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Xin Yi [a,b,c,1], Sijia Yin [a,b,1], Ling Huang [a,b], Hongli Li [a,b], Yangjun Wang [a,b], Qian Wang [a,b], Andy Chan [d], Dramane Traoré [a,b], Maggie Chel Gee Ooi [e], Yonghang Chen [c], David T. Allen [f], Li Li [a,b,*]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China
[b] Key Laboratory of Organic Compound Pollution Control Engineering (MOE), Shanghai University, Shanghai 200444, China
[c] College of Environmental Science and Engineering, Donghua University, Shanghai 201620, China
[d] Department of Civil Engineering, University of Nottingham Malaysia, Semenyih 43500, Selangor, Malaysia
[e] Institute of Climate Change, National University of Malaysia, Bangi 43600, Selangor, Malaysia
[f] Centre for Energy and Environmental Resources, University of Texas at Austin, Austin, TX 78758, United States
* Corresponding author at: School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China.
E-mail address: Lily@shu.edu.cn (L. Li).
[1] These authors contribute equally to this work.

A B S T R A C T

Chlorine radical plays an important role in the formation of ozone and secondary aerosols in the troposphere. It is hence important to develop comprehensive emissions inventory of chlorine precursors in order to enhance our understanding of the role of chlorine chemistry in ozone and secondary pollution issues. Based on a bottom-up methodology, this study presents a comprehensive emission inventory for major atomic chlorine precursors in the Yangtze River Delta (YRD) region of China for the year 2017. Four primary chlorine precursors are considered in this study: hydrogen chloride (HCl), fine particulate chloride (Cl^-) (Cl^- in $PM_{2.5}$), chlorine gas (Cl_2), and hypochlorous acid (HClO) with emissions estimated for twelve source categories. The total emissions of these four species in the YRD region are estimated to be 20,424 t, 15,719 t, 1556 and 9331 t, respectively. The emissions of HCl are substantial, with major emissions from biomass burning and coal combustion, together accounting for 68% of the total HCl emissions. Fine particulate Cl^- is mainly emitted from industrial processing, biomass burning and waste incineration. The emissions of Cl_2 and HClO are mainly associated with usage of chlorine-containing disinfectants, for example, water treatment, wastewater treatment, and swimming pools. Emissions of each chlorine precursor are spatially allocated based on the characteristics of individual source category. This study provides important basic dataset for further studies with respect to the effects of chlorine chemistry on the formation of air pollution complex in the YRD region.

Keywords: Chlorine, Emissions inventory, Yangtze River Delta

1. Introduction

Atomic chlorine radical (Cl·) plays an important role in tropospheric atmospheric chemical reactions. For instance, Cl· can oxidise volatile organic compounds (VOCs) at rates of about 1 to 2 orders of magnitude faster than that of hydroxyl radicals (OH·) and this, may enhance the formation of ozone (Chang et al., 2002; Chang and Allen, 2006; Knipping and Dabdub, 2003; Tanaka et al., 2003; Wang et al., 2005, 2014b; Aschmann and Atkinson, 1995; Martin and Martin, 2010; Wang et al., 2020; Qiu et al., 2019a, 2019b), secondary organic aerosol (Wang and Ruiz, 2017; Qiu et al., 2019a, 2019b; Wang et al., 2020) and atmospheric oxidation capacity in the troposphere (Li et al., 2020a, 2020b). Field measurements in China have reported high concentrations of chlorine gas (Cl_2) (up to 1000 pptv) and nitryl chloride ($ClNO_2$) (up to 1200 pptv) in urban areas (Zhou et al., 2018; Xia et al., 2020), demonstrating that both Cl_2 and $ClNO_2$ level in China's urban areas is much higher than those observed in northern coastal cities of the United States (Spicer et al., 1998; Glasow, 2010; Liu et al., 2017; Stephen et al., 2019). Further studies reveal the existence of chlorine species that originated from anthropogenic sources in China (Tham et al., 2016; Wang and Ruiz, 2017; Yang et al., 2018). A comprehensive analysis on observed particulate chlorine (Cl^-) suggests high Cl^- loading in eastern China and the high mass ratios of Cl^-/sodium ion (Na^+)(1.75– 3.40) also confirms the existence of non-marine source of chlo-rine, amongst which coal combustion and biomass burning are considered as one of the main sources of Cl^- (Yang et al., 2018).

While atomic chlorine precursors are largely generated through chemistries in the atmosphere, the primary emissions are not negligible. Major primary precursor emissions including HCl, Cl_2, HClO and particulate Cl^- are emitted from both anthropogenic and natural sources (Finley and Saltzman, 2006; Khalil et al., 1999). An early chlorine related emission inventory has been developed for Cl_2/HClO over the Houston area of the United States in 2000 (Chang et al., 2001). Liu et al. (2018) developed the first anthropogenic chlorine emissions inventory for China (ACEIC) for year 2012, which includes emissions of HCl and Cl_2 from coal combustion and HCl from waste incineration plants. Hong et al. (2020) further updated the ACEIC with datasets for the year 2014 following the estimation method applied in their previous study (Liu et al., 2018). These studies are of great importance as they fill the gap between traditional emissions and chlorine related species. However, both ACEIC 2012 and 2014 only include HCl and Cl_2 emission from coal combustion and HCl emission from waste incineration stations. The emissions of HCl and particulate Cl^- from coal combustion, industrial processes, biomass burning and municipal solid waste incineration for China for year 2014 are later estimated (Fu et al., 2018), but gaseous Cl_2 and HClO are not included, while other anthropogenic sources (e.g. cooking, disinfectant usage, etc.) are not considered either. The global model study of Wang et al. (2019) emphasises the importance of natural sources of Cl but explicitly omitted HCl emissions from coal combustion in China because estimates were considered uncertain and small from a global perspective. On the contrary, a higher resolution model study by Li et al. (2020a, 2020b) supports the importance of anthropogenic Cl emissions in China and the need for improved bottom-up emission inventories. There are a number of inconsistencies in the literatures, and it further identifies the need for more complete inventories that support detailed modelling studies. An emission inventory of Cl_2/HClO, HCl, and Cl^- is developed recently for Shanghai (Li et al., 2020a, 2020b; Yi et al., 2020), the largest city in the YRD region with serious ozone (O_3) pollution as well as secondary aerosol problems (Gao et al., 2016; Shu et al., 2016). This indicates the anthropogenic emissions are significant, but as Shanghai only covers around 3% of the YRD region in area, it is thus important to develop an emission inven-tory of chlorine precursors in order to enhance our understanding of the O_3 and secondary pollution issues in the entire YRD region.

With these research motivations, we develop a comprehensive up-to-date anthropogenic emission inventory of major chlorine precursors,

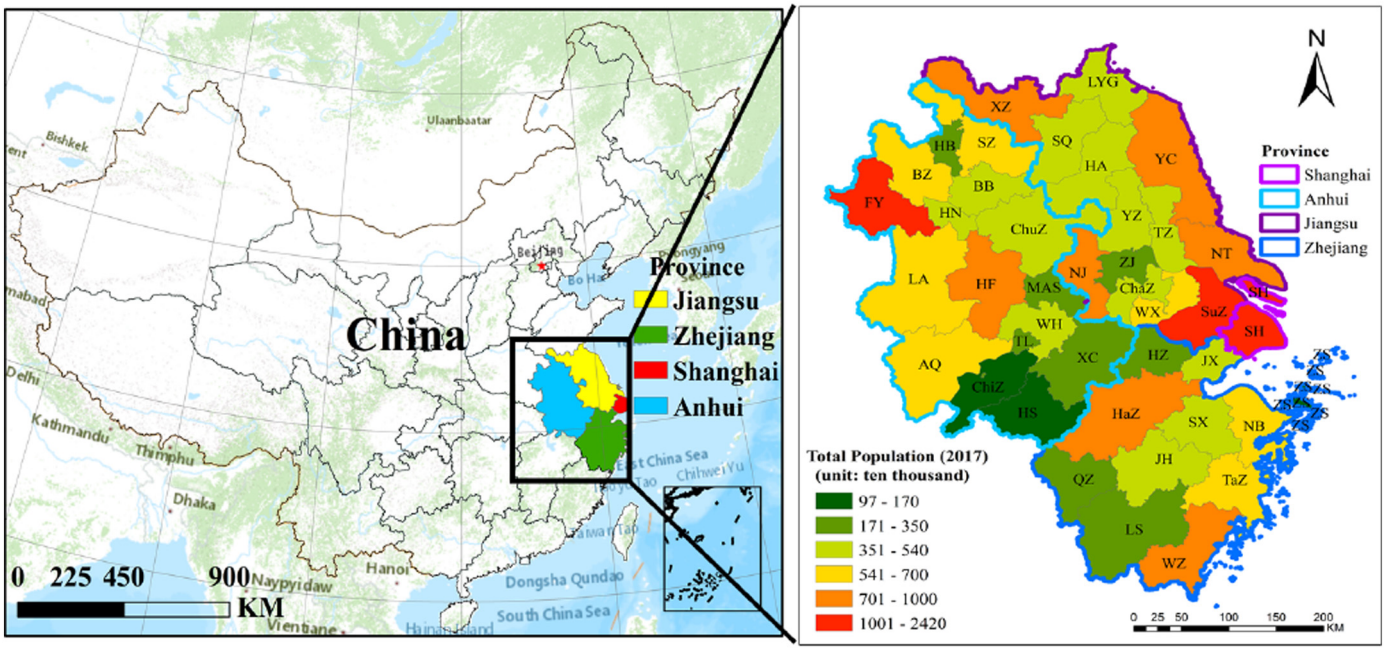


Fig. 1. Location of the Yangtze River Delta region and city-level population distribution.

including gaseous HCl, Cl_2, HClO, and fine particulate Cl^- for the YRD region for the year 2017. Anthropogenic emissions with a total of twelve source categories are included. Emissions of each chlorine precursor are spatially allocated based on the distribution of individual source category. The temporal profiles are also given based on the activity characteristics for each source category. Comparison with other studies and uncertainties are also discussed. This study serves as an essential input dataset for further study with respect to the role of chlorine chemistry in the formation of O_3 and secondary aerosols in the YRD city-cluster.

