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Chemical characteristics of precipitation in central Liaoning Province, Northeast China

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The chemical characteristics of precipitation were analyzed based on the chemical composition of principal ionic within acid rain (from February 2007 to January 2008) of Liaozhong Meteorological Station (LMS) located in Malong Village in central Liaoning Province of Northeast China, meteorological conditions on the corresponding period ground, and variation of several air pollutants concentration. The results indicated that (1) the precipitation of LMS was acidic; average pH of all samples was 4.76; the frequency of acid rain during the observation period was 70.7%; the frequency was 82.8% in summer and autumn; and the acidity was stronger in larger rainfall season; (2) in the chemical composition of precipitation, the primary anions were $\text{SO}_4^{2-}$ and $\text{NO}_3^-$; the primary cations were $\text{NH}_4^+$ and $\text{Ca}^{2+}$; the ratio of $\text{SO}_4^{2-}/ \text{NO}_3^-$ was 2.9; and the ratio of $\text{Na}^+/\text{Cl}^-$ was larger than 1; (3) all concentration of anions was higher in summer and winter, but relatively low in spring and autumn. This showed that the relationship between regional rainfall acidification and pollution was not significant. The correlation between $(\sum$ anionic / $\sum$ cationic) and pH was not obvious among the measured 9 kinds of main anions and cations, which explained the main 9 kinds of anions and cations in the current acid rain observation could not completely include precipitation ions composition; and (4) rainwater acidity and near floor gaseous pollution concentration were different from each other, and pH and $\text{NO}_x$, $\text{CO}$, $\text{NO}_2$ and $\text{O}_3$ concentrations showed significant negative correlation, but was not obvious with $\text{SO}_2$ concentration. However, the pH and alkaline pollutants, such as particulate, was positively correlative.

Key words: Precipitation, acid rain, chemical characteristics, central Liaoning Province of China.

INTRODUCTION

Recent observations show that precipitation in Northeast China, especially in many coastal cities of Liaoning Province, presents the tendency of acidification. Even acid rain is also very serious in the areas affected by less human pollutions. Studies have shown that since 2004, the pH value of acid rain is reduced more, but the acidity has increasing trend year by year (Hong et al., 2009). However, the formation mechanism of regional acid rain has received little attention.

The aim of this study is to analyze the variation characteristics of the acid rain observation data (from February 2007 to January 2008) of LMS located in Malong Village in central Liaoning Province, combining with ground meteorological conditions and other gases pollutant concentration in the same period, and to provide the theory basis on understanding the case of acid rain in rural area in northeast background situation and studying the causes of precipitation acidification and countermeasures of acid rain in the northeastern regions.

MATERIALS AND METHODS

Design of the station

The research station is located in the northwest corner of Malong Village of Liaozhong County, Liaoning Province (122° 40' - 15.66° E...
Monitoring and analysis method

The sampler, a polyethylene plastic bucket which is 40 cm in diameter and 20 cm in height, with colorless polyethylene bag, placed at relative height of 1.5 m was used for manual sampling. To prevent occurrence of wet deposition and help keep the sampler clean, the plastic cover was sealed throughout the whole process of rainfall (snow) from beginning to end. After sample collection, part of the sample (15 to 30 ml) was fetched to measure the conductivity and pH value. The remaining rain (snow) sample was filtered through a membrane filter with 0.45 mm pore size. Filtrate was collected into clean polyethylene bottle and sent to Shenyang Environmental Protection Monitoring Stations for ionic components analysis.

The monitoring methods were specified in the National standard method. pH value was measured with pH meter (RL060P, accuracy was 0.01) before each use; thereafter pH meter was corrected using the correction fluid for pH to be 6.86 and 9.18, respectively. Conductivity was measured with electrical conductivity meter (RL060C) before each use; thereafter conductivity values were corrected in the air and potassium chloride solution to be 1413 μs/cm respectively. Atomic absorption spectrophotometry and ion chromatography were used for ion analysis. Gaseous contaminants sampling for automatic sampler, is done using Hangzhou Earth Bianconeri Production API automatic sampling device; this device provided uninterrupted monitoring about atmospheric pollutants in 24 h.

