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Study on Chemical Characteristics of Rainfall in Tobacco-Growing Regions of Chenzhou, Hunan Province

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Abstract

In order to clarify the chemical properties of rainfall in typical tobacco areas in Chenzhou City, Hunan Province, and analyze its potential for soil and flue-cured tobacco planting, rainfall samples in 2020 were collected by rainfall instruments in Fangyuan Town and Aoquan Town of Guiyang County, and the chemical properties that are closely related to the quality of flue-cured tobacco were determined, such as pH, EC, total nitrogen (TN), nitrate nitrogen (NO_3^--N), ammonium nitrogen (NH_4^+-N) and ion concentrations (K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Al^{3+}, SO_4^{2-}, Cl^-, NO_3^-). The results show that the pH values of rainfall samples at Fangyuan and Aoquan monitoring sites are in the range of 4.92 - 6.17 and 4.93 - 5.69 respectively, with an average of 5.27 and 5.27 respectively. The acid rain characteristic is very obvious, which is mainly dominated by SO_4^{2-}. The variation of rainfall EC has seasonal characteristics. EC is low from January to September, in the range of 6.09 - 56.72 and 11.83 - 30.93 μS/cm respectively, besides, it is high from October to December, in the range of 102.63 - 174.60 and 25.05 - 86.37 μS/cm respectively. The annual deposition of TN was 22.19 and 20.76 kg/hm^2/yr respectively, which were higher than that in the western regions with less human disturbance, but lower than or equal to that in the developed agricultural regions in eastern China. The proportion of NH_4^+-N in the annual deposition of TN was higher than that of NO_3^--N at two monitoring sites, with an average of 56.51% and 38.86% respectively. Ammonia volatilization from agricultural activities contributed more to rainfall nitrogen content. The ratios of ammonium nitrogen to nitrate nitrogen deposition at two monitoring points were 1.84, 1.81, 1.86 and 1.34, 1.46, and 1.29 during the whole year, summer and autumn, winter and spring respectively. The ratio is higher in summer and autumn than in winter and spring. The weighted average equivalent concentrations of the main ions at two monitoring sites were 238.88 μeq/L and 211.21 μeq/L respectively, and the orders of the ion concentrations were slightly different. Both the concentrations of SO_4^{2-} and NH_4^+ are higher, while Mg^{2+}, NO_3^- and Al^{3+} are lower. NH_4^+, SO_4^{2-} and NO_3^- are mainly from human activities with a contribution rate between 91.90% and 99.35%. Ca^{2+} mainly comes from soil and ground dust, besides, Cl^- and Mg^{2+} mainly come from marine sources and K^+ mainly comes from terrestrial sources. In general, the acidic rainfall and higher SO_4^{2-} concentration are beneficial to reducing the high pH value of soil in Aoquan tobacco area and improving the quality of flue-cured tobacco. Higher concentrations of SO_4^{2-} and NH_4^+ in rainfall are not conducive to the improvement of flue-cured tobacco quality, because of the high content of soil available sulfur in Chenzhou tobacco area and the characteristics of flue-cured tobacco's preference for ammonium.

Keywords

Rainfall, Chemical Characteristics, pH, Nitrogen Form, Ion Composition, Tobacco-Growing Region, Chenzhou

1. Introduction

With the continuous development of human society, industrial production, automobile exhaust, fossil fuel combustion, construction dust, mining and other human activities [1] [2] release a large number of SO_2, nitrogen oxide, heavy metals, particulate matter and other pollutants into the atmosphere [3] [4] [5], resulting in serious air pollution [6] [7]. After diffusion, migration and transformation, these substances eventually will enter earth surface and water body in the form of wet and dry depositions [8] [9], and then will affect the ecological environment, agricultural production and human health [10] [11]. For example, atmospheric nitrogen deposition could lead to soil acidification, water eutrophication, biodiversity loss and greenhouse gas emissions increasing, etc. [12] [13] [14]. Particulate matter containing heavy metal elements in the air could enter into soil, water body and the ecological cycle or food chain through dry deposition [15]. Therefore, it is of great significance to study the chemical characteristics of regional rainfall in order to evaluate its impacts on agricultural production and ecological environment.

Chenzhou city of Hunan Province is a famous region of non-ferrous metals in the world, and its reserves of tungsten and bismuth rank first and second respectively in the world. In addition, molybdenum and graphite rank first, and tin and zinc rank third and fourth respectively in China. As the most typical region of

