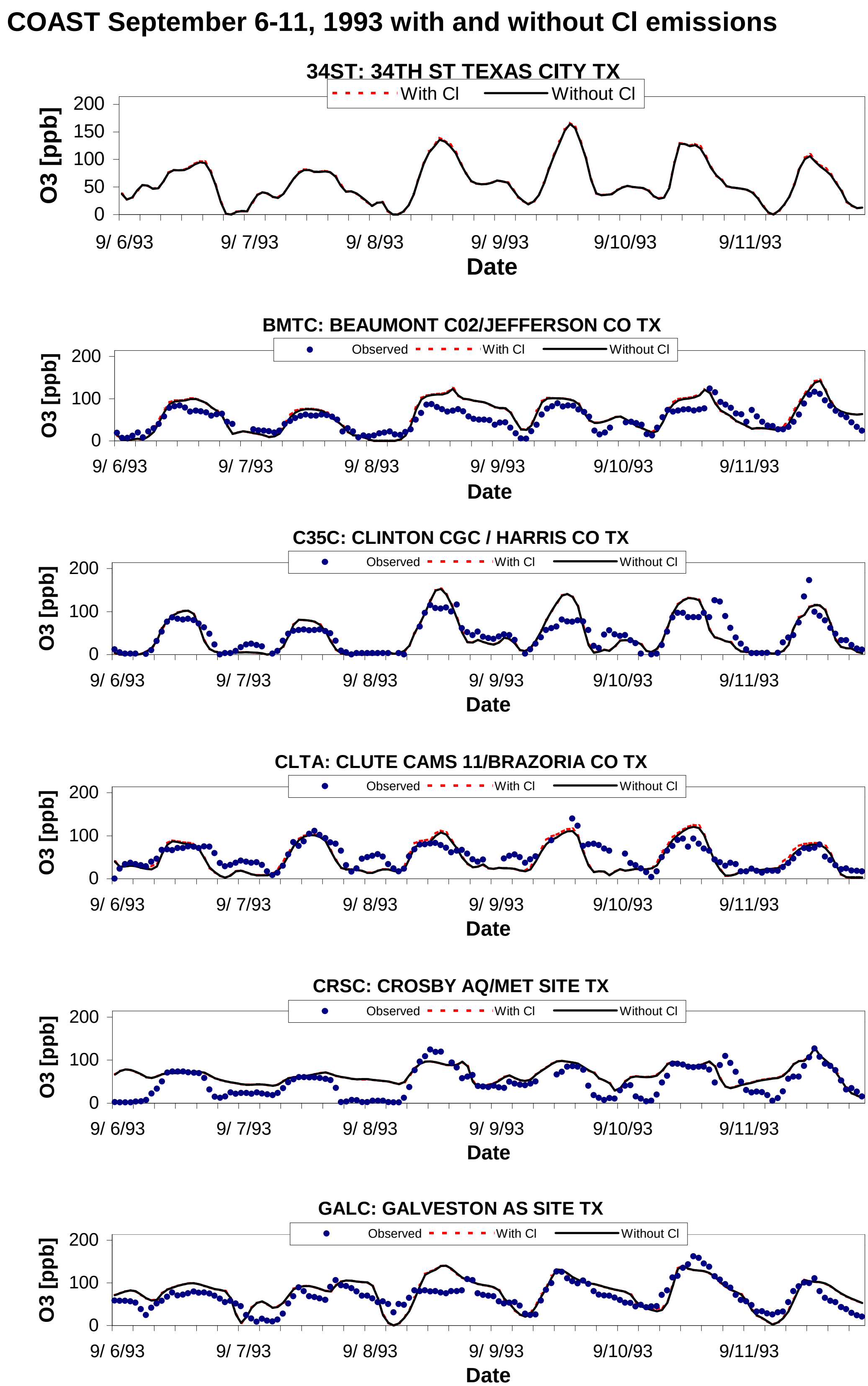
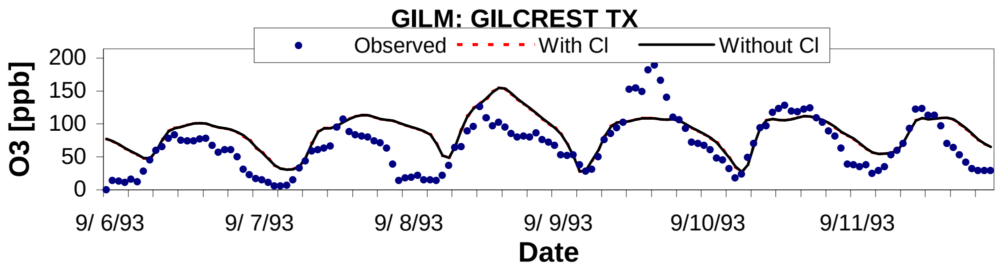
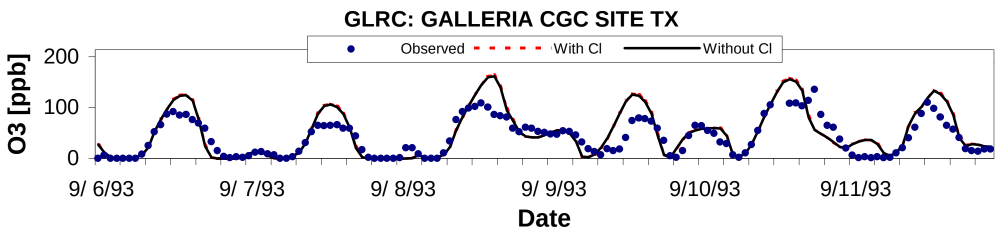
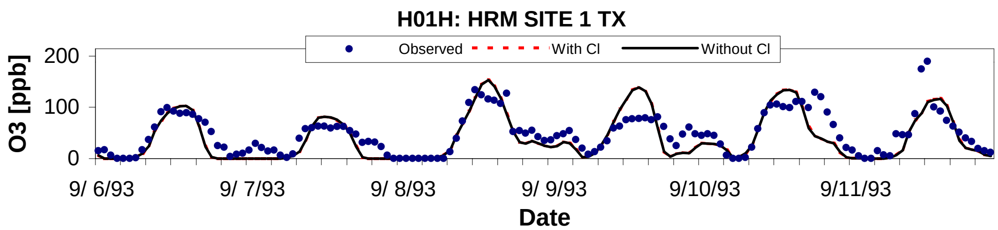


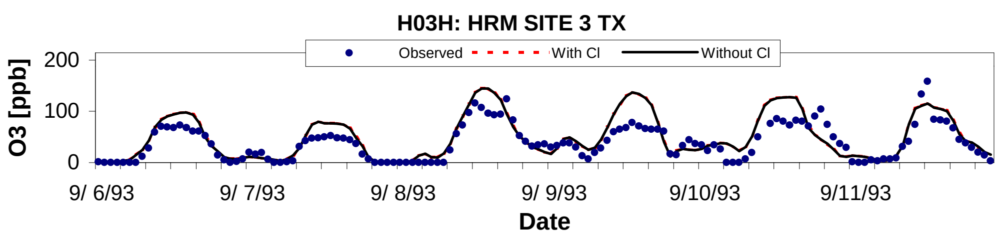
Figure 11. Time series of 1-hour ozone observations and predictions with and without chlorine emissions.

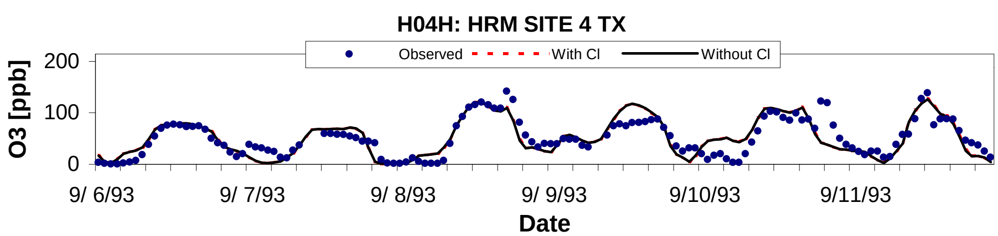
COAST September 6-11, 1993 with and without Cl emissions

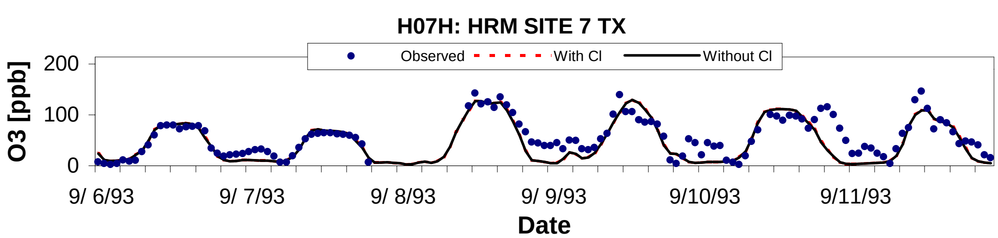




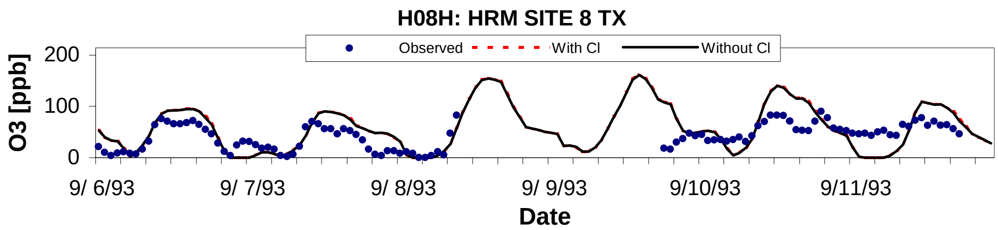


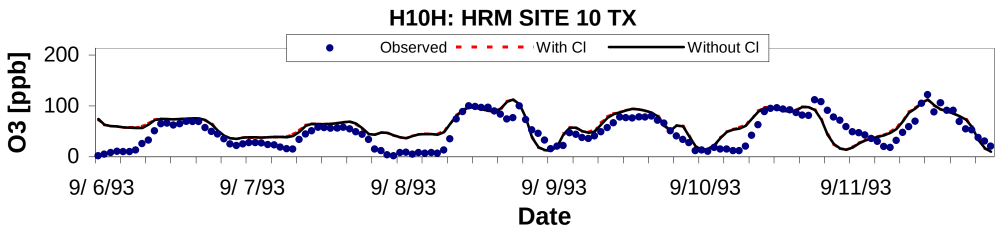


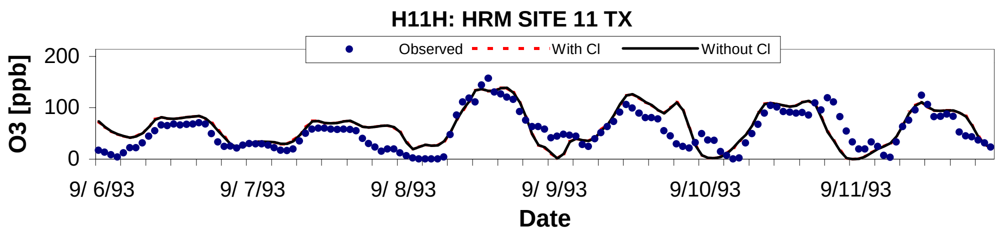


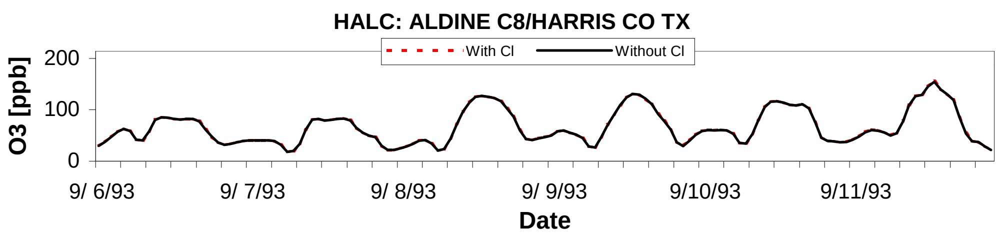


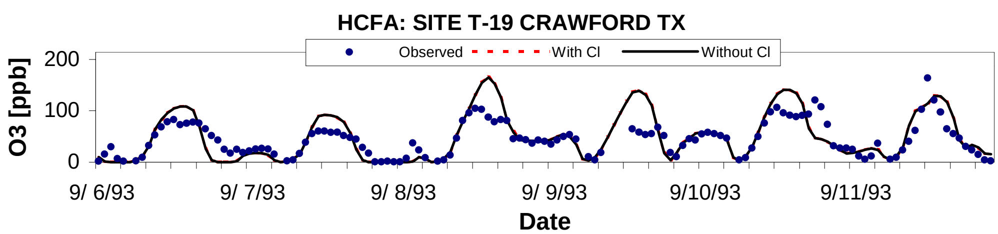
COAST September 6-11, 1993 with and without Cl emissions

