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An emission inventory for Cl_2 and HOCl in Shanghai, 2017

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HIGHLIGHTS

- An emission inventory for atomic chlorine precursors was developed for Shanghai in the year 2017 for the first time.
- Eight source sectors of chlorine precursors are considered.
- It provides a basis for further study regarding the influence of chlorine chemistry on ozone formation.

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ABSTRACT

Chlorine radical plays an important role in ozone formation. However, it has not generally been included in air quality modelling in China. In this study, an emission inventory for atomic chlorine precursors was developed for Shanghai in the year 2017. Total emissions of chlorine radical precursors were estimated at 8650 tons/year. The main source sectors of chlorine precursors in Shanghai include the volatilization of disinfectants, including in water treatment (850 tons/year, accounting for 9.8% among total emissions), in cooling towers (4,000 tons/year, 46.2%), in wastewater treatment (2,700 tons/year, 31.2%), in tap water (310 tons/year, 3.6%), in swimming pools (280 tons/year, 3.2%), and in the usage of chlorine-containing disinfectants (210 tons/year, 2.4%). The contribution of sea salt heterogeneous reactions with ozone to chlorine radical precursors is estimated as 90 tons/year; this represents a lower bound on the emissions from sea salt because of other reaction pathways (e.g., the reaction of particulate chloride with N_2O_5). Local emissions from coal combustion and chemical manufacturing were estimated to be relatively small. This study provides a basis for further study regarding the influence of chlorine chemistry on ozone formation in Shanghai.

1. Introduction

Ozone formation in urban atmospheres typically proceeds through a series of free radical reactions involving volatile organic compounds (VOCs) and nitrogen oxides (NOx) (Seinfield and Pandis, 1998). Some studies have shown that the chlorine radical (Cl·) may also play an important role in ozone formation (Chang et al., 2001; Chang and Allen, 2006; Finlayson-Pitts, 1993; Hov, 1985; Sarwar and Bhave, 2006; Tanaka et al., 2000, 2003a, 2003b, 2003c). For many hydrocarbons, Cl· initiated oxidation is on the order of 2 orders of magnitude faster than OH· initiated reactions (Atkinson et al., 1998). In particular, methane oxidation in urban atmospheres can become a significant reaction pathway affecting ozone concentrations if Cl· is present. The significantly greater reactivity of Cl· atoms across a broad range of hydrocarbons implies that even small concentrations of Cl· atoms can have an impact on ozone formation rates through increasing the rate of peroxyalkyl (RO_2) radical production. It has been confirmed that Cl· may enhance ozone concentrations in reactions with VOCs in Houston (Tanaka et al., 2000), Telemark (Isaksen and Hov, 1985) and inland regions in Texas (Chang et al., 2005). Field studies have identified photochemically active, gas-phase chlorine compounds other than hydrogen chloride (HCl) in the troposphere (Keene et al., 1993; Pszenny et al., 1993; Impey et al., 1997), but specific compounds have been difficult to identify. Many observations have detected molecular chlorine Cl_2 concentrations (Pszenny et al., 1993, 2003; Finley and Saltzman, 2006, 2008; Lopez and Glasow, 2012); high Cl_2 concentrations up

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to 150 pptv in night time ocean plumes have been observed, suggesting that chlorine chemistry in coastal cities may be more significant. Regional air quality modeling studies in southeast Texas indicated that Cl· can increase 1-h and 8-h ozone by up to 73 ppbv and 21 ppbv in localized areas, respectively(Chang et al., 2005).

Sources of chlorine radical in urban atmospheres are generally believed to include both direct anthropogenic emissions of chlorine radical precursors, such as Cl_2 and hypochlorous acid (HOCl), as well as the reactions of nitrogen pentoxide (N_2O_5) with particulate chloride to produce nitryl chloride ($ClNO_2$). In southeast Texas, where both of these sources of chlorine radical have been modeled and compared to observations, anthropogenic sources of chlorine radical precursors led to highly localized increases in ozone concentrations, while the production of $ClNO_2$ led to widely distributed, but relatively small increases in ozone concentrations.

It is unclear how these results may apply to coastal megacities in China. Liu et al. (2018) examined the impact of chlorine emissions from coal combustion and prescribed waste incineration on ozone in China. Fu et al. (2018) estimated the anthropogenic emissions of hydrogen chloride (HCl) and fine particulate chloride in China. Qiu et al. (2019) also estimated the particulate chloride emissions from cooking. However, the emissions for atomic chlorine precursors are still quite limited. Large populations have the potential to lead to relatively large anthropogenic emissions from sources related to disinfection, and relatively high concentrations of NOx and N_2O_5 can lead to significant production of $ClNO_2$. This work will develop an inventory of anthropogenic sources of chlorine radical precursors. Shanghai is chosen as a typical coastal megacity in China, since ozone concentrations have been increasing and those increases are not completely understood. Many studies have been conducted and possible reasons for the increases have been proposed (Li et al., 2019; Liu et al., 2019). However, due to the lack of estimates of chlorine emission in Shanghai, the effects of precursors of chlorine free radicals on atmospheric chemical reactions have not been considered in the photochemical modeling of atmospheric pollution in Shanghai. A first step in understanding the importance of these reactions is to develop an emission inventory of atmospheric chlorine precursors in Shanghai.

2. Methodology

In this study, we mainly followed Chang and Allen (2006); Chang et al. (2001)'s methodology to develop the emissions inventory for anthropogenic sources of atomic chlorine precursors in Shanghai. We also estimated formation due to reactions (secondary formation) with sea salt. Taking into account Shanghai's anthropogenic emissions and secondary formation due to reactions of sea salt, eight categories of sources are included in this study: (i) coal combustion; (ii) chemical industry; (iii)water and waste water treatment; (iv) use of biocides in cooling towers; (v)disinfection of swimming pools; (vi) tap water; (vii) usage of chlorine-containing disinfectants; (viii) reactions of sea salt aerosol. Temporal patterns of emissions, locations of emissions, and other data needed for photochemistry modeling were also estimated for these sources. For other less important sources, only total emissions were estimated.

2.1. Research area

Shanghai is the economic center of China and the most populous city, bounded by the sea to the east. Fig. 1 shows the research domain.

