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

Submitted by

Sunghye Chang
Paul Tanaka
Elena McDonald-Buller
David T. Allen

Center for Energy and Environmental Resources
The University of Texas
Austin, Texas 78712

512-471-0049
allen@che.utexas.edu
ecmb@mail.utexas.edu
juliejang7@hotmail.com
tanaka@che.utexas.edu

Aug 24, 2001

Summary

Emissions of chlorine atom precursors were estimated for seven source categories in southeast Texas. The most significant sources were volatilization of biocides from cooling towers (6 tons/day for the Houston/Galveston and Beaumont/Port Arthur regions), volatilization of disinfecting agents from swimming pools (5 tons/day for the Houston/Galveston and Beaumont Port Arthur regions), and point sources (1 ton/day for

the Houston/Galveston and Beaumont/Port Arthur regions). Less significant were emissions due to water treatment, wastewater treatment and water use. The release of chlorine atom precursors from the atmospheric reactions of sea salt and the atmospheric reactions of chlorinated organics are highly uncertain, but preliminary estimates of the releases due to the reactions of sea salt (0.3 ton/day) are provided. Spatial and temporal allocations of the emissions are described for each of the significant sources.

Introduction

Previous work (Tanaka, et al., 2000) has suggested that emissions of molecular chlorine, Cl_2, may have a significant impact on the formation of ozone in the Houston area. The emissions and reactions of molecular chlorine (Cl_2), and other precursors of chlorine radicals (Cl˙) are not accounted for, however, in current photochemical modeling for southeastern Texas. Therefore, the Texas Natural Resource Conservation Commission (TNRCC) contracted with the University of Texas to develop a reaction mechanism and a preliminary emission inventory that could be used in existing photochemical modeling for southeast Texas.

The University of Texas has developed a simplified reaction mechanism to account for the dominant features of the urban tropospheric chemistry of molecular chlorine (Tanaka and Allen, 2001). This mechanism is suitable for inclusion in the Carbon Bond IV reaction mechanism that has been used in photochemical modeling for southeast Texas. The mechanism accounts for two sources of atomic chlorine: photolysis of molecular chlorine (Cl_2) and photolysis of hypochlorous acid (HOCl). This report presents preliminary estimates of atmospheric releases of molecular chlorine and hypochlorous acid, suitable for use in photochemical modeling. As a preliminary emissions inventory for molecular chlorine and hypochlorous acid (which will be referred to as atomic chlorine, Cl˙, precursors), the goal of the estimates will be to assess the likely magnitude and the range of potential emissions of atomic chlorine precursors. The following categories of sources will be considered:

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

The emission estimates presented in this report indicate that three of these source categories - cooling towers, swimming pools and point sources – are likely to be major sources of chlorine. For these emission categories, locations, stack parameters, and other data needed for photochemical modeling will be estimated. For other emissions categories, which are less significant, only the magnitudes of the emissions are estimated. The exception is releases due to the reactions of sea salt. While small, these emission rates are highly uncertain, and a range of emission rates from this source could be examined in photochemical modeling studies. Therefore, spatial and temporal distribution patterns for this source are also estimated.

The sections below describe the emission estimation methods used for each of the source categories.

1. Molecular Chlorine Emissions from Industrial Point Sources in Southeastern Texas

Point source emissions of molecular chlorine were identified in eleven counties in Southeastern Texas using the Toxic Release Inventory (TRI) compiled by the United States Environmental Protection Agency (USEPA, www.epa.gov/tri) These counties were Jefferson, Brazoria, Galveston, Orange, Harris, Fort Bend, Montgomery, Liberty, Chambers, Waller, and Hardin. Data were assembled for 1993 (the year of the base case episode for the Houston Galveston area SIP modeling) and for 1998 (the most recent data available at the time the inventory was compiled).

Of the 11 counties, Jefferson, Brazoria, Galveston, Orange and Harris County had facilities with significant (>0.5 ton per year (tpy)) chlorine releases. The largest emissions of chlorine gas emissions were recorded in Brazoria, Harris and Jefferson counties that registered 170 tpy, 110 tpy, and 85 tpy, respectively. The chlorine emissions reported in Galveston and Orange counties were approximately 1 tpy. Fort Bend, Montgomery and Chambers counties had molecular chlorine emissions of less than 0.5 tpy. Liberty, Waller, and Hardin County had no documented chlorine emissions. Significant point sources (>0.5 tpy) from the eleven counties, based on the TRI data are compiled in Table 1.

The TNRCC also maintains records of point source releases of molecular chlorine in

their PSDB. In principle, the PSDB would contain the same information on point source emission rates as the Toxic Release Inventory, and would provide additional information such as stack characteristics and other parameters necessary for photochemical modeling. A comparison of the TRI and PSDB data (Table 1), indicates that the data on emission rates in the two databases mostly agree, but some discrepancies do exist.

The point source inventory that will be used in photochemical modeling uses the larger of the emission rates reported through the 1998 TRI and the PSDB. Stack parameters and other model input data were drawn from the PSDB. When these data were missing, they were assumed to be equal to default values recommended by the U.S. EPA for photochemical modeling. A summary of the magnitude, spatial allocation and temporal allocation of the point source emissions is given below.

