Development of an Area and Mobile Sources Inventory for Reactive Chlorine Compounds in Southeast Texas

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ABSTRACT

Reactive chlorine compounds are an often overlooked group of compounds that may have played a catalyst role in tropospheric ozone formation in the Houston area. In the Houston area an ozone episode occurred in August of 1993, when an alkane-rich hydrocarbon plume passed over anthropogenic sources of molecular chlorine (Cl_2). Although the troposphere contains over 200 reactive chlorine gases, eight of them have been reported to constitute a majority of the tropospheric chlorine burden. To investigate the importance of chlorine compounds in the atmospheric chemistry of ozone non-attainment areas in Texas, the Texas Natural Resources Conservation Commission (TNRCC) is conducting a series of inventories and atmospheric modeling studies for reactive chlorine emissions. As a component of these TNRCC studies, Eastern Research Group (ERG) developed an inventory methodology for reactive chlorine emissions from mobile and area sources, and conducted an emission inventory for Southeastern Texas to demonstrate the methodology. Some of the sources that were inventoried by ERG included swimming pools, commercial cooling towers, laundry bleach, sea salt aerosols and crustal dust chlorine.

BACKGROUND

Reactive chlorine compounds are an often overlooked group of compounds that may have recently been involved as a catalysts for tropospheric ozone formation in the Houston area. In the Houston area an ozone episode occurred in August of 1993, when an alkane-rich hydrocarbon plume passed over anthropogenic sources of molecular chlorine (Cl_2). Some hours after the plume had passed over the chlorine sources, the following circumstances were observed: hydrocarbon compounds (alkanes) were rapidly lost from the plume; and a large increase in ozone concentration was observed. Although the troposphere contains over 200 reactive chlorine gases, eight of them have been reported to constitute a majority of the tropospheric chlorine burden: methyl chloride (chloromethane), hydrochloric acid, methyl chloroform (1,1,1-trichloroethane), methylene chloride, chloroform, Cl_2^*, phosgene and chlorodifluoromethane. To investigate the importance of chlorine compounds in the atmospheric chemistry of ozone non-attainment areas in Texas, the Texas Natural Resources Conservation Commission (TNRCC) is conducting a series of inventories and atmospheric modeling studies for reactive chlorine emissions. As a component of these TNRCC studies, Eastern Research Group (ERG) was contracted by TNRCC to develop an inventory methodology for reactive chlorine emissions from mobile and area sources, and to conduct an emission inventory for Southeastern Texas to demonstrate the methodology. This paper presents the reactive chlorine inventory methodology developed for the TNRCC and shares the results of this inventory for area and mobile sources for Southeast Texas.

IDENTIFICATION OF REACTIVE SPECIES

Of the common trace elements in the troposphere, the reaction cycle of chlorine is the most poorly understood and delineated. Condensed “chlorine” phases consisting of sea salt aerosol and chloride in precipitation are abundant and frequently measured. Chlorine compounds occurring in the gas phase are divided between: (1) Fully halogenated and saturated (i.e., no carbon-carbon double bonds) organic compounds, unreactive in the troposphere yet studied extensively for their role in depleting stratospheric ozone; and (2) Reactive chlorinated compounds, reacting according to numerous pathways in the troposphere to produce the reactive chlorine species (Cl•) and contributing to the formation of ozone: infrequent measurement, budgets relatively unspecified.

The tropospheric reactive chlorine budget is significantly influenced by anthropogenic sources and is definitely not in equilibrium. Although the troposphere contains over 200 reactive chlorine gases, eight of them constitute almost all of the tropospheric chlorine burden: methyl chloride (chloromethane, $CHCl_3$), hydrochloric acid (HCl), methyl chloroform (1,1,1-trichloroethane, CCl_3CH_3), methylene chloride (dichloromethane, CH_2Cl_2), chloroform ($CHCl_3$), Cl_2^* (excited molecular chlorine), chlorodifluoromethane (CHF_2Cl) and phosgene ($COC1_2$), with three-fourths of the burden due to methyl chloride and methyl chloroform alone.[1] A review of the anticipated trends in several of the reactive chlorine gas sources suggests that global average concentrations of tropospheric chlorine are very likely to increase over the next several decades, with the most important factor in this trend being increased combustion of coal. Fossil fuels contain chlorine, and that chlorine is liberated as HCl and methyl chloride when coal is burned.[2,3,4] Chlorine chemistry in the tropospheric boundary layer is expected to assume increased importance in urban areas; the chemistry of sea salt aerosols will also assume importance in coastal areas.

The elucidation of chlorine reaction mechanisms in the atmosphere is an extremely active area of research, with two areas of agreement (and many areas of disagreement) among researchers: (1) The reactive chlorine species in atmospheric chemistry is the chlorine radical (denoted as Cl•), an atomic chlorine species with an unpaired electron; and (2) The mechanisms of reaction of this chlorine species are complex. The chlorine radical is formed photolytically, from the input of solar energy, and the species could also be formed from organochlorine compounds, from molecular chlorine (the diatomic molecule, Cl_2), from volatile inorganic chlorinated species (such as chloramines, formed from swimming pool chlorination) and sea salt aerosols. This atomic chlorine species reacts with alkanes up to two orders of magnitude faster than hydroxy radicals and can promote the formation of ozone in the presence of VOCs and oxides of nitrogen.[5] A few atmospheric chamber studies involving the introduction of chlorine-containing species into a synthetic atmosphere have been performed to characterize the reactivity of certain chlorine-containing species (trichloroethylene,[6] chloropicrin,[7] and molecular chlorine[8]) but many more environmental chamber studies and modeling studies will be needed to elucidate the complex reaction sequence of chlorine in the atmosphere.

