The pollution characteristics and source analysis of water-soluble ions in indoor PM$_{2.5}$ during the Spring Festival in Jingyue Suburb of Changchun City

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Abstract: The characteristics of water-soluble ions in indoor PM$_{2.5}$ during the Spring Festival in Changchun City were analyzed by ion chromatography. The results showed that the main water-soluble ionic components in the indoor and non-combustion periods were SO$_4^{2-}$ and Ca$^{2+}$, and the concentration of Na$^+$, K$^+$, Mg$^{2+}$, F$^-$, Cl$^-$ and NO$_3^-$ increased in the fireworks and firecrackers, among which Cl$^-$ and NO$_3^-$ increased the most. The concentration increased significantly compared with the non-combustion period, and peaked with PM$_{2.5}$ concentration in the first month of the first month and the first month of the first month; the correlation between NH$_4^+$ and SO$_4^{2-}$ during the discharge and non-combustion periods was greater than the correlation between NH$_4^+$ and NO$_3^-$, and secondary ions are mainly in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. Cluster analysis and correlation analysis indicate that the sources of water-soluble ions in indoor PM$_{2.5}$ during the Spring Festival can be classified into four categories. Biomass combustion source, automobile exhaust gas source, coal-fired emission source and soil dust, among which the main sources of Na$^+$, K$^+$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$ during the discharge period are the fireworks and firecrackers.

1. Introduction
Inhalable particulate matter is the main pollutant of the urban environment [1]. Although the particulate matter (PM$_{2.5}$) with particle size ≤ 2.5μm has a low content in the atmosphere, it is rich in a large number of toxic and harmful substances that stay in the atmosphere for a long time and have a long transportation distance [2], which has an important impact on human health and atmospheric environment quality[3]. PM$_{2.5}$ is complex in composition, including both primary aerosol particles and secondary aerosol particles generated by atmospheric chemical reactions of various gas molecules, such as nitrates, sulfates, ammonium salts [4-6]. These water-soluble substances are the main component of PM$_{2.5}$ scattering visible light, and also the main factor for the increase in particulate matter concentration, occupying a large proportion in PM$_{2.5}$. Studying the distribution characteristics of water-soluble ions in PM$_{2.5}$ is of great significance for tracking the source of PM$_{2.5}$. The Spring Festival is a traditional Chinese festival. During the Spring Festival, especially during the fireworks and firecrackers, the concentration of particulate matters and various water-soluble ions increased sharply in a short period time [7-8], resulting in a significant decrease in atmospheric visibility and a significant drop in air quality. At present, the research on water-soluble ions is mainly aimed at PM$_{2.5}$
in the atmospheric environment, while modern people spend 70%~90% of the time in the room every day, especially during the Spring Festival. Indoor PM$_{2.5}$ sources are divided into indoor and outdoor sources [3], where the outdoor source will pass through the building ventilation, the gap of the envelope structure and personnel to enter the room. Studies have shown that the amount of PM$_{2.5}$ inhaled by people staying indoors for a long time is four times that of outdoor. Even for these particulate matter originating outdoors, the exposure is often present indoors. Therefore, the research and control of indoor PM$_{2.5}$ and its water-soluble ions are more important. Based on this, this paper continuously collected the PM$_{2.5}$ samples from a non-smoking flower and firecracker residential area in the suburbs of Changchun City during the Spring Festival from Jun.21$^{th}$,2019 to Feb.19$^{th}$,2019 and water-soluble. ion component characteristics were correlated and analyzed at the same time.

2. Materials and methods

2.1 Sample collections

Sampling point and sampling time: the sampling point is located in a non-smoking flower and firecracker residential area in the suburbs of Changchun City, Jilin Province. The sampling area is convenient for transportation, there are many construction sites, no dense commercial areas and large industrial areas, which can be used at Changchun City. Representatives of non-smoking flower and firecracker residential areas responded to indoor PM$_{2.5}$ and the level of water-soluble ions in the indoors during the Spring Festival. The sampling time is set from Jun.21$^{th}$,2019 to Feb.19$^{th}$,2019. From Jun.21$^{th}$,2019 to Feb.3$^{rd}$,2019, the fireworks and firecrackers are non-burning period, and from Feb.4$^{th}$,2019 to Feb.19$^{th}$,2019 is the burning period.

