Formation of Rainwater Acidity in the Forested Basin of the Sikhote Alin Mountain Region

N. K. Kozhevnikova[a, *], **A. G. Boldeskul**[b, **], **T. N. Lutsenko**[b], **T. S. Gubareva**[b, c],
S. Yu. Lupakov[b], **and V. V. Shamov**[b]

[a] *Federal Scientific Center of the East Asia Terrestrial Biodiversity, Far East Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia*
[b] *Pacific Geographical Institute, Far East Branch, Russian Academy of Sciences, Vladivostok, 690041 Russia*
[c] *Water Problems Institute, Russian Academy of Sciences, Moscow, 119333 Russia*
*e-mail: nkozhevnikova@biosoil.ru
**e-mail: boldeskul@yandex.ru
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Abstract—The paper presents results of long-term (for seven years) monitoring and analysis of the formation of rainwater acidity in Primorsky Krai, southern Russian Far East. These results reveal the variability in the concentrations of both of total dissolved solids (TDS) and individual elements. Two groups of years were distinguished in the general dataset during which the character of the atmospheric circulation played an important role in the ionic balance of the rainwater. The study area was shown to be characterized by predominantly acidic precipitation, with the pH of the water rarely exceeding 5.3 even at low concentrations of strong acid anions. In order to identify the factors that form the acidity of rainwater, the paper proposes to rank the initial dataset according to the value of fractional acidity. In the course of this separation, data blocks with a high and low degree of neutralization of the acid potential are distinguished. Within each data block, the relationships between the pH value and the concentrations of the major ions are defined. During the analysis, it was found that the mechanism of acid rain generation is determined by the mutual influence of natural and human-made sources. It was shown that compounds of dissolved organic carbon (DOC) were involved in both acidification and neutralization of rainwater. The results obtained indicate the predominance of natural rain acidification factors. However, during periods of cyclonic activity, even a slight increase in anthropogenic load leads to an increase in the acidity of atmospheric precipitation to critical values.

Keywords: background reference region, major-component composition, acidity of rainwater, transboundary transport, monsoon climate

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INTRODUCTION

The chemical composition of atmospheric precipitation and its acidity have been intensely studied over the past four decades. Results of such studies provide unbiased information on the air quality and offer the easiest and most informative way for assessing the atmospheric—anthropogenic pollution of natural ecosystems. Monitoring sites for the quantitative assessments of the spatiotemporal variability of the concentrations of major components have been organized in practically all densely populated areas across the world (Vet et al., 2014). At the same time, inadequately little studies were focused on areas distant from sources of anthropogenic contamination. At the same time, data acquired at background sites provide important indicators for estimating the effects of anthropogenesis, variations in regional climate conditions and biogeochemical processes, and the introduction of nutrients into ecosystems (Arzhanova and Yelpatyevsky, 2005;

Likens et al., 1987). Areas distant from contamination sources are usually characterized by weakly acidic precipitation with pH < 5.6—5.8, which were theoretically calculated for background concentrations of ammonia (NH_3) sulfur dioxide (SO_2), and carbon dioxide (CO_2) in the atmosphere (Brimblecombe, 1986; Horvath, 1986). In contrast to industrial centers, where more than 60% of the acid precipitation is controlled by strong-acid anions, the acidity of precipitation in geochemically clean areas is defined first of all by CO_2 (Izrael' et al., 1989). However, modern measurements of atmospheric components at background territories often discover significant anthropogenic impacts related to the long-distance transfer of contaminated air masses (Obolkin et al., 2013; Kondrat'ev, 2018; Baranov et al., 2020; Keene et al., 2015).

An important feature of climatic processes in Primorskii Krai, Russian Far East, is that its territory is affected by tropical and extratropical cyclones. This

predetermines the alternation of dry and very wet years in this area and the annual variability of the atmospheric precipitation. The average annual precipitation is 500−1200 mm, with 80% of it in the form of rain. The cyclones are formed in different physiographic and climatic zones in Transbaikalia, Mongolia, and the Yellow Sea, as well as over adjacent parts of the Pacific Ocean (Mezentseva et al., 2019). The composition of admixtures in air masses involved in the circulation of cyclones over the territory is controlled by compositional features of the atmospheric precipitations. It has been determined that the transboundary transport of acid-bearing compounds is the dominant factor affecting the ion balance and acidity of precipitations (Mukha et al., 2012; Kondrat'ev, 2018). For example, the transboundary flux in the city of Vladivostok accounts for 30% of the total sulfate and nitrate fallouts, and the current decrease in the pH in the urban and rural territories compared to the 1990s is by more than 15% (Kondrat'ev et al., 2017). The transfer of air masses formed above industrial provinces of China leads to falls of precipitation that contain elevated concentrations of strong-acid anions and are anomalously acidic in the Russian Far East (Mukha et al., 2012; Kondrat'ev et al., 2013; *Review of the State*..., 2016). An increase in the frequency of cyclones formed above southeastern seas, Japan, Mongolia, and Transbaikalia results in that precipitation falling in the territory contains elevated concentrations of nitrates and terrigenous admixtures (Kondrat'ev, 2018; Mezentseva et al., 2019; *Review of the State*..., 2019).

Concentrations of acid-bearing components in precipitation in the Russian Far East are nowadays much lower than in industrially more developed states of East Asia and in industrial regions in Europe (Duan et al., 2016; Chang et al., 2017; Keresztesi et al., 2019; Vet et al., 2014). Nevertheless, an increase in the anthropogenic load and the introduction of acid-bearing compounds with precipitation undoubtedly affect the biogeochemical balance of the woodland ecosystems and poses the threat of acidification of the biotic complexes (Kozhevnikova and Boldeskul, 2014; Kozhevnikova et al., 2017; Skirina et al., 2015; Du et al., 2017; Zhang et al., 2020). In view of this, the ionic composition and acidity of precipitation in areas distant from the main contamination sources, with preserved natural forests call for their active studying. Data acquired in the course of such studies provide background parameters of the composition and acidity of precipitations in mountainous wooded catchments for the further indexing of anthropogenic impacts at increasing acid loads in the territory. This study was centered on the seasonal and annual variability of the ionic composition and acidity of rainwaters in the forested basin of the Sikhote Alin mountainous region and in the identification of the sources controlling the composition and acidity. Inasmuch as rainfall events were registered in a representative catchment area during seasons contrastingly different in climatic parameters and precipitation amounts, data of this research can adequately reflect the chemical characteristics of rainwaters in the Central Sikhote Alin.