Extensive research is currently being performed on the role of sea salt aerosols in the formation of molecular chlorine and precursors to reactive chlorine (Cl•). Sea salt particles formed by wave action are ubiquitous in the marine boundary layer and in coastal regions. Chlorine atoms formed from sea salt can destroy ozone through direct reaction, but can also react rapidly with organic molecules leading to ozone formation in the presence of sufficient quantities of oxides of nitrogen. A detailed mechanism for these reactions has not yet been determined; this area of research is currently very active, with many investigators pursuing facets of the reactivity of sea salt aerosols.[9]

In the identification of reactive species, due consideration must be given to local factors and potential local or regional sources of reactive chlorine. Emissions inventories of regional industries can assist in this process, giving appropriate consideration to the global budget of chlorine-containing compounds and local use/production of these specific (or related) compounds. Factors such as location in a coastal area and the timing and direction of prevailing winds must be considered. Local chlorine-using or -producing activities must also be considered. For example, both molecular chlorine and other organic and inorganic compounds that can decompose to yield molecular chlorine are used in swimming pools and cooling towers for the purpose of disinfection and to prevent the growth of biological organisms that may cause fouling of the pool or tower or possibly disease in humans, if levels of certain bacteria are allowed to be high enough. A variety of chlorine-containing compounds are used for the purpose of disinfection; the exact chemistry of all of these chemicals is still undefined. Regional agricultural use of chlorine-containing compounds as pesticides or herbicides must also be considered. The identification of reactive chlorine-containing compounds is a complex process, with the exact nature of the chlorine species of concern unique to a given area.

Some chlorine-containing compounds likely to be considered reactive chlorine precursors are summarized in Table 1. Reported experimental data has established that these compounds enhance ozone production and are likely to be precursors to the reactive chlorine species, Cl•. Even if the rate of production of Cl• is slow for a given compound, if relatively large amounts of the compound are present in the urban environment, this compound is important to include when inventorying chlorine emission sources and for use in atmospheric reaction models.

DEVELOPMENT OF A METHODOLOGY

After identifying the eleven reactive chlorine compounds listed in Table 1, we developed a methodology to estimate the emissions of these reactive chlorine compounds from area, biogenic and mobile sources in Southeast Texas. The methodology inventoried these compounds on two temporal scales: total annual emissions for the year 2000 and typical daily emissions for a ozone exceedence period in 2000. The ozone exceedence period was defined as a typical week-day in late August, 2000. The Southeast Texas study area is shown in Figure1.

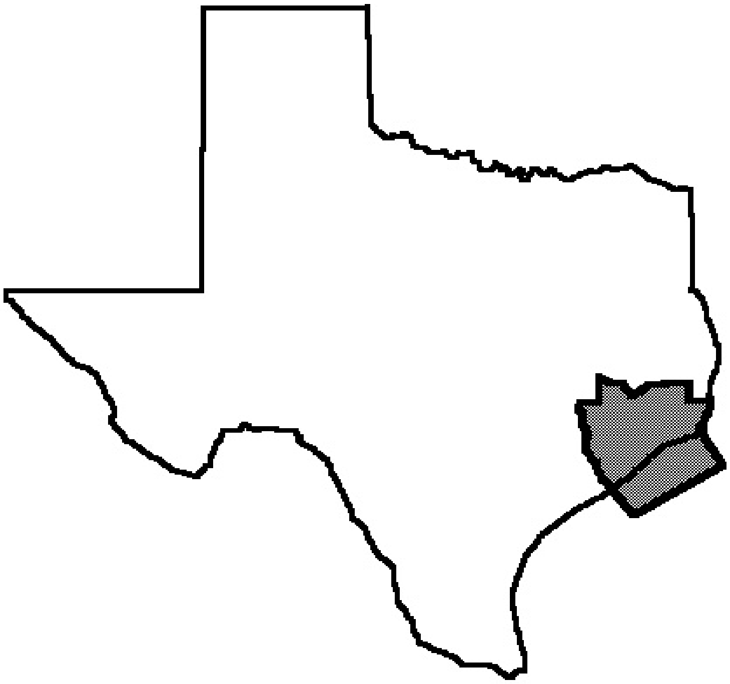

Figure 1. Southeast Texas Study Area

Table 1. Chlorine-Containing Compounds Likely to be Considered Primary Precursors of Reactive Chlorine

