

# An Updated Anthropogenic Emission Inventory of Reactive Chlorine Precursors in China

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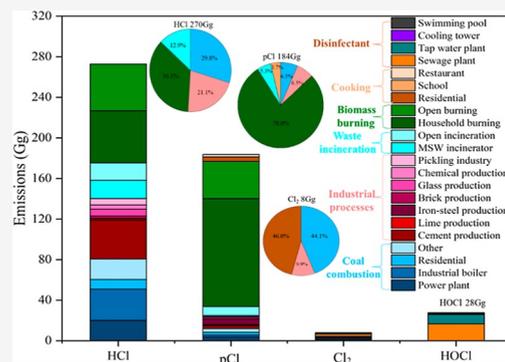
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**ABSTRACT:** The chlorine radical ( $\text{Cl}^\bullet$ ) plays an important role in the formation of secondary pollutants such as ozone and secondary organic aerosols. However, primary emissions of reactive chlorine species are not well known. Here, we develop an up-to-date emission inventory of major primary reactive chlorine precursors, including chlorine gas ( $\text{Cl}_2$ ), hypochlorous acid ( $\text{HOCl}$ ), hydrogen chloride ( $\text{HCl}$ ), and particulate chloride ( $\text{pCl}$ ) in mainland China for the year 2019 with a spatial resolution of  $0.1^\circ \times 0.1^\circ$ . The anthropogenic sources considered in this study include six major source categories (coal combustion, industrial processes, municipal solid waste incineration, biomass burning, cooking, and chlorine-containing disinfectants) and 22 sub-categories. The  $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{HCl}$ , and  $\text{pCl}$  emissions in mainland China in the year 2019 are estimated to be 7.8, 27.6, 270.3, and 183.5 Gg, respectively, with the major source contributors being use of chlorine-containing disinfectant (46%), use of chlorine-containing disinfectant (100%), biomass burning (36.1%), biomass burning (78.0%), respectively. The emission intensity of  $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{HCl}$ , and  $\text{pCl}$  for most provinces range from 0 to 3 tons-year<sup>-1</sup>·km<sup>-2</sup>. Emissions are highest in Eastern China, especially in the Beijing–Tianjin–Hebei and surrounding area, and the Yangtze River Delta region. The temporal distribution varies in different regions due to different human activities, industrial structures, and climatic conditions. The Monte Carlo method was applied to quantify the uncertainty of this emission inventory. The ranges of uncertainty in the emission of  $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{HCl}$ , and  $\text{pCl}$  were estimated to be 4.4–14.2, 9.7–51.6, 207.2–422.7, and 106.4–321.1 Gg·yr<sup>-1</sup>, respectively. This study provides an updated chlorine emission inventory with improved spatial and temporal resolution, enabling better quantification of chlorine production and its impact on the air quality in China.

**KEYWORDS:** chlorine, reactive chlorine precursors, anthropogenic sources, emission inventory, China



## 1. INTRODUCTION

Secondary air pollutants, such as ozone ( $\text{O}_3$ ) and secondary aerosols, are formed via oxidation of  $\text{NO}_x$  and VOCs by hydroxyl radicals ( $\text{OH}^\bullet$ ).<sup>1,2</sup> Recent research has indicated that, in addition to  $\text{OH}^\bullet$ , the chlorine atom ( $\text{Cl}^\bullet$ ) also plays an important role in urban atmospheric chemistry, which could have a significant impact on the atmospheric oxidation capacity<sup>3,4</sup> and thus the formation of ozone,<sup>5–7</sup> nitrate,<sup>8</sup> and secondary organic aerosols.<sup>9,10</sup> The daytime  $\text{Cl}^\bullet$  concentrations are estimated to be quite low (ranging between  $0.4 \times 10^4$  and  $4.0 \times 10^5$  molecules  $\text{cm}^{-3}$ )<sup>11–14</sup> due to its relatively high reactivity toward hydrocarbons, including alkanes and even methane.<sup>12</sup> This high reactivity allows chlorine to greatly affect the atmospheric oxidation capacity and radical production.<sup>15</sup> Recent field observations show that the concentrations of reactive chlorine species such as  $\text{Cl}_2$  and  $\text{ClNO}_2$  in inland areas of China are unexpectedly high,<sup>16–18</sup> indicating there are significant anthropogenic sources of chlorine in mainland China. Therefore, it is of great significance to understand their sources.<sup>19</sup>

Previous studies have pointed out that the sources of reactive chlorine species are complicated, including anthropogenic<sup>2,20</sup> and biogenic<sup>21</sup> sources. Primary anthropogenic emissions of  $\text{HCl}$ ,  $\text{pCl}$ ,  $\text{Cl}_2$ , and  $\text{HOCl}$  come from power plants,<sup>22</sup> industrial processes,<sup>20,23</sup> wastewater treatment plants,<sup>24</sup> cooling towers,<sup>6</sup> swimming pools,<sup>25</sup> tap water usage, coal combustion,<sup>20,26</sup> municipal solid waste (MSW) incineration,<sup>2,27</sup> biomass burning,<sup>28</sup> cooking,<sup>8</sup> chlorine-containing disinfectants,<sup>6,29–32</sup> and others.  $\text{HCl}$  is also released from sea-salt aerosol through acid displacement reactions involving  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .<sup>33</sup> A couple of studies have tried to develop emission inventories for chlorine species. The earliest anthropogenic chlorine emission inventory for China is

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Reactive Chlorine Emission Inventory (RCEI)\_1990, which was compiled for the year 1990 with a spatial resolution of  $1^\circ \times 1^\circ$ , developed by the International Global Atmospheric Chemistry (IGAC) program's Global Emissions Inventory Activity.<sup>34</sup> The first chlorine emission inventory based on local data in China was developed by Liu et al.<sup>26</sup> for the year 2012, with HCl and Cl<sub>2</sub> emissions from coal combustion and waste incineration considered. A relatively detailed chlorine emission inventory including pCl and HCl from coal combustion, MSW incineration, industrial processes, and biomass burning was developed for the year 2014 for China by Fu et al.,<sup>20</sup> which concluded that pCl and HCl emissions were mainly from biomass burning and MSW incineration. Later, Qiu et al.<sup>8</sup> further estimated pCl emissions from cooking for 2014 for Beijing. However, these studies mainly focus on emissions of HCl and pCl. Our previous study also takes into consideration primary emissions of reactive chlorine species such as Cl<sub>2</sub> and HOCl for Shanghai as well as the Yangtze River Delta region.<sup>29,30</sup>

