Spatial Distributions and Sources of Inorganic Chlorine in PM$_{2.5}$ across China in Winter

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Abstract: Chlorine is an important atmospheric photochemical oxidant, but few studies have focused on atmospheric chlorine. In this study, PM$_{2.5}$ samples were collected from urban and rural sites across China in January 2018, and concentrations of Cl$^-$ and other water-soluble ions in PM$_{2.5}$ were analyzed. The size-segregated aerosol Cl$^-$ data measured across Chinese cities by other studies were compiled for comparison. The observed data demonstrated that the Cl$^-$ concentrations of PM$_{2.5}$ in northern cities ($5.0 \pm 3.7$ μg/m$^3$) were higher than those in central ($1.9 \pm 1.2$ μg/m$^3$) and southern cities ($0.84 \pm 0.54$ μg/m$^3$), suggesting substantial chlorine emissions in northern cities during winter. The concentrations of Cl$^-$ in aerosol were significantly higher in urban regions (0.11–26.7 μg/m$^3$) compared to than in rural regions (0.03–0.61 μg/m$^3$) across China during winter, implying strong anthropogenic chlorine emission in cities. Based on the mole ratios of Cl$^-$/Na$^+$, Cl$^-$/K$^+$ and Cl$^-$/SO$_4^{2-}$ and the PMF model, Cl$^-$ in northern and central cities was mainly sourced from the coal combustion and biomass burning, but in southern cities, Cl$^-$ in PM$_{2.5}$ was mainly affected by the equilibrium between gas-phase HCl and particulate Cl$^-$. The size-segregated statistical data demonstrated that particulate Cl$^-$ had a bimodal pattern, and more Cl$^-$ was distributed in the fine model than that in the coarse mode in winter, with the opposite pattern was observed in summer. This may be attributed to both sources of atmospheric Cl$^-$ and Cl$^-$. This study reports the concentrations of aerosol Cl$^-$ on a national scale, and provides important information for modeling the global atmospheric reactive chlorine distribution and the effects of chlorine on atmospheric photochemistry.

Keywords: Cl$^-$; PM$_{2.5}$; spatial distribution; sources; China; winter

1. Introduction

Chlorine is one of the most abundant halogen species in the atmosphere, where it exists as both inorganic Cl (such as particulate Cl$^-$ and gas-phase HCl) and organic Cl (such as CH$_3$Cl and chlorofluorocarbons), and participates in many atmospheric photochemical reactions [1]. Cl$^-$-containing inorganic and organic compounds are considered to be one of the factors driving the global climate change [2]. It is well known that halogens decrease the atmospheric ozone concentration [3–7], and that halogens can participate in the NO$_x$ cycle, promoting heterogeneous formation of atmospheric nitrate in both the marine and terrestrial atmospheric boundary layers [8–10]. Using the GEOS-Chem model, halogens were estimated to account for as much as ~15–27% of the global oxidation of volatile organic compounds [7]. In addition, chlorine depletion is a common phenomenon for marine aerosol and the volatilization of gas-phase HCl from the surface of particles
may disturb the aerosol acidity \[11–14\], which further affects the water-soluble ion concentrations aerosol \[15,16\]. Although the Cl\(^-\) concentration in aerosol has been incidentally reported in many studies, very few studies have paid attention to Cl\(^-\) in terrestrial aerosols as compared to marine aerosol, let alone in situ observations on a large spatial scale.

The sources of atmospheric Cl\(^-\) have been identified using several different methods, such as determining stable isotopic compositions of Cl\(^-\) \[17–19\], monitoring the relationships between Cl\(^-\) and OC, EC, Na\(^+\), and K\(^+\) \[16,20–22\], and model simulations \[23,24\]. Atmospheric Cl\(^-\) has many natural sources, including sea water, wildfires, dust storms, and volcanic eruptions \[25–28\], as well as anthropogenic sources, such as coal combustion, biomass burning, industrial emissions, and the use of sodium chloride on icy roads \[20,21,29–35\]. The chlorine emissions from sea water (both particulate Cl\(^-\) and gas-phase HCl) were estimated to be 1792.6 Tg Cl yr\(^{-1}\) \[23\], which is considerably higher than emissions from other sources, such as dust (15 Tg Cl yr\(^{-1}\) as particulate Cl\(^-\)) and volcanic eruptions (2 Tg Cl yr\(^{-1}\) as gas-phase HCl) \[19\]. In terms of anthropogenic sources, the chlorine emission from biomass burning were 6.4 Tg Cl yr\(^{-1}\) \[24\], which were similar to the emissions of gas phase HCl from coal combustion (4.6 Tg Cl yr\(^{-1}\), \[19\]) and urban garbage burning (6–9 Tg Cl yr\(^{-1}\), \[21\]). The majority of atmospheric inorganic chlorine is returned to the Earth’s surface by dry or wet deposition. Unlike bioavailable nutrients, such as NO\(_3^-\), that can rapidly affect terrestrial ecosystems \[36–39\], Cl\(^-\) exhibits conservative behavior and very few studies have specifically investigated the influences of atmospheric Cl\(^-\) deposition on the biogeochemistry of terrestrial ecosystems \[40\]. With the high solubility and conservative behavior of Cl\(^-\), the mass balance of Cl\(^-\) has been used to evaluate the long-term groundwater recharge of regional hydrologic cycles \[41–43\]. In addition, studies have demonstrated that deposition of atmospheric Cl\(^-\) on the surface of steel may accelerate the corrosion rate and reduce the lifetime of construction steel \[44–46\]. A review of atmospheric corrosion in China reported that Cl\(^-\) plays an important role in the corrosion of metals in areas across China \[47\].