MATERIALS AND METHODS

Study Area

The study area is located in the continental part of Primorskii Krai, on the Ussuri−Khanka (western) macroslope of the Sikhote Alin mountainous territory. More than 90% of its surface area is overgrown by forests of different composition and age, which play a leading role in regulating the aquatic regime and significantly affect the amounts of precipitation and its chemical composition (Zhil'tsov, 2008; Kozhevnikova and Dyukarev, 2011; Kozhevnikova and Boldeskul, 2014). The distribution of the precipitation strongly depends on the mountainous topography of the territory and the character of the cyclonic activity. Monitoring sites for studying the chemical composition of the rainwaters were organized at the Upper Ussuri Forest Station (UUFS) of the Federal Scientific Center of the East Asia Terrestrial Biodiversity, Far East Branch, Russian Academy of Sciences. UUFS (43.6°−44.3° N, 133.5°−134.5° E) in the basin of the Upper Ussuri River is a biosphere site constrained between watersheds (Fig. 1b). The study area is surrounded by mountain ranges, is located at a distance of approximately 400 km away from the seashore, and is situated more than 20 km away from major traffic arteries and population centers. The UUFS landscapes have natural conditions typical of the middle mountainous belt of the Southern Sikhote Alin and are covered by mixed coniferous-broad leaved forests preserved in this area. The climate of the study area is humid and moderately cold. The average air temperature from May through October is 11.8°C (long-term data), and the precipitation over this period ranges from 330 to 1079 mm, with 70% of the falling out in June−September (Kozhevnikova, 2009). The cyclonic activity of variable intensity controls the annual distribution and long-term variations in the total amount of precipitation, with deviations from the norm reaching 40−170% in summer and autumn. The average number of days with precipitation of various intensity is 125 to 190 per year.

Sampling and Chemical Analysis of the Rainwaters

Rainwaters were systematically sampled for their chemical analysis from May to October at two sites at elevations of 560 and 670 m above sea level. Meteorological data were determined at these sites by an WS GP1 Delta-T (Great Britain) portable weather station, which registered (once in every 15 min) the temperature, air humidity, precipitation, and wind structure throughout the whole monitoring period. Rainwater samples were collected using cone-shaped plastic col-
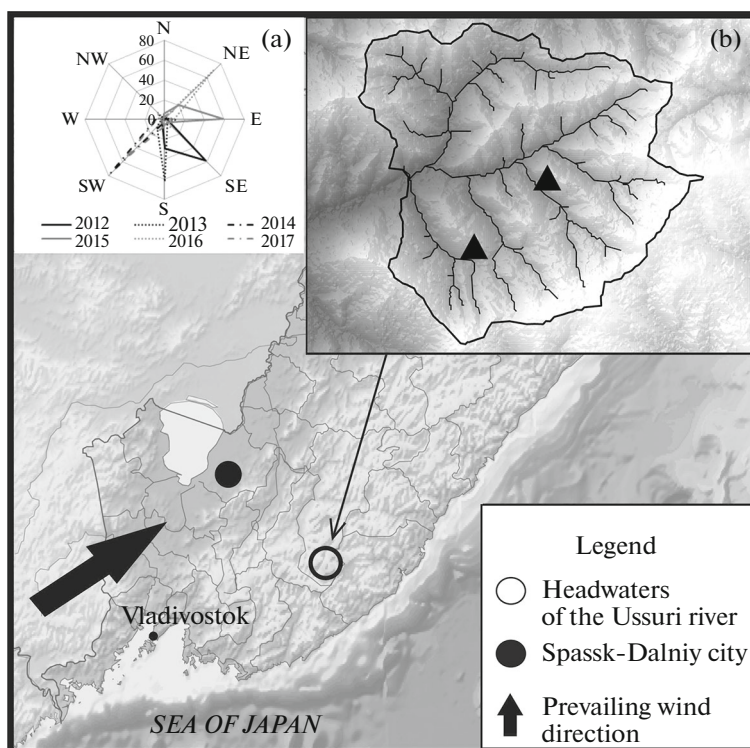
Fig. 1. Map of the Upper Ussuri Forest Station (UUFS). Solid triangles are sites with precipitation collectors. Insets: (a) wind diagram for UUFS during the warm period of 2012−2017; (b) location map of UUSF.

lectors coupled to plastic bottles (2−5 L). The collectors were installed in clearings in the woods at 3−4 m from trees and edifices and 100−150 cm above the soil surface. At least three rainfalls with precipitation more than 3 mm were sampled monthly. If a rainfall lasted for more than one day, two water portions were collected: one at the beginning and the other late in the event. The collectors were covered with a capron mesh to preclude falling large insects and organic remnants into the samples and were cleaned after each rainfall. In spite of these measures, the samples contained the material of mineral aerosol fallouts, fine pollen, etc. The total number of the collected and analyzed rainwater samples was 94, and we interpreted them as integral samples of the wet and dry deposition.

On the sampling dates, the atmospheric precipitation samples were analyzed for pH and alkalinity (by conventionally used potentiometric titration techniques; *Manual*..., 1977). Before their further analysis, the samples were filtered through preliminarily weighed membrane filters with 0.45-μm pores. The aliquots for analysis for cations were acidified by nitric acid to pH ~ 2. The samples were stored in a refrigerator for one to two weeks and delivered to the Center for Landscape Ecodiagnostics and GIS Technologies of the Pacific Geographical Institute, Far East Branch, Russian Academy of Sciences, to analyze the waters for all principal parameters. Concentrations of anions (Cl^-, NO_3^-, and SO_4^{2-}) were determined on a Shi-

madzu LC 10Avp liquid chromatograph, and cations were analyzed by atomic absorption (Ca^{2+} and Mg^{2+}) and emission spectrometry (K^+ and Na^+) on a Shimadzu AA 6800 spectrophotometer. Concentrations of dissolved organic carbon (DOC) in the waters were determined in the form of NPOC (nonpurgeable organic carbon) on a Shimadzu TOC-V$_{CPN}$ TOC analyzer.

The completeness and quality of the analytical data were controlled by the ion-balance method. The balance of cations and anions was assayed by the formula $R1 = 100\%(K - A)/(K + A)$, where K and A are the totals (in μeq/L) of all major cations and anions. Data on waters with TDS < 50 μeq/L deemed reasonably reliable at $R1 < \pm 30\%$ (*Network Center* ..., 2010). Deviations from this value for 10−25% were annually found in some of the rainwater samples. Because of technical limitations, we have not determined the NH_4^+ cation and organic acids. The most commonly identified misbalance was that in the totals of anions exceeded the totals of cations because the ammonium ion concentration was not determined. According to literature data, rainwaters in the territory contain 10 to 45% ammonium among the totals of cations (*Review of the State*..., 2016, 2019).

