forests

Article

Biogenic Elements of Atmospheric Fallout and Impact of Sub-Mediterranean Forest Communities of Downy Oaks on Changes in the Chemical Composition of Atmospheric Precipitation

Cam Nhung Pham [1,*], Roman Gorbunov [1], Vladimir Lapchenko [2], Tatiana Gorbunova [1,3] and Vladimir Tabunshchik [1]

[1] A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, 299011 Sevastopol, Russia
[2] T.I. Vyazemsky Karadag Scientific Station, Nature Reserve of RAS, Branch of A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, 298188 Feodosia, Russia
[3] Department of Subtropical and Tropical Ecology, Institute of Environmental Engineering, Peoples' Friendship University of Russia (RUDN University), 117198 Moscow, Russia
* Correspondence: nhung5782@gmail.com; Tel.: +7-9785291392

Abstract: In this work, a study of the biogenic composition of atmospheric precipitation and its change during the passage through the crowns of trees of a downy oak forest was carried out. First of all, the content of rainwater-soluble compounds of all the considered elements in rainwater under the forest canopy was higher than in rainwater in an open area. It was revealed that the main forms of nitrogen in the atmospheric fallout were nitrates and ammonium. The average concentrations of nitrogen anions in rainwater collected under the canopy were higher than in rainwater collected in the open area. The proportion of nitrite nitrogen in rainwater under the canopy was 6% higher than in rainwater collected in the open area. Simultaneously with the increase in the proportion of nitrite nitrogen, nitrate nitrogen decreased. For all considered biogenic substances, an increase in their content was observed in the warm period of the year. We found an inverse relationship between the concentration of inorganic nitrogen and phosphorus in precipitation and the relative air humidity and wind speed. It was established that the pH of precipitation falling under the crowns of trees was lower than the pH of precipitation in the open area. It was revealed that the increase in the concentration of biogenic elements was in accordance with the phase of plant development during the growing season.

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

check for updates

Citation: Pham, C.N.; Gorbunov, R.; Lapchenko, V.; Gorbunova, T.; Tabunshchik, V. Biogenic Elements of Atmospheric Fallout and Impact of Sub-Mediterranean Forest Communities of Downy Oaks on Changes in the Chemical Composition of Atmospheric Precipitation. *Forests* **2023**, *14*, 294. https://doi.org/10.3390/f14020294

Academic Editor: Zang Fei

Received: 6 January 2023
Revised: 30 January 2023
Accepted: 1 February 2023
Published: 3 February 2023

1. Introduction

Atmospheric precipitation not only contributes to the removal of impurities from the atmosphere, but also leads to the entry of various chemical elements into the surface waters of land and the world ocean. The high efficiency of forest functioning is achieved due to the intensive and constant exchange of matter in the system atmosphere–forest canopy–soil. The chemical transformation of atmospheric water occurs after its interaction with the aboveground phytomass of forest stands. Precipitation is included in the biogeocenosis and actively affects the biological cycles. At the same time, the atmosphere is a significant source of biogenic elements, such as, for example, nitrogen, phosphorus, and silicon, which most often limit the development of the productivity of aquatic ecosystems [1–3].

The forest ecosystems have a significant impact on changes in the chemical composition and amount of precipitation. Passing through the crowns of woody plants, atmospheric precipitation undergoes a number of transformations that lead to a change in its initial amount and chemical composition [1,2,4–7]. This leads to an increase in the content of most components in rainfall under the forest canopy, in comparison with atmospheric precipitation, including biogenic elements [2,6].

The study of the crown runoff of trees is considered in many works [8,9]. However, the study of changes in the chemical composition of precipitation is more limited. At the same time, there are studies on the influence of epiphytes and forophytes on changes in the chemical composition of precipitation [10–12], of precipitation in rainforest tropical ecosystems [13–15], of leaf litter [16,17]. However, the study of the influence of deciduous tree species, including oak forests, on the chemical composition of precipitation is presented to a much lesser extent [18].

The authors of a previous work [6] showed that in a forest canopy of deciduous-coniferous plantation, a combination of the ions HCO_3^-, K^+, NH_4^+, NO_3^-, Ca^{2+}, Na^+ and an amount of Cl^- and SO_4^{2-} is observed in precipitation. In another work [2], the authors showed that the pH value decreased from 5.8 to 5.5. At the same time, it was shown that under the influence of the canopy, the concentrations of most elements increased. For example, the content of hydrocarbonate ions in the water that passed the canopy increased almost fourfold. In particular, sodium and potassium were washed out directly from the leaves and tissues of plants [19]. Rainfall carries out the transfer of elements from the atmosphere to ecosystems and maintains biogenic cycles in the plant–soil system. Some authors [1,19] found that different types of woody vegetation have a different effect on the formation of rainwater acidity and the rainwater content of certain components. For all elements, there are both facies differences in their supply to the underlying surface and intrafacial differences, under different trees and within their under-canopy space. This is a consequence of the biochemical features of a tree and the actual landscape–geochemical conditions of its growth [2,20,21]. The effect of deciduous forest canopies on the chemical composition of rainfall and surface waters, especially their microelement composition, is poorly understood.

In an article [22], hydrological partitioning and changes in the solute composition of rainfall were studied in three tree species: Roystonearegia, Ficus microcarpa, and Lagerstroemia speciosa. A canopy model was used for estimating the contribution of canopy exchange and dry deposition to net rainfall (throughfall + stemflow) solute flux. At the same time, the concentrations of Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl, NO_3^-, and SO_4^{2+} in throughfall and stemflow were higher than in rainfall. The authors of another work [23], monitored I, Se, and Cs concentrations in both rainfall and throughfall of fourteen French forested sites and estimated dry deposition and canopy exchange fluxes for I, Se, and Cs.

The atmospheric inputs of selected Trace Metals, i.e., Cd, Cu, Ni, Pb, Sb, Zn, as well as Al, Fe, and Mn, in six forested sites in France were studied [7]. The authors noted that trace metals present in labile forms (Cd, Ni, Zn) interact with the canopy and are cycled in the ecosystem, and their concentration is either slightly increased or even decreased in throughfall. Sb, Pb, and Cu concentrations are increased through the canopy, as a consequence of dry deposition accumulation. In the work [24], the authors confirmed that the interactions between precipitation and forest canopy elements (bark, leaves, and epiphytes) control the quantity, spatiotemporal patterning, and chemical concentration, character, and constituency of precipitation to soils.

In other works [2,6], the authors pointed out that birch, spruce, and beech have different effects on the chemical composition of rainwater. The authors of [20] showed that the degree of influence on the chemical composition of rainwater also depends on the age of the forest.

The chemical composition of atmospheric precipitation and the content of biogenic elements in atmospheric precipitation on the territory of Crimea were studied earlier [25–31]. These works were carried out in Sevastopol, Katseveli, and Trudolyubovka, which are all under technogenic influence. In environmentally friendly places and reserves, the content of biogenic and other chemical elements in precipitation, as well as the influence of the forest canopy on the chemical composition of precipitation on the territory of the Crimean Peninsula, have not been studied.

The purpose of this paper was to assess the content of biogenic substances (nitrogen, phosphorus) in precipitation and its change when passing through the crowns of trees of a downy oak forest in the Karadag Nature Reserve territory.

2. Materials and Methods

The study was carried out on the territory of the Karadag Nature Reserve (Figure 1). The Karadag Nature Reserve is located in the southeastern part of the Crimean Peninsula at the junction of mountain forest, steppe, and coastal marine zones. The territory of the reserve includes the ground part and the sea area. The climate of the Karadag Nature Reserve is characterized by transitional Mediterranean features. It is characterized by moderately hot dry summers and mild wet winters. There are no permanent rivers in the reserve. Within the boundaries of the Karadag Nature Reserve, there are groundwater outlets, which often dry up in summer. The vegetation of the Karadag Nature Reserve is sub-Mediterranean with the addition of steppe species.