Previous chlorine emission inventories have provided an important basis for research regarding the impact of chlorine chemistry on air pollution. However, there are still high uncertainties regarding the previously established inventories, which can be demonstrated in the following ways. First, modeling results indicate that observed pCl concentrations are much higher than model predictions using the pCl and HCl emission inventory for 2014 as input,<sup>10</sup> suggesting that there are high uncertainties or missing sources in the previous RCEI. Second, there are clear inconsistencies in Cl<sup>•</sup> formation pathways based on observations and modeling studies. For example, Priestley et al.<sup>35</sup> pointed out that the Cl<sup>•</sup> mainly comes from Cl<sub>2</sub> photolysis (~74%) based on observations. However, modeling studies by Wang et al.<sup>36</sup> concluded that 90% of the annual mean Cl<sup>•</sup> radicals originate from ClNO<sub>2</sub> chemistry, while the remaining 10% comes from HCl + OH, Cl<sub>2</sub>, and HOCl photolysis; even in summer, the latter pathway contributes less than 25%. The big gap between observations and modeling is partially due to the underestimation of chlorine emissions or missing sources of Cl<sub>2</sub> and HOCl. Third, the previously established inventories are mostly focused on past years (e.g., 2012 or 2014). In recent years, China has implemented stringent control measures to control air pollutant emissions, including the Clean Air Act (2013–2017) and the Blue-Sky Protection Campaign (2018–2020). As a result, the activities and the emission factors related to chlorine species have changed a lot. For example, the amount of coal consumption has increased significantly, from 3565T<sub>g</sub> in 2012<sup>37</sup> to 4503T<sub>g</sub> in 2019.<sup>38</sup> Open biomass burning, one of the major sources of pCl and HCl, has been strictly prohibited, leading to a dramatic decrease of air pollutant emissions.<sup>39</sup> The emission control standards of air pollutants in industries and power plants have been strengthened year by year. In this case, the emissions of reactive chlorine species have changed significantly. As a result of these factors, it is necessary to develop an up-to-date, comprehensive, anthropogenic RCEI for China as a foundation for exploring the effects of high concentrations of reactive chlorine species on the atmospheric oxidation capacity in polluted inland regions.

In this study, we develop an up-to-date RCEI for China for year 2019, including emissions of Cl<sub>2</sub>, HOCl, HCl, and pCl from six major source categories (coal combustion, industrial processes, MSW incineration, biomass burning, cooking, and chlorine-containing disinfectant) and 22 sub-categories. The

emissions are also spatially and temporally allocated based on both point of interest (POI) and activity data. The results of this study provide an important basis for further investigation of the role of atmospheric chlorine in the formation of air pollution and for proposing better strategies in air quality management for policy-makers.

## 2. METHODOLOGIES

**2.1. Source Classification.** The species included in the RCEI include Cl<sub>2</sub>, HOCl, HCl, and pCl. Six major source categories are considered, with 22 sub-sectors. The details are presented in Table 1.

**Table 1. Classification of Sectors and Chlorine Species**

sector	sub-sector	chlorine species
coal combustion	power plants	Cl <sub>2</sub> , HCl, pCl
	domestic combustion	
	industrial boilers and kilns	
industrial processes	other combustion	HCl, pCl
	cement clinker production	
	lime production	
	iron-steel production	
	brick production	
	glass production	
waste incineration	chemical production	HCl, Cl <sub>2</sub>
	pickling industry	
	HCl	
waste incineration	msw incinerator	HCl, pCl
	open incineration	
biomass burning	household burning	pCl
	open burning	
cooking	residential	pCl
	restaurant	
	school	
chlorine-containing disinfectant	sewage plant (domestic sewage, medical sewage from hospitals)	Cl <sub>2</sub> , HOCl
	tap water plant	
	cooling tower	
	swimming pool	

**2.2. Emission Calculation.** A commonly used emission factor method is applied in this study to estimate emissions of reactive chlorine species, including Cl<sub>2</sub>, HOCl, HCl, and pCl from the various sectors, as shown in eq 1

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

where  $A$  is the activity data, representing the amount of coal combusted, industrial product production, biomass burned, MSW incinerated, and so forth.  $EF$  is the emission factor.  $i$  refers to the source sectors,  $j$  refers to the province within China, and  $k$  is the chlorine species.

**2.2.1. Coal Combustion.** Activity data for the coal consumption of power plants (electricity plants, heat plants, and cogeneration plants), residential, and other types of coal combustion (agriculture, transport, construction, restaurants, etc.) are derived from the China Energy Statistic Yearbook 2020.<sup>38</sup>

The emission factors of Cl<sub>2</sub> and HCl from coal combustion are calculated based on eq 2.

$$EF_{i,j,k,l} = C_j \times R_{i,j,k} \times \sum_k 1 - f_{s,i,j,k} \eta_{s,i,j,k} \times 1 - f_{d,i,j,k} \eta_{d,i,j,k} \times \rho \times \frac{1}{MW_l} \quad (2)$$

where  $C$  represents the chlorine content of the coal and  $R$  is the chlorine release rate.  $f_d$  and  $f_s$  are the application rates of conventional  $\text{SO}_2$  and particulate matter emission control technologies under strict emission control policies.  $\eta_d$  and  $\eta_s$  are the removal efficiencies of dust-removal facilities and sulfate-removal facilities.  $\rho$  is the proportion of chlorine species (HCl and  $\text{Cl}_2$ ) in the emitted flue gas; the values of 86.3 and 3.6% are used for HCl and  $\text{Cl}_2$ , respectively.<sup>40</sup>  $MW$  denotes the ratios of the molar mass of chlorine atom to the molecular weight of HCl and  $\text{Cl}_2$ .  $i$  refers to the source sector,  $j$  refers to the province within China, and  $k$  is the chlorine species (HCl and pCl). Coal resources in China are distributed very unevenly across source types and provinces. In order to estimate the chlorine emissions from coal combustion reliably, Fu et al.<sup>20</sup> calculated the Cl content in raw coal consumed by each province based on the vector of Cl content in raw coal produced by each province and the coal transportation matrix. The results of chlorine content in consumed coal obtained by Fu et al. were adopted in this study. Values of chlorine release rate, removal efficiency from dust-removal facilities, and removal efficiency from sulfate-removal facilities in different economic sectors and boiler types used in this study are the same as in Liu et al.<sup>26</sup> The selection of parameters related to the calculation of chlorine precursor emissions from coal-fired sources is listed in Table S1.

The emission factors of pCl ( $EF_{\text{pCl}}$ ) are calculated by the  $\text{PM}_{2.5}$  emission factors ( $EF_{\text{PM}}$ ) multiplied by the percentage of Cl in  $\text{PM}_{2.5}$  ( $P_{\text{Cl}}$ ), the parameters adopted being given in Table S2. The method of calculating pCl emissions from other source sectors was the same as for coal combustion, which is mainly based on the source profiles.

$$EF_{\text{pCl},i} = EF_{\text{PM},i} \times P_{\text{Cl},i} \quad (3)$$

**2.2.2. Industrial Processes.** The industrial processing sectors having reactive chlorine emissions mainly consist of pickling, chemicals production, glass production, brick production, iron–steel production, lime production, and cement production. The pickling industry uses hydrochloric acid to clean metal surfaces, and the hydrochloric acid volatilizes into the air during the pickling process. Some industries in chemicals production, such as the pharmaceutical and chemical manufacturing processes, emit HCl and  $\text{Cl}_2$ . Flat glass manufacturing generates HCl and pCl. The emission factors of chlorine precursors in industrial processes are shown in Tables S2 and S3. The emission factor method is applied in the estimation of chlorine emissions for industrial processing sources.