2.2. Emissions estimation

2.2.1. Molecular chlorine emissions from coal combustion

Liu et al. (2018) calculated chlorine emissions during coal combustion in China in 2014 based on chlorine content in coal, boiler types, pollution control technologies and an estimated percentage of molecular chlorine to released chlorine elements of 3.6% (Deng et al., 2014). The calculation formula is as follows:

$$E_x = M_x \times c_x \times \sum_t (R_{x,t} \times X_x \times (1 - \eta d_{x,t}) \times (1 - \eta s_{x,t})) \times \rho \quad (1)$$

where M represents coal consumption, ρ is the chlorine proportion of Cl_2 in emitted flue gas, x represents the sector, t represents the energy allocation type (type of boiler and control device combination), c represents chlorine content in coal, R is the chlorine release rate, X is the fraction of energy for a sector (energy allocation ratio), ηd is the removal efficiency of dust-removal facilities, and ηs is the removal efficiency of sulfate-removal facilities.

Based on this method, we collected coal combustion data (SMSB, 2018a), and updated the chlorine emission during coal combustion in Shanghai in 2017. The consumption of various sectors of coal and the release of Cl_2 in Shanghai in the year 2017 are shown in Table 1.

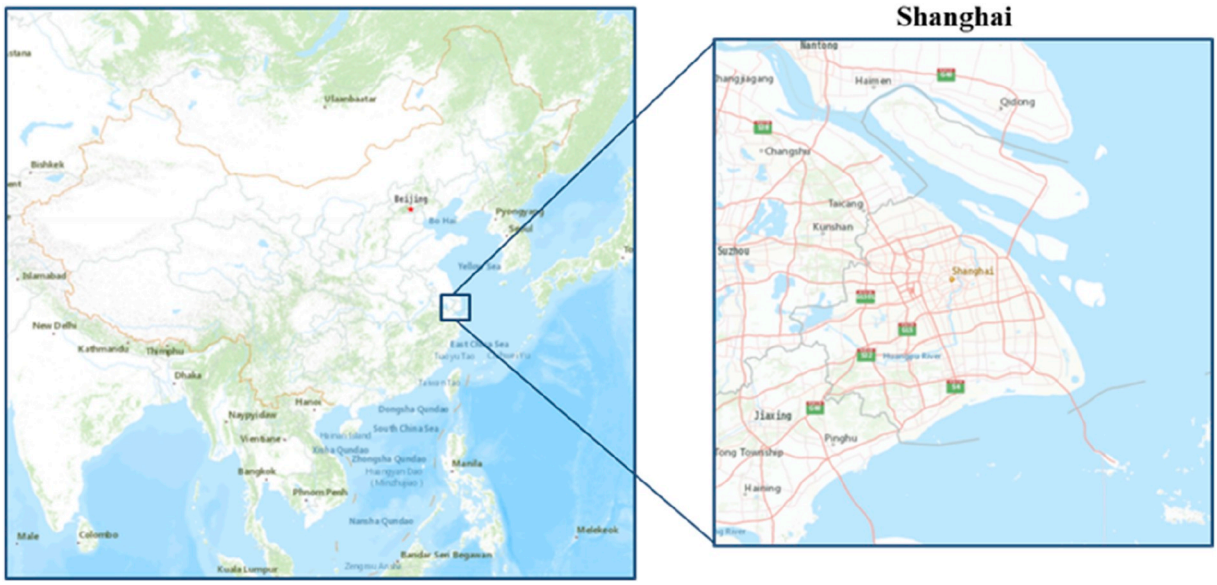

Fig. 1. Location of the study area: Shanghai.

2.2.2. Molecular chlorine emissions from chemical industry

In the chlor-alkali chemical production process, by-product chlorine gas will be produced in the process of caustic soda production by electrolysis. The following reaction stoichiometry shows the generation of chlorine.

$$2NaCl + 2H_2O = 2NaOH + H_2\uparrow + Cl_2\uparrow$$

Chlorine emissions in chlor-alkali manufacturing are controlled by absorbing chlorine gas in alkali solution. Chlorine gas is emitted into the atmosphere at a rate under 3 mg/m^3, which is required by the national emission standard (MEPC, 2006).

Emissions in chemical industry ($E_{chemical}$, tons/year) were estimated by multiplying emissions of waste gases (G, m^3/year) by concentration of chlorine in exhaust gas ($C_{chemical}$, mg/m^3):

$$E_{chemical} = G \times C_{chemical} \quad (2)$$

Based on the pollution survey data about industrial sources (SMSB, 2018a), we identified chemical manufacturing sites that belong to chlor-alkali industry. As shown in Table 2, we calculated the Cl_2 emissions from the waste gases from the chlor-alkali chemical industry in Shanghai.

2.2.3. Atomic chlorine precursor emissions associated with water and wastewater treatment

During the process of water treatment, chlorine-containing compounds are used to disinfect in water, which may release atomic chlorine precursors into the atmosphere. The use of chlorine-containing disinfectants such as Cl_2, HOCl and Chlorine Dioxide (ClO_2) in water treatment is a potential source of chlorine free radicals in the atmosphere.

Emissions (E_i, tons/year) were estimated by multiplying activity data (A_i, tons/year) by emission factors (EF_i):

$$E_i = A_i \times EF_i \quad (3)$$

where *i* represents the source sector, including water treatment, wastewater treatment and medical wastewater treatment. The difference between the chlorine dosage and the free chlorine residual is referred to as the chlorine demand, where chlorine demand is defined as:

Chlorine demand = Chlorine dose – Chlorine residual

Lawler (2001) estimated that 20% of the chlorine demand was due to volatilization, so here we adopt $EF_i = 0.2$, for an activity factor defined as chlorine demand.

The amount of chlorine-containing disinfectants used in water disinfection (chlorine demand, A_i) is calculated through formula (4):

$$A_i = W_i \times (Cd_i - Cr_i) \quad (4)$$

where *i* represents the sector, including water treatment, wastewater treatment and medical wastewater treatment. W represents the amount of water treated; C*d* represents the chlorine dose; C*r* represents the chlorine residual.

The chemical form is important, Cl_2 would be expected to photolyze very rapidly (less than 10–20 min), while the photolysis rate of HOCl will be a factor of 10 times slower (Tanaka et al., 2000; Tanaka and Allen, 2001). In addition, for a fixed amount of chlorine release, the formation of HOCl would lead to twice the production of free radicals as release of Cl_2. HOCl is formed when chlorine is added to water which can dissociate and also react with other chemical species present in water. At higher pH, only a fraction of HOCl may be available for volatilizing into the atmosphere. HOCl, Cl_2 or other chemical forms may be released in the use of chlorine-containing disinfectants, this is an uncertain factor. In this study, we assume that all sources are released in the form of Cl_2.

Table 1
Coal consumption and emissions of molecular chlorine in Shanghai 2017.

Sector	Coal consumption (Gg)	Cl_2 Emissions (ton)
Power plant	26082.6	9.8
Industry	26601.0	165.4
Residential	467.0	4.6
Others	1210.9	12.2
total	**54361.5**	**192.0**

Table 2
Waste gas and Cl_2 discharged from Chlor-Alkali Chemical Plants in Shanghai 2017.