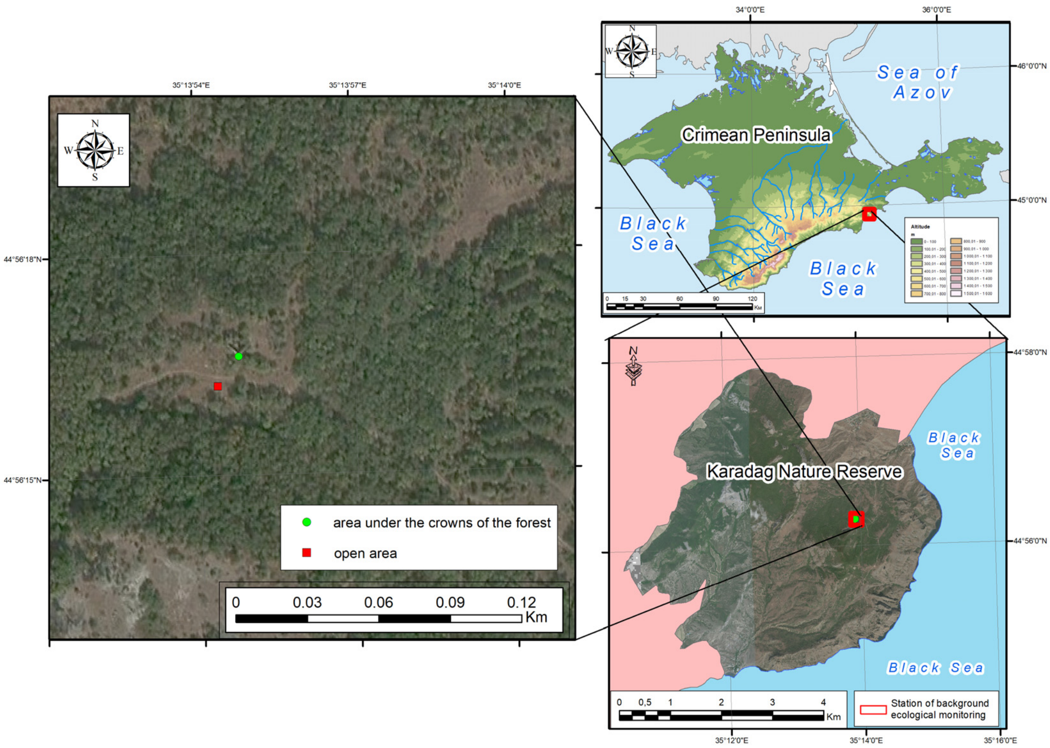


Figure 1. Study area map.

The Background Environmental Monitoring Station (BEMS) is located in the territory of the reserve, on the northeastern slope of mountain Svyataya in a site with steppe vegetation with isolated trees. The bordering forest area, in which precipitation was collected, is a downy oak–ash forest with dogwood in the undergrowth (crown density up to 60%). The distance to the nearest village, Koktebel, is about 1.5 km. The station is separated from the sea by the Kok-Kaya Ridge (320 m) [32].

Precipitation was collected monthly by sediment collectors with a height of 59 cm and a diameter of 26.5 cm. At the same time, accounting and analysis of atmospheric precipitation were carried out in an open area and under the forest canopy (Figure 2). After each rain, the precipitation was poured into sterile containers. The resulting rainwater was delivered to the laboratory. The preparation of the samples for analysis and the laboratory analysis of the content of biogenic substances in the atmospheric precipitation of the selected samples were carried out in the scientific and educational collaborative center "Spectrometry and Chromatography" at the Research Center of IBSS (Sevastopol).

(**a**) (**b**)

Figure 2. Monitoring point for the content of biogenic elements in atmospheric fallout: (**a**) open area; (**b**) under the forest canopy.

All studied biogenic elements were determined by spectrophotometry, on a KFK-3 ZOMZ photometer (JSC "ZOMZ", Sergiev Posad, Moscow region, Russia). The method for determining the nitrate ion is based on the reduction of nitrates to nitrites. Copper-plated cadmium is used as a reducing agent, and EDTA diatrium salt (Trilon B) is used as a complexing agent. The nitrite ion was determined by the Bendschneider and Robinson method. Ammonium nitrogen in precipitation was determined by the Seji–Solorzano method. Inorganic phosphate in the form of $H_2PO_4^-$ was determined by the Murphy–Riley method, which is based on the formation of a phosphomolybdenum complex and its subsequent reduction to a strongly colored blue compound [33].

Weather conditions data were recorded at the WS 600 weather station (OTT HydroMet Fellbach GmbH, Fellbach, Germany), which is installed on the territory of the BEMS. Climate data were recorded every hour.

For a detailed study of the relationship between factors (concentrations of nitrite ion, nitrate ion, ammonium ion, inorganic phosphorus, pH value, precipitation, relative humidity, wind speed), we calculated Pearson's correlation coefficients.

3. Results

3.1. Acidity

One of the most important indicators of the chemical composition of atmospheric precipitation is its acidity. Figure 3 shows the change in the pH of precipitation in the period from April 2021 to January 2022.

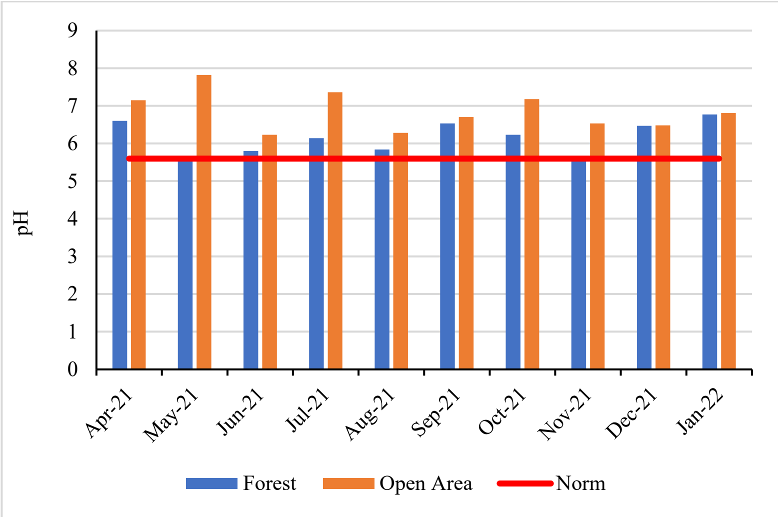


Figure 3. Changes in the pH of precipitation by month.

The chart shows that during the research period in this area, we measured a pH = 6.23 – 7.82 (average value 6.8). For rainwater that had passed through the canopy of trees, this indicator decreased to pH = 5.55–6.77 (average value 6.1). However, in May 2021, the pH of rainwater collected in the open area had the highest value (pH = 7.82), and the pH of rainwater under the forest canopy had the lowest value of 5.55. Figure 3 shows the average contents of all considered elements for the entire period of the study. It shows that the content of rainwater-soluble compounds of all the considered elements in the rainwater under the forest canopy was higher than in the rainwater in the open area.

3.2. Inorganic Nitrogen

Inorganic nitrogen compounds in natural water—ammonium ions, nitrous and nitric acids—appear mainly as a result of the final decomposition of protein-origin substances. The relative contribution of nitrogen-containing ions to the composition of atmospheric precipitation is shown in Figure 4. The average concentrations of nitrogen anions in rainwater collected under the canopy were higher than in rainwater collected in the open area.

