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Macro- and Microelements and the Impact of Sub-Mediterranean Downy Oak Forest Communities on Their Composition in Rainwater

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Abstract: In this study, we analyzed the content of chemical elements in rainwater and investigated the influence of forest cover on the composition of precipitation. The results obtained showed that the concentration of some elements in the rainwater collected under the forest canopy was higher than that in the open area. As part of the work, we calculated the enrichment factor and examined the sources of chemical elements in rainwater. We found that all macro-elements had increased values of the enrichment factors compared to the supporting elements of the Earth's crust. Ca had the highest value. The values of the remaining elements (Sr, Pb, Mn, Cr, Ba, V, Fe) indicated their lithogenic and anthropogenic origins. We noted that the enrichment factor under the forest canopy was significantly lower than in the open area, indicating the dilution of these elements during water passage through the canopy. Elements such as Zn, Co, Cu, and Ni also had high enrichment factors, which indicate their anthropogenic origin. In the open area, most elements had an inverse relationship with pH, except for the alkali metals Na, Mg, and Ca, which had a positive relationship with the pH value. The concentration of K was not dependent on pH. In rainwater that had passed through the forest canopy, the concentrations of Na, Mg, and Ca were also not dependent on pH, while the concentration of K had an inverse relationship with pH. As the concentration of heavy metals in rainwater increases, the role of Na, Mg, and Ca in the process of water neutralization decreases.

Keywords: atmospheric fallout; elemental composition of precipitation; under the forest canopy; rainwater; downy oak forests

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1. Introduction

In recent decades, due to growing environmental pollution, special attention has been paid to the study of the chemical composition of precipitation. Air pollution has become an acute problem in developing countries due to rapid economic development and the consequent increase in energy consumption. The composition of the atmosphere plays an essential role in the climate system and remains relatively constant. Atmospheric precipitation continuously transports a variety of dissolved substances to the Earth's surface, significantly impacting the nutritional balance of forests. The input of trace elements through both dry and wet deposition serves as a significant source of contamination for the system of plants–soil–water.

The efficiency of forest functioning is achieved through the intensive and continuous exchange of matter and energy within the atmosphere–forest canopy–soil system. When atmospheric precipitation passes through the vegetation cover, it undergoes changes in composition, leading to the removal of various products of plant life and anthropogenic pollutants. This process significantly influences the substance cycling within ecosystems [1]. Precipitation is part of biogeocenosis and has an active impact on the biological cycle. Forest ecosystems play a significant role in changing the chemical composition and quantity of rainwater. Factors such as forest type, rainfall and acidity, canopy density, and leaf area index play a major role in controlling the seasonal and spatial variability in the chemical composition of waters collected under the forest canopy [2,3]. As a result, the content of most components in rainwater under the canopy increases compared to rainwater collected in open areas [1–6]. In the forest canopy, interactions between precipitation and the forest canopy lead to ion exchange and changes in the concentration of elements [7,8]. Leaching from vegetation increases with the increasing acidity of precipitation [9], especially at $pH < 3.0$ [10,11], which is most true for divalent cations such as Mg^{2+} and Ca^{2+} [12]. The acidity of precipitation can be neutralized by ion exchange with H^+. The exchange of rainwater H^+ for Ca^{2+} and Mg^{2+} in the canopy can account for up to ~40% of pH neutralization [13]. However, there is little information on the exact chemical and quantitative mechanisms of complete neutralization processes through the canopy [14]. Metals in the atmosphere are formed mainly as a result of human activities and usually dissolve easily in rain [15]. In addition, they can easily adhere to the tree canopy due to the hydrophobic (waxy) nature of the leaf surface [16]. Under-canopy samples are often analyzed for the presence of chemical components to assess atmospheric deposits in forest ecosystems [17]. However, information regarding metals in these through samples is relatively limited [18]. The wet and dry deposition of metals has often been analyzed in open areas [19–21]. In [22], the authors showed that the concentrations of metals were higher in rainwater that had passed through the forest canopy than in rainwater collected in an open area.

The influence of deciduous forest stands on the chemical composition of rainfall, particularly its microelement composition, has not been sufficiently studied. Moreover, the mechanisms through which vegetation transforms precipitation are not fully understood. The available data concerning the effect of various tree species on the chemical composition of precipitation are inconsistent. It is essential to pay considerable attention to the monitoring system for trace elements in precipitation, especially in light of the increase in atmospheric pollution by substances of anthropogenic origin. This pollution has a regional and, for some components, even global character.

Previously, studies were conducted on the chemical composition of rainwater in the territory of the Crimean Peninsula, in areas affected by anthropogenic factors [23–29]. We have investigated the influence of tree canopy on the content of biogenic elements in rainwater under environmentally pristine conditions. This study focused on the impact of the forest on the chemical composition of rainwater, particularly its microelement composition. The findings of this study contribute to the understanding of the role of forests in regulating the chemical composition of rainwater and provide valuable information for monitoring trace elements in precipitation, especially in light of the increase in atmospheric pollution by substances of anthropogenic origin.

Typically, rainwater is analyzed for the presence of basic elements and acidic contaminants [3,4,9]. However, information on the content of these components in precipitation under tree canopies is scarce. In previous studies, the contents of various elements such as Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Sr, Ba, etc., in rainwater collected in open areas were considered [3,22,30–33]. In this study, we analyzed the concentration of 17 elements in rainwater including Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Sr, and Ba, which were collected in open areas and under forest canopies. The main goal of this work was to assess the impact of the forest on the changes in the macro- and microelements in rainwater as it passes through the crowns of trees in a downy oak forest as well as determining the origin of these precipitations.