Point source emission summary:

Total emissions in the 11 county-region and outlying areas: 1.416tons/day of molecular chlorine (1.087tons/day in 11 county area)

Spatial distribution of emissions: latitude and longitude are available for each source

Temporal distribution of emissions: constant emissions, 7 days/week, 365 days/year

Stack parameters: Some stack parameters provided in PSDB, otherwise default parameters were used. (Height=3m; Diameter=0.2m; T=294K; Stack gas vel.=0.5m/s)

Table 1a. Point source releases of molecular chlorine in Jefferson County

Facility	**Latitude**	**Longitude**	**1993 TRI reported releases lb/yr**	**1998 TRI reported releases (t/d) lb/yr**	**TNRCC PSDB (t/d) lb/yr**	**Proposed Emission Rate t/d**
Alac, Port Neches ASU	29.98403	-93.95175	1516			
Basf Corp.	29.97139	-94.05333	500	(0.00214) 1560	(0.0027) 1971	0.0027
Du PontDow Elastomers Beaumont Plant	30.01419	-94.03304	1573	(0.00246) 1792	(0.00131) 956	0.00246
Equistar Chemicals L.P.Port Arthur Plant	29.74356	-94.11179	6000	(0.00455) 3320	(0.00247) 1803	0.00455
Goodyear Tire & Rubber Co.	29.97456	-94.21658	1420	(0.002219) 1620		0.002219
Huntsman Corp.-C4/O&O Plant	29.96889	-93.92763	126000	(0.183836) 134200	(0.02333) 17,000	0.206712
Huntsman Corp.-Po/MTBE Plant	29.96808	-93.9455	13700	(0.014384) 10500		
Huntsman Corp. Port Arthur-A&O Plant	29.89325	-93.97334	12000	(0.008493) 6200		
Mobil Chemical Co.Olefins&Aromatics Plant	30.06658	-94.05967	3720	(0.00226) 1650		0.002260
Union Oil of CA, DBA Unocal	29.99933	-93.97934	2500			
Chevron Port	29.87306	-93.99333	1100			
Exxon Mobile Chemical Company	30.06954	-106.09062			(0.00206) 1503	0.00206
Total			170029	160842	21730	0.222955

Table 1b. Point source releases of molecular chlorine in Harris County

Facility	Latitude	Longitude	1993 TRI reported releases lb/yr	1998 TRI reported releases (t/d) lb/yr	TNRCC PSDB (t/d) lb/yr	Proposed Emission Rate t/d
Crown Central Petroleum Corp. Houston Refy.	29.719417	-95.211528	66723	(0.09249) 67518	(0.12604) 92001	0.12604
Deer Park Refining L.P.	29.724804	-95.133736		(0.015068) 11000		0.015068
Donohue Inds.Inc.	29.884734	-95.116083	12765	(0.02062) 15055	(0.0023) 1679	0.02062
Dow Chemical Co. La Poerte Site	29.711811	-95.082657	13	(0.0016) 1100	(0.0004) 292	0.0016
Equistar Chemicals – Bayport Chemicals Plant	29.617992	-95.085799		(0.00252) 1840		0.00252
Equistar Chemical LP(Deer Park)	29.7115	-95.0675			(0.00104) 759	0.00104
Equistar Chemical LP(Pasadena)	29.6323	-95.0805			(0.00252) 1840	0.00252
GB Biosciences Corp.	29.762846	-95.172676	10868	(0.03175) 23179	(0.03092) 22572	0.03175
Lubrizol Corp., Deer Park Facility	29.720194	-95.11333	28588	(0.003207) 2341	(0.00267) 1949	0.003207
Oxy Vinyls L.P. LA Porte- VCM Plant	29.726667	-95.077778	12304	(0.005205) 3800	(0.00863) 6300	0.00863
Oxy Vinyls L.P. Deer park C/A	29.7161	-95.1236	4400	(0.002236) 1632	(0.00516) 3767	0.00516
Phillips Petroleum Co. Houston Chemical Complex	29.735167	-95.179657	2400	(0.002877) 2100		0.002877
PPG Inds. Inc	29.65576	-95.037621	1000	(0.0014) 1022		0.0014
Simpson Pasadena Paper Co.	29.714463	-95.196193	16400	(0.006877) 5020		0.006877
Zeneca AG Prods. Inc. Bayport Plant	29.626778	-95.086639	1460	(0.001918) 1400	(0.00191) 1394	0.001918
AES Deepwater Generation Plant	29.617992	-95.085799	7368			
Air Liquide America Corp.	29.614289	-95.042998	5025	(0.0000068) 5		0.0000068
Aristech Chemical Corp.	29.701714	-95.087059	1073			
DXI IND. INC	29.757047	-95.13568	1000	(0.001303) 951		0.001303
Ethyl Corp	29.735245	-95.169899	3519	(0.001223) 893		0.001223
Millennium Petrochemical INC.La Porte Plant	29.713889	-95.068333	3700	(0.000055) 40	(0.00006) 44	0.00006

Mobil Chemical Co. Houston Olefins Plant	29.704948	-95.25354	2639			
Oxy Vinyls L.P Deer Park-VCM Plant	29.7161	-95.1236	4280	(0.001) 730	(0.00516) 3767	0.00516
Shell Chemical L.P	29.724804	-95.133736	15386		(0.00217) 1584	0.00217
Valero Refining Co.-Texas	29.718431	-95.253716	13015	(0.000342) 250		0.000342
Witco Corp., La Porte Plant	29.702778	-95.075556	2903	(0.000595) 434		0.000595
Shell Oil Corp.	29.72291	-107.12234			(0.00555) 4052	0.00555
Total			216829	140313	142043	0.2476368

