

Supporting Information for

**Atmospheric chlorine chemistry in southeast Texas:
Impacts on ozone formation and control**

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Emission Inventory of Atomic Chlorine Precursors

Emissions of molecular chlorine were estimated for the Houston-Galveston, Beaumont- Port Arthur (HGBPA) sub-domain shown in Figure 2 of the accompanying manuscript. Chlorine emission estimates were made for the following source categories:

- point sources of Cl₂ emissions reported through the US Environmental Protection Agency's Toxic Release Inventory (TRI) and the State of Texas' Point Source Database (PSDB),
- atomic chlorine precursors from the use of biocides in cooling towers,
- atomic chlorine precursors from swimming pool disinfection,
- atomic chlorine precursors associated with reactions of chlorides in sea salt aerosol,
- other sources of atomic chlorine precursors associated with tap water use, water and wastewater treatment, and chlorinated organics in the atmosphere.

Cl₂ emissions were estimated using the methodologies summarized below, using activity data from 2000. Details of the emission inventory development methods are reported by Chang (1).

Molecular Chlorine Emissions from Industrial Point Sources in Southeastern Texas

Point source emissions of molecular chlorine were estimated using the Point Source Data Base (PSDB), maintained by the State of Texas and by using the Toxic Release Inventory (TRI), maintained by the U.S. Environmental Protection Agency (2). Both inventories should provide the same information, but there are some discrepancies due to differences in reporting. For this work, the larger of the PSDB and 2000 TRI emissions was selected for the photochemical modeling inventory.

Modeling parameters such as stack parameters were determined using the methods described in Chang et al. (1). Hourly emissions were assumed to be constant throughout the day. Total Cl₂ emissions from industrial point sources in the region were 0.65 tons day⁻¹.

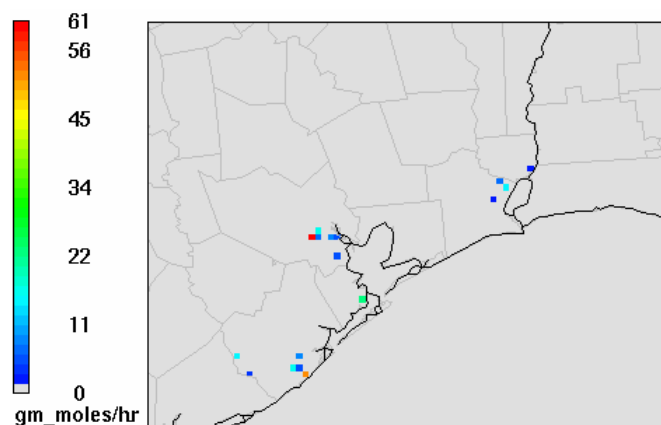


Figure S.1 Spatial distribution of chlorine emissions from industrial point sources

Emissions of atomic chlorine precursors from cooling towers in Southeastern Texas

Chlorine is added to water in cooling towers to control biofouling of the recirculating water. This chlorine can volatilize as the cooling tower evaporates water. The extent of these chlorine emissions was estimated using the method developed by Chang et al (1). Briefly, this method is based on mass transfer considerations of flash-off and field measurements reported by Exxon (3, 4). Data were collected before, during and after a typical shock chlorination cycle of a 1.2 million gallon system. The shock consisted of 3 hours of chlorine addition at a rate of 28,000 g molecular chlorine gas/hr, followed by 1.5-hours at 17,000 g/hr, and 3,800 g/hr for the remainder of a 24-hour period. The flow rate of make-up water for this cooling tower was 1.44 million gallons per day (mgd). Assuming a flash-off fraction of 0.1 and that the emissions are in the form of molecular chlorine leads to an emission estimate for the 1.44 mgd cooling tower of :

$$\begin{aligned}
 & (28 \text{ kg/hr} * 3\text{hr} + 17 \text{ kg/hr} * 1.5\text{hr} + 3.8 \text{ kg/hr} * 19.5\text{hr}) * 0.1 \\
 & = 18.4 \text{ kg chlorine emission per 24 hours a day for a 1.44 mgd cooling tower}
 \end{aligned}$$