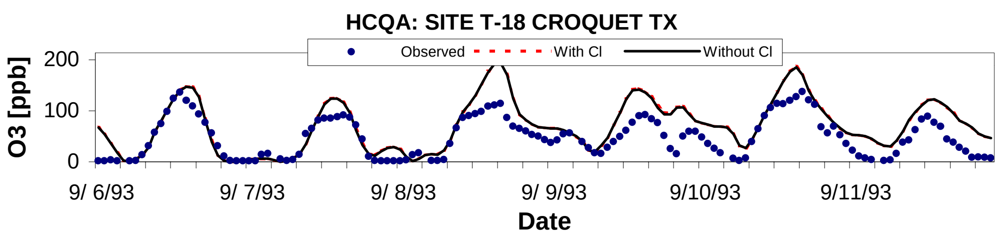












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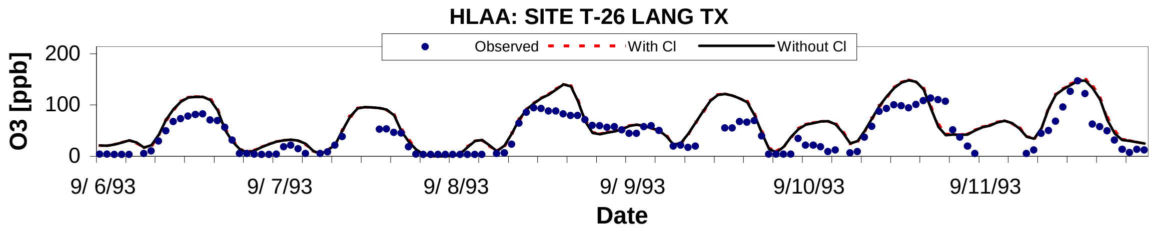
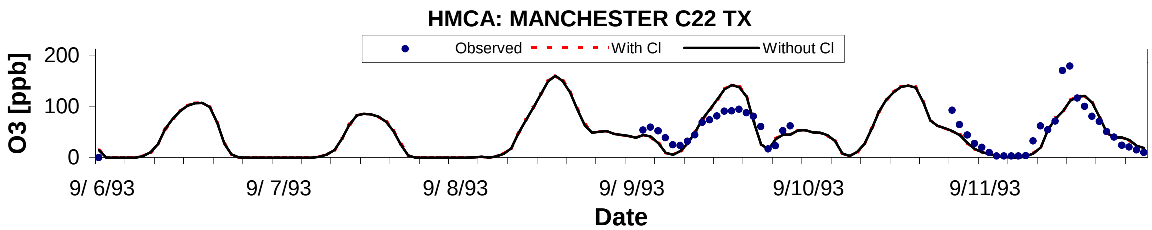
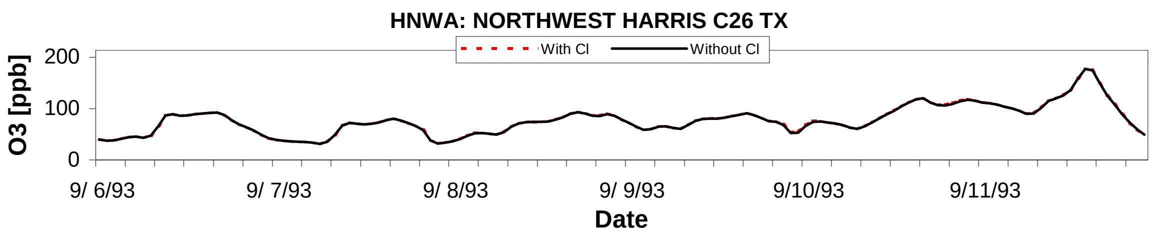
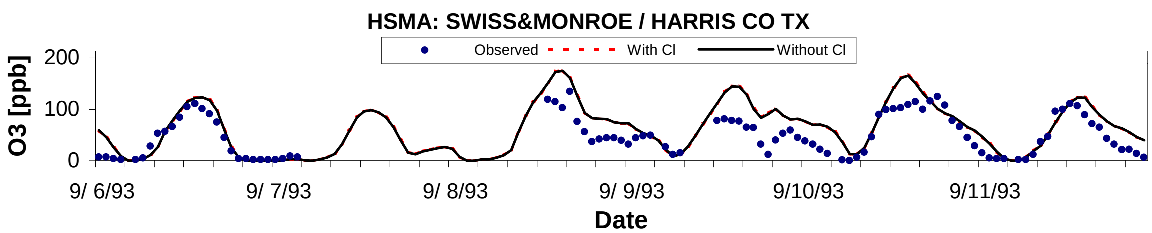
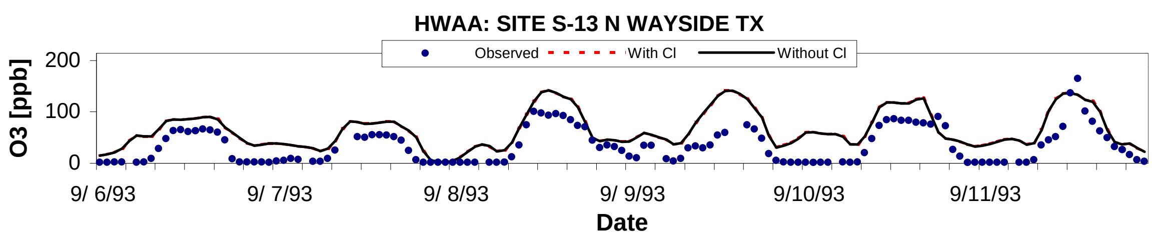
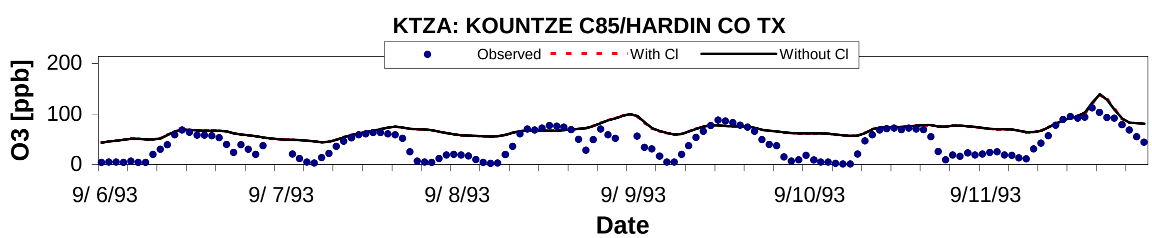




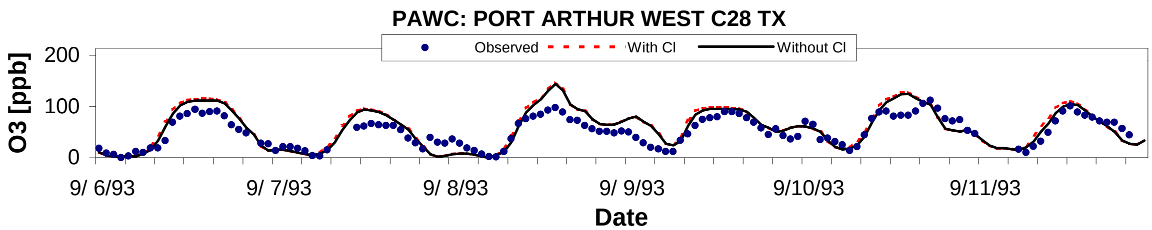


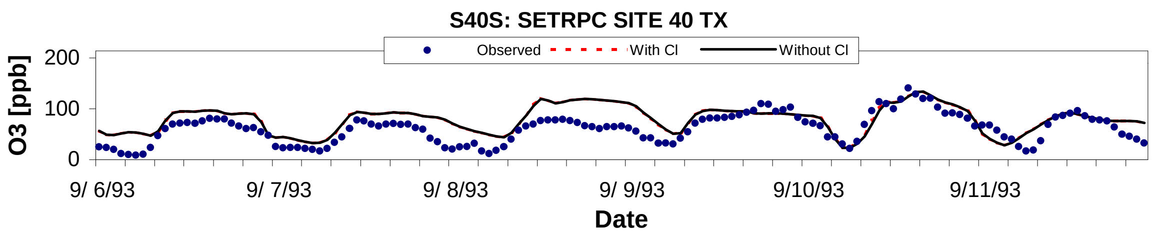


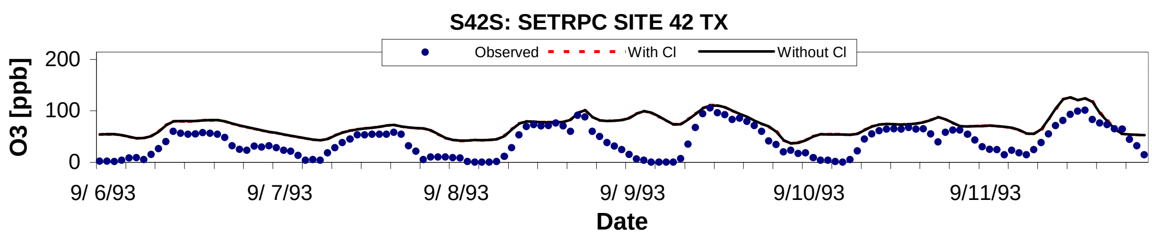


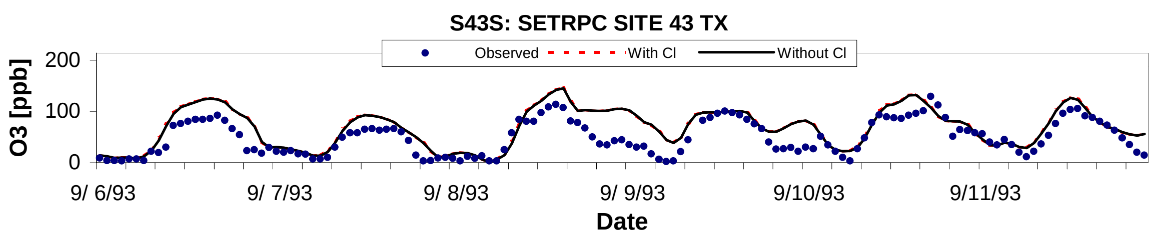


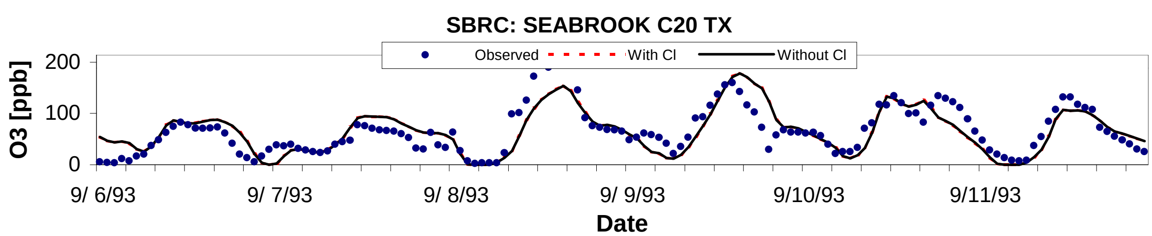
COAST September 6-11, 1993 with and without Cl emissions

