Chemical Characteristics and Cause Analysis of Precipitation in the South of Liaodong Peninsula

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Abstract

Based on the acid rain observation data of 12 observation points from 2007 to 2009 in Dalian Environmental Monitoring Center and Dalian Meteorological Bureau, the paper analyzes the spatial and temporal distribution status of acid rain and the chemical characteristics of precipitation in the south of Liaodong Peninsula, makes an initial cause analysis, and does the Spearman rank correlation coefficient test of materials since 2004. The results show that, the frequency of acid rain shows a trend of significant increase while the pH value shows a clear downward trend, it has already been at medium level of acid rain. The equivalent concentration ratio of sulfate to nitrate ion in precipitation is 2.7. The acid rain is not entirely caused by the local pollutant emission but affected by a wide range of regional pollution. The enhancement of the acid rain is because that the control of pollutant emissions results in the decrease of neutralization of alkaline substances.

Keywords: Southern Liaoning; acid rain; Chemical Characteristics of precipitation; cause analysis; neutralization effect

1. Introduction

Studies show that the acid rain has significant impact and damages to the ecological environment and human economy and society\textsuperscript{[1]}. In 2001, the State Environmental Protection Administration set forth the control objective of the total S0\textsubscript{2} and acid rain and air quality in the two control zones during the 10th Five-Year Plan. The program had been approved to implement by the State Council on September 19th.
2002[2]. However, during the 10th Five-Year Plan, China's national economy continued to develop rapidly and energy consumption continued to grow, which was a huge challenge to realize the control objective of the total S02 emission in the two control zones. Meanwhile, the acid rain pollution resulted from the complex and synthetic effect. It is a systematic and long-term project to control the acid rain, needing to keep in-depth study of acid rain pollution. The studies of Zhao Yanxia and others[3] show that, from a national perspective, the scope of acid rain is widening and the hard-hit area of acid rain pollution is gradually shifting from the southwest to Middle China and the central south China. Another distinguishing feature is that the intensity of acid rain has been strengthening obviously in the north. The acid rain pollution in the north has also got attention and study [4-7]. Dalian is located in the south of the northeast region of China. In recent years, the acid rain has been standing out at a serious level.

2. Observation Points and Analysis Principle

Dalian Environmental Protection Bureau has 10 conventional precipitation observation sites and Meteorological Bureau has 2 acid rain monitoring sites (OBS, WFD2). The operation of sampling meets the technical specifications. Routine analysis items in the laboratory include: pH value of precipitation, conductivity, and 9 ion components. The methods of precipitation analysis all meet the standard number GB13580 and are through rigid quality control. The pH value, conductivity and the average concentration of ion precipitation are calculated by the weighted average method of precipitation; the number of acid rain samples divided by the percentage of the total samples of precipitation is the frequency of acid rain. The evaluation criteria for the local acid rain are: heavy acid rain region, pH≤4.50; medium acid rain region, 4.50<pH≤5.0; light acid rain region, 5.0<pH≤5.60 and non-acid rain region, pH>5.6. Before the analysis of the chemical characteristics of precipitation, make a comparison between the calculated value and the measured value of anion cation balance and conductivity to test the validity of the analysis results of the precipitation sample. Invalid data are excluded from the statistics. It is usually assumed that all Na⁺ in the precipitation are from sea salt. Deduct the contribution of sea salt in proportion based on Na⁺ on other ions, and then analyze the concentration of each ion.

\[
\gamma_s = \sqrt{\frac{1}{n^2 - 1} \left( \sum_{t=1}^{n} R_t - \frac{n+1}{2} \right)^2} \times \left( 1 - \frac{6 \sum_{t=1}^{n} (R_t - r_t)^2}{n^3 - n} \right)
\]

Years of trend analysis adopts Spearman rank correlation coefficient method(1). Make a comparison between the absolute value of rank correlation coefficient \(r_s\) and the threshold value in the statistical table of Spearman rank correlation coefficient to determine whether the correlation is of great significance.