This estimate is consistent with the estimates of chlorine use in cooling towers from surveys performed on refineries in the South Coast Air Basin (5). Since data from South Coast Air Basin indicate that relative few small capacity cooling towers used chlorine as a biocide, it is assumed that virtually all chlorine use in cooling towers is confined to the chemical manufacturing and refining sectors. In order to arrive at an order of magnitude estimate of chlorine use in cooling towers, the current study assumed approximately 500 MGD of cooling water use (350 cooling towers in southeastern Texas with capacities of approximately 1.44 MGD)

$$18.4 \text{ kg/day/cooling tower} * 350 \text{ cooling towers} = 6,000 \text{ kg/day}$$

The estimate of cooling water use was based on an assumption of approximately 1 gal of cooling water used per pound of chemical produced (6), and that approximately 25% of the 300 million tons per year of commodity chemicals are produced in the region being modeled. Chang et al. (1) assumed that cooling towers were co-located with the top 50-point sources of NO_x emissions in the area, excluding electricity-generating units (EGU), using a 1995 base-year inventory. The fraction of the total chlorine emissions assigned to each site was based on the fraction of the point source NO_x emissions located at each site.

The inventory used in this work differed from the original inventory developed by Chang et al. (1) only in the spatial distribution of emissions. In this work, cooling towers, and their chlorine emissions, were assumed to be co-located with all the 596 point sources of NO_x emissions in the area, excluding electricity-generating units (EGUs). The NO_x source locations were based on a year 2000 inventory. The temporal distribution of chlorine emissions and the stack parameters used by Chang et al (1) were used in this work. The spatial distribution of chlorine emission from cooling towers in the revised inventory is shown in Figure S.2. The total chlorine emission rate from cooling towers in this region was 6 tons day⁻¹ of molecular chlorine as Cl₂.

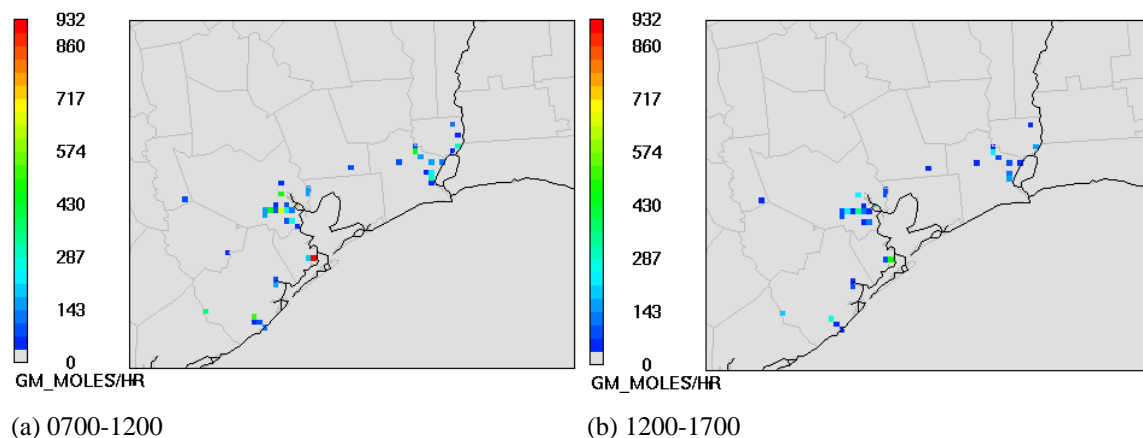


Figure S.2 Spatial distributions of chlorine emissions from cooling towers during (a) 0700-1200 and (b) 1200-1700 CDT.