Nanling Hill Ecological Zone of tobacco with the aroma style of burnt-pure sweet in China [16], Chenzhou City is the largest tobacco-rice rotation region in Hunan province, accounting for about 1/3 (2.67×10^4 hm^2) of the total tobacco-planting area in Hunan [17]. There were some studies [18] analyzed the variation trends of climate parameters (such as rainfall, temperature, sunshine duration, light intensity, etc.) in Chenzhou tobacco-planting regions over the years and their influence on the growth and quality of tobacco. There were also some studies conducted on the chemical characteristics of rainfall (2016-2020) in the urban region (Beihu district) of Chenzhou [19] and the adjacent regions [20] [21] [22] [23]. It is found that the weighted pH of the annual precipitation varied from 5.12 to 5.41, showing an overall downward trend leading to acid rain occurring frequently, and the seasonal weighted pH is higher in autumn and winter and lowest in summer, besides, the weighted average total ion equivalent concentration of precipitation was 1243.84 μeq/L, and the weighted EC annual average was 67.5 μS/cm, meanwhile, SO_4^{2-}, Ca^{2+}, Cl^-, NO_3^- and NH_4^+ were the main ions in precipitation, accounting for 89.1% of the total ion equivalent concentrations from 2016 to 2020 in Beihu District of Chenzhou [19]. In adjacent regions, for examples, the wet deposition of atmospheric nitrogen in Jinjing River Basin of Changsha city of Hunan Province was 26.2 $kg/hm^2 \cdot a$, and NH_4^+-N accounted for 49.7% of the total nitrogen in rainfall [24]. In Shenzhen City of Guangdong Province, the weighted average pH of precipitation was 4.68, among which NO_3^- and Cl^- had the greatest influence on precipitation acidity, besides, Cl^-, K^+ and Na^+ mainly came from marine sources [25]. In Chancheng of Foshan City, the pH value of rainfall is between 3.95 and 6.47, with an annual average of 5.35. In addition, the frequency of acid rain is 46.0%. The electrical conductivity is between 3.51 and 100.40 μS/cm, with an annual average of 22.48 μS/cm. Also, NO_3^- and SO_4^{2-} are the main anions in precipitation, while NH_4^+ and Ca^{2+} are the main cations, as a result, these 4 main ions make up 76.0% of the total ions [20]. The range of pH values of atmospheric precipitation in Guilin is between 4.13 and 7.37, besides, 48.0% of which is less than the critical value of acid rain, indicating that there is a certain acidification phenomenon in Guilin rainfall. The electrical conductivity (EC) varies from 4.53 to 128.10 $\mu S \cdot cm^{-1}$, and the weighted average is 16.44 $\mu S \cdot cm^{-1}$. The anions are mainly SO_4^{2-} and NO_3^-, with a weighted average content of 94.50 $\mu eq \cdot L^{-1}$ and 30.48 $\mu eq \cdot L^{-1}$, accounting for 65.28% and 21.06% of the total anions, followed by Cl-. The cations were mainly Ca^{2+}, with a weighted average of 97.67 $\mu eq \cdot L^{-1}$, accounting for 58.76% of the total cations, followed by NH_4^+, which accounted for 19.10% of the total cations. The average value of SO_4^{2-}/NO_3^- was 2.45, so that the atmospheric precipitation is of a mixed type of sulfuric acid and nitric acid. Ca^{2+} and Mg^{2+} mainly come from crustal and anthropogenic sources, while Na^+ mainly comes from ocean transport, and K^+ comes from human activities [21]. NH_4^+ and Ca^{2+} are the main cations in the atmospheric precipitation in Nanchang, with weighted average concentrations of 65.3 and 23.9 μmol/L, accounting for 57% and 21% of the total cations, respectively. In addition, SO_4^{2-} and NO_3^- are the main anions, with weighted average concentrations of 60.4 and 25.3 μmol/L, accounting for 56% and 23% of the total anions, respectively. Na^+ and Cl^- are obviously affected by sea salt, and most of K^+, Mg^{2+} and Ca^{2+} come from soil. SO_4^{2-}, NH_4^+ and NO_3^- are the main components of secondary particulate matter in the atmosphere, and coal combustion contributes the main F^- and part of SO_4^{2-}. The influence of SO_4^{2-} in the atmospheric precipitation in Nanchang gradually increased, which led to the gradual transformation from mixed type to sulfuric acid type [22]. The order of the content of anions in precipitation in Changsha City is $SO_4^{2-} > NO_3^- > Cl^- > F^-$,besides, SO_4^{2-} accounts for 65.8% of the total amount of anions, while the order of the content of cations in the precipitation of Changsha City is $NH_4^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$, in addition, the first two items account for 89.8% of the total amount of cations [23].

But so far there is no report on the chemical characteristics of rainfall in tobacco-planting region in Chenzhou, therefore, in this study, the rainfall samples were collected in 2020 from Fangyuan and Aoquan sites in Guiyang County, which is the main tobacco-planting region of Chenzhou. pH, EC, nitrogen in different forms and ion compositions of the rainfall samples were determined, and their potential impacts on soil and tobacco are preliminarily assessed.

2. Methods and Materials

2.1. Basic Information of Study Area

Guiyang County is located between 112˚13'26"E - 112˚55'46"E and 25˚27'15"N - 26˚13'30"N, with a total area of 2973 km^2. Tobacco has been planted since 1953, with tobacco-rice rotation as a main plantation system. Guiyang County has a subtropical humid monsoon climate with an average annual temperature of 17.2˚C, sunshine hours of 1705.4 h, and rainfall of 1385.2 mm [26].

2.2. Methods for Collecting and Analyzing Rainfall Samples

The rainfall sampling device is Ellen ISC-10 automatic continuous sampler for precipitation and dustfall, which is automatically opened during precipitation and automatically closed when the precipitation ends. They were set up in Fangyuan Tobacco Workstation (112˚40'0.03"E, 25˚40'48.65"N, 320.4 m above sea level) and Aoquan Tobacco Workstation (112˚34'35.62"E, 25˚55' 36.21"N, 250.0 m above sea level), about 20 m from the ground on the roof of the buildings to reduce the splash and contamination of surrounding substances.

The rainfall is sampled during the whole year of 2020. 90 and 119 rainfall samples were collected from the two monitoring sites in Fangyuan and Aoquan. The collected rainfall samples were stored in washed 1.5 L PVC bottles and placed in a 4˚C environment saving for backup. pH was measured with a pH meter (PB-21), besides, conductivity (EC) was measured with a conductivity meter (EC215), and total nitrogen, ammonium nitrogen and nitrate nitrogen were measured with a continuous flow analyzer (San++System). The main cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+}) were determined by inductively coupled plasma emission spectrometer (Optima 8000). After the rainfall samples filtered with a 0.22 μm pore size microporous membrane, the concentration of major anions (SO_4^{2-} , Cl^-) was analyzed and determined by a high-pressure dual-system ion chromatograph (ICS-5000+). The rainfall information at two monitoring sites come from the temperature and humidity recorder (179-TH) installed in the nearby farmland.