Table 1c. Point source releases of molecular chlorine in Brazoria County

Facility	**Latitude**	**Longitude**	**1993 TRI reported releases lb/yr**	**1998 TRI reported releases (t/d) lb/yr**	**TNRCC PSDB (t/d) lb/yr**	**Proposed Emission Rate t/d**
Alac, Freeport ASU	28.967338	-95.350066		(0.002014) 1470		0.002014
Dow Chemical Co. Freeport Texas	28.969389	-95.379528	220000	(0.490411) 358000	(0.09409) 68686	0.490411
Phillips 66 Co. Sweeny Complex	29.073317	-95.744797	17552	(0.020548) 15000	(0.00939) 6855	0.020548
Rhodia Inc.	28.990141	-95.358894	132	(0.001948) 1422		0.001948
Chevron Phillips Chemical Co.LP	29.0773	-95.7473			(0.01123) 8198	0.01123
Total			336622	375892	83738	0.526151

Table 1d. Point source releases of molecular chlorine in Galveston County

Facility	***Latitude***	***Longitude***	***1993 TRI reported releases lb/yr***	***1998 TRI reported releases (t/d) lb/yr***	***TNRCC PSDB (t/d) lb/yr***	***Proposed Emission Rate t/d***
BP AMOCO TEXAS CITY BUSINESS UNIT	29.349676	-94.929268	2200	(0.003425) 2500	(0.00406) 2964	0.00406
Valero Refining Co.	29.36893	-94.91407	320	(0.019726) 14400	(0.01973) 14403	0.01973
Total			2520	16900	17367	0.02409

Table 1e. Point source releases of molecular chlorine in Orange County

Facility	Latitude	Longitude	1993 TRI reported releases lb/yr	1998 TRI reported releases (t/d) lb/yr	TNRCC PSDB (t/d) lb/yr	Proposed Emission Rate t/d
Du Pont Sabine River Works	30.052603	-93.748169	2137	(0.002941) 2147	(0.00139) 1015	0.002941
Total			2137	2147	1015	0.002941

Table 1f. Point source releases of molecular chlorine in Chambers County

Facility	Latitude	Longitude	1993 TRI reported releases lb/yr	1998 TRI reported releases lb/yr	TNRCC PSDB (t/d) lb/yr	Proposed Emission Rate t/d
Bayer Corporation	29.75934	-106.9120			(0.002) 1460	0.002
Total					1460	0.002

2. Emissions of atomic chlorine precursors from cooling towers in southeast Texas

Cooling towers can be significant sources of atomic chlorine precursors. Molecular chlorine or hypochlorite are often added to the recirculating water used in cooling towers to control biofouling. There are three possible sinks for the chlorine added to cooling towers (Holzwarth et al, 1984a,b).

(1) *flashoff* occurs when the air stream flowing through the cooling tower strips volatile constituents from the water;
(2) The *blowdown* stream carries off a portion of the HOCl and its products; and
(3) A part of the HOCl is converted to other chemical species by reaction with contaminants in the water and the cooling system, referred to as *chlorine demand.*

In assessing atmospheric emissions from cooling towers, flash-off is the important factor to consider. Flash-off has been estimated both theoretically, based on mass transfer considerations, and through field measurements reported by Exxon (Holzwarth et al., 1984a,b) The field data are based on measurements made in November, 1981 at a U.S. refinery. Data were collected before, during and after a typical shock chlorination cycle. The shock consisted of 3 hours of chlorine addition at a rate of 28,000 g molecular chlorine gas/hr, followed by 1.5h 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 1000 gal/min (1,440,000gal/day or 1.44 mgd).

Field and laboratory data indicate that the fraction of chlorine that flashes is a strong function of pH and temperature, with higher pH and temperature leading to greater flash-off of atomic chlorine precursors. Reported flash-off fractions ranged from less than 0.1 to 1.0. To provide a preliminary estimate of the rate of atomic chlorine precursor release from cooling towers a flash-off fraction of 0.1 (10%) will be used. It should be recognized that this is only a preliminary estimate and actual values may vary by as much as an order of magnitude from this value.

Another uncertainty associated with estimating the rate of atomic chlorine precursors from cooling towers is the chemical form of the emissions. The chlorine may be released as HOCl, as Cl_2 or in other chemical forms such as chloramines (if ammonia is present in the water). The chemical form is significant because each compound

photolyzes at different rates. For example, Cl_2 would be expected to photolyze very rapidly (less than 10-20 minutes) after release, while the photolysis rate of HOCl will be a factor of 10 slower (Tanaka and Allen, 2001). For this work, Cl_2 emissions will be assumed, but it is recommended that the photochemical modeling also be performed assuming that emissions from cooling towers are in the form of HOCl.