Sampling instrument: The indoor sampler selects the LD-6SR laser dust monitor to realize the monitoring of PM$_{2.5}$ and the collection of filter samples. The instrument can effectively reduce the interference of humidity. The sampling period is 24h, and the sampling flow is 2L/min. The sampling filter adopts the Swedish Munktell quartz fiber filter membrane. The quartz component of the raw material is >99%, and the collection efficiency of 0.3μm particles in the air is >99.998%.

2.2 Sample analyses

To eliminate the residual volatile organic compounds in the filter film, the filter was placed in a 600°C muffle furnace for 4h before sampling and dried under constant temperature and humidity conditions (T=20°C, RH=50%) for 48h. With constant weight, the filtered membrane must still be dried under the same conditions, weighed three times to obtain the average value, and the low-temperature storage is to be tested. The filter membrane was cut and ultrasonically extracted with 20 ml of pure water for 40 min. The supernatant was transferred to a plastic tube and then entered into an ion chromatography.

The ion analysis was performed using a Metrohm 930 Compact IC Flex ion chromatograph. The cation detection was performed on a column of Metrosep C 6. The eluent was 1 mol of a solution of Pyridine dicarboxylic acid and HNO$_3$ at a flow rate of 0.9 ml/min. The anion was detected using a separation column Metrosep A Supp 5-250. The eluent was 3.2 mmol/L Na$_2$CO$_3$ and 1 mmol/L NaHCO$_3$ at a flow rate of 0.7 ml/min. The determination of 10 water-soluble ions in the PM$_{2.5}$ filter was carried out separately. (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, F$^-$, Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$)

2.3 Quality control

In order to ensure the accuracy of the test results, one blank parallel sample was added to each of the five filter samples for quality control analysis. The results of each ion test were lower than the lower limit of determination, and the relative deviation of the measured values of the blank parallel samples was≤10%. A standard solution of concentration gradient was set up and a standard curve was established with a correlation coefficient R$^2$ > 0.996.
3. Result and discussion

3.1 pH of PM$_{2.5}$

The pH is an important attribute of PM$_{2.5}$. Acidity promotes the heterogeneous reaction on the surface of particles, promotes the formation of secondary components, and endangers human health [9]. Calculate the molar charge numbers $N_1$ and $N_2$ of cations and anions by using equations (1) and (2), respectively, and determine the pH of PM$_{2.5}$ by analyzing the balance of anions and cations. When $N_1/N_2$>1, PM$_{2.5}$ is alkaline. When $N_1/N_2$<1, PM$_{2.5}$ is acidic. The calculated $N_1/N_2$ values for the burning period and the non-burning period are plotted in Fig. 1.

$$N_1 = \frac{c(\text{Na}^+)}{23} + \frac{c(\text{NH}_4^+)}{18} + \frac{c(\text{K}^+)}{39} + \frac{c(\text{Mg}^{2+})}{12} + \frac{c(\text{Ca}^{2+})}{20}$$  \hspace{1cm} (1)

$$N_2 = \frac{c(\text{F}^-)}{19} + \frac{c(\text{Cl}^-)}{35.5} + \frac{c(\text{NO}_2^-)}{46} + \frac{c(\text{NO}_3^-)}{62} + \frac{c(\text{SO}_4^{2-})}{48}$$  \hspace{1cm} (2)

![Figure 1. The ratio of cation to anion molar charge in the burning and non-burning periods](image)

It can be seen from Fig. 1 that the $N_1/N_2$ value of the burning period is concentrated in the interval of 0.9–1.1, and the lowest value is 0.7, which appears on February 16 (Jun. 1st of the lunar calendar). On this day, the indoor PM$_{2.5}$ is the most acidic. The highest value of $N_1/N_2$ is 1.1, and the median is 0.97. The data exceeding 50% shows that $N_1/N_2$<1.0, while the $N_1/N_2$ value of the non-burning period is concentrated in the range of 1.2–1.8, the lowest value is 1.1. The highest value is 2.1. It is indicated that most of the indoor PM$_{2.5}$ in the burning period is acidic and the cation is depleted. There is H$^+$ in the water-soluble component which cannot be detected by ion chromatography, and the indoor PM$_{2.5}$ in the non-burning period is alkaline.