Compound	Comments
Cl_2 HOCl	The excited molecular chlorine species, Cl_2*, cannot be measured directly; measurable forms include Cl_2 and HOCl. Both chlorine ($C1_{2)}$ and hypochlorous acid (HOC1) are used in disinfection of swimming pools and cooling towers, as well as in various types of water treatment.
HCl	HCl is not photochemically reactive. Coastal urban areas have higher ambient HCl concentrations than continental urban areas, but the range of HCl is such that local sources often must dominate natural background. The excited form, HCl*, possibly should include NOCl, $ClNO_2$, and $ClNO_3$, but these compounds are products of reaction of the reactive chlorine species (Cl•) with NO_x rather than industrial products or agents. Produced in the marine atmosphere by direct volatilization from deliquescent sea salt aerosol acidified by incorporation of HNO_3 and/or H_2SO_4
NaOCl sodium hypochlorite	Commonly known as bleach; predecessor to molecular chlorine (Cl_2) and widely used in many industrial applications. Would not be emitted as sodium hypochlorite; emitted form would be hypochlorous acid or possibly molecular chlorine.
methyl chloride (CH_3Cl)	Most abundant of the reactive chlorine-containing gases in the troposphere; oceans and biomas combustion are primary sources. More tropospheric reactive chlorine is contained in methyl chloride than in any other species; it is nearly half the total burden. Rate of reaction to produce Cl• is not known.
methyl chloroform (1,1,1-trichloroethane) CH_3CCl_3	Hydrohalocarbon used as a substitute for CFC compounds; widely used as a degreasing solvent in electronics applications Rate of reaction to produce Cl• is not known.
chlorodifluoromethane (CFC-22) $CHClF_2$	Hydrohalocarbon used as a substitute for CFC compounds; widely used in refrigeration and as a foam-blowing agent Rate of reaction to produce Cl• is not known.
perchloroethylene CCl_2=CCl_2	Has seen wide industrial use, present in the background atmosphere; use is under increasing restriction because of toxicity concerns; considered a “reactive chlorine compound” because of the unsaturation in the molecule Rate of reaction to produce Cl• is not known.
trichloroethylene TCE CHCl=CCl_2	Has seen wide industrial use as a degreasing solvent; use is under increasing restriction because of toxicity concerns; considered a “reactive chlorine compound” because of unsaturation in the molecule. TCE showed a positive effect on NO oxidation, ozone formation, and radical levels in simulated photochemical smog systems, though the positive effect on ozone declined to zero with sufficiently low NO_x/reactive organic gas levels. TCE also enhanced the rate of alkane consumption. Rate of reaction to produce Cl• is not known.
methylene chloride (dichloromethane) $CHCl_2$	Has seen wide industrial use, present in the background atmosphere; use is under increasing restriction because of toxicity concerns Rate of reaction to produce Cl• is not known.
chloroform $CHCl_3$	Has seen wide industrial use, present in the background atmosphere; use is under increasing restriction because of toxicity concerns Rate of reaction to produce Cl• is not known.
phosgene $COCl_2$	Industrial intermediate, highly toxic, highly reactive; usually not emitted directly but is a product of the atmospheric breakdown of other halocarbons Rate of reaction to produce Cl• is not known.

Identification of Reactive Chlorine Emission Sources

Our first activity was to develop a list of the specific reactive chlorine sources that compose the area, biogenic, and mobile source groups in Southeast Texas. An extensive literature search identified three important data references. In 1999 the IGAC developed the global Reactive Chlorine Emissions Inventory (RCEI) which served as a starting point for identifying the sources of reactive chlorine compounds that may be important in Texas.[10] Since nine of the eleven reactive compounds identified in Table 1 are toxic, they are inventoried in the TNRCC comprehensive inventory of major HAP sources in Texas.[11] The TNRCC is also in the midst of a study to develop atmospheric models for investigating the effects of reactive chlorine emissions on the formation of tropospheric ozone in their larger metropolitan areas.[12] A review of these three references provided a list of thirteen area, biogenic and mobile emission sources that emit reactive chlorine compounds and would require emission estimation methodologies.

Although these references identified chlorine emissions in the exhaust of gasoline-powered vehicles further investigation revealed that these emissions are attributable to chlorine additives used in leaded gasoline. The emission of these compounds dropped to insignificant levels where unleaded gasoline was introduced in Europe [13]. For this reason and the fact that chlorinated compounds have not been identified in any exhaust measurements on US vehicles fueled with either gasoline or diesel fuels, we concluded that vehicle exhaust does not require inventory methodologies. Chlorinated compounds have been identified only in the heavy residual oils that are consumed by large commercial marine vessels. Since Southeast Texas includes marine ports, a methodology was developed for residual oil-fired marine vessels.

Based on the above analysis, Table 2 lists the area sources that required methodology development for inventorying reactive chlorine emissions and lists the reactive chlorine compounds that are emitted from each source.

Estimation Methodology Development

Methodologies were developed for inventorying each reactive chlorine compound emitted from each source listed in Table 2. The development of inventory methodologies began with a literature search for inventory methodologies that have already been developed for these sources and pollutants. The literature search included work conducted by the TNRCC, by the EPA and other state agencies, and by the international environmental research community. The productive references that resulted from this literature search and the detailed methodologies that were developed for the Table 2 sources are presented in the Final Report on The Southeast Texas Reactive Chlorine Inventory.

Chlorine emission estimates were sometimes reported in literature for a group of chlorine compounds instead of for a specific chlorine compound. This occurred, in part, because some data was derived from test methods that did not distinguish between the various inorganic chlorine species and because some data was based on equilibrium and kinetic modeling which was inconclusive as to which specific chlorine compound would be emitted. For four chlorine compound groups, we created an emission inventory methodology for the compound group instead of specific compounds: atomic chlorine precursors, particulate and inorganic chlorine, sea salt chlorine, and chlorides. In our methodologies for these groups, we calculate only the emission rate of the chlorine component of these chlorine compound emissions. Therefore, the emission rate for a group of chlorine compounds which might be include NaCl, HOCl and HCl would be reported in units of lbs/yr of total chlorine atoms. The mass of the non-chlorine atoms is not included in this emission rate. Before the emissions of a compound group can be used in atmospheric chemistry models, they may have to be subdivided into