2. Materials and Methods

The Crimean Peninsula is a geographically diverse region located in the northern Black Sea. It is characterized by a complex topography, ranging from semi-desert low-lands to middle mountains. The peninsula has a temperate climate, with warm, dry summers and mild, wet winters. The average annual temperature is around 13 °C (55 °F), with average summer temperatures reaching up to 25 °C (77 °F) and average winter temperatures dropping to around 0 °C (32 °F). The Peninsula receives an average of 500–600 mm (20–24 in) of precipitation per year, with most rainfall occurring in the spring and autumn months. The studied area is located in the Southeastern Crimea, with a climate that is very dry, hot with very mild winters, with the Köppen designation Csa [34]. Sampling points are located at the Background Environmental Monitoring Station (BEMS) on the territory of the Karadag State Nature Reserve on the northeastern slope of the mountain Svyataya, Crimea Peninsula (Figure 1). The study area is dominated by steppe vegetation with separate patches of downy oak-ash forest with dogwood in the undergrowth, which have a crown density up to 60%. The distance from the station to the nearest village, Koktebel, is approximately 1.5 km. The BEMS is separated from the sea by the Kok-Kaya Ridge (320 m a.s.l.) [35].

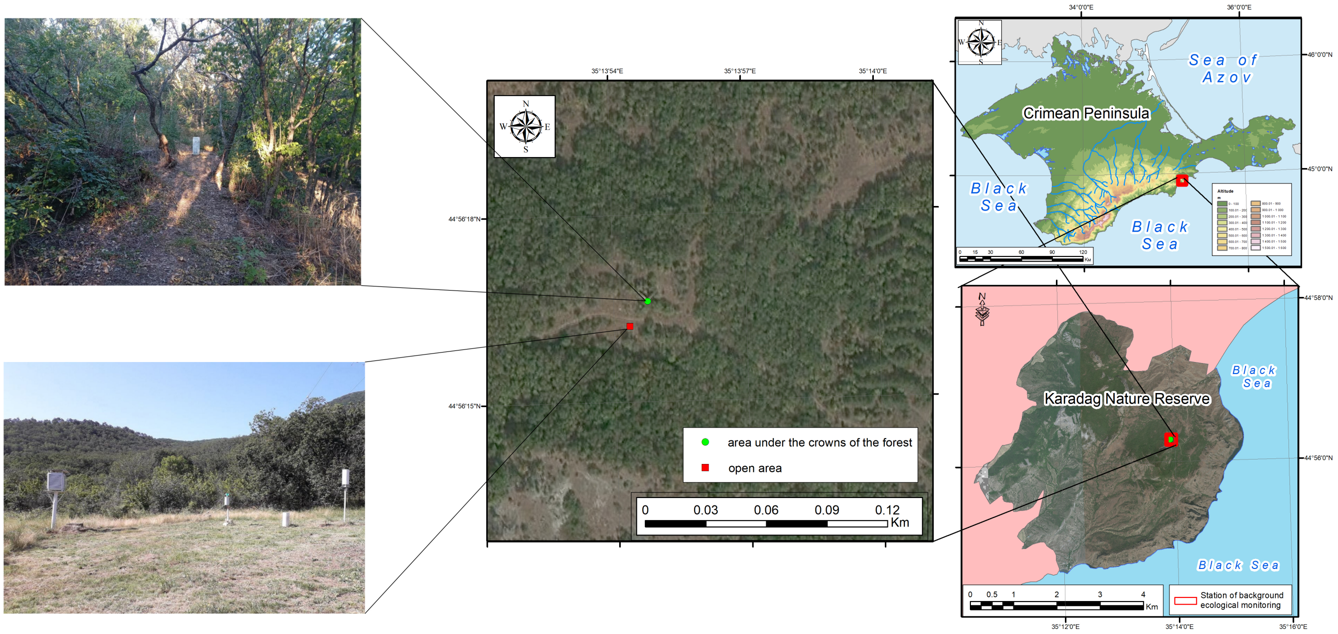

Figure 1. Study area and sampling sites.

Precipitation collectors included in the AGMS-NN-02 weather station were used to collect rainwater. Precipitation samples were collected from July 2020 to September 2020 and from April 2021 to January 2022. Precipitation was collected and analyzed monthly. We obtained 26 samples including 13 samples of rainwater in an open area and 13 samples of precipitation collected under the forest canopy. After each rainfall event, the collected precipitation was poured into sterile bottles, then refrigerated at 4 °C in the dark, and transported to the laboratory for further analysis. All samples were taken according to the National Standard of the Russian Federation GOST R 59024-2020 "Water: General requirements for sampling" [36]. The mean monthly sample quantities were proportional to the collected event volumes.

Rainwater samples were analyzed for pH using a pH-150MI instrument. Determination of the content of the studied elements in atmospheric samples was carried out using a mass spectrometer with inductively coupled plasma, PlasmaQuant MS Elite S-NR:11-6000ST043, at the scientific and educational collaborative center "Spectrometry and Chromatography" at the Research Center of IBSS. The LOD were 4.6 µg L^{-1} for Al, 8.2 µg L^{-1} for K, 1.59 µg L^{-1} for Na, 5.9 µg L^{-1} for Ca, 0.2 µg L^{-1} for Sr, 0.6 µg L^{-1} for Mg, 0.1 µg L^{-1} for Cd, Cr, Ni, Co, Pb, and V; 0.2 µg L^{-1} for Cu; 3.5 µg L^{-1} for Fe, 0.07 µg L^{-1} for Ba, 0.06 µg L^{-1} for Mn, and 0.3 µg L^{-1} for Zn. For descriptive purposes, the minimum, maximum, and mean values were calculated for each analyzed element.