**2.2.3. Biomass Burning.** Biomass burning can be divided into residential crop straw burning, firewood burning, and open biomass burning.

For crop straw burning, the burning mass of crop straw is calculated by the following equation

$$A_{i,j} = P_{i,j} \times N_{i,j} \times R_j \times D_j \times C_j \quad (4)$$

where  $i$  and  $j$  represent the type of crop and the province;  $A$  is the burning mass of crop straw;  $P$  is the crop yield;  $N$  is the straw-to-product ratio;  $R$  is the fraction of household biomass

burning;  $D$  is the dry matter fraction; and  $C$  is the combustion efficiency. Crop-yield data for each province are extracted from China Statistical Yearbook 2020.<sup>38</sup> It is reported that the amount of straw and firewood in rural energy consumption in 2018 decreased by 52.5% compared with 2012. Therefore, we assume that the proportion of biomass burning in households will be reduced by half in 2019 based on the studies of Zhou et al.,<sup>41</sup> which are given in Table S4. Values of the parameters  $N$ ,  $D$ , and  $C$  values are given in Table S5.

For firewood burning, the calculation method of activity data is as follows

$$A_{\text{firewood},j} = H_j \times T_j \times B_j \times f \quad (5)$$

where  $A_{\text{firewood}}$  is the amount of firewood burned;  $H$  is the number of rural households;  $T$  is the number of days of using firewood as fuel (260 days are used in this study), while the remaining days will use crop residuals as residential biofuel; and  $B$  is the daily average firewood consumption per household, for which 2 kg/day household is adopted in this study.<sup>42</sup>

For open biomass burning, the burned mass of straw, forest, and grassland ( $A$ ) was calculated using estimates of the burned area (BA), the biomass fuel loading (FL), and the combustion factor (CF)

$$A_{i,j} = \text{BA}_{i,j} \times \text{FL}_{i,j} \times \text{CF}_j \quad (6)$$

where  $i$  and  $j$  represent the land cover type and location, respectively. The data for burned area were derived from the Fire Inventory of the National Center for Atmospheric Research (FINN), which provides daily, 1 km resolution, global estimates of the trace gas and particle emissions from open burning of biomass, including wildfires, agricultural fires, and prescribed burning but does not include biofuel use and trash burning.<sup>43</sup> FL and CF values were obtained from a review of previous studies,<sup>41</sup> which integrated a collection of relevant literature.

Emission factors for calculating the emissions of HCl and pCl from biomass burning are listed in Tables S2 and S3, respectively.

**2.2.4. Waste Incineration.** The mass of MSW burned by incineration in the various provinces are extracted from the China Statistical Yearbook 2020.<sup>38</sup> With strict control of open waste incineration, the open burning of MSW has been banned in China. However, some rural solid waste was open burned occasionally in some rural areas. The mass of open waste incineration ( $W$ ) is estimated by

$$W_{i,j} = P_i \times \text{RSW}_i \times f_{\text{rural},i} \times B \quad (7)$$

where  $P$  is the rural population, obtained from the China Statistical Yearbook 2020;<sup>38</sup>  $\text{RSW}$  is the annual mass of per capita solid waste production in rural area (0.79 kg/capita/day is applied in this study<sup>44</sup>);  $f$  is the fraction of RSW that is open burned (0.05 is used<sup>45</sup>); and  $B$  is the proportion of waste that is burned (0.6 is used<sup>46</sup>).

The pCl emission factors for MSW incineration are listed in Table S2. In the previous work,<sup>20</sup> 3.58 g of HCl per kg solid waste ( $EF_{\text{HCl}}$ ) was used to calculate HCl emissions from open solid waste incineration. The emission factors of HCl for waste incineration are listed in Table S3.

**2.2.5. Cooking.** Using salt (sodium chloride, NaCl) during cooking causes pCl to release into the atmosphere.<sup>47</sup> Here, we estimate the pCl emissions from cooking oil fumes in

Table 2. Anthropogenic Emissions of Chlorine Radical Precursors in China in 2019

sector	sub-sector	emission/Mg			
		HCl	pCl	Cl <sub>2</sub>	HOCl
coal combustion	power plants	19,859	3522	852	
	industrial boilers and kilns	30,947	2181	1327	
	domestic combustion	9491	2538	407	
	other combustion	20,309	3616	871	
industrial process	cement clinker production	38,212	2995		
	lime production	1205	869		
	iron-steel production	597	5574		
	brick production	2478	2135		
	glass production	6612	302		
	chemical production	4196		783	
	pickling industry	3786			
waste incineration	MSW incinerator	18,083	1035		
	open incineration	16,928	8744		
biomass burning	household burning	51,530	10,6589		
	open burning	46,104	36,596		
cooking	residential		4411		
	school		146		
	restaurant		2288		
chlorine-containing disinfectant	sewage plant-domestic sewage			1495	11421
	sewage plant-medical sewage			657	5015
	tap water plant			1218	9304
	cooling tower			59	451
	swimming pool			179	1368
<b>total</b>		<b>270,337</b>	<b>183,541</b>	<b>7848</b>	<b>27,559</b>

residential cooking, restaurants, and schools. Based on the number of households from the China Statistical Yearbook 2020<sup>38</sup> and the number of catering companies from POI information, the waste gas from residential cooking, restaurants, and schools was calculated by eq 8.

$$G_i = N_i \times n \times V_i \times T_i \times (1 - f_i \times \eta_i) \quad (8)$$

where  $i$  refers to the number of households or restaurants;  $n$  is the number of stoves per household or restaurant;  $V$  is the volume of cooking waste gas per hour, with assumed values for the exhaust emissions of catering companies, households, and schools being 8000, 1300, and 2000 m<sup>3</sup>·h<sup>-1</sup> respectively;<sup>8,48</sup>  $T$  is the amount of cooking time per year; and  $\eta$  is the removal efficiency of any waste-gas purification facilities. The statistics used in each sector are derived from survey data.<sup>49</sup> The PM<sub>2.5</sub> emission factors and the proportion of pCl in PM<sub>2.5</sub> are listed in Table S2.