3.2. PM$_{2.5}$ and water-soluble ion pollution characteristics

The indoor water-soluble ion content and percentage in the discharge and non-burning periods were separately calculated and plotted in the figure. It can be seen from Fig. 2 that Na$^+$, K$^+$, Mg$^{2+}$, F$^-$, Cl$^-$, and NO$_3^-$ are higher than the non-burning period during the burning period, in which Cl$^-$ and NO$_3^-$ increase significantly and the concentration fluctuates greatly; NH$_4^+$, Ca$^{2+}$, The concentration of NO$_2^-$ in the non-burning period is higher than that in the burning period, in which the concentration of Ca$^{2+}$ changes significantly, the concentration of NH$_4^+$ and Ca$^{2+}$ is higher in the non-burning period, while the concentration of NO$_2^-$ in the burning period fluctuates greatly; while the concentration of SO$_4^{2-}$ is in the burning period. There was no significant difference between the concentration levels of non-burning and release periods. It can be seen from Fig. 3 that the proportion of SO$_4^{2-}$, Cl$^-$ and Ca$^{2+}$ in the burning period is the highest, respectively 25.27%, 21.94%, 10.98%, and the proportion of SO$_4^{2-}$, Ca$^{2+}$ and NH$_4^+$ in the non-burning period is the highest, 28.96%, 4.54%, 12.48%, SO$_4^{2-}$ and Ca$^{2+}$ have been the main ionic components in the room during the Spring Festival. Ca in nature enters the atmosphere mainly in the form of dust and floating dust, and exists in the form of CaCO$_3$, which reacts
with acid gases (HCl or HNO₃) in the atmosphere to form soluble Ca²⁺[10]. During the Spring Festival, construction activities and other activities are stopped, and dust is reduced, resulting in a decrease in Ca²⁺ concentration. According to the results of Section 3.1, PM₂.₅ is acidic during the burning period, and NO₂⁻ is unstable under acidic conditions, which is easy to decompose to form NO₃⁻, which is also a reason for the increase of NO₃⁻ concentration and the decrease of NO₂⁻ concentration during the burning period, and NO₂⁻ The conversion process to NO₃⁻ is affected by the acidity and the fluctuations of NO₂⁻ and NO₃⁻ during the burning period are large. At the same time, cerium nitrate is used as the main coloring agent to be mixed into the fireworks. When the temperature is lower than 15°C, NO₃⁻ mainly exists in the form of particles and is released into the environment[11], so that the concentration of NO₃⁻ increases.

![Graph showing indoor water-soluble ion concentration levels during the burning and non-burning periods](image1)

**Figure 2.** Indoor water-soluble ion concentration levels during the burning and non-burning periods

![Pie charts showing the proportion of water-soluble ions during the burning and non-burning periods](image2)

**Figure 3.** The proportion of water-soluble ions during the burning and non-burning periods

The monitoring results of water-soluble ion concentration in indoor PM₂.₅ during the non-burning period (Jun.21st, 2019–Feb.3rd, 2019) and the burning period (Feb.4th, 2019–Feb.19th, 2019) are shown in Fig.4. During the non-burning period, the average daily concentration of PM₂.₅ was 39~76μg/m³; the average daily concentration during the burning period was 72~117μg/m³, which was significantly higher than the non-burning period, and was on Feb.5th, 2019 and Feb.19th, 2019, the PM₂.₅ concentration reached a peak of 108μg/m³ and 117μg/m³, and the 3/4 days exceeded the 24h average concentration of PM₂.₅ in the Ambient Air Quality Standard (GB3095-2012). The secondary standard requires (75μg/m³) and the target days are only 25%. At the same time, the concentration of various water-soluble ions in PM₂.₅ increased to different degrees on Feb.4th, 2019 (New Year's Eve) and Feb.19th, 2019 (the Lantern Festival). Firecrackers are the traditional Chinese custom during the Spring Festival. New Year's Eve and Lantern Festival are the most concentrated and concentrated periods, while February is the cold month of Changchun City. The minimum temperature at night can reach -20°C, forming a thicker inversion layer. Inverse temperature, low mixed layer, high humidity, low wind speed and other conditions, the atmospheric structure tends to be stable and lasts for a long time,
which is not conducive to the spread of particulate matter near the ground. The continuous high burning dose on Feb.4th, 2019 makes PM$_{2.5}$ constant. The cumulative peak value, in which the concentrations of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ increased by 23.3%, 65.6% and 32.6% respectively compared with New Year’s Eve, because the water-soluble components produced by fireworks and firecrackers increased the relative humidity of PM$_{2.5}$. Large, it is conducive to the formation of NH$_4^+$, NO$_3^-$, SO$_4^{2-}$ by gaseous heterogeneous NH$_3$, NO$_x$, SO$_2$ through heterogeneous chemical reactions, and the secondary photons will continue to accumulate during the daytime photochemical reaction on Feb 5th. After Feb 6th, 2019 (Jun. 2nd of the lunar calendar), there was a slight downward trend as the amount of discharge decreased. At the same time, during the Spring Festival, the increase of artificial activities such as indoor cooking and cleaning will increase the indoor PM$_{2.5}$ concentration, and will also generate heat to increase the indoor temperature, resulting in an increase in indoor and outdoor temperature difference, an increase in pressure difference, and the penetration of outdoor particulate matter into the room. The amount of indoor PM$_{2.5}$ and its concentration of water-soluble ions during the Spring Festival are affected by both indoor and outdoor.