Using the enrichment factor (EF), it is possible to provide a rough estimate of the excess or deficiency of elements in rainwater in relation not only to marine, but also to continental sources. The enrichment factor (EF) is a factor that allows differentiating elements of anthropogenic origin from those of natural origin [37]. To determine the possible sources of dissolved ions in rainwater and to estimate their quantity, an analysis was carried out including the calculation of the enrichment factor (EF) for each ion in relation to sea salt. Na was conventionally assumed to come entirely from seawater. EF, calculated using Na as a reference element, reflects the depletion or enrichment of precipitation in relation to seawater. To assess the role of the sea surface as a source of components in precipitation, the EF for each element with respect to ocean water was calculated as follows:

$$\mathrm{EF_{sea}} = [\mathrm{X/Na}]_{\mathrm{samples}}/[\mathrm{X/Na}]_{\mathrm{sea}}$$

Usually, chemically stable and inactive elements with a continental source are used such as Al, Fe, Ti, Sc, and Si [38,39]. In this work, Al was used as the reference element for sources of continental origin. EF was calculated relative to the average composition of the Earth’s crust using the formula [40]:

$$\mathrm{EF_{crust}} = [\mathrm{X/l}]_{\mathrm{samples}}/[\mathrm{X/Al}]_{\mathrm{crust}}$$

where X is the content of the element (mg/L) in both the sample and the upper part of the continental crust.

The concentrations of elements in the Earth’s crust and seawater, mg/kg, are according to Vinogradov (1962) [41].

It is important to note that the main source of uncertainty in the calculations stems from the difficulty in determining the composition of the Earth’s crust and seawater sources. As such, the results should be interpreted qualitatively.

To investigate the potential relationship between target communities in rainwater and identify possible sources of contaminants, Pearson correlations were calculated among the metal concentrations in rainwater samples collected from open areas. Additionally, a matrix correlation was conducted to assess the relationship between the metal concentrations and both the pH value and average monthly precipitation. Furthermore, correlation coefficients were determined between the concentrations of elements in rainwater collected under forest canopies and in open areas.

3. Results

One of the most important indicators of the chemical composition of rainwater is its acidity. Figure 2 shows the change in the pH of rainwater during the observed periods from July 2020 to September 2020 and from April 2021 to January 2022.

From the analysis of the graph, it can be seen that during the research in this area, a wide range of pH values was observed in the collected rainwater. The average pH of rainwater collected in the open area was 6.56, while it was 5.97 under the forest canopy. Under normal conditions, rainwater has a pH = 5.6–5.7 [33]. In July 2020, slightly acidic rain was recorded in the reserve: the pH of rainwater collected in an open area was 5.53, and under the forest canopy, it was 5.22. Between July 2020 and September 2020, the rainwater passing through the canopy was also slightly acidic. In May 2021, the highest pH level (7.82) was recorded for rainwater collected in the open area. At the same time, one of the lowest pH values (5.55) was recorded in the rainwater under the forest canopy. There was a general trend that the pH of rainwater passing through the canopy was lower than the pH of rainwater collected in the open area.

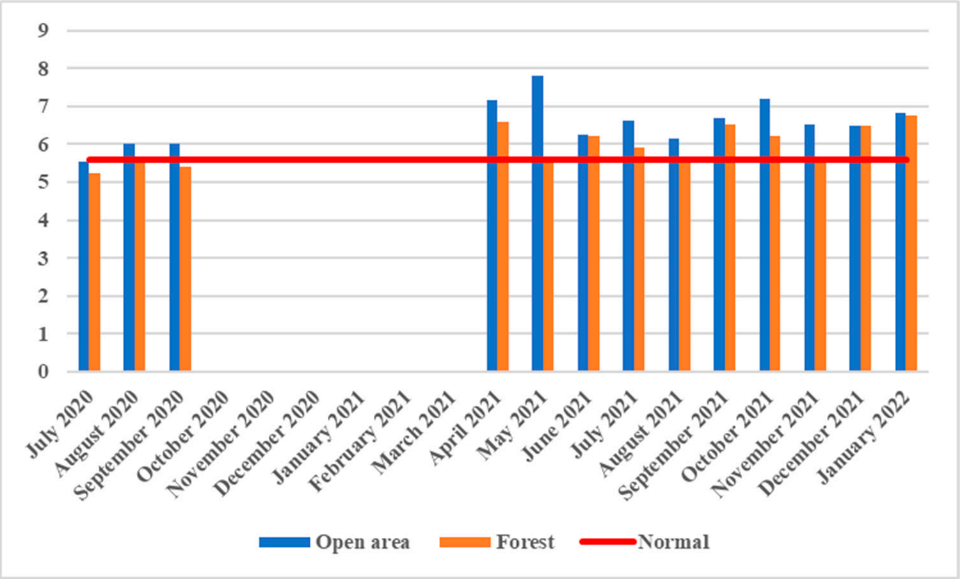

Figure 2. Monthly changes in rainwater pH.

The concentrations of the studied elements in rainwater are presented in Table 1.

Table 1. Concentrations of chemical elements in rainwater (μg/L).