Data quality control

The conductivity of each ionic component in precipitation is additional; therefore in the stations soluble ionic components in precipitation were measured, and conductivity data can be used to test completeness and accuracy of ionic components measurement. According to the additive property of conductivity, Tang et al. (2008) put forward the method of K - pH inequality data test.

The inequality in the measured conductivity of precipitation and pH value:

\[
K_m > K_{H^+} + K_{OH^-}
\]

\[
= A_{H^+} \times [H^+] + A_{OH^-} \times [OH^-]
\]

\[
= A_{H^+} \times 10^{-pH} + A_{OH^-} \times 10^{pH+14}
\]

Type: \(A_{H^+}\) and \(A_{OH^-}\) were ions; Moore conductivity of \([H^+]\) and \([OH^-]\) respectively, \([H^+]\) and \([OH^-]\) were ions concentration. Inequality left is the measured conductivity, and right is the calculated electrical conductivity by pH value. The measured conductivity of precipitation must be greater than the sum of conductivity \([H^+]\) and \([OH^-]\). If measured pH value and conductivity numerical generation going into the inequality was negative, it means that one or both of the pH value and conductivity measurement was significant errors.

Figure 1 is Liaozhong Acid Rain Monitoring Stations measured conductivity and the numerical calculation according to rainfall pH. From the Figure 1, measured conductivity were significantly greater than \(KH+KOH\). Except in 2007 March 28th, the rainfall sample does not conform to the rule; the rest of the samples conform to the K - pH inequality. The March 28 data may have some clear measurement errors that may originate from the pH value of measurement. As the rainfall pH value can reach 12.9, generally speaking the pH > 9 or less than 2 data can be eliminated, and therefore this sample was taken out. The quality of monitoring data is generally high and can be applied to chemical analysis of precipitation.

RESULTS AND DISCUSSION

Precipitation pH value

There were 39 cases of rainfalls and two cases of
snowfalls in 41 games due to wet deposition in Liaozhong station, with two snowfalls respectively occurring in March 3rd and 4th 2007. The rainfall season distribution is shown in Figure 2.

The rainfall of stations are mainly concentrated in July and August, in July, the highest rainfall was 180.4 mm, followed by August, was 81.2 mm, Precipitation mainly concentrated in summer and autumn season, less in winter or spring (Figure 2).

Figure 3 gives the changes in wet deposition of pH in Liaozhong station during the observation period. The pH range of Liaozhong station wet deposition change was large, the range was 3.4 to 7.34, the biggest difference was 4 pH unit, the rainfall weighted average mean was 4.76 and the acid was strong.

In the 41 effective samples collected in Liaozhong station, the rainfall pH less than 5.6 appeared 29 times, the non-acidic precipitation appeared 12 times, and the
frequency of acid rain was 70.7%. Of the 29 times rainfall in summer and autumn, 24 times were acidic, and the frequency of acid rain was 82.8%. The frequency of acid rain was relatively higher in summer and autumn; and was related to larger rainfall. The concentration of air particles and alkaline gaseous decreased because the continuous rain, the acid neutralizing capacity weakened.

According to the pH value of wet deposition, we can put forward three of the threshold value, respectively, 5.00, 5.60 and 4.50 (Zhang and Yang, 2009). The precipitation was divided into four classes by these three boundary value, namely the acidic precipitation, mild acidic precipitation, moderate acid rain and heavy acidic precipitation. Mild acidic precipitation appeared 8 times at a frequency of 19.5%; medium acidic precipitation appeared 6 times at a frequency of 14.6%; while heavy acidic precipitation appeared 15 times at a frequency of 36.6%. The frequency distribution of the pH value of Liaozhong wet deposition was shown in Figure 4.