Emissions of atomic chlorine precursors from swimming pools

Chlorine is added to water in swimming pools as a disinfecting agent. Estimates of the chlorine emissions from pools are generally based on an estimate of the number of pools and the emissions from each pool. Chang, et al. (1) estimated the number of pools in Houston based on national and Los Angeles pool ownership data, and arrived at an estimate of 150,000 pools in the

Houston area. The volatilization of chlorine from swimming pools was estimated using three different approaches. Rogozen et al. (5) assumed that the average rate of chlorine addition during summer months was 2 gallons of NaOCl solution (10-12.5% by weight) per pool per week. This leads to an estimate for summertime hypochlorous acid use of:

$$0.1 \text{ NaOCl} * 2 \text{ gal week}^{-1} (\text{week} / 7 \text{ days}) * 3.78 \text{ kg gal}^{-1} * 150,000 \text{ pools} \\ = 16,200 \text{ kg NaOCl day}^{-1} \text{ in 11 counties in Southeast Texas}$$

This suggests that approximately 16,200 kg day⁻¹ of NaOCl is added to pools in 11 counties, some fraction of which will volatilize.

Another approach to estimating the rate of volatilization from pools is to apply an overall mass transfer coefficient coupled with estimates of pool surface area and free chlorine concentration. Rogozen et al. (5) estimated an average pool surface area of 40 m² for southern California, and an average mass transfer coefficient for chloroform of 22 µg m⁻² min⁻¹, which is a weighted average of mass transfer coefficients under agitated and non-agitated conditions. This overall mass transfer coefficient is the product of an air phase mass transfer coefficient, a partitioning coefficient (Henry's law constant) and an aqueous phase concentration. Assuming that the air phase mass transfer coefficient is the same for chloroform and chlorine, the mass transfer coefficient for chlorine can be estimated by replacing the concentration and Henry's law constant for chloroform with the concentration and Henry's law constant for chlorine/hypochlorous acid. The data reported by Rogozen et al. (5), suggest that free residual chlorine concentrations in the water are a factor of 5 greater than aqueous chloroform concentrations. Assuming that the pH of the swimming pool water is maintained between 6.5 and 7.5, the Henry's law constant for chlorine (as HOCl in the aqueous phase) will be approximately a factor of 5 lower than the Henry's law constant for chloroform assumed by Rogozen et al. (5). After adjusting for the difference in molecular weights, this analysis suggests that an overall mass transfer coefficient for hypochlorous acid is approximately 10-100 µg m⁻² min⁻¹. The total surface area of swimming pools in the 11 counties is calculated based on the estimated number of swimming pools in Southeast Texas (1).

$$40 \text{ m}^2 \text{ per pool} * 150,000 \text{ pools in the 11 counties (5.18 million residents, US census Bureau)} = 6.0 * 10^6 \text{ m}^2$$

Mass volatilized:

$$10\text{-}100 \text{ } \mu\text{g m}^{-2} \text{ min}^{-1} * 6.0 * 10^6 \text{ m}^2 * 1440 \text{ min day}^{-1} * \text{kg } 10^9 \text{ } \mu\text{g}^{-1} = 90 - 900 \text{ kg day}^{-1}$$

The high end of the volatilization rate indicates that the chlorine evaporates at a rate of about 1000 kg day⁻¹, and this volatilization would occur during agitation when mass transfer coefficients are highest. Thus, the estimated emission rates based on a mass balance and on a mass transfer approach lead to very different estimates of emissions.

Yet another approach would be to assume that the volume of a typical pool is 50 m³ (an average surface area of 40 m² and an average depth of 1.25 m). Further assuming that the required residual chlorine concentration in the swimming pool is 2ppm (7), the residual chlorine available in a pool is

$$150,000 \text{ pools in 11 counties} * 50,000 \text{ L/pool} * 2\text{ppm} * 1 \text{ kg L}^{-1} = 15,000 \text{ kg.}$$

This suggests that a large stock of chlorine residues in the pool volume.