3. Analysis of the Present Situation of Acid Rain

3.1. Analysis of the Spatial and Temporal Distribution

The data from Dalian Environmental Monitoring Center shows that acid rain monitoring in Dalian started in 1982; from 1983 to 1985, the acid rain fell 3 times; from October 1985 to June 2004, no acid rain fell. Since July 2004, two sites in the downtown monitored the acid rain (the corresponding land area of 58.65 km²). In 2005, six sites in the urban area monitored the acid rain (the corresponding land area of 2414.66 km²). By the end of 2008, except PLD point, the remaining sites all monitored the acid rain (the corresponding land area of 9803.65 km²). The acid rain expanded from the downtown area to the entire
city, the county-level cities and counties, indicating that the scope of the acid rain has been gradually expanding. Acid rain frequency in the city was over 20% in 2005 and 2006 and the mean pH value was between 5.0 and 5.6. From 2007 to 2009, 12 monitoring sites in Dalian obtained totally 1085 samples. After test in the laboratory, the acid rain frequency was 25.6%, 43.7% and 44.9% respectively, increasing year by year; the weighted annual average pH value was 4.82, 4.84 and 4.75 respectively, indicating that the intensity of the acid rain was increasing. The frequency of acid rain in urban area (composed by 5 sites of HSJ, OBS, SDJ, GJZ and LSH) was stable between 50% and 60% in the three years and the weighted annual average pH value was 4.49, 4.67 and 4.59 respectively. In the last three years, Dalian was the moderate acid rain pollution area and the acid rain pollution was more serious in the city than that in the suburban counties.

Among the 12 acid rain monitoring sites in Dalian, the acid rain was mainly in HSJ, OBS, SDJ sites in 2007 (see Figure 1). In 2008, the acid rain pollution increased significantly. Except PLD, the acid rain fell in nearly all the cities and counties of each district at different levels. In 2009, the acid rain increased greatly in LSH and CHH. From the mean pH value, HSJ, OBS, SDJ, LSH, JZH, WFD2 and CHH had reached the level of the moderate acid rain region. From the conductivity analysis, PLD always had the highest conductivity, indicating that there were many pollutants around the site. WFD, JZH and GJZ sites also had high conductivity. The general trend was the conductivity in Dalian city and even the whole region showed a declining trend, especially in the city. The intensified pollution control and clean air made the conductivity of precipitation decreased sharply and the neutralization effect of the alkaline pollution reduced.

From the seasonal distribution (Figure 2), the frequency of acid rain is of maximum in summer, followed by autumn, and minimum in winter. From the perspective of acidity, the precipitation in fall is the most acid and the pH value reaches 4.6. It is followed by summer and winter. From the perspective of
conductivity, the conductivity is maximum in winter and minimum in summer. It is highly pollution in winter in Dalian. Especially, it is the heating period in winter, resulting in the largest emissions of the acid-causing pollutant SO₂. Therefore, the acid rain is not entirely caused by the local pollutant emissions but affected by the large-scale regional pollution. From Distribution of Air Pollution Index from 2007 to 2009 (Figure omitted), NO₂ has little change throughout the year; SO₂ has greater variation, its pollution index reaches the peak in winter and the bottom between July and August. In other words, the air pollution laws in Dalian, especially the SO₂ and NO₂ pollution laws which are directly related to the formation of acid rain can not explain the status of acid rain in Dalian.

3.2. The Relationship with Precipitation

It is found in the observations of the acid rain that the precipitation acidity is different under different precipitations. The observed precipitations are divided into 5 levels (drizzle, 0.1 ≤ R <2; light rain, 2 ≤ R <10; moderate rain, 10 ≤ R <25; heavy rain, 25 ≤ R <50; rainstorm, R ≥ 50; unit: mm) (See Table 1). The average pH value is lowest in moderate and heavy rains. The highest frequency of acid rain occurs in rainstorm, followed by moderate and heavy rain. The strong acid rain process in which the pH value is below 4.5 has the highest proportion in heavy rain, followed by moderate rain. The above analysis shows that the acid rain is more frequent in the heavy rainfall and the acid-causing opportunities are more in the clouds than washing under the clouds. It is learned from the meteorological analysis that the heavy precipitation will occur only in case of sufficient water vapor that generally comes from the south China by the southerly airstream, so it can be primarily concluded that the outside sources contribute most to the local acid rain.

