Revista de Chimie
https://revistadechimie.ro
https://doi.org/10.37358/Rev. Chim.1949

Analysis on Change of Precipitation *p*H and Chemical Characteristics of Acid Rain in Liaoning Province (2007–2018)

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Abstract: *Acid rain, as one of the outputs of toxic and harmful chemicals from factories, is a serious environmental problem, especially in China, which has harmful ecological consequences and has a direct impact on vegetation and human health. Based on the data of acid rain observation station of Liaoning Meteorological Bureau from 2007 to 2018, the variation of precipitation pH and the distribution of acid rain in Liaoning Province in the past 12 years were analyzed. The result shows: First, the average pH value of annual precipitation in Liaoning Province is 5.55, which belongs to weak acid rain area. The frequency of acid rain is 12.56%, and the ratio of acid rain to total precipitation is 15.48%. More than 1/5 of the stations are located in the acid rain prone area, among which Dalian and Dandong are seriously polluted, being close to the grade of acid rain frequent area. Second, from 2007 to 2018, the precipitation pH in Liaoning Province fluctuated and increased year by year, with an average annual increase of 0.077 pH, and the pollution of acid rain decreased year by year; especially after 2014, Liaoning Province has exited from weak acid rain area, with its precipitation pH tending to be neutral year by year. Third, acid rain pollution in Liaoning Province is most serious in winter, followed by autumn and summer; in the first six years (2007-2012), the pollution in February was the most serious, and in the last six years (2013-2018), the pollution in December was the most serious, which was significantly worse than the previous six years. Fourth, more efforts have been made to control air pollution in all parts of the country, and the annual decrease in acid precursor emissions is the fundamental reason for the variation of precipitation pH and the improvement of acid rain pollution in Liaoning Province, while the precipitation pH and acid rain distribution in Liaoning Province are sensitive to the relevant environmental control measures taken by the state in recent years. However, the change of acid rain pollution reminds us to attach great importance to new pollution components and causes.*

Keywords: *Chemical Characteristics, Precipitation pH, Acid rain frequency, Pollution trend, Affected area*

1. Introduction

The acidity and alkalinity of atmospheric precipitation are expressed by pH, which is defined as the negative logarithm of hydrogen ion concentration, belong to the dimensionless quantity. Acid rain refers to the atmospheric precipitation with pH less than 5.60 [1-8]. Because the long-term acid precipitation will have a great adverse impact on ecological environment, building surface and human health, and even affect global changes, acid rain has become one of the three global atmospheric environmental problems in the world, and attracted much attention [9-20].

China has carried out acid rain monitoring and research for more than 40 years. In the early 1990s, China Environmental Protection Administration and China Meteorological Administration established acid rain monitoring websites in various provinces and regions, and joined the East Asia acid deposition monitoring network (EANET) through international cooperation [21, 22]. The spatial distribution of acid rain in China is mainly characterized by more acid rain in the south than in the north, more alkaline precipitation in the northwest, and more acid rain in the urban areas than in the

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Revista de Chimie
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https://doi.org/10.37358/Rev. Chim.1949

suburbs [23, 24]. From 1993 to 2007, the scope of acid rain area in China expanded to the north with the increased acidity, and the pollution area of acid rain in general showed an expanding trend [25]; the annual direct and indirect economic losses caused by acid rain and main acid gas reached up to hundreds of billion yuan [26].

In the past decade, the Chinese government and relevant departments have taken a series of targeted measures to reduce pollutant emissions and increase environmental pollution control. Since 2008, pollution emissions in various regions of China have been effectively controlled, and the impact scope and pollution intensity of acid rain have been reduced [27-30]. Based on the data of acid rain station network in Liaoning Province of China Meteorological Bureau, and the ecological environment monitoring data released by the environmental protection department, the spatio-temporal variation of precipitation *p*H in Liaoning Province from 2007 to 2018, and its characteristics and trends of acid rain pollution were analyzed in this paper. The purpose of the study is mainly discusses the macro factors affecting the *p*H variation in Liaoning Province, in order to provide more effective suggestions for acid rain monitoring, evaluation, prediction and pollution control in Liaoning Province.

2. Materials and methods

2.1. Data Sources

The data of acid rain from 2007 to 2018 come from the routine observation records of 22 monitoring stations in Liaoning meteorological acid rain station, including precipitation, precipitation pH, conductivity K value, wind direction, wind speed and weather phenomenon. All the acid rain observation projects are implemented in accordance with the "Operational Specification for Acid Rain Observation" issued by China Meteorological Administration, and the automatic precipitation sampling and analysis are consistent with the national standards and the relevant requirements of the World Meteorological Organization.

The acid rain observation in Liaoning Meteorological Bureau started in 1992, and 22 stations had been built by the beginning of 2007, and then the number of conventional stations had gradually increased to 60 in 2018, whose geographical locations are shown in Figure 1. In order to facilitate trend analysis and comparison for many years, this paper only discusses the records of 22 acid rain stations that have been continuously observed for 12 years.