In this study, PM\(_{2.5}\) samples were collected during January 2018 from 20 cities and 2 rural sites across China (latitude from 22.8° N to 45.7° N and longitude from 102.7° E to 126.7° E; Figure 1). Concentrations of Cl\(^-\) in PM\(_{2.5}\) across Chinese urban and rural sites were measured, aiming to investigate the spatial distribution of Cl\(^-\) in PM\(_{2.5}\), and to explore the possible sources of Cl\(^-\) in PM\(_{2.5}\) during winter across China. We also summed the size distribution of aerosol Cl\(^-\) across China in both winter and summer to examine the seasonal patterns of size-segregated aerosol Cl\(^-\).

2. Materials and Methods

2.1. Sampling and Chemical Analysis

A high-volume total suspended particulate sampler equipped with a PM\(_{2.5}\) impactor (KC-1000; Laoshan Mountain Electronic Instrument Factory Co., Ltd, Qingdao, China) was used to collect PM\(_{2.5}\) samples. The sampling substrate was the Tissuquartz 2500QAT-UP filter (Pall Corp., Port Washington, WA, USA), which was combusted at 450 °C for 4 hours before use. The sampling campaigns were taken in January of 2018, and the sampling time for each PM\(_{2.5}\) sample in urban sites was 23.5 hours. According to the latitude distribution and ambient temperature of each sampling sites, the 20 urban sampling sites were divided into three regions: 1) Northern cities (blue solid circles in Figure 1), including Harbin (HRB), Shenyang (SY), Shijiazhuang (SJZ), Tianjin (TJ), Taiyuan (TY), Ji’nan (JN), Qingdao (QD), Xi’an (XA), and Lanzhou (LZ), where regions of heating supply are located in northern China and the average ambient temperature in January is lower than zero. 2) Central cities (yellow solid circles in Figure 1), including Shanghai (SH), Nanjing (NJ), Hangzhou (HZ), Nanchang (NC), Wuhan (WH), Chongqing (CQ) and Chengdu (CD), which are located between 28 °N and 32 °N, and the average ambient temperature ranges from 2 °C to 6 °C. 3) Southern cities (red solid circles in Figure 1), including Xiamen (XM), Guangzhou (GZ), Nanning (NN) and Kunming (KM), located south of 25 °N where the average ambient temperature is higher than 9 °C. We also sampled PM\(_{2.5}\)
samples from rural sites (Yudu and Puding, Figure 1), but the sampling time for each PM$_{2.5}$ sample was 47.5 hours and only 16 samples were collected from each rural site. The latitude distributions of ambient temperature and relative humidity for the urban sites are shown in Figure 1b,c.

The water-soluble ions analyzing processes can be referenced to Luo et al. [16] and Hsu et al. [48]. Briefly, a one-eighth piece of filter was extracted with 50 mL of Milli-Q water (conductivity 18.2 MΩ/cm) in a clear centrifuge tube. The centrifuge tube filled with filter and 50 mL Milli-Q water, was subjected to ultrasonically extraction for 30 minutes under room temperature, then centrifuged for 20 minutes at 2000 revolutions per minute. Finally, the extract was filtered using a 0.22 μm Millipore syringe filter. After filtering, the extract was stored at -20 °C for further chemical analysis. The water-soluble ions ($\text{Cl}^-$, $\text{NH}_4^+$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{NO}_3^-$, and $\text{SO}_4^{2-}$) were analyzed by a ion chromatograph (Thermo Fisher Scientific, Inc., Waltham, MA, USA). For the urban samples, all of the above ions were analyzed, but for the rural sites, only anions ($\text{Cl}^-$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$) were analyzed.