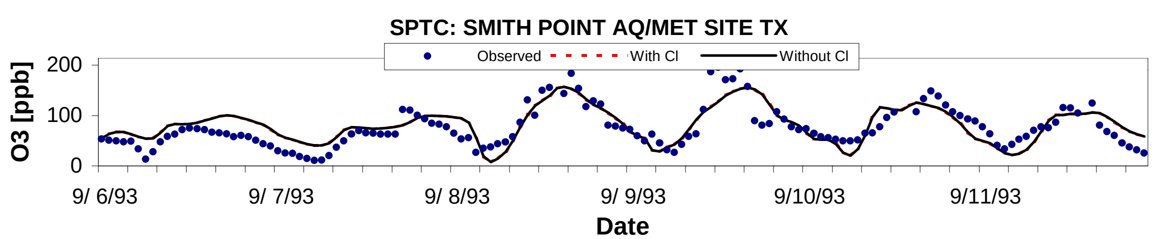




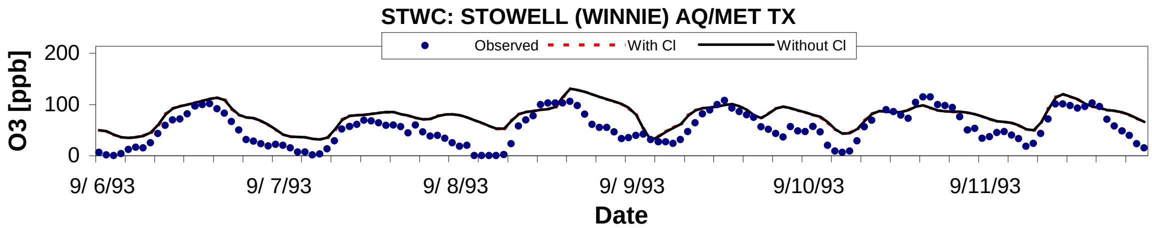


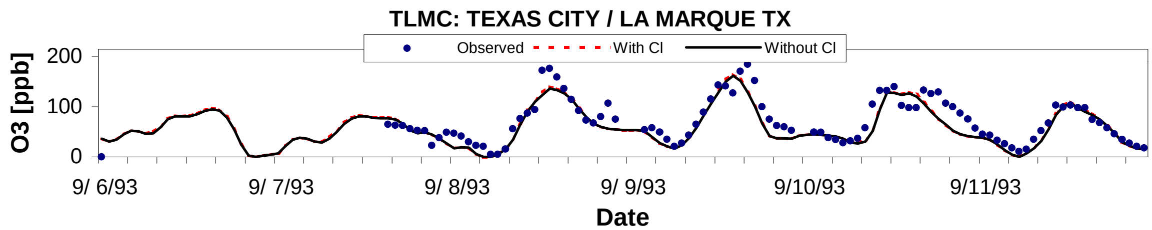


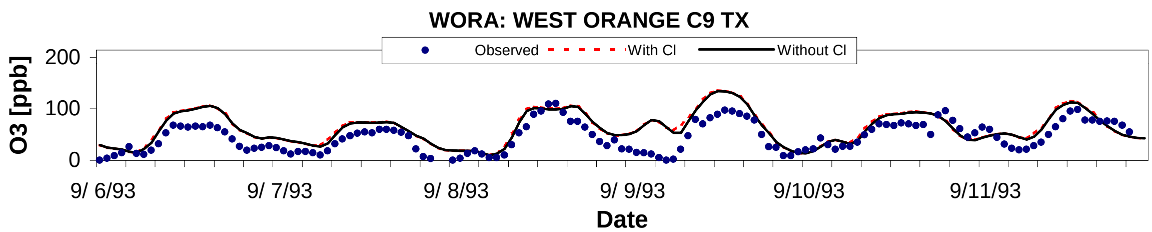


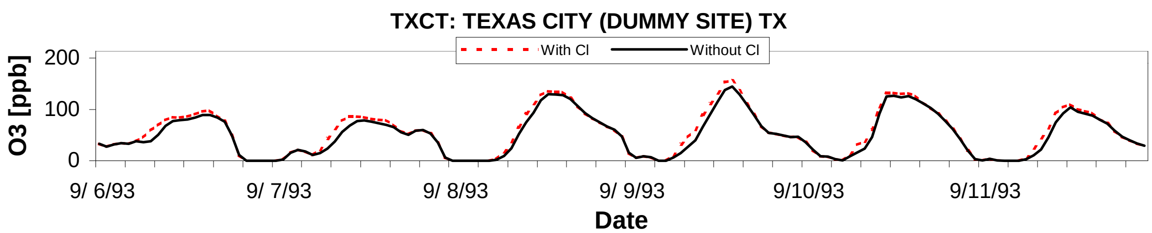


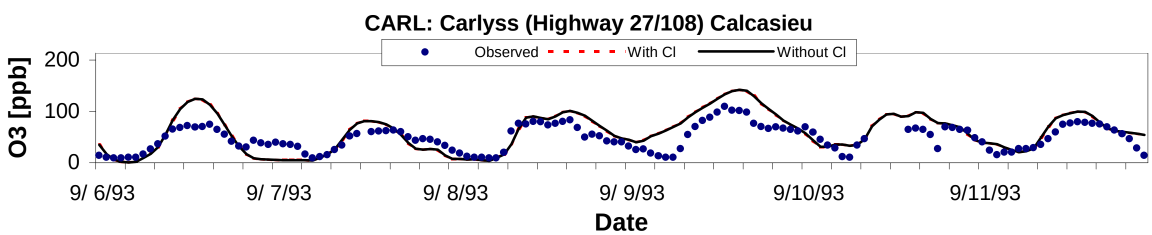
COAST September 6-11, 1993 with and without Cl emissions

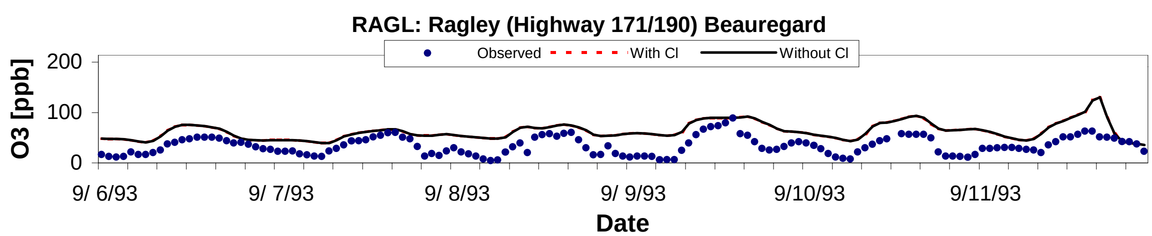




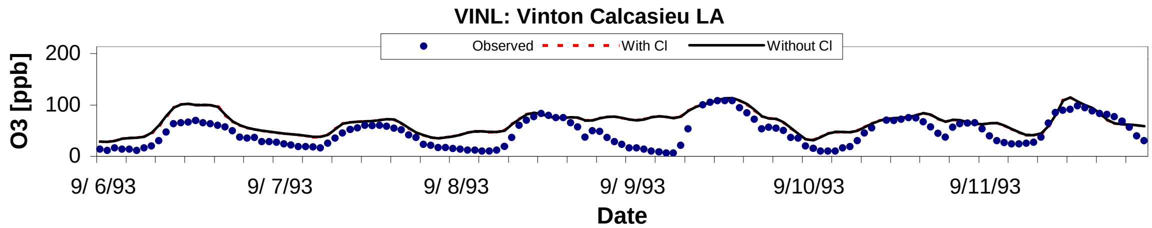


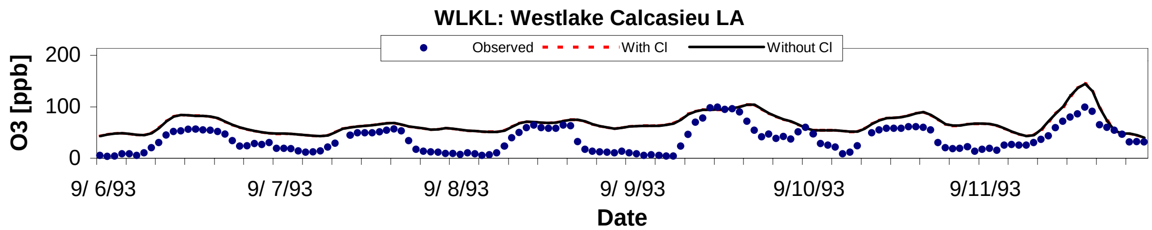






COAST September 6-11, 1993 with and without Cl emissions





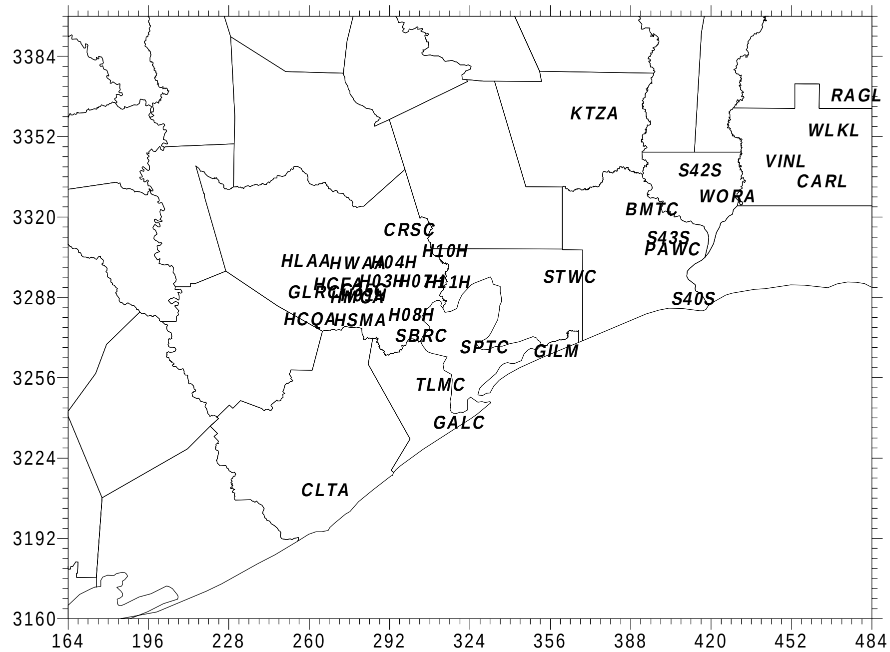
Appendix 4

CAMx results for the August 16-20, 1993 episode.

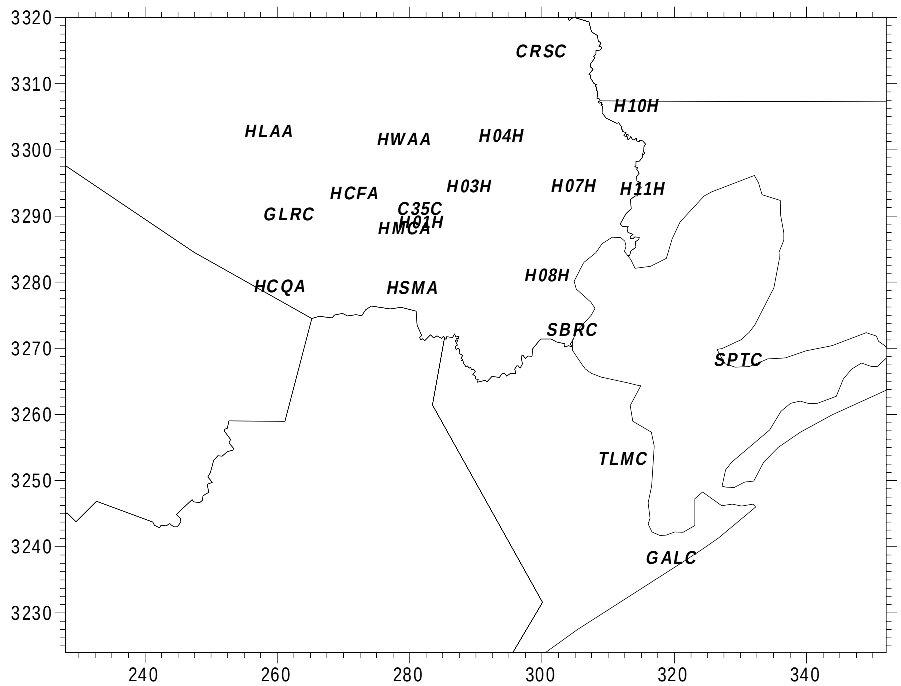
Table 1. Comparison of CAMx 1-hour ozone model performance statistics with and without Cl emissions.

	EPA Goal	17-Aug	18-Aug	19-Aug	20-Aug
Observed Peak (ppb)		119.0	139.0	231.0	187.0
			Without Cl Emissions		
Modeled Peak (ppb)		137.9	139.6	130.0	131.3
Unpaired Peak (%)	≤ ±20	15.9	0.4	-43.7	-29.8
Normalized Bias (%)	≤ ±15	-19.1	-5.3	-36.1	-35.2
Normalized Error (%)	≤ 35	31.0	24.0	40.2	37.3
			With Cl Emissions		
Modeled Peak (ppb)		138.5	139.6	131.2	132.7
Unpaired Peak (%)	≤ ±20	16.4	0.4	-43.2	-29.0
Normalized Bias (%)	≤ ±15	-18.2	-4.4	-34.9	-34.1
Normalized Error (%)	≤ 35	32.6	24.0	39.1	36.2

Statistical measures were calculated for valid data pairs with observed values > 60 ppb at 37 stations



Location of monitoring sites in 4-km grid



Location of monitoring sites in Houston area

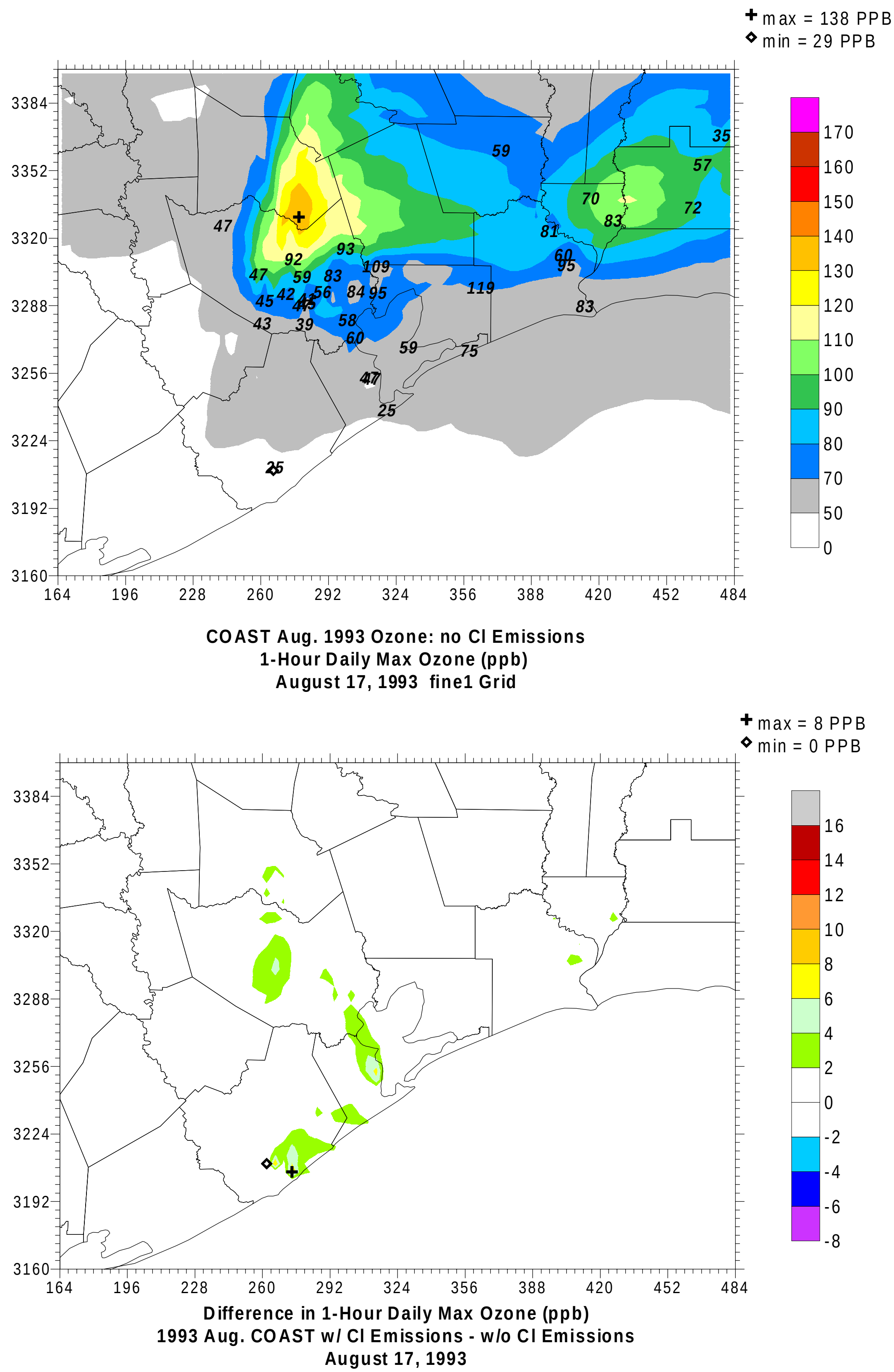


Figure 1. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results without Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.