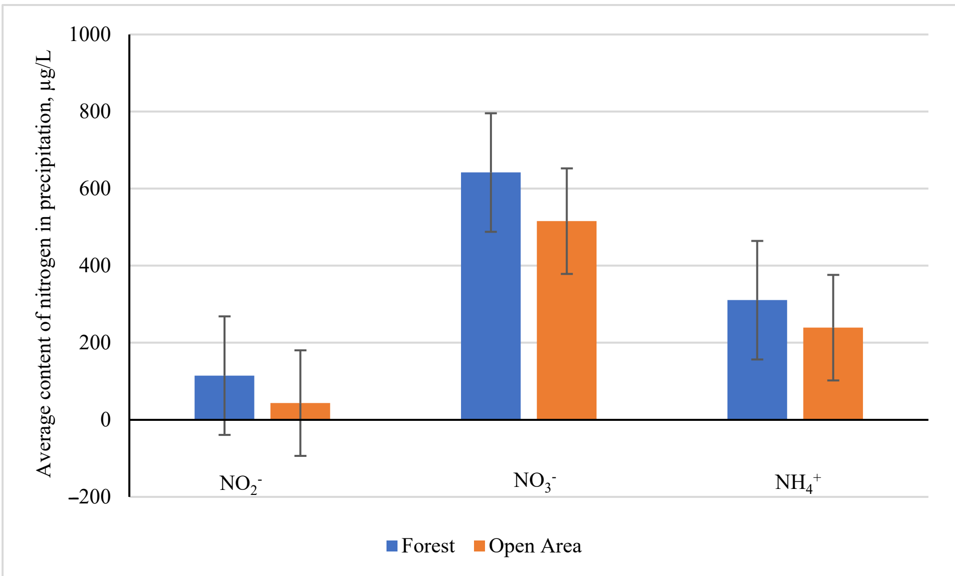
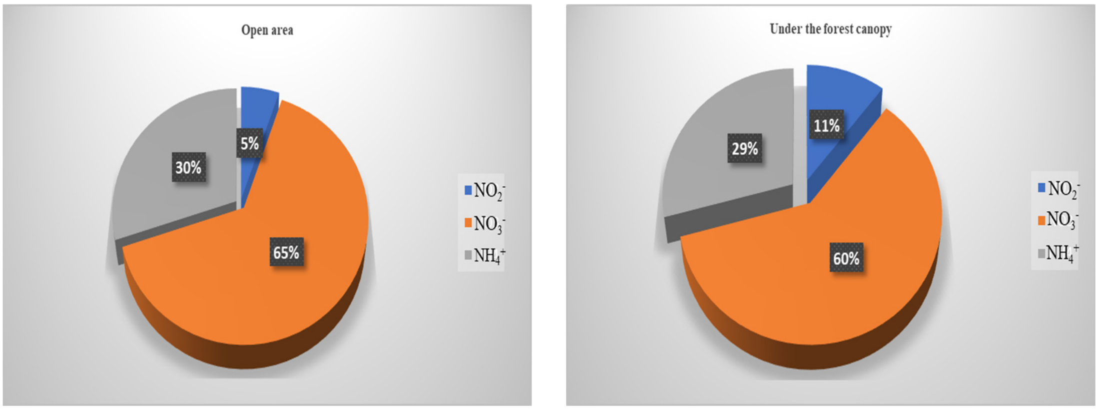


Figure 4. Average content of nitrogen in precipitation (µg/L) for the period 04.2021–01.2022.

The main forms of inorganic nitrogen were still nitrate and ammonium nitrogen (Figure 5). The share of nitrate nitrogen in rainwater under the canopy and the share in rainwater collected in the open area were 65% and 60%, respectively. However, the proportion of nitrite nitrogen in rainwater under the canopy was 6% higher than in rainwater collected in the open area, corresponding to 11% and 5%, respectively. Simultaneously with the increase in the proportion of nitrite nitrogen, nitrate nitrogen decreased from 65% in the open area to 60% under the canopy, and ammonium nitrogen from 31% in the open area to 29% under the canopy. Here, it should be noted that the order of the relative contribution of nitrogen-containing ions in rainwater in the open area and under the forest canopy did not change ($NO_3^- > NH_4^+ > NO_2^-$).



(**a**) (**b**)

Figure 5. Relative contribution of nitrogen-containing ions: (**a**) open area; (**b**) under the forest canopy.

The acidity of rainwater in one area may differ from the acidity of rainwater in another area. This depends on the types of gases contained in the atmosphere of a particular area, such as sulfur oxide and nitrogen oxides.

There was a sharp increase in nitrite in rainwater collected under the canopy in June. There was also a sharp increase in the content of the nitrate ion in May 2021 in the rainwater under the forest canopy and the ammonium ion in September 2021 (Figure 6). This increase affected the total content of the resulting nitrogen ions. The average content of nitrogen ions in rainwater under the forest canopy was higher than in rainwater collected in the open area (Figure 4). However, in fact, all year round, the content of inorganic nitrogen under the forest canopy was less than in the open area. Often, in rainwater that passed through the forest canopy (in some months), only "traces" of nitrite and ammonium were found, which testifies in favor of their absorption by woody vegetation.

3.3. Inorganic Phosphorus

The change in the concentration of inorganic phosphorus is shown in Figure 7 (μg/L). The content of phosphorus in rainwater was characterized by an increase in the summer. It can be seen in the figure that in June there was a sharp increase in the content of phosphorus up to 1157.67 μg/L. The content of phosphorus in the water collected under the forest canopy in all months was greater than its content in water from the open area. At the same time, the content of phosphorus in the rainwater under the forest canopy in June was higher than in July, and the content of phosphorus in the open area in June was lower than in July. The average concentration of inorganic phosphorus in atmospheric precipitation was 153.23 μg/L and 117.16 μg/L in rainwater collected under the canopy and in the open area, respectively. The average content of inorganic phosphorus in the rainwater under the forest canopy was not much higher than in the open area.

3.4. Dependence of the Biogenic Elements Content on Weather Conditions

Some works [30,31] studied the dependence of the content of elements on weather conditions. The authors of the work [30] stated that the intensity of precipitation is not a determining factor in the change in the concentration of nitrogen compounds in sediments. Therefore, in this work we studied the dependence of the biogenic elements content on weather conditions. The results are shown in Figure 8. The figure shows the dependence of the concentration of inorganic nitrogen and phosphorus on the amount of precipitation, on the relative humidity of the air, and on the wind speed during the study, from April 2021 to January 2022.