**2.2.6. Chlorine-Containing Disinfectant.** Our previous work<sup>29,30</sup> compiled a comprehensive emission inventory of Cl<sub>2</sub> and HOCl for Shanghai and the Yangtze River Delta region, including emissions from cooling towers, water and sewage treatment facilities, swimming pools, and various applications of chlorine-containing disinfectants (e.g., households, hospitals, toilets, and farming plants). Our research found that the contribution of dispersed use of chlorine-containing disinfectants to emissions can be considered to be negligible. The sources of disinfectants used in this study are tap water and sewage treatment plants, swimming pools, and cooling towers. Also, the calculation method was improved as follows:

Activity data: the mass of chlorine-containing disinfectant (A) used in the different sectors is calculated as follows

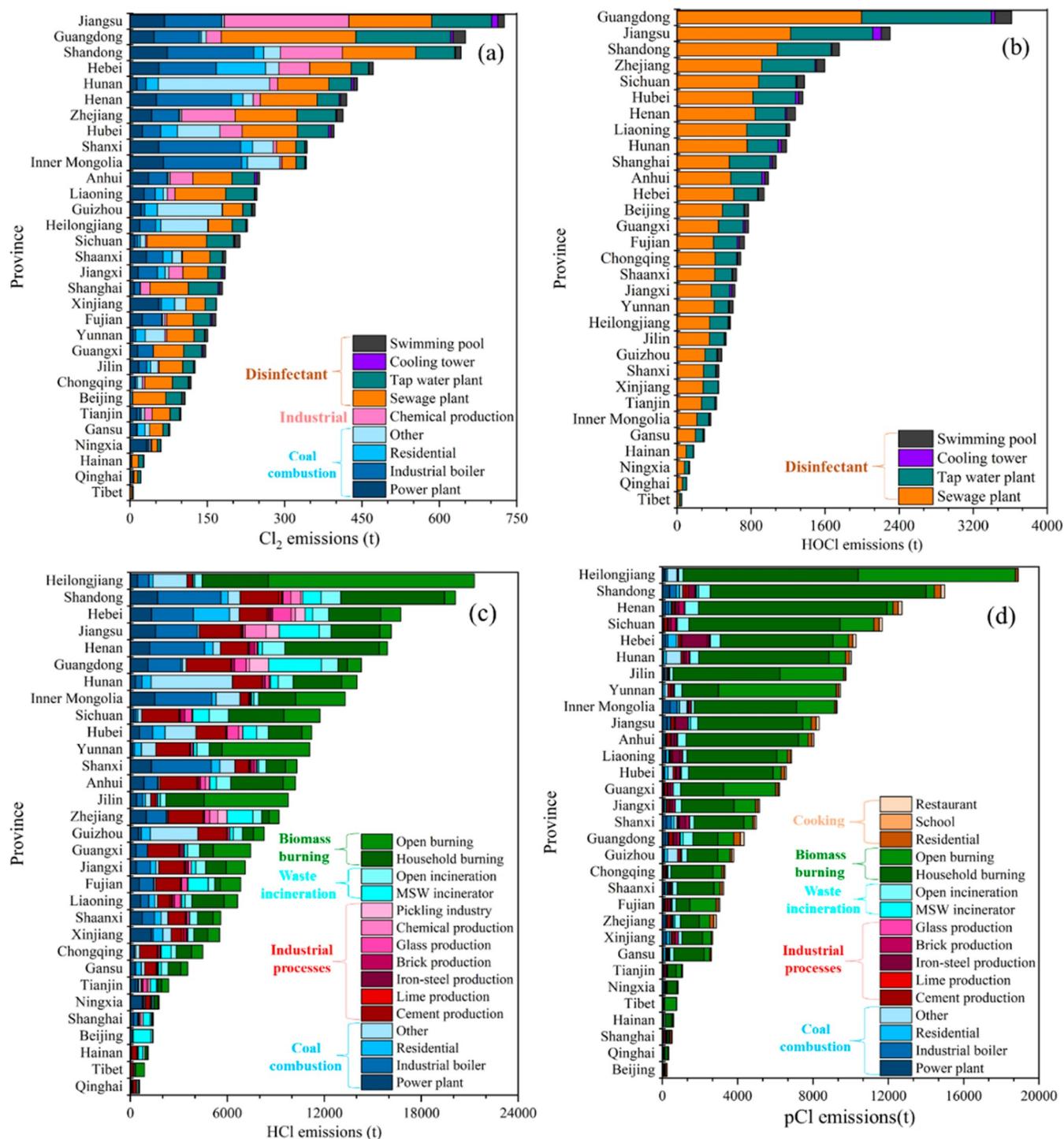
$$A_{i,j} = \sum_j W_{i,j} \times (C_d - C_r) \times f \quad (9)$$

where  $W$  represents the mass of water disinfection with chlorine-containing disinfectant in sector  $i$  (tap water plants, sewage treatment plants, swimming pools, and cooling towers) of each province  $j$ , and the amounts of tap water and process water that are treated were obtained from China Statistical Yearbook 2020.<sup>38</sup> The data for domestic sewage are derived from the China Urban Construction Statistical Yearbook 2019.<sup>50</sup> The cooling circulating water usually accounts for more than 60% of processing water.<sup>51</sup> For swimming pools, there were about 27,900 public swimming pools in China based on POI data. The method of calculating emissions from medical sewage (from hospitals) and swimming pools is documented in our previous work.<sup>29</sup>  $C_d$  and  $C_r$  represent the chlorine dose and residual chlorine for different sectors (Table S6), calculated as available chlorine (mg·L<sup>-1</sup>);  $f$  refers to the conversion from available chlorine to the amount of chlorine containing disinfectant with equivalent oxidation capacity; for NaClO,  $f = 1.05$ .

For tap water and sewage disinfection with chlorine-containing disinfectants, it is estimated that 20% of hypochlorous acid escapes into the atmosphere during the disinfection process.<sup>52</sup> For cooling circulating water, the supplementary amount of cooling water is less than 1%.<sup>23</sup> Emission factors are calculated by eq 10

$$EF_i = \frac{MW_{HOCl}}{MW_{NaClO}} \times V_i \times R_k \quad (10)$$

where  $MW$  represents the molecular weight and  $V$  is the proportion released into the atmosphere.  $R$  represents the fraction of released chlorine as HOCl or Cl<sub>2</sub>, for which the volumetric mixing ratio of HOCl to Cl<sub>2</sub> is taken as 10:1 from