Elements	Open Area		Under the Forest Canopy	
	Maximum–Minimum Value, μg/L	**Average Value**	**Maximum–Minimum Value, μg/L**	**Average Value**
Na	34,348.56–483.97	4414.32	16,746.47–244.74	4115.50
Mg	14,482.59–129.49	1401.68	4149.72–153.91	930.09
Al	38.45–0.00	10.59	52.73–0.24	20.73
K	10,246.75–180.62	2457.01	13,128.05–702.88	5405.70
Ca	28,872.74–699.74	10,316.33	17,439.83–728.05	8044.44
V	1.27–0.17	0.45	2.09–0.23	0.66
Cr	4.39–0.36	1.27	6.36–0.41	1.49
Mn	59.37–0.73	16.25	220.87–0.20	49.09
Fe	358.65–25.93	144.08	212.42–47.18	138.70
Co	27.79–0.41	4.87	12.15–0.17	2.23
Ni	32.33–0.17	9.96	14.14–0.54	4.97
Cu	31.88–0.19	8.79	33.93–0.55	11.09
Zn	629.44–6.72	127.90	254.00–3.23	55.76
Cd	3.32–0.00	0.71	3.06–0.01	0.74
Pb	7.46–0.00	1.16	5.96–0.02	1.34
Sr	268.60–1.56	30.58	109.94–1.93	25.78
Ba	19.15–1.16	6.37	40.36–1.87	8.38

Table 1 demonstrates that the concentration of macro-elements (Na, Mg, K, Ca) and heavy metals (Fe, Co, Ni, Sr) in rainwater collected in open areas was higher than in rainwater passing through the canopy. The remaining metals (V, Cr, Mn, Cu, Cd, Pb, Ba) displayed similar or slightly higher concentration values in rainwater under the canopy compared to rainwater in open air. The concentrations of Pb and Cd in rainwater in open areas were not detected in some samples, whereas they were detected in rainwater under the canopy. This suggests that V, Cr, Mn, Cu, Cd, Pb, and Ba particles accumulate on the tree canopy. As rainwater passes through the forest canopy, the dissolution of these particles occurs, leading to an increase in the concentration of these elements.

The decreasing order of elements in rainwater collected in the open area was as follows: Ca > Na > K > Mg > Fe > Zn > Sr > Mn > Al > Ni > Cu > Ba > Co > Cr > Pb > Cd > V.

The decreasing order of element content in rainwater under the forest canopy was as follows: Ca > K > Na > Mg > Fe > Zn > Mn > Sr > Al > Cu > Ba > Ni > Co > Cr > Pb > Cd > V.

The state of the elements could change while moving through tree crowns. For instance, it is known that Zn is absorbed or retained by tree canopies [18,42], resulting in a decrease in Zn concentration in rainwater collected under the forest canopy. Conversely, Mg is washed out from the surface of the tree canopy [18,43], leading to an increase in its concentration in rainwater collected under the forest canopy.

To distinguish elements of anthropogenic origin from those of natural origin, we calculated the enrichment factors (EF) in relation to their sources: lithogenic and marine (Figures 3 and 4). The total contribution of the marine component to the concentration of some elements was minimal, so we considered the marine enrichment factor only for elements such as Na, Mg, K, Ca, Sr, and Ba.

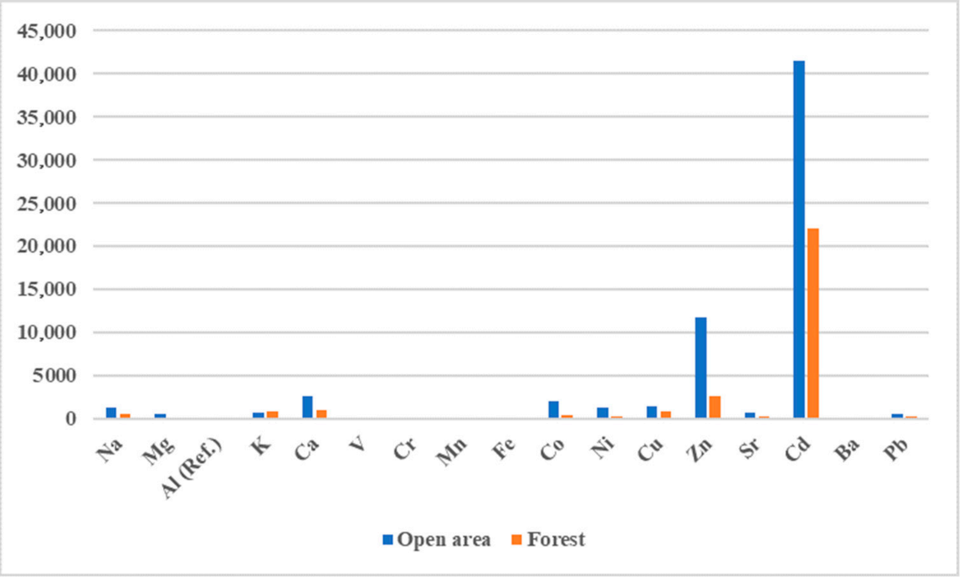

Figure 3. Enrichment factors for metals (rainwater vs. the Earth's crust).