![Figure 4. Changes in water-soluble ion concentrations during the burning and non-burning periods](image)

**3.3 The combination of secondary water-soluble ions in PM$_{2.5}$**

**3.3.1 Correlation analysis between SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$**

The correlation between the secondary particles NH$_4^+$ and SO$_4^{2-}$, NO$_3^-$ was compared, and the results are shown in Fig 5. The linear correlation coefficient $R_2$ of NH$_4^+$ and SO$_4^{2-}$, NO$_3^-$ during the burning period is 0.44 and 0.41, respectively. The linear correlation coefficient $R_2$ of the non-burning period NH$_4^+$ and SO$_4^{2-}$, NO$_3^-$ is 0.68 and 0.53. The correlation between NH$_4^+$ and SO$_4^{2-}$ is greater than NH$_4^+$ and NO$_3^-$. In relation to NO$_3^-$ and NH$_4^+$ preferentially combines with SO$_4^{2-}$ to form sulfate.

According to the Seinfeld theory, when $c$(NH$_4^+$)/$c$(SO$_4^{2-})$<2, it is indicated that SO$_4^{2-}$ is not completely neutralized by NH$_4^+$, but also exists in the form of other acid salts[12]. When SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ are present in the form of NH$_4$HSO$_4$ and NH$_4$NO$_3$, the actual NH$_4^+$ concentration in the environment can be calculated according to the formula (3), when SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ are present in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. The actual NH$_4^+$ concentration in the environment can be calculated according to the theory of equation (4)[13]. To determine the presence of sulfate the indoor environment, a linear regression analysis of the NH$_4^+$ concentration calculated by equations (3) and (4) and the actual measured NH$_4^+$ concentration is shown in Fig. 6. The slopes of the linear fit between the NH$_4^+$ concentration calculated by equations (3) and (4) and the measured NH$_4^+$ concentration during the burning period were 1.26 and 0.88, respectively. It shows that the actual NH$_4^+$ concentration in the environment is between the theoretical values calculated by the formula (3) and formula (4). In the indoor environment during the burning period, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ exist in the form of NH$_4$HSO$_4$, (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. The slopes of the linear fit between the NH$_4^+$ concentration calculated by
equations (3) and (4) and the measured NH₄⁺ concentration during the non-burning period are 0.58 and 0.95, respectively. It is indicated that SO₂⁻, NO₃⁻ and NH₄⁺ exist in the form of (NH₄)₂SO₄ and NH₄NO₃ in the indoor environment during the non-burning period.