Table 2. Sources of Reactive Chlorine Emissions

Source	Description	Major Compounds
1. Oceans	Gaseous emissions due to supersaturated surface waters, and sea salt aerosols that can undergo chemical transformations in the atmosphere, producing other reactive compounds	Methyl Chloride, Chloroform, Sea Salt, Cl^- , Methylene Chloride, Trichloroethene
2. Land	Gaseous emissions from soils, crustal dust particles, and emissions due to biological activity involving certain species of fungi	Methyl Chloride, Chloroform Particulate Cl^-
3. Residential Wood Burning	Gaseous and particulate emissions deriving from the use of wood in residential applications	Methyl Chloride, Particulate & Inorganic Chlorine, Methylene Chloride, Chloroform, Methyl Chloroform
4. Forest Wildfires	Gaseous and particulate emissions deriving from prescribed and naturally occurring forest fires	Methyl Chloride, Particulate & Inorganic Chlorine, Methylene Chloride, Chloroform, Methyl Chloroform
5. Agricultural Burning	Gaseous and particulate emissions due to agricultural field burning	Methyl Chloride, Particulate & Inorganic Chlorine, Methylene Chloride, Chloroform, Methyl Chloroform
6. Grassland fires	Gaseous and particulate emissions that are due to prescribed and naturally occurring grassland fires	Methyl Chloride, Particulate & Inorganic Chlorine, Methylene Chloride, Chloroform, Methyl Chloroform
7. Drinking Water Treatment	Gaseous emissions from drinking water treated with chlorinated compounds	Chloroform Atomic Chlorine Precursors
8. Swimming Pools	Gaseous Emissions from swimming pools treated with chlorinated compounds	Chloroform Atomic Chlorine Precursors
9. Cooling Water	Gaseous emissions from cooling towers treated with chlorinated compounds	Chloroform Atomic Chlorine Precursors
10. Domestic Bleach	Gaseous emissions from bleaching of laundry and similar applications	Chloroform Atomic Chlorine Precursors
11. Refrigerants and Foam Production	Gaseous emissions due to leakage by refrigeration systems and from foam blowing operations	Chlorodifluoromethane
12. Ruminants	Gaseous emissions due to livestock	Chloroform
13. Commercial Marine Vessels	Use of heavy fuel oils in large marine vessels while operating in coastal waters	Inorganic chlorides

specific compounds or else replaced by a surrogate chlorine compound that expresses similar ozone reactivity.

Our inventory methodology generally consists of an emission factor which was developed to be applicable to any metropolitan area of Texas, not to just Southeast Texas. An activity factor was also developed that contained data specific to Southeast Texas and would be multiplied by the emission factor to yield the inventory estimate for Southeast Texas. The resulting emission factors that were developed in this study for estimating both the annual emissions for 2000 and an ozone exceedence day in 2000 are presented in Table 3. This table also presents an estimate of the uncertainty associated with each emission factor, based upon information provided by the references.

Table 3. Annual and Ozone Day Emission Factors for Reactive Chlorine Species in Southeast Texas for the Year 2000

Source	Emission Compound	Annual Emission Factors		Ozone Day Emission Factors		Emission Factor Uncertainty
Oceans	Sea Salt Chlorine	6.61E-03	lb/m^2*yr	1.81E-05	lb/m^2*day	Within a factor of 2 or 3
	Methyl Chloride	1.72E-05	lb/m^2*yr	4.71E-08	lb/m^2*day	
	Chloroform	9.08E-06	lb/m^2*yr	2.49E-08	lb/m^2*day	
	Methylene Chloride	3.04E-06	lb/m^2*yr	8.32E-09	lb/m^2*day	
	Trichloroethene	2.98E-07	lb/m^2*yr	8.17E-10	lb/m^2*day	
	Tetrachloroethene	2.12E-07	lb/m^2*yr	5.81E-10	lb/m^2*day	
Land	Methyl Chloride	2.17E-06	lb/m^2 temperate forest*yr	5.95E-09	lb/m^2 temperate forest*day	Within a factor of 10
	Chloroform	6.43E-06	lb/m^2	1.76E-08	lb/m^2	90% confidence interval within a factor of 1/2
	Particulate Chlorine	2.50E-4	lb/m^2	6.85E-07	lb/m^2	Poorly constrained
Residential Wood Burning	Methyl Chloride	1.39E-01	lb/ton wood burned	1.39E-01	lb/ton wood burned	Within a factor of 2 or 3
	Particulate and Inorganic Chlorine	9.40E-01	lb/ton wood burned	9.40E-01	lb/ton wood burned	
	Methylene Chloride	1.02E-02	lb/ton wood burned	1.02E-02	lb/ton wood burned	
	Chloroform	3.98E-04	lb/ton wood burned	3.98E-04	lb/ton wood burned	
	Methyl Chloroform	4.64E-03	lb/ton wood burned	4.64E-03	lb/ton wood burned	
Forest Wildfires	Methyl Chloride	4.17E-06	lb/g CO	4.17E-06	lb/g CO	Within a factor of 2 or 3
	Particulate and Inorganic Chlorine	2.84E-05	lb/g CO	2.84E-05	lb/g CO	
	Methylene Chloride	3.05E-07	lb/g CO	3.05E-07	lb/g CO	
	Chloroform	1.19E-08	lb/g CO	1.19E-08	lb/g CO	
	Methyl Chloroform	1.39E-07	lb/g CO	1.39E-07	lb/g CO	