Data Analysis

The database for the calculations and statistical analysis was grouped according to time intervals. Con-

Table 1. Average values of meteorological parameters and concentrations of chemical components in the warm periods of 2012−2018

Meteorological parameter	2012	2013	2014	2015	2016	2017	2018	2012−2014	2015−2018
Temperature, °C	16.3	16.3	16.1	16.0	15.8	15.2	15.7	16.3	15.7
Air humidity, %	80	87	83	87	90	69	88	83	84
Precipitation, mm	510	438	517	334	723	382	872	489	578
% of normal value	114	98	116	75	162	86	196	102	121
Chemical components	Weighted mean, µeq/L								
HCO_3^-	9.50	2.89	2.63	15.8	24.7	30.8	20.2	5.00	22.9
Cl^-	25.5	5.95	10.6	17.3	6.80	4.98	8.45	14.0	9.38
SO_4^{2-}	31.2	28.6	30.5	17.5	25.3	22.7	5.33	30.1	17.7
NO_3^-	21.0	14.6	16.0	17.6	20.3	18.2	5.14	17.2	15.3
Ca^{2+}	22.3	7.58	17.0	8.89	21.6	23.8	13.5	15.6	16.9
Mg^{2+}	6.19	2.17	3.79	1.87	4.35	4.51	2.95	4.05	3.42
K^+	31.2	4.67	7.32	4.27	9.91	11.2	3.52	14.4	7.23
Na^+	5.27	2.63	6.89	1.67	5.37	5.96	1.27	4.93	3.57
H^+	16.4	17.4	9.36	17.0	9.11	6.37	9.01	14.4	10.4
TDS, mg/L	6.15	3.09	3.82	3.92	5.22	5.38	2.58	4.35	4.27
DOC, mg/L	2.69	1.34	1.85	1.29	2.27	2.52	1.18	1.96	1.82

* Here and below, TDS is total dissolved solids.

centrations of major components were determined as weighed means per volume of precipitation per warm season. In discussing the acid−base properties of the rainwaters, we used the method of fractional acidity (Balasubramanian et al., 2001; Walna, 2013; Keresztesi et al., 2019). Fractional acidity FA (Formula 1) was used to estimate the degree of neutralization of fallen rainwaters due to nitric and sulfuric acids. The closer the FA value to 1, the lower the acidity percentage neutralized by alkaline components.

$$FA = H^+/(SO_4^{-2} + NO_3^-). \qquad (1)$$

Formulas (1) and (2) were derived based on the fact that the key acidifying ions in the precipitations were assumed to be SO_4^{2-} and NO_3^-. The totals of these anions are often referred to as acidifying potential, whereas the totals of major cations are referred to as the neutralizing potential (Safai et al., 2004; Zhao et al., 2013; Zhang et al., 2014). The balance between major cations and acidifying anions was assayed by comparing the neutralizing (ΣK) and acidifying (ΣACK) potentials (Zhao et al., 2013)

$$\frac{\sum K}{\sum ACK} = \frac{Ca^{2+} + Mg^{2+} + K^+}{SO_4^{2-} + NO_3^-} \qquad (2)$$

In addition, the role of each cation K_i in the neutralization of acids was explained by calculating the neutralization factor (Zhang et al., 2014; Keresztesi et al., 2019)

$$NF = K_i/(SO_4^{-2} + NO_3^-). \qquad (3)$$

Concentrations of cations in the formulas is expressed in µeq/L.

For comparative analysis, we have statistically processed the data using the Statistica 10 (StatSoft) program package. The confidence level was assumed to be 95% ($p < 0.05$).

RESULTS AND DISCUSSION

Meteorological Conditions

The air temperature and humidity, the character of the precipitation, and the wind structure are the principal parameters able to affect the chemical composition of precipitation. Meteorological parameters were monitored in the immediate vicinities of the sampling sites. Analysis of these parameters has shown that the period of time in May through October in 2012−2018 were mildly humid, low-wind, and hot (Table 1). The air temperature was 5−12% higher than the mean annual values. The wind diagram (Fig. 1a) indicates that the dominant winds were southeasterly and south–

westerly. The wind velocity was only rarely higher than 2 m/s. The exceptions were the years 2016 and 2018, when the maximum wind velocities during cyclones reached 6−10 m/s.

Most of the studied years were characterized by uneven precipitation falls and by long-lasting dry periods in between. Moisture was often brought to the catchment in the form of brief showers, which were formed due to circulation of local air currents. The frequency of precipitation in an amount of >10 mm increased in the driest years and was close to 80% of all rainfall events. Most of the precipitations fell during cyclones. Precipitation of intensity >50 mm/day was detected annually, except only 2015. The total precipitation amounts in 2015−2018 were within the climatic norms. The summer through autumn of 2015−2018 were marked by alternating dry and extremely humid years (Table 1). The amounts of precipitation in July through September in 2015 and 2017, were 15 to 25% lower than the normal values, and those in 2016 and 2018 were 1.6 to 2 times above the normal values.

Ionic Composition of the Rainwaters

Table 1 presents principal data on the major-component composition of rainwaters in UUFS. The rains are characterized by broad variations in the concentrations of most ions, whereas their maximum concentrations were sometimes five- to tenfold higher than the average values for the warm period. This variability is explained by the amounts, frequency, and duration of the rainfalls, the background temperature, and the air humidity. As was mentioned in (Walna, 2013), the high variability of the concentrations of ions affects the ecological properties of the plants and can destabilize the ecosystem.

Rainwater samples from UUFS mostly had TDS = 3−15 mg/L, 4.81 ± 4.30 mg/L on average. These values correspond to the regional background (Chudaeva et al., 2008) and are close to values obtained for natural reserves in the Russian Federation (Svistov et al., 2015; *Review of the State...*, 2019). The maximum variability of the total concentrations of ions was found in precipitations whose amounts were no greater than 10 mm. Their average TDS = 7.10 ± 6.43 mg/L. During the vegetation season, the composition of the precipitation, particularly air-mass ones, strongly depends on the activation of biogenic processes (Arzhanova and Yelpatyevsky, 2005). The highly mineralized water samples taken during this period had TDS > 10 mg/L and DOC = 4−14 mg/L. The frequency of rainfalls with TDS higher than the mean annual precipitation is higher than 47%, and their balance is most often dominated by the anions of strong acids (Boldeskul et al., 2014). The TDS of rains whose precipitation amounts are >10 mm decreases to 11−0.5 mg/L at an average of 3.46 ± 2.55 mg/L, which is explained mostly by dilution. The frequency of rains with precipitation amounts >10 mm and TDS higher

than the mean annual precipitation is 22%, but only two of the samples had TDS > 10 mg/L. Discrete water samples collected at the end of long-lasting intense precipitation falls had TDS < 1 mg/L.