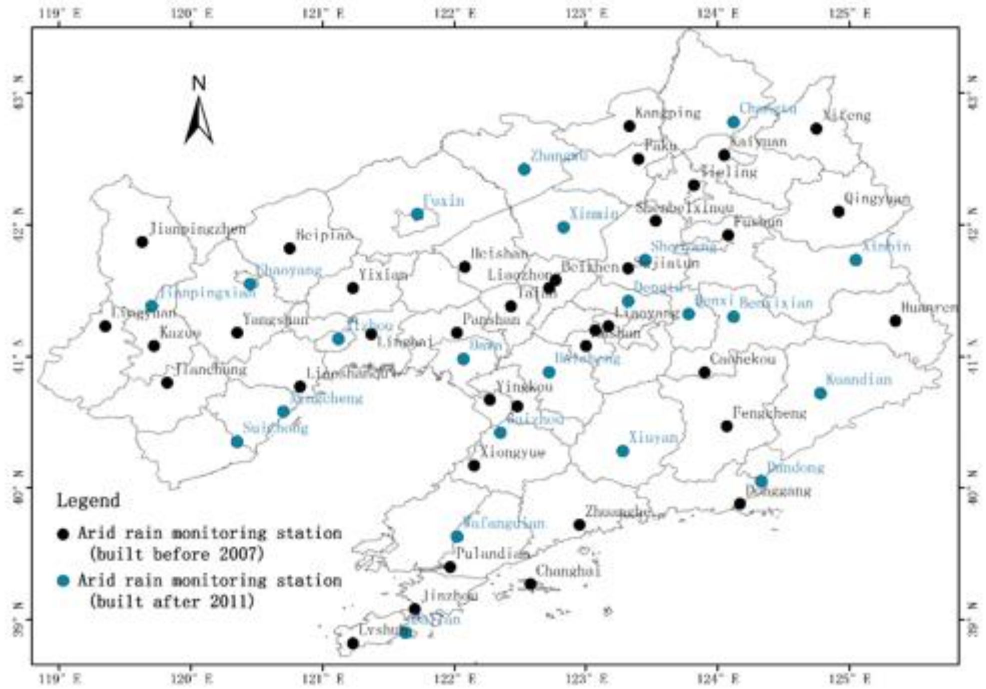


Figure 1. Location map of the meteorological acid rain monitoring stations in Liaoning Province

In this paper, except for special annotations, the data of air pollutant concentration in Liaoning Province are all from the bulletin of annual environmental conditions published on the website of Liaoning Provincial Department of Ecological Environment[31]; the content and release time of relevant policies and regulations are from the Internet and China government website[32].

2.2. Statistical method

According to the Operational Specification for Acid Rain Observation issued by China Meteorological Administration, the weighted average of precipitation is used to calculate the mean value of annual, seasonal and monthly precipitation *p*H and conductivity (commonly known as K value), and the calculation formula is as follows:

$$\mathrm{pH} = -\lg[H^+] = -\lg\left[\sum_1^n(10^{-pH_i} \times R_i) \Big/ \sum_1^n R_i\right] \quad (1)$$

$$\mathrm{K} = \sum_1^n K_i \times R_i \Big/ \sum_1^n R_i \quad (2)$$

In formula (1): pH_i=pH of the i-the precipitation; R_i=amount of precipitation;

In formula (2): K_i=K value of each precipitation; the conductivity K value represents the conductivity of atmospheric precipitation, which reflects the cleanliness of atmospheric precipitation, with the common unit of μS/cm.

The *p*H value of precipitation shall be conducted with statistics according to the following classification standards: Strong acid rain (*p*H<4. 5), weak acid rain (4. 5≤*p*H<5. 0), less weak acid rain (5. 0≤*p*H<5. 6) and non acid rain (5.6≤pH); non acid rain includes neutral precipitation (5. 6≤*p*H<7.0) and alkaline precipitation (7.0≤*p*H).

The evaluation of acid rain pollution area is divided by annual (or monthly, quarterly) average precipitation *p*H value, including three grades: lighter acid rain area (5.0 ≤ *p*H < 5.6), light acid rain area (4.5 ≤ *p*H < 5.0) and heavy acid rain area (*p*H < 4.5).

The calculation formula of acid rain frequency in different degrees is as follows:

$$F=n/N\times100\% \quad (3)$$

where, F represents the acid rain frequency in corresponding degree, n and N respectively represent the number of acid rain in corresponding degree and the total number of precipitation in the calculation period. The acid rain pollution frequency is divided by acid rain frequency, including five grades: occasionally occurred acid rain (F ≤5%), rarely occurred acid rain (5% ＜ F ≤20%), pronely occurred acid rain (20% ＜ F ≤ 50%), frequently occurred acid rain (50% ＜ F≤80%), and highly occurred acid rain (F＞ 80%).

Except for special annotations, the *p*H and K average values of all provinces in the following are the weighted average of rainfall of the measured values in the selected 22 stations.

2.3. Quality control of observation data

The *K-pH* inequality method[33] is used to eliminate the unreasonable data in the statistical analysis of acid rain observation records. From January 2007 to December 2018, there were 23,718 observation records (station-times), among which there were 8,913 station-times without pH measurement due to the precipitation less than 1.0 mm, and 8 unreasonable samples (accounting for 0.05% of total samples) were eliminated by *K-pH* inequality method, while 46 data samples without K value measurement (0.31% of total samples) were eliminated, with the valid data samples of 14,687 station-times (about 668 times/station). The total precipitation of 54 samples was 500.9 mm (0.29% of the total precipitation).

3. Results and discussions

3.1. *p*H Distribution Probability and Acid Rain Frequency

In order to investigate the *p*H property and grade of precipitation in Liaoning Province from 2007 to 2018, the probability distribution of daily *p*H value of all precipitation in 22 acid rain monitoring stations is calculated. The results show that the 12-year average probability of occurrence for 5.0 ≤ *p*H < 7.5 is more than 90%, with its annual change increasing year by year, from 76.46% in 2007 to 96.55% in 2018. Among them, the occurrence probability of 6.0 ≤ *p*H < 7.0 is the most, accounting for about half or even nearly 3 / 4 of the observation times in each year, followed by the occurrence probability of 5.0 ≤ *p*H < 6.0 and 7.0 ≤ *p*H < 8.0, accounting for about 20%. Some statistical results of 22 acid rain observation stations are shown in Table 1.

Table 1. Precipitation *p*H statistics and acid rain frequency in various stations in Liaoning Province from 2007 to 2018.