Chemical Plant	Emissions exhaust gases(m^3)	Emissions Cl_2 (ton)
IND1	262460000	0.79
IND2	815848250	2.45
IND3	2338748256	7.02
IND4	6010000	0.02
IND5	523960000	1.57
IND6	1183699200	3.55
IND7	28440000	0.09

2.2.3.1. Water treatment. Total supply of tap water in Shanghai in 2017 was 3.10 billion cubic meters, of which 2.45 billion cubic meters were sold (SMSB, 2018b). According to the statistics of the Yellow River waterworks of Jinan Water Supply Company, the average amount of chlorine added to the disinfection treatment of waterworks under normal conditions is about 2.2 mg/l (Wang et al., 2000), and the water quality monitoring data published by Shanghai Water Bureau of China show that the average residual chlorine of water at the end of Shanghai Pipe network in 2017 is 0.84 mg/l (SWBC, 2017).

Demand for chlorine-containing disinfectants in water treatment is:

3,101,000,000 m^3 × (2.2 mg/l - 0.84 mg/l) = 42,17.4 tons/year

Therefore, emissions of atomic chlorine precursors in water treatment are approximately 850 tons per year.

42,17.4 tons/year × 0.2 = 850 tons/year

Emissions of atomic chlorine precursors from water treatment were 850 tons/year of molecular chlorine as Cl_2 or 1275 tons/year as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl).

2.2.3.2. Wastewater treatment. The chlorine demand water quality of wastewater treatment is complex. Chlorine dose needs to be adjusted according to the characteristics of wastewater quality. According to *Code for design of outdoor wastewater engineering* (MCC, 2006), we assume that chlorine dose in wastewater is 6.0 mg/l. Regarding the chlorine residual in wastewater, we consulted *the Comprehensive Wastewater Discharge Standard*, but no discharge standard for chlorine residual in sewage was included (MEPC, 1996). On the other hand, the residual chlorine in general sewage is very small, so we assume that the residual chlorine in sewage can be neglected. Medical wastewater contains a large number of pathogenic bacteria, so the chlorine dose of medical wastewater is greater than other wastewaters. According to *The Discharge Standard of Water Pollutants in Medical Institutions*, the chlorine content of medical wastewater is 10 mg/l and the residual chlorine content is 0.5 mg/l (NHCC, 2012; Zhang, 2015).

There are 51 municipal wastewater treatment plants in Shanghai; the average daily wastewater treatment capacity is 5,942,800 m^3/day (SMSB, 2018b).

There were 134,607 beds in Shanghai medical institutions in 2017 (SMSB, 2018b), the sewage production of hospitals in China is generally 1.2–2.0 m^3/d·bed, and that of Shanghai is 1.58 m^3/d·bed (Huang, 2006). It is estimated that the medical wastewater production in Shanghai is around 212,679 m^3.

134,607 bed × 1.58 m^3/d·bed = 212,679 m^3/day

Emissions of atomic chlorine precursors from medical wastewater treatment are estimated to be:

212,679 m^3/day × (10 mg/l-0.5 mg/l) × 0.2 × 365 = 147.5 tons/year

Emissions of atomic chlorine precursors from other wastewater treatment facilities are:

(5,942,800 m^3/day-212,679 m^3/day) × 6 mg/l × 0.2 = 2,500 tons/year

In addition to chlorine volatilization occurring in the wastewater treatment process, residual chlorine in the treated sewage may also volatilize into the atmosphere. Normally, the residual chlorine in wastewater treatment except for medical wastewater is very small, so we neglect the volatilization of this part of chlorine.

Emissions of atomic chlorine precursors from wastewater treatment was 2,700 tons/year of molecular chlorine as Cl_2 or 4,000 tons/year as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl).

2.2.4. Atomic chlorine precursor emissions associated with the use of biocides in cooling towers

Chlorine-containing fungicides need to be added to the circulating water of the cooling towers to prevent the microorganisms growths, so cooling towers may be an important source of atomic chlorine precursors. There are generally three consumption pathways for chlorine-containing disinfectants added to circulating water (Holzwarth et al., 1984): (1) flash-off occurs when the air stream flowing through the cooling tower strips volatile constituents from the water; (2) the blow-down 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.

Emissions from cooling towers ($E_{cooling}$, tons/year) were estimated by multiplying evaporation of cooling water ($W_{cooling}$, m^3/year) by concentration of chlorine-containing disinfectants in cooling water ($C_{cooling}$, mg/m^3):

$$E_{cooling} = W_{cooling} \times C_{cooling} \quad (5)$$

Holzwarth et al. (1984) measured the chlorination content of cooling towers in a refinery in the United States. It was found that the amount of molecular chlorine used in cooling towers with supplementary water of 1,000 gallons per minute was 184 kg per day. The volatilization of molecular chlorine is related to the flash-off coefficient of chlorine. The flash-off coefficient of chlorine is 0.1–1.0 in general. The higher the pH and temperature, the greater the flash-off of atomic chlorine precursors, we conservatively assume that the flash-off fraction of chlorine-containing disinfectants in cooling towers is 0.1 (10%). Therefore, the volatilization of molecular chlorine in cooling tower with 1,000 gallons/minute supplementary water is 18.4 kg.

Rogozen et al. (1988) found that not all cooling towers use chlorine-containing disinfectants; small cooling towers generally do not use chlorine-containing disinfectants. Therefore, we estimate that chlorine-containing disinfectants will only be used in cooling towers with cooling water use greater than 100 m^3/h in chemical production and refining industries. Zhang and Ma (1998) conducted a statistical investigation on the water consumption of cooling towers in Shanghai in 1998. It was found that the supplementary water consumption of cooling towers with cooling water use capacity greater than 100 m^3/h in Shanghai in 1998 was 463,416 m^3/day. Based on the change of industrial scale (The industrial scale of Shanghai in 2017 is seven times that of 1998.) in Shanghai, the supplementary water quantity of cooling towers with cooling capacity greater than 100 m^3/h in 2017 is estimated.

Supplementary water for cooling towers with cooling capacity greater than 100 m^3/h in Shanghai in 2017:

463,416 m^3/day × 7 = 3,243,912 m^3/day

This leads to the estimated emissions of:

18.4 kg min/1,000 gal × 3,243,912 m^3/day × 365 = 4,000 tons/year

Emissions of atomic chlorine precursors from cooling towers is estimated to be 4,000 tons/year of molecular chlorine as Cl_2 or 6,000 tons/year as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl).