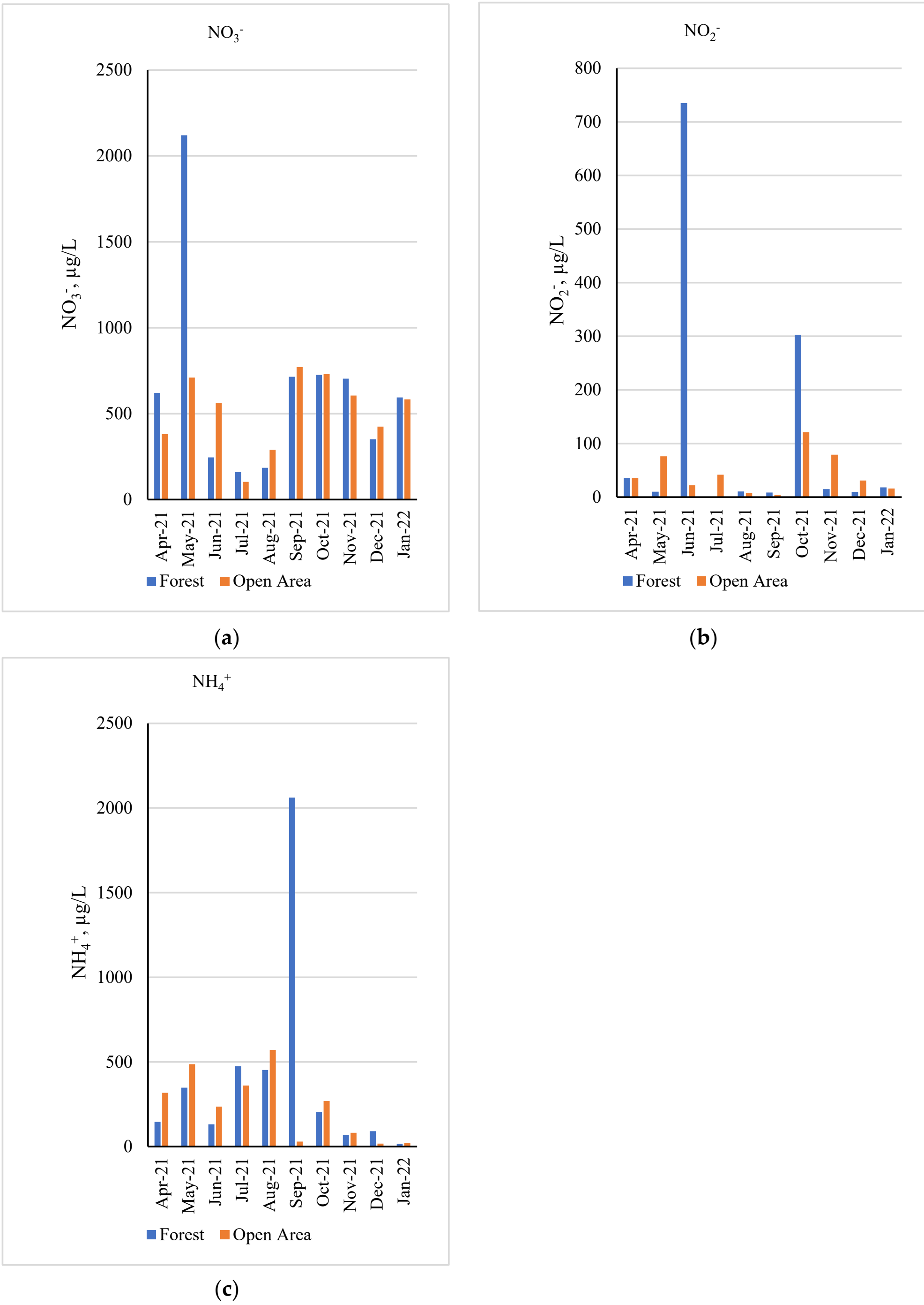


Figure 6. Change in the content of nitrogen ions by month (µg/L): (**a**) NO_3^-; (**b**) NO_2^-; (**c**) NH_4^+.

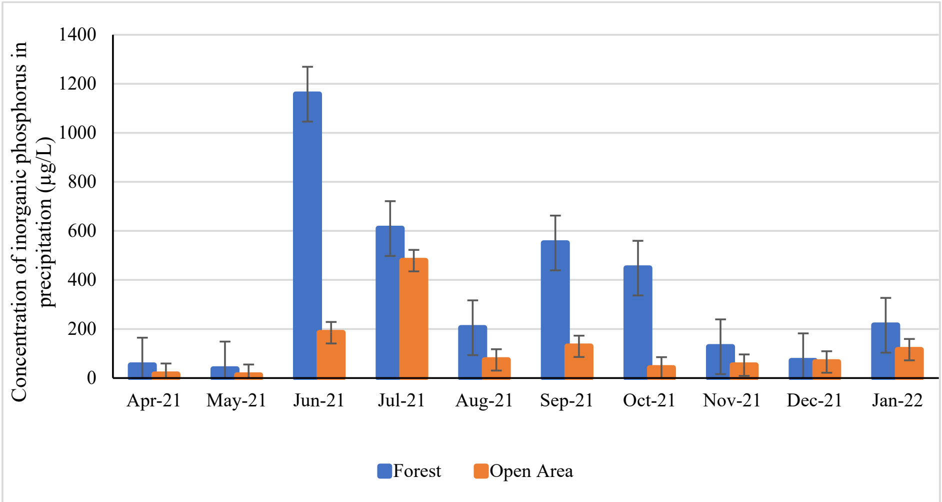


Figure 7. Change in the concentration of inorganic phosphorus in precipitation (µg/L).

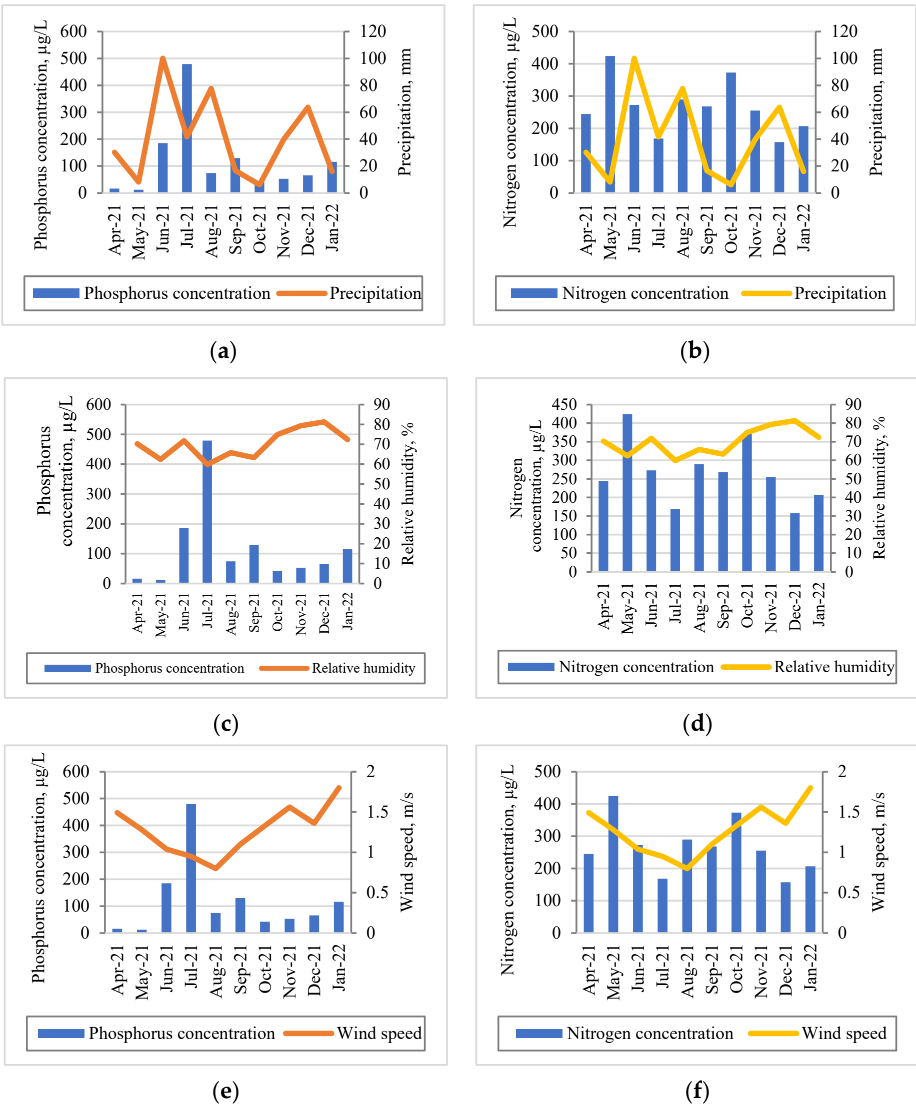


Figure 8. Dependence of the concentration of inorganic nitrogen and phosphorus on the amount of precipitation, on the relative humidity of the air and on the wind speed: (**a**) dependence of the concentration

of phosphorus on the amount of precipitation; (**b**) dependence of the concentration of inorganic nitrogen on the amount of precipitation; (**c**) dependence of the concentration of phosphorus on the relative humidity of the air; (**d**) dependence of the concentration of inorganic nitrogen on the relative humidity of the air; (**e**) dependence of the concentration of phosphorus on the wind speed; (**f**) dependence of the concentration of inorganic nitrogen on the wind speed.

During the period under consideration, a decrease in the concentration of inorganic nitrogen was observed with an increase for precipitation. At the same time, no such dependence was observed for inorganic phosphorus. An inverse dependence of the concentration of inorganic nitrogen and phosphorus in atmospheric precipitation on the relative air humidity was observed (Figure 8). The content of phosphorus increased with a decrease in wind speed, while a dependence of the content of inorganic nitrogen on wind speed was not observed.