Statistical analysis of observational data between February to August 2007 about Liaozhong stations rainfall pH value and Liaoning under comparison (Table 1 and Figure 5), pH average according to rainfall weighted average. Liaozhong station February - August pH weighted average was 4.75, this pH in Liaoning Provincial was medium low, the acidic level was stronger than non-coastal regions in Liaoning. According to the same period observation data, the average was 6.38 in Shenyang and comparatively closer to that of Liaozhong, the pH value was 6.44 in Qingyuan station which was the background station of Liaoning, but the pH value of Liaozhong was higher than that of coast Dandong station (4.19), which was about the same with Dalian (4.78). The pH level that was lower in the coastal station reflected the low concentration atmosphere alkaline particles and weak buffering capacity. In addition, Dimethyl sulphur (DMS) produced by the sea phytoplankton and zooplankton, became Sulfur dioxide as a result of product reaction with Hydroxyl (OH), then through homogeneous or out-of-phase reactions produced \( \text{SO}_4^{2-} \). These aerosol which are the condensate nuclear of cloud, have contributed to the rain natural acidity (Zhang and Yang, 2009). The pH of Liaozhong was closed with neighboring countries Korea and Japan, the average pH of 8 representative stations in Korean peninsula was 4.7, the pH of Japan was 4.8 (Bo, 2000; Hideaki et al., 2008).

**Concentration of the ions and composition of precipitation**

**Ion total concentration**

The ionic concentration of wet deposition (between February 2007 and January 2008) in Liaozhong station can be seen in Table 2. The weighted ion total
Table 1. Correlation coefficient of ion in Liaozhong station.

<table>
<thead>
<tr>
<th>Ion</th>
<th>H⁺</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻</td>
<td>1</td>
<td>0.897</td>
<td>0.72</td>
<td>0.731</td>
<td>0.925</td>
<td>0.818</td>
<td>0.591</td>
<td>0.454</td>
<td>0.777</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1</td>
<td>0.706</td>
<td>0.857</td>
<td>0.825</td>
<td>0.717</td>
<td>0.488</td>
<td>0.303</td>
<td>0.744</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F⁻</td>
<td>1</td>
<td>0.804</td>
<td>0.659</td>
<td>0.803</td>
<td>0.606</td>
<td>0.593</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1</td>
<td>0.617</td>
<td>0.866</td>
<td>0.5</td>
<td>0.624</td>
<td>0.791</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1</td>
<td>0.698</td>
<td>0.488</td>
<td>0.489</td>
<td>0.711</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1</td>
<td>0.442</td>
<td>0.59</td>
<td>0.844</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1</td>
<td>0.435</td>
<td>0.484</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>1</td>
<td>0.495</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Comparison of pH and ion concentration between Liaozhong station and other Liaoning stations.

Table 2. Change in ion concentration range of Liaozhong station (2007.2 - 2008.1) (μeq/L).

<table>
<thead>
<tr>
<th>Project</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>H⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>C+A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>862.23</td>
<td>497.21</td>
<td>53.16</td>
<td>191.94</td>
<td>394.95</td>
<td>653.77</td>
<td>919.50</td>
<td>422.50</td>
<td>345.22</td>
<td>57.95</td>
<td>3236.88</td>
</tr>
<tr>
<td>Minimum</td>
<td>14.58</td>
<td>1.61</td>
<td>1.40</td>
<td>7.89</td>
<td>0.05</td>
<td>2.22</td>
<td>1.00</td>
<td>1.61</td>
<td>6.52</td>
<td>1.41</td>
<td>82.11</td>
</tr>
<tr>
<td>Arithmetic mean</td>
<td>254.85</td>
<td>96.98</td>
<td>15.43</td>
<td>51.53</td>
<td>39</td>
<td>191.96</td>
<td>142.66</td>
<td>100.26</td>
<td>98.64</td>
<td>16.80</td>
<td>1008.11</td>
</tr>
<tr>
<td>Weighted average</td>
<td>162.77</td>
<td>56.62</td>
<td>11.26</td>
<td>38.48</td>
<td>38.67</td>
<td>126.96</td>
<td>84.15</td>
<td>60</td>
<td>66.53</td>
<td>12.68</td>
<td>658.14</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>37.52</td>
<td>14.89</td>
<td>2.19</td>
<td>6.82</td>
<td>6.08</td>
<td>29.63</td>
<td>22.12</td>
<td>15.41</td>
<td>14.39</td>
<td>2.4</td>
<td>144.62</td>
</tr>
</tbody>
</table>
Table 3. The concentration comparison of pH and ion between Liaozhong station and Liaoning other stations (2007.2-2007.8) – (unit: μeq/L).