Source	Emission Compound	Annual Emission Factors		Ozone Day Emission Factors		Emission Factor Uncertainty
Agricultural Burning	Methyl Chloride	6.89E-06	lb/g CO	6.89E-06	lb/g CO	Within a factor of 2 or 3
	Particulate and Inorganic Chlorine	4.69E-05	lb/g CO	4.69E-05	lb/g CO	
	Methylene Chloride	5.04E-07	lb/g CO	5.04E-07	lb/g CO	
	Chloroform	1.97E-08	lb/g CO	1.97E-08	lb/g CO	
	Methyl Chloroform	2.29E-07	lb/g CO	2.29E-07	lb/g CO	
Grassland Fires	Methyl Chloride	3.06E-06	lb/g CO	3.06E-06	lb/g CO	
	Particulate and Inorganic Chlorine	2.09E-05	lb/g CO	2.09E-05	lb/g CO	
	Methylene Chloride	2.24E-07	lb/g CO	2.24E-07	lb/g CO	
	Chloroform	8.76E-09	lb/g CO	8.76E-09	lb/g CO	
	Methyl Chloroform	1.02E-07	lb/g CO	1.02E-07	lb/g CO	
Drinking Water Treatment	Chloroform	1.88E-02	lb/people using public H2O*yr	1.03E-04	lb/people using public H2O*day	Within 60%
	Atomic Chlorine Precursors	7.73E-02	lb/people using public H2O*yr	4.25E-04	lb/people using public H2O*day	Within an order of magnitude
Swimming Pools	Chloroform	3.59E-02	lb/person*yr	1.80E-04	lb/person*day	
	Atomic Chlorine Precursors	5.81E-01	lb/person*yr	2.91E-03	lb/person*day	
Cooling Water	Chloroform	1.45E-03	lb/person*yr	7.24E-06	lb/person*day	
	Atomic Chlorine Precursors	8.48E-02	lb/person*yr	4.22E-04	lb/person*day	
Domestic Bleach	Chloroform	1.03E-03	lb/person*yr	2.81E-06	lb/person*day	
	Atomic Chlorine Precursors	2.75E-03	lb/person*yr	7.53E-06	lb/person*day	
Refrigerants and Foam Production	HCFC-22	6.10E-01	lb/person*yr	1.67E-03	lb/person*day	Within 1%
Ruminants	Chloroform	2.38E-03	lb/head*yr	6.52E-06	lb/head*yr	Within an order of magnitude
Commercial Marine Vessels	Chloride	3.47E-01	lb/1000 gal resid. Fuel	3.47E-01	lb/1000 gal resid. Fuel	Within a factor of 2 or 3

The equations or data that we used to construct activity factors for the thirteen area, biogenic and mobile sources of reactive chlorine compounds are presented in Table 4. When the activity factors are multiplied by the emission factors in Table 3, an inventory estimate is created for each source and reactive chlorine compound. Often there are several activity components comprising an activity factor. Table 4 lists these activity components and provides good sources of data for each of the components.

Table 4. Activity Data for Reactive Chlorine in Southeast Texas in 2000

Emission Source	Equation/Information Used to Construct Activity Factor	Components of the Activity Factor	References for the Activity Components
Oceans	Area of Ocean zone (m^2) = width of zone x length of zone	Width of ocean zone - Surface distance between two points on the earth (m)	U.S. Department of Agriculture, 2002. “Surface Distance Between two Points of Latitude and Longitude.” http://www.wcrl.ars.usda.gov/cec/java/lat-long.htm
		Length of ocean zone - Distance from shore in which a pollutant still affects the study area (m)	Lobert et al 1999, p.8379. "Global Chlorine Emissions from Biomass Burning: Reactive Chlorine Emissions Inventory."J.M. Lobert, W.C. Keene, J.A. Logan, R. Yevich. Scripps Institution of Oceanography, La Jolla, California. Journal of Geophysical Research, Vol. 104, No. D7, p. 8373-8389 (1999).
Land - Methyl Chloride	Area of temperate forest per county (m^2)= Fraction of county that is temperate forest * area of county	Fraction of county that is temperate forest	Wiedinmyer et al, 2001. “A land use database and examples of biogenic isoprene emission estimates for the state of Texas, USA.” Atmospheric Environment 35: 6465-6477.
			Yarwood et al, 1999. Development of GLOBEIS--A State of the Science Biogenic Emissions Modeling System. Final report, prepared for Texas Natural Resource Conservation Commission, 23 December 1999.
		Land area per county (m^2)	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Land - Chloroform, Particulate Chlorine	Land area per county (m^2)	Land area per county (m^2)	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Residential Wood Burning	Tons wood burned per county = tons wood burned in state/yr x Number wood burning households in county/ Number wood burning households in state	Tons of wood burned in state per year	EIA, 2001a. "Household Energy Consumption and Expenditures 1997." Energy Information Adminstration. Http://www.eia.doe.gov/aer
		Number of wood burning households by county	U.S. Census Bureau, 2001c. 1990 U.S. Census LOOKUP", U.S. Census Bureau, http://homer.ssd.census.gov/doc/lookup_doc.html
		Number of wood burning households statewide	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Forest Wildfires	Grams of CO from forest wildfire per county	Grams of CO from forest wildfire by county	Allen and Dennis, 2000. "Inventory of air pollutant emissions associated with forest, grassland and agricultural burning in Texas." Center for Energy and Environmental Resources, the University of Texas, Austin, Texas 78712. The Texas Natural Resources Conservation Commission, Contract #9880077600-05, February 2000.
Agricultural	Grams of CO from agricultural	Grams of CO from	Allen and Dennis, 2000. "Inventory of air