In summary, the secondary ions SO₄²⁻, NO₃⁻ and NH₄⁺ in the indoor environment of Changchun City mainly exist in the form of (NH₄)₂SO₄ and NH₄NO₃, but there are still existing forms between SO₂⁻, NO₃⁻ and NH₄⁺ during the fireworks and firecrackers in the Spring Festival. NH₄HSO₄. The reason is that PM2.5 is acidic in the fireworks and firecrackers during the Spring Festival, and the free H⁺ in the water-soluble component is easily combined with SO₄²⁻ to form HSO₄⁻.

\[ C(NH₄⁺) = 0.29C(NO₃⁻) + 0.19C(SO₄²⁻) \] (3)

\[ C(NH₄⁺) = 0.29C(NO₃⁻) + 0.38C(SO₄²⁻) \] (4)

Figure 5. Correlation between theoretical and actual values of NH₄⁺ during the burning and non-burning periods

Figure 6. The linear fit between SO₂⁻, NO₃⁻ and NH₄⁺ during the burning and non-burning periods

3.3.2 c(NO₃⁻)/c(SO₄²⁻)

SO₂⁻ and NO₃⁻ in the environment are mainly secondary ions generated by an oxidation reaction and the photochemical reaction of SO₂ and NOx, respectively. According to the N and S contents in coal, gasoline and diesel in China, the NO₃⁻/SO₂⁻ mass ratio emitted by coal combustion is 1:2, and the NO₃⁻/SO₂⁻ mass ratio discharged from gasoline and diesel is 8:1~13:1[14]. Therefore, NO₃⁻ can be used as a marker for vehicle exhaust sources (moving sources). SO₂⁻ can be used as a marker for coal-fired sources (fixed sources). Usually, c(NO₃⁻)/c(SO₄²⁻) is used to judge the source of movement. And the contribution rate of the fixed source to particulate matter[15-16], c(NO₃⁻)/c(SO₄²⁻)>1, indicating that the main source is the mobile source, c(NO₃⁻)/c(SO₄²⁻)<1, indicating The main source is a fixed source. The distribution of c(NO₃⁻)/c(SO₄²⁻) in indoor PM2.5 during the sampling period of this study is shown in Fig. 7. The median of the burning period c(NO₃⁻)/c(SO₄²⁻) is 0.32, 50%. The data shows that c(NO₃⁻)/c(SO₄²⁻)<0.32, the 3/4 quantile of the non-burning period c(NO₃⁻)/c(SO₄²⁻)is 0.23,
and 75% of the data shows $c(\text{NO}_3^-)/c(\text{SO}_4^{2-})<0.23$, indicating that the $c(\text{NO}_3^-)/c(\text{SO}_4^{2-})$ in the burning period is higher than the non-burning period. The discharge of fixed sources will not show large fluctuations in the short period of the sampling period. Except for mobile emission sources, the fireworks and firecrackers will change the $\text{NO}_3^-$ content in the environment in a short time. However, the overall presentation of $c(\text{NO}_3^-)/c(\text{SO}_4^{2-})<1$ indicates that the indoor PM$_{2.5}$ during the Spring Festival in Changchun City is dominated by fixed pollution sources.

![Figure 7. Distribution of $c(\text{NO}_3^-)/c(\text{SO}_4^{2-})$ in indoor PM$_{2.5}$](image)

3.4 Source analysis of water-soluble ions in PM$_{2.5}$

3.4.1 Correlation analysis

The correlation between water-soluble ions in indoor PM$_{2.5}$ during the burning period and the non-burning period was analyzed. The results show that for the fireworks and firecrackers, the correlation between Na$^+$, K$^+$, Mg$^{2+}$, Cl$^-$ and SO$_4^{2-}$ is higher. However, the correlation between ions in the non-burning period is reduced, indicating that the fireworks and firecrackers have a significant effect on Na$^+$, K$^+$, Mg$^{2+}$, Cl$^-$ and SO$_4^{2-}$. For the purpose of high flammability and safety, the main oxidant in fireworks is potassium perchlorate (KClO$_3$)[17] and reacts with sulfur, charcoal, and other components to produce K$_2$SO$_4$ or KCl along with the fireworks. Na is also used as the main color metal element[18], and Mg is added as a main reducing agent[19] to fireworks and firecrackers and is released into the environment with the discharge process. Therefore, it can be considered that the release period Na$^+$, K$^+$, Mg$^{2+}$, Cl$^-$ and SO$_4^{2-}$ mainly originates from the discharge of fireworks and firecrackers, and exists in the form of sulfate or hydrochloride. For the non-burning period, the correlation between K$^+$, F$^-$ and Cl$^-$ is higher. Among them, K$^+$ is usually used as an indicator substance for biomass combustion[20], while F$^-$ and Cl$^-$ sources are complex, mainly including sea salt and coal. Related studies have shown that most of NaCl come from sea salt, long-distance transport of marine aerosols[21], usually Cl$^-$/Na$^+]=1.81. However, Changchun City is an inland area. The northwest wind prevails in winter. The wind direction is blown by the land to the ocean, which is less affected by the ocean. At the same time, the non-flammable period of this study is Cl$^-$/Na$^+=2.56$, and there is no correlation, indicating that Cl$^-$ mainly originates from Emissions from the combustion process. Therefore, it can be considered that the K$^+$, F$^-$, and Cl$^-$ in the non-burning period are mainly derived from the biomass discharge, and exist in the form of hydrochloride or a fluoride salt. Besides, the correlation between Mg$^{2+}$ and Ca$^{2+}$ in the non-burning period is higher, which is 0.74. Both are often used as tracer ions for soil and dust[22]. It is believed that Mg$^{2+}$ and Ca$^{2+}$ are mainly derived from soil dust or building dust.