2.3. Determination of Ionic Characteristic of Rainfall Samples

The formula for calculating the sedimentation amount of ions is [27]:

$$F_i = P_i \times C_i \times A \tag{1}$$

$$F_m = \sum_{i=1}^{n} F_i \tag{2}$$

$$F_y = \sum_{i=1}^{n} F_i \tag{3}$$

In the above formula, F_i is the sedimentation amount of ions or elements in the sample after each rainfall (kg/hm^2/yr), P_i is the daily rainfall (mm), and C_i is the concentration of ions or elements in the sample (mg/L or ug/L), A is the unit conversion factor (A is 0.01 when C_i is mg/L, A is 10^{-5} when C_i is ug/L), F_m is the monthly sedimentation amount of ions or elements (kg/hm^2/yr), F_y is the annual deposition of ions or elements (kg/hm^2/yr).

The formula for calculating the ionic equivalent concentration is [28]:

$$N = 1000 \times C \times V/M \tag{4}$$

$$C_{vwm} = \sum_{i=1}^{n} \left(N_i \times P_i\right) \Big/ \sum_{i=1}^{n} P_i \tag{5}$$

In the above formula, N is the ion equivalent concentration (ueq/L), C is the ion concentration (mg/L), V is the absolute value of ion valence, M is the ion molar mass (g/mol), and C_{vwm} is the weighted average concentration of ion rainfall (ueq/L), N_i is the normal concentration of i ions in the sample (ueq/L), P_i is the daily rainfall (mm).

EF_{sea} and EF_{soil} are enrichment factors to identify the potential sources of ionic species in rainwater. EF_{sea}, EF_{soil}, contribution of sea salt fraction (SSF), non-sea salt fraction ($NSSF$), terrestrial fraction (TF), crust fraction (CF) and anthropogenic fraction (AF) were calculated using the following equations: [29] [30] [31] [32]

$$EF_{sea} = \left(X/Na^+\right)_{rainwater} \Big/ \left(X/Na^+\right)_{seawater} \tag{6}$$

$$EF_{soil} = \left(X/Ca^{2+}\right)_{rainwater} \Big/ \left(X/Ca^{2+}\right)_{soil} \tag{7}$$

$$\%SSF = 100\left(X/Na^+\right)_{seawater} \Big/ \left(X/Na^+\right)_{rainwater} \tag{8}$$

$$\%NSSF = \%TF = 100 - \%SSF \tag{9}$$

$$\%CF = 100\left(X/Ca^{2+}\right)_{crust} \Big/ \left(X/Ca^{2+}\right)_{rainwater} \tag{10}$$

$$\%AF = \%NSSF - \%CF \tag{11}$$

where X is the concentration of the desired ion, $\left(X/Na^{+}\right)_{seawater}$ is the ratio from seawater composition and $\left(X/Ca^{2+}\right)_{crust}$ is the ratio from crustal composition.

2.4. Data Processing, Analysis and Mapping

Data processing, analysis and graphing were performed using Microsoft Excel 2016 and IBM SPSS Statistics 26.

3. Results and Discussion

3.1. Analysis of Rainfall

Table 1 shows the 2020 rainfall data from National Weather Station (No. 57973, 112˚43'29"E, 25˚44'58"N, 329.1 m above sea level) in Guiyang County and the field temperature and humidity recorders (Temperature and Humidity Recorder 179-TH, Beijing Dingxuan Shengshi Technology Co., Ltd.) set in Fangyuan (112˚40'0"E, 25˚40'49"N, 320.4 m above sea level) and Aoquan (112˚34'36"E, 25˚55'36"N, 250.0 m above sea level), it can be seen that 1) the annual rainfall data of Fangyuan and Aoquan monitoring sites are higher than the national station data, The relative errors were 10.5% and 10.2%, respectively. 2) The inter-month high-low sequence and the rising -falling trend of rainfall data at the national station and the two monitoring sites were consistent, and the rainfall was mainly concentrated during the first half of the year (January to June, tobacco season), and it accounted for 67.8%, 72.7% and 77.5% of the annual rainfall at the national station and the two monitoring sites respectively, which was significantly higher than that in the second half of the year (July to December, the rice season).

Table 1. Precipitation of national meteorological station and two monitoring sites in 2020.

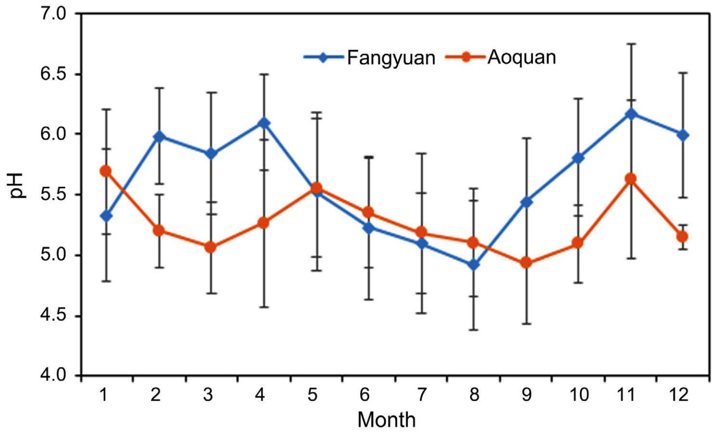
Month	National station	Fangyuan		Aoquan	
	Precipitation (mm)	Precipitation (mm)	Relative error (%)	Precipitation (mm)	Relative error (%)
1	71.1	96.2	35.3	134.6	89.3
2	157.3	195	24.0	211.7	34.6
3	299.9	372.2	24.1	435.0	45.0
4	174.8	245.5	40.4	162.2	−7.2
5	159.3	174.3	9.4	200.8	26.1
6	132.2	95.1	−28.1	108.3	−18.1
7	114.1	85.7	−24.9	1.3	−98.9
8	90.2	85.7	−5.0	76.5	−15.2
9	207	188.6	−8.9	237.2	14.6
10	22.8	38.7	69.7	25.0	9.6
11	7.3	12.8	75.3	7.8	6.8
12	30.7	31.6	2.9	16.2	−47.2
Year	1466.7	1621.4	10.5	1616.6	10.2