2. Methodology

The study area is the Yangtze River Delta (YRD) region, which includes Shanghai, Jiangsu, Zhejiang and Anhui provinces, as shown in Fig. 1.

Fig. 2 lists the emission sources of different chlorine precursors con-sidered in this study. Sources of HCl and Cl^- include the five main categories, namely: coal combustion, industrial processing, biomass burning, solid waste incineration and catering. Sources of Cl_2 and HClO include nine separate categories: coal combustion, chemical industry, cooling tower disinfection, water and wastewater treatment, usage of disinfectants, tap water use, and agriculture. Based on different technological processes and control measures, each source can be further divided into sub-categories. Details of sub-level sectors and associated chlorine precursors are listed in Table S1. A bottom-up method based on emission factors and activity data is applied to estimate the emissions of individual chlorine precursor from each source. The calculation method, sources of activity data and emission factors are summarized in Table 1. Details with respect to the emission calculations are provided in the Supplementary Information.

For spatial allocation of the emissions, the information on the latitude and longitude of power plants, industries, and waste incineration plants are collected and collated. Emissions from open biomass burning are allocated based on the locations provided in the National Center for Atmospheric Research (NCAR) - Fire Inventory from NCAR (FINN) fire spots. Emissions from other source sectors are mainly allocated based on population distribution of each city in the YRD region. For temporal allocation, we collect hourly activity intensity coefficients of various sources sectors (Mao et al., 2017; Zhang et al., 2015). In this study, the emission factor method is applied to calculate the emissions of the four chlorine precursors. The main calculation formulas are as follows:

a. HCl: The emissions of HCl are calculated based on the following equation,

$$E_{HCl} = \sum_{i,j} A_{i,j} \times EF_{(HCl)i,j} \quad (1)$$

where $A_{i,\ j}$ refers to the activity data, including the amount of coal combusted, industrial products, municipal solid waste incineration, straw combusted, etc.; $EF_{(HCl)i,\ j}$ represents the emission factors of HCl from different sources. i and j represents the county and subsectors respectively.

b. fine particulate Cl^-: The calculation method of $PM_{2.5}$ emissions has been established in details in previous studies (Zhao et al., 2013; Wang et al., 2014a, 2014b; Ma et al., 2017). The emissions of Cl^- are calculated based on the content of Cl^- in $PM_{2.5}$,

$$E_{Cl^-} = \sum_{i,j} A_{i,j} \times EF_{(PM_{2.5})j} \times M_j \quad (2)$$

where $A_{i,j}$ refers to activity data for $PM_{2.5}$ emissions, $EF_{(PM2.5)j}$ represents the emission factors of $PM_{2.5}$ from different sources; M is the fraction of Cl^- in primary $PM_{2.5}$ emissions. $_i$ and $_j$ represents the county and subsectors as above. The proportion of Cl^- in $PM_{2.5}$ adopted in this study is listed in Table S2.
The emission factors for Cl^- from biomass burning in China have been reported. Cl^- emissions from biomass burning are directly derivedfrom the activity level multiplied by the Cl^- emission factor. The emission factors of Cl^- from biomass burning adopted in this study are shown in Table S3.

c. Cl_2/HClO: The calculation methods of Cl_2 and HClO of different sources are slightly different. The main calculation method used is

$$E_{Cl_2/HClO} = \sum_i A_i \times (C_{ai} - C_{ri}) \times v \quad (3)$$

where $E_{Cl2/HClO}$ is the emission of Cl_2/HClO; A_i is the activity data; C_{ai} is the concentration of chlorine added in water, C_{ri} is the concentration of residual chlorine, v is the volatilisation rate. i represents the source type.

The detailed calculation methods for various sources including coal combustion, chemical industry, water and waste water treatment, use of biocides in cooling towers, disinfection of swimming pools, tap water and usage of chlorine-containing disinfectants have been reported in our previous study (Li et al., 2020a, 2020b). In addition, we also include emissions from agriculture in this article. There are many photochemical reactive chlorine-containing VOCs (e.g., fumigants and pesticides) in agricultural applications, which are especially important during the crop growing seasons. These chemicals can be precursors for chlorine radicals and may play a role in ozone or secondary organic aerosol (SOA) formation in agricultural regions. Zhang (2016) calculates that organic phosphorus, organic nitrogen, and organic sulphur pesticides accounted for approximately 70% of pesticide application in Guangdong, Jiangxi, and Hebei provinces. It is estimated that the use of organochlorine pesticides accounts for 30% of the total pesticides. The proportion of pesticides used is greater than 68%, and herbicides account for around 23% (Zhang, 2016). Information about several chlorine-containing pesticides and herbicides are shown in Table S4. The formula for calculating Cl_2/HClO emissions is shown in Eq. (4).

$$E_i = \sum_i \frac{T_i}{\rho} \times A_i \times C_i \times v, \quad (4)$$

where Ti is the amount of chlorine-containing pesticide used; ρ is the density of the insecticide; Ai is the effective component of chlorine; Ciis the proportion of molecular chlorine, v is volatile chlorine, and the value in this study is 30%, i represents the type of pesticide. The chlorine-containing herbicides are mainly liquid and have no density value, which do not need to be used ρ value in calculation.

3. Results and discussions

3.1. Estimated emissions of chlorine precursors

Table 2 shows the estimated emissions of chlorine precursors by source sector. The total emissions of HCl, Cl^-, Cl_2 and HClO in the YRD region in 2017 are estimated to be 20,424t (t), 15,719 t, 1556 t and 9331 t, respectively. The sectoral contributions from different emission category are presented in Fig. 3.

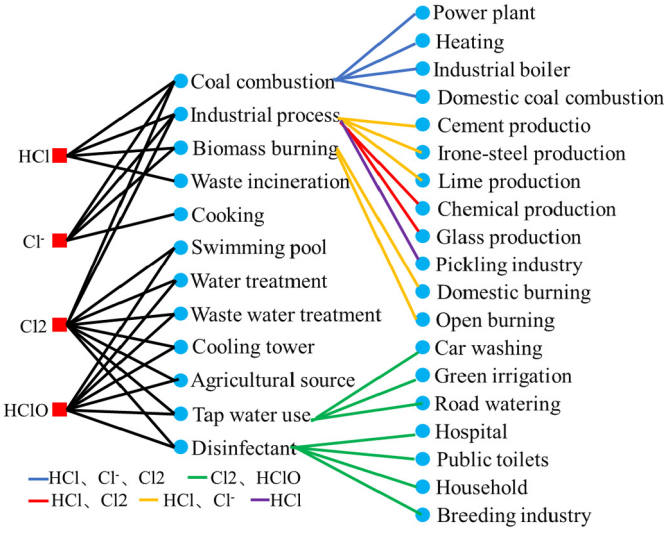


Fig. 2. Sources of chlorine precursors.

Table 1
Methods and data source applied to estimate chlorine emissions: Details of the activity data are listed in the Supporting Information.

Species	Source sector	Activity data	Emission factors
HCl	Coal combustion	The amount of coal burning, product output and waste incineration	Supplementary Eq. (19) (coal-fired)
	Industrial process		Table S8 (steel, cement, lime, chemical industry, biomass burning, garbage incineration)
	Waste incineration		
	Biomass burning-household-crop	Straw consumption	
	Biomass burning-household-firewood	Firewood consumption	
	Biomass burning-open	–	–
Cl^-	Coal combustion	The amount of coal burning, product output and waste incineration	Table S2 (the proportion Cl^- in $PM_{2.5}$)
	Industrial process		
	Waste incineration		
	Biomass burning	Biomass burning	Table S3 (biomass burning)
	Cooking	Number of households and catering companies	Wu et al., 2018
Cl_2	Coal combustion	Coal burning and exhaust gas production	Deng et al., 2014
	Industrial process		GB 31573-2015, GB 37823—2019
Cl_2/HClO	Swimming pool	Number of swimming pools	Chang et al., 2001
	Water treatment	Quantity of water and wastewater treatment	
	Waste water treatment		
	Cooling tower	Water supply of cooling tower	
	Agriculture source	Chlorine disinfectant usage	
	Tap water use-car washing	Car wash water consumption	
	Tap water use	Green irrigation and road watering	
	Disinfectant	Disinfectant usage in hospital	
		Public toilets and household	
		Breeding industry	

Major sources of HCl emissions include coal combustion (6283 t), industrial processing (3490 t), biomass burning (7543 t), and waste incin-eration (3108 t). Biomass burning represents the largest source of HCl emissions, accounting for 37% of total emissions, followed by coal com-bustion, industrial processing. The emissions of Cl^- are mainly from coal combustion (964 t), industrial process (1831 t), biomass burning (7222 t), waste incineration (4479 t) and cooking (1223 t). The largest anthropogenic source of Cl^- emissions is biomass burning, accounting for 46%.

Emissions of Cl_2 and HClO are mainly related to the usage of chlorine-containing disinfectants in water treatment (364 and 2746 t), wastewater treatment (510 and 3847 t) and swimming pools (170 and 1284 t). Cl_2 and HClO emissions from other sources including industrial processing, cooling towers tap water use, agricultural sources and disinfectant use are relatively small, each accounting for less than 10%of the total emissions.

Table 2
Emissions of chlorine precursors from various source sectors in the YRD in 2017.