The year-to-year variability in the concentrations of major ions in UUFS rainwaters (Table 1) may result from the activity of cyclones of various type coming to the territory. We have distinguished two groups of years in the general dataset (Table 1). In 2012−2014, precipitation was brought to UUFS mostly with continental cyclones, whose air masses were enriched in terrigenous admixtures and acid-bearing compounds (Mezentseva et al., 2019). Sulfates and nitrates dominated among the anions in these rainwaters. The cyclonal precipitations were also rich in major cations, especially, Ca. However the totals of major cations in 70% of the samples were lower than the totals of the strong-acid anions (Table 3). The formula of the rainwaters (proportions of major ions in %-equivalents) according to M.G. Kurlov (Posokhov, 1975) for this period is

$$M_{<0.01} \frac{SO_4^{2-}45NO_3^-24Cl^-19HCO_3^-12}{H^+41Ca^{2+}27K^+16Na^+9Mg^{2+}7} \, pH\,3.8\text{--}5.7. \quad (4)$$

It is also worth mentioning that the warm season of 2012−2014 was characterized by a brief duration of rainfalls and long-lasting (up to 7−14 days) interludes between them. After the rainless periods, we collected relatively concentrated solutions with elevated concentrations of potassium and chloride ions of continental provenance (Kozhevnikova et al., 2017). An analogous increase in K^+ concentrations in summertime was also registered in precipitations in other forested territories (Yelpatyevsky 1993; Stallard and Edmond, 1981; Likens et al., 1994; Berger et al., 2008). We believe that the high K^+ concentrations are explained by that they are brought with aerosols carrying mineral and biogenic compounds.

Active measures taken by the Chinese administration to reduce the SO_2 emissions (Zheng et al., 2018) and an increase in the frequency of southerly cyclones (Mezentseva et al., 2019) were most likely responsible for the decrease in the concentrations of major acid agents in the rainwaters in 2015−2018, and this strongly affected their concentrations among the anions (Formula (5)). According to (Zhang et al., 2020), the precipitation falling in high-mountain forested areas in China in 2017−2019 contained three-fold lower concentrations of sulfates and ~9% higher concentrations of nitrates compared to earlier data. These authors stress that the acidity of the precipitation decreased, but the pH of more than 46% of the samples was lower than 5.6. The role of typhoons in the decrease in sulfate concentrations and the increase in Ca ones in rainwaters was discussed in (Mkadam et al., 2008).

The rainwaters studied in UUFS in 2015−2018 were found out to be enriched in nitrates relative to
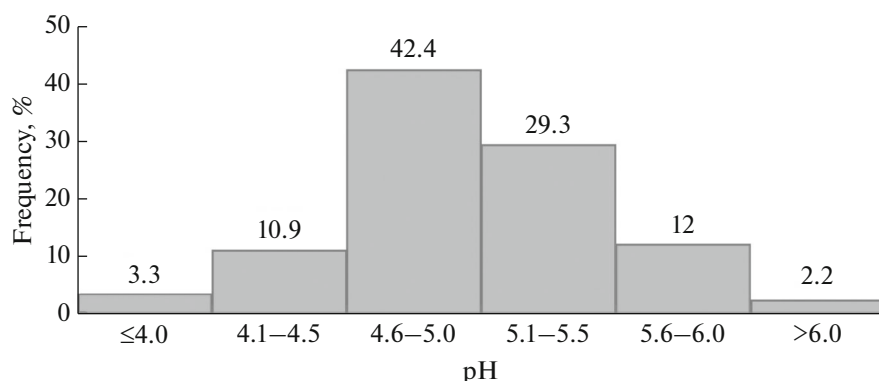
Fig. 2. Distribution of rainwaters in UUFS according to their acidity groups.

sulfates, more than twofold enriched in carbonates, and became ~1.5 times richer in calcium. Concentrations of hydrocarbonates in the summer–autumn precipitation were 14–28% higher than during the analogous period of 2012–2014 (Table 1). The equivalent content of HCO_3^- among the anions was 10–20% higher than in 2012–2014 and was 50% higher than the contents of sulfates during the passage of typhoons, which predetermined the hydrocarbonate type of the rainwaters. The chemical composition formula for the years 2015–2018 is

$$M_{<0.01} \frac{HCO_3^- 44 \ SO_4^{2-} 24 \ NO_3^- 20 \ Cl^- 12}{Ca^{2+} 39 \ H^+ 35 \ K^+ 12 \ Na^+ 9 \ Mg^{2+} 6} pH 4.3\text{--}6.1. \quad (5)$$

This group of years includes very humid years with long-lasting intense rains (Table 1). An increase in the frequency of rainfalls with precipitation amounts greater than 20 mm/day was the most probable reason for the decrease in the concentrations of major ions in 2015–2018 compared to the previous period of time. The average ratio of the totals of major cations and strong-acid anions was higher than 1 in half of the analyzed water samples. Consequently, the neutralizing effect enhanced, and the frequency of rainfalls with concentrations of H^+ free ions <5 μg/L increased.

Acidity of the Rainwaters

Atmospheric precipitation is usually characterized by a low buffer capacity (Yelpatyevsky, 1993). The main acidifying components of precipitation are sulfuric and nitric acids. The long-distance transfer of compounds and natural conditions of the rain generation affect the acidity of rainwaters. For example, more acidic rains occur when air humidity is higher (Svistov et al., 2015), with this parameter usually high in UUFS in June through September and reaching 75–90% (Table 1).

Biotic components in the study area can also be sources of natural emissions of carbon and sulfur dioxides, nitrogen oxide, and organic acids. The contribu-

tion of CO_2 to the acidity of precipitation in background areas is close to 80%, and natural SO_2 concentrations at low concentrations of alkaline agents can increase the acidity of rainwaters to pH 4.5 (Izrael' et al., 1989). Water-soluble low-molecular organic acids may also play an important part in the acidification of precipitation (Keene and Galloway, 1984; Sun et al., 2016). It has been determined (Likens et al., 1987; Huo et al., 2010; Keene et al., 2015; Conradie et al., 2016; Niu et al., 2018) that the contribution of organic anions to the potential acidity of rainwaters in background areas can amount to 10–69%, and their source during the vegetation period is plants. The carbon isotope composition indicates that more than 80% of the formic and acetic acids is generated by biogenic sources (Glasius et al., 2001). These organic acids are important acidification agents in areas distant from anthropogenic sources (Millet, 2012; Niu et al., 2018; Stavrakou et al., 2012).