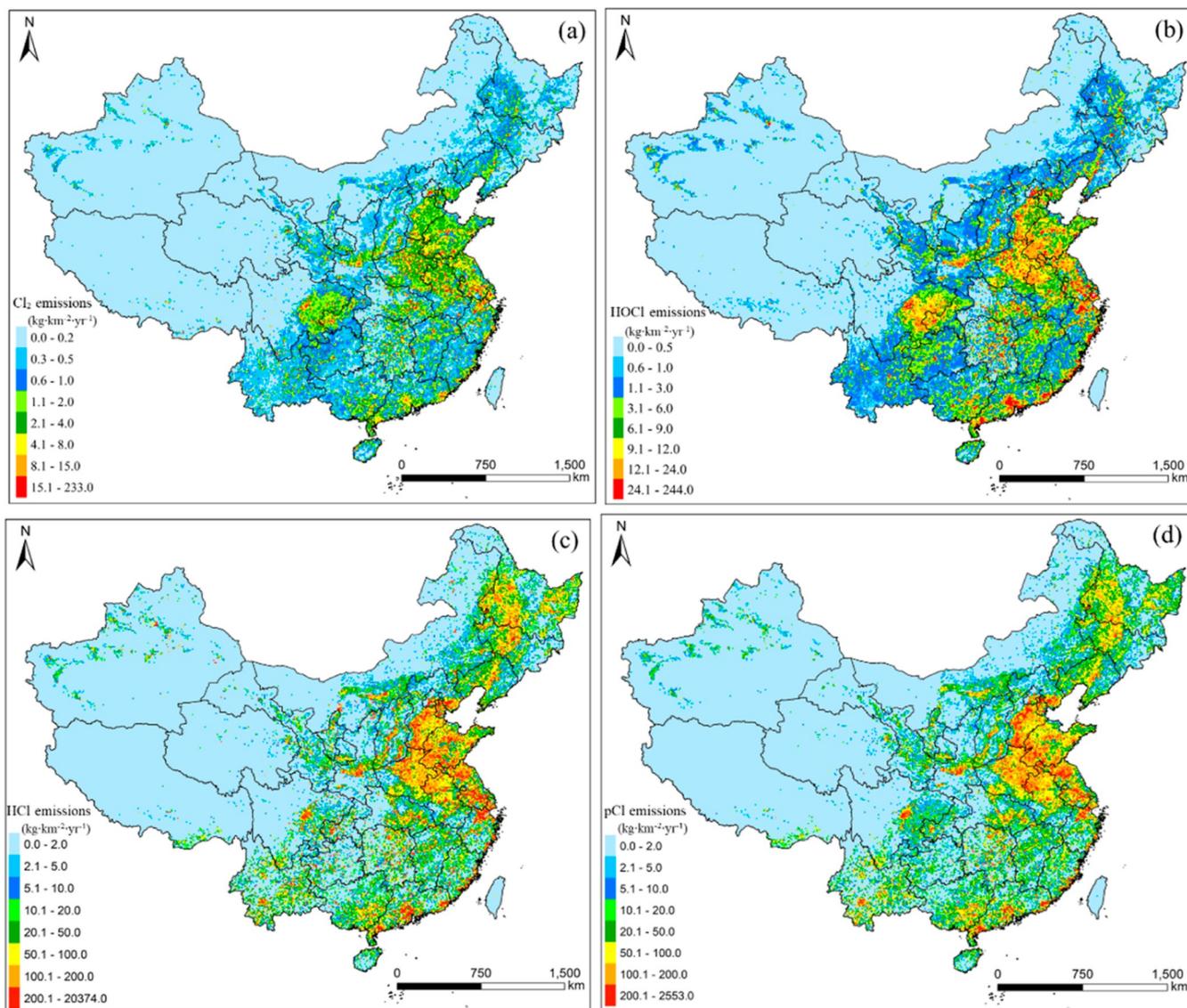
**Figure 1.** Reactive chlorine emissions in different provinces [ $\text{Cl}_2$  emissions (a), HOCl emissions (b), HCl emissions (c), and pCl emissions (d)].

Wong et al.,<sup>32</sup> this is converted into 0.84 for HOCl and 0.11 for  $\text{Cl}_2$ .

**2.3. Spatial Allocation.** We collected the longitude and latitude of power plants, industries, tap water plants, sewage water plants, restaurants, and swimming pools across the country based on both pollution statistical data as well as the POI data. Longitude, latitude, and waste handling capacity of waste incineration plants are extracted from the national website (<http://ljgk.envsc.cn/>). Emissions from power plants, industrial processes, water (tap and sewage) treatment plants, and swimming pools are distributed by power generation, coal

consumption, and water treatment capacity, respectively. For open biomass burning, the emissions are distributed using the FINN active fire products of 2019. For domestic biomass burning, residential and other-purpose coal combustion, and open waste incineration, emissions are allocated according to the distribution of rural population.

**2.4. Temporal Allocation.** The monthly, weekly, and hourly variations of emissions from power plants, industry, and residential energy consumption are allocated using the same method as Wang et al.<sup>53</sup> Based on the water supply of tap water plants,<sup>54</sup> the temporal profiles of HOCl and  $\text{Cl}_2$



**Figure 2.** Spatial distribution of chlorine precursors at  $0.1^\circ \times 0.1^\circ$  resolution [ $\text{Cl}_2$  (a), HOCl (b), HCl (c), and pCl (d)].

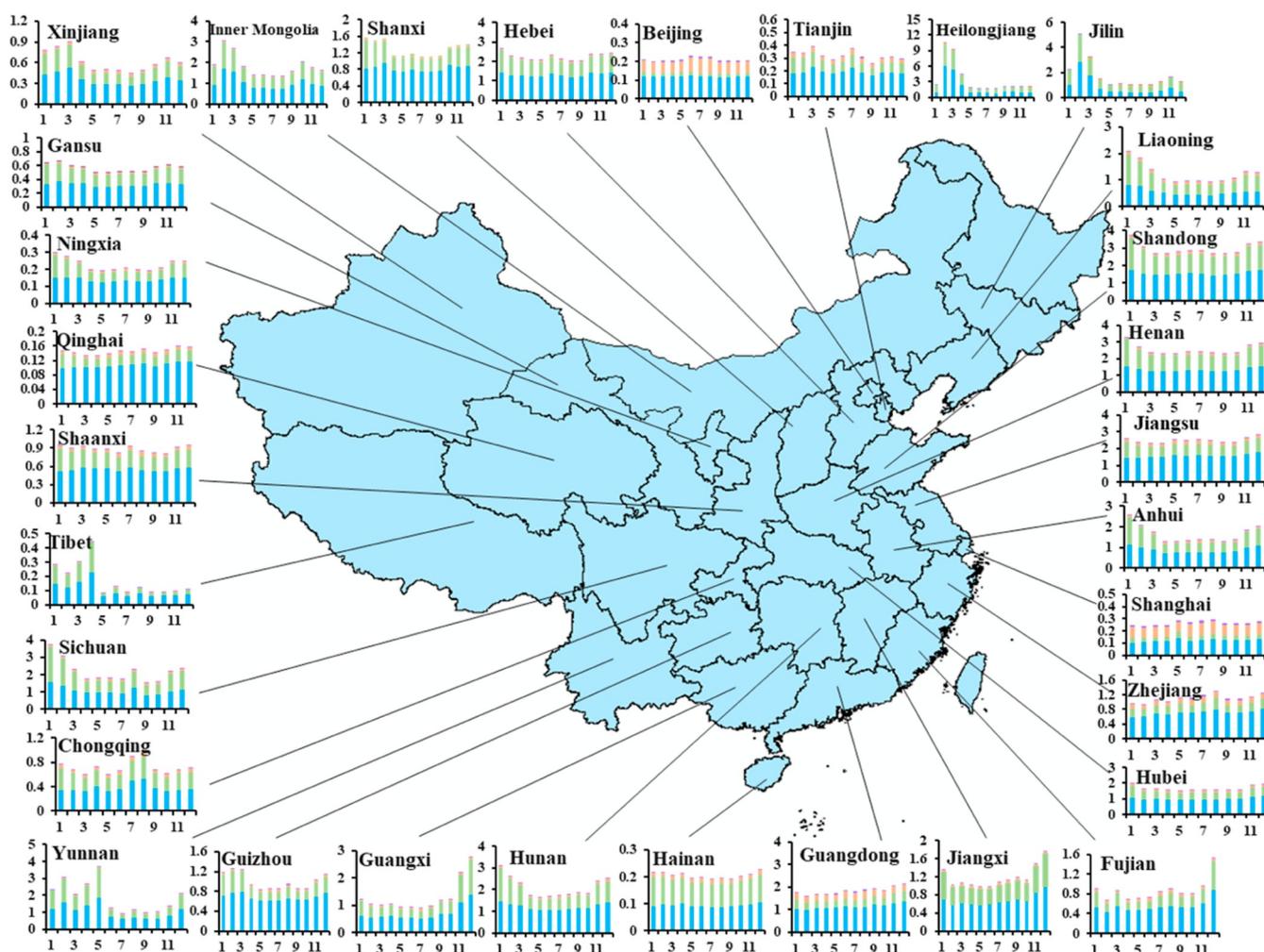
emissions from sewage plants and tap water plants are calculated. Using the FINN active fire products, the monthly variation of HCl and pCl emissions from open biomass burning was allocated. In this study, we assumed that the monthly and diurnal emission distribution of MSW incinerators, cooking, and cooling towers was uniform. Public swimming pools are only open during the summer (from June to August, 92 days). Detailed information of the statistics used for temporal allocation is listed in Tables S7 and S8.