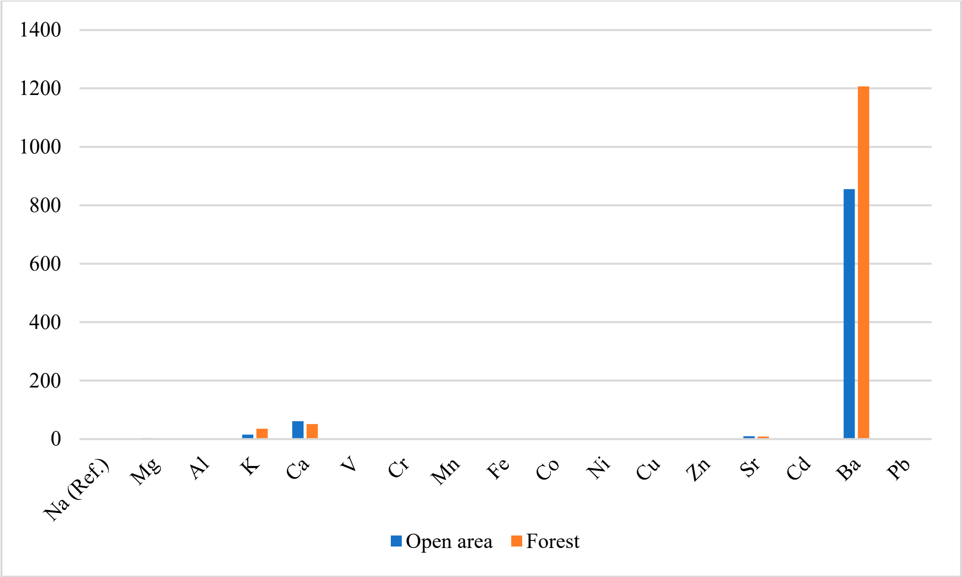

Figure 4. Enrichment factors for metals (rainwater vs. marine).

Therefore, metals with an EF_{crust} close to 1 are likely to have formed as a result of weathering of the Earth's crust, and EF_{crust} values from 1 to 10 may indicate the influence of the local soil's chemical composition [30,44]. Values between 10 and 500 indicate moderate enrichment, while numbers above 500 are clear evidence of extreme enrichment, signifying severe pollution from anthropogenic activities [30]. From Figure 3, it can be observed that, aside from K and Mn, all elements had higher EF_{crust} values in rainwater collected in open areas than in rainwater collected under the forest canopy. This indicates the presence of a dilution process for these elements as rainwater flows under the forest canopy. All of the studied elements had EF values well above 10, with most of them over 500. Moderately enriched elements ($10 < EF_{crust} < 500$): V, Fe, Ba, Cr, and Mn had EF_{crust} values in the open area of 38.01, 23.55, 74.49, 116.31, and 123.52, respectively. Simultaneously, the EF_{crust} values for V, Fe, Ba, Cr, and Mn under the forest canopy were 28.48, 11.58, and 50.06, respectively. Such values suggest the enrichment of material primarily from lithogenic and anthropogenic sources such as atmospheric pollution from emissions from industrial enterprises and transportation being transported over long distances. For example, there is a likelihood of the transboundary transfer of pollutants that may come primarily from the industrial region of the northern Black Sea (the area Mariupol and Taganrog) and southern European countries (Romania, Bulgaria, etc.) [45]. All other elements were characterized as highly enriched ($EF_{crust} > 500$).

For EF_{sea} (Figure 4): Ca and Sr had EF_{sea} values in the open area that were higher than the EF_{sea} values under the forest canopy. The rest of the elements had EF_{sea} values in the open area lower than the EF_{sea} values under the forest canopy. EF_{sea} values for Ca were 61.12 and 51.12 in the open area and under the forest canopy, respectively, which confirms its lithogenic origin. Additionally, Ba had EF_{sea} values of 855.40 and 1207.02, significantly more than 500, in the open area and under the forest canopy, respectively, which indicates strong enrichment of this element in rainwater and its anthropogenic origin. Mg and Sr had EF_{sea} values of 2.65 and 9.36, respectively, in the open area, and 1.88 and 8.46, respectively, under the forest canopy, indicating the influence of the local seawater's chemical composition. At the same time, K had EF_{sea} values of 15.00 and 35.39 for the open area and under the forest canopy, respectively, suggesting other natural sources besides the sea.

4. Discussion

During the study, rainwater was found in the reserve, collected in the open area with an average pH = 6.56, which shows the alkaline metal dominance [46]. The influence of lithogenic impurities in the atmosphere extended the range of pH values from 5.53 to 7.82. Notably, only 4% of the samples had a pH below 5.6, while 77% of the samples had a pH above 5.6, indicating contamination with alkaline atmospheric components. Such pollution can be explained by a large number of limestone rocks in the reserve, and the processes of erosion and weathering of these rocks lead to the alkalinization of precipitation. This result has been confirmed in the works of other authors [29]. During the vegetation period of woody plants, atmospheric precipitation interacts with the plants, and as a result, they are transformed under the influence of biological activity in this ecosystem. Rainwater passing through the forest canopy carries away and dissolves dust particles, organic, and mineral acidic substances. This leads to a decrease in the pH of rainwater from 6.56 to 5.97.

The authors of [47] found that the solubility of elements increases at a lower pH of precipitation. In particular, for Cr, Ni, and Pb, the solubility increased by a factor of two or more in samples with a pH below 5.0. However, the solubility of highly soluble elements such as Na, K, Mg, Ca, Cd, and V was not significantly affected by pH. Since the distribution of trace elements depends on the pH of rainwater, we calculated the Pearson correlation coefficients between the pH of rainwater and the concentration of the studied elements. The results obtained were distributed as follows: pH and concentrations of Na, Mg, Cr, Br, and Sr had a strong correlation with 0.63, 0.69, 0.51, 0.57, and 0.55, respectively. The concentrations of K, Fe, and Pb were practically independent of pH, with coefficients of −0.15, −0.16, and −0.06, respectively. pH and concentrations of Ca and V had an average positive correlation (0.22 and 0.41, respectively). The remaining elements—Al, Mn, Co, Ni, Cu, Br, Cd, and Ba—had an average negative correlation (−0.49, −0.37, −0.25, 0.22, −0.31, −0.22, 0.42, and 0.29, respectively).