2.2.5. Atomic chlorine precursors emissions associated with swimming pools

The amount of chlorine present in swimming pools ($Cl_{swimming}$, tons) were estimated by multiplying swimming pool volume (V, m^3) by concentration of chlorine in swimming pools ($C_{swimming}$, mg/m^3):

$$Cl_{swimming} = V \times C_{swimming} \quad (6)$$

In July 2017, the Shanghai Health Supervision Department conducted a random sampling of swimming pools in Shanghai. It was found that 737 swimming pools had obtained health permits for public places (SSBC, 2017). This data does not cover all swimming polls, we estimate that the total number of swimming pools in Shanghai is 1.5 times that of this data, that is:

737 × 1.5 = 1,106 swimming pools

Searching the number of swimming pools in Shanghai through Baidu Map (https://map.baidu.com/@13523265.31,3641114.64,12z.html) with the keyword "swimming pool", we found that the estimated data are similar to the search results. Zhang (2015) conducted a survey of swimming pools in Jinan City; 28% of Jinan public swimming pools are in standard size, 72% are semi-standard and other non-standard. The standard size of swimming pool is 50 m long, 21 m wide and 1.8 m deep; while the semi-standard swimming pool is 25 m long, 21 m wide and 1.8 m deep.

Due to the lack of relevant data on the number and scale of private swimming pools in Shanghai, we estimate the number of private swimming pools in Shanghai to be 12,000 according to the income ratio of permanent residents in Shanghai. The size of private swimming pool is 10 m long, 8 m wide and 1.4 m deep.

In China, concentrations of chlorine-containing disinfectants in swimming pools range from 0.3 mg/l to 1.0 mg/l, and combined residual chlorine in public swimming pools is less than 0.4 mg/l (QTSBC, 1996). We assume that the hypochlorite concentration in swimming pools in Shanghai is 1.0 mg/l. Hypochlorite is highly volatile, and chlorine disinfectant in swimming pools volatilize in less than a day. Therefore, we assume that all residual chlorine in swimming pools will volatilize into the atmosphere (in less than one day). This leads to an estimate for summertime chlorine-containing disinfectants use of:

$$\begin{aligned} &1,106 \text{ swimming pools} \times (50m \times 21m \times 28\% + 25m \times 21m \times 78\%) \times 1.8\mu + \\ &12,000 \text{ swimming pools} \times 10m \times 8m \times 1.4m = 2,681.8\ kg/day \end{aligned}$$

Rogozen et al. (1988) estimated that the weighted average mass transfer coefficient of chloroform under stirring and non-stirring conditions was 22 mg m^{-2}·min^{-1}. By adjusting the molecular weight difference between chloroform and hypochlorite and Henry's law constant, the total mass transfer coefficient of hypochlorite should be about 10–100 mg m^{-2}·min^{-1}.

Area of pools is approximately:

$$\begin{aligned} &1,106 \text{ swimming pools} \times (50m \times 21m \times 28\% + 25m \times 21m \times 78\%) + \\ &12,000 \text{ swimming pools} \times 10m \times 8m = 1,738,071m^2 \end{aligned}$$

Mass volatilized:

10 mg m^{-2}·min^{-1} × 1,738,071 m^2 × 1440 min/day = 2,508.2 kg/day

The use of swimming pools in Shanghai usually lasts 92 days from July to October in summer. Considering underestimation of the number

of swimming pools, these emissions can be assumed to be 3 tons per day, so emissions of atomic chlorine precursors from swimming pools is estimated to be 280 tons/year of molecular chlorine as Cl_2 or 420 tons/year as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl).

For 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 8:00.

2.2.6. Atomic chlorine precursor emissions associated with tap water

There is 0.84 mg/l residual chlorine in tap water, the residual chlorine in tap water may volatilize into the atmosphere during: (1) Car washing; (2) Lawn watering; (3) Road sprinkling; (4) Leakage during water conveyance.

Emissions from tap water (E_j) were estimated by multiplying usage of tap water (U_j) by concentration of chlorine-containing disinfectants in tap water (C_r):

$$E_j = U_j \times C_r \quad (7)$$

Where j represents the source sector, including car washing, lawn watering, road watering and leakage during water conveyance; C_r represents the residual chlorine in tap water, 0.84 mg/l.

(1) Car washing

Jing et al. (2014) found that the average daily consumption of water for car washing in Shanghai was about 6.6 m^3. And with "car washing" as the key word searched in Baidu Map, we found that there are 6,668 car washing spots in Shanghai. Therefore, the tap water consumption of car washing in Shanghai in 2017 is as follows:

$$6{,}668 \times 6.6\ m^3/day \times 365 = 16{,}063{,}212\ m^3/year$$

Emissions of atomic chlorine precursors from car washing:

$$16{,}063{,}212\ m^3/year \times 0.84\ mg/l = 13.5\ tons/year$$

(2) Lawn watering

In 2017, the green area of Shanghai was 13,637.2 ha (SMSB, 2018b). The water consumption per lawn watering is 1.5 L/m^2 (SWBC, 2018). We estimate that the frequency of lawn watering in Shanghai is 45 times/year in 2017. Emissions of atomic chlorine precursors from lawn watering:

$$136{,}327.2\ ha \times 0.84\ mg/l \times 1.5\ L/m^2 \times 45\ time/year = 77.3\ tons/year$$

(3) Road sprinkling

The road area of Shanghai in 2017 was 298,410,000 m^2 (SMSB, 2018b). The amount of water used for road sprinkling is 1.0 L/m^2·d (SWBC, 2018). We estimate that the frequency of road sprinkling in Shanghai in 2017 is 50 times/year. Emissions of atomic chlorine precursors from road sprinkling:

$$298{,}410{,}000\ m^2 \times 1.0\ L/m^2{\cdot}d \times 50\ time/year \times 0.84\ mg/l = 12.5\ tons/year$$

(4) Leakage during water conveyance

The water leakage rate in the process of tap water transportation in Shanghai was controlled below 8% in 2017 (SWBC, 2018). Due to the complexity of the factors leading to water leakage in the water supply process, we estimate that about 10% of the residual chlorine in the leaked water will volatilize into the atmosphere. Emissions of atomic chlorine precursors from leakage during water conveyance:

$$0.84\ mg/l \times 3{,}101{,}000{,}000\ m^3/year \times 8\ \% \times 10\ \% = 208.4\ tons/year$$

Total emissions from tap water:

$$13.5\ tons/year + 77.3\ tons/year + 12.5\ tons/year + 208.4\ tons/year = 311.7\ tons/year$$

In summary, emissions of atomic chlorine precursors from tap water are estimated to be 310 tons/year of molecular chlorine as Cl_2 or 470 tons/year as HOCl (assuming equal amounts of chlorine released as either Cl_2 or HOCl).