Assuming a flash-off fraction of 0.1 and that the emissions are in the form of molecular chlorine, an emission estimate for the 1.44 mgd cooling tower can be calculated:

(28 kg/hr * 3hr/day + 17 kg/hr * 1.5hr/day + 3.8 kg/hr * 19.5hr/day) * 0.1

=18.4 kg chlorine emission /day for a 1.44 mgd cooling tower

This estimate is consistent with other estimates of chlorine use in cooling towers. These corroborating measurements are from a study performed by SAI to estimate chloroform emissions in the South Coast Air Basin (Rogozen, et al., 1988). Based on surveys performed on refineries in the South Coast Air Basin, chlorine use in cooling towers (overwhelmingly in the form of chlorine gas) was 500,000 pounds per year for the 7 refineries that responded to the survey (half of the refineries in the region). This corresponds to 200 pounds of use per day per refinery. Assuming a flash-off fraction of 0.1, 200 pounds per day implies emissions of 20 pounds per day per facility.

To extrapolate the chlorine emission rate per tower to a region wide inventory requires an estimate of the number of cooling towers that use chlorination in the Houston Galveston area. There are both commercial and industrial cooling towers in the Houston Galveston area.

Frashier (2001) estimates that there are approximately 1000 commercial cooling towers in Houston, not including industrial cooling towers in chemical plants and refineries. The commercial towers are in a variety of facilities such as hotels, hospitals, schools and universities, and most large buildings. The data from Frashier indicate the "average" commercial cooling tower uses about 500,000 gallons of water per month, but can range from 50,000 gallons/month in small towers, such as in older apartment buildings, to 4,000,000 gallons per month for large systems such as the Bush Intercontinental Airport. 500,000 gallons per month (17,000 gallons per day) is the annual average, but commercial towers use twice as much water during the summer and much less during the cool winter months when there is little cooling demand on air conditioning systems.

While the number of cooling towers is substantial, and the net cooling demand from these towers is significant, data from the South Coast Air Basin (Rogozen, et al., 1988) indicate that relatively few small capacity cooling towers use chlorine as a biocide. Therefore, we will assume that virtually all chlorine use in cooling towers is confined to the chemical manufacturing and refining sectors. Despite assuming that chlorine use in cooling towers is limited to these sectors, it is still difficult to estimate total chlorine use in this application. Not all facilities use chlorine as a biocide, and data on cooling loads at chemical manufacturing and refining facilities are not publicly available. To accurately estimate chlorine use in cooling towers would require, at a minimum, systematic surveys of facility practices and/or surveys of chlorine suppliers. Collection of these data is beyond the scope of this project.

Therefore, to arrive at an order of magnitude estimate of chlorine use in cooling towers, we will assume that there are approximately 350 cooling towers with capacities of approximately 1 mgd in southeast Texas using chlorine as a biocide. This leads to estimated emissions of:

18.4 kg/day/cooling tower * 350 cooling towers = 6,000 kg/day

Thus, our best estimate for molecular chlorine emissions from cooling towers is 6 metric tons (mt) per day, however, this should be considered only an order of magnitude estimate and the emissions may be in the form of HOCl, rather than Cl_2.

For modeling purposes, the location of cooling towers using chlorine as a biocide will be assumed to be distributed in the same way as point source NOx emissions from chemical manufacturing and petroleum refining facilities. This assumption is based on the fact that both heating and cooling demands at large facilities will be greater than at small facilities. A summary of the magnitude, spatial allocation and temporal allocation of the emissions from cooling towers is given below.

Summary of emissions from cooling towers:

Total emissions in 11 county area: 6 tons/day of molecular chlorine as Cl_2 or 9 tons/day as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl)

Spatial distribution of emissions: spatial distribution pattern is assumed to be the same as the top 50 point source NOx emissions, excluding electricity generating units (EGU). The NOx emissions at a point source, divided by the total non-EGU point source NOx emissions, was multiplied by the total atomic chlorine precursor emissions from cooling towers to arrive at the emissions at each site.

Temporal distribution of emissions: It was assumed that shock chlorination would be done during 7AM-5PM shifts. The emission rate from 7-12 was assumed to be double the rate from 12-5, so the fraction of emissions released each hour was 0.133 for each hour between 7 and noon and .0666 for each hour between noon and 5PM.

Stack parameters: Stack parameters for a typical cooling tower were assumed to be: (Height=20m; Diameter=5m; T=294K; Stack gas vel.=1m/s) These data were drawn from the TNRCC PSDB as representative data for cooling towers.

3. Chlorine Emissions from Water and Wastewater Treatment in Metropolitan Houston

Water and wastewater treatment accounts for approximately 5% of chlorine use in the United States (Ayres, 1997) and therefore should be considered as a potential sources of Cl_2 or HOCl emissions. The subsections below separately estimate potential atomic chlorine precursor emissions for water and wastewater treatment.

3.A. Chlorination in Water Treatment

Houston obtains 65% of its municipal water supply from surface water sources and 35% from ground water sources. Houston water treatment plants adjust chlorine dosages according to the water source. For surface and ground water, the chlorine dosages are 3 ppm (mass) chloramines and 2 ppm free chlorine, respectively. Residual chlorine concentrations are 1-1.5 ppm and 1 ppm, respectively (Greenlee, 2001). The difference between the chlorine dosage and the free chlorine residual is referred to as the chlorine demand, where chlorine demand is defined as:

$$\text{Chlorine demand} = \text{Chlorine dose} - \text{Chlorine residual}$$

The chlorine demand is the result of a variety of potential chlorine sinks including reactions promoted by sunlight, reactions with inorganic compounds, reactions with ammonia, reactions with organic compounds and volatilization. Based on interviews with water treatment experts (Lawler, 2001), we suggest assuming that 20% of the chlorine demand is due to volatilization.