Acid rain observatory*	*pH*				*Frequency(%)*					Frequency of acid rain(%)
	F>80% interval	*Min*	*Max*	*Average*	*3.0≤pH<4.5*	*4.5≤pH<5.0*	*5.0≤pH<5.6*	*5.6≤pH<7.0*	*pH≥7.0*	
Dalain(DL)	4.5-6.5	3.21	7.74	4.86	9.16	15.37	24.87	26.42	1.56	49.40
Dandong(DD)	4.5-6.5	3.71	7.36	5.08	6.74	13.36	23.41	30.53	1.27	43.51
Wafangdian(WFD)	5.0-7.0	3.28	7.71	5.33	3.24	7.46	20.91	44.09	1.78	31.61
Kuandian(KD)	5.0-7.0	4.18	7.59	5.49	0.55	4.11	26.19	45.29	4.66	30.85
Benxixian(BXX)	5.0-7.5	3.53	8.52	5.26	4.01	6.06	10.30	40.50	26.09	20.37
Dawa(DW)	5.6-7.0	4.31	8.86	5.84	0.65	1.31	5.06	67.05	7.83	7.02
Suizhong(SZ)	5.6-7.0	4.59	7.34	6.02	0.00	1.07	5.71	61.78	1.25	6.78
Changtu(CT)	5.6-7.5	3.95	9.09	5.74	0.79	1.59	7.53	42.41	29.06	9.91
Fuxin(FX)	5.6-7.5	3.61	9.34	5.42	2.48	2.67	6.87	51.71	27	12.02
Zhangwu(ZW)	5.6-7.5	3.70	8.85	5.62	0.36	1.60	9.22	57.8	19.32	11.18
Shenyang(SY)	6.0-7.0	4.72	8.30	6.14	0.00	0.67	1.62	85.33	9.14	2.29
Xinmin(XM)	6.0-7.0	5.17	8.01	6.35	0.00	0.00	0.16	96.78	1.93	0.16
Xingcheng(XC)	6.0-7.0	3.85	7.32	5.86	0.42	3.81	2.33	85.63	0.85	6.56
Jinzhou(JZ)	6.0-7.0	5.19	7.79	6.57	0.00	0.00	0.36	88.89	10.2	0.36
Benxi(BX)	6.0-7.5	4.13	8.64	5.91	0.47	0.94	1.64	58.97	32.93	3.05
Xinbin(XB)	6.0-7.5	4.03	7.83	5.84	0.64	2.77	4.79	63.83	20.85	8.20
Dengta(DT)	6.0-7.5	4.15	7.84	6.14	0.47	0.94	1.64	58.97	32.93	3.05
Xiuyan(XY)	6.0-7.5	3.30	8.50	5.90	0.56	0.98	1.26	71.63	24.02	2.80
Haicheng(HC)	6.0-8.0	3.44	9.74	6.37	0.16	0.00	1.09	66.57	26.1	1.25
Gaizhou(GZ)	6.0-8.0	4.26	8.82	5.73	0.94	1.42	3.15	56.06	32.44	5.51
Chaoyang(CY)	6.0-8.0	4.16	8.36	6.04	0.39	0.77	6.55	47.01	40.47	7.71
Jianpingxian(JPX)	6.0-8.0	5.13	9.77	6.43	0.00	0.00	1.47	37.2	59.12	1.47

*The letters in parentheses are short for station names

As shown in Table 1, the precipitation *p*H in the whole province has large fluctuation range, with the minimum *p*H value of 3.21, and the maximum pH value of 9.77. The stations most seriously affected by acid rain (in order of severity) are DL, DD, WFD, KD, and BXX, with their 12-year average *p*H values of 4.86, 5.08, 5.33, 5.49 and 5.26, respectively. And the average annual acid rain frequency of those stations is respectively 49.40, 43.51, 31.61, 30.85, and 20.37%, all of which belong to acid rain prone areas, with their precipitation frequency with *p*H < 5.0 of 24.53%, 20.10, 10.70, 4.66, and 10.07%, respectively. Thus it is no less than that of Beijing, Tianjin and Hebei in North China and parts of South China with serious acid rain pollution [28, 33]. The nine stations of ZW, FX, CT, XB, DW, CY, SZ, XC, and GZ belong to the grade of less acid rain area. In which the pH value of annual precipitation in FX is 5.42, belonging to the grade of light acid rain area; the eight stations of BX, DT, SY, XY, JPX, HC, JZ and XM with acid rain frequency of F <5% belong to the grade of occasional acid rain area [33-44].

It also can be seen from Table 1 that in the 22 observation stations of the whole province, there are 17 stations that the number of non-acid precipitation days is more than 80% of the total precipitation days. However, about half of the stations have experienced super acid rain (pH < 4.0), and the 12-year average precipitation pH is less than 5.60, which is close to 1/3 of the whole province, thus the situation of acid rain pollution in Liaoning Province is still worthy of attention.

3.2. Inter-annual Variation of pH And Distribution of Acid Rain

The provincial average value and provincial annual average of each parameter are calculated by the method of weighted average of precipitation of the 22 stations. The statistical results show that the average precipitation pH value in 2007-2018 was 5.55, belonging to the grade of light acid rain pollution area; the conductivity K value was 73.03μS/cm, indicating that there are many pollutants in the atmospheric precipitation in Liaoning Province, resulting in poor air quality [33]. Figure 2 shows the change and trend curves of average pH and K value and acid rain frequency in Liaoning Province from 2007 to 2018.