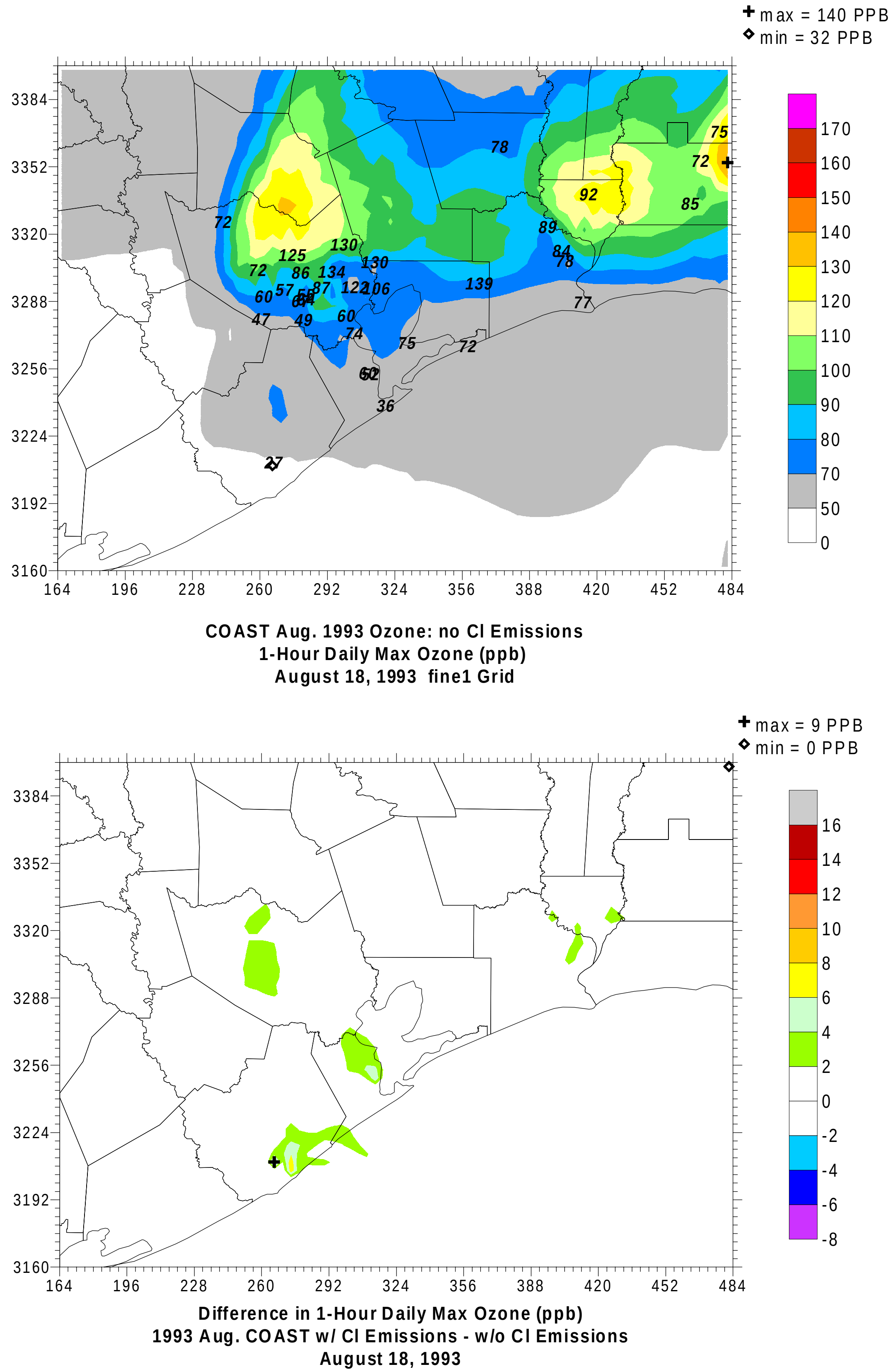


Figure 2. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results without Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.

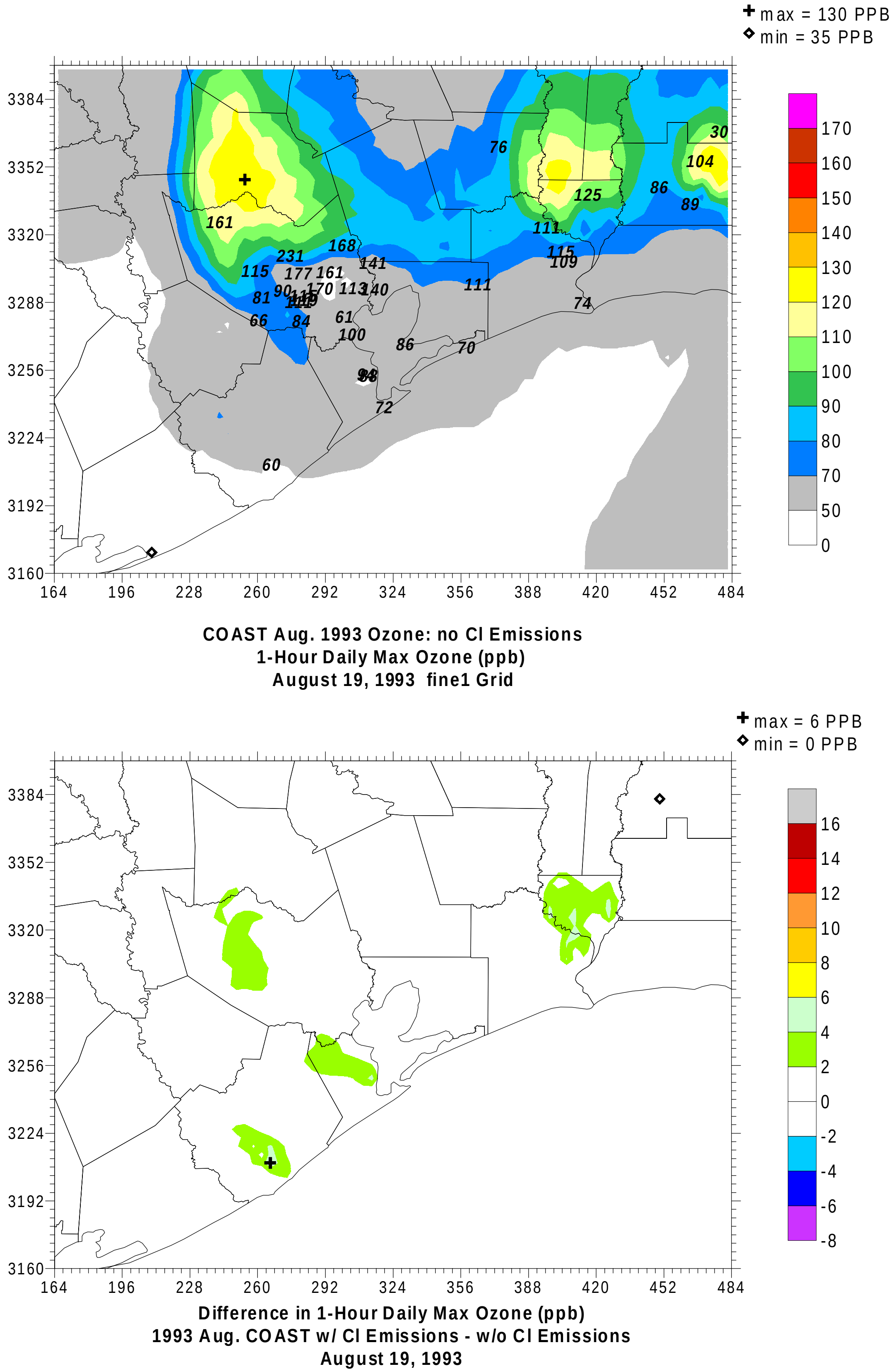


Figure 3. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results without Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.

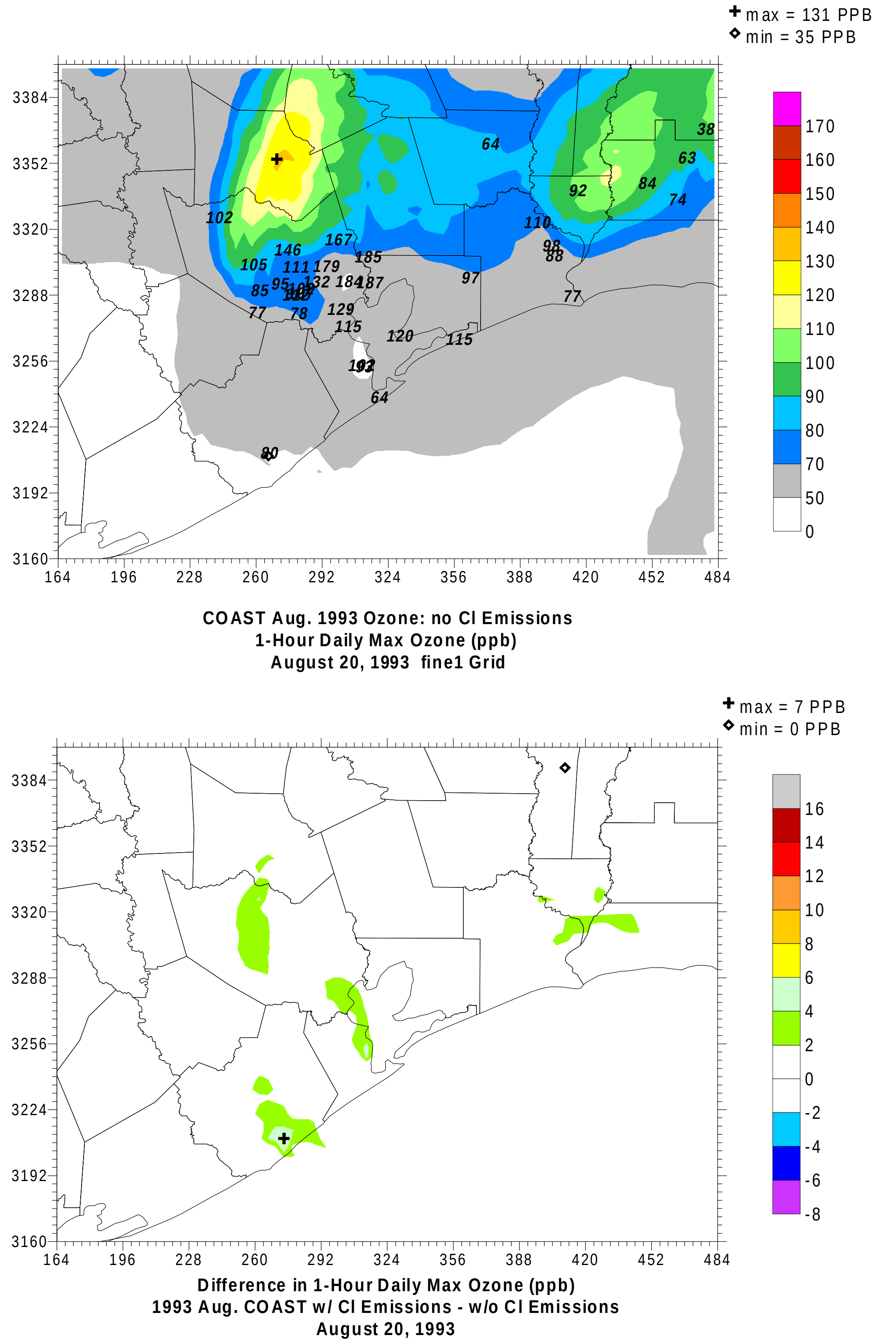
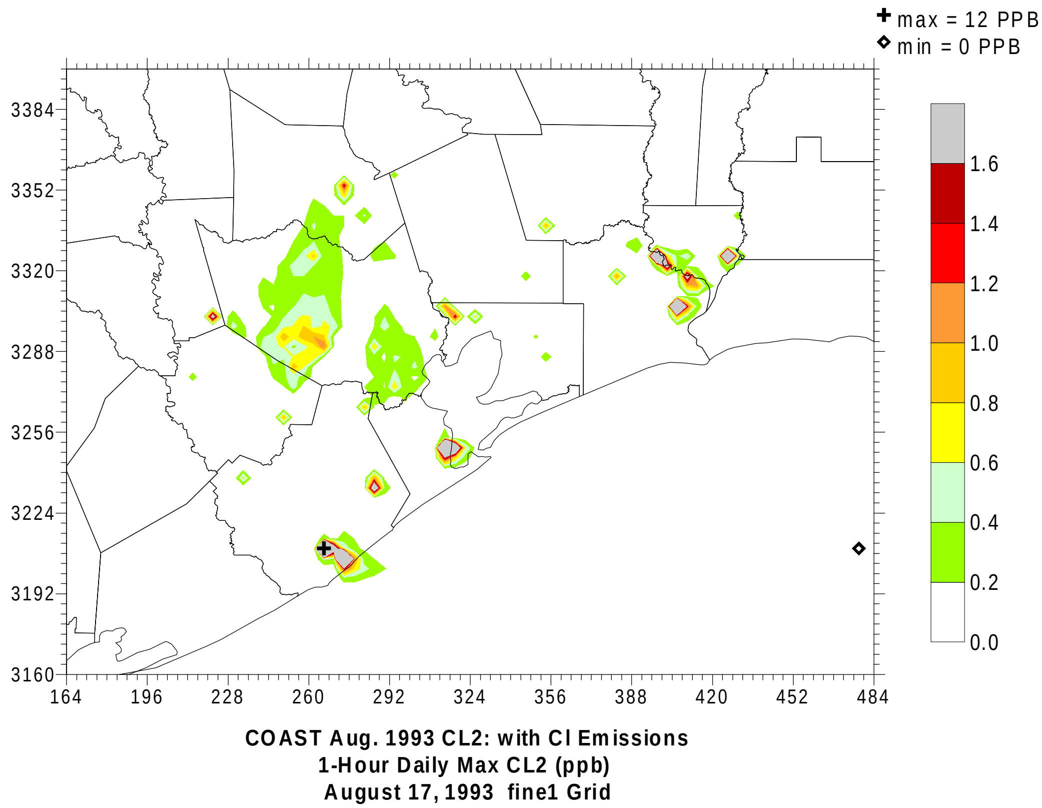


Figure 4. Top: Daily maximum 1-hour ozone plot showing observations and CAMx results without Cl emissions. Bottom: Difference in maximum 1-hour ozone with and without chlorine emissions.