Thus, three different estimation methods lead to estimates of 16,200 kg of NaOCl added per day to pools, a stock of 15,000 kg of free residual chlorine in the pools, and a volatilization rate of 100-1000 kg day⁻¹. Taking all of these divergent estimates into account, it was assumed that total emissions in the 11-county area in the current study were 5 tons day⁻¹ (4540kg day⁻¹) as Cl₂. This estimate is significantly larger than the rate suggested by limited mass transfer rate data, but only a small fraction of the available stock of free residual chlorine. Thus, this estimate may be uncertain by an order of magnitude.

Chlorine emissions were spatially allocated based on population and income distributions. Chang, et al. (1) used 1990 data on the spatial distribution of households with incomes above \$50,000; this study used 2000 census data on the spatial distributions of households with incomes above \$75,000 to spatially distribute swimming pool emissions. It was assumed that the chlorine emissions occur at a constant rate between 1200 and 2000 as the water was agitated by use. The spatial distribution of chlorine emissions from swimming pools is shown in Figure S.3.

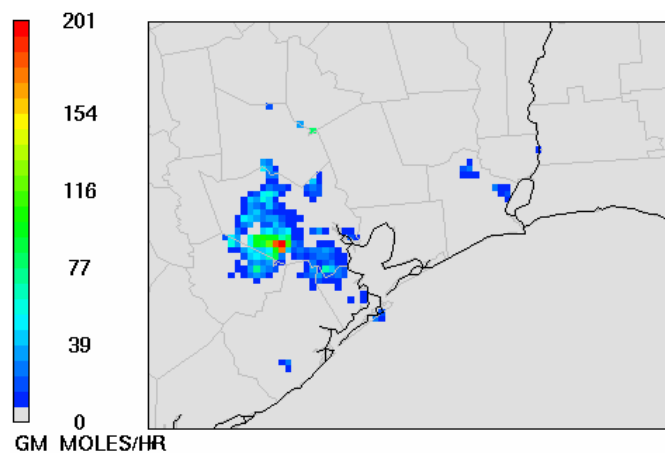


Figure S.3 Spatial distributions of chlorine emissions from industrial point sources during 1200 to 2000

Emissions of atomic chlorine precursors from the reactions of sea salt aerosol

Spicer et al (8) has suggested that ozone and other components in photochemical smog react with chloride in sea salt to release Cl_2 . Chang et al. (1) estimated the chlorine emission rate from this source in the Houston-Galveston region based on the rates of molecular chlorine generation by sea salt observed on Long Island by Spicer et al. (8). In this work, emissions were spatially allocated to grid cells that had both high sea salt concentrations and ozone (or other air pollutant) concentrations. This area was assumed to include the all grid cells in the photochemical model that were over water, but within 8 km of a coastline. The emission was modeled as an area source in each 4 km by 4 km grid cell with emissions of 1.6 kg day^{-1} per grid cell. Chlorine production was assumed to be evenly distributed over daylight hours, from 0600 to 1800 (1).

Emissions of atomic chlorine precursors associated with tap water use, water and wastewater treatment, and chlorinated organics in the atmosphere

Chang et al. (1) estimated the emissions of atomic chlorine precursors associated with tap water use, water and wastewater treatment, and chlorinated organics in the atmosphere. Since the emission estimates for these sources were estimated to be more than an order of magnitude less than other potential sources, these emissions will not be incorporated into the inventory used for modeling in this work.

Summary of emission inventory for atomic chlorine precursors

Figures S.4a and S.4b show the spatial distributions of total emissions of molecular chlorine from 0700 to 1200 and from 1200 to 1700. Figures S.4c and S.4d show the spatial distribution of emissions of molecular chlorine from cooling towers from 0700 to 1200, and the emission from swimming pools from 1200 to 2000.