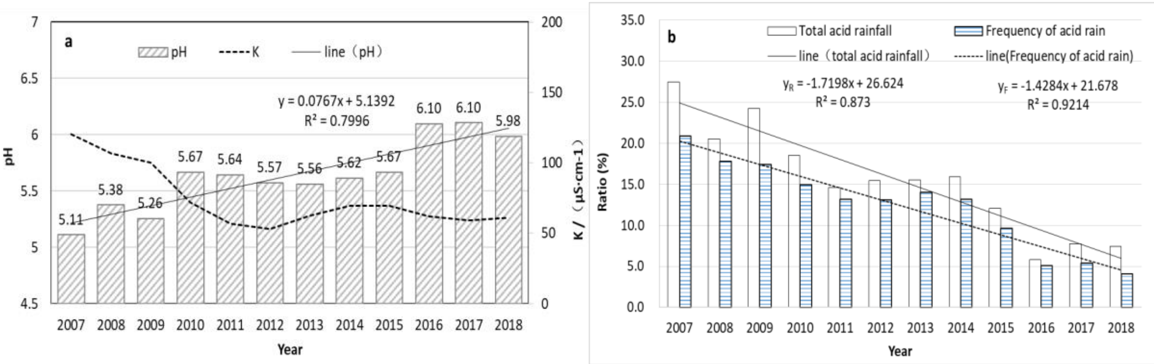
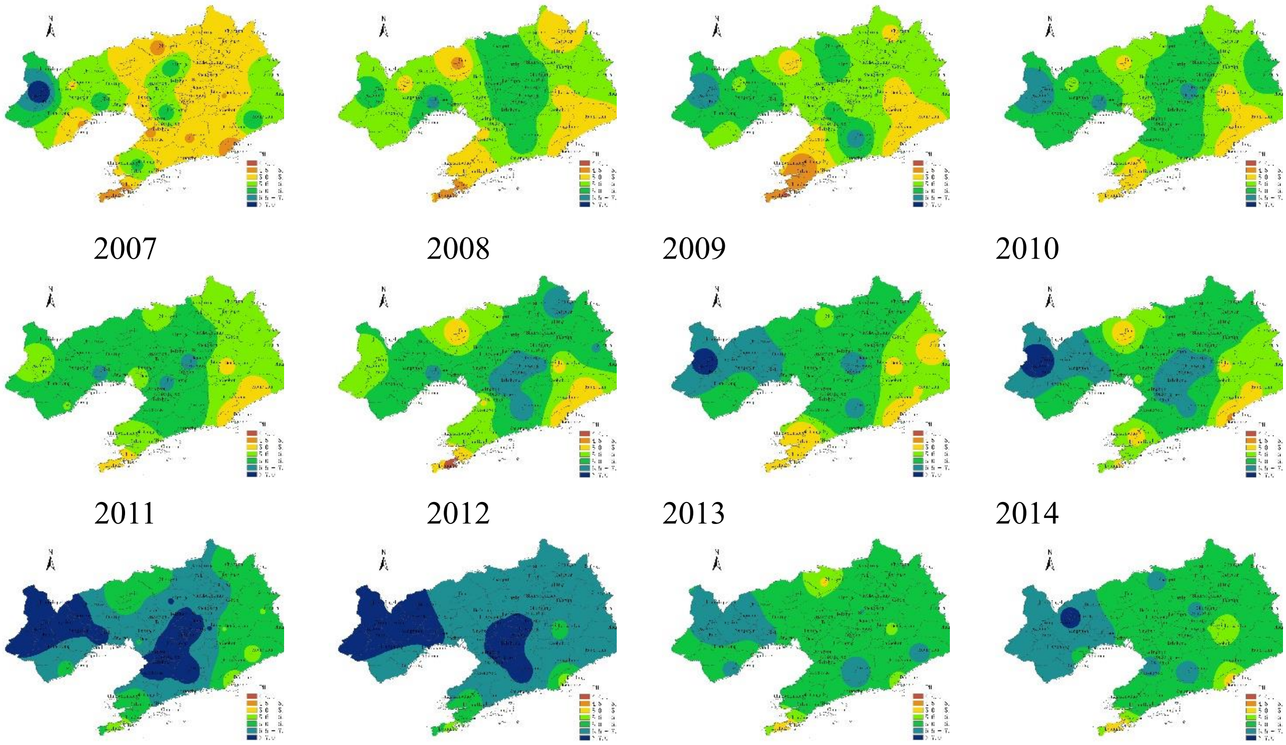


Figure 2. Annual variation of average pH value(a) and frequency of acid rainfall(b) in the province

As shown in Figure 2(a), the average pH value of precipitation in the whole province was 5.11 in 2007, followed by 5.26 in 2009, and then 5.38 in 2008, 5.57 in 2012 and 5.56 in 2013. Liaoning Province was in the light acid rain pollution area in the above five years and belonged to the non-acid rain area in the rest years. From the overall trend analysis, the annual change of average precipitation pH in the whole province shows a linear increasing trend year by year with the annual increase of about 0.077 pH, whose linear fitting degree is R^2 = 0.7996. The annual change of K value is the opposite. In 2007, the maximum K value was 120.18 μS/cm, and then decreased to 53.15 μS/cm, but it slightly rose again to 69.76μS/cm in 2013-2015, and fluctuated around 60 μS/cm in 2016-2018. In general, the annual K values of precipitation conductivity in Liaoning Province are all greater than 50 μS/cm, indicating the poor precipitation cleanliness [34, 45-47].

It can be seen from Figure 2(b) that in 2007, acid rain accounted for the highest proportion of total rainfall, about 27.49%, followed by 24.20% in 2009, with the lowest proportion of 5.83% in 2016. From 2007 to 2018, the annual variation of acid rain frequency and acid rain amount in the whole province showed a fluctuating and decreasing trend. And the proportion of acid rain in total rainfall decreased at a rate of 1.72% per year, with a linear fitting degree of R^2 = 0.873. While the proportion of acid rain frequency decreased at a rate of 1.43% per year, with a linear fitting degree of R^2= 0.921.