If the chlorine volatilization rate per volume of water treated is known, then a preliminary estimate of chlorine releases requires only an estimate of the volume of water processed. The population of Houston is 1.8 million and the population of the county metropolitan statistical area is 4.3 million (Greater Houston Press Kit, 2001). The City of Houston supplies water to about 2.35 million people (TNRCC, 2001). The annual average water flow rate, for the City of Houston, is 315 million gallons per day (MGD) (Greenlee, 2001). However, summer time water flow rates are significantly larger (469.546 MGD; City of Houston, 2001), and the summer water usage rates will be used in this analysis.

To estimate the magnitude of atomic chlorine precursor emissions from water treatment plants, it was assumed that 20% of chlorine demand was due to volatilization and that the water usage was 470 MGD. Table 2 summarizes the data used to estimate the emissions. The estimated releases are small (a few hundred kg/day) compared to estimated releases from cooling towers. Since this estimate is based on a relatively conservative (high) flash-off fraction (0.2) these emissions are likely to be negligible.

$$0.2 * (2-1) \text{ ppm} * 470 \text{ MGD} * 0.35 = 100 \text{ kg/day}$$
(chlorine treatment of ground water)

$$0.2 * (3-2.25) \text{ ppm} * 470\text{MGD} * 0.65 = 200 \text{ kg/day}$$
(chloramine treatment of surface water)

Table 2. Data on Chlorination Practices for Water Treatment in Houston

	Ground Water	Surface Water
Water Source Percentage	35%	65%
Free Chlorine Dosage	2ppm	3ppm
Residual Free Chlorine(Arithmetic Average)	1ppm	2.25ppm
Chlorine Reacted with Organic Matter	< 30ppb	<30ppb
Water Flow Rate during SummerTime	470MGD	

3.B. Chlorination in Wastewater Treatment Plant

Houston has 41 wastewater treatment plants (City of Houston, 2001b). Table 3 lists the name, address, and phone number of each wastewater treatment plant in Houston. The purpose of chlorinating during wastewater treatment prior to discharge of the final effluent is to kill pathogenic (disease causing) bacteria, viruses, and other microorganisms. Pathogenic microorganisms may enter the wastewater collection system from homes, hospitals, or other sources, and pose a threat to human health if the discharged effluent is later used for recreation or drinking water.

In order to estimate how much chlorine is released from wastewater treatment plants during chlorination, it was assumed that the quantity of chlorine used is similar to that used by water treatment plants since the City of Houston has no recorded chlorination data for wastewater treatment. The annual average quantity of wastewater that is treated in Houston is 234.588 MGD (Whitmey, 2001), which is two thirds of the annual water treatment flow rate. Wastewater may have a higher chlorine demand. Therefore, in the absence of specific data, it was assumed that the chlorine emissions during chlorination

of wastewater are similar to the emission rates due to water treatment, a few hundred kilograms per day.

In addition to volatilization during treatment, additional chlorine emissions may be associated with removal of residual chlorine. Following the chlorine contact basins, sulfur dioxide is added to the wastewater to remove residual chlorine to concentrations below 0.01 mg/L in order to protect fish and other aquatic life. The sulfur dioxide converts the free chlorine to chloride. It is reasonable to expect that the sulfur dioxide will scavenge a large fraction of the residual free chlorine. This dechlorination with sulfur dioxide is required if a wastewater treatment plant treats 1 MGD or more. However, if the plant treats less than 1 MGD, dechlorination is not required (Whitmey, 2001). Assuming that wastewater treatment plants handle more than 1 MGD, chlorine loss due to volatilization of residual chlorine is likely to be negligible.

Releases due to volatilization during wastewater treatment =
two thirds of the value assigned to water treatment based on the lower volumes of wastewater treated =
200 kg/day