Emission Source	Equation/Information Used to Construct Activity Factor	Components of the Activity Factor	References for the Activity Components
Crop Burning	crop burning per county	agricultural crop burning by county	pollutant emissions associated with forest, grassland and agricultural burning in Texas." Center for Energy and Environmental Resources, the University of Texas, Austin, Texas 78712. The Texas Natural Resources Conservation Commission, Contract #9880077600-05, February 2000.
Grassland Fires	Grams of CO from grassland fires by county	Grams of CO from grassland fires by county	Allen and Dennis, 2000. "Inventory of air pollutant emissions associated with forest, grassland and agricultural burning in Texas." Center for Energy and Environmental Resources, the University of Texas, Austin, Texas 78712. The Texas Natural Resources Conservation Commission, Contract #9880077600-05, February 2000.
Drinking Water Treatment	People using public water per county = county pop x No. county households using public water / No. county households with water	county population	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
		No. county households using public water in state, No. county households with water	U.S. Census Bureau, 2001b. "Housing characteristics, 1990. U.S. Census Bureau, 1990 Census of Population and Housing. Http://factfinder.census.gov
Swimming Pools	People per county	People per county	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Cooling Water	People per county	People per county	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Domestic Bleach	People per county	People per county	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Refrigerants and Foam Production	People per county	People per county	U.S. Census Bureau, 2001a. "State and County Quickfacts", U.S. Census Bureau, http://quickfacts.census.gov
Ruminants	Head of cattle per county	Head of cattle by county	U.S. National Agricultural Statistics Service, 2000. http://www.nass.usda.gov/census/
Commercial Marine Vessels	1000 gallons of residual fuel per county	1000 gallons of residual fuel per county	ERG, 200 lb, “Development of the 1999 Texas Toxics Inventory,” August 31, 2001

INVENTORY RESULTS

The results of the annual and ozone-day inventories of reactive chlorine emissions from area, biogenic and mobile sources for Southeast Texas in 2000 are presented in Tables 5 and 6, respectively. Figure 2 shows the contribution of major sources to reactive chlorine compound emissions from area and mobile sources on a typical ozone-day in Southeast Texas. The most significant source of annual reactive chlorine emissions for Southeast Texas is the ocean. Over 70 million pounds of chlorine compounds were released in 2000 from a 60 kilometer-wide band of ocean along the Southeast Texas coast, adjacent to the eleven counties inventoried. Land sources and swimming pools comprise the second and third most significant sources of reactive chlorine emissions. Because the emission factors for land sources have such a significant uncertainty, a factor of 10, land sources may actually be either the largest source or the sixth largest source of reactive chlorine emissions. Chlorodifluoromethane, emitted from refrigeration and foam blowing, and forest fires are the fourth and fifth largest sources of annual reactive chlorine emissions.

Very similar trends are exhibited by the ozone-day emission inventory presented in Table 6. Possibly the most significant difference between the annual and the ozone-day inventories is observed in the swimming pool source category. In the summer, the chlorination of swimming pools and the subsequent release of chlorine compounds is significantly greater than the annual average rate. This makes swimming pools almost equal to Land as the second most significant source of reactive chlorine emissions from area, biogenic and mobile sources during the late August ozone events.

Six sources had an uncertainty of “a factor of ten” (or an order of magnitude): land, drinking water chlorination, swimming pools, cooling towers, bleach, and ruminants. In Southeast Texas, ruminants contribute so little chlorine that this uncertainty is not significant. However, a factor of ten has a significant impact of the importance of the other sources and could greatly change their respective importance among area and biogenic sources.