### 3. RESULTS AND DISCUSSIONS

**3.1. Emission Characteristics of Reactive Chlorine in China.** The annual emissions of  $\text{Cl}_2$ , HOCl, HCl, and pCl in China in 2019 are estimated to be 7.8, 27.6, 270.3, and 183.5 Gg, respectively, as shown in Table 2. The largest contributor to  $\text{Cl}_2$  and HOCl emissions was the use of chlorine-containing disinfectant, accounting for 46% and 100%, respectively. Coal combustion contributed 44% of  $\text{Cl}_2$  emissions, among which power plants accounted for 10.9% and industrial boilers and kilns contributed 16.9%. Chlorine-containing disinfection accounted for 46.0% of  $\text{Cl}_2$  emissions, among which sewage

disinfection and tap water plant accounted for 27.4 and 15.5%, respectively. Looking at the sub-class source categories, sewage plants and tap water plants are the major sources of HOCl emissions at the national level, while cooling towers and swimming pools are the largest contributors at city and regional levels.<sup>6</sup> Sewage plants, including domestic sewage and medical sewage from hospitals, were the largest contributors to HOCl emissions, with a proportion of 59.6%. The second largest contributors were tap water plants, accounting for 33.8%. The disinfection of swimming pools and cooling towers contributed less than 10% for HOCl emissions. The loss of cooling circulation water was less than 1% with the upgrade of cooling circulation equipment, and most swimming pools were only used in summer. The disinfection of cooling towers and swimming pools with chlorine-containing disinfectant were not significant contributors to  $\text{Cl}_2$  and HOCl emissions.  $\text{Cl}_2$  and HOCl emissions from medical sewage from hospitals are also significant, with emissions of 657 and 5015 Mg, contributing to 8.4 and 18.2% of the total emissions nationally.

The largest contributor to HCl and pCl emissions was biomass burning, with a proportion of 36.1 and 78.0%,



**Figure 3.** Monthly variation of  $\text{Cl}_2$  (purple), HOCl (brown), HCl (blue), and pCl (green) emissions (Gg) in each province.

respectively. Coal combustion was the second largest contributor, accounting for 29.8% of HCl emissions and 6.5% of pCl emissions, respectively. Industrial processes and waste incineration contributed 21.1 and 12.9% for HCl emissions, 6.5 and 5.3% for pCl emissions, respectively. Satellite monitoring showed that the number of straw burning fires nationwide in 2019 dropped by 42% compared with 2015.<sup>55</sup> These activities have decreased sharply in recent years due to efforts of the Chinese government to prohibit open straw and waste burning.<sup>29</sup> Simultaneously, the installation of air pollution control devices on industrial plants and MSW incineration plants has increased. The emissions of HCl and pCl from those sectors have thus decreased.

**3.2. Reactive Chlorine Emissions across Different Provinces.** The emissions of reactive chlorine in different provinces are shown in Figure 1, indicating that the emissions of chlorine precursors have clear regional characteristics. Emissions of  $\text{Cl}_2$  mainly come from coal combustion, industrial processing and the use of disinfectants. Jiangsu, Guangdong, and Shandong are the top three provinces in terms of  $\text{Cl}_2$  emissions in China. The proportion of  $\text{Cl}_2$  emissions in the chemical industry in Jiangsu is as high as 33.3%, which is due to the large number of chemical enterprises there.  $\text{Cl}_2$  emissions in Guangdong province are also relatively high, which is due to the dense population and the large demand for tap water treatment and wastewater treatment. The proportion

of  $\text{Cl}_2$  emitted by industrial coal combustion in Shandong is relatively high. The emissions of HOCl mainly derive from the usage of chlorine-containing disinfectants. As can be seen from Figure 1b, water treatment and wastewater treatment are the main sources of HOCl emissions in the various provinces. Among them, the emissions of HOCl in Guangdong are as high as 3615.6 Mg, accounting for 13.1% of the total national HOCl emissions.

HCl and pCl are mainly derived from coal combustion, industrial processing, biomass burning, waste incineration, and cooking, of which cooking sources mainly emit pCl. Heilongjiang, Shandong, Hebei, Jiangsu, and Henan were the top five contributors for HCl emissions, accounting for 7.9, 7.4, 6.2, 6.0, and 5.9% of total HCl emissions, respectively. Heilongjiang, Shandong, Henan, Sichuan, and Hebei were the top five emitters, contributing 10.3, 8.1, 6.9, 6.4, and 5.6% of pCl emissions, respectively. It can be seen from Figure 1c,d that Heilongjiang province has the largest emissions of HCl and pCl. The HCl and pCl emissions from biomass burning in the Heilongjiang province account for 79.1% and 93.4%, respectively. This is mainly because Heilongjiang is the largest grain-producing province in China and therefore produces a large amount of straw. The proportion of open burning and residential burning is also significant. The HCl emissions from open biomass burning in Heilongjiang province is significantly higher than that of residential biomass burning, which may be