Table 1. pH and acid rain frequency at different precipitation levels in Dalian from 2007 to 2009

<table>
<thead>
<tr>
<th>item</th>
<th>drizzle</th>
<th>light rain</th>
<th>moderate rain</th>
<th>heavy rain</th>
<th>rainstorm</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>5.205</td>
<td>4.747</td>
<td>4.576</td>
<td>4.578</td>
<td>4.895</td>
</tr>
<tr>
<td>frequency of acid rain/%</td>
<td>41.67</td>
<td>54.55</td>
<td>62.58</td>
<td>58.57</td>
<td>69.7</td>
</tr>
<tr>
<td>probability of pH&lt;4.5/%</td>
<td>20</td>
<td>30.95</td>
<td>40.21</td>
<td>43.9</td>
<td>13.04</td>
</tr>
</tbody>
</table>

3.3. Chemical Analysis of Precipitation

From 2007 to 2009, there were total 347 valid samples of ion for analysis. Among the nine conventional ions for precipitation analysis, sulphate ion had the highest concentration in anions (See Table 2), it was followed by nitrate ion. Each ion in anions is in the following order: SO₄²⁻>NO₃⁻>Cl⁻>HCO₃⁻>F⁻. Calcium ion had the highest concentration in cations, it was followed by ammonium ion. Each ion in cations is in the following order: Ca²⁺>NH₄⁺>Na⁺>Mg²⁺>H⁺>K⁺. After deducting the influence of sea salt, the sum of sulphate and nitrate ions accounted for 85.9% of the total anions, the sum of calcium and ammonium ions accounted for 81.8% of the total cations.

Table 2. Concentration of Ions in the Precipitation in Dalian from 2007 to 2009 (Unit: µeq.L⁻¹)

<table>
<thead>
<tr>
<th>item</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean value</td>
<td>173.95</td>
<td>62.26</td>
<td>11.50</td>
<td>48.14</td>
<td>11.95</td>
<td>96.34</td>
<td>135.02</td>
<td>27.84</td>
<td>42.45</td>
<td>11.60</td>
<td>21.80</td>
</tr>
<tr>
<td>mean value</td>
<td>168.86</td>
<td>62.26</td>
<td>11.50</td>
<td>14.35</td>
<td>11.95</td>
<td>96.34</td>
<td>133.20</td>
<td>18.59</td>
<td>10.71</td>
<td>21.80</td>
<td></td>
</tr>
</tbody>
</table>
The ratio of sulphate to nitrate ion in precipitation decreased from 3.2 in 2007 to 2.55 in 2009 with an average of 2.7 which is lower than the national urban average value (4.8, see 2007 China Environmental Quality Report) indicating that nitrate makes higher contribution to the acid rain and is increasing year by year, which has much to do with the rapid growth of vehicle ownerships in the recent years in China and the increase of NOx in vehicle exhaust emissions year by year.

Table 3. Major ion comparison in acid rain and non-acid rain in Dalian from 2007 to 2009

<table>
<thead>
<tr>
<th>item</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$/NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>Ca$_{2+}$</th>
<th>Ca$_{2+}$ / (SO$_4^{2-}$ + NO$_3^-$)</th>
<th>(Ca$_{2+}$ + NH$_4^+$) / (SO$_4^{2-}$ + NO$_3^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid rain/µeq.L$^{-1}$</td>
<td>151.34</td>
<td>58.57</td>
<td>2.6</td>
<td>96.16</td>
<td>93.87</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Ratio%</td>
<td>31.7</td>
<td>12.3</td>
<td>—</td>
<td>20.1</td>
<td>19.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>non-acid rain/µeq.L$^{-1}$</td>
<td>199.23</td>
<td>68.66</td>
<td>2.9</td>
<td>103.28</td>
<td>203.53</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Ratio%</td>
<td>26.4</td>
<td>9.1</td>
<td>—</td>
<td>13.7</td>
<td>27.0</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