Source category	Sub-sector	HCl emissions (t)	Cl^- emissions (t)	Cl_2 emissions (t)	HClO emissions (t)	Percentage of total emissions (%)
Coal combustion	Power plant	2504	269	115	–	6.1
	Heating	625	193	32	–	1.8
	Industrial boiler	386	120	19	–	1.1
	Disperse coal combustion	2767	382	6	–	6.7
Industrial process	Cement production	1424	240	–	–	3.5
	Iron-steel production	204	1411	–	–	3.4
	Lime production	250	180	–	–	0.9
	Chemical production	811	–	137	–	2
	Glass production	211	–	10	–	0.5
	Pickling industry	591	–	–	–	1.3
Biomass burning	Domestic burning	6128	6117	–	–	26
	Open burning	1415	1105	–	–	5.4
Waste incineration	–	3108	4479	–	–	16.1
Cooking	–	–	1223	–	–	2.6
Swimming pool	–	–	–	170	1284	6.6
Water treatment	–	–	–	364	2746	9.3
Waste water treatment	–	–	–	510	3847	0.1
Cooling tower	–	–	–	3	26	1
Agricultural source	–	–	–	54	405	0.6
Tap water use	–	–	–	31	235	1.9
Disinfectant	–	–	–	105	788	6.1
Total		20,424	15,719	1556	9331	100

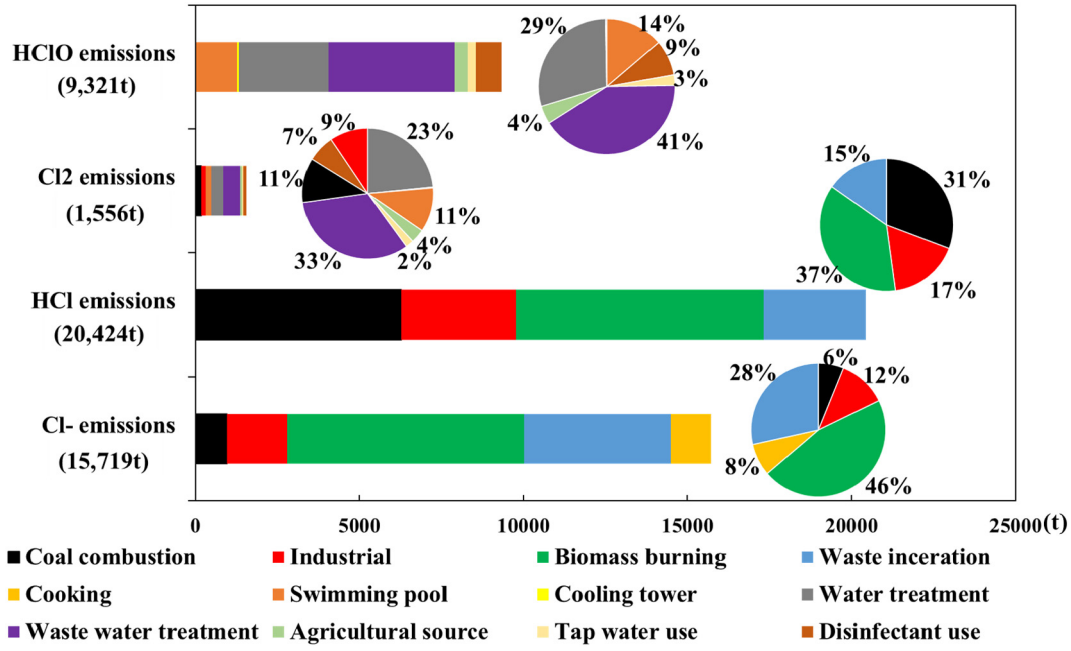


Fig. 3. Sectoral contributions of HCl, Cl^-, Cl_2 and HClO emissions in the YRD in 2017.

3.2. Spatial distribution of HCl, Cl^-, Cl_2 and HClO

The spatial distributions of annual total HCl, Cl^-,Cl_2 and HClO emis-sions are shown in Fig. 4. The chlorine precursors are mainly distributed around the central-east and northwest of the YRD region. The distributions of HCl and Cl^- are similar, with large emissions in Anhui and Jiangsu province, due to the relatively large amount of household biomass burn-ing and the relatively developed industry. The emissions of Cl_2 and HClO are higher in the central and eastern regions of the YRD region, especially in urban areas such as Shanghai, Suzhou, Hangzhou, Nanjing, mainly due to large amount of water treatment and wastewater treatment.

The spatial distributions of chlorine precursor emissions from different source sectors are shown in Fig. 5–6 and the Supporting Informa-tion. We obtain the specific latitudes and longitudes of coal-fired power plants, industrial coal-fired plants, steel plants, cement plants, garbage incineration plants and other enterprises from the 2018 environmental statistics. The domestic coal and household biomass burning according to rural population data, and cooking sources are allocated based on the respective commercial catering companies. Water treatment and wastewater treatment are allocated according to population, and is processed using SMOKE 3.7(Sparse Matrix Operator Kernel Emissions) for processing with a grid of 4 km × 4 km to obtain the result as shown in the Fig. 5. Coal combustion, industrial processing, waste incineration, water treatment and waste water treatment produce larger emissions in the central and eastern YRD region. Chlorine precursors produced by household biomass burning are mainly distributed in Anhui province, while large amounts of chlorine precursor emissions are produced by the open biomass burning in Anhui province. Cl_2 and HClO emissions in Shanghai, Suzhou, Nanjing, and Hangzhou are relatively high, with annual emissions exceeding 36 t and 350 t, respectively. This is mainly due to the large amount of water use, water and waste water treatment which is related to the population density. Huaibei, Chizhou, Huangshan, Xuancheng and Tongling (Anhui) have less Cl_2 and HClO emissions, with annual emissions lower than 6 t and 45 t respectively.

3.3. Temporal distribution of HCl, Cl^-, Cl_2 and HClO

The temporal profiles of different chlorine precursor emission sources are shown in Fig. 6. It is obvious that the emissions from 9:00 am to 12:00 am and from 17:00 pm to 19:00 pm are relatively high. Catering, household biomass burning, dispersed coal burning, industrial coal combustion and industrial processing have high contributions during this time period. From 22:00 pm to 5:00 am, the emission of chlorine precursors is relatively small, and the emissions from cooking sources, swimming pools, and water treatment sources are relatively small, which are closely related to people's daily activity. The opening hours of swimming pools are mainly distributed from July to September, which is obviously different from the emissions from other sources. The monthly changes in emissions from other sources have little variation.

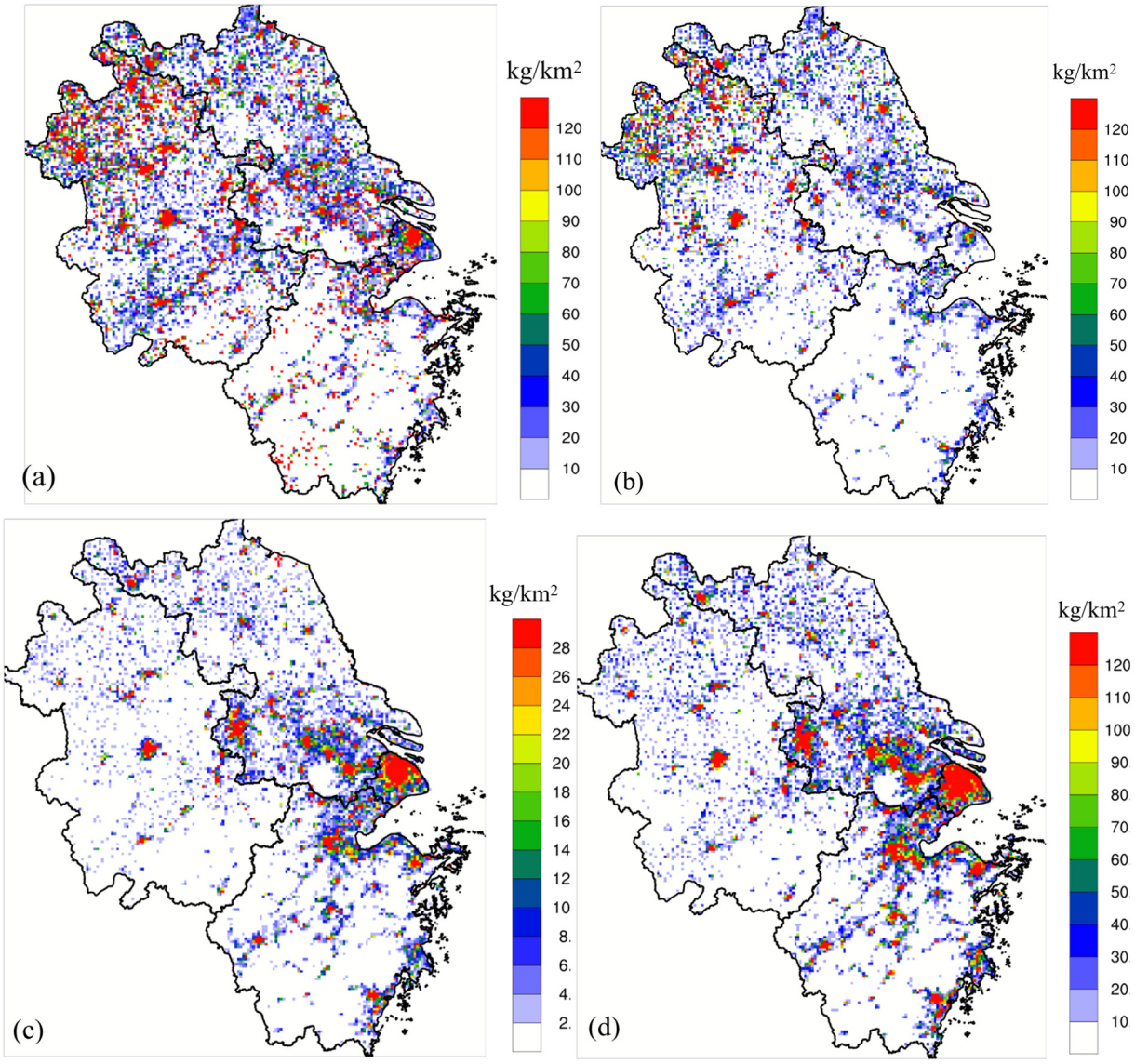


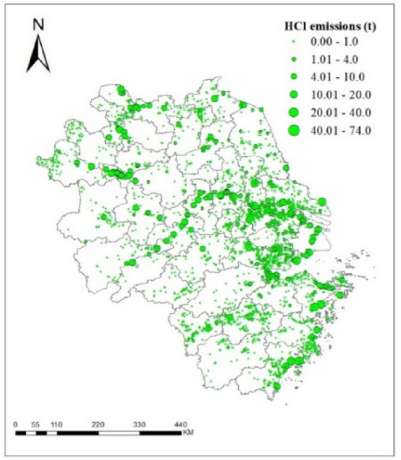
Fig. 4. Spatial distribution of (a)HCl, (b)Cl^-, (c)Cl_2 and (d)HClO emissions in the YRD in 2017.