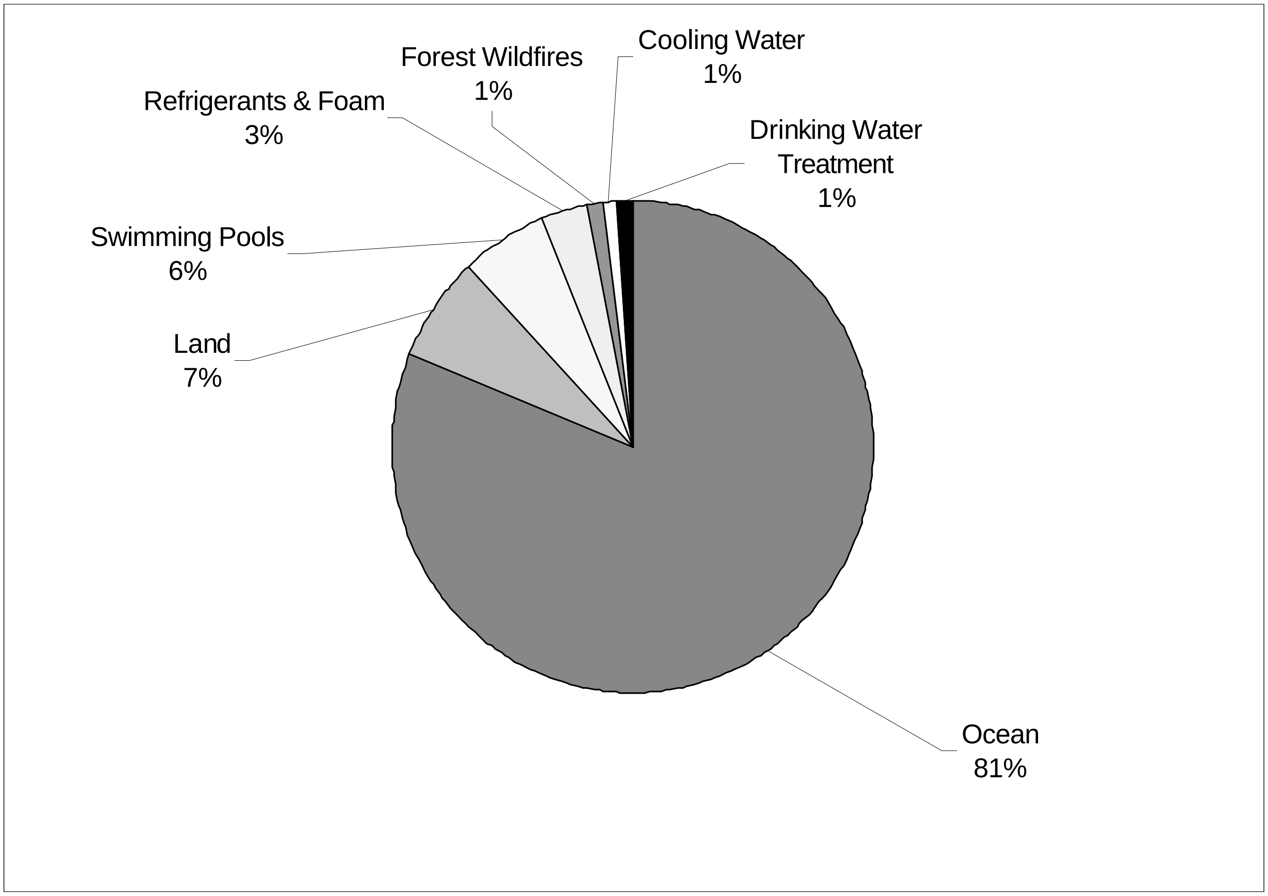

Figure 2. Contribution of individual sources to total area and mobile source reactive chlorine emissions on a typical ozone-day in Southeast Texas

Table 5. Inventory of Annual Reactive Chlorine Emissions in Southeast Texas in 2000 (lbs/yr)

Source	Methyl Chloride	Atomic Chloride Precursors	Chloroform	Particulate & Inorganic Chlorine	Methylene Chloride	Methyl Chloroform
Oceans	192,640	0	101,696	0	34,048	0
Land	34,731	0	164,224	0	0	0
Residential Wood Burning	15,768	0	45	106,630	1,157	526
Forest Wildfires	193,165	0	551	1,315,560	14,128	6,439
Agricultural Burning	5,222	0	15	35,545	382	174
Grassland Fires	16,456	0	47	112,394	1,205	549
Drinking Water Treatment	0	348,342	84,720	0	0	0
Swimming Pools	0	2,856,683	176,514	0	0	0
Cooling Water	0	416,948	7,129	0	0	0
Domestic Bleach	0	13,521	5,045	0	0	0
Refrigerants and Foam Production	0	0	0	0	0	0
Ruminants	0	0	950	0	0	0
Commercial Marine Vessels	0	0	0	0	0	0

Definitions:

Atomic Chlorine Precursors: Combined emissions of molecular chlorine and hypochlorous acid. When used with bleaching, this group refers to the hypochlorite compounds (AOX)released due to the use of NaOCl bleach.

Particulate and Inorganic Chlorine: Includes the various inorganic chlorine species in the particulate emissions from these combustion sources. HCl is a significant component in this species group.

Table 5 (Continued). Inventory of Annual Reactive Chlorine Emissions in Southeast Texas in 2000 (lbs/yr)

Source	Sea Salt Chlorine	Trichloro-ethene	Tetrachloro-ethene	Chloride	Chlorodifluoro-methane (HCFC-22)	Particulate Chlorine	Totals
Oceans	74,032,000	3,338	2,374	0	0	0	74,366,096
Land	0	0	0	0	0	6,385,075	6,584,030
Residential Wood Burning	0	0	0	0	0	0	124,126
Forest Wildfires	0	0	0	0	0	0	1,529,843
Agricultural Burning	0	0	0	0	0	0	41,337
Grassland Fires	0	0	0	0	0	0	130,650
Drinking Water Treatment	0	0	0	0	0	0	433,062
Swimming Pools	0	0	0	0	0	0	3,033,197
Cooling Water	0	0	0	0	0	0	424,077
Domestic Bleach	0	0	0	0	0	0	18,566
Refrigerants and Foam Production	0	0	0	0	2,999,271	0	2,999,271
Ruminants	0	0	0	0	0	0	950
Commercial Marine Vessels	0	0	0	10,113	0	0	10,113

Definitions:

Sea Salt Chlorine: Various ionic chlorine compounds present in sea salt aerosols.

Chloride: Refers to the ionic form of the chlorine atom.

Particulate Chlorine: Various inorganic chlorine species such as NaCl that naturally occur in crustal dust and become airborne particulates.

Table 6. Inventory of Ozone Day Reactive Chlorine Emissions in Southeast Texas in 2000 (lbs/yr)

Source	Methyl Chloride	Atomic Chloride Precursors	Chloroform	Particulate and Inorganic Chlorine	Methylene Chloride	Methyl Chloroform
Oceans	528	0	279	0	93	0
Land	95	0	450	0	0	0
Residential Wood Burning	0	0	0	0	0	0
Forest Wildfires	429	0	1.2	2,923	31	14
Agricultural Burning	18	0	0.05	124	1.3	0.60
Grassland Fires	0	0	0	0	0	0
Drinking Water Treatment	0	1,916	466	0	0	0
Swimming Pools	0	14,308	885	0	0	0
Cooling Water	0	2,075	36	0	0	0
Domestic Bleach	0	37	14	0	0	0
Refrigerants and Foam Production	0	0	0	0	0	0
Ruminants	0	0	2.6	0	0	0
Commercial Marine Vessels	0	0	0	0	0	0

Definitions:

Atomic Chlorine Precursors: Combined emissions of molecular chlorine and hypochlorous acid. When used with bleaching, this group refers to the hypochlorite compounds (AOX)released due to the use of NaOCl bleach.