3.2. Analysis of Rainfall pH and EC

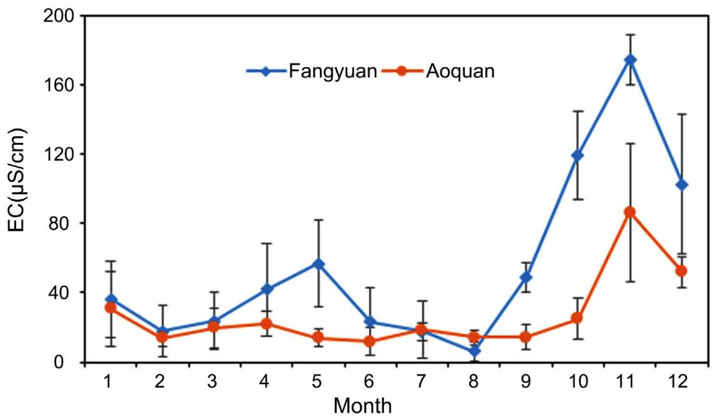
Figure 1(a) shows the pH variation trend of rainfall in Fangyuan and Aoquan in 2020. The pH of rainfall at two monitoring sites are in the range of 4.92 - 6.17 and 4.93 - 5.69, with an average of 5.62 and 5.27, respectively. The changing trends of pH between the two monitoring sites are slightly different, mainly reflected in the rising and falling trend from January to May. In general, 43.33% of rainfall at Fangyuan site and 73.11% of rainfall at Aoquan site were lower than 5.5 in the characteristic of pH, and acid rain characteristic [33] were obvious. Figure 1(b) shows that there are obvious seasonal changes in the mean value of rainfall EC at Fangyuan and Aoquan monitoring sites. It can be seen that: 1) The EC from January to September were all low, ranging from 6.09 to 56.72 μS/cm and from 11.83 to 30.93 μS/cm, respectively. After that, the electrical conductivity gradually increased and reached the maximum value in November, which were 174.60 and 86.37 μS/cm respectively, and then tended to decrease. 2) The variation range of the rainfall electrical conductivity at two monitoring sites after August (the coefficient of variation is 0.64 and 0.72, respectively) is larger than that before August (the coefficient of variation is 0.54 and 0.32, respectively). The EC of rainfall depends on the concentration of solute-containing salts or other chemical impurities that decompose into electrolytes, besides, the higher the concentration, the higher the conductivity [34]. It can be seen from Figure 1(b) that the high EC values of rainfall generally appear in October~December at both monitoring sites, but the EC of rainfall in January~September are both very low.

3.3. Analysis of Rainfall Nitrogen Form

The deposition amounts of total nitrogen (TN), NO_3^--N and NH_4^+-N and their changes in rainfall at Fangyuan and Aoquan monitoring sites are shown in Figure 2 and Figure 3, respectively. The deposition amounts were 22.19 kg/hm^2/yr and 20.76 kg/hm^2/yr, respectively. The variation trends of TN deposition at the two sites in different months are similar, with a peak in the first half and the second half of the year, respectively. The first peak appeared in March (4.87 kg/hm^2 and 5.71 kg/hm^2, respectively), and the second peak appeared in September (3.09 kg/hm^2 and 3.14 kg/hm^2, respectively). The annual deposition of NO_3^--N and NH_4^+-N at Fangyuan monitoring site were 6.80 kg/hm^2/yr and 12.54 kg/hm^2/yr, accounting for 30.66% and 56.51% of the annual deposition of TN, respectively. At Aoquan monitoring site the annual deposition rates of NO_3^--N and NH_4^+-N were 6.02 kg/hm^2/yr and 8.07 kg/hm^2/yr, accounting for 29.00% and 38.86% of the total deposition in TN, respectively. The variation trends of NO_3^--N and NH_4^+-N deposition in Fangyuan and Aoquan in different months are similar to that of TN, it can be seen that there is a peak in the first half and second half of the year, respectively, and the first peak appeared in March, while the deposition amounts of NO_3^--N and NH_4^+-N were 1.49 kg/hm^2, 2.75 kg/hm^2 and 1.66 kg/hm^2, 2.01 kg/hm^2, respectively. Meanwhile, the second peak appeared in September, and the NO_3^--N and NH_4^+-N deposition amounts were 0.99 kg/hm², 1.83 kg/hm² and 0.86 kg/hm² and 1.46 kg/hm², respectively.



(a)



(b)

Figure 1. Variation characteristics of rainfall pH and EC in 2020 in Fangyuan and Aoquan stations.