2.2. Model of Positive Matrix Factorization

The positive matrix factorization (PMF 5.0) is a factor-based receptor model used for quantifying the contribution of sources to samples based on the fingerprints of the sources [49]. In this study, 270 × 8 matrix (sample number × 8 species) data sets for northern cities, 214 × 8 matrix date sets for central cities and 156 × 8 matrix date sets for southern cities were introduced into the PMF 5.0 to quantify sources of $\text{Cl}^-$ in PM$_{2.5}$ across China during the winter. We ran PMF 5.0 with the number of runs set to 20 and the number of factors set from 3 to 6, and examined Q (Robust)/Qexp to choose the best number of factors for the model. The detailed model parameter settings can be found in the user guide (www.epa.gov) and other studies [50,51].
3. Results and Discussions

3.1. Spatial Distributions of Cl$^-$, SO$_2^-$, K$^+$ and Na$^+$ in PM$_{2.5}$

Overall, the Cl$^-$ concentrations in PM$_{2.5}$ ranged from 0.11 to 26.7 µg/m$^3$ over the 20 urban sites (Table 1; Figure 2a), which is consistent with previous observations of aerosol Cl$^-$ concentrations across China during winter [52–55]. The concentrations of Cl$^-$ in PM$_{2.5}$ across Chinese cities in our observations were significantly higher than previous studies of aerosol Cl$^-$ during wintertime in the northeastern United States (0.06~0.23 µg/m$^3$) [14], in Iasi (0.32 ± 0.15 µg/m$^3$) [30], and in Sao Paulo (1.4 µg/m$^3$) [56], suggesting intensive inorganic chlorine emissions in China. The aerosol Cl$^-$ concentrations in rural sites ranged from 0.07 ± 0.02 µg/m$^3$ to 0.55 ± 0.19 µg/m$^3$ across China during winter (Table 2, Figure 2b), which were significantly lower than those in urban sites (Table 1; Figure 2a), suggesting strong anthropogenic emissions of chlorine in urban sites. In addition, there were large spatial variations in aerosol Cl$^-$ in urban and rural sites. For example, the average Cl$^-$ concentration (9.81 ± 5.20 µg/m$^3$) in PM$_{2.5}$ observed in Shijiazhuang (located in northern China) was thirteen-fold times higher than those (0.69 ± 0.31 µg/m$^3$) occurred in Kunming (located in southwest China) during winter (Table 1). The average concentration of aerosol Cl$^-$ sampled in Changbai Mountain (0.39 ± 0.15 µg/m$^3$) was five times higher than that (0.07 ± 0.02 µg/m$^3$) the rural site of Yudu (Table 2).

Table 1. Concentrations of Cl$^-$ in urban PM$_{2.5}$ (µg/m$^3$) across China in January 2018.

| Locations       | Min   | Max   | Median | Mean $^1$ | Mean $^2$ | Mean $^3$ | SD  |
|-----------------|-------|-------|--------|-----------|-----------|-----------|-----|
| Harbin (HRB)    | 1.15  | 18.6  | 6.77   | 6.91      | 5.78      | 6.65      | 3.94|
| Shenyang (SY)   | 1.00  | 7.24  | 3.57   | 3.73      | 3.34      | 3.72      | 1.69|
| Tianjin (TJ)    | 0.39  | 16.4  | 4.30   | 5.29      | 4.19      | 5.24      | 3.53|
| Shijiazhuang (SJZ) | 1.29  | 26.7  | 9.46   | 9.81      | 8.44      | 9.7       | 5.20|
| Taiyuan (TY)    | 1.21  | 12.4  | 5.98   | 6.37      | 5.38      | 6.3       | 3.48|
| Ji’an (JN)      | 0.84  | 10.44 | 3.12   | 3.79      | 3.21      | 3.64      | 2.36|
| Qingdao (QD)    | 0.99  | 9.77  | 2.65   | 3.18      | 2.74      | 3.17      | 1.95|
| Xi’an (XA)      | 1.08  | 10.5  | 3.18   | 3.80      | 3.34      | 3.74      | 2.14|
| Lanzhou (LZ)    | 0.67  | 5.23  | 2.73   | 2.62      | 2.27      | 2.61      | 1.30|
| Shanghai (SH)   | 0.17  | 5.61  | 1.30   | 1.73      | 1.29      | 1.73      | 1.41|
| Nanjing (NJ)    | 0.69  | 5.83  | 2.11   | 2.30      | 2.05      | 2.29      | 1.14|
| Hangzhou (HZ)   | 0.42  | 4.75  | 1.91   | 1.94      | 1.55      | 1.92      | 1.24|
| Nanchang (NC)   | 0.27  | 3.37  | 0.95   | 1.13      | 0.90      | 1.05      | 0.79|
| Wuhan (WH)      | 0.28  | 4.60  | 2.12   | 2.27      | 2.07      | 2.13      | 0.88|
| Chongqing (CQ)  | 0.32  | 6.14  | 1.56   | 1.73      | 1.28      | 1.72      | 1.34|
| Chengdu (CD)    | 0.42  | 4.52  | 2.39   | 2.32      | 1.96      | 2.32      | 1.17|
| Kunming (KM)    | 0.26  | 1.55  | 0.63   | 0.69      | 0.63      | 0.69      | 0.31|
| Nanning (NN)    | 0.24  | 2.63  | 0.78   | 0.90      | 0.76      | 0.90      | 0.54|
| Guangzhou (GZ)  | 0.11  | 1.83  | 0.66   | 0.76      | 0.59      | 0.76      | 0.52|
| Xiamen (XM)     | 0.13  | 4.02  | 0.93   | 1.01      | 0.83      | 1.01      | 0.70|

$^1$ Arithmetic mean, $^2$ Geometric mean, $^3$ Volume mean.