<table>
<thead>
<tr>
<th>Project</th>
<th>pH</th>
<th>Σ Total ion</th>
<th>Σ Anionic</th>
<th>Σ Cationic</th>
<th>Σ Anionic / Σ Cationic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liaozhong</td>
<td>4.75</td>
<td>888.61</td>
<td>269.13</td>
<td>350.35</td>
<td>0.77</td>
</tr>
<tr>
<td>Shenyang</td>
<td>6.38</td>
<td>1496.77</td>
<td>543.47</td>
<td>409.83</td>
<td>1.33</td>
</tr>
<tr>
<td>Dandong</td>
<td>4.19</td>
<td>783.72</td>
<td>269.81</td>
<td>244.10</td>
<td>1.11</td>
</tr>
<tr>
<td>Dalian</td>
<td>4.78</td>
<td>987.46</td>
<td>364.14</td>
<td>259.18</td>
<td>1.40</td>
</tr>
<tr>
<td>Huludao</td>
<td>4.95</td>
<td>2405.04</td>
<td>841.82</td>
<td>721.40</td>
<td>1.17</td>
</tr>
<tr>
<td>Qingyuan County</td>
<td>6.44</td>
<td>358.47</td>
<td>102.72</td>
<td>153.03</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Figure 6. Annual change of the major ion concentration of Liaozhong station.

concentration was calculated by amount of rainfall. From the Table 2, it is known that during observation period, Liaozhong stations rainfall ion total concentration range change is larger, for 82.11 ~ 3236.88 μeq/L, the biggest difference was about 39.42 times. Compared ion concentration of Liaozhong station and other station (Table 1 and Figure 5), below the Shenyang station and Huludao station, closed to Dalian and Dandong which is located in the seaside, the low ions concentration in Liaozhong was related to small human activities impact. Qingyuan county is located in northeast of Liaoning Province, the ground was covered by the forest, there are less human activities, therefore ion total concentration was lowest.

Liaozhong station ion concentration showed significant seasonal variation (Table 3, Figures 6 and 7), all sorts of ion concentration, was higher in winter and spring, lower in summer and autumn. Ion total concentration changes and rainfall acidic pH change presented opposite tendencies, when ion total concentration was higher, acid was weak, acid was strong when ion total concentration was lower.

Ion composition

Figures 8 and 9 show that the cationic and anionic percentage composition, \( \text{SO}_4^{2-} \) are 61% of the total anionic anion, followed by \( \text{NO}_3^- \) that is 21%. The proportion of \( \text{NH}_4^+ \) was biggest in cationic, occupied 33 percent of the main cationic, followed by \( \text{Ca}^{2+} \) that was 22%, sodium was 17%. The ratio of \( \text{SO}_4^{2-} / \text{NO}_3^- \) was 2.9, less than 3.0, for sulfur denigration mixed acid rain. This was consistent with existing East Asia precipitation chemistry research results. The existing research thinks, East Asia precipitation chemical composition and major ionic components was cationic \( \text{Ca}^{2+} \) and \( \text{NH}_4^+ \), anionic \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \). There were more \( \text{Na}^+ \) and \( \text{Cl}^- \) in the main anion and cation in Coastal areas. Regarding acid rain areas, besides China southwest industrial underdeveloped areas that still experienced sulfuric acid type, other acid rain areas experienced sulfuric acid and nitric acid.
mixed (Ye et al., 2005; Huang et al., 2009).

The same ion concentration range change was larger in different screening precipitation, the concentration changes scope of $\text{Ca}^{2+}$ was biggest, which is $1 \sim 919.5$ μeq/L, followed by $\text{SO}_4^{2-}$ and $\text{NH}_4^+$, the concentration range change was $14.58 \sim 862.23$ μeq/L and $2.22 \sim 653.77$ μeq/L, respectively, standard deviation of the three were $22.12$ μeq/L, $37.52$ μeq/L and $29.63$ μeq/L, respectively, showing that the precipitation ion source was complex in this station. The rainfall chemical characteristics of Liaozhong was compared with other stations of Liaoning Province, and shown in Table 4 and Figure 9.