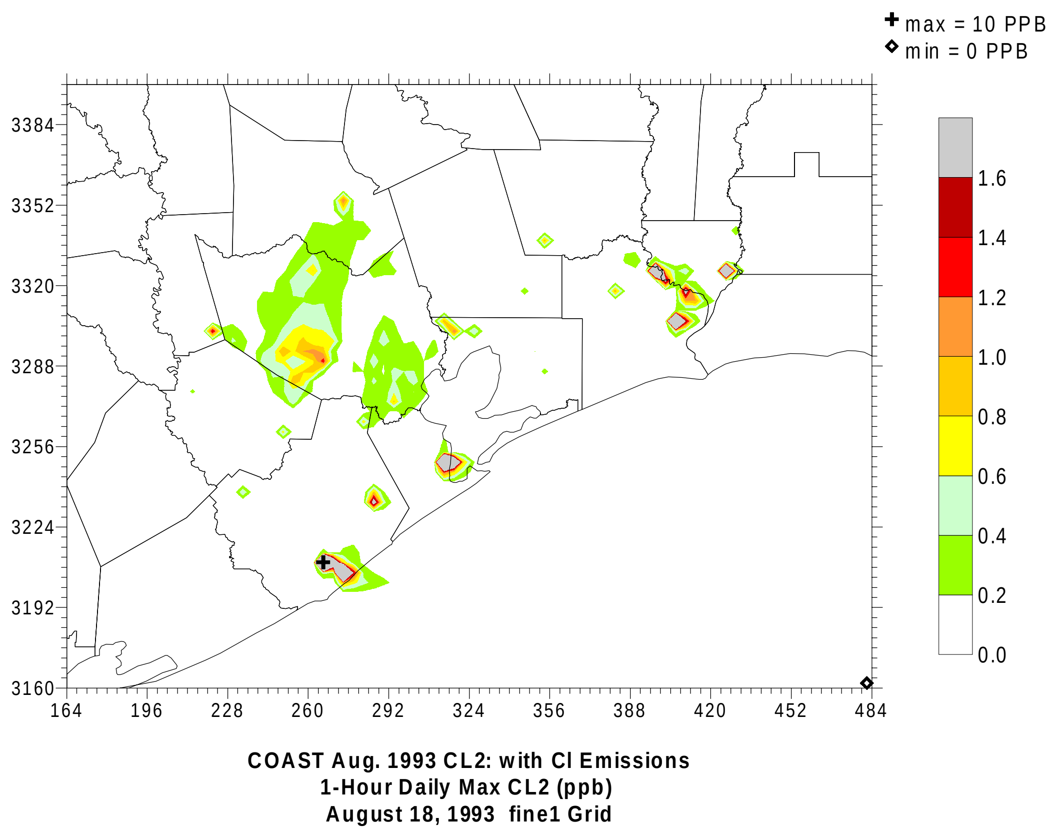
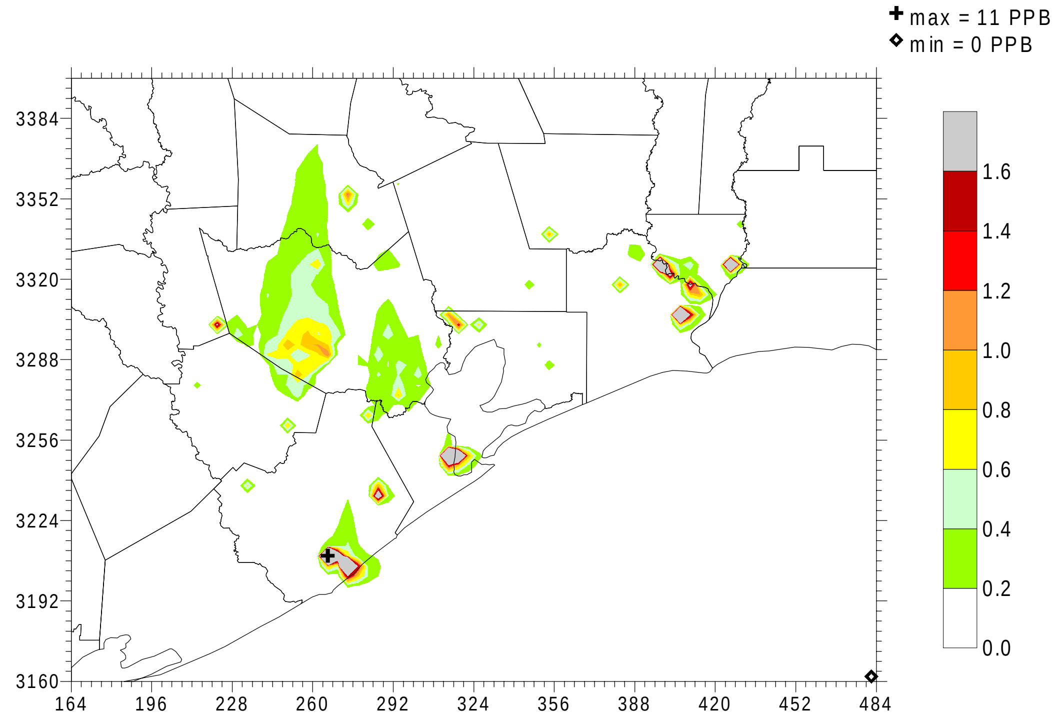
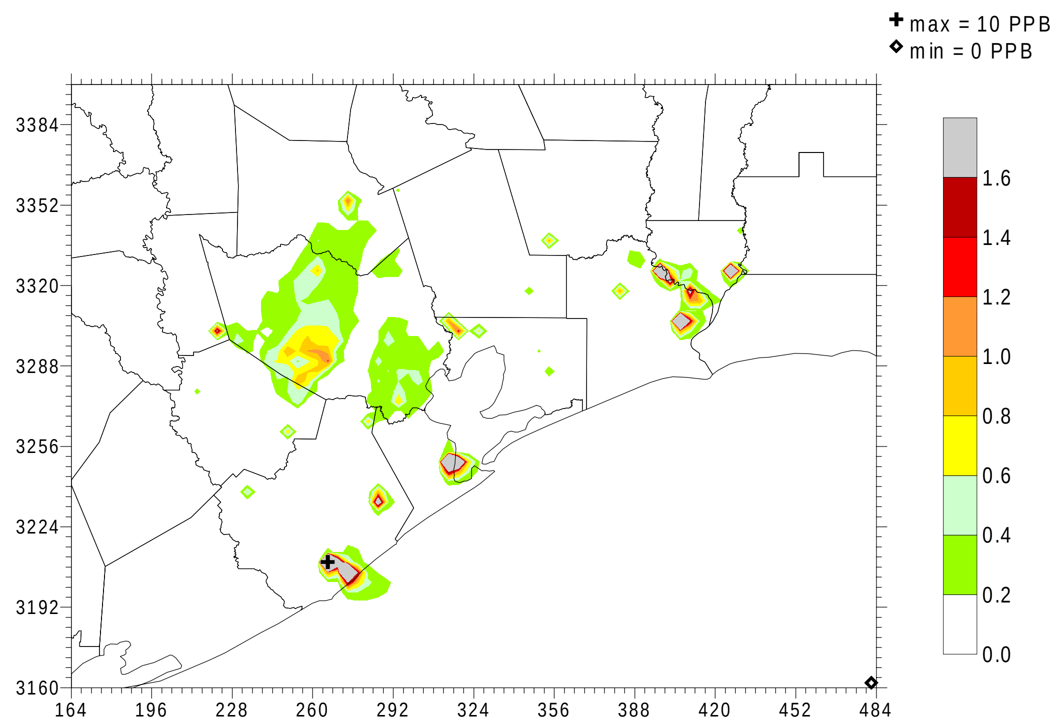


Figure 5. Daily maximum 1-hour CL2 plots showing CAMx results with Cl emissions.

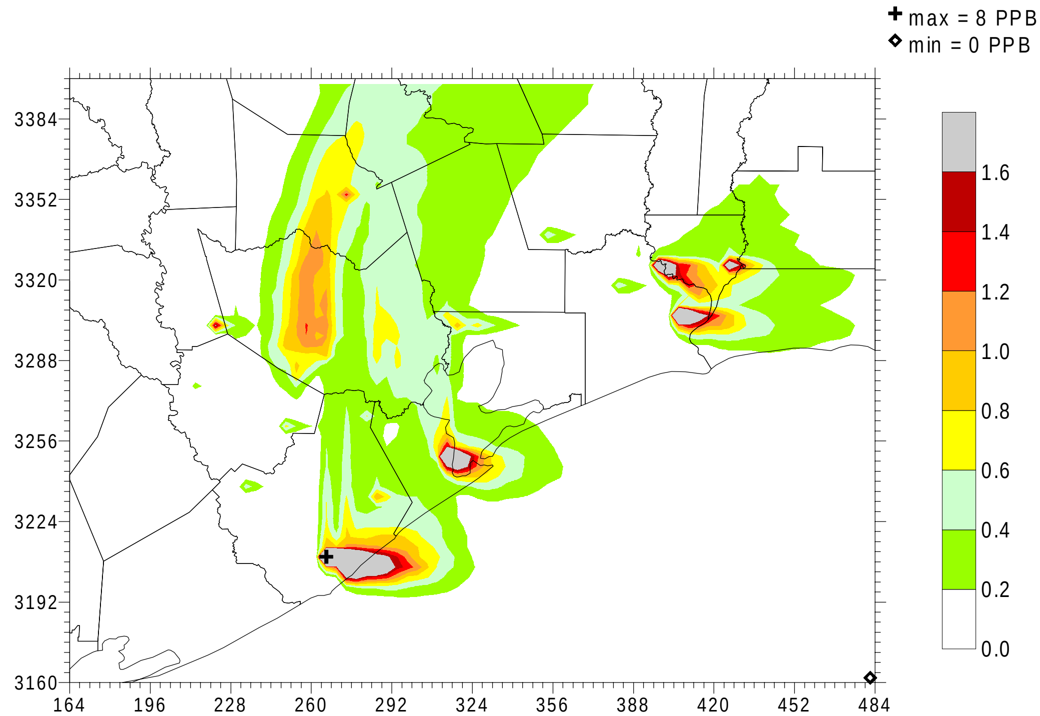


COAST Aug. 1993 CL2: with Cl Emissions
1-Hour Daily Max CL2 (ppb)
August 19, 1993 fine1 Grid

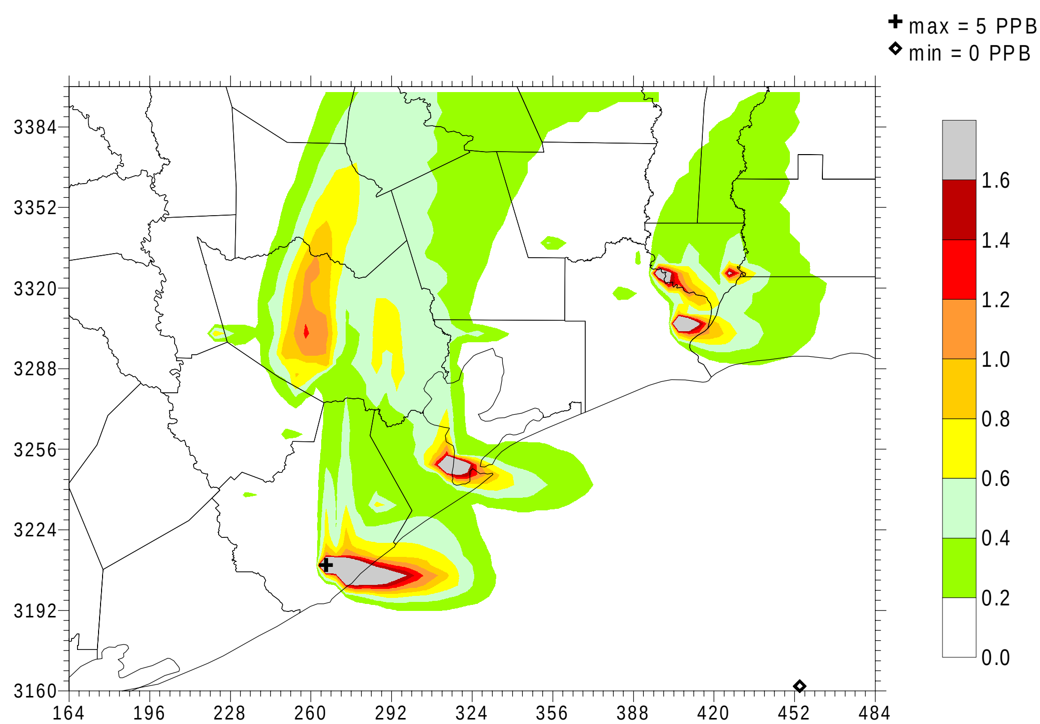


COAST Aug. 1993 CL2: with Cl Emissions
1-Hour Daily Max CL2 (ppb)
August 20, 1993 fine1 Grid

Figure 6. Daily maximum 1-hour CL2 plots showing CAMx results with Cl emissions.