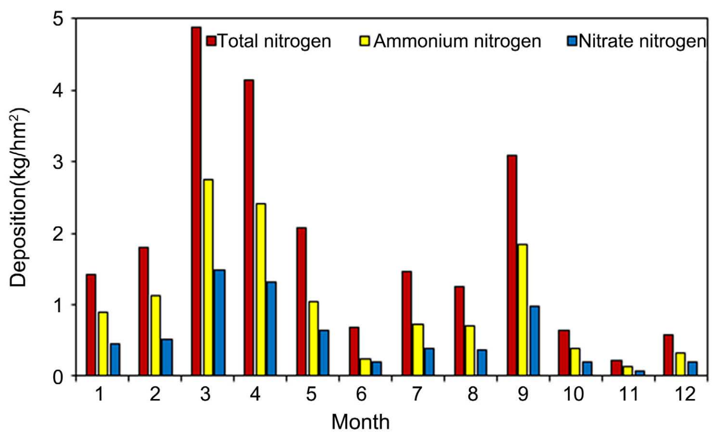


Figure 2. Deposition of total nitrogen, ammonium and nitrate at Fangyuan monitoring site in 2020.

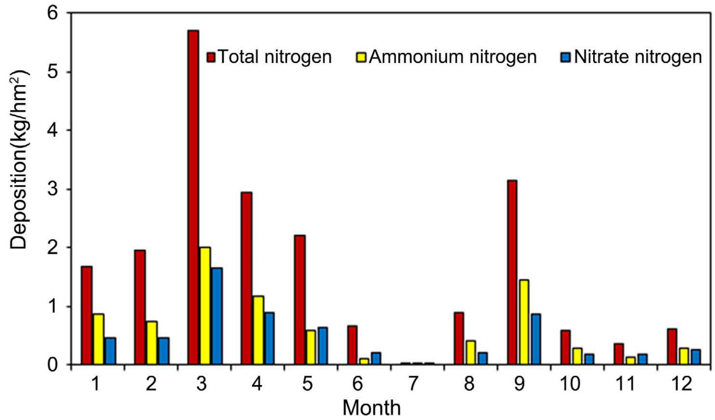


Figure 3. Deposition of total nitrogen, ammonium and nitrate at Aoquan monitoring site in 2020.

3.4. Analysis of Rainfall Ion Composition

Table 2 shows the annual and monthly equivalent concentrations of main ions at Fangyuan and Aoquan monitoring sites. The sums of the weighted average equivalent concentrations of all ions are 238.88 and 211.21 μeq/L, respectively, and the concentrations of each ion from high to low are $SO_4^{2-} > NH_4^+ > Na^+ > Ca^{2+} > K^+ > Cl^- > Mg^{2+} > NO_3^- > Al^{3+}$ and $SO_4^{2-} > NH_4^+ > Ca^{2+} > Na^+ > K^+ > Cl^- > NO_3^- > Mg^{2+} > Al^{3+}$, in which the sum of SO_4^{2-}, NH_4^+, Na^+, Ca^{2+}, K^+ and Cl^- concentrations exceeded 90%, which are the dominant ions in rainfall. The weighted average equivalent concentrations of Al^{3+} at the two monitoring sites were lower, which were 3.54 and 4.04 μeq/L, respectively. SO_4^{2-} was the main anion at the two monitoring sites, and its weighted average equivalent concentrations were 61.42 and 50.46 μeq/L, accounting for 73.18% and 69.13% of the total anions, respectively. NH_4^+, Na^+ and Ca^{2+} were the main cations, and their concentrations accounted for 74.39% and 76.99% of the total cations, respectively.

The sums of weighted average equivalent concentrations of main ions in Fangyuan and Aoquan monitoring sites in tobacco and rice seasons were 251 μeq/L, 263.29 μeq/L and 209.46 μeq/L, 456.27 μeq/L, respectively, in which the concentrations were both larger in rice season than taht in tobacco season. And the order were $SO_4^{2-} > NH_4^+ > Na^+ > Ca^{2+} > K^+ > Cl^- > Mg^{2+} > NO_3^- > Al^{3+}$, $SO_4^{2-} > NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+} > Cl^- > K^+ > NO_3^- > Al^{3+}$ and $SO_4^{2-} > NH_4^+ > Na^+ > Ca^{2+} > K^+ > Cl^- > NO_3^- > Mg^{2+} > Al^{3+}$, $Ca^{2+} > SO_4^{2-} > NH_4^+ > NO_3^- > Cl^- > Mg^{2+} > Na^+ > Al^{3+} > K^+$. SO_4^{2-}, NH_4^+, Na^+, and Ca^{2+} accounted for more than 70% of the total average equivalent concentration during tobacco season and rice season in Fangyuan and during tobacco season in Aoquan, while SO_4^{2-}, NH_4^+, NO_3^-, Ca^{2+} accounted for more than 85% during rice season in Aoquan.

At Fangyuan monitoring site, the weighted average equivalent concentrations of SO_4^{2-} and NH_4^+ reached a peak in April (155.84 and 105.11 μeq/L) and

December (281.50 and 126.57 μeq/L), respectively. The month-to-month changes of other ions were relatively stable. At Aoquan monitoring site, the weighted average equivalent concentrations of Ca^{2+} and SO_4^{2-} reached their peaks in November (466.35 and 323 μeq/L), and the weighted average equivalent concentration of NH_4^+ reached a peak in December (148.30 μeq/L), besides, the concentrations changes of other ions are relatively stable from month to month.

Table 2. Equivalent concentrations of various ions in rainfall at monitoring sites (ueq/L).