Table 3. Wastewater treatment facilities in Houston

FACILITY NAME	ADDRESS	PHONE NUMBER
ALMEDA SIMS	12319 1/2 ALMEDA ROAD	713 - 433 - 1717
BELTWAY CEDAR BAYOU	10518 BELLAIRE 2804 HUFFMAN EASTGATE	281 - 498 - 4127
CHOCOLATE BAYOU	9600 MARTIN LUTHER KING	
CLINTON PARK	9030 CLINTON DRIVE	713 - 672 - 2433
EASTHAVEN	8545 SCRANTON	713 - 948 - 9060
F.W.S.D.# 23	8219 KELLET	713 - 636 - 8209
GREENRIDGE	6301-#1 W.FUQUA	281 - 437 - 6299
HOMESTEAD	5565 KIRKPATRICK	713 - 675 - 3910
IMPERIAL VALLEY	15500 COTILLION	281 - 448 - 4226
INTERCONTINENTAL KEEGANS BAYOU	2450 RANKIN 9400 WHITE CHAPEL LN.	281 - 233 - 2572
METRO CENTRAL	12815 GALVESTON ROAD	
NORTHBELT	14506 SMITH	713 - 441 - 1786
NORTHBOROUGH	13131 NORTH FREEWAY	
NORTHEAST	655 MAXEY ROAD	713 - 453 - 2946
NORTHGATE	303 BENMAR	281 - 875 - 5551
NORTHWEST	5423 MANGUM	713 - 683 - 6789
PARK TEN	16500 PARK ROW	281 - 646 - 6606
SAGEMONT	11700 SAGEARBOR	281 - 922 - 2308
SIMS BAYOU	9500 LAWNDALE	713 - 926 - 1040
SIMS SOUTH SOUTHEAST	3005 GALVESTON ROAD 9610 KINGSPOINT	713 - 847 - 5158 713 - 731 - 6003
SOUTHWEST	4211 BEECHNUT	713 - 622 - 8031
TURKEY CREEK	1147 ENCLAVE PARKWAY	
UPPER BRAES	13525 OLD WESTHEIMER	281 - 752 - 2231
W.C.I.D.# 47	7410 GALVESTON	713 - 946 - 9057
W.C.I.D.# 76	13535 RIVER TRAIL DR.	281 - 590 - 6219
W.C.I.D.# 111	10601 HUNTINGTON POINT	281 - 568 - 7598
WEST DISTRICT	255 ISOLDE	713 - 468 - 0875
WESTWAY WHITE OAK	10273 GENARD 7103 GULF BANK RD.	 713 - 937 - 0433
WILLOWBROOK	7101 W. GREENS RD.	281 - 807 - 9586
69TH STREET	2525 MACARIO GARCIA	713 - 671 - 4200
TIDWELL TIMBER	10155 TIDWELL	
M.U.D.# 203	1215 GEARS ROAD	281 - 825 - 8124
M.U.D.# 48	SORTERS ROAD	281 - 358 - 6885
HUNTERWOOD	6230 S.LAKE HOUSTON PK WY	
KINGWOOD CENTRAL	3928 KINGWOOD DR.	
FOREST COVE	729 HAMBLEN RD.	

Summary of emissions from water and wastewater treatment:
Since the emission estimates for water and wastewater treatment are more than an order of magnitude less than other potential sources, these emissions will not be incorporated into the inventory used for modeling.

4. Atomic chlorine precursor emissions from swimming pool treatment

Swimming pools are chlorinated for sanitation. According to recent estimates by the National Spa and Pool Institute (as cited in Whitfield, 2000), there are about 7 million residential pools in the continental United States. Therefore, we can estimate the number of swimming pools in Houston as the ratio of the population as follows:

Number of swimming pools in Houston

= Number of total residential swimming pool in US * Population of Houston/U.S. Population

= 7,000,000*1,800,000/283,800,000 = 44,000 swimming pools

Because the average summer temperature in Houston is high, it was assumed that Houston has 1.5 times more swimming pools than the calculated average

.

44,000 * 1.5 = 66,000 swimming pools in the city of Houston (1.8 million population)

This estimate appears consistent with a more detailed estimate performed by SAI for the South Coast Air Basin, which concluded that the Los Angeles area had 250,000 in-ground swimming pools for a population of approximately 11 million (Rogozen, et al., 1988). The study further 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:

$$0.1 * 2 \text{ gal} / 7 \text{ days} * 3.78 \text{ kg} / \text{gal} * 66{,}000 \text{ pools} = 7000 \text{ kg/day}$$

If the population of the 11 county region is assumed to be roughly double the population of the City and if it is assumed that roughly half of the chlorine used in pools volatilizes, the total emissions from pools will be 7000 kg/day.

Another approach to estimating the rate of volatilization from pools would be to apply an overall mass transfer coefficient, coupled with estimates of pool surface area and free chlorine concentration.

Rogozen, et al. (1988) estimated an average pool surface area of 40 m^2 for southern California, and an average mass transfer coefficient for chloroform of 22 :g m^{-2} min^{-1}, which is a weighted average of mass transfer coefficients under agitated and non-agitated conditions. Adjusting for the difference in molecular weights and Henry's law constants between chloroform and hypochlorous acid suggests that an overall mass transfer coefficient for hypochlorous acid should be roughly 10-100 :g m^{-2} min^{-1}. This suggests the following calculations:

Area of pools:
$40m^2$ per pool * 66,000 pools per 1.8 million residents * 4.3 million residents =
$6.3* 10^6$ m^2

Mass volatilized:
10-100 :g m^{-2} min^{-1} * $6.3* 10^6$ m^2* 1440 min/day = 90,000 – 900,000 g/day

This calculation assumes a constant hypochlorous acid concentration of 2 ppm. The high volatilization rate indicates that the chlorine will evaporate in far less than a day and that it would be difficult to maintain a free chlorine concentration of 2 ppm for a pool without continuous chlorine addition.

The volatilization rates also suggest that if chlorination is done with batch application, most of the chlorine applied will evaporate in less than a day. Assuming that the volume of a typical pool is 50,000 L (5m * 5m * 2m = $50m^3$), and the required chlorine concentration in the swimming pool is 2-2.5 ppm (Taylor Technology, 2001), an estimate can be made of the residual chlorine available in a pool.

Number of swimming pools * average volume* required chlorine concentration in the swimming pool * volatilization factor (2/week) =

66000 * 4.3/1.8 number of swimming pool* 50000L * 2 ppm * 2/7 days =
4500 kg/day

All residual chlorine is assumed to be emitted to the atmosphere, implying that continuing chlorine demand after the initial chlorine demand, is relatively small. So, if a typical pool owner chlorinates twice per week until a residual chlorine concentration of 2 ppm is attained, and all residual chlorine evaporates (in much less than a day) then the daily emission rate in the Houston Galveston area is of order 4 mt/day.