2.2.7. Atomic chlorine precursors associated with usage of chlorine-containing disinfectants

Chlorine-containing disinfectants are used in small-dose for,: (1) Disinfection of equipment and ground environment in hospitals; (2) Disinfection of livestock, poultry and aquaculture environments; (3) Disinfection of public toilets and households; (4) Food cleaning and disinfection in food processing industries; (5) Disinfection of the floor and toilet of hotels. Due to the lack of data on the use of chlorine-containing disinfectants in food processing industries and hotels, we only counted the volatilization of chlorine precursors during the use of chlorine-containing disinfectants in hospitals, public toilets and household toilets, livestock and poultry, and aquaculture.

Emissions from usage of chlorine-containing disinfectants (E_k) were estimated by multiplying use of chlorine-containing disinfectants (A_k) by emission factors (EF_k):

$$E_k = A_k \times EF_k \quad (8)$$

where k represents the sector, including hospital, livestock and poultry, aquaculture, and public toilets and households.

(1) Disinfection of instruments and ground environment in hospitals

Based on the surveys and statistics of Sun et al. (2007) in Taizhou City, the average amount of chlorine-containing disinfectants used in hospitals in Taizhou City is 232,920 L/year. *The Technical Specification for Disinfection in Medical Institutions* stipulates that the concentration of chlorine-containing disinfectants is generally 500–2,000 mg/L (NHCC, 2012) for different disinfection needs. We estimate that the average use of chlorine-containing disinfectants in hospitals in Shanghai was 232,920 L/year, and the concentration of chlorine-containing disinfectants was 1,000 mg/L. There were 363 hospitals in Shanghai in 2017 (SMSB, 2018b), so the amount of chlorine-containing disinfectants used in hospitals in Shanghai in 2017 was as follows:

$$363 \times 232{,}920\ L/year \times 1{,}000\ mg/L = 84.6\ tons/year$$

Since this kind of chlorine-containing disinfectants is mainly used for spraying and mopping disinfection, its dispersion area is large, hence the volatilization ratio of chlorine precursors will be larger than that in water treatment. We assume $EF_{hospital}$ to be 0.3. Emissions of atomic chlorine precursors from disinfection of instruments and ground environment in hospitals:

$$84.6\ tons/year \times 0.3 = 25\ tons/year$$

(2) Disinfection of livestock, poultry and aquaculture environment

The annual stocks of pigs and poultry in Shanghai at the end of 2017 were 606,300 and 12.52 million respectively (SMSB, 2018b). We estimate that the breeding density of pigs is 1.2 m^2/per pig, that of poultry is 0.05 m^2/per poultry, thus, the breeding area for livestock and poultry is:

$$606{,}300\ pigs \times 1.2\ m^2/pigs + 12{,}520{,}000 \times 0.05\ m^2/\ poultry = 1{,}353{,}560\ m^2$$

The disinfection frequency of livestock and poultry farming is once a week, and the dosage of chlorine-containing disinfectants is 1 g/m^2. The volatilization rate of chlorine-containing disinfectants in livestock and poultry farming is estimated to be 0.3. Emissions of atomic chlorine

precursors from disinfection of livestock and poultry environment:

$0.3 \times 1{,}353{,}560 \times 52$ time/year $\times$ 1 g/m^2 = 21.1 tons/year

Total amount of aquatic products in Shanghai in 2017 was 231,400 tons (SMSB, 2018b), the average aquaculture density was 2.25 kg/m^2, and the area of aquaculture was:

231,400 ton /2.25 kg/m^2 = 102,800,000 m^2

According to the suggestion of fishery disinfectant vendors, the amount of chlorine-containing disinfectants used in aquaculture is generally 0.3 g/m^2, and the frequency of disinfection in aquaculture is generally 1.5 times/month. The volatilization ratio of chlorine precursors in aquaculture disinfection process is similar to that in water treatment process. The volatilization ratio of chlorine precursors in aquaculture disinfection process is 0.2. Emissions of atomic chlorine precursors from disinfection of aquaculture environment:

102,800,000 m^2 $\times$ 0.3 g/m^2 $\times$ 18 times/year $\times$ 0.2 = 110 tons/year

(3) Disinfection of public toilets and homes

There were 6,221 public toilets in Shanghai in 2017 (SMSB, 2018b). We estimated that 500 ml of chlorine-containing disinfectants with 5% effective chlorine content will be consumed for each disinfection of public toilets, and the disinfection frequency is once per day. The proportion of volatilization of chlorine precursors in toilet disinfection was 0.3. Emissions of atomic chlorine precursors from disinfection of public toilets:

6,221 public toilets $\times$ 500 ml $\times$ 5% $\times$ 365 days $\times$ 0.3 = 17.0 tons/year

Chlorine-containing disinfectants are mainly used in households to disinfect and clean toilets. At present, only a few residents use hypochlorite-containing disinfectant for toilet disinfection, and there are few relevant data on the use of chlorine-containing disinfectants in Shanghai residents. Therefore, we estimate that emissions of atomic chlorine precursors from disinfection of households are 2 times that of public toilets:

17.0 tons/year $\times$ 2 = 34.1 tons/year

Total emissions from usage of chlorine-containing disinfectants are:

25.4 tons/year+21.1 tons/year+111.1 tons/year+17.0 tons/year+34.1 tons/year = 210 tons/year

2.2.8. Atomic chlorine precursor emissions associated with the reactions of sea salt aerosol

Spicer et al. (1998) found that hydroxyl radicals and ozone in the atmosphere react with sea salt to form Cl_2. The formation rate of molecular chlorine can reach 330 parts per trillion per day.

In order to quantify the effect of Cl_2 produced by photochemistry of sea salt on Shanghai, we assume that the reaction occurs in a volume 250 km by 10 km by 1 km located over the Yangtze Estuary and Hangzhou Bay. The rate of Cl_2 formation in the photochemistry of sea salt in the offshore area of Shanghai is as follows:

250 km $\times$ 10 km $\times$ 1 km $\times$ 10^9 m^3 $\times$ 330 $\times$ 10^{-12} mol chlorine per mole air $\times$ 1 mol air / 0.0224 m^3 $\times$ 0.071 kg chlorine/mole Cl_2 = 250 kg/day

The contribution of sea salt heterogeneous reactions with ozone to chlorine radical precursors is estimated as 91 tons/year (250 kg/day); this represents a lower bound on the emissions from sea salt because of other reaction pathways (e.g., the reaction of particulate chloride with N_2O_5). The impact of sea salt reactions on Shanghai remains highly uncertain. However, compared with human sources, this source has potentially important implications.