When precipitation passes through the forest canopy, there is a negative correlation between pH and Ni content (r = −0.67) as well as an average negative correlation between pH and the concentration of Al, K, Mn, Fe, Ni, Co, Cu, Zn, Sr, Cd, Ba, and Pb (respectively −0.48, −0.48, −0.49, −0.39, −0.67, −0.22, −0.36, −0.35, −0.42, −0.32, and −0.47). With an increase in the concentration of metals, the correlation dependency changes, and most elements have an inverse relationship with pH. This is due to the fact that the pH of precipitation that has passed through the forest canopy is more acidic than the pH of precipitation in an open area.

Consider the correlation between pH and alkali metals Na, Mg, and Ca. In the open area, there was a positive relationship between pH and these metals, which suggests that they play an important role in the process of neutralizing rainwater in the study area. At the same time, the concentration of K in rainwater collected in an open area had almost no effect on pH. However, for rainwater under the forest canopy, pH was almost independent of the concentration of Na, Mg, and Ca, but had an inverse relationship with the concentration of K. With an increase in the concentration of heavy metals in rainwater, Na, Mg, and Ca lose their role in the process of rainwater neutralization. To draw accurate conclusions about the neutralization coefficient, it is necessary to carry out additional calculations that were not considered in this paper.

At 100% humidity, the atmosphere is saturated with water vapor, and water condenses on large aerosol particles, enriching their chemical composition. Soil is the main source of aerosols in the surface layer of the atmosphere, providing about 50% of all aerosol particles [48]. Sea salt is also an important source of aerosols in the atmosphere. The anthropogenic factor including industrial emissions, vehicles, agriculture, and deforestation also influences the formation of the chemical composition of rainwater. To examine the possible relationship between target communities in rainwater and hence the sources of contaminants, Pearson correlations between metal concentrations in open area rainwater were assessed in all of the rainwater samples collected (Table 2). According to the correlation analysis data, Al showed a good correlation with Mn (r = 0.74), Co (r = 0.68), Ni (r = 0.76), Cu (r = 0.94), Zn (r = 0.80), Cd (r = 0.83), Ba (r = 0.85). A good correlation was also observed between Na and V and Cr (r = 0.84 for both), Mg and V and Cr (r = 0.83 and 0.84, respectively), K–Ca (r = 0.74), Ca–Fe (r = 0.81), V–Sr (r = 0.80), Cr–Sr (r = 0.74), Mn–Ba (r = 0.71), Co–Ni (r = 0.71), Co–Zn (r = 0.91), Ni–Cu (r = 0.88), Ni–Zn (r = 0.88), Ni–Ba (r = 0.90), and Cu–Ba (r = 0.91). According to Topchaya [32], if the significant correlation relationship between the concentrations of elements r > 0.87, then the elements are of lithogenic origin; when r = 0.70–0.87, then the elements are of both lithogenic and anthropogenic origin. In [49], as the authors indicated the elements that have a good correlation relationship with Al (r > 0.5), we can assume the lithogenic origin of these elements. Good and positive correlations (Table 2) were found between all elements, indicating a common source. Thus, we can assume that Cu is of lithogenic origin. The elements Ni, Mn, Co, Zn, Cd, and Ba are of both lithogenic and anthropogenic origin. The remaining elements Mg, Ca, V, Cr, Fe, Sr, and Pb may presumably indicate the multiple sources of these metals.

The change in the average monthly concentration of chemical elements in rainwater varied greatly from month to month. The highest concentrations of all species were observed during the dry months of May, September, and October 2021, where the average rainfall during these months was below 16 mm. Less rainfall should result in a higher concentration of chemical elements in rainwater [50–52]. The relationship between the volume of precipitation and the concentration of chemical elements is presented in Table 3.

Table 2. Correlation coefficient between the element concentrations in rainwater ($\alpha = 0.05$, $n = 13$).

	Na	Mg	Al	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Cd	Ba	Pb
Na	1.00	0.98	−0.08	−0.01	0.37	0.84	0.84	−0.10	0.41	−0.06	0.24	0.07	0.02	0.96	−0.12	0.24	0.00
Mg		1.00	−0.22	0.06	0.44	0.83	0.84	−0.16	0.40	−0.15	0.11	−0.07	−0.09	0.93	−0.25	0.10	−0.10
Al			1.00	−0.07	−0.45	−0.04	−0.17	0.74	0.11	0.68	0.76	0.94	0.80	0.10	0.83	0.85	0.32
K				1.00	0.74	0.11	0.18	0.07	0.75	−0.28	−0.19	−0.21	−0.33	−0.09	−0.14	−0.14	−0.02
Ca					1.00	0.38	0.56	−0.41	0.81	−0.49	−0.34	−0.49	−0.55	0.17	−0.55	−0.29	−0.12
V						1.00	0.88	−0.03	0.42	−0.04	0.18	−0.01	0.00	0.80	−0.13	0.20	−0.16
Cr							1.00	−0.17	0.55	−0.15	0.10	−0.10	−0.10	0.74	−0.33	0.11	−0.12
Mn								1.00	0.04	0.59	0.65	0.69	0.60	0.08	0.65	0.71	0.12
Fe									1.00	−0.05	0.17	0.07	−0.04	0.31	−0.13	0.25	0.13
Co										1.00	0.77	0.71	0.91	0.10	0.30	0.75	0.36
Ni											1.00	0.88	0.85	0.37	0.52	0.90	0.50
Cu												1.00	0.86	0.25	0.76	0.91	0.40
Zn													1.00	0.19	0.49	0.81	0.42
Sr														1.00	0.04	0.39	−0.03
Cd															1.00	0.59	0.30
Ba																1.00	0.27
Pb																	1.00

Table 3. Correlation coefficient between the element concentrations and mean monthly precipitation ($\alpha = 0.05$, $n = 13$).