COAST Aug. 1993 HCL: with Cl Emissions
1-Hour Daily Max HCL (ppb)
August 17, 1993 fine1 Grid



COAST Aug. 1993 HCL: with Cl Emissions
1-Hour Daily Max HCL (ppb)
August 18, 1993 fine1 Grid

Figure 7. Daily maximum 1-hour HCL plots showing CAMx results with Cl emissions.

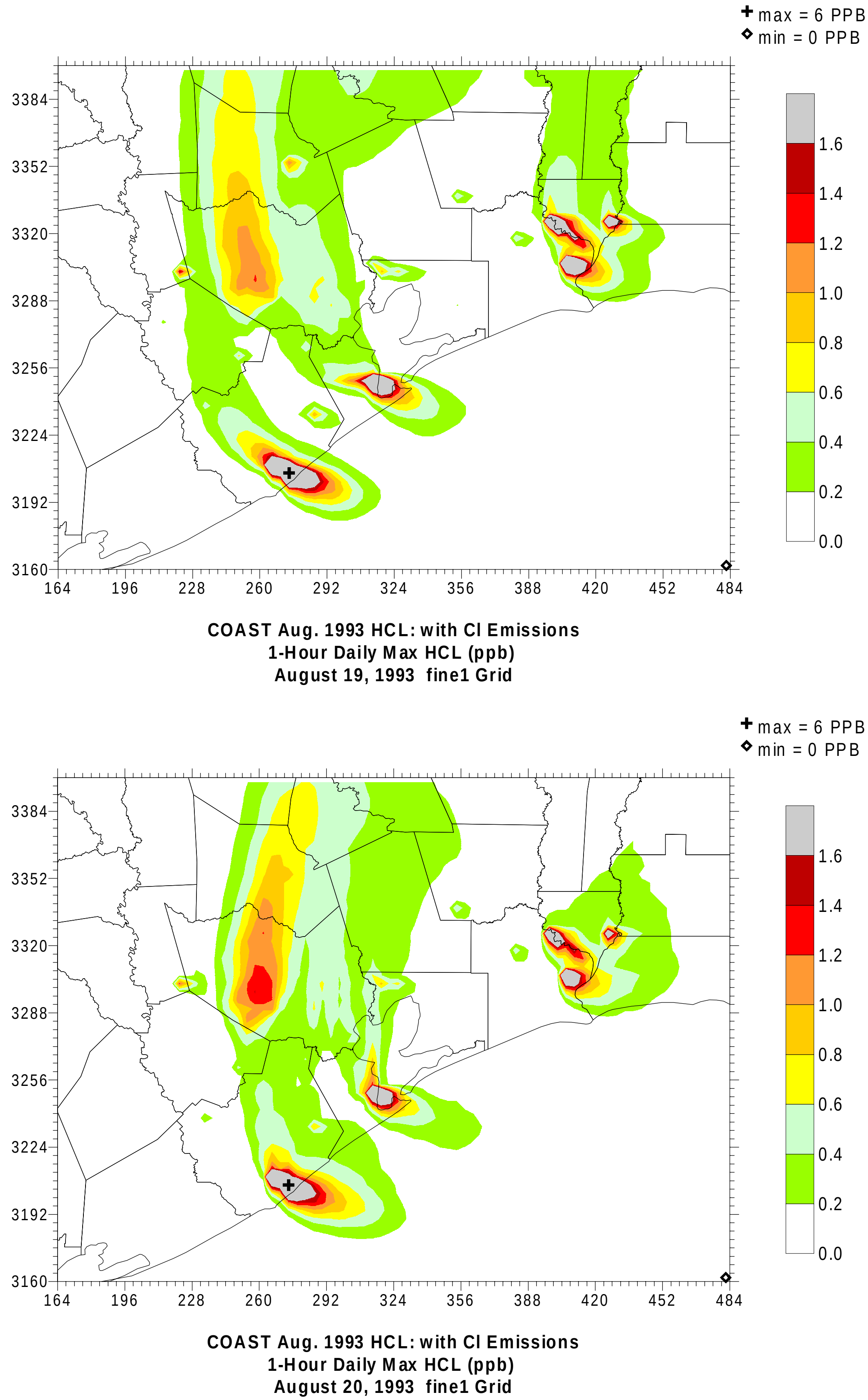


Figure 8. Daily maximum 1-hour HCL plots showing CAMx results with Cl emissions.

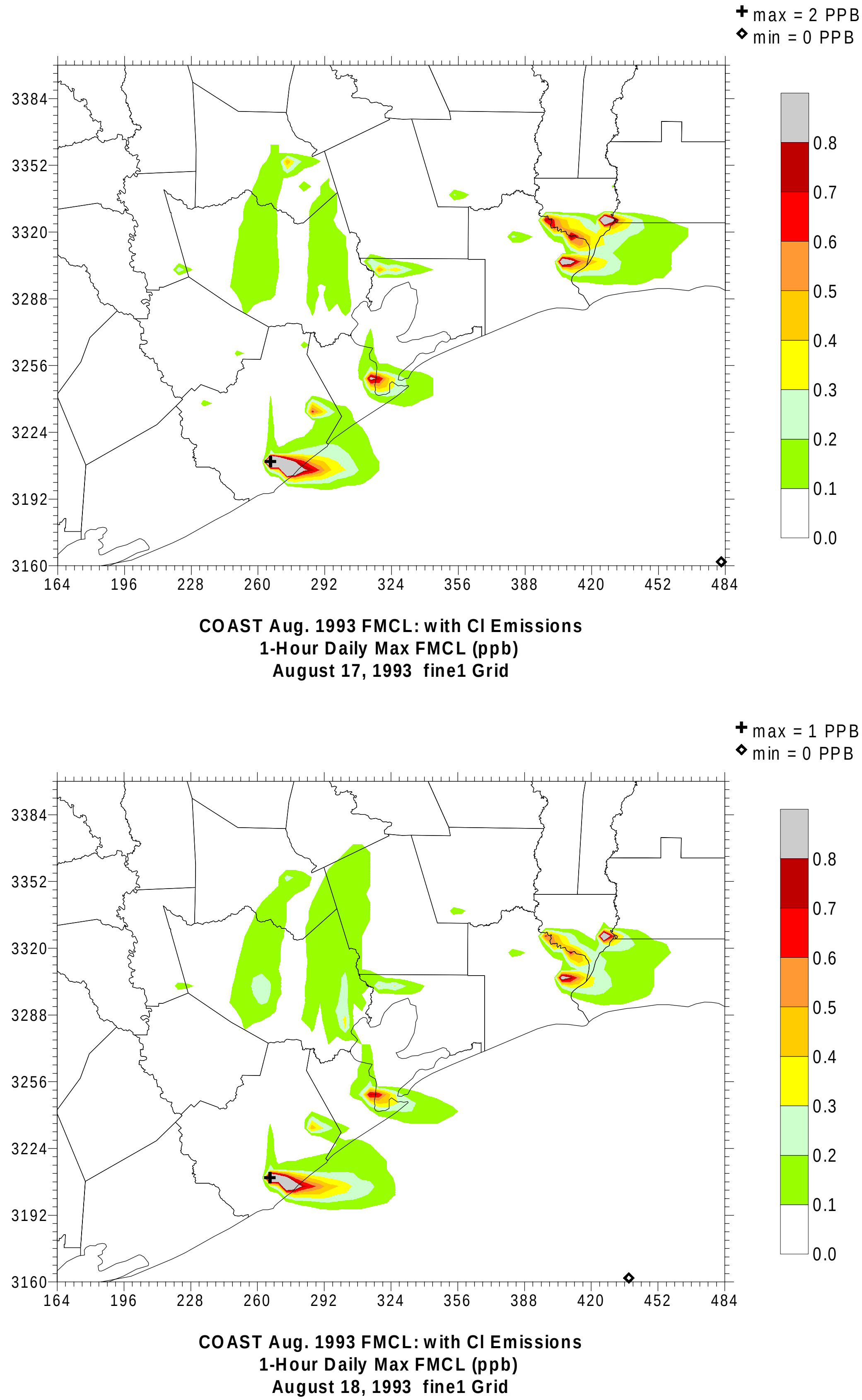


Figure 9. Daily maximum 1-hour FMCL plots showing CAMx results with Cl emissions.

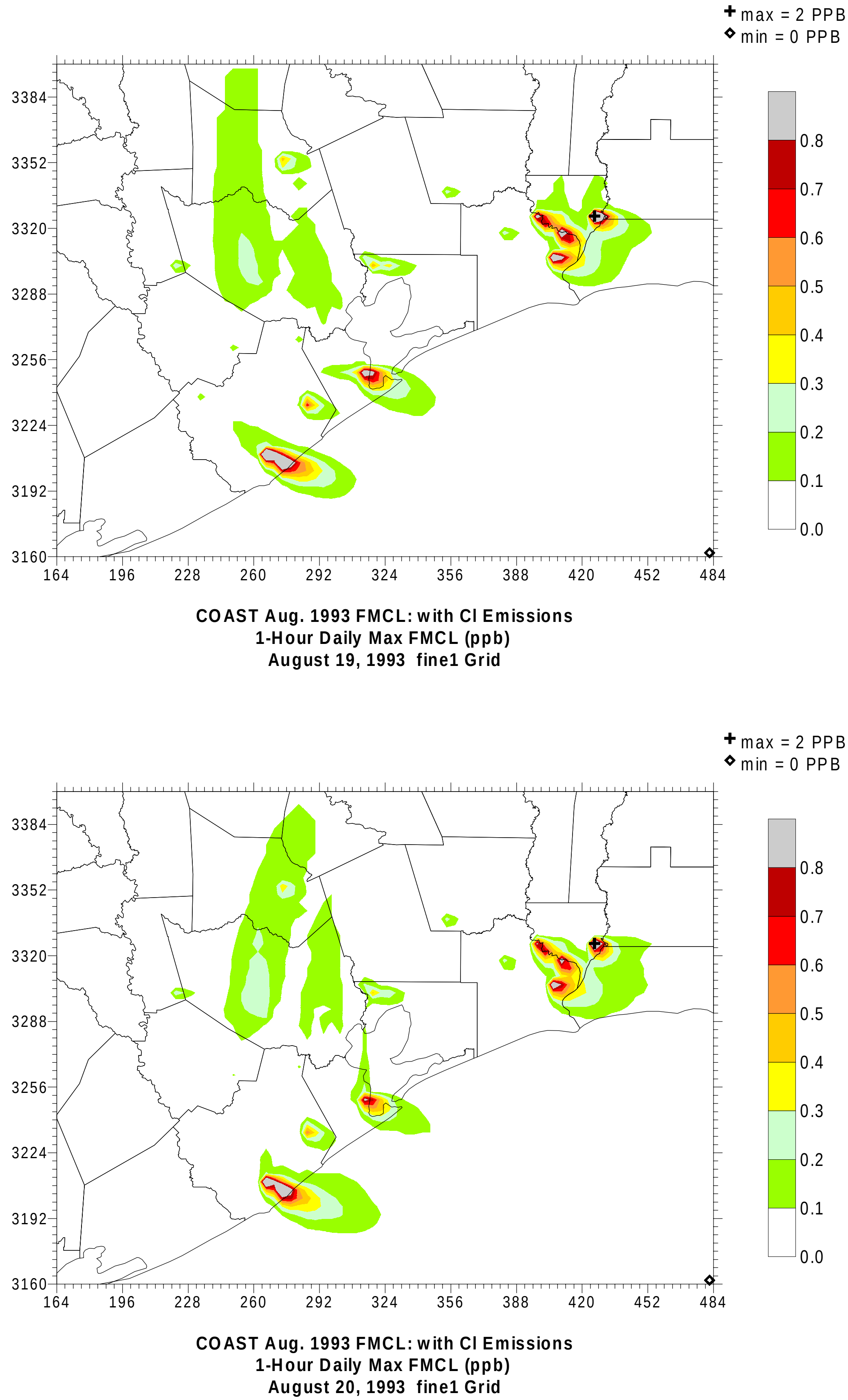


Figure 10. Daily maximum 1-hour FMCL plots showing CAMx results with Cl emissions.