For the secondary particles NH$_4^+$, NO$_3^-$, SO$_4^{2-}$ in the environment, the correlation between non-burning period NH$_4^+$ and NO$_3^-$ or SO$_4^{2-}$ is higher, respectively 0.72 and 0.96, indicating that NH$_4^+$ and NO$_3^-$ or SO$_4^{2-}$ are very strong. Homology. SO$_4^{2-}$ mainly originates from the formation of coal-fired products through a secondary reaction process. NO$_3^-$ mainly originates from the oxidation reaction or
photochemical reaction of automobile exhaust gas, and $\text{NH}_4^+$ is mainly derived from the discharge of related processes such as fossil fuel combustion[23]. The three ion sources are more complicated during the burning period, and there is also a correlation between $\text{NO}_2^-$ and $\text{NO}_3^-$ during the burning period. $\text{NO}_2^-$ is also mainly caused by the reaction of the vehicle exhaust gas, and is converted to $\text{NO}_3^-$ depending on the pH of the atmospheric environment or other factors. Therefore, $\text{SO}_4^{2-}$ in the environment is mainly derived from coal-fired emission sources. $\text{NO}_2^-$ and $\text{NO}_3^-$ are mainly derived from motor vehicle emission sources and are mostly in the form of ammonium salts.

### Table 1. Correlation matrix of water-soluble ions during the burning and non-burning periods

| Time          | Ion | Na$^+$ | NH$_4^+$ | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ | F$^-$ | Cl$^-$ | NO$_2^-$ | SO$_4^{2-}$ | NO$_3^-$ |
|---------------|-----|--------|---------|------|-----------|-----------|-------|-------|---------|-----------|---------|
| **Burning**   | NH$_4^+$ | 0.09   |         |      |           |           |       |       |         |           |         |
|               | K$^+$    | -0.07  | 0.68    |      |           |           |       |       |         |           |         |
|               | Mg$^{2+}$ | 0.35   | -0.03   | 0.34 |           |           |       |       |         |           |         |
|               | Ca$^{2+}$ | -0.17  | 0.06    | -0.36| -0.22     |           |       |       |         |           |         |
|               | F$^-$    | 0.1    | 0.17    | 0.16 | -0.05     | -0.4      |       |       |         |           |         |
|               | Cl$^-$   | 0.27   | -0.14   | 0.61 | 0.29      | 0.29      | 0.55  |       |         |           |         |
|               | NO$_2^-$ | 0.24   | -0.31   | 0.37 | 0.18      | 0.18      | 0.40  | 0.54  |         |           |         |
|               | SO$_4^{2-}$ | 0.23  | 0.69    | 0.02 | -0.08     | -0.08     | 0.28  | 0.31  | 0.12    |           |         |
|               | NO$_3^-$ | -0.23  | 0.67    | -0.26| -0.07     | -0.07     | -0.20 | -0.64 | -0.58   | -0.02     |         |
| **Non-burning** | NH$_4^+$ | -0.13  |         |      |           |           |       |       |         |           |         |
|               | K$^+$    | 0.08   | -0.05   |      |           |           |       |       |         |           |         |
|               | Mg$^{2+}$ | -0.10  | 0.18    | 0.08 |           |           |       |       |         |           |         |
|               | Ca$^{2+}$ | -0.15  | -0.02   | -0.32| 0.74      |           |       |       |         |           |         |
|               | F$^-$    | -0.01  | 0.06    | 0.75 | -0.05     | 0.58      |       |       |         |           |         |
|               | Cl$^-$   | -0.04  | -0.39   | 0.83 | -0.04     | 0.29      | 0.51  |       |         |           |         |
|               | NO$_2^-$ | 0.09   | 0.17    | -0.11| 0.17      | 0.02      | -0.15 | -0.25 |         |           |         |
|               | SO$_4^{2-}$ | 0.04  | 0.96    | -0.07| 0.23      | -0.12     | -0.04 | -0.52 | 0.32    |           |         |
|               | NO$_3^-$ | -0.28  | 0.72    | 0.10 | 0.10      | -0.02     | 0.19  | -0.03 | -0.44   | 0.54      |         |