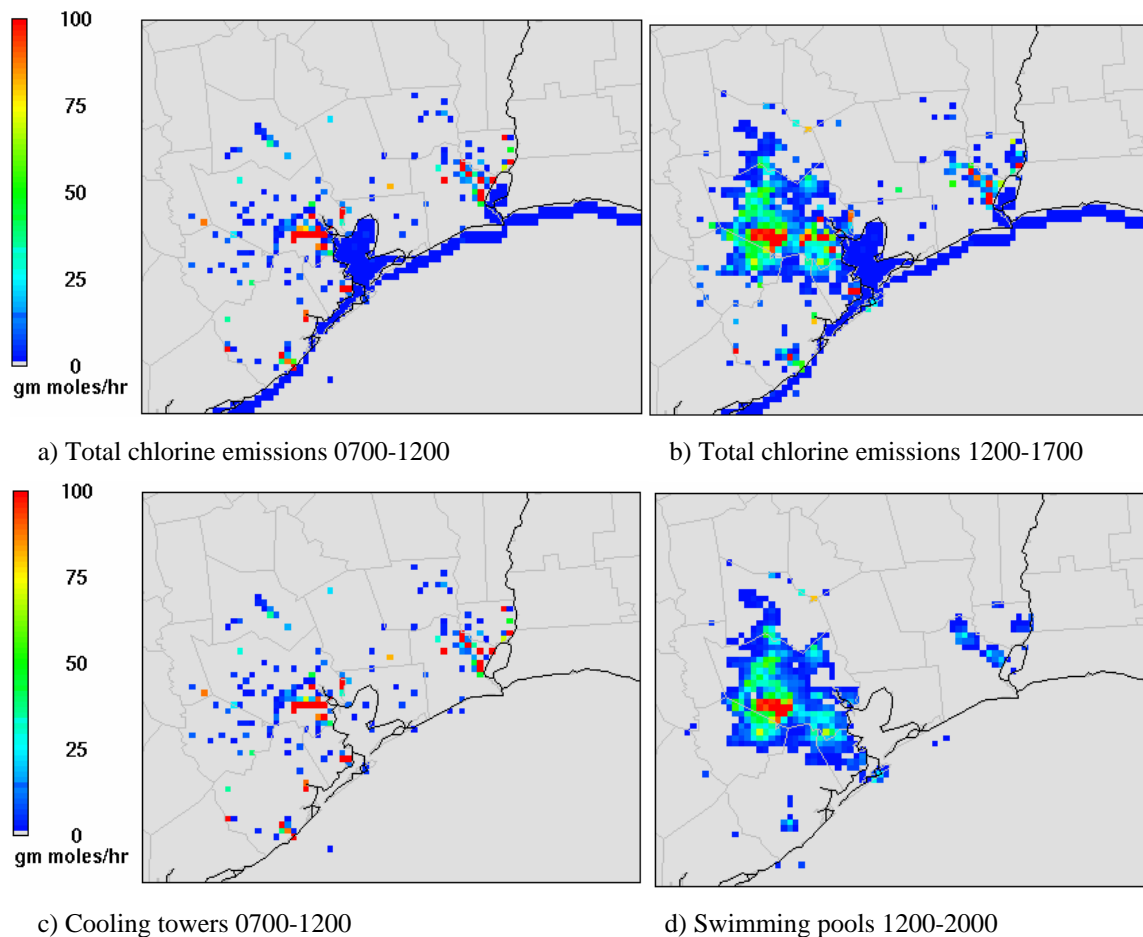


Figure S.4 Estimated chlorine emissions in southeastern Texas nested CAMx modeling domain (4km HGBPA subdomain). a) Total emissions of molecular chlorine from cooling towers, swimming pools, point sources, and reactions of sea salt between 0700 and 1200, b) total emissions of molecular chlorine between 1200 and 1700; c.) emissions of molecular chlorine from cooling towers between 0700 and 1200; this is the largest estimated source of emissions in the inventory; d.) emissions of molecular chlorine from swimming pools between 1200 and 2000; this is the second largest estimated source of emissions in the inventory

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