Site	Month	NO_3^-	NH_4^+	Al^{3+}	Mg^{2+}	SO_4^{2-}	Ca^{2+}	Na^+	K^+	Cl^-
Fangyuan	1	10.81	66.65	7.44	7.97	73.41	31.42	46.75	7.83	22.97
	2	5.51	50.10	2.33	4.91	27.07	22.41	32.51	6.64	11.06
	3	8.92	55.75	2.26	4.82	50.09	20.60	29.72	30.53	11.57
	4	17.86	105.11	13.31	12.22	155.84	43.34	39.63	54.13	12.45
	5	9.86	59.03	2.30	35.33	73.20	39.25	38.85	38.33	15.67
	6	3.98	17.73	0.95	2.41	16.58	13.67	29.50	27.07	14.05
	7	5.86	51.37	1.80	5.93	37.51	37.13	31.37	27.60	14.74
	8	2.56	22.05	1.07	3.19	19.10	17.63	9.46	2.93	9.26
	9	2.58	13.89	0.97	2.77	19.38	16.00	41.74	23.59	9.30
	10	3.71	31.67	0.22	43.92	14.38	51.00	33.61	16.00	14.08
	11	15.32	50.56	1.08	8.00	81.25	52.50	42.61	25.13	18.31
	12	39.02	126.57	26.00	21.58	281.50	53.00	15.04	4.82	28.09
	Year	8.44	53.97	3.54	10.99	61.42	28.37	32.92	25.16	14.07
Aoquan	1	10.37	82.98	10.71	16.53	74.78	64.75	75.34	69.42	40.83
	2	3.80	20.08	2.54	4.79	33.36	18.76	35.26	66.54	13.43
	3	7.55	42.30	2.00	4.49	44.81	16.53	27.82	11.26	12.41
	4	11.82	53.24	3.26	5.66	61.14	31.83	31.51	21.14	13.15
	5	6.35	22.46	2.12	5.38	37.09	24.90	27.81	12.07	12.79
	6	3.04	13.30	1.24	2.12	24.13	14.47	25.91	5.89	11.61
	7	3.19	47.57	2.71	5.05	31.19	36.64	24.45	4.71	11.82
	8	5.96	31.62	5.22	6.18	52.14	46.42	9.92	1.57	10.44
	9	6.15	35.66	4.07	5.22	44.79	33.03	8.86	2.22	8.61
	10	16.35	109.71	4.81	6.15	74.53	38.20	11.65	1.51	18.93
	11	64.26	125.18	12.56	44.67	323.00	466.35	23.70	14.18	40.61
	12	42.39	148.30	19.94	18.04	177.69	121.80	12.96	6.14	19.71
	Year	7.87	42.54	4.04	6.47	50.46	36.60	27.19	21.27	14.76

3.5. Discussion

There are various reasons for the formation of acid rain in Guiyang County [35] [36], mainly including nitrogen oxides from industrial and automobile exhaust emissions [37], sulfides from coal combustion [38], and from emissions of acid gas from neighboring provinces (Guangdong, Sichuan, Guizhou) [39]. Studies have shown that the areas with severe acid rain in China are mainly distributed in Sichuan Basin and vast area in the south of the Yangtze River [40], and Hunan Province is located in the area with severe acid deposition in China. The energy consumption structure of Hunan Province is dominated by coal [41] [42], so a large amount of SO_2 and NO_x will be generated when coal resources are consumed. These acid gases are the main precursors for the formation of acid rain. Therefore, the formation of acid rain in Hunan Province is related to the energy structure and consumption [43].

In terms of flue-cured tobacco planting, the suitable soil pH for high-quality flue-cured tobacco is 5.5 - 7.0 [44] [45] [46]. There are literatures report that about 2/3 of tobacco fields in Chenzhou were higher in pH (≥7.0) in 2015, which could be attributed to the application of superphosphate fertilizer and the habit of local farmers using fired soil to improve soil quality [47] [48], and may also be related to the continuous supply of Ca^{2+} and Mg^{2+} dissolved from the limestone in the hills and mountains [49]. In 2020, the soil pH values at Fangyuan and Aoquan tobacco fields are in the range of 6.10 - 6.97 (suitable) and 8.16 - 8.40 (higher), respectively. Therefore, acidic rainfall is beneficial to reduce the high soil pH value at Aoquan tobacco fields, as a result, it is conducive to the improvement of flue-cured tobacco quality in Aoquan, but there is a potential adverse effect on Fangyuan tobacco fields.

The high EC values of rainfall generally appeared from October to December at both monitoring sites, due to less rainfall (27.7 mm and 16.3 mm on average) at that time, resulting in more particulate matter and soluble ions in the air [50]. However, the EC values of rainfall were very low from January to September because of its high rainfall (average of 170.9 mm and 174.2 mm, respectively), which effectively reduces the soluble ions and particulate matter in the air. The EC values of the rainfall during the tobacco season (January to July) were low (17.65 - 56.72 μS/cm and 11.83 - 30.93 μS/cm, relatively), indicating that the rainfall was relatively pure with few impurities, which was beneficial to the maintenance of soil and water environment during the tobacco season.