DOC concentrations in UUFS rainwaters varied from 0.3 to 6.7 mg/L, which is comparable to the totals of the mineral components. The weighted mean values (Table 1) are consistent with data on 86 monitoring sites worldwide (Iavorivska et al., 2016). The DOC concentrations increased during periods of active vegetation and elevated temperature, which may indicate that biogenic emissions of plants can serve as an important source of organic compounds in rainwaters. DOC in cyclonal precipitation generated above industrial centers and southeastern seas can partly be brought from anthropogenic and/or marine sources (Sun et al., 2016).

Over the monitoring period, pH varied in UUFS from 3.82 to 6.10 and was 4.90 ± 0.51 on average. If precipitation with pH ≤ 5.0 is viewed as acidic, it can be concluded that more than 50% of the analyzed waters belong to this category (Fig. 2). About 14% of the rains were very acidic (pH ≤ 4.5), and 3% of them had pH < 4.0. Precipitation with pH ≥ 5.6 was determined in 14% of the analyzed samples. Comparison of pH values in UUFS and in a forested basin in southern China (Huang et al., 2012) shows an analogous fre-

Table 2. Matrix of the Pearson correlation coefficients ($n = 92$, $p < 0.05$) for the major chemical components of rainwaters in the Upper Ussuri Forest Station (UUFS)

Component	DOC	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+
DOC	1.00									
HCO_3^-	–	1.00								
Cl^-	0.61	–	1.00							
SO_4^{2-}	0.47	−0.31	0.21	1.00						
NO_3^-	0.48	–	0.30	0.80	1.00					
Ca^{2+}	0.53	–	0.35	0.69	0.64	1.00				
Mg^{2+}	0.67	–	0.49	0.43	0.67	0.81	1.00			
K^+	0.69	–	0.81	0.24	0.41	0.62	0.70	1.00		
Na^+	0.44	–	0.46	0.29	0.32	0.43	0.42	0.46	1.00	
H^+	0.21	−0.49	–	0.68	0.42	0.35	0.39	–	–	1.00
TDS	0.70	–	0.57	0.78	0.80	0.70	0.62	0.62	0.45	0.28

Dashes mean the absence of correlations.

quency of precipitation with pH > 5.5. However, acid rains (pH < 4.5) are more abundant in southern China, and those with pH from 4.5 to 5.5 are 28% less abundant than in UUFS. These differences in the distribution of acidity are explained by higher concentrations of both acidic anions and acid-neutralizing cations in China (Du et al., 2018).

The acidification of precipitation in summer–autumn, 2012–2017, was detected at most rural sites of the EANET monitoring network (Table 3). It should be stressed that the average pH values in UUFS rainwaters are lower than the values measured at the Primorskaya EANET rural site in the study area, although the total (SO_4^{2-} + NO_3^-) content at this site is approximately twice higher. This fact may be explained by higher concentrations of neutralizing cations in the rainwaters (Table 3).

The year-to-year and season-to-season variability in the acidity of rainwaters is related to the variability of the concentrations of major components responsible for the cation–anion balance. The seasonal average pH values were only occasionally higher than 5.3. The smallest pH variations were found in 2012–2014. The pH values of more than 70% of the rainwater samples were no higher than 5, and the seasonal average pH value was then 4.85. In 2015–2018, the frequency of rains with pH< 5 decreased to 49%, and the average pH values increased to 5.18.

The enhancement of the acidity of rainwaters during this period was associated with a proportional increase in the concentrations of sulfates, nitrates, and organic carbon (Table 2). As seen in the table, the main contribution to the acidification of the rainwaters was made by SO_4^{2-} and NO_3^- ions. Their equivalent

fractions among the anions varied from 3 to 72 and from 3 to 48%, respectively. The average SO_4^{2-} and NO_3^- concentrations can be characterized as corresponding to the background level (*Review of the State*..., 2019), although their concentrations in some of the rainwater samples reached 3−14 and 1−10 mg/L, respectively. According to qualitative estimates of environmental changes, these concentrations of acid-forming anions exceed the standardized ecologic values (Svistov et al., 2010). In view of this, in discussing the sources of the acidity, concentrations higher than 3 mg SO_4^{2-} and 1 mg NO_3^- were viewed as elevated. The relatively high SO_4^{2-} and NO_3^- concentrations indicate that they were caused by analogous sources. The low correlation coefficients between H^+ and SO_4^{2-} and NO_3^- anions may be explained by that the acidity is controlled not only by these ions but also by interactions with other components in the waters (Huang et al., 2008). Rainwaters with elevated SO_4^{2-} and NO_3^- concentrations can be, in the same area, either alkaline or acidic (Anatolaki and Tsitouridou, 2009). These authors presented arguments to prove that the pH of precipitation in their study area is controlled by calcium concentrations in the waters. Moreover, the acidity of rainwater may also depend on the variation dynamics of its anionic composition. For example, sulfates were dominant in the salt balance of waters (Formula 4) in our study area in 2012–2014. Comparative analysis of the pH values and SO_4^{2-} concentrations in the rainwaters during this period indicates that the correlation between these parameters was nearly linear: $r = -0.75$, $p < 0.05$. No correlation between pH

Table 3. Medians of the acidity (pH) and ratios of major ions in the rainwaters of UUFS and EANET rural monitoring sites in June$-$September, 2012$-$2017

Site	Country	pH	SO_4/NO_3	$\Sigma K/\Sigma ACK$	$SO_4 + NO_3$, μeq/L	FA	NF Ca^{2+}	NF K^+	NF Mg^{2+}	NF NH_4^+
UUFS (this study)	Russia	4.80	1.26	0.67	30.1	0.49	0.53	0.15	0.10	$-$
Listvyanka	Russia	4.76	3.32	0.46	38.0	0.39	0.30	0.04	0.07	0.31
Mondy		5.28	1.45	0.76	12.9	0.37	0.68	0.11	0.13	0.48
Primorskaya		5.23	2.04	0.69	54.3	0.09	0.38	0.08	0.13	0.44
Jin Yun Shan	China	4.73	2.74	0.54	95.8	0.12	0.45	0.03	0.06	0.45
Xiaoping		4.77	1.51	0.64	56.8	0.17	0.42	0.04	0.10	0.49
Oki	Japan	4.84	2.08	0.75	39.3	0.40	0.15	0.07	0.41	0.22
Yusuhara		4.90	2.97	0.36	17.8	0.79	0.10	0.03	0.17	0.24
Imsil	S. Korea	5.52	1.12	0.63	40.0	0.05	0.08	0.12	0.03	0.73
Kanghwa		4.65	1.17	0.41	65.6	0.25	0.09	0.09	0.03	0.83
Kanchanaburi	Thailand	5.78	1.58	1.16	6.96	0.15	0.94	0.11	0.36	0.88
Sakaerat		5.35	1.06	0.76	18.4	0.20	0.63	0.04	0.09	1.00