In order to have a clear understanding of the spatial distribution of precipitation pH value in Liaoning Province from 2007 to 2018, the spatial distribution of weighted average pH value of precipitation at 22 stations in each year is drawn by the method of calculating grid interpolation based on the weighted average of the distance between longitude and latitude of three adjacent stations, as shown in Figure 3.



2007 2008 2009 2010

2011 2012 2013 2014

2015 2016 2017 2018

Figure 3. Spatial distribution of annual *p*H value of precipitation in Liaoning Province from 2007 to 2018

It can be seen from Figure 3 and Table 1 that the impact range of acid rain in Liaoning Province has a trend of year-on-year fluctuation and reduction. In 2007, acid rain had the largest impact range, with 72.73% of stations having an average annual precipitation *p*H value less than 5.60; among them, 31.82% of stations have an average annual precipitation *p*H value less than 5.0, reaching the pollution grade of weak acid rain or even strong acid rain. In 2008, the area affected by acid rain in the whole province was reduced to 40.91% significantly, among which the stations reaching and exceeding the pollution level of weak acid rain are reduced to 9.09%. By 2011, the area affected by acid rain was decreased to 18.18%, and there was no station with annual precipitation *p*H reaching and exceeding the pollution grade of weak acid rain. In 2012, the area affected by acid rain had been slightly increasing to 2014, and the stations with annual average precipitation *p*H reaching acid rain grade had been kept in the range of 27.27%; after 2010-2015, the impact scope of acid rain has been further reduced, and the pollution intensity of acid rain has also been reduced significantly.

3.3. Seasonal Variation of pH and Characteristics of Acid Rain Pollution

In order to visually compare the seasonal variation of precipitation *p*H value and the characteristics of acid rain pollution in Liaoning Province, the spatial contour distribution of precipitation *p*H value and conductivity K value in each season of Liaoning Province from 2007 to 2018 is plotted in Figure 4.

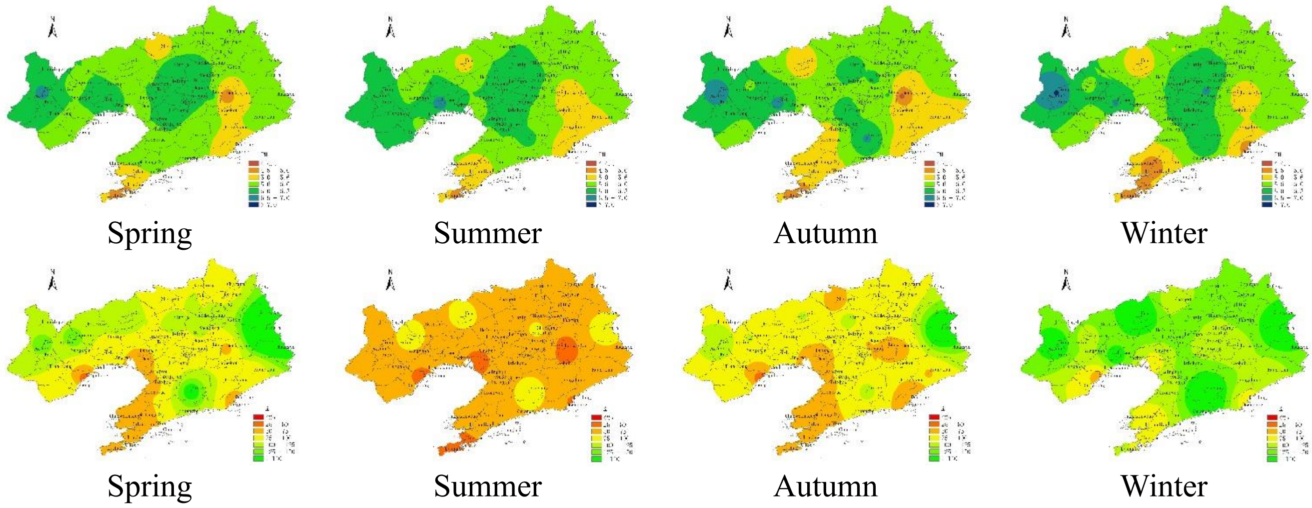


Figure 4. Seasonal average spatial distribution of precipitation pH (up) and conductivity K value (blow)in Liaoning Province from 2007 to 2018

As shown in Figure 4, the acid rain pollution in Liaoning Province from 2007 to 2018 was the most serious in winter, followed by autumn and the lightest in summer; the precipitation cleanness was the best in summer, followed by autumn and the worst in winter. This result is obviously different from the distribution characteristics of the most serious acid rain pollution in summer of Liaoning Province from 2004 to 2008, which shows that the variation of *p*H value in Liaoning Province in recent 10 years is not only reflected in the pollution intensity, but also in the distribution of time and space.

The further analysis on monthly variation of precipitation *p*H in Liaoning is helpful to understand the factors affecting the variation and explore the sources of pollution. According to statistics, the monthly change characteristics of acid rain pollution in 2013-2018 are obviously different from that in 2007-2012. In order to facilitate analysis and comparison, 2007-2012 (hereinafter referred to as: the previous 6 years) and 2013-2018 (hereinafter referred to as the following: 6 years) is divided into two stages, and the monthly changes of precipitation *p*H and acid rain frequency are counted and plotted in Figure 5 respectively.