The Cl$^-$ concentrations in PM$_{2.5}$ gradually decreased from the northern cities (5.0 ± 3.7 µg/m$^3$) to the central cities (1.9 ± 1.2 µg/m$^3$), and then to the southern cities (0.84 ± 0.54 µg/m$^3$) across China during winter (Figure 3a). Similar aerosol Cl$^-$ spatial patterns were also seen for the rural sites over China (Figure 2b). These results indicated a national pattern of aerosol Cl$^-$ across China in winter. Moreover, the decreased concentrations of aerosol Cl$^-$, along with the path of the Asian winter monsoon from the northern to southern China, suggested that the atmospheric chlorine may be transported along the wind field. Although ambient temperature and RH have an obvious latitude distribution from north to south China (Figure 1b,c), there were no positive or negative correlations between aerosol Cl$^-$ and temperature, and between aerosol Cl$^-$ and RH for all the study regions. In addition, the observations of Cl$^-$ concentrations were not consistent with the spatial distribution of the emission of
chlorine (HCl + Cl₂) modeled by the coal consumption and chlorine content of coal in each province for the whole year of 2012 [57]. Liu et al. showed that high chlorine emissions are mainly distributed in the Sichuan Basin, the Yangtze River Delta and the North China Plain, with no latitude variations across China [57]. Due to a lack of coal consumption in January 2018 for the observed cities, we cannot estimate the chlorine emissions from coal combustion. The discrepancies between the observed aerosol Cl− concentrations and the modeled chlorine emissions across China may be related to the seasonal differences (for example higher chlorine in winter than summer [58]), and the study scale differences (for example, our study focused on the cities, but the study of Liu et al. [57] including both cities and countryside).

| Locations       | Types | Min  | Max  | Mean | SD   |
|-----------------|-------|------|------|------|------|
| Mt. Hua (HS)    | PM 2.5| 0.3  | 0.2  | -    | -    |
| Mt. Longfeng (LF) TSP | -     | 0.55 | 0.19 | [63] |
| Mt. Waliguan (WLG) TSP | -     | 0.37 | 0.13 | [63] |
| Mt. Changbai (CBS) PM 2.5 | -     | 0.39 | 0.15 | [62] |
| Harbin (HRB)    | PM 2.5| 1.15 | 18.6 | 6.77 | 6.91 |
| Taiyuan (TY)    | PM 2.5| 1.21 | 12.4 | 5.98 | 6.37 |
| Shijiazhuang (SJZ) 1.29 26.7 9.46 9.81 8.44 9.7 5.20 | PM 10 | 0.05 | 1.13 | 0.26 | - [61] |
| Ji`nan (JN)     | PM 10 | 0.84 | 10.44| 3.12 | 3.79 |
| Lanzhou (LZ)    | PM 10 | 0.67 | 5.23 | 2.73 | 2.62 |
| Xi`an (XA)      | PM 2.5| 1.08 | 10.5 | 3.18 | 3.80 |
| Nanjing (NJ)    | PM 10 | 0.69 | 5.83 | 2.11 | 2.30 |
| Kunming (KM)    | PM 2.5| 0.26 | 1.55 | 0.63 | 0.69 |
| Chengdu (CD)    | PM 2.5| 0.42 | 4.52 | 2.39 | 2.32 |
| Xiamen (XM)     | PM 2.5| 0.13 | 4.02 | 0.93 | 1.01 |
| Puding (PD)     | PM 2.5| 0.03 | 0.61 | 0.23 | 0.19 |
| Jincheng (JC)   | PM 2.5| 0.03 | 0.11 | 0.07 | 0.02 |
| Yudu (YD)       | PM 2.5| 0.03 | 0.11 | 0.07 | 0.02 |

In addition, there was a positive relationship between concentrations of Cl− and PM2.5 in northern China ($R^2 = 0.71$), central China ($R^2 = 0.78$) and southern China ($R^2 = 0.63$) (Figure 3b), which indicated that Cl− accumulates as concentration of particulate matter increases. The average mass ratios of Cl−/PM2.5 in northern cities (6.0 ± 4.8%) were higher than those in central cities (2.7 ± 2.1%) and southern cities (1.8 ± 1.8%) (Figure 3c), and were also higher than previous studies (ranging from 0.34 to 4.55) [54,58]. The anomalous high mass ratios of Cl−/PM2.5 in northern cities may be connected with the high emission of anthropogenic chlorine [58], or with the higher gas-phase HCl partition into
particulate Cl− [57], or with the implementation of air pollutant emission reduction measures, which dropped the concentrations of PM2.5 during this study period. Such high mass ratios of Cl−/PM2.5 in widespread northern cities deserve further explanation.