Elements	R	Elements	R
Na	−0.44	Co	0.34
Mg	−0.41	Ni	−0.20
Al	0.36	Cu	−0.01
K	−0.05	Zn	0.49
Ca	−0.30	Sr	−0.40
V	−0.16	Cd	0.31
Cr	−0.25	Ba	−0.18
Mn	0.37	Pb	−0.11
Fe	−0.26		

The concentrations of most elements in rainwater showed a moderate negative correlation with the amount of precipitation. This may indicate that these metals mainly entered the rainwater as a result of the removal of airborne particulate matter, but also, in the case of throughfall, as a result of the rapid dissolution and washing of metals from canopy deposits at the onset of rain. The latter process can be supported by the fact that a relatively large number of elements were dissolved in the initial washings during successive washings of tree leaves [22]. According to A.M. Nikanorov [48], the salt content in atmospheric precipitation is directly dependent on the dustiness of the atmosphere and inversely on the amount of precipitation.

For a more detailed study of the behavior of atmospheric precipitation components, a correlation analysis of rainwater collected under the forest canopy and in an open area was carried out. The results of the correlation analysis are presented in Table 4.

The table shows that most of the elements had a positive correlation between the open area and under the forest canopy including Na, Mg, Ca, V, Cr, Ni, Cu, Sr, and Ba (r = 0.88, 0.81, 0.66, 0.84, 0.73, 0.62, 0.52, 0.97, 0.89, respectively). The concentrations of these elements in rainwater collected in the open area proportionally affected the concentrations of elements in rainwater collected under the forest canopy. At the same time, Al, K, Co, Cd, and Pb had a slight negative correlation between the open area and under the canopy space (r = −0.16, −0.13, −0.14, −0.25, −0.12, respectively). The remaining elements (Mn, Fe, Zn) had a weak positive correlation between the open area and under the canopy space (r = 0.35, 0.26, and 0.37, respectively). Metals were positively correlated, which clearly indicated that metal fluxes from the atmosphere increased with increased precipitation, even though the metal concentrations were often very high in small amounts of rainwater during dry periods. The increase in element concentrations after the forest canopy indicates that more metals were dissolved from the canopy deposits as the rainwater volume increased, and the degree of solubilization may depend on the amount of the deposits.

Table 4. Correlation coefficients between the concentrations of elements in rainwater collected under the forest canopy and in the open area ($\alpha = 0.05$, $n = 13$).

Elements	R	Elements	R
Na	0.88	Co	−0.14
Mg	0.81	Ni	0.62
Al	−0.16	Cu	0.52
K	−0.13	Zn	0.37
Ca	0.66	Sr	0.97
V	0.84	Cd	−0.25
Cr	0.73	Ba	0.89
Mn	0.35	Pb	−0.12
Fe	0.26		

These dependencies indicate that the amount of precipitation, the properties of the forest canopy, and the atmospheric dustiness affect the concentrations of elements in rainwater. Therefore, the chemical composition influences the pH of the rainwater.

Comparing our studies with the results in [29], which were conducted on the Crimean Peninsula more than 10 years ago, we found that the enrichment values obtained by in our study were an order of magnitude higher. The reasons may vary: anthropogenic activity (high rates of urbanization, population growth, and motorization), changed weather conditions, climate change, and changes in biogeochemical processes in the ecosystem. Trace elements can be carried by the winds. The authors of [29,32] indicate that the main reason for bringing dust with trace element content is the wind that comes from industrial facilities. Apart from Na, Mg, K, Ca, Fe, Co, Ni, and Sr, the other studied elements had concentrations in rainwater collected in the open area that were lower than in rainwater under the forest canopy. This confirms the fact that the leaf surface has the ability to trap solid particles [31,53].

A comparison of element content in rainwater samples from various literature sources with our selected samples is shown in Table 5. In our samples, a decrease in the concentration of macro-elements Na, Ca, and Mg was observed after passing through the forest canopy, while the literature sources presented the opposite trend [2,3,6]. In other studies, these concentrations increased in samples under the forest canopy. At the same time, the concentrations of macro-elements in the study area were significantly higher than their concentrations in other reserves in Russia [3,6]. We could only compare the concentration of trace elements in our samples with studies by other authors in open areas, since most works have not provided data on the precipitation collected under the forest canopy. However, the concentrations of trace elements in our samples were much higher than those in [3], which was conducted at the Lyalsky Forest Ecological Station of the Institute of Biology of the Federal Research Center of the Komi Scientific Center of the Ural Branch of the Russian Academy of Sciences in the Komi Republic. The concentrations of trace elements in our samples were similar to those found in samples collected near settlements [29,40,49,54]. Despite this, we did not find any exceedance of the MPC [55]. Thus, there was no pollution in the rainwater in the study area.

Table 5. Average values of element concentrations in precipitation (μg/L).