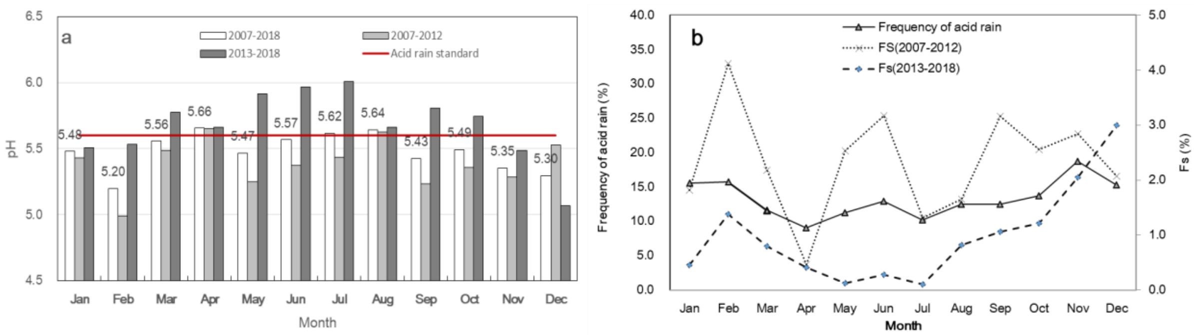


Figure 5. Monthly variation of average *p*H value (a) and of acid rain characteristic value (b) in the province

As shown in Figure 5(a), in the first six years, the minimum *p*H value appeared in February, followed by September and May; April and August with *p*H value more than 5.60 belonged to the non-acid rain, and the rest ten months belonged to the weak acid rain. In the second six years, the minimum pH value appeared in December, which was significantly lower than the value of the same period in the first six years; the *p*H values in the rest eleven months were all greater than the average of the same period in the first six years. The months reaching the grade of weak acid rain are January, February, November and December, which is 6 months less than the first six years. According to the monthly variation of acid rain characteristic quantity in the whole province (Figure 5(b)), the number of acid rain days is the most in June, with an annual average of 23.8 station-times, followed by 22.8 station-times in August. The months with few acid rain days are January, February, March, December and April, respectively as 4.3, 6.3, 6.4, 6.7, and 8.5 station-times. However, the month with high frequency of acid rain does not appear in the month with more acid rain days, and the highest frequency of acid rain in November is 18.75%, followed by February and December, which are 15.70 and 15.30%, respectively, while the lowest frequency of acid rain in April is 9.03%.

There are different characteristics in the monthly variation of strong acid rain frequency between the first six years and the second six years. In the first six years, the frequency of strong acid rain showed the multimodal fluctuation, with the highest frequency of 4.12% in February, followed by 3.17% in June and 3.16% in September, and the lowest frequency of 0.47% in April. In the second six years, the monthly variation of the frequency of strong acid rain basically showed the bimodal arrangement, with the maximum peak value of 2.99% in December, which increased by 0.91 percentage points compared with the same period of the first six years. The second peak occurred in February with the frequency of 1.38%, which was less than the frequency of strong acid rain in November. In general, the frequency of strong acid rain from January to November in the second six years was lower than that in the first six years, and only the frequency in December was higher than that in the first six years.

3.4. Variation characteristics of precipitation ion composition

The pH value of precipitation depends on the ionic composition of precipitation, not only related to the concentration of acid ions, but also related to the basic ions that can neutralize acid ions. According to the detection data of precipitation ion components of Liaoning Environmental Monitoring and Experiment Center in different years, the change trend of precipitation acidity and composition in Liaoning Province in recent years was analyzed. By revealing the reasons for its changes, we can deepen our understanding of the characteristics of atmospheric precipitation pollution in this area and the impact of human activities, and further analyze and determine the sources of pollutants in precipitation. Tables 2 and 3 give the respective ion concentrations and their proportions of precipitation in different years in Liaoning Province (Table 3 from cological Environment Bulletin of Liaoning Province in 2018).

Table 2. Ions compositions of precipitation at different locations in Liaoning Province (μeq/l)

Location	Year	SO_4^{-2}	NO_3^-	Cl^-	F^-	NH_4^+	Ca^{+2}	Mg^{+2}	Na^+	K^+	$[SO_4^{-2}]/[NO_3^-]$	literature
Liaoning (13 stations)	1991 -1995	509.7	56.4	83.5	-	127.8	692.1	188.7	91.7	35.6	9.04	16
DL	1991 -1995	517.8	63.5	92.9	-	164.5	968.1	123.8	52.6	162.7	8.15	16
DL	2007	212.8	62.99	72.05	16.95	127.14	139.61	32.81	41.00	8.15	3.38	17
SY	1991 -1995	984.0	102.1	132.2	-	205.4	1369.2	486.2	64.5	130.2	9.64	16
SY	2007	352.42	61.3	83.14	56.2	171.82	307.66	67.69	42.86	17.28	5.75	17
JZ	2007	97.04	21.89	39.72	0.48	3.42	37.19	13.44	36.14	1.82	4.43	18
JZ	2013	20.30	9.31	9.86	0.60	5.00	7.66	8.92	10.12	18.48	2.18	18
Liaoning (13 stations)	2007	371.16	45.11	114.68	19.63	103.90	210.05	56.28	37.47	52.30	8.23	17
Liaoning (13 stations)	2009	104.72-795.30	11.90-244.44			42.88-281.73	41.22-693.41	22.41-249.37			3.9	19
Liaoning (62 stations) (mg/L)	2011 -2015	11.00-15.21	3.58-7.19	1.93-3.57	0.24-0.36	1.50-2.47	3.79-5.43	-	-	-	3.3	20