The coefficients were calculated by Formulas (1)$-$(3), dashes mean the absence of data. Source data obtained from open sources of EANET monitoring network (https://monitoring.eanet.asia/document/public/index).

and concentrations of the anions of strong acids was detected in 2015$-$2018. This is likely explained by the increase in the concentrations of hydrocarbonates and calcium (Formula (5)). A weak but significant correlation at $p < 0.05$ between H^+ and DOC is due to inverse relationship between these components in the less-acid rainwater as shown below. With regard to the aforementioned, it should be emphasized that the database on many years requires a more detailed analysis of dependences between chemical components in various pH ranges.

Analysis of Factors Controlling the Acidity of Rainwaters

To evaluate the contribution of the various acidifying and neutralizing compounds of the rainwaters by Formulas (1)$-$(3), we have calculated the fractional acidity and neutralizing capacity of the cations. In addition, we have determined the rations of the equivalents of SO_4^{2-}/NO_3^-, which is a measure of the relative contributions of sulfur and nitrogen to the total acidity of rainwaters (Migliavacca et al., 2005).

The average SO_4^{2-}/NO_3^- ratio at UUFS over seven years was 1.73 ± 1.65, which is consistent with data on rural sites in the EANET monitoring network (Table 3) and provides grounds to think that sulfur is the main acidifying element. In 2015$-$2018, the sulfur concentration had decreased, whereas the contribution of nitrates had increased in 37% of the studied samples. The decrease in both the concentration and the equivalent content of sulfates among the anions was likely one of the factors responsible for the decrease in the acidity of the rains in 2015$-$2018 compared to earlier years.

The calculated fractional acidity (Formula (1)) shows that the FA of the rainwaters varied from 0.02 to 2.12 and was 0.60 ± 0.52 on average. The FA value was higher than at most of the EANET monitoring sites (Table 3), which indicates that acidity caused by SO_4^{2-} and NO_3^- was only partly (by approximately 40%) neutralized by major cations. The conditions of acidic components in rainwaters were different in forested mountainous basins in Bulgaria and in rural areas in China (Zhao et al., 2013; Niu et al., 2017) and Europe (Keresztesi et al., 2019; Szep et al., 2018). The loads of strong acids in the rains of these areas were almost one order of magnitude higher than that measured in UUFS, and they were neutralized by 60$-$98% (FA = 0.01$-$0.40). This is reportedly explained by that precipitations in these areas contain much calcium. In a high-mountain background site, the average FA was 1.16 ± 0.89 (Khan et al., 2018). The acidic nature of the rains (pH 4.98) was explained by these authors by that the concentrations of introduced cations were lower than those of strong-acid anions. It is obvious that Ca^{2+} plays an important role in neutralizing the acidity of precipitations, and this has been emphasized by many researchers (Smolyakov et al., 2006; Conradie et al., 2016; Safai et al., 2004). Zhao et al. (2013) state that the acidification of rainwaters is weaker if the waters contain more calcium than ammonium because calcium hydroxide is a stronger base. The calculated neutralization factor NF (Formula (3)) also indicates that the dominant cation controlling the acidity caused by SO_4^{2-} and NO_3^- in this basin was also Ca^{2+} (Table 3). The farness of the area from seashores predetermines the very low (compared to rainwaters in typical coastal areas; Chudaeva, 2008; Huang et al.,

Table 4. Median values of the concentrations of major components and TDS (mg/L) in rainwaters with various changes in the fractional acidity (FA) and pH

Component	FA < 0.5		FA > 0.5		FA > 1.0
	pH < 5.0	pH ≥ 5.0	pH < 5.0	pH ≥ 5.0	
HCO_3^-	0.18	1.46	0.05	1.70	0.98
Cl^-	0.48	0.287	0.20	0.10	0.10
$SO_4^{2-} + NO_3^-$	3.09	1.95	2.54	0.51	0.40
ΣK	1.37	0.67	0.70	0.24	0.27
TDS	5.48	4.40	3.55	2.37	1.89
DOC	3.54	1.20	2.14	0.75	0.50

2008) calcium and magnesium concentrations, which were <0.1 mg/L in 80% of the analyzed samples (Table 1). The average potassium concentrations were notably higher, and it was determined to be the second most important cation neutralizing strong acids (Table 3). Analysis of the Ca^{2+} and K^+ concentrations shows that the concentrations of these cations most commonly lie within the range of 0.1–0.5 mg/L. Samples with Ca^{2+} and K^+ concentrations higher than 1 mg/L were found in 7–8% of the analyzed rains. The contributions of potassium to the cation balance is greater during dry seasons, whereas the contributions of calcium and magnesium are more significant during wet periods.

Thus, we assumed the total Ca^{2+}, K^+ and Mg^{2+} concentration as the neutralizing potential (ΣK in Formula (2)). In ~59% of the analyzed samples, ΣK was lower than the acidifying potential (ΣACK in Formula (2)). Inasmuch as the acidity of the rainwaters is controlled by the balance between cations and anions, a deficit in major cations in rainwaters may be an important factor of their acidification.

To analyze in more detail how the acidity and major-component composition of the rainwaters are correlated, we have ranked data on them according to their fractional acidity FA values. The data of each FA set were further subdivided into those on rains with pH < 5.0 and pH > 5.0 (Table 4). As mentioned above, if the acidity of rainwater is caused by nitric and sulfuric acids and is not neutralized, then the fractional acidity FA should be 1 (Keresztesi et al., 2019). The lower the FA value, the greater the degree of neutralization of acidic anions. Because of this, we denoted the dataset with FA < 0.5 as rains with a high degree of neutralization, and those with FA > 0.5 were regarded as insignificantly neutralized. A separate group comprised rains in which the proton load was greater than the concentrations of major acidifying anions (FA > 1). Acidity in Table 4 was subdivided based in the fact that pH 5.0 in background forested areas is often assumed as the lower boundary for the natural acidification of precipitation (Galloway et al., 1982; Arzhanova and Yelpatyevsky, 2005).