### Table 2. Concentrations of aerosol Cl− in rural sites (µg/m³) during winter.

| Locations | Types | Min   | Max   | Mean   | SD    | References |
|-----------|-------|-------|-------|--------|-------|------------|
| Yudu (YD) | PM2.5 | 0.03  | 0.11  | 0.07   | 0.02  | This study |
| Puding (PD) | PM2.5 | 0.03  | 0.61  | 0.23   | 0.19  | This study |
| Mt. Hua (HS) | PM10  | -     | 0.3   | 0.3    | 0.2   | [59]       |
| Mt. Yulong (YL) | TSP  | 0.13  | 0.46  | 0.26   | 0.08  | [60]       |
| Mt. Gongga (GG) | PM2.5 | 0.03  | 0.52  | 0.17   | -     | [61]       |
| Mt. Gongga (GG) | PM10  | 0.05  | 1.13  | 0.26   | -     | [61]       |
| Mt. changbai (CBS) | PM2.5 | -     | -     | 0.39   | 0.15  | [62]       |
| Mt. Longfeng (LF) | TSP  | -     | -     | 0.55   | 0.19  | [63]       |
| Mt. Waliguan (WLG) | TSP  | -     | -     | 0.37   | 0.13  | [63]       |

Concentrations of SO4^2−, K+ and Na+ also decreased from the northern cities to the southern cities (Figure 4). These results, on the one hand, validate our regional divisions (i.e., northern, central and southern cities), but on the other hand, imply that the strongest anthropogenic emission of SO4^2−, K+ and Na+ occurred in northern China. Most urban aerosol SO4^2− is associated with the coal combustion [20,22]. The highest concentration of SO4^2− in PM2.5 in northern cities (13.3 ± 9.0 µg/m³) in these measurements (Figure 4a) may be attributed to increasing consumption of coal in winter for heating supply. The SO4^2− in central cities (11.7 ± 6.7 µg/m³) may be sourced from the local emissions or transport from the northern China. High K+ emission is a characteristic of biomass burning [64–66]. In these observed campaigns, the highest concentration of K+ occurred in northern cities (0.98 ± 0.78 µg/m³), followed by central cities (0.77 ± 0.52 µg/m³), and then southern cities (0.59 ± 0.48 µg/m³) (Figure 4b). However, the active fire points from the Aqua and Terra MODIS data in January 2018 displayed an opposite trend for K+, i.e., less fire points in northern China but more in southern China (Figure 5). For the highest concentrations of K+ in northern China, we speculate that coal combustion may be an important source of K+ [64,66], but the contribution from residential biofuel combustion may not be negligible [58]. In southern China, K+ may be mainly from the biomass burning (Figure 5). Significantly higher Na+ in northern cities (0.75 ± 0.58 µg/m³) compared to central (0.26 ± 0.19 µg/m³) and southern (0.21 ± 0.16 µg/m³) cities (Fig. 4c) further indicated that there is higher consumption of coal in northern cities, as Na+ emission is a characteristic of coal combustion [67,68].

**Figure 4.** Concentrations of SO4^2− (a), K+ (b) and Na+ (c) in northern, central and southern cities, respectively. The large boxes represent the interquartile range from the 25th to 75th percentile. The line inside the box indicates the median value. The whiskers extend upward to the 90th and downward to the 10th percentile. Significant differences at the p < 0.05 level among different regions are marked with uppercase letters.
which were still higher than seawater. These results indicate that the oceanic source of chlorine is (Figure 6b), agrees with the relatively high potassium released from the biomass burning [64,65] and (Figure 6a). This may be ascribed to, on the one hand, the chlorine released from biomass burning and ±\(1.17\) [69]. Even for coastal cities, the average ratios of Cl\(^-\)/Na\(^+\) were 5.5 \(\pm\) 3.8, 5.5 \(\pm\) 2.5 and 4.5 \(\pm\) 3.9 in northern, central and southern cities (Figure 6a), respectively, which were significantly higher than sea water (1.17) [69]. Even for coastal cities, the average ratios of Cl\(^-\)/Na\(^+\) were (5.5 \(\pm\) 3.1 in northern cities (TJ and QD), 4.7 \(\pm\) 2.8 in central cities (SH and HZ) and 2.9 \(\pm\) 2.5 in southern cities (XM and GZ)), which were still higher than seawater. These results indicate that the oceanic source of chlorine is minor for all observed inland cities. Moreover, the mole ratios of Cl\(^-\)/Na\(^+\) in PM\(_{2.5}\) were higher than that (1.3 \(\pm\) 0.87) in urban dust [70], implying the urban dust source of chlorine is also minor for atmospheric aerosol chlorine. For the aerosol chlorine in an urban atmosphere, excluding the natural origins, anthropogenic emissions (such as coal combustion and biomass burning (including burning of residential and industrial biofuel, agricultural waste and wildfires)) have been widely mentioned in the literature [32,57,58]. However, the mole ratios of Cl\(^-\)/Na\(^+\) in PM\(_{2.5}\) for all the cities in our observations during winter were higher than the Cl\(^-\)/Na\(^+\) mole ratios in PM\(_{2.5}\) that collected directly from the flue gas of biomass burning (3.2 \(\pm\) 2.7) [71–74] and coal combustion (1.2 \(\pm\) 1.9) [73,75–79] (Figure 6a). This may be ascribed to, on the one hand, the chlorine released from biomass burning and coal combustion, including both gas-phase HCl and particulate Cl\(^-\) [76], and sampling the PM\(_{2.5}\) from the flue gas only, which would filter the particulate Cl\(^-\). On the other hand, Cl\(^-\) sampled in urban PM\(_{2.5}\) not only involves the primary particulate Cl\(^-\), but also contains the transformation of gas-phase HCl to particulate Cl\(^-\) [14].