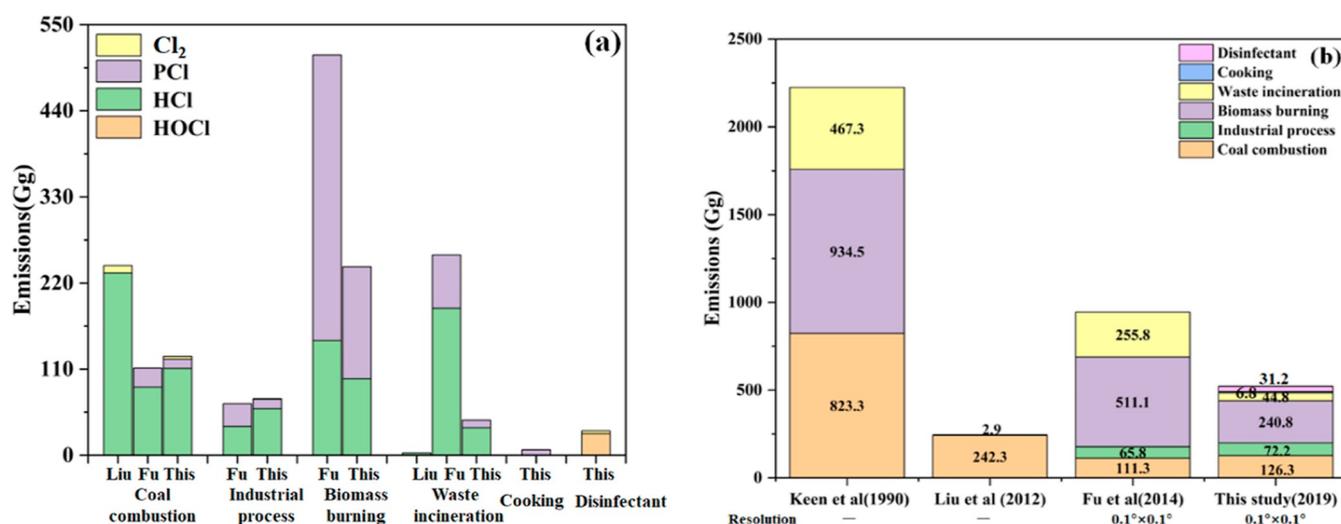


Figure 4. Comparisons of RCEI among various studies.

due to the large amount of open biomass burning in Heilongjiang province. In all provinces, biomass burning is the main source of pCl emissions and accounts for more than 60%.

**3.3. Spatial Distributions.** As shown in Figure 2, the emissions of reactive chlorine with  $0.1^\circ \times 0.1^\circ$  spatial distribution have been developed. In addition to residential coal combustion, other coal combustion, household straw combustion, open waste incineration, cooking sources, and cooling towers, we also collected information for other source companies and allocated emissions based on environmental statistics and POI data. The emission intensity of  $\text{Cl}_2$ , HOCl, HCl, and pCl for most provinces ranged between 0 and 3 tons-year<sup>-1</sup>·km<sup>2</sup>. For  $\text{Cl}_2$  and HOCl, the emissions were concentrated on economically developed eastern coastal cities. While for HCl and pCl, the emissions are concentrated in the North China Plain and northeast China where biomass burning occurs frequently.

**3.4. Temporal Distribution.** Figure 3 presents the monthly emissions of  $\text{Cl}_2$ , HOCl, HCl, and pCl in each province, indicating that the emissions of monthly distributions are distinctly different among the various regions. It can be seen that, except for Beijing and Shanghai, the emissions of chlorine precursors in other provinces are mainly HCl and pCl, which is primarily due to the large amount of coal combustion, the relatively developed industry, and the extent of biomass burning in these regions. The highest emissions occur in winter (December, January, February) for most provinces, due to the increase of domestic biomass burning and domestic coal combustion in that season. The HOCl and  $\text{Cl}_2$  emissions from chlorine-containing disinfectant use in Beijing, Guangdong, and Shanghai is much larger than other provinces, which is due to the high population density and the high economic level that promotes the demand for cleaning products.

**3.5. Comparisons with Previous Studies.** We compared our results with previous studies,<sup>20,26,52</sup> as illustrated in Figure 4. It is clear from the figure that the emissions of reactive chlorine from different sources vary greatly in different years. The emissions of HCl generated by coal combustion estimated by Liu et al.<sup>26</sup> are higher than the estimates of Fu et al.,<sup>20</sup> which is mainly due to their different activity level data and calculation method. The HCl emissions from coal combustion

in this study are lower than those of Liu et al.,<sup>26</sup> which is mainly due to the improvement of exhaust gas removal facilities and efficiencies. The HCl emissions from industrial processing in this study are higher than those estimated in the study by Fu et al.,<sup>20</sup> which is probably due to an increase in industrial production and categories involved in the industrial process sources. The HCl produced by biomass burning in this study is lower than in Fu et al.,<sup>20</sup> which may be attributable to the implementation of policies such as the ban on straw burning. The HCl emissions from waste incineration in this study are midway between results of Liu et al.<sup>26</sup> and Fu et al.<sup>20</sup> The amount of waste incineration shows an upward trend in recent years, and the large change in emissions is mainly due to the choice of HCl emission factor for waste incineration. The emissions of pCl from different sources in this study are lower than the estimates of Fu et al.,<sup>20</sup> which is mainly due to the stringent controls imposed on major air pollution sources in recent years.

Total emissions of reactive chlorine estimated by Keene et al.,<sup>34</sup> Liu et al.,<sup>26</sup> Fu et al.,<sup>20</sup> and this study were 2225 Gg (1990), 245 Gg (2012), 944 Gg (2014), and 522 Gg (2019), respectively. These results are broadly consistent. The results of Keene et al. are significantly higher than those of the other studies because of the massive combustion of coal and biomass in 1990 that resulted in very large emissions of inorganic chlorine. The lowest results of Liu et al.<sup>26</sup> are mainly due to the omission of some anthropogenic sources, while the results of Fu et al.<sup>20</sup> are high, which can be attributed to the large amount of biomass burning and the high emission factor chosen for the waste incineration source. Overall, the differences between the results of this study and previous studies are within an acceptable range and can be satisfactorily explained.

**3.6. Uncertainty Analysis.** The commonly used Monte Carlo method was applied to quantify the uncertainty of this emission inventory. The coefficients of variation (the standard deviation divided by the mean) of activity data and emission factors were referenced from previous studies.<sup>29,30</sup> Table 3 shows the uncertainty ranges of reactive chlorine emissions calculated by 100,000 Monte Carlo simulations with a 95% confidence interval. The ranges of uncertainty in emission of  $\text{Cl}_2$ , HOCl, HCl, and pCl were estimated to be 4.4–14.2, 9.7–

**Table 3. Range of Uncertainty in Emission Compared with Previous Studies**

species	emission estimate/Gg·yr <sup>-1</sup>		the range of uncertainty/Gg·yr <sup>-1</sup>		refs
	this work	previous study	this work	previous study	
Cl <sub>2</sub>	7.8	2 <sup>a</sup>	4.4–14.2	0–5 <sup>a</sup>	30
HOCl	27.6	9 <sup>a</sup>	9.7–51.6	2–18 <sup>a</sup>	30
HCl	270.3	458	207.2–422.7	307–838	20
pCl	183.5	486	106.4–321.1	292–885	20

<sup>a</sup>The study area was the Yangtze River Delta.