3.4. Uncertainty analysis

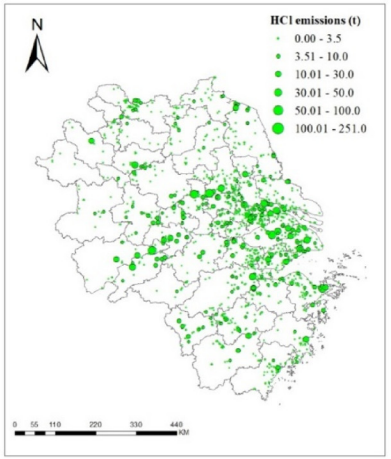
We estimate the uncertainty of the chlorine emission inventory based on Monte Carlo methods (Zhao et al., 2011; Zheng et al., 2009). We obtain the pertinent activity level data and the uncertainty distribution of emission factors from literatures (Zhou et al., 2017; Zhao et al., 2011) (Table S9). The uncertainty of HCl, Cl^-, Cl_2 and HClO emissions in YRD in 2017 is shown in Fig. 7, with uncertainties range of −26.8 to 16.8%, −57.4% to 56.8%, −105.7% to 166.5%, −75.1% to 94.5% at 95%confidence intervals, respectively.

The uncertainty of HCl and Cl^- mainly comes from the chlorine content in coal, the removal efficiency of HCl by coal-fired facilities and different coal-fired control measures, and the data of household biomass combustion activity has greater uncertainty. The uncertainty of Cl_2 and HClO mainly comes from the use of chlorinated pesticides in agricultural sources and the volatilisation factor of chlorinated substances, and the lack of detection values for the amount of chlorine and residual chlorine in the water and wastewater treatment processes. The amount of water treatment and sewage treatment also has large uncertainty.

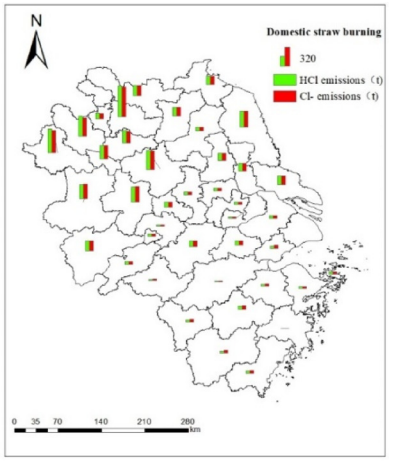
In order to reduce the uncertainty of the inventory, more emission measrurement data are needed, for example, the emission factors of HCl and Cl^- in industries such as steel, chemical and cement production, and the removal efficiency of HCl and Cl^- by different coal combustion control measures. Increasing the investigation of the use of chlorine-containing disinfection in the water treatment and waste-water treatment process, and obtain more information on the amount of chlorination and residual chlorine in the water treatment process. The proportion of Cl_2 and HClO volatilised in daily life applications are needed through experimental testing. In order to further verify the emission inventory, we recommend that chlorine precursors be observed in more locations and in different seasons, and the observed data is compared with the simulated data. Despite the uncertainty, the current inventory provides the latest and more comprehensive estimates of chlorine precursor emissions in the YRD region through detailed local data, so as to better understand the impact of chlorine chemistry on the generation of air pollution in the YRD region.



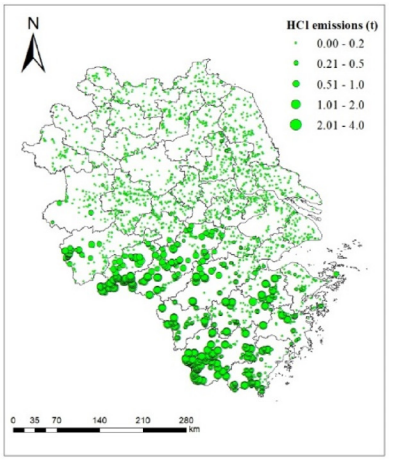
(a) HCl from coal combustion



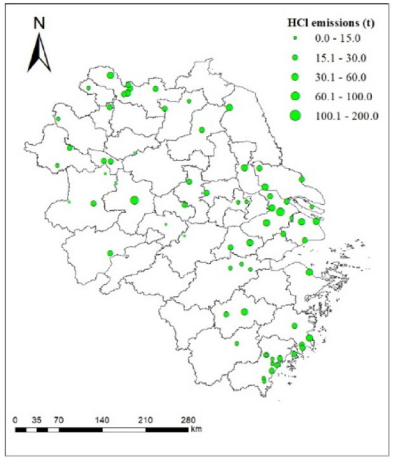
(b) HCl from industrial processing



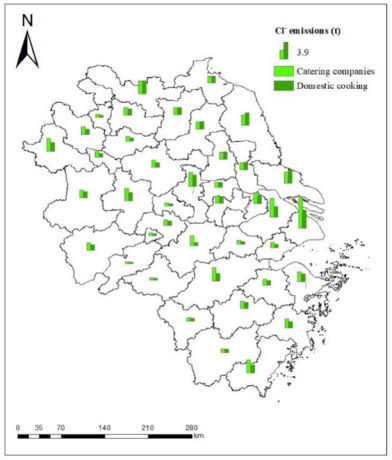
(c)HCl from household biomass burning



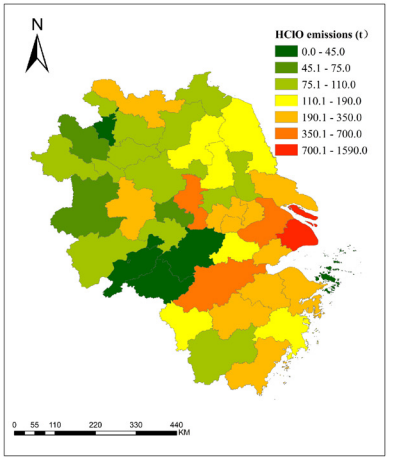
(d) HCl from open biomass burning



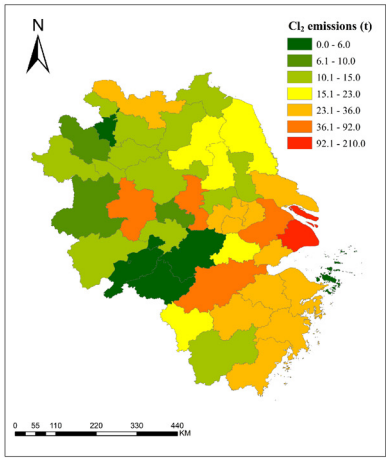
(e) HCl from waste incineration



(f) Cl^- emissions from cooking



(g)Area source of HClO emissions



(h) Area source of Cl_2 emissions

Fig. 5. Spatial distribution of HCl, Cl_2, Cl^- and HClO from different emission sources.

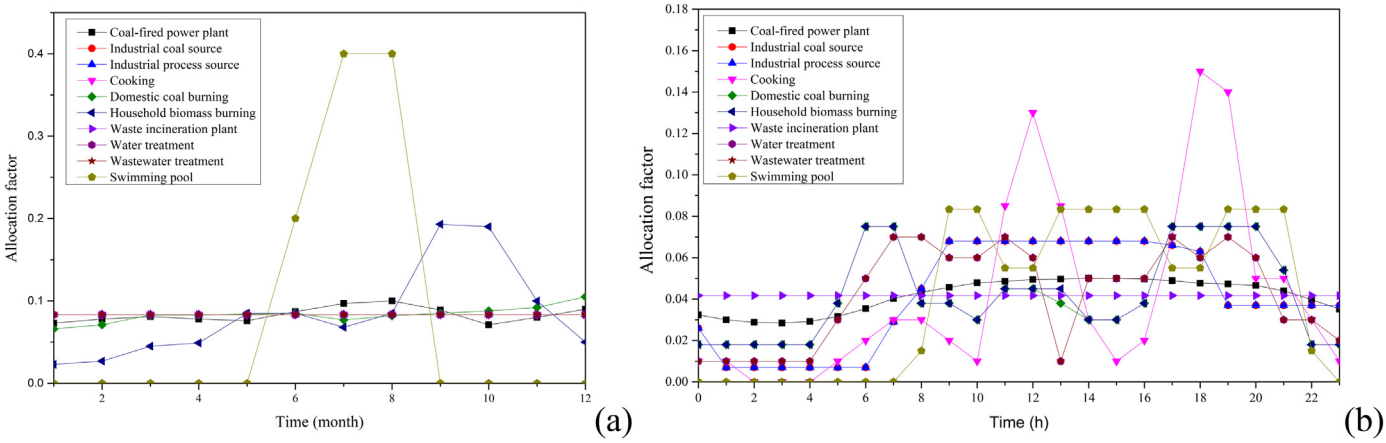


Fig. 6. Temporal distribution of different sources (a) monthly profile and (b) daily profile.

3.5. Comparisons with other studies

Table 3 shows comparisons between our results and previously reported data. The total emission intensity (emissions per unit area) over the YRD region is approximately one tenth of that estimated in Southeast Texas and 1.2 times higher than Beijing. The result of Cl_2 emissions estimated in our study is far lower than the emissions in Southeastern Texas. The main reason is that the use of chlorine-containing disinfectants in cooling towers in Southeastern Texas is more common, with a value of 6 t/day. There are few reports and studies on the use of chlorine-containing disinfectants in cooling towers in China. We use the industrial water consumption in the statistical yearbook and calculate the volatilisation of Cl_2 and HClO based on the circulating water volume of the cooling tower. The chlorine emissions from cooling towers in YRD (29 t) is much lower than that in Southeast Texas (2190 t).