Studies have shown that the annual deposition of TN in farmland in Zhejiang is 18 - 32 $kg/hm^2/yr$ [51], besides, the total annual deposition of atmospheric nitrogen in agro-ecological regions in southeastern China can reach 33.93 $kg/hm^2/yr$ [52]. In alpine meadow area of Qilian Mountains, the annual deposition of TN, NH_4^+-N and NO_3^--N is only 3.19, 1.78 and 1.40 $kg/hm^2/yr$, respectively [53]. Also, the annual deposition of TN in Nyingchi City of Tibet is only 2.19 $kg/hm^2/yr$ [54]. Comparing with the above data, it can be found that the annual deposition of TN in this study area is higher than that in the western regions with less human disturbance, but equal to or lower than that in the eastern regions with developed agricultural activities. In areas with less anthropogenic interference, there is less exhaust gas from automobiles and factories and less ammonia from agricultural activities, so the TN deposition of rainfall is less. While in the developed eastern areas, ammonia and nitrogen oxides were produced more due to the strong anthropogenic activities such as transportation, industry, and agriculture, so the TN deposition of rainfall is larger. In this study, the ratio of NH_4^+-N to TN at two monitoring sites was higher than that of NO_3^--N, indicating that the nitrogen deposition at two monitoring sites was more affected by the volatilization of ammonia from agricultural activities [55] [56], especially during the rice season [57] [58], while the effects of nitrate nitrogen generated by factors such as industrial emissions and traffic exhaust [59] are relatively small. Two peaks of nitrogen deposition occurred in March in the first half of the year and in September in the second half of the year, which may be related to the concentrated fertilization for flue-cured tobacco and late rice at that time. The ratios of ammonium nitrogen to nitrate nitrogen deposition at two monitoring sites were 1.84, 1.81, 1.86 and 1.34, 1.46, 1.29 for the whole year, summer and autumn, and winter and spring, respectively. The ratio of NH_4^+-N and NO_3^--N deposition is higher in summer and autumn (June-November) than that in winter and spring (December-May) as a result of the facts that the frequent agricultural activities and high temperature in summer and autumn can promote ammonia volatilization, while in winter and spring the contribution of agricultural activities to ammonium is reduced, and the nitrate content is slightly increased due to traffic exhaust and fossil fuels [60].

The annual application of pure N in the tobacco season of Chenzhou is generally 157.5 - 195 kg/hm^2. This study shows that the annual nitrogen depositions in Fangyuan and Aoquan sites are 22.19 and 20.76 kg/hm^2/yr, respectively, which is equivalent to 10.7% - 14.1% of the pure N application rate. Flue-cured tobacco is nitrate-liking and ammonium-disliking [61] [62]. During tobacco season, the proportions of NH_4^+-N and NO_3^--N in annual TN deposition at Fangyuan and Aoquan monitoring sites were 55.84%, 30.34% and 36.32%, 28.56%, respectively. And the proportion of NH_4^+-N in the annual deposition of TN was 84.05% and 27.17% higher than that of NO_3^--N, which was not conducive to the growth of high-quality flue-cured tobacco in general.

SO_4^{2-} is the main anion at two monitoring sites, and its weighted average equivalent concentration is 61.42 and 50.46 μeq/L, accounting for 73.18% and 69.13% of the total anions, respectively. The higher concentration of SO_4^{2-} is related to the large amount of fossil fuels combustion and SO_2 emissions from vehicle exhaust [63]. The acidification of rainfall at two monitoring sites was dominated by sulfuric acid rather than nitric acid because the concentration of SO_4^{2-} was higher than that of NO_3^- [64]. NH_4^+, Na^+ and Ca^{2+} are the main cations, and their concentrations account for 74.39% and 76.99% of the total cations, respectively. The higher concentration of NH_4^+ is related to local agricultural production activities, because agricultural activities increase the amount of ammonia and particulate ammonia in the atmosphere [65]. The concentration of Ca^{2+} mainly comes from soil and ground dust, etc., as the concentration of Ca^{2+} in rainfall will be increased when the dust, sand dust and construction dust enter the air [66].

Table 3 shows the enrichment factors of main ions components relative to seawater (EF_{sea}) and soil (EF_{soil}) at Fangyuan and Aoquan monitoring sites, and **Table 4** shows the main ions components contributed source in rainfall at Fangyuan and Aoquan monitoring sites, meanwhile, the analysis method is shown in the literature [67] [68]. The EF_{soil} of Cl^- is much greater than 1 and the EF_{sea} is less than 1, indicating that Cl^- in the rainfall at two monitoring sites mainly comes from marine sources [69], and the proportion of Cl^- input from marine sources in both places is greater than 99%. The EF_{sea} of K^+ were 34.74 and 35.55, respectively, and the EF_{soil} were 1.76 and 1.15, respectively, indicating that K^+ was mainly contributed by terrigenous sources. Most of Mg^{2+} comes from marine sources, and the proportions of marine sources account for 68.02% and 95.35%, respectively. The concentrations of Mg^{2+} and Cl^- were significantly and positively correlated at two monitoring sites ($p < 0.01$, **Table 5**). The sources of NH_4^+, SO_4^{2-} and NO_3^- are mainly contributed by anthropogenic activities, and their anthropogenic contributed source components are 99.35%, 92.43%, 96.88% and 99.25%, 91.90%, 96.88% respectively at two sites. And there were significantly positive correlations among these three ions ($p < 0.01$, **Table 3**).The content of SO_4^{2-} is the highest, followed by NH_4^+. The content sums of the two ions account for 48.30% and 44.03% of the total main ions at two monitoring sites, and both are mainly affected by human activities, indicating that the soluble ions in rainfall mainly come from human production and life [70].

This study shows that the concentrations of SO_4^{2-} and NH_4^+ are relatively high in ion compositions of rainfall in Chenzhou tobacco area. The former has both advantages and disadvantages for the growth of high-quality flue-cured tobacco, as it can reduce high pH values of tobacco fields soil in Aoquan which are relatively high at present, but it can also increase the supply of sulfur in tobacco fields while the content of sulfur in the soil of Chenzhou tobacco area is mostly too high for high-quality flue-cured tobacco [71] [72]. High NH_4^+ concentration is also disadvantageous for the growth of high-quality flue-cured tobacco, because flue-cured tobacco is nitrate-liking and ammonium-disliking [61] [62].

Table 3. Enrichment factors of ionic components in rainfall relative to seawater and soil.