	Present Work		**Bakhchisarai (Crimea) [29]**	**Kaliningrad Region [31]**	**Spain [49]**	**Poland [54]**	**Republic of Komi [3]**		**China [2]**		**Canada [30]**	**Kivach [6]**		**MPC**
Elements	**Open Area**	**Under the Forest Canopy**					**Open Area**	**Under the Forest Canopy**	**Open Area**	**Under the Forest Canopy**		**Open Area**	**Under the Forest Canopy**	
Na	4414.32	4115.50	1,780,000		188,200		200,000	290,000	13,000	25,600		370,000	820,000	200,000
Mg	1401.68	930.09	880,000		53,700		70,000	700,000	37,000	65,800		170,000	810,000	50,000
Al	10.59	20.73	172.4	8762	49.4		7.48	8.65			17.5			500
K	2457.01	5405.70	2,370,000		15,100		540,000	7,380,000	17,400	100,400		850,000	6,960,000	
Ca	10,316.33	8044.44	6,340,000		121,700		310,000	2,460,000	150,000	382,000		600,000	1,430,000	
V	0.45	0.66	0.787	17.3	0.83						0.75			100
Cr	1.27	1.49	5.19	32.6	0.28	1.64	0.01	*			1.52			500
Mn	16.25	49.09	13.38	232	6.4		2.66	9.65			9.46			100
Fe	144.08	138.70	366.2	11.4	11.4						90.5			300
Co	4.87	2.23	0.177	4.9	5.0		0.01	*			0.13			100
Ni	9.96	4.97	6.78	73.9	1.0	6.42	0.36	1.28			2.82			20
Cu	8.79	11.09	30.43	81.5	2.1	11.94	1.46	2.54			4.00			1000
Zn	127.90	55.76	78.22	438	55.7	37	22.02	32.47			28.1			1000
Sr	30.58	25.78	37.49	34	5.5						7.74			7000
Cd	0.71	0.74	0.117	3.7		0.14	0.18	0.13			0.26			1
Ba	6.37	8.38	148.8	94	15.2									100
Pb	1.16	1.34	4.279	73.3	0.51	13.23	*	0.05			5.14			10

* Lower detection limit of the device.

Excess or deficiency of elements in precipitation in relation to sources of marine and continental origin can be approximately estimated by enrichment factors. The analysis of the enrichment factor (Table 2) for rainwater collected in open areas and under the forest canopy allowed the elements to be arranged in the following order: Na < Al < Fe < V < Ba < Cr < Mn < Pb < Mg < Sr < K < Ni < Cu < Co < Ca < Zn < Cd (outdoor), Na < Al < Fe < V < Ba < Cr < Pb < Mg < Mn < Sr < Ni < Co < K < Cu < Ca < Zn < Cd (under the forest canopy). Despite the fact that Zn is a marker element in the combustion of fossil fuels, smelting of non-ferrous metals, and spraying of agrochemicals [56], Zn released as a result of such processes can easily dissolve in rainwater [57]. The obtained EF_{crust} results for Zn were 4.42 and 2.47, which were significantly lower than the results in other studies: from 50 to 500 in Norway [58], and in Tsukuba (Japan), higher than 1000 in open areas and under the forest canopy ranging from 900 depending on plant species [22]. This indicates that Zn is mainly of lithogenic origin.

All macro-elements had elevated EF_{crust} values relative to the supporting elements of the Earth's crust, but Ca had the highest values: EF_{crust} = 2649.31 (in the open area) and 1055.36 (under the forest canopy). This is probably due to the natural features of the territory (geological, lithological, climatic, etc.); in some cases, anthropogenic sources may contribute. The order of decreasing EF for macronutrients is as follows: Ca > Na > K > Mg (in the open area) and Ca > K > Na > Mg (under the forest canopy). The order of decrease in EF under the forest canopy was similar to the order of decrease found in [29]. The chemical composition of aerosol particles in the atmosphere is not entirely identical to the chemical composition of soils (not all minerals and soil products are equally dispersed). Dust is significantly enriched in iron and manganese oxides compared to its source, the soil; in addition, soil aerosols contain silicon, alumina, carbonates, and calcite [48]. When atmospheric CO_2 interacts with silty particles of carbonates (which saturate the atmosphere due to the weathering of widely developed limestones and marl dolomites), HCO_3^- and Ca^{2+} are formed.

Regarding the micro-elements, the vast majority had EF_{crust} values relative to the supporting elements of the Earth's crust greater than 500, and the order of decreasing EF_{crust} was as follows: Cd > Zn > Co > Cu > Ni > Sr > Pb > Mn > Cr > Ba > V > Fe (in the open area) and Cd > Zn > Cu > Co > Ni > Pb > Sr > Mn > Cr > Ba > V > Fe (under the forest canopy). At the same time, Cd had a very high EF_{crust}: 41,515.94 and 22,104.72 in the open area and under the tree crowns, respectively. Other heavy metals such as Zn, Co, Cu, and Ni also had high EF_{crust} values, which indicate their anthropogenic origin. The EF_{crust} values of other elements indicated their lithogenic and anthropogenic origins. It should be noted that their EF_{crust} values under the forest canopy were much lower than in the open area. This confirms that when rainwater passes through the forest canopy, these elements are diluted. It also suggests that the forest canopy can be viewed as a self-regulating system filtering certain trace elements in precipitation.

5. Conclusions

From July 2020 to January 2022, we analyzed the macro- and micro-elements in rainwater collected in the Karadag State Nature Reserve. The forest canopy was found to filter certain trace elements in precipitation, with the concentrations of most elements higher in rainwater under the canopy than in the open area. The study identified the sources of chemical elements in rainwater using enrichment factors. From the research results, it can be said that Cu has a lithogenic origin. The elements Ni, Mn, Co, Zn, Cd, and Ba are of both lithogenic and anthropogenic origin. The remaining elements Mg, Ca, V, Cr, Fe, Sr, and Pb may presumably indicate a variety of sources for these metals. The enrichment factor under the forest canopy was generally lower than in the open area. Element concentrations showed an inverse relationship with pH, except for alkali metals (Na, Mg, Ca) in the open area. Heavy metals competed with alkali metals in the rainwater neutralization process. The study suggests that metals entered rainwater through the removal of airborne particulate matter and the dissolution and leaching of metals from forest canopy deposits. The concentration of most elements increased with rainfall volume, indicating that more metals were dissolved from canopy deposits with increased rainfall. Despite their anthropogenic sources, heavy metal concentrations did not exceed the maximum permissible concentrations.

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