The lower molar ratios of Cl\(^-\)/K\(^+\) from the flue gas of biomass burning than coal combustion (Figure 6b), agrees with the relatively high potassium released from the biomass burning [64,65] and implies that more chlorine is released from coal combustion than biomass burning. High Cl\(^-\)/K\(^+\) ratios in northern cities (Figure 6b), together with high concentrations of Cl\(^-\) and K\(^+\) in northern cities (Figures 3a and 4b), suggests that chlorine is mainly related to potassium in PM\(_{2.5}\). Moreover, the lower Cl\(^-\)/K\(^+\) ratios in southern cities, coupled with the lower concentrations of Cl\(^-\) and K\(^+\) in southern cities, suggests that more K\(^+\) than Cl\(^-\) is emitted, which is consistent with the more active fire points in southern China than central and northern China (Figure 5). Furthermore, the well correlation coefficients (0.78) between Cl\(^-\) and K\(^+\) in northern cities implies that there are similar sources of Cl\(^-\) and K\(^+\). These results suggested that Cl\(^-\) and K\(^+\) in northern cities is mainly sourced from the coal combustion. A significantly higher Cl\(^-\)/SO\(_4^{2-}\) ratio from biomass burning than coal combustion.

Figure 5. Active fire point across China from Aqua and Terra MODIS data in January 2018.

3.2. Source Apportionment of Cl\(^-\) in PM\(_{2.5}\)

To explore the possible sources of Cl\(^-\) in PM\(_{2.5}\) over Chinese cities in winter, the mole ratios of Cl\(^-\)/Na\(^+\), Cl\(^-\)/K\(^+\) and Cl\(^-\)/SO\(_4^{2-}\), and the PMF 5.0 model, were employed to explore and estimate the origins of Cl\(^-\). The mole ratios of Cl\(^-\)/Na\(^+\) were 5.5 \(\pm\) 3.8, 5.5 \(\pm\) 2.5 and 4.5 \(\pm\) 3.9 in northern, central and southern cities (Figure 6a), respectively, which were significantly higher than sea water (1.17) [69]. Even for coastal cities, the average ratios of Cl\(^-\)/Na\(^+\) were (5.5 \(\pm\) 3.1 in northern cities (TJ and QD), 4.7 \(\pm\) 2.8 in central cities (SH and HZ) and 2.9 \(\pm\) 2.5 in southern cities (XM and GZ)), which were still higher than seawater. These results indicate that the oceanic source of chlorine is minor for all observed inland cities. Moreover, the mole ratios of Cl\(^-\)/Na\(^+\) in PM\(_{2.5}\) were higher than that (1.3 \(\pm\) 0.87) in urban dust [70], implying the urban dust source of chlorine is also minor for atmospheric aerosol chlorine. For the aerosol chlorine in an urban atmosphere, excluding the natural origins, anthropogenic emissions (such as coal combustion and biomass burning (including burning of residential and industrial biofuel, agricultural waste and wildfires)) have been widely mentioned in the literature [32,57,58]. However, the mole ratios of Cl\(^-\)/Na\(^+\) in PM\(_{2.5}\) for all the cities in our observations during winter were higher than the Cl\(^-\)/Na\(^+\) mole ratios in PM\(_{2.5}\) that collected directly from the flue gas of biomass burning (3.2 \(\pm\) 2.7) [71–74] and coal combustion (1.2 \(\pm\) 1.9) [73,75–79] (Figure 6a). This may be ascribed to, on the one hand, the chlorine released from biomass burning and coal combustion, including both gas-phase HCl and particulate Cl\(^-\) [76], and sampling the PM\(_{2.5}\) from the flue gas only, which would filter the particulate Cl\(^-\). On the other hand, Cl\(^-\) sampled in urban PM\(_{2.5}\) not only involves the primary particulate Cl\(^-\), but also contains the transformation of gas-phase HCl to particulate Cl\(^-\) [14].