Besides the above 8 sources, photochemical reactions of organochlorine compounds in the atmosphere may be another potential important source of atomic chlorine precursor. On the one hand, the mechanism of this reaction remains to be studied. On the other hand, due to the lack of relevant data, it is not possible to determine the emissions from this source right now. However, a closer consideration of these compounds should be made if a more detailed inventory of atomic chlorine precursors is performed in the future.

3. Results and discussions

3.1. Total emissions amount of atomic chlorine precursors in Shanghai

Table 3 shows the total emissions of atomic chlorine precursors in Shanghai in the year 2017. It is estimated that total atomic chlorine precursor emissions in Shanghai in 2017 were 8,650 tons, among which, water treatment takes an account of 9.8%, cooling towers accounts for 46.2%, wastewater treatment accounts for 31.2%. These three sectors are the major emission source categories of atomic chlorine precursor emissions in Shanghai.

3.2. Spatial allocation of chlorine emissions

3.2.1. Water and wastewater treatment plants

Since it is impossible to obtain the chlorine consumption data of each water plant in the disinfection process, we calculate the release of atomic chlorine precursors based on the amount of water treatment in the water treatment plants.

As shown in Fig. 2(a), a large number of small-scale water treatment plants are concentrated in the densely populated central urban area, while large-scale water plants are scattered around the urban area.

We also collected the longitude and latitude of the main wastewater treatment plants and the daily wastewater treatment volume in Shanghai 2017, and calculated the discharge intensity according to the daily sewage treatment volume of each wastewater treatment plant. The distribution of wastewater treatment plants in Shanghai is scattered. Except for a small number of large-scale wastewater treatment plants in the central and eastern parts, the treatment capacity of other wastewater treatment plants is almost the same. Emissions of chlorine precursors from wastewater treatment plants are shown in Fig. 2(b).

Table 3
Total emissions of atomic chlorine precursors in Shanghai 2017

Source		Total emissions (ton)		Percentage (%)	
First level sector	Second level sector	First level sector	Second level sector	First level sector	Second level sector
water treatment		850		9.8%	
cooling towers		4000		46.2%	
wastewater treatment		2700		31.2%	
swimming pools		280		3.2%	
tap water	water leakage	310	208.4	3.6%	2.4%
	lawn watering		77.3		0.9%
	road sprinkling		12.5		0.1%
	car wash		13.5		0.2%
usage of chlorine-containing disinfections	breeding plant	210	132.1	2.4%	1.5%
	household		34.1		0.4%
	hospital		25.4		0.3%
	toilets		17		0.2%
coal combustion		190		2.2%	
sea salt		90		1.0%	
chemical industry		20		0.2%	
Total		16200		100.0%	

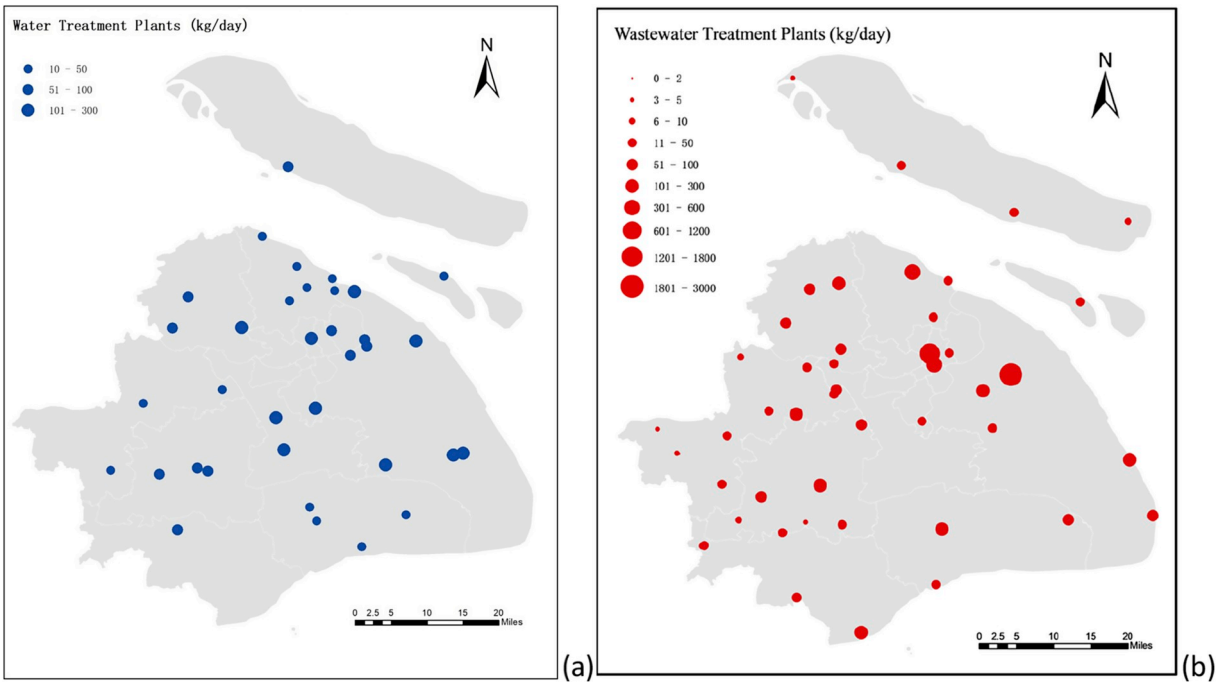

Fig. 2. Spatial distributions of atomic chlorine precursor emissions from water plants (a) and wastewater treatment plants(b).

3.2.2. Cooling towers

Large cooling towers are mainly concentrated in power plants. We collected latitude and longitude information and power generation capacity of the 26 power plants in Shanghai. The release intensity of atomic chlorine precursors was calculated according to the power generation of each power plant.

As shown in Fig. 3, Shanghai's large-scale power plants are mainly distributed in the northern and southern coastal areas while there is also a small distribution in the east and west.

3.2.3. Swimming pools

Longitudinal and latitudinal information of swimming pools are collected from Baidu Map (https://map.baidu.com/@13523265.31,3641114.64,12z. html). Emission intensity was calculated according to the volume of swimming pool. As can be seen from Fig. 4, large-scale swimming pools are mainly concentrated in densely populated urban centers, while small-scale swimming pools are scattered in the surrounding suburban.

3.2.4. Total emissions

Fig. 5 shows the spatial distribution of atomic chlorine precursor emissions from major sources in Shanghai in 2017. The central region is the main source of atomic chlorine precursors, where a large number of water treatment plants, wastewater treatment plants and swimming pools are concentrated. Several large point sources in northern Shanghai mainly come from cooling towers in power plants. The other major point source discharges come mainly from disinfection processes in wastewater and water plants.