It can be seen from Table 2 that the main cation of precipitation ions in Liaoning Province is Ca^{+2}, followed by Mg^{+2} and NH_4^+; the main anion is SO_4^{-2}, followed by NO_3^- and Cl^-.The total ion concentration in precipitation in Liaoning Province is very high, especially in the 1990s and early 2000s. The economic pillars of major cities in Liaoning, known as "China's old industrial base", are dominated by heavy industry. Due to lack of technology and backward plant equipment, the factory has not effectively purified and reduced pollutants before pollutant discharge. Since the early 2010s, the emission of sulfur dioxide and nitrogen oxides has decreased, and the level of pollution has fallen sharply due to the government's effective control measures. In recent years, the ratio of SO_4^{-2} to NO_3^- has decreased year by year, indicating that the precipitation pollution has changed from sulfuric acid type to mixed type of sulfuric acid + nitric acid or even sulfuric acid + nitric acid + hydrochloric acid. The average annual concentration order of water-soluble inorganic ions in precipitation in the 1990s is: $Ca^{+2}>SO_4^{-2}>NH_4^+>Mg^{+2}>Na^+>Cl^->NO_3^->K^+$. The average annual concentration order of water-soluble inorganic ions in precipitation in the 2010s is: $SO_4^{-2}>Ca^{+2}>Cl^-> NH_4^+>Mg^{+2}>K^+> NO_3^->Na^+$.

Table 3. Proportion of ions in precipitation in Liaoning Province(%).

Year	SO_4^{-2}	NO_3^-	Cl^-	F^-	NH_4^+	Ca^{+2}	Mg^{+2}	Na^+	K^+	∑Cation	∑Anion	literature
2009	30.8	7.9	6.6	1.8	13.7	23.8	8.1	5.5	1.8	52.9	47.1	19
2011-2015	29.4	8.8		1.6	11.1	26.5			2.4			20
2018	21.4	6.7	9.3	1.7	12.3	30.8	8.8	7.0	2.0	60.9	39.1	
Range of change(%)	-30.52	-15.19	40.91	-5.56	-10.22	29.41	8.64	27.27	11.11	15.12	-16.99	

Compared with the difference in the proportions of major ion components in the precipitation in 2018 and 2009, it is not difficult to find that the proportions of SO_4^{2-}, NO_3^- and F^- in the anions have been reduced in varying degrees, while the proportion of Cl^- has been significantly increased. At the same time, compared with the proportion variations of Na^+, Mg^{2+} and K^+ as the cation of crustal elements, the total increase of Na^+ and K^+ is equivalent to the increase of Cl^-. In the free atmosphere, sodium (potassium) ions and chloride ions can combine to form NaCl (KCl), that is, $Na^++ Cl^- \rightarrow NaCl$ ($K^++ Cl^- \rightarrow KCl$). The main components of sea salt are NaCl and KCl, which It can be inferred that the influence of sea salt composition on atmospheric precipitation in Liaoning Province has increased significantly in recent years. There are also $Ca^{+2} + 2\ Cl^- \rightarrow CaCl_2$ and $Mg^{+2} + 2\ Cl^- \rightarrow MgCl_2$. Thinking further, we will ask a question. Why is Shenyang, an inland city far from the ocean, the chloride ion content of its precipitation higher than Dalian, a coastal city? In fact, $CaCl_2 + MgCl_2 +KCl$ is the main component of the snow remover. From here, we think of the situation in which snow removal agents are often used by people in Liaoning during the winter.

Although snow trucks have been used to remove snow in large urban streets in recent years, relatively low-cost snow removers are still used in small areas and economically backward areas. Reflected in atmospheric precipitation shows that in inland cities like Shenyang, sea salt has gradually become the main ionic component. KCl is the main component of the snow remover, so it is associated with the use of snow removers by people in Liaoning during the winter snowfall. Although in recent years, snow trucks have been used to remove snow in large urban streets, but because of cost inexpensive relatively, snow removal agent is still used in some small places and economically backward regions. The ensuing phenomenon will appear in the atmospheric precipitation of inland cities, and the composition of sea salt ions is higher than that of coastal cities. Of course, the final conclusion needs further observation, analysis and verification [48-58].

The causes for the variation of precipitation *p*H are very complex, including the effects of atmospheric composition, particulate matter and meteorological factors. On source investigation, the influence of the concentration of sulfur dioxide and nitrogen oxides on the pH value is the basic reason for the formation of acid rain. The annual and monthly variations of air pollutant concentration in Liaoning Province in recent years are shown in Figure 6.

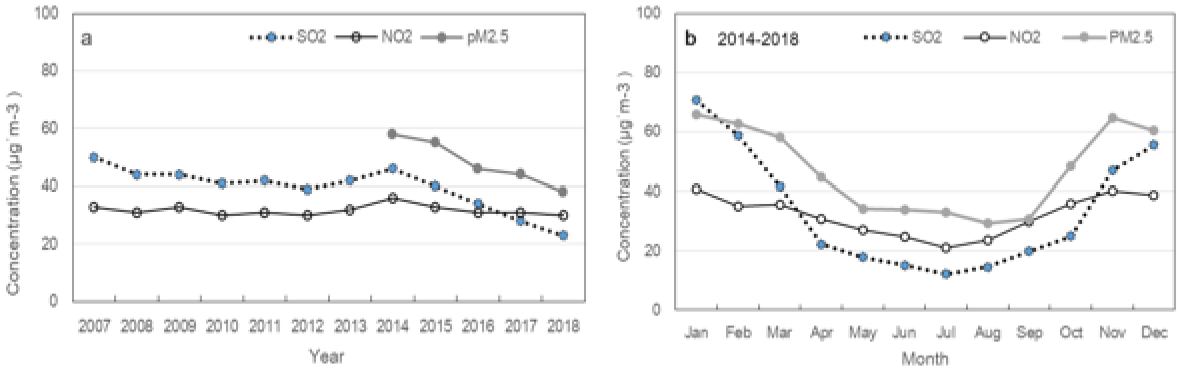


Figure 6. Annual changes(a) and monthly changes from 2014 to 2018 (b) of atmospheric pollutant concentrations in Liaoning Province