The lower molar ratios of Cl\(^-\)/K\(^+\) from the flue gas of biomass burning than coal combustion (Figure 6b), agrees with the relatively high potassium released from the biomass burning [64,65] and implies that more chlorine is released from coal combustion than biomass burning. High Cl\(^-\)/K\(^+\) ratios in northern cities (Figure 6b), together with high concentrations of Cl\(^-\) and K\(^+\) in northern cities (Figures 3a and 4b), suggests that chlorine is mainly related to potassium in PM\(_{2.5}\). Moreover, the lower Cl\(^-\)/K\(^+\) ratios in southern cities, coupled with the lower concentrations of Cl\(^-\) and K\(^+\) in southern cities, suggests that more K\(^+\) than Cl\(^-\) is emitted, which is consistent with the more active fire points in southern China than central and northern China (Figure 5). Furthermore, the well correlation coefficients (0.78) between Cl\(^-\) and K\(^+\) in northern cities implies that there are similar sources of Cl\(^-\) and K\(^+\). These results suggested that Cl\(^-\) and K\(^+\) in northern cities is mainly sourced from the coal combustion. A significantly higher Cl\(^-\)/SO\(_4^{2-}\) ratio from biomass burning than coal combustion.
indicates that there is relatively high Cl$^-$ emission from the biomass burning (Figure 6c). The decreasing trend in the Cl$^-$/SO$_2^{4-}$ ratio from the northern cities to the southern cities (Figure 6c) suggests that the contribution of biomass burning to aerosol Cl$^-$ cannot be neglected in northern cities. Similarly, coal combustion also may be an important source of aerosol Cl$^-$ in central and southern cities.

![Figure 6](image)

**Figure 6.** Mole ratios of Cl$^-$/Na$^+$ (a), Cl$^-$/K$^+$ (b) and Cl$^-$/SO$_2^{4-}$ (c) in aerosol collected from the northern, central and southern cities, and from the gas flue directly from biomass burning (BB) and coal combustion (CC).

To quantify the possible contributions of different sources of Cl$^-$ in PM$_{2.5}$, four resolved source profiles for Cl$^-$ and other water-soluble ions in PM$_{2.5}$ were performed by the PMF model (Figure 7). The first factor with high loading of K$^+$ indicated the sources of coal combustion and biomass burning. The second factor was characterized by high amounts of secondary formation ions (NO$_3^-$, SO$_2^{4-}$ and NH$_4^+$), giving the secondary formation source. A high Ca$^{2+}$ level indicated that the third factor was related to the soil dust. The fourth factor showed a high amount of Na$^+$, which may be associated with the sea salts or with sodium-containing salts in urban spray water (hereafter, ‘salts’ includes both sodium-containing salts in spray water and sea salts). In order to improve the urban air quality, water is frequently sprayed into the air by a sprinkler in many Chinese cities, governed by the local government. The mode results showed that the dominant contribution of Cl$^-$ in PM$_{2.5}$ was from coal combustion and biomass burning, and the soil dust and salts were the other contributors in northern cities (Figure 7, Panel A). In central cities, 60% of Cl$^-$ in PM$_{2.5}$ is from coal combustion and biomass burning, but the remainder is from the salts (Figure 7, Panel B). However, in southern cities, around 60% of Cl$^-$ in PM$_{2.5}$ is associated with the secondary formation ions (Figure 7, Panel C), implying an abundant partition of gas-phase chlorine into particulate Cl$^-$. 
Figure 7. Cont.
was dominantly distributed in size ranges from 4.7 to 5.8 µm [88], and during dust periods, aerosol Cl⁻ was mainly located in the coarse mode [89]. Primary particulate Cl⁻ sources, such as sea salt and mineral dust, were mainly distributed in the coarse mode. For example, Cl⁻ in aerosols that were sampled in the open ocean was dominantly distributed in size ranges from 4.7 to 5.8 µm [88], and during dust periods, aerosol Cl⁻ was mainly located in the coarse mode [89]. Primary particulate Cl⁻ emitted directly from coal combustion and biomass burning was distributed in the fine mode [34,75]. However, most of the chlorine was emitted into the atmosphere from coal combustion and biomass burning as gas-phase HCl [90,91]. The equilibrium of gas-phase HCl and particulate Cl⁻ may affect the size distribution of aerosol Cl⁻. Previous studies have shown that the partitioning of gas-phase HCl and particulate Cl⁻ depends on particulate pH, atmospheric relative humidity, ambient temperature, particle loading and particle water content [14,30]. Thus, it is hard to discuss the size distributions of aerosol Cl⁻ during gas-particulate partitioning of chlorine for the in-situ observations. In addition, the neutral reaction between gas-phase HCl and mineral particles may enhance the Cl⁻ distribution in coarse.

**Figure 7.** Source profiles of chlorine and other water-soluble ions deduced from the PMF5.0 analysis in northern (Panel A), central (Panel B) and southern (Panel C) cities.