Enrichment Factor	Site	SO_4^{2-}/Na^+	NH_4^+/Na^+	Ca^{2+}/Na^+	K^+/Na^+	Cl^-/Na^+	Mg^{2+}/Na^+	NO_3^-/Na^+
EF_{sea}	Fangyuan	14.92	184.20	19.58	34.74	0.37	1.47	-
	Aoquan	14.84	175.79	30.59	35.55	0.47	1.05	-
		SO_4^{2-}/Ca^{2+}	NH_4^+/Ca^{2+}	Na^+/Ca^{2+}	K^+/Ca^{2+}	Cl^-/Ca^{2+}	Mg^{2+}/Ca^{2+}	NO_3^-/Ca^{2+}
EF_{soil}	Fangyuan	115.15	905.92	2.04	1.76	160.01	0.69	141.65
	Aoquan	73.32	553.46	1.31	1.15	130.11	0.32	102.42

Table 4. Relative contributions of different ionic components in rainfall.

Site	ions	Marine source input	Terrene source input	
			Soil and rock weathering	Anthropogenic activities
Fangyuan	SO_4^{2-}	6.70%	0.87%	92.43%
	NH_4^+	0.54%	0.11%	99.35%
	Ca^{2+}	5.11%	94.89%	
	K^+	2.88%	56.83%	40.29%
	Cl^-	99.38%	0.62%	
	Mg^{2+}	68.02%	31.98%	
	NO_3^-	2.42%	0.71%	96.88%
Aoquan	SO_4^{2-}	6.74%	1.36%	91.90%
	NH_4^+	0.57%	0.18%	99.25%
	Ca^{2+}	3.27%	96.73%	
	K^+	2.81%	86.74%	10.45%
	Cl^-	99.23%	0.77%	
	Mg^{2+}	2.14%	0.98%	96.88%
	NO_3^-	95.35%	4.65%	

Table 5. Correlation analysis of main ion concentrations in rainfall.

Site		NO_3^-	NH_4^+	Al^{3+}	Fe^{3+}	Mg^{2+}	SO_4^{2-}	Ca^{2+}	Na^+	K^+	Cl^-
Fangyuan	NO_3^-	1									
	NH_4^+	0.85 **	1								
	Al^{3+}	0.90 **	0.80 **	1							
	Fe^{3+}	0.57 **	0.39 **	0.58 **	1						
	Mg^{2+}	0.26 *	−0.01	0.07	−0.03	1					
	SO_4^{2-}	0.71 **	0.51 **	0.61 **	0.36 **	0.56 **	1				
	Ca^{2+}	0.37 **	0.55 **	0.25 *	0.26 *	0.06	0.31 **	1			
	Na^+	0.42 **	0.47 **	0.33 **	−0.04	0.36 **	0.36 **	0.33 **	1		
	K^+	0.25 *	0.33 **	0.21	−0.02	0.22	0.23	0.33 **	0.39**	1	
	Cl^-	0.44 **	0.27 *	0.28 *	0.36 **	0.48 **	0.41 **	0.34 **	0.49 **	−0.01	1
Aoquan	NO_3^-	1									
	NH_4^+	0.77 **	1								
	Al^{3+}	0.66 **	0.69 **	1							
	Fe^{3+}	0.55 **	0.52 **	0.51 **	1						
	Mg^{2+}	0.79 **	0.65 **	0.76 **	0.43 **	1					
	SO_4^{2-}	0.94 **	0.77 **	0.72 **	0.52 **	0.88 **	1				
	Ca^{2+}	0.83 **	0.56 **	0.61 **	0.47 **	0.89 **	0.86 **	1			
	Na^+	0.08	0.17	0.18	0.03	0.43 **	0.18	0.18	1		
	K^+	−0.02	0.04	0.15	0.16	0.15	−0.02	0	0.35 **	1	
	Cl^-	0.30 **	0.23 *	0.24 *	0.16	0.52 **	0.34 **	0.38 **	0.74 **	0.28**	1

Note: ** and * indicate significant correlations (two-sided) at the 0.01 and 0.05 levels, respectively.

There are still some shortcomings in this study. 1) Due to the variability of climate, the characteristics of rainfall in different years may be different, and its chemical properties and monthly trends may be different. Generally, several years' research data is needed to reliably reveal the chemical properties of rainfall in a certain area. However, in this study we only analyzed the research data in 2020, and continuous monitoring is still required. 2) Due to limited conditions, neither information about the types of factories and mines around the two monitoring sites nor relevant data about three-waste-discharges was obtained, which would affect the interpretations of the research results.

4. Conclusion

This study shows that the rainfall in the tobacco area of Chenzhou City has obvious acid rain characteristics, which is mainly dominated by SO_4^{2-}. The EC of rain is lower from January to September but higher from October to December. The annual deposition of TN is higher than that of the western regions with less human disturbance, but lower than or equal to that in the developed agricultural regions in eastern China. The ratio of NH_4^+-N in rainfall to the annual deposition of TN was higher than that of NO_3^--N, and ammonia volatilization from agricultural activities contributed the most to the nitrogen content in rainfall. As for the ion compositions of rainfall, SO_4^{2-} and NH_4^+ are higher, while Mg^{2+}, NO_3^- and Al^{3+} are lower. NH_4^+, SO_4^{2-} and NO_3^- are mainly from anthropogenic activities, and Ca^{2+} is mainly from soil and ground dust, while Cl^- and Mg^{2+} are mainly from marine sources, besides, K^+ is mainly from terrestrial sources. In general, the acidic rainfall was beneficial to reduce the high soil pH value at Aoquan tobacco fields, and the high NH_4^+ and SO_4^{2-} concentrations were not conducive to the improvements of flue-cured tobacco quality.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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