51.6, 207.2–422.7, and 106.4–321.1 Gg·yr<sup>-1</sup>, respectively. The contribution of different sources to the uncertainty of chlorine precursors is highly variable. The major contributor to HCl and pCl emissions is the waste incineration source, and its uncertainty ranges are 15.8–87.5 and 3.3–27.2 Gg·yr<sup>-1</sup>, respectively. This is followed by biomass burning, whose ranges of emissions are 41.9–231.3 and 63–316.5 Gg·yr<sup>-1</sup>, respectively, which is mainly due to the large uncertainty of the mass of open waste incineration and biomass burning, as well as the lack of measurements of a large number of emission factors. The main contributors to the uncertainty of Cl<sub>2</sub> and HOCl are cooling towers, with uncertainties ranging between 1–234 and 103–1592 kg·y<sup>-1</sup>, respectively. This is primarily due to the high uncertainty of disinfection activity data for cooling towers.

To reduce uncertainties in chlorine precursor emissions, more field measurements are needed, such as the measurement of emission factors for open burning of MSW, industrial processing sources, and usage of disinfectants. The proportion of pCl in particulates from different sources needs more measurement data to improve the accuracy of particulate chlorine emissions. In future research, it is recommended to use a more accurate method to estimate the usage of chlorine-containing disinfectants to further reduce the uncertainty of Cl<sub>2</sub> and HOCl. To further validate this emission inventory, we propose observations of HCl, pCl, Cl<sub>2</sub>, and HOCl at more locations and in different seasons. Despite the uncertainties in this study, the current inventory provides an up-to-date and relatively comprehensive estimate of reactive chlorine emissions in China with detailed local data, which lays a solid foundation for incorporating chlorine emissions into air quality models and studying the effects of chlorine radicals on air quality.

Sea-salt aerosol is considered to be an important natural source of particulate chlorine, especially in coastal regions. Sea-salt aerosol is the largest biogenic source of reactive chlorine precursors, contributing a large proportion of pCl to the atmosphere in coastal regions.<sup>56</sup> A few studies have investigated the impacts of sea-salt emissions on air quality. For example, Dai et al.<sup>57</sup> found that ClNO<sub>2</sub> from sea-salt chloride increased the O<sub>3</sub> mixing ratios by up to 2.0 ppb (4%) over the inland areas during marine winds and up to 3.8 and 6.5 ppb over the South China Sea. Studies by other researchers have also shown that pCl from sea salt promotes the formation of ClNO<sub>2</sub> and thus the formation of ozone.<sup>58,59</sup> Simulation of sea-salt aerosols is affected by several processes, including the deposition<sup>60</sup> and loss of chlorine in sea salt by chemical reactions.<sup>61</sup> Uncertainties exist with the estimation of sea-salt emissions, which are related to the meteorological parameterization scheme (10 m wind speed) and the resolution of the

models, and thus, these uncertainties could also contribute to the inconsistencies between observation and modeled values. More observations, especially over coastal regions, are warranted to constrain sea-salt emissions.

Although there are uncertainties with the updated RCEI emission inventory, results of this study are of importance and significance. As illustrated in the **Introduction**, there are several issues remaining in this field, for example, (1) the concentrations of reactive chlorine species such as Cl<sub>2</sub> and ClNO<sub>2</sub> in inland areas of China are unexpectedly high, indicating that there are significant anthropogenic sources of chlorine in mainland China; (2) observed Cl<sub>2,5</sub><sup>-</sup> concentrations are much higher than model predictions using the pCl and HCl emission inventory for 2014 as input, suggesting that there are high uncertainties or missing sources in the previous RCEI; and (3) there are clear inconsistencies in Cl<sup>•</sup> formation pathways based on observations and modeling studies, partially due to the underestimation of chlorine emissions or missing sources of Cl<sub>2</sub> and HOCl. These issues are likely due to three reasons. First, part of the inconsistency may be attributable to the underestimation of emissions such as Cl<sub>2</sub> and HOCl and the absence of some anthropogenic source categories such as the use of disinfectants. Second, the impact of natural sources such as sea-salt aerosol on air quality can be significant in coastal regions but has large uncertainties. Third, there are still high uncertainties with the chemical mechanisms of reactive chlorine species. This work quantifies the emissions of HCl, pCl, Cl<sub>2</sub>, and HOCl emissions from a comprehensive array of anthropogenic sources. We believe that this work will minimize the gap between modeling and observation to a certain extent, but it cannot fully address the issues raised. Continuous studies including field campaigns as well as modeling studies need to be further conducted.

#### 4. CONCLUSIONS

The chlorine radical (Cl<sup>•</sup>) plays an important role in the atmospheric oxidization capacity and the formation of secondary pollutants. Recent field observations reveal that the concentrations of reactive chlorine species are unexpectedly high over China, indicating that there are previously underestimated or missing anthropogenic sources of reactive chlorine species. Here, we develop an up-to-date emission inventory of the major primary reactive chlorine precursors, including Cl<sub>2</sub>, HOCl, HCl, and pCl, in China for the year 2019 with a spatial resolution of 0.1° × 0.1°. The Cl<sub>2</sub>, HOCl, HCl, and pCl emissions in China in the year 2019 are estimated to be 7.8, 27.6, 270.3, and 183.5 Gg, respectively, with the major source coming from the use of chlorine-containing disinfectants (accounting for 46% of total Cl<sub>2</sub>), chlorine-containing disinfectants (accounting for 100% of total HOCl), biomass burning (36.1% to HCl), and biomass burning (78% to pCl), respectively. The emission intensity of Cl<sub>2</sub>, HOCl, HCl, and pCl for most provinces ranges between 0 and 3 tons·year<sup>-1</sup>·km<sup>2</sup>. Emissions are high in eastern China, especially in the Beijing–Tianjin–Hebei and surrounding area, and the Yangtze River Delta region. The ranges of uncertainty in emission of Cl<sub>2</sub>, HOCl, HCl, and pCl were estimated to be 4.4–14.2, 9.7–51.6, 207.2–422.7, and 106.4–321.1 Gg·yr<sup>-1</sup>, respectively. Our research shows that emission sources such as biomass burning, chlorine-containing disinfectants, industrial processing, and coal combustion contribute significantly to RCEI emissions, which further affects the atmospheric oxidation, causing increase of ozone and fine particles. In

future studies, it is recommended to measure localized emission factors of major source sectors to reduce the uncertainties of RCEI estimation. Air quality modeling studies are encouraged to further investigate the impact of chlorine chemistry on air quality, and policies to control RCEI emissions are necessary to be further explored.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00096>.

Activity data and emission factors adopted in this study; parameters adopted to calculate the chlorine emissions from coal combustion; domestic straw burning percentage; straw-to-product ratio, dry matter fraction, and combustion efficiency of crop straw; chlorine dose and residual chlorine for water treatment; monthly variation of emissions for different source sectors; diurnal profiles of different source sectors; and distribution of HCl, Cl<sub>2</sub>, and Cl<sub>2</sub> emissions (PDF)

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### Notes

The authors declare no competing financial interest.

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