### 3.3. Size Distributions of Aerosol Cl⁻: A Review

Here, the published datasets of size-segregated urban aerosol Cl⁻ that were sampled during both winter and summer in China were compiled for comparison [30,52,68,80-87] (Figure 8). The compiled size distribution results of aerosol Cl⁻ displayed a bimodal pattern, with peaks located between 0.43-0.65 µm for fine mode particles and 4.7-5.8 µm for coarse mode particles both in winter (Figure 8a) and summer (Figure 8b). The dual peak distribution of aerosol Cl⁻ might be ascribed to both the sources of chlorine and the gas-particulate partitioning of chlorine. The sources of aerosol Cl⁻ in the urban atmosphere include primary particulate Cl⁻ emission (particulate Cl⁻ directly emitted from the coal combustion, biomass burning, mineral dust and sea salts) and the transformation of gas-phase HCl (mainly emitted from the coal combustion, biomass burning and industrial emissions) into particulate Cl⁻ [21,32,67]. The primary particulate Cl⁻ sources, such as sea salt and mineral dust, were mainly distributed in the coarse mode. For example, Cl⁻ in aerosols that were sampled in the open ocean was dominantly distributed in size ranges from 4.7 to 5.8 µm [88], and during dust periods, aerosol Cl⁻ was mainly located in the coarse mode [89]. Primary particulate Cl⁻ emitted directly from coal combustion and biomass burning was distributed in the fine mode [34,75]. However, most of the chlorine was emitted into the atmosphere from coal combustion and biomass burning as gas-phase HCl [90,91]. The equilibrium of gas-phase HCl and particulate Cl⁻ may affect the size distribution of aerosol Cl⁻. Previous studies have shown that the partitioning of gas-phase HCl and particulate Cl⁻ depends on particulate pH, atmospheric relative humidity, ambient temperature, particle loading and particle water content [14,30]. Thus, it is hard to discuss the size distributions of aerosol Cl⁻ during gas-particulate partitioning of chlorine for the in-situ observations. In addition, the neutral reaction between gas-phase HCl and mineral particles may enhance the Cl⁻ distribution in coarse.
mode particles [26], and the reaction of gas-phase HCl with NH₃ to form solid NH₄Cl is located in the fine mode [31].

Figure 8. Size distributions of Cl⁻-containing aerosol particles in winter (a) and summer (b) in China. (c) The mass ratios of Cl⁻ in fine and coarse particles during winter and summer using the data from (a) and (b).

The statistical results also showed that urban aerosol Cl⁻ concentration distributed in the fine mode was similar to that in the coarse mode during winter, but significantly higher Cl⁻ concentration was distributed in the coarse mode than in the fine mode during summer (Figure 8c). The seasonal discrepancies in size-segregated aerosol Cl⁻ concentration may be attributed to several possible factors. First, during summer, the prevailing wind direction is from the ocean to the land, which may carry the sea salt into the inland, which may enhance aerosol Cl⁻ in the coarse mode. On the contrary, during winter, the wind direction of the Asian winter monsoon is from the land to the ocean, which weakens the influences of sea salt. Second, more coal and biomass consumption for heating occurs in winter than summer in northern China, which may enhance the primary fine mode aerosol Cl⁻ during winter. Third, concentrations of PM$_{2.5}$ are generally higher in winter than summer [92], and fine particles provide a relatively large specific surface area, which may enhance Cl⁻ in the fine mode in winter [31]. Fourth, acidic ions, such as SO$_4^{2-}$ and NO$_3^-$, distributed in the fine mode [52,85], can acidize fine mode aerosols [93]. In summer, strong solar irradiation can enhance gas-phase HCl release from the acidic fine particles through acid displacement between sulfuric acid or nitric acid and deliquesced Cl⁻ (HNO$_3$(g) + Cl⁻(aq) → NO$_3^-$(aq) + HCl(g) or H$_2$SO$_4$(g) + Cl⁻(aq) → SO$_4^{2-}$(aq) + HCl(g)) [89]. On the contrary, more Cl⁻ may reside in fine mode aerosol in winter than summer.

4. Conclusions

Samples of PM$_{2.5}$ were collected from 20 urban and two rural sites across China during winter, and the water-soluble ions were analyzed. The aerosol Cl⁻ concentrations decreased from northern to southern China, both in urban cities and rural sites, indicating a national spatial pattern of aerosol Cl⁻ during winter across China. The high concentration of Cl⁻ in northern China, coupled with the high concentrations of SO$_4^{2-}$, K$^+$ and Na$^+$ and the high mole ratios of Cl⁻/Na$^+$, Cl⁻/K$^+$ and Cl⁻/SO$_4^{2-}$ in northern cities, suggests that coal combustion and biomass burning are the dominate sources of Cl⁻ in PM$_{2.5}$. However, for the southern cities, the Cl⁻ in PM$_{2.5}$ was mainly affected by partition of gas-phase chlorine to particulate Cl⁻. Statistical analysis of the size distributions of Cl⁻-containing aerosols exhibited a bimodal pattern during both winter and summer. This bimodal pattern may be attributed to chlorine sources, Cl⁻ involved photochemical reactions and partition of gas-phase chlorine to particulate Cl⁻. Our simultaneously in-situ observations of Cl⁻ concentrations in PM$_{2.5}$ across China provides information for accurately modeling the spatial distribution of atmospheric chlorine and its effect on atmospheric photochemistry.
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