3.3. Comparisons of chlorine emissions between Shanghai and Texas

Chang et al. (2001) made preliminary statistics on atomic chlorine precursors in south eastern Texas in 2000. Based on Chang's methodology, we further considered the contributions from coal combustion, public swimming pools, road sprinkling, water leakage, households, public toilets, livestock farming, aquaculture and hospitals to atomic chlorine precursors. At the same time, we have updated more reliable activity data.

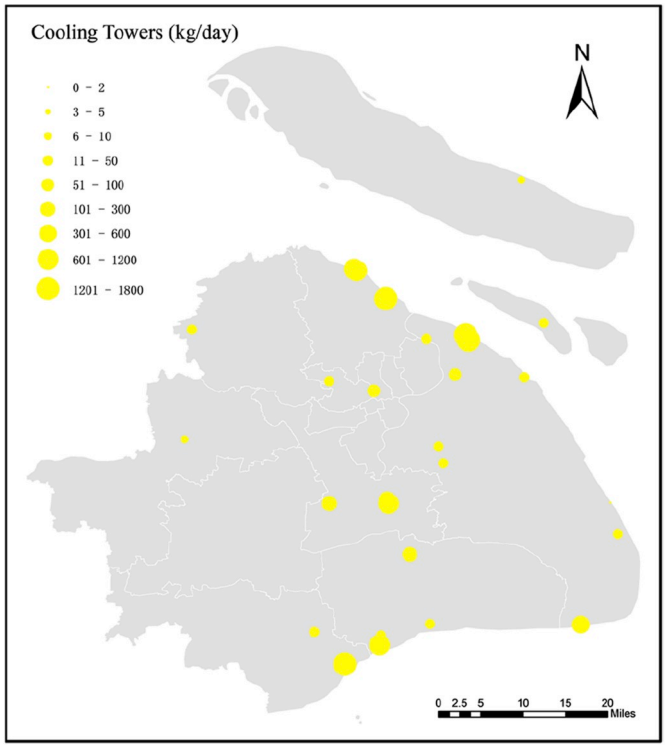

Fig. 3. Spatial distributions of atomic chlorine precursors emissions from Cooling Towers.

Table 4 shows the comparison between emissions of atomic chlorine precursors from Shanghai in 2017 and Southeast Texas in 2000. In 2000, the main sources of atomic chlorine precursors from Southeast Texas were cooling towers, swimming pools and industrial point sources. In 2017, the main sources of atomic chlorine precursors from Shanghai were water treatment plants, wastewater treatment plants, cooling towers and swimming pools. Compared with south eastern Texas, the

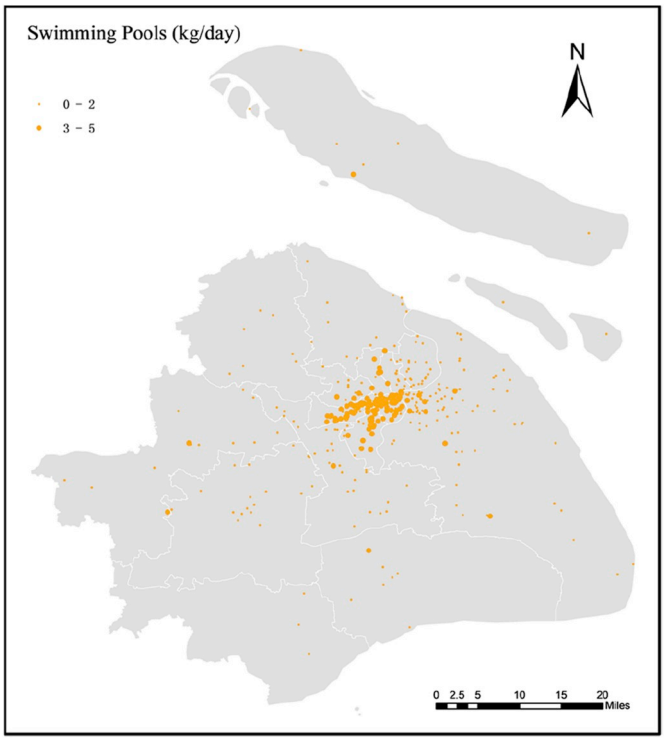

Fig. 4. Spatial distributions of chlorine emissions from Swimming Pools.

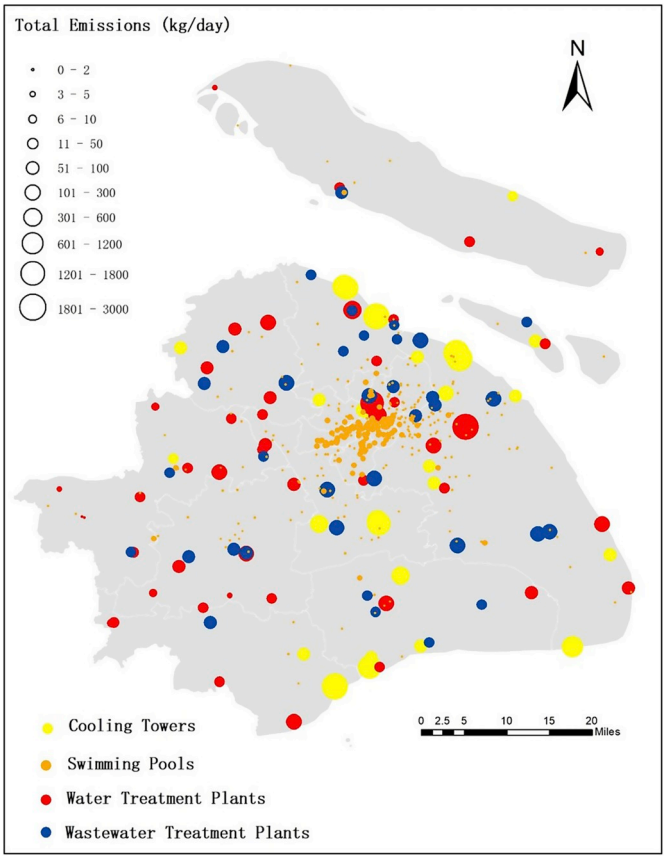

Fig. 5. Total emissions of molecular chlorine from wastewater treatment plants, cooling towers, water treatment plants, and swimming pools.

Table 4
Comparisons of chlorines emissions between Shanghai and Southeast Texas.