We apply the same methods employed previously (Fu et al., 2018; Qiu et al., 2019a, 2019b) to estimate HCl and Cl^- emissions. However,

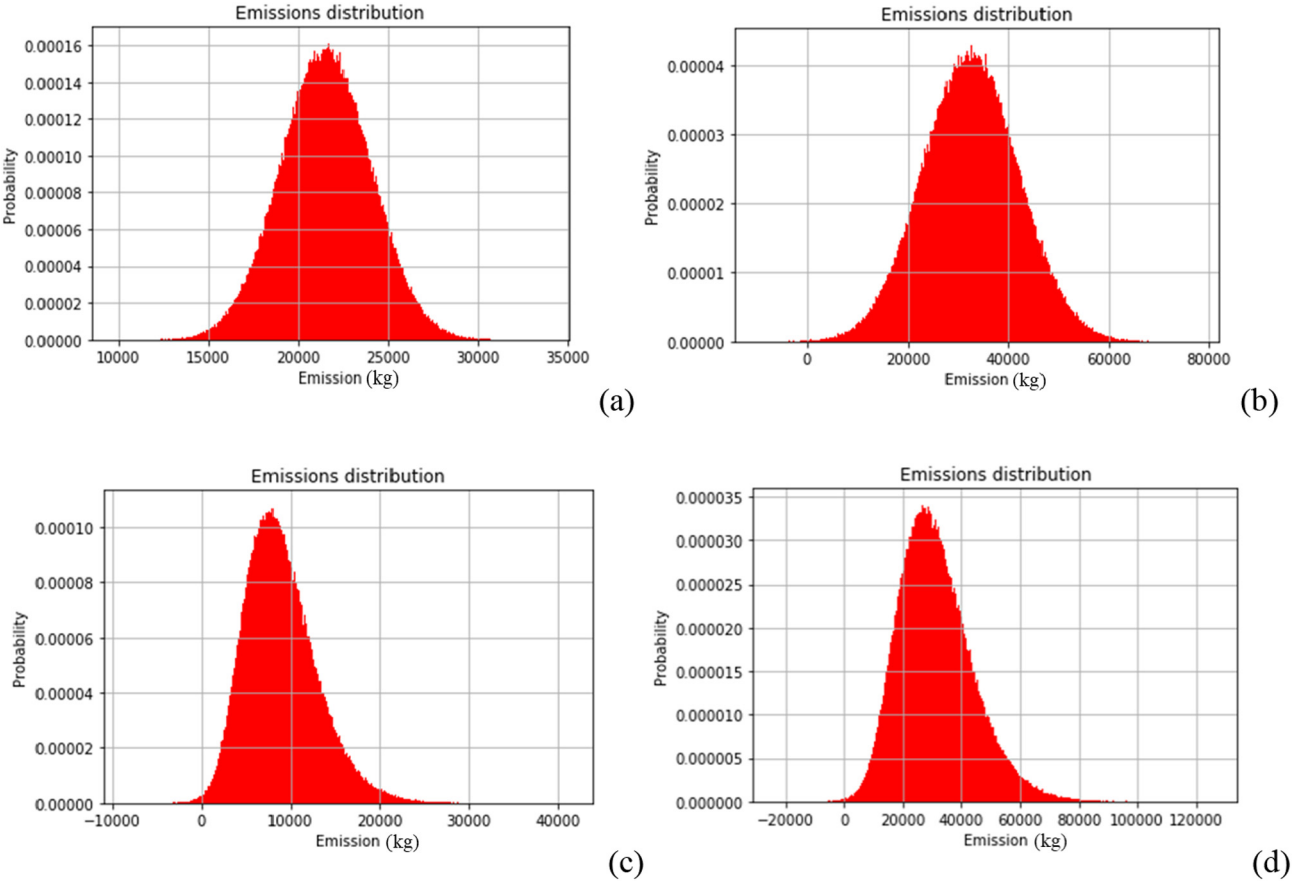


Fig. 7. Uncertainty distribution of HCl (a), Cl^- (b), Cl_2 (c) and HClO (d) emissions estimation.

Table 3
Comparisons of chlorine precursor emissions in different regions.

Region	Year	HCl emissions (t)	Cl^- emissions (t)	Cl_2 emissions (t)	HClO emissions (t)	Total chlorine emission rate by area (g/m^2)	Total chlorine emission rate by population ($g/per\ person*10^{-3}$)	Reference
Southeast Texas	2000	–	–	3453[a]	0	1.939	1.427	Chang et al., 2001
China	2012	235,800[b]	–	9400[c]	0	0.026	0.175	Liu et al., 2018
China	2014	223,400[d]	–	8900	–	0.024	0.166	Hong et al., 2020
China	2014	458,000[e]	486,000[f]	–	0	0.098	0.674	Fu et al., 2018
Beijing	2017	1893[g]	566[h]	29[i]	0	0.152	0.116	Qiu et al., 2019a, 2019b
Shanghai	2017	–	–	8650[j]	0	0.136	0.036	Li et al., 2020a, 2020b
Shanghai	2017	1207[k]	820[l]	–	0	0.32	0.083	Yi et al., 2020
YRD	2017	20,424[m]	15,719[n]	1556[o]	9331[p]	0.182	0.287	This study

[a] Water treatment: 110 t, waste water treatment: 73 t, disinfection of cooling tower: 2190 t, disinfection of swimming pools: 460 t, industrial sources: 365 t, sea salt: 110 t, tap water use: 110 t.
[b] Coal combustion: 232,900 t, waste incineration: 2900 t.
[c] Coal combustion: 9400 t.
[d] Coal combustion: 219,200 t, waste incineration: 4200 t.
[e] Coal combustion: 92,150 t (power plants, industrial boilers, domestic combustion), sources of industrial processes: 36,640 t (production of cement, steel, lime, bricks, HCl), biomass burning: 146,560 t (household, open), waste incineration: 187,780 t (incineration plant, open).
[f] Coal combustion: 24,300 t (power plants, industrial boilers, domestic combustion), sources of industrial processes: 29,160 t (production of cement, steel, lime, bricks, HCl), biomass burning: 364,500 t (household, open), waste incineration: 68,040 t (incineration plant, open).
[g] Coal combustion: 225 t (power plant, home combustion), industrial sources: 587 t, biomass burning: 0.18 t, waste incineration: 1080 t.
[h] Coal combustion: 41 t (power plant, home combustion), industrial sources: 89 t, biomass burning: 0.14 t, waste incineration: 8.5 t, cooking: 427 t.
[i] Coal combustion: 9 t (power plant, home combustion), industrial sources: 20 t.
[j] Coal combustion: 190 t (power plants, industrial, residential, other), industrial process sources: 20 t (chemical), water treatment: 850 t, wastewater treatment: 2700 t, cooling tower disinfection: 4000 t, swimming pool disinfection: 280 t, tap water use: 310 t, disinfectant use: 210 t, sea salt: 90 t.
[k] Coal combustion: 327 t (power plants, industrial boilers, domestic combustion other), sources of industrial processes: 134 t (production of cement, steel, HCl), biomass burning: 24 t (household, open), waste incineration plant: 722 t.
[l] Coal combustion: 82 t (power plants, heating, industrial boilers, domestic combustion, other), industrial process sources: 153 t (cement, steel), biomass combustion: 47 t (household, open), waste incineration: 498 t (incineration plant, open), cooking: 39 t (household, school, government agency, commercial catering), sea salt: 0.6 t.
[m] Coal combustion: 6283 t (power plants, heating, industrial boilers, household combustion), industrial process sources: 3490 t (cement, steel, lime, glass, chemical, pickling), biomass combustion: 7543 t (household, open), waste incineration: 3108 t (incineration plant, open).
[n] Coal combustion: 964 t (power plants, heating, industrial boilers, household combustion), industrial process sources: 1831 t (cement, steel, lime), biomass combustion: 7222 t (household, open), waste incineration: 4479 t (incineration plant, open), cooking: 1223 t, sea salt: 18,104 t.
[o] Coal combustion: 172 t (power plants, heating, industrial boilers, household combustion), industrial process sources: 147 t (chemical, glass), water treatment: 364 t, wastewater treatment: 510 t, cooling tower disinfection: 3 t, swimming pool disinfection: 170 t, tap water use: 31 t, disinfectant use: 104 t, agricultural sources: 54 t.
[p] Water treatment: 2746 t, wastewater treatment: 3847 t, cooling tower disinfection: 26 t, swimming pool disinfection: 1284 t, tap water use: 235 t, disinfectant use: 788 t, agricultural sources: 405 t.

both studies do not consider the emissions of chlorine precursors in the pickling, glass, and chemical industries. The industrial source of HCl in this study is more comprehensive. Compared with these studies (Fu et al., 2018) our results show a large contribution of HCl emissions from industrial sources while waste incineration only contributes a small proportion. The emissions calculated in this study are significantly different from those estimated due to the expansion of source categories and the different base year selected (Fu et al., 2018).

The HCl and Cl2 emissions from coal combustion and waste incineration sources in China are estimated in a previous study (Liu et al., 2018), with emissions from coal combustion processes estimated at 232,900 t and 9400 t, respectively for the year of 2014. In this study, the emissions of HCl and Cl2 from coal combustion in the YRD region are 6283 t and 172 t, respectively. The emissions of HCl from coal combustion are about 36 times higher than that of Cl2, and our results are higher than the results reported earlier, which is 25 (Liu et al., 2018). The most likely reason is that the annual coal consumption for the year 2012 calculated is higher than the coal consumption adopted in our study (year 2017), and the efficiency of related flue gas treatment facilities has also improved thus the emissions of HCl and Cl2 are lower in our study. This comparative results also indicate that the update of emissions inventory is very important due to the strict air pollution control measures conducted in China.

Cl^- emissions from commercial restaurants and households in the YRD region are also included in this study. Cl^- emissions from cooking in Beijing are estimated at 426.8 t, accounting for 75% of total Cl^- emissions (Qiu et al., 2019a, 2019b). In this study, Cl^- emissions in the YRD are estimated to be 1223 t, accounting for only 8% of anthropogenic Cl^- emissions. The large discrepancy is possibly due to the proportion of Cl^- in $PM_{2.5}$ in the cooking source in Beijing area (10%) is quite different from the factor applied in our study (1%) and the emissions from other sources may have been underestimated.