4. Discussion

4.1. Acidity

Usually, under normal conditions, rainwater has a pH = 5.6–5.7 [34]. During the study period, alkaline precipitation was observed in the examined area, with an average pH value in the open area of 6.8 and under the forest canopy of 6.1. The decrease in the pH value can be explained by the fact that rainwater, flowing down from the crowns of trees, washes away and dissolves dust particles and organic and mineral substances of an acidic nature. Thus, a relatively "alkaline" precipitation, passing through the canopy of the studied forest, is acidified and becomes slightly acidic. Consequently, in the rainwater that had passed through the crowns of the forest, the content of rainwater-soluble compounds of all the considered elements in total increased significantly (Figure 3). The analysis of sediment samples allows us to say that a weakly alkaline precipitation falls mainly on the territory of the Karadag Reserve. This is explained by the fact that there are many limestone rocks in the territory of the peninsula, and the processes associated with the erosion and weathering of limestones lead to the alkalinization of sediments ($CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$). This result coincides with the results of [31].

4.2. Inorganic Nitrogen

The decrease in the ammonium content can be explained by the fact that while rainwater flows through the forest canopy, the process of ammonium oxidation occurs due to contact with protein products and the presence of corresponding microorganisms accumulated on the surface of the leaves. The low content of nitrites, apparently, is explained by the fact that they are an intermediate product of the oxidation of ammonium to nitrates. These results are consistent with the available data on the ratio of nitrogen species in samples of atmospheric precipitation [35–38].

In previous works [2,33,39,40], the order of contribution of nitrogen-containing ions was $NH_4^+ > NO_3^- > NO_2^-$. In addition, in [25,31], the contribution of nitrogen-containing ions was $NO_3^- > NH_4^+ > NO_2^-$. This order is identical to our result. Moreover, the order of contribution can be explained by differences in the characteristics of the study areas.

When comparing the open area and the area under the forest canopy, it can be seen that the nitrogen content in the rainwater under the canopies was greater than in the rainwater collected in the open area (Figure 4). These results correspond to the results obtained in [31].

The maximum values of nitrates were recorded both in the open area and under the forest canopy in May 2021, which amounted to 710 µg/L and 2120 µg/L, respectively. The maximum nitrite values were recorded in May and June 2021 in the open area (76 µg/L) and under the forest canopy, respectively (735 µg/L). At the same time, the maximum values of ammonium were recorded in August and July, respectively, in the open area (570 µg/L) and under the forest canopy (474 µg/L). No simultaneous high concentrations of all inorganic forms of nitrogen were observed in one sample. For a detailed study of the relationships between the concentrations of nitrite ion, nitrate ion, ammonium ion, and pH value, we calculated the Pearson correlation coefficients (Table 1).

Table 1. Correlation coefficients for the concentrations of nitrite ion, nitrate ion, ammonium ion, and pH value ($p = 0.05$, $n = 10$) under the forest canopy.

	NO_2^-	NO_3^-	NH_4^+	pH
NO_2^-	1			
NO_3^-	−0.22	1		
NH_4^+	−0.20	0.05	1	
pH	−0.24	−0.33	0.19	1

Tables 1 and 2 show that in the open area, all components (except NH_4^+-NO_3^-) showed a proportional correlation (r > 0). At the same time, the pH strongly depended on the NO_2^- and NH_4^+ ions (r = 0.51 and 0.34, respectively); pH and NO_3^- were almost independent of each other, r = 0.07, a value almost equal to 0. NO_3^- and NO_2^- proportionally depended on each other (r = 0.34). The good correlation between nitrate and nitrite nitrogen can be explained by the fact that they enter the atmosphere from similar sources, as well as by the fact that they are elements of mutual transformation. At the same time, the difference in the sources of ammonium, nitrite, and nitrate nitrogen entering the atmosphere apparently explains the lower correlation between these elements. At the same time, NH_4^+ and NO_3^- are inversely dependent on each other (r = −0.37). Under the forest canopy, on the contrary, almost all components were inversely correlated (r < 0), except for NH_4^+ and NO_3^- and pH and NH_4^+. At the same time, NH_4^+ and NO_3^- were almost independent of each other, with r = 0.05, a value almost equal to 0. Here, unlike in the open area, pH and NO_3^- showed an inverse relationship r (r = −0.33). This is logical, because the acidity of rainwater depends on the concentration of nitrate ions, and the more NO_3^- in rainwater, the lower its pH value.

Table 2. Correlation coefficients between the concentrations of nitrite ion, nitrate ion, ammonium ion, and pH value ($p = 0.05$, $n = 10$) in the open area.

	NO_2^-	NO_3^-	NH_4^+	pH
NO_2^-	1			
NO_3^-	0.34	1		
NH_4^+	0.14	−0.37	1	
pH	0.51	0.07	0.34	1

4.3. Inorganic Phosphorus

Our result corresponds to the results obtained in [25,41] and is explained by the influx of phosphorus through the products of plant metabolism. In addition, this can be explained by the peculiarities of phosphorus migration in the biosphere, which is also associated with the influx of mineral forms of the element together with dust particles formed during soil and rock erosion. pH and $H_2PO_4^-$ in rainwater under the forest canopy showed a weak inverse relationship r (r= −0.18). At the same time, pH and $H_2PO_4^-$ in rainwater in the open area were almost independent of each other (r = 0.08, almost equal to 0) as shown in Figure 9.

4.4. Dependence of the Biogenic Elements Content on Weather Conditions

The decrease in the concentration of inorganic nitrogen with an increase in precipitation is explained by the effect of sample dilution. In addition, the lack of dependence of inorganic phosphorus on the amount of precipitation can be explained by the strong spatiotemporal variability of phosphorus sources in the atmosphere [25]. With an increase in the relative humidity of the air, the amount of precipitation increases, and, consequently, its content of pollutants decreases, resulting in an inverse relationship between the concentration of inorganic nitrogen and phosphorus in precipitation and the relative humidity of the air [42,43].

As can be seen in Table 3 and Figure 8, the values of the correlation coefficients between the series of concentrations of the considered substances in precipitation falling on the territory of the reserve during the study period and the amount of precipitation did not exceed the threshold for a reliable correlation. This allows us to conclude that the intensity of precipitation is not a determining factor in the change in the concentration of inorganic nitrogen compounds in sediments. In general, it has a slight inverse effect on the change in nitrogen concentration. The amount of precipitation proportionally affected the change in the concentration of phosphorus in precipitation. Relative humidity showed an inverse relationship with respect to the change in the concentration of the various components. Wind speed was also a determining factor in changing the concentration of phosphorus compounds, while nitrogen had almost no effect. Phosphorus was inversely correlated with inorganic nitrogen (Figure 10), so that as the concentration of phosphorus in rainwater increased, the concentration of nitrogen decreased, especially the concentration of nitrate.

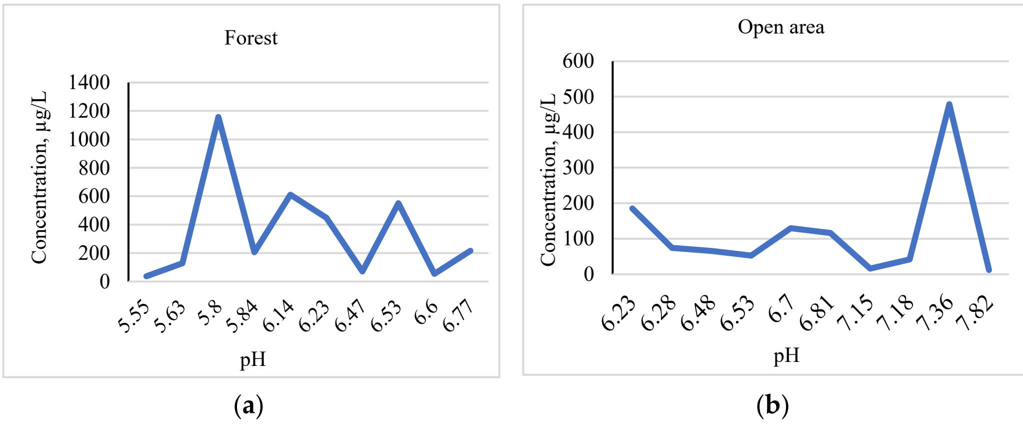


Figure 9. Relationship between pH and the concentration of inorganic phosphorus in precipitation: (**a**) forest; (**b**) open area.