As with the table and figure, compared with Shenyang,
Figure 9. Ion concentration of Liaozhong station compared with other stations in Liaoning Province.

Table 4. The ion concentration of wet deposition in Liaozhong compared with other cities in Liaoning Province (2007.2 - 2007.8) (unit: μeq/L).

<table>
<thead>
<tr>
<th>Project</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>F$^-$</th>
<th>Cl$^-$</th>
<th>NH$_4^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>SO$_4^{2-}$/NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liaozhong</td>
<td>162.77</td>
<td>56.62</td>
<td>11.26</td>
<td>38.48</td>
<td>126.99</td>
<td>84.15</td>
<td>60</td>
<td>66.53</td>
<td>12.68</td>
<td>2.87</td>
</tr>
<tr>
<td>Shenyang</td>
<td>333.13</td>
<td>64.19</td>
<td>52.63</td>
<td>93.52</td>
<td>155</td>
<td>147.25</td>
<td>36.25</td>
<td>52.61</td>
<td>18.72</td>
<td>5.19</td>
</tr>
<tr>
<td>Dandong</td>
<td>176.04</td>
<td>37.10</td>
<td>15.26</td>
<td>41.41</td>
<td>51.11</td>
<td>98.75</td>
<td>30</td>
<td>47.83</td>
<td>16.41</td>
<td>3.59</td>
</tr>
<tr>
<td>Dalian</td>
<td>209.38</td>
<td>60.81</td>
<td>17.89</td>
<td>76.06</td>
<td>120.56</td>
<td>68.50</td>
<td>16.26</td>
<td>45.65</td>
<td>8.21</td>
<td>3.61</td>
</tr>
<tr>
<td>Huludao</td>
<td>445.83</td>
<td>100.65</td>
<td>34.21</td>
<td>261.13</td>
<td>202.22</td>
<td>206.50</td>
<td>37.08</td>
<td>83.04</td>
<td>192.56</td>
<td>4.18</td>
</tr>
<tr>
<td>Qingyuan County</td>
<td>65.83</td>
<td>19.35</td>
<td>6.84</td>
<td>10.70</td>
<td>43.33</td>
<td>58.25</td>
<td>10.00</td>
<td>14.78</td>
<td>26.67</td>
<td>3.40</td>
</tr>
</tbody>
</table>

anionic SO$_4^{2-}$, Cl$^-$ and F$^-$ were obviously lower, cation Mg$^{2+}$ and Na$^+$ were higher.

Relationship between concentration of anion, cation and pH

Precipitation acidity depends on ion composition of precipitation; pH value was not only related with acidic ion, but also related with the alkaline ions which played neutralisation in the rain. By this observation analysis, it showed that the correlation was complex, as displayed in:

1) The rainfall was not necessarily acidic when anionic/cationic was high: The ratio of $\sum$ anionic / $\sum$ cationic was 0.77 in the major ions monitored in Liaozhong station, namely anionic total concentration was far less than cationic total concentration, but acid is stronger, and the average pH value was 4.76. The pH value of Shenyang station and background station Qingyuan station was nearly the same, 6.38 and 6.44 respectively, but anion and cation concentration ratio had a big difference, the ratio of $\sum$ anionic / $\sum$ cationic values was 0.67 and 1.33 respectively. From 9 types of ion concentration analysed in this study, this situation was not reasonable. This shows that the atmosphere could be having other anion and cation interference. Some scholars believe that some organic acid, such as formic acid and acetic acid are likely to have such contribution. In American urban areas, the contribution of organic acid was 16 ~ 35% in precipitation free acidity. It may be that the main components build the precipitation acid.
(Stumm and Morgan, 1996). In order to explain the problem, we monitored all the samples of Liaozhong and Qingyuan in this research and did not detect formic acid and acetic acid (The Environmental Monitor Station of Liaoning, 2008). Visible, existing rain monitoring ion project cannot fully explain the acid and alkaline of precipitation. To explain the formation mechanism of acid rain, there is need to increase the project analysis of anion and cation.