Rains with high degrees of neutralization of sulfuric and nitric acids (FA < 0.5) made up 51% of the analyzed samples. Their waters are more concentrated than in other rains (Table 4), with a broad pH range of 4.0–6.1. Although the degree of neutralization of the rains is high, rainwater samples with pH < 5.0 make up 60% of the dataset with FA < 0.5. The pH of these rains strongly correlated with their sulfate and nitrate concentrations (Fig. 5), with these anions accounting for 40%-equiv. of all anions in most of the samples. The neutralization of strong acids was 65% on average and was caused mainly by the elevated calcium concentrations. The correlation ($r = 0.83$) indicates that the Ca^{2+} originated from the same sources as the sulfates. The concentration of the former in the rains was 1.4 to 4 times higher than the average values over the monitoring years. This Ca^{2+} concentration at low concentrations of other cations seems to be insufficient for the complete neutralization of the acids, and this resulted in the acidification of the rainwaters. Inasmuch as high SO_4^{2-}, NO_3^-, and Ca^{2+} concentrations were found in the cyclonal precipitation coming to Primorsky Krai from economically well-developed areas in southeastern Asia, it is reasonable to conclude that the components can be transferred for long distances and that anthropogenic contamination takes place (Kondrat'ev et al., 2017).

At acidity of the precipitation up to 10 µg/L (pH > 5.0), the neutralization of strong acids is enhanced and is >80%. This strong neutralizing effects stems from that the totals of major cations are greater than that of ($SO_4^{2-} + NO_3^-$) in 70% of the samples. The rainwaters are sulfate–carbonate and mostly contain 2 to 7 mg/L DOC. This group includes the most strongly mineralized precipitations whose pH is close to the equilibrium value of 5.6. The acidic potential of these rains is almost completely (75–98%) neutralized. The precipitations with pH > 5.0 show a direct correlation between their pH and DOC (Fig. 3a), which may indicate that organic compounds may have been one of the factors neutralizing strong-acid anions under these conditions.
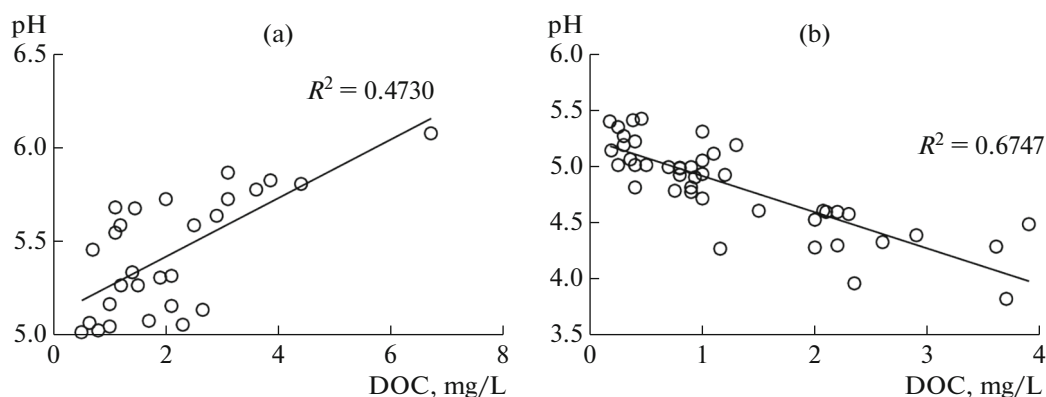
Fig. 3. Correlation between the acidity of precipitation and its DOC concentration: (a) for rainwaters with FA < 0.5 (pH > 5.0) and (b) rainwaters with FA > 0.5.

Regression analysis of the dataset on the rains whose fractional acidity FA = 0.5 to 3.2 shows a negative linear correlation between their pH and DOC (Fig. 3b). The pH range of the rains with a low degree of neutralization (FA > 0.5) was 3.8−5.4. The precipitation is characterized by a high variability of its TDS, concentrations of ions, and the $\Sigma K/\Sigma ACK$ ratios. The rainwaters with pH 3.8−4.9 have the maximum concentrations of both strong acids and major cations (Table 4), and their TDS lies commonly in the range of 3−7 mg/L. The equivalent concentrations of $(SO_4^{2-} + NO_3^-)$ among all ions in half of the rainwater samples fall within the range of 50−76%, whereas the concentrations of major cations were no lower than 20%-equiv. The role of the neutralizing potential (ΣK) was significant (Table 5), but the coupled effects of strong acids (ΣACK) and organic components (Fig. 3b) likely played a determining role in the acidification of the rains. The low mineralized waters (M < 3 mg/L) with acidity up to 10 $\mu g H^+/L$ came from the atmosphere washed by frequent rains. Concentrations of strong acids in these samples were at the background level (0.1−0.7 mg/L), and the concentration of hydrocarbonates increased to 63%-equiv. A determining role in the neutralization of strong anions was played by calcium and potassium, but their concentrations were two to three times lower than in the rains with pH < 5.0. More than half of the rains was brought with tropical cyclones, whose trajectories usually pass above Japan (Mezentseva et al., 2019). The emissions of this country are dominated by nitrogen oxides (Kim et al., 2004), and this was reflected in the SO_4^{2-}/NO_3^- ratios of the rainwaters. The main donor of hydrogen ions was determined to be nitric acid. The low degree of neutralization of the rainwaters with pH > 5.0 may have been caused by the introduction of hydrogen ions with chlorides and organic components (Table 5, Fig. 3b). The acidification of precipitations of low degree of neutralization is thus a coupled affect of anthropogenic and natural sources, with the obvious predominance of the latter.

Water samples with FA > 1 corresponded to periods of long-lasting precipitation falls in amounts no less than 25 mm, and these samples made up approximately 16% of all of the analyzed rainwater samples. The fractional acidity coefficient FA = 1.1−3.2. The rainwaters were weakly acidic, with low TDS. The pH values varied from 4.6 to 5.3, and the TDS was no higher than 2.8 mg/L. Correlation analysis has revealed strong significant correlations between pH and the concentrations of nitrates and chlorides (Table 5). It is quite probable that additional protons were brought together with chlorides, and this may explain the increase in the threshold FA value and the acidification of the rains to pH < 5. The background concentrations of sulfates and nitrates, the dominance of hydrocarbonates among the anions, and the low TDS (Table 4) suggest natural acidification of the precipitation with FA > 1.