4. Conclusions

In this study, we establish a comprehensive emission inventory of chlorine precursors in the YRD region for the first time. Annual emissions of HCl, Cl^-, Cl_2 and HClO for the YRD region in the year 2017 are estimated at 20,424 t, 15,719 t, 1556 t and 9331 t, respectively. For HCl and Cl^-, biomass burning is the dominant contributor, accounting for 37% and 46% of total emission, respectively. Cl_2 emissions are primarily contributed by water and wastewater treatment, and swimming pool disinfection. Uncertainty analysis suggests that Cl_2 emissions have the largest uncertainty. Measurement of emission factors and atmospheric concentrations of atmospheric chlorine species are recommended in order to constrain and improve the accuracy of the inventories. Results from this study serve as a basis for further research regarding the impact of chlorine chemistry on the formation of ozone and secondary aerosols.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Supporting Information for "Anthropogenic emissions of atomic chlorine precursors in the Yangtze River Delta Region, China"

Xin Yi [a,b,c#], *Sijia Yin* [a,b,#], *Ling Huang* [a,b], *Hongli Li* [a,b], *Yangjun Wang* [a,b], *Qian Wang* [a,b], *Andy Chan* [d], *Dramane Traoré* [a,b], *Maggie Chel Gee Ooi* [e], *Yonghang Chen* [c], *David T. Allen* [f], *Li Li* [a,b*]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai, 200444, China

[b] Key Laboratory of Organic Compound Pollution Control Engineering (MOE), Shanghai University, Shanghai 200444, China

[c] College of Environmental Science and Engineering, Donghua University, Shanghai 201620, China

[d] Department of Civil Engineering, University of Nottingham Malaysia, Semenyih 43500, Selangor, Malaysia

[e] Institute of Climate Change (IPI), National University of Malaysia (UKM), 43600, Bangi, Selangor, Malaysia

[f] Centre for Energy and Environmental Resources, University of Texas at Austin, Austin, TX 78758, United States

 # These authors contribute equally to this work.

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* Correspondence to Li Li: Lily@shu.edu.cn

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Figure S3. Distribution of Cl^- emissions from open biomass burning

Figure S4. Distribution of Cl^- emissions from waste incineration plants

Data:

S1. Activity data

S1-1 Coal Combustion

Coals are mainly used for power plants, heating, industries, and residential purposes. Coal is also consumed in the production of cement, steel, glass, and lime in industrial processing sources. The amount of coal combusted from various sources is derived from the 2018 environmental statistics and statistical yearbooks. Calculation methods are mainly based on product output and exhaust emissions.

S1-2 Industrial processes

Chemical industry The chlor-alkali industry and the production of chlorine-containing chemicals, reagents and pesticides will release HCl and Cl_2. The direct chlorine-related product from the chlor-alkali industry is chlorine while indirect

products include hydrochloric acid, bleaching powder, disinfectant, and liquid chlorine. Exhaust gas is emitted during the production of chlorine-containing chemicals, reagents, and pesticides with HCl and Cl_2 in the exhaust gas. Exhaust emissions are derived from 2018 environmental statistics.

Pickling industry Pickling of metal surfaces (the removal of oxidic scale and rust on steel surfaces with common acids of sulphuric acid and hydrochloric acid) consumes a large amount of hydrochloric acid, which produces volatile HCl. Exhaust emissions are derived from 2018 environmental statistics.

Cement, Steel, Glass, and Lime production Fu et al. (2018) indicates that the main chlorine precursors released during the production of cement, steel, and lime are HCl and Cl^-, and Wang et al. (2014) finds that HCl and Cl_2 are contained in glass production flue gas. The output of cement, steel, lime and flue gas from the glass production processes are derived from 2018 environmental statistics.

S1-3 Biomass burning

Biomass burning includes domestic burning and open biomass burning. In the sector of domestic burning, the amount of crop straw burning amount is calculated using Eq (1), while the mass of firewood burning is calculated by Eq (2).

$$A_j = P_j \times R_j \times F_j \times D_j \times C_j \quad (1)$$

$$A_j = H_j \times T_j \times B_j \quad (2)$$

where A_j is the mass of crop straw and firewood; P_j is the crop yield; R_j is the ratio of straw to product; F_j is the proportion of household straw burning; D_j is the dry matter fraction; C_j is the combustion efficiency. j represents the type of crop; the

value of F_j is from the existing research (Zhou et al.,2017), and the values of R_j, D_j, and C_j are from Zhou et al. (2017), which are shown in Table S5. H_j is the number of rural population households; T_j is the number of firewood burning days. Considering the domestic burning of crop straw, the number of days of firewood burnt is 260 days; and B_j is the daily amount of firewood burned by rural households. Investigation revealed that the value of B_j was 2 kg per family per day.

In terms of open biomass burning, we use the $PM_{2.5}$ emissions from the FINN emissions inventory. The Cl^- emission is calculated based on the Cl^- content in $PM_{2.5}$. There are already $PM_{2.5}$ emissions in the wildfire inventory, and the HCl emissions are estimated based on the ratio method of $PM_{2.5}$ and HCl emission factors, which is 22:1 ($PM_{2.5}$: HCl) (Fu et al., 2018; Zhou et al.,2017).

S1-4 Waste incineration

Incineration is an important technology for municipal waste treatment. HCl and Cl^- are released during the incineration process. The waste incineration mass of each plant was derived from 2018 environmental statistics. The mass of open waste incineration is negligible in content of strict control of open waste incineration.

S1-5 Cooking

The number of households and commercial enterprises in the cooking source category is obtained from statistical yearbooks at city level. The Cl^- containing in smoke is emitted during cooking, which will be released into the air.

S1-6 Disinfection of cooling towers

Industrial cooling towers are mainly used in coal fired power plant, steel, cement,

chemical industry, and refining industry (Chang et al.,2001; Yan et al.,2018; Zhao et al.,2017).

S1-7 Swimming pool disinfection

The number of swimming pools and their locations are derived from Baidu maps. Outdoor swimming pools are usually open in summer.

S1-8 Water treatment and wastewater treatment

The total water supply and sewage treatment volume of each city are derived from the 2018 statistical yearbook of each city.

S1-9 Agricultural sources

The use of chlorinated fertilizers and pesticides in agricultural sources may lead to the volatilization of chlorine precursor materials. Commonly used chlorinated fertilizers are potassium chloride (KCl) and ammonium chloride (NH_4Cl). KCl is relatively stable and not easy to volatilize. NH_4Cl will not decompose under normal temperature, but it decomposes when heated to 100 ℃, which can be completely decomposed into ammonia gas and hydrogen chloride gas at 337.8 ℃. Therefore, the release of chlorine precursors from the use of chlorinated fertilizers is negligible. Chlorine-containing pesticides are used less because of their persistence in the environment, low water solubility, difficulty in degradation and metabolism, and long-distance transmission, such as HCHs, dichlorodiphenyltrichloroethane (DDTs), chlordane, entozoan, etc. Chlorine-containing pesticides have been banned from production and use in most countries (Yang et al.,2012; Deng et al.,2014). According to information obtained in recent years, the use of pesticides containing chlorinated

pesticides include cyhalothrin, lambda-cypermethrin and chlorantraniliprole. Chlorine-containing herbicides are mainly sodium dimethyl tetrachlorochloride, triflufenacil and clofensulfuron. We assume that part of the chlorine in chlorinated pesticides and herbicides is released into the air as Cl_2/ HClO. The total amount of pesticide used is from the statistical yearbook of each city, from which the amount of chlorine-containing pesticides is calculated based on the proportion of various pesticides used in the literature.

S1-10 Use of tap water

The values of green irrigation area, number of passenger vehicles and road area are obtained from the statistical yearbooks of each city.

S1-11 Usage of disinfectants

The number of hospitals, public toilets, households, and breeding (aquatic products, pig and poultry production) are derived from the statistical yearbooks of each city.

S2 Emission factors

S2-1 Coal combustion

The calculation for the emission factors of HCl produced by coal combustion is

$$EF_{(HCl)i,j,k} = C_i R_{j,k} \sum_l \left(1 - f_{(so_2)i,j,k,l}\eta_{(so_2)i,j,k,l}\right) \sum_m \left(1 - f_{(PM)i,j,k,m}\eta_{(PM)i,j,k,m}\right) \quad (3)$$

where C_i is the average chlorine content in the coal consumed; $R_{j,k}$ is the release rate of HCl; $f_{(so_2)i,j,k,l}$ and $f_{(PM)i,j,k,m}$ are the application rates of traditional sulphur dioxide and respirable particulate matter (PM) emission control technologies, which are

obtained in previous studies (Zhao et al.,2013; Wang et al.,2014; Ma et al.,2017); $\eta_{(so_2)i,j,k,l}$ and $\eta_{(PM)i,j,k,m}$ are removal efficiency of traditional sulphur dioxide and PM emission control technology for HCl; i,j,k,l and m represent the province, department, technology / fuel type, SO_2 and PM emission control technology, respectively. i represents different provinces.

The values of chlorine content in coal are taken from Fu et al. (2018) study, which are shown in Table S6.

The release rate of HCl depends on the combustion technology. In this study, coal combustion facilities are divided into four types: pulverized coal boilers, circulating fluidized bed boilers, stove and stoker furnaces. The proportion of combustion technology for power plants, industrial boilers and domestic combustion were derived from the emission database established in our previous studies (Zhao et al.,2013; Wang et al.,2014; Ma et al.,2017). Based on the field measurements of 6 power plants in China (Deng et al.,2014), the HCl release rate of pulverised coal boilers was set at 87%, with values ranging from 78% to 93%. Paradiz et al. (2015) measures the HCl release rate of coal with different Cl content in the furnace. In this study, an average HCl release rate of 68% is used as the HCl release rate of the furnace. Due to the lack of measurement results, the HCl release rates of circulating fluidized bed boilers and stoker furnaces were set to 87% and 80%, respectively, referring to the SO_2 release rate used in previous studies coal burning (Fu et al., 2018; Zhao et al.,2013; Wang et al.,2014).

In order to improve air quality, a series of emission control devices have adopted

in China's power plants and industrial boilers. Analysis of field measurement data shows that these conventional air pollution control devices can also reduce HCl emissions. We use the values of Fu et al. (2018), as shown in Table S7.

S2-2 Chemical industry and pickling industry

Discharge of chlorine-containing substances in the chemical industry mainly involves the production of hydrochloric acid, the manufacture of chlorine-containing chemicals, pesticides, and reagents. HCl and Cl_2 are mainly produced during the production process and pickling industry only produces HCl, which can be calculated by Eq (19).

$$E_i = G_i \times C_i \tag{19}$$

where E_i is the mass of emissions; G_i is the amount of exhaust emissions; C_i is the concentration of HCl and Cl_2. i represents different industries. The concentrations of HCl and Cl_2 in the chlor-alkali industry and in the production of chemicals, pesticides, and reagents come from the national standard (GB 31573-2015; GB 37823-2019). Cao et al. (2009) gives the content of HCl in the waste gas of the pickling industry.