2) The total ion concentration (pollution degree) and acid rain strength were not related: The total concentration of major ions tested in Liaozhong was 888.61 μeq/L lower than the Shenyang station (1496.77 μeq/L). The total concentration of Anion and cation were both far below the Shenyang station (Table 3). The weighted average of SO$_4^{2-}$ concentrations were 162.77 and 333.13 μeq/L, respectively, showing that the atmospheric pollution degree of Shenyang station is far higher than Liao Zhong, but Shenyang average pH was 6.38, acid rain appeared less. The precipitation during 1st to 21st August, 2007, only produced four times pH value lower than 5.6, the frequency of acid rain was 19%, including pH lower than 5.0 only once. The ion concentrations in several coastal zones representing stations in Liaoning were also lower, and the total ion concentration in Dandong and Dalian were 783.72 and 987.46 μeq/L.

It can be seen in the relationship between intensity of acid rain that atmospheric pollution degree was not obvious. The earliest established number (five) background station by America’s global precipitation chemistry research project (GPCP) was Sulzberger Frito (Poker flat, Alaska). George’s biological station (Bermuda), San Carlos (San Carlos, Venezuela), Catherine station (Australia), Amsterdam (little volcanic island in Indian Ocean, Southern hemisphere), the ions concentration of this 5 stations were very low, but their pH were significantly lower than 5.6, were 4.92, 4.96, 4.78, 4.81, 4.79, respectively (Stumm and Morgan, 1996). Consequently, it is not possible to judge regional air pollution degree and strength human impact by strength of acid rain.

Ion correlation and preliminary analysis of ion source

The relationship between various ions can explain the possible existence state of corresponding pollutant in the atmosphere before entering the deposition, some ion displayed good correlation due to the same or similar source. The correlation between various ions in Liaozhong station was shown in Table 1, with significant level valued at 0.01. It can be found in the correlation between mainly acid SO$_4^{2-}$, NO$_3^-$ and alkali neutralization that Ca$^{2+}$, NH$_4^+$ are very significant, and also stated that in the atmosphere, SO$_4^{2-}$ and NO$_3^-$ mainly in the form of (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, Ca(NO$_3$)$_2$, and CaSO$_4$, CaCl$_2$ are present before wet deposition.

NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ are mainly related with human activities. SO$_4^{2-}$ and NO$_3^-$ have a good correlation, because they have the same sources - coal combustion. In addition, Malone located in the countryside, station around land are farmland, quite a lot of research shows, pesticide and fertilizer is the main source of atmospheric nitrogen (Zhang et al., 2008). Liaozhong stations rainfall occurred mainly in summer crops growth season. Ammonium sulfate, ammonium nitrate etc N-fertilizer application and release, added into the atmosphere NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$. Ca$^{2+}$ while Mg$^{2+}$ mainly come from soil dust. Traditionally, people think Na$^+$ and Cl$^-$ mainly from sea; the ratio of Na$^+$ and Cl$^-$ in seawater is 0.86. During Observation period, the correlation between Na$^+$ and Cl$^-$ was significant, and the correlation coefficient r was 0.624, but the average of Na$^+$/Cl$^-$ was 1.73, far higher than the proportion in seawater (Khashman, 2005). Comparison of the concentration material of other acid rain areas representing stations in Liaoning Province shows that, the ratio of Na$^+$/Cl$^-$ more than 1 were Dandong (1.15), Qingyuan (1.38), the ion total concentration and SO$_4^{2-}$ concentrations was relatively low, air was relative cleaner and less affected by humans. Shenyang, Huludao Na$^+$/Cl$^-$ were far less than 0.86. The pollution in these two stations was relatively larger in Liaoning Province and the total ion concentration was higher. Xu Jianzhong’s research shows that Na$^+$/Cl$^-$ ratio is larger in the Arctic Circle (Xu et al., 2007). It also shows that the Cl$^-$ concentration in acid rain due to human sources of influence increased obviously, Na$^+$/Cl$^-$ ration is greater in man-made lighter pollution area.