Table 3. Results of the correlation analysis of time series of precipitation intensity and rainwater concentrations of nitrogen and $H_2PO_4^-$ (p = 0.05, n = 10).

	$H_2PO_4^-$	N	Amount of Precipitation	Relative Humidity	Wind Speed
$H_2PO_4^-$	1				
N	−0.48	1			
Amount of precipitation	0.22	−0.34	1		
Relative humidity	−0.47	−0.22	0.18	1	
Wind speed	−0.44	−0.09	−0.50	0.57	1

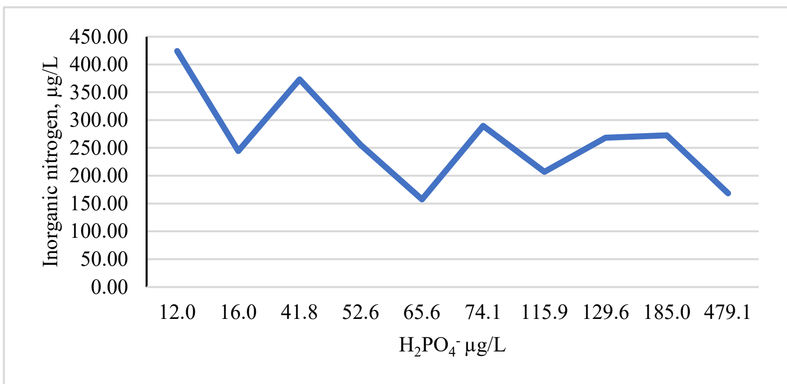


Figure 10. Linear dependence of inorganic nitrogen on inorganic phosphorus.

In order to study the mutual influence of the components in rainwater in more detail, we carried out a correlation analysis for rainwater collected under the forest canopy and in the open area. The results of the correlation analysis are shown in Table 4.

Table 4. Results of the correlation analysis for rainwater collected in the forest and in the open area (p = 0.05, n = 10).

		Open Area			
		$H_2PO_4^-$	**NO_2^-**	**NO_3^-**	**NH_4^+**
Forest	$H_2PO_4^-$	**0.56**	−0.18	0.01	−0.06
	NO_2^-	0.06	**0.09**	0.21	0.01
	NO_3^-	−0.52	0.44	**0.59**	0.20
	NH_4^+	0.15	−0.36	0.28	**−0.14** [1]

[1] Bold indicates significant correlation coefficients.

Table 4 shows that the combination of nitrogen and phosphorus in rainwater collected under the forest canopy and in the open area were well correlated other. Phosphorus and nitrate proportionally affected each other, so that with their increase in the concentration in rainwater collected in the open area, an increase in their concentration in rainwater collected under the forest canopies was observed; this was not observed for NH_4^+, as shown in Figure 11. In Figure 11, we can see that NO_2^- and NH_4^+ in rainwater in the open area and in rainwater in the forest were not dependent upon each other. This may be due to the abnormal values of their concentrations.

With an increase in the concentration of ammonium and nitrite in the open area, there was an increase in the concentration of nitrate in rainwater under the forest canopy. This can be explained by the fact that all these substances were converted into the final form of nitrate. This means that while rainwater passed through the crowns of the forest, the reaction of oxidation of ammonium and nitrite to nitrate occurred. Nitrate in the open area was not a determining factor in changing the concentration of phosphorus under the trees. Similar results were also observed for ammonium in the open area and phosphorus under the forest canopy, and for phosphorus in the open area and nitrite under the canopy. At the same time, ammonium and phosphorus showed a strong relationship: phosphorus in rainwater in the open area proportionally affected the content of ammonium ion in rainwater under the forest canopy, and ammonium in rainwater in the open area influenced the content of phosphorus in rainwater under the forest canopy. An increase in the concentration of nitrate in rainwater in the open area led to an increase in the concentration of nitrite under the forest canopy. This is because the reduction reaction of nitrate to nitrite occurred.

Intensive processes on the surface of actively functioning trees can explain a more intensive supply of elements in under-crown spaces, as well as the washing off of dust from the crown, which has a high sorption capacity.

The intake of biogenic substances (inorganic nitrogen, phosphorus) with atmospheric precipitation in the area of the Karadag Nature Reserve was determined from April 2021 to January 2022. It was established that the main forms of nitrogen in atmospheric precipitation were nitrates and ammonium. For all considered biogenic substances, an increase in their content in the warm period of the year was observed, which is explained both by the inverse dependence of the concentration of elements on the amount of precipitation, and by the peculiarity of their migration and sources. There was an inverse relationship between the concentration of inorganic nitrogen and phosphorus in precipitation and the relative air humidity and wind speed.

The influence of oak forests on the chemical composition of precipitation was not previously studied in the territory of the Crimean Peninsula within protected natural areas. Therefore, our research is new. It shows previously unexplored aspects of the functioning of the oak forests of the Karadag Nature Reserve. At the same time, we can say that the data obtained can be representative of oak forest ecosystems within the Greater Mediterranean, taking into account regional characteristics. It should be taken into account that juniper, pine, beech, and hornbeam forests also grow within the Crimean Peninsula. In the future, it is necessary to study the influence of these forests on the chemical composition of precipitation in order to obtain a complete picture of all the types of forest ecosystems of the Crimean Peninsula. This would make it possible to explore the forest conditions and provide more detailed information about the ecology of the study area.

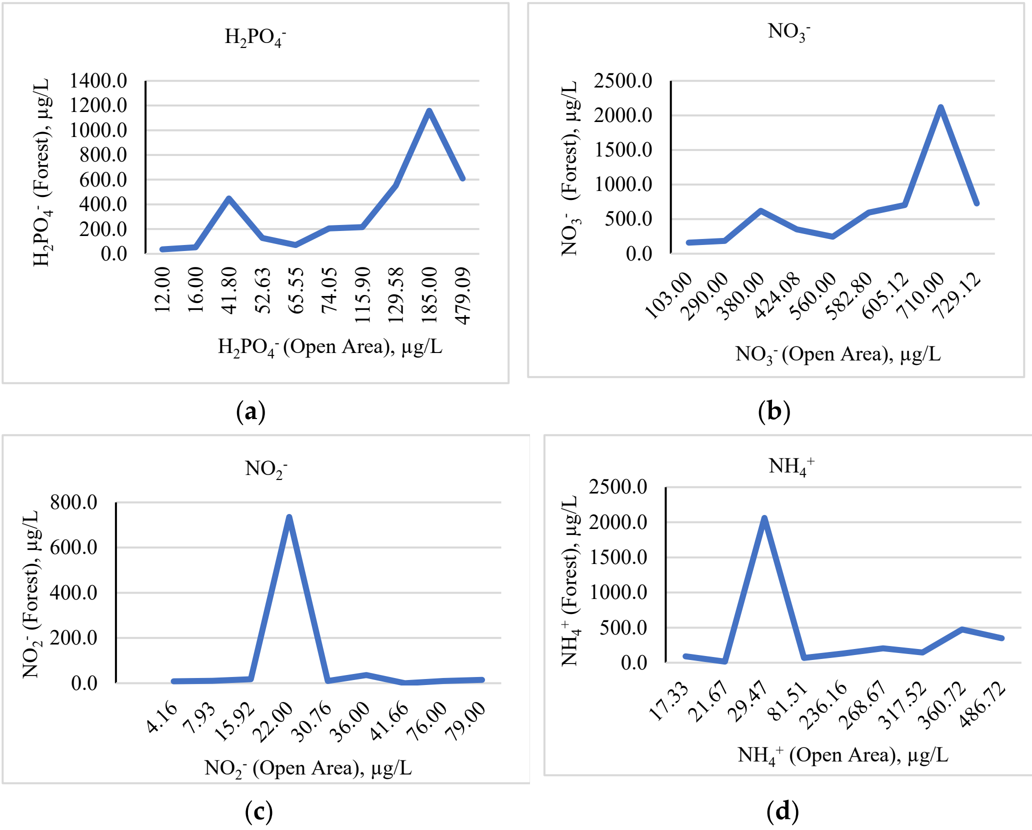


Figure 11. Relationship between the concentrations of $H_2PO_4^-$ (**a**), NO_3^- (**b**), NO_2^- (**c**), NH_4^+ (**d**) in rainwater in the open area and in the forest.