3.4.2 Cluster analysis

Cluster analysis of water-soluble ions in indoor PM$_{2.5}$ during the Spring Festival, the results are shown in Fig.8. Combined with the results of the correlation analysis in Section 3.4.1, 10 water-soluble ions can be divided into four categories.

Figure 8. Water-soluble ion clustering analysis tree
The first category contains K⁺, F⁻, Na⁺, Cl⁻, which is considered to be mainly derived from the fireworks and pyrotechnics during the Spring Festival and is considered to be mainly derived from biomass combustion products during the non-burning period. Therefore, the first category is defined as the source of biomass combustion emissions.; the second category contains NO₂⁻, NH₄⁺, NO₃⁻, defined as the vehicle emission source, which can be called the mobile source; the third category contains Ca²⁺, Mg²⁺, defined as soil dust; the fourth category contains SO₄²⁻, defined as coal combustion Source of emissions, which can be called the fixed source. In summary, the main sources of water-soluble ions in indoor PM₂.₅ during the Spring Festival are biomass combustion sources, vehicle emissions, soil dust, and coal-fired sources.

4. Result and discussion

(1) The PM₂.₅ in the fireworks and firecrackers during the Spring Festival is acidic, the non-burning period is alkaline, and the burning period is significantly higher than the non-flammable period. The main water-soluble ionic components are SO₄²⁻ and Ca²⁺. The concentration of NH₄⁺, Ca²⁺, and NO₃⁻ in the fireworks and firecracker period decreased compared with the non-burning period, while the concentrations of Na⁺, K⁺, Mg²⁺, F⁻, Cl⁻, and NO₃⁻ increased significantly, and with PM₂.₅ concentration peaking in the Jun.16th of the lunar calendar and Jun.16th of the lunar calendar, while the SO₄²⁻ has no significant difference between the burning period and the non-burning period concentration level.

(2) Compare the correlations between secondary ions NO₃⁻, SO₄²⁻ and NH₄⁺ in the indoor environment during the Spring Festival, and find that NH₄⁺ preferentially combines with SO₄²⁻ to form sulfate, and secondary ions mainly exist in the form of (NH₄)₂SO₄ and NH₄NO₃. However, during the fireworks and firecrackers, the secondary ions exist in the form of NH₄HSO₄.

(3) Indoor c(NO₃⁻)/c(SO₄²⁻)<1 during the Spring Festival in Changchun City indicates that the contribution of fixed emission sources to PM₂.₅ and water-soluble ions is greater than that of mobile emission sources.

(4) For the burning period, Na⁺, K⁺, Mg²⁺, Cl⁻, SO₄²⁻ mainly originate from the fireworks and firecrackers, while for the non-burning period, K⁺, F⁻, and Cl⁻ are mainly derived from biomass combustion emissions, Mg²⁺ and Ca²⁺ are mainly derived from soil dust or building dust. SO₄²⁻ mainly originates from coal-fired emission sources. NO₃⁻ and NO₂⁻ mainly originate from motor vehicle emission sources and are mostly in the form of ammonium salts.

(5) Cluster Analysis of the springs during the Spring Festival and the non-burning period in Changchun City can be classified into four categories: biomass combustion sources, automobile exhaust sources, coal-fired sources, and soil dust.

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