Table S1. Activity data of different emission sources

Province	City	Coal combustion($\times10^4$t)			Cement production($\times10^4$t)	Waste incineration($\times10^4$t)	Water volume ($\times10^6$ m^3)		
		Power plant	Heating	Industrial boiler			Water treatment	Wastewater treatment	Cooling tower water supply
Shanghai		2608.3	163.2	250.2	303.4	190.9	3055	2655	433
Zhejiang	Hangzhou	272.3	233.1	194.3	3109.3	44.2	694.5	635.2	653.9
	Ningbo	2917	167.9	371	1746.8	118.7	444	406.1	418.1
	Wenzhou	1339.9	25.1	57.3	200	217.6	380.9	348.4	358.7
	Jiaxing	1187.5	264.5	341.8	1428.4	23.1	401.2	367	377.8
	Huzhou	529.4	79.7	83.5	2570	111.1	299.7	274.1	282.2
	Shaoxing	586.7	286.1	89.3	972.4	22.8	386.9	353.9	364.3
	Jinhua	498.1	31.6	74.4	2220.4	75.6	348.2	318.5	327.9
	Quzhou	96.6	171	102.7	2644.2	0	249.2	227.9	234.6
	Zhoushan	612	0	23.8	94.9	0	34.6	31.7	32.6
	Taizhou	1463.1	64.1	43.2	291.1	155.1	330.2	302.1	310.9
	Lishui	30.4	0.7	41.8	270.8	15.7	147.6	135	139
Anhui	Hefei	667.5	80.4	65.6	3278.8	90.8	608.8	566.2	108.6
	Huaibei	1017.4	31.2	9.2	615.4	30.8	59.4	48.4	20
	Bozhou	378.4	9.2	13.3	235.9	14.5	48	52.9	12.7
	Suzhou	263.9	188.8	44.4	1284.3	12.6	58.3	41.1	31
	Bengbu	294.9	34.1	32.2	510.7	4.8	184.4	134.1	85.4
	Fuyang	241.6	0.8	59.8	319	40	98.1	86.2	28.3
	Huainan	2524.6	137.2	86.6	938.9	59.8	97.2	83.4	15
	Chuzhou	192.9	0.5	75.4	2091.9	0	118.2	109.7	29.7

	Luan	258.3	1	11	493.3	34.9	73.2	53.2	8.9
	Maanshan	794.1	0	112	2410.2	22.3	136.1	96.7	65.1
	Wuhu	249.2	281	52.6	4383	75.7	193.5	157.3	56.8
	Xuancheng	246.8	0	54.7	2196	10.3	55.7	45.4	13.6
	Tongling	671.3	16.4	34.5	4077.7	0	77.9	49.8	11.9
	Chizhou	127.4	0	46.8	1719.6	0	34.8	29.8	8.2
	Anqing	508.1	124.2	39.8	1577.2	27	116.4	90	37
	Huangshan	0	1.1	11.8	279.8	0	48.4	33.7	12.8
	Nanjing	1076.1	609.9	351.7	1542	68.5	1340	1160.8	475.1
	Wuxi	944.3	1130.2	190.7	1983.3	93	458	396.8	166.1
	Xuzhou	1263.3	1070.5	61.6	2728.1	93.1	318	275.5	112.2
	Changzhou	11.2	558.9	85.7	3110.6	42.5	360	311.9	112.9
	Suzhou	3148.8	722.3	792.7	1049.2	283	780	675.7	332.6
	Nantong	1473.6	236.9	217.5	806.4	184.3	297	257.3	121.4
Jiangsu	Lianyungang	417.2	80.7	168.2	317.4	0	121	104.8	31.8
	Huaian	237.5	216.2	333.8	574.1	33.9	222	192.3	102.7
	Yancheng	409.9	633.7	161.5	1630.2	11.9	116	100.5	16.6
	Yangzhou	661.6	54.2	243.8	594.9	0	200	173.3	53.2
	Zhenjiang	1612.3	30.5	192.6	2255.6	25.6	160	138.6	71.2
	Taizhou	297.1	1020.6	134.9	722.2	35	110	95.3	35.1
	Suqian	100	60.2	31.8	247.7	59.2	88	76.2	36.5
YRD		32230.6	8817.7	5389.5	59825.1	2328.3	13350.4	11691.8	6145.4

Table S2. Content of Cl^- in primary $PM_{2.5}$ emissions

Source Categories	Cl^- percentage in primary $PM_{2.5}$ emission (%)	Reference
Pulverized coal boiler	1.1	Kong, 2012; Pei et al., 2016; Wang et al., 2016; Zheng et al., 2013; Ma et al., 2015; Liang et al., 2016
Circulating fluidized bed boiler	0.78	Pei et al., 2016; Ma et al., 2015; Li et al., 2009; Zhao et al., 2015; Liu et al., 2014
Stoker furnace	3.49	Kong, 2012; Li et al., 2009; Liu et al., 2014; Cao et al., 2014; Xu et al., 2018; Shang et al., 2012; Wang et al., 2008
Stove	0.82	Kong, 2012; Zhang et al., 2012
Sinter production	3.9	Zhao et al., 2014; Wang et al., 2015; Ma, 2009
Puddling	3.54	Zheng et al., 2013; Zhao et al., 2014; Ma, 2009
Cement kiln	0.875	Kong, 2012; Ma et al., 2015,2010
Lime kiln	1.53	Fu et al.,2018
Brick kiln	0.82	Fu et al.,2018
Waste incineration	7.58	Fu et al.,2018; Mugica et al.,2008

Table S3. Cl^- emission factors of biomass burning

Biomass	Emission Factor (g/kg)	Reference
Rice straw	0.4635	Hong et al., 2015; Ju et al., 2018; Tian, 2016; Ye et al., 2019; Wang et al., 2016,2007; Zhang et al., 2013
Wheat straw	0.5271	Ju et al., 2018; Tian et al., 2016; Ye et al., 2019; Wang et al., 2016,2007
Corn straw	0.4146	Ju et al., 2018; Tian et al., 2016; Ye et al., 2019; Wang et al., 2007
Soybean straw	0.233	Ju et al., 2018; Ye et al., 2019
Rape straw	0.246	Ju et al., 2018
Branch	0.16	Liu et al., 2016; Sen et al., 2014; Ju et al., 2019

Table S4. Types of insecticides and herbicide

Type	Name	Density (g/ml)	Active ingredient	Chlorine content (%)
Insecticide	Lambda-cyhalothrin	1.25	25g/l	7.89
	Lambda cypermethrin	1.32	200g/l	14.49
	Chlorantraniliprole	1.507	59.4g/l	16.86
Herbicide	Sodium dimethyltetrachloride	—	56%	16.46
	Carbendazim	—	75%	9.81
	Clopyrsulfuron	—	75%	8.16

Table S5. Values of *R*, *D*, and *C* in this study

Crop	*R* (Straw-to- product ratio)	*D* (dry matter fraction)	*C* (combustion efficiency)
Corn	1.27	0.87	0.92
Wheat	1.30	0.89	0.92
Rape	1.50	0.83	0.9
Rice	1.32	0.89	0.93
Bean	1.60	0.91	0.68

Table S6. Chlorine content in coal

Province	Chlorine content（ppm）	Reference
Anhui	244	Fu et al.,2018
Jiangsu	258	Fu et al.,2018
Zhejiang	273	Fu et al.,2018
Shanghai	214	Fu et al.,2018

Table S7. Removal efficiency of different HCl control equipment

Control devices	Removal efficiency (%)	Reference
Wet flue gas desulfurization	96.5	Fu et al.,2018
Other-flue gas desulfurization	89.7	Fu et al.,2018
Fabric filter	10.4	Fu et al.,2018
Wet scrubber	50	Fu et al.,2018
Electrostatic precipitator	5.2	Fu et al.,2018

Table S8. HCl emission factors from other sources

Source category	Emission factor	References
Iron-steel production（$g \cdot t^{-1}$）	0.6	Fu et al.,2018
Lime production（$g \cdot t^{-1}$）	29.72	
Cement kiln（$g \cdot t^{-1}$）	1.435	Ma et al., 2010
Chemical production（$mg \cdot m^{-3}$）	10	GB 31573-2015
Pickling industry（$mg \cdot m^{-3}$）	28.75	Cao et al.,2009
Glass production（$mg \cdot m^{-3}$）	4.165	Wang et al.,2014
Rice straw（$g \cdot kg^{-1}$）	0.44	Stockwell et al.,2014
Wheat straw（$g \cdot kg^{-1}$）	0.6	
Other-straw（$g \cdot kg^{-1}$）	0.52	Fu et al.,2018
Wood（$g \cdot kg^{-1}$）	0.06	
MSW incineration plants−grated firing incinerator ($g \cdot kg^{-1}$)	0.2	Tian et al.,2012
MSW incineration plants−fluidized bed incinerator($g \cdot kg^{-1}$)	0.089	

Table S9. Assumptions for uncertainty analysis.