5. Conclusions

In this paper, the study of the biogenic composition of atmospheric precipitation under the forest canopy in the territory of the Karadag Nature Reserve was carried out. It was established that the transformation of precipitation under the forest canopy led to an increase in the concentration of most of the determined biogenic components. We showed that the pH of precipitation falling under the forest canopy was significantly lower than the pH of precipitation in the open area. It was observed that rainwater pH under the forest canopy was inversely related to the concentrations of almost all observed components, except ammonium. At the same time, in the open field, it showed a proportional relationship with the concentration of nitrogen ions. The forest canopy significantly increased the concentrations of NO_3^-, $H_2PO_4^-$, NH_4^+ ions and reduced the amount of NO_2^- in precipitation. It was found that nitrate in the open area was not a determining factor in changing the concentration of phosphorus under the forest canopy. At the same time, ammonium and phosphorus ions were strongly linked to each other. Nitrogen ions in the open field and under the forest canopy showed a good relationship with each other. Edificatory plants determine the transformation of atmospheric precipitation penetrating through the vegetation cover. It was revealed that the increase in the concentration of biogenic elements was in accordance with the phase of plant development during the growing season (from spring to summer and autumn).

Author Contributions: Conceptualization, R.G.; methodology, R.G. and C.N.P.; validation, V.T.; formal analysis, T.G., V.T. and V.L.; investigation, C.N.P., R.G., and T.G.; resources, V.L.; data curation, V.T.; writing—original draft preparation, C.N.P.; writing—review and editing, R.G. and T.G.; visualization, V.T.; supervision, R.G.; project administration, R.G. All authors have read and agreed to the published version of the manuscript.

Funding: The research was conducted within the framework of the research topic of IBSS, registration number: 121040100327-3, of KSS–NR RAS–Branch of IBSS, registration number: 121032300023-7. The RUDN University Strategic Academic Leadership Program supported this research.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors are grateful to Bovko N.I. (A.O Kovalevsky Institute of Biology of the Southern Seas of RAS) for support of the study.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Pierret, M.-C.; Viville, D.; Dambrine, E.; Cotel, S.; Probst, A. Twenty-five year record of chemicals in open field precipitation and throughfall from a medium-altitude forest catchment (Strengbach—NE France): An obvious response to atmospheric pollution trends. *Atmos. Environ.* **2019**, *202*, 296–314. [CrossRef]
2. Shiltsova, G.V.; Lastochkina, V.G. Influence of the canopy of pine and birch forests on the chemical composition of precipitation in the Kivach Nature Reserve. *Proc. Karal Sci. Cent. Russ. Acad. Sci.* **2006**, *10*, 180–184.
3. The 16th Baltic Sea Parliamentary Conference, Berlin, Germany, 27–28 August 2007. Available online: http://www.bspc.net/page/show/26 (accessed on 2 August 2022).
4. De Schrijver, A.; Geudens, G.; Augusto, L.; Staelens, J.; Mertens, J.; Wuyts, K.; Gielis, L.; Verheyen, K. The effect of forest type on throughfall deposition and seepage flux: A review. *Oecologia* **2007**, *153*, 663–674. [CrossRef] [PubMed]
5. Zhang, G.; Zeng, G.-M.; Du, C.-Y.; Jiang, Y.-M.; Su, X.-K.; Xiang, R.-J.; Huang, L.; Xu, M.; Zhang, C. Deposition patterns in bulk precipitation and throughfall in a subtropical mixed forest in central-south China. *For. Int. J. For. Res.* **2007**, *80*, 211–221. [CrossRef]
6. Pristova, T.A. Chemical composition of atmospheric precipitation, undercrown and surface waters in the middle taiga deciduous plantations of post-cutting origin. *Theor. Appl. Ecol.* **2022**, *2*, 63–69. [CrossRef]
7. Gandois, L.; Tipping, E.; Dumat, C.; Probst, A. Canopy influence on trace metal atmospheric inputs on forest ecosystems: Speciation in throughfall. *Atmos. Environ.* **2010**, *44*, 824–833. [CrossRef]
8. Yang, B.; Lee, D.K.; Heo, H.K.; Biging, G. The effects of tree characteristics on rainfall interception in urban areas. *Landsc. Ecol. Eng.* **2019**, *15*, 289–296. [CrossRef]
9. Dubenok, N.N.; Lebedev, A.V.; Gemonov, A.V. Hydrological Role of Forest Stands in a Small Catchment Basin. *Russ. Agric. Sci.* **2021**, *47*, 323–327. [CrossRef]
10. Chen, L.C.; Wang, L.J.; Martin, C.E.; Lin, T.C. Mediation of stemflow water and nutrient availabilities by epiphytes growing above other epiphytes in a subtropical forest. *Ecohydrology* **2019**, *12*, e2140. [CrossRef]
11. Hargis, H.; Gotsch, S.G.; Porada, P.; Moore, G.W.; Ferguson, B.; Van Stan, J.T., II. Arboreal Epiphytes in the Soil-Atmosphere Interface: How Often Are the Biggest "Buckets" in the Canopy Empty? *Geosciences* **2019**, *9*, 342. [CrossRef]
12. Knops, J.M.H.; Iii, T.N.; Boucher, V.L.; Schlesinger, W.H. Mineral cycling and epiphytic lichens: Implications at the ecosystem level. *Lichenology* **1991**, *23*, 309–321. [CrossRef]
13. Townsend, A.R.; Asner, G.P.; Cleveland, C.C. The biogeochemical heterogeneity of tropical forests. *Trends Ecol. Evol.* **2008**, *23*, 424–431. [CrossRef]
14. McDowell, W.H.; Pérez-Rivera, K.X.; Shaw, M.E. Assessing the ecological significance of throughfall in forest ecosystems. In *Forest-Water Interactions*; Springer: Cham, Switzerland, 2020; pp. 299–318.
15. Asner, G.P.; Martin, R.E.; Knapp, D.E.; Tupayachi, R.; Anderson, C.; Carranza, L.; Weiss, P. Spectroscopy of canopy chemicals in humid tropical forests. *Remote Sens. Environ.* **2011**, *115*, 3587–3598. [CrossRef]
16. Tao, J.; Zuo, J.; He, Z.; Wang, Y.; Liu, J.; Liu, W.; Cornelissen, J.H. Traits including leaf dry matter content and leaf pH dominate over forest soil pH as drivers of litter decomposition among 60 species. *Funct. Ecol.* **2019**, *33*, 1798–1810. [CrossRef]
17. Rahman, M.M.; Tsukamoto, J. Leaf traits, litter decomposability and forest floor dynamics in an evergreen-and a deciduous-broadleaved forest in warm temperate Japan. *Forestry* **2013**, *86*, 441–451. [CrossRef]
18. Jochheim, H.; Lüttschwager, D.; Riek, W. Stem distance as an explanatory variable for the spatial distribution and chemical conditions of stand precipitation and soil solution under beech (*Fagus sylvatica* L.) trees. *J. Hydrol.* **2022**, *608*, 127629. [CrossRef]
19. Kozhevnikova, N.K.; Lutsenko, T.N.; Boldeskul, A.G.; Lupakov, S.Y.; Shamov, V.V. Water migration of macroelements in coniferous-broad-leaved forests of Sikhote-Alin. *Sib. For. J.* **2017**, *3*, 60–73.