Taking all of these estimates into account, the emissions of HOCl or Cl_2 from pools could be expected to be 4-7 mt/day. As a first approximation, these emissions can be assumed to be 5 t/day and should be distributed according to population and income level.

Summary of emissions from swimming pool disinfection:

Total emissions in Houston area: 5 tons/day of molecular chlorine as Cl_2 or 7.5 tons/day as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl)

Spatial distribution of emissions: The spatial distribution pattern is assumed to be primarily dependent on population and income distributions. The number of households with annual incomes greater than $75,000 were determined for each grid cell in the region. The fraction of residential pools in each grid cell is assumed to be equal to the fraction of the households in the region with greater than $75,000 in annual income that are in that grid cell. In addition to the information on the spatial distribution of residential pools, by household income, a survey of the locations of municipal pools was conducted using a map provided by the City of Houston. The number of municipal pools in each grid cell was determined and it was assumed that a municipal pool had emissions equal to 10 residential pools. Pools associated with schools were not counted based an interview with a competitive swimmer from the Houston area who indicated that most school pools were indoors.

The emissions will either be modeled as an area source or will be modeled as a point source in the middle of each grid cell. The point source would be given default stack parameters that would confine the emissions to the first vertical layer in the model, and no plume-in-grid calculations would be performed on these emissions. Therefore, the point source approach would be equivalent to the area source approach.

Temporal distribution of emissions: It was assumed that shock chlorination would be

done relatively early in the day and that this would result in volatilization throughout the afternoon. Emissions will be assumed to occur at a constant rate between noon and 8 PM.

5. Atomic chlorine precursor emissions from the reactions of sea salt aerosol

A number of investigators (for example, Spicer, et al., 1998) have suggested that ozone and other components in photochemical smog react with chloride in sea salt to release Cl_2. Direct, observational data on the rates of chlorine release via this process are very limited. However, based on measurements made near the coast of Long Island, New York, Spicer, et al. (1998) have estimated that the formation rate of molecular chlorine can be up to 330 parts per trillion per day. This formation rate is based on typical sea salt aerosol concentrations (30 sea salt particles of diameter 1 :m per cm^3) and moderate ozone concentrations (40 ppb).

To apply this formation rate to the Houston-Galveston area, it will be assumed that the formation occurs in a volume 300 km by 10 km by .1 km located over the Gulf of Mexico, between the Louisiana border and Corpus Christi. The production rate of molecular chlorine would be:

$$300 * 10 * .1 * 10^9 \text{ m}^3 * 330 * 10^{-12} \text{ moles chlorine per mole air} * 1 \text{ mole air} / .0224 \text{ m}^3 * .071 \text{ kg chlorine/mole } Cl_2 = 300 \text{ kg/day}$$

This source of Cl_2 is potentially significant, compared to anthropogenic sources, but the emission estimates are highly uncertain and the source is distributed over a very large area.

This source will be represented in the model as an area source of molecular chlorine over the Gulf of Mexico. The source strength will be assumed to be 10^{-4} g/m^2 (10^{-7} kg/m^2) of sea surface area per day.

Summary of marine emissions based on the conversion of sea salt chloride to atomic

chlorine precursors:

Total emissions: 10^{-7} kg/m^2 of Cl_2 per day or $4*10^{-1}$ kg per day per 2 km by 2 km grid cell or 1.6 kg per day per 4 km by 4 km grid cell.

Spatial distribution of emissions: Emissions will be assigned to grid cells that are anticipated to have both relatively high sea salt concentrations and ozone (or other air pollutant) concentrations sufficient to convert the sea salt to atomic chlorine precursors. This will include the two grid cells closest to the coast, over the entire length of the Gulf coast, plus all grid cells covering Galveston Bay. The emissions will either be modeled as an area source or will be modeled as a point source in the middle of each grid cell. The point source would be given default stack parameters that would confine the emissions to the first vertical layer in the model, and no plume-in-grid calculations would be performed on these emissions. Therefore, the point source approach would be equivalent to the area source approach.

Temporal distribution of emissions: It will be assumed that the emissions are evenly distributed over daylight hours (6 AM – 6 PM).

6. Area sources of atomic chlorine precursors associated with tap water use

On average, individuals use almost 100 gallons of drinking water per person per day. Traditionally, water use rates are described in units of gallons per capita per day (gpcd), gallons used by one person in one day (U.S. EPA, 2001). Water use amounts per capita per day are shown in the following table:

Table 4. Water Use per Capita

Water Use	Flow Rate
Bath	20gpd
Toilet,flushing	24gpd
Laundary	8.5 gpd
Dish washer	4 gpd
Garbage Disposal	1gpd
Drinking and Cooking	2gpd
Car washing	2.5 gpd
Lawn watering and pools	25gpd

Among these water uses, car washing and lawn watering are potential outdoor sources of chlorine emissions. Water use for these sources is:

2.5 + 25 = 27.5 gpd

27.5 gpd * 1,800,000 population = 50,000,000 Gallons per day

Tap water residual chlorine concentration is calculated as follows using the residual chlorine concentrations of 2.25 ppm for 65 % surface water and 1ppm for 35% ground water:

2.25ppm * 0.65 surface water + 1ppm *0.35 ground water =1.81 ppm

1.81ppm *50,000,000 gpd =190 * 10^6 L/day *1.81= 300 kg/day

Summary of emissions from water use:
Since the emission estimates for water use are more than an order of magnitude less than other anthropogenic sources, these emissions will not be incorporated into the inventory used for modeling.