As shown in Figure 6(a), after 2014, the SO_2 and NO_2 concentrations of the acid rain precursors in the atmosphere of Liaoning Province decreased in varying degrees, especially SO_2 and $PM_{2.5}$ decreased significantly. However, NO_2 concentration has exceeded SO_2 concentration in the last two years (2017 and 2018), which was contrary to the state in the past ten years that NO_2 concentration was always lower than SO_2 concentration. The monthly variations of the concentrations of various pollutants in Liaoning Province from 2014 to 2018 are shown in Figure 6(b). It indicates that the difference between the heating season (January to March and November to December) and non heating season (April to October) is very obvious, and the SO_2 concentration in the heating season is 2-4 times higher than that in the non-heating season, and significantly higher than the NO_2 concentration in the same period. The SO_2 concentration in the non-heating season is significantly lower than the NO_2 concentration.

It can be seen from Figure 6(a) and Figure 2(a) that in recent 12 years, the annual variation of SO_2 and NO_2 concentrations in Liaoning Province has been reverse consistent with the annual variation trend of precipitation *p*H value. The concentrations of SO_2 and NO_2 are generally decreasing year by year, while the variation trend of *p*H value is increasing year by year. However, the variation of precipitation *p*H in Liaoning Province is not only affected by local pollution sources, but also by some external sources, so there is no fully synchronous correlation in its variation ranges. By further exploring the detailed characteristics of the inter-annual variation of precipitation *p*H in Figure 2(a), it is found that each year with a large variation range of *p*H value is closely related to the time nodes for implementing the major national initiatives in atmospheric environmental governance in recent years [59-61].

First, the success of Beijing Olympic Games in 2008 had greatly promoted the comprehensive treatment of environmental pollution by the government and relevant departments. Then with the obvious improvement of national air quality, the annual average *p*H value of precipitation in Liaoning Province in 2008 increased by 0.27 than that in 2007, which was 3.5 times of annual average increment. In 2010, the average *p*H value of precipitation in Liaoning Province increased by 0.41, which was 4.3 times higher than that in 2009, and the pollution intensity of acid rain in this year was reduced significantly, thus Liaoning Province had changed from the lighter acid rain area to the non-acid rain area. The administrative measures closely related to this change are as follows. The "*key points of national pollution prevention and control in 2009-2010*" and the "*guidance on promoting joint prevention and control of air pollution to improve regional air quality*" respectively launched in March 2009 and May 2010 by the Ministry of Environment Protection [60-68].

Further strengthen the prevention and control of key pollutants, including the measures of strengthening the total sulfur dioxide control system and strengthening the NOx pollution reduction. From 2010 to 2015, the average *p*H value of precipitation in Liaoning Province remained stable at 5.60. Since May 2015, the state has launched a series of measures such as the "*overall plan for the reform of ecological civilization system*" and the "*pilot plan for the reform of ecological environment* *damage compensation system*". Then Liaoning Province, like the whole country, has carried out key projects such as blue sky and clear water, with the focus on solving outstanding environmental problems, thus it makes the environmental quality in 2016 show the obvious effect of periodic improvement again. The average *p*H value of precipitation in Liaoning Province in 2016 was 0.43 higher than that in 2015, which was 4.6 times more than the annual average increment. After 2016, the frequency of acid rain pollution in Liaoning Province decreased year by year to less than 5.0% in 2018, thus making Liaoning Province change from the acid rain prone area maintained for more than 10 years (2007-2017) to the acid rain occasional area. Moreover, the concentration of distribution probability of precipitation pH in Liaoning Province is higher, and in 2016, more than 3/4 of precipitation was in the neutral level ($5.6 \leq p\text{H} < 7.0$).

4. Conclusions

(I) In 2007-2018, more than 90% of the precipitation *p*H in Liaoning Province were between 5.0-7.5, and acid rain appeared at 22 stations in varying degrees, especially in the South and southeast of Liaoning Province, where the acid rain pollution was the most serious, and Dalian and Dandong continued to maintain a stable status of acid rain area.

(II) Generally speaking, the lowest pH value in Liaoning Province is 5.11 in 2007, with the most serious acid rain pollution. After 2008, it has been reduced year by year, and Liaoning Province has changed from the acid rain prone area in 2007 to the acid rain rare area in 2008-2017, and then become an acid rain occasional area in 2018. Which shows that the measures taken by the Chinese government and relevant departments have played a significant role in reducing pollutant emissions and strengthening environmental pollution control.

(III) The acid rain pollution in Liaoning Province is the most serious in winter, followed by autumn and summer, which is caused by the high concentration of SO_2 emission due to the coal combustion in heating season. The monthly distribution of *p*H value was the smallest in February of the first six years (2007-2012). The precipitation acidity in February of the six years after 2013 was significantly improved, which may be related to the prohibition of fireworks and firecrackers during the Spring Festival, but the acid rain pollution in December was significantly worse than that in the first six years, and the cause needs further study.

(IV) The concentration of various ions in atmospheric precipitation in Liaoning Province has been significantly lower than in the 1990s, but the overall content is still at a relatively high level, and the cleanliness of atmospheric precipitation in Liaoning Province still needs to be further improved.

(V) Since 2014, the obvious decrease of SO_2 emission concentration in Liaoning Province has been the main reason for the increase of precipitation pH and the decrease of acid rain. However, more attention should be paid to the significant increase of Cl^- in precipitation.

Acknowledgements: his work was supported by the National Key R&D Program of China (Grant No. 2018YFC1507900), Chinese National Natural Science Foundation (41440036) and Chinese National Natural Science Foundation (41505120).

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Manuscript received: 17.03.2020