From Table 3, the biggest difference of the major ion components in acid rain and non-acid rain is reflected in the calcium ion. The concentration of calcium ion in the non-acid rain is much higher than that in the acid rain and the ratio of calcium ion to the main ion of anions is 0.8 (0.4 in the acid rain), indicating that calcium ion plays the foremost role of neutralization in the precipitation. When the proportion of calcium decreases, the acidity of precipitation will strengthen. Also, the ratio of sulphate to nitrate is 2.6, lower than 2.9 in the non-acid rain, so nitrate plays a very important role of acidification.

Fig.3. The contrast of the major ions in precipitation in the main sites (a) and acid rain frequency and pH value in 10 sites from 2004 to 2009(b)

See Figure 3a, the concentration of sulphate and calcium ion is significantly higher in GJZ, mainly because this site is located in the industrial zone and the local pollution is relatively heavy. The concentration of sulphate ion here is 2.4 times more than that in HSJ; calcium ion is 3.0 times more than that in HSJ; SO$_4^{2-}$/NO$_3^-$ is 3.9, far higher than that in other sites. But hydrogen ion in GJZ is the lowest, corresponding to the low frequency of acid rain, indicating that the contribution of the local pollution to acid rain is reflected in the neutralization effect.

3.4. The Variation Trend of the Acid Rain

See Figure 3b. The annual pH value of the precipitation in 10 sites for 6 years reduced from 5.24 to 4.84. Rank correlation test results $r_s = -0.943$, $|r_s| > W_p$ (0.829, 95% confidence level) indicate that the pH value decreases significantly. In addition, for the frequency of acid rain, rank correlation test results $r_s$,
= 0.943, \( r_s > W_p (0.829, 95\% \text{ confidence level}) \) indicate that the acid rain frequency increases significantly, so the development of acid rain pollution needs concern. From the variation of concentration of four major ions in the precipitation from 2004 to 2009, in 2006, the concentration of various ions was high and then decreased significantly. Compared with sulphate ion, calcium ion had a sharper drop after 2006, which is the direct cause of the continuous decrease of pH value. In recent years, \((\text{Ca}^{2+} + \text{NH}_4^+) / (\text{SO}_4^{2-} + \text{NO}_3^-)\) in the precipitation has showed a downward trend, which was consistent with the trend of the pH value. It further explains that the enhancement of the acid rain is due to the control of pollution emissions, resulting in the reduction of the neutralization of alkaline substances.

4. Conclusions

(1) Since 2004, the frequency of acid rain in southern Liaoning has been showing a significant upward trend and the pH value a clear downward trend. The acid rain pollution is more serious in the downtown than in the suburban counties. The south of Dalian has been at the moderate acid rain level and the north at the light acid rain level. It is the cleanest in summer, but the frequency of acid rain is the highest. The air pollution can not explain the status of the acid rain. The acid rain in Dalian is not entirely determined by the local pollutant emissions but affected by the large-scale regional pollution.

(2) Acid rain is more frequent in the heavy rainfall and the acid-causing opportunities are more in the clouds than washing under the clouds. The outside sources contribute more to the local acid rain.

(3) In the southern Liaoning, the acid rain pollution is still mainly the sulphuric acid. The equivalent concentration ratio of sulphate ion and nitrate ion is 2.7 in average, below the average value of the cities all over the country. Nitrate ion plays an important role of acidification.

(4) The concentration of calcium ion in the non-acid rain is much higher than that in the acid rain; the concentration of calcium ion has the sharpest drop, which is the direct reason for the continuous drop of the pH value in the precipitation. The enhancement of the acid rain in southern Liaoning is because that the control of pollutant emissions results in the decrease of neutralization of alkaline substances.

References