7. Area sources of atomic chlorine precursors associated with reactions of chlorinated organics in the atmosphere

Another possible source for chlorine atoms in the troposphere is the photochemical decomposition of organochlorine compounds. Chlorine atoms are produced from the photochemical reactions of organochlorine compounds such as chlorinated solvents and pesticides (Carter, et al., 1997a,b). For the chlorinated solvent, trichloroethene (TCE), the yield of chlorine atoms has been estimated at 60% of the moles of TCE initially present (Carter, et al, 1997b; Tuazon, et al., 1988). For the agricultural pesticide, chloropicrin, the yield is expected to be near unity because photolysis is the primary consumption pathway and this compound does not react with hydroxyl radical to a significant extent (Carter, et al., 1997a).

A detailed inventory of organochlorine compound emissions for the eleven-county Houston-area is not within the present scope of work. Therefore, the contribution of organochlorine compounds is not considered here. However, a closer consideration of these compounds should be made if a more detailed inventory of chlorine atom

precursors is performed in the future.

References

R.U. Ayres, The Life Cycle of Chlorine, Part II, *Journal of Industrial Ecology*, 1 (2), 6 5-89 (1997).

W.P.L. Carter, D.Luo, and I.L. Malkina, "Investigation of the Atmospheric Reactions of Chloropicrin," *Atmos. Env.*, **31**, 1425 (1997a).

W.P.L. Carter, D. Luo, and I.L. Malkina, "Investigation of the Atmospheric Ozone For mation Potential of Trichloroethylene," Draft Report to the Halogenated Solvents Indust ry Alliance, August 29, 1997b.

City of Houston Homepage (2001a) http://www.cityofhouston.org ; data for 06/19/2000 to 09/18/2000 water usage

City of Houston Homepage (2001b) wastewater.controlcenter@cityofhouston.net and letter of City of Houston.

City of Houston Homepage (2001c) municipal swimming pool map, http://www.ci.houston.tx.us/department/parks/masterplan/pools.jpg

Greater Houston Convention and Visitors Bureau Press Kit, (2001) http://www.houston-guide.com/press/

G. Holzwarth, R.G. Balmer and L. Soni, The fate of chlorine and chloramines in cooling towers, *Water Res.*, 18, 1421-1427 (1984a).

G. Holzwarth, R.G. Balmer and L. Soni, The fate of chlorine in recirculating cooling to wers, *Water Res.*, 18, 1429-1435 (1984b).

City of Houston Homepage (2001) http://www.ci.houston.tx.us/pwe/wateruse.html; data for 06/19/2000 to 09/18/2000 water usage

David Frashier (2001), Cost Containment Engineering, 210-509-0825, http://twri.tamu.edu/twripubs/WtrSavrs/v6n1/article-3.html

Jim Greenlee (2001), Acting Deputy Assistant Director, Water Production Branch, City of Houston, jim.greenlee@cityofhouston.net

D. Lawler, University of Texas at Austin, preliminary estimate of upper bound of potenti al volatilization of free chlorine in water and wastewater treatment, based on profession al judgement, 2001.

M.B. Rogozen, H.E. Rich, M.A. Guttman, D. Grosjean, and E.L. Williams "Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin", Science Applic ations International Corporation, Final Report to the State of California Air Resources B oard, Contract A4-115-32, April, 1988.

C.W. Spicer, E.G. Chapman, B.J. Finlayson-Pitts, R.A. Plastridge, J.M. Hubbe, J.D. Fast, and C.M. Berkowitz, Unexpectedly high concentrations of molecular chlorine in coastal air, *Nature*, 394, 353-356 (1998).

P.L. Tanaka, P.L., et al. "Anthropogenic Sources of Chlorine and Ozone Formation in Urban Atmospheres," *Env. Sci. Tech*., 34, 4470 (2000).

P.L. Tanaka and D.T. Allen, "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

Taylor Technology, Inc. , Brochure on swimming pool treatment chemicals, Austin, 512-451-5254

Texas Natural Resource Conservation Commission, TNRCC (2001), http://www.tnrcc.state.tx.us/permitting/waterperm/pdw/droughtw.html, this site indicates that the population served by the City of Houston is 2,354,040

E.C. Tuazon, R. Atkinson, S.M. Aschmann, M.A. Goodman, and A.M. Winer, "Atmospheric Reactions of Chloroethanes with the OH Radical," *Int. J. Chem. Kinet.*, 20, 241 (1988).

U.S. Environmental Protection Agency, 2001, http://www.epa.gov/OGWDW/wot/howmuch.html

T.W. Whitfield (2000) An evaluation of swimming pool alarms, Cosumer Product Safety Commission, http://www.cpsc.gov/library/alarm.pdf

Roger Whitmey Chief Engineer in Wastewater Operations in City of Houston. 713-641-9189, roger.whitney@cityofhouston.net

Randell Meyer, competitive swimmer in Houston area, interview of school swimming p ool , randellm@che.utexas.edu

.