Emissions/Emission intensity	Shanghai, 2017	Southeast Texas, 2000
total emissions (ton)	8650	3453.0
water treatment (ton)	850	109.5
cooling towers (ton)	4000	2190.0
waste water treatment (ton)	2700	73.0
swimming pools (ton)	280	460.0
Industry (ton)	20	511.0
sea salt (ton)	90	109.5
emission rate by area (kg/m^2)	1379.1	132.7
emission rate by population (kg per capita)	0.4	0.6

emission of atomic chlorine precursors from the water and wastewater treatment in Shanghai cannot be neglected. This is because Shanghai's water use in 2017 was 7 times that of southeast Texas in 2000, which means that the chlorine-containing disinfectant consumption is very large. On the other hand, fewer swimming pools lead to fewer atomic chlorine precursors volatilized from this sources and emissions from the chlor-alkali industry in Shanghai is much lower than that in Texas.

3.4. Uncertainty analysis

We used a Monte Carlo method to analyse the uncertainty of this emission inventory. Since there are no similar emission factors and other parameters for reference, we assumed the probability distribution coefficients of the data based on the reliability of the data source (Table 5). As shown in Fig. 6, the uncertainty of chlorine emission in Shanghai in 2017 is -84.60% ~ 84.60% at 95% confidence interval. Emission factors, subjective assumption and activity data are the main causes of uncertainty. In order to reduce the uncertainty, future studies are needed to perform in-situ measurements and conduct local surveys to obtain more accurate emission factors as well as activity data.

In this study, the statistical results of the emissions of atomic chlorine precursors in Shanghai in 2017 represent only an order of magnitude estimation. This is because the emission factors of atomic chlorine precursors emitted by various sources are not from field measurement, but from estimation based on engineering estimates, leading to potentially large uncertainties On the other hand, atmospheric organic chlorine is potentially an important source that is not considered in this study. It is mainly due to the unclear mechanism of photochemical reactions of sea salt and atmospheric organic chlorine, and subsequently the atomic chlorine precursors produced in this process cannot be effectively counted.

Despite the uncertainty, this study estimates the amount of chlorine emitted by Shanghai in 2017, provides basic information for follow-up study, so as to better quantify the impact of the chemical mechanism of chlorine in the atmosphere on air pollution in Shanghai.

4. Conclusions

An emissions inventory was developed for chlorine precursors in Shanghai in the year 2017. Based on the activity data and some empirical judgment, emissions of atomic chlorine precursors from coal combustion, chemical industry, water treatment, wastewater treatment, cooling towers, swimming pools, water leakage, lawn watering, road sprinkling, car wash, hospitals, farms, household, public toilets and sea salt reactions were estimated separately. Results show that the emissions of atomic chlorine precursors from Shanghai in 2017 total emissions reaching 8650 tons. The main sources of chlorine precursors are the annual discharge of water treatment with 850 tons/year, accounting for 9.8% of the total discharge; cooling tower 4,000 tons/year, 46.2%; wastewater treatment 2,700 tons/year, 31.2%; swimming pool 280 tons/year, emissions in summer, accounting for 3.2% of the annual

Table 5
Assumptions for uncertainty analysis.

Parameter	Distribution
Water treatment	
Treatment water volume	Normal(CV:5%)
Chlorine dose	Lognormal(CV:50%)
Free chlorine	Normal(CV:5%)
Emission factor	Uniform(15%, 25%)
Cooling towers	
Supplementary water volume	Normal(CV:50%)
Scale of change	Lognormal(CV:50%)
Chlorine dose	Normal(CV:20%)
wastewater treatment	
Treatment water volume	Normal(CV:5%)
Chlorine dose	Lognormal(CV:50%)
Free chlorine	Lognormal(CV:50%)
Emission factor	Uniform(15%, 25%)
Swimming pools	
Number of swimming pools	Normal(CV:20%)
Volume of pools	Normal(CV:50%)
Chlorine concentration	Lognormal(CV:50%)
Tap water use	
Water consumption	Lognormal(CV:50%)
Free chlorine	Normal(CV:5%)
Usage of disinfectants	
Disinfectant consumption	Lognormal(CV:50%)
Emission factor	Uniform(20%, 40%)
Coal combustion	
Coal consumption	Normal(CV:10%)
Emission factor	Lognormal(CV:50%)
Chemical industry	
Waste gas volume	Normal(CV:10%)
Chlorine concentration	Lognormal(CV:50%)
Sea salt	
Emission	Lognormal(CV:50%)

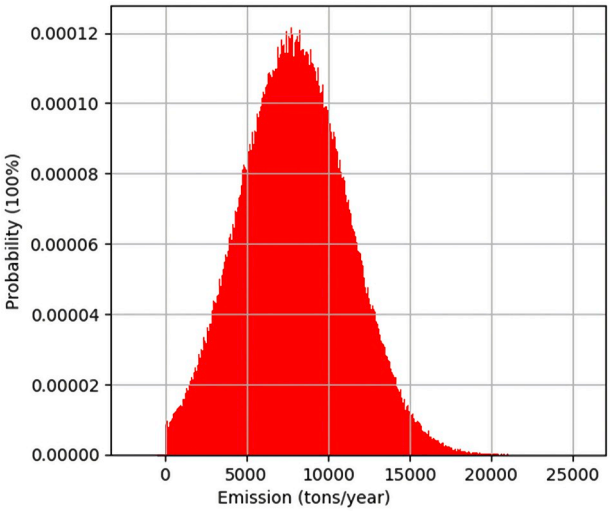

Fig. 6. Emission probability distribution.

discharge; 820 tons per year of water leakage, lawn watering, road sprinkling, car washing, forms, hospitals, household, public toilet, coal combustion and chemical industry, accounting for 9.5% of the total emissions. Average daily emissions from chlor-alkali chemical industry, sea salt reaction, coal combustion, farms, households, lawn watering, car washing, road sprinklers, toilets and leaks are relatively insignificant compared to the other sources.

Compared with Texas and its surrounding areas in 2000, where main sources of emissions were industrial sources and cooling towers, the main source of atomic chlorine precursors in Shanghai in 2017 is water-related disinfection processes. This is because Shanghai, as one of the largest city with the world's population, consumes a large amount of tap water every year and produces a large amount of sewage. The water-related disinfection process requires a large number of chlorine-containing disinfectants.

Photochemical reactions of organochlorine compounds in the atmosphere may be an important source of atomic chlorine precursors, and subsequent studies should quantify the emissions from such sources. This work provides a start for further study regarding chlorine chemistry on secondary air pollution.

Author contributions

LL designed this study and wrote the paper. Sijia Yin and Xin Yi conducted the data collection and calculation. Ling Huang, Yangjun Wang, Kun Zhang, Chel Gee Ooi and David T. Allen joined in discussions, and revisions of the manuscript. David T. Allen helped revise and polish the article and gave advice on paper writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.117220.

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