COAST August 16-20, 1993 with and without Cl emissions

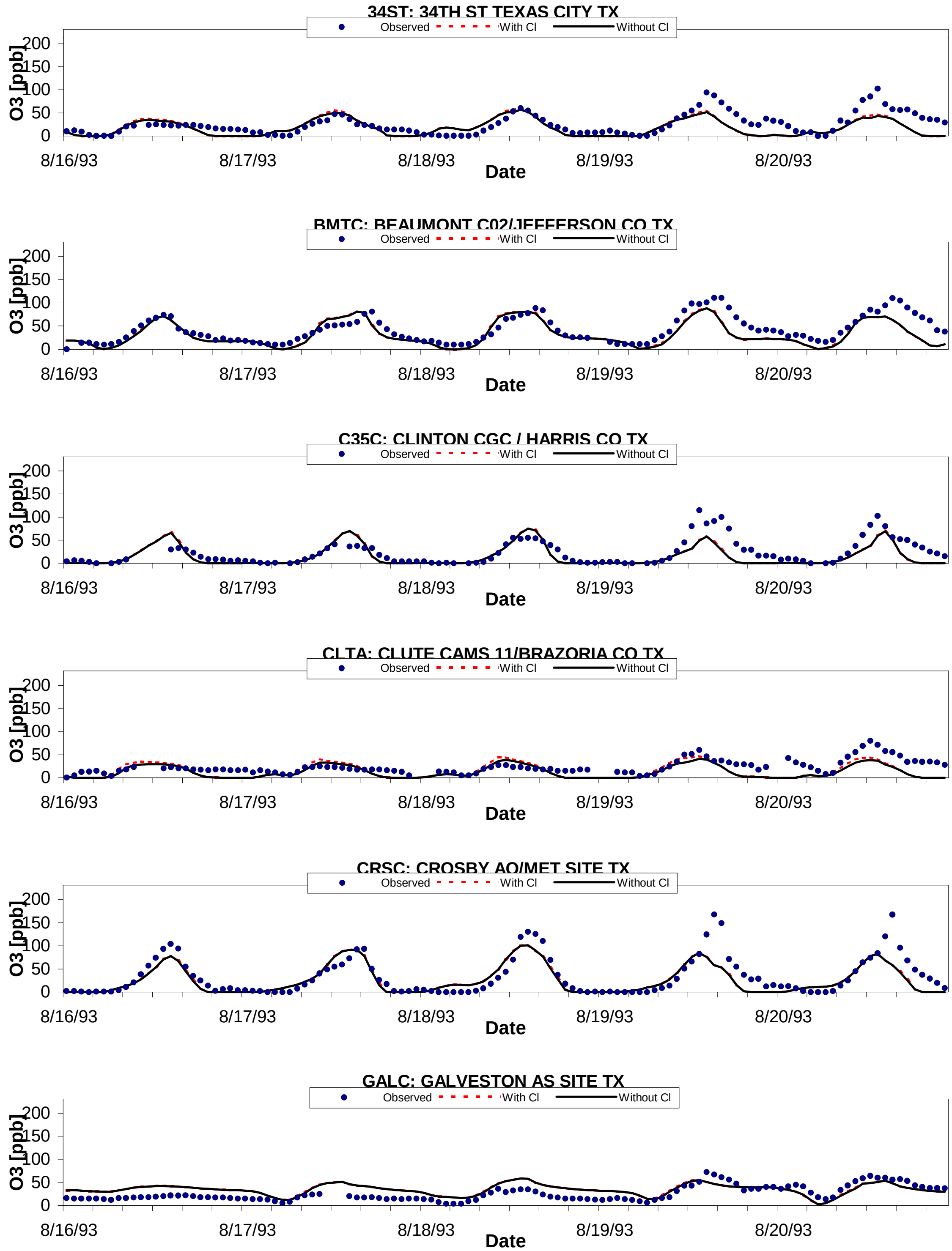
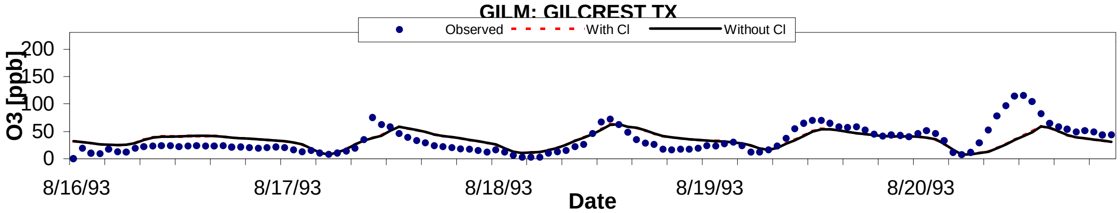
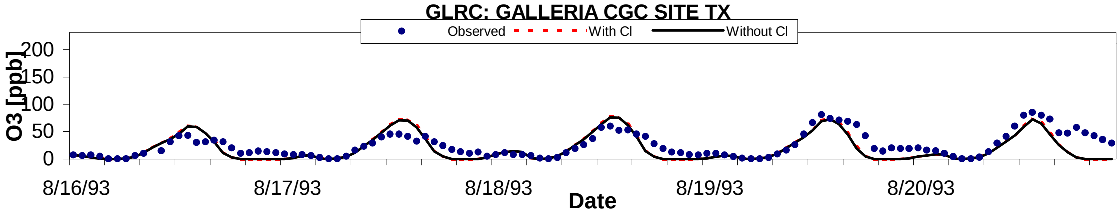
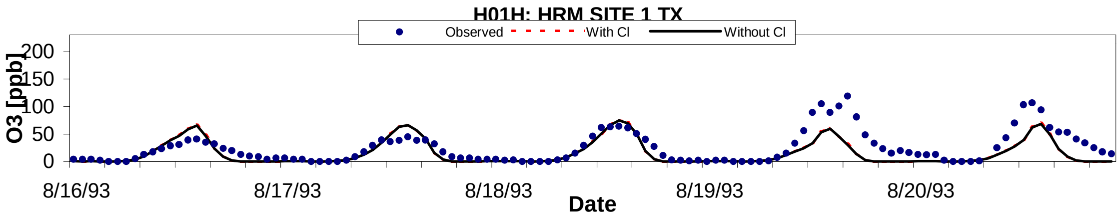


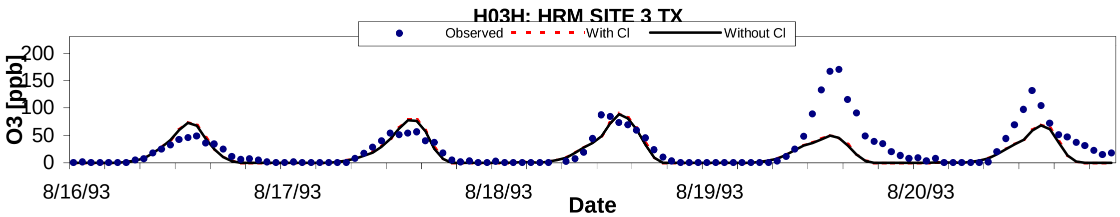
Figure 11. Time series of 1-hour ozone observations and predictions with and without chlorine emissions.

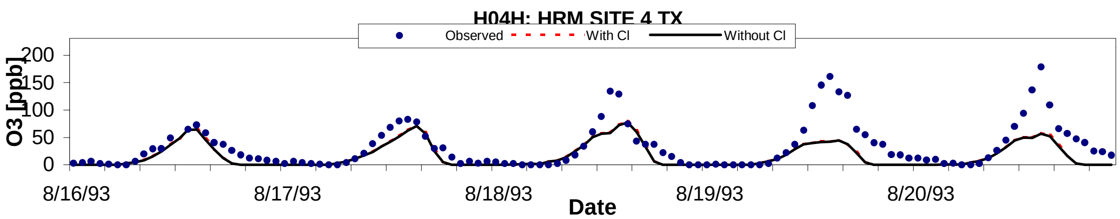
COAST August 16-20, 1993 with and without Cl emissions

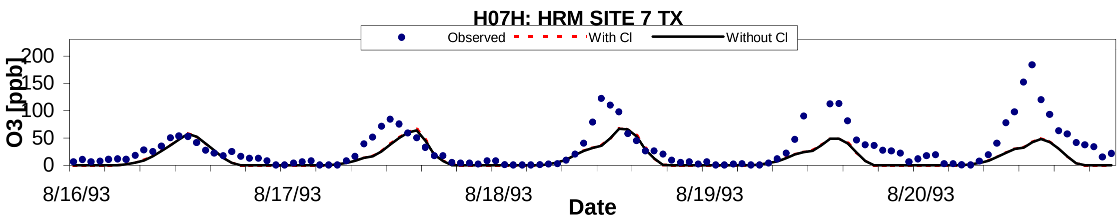




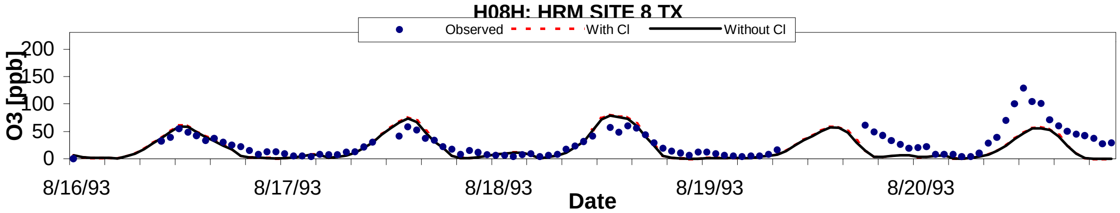


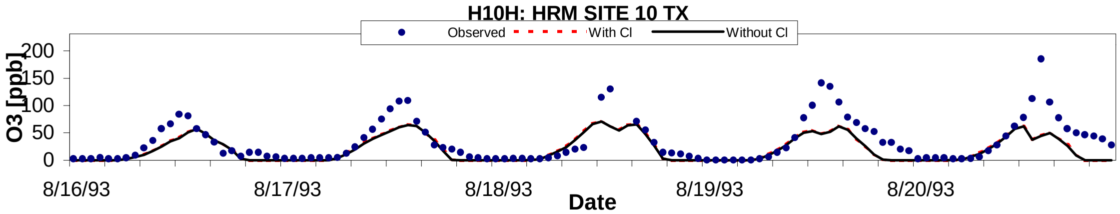


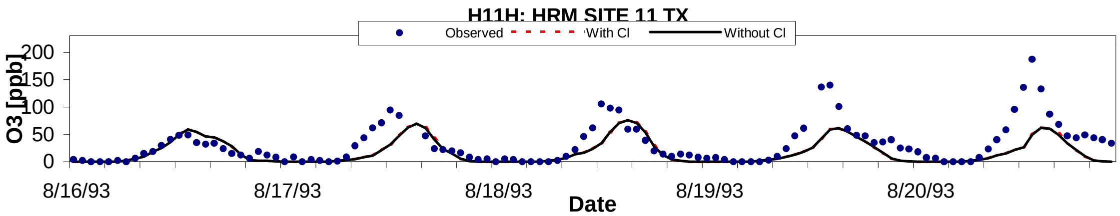


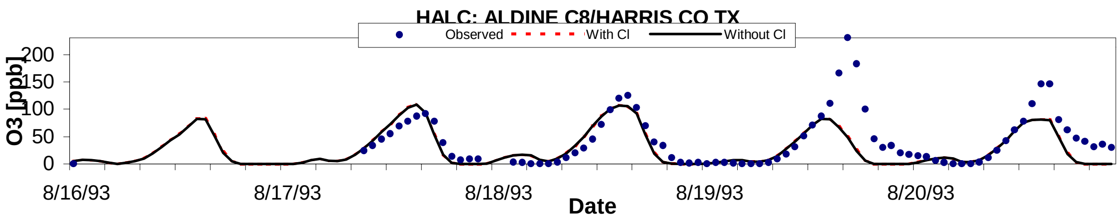


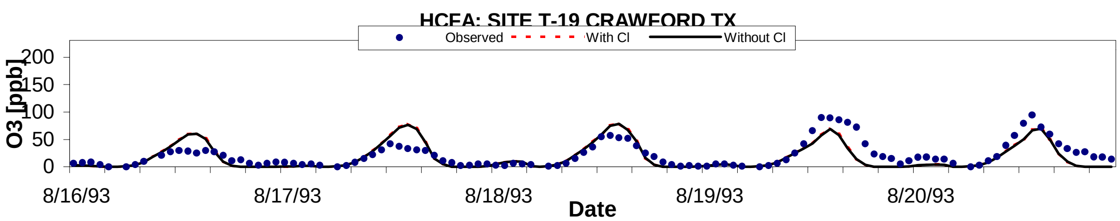
COAST August 16-20, 1993 with and without Cl emissions