Parameters	Distribution
Activity data	
Power plants	Normal（CV：5%）
Heating	Normal（CV：5%）
Industrial boilers	Normal（CV：5%）
Disperse coal	Normal（CV：50%）
Steel production	Normal（CV：10%）
Cement production	Normal（CV：10%）
Lime production	Normal（CV：10%）
Glass production	Normal（CV：10%）
Chemical industry	Normal（CV：20%）
Pickling industry	Normal（CV：20%）
Biomass burning	Normal（CV：30%）
Waste incineration	Normal（CV：5%）
Cooking	Normal（CV：50%）
Numbers of cooling tower	Normal（CV：50%）
Surface area of swimming pool	Normal（CV：20%）
Water treatment	Normal（CV：10%）
Wastewater treatment	Normal（CV：10%）
Tap water use	Normal（CV：30%）
Usage of disinfectants	Normal（CV：30%）

Use of pesticides	Normal（CV：40%）
HCl release ratio	
Pulverized coal boiler	Uniform (78%,93%)
Circulating fluidized bed boiler	Uniform（86%,93%）
Stoker furnace	Uniform (75%,85%)
Stove	Normal（CV:50%）
HCl removal efficiency	
WFGD	Uniform (90%,99.29%)
Other-FGD	Uniform (85%,93.9%)
Wet scrubber	Uniform (9.46%,11.26%)
ESP	Uniform (0.9%,6.53%)
Wet scrubber	Lognormal (CV:50%)
HCl emission factor	
Steel production	Lognormal (CV:50%)
Cement production	Lognormal (CV:10%)
Lime production	Normal（CV：10%）
Chemical industry	Lognormal (CV:30%)
Pickling industry	Lognormal (CV:30%)
Glass production(mg/m^3)	Uniform (1.5,11.23)
Grated firing incinerator（g/kg）	Uniform (0.0761,0.3504)
Fluidized bed incinerator（g/kg）	Uniform (0.089,0.0891)
Biomass burning-rice straw(g/kg)	Uniform (0.0393,0.8065)
Biomass burning-wheat straw(g/kg)	Uniform (0.0201,1.0034)
Biomass burning-other crop straw (g/kg)	Lognormal (CV: 50%)
Biomass burning-wood(g/kg)	Uniform (0.0376,0.087)
Fine particle Cl^- percentage	
Pulverized coal boiler	Uniform (0.2%,3%)
Circulating fluidized bed boiler	Uniform (0.62%,1.2%)
Stoker furnace	Uniform (0.1%,16.27%)
Stove	Uniform (0.64%,1%)
Cement production	Uniform (0.3%,1.92%)
Steel production	Uniform (0.74%,8.37%)
Lime production	Lognormal（CV：30%）
Waste incineration	Uniform (2.5%,13.8%)
Cooking source	Lognormal（CV：20%）
Cl^- emission factor	
Biomass burning-rice straw(g/kg)	Uniform (0.187,0.83)
Biomass burning-wheat straw(g/kg)	Uniform (0.1317,0.939)
Biomass burning-corn straw(g/kg)	Uniform (0.059,1.026)
Biomass burning-bean straw(g/kg)	Uniform (0.068,0.361)
Biomass burning-rape straw(g/kg)	Lognormal (CV:50%)
Biomass burning-wood(g/kg)	Uniform (0.086,0.276)

Cl_2/HClO emission	
Coal combustion	Lognormal (CV:50%)
Water treatment	Uniform（10%,30%）
Chlorine dose	Lognormal (CV:50%)
Free chlorine	Normal (CV:5%)
Wastewater treatment	Uniform（10%,30%）
Chlorine dose	Lognormal (CV:50%)
Free chlorine	Normal (CV:30%)
Cooling tower	Normal (CV:50%)
Swimming pool	Uniform（10,100）
Tap water use	Normal (CV:50%)
Free chlorine	Normal (CV:10%)
Usage of disinfectants	Uniform（20%,40%）
Chemical industry	Lognormal (CV:50%)
Use of pesticides	Normal (CV:50%)

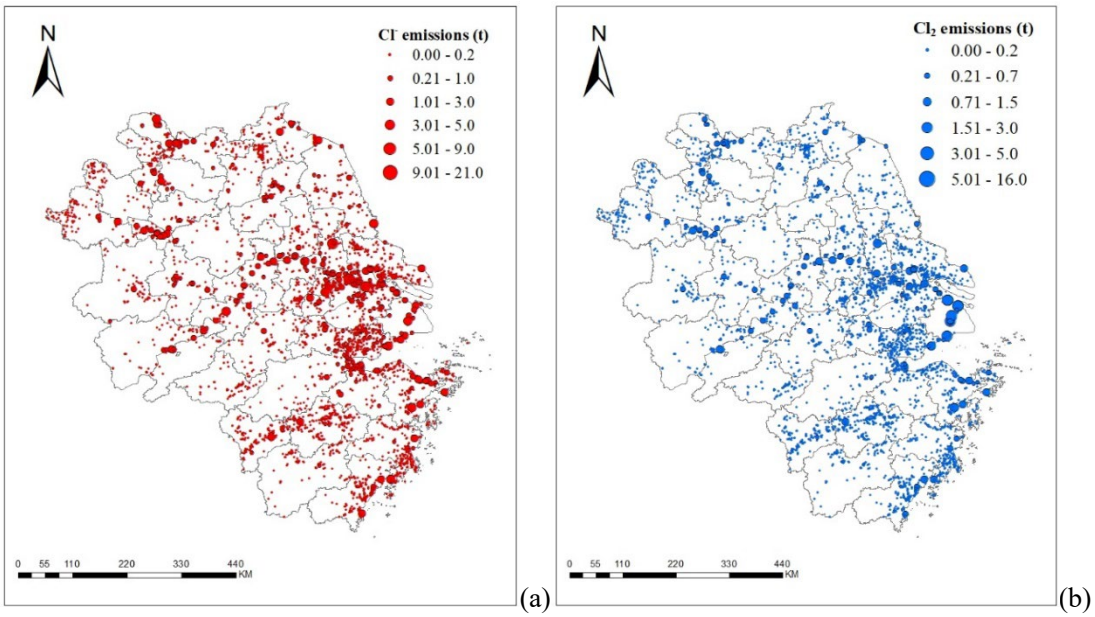

Figure S1. Emission distribution of Cl^-(a) and Cl_2(b) from coal combustion sources

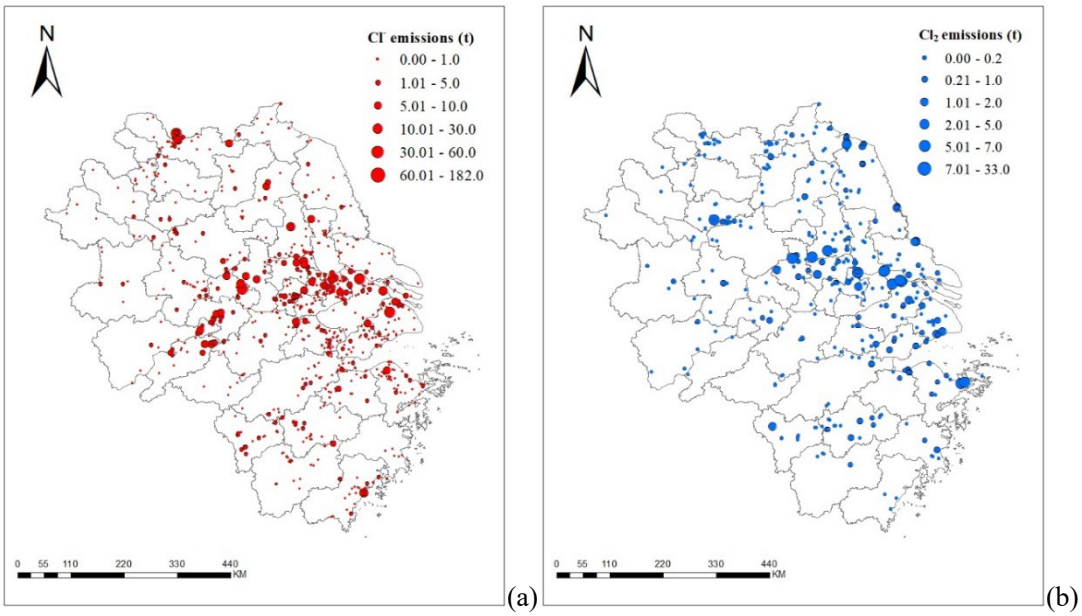

Figure S2. Distribution of Cl^-(a) and Cl_2(b) emissions from industrial processing

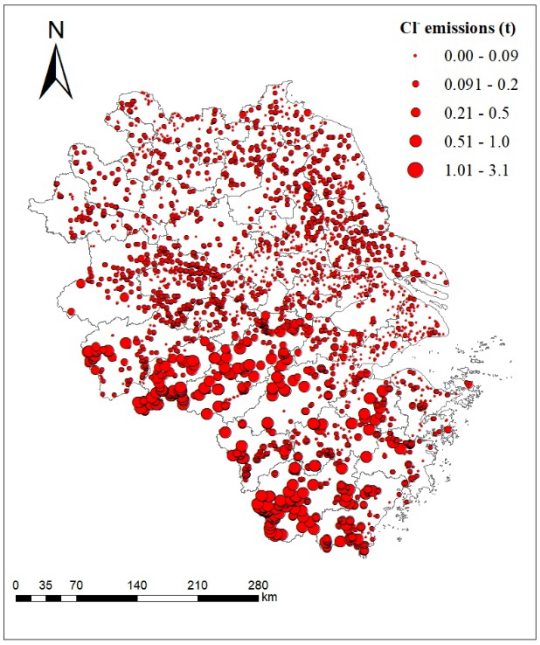

Figure S3. Distribution of Cl^- emissions from open biomass burning

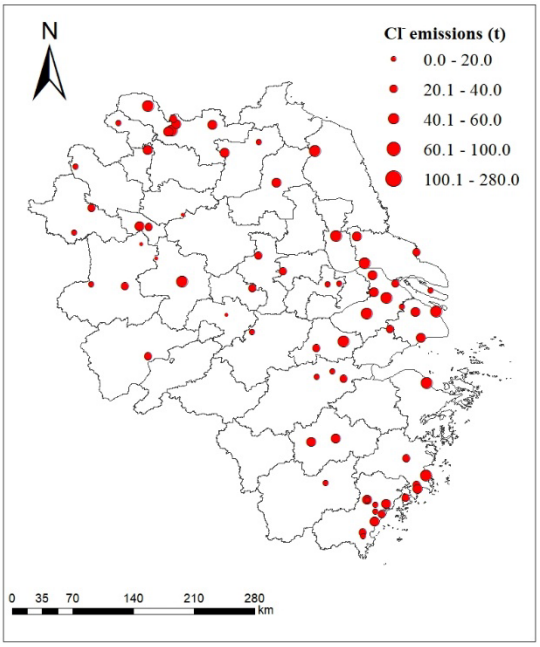

Figure S4. Distribution of Cl^- emissions from waste incineration plant

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