Particulate and Inorganic Chlorine: Includes the various inorganic chlorine species in the particulate emissions from these combustion sources. HCl is a significant component in this species group.

Table 6 (Continued). Inventory of Ozone Day Reactive Chlorine Emissions in Southeast Texas in 2000 (lbs/yr)

Source	Sea Salt Chlorine	Trichloro-ethene	Tetrachloro-ethene	Chloride	Chlorodifluoro-methane (HCFC-22)	Particulate Chlorine	Totals
Oceans	202,755	9.2	6.5	0	0	0	203,670
Land	0	0	0	0	0	17,493	18,039
Residential Wood Burning	0	0	0	0	0	0	0
Forest Wildfires	0	0	0	0	0	0	3,399
Agricultural Crop Burning	0	0	0	0	0	0	144
Grassland Fires	0	0	0	0	0	0	0
Drinking Water Treatment	0	0	0	0	0	0	2,382
Swimming Pools	0	0	0	0	0	0	15,193
Cooling Water	0	0	0	0	0	0	2,111
Domestic Bleach	0	0	0	0	0	0	51
Refrigerants and Foam Production	0	0	0	0	8,217	0	8,217
Ruminants	0	0	0	0	0	0	3
Commercial Marine Vessels	0	0	0	28	0	0	28

Definitions:

Sea Salt Chlorine: Various ionic chlorine compounds present in sea salt aerosols.

Chloride: Refers to the ionic form of the chlorine atom.

Particulate Chlorine: Various inorganic chlorine species such as NaCl that naturally occur in crustal dust and become airborne particulates.

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REFERENCES

1. Gradel, T.E. “Tropospheric Budget of Reactive Chlorine”. Global Geochemical Cycles, Vol. 9, No. 1, pp. 47-77 (1995).
2. Gerstle, R.W.; Devitt, T.W. “Chlorine and Hydrogen Chloride Emissions and Their Control”. Paper 71-25 presented at 64th Annual Meeting, Air Pollution Control Association, Atlantic City, N.J., June 27-July 2, 1971.
3. Knapp, K.T.; Cheney, J.L. “Measurement of Sulfuric Acid and HC1 in Stationary Source Emissions”. Report EPA-600/83-069 Environmental Protection Agency Research Triangle Park, NC.
4. McCulloch, A.; Aucott, M.L.; Graedel, T.E.; Kleiman, G., Midgley, P.M.; Li, Y.F. “Industrial Emissions of Trichloroethene, Tetrachloroethene, and Dichloromethane: Reactive Chlorine Emissions Inventory”. Journal of Geophysical Research, Vol. 104, No. D7, p. 8417-8427 (1999).
5. Tanaka, P.L; Oldfield, S.; Mullins, C.B.; Allen, D.T. “Anthropogenic Sources of Chlorine and Ozone Formation in Urban Atmospheres”. Environmental Science Technology, Vol. 34, pp. 4470-4473 (2000).
6. Carter, W.P.L.; Luo, D.; Malkina, I.L. “Investigation of the Atmospheric Ozone Formation Potential of Trichloroethylene”. Draft Report to the Halogenated Solvents Alliance.
7. Carter, W.P.L.; Luo, D.; Malkina, I.L. “Investigation of the Atmospheric Reactions of Chloropicrin”. Revised and submitted to Atmospheric Environment.
8. Allen, D.; Dennis, A. “Inventory of Air Pollutant Emissions Associated with Forest Grassland and Agricultural Burning in Texas”. The Texas Natural Resources Conservation Commission Contract #9880077600-05, February, 2000.
9. Erickson III, D.J.; Seuzaret, C. “A General Circulation Model Based Calculation of HC1 and $CINO_2$ Production from Sea Salt Dechlorination: Reactive Chlorine Emissions Inventory”. Journal of Geophysical Research, Vol. 104, No. D7, pp. 8347, 1999.
10. Keene, W.C.; Khalil, M.A.K; Erickson, D.J.; McCulloch, A.; Graedel, T.E.; Lobert, J.M.; Aucott, M.L.; Gong, S.L.; Harper, D.B.; Kleiman, G.; Midgley, P.; Moore, R.M.; Seuzaret, C.; Sturges, W.T.; Benkovitz, C.M.; Koropalov, V.; Barrie, L.A.; Li, Y.F. “Composite Global Emissions of Reactive Chlorine from Anthropogenic and Natural Sources: Reactive Chlorine Emissions Inventory”. Journal of Geophysical Research, Vol. 104, No. D7, pg. 8429-8440, 1999.
11. Ogbeide, Peter. “Texas Toxics Inventory Program”. Texas Natural Resource Conservation Commission, 2001.
12. Change, S.; Tanaka, P.; Mcdonald-Buller, e.; Allen, D.T. “Emission Inventory for Atomic chlorine Precursors in Southeast Texas”. The Texas natural Resources Conservation Commission Contract #9880077600-18, June 7, 2001.
13. Rogozen, M.B.; Rich, H.E.; Guttman, M.A.; Grosjean, D.; Williams, E.L. “Sources and Concentrations of Chloroform in the South Coast Air Basin”. State of California Air Resources Board, SAIC-86/1105, April 8, 1988.