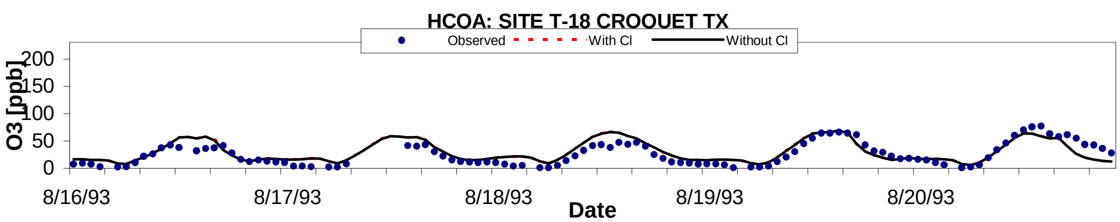




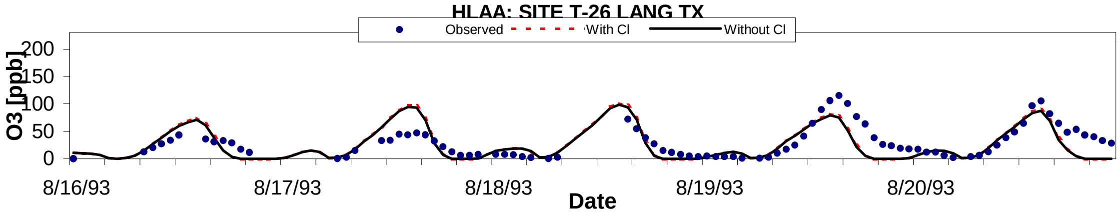


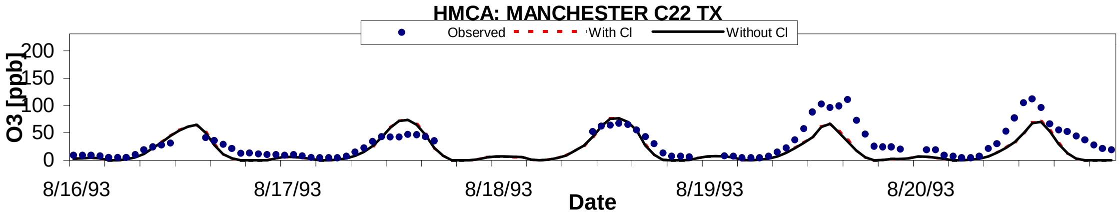


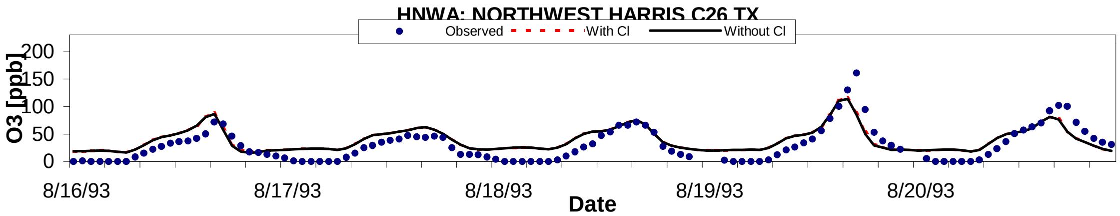


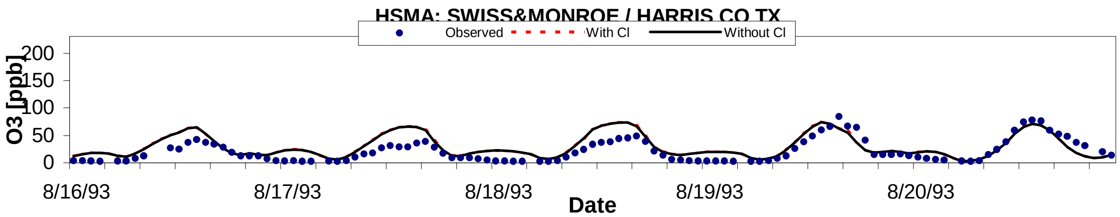


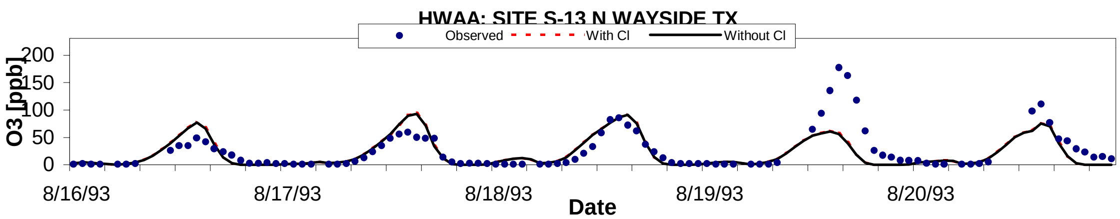
COAST August 16-20, 1993 with and without Cl emissions

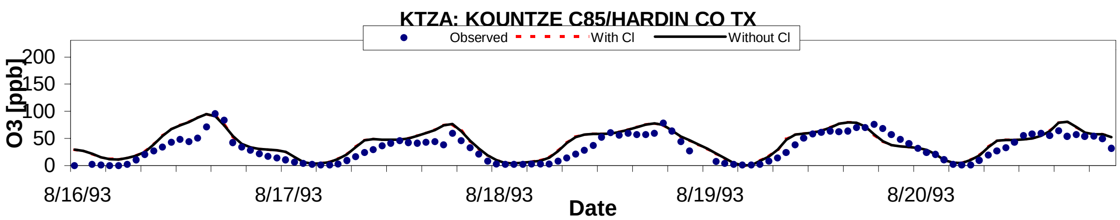












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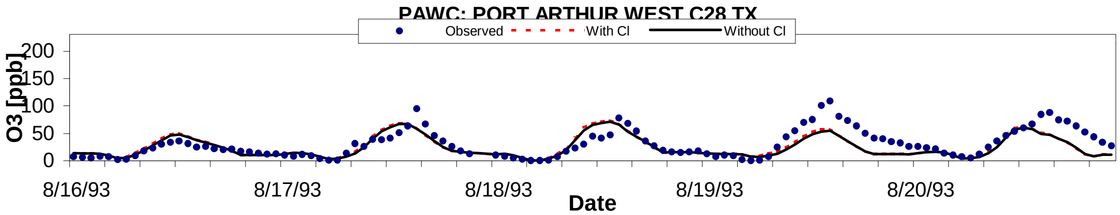
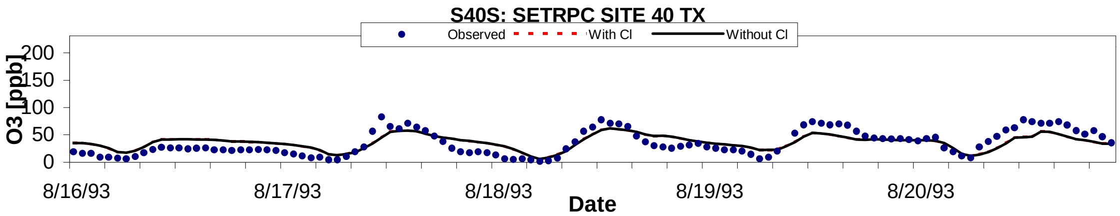
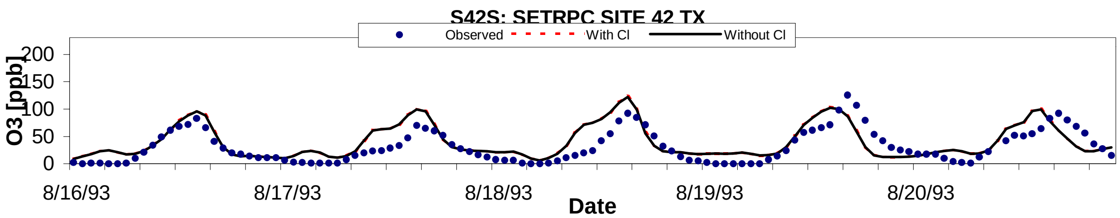
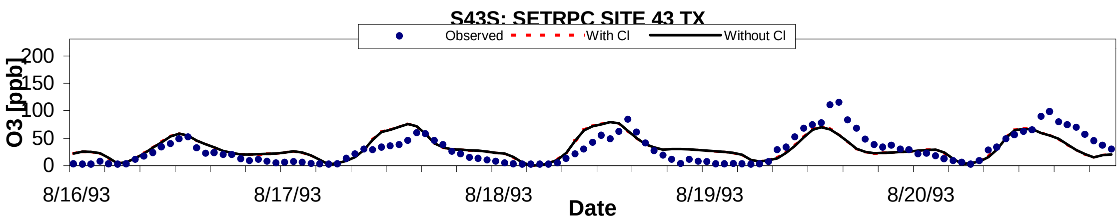
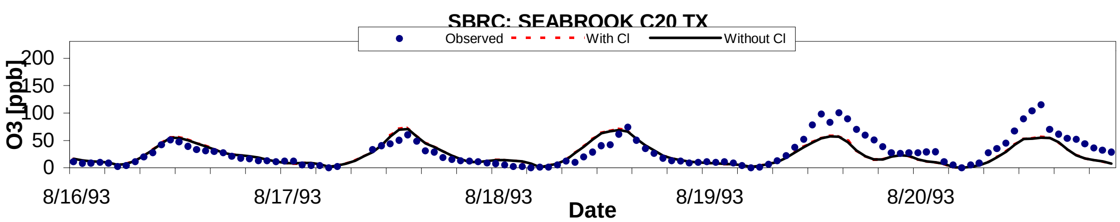
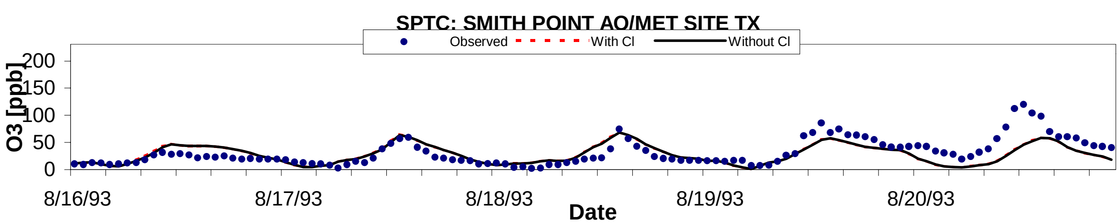




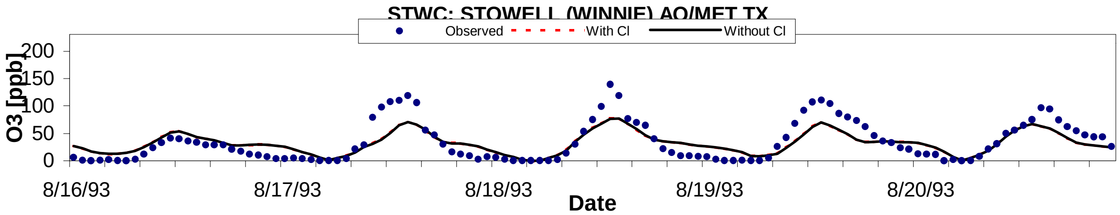


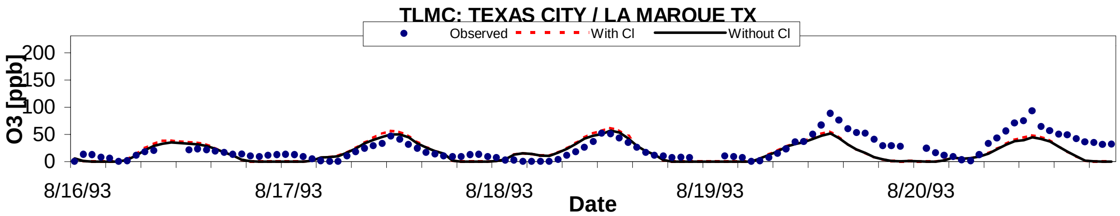


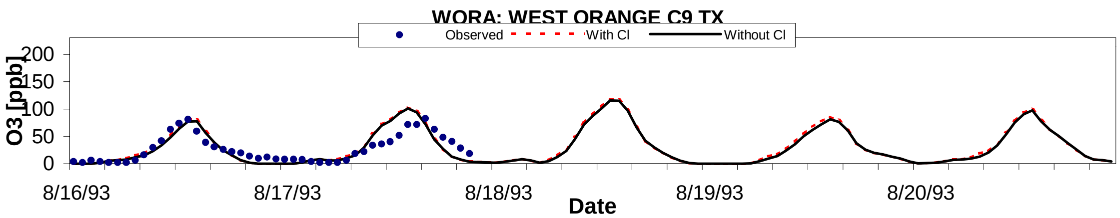


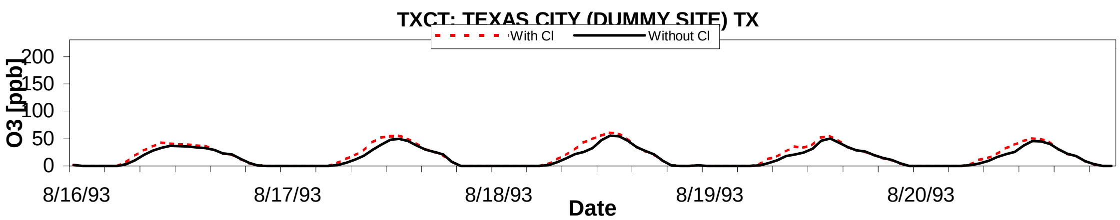


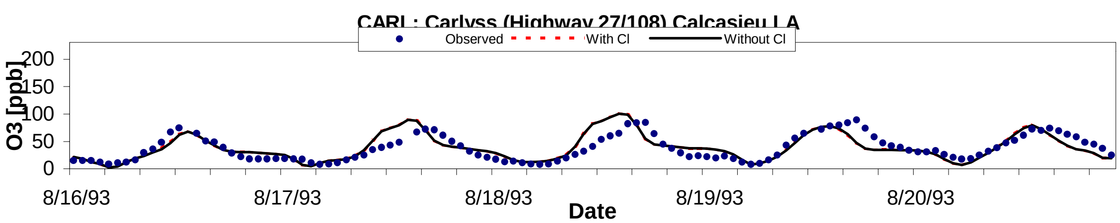
COAST August 16-20, 1993 with and without Cl emissions

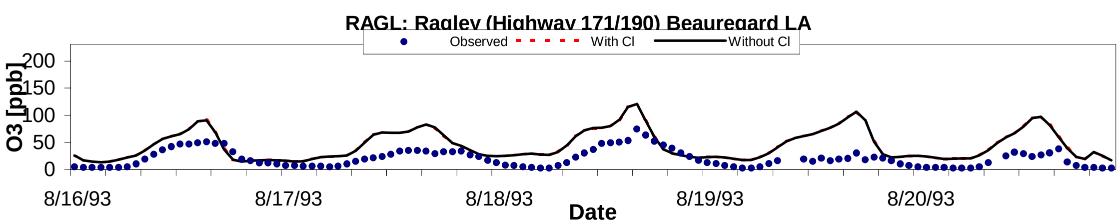












COAST August 16-20, 1993 with and without Cl emissions