Correlation between pH value of precipitation and air pollution in the near-face air

In order to explore the relationship between chemical composition of precipitation and local air pollution, while observing rainfall chemical characteristics executed in Liaozhong station, the air pollution concentration was monitored, the relationship between the two is shown in Figure 10.

pH and near ground NOx concentration had obvious inverse relationship, explaining why acidic gas NOx had obvious influence on the local pH. However, in pHs with another major acidic gas, SO2 near the ground surface concentration inverse relationship was not apparent. During the observation period, near ground SO$_2$ average concentration had only 0.012 mg/m$^3$, NOx average concentration for 0.050 mg/m$^3$, while in precipitation SO$_4^{2-}$ and NO$_3^-$ concentrations were 162.77 and 56.62 μeq/L, explaining why stations near the ground surface SO$_2$ have less influence on acid rain. The SO$_4^{2-}$ concentration and precipitation aerial long-distance transmission are connected. On the other hand, related with fertilizer of ammonium sulfate ion release. The
conveying study of Zhang et al. (2004) about pollution in North China shows that SO$_2$ concentration distributions and emission source distribution have a close relationship. However, SO$_4^{2-}$ quality concentration and emission source does not hold an obvious relationship. SO$_4^{2-}$ quality concentration are uniformly distributed, indicating that SO$_4^{2-}$ is mainly composed from SO$_2$ diffusion process in the atmosphere, consequently pollution emissions may affect regional SO$_4^{2-}$ quality concentration away from it. Comparison of the center of SO$_4^{2-}$ quality concentration value and position of heavy pollution, found that some center of SO$_4^{2-}$ quality concentration balanced value relative to grid of

Figure 10. The relationship between precipitation pH value and other air pollution in the near-surface ground.
heavy pollution center, and moved along the prevailing wind direction. The effect of the wind was the important factor that determined the concentration of \( \text{SO}_4^{2-} \). 30% of the adventive sulfur settlement of Beijing came from Tianjin and about 70% came from Hebei.

The inverse correlation between pH and other acidic gas CO and NO\(_2\) concentration near the ground surface was also obvious. pH and O\(_3\) also assumed certain inverse relationships. Consequently, the fact that O\(_3\) can be an oxidant prompted \( \text{SO}_2 \) shift to \( \text{H}_2\text{SO}_4 \), thereby reducing the pH.

pH and the concentration of surface PM\(_{10}\) showed positive correlation because the local and surrounding (except northeastern direction) soil is alkalescent, Ca\(^{2+}\) and Mg\(^{2+}\) in particulate played neutralize effect to acidic ion.

**Conclusion**

Statistical analysis of observational data about Acid rain in MaLong village, Liaozhong County and Liaoning Province from February 2007 to 2008 January shows that, Liaozhong stations rainfall become acidic, pH average for all samples were 4.76, acid rain occurred frequency for 70.7%, the frequency was 82.8% in summer and autumn. The chemical composition of precipitation anionic is mainly \( \text{SO}_4^{2-}, \text{NO}_3^- \), cationic mainly Ca\(^{2+}\), NH\(_4^+\), \( \text{SO}_4^{2-}/\text{NO}_3^- \) for 2.9; Na\(^+\)/Cl\(^-\), ratio is larger, more than 1. The change of total ion concentration and pH present opposite tendency, when there is higher total ion concentration, acidic is weak, when there is lower total ion concentration, acidic is strong. There is strong acid rain in the rainy season when precipitation is stronger and when there is a lack of precipitation in winter acid rain is weak. Measurement results for 9 kinds of main anion and cation total concentration \( \Sigma \) anionic / \( \Sigma \) cationic than with pH correlation is not high. This explains that the main anion and cation in current acid rain observation cannot completely include precipitation ions composition. Rainwater acidity and near floor air pollution concentration related differently, pH and NOx concentration had obvious inverse relationship while in \( \text{SO}_2 \) concentration, inverse relationship was not apparent. In pH and other acidic gas CO, NO\(_2\) concentration of inverse correlation was also more apparent, pH and O\(_3\) concentration represented certain inverse relationship. pH and alkaline pollutants such as particulate were inversely obvious.

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