20. Kravchenko, I.Y. Influence of the coniferous forest canopy on the chemical composition of atmospheric precipitation. In *Geography: The Development of Science and Education*; Solomin, V.P., Rumyantsev, V.A., Subetto, D.A., Lovelius, N.V., Eds.; Herzen University: Saint Petersburg, Russia, 2018; pp. 108–112.
21. Martynyuk, A.A.; Doronicheva, E.V.; Rykova, T.V. Changes in the chemical composition of natural sediments under the canopy of pine plantations under conditions of technogenic pollution of the environment. *Lisoviy Zhurnal* **2011**, *1*, 8–11.
22. Jiang, Z.-Y.; Zhi, Q.-Y.; Van Stan, J.T.; Zhang, S.-Y.; Xiao, Y.-H.; Chen, X.-Y.; Yang, X.; Zhou, H.-Y.; Hu, Z.-M.; Wu, H.-W. Rainfall partitioning and associated chemical alteration in three subtropical urban tree species. *J. Hydrol.* **2021**, *603*, 127109. [CrossRef]
23. Roulier, M.; Bueno, M.; Coppin, F.; Nicolas, M.; Thiry, Y.; Rigal, F.; Pannier, F.; Le Hécho, I. Atmospheric iodine, selenium and caesium depositions in France: II. Influence of forest canopies. *Chemosphere* **2021**, *273*, 128952. [CrossRef]
24. Van Stan II, J.T.; Pypker, T.G. A review and evaluation of forest canopy epiphyte roles in the partitioning and chemical alteration of precipitation. *Sci. Total Environ.* **2015**, *536*, 813–824. [CrossRef]
25. Varenik, A.V.; Kozlovskaya, O.N. Supply of biogenic elements with atmospheric precipitation to the surface of the Black Sea in 2010-2013. *Ecol. Saf. Coast. Shelf Zones Integr. Use Shelf Resour.* **2014**, *28*, 105–114.
26. Ilyin, Y.P.; Ryabinin, A.I.; Malchenko, Y.A.; Bobrova, S.A.; Klimenko, N.P.; Chaikina, A.V.; Katunina, E.V.; Saltykova, L.V.; Danilova, E.A.; Senicheva, M.I.; et al. The state of pollution of atmospheric precipitation in the city of Sevastopol in 1997–2006. *Sci. Work. Ukr. Res. Hydrometeorol. Inst.* **2006**, *255*, 166–184.
27. Myslina, M.A.; Varenik, A.V. Supply of inorganic nitrogen with atmospheric precipitation to the water area of the Sevastopol Bay in 2015-2016. *Ecol. Saf. Coast. Shelf Zones Sea.* **2019**, *1*, 78–82.
28. Varenik, A.V.; Konovalov, S.K. Contribution of atmospheric precipitation to the supply of biogenic elements in the area of the Crimean coast. In Proceedings of the III International Scientific Conference in Memory of Corresponding Member of the Russian Academy of Sciences D.G. Matishov—Regularities of Formation and Impact of Marine, Atmospheric Hazards and Disasters on the Coastal Zone of the Russian Federation in the Context of Global Climatic and Industrial Challenges, Rostov-on-Don, Russia, 15–19 June 2021; SSC RAS Publishing House: Rostov-on-Don, Russia, 2021; pp. 253–256.
29. Varenik, A.V.; Konovalov, S.K.; Metik-Diyunova, V.V. Quantitative assessment of the input of biochemical elements with atmospheric precipitation in the coastal regions of the Crimean Peninsula. In Proceedings of the II All-Russian Conference Hydrometeorology and Ecology: Achievements and Development Prospects, St. Petersburg, Russia, 19–20 December 2017; Chemizdat: St. Petersburg, Russia, 2018; pp. 124–127.
30. Chaikina, A.V.; Kholoptsev, A.V. Peculiarities of hydrochemical composition of atmospheric precipitation in summer 2004 near the village of Katsiveli (Southern coast of Crimea). *Ecol. Saf. Coast. Shelf Zones Integr. Use Shelf Resour.* **2005**, *12*, 215–219.
31. Kayukova, E.P. Features of the chemical composition of precipitation of the Crimean training site of Saint-Petersburg University. *Vestn. St. -Petersburg Univ. Ser. 7 Geol. Geogr.* **2011**, *3*, 26–42.
32. Andreev, V.V.; Arshinov, M.Y.; Belan, B.D.; Davydov, D.K.; Elansky, N.F.; Zhamsueva, G.S.; Zayakhanov, A.S.; Ivlev, G.A.; Kozlov, A.V.; Kotel'Nikov, S.N.; et al. Surface ozone concentration over the Russian territory in the first half of 2020. *Opt. Atmos. I Okeana J.* **2020**, *33*, 710–721. [CrossRef]
33. Sapozhnikov, V.V. *Methods of Hydrochemical Studies of the Main Biogenic Elements*; VNIRO: Moscow, Russia, 1988; p. 118.
34. Trushkina, L.Y.; Trushkin, A.G.; Demyanova, L.M. *Hygiene and Human Ecology*, 4th ed.; TK Velby, Prospekt Publishing House: Moscow, Russia, 2006; p. 528.
35. Guerzoni, S.; Chester, R.; Dulac, F.; Herut, B.; Loÿe-Pilot, M.-D.; Measures, C.; Migon, C.; Molinaroli, E.; Moulin, C.; Rossini, P.; et al. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Prog. Oceanogr.* **1999**, *44*, 147–190. [CrossRef]
36. Jickells, T. Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects. *Mar. Chem.* **1995**, *48*, 199–214. [CrossRef]
37. Koçak, M.; Kubilay, N.; Tuğrul, S.; Mihalopoulos, N. Atmospheric nutrient inputs to the northern levantine basin from a long-term observation: Sources and comparison with riverine inputs. *Biogeosciences* **2010**, *7*, 4037–4050. [CrossRef]
38. Medinets, S.; Medinets, V. Investigations of atmospheric wet and dry nutrient deposition to marine surface in western part of the Black Sea. *Turk. J. Fish. Aquat. Sci.* **2012**, *12*, 497–505. [CrossRef] [PubMed]
39. Gashkina, N.A.; Moiseenko, T.I.; Dinu, M.I.; Tatsii, Y.G.; Baranov, D.Y. Biogeochemical migration of elements in the "Atmospheric precipitation-crown water-soil water-lake" system in the background region (Valdai National Park). *Geochemistry* **2020**, *65*, 693–710. [CrossRef]
40. Kalinskaya, D.V.; Varenik, A.V.; Papkova, A.S. Phosphorus and silicon as markers of dust aerosol transport over the Black Sea region. *Mod. Probl. Remote Sens. Earth Space* **2018**, *15*, 217–225.
41. Savchenko, V.S. Phosphorus in precipitation. *Water Resour.* **1996**, *185*, 11–17.
42. Salukvadze, M. Study of the Influence of Meteorological, Anthropogenic and Terrigenous Factors on the Chemical Composition of Atmospheric Precipitation in Eastern Georgia. Dissertation Abstract, TSU M. Nodia Institute of Geophysics, Tbilisi, Georgia, 2006; pp. 1–22.
43. Jiang, X.; Gao, G.; Deng, J.; Zhu, G.; Tang, X.; Shao, K.; Hu, Y. Nitrogen concentration response to the decline in atmospheric nitrogen deposition in a hypereutrophic lake. *Environ. Pollut.* **2022**, *300*, 118952. [CrossRef]