Sources of the Acidity

The analysis of the ionic balance of the rains presented above has shown that their acidity is controlled by natural and anthropogenic factors. The principal criteria applied to identify the sources of acidification of the rainwaters in the forester mountainous basin were as follows: (1) the $(SO_4^{2-} + NO_3^-)$ concentration, (2) the equivalent content of HCO_3^- relative to that of $(SO_4^{2-} + NO_3^-)$, and (3) the ratio of the neutralizing and acidifying potentials ($\Sigma K/\Sigma ACK$).

A leading role of natural sources of acidification is evident from the background-level (<1 mg/L) concentrations of major acidic anions and elevated concentrations of hydrocarbonates ($HCO_3^- > SO_4^{2-} + NO_3^-$) and major cations (Table 6) in the waters. The TDS = 95% of these rainwaters is within the range of 1−3.5 mg/L. This group also comprises all samples with FA > 1. The donors of hydrogen ions in these waters were determined to be the anions of strong, and perhaps weak, acids. The concentrations of major cations,

Table 5. Correlation between pH and major components and relations between major cations and strong-acid anions ($\sum K/\sum ACK$) in rainwaters in UUFS with various changes in the fractional acidity (FA) and pH

Component	FA < 0.5		FA > 0.5		FA > 1.0
	pH < 5.0	pH ≥ 5.0	pH < 5.0	pH ≥ 5.0	
HCO_3^-	0.48	**0.64**	**0.74**	0.40	−
Cl^-	−	−	−	**−0.55**	**−0.60**
SO_4^{2-}	**−0.72**	−	**−0.92**	**−0.63**	**−0.48**
NO_3^-	**−0.65**	−	**−0.89**	**−0.88**	**−0.66**
DOC	−	**0.70**	**−0.74**	−0.47	**−0.78**
$\sum K/\sum ACK$	0.35	0.33	**0.64**	**0.95**	−

Numerals printed in semibold correspond to significant, $p < 0.05$, correlations, correlations for the rest are at $p < 0.10$, dashes mean the absence of correlations.

Table 6. Fractional acidity (FA), TDS, and concentrations of major components in the rainwaters of various sources controlling their composition

Source	n	FA	pH	% of the totals of anions				% of the totals of cations		TDS, mg/L	DOC, mg/L
				HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	H^+		
Natural	40	0.99	5.09	58.7	11.1	15.3	13.0	28.8	46.8	2.31	0.90
Mixed	32	0.24	5.21	36.2	11.8	28.8	22.9	35.7	19.6	4.16	1.90
Anthropogenic	20	0.24	4.79	2.62	7.51	49.7	30.5	34.7	32.6	6.87	2.30

The table presents median concentrations of components, n is the number of samples.

chlorides, and nitrates in the waters are strongly interrelated with the DOC concentrations. The common source providing all of them for the atmosphere may be the biogeocenosis. The natural acidification of the rest of the low-mineralization rainwaters proceeds proportionally to the decrease in their TDS ($r_{pH-M} = 0.79$, $p < 0.05$). Therewith the greater the contribution of cations, the lower the acidity of the rains.

The acidify of the rainwaters with a total concentration of ($SO_4^{2-} + NO_3^-$) within the range of 1 to 3 mg/L is controlled by an interplay of natural and anthropogenic factors. The HCO_3^- fraction among the anions increases but is still lower than the ($SO_4^{2-} + NO_3^-$) concentration in 65% of the samples (Table 6). The pH varies from 4.3 to 6.1. The waters show strong positive correlations between pH and TDS ($r_{pH-M} = 0.72$, $p < 0.05$), and hydrocarbonates and organic anions may operate as neutralizing agents.

A mandatory criterion for the identification of anthropogenic factors of the acidification of the rainwaters was that the total concentration of ($SO_4^{2-} + NO_3^-$) > 3 mg/L (Svistov et al., 2010). Compared to other precipitations, these waters are more mineralized, with an obvious dominance of the acidifying potential in the anion balance ($HCO_3^- \ll SO_4^{2-} + NO_3^-$). The total concentrations of major cations were higher than the average long-term values. Although their totals were much lower than those of strong acids (Table 6), the neutralizing effect most commonly amounted to 76−91%. The pH thereby varied from 4.37 to 5.07. The aforementioned decrease in the acidity to pH > 5.5 was induced by that the concentrations of Ca^{2+}, the main neutralizing cation, was higher than the concentrations of sulfates: $Ca/SO_4 > 1.1$. The correlation coefficient between the pH and Ca/SO_4 was 0.74 ($p < 0.05$).

CONCLUSIONS

The results of monitoring of rain precipitation in UUFS demonstrate significant intra-season and year-to-year variability of the concentrations of major ions in these waters. Our data on the rainwaters are generally consistent with EANET data. The average TDS = 4.70 ± 3.02 mg/L corresponds to the regional background and is close to the values obtained for natural reserves in the Russian Federation.

The rainwater composition was determined to change from sulfate−calcic in 2012−2014 to hydrocarbonate−calcic in 2015−2018, which is explained by the increase in the number of the cyclones formed over industrial centers in China. The average pH values tend to increase. One of the probable factors of the decrease in the acidity of the rains in 2015−2018 seems to be a decrease in both the concentrations of sulfates and their percentage among the anions.

Based on a long-term dataset, we have determined relationships between the acidity of the rainwaters and content of their major components in various ranges of their fractional acidity and pH values. In the course of this analysis, correlations between chemical components turned out to be stronger and more reliable than for the long period as a whole, and this allowed us to distinguish the main factors controlling the acidity of the rainwaters.

We have established that natural acidification of low-TDS rainwaters occurs proportionally to the decrease in the total mineralization. Thereby the higher the percentages of major cations, the lower the acidity of the falling rains, and the DOC shows buffering properties. In higher-TDS rainwaters, acidity is efficiently neutralized due to the increase in the calcium concentration. In such situations, DOC can serve as one of the factors neutralizing the anions of strong acids. Inasmuch as SO_4^{2-} ions play a more significant role in controlling the anthropogenically induced acidity, the Ca/SO_4 ratio may be a decisive criterion of the degree of neutralizing of rainwaters with the maximum acid load.

Our seven-year-long monitoring of the chemical composition of warm-season precipitation in an area with well preserved natural forests allowed us to identify the roles of natural and anthropogenic sources in the acidification of the rainwaters. In general, our results demonstrate that natural factors are dominant in controlling the ionic balance and acidity of the rains. However, an even insignificant increase in the anthropogenic load during periods of cyclonal activity leads to an increase in the acidity of the precipitations to critical values. The mechanisms forming acid rains are governed by mutual effects of natural and anthropogenic sources. Inasmuch as forested mountainous ecosystems in the territory are susceptible to acidic fallouts, one should pay special attention to the geochemical monitoring of precipitation water in such area.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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